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CONFERENCE ON HIGH TEMPERATURE POLYMER AND FLUID RESEARCH

compiled by
Robert J. McHenry, 1/Lt, USAF

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-372

August 1962

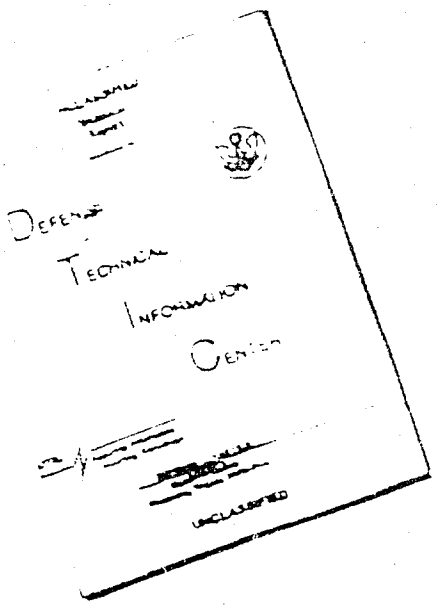
Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7340, Task No. 734004

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FOREWORD

This technical documentary report was compiled under Task No. 734004, "New Organic and Inorganic Polymers," Project No. 7340, "nonmetallic and Composite Materials" by Lt. R. J. McHenry of the Nonmetallic Materials Laboratory, Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio

ABSTRACT

This report is a collection of the papers presented at the Directorate of Materials and Processes ASD conference on "High Temperature Polymer And Fluid Research" held in Dayton, Ohio, on 8-11 May 1962.

The purpose of this conference was to review the recent progress in both contractual and internal research programs sponsored by the Polymer Branch of the Nonmetallic Materials Laboratory in the area of synthesis of new polymers and fluids.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Acting Chief, Polymer Branch
Nonmetallic Materials Laboratory
Directorate of Materials And Processes

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Polyaromatics

By C. S. Marvel

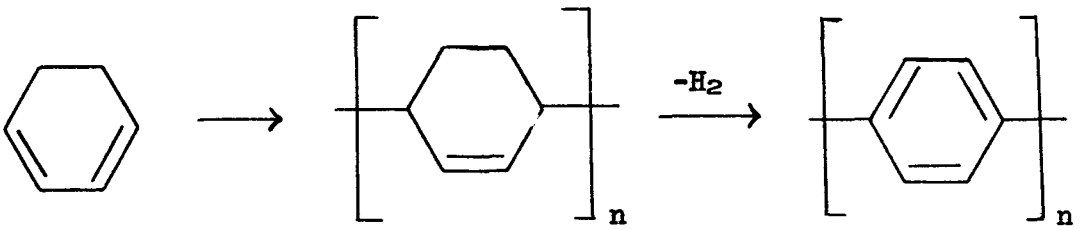
University of Arizona

[Experimental work by M. Hasegawa, D. A. Frey, H. Vogel, J. J. Bloomfield and J. E. Mulvaney]

Research on polymers with recurring aromatic units has been in progress in our group for the past three years at the University of Illinois and University of Arizona. It is not intended that this report is a complete coverage of all work performed, but it will include a discussion of the research on poly-p-phenyls, polybenzimidazoles, polybenzborimidazolines and lattice-type aromatic polymers.

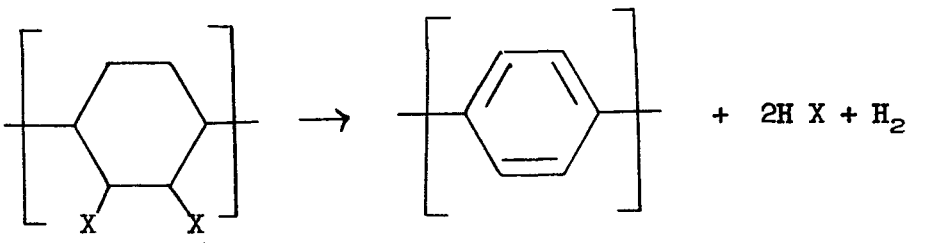
Poly-p-phenyls

These polymers are being prepared via the polymerization of 1,3-cyclohexadiene and subsequent dehydrogenation.



The polymerization has been achieved by means of Ziegler-type catalysts and by cationic initiation with boron fluoride in methylene chloride. It has been impossible to obtain high molecular weight polymer. However, it is consistently possible to produce a soluble polymer with an inherent viscosity of 0.10 to 0.15.

Dehydrogenation has been accomplished by preparing either the bromine or chlorine adduct of the polymer and then heating the halogenated polymer to 350-400°C. to eliminate hydrogen halide and hydrogen.



When the bromine derivative is used this treatment leads to a dark brown powdery product which is soluble in 1-methylnaphthalene and slightly soluble in concentrated sulfuric acid. The very dilute solution in sulfuric acid shows a λmax at 325 mμ. The inherent viscosity of this material (0.25 g./100 g. 1-methylnaphthalene) was 0.09. It still contained about 0.01 mole per cent of bromine. If one assumes one bromine atom per polymer chain this would suggest a

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degree of polymerization of at least 100.

This polymer when heated with sulfuric acid is sulfonated to yield a polymer which has one sulfur atom for about each 12 carbon atoms. This sulfonated material is slightly water soluble. This polyphenyl is probably not completely aromatized but it is quite stable to heating in air and is very slowly oxidized at 420°C.

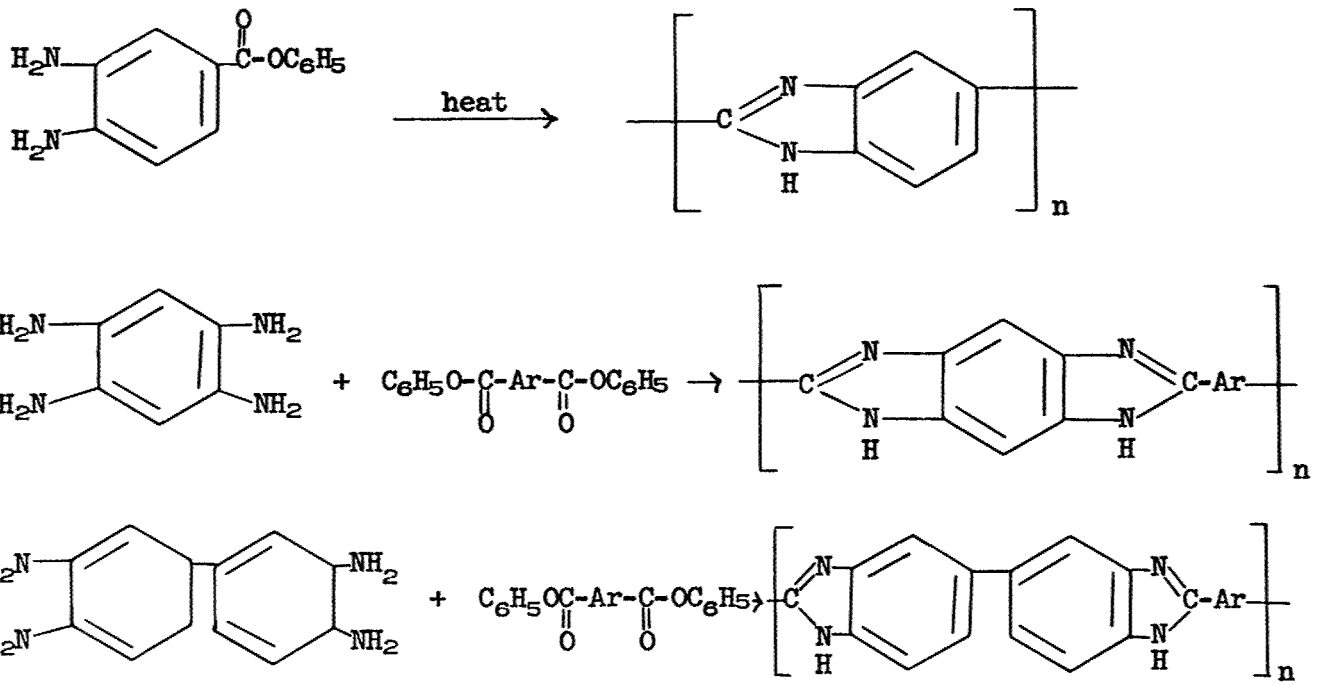
When the chlorine derivative is heated to 350°C. in nitrogen for 8 hours and then at 400°C. under diminished pressure for about 8 hours, a black shiny polymer is obtained which still contains some chlorine and is essentially insoluble in all solvents. The material is so stable to oxidation that we are still having trouble with analyses on samples. This black polymer also seems to be capable of sulfonation. When this polyphenyl (0.005 g.) is heated in an open crucible over a Meker burner at full heat for 5-10 minutes it is gradually burned completely.

Future work is planned to seek higher molecular weight polymers and some other dehydrogenation processes.

Polybenzimidazoles

The reaction of tetraamino aromatic compounds and diphenyl esters of aromatic dibasic acids to yield polybenzimidazoles has been successfully carried out to give a wide variety of new, high molecular weight, heat stable, polymers with good tensile properties. A polymer of this type has also been obtained from the phenyl ester of 3,4-diaminobenzoic acid.

The general classes of polymer which have been obtained are illustrated by the following:



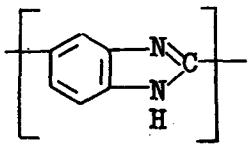
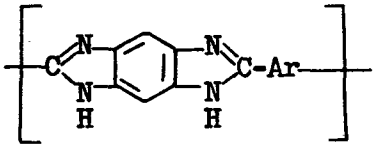
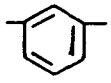
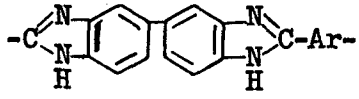
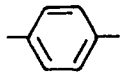
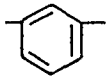
The general procedure for the preparation involves heating the monomer or mixture of monomers in an oxygen-free atmosphere at temperatures of 250-270°C. until the evolution of phenol and water slows down. The solid cake of polymer

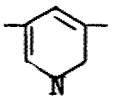
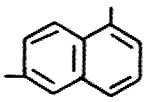
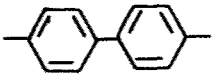
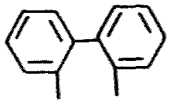
thus produced is then broken up and heated under about 0.1 mm. pressure for several hours with the temperature gradually increasing to 400°C. It is significant that the polymer increases in molecular weight during this heating of the solid prepolymer. The polymer mass never melts during this phase of the polymerization. All of the polymers are soluble in formic acid and sulfuric acid. A few are soluble in other solvents.

The following table lists polymers which have been prepared and some of their important properties.

Table I

Polybenzimidazoles

	m.p. °C.	Inherent viscosity (0.2% in HCO_2H)	Wt. loss at 600°C. in N_2- 5 hrs.	Crystallinity	Solvents
	>600°	1.27	7.3%	?	--
					
-Ar- = 	>600°	0.80	10.2	+	--
Ar = 	>600°	1.10	5.2	+	--
					
-Ar = 	>600°	1.00	4.7	+	--
-Ar- = 	>600°	3.34	4.5	-	{DMF, DMAC, DMS, NMP, HMP}[a]

Ar = 	>600°	4.13	8.2		
-Ar- = 	>600°	1.48	5.6	+	DMS[a]
-Ar- = 	480°	0.74	10.0	+	DMS, DMF[a]
-Ar- = 	>600°	2.70	6.5	-	DMS[a]
-Ar- = 	>600°	0.86 (in H_2SO_4)	3.5	+	--
-Ar = 	430°	2.99	17.5	-	DMS, DMF[a]

a - DMF = dimethylformamide
DMA = dimethylacetamide
DMS = dimethyl sulfoxide
NMP = N-methyl pyrrolidone
HMP = hexamethyl phosphoramide

All polymers are colored and the color varied from light yellow to deep yellowish brown.

The polymers which are listed as melting above 600°C. are cross-linked since after heating at about 450-500°C. none is soluble in any solvent which has been tried. It seems probable that this cross-linking is due to loss of hydrogen and formation of diphenyl links since benzene is known to give diphenyl at about 500°C.

The polymer from 3,3'-diaminobenzidine and diphenyl isophthalate can be cast from dimethyl sulfoxide solution to yield films with fair tensile strength (0.7 g. per denier) and the tensile at 200°C. is essentially the same as the tensile at 25°C. This is an outstanding property of this polymer.

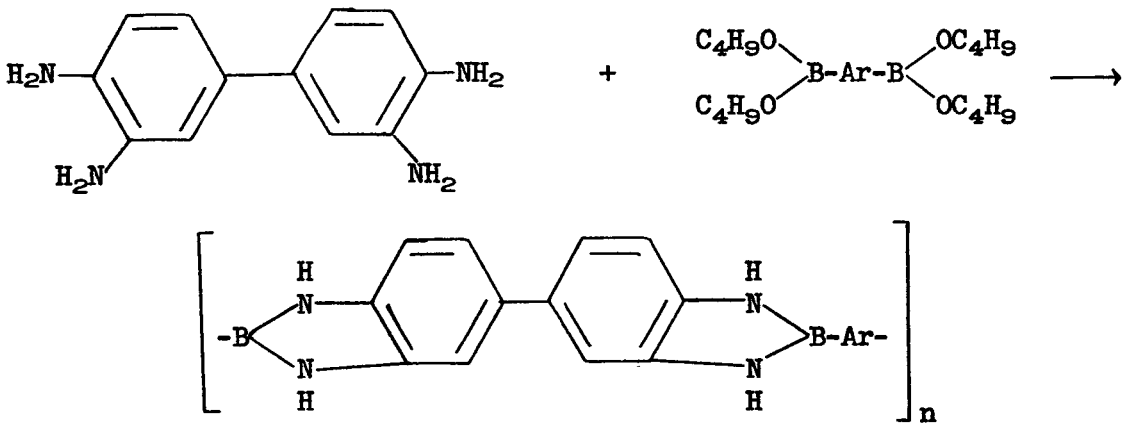
Thermal gravimetric analysis curves on this polymer show only slight weight loss in nitrogen up to 600°C. and then approximately 30% weight loss up to 900°C.

In air the weight loss becomes rapid at 450°C. Although in air there is little weight loss up to 450°C. there is obvious degradation of the polymer above 350°C. since thin films quickly lose their strength at this temperature. The polybenzimidazoles are extremely stable to hydrolysis. Samples of the m-phenylene polymer were refluxed with 70% sulfuric acid and with 25% potassium hydroxide solution for 10 hours each and recovered with no change in inherent viscosity.

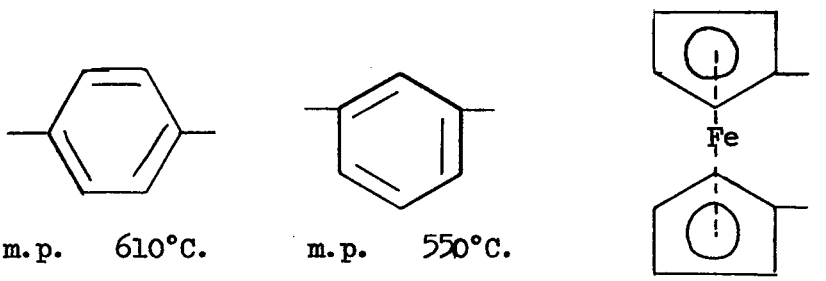
Work is currently under way to try to further modify this type of polymer so that a thermo plastic can be obtained. Also, attempts are in progress to make derivatives which it is hoped may be metal adhesives.

Polybenzborimidazolines

These polymers which are boron analogs of the polybenzimidazoles have been prepared by heating 3,3'-diaminobenzidine with tetraalkyl aryldiboronates under the same general conditions used to make the polybenzimidazoles.



The aryl groups used were the following:

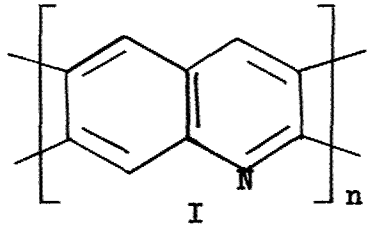


m.p. 610°C. m.p. 550°C. dec. about 350°C.

Some polymers were prepared in dimethylacetamide solution and this in general gave lower molecular weight materials. Film forming polymers were obtained but the films were brittle. The polymers first prepared were white but gradually darkened on standing. The polybenzborimidazolines were obtained with inherent viscosities of 0.13 to 0.35. Heat stabilities were about the same as those of the polybenzimidazoles except that the ferrocene derivative is decomposed at about 350°C. The boron derivatives were however much less stable to acids. In general this class of materials seemed less interesting than the polybenzimidazoles and work has been suspended.

Lattice Polymers

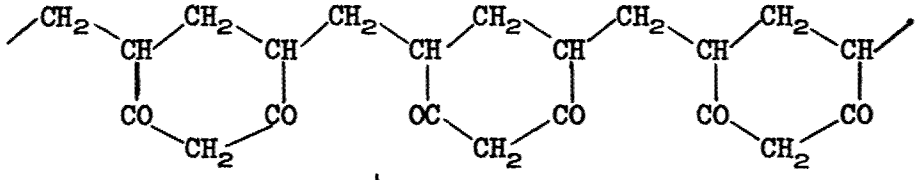
For some time attempts have been under way to produce a lattice polymer with an all aromatic recurring unit. Particularly the polyquinoline (I) has been the



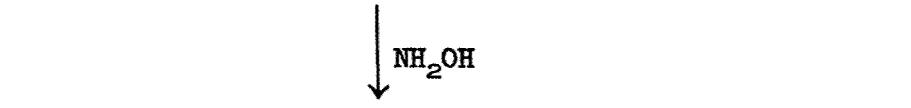
I

object of our research. A method which looks feasible to use for the synthesis of this polymer is the following:

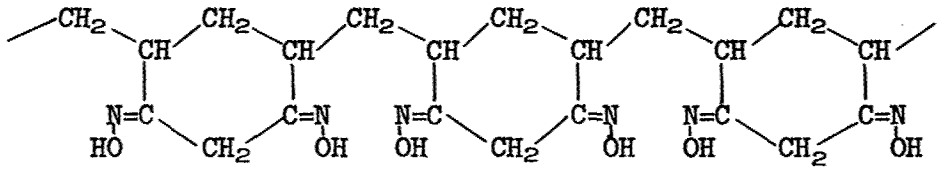
1. $CH_2=CH-CO-CH_2-CO-CH=CH_2$



2.

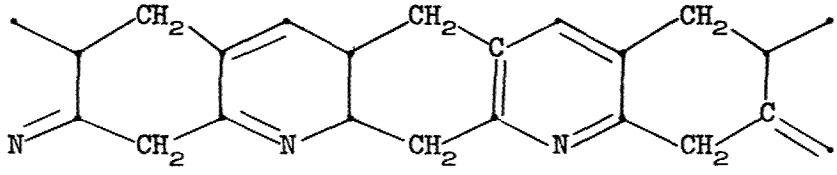


NH_2OH



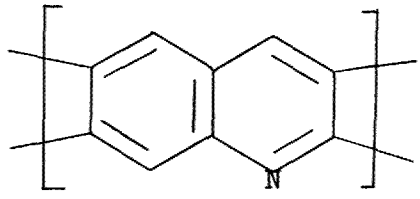
3.

Heat HCl



4.

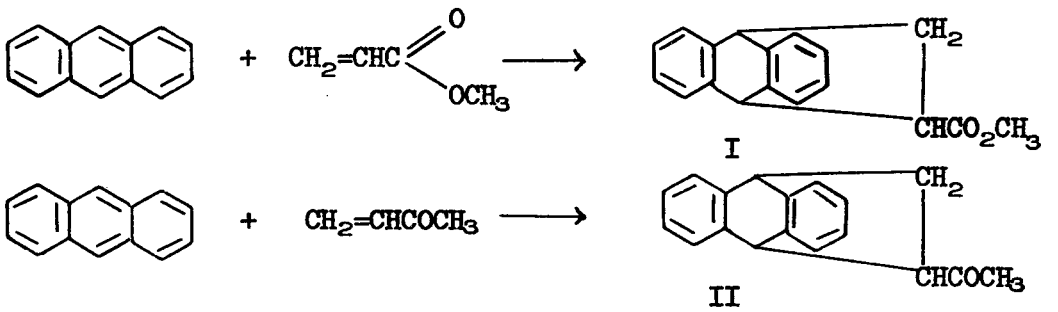
$-H_2$

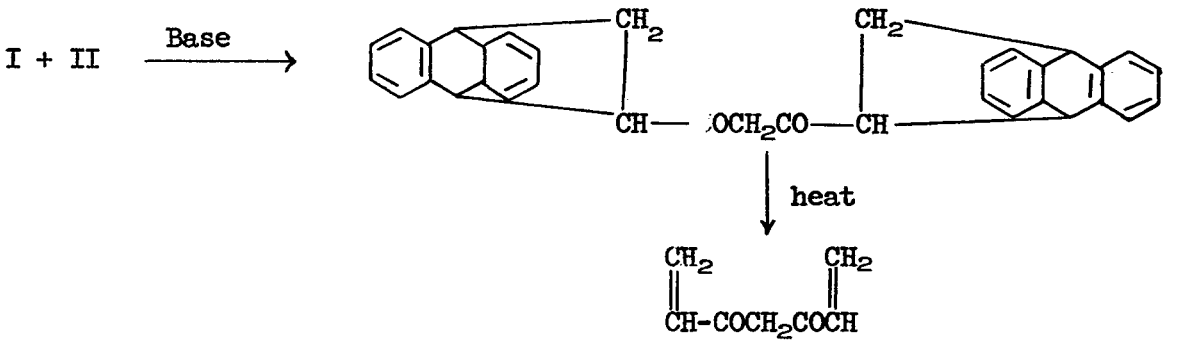


5.

The cyclic polydiketone indicated at step 2 has been claimed in a patent by Jones of Goodrich but his product is obviously not a pure homopolymer but probably contains units of methyl vinyl ketone. His monomer was never isolated as a pure product but was polymerized as made in the presence of methyl vinyl ketone.

A synthesis of this pure monomer has now been realized and the rest of the series of reactions are now being studied.





In conclusion it can be stated that several varieties of polymers with recurring aromatic units have been prepared and all have good thermal stability. Polybenzimidazoles have been obtained which are high molecular weight, have good tensile strength even at 200°C. and possess excellent hydrolytic stability.

SYNTHESIS AND PROPERTIES OF HETEROCYCLIC POLYMERS
I) POLYBENZIMIDAZOLES
II) POLY(1,3,4-OXADIAZOLES)

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James J. Kane
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ABSTRACT

Dimethylacetamide and dimethylsulfoxide have been successfully employed as dry-spinning solvents for poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole. The physical properties of both fibers appear to be comparable. Since dimethylacetamide produces a lighter colored yarn and in general lends itself to easier solvent removal, it emerges as the more desirable solvent for dry-spinning operations.

The fibers exhibit remarkably high resistance to hydrolysis and thermal ageing although under the more realistic condition of air ageing the thermal properties are not nearly as impressive as under nitrogen. The N-H bond in polybenzimidazoles is suspect as the weak link leading to degradation in the hot oven. This hypothesis will be tested by preparation of N-substituted polymers although such substitution appears to introduce increased solubility problems and may render dry-spinning impossible.

Polyhydrazide fibers have been prepared and were converted into polyoxadiazole fibers by thermal cyclodehydration. Good yarn properties and potentially high temperature resistance were observed. Specifically, alt. poly(1,3-/1,4-phenylene hydrazide) (50:50) fiber [T/E/Mi = 5/24/94], alt. poly[1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole)] (50:50) fiber [T/E/Mi = 3/3/124] were prepared. The investigation also afforded interesting chelating properties of polyhydrazide fibers and a study of thermal cyclodehydration of model compounds consisting of oligohydrazides and oligooxadiazoles which were prepared for the purpose of studying the reaction mechanism.

INTRODUCTION

The preparation of high molecular weight highly aromatic polymers has been a long-standing goal of polymer chemists. Such polymers would be expected to have the high degree of thermal and chemical inertness displayed by simple model systems, combined with new dimensions in mechanical properties.

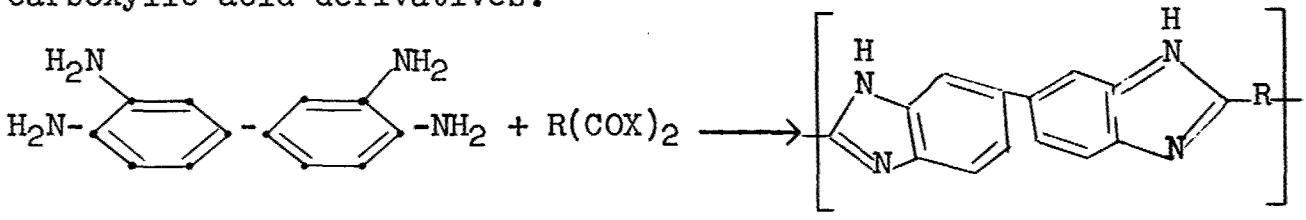
Two such highly aromatic polymeric systems which appear to meet the above specifications - the polybenzimidazoles and the poly(1,3,4-oxadiazoles) - have been the subject of the following research effort.

I. Polybenzimidazoles

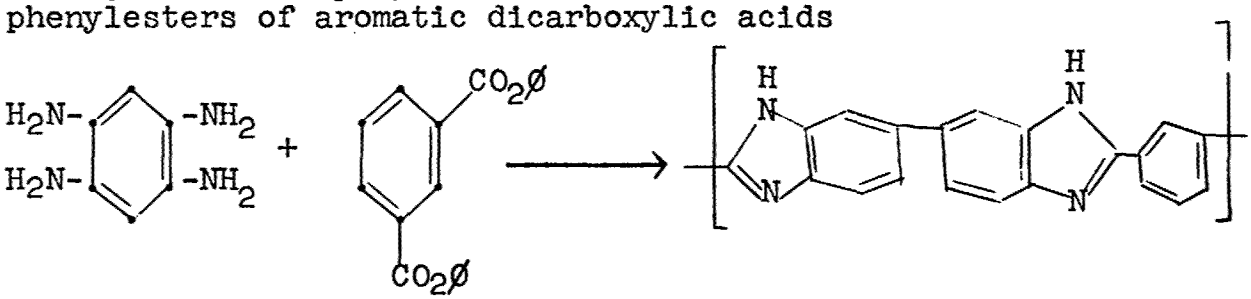
Introduction

Recently, Marvel and Vogel[1] reported the synthesis of a series of polybenzimidazoles having the general property of high thermal stability and therefore of interest for candidacy in satisfying the present demand for super thermal stability in synthetic yarns.

Benzimidazole derivatives are synthesized from o-phenylene diamines and carboxylic acids or derivatives[2]. Extension of this reaction to polymer synthesis was accomplished by Brinker and Robinson[3] by the reaction of bis-o-phenylene diamines and bis-carboxylic acid derivatives:



A modification of this method to produce polybenzimidazoles containing recurring aromatic units was developed by Marvel and Vogel[1] through the melt polymerization of aromatic tetraamines and diphenylesters of aromatic dicarboxylic acids



The work herein reported is concerned with the preparation of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, spinning of this polymer from the solvents dimethylsulfoxide and dimethylacetamide, and the physical properties of yarns so obtained. Further, attempts to prepare the polybenzimidazole based on 3,3',4,4'-tetraaminodiphenylsulfone and isophthalic acid will be reported.

Discussion

Benzimidazoles are generally high melting crystalline solids possessing both acidic and basic characteristics. They are quite resistant to acids, bases, and oxidizing agents[4]. The tautomeric nature of benzimidazole is a well known phenomena rendering both nitrogens in the heterocyclic system equivalent. Hydrogen bonding in benzimidazole unsubstituted in the 1 position has been demonstrated and appears to be due to association via hydrogen bonds between the imino grouping and the tertiary nitrogen[4].

The polymers prepared by Marvel and Vogel exhibited unusually high thermal stabilities and it was decided to prepare one of them in sufficient quantity for spinning and fiber evaluation. Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole was chosen as the first to be evaluated because of the commercial availability of 3,3'-diaminobenzidine tetrahydrochloride, the salt precursor to the required tetraamine.

Techniques employed for purification of tetraamine and polymerization were those devised by Marvel and Vogel. The reactants are polymerized at 260-290° under nitrogen followed by removal of most of the water and phenol by-products by reducing the pressure to 0.1 mm. The resulting low polymer is ground and powder polymerized at temperatures ranging from 290-400° and 0.1 mm. The reaction appears to involve simultaneous or nearly simultaneous evolution of water and phenol rather than preliminary condensation and evolution of phenol to produce a polyaminoamide which then undergoes cyclic dehydration to yield polybenzimidazole. This supposition is given credence by the fact that polyaminoamide prepared by low temperature condensation of isopathalyl chloride and diaminobenzidine does not cyclize on heat treatment to yield polybenzimidazole[5].

Product yields of the polymerization are generally 95%. The bulk polymer is reprecipitated from dimethylsulfoxide or dimethylacetamide with water. In the reprecipitation process about 10% of the solids are insoluble, probably crosslinked materials.

The polymer has been spun from dimethylsulfoxide and dimethylacetamide solvents. Typical fiber properties are summarized in Table I. Yarn obtained by spinning from DMAc is golden yellow in color while the material spun from DMSO is brown. The physical

properties of the two yarns are, in general, comparable although the one spun from DMSO exhibits superior loop and knot properties. It is unlikely that this result is a solvent effect. The polymer spun from DMAc was lower molecular weight material than that spun from DMSO. This fact would account for the inferior loop and knot properties of the former material.

The fibers exhibit strong resistance to concentrated acid and basic solutions. Samples subjected to 40% aqueous sodium hydroxide or 40% aqueous sulfuric acid for 24 hours retained 66% of their original tenacity. Data for hydrolytic stability is summarized in Table II.

Thermal stabilities for poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole fibers were conducted in air. The results of these tests are summarized in Table III and indicate impressive stability at elevated temperatures. Under nitrogen atmosphere the polymer is reported[1] to retain 99% of its original weight after one hour at 500° while in air a sample of fiber disappeared in the oven (Table IV) after one hour at 500°.

The fibers were steam drawn and subsequently re-drawn over a hot pin at temperatures up to 400°. All fibers so treated were highly oriented but amorphous as demonstrated by x-ray diffraction patterns. Additional heat setting experiments failed to induce any crystallinity in the fiber. Mixed solvent experiments employing various concentrations of dimethylformamide-water were also ineffective. A small degree of crystallinity was induced in samples treated with a mixture of formic acid; water (50:50 by volume).

Fiber samples exposed to ultra-violet radiation darken quickly but their physical properties are virtually unaltered after periods up to 220 hours in the Xenotester.

With the hope of reducing the rigidity of the polybenzimidazole chain and possibly enhancing solubility properties, several attempts have been made to prepare the polymer based on 3,3',4,4'-tetraaminodiphenylsulfone and isophthalic acid. Thus far the reactions have yielded only low molecular weight polymer in poor yield. The tetraamine is prepared by conversion of 3,3'-dinitro-4,4'-dichlorodiphenylsulfone to the 4,4'-diamino analog and subsequent reduction of the nitro functions to yield the tetraamine. Purification has proven to be a problem and impurities are probably the cause of the unsatisfactory polymerization experiments.

TABLE I

A) Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole spun from DMAc
fiber properties

1) Drawn 1.65 times at 5# steam and redrawn 1.6 times at 350°C.

				TR			WR		
	T	E	Mi	3	5	10	3	5	10
Straight	4.33	10.8	110	75	58	41	48	31	18
Loop	0.64	1.8	-						
Knot	0.67	2.2	30.3						
Hot-Wet	1.94	18.1	47.0						

B) Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole spun from DMSO
fiber properties

1) Drawn 1.8 times at 12# steam and redrawn 1.2 times at 360°C.

				TR			WR		
	T	E	Mi	3	5	10	3	5	10
Straight	4.16	6.9	121	88	68	--	62	36	--
Loop	1.60	1.5	104						
Knot	2.80	4.0	67						
Hot-Wet	2.40	23.4	74						

a) T = Tenacity (gr./denier)

b) E = Elongation (gr./denier)

c) Mi= Initial Modulus (gr./denier)

d) TR= Tensile Recovery

e) WR= Work Recovery

TABLE II

HYDROLYTIC STABILITIES OF POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE FIBERS

Medium	Time (Hours)	T/E/Mi[a]
None	-	4.5/13/97
10% NaOH 95-100°	1	3.9/22/74
"	3	3.8/26/61
"	6	4.2/29/70
"	24	3.9/38/55
20% NaOH 95-100°	1	4.4/23/75
"	3	4.0/23/70
"	6	3.8/25/65
"	24	3.8/25/68
40% NaOH 95-100°	1	4.1/49/56
"	3	3.0/56/50
"	6	2.8/50/39
"	24	3.0/54/33
10% H_2SO_4 95-100°	1	3.6/36/50
"	3	3.2/35/48
"	6	3.6/42/44
"	24	3.4/38/52
20% H_2SO_4 95-100°	1	3.4/42/44
"	3	3.5/37/45
"	6	3.3/49/39
"	24	3.6/37/52
40% H_2SO_4 95-100°	1	3.4/36/46
"	3	3.6/45/53
"	6	3.4/50/44
"	24	3.1/52/43

a) See footnote in Table I

TABLE III

1) THERMAL STABILITY OF POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE FIBERS

T (in air) °C	Time (Hours)	T/E/Mi[a]
Room Temp.	-	4.5/13/79
300	24	4.1/13/79
"	48	3.6/9/66
"	72	3.6/9/66
"	144	2.8/6/22
"	240	2.5/6/22
350	18	3.0/4/66
"	24	2.4/3/40
400	1	3.8/15/80
"	2.5	2.3/10/60
"	6	1.0/6/60
"	18	TWTT
450	1	2.5/2.5/27
"	3	Disintegrated
500	0.25	TWTT
"	1	Disappeared

2) ULTRAVIOLET STABILITY OF POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE FIBERS

Exposure Time[b] (Hours)	T/E/Mi
0	4.5/13/97
24	4.3/13/97
48	4.3/9/80
78	4.1/7/85
96	4.2/10/80
220	4.1/10/83

a) See footnotes in Table I.

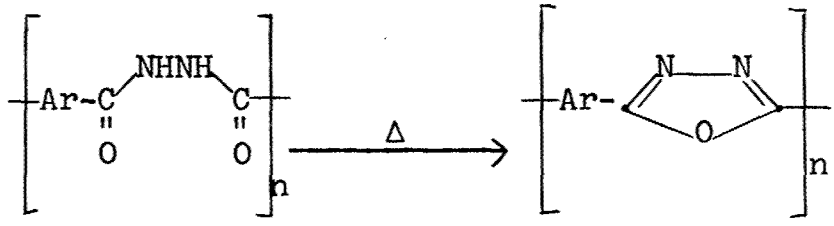
b) One hour in Xenotester is the equivalent of the Florida sunlight.

II. Poly(1,3,4-Oxadiazoles)

1. Introduction

The search for high temperature resistant fibers in the past years has resulted in two major developments. One was the preparation of poly[2,2'-(1,3-phenylene)-5,5'-benzimidazole] bulk polymer and films by Vogel and Marvel[1] and the subsequent fabrication of this polymer into tough fibers by Frazer and Kane.

The other development was, that Frazer[6] discovered and reported aromatic poly[2,5-(1,3,4-oxadiazole)] fibers which had superior high-temperature resistance and excellent fiber properties. Their preparation was accomplished by cyclodehydration of aromatic polyhydrazide fibers at elevated temperature. This fiber conversion is presently the only



route to polyoxadiazole fibers since appropriate preparative and spinning solvents are unavailable[6,7].

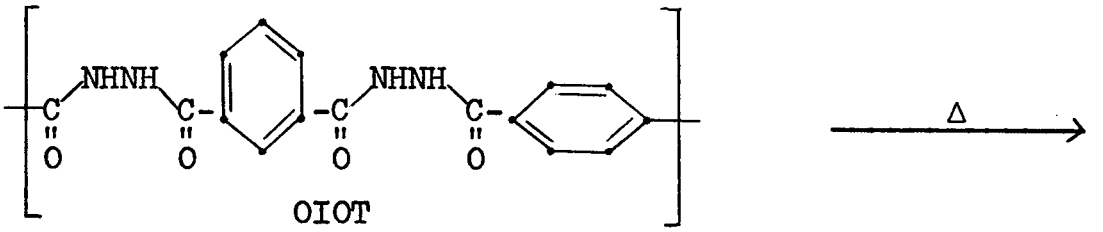
The most promising polyoxadiazole fiber, alt. poly[1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole)]*, was that obtained from alt. poly(1,3/1,4-phenylene hydrazide)** (50:50). The fiber conversion must be quantitative from the chemical standpoint in order to afford the desired high-temperature properties. The fiber conversion must be carefully controlled from a mechanical standpoint in order to maintain the fiber properties through various intermediate polyhydrazide-polyoxadiazole stages. A combination of both requirements is even more difficult to meet on a practical scale since temperatures of at least 280°C. are required for a reasonable rate of the chemical reaction and since sustained temperatures above 320° would degrade the polyhydrazide or any remaining hydrazide link.

As a matter of fact, Stolle[8] and Pellizzare[9] reported that the thermal cyclodehydration of dibenzoylhydrazine, the simplest model, at a temperature of 250-280°C., gave 2,5-diphenyl-1,3,4-oxadiazole, but also traces of diphenyltriazole as signal of such possible degradation and side reactions.

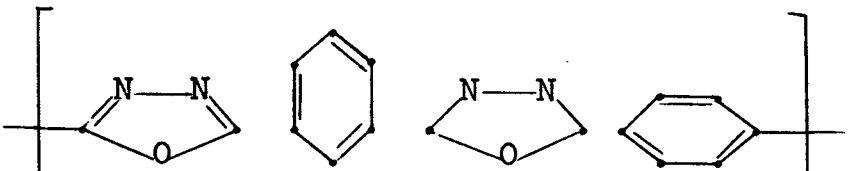
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* Abbreviated and coded as PODZ-I/T.
** Abbreviated and coded as OIOT.

When PODZ-I/T fibers with thermal stabilities and fiber properties superior to those of polybenzimidazoles had been obtained by Frazer[6] it was not unexpected to find that reproducibility (in the context of the foregoing) would be difficult. At least it would require research under most accurately defined reaction conditions using most sensitive analytical tools.



OIOT



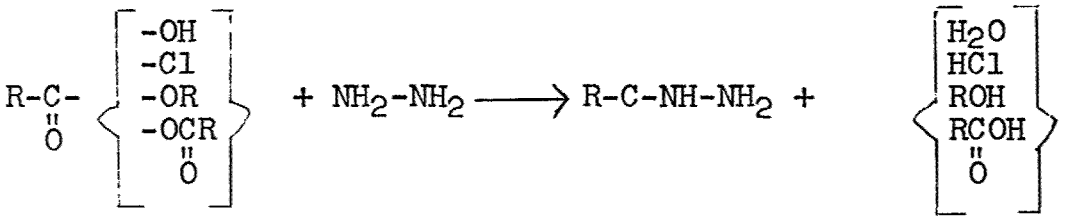
PODZ-I/T

Such an investigation was initiated and the initial effort is reported here. It involved a study of preparing the polyhydrazide OIOT as bulk polymer under various conditions, it involved a study of spinning solvents for OIOT, of drawing ratios and conditions for the yarn and a number of conversion studies of OIOT into PODZ-I/T. Chelation of OIOT fibers, as observed, was noted and assessed and model oligohydrazides and oligooxadiazoles were prepared to aid the study of conversion conditions. Alternate preparations of polyoxadiazoles, such as that by Abshire and Marvel[10] was repeated in amide solvents. New approaches were attempted by reacting bis orthoesters and with dihydrazides and by cyclizing polyhydrazides in solution with the phosphoazo-derivative of cyclohexylamine, and other cyclizing agents.

In short, this report summarizes our present knowledge of polyoxadiazoles, polyhydrazides, polyhydrazide chelates, and of model compounds.

2. Polyhydrazides

For a long time it has been recognized that the reaction between carboxylic acids, esters[11], anhydrides[12], or carbonyl chlorides[13] with hydrazine affords carboxylic hydrazides.



The reaction of esters with hydrazine or 85-100% hydrazine hydrate is regarded to be quantitative while the other acid derivatives frequently lead to undesirable mixtures of mono-, di-, tri-, and tetra-acyl hydrazines[12,14,15,16]. Diesters, when treated with hydrazine hydrate in alcohol yield nearly quantitatively the desired dihydrazides which are polymer intermediates.

Low temperature polymerization of equimolar amounts of dihydrazide and carbonyl chloride in amide solvents such as hexamethylphosphoramide (HMPA), N-methylpyrrolidone (NMP), and N-methylpyrrolidone containing 2-5% lithium chloride was found to be the only preparative method that consistently yielded high molecular weight polyhydrazides.

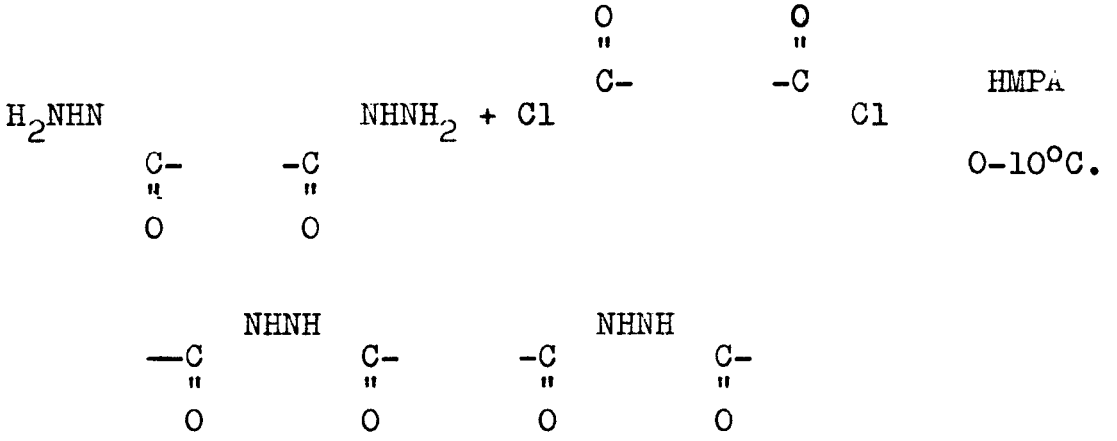
This preparation was discovered by Frazer[6] and was successfully employed[6,7] to cover the whole range of all-aromatic heteroaromatic, aromatic-oxalic, aromatic-aliphatic and all-aliphatic polyhydrazides. For high-temperature resistant polymers it was of course of greatest interest to prepare all-aromatic polyhydrazides and to study their properties and utility. Such polyhydrazides, when obtained in above manner, possessed high melting points (>300°C.) and were of high molecular weight. They were soluble in hot dimethyl sulfoxide, but insoluble in conventional polymer solvents.

3. Polyhydrazide Fibers

At the outset of this program, the polyhydrazide derived from terephthaloyl chloride and isophthalic hydrazide, poly(isophthalic-terephthalic hydrazide), OIOT, was selected for the conversion of its fibers into polyoxadiazole fibers.

a. Preparative Procedures

This polyhydrazide, OIOT, is best prepared in hexamethylphosphoramide (HMPA) from equal amounts of intermediates and in the absence of inorganic salts. The polymerization proceeds for 4-15 hours at room temperature.



The polymer is then washed several times with distilled water and several times with dry methanol and is dried at 80°C. in a vacuum oven. This routine polymerization has been carried out several times during the period covered by this report. Since it was noticed that resulting polyhydrazides contain still small amounts of ash after combustion, it was decided that the polymerization should be carried out in polyethylene flasks with a stirrer manufactured from a nylon rod and a "Teflon"* blade.

Further washings are now carried out with distilled water and deionized water.

b. Spinning Solvents

The polyhydrazide, OIOT, prepared and dried in above manner may be spun from dimethylsulfoxide (DMSO), but is best spun from dimethylacetamide (DMAc). The latter solvent is extremely useful because it allowed to lower the spinning temperature. Various spins have been carried out with DMAc as solvent containing small amounts (2-5%) of lithium chloride. When DMAc without lithium chloride was used as spinning solvent, it was necessary to spin between 100-105°C. because crystallization of the polymer was observed at higher temperatures. Dimethylformamide (DMF) causes rapid crystallization below 100°. The use of DMAc as spinning solvent as compared to DMSO or DMF has other advantages: DMAc is easier removed from the fiber by washing with water than is DMSO; unlike DMSO it does not attack the fiber on heat drawing. This is very important because any degradation of the polyhydrazide from heat drawing prior to conversion influences the fiber properties of the resulting polyoxadiazoles. DMAc as spinning solvent allows to draw the yarn to different levels of properties. Oriented and crystalline yarns are now available with a tenacity ranging from 3 to 6 gpd, elongations ranging from 4 to 24% and moduli ranging from 94 to 169. Table I contains a comparison of fiber properties obtainable when OIOT is spun from DMSO and DMAc. In addition, this spinning solvent affords yarn with various intermediate levels of orientation and crystallinity. Thus, wide ranges of properties are now attainable to

*Trademark for Du Pont's TFE-fluorocarbon resin

study the conversion of polyoxadiazole fibers. For the present report, it has to be noted that conversion studies have been carried out with yarn (OIOT) which still contains appreciable amounts (0.2-0.7%) of ash. Polyhydrazide fibers from ash-free yarn have not been studied up to the present time.

d. Ultraviolet Stability

Films of OIOT were not only used to determine the retention of the polymer but also to study the ultraviolet stability of the material. Polyhydrazide films cast from DMAc or from HMPA showed no color break up to 1000 hours in the Fade-Ometer.

e. Chelate Films

Initial chelating studies of OIOT polymer were also carried out with film because of greater ease of handling. These studies of chelation are now being carried out with fibers (see below). As far as our studies with chelating films are concerned, we have prepared a OIOT/$HgCl_2$ chelate film which was completely transparent, colorless, and could be dried in vacuum at 80° over the weekend without change of appearance. When the same film was heated at 80° in an air atmosphere this film turned brown. Other metal salt chelate polymers of OIOT were prepared but films could not be cast, owing to their insolubility in various solvents. The mercuric chloride/OIOT chelate film was placed in a Fade-Ometer and did not show the usual color break to yellow expected from ultraviolet ageing. Instead, the exposed side of the film turned dark gray and became very brittle after 150 hours of exposure.

The most interesting results in our chelation studies with OIOT films were obtained when these films were cast on aluminum plates or on brass plates. These still preliminary results may be indicative of OIOT chelating of metal. The film cast on brass adhered well for four hours in boiling water. Discoloration of the OIOT occurred simultaneously which is indicative of a picking up of metal ions. More interesting was the film of OIOT cast on aluminum. It could not be removed by boiling the film with the aluminum plate in hot water. It was still firmly attached to the aluminum base after boiling the sample for 3-4 days. This interesting adhesion is possibly due to a polymer-to-metal self-bonding.

f. Chelate Fibers

The rather qualitative results observed for chelate films were followed up with more detailed experiments of chelating on polyhydrazide fibers. This study involves OIOT fibers of various degrees of orientation and crystallization.

TABLE I

POLYHYDRAZIDE (OIOT) FIBER PROPERTIES

Spinning solvent	Dimethylsulfoxide		Dimethylacetamide	
% Solids	25		25	
Spinning & column temp. °C.	125/214		105/220	
Draw ratio/°C.	2X; 10# steam		2X; 10# steam	
Redrawn/°C.	-	1.2X; 310	-	2.0X/310
Ten. (T), % Elong. (#), Mod. (Mi)	3.3/20/76	4.9/24/94	1.9/21/56	3.8/5.6/122
Denier	6.2	5.4	4.4	2.4
Loop T/E/Mi	1.6/5.5	1.9/6.3	1.1/4.6/52	0.4/0.5/85
Denier	5.5	4.7	4.5	2.3
Knot T/E/Mi	2.3/9/52	2.9/10/56	1.4/7.7/40	1.5/1.9/87
Denier	7.1	7.4	4.5	2.1
Elevated T/E.Mi (90°C. air)			2.2/27/46	6.0/11/110
Denier			5.3	2.1
Work Recovery, WR, 3% [RT/RT wet/ 90°C. wet]	35/26/25	34/33/36	33/17/18	39/23/24
Work Recovery, WR, 5%	29/25/26	27/35/39	31/18/16	42/29/31
Ten. Recovery, TR, 3% [RT/RT wet/ 90°C. wet]	66/52/48	65/64/78	63/35/35	68/45/47
Tensile Recovery, TR, 5%	57/52/52	55/62/67	62/38/34	71/56/58
Wash-Set Recovery Angle	120	140	130	145
X-ray crystal. (amt./perf.)	amorph.	med./med.	low/med.	low/low
X-ray orient. (degrees)	64°	good	low	med.
Fiber Stick Temperature FST °C.				305°
Melting Point °C.				370°

The study of chelating fibers was carried out because it was felt that we could produce high temperature resistant fibers other than polyoxadiazoles from OIOT by chelating the fibers with metal salts and if possible, by reducing the metal salts to Me°.

We have, therefore, started up a program of chelating OIOT fibers in a DMF/salt bath. The salt bath contained about 10-15% of metal salt. The bath temperature was maintained as 100 ± 5°C. In some cases, there was added a small amount of tertiary amine in order to make the salt bath more basic. Visually, there was observed differences in chelation, and generally more chelation occurred at the less basic conditions. Table II summarizes the results obtained with amorphous OIOT fiber. The most interesting case observed so far is the chelation of OIOT fiber with silver nitrate. While silver nitrate gives a straw colored chelate fiber, this fiber can be run through a subsequent bath of a tertiary amine such as dimethylaniline. Interestingly enough this tertiary amine bath has reduced $AgNO_3$ on OIOT to Ag°. The resulting polyhydrazide chelate fibers had a silvery gray to black appearance.

4. Model Compounds

The investigation described in this study necessitated the preparation of model compounds for polyhydrazides, polyoxadiazoles and the cyclodehydration reaction. Huisgen[17,18] has reported aromatic oligooxadiazoles but they are exclusively para-linked and not immediately useful here.

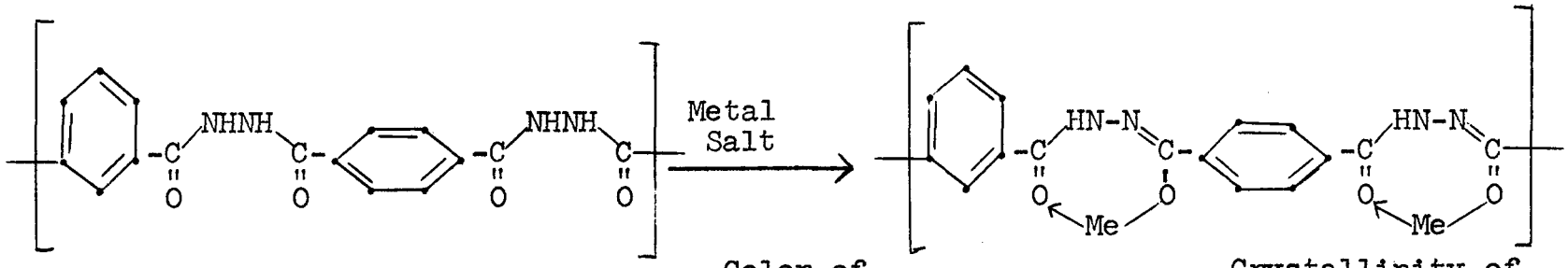
a. Oligohydrazides

A number of model compounds have been prepared which have the alternating sequence of isophthalic and terephthalic hydrazide links. These oligohydrazides are listed in Table III.

Examples 1 and 2 were prepared from dimethyl terephthalate and dimethylisophthalate by treating the respective methanol solution with hydrazine hydrate. Example 3 was prepared by reacting an aqueous solution of hydrazine sulfate simultaneously with sodium hydroxide and benzoyl chloride[19] or by reacting a pyridine solution of benzoyl chloride with hydrazine hydrate. Examples 4 and 5 were obtained by reacting DMAc or pyridine solutions of isophthalic or terephthalic dihydrazide carefully with benzoyl chloride. Example 6, OIOT, is shown in Table III, to depict the relevance of the model compounds for this study.

TABLE II

POLYHYDRAZIDE/CHELATE FIBER PROPERTIES

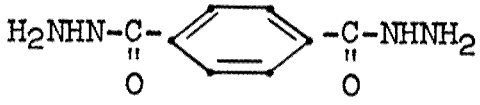


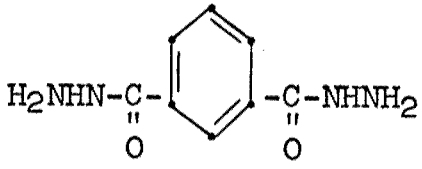
Sample	DMF Bath (I)	Bath II	Color of Dry Yarn	T/E/Mi***	Crystallinity of Yarn/Additive
3	13.9% $CoCl_2$	-	Dk. green	0.5/16/22	Amorphous/ Amorphous
4	13.2% $CoCl_2$ + 4.7% DMA*	-	Lemon	1.1/96/38	Amorphous/ Crystalline
6	16.7% $AgNO_3$	-	Straw	0.7/5/32	Amorphous/ Cryst. (random)
7-I	9.7% $AgNO_3$	DMA*	Black [Ag°]	0.9/65/34	Amorphous/ Crystalline
7-II	9.7% $AgNO_3$	DMA*	Dk. grey [Ag°]	1.3/99/36	Amorphous/ Crystalline
9	10.6% $AgNO_3$**	DMA*	Silvery [Ag°]	1.3/101/36	Amorphous/ Trace Cryst.
10	9.7% $CrCl_3$	-	Olive	1.2/82/37	Amorphous/ Amorphous
11	9.2% $CrCl_3$ + 4.9% DMA*	-	Green	1.2/90/38	Amorphous/ Trace Cryst.

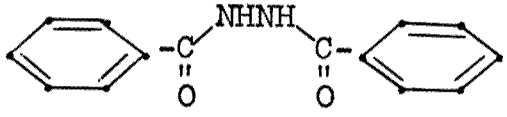
* N,N'-Dimethylaniline
** Short contact time
*** Control 1.8/118/41, undrawn, amorphous

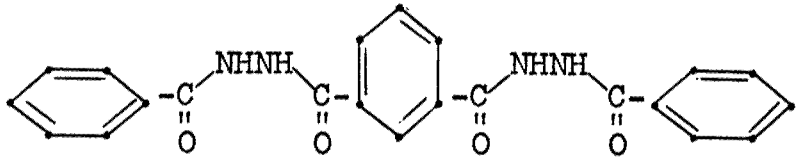
TABLE III

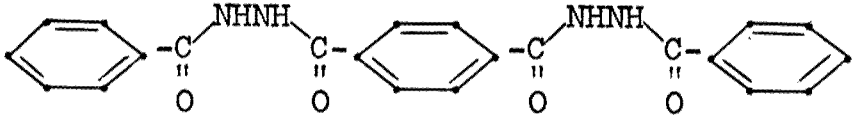
OLIGOHYDRAZIDES

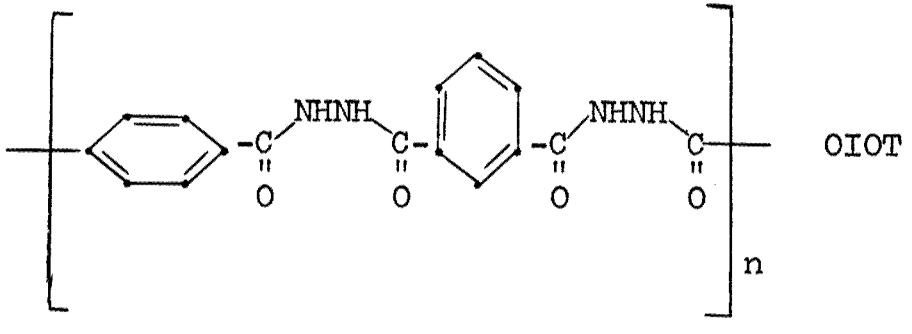
1. 

2. 

3. 

4. 

5. 

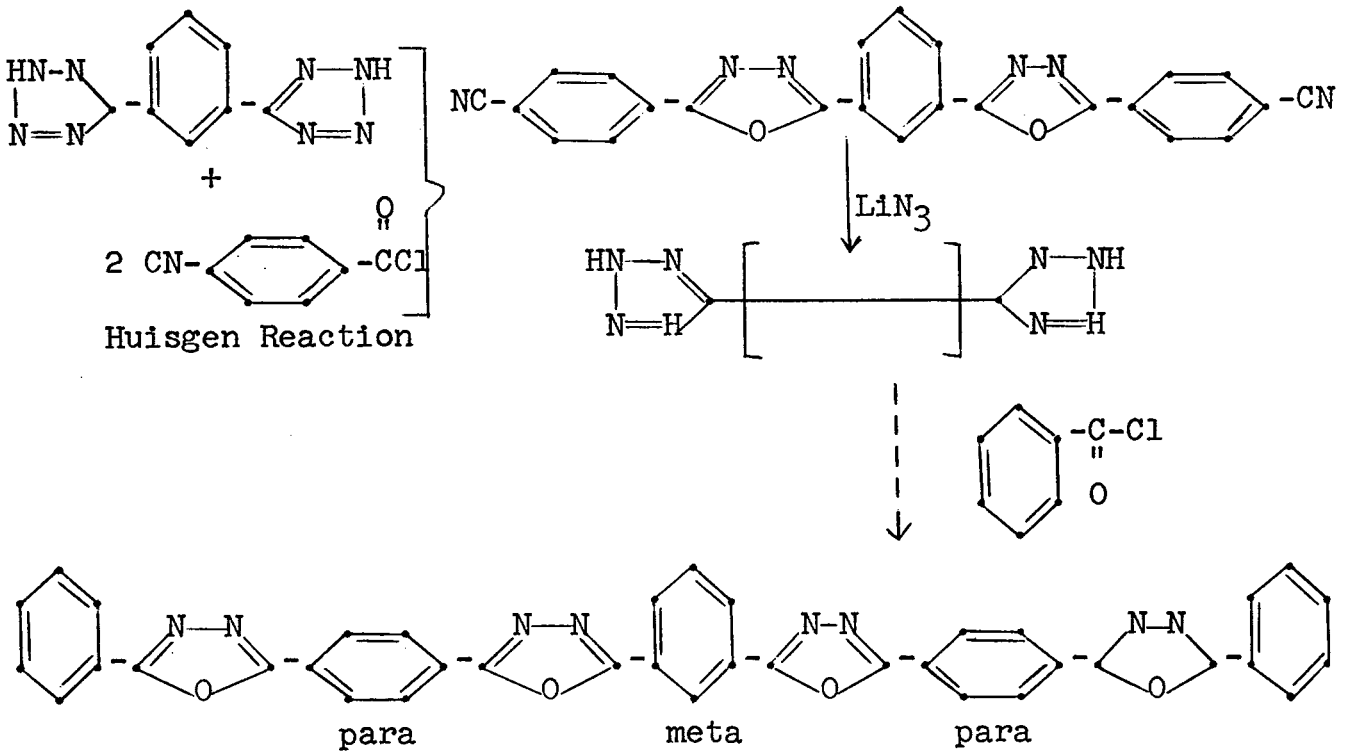
6. 

These hydrazides were prepared as model compounds for the conversion into the corresponding oligo-1,3,4-oxadiazoles by thermal cyclation and dehydration. This conversion is analogous to the conversion of polyhydrazides into polyoxadiazoles. It is presently carried out on a thermogravimetric balance in order to study the exact course and possible kinetics of the conversion.

b. Oligo-1,3,4-oxadiazoles

A number of model compounds containing the polyoxadiazole unit have also been prepared and in some cases are still in the preparative stage (Table IV). These are model oxadiazoles which have two oxadiazole rings per three benzene rings, one of them meta- or paraphenylene rings. They have either been prepared by cyclodehydration of oligohydrazides in pyridine[20] or DMAc or by the Huisgen reaction [17,18], whereby high yields of 1,3,4-oxadiazoles result from treatment of acid chlorides with tetrazoles.

The preparation of the 9-membered oligo-1,3,4-oxadiazole (see below) is analogous to that described by Huisgen for a 9-membered oxadiazole consisting of exclusively p-phenylene rings and oxadiazole rings. The oligooxadiazole described here, however, is much more pertinent as model compound for PODZ-I/T because of its alternating structure, consisting of m-phenylene, p-phenylene and 2,5-disubstituted 1,3,4-oxadiazole rings.



The dinitrile was prepared from p-cyanobenzoyl chloride[21], and was subsequently treated with lithium azide. This is essentially the principle of the Huisgen Reaction[17,18] which allows building up of oligooxadiazoles resembling polyphenyls.

5. Poly(1,3,4-oxadiazoles)

a. Preparative Methods

Abshire and Marvel[10] have reported the preparation of polyoxadiazoles from ditetrazoles with diacid chlorides in inert solvents. This type of preparation was repeated with amide solvents such as hexamethylphosphoramide (HMPA). It was hoped that higher molecular weight polyoxadiazole would result. A few experiments using this variation of Marvel's route yielded polyoxadiazole with low viscosities ($\eta inh < 0.3$). No solvents other than sulfuric acid were found.

Another method for preparing polyoxadiazoles was briefly studied. It involves the reaction of bis orthoesters and dihydrazides as an application of the nonfunctional model reaction reported by Ainsworth[22]. Thus the diethyl succinate was prepared with great difficulty[23] in reasonably pure form but no high molecular weight polymer was obtained in this condensation. Three other intermediates[24,25] for the preparation of bis orthoesters were also prepared: dimethyliminosuccinate, diethyliminosuccinate and diethyliminoisophthalate. No further attempts are contemplated to prepare polyoxadiazoles by these or other routes. Hence no further effort will be made to prepare the bis orthoesters from these iminosuccinates by treatment with absolute alkanols.

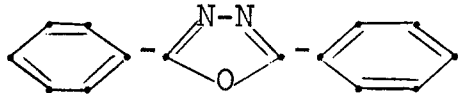
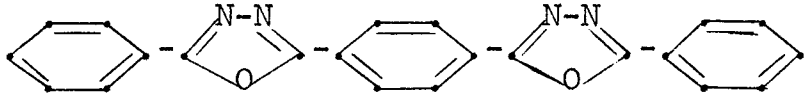
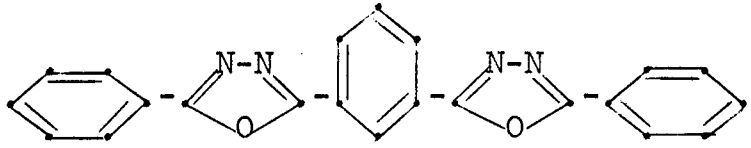
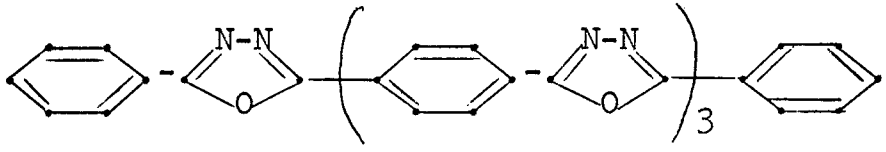
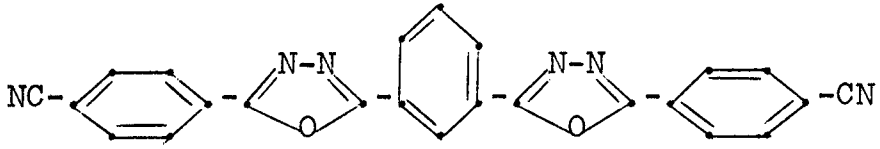
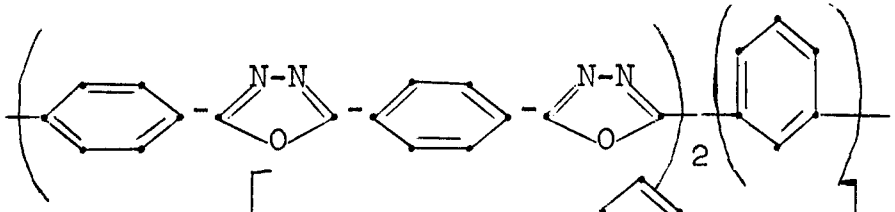
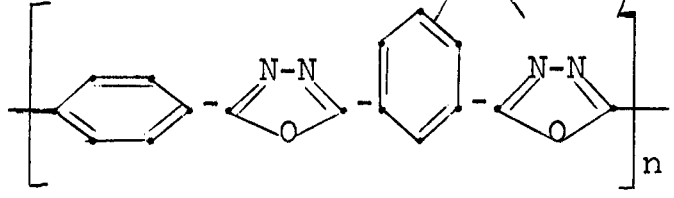
b. Cyclodehydration of Polyhydrazides

The inaccessibility of polyoxadiazoles by such routes as described above, the lack of solvents for such polymers and the excellent synthesis of high-molecular weight polyhydrazides discovered by Frazer[6], made this polymer and its fibers the potential intermediate for polyoxadiazole fibers. For example, the alternating isophthalic/terephthalic polyhydrazide, poly-(1,3-/1,4-phenylene hydrazide) (50:50), as bulk polymer, was shown to be more or less convertible into polyoxadiazole under a variety of conditions patterned after monomeric model reactions.

The cyclodehydration of monomeric model reactions[26] is carried out at elevated temperatures (thermal conversion) or in solution with chlorosulfonic acid, sulfuryl chloride, toluene sulfonic acid, tosyl chloride, organic anhydrides, and sulfuric acid.

TABLE IV

OLIGO-1,3,4-OXADIAZOLES

	Ref.	Max.	log	Solvent
	17	280.0 280.0	4.44 4.45	EtOH DMF
	1 17,18 -	323 312.5 312.0	- 4.69 4.69	H_2SO_4 DMF DMF
	- 1	287.5 297.0	4.74 -	DMF H_2SO_4
	18	327.5	-	DMF
	-	295.0	4.80	DMF
	-	-	-	-
Polymer: PODZ-I/T 	-	332.0	-	H_2SO_4

Hence, several types of conversions were studied and are described in the following paragraphs. They are thermal cyclization of polyhydrazide bulk and fiber samples in the absence of a solvent, and cyclodehydration in solution by thermal or chemical means.

Thermal conversion of polyhydrazide fibers is described in a later chapter. Conversion of polyhydrazide (OIOT) bulk samples at elevated was studied by various means. A finely ground (40 mesh) sample of polyhydrazide was heated for 48 hrs. at 283° (0.4 mm). The resulting sample analyzed clearly for polyoxadiazole, as judged by carbon, hydrogen, and oxygen analyses.

Six samples of polyhydrazide fiber were heated in a steel bomb with steam at 254°C. (inside temperature) and 585 lbs. pressure. It was hoped that steam at this temperature might effect cyclization. However, the fiber degraded badly.

Thermal conversions of polyhydrazides in solution were also attempted in hexamethylphosphoramide at 200°C. by heating a 10% solution for 24 hrs. under nitrogen. During the course of the reaction, solid polymer precipitated which analyzed for polyoxadiazole with a 90% degree of conversion as judged by carbon, hydrogen, and oxygen analyses.

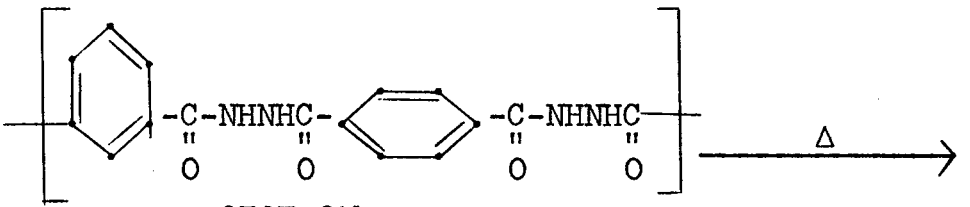
Mild dehydrating agents in solution, such as N,N'-dicyclohexylcarbodiimide, trichloroacetonitrile, and tetrachlorodifluoroacetone were without effect. No change in oxygen analysis was obtained when samples were withdrawn over a period of four days. Strong dehydrating agents such as acids or bases degraded the polyhydrazide partially or totally while conversion occurred.

Klingsberg[27] had reported that symmetrical aromatic dihydrazides could be converted into 2,5-disubstituted oxadiazoles by the reaction of phosphoazo-derivatives of cyclohexylamine [$C_6H_{11}N{=}PNHC_6H_{11}$]. In an attempt to convert polymeric hydrazides into polymeric oxadiazoles, a 2.5% solution of OIOT in a mixture of dimethylsulfoxide and o-dichlorobenzene was treated with the phosphoazo-derivative of cyclohexylamine and of aniline. After heating on a steam bath, a yellow color appeared in each case; both solutions were precipitated with acetone. The microanalytical results on the dry specimens showed that high molecular weight polyhydrazide was recovered unchanged in each case. Hence, this method is not suitable for conversion of polyhydrazides into polyoxadiazoles.

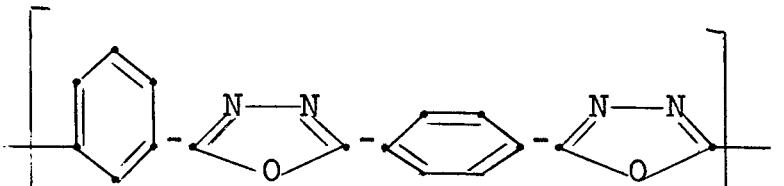
The polymer from the solution and bulk conversions was not soluble in trifluoroacetic acid which occasionally dissolves this polyoxadiazole. Owing to insolubility of polymeric oxadiazoles in a large number of solvents, it appeared that thermal conversion of solid polyhydrazides into solid polyoxadiazoles was the most promising route for this polymer post-reaction. Hence, polyhydrazide fibers were converted into polyoxadiazole fibers.

6. Polyoxadiazole Fibers

A study of thermal conversion of OIOT into the corresponding oxadiazole (PODZ-I/T) was carried out and is still in progress. This study was designed to furnish information about the dehydration-cyclization mechanism with the objective to find the



OIOT fiber



PODZ-I/T fiber

optimum conversion conditions. Such conversions were attempted on polyhydrazide fibers in vacuum at 222, 242, 265, and 283°C. Thermal conversions were also attempted on finely ground (40 mesh) polyhydrazide powder at 283° in vacuum. In addition, a number of attempts of thermal and chemical conversions of polyhydrazide solutions were studied.

a. Conversion in Vacuum

The thermal conversion studies on polyhydrazide yarn (T/E/Mi = 5/24/80) in vacuum were carried out by heating 3 to 6 samples of yarn wound around a perforated metal bobbin. Periodically samples were withdrawn to follow the conversion with time. Withdrawn samples were analyzed and showed the following results: No conversion occurred at 222°C. within 72 hrs., as evidenced by virtually unchanged oxygen analysis. At 242°, there was a slow conversion (about 50% in 50 hrs.) with gross deterioration of yarn properties. At 265°, the conversion proceeded fairly rapidly. However, the final yarn properties were poor. At 283°, complete conversion was noticed in less than 12 hrs. When this sample was further heated at 283°, it was noted that a continuous drop in yarn properties occurred which leveled off after about 100 hrs. (T/E/Mi = 0.6/0.8/87).

This suggests that the history of the starting polyhydrazide, despite its excellent yarn properties, is definitely important for the subsequent conversion characteristics. Traces of solids such as ash or degradation products of the spinning solvents may clearly influence the final polyoxadiazole properties.

b. Conversion in Solvent Vapors

A bobbin of oriented and crystalline polyhydrazide yarn (T/E/Mi = 5/24/80) was boiled in diphenylmethane vapors (b.p. 265°) for 100 hrs. Eighty to ninety percent conversion, as judged by oxygen analysis, occurred but the properties of the resulting polyoxadiazoles had decreased to T/E/Mi=2.2/3/92. A similar conversion in boiling diphenylethane (b.p. 284°) was found to be complete after about two days (T/E/Mi = 0.7/0.7/85). Yarn converted in boiling diphenylmethane degraded badly after one-hour exposure to 400°C.

The properties of polyoxadiazole fibers listed in Table V are the result of a more detailed study to develop techniques for the conversion rather than large amounts of yarn sample. These fibers were obtained in an oven in nitrogen atmosphere using good circulation at 280°C. Because of the chelating tendency of polyhydrazide, it was advisable to use "Teflon" bars to support the skeins of polyhydrazides during conversion studies rather than glass or metal bars.

TABLE V

POLY-1,3,4-OXADIAZOLE (PODZ-I/T) FIBER PROPERTIES

Ten. (T), % Elong. (E), Mod. (Mi)	2.6/3.1/124
Denier	3.0
Loop (Tenacity/Elongation)	1.8/2.8
Denier	3.9
Knot (Tenacity/Elongation/Modulus)	2.3/2.8/79
Denier	3.0
X-ray Crystallinity (amount/perfection)	low/low
X-ray Orientation (degrees)	31° (outer) 38°
Wash-Set Recovery Angle	290°

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THE PREPARATION AND EVALUATION OF POLY(PHENYLENE)TRIAZOLES

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ABSTRACT

This research was carried out for the purpose of evaluating poly(phenylene)triazoles for use in fiber and film applications at high temperatures. Initial work emphasized the preparation, purification and characterization of the necessary intermediate compounds for the preparation of poly(phenylene)triazoles from reactions of phenylene-bis-tetrazoles.

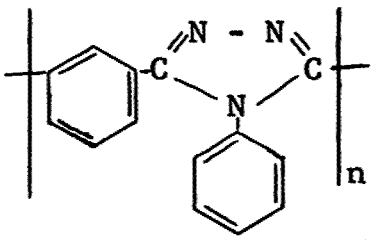
1,4- and 1,3-Bis[3,4-diphenyl-1,2,4-triazolyl-(5)]benzenes were prepared as model compounds containing the desired triazole structure in combination with the para- and meta-phenylene groups. Thermal evaluation of these compounds by differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) showed them to be stable to their melting points with no weight-loss up to 500°C.

Efforts to prepare high molecular weight poly(phenylene)-triazoles by the reactions of phenylene-bis-tetrazoles with diimino-chlorides under a variety of conditions have thus far been unsuccessful. Improved solvent systems are being sought, and butyrolactone-pyridine mixtures appear to be the most promising of those tried.

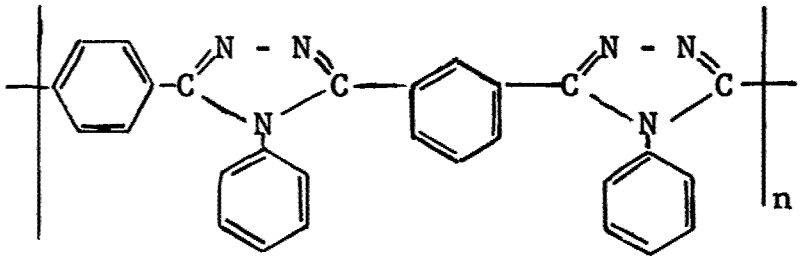
An alternate synthesis approach to prepare polytriazoles by condensing diacid hydrazides with diamides in the presence of hydrazine at elevated temperatures and pressures has resulted in products of uncertain compositions.

I. INTRODUCTION

Among the polyaromatic systems investigated by Abshire and Marvel,[1] two examples of poly(phenylene)triazoles, poly(3,5-bis-m-phenylene-4-phenyl)-1,2,4-triazole,



and poly(3-m-,5-p-phenylene-4-phenyl)-1,2,4-triazole,



were reported. These polymers showed reasonably good thermal stability and were considered to be potential candidates for high temperature fiber and film applications. However, in order to obtain fibers and films of the poly(phenylene)-triazoles for evaluations in high temperature applications, it is necessary to find means for preparing higher molecular weight polymers; this is the principal objective of the work reported in this paper. Approaches taken to attain this goal include:

(1) The preparation of high-purity polymerization intermediates.

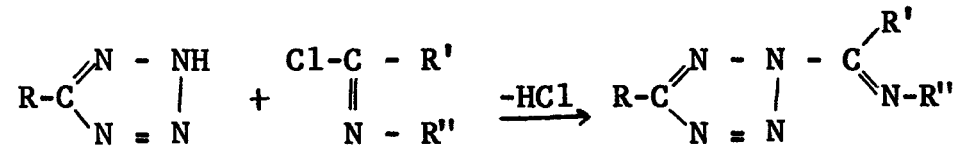
(2) The preparation and characterization of model phenylene-triazole compounds for reference purposes.

(3) The screening and evaluation of polymerization solvents and techniques.

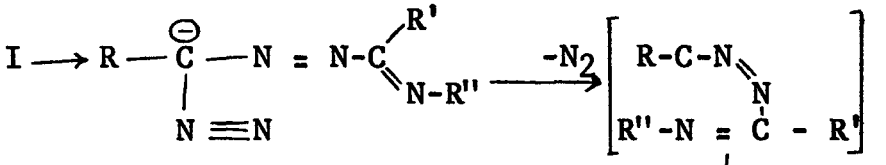
II. DISCUSSION

A. Poly(phenylene)triazoles from reactions of Phenylene-bis-tetrazoles

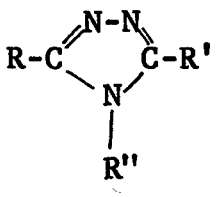
Huisgen, Sauer and Seidel[2] reported a general preparation of 1,2,4-triazoles from the reaction of 5-substituted tetrazoles with imino-chlorides. They proposed the mechanism of the reaction to be as follows:



I



II



III

Whether the liberation of nitrogen from II and the ring closure to III took place by a stepwise or a conserted process was an open question. These authors suggested the use of this type reaction with phenylene-bis-tetrazoles and imino-chlorides as a route to linear polyaromatic substances. Abshire and Marvel[1] applied this general reaction to obtain low molecular weight poly(phenylene)-triazoles from the reactions of m- and p-phenylene-bis-tetrazoles with N,N'-diphenylisophthaliminochloride. We chose this route as the starting point for our investigations, because the reactions involved were reasonably well defined and the chances for interfering side reactions appeared small.

1. Preparation of High-Purity Polymerization Intermediates

In most condensation polymerizations high-purity reactants are necessary to obtain high molecular weight polymers of known composition and properties. Therefore, a program of synthesis, purification and characterization was undertaken to provide supplies of high-purity m- and p-phenylene-bis-tetrazoles and N,N'-diphenyl-iso- and tere-phthalimino-chlorides for use in subsequent condensation polymerization studies. The synthesis routes used for preparing these compounds were those followed by Abshire and Marvel[1] with some modifications to individual reactions. The purifications of these compounds were greatly facilitated by the use of high-purity intermediates in their preparations. Consequently, the iso- and tere-phthalonitriles used in the preparations of the bis-tetrazoles, and the N,N'-diphenyl-iso- and tere-phthalamides used in the preparations of the imino-chlorides were rigorously purified.

High-purity iso- and tere-phthalonitriles were obtained from the corresponding acids in 50-60% yields by a single-step synthesis. A mixture of the acid, urea and dehydrating catalyst was stirred and heated in adiponitrile until all of the dinitrile had distilled from the mixture with the aid of an ammonia sweep gas. The isophthalonitrile, thus obtained, was purified by recrystallization from methanol; and the tere-phthalonitrile was recrystallized from dimethylformamide (DMF) and/or n-butyl alcohol.

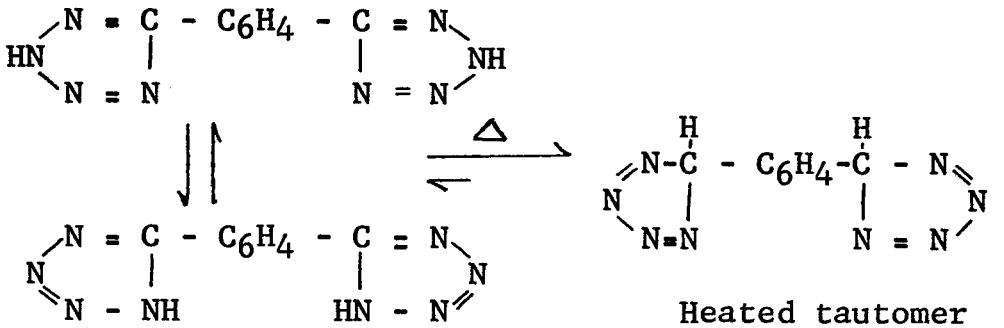
N,N'-Diphenyl-iso- and tere-phthalamides were prepared in 90-95% yields by use of the Schotten-Baumann technique. Aniline was added to a mixture of a benzene solution of the diacid chloride slurried with an aqueous sodium bicarbonate solution. Analytically pure N,N'-diphenylisophthalamide (m.p. 282-283.5°C; reported[3] m.p., 245-250°C) was obtained by recrystallizations from cyclohexanone and butyrolactone. Analytically pure N,N'-diphenylterephthalamide (m.p. 336.0-336.2°C) was obtained by recrystallizations from DMF and butyrolactone.

Several improved synthesis procedures for 5-aryltetrazoles have been reported in the recent literature[4,5,6]. Herbst and Wilson[4] pointed out that higher boiling solvents facilitated the reaction of hydrazoic acid with arylnitriles to

give 5-aryltetrazoles. They developed a procedure wherein n-butyl alcohol was used as the reaction solvent, and hydrazoic acid was generated in situ from sodium azide and glacial acetic acid. The reaction was complete after heating under reflux for six days. Huisgen, Sauer, Sturm and Markgraf[5] prepared 5-aryltetrazoles in ethylene glycol monomethyl ether as the solvent. They used lithium azide in place of hydrazoic acid. By this procedure the reaction was complete after heating under reflux for five days. Finnegan, Henry and Lofquist[6] prepared 5-phenyltetrazole in quantitative yield by heating benzonitrile and ammonium azide in DMF at 125°C for seven hours. These authors also pointed out that the reaction was subject to acid catalysis.

A quantitative yield of p-phenylene-bis-tetrazole was obtained after only three hours by heating under reflux a mixture of terephthalonitrile and hydrazoic acid (generated in situ) in diethylene glycol monoethyl ether. A 95% yield of m-phenylene-bis-tetrazole was similarly obtained after 24 hours of heating under reflux in ethylene glycol monomethyl ether. Analytically pure p-phenylene-bis-tetrazole (decomposition point 302°C) was obtained by recrystallization from DMF. m-Phenylene-bis-tetrazole (decomposition point 275°C) was purified by recrystallizations from methanol and pyridine.

Interesting phenomena observed in the determinations of some of the physical properties of m- and p-phenylene-bis-tetrazoles led us to propose the occurrence of the following heat sensitive tautomeric shift:



Unheated tautomer(s)

Heated tautomer

The tautomerization of the unheated tetrazole in solution was discussed by Herbst[7]. Occurrence of a thermal tautomerization is supported by the following observations:

The DTA thermograms of p-phenylene-bis-tetrazole (Figure 1) and m-phenylene-bis-tetrazole (Figure 2) exhibited very strong endothermic peaks in the temperature range of 90-180°C. A TGA weight-loss plot of m-phenylene-bis-tetrazole showed negligible weight-loss below its decomposition point. DTA thermograms of samples of p-phenylene-bis-tetrazole and m-phenylene-bis-tetrazole which had been heated at 125°C overnight and then cooled to room temperature showed no endothermic peaks (Figures 3 and 4, respectively). Also, the infrared spectra of the heated samples showed no characteristic peaks for >N-H (3350 cm^{-1}) or >C = N- (1600 cm^{-1}) which were present in the spectra of the unheated samples. X-ray diffraction patterns of the heated and unheated m-phenylene-bis-tetrazole showed distinctly different crystalline lattices. Microscopic examination of the unheated m-phenylene-bis-tetrazole on a hot stage, under polarized light, revealed the formation of minute, weakly birefringent crystals around the original sample at about 130°C. Similar examination of a preheated sample of m-phenylene-bis-tetrazole showed no such crystal formation in this temperature range.

Samples of the two tetrazoles which were heated at 130°C overnight, dissolved in sodium carbonate solution and reprecipitated by the addition of acid, showed identical characteristics to those of the unheated samples. Also, a sample of the m-phenylene-bis-tetrazole which had been heated and then recrystallized from methanol showed identical characteristics to those of the unheated tetrazole. A sample of heated m-phenylene-bis-tetrazole, after standing at room temperature for one week, exhibited an identical infrared spectrum to that of the freshly heated sample. However, after standing for three weeks in a desiccator, the infrared spectrum of the sample showed the presence of a small, but significant >N-H peak at 3350 cm^{-1}.

In light of the facile reversion in solution of the heated tetrazole forms to those of the unheated forms, the identical ultraviolet spectra of the heated and unheated p-phenylene-bis-tetrazole in methanol was not surprising. Both samples of p-phenylene-bis-tetrazole showed strong absorption peaks at 265 $m\mu$.

Abshire and Marvel[1] reported the preparation of N,N'-diphenylisophthalimino-chloride by heating a mixture of N,N'-diphenylisophthalamide and excess thionyl chloride under reflux for twelve hours. This was an application of the general procedure developed by von Braun and Pinkernelle[8] for the preparation of imino-chlorides from amides derived from aromatic acids. We obtained N,N'-diphenylisophthalimino-chloride in 92% yield by heating a mixture of the amide and a large excess of thionyl chloride under reflux overnight. Similarly, we obtained a 40% yield of crude N,N'-diphenylterephthalimino-chloride, although Marvel[3] had noted that they had been unsuccessful in preparing the para-isomer by this general procedure.

Bosshard et al.[9] reported the excellent catalytic effect of DMF on the preparations of acid chlorides from free acids which did not react with thionyl chloride in the absence of a catalyst. These authors attributed the catalytic activity of the DMF to the formation of a more reactive intermediate.

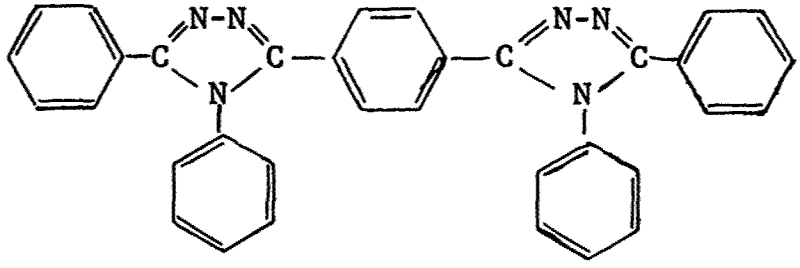
$$(CH_3)_2N\text{-}CHO + SOCl_2 \longrightarrow \left[(CH_3)_2\overset{+}{N} = CHCl \rightleftharpoons (CH_3)_2N\text{-}\overset{+}{C}HCl\right] \bar{C}l + SO_2\uparrow$$

$$RCOOH + \left[(CH_3)_2\overset{+}{N} = CHCl\right] \bar{C}l \longrightarrow RCOCl + (CH_3)_2N\text{-}CHO + HCl\uparrow$$

Similarly, we found DMF to be a catalyst in the preparations of imino-chlorides by the method of von Braun and Pinkernelle[8]. By adding a catalytic amount of DMF to the reaction mixture, N,N'-diphenylisophthalimino-chloride (m.p. 149-150.4°C; reported[1] m.p., 155-156°C) was obtained in 98.5% yield after heating under reflux for only three hours. The imino-chloride, which is extremely sensitive to moisture, was purified by recrystallization from isooctane under anhydrous conditions. N,N'-Diphenylterephthalimino-chloride (m.p. 194-195°C) was similarly obtained in 84% yield after heating the reaction mixture under reflux for a day. This imino-chloride, also extremely moisture sensitive, was recrystallized from tetrahydrofuran under anhydrous conditions.

2. Preparation and Characterization of Model Phenylenetriazole Compounds

Huisgen, Sauer and Seidel[2] reported the preparation of 1,4-bis [3,4-diphenyl-1,2,4-triazolyl-(5)] benzene,



from the reaction of p-phenylene-bis-tetrazole and N-phenyl-benzimino-chloride. This compound contains the p-phenylene-triazole repeating unit, which we hope to obtain in the polymer from the reaction of p-phenylene-bis-tetrazole with N,N'-diphenylterephthalimino-chloride. This p-phenylenetriazole (m.p. 425.5°C) was prepared according to the procedure described by Huisgen et al.[2] to serve as a model compound. The infrared spectrum of this compound should serve as a useful reference for detecting or substantiating the presence of the p-phenylene-triazole system in polymerization products. A study of the thermal stability of this model compound should give some insight into the general thermal stability of the p-phenylene-triazole polymer system. A DTA thermogram (Figure 5) showed it to be stable up to its melting point at 430°C, but an exo-thermic reaction commenced immediately after, or simultaneously with, the melting. However, a TGA weight-loss plot (Figure 6) showed no significant weight-loss up to 500°C, at which temperature general degradation occurred. Inherent viscosity data were obtained on the model compound (M.W. 517) in formic acid to be used as a guide in estimating the molecular weights of low molecular weight p-phenylenetriazole polymer samples.

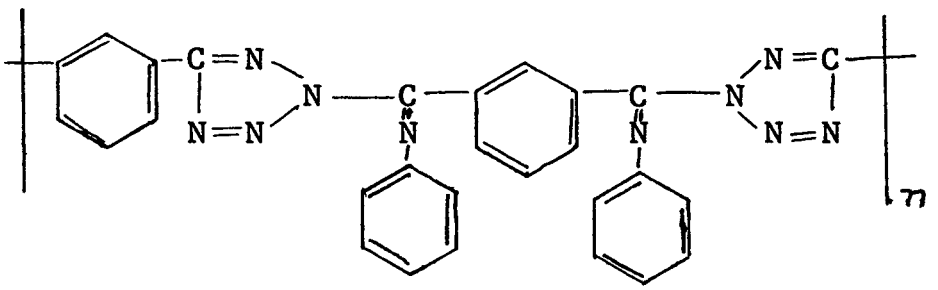
The corresponding m-phenylenetriazole model compound, 1,3-bis [3,4-diphenyl-1,2,4-triazolyl-(5)]benzene, a previously unreported compound, was prepared by the reaction of m-phenylene-bis-tetrazole and N-phenylbenzimino-chloride. The melting point of this meta-phenylenetriazole model compound, 243.5°-244.0°C, was surprisingly low compared to that of the para-isomer, 425.5°C. However, the TGA weight-loss plot of the model meta-compound (Figure 7), like that of the para-compound, showed no significant weight-loss below its decomposition point at 500°C. Again, the DTA thermogram of this model compound (Figure 8) showed it to be stable up to its melting point with a slowly

increasing exothermic reaction beginning immediately after melting had occurred. The infrared spectrum of the meta-compound was quite similar to that of the para-isomer, having similar principal peaks at 1500 cm^{-1}, 1470 cm^{-1}, and 1425 cm^{-1}. Substantiation of the identity of the meta-model compound was fairly well completed by a satisfactory elemental analyses report.

3. Screening and Evaluation of Polymerization Solvents and Techniques

Huisgen et al.[2] and Marvel[3] prepared triazole compounds by heating 5-substituted tetrazoles and imino-chlorides in pyridine. We followed this general procedure using the phenylene-bis-tetrazoles and phthalimino-chlorides at reflux temperature (115°C) and at 90°C for 96 and 120 hours, respectively. Precipitation of the polymers from the hot reaction mixtures resulted in products of low molecular weights. At 90°C, the reaction appeared to produce a mixture of polymers containing both triazole and tetrazole rings. Evidence for this was the evolution of gas on heating the polymer and an exothermic reaction at 275-285°C as shown by a DTA thermogram. This led us to prepare and isolate the intermediate tetrazole polymer and study its thermal conversion to the polytriazole structure.

Polymerization of m-phenylene-bis-tetrazole and N,N'-diphenyl-isophthalimino-chloride in refluxing tetrahydrofuran (THF), containing sufficient potassium carbonate to neutralize the hydrogen chloride released, produced a product believed to be largely the intermediate tetrazole polymer:

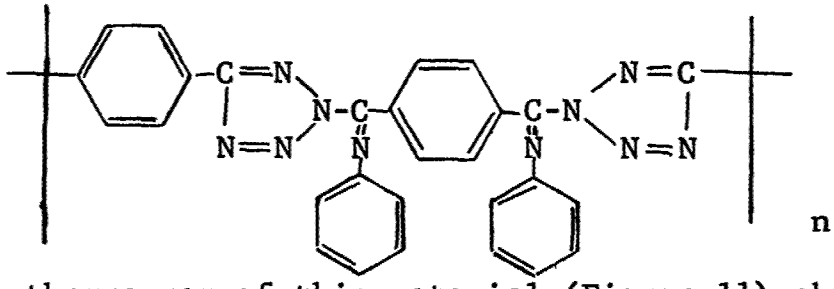


The DTA thermogram of this material (Figure 9) showed a very strong exotherm at 290-310°C. This type of exotherm was also observed for the tetrazole monomer (Figure 2) at a slightly

higher temperature and was interpreted as decomposition of the tetrazole ring. A TGA weight-loss plot (Figure 10) for this sample showed little weight-loss below 290°C. At 290°C a sudden weight-loss of 12.7% occurred. This temperature corresponded to the DTA exotherm and the weight-loss compared favorably with the calculated weight-loss of 12.95% in going from a polytetrazole to a polytriazole structure. There was little additional weight-loss from 290°C to 450°C, indicating good thermal stability for the assumed triazole structure in that range. From 450°C to 600°C, considerable weight was lost leaving a completely carbonized residue. The weight-percent of this residue agreed with the theoretical carbon content (68%) of the starting polytetrazole sample. The tetrazole polymer was soluble in formic acid; however, low viscosity values indicated a very low molecular weight for the polymer.

A sample of the tetrazole polymer in adiponitrile was slowly heated to 270°C. The evolution of gas during heating and the almost complete elimination of the exotherm at 300°C from the DTA thermogram of the resulting material were strong indications of conversion to the polytriazole structure. Infrared absorption spectra of the heated and unheated polymer, while different, could not be conclusively interpreted. On heating the dry, powdered tetrazole polymer to 300°C, vigorous evolution of gas occurred resulting in a brittle, amber-colored foam. Carbonization occurred more readily with the dry polymer than with an adiponitrile solution of the material.

The polymerization procedure using refluxing THF as solvent was repeated with p-phenylene-bis-tetrazole and N,N'-diphenyl-terephthalimino-chloride to give the isomeric p-phenylene tetrazole polymer:



The DTA thermogram of this material (Figure 11) showed the characteristic tetrazole decomposition exotherm at 305-325°C. The TGA weight-loss plot (Figure 12) was similar to that of

the poly(m-phenylene)tetrazole except in the upper temperature range. A 3.8% loss of weight occurred up to 300°C. The sharp loss of 13.3% of sample weight observed at 300°C compared well with the calculated theoretical loss of nitrogen in going from the polytetrazole to the polytriazole structure. Above 300°C this material was less stable than the poly(m-phenylene)triazole product. A weight-loss of 6.2% occurred between 300°C and 400°C and rapid carbonization was indicated above 400°C.

Sauer, Huisgen and Sturm[10] reported the tetrazole anion to be more thermally stable than the substituted or free tetrazoles. Previous poly(phenylene)triazoles obtained by the reactions of the phenylene-bis-tetrazoles and the diimino-chlorides have contained some residual tetrazole rings. It seemed possible that the triazole rings would be formed progressively at the ends of the growing polymer chains if the diimino-chloride were added to the disodium salt of the phenylene-bis-tetrazole at a temperature such that the less thermally stable substituted tetrazole rings would decompose as they were formed. To investigate this possibility, the disodium salt of m-phenylene-bis-tetrazole was prepared in DMF and heated to 140-145°C which effected complete solution of the tetrazole salt. A hot solution of N,N'-diphenylisophthalimino-chloride in DMF was added dropwise to the hot salt solution causing simultaneous gas evolution and the precipitation of an orange-colored solid. Work-up of this reaction mixture by a rather tedious procedure resulted in the isolation of an 82.6% yield of polymer. However, this polymer was shown by a DTA thermogram to contain some unchanged tetrazole rings. Viscosity data indicated a molecular weight of probably not much more than 1000.

The difficulties encountered in the preparations of poly-(phenylene)triazoles of sufficiently high molecular weight to have fiber forming characteristics seemed to center around the insolubility of the initially formed polymers in the solvent media used. Hot DMF containing 5% dissolved lithium chloride was found to dissolve about 15% of its weight of the low molecular weight polymer. However, only decomposition products were obtained from the addition of N,N'-diphenylisophthalimino-chloride to disodium m-phenylene-bis-tetrazolate in this salt solution at 140-150°C.

The possibility existed that the imino-chloride may have been reacting with the hot DMF. Therefore, hot pyridine containing

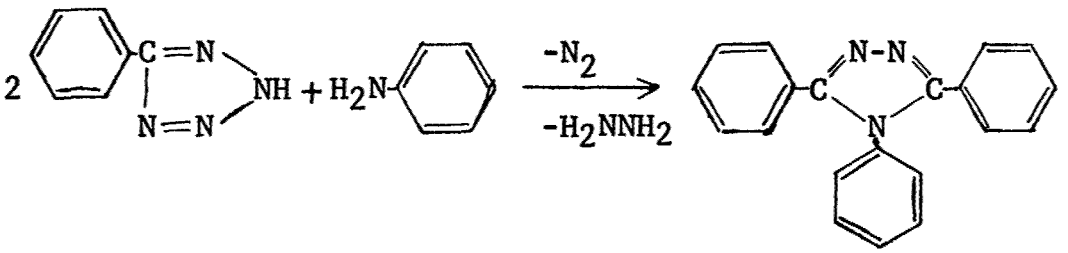
5% dissolved lithium chloride was substituted for the DMF-lithium chloride solvent, and a warm solution of the free tetrazole was added to a hot solution of the imino-chloride. The only product isolated was a light brown powder which decomposed to tar with gas evolution above 270°C.

Low molecular weight m-phenylenetriazole polymer was observed to be soluble in boiling nitrobenzene forming a viscous dope. However, m-phenylene-bis-tetrazole was not readily soluble in this solvent and appeared to react with the nitrobenzene under reflux. In hopes that nitrobenzene would prove to be a satisfactory polymerization medium, N,N'-diphenylisophthalimino-chloride and m-phenylene-bis-tetrazole were mixed in nitrobenzene at room temperature. No noticeable reaction occurred, although the imino-chloride dissolved. On heating, gas evolution occurred at about 100°C. The only product isolated from the mixture decomposed to a viscous black tar at 360°C.

Attempts were also made to prepare the polytriazoles from the tetrazoles and imino-chlorides in the presence of quinoline, tri-n-butylamine and dimethylacetamide. Again product precipitated from the hot reaction mixtures and only low molecular weight polymers were obtained.

Further efforts to find satisfactory solvents in which to prepare high molecular weight poly(phenylene)triazoles by solution techniques have indicated that N-methyl-2-pyrrolidone and mixtures of butyrolactone and pyridine may have promise for this purpose.

Huisgen[11] reported that the thermolysis of 5-phenyltetrazole in aniline gave a 63% yield of 3,4,5-triphenyl-1,2,4-triazole.



This reaction offers a potentially much easier route to the poly(phenylene)triazole systems which avoids the use of the difficultly obtainable imino-chlorides. To investigate this

route, a study of the thermolysis of m-phenylene-bis-tetrazole in aniline was initiated. After stirring a sample of m-phenylene-bis-tetrazole in a large excess of refluxing aniline for three days, the solution was quite dark and there appeared to be no increase in the viscosity of the solution. Only a small amount of resinous material was isolated. This product decomposed at about 230°C with distillation of a clear, colorless liquid. The infrared spectrum of this resinous product showed the presence of the triazole ring, but more closely resembled that of a p-phenylene compound than that of a m-phenylene compound. This indicated the occurrence of a thermally induced rearrangement on the phenylene ring. Another thermolysis reaction between m-phenylene-bis-tetrazole and aniline with dimethylsulfoxide as a solvent and anhydrous zinc chloride as a catalyst resulted in a vigorous decomposition of the reaction mixture.

High molecular weight polymers are usually obtained from polymerizations in which interfacial techniques are employed. However, the extreme susceptability of the imino-chlorides to hydrolysis makes the use of these compounds impractical in interfacial polymerizations. Addition of a basic aqueous solution of m-phenylene-bis-tetrazole to a solution of N,N'-diphenylisophthalimino-chloride in chloroform resulted in the complete hydrolysis of the imino-chloride and the recovery of the corresponding amide.

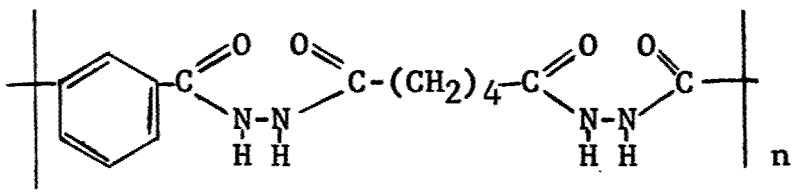
Exploratory attempts to prepare poly(phenylene)triazoles by heating finely ground mixtures of the phenylene-bis-tetrazoles and phthalimino-chlorides in the solid state resulted in products which were soluble in concentrated sulfuric acid. These materials appeared to contain tetrazole units as was evidenced by DTA exotherms in the range of 260-280°C.

B. Polytriazoles from Diacid Hydrazides

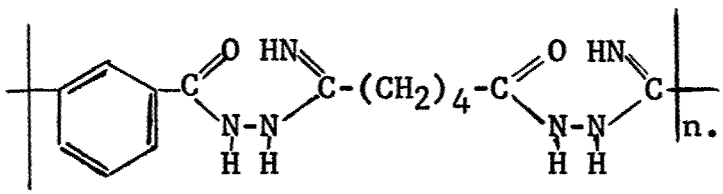
In view of the lack of success of efforts to produce high molecular weight poly(phenylene)triazole by the bis-tetrazole route, the study of a dihydrazide approach to polytriazoles was initiated. Bates, Fisher and Wheatly[12] described the polymerization of various aliphatic diacid hydrazides in the presence of hydrazine to give 4-amino-1,2,4-polytriazoles. When a diamide was reacted with the diacid hydrazide, a 1,2,4-polytriazole was formed.

We chose to study the reaction, first using an aliphatic diamide (adipamide) and an aromatic dihydrazide (isophthalic or terephthalic dihydrazide) in order to form a product which might be fusible and thus more easily handled. The intermediate dihydrazides, isophthalic dihydrazide and terephthalic dihydrazide, were easily synthesized by reacting the dimethyl esters with hydrazine according to the general procedure of Davidis[13]. Ethanol was found to be a satisfactory reaction solvent for the preparation of isophthalic dihydrazide, but was less suitable for the terephthalic analog. However, reasonably high yields (65%) of the terephthalic dihydrazide were obtained in dimethylacetamide. Recrystallizations of the crude reaction products from hot water provided convenient means of purification. The dihydrazides were characterized by melting points, infrared spectra and elemental analyses.

Initial polymerization reactions were carried out at atmospheric pressure in the absence of hydrazine. The reaction of equimolar quantities of isophthalic dihydrazide and adipamide at 200°C and atmospheric pressure produced a clear melt from which ammonia was evolved as the viscosity gradually increased. The viscosity of the reaction melt increased rapidly when the pressure was lowered to 0.5 mm. Hg. Long fibers were easily drawn from this viscous melt; however, they became brittle on cooling, probably because of low polymer molecular weight. Elemental analyses indicated a probable polyhydrazide structure for the material:



However, the fact that the nitrogen content was somewhat high (20.24% vs. 18.42% calculated) and the oxygen content low (20.55% vs. 21.05%) showed contamination by a material of higher nitrogen content, perhaps a structure of the type:



Heating the polymer for several hours at 250°C resulted in some discoloration and loss of water. The viscosity of the resulting polymer, though somewhat higher, did not indicate crosslinking to any significant degree. Solubility in warm formic acid also helped to rule out crosslinking. Elemental analyses indicated a polyoxadiazole structure to be the main product; possibly with some polytriazole as a contaminant. These structures would result from the dehydration of the structures proposed above for the initial polymer.

The above polymerization reaction was repeated in the presence of hydrazine in a small, stirred autoclave. The temperature was maintained at 200°C and the pressure was held at 250 psig for a period of four hours. After a vacuum finishing cycle, a fusible polymer was obtained (m.p. 220°-225° with gas evolution at 240°C). This material was soluble in formic acid, had an inherent viscosity of 0.349 (0.5% in formic acid) and was found to contain 32.77% nitrogen and 6.81% oxygen. Since these values fit none of the anticipated structures, it was concluded that the polymer probably contained several structures. On heating the polymeric reaction product to 280°C over a period of two hours, the material became infusible, though soluble in hot formic acid; and the inherent viscosity increased to 1.174.

It seemed of interest to explore the possibilities of spinning the original polymer into fiber and then, through a heat treatment of the fiber, convert it into the more stable material. However, fibers formed from the molten polymer were too brittle for evaluation. Efforts made to obtain a less brittle fiber by wet-spinning a 30% solids, formic acid dope were unsuccessful. Extremely poor coagulation of the fiber in the spin bath occurred as a probable result of the low molecular weight of the polymer. It had been hoped that sufficient orientation of the polymer could have been attained in the swelled state to impart strength to the fiber. Studies are planned to determine the proper set of reaction variables for increasing the molecular weight of the polymer and to extend the polymerization reaction to include aromatic intermediates.

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Figure 1

DTA Thermogram of p-Phenylene-bis-tetrazole

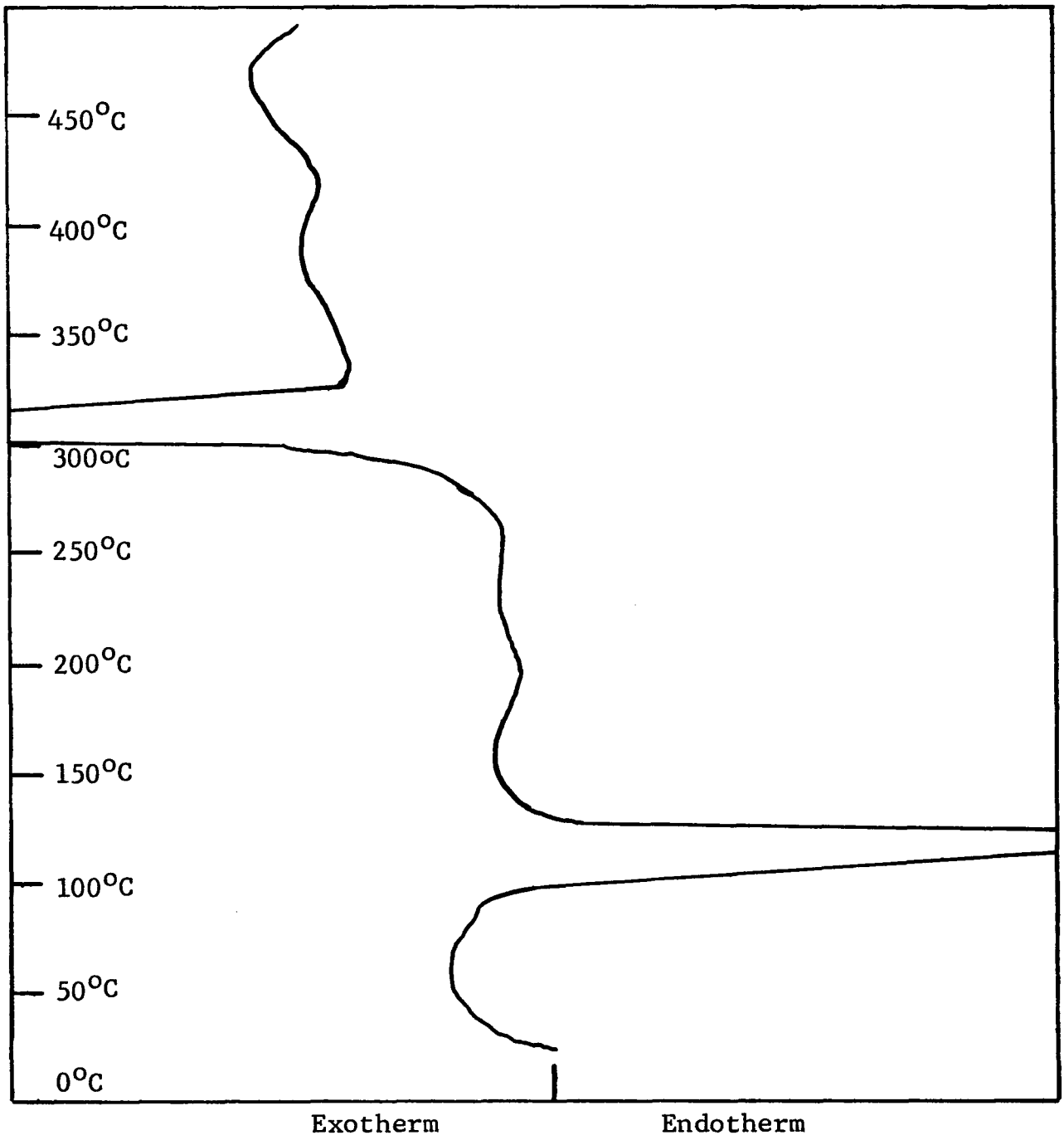


Figure 2

DTA Thermogram of m-Phenylene-bis-tetrazole

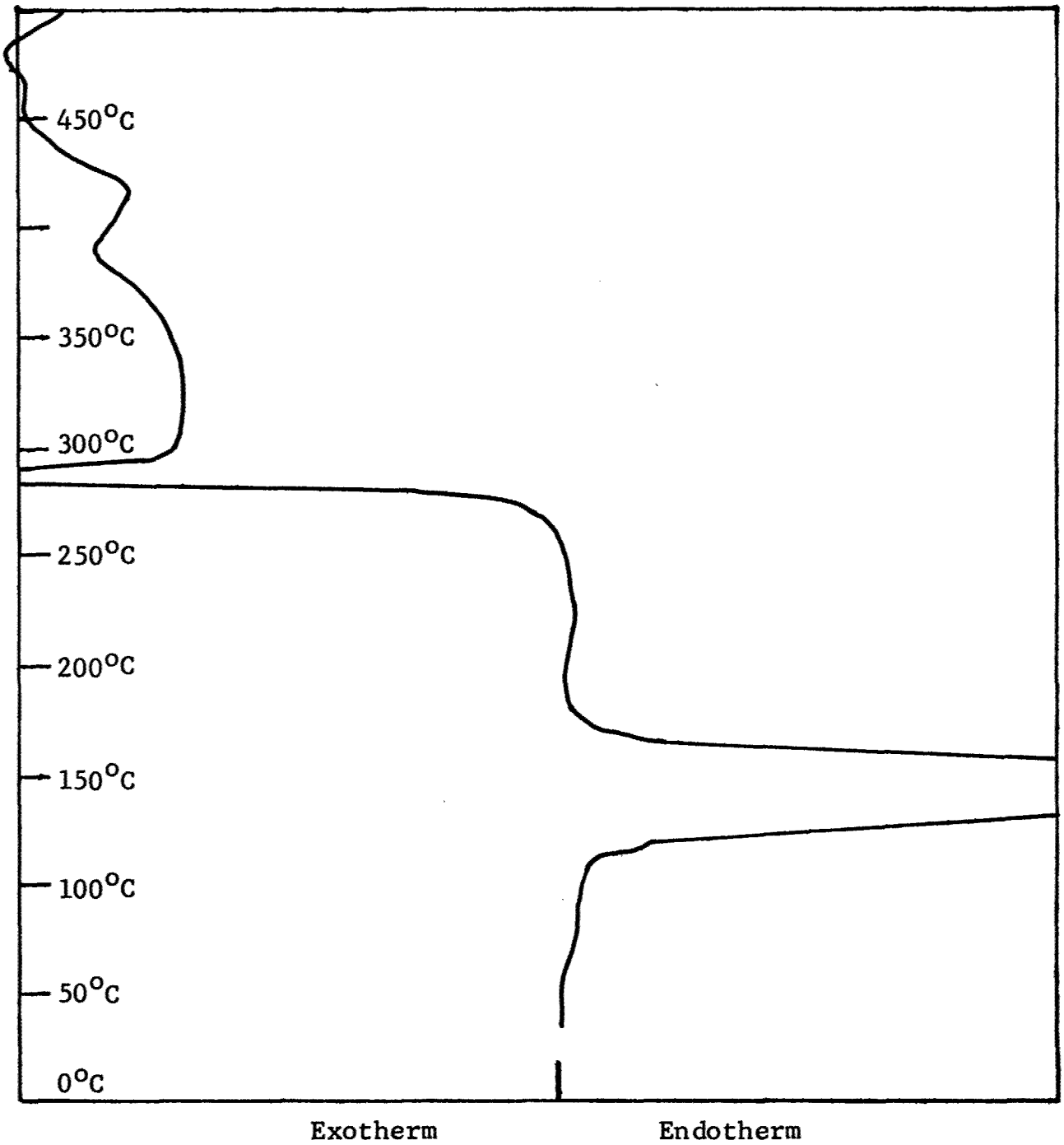


Figure 3

DTA Thermogram of Heated p-Phenylene-bis-tetrazole

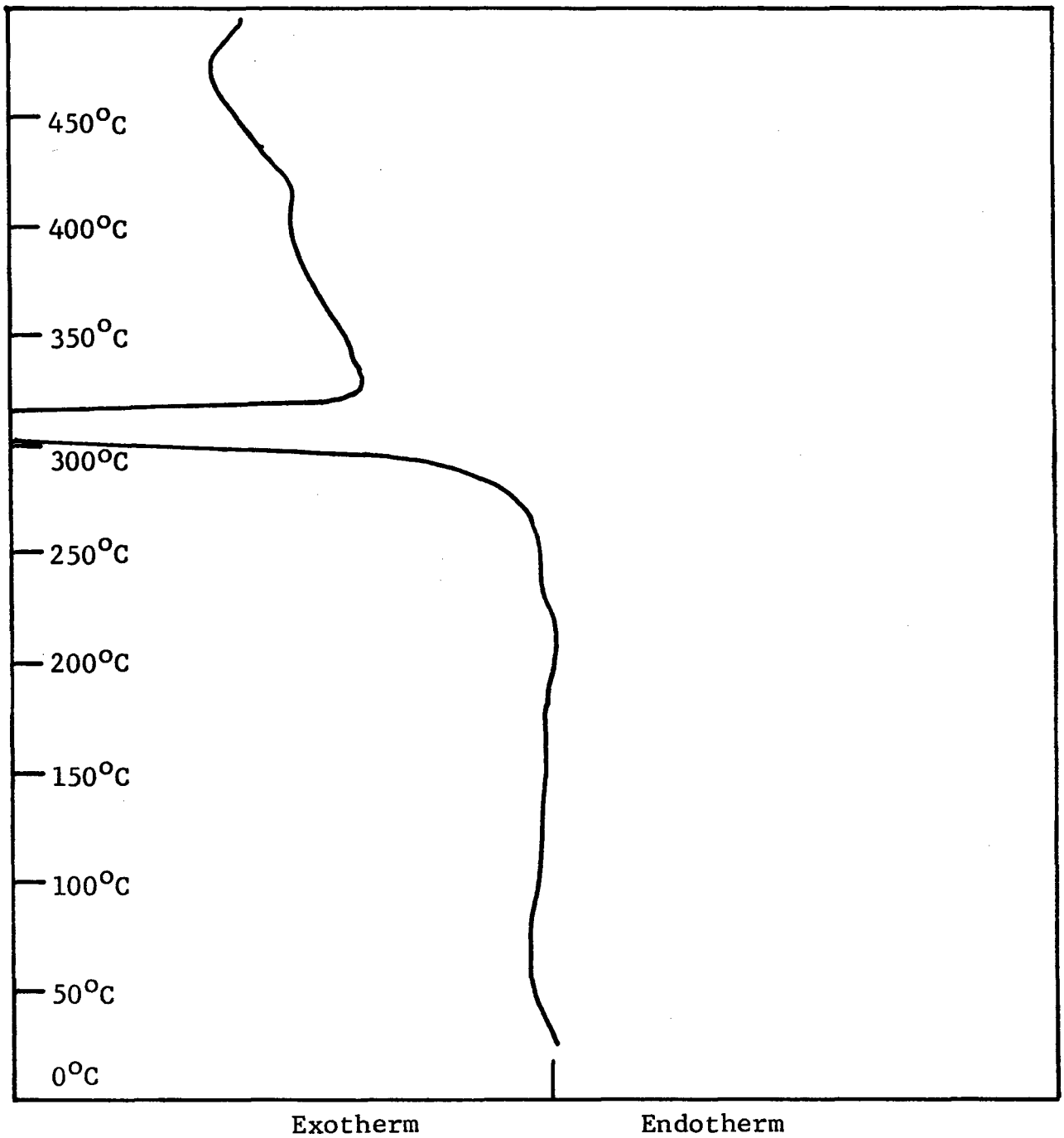


Figure 4

DTA Thermogram of Heated m-Phenylene-bis-tetrazole

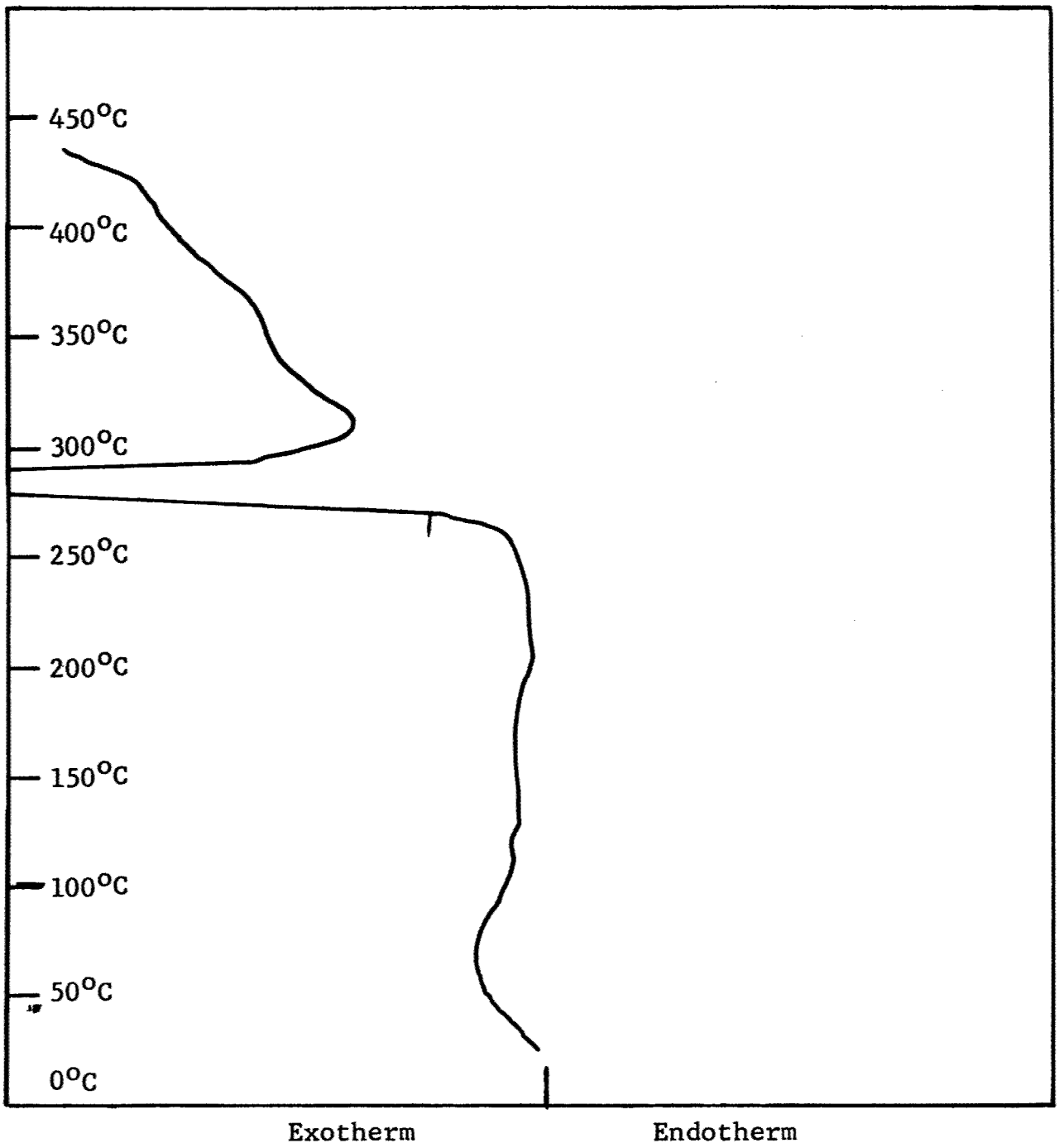


Figure 5

DTA Thermogram of 1,4-Bis[3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

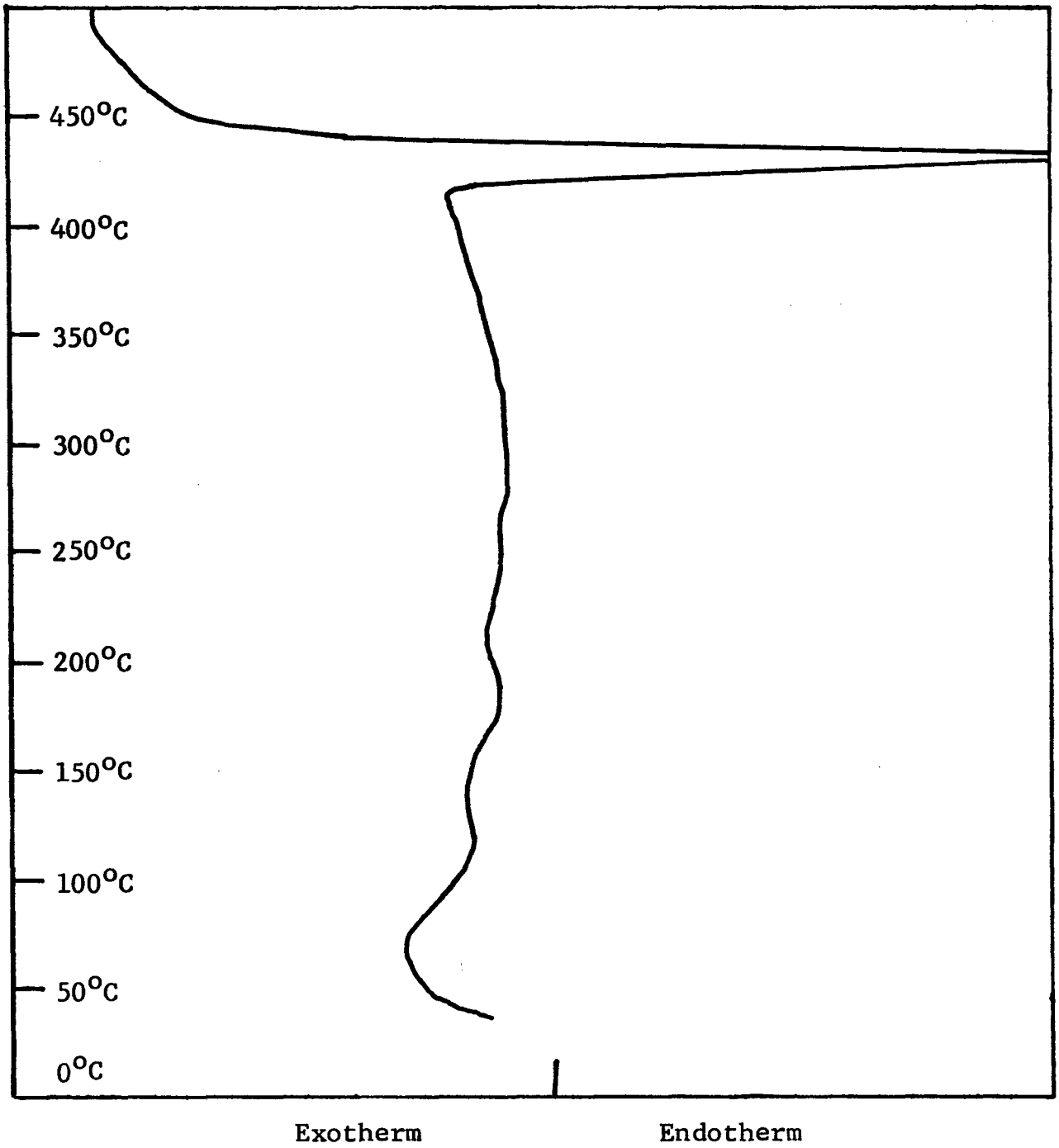


Figure 6

TGA Weight-loss Plot of
1,4-Bis[3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

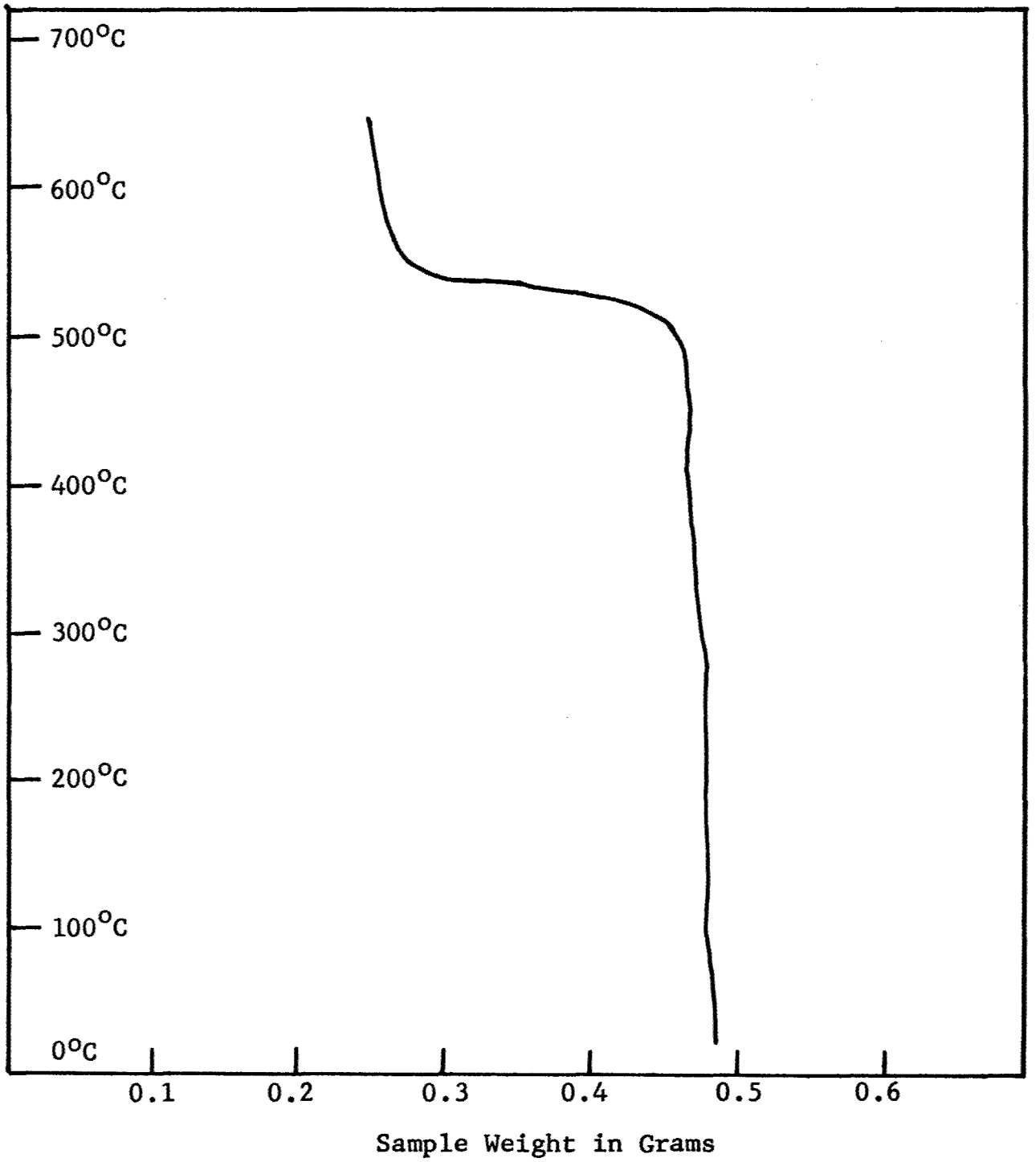


Figure 7

TGA Weight-loss Plot of
1,3-Bis[3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

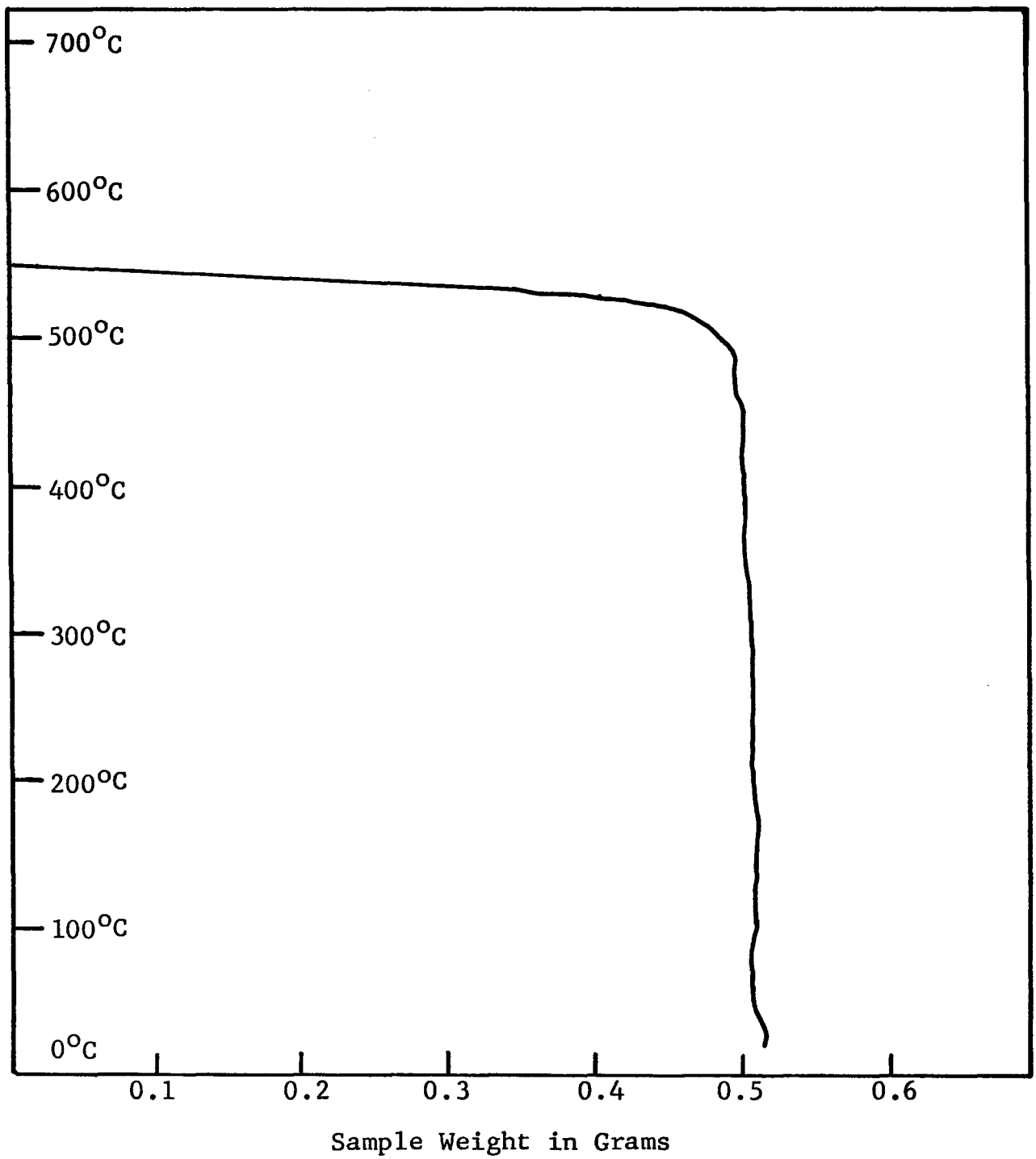


Figure 8

DTA Thermogram of 1,3-Bis [3,4-diphenyl-1,2,4-triazoyl-(5)]benzene

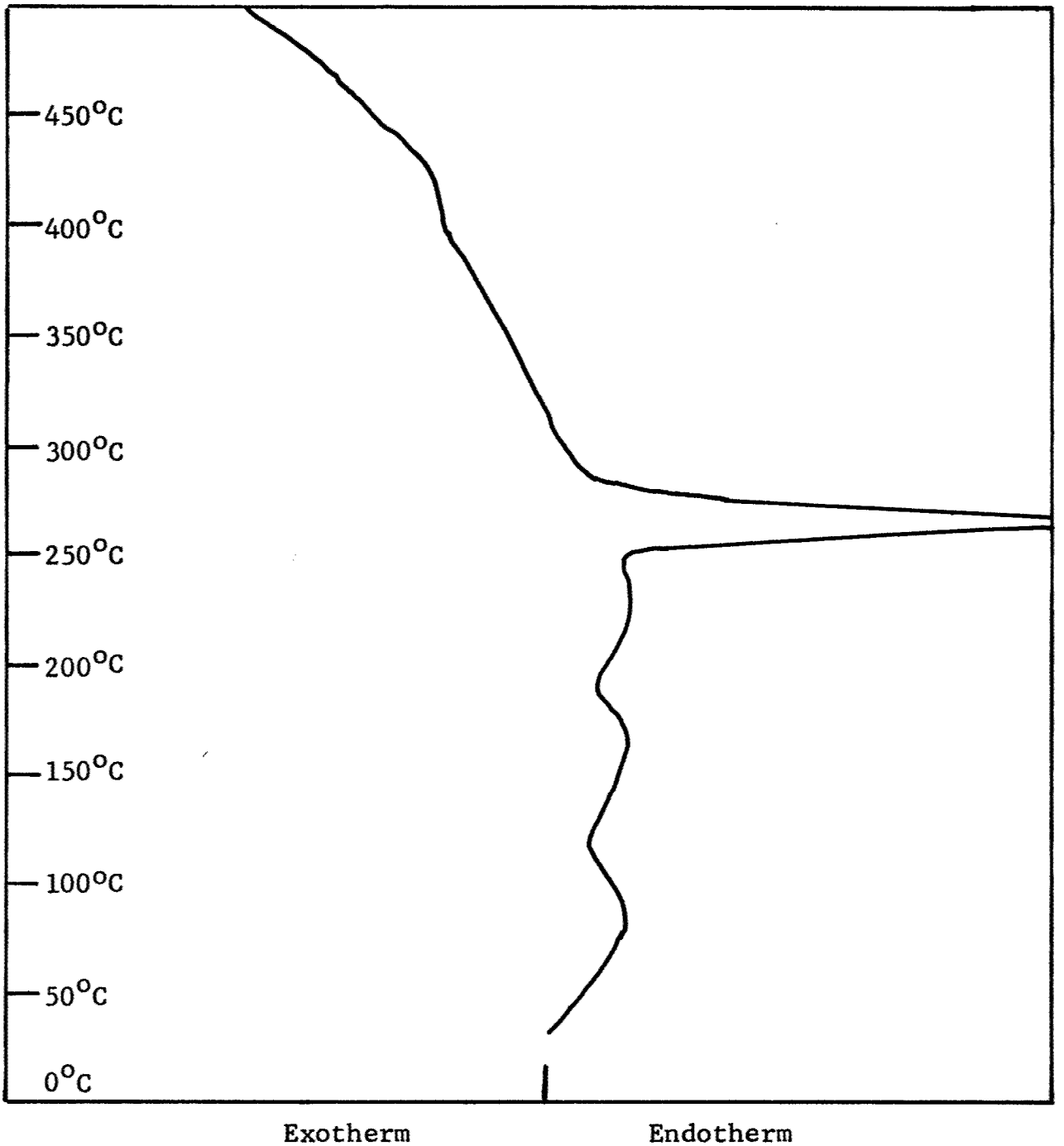


Figure 9

DTA Thermogram of Poly(m-phenylene)tetrazole

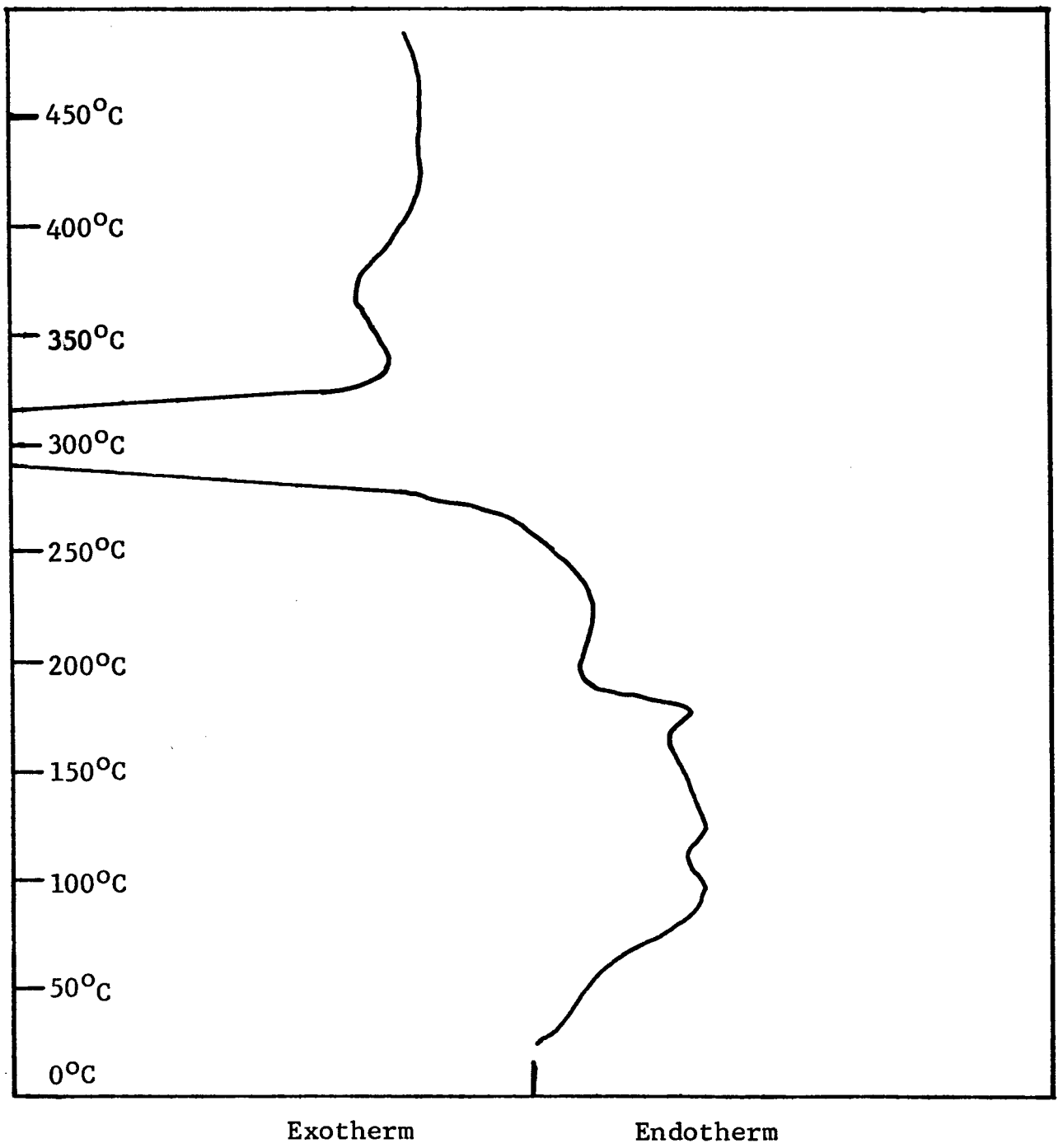


Figure 10

TGA Weight-loss Plot of Poly(m-phenylene)tetrazole

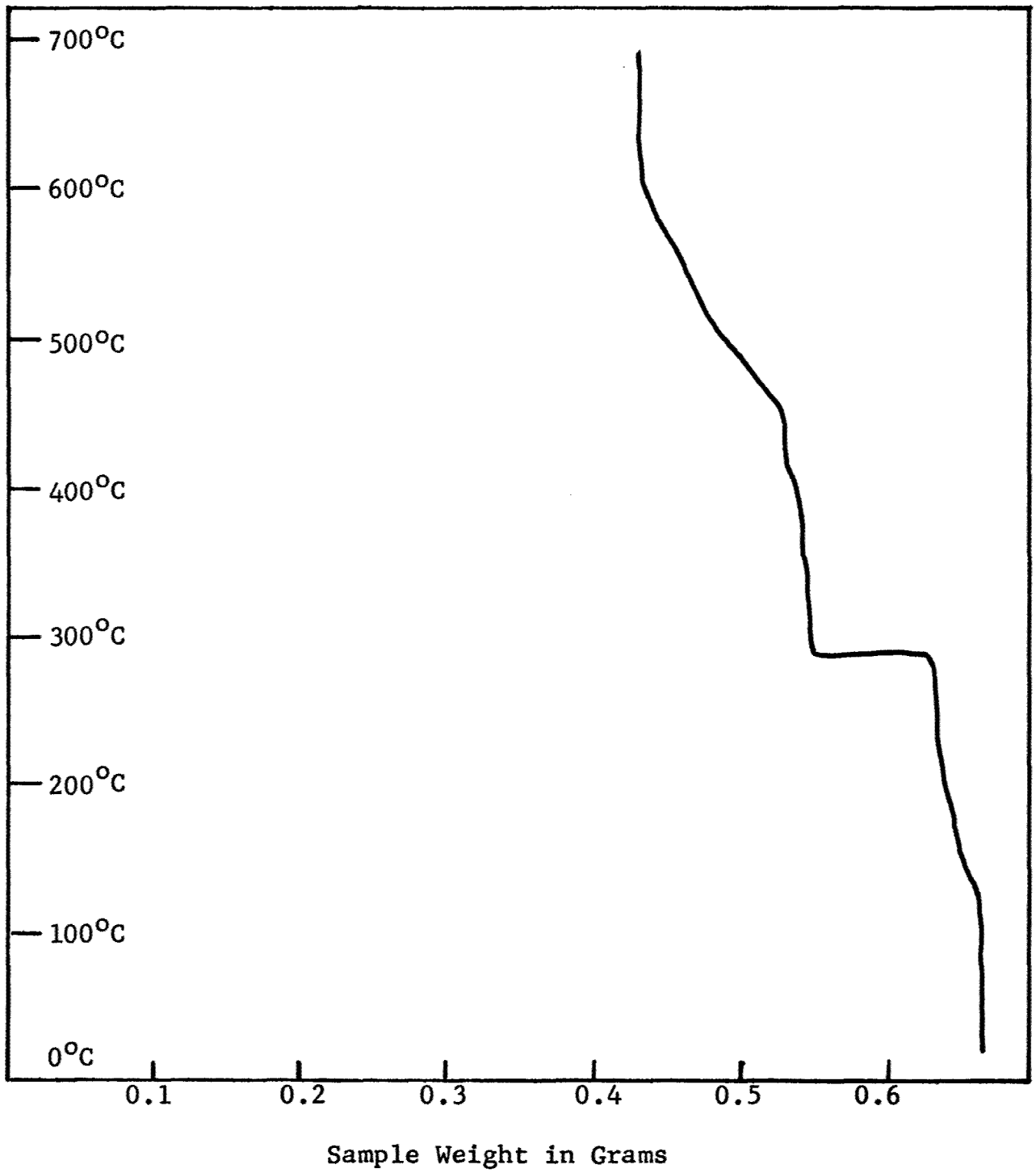


Figure 11

DTA Thermogram of Poly(p-phenylene)tetrazole

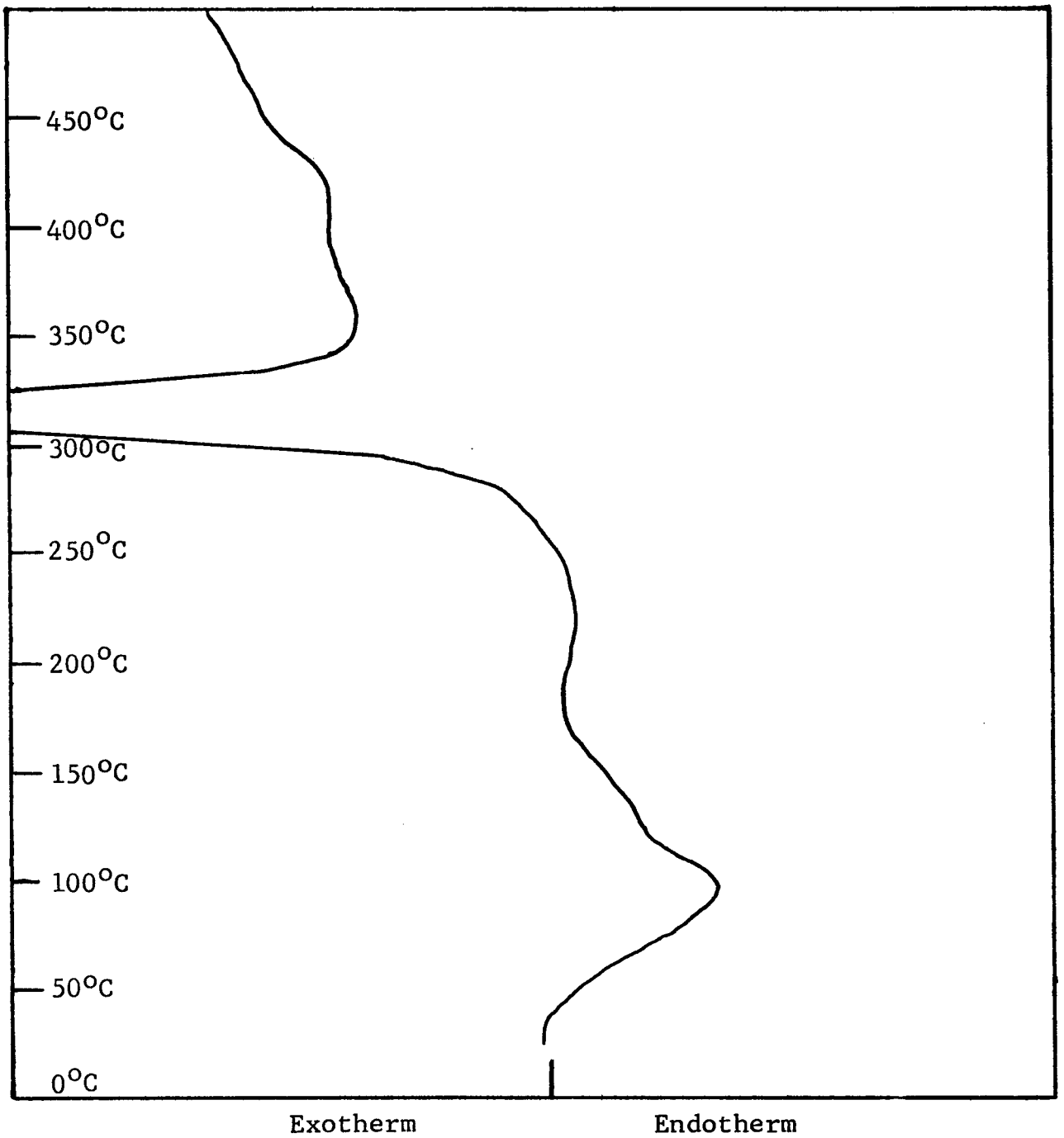
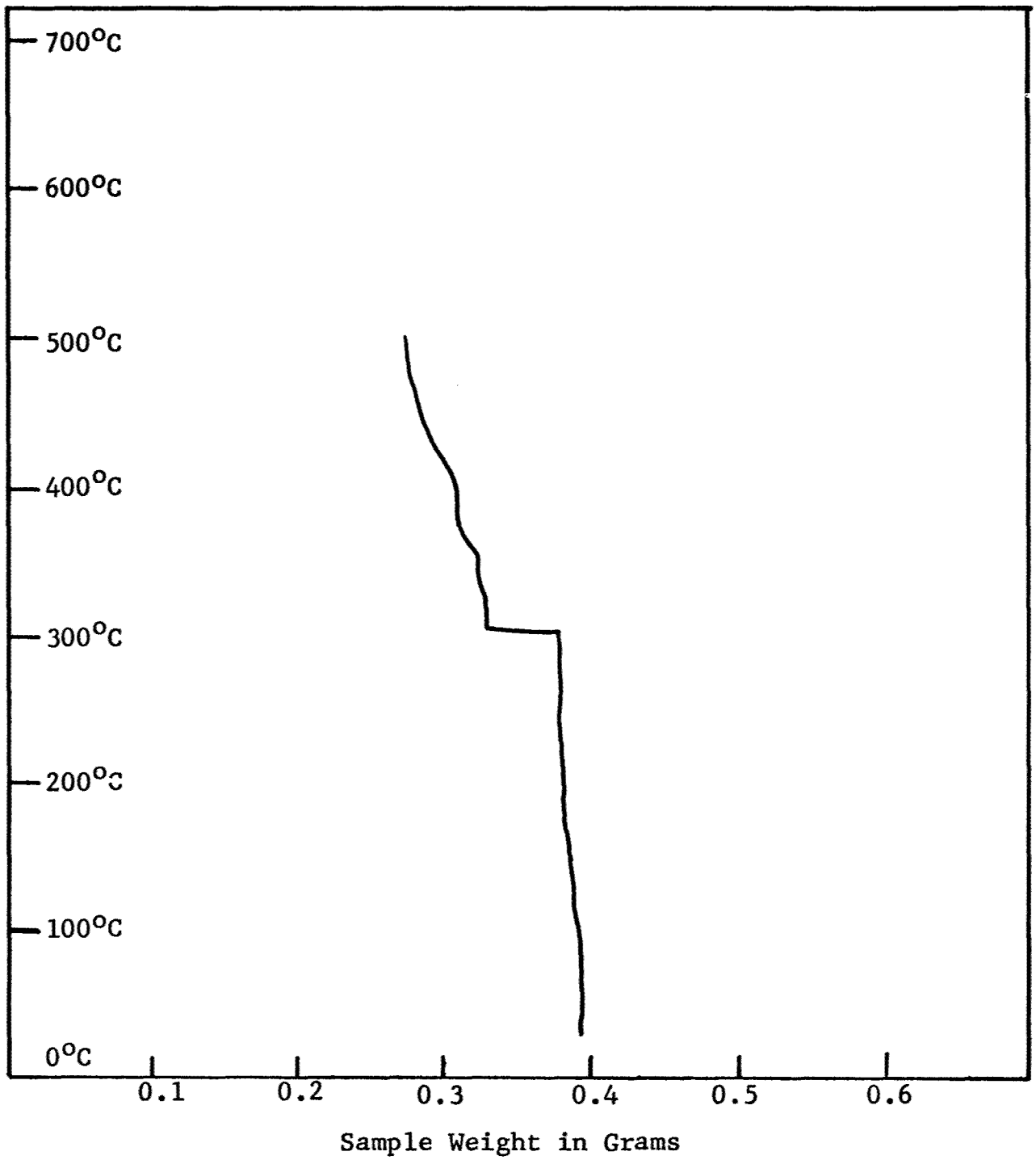


Figure 12

TGA Weight-loss Plot of Poly(p-phenylene)tetrazole



SYNTHESIS OF POLYTHIAZOLES AND POLYFLUOROOLEFINS

P. E. Brumfield, A. V. DiGiulio, A. Lebovits and P. M. Hergenrother

Koppers Company, Inc.

Abstract

This project has as its goal the synthesis of organic polymers of high thermal stability. Two approaches are being followed; namely, the condensation polymerization of a chain of aromatic nuclei joined through heterocyclic groups and the polymerization of fluoroolefins containing heterocyclics groups to give fluorocarbon polymers with pendant heterocyclic substituents.

In a preliminary study, eight model thiazole compounds with aryl substituents were prepared and compared as to thermal stability as a guide to designing polymer chains. The benzothiazole unit and 2,4-aryl-substituted thiazole structure appeared to be most stable. Two poly-(benzothiazole) products, a poly-(benzimidazole-benzothiazole) product, a poly(arylene-thiazolothiazole) product and a poly(azo-arylene-thiazole) product have been obtained in small scale reactions. All of these products were dark, infusible powders. One of the poly-(benzothiazole) products was prepared in sufficient quantity to determine certain properties. It was insoluble in all solvents tested, formed a brittle disc by compression molding at 600°F, and showed thermal stability to over 600°C by TGA.

The synthesis of perfluorocarbon polymers with pendant heterocyclic groups first requires the preparation of monomers with the structure $RCF=CF_2$, where R is a stable heterocyclic ring. Several methods designed to produce such monomers have been examined without success. The first approach involved the reaction of the lithium derivative of a heterocycle with tetra-fluoroethylene. With 2-pyridyllithium, the product obtained was 1,2-di(2-pyridyl)-1,2-difluoroethylene, instead of the desired 2-(trifluorovinyl)pyridine. A similar approach, the reaction of an organometallic with dibromotetrafluoroethylene, led to the formation of tetrafluoroethylene and a bromocyclic. Next, N-(tetrafluoroethyl)-carbazole was prepared and treated with alkaline reagents to effect dehydrofluorination. Mild alkaline treatments were ineffective and forcing conditions led to the regeneration of carbazole. Currently attempts are underway to prepare 2-(trifluorovinyl)benzazoles via condensation of the properly substituted fluoroacids with ortho-substituted anilines. The precursors, several of which have been prepared, include tetrafluoroethyl-, dihalotrifluoroethyl-, and tetrafluorocarboxyethyl-benzazoles. Attempts are underway to synthesize the monomers by dehydrofluorination, dehalogenation, or decarboxylation.

Introduction

In postulating structures for polymeric materials that would have a high degree of thermal stability, first consideration should be given to the relative stabilities of potential building units. Reference to various reports on decomposition temperatures for simple organic compounds will show that some structures, such as aromatic compounds, certain heterocyclic compounds, and fluorocarbons,

have favorably high thermal resistance. A few examples of heat stable compounds are given in Table 1:

TABLE 1

Vapor Phase Decomposition of Simple Compounds[1]

Compound	Decomposition Temperature, °F
Perfluorocyclohexane	1150-1200
Naphthalene	1150-1200
Thiophene	1100-1150
2-Phenylimidazole	1100
Benzothiazole	1025-1050
Biphenyl	950-1000
Benzimidazole	750-800
1,2,4-Triazole	800

In this contractural program, the goal is the preparation of thermally stable polymers incorporating certain of these more stable structures.

One part of this program is the preparation of polymeric chains incorporating heterocyclic rings, particularly thiazoles, with connecting arylene units. The preferred approach is the condensation of polyfunctional arylene compounds with the formation of the heterocyclic ring as the polymer-forming reaction. The polymer chain is to contain no readily removable hydrogen, as represented by an aliphatic chain or a primary amide group.

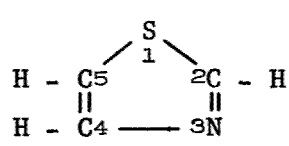
In the other part of this program, perfluoroolefin derivatives of heterocyclic compounds are to be prepared. Addition polymerization of such monomers will lead to a fluorocarbon backbone with pendant heterocyclic groups. As in the preceding program, presence of labile hydrogens is to be avoided.

I. Condensation Polymers Containing Thiazole Groups

This work can be divided into three phases. The first phase was the synthesis of a series of model compounds for a comparison of thermal stability. The other two phases are the preparation of monomers and the study of polymerization of these monomers.

A. Model Aryl-Substituted Thiazoles

A series of eight model thiazole derivatives was prepared, following standard preparative methods[2]. These compounds included various combinations of aryl substitution on the thiazole ring (formula I).



(I)

Highly purified samples of these compounds were submitted to ASD for testing in a high pressure isoteniscope. The eight model thiazole derivatives are listed,

with their decomposition temperatures, in Table 2, along with selected results for other compounds as determined by the operators of the isoteniscope[1,3]. As will be seen in the subsequent discussion of polymeric materials, correlation of relative thermal stability of a monomer structure with the thermal stability of a polymer chain of the same basic structure is not absolute. With respect to the model thiazole derivatives tested, the simple phenyl group seems to exhibit greater stability than other groups. The greater stability of compound b compared to compounds e and f suggests attachment through the 2,4-positions of the thiazole ring. The most stable of the thiazole derivatives was 2-phenylbenzothiazole, which would indicate that the fused ring system of the benzothiazole structure would produce the most heat resistant polymers.

B. Synthesis of Monomer Intermediates

Some of the simpler types of monomers have been prepared by known synthetic methods. The chief problem has now become the preparation of monomers containing heat stable connecting groups which will add flexibility to the polymer chain and impart a solubilizing effect. Some of the monomers being synthesized are indicated in the following discussion.

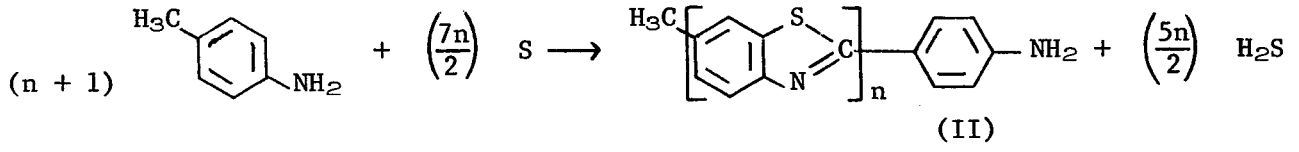
TABLE 2

Thermal Stability in a High Pressure Isoteniscope

Compound	Decomposition Temperature, °F
a. 2-Phenylbenzothiazole	943
b. 2,4-Diphenylthiazole	916
c. 2,4,5-Triphenylthiazole	897
d. 2-(1-Naphthyl)-4-phenylthiazole	876
e. 2,5-Diphenylthiazole	813
f. 4,5-Diphenylthiazole	783
g. 2-(4'-Benzamidophenyl)benzothiazole	667
h. 2-Anilino-4-phenylthiazole	613
i. Naphthalene	1053
j. Biphenyl	1010
k. Quinoline	950-1000
l. Diphenyl ether	1000
m. 1-Phenylimidazole	890
n. Diphenylmethane	850

1. Derivatives of Dehydrothio-p-toluidine

The ready availability of dehydrothio-p-toluidine (II, n = 1) from the p-toluidine-sulfur fusion reaction of dye chemistry, suggested derivatives of this



(II)

compound as polymer intermediates with a benzothiazole unit already in the monomers. Some of the intermediates obtained and their methods of synthesis are as follows:

a. 2-(4'-Acetamidophenyl)benzothiazole-6-carboxylic acid

This compound was prepared by the oxidation of the acetyl derivative of dehydrothio-p-toluidine (II) by potassium permanganate in pyridine.

b. 2-(4'-Cyanophenyl)-6-methylbenzothiazole

This compound was prepared by diazotization of II, followed by reaction with cuprous cyanide.

c. 2-Phenylbenzothiazole-4',6-dicarboxylic acid

This compound was prepared by the oxidation and hydrolysis of the preceding compound with permanganate.

d. 2-(4'-Amino-3'-mercaptophenyl)benzothiazole-6-carboxylic acid

Preparation of this compound was unsuccessfully attempted by the reaction of sulfur monochloride (the Herz reaction[4]) with 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid.

2. Derivatives of Arylene Diamines

Both in this study of thiazoles and in the work of Marvel[5] with imidazoles, the formation of fused ring systems is dependent upon the reaction of a carboxylic acid group with an aryl amine, having an ortho mercapto group (to permit formation of a benzothiazole) or having an ortho amino group (to permit formation of a benzimidazole). Such intermediates as have been studied are as follows:

a. 3,3'-Dimercaptobenzidine

This compound was prepared by the reaction of benzidine with sulfur monochloride[4].

b. 3,3',4,4'-Tetraaminobiphenyl

This compound was obtained from the Chemical and Dyestuffs Division of Koppers Company, Inc.

c. Bis(4-amino-3-mercaptophenyl) ether

Preparation of this compound was unsuccessfully attempted by the reaction of oxy-dianiline with sulfur monochloride[4].

C. Polymers Prepared

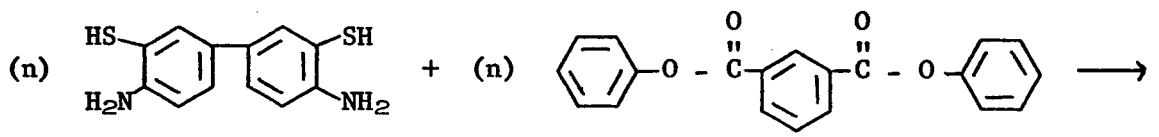
Polymeric products have been produced from some of the monomer intermediates described in the preceding section and from some other reactions of an exploratory nature. The preliminary results for polymers produced in this program thus far indicate that poly(benzothiazoles) are indeed quite thermally stable.

1. Extension of the Primuline Fusion Reaction

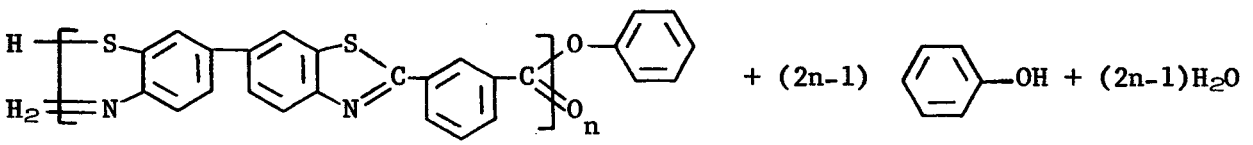
The old reaction of p-toluidine with a sulfur melt (as previously noted in paragraph B.1.) produces dehydrothio-p-toluidine (II, n = 1) and primuline base (II, n = 2) as the major products. The reaction could theoretically proceed to the polymer range with "n" becoming a large number, were the higher homologs more readily fusible. Use of high boiling organic solvents with p-toluidine and sulfur resulted in the same products as the melt reaction. When a mixture of anhydrous sodium tetrasulfide and potassium pentasulfide was used as a molten reaction medium, sulfur converted dehydrothio-p-toluidine (at 260° maximum reaction temperature) and primuline base (at 285° maximum reaction temperature) to apparently identical brown powders. Characterization of these products by infrared absorption analysis and by elemental analysis indicated that each was a poly(benzothiazole), probably cross-linked by sulfide bonds. This polymer was insoluble in phenol, 97% formic acid, dimethylsulfoxide, dimethylformamide and sulfuric acid. A study of the physical properties of this product will be given in a later paragraph.

2. Condensation of 3,3'-Dimercaptobenzidine with Diphenyl Isophthalate

An equimolar mixture of 3,3'-dimercaptobenzidine (III) and diphenyl isophthalate (IV) was intimately mixed and heated first to 300° under nitrogen



(III) (IV)

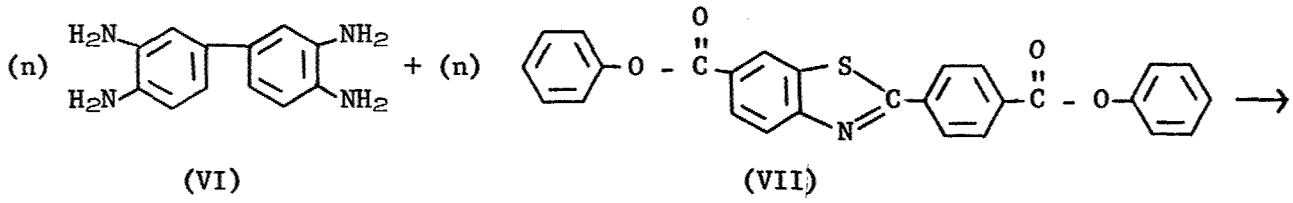


(V)

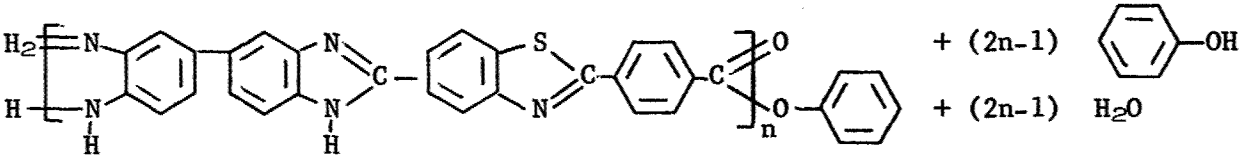
and, after pulverizing, to 400° under vacuum. The infrared absorption analysis was consistent with the proposed structure for the poly(benzothiazole) (V). The elemental analysis values for C, H, N and S were low, presumably because of incomplete combustion. This dark green solid was infusible and insoluble in the common solvents.

3. Condensation of 3,3',4,4'-Tetraaminobiphenyl with Diphenyl 2-Phenylbenzothiazole-4',6-dicarboxylate

Since the benzimidazole polymers prepared by Marvel[5] possessed such excellent thermal stability, a combined benzothiazole-benzimidazole polymer might be expected to have high thermal resistance. A mixture of 3,3',4,4'-tetraaminobiphenyl (VI) and diphenyl 2-phenylbenzothiazole-4',6-dicarboxylate (VII) was condensed by the same procedure as in the preceding paragraph. The infrared absorp-



(VI) (VII)

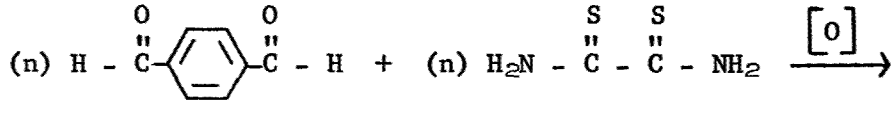


(VIII)

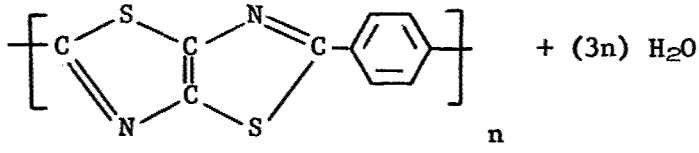
tion analysis was consistent with the proposed structure for the poly(benzimidazole-benzothiazole) (VIII). Elemental analysis values for C, H, N and S were again low, especially the values for carbon and nitrogen. The dark brown product was infusible and insoluble in common solvents.

4. Condensation of Terephthaldehyde with Rubeanic Acid

The availability of rubeanic acid (dithiooxamide) suggested this intermediate for the preparation of polymer chains with pairs of thiazole rings /condensation with bis(haloacetyl)compounds/ or with thiazolothiazole[6] units (condensation with dialdehydes). By heating a solution of terephthalaldehyde (IX) and rubeanic acid (X) in triglyme, first with air as the oxidant, and in a second



(IX) (X)

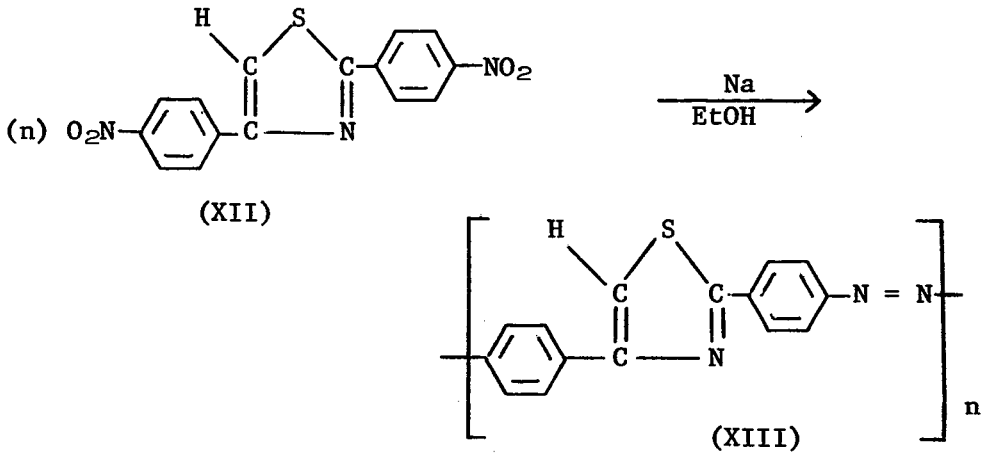


(XI)

experiment with sulfur added to the reaction mixture, a brown powder was obtained in each case. The infrared absorption analysis of the two products showed the same absorption peaks, but the presence of the thiazolothiazole group could not be confirmed. The elemental analysis for C, H, N and S was low, possibly due to incomplete combustion, relative values for nitrogen and sulfur being too low for the expected poly(phenylene-thiazolothiazole) (XI).

5. Partial Reduction of 2,4-Bis(p-nitrophenyl)benzothiazole

The favorable thermal stability of 2,4-diphenylthiazole suggested that linking units of the compound through the phenyl rings might produce thermally stable polymers. The mixed acid nitration of 2,4-diphenylthiazole produced 2,4-bis(p-nitrophenyl)thiazole (XII). The reduction of this compound over sodium amalgam gave a brown, infusible powder. Infrared absorption analysis showed absorption peaks characteristic of 1,4-phenyl substitution and of thiazoles, but the presence of an —N = N— group could not be established. The elemental analysis was too low for all elements, except hydrogen, for the expected poly(azo-phenylene-thiazole) (XIII).



II. Perfluorocarbon Polymers with Pendant Heterocyclic Groups

The first part of this phase of the project, the synthesis of monomers which will yield a polymer with a fluorocarbon backbone and pendant heterocyclic groups, $-(CFCF_2)_n$ (R), has not been completed. The second part, polymerization of the monomers to high molecular weight materials and a study of their thermal stability, will be inaugurated when the monomers become available. The attempts to prepare the desired monomers are discussed in what follows.

A. Reaction of Organolithium Compounds with Tetrafluoroethylene (TFE)

It had been originally planned to synthesize monomers of the type $RCF=CF_2$, where R was pyridyl, carbazolyl and fluorenyl.

The first approach consisted of reacting, tetrafluoroethylene (TFE) with organolithium compounds in a manner analogous to the preparation of 1-phenyl-1,2,2-

trifluoroethylene (alpha, beta, beta-trifluorostyrene) by Dixon[7].

$$CF_2 = CF_2 + RLi \longrightarrow RCF = CF_2 + LiF$$

(XIV)

$$RCF = CF_2 + RLi \longrightarrow RCF = CFR \longrightarrow R_2C = CFR \longrightarrow R_2C = CR_2$$

(XV)

Dixon recommended using an excess of TFE and a low temperature in order to obtain XIV, where R was alkyl or phenyl. In the reaction of 2-pyridyllithium with TFE, Dixon isolated a 10% yield of XV, R = C_5H_4N. No mention was made of the isolation of the type XIV product. A reinvestigation of the reaction of 2-pyridyllithium with a three-fold excess of $CF_2 = CF_2$, at -60°C, gave no evidence that XIV, R = C_5H_4N, was obtained in the final product. Instead a high yield of crude 1:2 product, XV, R = C_5H_4N was obtained. The failure to obtain XIV, 2-(trifluorovinyl)pyridine under conditions that gave alpha, beta, beta-trifluorostyrene, was ascribed to the greater contribution of the pyridyl group to the positive nature of the terminal CF_2 group in XIV.

In a similar reaction between 9-fluorenyllithium and TFE, only 1,2-di-(9-fluorenyl)-1,2-difluoroethylene was isolated. In this case, reaction occurred only above 0°C, a temperature at which an excess of TFE could not be maintained. Thus it is possible that, if this reaction were carried out under pressure in order to maintain an excess of TFE, the desired 9-fluorenyllithium might form.

B. Reaction of Organolithium Compounds with Tetrafluorodibromoethane (TFDE)

A second approach was explored in which organolithium compounds were made to react with 1,1,2,2-tetrafluoro-1,2-dibromoethane (TFDE). It was hoped that bromotetrafluoroethyl derivatives would form, which could then be dehalogenated to trifluorovinyl compounds.

$$RLi + BrCF_2CF_2Br \longrightarrow RCF_2CF_2Br + LiBr$$

$$RCF_2CF_2Br + Zn \longrightarrow RCF = CF_2 + ZnBrF$$

Reactions occurred very readily at -50° and -30° with butyllithium and fluorenyllithium, but did not give the desired products. Instead, TFE and butyl bromide were formed in the first case, and TFE, 9-bromofluorene, and bifluorene were formed in the second case.

$$RLi + BrCF_2CF_2Br \longrightarrow RBr + LiBr + CF_2 = CF_2$$

Carbazolyllithium did not react with TFDE at 100°C. At 140°C a reaction occurred, but investigation of the reaction product showed that the desired N-(bromotetrafluoroethyl)carbazole, if formed at all, was not a major constituent of the mixture.

C. Attempted Dehydrofluorination of N-(1,1,2,2-tetrafluoroethyl)carbazole

The next approach was to attempt the preparation of a monomer, $R_2NCF = CF_2$, by dehydrofluorination of the precursor $R_2NCF_2CF_2H$ compound. For this purpose, it was decided to attempt the dehydrofluorination of N-(1,1,2,2-tetrafluoroethyl)carbazole (XVI). This compound can be prepared according to U. S. Patent 2,861,990 from carbazole and TFE under pressure in the presence of carbazolylpotassium and dimethylformamide. We have found that this reaction occurred at atmospheric pressure in dioxane, so that no special equipment was necessary. However, attempts to dehydrofluorinate XVI with potassium ethoxide in ethanol or 50% aqueous KOH at reflux gave back unchanged XVI. Heating with KOH in ethylene glycol at 190°C led to regeneration of carbazole and TFE. It is postulated that in the intermediate XVII which resulted from abstraction of a proton by the base, displacement of nitrogen rather than fluorine occurred. Thermal cracking of XVI at

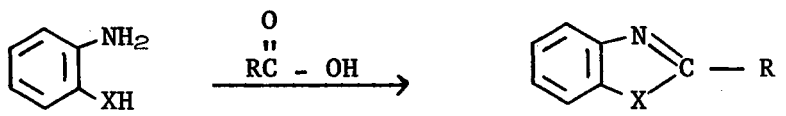
$$\underset{\text{(XVI)}}{C_{12}H_8NCF_2CF_2H} + B^{\ominus} \longrightarrow \underset{\text{(XVII)}}{C_{12}H_8NCF_2CF_2^{\ominus}} \longrightarrow C_{12}H_8N^{\ominus} + CF_2 = CF_2$$

about 260°C gave a black residue and a blue-violet sublimate which were not identified. The lack of success in the synthesis of the desired monomers by the reaction of organometallics with TFE and TFDE led to a shift to another synthetic approach which is described below.

D. Attempted Preparations of 2-(Trifluorovinyl)benzazoles

The synthetic route envisioned here is the preparation of benzimidazoles, benzothiazoles, and benzoxazoles substituted in the 2-position with a fluoroalkyl group which can subsequently be converted to the trifluorovinyl group.

2-Substituted benzimidazoles, benzoxazoles, and benzothiazoles are frequently prepared by the condensation of organic acids with the proper ortho-substituted aniline as shown below:



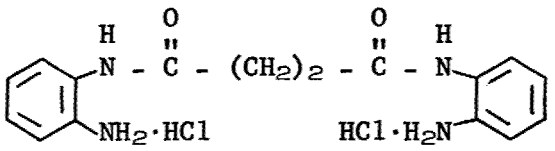
X = NH, O, S

X = NH, O, S

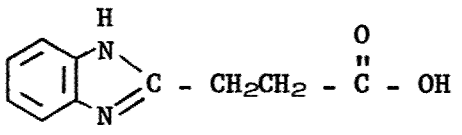
(XVIII)

Recently a number of 2-perfluoroalkylbenzimidazoles, (XVIII), X = NH, R = CF_3, CF_2CF_3, and $CF_2CF_2CF_3$ [8a,b,9] have been synthesized by this method.

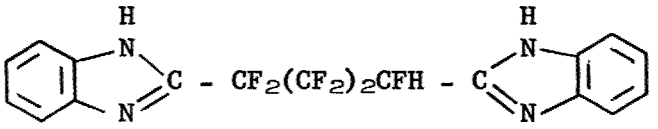
A number of dibasic acids also have been condensed with ortho-phenylenediamine. Succinic acid when reacted in a 1:1 molar ratio with ortho-phenylenediamine in 4N hydrochloric acid[10] has been reported to give a mixture of the compounds XIX and XX. Quite recently Lane[8a] reported the formation of the heptafluoroadipobis-2-benzimidazole (XXI). It appears to us, therefore, that this general route should prove fruitful in the preparation of the desired trifluorovinyl benzazoles. By the judicious selection of the acid, a variety of monomer



(XIX)



(XX)



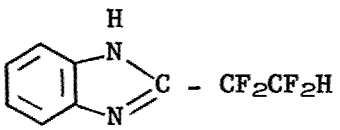
(XXI)

precursors would become available. These would enable us to investigate and to evaluate three of the general methods, dehydrohalogenation, dehalogenation and pyrolysis, for introducing the double bond in fluorocarbons.

To date, a number of 2-(perfluoroalkyl)benzimidazoles and benzothiazoles have been prepared and their attempted conversion to the desired 2-(trifluorovinyl) benzazoles have been or are currently in progress.

1. 2-(1,1,2,2-Tetrafluoroethyl)benzimidazole (TFB) and Its Attempted Dehydrofluorination

The condensation of 2,2,3,3-tetrafluoropropionic acid with ortho-phenylenediamine in 4N hydrochloric acid yielded 2-(1,1,2,2-tetrafluoroethyl)-benzimidazole (TFB) (XXII) in 46% yield. Attempts to dehydrofluorinate TFB in refluxing triethylamine, and with potassium t-butoxide in dimethylsulfoxide at



(XXII)

temperatures ranging from 35° to 130° were unsuccessful, TFB being recovered for the most part unchanged.

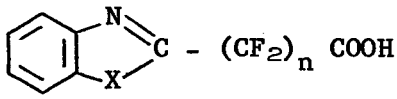
The attempted dehydrofluorination of TFB in refluxing 17% sodium hydroxide solution was unsuccessful and led to the formation of the disodium salt of oxalic acid, inorganic fluoride ion and a 60% yield of benzimidazole. Further attempts to dehydrofluorinate this compound has been temporarily suspended.

2. The Reaction of Dibasic Perfluoro-Acids with ortho-Phenylenediamine and ortho-Aminothiophenol. The Pyrolysis of 2-(1,1,2,2-Tetrafluoro-2-carboxyethyl)benzimidazole and Its Salt

The pyrolysis of the sodium salts of perfluoro-acids is a useful method for the preparation of terminal olefins[11].

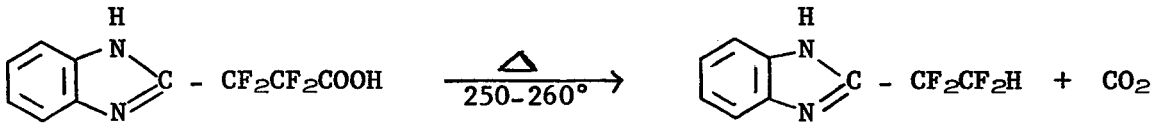
$$RCF_2CF_2COO^{\ominus}Na^{\oplus} \xrightarrow{\Delta} RCF = CF_2 + CO_2 + NaF$$

The condensation of perfluorosuccinic acid and perfluoroglutaric acid with ortho-phenylenediamine yielded the novel acids XXIII, (X = NH, n = 2), 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzimidazole, and XXIII, (X = NH, n = 3), 2-(1,1,2,2,3,3-hexafluoro-3-carboxypropyl)benzimidazole, in 60% and 46% yield respectively. In a similar fashion, the acid XXIII, (X = S, n = 2), 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzothiazole, has been prepared in ca. 60% yield.



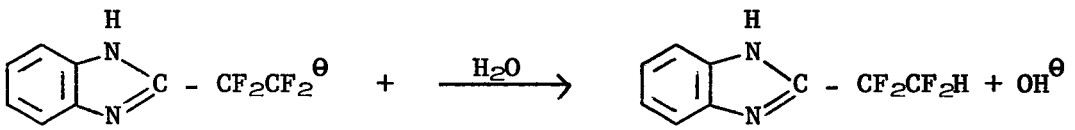
(XXIII)

Initial pyrolyses studies of the acid XXIII, (X = NH, n = 2) and its sodium salt have been carried out. This acid when heated at 250-260° decarboxylates with the formation of TFB. Likewise the decarboxylation of the moist sodium



(XXIII)

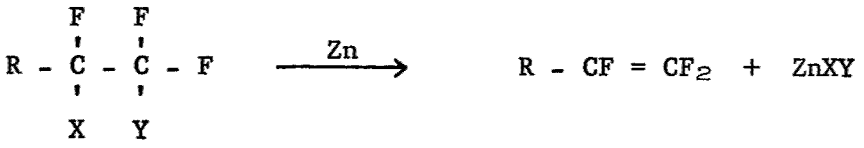
salt at 260-290° at atmospheric pressure occurs with the formation of TFB. A reasonable explanation for the formation of TFB is indicated.



However, the pyrolysis of the anhydrous sodium salt at 240-280°/0.2 mm. in a sublimation unit, yielded sublimates, which were obviously mixtures, carbon dioxide, and a residue which was predominantly inorganic fluoride. The infrared spectra of the sublimates showed new absorptions at 5.55μ, 5.65μ, and 5.82μ not present in the starting material. The trifluorovinyl group, as well as alpha-fluorocarbonyls, are known to absorb in this same general region. However, it is possible that conjugation with an aromatic system may cause a shift to shorter wavelengths. These results indicate that the reaction has proceeded to a certain extent in the desired direction. Initial efforts to separate the components of the mixture by fractional sublimation have been unsuccessful. Further efforts to separate the mixture are currently in progress.

3. 2,3,3-Trifluoro-3-bromo-2-chloropropionic Acid and 2-(1,2,2-Trifluoro-2-bromo-1-chloroethyl)benzimidazole

A third general method for preparing terminal fluoroolefins under rather mild conditions utilizes the dehalogenation of a properly substituted fluoro-compound with zinc as shown below:



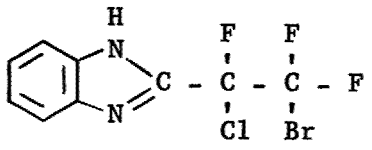
$$R - \overset{F}{\underset{X}{C}} - \overset{F}{\underset{Y}{C}} - F \xrightarrow{Zn} R - CF = CF_2 + ZnXY$$

X = Y = Cl, Br, I or any combination of these.

Efforts were therefore made to prepare a suitably substituted fluoro-acid which could be condensed to form benzazoles.

The ozonization of the olefin, 3,4,4-trifluoro-4-bromo-3-chlorobutene, followed by aqueous hydrogen peroxide oxidation, yielded a pure fluoro-acid, as determined by gas phase chromatography, having the correct neutralization equivalent for the desired acid 2,3,3-trifluoro-3-bromo-2-chloropropionic acid. However, the elemental analyses, (C,H) for this compound was very poor. An aqueous potassium permanganate oxidation of the same olefin also yielded the same acid in ca. 25-30% yield.

On the assumption that the above fluoro-acid was the desired acid, a small amount of this material (2.0 g.) was reacted with ortho-phenylenediamine to give a trace amount of a product, believed to be the desired intermediate (based on infrared spectrum, and C, H, N analyses), 2-(1,2,2-trifluoro-2-bromo-1-chloroethyl)benzimidazole (XXV). However, if the zinc dehalogenation procedure is to prove feasible, the yield of the condensation reaction must be greatly improved. Efforts in this direction are currently underway.



(XXV)

III. Characterization of Polymers

Polymers prepared under this program are to be studied for thermal stability, solubility, moldability and structural strength. Most of the reactions were first trials, being carried out on a small scale. Only the poly(benzothiazole) from the primuline fusion reaction has been obtained in sufficient quantity for testing.

1. Thermogravimetric Analysis

The ASD has requested that samples of polymers be submitted for thermogravimetric analysis and other characterizing tests. The TGA curve obtained for poly(benzothiazole), 910-W51A (the primuline fusion reaction), is shown on

Figure 1. On the figure are also plotted values for polyphenyl and "Teflon", as reported by Doyle[13]. The TGA determination of ASD and of Doyle are carried out in the same manner. Calculation of decomposition temperatures was therefore adapted from the report by Doyle. The "differential procedural decomposition temperature", DPDT, was calculated from a plot of weight loss per hour, the temperature where the loss amounted to 10% per hour being taken as the DPDT, found to be 620° for Sample 910-W51A. The "integral procedural decomposition temperature", IPDT, was calculated from the ratios of areas under the TGA curve, using Doyle's equation:

$$T_{A*K*} = 875\ A*K* + 25$$

For Sample 910-W51A, the IPDT was 690°C. Some representative values of decomposition temperatures are shown in Table 3, for comparison with the poly(benzothiazole). As was noted earlier in this report, relative stabilities of simple compounds do not necessarily predict the relative stabilities for the corresponding

TABLE 3

Thermogravimetric Analysis - Calculated Decomposition Temperatures

Polymer	IPDT, °C	DPDT, °C
Poly(benzothiazole) 910-W51A	690	620
Teflon	555	490
Polyphenyl	535	510
Silicone (SR32)	505	450
Nylon 66	420	360
Polystyrene	395	330
Plexiglass	345	280

polymer. For example, the decomposition point for biphenyl (1010°F)[a] is higher than that of 2-phenylbenzothiazole (943°F)[b], as shown in Table 2. The corresponding polymers, however, reverse the order of thermal stability, poly(benzothiazole) (620°C) showing a higher TGA value than does polyphenyl (510°C) as shown in Table 3 and Figure 1.

(a) 1010°F equals 543°C
(b) 943°F equals 505°C

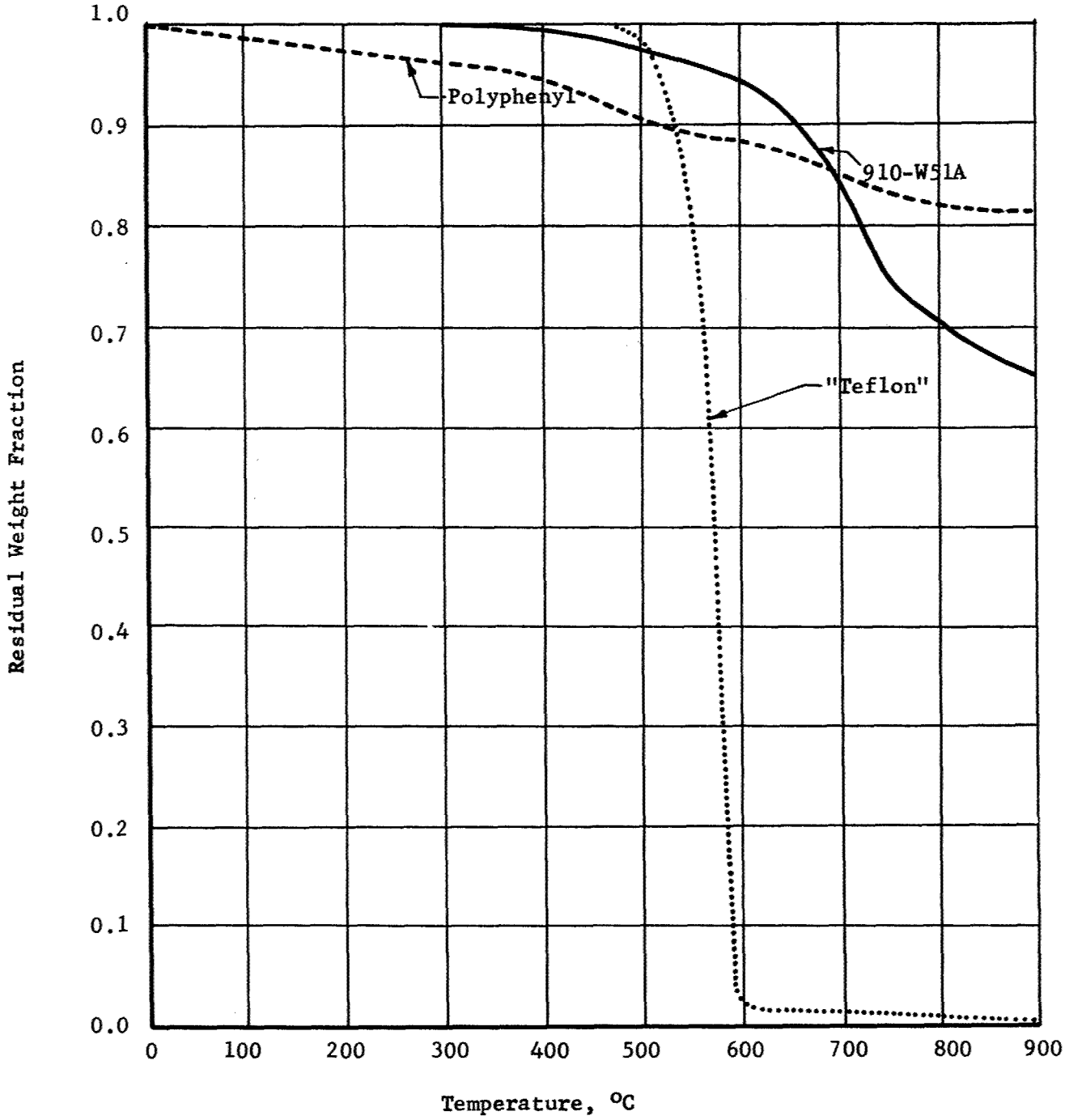
2. Solubility Studies

The discussion of the poly(benzothiazole), 910-W51A, in an earlier paragraph noted the unsuccessful attempts to effect solution of this polymer. The range of solubility attempted was at the 1% solution level, in order to develop a means of obtaining molecular weight value. The following solvents were tested, under a nitrogen atmosphere:

Figure 1

Thermogravimetric Analysis Data[13]

(ΔT 150°C per hour, nitrogen)



Sample (g.)	Solvent (g.)	Temp. (°C)	Time (hrs.)	Residue* (g.)
0.13	Sulfolane (14.4)	235-9	2.0	0.13
0.08	Hexachlorobenzene (11.6)	235-9	2.0	0.07
0.10	N-methyl-2-pyrrolidone (14.7)	193-9	5.0	0.07
0.40	2-Phenylbenzothiazole (14.1)	255-71	2.0	0.39
0.40	Dimethylsulfoxide (32.8)	164-70	4.0	0.40

*Some residues were not recovered quantitatively, because of mechanical losses. No detectable solid separated out of any of the solvent filtrates.

Concentrated sulfuric acid was slightly colored, but a slight floc observed upon neutralization of the diluted acid filtrate was too minute to be isolated.

3. Moldability of Polymers

Since the poly(benzothiazole), 910-W51A, was infusible and insoluble, a compression molding at high temperature was attempted. A small electrically-heated mold with a 7/8" diameter cylindrical cavity was adapted to a Vicat press capable of a maximum pressure of 20 tons. A 3/16" thick disc of the polymer was produced by a temperature of 600°F at a pressure of 20 tons after a holding time of 5 minutes. This disc was hard, but rather brittle. In a statistically designed experiment, 1/16" discs were prepared at varying temperatures (400 to 600°F), varying pressures (5 to 20 tons) and varying holding times (5 to 20 minutes). Many of the discs were too fragile to remove from the mold intact, and most were too brittle to obtain a relative hardness value.

4. Structural Strength of Molded Polymers

The poly(benzothiazole) could not be tested for tensile modulus or flexural modulus, since molded shapes for these tests could not be obtained.

IV. Conclusions

Polymers containing thiazole and benzothiazole units have been shown to have high thermal stability. The major problem is the formation of polymers with structural modifications in the connecting groups which will enhance solubility and moldability without greatly reducing thermal stability.

The major problem in the preparation of fluorocarbon polymers with pendant heterocyclic groups is the synthesis of the perfluorovinylheterocyclic monomers. The benzazole derivatives of the perfluoro acids appear to be promising intermediates.

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RESEARCH ON CONDENSATION OF DINITRILES, COORDINATION POLYMERS OF TRIAZINE, AND CONDENSATION POLYMERS OF TRIAZINE

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ABSTRACT

The research reported here arose from two discoveries. First, the nitriles of the lower dibasic acids condense at high pressure and elevated temperature to yield insoluble and fairly stable polymeric substances containing the -C=N-C=N- chain. Second, the zinc and beryllium coordination compounds of tris(2-hydroxyphenyl)-s-triazine are polymeric and exhibit phenomenal thermal stability. This report summarizes the general structural principles of thermal stability and reviews the work on nitrile condensations and the synthesis of bifunctional aryl triazines which yield stable linear coordination polymers and stable condensation polymers.

INTRODUCTION

This research has employed the following five general principles of thermal stability: (1) only the strongest chemical bonds must be used, (2) the structure must allow no easy pathways for rearrangement, (3) there must be maximum use of resonance stabilization, (4) all ring structures must have normal bond angles, and (5) the polybonding principle must be utilized as much as possible.

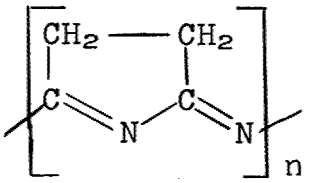
The polybonding principle requires that each skeletal atom be linked in the chain by more than one route. Polybonding is to be distinguished from multiple bonding as this latter term is defined in organic chemistry. Condensed rings are good examples of polybonded structures. Thus the "chains" in such extended compounds as anthracene, tetracene, pentacene, etc., cannot be broken by the rupture of only one carbon-carbon bond. Furthermore, if one bond is ruptured the natural bond angles of the structure hold the atoms near enough so that the bond can heal after the excess energy has dissipated by vibration through the molecule.

When the polybonding principle is applied to its fullest extent the products lack flexibility. They are the familiar "brick dust" and resist sintering into useful shapes even at very high pressure and temperatures. It is therefore necessary to build into the molecules some flexibility by means of single bonds. These flexible links should be made through inorganic units if great sacrifice of thermal stability is to be avoided.

It seems to be unimportant whether the building blocks are organic or inorganic since adequate stability can be realized by application of the principles mentioned above. In the present research several structures have been synthesized which are stable

to 500°C. It is in the flexible links that the strongest bonds are required, which probably can be realized only by employing elements other than carbon.

The work reported here falls into three general areas: First, the condensation of some dinitriles at very high pressure and temperature, which, in the case of succinonitrile, results in a poly ring system in which the repeating unit is



Second, the coordination polymerization of the bifunctional triazine, 2-(2-phenoxyphenyl)-4,6-bis(2-hydroxyphenyl)-s-triazine, resulting in a thoroughly polybonded structure;

Third, the condensation of the bifunctional triazine, 2-phenyl-4,6-bis(3-hydroxyphenyl)-s-triazine with diphenyldichlorosilane.

DISCUSSION

HIGH PRESSURE EQUIPMENT

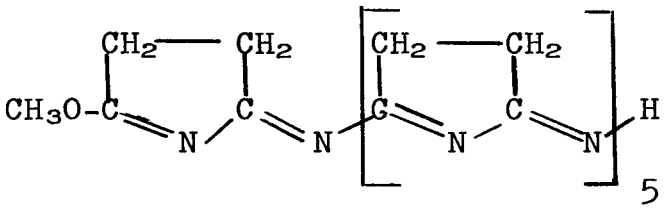
For the high pressure work various modifications of the piston and cylinder apparatus and also the Bridgman anvil apparatus have been used. In some experiments internal thermocouples have been used for differential thermal analysis for observation of reaction rates. The piston and cylinder equipment has been used to 25,000-28,000 atmospheres and up to 450-500°C. The anvil apparatus has been used to 38,000 atmospheres and to 525°C.

CONDENSATION OF NITRILES

The work of Cairns, et al., and of Bengelsdorf has shown that mononitriles condense under high pressure to yield sym-triazines. The condensation proceeds with moderate speed, as compared with the chemical trimerization at one atmosphere. In the case of the nitriles of the lower dibasic acids a more complicated reaction occurs which can proceed with explosive violence unless moderated by dilution with an inert solvent. Such compounds as malononitrile, fumaronitrile, and succinonitrile must be handled with great care under high pressure. Anionic catalysts such as sodium methoxide and sodium 2,4-dichlorophenate markedly lower the temperature and pressure required for initiation of condensation.

The effect of pressure on the condensation is exactly as expected for a bimolecular addition reaction. The rate is increased at any given temperature by increasing the pressure, while the temperature at which reaction is initiated is lowered by increasing the pressure.

Analysis and end-group determinations show that the product from succinonitrile, initiated by sodium methoxide in methanol, has the structure:



The infrared spectrum shows the complete absence of -C≡N groups and the presence of -C=N- groups. When sodium dichlorophenate in methanol was used as catalyst, the product has a degree of polymerization of 66 and the chain is initiated by a dichlorophenoxy group.

The measured thermal stability of these products was somewhat disappointing. Gases were slowly evolved at 300°C. Ammonia was the principal gaseous product. The limited thermal stability is obviously due to the large number of single bonds per molecule.

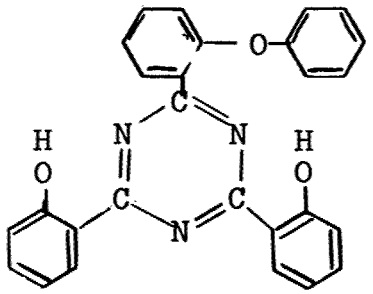
Other nitriles were studied at high temperature and pressure. Terephthalonitrile mixed with benzonitrile yielded the three expected products; namely, triphenyltriazine, the double triazine of terephthalonitrile with four benzonitrile molecules, and the polymeric triazine of terephthalonitrile alone. This latter compound is an infusible, insoluble, tan powder. The condensation of 2,6-dicyanopyridine yielded a very hard black solid. Infrared spectra show that the nitrile groups had condensed to triazine rings to form a network polymer. The diimide of pyromellitic acid and p-aminobenzonitrile condensed via the terminal nitrile groups only partially at 20,000 atmospheres and 500°C. About 80% of the nitrile groups remained after 20 minutes at these severe conditions.

Not all nitriles will condense under these conditions. Anthranilonitrile refused to condense; salicylonitrile, however, easily yields the corresponding triazine. The phenyl ether of salicylonitrile, o-cyanodiphenyl ether, has resisted all our efforts to trimerize it.

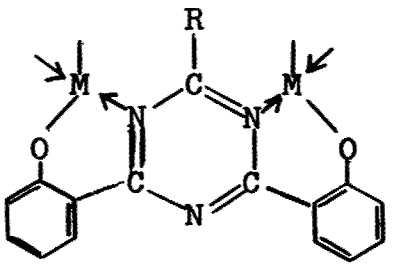
COORDINATION POLYMERS

The structure of the trimer of salicylonitrile, 2,4,6-tris(2-hydroxyphenyl)-s-triazine, suggests that it should coordinate with divalent tetracoordinate metal ions to form polymeric products. Since there are three sites for coordination in this triazine the products are likely to be somewhat crosslinked even when only enough metal ion is used to satisfy two sites. An extensive study of this ligand and its metal chelates was made, which is presented in a paper in the Journal of Organic Chemistry, vol. 27, p. 592. The zinc and the beryllium compounds are completely stable at 500°C.

Truly linear coordination polymers can be prepared from bifunctional triazines such as the monophenyl ether of the above compound. To investigate this possibility 2-(2-phenoxyphenyl)-4,6-bis(2-hydroxyphenyl)-s-triazine was prepared. It can coordinate with metal ions at only two sites and should yield a linear polymer that is thoroughly polybonded. The ligand has the structure shown here, where R is the phenoxyphenyl group:



The coordination compounds with bivalent tetracoordinate metal ions have the structure:



The infinite linear polymer contains one metal ion per triazine unit. This composition is never obtained exactly because the polymer chains are rather short, containing 6 to 8 triazine units. The chains are terminated by metal ions carrying small groups such as acetate, acetylacetone, or hydroxyl, from the solution. For this reason the metal content is always slightly higher than that calculated for the infinite polymer. No method is yet available for determination of molecular weight except the metal or end-group analyses, which are uncertain because thorough purification of the polymer has not been possible.

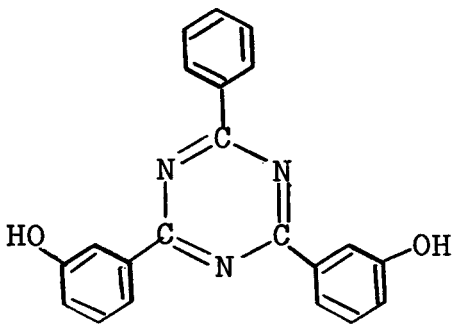
The phenoxyphenyl group, at R, greatly improves the sinterability of the polymer, as was expected. Although the zinc compound is infusible at 500°C it sinters at only 240°C under a pressure of 12,000 atmospheres to yield a strong, hard, translucent yellow solid.

The thermal stability of these coordination polymers is due to the fact that they comply well with the principles mentioned in the introduction. The polybonding principle is particularly well illustrated. The main chain of the polymer cannot be broken by the rupture of any one bond. Resonance extends throughout the whole molecule. Only strong chemical bonds are employed and bond

angles are normal. Models of the compound show that the structure is tightly packed but not strained. Beyond doubt strong Van der Walls forces give high crystal lattice energy, which contributes to the thermal stability as well as to the high melting point. A careful study of these principles in relation to structure will lead to even more substantial polymers.

CONDENSATION POLYMERS

The lack of flexibility of the above coordination polymers suggested that this physical property might be improved by coupling stable triazine molecules by single bonds. It is obvious that the coupling must be done through very strong chemical bonds if great sacrifice of thermal stability is to be avoided. Even so, the loss of polybonding will be detrimental. The -O-Si-O- linkage was the obvious choice. It was also clear that coupling could be done more easily at the meta- or para- positions on the benzene rings than at the ortho-position. To investigate this system the synthesis of 2-phenyl-4,6-bis(3-hydroxyphenyl)-s-triazine was undertaken. The structure of the triazine is:



The synthesis involved the preparation of the dinitro derivative, 2-phenyl-4,6-bis(3-nitrophenyl)-s-triazine by the Eitner and Krafft synthesis, using 3-nitrobenzonitrile and benzoylchloride with aluminum chloride and ammonium chloride. After careful purification this product was hydrogenated with platinum oxide and 50 psi hydrogen to yield 2-phenyl-4,6-bis(3-aminophenyl)-s-triazine, which was then diazotized to yield the desired compound. Purification of the product was accomplished by preparation of the dibenzoate and subsequent hydrolysis.

The condensation polymer was prepared by heating the pure dihydroxy compound with diphenyl dichlorosilane in diglyme under dry nitrogen, while titrating the slowly evolved gaseous HCl with standard sodium hydroxide solution. The product is a brown solid that softens at 175°C. It is completely stable at 360°C and can be sintered under high pressure to yield a coherent, but somewhat brittle solid. Analysis indicates that the polymer molecule contains seven triazine units and six silicon atoms.

CONCLUSIONS

1. The high pressure condensation of dinitriles yields reasonably stable solid, black polymers. The products are very insoluble, brittle, and unsinterable. A more thorough study of the structure of these products and the mechanism of the reaction must be made before useful materials can be prepared.

2. Coordination polymers whose structures agree with the principles for thermal stability offer great promise.

3. Methods are needed for control of chain length in the coordination reaction, as are also methods for determination of chain length.

4. Polymers produced by linking thermally stable bifunctional units by means of single bonds will require the strongest inorganic links if maximum thermal stability is to be realized.

SYNTHESIS STUDIES OF POLY-m-PHENOXYLENE*

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ABSTRACT

Many of the variables affecting the synthesis of poly-m-phenoxylene via self-condensation of potassium m-halophenoxides have been studied. The most significant factors affecting the molecular weight are carbon-carbon rather than carbon-oxygen coupling and cyclization. Non-polar solvents reduce the ionization of the starting salt and so reduce carbon-carbon coupling. Cyclization is less at high concentration of starting materials relative to solvent and since bulk polymerization is not feasible due to the exothermic nature of the reaction, heterogeneous reaction in highly non-polar medium gives highest degree of polymerization yet attained.

Basically there is little novelty in suggesting that polymers composed of alternating phenylene and oxygen units might have interesting thermal stability. Recent publications by Hay, et al[1], Staffin and Price[2] in this country, and by Golden[3], abroad, indicate the continuing interest in polymers of such structure. Interestingly the bulk of the published work in this field covers poly-p-phenoxylene (or poly-p-phenylene oxide) and substituted poly-p-phenoxylenes only. Indeed except for work on the "chain-stopped" oligomers of interest as lubricants[4,5,6], poly-m-phenoxylene has received scant attention. The only mention of such a polymer, of which the authors are aware, is that of thermal stability data presented by Wright[7]. The fact is, that in addition to the obvious, attractive thermal stability possible in poly-m-phenoxylene, the "amorphous nature"[4] of the m-phenoxylene unit suggests interesting physical properties for such a polymer, including the possibility of elastomeric properties. Such was the basis for conducting the work herein reported.

Synthesis of the desired poly-m-phenoxylene, because of the desired configuration, obviously cannot be approached through the attractive oxidative and free-radical reactions developed by Hays and Price, respectively. The only alternative is a displacement reaction such as that of the Ullman ether synthesis, utilizing reaction of the alkali metal salt of a phenol with a halogenated compound under the influence of copper catalyst. For polymer formation two routes are theoretically feasible, condensation of a dihydroxy compound with a dihalo compound or self-condensation of a material having both hydroxyl and halogen in the same

*Poly-m-phenylene oxide, $(m\text{-}C_6H_4O\text{-})_n$

compound. In earlier work on the synthesis of oligomers of poly-m-phenoxylene for lubricants it was shown that the only readily accessible dihydric compound, resorcinol, failed to undergo the desired reaction. This leaves only the second alternative, that of self-condensation of (salts of) m-halophenol, and higher analogs, as the sole available route (by straightforward reaction schemes) for preparation of poly-m-phenoxylene.

Limited self-condensation of alkali-metal salts of m-bromophenol had previously been used for the preparations of intermediates for lubricants with reasonable success. This only means, however, that the products of such reaction were not so grossly contaminated that they could not be adequately purified by conventional techniques. Since essentially zero per-cent is the limiting amount of side-reaction that can be tolerated in a polymer forming reaction, a series of studies involving investigation of homogeneous vs heterogeneous conditions, effect of solvent, catalyst, catalyst addition temperature, light, concentration and alkali metal were undertaken. The effects of some of these variables on the polymerization as indicated by effect on the molecular weight are discussed.

EXPERIMENTAL

A. "Homogeneous" Conditions

Homogeniety in a variety of solvents was sought by allowing water present in the starting 87% KOH, water of reaction and, in some cases, added water to remain in the reaction mixture. In general, the moist solvent so attained provided homogeneous reaction mixtures. Solvents used in these experiments included dimethylformamide, phenyl ether, pyridine, nitrobenzene, dimethyl sulfoxide, xylene, pyridine and diethyl carbitol. Reaction temperatures varied from 110°C for pyridine to 180°C for phenyl ether and for nitrobenzene. Two slightly different methods of performing the reactions were used; in the first 87% KOH pellets (0.5 mole), m-bromophenol (0.5 mole), 1 to 2 grams of copper powder catalyst, and solvent were charged together and allowed to react under N_2 flow with stirring. In the second reaction method, m-bromophenol, copper catalyst, and solvent were charged and heated to the reaction temperature and then an equimolar quantity of KOH in concentrated aqueous solution was added dropwise. Products were isolated by extraction or precipitation, as fitted the individual case, and were redissolved and reprecipitated before analyses. Determination of molecular weight by freezing point depression of p-dibromobenzene was performed where solubility was appropriate, and analyses for bromine and hydroxyl[8] were carried out.

Comparison of end group analyses, as confirmed by infrared spectra, indicated that none of the polymers so prepared was authentic poly-m-phenoxylene. Results for these preparations are exemplified by results for a run in phenyl ether and one in nitrobenzene as shown in Table I.

B. Anhydrous Conditions

m-Bromophenol and m-chlorophenol (Eastman) were purified by passage of a 50% solution in one to one benzene/ether mixture through an alumina column, followed by removal of solvents by distillation and then distillation at reduced pressure. The anhydrous alkali metal salts of m-halophenols were prepared by azeotropic distillation of water with benzene from a concentrated aqueous salt solution under nitrogen. Benzene was displaced by addition of solvent with

concurrent distillation. Copper powder catalyst (originally 1 g. but in later experiments 3 g.) was added, preferably before the reaction mixture temperature reached 100°. Reaction times and temperatures were varied from 2 to 88 hours and from 120° to 250°C with preferred temperatures being 180° to 200°C.

In general, the reaction mixtures were cooled to room temperature, diluted with benzene and the benzene solution filtered and washed. The solution was then concentrated to 50-75 ml and the polymer precipitated by addition to 2-1/2 to 3 liters of methanol. The polymer was taken up in 50 to 100 ml of benzene, or in later experiments a 1 to 1 mixture of benzene/chloroform, chilled and filtered. At this point the precipitate was a mixture of small amounts of unidentified "trash" and in some cases low molecular weight cyclic oligomers. The filtrate was then added to methanol to precipitate polymer, which was the recycled through the above steps before final freeze-drying from benzene solution. Polymers so prepared in general have flow points of 120 to 130°, except where cyclization has been extensive, in which case flow points may be as low as 65 to 75°C.

Microanalytical analyses for carbon, hydrogen and halogen were obtained from either Schwartzkopf Microanalytical Laboratories, Woodside, Long Island, N.Y. or Dr. Carol K. Fitz, Needham Heights, Mass. Analysis for active hydrogen was by Schwartzkopf Microanalytical Laboratories. Vapor pressure osmometric (VPO) molecular weight determinations were performed in this Laboratory using a Mechrolab Model 301 Vapor Pressure Osmometer. Determination of molecular weights by viscometry measurements were carried out in phenyl ether and/or benzene using the approximations $a = 1$ and $K = 2 \times 10^{-5}$ in the Staudinger equation, $/\eta/ = KM^a$.

C. Cyclic Oligomers

Small quantities of crystalline products were isolated from several of the polymer preparations by precipitation from a benzene or benzene/chloroform solution of poly-m-phenoxylene, or were collected as a sublimate in reactions run under reduced pressure. In general yields were 100 mg or less though in two cases yields were on the order of 250 mg. The crystalline products were separated into two components when sufficient quantities were on hand by recrystallization from benzene. Where yields were insufficient to allow separation, both fractions were nevertheless demonstrable by infrared spectra.

One of the larger batches was separated and analyzed as follows: the crystalline precipitate was recrystallized from benzene to afford two fractions. The larger first crop melted at 236°, while the second melted at 275°.

Microanalysis: Calculated for (C_6H_4O) : C, 78.25%; H, 4.38%.

Found*: 275° fraction: C, 78.93%; H, 4.79%; Br, 0%, Active H, 0%; Mol. wt. 312.
236° fraction: C, 78.51%; H, 4.33%; Br, 0%, Active H, Trace; Mol. wt. could not be determined due to insolubility.

Theoretical molecular weight for $(C_6H_4O)_3$ is 276 and for $(C_6H_4O)_4$ is 368.

*By Schwartzkopf Microanalytical Laboratories

The analysis for another batch of material which was not separable because of the small sample size but which contained both components (by infrared spectra) was:

Found*: C, 78.97%; H, 4.69%, Br, 0%; Active H, 0.05% and Mol. wt. 339.

RESULTS AND DISCUSSION

The results for representative syntheses are shown in Tables 1 through 5 in which are tabulated significant experimental details together with results of various measures of the molecular weights of the resultant polymers.

Table 1 shows results for two runs made under "homogeneous", that is to say moist, conditions. In both of these, as well as in several more for which results are not presented, the equivalent weight based on hydroxyl content is significantly lower than that based on bromine content. This would serve to indicate that extensive carbon-carbon coupling occurred.

The importance of the use of copper as a catalyst is illustrated by the results given in Table 2. Without added catalyst the reaction proceeds only to a limited extent. Cuprous oxide apparently has some catalytic activity, but is obviously less efficient than powdered copper metal. These reactions illustrate an important further point. Both the cuprous oxide and the metallic copper catalyzed reactions yielded crystalline cyclic oligomers and the end group analyses for both polymers, as compared to the vapor pressure osmometry (VPO) values, indicate that these also contain (large) cyclic components.

Since many of the polymerizations were carried out over extensive periods of time, it was inevitable that attack on glassware would be evident. Such attack shows up in etching of the glassware itself (noticeable after several runs have been made in the same flask) and in ash content found on microanalysis. In an effort to avoid this factor several runs were made in Monel metal flasks (results not presented) in which it was found that reaction either did not take place at all or else was seriously inhibited. In an effort to differentiate between the possible causes of this inhibition, either inhibition by Monel or by lack of illumination of the reactants, a series of runs were set up using identical conditions except for the flask. These experiments are shown in Table 3 and tend to indicate a minor role for the effect of light.

The effect of concentration on the degree of polymerization is indicated in Table 4. Decreasing the amount of solvent tends to promote higher degree of polymerization. Several attempts to achieve bulk polymerization of potassium m-bromophenoxide gave only very low yields of polymer, however, due largely to decomposition engendered by uncontrollable exothermic heating. The closest approach to true bulk polymerization is that of beginning the reaction in a solvent followed by removal of solvent by reduced pressure distillation while holding constant temperature. This technique is represented in the table as 100 → None under the heading Vol. of Solvent and is shown by the analytical results as being no more effective than the use of high concentration of starting material relative to solvent.

*By Schwartzkopf Microanalytical Laboratories

TABLE 1. ATTEMPTED SYNTHESIS OF POLY-m-PHENOXYLENE, "HOMOGENEOUS REACTION CONDITIONS"

Reagents: m-Bromophenol, aqueous KOH, copper catalyst

Time: 2 Hours @ 180°C

SOLVENT	MOLECULAR WEIGHT		
	Cryoscopic	Bromine	Hydroxyl
Phenyl Ether	--	16,500	265
Nitrobenzene	5400	3,300	800

TABLE 2. SYNTHESIS OF POLY-m-PHENOXYLENE, "EFFECT OF COPPER CATALYST"

Reagents: Anhydrous potassium m-bromophenoxide

Solvent: Phenyl ether

			Molecular Weight		
Catalyst	Time (hrs.)	Temp. °C	VPO*	Bromine	Active H
None	60	175-180	930	1100	--
Cu_2O	60	150	1400	3700	5000
Cu	36	150	2000	7200	5000

*Vapor Pressure Osmometry

TABLE 3. SYNTHESIS OF POLY-m-PHENOXYLENE, "EFFECT OF LIGHT"

Reagents: Anhydrous potassium m-chlorophenoxide, copper catalyst

Solvent: Phenyl ether

Time: 40 Hours at 185°C

	Molecular Weight			
Flask	VPO	Chlorine	Active H	Viscosity
Copper	1500	7100	3300	3700
Amber Coated Pyrex	1500	7100	3300	3250
Regular Pyrex	1900	5900	2500	3500

TABLE 4. SYNTHESIS OF POLY-m-PHENOXYLENE, "EFFECT OF CONCENTRATION"

Reagents: One-quarter mole anhydrous potassium m-chlorophenoxide, copper catalyst

Solvent: Phenyl ether

Time: 40 Hours at 185°C

Vol. of Solvent ml	Molecular Weight			
	VPO	Chloride	Active H	Viscosity
200	2000	5900	2500	3250
100	2400	5500	5000	3250
50	2900	6500	3333	7300
100 → None*	2800	7100	5000	5000

* Reaction started in 100 ml of phenyl ether, then solvent removed by reduced pressure distillation keeping temperature constant.

TABLE 5. SYNTHESIS OF POLY-m-PHENOXYLENE, "ANHYDROUS CONDITIONS"

Reagents: Anhydrous Potassium-m-Bromophenoxide, Copper Catalyst

Solvent	Time	Temp.	Molecular Weight VPO	Halogen	Active H	Visc.
Phenyl Ether	5	180	2700	3000	3300	3100
Diphenyl	6	170	3600	20,000	3300	----
Benzophenone	7	185-205	1600	29,000	--	1900
Phenyl Ether → None*	80	155	3900	5,600	4000	8000
Phenyl Ether	48+ 18	120+ 150	3100	20,000	>4000	6800
Reagents: Anhydrous Potassium m-chlorophenoxide, copper catalyst						
Phenyl Ether → None*	88	175	5500	5,900	2500	--
Eicosane	62	180	6900	--	--	9800

* Reaction started in phenyl ether, then solvent removed under reduced pressure.

Table 5 presents the results for a number of representative polymerizations conducted in various solvent media. The results indicate a higher degree of polymerization is attained the less polar is the solvent. Also, indicated is a higher degree of polymerization with higher temperature and longer reaction times. Noteworthy also is a tendency for the molecular weight as determined by viscometry vs that obtained by VPO to rise from a one to one relationship to as high as two to one with longer reaction times.

The results for the reaction conducted in eicosane were incomplete at the time of writing. They are of expecial interest though in that the molecular weight as measured by both VPO and viscometry were the highest yet attained and since reaction in eicosane is the only instance of a completely heterogeneous reaction. All other solvent systems were found to give homogeneous reaction, either dissolving the starting metal halophenoxide (as in the case of benzophenone) or dissolving the oligomeric products at onset of polymerization.

At the beginning of this program, it was acknowledged that the probability of preparing high molecular weight poly-m-phenoxylene via the Ullmann reaction was poor unless all competing side reactions could be effectively surpressed. In this connection particular attention was given to the results of Kornblum and Lurie[9] who had shown that in the preparation of phenyl benzyl ethers carbon-carbon coupling was enhanced by heterogeneous reaction and was surpressed by homogeneous reaction conditions. These results led us to undertake experiments designed to give homogeneous reaction conditions, which were largely conditions such that water was present in the reaction mixture. The results for these reactions indicated that in the presence of water carbon-carbon coupling was high. Further, comparison of results for polymerizations run under anhydrous conditions show that for the preparation of poly-m-phenoxylene the more non-polar is the solvent, then the more heterogeneous is the reaction, and that under such conditions, the degree of polymerization reaches higher values. It is not possible to rigorously prove that the higher molecular weight polymers receive no contribution from carbon-carbon coupling since analyses for residual hydroxyl (or active hydrogen) are not sufficiently accurate by virtue of the very low percentage content of these groups. It bears noting, however, that the greater the polarity of the solvent, then the higher would be the degree of ionization of the metal halophenoxide, and as ionization increases, so should carbon-carbon coupling increase.

On the other hand, the higher degree of polymerization achievable under heterogeneous conditions may be due at least in part to still another factor. Cyclization is strongly evident under conditions leading to low reaction rates and under conditions of high dilution. Heterogeneity should provide more intimate contact between catalyst and reactant thus maximizing reaction rates at a given temperature and at the same time should remove the concentration effect. Thus, reaction under heterogeneous conditions would be expected to give higher degree of polymerization due to suppression of cyclization.

THERMOGRAVIMETRIC ANALYSIS OF POLY-m-PHENOXYLENE

Figures 1 and 2 show typical results of thermogravimetric analyses (TGA) of poly-m-phenoxylene in nitrogen and in air, respectively, at a heating rate of 180°C per hour. Except for the expected difference in final weight of residue, there is essentially no difference in the character of the plots or temperature of decomposition due to the atmosphere. These results tend to indicate that the oxidation of the polymer is a non-chain reaction and is the result of oxidative attack on the products of thermal decomposition of the polymer.

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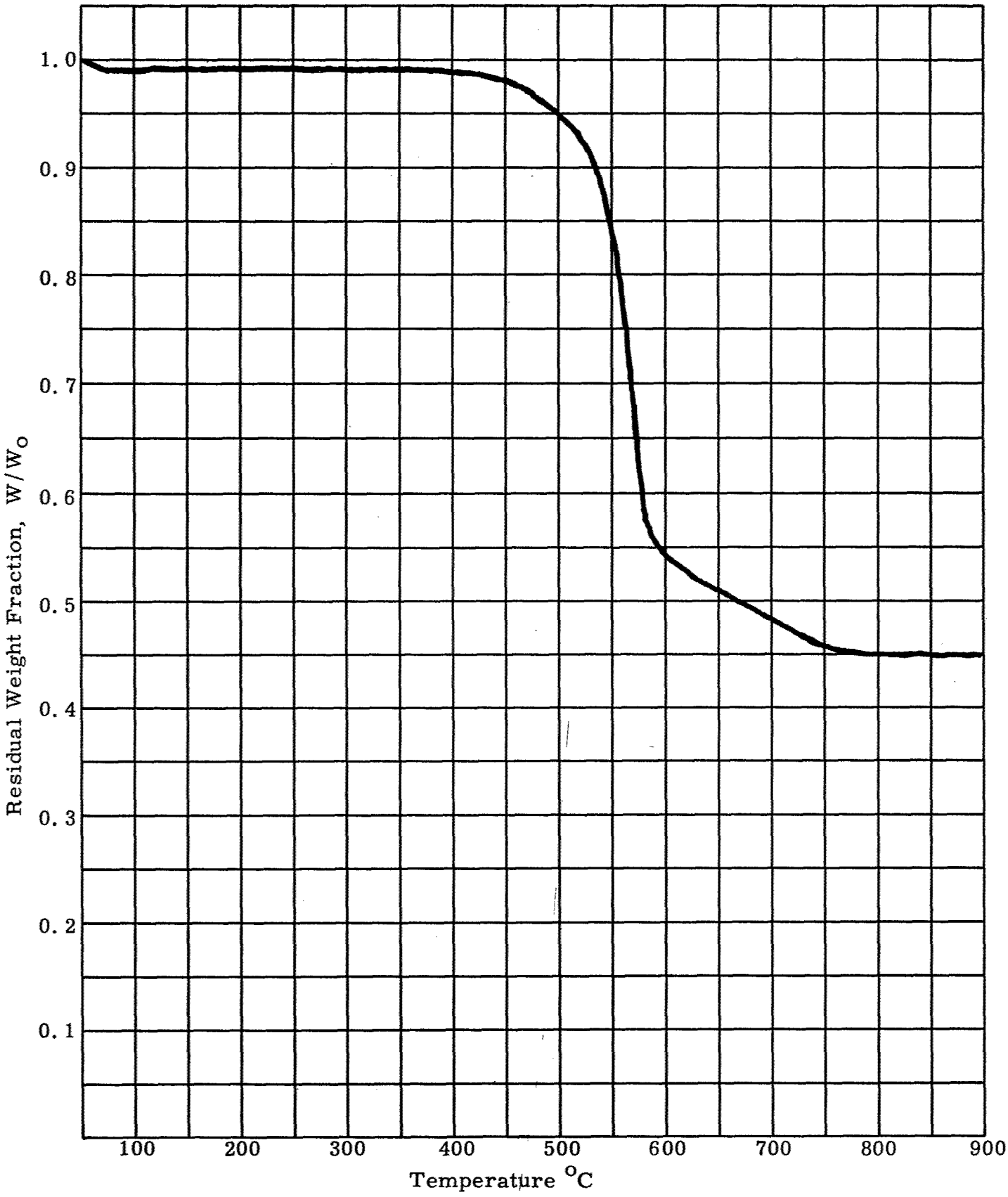


Figure 1. TGA In Dry Nitrogen At 180°C Per Hour For Poly-m-phenoxylene ($\bar{M}_{VPO}$ = 3900)



Figure 2. TGA In Air At 180°C Per Hour For Poly-m-phenoxylene ($\bar{M}_{VPO}$ = 3900)

INVESTIGATION OF PHENYLENE SULFIDE POLYMERS

by

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Abstract

The investigation of phenylene sulfide polymers has been divided into four areas of endeavor. These are a kinetic study of a model reaction, monomer synthesis, polymerization, and determination of polymer properties. From the results of the kinetic study and monomer synthesis coupled with the early results in the other two fields cuprous p-bromothiophenoxide has been chosen as the monomer of choice for the preparation of linear phenylene sulfide polymers. Later work on this monomer has shown that a number average degree of polymerization greater than 400 can be obtained either by solid state or solution polymerization. This polymer which has useful polymeric properties is stable in air or nitrogen to 450°C and forms a polymeric residue stable to 900°C under nitrogen.

Introduction

The investigation of phenylene sulfide polymers is being conducted under Air Force Contract Number AF 33(616)-7251; Project Number 7340, "Non-metallic and Composite Materials"; Task Number 73404, "New Chemicals and Methods". It is administered under the direction of Materials Central, Directorate of Materials and Processes, Aeronautical Systems Division with Mr. G. A. Loughran as the Project Engineer. This work is being performed in the Plastics Department Research Laboratories of The Dow Chemical Company, Midland, Michigan. The purpose of this work is to obtain a useful plastic material which is thermally stable.

The initial work on phenylene sulfide polymers was done by Dr. A. D. Macallum of London, Ontario. He discovered that this polymer could be prepared by the sequence of reactions shown in Figure 1.

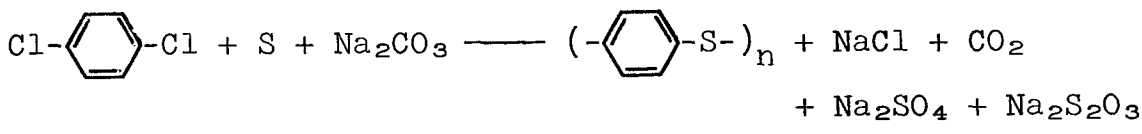


Figure 1. Macallum Polymerization

Since Dow makes p-dichlorobenzene and the other two starting materials are inexpensive, the patents for this work were purchased from Dr. Macallum by The Dow Chemical Company in 1954. Subsequent studies were carried on in the Plastics Department Research Laboratories.

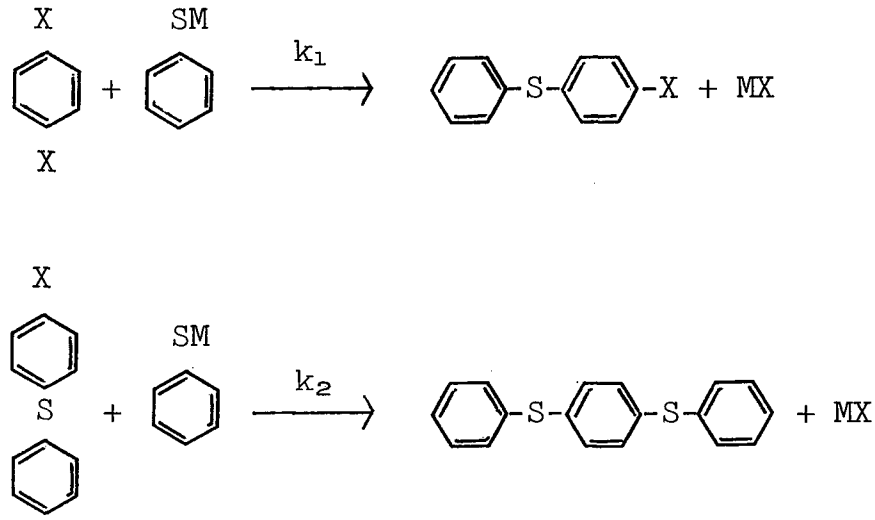
It soon became apparent that the Macallum polymerization would be a difficult reaction to control since the yields and the polymer properties were very unpredictable. In addition the polymeric material obtained was somewhat branched and or lightly crosslinked, and also there was always found an insoluble, infusible highly crosslinked material. Consequently, it was decided to prepare a more readily characterizable polymer namely a linear polymer from the condensation polymerization of such species as p-halothiophenoxides. In the course of the investigation on linear phenylene sulfide polymers four different aspects of the problem were studied. These were (1) a kinetic study of the polymerization on model compounds, (2) monomer synthesis, (3) polymerization studies, and (4) determination of the polymer properties.

Kinetic Studies

The first phase of our work was to study the basic polymerization reactions. Since isolation of individual products from a polymerization reaction would be at best difficult, it was decided to investigate a model reaction. From this it was hoped to determine the relative reactivities of the various halogens and cations used as well as the side reactions involved in the use of each halogen and cation. Having this information then, a monomer system could be chosen which would have the greatest possibility of producing a high molecular weight polymer by condensation polymerization.

The system studied is depicted in Figure 2. As can be seen, the reaction takes place in two steps. In the first step p-dihalobenzene and thiophenoxide react to give p-halophenyl phenyl sulfide. This then reacts with more thiophenoxide in the second step to give 1,4-bis(phenylthio)benzene.

For the kinetic consideration of the reaction, it was treated as a competitive, consecutive second order reaction. Due to the nature of this type of kinetic treatment the individual rate constants are extremely difficult to determine accurately. However, thanks to Dr. Turner Alfrey, Jr. who worked out the mathematical treatment we were able to obtain quite easily the ratio of the rate constants. This ratio then makes it possible to determine whether a halogen opposite a sulfide linkage (k_2) is more reactive than one opposite the same halogen (k_1). It should be mentioned that when the two halogens have the same reactivity, the ratio of k_2/k_1 equals 0.5.



X = F, Cl, Br, I
M = Na, Li, K, Cu

Figure 2. MODEL REACTION FOR KINETIC STUDIES

The starting materials for this study needed to be very pure since by-products were going to be studied also. Consequently the commercial p-dihalobenzenes were recrystallized and then checked for purity by gas-liquid chromatography prior to use. The thiophenoxide after purification was checked for purity by potentiometric titration with silver nitrate. Both reagents had a purity of greater than 99%.

All the reaction and workup procedures were standardized to avoid introducing errors from this source. The reactions were run in sealed glass ampoules under an argon atmosphere. The ampoules were placed in steel jackets and preheated in a molten salt bath at 500°C for one minute and forty seconds. Then they were placed in the preheated bomb rocker and allowed to react for the desired time. Zero time for reactions carried out at 250°C was taken as four minutes after the introduction of the bomb into the molten salt bath since calibration runs had indicated that this was the time required for the bomb to reach the reaction temperature. For reaction times of greater than six hours preheat treatment was felt to be unnecessary.

After the reaction was completed, the ampoules were frozen in liquid nitrogen and opened. The contents were extracted with carbon disulfide and then with water. The water extract was titrated with silver nitrate to determine the amount of halide ion liberated. The carbon disulfide extract was analyzed on a model 300 F&M high temperature, linear programmed gas-liquid chromatograph. A sample chromatogram is shown in Figure 3. This figure shows the separation of the products obtained in a typical reaction mixture and their order of elution. Durene, peak 4, is an internal standard. Peaks 8 and 9 are the products of the first and second reactions, respectively (Figure 2). An example of the results from a typical analysis is shown in Table I. As can be seen the results are quite good giving essentially a complete material balance. On the average, however, the results fall in a range of $\pm$ 5% of the values given in Table I.

Two of the products listed in Table I, diphenyl sulfide and diphenyl disulfide, occur in rather small amounts. These are the major by-products in the reaction and amount to 0.2-0.4% of the total products in a solution reaction and 0.2-0.7% in a reaction without solvent. The diphenyl disulfide undoubtedly arises from thiophenoxide being oxidized during the workup. The diphenyl sulfide may arise from disproportionation of the thiophenoxide during the reaction. Other by-products found in only trace quantities are benzene, halobenzene, and free halogen. From the by-product studies it became apparent that in the reaction of sodium thiophenoxide with p-dihalobenzene the order of by-product production for the respective halogens was $I > F > Br \sim Cl$.

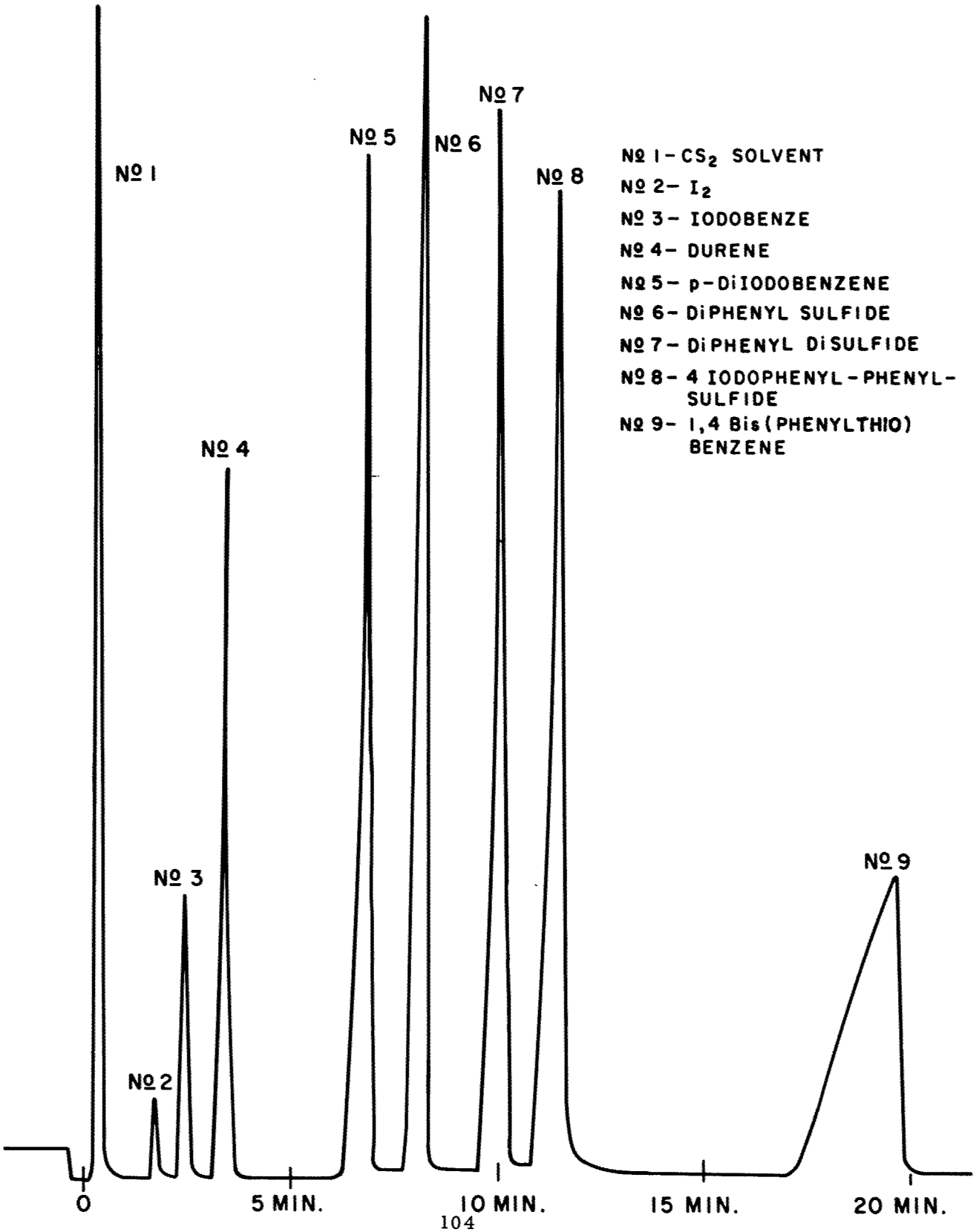


FIGURE 3. MODEL GAS-LIQUID CHROMATOGRAM OF REACTION PRODUCTS

TABLE I

Complete Material Balance of the Reaction of Sodium Thiophenoxide with p-Diiodobenzene

Reactants:	Moles
sodium thiophenoxide	0.0200
p-diiodobenzene	0.0100
Products:	
sodium iodide	0.01635
sodium thiophenoxide	0.00342
p-diiodobenzene	0.00033
p-iodophenyl sulfide	0.00297
p-bis (phenylthio) benzene	0.00660
phenyl sulfide	0.00011
phenyl disulfide	0.00035
Material Balance:	%
iodine accounted for	99.9
sulfur accounted for	102.0
benzene accounted for	101.4

The order of ease of halogen displacement, however, does not parallel exactly that for by-product production. Some of the kinetic data from the model reactions is shown in Table II. The relative reactivities of the various halogens can be ascertained from the percent dihalobenzene reacted in a given length of time. Seventy-seven percent of the p-difluorobenzene reacted in twelve hours while in the case of the chloro, bromo, and iodo compounds the same extent of reaction is achieved in about five hours, fifteen minutes, and ten minutes respectively as shown by Table II. Therefore the order of reactivity of the dihalobenzenes must be I>Br>Cl>F for the overall reaction.

In order to determine the relative reactivities of the respective halogens under the same circumstances in each case and without complications by consecutive, competing reactions, the reaction of p-halophenyl phenyl sulfide with thiophenoxide was studied. The results are given in Table III. It can immediately be seen that the order of replaceability of a halogen opposite a sulfide linkage is I>Br>F~Cl or essentially the same order exhibited in Table II.

Table II also contains some interesting data in the form of k_2/k_1 ratios. These ratios show that an iodine opposite an iodine has about the same reactivity as one opposite a sulfide. (The ratio is about 0.5.) In the case of bromine, however, the bromine opposite a sulfide is 1.5 times more reactive than one opposite a bromine. With chlorine this factor goes to about three times and with fluorine to seventy times. This suggests that in a monomer system containing an aryl fluoride a preferential formation of polymer might be observed. If this happens, it would be possible to obtain high molecular weights at relatively low conversions. Some results in the polymerization studies shed some light on this subject, and it will be discussed further.

It might be mentioned that the k_2's given in Table III should represent the k_2's in the model reaction. Therefore these in conjunction with the k_2/k_1 ratio should allow the k_1's for the model reaction to be calculated.

In addition to the effect on reactivity that the halogen substituent had, it might be expected that the cation associated with the thiophenoxide might show some effect. The results of this study are given in Table IV. From the percent dihalobenzene reacted in a given time it can be seen that the lithium and cuprous salts are both more reactive than the sodium. In addition, since the cuprous salt is reacting with a less reactive halogen and still gives about the same percent reaction as the lithium salt, the cuprous salt must be the more reactive of the two. This gives an order of reactivity of Cu>Li>Na.

TABLE II

Rates of Solution Reactions of Various p-Dihalobenzenes

p-Dihalobenzene	Time (hrs.)	% X-⬡-X Reacted	k_2/k_1	Average
ϕF_2	4.25	50.2	37.9	34.2
	12.0	76.9	30.4	
ϕCl_2	0.25	17.1	1.77	
	0.25	13.4	1.64	1.84
	5.00	70.3	1.98	
	5.00	70.3	1.95	
ϕBr_2	0.25	79.0	0.900	
	0.25	69.9	0.870	0.860
	0.50	83.7	0.804	
ϕI_2	0.18	75.3	0.548	0.543
	0.18	80.0	0.537	

TABLE III

Solution Reactions of
4-Halophenylphenyl Sulfide

Compound	Second Order Rate Constant k_2 (l/mole min.)
FØSØ	0.10 ± 0.02
ClØSØ	0.094
BrØSØ	0.15 ± 0.03
IØSØ	0.65 ± 0.17

TABLE IV

Reactivity of Thiophenoxide Salts
with p-Dihalobenzene

Salt	Dihalo-benzene	Time (hrs)	Temp. °C	% X-⬡-X Reacted	k_2/k_1	Average
LiSØ	$ØI_2$	0.25	250	87.5	0.584	0.579
		0.25	250	90.0	0.573	
NaSØ	$ØI_2$	0.25	250	75.3	0.548	0.543
		0.25	250	80.0	0.537	
NaSØ	$ØBr_2$	0.25	250	79.0	0.900	
		0.25	250	[illegible].9	0.870	0.860
		0.50	250	83.7	0.804	
CuSØ	$ØBr_2$	0.17	250	83.9	-	
		1.00	200	80.1	-	
		2.00	200	87.5	-	

The above results coupled with the ease of preparation of the various species, should enable a choice of a monomer to be made. It has been found that the ease of preparation of the thiophenoxides was Cu>Na~K>Li while that for the aryl halide was Br>Cl>F>I. This along with the orders of reactivity and of by-product production indicates that the best choice for monomer would be cuprous p-bromothiophenoxide. In addition, due to the possibilities of preferential formation of polymer, p-fluorothiophenoxide should be considered.

Monomer Synthesis

At the same time that the kinetic studies were being carried out, attempts were being made to synthesize all the possible monomer variations. There were three general methods used for the synthesis of the substituted thiophenols desired for the monomers. These are shown in Figure 4. The first involves preparation of the diazonium salt from the appropriate p-haloaniline. This is converted to the xanthate.[1] The xanthate is then pyrolyzed to the desired p-halothiophenol.[1] This technique, however, is long and tedious resulting in a low overall yield of approximately 35-40%. Consequently simplier methods which could give higher yields were desired for the three p-halothiophenols, fluoro, bromo and iodo, which could not be obtained commercially.

It was described in the literature[2] (reaction 2, Figure 4) that treatment of thiophenol with bromine gave the bis-(4-bromophenyl) disulfide in essentially a quantitative yield. This material can be reduced to p-bromothiophenol by zinc-acid reduction (80% yield),[3] by sodium borohydride-aluminum chloride reduction (95-99% yield),[4] or by a sodium hydroxide-dextrose reduction (70% yield).[5]

When an attempt was made to prepare p-iodothiophenol by the same procedure as used for the preparation of bis-(4-bromophenyl) disulfide it was discovered that very little iodo disulfide was formed from iodine and thiophenol. The major product is thianthrene. Consequently a different process was needed, and this is shown in the third reaction and its alternate in Figure 4. Treatment of iodobenzene with sulfur trioxide results in an 81% of p-iodobenzenesulfonic acid anhydride monohydrate after seven hours at -60°C.[6] Treatment of the anhydride so formed with hydrobromic acid in acetic acid converts it to the disulfide in a 70% yield.[7] Overall yield to p-iodothiophenol is about 57%. The alternate route, treatment of iodobenzene with chlorosulfonic acid, suffers from a serious side reaction namely the formation of sulfone. Consequently the maximum yield of sulfonyl chloride obtained was 48%. The reduction of the sulfonyl chloride to the disulfide, however, was almost quantitative using hydrobromic acid in acetic acid.[7] This gives an overall yield to p-iodothiophenol of 45%.

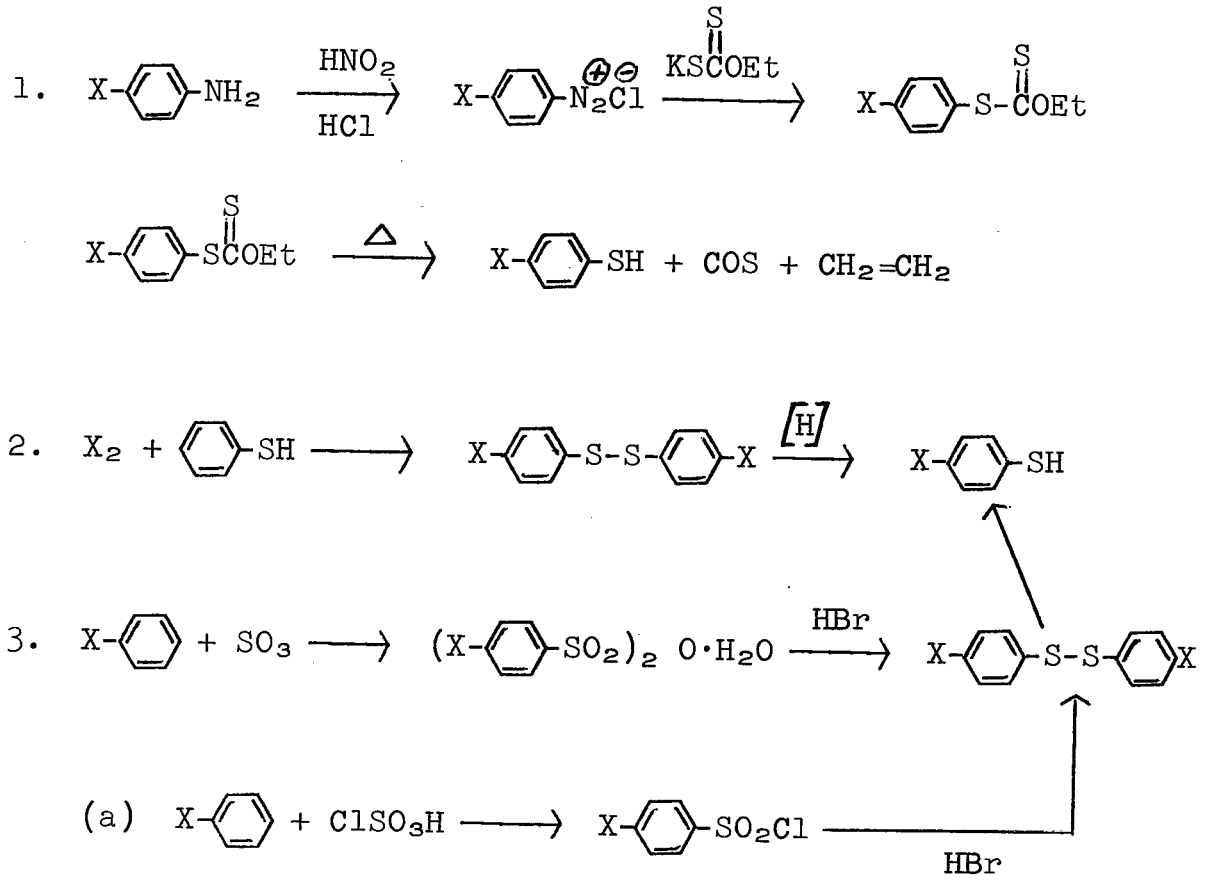


Figure 4. THIOPHENOL SYNTHESIS

A point in the favor of the p-iodobenzenesulfonyl chloride route is that the sulfonyl chloride is not converted to an unusable product if it becomes warm as the corresponding sulfonic acid anhydride monohydrate is.

From the substituted thiophenols the salts could be obtained in greater than 95% yield as shown in Figure 5. Reaction (1), the first one tried in an effort to prepare the sodium salts, was successful. Purity and yield, however, frequently suffer due to the environmental instability of the sodium hydride. Consequently a better method of preparing sodium salts in addition to techniques for preparing the other salts was desired.

Lithium salts are conveniently prepared by reaction (2) while reaction (3) provides an easy route to the cuprous salts. The cuprous salts provide one distinct advantage over the other monomers. This is their much greater stability to air and moisture which allow them to be handled outside of a drybox during workup.

The reaction shown in method (4) provides a very good synthesis of sodium and potassium salts. This involves treatment of the thiophenol with a sodium-naphthalene complex for sodium salts and a potassium-anthracene complex for potassium salts. The complexes are very readily prepared and react instantly with the thiophenol. Further work showed that reduction of the appropriate disulfide to the substituted thiophenol was unnecessary when using the complexes since the complex was capable of a selective reduction of the disulfide bond yielding the desired salt.

Reaction (5a) illustrates an alternate means of obtaining the cuprous salt. This procedure suffers only from contamination of the monomer by unreacted copper metal while that in reaction (3) suffers from impurities in the cuprous oxide. As yet neither technique has been chosen as the preferred one.

Listed in Table V are the various monomers synthesized along with the monomer purities and the overall yields from the starting materials. In the four cases showing yields of less than 90% the cause is in the substituted thiophenol synthesis with the exception of lithium p-bromothiophenoxide. In this case the low yield is due to the lithiation reaction.

Some explanation concerning the entries for the copper salt purities is needed. Since the insolubility of the copper monomers eliminated most analytical methods for purity determinations and since elemental analysis was not accurate enough to give precise values, the purity of these materials were not known more exactly than indicated in Table V.

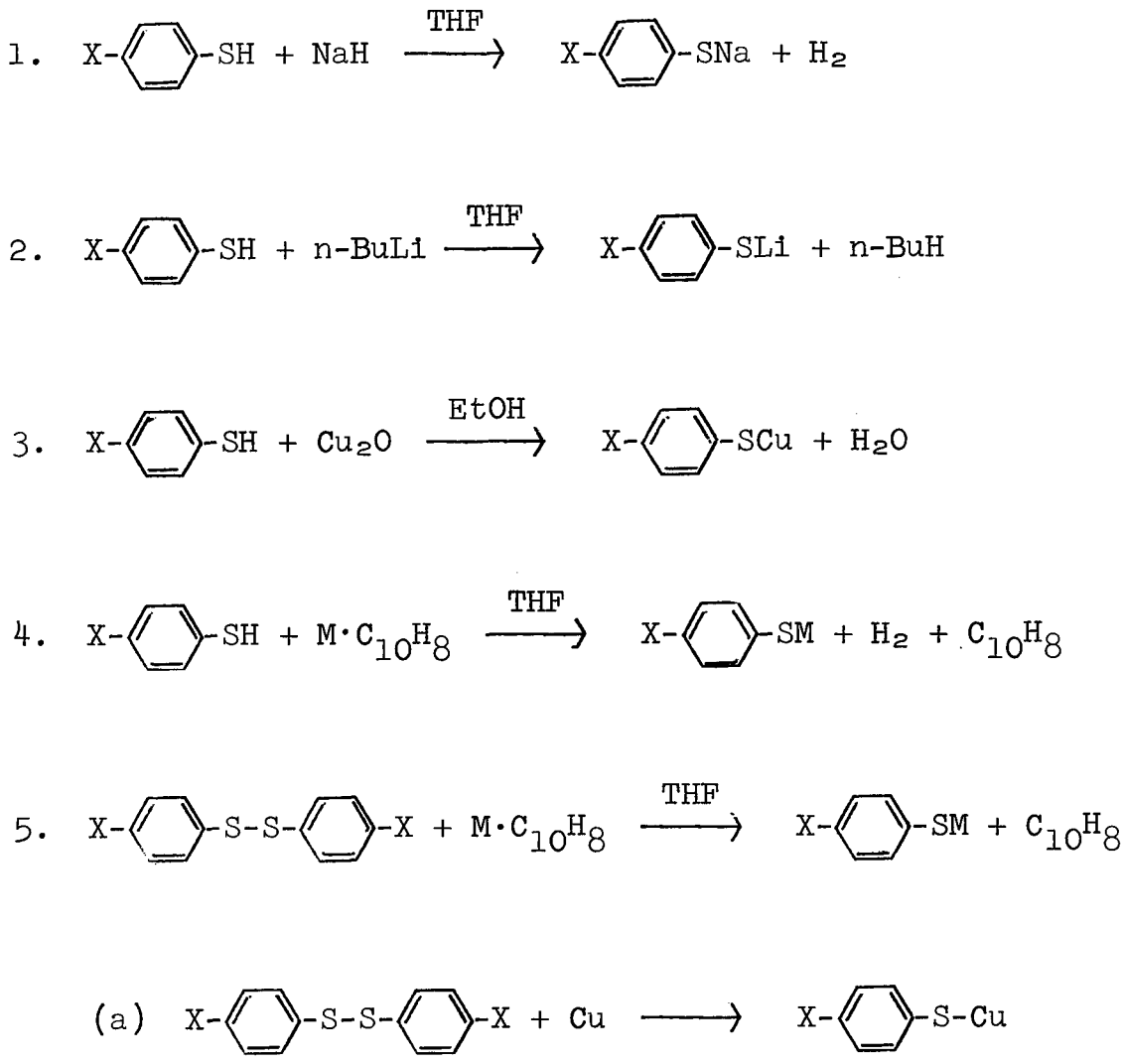
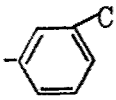
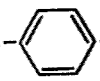
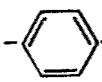
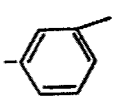
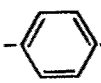


Figure 5. SALT PREPARATION

TABLE V

Monomer	Overall Yield %	Purity %
LiS-  -Cl	95.0	96.3
LiS-  -Br	37.0	90.0
NaS-  -F	50.5	98.8
NaS-  -Cl	95.0	97.2
NaS-  (Cl)	95.0	98.0
NaS-  -Br	91.0	96.5
NaS-  -I	30.0	100
KS-  -Br	92.5	100
CuS-  -Cl	97.9	>95.0
CuS-  -Br	91.9	>95.0
CuS-  (Br)	36.2	> 95.0
LiS-  -SLi	68.0	96.0
NaS-  -SNa	93.0	100

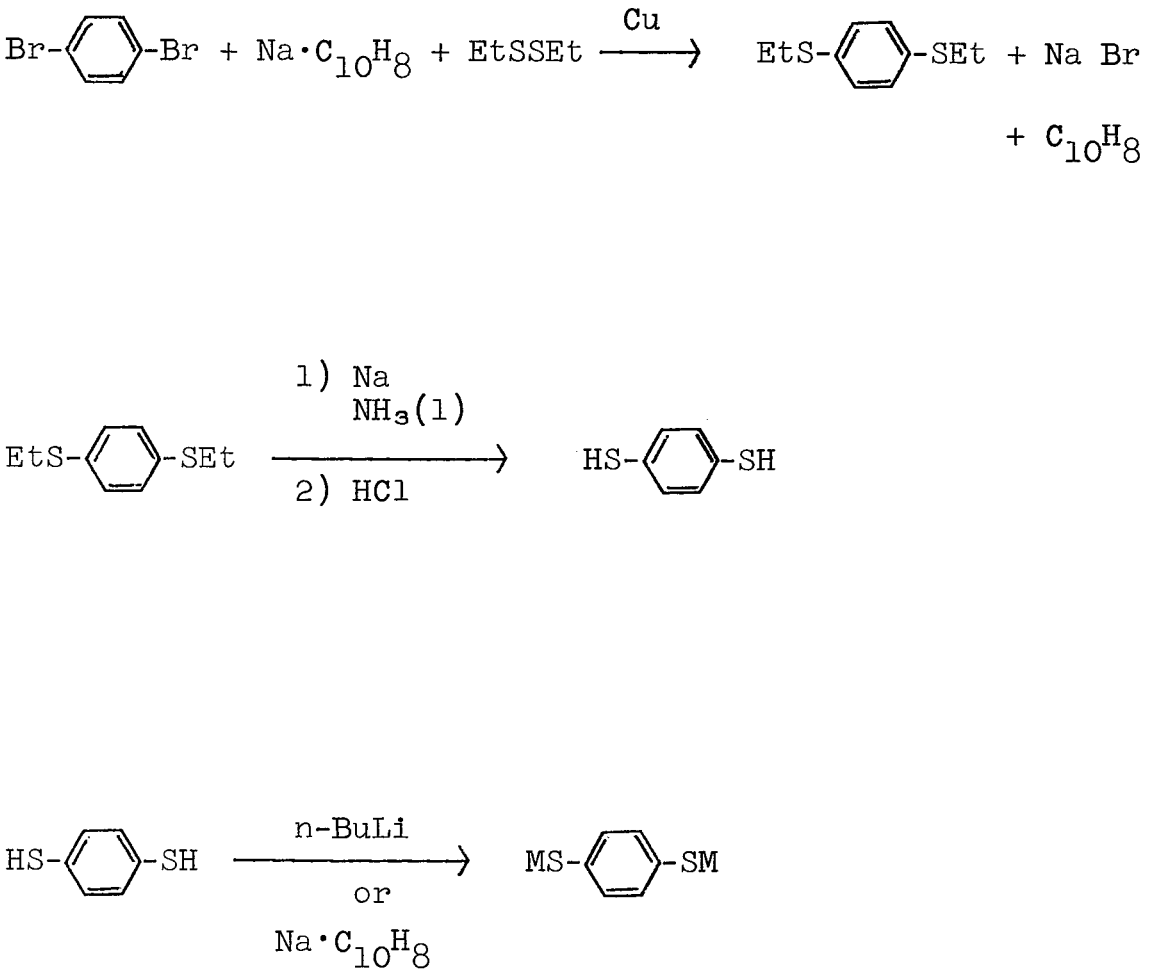


Figure 6. DISALT SYNTHESIS

The last two entries in Table V are examples of monomers, which would be used in an A-A, B-B condensation system where the B-B monomer would be a p-dihalobenzene. These disalts were prepared in the manner shown in Figure 6. The p-dibromobenzene is treated with the product from the reaction of sodium-naphthalene complex with diethyl disulfide in the presence of copper dust, namely sodium ethylmercaptide. This results in the formation of 1,4-bis(ethylthio)benzene. The bis sulfide so formed is cleaved by sodium in liquid ammonia to give, on acidification, 1,4-benzenedithiol. Treatment of the 1,4-benzenedithiol with n-butyllithium results in the dilithium salt. Alternatively the 1,4-benzenedithiol can be treated with sodium-naphthalene complex to give the disodium salt in the yields and purities shown in Table V.

Polymerization

Once the monomers had been synthesized, their polymerization reactions were studied. The ampoules were prepared by the same general technique used in the kinetic studies. The workup, however, was somewhat different. After the ampoule was cooled and opened, the contents were extracted twice with boiling water, and the water extract was titrated potentiometrically for halide ion with silver nitrate to determine the monomer conversion. The residue was heated to reflux in diphenyl ether. Then the resulting solution was filtered, and the filtrate poured into cold methanol to precipitate the polymer. The precipitate was filtered off, washed with acetone and dried under vacuum at 80-120°C for several hours. Yields were based on the vacuum dried polymer obtained.

Polymerizations were carried out in the solid state or in solution. It was found earlier that if the monomer was polymerized above its melting point in the absence of solvent an uncontrollable reaction ensued leading to a black charred mass. The maximum temperature that could be used was 10-15° below the monomer melting point. The usual temperatures employed were 200° and 250°C. The solid state polymerization appears to be just that. In no instance was the presence of liquid observed and the particle size of the material in the ampoule appeared to be unchanged. The only visual change appeared to be a very slight change in color.

The solution reactions were run in quinoline, diphenyl ether and pyridine at about 1 M concentration. Pyridine seemed to give the best results and showed a fifty fold enhancement in rate over the solid state reactions at the same temperatures.

Two types of monomer systems were investigated, the A-A, B-B and the A-B. In the first system there is one inherent disadvantage; the two monomers must be present in exactly stoichiometric quantities to achieve a high molecular weight polymer. With the A-B monomers this is automatically taken care of due to the nature of

the monomer.

In the A-A, B-B system, two different monomer sets have been briefly considered. The results are given in Table VI. In the case of the dilithium salt a low yield of low melting polymer was obtained. With the disodium salt very little, if any, polymeric material was obtained.

Some results from the kinetic studies could shed some light on the above results. When sodium thiophenoxide was heated in pyridine for twelve hours at 250°C no apparent reaction occurred. When p-dibromobenzene was treated under the same conditions a black insoluble, infusible mass was obtained. Therefore what may be occurring is that, due to the low reactivity of the disodium salt, the pyridine is degrading the p-dibromobenzene before any appreciable amounts of polymer can be formed. However, the more reactive dilithium salt reacts with the p-dibromobenzene to give some polymer before the pyridine degradation reaction becomes dominate.

Since the A-B system has a built in stoichiometric balance, since it is easier to prepare, and since the results have been much better with this system than with the A-A, B-B system the A-B monomers have been studied more extensively.

One of the monomers studied was sodium p-fluorothiophenoxide. The results are given in Table VII. Although the first two runs are at somewhat higher temperatures than is usually employed, their results are quite interesting. As has been mentioned previously fluoroderivatives have a potentiality for preferential polymer formation. In the first two runs we have some evidence which bears on this question. Condensation polymerization theory predicts that for conversions of 58% and 79% the number average degree of polymerization, $\bar{x}_n$, obtained for the polymers would be 2 and 3 respectively. However, the $\bar{x}_n$'s observed were 9 and 7 respectively. This may be an indication that preferential polymer formation is taking place.

Tables VIII and IX show the results for two more monomers, the sodium and potassium salts of p-bromothiophenol. The results in Table VIII exhibit several interesting features. One is the effect of pyridine that was mentioned before, a fifty fold enhancement in rate over the solid state reaction. Another is the rate enhancement of pyridine over quinoline. In addition it might be noted that the percent of bromine continues to decrease, indicating continued polymerization, even after titration of liberated bromide ion indicates a complete reaction. One feature of distinct importance is the fact that $\bar{x}_n$ reaches a maximum, at 24 hours, and then decreases. This apparent decrease in molecular weight after an optimum reaction time appears in all of the polymerizations studied and is signalled by a drop in melt viscosity, melting point and

TABLE VI

A-A and B-B Polymerizations

250° Pyridine Solvent

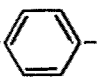
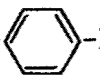
A-A	B-B	Time (hrs)	Polymer Yield %	M. P. °C
LiS-  -SLi	Br-  -Br	6	39	220-230
NaS-  -SNa	Br-  -Br	1	7	<100
NaS-  -SNa	Br-  -Br	6	6	<100
NaS-  -SNa	Br-  -Br	12	8	<100

TABLE VII

Polymerization of NaS-  -F

Time (Hrs)	Temp. °C	% Conversion	M. P. °C	$\overline{DP}_{Br}$	System
2	320	58.0	~265	9	Pyridine
72	320	79.0	>300	7	Solid State
6	250	91.0	272-280	-	Pyridine

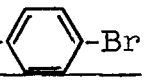
TABLE VIII

Polymerization of NaS-  -Br at 250°C

Solvent	Time (hrs)	% Conversion	Polymer			
			% Br	% S	M. P. °C	$\overline{DP}_{Br}$
None	36	79.2	-	-	-	-
None	140	93.0	-	-	-	-
Quinoline*	24	91.3	-	-	-	-
Pyridine	1	72.0	13.2	31.3	160-200	5
Pyridine	2	97.8	6.00	28.9	240	12
Pyridine	3	97.6	3.75	27.1	240-250	19
Pyridine	6	100.0	1.50	29.1	260	48
Pyridine	12	100.0	0.67	29.4	265	122
Pyridine	24	100.0	0.58	29.0	-	156
Pyridine	36	100.0	0.69	29.2	265	107

*Reaction Temperature 280°C.

TABLE IX

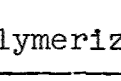
Solution Polymerization of KS-  -Br

Temp. °C	Time (hrs)	% Conversion	% Polymer	M. P. °C	$\overline{DP}$*
250	1	80.7	-	~260	-
250	2	90.6	-	~264	20
250	3	100.0	-	~265	36
250	8	100.0	55	262-269	33
250	24	100.0	77	257-263	78
250	36	100.0	60	238-245	202
250	3**	100.0	54	263-268	38
250	8**	100.0	47	260-265	32
200	38	92.3	64	262-266	17
200	53	92.5	59	263-268	18

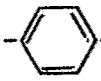
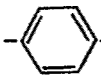
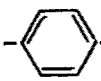
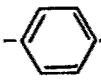
*$\overline{DP}$ from Br end group analysis

**CuBr added

TABLE X

Polymerization of (p)X-  -SM

at 250°C in Pyridine

Monomer	Polymer % Yield	M. P. °C	k_2
NaS-  -F	63	272-280	0.026
NaS-  -Cl	62	245-260	0.011
NaS-  -Br	75-80	260-265	0.13
NaS-  -I	42	225-240	1.01
LiS-  -Br	20	243-248	2.57
KS-  -Br	80	265-269	0.096
CuS-  -Br	97	283-287	>3.0

yield. Table IX shows both the drop in melting point and yield occurring after 24 hours reaction time.

Table IX also shows two other features of interest. One is the lack of catalytic effect of cuprous bromide as shown by runs 7 and 8 versus 3 and 4. The other is a temperature effect on the rate as shown by the last two runs. This latter effect amounts to a sixteen fold decrease in rate for the 50° drop in temperature.

Table X summarizes the results of the preliminary studies on all the A-B type monomers investigated. The yields given are the maximum polymer yields obtained with the particular monomer. The melting points are also maxima and give an indication of relative molecular weights attained in each case. The last statement is true since we have found that the higher the melting point the higher average molecular weight up to the crystalline melting point of the polymer, 287°C. The rate constants are overall constants based on second order kinetics.

From the first four entries it can be seen that the ease of halogen displacement is essentially the same as that found in the model reactions namely I>Br>F>Cl. In addition it can be seen that the best polymer, as indicated by melting point, resulted from the p-fluoro and p-bromothiophenoxides with the p-bromo giving the best yield.

From the third, fifth, sixth and seventh entries it can be seen that the effect of the cation on the rate is also the same as that found in the model reactions being Cu>Li>Na>K. In this set of entries, however, cuprous p-bromothiophenoxide has by far the best yield and melting point. In fact these values are the best of all those obtained. Consequently the monomer chosen for further study was cuprous p-bromothiophenoxide. This is the same monomer that the kinetic studies indicated to be the preferable one.

Cuprous p-bromothiophenoxide, therefore was extensively studied under four different reaction conditions. These were 200° and 250°C in the solid state and in pyridine. The results are given in Figures 7-10. The solid line represents the yields observed while the dashed line refers to the melting points. In each case a maximum is reached after a given reaction time beyond which the yield and the melting point decrease. These maxima in melting point and yield are 280°C and 90% yield for five days at 200°C in the solid state; 278°C and 78% yield for two and one-half days at 250°C in the solid state; 278°C and 95% yield for 32 hours at 200°C in pyridine; and 287°C and 90% yield for 16-32 hours at 250°C in pyridine. From these results the best polymerization conditions would appear to be 16-32 hours at 250°C in pyridine or five days at 200°C in the solid state.

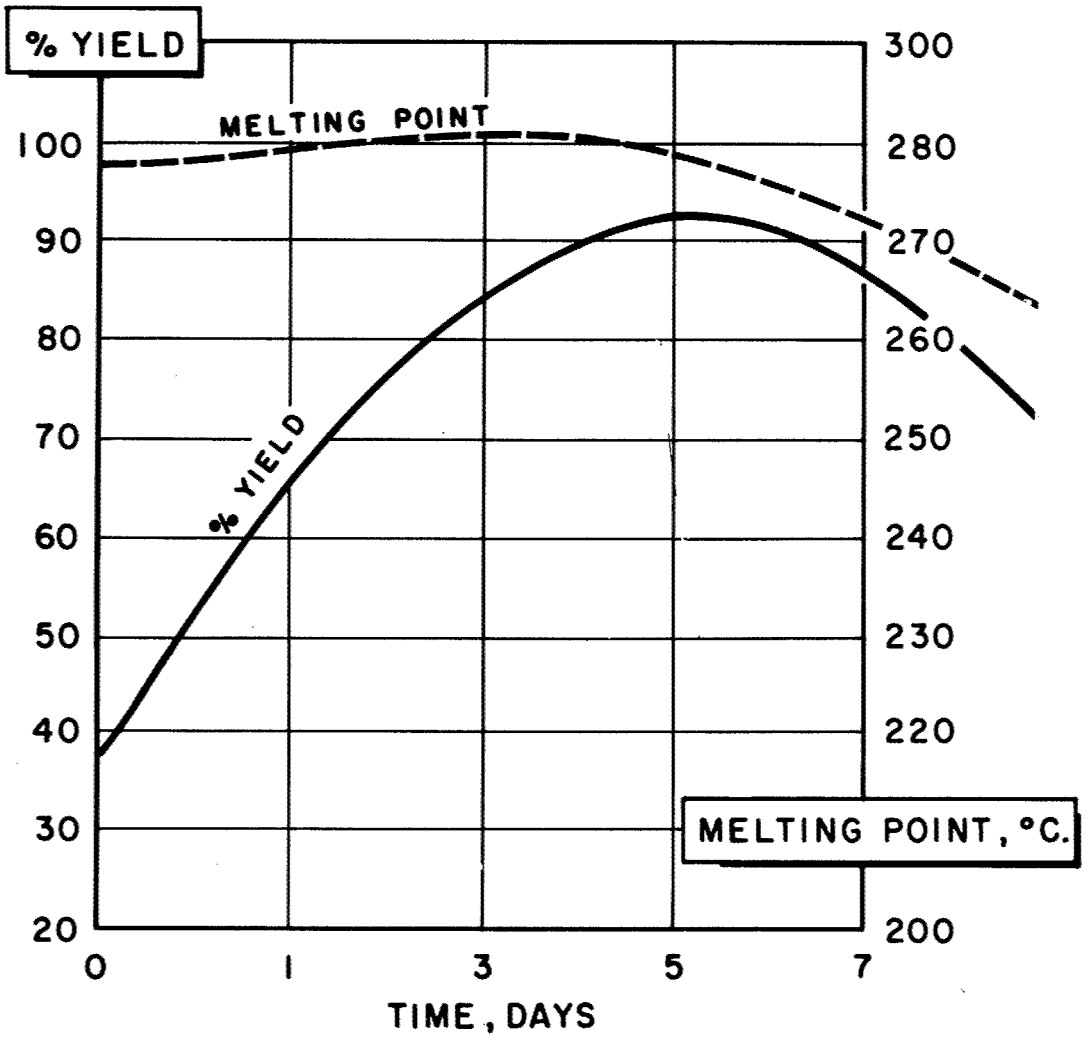


FIGURE 7. Br ϕ S Cu, SOLID STATE, 200°C.

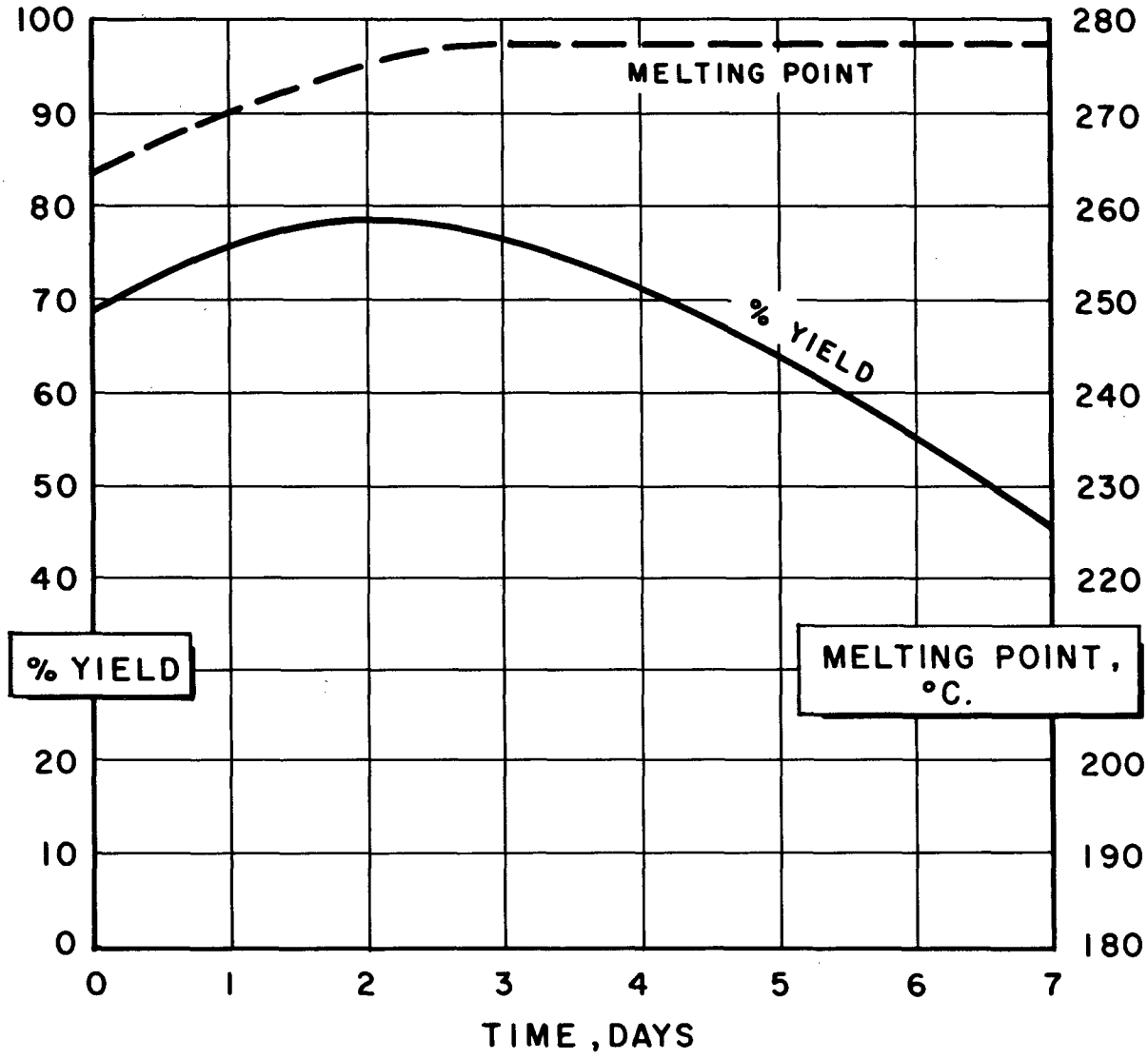


FIGURE 8. CuS ϕ Br, SOLID STATE, 250°C.

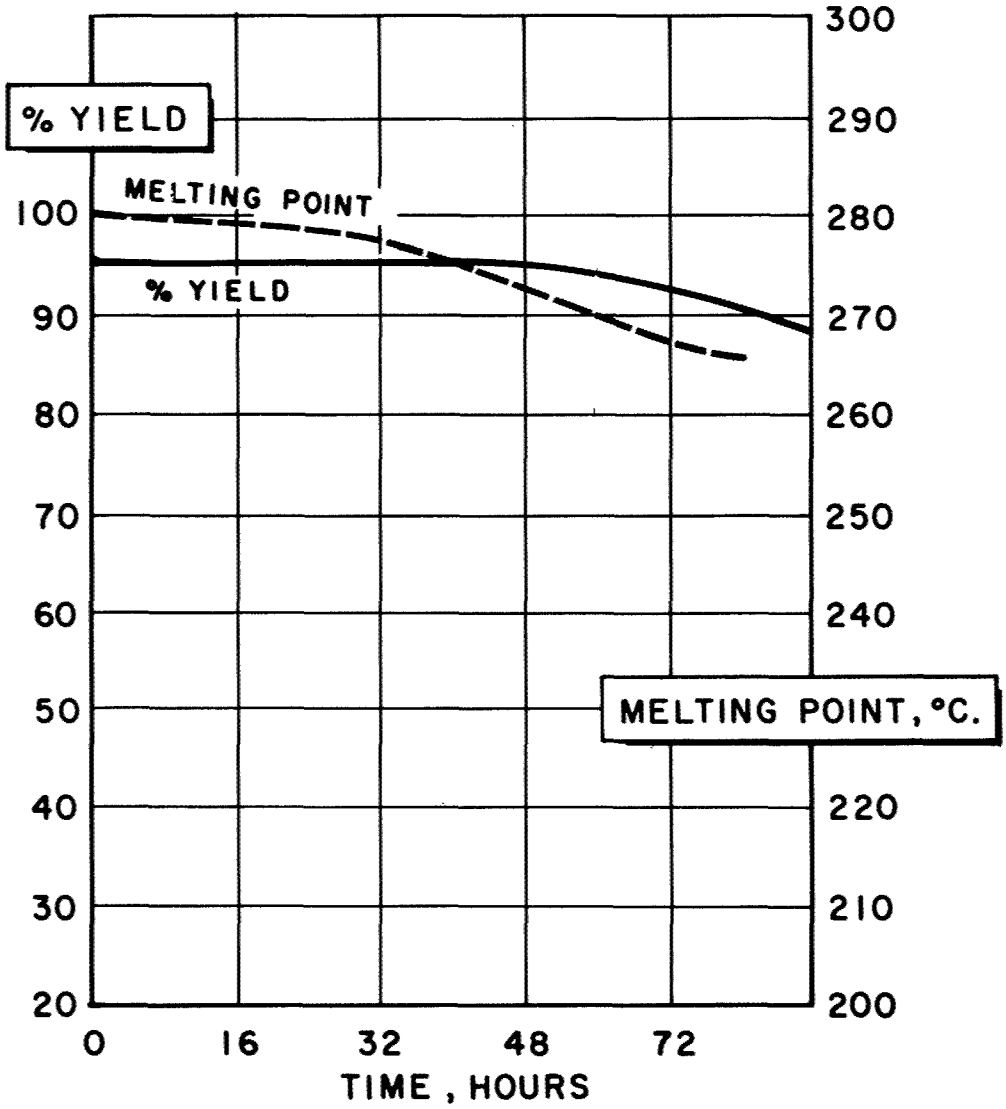


FIGURE 9. BrϕSCu, PYRIDINE, 200°C.

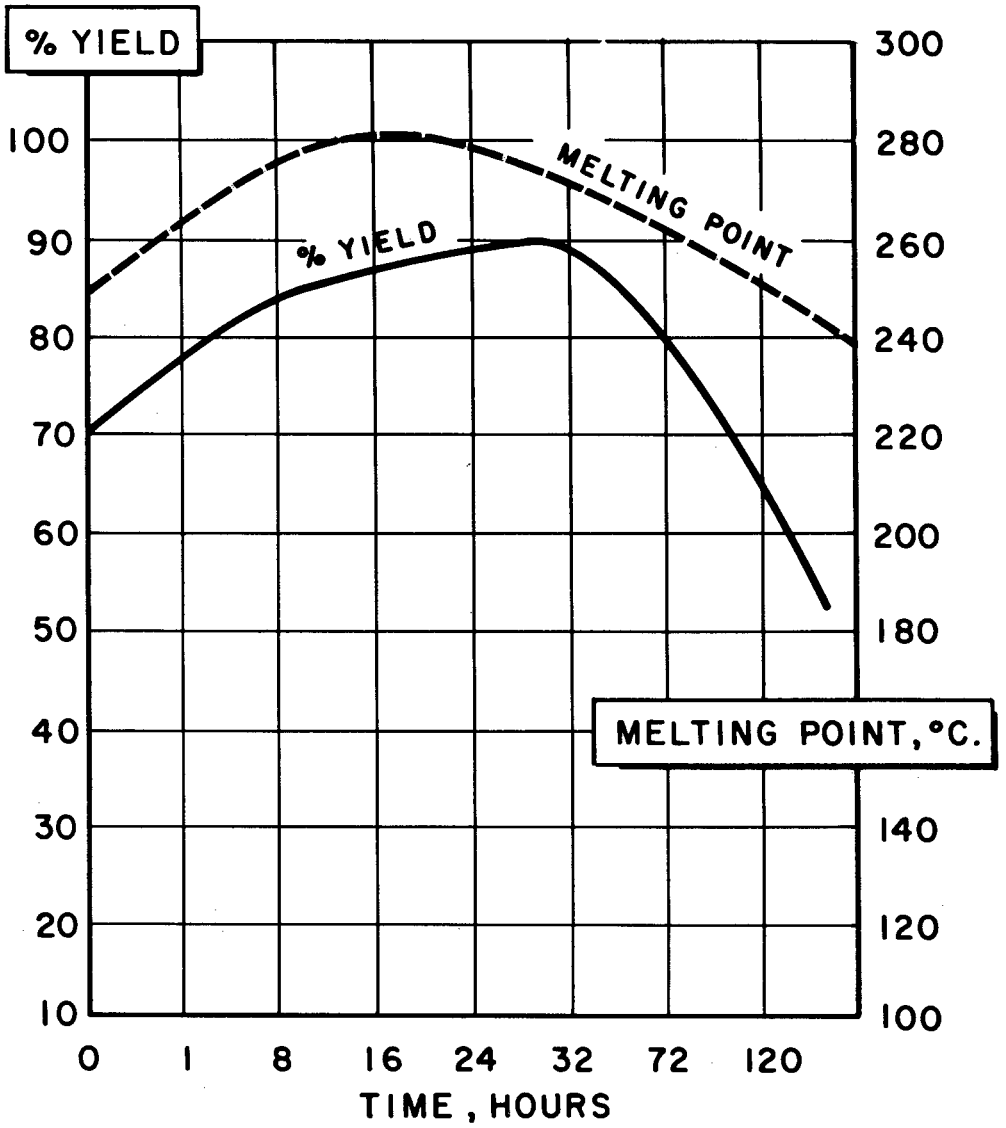


FIGURE 10. Br ϕ S Cu, PYRIDINE, 250° C.

Therefore when a scale up in the polymerization reaction was desired, 16 hours at 250°C in pyridine was selected for the reaction conditions. The first attempts were carried out in glass lined high pressure reactors. In each case, however, the liner broke and low yields resulted. In addition to the low yield, the bomb temperature could not be measured any closer than 50-60°C in the second experiment since the thermowell had to be removed. Consequently the polymer in this case was very poor, as indicated by the melting point, undoubtedly due to too low a reaction temperature.

In order to avoid the difficulties, at least temporarily, of the solution polymerizations, it was decided to polymerize at 212°C in the solid state. The last three runs in Table XI show the results of this work. The runs were made for five, six and one-half, and nine days. The fact that reaction times greater than five days were needed to obtain a polymer with good properties, run 5, is probably due to the lack of agitation in the ampoules. This would probably cause a temperature gradient in the reactants from 212°C on the outside of the ampoule to much less than 200°C in the center. After prolonged reaction times this gradient would disappear, but the overall reaction would be slowed down.

In addition to the polymerization studies a preliminary investigation of repolymerization of low molecular weight material was made. From the elemental analyses of the polymers it was discovered that the amounts of copper and bromine in the polymer were about equal. This suggested that the polymer end groups remained intact during workup. Consequently it should be possible to polymerize the polymers further by subjecting them again to polymerization conditions. The results of these attempts are given in Table XII. It can immediately be seen from the melting points that essentially no change has taken place under any of the conditions used. However, some increase in molecular weight is indicated by an increase in solution viscosity (Figure 15).

Polymer Properties

During the course of the polymerization studies the properties of the polymers produced were investigated. Much of this investigation was concerned with molecular weight determinations on the polymer. From the scatter observed in the percent sulfur in the polymer, Table VIII, it can be seen that sulfur analysis is of no use for molecular weight determinations. The percent bromine is useful for determinations at lower molecular weight, Table VIII, but as would be expected it fails at higher molecular weight. Therefore it was decided to investigate the melt viscosity of the polymers.

TABLE XI

Large Bomb Polymerizations

Time (Hrs)	Temp. °C	Solvent	% Yield	M. P. °C
15-1/2	250	Pyridine	52.7	278-285
16	250	Pyridine	78.7	255-265
120	212	None	71.8	259-260
156	212	None	61.7	264-274
216	212	None	>95.0	279-290

TABLE XII

Repolymerization

Temp. °C	Time (hrs)	Solvent	% Yield	M. P. °C
250	0	Pyridine	-	265-278
250	12-1/2	Pyridine	62.4	265-275
250	12	Pyridine	69.3	275-282
200	0	None	-	265-272
200	24	None	94.0	255-270
200	72	None	89.7	265-273

The apparatus used is shown in Figure 11. The polymer is packed into the capillary in the viscometer so as to give a bubble free column. The side arm on the tube is for introduction of a vacuum or an inert gas. The calibration lines on both tube and plunger serve as a means of timing the plunger drop. The plunger has a narrow tip which slides into the capillary as well as a cap on which weights can be placed.

The heating apparatus for the viscometer is shown in Figure 12. The central well is used for the viscometer and the two thermowells for determining the temperature at both ends of the capillary tube in the viscometer. The temperature in the center well was calibrated against thermometers in both thermowells in order to provide two independent measures of the center well temperature.

Since viscosity determinations are capable of giving only relative molecular weights, it was necessary to calibrate the technique. This was done by determining the viscosities of polymers whose bromine analyses were believed to be reliable.

The results of the melt viscosity determinations at 303°C are given in Figures 13 and 14 for solution polymerizations at 200° and 250°C and for solid state polymerizations at 200° and 250°C respectively. In each case the viscosity rapidly increases to a maximum and then falls off about as rapidly. The maxima occur at 8000 poises for 32 hours at 200°C in pyridine, 230,000 poises for 16 hours at 200°C in pyridine, 26,000 poises for 5 days at 200°C in the solid state, and 6000 poises for 3 days at 250°C in the solid state. The highest two maxima 230,000 poises and 26,000 poises correspond roughly to $\bar{x}_n$'s of 400 and 200 respectively. These maxima occur at about the same regions in reaction time that polymer melting points and percent yields show maxima. Apparently some degradation process is taking place which becomes dominate after the polymerization reaction has slowed down. In addition infusible, insoluble materials are found at prolonged reaction times indicating a crosslinking reaction also. The fact that the appearance of maxima occurs in both solution and solid state polymerizations would indicate that pyridine is not responsible for the degradation. The actual culprit may be the salt produced during polymerization. This is suggested by the data in Figure 15. These are the results of solution viscosity determinations on repolymerization reactions. As can be seen no maxima occur. Instead the viscosity rises steadily with increasing reaction time. Since on workup of the polymer prior to repolymerization the halide salt was removed, this would seem to indicate that this material is indeed the culprit.

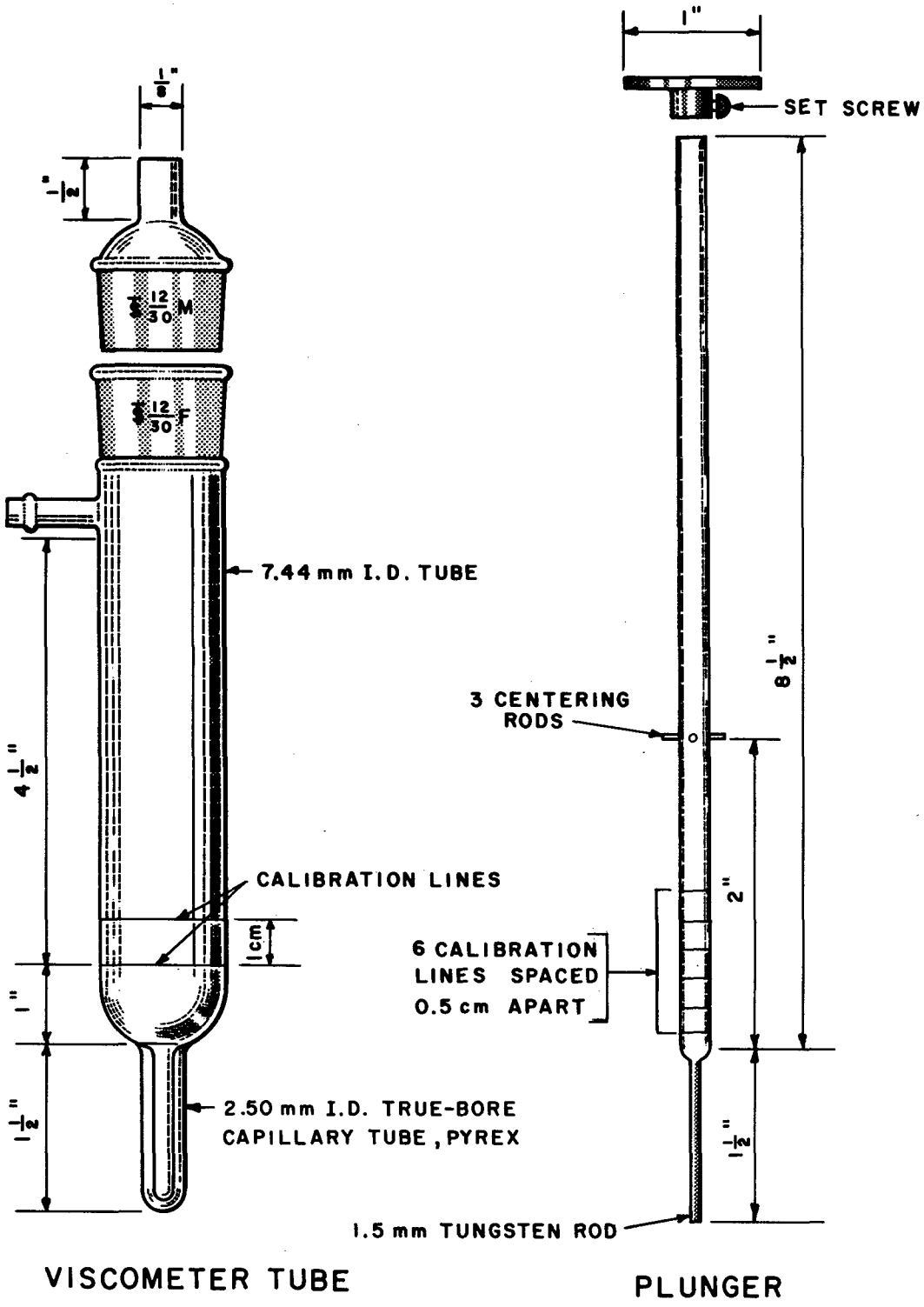


FIGURE 11. MELT VISCOMETER

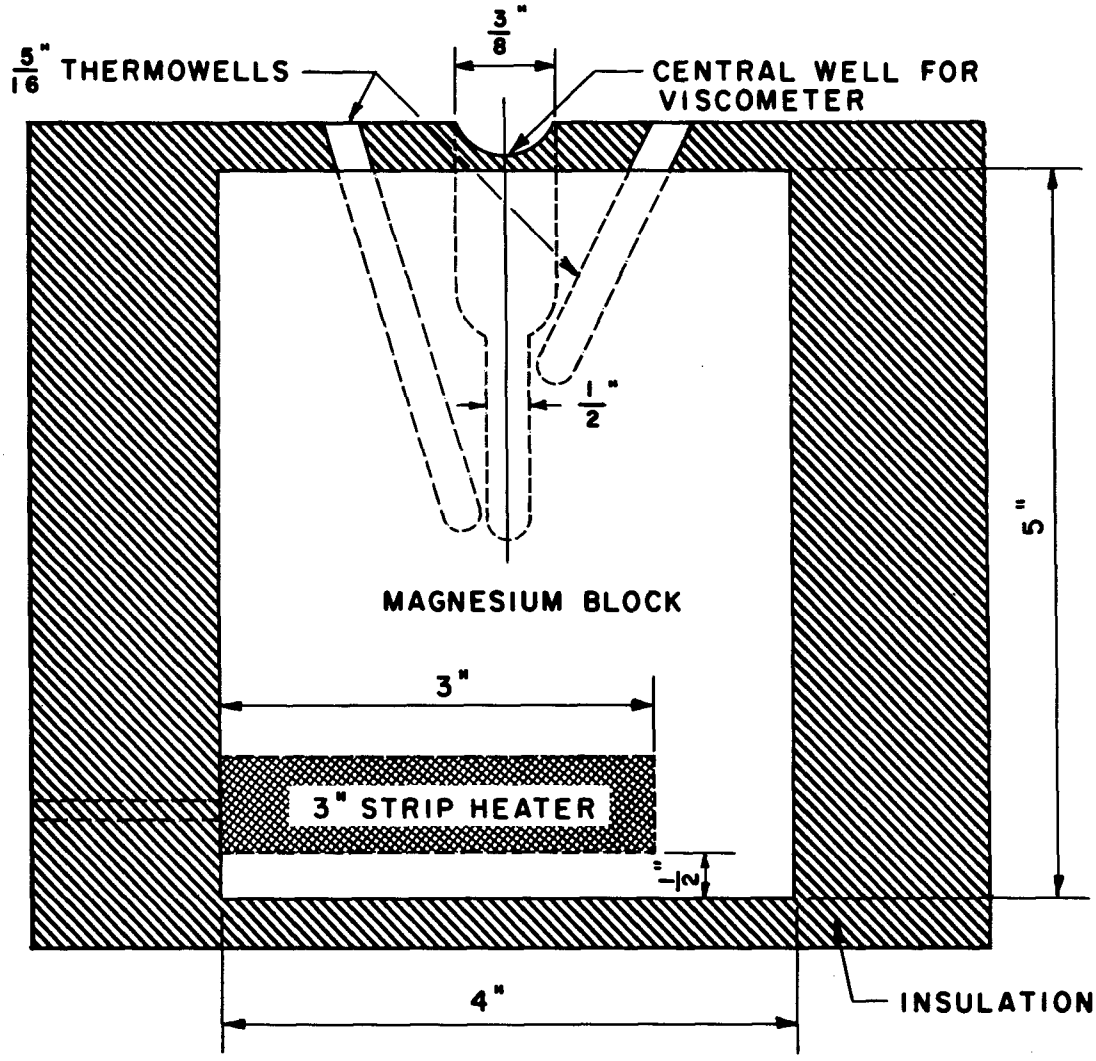


FIGURE 12. HEATING BLOCK FOR VISCOMETER

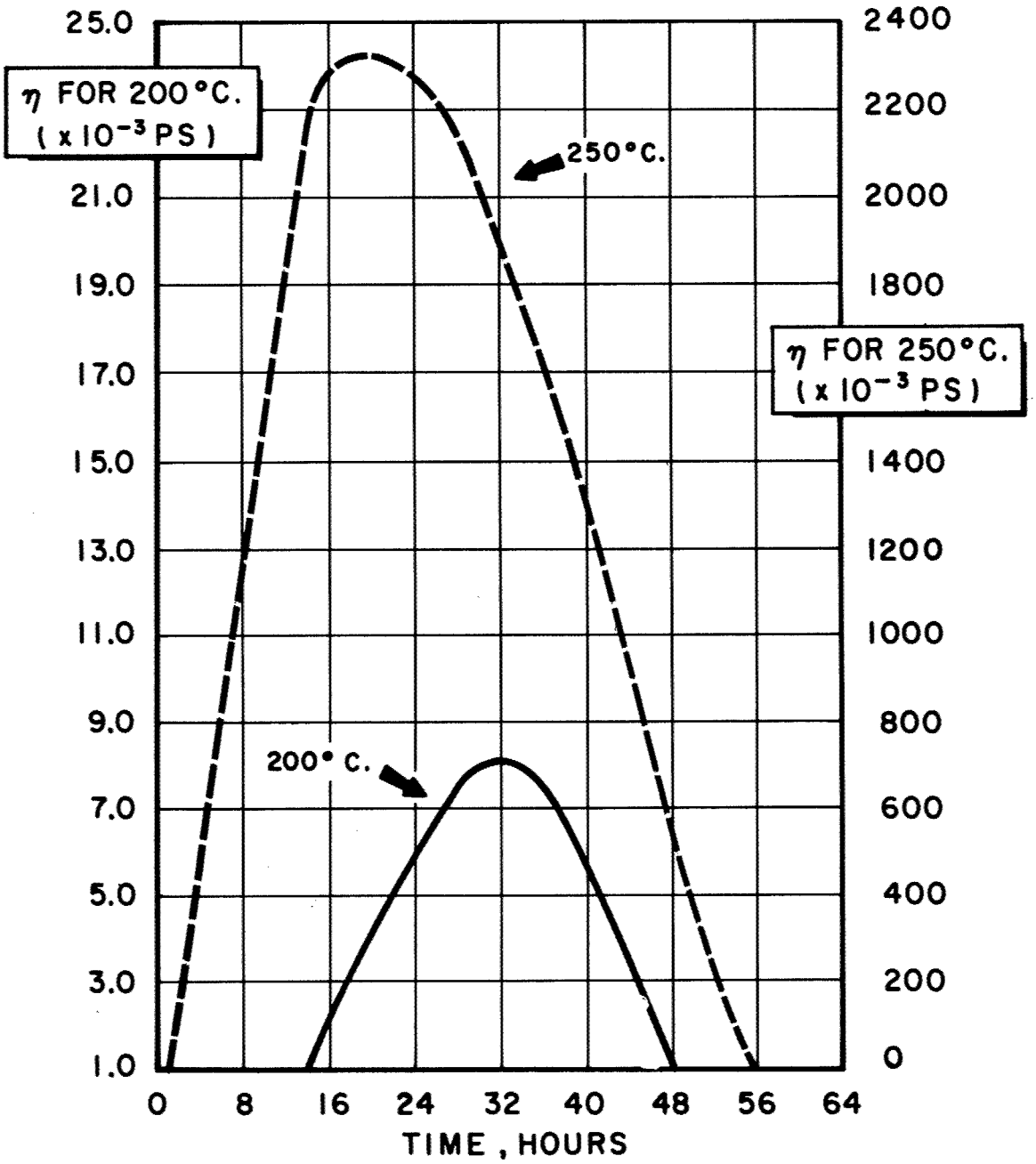


FIGURE 13. MELT VISCOSITY–POLYMERIZED IN SOLUTION

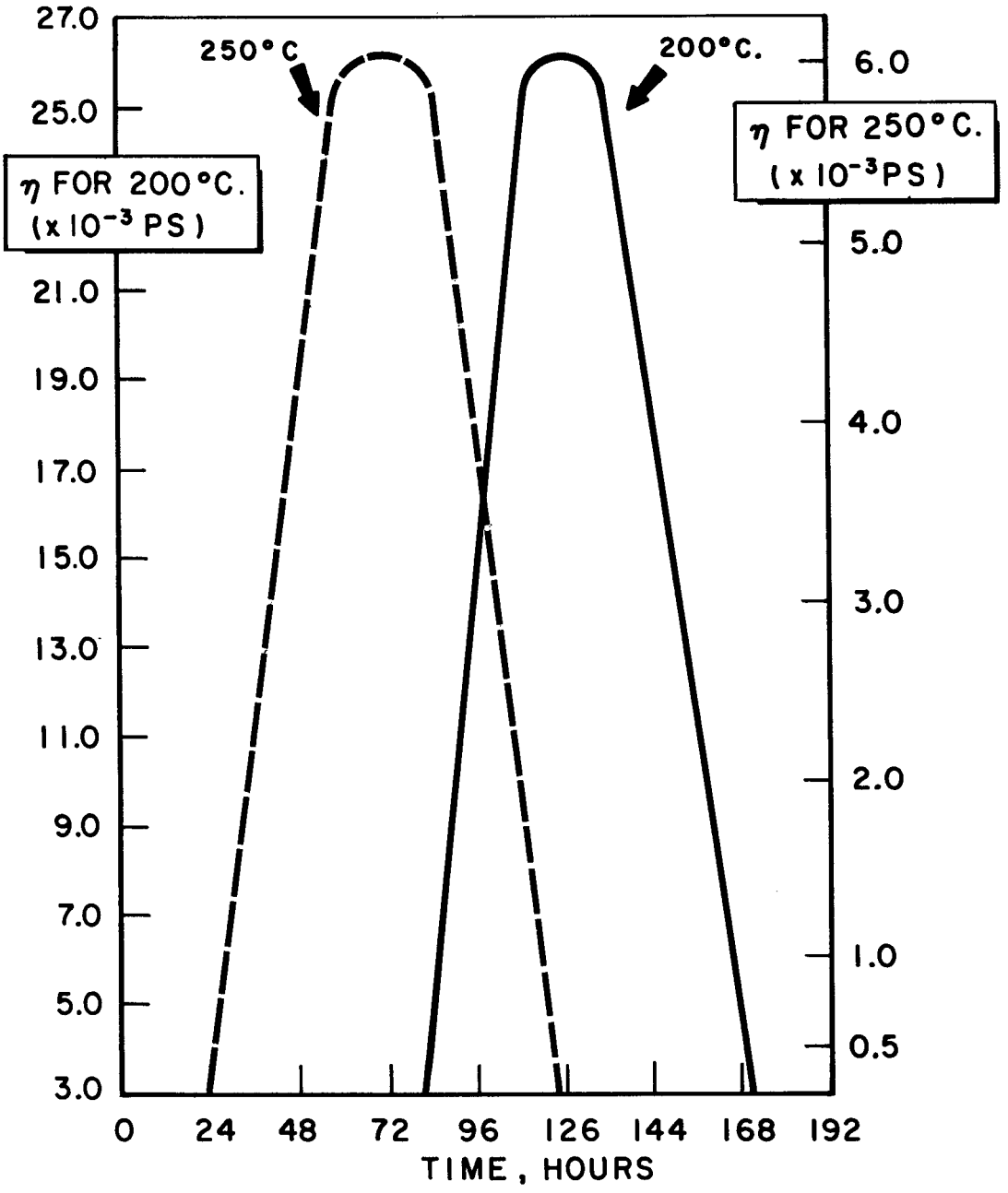


FIGURE 14. MELT VISCOSITY-POLYMERIZED IN SOLID STATE

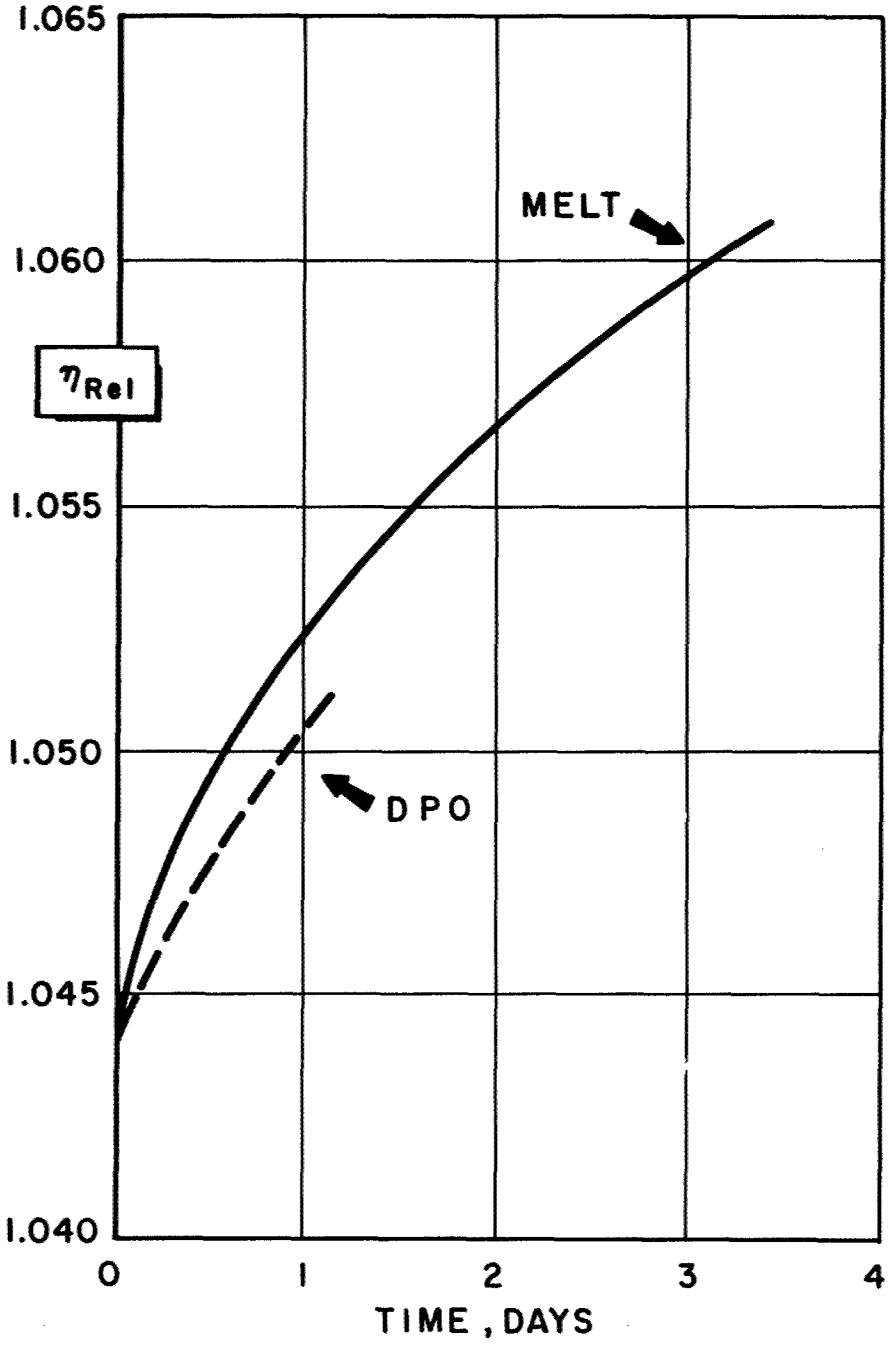


FIGURE 15. SOLUTION VISCOSITY-REPOLYMERIZATION

In addition to the melt viscosity work, solution viscosities have also been determined. These were carried out on a 1% polymer solution in diphenyl ether at 250°C. The results correlate quite well with the melt viscosity results. However, this technique has one advantage in that it can be used to classify polymers as to molecular weight whose melt viscosity is too low to measure.

Another property investigated was the solubility of the polymer. Since phenylene sulfide polymer is a highly crystalline material, a high boiling solvent is required. The results of solubility tests with such solvents is given in Table XIII. The polymer is insoluble in the first four solvents listed, and it reacts with sulfuric acid. In diphenyl ether and diphenyl sulfide, however, at least a 1% solution can be attained at reflux. The polymer, due to its crystalline nature, then precipitates on cooling at about 200°C in diphenyl ether and somewhat lower, 170°C, in diphenyl sulfide. It is the solubility of the polymer in diphenyl ether which made solution viscosity determinations possible as well as providing a means of separating the polymer from the other products of polymerization.

A preliminary investigation of the fabrication properties of the polymer was also made. It was found that a fiber could be pulled from the melt of a polymer of high enough molecular weight. This fiber was fairly strong and flexible.

Somewhat more time was spent on the compression molding properties. The higher molecular weight materials could be molded into a fairly tough, flexible film that was at least partially transparent. The film could be folded and creased without cracking. An additional property was noted during the molding operations. This was the great tenacity with which the polymer adhered to the metal molding plates or to glass. In one case the polymer stripped the metal coating from the plate instead of breaking free from it. The polymer did not adhere to Teflon, but the color and transparency of the film were much worse when Teflon was used as a molding plate.

One of the most important properties investigated was the thermal stability of the polymer. Figure 16 shows the results of the thermal gravimetric analysis of some polymer samples sent to Wright-Patterson Air Force Base for testing. Under either air or nitrogen polyphenylene sulfide is stable to about 450°C. At this point degradation sets in slowly until, in air, the polymer is essentially gone at 700°C. In nitrogen, however, degradation appears to cease at 600°C, and a thermally stable residue is formed which resists further degradation up to 900°C.

Since it would be very desirable to know if this thermally stable residue has useful properties, several samples were treated

TABLE XIII

Solubility of Phenylene Sulfide Polymers

Solvent	Solubility at Reflux	Precipitation Temperature
Pyridine	0.0%	-
2,4-Lutidine	0.0%	-
Toluene	0.0%	-
Polyether	0.0%	-
Diphenyl Oxide	$\geq$ 1.0%	200°C
Diphenyl Sulfide	$\geq$ 1.0%	170°C
H_2SO_4	Reacts	-

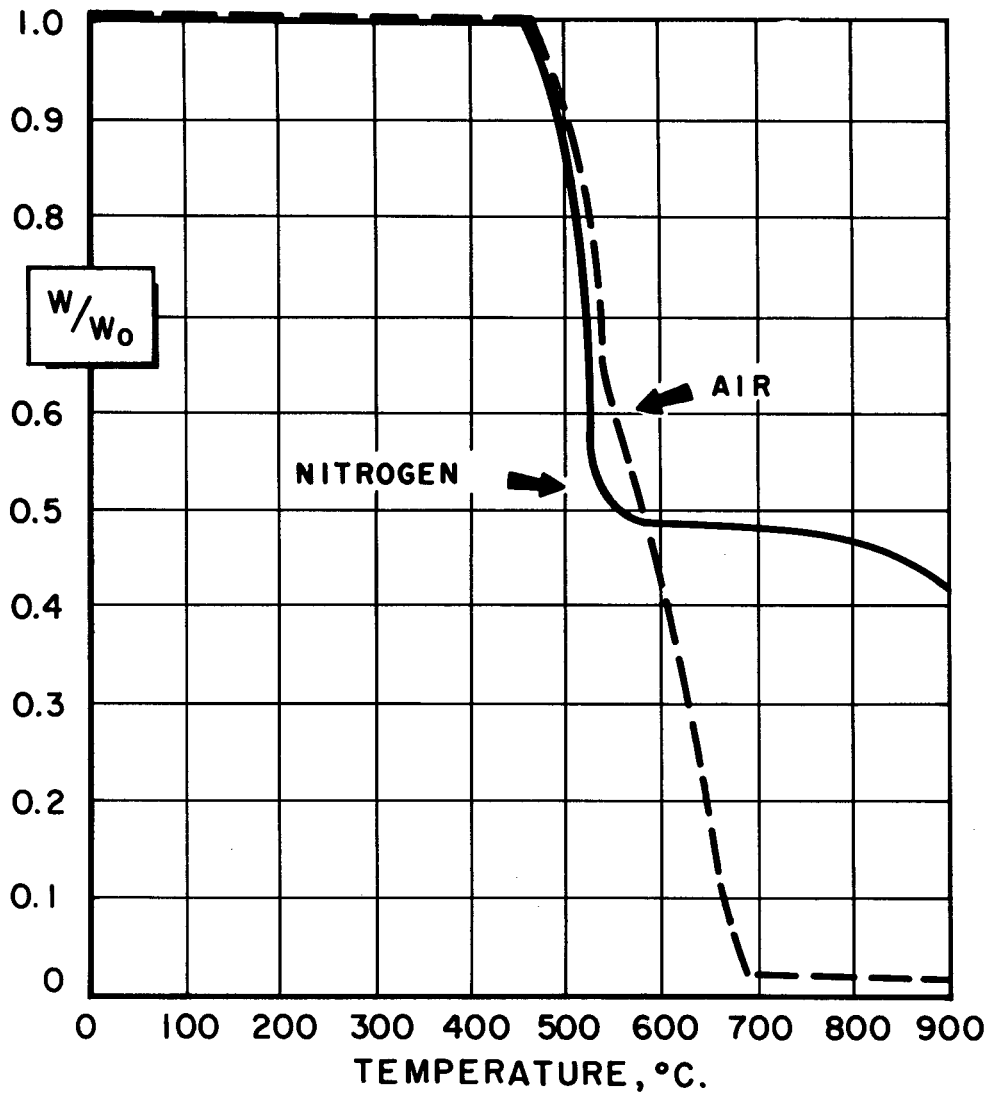


FIGURE 16. THERMAL GRAVIMETRIC ANALYSIS

at 400°C and 500°C under nitrogen to determine what properties the residue did have. The results are given in Table XIV. In each case a black glassy material was obtained which probably was cross-linked. The best material resulted from treatment at 400°C for 65-70 hours which gave a material with better properties than the original material even though some degradation had occurred. Treatment at 500°C for prolonged periods of time seems to be too drastic resulting in a material with poor molding properties. After only three hours at 500°C, though, the material still has good molding properties.

One interesting feature of the heat treatment was that material having good molding properties appeared only after solubility in diphenyl ether had disappeared. Thus the two runs that produced material that was still soluble in diphenyl ether gave only poor to fair films while the insoluble materials with the exception of that from 24 hours at 500°C gave good to excellent films.

Another interesting feature was the effect of molecular weight on weight loss and film properties. The molecular weights are roughly in the order polymer (3)> polymer (1) > polymer (2). The weight losses for a given treatment time, however, are in the reverse order, polymer (2) > polymer (1) > polymer (3). The film properties also appear to correlate with the molecular weight of the starting materials. In other words the material produced from the highest molecular weight starting material gave the best film and vice versa.

From the results obtained with the larger polymerizations along with the properties of the polymer and the heat treated material the phenylene sulfide polymer appears to be potentially a very useful material.

Acknowledgments

We wish to express our appreciation for the able direction of the contract work provided by the former director of the contract, Dr. R. W. Lenz, from the inception of the contract in April, 1960 to August, 1961 when he left the Midland Division to join the Eastern Research Laboratory of The Dow Chemical Company.

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7. Ibid., 103, 627 (1955).

TABLE XIV

Heat Treatment of Low Molecular Weight Polymer

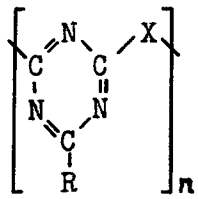
Starting Polymer	Time (hrs)	Temp. °C	M. P. °C	Weight Loss %	Diphenyl Ether Solubility %	Film Properties		
						Toughness	Adherance	Appearance
Polymer 1	0	-	265-270	-	100	Very poor	Very poor	Opaque
	3	500	> 600	30	0	Good	Very good	Transparent
	24	500	>600	56	0	Too high melting and brittle		
	20	400	283-287	16	99	Very poor	Very poor	Opaque
	40	400	285-290	22	99	Fair	Good	Transparent
	68.5	400	> 600	27	0	Very good	Very good	Transparent
Polymer 2	0	-	262-265	-	100	Poor	Poor	Opaque
	3	500	>600	38	0	Good	Good	Transparent
Polymer 3	0	-	264-274	-	100	Very poor	Very poor	Opaque
	70	400	>600	18	0	Excellent	Excellent	Transparent

SYNTHESIS, STRUCTURE AND THERMAL STABILITY OF NITROGEN AND SULFUR-BRIDGED-S-TRIAZINE OLIGOMERS

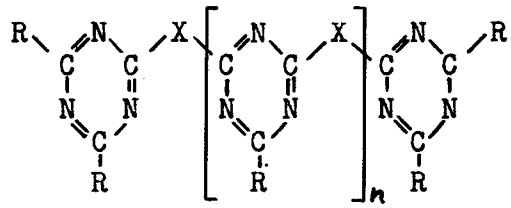
G. A. Loughran and G. F. L. Ehlers
Aeronautical Systems Division

I. INTRODUCTION

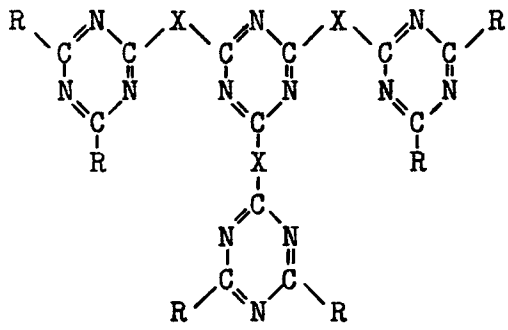
The purpose of this work is to synthesize model compounds and polymers containing the s-triazine ring system in the "backbone" of the polymeric chain, to evaluate their thermal stability, and if possible to compare them with other aromatic systems. Properties, such as radiation stability, fibre forming ability, film strength and flexibility are also of interest. In general the model compounds and polymers discussed in this report consist of structures in which alkyl or aryl substituted s-triazine molecules are linked with each other through nitrogen or sulfur bridges. Their general structures can be formulated as follows:



I



II



III

where R is alkyl, or phenyl, X is-N-H; -N-CH_3; -N-C_6H_5; or S, and n is an integer.

A. Synthesis of N-Bridged S-Triazines

1. Model Reactions

As a guide for the estimation of optimal conditions for the formation of condensation polymers from the reaction of -A-A- and -B-B- type monomers, and for later self condensation of -A-B type monomers, certain model melt reactions and solution reactions in diphenylether were run at 150° to 400°C in a stream of nitrogen or under vacuum between a number of halogen and amino-substituted

-s-triazines. The per cent conversion was determined by titrating the HCl evolved with N/10NaOH.

The model reactions were run between such halogen substituted -s-triazines as cyanuric chloride, I, 2-methyl-4,6 dichloro-s-triazine, II, 2-phenyl-4,6 dichloro-s-triazine, III, and 2,4 diphenyl-6-chloro-s-triazine, IV, and such amino substituted -s-triazines as 2,4 diphenyl-6-N-methylamino-s-triazine, V, 2-phenyl-4,6-bis-(N-phenylamino)-s-triazine, VI, 2,4 diphenyl-6-(N-phenylamino)-s-triazine, VII, and 2-phenyl-4,6-bis-(N-methylamino)-s-triazine, VIII.

The reactions were conducted either as melt reactions or in solution in diphenylether (DPE). The sample was placed in a 1" x 5" reaction tube and heated in an aluminum block by a heating mantle. The temperature was controlled by a thermocap relay with an accuracy of better than $\pm 1^{\circ}C$. N_2 was swept through the apparatus from a tube fitted to the adaptor attached above the reaction tube. The evolved HCl was absorbed in water and titrated at short intervals with N/10NaOH. When vacuum was used, a trap (containing NaCl) was cooled in a dry ice-acetone bath followed by a drying tower packed with Drierite.

Reactions went to completion more rapidly under vacuum than under N_2 at the same temperature, presumably due to a high loss of starting material by sublimation. Conversion generally was higher under N_2 than vacuum. Cyanuric chloride, I, 2-methyl-4,6 dichloro-s-triazine, II, and 2-phenyl-4,6 dichloro-s-triazine, III, all exhibit a high degree of sublimation at the temperatures used. The degree of sublimation varied from two to sixteen per cent under nitrogen, and up to 50% under vacuum, in the temperature range of 200° - $250^{\circ}C$. Hence, calculation of the per cent conversion involved corrections for the amount of sublimation. Reactions conducted at $150^{\circ}C$ usually were incomplete, while at $400^{\circ}C$ the reaction products appeared to be partially degraded although conversion was 100%. Reaction under nitrogen at 200° - 250° for from 12 to 30 hours appear to give optimum results.

After reaction was complete the crude products were crystallized from a suitable solvent such as benzene, toluene, dioxane, or THF. The pure products were high melting white crystalline compounds and have not been described previously in the literature. They can be considered as low molecular weight nitrogen linked triazine oligomers which can be expected to possess some of the properties of higher molecular weight nitrogen linked -s-triazine polymers. The new compounds have been defined as:

1. 2,2'-(N-phenyl)-bis-(4,6 diphenyl-s-triazine), IX.
2. Bis-[N-phenyl-N-(4',6'-diphenyl-s-triazinyl-27) -2,4-diamino-6-methyl s-triazine, X.
3. Bis-[N-phenyl-N-(4',6'-diphenyl-s-triazinyl-2)] -2,4 diamino-6-phenyl-s-triazine, XI.
4. Tris-[N-phenyl-N-(4',6' diphenyl-s-triazinyl-2')] -2,4,6-triamino-s-triazine, XII.
5. Tris-[N-methyl-N-(4',6'-diphenyl-s-triazinyl-2')] -2,4,6-triamino-s-triazine, XIII.

Their reaction schemes are given in Figure 1 and their properties are shown in Table I.

Figure 1
Preparation of N-Linked-S-Triazinylene Oligomers

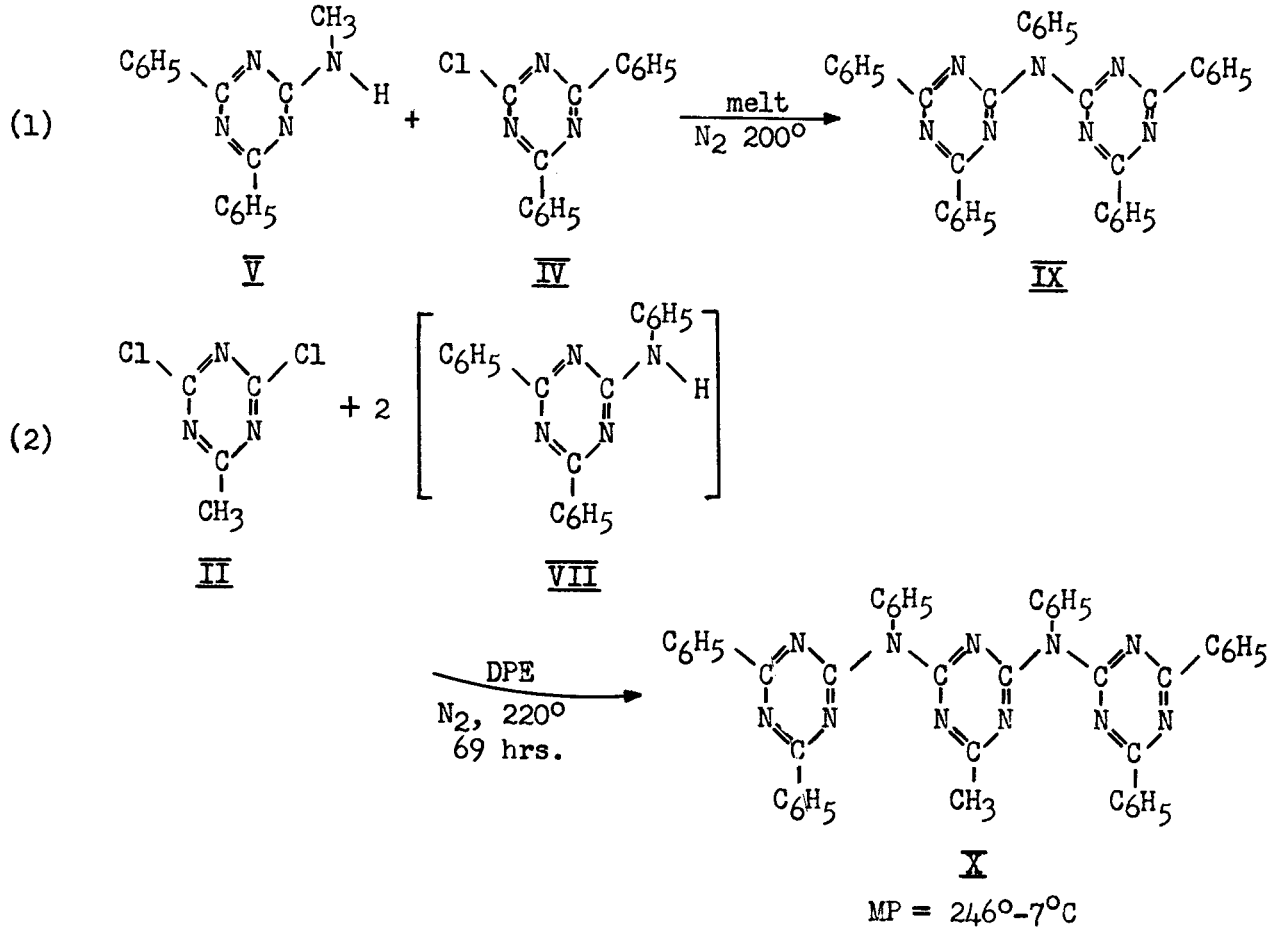
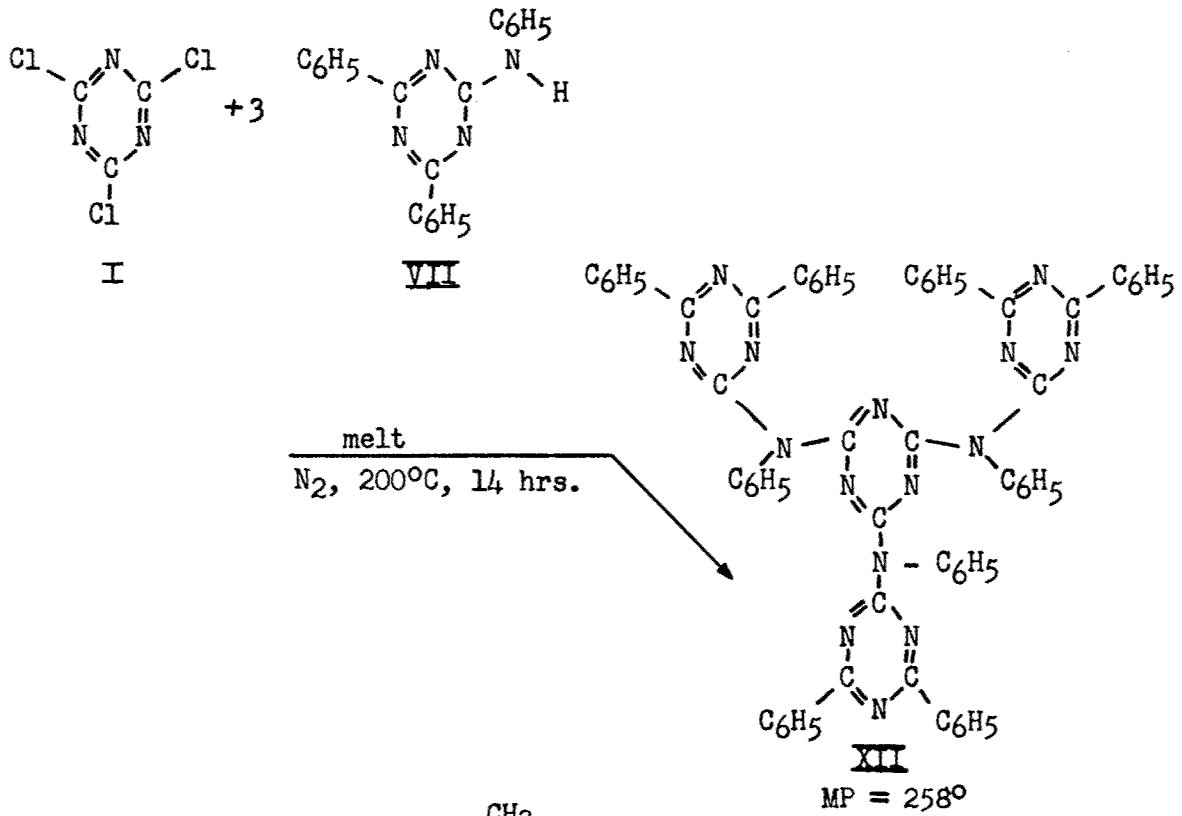


Figure 1 (Cont'd.)

(5)



(6)

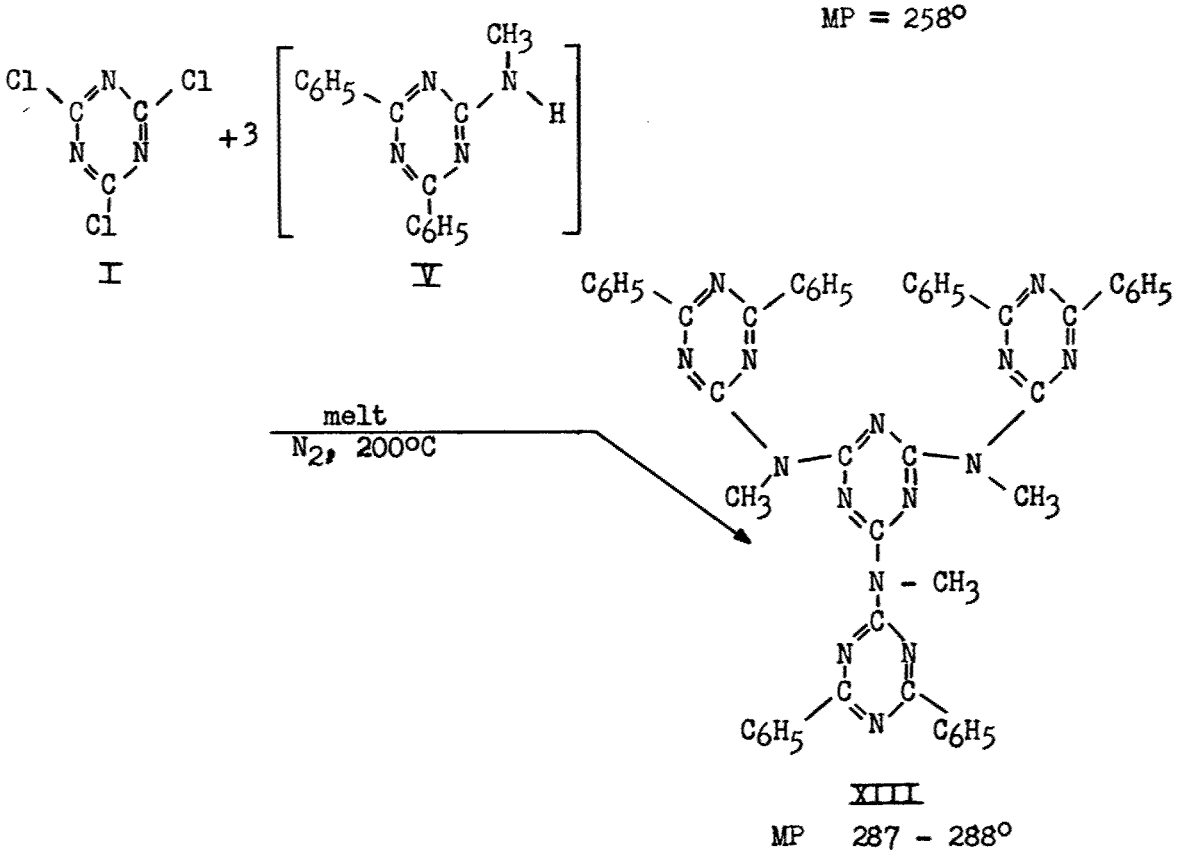


TABLE I

MODEL REACTION BETWEEN CHLORO-S-TRIAZINES AND ANILINO-S-TRIAZINES

Trial No.	Reactants	Solvent	Temp. °C	Reaction Time (hrs)	% Conversion	M.P. of Residue in °C
1	I + VII	None	150	34	68.7	204-215
2	I + VII	"	200	13	95.0	237-238.5
3	I + VII	"	200	8	85.8	193-196
4	I + VII	"	250	5	88.0	120-133
5	I + VII	"	150	311	83.5	208-220
6	I + VII	"	200	27	93.6	230-235
7	I + VII	"	200	29½	91.5	210-229
8	I + VII	"	250	6½	93.7	233-242
9	I + VII	"	200-400*	54	100.0	200
10	III + VII	"	200	30	97.3	126-130
11	III + VII	"	200	46	96.1	125-132
12	IV + VI	DPE	200-220	112	96.4	---

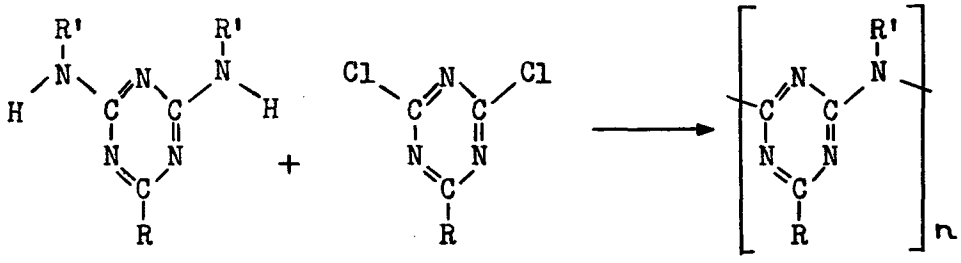
* 47 hrs. at 200°C; 2 hrs. at 300°C; 5 hrs. at 400°C.

A	I	Cyanuric Chloride
B	III	2-phenyl-4,6 dichloro-s-triazine
C	IV	2-4 diphenyl-6-chloro-s-triazine
D	VI	2-phenyl-4,6 dianilino-s-triazine
E	VII	2,4 diphenyl-6-anilino-s-triazine

After a study of the model reactions, and the experimental techniques, essentially two basic methods were used for the synthesis of -N-bridged s-triazine polymers, both of them involving melt condensations, reactions in solution, and interfacial condensation.

2. Condensation of -A-A With -B-B Type Monomers.

The first method involves the condensation reaction of two difunctional monomers, -A-A, and B-B with eachother, as represented by reaction between equimolar quantities of a 2-alkyl or aryl substituted -4,6-bis-(N-alkylamino or N-arylamino)-s-triazine, VI or VIII, and a 2-alkyl or aryl substituted -4,6-dichloro-s-triazine, II or III.



VI R = C_6H_5, R' = C_6H_5

VIII R = C_6H_5, R' = CH_3

II R = CH_3

III R = C_6H_5

Melt condensation of equimolar quantities of 2-phenyl-4,6-dianilino-s-triazine, VI, and 2-phenyl-4,6 dichloro-s-triazine, III, as described previously, gave low molecular weight products with inherent viscosities in the order of 0.01 to 0.07. When an "interfacial" condensation was attempted between a suspension of VI in a solution of III in CCl_4, no reaction occurred. However, a melt condensation between equimolar quantities of III and 2-phenyl-4,6-bis-(N-methylamino)-s-triazine, VIII, at 200° for 160 hours under N_2 gave poly-6-phenyl-N-methyl-2,4 triazinylene imine, XV, MP = 432°. The polymer had a relative viscosity of 0.35, and this represents a significant increase in molecular weight. The same reaction in phenol at 170° for 96 hours lowered the inherent viscosity to 0.035 while no reaction occurred in DPE at 200°C over 24 hours. The improvement in molecular weight by substitution of an N-methyl group in place of the N-phenyl group led to an investigation of the effect of substitution of alkyl groups for phenyl groups both on the triazine ring and attached to the nitrogen bridge. In general, increase in viscosities were noted although not as great as expected. Presumably, this may be due not only to difficulty in the stoichometry of -A-A- plus -B-B-type condensation reactions, but also to sublimation and other experimental factors. The results are shown in Table II.

TABLE II
CONDENSATION OF -A-A-PLUS-B-B-TYPE MONOMERS

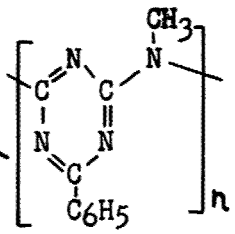
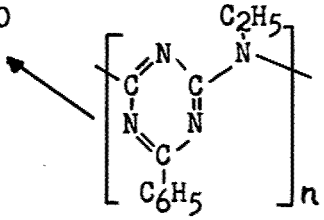
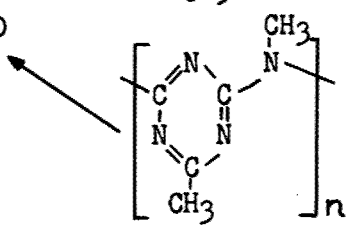
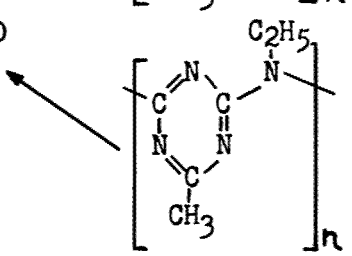
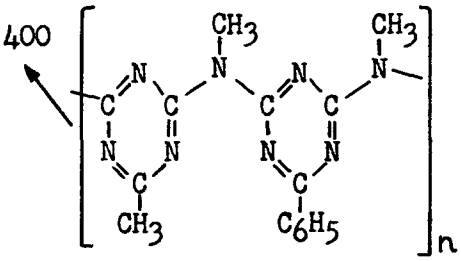
Reactants	Solvent	Temp. °C	Time Hrs.	[η]	M.P. °C	Structure
B + C	None	200	160	0.35	432	
B + C	DPE	200	24	no	reaction	
B + C	Phenol	170	96	0.035	230-70°	
B + D	None	200	41	0.07	365-400	
A + E	None	200	49	0.18	400	
A + F	None	200	42	insol.	400	

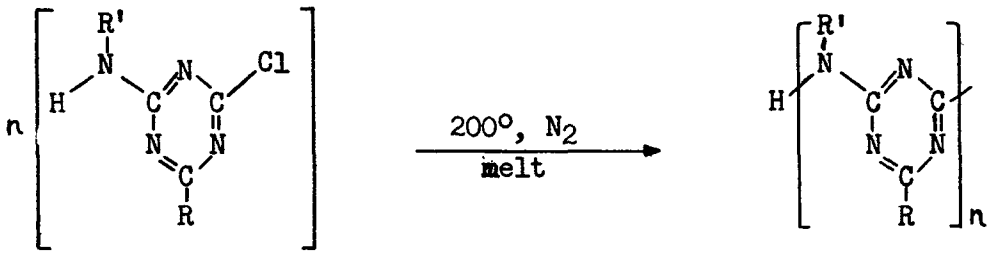
TABLE II (Cont'd.)

Reactants	Solvent	Temp. °C	Time Hrs.	[η]	M.P. °C	Structure
B + E	None	200	49	0.06	400	

A: 2-Methyl-4,6-dichloro-s-triazine.
B: 2-phenyl-4,6-dichloro-s-triazine.
C: 2-phenyl-4,6-bis-(N-methylamino)-s-triazine.
D: 2-phenyl-4,6-bis-(N-ethylamino)-s-triazine.
E: 2-methyl-4,6-bis-(N-methylamino-s-triazine).
F: 2-methyl-4,6-bis-(N-ethylamino-s-triazine).

3. Self Condensation of -A-B Type Monomers

The second method involves the self condensation of -A-B-type monomers as represented by 2-alkyl or aryl substituted -4-chloro -6-alkylamino or arylamino-s-triazines.



A number of melt polycondensations were carried out with 2-phenyl-4-chloro-6-anilino-s-triazine, XIV, alone or in the presence of a catalytic amounts of acidic and alkaline materials, and peroxide under nitrogen. The reaction product, poly-6-phenyl-N-phenyl-2,4-triazinylene imine, XVI, was washed with water for several hours where water soluble additives had been used. All the crude products were extracted with ether to remove starting materials, and then melting points, chlorine content, inherent viscosity were determined and I.R spectra were obtained. No improved products were obtained and the best products had an estimated D.P. between 2 and 10 based on inherent viscosities of up to n = 0.07. D.P.'s calculated on the basis of chlorine and end group analyses were low and unreliable. The results of these runs are listed in Table III.

When an attempt was made to condense 2-phenyl-4-chloro-6-anilino-s-triazine, XIV, in con. H_2SO_4 at 105°C partial decomposition occurred, and the inherent viscosity was found to be lower than products from the melt reaction.

Replacement of the N-phenyl group with N-methyl resulted in a substantial increase in molecular weight. The resulting polymer, poly-2 phenyl-N-methyl-4,6 triazinylene imine, XV, had a M.P. of 395°C and an inherent viscosity

TABLE III

SELF-CONDENSATION REACTIONS OF 2-PHENYL-4-CHLORO-6-ANILINO-S-TRIAZINE

Trial No.	Atmosphere	Temp. °C	Time (hrs)	Additives (Catalysts)	M.P. (°C)	[n]	% Cl	D.P. Viscosity	From Cl Content
1	N_2	200	67	None	222-7	0.07-0.09	0	5-16	Infinite or cyclic!
2	N_2	200	56	0.05g of $FeCl_3$	246-52	0.07	0.74	5-9	20
3	N_2	200	24	0.05g of BF_3-400	210-225	0.02	0.17	1-2	80
4	N_2	200	21	0.05g of cu par.	215-240	0.05	1.95	3-6	8
5	N_2	200	23	2g of H_3PO_4	310	--	--	--	--
6	N_2	200	--		--	--	--	--	--
7	N_2	190	48		138-260	--	0	--	Infinite or cyclic!
8	N_2	200	48		204-260	0.04	2.50	2-5	6
9	N_2	200	42		273-305	0.08	0.35	6-16	40
10	N_2	115	70		230-265	0.03	--	2	--

of 0.30, corresponding quite closely to the properties of the same polymer obtained from the -A-A- plus -B-B- reaction. Further increases in molecular weight can be expected in runs now being conducted by prolonged heating at higher temperatures. The results of the self-condensation of A-B-type monomers are listed in Tables III and IV.

B. Synthesis of Sulfur Bridged S-Triazinylene Oligomers and Polymers

1. Model Compounds

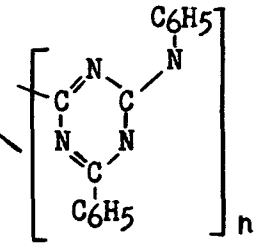
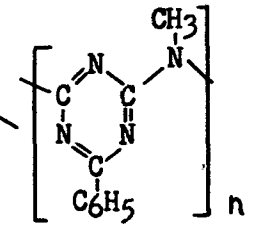
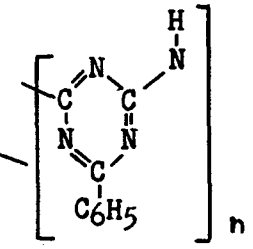
The synthesis of a limited number of pure low molecular weight sulfur bridged 2-phenyl substituted-s-triazine oligomers was begun in order to determine their structure and physical properties, and to obtain thermal stability data which may be useful for predicting the thermal stability characteristics of higher molecular weight polymers of the triazinylene sulfide structure.

(a) Linear straight and branched oligomers.

Dimeric, trimeric, and tetrameric -2-phenyl s-triazinylene 2,4 monosulfides were prepared in solution (usually dioxane) by reaction of 2,4 diphenyl-6-chloro-s-triazine, IV, with the appropriate thiol derivative, XXII, XXIII, or XXIV (see Figure 3), or by reaction of 2,4 diphenyl-6-mercapto-s-triazine, XXII, with the appropriate dichloro derivative, II, III, or XXV in the presence of an acid acceptor such as pyridine, sodium hydroxide, or sodium ethylate. In some cases the sodium salts of the thiol derivatives, XXII, XXIII,

TABLE IV

SELF CONDENSATION OF 2-ALKYL-OR-ARYL-4-CHLORO-6-(N-ALKYL OR ARYL)-S-TRIAZINES

Monomer	Solvent	Temp. °C	Time Hrs.	[n]	M.P.	Structure
G	None	200	67	0.076	222-7	
G	Con H_2SO_4	105	24	0.04	350	
H	None	220	10	0.30	395	
H	DPE	200	48	Insufficient Product	275	
I	None	230	10	Insol	463	

G: 2-phenyl-4-chloro-6-(N-phenylamino)-s-triazine.
H: 2-phenyl-4-chloro-6-(N-methylamino)-s-triazine.
I: 2-phenyl-4-chloro-6-amino-s-triazine.

or XXIV, were prepared in situ and reacted with the chloro derivatives. The new compounds were obtained in relatively high yields, 70 to 90% or better and were purified by crystallization from dioxane, benzene or chlorobenzene. The pure monosulfide oligomers are all white crystalline high melting compounds as is the dimeric disulfide, 2,2' dithiobis-(4,6 diphenyl-s-triazine), XXX, which was prepared by nitrous acid oxidation of 2,4 diphenyl-s-triazine-6-thiol. These oligomers are new compounds and have not yet been described previously in the literature. The new compounds have been defined as:

1. 2,2' thiobis-(4,6 diphenyl-s-triazine) XXVI.
2. 2,4 bis-(2'-thio-4',6'-diphenyl-s-triazinyl)-6-phenyl-s-triazine, XXVII.
3. 2,2' diphenyl-4,4' bis-(2"-thio-4",6" diphenyl-s-triazinyl)-6,6'-s-triazinyl sulfide, XXVIII.
4. Tris-(2'-thio-4',6'-diphenyl-s-triazinyl)-s-triazine, XXIX.
5. 2,2' dithiobis-(4,6 diphenyl-s-triazine), XXX.

Their reaction schemes are given in Figure 2 and their properties are summarized in Table V.

Figure 2
Synthesis of Linear S-Triazine Sulfide Oligomers

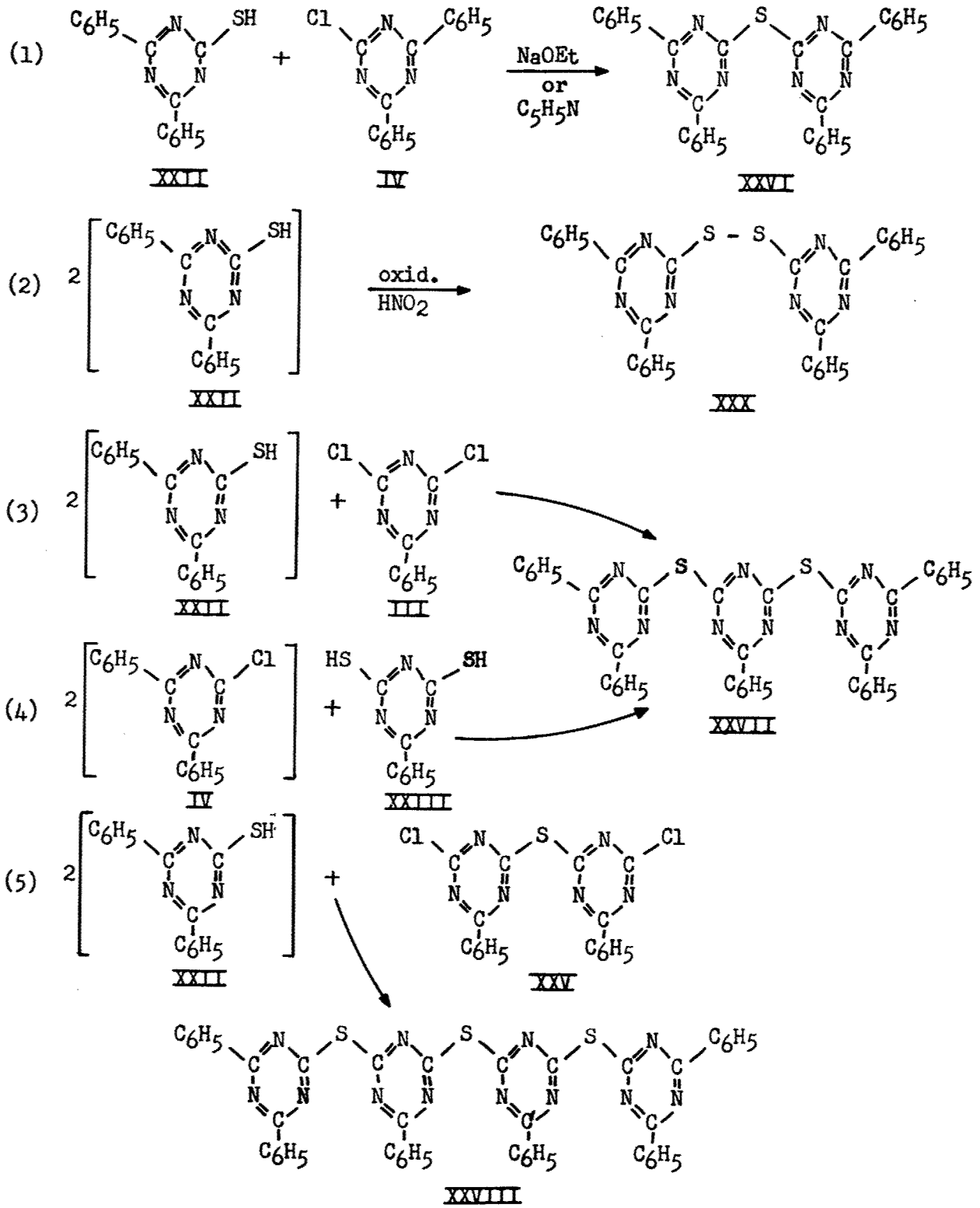


Figure 2 (Cont'd.)

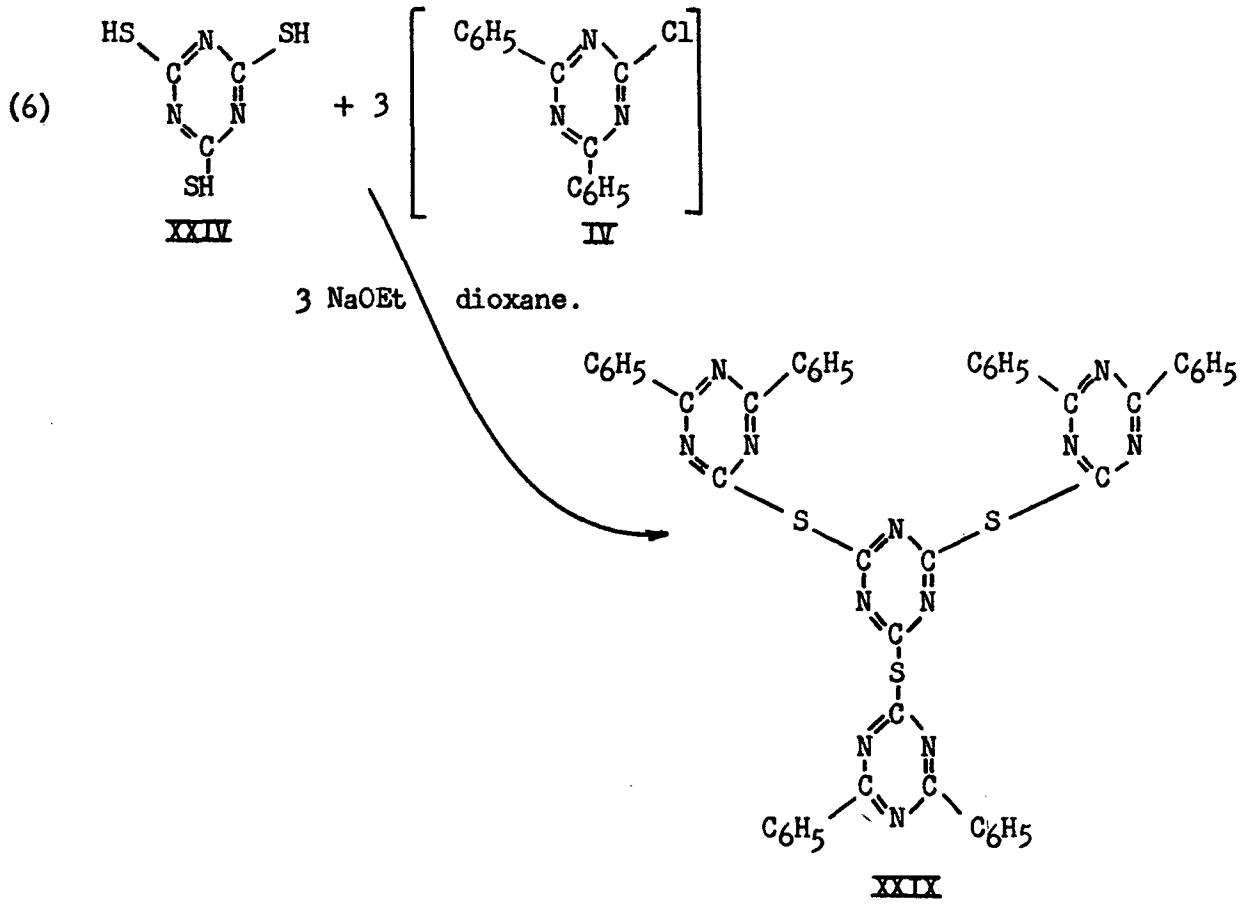


TABLE V

PROPERTIES OF LINEAR S-TRIAZINYLENE SULFIDE OLIGOMERS

Compound	Empirical Formula	% Yield	M.P.(°C)	Molecular Weight* Calc'd.	Obs.
1. (XXVI)	$C_{30}H_{20}N_6S$	95	223-4°	496	528 454
2. (XXX)	$C_{30}H_{20}N_6S_2$	99	275-6°	528.6	566 540 528
3. (XXVII)	$C_{39}H_{25}N_9S_2$	90	249-52°	684	732
4. (XXVIII)	$C_{48}H_{30}N_{12}S_3$	90	251-3°	871	602 638
5. (XXIX)	$C_{48}H_{30}N_{12}S_3$	86	230-5°	871	630

* ebullioscopic, benzene

(b) Cyclic Oligomers

Dropwise addition of aqueous sodium sulfide to an equimolar quantity of 2-phenyl-4,6 dichloro-s-triazine, III, in dioxane at room temperature or at 100°C gave a white fibrous material, XXXI, $C_9H_5N_3S$, MP = 265-7°C. Its molecular weight (ebulloscopic, benzene) was 531 indicating that the compound is a poly-2-phenyl-s-triazinylene 4,6 monosulfide, XXXI with a degree of polymerization of 2.84. Absence of Cl end groups suggests that the product has a cyclic structure, containing three triazinylene units. Similarly, addition of aqueous NaSH to a dioxane solution of 2-methyl-4,6 dichloro-s-triazine, II gave a white granular solid, $C_4H_3N_3S$, M.P. = 212-15°C. Its molecular weight was 361, indicating a degree of polymerization of about 2.9. This compound was identified as cyclotrimeric 2-methyl-s-triazinylene 4,6-monosulfide, XXXII.

Oxidation of 2-phenyl-4,6 dimercapto-s-triazine, XXIII, with nitrous acid at 90°C gave a white crystalline product, $C_9H_5N_3S_2$, M.P. = 282-3°C. The compound had a molecular weight of 791, indicating a degree of polymerization of 3.6. Absence of end groups suggest that this product also has a cyclic structure, XXXIII, corresponding to cyclotrimeric or tetrameric 2-phenyl-s-triazinylene-4,6-disulfide.

Attempts to prepare the corresponding 2-methyl derivative under the same conditions were unsuccessful due to ring scission.

When 2-phenyl-4,6 dichloro-s-triazine, III, was added to a solution of 2-phenyl-4,6 dimercapto-s-triazine, XXIII, and sodium ethylate in alcohol at 70°-80°C, a white crystalline product, XXXIV, M.P. 265-7°C was formed. Infrared spectra indicates that this product is identical with that of the previously prepared cyclotrimeric 2-phenyl-s-triazine-4,6-monosulfide.

The properties of the cyclic poly-triazinylene sulfides and disulfides are compared in Table VI, reaction schemes are given in Figure 3.

TABLE VI
PROPERTIES OF CYCLIC POLYTRIAZINYLENE SULFIDES

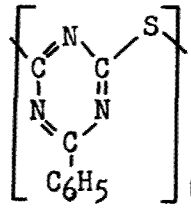
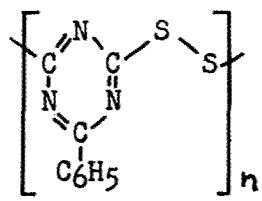
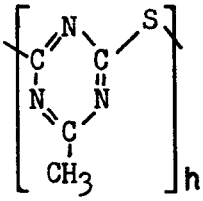
Reactants	Polymer	Yield (%)	M.P. (°C)	MW	D.P.
III + Na_2S		96	265-7	638[a]	3.4
III + Na_2S		92	266-7	530[b]	2.9
III + XXIII 2NaOEt		--	265-7	—	—
III + XXIII 2NaOEt		--	243-8	—	—
III + XXIII NaOH oxid.		99	267-9	791[b]	3.6
XXIII + HNO_2		96	282-3	774[b]	3.5
XXIII + HNO_2		--	265-7	—	—

TABLE VI (CONT'D.)

Reactants		Polymer	Yield (%)	M.P. (°C)	MW	D.P.
II	NaSH		69	d	385[b]	3.1
II	NaSH		71	d	360[b]	2.9

[a] Neumayer Method (osmotic pressure) in chloroform.
[b] Ebullioscopic in benzene.

Figure 3
Preparation of 2-Alkyl or Aryl-s-Triazinylene-4,6-Mono and Disulfide Cyclopolymers

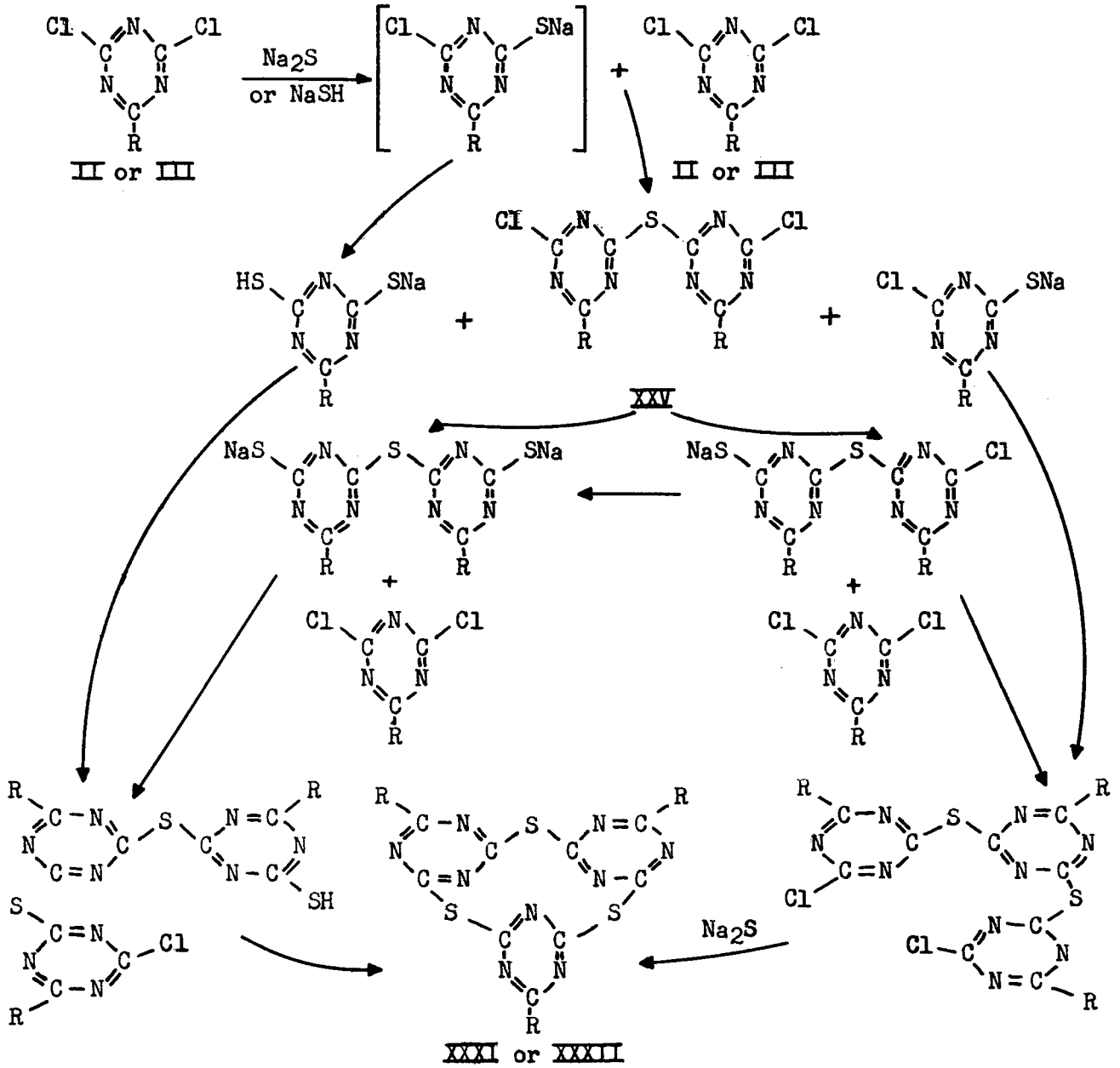
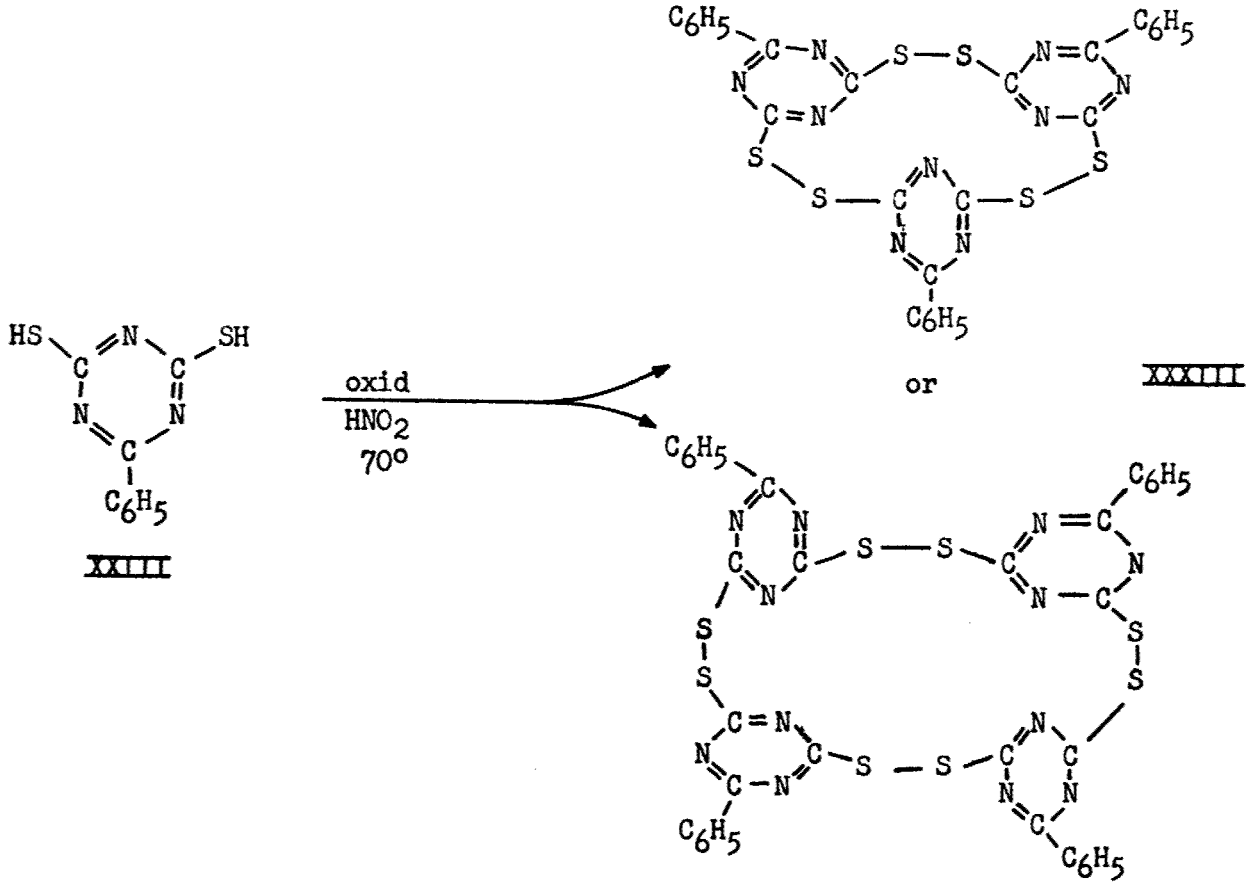


Figure 3 (Cont'd)



2. Melt Condensations of -A-A-and -B-B-Type Monomers

A number of A-A plus B-B melt condensations were carried out. For these condensations highly purified recrystallized samples of 2-phenyl-4,6 dichloro-s-triazine, III, and 2-phenyl-4,6 dimercapto-s-triazine, XXIII, were used in equimolar amounts, at temperatures ranging from 200° to 300°C under nitrogen. The conversions as measured by HCl evolution varied from 97.5 to 97.8%. Several difficulties were encountered during the reaction. The most serious problem was sublimation of 2-phenyl-4,6 dichloro-s-triazine, III. From time to time, the reaction mixture was cooled and the sublimed material was "scraped" back into the reaction mixture which then had to be broken up and "pulverized" as well as possible. It was difficult to maintain a homogeneity throughout the reactions. In all cases the reaction products consisted of two components: (1) about 47% of a hard brittle dioxane insoluble resin, possibly of high molecular weight, and (2) about 53% of a low melting dioxane soluble polymer with a relative viscosity of 0.042 to 0.045. This suggests a low polymer with a possible molecular weight range of 700 to 1400, or a degree of polymerization between 3.7 and 7.5. Prolonged heating did not improve the molecular weight of the dioxane-soluble material.

Investigation of the properties of the dioxane-insoluble polymer has not been completed. It appears to be partially soluble to a low degree in

hot diphenylether, which suggests that viscosity measurements may be feasable in this solvent with a sample of the fractionated material. It is difficult at this stage to conclude whether the melt viscosity technique will be helpful, because the product which is a hard resin at 200°C and which softens gradually with increasing temperature did not appear to melt to a flowable liquid before decomposition began at about 400°C. It therefore will be necessary to find a method to fractionate and purify this resinous product before further evaluation can be made.

Another melt condensation was carried out in a sealed tube under nitrogen at 200°C for 16 hours with equimolar quantities of 2-phenyl-4,6 dichloro-s-triazine, III, and the disodium salt of 2-phenyl-4,6 dimercapto-s-triazine, XXIII. The salt was prepared by reaction of 2-phenyl-4,6 dimercapto-s-triazine, XXIII, with the sodium-naphthalene complex in dry THF. The reaction product as before consisted 46% of a dioxane-soluble fraction with an inherent viscosity of 0.038 and the remaining component was insoluble in dioxane. The properties of the polymers are given in Table V. As before, the chief difficulties encountered were sublimation and lack of homogeneity.

TABLE VII

MELT CONDENSATION OF 2-PHENYL-4,6 DICHLORO-S-TRIAZINE, III, AND 2-PHENYL-4,6 DIMERCAPTO-S-TRIAZINE XXIII

Reactants	Reaction Time	Temp. (°C)	Conversion %	Products Soluble	Products Insoluble	[n]
HS-$C_9H_5N_3$-SH + Cl-$C_9H_5N_3$-Cl	148	200°	98.5	47	53	0.045
	18	200°	98.0	46	54	0.042
	$4\frac{1}{2}$	to 300°				
NaS-$C_9H_5N_3$-SNa + Cl-$C_9H_5N_5$-Cl	16	200°	--	45	55	0.038

D. Thermogravimetric Analysis

Thermogravimetric analyses were run on the "high" molecular weight sample of linear poly-2-phenyl-N-methyl-4,6-triazinylene imine, XV, of an inherent viscosity of 0.30, and on samples of the branched oligomers X, XI, XII, and XXIX, under nitrogen on a modified Chevenard thermal balance. The heating rate was set at 150°C per hour.

The T.G.A. curve for poly-2-phenyl-N-methyl-4,6-triazinylene imine XV, as shown in Figure 4, exhibits initial breakdown in the 350° to 420°C region with a loss of about 10%, followed by rapid decomposition to the extent of about 55% up to 460°C. Subsequently, the rate of decomposition begins to show down at 900°C, only about 10% residue remains. This appears to indicate that the polymer would be servicable for only a short period of time in the 400 to 450°C range.

The T.G.A. curves for the branched oligomers are plotted together in Figure 5. The nitrogen branched oligomers gave similar curves with decreasing

stability in the order, X, XII, and XI, with corresponding initial breakdown temperatures at about 475°C, 450°C, and 390°C. With all these materials rapid breakdown occurs in the 400° to 500°C range with losses of 70 to 90%. The sulfur branched oligomer exhibited earlier breakdown beginning at about 340°C losing up to 50% of its weight at 440°C, and up to about 87% to 480°C. Since, sublimation is observed when XXIX is heated at 350 to 400°C in a tube under nitrogen it can be inferred that the early weight loss between 340°C and 440°C may be partially due to sublimation, because the remainder of the weight loss curve appears in the same region as those of the nitrogen branched oligomers, and the polymer XV.

While all of these compounds appear to show different degrees of stability, these differences actually are minor, and the overall stability of the nitrogen or sulfur-branched oligomers and polymers is limited to the 400°C to 500°C range where complete breakdown occurs. It is also of some significance that the relative thermal stability of a polymer system can be estimated from thermogravimetric data obtained from low molecular weight oligomers thus eliminating the necessity for a major research effort to synthesize high molecular weight polymers for testing.

ACKNOWLEDGEMENTS

Some of the synthetic work and evaluations were performed by Mr. James Kay and Mr. Gerald Burkett.

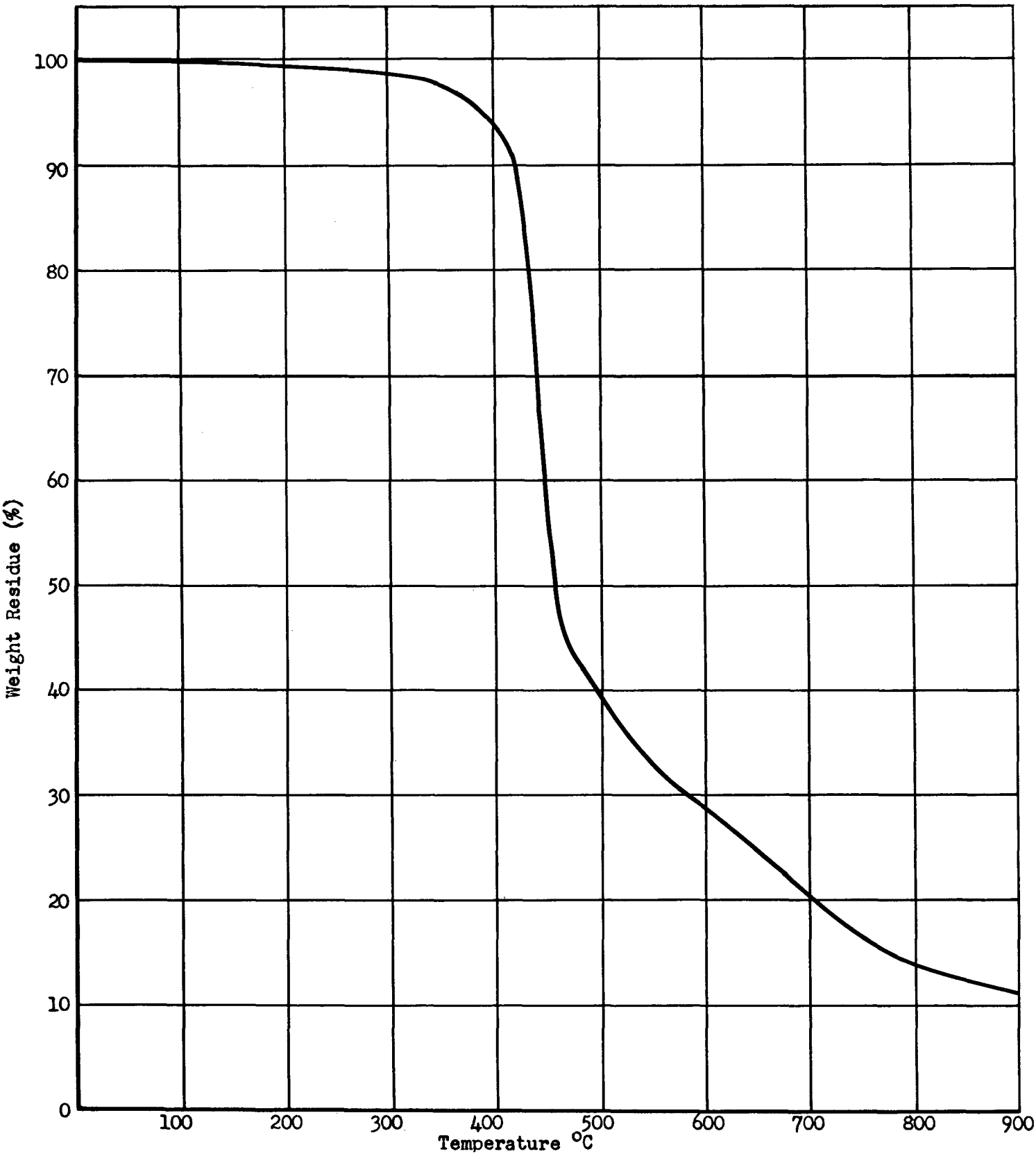


Figure 4. T.G.A. Curve Poly-2-phenyl-N-methyl-4,6 Triazinylene Imine..

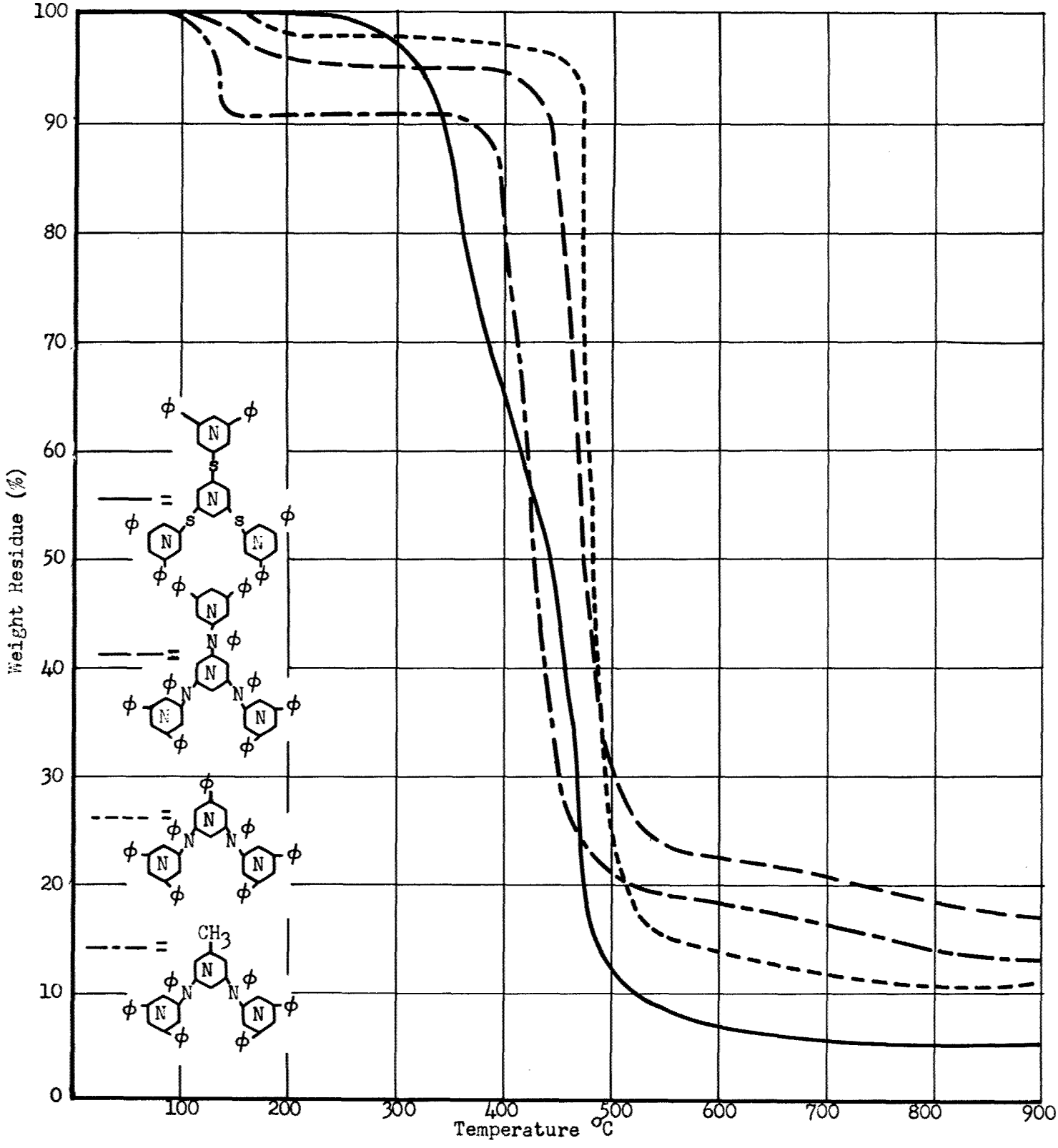


Figure 5. T.G.A. Curves. Branched Nitrogen and Sulfur Linked Triazine Oligomers.

THERMALLY STABLE PERFLUOROALKYL SUBSTITUTED POLYMERS

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INTRODUCTION

The perfluoroalkyl-substituted sym. triazine molecule has been shown to have exceptional stability to high temperatures and strong oxidizing agents. The formation of this ring structure from the condensation of perfluoroalkyl amidines and some of its characteristics have been described[1,2]. The incorporation of the perfluoroalkyl-substituted triazine group into a polymer structure was reported at the previous conference and has been described in the literature[3]. Condensation polymerization of a difunctional perfluoroalkylamidine produced hard, infusible, insoluble products that were obviously completely cross linked. Copolymerization of perfluoroadipoamidine or perfluoroglutarimidine with perfluorobutyramidine produced elastomeric gums, presumably with the structure shown in Fig. 1, where the values of x and y depend on the

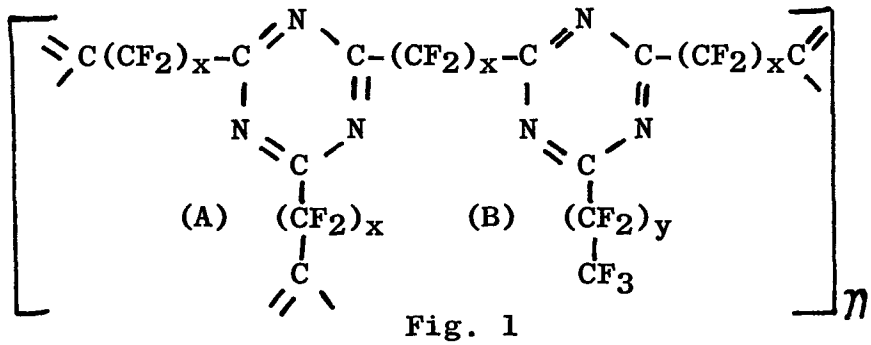


Fig. 1

particular diamidine or monoamidine used, and the groups at (A) and (B) may be continuing or terminal, depending on the monomer which reacted at this point. These polymerizations were carried out with melts or solutions of the two solid monomers.

The structure shown in Fig. 1 is randomly crosslinked, and, by the method of preparation used, this crosslinking apparently cannot be prevented. Obviously, to attain the maximum desired physical properties, a completely linear structure in which (A) and (B) were always terminal would be desirable in the original product, though subsequent partial crosslinking might be used for modification.

This report describes work carried out on the perfluoroalkyltriazine polymer system since the last conference. Three areas of research are described: (1) the mechanism of triazine ring

formation in this system; (2) the preparation of intermediate or prepolymer; (3) catalytic trimerization and polymerization of perfluoroalkylnitriles. All areas have as their objective the attainment of a more complete understanding of this polymer system.

MECHANISM OF FORMATION OF THE TRIAZINE RING FROM CONDENSATION OF PERFLUOROALKYLAMIDINES.

A simple picture of the overall reaction to produce tris-(perfluoroalkyl)sym. triazines is shown in Fig. 2.

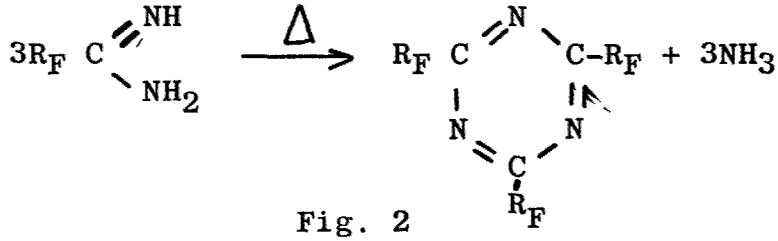


Fig. 2

Here three moles of a perfluoroalkylamidine condense upon heating to form the tris-perfluoroalkyl sym. triazine with the evolution of ammonia.

The first approach to the problem of the mechanism of this reaction was to obtain kinetic data by determining the rate of evolution of ammonia when a solution of the perfluoroalkylamidines in toluene was heated at 100°C. Since a termolecular reaction seemed quite improbable, an assumption was made that the initial step was the reaction of two molecules of amidine to produce one molecule of ammonia and a condensation product represented by the tautomeric structures shown as A + B in Fig. 3.

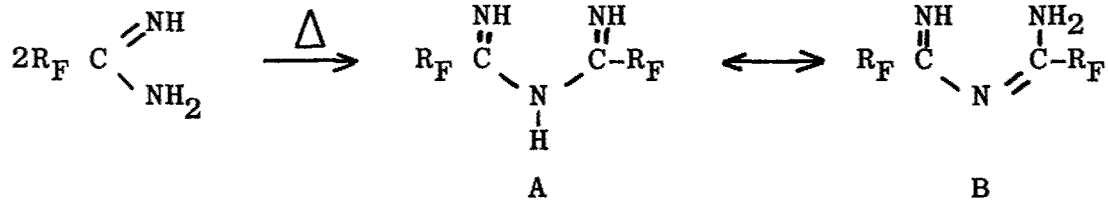


Fig. 3

Graphing of the rate data obtained definitely indicated a bimolecular or second order reaction for the initial stages of the deammonation. A fairly uniform value for the reaction rate constant was obtained during this initial stage and it was assumed that the intermediate shown was being formed.

If we examine the structure of this intermediate, particularly the form shown as B, it is obvious that there is a possibility of chelate formation with metal ions. The solutions used in the rate

studies were, therefore, treated with a solution with cupric acetate and a stable, water-insoluble chelate was isolated.

For the purposes of determining the overall mechanism of triazine formation from the perfluoroalkylamidines, it was obviously necessary to learn something of the intermediate products formed and their properties. Although isolation of this intermediate, which we have termed an N'(perfluoroacylimino)perfluoroalkylamidine, is possible from the deammonation solutions of the original amidine, the procedure is difficult and cumbersome. It was, therefore, desirable that this intermediate be synthesized directly and this was done as shown in Fig. 4.

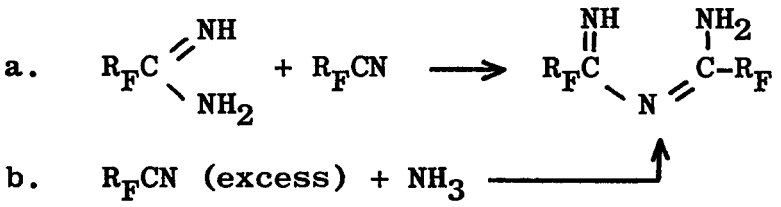


Fig. 4

In reaction (a), a perfluoroalkylamidine is simply reacted with an excess of perfluoroalkylnitrile at a relatively low temperature and the resulting N'(perfluoroacylimino)perfluoroalkylamidine is formed in good yield. The reaction can be carried out even more simply by reacting an excess of the nitrile with the desired amount of ammonia as shown in reaction (b). Reaction (a), of course, offers the opportunity of placing unlike perfluoroalkyl groups in the structure.

In Table 1 are shown some of the properties of the N'(perfluoroacylimino)perfluoroalkylamidines prepared to date.

TABLE 1

N'(PERFLUOROACYLIMINO)PERFLUOROALKYLAMIDINES

$R_F-C(=NH)-N=C(NH_2)-R'_F$

R_F	R'_F	BP, °C	MP, °C	d^{25}	N_D^{25}	Nitrogen	
						calc.	found
CF_3	CF_3		38-42[a]			20.28	19.16
C_2F_5	C_2F_5	35.9-36.1 (6.8 mm)		1.6128	1.3438	13.67	13.41

TABLE 1 (continued)

C_3F_7	C_3F_7	44.3-44.7 (1.5 mm)	1.6854	1.3386	10.31	10.05
CF_3	C_3F_7	50.0-50.8 (13.0 mm)	1.6521	1.3508	13.67	13.51
C_2F_5	C_3F_7	39.2-40.0 (3.8 mm)	1.6561	1.3398	11.76	11.38
C_7F_{15}	C_3F_7	b				

a Decomposes at room temperature
b Viscous liquid, isolated as its copper II chelate

If both of the perfluoroalkyl groups were CF_3, a low melting solid was obtained which was not stable for any length of time at room temperature. If these groups were C_2F_5 or C_3F_7, liquids were obtained which, surprisingly enough, can be distilled without appreciable decomposition. The last three compounds do not have identical perfluoroalkyl groups. Their properties are in line with what we might expect. The last compound, in which one of the perfluoroalkyl groups is C_7F_{15}, was a viscous liquid and could not be distilled. It was actually isolated and purified as a copper chelate.

Fig. 5 shows the formation of the copper chelate of a (perfluoroacylimino)perfluoroalkylamidine.

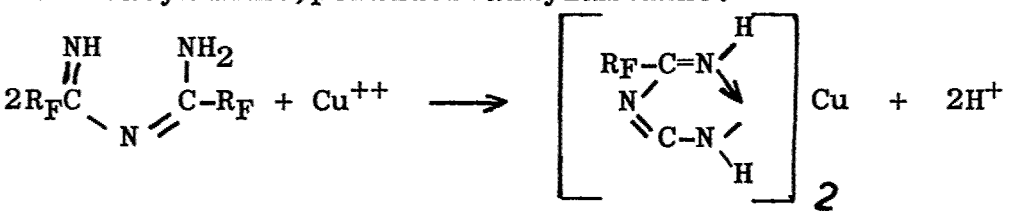


Fig. 5

The structure of the chelates shows one covalent copper-nitrogen bond, one coordinate covalent copper-nitrogen bond and the equation shows the production of hydrogen ion on chelate formation. This is a true picture and the course of this chelate formation can be followed by the determination of the hydrogen ion concentration of the solution.

The absorption spectra of the metal chelates in the visible region was determined as a method of characterization. The copper and nickel chelates are colored where the mercury and zinc chelates are not.

The absorption spectra in the ultra-violet region is of

considerably more interest in helping to understand the structure of the chelate and of the ligand itself. In Fig. 6 the structure of the metal chelate is shown at (B), and the log of the molar extinc-



$\log \epsilon_{max} = 3.93$
$\lambda_{max} = 262\ m\mu$

$\log \epsilon_{max} = 4.35$
$\lambda_{max} = 2.85$



No absorption 220-340 mμ

No absorption 220-340 mμ

Fig. 6

tion coefficient shown as 4.35 at a maximum wave length of 285 mμ. Obviously, the absorption in this region cannot be attributed simply to the two conjugated C=N bonds. The C=N bond is reported to absorb in the region of 190 mμ with a log molar extinction coefficient of about 3.7. Conjugation might shift this absorption maxima towards the red by about 30 mμ but certainly not to the extent shown by the results obtained. The picture, therefore, of the structure of the chelate indicates considerable delocalization of the π electrons from the carbon-nitrogen double bond, but probably not a completely conjugated ring structure since this would involve an unlikely contribution to the bond formation from the metal atom. The ring must have some aromatic character.

Subsequent to the determination of the ultra-violet absorption spectra of the metal chelates, the ultra-violet spectra of the ligand itself, the (perfluorobutyrimino)perfluorobutyramidine, (A) was determined and somewhat unexpectedly showed a fairly intense absorption maxima with the $\log \epsilon = 3.93$ at 262 mμ. Resonance structures might be proposed for the ligand to account for absorption in this region and this, of course, brings up the question of the position of the hydrogen atom which is involved in the hydrogen bonding as shown. It seems likely at present that this is one of the rare incidences where the hydrogen is actually equi-distant

between the two nitrogen atoms, although this is not usually the case in hydrogen bonding.

The compound shown at (C) is N'(perfluorobutyrimino)N-methyl perfluorobutyramidine and at (D) is N'(perfluorobutyrl)perfluorobutyramidine. Neither of these compounds showed absorption in the ultra-violet region between 220 and 340 mμ. Compound (C) was prepared by the reaction of a perfluorobutyronitrile on N-methyl perfluorobutyramidine. The attack of the nitrile on the N-methyl amidine was obviously on the amino nitrogen and resulted in the CH_3 group being attached to the central nitrogen atom. An alternative attack on the imino nitrogen would have resulted in an $NHCH_3$ group being formed and this structure should have shown the characteristic ultra-violet absorption spectra of the unsubstituted compound and also the chelate formation. No chelate formation was observed when compound (C) was treated with metallic ions.

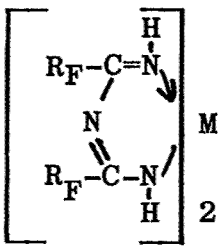
Compound (D) could be produced either by hydrolysis of the N'(perfluoroacylimino)perfluoroalkylamidine or by acylation of a perfluoroalkylamidine with the appropriate anhydride. The structure shown has been selected rather than the tautomeric form in which an OH group would be present on the basis of its infrared spectra which shows a strong absorption for C=O and also on the basis of the inability of this compound to form a metal chelate.

Typical metal chelates that have been formed from the N'(perfluoroacylimino)perfluoroalkylamidine are shown in Table 2.

TABLE 2

N'(PERFLUOROACYLIMINO)PERFLUOROALKYLAMIDINE

Metal Chelates



R_F	Metal	MP, °C	Analysis			
			Metal		Nitrogen	
			calc.	found	calc.	found
CF_3	Cu	223 dec.	13.35	13.19	17.67	17.52
C_2F_5	Cu	134-135	9.40	9.34	12.43	12.02

TABLE 2 (continued)

C_3F_7	Cu	148.5-149.5	7.26	7.21	9.58	9.67
C_3F_7	Zn	108.5-108.8	7.41	7.31	9.58	9.39
C_3F_7	Ni	152-153	6.77	6.66	9.64	9.52
C_3F_7	Hg	126-127	19.93	20.39	8.30	8.53

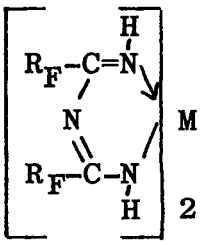
These are all solid compounds that are not wetted by water but are soluble in a variety of organic solvents.

Electronic Spectra

Table 3 shows the ultra-violet and visible spectra of representative chelates.

TABLE 3

ULTRA-VIOLET AND VISIBLE SPECTRA OF REPRESENTATIVE CHELATES



Ligand, R_F	Metal	λ_{max}	$\log \epsilon_{max}$	λ_{max}	$\log \epsilon_{max}$	λ_{max}	$\log \epsilon_{max}$
CF_3	Cu	500	1.69	394	1.87	282	4.13
C_2F_5	Cu	485	1.65	400	1.85	285	4.00
C_3F_7	Cu	490	1.69	405	1.89	285	4.35
C_3F_7	Zn	---	---	---	---	290	4.18
C_3F_7	Ni	492	1.72	241	4.37	305	3.75
C_3F_7	Hg	---	---	---	---	289	3.83
C_3F_7	H	---	---	---	---	262	3.93

Spectroscopic data were determined on methanol solutions of the

metal chelates and ligand using a Beckman DK-2 recording spectrophotometer. It can be seen that there are two absorption maxima in the visible region for the copper chelates in the region of 500 mμ and 400 mμ and that the log of the molar extinction coefficients at this maximum range from 1.65 to 1.9. The ultra-violet absorption maxima for the copper chelates in the region of 280 to 285 mμ show much higher extinction coefficients with log ϵ values of around 4. The nickel chelates are of approximately the same color and, therefore, show absorption in the visible about the same region as the copper chelates. In the ultra-violet region, however, the two absorption maxima for Ni chelates at 241 mμ and 305 mμ again are much more intense than those in the visible region. The mercury and zinc chelates as mentioned before are colorless, but absorb in the ultra-violet region of about 290 mμ with a fairly high extinction coefficient. In the last line is shown the ultra-violet absorption maxima for the ligand at 262 mμ with the log ϵ_{max} 3.93. for comparison.

Infra-Red Absorption Spectra

A considerable effort has been made to establish assignments in the infra-red region for the various N-H and C-N structural features found in the compounds that are pertinent to the objectives of this research. As an aid in establishing these assignments, infra-red spectral data was obtained on several representative compounds and their deuterated analogs in which deuterium has been exchanged for hydrogen. Preparation of the deuterated compounds made use of ammonia-d_3 which was synthesized by the reaction of magnesium nitride with deuterium oxide.

Table 4 shows the infra-red absorptions spectra assignments made to date in the 2.5-7.4μ region. Absorption bands at higher wave lengths are not generally useful in this series of compounds since the carbon-fluorine absorption frequencies obscure the other bands which would be of interest. With the exception of those spectra indicated by footnotes, all of these spectra were obtained by observation of the sample in a mull in Kel F Polymer Oil.

A shift to lower vibration frequencies would be expected upon exchanging deuterium for hydrogen in an NH group.

According to Hooke's Law:

$$\nu = \left(\frac{1}{2\pi C}\right)\left(\frac{K}{\mu}\right)^{1/2}$$

in which ν = frequency in $cm.^{-1}$, C = velocity of light, K = force constant of the bond, and μ = reduced mass.

For the bond X-H,

$$\mu = \frac{M_X\ M_H}{M_X + M_H} \quad \text{where M = atomic weight}$$

The force constants of X-H and X-D are not significantly different, but the reduced mass changes greatly when D is substituted for H. Therefore the approximate shifts to be expected upon deuteration of an X-H bond may be calculated by:

$$\frac{\nu_{X-D}}{\nu_{X-H}} = \left(\frac{\frac{K_1}{\mu_D}}{\frac{K_2}{\mu_H}} \right)^{1/2} = \left(\frac{\mu_H}{\mu_D} \right)^{1/2} \qquad (\text{since } K_1 = K_2)$$

$$\frac{\nu_{X-D}}{\nu_{X-H}} = \left(\frac{\frac{M_X\ M_H}{M_X + M_H}}{\frac{M_X\ M_D}{M_X + M_D}} \right) = \left(\frac{(M_X)^2 + 2M_X}{2(M_X)^2 + 2M_X} \right)^{1/2} = \left(\frac{M_X + 2}{2M_X + 2} \right)^{1/2}$$

For X = Nitrogen

$$\frac{\nu_{N-D}}{\nu_{N-H}} = \left(\frac{16}{30} \right)^{1/2} = \sqrt{.534} = 0.732$$

The frequency shifts found for the N-H to N-D stretching absorption are shown in Table 5. The shifts obtained agree in general with the values that would be expected.

The N-H stretching frequencies of the compounds listed in Table 4 fall within a rather narrow range; the ND stretching frequencies are somewhat more spread but are fairly consistent.

Deuteration of an NH group should cause a similar shift in the deformation frequency to that described above for the stretching absorption. Since this shift would place the absorption maxima at wave lengths greater than 7.4 μ (in which region it would be obscured by other absorption of the fluorocarbon molecule), we would not expect to see the ND deformation maximum. The net result, of course, would be the disappearance of a maximum observed in the NH compound upon deuteration. In the compounds observed, with the exception of perfluorobutyramide, there were no strong and distinct absorption bands which could be assigned to NH deformation. In perfluorobutyramide, a band at 6.15 μ (distinct and of medium strength) disappeared completely upon deuteration. In N'(perfluorobutyrimino)-

TABLE 4

INFRA RED ABSORPTION SPECTRA ASSIGNMENTS IN THE 2.5-7.4 μ REGION (IN μ)

Compound	NH			ND		
	asym. str.	sym. str.	assoc.	asym. str.	sym. str.	assoc.
$C_3F_7C(=O)-NH_2$ 1	2.82(m) (3546)	3.03(m) (3300)		4.00(m) (2500)	4.30(m) (2326)	
$C_3F_7C(=NH)-NH_2$	2.86(m) (3497)	3.05(m) (3279)		3.85 to 4.01(m)[2] (2545)	4.20(m) (2370)	
$C_3F_7C(=NH)-N=C(NH_2)-C_3F_7$ 4	2.86(m) (3497)	3.00(w) (3333)	3.20(w-b) (3125)	3.87(m) (2584)	4.07(m) (2457)	4.24(w) (2358)
$C_3F_7C(=O)-N(H)-C(=NH)-C_3F_7$	2.99(s)		3.31(m) (?)	---	---	---
$[C_3F_7C(H)=N-C(=N-C(H)=C_3F_7)-]_2Cu$	2.93(w) (3413)			4.00(w) (2500)		
$CF_2(CF_2-C(NH_2)=N-C(=NH)-CF_2)_2$	2.89(m)[3] (3460)	3.12(m) (3205)		3.95(m) (2532)		4.25(m) (2353)

(1) Nujol Mull (2) triplet (3) shoulder (4) liquid state

TABLE 4 (cont.)

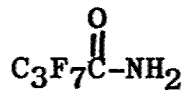
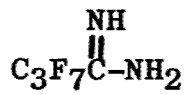
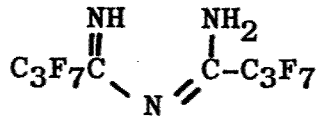
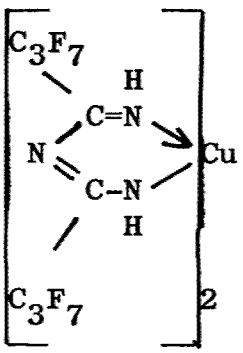
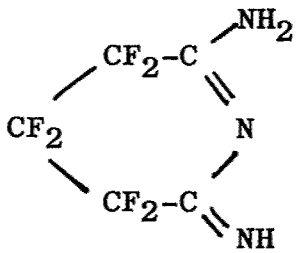
INFRA RED ABSORPTION SPECTRA ASSIGNMENTS IN THE 2.5-7.4μ REGION (IN μ)

Compound	C=N str. -C=NH	C=N str. -C=N-	C=N str. (d) -C=ND	C=N str. (d) -C=N-	N-H def.	N-D def.	Unassigned
$C_3F_7C(=O)-NH_2$ 1	C=O 5.85(s)		C=O 6.02(s)		6.15(m)	$\lambda > 7.4\mu$	7.00(m) for (d) 6.70(w) 7.00(m)
$C_3F_7C(=NH)-NH_2$	5.71(m)[3] 5.97(s) 6.10(m)[3]		5.75(w)[3] 6.02(s) 6.20(w)[3]				6.90 for (d) 7.00
$C_3F_7C(=NH)-N=C(NH_2)-C_3F_7$ 4	6.13(s)	6.30(s) (conj.)	6.17(s)	6.36(s) (conj.)	6.60(w)	$\lambda > 7.4\mu$	6.80 7.00 for (d) 6.80 7.00
$C_3F_7C(=O)-N(H)-C(=NH)-C_3F_7$	C=O 5.82(s) 6.02(s)		---	---			
$[C_3F_7C(H)=N\rightarrow Cu\leftarrow N=C(H)-C_3F_7]_2$	6.25(s)	6.45(s) (conj.)	6.29(s)	6.47(s) (conj.)	6.54(m)[3]	$\lambda > 7.4\mu$	6.70 6.95 for (d) 6.90
$CF_2(CF_2-C(NH_2)=N-)_2NH$	6.10(m)	6.30(s) (conj.)	6.10(m)[3]	6.30(s) (conj.)			5.87 (N-H def.?)

(1) Nujol Mull (2) triplet (3) shoulder (4) liquid state

TABLE 5

FREQUENCY SHIFTS ON DEUTERATION OF N-H BONDS

Compound	Frequency Shift, $\frac{\nu cm^{-1}\ N-D}{\nu cm^{-1}\ N-H}$		
	asym. str.	sym. str.	assoc.
	.705	.705	
	.728	.724	
	.739	.744	.753
		.732	
	.732	.733	

perfluorobutyramidine, a weak band appeared at 6.60μ which was not apparent in the deuterated structure. The copper chelate of this compound exhibited an absorption maxima of 6.54μ as a shoulder that disappeared on deuteration. A somewhat puzzling absorption at 5.87 microns in the spectra of perfluoroglutarimidine disappeared upon deuteration. The assignment of this maxima to NH deformation, however, does not agree with the assignment made from our previous work with the N(methyl) substituted perfluoroglutaramidines.

Assignments for C=N stretching are divided into those attributed to C=NH and to C=N-; all of those in the latter category are conjugated double bonds. The assignments for C=N are consistent when the variation in structures of the compounds recorded are taken into account. In all cases the C=N in a conjugated chain absorbed at lower frequencies. The exchange of deuterium for hydrogen has very little effect on the C=N stretching frequency as is shown by the data in the table.

During the preparation of the mulls of the compounds listed in Table 4 for determination of their infra-red spectra the following observations were made on the rate of exchange of hydrogen for deuterium when the compounds were exposed to atmospheric moisture:

(a) perfluorobutyramidine-detectable exchange in 24 hrs.
(b) perfluoroglutarimidine-detectable exchange in 15 min.
(c) N(perfluorobutyrimino) perfluorobutyramidine Cu II chelate-no exchange in 24 hrs.
(d) N(perfluorobutyrimino)perfluorobutyramidine-considerable exchange in 2 min.

PERFLUOROALKYL-TRIAZINE POLYMERS

The structure of the perfluoroalkyl-triazine polymer shown in Fig. 1 indicates a considerable degree of crosslinking. Since a linear structure would be desirable in terms of improved physical properties, efforts to produce a polymer in which all groups at (A) and (B) were terminal were made by reacting perfluoroglutaronitrile with perfluorobutyramidine to produce a prepolymer with subsequent cyclization along the chain to form triazine rings. An idealized picture of this reaction is shown in Fig. 7. In this reaction, the primary amino group of the perfluorobutyramidine adds to the nitrile of perfluoroglutaronitrile with a subsequent tautomeric shift to give III. The primary amino group of this structure then adds to another molecule of perfluoroglutaronitrile to continue chain formation, IV; such a linear polymer could then form the triazine ring in the chain by deammonation.

The first experiments were carried out in benzene by adding a dilute solution of perfluorobutyramidine to a solution of perfluoroglutaronitrile. Samples were taken periodically from this reaction

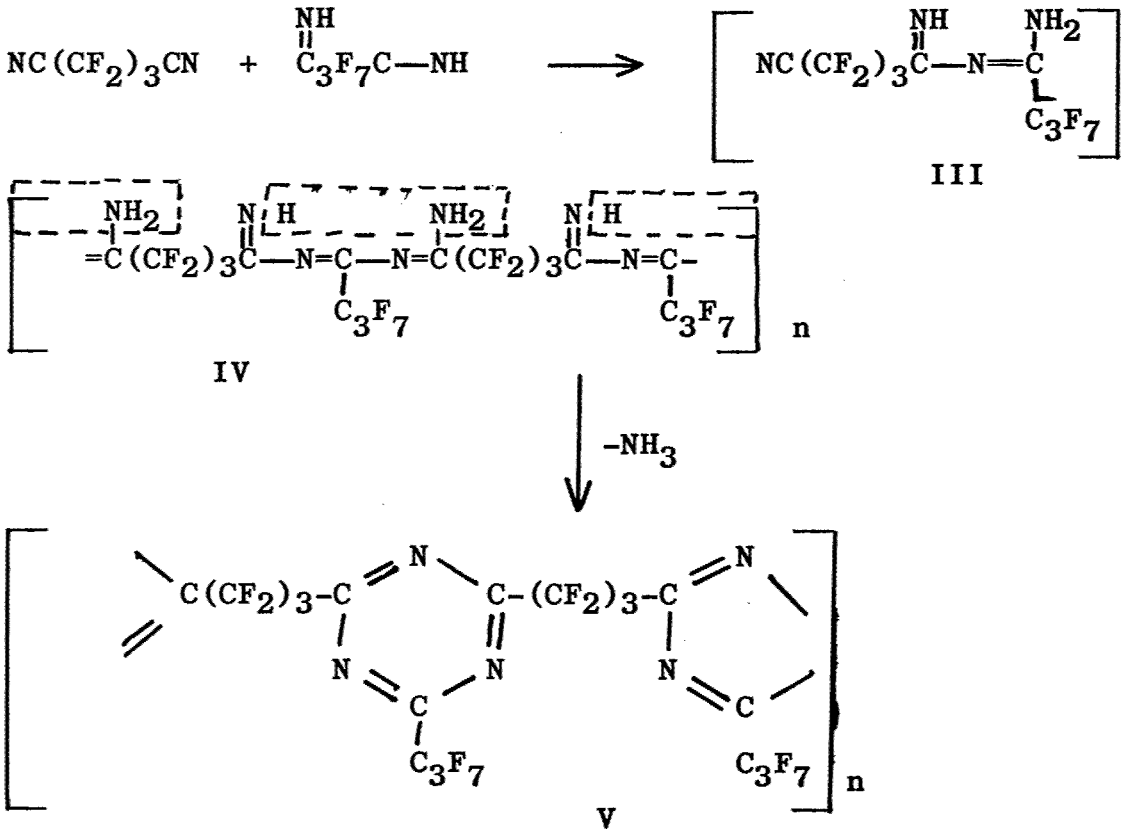


Fig. 7

mixture and the infrared spectra examined. Disappearance of the C≡N absorption band at 4.3 - 4.4μ was followed easily as the reaction took place.

Evaporation of the solvent from a portion of this reaction solution produced a tacky, fusible material which has been termed the intermediate polymer. Subsequent heating of the intermediate polymer at 150° for 2 1/2 days and at 300° for several hours produced an amber, thin, homogenous sheet which was elastic and had appreciable tensile strength.

Toluene was chosen as a solvent for subsequent prepolymer preparations with the thought that the higher boiling point of this solvent would favor complete reaction in a shorter time. A few examples of these prepolymers and their subsequent treatment are described below.

Polymer No. 39 was prepared in toluene with no attempt at protection from the effects of atmospheric oxygen or moisture. The reaction solution was not refluxed but, after stirring briefly, was distilled until about 85% of the solvent was removed. The remainder of the solvent was removed under reduced pressure and the intermediate polymer was then placed in an oven at 150° for 4 hours, 200°

for 15 hours, and 250° for 6 hours. The final product obtained was a thin, soft, flexible, somewhat elastic sheet that was a clear, light amber color. A portion of this polymer was heated further at 400° for 48 hours with very little change other than a slight darkening in color.

Polymer No. 343 was prepared from perfluoroglutaronitrile and perfluorobutyramidine in toluene and after removal of the solvent the intermediate polymer was divided and used for a variety of subsequent treatments. The intermediate polymer No. 343 was a clear, pale yellow-green, very viscous and very tacky material.

A portion of No. 343 (designated No. 343.2) was heated in an oven at 150° for 3 hours and at 200° for 16 hours. The product from this treatment was a light amber sheet, containing some large bubbles, that was elastic and very slightly tacky.

A portion of the polymer sheet No. 343.2 was heated at 375° for 24 hours with no physical change except a darkening to a clear amber color.

Other portions of Polymer No. 343.2 were reacted with perfluoroglutaronitrile by sealing the polymer sample and various percentages of perfluoroglutaronitrile in previously evacuated tubes and heating the tubes at 250° for 16 hours. The amounts of perfluoroglutaronitrile employed in this procedure ranged from over 200% to 10% by weight of the polymer. In each case, all of the perfluoroglutaronitrile was reacted with the polymer. The high percentages produced a very brittle but very hard product, with properties for the lower percentages ranging down to the 10% sample which was somewhat stiffer than the original polymer but was not broken by repeated flexing. These polymer samples after reaction with perfluoroglutaronitrile were heated at 375° for 24 hours with no further physical change except a slight darkening of color.

A small amount of the intermediate polymer No. 343 was placed in a 4" test tube and heated in an oven at increasing temperatures up to a maximum of 170°. When it was apparent that the intermediate polymer was beginning to gel, a glass plunger was forced into the tube to compress the gel and prevent bubble formation. The compressed product was then heated for 1 hour at 170° and cooled to room temperature. The test tube was broken, the pellet removed and placed in an oven at 200° for 1 hour at 250° for 12 hours. There was no deformation or bubble formation in the polymer pellet after this heat treatment and it is evident from this procedure that molding of the intermediate polymer after a suitable heating cycle would be possible.

The infrared spectra of polymer No. 343.2 was typical. There was strong absorption at 5.7μ, probably due to the C=O group, and at 6.45μ due to C=N stretching in the triazine rings. The treatments of this polymer with 40% by weight of perfluoroglutaronitrile

produced no appreciable change in the spectra. The dinitrile evidently reacted completely with the NH or NH_2 groups in the polymer, since there were no evidence of the C=N in the spectra. All of the samples heated at 375-400° showed quite similar infrared spectra with absorption at 6.45 μ, which is characteristic of a triazine ring.

Intermediate Polymer Preparation in Sealed Tubes

From a series of experiments in which preparation of the intermediate polymer was carried out simply by sealing the required quantities of perfluoroglutaronitrile and perfluorobutyramidine in a previously evacuated glass tube and allowing the reaction between the two to take place as the tube warmed, it appeared that this might be a more desirable method of preparation of the intermediate polymer than that described above with the use of solvents. The work to date in this area has not included a detailed study of the properties of the intermediate polymer, such as molecular weight determination, but has dealt principally with the characteristics of the products obtained by oven heating procedures.

Polymer No. 47a was prepared by sealing equimolar quantities of perfluoroglutaronitrile and perfluorobutyramidine in a tube, warming the tube to room temperature and allowing the exothermic reaction to take place. This intermediate polymer was a clear yellow-green liquid that was not viscous immediately following the initial reaction but on standing at room temperature became very viscous after approximately 1 hour and finally set to a hard resin. Subsequent heating of this intermediate polymer, after removal from the reaction tube, at 150° for 2 hours and at 200° for 2 hours produced a clear, water-white elastic, non-tacky sheet with scattered bubble formation. A small portion of this polymer product was heated at 375° for 24 hours and retained all of its previous characteristics with the exception of a slight darkening in color.

A qualitative examination of the product produced by the procedure described above indicates that the final polymer is quite similar to those produced in the best runs made in solvents.

Polymer No. 47b was a repeat of No. 47a with the exception that the sealed tube was heated to 150° for 30 minutes before opening. This procedure produced a marked change in the appearance of the intermediate polymer, which became an opaque white, and subsequent oven heating of the intermediate polymer did not produce a gel but rather a stiff, tacky gum which was partially fusible. Heating this material at 375° caused foaming and the formation of a cellular product.

Small portions of No. 47b were reacted with additional perfluoroglutaronitrile as previously described, and upon this treatment, became infusible and considerably harder.

Polymer No. 348 was prepared in approximately the same manner as No. 47a but with somewhat more extensive investigation of the effect of various treatments on the intermediate polymer.

A portion of No. 348 (designated 348a) was heated in an oven at 100° for 1 hour, 150° for 3 hours, and 200° for 12 hours. The final product from this treatment was an elastic, leathery sheet, containing some bubbles, and very pale amber in color. No. 348a was heated at 375° for 24 hours with no change in physical characteristics. Further reaction of No. 348a with 10% by weight of perfluoroglutaronitrile produced a product that was somewhat stiffer but not brittle. This nitrile treated product appeared to be completely stable when heated at 375° for 24 hours.

The infrared spectra of the polymers obtained in this experiment show all of the characteristic peaks found in the spectra of similar polymers prepared originally in solvents. For example, No. 348a showed a very weak absorption in the NH stretching region (2.6-3.0 μ), a strong absorption peak at 5.75μ and another strong absorption peak at 6.48 μ. After heating at 375° the NH stretching absorption had disappeared and there was no significant peak at 5.75 μ. The characteristic triazine absorption peak at 6.45μ remains.

Determination of the Volatile Products from Controlled Heating of the Intermediate or Pre-Polymer

Since it was quite evident from the work described above on the intermediate or pre-polymers produced from perfluoroglutaronitrile and perfluorobutyramidine that further knowledge was needed concerning the subsequent heat treatment of these products, a detailed study was started in this area with the objective of determining a suitable heating schedule for the pre-polymer in which the loss of the fluorocarbon monomers would be at a minimum and in which the deammonation would be carried to its maximum with a minimum amount of gel formation in the polymer. The pre-polymer product was prepared by reacting equal molar quantities of perfluorobutyramidine and perfluoroglutaronitrile in an evacuated tube at temperatures below 0°. The intermediate product was then held at 0° for 2 - 3 days before the heating schedule was begun. The pre-polymer product was then heated in a glass tube and the volatile products swept out with a constant flow of nitrogen which passed through a trap to collect sublimed solids or high boiling liquids, then through tubes containing a chemical reagent to combine with the evolved ammonia, and finally through a liquid air trap to condense perfluoroalkylnitriles.

In a typical run, No. 20, the first trap was cooled to -30° to trap the higher boiling liquids or sublimed solids. This particular temperature, slightly above the boiling point of ammonia, was chosen in the hope that no ammonia would condense. Liquid ammonia has been found to react rapidly with perfluoroalkylnitriles but

ammonia in the gas phase is very slow to react.

Table 6 shows the evolution of ammonia during the various stages of heating in Run No. 20.

TABLE 6

EVOLUTION OF AMMONIA IN RUN NO. 20

Temp., °C. (furnace)	Total NH_3 Collected, g.	Total NH_3 Collected, g. (at °C.)	Time of Collection, hrs.	Rate of Evolution g./hr
100	.0027	---	1.5	.0018
100	none	.0027 (100)	2.0	---
125	.0096	---	1.0	.0096
125	.1182	---	2.0	.0591
125	.0272	---	1.3	.0204
125	.0187	.1737 (125)	1.17	.0160
150	.0167	---	0.5	.0334
150	.0775	---	1.0	.0775
150	.0419	---	1.0	.0419
150	.0136	.1497 (150)	0.5	.0272
Total NH_3	.3261			

It is apparent from these data that deammonation is not appreciable until a temperature of 100° is reached.

Table 7 shows the various volatile compounds collected during the heating schedule of Run No. 20. In Run No. 20 the combined nitrile portion from the liquid air trap apparently contained about 23% perfluorobutyronitrile and 77% perfluoroglutaronitrile. Thus the weight of perfluoroglutaronitrile (0.0305 g.) represents only 0.61% of the dinitrile originally charged to the reaction tube. The loss of perfluorobutyramidine, however, was high, both at 125° and at 150°. The solid amidine and the C_3F_7 substituted triazine collected in the -30° trap represent, of course, loss of the original perfluorobutyramidine. If one assumes that the materials trapped

at -30° from the 125° heating are 50% perfluorobutyramidine and 50% C_3F_7 substituted triazine and that the material from the 150° heating is 50% C_3F_7 substituted triazine, one can calculate that 0.918 g. of perfluorobutyramidine has been lost. This represents 17.5% of the original charge.

TABLE 7

VOLATILE MATERIALS COLLECTED IN RUN NO. 20

Source of Recovered Volatile Material	Furnace Temp., °C.	Wgt. of Collected Fraction, g.	Identification
$AlCl_3$ trap	100	0.0027	NH_3
$AlCl_3$ trap	125	0.1737	NH_3
$AlCl_3$ trap	150	0.1497	NH_3
-30° trap	100	0.0357	Unidentified liquid.
-30° trap	125	0.6526	$C_3F_7C(NH)NH_2$ and $(C_3F_7CN)_3$ [1]
	150	0.4349	$(C_3F_7CN)_3$ + unidentified liquid.
Liquid Air trap	100	0.0347	$(CF_2)_3(CN)_2$, C_3F_7CN and unidentified liquid.

[1] This mixture appears to be about 50% $C_3F_7C(NH)NH_2$

A member of subsequent runs established the fact that gelation of the polymer occurred when 45-55% of the ammonia had been liberated from the perfluoroglutaronitrile-perfluorobutyramidine system. Heating the prepolymer in a sealed tube to 150°-165° with subsequent removal of ammonia produced a fusible product but intrinsic viscosity measurements indicated a very low molecular weight.

The perfluorocaprylamidine-perfluoroglutaronitrile polymer system was investigated in order to study the effect of lengthening of the perfluoroalkyl chain of the monoamidine on this type of polymerization reaction and also to provide a monoamidine that was less

volatile than those previously used in order to minimize sublimation of the starting materials. The reaction of perfluorocaprylamidine with perfluoroglutaronitrile was slower than that of perfluorobutyramidine; the prepolymer prepared from the C_8 amidine required three hours to gel when heated at 150° while that formed from the C_4 amidine gelled in approximately seventy five minutes. The total weight losses, representing in large part sublimed solids, were also significantly lower in runs made employing the C_8 amidine; the total loss was less than 6%. Another apparent advantage of this system is the fact that the polymer does not reach a gel point until approximately 83-85% of the total contained ammonia has been evolved. This should be an advantage in future fabrication of the polymer.

Table 8 shows the volatile products produced from a typical run (No. 50). At the gel point (after heating 1.5 hours at 150°), 84.7% of the ammonia had been liberated and at the end of the run 90.3% of ammonia was evolved.

TABLE 8

VOLATILE PRODUCTS FROM RUN NO. 50

Temp., °C. Time, hrs.	Source of Collected Material	Wgt. g.	Identification
Room Temp.	$AlCl_3$ trap	0.0039	NH_3
	Liq. Air Trap	0.0323	(Mol. Wgt. 139)
100/2.0	$AlCl_3$ trap	0.0005	NH_3
	Liq. Air Trap	0.0144	HCl [1]
125/2.5	$AlCl_3$ trap	0.0845	NH_3
	-30° Trap	0.0069	(Mol. Wgt. 19.5)[1]
	Liq. Air Trap	0.0211	HCl
150/2.0	$AlCl_3$ trap	0.0988	NH_3
	-30° Trap	0.0052	(Mol. Wgt. 16)[1]
	Liq. Air Trap	0.0128	HCl
Sublimed solids (entire run)		.1618	
Total volatile		.4422	

Total NH_3- 0.1877 g. (90.3% of NH_3 present in starting materials)
Total wgt. loss of prepolymer 0.4428 g.

1. The material collected in the -30° trap was not identified. There is a possibility, however, that it was HF since the C_7F_{15} group of the C_8 amidine is not a solely straight chain and some HF may be formed by decomposition in this reaction environment. If this happens, then sweeping of a portion of the HF through the $AlCl_3$ trap would account for the HCl formed in the liquid air trap.

The perfluoroacetamidine-perfluoroglutaronitrile system was investigated in the hope that the increased reactivity of perfluoroacetamidine (as compared with perfluorobutyramidine) would more than offset its increased volatility, and make possible the preparation of copolymers with lower weight losses than were encountered with the C_4 monoamidine.

The reaction of perfluoroacetamidine with perfluoroglutaronitrile was difficult to control. At a temperature -45° the reaction apparently does not take place; upon warming to -40° the reaction is virtually complete and about 25 seconds. Stirring the reaction mixture to obtain an homogeneous product is not possible.

A further difference in the activity of perfluoroacetamidine as compared to perfluorobutyramidine was evident in the time required for gelation of the prepolymer. The perfluoroacetamidine product required approximately forty minutes at 150° while the average time for the perfluorobutyramidine product was around seventy five minutes at this same temperature. This more rapid gelation may be due in part to the tendency for the perfluoroacetamidine group to react with itself to form the volatile N-(perfluoroacetimino) perfluoroacetamidine and tris(trifluoromethyl) sym. triazine which are then removed from the reaction zone. This, of course, requires that the original prepolymer product chain be broken; an examination of the volatile products produced and of the final polymers indicates that this is probably taking place. All of the final polymers were amber colored and brittle, resembling more the homopolymers of perfluoroglutaromidine than previously described copolymers.

CATALYTIC TRIMERIZATION AND POLYMERIZATION OF PERFLUOROALKYLNITRILES

In the course of our study of the perfluoroalkyltriazine polymer system, the question arose as to whether a small amount of ammonia could function as a catalyst for the trimerization of perfluoroalkylnitriles or the polymerization of the dinitriles to give final products of the same type as those obtained by heating the ammonia addition products.

A study was begun, therefore to determine the effect of catalytic amounts (0.1-10.0 mole% of ammonia on the various perfluoro-

alkylnitriles at elevated temperatures; this study was later extended to other weakly basic or nucleophilic catalysts (with preferential selection of volatile compounds since the conditions chosen indicated a gas phase reaction) in order to gain more information concerning the variables influencing the rate and direction of the reaction.

The results of the work on the mononitriles, particularly the indication of the formation of an activated complex, led to the extension of this type of reaction to the cotrimerization of perfluoroalkylnitriles with aromatic nitriles. Further extension involved the homopolymerization of perfluoroglutaronitrile and the copolymerization of perfluoroglutaronitrile with perfluorobutyronitriles.

Catalytic Trimerization of Perfluoroalkylnitriles

Perfluoroacetonitrile was trimerized at 300° in the presence of 10 mole % or less of weakly basic compounds, or compounds capable of functioning as nucleophiles, to give 2,4,6-tris(trifluoromethyl)-triazine. The reactions were carried out under uniform conditions so that a comparison could be made between the efficiencies of the various catalysts; no attempt was made to find conditions of maximum yield for a given catalyst. The results of these experiments are shown in Table 9.

TABLE 9

TRIMERIZATION OF CF_3CN WITH VARIOUS CATALYSTS

(300°C./24 hrs.)

Catalyst	Mole %	Yield, 2.46, tris(trifluoromethyl)-1,3,5-triazine, %
Ammonia	1	9
	10	85
Triethylamine	1	6
	10	45
p-Toluidine	1	4
	10	55
Diethyl ether	10	trace
Water	10	63

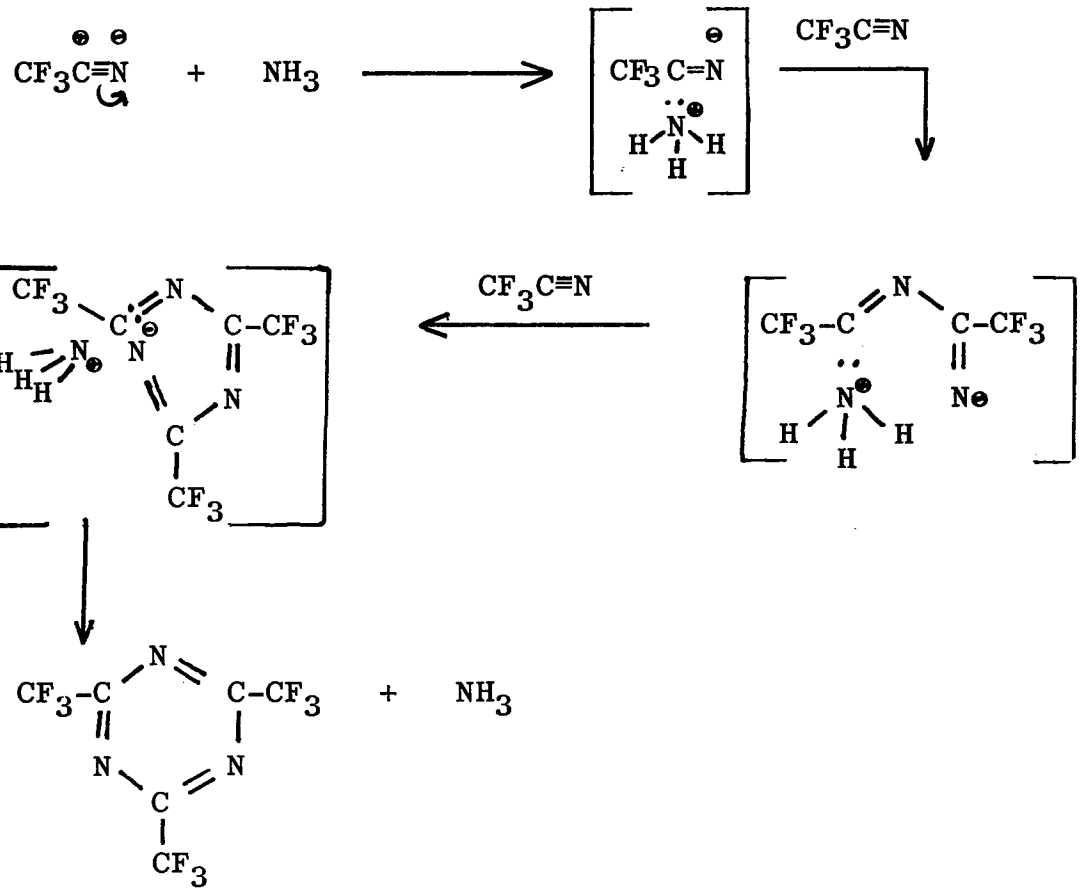
TABLE 9 (continued)

Perfluoroacetamide	1	4
	10	65

Ammonia also was found to be an excellent catalyst for the conversion of perfluoropropionitrile and perfluorobutyronitrile to the corresponding s-triazines.

A mechanism for reaction under these conditions has been considered; two possibilities present themselves as shown in (1) and (2) of Fig. 8.

(1)



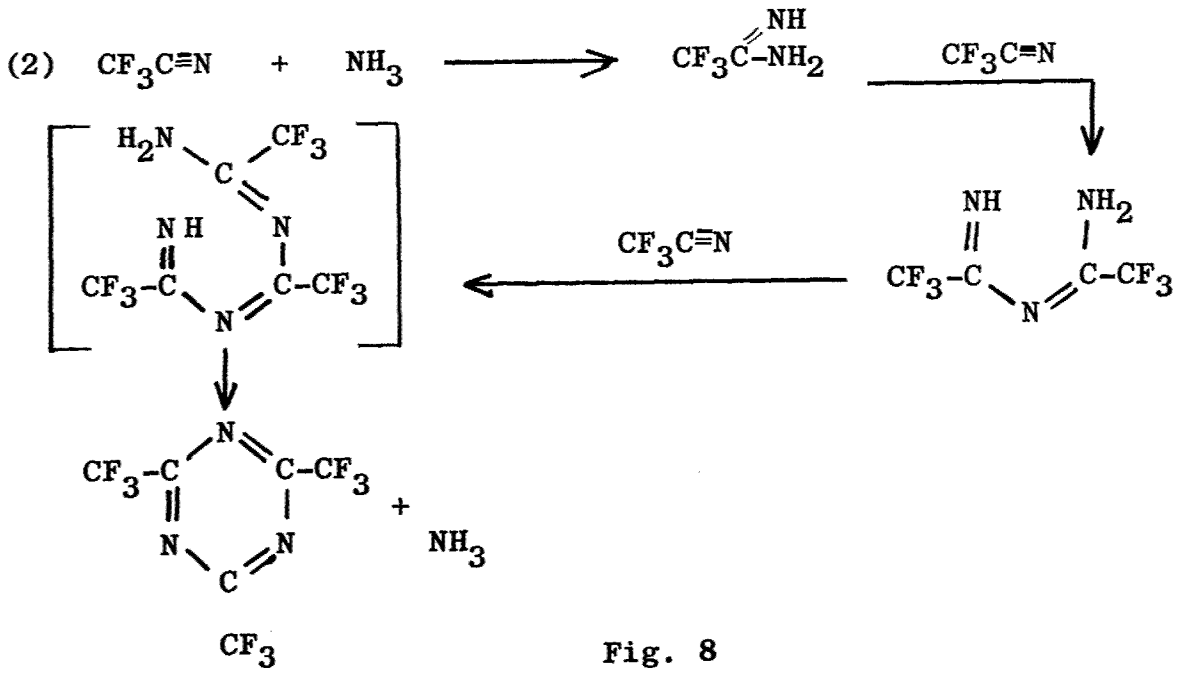


Fig. 8

A mechanism similar to that shown in (2) has been previously discussed by Schaefer et al[4] to explain triazine formation from heating amidines; our initial work on the N'(perfluoroacylimino)-perfluoroalkylamidines led toward a similar conclusion. However, the trimerizations in the present work occurred in the gas phase at a high temperature and neither the perfluoroalkyl amidines nor the N'(perfluoroacylimino)perfluoroalkylamidines are stable under these conditions. In addition, this reaction was catalyzed by trimethylamine, where formation of addition products as shown in (2) is not possible.

We therefore propose the mechanism shown in (1), wherein a nucleophilic attack by ammonia, trimethylamine, water or other nucleophile results in the formation of an activated complex; this complex then reacts with another molecule of nitrile to give an activated dimer, then a trimer. At this stage cyclization occurs to give the resonance-stabilized triazine ring with release of the nucleophile.

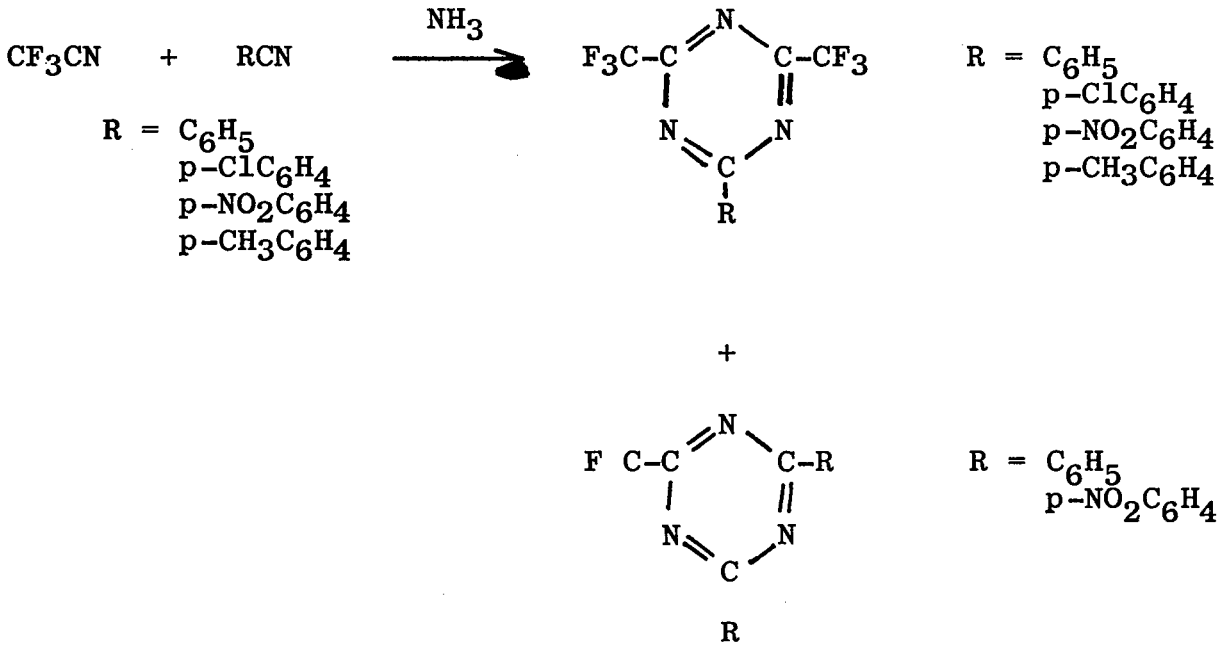
The highest yield of tris(perfluoroalkyl)-s-triazine was obtained with ammonia; triethylamine, a slightly stronger base, gave lower yields, as did p-toluidine, with some decomposition. Steric effects possibly prevented these amines from functioning as effectively as ammonia.

Ethyl ether was an ineffective catalyst and must be considered a poor nucleophile under these conditions. Water was quite effective; perfluoroacetamide, which must be a considerably weaker nucleophile than water, probably is unstable at 300° and the actual catalyst in this experiment was water.

Nitriles containing no fluorine, for example, acetonitrile and benzonitrile, were not trimerized by this procedure.

Catalytic Cotrimerization of Perfluoroacetonitrile with Aromatic Nitriles

Perfluoroacetonitrile was found to cotrimerize with several aromatic nitriles in sealed Pyrex tubes at 300° in the presence of 1-5 mole % ammonia.



Yields of the s-triazines with unlike substituents were less than 30% with the exception of 2-phenyl-4,6-bis(trifluoromethyl)-1,3,5-triazine, which was recovered in 53% yield. tris(Trifluoromethyl) s-triazine was produced in each reaction; no s-triazines of the aromatic nitriles were detected.

Since the aromatic nitriles dó not trimerize under the conditions of these experiments, the cotrimerization with trifluoroacetonitrile must have been promoted by the formation of an activated complex, as previously described, of the ammonia and perfluoroalkyl nitrile.

It is anticipated that these cotrimers may furnish useful monomers for polymers incorporating both triazine and phenyl rings in the polymer structure.

Catalytic Polymerization of Perfluoroalkylnitriles

Our report at the previous conference discussed briefly catalytic polymerization of perfluoroglutaronitrile by basic

(ammonia), Lewis acid (aluminum chloride), and free radical (benzoyl peroxide) catalysts.

It is obvious from our work on trimerization of nitriles that the principal interest now lies in the area of basic or nucleophilic catalysts. The present extension of this type of polymerization has involved the use of ammonia, various amines and water. Table 10 shows tha catalysts, conditions and yield of homopolymers of perfluoroglutaronitrile obtained. In general, the yields shown are average values of the runs made.

TABLE 10

CATALYTIC POLYMERIZATION OF PERFLUOROGLUTARONITRILE AT 200°C.

Catalyst (Mole %)	Relative Pressure of PFGN	Polymer Yield %
None	1.0	7.4*
None	2.0	9.1*
Ammonia (0.1)	1.0	26.5
Ammonia (0.1)	2.0	14.0
Ammonia (0.5)	0.5	77.3
Ammonia (0.5)	1.0	48.6
Ammonia (0.5)	2.0	36.1
Ammonia (1.0)	0.5	91.2
Ammonia (1.0)	1.0	84.0
Ammonia (1.0)	2.0	51.5
Methylamine (1.0)	0.5	89.6
Methylamine (1.0)	1.0	85.4
Dimethylamine (1.0)	0.5	47.8

TABLE 10 (continued)

Dimethylamine (1.0)	1.0	52.6
Trimethylamine (1.0)	0.5	18.6
Trimethylamine (1.0)	1.0	37.4
Pyridine (3.2)	1.0	46.7
p-Toluidine (1.0)	1.0	87.9**
Piperidine (1.0)	1.0	52.8**
p-Phenylendiamine (1.0)	1.0	91.7**
Perfluoroacetamide (1.0)	1.0	13.4
Perfluoroglutaramide (1.0)	1.0	98.9

*reproducibility poor
**possibly decomposition of the catalyst

For the polymerizations catalyzed by ammonia, the yield of polymer increased, as expected, with increase in catalyst concentration; for each catalyst concentration, it will be noted however, that yields increased with decreasing initial pressure. Additional study of the nature of the activated complex formed in this polymerization would help explain this effect.

The decreasing yields in the series CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ may be explained by steric hindrance to formation of the complex. Some of the other amines may have decomposed under the conditions of the reaction. No significant conclusions may be drawn concerning the effect of the basicity of the catalyst on this reaction.

The polymerization catalyzed by perfluoroglutaramide almost certainly indicates that water derived from catalyst decomposition was the effective nucleophile. At this temperature (200^{o}) dehydration of perfluoroacetamide appears to be much less extensive than in the trimerization experiments at 300^{o}.

Copolymers of the type previously described in this report were prepared by catalytic copolymerization of perfluoroglutaronitrile with perfluoroalkylmononitriles. Table 11 shows the results obtained.

TABLE 11

CATALYTIC COPOLYMERIZATION OF PERFLUOROGLUTARONITRILE

WITH PERFLUOROALKYLNITRILES AT 300° WITH

1.0 MOLE % AMMONIA

Perfluoroalkylnitrile	Molar Ratio PFGN : PFAN	% Yield (of total reactants)
CF_3CN	1 : 1	86
CF_3CN	1 : 2	77
CF_3CN	1 : 3	50
C_2F_5CN	1 : 1	66
C_3F_7CN	1 : 1	89
C_3F_7CN	1 : 2	53

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NOVEL POLYMERS BY THE DIELS-ALDER REACTION, CYCLOPOLYMERIZATION, AND THE POLYMERIZATION OF OPTICALLY ACTIVE MONOMERS

by C.G.Overberger, H.Jabloner, W.H.Daly and S.Ishida

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The purpose of this work is to find new ways to prepare polymers which are resistant at high temperatures. Three approaches are described here:

1) The preparation of asymmetric polymers. Currently we are concentrating our efforts on polycondensation polymers which have asymmetric units in the chain although we are also considering polymers with asymmetric units in the main chain and the side chain as well. Results to date have indicated that new polyamides having high melting points and high crystallinity can be prepared in this way while retaining increased solubility over non-branched structure.

2) Synthetic techniques devised to prepare ladder or strand polymers.

3) Preparation of cyclo polymers which result in stiffer chains, higher order and higher melting points.

ABSTRACT

D(-) β methyl-ε-caprolactam has been prepared and polymerized to give a high melting, crystalline polymer.

The optical activity and intrinsic viscosity of the polymer have been determined and in mixtures of cresol and chloroform and the results given a tentative explanation.

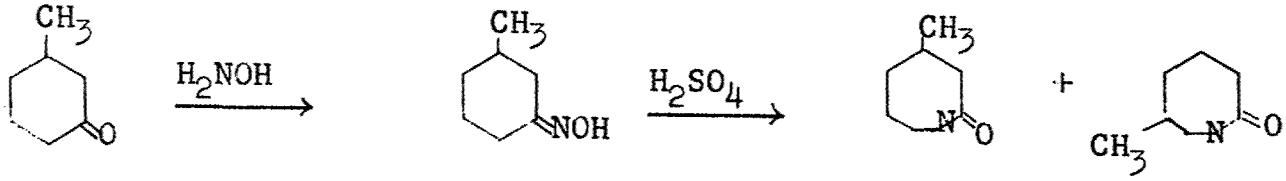
Dibenzylidene succinic anhydride and diisopropenyl succinic anhydride have been prepared. A material has been prepared from dibenzylidene succinic anhydride and maleic anhydride.

Glutaraldehyde has been polymerized thermally to give a soluble polymer. From its infrared spectrum the polymer is thought to have the structure of cyclopolymers. The polymer is soluble but unstable. Glutaraldehyde also has been polymerized at -80°C. with aluminum triisobutyl. The polymer is insoluble but stable. The polymer has been shown by X-ray analysis to have some crystallinity.

OPTICALLY ACTIVE POLYAMIDES - Naturally occurring proteins and polypeptides are the best known examples of polymers containing optically active centers in the main chain. Many of the unusual properties of these materials such as the formation of an α helix in the solid state (1) and in solution (2) are directly or indirectly due to the presence of an optically active asymmetric carbon atom.

The number of synthetic polymers other than poly α amino acids which possess an optically active carbon atom include, polypropylene oxide (3,4), lactide (5) and propylene imine (6). Volkenstein (7) has prepared polymers from D(+) 3-methyl adipic acid and 1,6-hexanediamine and from the corresponding racemic diacid and 1,6-hexanediamine. In all of these cases, the melting point and crystallinity is higher in the optically active polymer than its racemic analogue. We have undertaken a study of these effects on polymers derived from D(-) β-methyl-ε-caprolactam and D,L β-methyl-ε-caprolactam.

DL-β-Methyl-ε-caprolactam and D(-) β-methyl-ε-caprolactam were chosen because of their easy accessibility. The optically active compounds were first prepared by Wallach (8) from naturally occuring pulegone. The optically inactive compounds and their polymers were described by Schaffler and Ziegenbaum (9). The monomer preparation is shown below.



Lactam separation is effected through fractional crystallization, the δ-methyl-ε-caprolactam being the more soluble.

Polymerization of the racemic and optically active β-methyl-ε-caprolactam was carried out according to the procedure of Rogovin et al (10). Water (1%) was used as catalyst at 230° for 20 hrs. The racemic DL β-methyl-ε-caprolactam yielded a discolored rubbery solid; the optically active compound yielded a white fibrous solid. Yields and melting points for these compounds and Nylon 6 prepared by the same procedure are shown below.

Properties of Polyamides

Monomer	D(-)β-Methyl-ε-caprolactam	DL β-Methyl-ε-caprolactam	ε-Caprolactam
Yield %	52	56	90
M.P.*	220-225	135-145	210-215

*Hot stage polarizing microscope

In order to raise the yield and molecular weight of poly D(-) β-methyl-ε-caprolactam over that which was obtained at 230° we have also used polymerization at temperatures below the polymer melting point. Wichterle (27) has recently reported the polymerization of ε-caprolactam at temperatures below the melting point of the polymer. He used anionic initiators in order to obtain reasonable rates at temperatures of from 150-200°. He was able to show that at these temperatures the amount of monomer in equilibrium with the polymer is considerably lower than would be expected from extrapo-

lation of results obtained at temperatures above the polymer melting point. These results are explained in terms of the crystalline polymer phase being excluded from the monomer polymer equilibrium. We found that polymerization using 1/2 percent water as catalyst at 200° was very slow but resulted in substantial increase in the yield (80%) and in the molecular weight (=0.96) over results obtained at 230°.

Solution Properties of Poly D(-) β-Methyl-ε-Caprolactam - The relationship between polymer conformation and the optical activity of optically active polyamides has been discussed only in terms of α-helix formation (11). Poly D(-) β-methyl-ε-caprolactam solutions in cresol-chloroform mixtures have been found to give curves which show a strong dependence of the specific rotation, at the D line of sodium one the solvent composition and exhibit a very sharp maximum. Doty et al (11) for solutions of poly-γ-benzyl glutamate in dichloroacetic acid-chloroform obtained curves of $[\alpha]_D^{25}$ versus solvent composition which are discontinuous and clearly show the formation of an α-helix by rotatory dispersion measurements. Tanford et al (12) for solutions of β lactoglobulin in mixtures of water and organic solvents obtained curves which are similar to the curves obtained for poly D(-) β-methyl-ε-caprolactam which we have studied.

To determine the conformation of the polymer in the cresol - chloroform mixtures the optical rotatory dispersion of the solutions was measured at four wavelengths. For a simple non-helical conformation one would expect (13) the dispersion to follow the Drude relationship. $[\alpha]_\lambda^{25} = K'/\lambda^2 - \lambda_c^2$ where λ_c equals the characteristic or cotton effect wavelength. For helical polyamides the Moffitt equation has been shown to apply (14): $[\alpha]_\lambda^{25} = a_o \frac{\lambda_o^2}{\lambda^2 - \lambda_o^2} + b_o \frac{\lambda_o^4}{(\lambda^2 - \lambda_o^2)^2}$, where b_o is a measure of helix content. The conformation of a polymer may also be followed by measurements of its intrinsic viscosity (14).

The data which we have obtained for poly D(-) β-methyl-ε-caprolactam is summarized in Table I and figures 1,2 and 3. Rotations at wavelengths other than the sodium D line have been omitted.

TABLE 1

Relationship of Polymer Conformation and Optical Activity of Poly D(-) β Methyl-ε-Caprolactam in Cresol-Chloroform Mixtures

Mole % Chloroform	$[\alpha]_D^{25}$	$[\eta]$ dl/g	λ_c mμ (Drude equation)
29.14	44.09	0.980	173
77.46	57.19	1.160	-
71.71	56.01	1.447	220
20.34	45.92	0.980	182
52.38	50.30	1.375	200
62.35	54.00	-	-
75.34	58.32	1.316	178

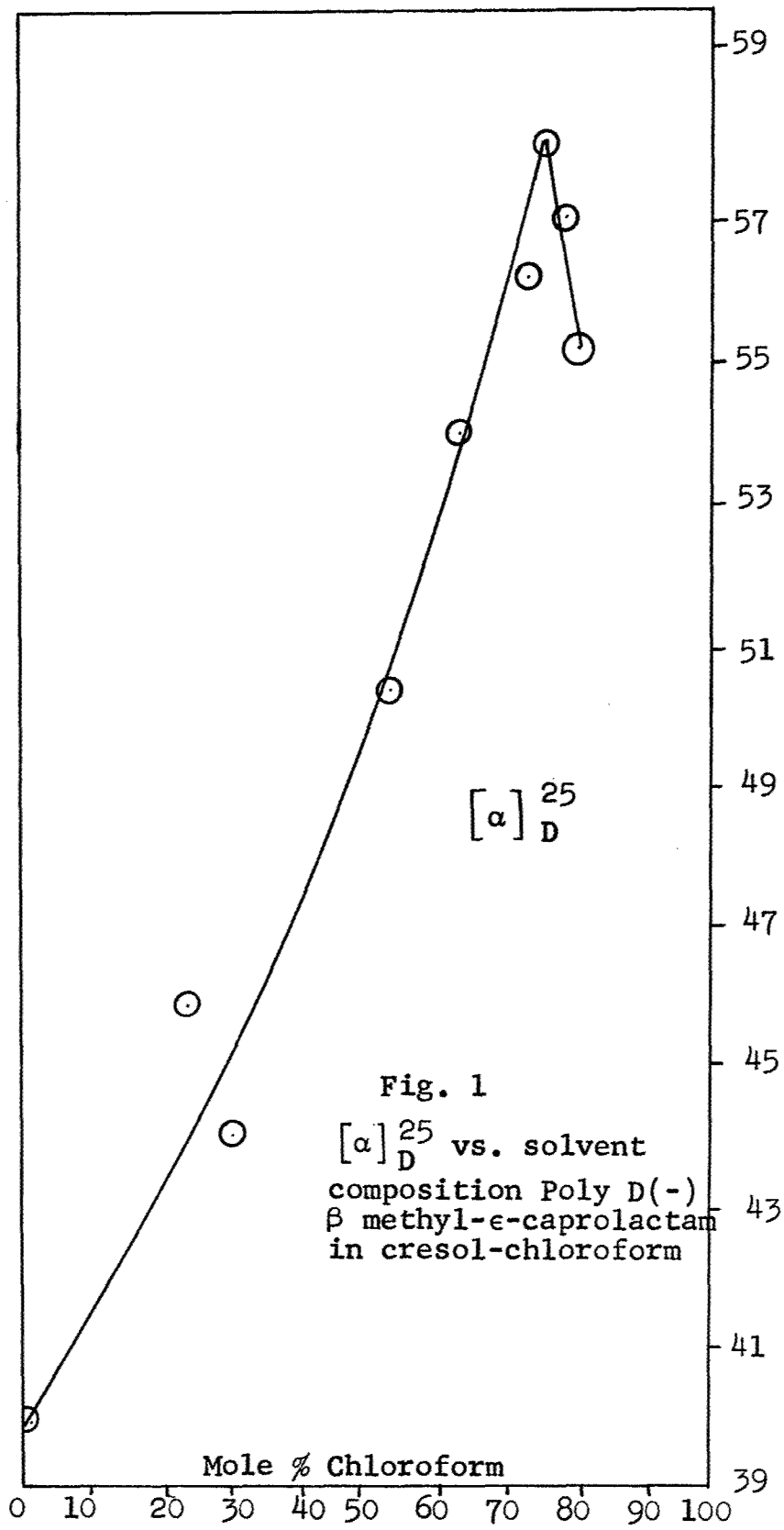


Fig. 1

$[\alpha]_D^{25}$ vs. solvent composition Poly D(-) β methyl-ε-caprolactam in cresol-chloroform

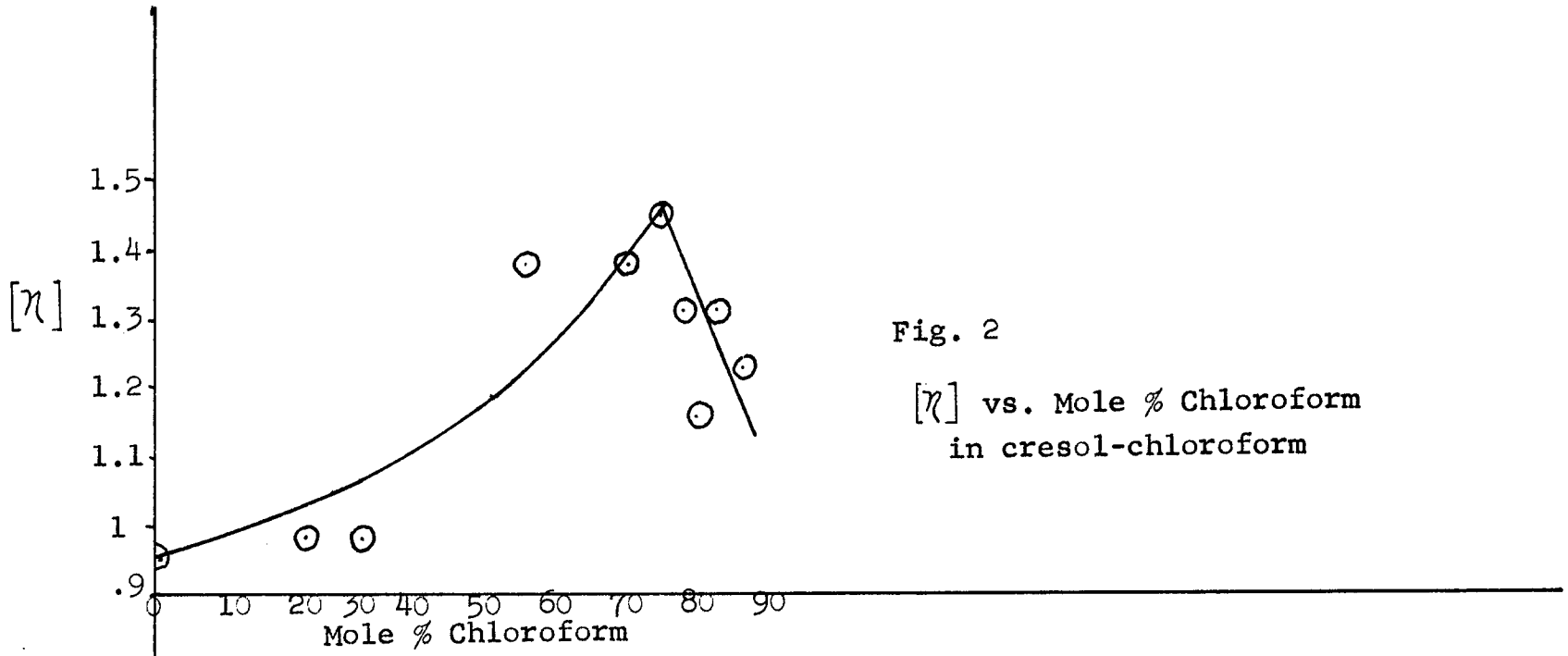


Fig. 2

[η] vs. Mole % Chloroform in cresol-chloroform

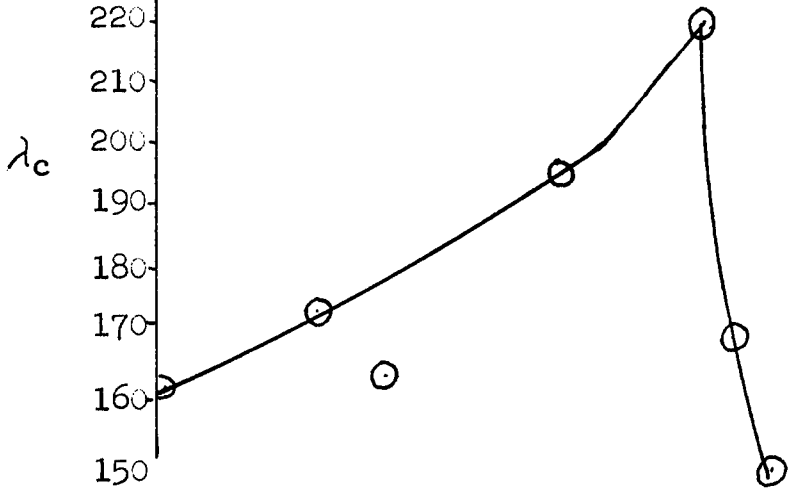


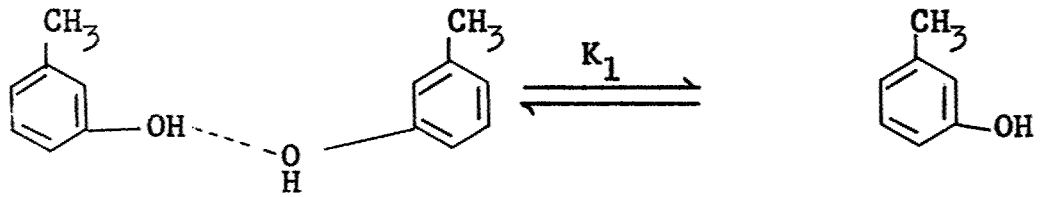
Fig. 3

λc vs. Mole % Chloroform

Table I (Continued)

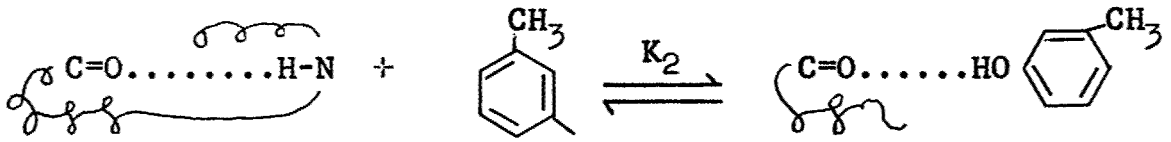
Mole % Chloroform	$[\alpha]_D^{25}$	$[\eta]$ dl/g	λc mμ (Drude equation)
0	39.60	0.960	171
83.52	-	1.227	-
66.87	-	1.372	-

The optical rotatory dispersion data follow the Drude equation for all solvent compositions indicating that there is no helix present in these solutions. The data can be interpreted as a gradual solvation of the coil as the cresol is diluted with chloroform. Pakshver, et al (15) have postulated that the solution of polyamides, in mixtures of hydrogen bonding and non-hydrogen solvents, can be interpreted in terms of increasing chain solvation as the hydrogen bonding component is diluted. There are two equilibria which seem to be important



+

higher aggregates

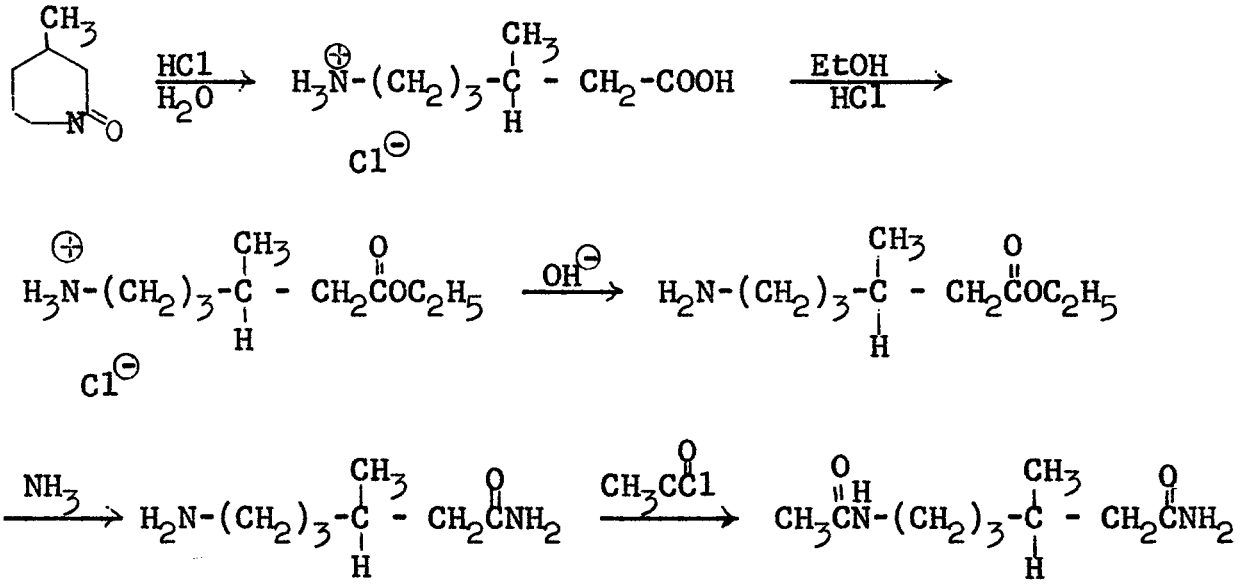


The addition of chloroform would shift both equilibria to the right thus changing the hydrogen bonding of the amide carbonyl from an intramolecular C=O....HN bond to a C=O...HO  bond. The values of λ_c shown in Table I demonstrate that the optically active chromophore is indeed the amide carbonyl (13). Thus both the optical activity and the intrinsic viscosity would be reflections of the solvation of the polymer. While the absolute magnitude of the rotation of a carbonyl hydrogen bonded to an amide nitrogen and the absolute magnitude of a carbonyl hydrogen bonded to cresol cannot be estimated, it is reasonable to assume that the measured rotation is simply a linear sum of the individual rotation of free carbonyl plus the two hydrogen bonded species.

$$[\alpha]_{exp} = [\alpha]_{C=O} + [\alpha]_{C=O-HN} + [\alpha]_{C=O....H-solvent}$$

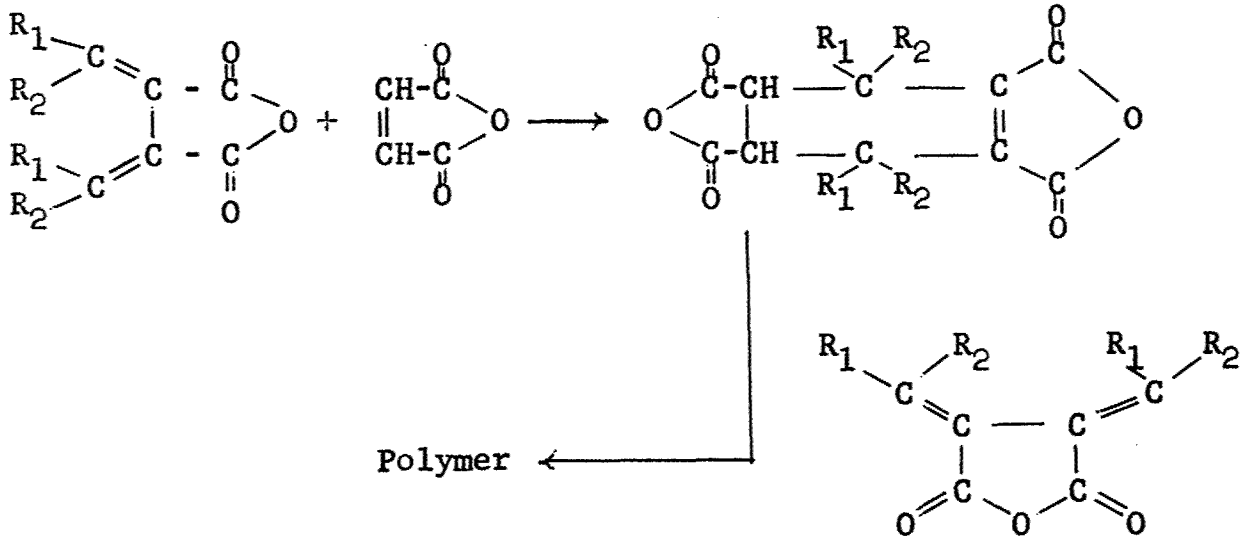
The intrinsic viscosity of a polymer also represents this hydrogen bonding in a poor solvent most of the hydrogen bonds would be intramolecular ones to amide nitrogen as the carbonyl became more highly solvated the random coil would simultaneously expand.

In the previous explanation generalized solvent effects have been neglected. If the argument is to be strengthened further it is necessary to find the optical rotation of the low molecular weight analogue of the polymer. Work has therefore begun on the synthesis of D(-) 6-acetamido-3-methyl-hexanamide. The projected route is similar to Marvel's (16) synthesis of 6-aminohexanamide and is shown below:



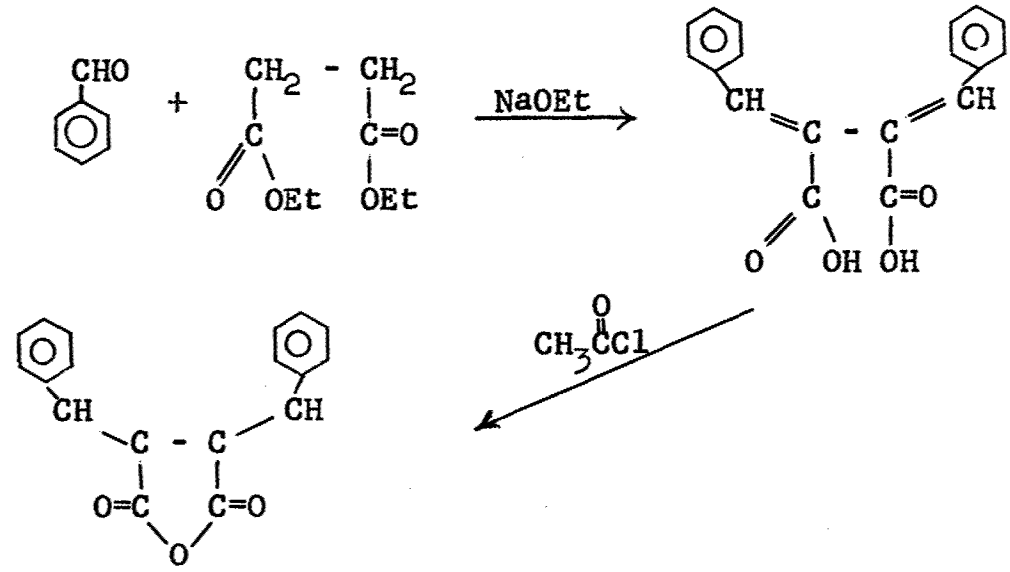
DIELS-ALDER POLYMERS - The preparation of ladder polymers via the Diels-Alder reaction is being studied as a means of preparing soluble, high melting, thermally stable polymers. A Diels-Alder polymer can be prepared by condensation of a bifunctional diene with a bifunctional dienophile or by self-condensation of a molecule which can function both as a diene and as a dienophile. Polymers of the first type have been studied by Bailey (17), Stille (18), Whelan (19), and Kraiman (20). Soluble polymers with good thermal stability have been prepared. However, high molecular weight materials were not obtained because monomer impurities prevented exact stoichiometry.

We are investigating Diels-Alder monomers of the second type. Dimethylene succinic anhydride and several substituted analogs are being prepared as monomers. These materials should polymerize as follows:



R_1R_2=H, CH_3, C_6H_5

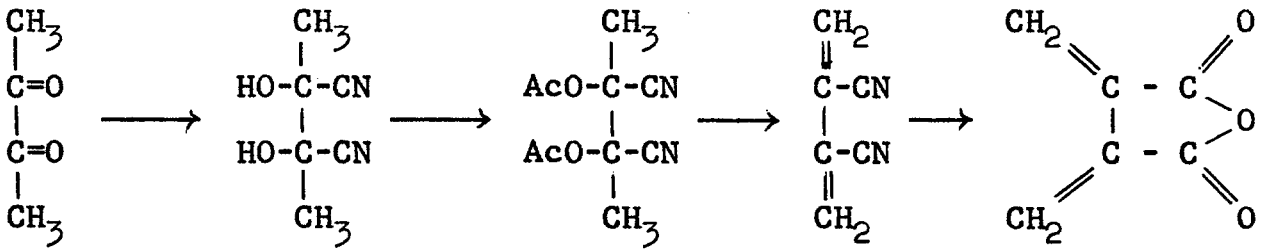
Dibenzylidene succinic anhydride (R_1=H, R_2-C_6H_5 and diisopropenyl succinic anhydride (R_1R_2=CH_3) have been prepared by Stobbe (21) condensation of the corresponding aldehyde or ketone with diethyl succinate.



Initial attempts to polymerize these monomers at atmospheric pressure and 200°C. with a small amount of maleic anhydride as an initiator did not yield polymer. However, reaction of dibenzylidene succinic anhydride in a closed system at 200° and 200 psi has yielded a material with a melting point of 255-256°C. This material may be a polymer but preliminary characterization indicates it may be 3,4-diphenyl-1,2-dicarboxy-cyclobutene-1 anhydride. Further

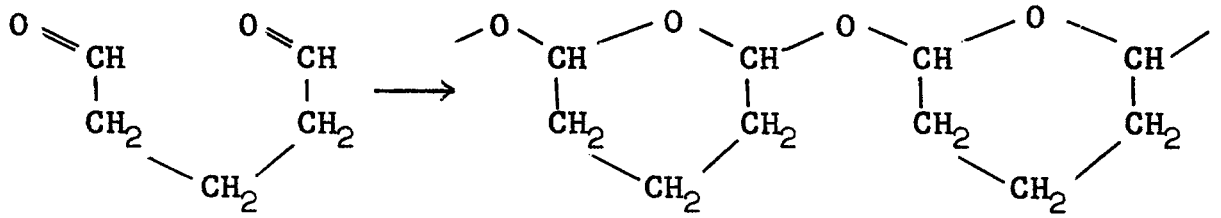
characterization is in progress.

2,3-Dicyanobutadiene has been prepared by pyrolysis of 2,3-butadiene bis cyanohydrin diacetate as described by Prill (22).



This monomer will also be used for the preparation of α,β-dimethylene succinic anhydride.

CYCLOPOLYMERIZATION OF GLUTARALDEHYDE - A number of aliphatic aldehyde polymers have been described (23,24,25). These materials range from solid crystalline polymers to rubbery amorphous ones. The cyclopolymerization of dialdehydes is being undertaken to improve the thermal stability of these polyethers. Glutaraldehyde is the first dialdehyde which has been selected for the preparation of cyclic polyethers. It is expected to polymerize as shown below:



Pure glutaraldehyde itself has a tendency to polymerize at room temperature without any additional catalyst (26). We have found that the polymer is soluble in common organic solvents. It is unstable at room temperature, if freed from the monomer by reprecipitation, a monomer-polymer equilibrium seems to be reestablished. The infrared absorption at 1730 cm.$^{-1}$ due to carbonyl group is fairly weak in freshly precipitated polymer. The absorption due to hydroxyl groups can be seen at approximately 3500 cm.$^{-1}$. These facts seem to imply that the polymer is mainly composed of the structure shown above with hydroxyl groups at the ends. The instability of the polymer makes it difficult to elucidate more fully the structure by elementary analysis or some other means.

Glutaraldehyde also polymerizes at low temperatures with aluminum triisobutyl as a catalyst. The polymerization has been carried out in toluene at the temperature of a Dry-Ice acetone bath (-80°C.). The reaction mixture appears to be homogeneous and becomes thick after a certain time. The polymer when precipitated and freed from the solvent is insoluble in solvents so far tried such as toluene, dimethylformamide, chloroform, or tetrahydrofuran.

A trace portion of the polymer is extractable with chloroform. After the extraction, the polymer shows the presence of a crystalline part by X-ray analysis. The infrared spectrum of the polymer is essentially the same as that of the thermally polymerized material. The insolubility of the polymer is presumably due to its crystallinity, although the possibility of the presence of crosslinkages cannot be excluded. The insoluble polymer is much more stable.

In an attempt to obtain soluble stable polymer, other catalysts such as boron trifluoride - etherate and other conditions such as thermal polymerization in toluene solution are under investigation.

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Mass Spectrometric Techniques Applied to the Investigation of the Thermal Degradation of Polymers

by

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Abstract

The problems of analyzing mixtures of fluorocarbons by mass spectral techniques are discussed. The effects of temperature and of the energy of the ionizing electrons on mass spectra are illustrated. The application of the linear, pulsed time-of-flight mass spectrometer to the study of reacting fluorocarbon systems is discussed and the expecimental program based on this application is outlined.

Introduction.

The mass spectrometric research program at the National Bureau of Standards applied to the problem of thermal degradation of polymers has been primarily occupied with completing the instrumentation necessary for investigation of fast reactions and the analysis of fluorocarbon mixtures. The laboratory now has two instruments available for these studies. They are a modified Consolidated Electrodynamics Corporation Model 21-102, 5-inch radius of curvature, 180° magnetic deflection mass spectrometer and a Bendix Corporation Model 14 time-of-flight mass spectrometer.

The mass spectral analysis of fluorocarbon systems is quite difficult due to the similarity of the mass spectra of the fluorocarbons and the lack of high mass ions. In order to analyze the products of the reactions of fluorocarbon radicals to be studied with the Bendix instrument it is necessary to have a fairly complete understanding of the ionization-dissociation processes of the fluorocarbons involved and to know the effect of temperature on these processes.

The Consolidated Electrodynamics Corporation 21-102 Mass Spectrometer and its Applications.

1. Description

The CEC instrument has been rebuilt to provide better sensitivity and stability. A heated inlet system has been added to permit examination of liquid and solid materials. The instrument now consists of a heated inlet oven with a stainless steel inlet block, high resolution analyzer and associated electronics. The valves and expansion volume of the inlet system are stainless steel with teflon seats and gaskets. This system can be maintained at 200°C or raised to over 250° for several hours at a time. A new high resolution analyzer is used with a four coil, high temperature magnet which has had the pole faces cut to accomodate this analyzer.

To improve the stability of the instrument the following changes have been made:

a. The instrument power is supplied by a 3 kva constant voltage transformer having low harmonic output. This transformer receives its input power from one isolated output of a 7.5 kva isolation transformer. A second output from an isolation transformer supplies power for the mechanical requirements of the instrument. A single ground return point is provided for the entire instrument.

b. The regulation circuit of the magnet power supply has been changed so that it now acts as a constant current supply rather than a constant voltage supply thus correcting for the temperature variation of the magnet coil resistance.

c. The high voltage supply and regulation circuit have been replaced with a commercial 6000v 20ma supply having greater stability.

d. The r-c controlled sweep circuit has been replaced by an electromechanical sweep which is quite stable and very easily controlled.

e. The dc amplifier has been replaced by a vibrating reed electrometer which drives a pen recorder. This change reduced the noise level significantly thereby increasing the sensitivity of the instrument.

f. Some slight modifications were made in the filament emission control circuits which give greater stability of operation when using low energy electrons to produce ionization.

The instrument is capable of remaining on a mass peak for many hours, and has sensitivity and noise level equivalent to currently available commercial instruments. The 180° mass spectrometer is suited to several studies applicable to the better understanding of the mechanism of thermal degradation of polymers.

2. Applications.

Utilizing the heated inlet system it is possible to examine material not volatile at room temperatures. After analytical schemes are devised this may give some information as to the nature of some of the waxy products and residues formed in thermal degradation experiments.

Investigations of the ionization-dissociation processes occurring in the "low molecular weight polymers" such as the straight chained hydrocarbons and fluorocarbons can also be carried out with this mass spectrometer. The resulting information coupled with knowledge of radical ionization potentials may permit estimation of bond strengths and heats of formations. There are many problems involved in obtaining good values for these quantities from the interpretation of experimental ionization efficiency curves [1,2] These problems are both theoretical and experimental, arising primarily from the lack of knowledge of the exact processes involved in the dissociation, from the experimental difficulties in completely accounting for all the energy involved in these processes, and from the distortion of the ionization efficiency curves produced by the instrument itself. The ionization efficiency curves of the radicals being studied would also lead to a means of identifying the radicals in reacting systems.

The information on the ionization efficiencies of the various ions in the mass spectra of such homologous series also provides the basis for analysis of mixtures of these materials. The low voltage mass spectra can be used to help identify the species present in a gaseous mixture since the number of dissociation processes can be greatly reduced when ionization is produced by low energy electrons thereby simplifying the mass spectra. In the fluorocarbon systems being investigated this reduction of the mass spectral data produced by ionizing with low energy electrons will simplify the analytical problem. However, the similarity of the cracking patterns of the fluorocarbons will still make the analysis of such reacting systems difficult. This will be further complicated by the variation of the mass spectra with temperature.

The difficulty in analyzing a mixture of fluorocarbons solely on the basis of the information obtained from the 70 volt mass spectra can be seen by referring to Table I. This table presents the 70 volt mass spectrum for some saturated fluorocarbons and for C_2F_4 [2]. The saturated fluorocarbons are seen to have their major mass peak at m/e = 69, the CF_3^+ ion, with generally no parent molecular ion $[C_nF_{2n+2}^+]$. Mixtures of certain of these components could easily be analyzed, e.g. CF_4, C_2F_4, and C_2F_6 or C_3F_8, since the mass spectral contribution due to C_2F_4 can be based upon the C_2F_4 (m/e = 100) peak; the contribution due to C_2F_6 or C_3F_8 can be based upon the C_2F_5 (m/e = 119) or C_3F_7 (m/e = 169) peaks respectively with the remaining portion of the mixture mass spectrum due to CF_4, which could be checked by comparison with its mass spectrum. This analysis along with the knowledge of the relative ionization cross sections for these compounds with 70 volt electrons would yield the partial pressure of each component in the original gaseous mixture. However, if the mixture contains several saturated fluorocarbons then the analysis becomes difficult and ambiguous when based solely on the 70 volt electron mass spectra. This is a result of the similarity of the mass spectra of the saturated fluorocarbons and the relatively small contribution of the high mass ions to the mass spectra of these compounds. A quantitative analysis is difficult if it has to be based upon a minor mass peak which would be the case if the mixture contained a heavier fluorocarbon, e.g. perfluorobutane, C_4F_{10}, in which the highest mass peak m/e = 219, $C_4F_9^+$ ion, is 2.6% of the major peak CF_3^+ or less than 0.7% of the contribution of C_4F_{10} to the total mass spectrum of the mixture. The 70 volt mass spectra of higher members of the perfluoroalkane series are even more similar and contain less information on which an analysis can be based.

The dependence of these mass spectra on temperature is also necessary information. If there is a significant temperature dependence then a quantitative determination will be impossible for a reaction performed and analyzed at a temperature other than that at which the comparison cracking pattern was obtained.

3. Experimental.

Using a modification of the technique of Reese et al [4] the dependence of the cracking pattern of C_3F_8 on temperature was studied. The temperature of the ion source was adjusted in the range of 150°C to 300°C by varying the power to the auxiliary source heater of the isatron on the CEC 21-102 mass spectrometer. When the temperature stabilized, the cracking pattern of the perfluoropropane was obtained. The experimental parameters of interest during this procedure were as follows:

a) pressure against the mass spectrometer leak was approximately 50 microns of C_3F_8;

b) time delay between admitting the sample and obtaining the mass spectrum was 2 minutes;

c) 70 volt ionizing electrons at a collector current of 10 microamperes were used;

d) the magnet current was 0.81 amperes. This value gave ample coverage of the mass range studied.

The cracking pattern was obtained by scanning (electrostatically) from high mass to low mass and back again. To remove the effect of the decrease in pressure against the leak with time the two values for each mass peak were averaged for each determination. The results of these studies on C_3F_8 are given in Table II. The pattern coefficients, percent change per degree centigrade, in Table II, are calculated at 250°C and are expressed relative to the CF_3^+ peak. The absolute temperature coefficient and sensitivity can be obtained from this data if the variation in equilibrium source pressure with temperature is known. This information was obtained by studying the temperature effect on the mass spectral sensitivity of a rare gas, argon. The results of this study are found in Table III. The variations in equilibrium ion source pressure with temperature, as studied with argon, were performed by recording the ion current of Ar^+ ($m/e = 40$) with the same experimental parameters listed. In this case the temperature was varied by removing the power to the isatron heater and allowing the ion source to cool. The variations of temperature with time and of inlet pressure with time are found in Table IV. With this information the variation in source equilibrium pressure can be obtained by correcting the experimental data in Table III for inlet pressure variation, this data being found in the column headed corrected peak height.

4. Discussion.

It is seen in Table II that there is a small but significant temperature dependence for all the ions even for the small range of temperatures studied. To correct these temperature coefficients for the variation in equilibrium source pressure with temperature and obtain the absolute temperature coefficients requires interpretation of the data found in Table III. For this purpose it is convenient to assume that the mass spectrometer system is composed of three regions as follows:

a) the inlet system to the gold leak,

b) the inlet tube from the gold leak to the mass spectrometer and the ion source,

c) the mass spectrometer analyzer and pumping system.

From Table IV the pressure in the inlet system can be corrected for the loss of molecules through the gold leak and therefore the inlet system can be considered as an infinite supply of gas molecules for the mass spectrometer. The number of molecules entering the ion source through the gold leak must be equal to the number leaving the ion source through the ion exit slit, electron beam slit and any other openings in the source. This number per unit time becomes a constant, n, after the inlet pressure variation with time is corrected as discussed above. The number of molecules leaving the ion source per unit time is now dependent upon the number of molecules present in the source, n_o, and the mean velocity of these molecules, since the mean lifetime of a molecule in the source will depend only on its mean velocity for a fixed source geometry, i.e.

$$N = kn_o\bar{c} \qquad (1)$$

where k is the geometry factor. The mean velocity is given by

$$\bar{c} = \sqrt{\frac{8RT}{\Pi M}} \qquad (2)$$

and therefore the number of molecules in the source at any time is

$$n_o = \frac{n}{k}\sqrt{\frac{\Pi M}{8RT}} \qquad (3)$$

The data in Table III when plotted as sensitivity vs $(T)^{-1/2}$ is a straight line whose slope at 250° gives a temperature coefficient for argon of -0.17% per °C. Since the ionization cross section for argon is independent of temperature in this range, the pattern coefficients for C_3F_8 can be corrected for this variation in n_o. This results in the corrected pattern coefficients in Table V.

The studies of the ionization-dissociation processes, of both the positive and negative ion mass spectra and the temperature dependence of the mass spectra of the perfluoro-alkanes and selected other perfluoro compounds are being continued.

The Bendix Corporation Model 14 Mass Spectrometer and its Applications.

1. Description.

This instrument is capable of obtaining a positive ion or negative ion mass spectrum produced by pulsed (10 kc rate) or continuous ionization. The mass spectrum can be displayed on an oscilloscope, from which the individual mass spectra (obtained every 100 μ sec) can be recorded by a revolving drum camera. Alternately, a slower recording camera can integrate these mass spectra optically at shutter speeds from 1/10 sec to 1/100 sec. The output of the ion multiplier can be monitored by means of six gating-electrometer circuits so that the variation with time of six different mass peaks can be recorded simultaneously (at a frequency response of 150 cycles for maximum fidelity). The mass spectrum can be obtained by time scanning with the gating circuits. Thus, this instrument has the capability of recording rapid changes in dynamic reactions or the variation of steady state reactions (e.g. in flow reactors) with experimental parameters, i.e. concentration, temperature, time. These features together with the physical construction and geometry of its ion source make the Bendix instrument highly suited for the study of reactive species. These studies to be performed in flow systems are directed towards the evaluation of rate constants and energetics for radical recombination, abstraction and disproportionation reactions.

2. Discussion.

In the system chosen to begin the study of fluorocarbon reactions with the Bendix mass spectrometer, $CF_3 + C_2F_6$, the following fluorocarbon molecules and radicals can be expected: CF_3, C_2F_5, C_2F_4, C_2F_6, C_3F_8, C_4F_{10}. These would be produced from the following probable reactions:

$$CF_3 + C_2F_6 \longrightarrow C_2F_5 + CF_4 \qquad (4)$$

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (5)$$

$$CF_3 + C_2F_5 \longrightarrow C_3F_8 \qquad (6a)$$

$$\searrow\ CF_4 + C_2F_4 \qquad (6b)$$

$$C_2F_5 + C_2F_5 \longrightarrow C_4F_{10} \qquad (7a)$$

$$\searrow\ C_2F_6 + C_2F_4 \qquad (7b)$$

To understand the proposed reaction, the CF_3 radical concentration and the concentrations of the stable products C_3F_8, C_4F_{10}, C_2F_4 have to be known as functions of temperature, time and initial concentration of C_2F_6. There are many analytical problems which must be solved before this can be done.

A group of ions can be selected on the basis of the information in Table I which will permit the analysis of this system provided that the concentration of CF_3 radicals can be determined and that the mass spectra of the products are a known function of temperature. The low voltage mass spectra will permit the determination of the CF_3 radical since its ionization potential is 10.1 ev [5] while the appearance potential of the mass 69 peak from the fluorocarbons is about 15 ev (15.4 from CF_4, 14.3 from C_2F_5, 14.4 from C_3F_8 [6] etc.) Thus if the mass spectra of these compounds produced by low energy electrons (suitable values to be experimentally determined to give maximum analytical information) are known then the composition of the reacting system can be determined.

It is also necessary to know the effect of temperature on the mass spectra since the open ion source of the Bendix mass spectrometer (which makes it a good instrument for studying reactive species) minimizes collisions of the gases with the ion source walls. Therefore, the temperature of the gases being ionized is essentially that of the reacting system. Thus the mass spectra obtained with this instrument is influenced much more by the sample temperature than in the CEC instrument where the molecules come into thermal equilibrium with the ion source walls before ionization.[7]

Conclusion.

This research involves closely interrelated experimental programs on these two mass spectrometers which will add to the small but growing compilation of data available on the thermochemistry of fluorocarbons. This data along with the mass spectrometric analytical schemes being developed in these studies will help provide the basis for analyzing and understanding fluorocarbon polymers systems at elevated temperatures.

Table I

Mass Spectra of some Fluorocarbons at 270°C

Ion	CF_4	C_2F_6	C_3F_8	C_4F_{10}	C_2F_4	m/e
C	7.8	1.49	2.4	0.19	12.6	12
F	6.7	1.22	0.98	.14	2.77	19
CF	4.9	18.3	28.8	12.2	100.	31
CF_2	11.8	10.1	9.3	4.16	29.5	50
CF_3	100	100	100	100	2.83	69
CF_4	0	-	-	-	-	88
C_2	-	-	-	-	3.03	24
C_2F	-	-	-	-	1.44	43
C_2F_2	-	-	-	-	0.99	62
C_2F_3	-	-	-	-	63.1	81
C_2F_4	-	0.55	6.55	8.40	33.8	100
C_2F_5	-	41.3	9.0	18.3	-	119
C_2F_6	-	0.15	-	-	-	138
C_3F_3	-	-	0.55	1.20	-	93
C_3F_5	-	-	.23	8.37	-	131
C_3F_6	-	-	.05	2.55	-	150
C_3F_7	-	-	24.6	2.14	-	169
C_3F_8	-	-	0	-	-	188
C_4F_7	-	-	-	0.03	-	181
C_4F_9	-	-	-	2.57	-	219
C_4F_{10}	-	-	-	0	-	238

Table II

Variation of the Mass Spectra of C_3F_8 with Temperature

		Temperature °Centigrade					
		210	236	258	279	291	Pattern** Coefficients
m/e	Ion	Relative Abundance*					
31	CF^+	24.0_0	24.1_8	23.7_2	24.1_1	23.6_4	-0.04
50	CF_2^+	7.6_7	7.5_6	7.5_9	7.6_7	7.6_8	+0.02
69	CF_3^+	100	100	100	100	100	-
100	$C_2F_4^+$	6.1_0	5.8_3	5.6_2	5.7_6	5.8_4	-0.07
119	$C_2F_5^+$	9.1_9	9.3_0	9.4_3	9.5_0	9.4_1	+0.06
169	$C_3F_7^+$	22.2_4	20.9_8	19.9_6	19.0_7	18.9_6	-0.22

*Relative abundance of the ions compared to the largest peak CF_3^+, m/e 69.

**Percent change in relative abundance at 250°C per degree centigrade.

Table III

Mass Spectrometric Sensitivity for Argon as a Function of Temperature

	Ar^+ peak height		Sensitivity[a]			
Time	Uncorrected	Corrected	mv/u	T	$\frac{1}{T}x10^4$	$\sqrt{\frac{1}{T}}x10^2$
0[b]	4705	4705	72.74	574	17.42	4.17
1	4700	4716	72.91	574	17.42	4.17
2[c]	4685	4717	72.93	574	17.42	4.17
3	4700	4748	73.40	563	17.76	4.22
4	4705	4769	73.73	555	18.01	4.24
5	4705	4785	73.98	548	18.24	4.27
6	4710	4806	74.30	542	18.45	4.30
7	4720	4832	74.70	535	18.69	4.32
8	4725	4853	75.03	530	18.86	4.34
9	4750	4894	75.66	527	18.97	4.35
10	4755	4915	75.99	522	19.15	4.38
11	4760	4936	76.31	518	19.30	4.39
12	4770	4962	76.71	515	19.41	4.40
13	4780	4988	77.11	513	19.49	4.41
17	4798	5070	78.38	501	19.96	4.47
22	4795	5147	79.57	488	20.49	4.52
27	4790	5222	80.73	480	20.83	4.56
32	4765	5277	81.58	475	21.05	4.59
42	4690	5362	82.90	463	21.59	4.64

a) Input resistance to electrometer was $10^{11}\Omega$.
b) Inlet system opened to mass spectrometer.
c) Power to isatron heater shut off.

Table IV

Variation of Inlet Pressure and Isatron Temperature with Time

Time (Minutes)	Temp. °C	Pressure Microns
0	301	55.97
1	290	-
2	284	55.68
3	275	-
4	269	55.39
5	262	-
6	257	54.96
7	254	-
8	249	54.60
9	245	-
10	242	54.24
12	-	53.96
15	228	53.24
17	-	52.88
20	215	-
21	-	52.16
23	-	51.73
25	207	51.37
27	-	51.09
29	-	50.66
30	202	-
31	-	50.30
35	195	-
40	190	-

Table V

Pattern Coefficients* for C_3F_8 Corrected for Change in Source Gas Density with Temperature

m/e	31	50	69	100	119	169
ion	CF^+	CF_2^+	CF_3^+	$C_2F_4^+$	$C_2F_5^+$	$C_3F_7^+$
Pattern Coefficient	+0.13	+0.17	-	+0.10	+0.23	-0.05

*Pattern Coefficient is given in terms of the percent change in the relative abundance of the ion per degree centigrade at 250°C.

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MECHANISM OF THERMAL DEGRADATION OF POLYMERS

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I. INTRODUCTION

No mathematical analysis of the kinetics of the thermal degradation of polymers can be regarded as adequate until all of the contributing elementary rate processes have been considered in a model which predicts the measurable changes which occur during degradation. Therefore, research in this field falls into four general categories:

1. Identification of contributing rate processes,
2. Collection of data for describing these processes,
3. Synthesis of this data into a model which predicts the measurable changes, and
4. Measurement of these changes.

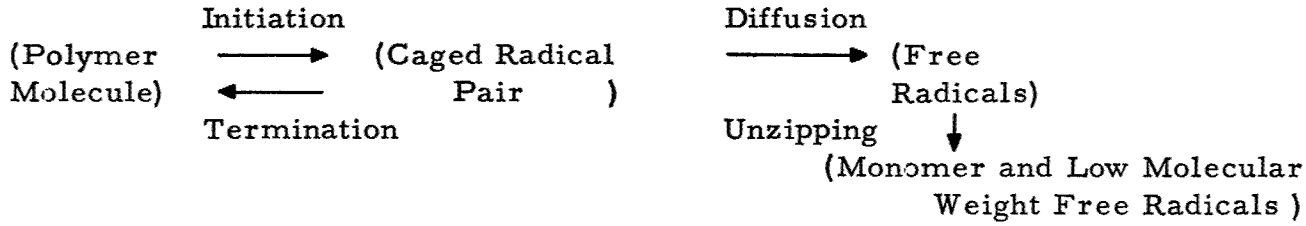
This report is broken down into three sections corresponding to the first two and last of these categories.

II. IDENTIFICATION OF CONTRIBUTING RATE FACTORS, THE "CAGE EFFECT"

In thermal degradation studies, the "cage effect" has been completely ignored. In order to demonstrate that this effect is a contributing rate factor, an extremely simple mathematical model including it is discussed below.

Assume that a polymer degrades by random chain scission followed by complete unzipping of both radicals to very low molecular weight radicals and monomer, which diffuse out of the sample before undergoing further reaction. Also, assume that the density of the polymer sample stays constant during degration.

Polymer radicals formed during initiation in an amorphous polymer sample should have a higher probability of immediate termination before unzipping than the similar initiation of linear molecules in the gas phase. Radical pairs which have just formed and have not separated to any extent will be called "caged radical pairs." Using this definition, the process of degradation may be represented in the following manner.



From this it follows that the rate of increase of concentration of "caged radical pairs" is

$$\frac{d\left[R_p\right]}{dt} = \alpha N K_i\left[P\right] - K_T\left[R_p\right] - K_D\left[R_p\right] \qquad (1)$$

where $\left[R_p\right]$ is the concentration of "caged radical pairs," t is time, N is the number average degree of polymerization of polymer molecules, $\left[P\right]$ is polymer molar concentration and K_i, K_T, and K_D are rate constants for initiation, termination of "caged radical pairs" and separation of caged radical pairs. α is the number of carbon-carbon bonds contributed by each monomer unit. For vinyl polymers, the case considered here, α is equal to two.

The rate of formation of uncaged free radicals per unit volume is,

$$\frac{d\left[R\right]}{dt} = 2K_D\left[R_p\right] \qquad (2)$$

Assuming the steady state for "caged radical pairs", $d\left[R_p\right]/dT=0$,

$$\frac{d\left[R\right]}{dt} = 2K_D\left(\frac{2NK_i\left[P\right]}{K_T+K_D}\right) = \left(\frac{K_D}{K_T+K_D}\right)\left(4NK_i\left[P\right]\right) \qquad (3)$$

The rate of formation of monomer is

$$\frac{dM}{dt} = -\frac{1}{M}\frac{dw}{dt} = \frac{N}{2}\left(\frac{d\left[R\right]}{dt}\right)V \qquad (4)$$

where V is the sample volume, m is the molecular weight of a monomer unit, and w is the weight of the sample. Substituting 3 into 4 and then substituting the relation $\left[P\right] = \frac{w}{VmN}$

$$\frac{dw}{dt} = -\left(\frac{K_D}{K_T + K_D}\right)\left(2NK_i\right) w \qquad (5)$$

If K_D is much greater than K_T, $K_D/(K_T + K_D)$ will equal one and $dw/dt = -2NK_i W$, (6)

the rate equation for the case where the cage effect is negligible.[1]

In order to find $K_D/(K_T + K_D)$ for the other case where K_D is not much greater than K_T, one utilizes the fact that the rate constants may be expressed in terms of an Arrhenius equation, that is

$$K_D = A_D\ e^{-E_D/RT}$$

$$K_T = A_T\ e^{-E_T/RT}$$

Also it is assumed that a liquid cell model holds where molecules may move only in six perpendicular directions and that once one of the free radicals in a "caged radical pair" makes a jump which does not lead to termination, the probability of termination of the radical pair is zero. Therefore, for this model $A_D = 5A_T$.

In order to put numbers into these expressions, polytetrafluoroethylene is taken as an example. E_T for radical recombination is generally quite small, and in this case due to the high degree of orientation given the free radical, it will be assumed that $E_T = 0$. From diffusion data in a following section of this paper E_D may be estimated to be 9 kcal for tetrafluoroethylene. Therefore,

$$K_D/(K_T + K_D) \approx 5e^{-9\text{kcal}/RT} = .015$$

at 500° C. It is to be expected that a chain end would have a much higher activation energy for diffusion due to the stiffness of a polytetrafluorethylene chain. In any case, the cage effect appears to make a significant contribution to the overall rate even if one of the free radicals is as small as tetrafluoroethylene.

In order to give an example of the type of effect that the "cage effect" may have on a rate expression, the rate expression obtained from substituting values into equation 5 and 6 are compared. Comparison with the experimental rate expression is interesting also because the theoretical expression including the "cage effect" is in surprisingly good agreement with experiment.

The three expressions are:

1. Theoretical, neglecting the "cage effect"

$$\frac{dw}{dt} = \left[-2 \times 10^{18} e^{-74,000/RT}\right] W$$

2. Theoretical, including the "cage effect"

$$\frac{dw}{dt} = \left[-10^{19} e^{-83,000/RT}\right] W$$

3. Experimental[2]

$$\frac{dw}{dt} = -\left[9.4^{+7.4}_{-4.2} \times 10^{18} e^{-81,400/RT}\right] W$$

The first two expressions were obtained from substituting the values $N=10^4$ and $K_i = 10^{14} e^{-74,000/RT}$ [2] for gas phase reactions into equations 6 and 5 respectively. The experimental expression is the least square line of the Arrhenius plot of the data of Madorsky, and Siegle and Muus.

While this theoretical model is in good agreement with significant experimental results, it is open to question. Nevertheless it is felt that the cage effect itself cannot be ignored.

III. COLLECTION OF DATA FOR DESCRIBING DEGRADATION PROCESSES

A. Diffusion

The purpose of this part of the research program is to obtain diffusivity and solubility coefficients of the evolved products of degradation in parent polymer. At the present, the time-lag method[3] is being used to study the flow of hexafluoropropene and tetrafluoroethylene in polytetrafluoroethylene. This type measurement is begun by evacuating a polymer sample from both sides. Then a vapor of a known pressure is introduced on one side and the increase in pressure of the other side is recorded against time.

At very high temperatures the time-lag is very short and difficult to measure, but permeabilities can be obtained. These permeabilities can be combined with independently determined solubility coefficients to yield diffusivity coefficients. Solubility coefficients can be determined by both theoretical and experimental techniques. A theoretical method is described later in this paper.

Theory

Published derivations of the equations used in this work are more complex than necessary because other authors have tried to maintain a high degree of generality.[4] For this reason a comparatively simple derivation is presented.

The basic hypothesis of the mathematics of diffusion is Fick's First Law,

$$F = -D\frac{dC}{dx} \quad \text{where}$$

F is the rate of diffusion per unit area, C is the concentration of the diffusing gas, x is distance measured normal to the above area and parallel to the path of the diffusing vapor, and D is a constant called the diffusion coefficient and diffusivity. From this law, Fick's Second Law follows,

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \quad \text{where t is time}$$

In this experiment both sides of the polymer film are evacuated for a long period before the gas is admitted to the chamber on one side of the film. Since diffusion is slow this vapor stays effectively at a constant pressure ϕ_0 Therefore, its concentration C_0, at the surface of the sample is assumed to be constant.

Since the pressure on the other side is always less than one thousandth of ϕ_0, the concentration of gas at this surface of the polymer film can be assumed to be zero.

From this discussion we can write the boundary conditions.

1. At all time at $x = 0$, $C = 0$

   at $x = \ell$, $C = C_0$ where ℓ is film thickness.

2. At $t = 0$ and at $0 \leq x \leq \ell$, $C = 0$

A solution of Fick's Second Law is

$$C = Ax + \sum_n (B_n \sin \lambda_n x) e^{-\lambda_n^2 Dt} \qquad (7)$$

where A, B_n, and λ_n are to be determined.

Applying condition 1. starting with $t \longrightarrow \infty$ equation (7) reduces to C=0 at $x = 0$ and to $C = C_0$ at $x = \ell$ if $C_0 = A\ell$. Therefore, $A = \frac{C_0}{\ell}$. At other values of t, $C = 0$ at $x = 0$ and $C = C_0$ at $x = \ell$ if $0 = \sum_{n=1}^{\infty} (B_n \sin \lambda_n x) e^{-\lambda_n^2 Dt}$ which is true if $\lambda_n = n \pi / \ell$.

Applying condition 2 where $0 \leq x \leq \ell$ at $t = 0$ and $C = 0$ we find $0 = \frac{C_0 x}{\ell} + \sum_{n=1}^{\infty} (B_n \sin \frac{n\pi x}{\ell})$. By multiplying this equation by $\sin p \frac{\pi x}{\ell}$ and integrating from $x = 0$ to $x = \ell$ we find that $B_n = \frac{2C_0(-1)^n}{n\pi}$.

On substituting these realtions into equation (7) we find $C = \frac{C_0 x}{\ell} + \sum_{m=1}^{\infty} \frac{2C_0}{m\pi} (-1)^m (\sin \frac{m\pi x}{\ell}) e^{-(\frac{m\pi}{\ell})^2 Dt}$. From this relation the rate of flow at the surface $x = 0$ is found to be

$$D \left(\frac{dc}{dx}\right)_{x=0} = \frac{DC_0}{\ell} + \frac{2DC_0}{\ell} \sum_{m=1}^{\infty} (-1)^m e^{-(\frac{m\pi}{\ell})^2 Dt}$$

The overall quantity Q_t which has diffused out of side $x = 0$ at any time is

$$Q_t = \int_0^t D \left(\frac{dc}{dx}\right)_{x=0} dt = \frac{Dc_0 t}{\ell} - \frac{2C_0 \ell}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)m}{m^2} e^{-(\frac{m\pi}{\ell})^2 Dt} + \frac{2C_0 \ell}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2}$$

As $t \longrightarrow \infty$ and equilibrium is reached Q_t becomes a linear function of time,

$$Q_t = \frac{DC_0 t}{\ell} + \frac{C_0 \ell}{6}$$

This line may be extrapolated back to Q_t equals 0 to give an intercept, L, or the time axis. Therefore, the diffusion coefficient may be obtained from this intercept and the thickness of the sample.

$$D = \frac{\ell^2}{6L}$$

At a given temperature the equilibrium concentration of dissolved vapor in a high polymer may be related to the pressure in the following manner,[5] $C = (S_0 e^{QC})\ \phi = S\phi$ where Q is a constant, S is the solubility coefficient and S_0 is the zero concentration solubility coefficient. For highly volatile vapors at low vapor activities e^{QC} approaches one and the ratio C/P is nearly equal to the constant S_0. Even at fairly high concentrations $S/S_0 = 1$ due to the low magnitude of Q.

On substituting the relation $C = S\phi$ into Fick's First Law, $F = -SD\frac{d\phi}{dx}$. The product SD is defined as P, the permeability or SD = P.

It follows from Fick's Second Law that, at the steady state, concentration varies linearly, therefore, if $C = S\phi$ the following relation holds: $F = P(\phi_2 - \phi_1)/x$ where ϕ_1 and ϕ_2 are two pressures x distance apart.

With these assumptions, we can find P from the slope of the ϕ vs T plot at steady state and D from the intercept of the steady state line with the t axis. From these two values we can calculate S.

B. Diffusion Measurements

A schematic diagram of the vacuum apparatus used is shown in Figure I. Volume 1 is filled with the specimen gas and volumes 2 and 3 are evacuated overnight. Then stopcock D is closed and B is opened. The increase in pressure in volume 3 is then measured with a McLeod gauge. The "leak rate" is determined by measuring the increase in pressure in volume 3 before opening B to admit the specimen gas to volume 1.[6]

Figure II shows a typical plot of experimental data. The gas is admitted to volume 2 at the time indicated by the arrow. It is assumed that the established "leak rate" stays the same through the diffusion run so that subtraction from the observed pressure yields the pressure increase due to diffusion.

Two diffusion cells were used. The first was a very crude arrangement. The area was small, and stopcock grease was used to seal in the polymer film.

The second diffusion cell is shown in Figures III and IV. This cell was constructed from stainless steel and put together with silver solder. The polymer film was put between the two halves of the cell and the two halves were bolted tightly together. The closed cell was put in a carefully machined copper block inside a specially built furnace.

The temperatures in the copper block, in the stainless steel cell and inside the cell where the high pressure vapor is stored were measured with thermocouples. The temperature differences and fluctuation were less than $\pm$ 1° C.

The measurements were made between 25 and 350° C. The latter being the highest temperature at which a polytetrafluoroethylene film can be maintained without its collapsing.

The tetrafluoroethylene was prepared by degrading polytetrafluoroethylene slowly and collecting the vapor. The vapors which could not be condensed with liquid nitrogen were pumped off and vapors which could be condensed with dry ice were removed from the tetrafluoroethylene. This procedure gives better than 96.7% pure tetrafluoroethylene.[7] The pressure ϕ_0 was varied from 12 to .1 cm Hg.

The polytetrafluoroethylene films were provided by Dilectrix Corporation and designated as Type C Teflon Films. They varied from 1 to 5 mil in thickness.

It was found necessary to develop a reliable pressure measuring technique. The measurements were made with a carefully calibrated McLeod gauge Five minutes were allowed for the mercury level in the gauge to settle down after it was brought up to a proper height. To save time no attempt was made to exactly zero the mercury in the standard column. As a result, it was necessary to measure the height of both columns with a cathetometer and calculate each pressure.

Table I and Figure V present the data collected to the present. Since both systems used with each of the two cells were completely different, the maximum absolute error should be indicated fairly well by differences in values of the room temperature permeabilities, $\pm .7 \times 10^{-9}$ (cc x mm)/(cmHg x cm^2xsec)

C. Theoretical Determination of Zero Concentration Solubility Coefficients of the Low Molecular Weight Homologs of Vinyl Polymers in the Parent Polymer

In the following paragraphs, the zero concentration solubility coefficients of the low molecular weight homologs of vinyl polymers in the parent polymer are related to known properties of the vapor and polymer in order that the value of the solubility coefficients may be theoretically determined. This is necessary because at high temperatures solubility coefficients become very small and difficult to measure.

The following assumptions are made:

1. The enthalpy of solution of the condensed vapor with polymer at a given temperature is zero, i.e. $\Delta H = 0$
2. The ideal gas law is assumed for the gaseous state.
3. The total number of available sites for vapor molecules inside the polymer sample is equal to the difference in volume between the given polymer sample, and a hypothetical polymer sample of 100% crystallinity of the same mass, divided by the volume of a vapor molecule.
4. All of these sites are equivalent.

The difference in chemical potential of the vapor in equilibrium with the solution and the vapor in equilibrium with pure condensed vapor can be shown to be equal to

$$RTLn \frac{Pi}{P_i^o} = \left[\frac{d(\Delta H - T \Delta S)}{dn_i}\right]_{P,\ T,\ n_p}$$

where P_i^o is the equilibrium vapor pressure of pure vapor i, P_i is the vapor pressure of component i in equilibrium with the solution, n_i is the number of moles of vapor component i in the solution, n_p is the number of moles of polymer, and P, T, R, ΔH, and ΔS have their usual meaning.

Since $\Delta H = 0$

$$RTLn \frac{Pi}{P_i^o} = -\left[\frac{d(T \Delta S)}{dn_i}\right]_{P, T, n_p}$$

The difference in entropy between vapor in the solution and the pure condensed state equals

$$\Delta S = K \, Ln\Omega$$

where Ω is the number of distinguishable arrangements of vapor molecules in the polymer sample. The configurational entropy of the vapor in the pure condensed state at the same temperature is taken as zero.

If Z is the number of sites in the polymer sample and V is the number of dissolved vapor molecules, then

$$\Omega = \frac{Z!}{V!\ (Z-V)!}$$

Using Stirling's Formula, $LnN! = NLnN-N$

$$K Ln\Omega = Z Ln\ Z - Z - V Ln\ V + V - (Z-V)\ Ln\ (Z-V) + (Z-V)$$

$$= Z Ln\ Z - V\ Ln\ V - (Z-V)\ Ln\ (Z-V)$$

The difference in chemical potential is

$$RT Ln \frac{Pi}{P_i^o} = -N\left[\frac{d(T\Delta S)}{dV}\right]_{P, T, n_p}$$

$$= -NKT\left[\frac{(Ln\,\Omega)}{dV}\right]_{P, T, n_p}$$

$$= -RT\left[-LnV - 1 + Ln\,(Z-V) + 1\right]$$

$$= RT\ Ln\left(\frac{V}{Z-V}\right)$$

and $$\frac{Pi}{P_i^o} = \frac{V}{Z-V}$$

If $Z \gg V$, then

$$\frac{Pi}{P_i^o} = \frac{V}{Z}.$$

The fraction of sites occupied is equal to

$$\frac{V}{Z} = \frac{Pi}{P_i^o} = \frac{C}{d_v\left(\frac{1}{d_p} - \frac{1}{d_c}\right)}$$

where C is the concentration of vapor (gm vapor/gm polymer), d_v is the density of the vapor, d_p is the density of the polymer after dissolving the vapor, and d_c is the density of the hypothetical 100% crystalline polymer.

The solubility coefficient at zero concentration is equal to

$$\lim_{C \to 0} \frac{C}{P_i} = S_0$$

or

$$S_o = \frac{d_v}{P_i^o} \left(\frac{1}{d_p} - \frac{1}{d_c} \right) \qquad (8)$$

Equation 8 was used to calculate the theoretical solubility coefficients of low molecular weight homolog vapors of polyethylene in polyethylene as shown in table II.

The assumption was made that the degree of crystallinity does not change over the temperature range considered.[8] The specific volume of the amorphous polyethylene was taken as $\overline{V} = 1.192 + 8.8 \times 10^{-4} T$ and the specific volume of crystalline linear polyethylene was taken as $\overline{V}c = .993 + 3.0 \times 10^{-4} T$.[8]

From Table II it is apparent that all of the calculated values are in good agreement with experiment. The higher molecular weight vapors are in better agreement as would be expected from theory. While neither of the papers from which the experimental solubility coefficients were taken have a complete discussion of error, Brandt[6] gives a 6% precision for his diffusion coefficients and states that solubility coefficients have a larger error than the corresponding diffusion coefficients.

While none of the vapors compared in Table II were above their critical temperatures it is possible to extrapolate equilibrium vapor pressures of pure vapors above their critical temperatures to obtain fair estimates of solubilities.[9] Also the experimental data in Table II consists of measurements from both linear and branched polyethylenes. This theory seems to be adequately general to cover both cases. The greatest advantage of this theory is that it involves no parameters and the experimental data required for its application are, relatively speaking, readily available.

IV MEASUREMENT OF CHANGES WHICH OCCUR DURING DEGRADATION

A. Gradient Elution

Since it is necessary to obtain molecular weight distributions of the residue of the polymer after degradation, some work has been started to develop a gradient elution analysis apparatus. This apparatus is based on the principle that addition of solvent progressively dissolves fractions of precipitated polymer of increasing molecular weight. Superimposed upon this concentration gradient is a temperature gradient.

The apparatus which is being developed is shown in Figure VI. The design of this apparatus has some improvements over other apparatus used up to the present while still remaining as inexpensive as a gravity flow system. Since there will be no air space in the apparatus, there will be no need to adjust seperate flow rates.

In a gravity feed system there is a rate controlling capillary at the bottom of the column which can become clogged with polymer and change the flow rate. In this apparatus, the rate controlling parts are the nitrogen pressure and the sinter filter. The pressure may be easily regulated and the sinter filter is not in danger of becoming clogged during the run since only pure solvent passes through it.

The major problem encountered has been to find suitable greases for joints and stopcocks.

B. High Vacuum Therman Balance

In order to measure weight changes of polymers undergoing thermal degradation as well as the temperature of the polymer, the apparatus shown in Figures VII and VIII was constructed. The polymer is suspended from an automatic recording balance by a fine thermocouple into a "Vycor" pyrolysis tube. The balance is mounted in a bell jar, has a 350 milligrams capacity and can measure weight changes over a range of 100 milligrams with .05% accuracy. The furnace is a cylindrical polished aluminum reflector with eight one kilowatt infrared heating lamps mounted inside. This method of heating raises the polymer to a constant degradation temperature before much reaction can occur at

intermediate temperatures.

Since it is quite unlikely that a polymer undergoing degradation is at the same temperature as its surroundings, it is desirable to measure the temperature of the polymer itself. Therefore, thermocouple wires are used to suspend the sample and contact is made intermittantly by raising the level of the cups of mercury so as to make contact with the thermocouple wires.

With this apparatus it will be possible to measure the rate of weight loss and the volatile products formed during degradation of polymers at well defined temperatures.

TABLE I

DIFFUSION DATA FOR TETRAFLUOROETHYLENE

IN POLYTETRAFLUOROETHYLENE

Cell	Temperature	Permeability $\times 10^9$ $\frac{cc \times mm}{(cm\ Hg) \times cm^2 \times sec}$	Diffusivity $\times 10^9 cm^2/sec$	Solubility Coefficient cc/(ccxatm)	Density of Polymer gm/cc
1	25.	2.7	7.2	2.2	2.18 ±01
	28.	2.2	7.9	2.1	"
	24.	2.5	6.7	2.9	"
	24.	2.5	7.2	2.7	"
2	25.	1.80	8.0	1.7	2.184±.0006
	24.	1.85	8.5	1.65	"
	114.	14.4			"
	118.	21.8			2.161
	119.	23.6			"
	121.	16.5			2.184
	175.	63.9			2.161
	182.	73.1			"
	183.	79.0			"
	198.	87.0			"
	229.	164.0			2.161
	241.	167.0			2.184
	252.	171.0			"
	338.	1340.0			"
	342.	1310.0			2.161

TABLE II

COMPARISON OF THEORETICAL AND EXPERIMENTAL

SOLUBILITY COEFFICIENTS OF ALKANE VAPORS IN POLYETHYLENE

Vapor	Temperature °C	Density of Polyethylene	Solubility Coefficients $\times 10^4$ (gm vapor/(gm Polymer x cm Hg))		Source of Experimental Data
			Experimental	Theoretical	
Ethane	-5	.9511	.0483	.123	6
	0	.9505	.147	.110	6
	0	.9185	.173	.188	6
	0	.9103	.206	.209	6
	7	.9505	.106	.0945	6
	8	.9185	.138	.155	6
	25	.9505	.0743	.0549	6
	25	.9511	.0557	.0542	6
	25	.9508	.0538	.0546	6
	25	.9637	.0733	.0396	6
	25	.9182	.114	.0944	6
	25	.9639	.0787	.0394	6
	25	.9103	.112	.104	6
	25	.9206	.0997	.0913	6
	25	.9185	.127	.0940	6
Propane	25	.9511	.248	.339	6
Butane	25	.9511	.197*	1.53	6
Pentane	25	.9220	11.0	10.2	5
	25	.9505	6.24	6.25	6
	27	.9185	8.76	9.97	6
	50	.9185	4.61	4.77	6
	50	.9505	2.54	2.79	6
Hexane	0	.9540	67.0	65.3	5
	0	.9220	110.0	115.	5
	0	.9380	87.0	89.8	5
	25	.9220	39.0	36.4	5
	30	.9220	36.0	29.7	5
	30	.9540	20.0	16.9	5
	30	.9380	23.0	23.2	5
Heptane	25	.9220	140.0	125.0	5
Octane	25	.9220	460.0	420.	5

*Comparison of experimental data with itself indicates possible decimal error here.

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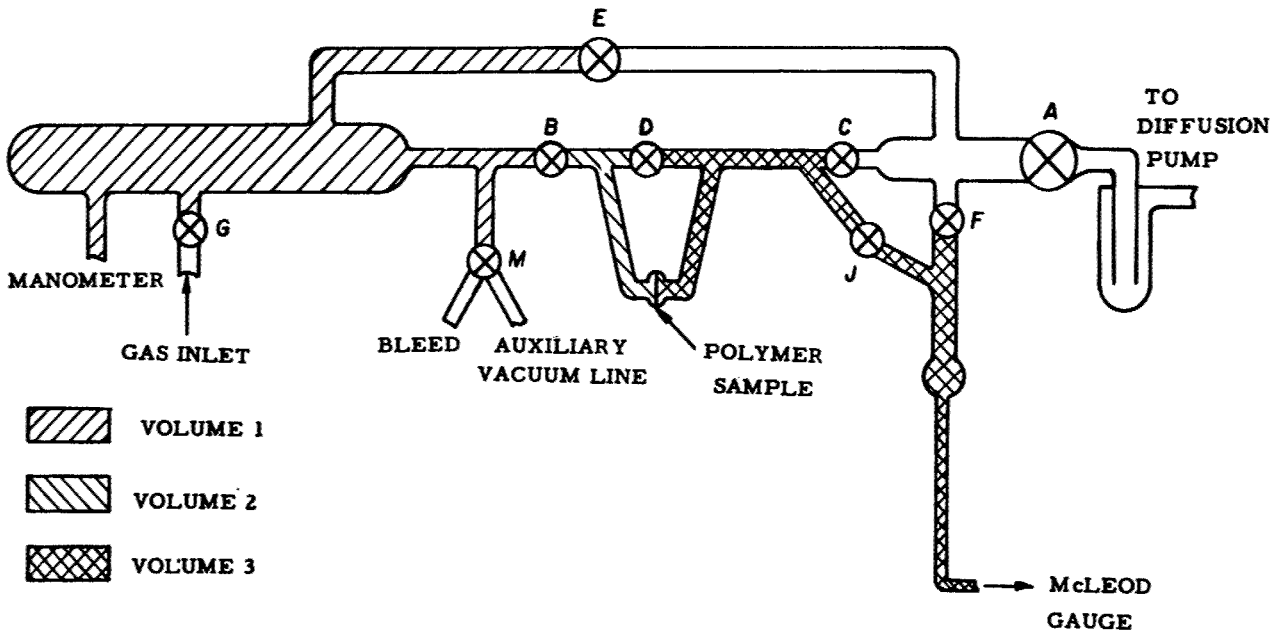


Figure I. Diffusion Apparatus

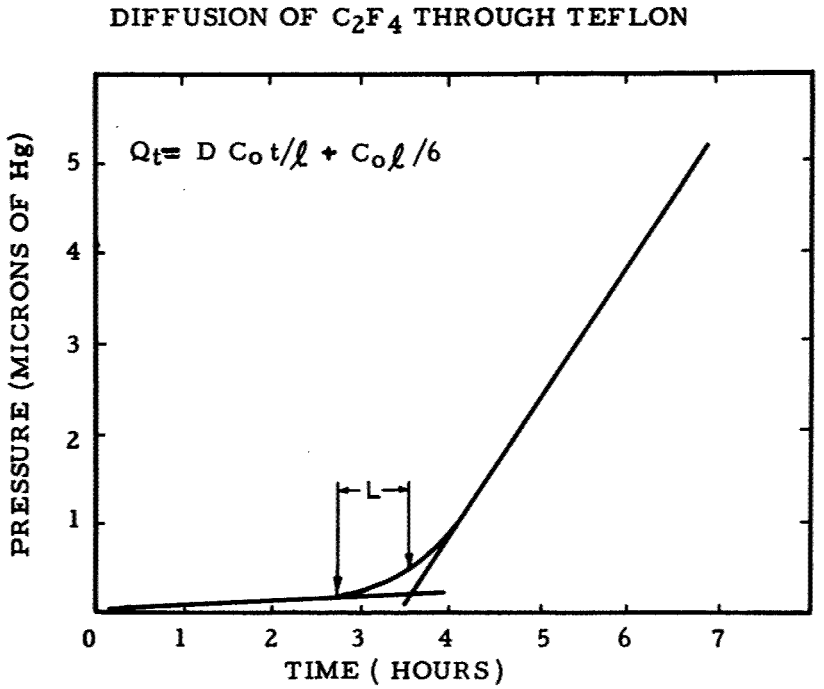


Figure II. Diffusion of C_2F_4 Through Teflon

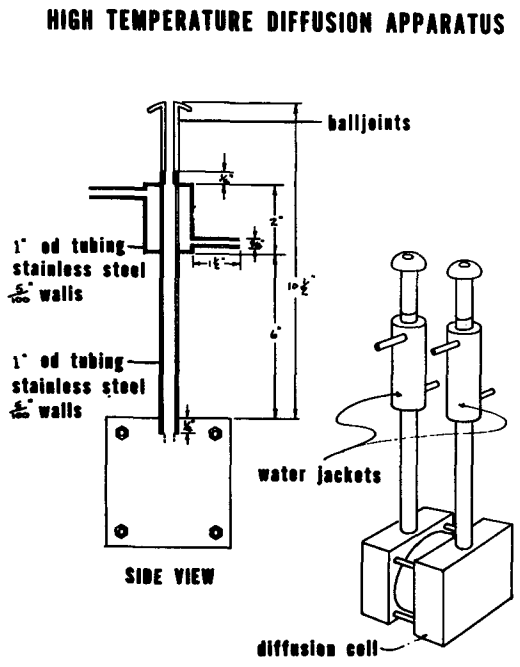


Figure III. High Temperature Diffusion Apparatus

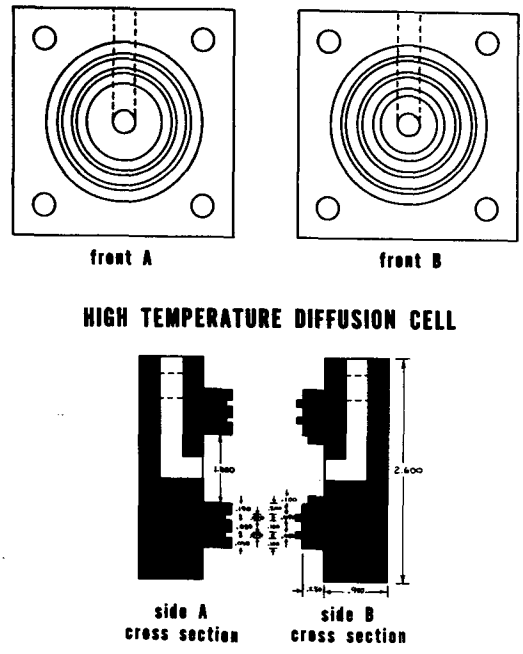


Figure IV. High Temperature Diffusion Cell

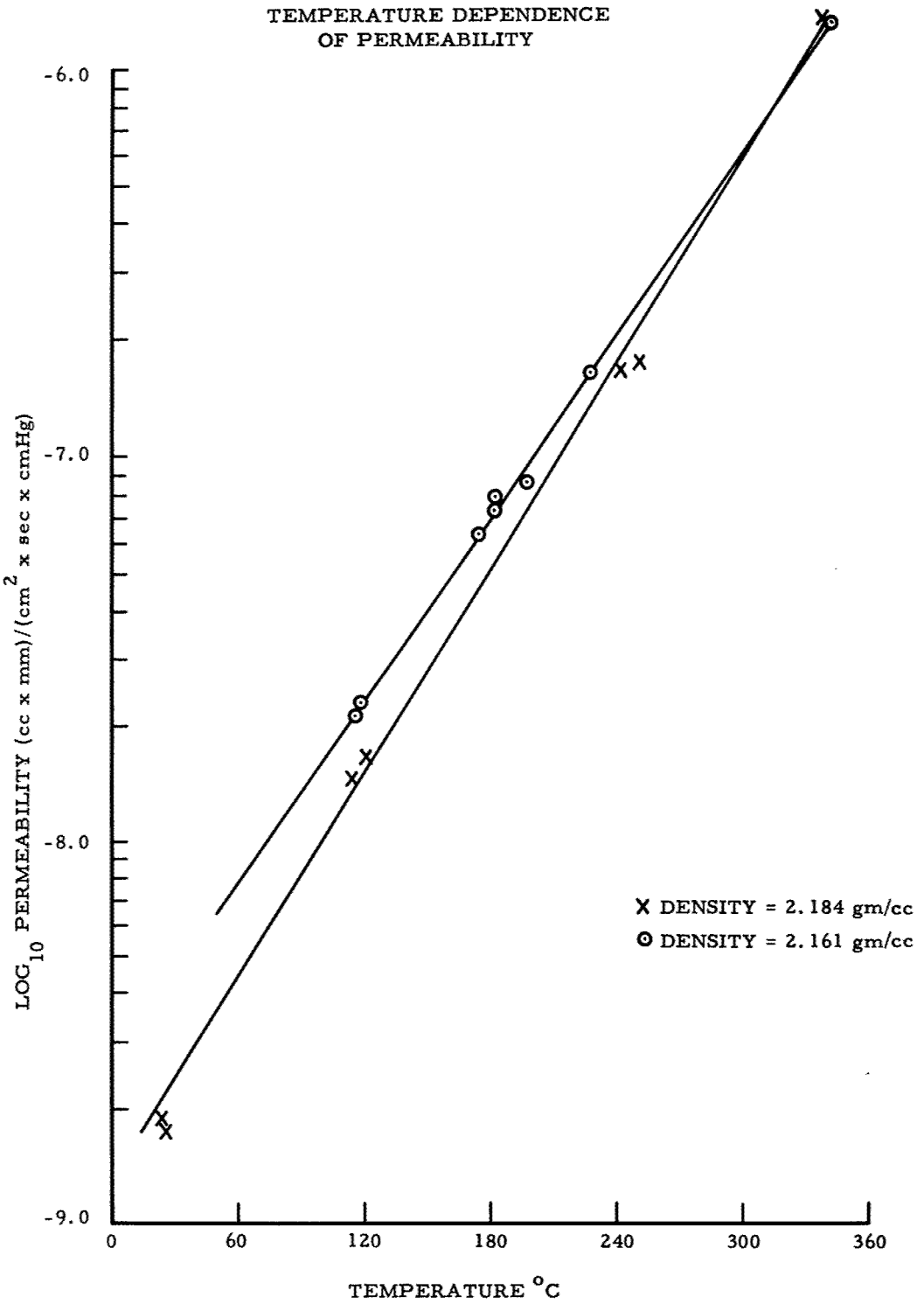


Figure V. Temperature Dependence of Permeability

APPARATUS FOR GRADIENT ELUTION

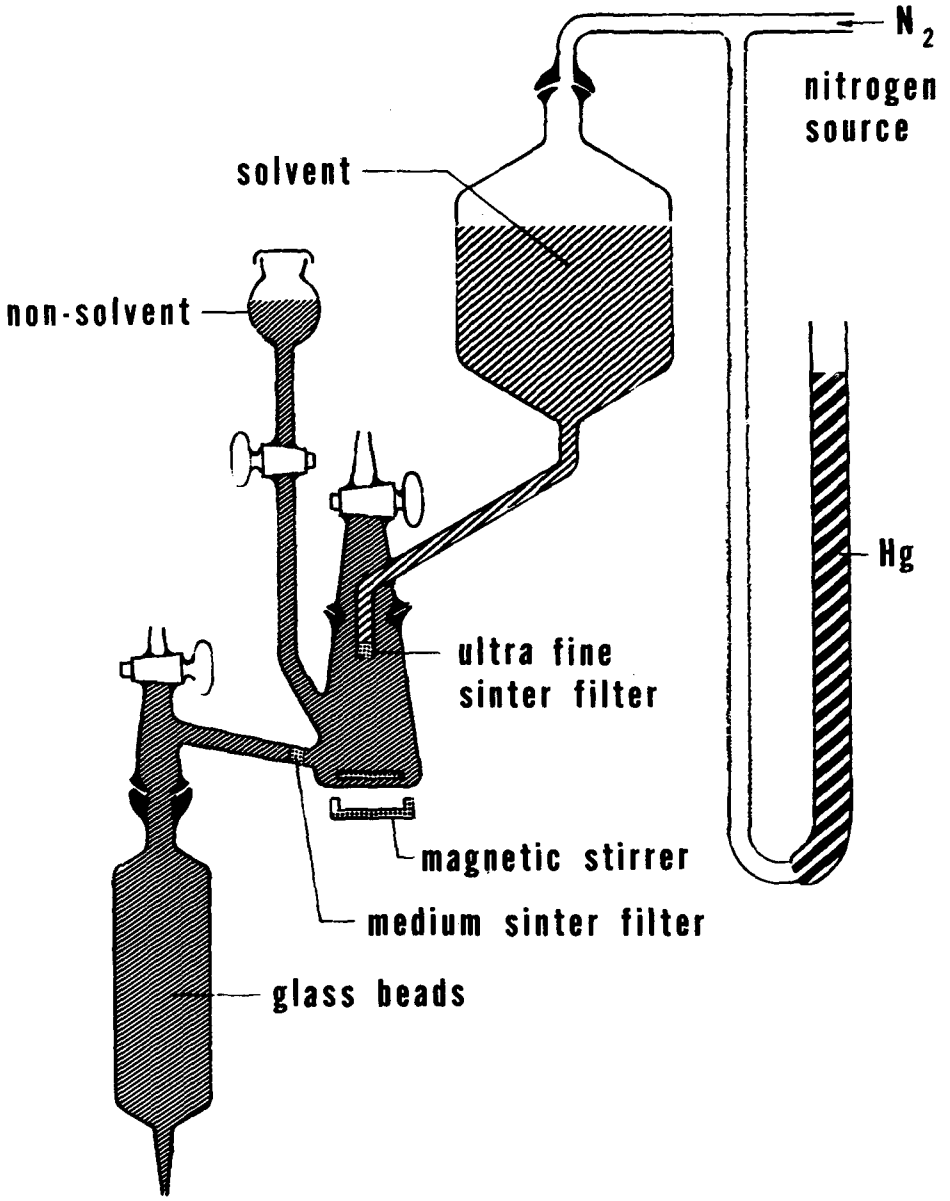


Figure VI. Apparatus for Gradient Elution

Figure VII. Thermai Balance

Figure VIII. High Vacuum Thermalbalance

Termination mechanisms of the radical polymerisation of acrylamide.

By

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Abstract

A kinetic study of the polymerisation of acrylamide initiated by 4-4'-azo-bis-4-cyanopentanoic acid has shown that up to 10% conversions, the rate of polymerisation is directly proportional to the concentration of monomer and to the square root of the concentration of initiator. Molecular weight measurements indicate that non-degradative transfer to monomer occurs and that mutual termination is probably by disproportionation.

The addition of ferric salts greatly reduces the overall rate of polymerisation, the chloride being more effective in this respect than the perchlorate. At sufficiently high concentrations of ferric salts, the order of the polymerisation reaction approximates to one with respect to initiator and minus one with respect to the ferric salt. It has been shown that under these conditions, radical chains are being terminated by electron transfer, involving the reduction of the iron salt to the ferrous state.

Introduction

In the presence of a suitable initiator, acrylamide readily undergoes polymerisation in aqueous solution even at room temperature, although the rate of reaction displays an extreme sensitivity to traces of certain impurities. Particularly effective in retarding polymerisation are salts of metals of variable valency and it is with the effect of such salts on the kinetics and mechanism of the termination reaction in the radical polymerisation of acrylamide, that this investigation is primarily concerned.

The initiator chosen for the present series of experiments was the water-soluble, thermal catalyst, 4-4'-azo-bis-4-cyanopentanoic acid, a substance which had not previously been used to initiate polymerisation of acrylamide. A preliminary study of the kinetics of the reaction was, therefore, undertaken to ensure that the mechanisms of initiation and propagation were free from undesirable complications.

Kinetics of polymerisation with no metal salt present

Rates of polymerisation obtained with varying concentrations of monomer and of catalyst are summarised in Tables I and II. Analysis of these kinetic data by the method of least squares has shown that for conversions of up to 10%, the rate of polymerisation (R_p) of acrylamide, under the conditions prevailing in our experiments, is proportional to $[\text{monomer}]^{1.04}$ and to $[\text{catalyst}]^{0.49}$. We may conclude, therefore, that apart from transfer processes, the principal reactions involved in the polymerisation are as follows:-

Initiation	$\text{Cat} \rightarrow 2Q-$ $Q- + m_1 \rightarrow m_1^*$	Rate $= f_i k_i [\text{Cat}]$
Propagation	$m_j^* + m_1 \rightarrow m_{j+1}^*$	Rate $= k_p [m_1][m_j^*]$
Termination	$m_r^* + m_s^* \rightarrow P_r + P_s$ $m_r^* + m_s^* \rightarrow P_{r+s}$	Rate $= (k_t + k_t')[m_r^*][m_s^*]$

where m_j^* represents a live polymeric radical consisting of j monomeric segments (m_1) and a single initiator fragment ($Q-$), P_r a dead polymer molecule having r monomer units, k_t and k_t' the velocity coefficients for termination by disproportionation and by combination respectively. With the usual simplifying assumptions, this kinetic

Table I

$[\text{catalyst}] = 1.64 \times 10^{-4}$ M. Temp. $= 25.00 \pm 0.01^\circ$ C.

$[\text{monomer}]$	$10^4 R_p$ mol. l^{-1} min^{-1}	$10^2 R_p/[m_1][\text{Cat}]^{\frac{1}{2}}$
0.313	3.78	9.5
0.419	4.52	8.4
0.528	6.42	9.5
	6.86	10.2
	6.30	9.3
0.640	6.90	8.4
	7.90	9.6

scheme requires $k_p f_i k_i/(k_t + k_t')^{\frac{1}{2}}$ to equal $R_p/[m_1][\text{Cat}]^{\frac{1}{2}}$, the average value of which from all our kinetic experiments was found to be $(1.70 \pm 0.17) \times 10^{-3}$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec^{-1} at 25.0° C. However, at this temperature the propagation (k_p) and termination ($k_t + k_t'$) coefficients are known[1] to be $(1.80 \pm 0.15) \times 10^4$ litre mole^{-1} sec^{-1} and $(1.45 \pm 0.20) \times 10^7$ litre mole^{-1} sec^{-1} respectively.

Table II

monomer = 0.528M. Temp. = 25.00 ± 0.01° C.

10^4 catalyst	$10^4 R_p$ mol. l^{-1} min^{-1}	$10^2 R_p / m_1$ Cat$^{1/2}$
0.096	1.78	10.9
0.236	3.51	13.7
0.517	4.54	11.9
0.548	3.51	9.0
0.835	4.80	9.9
0.866	4.92	10.0
1.64	6.53	9.7
3.34	9.24	9.6
3.53	12.8	12.9
5.89	12.6	9.9
12.9	20.8	11.0

Our experimental data may, therefore, be used to evaluate the initiation coefficient ($f_i k_i$), which was found to be (1.29 ± 0.29) x 10^{-7} sec^{-1} and it is this value which has been used to compute kinetic chain lengths ( ) given in Table III, where

$$= \frac{k_p m_1}{(k_t + k_t) f_i k_i \text{ Cat}^{1/2}} \qquad (1)$$

Molecular weights of polymers

Average degrees of polymerisation ($\bar{r}_v$) of the polymers produced are summarised in Table III. They were calculated from limiting viscosity numbers by means of Scholtan's relation[2], which for polymer concentrations expressed in gm. per 100 ml. is

$$= 6.31 \times 10^{-5} (71.1 \bar{r}_v)^{0.80} \qquad (2)$$

Over the range of polyacrylamide concentrations used in our viscosity measurements, the ratio of specific viscosity to polymer concentration was itself found to vary linearly with polymer concentration, so that limiting viscosity numbers were obtained by graphical extrapolation.

However, average degrees of polymerisation so obtained, which are close to weight-average values, are significantly smaller than would be expected from the corresponding kinetic chain lengths, indicating that non-degradative chain transfer processes are relatively important in the polymerisation of acrylamide under our experimental conditions. Now, in aqueous solution the most likely transfer reactions seem to be:-

Table II

[monomer] = 0.528M. Temp. = 25.00 ± 0.01° C.

10^4 [catalyst]	$10^4 R_p$ mol. l^{-1} min^{-1}	$10^2 R_p/[m_1][Cat]^{\frac{1}{2}}$
0.096	1.78	10.9
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3.53	12.8	12.9
5.89	12.6	9.9
12.9	20.8	11.0

Our experimental data may, therefore, be used to evaluate the initiation coefficient ($f_i k_i$), which was found to be (1.29 ± 0.29) x 10^{-7} sec^{-1} and it is this value which has been used to compute kinetic chain lengths ($\bar{\nu}$) given in Table III, where

$$\bar{\nu} = \frac{k_p[m_1]}{\left\{(k_t + k_t')f_i k_i[Cat]\right\}^{\frac{1}{2}}} \qquad (1)$$

Molecular weights of polymers

Average degrees of polymerisation ($\bar{r}_v$) of the polymers produced are summarised in Table III. They were calculated from limiting viscosity numbers [ɣ] by means of Scholtan's relation[2], which for polymer concentrations expressed in gm. per 100 ml. is

$$[\gamma] = 6.31 \times 10^{-5} (71.1\ \bar{r}_v)^{0.80} \qquad (2)$$

Over the range of polyacrylamide concentrations used in our viscosity measurements, specific viscosity was found to vary linearly with polymer concentration, so that limiting viscosity numbers were obtained by graphical extrapolation.

However, average degrees of polymerisation so obtained, which are close to weight-average values, are significantly smaller than would be expected from the corresponding kinetic chain lengths, indicating that non-degradative chain transfer processes are relatively important in the polymerisation of acrylamide under our experimental conditions. Now, in aqueous solution the most likely transfer reactions seem to be:-

Table III

$10^4[\text{Cat}]$	Kinetic chain length ($\bar{\nu}$) x 10^{-4}	Degree of polymerisation ($\bar{r}_v$) x 10^{-4}	10^5 ($\delta = 2/\bar{r}_v - 1/\bar{\nu}$)
12.9	19.3	9.04	1.69
5.89	28.6	9.60	1.73
3.53	36.9	9.35	1.87
3.34	38.0	9.04	1.95
1.64	54.1	7.91	2.33
0.84	75.8	7.02	2.72

$$m_j^* + m_1 \longrightarrow P_j + m_1^* \qquad \text{Rate} = k_{fm}[m_1][m_j^*]$$

and

$$\left.\begin{aligned} m_j^* + \text{Cat} &\longrightarrow P_j + Q^! \\ Q^! + m_1 &\longrightarrow m_1^* \end{aligned}\right\} \qquad \text{Rate} = k_{fc}[\text{Cat}][m_j^*]$$

The inclusion of such reactions in the overall scheme leads to the following relationship for the number average degree of polymerisation ($\bar{r}$)

$$\frac{1}{\bar{r}} - \left\{\frac{k_t + k_t^!/2}{k_p[m_1]}\right\}\left\{\frac{f_i k_i[\text{Cat}]}{k_t + k_t^!}\right\}^{\frac{1}{2}} = \frac{k_{fm}}{k_p} + \frac{k_{fc}[\text{Cat}]}{k_p[m_1]} \qquad (3)$$

However, the values of the individual termination coefficients, k_t and $k_t^!$, are not known. We have, therefore, assumed for present purposes that termination proceeds predominantly by disproportionation, i.e. $k_t^! \sim 0$, and that the average degrees of polymerisation computed using Scholtan's equation are twice the number average values, and we have evaluated the L.H.S. of equation (3), which now equals δ, accordingly. It is clear from the figures given in Table III that δ does not increase with increasing catalyst concentration as required by equation (3). On the contrary, there is a marked tendency for it to increase as the catalyst concentration is diminished. This behaviour suggests the existence of an additional transfer reaction involving a substance, the concentration of which is an inverse function of that of the catalyst. The substance concerned, which could be an impurity, possibly a decomposition product either of the catalyst itself or of the monomer, must be capable of being rendered inactive as far as transfer is concerned by a reversible reaction with the catalyst. Indeed our experimental data are represented fairly well by the empirical relationship

$$\delta = 1.6 \times 10^{-5} + 1 \times 10^{-9}/[\text{Cat}] \qquad (4)$$

in which the constant term, 1.6×10^{-5}, presumably corresponds to

the transfer constant for monomer (k_{fm}/k_p), for which Dainton and Tordoff[1] obtained a value of 1.2×10^{-5} at 25.0° C.

Experimental confirmation of the assumption that termination of polymerisation is primarily by disproportionation seems to be limited to an observation of residual unsaturation in the polymer[3]. Attempts in the present investigation to determine the terminal carboxyl groups by titration were unsuccessful, so that conclusive evidence for the mechanism of termination is not yet available.

Effect of ferric perchlorate on kinetics of polymerisation

Commercial acrylamide is said to contain some 50 parts per million of iron[4], probably as sulphate. A consideration of the effect of added ferric salts is therefore an appropriate point at which to start. The perchlorate appears to be the least complicated of all ferric salts in aqueous solutions. Its effect on the X- and γ-ray initiated polymerisation of acrylamide has been investigated by Collinson, Dainton and McNaughton[5], so that a comparison is possible between the results obtained in the present investigation and those given by an independent method.

The most obvious effect of the addition of ferric perchlorate is the reduction in the overall rate of polymerisation, the extent of which increases with an increasing concentration of ferric salt, as illustrated by the data given in Table IV. Perchloric acid, itself, has no detectable effect on the rate of polymerisation and no significant amount of polymer was produced by ferric perchlorate and perchloric acid in the absence of the initiator. However, for the range of concentrations examined, the rate of polymerisation was found to be directly proportional to $[\text{catalyst}]^{0.77}$ but inversely proportional to $[\text{ferric salt}]^{0.74}$. In addition, we have shown using o-phenanthroline that the ferric salt is continuously reduced to the ferrous state during the course of the polymerisation.

These observations are all consistent with the conclusion that in the presence of ferric perchlorate, the following alternative mechanism of termination is operative:-

$$m_j^{*} + Fe^{3+}_{aq.} + H_2O \rightarrow P_j + Fe^{2+}_{aq.} + H_3^{+}O \qquad \text{Rate} = k_4\left[Fe^{3+}_{aq.}\right]\left[m_j^{*}\right]$$

in addition to the normal bimolecular termination reaction discussed above. Infra-red absorption studies have shown that polyacrylamide produced in the presence of ferric perchlorate contains some vinyl groups[6], an observation which suggests that the polymeric carbonium ion, produced by loss of an electron to the ferric ion, stabilises itself by proton transfer to a solvent molecule. The implications of including this additional mode of chain termination in the overall kinetic scheme are such that the termination coefficient (k_4) for this reaction may be calculated from the equation

Table IV

[monomer] = 1.00M; $[HClO_4]$ = 0.11M; Temp. = 25.00 ± 0.01° C.

(a) Variation of R_p with concentration of ferric perchlorate

[catalyst] = 4.00×10^{-4}M

10^5 $[Fe(ClO_4)_3]$	10^4 R_p mol. l^{-1} min^{-1}	$10^{-4}k_4$ l. mol^{-1} min^{-1}
1.39	14.3	8.7
5.58	5.29	10.6
9.28	3.54	9.9
9.28	3.48	10.1

(b) Variation of R_p with concentration of catalyst

$[Fe(ClO_4)_3]$ = 9.28×10^{-5}M

10^4 [catalyst]	10^4 R_p mol. l^{-1} min^{-1}	10^{-4} k_4 l. mol^{-1} min^{-1}
2.60	2.96	7.7
2.60	2.98	7.6
4.00	3.48	10.1
4.00	3.54	9.9
4.51	5.06	7.6
6.00	5.62	9.2

$$k_4 = \frac{f_i k_i k_p [Cat][m_1]}{R_p[Fe(ClO_4)_3]} - \frac{k_t \cdot R_p}{k_p[m_1][Fe(ClO_4)_3]} \qquad (5)$$

The mean value of k_4 so obtained from the data given in Table IV was $(1.49 \pm 0.17) \times 10^5$ litre $mole^{-1}$ $sec.^{-1}$

However, ferric salts are known to be subject to a series of complex hydrolytic reactions in aqueous solutions, of which the following are said to be the most important:-

$$Fe^{3+}_{aq.} + 2H_2O \rightleftharpoons FeOH^{2+} + H_3^+O \qquad K_1$$

$$FeOH^{2+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + H_3^+O \qquad K_2$$

$$2FeOH^{2+} \rightleftharpoons Fe_2(OH)_2^{4+} \qquad K_d$$

The termination coefficient k_4 is, therefore, a composite quantity, which under appropriate experimental conditions might be expected to vary with the total concentration of ferric salt present, particularly as the relative terminating efficiencies of the ionic species $Fe^{3+}_{aq.}$, $FeOH^{2+}$, $Fe(OH)^{+}_{2}$, and $Fe_2(OH)^{4+}_{2}$, are known[5] to be in the ratio 1 : 5.5 : 50 : 200. This variation is not observed in the present series of experiments, however, partly because of low concentrations of ferric salt employed and partly because of the low pH of the solutions. However, in order to illustrate the relative importance of the various ionic species present, we have calculated their concentrations (Table V) from the values of K_1 and K_d given by Milburn and Vosburg[7] and from that for K_2 obtained by Hedström[8], K_2 being assumed to vary with ionic strength in the same way that K_1 does. It is clear that despite their greater terminating

Table V

$[HClO_4] = 0.11M$; $[Fe(ClO_4)_3] = 9.28 \times 10^{-5} M$; Temp. = 25.0° C.

$K_1 = 2.83 \times 10^{-3}$	$10^5 [FeOH^{2+}] = 0.232$
$K_2 = 1.2 \times 10^{-3}$	$10^5 [Fe(OH)^{+}_{2}] = 0.0025$
$K_d = 192$	$10^5 [Fe_2(OH)^{4+}_{2}] = 0.0001$
	$10^5 [Fe^{3+}_{aq.}] = 9.04$

efficiencies, the effect of both the second hydrolysis product and of the dimer on the kinetics of termination may be neglected. In addition, it should be noted that the high concentration of acid used ensures that relative proportions of Fe^{3+}_{aq} and $FeOH^{2+}$ are independent of the total concentration of ferric perchlorate, so that the absolute value of the termination coefficient for the aquated ferric ion (k_{40}) may be evaluated from the relation

$$k_4 = k_{40}(1 - \alpha) + k_{41}\alpha = k_{40}(1 - \alpha) + 5.5k_{40}\alpha \qquad (6)$$

in which k_{41} is the termination coefficient for $FeOH^{2+}$ and α is the degree of hydrolysis, viz. 0.0251 for $[H_3^+O] = 0.11M$. After making due allowance for the relatively large uncertainty in the value of the initiation coefficient ($f_i k_i$), we find k_{40} to be $(1.3 \pm 0.4) \times 10^3$ litre mole^{-1} sec^{-1} compared with values of $(2.0 \pm 0.6) \times 10^3$ and $(2.2 \pm 0.3) \times 10^3$ reported by other investigators[1,5].

Effect of ferric chloride on kinetics of polymerisation

The chloride ion is known[9,10] to catalyse electron transfer reactions involving ferric ions. It is not surprising, therefore,

that for a given concentration of ferric chloride the reduction in the rate of polymerisation observed is significantly larger than for the same concentration of ferric perchlorate. The appropriate kinetic data are summarised in Tables VI and VII and for the range of concentrations studied we have found that R_p is directly proportional to $[\text{catalyst}]^{0.88}$ and inversely proportional to $[\text{ferric chloride}]^{0.89}$. However, by restricting attention to sufficiently high concentrations of ferric salt and low concentrations of catalyst, both exponents can be made to approach unity more closely.

We have again found that with ferric chloride present, polymerisation is accompanied by the production of ferrous ions. Hydrochloric acid by itself had no effect on the rate of polymerisation and no significant amount of polymer was produced in solutions of monomer containing ferric chloride and acid in the absence of the initiator. Evidently linear termination of radical chains by an electron transfer process involving the ferric salt is again operative in addition to the normal bimolecular mode of mutual termination of chains. The essential difference in behaviour with chloride ions present is that the rate of linear termination is faster than with perchlorate ions.

Table VI

$[\text{monomer}] = 1.00\text{M}$; $[FeCl_3] = 2.58 \times 10^{-5}\text{M}$; $[HCl] = 0.122\text{M}$.
Temp. = $25.00 \pm 0.01^{\circ}$ C.

10^4 [catalyst]	$10^4 R_p$ mole litre^{-1} min^{-1}	$10^{-4} k_l'$ litre mole^{-1} min^{-1}
1.00	2.14	14.5
1.00	2.17	14.3
2.00	4.12	14.5
2.00	3.34	18.4
2.00	4.17	14.3
3.00	4.80	18.8
4.00	8.57	13.5
5.00	9.56	14.0
5.00	8.02	17.7
5.08	8.59	16.5

The greater efficiency of ferric chloride as a chain terminator is undoubtedly due to the greater complexity of its solutions as compared with those of ferric perchlorate. This complexity arises from the tendency for ionic association to occur in aqueous solutions in addition to the usual hydrolytic reactions common to all ferric salts, and the following equilibria have been recognised and investigated by several authors[9, 10, 11]

Table VII

[monomer] = 1.00M; [HCl] = 0.122M; Temp. = 25.00 ± 0.01° C.

$10^5[FeCl_3]$	$10^4 R_p$ mole litre^{-1} min^{-1}	$10^{-4} k'_4$ litre mole^{-1} min^{-1}
[catalyst] = 8.01 x 10^{-4}M		
3.60	10.0	16.4
6.00	6.26	17.0
6.00	5.88	18.2
[catalyst] = 5.08 x 10^{-4}M		
2.58	8.59	16.5
4.20	6.79	13.6
5.15	4.94	16.0
6.00	4.35	15.8
6.00	4.07	16.9
7.72	3.03	17.9
7.72	3.84	13.8

$$Fe^{3+}_{aq.} + Cl^- \rightleftharpoons FeCl^{2+} \qquad K_3$$

$$FeCl^{2+} + Cl^- \rightleftharpoons FeCl^+_2 \qquad K_4$$

However, the use of decimolar hydrochloric acid in the present experiments ensures that the only hydrolysis product which need be considered is $Fe(OH)^{2+}$, and also that the relative proportions of all ionic species present, including $FeCl^{2+}$ and $FeCl^+_2$, are independent of the total ferric chloride concentration since this is very small compared with that of hydrochloric acid.

By means of the semi-empirical relationship of Rabinowitch and Stockmayer[11], the constants appropriate to the ionic strengths of the solutions used in kinetic measurements, for each of the above equilibria, have been evaluated and are given in Table VIII, together with proportions of the total ferric chloride present in the different forms.

The average value of the composite termination coefficient (k'_4) evaluated from the experimental data given in Tables VI and VII by means of equation (5) was found to be (2.65 ± 0.27) x 10^3 litre mole^{-1} sec.$^{-1}$ Although k'_4 is related to the individual coefficients of the various ionic species present by the expression

$$k'_4 = (1 - \alpha - \beta - \gamma)k_{40} + \alpha k_{41} + \beta k_{43} + \gamma k_{44} \qquad (7)$$

Table VIII

$[HCl] = 0.122M$ Temp. = 25.0° C.

$K_1 = 2.76 \times 10^{-3}$; $K_3 = 7.73$; $K_4 = 2.5$

Species	Fraction of total $FeCl_3$	Rate coefficient symbol
$FeOH^{2+}$	$\alpha = 0.010$	k_{41}
$FeCl^{2+}$	$\beta = 0.403$	k_{43}
$FeCl_2^+$	$\gamma = 0.127$	k_{44}

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it is not possible at this stage without more experimental data to evaluate k_{43} and k_{44} separately. We hope to obtain the necessary additional experimental information by measuring the rate of polymerisation in the presence of different concentrations of chloride ion. At the moment it is only possible to evaluate an average value for the termination coefficients of the ions, $FeCl^{2+}$ and $FeCl_2^+$, viz. $(\beta k_{43} + \gamma k_{44})/(\beta + \gamma)$, and this turns out to be 3.7×10^3 litre $mole^{-1}$ sec^{-1}. These ions therefore terminate radical chains at about three times the rate of the aquated ferric ion.

One final question still to be settled is whether termination of polymer chains by species such as $FeCl^{2+}$ involves the incorporation of chlorine into the polymer molecule produced,

$$\text{i.e.} \quad m_j^* + FeCl^{2+} \rightarrow P_jCl + Fe^{2+}_{aq.}$$

instead of producing a molecule having a terminal vinyl linkage as with ferric perchlorate. There is evidence that in non-hydroxylic media, e.g. dimethyl formamide, the termination of polymerisation of some vinyl monomers by ferric salts does sometimes involve the incorporation of the anion concerned into the resulting polymer[12,13]. As far as the aqueous polymerisation of acrylamide is concerned, this point has still to be settled.

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POLYMERS FROM DIAZOALKANES

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The aim of this paper is to describe the work done up to the present time in the Chemistry Department of the University of Torino on the preparation of polyalkylidenes from the catalytical decomposition of diazoalkanes. The interest of this research chiefly lies in the peculiar polyalkylidene chain which is constituted by a sequence of tertiary carbon atoms without any intermediate $-CH_2-$ group, as in the case of the polymers obtained by polymerization of monomers of the vinyl or vinylidene types.

Some kinds of polyalkylidenes have been recently obtained from the polymerization of monomers having an internal double bond a such as maleic anhydride (1) and maleinimide (2). Worth of mention is also the stereospecific copolymerization of ethylene with cis-but-2-ene to form steroregular crystalline copolymers (3).

Up to the present time, however, the easiest way to get polyalkylidenes is to prepare the form the catalytical decomposition of diazoalkanes. It is well known that diazoalkanes, in the presence of boron compounds, such as boron trifluoride, boron alkyls and the ester of boric acid (4), or of some copper derivatives, such as copper stearate (5), decompose diazoalkanes and form polyalkylidenes. It is to be pointed out that boron compounds are very active catalysts in giving polymethylene from diazomethane, but their catalytic activity towards polyalkylidene formation decreases with higher diazoalkanes, such as diazoethane, diazopropane and so on (6). On the other hand copper derivatives are much more efficient catalysts in giving polymers from the decomposition products of the higher diazoalkanes than from diazomethane (6, 7).

Some years ago, being interested in the properties of polymers having side chains, we started to prepare them from the catalytical decomposition of diazoalkanes, looking at the same time for an efficient catalyst. It was thought that $AuCl_3$, being a Lewis acid as well as boron trifluoride, and the salt of an heavy metal belonging to the same subgroup of copper in the periodic system, could be a suitable catalyst for obtaining polyalkylidenes from the decomposition of diazoalkanes.

Our first experiments (8) confirmed this hypothesis: $AuCl_3$, in the presence of an ethereal solution of diazomethane was reduced as soon to a red gold colloid and polymethylene occluding colloidal gold was obtained with nearly quantitative yield. But the most interesting result arose from the $AuCl_3$ catalyzed decomposition of diazoethane, diazopropane and diazobutane. The behaviour of these

diazoalkanes was, generally speaking, similar to the one of diazomethane: $AuCl_3$ was reduced to colloidal gold, but the reaction was not as fast as in the case of diazomethane; the polyalkylidenes were formed but the yields were lower than with diazomethane (about 35% of polyethylidene from diazoethane and about 10% of polypropylidene and polybutylidene from diazopropane and diazobutane respectively) and, this is the point of interest, in addition to the amorphous polymers, soluble in cold solvents, highly crystalline polyalkylidenes, insoluble in cold solvents, were obtained. The yields of crystalline polyalkylidenes obtained in such a way were about 5% for crystalline polyethylidene and about 2% for crystalline polypropylidene and polybutylidene respectively (8, 9).

A thorough investigation of the reaction of polyalkylidene formation from the $AuCl_3$ catalyzed decomposition of diazoalkanes lead to the conclusion that the catalyst was not the gold salt itself, but the colloidal gold formed from the reduction of $AuCl_3$. The arguments which support this conclusion are:

(1) polymethylene occluding collaidal gold (the polymer acts as a protective agent of the colloid) decomposes a fresh solution of diazomethane, polymethylene is formed in nearly quantitative yields, and the rate of the reaction does not appreciably differ from that observed if the experiment is performed using the corresponding amount of $AuCl_3$ and diazomethane (10). The same happens when crystalline polyethylidene, polypropylidene or polybutylidene occluding colloidal gold are put in contact with a fresh solution of the corresponding diazoalkane (8, 9, 10);

(2) gold hydrosols, prepared according to Turkevich (11) by reducing $HAuCl_4$ in aqueous solution with sodium-citrate, decompose diazomethane and diazoethane as well (12). If the reaction is carried out on a holder for electron microscopy, it is easy to observe that, after a few minutes, the gold particles are surrounded with a layer of polymer, which becomes thicker if the diazoalkanes have been allowed to react for a longer time;

(3) if an ethereal solution of diazomethane is put in contact with a gold film prepared by evaporating gold metal under high vacuum, the diazoalkane decomposes and polymethylene is formed in nearly quantitative yield. The same happens with diazoethane, and both amorphous and crystalline polyethylidene are formed (9, 12, 13).

In addition to gold, many other metals, as evaporated metal films, have been found to be suitable catalysts for polyethylidene formation from the decomposition products of diazoethane, while some other metals are only active in decomposing diazoethane, but without any polymer formation (12, 13). Among the metals catalytically active in giving polyethylidene from the decomposition of diazoethane in ethereal solution, copper is to be remembered, which gives practically quantitative yield of the polymer, and among those metals which only decompose diazoethane in ethereal solution without polymer formation, we

indicate silver. An investigation upon the action of twenty four metallic surfaces on polymer formation from the decomposition products of diazoethane showed that, although no correlations can be found between electronic and geometric factors of the metals and their polymer forming ability, themetals which do not catalyze any polymer formation, although diazoethane is decomposed in a relatively short time, are those transition metals belonging to the second long period of the periodic system and those immediately following them, such as silver. Among the metals which catalyze polymer formation from the decomposition products of diazoethane, gold only is endowed with a stereoregulating activity, and gives rise to crystalline polyalkylidenes.

The gaschromatographic analysis of the products formed, besides polyethylidene and nitrogen, in the metal catalyzed decomposition of diazoethane in ethereal solution, showed that they are chiefly ethylene, cis-but-2-ene and trans-but-2-ene, and that relative amount of these light hydrocarbons depends upon the ability of the metal surface to give polymer or not (14). As a matter of fact, the light hydrocarbons evolved during the decomposition of an ethereal solution of diazoethane catalyzed by metals active towards polymer formation, such as copper and gold, are essentially a mixture in nearly equal parts of trans-but-2-ene and cis-but-2-ene, which of course, arise from coupling of two ethylidene fragments. When the decomposition of diazoethane in ethereal solution occurs without polymer formation, ethylene represents the main fraction of the light hydrocarbon formed, as the result of the isomerization of the ethylidene fragment arising from diazoethane.

The crystallinity in polyalkylidenes is, of course, to be attributed to a regular steric arrangement of the side alkyl groups bound to every one of the tertiary carbon atoms which constitute the backbone of the polymer chain. The crystal structure of the polyalkylidenes we prepared is still under investigation, and it is rendered difficult by the fact that, up to the present time, it has not been possible to obtain completely oriented fibers of the polymers, much probably be cause of their low molecular weights. The results so far obtained on polyethylidene from the study of the electron diffraction spectra seem to be in agreement with the model of a syndiotactic chain fully extended in the plane (9).

The infrared spectra of both amorphous and crystalline polyalkylidenes prepared by the metal catalyzed decomposition of diazoalkanes show absorption band due to the presence of unsaturations of the vynil type in the polymer chain (9). It is worth of note the fact that the realative intensity of the absorption bands due to unsaturations of the vynil type in the polymer molecule, depends upon the metal used as a catalyst, but in this case too, no correlations seem to exist with the metal properties.

On the basis of the main experimental evidences reported here, some working hypotheses can be drawn about the path of the reaction leading to polyalkylidenes from the metal catalyzed decomposition of diazoalkanes. It is reasonable to assume that the first step of the reaction might be the decomposition of the diazoalkane molecules reaching the active sites of the metal surface, with nitrogen liberation and consequent formation of active carbenes, which can be held on themetal surface. These active carbene can then isomerize, dimerize and polymerize, depending upon the metal surface used as a catalyst. A mechanism of polymerization involving a two-sites attachment on the metal surface during the growth of the polyalkylidene chain, might probably explain the formation of stereoregular polyalkylidenes, when metals having the proper geometric and electronic factors are used as catalysts. From the results of our investigation it seems that the limits are very crytical, as shown by the fact that gold only, up to the present time, has been found to possess a stereoregulating catalytic activity in the course of the growth of the polyalkylidene chain.

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The Preparation and Thermal Stability Properties of Certain Silicon and Phosphorus Containing Heterocyclic Polymers

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ABSTRACT

A number of monomers containing silicon and phosphorus have been synthesized which are functionally capable of undergoing polymerization by an alternating intramolecular–intermolecular mechanism to produce soluble, linear polymers. Three different types of monomers have been prepared: (a) di–unsaturated silanes capable of closing five–, six– or, seven–membered rings, (b) di–unsaturated phosphonium salts, and (c) di–unsaturated phosphine oxides. As intermediates for the phosphorus containing monomers a number of unsaturated phosphines have been prepared. Both free radical initiators and Ziegler–type initiators have been used, when appropriate, to initiate polymerization of the monomers prepared. In addition, polyphosphine oxides of high molecular weights were obtained by alkaline degradation of appropriate polyphosphonium salts. The silane polymers tested have been found to be thermally stable up to the range of 410 – 530° C. The phosphine oxide polymers tested decompose in the range of 392 – 450° C.

I. INTRODUCTION

The purpose of this research program was to investigate the possibility of producing new and useful heterocyclic polymers containing silicon and phosphorus through use of monomers functionally capable of polymerization by an alternating intramolecular–intermolecular chain propagation. It has previously been reported[1] that such monomers as diallyldimethylsilane and diallylphenylphosphine oxide are capable of undergoing such a chain propagation to produce soluble, linear polymers containing cyclic recurring units. Reports on the diallyldimethylsilane polymer[18,19] indicate that it possesses considerable thermal stability. It is the purpose of this paper to report on additional monomer and polymer syntheses and to discuss some of the properties of the polymers.

II. MONOMERS AND POLYMERS CONTAINING SILICON

(a) Monomers

Monomers in addition to those previously reported[1] which have been synthesized include the following: diallylmethylphenylsilane, dimethallylmethylphenylsilane, diallylcyclotetramethylenesilane, diallylcyclopentamethylenesilane, dimethallylcyclopentamethylenesilane, allyltrimethylsilane, allylvinyldimethylsilane, and 3–butenylallyldimethylsilane. The synthetic method employed was reaction of an appropriate Grignard reagent with an appropriate chlorosilane.

Allyldimethylvinylsilane was prepared both by the reaction of vinyl Grignard reagent with allyldimethylchlorosilane and by the reaction of allyl

Grignard reagent with vinyldimethylethoxysilane. The products of the two reactions were identical in their physical properties and infrared spectra, providing a definite structure proof for this compound in addition to the analysis and molar refraction. The infrared spectrum of this compound exhibits two distinct peaks for the two carbon–carbon double bonds at 1635 and 1595 cm.$^{-1}$. The peak at 1595 cm.$^{-1}$ appears in the spectra of other vinylsilanes and can be attributed to the vinyl group attached to silicon. The peak at 1635 cm.$^{-1}$ appears in all of the spectra of the allylsilanes and is assigned to the allyl double bond. This shift indicated that the carbon–carbon double bond of the vinyl group is of lower energy than is that of the allyl group. This suggests a polarization of the vinyl double bond due to the presence of the silicon atom. The physical properties, analytical data, yields, and appropriate references for these monomers are summarized in Table I.

(b) Silane Polymers and Polymerization

It was decided to attempt the polymerization of the diunsaturated silanes with both Ziegler catalysts and with free radical initiators. Due to "degradative chain transfer" most free radical initiated allylic polymerizations tend to give relatively low degrees of polymerization. The Ziegler catalysts might be expected to give higher molecular weight polymers. A great deal of work has been published concerning polymerizations by use of these complex metal catalysts in the past five years. With these catalyst systems it is possible to obtain high molecular weight polymers of α-olefins which could not be polymerized with free radical initiators. There are, however, some types of α-olefins which cannot be polymerized with conventional Ziegler catalysts. It has been reported[30] that α-olefins with branching closer than the 3- or 4-position to the double bond cannot be polymerized by this method. In view of this evidence it would be unlikely that the dimethallylsilanes and possibly the vinylsilanes would polymerize with the Ziegler catalysts. If these findings hold true for these compounds it will be necessary to polymerize them by means of free radical initiators.

The Ziegler catalyst system chosen for the polymerizations was triethyl aluminum–titanium tetrachloride. This is a common catalyst system and both of these materials are readily obtainable. The free radical initiator chosen was di-t-butyl peroxide. This initiator was chosen because it is readily obtainable and is soluble in the non-polar system which will be used in the polymerizations.

Intrinsic viscosity measurements will be made on samples of the polymers obtained in order to get an approximation to the relative degree of polymerization.

The polymerization of the diallyl- and dimethallylsilanes was accomplished by two different methods. The Ziegler catalyst was effective for the polymerization of the diallylsilanes while free radical initiators were effective for the polymerization of the dimethallylsilanes.

All of the diallylsilanes gave solid, benzene soluble polymers when treated with the Ziegler catalyst. A wide variety of conditions were used in some of the polymerizations in order to obtain the best conversion of the monomer to polymer. The factors varied were: mole ratio of the co-catalyst components, reaction time, temperature, and aging time of the catalyst.

It is reported[31] that the aluminum triethyl–titanium tetrachloride mole ratio should be 2 or 3 to 1 in order to obtain the most active catalyst. It was found, in the polymerization of diallyldimethylsilane that when the catalyst was not aged, the best conversion was obtained with a mole ratio of

Table I

Physical Properties, Analytical Data and Yields of Unsaturated Silanes

Silane	Physical Properties	Analysis	Yield %	Ref.
Diallyldimethyl	B.P. 135° n_D^{20} 1.4405		76	(16) (19) (18)
Diallyldiphenyl	B.P. 137–38/1.5mm n_D^{20} 1.5742		71	(15) (19) (18)
Dimethallyldimethyl	B.P. 75–79/25mm n_D^{20} 1.4525		72	(16) (20)
Dimethallyldiphenyl	B.P. 148/0.5mm n_D^{22} 1.5650		55	(16) (8)p.14
Diallylmethylphenyl	B.P. 124/15mm n_D^{20} 1.5200		75	(16) (8)p.14
Dimethallylmethylphenyl	B.P. 138/12mm n_D^{22} 1.5180		51	(16) (8)p.14
Diallylcyclotetramethylene	B. P. 142° n_D^{20} 1.5813	Calcd. for $C_{10}H_{18}Si$: C, 72.20; H, 10.90; Si, 16.88 Found: C, 69.80; H, 11.64; Si, 17.33	79	(20)p.11 (5)p.8 (3)p.11
Diallylcyclopentamethylene	B.P. 104/24mm n_D^{20} 1.4815	$C_{11}H_{10}Si$: C, 73.28; H, 11.18; Si, 15.54 C, 72.07; H, 10.82; Si, 15.06	68	(20)p.12 (3)p.11
Dimethallylcyclopentamethylene	B.P. 95/2mm n_D^{24} 1.4900	$C_{13}H_{24}Si$: C, 74.94; H, 11.61; Si, 13.45 C, 74.01; H, 11.36; Si, 13.77	60	(20)p.14 (7)p.14
Allyltrimethyl	B.P. 85° n_D^{20} 1.4058		54	(7)p.14 (5)p.7
Allylvinyldimethyl	B.P. 111° Density: 0.7594 n_D^{20} 1.4290	$C_7H_{14}Si$: C, 66.57; H, 11.17; Si, 22.24 C, 66.61; H, 10.95	51	(20)p.15 (9)p.14 (12)p.29 (14)p.4
3-Butenylallyldimethyl	B.P. 71–2/40mm n_D^{20} 1.4436		60	(14)p.7

2.5 to 1. It was found, as expected, that the conversion was increased by raising the reaction temperature from 30 to 85°. The reaction time seemed to have only a small effect upon the yield of polymer obtained.

The effect of aging of the catalyst upon the conversion to polymer was studied for the polymerization of diallyldimethylsilane. It is reported[31] that the aging of the catalyst decreases its activity. It was found that the aging of the catalyst actually increased the conversion of this monomer to solid, linear polymer. The best conversion was obtained with a co-catalyst mole ratio of 1 to 1 and a one hour aging time for the catalyst. The conversion dropped off slowly as the catalyst was aged for a longer period.

In the polymerization of diallyldiphenylsilane it was found that the mole ratio of the co-catalyst components had a smaller effect upon the conversion, between mole ratios of 2.2 and 4.4 to 1. With this monomer the temperature and reaction time seem to have only a small effect upon the conversion.

In some polymerizations of diallyldiphenylsilane, titanium tetrachloride was replaced in the catalyst by dicyclopentadienyltitanium dichloride, to give a soluble Ziegler type catalyst. Diallyldiphenylsilane was chosen for these experiments due to the fact that good yields of solid polymer had been obtained in previous polymerizations of this monomer with the conventional Ziegler catalyst. Only small amounts of solid polymer were obtained with the soluble catalyst mixture. Natta has reported that this soluble catalyst is less active than is the conventional catalyst.

Polymerization of the remaining diallylsilanes was accomplished with the conventional Ziegler catalyst. Conditions for these polymerizations were not significantly varied and no attempts were made to obtain optimum conditions for the polymerizations.

Attempts were made to polymerize dimethallyldimethylsilane with the Ziegler catalyst but no polymer was isolated. This was not surprising in view of previously published reports of attempts to polymerize olefins with branching close to the double bond.[30]

Free radical polymerization of the dimethallylsilanes led to soluble polymers. Di-t-butyl peroxide was used as the initiator for these polymerizations. Diallyldimethylsilane and diallyldiphenylsilane were also polymerized with this initiator.

Lower melting points and lower intrinsic viscosity values for these free radical initiated polymers indicate that the polymers are of lower molecular weight than are those obtained with the Ziegler catalyst. The dimethallyl-silanes all have very low intrinsic viscosities which indicate that they have a low degree of polymerization. The low degree of polymerization is probably due to "degradative chain transfer" involving the allylic hydrogen atoms. In the dimethallylsilanes, this effect should be more important due to the greater number of allylic hydrogens. Diallylsilanes have four allylic hydrogens while the dimethallylsilanes have ten. Comparison of the results of the free radical polymerization of diallyldiphenylsilane and of dimethallyldiphenylsilane shows that although both have low intrinsic viscosity value, those for the diallyl polymers are about twice those for the dimethallyl polymers. Since these compounds are very similar it seems likely that the molecular weights for these two polymers would be in about the same ratio as are their intrinsic viscosities.

All of the diallyl- and dimethallylsilanes gave polymers which were soluble in benzene although small fractions of a few polymers were insoluble. These soluble polymers exhibited little or no residual unsaturation in the

infrared spectra. In most cases the abosrption bands for carbon–carbon double bond stretch and for terminal methylene deformation could be removed from the spectra by further purification of the polymer.

The analytical results of the polymers are in many cases rather far from the theoretical value for carbon. It is reported, that in the analysis of silicon polymers, combustion of the sample may lead to the formation of some silicon carbide which is not completely oxidized. The formation of this compound would account for the low per cent of carbon found in the analyses of these polymers. The per cent silicon would not be affected by this due to the fact that the silicon analyses are performed on a separate sample using wet oxidation methods. The silicon and hydrogen analyses of these polymers are fairly close to the theoretical values and it seems certain that the formulae assigned to the polymers are correct.

The polymerization of allyldimethylvinylsilane was attempted with several catalysts but no solid, soluble polymer was obtained. The polymerization with free radical initiators gave varying results. With di–t–butyl peroxide both an insoluble solid and a heavy oil were obtained. The infrared spectra were very similar and showed absorption for both allyl and vinyl groups. The allyl double bond absorption was decreased a great deal in the two polymers however. Benzoyl peroxide gave a low yield of heavy oil which had an infrared spectrum similar to that of the polymers above. Use of α,α'–azobisisobutyronitrile gave no polymerization.

It has been reported that vinylsilanes do not polymerize with benzoyl peroxide. The reason for this lack of polymerization can be explained by consideration of the radical which would be formed by a free radical attack on a vinylsilane. It has been mentioned earlier in this section that there is a polarization of the vinyl group attached to silicon. This polarization is due to the "electron sink" effect of silicon. This "electron sink" effect would stabilize the free radical formed above. This radical stability is apparent in the free radical chlorination of tetraalkylsilanes. The chlorination of tetraethylsilane gives the α–chloro compound exclusively. This indicates that the radical on a carbon atom adjacent to a silicon atom of a tetraalkylsilane is very stable. The stability of this radical may account for lack of polymerization through the allylic double bonds. This type of polymerization leaves a vinyl group on the chain which may, under proper conditions, react to form a crosslink leading to insoluble polymer.

Attempts to polymerize this monomer by use of Ziegler catalysts gave results similar to those obtained with free radical initiators. In this case the vinyl double bond does not take part in the polymerization due to steric factors. The allyl double bond undergoes polymerization, however, to give low molecular weight oils. It was not possible to purify the polymers obtained with this monomer to any large extent due to the fact that the polymers were non–volatile and liquid at even very low temperatures. Infrared spectra, however, indicate that the only major changes from the monomer is the decrease of allyl double bond content in the polymer.

A sample of polydiallyldiphenylsilane was fractionated and molecular weight determinations of each of the twelve fractions was done using light scattering technique. The results are shown below:

Fraction	Molecular Weight
1–6	$4–5 \times 10^4$
7	6.7×10^4
8	9.1×10^4

9	1.5×10^5
10	1.8×10^5
11	2.4×10^5
12	2.0×10^6

A molecular weight determination of Fraction 5 by the osmotic pressure method gave a value of 3.6×10^4, in fair agreement with that obtained by the light scattering method.

Differential thermal analysis of several of the polydiallyldiphenylsilane samples gave the following results:

Fraction	Decomposition
1	410–530°C
4	410–530°C
8	410–530°C

Although the sample of polydiallyldiphenylsilane did not fractionate into consistently increasing molecular weight groups in the first several fractions, a distribution is implied which appears to be consistent with the results of other workers who have used the column fractionation technique. From the values obtained it is seen that most of the sample weight, approximately 75 per cent, lies in the molecular weight range of $10^4 - 10^5$, while only about 3 per cent of the sample has a molecular weight greater than 10^6. This may be compared to molecular weight distributions determined by a similar fractionation technique at Monsanto Chemical Company on samples of polystyrene and polyethylene. The integral molecular weight curves which have been published for these polymers indicate that as much as 60 per cent – 75 per cent of the sample weight has molecular weights ranging in value over a factor of ten, with only a very small amount greater than a factor of a hundred above the lowest measured weight. The results obtained for polydiallyldiphenylsilane are in good agreement with these values, even though very little fractionation occurred among the light fractions.

In addition, the range of molecular weights serves as a confirmation of the value obtained for the average molecular weight determined on a different sample of polydiallyldiphenylsilane in the earlier part of this work. The measured average value of 6.7×10^4 is well within the limits of the range, and it is believed that this agreement indicates the methods developed for removing the micro-gel from the solutions are effective, and that the measurements are a true indication of the polymer molecular weight.

The absence of fractionation among the light fractions was probably caused by the fact that the Cellosolve used as the nonsolvent actually dissolved the light fractions, which constituted a large part of the sample weight, and was not initially present in large enough quantity to remove all of this portion. As previously stated, Cellosolve was the best non-solvent available for use at the desired temperature, and was not expected to remove material from the column. However, when heated to the operating temperature, some of the polymer dissolved and was precipitated from the Cellosolve used to keep the column wet while heating the system. The first several mixtures of Cellosolve and toluene contained only small precentages of toluene, and, with the warm Cellosolve acting as a solvent, it is possible that the toluene added did not cause a large increase in solvent power over that of the Cellosolve itself. Only a limited amount of the polymer was available, and extensive testing was not done prior to the fractionation run.

An additional complication was encountered in measuring the molecular weight of these light fractions. While performing the calculations, it was apparent that these molecular weights may have been near the lower limit which can be measured by this method. While the lower limit of molecular weights measurable by means of light scattering is usually given as around 1 X 10^4, it is seen that this limit depends somewhat upon the solvent–polymer pair being measured insofar as the refractive index gradient, dn/dc, is involved. In general, the measured turbidity will be greater for a given concentration in a system having a larger value for this gradient. While the value of the refractive index gradient of the system measured was not particularly low, the loss in sensitivity which was encountered caused difficulty in extrapolating the curves, so that some molecular weight separation may have occurred even though no consistent increase was obtained from the measurements.

The appearance of micro–gel upon dissolving the last, or heaviest, fraction was surprising. It had been thought that the micro–gel encountered previously was caused by the cross–linking of several polymer molecules during the polymerization process, since one characteristic of a cross–linked polymer is that it will not dissolve. However, in this case the polymer was filtered before fractionation in order to remove such insoluble material, and the eluting mixtures underwent further filtration in the column while passing over the bed of uncoated Celite and through the glass frit which held the Celite. This should have removed any micro–gel which may have been present, and it is difficult to understand how the polymer could have cross–linked after fractionation, as no catalyst was present. In addition, all of the fractions received similar treatment, and if cross–linking had occurred at this stage it should have shown up in some of the other fractions as well. Another possibility is that the polymer molecules were brought very close together in the precipitation step, and that this allowed dipole interaction between molecules strong enough to hold them together when placed again in solvent. This may have taken the form of a crystallization process, as it is known that a crystalline polymer is more difficult to dissolve than an amorphous one. The presence of dipoles in this polymer is very likely, since it contains silicon as well as carbon atoms. As the micro–gel appeared only in the fraction having the highest molecular weight, it is also possible that it is simply the result of chain entanglement occuring during precipitation. If this is the case, there should be a solvent effect, the micro–gel being less pronounced in a better solvent. It seems most likely that all of these factors contributed to the sudden appearance of micro–gel in this heaviest fraction.

The physical properties and other data for the silane polymers are reported in Table II.

III. PHOSPHONIUM MONOMERS AND POLYMERS

(a) Phosphonium Monomers

As intermediates for the phosphonium salts to be prepared, a number of unsaturated phosphines were prepared by the method of Jones and Davies.[29] The physical properties and other data for these phosphines are reported in Table III.

The phosphonium salts were prepared by reaction of the appropriate phosphine with the appropriate alkyl halide. The pronounced reactivity of the allyl and methallyl halides with phosphines was taken advantage of when possible in order to facilitate preparation of the phosphonium salts. Due to the

Table II

Physical Properties, Analytical Data and Yields of Silane Polymers

Silane Polymers	Initiator	Yield %	Analysis Calculated for:		Found:	Polymer Properties	References
Diallyldimethyl	$AlR_3/TiCl_4$	59	$(C_8H_{16}Si)_n$:	C, 68.52	65.84	M.R. 115–140	(3)p.11,(17)
				H, 11.50	10.95	Decomp. 330	(8)p.16,(18)
				Si, 19.98	19.73	η = 0.13	(12)p.30,(19)
							(20)p.20
Diallyldiphenyl	$AlR_3/TiCl_4$	60	$(C_{18}H_{20}Si)_n$:	C, 81.78	80.74	M.R. 142–180	(3)p.12,(18)
				H, 7.63	7.60	Decomp. 315	(8)p.16,(19)
				Si, 10.60	10.40	η = 0.08	(11)p.5
						MW = 4.5×10^4–2.0×10^6	(12)p.35
							(20)p.21
Dimethallyldimethyl	Di-t.BP[a]	38	$(C_{10}H_{20}Si)_n$:	C, 71.34	71.04	Viscous liquid	(8)p.17
				H, 11.97	11.31		(3)p.13
				Si, 16.68	16.75		(20)p.21
Dimethallyldiphenyl	Di-t.BP	75	$(C_{20}H_{24}Si)_n$:	C, 82.12	80.88	M.R. 110–125	(9)p.15
				H, 8.27	8.72	η = 0.030	(12)p.36
				Si, 9.60	9.43		(20)p.23
Diallylmethylphenyl	$AlR_3/TiCl_4$	56	$(C_{13}H_{18}Si)_n$:	C, 77.15	71.60	M.R. 90–130	(5)p.9,(20)p.21
				H, 8.96	8.72	η = 0.12	(8)p.16,(12)p.36
				Si, 13.88	13.79		(9)p.15
Dimethallylmethylphenyl	Di-t.BP	40	$(C_{15}H_{24}Si)_n$:	C, 78.18	76.31	M.R. 65.75	(8)p.18
				H, 9.62	9.38	η = 0.03	(20)p.24
				Si, 12.18	12.76		
Diallylcyclotetramethylene	Di-t.BP / $AlR_3/TiCl_4$	30–50	$(C_{10}H_{18}Si)_n$:	C, 72.20	69.80	M.R. 85–87 / M.R. 130–140	(9)p.15,(20)p.22
				H, 10.90	11.64		(3)p.12,(5)p.9
				Si, 16.88	17.41	Decomp. 325;n = 0.11	(8)p.16
Diallylcyclopentamethylene	$AlR_3/TiCl_4$	60	$(C_{11}H_{20}Si)_n$:	C, 73.28	69.07	M.R. 95–110	(3)p.11,(8)p.16
				H, 11.18	10.58	n = 0.12	(5)p.9,(20)p.22
				Si, 15.54	15.95		(9)p.15,(12)p.36
Dimethallylcyclopentamethylene	Di-t.BP	50	$(C_{13}H_{24}Si)_n$:	C, 75.64	73.68	M.R. 75–90	(8)p.18
				H, 10.74	10.84	η = 0.04	(20)p.24
				Si, 13.60	14.77		

Table II (Continued)

Allyltrimethyl–Diallyldimethyl Copolymer	$AlR_3/TiCl_4$	10		(5)p.9 (8)p.16
Allylvinyldimethyl	$\frac{AlR_3/TiCl_4}{Di\text{–}t.BP}$		$\frac{Oil}{Oil}$	$\frac{(12)p.30,(20)p.24}{(12)p.30}$

3–Butenylallyldimethyl

a. Di–t.BP = Di–tert. Butyl Peroxide

Table III

Physical Properties, Analytical Data and Yields of Intermediate Unsaturated Phosphines

Phosphine	Physical Properties	Analysis	Yield %	Ref.
Diallylphenyl	B.P. 79°/0.7mm n_D^{25} 1.5670		45	(27)p.7 (12)p.24 (29)
Dimethallylphenyl	B.P. 98°/1.5mm n_D^{25} 1.5485			(8)p.8 (10)p.3 (29)p.3
Allyldiphenyl	B.P. 114–116°/0.5mm			(9)p.7 (12)p.25
Methallyldiphenyl	B.P. 118–121°/0.45mm			(9)p.7 (12)p.25
Divinylphenyl	B.P. 48–50°/0.2mm	Calcd. for $C_{10}H_{11}P$: C, 74.07; H, 6.79; P, 19.13 Found: C, 73.96; H, 6.80; P, 18.94	66	(12)p.20 (9)p.9 (28)
Vinyldiphenyl	B.P. 104°/0.25mm $n_D^{24.5}$ 1.6260	Calcd. for $C_{14}H_{13}P$: C, 79.24; H, 6.13; P, 14.62 Found: C, 79.43; H, 6.12; P, 14.42	57	(12)p.21 (9)p.10 (13)p.6 (26)
3-Butenyldiphenyl	B.P. 142–43°/1.25mm n_D^{20} 1.5991		40	(13)p.5

hygroscopic nature of these salts, and the tendency for the intermediate phosphine to react with oxygen and to absorb water from the atmosphere, it was necessary to work under an inert atmosphere and under anhydrous conditions. Several phosphonium salts have been prepared which are functionally capable of producing other ring sizes during polymerization. The physical properties and other pertinent data on these compounds are reported in Table IV.

(b) Phosphonium Polymers

Free radical initiation was chosen as the method for polymerizing the monomers prepared. Since the phosphonium compounds are somewhat ionic in character, the use of anionic or cationic initiation is precluded. Compounds of this type are also known to poison the Ziegler catalyst system. Free radical initiation then becomes the only remaining choice. This is unfortunate because of difficulties which have been observed in attempting the polymerization of allylic materials by means of free radicals. The phenomenon known as degradative chain transfer arises due to the labile hydrogen atoms attached to the carbon alpha to the double bond. Abstraction of one of these hydrogens by a free radical leads to a new radical which is stabilized by free radical resonance. Due to this stability, the new radical is not active enough to act as a chain carrier. Although degradative chain transfer leads to a new radical, it in effect is a chain termination step.

Solution polymerization was used throughout this study. It is not known definitely if other free radical initiated systems will produce linear polymers from these compounds. Bulk polymerization has been found to yield linear polymers from 1,6-diunsaturated phosphine oxides.[24] No bulk polymerizations were attempted using phosphonium type monomers due to the high melting points of these compounds. The concentrations used for the solution polymerizations were near saturation. The solvent acted only to bring the monomer and initiator into a single phase.

The polymers prepared from the monomers discussed earlier have several things in common. All of them are soluble in ethanol and dimethylformamide. All had infrared spectra which contain very little or no absorption corresponding to unsaturation. The softening points of the polymers are higher than the melting points of the monomers. The analyses of the polymers were, in every case, consistent with the analyses calculated for the monohydrates.

The increased softening points indicate an increase in molecular weight. The analyses corresponding to hydrated products are also indicative that larger molecules were formed by the polymerization reaction. Phosphonium compounds are known to form hydrates, and water of hydration would be more difficult to remove from high molecular weight compounds. The fact that the materials formed are soluble indicates that they are linear. The cyclic mechanism accounts for the reaction of two double bonds per repeating unit in the polymer chain. The infrared data and solubility of these materials is then consistent with the formation of cyclic units, separated by methylene groups, for these materials.

Poly-(triallylphenylphosphonium bromide) was also prepared as part of this study. In the light of information gained from the polymerization of triallylammonium bromides, triallylphenylphosphonium bromide was expected to form a cross-linked material. Poly-(triallylphenylphosphonium bromide) was indeed cross-linked. The material is an amber, glass-like, insoluble solid. The similarity between the ammonium and phosphonium type polymers is strengthened by the production of this cross-linked material.

Two of the polymers prepared appeared to be highly unsaturated upon first examination. Both poly-(diallylphenylmethylphosphonium bromide) and

Table IV

Physical Properties, Analytical Data, and Yields of Unsaturated Phosphonium Salts

Phosphonium Salt	Physical Properties	Analysis		Yield %	Ref.
Diallylhydrogen-phenyl Cl	M.P. 105–110°			26	(4)p.8 (3)p.2
Diallylmethyl-phenyl Br	M.P. 98–99°	Calcd. for $C_{13}H_{18}PBr$:	P, 10.86; Br, 28.03	53	(4)p.7
		Found:	P, 10.86; Br, 28.22		(7)p.4
Diallylethyl-phenyl Br	M.P. 123–130°	$C_{13}H_{20}PBr$:	P, 10.37; Br, 26.76	23	(8)p.7
			P, 10.31; Br, 25.87		(4)p.7 (5)p.4
Diallyl-n-propylphenyl Br	M.P. 85°	$C_{14}H_{22}PBr$:	P, 9.90; Br, 25.50	30	(5)p.5
			P, 9.84; Br, 25.20		(6)p.2 (8)p.7
Triallyl-phenyl Br	M.P. 109–111°	$C_{15}H_{20}PBr$:	P, 9.97; Br, 25.63		(5)p.4
			P,10.12; Br, 25.37		(8)p.7
Dimethallyl-methylphenyl Br	M.P. 175–78°	$C_{15}H_{22}PBr$:	P, 9.81; Br, 25.32	51	(8)p.8
			P, 9.68; Br, 24.81		(23)p.31
Dimethallyl-ethylphenyl Br	M.P. 77–79°	$C_{16}H_{24}PBr$:	P, 9.48; Br, 24.47	11	(6)p.3
			P, 9.40; Br, 24.63		(8)p.8 (7)p.3
Dimethallyl-n-propylphenyl Br	M.P. 107–110°	$C_{17}H_{26}PBr$:	P, 9.09; Br, 23.40	7	(8)p.9
			P, 9.18; Br, 23.07		
Diallyldiphenyl Br	M.P. 155–157°	$C_{18}H_{20}PBr$:	P, 8.94; Br, 23.01	57	(9)p.7
			P, 8.75; Br, 23.14		(12)p.25
Dimethallyl-diphenyl Br	M.P. 179–180°	$C_{20}H_{24}PBr$:	P, 9.27; Br, 21.33	18	(9)p.8
			P, 8.39; Br, 21.39		
Allylmethallyl-diphenyl Br	M.P. 162–164°	$C_{19}H_{22}PBr$:	P, 8.59; Br, 22.18	42	(12)p.26
			P, 8.61; Br, 22.19		(9)p.8
Di-3-butenyl-diphenyl Br	M.P. 115–117°	$C_{20}H_{24}PBr$:	C, 63.85; H, 6.45; P, 8.25	35	(14)p.6
			C, 63.36; H, 5.74; P, 8.57		
Vinyl-3-butenyl-diphenyl Br	M.P. 115–117°			35	(9)p.6
					(14)p.6
Allylvinyl-diphenyl Br	M.P. 173–175°	$C_{17}H_{18}PBr$:	C, 61.28; H, 5.44; P, 9.23		(12)p.25
			C, 61.19; H, 5.59; P, 9.14		
Allylvinyl-diphenyl Cl				13	(12)p.25

poly-(dimethallylphenylmethylphosphonium bromide) gave infrared spectra which showed strong absorption in the 930 cm.$^{-1}$ region. This is the region where absorption due to terminal unsaturation was expected. All of the monomers prepared absorbed in this area. The polymers produced, however, did not absorb in this area with these two exceptions. Poly-(dimethallylphenylmethylphosphonium bromide) was catalytically hydrogenated at 25 p.s.i. in order to eliminate the infrared absorption at 930 cm.$^{-1}$. The product of the hydrogenation gave a spectrum which was identical with the spectrum of the material before hydrogenation. The failure to produce a change in the infrared spectrum leads to the conclusion that the absorption was due to some anomaly of these methyl substituted compounds rather than to unsaturation in the polymers. Infrared spectra of triphenylmethylphosphonium bromide and triphenylallylphosphonium bromide were compared with the spectra from the monomer and the polymer of dimethallylphenylmethylphosphonium bromide and diallylphenylmethylphosphonium bromide. These spectra show a strong absorption at 916 cm.$^{-1}$ which may be assigned to phosphorus-methyl bonds. Double bond absorptions for these compounds are found at 1017 and 872 cm.$^{-1}$. These two absorptions, which appear in the spectra of the methyl-substituted monomers, do not appear in the spectra of the polymers. It has been concluded from this evidence that what had appeared to be unsaturation in poly-diallyl- and poly-(dimethallylphenylmethylphosphonium bromide) is due rather to phosphorus-methyl bonds. These polymers are now thought to be saturated materials.

It has been established that amines act as inhibitors for free radical reactions. It was assumed that phosphines would act in a similar fashion. If this were true it would not be possible to polymerize diallylphenylphosphine by a free radical reaction. An attempt was made to polymerize diallylphenylphosphine using a free radical initiator in order to test this assumption. The monomer was placed in a benzene solution along with five per cent ABN and refluxed 11 days. The product, which was isolated, possessed physical properties and an infrared spectrum nearly identical with diallylphenylphosphine oxide. Since no polymeric material was isolated it was concluded that the phosphine had acted as an inhibitor.

Reference was made earlier to intrinsic viscosity values obtained for the polyelectrolyte polymers obtained. Polyelectrolyte materials behave differently in solution than non-electrolyte materials. In solution, the polyelectrolytes obtained are free to ionize. The bromide ions formed by ionization are free to move about in solution. The positive phosphonium ions formed are not free to move about as they are bound together by the polymer chain. These positive ions repel each other and force the polymer chain to uncoil. The greater the extent of ionization, the more the polymer chain is extended. Dilution of a sample of polymer causes greater ionization. Intrinsic viscosity cannot be measured under these conditions due to the change in interaction between molecules in the system. Ionization of these polyelectrolytes was held constant enough for viscosity measurements to be made through the use of added electrolyte. Intrinsic viscosity values were obtained by the usual method. These values are small when compared to values obtained for other polymer systems. The magnitude of these values may have several meanings. First, the polymers may be of low degree of polymerization. Or, the degree of polymerization is large but the added electrolyte has supressed the ionization to a point where the polymer molecules remain tightly coiled and do not act as long chains. Two polyelectrolyte polymers were degraded to give non-electrolyte polymers. This reaction and the polymers obtained by this method will be discussed later. The intrinsic viscosities obtained for non-electrolyte polymers obtained by degradation are shown in Table VII. These values are considerable larger than values obtained from the

polyelectrolytes from which they were obtained. Due to the change in intrinsic viscosity between the compounds it was thought that both types of polymers have longer chains than was indicated by the intrinsic viscosities of the electrolyte materials. It then seems that the added electrolyte is suppressing ionization and that the coiled molecules give very little indication as to their degree of polymerization in this system.

The physical properties and other pertinent data for the polyphosphonium salts are recorded in Table V.

IV. PHOSPHINE OXIDE MONOMERS AND POLYMERS

(a) Phosphine Oxide Monomers

The preparation of diallylphenylphosphine oxide was previously discussed[1] and its preparation along with that of dimethallylphenylphosphine oxide has been published.[24] Additional phosphine oxides as suitable monomers for this study are reported in this paper. The physical properties, and other pertinent data on these monomers are included in Table VI.

(b) Polyphosphine Oxides

Diallylphenylphosphine oxide could be polymerized in bulk with benzoyl peroxide; yields 15–30%. Poly–(diallylphenylphosphine oxide) was soluble in alcohol, dimethylformamide and glacial acetic acid. An intrinsic viscosity determination of a sample melting at 85–115° gave a value of 0.026 (inalcohol). An infrared examination of the polymer showed only a small peak for a carbon–carbon double bond (1640 cm.$^{-1}$). Absorption assigned to the terminal methylene group (910 cm.$^{-1}$) in the monomer did not appear in the polymer. A sample of poly–(diallylphenylphosphine oxide) lost 21.9% of its original weight when heated at 210° for four hr. It began to darken in 10 min. and had the appearance of tar after 48 hr.

Polymerization of dimethallylphenylphosphine oxide was initiated by either α,α'–azodi–isobutyronitrile or benzoyl peroxide at 75°. The yields of polymer were low (less than 30%) with either initiator. Poly–(dimethallylphenyl–phosphine oxide) was soluble in alcohol, glacial acetic acid and dimethylformamide. A value of 0.04 was found for the intrinsic viscosity of an alcohol solution of the polymer; the sample melted at 130–165°. The infrared spectrum has only a small hump to indicate a carbon–carbon double bond (1635 cm.$^{-1}$) and does not have a peak for a terminal methylene group (892 cm.$^{-1}$) as is present in the spectrum of the monomer. When heated at 210° for four hr., the polymer decreased in weight by 32.5%.

In view of the low intrinsic viscosity measurements it appears likely that the polymers are not of high molecular weight. Polymerizations involving allyl groups have been reported to terminate through degradative chain transfer which may be influential in retarding growth in samples.

A molecular weight determination of a poly–(diallylphenylphosphine oxide) by the light scattering method gave a value of 2.8×10^4.

Differential thermal analysis of two of the polyphosphine oxides gave the following results: Polydiallylphenylphosphine oxide (M.R. 165–205°), Decomp. 438–450°; Polydimethallylphenylphosphine oxide (M.R. 198–225), Decomp. 392–438°.

Treatment of dimethallylmethylphosphine oxide in bulk with catalytic amounts (up to 5%) of benzoyl peroxide apparently initiated little or no polymerization as unreacted monomer could be recovered in high yield. This is in contrast to the behavior of diallyphenylphosphine oxide and dimethallylphenyl–

Table V

Physical Properties, Analytical Data and Yields of Phosphonium Polymers

Phosphonium Salt Polymers	Initiator	Yield %	Analysis Calculated for:	Found:	Polymer Properties	References
Diallylhydrogen-phenyl Cl	t-BHP[a]				M.P. > 350°	(4)p.9
Diallylmethyl-phenyl Br	t-BHP		$(C_{13}H_{18}PBr)_n$: P,	10.88 10.34	Soft. 230°	(4)p.9, (9)p.9
			Br,	28.03 26.77	M.P. 270°;n = 0.035	(12)p.27
Diallylethyl-phenyl Br	t-BHP	95	$(C_{14}H_{20}PBr \cdot H_2O)_n$:			(5)p.4, (9)p.9
			P,	9.78 9.30	M.P. 260-300°	(8)p.9, (12)p.27
			Br,	25.20 24.05	η = 0.034	(23)p.22
Diallyl-n-propyl-phenyl Br	t-BHP		$(C_{15}H_{22}PBr \cdot H_2O)_n$:			(6)p.3, (9)p.7,9
			P,	9.36 8.80	M.P. 235°	(12)p.26,27
			Br,	24.10 23.34	η = 0.02	
Triallyl-phenyl Br	t-BHP	Quant.	$(C_{15}H_{20}PBr \cdot H_2O)_n$:		Insoluble,	(8)p.9
			P,	9.43 9.10	Cross-linked	(5)p.5
			Br,	24.30 23.34		
Dimethallyl-methylphenyl Br	t-BHP	95	$(C_{15}H_{22}PBr \cdot H_2O)_n$:		Soft. 220°	(9)p.7,9
			P,	9.36 9.41	M.P. 344°	(12)p.26,27
			Br,	24.18 24.08	η = 0.018	(23)p.33
Dimethallyl-ethylphenyl Br	AIBN,[b] BP[c] t-BHP	90	$(C_{16}H_{29}PBr \cdot H_2O)_n$:		M.P. 180-200°	(7)p.4
			P,	8.98 8.63	η = 0.025	(23)p.33
			Br,	23.18 23.40		(8)p.9
Dimethallyl-n-propylphenyl Br	AIBN	60	$(C_{17}H_{26}PBr \cdot H_2O)_n$:		Soft. 170°	(9)p.7,9
			P,	8.60 8.46	M.P. 220°	(12)p.26,27
			Br,	22.18 21.67	η =0.031	
Diallyldi-phenyl Br	AIBN	97	$(C_{18}H_{20}PBr \cdot H_2O)_n$:		Soft. 250°	(9)p.8,9
			P,	8.50 8.49	M.P. 295-315°	(12)p.26,27
			Br,	21.90 21.80	η = 0.031	
Dimethallyl-diphenyl Br	AIBN	89	$(C_{20}H_{24}PBr \cdot H_2O)_n$:		Soft. 256°	(9)p.8,9
			P,	7.90 8.05	M.P. 326°	(12)p.26,27
			Br,	20.35 20.48	η = 0.013	
Allylmethallyl-diphenyl Br	AIBN	96	$(C_{19}H_{22}PBr \cdot H_2O)_n$:		Soft. 240°	(9)p.8,9
			P,	8.19 7.90	M.P. 270°	(12)p.26,27
			Br,	21.10 20.68	η = 0.038	
Di-3-butenyl-diphenyl Br						
Vinyl-3-butenyl-diphenyl Br						
Allylvinyldiphenyl Br	AIBN					(14)p.6

a. t-BHP = tert-Butylhydroperoxide
b. AIBN = Azo-di-iso-butyronitrile
c. BP = Benzoylperoxide

Table VI

Physical Properties, Analytical Data and Yields of Unsaturated Phosphine Oxides

Phosphine Oxide	Physical Properties	Analysis	Yield %	Ref.
Diallylphenyl	M.P. 42.5	Calcd. for $C_{12}H_{15}OP$: C, 69.90; H, 7.28; P, 15.05 Found: C, 69.87; H, 7.40; P, 14.89	56	(4)p.11 (5)p.6 (24)
Dimethallylphenyl	B.P. 156–61/3mm	$C_{14}H_{19}OP$: C, 71.79; H, 8.11; P, 13.24 C, 71.89; H, 8.39; P, 13.01	47	(4)p.11 (5)p.6 (24)
Diallylmethyl	B.P. 145–52/1–3mm n_D^{22} 1.4870		43	(4)p.12 (3)p.7,8
Diallylethyl	B.P. 148–52/1–2mm n_D^{24} 1.4846		42	(4)p.14 (3)p.8,9
Dimethallylmethyl	B.P. 135–41/2mm	$C_9H_{17}OP$: C, 62.79; H, 9.88; P, 18.02 C, 62.56; H, 9.82; P, 17.98	57	(8)p.11 (4)p.13 (25) (27)p.19
Dimethallylethyl	B.P. 115–18/0.3mm	$C_{10}H_{19}OP$: C, 64.51; H, 10.21; P, 16.66 C, 64.49; H, 10.32; P, 16.46	43	(8)p.11 (7)p.4 (25)
Divinylphenyl	B.P. 133–36/0.75mm		37	(9)p.10 (12)p.20
Diphenylvinyl	M.P. 115–17	$C_{14}H_{13}OP$: C, 73.66; H, 5.70; P, 13.59 C, 73.40; H, 5.88; P, 13.60	48	(9)p.11 (12)p.21 (26)
Phenylcyclopenta–methylene	M.P. 128–29	$C_{11}H_{15}OP$: C, 68.04; H, 7.71; P, 15.97 C, 68.22; H, 7.79; P, 15.73	9	(8)p.12

phosphine oxide. The highest conversions of the trialkylphosphine oxides to soluble polymers were obtained by using azobisisobutyronitrile (5%) at a temperature of 110°. That poly(dimethallylmethylphosphine oxide) was not of high molecular weight was inferred by a low value (0.042) for its intrinsic viscosity. Infrared data demonstrated the existence of a small amount of residual unsaturation.

The small conversions of monomers with azobisisobutyronitrile as well as the negative results with benzoyl peroxide can probably be explained in part as another example of degradative chain transfer.

Diphenylvinylphosphine oxide was polymerized in presence of free radical initiators either in bulk or in solution. The polymer is soluble in dimethylformamide and alcohol, and one sample (M.P. 220-242°) in alcohol gave a value of 0.047 for its intrinsic viscosity.

Polyphosphine oxides have also been prepared by reaction of polyphosphonium salts with sodium hydroxide. When poly-(diallyldiphenylphosphonium bromide) was treated, a phenyl anion was lost. The product of the reaction was poly-(diallylphenylphosphine oxide). No reliable analysis could be obtained for this product. Poly-(diallylphenylphosphine oxide) had been prepared by the free radical polymerization of diallylphenylphosphine oxide.[24] It was found that it also was difficult to obtain an acceptable analysis on the polymer obtained in this manner. The infrared spectrum of the poly-phosphine oxide prepared by hydroxide degradation was identical with the spectrum obtained by Berlin.[24]

When poly-(diallylphenylethylphosphonium bromide) was degraded by this method, the product was found to be poly-(diallylethylphosphine oxide). The phenyl radical was eliminated rather than the ethyl radical due to its greater stability. Again, analyses obtained for the product were inconclusive. An examination of the infrared spectrum showed a strong absorption at 1180 $cm.^{-1}$ for the phosphoryl group. No absorptions appeared in the spectrum which could be assigned to the phenyl group. The spectrum was very similar in other respects to the spectrum of poly-(diallylphenylphosphine oxide).

The intrinsic viscosities of the polyphosphine oxides were considerably larger than the intrinsic viscosities of the poly-phosphonium bromides from which they were prepared, as was mentioned earlier. The intrinsic viscosity found for poly-(diallylphenylphosphine oxide) prepared by degradation was 0.109. Berlin[24] reported an intrinsic viscosity of 0.026 for the same polymer produced by the polymerization of diallylphenylphosphine oxide. It appears that the phosphonium bromide polymerized to give a product having a considerably greater degree of polymerization than the corresponding oxide.

The poly-phosphine oxides produced by both methods appear to be identical except for chain length. This is considered to constitute an alternate synthesis of this cyclic polymer and lends support, along with other evidence presented, to the theory of cyclic polymerization of 1,6-diolefinic phosphonium bromides.

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Table VII

Physical Properties, Analytical Data and Yields of Phosphine Oxide Polymers

Phosphine Oxide Polymers	Initiator	Yield %	Analysis Calculated for:		Found:	Polymer Properties	References
Diallylphenyl	t-BHP[a] NaOH on Diallyl-diphenylphos-phonium Br	20-30	$C_{12}H_{15}OP$:	C, 69.90 H, 7.28 P, 15.05	68.98 7.15 14.05	M.R. 90-115 η = 0.026 MW = 28,000 M.R. 250°;n = 0.109	(3)p.9,10,(24) (4)p.14 (9)p.8,(10)p.3
Dimethallyl-phenyl	BP[b] AIBN[c]	11	$C_{14}H_{19}OP$:	P, 13.24	12.96	M.R. 130-165 η = 0.04	(8)p.13,(24) (4)p.15,(27)p.19
Diallylmethyl							
Diallylethyl	NaOH on Diallylphenyl-ethylphosphonium Br					M.R. 192-310 η = 0.103	(6)p.3 (12)p.24-25
Dimethallyl-methyl	AIBN	15	$(C_9H_{17}OP\cdot H_2O)_n$:	C, 59.99 H, 10.55	59.95 10.01	M.R. 162-170 η = 0.042	(7)p.5,(25) (8)p.13 (5)p.7
Dimethallyl-ethyl	AIBN	5	$(C_{10}H_{19}OP\cdot H_2O)_n$:	C, 58.82 H, 9.31 P, 14.21	59.17 9.99 13.18	M.R. 165-185	(8)p.13-14 (25)
Divinylphenyl Copolymer with Malaic Anhydride	AIBN	15				White solid	(12)p.24
Diphenylvinyl	AIBN t-BHP	Quant.	$(C_{14}H_{13}OP\cdot H_2O)_n$:	C, 68.29 H, 6.09 P, 12.60	67.85 5.99 11.79	M.R. 220-224 η = 0.047	(9)p.13 (12)p.23, (26)

a. t-BHP = t-Butyl hydroperoxide
b. BP = Benzoyl peroxide
c. AIBN = Azo-isobutyronitrile

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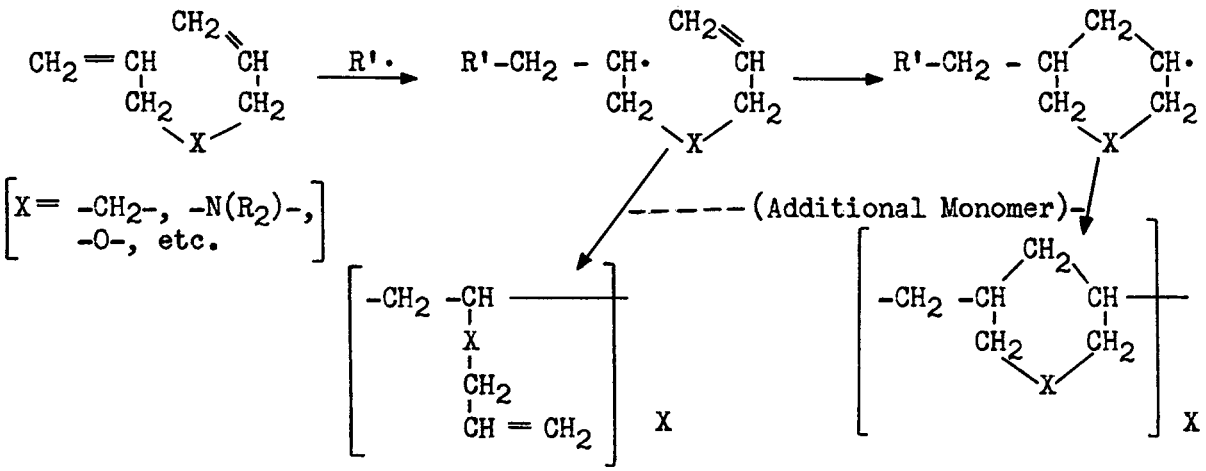
POLYMERIZATION OF NON-CONJUGATED DIOLEFINS

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I. INTRODUCTION

The concept of alternating inter-intramolecular propagation (cyclopolymerization) occurring during the polymerization of certain non-conjugated diolefins, as first discovered by Butler (1) (2), has become a subject of considerable interest (3) (4). During the past one to two years our laboratory has carried on a research program in an effort to achieve two main objectives: (a) to elucidate more fully the nature of the cyclopolymerization mechanism and (b) to extend the boundries of the known scope of the reaction to obtain additional new and/or unique structures. This paper describes work in both of these areas. In the first section a summary is given of our efforts and those of others, to elucidate, more completely, the reaction mechanism. In the second section some experimental studies are reported on a cyclopolymerization process which occurs in the solid state.

Basically the inter-intramolecular propagation reaction may be illustrated as:



II. CYCLOPOLYMERIZATION IN SOLUTION

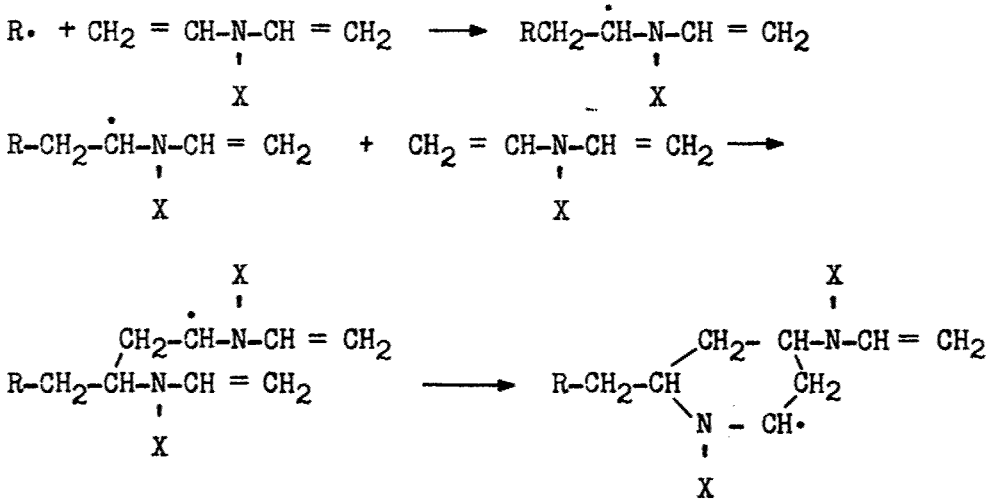
The detailed kinetics of cyclopolymerization have not been reported in the literature. The following scheme is set forth to describe free radical initiated reactions which may take place and to evaluate the rate expression obtained when various methods of chain termination are postulated which appear to be applicable.

Type	Reaction	Rate Constant	Reaction
Initiator Decomposition:	$A_2 \rightarrow 2A\cdot$	k_d	(a)
Chain Initiation:	$A\cdot + M_1 \rightarrow M_1\cdot$	k_I	(b)

Type	Reaction	Rate Constant	Reaction
Chain Propagation:	$M_1\cdot + M_1 \rightarrow M_1\cdot$	k_{11}	(c)
(cyclization)	$M_1\cdot \rightarrow M_2\cdot$	k_c	(d)
	$M_2\cdot + M_1 \rightarrow M_1\cdot$	k_{21}	(e)
(crosslinking)	$M_1\cdot + M_3 \rightarrow M_3\cdot$	k_{13}	(f)
(crosslinking)	$M_2\cdot + M_3 \rightarrow M_3\cdot$	k_{23}	(g)
(crosslinking)	$M_3\cdot + M_3 \rightarrow M_3\cdot$	k_{33}	(h)
	$M_3\cdot + M_1 \rightarrow M_1\cdot$	k_{31}	(i)
Chain Termination:	$2M_1\cdot \longrightarrow$	k^{11}	(j)
	$2M_2\cdot \longrightarrow$	k^{22}	(k)
	$M_1\cdot + M_2\cdot \longrightarrow$	k^{21}	(l)
	$M_3\cdot + M_1\cdot \longrightarrow$	k^{31}	(m)
	$M_3\cdot + M_2\cdot \longrightarrow$	k^{32}	(n)
	$2M_3\cdot \longrightarrow$	k^{33}	(o)

In the above treatment, M_1 is either double-bond of the previously unreacted diolefinic monomer, $M_1\cdot$ is the unsaturated radical produced directly from M_1, $M_2\cdot$ is the cyclized radical, M_3 is a pendant double-bond and $M_3\cdot$ is the pendant radical from M_3. It may be noted that the radical $M_1\cdot$ also contains a double-bond. The formation of M_3 is by reactions (c) and (f) as well as by (j), (l), and (m).

One series of reactions is not represented in the scheme which may be of considerable consequence when the diolefin is capable of forming only a four or five membered ring. This may be illustrated as:



This resulting cyclic radical may possibly react intramolecularly once again to give a bicyclo radical or it may attach monomer directly, leaving residual unsaturation in the polymer. This series of reactions is not treated in the following discussion.

The disappearance of carbon-carbon double-bonds (DB) in the systems of interest here may be written formally as

$$-d(DB)/dt = k_{11}(M_1\cdot)(M_1) + k_c(M_1\cdot) + k_{13}(M_1\cdot)(M_3) + k_{33}(M_3\cdot)(M_3) + k_{21}(M_2\cdot)(M_1), \quad (1)$$

following the usual procedures of neglecting the monomer consumed in the initiation reaction (b) for reasonably long kinetic chains. Since crosslinking represents only a minor disappearance of double-bonds, further dimplification results from neglecting the double-bonds consumed in crosslinking reactions (f), (g), and (h).

$$-d(DB)/dt = k_{11}(M_1\cdot)\ (M_1) + k_c(M_1\cdot) + k_{21}(M_2\cdot)(M_1) \quad (2)$$

Furthermore, for a monomer capable of undergoing essentially complete cyclization, reaction (c) is rare, hence:

$$-d(DB)/dt = k_c(M_1\cdot) + k_{21}(M_2\cdot)(M_1) \quad (3)$$

Following conventions established in treatment of copolymerization kinetics, the steady-state relationships may be listed as:

$$d(M_1\cdot)/dt = k_{21}(M_2\cdot)(M_1) - k_c(M_1\cdot) = 0 \quad (4)$$

$$d(M_2\cdot)/dt = k_c(M_1\cdot) - k_{21}(M_2\cdot)(M_1) = 0 \quad (5)$$

Hence: $$(M_2\cdot) = k_c(M_1\cdot)/k_{21}(M_1) \quad (6)$$

Therefore, equation (3) may be written as:

$$-d(DB)/dt = 2k_c(M_1\cdot) = 2k_{21}(M_1)(M_2\cdot) \quad (7)$$

In this system there are three main methods possible for radical chain termination. These involve (A) termination by interaction of two cyclized radicals ($M_2\cdot$), (B) termination by interaction of two non-cyclized radicals ($M_1\cdot$), and (C) crossed termination.

(A) Termination Involving Only ($M_2\cdot$) Radical Interaction

Following usual procedures of equating the formation and termination of chain radicals:

$$k_I(A\cdot)(M_1) = 2k^{22}(M_2\cdot)^2 \quad (8)$$

Hence: $$(M_2\cdot) = ((A\cdot)(M_1)k_I/2k^{22})^{\frac{1}{2}} \quad (8a)$$

From the steady state assumption

$$d(A\cdot)/dt = 2fk_d(A_2) - k_I(A\cdot)(M_1) = 0 \quad (9)$$

or $$(A\cdot) = 2fk_d(A_2)/k_I(M_1) \quad (9a)$$

Thus equation (8a) becomes

$$(M_2\cdot) = (fk_d(A_2)/k^{22})^{\frac{1}{2}} \quad (8b)$$

and substitution of $M_2\cdot$ into equation (7) gives the following rate expression:

$$-d(DB)/dt = 2k_{21}(M_1)(fk_d(A_2)/k^{22})^{\frac{1}{2}} \quad (10)$$

(B) Termination Involving Only ($M_1\cdot$) Radical Interaction

Following a procedure similar to that used in (A) above:

$$k_I(A\cdot)(M_1) = 2k^{11}(M_1\cdot)^2 \quad (11)$$

Hence: $$(M_1\cdot) = ((A\cdot)\ (M_1)k_I/2k^{11})^{\frac{1}{2}} \quad (11a)$$

Utilizing the expression for $(A\cdot)$ from equation (9a) above, equation (11a) becomes:

$$(M_1\cdot) = (fk_d(A_2)/k^{11})^{\frac{1}{2}} \quad (11b)$$

Therefore, termination by only $M_1\cdot$ leads to a rate expression independent of monomer concentration:

$$-d(DB)/dt = 2k_c(fk_d(A_2)/k^{11})^{\frac{1}{2}} \quad (12)$$

(C) Termination Involving Only Unlike Radical Interaction

For the case of termination by inaction of $M_1\cdot$ and $M_2\cdot$ as depicted by reaction (1) of the kinetic scheme:

$$k_I(A\cdot)\ (M_1) = 2k^{21}(M_2\cdot)(M_1\cdot) \quad (13)$$

From equation (6) and (13) it follows that

$$k_I(A\cdot)(M_1) = 2k^{21}k_c(M_1\cdot)^2/k_{21}(M_1)$$

or $$(M_1\cdot) = (k_{21}k_I(A\cdot)(M_1)^2/2k^{21}k_c)^{\frac{1}{2}} \quad (14)$$

Equation (9a) is again employed to remove $(A\cdot)$. Thus, equation (14) may be expressed as follows:

$$(M_1\cdot) = (k_{21}fk_d(A_2)(M_1)/k^{21}k_c)^{\frac{1}{2}} \quad (15)$$

This expression for $(M_1\cdot)$, when substituted into equation (7) gives the following rate equation for disappearance of double bonds:

$$-d(DB)/dt = 2(k_ck_{21}fk_d(A_2)(M_1)/k^{21})^{\frac{1}{2}} \quad (16)$$

It may be noted that the derived rate expressions, (10), (12) and (16), differ markedly with regard to dependence upon monomer concentration for the various termination mechanisms listed. The bimolecular termination of the cyclized ($M_2\cdot$) radicals leads to an expression with a first-order dependence on monomer concentration (eq. 10); the bimolecular termination of the non-cyclized ($M_1\cdot$) radicals leads to a non-dependence of rate on monomer concentration (eq. 12);

whereas the crossed-termination mechanism yields a square-root dependence of rate upon monomer (eq. 16). All rate expressions show a square-root dependence upon initiator concentration.

Other interesting relationships may be derived from a further consideration of copolymerization type treatments. For example, when comparing the relative rates of formation of various structures in the polymer:

$$d(M_1)/dt = k_{11}(M_1\cdot)(M_1) + k_{21}(M_2\cdot)(M_1) \quad (17)$$

$$= (M_1\cdot)(M_1)(k_{11} + k_c/(M_1)) \quad (17a)$$

$$d(M_3)/dt = k_{11}(M_1\cdot)(M_1) \quad (18)$$

$$d(M_1)/d(M_3) = 1 + (k_c/k_{11})(1/(M_1)) \quad (19)$$

The conditions under which these expressions are valid are relatively high dilution of monomer and low conversion of monomer to polymer. Under these conditions reactions of (M_3) and $(M_3\cdot)$ may be safely disregarded. In addition, since the conversions are low, the actual polymer composition may be used as the differential ratio:

$$m_1/m_3 = 1 + (k_c/k_{11})(1/(M_1)) \quad (20)$$

Therefore, from the concentration of pendant groups in the polymer and the total weight of polymer, one may evaluate the k_c/k_{11} ratio.

Mercier and Smets[5] have reported a measurement of k_c/k_p (units unspecified) where k_p is probably the same as k_{11} here for acrylic anhydride in cyclohexanone at 35°C. The k_c/k_p ratio was 0.17. In addition, they report an activation energy for cyclization 2.4 kcal./mole higher than that of propogation.

The experimental work in our laboratory has been concerned with the cyclopolymerization of methacrylic anhydride (MA). Some of the results of this work have been reported[6]. This monomer was known to yield high molecular weight polymer by a cyclopolymerization process[7]. In addition, some information was available on the properties of its hydrolysis product, poly(methacrylic acid).

Figure 1 illustrates a typical reaction rate curve obtained in this work. A linear conversion-time curve was observed from 1-2% conversion up to at least 15-20% conversion, so no ambiguities were involved in calculation of the rate data.

The variation of R_p with initial monomer concentration, observed at six monomer concentrations covering nearly a twenty-fold range, was found to vary as the 3/2 power of the monomer concentration (see Figure 2). At the highest initial monomer concentration used (4.799 moles/liter), which is not shown on this plot, R_p was observed to be higher than would be predicted from this relation.

A 3/2 power dependency has been previously observed to occur when the efficiency of initiation is low[8] (i.e., the styrene-benzoyl peroxide system in benzene)[9], although methyl methacrylate, a monomer which one might expect to

more closely resemble MA, does show ideal behavior with AIBN[10]. The kinetic scheme presented earlier does not offer any other basis than low efficiency of initiation to account for the 3/2 order in monomer found.

The variation of R_p with initiator concentration was observed to obey the square-root law over a sixteen-fold change in initial initiator concentration. This is illustrated in Figure 3.

A consideration of the kinetic schemes presented earlier also leads to various relationships for the activation energies of the several processes occurring in cyclopolymerization. Assuming that the sole process of chain termination is the bimolecular termination of $M_2\cdot$ radicals the overall activation energy (E_T) is related to the activation energies for: initiator decomposition (E_d); the reaction of $M_2\cdot$ with M_1 (E_{21}); and chain termination E^{22} by:

$$E_T = E_d/2 + (E_{21} - E^{22}/2) \qquad (21)$$

This may be compared with the equation obtained for vinyl polymerization[11]:

$$E_T = E_d/2 + (E_p - E_t/2) \qquad (22)$$

In order to determine the overall activation energy in cyclopolymerization, measurements of the R_p values of MA in DMF were carried out in the temperature range between 35 and 50°C. In addition, a study was also made with methacrylic acid. The logarithm of R_p values of both these systems are plotted versus 1/T in Figure 4. The values calculated from the slopes of these curves are given in Table 1, along with values available in the literature for methyl methacrylate, styrene, and butadiene.

TABLE 1

ACTIVATION ENERGIES FOR METHACRYLIC ANHYDRIDE AND METHACRYLIC ACID

Monomer	E_T(*)	$E_d/2$(*)	$(E_p-E_t/2)$(*)
Methacrylic Anhydride	23.0	15	8.0
Methacrylic Acid	24.8	15	9.8
Methyl Methacrylate(17)	--	--	5.0
Styrene (18)	--	--	6.5
Butadiene (19)	--	--	9.8 - $E_t/2$

*Units of kcal/mole

It is obvious from Table 1 that the E_T terms for MA and methacrylic acid (the latter chosen because it bears a very strong resemblance to one half of a MA monomer) are very close together--almost within experimental error. Significantly, (the E_p-$E_t/2$) values for both MA and methacrylic acid are in the proximity of, however slightly higher than, values for other typical monomers. These data would suggest that there is very little, if any, difference in the energetics for inter-inter- and inter-intramolecular propagation. This is in opposition to previously reached conclusions based upon data obtained with allylsilanes[12].

Mikulasova and Hrivik[12] compared the bulk polymerization of monoallyltrimethylsilane and diallyldimethylsilane by t-butyl peroxide and reported apparent overall activation energies (E_T) of 35 and 50 kcal/mole, respectively. These authors did not acknowledge the possibility of cyclopolymerization occurring with the diallyl monomer, although this is known to be the case when Ziegler type catalysts are used[13][14]. Making the likely assumption that cyclization does occur with the diallyl silane monomer and that effective termination in both cases is first order in radical concentration, Mikulasova and Hrivik[12] report that the R_p values for both monomers were functions of the first power of the initiator concentration, the simplest expression for the activation energies would be:

$$E_T = E_d + E_p - E_t \qquad (23)$$

where the subscripts have the same meaning as before. For the diallyl silane monomer, however, E_p is E_{21} as in the case of MA (reaction (e) in kinetic scheme). Based on the variation in R_p or degree of polymerization with temperature for these allylic systems, it is possible to calculate various activation energies. These values are given in Table 2. The values of (E_p-E_t) from the variation in

TABLE 2

POLYMERIZATION OF MONO- AND DI-ALLYLMETHYLSILANES				
Activation Energies of Silanes	Observed[a]	Calculated[b]		Calculated[c]
	E_T	E_d*	E_p-E_t	E_p-E_t
Monoallyltrimethyl-	35	38	-3	3.7
Diallyldimethyl-	50	38	12	12.6

(a) Mikulasava and Hrivik[12].
(b) Assuming that $E_T = E_d + E_p-E_t$ (Eq. 23) applies.
(c) From the $\overline{P}_n(=k_p/k_t)$ vs. T data of Mikulasova and Hrivik[12].
* From the data of Lossing and Tickner (gas phase)[15].

molecular weight are believed more reliable for the monoallyl silane monomer than those based on the rate measurements. This is due to the fact that the degree of polymerization gives directly the ratio k_p/k_t whereas rate measurements are more complicated in these cases.

It may be noted that the E_p-E_t terms are considerably different for the two silane monomers. The E_p-E_t term for the cyclopolymerizing monomer is about 3.5 times greater than for the monoallyl silane monomer.

In our work with the methacrylic acid and anhydride pair this large difference is not obtained. Some preliminary data obtained in our laboratory on the dimethyl - 2,2' - dimethylenepimelate system (which also undergoes cyclopolymerization) indicates an overall activation energy comparable to methyl methacrylate.

To our way of thinking it is not too surprising that no large differences in activation energies are found between mono vinyl polymerization and

the cyclopolymerization systems we have examined. The difference between the alternating inter-intra and the usual inter-inter types of polymerization is the occurrence of intramolecular cyclization in the former. The ring formation reaction step involves a very specific orientation for the radical and double-bond. As with most reactions which involve such a rigid transition state, the reaction should take place with a significant decrease in entropy. This should result, therefore, in a markedly different frequency term for the intramolecular step as compared with the intermolecular step.

Occasionally IR spectra of poly(MA) revealed relatively small amounts of residual unsaturation, although attempts to accurately determine these amounts were not satisfactory for quantitative conclusions.

To obtain more information on the contribution of the inter-inter reaction in the polymerization of MA, the intrinsic viscosities of polymers formed at varying stages in the polymerization were examined. At high enough concentration, unsaturated pendant groups in the polymer, would be expected to participate in crosslinking to a detectable degree. Since the intrinsic viscosity is more sensitive to the higher molecular weight species present, and the higher molecular weight species are more subject to crosslinking (on a molecule to molecule basis), a convenient and sensitive measure of the occurrence of crosslinking was afforded by intrinsic viscosity-conversion measurements. Such measurements were carried out at 40.0°C at three initial monomer/solvent ratios: 17.0/83.0, 34.9/65.1 and 50.0/50.0, by weight. The data obtained are given in Table 3.

TABLE 3

INTRINSIC VISCOSITY - CONVERSION DATA FOR METHACRYLIC ANHYDRIDE

Monomer Concentration (%)	Conversion (%)	$[\eta]$ (dl/g)
17.0	6.2	1.04
	12.2	1.04
	17.9	1.03
	20.7	0.99
34.9	6.2	1.4
	17.4	0.8
	24.1	2.2
	27.3	1.1
	37.1	3.0
50.0	7.0	0.36
	11.6	0.56
	12.7	0.52
	16.6	0.50

At the lowest initial monomer level, the intrinsic viscosity data is essentially constant, at least as far as the highest conversion point recorded (20.7 percent). The polymer was completely soluble in DMF. At 34.9 percent monomer gel was detected in all samples taken. These data show a wide variation between 0.8 and 3.0 dl·/g·. At 50.0 percent monomer concentration the intrinsic

viscosities are all lower than those at 17.0 or 34.9 percent, but appear to have a much smaller overall variation than at 34.9 percent. Gel was present in these samples as well.

The data suggest, as might be expected, that the concentration of monomer markedly affects the course of the reaction. This would be expected on two accounts. Firstly, at low monomer concentrations, the intramolecular reaction is given a greater time interval in which to occur. Secondly, at low monomer concentrations there is the possibility of forming highly branched structures which are still soluble via the crosslinking reaction[16]. The data obtained at 17 percent monomer, however, indicate that the molecular weight of the polymer formed is essentially constant. Hence, the branching is probably negligible at the dilution.

III. CYCLOPOLYMERIZATION IN THE SOLID STATE

Inter-intramolecular polymerization in the solid state was also investigated in our laboratory[17]. The non-conjugated diolefin used in this study was N,N-diallylmelamine (DAM), m.p., 140-1°C.

Although several studies of solid state polymerizations had appeared in the literature, evidence that cyclopolymerization could occur in the solid state had not been reported. Comprehensive studies of vinyl polymerizations of acrylamide have appeared[18][19].

Solid state polymerizations of DAM were carried out in our laboratory by irradiating evacuated ampules containing monomer in a Co^{60} source and subsequently thermostatting the unopened samples at various constant temperatures for various time intervals. Polymers were then isolated by gravimetric precipitation techniques.

The general effects of varying conditions upon percent conversion to polymer can be observed in Table 4 for room temperature irradiations. In-source

TABLE 4

SOLID STATE POLYMERIZATION OF DAM

Run No.	Rads ($\times 10^{-5}$)	Post-Irradiation Treatment		Total Conversion(%)
		Time(Hrs)	Temp.(°C)	
1	7	24	50	1
2	7	120	50	2
3	7	120	60	3
4	290	120	50	54
5	560	96	60	92
6	360	0	—	48
7	"	24	65	66
8	"	24	85	71
9	"	48	65	76
10	"	48	85	82

polymerization occurs as evidenced by Run No. 6. By irradiating at liquid nitrogen temperature, in-source polymerization could be eliminated to permit the measurement solely of the post-irradiation reaction. The effect of varying thermostat temperatures for such reactions can be noted in Figure 5. The polymers were soluble in acids.

Soluble polymers were also obtained in DMSO solution using AIBN as initiator. Infrared spectra of these polymers indicated that they were identical with those produced in the solid state, but in order to dissolve the solid state polymers in DMSO the addition of dimethylsulfone was required. All polymers were insoluble in other common organic solvents, and they were essentially amorphous, as evidenced by X-ray diffraction examination. The intrinsity viscosities of several poly(DAM) samples were all found to be of a low order as is generally found for allylic polymerization products. Some effect of percent conversion upon the intrinsic viscosity values obtained for solid state polymers was observed.

Since the polymerization of DAM, solely by an inter-intramolecular propagation mechanism would involve the complete loss of unsaturation without producing crosslinks, studies to determine residual unsaturation in polymers were undertaken. IR studies were found to be the more useful in determining poly(DAM) structure than either microcatalytic hydrogenation or NMR analysis. Spectra of monomer, polymer and reduced monomer (N,N-di-n-propylmelamine) were compared. The most commonly used absorption regions for detecting carbon-carbon unsaturation[20] were complicated by characteristic absorptions of melamine. Our studies were therefore confined mainly to the 10-11μ region where two vinyl absorption peaks resulting from out-of-plane deformation vibrations are described near 10.1 and 11.0μ. Figure 6 illustrates the comparison of spectra where the loss of monomer unsaturation in the reduced monomer and the polymer spectra is observed. We have tentatively interpreted the splitting of the two vinyl bands of monomer in this region to be the result of non-equivalent positioning of allyl groups -- a steric influence.

The low level of residual unsaturation (5 mole percent or less), in conjunction with the solubility properties, would indicate that non-crosslinked, essentially linear polymers resulted from both solid state and solution reactions.

Light-scattering measurements were made on a polymer prepared in solution and a molecular weight of approximately 7,500 was obtained for the weight average molecular weight polymer. By assuming this to be the primary weight average molecular weight and by utilizing the relationships of Stockmeyer[21] (the presence of one crosslink per weight average molecule is sufficient to produce gelation or insolubility) one can expect the ratio of propagation to crosslinking to be at least 30, and perhaps significantly higher. This also lends support for concluding that if the crosslinking reaction occurs, its magnitude is of a relatively low order.

A comparison of the energetics of propagation between the cyclopolymerization mechanism of DAM and that of the vinyl polymerization of acrylamide[18][19] was of interest. Fadner and Morawetz[18] proposed a kinetic scheme for post-irradiation polymerization based upon the bimolecular termination of active chain end radicals (R):

$$-d(R)/dt = k_t(R)^2 \qquad (24)$$

where $(R) = (R_o)/(1 + k_t(R_o)t)$. (25)

Substituting this expression of (R) into the rate expression, $d(M)/dt \quad k_p(M)(R)$, the following rate equation was obtained:

$$-\ln(1-Y) = (k_p/k_t)\ln(1 + k_t(R_o)t) \quad (26)$$

where Y equals the weight fraction of polymer at time t; $-\ln(1-Y) = -\ln(M/M_o)$. These workers irradiated at low temperature to eliminate in-source polymerization. They found their experimental curves to be of the form suggested by equation(26), but nevertheless, they point out the inconsistency of such a simplified scheme in light of the fact that the radical concentration was found to decay more slowly than the rate of polymerization.

Fadner and Morawetz found the activation energy for post-irradiation polymerization of acrylamide to be 25 kcal/mole at 25-65°C. Our data on DAM, obtained by similar methods, gave a value of 15.5 ± 1.5 kcal/mole for the activation energy at 50-70°C. A plot of the data is shown in Figure 7.

Baysal, Adler, and coworkers(19) found the following expressions to adequately express their results for post-irradiation polymerizations of acrylamide, where irradiation was carried out at temperatures permitting in-source reaction:

$$-d(M)/dt = k_p(M)(R_o)$$

where $(R_o) = (R) =$ constant. Thus,

$$\ln((M_o)/(M)) = k_p(R_o)t$$

These workers(19) described in-source polymerization by:

$$-d(M)/dt = k_p k_i f I t(M)$$

Here, (R) is related to radiation intensity (I), an initiation rate constant (k_i), and an efficiency factor (f). Activation energies of 3 kcal/mole (in-source) and 10 kcal/mole (post-irradiation) were determined.

Although the complexities of solid state polymerization are not fully elucidated at this time, it does appear that cyclopolymerization is as energetically feasible as vinyl polymerization in the solid state.

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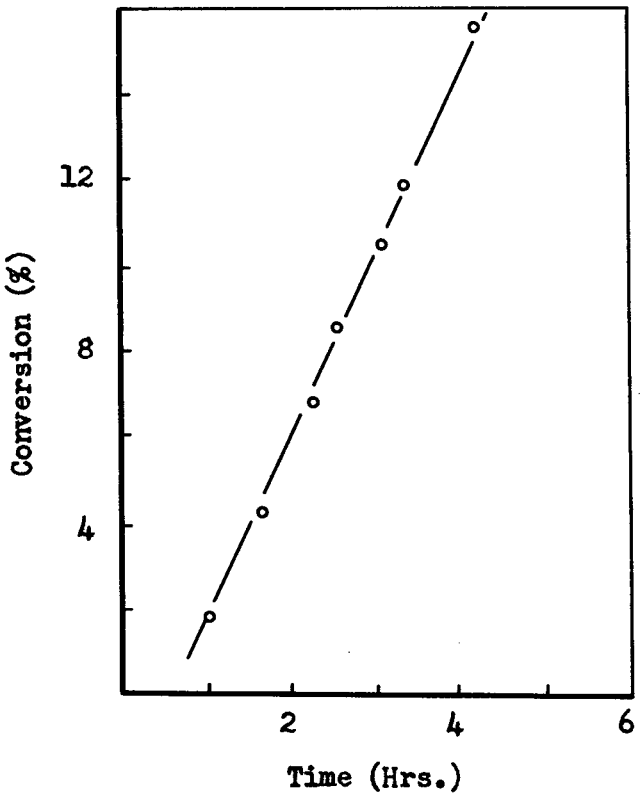


Figure 1. Methacrylic Anhydride Polymerization.

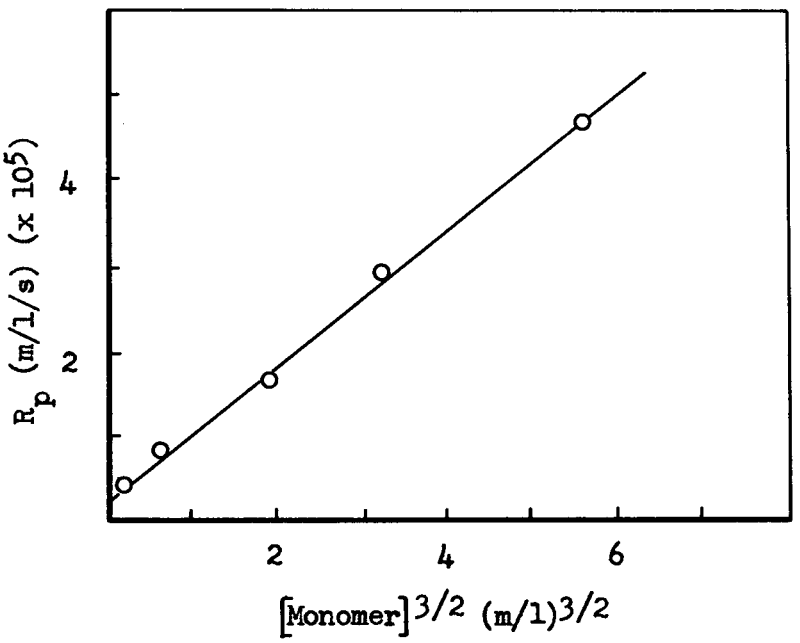


Figure 2. Variation of R_p with Methacrylic Anhydride Concentration.

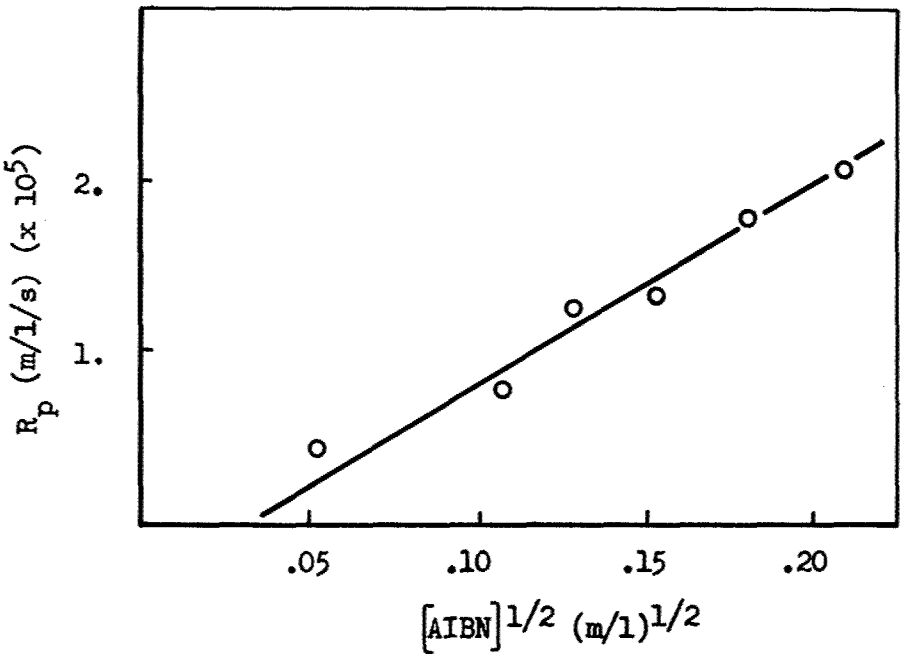


Figure 3. Variation of R_p with Initiator Concentration (AIBN).

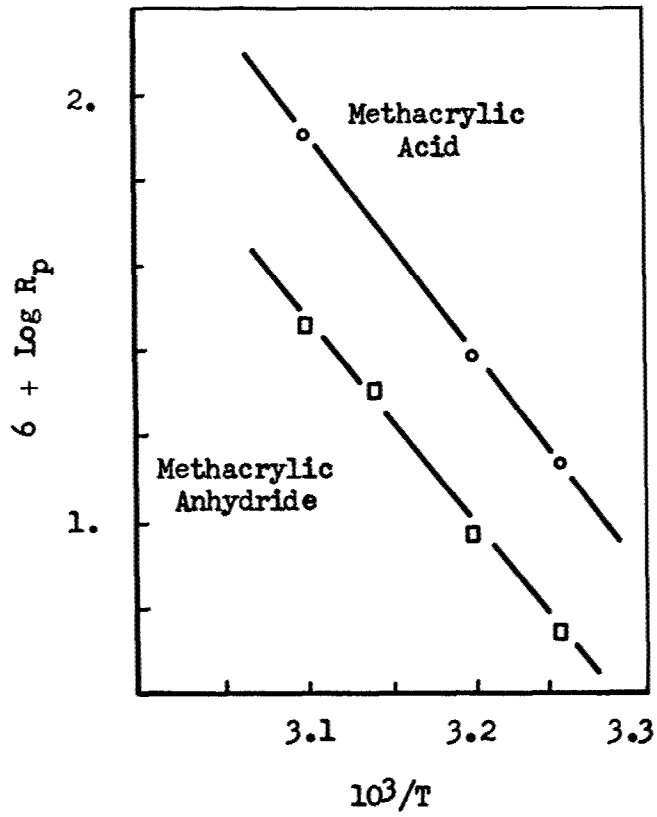


Figure 4. Arrhenius Plot for Methacrylic Acid and Methacrylic Anhydride.

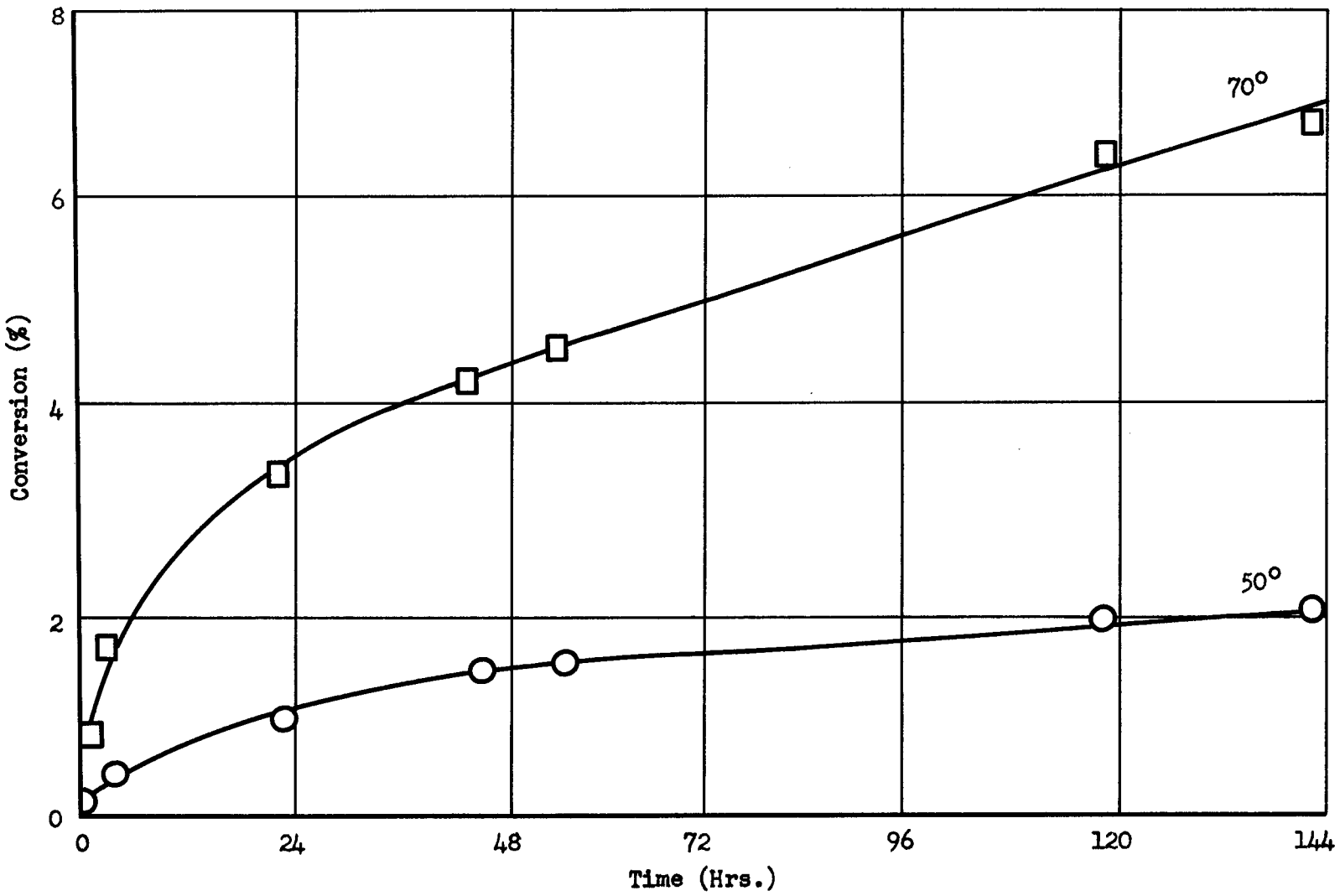


Figure 5. Effect of Time and Temperature upon Post-irradiation Conversion of DAM.

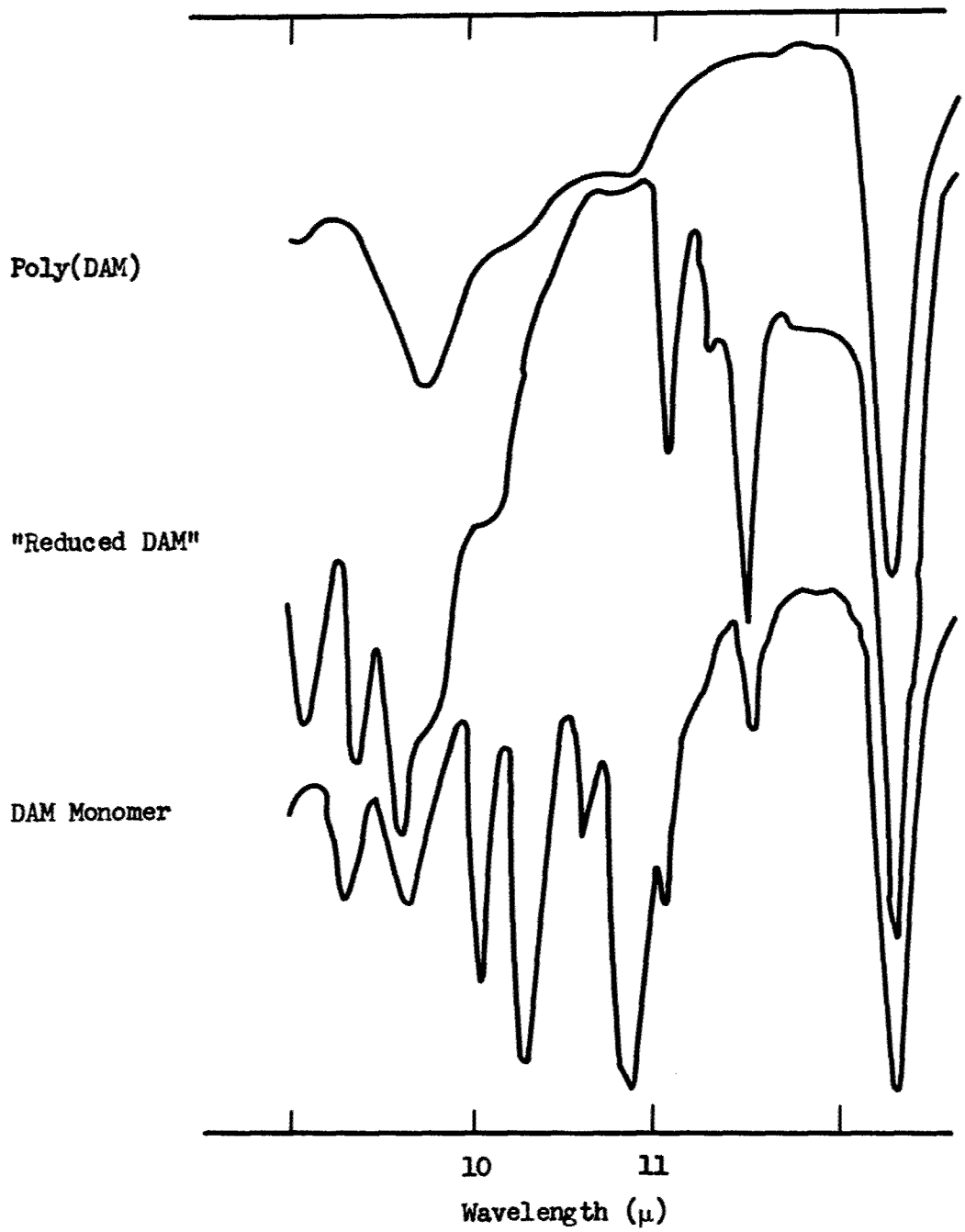


Figure 6. Comparison of IR Absorption Characteristics in 10-11 Micron Region.

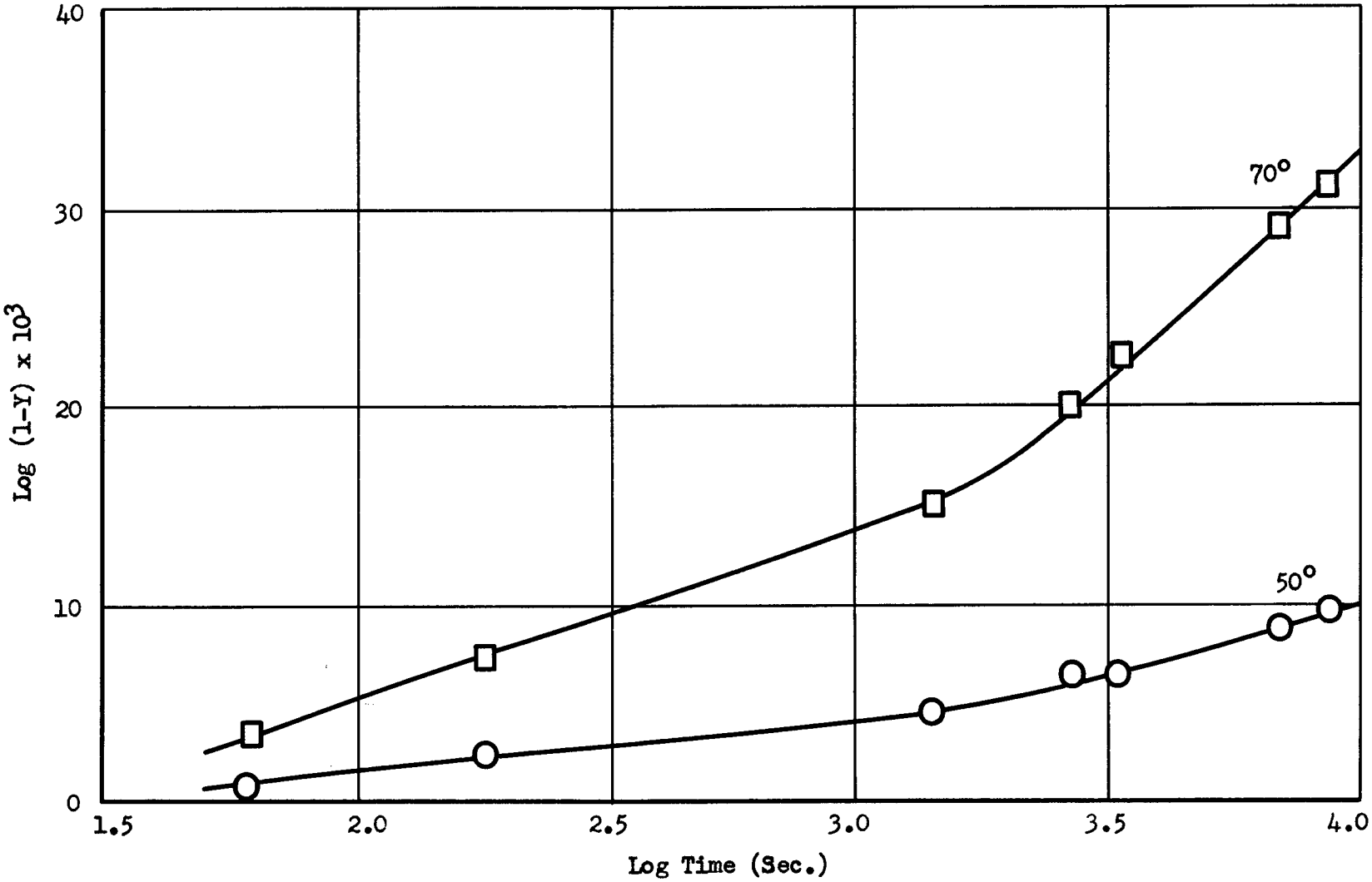
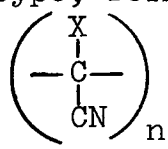


Figure 7. Post-irradiation Data Plotted According to Fadner and Morawetz (18).

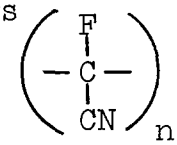
CYANOFLUOROCARBON POLYMERS

C. N. Matthews, R. M. Kliss and R. J. Wineman
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ABSTRACT

The purpose of this investigation is to synthesize cyanofluorocarbon polymers through the intermediate formation of cyanofluoromethylene FC(CN). Polymeric products were formed in reactions yielding cyanomethylenes XC(CN) under neutral or basic conditions. Where X = H, $COOC_2H_5$, Cl or F, polymeric cyanomethylenes were isolated as dimers (olefins), trimers (cyclopropanes) or solid brown-black polymers. The brown-black polymers are believed to have conjugated structures of the "black orlon" type, formed by cyclization of linear cyanomethylene polymers 

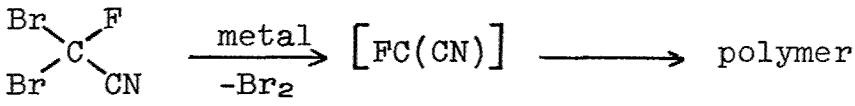
INTRODUCTION

The main aim of this research is to synthesize cyanofluorocarbon polymers  through the intermediate formation of cyanofluoromethylene FC(CN). Such polymers would be expected to be thermally stable because of the high dissociation energies[3] of C-F bonds (106 Kcals) and C-CN bonds (103 Kcals), and because fluorine atoms and nitrile groups would have exceptional covering power for a carbon skeleton.

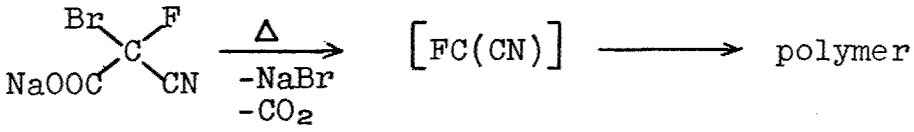
By analogy with the known diradical species propargylene[5], HC(C≡CH), the postulated divalent carbon intermediate FC(C≡N) should probably be regarded as a methylene[5] possessing diradical character (triplet state) rather than as a carbene (singlet state). Polymerization, including dimerization, of such cyanomethylenes would be expected under suitable conditions. Experiments were therefore directed toward forming cyanomethylenes XC(CN), where X = H, $COOC_2H_5$, Cl and F, under conditions that would give rise to polymers. Three known methods for forming divalent carbon intermediates were used, based on dehalogenation, decarboxylation, and dehydrohalogenation experiments. For the formation of cyanofluoro-

methylene the methods are represented by the following equations:

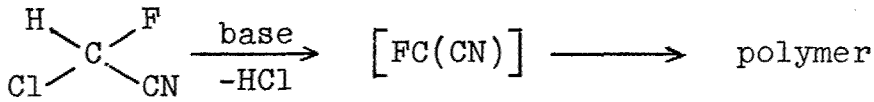
1. Dehalogenation of dibromofluoroacetonitrile[2].



2. Decarboxylation of sodium cyanobromofluoroacetate[9]



3. Dehydrohalogenation of chlorofluoroacetonitrile[4]

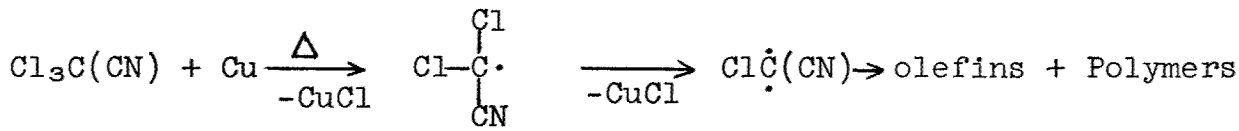


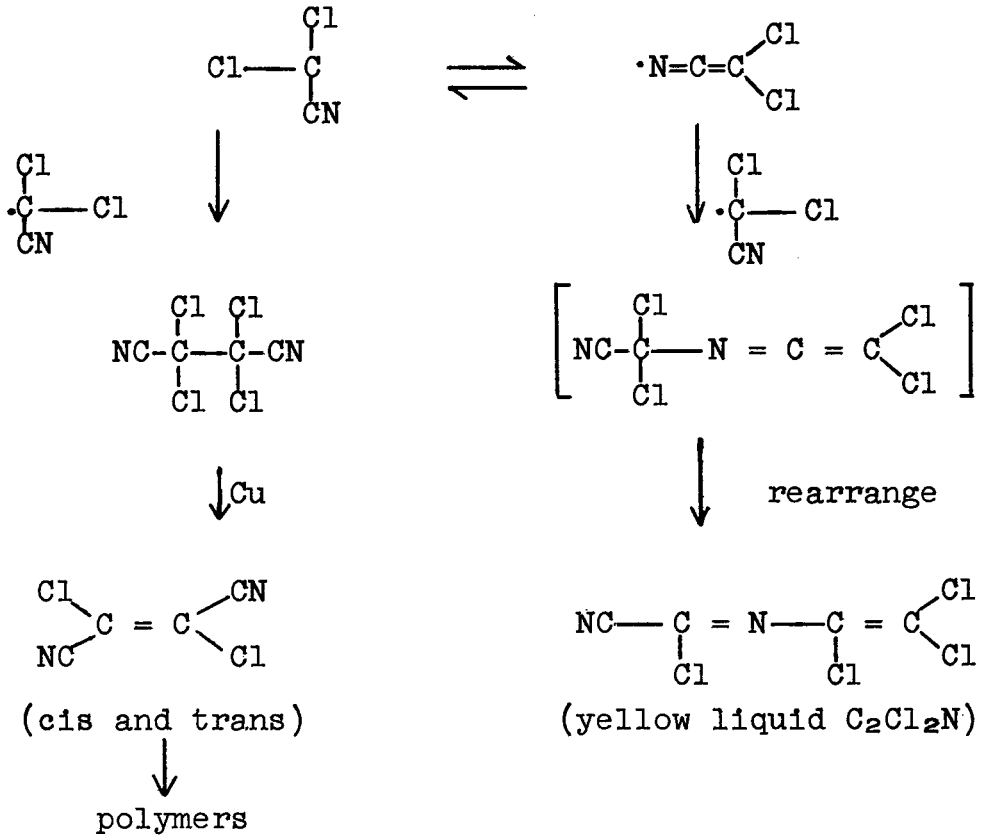
RESULTS AND DISCUSSION

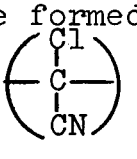
1. Dehalogenation Reactions

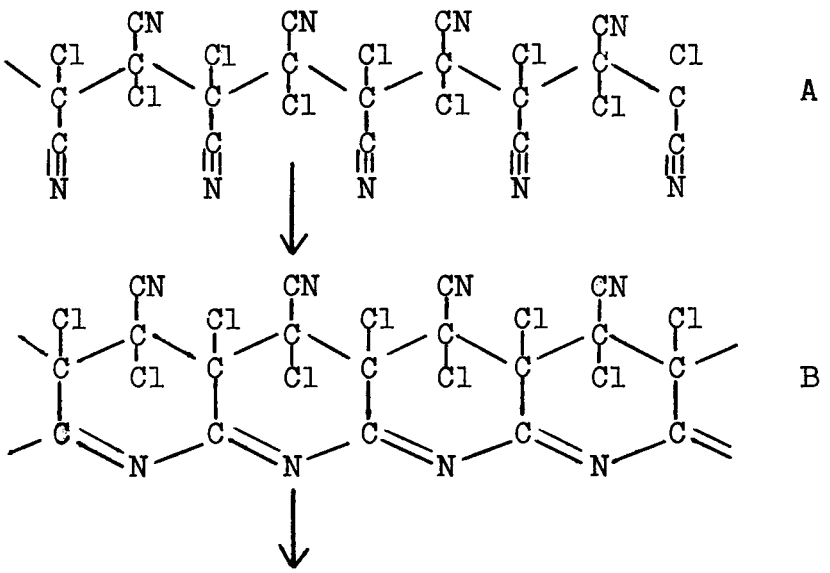
(a) Reactions of cyanohalomethanes with copper (no solvent) Refluxing of trichloroacetonitrile with finely divided copper yielded a mixture of products that were separated and characterized by elemental analysis and infrared spectroscopy. The products were cuprous chloride; a brown-black solid polymer, infusible and insoluble, with infrared spectrum bands at 3.0 μ (broad), 4.5 μ (sharp), and 6.2 μ (broad); tetrachlorosuccinonitrile; dichloromaleonitrile; dichlorofumaronitrile; and a yellow liquid C_2Cl_2N (bp 54°C/4.5 mm) with infrared spectrum bands at 4.46 μ, 4.50 μ, and 6.0-6.55 μ, believed to be NC-C(Cl)=N-C(Cl)=C(Cl)Cl.

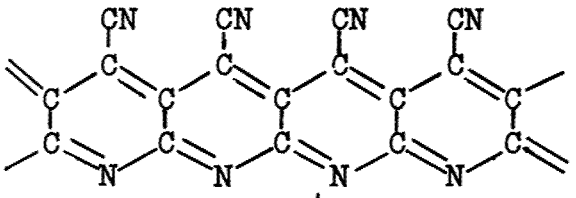
The products from this reaction suggest the formation of the dichlorocyanomethyl radical and its ketenimine form[7] as primary intermediates. Polymer formation could then occur as outlined below, or through the intermediate formation of cyanochloromethylene:



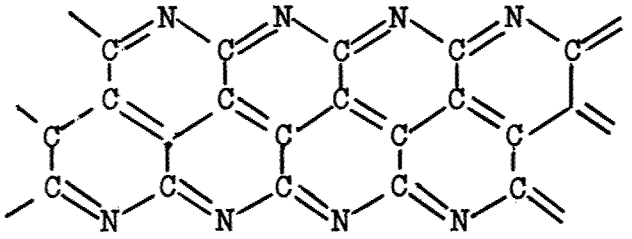


To explain the color of the brown-black polymeric material and its infrared spectrum it is proposed that conjugated structures of the "black orlon" type (B) are formed spontaneously from the linear polycyanochloromethylene  initially formed (A).





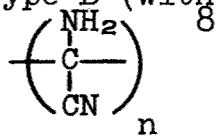
C



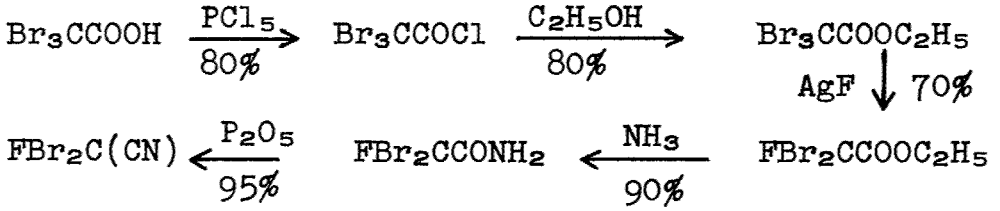
D

Further dechlorination could occur to give the doubly conjugated polymer C, which could undergo further cyclization to give the triply conjugated polymer D.

The infrared spectrum peak at 4.5 μ can be attributed to nitrile groups. The broad band at 6.2 μ can be attributed to >C=N- groups, while the broad band at 3.0 μ can be attributed to $-NH_2$ or =N-H groups, perhaps present as end groups. The infrared spectra[1] of "black orlon" structures of type B (with H replacing Cl and CN) possess broad bands in the regions 3.0 μ and 6.2 μ. Polymers closely resembling the brown-black solid in appearance and with very similar infrared spectra[8] have been obtained by the polymerization of hydrocyanic acid, and have been assigned structures of the type B (with Cl replaced by NH_2), derived from the linear polymer



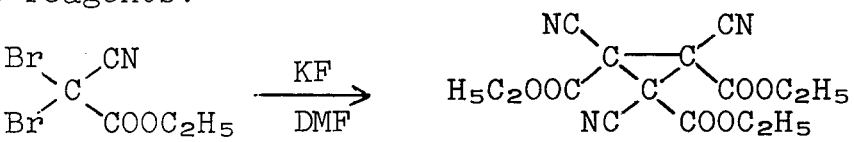
Reactions of dichloroacetonitrile and dibromoacetonitrile with copper have also yielded brown-black polymeric products at present being purified and characterized. Initial reactions of dibromofluoroacetonitrile with copper are being investigated. This cyanofluoromethylene precursor was synthesized by a five-step procedure starting with tribromoacetic acid:

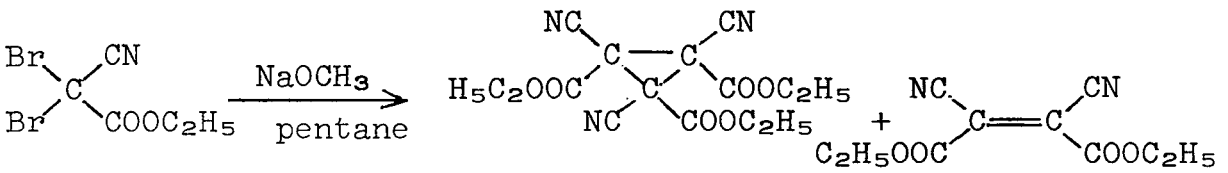


In general, the above results suggest that reactions of polyhalocyanomethanes with copper yield conjugated polymers formed by the cyclization of linear cyanomethylene polymers.

(b). Reactions of cyanohalomethanes with zinc-copper couple (in polar solvents). Reaction of trichloroacetonitrile or dibromoacetonitrile with zinc-copper couple[6] in refluxing tetrahydrofuran yielded brown-balck solid polymers, insoluble and infusible. The infrared spectra of the polymers resembled the spectra of the polymers obtained in the reactions with copper alone, with strong bands in the regions 3.0 μ, 4.5 μ and 6.2 μ. Metal complexing with the polymers occurs.

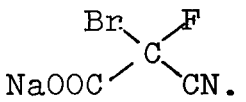
(c). Reactions of ethyldibromocyanoacetate with bases. Evidence for the formation of the cyanomethylene $(NC)C(COOC_2H_5)$ was obtained by isolating the dimer (olefin) and trimer (cyclopropane derivative) from reactions of ethyldibromocyanoacetate with basic reagents:



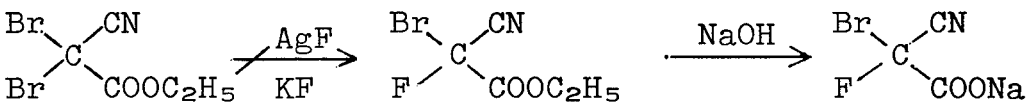


2. Decarboxylation Reactions

Unsuccessful attempts were made to synthesize sodium cyanobromofluoroacetate



Attempts to convert ethyldibromocyanoacetate to ethylcyanobromofluoroacetate by using silver fluoride or potassium fluoride under a variety of conditions were unsuccessful:



Attempts were made to form cyanofluoromethylene indirectly by decarboxylating sodium chlorodifluoroacetate in the presence of excess sodium cyanide:

$$ClF_2CCOONa \xrightarrow[DMF]{\Delta} [F_2C] + CO_2 + NaCl$$

$$[CF_2] \xrightarrow{CN^-} [F_2C(CN)]^- \longrightarrow F^- + [FC(CN)] \longrightarrow \left(-\underset{\displaystyle CN}{\overset{\displaystyle F}{\overset{|}{\underset{|}{C}}}}-\right)_n$$

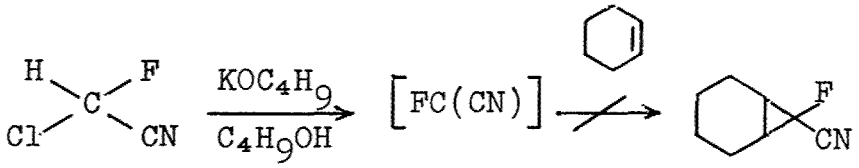
Brown-black polymeric solids were obtained with infrared spectra bands at 3.0 μ, 4.5 μ, and 6.2 μ, suggesting that conjugated "black orlon" types of structures had been formed.

3. Dehydrohalogenation Reactions

Chlorofluoroacetonitrile was prepared from 2-chloro-1,1,2-trifluoroethyl ethyl ether by the method of Young and Tarrant[10]:

$$H\text{-}\underset{F}{\overset{Cl}{C}}\text{-}\underset{F}{\overset{F}{C}}\text{-}OC_2H_5 \xrightarrow[60\%]{H_2SO_4} H\text{-}\underset{F}{\overset{Cl}{C}}\text{-}\underset{O}{C}\text{-}OC_2H_5 \xrightarrow[79\%]{NH_3} H\text{-}\underset{F}{\overset{Cl}{C}}\text{-}\underset{O}{C}\text{-}NH_2 \xrightarrow[39\%]{P_2O_5} H\text{-}\underset{F}{\overset{Cl}{C}}\text{-}CN$$

Reactions with potassium tert-butoxide in the presence of cyclohexene yielded mixed products, including chlorofluoroacetamide, but no cyclopropane derivatives:



A control experiment with bromoform[4] yielded dibromonorcarane (63%). With sodium methoxide (no solvent) at least twelve products were obtained (V.P.C.). Brown solids isolated from the alkoxide reactions are being characterized. Reactions of chlorofluoroacetonitrile with lithium butyl (in pentane at ~-50°C) in the presence of cyclohexene yielded mixtures of products (V.P.C.) but not cyclopropane derivatives.

These unsuccessful attempts to trap cyanofluoromethylene with olefins suggest that the methylene intermediate reacts rapidly as a radical with neighboring molecules to give a variety of products including polymers.

CONCLUSIONS

Polymeric products are formed from reactions yielding cyanomethylenes XC(CN) under neutral or basic conditions. Where X = H, $COOC_2H_5$, Cl or F, polymeric cyanomethylenes have been

isolated as dimers (olefins), trimers (cyclopropanes) or solid brown-black polymers. The brown-black polymers are believed to have conjugated structures of the "black orlon" type, formed by cyclization of linear cyanomethylene polymers $\left(-\underset{\underset{CN}{|}}{\overset{\overset{X}{|}}{C}}-\right)_n$.

Investigation of the synthesis, structure, and thermal stability of such polymers is in progress. Of special interest are the polymers derived from cyanofluoromethylene FC(CN).

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PHYSICAL CHEMISTRY OF POLYMERS IN DILUTE SOLUTION

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H. Nakayasu, T. A. Orofino, D. J. Plazek
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Pittsburgh, Pennsylvania

Research at Mellon Institute on the dilute solution properties of high polymers is reviewed. Of concern in theoretical studies have been: the dimensions of branched chain molecules in poor solvents; the effect of heterogeneity in molecular weight on the second virial coefficient for linear polymers; and the effect of intermolecular correlations on Rayleigh scattering when both molecular dimensions and thermodynamic interactions are large. In experimental investigations, polystyrene has been studied to explore the properties of a particular branched structure and the nature of specific solvent effects on configurational and thermodynamic properties. The intrinsic viscosity-molecular weight relation for poly-(vinyl acetate) in butanone has been confirmed for molecular weights lower than have been studied previously. A precision light scattering photometer has been designed and built to meet the exacting requirements of projects now getting under way.

Introduction

Since 1960, research in polymer science at Mellon Institute has been aided by contracts with the Wright Air Development Division. In this paper we present a review of activities in one major division of this effort: that of dilute solution properties of synthetic polymers. Investigations have been both theoretical and experimental in character and have been pursued by a number of investigators individually and collaboratively as indicated by the following subdivision, which will be adopted for the ensuing discussion.

(a) Conformation of branched-chain structures (G. C. Berry, T. A. Orofino)

(b) Properties of branched polystyrene (T. A. Orofino)

(c) Dimensions of polymers: specific solvent effects (T. A. Orofino)

(d) The second virial coefficient for heterogeneous polymers in good solvents (E. F. Casassa)

(e) Theory of Rayleigh scattering: effect of intermolecular correlations (E. F. Casassa)

(f) Viscosity-molecular weight relationship for poly-(vinyl acetate) (R. E. Kerwin, H. Nakayasu)

(g) Light scattering photometer (G. C. Berry, E. F. Casassa, D. J. Plazek)

Detailed discussions of some of these topics will be found in a Technical Report[1] entitled "Polymer Structures and Properties."

(a) Conformation of Branched Chain Structures

Except at the Flory temperature, the configuration of a polymer chain is not described by the average magnitudes arising straightforwardly from random-flight statistics since the existence of net interaction forces between remotely connected chain segments weights the probability of occurrence of many configurations. The effect may be regarded as the manifestation of a volume which the presence of one segment denies to occupancy by another, and thus the determination of chain properties as a function of this parameter is referred to as the now-famous problem of the "excluded volume."

In very good solvents the large volume effect has so far defied truly rigorous analysis, but for sufficiently small excluded volume, perturbation treatments have been carried out as far as the linear or quadratic approximation to the expansion in terms of a variable

$$z = \left(\frac{3}{2\pi b_0^2}\right)^{3/2} \beta N^{1/2}$$

where b_0 is the equivalent segment length, N is the number of statistically effective segments in the chain and β is the mutually excluded volume for a pair of segments. For the mean square radius of gyration $\langle R^2 \rangle$ of a linear chain the result is well known.[2]

$$\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0 = 134z/105 + \cdots \qquad (1)$$

where $\langle R^2 \rangle_0 = Nb_0^2/6$ represents the mean square radius for a true random flight. In the present investigation it has been found possible to generalize this result to the case of the star molecule with f branches radiating from a single point. Aside from being an abstraction amenable to mathematical treatment, this model is of genuine interest in that useful procedures for synthesis of such molecules have now been developed in this laboratory (cf. below). The basis of the calculation is the general relation

$$\langle R^2 \rangle = \frac{1}{2N^2} \sum_i \sum_j \langle L_{ij} \rangle$$

together with the expression from the perturbation treatment[2]

$$\langle L_{ij}^2 \rangle = \langle L_{ij}^2 \rangle_0 - \beta \int \sum_k \sum_l L_{ij}^2 \Big[P(L_{ij}, O_{kl}) - P(L_{ij}) P(O_{kl}) \Big] dL_{ij} + \cdots \qquad (2)$$

Here, N is the total number of segments in the molecule, whatever may be its structure and $\langle L_{ij}^2 \rangle$ is the mean square of the vector distance $\underline{L}_{ij}$ separating segments i and j. The probability densities $P(\underline{L}_{ij})$ for the occurrence of L_{ij}, $P(O_{kl})$ for the existence of a contact ($L_{kl} \to 0$) between segments k and l, and $P(L_{ij}, O_{kl})$ for both events simultaneously, are given by random flight statistics, and are thus readily formulated.[2] The integration over space assumes a standard form and one is left with the laborious summations (integrations) with respect to i, j, k, l. It is clear that to obtain a result correct through the second term in equation 2 configurations must be considered in which the separation $\underline{L}_{ij}$ and the contact O_{kl} are specified. The pertinent configurations occur in three groups (a) segments i, j, k, l all in one of the f branches, (b) the segments distributed within two branches, (c) the four segments distributed among three branches. The first two types are equivalent and relate simply to results already known (cf. equation 1) for linear chains having respectively (for the case of equal branches of n segments) n and 2n segments. Since configurations with i, j, k, l distributed simultaneously among four branches contribute nothing to the second term of equation 2, only the third category of configurations introduces anything new in the calculation for the f-functional star.

The final result for the star molecule with equal arms of length n = N/f is

$$\alpha^2 = 1 + C_f z + \cdots$$

where

$$C_f = \frac{2}{f^{1/2}(3f-2)} \left[(f-1)\,\frac{268\sqrt{2}}{105} - (f-2)\,\frac{67}{105} + (f-1)(f-2)\left(\frac{202\sqrt{2}}{15} - \frac{92}{5}\right) \right]$$

Numerical results for a few cases are given in Table I.

It is evident from the tabulation, first that the requirement of identical results for f = 1 and f = 2 is met, and second that the effect of increasing branching at fixed molecular weight (fixed N) is to increase the expansion factor. The latter finding is consistent with the intuitive notion that the volume exclusion effect should become more marked as the segment density is increased. Every test indicates the correctness of the foregoing results: however, it must be remarked that they are at variance with $C_4 = 1.12$ reported by Fixman.[2] We have confirmed that Fixman's somewhat different method does give his numerical result (and find also that it gives C_2 incorrectly); but we have so far not been able to discover the origin of the discrepancy.

In current studies the same methods are being applied in elucidating the initial effect of volume exclusion on the dimensions of regular-comb molecules--the branched structures formed by attaching uniform chains at equal distances along a backbone chain.

TABLE I

Expansion of the Mean-square Radius for Star Molecules

f	C_f	
1	$\frac{134}{105}$	$= 1.276$
2	$\frac{134}{105}$	
3	$\sqrt{3}\left(\frac{6728}{2205}\sqrt{2} - \frac{7862}{2205}\right)$	$= 1.298$
4	$\frac{1548\sqrt{2}}{175} - \frac{5863}{525}$	$= 1.342$
8	$\frac{30632}{1155} - \frac{13591\sqrt{2}}{770}$	$= 1.559$
∞	$f^{1/2}\left(\frac{404\sqrt{2}}{45} - \frac{184}{15}\right)$	

(b) Properties of Branched Polystyrene

Two polystyrene samples closely approximating the idealized uniform three-branched star were employed in a preliminary experimental investigation. These materials were two fractions (of molecular weight about 3×10^5) isolated from an already narrowly distributed mixture of trifunctionally branched molecules prepared (by Dr. F. Wenger of this laboratory) by coupling nearly monodisperse polystyryl lithium with an aromatic compound containing three chloromethyl groups The synthesis is described in detail elsewhere.[3] From fractionation data the weight to number average molecular weight ratio of the parent linear polymer was found to be 1.03; and for one of the branched fractions the same ratio was unitv within the error inherent in the comparison of molecular weights from osmotic pressure and light scattering.

The results of the measurements may be summarized as follows:

The Flory temperature[4] θ, at which the second virial coefficient A_2 vanishes, is 34.3 ± 0.5°C in cyclohexane irrespective of branching.

The Huggins constant k' in good solvents (benzene at 25°, toluene at 30°) is 0.38 ± 0.02 and unaffected by branching; but there are indications that in a theta solvent k' is slightly larger than that found for the linear polymer.

The intrinsic viscosity ratio $g' = [\eta]_{branched}/[\eta]_{linear}$ in cyclohexane at θ is 0.90 in good agreement with the theoretical value predicted by Zimm and Kilb. Results indicate, however, that in good solvents, the Zimm-Kilb relation is not applicable.

Near θ, the second virial coefficient is about one-third smaller (in absolute magnitude) than that found for the linear polymer of the same molecular weight. To put it another way: the entropy parameter[4] ψ_1 is reduced from 0.33 to 0.21. In the good solvent toluene, however, the virial coefficients are indistinguishable.

The unperturbed mean square radius of the trifunctionally branched chain calculated from intrinsic viscosity and virial coefficient data is in good agreement with the random-flight relation

$$\frac{\langle R^2 \rangle_0}{M} = \frac{3f - 2}{6f^2} \times \text{constant}$$

and the constant established for linear polystyrene either directly[5] by light scattering or by the combination of viscosities and virial coefficients.[6]

(c) Dimensions of Polymers: Specific Solvent Effects

According to the familiar theory developed by Flory and Fox,[7] the intrinsic viscosity of a polymer solution may be expressed by the relation

$$[\eta] = KM^{1/2}\alpha^3$$

where the constant K is given by

$$K = \Phi'(\langle R^2 \rangle_0/M)^{3/2}$$

and Φ' is a universal numerical constant. Viscosity measurements at the Flory

temperature, where α is unity, can thus be used to determine K. If the unperturbed chain size $\langle R^2 \rangle_0$ is a characteristic of the polymer chain at a given temperature without regard to the nature of the solvent, K must similarly be dependent only on temperature and the polymer. Many experimental studies indicate this view to be correct as a first approximation; but it is only reasonable to expect that specific interactions between solvent and polymer may modify $\langle R^2 \rangle_0$ to some degree, and there does exist some experimental evidence supporting the idea that variations of K with solvent may occur.[8,9]

In order to study solvent effects it is necessary to eliminate the possibly predominant effect of temperature per se. Evidently, this can be done if a polymer is found to exhibit sufficiently similar values of θ in two different solvents. In a preliminary screening, polystyrene with the solvents cyclohexane and diethyl malonate proved to be one combination with the requisite properties In order that unambiguous results might be obtained it was considered that the polymer used should be relatively homogeneous, to eliminate possible complications from a dispersion of molecular weights; and that it should be of such molecular weight that accurate osmotic pressure, light scattering, and viscosity measurements could be made without difficulties from leakage through osmotic membranes, from high dissymmetry in light scattering, from shear corrections in viscosity, or from phase separation too near θ. Further, enough material should be available to permit all measurements to be made on the same sample. A thirty gram sample of anionically polymerized polystyrene of molecular weight about 4×10^5 (prepared by Dr. F. Wenger) was considered to meet these criteria and was used in the measurements.

The second virial coefficient A_2 was measured by light scattering for both systems over a range of temperatures including θ. Interpolation to $A_2 = 0$, yielded $\theta = 34.8 \pm 0.3°C$ in cyclohexane and $\theta = 35.9 \pm 1.0°$ in diethylmalonate, the reduced precision in the latter figure arising from the relatively small temperature dependence of A_2 in this system. The value of θ was confirmed for the cyclohexane system by osmotic pressure, which gave $\theta = 34.6 \pm 0.2°$, in good agreement also with published results.[10] Since $\langle R^2 \rangle_0$ does not vary rapidly with temperature, comparison of the intrinsic viscosities at the respective values of θ will indicate whether there exist differences in specific solvent effects in these two systems. From viscosity measurements at θ and two degrees above and below it was concluded that for polystyrene-cyclohexane $[\eta]_\theta$ is 0.555, but for polystyrene-diethylmalonate $[\eta]_\theta = 0.491$. The difference is small but well beyond the limits of experimental uncertainty.

The significance of this effect and its relevance in other systems is of continuing interest. The comparisons made here will be supplemented by data on polystyrene in 1-chloro-n-undecane which also exhibits θ near 35°. Direct determinations of $\langle R^2 \rangle$ for a high molecular weight polymer in all three solvents are also planned.

(d) The Second Virial Coefficient for Heterogeneous Polymers in Good Solvents

Available theoretical treatments of the second virial coefficient in the equation of state for polymers in good solvents give results in complicated forms

which it has not been found possible to apply to the general case of solutes heterogeneous in molecular weight. Mathematically, the task involved generally is a double integration, over a molecular weight distribution, of a function that cannot itself be expressed analytically.[11-13]

In a new approach to the problem we abandon all pretense of a sophisticated model and simply assume that the virial coefficient for a homogeneous polymer is proportional to a negative power of molecular weight. This assumption is quite without theoretical justification, but empirically it conforms to virtually all experimental data on well-fractionated polymers to within the limits of experimental accuracy. Hence we regard it merely as a convenient representation of empirical results, but one which is a vital factor in the avoidance of mathematical difficulty. Thus we write for a homogeneous polymer of degree of polymerization $\underline{n}$ (which need not be identified with the number n of chain segments discussed earlier)

$$A_2 = B_0 n^{-a} \tag{3}$$

where B_0 and $\underline{a}$ depend on the nature of the polymer-solvent pair and the temperature, but not on molecular weight. The virial coefficient A_2 is defined in the usual way as the coefficient of the linear term in the equation of state: e.g., for the osmotic pressure Π

$$\frac{\Pi}{RTc} = \frac{1}{M} + A_2 c + \cdots$$

with c the concentration in units of mass/volume.

Since equation 1 still implies little about the virial coefficient for heterogeneous polymers an additional condition is required; that is, we require some relation among the coefficients B_{ij} in the two general expressions

$$A_2^{(\Pi)} = \sum_i \sum_j B_{ij} w_i w_j \tag{4}$$

for the osmotic pressure, and

$$A_2^{(R)} = \sum_i \sum_j B_{ij} n_i w_i n_j w_j \Big/ \left(\sum n_i w_i \right)^2 \tag{5}$$

for light scattering, in which w_i is the weight fraction of component i in the solute. Probably the simplest assumption with some physical basis is that the unlike molecules interact as hard spheres of equivalent radii defined by the B_{ii} from equation 3. An elementary calculation in statistical mechanics gives the appropriate result:

$$2(B_{ij} n_i n_j)^{1/3} = (B_{ii} n_i^2)^{1/3} + (B_{jj} n_j^2)^{1/3} \tag{6}$$

As a test of the averaging assumed in equation 4, we can examine the special case of a solute consisting of a mixture of two sharp fractions[11,14,15] of the same polymer. The very simple theory derived here indicates, interestingly, that there are physically reasonable conditions, determined by the value of $\underline{a}$ and the molecular weight ratio of the two solutes, for which $A_2^{(\pi)}$ and $A_2^{(R)}$ both pass through a maximum as a function of the relative amounts of the two polymers in the solute. At least qualitatively, this result is in agreement with more sophisticated theory[11] and with some experimental results.[14,15]

In dealing with continuous molecular weight distributions we adopt the Schulz distribution function[16]

$$f(n) = y^{Z+1} \frac{n^Z}{\Gamma(Z+1)} e^{-yn} \qquad (7)$$

$$y = (Z+1)/n$$

where $f(n)dn$ is the weight fraction of polymer with n lying between n and n + dn. The parameters of the distribution are $\langle n \rangle$ the weight average value of n and the parameter Z, which increases with decreasing heterogeneity: the limit of infinite sharpness corresponds to $Z = \infty$ while $Z = 1$ denotes the "most probable" or "polyester" distribution.

Substitution of equations 3, 6, and 7 in the integral forms equivalent to equations 4 and 5, yields integrals involving only a single standard form, the Γ function. We obtain for the second virial coefficient from osmotic pressure

$$A_2^{(\pi)} = B_0 y^a \phi^{(\pi)} / 4[\Gamma(Z+1)]^2$$

$$\phi^{(\pi)} = \Gamma(Z+2-a)\Gamma(Z) + 3\Gamma[3Z+4-2a)/3]\Gamma[(3Z+2-a)/3]$$

and for light scattering

$$A_2^{(R)} = B_0 y^a \phi^{(R)} / 4[\Gamma(Z+2)]^2$$

$$\phi^{(R)} = \Gamma(Z+3-a)\Gamma(Z+1) + 3\Gamma[3Z+7-2a)/3]\Gamma[(3Z+5-a)/3]$$

These results are such that the form of relation between the virial coefficient and average molecular weight is still that of equation 3 for a single species: hence for a given Z, plots of log A_2 versus log $\underline{n}$ for a sharp fraction, and of log $A_2^{(\pi)}$ versus the logarithm of the number average $\underline{n}$ or of log $A_2^{(R)}$ versus log $\langle n \rangle$ are all predicted to be straight lines of the same slope $-\underline{a}$. If the three functions (for empirically meaningful values of $\underline{a}$) are superimposed on a single graph, the plots for a heterogeneous system lie above that for the homogeneous case

with the $A_2^{(\pi)}$ plot uppermost; and the difference increases as heterogeneity increases.[2] In this definite sense, A_2 is predicted to be increased by heterogeneity, and more strongly for osmotic pressure than for light scattering. In the case of the polyester distribution with a = 1/4 (a typical value for systems in good solvents) $A_2^{(\pi)}/A_2^{(R)}$ for a given polymer exhibits, according to this theory, a value equal to 1.26, and thus a difference from unity sufficiently great to be detected by careful measurements. However, in the same instance, the ordinates of $A_2^{(\pi)}$ versus number average $\underline{n}$ and of $A_2^{(R)}$ versus $\langle n \rangle$ should be in the ratio 1.26;[2] and thus it appears that these two functions may not show experimentally significant differences.

It is possible to apply the theory outlined here to more complicated distributions made up from several Schulz distributions, each determined by a certain Z and $\langle n \rangle$. The results can become cumbersome indeed, but the necessary integrations are as elementary as before. Perhaps the most interesting prediction is that the maximum in A_2 obtained for some mixtures of two homogeneous polymers should in fact be enhanced by heterogeneity if both fractions have the same Z.

(e) Theory of Rayleigh Scattering: Effect of Intermolecular Correlations

A statistical model developed earlier[13] in deducing approximately the osmotic properties of solutions of polymers in thermodynamically good solvents has been applied to the problem of the scattering of light for the general case in which solutions do not obey van't Hoff's law and the polymeric solute molecules are so large that intramolecular optical interferences cannot be ignored.

In our molecular model a bimolecular cluster (two solute molecules in contact) is represented as a spherically symmetrical distribution of chain segments centered about an arbitrarily chosen "initial contact." With this model it was found that the series expansion for the second virial coefficient in powers the excluded volume β (or of z), as derived by Zimm,[17] could be summed in closed form prior to a final summation (integration) required for averaging over all intermolecular segment-segment pairs as initial contacts. Although this final step could not be performed analytically, it was possible to show that a simple approximation yielded a result very close to the exact integral. Comparison of this result with that of Flory and Krigbaum,[11] (based on the representation of the bimolecular cluster as the interpenetration of two spherically symmetrical distributions of polymer segments centered at the positions of the respective molecular centers of mass) showed a more rapid decrease in A_2 with increasing molecular weight. In some cases, at least, this behavior appeared in better accord with experiment.[13]

In brief, the present study constitutes an attempt to calculate from theory for a homogeneous solute the function $Q(\theta)$ in

$$\frac{Kc}{R(\theta)} = \frac{1}{MP(\theta)} + 2A_2Q(\theta)c + \cdots$$

where $R(\theta)$ is the light intensity scattered through the angle θ; M is the polymer molecular weight; c is the weight concentration; and $P(\theta)$, $Q(\theta)$, are functions, normalized to unity at $\theta = 0$, that determine the angular distribution of scattered radiation. The theory may be regarded as providing some degree of correction to the well-known treatment of light scattering by Zimm in which $Q(\theta)$ is unity at all angles.[18] Zimm's theory is based on the so-called "single contact" approximation by which, in the enumeration of the configurations of a bimolecular cluster, simultaneous multiple intermolecular contacts are not considered. The electromagnetic aspects of our derivation include nothing novel and the statistical mechanical treatment follows Zimm's procedure[17,18] rather closely except for the introduction of the particular properties of the model. In spite of the simplifications involved, the single-contact contributions are accounted for properly. Unlike the case of the virial coefficient,[13] however, double-contact configurations are not treated rigorously. This means that the expression of A_2 in this theory as a series in powers of z reproduces the first two terms of the exact series while only the first term is correct in the analogous development of $Q(\theta)$. In both cases, higher order terms involve approximations of uncertain effect since, of course, an exact result is not available for comparison.

The final result

$$Q^*(\theta) = \frac{w_0}{w_u}\left[\frac{1 - \exp(-\psi w_u)}{1 - \exp(-\psi w_0)}\right] \tag{8}$$

depends on two variables: the thermodynamic parameter

$$\psi = 4z/\alpha^3$$

and a quantity characterizing the optical interference effects (and thus the molecular size)

$$u = \frac{8^2 n b_0^2 \alpha^2}{3\lambda^2} \sin^2\left(\frac{\theta}{2}\right)$$

where λ is the wavelength in the medium. The function w_u is extremely complicated but actually turns out to be nearly constant: it is $w_0 = 1.433$ for $u = 0$, increases with increasing u to about 1.469 and then decreases again to w_0 as u becomes infinite. It must follow that $Q^*(\theta)$ is always close to unity whatever the value of ψ and hence that the single-contact approximation of Zimm should <u>always</u> apply for practical purposes.

This is a rather surprising and perhaps implausible result although there seem to be no completely unequivocal experimental data to cite in comparison. It is, however, very much at variance with the predictions of Flory and Bueche[19] who derived $Q(\theta)$ from the Flory-Krigbaum molecular model[11] and found a marked decrease from unity with increasing ψ at sufficiently large, but physically reasonable, values of u. Equation 8 also predicts a decrease in $Q(\theta)$, at first, as either u or ψ increases, but the effect is small as compared both to that found by Flory and Bueche and to the limiting dependence at $\psi u = 0$ indicated by exact theory. It

seems to us that this behavior is a consequence of the extreme symmetry of our model in which all configurations of a bimolecular cluster are represented as spherically symmetrical. The Flory-Krigbaum model is undoubtedly a much more realistic model for the intermolecular interference effects, although it may perhaps err in the opposite direction of underemphasizing the contributions from highly symmetrical configurations.

In the derivation leading to equation 8, it is assumed that the expansion factor α is the same for a single molecule and for a bimolecular cluster. However a completely consistent treatment of the statistical model we have employed, suggests that the expansion α_1 of a single chain is less than that α_2 of the cluster, according to the relation[20]

$$\alpha_2^5 - \alpha_2^3 = 1.601(\alpha_1^5 - \alpha_1^3)$$

The scattering function obtained if this modification is adopted is

$$Q^{\dagger}(\theta) = \frac{w_0[1 - \exp(-\psi w_{u_2})][P(\theta,u_2)]^2}{w_{u_2}[1 - \exp(-\psi w_0)][P(\theta,u_1)]^2}$$

where u_1, u_2 indicate the quantities u determined by the respective expansion factors α_1, α_2.

With this refinement, values of $Q^{\dagger}(\theta)$ are found significantly less than unity though the effect is still very much smaller than that predicted by Flory and Bueche. Some numerical values are listed in Table II.

TABLE II

The Scattering Function $Q(\theta)$ in Two Approximations

$u = u_2$	w_u	$Q^*(\theta)$ ($\psi > 7$)	$Q^{\dagger}(\theta)$ $\psi = 1$	$Q^{\dagger}(\theta)$ $\psi = 2$	$Q^{\dagger}(\theta)$ $\psi = 10$
0	$1.433 = w_0$	1	1	1	1
2	1.458	0.983	0.905	0.876	0.841
4	1.467	0.977	0.863	0.822	0.774
8	1.468	0.976	0.836	0.787	0.729
18	1.459	0.982	0.824	0.772	0.710
∞	w_0	1	0.822	0.771	0.707

To gain some sense of the physical meaning of these results it is useful to make an estimate of magnitudes of u and ψ attainable in experiment. Choosing polystyrene in toluene as a typical instance of a polymer in a good solvent and

calculating the desired quantities from intrinsic viscosity parameters we obtain, at four molecular weights the results given in Table III.

TABLE III

Parameters for the System Polystyrene-Toluene

M	ψ	u_1^*	u_2^*	R(45)/R(135)*
10^5	1.4	0.22	0.25	1.05
10^6	2.7	3.0	3.5	1.9
5×10^6	4.1	19.1	22.3	1.9
10^7	4.9	42.8	50.2	5.2

*For blue light (436 mμ)

(f) Viscosity-Molecular Weight Relationship for Poly-(vinyl acetate)

The intrinsic viscosity-molecular weight relationship for linear poly-(vinyl acetate) in methyl ethyl ketone has been studied previously,[21-24] but most of the investigations have dealt principally with polymers of molecular weights in excess of 100,000. In connection with other work under way in this laboratory it has become important to know the relationship accurately in a lower weight range. Accordingly, intrinsic viscosity and light scattering measurements on this system have been carried out with nine fractionated polymers of molecular weights from 6,000 to 30,000.

Viscosity measurements were made at 25°C in a Cannon-Ubbelohde viscometer such that kinetic energy corrections were negligible. Light scattering measurements were made at four solute concentrations and at least seven scattering angles and the data were analyzed according to the familiar method of Zimm. Molecular weight calculations were based on a refractive index increment of 0.089 cm^3/g, as reported by Shultz,[21] and Matsumoto and Ohyanagi.[24]

The new data are well fitted by the equation

$$\log [\eta] = -1.871 + 0.71 \log M_w \qquad (9)$$

which also describes the results of Schultz and Howard[22] covering the high molecular weight range 240,000 to 3,460,000.

Combining molecular weights from both light scattering and sedimentation diffusion data, Elias and Patat[23] obtained an equation which differs by about 25 per cent from the lowest molecular weight data of this study. However, if their light scattering data alone are considered and one point for a poorly fractionated sample is rejected, the agreement with the present data and those of Shultz is much

improved. Matsumoto and Ohyanagi obtained intrinsic viscosities about 15 per cent lower than given by equation 9 but showing the same molecular weight dependence. However, their polymers were not fractionated and it is perhaps possible that their method of sample preparation leads to some hydrolysis of acetate groups.

We can conclude therefore that Shultz's equation is valid over the entire molecular weight range so far studied 6×10^3 to 3.5×10^6. From theoretical considerations an abrupt change in slope of the log $[\eta]$ versus log M_w relation is expected at some rather low molecular weight, hence further experiments are planned at still lower molecular weights to determine if possible the lower limit of validity of the relation.

(g) Light Scattering Photometer

A precision light scattering photometer has been designed and built with a view to its use in studies of configurational and thermodynamic properties of polymers in dilute solutions. Since a comprehensive description will be found in an ASD Technical Report[1] we offer here only an outline of the main characteristics of the instrument. Most elements of the design are fairly conventional and individually nearly all may be found in instruments constructed previously: a mercury arc light source, glass filters to isolate either the strong blue or green line of the spectrum; a rotating sector to modulate the light source; optical elements to concentrate, collimate and define the incident beam; photomultiplier tubes to detect both scattered radiation and a reference intensity deducted from the incident beam; a tuned bridge circuit for balancing the two photocurrents; a sensitive amplifier-voltmeter as the null detector, a goniometer permitting accurate measurement of scattering angle, and a thermostat for control of sample temperature. While there is thus nothing exceptional in the conception, the abiding goal has been to achieve the utmost of which such apparatus ought reasonably to be capable in precision and reproducibility of measurements. To this end much effort has been put into the finer details of design and in tracking down and eliminating effects that might be characterized as of a second order in regard to influencing accuracy. For example, it is expected that the optical system will prove of such quality that in comparison to commercial instruments there can be attained more accurate measurements of depolarization and better angular resolution of scattered light over a wider range of scattering angles. Also, by a rather simple but effective thermostat design, the precise temperature control needed for meaningful thermodynamic studies over an extended temperature range can be achieved.

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PREPARATION AND PROPERTIES OF MONODISPERSE BRANCHED POLYSTYRENE

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ABSTRACT

Model branched polymers have been prepared by the reaction of relatively monodisperse polystyryl lithium with silicon tetrachloride. The branched molecules have been carefully characterized by light scattering and osmotic pressure measurements. A study of the dilute solution properties of the branched molecules has confirmed the theoretical development of the branching coefficient, g', by Zimm and Kilb. The second virial coefficient, A_2, has been found to decrease with increased branching. In addition, the Huggins constant, k', has been found to be a poor measure of branching in molecules.

INTRODUCTION

Zimm and Kilb[1] have presented theoretical formulas for the intrinsic viscosity and viscoelastic properties of some model branched molecules in dilute solution. Using their theoretical expression, they were able to calculate the ratio of the intrinsic viscosities of several model branched molecules to that of linear molecules having the same molecular weight. This ratio is expressed by the following equation,

$$g' = \frac{[\eta]_b}{[\eta]_l}$$

Although they referred to data available in the literature to substantiate the validity of their work, the inherent uncertainties in the branched polymer characterizations detracted from the test of the mathematical treatment.

In order to resolve this uncertainty, it was the purpose of this work to prepare well-characterized model branched polymers and study their dilute solution behavior. The unique characteristics of anionic polymerization lend themselves very well to the purpose intended. The anionic polymerization of styrene can be used to prepare relatively homogeneous linear polymer of predetermined molecular weight. In addition, the "living" nature of the polystyryl anion can be used to further advantage in the preparation of the branched molecules. In this work, the polystyryl anion was reacted with silicon tetrachloride to yield molecules with three and four uniform branches emanating from a single point. These "star" type molecules were then used to experimentally

determine the g' factor, the second virial coefficient, A_2, and the Huggins constant, k'.

EXPERIMENTAL

Preparation of Linear Polystyrene

In order to prepare model branched compounds consistent with the models used in the calculations of Zimm and Kilb, it was necessary to prepare relatively monodisperse linear polystyrene. To accomplish this task, styrene monomer was polymerized using anionic polymerization techniques under high vacuum [10^{-6} mm Hg]. The details concerning purification of solvent and monomer and the use of catalyst seed have been described elsewhere[2]. The polymerization apparatus is shown in Figure 1 and the procedures used, with exception of one modification, have already been described[2]. The modification consisted of distilling the styrene monomer from the ampoule into the frozen benzene seed solution in flask F_1 (see Figure 1). This distillation insured the addition of pure monomer to the reaction flask, whereas the freezing of the mixture prevented polymerization during distillation. After thawing, the monomer-seed solution was thoroughly mixed and a substantial portion was transferred to flask F_2. Having transferred some of the solution, flask F_2 was cut away. The solutions in both flasks were kept at room temperature for 24 hours with continuous stirring. The polymerization was considered complete after the 24 hour interval.

In order to determine the molecular weight of the linear polymer prepared in this manner, the catalyst concentration of the polymer in flask F_1 was determined by titrating the orange colored polystyryl anions with a standard n-butanol solution by means of a slow-leaking burette, B (see Figure 1). The butanol termination of the polystyryl anions caused a loss of color, and thus the titration end-point was a colorless solution. After titration, the polymer was precipitated from solution with methanol, filtered, dried and weighed. Hence, from the weight of polymer and the number of moles of catalyst, it was possible to estimate the molecular weight of the linear polymer. This linear polymer is referred to as the S_{10} sample.

Preparation of Branched Polystyrene

The polymer remaining in flask F_2 was used to prepare the branched molecules. Knowing the amount of monomer initially used, and the weight and molecular weight of the polymer in flask F_1, it was possible to calculate, by difference, the number of moles of polymer in flask F_2. To this flask was added a less than equivalent amount of silicon tetrachloride calculated on the assumption that all four chlorines would be replaced by polystyryl anions. The excess of polystyryl anions was necessary to insure that the linking reaction would go to completion.

The silicon tetrachloride used in the linking reaction was treated in the following manner. It was dried over anhydrous sodium sulfate and distilled twice before collecting into weighed ampoules. Benzene solutions were made and the concentration of silicon tetrachloride was determined by breaking an ampoule in ice water and titrating the liberated hydrochloric acid with standard sodium hydroxide solution using phenolphthalein as an indicator.

Having introduced the silicon tetrachloride into the polymer solution, the mixture was allowed to stand for 48 hours at 50°C. At the end of this period, any remaining polystyryl anions were terminated by the addition of n-butanol. The resulting polymer mixture was precipitated in methanol, dried, and weighed. This polymer sample is referred to as the $4S_{10}$ sample.

Polymer Characterization

The polymer sample $4S_{10}$, which was the total polymer product of the linking reaction of polystyryl-lithium and silicon tetrachloride, was initially expected to contain the tetra-linked star molecules and the excess linear polymer S_{10}. Hence, fractionation was considered necessary to isolate the pure, linked product. However, careful fractionation became even more important when, in initial attempts at preparing the linked products, it was observed that mixed products of tetra- and tri-linked molecules were being formed.

Fractionation

The mixed polymer product, $4S_{10}$ was dissolved in benzene to give a 0.12% solution by weight. The non-solvent used for the fractionation was methanol. The fractionation was carried out at a constant temperature of 30°C. Upon separation, the fractions were precipitated in methanol, dried in vacuo, and weighed. The weight fraction data for the fractionation are listed in Table I.

Molecular Weight Determinations

In order to establish the efficiency of fractionation, the degree of linking and the homogeneity of both linear polymer and the fractions, it was necessary to determine both the weight- and number-average molecular weights of the samples. To obtain this information, osmotic pressure and light scattering measurements were made.

The light scattering measurements were made using a Brice-Phoenix light scattering photometer, Universal 1000 series. Calibration was accomplished through the use of a reference standard opal provided with the instrument. In order to recheck the calibration, the absolute turbidity of benzene was determined, and it agreed to 0.6% with the value listed by Carr and Zimm[3]. All the solutions were filtered through sintered glass frits to remove insoluble impurities. The scattering intensities of the solutions

were determined at various angles through the use of a cylindrical cell having the dimensions, 75 x 26 mm. The scattering system was a polystyrene-benzene solution and the refractive index increment for a wave-length of 436 millimicrons was 0.1151 ml gm^{-1}. The data obtained were interpreted through the use of a Zimm plot. The weight-average molecular weights thus obtained are listed in Table I.

The number-average molecular weights were obtained through osmotic pressure measurements. The osmometers used were of the design developed by Immergut and Stabin[4]. The membranes used were gel cellophane, grade No. 600. The osmotic molecular weight of the linear S_{10} sample was determined in benzene solution at 30°C. For fractions, A-$4S_{10}$ and B-$4S_{10}$, the measurements were made in butanone at 25°C. All the osmotic pressures were obtained by the static method and the equilibrium times were of the order of 20 hours. The number-average molecular weights are listed in Table I.

Viscosity Determinations

In order to obtain g', it was necessary to experimentally determine the intrinsic viscosity of the branched molecules. The viscosities were determined in two solvents, toluene at 25°C and cyclohexane at 34°C, the former being a good solvent and the latter a theta, Θ, solvent. The measurements were made using a Ubbelohde dilution viscometer having a flow time of 123 sec. for toluene and 193 sec. for cyclohexane, and having a negligibly small kinetic energy correction.

RESULTS AND DISCUSSION

The fractionation data and weight-average molecular weight values are listed in Table I. The agreement between the weight-average molecular weight of $4S_{10}$ which was determined experimentally to be 1.93×10^5, and the calculated value of 1.90×10^5 for this sample calculated from the data for the individual fractions, indicates that the fractionation was efficient and complete. However, to insure that the fractions were homogeneous, number-average molecular weights were determined (see Table I) and were used to determine the heterogeneity ratio, M_w/M_n, for the A-$4S_{10}$ and B-$4S_{10}$ samples. In addition, the heterogeneity ratio was determined for the linear S_{10} sample. The ratios obtained indicated that the fractionation was indeed very efficient and that both fractions of the linked polymer and the linear polymer were homogeneous enough for the purposes intended.

Having established the fact that homogeneous fractions were obtained, it was still necessary to determine the degree of branching that had taken place to produce each fraction. This was done by calculating the linking ratio, i.e., the number-average molecular weight of the branched molecule divided by the number-average

TABLE I

Fractionation and Molecular Weight Data

Sample	Weight Fraction	$\bar{M}_w \times 10^5$	$\bar{M}_n \times 10^5$	$\frac{\bar{M}_w}{\bar{M}_n}$	$\frac{4S-\bar{M}_n}{S-M_n}$
S_{10}	-	0.606	0.574	1.06	-
$4S_{10}$	-	1.93	-	-	-
A-$4S_{10}$	0.252	2.57	2.35	1.09	4.09
B-$4S_{10}$	0.349	1.70	1.70	1.00	2.96

molecular weight of the linear sample, S_{10}, i.e. $4S_{10}-M_n/S_{10}-M_n$. The reasons for using the number-averages to determine the degree of linking are given in the Appendix, where the effects of molecular weight distribution are considered. In the case of the A-$4S_{10}$ sample, the ratio was, within experimental error, 4.0, whereas for B-$4S_{10}$ the ratio was 3.0, as shown in Table I. Thus, having shown the linear polymer to be relatively homogeneous, and having demonstrated the separation of homogeneous branched polymers it can be assumed that the A-$4S_{10}$ sample is a "star" type molecule with four branches, of essentially the same length, emanating from a single point. The B-$4S_{10}$ sample is a "star" with three such branches.

Viscosity measurements were made for both branched polymers in toluene at 25°C, a good solvent, and in cyclohexane at 34°C, the theta solvent. The data are listed in Table II. In order to determine the branching coefficient, g', as defined by Zimm and Kilb[1], it was necessary to obtain the intrinsic viscosity of a linear polymer having the same molecular weight as each of the branched polymers. It was originally intended to calculate these values using the viscosity-molecular weight relationship reported by Outer, Carr and Zimm[5] for polystyrene-toluene at 25°C. However, the linear polymer prepared by anionic polymerization in benzene did not exactly obey the equation reported by Outer, Carr and Zimm[5]. The viscosities experimentally determined were observed to be consistently lower than those calculated from the literature equation. Therefore, it was necessary to establish the viscosity-molecular weight equation experimentally. The equation determined for toluene at 25°C was as follows,

$$[\eta] = 1.46 \times 10^{-4} M_w^{0.69}$$

The reason for the slight difference between this equation and that reported by Outer, Carr and Zimm is unknown at the present time. There is a remote possibility that there is a consistent error in these measurements. However, the procedure used herein eliminates any error in the g' calculations.

In order to calculate the viscosity of the linear polymer in cyclohexane at 34°C, it was necessary, due to the discrepancy observed in toluene, to apply a proportionate correction to the viscosity-molecular weight equation reported for cyclohexane at 34°C by Krigbaum and Flory[6]. The equation determined for these polymers is as follows,

$$[\eta] = 7.45 \times 10^{-2} M^{0.5}$$

The viscosities calculated, using the above equations for linear molecules of the same molecular weight as the branched molecules, are listed in Table II. The ratios of the branched to linear intrinsic viscosities for both toluene and cyclohexane have been calculated and the agreement between the experimentally and theoretically determined g' factors is very favorable (see Table II). Thus, within the degrees of experimental error involved, this viscosity study lends considerable support to the theoretical work of Zimm and Kilb.

TABLE II

Viscosity Data

Polymer	$[\eta]_b$ Expt.		$[\eta]_l$ Calc.		g' Expt.		g' Theory
	*C_7H_8	C_6H_{12}	C_7H_8	C_6H_{12}	C_7H_8	C_6H_{12}	
A-$4S_{10}$	70.5	30.9	84.0	37.8	0.84	0.82	0.81
B-$4S_{10}$	56.3	28.8	63.0	30.7	0.90	0.94	0.91

$[\eta]$ - ml gm^{-1} $\quad$ $[\eta]_l$ - linear $\quad$ $[\eta]_b$ - branched

*Toluene at 25°C, cyclohexane at 34°C.

The second virial coefficient, A_2, was obtained for the branched molecules in benzene and butanone. The A_2 values in benzene were obtained from light scattering data, whereas the values in butanone were obtained from osmotic pressure measurements. The A_2 values for linear molecules corresponding to the molecular weights of A-$4S_{10}$ and B-$4S_{10}$ were obtained from a plot of the log A_2 vs. log $\bar{M}_w$ for linear molecules (see Table III). From the data, it can be observed that, in going from linear to branched molecules, the A_2 value decreases. In addition, this decrease is proportionally greater when the degree of branching is increased. On changing from a good to poor solvent, the A_2 value is further decreased and, as would be expected, the difference in the A_2 values for A-$4S_{10}$ and B-$4S_{10}$, due to branching, becomes less obvious as the second virial coefficient decreases. These results are in agreement with theory and support the corresponding suggestions of Thurmond and Zimm[7]. It can be concluded that the second virial coefficient may be used as a qualitative measure of branching, but only in a good solvent.

TABLE III

Second Virial Coefficient Data

Polymer	$A_2 \times 10^3$		
	Linear *	Branched	
	(Benzene)	Benzene	Butanone
A-4S$_{10}$	0.54	0.33	0.19
B-4S$_{10}$	0.57	0.49	0.19

TABLE IV

Huggins Constant Data

Polymer	k'		
	Linear *	Branched	
	(Toluene)	C_7H_8	C_6H_{12}
A-4S$_{10}$	0.31	0.38	0.85
B-4S$_{10}$	0.31	0.41	0.88

*Determined for linear molecules having molecular weights corresponding to those of the branched polymers.

The Huggins constant, k', was determined for the branched molecules, A-4S$_{10}$ and B-4S$_{10}$, and for linear molecules of the same molecular weights, in toluene at 25°C. In addition, the k' values were obtained in cyclohexane at 34°C for both branched samples (see Table IV). The data obtained indicate an increase in the k' value on going from linear to branched molecules and from good to poor solvents. In spite of this, the value of k' actually decreases when going from the less branched B-4S$_{10}$ to the more branched A-4S$_{10}$. Hence, it appears that k' does not behave in any simple way with degree of branching.

This is not unexpected when one notices that in the equation defining the Huggins constant,

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c.$$

The factor k' $[\eta]^2$ is the proper measure of intermolecular interference at concentration c. The quantity $[\eta]^2$ decreases or increases as the molecule shrinks or grows larger. It is the primary measure of the way in which the molecules will interfere with each other at a given concentration. The factor k' varies only slightly in comparison with $[\eta]^2$ and can be thought of as a correction factor necessary to compensate for small inaccuracies introduced by the use of the simple, but not rigorously correct,

factor $[\eta]^2$. It is to be expected that the variation of k' with branching and solvent power will not be understood until a very accurate theory for the concentration dependence of viscosity is available.

As the data indicate, even in a good solvent, the effect of branching on k' approaches the limits of experimental error. Thus the value of determining k' to establish the degree of branching is very limited. In addition to this fact, a dependence of k' on molecular weight has been reported by Cragg and Sones[8], and this will further complicate the interpretation of k' values. Thus, because of these various limitations, k' becomes, at best, a very poor indication of the degree of branching.

CONCLUSIONS

The present studies have been successful in clarifying the following points: 1. Branched molecules of accurately determined form can be prepared by the methods used in this study. 2. The theory of Zimm and Kilb[1] for the intrinsic viscosity of branched molecules is valid. In addition, g' values are nearly the same for both good and poor solvents. 3. The value of the second virial coefficient, A_2, is lower for a branched molecule than for a linear molecule of the same molecular weight. This effect is most easily observed in the case of good solvents. 4. Branching is not easily determined by measurement of the Huggins constant, k'. Although small changes are observed, they are not easily interpreted.

Since the molecules prepared for this study have been uniform and well characterized, other data in the literature, which may at times conflict with the above conclusions, should be used with caution.

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LEGEND FOR FIGURE 1.

Polymerization Apparatus

A - standard n-butanol solution ampoule

B - slow leaking burette

C_1 - catalyst seed for purging

C_2 - catalyst seed for polymerization

F_1 and F_2 - flasks with magnetic stirrers for polymerization and linking reaction

F_3 - flask to remove purging solution

M - monomer ampoule

S - solvent ampoule

V - vacuum outlet

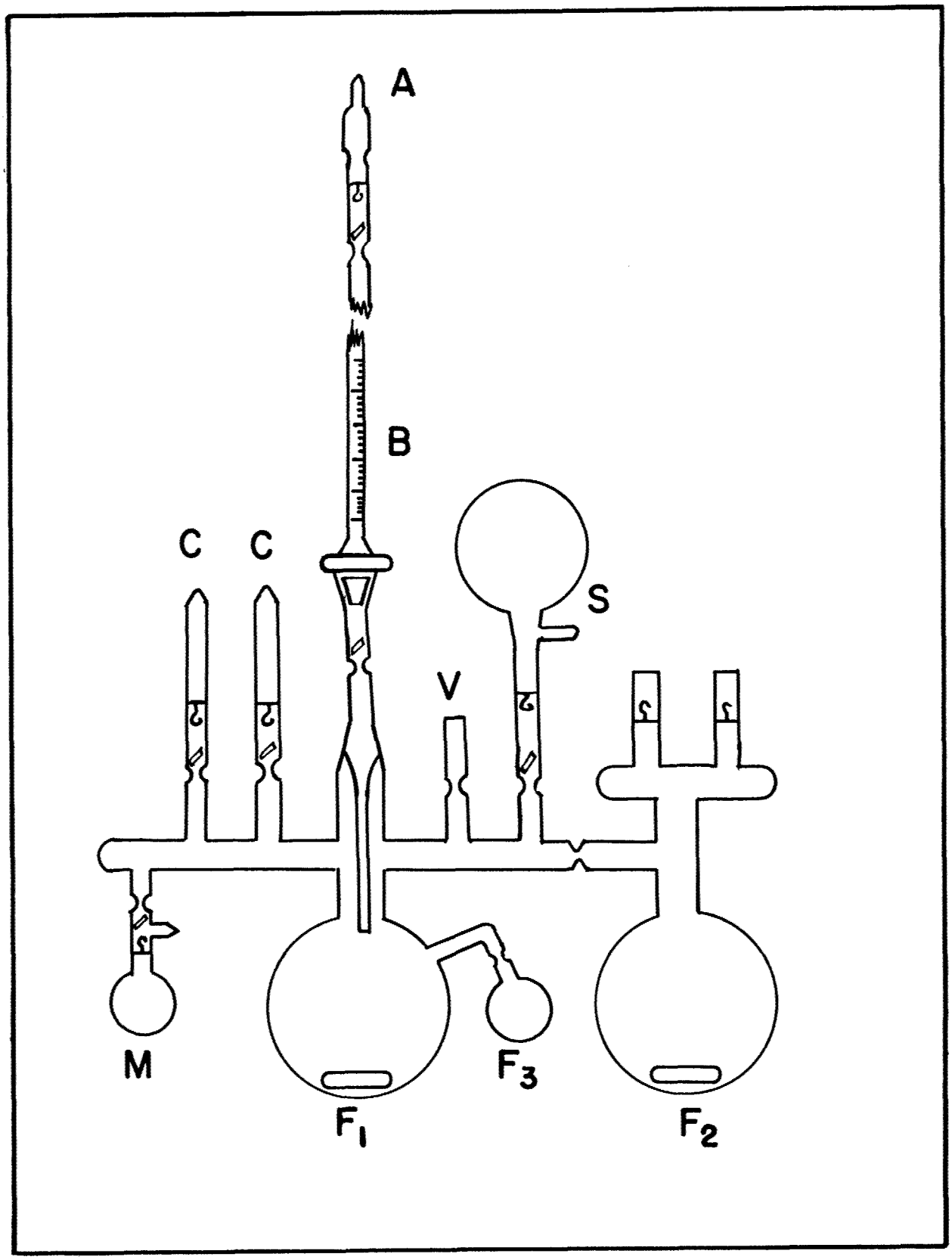


FIGURE 1 - POLYMERIZATION APPARATUS

THE INFLUENCE OF STRUCTURE ON THE MOLECULAR MOBILITY AND RHEOLOGY OF AMORPHOUS MACROMOLECULAR SYSTEMS

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A brief review with emphasis on the important open questions is presented of our knowledge of the factors influencing the chain mobility and mechanical properties of amorphous polymeric systems. It is necessary to give more precise meaning to the concepts of "chain entanglement" and "free volume" and to relate these to the structure of the repeating unit and to the gross chain structure of the macromolecules. From studies of the viscosity in bulk or in concentrated solution of model polymers and novel polymers, we propose to determine the influence on the mobility of heterogeneity in chain length distribution, of added diluent, and of the stereochemical chain structure. The initial data on polystyrenes of narrow distribution prepared in anionic synthesis, and of mixtures of these are presented here.

Introduction

Extensive data obtained over the past twenty-five years for amorphous polymer systems[1,2] have indicated that quite generally the chain mobility is goverened by two factors: (1) by the density of packing of the chain segments, which determines both the magnitude of the local friction factor and its temperature coefficient; and (2) by the interactions of units remote from each other in the liquid, but joined by primary valence bonds into long chains, and through "entanglements" of those chains into larger network structures. Stated more directly, both the viscosity and the time dependent rubber-like elastic response are sensitive to the total molecular chain length Z relative to the average number of chain atoms Z_c between interchain entanglements, and the temperature coefficient of these responses to stress is sensitive to the "free volume" which is itself dependent on the difference between the temperature and the glass temperature of the system.

Obviously it is important to give more precise meaning to the concepts of "chain entanglement" and "free volume," and to determine how these are influenced by the gross structural features such as chain length and its distribution, chain branching, and the dimensions of the polymer coil, and by the local structural details such as the steric and polar character of the repeating structural units and their relative stereochemical arrangements. It is the object of these studies to define more fully these relationships by viscosity studies in bulk or in concentrated solution of model polymers and of new and novel structures when they are available.

The immediate goals in our present investigations are to determine the influence on the melt viscosity of linear polymers:

(1) of the heterogeneity in chain length distribution, employing mixtures of monodisperse polystyrenes prepared by anionic techniques

(2) of added diluent, for a variety of polymer-diluent pairs

(3) of the stereochemical structure of these polymers.

The results of the latter two studies should provide evidence on the important question[3,4] as to whether the chain entanglements are similar to those between long coiled ropes or whether specific interactions are involved. The result of the first study will provide further test of the present theory of flow, and should provide a better knowledge and understanding of the complex and incompletely defined flow relationships for polymeric substances of moderate chain length ($Z < Z_c$)[5].

Here we report the few initial results of studies of the viscosities of mixtures. Data on the effect of diluent on the viscosity of homogeneous polystyrene samples will be available soon. The results of an attempt to prepare stereoregular polyvinyl acetate are given elsewhere[6]. Further, we take this opportunity to present a brief review of the background in this field.

Background

Studies on the viscosity-temperature-molecular weight relations for fractions of polystyrene and of polyisobutylene yielded the following result[1,7,8]

$$\eta = A Z^{3.4} \qquad Z \geq Z_c \qquad (1)$$

$$\eta = B Z^{a} \qquad Z \leq Z_c \qquad (2)$$

$$\frac{d \log \eta}{d_{(1/T)}} = F(T) \cdot f(1/Z) \qquad \text{any } Z \qquad (3)$$

Here η is the viscosity, T is the absolute temperature, and A, B, Z_c, and $\underline{a}$ are empirical constants characteristic of the polymer type. As an approximation, the dependence in Eq. (3)

$$f(Z) \sim (1 - \frac{1}{Z}) \qquad (4)$$

was observed[8] to parallel the dependence on Z of the specific volume v and of the glass temperature T_g

$$v = v_o + \frac{k_1}{Z} \qquad (5)$$

$$T_g = T_g - \frac{k_2}{Z} \qquad (6)$$

Values of v, T_g, and f(Z) are all sensibly constant if $Z > Z_o$, and increase (or decrease) at an accelerating rate with decreasing Z below this limit.

Subsequent studies of other systems indicated that the characteristics noted above are general for different polymer systems[1]. It was suggested that the isothermal dependence of η on $Z^{3.4}$ for long chains in Eq. (1), and of η on Z^a for short chains (with values of a of 1 to 2.4 depending on the system) express the mutual restriction on the flow of two chain segments far removed from each other in the liquid arising from the long chain structure; the increase in the temperature coefficient with decreasing Z below Z_o was thought to be due to the decrease in "free volume" associated with the increased concentration of chain ends for shorter chains.

In an approximate theoretical treatment[9], Bueche obtained the following limiting relations for monodisperse polymer chains;

$$\eta \sim Z^{3.5} f_o \qquad Z > Z_c \qquad (1')$$

$$\eta \sim Z\, f_o \qquad Z < Z_c \qquad (2')$$

For the short chains ($Z < Z_c$) he assumed that the long range interactions mentioned above are communicated solely through the primary valence bonds in a given chain, i.e., the molecular friction factor is equal to the product of Z and the friction factor f_o per chain atom. For the long chains ($Z > Z_c$) he considers the long range interactions to be communicated through the valence bonds in a given chain and through interchain entanglements, and in this case the molecular friction factor is $Z^{3.5} f_o$. Here the flowing system is considered to consist of an infinite network of entangled chains, which tend to drag one another along as they slip over each other in flow.

Comparison of Bueche's theory with Eq. (1) and (2) suggests: that network formation occurs first when $Z/Z_c = 1$; that the behavior predicted by Eq. (1') applies when $Z/Z_c \geq 1$; and that Bueche's theory does not predict accurately the result for $Z/Z_c < 1$ since the exponent a in (2) is generally greater than the value of unity predicted in (2').

Viscosity data[7,8] on mixtures of polystyrene fractions or of polyisobutylene fractions indicated that for heterogeneous systems

$$\eta = A\, Z_w^{3.4} \qquad Z_w > Z_c;\ Z_n > Z_o \qquad (1'')$$

$$\eta = B\, Z_w^{a} \qquad Z_w < Z_c;\ Z_n > Z_o \qquad (2'')$$

$$\frac{d \log \eta}{d_{(1/T)}} = F(T) \cdot f(1/Z_n) \qquad \text{any } Z_n \qquad (3'')$$

i.e., for such heterogeneous systems the viscosity-temperature coefficient is uniquely a function of the number average chain length, Z_n, whereas the isothermal viscosity for systems with $Z_n > Z_o$ is uniquely a function of the weight average chain length, Z_w. No adequate specification of the molecular weight dependence of η was found for heterogeneous polymers with $Z_n < Z_o$.

Recently Bueche[10] has suggested a further complication in the effect of heterogeneity of chain length distribution. Employing the aforementioned approximate theoretical treatment[9] he predicts for heterogeneous polymers with

components of $Z \gg Z_c$:

$$\eta \sim Z_\eta^{3.5} \qquad Z > Z_c \qquad (7)$$

where $Z_\eta = Z_w \qquad Z_z/Z_w < 1.8 \qquad (7\text{-}1)$

$$Z_\eta \rightarrow Z_z \qquad Z_z/Z_w > 1.8 \qquad (7\text{-}2)$$

Here Z_η is the chain length of a homogeneous polymer with a viscosity equal to that of the mixture.

Experimental and Results

Nearly twenty polystyrene samples of molecular weight ranging from 10^4 to 1.4×10^6 and of M_w/M_n of 1.01 to 1.06 prepared by the anionic polymerization techniques of Wenger and Yen[11] are available in our laboratory. These were further separated into fractions by addition at 30° of methanol to solutions of the polymer in benzene or in butanone. The molecular weights of the fractions were calculated from the measured values of the intrinsic viscosity in benzene according to the relations[12,13]

$$\log M_v = (\log [\eta] + 4.013)/0.74 \qquad M \geq 30{,}000 \qquad (8)$$

$$\log M_v = (\log [\eta] + 3.380)/0.60 \qquad M \leq 30{,}000 \qquad (9)$$

Mixtures of polymer fractions were prepared by dissolving weighed quantities in benzene, and by subsequent evaporation to dryness. A small amount (0.3 wt %) of phenyl-β-naphthylamine was added to minimize degradation during the melt viscosity determinations.

Melt viscosities were determined at 218° and at lower temperatures employing capillary viscometers and the techniques described earlier[1,7,14]. Intrinsic viscosities in benzene were measured on the sample after the melt viscosity measurement in order to determine the extent of degradation, if any.

The data on the viscosity-molecular weight relation at 218° for the present fractions of polystyrene prepared anionically are given in Table 1 and Figure 1. The lines in the latter are drawn in accord with the η-Z relations determined previously[8] for fractions of polystyrene prepared by free radical techniques. The fit of the present experimental points to these lines indicates excellent agreement between the observed behavior of the two sets of polymers.

In Table 2 the data obtained in our initial studies on mixtures of fractions are summarized. Although these data and the data assembled from the literature support (Figure 1) the earlier finding that the viscosity for heterogeneous systems with $Z_n > Z_o$ is determined by Z_w and not by Z_z, even when $Z_\eta/Z_w > 1.8$, it may be that the components of the mixtures do not satisfy Bueche's requirement that $Z \gg Z_c$. Thus conclusions on the effect of chain heterogeneity await completion of the measurements in progress on mixtures of both higher and lower chain lengths.

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TABLE I

Preliminary Viscosity Data on Fractions of Anionic Polystyrene

Designation		$M_w \times 10^{-3}$ [a]	η_{218}	$[\eta]$ [b]
Polymer	Fraction		poises	dl/gm
Molecular Weight Dependence				
8	AA	16.6	41.1	0.141
8	CB	18.7	42.5	0.151
8	CB	18.7	44.5	0.151
7	AA	38.1	204	0.238
7	AA	28.1	185	0.238
12	CB	45.0	220	0.277
11	CA	61.0	620	0.340
11	CA	61.0	685	0.340
D-1	CA	66.0	1,330	0.358
D-1	BA	71.0	1,390	0.378
11	BA	75.5	1,920	0.390
D-1	(Unfract.)	82.0	1,460	0.418
D-4	(Unfract.)	137.0	11,900	0.592
D-3	BA	141.0	14,600	0.620
D-4	CA	158.0	20,100	0.680
D-5	BA	195.0	43,200	0.792
D-6	BA	220.0	63,000	0.860

Temperature Dependence

		$\log \frac{\eta_{203}}{\eta_{218}}$	$\log \frac{\eta_{193}}{\eta_{218}}$	$\log \frac{\eta_{180}}{\eta_{218}}$	$\log \frac{\eta_{156}}{\eta_{213}}$
7	AA	--	0.76	1.09	2.25
11	CA	--	--	--	2.30
D-1	BA	0.69			
D-3	BA	0.35			
D-4	CA	0.34			
Reference 7		0.37	0.69	1.17	2.38

[a] $\log M_V = (\log [\eta] + 4.013)/0.74 \quad (M > 30 \times 10^3)$ [7]
$\log M_V = (\log [\eta] + 3.380)/0.60 \quad (M < 30 \times 10^3)$ [8]

[b] Measured in benzene at 30°C.

TABLE II

Viscosity Molecular Weight Data on Mixtures of Polymer Fractions of $Z_n > Z_o$

Mol. Wt. ($\times 10^{-3}$) + Wt. % of Components	calc'd M_z/M_w	M_η/M_w [a]	calc'd M_v/M_w	$\times 10^{-3}$ calc'd M_w	M_n	poises $\times 10^{-3}$ observed η_{218}
Present Preliminary Data on Anionic Polystyrene						
2,170 (3.85) 123 (96.15)	4.8	0.80	0.86	202	128	15.4
426 (41) 18.5 (59)	2.2	1.05	0.82	185	30	27.9
200 (50) 10 (50)	1.8	1.06	0.89	105	19	3.9
Free Radical Polystyrene[7]						
389 (50) 35 (50)	1.7	1.05	0.88	212	64	50
389 (50) 78 (50)	1.45	1.06	0.92	233	130	80.5
100 (50) 31 (50)	1.28	1.01	0.97	65.5	47.3	0.796
78 (50) 31 (50)	1.18	0.98	0.95	54.5	44.4	0.532
Polyisobutylene[7]						
233 (50) 38.2 (50)	1.5	1.00	0.83	204	66	4.56
81.5 (50) 30.0 (50)	1.2	0.98	0.96	55.8	44	0.321
Polyvinyl Acetate[15]						
2,870 (56.5) 1,040 (43.5)	1.3	0.95	0.96	2,070	1,620	--

[a] Calculated from the ratio of the molecular weight of a fraction having the same η_{218} as observed for the mixture to the calculated value of M_w for the mixture adjusted so that the calculated and observed M_v (after heating) are equal. The latter adjustment (generally indicating some degradation) was $\leq$ 6% except for the first mixture, where it was 9%.

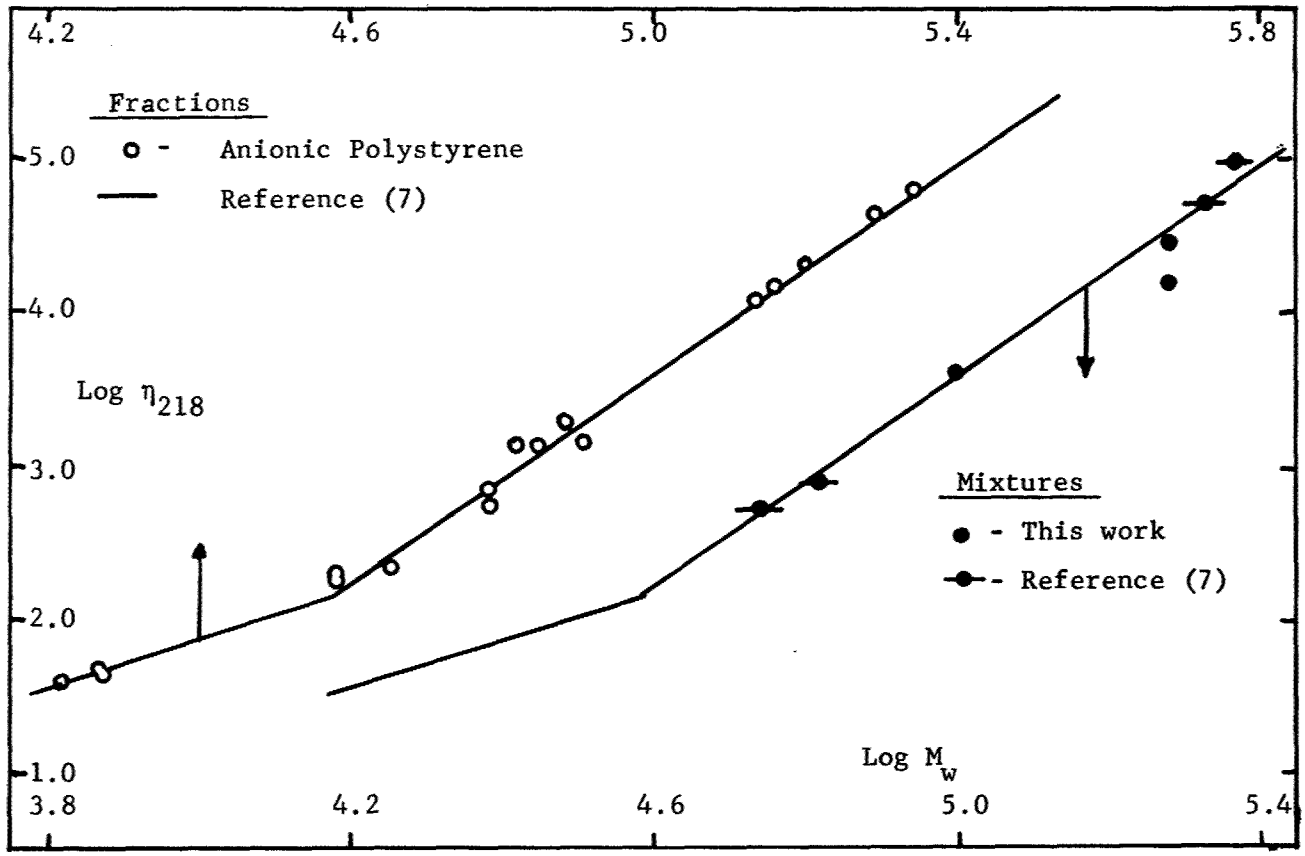


Figure 1. Preliminary η_{218}-M Data for Polystyrene Fractions and Their Mixtures.

Appendix

The various average molecular weights for heterogeneous polymers are defined by the usual equations

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \qquad \text{number average } (M_n) \qquad \text{(A-1)}$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad \text{weight average } (M_w) \qquad \text{(A-2)}$$

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \qquad \text{z-average } (M_z) \qquad \text{(A-3)}$$

$$[\eta]_{av} = \sum_i w_i [\eta]_i$$

$$M_v = \left[\frac{[\eta]_{av}}{K}\right]^{1/a} \qquad \text{viscosity average } (M_v) \qquad \text{(A-4)}$$

For a mixture of two homogeneous fractions consisting of weight fraction w_1 of molecular weight M_1 and $w_2 = 1 - w_1$ of molecular weight M_2,

$$M_n = \frac{M_2}{w_2}\left(\frac{r}{R} + 1\right)^{-1} \qquad \text{(A-5)}$$

$$M_w = w_2 M_2 (rR + 1) \qquad \text{(A-6)}$$

$$M_z = M_2 \left(\frac{rR^2 + 1}{rR + 1}\right) \qquad \text{(A-7)}$$

$$M_z/M_w = (r + 1)\frac{rR^2 + 1}{(rR + 1)^2}; \qquad M_w/M_n = \frac{(rR + 1)(r + R)}{(r + 1)^2 \cdot R} \qquad \text{(A-8)}$$

$$\text{where } r = \frac{w_1}{w_2}; \quad R = \frac{M_1}{M_2} \qquad \text{(A-9)}$$

In the special case where $w_1 = w_2 = 0.5$ and $r = 1$

$$M_z = \frac{M_1^2 + M_2^2}{M_1 + M_2}; \quad M_w = (M_1 + M_2)/2; \quad M_n = \frac{2M_1M_2}{M_1 + M_2} \qquad \text{(A-10)}$$

$$\frac{M_z}{M_w} = 2\frac{R^2 + 1}{(R + 1)^2}; \quad \frac{M_w}{M_n} = \frac{(R + 1)^2}{4R} \qquad \text{(A-11)}$$

It can be shown that M_z/M_w for a mixture of two fractions is maximum where $r = 1/R$. Then

$$\frac{M_z}{M_w} = \frac{(R+1)^2}{4R} \qquad r = 1/R \qquad \text{(A-12)}$$

$$\frac{M_w}{M_n} = \frac{2(R^2+1)}{(R+1)^2}$$

The relations in the following Table are useful here:

r	R	M_z/M_w	M_w/M_n
1	5	1.44	1.8
1	10	1.67	3.3
1	∞	2	∞
0.5	2	1.125	1.111
0.2	5	1.8	1.44
0.1	10	3.03	1.67
0.05	20	5.01	1.81
0.01	100	25	1.96
0	∞	∞	2

EFFECTS OF ULTRAHIGH PRESSURES ON THE FORMATION AND PROPERTIES OF ORGANIC, SEMIORGANIC, AND INORGANIC MATERIALS

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ABSTRACT

Studies on the effect of ultrahigh pressures (up to 90,000 atmospheres) were carried out on organic polymers and a variety of semiorganic and inorganic materials. The experimental work was done in a Belt-type internally heated high-pressure apparatus calibrated by means of electrical-resistance discontinuities in Bi, Tl, and Ba using the fixed pressure points of the "new" post-1960 absolute pressure scale.

With organic polymers results to date indicate that the effect of compression is influenced by: (1) The compression attained, (2) the compression rate, (3) the holding period, and (4) the polymer used. The most influential parameters within the target range of compression appear to be the polymer and the holding period. Results to date do not show any generalized pattern of behavior for polymers. Rather the limited data suggest that each material may well have its individual response to compression.

Among the semiorganic compounds studied, dimethyldicyano silane apparently polymerized at 60,000 atmospheres through conversion of the nitrile groups to > C = N -. Other semiorganics, alumino-siloxanes, ethyldicyanophosphine, arseno-siloxane, phosphonitrilic chloride trimer and diphenylphosphinoborine showed little effect of pressure or decomposed.

In the work with inorganic materials, ultrahigh-pressure high-temperature studies of two heteropolynuclear acids (silicotungstic and phosphotungstic acid) and two heteropolynuclear salts (ammonium-arseno-vanado tungstate and ammonium-phospho-vanado tungstate) revealed what appear to be pressure-dependent modifications over a broad pressure-temperature range to 75,000 atmospheres and 1300 C. The results of preliminary high-pressure experiments on a group of sulfides, including Sb_2S_3 and As_2S_3, and on apatite [$Ca_5(PO_4)_3(OH,F)$] were negative.

INTRODUCTION

Relatively recently (in the past few years) equipment and techniques for ultrahigh pressure* have been developed to the point where it is available for use as a method to modify or synthesize polymers.

Bridgman pioneered studies in the 1930's on very high pressures and interest continued but at a relatively low level until the last decade. At that time internally heated high-pressure devices, such as the Belt, were developed making the attainment of ultrahigh pressures at elevated temperatures feasible. Shortly thereafter came the development of a process (which quickly became commercial) for the production of diamonds from graphite and later the production of the heretofore unknown Borazon.

With this precedence, the question arose as to the possibility of improved polymers through such ultrahigh pressures and to answer this the Aeronautical Systems Division of the Air Force has sponsored this present study.

As the background relating to the effects of ultrahigh pressure was quite limited, this program was directed primarily towards a screening of the effects upon three classes of polymers, organic, semiorganic, and inorganic. Past efforts in the field of ultrahigh pressures were reviewed in a separate, initial phase of this study.

In the case of organic polymers, two general types of changes can be expected -- physical in which some property such as crystallinity is enhanced and chemical in which new bonds are established. It is the latter case which offers the most promise. It is expected that bonds which do not normally participate in polymerization reactions will be activated by the pressures exerted. These bonds include double and triple bonds, carbonyl linkages, aromatic carbon-carbon double bonds, nitrile, and the like. As has been already noted, evidence has been found of reaction of nitrile triple bonds under extreme pressure. It is known that rates and molecular weight increase as the pressures are increased in polymerizations but the phenomena have been studied only to much lower pressures than the target of this work. Possibilities here lie not only in the production of higher molecular weight materials but also in products of higher density through more complete crystallization. Unconventional routes to polymers through normally inactive groups are also of interest as is possible grafting to preformed polymers.

As was stated before, this program was designed to determine whether the extreme pressures would cause any of these changes in starting materials of the

*Ultrahigh pressures is here meant to be equal or greater than 30,000 atmospheres (new 1960 scale).

three classes of interest. Detection of these changes was to be made by measurement of physical or chemical properties by any one or combination of suitable methods.

APPARATUS

The high-pressure device used in all the studies on this project was the G.E. Belt based on the original design of H. T. Hall. Essentially, the Belt device consists of a pair of truncated tungsten carbide pistons which are forced by a hydraulic ram into a tungsten carbide die. Both the die and the pistons are surrounded by a series of concentric steel binding rings to afford massive support, and the device may be internally heated and instrumented. Hydraulic ram force was supplied by either a 1,000-ton Hall multiple-piston ram, a 100-ton Blackhawk jack, or a 150-ton Watson-Stillman press. Figure 1 shows an over-all view of the Belt apparatus and Figure 2 shows details of the apparatus as used with organic materials.

It should be noted that the pressure scale used in this research is the new (mid-1960) scale which is now generally accepted by workers in this field.

EFFECT OF PRESSURE ON ORGANIC MATERIALS

Polymer Compression

Compression studies conducted during the course of this program have been divided into two categories for convenience in discussion. First, those conducted in an intermediate range to investigate the effects of different parameters, and, second, compressions conducted within target range. Characterization in all instances was based upon net density change of the polymer.

Parameter Investigation at Intermediate Compression

Effect of Compression on Density. Currently the density-gradient apparatus appears to be the most satisfactory method for rapidly determining the extent of change in the polymers used in this study. At present, the columns are designed to give resolution to one in the fourth decimal place. Density gradient columns were used to provide a comparison of the density of molding materials with extruded material. There generally was a slight increase, possibly due to some

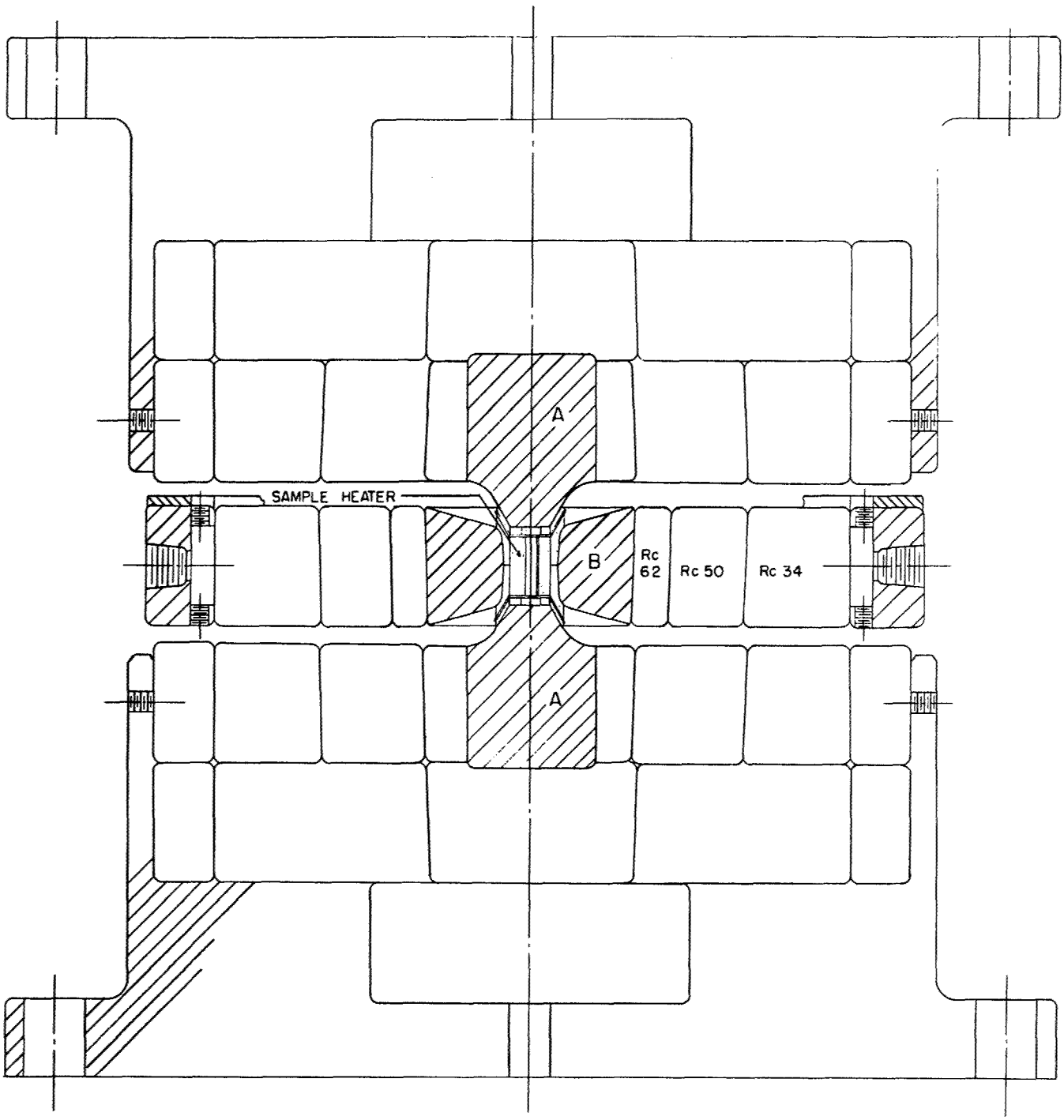


FIGURE 1. BELT ULTRAHIGH-PRESSURE APPARATUS

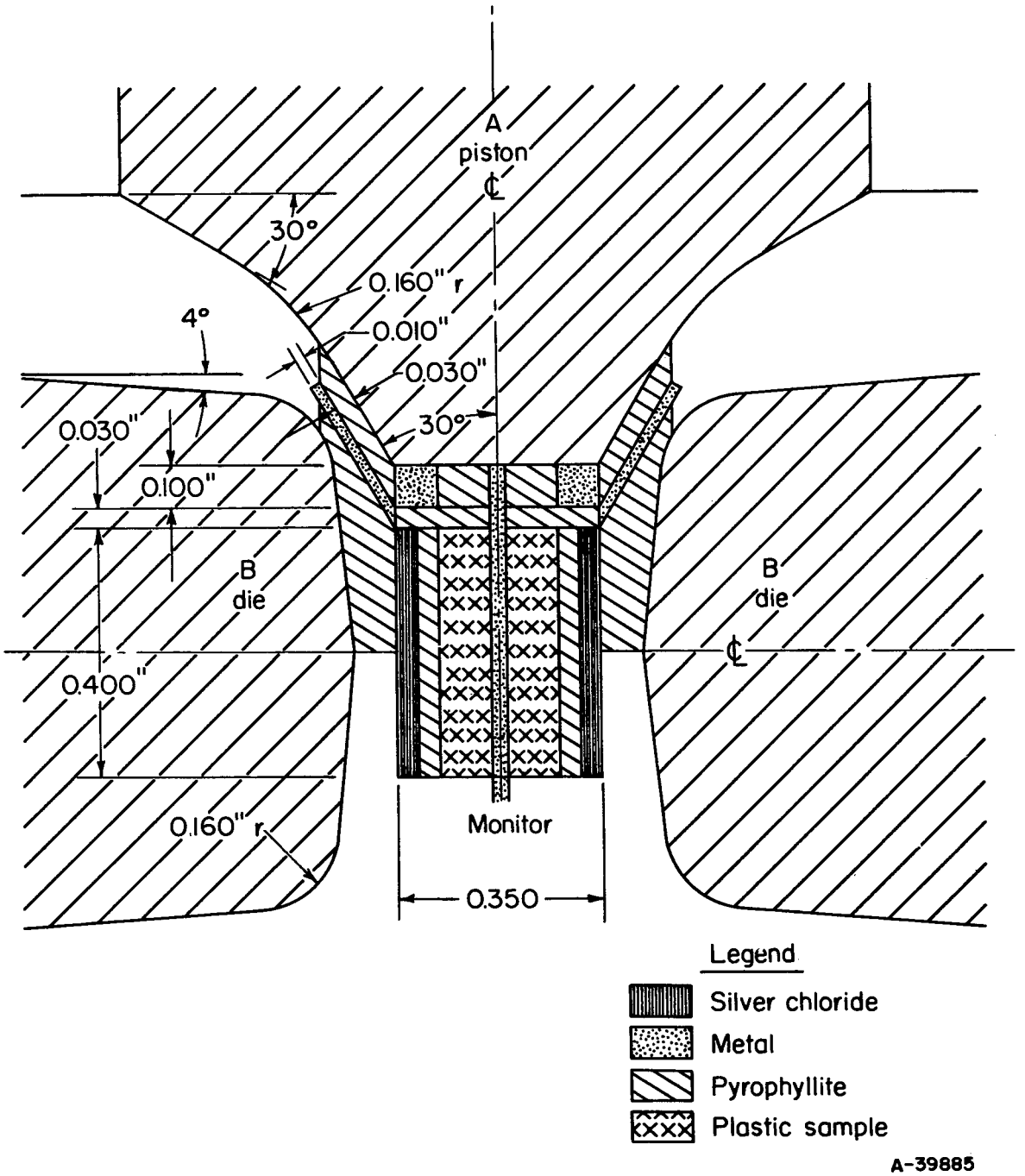


FIGURE 2. ULTRAHIGH PRESSURE ASSEMBLY USED IN POLYMER COMPRESSION

loss of volatile components, but more likely due to slower cooling rates after molding, permitting a higher degree of crystallization than is found in the molding pellets. This effect was rather pronounced in the case of the high-density polyethylene. Initially, the density was determined to be 0.9581, but after molding the density was 0.9647.

The effect of compression on polymers appeared to vary with the material, maximum pressure, rate and time of loading and temperature. These factors were not comprehensively studied during the intermediate compression program, nor have these preliminary results been verified by confirmatory runs.

Reductions in density were observed for most of the short-period runs at moderate compressions. This was true for runs with low- and high-density polyethylene, and polypropylene. However, several runs were made in which reductions either were not observed or the density was increased by the compression conditions used. These runs were made either by slow compression, prolonged holding under pressure, or by heating under pressure. This behavior was observed for low-density polyethylene which was used for the greater part of the study directed toward an extension of techniques. It appears reasonable to expect somewhat similar behavior with the high-density polyethylene and possibly polypropylene.

Compressions with polystyrene and polymethylmethacrylate, on the other hand, showed increasing densities roughly correlatable with estimated compression pressures. Results for work to date appear to be in general agreement with work reported by several investigators [1,2]. Larsen and Drickamer applied a shearing force to polymers under 50,000 atmospheres. Short-time loads were used in which degradation was observed for polyethylene, polymethylmethacrylate, and others. Polymers containing unsaturation (olefinic or aromatic), such as polyisoprene or polystyrene, were crosslinked by this treatment. The mechanism postulated was free-radical formation by bond rupture. In systems containing unsaturation, the free radicals apparently reacted readily to form crosslinked materials. Similar studies by Professor Roy were reported to give degradation with polyethylene and polyacrylonitrile, but to have no effect on polystyrene.

It is interesting to note that in this work with hydrostatic loading, density reductions, suggestive of degradation, occurred with moderate super-pressures up to 35,000 to 40,000 atmospheres, under fairly rapid loading and short holding periods. This conceivably could produce sufficient stress to cause bond rupture similar to that reported by Larsen and Roy. However, slower loading, longer compression periods, higher temperatures or pressures have in several cases shown a reversal of this trend.

It is suspected that the effect of the currently used hydrostatic compression would be considerably less drastic than the effect of high-pressure shearing of a polymer. Correlations of over-all experimental results to date with Larsen-Drickamer's results appear to confirm this. Since their studies indicate the degradation reaction, as determined by infrared methods, is virtually complete within a minute compared to the very small changes noted in the present work.

During preparation of equipment capable of attaining pressures of about 100,000 atmospheres, the effect of several compression parameters on density were studied for polyethylene and two types of polyamides. It was hoped that critical parameters could be further defined during this period to minimize the runs required to obtain a fairly valid appraisal of the maximum effect of 100,000-atmosphere compression. The results of work suggest that both loading rate and maximum compression modify the effect on a given polymer. However, in the range of parameters studied in the intermediate compression range, the most critical parameter still seems to be the polymer used.

Effect of Loading Rate on Polymer Density and Compression. Studies to evaluate the effect of this factor were conducted on polyethylene, and two types of polyamides.

Results of this study are shown in Figures 3 and 4. In general, results for polyethylene (Petrothene) and polyhexamethylenediamine sebacic acid (Nylon 610) show fairly well-defined patterns at least in the lower compression ranges. The polyethylene showed some irregularities above 35,000 atmospheres, but results qualitatively agree with the projected trend. Generally, results to date with it and Nylon 610 indicate that slow compression of a sample tends to produce increased density reduction. However, the tendency for the polyethylene patterns to converge might imply that density increases would be effected at sufficiently high compressions. The pattern is more random for the polyamide, and projection, at present, less meaningful. Where polyethylene and Nylon 610 appear to show higher relative densities as compression pressures are raised at constant time, the reverse is shown for polycaprolactam (Nylon 6). The more rapid loading rate appears to produce greater reductions in density. The data for studies with this polymer do not show the well-defined patterns of polyethylene and Nylon 610, but graphical interpretation of the data tends to support the observation.

Concurrently with the evaluation of the effect of loading rate on density, a brief study was made of the effect of loading rate on internal compressions. This work conducted on Nylon 610 compared the behavior of this system through the lower bismith transition at three different loading rates. Results of this work, Figure 5, indicate that, at least for this system, slower loading rates are more

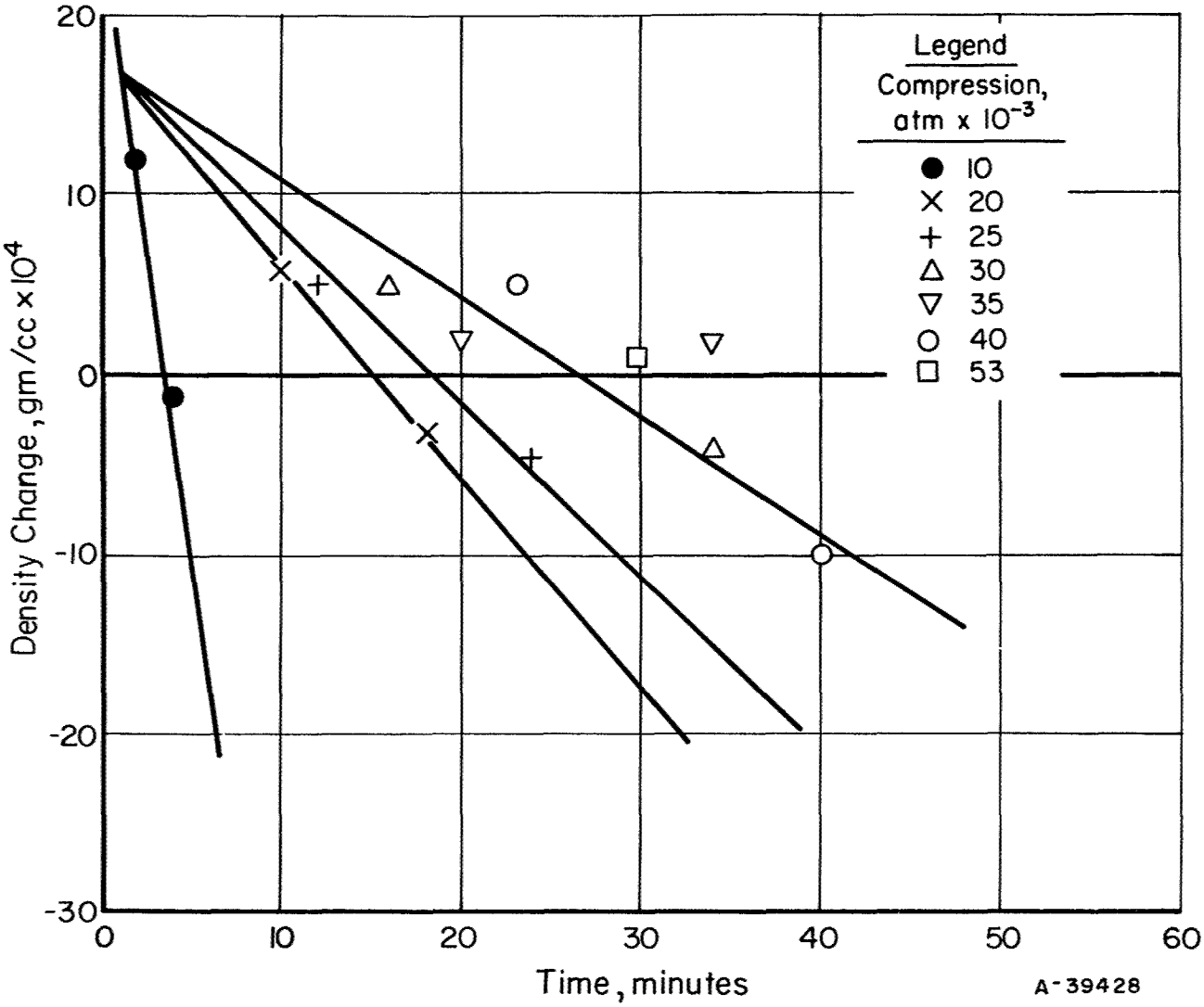


FIGURE 3. EFFECT OF TIME TO REACH MAXIMUM LOAD ON POLYETHYLENE DENSITY

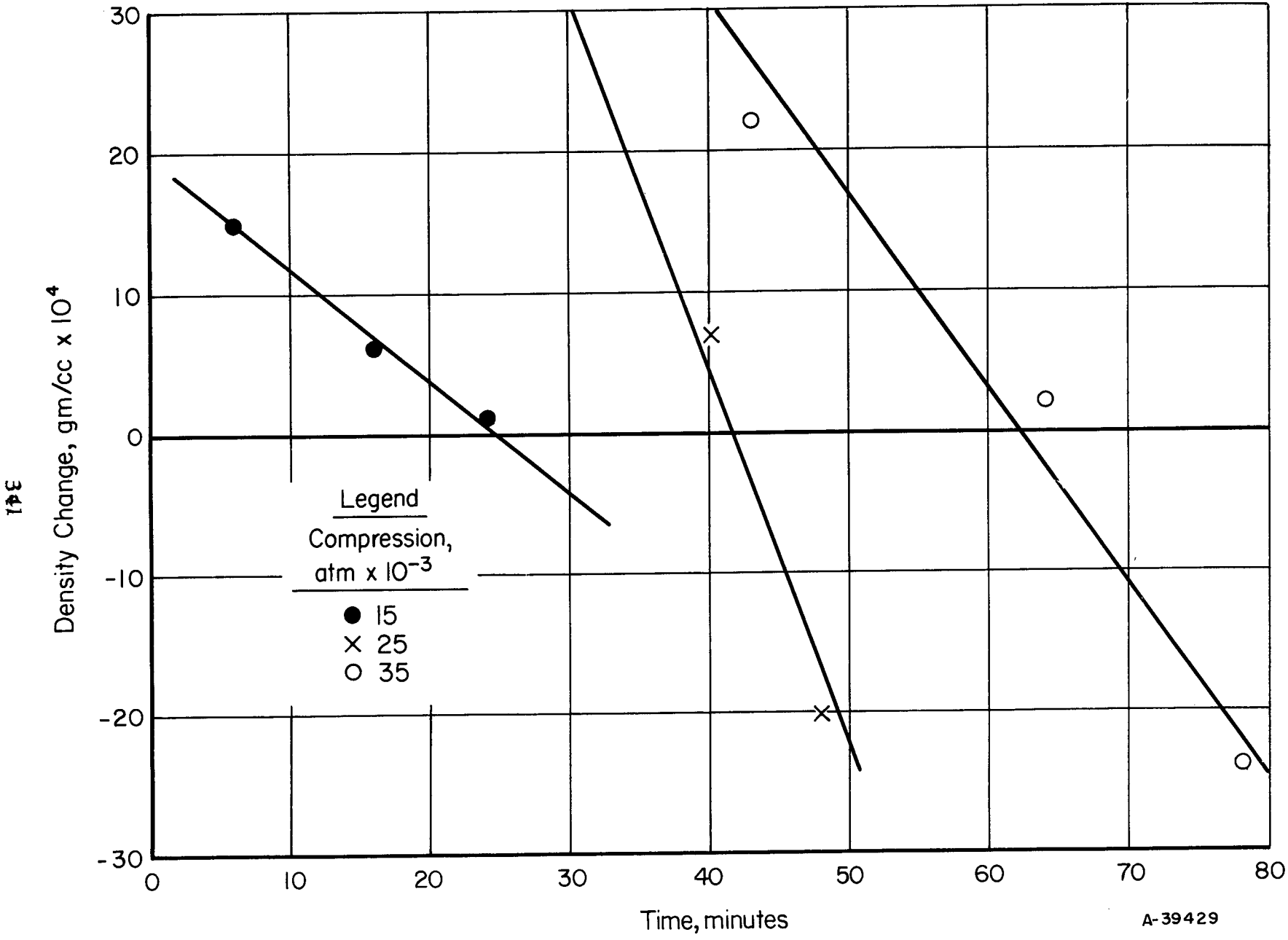


FIGURE 4. EFFECT OF TIME TO REACH MAXIMUM LOAD ON NYLON 610 DENSITY

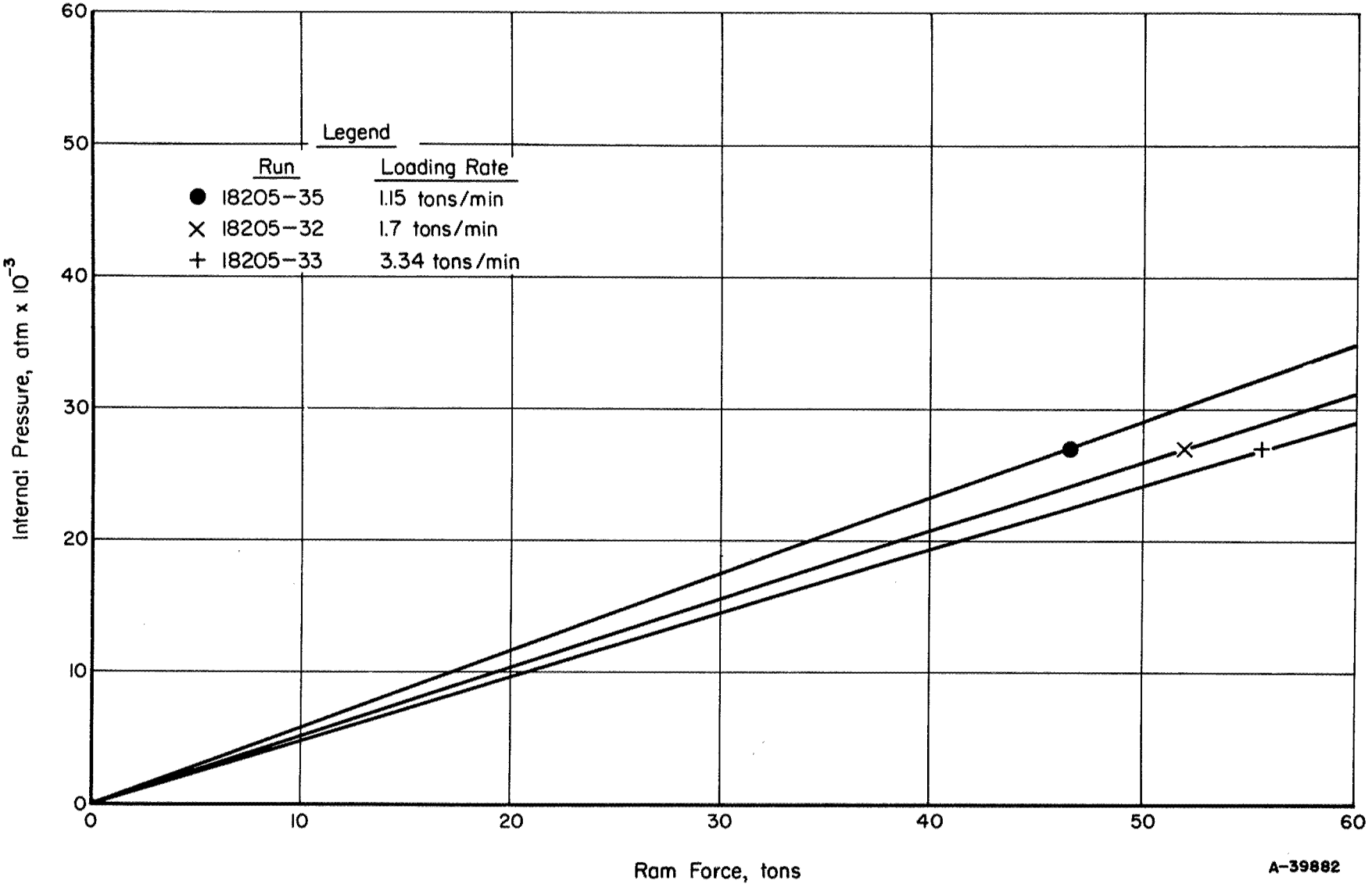


FIGURE 5. EFFECT OF LOADING RATE ON INTERNAL COMPRESSION IN NYLON 610

efficient. About 20 per cent more loading was required to produce the bismuth I-II transition at a loading rate of 3.3 tons per minute than at a loading rate of 1.1 tons per minute.

Correlation of Polymer Compression Studies. Although data from an adequate number of runs to determine the interrelationship of internal compression, loading rate, and density change with unquestionable validity for the polymers studied was not available, an attempt was made to correlate these effects to determine possible trends. Sufficient data were obtained for polyethylene and polyhexamethylenediamine sebacic acid (Nylon 610) to show slight similarity in pattern. Polycaprolactam (Nylon 6) appeared to behave differently. Preliminary work with these materials was conducted with a short holding time (two minutes) at maximum compression.

In the case of polyethylene, Figure 6, the effect of compression rate appears to diminish as compression pressures are raised. Rapid loading, however, appears to give the greatest increase in density. While data suggest the convergence of polymer densities under higher compressions to minimize the effect of compression rate, the projection suggests that only limited density increases may be obtained. A somewhat similar situation exists for Nylon 610. Fewer data, however, were available for correlation with this system and results are inconclusive at present.

Data available for Nylon 6 on the effect of time to reach maximum load were interpolated to provide a pattern for projecting Figure 7. This also indicates a tendency for the rate effect to diminish as the compression pressure is raised. This projection, however, indicates a marked tendency for a reduction of polymer density with increasing compression.

Projected correlation of data for polyethylene and Nylon 610 suggested that under present target compression, around 100,000 atmospheres, present compression rates and short holding times, very little net density change would be predicted. Data for Nylon 6, however, suggested that similar super-pressure treatment might effect significant density reductions.

Present conclusions based upon data available to date are: (1) that compression rate, compression used, temperature, and undoubtedly holding time, effect the net density change, (2) that different polymers may have a characteristic response to a given set of compression conditions.

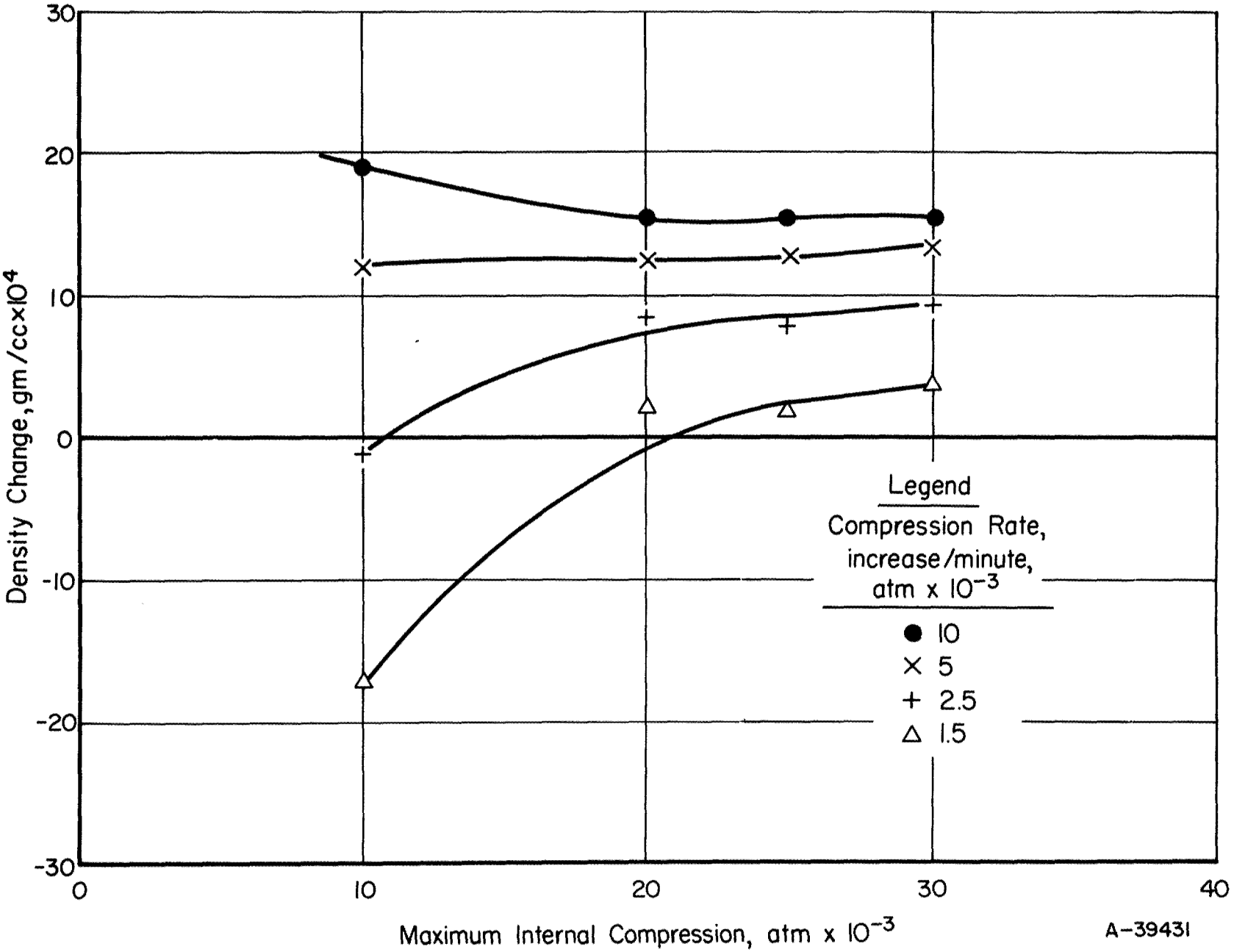


FIGURE 6. PROJECTED EFFECT OF INTERNAL COMPRESSION AND COMPRESSION RATE ON DENSITY OF POLYETHYLENE TO 30 KILOBARS

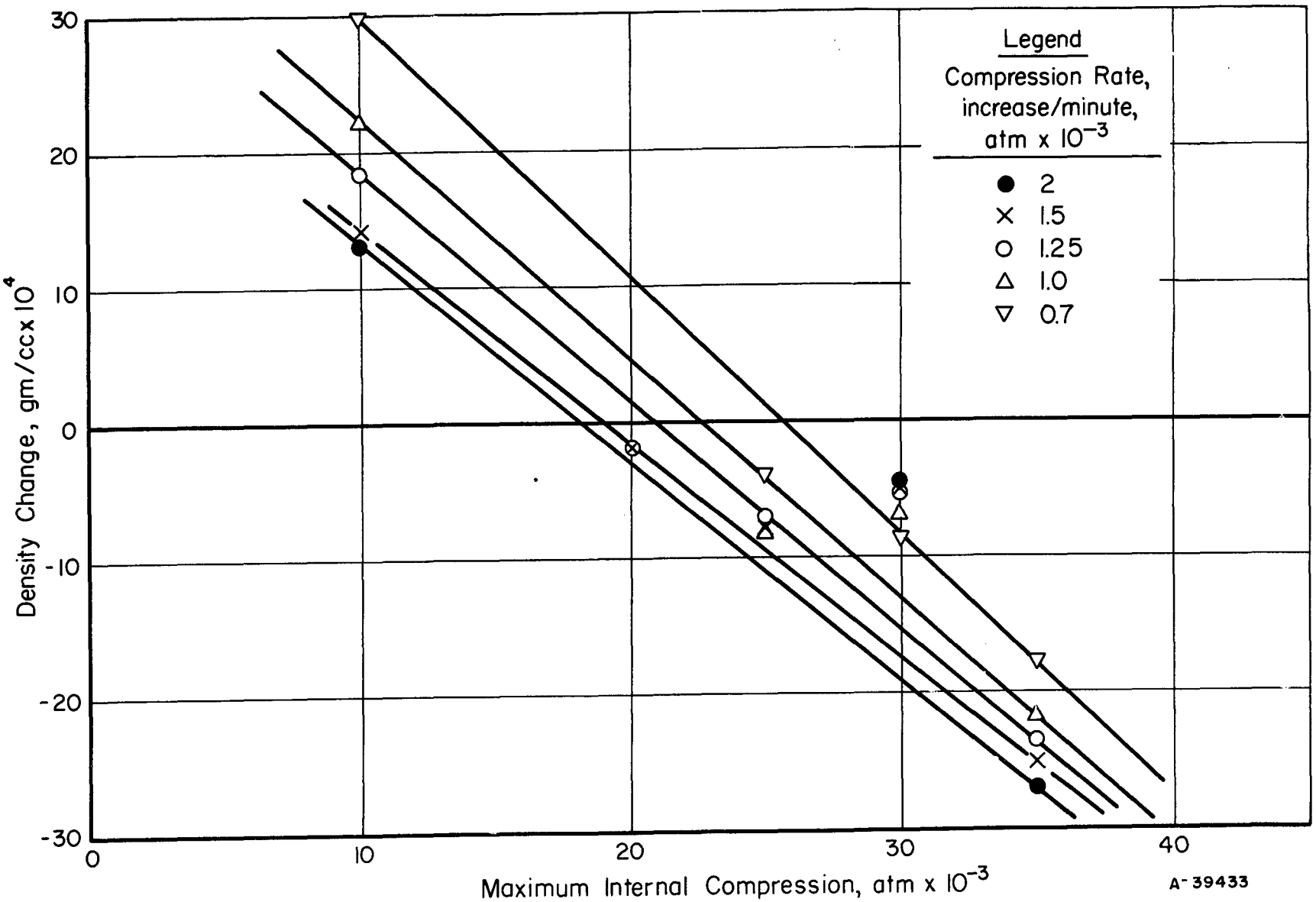


FIGURE 7. PROJECTED EFFECT OF INTERNAL COMPRESSION AND COMPRESSION RATE ON POLYMER DENSITY FOR NYLON 6 TO 35 KILOBARS

Polymer Compression in Target Range

Effect of Compression Holding Time and Correlation With Intermediate Compression Data. Work was conducted with polyethylene to verify the projected trend and runs of longer duration made to determine the effect of compression holding time. The predicted effect of negligible density change for a 2-minute holding period was confirmed at 90,000 atmospheres with an observed net density change of (-0.0001 gm/c.c.) Figure 8. However, prolonged holding periods (30 and 60 minutes) at comparable compressions produced significant density increases (0.0010 — 0.0026 gm/c.c.). Similarly density increases were observed for ethyl cellulose and polystyrene. Prolonged holding of polycaprolactam (Nylon 6) Figure 9, did produce net density increases greater than that predicted from the preliminary correlation, but increasing compressions continued to show reductions in density which were consistent with the established behavior at lower compressions. Similar prolonged compressions of polyformaldehyde (Delrin) will require evaluation in a salt column since the compressed material appears sensitive to the solvent column.

Effect on Polymer Properties. This factor has not been studied in detail. Density evaluations have been used for the most part to determine whether pressure induced changes have been effected. Early studies with high-density polyethylene and polypropylene revealed that electron microscopy techniques could be used to show differences in fine structure of control and compressed polymers. This, however, has not been employed in the more recent runs at the higher pressures. Some evidence has been obtained to indicate changes in the solubility characteristics of compressed polymers. Polyformaldehyde appears unaffected by the solvent density gradient columns before compression. Solvent absorption of the compressed polymer, however, appears so rapid that meaningful density data cannot be obtained with the solvent columns.

Effect of Generic Types on Polymer Compression. The fact that early work indicated varying behavior for different polymers under compression makes this correlation of extreme interest. The program was set up to study a broad spectrum of carbon backbone polymers modified either in the main chain or on a side chain. Materials scheduled in the study included several types of polyethylenes, and polyamides, polypropylene, polystyrene, polyacrylonitrile, polymethylmethacrylate, and ethyl cellulose. Results of work to date suggest differing behavior for individual polymers. Data presently are incomplete for all materials under target conditions, but polymer behavior under compression appears, to date, to be more influenced by the generic structure than by the types within a given generic structure.

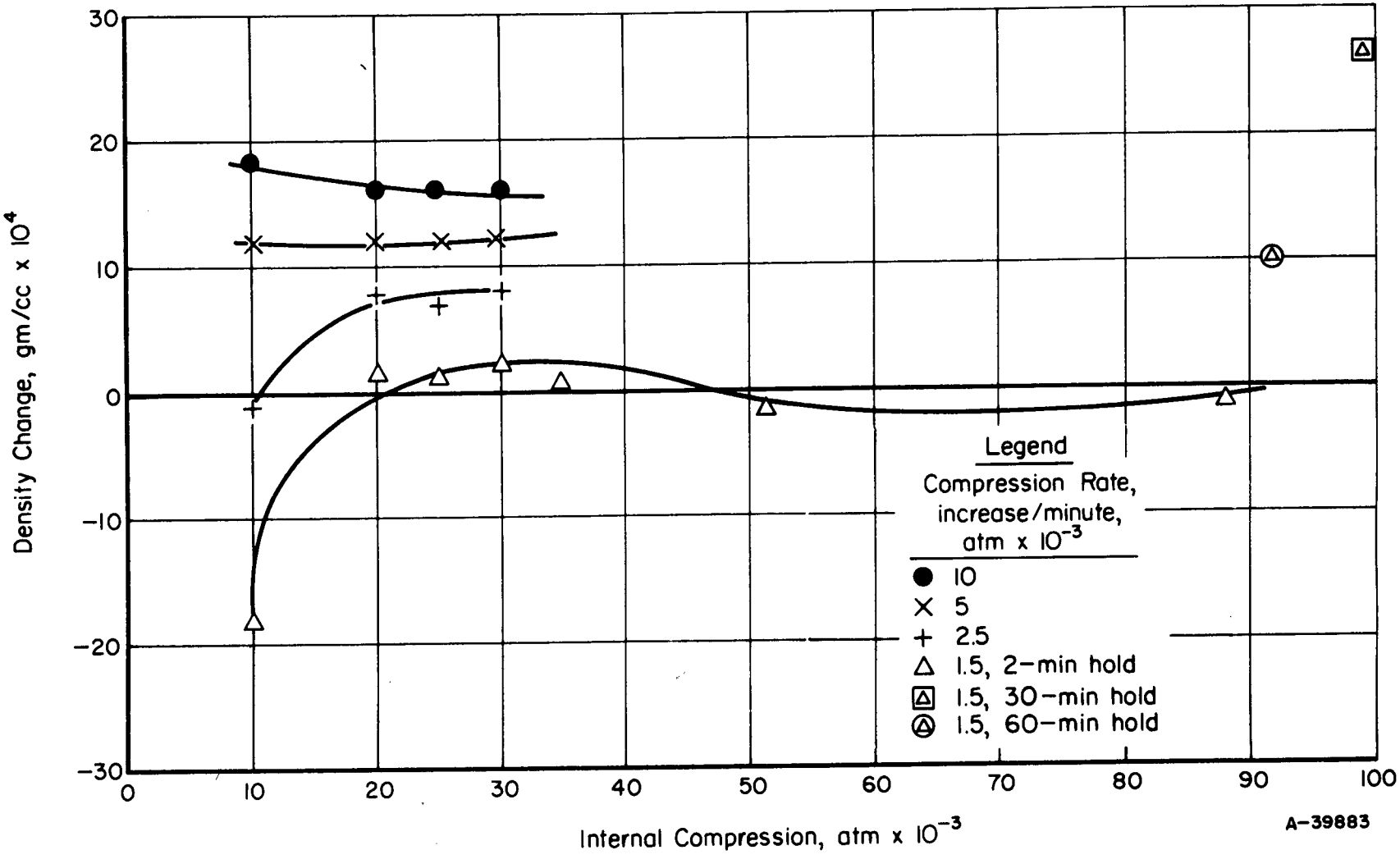


FIGURE 8. EFFECT OF COMPRESSION HOLDING TIME ON POLYMER DENSITY-POLYETHYLENE

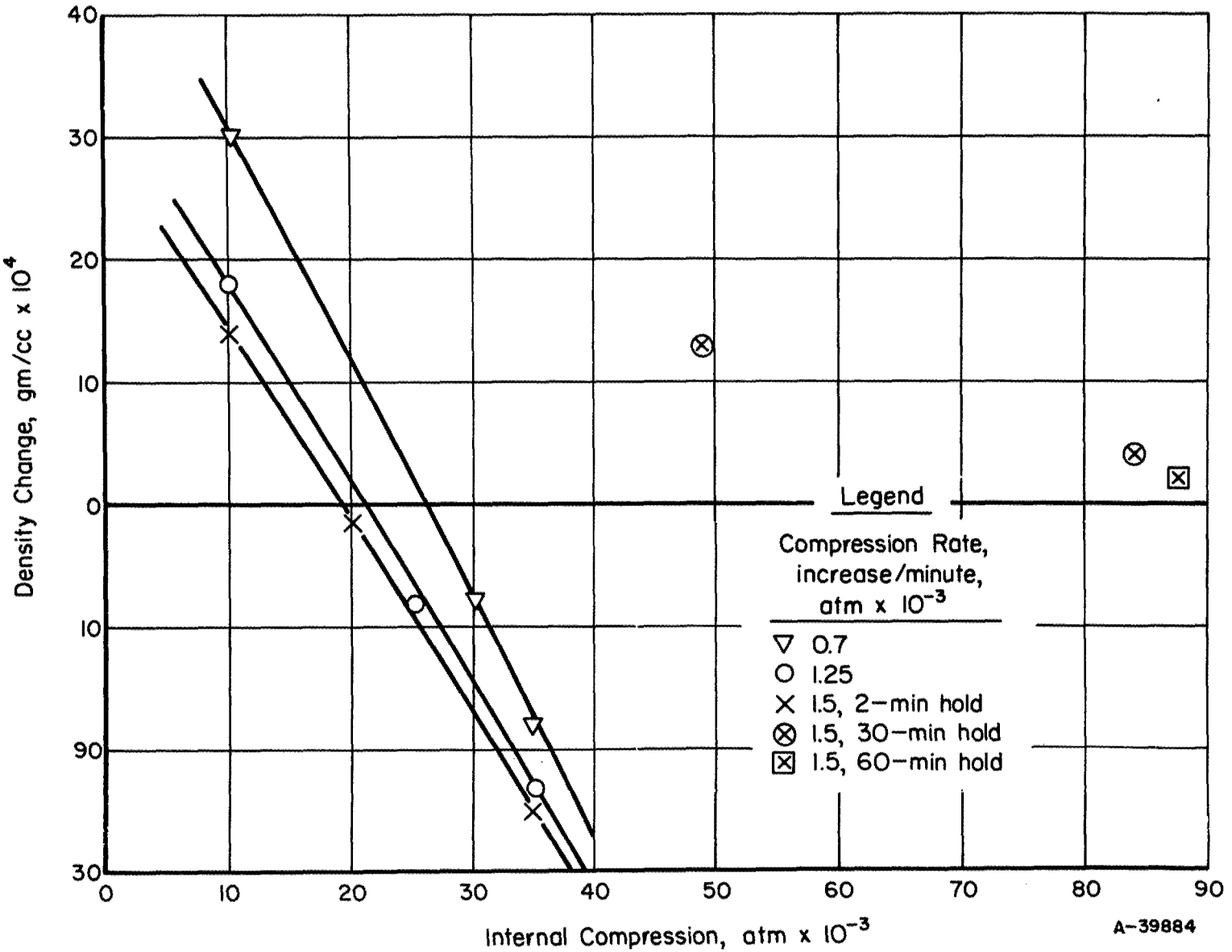


FIGURE 9. EFFECT OF COMPRESSION HOLDING TIME ON POLYMER DENSITY-NYLON 6

Current Status of the Program

Compression techniques, instrumentation and critical parameters of this phase of study have been resolved and a number of polymers compressed in the target range. The most influential parameter appears to be the holding time. Data pertinent to this observation are summarized in Table 1. Results indicate that increased holding time is effective in increasing polymer density under compression. Prolonged runs, however, have not been made to determine whether equilibrium densities of compressed polymers ultimately reach the same value regardless of compression. Runs are contemplated under target conditions to explore this effect and with the remainder of the polymer series to further clarify the generic effect on polymer compression.

EFFECT OF PRESSURE ON SEMIORGANIC MATERIALS

Pressurization Experiments

The semiorganic materials were subjected to compressive forces which produced 60,000 to 75,000 atmospheres when silver chloride was used as a calibration medium. The semiorganic materials studied in this phase were synthesized as a part of the work.

Dimethyldicyanosilane

This compound is very sensitive to moisture and changes from a white crystalline solid to a colorless oil in 1 — 2 min. when exposed to the atmosphere. Consequently, it was loaded into the platinum capsule under dry argon.

When this material is pressurized (at 60,000 atm), reaction as indicated by changes in its infrared spectrum does not occur until the temperature is raised to 100°C. Heating the compound in a sealed Pyrex tube at 100°C for 3 hrs. leaves it unchanged, but combined pressure and heat cause the dimethyldicyanosilane to change to a brownish-black product, which is not moisture sensitive and is no longer soluble in common organic solvents. The infrared spectrum of the product indicates the formation of some C=N bonds, although not all of the C≡N character has disappeared. Analysis for C, H, and N shows a loss of all three components which is equivalent to the loss of 3 HCN from 4 molecules of $(CH_3)Si(CN)_2$. However, the result is complicated by the appearance of absorption bands in the spectrum, which may come from water introduced from the pyrophyllite gasket

TABLE 1. EFFECT OF EXTREME COMPRESSION IN THE DENSITY OF ORGANIC POLYMERS

Run[1]	Material	Maximum Press Load, tons	Estimated Maximum Compression, atmospheres x 10^3	Holding Time, minutes	Density Change, grams/cc
64	Petrothene	140	90	2	-0.0001
65	Petrothene	150	92	30	+0.0010
66	Petrothene	150	98	60	+0.0020
68	Nylon 6	50	30	Blow-out	-0.0007
67	Nylon 6	80	49	30	+0.0013
68	Nylon 6	145	83	30	+0.0004
69	Nylon 6	150	86	60	+0.0002
71	Ethocel	125	72	30	+0.0040
70	Ethocel	150	84	60	+0.0045

material. Further investigation with baked-out pyrophyllite will be made. Increasing the pressure to 75,000 atm at 100°C increases the amount of C=N that appears.

Figure 10 shows the conditions of temperature and pressure under which reaction has been observed. It is expected that subsequent experiments will define a boundary between the regions of reactivity and inactivity. Efforts will also be made to resolve the nature of the C=N bonding. It could be the result of either partial condensation to a triazine structure, or linking of adjacent molecules in a linear structure.

Aluminum-Oxygen-Silicon Polymers

The pressure experiments on the four polymeric materials having Al-O-Si bonds were all performed at 60,000 atm. The temperature ranged from 100 to 400°C and the time of pressurization varied from 2 to 8 hours.

Dimethylsiloxy-Aluminum-Acetylacetonate Polymer. The combined heat and pressure had no permanent effect on this material at 100 or 200°C. At 300°C no change was observed after 2 hours at pressure. However, when the time was extended to 8 hours, some of the silicon-carbon bonds were broken, as indicated by the infrared spectrum, with consequent reduction in carbon and hydrogen content. A comparison experiment, run at 300°C and atmospheric pressure, resulted in breaking of the acetylacetonate ring in addition to silicon-carbon bonds and showed greater loss of carbon and hydrogen. At 400°C pyrolysis occurred.

Diethylsiloxy-Aluminum-Acetylacetonate Polymer. This material was unchanged under pressure at 100°C and at 200°C in three-hour experiments. The silicon-carbon bonds were affected at 300°C and, as the time of exposure at this temperature was increased to 8 hours, differences between the pressurized and unpressurized samples were observed. The acetylacetonate ring was broken in the case of the unpressurized sample, but the over-all loss of carbon and hydrogen was less than that for the pressurized sample. This material also underwent pyrolysis at 400°C.

Diethylsiloxy-Aluminum-Isopropoxide Polymer. This material was unaffected by the combined heat and pressure at 100°C and 200°C. At 300°C, the breaking of the silicon-carbon bonds occurred more rapidly than it did for the polymers in which the acetylacetonate was bonded to the aluminum.

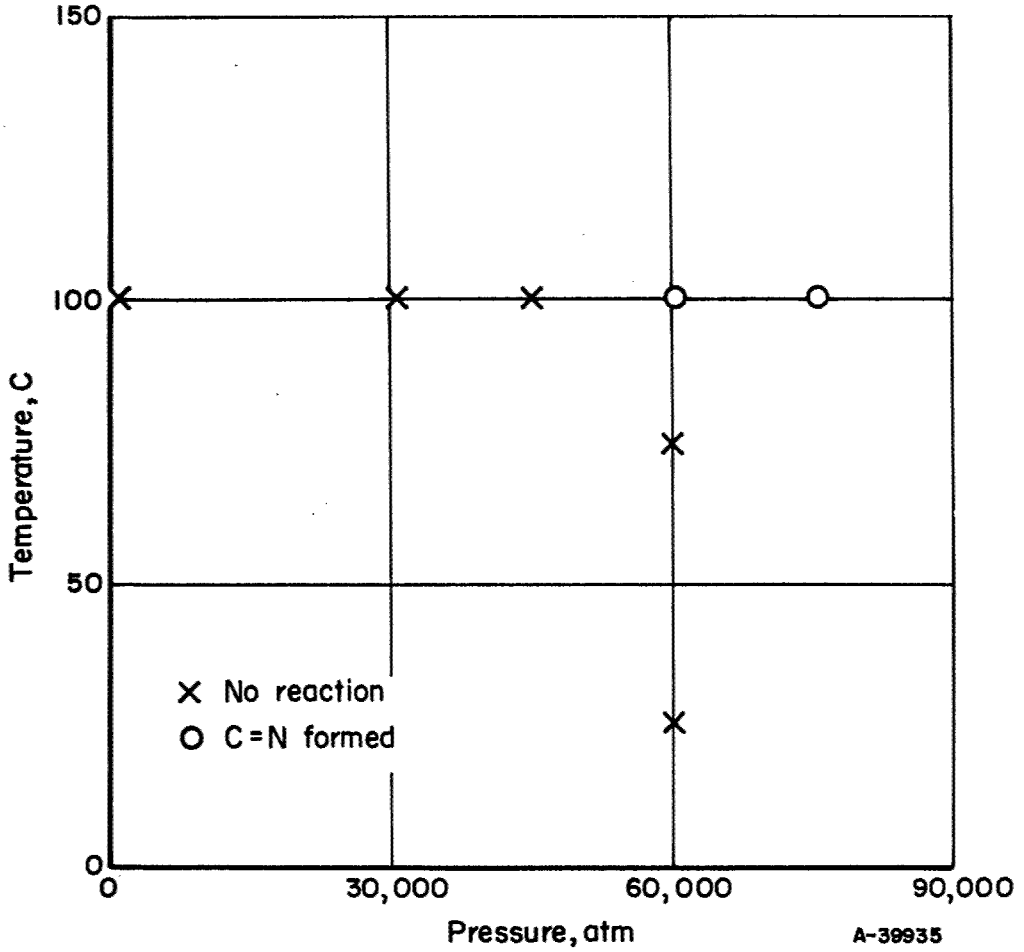


FIGURE 10. EFFECT OF PRESSURE AND TEMPERATURE ON C=N FORMATION IN $(CH_3)_2Si(CN)_2$

The unpressurized sample showed greater effect on the group bonded to aluminum than on that bonded to silicon. Pyrolysis occurred at 400°C in this case also.

Diphenylsiloxy-Aluminum-Isopropoxide Polymer. No change occurred in this material when pressurized at 100 or 200°C, but when the temperature was raised to 300°C, pyrolysis took place rapidly.

Ethyldicyanophosphine

This compound is extremely sensitive to atmospheric moisture and had to be loaded into the pressure capsules under the blanket of dry argon. Extensive decomposition of this compound began at 50°C under 60,000 atm pressure. Pressurization at room temperature resulted in the disappearance of C≡N bonding, as indicated by infrared spectra. However, allowing the compound to stand uncovered in air at ambient temperature brought about these same structural changes. In future experiments, it may be possible to separate the effects of moisture and oxygen from those of pressure on this compound, to establish whether or not there is any real effect of pressure.

Tris(Diphenylsiloxy) Diarsenic (III)

This cyclic material having As-O-Si bonding, $As[OSi(C_6H_5)_2O]_3As$, was unaffected by pressures of 60,000 atm at temperatures as high as 400°C for periods of several hours. When pressurization was conducted at 500°C for three hours, definite structural changes occurred. As indicated by the infrared spectra, these appear to be breaking of the silicon-carbon bonds. Unpressurized samples held at 500°C for a 3-hour period did not degrade quite as extensively. This case was the first encountered in this study in which high pressure appears to have increased the rate of decomposition of a material.

Diphenylsiloxy-Arsenoxane Polymer

The linear polymer of the As-O-Si series, which has been formulated as $AsO(OH)_2[OSi(C_6H_5)_2OAsO(OH)]_nOH$ started decomposing when subjected to 60,000 atm at 100°C for 3 hours. Pyrolysis occurred readily when the material was pressurized at 200°C.

Phosphonitrilic Chlorides

The phosphonitrilic chloride trimer, $(PNCl_2)_3$, was subjected to 60,000 atm pressure and a temperature of 240°C was maintained for 30 min. The sample changed in color from white to tan and the melting point was lowered from 113-114°C to 106-107°C. However, identical results were obtained by simply heating a sample of the trimer at 240°C for 30 min. The infrared spectra of the two samples were identical also. In another experiment the temperature was maintained at 300°C while the pressure was applied. A high polymer which could be heated to 500°C without melting was obtained. However, in this case also, the same result was obtained by application of heat alone. Thermal energy appears to be sufficient to break the bonds in the ring structure of the $PNCl_2$ trimer, and pressure does not contribute any permanent effect.

The linear polymer fraction of phosphonitrilic chloride, which had been extracted from a mixture of the cyclic and linear polymers, was subjected to 60,000 atm also. After 3 hours at 200°C the thermal stability of the material was altered. The starting material did not melt, but slowly charred as the temperature was raised to 300°C. However, the pressurized product melted in the range 270-300°C. This result points to the formation of lower molecular weight polymers than the starting material, but no suitable solvent for molecular weight determination could be found. Infrared analyses were inconclusive also, as there was no significant absorption in the infrared region for either the treated or untreated specimens.

Phosphinoborine Polymers

Diphenylphosphinoborine trimer, $[(C_6H_5)_2PBH_2]_3$, was pressurized at 60,000 atm at temperatures up to 400°C, where pyrolysis occurred. Only slight structural changes were observed below the pyrolysis temperature, and these could be brought about by heat alone.

A solid which separated during the preparation of the diphenylphosphinoborine trimer appears to have some unusual properties, although it has not been characterized completely. This material melted at 188-192°C and remained liquid to 360°C, where it volatilized slowly. Analysis showed lower carbon and hydrogen content than the trimer, and molecular weight determinations were inconclusive. Under pressure it did not pyrolyze until the temperature reached 500°C, although an unpressurized sample held at 400°C for 8 hours in a sealed Pyrex tube degraded extensively. Further study of this material seems to be warranted.

EFFECT OF PRESSURE ON INORGANIC MATERIALS

Effect of Pressure on Heteropolynuclear Acids and Salts

Experimental high-pressure high-temperature work was done on two heteropolynuclear acids and two heteropolynuclear salts. The former pair are silicotungstic acid ($H_4SiW_{12}O_{40}\cdot nH_2O$) and phosphotungstic acid ($H_3PW_{12}O_{40}\cdot nH_2O$), and the latter pair are hydrated ammonium phospho-vanado-tungstate [$(NH_4)_{3+x}PV_xW_{12-x}O_{40}\cdot nH_2O$ in which x approximates 1, crystallized from solution at high pH with initial solution weight ratios of P:V:W = 1:1:16] and hydrated ammonium arseno-vanado-tungstate [$(NH_4)_{3+x}AsV_xW_{12-x}O_{40}\cdot nH_2O$ in which x approximates 2, crystallized from solution at high pH with initial solution weight ratios of As:V:W = 1:3:16].* The experimental runs and the results obtained are summarized in a set of temperature-pressure diagrams (Figures 11, 12, 13, 14). The boundary lines on the diagrams which delineate the stability fields for the various structural modifications are, of course, solely schematic, and many more experimental data are required to determine their positions accurately. At this juncture, however, they are useful as guides for further experimental work. The products corresponding to the points on the diagrams have been evaluated by X-ray powder diffraction methods and, for some of the silicotungstic acid products, by optical crystallographic methods as well. X-ray powder diffraction data have been obtained for the various structural modifications found in experimental products. As a control on the validity of any conclusions regarding pressure-induced transformations, the effects of temperature at 1 atmosphere on each of the materials under study has been determined.

Experimental High-Pressure Products From Silicotungstic Acid

Silicotungstic acid has been studied in greater detail than the other materials, and, accordingly, descriptive notes on some of the products are recorded.

The starting material (Fisher Reagent A-289) is a colorless coarsely crystalline powder composed of single-crystal grains up to 2 mm in size. It is uniaxial negative with $\omega = 1.724$, $\epsilon = 1.692$, and a moderately high birefringence. It is probably a higher hydrate than the cubic material with 8 H_2O listed in the ASTM index of X-ray powder diffraction patterns (data of Scroggie and Clark[3]). When the Fisher compound is heated in air at 1 atmosphere it transforms above about 125°C to a colorless isotropic material with an index of refraction of 1.915 ± 0.005 and a powder pattern corresponding to a body-centered cubic cell

*Synthesized by J. J. Bulloff and P. F. Kurz at Battelle Memorial Institute.

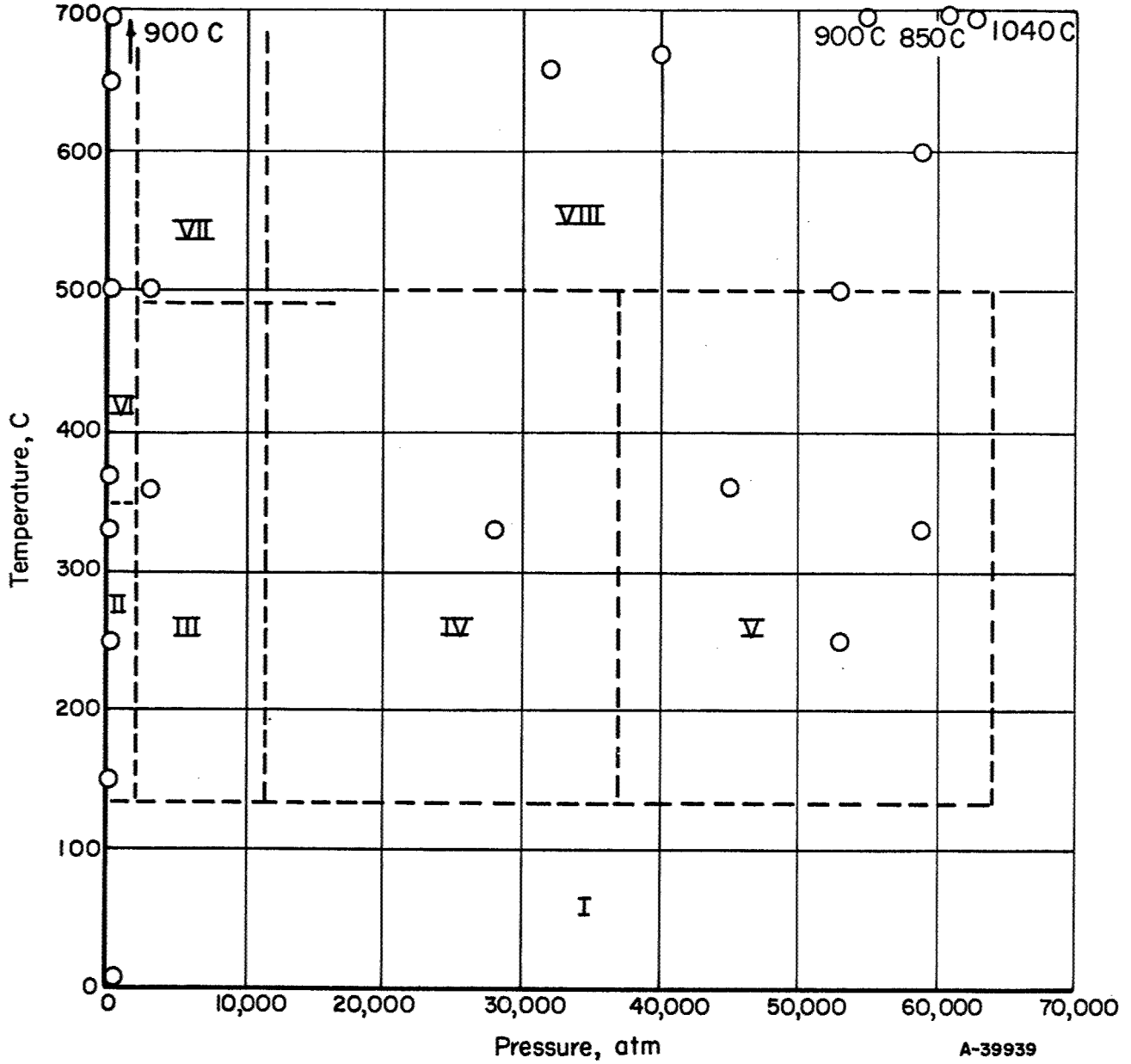


FIGURE 11. PILOT OF EXPERIMENTAL RUNS ON SILICOTUNGSTIC ACID

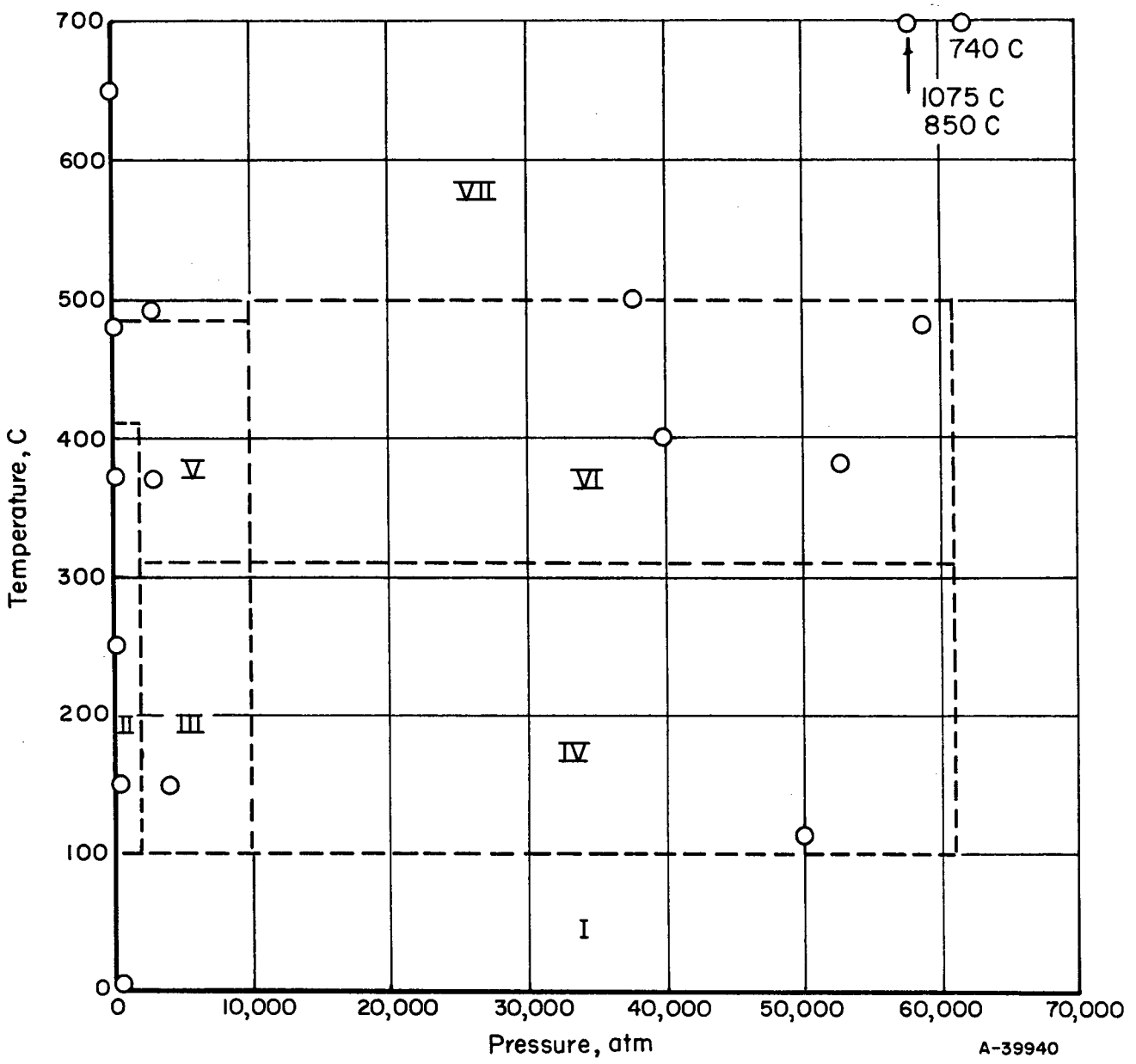


FIGURE 12. PLOT OF EXPERIMENTAL RUNS ON PHOSPHOTUNGSTIC ACID

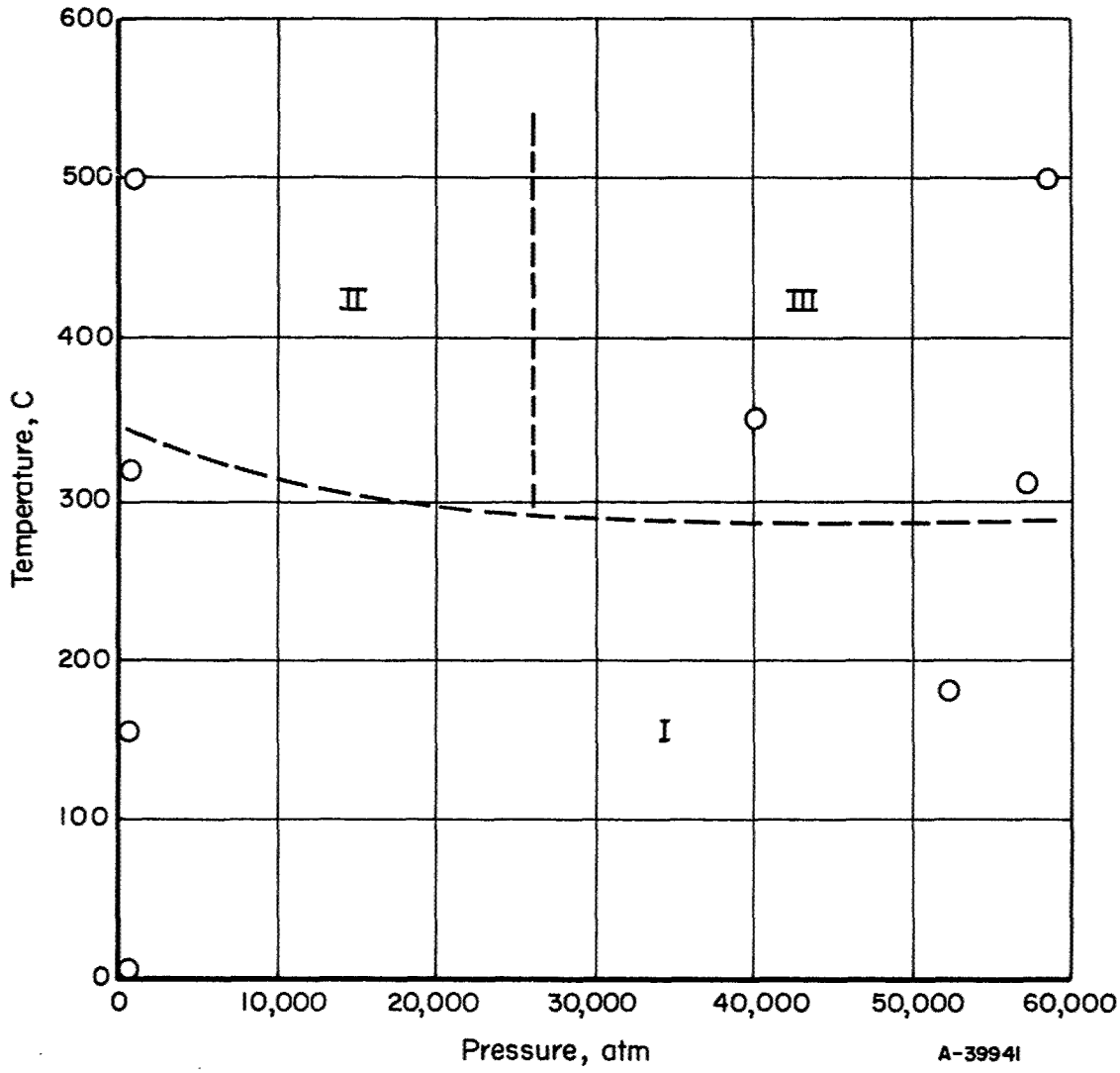


FIGURE 13. PLOT OF EXPERIMENTAL RUNS ON HYDRATED AMMONIUM-ARSENO-VANADO-TUNGSTATE

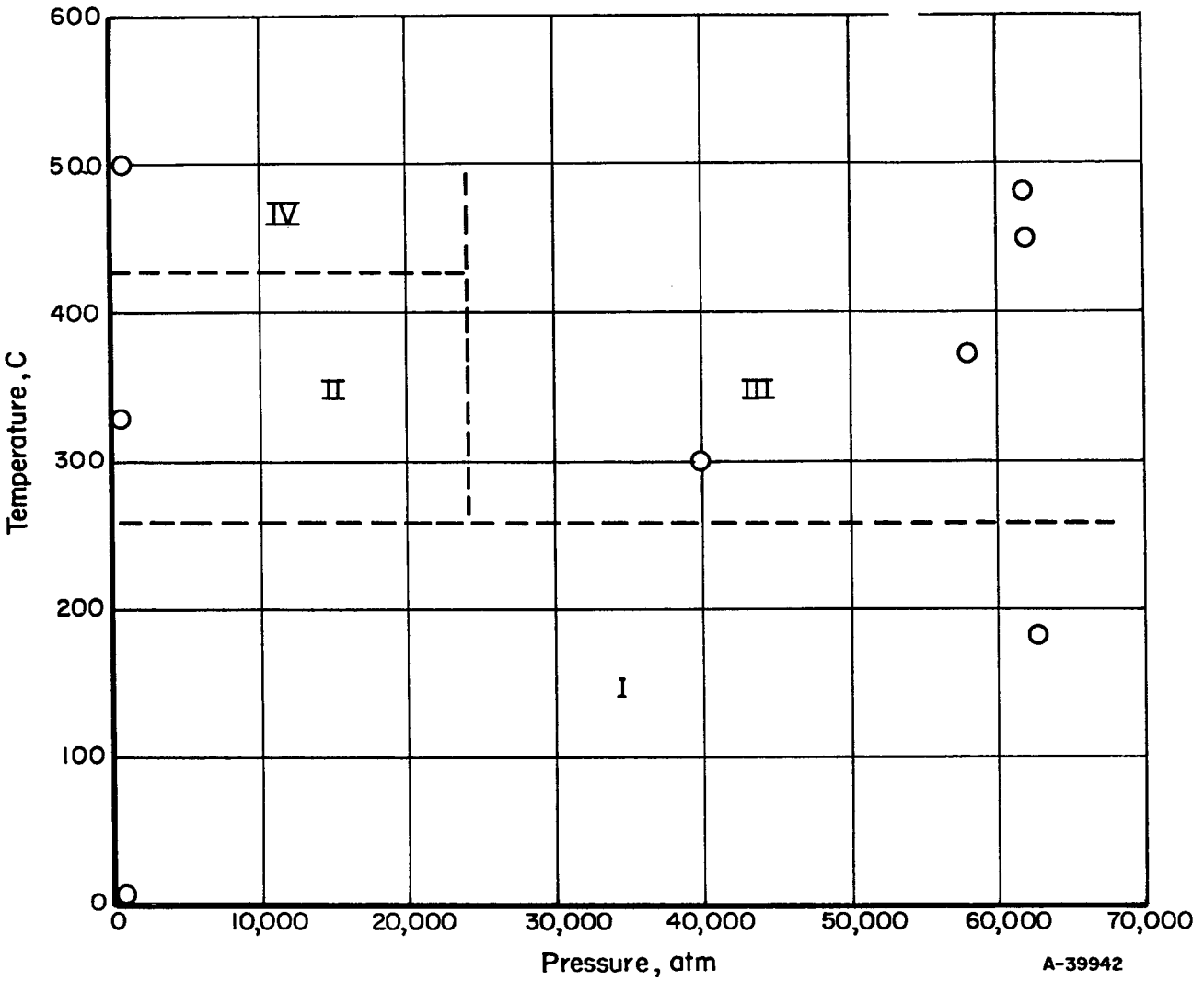


FIGURE 14. PLOT OF EXPERIMENTAL RUNS ON HYDRATED AMMONIUM-PHOSPHO-VANADO-TUNGSTATE

with a_o = 12.16 Å, which is equivalent to that given on the ASTM card. Two spacings (d = 8.6 Å and d = 6.08 Å for hkl of 110 and 200, respectively) were not obtained on a cylindrical film by Scroggie and Clark but were verified by them on a flat film. Because of these experimental differences the relative intensities of these two lines with respect to the rest of the pattern were not recorded, and, probably for this reason, these lines were not listed on the ASTM card. In the present study, both of these spacings were obtained with the entire pattern on a cylindrical film, using a 114.6-mm camera, and the 8.6-Å spacing was found to be the strongest (100) line of the pattern; the 6.08-Å spacing has a relative intensity of about 35.

When the Fisher reagent is heated to 500°C at 2600 atmospheres, a black powder with a unique pattern and optical properties is obtained.

The powder is composed of square to rectangular tablets with an average side length of about 10 microns; a few are as long as 35 microns. The tablets have an intense pleochroism with extraordinarily strong absorption when observed in transmitted light in the direction of the optic axis which is normal to the broad face of the tablets. The pleochroic formula is ω = deep green-blue to practically opaque even in strongly convergent light depending on thickness, and ϵ = pale yellow to colorless. Because of the strong absorption it is not possible to measure the index of refraction, but; is probably greater than 2.00. The tablets show extinction between crossed nicol prisms parallel to their sides; this suggests tetragonal symmetry. The product might be anhydrous ($SiO_2 . 12WO_3$), possibly a defect structure, and it may have useful properties as a pigmenting and opacifying agent in refractory paint. It should impart a jet black appearance to paints because the tablets tend to lie on their broad faces whose poles are the direction of greatest light absorption.

The product obtained at 28,000 atmospheres and 350°C (Figure 2, Field IV) is a white fine-grained material which is barely resolvable with the light microscope. It has a high birefrigence and indices of refraction greater than 2.00. By contrast, Field V is occupied by a fine-grained canary-yellow material with an average crystallite size of 1 to 2 microns and individual crystals as large as 5 microns. The crystals are yellow square to rectangular tablets, probably tetragonal in symmetry, and with the optic axis apparently normal to the broad face of the tablets. The extinction positions are parallel to the diagonals of the tablets, and the indices of refraction are $\omega > 2.10$ and $\epsilon \approx 2.00$ with high birefringence.

The product obtained at 53,000 atmospheres and 500°C was zoned, with a yellow core and a pale, greenish peripheral zone. The yellow core material was shown to be equivalent to Field V by both optical measurements and by X-ray

powder diffraction. It is, however, more coarsely crystalline, and many tablets have side lengths up 10 microns. The greenish peripheral zone gives the diffraction pattern of Field VIII. The peripheral zone is composed of relatively large square and rectangular tablets commonly with side lengths as great as 30 microns and, rarely, as great as 90 microns. The tablets are pale yellow to colorless in transmitted light and have extinction positions parallel to the sides, which suggests tetragonal symmetry. Most of the crystals have a very high birefringence when viewed normal to their broad faces; this suggests that the optic axis is probably in the plane of the tablets. Many crystals of this green peripheral zone are internally zoned with a central, irregularly shaped, deep-blue core (Field VII material) which is in apparent optical continuity with the pale yellow to colorless peripheral zone.

The product obtained at 59,000 atmospheres and 600°C is a pale yellowish-green well crystallized powder composed of crystals with rectilinear outlines, many of which approach the equidimensionality of cubes. Eighty-five to 90 per cent of the crystals are homogeneous and pale yellow to colorless in transmitted light. Their mean index of refraction is greater than 2.10. The remaining 10 to 15 per cent are zoned with deep blue to almost opaque irregular cores (Field VII material) and pale yellow to colorless peripheral zones. The cores of the zoned crystals are typically volumetrically dominant and are in optical continuity with peripheral zones, and the direction with the deep blue color appears to coincide with the direction of an optic axis. The crystals are probably tetragonal and uniaxial negative. They appear to be equivalent to those which constitute the greenish peripheral zone of the zoned product, described in the preceding paragraph.

General Conclusions

The experimental results to date may be summarized as follows:

(1) Silicotungstic acid transforms above 475°C to a phase which is stable at pressures between 20,000 atmospheres and 60,000 atmospheres and at temperatures to at least 1100°C. This phase may be obtained by pressurizing either reagent-grade hydrated silicotungstic acid as received or silicotungstic acid which was preheated in air at 1 atmosphere at 650°C. The phases obtained by preheating reagent-grade silicotungstic acid in air at 1 atmosphere between 300 and 700°C are not equivalent to the stable phase obtained by pressurization above 450°C and 20,000 atmospheres.

(2) Phosphotungstic acid transforms above 500°C to a phase which is stable at pressures between 1 atmosphere and 60,000 atmospheres to at least 1075°C. This phase is obtained by pressurizing either reagent-grade hydrated phosphotungstic acid as received or phosphotungstic acid which was preheated in air at 1 atmosphere at 650°C. It may also be obtained by heating reagent-grade phosphotungstic acid to 650°C in air at 1 atmosphere. This phase is not equivalent to other phases obtained from both preheated and hydrated phosphotungstic acid at temperatures below 500°C and at pressures up to 60,000 atmospheres.

(3) Both silicotungstic acid and phosphotungstic acid appear to have at least three pressure-dependent hydrated(?) forms which occupy regions on a P-T diagram between 200 and 500°C and between 5,000 and 75,000 atmospheres.

(4) It is interesting to note that although silicotungstic acid preheated at 650°C will transform at 60,000 atmospheres and between 850 and 1000°C to the same phase as is obtained by application of the same P-T conditions to reagent grade silicotungstic acid, both silicotungstic and phosphotungstic acid preheated to 370°C at 1 atmosphere and then subjected to 75,000 atmospheres at 370°C remain unchanged. The reason for this anomalous condition is unknown.

(5) The heteropolynuclear salts also appear to have pressure-dependent (ammonia-deficient ?) modifications (Figures 12 and 13).

Effect of Pressure on Polynuclear Sulfides

In preliminary experimentation prior to intensive study of polynuclear sulfides, a group of sulfides of diverse structure including As_2S_3, Bi_2S_3, Ag_3SbS_3, $PbCuSbS_3$, FeS, and HgS were subjected to pressures between 60,000 and 75,000 atmospheres at temperatures between 250 and 1000°C under anhydrous conditions. Finely ground natural crystalline compounds were used as reactants. Experimental details are assembled in Table 5. No pressure-dependent changes were found in any of these materials, but one problem has arisen, namely, that Sb_2S_3 reacted with and largely digested the platinum tube at high pressures and at temperatures above 550°C. The reaction products are a crystalline multiphase

TABLE 2. HIGH PRESSURE EXPERIMENTS ON SULFIDES

Starting Material	Temperature, °C	Pressure, (10^3 atms)	Time, hr
STIBNITE (Sb_2S_3)	200	75	42
Ditto	300	60	45
"	490	75	25
"	550	60	25
Troilite (FeS)			
Ditto	200	50	24
"	500	65	24
	1000	60	24
Pyrrhotite ($Fe_{1-x}S$)	700	50	20
Pyrargyrite (Ag_3SbS_3)	400	60	14
Bournonite ($PbCuSbS_3$)	200	75	15
Ditto	400	75	20
Bismuthinite (Bi_2S_3)	400	60	16
Orpiment (AS_2S_3)	240	60	15
Cinnabar (HgS)	400	60	15

mixture, the components of which may be revolved microscopically in incident light in polished section. The phases have thus far defied identification by either optical or X-ray powder methods. Reactions between sulfides and metallic platinum at relatively low pressures (<3000 atmospheres) and temperatures between 300 and 800°C have long been known and have been ascribed to the formation of stable sulfides of platinum. Recent hydrothermal investigations [4] on sulfide systems between 200 and 800°C and up to 6000 atmospheres have shown that gold may be employed successfully as an inert sample container. Accordingly, experiments are now under way in which gold is being used as both sample container and heater tube in the Belt apparatus. In addition, high pressure experiments on sulfides in which mineralizers will be employed are being planned.

Effects of Pressure on Phosphates

An exploratory study of the effects of combined pressure and temperature on phosphates of diverse atomic structure has been started. In preliminary experimentation finely ground natural crystalline apatite [$Ca_5(PO_4)_3(OH,F)$] was subjected anhydrously to 60,000 atmospheres at 1100°C for 15 hours. No change was detected. Other experiments are under way with this and other phosphates using hydrothermal as well as anhydrous conditions and finely divided chemical components to prepare the reactant.

Effects of Pressure on Germanium Dioxide And Zirconium Orthosilicate

In the early stages of this experimental program a number of exploratory high-pressure high-temperature runs were made on stable substances of simple chemistry, fixed stoichiometry, and known structures. Although this work was only of a cursory nature, some of the results and observations are considered to be worthy of record.

The dimorphism of GeO_2 has long been known [5]. The low-temperature high-density "insoluble" modification is tetragonal and has the rutile structure whereas the high-temperature low-density "soluble" form is hexagonal and has the low-quartz structure. The enantiotropic inversion point is 1033°C ± 10°C. The soluble form is obtained by hydrolysis of germanium tetrahalides and the insoluble form may be prepared from the "soluble" form by hydrothermal methods at a few hundred degrees C. In view of the structural equivalence of the soluble form with low quartz, the possibility of producing a coesite[6] analogue from this form of GeO_2 was considered, and several exploratory runs were made at 1000°C and

between 40,000 and 50,000 atmospheres. The resultant products were composed of well-developed tetragonal prisms of the "insoluble" form of GeO_2 as large as 80 microns in length and 30 microns in width. The measured indices of refraction are: $\epsilon = 2.04 \pm 0.01$ and $\omega = 1.96 \pm 0.005$. These data are believed to be more accurate than those given by Mason [7] who "estimated" the indices as $\epsilon = 2.05\text{-}2.10$, $\omega = 1.99$ at time when calibrated sets of stable high-refractive index liquids were not readily available. The X-ray powder diffraction pattern of these products is equivalent to that given for insoluble GeO_2 prepared hydrothermally at the National Bureau of Standards [8]. Shortly after this experimental work was started, it was found that a paper [9] by Dachille, Shafer, and Roy entitled "High Pressure Studies in the System GeO_2-SiO_2" was in press. As a result, further work on GeO_2 was stopped pending the publication of this paper.

Zircon ($ZrSiO_4$) is a refractory substance with a melting point of 2550°C and a density of 4.7 which is commonly used as a molding sand in foundries. It is a tetragonal nesosilicate built of isolated SiO_4 tetrahedral and zirconium in eightfold coordination with oxygen. The effect of pressure on such a material is of interest. Two runs were made with natural zircon molding sand* composed of closely sized single-crystal prismatic grains with c-axes between 150 and 250 microns in length. The first run was made using ammonium chloride as a mineralizer at 900°C and 60,000 atmospheres for 14 hours. The product was fine-grained zircon which was evidently the comminuted and recrystallized equivalent of the original zircon in view of the small but measurable changes in indices of refraction from $\epsilon = 1.988$ and $\omega = 1.927$ to $\epsilon = 1.972$ and $\omega = 1.920$ (Na light, all indices ± 0.002). The second run was made with ammonium fluoride as a catalyzer at 1300°C and 60,000 atmospheres for 15 hours. The fine-grained product was equivalent to the first run. Both products give the X-ray diffraction pattern of zircon. Two additional runs were made using a charge of zirconium nitrate and silicic acid which were mixed in the proportions required for zircon and a small amount of excess silica. These charges were pressurized at 60,000 atmospheres at 600 and 800°C for 19 and 16 hours, respectively. The products were composed of very fine-grain zircon as shown by X-ray diffraction powder patterns.

*Zircon Sand, Titanium Alloy Division, National Lead Corporation.

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EVALUATION TECHNIQUES FOR SMALL POLYMER SAMPLES

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In earlier reports on evaluating experimental polymers, the General Engineering Laboratory has presented empirical methods for assessing the intrinsic thermal stabilities of small research samples, including those furnished in the form of intractable powders or gels (1). The more recent work to be reviewed here has been directed toward the development of methods for the further evaluation and characterization of the survivors of thermal stability testing. Again, such secondary screening methods have been chosen from among those which can be applied to small samples of indefinite form.

Of the dozen or so techniques which have been considered so far, only five will be discussed here. Two of them arose as logical extensions of the scopes of the two principal empirical thermal stability methods used in the earlier work, namely, thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The three additional techniques are: nuclear magnetic resonance spectroscopy (NMR), the micro-softening-range test (MSR) and dielectric testing.

All of these techniques, excepting TGA, have been studied as means of determining whether the survivors of thermal stability screening can be expected to retain useful properties over appropriately broad temperature ranges. TGA, on the other hand, has been applied to the problem of expressing empirically demonstrated thermal stability in terms of the kinetics of volatilization in inert atmosphere.

A single TGA graph of residual weight fraction vs temperature constitutes a rich source of kinetic data, since it is equivalent to a vast number of comparable isothermal aging curves. Much of this generous store of information is wasted, however, when the kinetic analysis is accomplished in the usual way by plotting the Arrhenius rate equation. This is because it is only in the knee regions of

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1. Doyle, C.D., Anal. Chem. 33, 77-9 (1961)

thermograms that slopes can be determined and matched to their corresponding temperatures with anything like reasonable precision.

To circumvent this difficulty, the equation of the TGA curve itself is used, rather than that of its slope. This expression, obtained by integrating the simple Arrhenius equation, is given at the top of Figure 1. Here, a and b are the desired kinetic constants, namely, the apparent frequency factor and the apparent activation energy for volatilization. They are found by first approximating b separately with the help of the second and third equations in Figure 1, then closing in on the value of b which affords the best fit of the equation to the experimental TGA curve. The great advantage of this procedure is that the resulting kinetic constants for a volatilization step of interest are valid over the entire step, rather than just the knee region.

The constants B and R are the TGA heating rate and the molar gas constant. The variable T is the absolute TGA temperature, preferably as measured in the sample material. The negative reciprocal thermogram slope dT/dv is measured at a point, denoted by the subscript - a, on the knee of the curve. The variable h is the true residual weight fraction calculated on the total weight fraction H lost during a particular volatilization step.

The functions p(x) and q(x), having been tabulated for the commonly encountered range of x (2), are readily evaluated. The evaluation of f(h) and g(h), on the other hand, is not straightforward, since the specific forms of these functions depend on the order of the rate process (2). Fortunately, it is frequently possible to describe matters adequately in terms of one of the simpler processes. Failing this, however, b can be determined without reference to the nature of the kinetic process by the use of the fourth equation in Figure 1. In this approach, compensation for the lack of information about the type of process is furnished by an additional data curve, namely, an aging curve determined at a constant temperature, denoted by the subscript - c, with all other experimental conditions kept identical with those of the corresponding TGA run. The equivalent life equation gives the relationship between isothermal aging times and TGA temperatures at equal residual weight fractions, as denoted by the subscript - i.

The reason why it is possible to determine b for undefined kinetic processes by using the equivalent life equation is that,

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2. Doyle, C.D., J. Appl. Pol. Sci. 5, 285-92 (1961)

fortunately, log p(x) is a nearly linear function of x for values of x greater than about 20. Thus b (in Kcal) can be approximated from a plot of log t_i vs $10^3/T_i$ by multiplying its slope by -4.351 (3). Thereafter, the best-fit value of b can be sought, using tabulated values of p(x) in the equivalent life equation.

The equations in Figure 1, together with the tables of p(x) and q(x), have proven most helpful in utilizing the TGA curve as a source of preliminary kinetic information.

In considering other secondary screening test methods, interest has been centered on heat softening and such underlying causes of heat softening as relaxations and thermodynamic transitions. Of the techniques to be discussed briefly here, differential thermal analysis (DTA) is applied solely as a means of observing thermodynamic transitions, while nuclear magnetic resonance spectroscopy (NMR) and dielectric testing are used in observing both transitions and relaxations. Dielectric testing has the added advantage of affording information of immediate value to designing engineers. The micro-softening-range test (MSR) was developed as a means of observing heat-softening directly and quantitatively. As an added advantage, the mechanical creep characteristics of a material can be inferred from its MSR curve.

For the observation of transitions by DTA up to about 300°C, the sample holder shown in Figure 2 has been devised for use on an ordinary lab hotplate plugged into a temperature programmer. The unit is highly sensitive and comparatively easy to load and clean. It comprises three 3-in. dia. x $\frac{1}{2}$-in. thick aluminum discs bolted together in a stack. The top disc serves to position three Baldwin-Lima-Hamilton micro-miniature thermocouples, each of which is contained in and insulated from a 14-mil dia. stainless steel sheath. The thermocouples were specially ordered with long leads to minimize the number of junctions in the heated zone.

The thermocouple sheaths terminate within $\frac{1}{4}$-in. dia. sample and reference wells equally spaced on a $\frac{1}{4}$-in. radius in the center disc. Since these wells pass completely thru the center disc, they are easily cleaned by disassembling the stack. As a further aid to cleaning, a layer of aluminum foil is inserted between the bottom and center plates.

For the observation of first-order transitions, especially the melting of crystalline materials, the apparatus shown in Figure 2

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3. Doyle, C.D., to be published in J. Appl. Pol. Sci. in 1962

has been highly satisfactory. This has held true even for those powdered polymers which shrink to as little as 10% of initial volume on melting. Second-order transitions and glass transitions, on the other hand, are usually difficult to distinguish from capriciously varying base-line drift in DTA, and in this regard, the apparatus of Figure 2 offers little or no advantage over previous designs.

Where DTA senses only changes in heat content and can, therefore, be used only in observing thermic events, such as thermodynamic transitions, NMR senses molecular motions and therefore permits the observation of both transitions and relaxations. This powerful technique has been studied briefly thru the courtesy of Dr. C.M. Huggins, of the G.E. Research Laboratory, using a family of styrene-divinylbenzene copolymers kindly furnished by Dr. G.F.L. Ehlers, of A.S.D.

The findings are presented in Figure 3, where the effect of increased degree of crosslinking is shown as an increase in the temperature of the relaxation observed at about 20 kc. In each case, this relaxation involves molecular motions which commenced at the glass transition temperature some 40°C lower than the corresponding relaxation temperature.

NMR is a fascinating research tool, but for use in general prospecting for transitions and relaxations, it has some serious disadvantages. For one thing, the method is insensitive to molecular motions at frequencies below about 10 kc, so that most of the frequency range of interest in the study of mechanical behavior is inaccessible. Further, NMR is insensitive even to transitions if sufficiently vigorous molecular motions have already begun in preceding transitions.

From the standpoint of broad practical interest, both DTA and NMR are of questionable value as secondary screening tests for experimental materials. In this view, a direct heat-softening test which sums up the contributions of all the underlying causes of heat-softening is preferable to specialized methods for observing relaxations and transitions. To fulfill this need, the micro-softening-range apparatus shown in Figure 4 was devised for use with small powdered samples.

The MSR apparatus affords means of heating the sample under a weighted foot whose vertical height is recorded continuously along with the temperature of the sample holder. The stationary assembly of the apparatus comprises an aluminum baseplate and sample holder (again designed for use on an ordinary lab hotplate), a set of three Invar 36 support columns, an aluminum topplate bolted to the housing of a Starrett No. 25-611 dial gage, which in turn, supports a Schaevitz 100 SSL linear variable differential transformer (LVDT). The LVDT is loosely supported by a ringstand clamp to permit free

expansion and contraction of the stationary assembly. The movable assembly comprises an Invar 36 loading rod connected to the dial gage foot and, thru the dial gage, to the movable core of the LVDT, which in turn, supports a pan for added weights. The LVDT core can also be positioned independently on its threaded supporting stud by turning the weight pan.

Before conducting a test, the $\frac{1}{4}$-in. dia. loading foot and the inner surface of the sample cup, 5/16-in. dia. x 50 mils deep, are covered with metal foil, usually a layer of 0.5 mil aluminum. Then, with the foil pressed firmly in place and with the weighted loading foot firmly bottomed in the sample cup, the dial indicator is zeroed. Next, the sample cup is filled, and the powdered sample in tamped under the loading foot by repeatedly lifting and lowering the weight pan with the weight in place. When the dial indicates a tamped sample depth near 50 mils, and when any creeping of the sample under load has become imperceptibly slow, the recorder is zeroed by turning the weight pan, and the heating program is started.

The instruments used with the MSR apparatus are shown in Figure 5. They comprise a temperature programmer, a demodulator for the output of the LVDT and a two-channel, time-base recorder. The temperature programmer, shown on the shelf in the upper portion of Figure 5, consists of four basic units mounted in a shop-made case: a Leeds and Northrup "10170" cam-type program unit, a "Speedomax H" recorder for the hotplate temperature, a "2-Action Duration-Adjusting Type"("DAT") control unit and an H.B. Instrument Company mercury relay, Cat. No. 7080, not visible in the photo.

To the right of the MSR test apparatus in Figure 5 is the demodulator for the output of the LVDT, a Schaevitz "DM-60-C" unit, powered by a "PS12A" supply. The output of the demodulator is fed to one channel of a Varian "G-22" recorder. The second channel receives the output of the sample thermocouple, a Baldwin-Lima-Hamilton "TCS-IS-50", specially supplied with long leads.

The gratifying reproducibility and sensitivity of the MSR test are illustrated in Figure 6 for a family of emulsion copolymers of styrene and divinylbenzene, some members of which were also examined by means of NMR, as noted earlier. Figure 6 clearly shows that, as contrasted with DTA and NMR, the MSR test indicates not only the temperature range, but also the extent of heat-softening. In further contrast with DTA and NMR, which are sometimes insensitive to the underlying causes of heat-softening, the MSR test affords a consistently dependable means of determining softening temperatures. Moreover, the MSR data curve has immediate practical value as an index of the temperature range where the rate of creep under load becomes rapid.

Considerations of potential practical value, more than anything else, led to the study of dielectric testing as a secondary screening procedure for experimental polymers--in spite of all the well-documented ancient and essentially still-unsolved problems associated with measuring the dielectric characteristics of powders. Even as a means of observing relaxations and transitions in distinctly formed specimens, the scope of dielectric testing is limited by insensitivity to the motions of non-polar molecular aggregations.

Primarily as a matter of ultimate engineering interest, then, a comparative study was made of the temperature-dependence of the dielectric characteristics of compressed powdered materials and the same materials in solid disc form. The standard disc specimens carried circular silver-painted electrodes on the opposite faces. One electrode was made smaller than the other and covered with a guard electrode during the measurements to eliminate fringing capacitance and loss.

For the measurements on powders, the cell shown disassembled in Figure 7 was used. It comprises an alumina ceramic ring with a close-fitting stainless steel cylinder in the bottom serving as one of the electrodes. The other electrode is a ceramic cylinder metallized with platinum paint on the side and on one end, and with a platinum wire run thru from the metallized end to the opposite end. A guard gap 18 mils wide and 15 mils deep was machined in the metallized end.

Measurements at 1 kc on an epoxy resin in disc form and in the form of a powder under 15,000 psi are compared in terms of their temperature dependence in Figures 8 and 9. In Figure 8, it is seen that, while the apparent dielectric constant of the compressed mixture of powdered resin and air scarcely resembles that of the solid resin, the same temperature-dependence is found in both cases. Similarly, from Figure 9, the temperature-dependence of the dissipation factor is the same in both cases.

Again for reasons of practical interest, dielectric testing will be studied further in future work, with special emphasis on developing ways of measuring the true dielectric constants of powdered materials. At this writing, however, the best of the secondary screening methods developed so far are the micro-softening-range test and TGA applied as a means of determing preliminary kinetic constants. In the further development of the MSR test, it will be interesting to conduct parallel creep tests on distinctly formed specimens. Presumably the further development of TGA as a source of kinetic data would proceed along the lines of separate studies aimed at applying preliminary kinetic constants in solving practical problems involving special conditions of geometry, function and environment.

$$g(h) = \frac{ab}{BR} p(x)$$

$$x = \frac{b}{RT}$$

$$q(x_a) = H\left[\frac{f(h)g(h)}{T}\left(\frac{dT}{dv}\right)\right]_a$$

$$t_i = \frac{be^{x_c}}{BR} p(x_i)$$

FIGURE I VOLATILIZATION KINETICS EQUATIONS

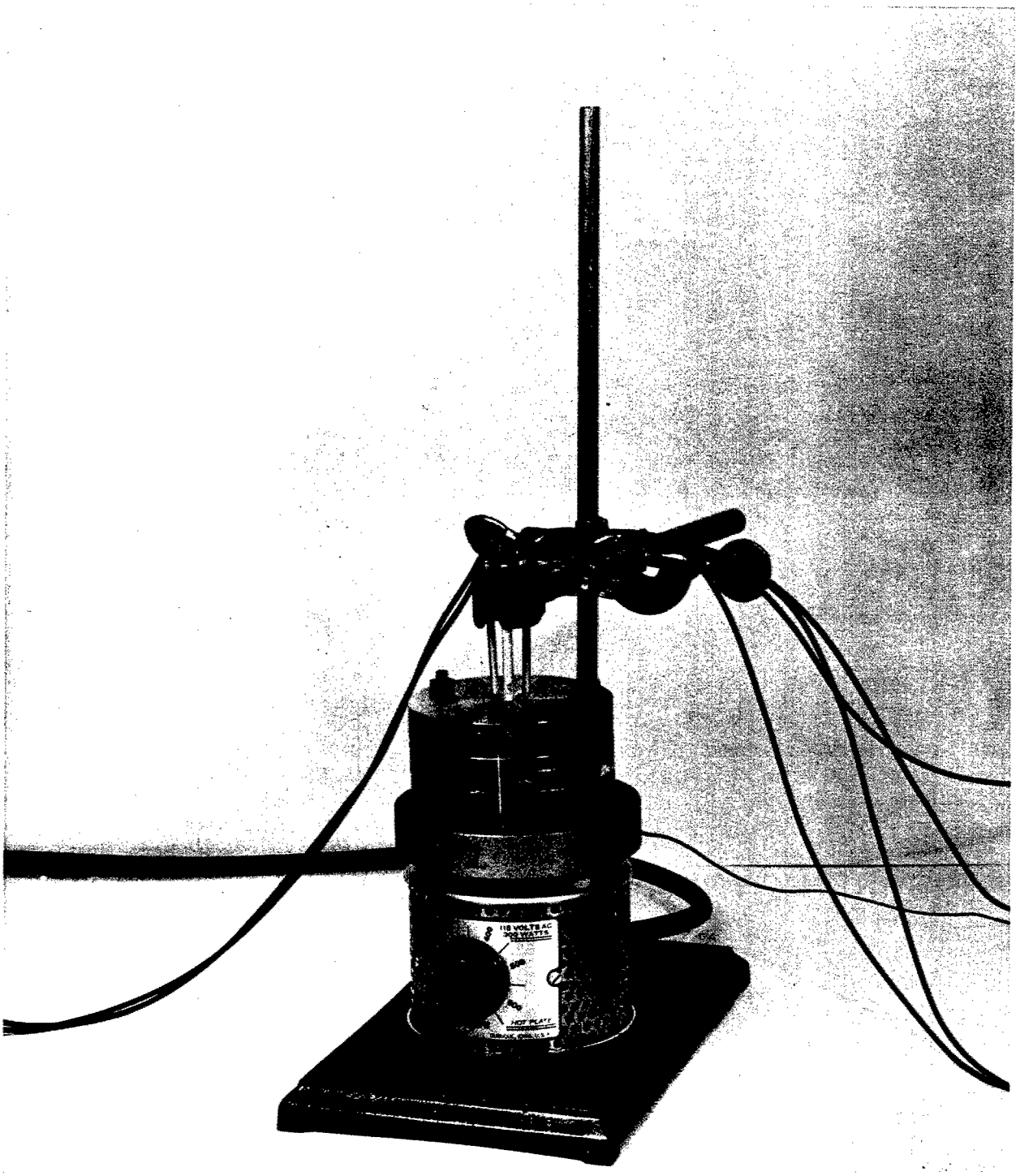


FIGURE 2 DTA APPARATUS

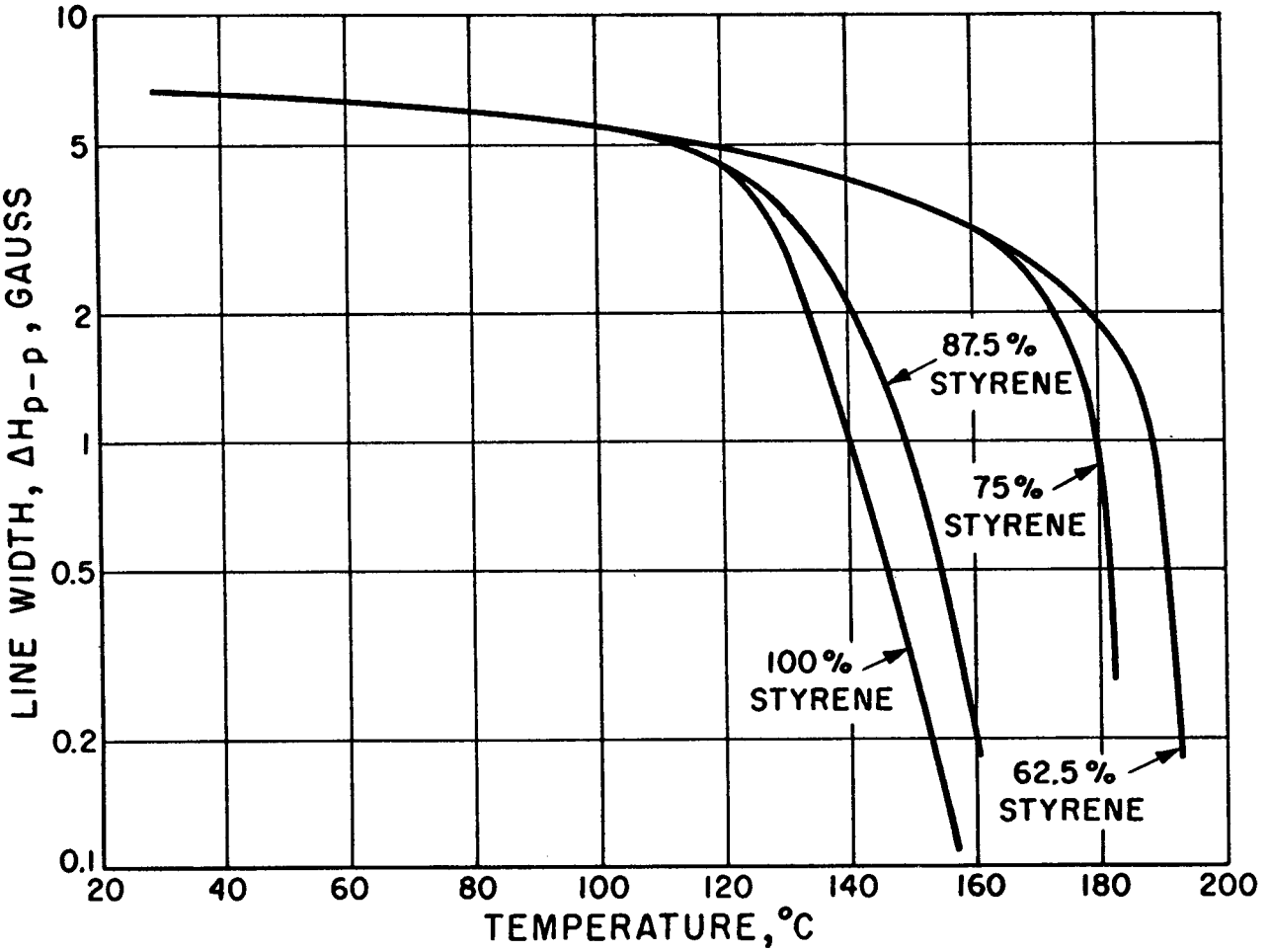


FIGURE 3 TEMPERATURE DEPENDENCE OF THE PROTON MAGNETIC RESONANCE LINE WIDTH FOR CO-POLYMERS OF STYRENE AND DIVINYLBENZENE

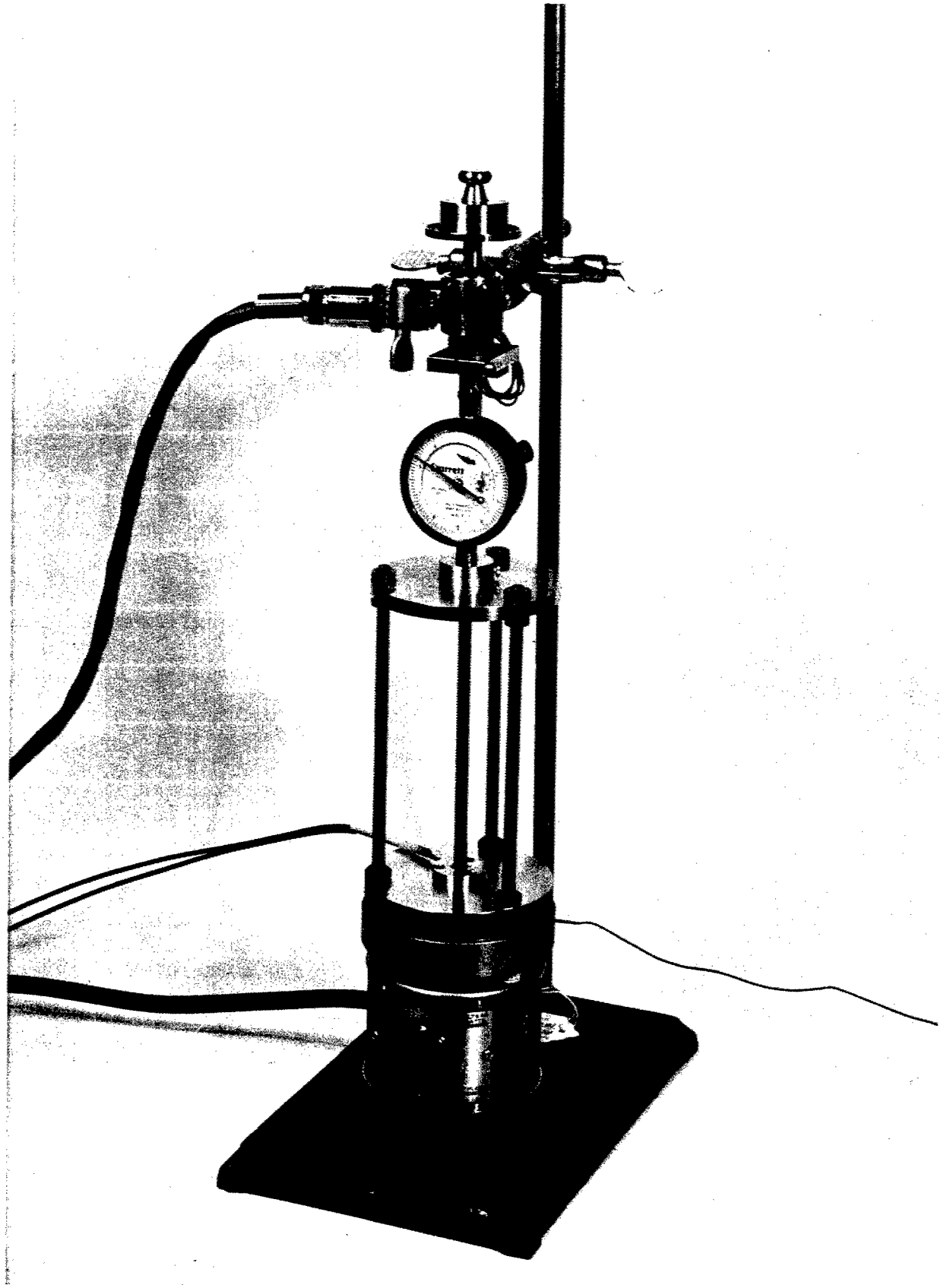


FIGURE 4 MSR APPARATUS

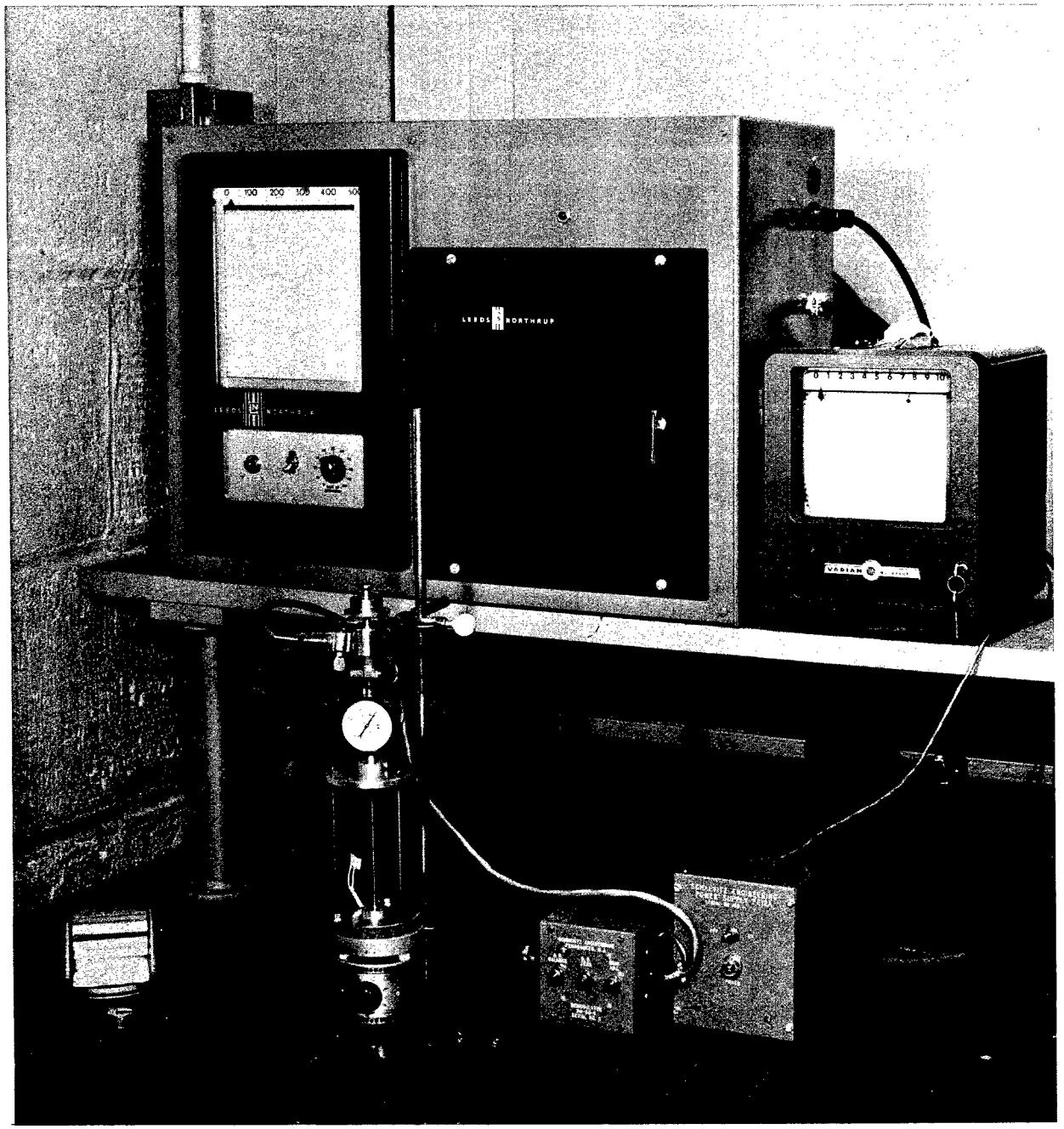


FIGURE 5 MSR APPARATUS AND INSTRUMENTATION

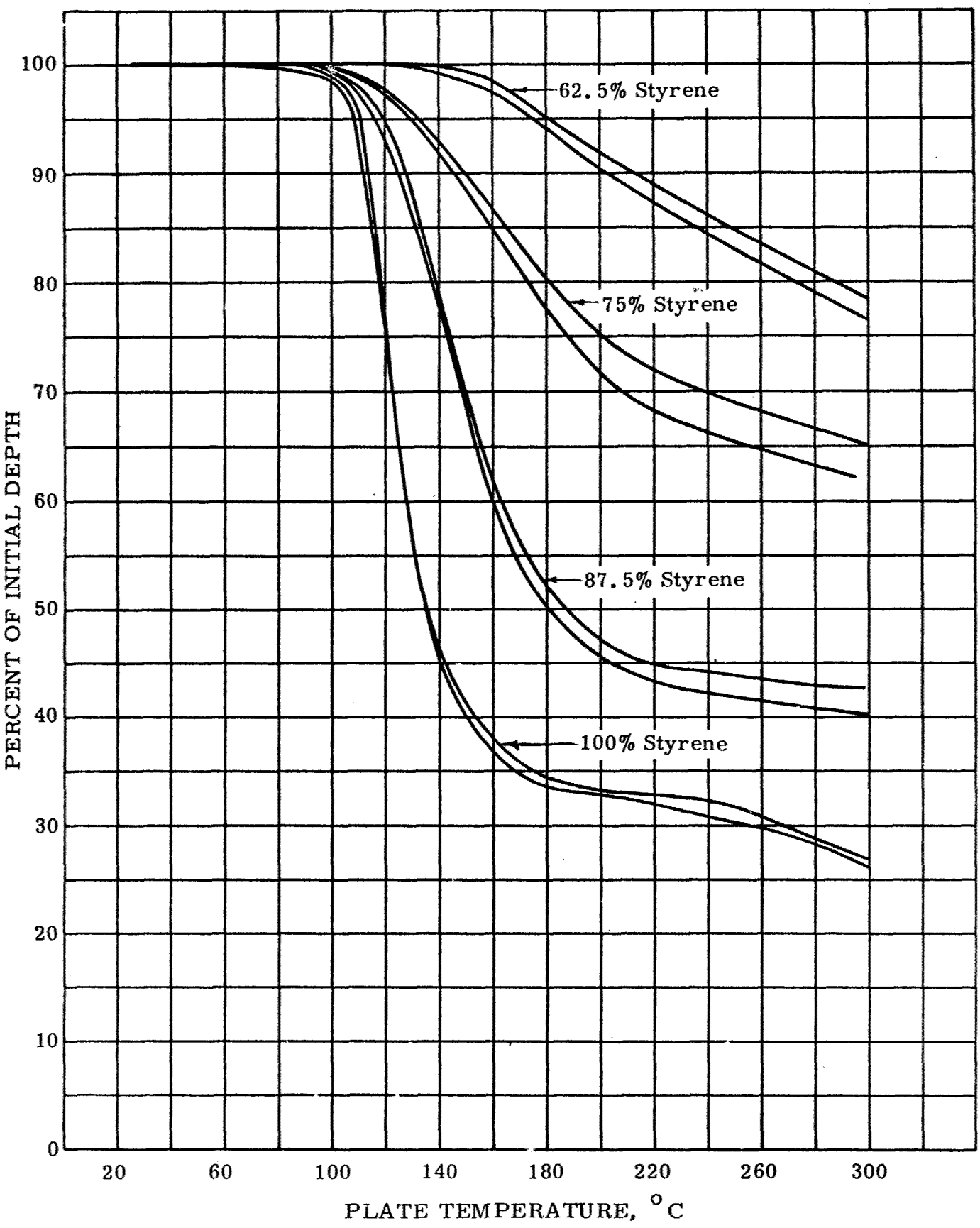


Figure 6 MSR Test at 10°C per Minute, under 100 g Added Load, Styrene - Divinylbenzene Copolymers

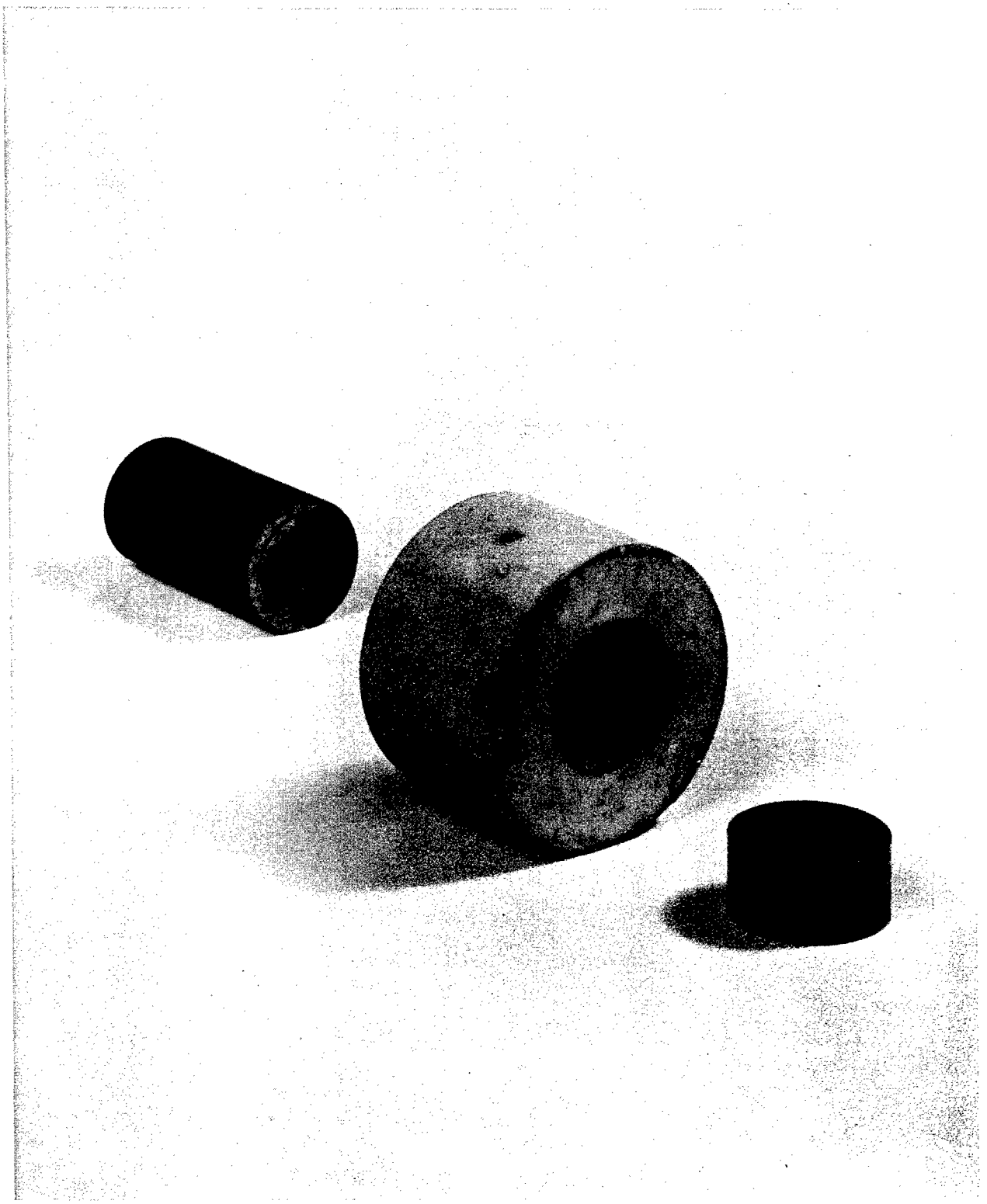


FIGURE 7 DIELECTRIC TEST CELL

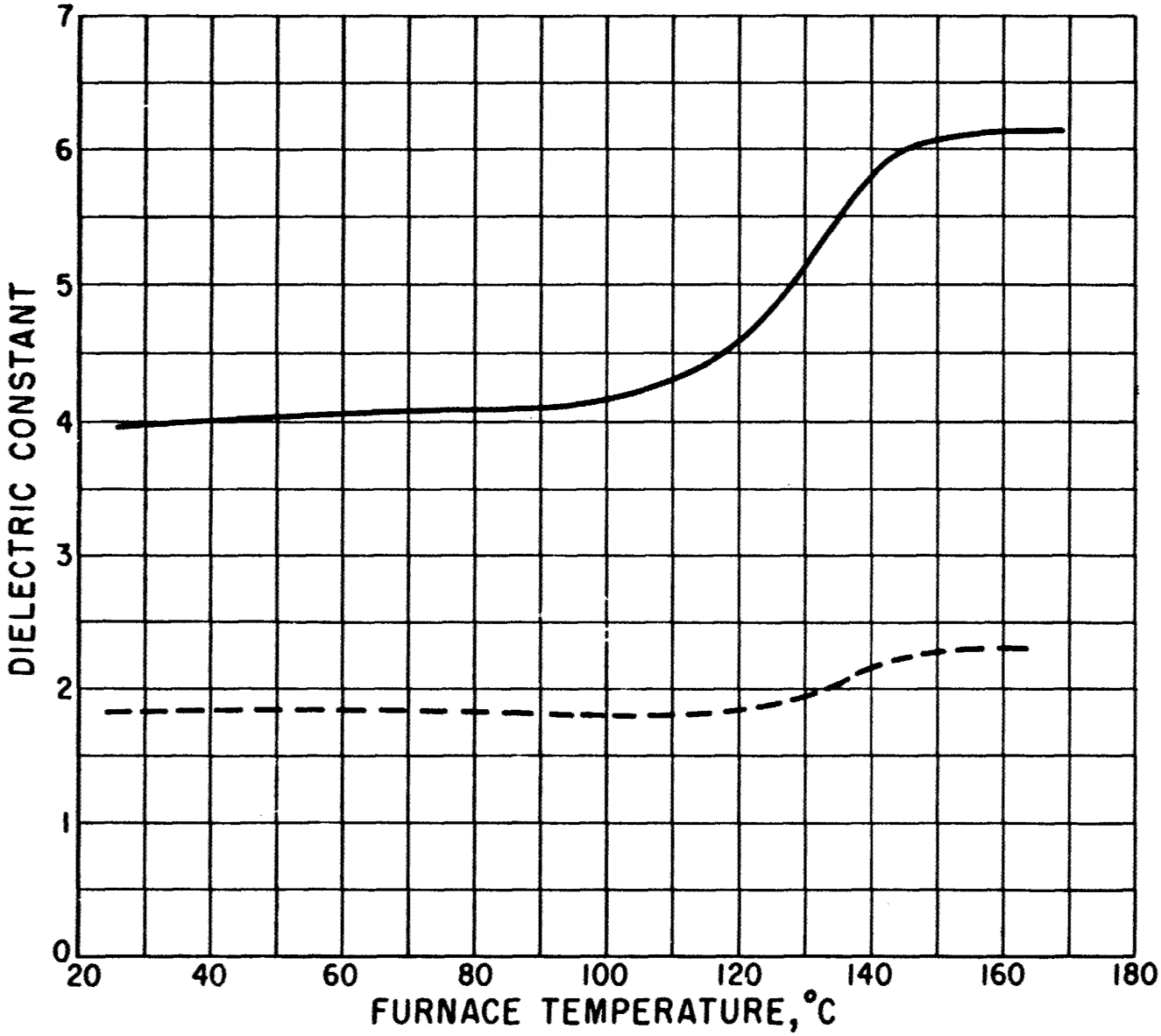


FIGURE 8 MDA EPOXY TESTED AT 1000 CPS

——— SOLID

– – – – POWDER PRESSED AT 15000 PSI

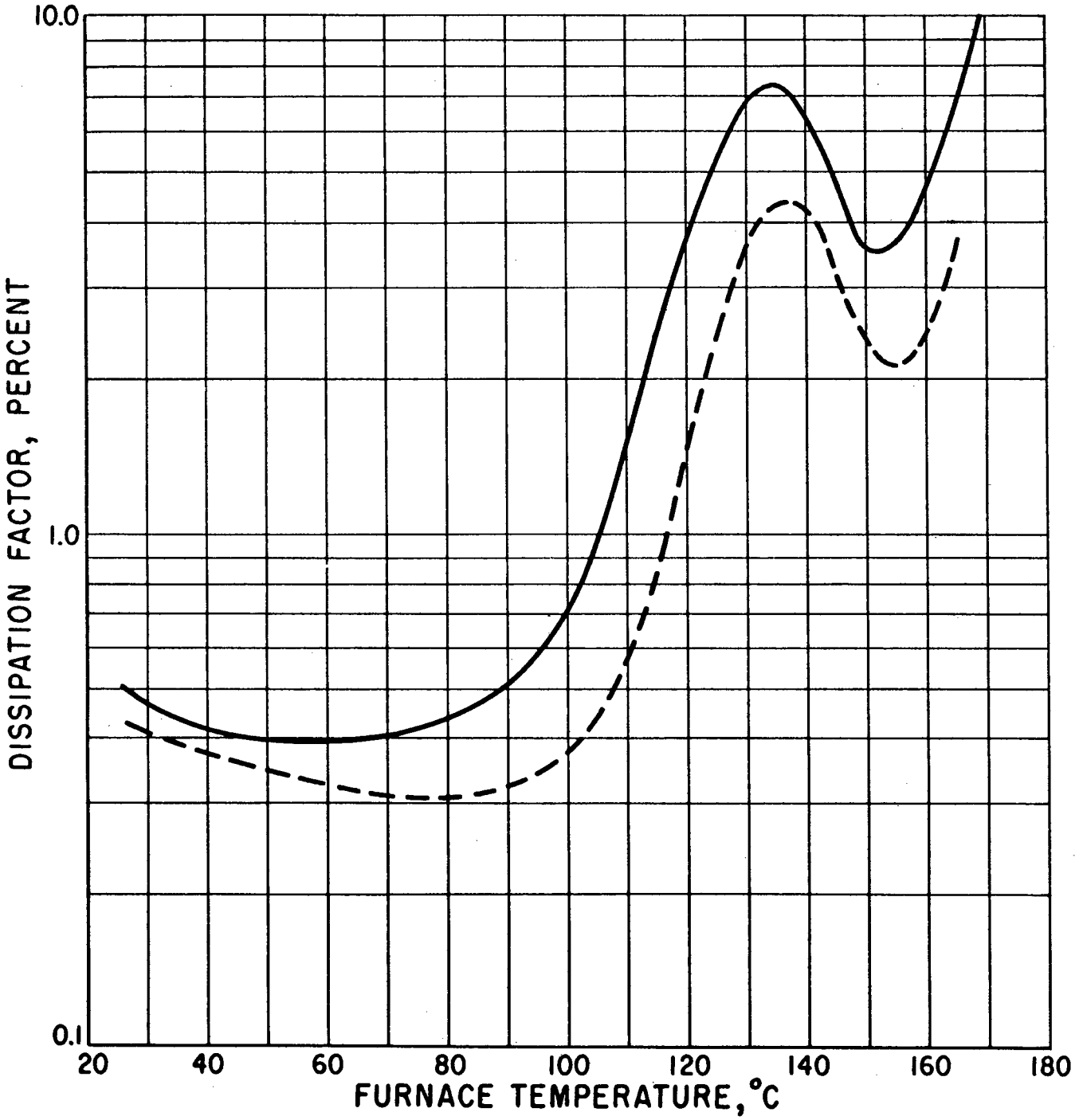


FIGURE 9 MDA EPOXY TESTED AT 1000 CPS

——— SOLID

– – – – POWDER PRESSED AT 15000 PSI

Specific Diluent Effects on the Elastic Properties of Polymeric Networks

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Introduction

At present the elastic properties of rubber-like materials are rather well understood. The form of the stress-strain curve and the temperature dependence of the stress at fixed strain can be explained on a molecular basis. Recent theoretical work[1,2] on the chain dimensions as a function of intramolecular forces has been related to thermoelastic properties of idealized models of networks. However, real networks may deviate from those models in several important aspects. The present status may be summarized as follows.

All theories assume that the chains are Gaussian in the unconstrained state. This assumption is not severely restrictive and appears to be a good approximation for networks of chains consisting of many links.

A second assumption is that interactions between chains are independent of deformation. This assumption has not yet been evaluated theoretically, although some recent experimental evidence[3] suggests that effects of this nature are not large.

A third assumption is that the unperturbed chain dimensions of free unperturbed chains are independent of specific diluent effects. These diluent effects may be important in a study of the elastic properties of swollen networks. Contrary to the former two assumptions, the third one may be relaxed from a theoretical point of view. The consequences of this more general approach are investigated below.

Flory[4] has given the following equation for a network in the unswollen state

$$f = \nu k T(<\alpha>^2/L_{io})(\alpha - \alpha^{-2}). \quad (1)$$

For a network at force zero in swelling equilibrium with a diluent, he obtained[4]

$$(\nu V_1/N_a V_o)[<\alpha>^2 v_2 - v_2/2] = -[\ln(1-v_2) + v_2 + \chi_1 v_2^2] \quad (2)$$

and for a force f,

$$(\nu V_1/N_a V_o)\,[<\alpha>^2 (v_2')^{2/3}(L_{io}/L) - v_2'/2] = -[\ln(1-v_2') + v_2' + \chi_1 (v_2')^2], \quad (3)$$

combined with

$$f = \nu k\, T(<\alpha>^2/L_{io}^2)\ (v_2')^{2/3} L(1 - L_{io}^3/v_2' L^3). \qquad (4)$$

ν is the number of chains in the sample; k and N_a are respectively Boltzmann's constant and Avogadro's number. T is the absolute temperature. L_{io} and L_i are the lengths of the isotropic sample in the unswollen and swollen state respectively, and L is the length corresponding to the force f, either for the swollen or unswollen sample. By definition $\alpha = L/L_i$. v_2 and v_2' are the volume fractions of polymer in the swollen sample in respectively the isotropic state and the deformed state, corresponding to f. χ_1 is the interaction parameter for diluent-polymer interaction. V_1 is the molar volume of the diluent and V_o is the volume of the unswollen polymer. $<\alpha>^2 = <r_i^2>/<r_o^2>$, where $<r_i^2>$ is the mean square end-to-end distance of the polymer chains in the isotropic sample at the volume, corresponding to f, and $<r_o^2>$ is the mean square end-to-end distance for uncrosslinked chains.

Earlier theories have assumed that $<r_o^2>$ is constant, independent of temperature and specific diluent effects. However, it has recently[3,5] been shown that the temperature dependence of $<r_o^2>$ may be introduced in rubber elasticity theory. In fact, at present, this theory is successfully used to evaluate $d \ln <r_o^2>/dT$ for various polymers.

We will critically examine the implicit assumption that $<r_o^2>$ is independent of diluent effects. The relative probabilities of different conformations may conceivably depend on the diluent, as has been observed for 1,2 dichloroethane[6] in different solvents. If these effects also exist for polymeric chains, $<r_o^2>$ depends on the diluent. It follows then that $<\alpha>^2$, and through eq. 4 the force on an elongated swollen sample, is a function of the diluent.

Experimental

Linear polyethylene ("Super Dylan", low pressure polyethylene, obtained from the Koppers Company) was chosen as the polymer. The diluents chosen were paraffin, melting range 65-70°C, n-hexadecane, α-chloronaphthalene and di-2-ethylhexyl azelate (DEHA). The latter three solvents were "Reagent Grade" and no attempt was made to purify them further.

Polyethylene films of a uniform thickness of 1-2 mm. were pressed at about 150°C and samples were cut at room temperature with a mold in the shape of a dumbbell. These samples are of uniform width of 3.1 mm. over a length of 25 mm. In order to crosslink the samples, they were irradiated at room temperature in evacuated glass containers by γ-radiation from a cylindrical Co^{60} source with a uniform dose rate of 0.61 megarep/hr. The samples investigated below received doses of 10 to 40 megarep. The dumbbell shape enabled the samples to be clamped in and stretched without breakage at the clamps. The clamps consisted of a pair of small metal plates, held together by screws. The lower clamp was fixed, while the upper clamp was suspended from a strain gauge which could be

adjusted vertically. The strain gauge (Statham Instrument Company, Transducer Model G-1) had a capacity of 750 g. and a linear response of 0.05 mv. per g. under a supplied e.m.f. of 12 v. The output of the strain gauge was displayed on a Leeds and Northrup recorder, giving a full scale deflection of 10 mv. The instrument was calibrated by addition of known weights before and after each experiment.

The length of the sample was measured with a cathetometer. Two thin metal pins, perforating the uniform section 20 mm. apart, served as markers.

A stream of high purity nitrogen was passed through the sample chamber in order to prevent oxidative degradation. Samples were swollen by diluent in the sample chamber. After the stress-strain experiment, the polyethylene sample was extracted with boiling xylene and evaporated to dryness at 150°C in vacuum. The stress-strain curve in the unswollen state after this treatment was usually identical, within experimental error, to that before swelling; otherwise the experiment was discarded.

The liquid thermostat (containing Silicone Oil DC-550, Dow Corning Corporation) maintained a constant temperature of 150 $\pm$ 0.1°C.

Stress-strain curves were obtained by stretching the sample at intervals to an extension ratio of about 1.3 and decreasing the length in similar intervals until the relaxed, isotropic state was reached. At each interval the length was kept constant for 15 minutes before the force was read.

The procedure for obtaining the ratio R, defined as $< r_o^2 >_{swollen} / < r_o^2 >_{unswollen}$, was as follows. From the stress-strain curve in the unswollen state $\nu < \alpha >^2$ was obtained through eq. 1. Substituting this value and the measured value of v_2 in eq. 2, we obtained χ_1. Subsequently v_2' corresponding to the length L was calculated with the aid of eq. 3 and with this value f was calculated according to eq. 4. During this procedure $< r_o^2 >$ was assumed to be equal to $< r_o^2 >_{unswollen}$. On comparing the calculated value of the force with that measured at the same L, we have that $R = f_{calculated}/f_{measured}$.

Results and Discussion

Table I

Ratio $R = \langle r_o^2 \rangle_{swollen} / \langle r_o^2 \rangle_{unswollen}$ for different diluents

Solvent	α	$f_{unswollen}$ g.	$f_{swollen}$ g.	v_2'	calculated $f_{swollen}$ g.	R
DEHA	1.35	60.0	75.8	0.394	74.0	0.98
α-Cl. n.	1.275	55.5	95.5	0.217	81.3	0.86
α-Cl. n.	1.32	61.3	104.5	0.230	90.3	0.86
n-hexad.	1.35	63.5	103.0	0.221	89.8	0.87
n-hexad.	1.31	56.4	96.0	0.196	82.2	0.86

The results obtained are given in Table I. It is to be remarked, however, that the data are preliminary and need further confirmation. Eqs. 1-4 are valid for measurements performed in equilibrium. It was apparent from the stress-strain curves for the unswollen samples, however, that the force was not constant after a period of 15 minutes. This results in hysteresis loops in the stress-strain curves. Attempts to increase this period showed that the time required would be impractically long. The results for the dry state are therefore open to doubt.

The measurements performed in the swollen state are more reliable, since hysteresis is small in this case. We are inclined to believe that the value of $\langle r_o^2 \rangle$ in n-hexadecane is close to that in polyethylene in the bulk, in view of the similarity of the molecules. If this is accepted, the value of $\langle r_o^2 \rangle$ in α-chloronaphthalene is the same as that in polyethylene in the bulk, but $\langle r_o^2 \rangle$ would be about 15 percent greater in di-2-ethylhexyl azelate.

From our theoretical calculations it has become apparent that $< r_o^2 >$ is very sensitive to slight changes in intramolecular interactions. Nevertheless, as is apparent from Table I, the chain dimensions are remarkably invariant with respect to such great changes in solvent from an aliphatic to an aromatic medium, or to molecules containing ester groups. Therefore, the implicit assumption adopted in rubber elasticity theory that unperturbed chain dimensions are independent of solvent medium, seems justified at least to a first approximation.

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RESEARCH ON INORGANIC POLYMER SYSTEMS CONTAINING BORON AND ALUMINUM

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ABSTRACT

The present investigation has been directed toward the preparation of thermally stable inorganic or semi-inorganic polymers. Initial work included investigations of polymers based on boron-boron and aluminum-oxygen bonding systems. Work was subsequently suspended in these areas in favor of more promising boron-nitrogen and boron-oxygen systems. Conversion of borazoles to linear boron-nitrogen systems or to polyborazoles has not given satisfactory materials, but more promising linear boron-nitrogen systems have been prepared by an alternative method. Recently a series of polymers with boron-oxygen or boron-nitrogen bonds and aromatic groups in the basic chains have been investigated.

I. INTRODUCTION

The objective of this research program is the preparation of new inorganic or semi-inorganic polymers which show sufficient thermal stability to meet a variety of current and future Air Force operating requirements. Initial research efforts involved a comprehensive study of systems based on B-B, B-N, and Al-O bonding. Early in this work numerous monomers and prototypes containing these bonding systems were prepared and evaluated; subsequently, monomers and polymers based on other bonding systems have also been investigated. As more information developed, overall emphasis on the program was gradually shifted from B-B and aluminum based systems to B-N bonded materials. More recently promising systems with B-O bonding and with various aromatic groups in the polymer chains have also been initiated including studies of polymer properties, polymerization techniques, and evaluation of end-use products, particularly glass fiber laminates. The results of our initial research on the B-B, Al-O, and B-N systems through December, 1960 have been described previously in Summary Technical Reports, (References 1 and 2). Some of this work has also been published in the open literature, and these references are given in the text. In the present paper, an attempt has been made to summarize our investigations of these systems and to discuss reasons for suspending work in the areas of the B-B and Al-O types. Subsequent work on B-N and borazole polymers will be discussed in addition to initial investigations of a variety of aromatic B-O and B-N materials.

II. POLYMERS CONTAINING BORON-BORON BONDS

A. INTRODUCTION

At the time of the inception of the present research program there was little published information on materials with covalent boron-boron bonds and essentially none on polymers containing this linkage. Excluded from this discussion are the boron hydrides, some of which have boron-boron single bonds in addition to the bridged bonding which is characteristic of these materials. The initial stage of the present program involved the synthesis and study of simple prototype systems. A major accomplishment of this early work was the development of the first practical syntheses of a variety of diboron compounds, the simplest boron-boron bonded derivatives (References 3-5). Using knowledge gained during the subsequent prototype investigations, various polymerization reactions and methods were studied. Three general types of high molecular weight materials containing boron-boron bonds were prepared. The preparation and some specific properties of selected derivatives of each system are described in the following sections.

B. DISCUSSION

1. Polyborons, $\leftarrow \overset{R}{\underset{|}{B}} \rightarrow_n$

a. Disproportionation of Diboron Compounds

The disproportionation of diboron compounds appears to be an ideal method for the preparation of polyboron polymers. Diboron tetrachloride, for example, disproportionates at room temperature and above to give boron trichloride and polyboron polyhalides (Reference 6), but the poor thermal stability of the

$$B_2Cl_4 \longrightarrow BCl_3 + \frac{1}{n}(BCl)_n \qquad (1)$$

resulting polyhalides eliminates them from any consideration for high temperature applications. During the present prototype studies, however, it became apparent that diboron compounds with substituents having available electrons on the substituent atom adjacent to the boron were significantly more stable than the halogen derivatives. Therefore, the disproportionation of tetraalkoxy and tetra(dialkylamino)diborons to polyborons was investigated. This type of disproportionation is

$$B_2Y_4 \longrightarrow BY_3 + \frac{1}{n}\leftarrow \overset{Y}{\underset{|}{B}} \rightarrow_n \qquad (2)$$

$$Y = OR,\ NR_2$$

ideal for the formation of high molecular weight materials because the volatile condensation products formed can be removed continuously. However, attempted thermal disproportionation of tetra(dialkylamino)-diborons always led to degradation of the diboron molecule rather than

the desired reaction. Polyalkoxy polyborons, $\left(\text{B}(\text{OR})\right)_n$, were obtained from tetraalkoxydiborons by careful heating at about 100°C. However, these systems always tended to eliminate ethers during the heating period, and it was difficult to eliminate this undesirable cross-linking reaction. The final products contained 10-15 ROB units (measured cryoscopically) and decomposed rapidly at 200°C. No additional work was done on these systems because of this lack of thermal stability and their difficulty of preparation.

b. Sodium Reduction

Our recently developed reaction of halo-bis(dimethylamino)boranes with sodium (Equation 3) is an excellent preparative method for diboron compounds (Reference 3). The analogous

$$2\ (Me_2N)_2BX + 2\ Na \longrightarrow B_2(NMe_2)_4 + 2\ NaX \qquad (3)$$

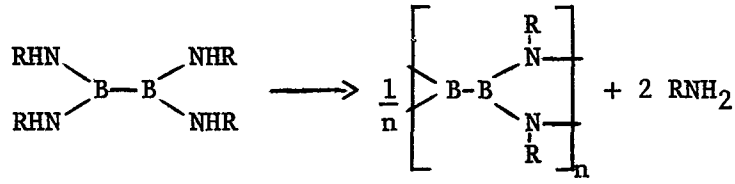
reaction of dihalo(dialkylamino)boranes with sodium is a potential method for preparing polymers, although the probable difficulty of obtaining high molecular weight products from this reaction is

$$Me_2NBX_2 + 2\ Na \longrightarrow \frac{1}{n}\left(\text{B}(\text{NMe}_2)\right)_n + 2\ NaX \qquad (4)$$

recognized. The reaction of dichloro(dimethylamino)borane with sodium yielded a material which appeared to be $\left(\text{B}(\text{NMe}_2)\right)_n$ where n was about 15. Elemental analysis suggested the presence of one or more bridging or crosslinking boron atoms, $>\text{B-B-B}<$, in the structure. This material decomposed at temperatures below 200°C. whereas the simple diboron analog, $B_2(NMe_2)_4$, is stable to 300°C. This poor thermal stability of dimethylamino polyboron suggests that related materials will not be sufficiently heat resistant for projected high-temperature uses, because prototype studies showed that diboron compounds with amine substituents were the most thermally stable of the derivatives investigated.

2. B-B-N Systems, $(\text{-B-B-N-})_n$

a. A number of materials have been prepared in which the boron-boron bonds in the polymer chain are interspersed with nitrogen atoms. These compounds were obtained by the elimination of amines from diboron derivatives of primary amines as shown in Equation 5. The

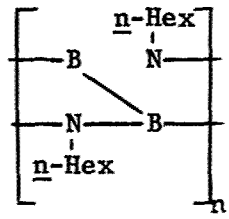


(5)

final products formed by the elimination of two amine groups from every diboron molecule would be a highly crosslinked material as shown.

b. The initial diboron compound formed in the reaction of excess ammonia with tetra(dimethylamino)diboron was apparently unstable and decomposed spontaneously below room temperature with the evolution of ammonia. The products from this reaction were white crystalline polymers with compositions approaching $\leftarrow B(NMe_2)-B(NH_2)-NH\rightarrow_n$. These materials were insoluble in common solvents and did not char when heated in an open flame. However, further heating at 500°C. led to continued amine evolution, and it is probable that boron-nitride-like structures such as $\leftarrow NHB(NH_2)-B(NH_2)-NH\rightarrow_n$ were approached.

c. Tetra(methylamino)diboron decomposed at about 75°C. to give approximately one mole of methylamine and low-molecular weight products. Heating tetra(n-hexylamino)diboron at 140°C. yielded one mole of n-hexylamine and an intermediate which was probably a borazole derivative (based on analyses and molecular weight). Further heating at 364°C. gave a viscous green liquid (molecular weight, 1750) which decomposed rapidly at 500°C.; there was some evidence for structural degradation even at 364°C. The elemental analysis of this product suggests a composition approaching



d. The thermal treatment of tetra(anilino)diboron was studied in detail. In this system the initial product evolved on heating at 300-500°C. was one molar equivalent of hydrogen. Varying amounts of aniline were also obtained depending on the conditions used. The results suggest that the initial step is cleavage of the boron-boron bond to give an intermediate borazole followed by amine elimination leading to polyborazoles as shown.

$$B_2(NHPh)_4 \longrightarrow (PhNHBNPh)_3 + 3\ H_2 \xrightarrow{-PhNH_2} \text{Polyborazoles} \qquad (6)$$

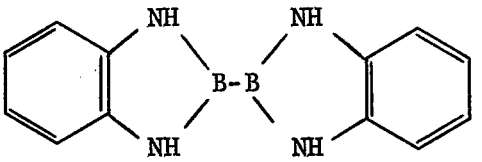
Initial products from this reaction were soluble in organic solvents and had molecular weights in the range of 1000-1100. Continued heating led to the evolution of additional amine and insoluble resins which had good thermal stability. However, these materials, which did not retain any boron-boron bonds, offered little advantages over resins which could be obtained more directly from simple boranes.

3. Aromatic B-B-N Systems, $\leftarrow B-B-N-(\text{aromatic})\rightarrow_n$

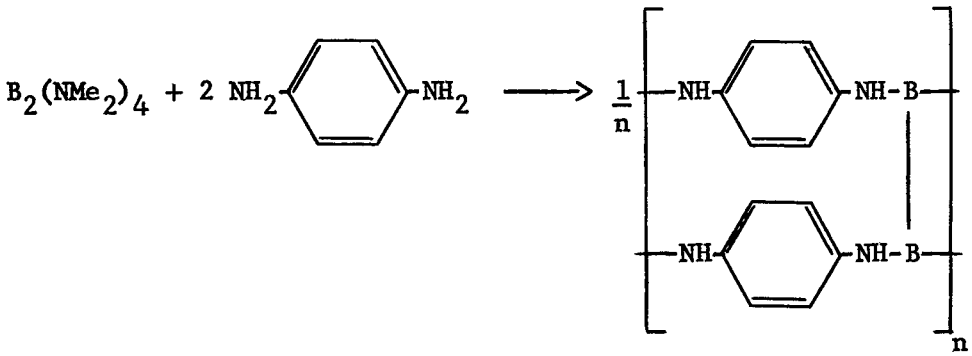
a. Phenylenediamine Derivatives

The reaction of tetra(dimethylamino)diboron with phenylenediamines led to a series of thermally stable, intractable

materials. The product from the reaction with o-phenylenediamine was a crystalline compound which appeared to be monomeric, possibly



This compound lost little weight up to 500°C., but heating at 500°C. for one hour resulted in the formation of one mole of hydrogen with probable cleavage of the B-B bond. Reactions with various molar ratios of o-phenylenediamine showed that the second hydrogens of the amine groups were very difficult to replace. Reaction with two molar equivalents of p-phenylenediamine yielded the polymer shown in Equation 7. This crosslinked product was insoluble in organic solvents



(7)

and lost only 4 wt.% when heated to 500°C. During this heating at 500°C., it evolved approximately one mole of hydrogen per boron-boron bond indicating almost complete cleavage as in the case of the ortho derivative. Comparable products from m-phenylenediamine were also prepared and found to be significantly less stable at 500°C. than those from o- and p-phenylenediamines.

b. Other Aromatic Polymers

Several polymers of the "polybenzborimidazoline" type have been prepared from tetra(dimethylamino)diboron. These materials are discussed in Section IV-D-3-c.

III. ORGANOALUMINUM POLYMERS

A. INTRODUCTION

The original decision to investigate aluminum-oxygen polymers was based on the known stability of alumina and several reports of thermally stable high-molecular weight aluminum-oxygen derivatives. During this investigation, aluminum-oxygen, aluminum-oxygen-silicon, aluminum-nitrogen, and several other aluminum-based materials were prepared and studied. Earlier prototype studies had shown that aryloxy substituents on aluminum led to materials with optimum stability,

and most of the polymers prepared contained aryloxy substituent groups. The present discussion will include a summary of the major polymerization reactions studied and the properties of the best aluminum-based materials obtained.

B. ALUMINUM-OXYGEN SYSTEMS

1. A number of aluminum-oxygen polymers were prepared by various condensation-polymerization methods. The simplest aluminum-oxygen polymers were prepared by partial hydrolysis-condensation reaction as shown, but they showed poor thermal stability and disproportionated in some cases.

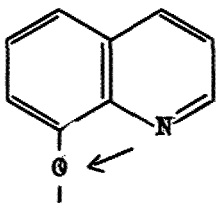
$$ArOAlEt_2 + H_2O \longrightarrow \left[\begin{array}{c} OAr \\ | \\ EtAlOH \end{array}\right] + EtH \longrightarrow \frac{1}{n}\left[\begin{array}{c} OAr \\ | \\ -Al-O- \end{array}\right]_n + EtH \qquad (8)$$

2. Related aluminum-oxygen materials with mixed substituents were prepared by reorganization and pyrolysis with the elimination of alcohols and olefins as shown in Equation 9. These products were

$$4\ Al(O\text{-}\underline{i}\text{-}Pr)_3 + Al(Ox)_3 + Al(OAr)_3 \longrightarrow \frac{3}{n}\left[\begin{array}{cc} Ox & OAr \\ | & | \\ -Al-O-Al-O- \end{array}\right]_n \qquad (9)$$

$$+ 6\ \underline{i}\text{-}PrOH + 6\ CH_2{=}CHCH_3$$

Ox = oxinate,



I, Ar = Ph

II, Ar = $SiMe_3$

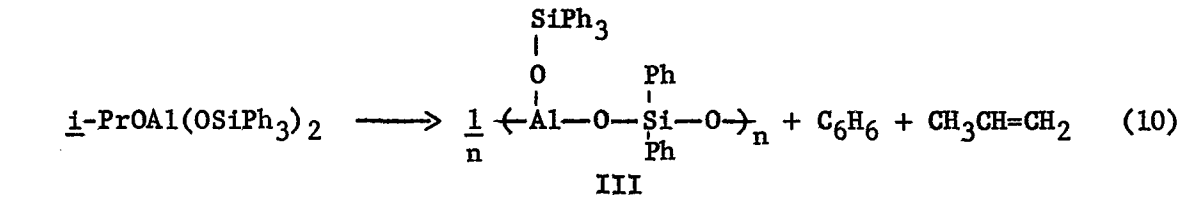
more soluble than the simple aryloxyaluminoxanes prepared as shown in Equation 8 and had molecular weights ranging from 2000-2500. Thermogravimetric analysis of I, which proved to have the best thermal stability of any aluminoxane prepared during this program, showed 29% weight loss at 500°C.*

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* All TGA (Thermogravimetric analysis) results were determined under vacuum at a heating rate of 150°C. per hour.

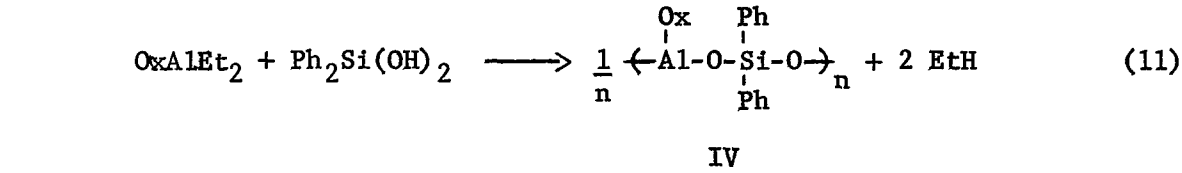
C. ALUMINUM-OXYGEN-SILICON SYSTEMS

On the basis of thermal stability, the most promising aluminum-based polymers prepared during this program have been aluminosiloxanes obtained by the two general methods illustrated by Equations 10 and 11. The product (III) from Equation 10 had an



$$\text{i-PrOAl(OSiPh}_3)_2 \longrightarrow \frac{1}{n}\left(\text{Al(OSiPh}_3)\text{O—Si(Ph)}_2\text{—O}\right)_n + \text{C}_6\text{H}_6 + \text{CH}_3\text{CH=CH}_2 \quad (10)$$

III



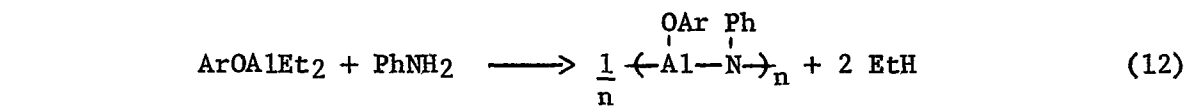
$$\text{OxAlEt}_2 + \text{Ph}_2\text{Si(OH)}_2 \longrightarrow \frac{1}{n}\left(\text{Al(Ox)—O—Si(Ph)}_2\text{—O}\right)_n + 2\ \text{EtH} \quad (11)$$

IV

approximate molecular weight of 2000 in benzene but decomposed readily at 350-500°C. It lost about 14% by weight when heated to 500°C. in the TGA equipment. The oxinate derivative (IV) had a measured cryoscopic molecular weight of about 6000 and lost 17% by weight when heated to 500°C. in the TGA equipment. These are the most thermally stable aluminum-based materials studied, but their stability still does not approach that of some of the boron-nitrogen and boron-oxygen systems described in other sections of this paper.

D. ALUMINUM-NITROGEN SYSTEMS

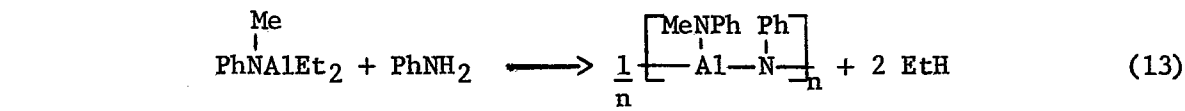
The following aluminum-nitrogen based materials were prepared:



$$\text{ArOAlEt}_2 + \text{PhNH}_2 \longrightarrow \frac{1}{n}\left(\text{Al(OAr)—N(Ph)}\right)_n + 2\ \text{EtH} \quad (12)$$

V, Ar = Ph

VI, Ar = oxinate



$$\text{PhNAlEt}_2 + \text{PhNH}_2 \longrightarrow \frac{1}{n}\left[\text{Al(MeNPh)—N(Ph)}\right]_n + 2\ \text{EtH} \quad (13)$$

All of these aluminum-nitrogen materials decomposed more readily than the most promising aluminum-oxygen systems; significant decomposition became apparent at 300-400°C.

IV. BORON-NITROGEN AND BORON-OXYGEN SYSTEMS

A. INTRODUCTION

One of the bonding types chosen for initial study was the boron-nitrogen system. This was based primarily on the known thermal stability of boron nitride and other boron-nitrogen compounds. Initial prototype studies involved the synthesis and evaluation of simple aminoboranes and borazoles. Various polymerization methods were developed, but direct preparation of linear boron-nitrogen compounds proved to be very difficult. Subsequent effort was directed toward the preparation of polyborazoles and aromatic boron-nitrogen polymers. More recently, boron-oxygen systems have also been investigated and found to have comparable thermal stability to boron-nitrogen systems. In addition, the boron-oxygen derivatives generally have better solubilities and improved adhesive properties. Work on linear boron-nitrogen systems, polyborazoles, and aromatic systems linked by boron-nitrogen and boron-oxygen bonding is summarized in the following sections.

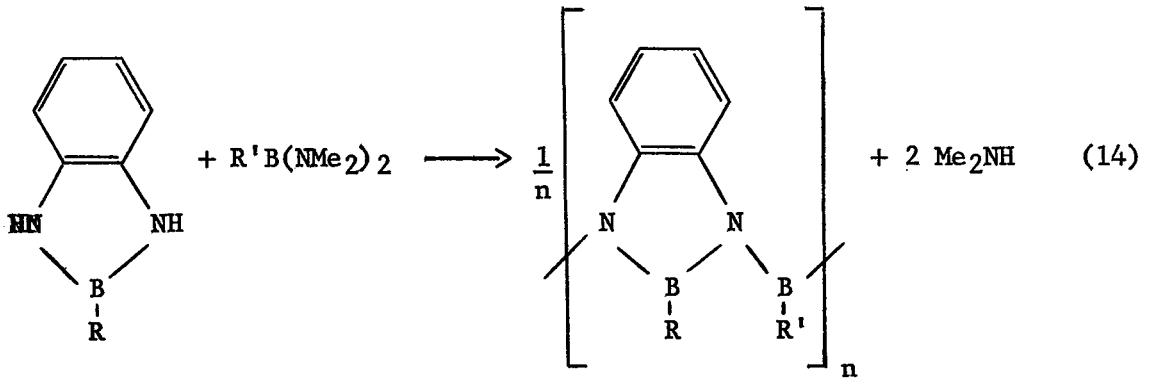
B. LINEAR BORON-NITROGEN POLYMERS

1. Attempted Preparation from Borazoles

This portion of the program involved prototype studies of monomeric borazoles and attempts to linearize the borazole ring by a variety of methods. The prototype studies demonstrated the encouraging thermodynamic stability of the borazole ring (Reference 5) and the relative stabilizing effects of various substituent groups; for example, methyl groups are particularly advantageous. Linearization of borazoles proved to be very difficult. High molecular weight materials could not be obtained, and the products were not as thermally stable as those which have been developed subsequently. An alternative approach to linear BN polymers is discussed in the next paragraph. Subsequent attempts to polymerize borazoles have been directed toward the preparation of polyborazoles which retain the borazole ring system.

2. Preparation from Benzodiazaborolines

The reaction of difunctional boranes with benzoborolines should lead to linear polymers as shown in Equation 14, since formation

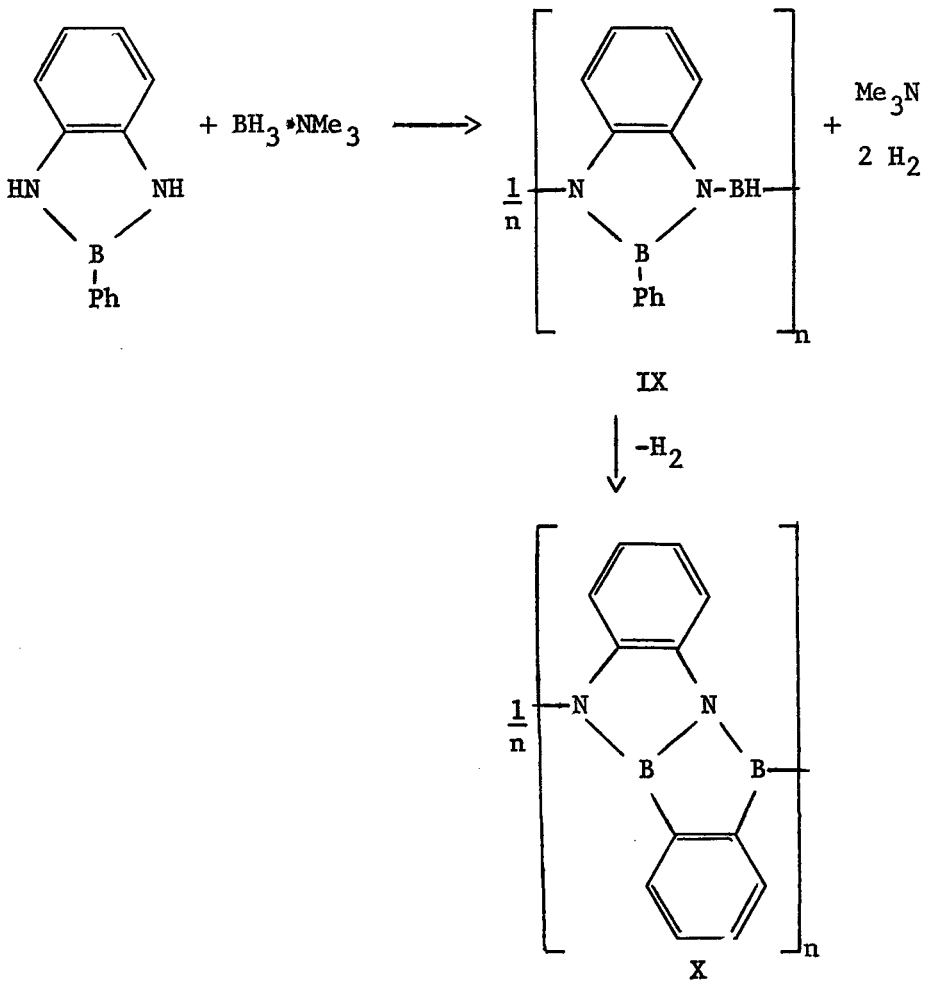


(14)

VII, R = R' = Ph

VIII, R = Me, R' = Ph

of the favored borazole structure is prohibited. The completely aromatic polymer (VII) exhibited excellent thermal stability and remained soluble in organic solvents after it was heated to 500°C. The phenylmethyl derivative VIII has not been evaluated. A related compound (IX) has also been prepared recently and found to have good thermal stability. Compounds VII-X have not been completely characterized,

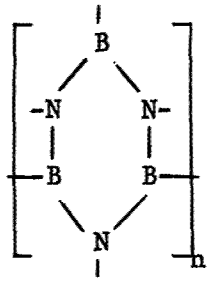


(15)

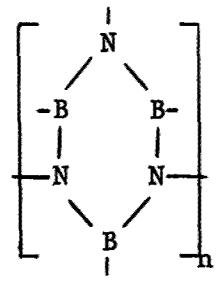
but it is probable that they approach the idealized structures shown.

C. POLYBORAZOLES

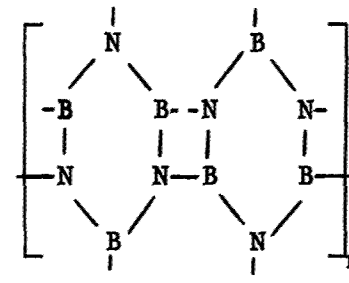
1. One of the difficulties in preparing workable polyborazoles is the trifunctional or multifunctional nature of the borazole ring. In order to prepare linear polyborazoles and to avoid intractable crosslinked structures, difunctional borazoles are required. A facile synthesis of these difunctional monomers has been one of the major problems limiting the synthesis of linear polyborazoles. Borazoles can be linked directly as shown in XI, XII, and XIII or through extraneous groups (XIV, XV, and XVI). Little work



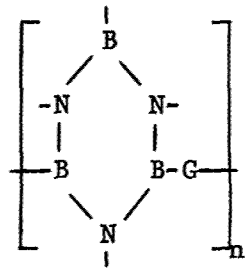
XI



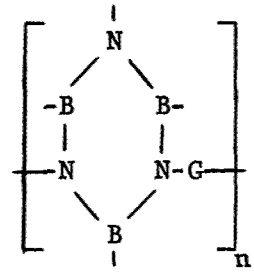
XII



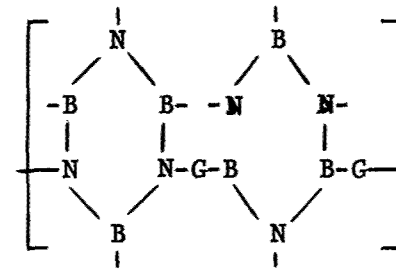
XIII



XIV



XV

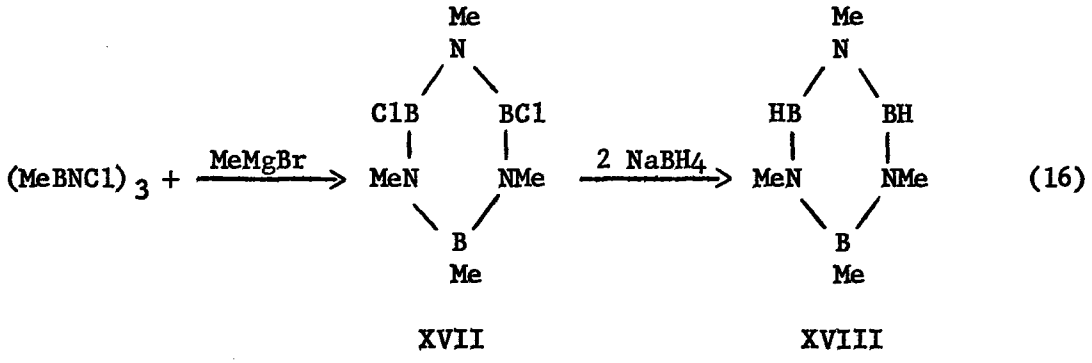


XVI

has been done on the preparation of polyborazoles of types XI-XIII, although prototypes of XI have been prepared by the action of sodium on monohaloborazoles. It is believed that the lack of flexibility of these systems and the steric problems introduced by the presence of substituent groups make these materials less attractive than types XIV-XV. No attempt has been made to prepare an example of XVI but approaches to XIV and XV are outlined in the following paragraphs.

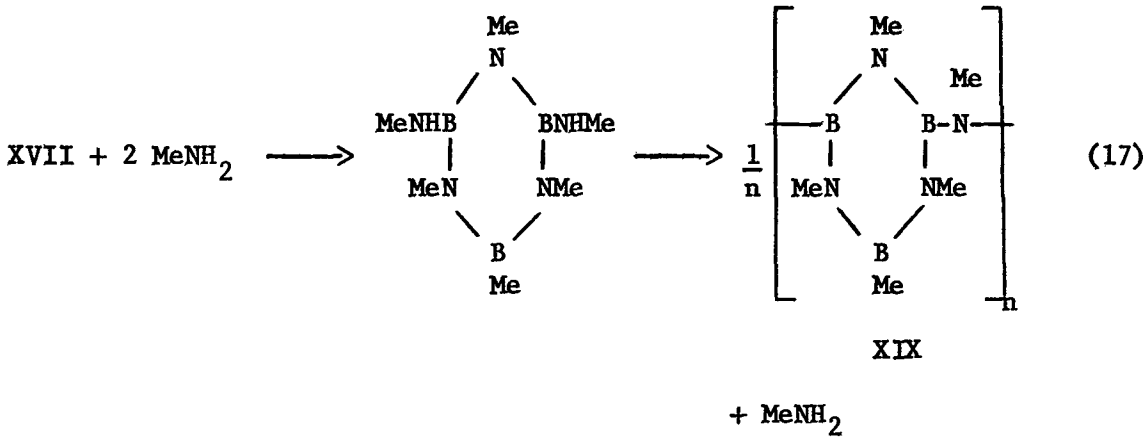
2. Linked Through Boron (Type XIV)

Difunctional borazole monomers for the preparation of polyborazoles linked through boron have been prepared by the following reaction sequence. The dichloro derivative has only been obtained in

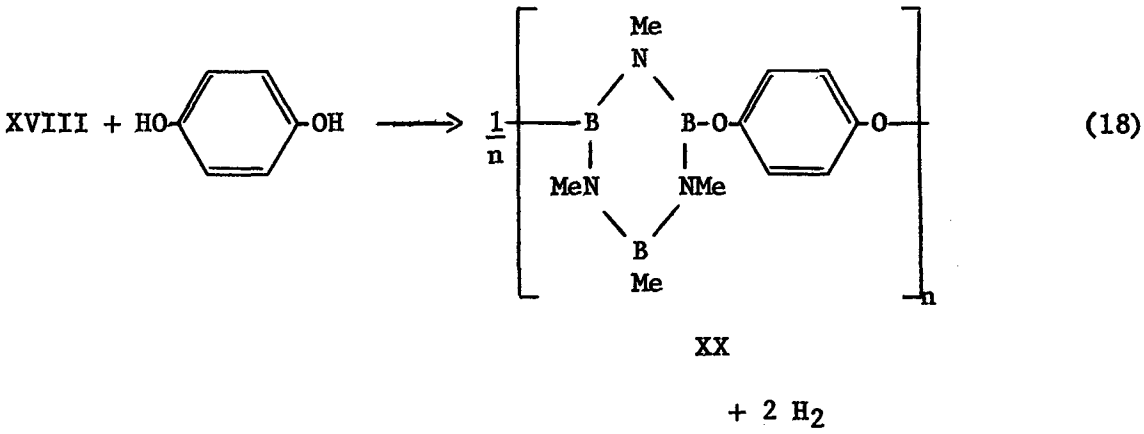


(16)

76-84% purity, but it is readily reduced to the pure dihydro compound as shown. Two promising polyborazoles which have been prepared from these difunctional monomers are shown below. The reaction represented



(17)



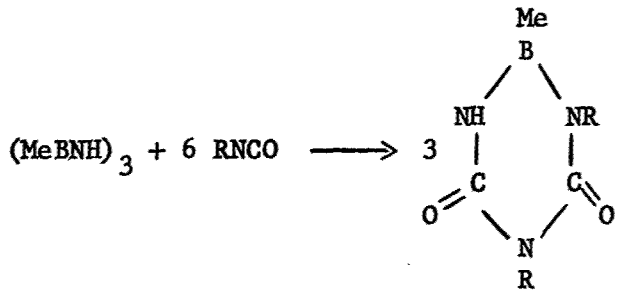
(18)

by Equation 17 proceeded readily to give 95% of the theoretical dimethylamine. The polymeric product XIX was infusible and also insoluble in organic solvents but lost 32 wt.% when heated to 500°C. on the TGA equipment. The hydroquinone polymer XX was soluble in

organic solvents and softened at 250-400°. It lost 27 wt.% when heated to 500°C. The structure of this material approaches the idealized polymer XX, but some ring cleavage also occurred.

3. Linked Through Nitrogen (Type XV)

The preparation of polyborazoles linked through nitrogen has been difficult, since the NH linkage of the borazole ring is very unreactive. Reactions with even the most active electrophilic organic reagents (acid chlorides, for example) did not give the desired products. Reactions with isocyanates also failed to give the expected addition of the borazole NH linkage, but did yield a new type of heterocyclic compound (XXI). These materials were soluble



(19)

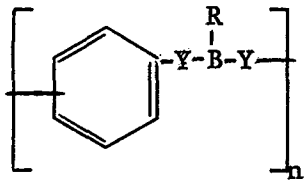
XXI

in organic solvents and decomposed at 200-300°C. Reaction of NH borazoles with aromatic diisocyanates should yield polymers incorporating this new ring system. The polymer from toluene diisocyanate and B-trimethylborazole was a white powder which was soluble in some organic solvents and darkened at 320°C. This material will be evaluated further.

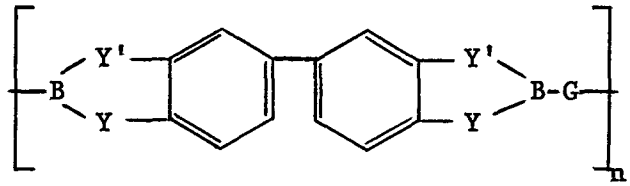
D. POLYMERS CONTAINING BO OR BN BONDS AND AROMATIC GROUPS

1. Introduction

Most of the polymeric products based on completely inorganic BN and BO chains were intractable and insoluble in organic solvents. In an attempt to improve these properties, semi-inorganic materials with stable aromatic groups in their backbone have been investigated. The two types which have received the most attention are represented by Structures XXII and XXIII. A number of variations



XXII



XXIII

Y' or Y = O, NH

R = Me, Ph, ArO

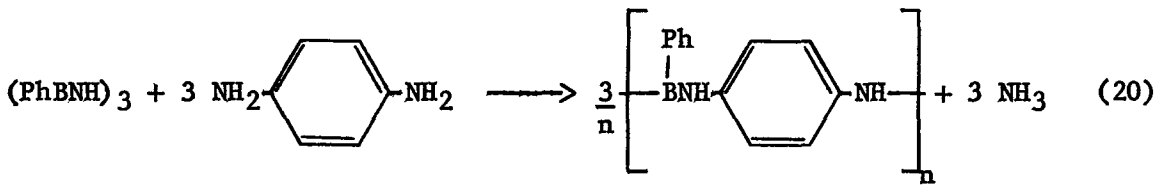
G = a variety of linking groups

of these systems have been investigated and materials with promising properties prepared. As a general class, compounds of type XXIII are the most thermally stable polymers prepared during the present program.

2. Polymers of Type XXII

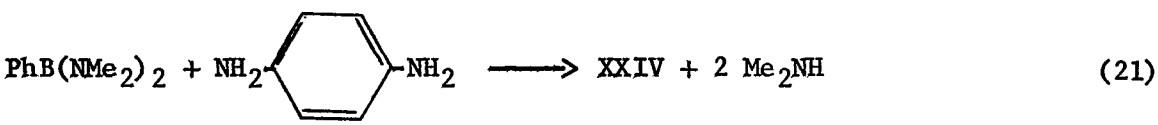
a. B-N Bonded Materials

The reactions of phenylenediamines with borazoles or with phenyl-bis(dimethylamino)borane led to a series of related polymers. The major difficulty in all polymerization reactions of this type has been elimination of the theoretical amount of volatile condensation products and the consequent formation of high-molecular weight materials. Theoretical amine evolution has been obtained from the reaction of hexamethylenediamine with phenyl-bis(dimethylamino)borane, but the resulting polymers are not thermally stable as might be expected with aliphatic carbon-carbon bonds present. In related reactions with aromatic diamines (Equations 20-25) only 50-90% of the theoretical displaced amine was obtained. The most thermally stable

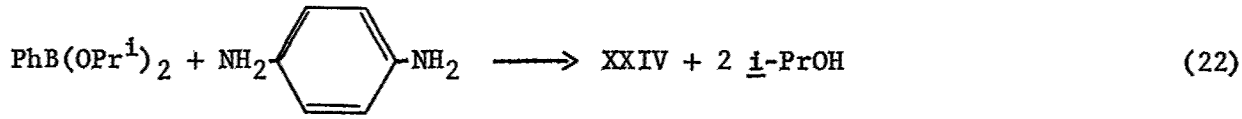


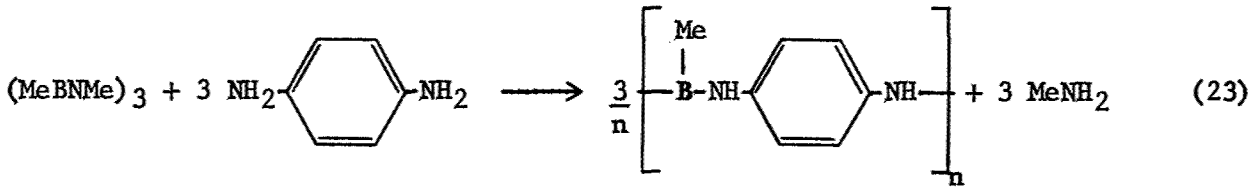
(20)

XXIV

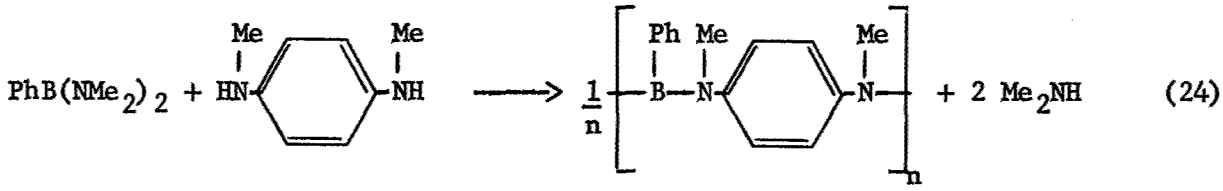


(21)

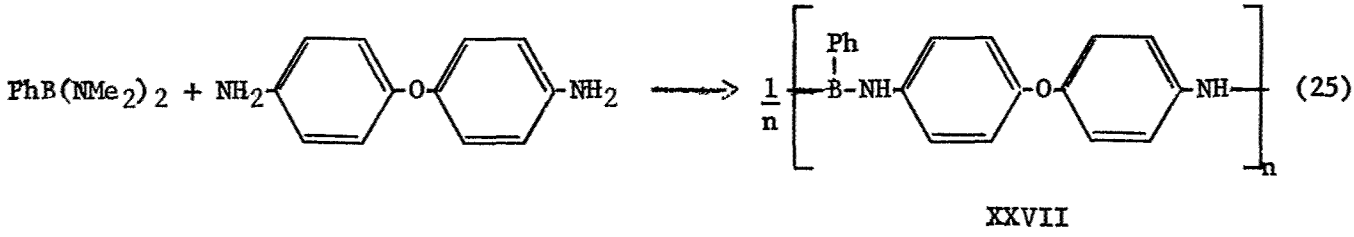




XXV



XXVI



XXVII

+ 2 Me$_2$NH

product of this type, XXIV, prepared by the reaction indicated in Equation 21, lost only 8 wt.% when heated to 500°C. on the TGA equipment. All of the other materials listed had significant weight losses at 500°C. Most of these boron-nitrogen derivatives had poor glass adhesion properties and poor to fair solubility in organic solvents. The study of type XXII aromatic systems has recently been expanded to include related boron-oxygen systems, most of which have excellent adhesive properties and give promise of better handling characteristics.

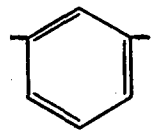
b. Boron-Oxygen Derivatives

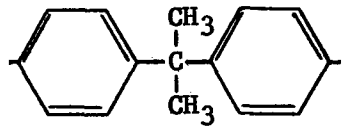
The boron-oxygen polymers of type XXII are characterized by excellent adhesion to either glass or metal surfaces and solubility in organic solvents in some cases. Their thermal stability

is good but not as favorable as those of type XXIII. Various boron-oxygen polymers of type XXII have been prepared as shown in the following general equations. The preparation and properties of the resorcinol polymer (XXIX) derived from hexamethylborazole was studied in some detail. This product bonded very strongly to glass and metals and after pretreatment at high temperatures lost 7 wt.% when heated to 500°C. on the TGA equipment. It was soluble in organic solvents but softened at temperatures below 200°C. Polymer XXIX has also been prepared from methyldi-n-butoxy borane (Equation 27) and its properties appear to be similar to the material from hexamethylborazole.

$$(MeBNMe)_3 + 3\ HO\text{-}Ar\text{-}OH \longrightarrow \underset{n}{1}\left\leftarrow \overset{Me}{\underset{|}{B}}\text{-}O\text{-}Ar\text{-}O\right\rightarrow_n + 3\ MeNH_2 \qquad (26)$$

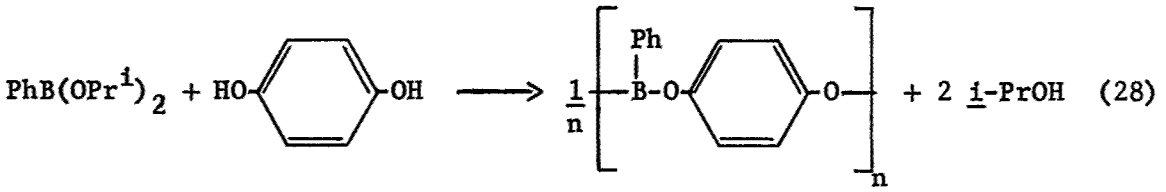
XXVIII, Ar = 

XXIX, Ar = 

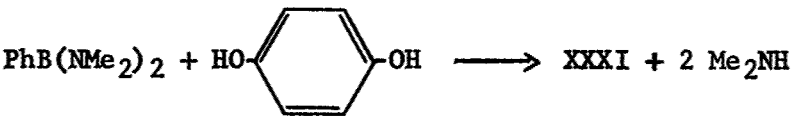
XXX, Ar = 

$$MeB(OBu^n)_2 + HO\text{-}\langle\bigcirc\rangle\text{-}OH \longrightarrow XXIX + 2\ n\text{-}BuOH \qquad (27)$$

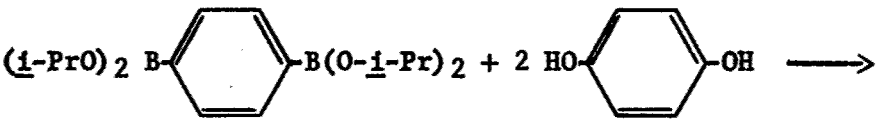
The related hydroquinone derivative (XXVIII) softened at 300-400°C. but was significantly less soluble. Its thermal stability was comparable to that of the resorcinol derivative. In an attempt to increase the softening point and possibly the solubility of this type of polymer, the related compound from bisphenol-A (XXX) was prepared. This material did have improved solubility but softened at 200-300°C. and lost 22 wt.% when heated to 500°C. on the TGA equipment. A polymer (XXXI) related to XXVIII with a phenyl group on boron in place of methyl has also been prepared from phenyldiisopropoxy- or phenyl-bis(dimethylamino)boranes (Equations 28 and 29). Its properties are similar to XXVIII with somewhat poorer thermal stability.

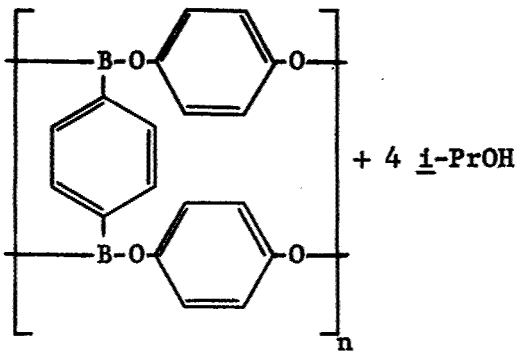


XXXI



The "ladder" polymer, XXXII, does not soften up to at least 300°C. and is slightly soluble in dimethylsulfoxide.



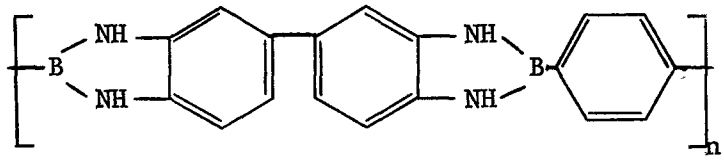


XXXII

3. Polymers Related to the Benzborimidazolines (Type XXIII)

a. Introduction

In September of 1960 (Reference 8) Bamford and Fordham announced the preparation of a new class of boron-nitrogen polymers, the polybenzborimidazolines, illustrated by XXXIII. Professor C. S. Marvel and co-workers (Reference 9) have also prepared

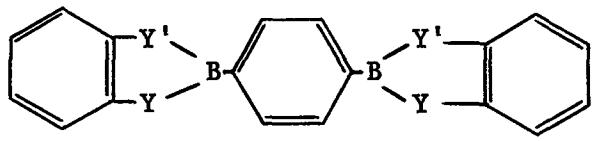


XXXIII

XXXIII and the related derivative of 1,3-benzenediboronic acid as a logical development of their studies on polybenzimidazolines. These polymers are very stable thermally but are infusible and essentially insoluble in organic solvents. The approach followed in the present program was to investigate a series of boron-nitrogen and boron-oxygen substituted analogs of XXXIII in an attempt to improve its solubility and fusibility characteristics with retention of its excellent thermal stability.

b. Derivatives of Diboronic Acids

Prototype compounds (XXXIV-XXXVI) were prepared and found to have comparable thermal stability. However, the oxygen-containing derivatives (XXXV and XXXVI) melted at about 300°C. compared to about 400°C. for XXXIV. They were all soluble

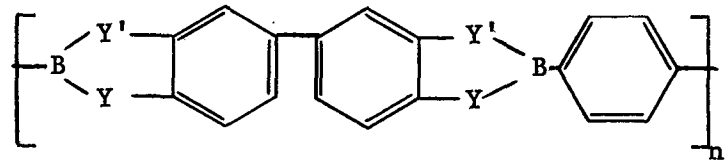


XXXIV, Y = Y' = NH

XXXV, Y = NH, Y' = O

XXXVI, Y = Y' = O

in dimethylsulfoxide and dimethylformamide. The related polymers (XXXVII-XXXIX) were also prepared from the 1,4-diboronate and evaluated. Each had excellent thermal stability losing less than 6 wt.% when



XXXVII, Y = Y' = NH

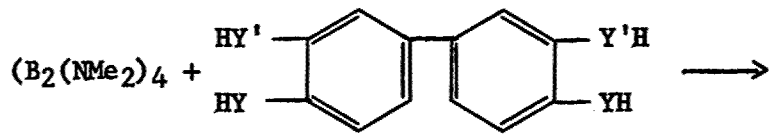
XXXVIII, Y = NH, Y' = O

XXXIX, Y = Y' = O

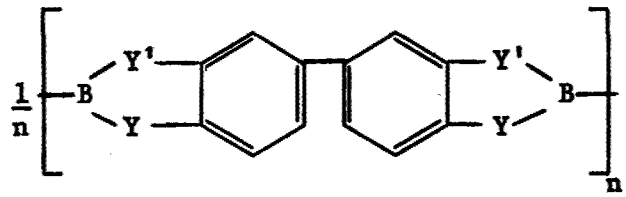
heated to 500°C. on the TGA equipment. They were infusible and essentially insoluble in organic solvents.

c. Derivatives of Diboron Compounds

Although the boron-boron bond is not stable in many simple derivatives, aromatic boron-boron containing compounds from phenylenediamines have shown good stability (References 1 and 2). Boron-boron polymers analogous to the derivatives of diboronic acids above have been prepared as follows:



(31)



XL, Y = Y' = NH

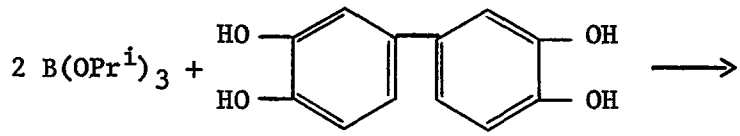
XLI, Y = NH, Y' = O

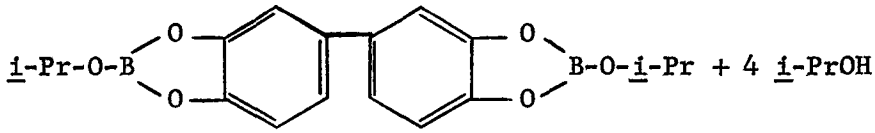
XLII, Y = Y' = O

These polymers have the same general characteristics as those prepared from the diboronic acids; infusibility, insolubility, and excellent thermal stability. However, TGA analysis did show XLI and XLII to be slightly less stable than XXXVIII and XXXIX.

d. Other Boron-Oxygen Derivatives

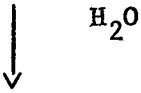
In addition to having the poor handling characteristics noted, the materials described in the two proceeding sections have poor adhesive properties. Subsequently, several related compounds have been prepared which have good adhesive properties and improved solubilities and softening points. Evaluation of these compounds is in its initial stages, but TGA tests on XLIV and XLV showed 4 and 6 per cent weight losses respectively on heating to 500°C. The B-O-B polymer XLIV was prepared as shown by

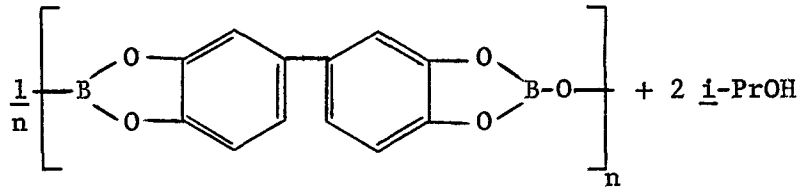




(32)

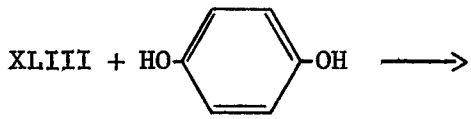
XLIII



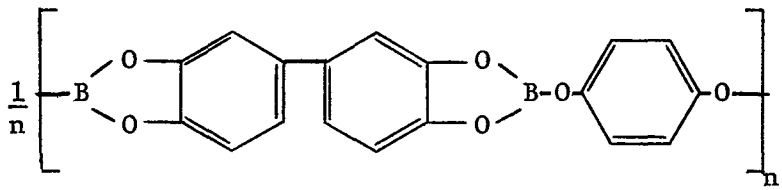


XLIV

a partial hydrolysis-condensation technique similar to that which has been used for the preparation of aluminoxanes. The evaluation of these



(33)



XLV

materials is only in its initial stages, but they appear to be very promising. Their handling characteristics and adhesive properties are better than any of the related compounds described previously.

V. ACKNOWLEDGEMENT

A. This work was supported by the Aeronautical Systems Division, Wright Air Development Center, under Contracts AF 33(616)-5931 and AF 33(616)-7303.

B. It is a pleasure to acknowledge the contributions of A. L. McCloskey and H. Steinberg who have been responsible for the overall supervision of this program and to the following scientists who have been directly responsible for the work discussed.

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4. R. J. Brotherton, A. L. McCloskey, J. L. Boone, and H. M. Manasevit, J. Am. Chem. Soc., 82, 6245 (1960).

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BORON NITROGEN COMPOUNDS

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Indiana University

Compounds containing boron and nitrogen have unusual chemical reactivity and provide a challenge in fields for synthesis of new, basically inorganic molecules. The high thermal stability and hydrolytic stability of certain derivatives suggests said further information about the basic nature of boron-nitrogen compounds can be of use in a program concerned with polymeric species.

A relatively high percentage of studies carried out during the last thirty-five years have concentrated on derivatives of the so-called inorganic benzene, $B_3N_3H_6$. In contrast, the majority of studies of boron-phosphorus compounds of a similar character have concentrated on materials bearing a closer resemblance to cycloalkane or alkane structures. Only recently has it become possible to prepare for direct comparison the analogous compounds of the boron-nitrogen series. This paper is concerned with the preparation and properties of the parent molecule itself, hexahydroborazole, $B_3N_3H_{12}$.

Studies thus far carried out serve to focus attention on possible importance of hexahydroborazole in two major lines of investigation. The chemical reactions of hexahydroborazole are frequently more easily controlled than those of borazole itself and can lead to unsymmetrical substitution products. Thermal decomposition or catalytic decomposition affords direct routes to new borazole molecules.

Experimental

A. Preparation of $B_3N_3H_{12}$. - Thirty cc. of dry diethyl ether was condensed into a dry 50 cc. flask at -196° and 2.5 g. (31 mmoles) of pure borazole condensed on top of the ether. The mixture was warmed to -80° and with continous stirring allowed to absorb an excess (about 120 mmoles) of hydrogen chloride. Within minutes a white precipitate of $B_3N_3H_6 \cdot 3HCl$ was observed. After apparent completion of the reaction the mixture was allowed to slowly warm to room temperature. Ether and excess hydrogen chloride were pumped off and the solid residue was heated to 60° with pumping with a mercury diffusion pump to remove all possible volatile reactants. About 35 cc. of dry diglyme was condensed onto the solid and on warming to room temperature all of the solid dissolved. The flask then was chilled with liquid nitrogen and 4.5g. of sodium borohydride dropped onto the frozen solution under cover of a dry helium stream. The flask then was evacuated again and warmed to room temperature with continuous stirring. Diborane evolution and deposition of a white solid began at once; after several hours a 75% yield of diborane was found to have been produced based on the equation

$$2B_3H_3Cl_3N_3H_6 + 6NaBH_4 \rightarrow 2B_3N_3H_{12} + 3B_2H_6 + 6NaCl$$

Volatile ether cleavage products were present as by-products and were discarded without further study. Decantation of the supernatant liquid from the white solid followed by removal of the diglyme by vacuum distillation left a white solid (undoubtedly containing some excess sodium borohydride). On slow warming with continuous pumping a white solid began to sublime between 90 and 100° at pressures below one micron. This substance was resublimed and used for the studies reported below.

B. Analysis. - Samples of the solid substance were treated with 6 M

aqueous hydrogen chloride for 12 hr. at 100°. Substantially lower acid concentrations or shorter times resulted in incomplete hydrolysis. Hydrogen produced by hydrolysis was measured in the vacuum system, nitrogen was determined by a Kjeldahl procedure and boron was determined by the usual titration in the presence of mannitol following removal of the ammonia. Calcd. for $B_3N_3H_{12}$: B, 37.5%; N, 48.6%; H by hydrolysis, 6.93%. Found: B, 38.4%, 36.9%; N, 47.6%, 47.5%; H, 6.92%, 6.93%.

C. Stability. - When obtained in pure form, hexahydroborazole appears to be remarkably stable towards hydrolysis in comparison with other boron-nitrogen compounds. Thus the compound has been recrystallized from water and yielded only a trace of hydrogen after a solution in 0.5 N hydrochloric acid had been heated for five hours at 115°.

In common with most boron-nitrogen compounds containing hydrogen attached to adjacent atoms, thermal stability of saturated borazole leaves considerable to be desired if the compound itself is considered as a potentially stable molecule. In the present case studies of vapor pressure curves have produced reproducible vapor pressures in the region from 27° to 125° (where the vapor pressure is 5.7 mm.), but hydrogen evolution begins to be important shortly above this temperature. On the other hand, high yields approaching quantitative of borazole have been produced by the thermal decomposition reaction suggesting that substituted hexahydroborazoles can be an important source of new substituted borazoles.

D. Chemical Reactions. - An important type of reaction that has received considerable attention in our laboratory is the reaction of saturated borazole with amides and other potential metallating agents. Study of reaction of sodium amide with saturated borazole in ammonia shows that three moles of hydrogen are rapidly produced per mole of saturated borazole used suggesting complete dehydrogenation to borazole itself. The rate of reaction of borazole with ammonia is too great to permit isolation but in the case of substituted saturated borazoles recovery of the borazole itself has been made. In similar studies reactions of phenyl and butyl lithium with saturated borazole have been carried out in hexane, ether, and tetrahydrofuran to produce solid products which yield borazole when treated with methyl bromide.

Preparation of alkoxy substituted saturated borazoles has been carried out by two separate paths. Saturated borazole is quite soluble in alcohols and relatively stable in the absence of catalysts. In the presence of catalytic quantities of hydrogen chloride, however, a solid product soon precipitates from homogeneous solution in methanol and has been identified as B-monomethoxy saturated borazole. In a parallel reaction, advantage has been taken of the reducing property of the B-H bond to prepare the identical compound by reaction between formaldehyde and saturated borazole and methanol as solvent. In both cases the insolubility of the product in methanol serves to allow preparation in good yields without appreciable further attack of the molecule.

In contrast reaction of saturated borazole with ethanol leads to extensive further substitution without precipitation of a monoethoxy product. The reductive route was successful however. In a typical reaction acetaldehyde and saturated borazole were dissolved in a one to one molar ratio in ethanol and warmed gently with a hair dryer for ten minutes to effect complete solution. On cooling to room temperature a white crystalline material was deposited but no hydrogen had been evolved in the reaction. Recrystallization from ethanol produced a 70% yield of B-monoethoxy saturated borazole. Further studies of the preparations of alkoxy substituted saturated borazoles are in progress.

One of the most remarkable properties thus far observed for saturated borazole is the relatively high stability of the nitrogen-hydrogen bond. In general N-H compounds exchange readily with liquid ammonia, but observations of the nuclear magnetic resonance of saturated borazole in deuterated ammonia show that exchange is effected only over a period of several days at room temperature. Eventually exchange is complete however. Exchange of hydrogen attached to boron can be readily effected by treatment with deuterated diborane.

Nuclear magnetic resonance experiments provide substantial conformation of the structural assignments above and will be presented.

RESEARCHES ON MODEL COMPOUNDS RELEVANT TO LINEAR BORON-NITROGEN POLYMERS.

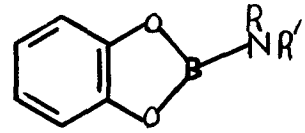
By R.H.Cragg, M.F.Lappert, and B.P.Tilley.

(The Manchester College of Science and Technology, University of Manchester, Manchester,1, U.K.)

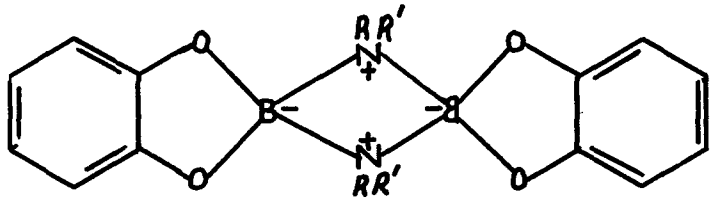
ABSTRACT

1. The following new organic boron-nitrogen compounds were synthesised:

o-phenylene t-butylaminoboronate
o-phenylene ethylaminoboronate
o-phenylene isopropylaminoboronate
o-phenylene phenylaminoboronate
o-phenylene dimethylaminoboronate



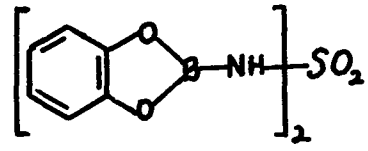
The last four compounds were all obtained as hydrolytically stable dimers.

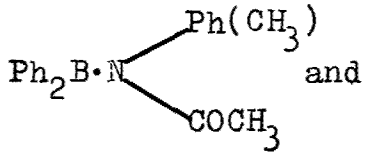
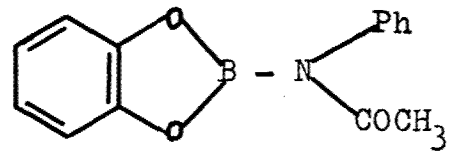


The problem of monomer ⇌ dimer, equilibrium and the influence thereon of substituents on the nitrogen atom has been studied qualitatively.

2. A preliminary study of the novel classes - acylamino- and sulphonylamino- boron compounds has been undertaken. Among the compounds characterised are

Bis(o-phenylenedioxyboron) sulphamide

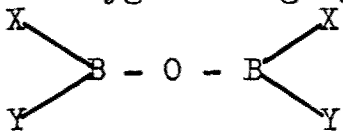


and the amides  and 

Stabilisation by chelation or autocomplexing is expected



3. Oxygen-bridging is being investigated and model compounds

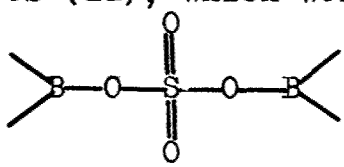
 are being examined.

4. Attempts to prepare organic boron sulphates were unsuccessful.

DISCUSSION

1. BORON SULPHATES

The initial programme was concentrated on the organo-boron sulphates (II), which were (and are) unknown.

 (II)

It was hoped that such compounds might be stabilized, particularly towards hydrolytic attack, by either intra-(chelation) or inter-molecular donation (O= S=O ···· B). Such chelation has previously been demonstrated to occur in the acyloxy boron compounds.[1]

The synthetic routes so far investigated, all of which yielded negative results as far as boron sulphate formation was concerned, were (i) - (v).

(i) The interaction of a boron halogen compound (o-phenylene chloro- or bromo-boronates, dibutyl chloroboronates or phenyldichloroborane) with dry silver sulphate in the absence or presence of various solvents (benzene, ether, acetonitrile, methylene dichloride or chloroform) under reflux.

(ii) Potassium sulphate with o-phenylene chloroboronate in the

presence of liquid sulphur dioxide, under reflux.

(iii) o-Phenylene chloroboronate and dimethyl sulphate at 60° for 1 hour.

(iv) o-Phenylene ethyl borate and sulphuryl chloride under reflux.

(v) o-Phenylene isocyanatoboronate and mercuric sulphate in the presence of benzene under reflux.

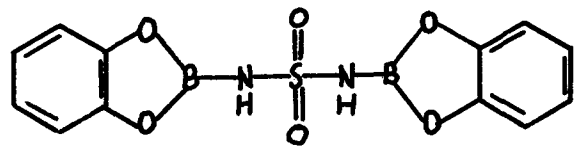
A possible explanation for the lack of formation of organoboron sulphates may be due to the considerable electron attracting capacity of the sulphonyl group.[2] Thus a sulphonyl group and a boron atom would in a boron sulphate be in competition for the electrons of the oxygen atom. In a recently published patent there is claimed the synthesis of organoboron sulphates, by refluxing dialkyl sulphates with dialkylboron chlorides, using an initial reflux temperature 100° - 150°;[3] it was stated that these compounds are highly reactive and decompose above the upper reflux limit. It is proposed to repeat these experiments at a later date.

2. SULPHAMIDES OF BORON

Due to the possibility that the electron-acceptor strength of the sulphonyl group prevents sulphate formation, it was thought that if a stronger electron-donor group was attached to the sulphur, it would be possible to effect bridging of two boron atoms by a substituent containing a sulphonyl group. As sulphamic acid had previously been tried,[4] but without success, it was decided to attempt to synthesise boron-substituted-sulphamides. In sulphamide, the diamide of sulphuric acid, it was considered that the nitrogen atoms would satisfy the requirements, and this lead to two approaches to the synthesis of boron sulphamides.

(i) By direct metathesis of chloroboronates with sulphamide or substituted-sulphamides: thus on refluxing o-phenylene chloroboronate with sulphamide in benzene, hydrogen chloride was evolved, leaving a white benzene-insoluble solid, which analysed as the N,N'bis(o-phenylenedioxyboron) sulphamide (III)

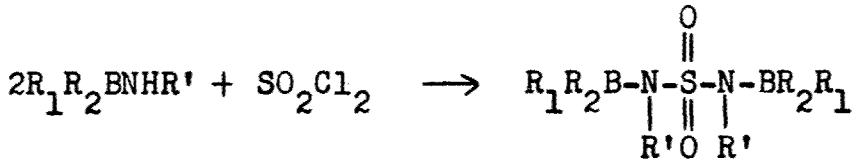
$$SO_2(NH_2)_2 + 2C_6H_4O_2BCl \rightarrow$$



(III)

Compound (III) was not very stable to hydrolysis.

(ii) The second approach was to react alkylaminoboronates with sulphuryl chloride.

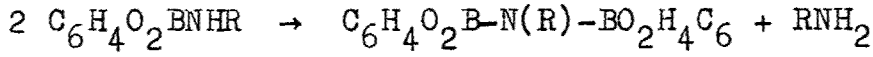


This second approach has not up to the present time been investigated, since synthesis of the o-phenylene alkylamino-boronates, which are the required precursors has lead to other interesting chemistry (see Section 3).

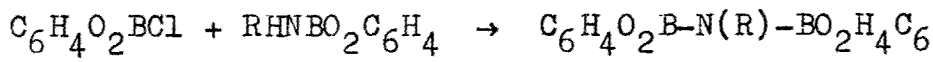
3. o-PHENYLENE ALKYL- OR ARYL- AMINOBORONATES

Investigation of o-phenylene alkylaminoboronates was undertaken partly in order to provide starting materials for borosulphamides and partly as a means of producing new boron compounds with boron-nitrogen-boron linkages. The latter problem was envisaged as involving the following alternative reaction sequences.

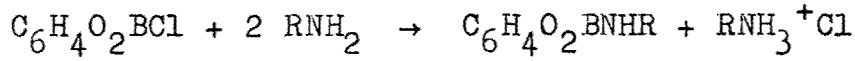
(i) By analogy with the pyrolysis of tris(alkylamino)boranes, which eliminate amine to produce boron-nitrogen-boron linkages;[5] thus, it was intended to pyrolyse the o-phenylene alkylaminoboronates to give the required compounds.



(ii) By direct metathesis between o-phenylene alkylaminoboronates and o-phenylene chloroboronates.



A number of o-phenylene alkylaminoboronates were synthesised, and two methods of preparation were used. The first method was by the reaction of o-phenylene chloroboronate and the appropriate amines in the presence of benzene or light petroleum, and subsequent removal by filtration of the amine hydrochloride.

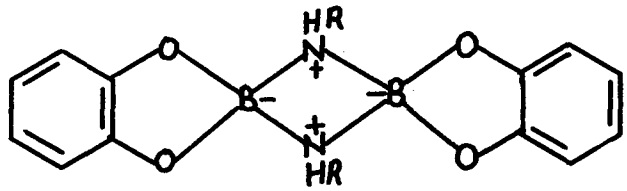


The second method of synthesis was by transaminating o-phenylene diethylaminoboronate, by the use of the appropriate amine in the presence of light petroleum. This method was preferred due to the speed and efficiency of reaction. The o-phenylene phenyl-, isopropyl-, ethyl-, and t-butyl-aminoboronates were prepared by the methods outlined. Some of the properties of the above amino-boronates are summarised in Table 1.

TABLE 1.

Compound	Ref. No.	B.p. (°/mm.)	M.p. (°)	Normal state of Aggregation	Miscellaneous
$C_6H_4O_2BNHBu^t$	IV	68/0·3		Monomer	Readily attacked by moist air
$C_6H_4O_2BNHPr^i$	V	54/0·2		Monomer ⇌ Dimer	Slowly attacked by moist air
$C_6H_4O_2BNHEt$	VI		265-75	Dimer	Stable but slowly attacked by cold water
$C_6H_4O_2BNHPh$	VII		266-8	Dimer	Stable and very slowly attacked by cold water

Structurally, compounds (V) - (VII) are considered to be dimers (VIII), due to their low reactivity, moleculare weights, infrared spectra (see below) and steric requirements.



(VIII)

Compound (IV) is considered to be monomeric from similar evidence.

Infrared spectra of compounds (V) - (VII) show broad bands attributed to BN stretching frequencies at 920± 10cm.$^{-1}$ which is in accord with previous observations for the BN stretching frequencies of the other similar dimer $(Me_2NBCl_2)_2$.[6] The monomeric o-phenylene t-butyl-aminoboronate has a BN stretching frequency at 1535± 2cm.$^{-1}$, which is in good agreement with BN stretching frequencies in other borazens,[7] (including monomeric Me_2NBCl_2).[6]

The spectra of all of the dimeric compounds show rather low NH stretching frequencies at 3225 - 3125cm.$^{-1}$, this may be compared with the NH stretching frequency of the monomeric o-phenylene t-butylaminoboronate located at 3472 ± 2cm.$^{-1}$

Compound (V), when freshly prepared and prior to distillation, was a liquid and had the BN stretching frequency at 1543± 2cm.$^{-1}$ and the NH frequency at 3425± 2cm.$^{-1}$ After distillation it solidified and although both these peaks still persisted to a small degree in a spectrum of the solid, the dimer peaks were very much more predominant. There thus appears to be an equilibrium between the monomeric and dimeric states for compound (V). The significant spectroscopic data are summarised in Table 2.

TABLE 2.

R in $C_6H_4O_2BNHR$	Bu^{t*}	Et	Pr^{i*}	Pr^{i}	Ph
NH (cm^{-1})	3472±2	3174±2	3425±2	3195±2	3125±2
BN (cm^{-1})	1535±2	915±10	1543±2	922±10	918±10

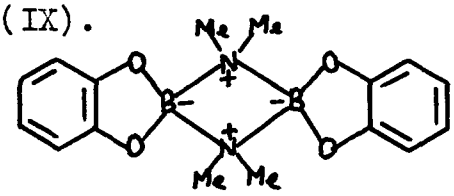
* monomers

The reason for dimerisation is clearly due to the thermodynamic preference for existence in this state, but may be prevented if the steric effects of the substituent groups introduce a high entropy term. The low steric requirement of the o-phenylene dioxyboron ring enables the thermodynamic factor for dimerisation to be greatly enhanced. This is instanced by the fact that even o-phenylene isopropylaminoboronate is dimeric, despite the presence of the bulky isopropyl group.

4. o-PHENYLENE DIALKYLAMINOBORONATES

In the light of the discovery of the dimeric o-phenylene-dioxyborons described in Section 3, it was decided to investigate the dialkylamino series also. The o-phenylene diethyl- and di-n-butyl-aminoboronates had previously been prepared and were monomeric high boiling liquids,[8] which were very susceptible to hydrolytic attack. Therefore any possibility of isolating a dimer in this series, was only likely with the lowest homologue, namely o-phenylene dimethylaminoboronate. This compound was synthesised by direct transamination of o-phenylene diethylaminoboronate with dimethylamine, using light petroleum as solvent. Distillation afforded a crystalline solid, which from molecular weight, its hydrolytic stability and molecular model consideration was assigned

the dimeric structure (IX).



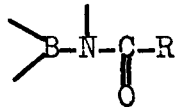
(IX)

Infrared data also indicated the dimeric structure, since the BN stretching frequency was considered to be at 946± 10cm.$^{-1}$ (broad), which is much lower than the 1354± 2cm.$^{-1}$ assigned to the BN stretching in the other o-phenylene dialkylaminoboronates.[9]

Isolation of dimeric o-phenylene dimethylaminoboronate was of further interest, since it provides the first example of a dimeric tetrasubstituted borazen,[10] thus also confirming our view regarding the low steric requirements of the planar fused o-phenylenedioxyboron ring.

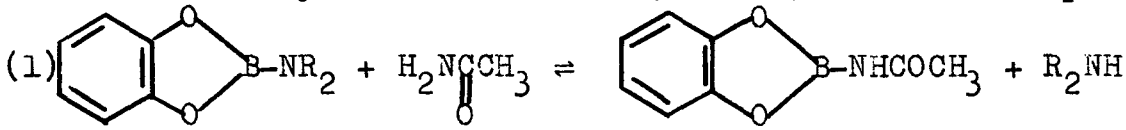
5. AMIDOBORON COMPOUNDS

These compounds have the functional group (X).

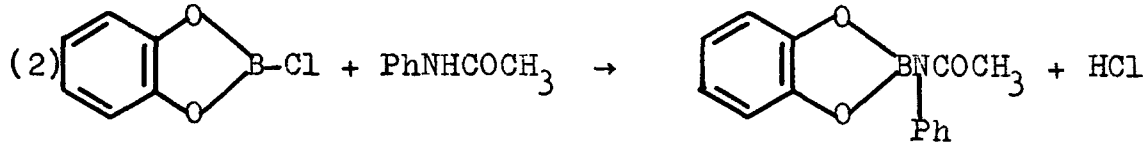


(X)

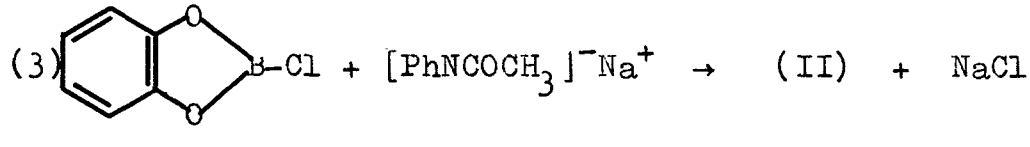
The idealised synthetic routes (i) to (v) have been explored.

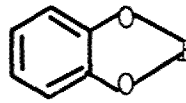


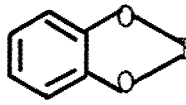
R = Et, Pr^{i}

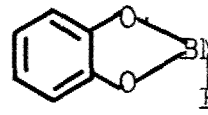


(II)

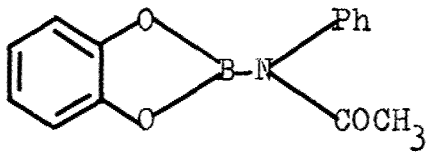


(4)  + $PhNHCOCH_3$ + Et_3N → (II) + Et_3N,HCl

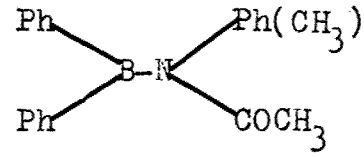
(5)  + CH_3COCl + C_5H_5N →

 + $[C_5H_5NH]^+Cl^-$

Routes (3) and (4) appear promising, but the others less so. Using method (3), the amides (XI) and (XII) have been made. Their properties are being investigated.



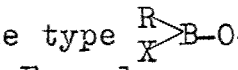
(XI)



(XII)

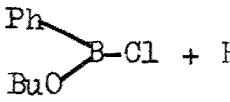
6. OXYGEN-BRIDGING

A major purpose of our research is the synthesis of model compounds for polymers, having two boron atoms attached through a bridging group. In the present case, bridging through an oxygen atom was explored.

Compounds of the type  although known are very limited in number. Examples are where R = AcO, Bu, Ph and X = AcO, Bu, Ph or halogen. A survey of the literature of these compounds was carried out in order to find methods to extend the series. It is proposed also to use these compounds to attempt the preparation of novel ring systems, e.g. tetrameric boroxoles.

The synthesis of $[Ph(BuO)B]_2O$, (XIII), from n-butoxychlorophenylborane was attempted.

Two reaction schemes were carried out (see below), but in neither case was (XIII) isolated. It may have been an unstable intermediate, however, in reactions (6) and (7)

(6) 2  + HgO → $\frac{1}{3}(PhBO)_3$ + $PhB(OBu)_2$ + $HgCl_2$

(7) $2\ \begin{matrix} Ph \\ BuO \end{matrix}\!\!>\!B\text{-}Cl + [(CH_3)_3Si]_2O \rightarrow \frac{1}{3}(PhBO)_3 + PhB(OBu)_2 + 2(CH_3)_3SiCl.$

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RESEARCH ON BOROPHANE, BORAZINE, AND PHOSPHORANE POLYMERS

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ABSTRACT

The synthesis of linear borophane polymers has been improved and expanded in terms of yields, molecular weights, and variety of substituent groups. Thermal stability of the polymers has also been improved, but their thermal depolymerization at 200-250°C. has not yet been overcome.

Several reactions have been developed which allow introduction of new substituent groups in cyclic borophane polymers, and these now open the way to new polymer types.

Significant advances have been made towards the development of both laminating resins and wide liquid range fluids based on cyclic borophane polymers.

Linear borazylene and borazylene oxide polymers have been synthesized and characterized.

New approaches to phosphorus-nitrogen polymers have resulted in the synthesis of arylphosphonyl azides and arylphosphonimidophosphoranes.

I. Introduction

The primary objective of our research program is to develop new candidate materials for application as elastomers, adhesives, resins and/or fluids at elevated temperatures. The borophanes (phosphinoborines), borazines, and phosphorus-nitrogen compounds offer promising fields of study since each of these classes of compounds show good thermal, hydrolytic, and oxidative stabilities.

The early work on borophane compounds led mainly to the cyclic triborophanes which gave the first indication of the inherent stability of the boron-phosphorus bond and indicated further work. The triborophanes have subsequently been used as model compounds to study the effects of substituents on physical and chemical properties. Means of preparing linear borophane polymers were developed but stability of these polymers was low relative to the cyclic compounds. Useful chemical reactions of the borophanes have more recently been developed but are still of limited scope.

Our research on borazine polymers, consisting of developing suitable syntheses for mono- and di-functionally substituted borazine derivatives and their subsequent polymerization, has all been done since the last Contractors' Conference.

Similarly, research in phosphonyl azide chemistry is of recent origin. The objective of this phase of the work has been to investigate new approaches to thermally stable materials. Most of the effort has been devoted to a study of the reaction of phosphonyl azides with trivalent phosphorus compounds to yield phosphoranes.

II. Borophane Polymers

A. Discussion

1. Linear Borophane Polymers

a. Synthesis

A number of new linear borophane polymers have been prepared during the past three years. Among these are the series of poly-P-methyl-n-alkylborophanes where the n-alkyl group is methyl through n-octyl. Pyrolysis of the methyl-n-alkylphosphine boranes in the presence of 20 mole per cent triethylamine provided the linear polymeric products in increasing yield but with decreasing molecular weight as the chain length of the n-alkyl substituent increased. Presumably an increasing steric requirement of the n-alkyl substituent makes initiation of new chains more favorable than growth of existing chains. Aside from the highly crystalline dimethyl member, these polymers are viscous liquids.

The tentatively characterized poly-P-(3,3-dimethylcyclotrimethylene)borophane was prepared by pyrolysis of 3,3-dimethylcyclotrimethylenephosphine borane in the absence of excess base to test the hypothesis that a small CPC bond angle would favor linear polymer formation. That the polymeric product was formed without ring opening has not been conclusively established.

A series of experiments using both dimethyl- and methylethylphosphines showed that linear polymers could be prepared when these phosphines were heated with approximately equimolar quantities of triethylamine borane. The yields of polymers were comparable to those obtained from approximately equimolar mixtures of secondary phosphine borane and triethylamine suggesting that rapid equilibration of the system (Eq. 1) precedes thermal dehydrogenation.

$$R_2PH + R'_3N{:}BH_3 \rightleftharpoons R'_3N + R_2PH{:}BH_3 \qquad (1)$$

Attempts to prepare the fully methylated linear polymer, $[(CH_3)_2PB(CH_3)_2]_n$, by methylation of either $[H(CH_3)PB(CH_3)_2]_n$ or $[(CH_3)_2PBCl_2]_n$ failed. Reaction of $[H(CH_3)PB(CH_3)_2]_n$, prepared by dehydrohalogenation of methylphosphine dimethylbromoborane, gave as the principal product: (1) with methyllithium, trimethylphosphine trimethylborane; and (2) with sodium amide and

methyl bromide, aminodimethylborane trimer. From the reaction of trimethylaluminum with $[(CH_3)_2PBCl_2]_n$, prepared by halogenation of the linear poly-P-dimethylborophane, no identifiable product was obtained.

b. Degradation

Thermal degradation of poly-P-dimethylborophane at 180°C. during 21 hrs. resulted in conversion of approximately half of the polymer to P-hexamethyltriborophane. During the first few hours of heating, 2-3 mole per cent each of hydrogen and a condensable gas (presumably dimethylphosphine and triethylamine) were evolved. The molecular weight of the polymer showed a moderate increase. At the higher temperature of 202°C., 27 ± 4% of the polymer depolymerized during 1 hr. to P-hexamethyltriborophane containing 2-4 per cent P-octamethyltetraborophane. Pyrolyses of both a physical equimolar mixture of P-dimethylborophane and P-methylethylborophane and a similar mixture which had been treated with hydrogen chloride to produce some block copolymer, yielded the same nearly statistical mixture of the four possible triborophane derivatives, $[(CH_3)_2PBH_2]_{3-n}[CH_3(C_2H_5)PBH_2]_n$. Based on these and other results the depolymerization appears to proceed by an unzipping of monomer units which recombine to form the observed cyclic products.

Thermal depolymerization of two other linear borophane polymers, P-cyclotetramethyleneborophane and P-(3,3-dimethylcyclotrimethylene)-borophane, gave in the case of the former, P-tris(cyclotetramethylene)triborophane as the principal product, while the latter polymer gave primarily a nonvolatile material together with some of the expected cyclic degradation product. Whether opening of the tetratomic phosphorus heterocyclic substituent occurred during synthesis or degradation of the polymer cannot be decided from the available data.

c. Stabilization

Treatment of poly-P-dimethylborophane with a variety of acidic and basic reagents was done in an effort to modify the chain ends and inhibit the depolymerization. After treatment with hydrogen chloride, acetic acid-acetic anhydride, sulfuric acid-acetic anhydride, maleic anhydride, nickel carbonyl or butyllithium, the polymer showed a decrease in the amount of depolymerization during 1 hr. at 202°C. from 27 ± 4% to less than 6% in each case. Polymer treated with triethylenediamine showed no stabilization.

2. Cyclic Borophane Polymers

a. Synthesis

New methods for synthesis of cyclic triborophanes were demonstrated in the preparation of P-hexamethyltriborophane by pyrolysis of the products resulting from the reaction of dimethylphosphonium chloride with lithium borohydride and from the reaction of dimethylphosphine chloroborane with triethylamine.

Pyrolysis of the secondary phosphine borane adducts in the usual manner provided the new triborophanes, P-hexaneopentyl-, P-trineopentyltri-

phenyl-, P-trimethyltriphenyl-, and P-trimethyltris(3-dimethylaminopropyl)triborophane without complication. The stereoisomers of both P-trineopentyltriphenyl- and P-trimethyltriphenyltriborophanes have been isolated. The functionally substituted P-trimethyltris(3-dimethylaminopropyl)triborophane was converted by way of the amine oxide derivative to P-trimethyltriallyltriborophane.

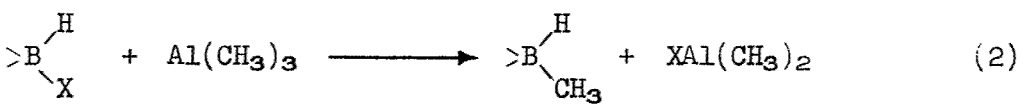
b. Reactions

Halogenation of P-hexamethyltriborophane has been accomplished with cyanogen bromide, mercuric bromide and N-halosuccinimides. With the last reagent and related compounds halogenation was accomplished with sufficient selectivity to prepare the entire series of B-chloro-derivatives of P-hexamethyltriborophane. The stepwise halogenation becomes more difficult as the steric requirement of the halogen increases. With the exception of the B-pentabromo- and B-tetra- and pentaiodo-derivatives, all 18 of the B-substituted chloro-, and iodo-derivatives of P-hexamethyltriborophane have been prepared. Only a few of the stereoisomeric mixtures have been resolved.

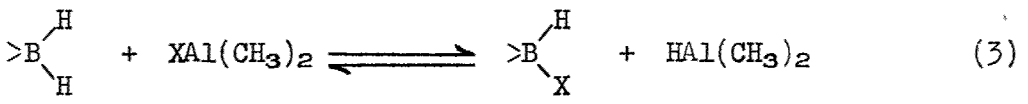
P-Hexamethyltriborophane reacts degradatively at elevated temperatures with silver oxide, sulfur, maleic or acetic anhydrides and formic acid and at ambient temperature with permanganate; reduction of mercuric acetate to mercury in hot methanol was observed but the other products of the reaction were obscure.

A number of reactions of B-halo-substituted P-hexamethyltriborophanes have been discovered using in most instances the monoiodo-derivative to simplify product characterization. The reactions may be divided into three types: reactions with organometallic reagents, carboxamide derivatives, and metallic salts.

Organic derivatives of lithium, magnesium, zinc, cadmium, mercury, boron and aluminum have been used with varying degrees of success to prepare B-alkyl and B-aryl-derivatives of P-hexamethyltriborophane, with the zinc, cadmium and aluminum compounds providing the higher product yields. Analysis of the reaction products showed that the reactions were nonspecific and that, in addition to the expected B-alkyl or B-aryl-derivative corresponding to the B-halo compound used, both more and less highly substituted products were formed in substantial amounts.



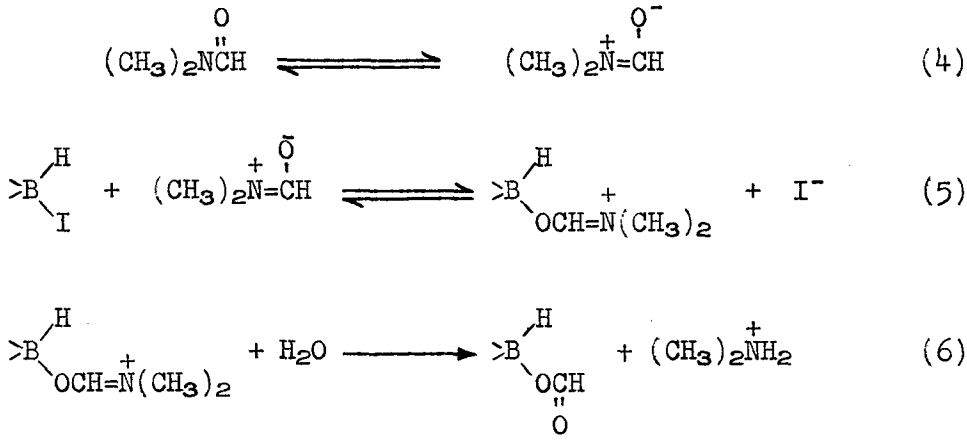
(2)



(3)

The apparent disproportionation reaction may be rationalized as an initial displacement of a halogen by the organometallic reagent (trimethylaluminum for example) followed by halogenation of the triborophane derivative by the by-product dimethylaluminum halide. Repetition of this process would result in more highly methylated products than expected since trimethylaluminum alone fails to react with P-hexamethyltriborophane. The less highly methylated products must arise of necessity from methylation of a partially reduced B-halo-triborophane derivative since disproportionation of the partially B-halogenated compounds has not been observed under the experimental conditions. Dimethylaluminum hydride, formed when dimethylaluminum halide halogenates the triborophane derivative, presumably is responsible for the observed reduction products. That lesser quantities of apparent disproportionation products are observed as the relative stabilities of the respective metal (Al, Zn, and Cd) hydrides decreases, suggests either supression of the forward reaction (equation 3) or degradation of the organometal hydride.

Attempts to use dimethylformamide as a reaction solvent for B-halo-derivatives of P-hexamethyltriborophane invariably resulted in the formation of a small amount of a carbonyl-containing product, the yield of which was greater with less carefully dried solvent. A direct study of the reaction of P-hexamethyl-B-iodotriborophane with aqueous dimethylformamide showed that the carbonyl-containing product was P-hexamethyl-B-formoxytriborophane. A proposed mechanism for this reaction is as follows:



Similar reactions were observed with formamide and dimethylacetamide.

The reaction of simple metallic salts with P-hexamethyl-B-iodotriborophane provided a synthetic method for a wide variety of B-substituted derivatives. Reaction of the silver salts of formic, acetic, and benzoic acids in benzene resulted in formation of silver iodide and the corresponding carboxy-compounds, the first two of which were identical with those formed by reaction of the aqueous carboxamides. The reaction of sodium cyanide with P-hexamethyl-B-halotriborophane (chloro-, bromo-, or iodo-) in dimethylformamide or ethanol provided the B-cyano-derivative in high yield; similar reaction of the B-dihalo-derivative yielded P-hexamethyl-B,B'-dicyanotriborophane. Other alkali metal salts were reacted with B-halo-derivatives to obtain the following derivatives of P-hexamethyltriborophane: isocyanato, thiocyano, mercapto and methanethio.

Reaction of P-hexamethyl-B-isocyanatotriborophane with diethylamine converted it to the corresponding diethylureido derivative. Repeated attempts to hydrolyze the cyano group in P-hexamethyl-B-cyanotriborophane to a carboxylic acid failed as did efforts to reduce it to an amine although some reductive cleavage was observed.

c. Evaluation

Relative oxidative stabilities of triborophane derivatives were measured by the spontaneous ignition temperatures of the compounds in air. In the series of 1,3,5-trimethyl-1,3,5-tri-n-alkyltriborophane fluids the spontaneous ignition temperature shows an increasing trend with decreasing volatility as might be expected. Although this series of liquid triborophanes (particularly the higher members) showed a good liquid range, viscosity, and lubricity, the oxidative stability was not sufficient to make them attractive for high temperature applications. P-Neopentyl groups offered no steric inhibition of the oxidation reaction. B-Cyano-derivatives appeared significantly more oxidatively stable than the parent compounds while the reverse was observed with the B-carboxy-derivatives.

The resin, poly-P-methylsesquimethyleneborophane, was used to prepare a glass cloth laminate. The low heat distortion temperature of the resin, presumably due to either thermoplasticity or insufficient cross-linking or both, precluded use of high temperatures. Other resin systems are under investigation.

3. Phosphines

The reaction of an alkyl halide with a metal phosphinide in liquid ammonia was successfully employed to prepare without complication eight new phosphines: methyl-n-alkylphosphine (n-alkyl = C_4-C_8), 3,3-dimethylcyclotrimethylenephosphine, methyl-3-dimethylaminopropylphosphine, and methyl-β-hydroxyethylphosphine (from ethylene oxide).

The reaction of organometallics with aminochlorophosphines has been used to prepare P,P'-bis(methyldimethylamino)-p-phenylenediphosphine, bis-(dimethylamino)methylphosphine, dineopentyldimethylaminophosphine, and neopentylphenyldimethylaminophosphine. The last two compounds were converted through the chloro-derivatives to the corresponding secondary phosphines.

B. Summary and Conclusions

Stabilization toward thermal depolymerization of linear P-dimethylborophane polymer with a variety of acidic and basic reagents has been accomplished, although the improvement observed still is insufficient to permit high temperature applications. Further work directed toward discovery of stable chain terminating groups will be undertaken.

The synthesis and investigation of the chemistry of triborophane derivatives functionally substituted on both boron and phosphorus has markedly accelerated since the discovery of the reactivity of partially B-halogenated triborophanes relative to that of the fully B-halogenated derivatives. Further

work will be directed toward substitution of groups which will either enhance the thermal, oxidative, or hydrolytic stabilities, influence the degree of polymerization, or in themselves be capable of further reaction including polymerization.

III. Borazine Polymers

1. Synthesis of Starting Materials

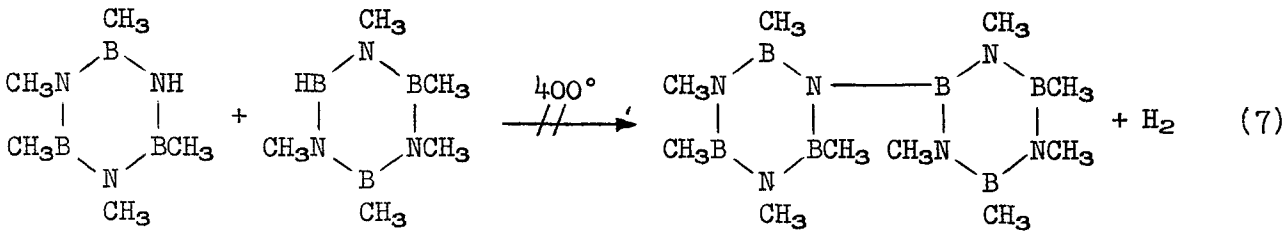
Only a few borazine derivatives which are unsymmetrically substituted with respect to one or both of the skeletal atoms have been reported. During the course of an investigation directed toward preparation of linked-ring borazine polymers a new type of borazine derivative was prepared which can be used to effect unsymmetrical substitution on the nitrogen atom of the borazine ring, i.e., N-lithio-derivatives. The N-lithioborazine compounds were prepared by reaction of the stoichiometric quantities of the borazine and methyllithium.

B-Mono- and -dihalo-substituted borazines were conveniently prepared in high yield and purity by reaction of a borazine suitably blocked with one or two B-methyl substituents with a hydrogen halide at such a temperature that only the B-H bonds and not the B-CH_3 bonds were cleaved. The same compounds, prepared by partial methylation of a B-trichloroborazine derivative with an organometallic reagent, were obtained as mixtures which were only partially resolved after tedious attempted purification.

2. Polymerization of Borazine Rings

Three means of effecting direct condensation polymerization of borazines were investigated: pyrolytic dehydrogenation, dehydrohalogenation, and lithium chloride elimination. Only the last reaction was successful in effecting direct B-N bonding between borazine rings.

Pyrolysis of an equimolar mixture of isomeric pentamethylborazines gave only a trace of decamethyl-N,B′-biborazyl (I) indicating a remarkable resistance of these substituted derivatives toward elimination of hydrogen.



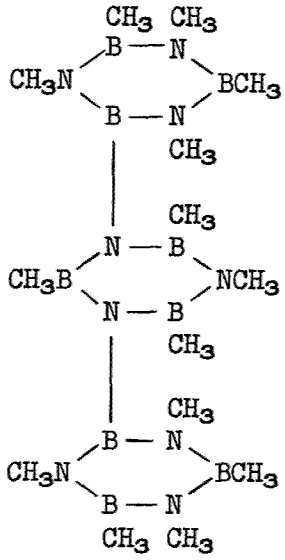
(7)

I

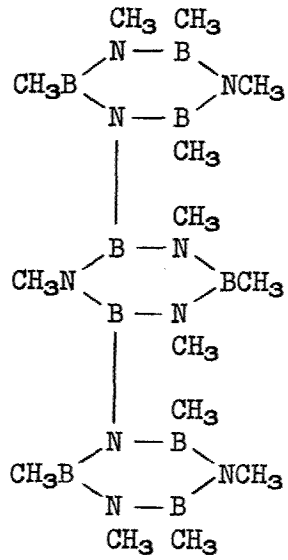
In each of the independent pyrolyses of the pentamethylborazine isomers the major portion (ca. 89%) of the starting material was recovered and all but a trace of the remainder was accounted for as disproportionation products (tri-, tetra-, and hexamethylborazines). Exchange of methyl groups and hydrogen atoms

occurred only between like skeletal atoms.

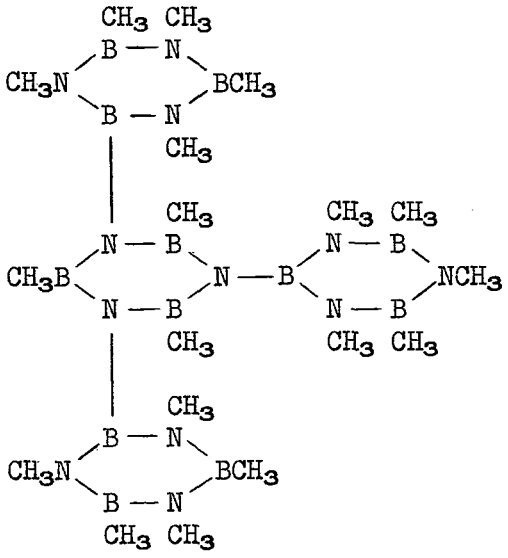
Elimination of lithium chloride between N-lithiopentamethylborazine and pentamethyl-B-chloroborazine gave (I) in good yield. Extension of this type of reaction to polyfunctional borazine derivatives led to the preparation of two isomeric diborazylborazines (II), one of the isomeric triborazylborazines (IIIb), and finally a biborazylene polymer (IV).



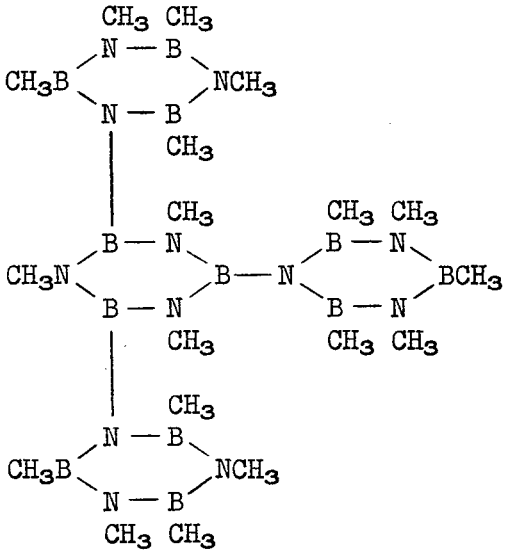
IIa



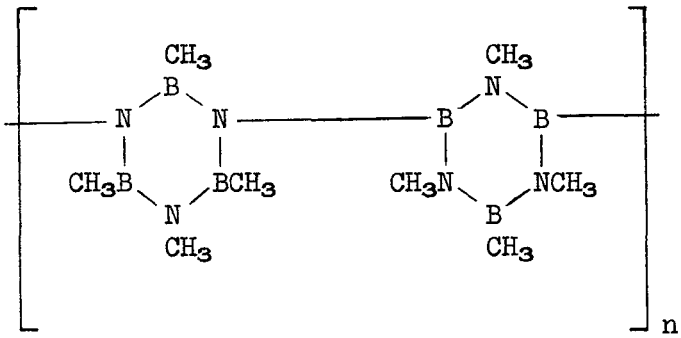
IIb



IIIa

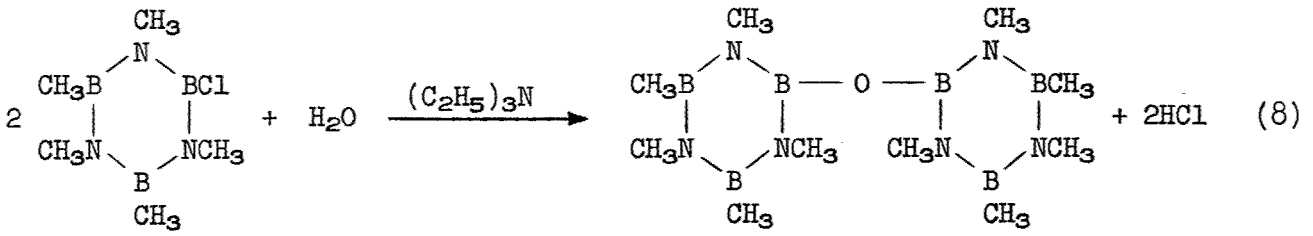


IIIb

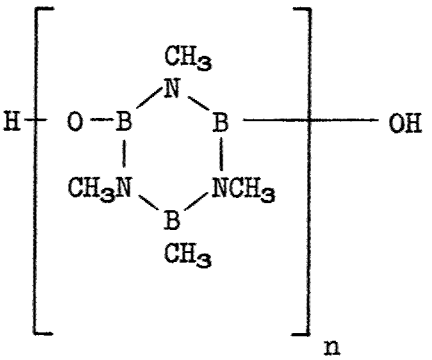


IV

Attempts to prepare (I) (and related compounds) by dehydrohalogenation of mixtures of borazines carrying N-H and B-Cl substituents gave instead a compound (V) which was identical to that obtained by hydrolysis of the chloro-substituted derivative alone. Hydrolysis of tetramethyl-B-dichloroborazine with the stoichiometric quantity of water produced, as a glassy product, a polymeric chain of rings (VI) with a degree of polymerization of approximately 23.



V



VI

IV. Phosphorus-Nitrogen Chemistry

A. Introduction

Aside from the phosphonitrilic halides, phosphorus-nitrogen bonded compounds have not been systematically investigated as possible thermally stable polymer systems or precursors. We wished to explore routes to such compounds by means of reactions in which either no by-product is formed, or only volatile by-products are formed. As a starting point we have investigated the preparation and reactions of organophosphorus azides.

B. Azides

1. Preparation

It was found that equal molar quantities of diarylphosphonyl chlorides (VII) and sodium azide undergo reaction in anhydrous pyridine or acetonitrile to provide the corresponding diarylphosphonyl azides (VIII) in essentially quantitative yields (Eq. 9).

$$(R\text{-}C_6H_4)_2\overset{\overset{Z}{\uparrow}}{P}Cl + NaN_3 \longrightarrow (R\text{-}C_6H_4)_2\overset{\overset{Z}{\uparrow}}{P}N_3 \qquad (9)$$

VII

VIII a, R = H, Z = O

b, R = p-CH_3-, Z = O

c, R = p-Cl, Z = O

d, R = H, Z = S

2. Properties

The diarylphosphonyl azides were found to be unexpectedly stable; they were distilled, burned, and hit with a hammer without any evidence of violent decomposition. Also, a sample of distilled diphenylphosphonyl azide was stable for 8 months in a sealed ampule under ambient conditions, and a sample of crude material exhibited no decomposition in the presence of 316 stainless steel during several weeks. Diphenylphosphonyl azide was distilled at 137-140°C. at 0.05 mm.; bis-(p-tolyl)phosphonyl azide distilled at 190-195°C. at 0.5 mm. with slow decomposition; bis-(p-chlorophenyl)phosphonyl azide distilled at 10^{-5} mm. without apparent decomposition; diphenylthiophosphonyl azide turned red and could be distilled only with difficulty at 10^{-4} mm. The infrared spectra of crude (yellow) and distilled diphenylthiophosphonyl azide were identical. The red color changed to yellow on standing; there was no apparent evolution of nitrogen accompanying the color changes from yellow-to-red and red-to-yellow. These observations suggest the following qualitative order of thermal stability for the diarylphosphonyl azides:

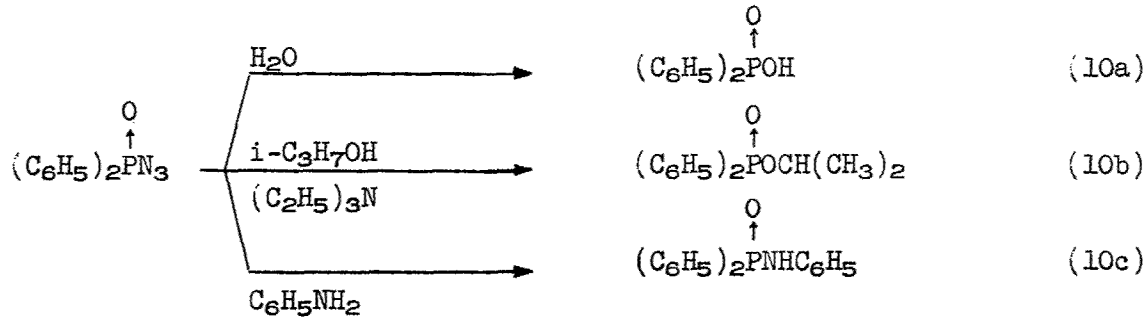
$$(Cl\text{-}C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}N_3 > (CH_3\text{-}C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}N_3 > (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}N_3 > (C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}N_3$$

The hydrolytic stability of the diarylphosphonyl azides varies markedly; diphenylphosphonyl azide appears to hydrolyze in a matter of minutes whereas under the same conditions diphenylthiophosphonyl azide is not completely hydrolyzed after several hours. Qualitatively, the relative order of hydrolytic stability appears to be:

$$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}N_3 > (Cl\text{-}C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}N_3 \sim (CH_3\text{-}C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}N_3 > (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}N_3$$

3. Reactions of Diarylphosphonyl Azides

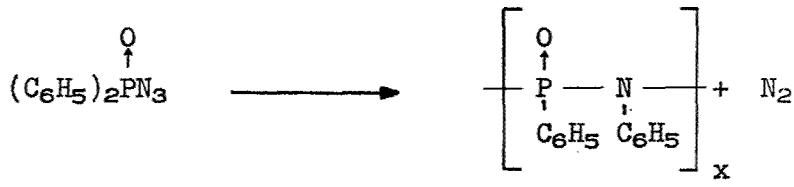
Diphenylphosphonyl azide undergoes solvolytic reactions such as hydrolysis (Eq. 10a), alcoholysis (Eq. 10b), and aminolysis (Eq. 10c).



(10a) (10b) (10c)

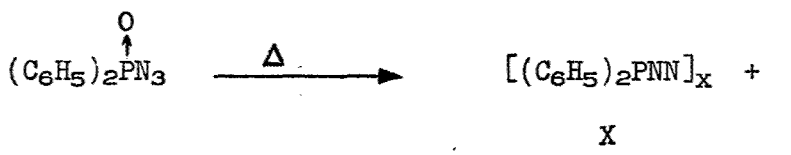
The alcoholysis reaction (Eq. 10b) must be performed under anhydrous conditions to prevent the preferential formation of diphenylphosphonic acid. Furthermore, the alcoholysis reaction did not occur readily except in the presence of a tertiary amine.

The attempted conversion of diphenylphosphonyl azide to a linear P-N polymer (IX) was unsuccessful under a variety of conditions (Eq. 11).



(11)

The use of sulfuric acid in an attempted acid catalyzed reaction was unsuccessful; the azide hydrolyzed and the only product isolated was diphenylphosphonic acid. In a further attempt to cause the rearrangement shown in Equation (11) using boron trifluoride in ether at reflux for 48 hrs. there was no nitrogen evolution or other evidence of reaction; infrared examination of the reaction mixture indicated that little or no reaction had occurred. Attempted thermal rearrangement according to Equation (11) did not yield the expected one mole of nitrogen but, instead, one-half mole of nitrogen was obtained (Eq. 12).



(12)

The product, X, has the empirical composition shown; the structure of X has not been determined.

In a preliminary experiment it was observed that diphenylphosphonyl chloride and sodium azide reacted in dimethylformamide to give an immediate evolution of nitrogen. However, when diphenylphosphonyl azide was added to dimethylformamide (dried over anhydrous sodium sulfate), no nitrogen evolution was observed. When the dimethylformamide was dried by distillation

from calcium hydride it was found to contain some free amine, and the impure dimethylformamide appeared to cause gas evolution (see below). It has also been found that diphenylphosphonyl azide reacts with dimethylsulfoxide with the liberation of nitrogen. The nature of the products obtained in the dimethylformamide and dimethylsulfoxide reactions has not been determined.

Arenesulfonyl azides have been reported to undergo reaction with aromatic compounds to yield arenesulfonanilides[1]. It appeared possible that a similar reaction between diarylphosphonyl azides and aromatic compounds might occur. Such a reaction would extend the chemistry of the phosphonyl azides and would provide a convenient route to a variety of phosphonanilides (Eq. 13).

$$(C_6H_5)_2P(O)N_3 + ArH \xrightarrow{R\cdot} (C_6H_5)_2P(O)NHAr + N_2 \qquad (13)$$

Such reactions were attempted in refluxing benzene and in p-xylene using azo-bis-isobutryonitrile as a radical source. In both cases, no phosphonanilide was obtained and no nitrogen evolution was observed; infrared examination of the residual liquids indicated that the strong azide absorption at 4.65 μ was unchanged. In this same connection, pyridine appears to be an excellent solvent for the preparation of diarylphosphonyl azide with no apparent reaction occurring with the solvent. However, arenesulfonyl azides have been shown to react with pyridine[2,3]. Diphenylphosphonyl azide reacts with triethylenediamine with the immediate formation of a white, water-soluble salt without the evolution of nitrogen. Infrared examination of this material did not show a distinct azide band at 4.65 μ, but exhibited a broad, strong absorption characteristic of a phosphorus-ammonium salt. The material melted at 172-180°C. and was soluble in ethanol. When a water solution of the material was acidified, diphenylphosphonic acid precipitated.

Diarylphosphonyl azides react with trivalent phosphorus compounds to yield phosphoranes (Eq. 14). This reaction is discussed separately, below. The reactions of diphenylphosphonyl azide are summarized in Fig. 1.

C. Phosphoranes

1. From Phosphonyl Azides

Equal molar quantities of diarylphosphonyl azides and trivalent phosphorus compounds (Eq. 14) react to provide excellent yields of diaryl-phosphonimidophosphoranes (XI a-g).

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1. T. Curtius and J. Rissom, J. Prakt. Chem. 125, 303 (1930)
2. T. Curtius and K. Vorbach, J. prakt. Chem. 125, 303 (1930).
3. R. M. Levine and G. L. Buchanan, J. Chem. Soc., 2248 (1950).

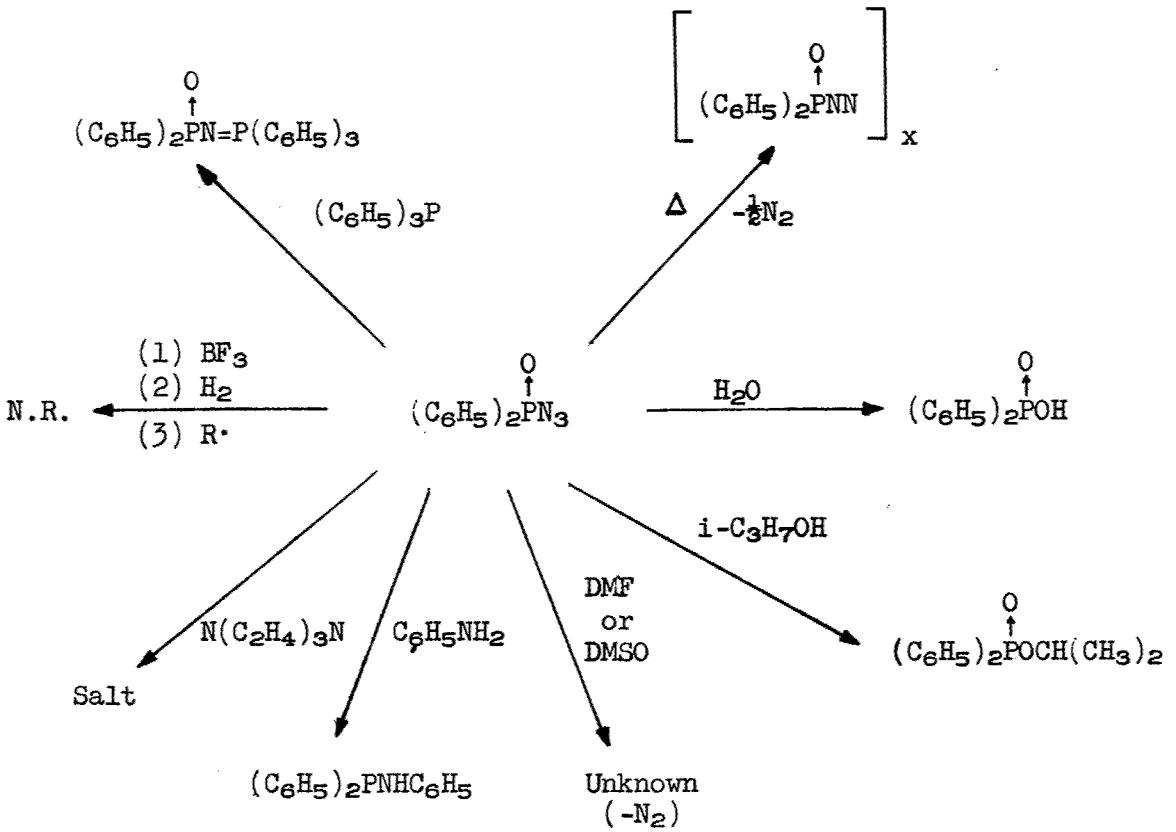


Figure 1. Reactions of Diphenylphosphonyl Azide

$$(R\text{-}C_6H_4)_2\overset{\overset{Z}{\uparrow}}{P}N_3 + R'R''R'''P \longrightarrow (R\text{-}C_6H_4)_2\overset{\overset{Z}{\uparrow}}{P}N{=}PR'R''R''' + N_2 \qquad (14)$$

XI. a. $R=H;\ R'=R''=R'''=C_6H_5;\ Z=O$

b. $R=p\text{-}Cl;\ R'=R''=R'''=C_6H_5;\ Z=O$

c. $R=p\text{-}CH_3;\ R'=R''=R'''=C_6H_5;\ Z=O$

d. $R=H;\ R'=R''=R'''=C_6H_5;\ Z=S$

e. $R=H;\ R'=R''=R'''=p\text{-}Cl\text{-}C_6H_4;\ Z=O$

f. $R=H;\ R'=R''=R'''=p\text{-}CH_3\text{-}C_6H_4;\ Z=O$

g. $R=H;\ R'=R''=CH_3;\ R'''=C_6H_5;\ Z=O$

Diphenylphosphonyl azide reacts slowly with triphenylphosphine in ether to yield diphenylphosphonimidotriphenylphosphorane with the concurrent liberation of equal molar quantities of nitrogen. However, pyridine appears to be a more generally useful solvent for this reaction. Whereas diphenylphosphonyl azide reacts only slowly in ether at reflux, the reaction is essentially quantitative in pyridine at reflux within about one-tenth the time required for ether.

The reaction of phenyldimethylphosphine and diphenylphosphonyl azide in cold ether is so vigorous that it cannot be simply controlled. However, the same reaction occurs in pyridine solution at 0°C. to give a vigorous but controllable evolution of nitrogen and a good yield of diphenylphosphonimido-phenyldimethylphosphorane (XI g).

In a survey of the scope of phosphorane formation, diphenylphosphonyl azide was allowed to react with a variety of Lewis bases in different solvents. Qualitatively, it appears that the rate of reaction of various Lewis bases with diphenylphosphonyl azide is in the order:

$$C_6H_5P(CH_3)_2 > (CH_3O)_3P > (C_6H_5)_3P > (p\text{-}CH_3\text{-}C_6H_4)_3P > (p\text{-}Cl\text{-}C_6H_4)_3P >$$

$$p\text{-}(C_6H_4)_2P\text{-}C_6H_4\text{-}P(C_6H_5)_2 > (C_6H_5)_3Sb$$

2. In Situ Procedure

An in situ procedure for the preparation of diarylphosphon-imidotriphenylphosphoranes and other metalloid phosphoranes has been developed

which does not require isolation of the phosphonyl azide or other metalloid azide. In the in situ procedure, a mixture of sodium azide and triphenylphosphine in pyridine solvent is warmed to gentle reflux under an argon atmosphere and then the phosphonyl chloride in pyridine is slowly added at such a rate that an easily controlled evolution of nitrogen is obtained (Eq. 15). The pyridine is removed at reduced pressure and the solid residue washed with ether and ammonium hydroxide. The in situ procedure offers some advantages in

$$(R\text{-}C_6H_4)_2\overset{O}{\overset{\uparrow}{P}}\text{-}Cl + NaN_3 + (C_6H_5)_3P \xrightarrow[-N_2]{\text{Pyridine}} (R\text{-}C_6H_4)_2\overset{O}{\overset{\uparrow}{P}}\text{-}N{=}P(C_6H_5)_3 + NaCl \quad (15)$$

choice of solvent. For example, when diphenylphosphonyl chloride and sodium azide were allowed to react in dimethylformamide there was an immediate evolution of nitrogen indicating decomposition of the azide (see above). However, when the diphenylphosphonyl chloride was added to a hot solution of sodium azide and triphenylphosphine in dimethylformamide a good yield of diphenylphosphonimidotriphenylphosphorane was obtained.

A useful modification of the in situ procedure just described involves the addition of the phosphonyl chloride to sodium azide in pyridine followed by removal of the precipitated sodium chloride by filtration. This leaves a pyridine solution of the phosphonyl azide which can then be allowed to react with a phosphine to yield a phosphorane.

Using the in situ procedure most of the phosphorane preparations can be completed within 10-15 minutes in a small run (10 g.), and the yields of phosphorane are generally about 95%.

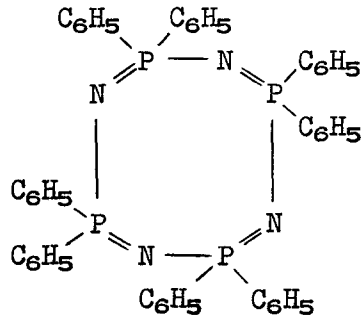
D. Anomalous In Situ Reaction: Formation of Diphenylphosphinic Nitride

When an attempt was made to use the in situ procedure for the preparation of diphenylthiophosphonimidotriphenylphosphorane, none of the desired material was obtained. Instead, an 87% yield of triphenylphosphine sulfide and a yellow, gummy material which was insoluble in benzene was obtained (Eq. 16).

$$(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}Cl + NaN_3 + (C_6H_5)_3P \begin{cases} \xrightarrow{//} (C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}N{=}P(C_6H_5)_3 + NaCl + N_2 \\ \longrightarrow (C_6H_5)_3PS + [(C_6H_5)_2PN]_x + NaCl + N_2 \end{cases} \quad (16)$$

After heating a portion of the yellow material at 275-280°C. for 3 hrs. in a high vacuum, it was extracted with benzene. A white solid was obtained from the benzene extract which was identified as diphenylphosphinic nitride tetramer (XII) by a comparison of the melting points and infrared spectra with an

authentic sample*



XII

Herring[4] found that the reaction of diphenylchlorophosphine and sodium azide at 165°C. yielded a mixture of diphenylphosphinic nitride polymers (Eq. 17).

$$(C_6H_5)_2PCl + NaN_3 \xrightarrow{165°} [(C_6H_5)_2PN]_x + NaCl + N_2 \quad (17)$$

However, when we attempted to prepare diphenylphosphinimidotriphenylphosphorane by the in situ reaction of diphenylchlorophosphine, sodium azide, and triphenylphosphine in pyridine at 115°C., there was no evidence of reaction (Eq. 18).

$$(C_6H_5)_2PCl + NaN_3 + (C_6H_5)_3P \xrightarrow[115°C.]{C_5H_5N} \text{N.R.} \quad (18)$$

On the other hand, while the in situ reaction of diphenylthiophosphonyl chloride, sodium azide, and triphenylphosphine underwent reaction in pyridine to yield Herring's polymer mixture (Eq. 16), diphenylthiophosphonyl azide reacted readily with triphenylphosphine in pyridine solution (Eq. 14) to give an 87% yield of diphenylthiophosphonimidotriphenylphosphorane. In contrast, diphenylphosphonimidotriphenylphosphorane was obtained in 85% yield from diphenylphosphonyl azide (Eq. 14) and in 97% yield by the in situ reaction of diphenylphosphonyl chloride, sodium azide and triphenylphosphine (Eq. 15).

In an attempt to better understand this anomalous in situ reaction of diphenylthiophosphonyl chloride, sodium azide, and triphenylphosphine (Eq. 16), it was found that diphenylthiophosphonyl chloride and triphenylphosphine react in pyridine at 115°C. to form triphenylphosphine sulfide in about 95% yield (Eq. 19).

4. D. L. Herring, Chemistry and Industry, 717, 1960.

* We wish to thank Mr. D. L. Herring, U. S. Naval Ordnance Laboratory, Corona, California, for a sample of diphenylphosphine nitride tetramer and its infrared spectrum.

$$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}Cl + (C_6H_5)_3P \xrightarrow[115°C.]{C_5H_5N} (C_6H_5)_3PS + (C_6H_5)_2PCl \qquad (19)$$

It seems unlikely, however, that Equation (19) represents the first step in the formation of diphenylphosphinic nitride polymer, since diphenylchlorophosphine was not observed to react under the same conditions (Eq. 18). It was also determined that diphenylthiophosphonimidotriphenylphosphorane does not react with triphenylphosphine under the same conditions (Eq. 20).

$$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}N{=}P(C_6H_5)_3 + (C_6H_5)_3P \longrightarrow \text{N.R.} \qquad (20)$$

The above information and the facts that phosphonyl chlorides and diphenylphosphonyl azide form salts with amines, suggest that the intermediate step in the formation of triphenylphosphine sulfide and diphenylphosphinic nitride polymer might be a displacement or rearrangement reaction of a phosphonium salt, such as XIII.

$$\left[\,(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}P(C_6H_5)_3\,\right]^{+} \quad Cl^{-}$$

XIII

This possibility remains to be proven.

E. Properties of Phosphoranes

In preparing a large quantity of diphenylphosphonimidotriphenylphosphorane by the in situ procedure (Eq. 15) the product obtained had a higher melting point (170-171°C.) than the product first obtained (149-150°C.) by the reaction of diphenylphosphonyl azide with triphenylphosphine (Eq. 14). Subsequent reactions of diphenylphosphonyl azide and triphenylphosphine gave the higher melting product. Elemental analyses and molecular weights were virtually the same for both products. Solution infrared and ultraviolet spectra of both materials were identical but shifts in several absorption bands were observed on comparison of the infrared spectra of the solids in potassium bromide pellets. A sample of the lower melting material which had been standing for several months had a wide melting range, 147-167°C., which suggests a slow conversion of low-melting to high-melting material. The low-melting material was readily converted to the high-melting material by recrystallization from isopropyl alcohol-water mixture. Although it is conceivable that the observed differences in physical properties are due to a difference in purity, the data suggest that diphenylphosphonimidotriphenylphosphorane exhibits two crystal forms (see below).

When diphenylphosphonimidotriphenylphosphorane was heated in an

evacuated tube at 216-244°C. for 20 hrs. a glass was obtained whose infrared spectral absorptions were in between those of the high and low-melting forms discussed above. However, recrystallization of the glass from isopropyl alcohol-water mixture gave an essentially quantitative recovery of diphenylphosphonimido-triphenylphosphorane melting at 170-171°C.

The general thermal and oxidative stability of the phosphoranes was demonstrated by dropping samples of the materials onto a heated copper block as previously described[5]. Diphenylphosphon-, bis-(p-chlorophenyl)phosphon-, bis-(p-tolyl)phosphon-, and diphenylthiophosphonimidotriphenylphosphorane, and diphenylphosphonimidophenyldimethylphosphorane did not auto-ignite up to the temperature limit of the apparatus which was approximately 450°C. Furthermore, diphenylphosphonimidotriphenylphosphorane would not support combustion; it burned only when in direct contact with a Bunsen flame.

All of the phosphoranes isolated and characterized were found to be hydrolytically stable toward warm, dilute ammonium hydroxide and dilute hydrochloric acid. In addition, the hydrolytic stability of diphenylphosphonimido-triphenylphosphorane was tested under more vigorous conditions. It was found to be stable toward 6N sulfuric acid at 100°C. for 18 hrs. and to be stable toward boiling alcoholic sodium hydroxide for 18 hrs. The combination of excellent hydrolytic, oxidative and thermal stabilities of the diarylphosphonimido-phosphoranes appears to be much better than the most closely related materials containing phosphorus-nitrogen bonds. For example, the preparation of a series of sulfonimidophosphoranes having relatively good thermal stability but having poor hydrolytic stability was reported recently (Eq. 21)[6]. Also benzoimidotri-phenylphosphorane has been reported to undergo a thermal redistribution at 150°C.

$$ArSO_2N_3 + (RO)_3P \longrightarrow ArSO_2N{=}P(OR)_3 + N_2 \qquad (21)$$

(Eq. 22) and phenyliminotriphenylphosphorane is cleaved by hydrochloric acid (Eq. 23)[7].

$$C_6H_5\overset{O}{\overset{\|}{C}}N{=}P(C_6H_5)_3 \xrightarrow{150°C.} C_6H_5CN + (C_6H_5)_3PO \qquad (22)$$

$$C_6H_5N_3 + (C_6H_5)_3P \longrightarrow C_6H_5N{=}P(C_6H_5)_3 \xrightarrow{HCl} C_6H_5NH_2 + (C_6H_5)_3PO \qquad (23)$$

F. Structure and Spectra

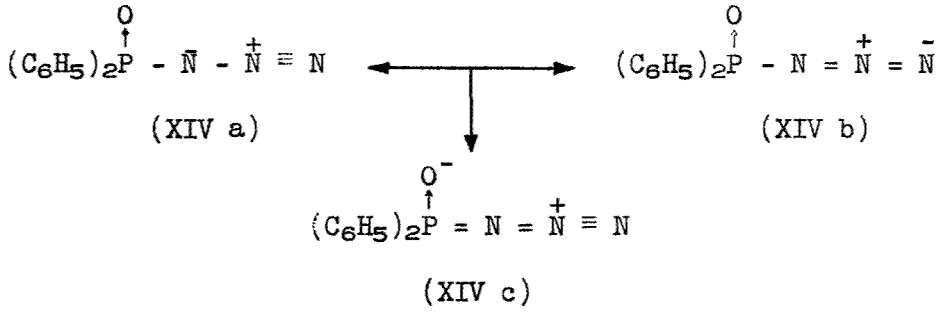
The unusual properties of the diarylphosphonyl azides and diaryl-phosphonimidophosphoranes can be rationalized by considering the resonance forms

5. R. I. Wagner, et al., WADC Technical Report, 57-126, Part I, March 1957, p. 31.

6. J. Goerdler and H. Ullmann, Ber. 94, 1067 (1961).

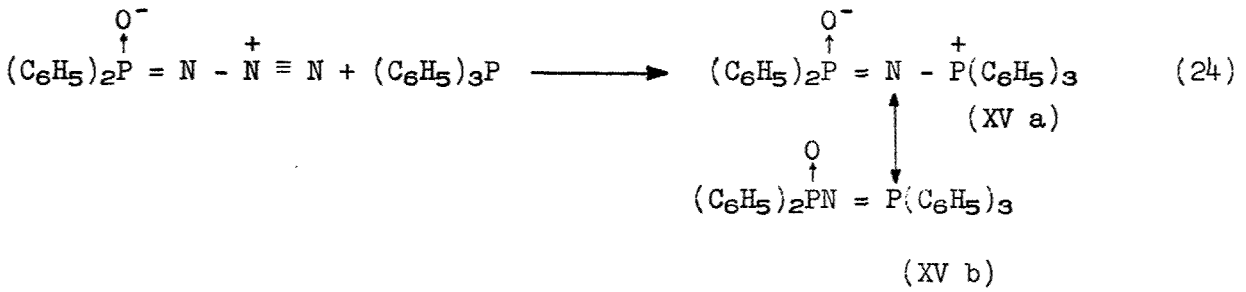
7. N. Staudinger and E. Hauser, Helv. Chim. Acta 4, 861, (1921).

which contribute to the total structure (XIV, a-b).



(XIV a) (XIV b) (XIV c)

Infrared absorptions at 1265 cm^{-1} (P=N) and at 1230 cm^{-1} P → O) suggest that the phosphonyl azides exist primarily as the charge-separated structure, XIV c. Structure XIV c is also suggested by the reaction of the azides with trivalent phosphorus compounds to yield phosphoranes (Eq. 24).



(XV a) (XV b) (24)

There are insufficient data available to draw definite conclusions concerning the nature of the intermediate in the reaction of phosphonyl azides with trivalent phosphorus compounds. By analogy with the sulfonyl azides, it might be argued that a highly reactive triplet state nitrogen would obtain; however, this does not appear to be the case up to temperatures of about 137°C. as evidenced by the lack of reactivity of diphenylphosphonyl azide with benzene and xylene. Under similar conditions, sulfonyl azides react to form sulfonanilides[1,8]. This difference in apparent reactivity may involve stabilization of the intermediate by electron delocalization as shown for XVIa and b so that a higher activation energy would be necessary for reaction. In this connection it



(XVI a) (XVI b)

8. O. C. Dermer and M. T. Edmison, J. Am. Chem. Soc. 77, 70 (1955).

appears that diphenylphosphonyl azide is considerably more stable thermally than benzenesulfonyl azide. The two forms of diphenylphosphonimidotriphenyl phosphorane shown as energetically equivalent (XVa and b) actually would be expected to have different potential energies. It is possible that XVa being a higher energy form is capable of existence provided that the potential energy barrier necessary for conversion to the thermodynamically more stable XVb is not exceeded. This might account for the low melting (150°C.) and high melting forms (170-171°C.) of diphenylphosphonimidotriphenylphosphorane referred to above. It is also possible that diphenylphosphonimidotriphenylphosphorane can exist in two energetically different geometric isomers; models show that there is possible restricted rotation about the phosphorus-nitrogen single bond due to the phenyl groups.

Examination of the infrared spectra of the diarylphosphonyl azides and the diarylphosphonimidophosphoranes shows two absorptions of interest which are common to both classes of compounds. The absorption at about 1180 cm^{-1} in the phosphoranes and at about 1250 cm^{-1} in the phosphonyl azides has been assigned to the P → O absorption. For comparison, triphenylphosphine oxide absorbs at 1190 cm^{-1}.[9] The second absorption of even more interest is that at 1316-1212 cm^{-1} in the phosphoranes and at about 1258 cm^{-1} in the azides. These absorptions have been assigned to a P=N absorption, in accord with similarly assigned absorptions in phosphonitrilic chloride trimer and tetramer[10], in diphenylphosphinic nitride trimer and tetramer, and in the recently reported sulfonimidophosphoranes[6]. The P → O and P=N absorptions for the compounds studied are given in Table I.

The ultraviolet spectra of the phosphonyl azides and phosphoranes have been determined using ethanol or acetonitrile as the solvent. The phosphoranes show greatly enhanced aromatic absorptions at 264-5 and 266-7 mμ (log ε 3.2, 3.5) and at about 224-5 mμ (log ε > 4.5). Diphenylthiophosphonimidotriphenylphosphorane exhibits enhanced aromatic absorptions (log ε 3.7, 3.85) at the same wavelengths as the oxygen analog and triphenylphosphine sulfide also exhibits a similar enhancement of the aromatic absorptions compared to triphenylphosphine oxide. Diphenylphosphonyl azide has an ultraviolet spectrum similar to that of the phosphoranes.

G. Applications

Two interesting applications for the phosphonyl azides and phosphoranes have been briefly investigated. Firstly, the addition of diphenylphosphonimidotriphenylphosphorane to epoxy resins appears to impart useful fire retardant properties and, secondly, if the phosphorane is prepared *in situ* the nitrogen gas liberated effectively acts as a blowing agent for the preparation of epoxy foams.

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9. L. W. Daasch and D. C. Smith, Anal. Chem. 23, 853 (1951).

10. L. W. Daasch, J. Am. Chem. Soc. 76, 3403 (1954).

TABLE I

Infrared Assignments (cm^{-1})

Compound	P → O	P = N
$(C_6H_5)_3PO$	1190	--
$(C_6H_5)_2\overset{O}{\uparrow}P\text{-}N{=}P(C_6H_5)_3$	1167	1316, 1302
$(p\text{-}CH_3C_6H_4)_2\overset{O}{\uparrow}P\text{-}N{=}P(C_6H_5)_3$	1170	1227
$(p\text{-}ClC_6H_4)_2\overset{O}{\uparrow}P\text{-}N{=}P(C_6H_5)_3$	1176	1239
$(C_6H_5)_2\overset{S}{\uparrow}P\text{-}N{=}P(C_6H_5)_3$	--	1230
$(C_6H_5)_2\overset{O}{\uparrow}P\text{-}N{=}P(C_6H_4\text{-}p\text{-}Cl)_3$	1170	1212
$(C_6H_5)_2\overset{O}{\uparrow}P\text{-}N{=}P(C_6H_4\text{-}p\text{-}CH_3)_3$	1176	1266
$(C_6H_5)_2\overset{O}{\uparrow}P\text{-}N{=}P(CH_3)_2C_6H_5$	1170	1250
$(C_6H_5)_2\overset{O}{\uparrow}PN_3$	1229	1263
$(C_6H_5)_2\overset{S}{\uparrow}PN_3$	--	1255
$(p\text{-}Cl\text{-}C_6H_4)_2\overset{O}{\uparrow}PN_3$	1227	1258

POLYMER COMPONENTS INVOLVING PHOSPHORUS(III)

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The stability of the ring $(R_2PBH_2)_3$ trimers relative to the open-chain $(R_2PBH_2)_n$ high-polymers is discussed theoretically in relation to other polymer types. Some stabilization of the trimers by B-H to P_{3d} pi-dative bonding is indicated by infrared spectroscopy but not thereby proved. For stabilization of phosphinoborine high-polymers it seems best to form more cross-linkages, as in resins made by incorporating R_2P units in boron-hydride polymers. Toward the further development of this possibility, new kinds of polyphosphine derivatives have been extensively explored. Some of the new types may be of interest in relation to other kinds of polymers as well.

The strongly bonded multivalence of phosphorus makes it an important connecting atom for polymers; but in its development as a polymer component it has been mostly pentavalent, as in the well-known polyphosphates and polymeric phosphate esters or the $(X_2PN)_n$ system. Utilization of trivalent phosphorus for polymers has been slow, perhaps mostly because most substituted phosphines are very reactive, labile, or unstable substances. However, a more thorough study of phosphorus(III) chemistry has brought forth a variety of new types of combination and may yet offer new paths to thermally stable polymers. Especially, the incorporation of new phosphine bases in boron-hydride networks offers considerable promise but should be investigated much further in detailed variety.

Such a more thorough study requires many new organophosphine derivatives, and accordingly much of our recent work has been turned toward the discovery of novel phosphines and polyphosphines which might be applicable to polymer development. The possible value of these new phosphorus(III) compounds need not be limited to P-B-H resins; for example, the CF_3-phosphines point toward interesting new ways to connect or cross-link fluorocarbon polymer chains, or to vulcanize rubber, or to make $(X_2PN)_n$ polymers in which X is a ring-connecting polyfunctional fluorocarbon or hydrocarbon moiety. Such phosphines even can connect nickel carbonyl units to make a polymer, and may relate even more broadly to coordination polymers of the transition elements. Further relations to polymer chemistry will appear as the properties of the new phosphine types are discussed in more detail. The possible lines of new knowledge in this field are so numerous that this presentation must be regarded only as a start rather than as a mature development.

New Knowledge of Phosphinoborine Polymers

The Stability of $[(CH_3)_2PBH_2]_n$ Polymers. Open-chain polymers of the $(CH_3)_2PBH_2$ unit have been made by using a phosphine base or amine to complete the four-coordination of a chain-ending boron atom; but heat converts such polymers to the very stable trimer $[(CH_3)_2PBH_2]_3$. Various devices may be suggested for preserving the high-polymer chain: one might seek a Lewis acid which would serve to coordinate the chain-ending phosphorus atom without being quite strong enough to remove the base from the other end; or the chain might gain some stability if it were employed as a plasticizer incorporated in an otherwise too brittle but thermally stable resin made from B_5H_9 and a phosphine base; or one might place large hydrocarbon units on the phosphorus atom so that the chair-form $(PB)_3$ ring would be strained by axial-group interference. However, none of these devices would offer much advantage if thermodynamics should fail to confer upon the open-chain polymers any special stability of their own, as it seems to do for the trimer form. Thus a thermodynamic argument is needed to decide whether the instability of the open chains can be overcome.

One factor strongly affecting the stability of simple open-chain polymers is the increase of translational entropy when one large polymer molecule is converted to many small rings such as the trimer. Designating the polymer unit as U, we can define for the breakdown an equilibrium constant $K = (U_3)^n/(U_{3n})$, and $\Delta F = \Delta H - T\Delta S = -RT\ln K$, so that a positive ΔS means a larger value of K, favoring the trimer form. Still smaller molecules would be favored even more by the entropy effect, but they often would represent too great a loss of bond energy, which is part of the term ΔH.

Favorable to the high polymers would be the entropy of their bond bending and rotation, whereby many distinct configurations are possible, in contrast to the relatively fixed structures of small rings. This effect probably does not ever quite compensate for the complete freedom of separate molecules, but its importance must vary greatly from one polymer system to another. In polymer chains with very small polarity between adjacent chain atoms there would be little chain-to-chain attraction, so that the packing of chains would be fairly random and the entropy high; but when the polarity alters from atom to atom down the chain, the packing tends to become fixed and the entropy is far less. A good example is the base-supported chain $(Base^+):(\underset{H_2}{B^-}\!\!-\!\!\underset{Me_2}{N}:)_n$, which rapidly and completely breaks down to the free base, the monomer $(CH_3)_2NBH_2$, and the dimer $[(CH_3)_2NBH_2]_2$. But even this monomer-dimer mixture is metastable relative to the trimer $[(CH_3)_2NBH_2]_3$, even though this has some steric strain because of contact among the axial methyl groups. There must also be some alternating polarity in the $(Base^+):(\underset{H_2}{B^-}\!\!-\!\!\underset{Me_2}{P}:)_n$ chain, although this charge effect is diminished by the larger volume of the phosphorus atom as well as some special electronic effects. In sum, the entropy effect probably is a major reason for the low stability of the long-chain $(CH_3)_2PBH_2$ polymers relative to the trimer.

Another approach toward stabilization of long-chain polymers would be to choose a bonding situation such as to demand bond angles wider than could occur in small rings. Then the high polymer may be actually stabler than small rings of the same unit, if alternation of polarity in the chain can be minimized at the same time. A good example would be the $(CH_3)_2SiO$ (silicone) polymers, in which the normal Si-O-Si bond angle seems to be nearly 145°, while the O-Si-O angle also is definitely wider than the tetrahedral 109.5°. Such wide angles would correlate with the use of two lone electron-pairs on each oxygen for two-way 2p-3d pi-dative bonding to silicon. This supplementary bonding not only widens the chain-bond angles and lends extra strength, but also overcomes much of the alternating polarity in the chain, so that the high-polymer chain can be fairly free to develop the many attitudes leading to high entropy. In the $(X_2PN)_n$ polymers the N-P pi dative bonding is even more obvious, and is especially strong when X is Cl or some more electronegative group. Then the wide P-N-P angles and the minimization of chain polarity mean that small rings actually convert to higher polymers on heating.

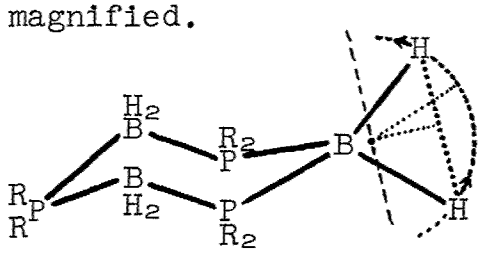
A somewhat similar bond-widening effect seems to be present also in $[(CH_3)_2PBH_2]_3$, for W.C. Hamilton's X-ray study (Acta Cryst. 8, 199 -- 1955) showed the B-P-B angle to be near 118° and the P-B-P angle near 112°. But if there is to be any plan to improve this bond-widening effect, in order to maintain a high-polymer form with no loss of bond-strength, the situation needs to be understood from a theoretical viewpoint, supported by experimental facts.

Spectroscopic Evidence of Structure. The relatively wide bond angles in the $[(CH_3)_2PBH_2]_3$ ring suggest that the B-P bonding includes some B to P pi bonding effect, which would be possible only through some delocalization of the B-H bonding electrons for interaction with the appropriate P_{3d} orbitals. One effect of this would be to widen the H-B-H angle, which Hamilton actually reports as 119.3°— well above the rough prediction of 108°, based upon the normal effect of a 112° P-B-P angle. Another effect would be to improve the P to B sigma dative bonding by partially neutralizing the formal charge, normally written as P^+B^-. A contrary argument, to the effect that both P to B dative bonds on each boron atom would have relatively low electron-density on boron, and so permit the H atoms to turn toward a linear pattern, would fail to account for the high stability of the trimer ring. However, the whole structural hypothesis rests upon the assumption that the H-B-H bond angle really is as wide as reported. A really dependable placement of hydrogen in a molecule having the scattering power contributed by the three nearby P atoms is so difficult that an independent approach to the subject, as by way of infrared spectroscopy, seems necessary.

Toward this purpose we have recorded the infrared spectra of $[(CH_3)_2PBH_2]_3$, $[(CH_3)_2PBD_2]_3$, $[(CF_3)_2PBH_2]_3$, and $[(CF_3)_2PBD_2]_3$ in a definitive manner, with $[(CH_3)_2NBH_2]_3$ for comparison and with some data also for the new trimer $(CH_3CF_3PBH_2)_3$.

Of primary interest in relation to the above theory was the indication that the BH_2 wagging mode increases frequency much more sharply than does the BH_2 rocking mode, with step-wise replacement

of CH_3 by the far more electronegative CF_3 groups. This result may be explained as due to an increase in the H-B-H angle as phosphorus becomes more electronegative. To understand this situation, we must define the BH_2 rocking and wagging vibrations in terms of the following picture of a phosphinoborine trimer with one BH_2 group magnified.



For both the rocking and wagging modes we assume that the BH_2 group retains a fixed shape. Then rocking is an in-plane motion of the pair of H atoms along the dotted circle, while boron performs a small back-lash. Wagging is an out-of-plane motion of the pair of H atoms along a cylindrical surface with the dashed line as the axis, while boron performs a small out-of-plane back-lash. Evidently the radius of gyration will change little with increasing H-B-H angle as far as the rocking mode is concerned, but for wagging the radius of gyration decreases with the cosine of the half-angle, measured at the center of gyration. Now for the same reduced mass, the vibrational frequency increases inversely to the decreasing radius of gyration; hence for a wider H-B-H angle we must expect a higher vibrational frequency for wagging, but little change of rocking frequency.

The actual frequencies for these wagging and rocking modes, as recognized by BH_2-BD_2 comparisons, are shown in the following table.

Trimer of	$(CH_3)_2PBH_2$	$(CH_3)_2PBD_2$	$CH_3CF_3PBH_2$	$(CF_3)_2PBH_2$	$(CF_3)_2PBD_2$
Wagging	810 w	603 ms	903 ms	995 mw	755 w
Rocking	665 mw	515 w	695 m	711 ms	535 w

Thus the results agree with the qualitative predictions from the theory, which needs to be developed in a more nearly quantitative manner if it is to be tested rigorously by reference to the observed frequencies. It is apparent that the H-B-H angle is widened by making phosphorus more electronegative, but the exact meaning of this effect can be judged only through rigorous and very difficult wave-mechanical calculations. It does seem that the trifluoromethyl compound $[(CF_3)_2PBH_2]_3$ is far stabler than it could be if there were no B-H to P_{3d} interaction, but the indicated increase in this effect, relative to $[(CH_3)_2PBH_2]_3$, is not enough to compensate for the weaker P-B sigma bonding by the more electronegative phosphorus atom. Then the main problem is still with us: how to improve the action of the P_{3d} orbitals toward linearizing the polymer bonding, without at the same time weakening the whole bonding pattern.

In the meantime, the phosphino-polyborane resins seem well worthy of further development. The possible pattern of invention of such resins is considerably broadened by the discovery of new areas of polyphosphine chemistry, as next described.

Polyphosphine Chains and Rings

Polyphosphines based upon P-P bonding have been very rare and little understood; yet their study is important not only on account

of their possible utility for making thermally stable phosphorus-polyborane resins, but also because they raise significant questions concerning the theory of polymer bonding. For example, the slightly volatile ring compounds $(CF_3P)_4$ and $(CF_3P)_5$, although interconvertible by a catalyst such as trimethylphosphine, are thermodynamically stabler than any other $(CF_3P)_n$ polymers; nevertheless these rings are easily opened by alcoholysis reactions to form the far less stable open-chain $H(CF_3P)_mH$ polyphosphines, along with less-studied alkoxy-polyphosphines of the types $H(CF_3P)_mOR$ and $RO(CF_3P)_mOR$. The initial reaction evidently forms $H(CF_3P)_nOR$; and then a second P-P bond cleavage occurs almost at random, forming polyphosphines and alkoxy-polyphosphines with m varying from 1 to n - 1. The dihydrogen polyphosphines decompose most easily when the P_m chain is longest, according to the general equation $H(CF_3P)_mH \rightarrow \frac{1}{n}(CF_3P)_n + H(CF_3P)_{m-1}H$, arriving finally at a mixture of $(CF_3P)_4$, $(CF_3P)_5$, and CF_3PH_2.

Other chain polyphosphines can be built up by reactions such as $CF_3PH_2 + 2(CF_3)_2PI + (CH_3)_3N \rightarrow 2(CH_3)_3NHI + P_3(CF_3)_5$. Again the stability decreases sharply with increasing chain length. Thus the decomposition $P_2(CF_3)_4 \rightarrow \frac{1}{n}(CF_3P)_n + (CF_3)_3P$ requires heating above 300°C., whereas the process $P_3(CF_3)_5 \rightarrow \frac{1}{n}(CF_3P)_n + P_2(CF_3)_4$ can be observed at room temperature.

The evident metastability of these open-chain polyphosphines can be ascribed to the greater stability of the $(CF_3P)_n$ rings. To explain that, one must consider several contributing causes. First is the increased entropy as the open-chain polyphosphines decompose to form a larger number of molecules: the general process $nH(CF_3P)_mH \rightarrow nCF_3PH_2 + (m-1)(CF_3P)_n$ increases the translational entropy in accord with m - 1 more molecules per n moles of the chain polyphosphine. However, the entropy of bond rotation and bending in the open chains is higher than in the relatively fixed ring structures, so that the net increase of entropy in the conversion to the monophosphine and the ring compounds is less than the increase of translational entropy alone.

Another cause of the special stability of ring polyphosphines is the behavior of the lone-pair electrons on phosphorus. In any -P̈-P̈- bonding situation we must expect a delocalization of these lone pairs through interaction with the nearest P3d orbitals. In a chain, this effect gives less supplementary bond energy for the end phosphorus atoms than for those in the middle; and in a ring the delocalization contributes the most bond energy per phosphorus atom. But then in $(CF_3P)_4$ and $(CF_3P)_5$ there is still another effect: a bonding action by the lone-pair electrons reaching across the ring. This effect is strong enough to distort the P_4 ring from the expected square form into a bisphenoid pattern, with P-P-P bond angles of 84.7° instead of 90° (Donohue and Palenik, Acta Cryst., in press); and the P_5 ring has a similar twist in its pattern. All of the factors here cited—entropy and two kinds of P_{3p}-P_{3d} bonding, serve to make $(CF_3P)_4$ and $(CF_3P)_5$ not only stabler than open chains, but also stabler than the higher $(CF_3P)_n$ ring compounds.

For all their stability, however, $(CF_3P)_4$ and $(CF_3P)_5$ can be

depolymerized quite easily by reaction with trimethylphosphine, to make the monomer-complex $(CH_3)_3P\text{-}PCF_3$. Here we recognize that the sigma-dative P-P bond is supplemented by pi-dative bonding in the opposite direction, by the two lone-pairs on the PCF_3 group; however, there could be no such pi-bonding in the similarly stable complex $(CH_3)_3N\text{-}PCF_3$. Both of these monomer-complexes can be dissociated in vacuo, with recovery of the tertiary bases and an equilibrium mixture of $(CF_3P)_4$ and $(CF_3P)_5$. Thus a base catalyzes the interconversion of these ring polymers; and the same effect accounts for the base-catalysis of the decomposition of the open-chain polyphosphines. It is also interesting that the dissociation of the PCF_3 complexes makes this unit available for many chemical reactions which would be far harder to perform by the direct use of the $(CF_3P)_n$ ring compounds.

Hydrocarbon-Fluorocarbon Phosphines

It is well established that hydrocarbon substituents on P in phosphines greatly enhance the base strength of phosphorus, whereas fluorocarbon groups have the opposite effect, actually causing the phosphorus to behave as an electron-acceptor (Lewis acid) in some compounds. The resulting extreme chemical differences between the $(CH_3)_2P$ and $(CF_3)_2P$ groups make it important to know more about the chemistry of the intermediate CH_3CF_3P group. Another reason for developing syntheses of CH_3CF_3P compounds is for comparison of methyl with trifluoromethyl in regard to ease of P-C bond cleavage. If the present indications are borne out— to the effect that it is much easier to remove CF_3 than CH_3 from its bond to phosphorus— we may expect that the projected hydrocarbon-connected double phosphine $CH_3CF_3PC_2H_4PCH_3CF_3$ could be brought to reaction with B_5H_9 to make phosphino-polyborane resins from which HCF_3 could be driven out by heat. Thus as the temperature is raised the cross-linking must increase, tending to maintain the mechanical properties of the resin during the rise of temperature. If all of the CF_3 groups were taken off, the final bonding unit would be $CH_3PC_2H_4PCH_3$, which should give resins having mechanical strength quite superior to that of resins incorporating only $(CH_3)_2P$ groups in the boron-hydride polymer.

Synthesis of CH_3CF_3-Phosphines. Fair yields of CH_3CF_3PI can be obtained by the addition of methyl iodide to $(CF_3P)_4$ at 150°C. (a process requiring critical control of time and temperature) or by the action of iodine on $CH_3P(CF_3)_2$ at 200°C. Or one can attach methyl iodide to the monomer-complex $(CH_3)_3P\text{-}PCF_3$ and treat the solid product with HCl to make a mixture which dimethylamine converts to the aminophosphine $(CH_3)_2NPCH_3CF_3$. From this it is easy to make a CH_3CF_3P-halide by reaction with the hydrogen halide.

The phosphine CH_3CF_3PH can be made in reasonable yields by the process $2CH_3PH_2 + CF_3I \rightarrow CH_3PH_3I + CH_3CF_3PH$, during two weeks at -78°C.; or one can use PH_3 to displace iodine from CH_3CF_3PI, for a very efficient conversion to CH_3CF_3PH. This use of phosphine is closely related to our synthesis of a new diphosphine and a new triphosphine, as described in the following section.

For the diphosphine $CH_3CF_3P\text{-}PCH_3CF_3$ a number of procedures are effective, but the most unusual is the action of HCl on the adduct

$(CH_3)_3P \cdot PCF_3 \cdot CH_3I$ in liquid sulfur dioxide. The production of the $R_2P\text{-}PR_2$ type of compound here must be accompanied by the oxidation of some other component of the mixture, but at present writing it is difficult to conjecture what the oxidation product may be.

The Reaction of $(CF_3)_2PI$ with CH_3PH_2. The reaction $(CF_3)_2PI + 2CH_3PH_2 \rightarrow CH_3PH_3I + CH_3HP\text{-}P(CF_3)_2$ was nearly quantitative at -78°C. The resulting new diphosphine (b.p. est. 92°C.) was decomposed by light or heat, quantitatively forming $(CF_3)_2PH$ and viscous oily material which might have included $(CH_3P)_n$ polymers.

The reaction of $CH_3HP\text{-}P(CF_3)_2$ with more $(CF_3)_2PI$ and $(CH_3)_3N$ gave a very high yield of the new triphosphine $CH_3P[P(CF_3)_2]_2$ (b.p. est. 136°C.), which proved to be stable on heating to 74°C. but decomposed completely during 20 hours at 160°C.

Both the diphosphine and the triphosphine showed ultraviolet absorption, with wide, flat peaks near 2200 Å. and very shallow minima at 2025 and 2100 Å.— results suggesting a complex pattern of lone-pair electronic delocalizations from two different phosphorus-atom situations in each compound. The potential for further syntheses from these new polyphosphines has not been much explored.

Hydrocarbon-Connected Polyphosphines. Diphosphines of the type $R_2P\text{-}PR_2$ have the pseudohalogen property of adding into carbon-carbon pi bonds, more easily when the R groups are more electronegative. For example, $(CF_3)_2P\text{-}P(CF_3)_2$ reacts with $H_2C{=}CH_2$ at room temperature to give 95% yields of $(CF_3)_2PC_2H_4P(CF_3)_2$ (b.p. est. 135°C.), whereas the similar action of $(CH_3)_2P\text{-}P(CH_3)_2$ to give high yields of the bis-phosphine $(CH_3)_2PC_2H_4P(CH_3)_2$ (b.p. est. 188°C.) requires heating nearly to 300°C. In both cases there are minor side reactions; for example the $C_2H_4\text{-}P_2(CF_3)_4$ reaction at 65°C. gives a 1.5% yield of $(CF_3)_3P$, showing that there is some cleavage and new connections of $P\text{-}CF_3$ bonds.

The addition of $P_2(CF_3)_4$ to C_2F_4 is less spontaneous, but can be promoted by a catalytic trace of iodine. However, one effect of iodine is to form C-I bonds, which add across the $F_2C{=}CF_2$ pi bond, so that larger fluorocarbon units are formed. Thus after a 34-hour heating at 165°C., nearly 14% of the consumed C_2F_4 had been converted to cyclo-C_4F_8; and twice as much had gone to form the heterocyclic phosphine $CF_3PC_4F_8$. Even so, the yield of $(CF_3)_2PC_2F_4P(CF_3)_2$ (b.p. est. 127°C.) represented nearly 60% of the consumed $P_2(CF_3)_4$, about 8% of which went to form $(CF_3)_3P$. The non-volatile by-products were assumed to be polymeric.

The reaction of $P_2(CF_3)_4$ with acetylene also required catalysis by iodine, and gave a still wider variety of by-products arising from the cleavage of $P\text{-}CF_3$ bonds. The nearly equimolar mixture was heated with a trace of iodine for 67 hours at 100°C., giving a 57% yield of $(CF_3)_2PC_2H_2P(CF_3)_2$, 7% $(CF_3)_3P$, 3% $(CF_3)_2PC_2H_2CF_3$, 6% of the tris-phosphine $CF_3P[C_2H_2P(CF_3)_2]_2$, and smaller yields of polyphosphines slightly less volatile than this last. A non-volatile oil probably represented a polymer-chain principle. The new bis-phosphine $(CF_3)_2PC_2H_2P(CF_3)_2$ proved to have a trans configuration, probably because the cis form would be sterically unfavorable; and steric

interference also may be the chief reason that this double tertiary phosphine cannot receive another $P_2(CF_3)_4$ into the remaining pi bond.

Yet another bis-phosphine was made by the fairly easy reaction $2(CF_3)_2PCl + C_2H_2 + 2(CH_3)_3N \rightarrow 2(CH_3)_3NHCl + (CF_3)_2P\text{-}C{\equiv}C\text{-}P(CF_3)_2$. This also failed to add $P_2(CF_3)_4$ to the carbon-carbon pi bonds.

Hydroboration of These Polyphosphines. Of the above hydrocarbon-connected polyphosphines, those having C-C pi bonds all reacted with diborane at room temperature or even lower, adding one BH_3 to each such pi bond. Thus the compound $(CF_3)_2PC_2H_2P(CF_3)_2$ formed the RBH_2 type $(CF_3)_2P\text{-}\underset{H\ BH_2}{\overset{H\ H}{C\text{-}C}}\text{-}P(CF_3)_2$, having an infrared spectrum and average molecular weight indicating two forms: the bridged dimer $\begin{matrix} H & & H & & H \\ R & B & H & B & R \end{matrix}$ and a monomer having a P-B dative-bonded four-atom ring. Similarly, $(CF_3)_2P\text{-}C{\equiv}C\text{-}P(CF_3)_2$ added two BH_3 groups to make an $R(BH_2)_2$ type, with some uncertainty whether both boron atoms went to the same carbon atom. Also, $CF_3P[C_2H_2P(CF_3)_2]_2$ formed an $R(BH_2)_2$ type with a considerable variety of possible structures.

These hydroboration reactions show the possibility of using C-C pi-bonded polyphosphines for making phosphorus-polyborane resins in which the phosphine-base units not only would be incorporated in the boron hydride polymer, but also would be connected by C_2H_n units acting at the same time as substituents for hydrogen on boron. For best results, however, it might be well to develop polyphosphines of this type with CH_3 groups instead of CF_3. The resulting resins then should have at least as much resistance to elevated temperatures as the monophosphine-polyborane resins, but far better mechanical strength.

Oxyphosphines

Possible Polymers. It is interesting to consider high-polymer chains in which trivalent phosphorus alternates with oxygen, not only because they would belong to a new polymer system which would be useful for testing theories of the stability of long open chains, but also because the phosphorus lone-pair electrons could attach oxidizing groups to make useful new polymers of pentavalent phosphorus. For stability, however, the $\text{--O-}\underset{R}{\overset{}{P}}\text{-O-}\underset{R}{\overset{}{P}}\text{--}$ chains probably must have just the right R groups on phosphorus. For example, our new compound $(CF_3)_2POP(CF_3)_2$ proved to be quite stable, whereas all attempts to make the corresponding methyl derivative $(CH_3)_2POP(CH_3)_2$ led only to equimolar yields of $(CH_3)_2P\text{-}P(CH_3)_2$ and $(CH_3)_2\underset{O}{P}\text{-}\underset{O}{P}(CH_3)_2$. In order to understand this result we may suppose that tetramethyldiphosphoxane would easily rearrange in the Arbuzov manner $R_2POR' \rightarrow R_2R'PO$, with one $P(CH_3)_2$ group playing the role of R', for P-P bonding to $(CH_3)_2PO$. Then the resulting diphosphine monoxide $(CH_3)_2\underset{O}{P}\text{-}P(CH_3)_2$ would very rapidly disproportionate by exchanging a $(CH_3)_2PO$ group for $(CH_3)_2P$ to give the observed result. The initial rearrangement to the diphosphine monoxide would be far more difficult in the case of $(CF_3)_2POP(CF_3)_2$ because here phosphorus lacks the base strength to bond a $(CF_3)_2P^+$ group effectively, and the P-O-P bonding should be

greatly strengthened by O_{2p}-P_{3d} pi bonding. For similar reasons, the $(CF_3PO)_n$ polymers might well be stable (with a preference for long chains and wide bond angles), whereas the analogous $(CH_3PO)_n$ polymers might not exist at all. Actually, a polymer-bonding of CF_3PO units does seem to exist, according to results obtained in the following study of acetoxyphosphines

The Acetoxyphosphine Approach. It was considered probable that $(CF_3PO)_n$ polymers would be formed by loss of Ac_2O from a compound of the type $CF_3P(OAc)_2$. For the preliminary exploration of this kind of chemistry, the new compound $(CF_3)_2POOCCF_3$ (I) was made from $AgCO_2CF_3$ and $(CF_3)_2PI$. Its dissociation to $(CF_3)_2POP(CF_3)_2$ (II) and $(CF_3CO)_2O$ (III) proved to be fairly fast at room temperature, but limited in extent. An infrared spectroscopic study gave a rough estimate of the dissociation constant as $K = [II][III]/[I]^2 = 0.11$. The acetoxyphosphine (I) proved to be a readily volatile liquid, but its dissociation was too rapid to permit accurate characterization. Attempts to make the diacetoxyphosphine $CF_3P(OOCCF_3)_2$ from $AgCO_2CF_3$ and CF_3PI_2 gave the anhydride $(CF_3CO)_2O$ as the only volatile product. It seemed probable that a $(CF_3PO)_n$ polymer was mixed with the silver iodide, and could not have disproportionated without forming the volatile compounds $(CF_3P)_4$ and $(CF_3P)_5$.

Next it was argued that the acetoxyphosphine $(CF_3)_2POOCCH_3$ would be stabler than the corresponding trifluoroacetoxyphosphine, for a less electronegative oxygen in the C-O-P bond would form a stronger $O_{2p}P_{3d}$ pi bond, while other differences would cancel out. Accordingly, $(CF_3)_2PI$ was allowed to react with $AgCO_2CH_3$ to make $(CF_3)_2POOCCH_3$, which proved to be entirely stable and not difficult to characterize: m.p. -58°C.; b.p. est. 96°C.

The analogous reaction of CF_3PCl_2 with $AgCO_2CH_3$ produced a major yield of acetic anhydride, along with nearly one-third of the calculated yield of a slightly volatile liquid purporting to be the desired diacetoxyphosphine $CF_3P(OOCCH_3)_2$. On standing, this formed more acetic anhydride and a non-volatile white solid. This most probably was a diacetoxy-polyphosphoxane embodying a short $(CF_3PO)_n$ chain with acetoxy- end groups. It showed no tendency toward a disproportionation into $(CF_3P)_n$ rings and $(CF_3PO_2)_n$ polymers, but on long standing it did form a red-brown gum in which the CF_3 groups seemed to exist in a wide variety of environments, leading to wide bands in the infrared spectrum. Thus the conversion of the presumed diacetoxy-polyphosphoxane to a simple open-chain high polymer may be very difficult.

Acknowledgements

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π-BONDING IN INORGANIC SYSTEMS

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ABSTRACT

Evidence from nuclear magnetic resonance studies for π-bonding between boron and nitrogen in the borazens is presented. Preliminary experiments, by infrared spectroscopy, which indicate that a similar situation might exist between phosphorus (III) and nitrogen, in open chain compounds, are also reported.

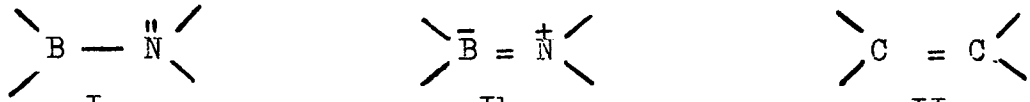
The energy barrier to rotation about the BN bond in dimethylaminophenylchloroborane is calculated (from four different observations on the N.M.R. spectra) as 18 ± 2 kcals.

Exploratory measurements on certain boron-oxygen compounds are also presented.

INTRODUCTION

It has been suggested that the search for monomers, suitable as intermediates in the synthesis of inorganic polymers, might well be pursued among those inorganic compounds in which a high degree of π-bonding occurs.

The borazens, (I), i.e. open-chain compounds in which both boron and nitrogen are three co-ordinate, are isoelectronic and isosteric with the corresponding olefins, (II). This point is particularly emphasized by the canonical form (Ib).

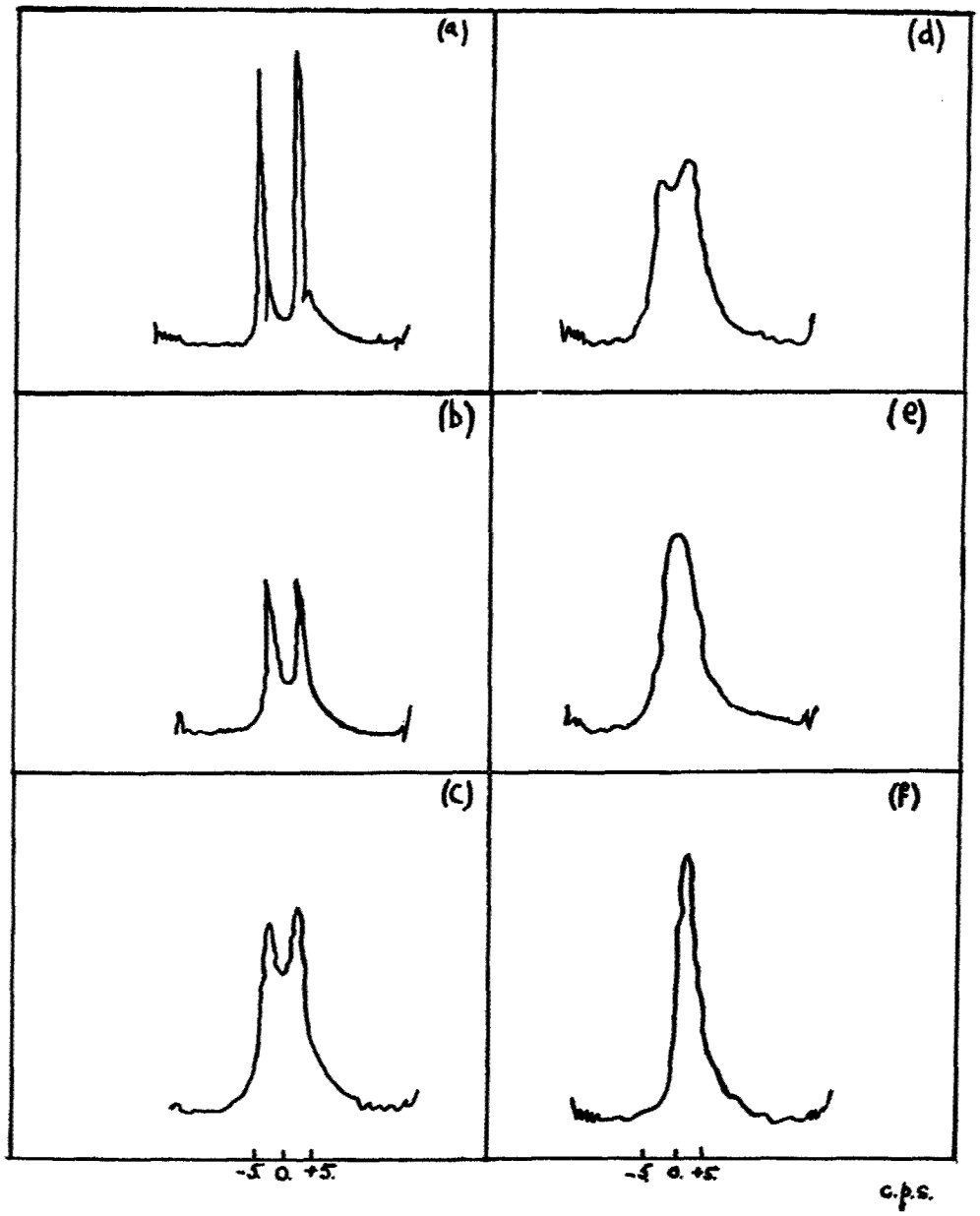


Ia Ib II

Much circumstantial experimental evidence for the occurence of π-bonding in the borazens is available (see ref.1. and references cited therein) and it seemed likely that more direct evidence for the phenomenon could be obtained from nuclear magnetic resonance data and especially from studies on energy barriers to rotation.

Results of ^{1}H nuclear magnetic resonance experiments on methylphenylaminodimethylborane,[2] $C_6H_5NCH_3B(CH_3)_2$, and phenyldimethylaminochloroborane,[3] $C_6H_5BClN(CH_3)_2$, have been

DIAGRAM 1



^1H SPECTRA OF PHENYLDIMETHYLAMINOCHLOROBORANE AT SEVERAL TEMPERATURES (a) 23°, (b) 93°, (c) 103°, (d) 109°, (e) 118°, (f) 137°.

SPECTRA WERE RECORDED AT 40 Mc/Sec., ABSORPTION OCCURED AT γ 2.72

published. These results confirm that a high barrier to rotation (estimated at 15 ± 3 kcals in the former and 18 ± 2 kcals in the latter) exists between boron and nitrogen and we[3] have shown in a preliminary way, by comparing $PhB(Cl)NMe_2$ and $PhB(NMe_2)_2$, that the high barrier in the former is essentially due to π-bonding and not to steric considerations. Our evidence will be elaborated upon in this paper.

DISCUSSION

1. THE BORON-NITROGEN SYSTEM

In the borazens a "partial" double bond, due to delocalisation of p_π-type nitrogen electrons into a vacant p_π-type boron orbital, is to be expected.

The ^1H nuclear magnetic resonance spectrum of the compound phenyldimethylaminochloroborane, $C_6H_5BClNMe_2$ (I), examined at 40 Mc/sec, showed a doublet at $\tau \simeq 7{\cdot}2$ (fig. 1a.) attributed to methyl absorption, the occurence of a doublet being consistent with the presence of two sets of protons in chemically-different and equally-abundant environments (cis- or trans- to the phenyl group). At progressively higher temperatures band broadening and decrease of maxima separation were observed (fig. 1b - 1d.), and at about 118° the doublet structure collapsed into a single broad band. At still higher temperatures the single band became increasingly narrow (fig. 1e, 1f.). The association of this kind of spectral behaviour with variable isomeric interconversion is well-established.[4]

From observations on the recorded spectra, a value of 18 ± 2 kcals has been calculated for the energy barrier to rotation about the BN bond.

The ^1H nuclear magnetic resonance spectrum of bis-(N,N-dimethylamino)phenylborane, $C_6H_5B(NMe_2)_2$, (II), showed no splitting of the methyl absorption at room temperature and this is taken to indicate that the energy barrier to rotation about the BN bond in this compound is rather low, probably less than 10 kcals. Similar observations were also made on bis(N-methylamino)phenylborane, $C_6H_5B(NHMe)_2$, (III).

Steric effects with respect to rotation about the BN bond would undoubtedly be greater in compound (II) (and III) than in (I). The presence of a lower barrier in (II), where back donation from two nitrogen atoms can occur, proves that the restriction to rotation in (I), where the boron atom is linked to a single nitrogen, must be due to electronic effects (i.e. π-bonding) rather than to steric factors. Furthermore these

TABLE 1.

Compound	B.p. °C/mm.	n_D^{20}	Method of Synthesis	Ref.
I. $PhBClNMe_2$	75/2	1·53202	$PhBCl_2 + Me_2NH \xrightarrow{Et_3N} PhBClNMe_2 + Et_3N.HCl$	10
II. $PhB(NMe_2)_2$	60/0·4	1·51684	$PhBCl_2 + 4Me_2NH \xrightarrow{-78^\circ} PhB(NMe_2)_2 + 2Me_2NH.HCl$	-
III. $PhB(NHMe)_2$	86/3	1·52902	$PhBCl_2 + 4MeNH_2 \xrightarrow{-78^\circ} PhB(NHMe)_2 + 2MeNH_2.HCl$	-
IV. Ph.BClNMePh	102/0·2	1·58774	$PhBCl_2 + PhNMeH \xrightarrow{Et_3N} PhBClNMePh + Et_3N.HCl$	10
V. $PhBClNMe^iPr$	90/2	1·51932	$PhBCl_2 + MeNH^iPr \xrightarrow{Et_3N} PhBClNMe^iPr + Et_3N.HCl$	-
VI. PhBClNMeEt	82/~~0·2~~	1·52844	$PhBCl_2 + MeNHEt \xrightarrow{Et_3N} PhBClNMeEt + Et_3N.HCl$	-
VII. $PhBBrNMe_2$*	63/0·8		$PhBBr_2 + PhB(NMe_2)_2 \rightarrow 2PhBBrNMe_2$.	-
VIII. $PhBFNMe_2$*	62/3	1·50581	$3PhBClNMe_2 + SbF_3 \rightarrow 3PhBFNMe_2 + SbCl_3$.	-
IX. PhBClOMe*	57/5	1·51110	$PhBCl_2 + PhB(OMe)_2 \rightarrow 2PhBClOMe$	11
X. $PhB(OMe)_2$	46/3	1·49599	$PhBCl_2 + 2MeOH \xrightarrow{0^\circ} PhB(OMe)_2 + 2HCl$	11
XI. $PhPClNMe_2$	80/0·1	1·57530	$PhPCl_2 + Me_2NH \xrightarrow{Et_3N} PhPClNMe_2 + Et_3N.HCl$	-
XII. $PhP(NMe_2)_2$	58/0·1	1·54791	$PhPCl_2 + 4Me_2NH \rightarrow PhP(NMe_2)_2 + 2Me_2NH.HCl$	-

* Not yet completely analysed.

results show that cis/trans isomerism due to restricted rotation about inorganic atomic pairs, can be extended beyond the only hitherto established case of - N = N - .

Further investigations into the borazen system have been based upon the compounds IV - VIII (Table 1). The spectrum of compound IV, methylphenylaminophenylchloroborane, $C_6H_5BCl(CH_3NC_6H_5)$, showed no splitting of the methyl resonance in the range 25 - 200°, and this may be due to a high barrier to rotation about the BN bond, mainly for steric reasons, and a steric preference for the less hindered isomer. Likewise, aryl-substituted amides (e.g. N-methylacetanilide) show a single methyl resonance whereas N,N-dimethylamides show a doublet, and it has been suggested[5] that at least 10% of the less-favoured isomer is required to give a recognisable signal. Chemical and spectroscopic evidence for steric hindrance in the borazens, particularly in the N-aryl derivatives, is available.[1]

The spectra of the remaining compounds have only recently been recorded.

2. THE BORON-OXYGEN SYSTEM

Thermochemical[6a] and spectroscopic[1,6b] evidence shows that although a B-O bond has some double bond character, the ability to form π-bonds with boron is greater for nitrogen than oxygen.

In order to investigate this further we have synthesised samples of the esters chloromethoxyphenylborane, $C_6H_5BCl(OMe)$, (IX), and dimethoxyphenylborane, $C_6H_5B(OMe)_2$, (X).

The ^1H nuclear magnetic resonance spectrum of these compounds recorded at 60 Mc/sec (room temperature) reveals, in both cases, a broad low field signal characteristic of the phenyl group, together with a single line at somewhat higher field which is attributable to the methyl group resonance.

This section of the work is being continued.

3. THE PHOSPHORUS(III)-NITROGEN SYSTEM

π-Bonding in the phosphorus nitrogen bond has been invoked in the discussion of a PN compound and its suggested pseudoaromaticity.[7] Spectroscopic investigations into the three co-ordinate phosphorus nitrogen system have therefore been undertaken.

The infrared spectrum of N,N-dimethyl-P-phenylphosphonamidous chloride, $C_6H_5PClNMe_2$, (XI), shows a medium band in the 1600 $cm.^{-1}$ region, characteristic of monosubstituted aromatic compounds. This is accompanied by another band at approximately 20 $cm.^{-1}$ lower and this may be due to the presence of an

unsaturated side chain which allows extended conjugation with the aromatic ring. Similar features have been observed in the spectra of borazens.[1] It is significant that the low intensity band is absent in N,N,N',N'-tetramethyl-P-phenylphosphonous diamide, $C_6H_5P(NMe_2)_2$, (XII), where the extent of π-bonding would be expected to be reduced.

The ^1H nuclear magnetic resonance spectra of these compounds recorded at 60 Mc/sec, are both characterised by a broad low field band, attributed to phenyl group resonance, and a doublet at higher field. This doublet was shown to arise from spin-spin interaction between the phosphorus and hydrogen nuclei by measurements at 25 Mc/sec.

SYNTHESIS OF MODEL COMPOUNDS

The compounds which have been prepared for use in these investigations, are listed in Table 1. Methods used for their synthesis are also indicated in the Table.

All the compounds, except for the dimethylaminohalogenophenylboranes, (VII) - (IX), were fully characterised by elemental analyses.

PHYSICAL MEASUREMENTS

Infrared spectra were recorded on a Perkin Elmer Model 21 (Sodium Chloride optics) and on a P.E.Model K14 (potassium bromide optics). Samples were studied as pure materials. Compounds (I) - (VIII) were each characterised by having a strong absorption band in the range 1450 ± 100 $cm.^{-1}$, which may be attributed to the BN stretching frequency.[1] Comparison of the spectra of the phosphorus compounds (XI) and (XII) with their boron analogues (I) and (II) confirms this assignment and moreover reveals that the PN stretching vibrations fall at 986 $cm.^{-1}$ for $PhPClNMe_2$ and at 971 $cm.^{-1}$ (asymmetric) and 957 $cm.^{-1}$ (symmetric) for $PhP(NMe_2)_2$.

Nuclear magnetic resonance spectra were recorded on a Varian Associates Model V4300B equipped with variable temperature probe or on an A.E.I. RS2 spectrometer. Spectra were recorded at 60, 40, and 25 Mc/sec.

Mathematical calculations were carried out on the Ferranti Mercury computer in the Department of Electrical Engineering, University of Manchester.

RESULTS AND

Mathematical Approach to the Calculation of Barriers to Internal Rotation.

A quantitative treatment for the study of internal rotation in molecules by nuclear magnetic resonance has been developed, by suitable modification of the Bloch equations to take into account exchange between two equally abundant sites with equal transverse relaxation times (T_2). The most general treatment is that of McConnell[8], who has shown that the total r.f. magnetisation in such a system is given by

$$G = \frac{iw_1 M_z \tau \left\{ 2 + \left[{}^1/T_2 - i(\Delta w_A + \Delta w_B)/2 \right] \tau \right\}}{\tau^2 ({}^1/\tau_2 - i\Delta w_A)({}^1/\tau_2 - i\Delta w_B) - 1.}$$

where M_z = total magnetisation

T_2 = Transverse Relaxation Time (assumed equal for the two environments)

τ = Mean lifetimes of environments A and B

${}^1/\tau_2 = {}^1/T_2 + {}^1/\tau$

$\Delta w_A = \Delta w_{OA} - w.$

w_{OA} = Larmor Precession angular velocity of nuclei in environment A in the STATIC field only.

w = Angular velocity of the rotating magnetic field, H_1.

$w_1 = \gamma H_1$

γ = Magnetogyric Ratio

If the internal chemical shift $w_{OA} - w_{OB} = \delta w$, and the separation of the angular velocity, w, from the mean shift $\frac{w_{OA} - w_{OB}}{2} - w = \Delta w$

Then:

$$\Delta w_A + \Delta w_B = 2\,\Delta w.$$
$$\Delta w_A - \Delta w_B = \delta w$$
$$\Delta w_A = \Delta w + \delta w/2.$$
$$\Delta w_B = \Delta w - \delta w/2.$$

and $$G = \frac{iw_1 M_z \tau \left(2 + \tau/T_2 - i\Delta w \tau\right)}{\left[1 + \tau\left(1/T_2 - i\Delta w - i\delta w/2\right)\right]\left[1 + \tau\left(1/T_2 - i\Delta w + i\delta w/2\right)\right] - 1.}$$

An expression for the out of phase component of the r.f. magnetisation ν, which is proportional to the intensity of absorption, can be obtained from the imaginary part of this expression for G.

$$\nu = \frac{w_1 M_z \left[\left(1 + \tau/2T_2\right)P + \tau/2(\Delta w)^2\left(1 + \tau/T_2\right)\right]}{P^2 + (\Delta w)^2 (1 + \tau/T_2)^2.}$$

$$P = \tau/2\left[\left(1/T_2{}^2\right) - \Delta w^2 + \left(\delta w/2\right)^2\right] + 1/T_2$$

Differentiation of this expression to obtain extreme values of ν, yields a fifth order equation in $(\Delta w)^5$

$$\frac{\tau^4}{T_2}(\Delta w)^5 + 8\tau^2 S\left(1 + \frac{\tau}{2T_2}\right)(\Delta w)^3 + 16\left[\left(1 + \frac{\tau}{2T_2}\right)^2 1 + \frac{2}{T_2} - \frac{\tau S}{2}\left(2 + \frac{3\tau}{2T_2}\right)\right] S\,\Delta w = 0$$

$$S = 1/T_2 + \tau/2T_2{}^2 + \tau/2\left(\delta w/2\right)^2$$

The solutions to this equation are at $\Delta w = 0$, or

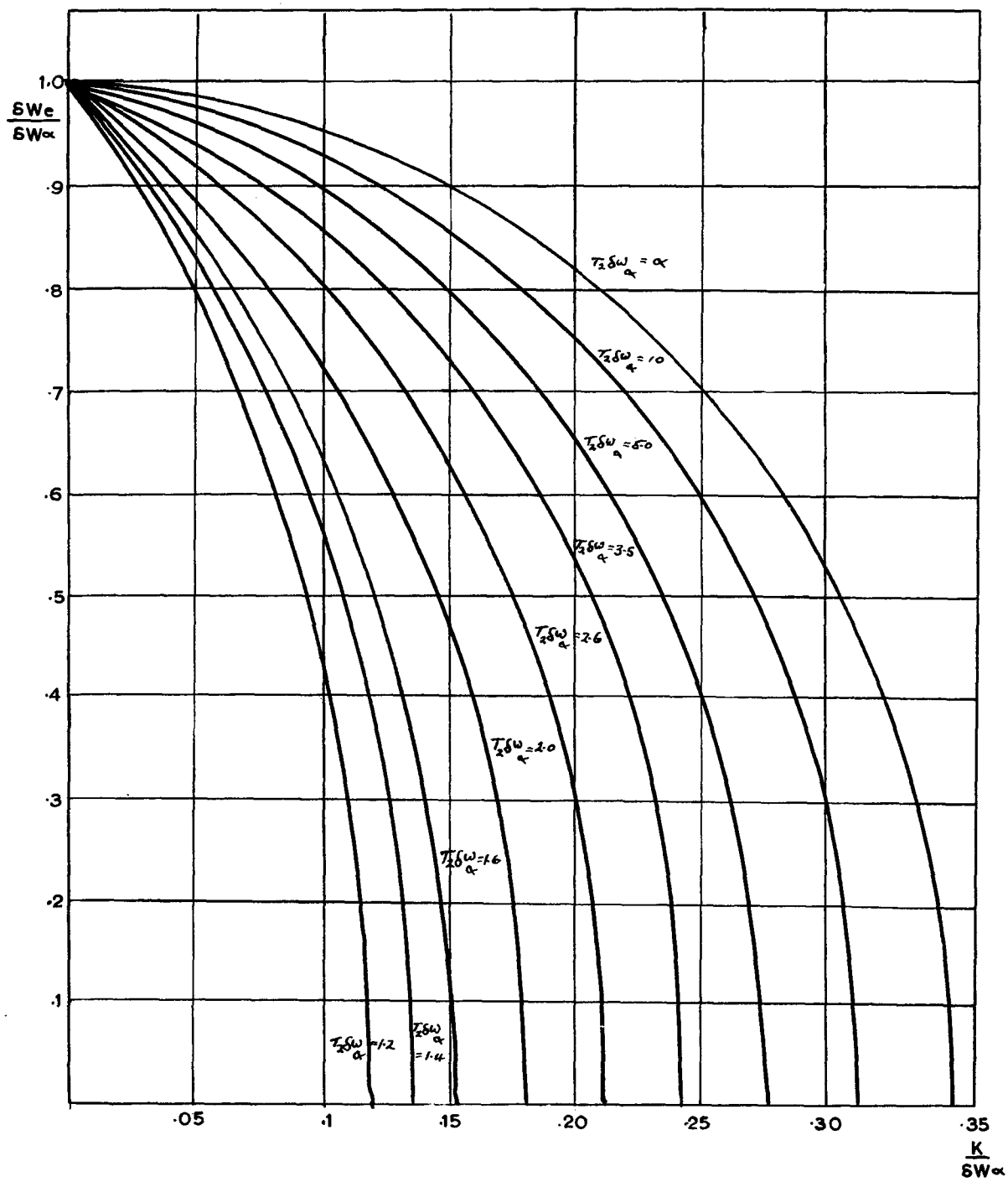
$$\Delta w = \pm\left[-2S\left(1/\tau + \frac{2T_2}{\tau^2} \pm S^{\frac{1}{2}}(\delta w)\,\frac{2T_2{}^2}{\tau^3} + \frac{4T_2}{\tau^2} + \frac{2}{\tau}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

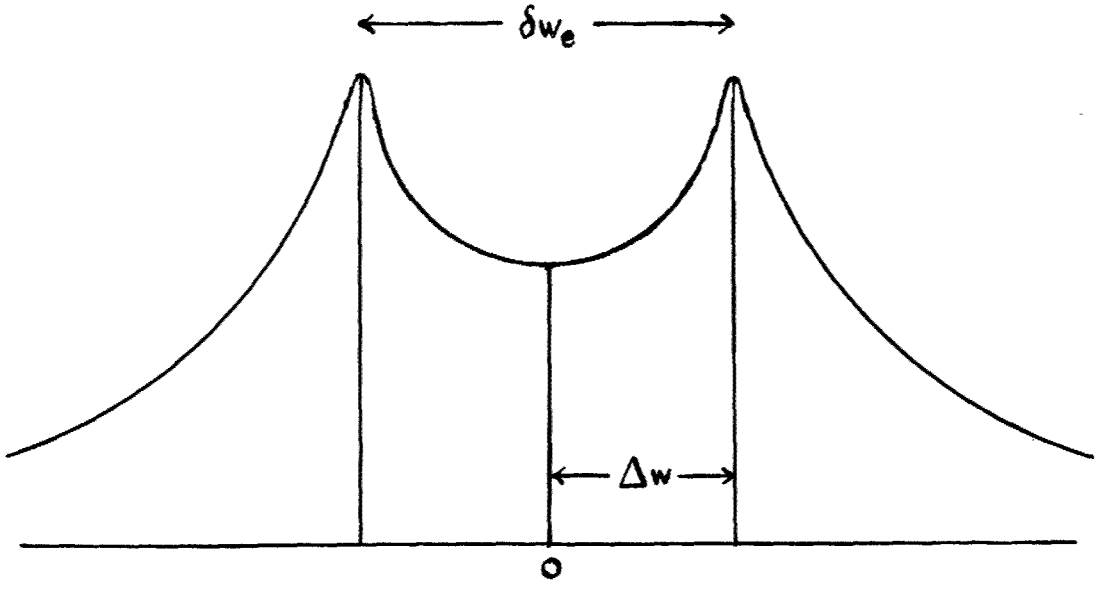
The negative possibility in the second choice of signs may be disregarded since this will lead to complex roots.

If the second term of this expression is numerically greater than the first, then the resultant two real roots will give an expression for the two maxima which will occur at positions Δw from a zero line and be given by

$$\Delta w = \pm\left[-2S\left(\frac{1}{\tau} + \frac{2T_2}{\tau^2}\right) + S^{\frac{1}{2}}(\delta w)\left(\frac{2T_2{}^2}{\tau^3} + \frac{4T_2}{\tau^2} + \frac{2}{\tau}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

DIAGRAM 2


1.0
δWe/δWα
.9
.8
.7
.6
.5
.4
.3
.2
.1
.05
.1
.15
.20
.25
.30
.35
K/δWα
T₂δω_α = ∞
T₂δω_α = 10
T₂δω_α = 5.0
T₂δω_α = 3.5
T₂δω_α = 2.6
T₂δω_α = 2.0
T₂δω_α = 1.6
T₂δω_α = 1.4
T₂δω_α = 1.2



The observed separation of the two peaks $\delta w_e = 2|\Delta w|$

$$\delta w_e = 2\left[-2S\left(\frac{1}{\tau} + \frac{2T_2}{\tau^2}\right) + S^{\frac{1}{2}}(\delta w)\left(\frac{2T_2^2}{\tau^3} + \frac{4T_2}{\tau^2} + \frac{2}{\tau}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

Hence $$\frac{\delta w_e}{\delta w} = 2\left[-2\left(\frac{1}{T_2\,\delta w} + \frac{\tau\,\delta w}{2(T_2\,\delta w)^2} + \frac{\tau\,\delta w}{8}\right)\left(\frac{1}{\tau\delta w} + \frac{2T_2\,\delta w}{(\tau\,\delta w)^2}\right) + \left(\frac{1}{T_2\,\delta w} + \frac{\tau\,\delta w}{2(T_2\,\delta w)^2} + \frac{\tau\,\delta w}{8}\right)^{\frac{1}{2}}\left(\frac{2(T_2\,\delta w)^2}{(\tau\,\delta w)^3} + \frac{4T_2\,\delta w}{(\tau\,\delta w)^2} + \frac{2}{\tau\,\delta w}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

At zero exchange $\tau = \infty$ and δw_e, represented in this special case by δw_∞, is given by

$$\frac{\delta w}{\delta w_\infty} = \left[\frac{1}{3} - \frac{4}{3(T_2\,\delta w_\infty)^2} + \frac{2}{3}\left(1 + \frac{4}{(T_2\,\delta w_\infty)^2} + \frac{16}{(T_2\,\delta w_\infty)^4}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

Using these expressions the variation of $\delta w_e / \delta w_\infty$ with $1/\tau\,\delta w$ for various values of $T_2\,\delta w$ have been computed. The results are shown graphically in diagram 2.

In addition to observations on peak maxima separation[5],

information on reaction rates have been obtained from observations on

(i) The intensity ratio of central minimum/maximum[9]
(ii) The band width at half height after coalescence.

Using the information briefly outlined above, equations have been derived which allows use to be made of these parameters. The resultant expressions are

$$\text{(i)}\quad \frac{\text{Minimum intensity}}{\text{Maximum intensity}} = \frac{(1 + \tau\delta w/2T_2\,\delta w)\left[\left(\frac{P}{\delta w}\right)^2 + \frac{1}{4}\left(\frac{\delta w_e}{\delta w}\right)^2\left(1 + \frac{\tau\delta w}{T_2\delta w}\right)^2\right]}{(S/\delta w)\left[\left(1 + \frac{\tau\delta w}{2T_2\delta w}\right)\frac{P}{\delta w} + \frac{\tau\delta w}{8}\left(\frac{\delta w_e}{\delta w}\right)^2\left(1 + \frac{\delta w}{T_2\delta w}\right)\right]}$$

$$\frac{P}{\delta w} = \frac{\tau\delta w}{2}\left[\frac{1}{(T_2\,\delta w)^2} - \frac{1}{4}\left(\frac{\delta w_e}{\delta w}\right)^2 + \frac{1}{4}\right] + \frac{1}{T_2\,\delta w}$$

$$\frac{S}{\delta w} = \frac{1}{T_2\,\delta w} + \frac{\tau\delta w}{2(T_2\,\delta w)^2} + \frac{\tau\delta w}{8}$$

$$\text{(ii)}\quad \frac{\delta w_{\frac{1}{2}}}{\delta w} = 2\left\{\frac{4(S/\delta w)}{\tau\delta w}\,\frac{\tau\delta w + T_2\,\delta w}{\tau\delta w + 2T_2\,\delta w} - \frac{2}{(\tau\delta w)^2}\left(1 + \frac{\tau\delta w}{T_2\,\delta w}\right)^2 + 2\left[\frac{1}{(\tau\delta w)^4}\left(1 + \frac{\tau\delta w}{T_2\,\delta w}\right)^4 - \frac{4(S/\delta w)}{(\tau\delta w)^3}\,\frac{\tau\delta w + T_2\,\delta w}{\tau\delta w + 2T_2\delta w}\left(1 + \frac{\tau\delta w}{T_2\,\delta w}\right)^2 + \frac{4(S/\delta w)^2(\tau\delta w + T_2\,\delta w)^2}{(\tau\delta w)^2(\tau\delta w + 2T_2\,\delta w)^2} + \frac{(S/\delta w)^2}{(\tau\delta w)^2}\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}}$$

Both these expressions only contain terms in $T_2\,\delta w$ and

DIAGRAM 3

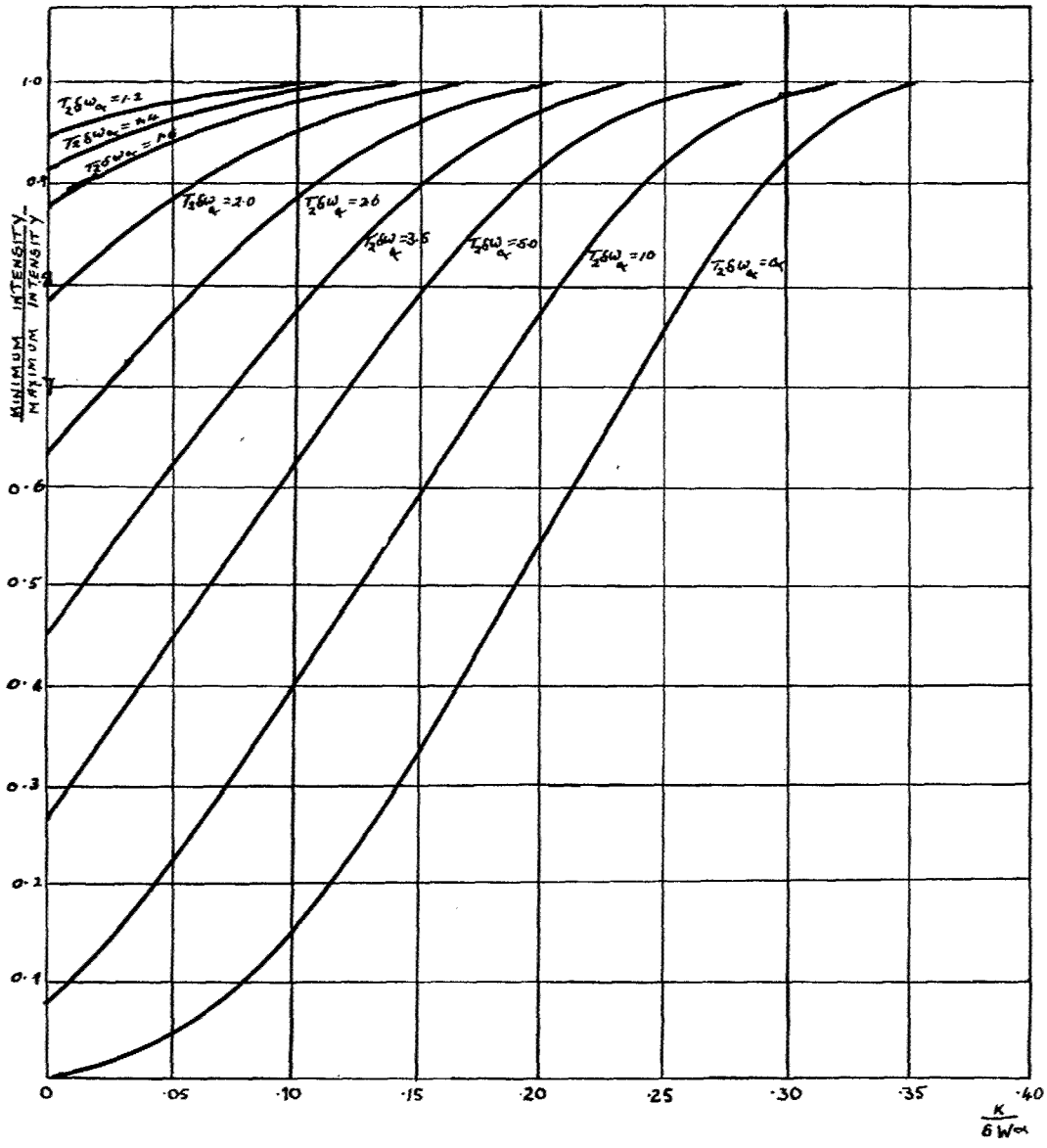
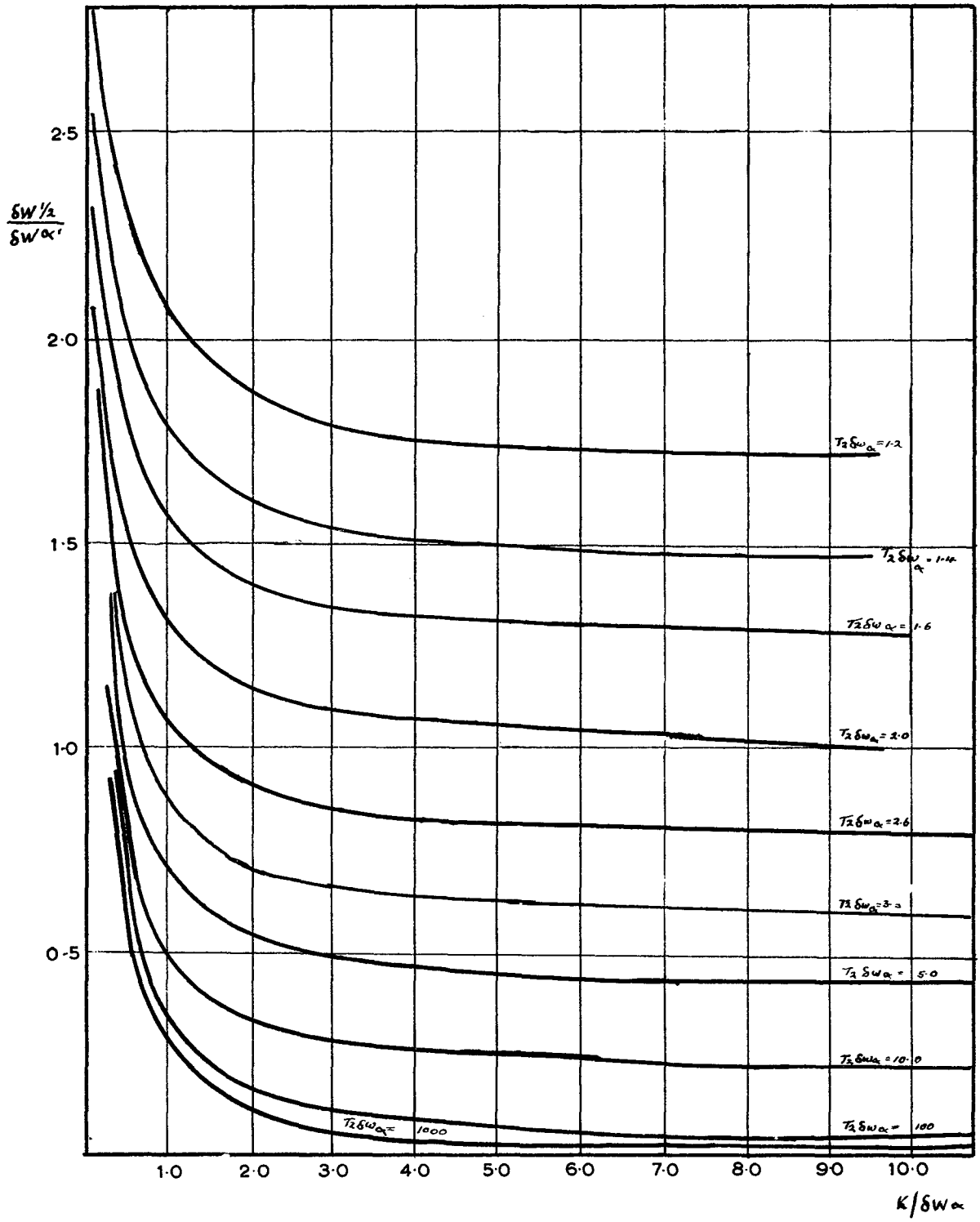

MINIMUM INTENSITY / MAXIMUM INTENSITY
1·0
0·9
0·6
0·5
0·4
0·3
0·2
0·1
0
·05
·10
·15
·20
·25
·30
·35
·40
K / δW∝
T₂δω = 1·2
T₂δω = 1·4
T₂δω = 1·6
T₂δω = 2·0
T₂δω = 2·6
T₂δω = 3·6
T₂δω = 5·0
T₂δω = 10
T₂δω = ∞

DIAGRAM 4


$\frac{\delta W_{1/2}}{\delta W_{\alpha'}}$
2·5
2·0
1·5
1·0
0·5
$T_2\delta\omega_\alpha = 1\cdot2$
$T_2\delta\omega_\alpha = 1\cdot4$
$T_2\delta\omega_\alpha = 1\cdot6$
$T_2\delta\omega_\alpha = 2\cdot0$
$T_2\delta\omega_\alpha = 2\cdot6$
$T_2\delta\omega_\alpha = 3\cdot3$
$T_2\delta\omega_\alpha = 5\cdot0$
$T_2\delta\omega_\alpha = 10\cdot0$
$T_2\delta\omega_\alpha = 100$
$T_2\delta\omega_\alpha = 1000$
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
$K/\delta W_\alpha$

$1/\tau\delta w$ and therefore the variation of the appropriate parameter (min/max. or $\frac{\delta w_{\frac{1}{2}}}{\delta w_{\infty}}$) with $1/\tau\delta w$ for various values of $T_2\ \delta w$ can be computed. The results of such calculations are shown in diagrams 3 and 4.

It is well known that the reaction rate constant (k) for a first order reaction = $1/\tau$.

$$\frac{1}{\tau\delta w} = \frac{k}{\delta w}$$

Observations upon (i) Separation of peak maxima
(ii) Minimum/maximum ratio
(iii) Band width at half height after coalescence will allow values of k to be calculated

from experimental observations at various temperatures. If the Arrhenius expression, $k = Ae^{-Ea/RT}$, is assumed to apply then Ea, the energy of activation for the reaction, can be calculated.

In practice the graphical results reproduced in diagrams 2, 3 and 4 are used as master graphs from which values of $k/\delta w$ can be read for each experimental observation.

Calculated from observations on	Energy Barrier to Rotation (k.cals) based upon		
	$T_2\ \delta w_{\infty} = 10$ Radians	$T_2\ \delta w_{\infty} = 5$ Radians	$T_2\ \delta w_{\infty} = \infty$ Radians
Band Maxima Sep^{n}	14·5	19·4	5·7
Minimum/Maximum Intensity Ratio	18·1	45·0	12·0
Band Width at Half Height	19·5	27·4	9·2
Transition State Theory	(Δ G) = 20·7	(ΔG) = 20·8	(ΔG) = 20·6

TABLE 2. - Showing values of Ea for $C_6H_5BCl\cdot NMe_2$, at three values of $T_2\ \delta w_{\infty}$; calculated from various experimental observations. Experimental value of $T_2\ \delta w_{\infty}$ = 9·6 Radians

A value for the energy barrier to rotation can also be calculated from the temperature at which the doublet collapses to a single peak and the value of ~~the~~ k at this temperature by substitution in the transition state expression $k = \frac{kT}{h} e^{-\Delta G/RT}$

Values of the energy barrier to rotation about the BN bond in phenyldimethylaminochloroborane, calculated from the experimental observations discussed above, are given in Table 2. Values of Ea for three values of $T_2 \delta w_\alpha$ (5, 10 and α radians) have been calculated, for each kind of experimental observation. The closest agreement occurs when $T_2 \delta w_\alpha = 10$, and this value is the nearest of the three to the value obtained experimentally (9·6 radians).

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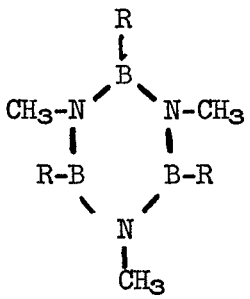
Organosilicon Derivatives of Inorganic "Benzenoid" Compounds.

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I. Introduction.

In a previous report[1] the synthesis of thermally and oxidatively stable silicon-substituted borazines (I) was reported. The present report summarizes our



I

[R= $(CH_3)_2R'SiCH_2$- , where R' = CH_3, C_2H_5, n-C_4H_9 and $(CH_3)_3SiO$]

further efforts in the borazine area and describes as well work devoted to the preparation of silicon-substituted phosphazenes and to the synthesis and characterization of perfluorovinyllithium. The latter reagent seemed of possible interest in connection with our studies of organofunctional borazines.

The work reported here was carried out principally by Drs. H. P. Kögler, G. Raab, W. Freyer and J. F. Helling and is being continued since September by Drs. H. Yamazaki and M. Takamizawa. The period 1 March 1959 - 30 November 1961 is covered in this summary.

II. Discussion.

A. Preparation of Silicon-substituted Borazines.

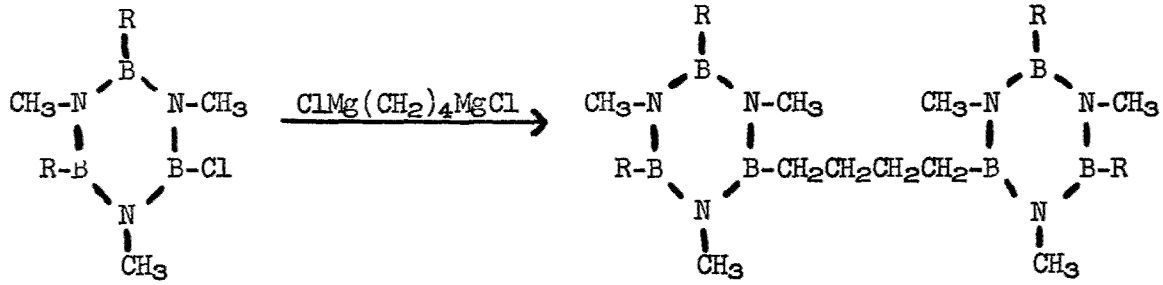
A compound containing a B-Si linkage (I, R= $(C_6H_5)_3Si$-) was prepared by the reaction of triphenylsilyllithium in THF with B-trichloro-N-trimethylborazine[2]:

$$3(C_6H_5)_3SiLi + (ClBNCH_3)_3 \longrightarrow [(C_6H_5)_3SiBNCH_3]_3 + 3LiCl$$

This borazine, a white solid of m.p. 248-251°, was hydrolytically unstable:

$$[(C_6H_5)_3SiBNCH_3]_3 + 9\ H_2O \longrightarrow 3\ (C_6H_5)_3SiH + 3\ B(OH)_3 + 3\ CH_3NH_2$$

Silicon-substituted borazines of higher molecule weight could be prepared by the reaction of B-chloro-B-bis(trimethylsilylmethyl)borazine with α,ω-di-Grignard reagents:



[R= $(CH_3)_3SiCH_2$- ; m.p. 93-94°]

This approach to stable borazines of higher molecular weight should be applicable to other novel systems, including cross-linked polymers when B-dichloro-B-trimethylsilylmethyl-N-trimethylborazine is used in place of the monochloro compound.

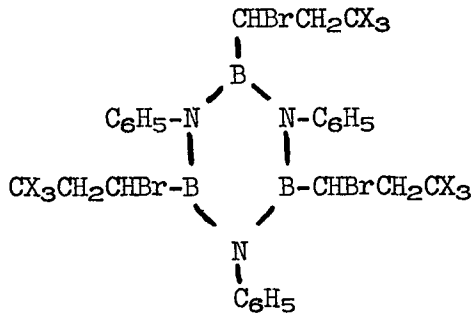
Other studies showed that facile introduction of bulky trimethylsilylmethyl groups into borazines by the Grignard reaction is limited to those cases in which the groups on the nitrogen atom are fairly small. Thus various N-triphenylborazines did not react with trimethylsilylmethylmagnesium chloride or bromide, although they did react well with methylmagnesium bromide.

B. Reactions of B-Trivinyl-N-triphenylborazine.

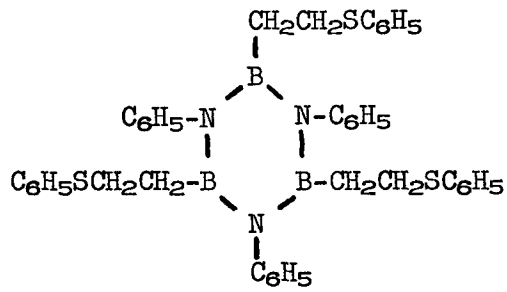
The preparation of B-trivinyl-N-triphenylborazine has been reported and its polymerization properties have been studied.[3] We have begun an investigation of the reactions of this compound with a variety of reagents with the object of preparing a wide variety of organofunctional borazines.

It might have been expected that phenyllithium would add across the double bonds in the vinylborazine, as it does with vinylsilanes and vinylgermanes. However, this was not the case; phenyllithium appeared not only to disrupt completely the borazine ring system, but also to displace the vinyl group on boron. The major boron-containing product of this reaction was triphenylborane (isolated as $(C_6H_5)_3B{\cdot}NH_3$).

A variety of radical reagents added to the C=C bond in B-trivinyl-N-triphenylborazine. These included bromotrichloromethane, carbon tetrabromide and benzenethiol, and borazines II, III and IV, respectively, were obtained. Dimethylphosphite and trichlorosilane reacted with the vinylborazine in the presence of peroxide initiators, but pure products have not yet been isolated. Methyldichlorosilane also added to the vinylborazine when chloroplatinic acid was used as the catalyst, but again a noncrystallizable oil resulted.



II, X=Cl ; III, X=Br



IV

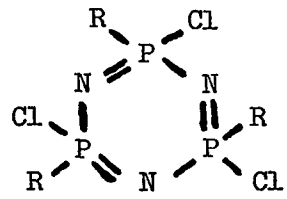
C. Attempted Preparation of Silicon-substituted Phosphazenes.

It has been reported that trimeric and tetrameric phosphonitrilic chlorides can be arylated by the Grignard and by the Friedel-Crafts procedures. However, more useful procedures for obtaining alkyl or aryl derivatives of the cyclic phosphonitrilic chlorides involve using alkyl(or aryl)tetrachlorophosphoranes and dialkyl(or diaryl)trichlorophosphoranes in place of pentachlorophosphorane in the phosphazene ring closure reaction[4]:

$$RPCl_4 + NH_4Cl \longrightarrow [NP(R)Cl]_n$$

It was decided to test this approach to organosilicon-substituted phosphazenes in this research.

The compound whose preparation was desired was:



[R= $(CH_3)_3SiCH_2$]

and its synthesis was attempted using the following reactions:

$$Me_3SiCH_2\text{-Metal Cpd.} + PCl_3 \longrightarrow Me_3SiCH_2PCl_2 \quad (1)$$

$$Me_3SiCH_2PCl_2 + Cl_2 \longrightarrow Me_3SiCH_2PCl_4 \quad (2)$$

$$Me_3SiCH_2PCl_4 + NH_4Cl \longrightarrow [NP(Cl)(CH_2SiMe_3)]_n \quad (3)$$

Conventional methods used to prepare alkyldichlorophosphines utilize the reaction of phosphorus trichloride with mild alkylating reagents such as dialkylmercury[5] or tetraalkyllead[6] compounds. Accordingly, bis-(trimethylsilylmethyl)mercury and tetrakis-(trimethylsilylmethyl)lead, both new compounds, were prepared by the usual Grignard procedure, and their action on phosphorus trichloride was investigated. The mercurial did not react with phosphorus trichloride either when a mixture of the reactants was refluxed in hexane solution, or in the absence of solvent at ca. 76°. In contrast, the lead compound was cleaved by phosphorus trichloride, giving crystalline, sublimable tris-(trimethylsilylmethyl)lead chloride and trimethylsilylmethyldichlorophosphine. However, the isolated yield of the phosphine was not very high, and a better synthesis was desired.

$$(Me_3SiCH_2)_4Pb + PCl_3 \longrightarrow (Me_3SiCH_2)_3PbCl + Me_3SiCH_2PCl_2$$

Although the Grignard procedure is not generally applicable to the preparation of pure alkyldichlorophosphines because mixtures of mono-, di- and trisubstituted products result, it seemed possible that with the relatively bulky trimethylsilylmethyl group, monosubstitution could be realized in acceptable yield. Indeed, our previous work[7] showed that complete substitution of all three chlorine atoms in phosphorus trichloride with trimethylsilylmethyl groups by the Grignard procedure requires drastic conditions. It was found in the present work that addition of one equivalent of trimethylsilylmethylmagnesium chloride to one mole of phosphorus trichloride in ether at low temperature resulted in the desired trimethylsilylmethyldichlorophosphine in ca. 40% yield. Further study of this reaction aimed at improvement of the yield was deferred until the practicality of reactions (2) and (3) could be assessed.

Attempted conversion of trimethylsilylmethyldichlorophosphine to trimethylsilylmethyltetrachlorophosphorane (reaction 2) was not successful. Even at -20° in the dark, addition of a solution of chlorine in 1,1,2,2-tetrachloroethane to trimethylsilylmethyldichlorophosphine caused cleavage of the carbon-silicon bond to form trimethylchlorosilane. This facile cleavage of the carbon-silicon bond may be due to the inductive effect of the PCl_4 group; electron withdrawal by this group would make the silicon-carbon bond more polar, hence more susceptible toward ionic fission. Investigation of the solid formed in the chlorination reaction showed it to be impure pentachlorophosphorane rather than the expected chloromethyltetrachlorophosphorane. The hydrolysis product of this solid formed a barium salt of very low carbon content, and an anilinium salt could be prepared which was shown to be $[C_6H_5NH_3][H_2PO_4]$. It is not known at what point fission of the phosphorus-carbon bond took place, nor is the fate of the methylene group of the trimethylsilylmethyldichlorophosphine known. It is, however, very likely that such cleavage took place after the cleavage of the silicon-carbon bond, since initial cleavage of trimethylsilylmethyldichlorophosphine at the phosphorus-carbon bond would have given chloromethyltrimethylsilane. This compound is stable to

silicon-carbon bond cleavage under these experimental conditions, although side chain chlorination does take place.

Since the proposed synthesis of silicon-substituted phosphazenes failed in the second of the three steps, this approach was abandoned.

B. The Synthesis of Perfluorovinyllithium.

It would be most desirable to introduce unsaturated groups, such as the vinyl and the perfluorovinyl group, into borazines. Hopefully, functionality of this type would allow polymerization reactions to be carried out with the object of linking borazene rings. Also, addition of various reagents to the unsaturated groups would permit the preparation of a large variety of borazines containing organofunctional alkyl groups linked to boron.

Active metal vinyl compounds - vinylmagnesium chloride and bromide, vinyllithium and vinylsodium - have been developed in recent years. More recently perfluorovinylmagnesium bromide[8] was described. After our early attempts to prepare B-vinylated borazines, the synthesis of B-trivinyl-N-triphenylborazine was reported in the patent literature[3]. For this reason we initiated a study directed toward the synthesis of B-perfluorovinylborazines.

Perfluorovinylmagnesium bromide is known as a relatively unstable species that must be prepared and used in tetrahydrofuran solution[8]. It was thought that perfluorovinyllithium might be capable of existence and that this reagent might be prepared in other, lower boiling solvents, thus extending the versatility of perfluorovinylation procedures. Our first efforts showed that perfluorovinyllithium could not be prepared by the direct reaction between metallic lithium and bromotrifluoroethylene. Accordingly, the transmetalation procedure which had proven of exceptional utility in the synthesis of vinyllithium[9] and allyllithium[10], was applied in this case. Perfluorovinyltin compounds had been the subject of previous study in these Laboratories[11], and the action of organolithium reagents on perfluorovinyltin compounds was examined as a possible route to perfluorovinyllithium. The reaction between triphenylperfluorovinyltin and phenyllithium, carried out in diethyl ether at room temperature, demonstrated that the exchange reaction did indeed occur, since tetraphenyltin was isolated in nearly quantitative yield. However, no evidence could be obtained for the presence of perfluorovinyllithium in the dark brown solution which was formed. Since perfluorovinyllithium did not appear to be stable under these conditions, it was felt that either lower reaction temperatures in the diethyl ether system or a change to a less polar solvent might favor the stability of the desired reagent. Subsequent experiments showed that perfluorovinyllithium could be prepared as a stable entity either in diethyl ether or in pentane at -40° to -30°. The reaction of phenyllithium with phenyltriperfluorovinyltin (3:1 molar ratio) in ether at ca. -40° proceeded rapidly, giving a precipitate of tetraphenyltin and a brown solution of perfluorovinyllithium. Exploratory experiments showed this reagent was best characterized by its reaction with triethyltin chloride:

$$C_6H_5Sn(CF{=}CF_2)_3 + 3\ C_6H_5Li \longrightarrow (C_6H_5)_4Sn + 3\ CF_2{=}CFLi$$

$$CF_2{=}CFLi + (C_2H_5)_3SnCl \longrightarrow (C_2H_5)_3SnCF{=}CF_2 + LiCl$$

The yield of triethylperfluorovinyltin obtained was ca. 40%, and this represents a minimum figure for the yield of perfluorovinyllithium in the transmetalation reaction. Perfluorovinyllithium also reacted normally with trimethylbromosilane and carbon dioxide.

A similar exchange reaction could be effected in pentane between n-butyllithium and n-butyltriperfluorovinyltin. However, in this solvent exchange was not complete, and it was found best to use the lithium reagent and the tin compound in 2:1 molar ratio. When the perfluorovinyllithium preparation was carried out in -30° and triethyltin chloride used to characterize the lithium reagent formed, the work-up procedure gave triethylperfluorovinyltin in 46 - 50% yield. Since the exchange was not complete under these conditions, and since in fact a deficiency of n-butyllithium was used, the possibility existed that triethyltin chloride could undergo direct exchange with any perfluorovinyltin compounds still present in the reaction mixture. To completely exclude this possibility the reaction mixture was shaken with aqueous-alcoholic potassium fluoride solution prior to removal of solvent and distillation of the products. This treatment removed unreacted triethyltin chloride as the insoluble fluoride. Other experiments showed that the exchange reaction between triethyltin chloride and di-n-butyldiperfluorovinyltin occurred only when this mixture was heated. Thus distillation at reduced pressure of a mixture of triethyltin chloride and di-n-butyldiperfluorovinyltin produced triethylperfluorovinyltin in ca. 9% yield.

Perfluorovinyllithium was more stable in pentane than in ether solution. It appeared to be stable in pentane at 0°, but short refluxing of its pentane solution caused complete decomposition.

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THERMALLY STABLE PHOSPHONITRILE COMPOSITIONS

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ABSTRACT

Phosphonitrilic chloride polymers stabilized against high-temperature polymerization by bonding to various metal halides have been prepared. Reactions of $SbCl_3$, $SbCl_5$, $AlCl_3$, $AlBr_3$, BCl_3, BF_3, $TiCl_4$, $ZnCl_2$, $FeCl_3$, CuCl, and TlCl with PCl_5 and NH_4Cl gave thermally stable compositions which are liquid from room temperature or below up to 1000°F. or higher, pyrolytically stable to 1000°F., and sensitive to hydrolysis to varying degrees. Their exact structure has not been rigorously established.

Several liquid aryloxy phosphonitriles prepared are thermally stable to approximately 750°F. and have pour points below room temperature. They are hydrolytically stable and have very low vapor pressures.

INTRODUCTION

The two most widely studied and well-defined inorganic homologous series are the siloxanes $(R_2SiO)_n$ and the phosphonitrilic chlorides $(PNCl_2)_n$. The former series has received the greatest attention because of the wide range of useful products based on the siloxane backbone. Utility of phosphonitrilic chlorides and derivatives has been impaired by their tendency to polymerize or decompose at elevated temperatures. If this tendency could be overcome, the phosphonitriles would be valuable materials for a variety of purposes including high-temperature fluid applications.

This investigation has been entirely within the area of phosphonitrile chemistry and, in part, represents an extension of studies reported at an earlier Contractor's Conference, May 26-28, 1959 (Ref. 1). The objective of this research has been the synthesis and evaluation of primarily inorganic polymer liquids with potential utility as lubricants, greases, and hydraulic fluids at temperatures up to 1000°F.

Progress toward the objectives has been made in two particular areas of phosphonitrile chemistry as discussed below. The first is that of phosphonitrilic chloride polymers stabilized against polymerization by bonding to various metal halides, these products being designated as $(PNCl_2)_n$/metal halide. The second is that of aryloxy phosphonitriles.

DISCUSSION

$(PNCl_2)_n/SbCl_3$

In an attempt to form a copolymer of phosphorous and antimony nitrilic chlorides by the reaction

$$nPCl_5 + nSbCl_5 + 2nNH_4Cl \longrightarrow \left(\begin{array}{c} Cl \quad Cl \\ | \quad | \\ P{=}N{-}Sb{=}N \\ | \quad | \\ Cl \quad Cl \end{array}\right)_n + 8nHCl$$

a liquid phosphonitrilic chloride product containing antimony was obtained that displayed several striking differences from cyclic $(PNCl_2)_n$ polymers. It was soluble only in polar solvents, was very sensitive to hydrolysis, and most important, it did not polymerize on heating to 430°C. In view of the significant effect of antimony in inhibiting polymerization and thereby extending the liquid range of the product, the system was studied in greater detail. It was found that essentially the same products could be obtained more simply by using $SbCl_3$ in place of $SbCl_5$. When the molar concentrations of PCl_5 and $SbCl_3$ in the reaction mixtures were varied from 10 to 1 through 1 to 1, the proportion of liquid product increased progressively from 60% in the 10 to 1 case to 100% liquid at a PCl_5 to $SbCl_3$ ratio of 2 to 1. Elemental analyses and molecular weights of these crude liquids varied with the PCl_5 to $SbCl_3$ ratio, indicating that different products were obtained in each case. The liquids varied in color from brown to black and all were sensitive to moisture.

Several components of the $(PNCl_2)_n/SbCl_3$ crude liquid products were isolated and identified by partial distillation at reduced pressure. $SbCl_3$ was one of the main components removed by distillation, the amount ranging from essentially none in the 10 to 1 case to nearly 50% of the total liquid product in the 1 to 1 case. Small amounts of $(PNCl_2)_n$ trimer, tetramer, and oil were also separated. After removal of all volatile components, the physical and chemical properties of the final liquid products from all of the $(PNCl_2)_n/SbCl_3$ preparations were practically identical. They are soluble only in polar solvents such as methylene chloride and nitrobenzene, and insoluble in nonpolar solvents such as benzene and petroleum ether. They are very sensitive to hydrolysis, being decomposed immediately on contact with water. Their appearance is the same except that the products from reactions involving high PCl_5 to $SbCl_3$ ratios are more viscous than those where the ratio is low.

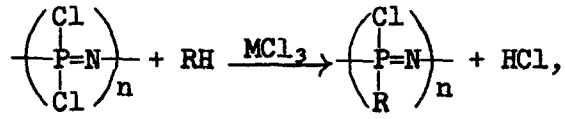
The final liquid from a preparation involving a PCl_5 to $SbCl_3$ ratio of unity boiled above 347°C./0.38 mm. and could be heated to 560°C. in an open tube before polymerizing. Elemental analysis gave an approximate empirical formula of $P_6N_5SbCl_{18}(CH_5)$ as compared with the approximate empirical formula $P_9N_8SbCl_{28}(C_4H_4)$ found for the liquid portion of the product from a reaction involving a PCl_5 to $SbCl_3$ ratio of 10 to 1. The latter product had the same resistance to polymerization at high temperatures as the former.

A more thorough investigation of the lower boiling components of the crude liquid products prepared in sym-tetrachloroethane was accomplished by vapor-phase chromatography (V.P.C.). The following components were isolated and identified: trichloroethylene, tetrachloroethylene, 1,1,2,3,4,4-hexachlorobutane,

sym-tetrachloroethane, antimony trichloride, phosphorous oxychloride, and phosphonitrilic chloride trimer and tetramer. The presence of several additional components in very small concentration was also demonstrated by V.P.C. These were not completely identified but they were found to contain carbon, hydrogen, and chlorine. In some cases peaks were found which were attributed to $(PNCl_2)_n$ pentamer, hexamer, and heptamer. These peaks were assigned by comparison with results obtained for $(PNCl_2)_n$ trimer, tetramer, pentamer, hexamer, and heptamer which could be satisfactorily separated from a normal $(PNCl_2)_n$ liquid by V.P.C. on a silicone grease on "Celite" column at 320°C. In no case was a definite $(PNCl_2)_n/SbCl_3$ component isolated by V.P.C. Adsorption column chromatography confirmed the V.P.C. work but did not lead to identification of other species.

The results demonstrated the instability of sym-tetrachloroethane as a solvent under the conditions used since trichloroethylene, tetrachloroethylene, and 1,1,2,3,4,4-hexachlorobutane definitely are products resulting from the decomposition of sym-tetrachloroethane. It is probable that several of the unidentified minor components are chlorinated hydrocarbons resulting from solvent decomposition.

The discovery that the sym-tetrachloroethane solvent undergoes decomposition in the reaction mixture appears to be significant to the understanding of the instability of ordinary $(PNCl_2)_n$ polymers prepared by the method of Schenk and Römer (Ref. 2). From the nature of the decomposition products isolated and identified, it is apparent that chloroalkyl radicals are present during reaction in significant concentrations and may undergo interchange with the chlorines in the phosphonitrilic chloride polymers. It is also possible that the presence of $SbCl_3$ (or other metal chlorides as discussed later) catalyzes reactions of the following type:



wherein R is $-CCl_2CHCl_2$. Elemental analysis of $(PNCl_2)_n/MCl_3$ liquids prepared in sym-tetrachloroethane confirmed the presence of carbon and hydrogen, and more chlorine than could be accounted for by any reasonable phosphonitrilic chloride structure.

The presence of chloroalkyl groups randomly attached to phosphorous in the $PNCl_2$-type polymers should lead to an inhomogeneous, dark colored product.

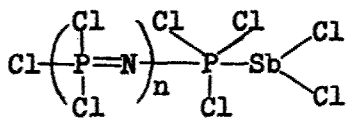
Previous work in this Laboratory (Ref. 3) showed that dark $(PNCl_2)_n$ liquids prepared in sym-tetrachloroethane (with or without $SbCl_3$) could be lightened considerably by treatment with chlorine. If, through decomposition of the solvent, a number of chloroalkyl groups become attached to phosphorous in the $(PNCl_2)_n$ chains or cycles, chlorination would then replace these groups with Cl leaving a uniform perchlorinated product.

On the basis of the above evidence for breakdown and subsequent reaction of sym-tetrachloroethane during phosphonitrilic chloride preparations, 1,2,4-trichlorobenzene (TCB) was evaluated as a less reactive solvent and showed the following advantages: (1) the fluids were clear yellow in color rather than

very dark, (2) the fluids did not become black on heating to 400°C., (3) the fluids appeared to be more homogeneous, and (4) product work-up was greatly facilitated. These comparisons are based on equivalent reaction times and temperatures.

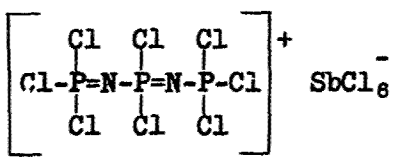
It is apparent that the reaction of PCl_5, NH_4Cl, and $SbCl_3$ does not usually lead to molecular species containing the same P to Sb ratio as in the reaction mixture. In the 10 to 1 case, the liquid portion of the product contains species with P to Sb ratios of approximately 9 to 1. As the molar concentration of $SbCl_3$ is increased, the P to Sb ratio in the crude liquid product follows directly, but this is accomplished by only a small reduction in the P to Sb ratio in the $(PNCl_2)_n/SbCl_3$ species plus solution of unreacted $SbCl_3$ in these species. Thus when the PCl_5 to $SbCl_3$ ratio in the reaction mixture is unity, the crude liquid product is approximately 50% by weight unreacted $SbCl_3$ plus $(PNCl_2)_n/SbCl_3$ compounds having an average elemental composition corresponding to a P to Sb ratio of 6 to 1.

The $(PNCl_2)_n/SbCl_3$ compositions have solubility and hydrolytic properties similar to those of the $(PNCl_2)_n \cdot PCl_5$ polymers which are assumed to be linear in structure (Ref. 4). The infrared spectra of the antimony-containing liquids are similar to those of medium weight $(PNCl_2)_n$ cyclic polymers. On the basis of elemental analysis, molecular weight, and physical and chemical properties, it is suggested that the $(PNCl_2)_n/SbCl_3$ compounds are linear $(PNCl_2)_n$ chains end-capped with the elements of $PSbCl_8$ as follows:



For n = 8 this would give an empirical formula of $P_9N_8SbCl_{22}$ which differs from that actually found for one of the $(PNCl_2)_n/SbCl_3$ oils discussed earlier by omission of the elements $C_4H_4Cl_4$. If it is assumed that two of the chlorines in the above structure have been replaced during reaction by $-CHClCHCl_2$ groups, the formula would then become $P_9N_8SbCl_{26}C_4H_4$ which is in agreement with the elemental analysis of the $(PNCl_2)_n/SbCl_3$ liquid prepared in sym-tetrachloroethane.

Preparations of $(PNCl_2)_n/SbCl_3$ compositions in TCB have led to solid products exclusively. The reactions involved PCl_5 to $SbCl_3$ ratios ranging from 1 to 1 to 10 to 1. These results indicate that the $(PNCl_2)_n/SbCl_3$ products obtained when sym-tetrachloroethane is used as solvent are liquids rather than solids because of a small number of chloroalkyl groups randomly incorporated in the polymer. One of the $(PNCl_2)_n/SbCl_3$ products (38% of the total product) from a preparation in TCB involving a $PCl_5/SbCl_3$ ratio of 5 to 1 was a white, poorly crystalline solid melting at 235-250°C. The remaining 62% of the product was a straw-colored solid melting at 60-76°C. Both of these solids have similar infrared spectra which are consistent with a phosphonitrilic chloride structure. Elemental analysis of the higher melting material gave an approximate empirical formula of $P_3N_2SbCl_{14}$. Thus it is quite possible that the compound has the following structure



analogous to the P_3NCl_{12} compound reported by Becke-Goehring and Lehr (Ref. 5) for which the structure $(Cl_3P{=}N{-}PCl_3)^+PCl_6^-$ was given.

$(PNCl_2)_n/AlCl_3$

It was found that when $AlCl_3$ was included in the reaction mixture for the preparation of $(PNCl_2)_n$ polymers, the liquid portion of the product was resistant to polymerization at elevated temperatures much the same as when $SbCl_3$ or $SbCl_5$ were employed. This result is very reasonable in view of the similarity of $SbCl_3$ and $AlCl_3$ as Lewis acids.

A series of reactions of PCl_5 with NH_4Cl in sym-tetrachloroethane was carried out in the presence of $AlCl_3$ with PCl_5 to $AlCl_3$ ratios of 10 to 1, 5 to 1, and 2 to 1. In each case, reaction proceeded smoothly. The yields were 63.4 g. oil and 59.2 g. solid, 107.2 g. oil and 32.2 g. solid, and 114.9 g. oil and 80.9 g. solid, respectively, based on one mole of PCl_5. The relative amounts of liquid and solid products in these preparations were nearly the same as when $SbCl_3$ was used. One marked difference between the two cases is that unreacted $SbCl_3$ remained in solution whereas $AlCl_3$ not incorporated in the fluid crystallized out in some complex form. These reactions will go rapidly at 95°C. once initiated by heating to about 110°C. Furthermore, they are endothermic and are essentially complete in 30 minutes at 95°C.

The $(PNCl_2)_n/AlCl_3$ liquids ranged from nearly colorless to yellow-brown and were very moisture-sensitive. If these fluids were agitated in the presence of moisture, they became cloudy and lost their stability toward polymerization.

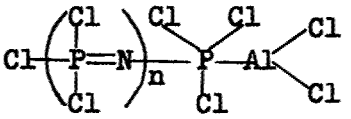
The solid portion of the product obtained with PCl_5 to $AlCl_3$ ratios of 10 to 1 and 5 to 1 was off-white in color and was found to be mostly $(PNCl_2)_n$ trimer and tetramer. The liquid portions of the products in these two cases were too high in molecular weight to be distilled. In the 2 to 1 case, however, the solid product was brown and violently moisture sensitive. On heating and subsequent distillation of this solid mixture, a light brown fluid was collected at ~245°C./0.1 mm. (m.p. ≃ 27°C.). Distillation of the liquid product from the case where the PCl_5 to $AlCl_3$ ratio was 2 to 1 yielded a fraction boiling at 420°C./1.1 mm. (pour point = -55°C.). These two products represent the only $(PNCl_2)_n$/metal halide compositions which have been successfully distilled.

Chemical analysis of the lower boiling fraction gave an empirical formula of P_2NAlCl_8 while that of the higher boiling fraction was $P_4N_3AlCl_{12}$. Both compounds are polar and soluble in polar solvents such as nitrobenzene but are insoluble in nonpolar solvents such as benzene. Both compounds undergo hydrolysis vigorously in water.

The infrared spectrum of the higher boiling fraction had one very strong absorption band at 1270 $cm.^{-1}$ which is midway between that for $(PNCl_2)_n$ trimer and tetramer (Ref. 6). This band is not far removed from the 1240 $cm.^{-1}$ band attributed to linear $(PNCl_2)_{8-9}\cdot PCl_5$ (Ref. 6). The $(PNCl_2)_n/AlCl_3$ compound also had weak bands at 865 $cm.^{-1}$ and 765 $cm.^{-1}$ which are consistent with a $(PNCl_2)_n$-type structure (Ref. 7). If the sample was allowed to contact atmospheric moisture, an hydrolysis band appeared at 3100 $cm.^{-1}$. The lower boiling $(PNCl_2)_n/AlCl_3$ fraction had strong absorption bands at 1330 $cm.^{-1}$, 1175 $cm.^{-1}$, and 810 $cm.^{-1}$. The first two bands are in the region of phosphorous-nitrogen stretching

frequencies in $(PNCl_2)_n$ polymers. The 810 cm.$^{-1}$ band is also in a region where $(PNCl_2)_n$ polymers absorb, but has not been definitely assigned to a particular group.

The following structure is proposed for the two $(PNCl_2)_n/AlCl_3$ compounds discussed above:



where n = 1 and 3, respectively. This structure would be polar and water sensitive and is consistent with the observed infrared spectra. It is exactly analogous to that proposed earlier for the $(PNCl_2)_n/SbCl_3$ compounds. Other ionic or covalent structures are possible but a rigorous structure assignment must await the results of N.M.R. studies and a more complete investigation of chemical properties.

John and Moeller (Ref. 8) report the preparation of a compound having an empirical formula of P_2NBr_7. It has the same solubility characteristics and hydrolytic instability as the two $(PNCl_2)_n/AlCl_3$ compounds, and they suggest that their compound is a $PNBr_2 \cdot PBr_5$ adduct. Preparation of the corresponding P_2NCl_7 compound is reported by Groeneveld, et al. (Ref. 9). The general class of assumed linear $(PNCl_2)_n$ molecules end-capped with the elements of PCl_5 also have similar solubility and hydrolytic properties (Ref. 4). A $(Cl_3P{=}N{-}PCl_3)^+AlCl_4^-$ compound analogous to $(Cl_3P{=}N{-}PCl_3)^+PCl_6^-$ has not been obtained in the present work.

The relative yields of the two distillable $(PNCl_2)_n/AlCl_3$ compounds varied with the relative mole ratios of PCl_5, NH_4Cl, and $AlCl_3$ in the reaction mixture. If a PCl_5 to $AlCl_3$ mole ratio of 2 to 1 was used, the product was predominantly the higher boiling component provided NH_4Cl was present in molar excess of PCl_5. When the molar amount of PCl_5 exceeded that of NH_4Cl, the yield of the lower boiling compound was increased.

A higher molecular weight product obtained from the reaction of NH_4Cl, PCl_5, and $AlCl_3$ (mole ratios 1.6 to 1.0 to 0.1, respectively) in sym-tetrachloroethane solvent had an elemental analysis closely corresponding to the structure shown earlier for $(PNCl_2)_n/AlCl_3$ compounds where n = 7.5 (i.e., a mixture of n = 7 and n = 8) and two chlorines per molecule were replaced by $CHCl_2\text{-}CCl_2\text{-}$ groups.

$(PNCl_2)_n/AlBr_3$

Aluminum bromide was found to react analogously to $AlCl_3$ when included in the reaction mixture of PCl_5 and NH_4Cl using TCB as solvent. With a PCl_5 to $AlBr_3$ ratio of 5 to 1, a red liquid, stable to polymerization at approximately 500°C., was obtained. It was very fluid at room temperature, had a pour point of -49°C., and was very moisture sensitive. Decreasing the PCl_5 to $AlBr_3$ ratio should lead to distillable products but this system appears to offer no advantages over the $AlCl_3$ system.

$(PNCl_2)_n/BCl_3$

The presence of BCl_3 during the preparation of $(PNCl_2)_n$ polymers in TCB also led to a liquid product stable to polymerization at elevated temperatures. The fluids were pale yellow and extremely moisture sensitive. Exposure to moisture led to a white precipitate and loss of polymerization stability.

All attempts to prepare a polymerization-stable $(PNCl_2)_n/BCl_3$ liquid in sym-tetrachloroethane failed. The products polymerized at approximately the same temperature as for ordinary $(PNCl_2)_n$ polymers (280°C. in one case).

Samples were heated to 400°C. in open tubes to remove volatile components before testing in evacuated sealed tubes at higher temperatures. Ten-hour tests were made at 500°C. and 538°C. After the tests the samples were still fluid at room temperature but contained white crystals suspended throughout.

When the $(PNCl_2)_n/BCl_3$ products were heated above 400°C. at atmospheric pressure, vigorous gas evolution and white solid formation occurred up to about 550°C. where polymerization to a dark brown elastomer occurred. At this point only about 30% of the original sample volume remained. These results and those from tests in sealed systems suggest that the decomposition is an equilibrium process. Apparently so long as the system is confined decomposition can proceed only to an equilibrium value on heating with perhaps partial reversal toward the original state on cooling.

Elemental analysis of a $(PNCl_2)_n/BCl_3$ oil (pour point = -44°C.) prepared from a reaction involving a PCl_5 to BCl_3 ratio of 5 to 1 gave the empirical formula $P_2N_2BCl_8$. A definite molecular structure was not established for this material, but the species involved does have an equivalent number of P and N atoms. In all other $(PNCl_2)_n$/metal halide compositions studied, except for the $(PNCl_2)_n/BF_3$ case, there is one more P than N per metal atom. The infrared spectrum of the $(PNCl_2)_n/BCl_3$ liquids has a major band in the region of PN stretching frequencies in $(PNCl_2)_n$ polymers.

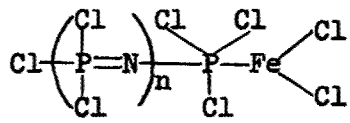
$(PNCl_2)_n/BF_3$

Boron trifluoride had the same effect as BCl_3 in increasing the polymerization stability of the product over that of the normal $(PNCl_2)_n$ cyclic polymers. The method of preparing $(PNCl_2)_n/BF_3$ fluids was the same as that used for BCl_3. It is assumed that the structures of the products are essentially the same. Elemental analyses are consistent with this assumption. The pour point of one of these liquids was -52°C.

$(PNCl_2)_n/FeCl_3$

Ferric chloride reacted with PCl_5 and NH_4Cl to give a high yield of dark liquid product with a pour point of -46°C. The material could be heated to 670°C. in an open tube without polymerization, even though some decomposition occurred. It was slightly soluble in benzene, soluble in nitrobenzene, and insoluble in water although it hydrolyzed slowly therein. The physical and chemical properties and infrared spectrum of this $(PNCl_2)_n/FeCl_3$ liquid indicated that it was similar in structure to other $(PNCl_2)_n$/metal halides. Elemental analysis gave an approximate empirical formula of $P_7N_5Fe_2Cl_{22}$ which could result from a nearly equimolar

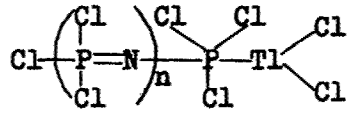
mixture of two polymers having the following structure.



where n = 2 and 3.

$(PNCl_2)_n/TlCl$

Thallous chloride interacted with PCl_5 and NH_4Cl (mole ratios of 1 to 5 to 5, respectively) in TCB solvent to give a good yield of a light brown liquid which was stable to polymerization above 450°C. It had a pour point of -50°C., boiled above 450°C./1.0 mm., was soluble in nitrobenzene, insoluble in benzene, and reacted with water to form an unidentified liquid immiscible with water. Elemental analysis gave an approximate empirical formula of $P_4N_3TlCl_{13}$ which is close to $P_4N_3TlCl_{12}$ obtained by replacing Fe by Tl in the structure given above for $(PNCl_2)_n/FeCl_3$ and assuming that thallium was oxidized to the +3 state, viz.



where n = 3. Its infrared spectrum is very similar to that of the other metal halide-stabilized $(PNCl_2)_n$ polymers. An attractive feature of the $(PNCl_2)_n/TlCl$ liquid was its failure to deteriorate rapidly in air.

$(PNCl_2)_n/SnCl_4$, CuCl, and $TiCl_4$

Reaction of PCl_5 and NH_4Cl in the presence of $SnCl_4$ did not lead to a product with greater resistance to polymerization than ordinary cyclic $(PNCl_2)_n$ polymers. This result may be attributed to formation of the stable $PCl_5 \cdot SnCl_4$ complex which precipitated from the reaction mixture, thus preventing the Sn from undergoing any further reaction. In order to retain part of the Sn in solution during reaction, triphenyltin chloride was used in place of $SnCl_4$ in the reaction of PCl_5 and NH_4Cl in TCB solvent. The products obtained included benzene, chlorobenzene, and a brown liquid $(PNCl_2)_n$ polymer presumably end-capped with $SnCl_3$. The latter product was insoluble in benzene, soluble in nitrobenzene, hydrolyzed slowly in water, had an infrared spectrum similar to other $(PNCl_2)_n$/metal halide compositions, and did not polymerize when heated to 520°C./1 atm. The yield of tin derivative was low, and there is no evidence to indicate that the $(PNCl_2)_n/SnCl_4$ system offers any advantages over $(PNCl_2)_n$/metal halides previously prepared.

When cuprous chloride was reacted with PCl_5 and NH_4Cl in TCB solvent, a very dark brown oil was obtained in low yield. It was stable to polymerization at 400°C., readily oxidized by air, soluble in acetone, and insoluble in benzene. It was insoluble in but reacted with nitrobenzene and water. It had an infrared spectrum similar to that of other $(PNCl_2)_n$/metal halides. Since the $(PNCl_2)_n/CuCl$ system did not have desirable characteristics, no further work with the system was done.

Reaction of PCl_5 and NH_4Cl in the presence of $TiCl_4$ was much slower than with the other compounds previously described. This may be due to formation of a $PCl_5 \cdot TiCl_4$ complex similar to but less stable than that from PCl_5 and $SnCl_4$. The all-liquid product (pour point = -26°C.) from a preparation involving a PCl_5 to $TiCl_4$ ratio of 5 to 1 was very dark brown and upon long standing at room temperature partly crystallized. A sample of the product was heated at atmospheric pressure with the following results. At 400°C. the sample was somewhat darkened but very little gas evolution occurred. Moderate boiling took place at 475°C., and at 500°C. there was vigorous boiling with deposition of yellow solids along the cooler portions of the system. After continuing the heating to 526°C., the sample was cooled to room temperature and remained as a very dark fluid. When tested for 10 hours at 538°C. in an evacuated sealed "Pyrex" tube the $(PNCl_2)_n/TiCl_4$ product was stable to polymerization.

$(PNCl_2)_n/ZnCl_2$

Pale yellow, viscous liquid products were obtained from the interaction of NH_4Cl, PCl_5, and $ZnCl_2$ in TCB. Reactions were essentially complete in one hour as determined by HCl evolution. When cool, the reaction mixtures separated into two layers; the upper solvent layers contained by-product $(PNCl_2)_n$ trimer and tetramer and the lower layer was the desired fluid product plus a small amount of solvent. This is the only case studied where a $(PNCl_2)_n$/metal halide fluid separated from the solvent in this manner. Essentially all of the products obtained were liquids containing only a small amount of volatile components. The fluids could not be distilled at 500°C./0.5 mm., thus indicating a high molecular weight. During the process of heating to 500°C. some unidentified black solid material formed in the samples. This was removed by filtration, leaving the product as a pale yellow fluid. These fluids had remarkable pyrolytic stability as judged by tests in evacuated sealed "Pyrex" tubes; for example, 10 hours at 600°C. produced no change in appearance, viscosity, nor infrared spectrum. A sample heated in an open tube to 610°C. did not polymerize, but some decomposition led to deposits of unidentified white solids on the cooler portions of the tube.

The $(PNCl_2)_n/ZnCl_2$ fluids were less sensitive to atmospheric moisture than most of the other $(PNCl_2)_n$/metal halide compositions investigated. They reacted slowly with water, as compared to the vigorous reaction of the $AlCl_3$, BCl_3, BF_3, and $SbCl_3$ compositions.

Elemental analysis of the liquid obtained from a reaction involving a PCl_5 to $ZnCl_2$ ratio of 5 to 1 gave an empirical formula of $P_7N_5Zn_2Cl_{20}$. Its molecular weight was determined as 1140 which is consistent with 1128 for the above empirical formula. Although a definite structure cannot be assigned from these data, it is almost certain that each molecule contains two zinc atoms. Its infrared spectrum has a very strong band at 1270 $cm.^{-1}$ and a smaller band at 760 $cm.^{-1}$, both of which are consistent with $(PNCl_2)_n$ polymers, especially the linear $(PNCl_2)_n \cdot PCl_5$ series.

The result of variations in mole ratios of $PCl_5/NH_4Cl/ZnCl_2$ on the yield and pour point of the resulting products is shown below.

Mole Ratios $PCl_5/NH_4Cl/ZnCl_2$	Liquid Product Wt. (g.)	Pour Point (°C.)
10/10/1	20.0	-15
5/7/1	61.5	- 5
4/2/1	96.3	- 3
2/2/1	151.6	0
1/1/1	105.0	30

It appears that the molecular weight of the product increases as the $ZnCl_2$ to PCl_5 ratio in the reaction mixture is raised, causing a corresponding increase in viscosity and pour point. This may be the result of forming a phosphonitrilic chloride-zinc copolymer.

Nonbonding Metal Halides

Preparations of phosphonitrilic chloride polymers from PCl_5 and NH_4Cl in TCB solvent were carried out in the presence of LiCl, phenylmercuric chloride, $MgCl_2$, $CdCl_2$, AgCl, and $PbCl_2$. There was no evidence that any of these halides became incorporated in the phosphonitrilic chloride products. The materials obtained polymerized at or below 300°C. in each case. A reaction including $SiCl_4$ was inconclusive.

LiCl

When PCl_5 and NH_4Cl were reacted in TCB in the presence of LiCl (PCl_5 to LiCl mole ratio of 5 to 1) a small percentage of the product was obtained as a dark viscous liquid which did not polymerize at approximately 500°C. when initially heated. However, on reheating, it polymerized at 300°C. Elemental analysis of the oil showed no lithium and gave the empirical formula $PNCl_2$. This is reasonable since LiCl would not be expected to react similarly to the Lewis acids discussed earlier. The temporary resistance to polymerization at elevated temperature is not understood. The rate of gas evolution during the preparation was slower than when LiCl was not present.

Preparations of $(PNCl_2)_n$ in the presence of LiCl have been carried out under a variety of conditions but the results have not led to a satisfactory understanding of the effect of the LiCl. Although the results have not been very reproducible, common features of these reactions are the slow evolution of HCl and the fact that these phosphonitrilic chloride products have improved polymerization stability over ordinary $(PNCl_2)_n$ polymers.

Conditions for Formation of $(PNCl_2)_n$/Metal Halides

The results of all reactions between PCl_5, NH_4Cl, and various metal halides fall into a pattern which may be defined in terms of electronegativity. When the metallic element in the metal halide has an electronegativity value (Ref. 10) below 1.2, e.g., Li (1.0), Hg (1.0), Cd (1.1), and Mg (1.2), bonding to $(PNCl_2)_n$ does not occur. Halides of all the elements investigated having electronegativities between 1.2 and 2.0, e.g., Zn (1.2-1.5), Tl (1.3-1.5), Al (1.5), Ti (1.6), Sn (1.6-1.8), Sb (1.8), Cu (1.8), and B (2.0), were found to bond to a $(PNCl_2)_n$ moiety, thereby stabilizing it against polymerization at elevated temperatures. Elements studied that may have electronegativities greater than 2.0 are

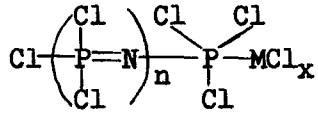
Pb (1.6-2.4), Ag (1.8-3.2), and As (2.0-2.2). Neither $PbCl_2$, AgCl, nor $AsCl_3$ imparted increased polymerization stability to the phosphonitrilic chlorides prepared in their presence.

There are a number of untried metal halides which fall into the class where the metal portion has an electronegativity between 1.2 and 2.0. It is expected that many of these would also bond to $(PNCl_2)_n$ groups. The boundary conditions for formation of $(PNCl_2)_n$/metal halides should not be a function alone of the electronegativity of the metallic, or more electropositive, portion of the metal halide, but should also depend on the relative electronegativities of the metal and halogen. In other words, the degree of ionic character of the bonding in the metal halide must be considered. Thus, highly ionic fluorides would not be expected to bond to $(PNCl_2)_n$ chains, but would be more likely to react with $(PNCl_2)_n$ products formed from PCl_5 and NH_4Cl to produce partially fluorinated phosphonitrilic polymers.

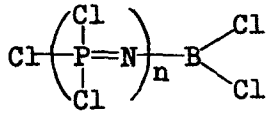
Properties of $(PNCl_2)_n$/Metal Halide Compositions

The similarity of the various $(PNCl_2)_n$/metal halide products suggests that they have similar structures. Although single molecular species could be isolated only in the $AlCl_3$ case, the elemental analyses of the other products indicates that P, N, and the "metal" always occur in ratios of n to n-1 to 1, respectively, where n may be 2 through 9, except for the BCl_3 and BF_3 cases in which the ratio of P to N is more nearly unity. It is therefore assumed that the boron halides react with PCl_5 and NH_4Cl in a slightly different manner. The $(PNCl_2)_n$/boron halide compositions tend to decompose when heated in open tubes at a faster rate than the other metal halide compositions. This effect may be the result of a different type of bonding.

An explanation of the difference between boron and the other elements under consideration may result from a comparison of their electronegativities. The electronegativity of B (2.0) is very close to that of P (2.1), whereas electronegativities of the other "metals" are significantly lower. Thus boron may replace phosphorous at one end of the $(PNCl_2)_n$ chain in the structure.

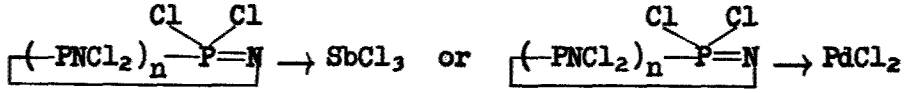


(where x is 1 less than the normal valency of M) so that the following structure is obtained for the $(PNCl_2)_n/BCl_3$ species



The above argument is speculative and further study will be needed before rigorous structural formulas can be assigned.

No reaction was observed when phosphonitrilic chloride trimer was heated with $SbCl_3$, $SnCl_4$, $PdCl_2$, or $CuCl_2$, indicating that cyclic complexes of the type



are not important in cases where high pyrolytic stability was found.

The hydrolytic stability of the $(PNCl_2)_n$/metal halide products varies approximately as the hydrolytic stability of the corresponding metal halide itself varies. The $(PNCl_2)_n$/metal halide products obtained with $SbCl_5$, $SbCl_3$, $AlCl_3$, $AlBr_3$, $TiCl_4$, BCl_3, and BF_3 are all vigorously hydrolyzed by water. Zinc chloride and $(PNCl_2)_n$/$ZnCl_2$ are both less reactive with water. This correlation indicates that the initial site of hydrolysis is the metal halide portion of the $(PNCl_2)_n$/metal halide molecule.

A comparison of liquid ranges of various metal halide stabilized phosphonitrilic chloride polymers is given in Table I. The results of thermal stability tests of $(PNCl_2)_n$/metal halide compositions in evacuated sealed "Pyrex" tubes are summarized in Table II. Viscosities at several temperatures for certain $(PNCl_2)_n$/metal halides are listed in Table III.

Aryloxy Derivatives of $(PNCl_2)_n$ Polymers

The chlorine atoms in phosphonitrilic chloride polymers can be readily replaced by alkoxy groups by the reaction of $(PNCl_2)_n$ with a sodium or potassium alkoxide (Ref. 11). Unfortunately, the alkoxy phosphonitriles are unstable at elevated temperatures, and chemically reactive. The preparation and properties of several aryloxy phosphonitriles have been described (Ref. 12, 13, 14). Their thermal and chemical stability was reported to be good but only in a qualitative manner.

The preparation of aryloxy phosphonitriles was reinvestigated and it was found that phenoxy and substituted phenoxy derivatives of $(PNCl_2)_n$ polymers could be obtained in yields of 70% or higher by reaction of $(PNCl_2)_n$ with the potassium salt of a phenol or substituted phenol in xylene at the reflux temperature. By this procedure phenoxy, o- and p-biphenyloxy, o- and p-chlorophenoxy, m- and p-phenoxyphenoxy, p-benzenesulfonylphenoxy, and m-trifluoromethylphenoxy phosphonitriles were prepared. The boiling points and melting or pour points of these compounds are given in Table IV.

Hexaphenoxytriphosphonitrile is a white crystalline solid melting at 115.0-115.5°C. and boiling at 290°C./0.14 mm. Octaphenoxytetraphosphonitrile was obtained as a white crystalline solid melting at 84.0-85.0°C. and boiling at 340°C./0.44 mm. It had a strong tendency to supercool to a viscous liquid at 25°C. and crystallized only on long standing or agitation. Based on the freezing properties of the trimer and tetramer, it is probable that the pentameric and higher phosphonitrilic phenoxide polymers would be noncrystalline or have very low melting points. As the trimeric and tetrameric phosphonitrilic phenoxide could be readily distilled at reduced pressure, it is reasonable to expect that some of the higher polymers could also be purified by distillation.

Two possible routes to liquid aryloxy phosphonitriles appeared possible: (1) synthesis of completely phenoxy derivatives of $(PNCl_2)_n$ polymers where n is 5 or higher, or where n is mixed, e.g., n = 3, 4, 5, 6, ··· and

(2) synthesis of unsymmetrical triphosphonitriles, e.g., mixed phenoxy and substituted phenoxy derivatives. The former approach was tested by making a phenoxy derivative of a $(PNCl_2)_n$ liquid having an average n value of approximately 7. The product was a very viscous orange liquid with a pour point near 28°C. Fractionation of this product was not attempted, but the results indicated that high fluidity could be expected only for n values near 5. The second approach was then investigated in some detail.

Several derivatives of $(PNCl_2)_3$ in which all six chlorines were replaced by identical substituted phenoxy groups were made in order to ascertain the desirability of different substituted phenols as desymmetrizing agents for phenoxy phosphonitriles. Hexa(o-biphenylyloxy)triphosphonitrile was obtained as a brown, noncrystalline, solid product with a pour point of about 70°C. It was stable to 5% aqueous KOH and became black on heating to 430°C. The sample could not be purified by either crystallization or distillation.

Hexa-m-phenoxyphenoxytriphosphonitrile and hexa-p-phenoxyphenoxytriphosphonitrile were noncrystalline, tacky solids at 25°C. with pour point values near 50°C. The colorless meta compound was found to change little during 6 hours at 400°C. under a dry, oxygen-free, nitrogen atmosphere. The para compound as prepared was light brown and decomposed rapidly at 400°C. The difference in stability of these two materials is attributed to impurities in the para isomer and not to the different position of substitution. No attempt was made to distill either of these high boiling materials.

A very high thermal stability has been reported (Ref. 15) for bis(o-chlorophenyl)-4-biphenylyl phosphate. Thus the o-chlorophenoxy group was investigated by preparing pentaphenoxy-mono(o-chlorophenoxy)triphosphonitrile. This compound melts at 106.5-107.5°C. and boils at 305°C./0.21 mm. Its thermal stability is slightly less than that of hexaphenoxytriphosphonitrile; hence the o-chlorophenoxy group is not considered a desirable substituent in aryloxy phosphonitriles.

Hexa(p-chlorophenoxy)triphosphonitrile (m.p. = 155-156°C.) was prepared and found to have a lower limit of thermal stability than pentaphenoxy-mono(o-chlorophenoxy)triphosphonitrile. This is the expected result of increasing the number of chlorine to phenyl bonds.

The above reactions showed that the potassium salts of chlorophenols, phenylphenols, and phenoxyphenols all react with $(PNCl_2)_3$ at approximately the same rate as does potassium phenoxide. Thus, mixtures of phenol and these substituted phenols should give phosphonitrile products having a statistical distribution of aryloxy substituents.

Reaction of a mixture of potassium phenoxide and sodium o-biphenylyl oxide in 5 to 1 mole ratio with $(PNCl_2)_3$ gave a pale yellow, viscous liquid which was obtained by distillation at 320 to 337°C./0.6 mm. It had a pour point slightly below room temperature and could be heated to 400°C. without discoloration. However, after 10 hours at 427°C. in an evacuated sealed "Pyrex" tube, it became a black solid. The major portion of the sample was assumed to be pentaphenoxy-mono(o-biphenylyloxy)triphosphonitrile.

Since it is reasonable to expect the meta- and para-biphenylyloxy groups to have higher thermal stability than the ortho-biphenylyloxy group, a phosphonitrilic

derivative involving a combination of p-biphenylyloxy and phenoxy groups was prepared. This product was a white crystalline solid melting at 96-98°C. and boiling at ~313°C./0.16 mm. The increased symmetry of the p-biphenylyloxy group over that of the o-biphenylyloxy was apparently sufficient to give a crystalline compound. Results of elemental analysis were consistent with the proposed composition of the desired product, viz., pentaphenoxy-mono(p-biphenylyloxy)triphosphonitrile.

A mixture of aryloxy phosphonitriles consisting of approximately 80% pentaphenoxy-mono(m-phenoxyphenoxy)triphosphonitrile, and 10% each of hexaphenoxytriphosphonitrile and tetraphenoxy-di(m-phenoxyphenoxy)triphosphonitrile (designated as Mixture I) was prepared in good yield from reaction of $(PNCl_2)_3$ with a mixture of phenol and m-phenoxyphenol (in 5 to 1 mole ratio) and KOH. Mixture I is a colorless, viscous liquid having a pour point of 10°C. and boiling between 316 and 345°C./0.18 mm.

A 200-g. sample of Mixture I was evaluated by ASD as a possible high temperature fluid candidate; the results are given in Table V. When compared to the polyphenyl ethers, one of the best classes of high temperature fluids presently available, Mixture I has several advantages such as low evaporative loss, high flash and fire points, and good viscosity properties at high temperatures, all of which are associated with the high molecular weight and correspondingly low vapor pressure of this phosphonitrile composition. Improvements in low temperature viscosity characteristics and stability to oxidation and pyrolysis at elevated temperatures would greatly increase the utility of aryloxy phosphonitriles such as Mixture I.

The para-substituted counterpart of Mixture I, consisting of approximately 80% pentaphenoxy-mono(p-phenoxyphenoxy)triphosphonitrile and 10% each of hexaphenoxytriphosphonitrile and tetraphenoxy-di(p-phenoxyphenoxy)triphosphonitrile (designated Mixture II) was prepared by a two-step procedure from $(PNCl_2)_3$. First, interaction of phenol and p-chlorophenol, in 5 to 1 mole ratio, with $(PNCl_2)_3$ yielded a mixture with a main component of pentaphenoxy-mono(p-chlorophenoxy)triphosphonitrile and minor portions of hexaphenoxytriphosphonitrile and tetraphenoxy-di(p-chlorophenoxy)triphosphonitrile. Second, this product was treated with potassium phenoxide using copper powder catalyst at 250°C. to give the desired Mixture II. Use of p-bromophenol in the first step was found to work as well. Mixture II has approximately the same physical and chemical properties as Mixture I. It is interesting that the para-substituted material is not crystalline.

Thermal stability tests of other phenoxyphenoxy phosphonitriles indicated that the meta-phenoxyphenoxy group might be more stable at elevated temperatures than the para-phenoxyphenoxy group, but Mixture II was found to have approximately the same thermal stability as Mixture I when tested in evacuated sealed "Pyrex" tubes at 400°C.

A phosphonitrile incorporating the p-benzenesulfonylphenoxy group was made by reaction of equimolar quantities of hexaphenoxytriphosphonitrile and benzenesulfonyl chloride. Analysis indicates that the desired pentaphenoxy-p-benzenesulfonylphenoxytriphosphonitrile was obtained. It had a high pour point (30°C.) and poor thermal stability; thus, the p-benzenesulfonylphenoxy group was ruled out as a useful desymmetrizing group for aryloxy phosphonitriles.

Diphenyl-tetrachlorotriphosphonitrile was prepared by the method of Bode and Bach (Ref. 16) and reacted with potassium phenoxide to give diphenyl-tetraphenoxy-triphosphonitrile (both phenyl groups are assumed to be bonded to the same phosphorous) as a white crystalline solid, m.p. = 97-98°C. No attempt was made to distill the compound although this should be possible since it does not decompose rapidly below 400°C.

Trifluoromethylphenoxy Phosphonitriles

An investigation of the m-trifluoromethylphenoxy group has led to very interesting phosphonitrile products. Reaction of $(PNCl_2)_3$ with m-hydroxybenzotrifluoride and KOH in xylene under reflux gave a 71% yield of hexa(m-trifluoromethylphenoxy)triphosphonitrile a colorless liquid having a pour point of -5°C. and a boiling point of 250°C./0.2 mm. Hg. Replacement of $(PNCl_2)_3$ by $(PNCl_2)_4$ in the above reaction gave octa(m-trifluoromethylphenoxy)tetraphosphonitrile a white crystalline solid melting at 54-55°C. and boiling at 280°C./0.20 mm. It readily supercools as a colorless liquid having a pour point of -10°C. The m-trifluoromethylphenoxy phosphonitriles are analogous to the chlorophosphonitriles in that the tetramer is more crystalline than the trimer. The situation is reversed for phenoxyphosphonitriles.

A mixture of $\overline{[PN(m\text{-}CF_3C_6H_4O)_2]}_n$ polymers (where n = 3, 4, 5, 6, and probably higher) was obtained by reaction of a $(PNCl_2)_n$ liquid sample (n = 3, 4, 5, 6 ····) with m-hydroxybenzotrifluoride and KOH in p-xylene. The product was separated into fractions ranging in boiling point from 250 to 375°C./0.07 mm. Preliminary property determinations indicate that trimer, tetramer, pentamer, hexamer, and perhaps heptamer were thus distilled.

Reaction of $(PNCl_2)_3$ with phenol and m-hydroxybenzotrifluoride (mole ratio of 2 to 1) and KOH in xylene gave a 70% yield of colorless liquid having a pour point of -2°C. This material was distilled between 252 and 270°C./0.2 mm. and is assumed to be a mixture of triphosphonitriles having approximately a statistical distribution of phenoxy and m-trifluoromethylphenoxy groups (the rate of reaction of m-trifluoromethylphenol and KOH with $(PNCl_2)_3$ appears to be approximately the same as for phenol and KOH). A mixed phenoxy and m-trifluoromethylphenoxy derivative of a mixture of phosphonitrile trimer (~85%) and tetramer (~15%) where the phenoxy and m-trifluoromethylphenoxy groups are statistically distributed in the ratio of 2 to 1, respectively, on the trimeric and tetrameric phosphonitrile rings was also made.

All of the m-trifluoromethylphenoxy phosphonitriles discussed above darkened on heating to 400°C. for 10 hours in evacuated sealed "Pyrex" tubes. However, there were no solids formed and little change in viscosity occurred. This stability is somewhat surprising since the CF_3 group greatly lowers thermal stability when incorporated in polyphenyl ethers (Ref. 17).

Relative Properties of Aryloxy Phosphonitriles

Comparison of the properties of the aryloxy phosphonitriles has been made and the results of thermal stability tests in evacuated sealed "Pyrex" tubes are given in Table VI. (Hexaphenyltriphosphonitrile was included for comparison.) The highest stability was found for hexaphenyltriphosphonitrile. Next, the phenoxy, p-biphenylyloxy, m- and p-phenoxyphenoxy, and m-trifluoromethylphenoxy

phosphonitrile derivatives all appear to have approximately the same thermal stability. The o-biphenylyloxy, chlorophenoxy, and benzenesulfonylphenoxy derivatives were of lower stability and consequently of less interest.

The low temperature viscosity and pour point are generally high for molecules with molecular weights as high as the aryloxy phosphonitriles. Thus it is important to utilize any factors that might lead to greater fluidity at low temperatures without sacrificing thermal stability. Table VII lists the pour points of several of the aryloxy phosphonitriles. The benzenesulfonylphenoxy group leads to the highest increase in pour point. This effect is presumably due to the highly dipolar nature of the sulfone linkage causing a certain amount of molecular association. The biphenylyloxy group imparts a higher viscosity than the phenoxyphenoxy group because of the inflexibility of the phenyl to phenyl linkage. This effect is exemplified by the vast difference in fluidity of polyphenyls and polyphenyl ethers. Hexaphenoxytriphosphonitrile can be easily supercooled below its melting point while hexaphenyltriphosphonitrile cannot. The most striking effect on the pour point resulted from the introduction of the m-trifluoromethylphenoxy group. The pour point of hexa-m-trifluoromethylphenoxytriphosphonitrile is 15°C. lower than that of hexaphenoxytriphosphonitrile.

All of the aryloxy phosphonitriles prepared have approximately the same hydrolytic stability, i.e., they are stable to hot 5% aqueous KOH. Furthermore, they have low vapor pressures, generally boiling above 300°C. at 1.0 mm. Hg. The trifluoromethylphenoxy derivatives have the highest vapor pressures (hexa-m-trifluoromethylphenoxytriphosphonitrile boils at 250°C./0.2 mm. Hg) which is characteristic of fluorocarbons.

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TABLE I

Comparison of Liquid Ranges
of $(PNCl_2)_n$/Metal Halides

Compound	Pour Point (°C.)	Boiling Point (°C./mm. Hg)
$(PNCl_2)_n/SbCl_3$	~80 (m.p.)	> 500/760
$(PNCl_2)_n/SbCl_3$*	< 0	> 560/760
$(PNCl_2)_n/AlCl_3$*	< 0	> 588/760
P_2NAlCl_8*	~27 (m.p.)	245/0.1
$P_4N_3AlCl_{12}$*	-55	420/1.1
$(PNCl_2)_n/AlBr_3$	-49	> 500/760
$(PNCl_2)_n/BCl_3$	-44	> 550/760
$(PNCl_2)_n/BF_3$	-52	> 500/760
$(PNCl_2)_n/TiCl_4$	-26	> 526/760
$(PNCl_2)_n/FeCl_3$	-46	> 670/760
$(PNCl_2)_n/TlCl_3$	-50	> 450/1.0
$(PNCl_2)_n/ZnCl_2$	- 5	> 500/0.5
$(PNCl_2)_n/SnCl_4$	< 25	> 520/760
$(PNCl_2)_n/CuCl$	< 25	> 400/760

* Prepared in sym-tetrachloroethane solvent; all other compounds were prepared in 1,2,4-trichlorobenzene.

TABLE II

Thermal Stability of $(PNCl_2)_n$/Metal Halides in Evacuated Sealed "Pyrex" Tubes

Compound	Temp. (°C.)	Time (hrs.)	Result
$(PNCl_2)_n$ liquid	400	0.1	Black polymerized rubber.
$(PNCl_2)_n/SbCl_3$	538	10	No color change; fluid; small amount of dark solid formed.
$(PNCl_2)_n/AlCl_3$	538	10	No color change; fluid; small amount of dark solid formed.
$(PNCl_2)_n/BCl_3$	538	10	No darkening; fluid; white crystals slowly forming at 25°C.
$(PNCl_2)_n/BCl_3$	600	10	Color changed from pale yellow to pale greenish yellow; rubber.
$(PNCl_2)_n/BF_3$	538	10	No darkening; fluid; some white crystals formed at 25°C.
$(PNCl_2)_n/TiCl_4$	538	10	Color changed slightly from brown to greenish brown; fluid which crystallized on long standing at 25°C.
$(PNCl_2)_n/ZnCl_2$	600	10	No color change; fluid at 25°C.

TABLE III

Viscosities of $(PNCl_2)_n$/Metal Halides

Compound	Viscosity in cs. at 0°F.	77°F.	100°F.	210°F.	400°F.	700°F.
$(PNCl_2)_n/AlCl_3$	169.8	30.7	20.8	5.87	1.88	0.73
$(PNCl_2)_n/ZnCl_2$		2433	906	65.3	9.44	
$(PNCl_2)_n/BCl_3$		46.2	29.7	7.45		
$(PNCl_2)_n/BF_3$		29.7	22.9	6.46		
$(PNCl_2)_n/FeCl_3$		30.2	20.2	5.76		
$(PNCl_2)_n/TlCl_3$		28.6	18.0	4.91		

TABLE IV

Comparison of Liquid Ranges of New Aryloxy Phosphonitriles

Compound	Pour Point (°C.)	b.p. (°C./mm. Hg)
$P_3N_3(C_6H_5O)_5(m\text{-}C_6H_5OC_6H_4O)_1$	10	328-330/0.30
Mixture I (see text)	10	315-362/0.35
Mixture II (see text)	10	315-362/0.35
$P_3N_3(m\text{-}C_6H_5OC_6H_4O)_6$	50	-
$P_3N_3(p\text{-}C_6H_5OC_6H_4O)_6$	50	-
$P_3N_3(o\text{-}C_6H_5C_6H_4O)_6$	70	-
$P_3N_3(C_6H_5O)_4(C_6H_5)_2$	100 (m.p.)	-
$P_3N_3(C_6H_5O)_5(o\text{-}ClC_6H_4O)_1$	108 (m.p.)	305/0.21
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5C_6H_4O)_1$	100 (m.p.)	360/0.60
$P_3N_3(C_6H_5O)_5(o\text{-}C_6H_5C_6H_4O)_1$	23	335/0.65
$P_3N_3(C_6H_5O)_{\sim4}(m\text{-}CF_3C_6H_4O)_{\sim2}$	-2	252-270/0.20
$P_3N_3(m\text{-}CF_3C_6H_4O)_6$	-5	250/0.20
$P_4N_4(m\text{-}CF_3C_6H_4O)_8$	56 (m.p.)	280/0.20
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5SO_2C_6H_4O)_1$	30	365/0.23

TABLE V

Results of ASD Evaluation of Mixture I

(Major Component: Pentaphenoxy-m(phenoxyphenoxy)triphosphonitrile)

1. Pour point (°F.) = +60

2. Flash point (°F.) = 640

3. Fire point (°F.) - did not obtain (appeared to boil at 765°F. to 770°F.)

4. Viscosity (cs.) °F. at 100 - 1598
   210 - 29.8
   400 - 3.34
   700 - 0.917

5. Shell-4-ball wear - conducted at Wyandotte at 400°F., 1 hr., 1200 r.p.m.
   40 kg. = 1.0 mm. wear scar
   MIL-L-9236 base stock under same conditions = 1.0 mm. wear scar

6. Thermal - DTA 730°F.
   - Isoteniscope 790°F. (rerun by Monsanto)

7. Oxidation stability (10 cc.) at 500°F., 6 hrs., 1 liter air/hr.
   Acid value - no change
   Viscosity change = +22 cs. from original
   Color change = (to slight pink from clear)
   Oxidation stability is good. However, ethers exhibit no change at all in this test.

8. Properties of a grease utilizing 10% carbon black thickener
   a. Unworked penetration 368
   b. Dropping point above 700°F.
   c. Evaporation (22 hrs. at 600°F.) 48.4%
   d. Separation (30 hrs. at 600°F.) 62.1%

TABLE VI

Thermal Stability of Aryloxy Phosphonitriles in Evacuated Sealed "Pyrex" Tubes

Compound	Temp. (°C.)	Time (hrs.)	Result
$P_3N_3(C_6H_5O)_6$	400	10	Slight darkening; I.R. indicates some formation of $P_4N_4(C_6H_5O)_8$.
$P_4N_4(C_6H_5O)_8$	400	10	Slight darkening; I.R. indicates some formation of $P_3N_3(C_6H_5O)_6$.
$P_3N_3(p\text{-}ClC_6H_4)_6$	400	1	Became very dark brown.
$P_3N_3(C_6H_5O)_5(o\text{-}ClC_6H_4O)_1$	400	10	Became dark brown; large increase in viscosity.
$P_3N_3(C_6H_5O)_5(o\text{-}C_6H_5C_6H_4O)_1$	400	10	Became dark green; very large increase in viscosity.
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5C_6H_4O)_1$	400	10	Slight darkening; tacky and non-crystalline at 25°C.
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5SO_2C_6H_4O)_1$	400	1	Became black.
$P_3N_3(C_6H_5O)_4(C_6H_5)_2$	400	10	Became a dark brown, noncrystalline solid.
$P_3N_3(C_6H_5O)_5(m\text{-}C_6H_5OC_6H_4O)_1$	400	10	Slight darkening; I.R. indicates some formation of tetrameric phosphonitrile; 67% increase in viscosity at 210°F.
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5OC_6H_4O)_1$	400	10	Slight darkening; I.R. indicates some formation of tetrameric phosphonitrile.
$P_3N_3(C_6H_5O)_4(m\text{-}CF_3C_6H_4O)_2$	400	10	Became brown; I.R. indicates some formation of tetrameric phosphonitrile; 12% increase in viscosity at 210°F.
$P_3N_3(m\text{-}CF_3C_6H_4O)_6$	400	10	Became brown; I.R. indicates some formation of tetrameric phosphonitrile; 1% increase in viscosity at 210°F.
$P_4N_4(m\text{-}CF_3C_6H_4O)_8$	400	10	Became brown; I.R. shows formation of some trimeric phosphonitrile; 12% decrease in viscosity at 210°F.
$P_3N_3(C_6H_5)_6$	400	10	No change.

TABLE VII

Pour Points of Aryloxy Phosphonitriles

Compound	Pour Point (°C.)
$P_3N_3(C_6H_5O)_6$	10 (supercooled)
$P_3N_3(C_6H_5O)_5(m\text{-}C_6H_5OC_6H_4O)_1$	10
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5OC_6H_4O)_1$	10
$P_3N_3(m\text{-}C_6H_5OC_6H_4O)_6$	50
$P_3N_3(p\text{-}C_6H_5OC_6H_4O)_6$	50
$P_3N_3(o\text{-}C_6H_5C_6H_4O)_6$	70
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5SO_2C_6H_4O)_1$	30
$P_3N_3(C_6H_5O)_4(m\text{-}CF_3C_6H_4O)_2$	-2
$P_3N_3(m\text{-}CF_3C_6H_4O)_6$	-5
$P_4N_4(m\text{-}CF_3C_6H_4O)_8$	-10 (supercooled)

PHOSPHORUS-CONTAINING INORGANIC AND SEMIORGANIC POLYMERS

ABSTRACT

The synthesis of new phosphorus-containing polymers expected to have high thermal stability was the object of this research. Accompanying this effort has been a study of model compounds and prototype reactions, to obtain information on bond formation and bond stability.

Among phosphorus-containing compounds, those containing the P-C-P linkage have unusual thermal stability. For example, several methylene and phenylene bis diphenylphosphine oxides are stable to 425-450°C (797-842°F). For this reason, the preparation of P-C-P type polymers by addition and condensation reactions using a variety of monomers under widely varied conditions was attempted.

Fundamental studies of the chemistry of P-C compounds are described. Reorganization studies indicated that the C_6H_5-P bond is probably stable to at least 400°C.

Polymers of the polyamide type with phosphorus in the backbone are described. Some prepared from a bibenzimidazole were stable to 425-450°C. (797-842°F), albeit of low molecular weight. Model compounds containing the phosphorus-imidazole bond showed stabilities as high as 500°C. (932°F.).

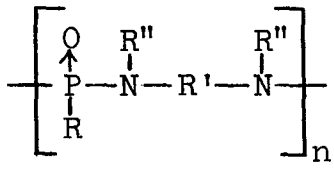
PART I. CONDENSATION POLYMERS FROM DIFUNCTIONAL PHOSPHORUS COMPOUNDS AND DIAMINES

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INTRODUCTION

Polyamides containing phosphorus appeared to be a promising type of linear polymer containing the very stable PN bond. Reactions were therefore investigated which would yield polymers of the type

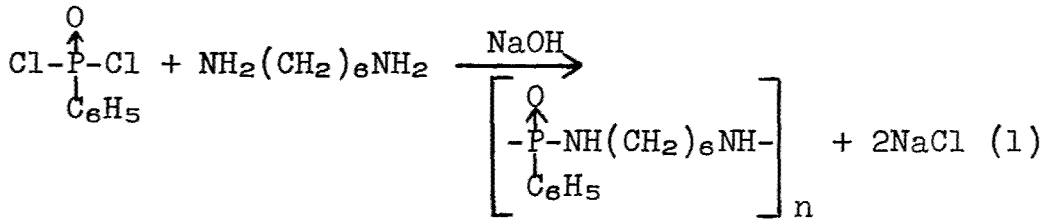


with the desired thermal stability to be obtained through selection of R, R' and R".

RESULTS

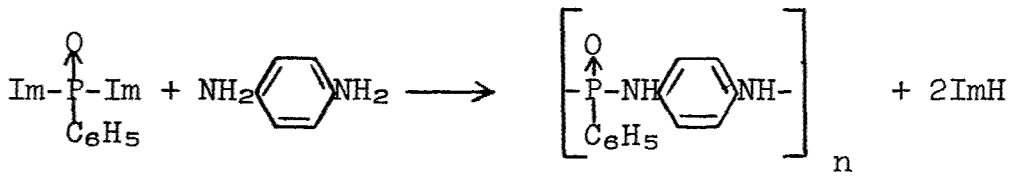
Preparation of Polymers

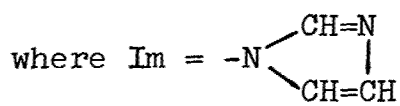
The reaction of suitable difunctional phosphorus compounds with diamines was used to form polymers. Thus, a dichlorophosphorus compound (e.g., phenylphosphonic dichloride) was reacted with 1,6-hexanediamine in the presence of a neutralizing agent such as sodium hydroxide or pyridine.



This method was used with several variations: reaction in an anhydrous medium with a homogeneous neutralizer such as triethylamine or with a dispersed phase neutralizer such as sodium hydride, and reaction in a two-phase (interfacial) system using aqueous sodium hydroxide as the neutralizer. The last variation, which has been investigated in detail by Wittbecker and Morgan[1] using reactants not containing phosphorus, was successful with aliphatic and aryl-aliphatic diamines. With aromatic diamines, however, polymer formation was precluded by preferential reaction of the dichloro compound with water.

Another method which proved useful for aromatic diamines involved transamination: heating a diimidazolyl phosphorus compound with a diamine caused release of the imidazole and formation of the polymer. This approach has been pursued by Staab[2] and coworkers in preparing nonpolymeric materials.





Typical polymers and their properties are listed in Table 1.

Properties of Polymers

As shown in Table 1, the various polymers varied widely in softening point and decomposition point. In general, the polymers from aliphatic diamines had low softening points and decomposed below 325°C. Those containing aromatic moieties softened at higher

Table 1.

Polyamides Containing Phosphorus

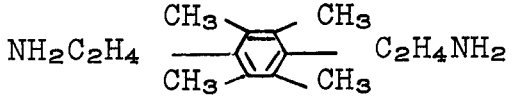
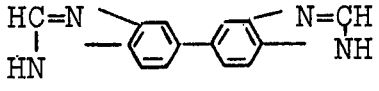
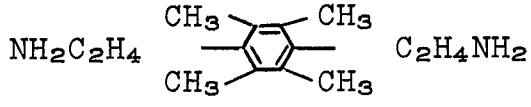
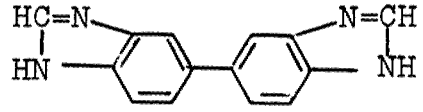
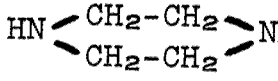
Phosphorus Compound	Diamine	Method[1]	Yield	Visc. η_{inh}	Soft. Pt., °C.	Decomp. Pt., °C
$C_6H_5P(O)Cl_2$	$NH_2(CH_2)_6NH_2$	A	93	0.14[2]	90-100	300
$C_6H_5P(O)Cl_2$	$NH_2(CH_2)_6NH_2$	B	42	0.05		
"	$C_4H_9NH(CH_2)_6NH_2$	A	61	0.04	75	320
"	$NH_2(CH_2)_3NH_2$	A	34	0.03	60	260
"	$NH_2(CH_2)_3O(CH_2)_3NH_2$	A	62	0.10[3]	60	260
"	$NH_2(CH_2)_3NH(CH_2)_3NH_2$	A	50	0.03	70	295
"	$NH_2(CH_2)_2NH(CH_2)_2NH_2$	A	11		100	285
"	$NH_2CH_2C_6H_4CH_2NH_2$	A	48	0.06	120	270
"		A	96	0.15	210	320
"		B	94		280	275
$C_6H_5P(S)Cl_2$	$NH_2(CH_2)_6NH_2$	A	75	0.05	80	225
$C_6H_5OP(O)Cl_2$	$NH_2(CH_2)_6NH_2$	A	95	0.17[4]	70	325
"		A	100	0.21	170	325

Table 1. (Contd.)

Phosphorus Compound	Diamine	Method[1]	Yield	Visc. inh	Soft. Pt., °C	Decomp. Pt., °C.
$C_6H_5N(CH_3)P(O)Cl_2$		B	100	0.02	>440	430-450
$(C_6H_5)_2NP(O)Cl_2$	"	B	16		>430	430
$(C_6H_5)_2NPCl_2$	"	B	28		225	320
$C_6H_5P(O)Im_2$	$NH_2(CH_2)_6NH_2$	C	35	0.08	80-85	250
$C_6H_5P(O)Im_2$	$NH_2C_6H_4NH_2$	C	83	0.05	245-255	350
"	$NH_2C_6H_4CH_2C_6H_4NH_2$	C	67	0.07	185-190	370-390
"	$NH_2C_6H_4C_6H_4NH_2$	C	77		210-215	330
"		C	51	0.08	185-190	210
"	$C_6H_5NHC_6H_4NHC_6H_5$	C	No reaction			

[1] Methods A - Two-phase (interfacial) condensation
B - Anhydrous condensation
C - Transamination

[2] Ebulliometric molecular weight: 2600

[3] Ebulliometric molecular weight: 1285

[4] Ebulliometric molecular weight: 2160

temperatures and were more stable. For example, 4,4'-methylenedianiline gave a polymer softening at 185-190°C. and decomposing at 370-390°C.

The most stable polymers were those prepared from 5,5'-bibenzimidazole, which did not soften at their decomposition points, 430-450°C.

Based on their viscosities, it appears that the degree of polymerization of all these polymers was low. This was also shown in some instances by ebulliometric molecular weight determinations.

Model Reactions and Compounds

Prototype condensations were conducted with monofunctional reactants to learn something about the problems that would be encountered in polymer-forming reactions. Incomplete reactions or reactions involving undesirable by-products are undesirable in forming condensation polymers.

Thus, the reaction of various chlorophosphorus compounds with aromatic amines proceeded as follows:

$$C_6H_5P(O)Cl_2 + 4C_6H_5NH_2 \xrightarrow{80°}$$

$$C_6H_5P(O)(NHC_6H_5)_2\ (98\%) + 2C_6H_5NH_2\cdot HCl \qquad (2)$$

$$C_6H_5OP(O)Cl_2 + 4C_6H_5NH_2 \xrightarrow{RT}$$

$$C_6H_5OP(O)(NHC_6H_5)_2\ (70\%) + 2C_6H_5NH_2\cdot HCl \qquad (3)$$

$$C_6H_5N(CH_3)P(O)Cl_2 + 4C_6H_5NH_2 \xrightarrow{70°}$$

$$C_6H_5N(CH_3)P(O)(Cl)NHC_6H_5\ (30\%) + C_6H_5NH_2\cdot HCl \qquad (4)$$

$$C_6H_5P(O)Cl_2 + \text{xs } C_6H_5NHCH_3 \xrightarrow{RT}$$

$$C_6H_5P(O)(Cl)N(CH_3)C_6H_5\ (90\%) + C_6H_5NHCH_3\cdot HCl \qquad (5)$$

$$POCl_3 + \text{xs } C_6H_5NHCH_3 \xrightarrow{180°}$$

$$(C_6H_5NCH_3)_3PO\ (43\%) + C_6H_5NHCH_3\cdot HCl \qquad (6)$$

$$+ (C_6H_5NH)_3PO\ (16\%)$$

In reaction (4) the phosphoramidic chloride appears relatively unreactive compared to nonamidic chlorides (cf. reactions (2) and (3)). This is attributed to the ability of the N-methylanilido radical to reduce the positive character of the phosphorus atom. This is further illustrated in the following transamination reactions:

$$C_6H_5P(O)Im_2 + C_6H_5NH_2 \xrightarrow{70°}$$

$$C_6H_5P(O)(NHC_6H_5)_2 + 2ImH \ (78\%) \qquad (7)$$

$$C_6H_5P(O)Im_2 + C_6H_5NHCH_3 \xrightarrow{70°}$$

$$C_6H_5P(O)(Im)N(CH_3)C_6H_5 \ (52\%) + IMH \qquad (8)$$

$$C_6H_5P(O)Im_2 + (C_6H_5)_2NH \xrightarrow{70°}$$

$$C_6H_5P(O)(Im)N(C_6H_5)_2 \ (68\%) + IMH \qquad (9)$$

$$C_6H_5N(CH_3)P(O)Im_2 + C_6H_5NH_2 \xrightarrow{70°} \text{No reaction} \qquad (10)$$

In reaction (8) substitution by one N-methylanilido group reduced the positive character of phosphorus atom to such an extent that no further substitution occurred. The same was true in reaction (9). In the absence of the N-methylanilido group, disubstitution took place, as indicated in reaction (7).

The use of sodium derivatives in preparing amides appears promising. In comparison with reaction (6), the use of a sodium amide derivative gave a better yield of the triamide:

$$POCl_3 + 3C_6H_5N(CH_3)Na \xrightarrow{RT} (C_6H_5NCH_3)_3PO \ (62\%) + 3NaCl \qquad (11)$$

Also, the formation of N,N',N"-phenylphosphoric triamide was not encountered in the latter reaction.

Another successful use of an N-sodium derivative was:

$$(C_6H_5O)_2P(O)Cl + NaN(CH_3)P(O)(OC_6H_5)_2 \xrightarrow{80°}$$

$$(C_6H_5O)_2P(O)N(CH_3)P(O)(OC_6H_5)_2 \ (23\%) + NaCl \qquad (12)$$

The analogous reaction of the free amide did not go:

$$(C_6H_5O)_2P(O)Cl + HN(CH_3)P(O)(OC_6H_5)_2 \qquad (13)$$

Model compounds have been used to compare the relative stability of chemical bonds. Table 2 lists a series of such compounds, one of which decomposes above 500°C.

Table 2.

Thermal Stability of Model Compounds

	Decomp. Pt., °C.
$C_6H_5P(O)(NHC_6H_5)_2$	210
$C_6H_5P(O)\begin{matrix}N(CH_3)C_6H_5\\ Im\end{matrix}$	> 460
$C_6H_5P(O)\begin{matrix}N(C_6H_5)_2\\ Im\end{matrix}$	> 500

New Compounds

New compounds prepared under this contract are listed in Table 3. X-ray diffraction data for many of these compounds have been submitted for publication.

Table 3.

New Compounds Prepared

Compound	m.p., °C	b.p., °C/mm
Disodium phenylphosphonate dihydrate		
Monosodium phenylphosphonic acid		
N-1,3-Propanediamine phenylphosphonamidic acid	248-50	
N-1,3-Diamino-2-propanol phenylphosphonamidic acid	204-7	
1,2-Propanediamine salt of phenylphosphonic acid	214-17	
1,2-Propanediamine salt of phenylphosphonic acid, 1.5-hydrate	194-8	
1,3-Propanediamine salt of phenylphosphonic acid, 1.5-hydrate	238-42	
1,3-Diamino-2-propanol salt of phenylphosphonic acid	217-21	
N-Cyclohexyl phenylphosphonamidic acid	235-55	

Table 3. (Contd.)

Compound	m.p., °C.	b.p., °C/mm
1,3-Diethyl-2-phenyl-2-oxo-1,3,2-diazaphospholidine		155-75/2.5
N,N'-Dicyclohexyl methylphosphonothionic diamide	117-19	
Piperazine bis(phenylphosphonochloridic acid)	110-20	
N,N'-Dicyclohexyl phenylphosphonic diamide	164-7	
N-Methyl-N-phenyl-N'-phenylphosphorodiamidic chloride	162-3	
N,N'-Dicyclohexyl-N"-methyl-N"-phenylphosphoric triamide	97-8	
N,N'-Dicyclohexyl-N",N"-dimethylphosphoric triamide	103-4	
N-Methyl-N-phenyl-P-phenylphosphonamidic chloride	40	
N-Cyclohexyl-N'-methyl-N"-phenyl-phenylphosphonic diamide	123-4	
Bis(1-imidazolyl)-phenylphosphine oxide	98-100	
P,P-Bis(1-imidazolyl)-N-Methyl-N-phenylphosphinic amide	122-3	
N,N'-Dicyclohexyl-phenylphosphonic diamide	162-4	
N,N'-Dimethyl-2,2,3,3,4,4-hexafluoro-1,5-diaminopentane	80-4	
N,N'-Dicyclohexyl-1,4-diaminocyclohexane	82-5	
P-1-Imidazolyl-N,N-diphenyl-P-phenylphosphinic amide	170-174	
P-1-Imidazolyl-N-methyl-N-phenyl-P-phenylphosphinic amide	108-120	
Hexaphenylphosphorous triamide	281-7	

Table 3. (Contd.)

Compound	m.p., °C.	b.p., °C/mm
Diphenylphosphoramidous dichloride	40-41	
Sodium diphenylamide monoammoniate		
5,5'-Bibenzimidazole	280-3	

SUMMARY

New phosphorus polyamides containing the bibenzimidazole moiety showed decomposition points of 425-450°C. (797-842°F.) and did not soften below this temperature. The molecular weights, as indicated by viscosities, were low. One model compound, P-1-imidazolyl-N,N-diphenyl-P-phenylphosphinic amide, showed a decomposition point of about 500°C (932°F.).

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PART II. P-C-P POLYMERS

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INTRODUCTION

Theoretical considerations indicate that molecular stability with respect to breaking and making of bonds can be divided into two categories:

a. Reaction of a compound with its environment with concomitant reduction in the over-all free energy at the temperature under question.

b. Structural reorganization in which neighboring molecules which are identical or belong to the same chemical family react with each other by exchange of individual ligands.

The widely accepted opinion that high values of bond energies in polymers will lead to good thermal stability is not correct for either reaction with the environment or structural reorganization. Instead of bond energies, however, the important factors with respect to the thermal stability are the activation energies and free energies of the reactions responsible for thermal degradation. Based on studies of the rate of reorganization of various ligands attached to triply and quadruply connected phosphorus atoms, it was concluded that quadruply connected structures with P-C-P linkages should exhibit a higher thermal stability than the majority of other phosphorus compounds. As a result, considerable effort has been spent on the preparation, separation and evaluation of such types of structures. Major difficulties have been encountered in forming the essential P-C-P bridge in polymers, a problem which has not yet been solved to any degree of satisfaction in spite of the study of many different, apparently promising synthetic approaches. Because it has not been possible to prepare and separate satisfactorily a pure polymer with P-C-P backbone, efforts have also been directed toward the preparation of dimers and trimers, the thermal stability of which would be a good indication of what can be expected from the longer polymers themselves. Thus, it was found that tetrasodium methylenediphosphonate $[(NaO)_2P(O)-CH_2(O)P(ONa)_2]$ was stable up to 500°C in a nitrogen atmosphere and up to 400°C in air. This result has been very encouraging to the research directed toward the preparation of P-C-P polymers.

In phosphorus chemistry, the more stable compounds are based on either a triply connected or quadruply connected phosphorus. Let us assume that the compound PX_3 (or alternately, say, OPX_3) undergoes structural reorganization with the compound PY_3 (or alternately OPY_3). In this case, the intermediate compounds PX_2Y and PXY_2 are formed. All of the multitude of reorganization reactions involving compounds from the group PX_3, PX_2Y, PXY_3, and PY_3 to give other compounds in this group can be derived from the following pair of equations for which equilibrium constants are given.

$$2PX_2Y = PX_3 + PXY_2 \qquad (1)$$

$$K_1 = (PX_3)(PXY_2)/(PX_2Y)^2 \qquad (2)$$

$$2PXY_2 = PY_3 + PX_2Y \qquad (3)$$

$$K_2 = (PY_3)(PX_2Y)/(PXY_2)^2 \qquad (4)$$

It has been shown mathematically[1] that K_1 and K_2 will equal 1/3 if the X's and Y's exchange with each other in a completely random manner. Examples of reorganization in phosphorus chemistry have been the subject of a recent series of papers from this laboratory.[1,2,3,4,5]

When X is chosen to be a monofunctional ligand (e.g. a chlorine atom) and Y a difunctional ligand (e.g. a bridging oxygen atom), the POX_2Y, $POXY_2$, and POY_3 groupings do not represent molecules but are parts of molecules--end groups, middle groups, and branch groups, respectively, making up polyphosphorus structures. It is quite obvious that these structural building units can never appear independently and must always be connected together in the form of molecules, so that equations 1 and 3 then represent only part of the over-all reorganization process--that part involving only change in functionality of a building unit. The true reorganization consists of the concomitant action of this change of functionality with a process which is mathematically equivalent to the sorting or reshuffling of these building units between and within molecules. Completely random reshuffling can be treated mathematically.

Although kinetic studies have not previously been carried out on the rates of reorganization, approximate values of these rates were obtained. Examples of this type of work are the following: The phosphorus trihalides show detectable reorganization at room temperature fifteen minutes after being mixed. Equilibrium appears to be reached in less than a week at room temperature. Correspondingly, the oxyhalides or thiohalides reorganize much more slowly at room temperature; but, at 265°F., detectable reorganization is found in about an hour, with equilibrium being achieved in less than a week. Reorganization of methyldichlorophosphine to give the equilibrium mixtures of PCl_3,

$(CH_3)PCl_2$, $(CH_3)_2PCl$, and $(CH_3)_3P$ is so slow at 450°F. that no chemical change could be detected after 65 hours, with equilibrium taking much longer. However, at 575°F., equilibrium is achieved in 65 hours. At this same temperature, methylthionophosphonic dichloride shows no appreciable reorganization.

From these types of studies, several broad conclusions were made: First, it appears that the rate or reorganization of various bonds to phosphorus lie in the following order:

$$P - F > P - Cl > P - Br > P - S > P - O \gg P - C$$

Secondly, bonds to triply connected phosphorus reorganize much faster than bonds to quadruply connected phosphorus. This means that chain structures based on P - C - P linkages, with the phosphorus being quadruply connected, should exhibit a higher order of thermal stability than the majority of compounds based on either carbon or phosphorus.

DISCUSSION

This research included a number of different attacks on the general problem of producing polymeric structures containing phosphorus. Among them are studies of compounds of the following types: P-C-P, P-C-S-P, P-C-O-P, polyphosphinates, polyphosphines, phosphonium salts, phosphosilicones, P-N-C-P polymers, and P-B polymers.

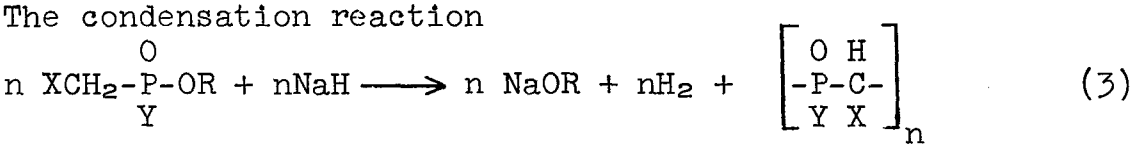
P-C-P Type Polymers

A satisfactory method for making polyphosphine oxides or sulfides has not been found. The most promising reaction is the condensation of methyl, chloromethylphosphinic chloride with zinc or magnesium.

$$n\ Cl\text{-}\overset{\overset{O}{\|}}{\underset{CH_3}{P}}\text{-}CH_2Cl + n\ Mg \longrightarrow \left[\begin{matrix} O \\ -P- \\ CH_3 \end{matrix}\right]_n\!\!\!

phosphine could not be prepared.

The condensation reaction

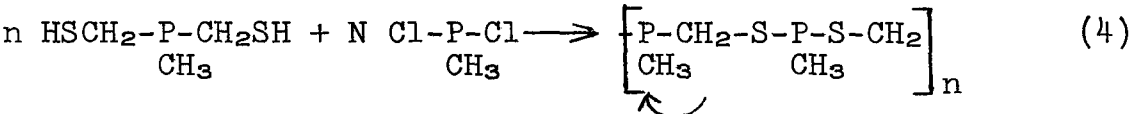


$$n\ XCH_2\text{-}\underset{\underset{Y}{|}}{\overset{\overset{O}{|}}{P}}\text{-}OR + nNaH \longrightarrow n\ NaOR + nH_2 + \left[\begin{matrix} O & H \\ -P & -C- \\ Y & X \end{matrix}\right]_n \qquad (3)$$

in which R = alkyl or aryl group, X = H or R and Y = R or OR was investigated. Various reaction products were obtained in complicated mixtures and definite proof of the presence of even small amounts of the desired structures could not be obtained.

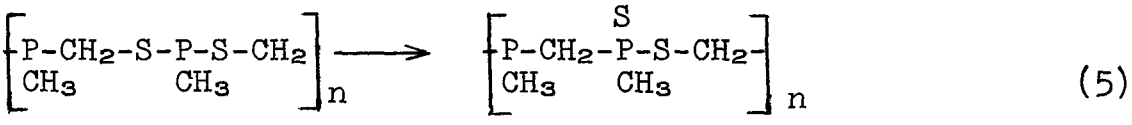
P-C-S-P Polymers

By reacting methyl, bishydrothiomethylphosphine with methyldichlorophosphine, a P-S-C-P type polymer can be expected to form:



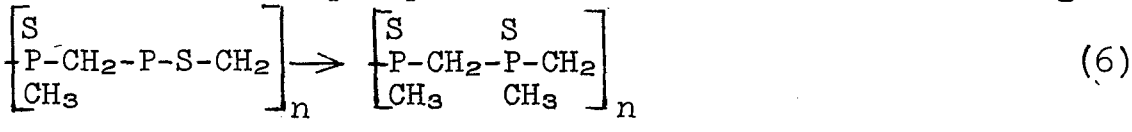
$$n\ HSCH_2\text{-}\underset{CH_3}{P}\text{-}CH_2SH + N\ Cl\text{-}\underset{CH_3}{P}\text{-}Cl \longrightarrow \left[\begin{matrix} P\text{-}CH_2\text{-}S\text{-}P\text{-}S\text{-}CH_2 \\ CH_3 \qquad\quad CH_3 \end{matrix}\right]_n \qquad (4)$$

Upon heating, an Arbusov type rearrangement can be expected to occur:



$$\left[\begin{matrix} P\text{-}CH_2\text{-}S\text{-}P\text{-}S\text{-}CH_2 \\ CH_3 \qquad\quad CH_3 \end{matrix}\right]_n \longrightarrow \left[\begin{matrix} \qquad\quad S \\ P\text{-}CH_2\text{-}P\text{-}S\text{-}CH_2 \\ CH_3 \qquad CH_3 \end{matrix}\right]_n \qquad (5)$$

The sulfur in the nonbridging position is attached to a phosphorus connected to two carbon atoms and one other sulfur. According to previous findings, it would be expected that this sulfur will be attracted by the triply connected phosphorus atoms which are bonded to three carbon atoms, thus freeing the isolated position of the first phosphorus for another Arbusov rearrangement:

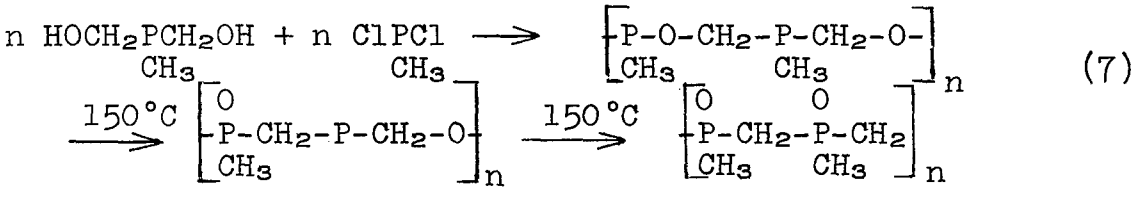


$$\left[\begin{matrix} S \\ P\text{-}CH_2\text{-}P\text{-}S\text{-}CH_2 \\ CH_3 \end{matrix}\right]_n \longrightarrow \left[\begin{matrix} S \qquad S \\ P\text{-}CH_2\text{-}P\text{-}CH_2 \\ CH_3 \qquad CH_3 \end{matrix}\right]_n \qquad (6)$$

A major problem in this scheme is the preparation of the starting material methyl, bishydrothiomethylphosphine. Although methyl bis(hydroxymethyl)phosphine was easily prepared from methyl phosphine, the preparation of the analogous compound, methyl bis-(hydrothiomethyl)phosphine was unsuccessful.

P-C-P Polymers by Reorganization of PCOP Linkages

It was expected, from chemical analogy, that the reactions



$$n\ HOCH_2\underset{CH_3}{P}CH_2OH + n\ Cl\underset{CH_3}{P}Cl \longrightarrow \left[\begin{matrix} P\text{-}O\text{-}CH_2\text{-}P\text{-}CH_2\text{-}O \\ CH_3 \qquad\quad CH_3 \end{matrix}\right]_n \qquad (7)$$

$$\xrightarrow{150^\circ C} \left[\begin{matrix} O \\ P\text{-}CH_2\text{-}P\text{-}CH_2\text{-}O \\ CH_3 \end{matrix}\right]_n \xrightarrow{150^\circ C} \left[\begin{matrix} O \qquad O \\ P\text{-}CH_2\text{-}P\text{-}CH_2 \\ CH_3 \qquad CH_3 \end{matrix}\right]_n$$

would proceed, one of the oxygens migrating over a carbon and a phosphorus atom to the isolated position. It is known[6] that the P-O bond breaks easily at 150°C.

The hydrogen n-m-r spectra of the product showed that the expected P-CH_2-P grouping was not present.

Polyphosphinates

The reaction of sodium hydride with phosphonate esters might be expected to be analogous to the acetoacetic ester condensation and proceed by the equation:

$$n\ XCH_2\text{-}\overset{\overset{O}{\|}}{\underset{Y}{P}}OR + n\ NaH \rightarrow n\ H_2 + nNa^+\ {}^-CHX\text{-}\overset{\overset{O}{\|}}{\underset{Y}{P}}OR \rightarrow n\ NaOR + \left[\begin{matrix} H & O \\ C & P \\ X & Y \end{matrix}\right]_n \quad (8)$$

The proposed reaction seems to be workable with phosphonate esters to produce polyphosphinates. The following phosphonates were tried (X, Y and R in Reaction (12) are given)

X	Y	R
H	OCH_3	CH_3 (three attempts)
Cl	OC_2H_5	C_2H_5
$PO_3(C_2H_5)_2$	OC_2H_5	C_2H_5
H	OC_4H_9	C_4H_9 (two attempts)
C_6H_5	OC_2H_5	C_2H_5

In each case, the desired reaction was aborted through loss of reactants as insoluble ester-salts. Minor amounts of new materials have been detected, but could not be separated, and the approach has been abandoned.

Polyphosphines

The successful utilization of the reaction described in the literature to give the diphosphine $(C_6H_5)_2PCH_2P(C_6H_5)_2$:

$$2\ (C_6H_5)_2PK + CH_2Cl_2 \longrightarrow (C_6H_5)_2P\text{-}CH_2\text{-}P(C_6H_5)_2 + 2\ KCl \quad (9)$$

prompted us to study the application of this type of reaction to the synthesis of polymers according to the following equation.

$$(C_6H_5)PK_2 + CH_2Cl_2 \longrightarrow 1/n\ \left[P(C_6H_5)\text{-}CH_2\right]_n + 2\ KCl \quad (10)$$

When the above reaction was run in dioxane as solvent, it was found, however, that only about 34% of the Cl available in methylenedichloride could be detected as KCl in the insoluble residue of the reaction product. The P^{31} n.m.r. spectrum of the concentrated dioxane solution containing the reaction product showed about 10 peaks in the range -50 to -7 ppm. No efforts have been

made to separate the various products.

One of the reasons for the failure of this research seems to be the intermediate formation of a carbene,

$$CH_2Cl_2 \xrightarrow{K} CH_2Cl^+ + KCl \xrightarrow{base} CHCl \qquad (11)$$

which may enter several side reactions with the present phosphorus compounds. Such a reaction is favored by a basic reaction medium as is the case in solutions of dipotassium, phenylphosphine.

Intermediate carbene formation could very well be the reason for several other unsuccessful reactions using methylene dichloride or its derivatives in basic media for syntheses, e.g., $CH_2Cl_2 + NaPO(OEt)_2$, and $(C_6H_5)_2P(O)CH_2Cl + KP(C_6H_5)_2$.

Phosphonium Salts

The principle of the phosphonium salt formation applied to a phosphorus compound containing the iodomethyl group and the lone electron pair of a triply connected phosphorus atom in one molecule should yield polymeric structures.

$$\begin{matrix} C_6H_5 \\ | \\ P - CH_2I \\ | \\ C_6H_5 \end{matrix} \longrightarrow 1/n \left[\begin{matrix} C_6H_5 \\ | \\ - P - CH_2 - \\ | \\ C_6H_5 \end{matrix} \right]^+ I^- \qquad (12)$$

A model reaction has shown that an iodomethyl group directly attached to phosphorus quaternizes easily with triphenylphosphine.

$$(C_6H_5)_3P + ICH_2P(O)(OEt)_2 \longrightarrow [(C_6H_5)_3PCH_2PO(OEt)_2]^+ I^- \qquad (13)$$

The quaternized product gave a P^{31} n.m.r. shift (-22.2 ppm) which is typical for triphenylphosphonium salts: $(C_6H_5)_3CH_3P^+ I^-$ gives -21.0 ppm. Since only one peak was obtained, it must be concluded that the other phosphorus atom in the molecule, the "phosphonate" phosphorus, has its n.m.r. peak at about the same position and thus causes an overlap of the two resonances.

An intermediate for the monomer starting material was prepared according to a procedure which has been reported in the literature for n = 2:

$$(C_6H_5)_2PK + (CH_2)_nO \rightarrow (C_6H_6)_2P(CH_2)_nOK \xrightarrow{H_2O} (C_6H_5)_2P(CH_2)_nOH \qquad (14)$$

The resulting hydroxyphosphine should be converted to the corresponding iodocompound.

$$(C_6H_5)_2P(CH_2)_nOH \xrightarrow{HI} (C_6H_5)_2P(CH_2)_nI \qquad (15)$$

which is expected to quaternize as stated above.

The reaction product according to reaction 41 for n = 2 proved to be the β-hydroxyphosphine as indicated by its P^{31}n.m.r. shift of +22.9 ppm. The corresponding compound for n = 1 which was obtained from potassium, diphenylphosphine and paraformaldehyde gave an n.m.r. peak at -29.8 which would be consistent with a phosphine oxide structure: e.g. $(C_6H_5)_2(CH_2Cl)PO$:

$$(C_6H_5)_2PCH_2OH \longrightarrow (C_6H_5)_2CH_3PO \qquad (16)$$

had occurred.

Phosphosilicones.

The exceptional thermal and hydrolytic stability of silicones suggested the synthesis of structures in which every second silicon atom was substituted by phosphorus. The best suitable approach seemed to be the elimination of HCl from equimolar amounts of a phosphonic acid and a dialkyl or diaryldichlorosilane.

$$\begin{matrix} R \\ Cl\text{-}Si\text{-}Cl \\ R \end{matrix} + \begin{matrix} O \\ HO\text{-}P\text{-}OH \\ R \end{matrix} \longrightarrow 1/n \left[\begin{matrix} R & O \\ Si\text{-}O\text{-}P\text{-}O \\ R & R \end{matrix}\right]_n + 2HCl \qquad (17)$$

The products obtained for R = CH_3 and C_6H_5 were viscous liquids or low-melting solids. For R = CH_3, the polymer appears to be quite stable in cold water, but hydrolyzes readily in boiling water to form methylphosphonic acid and silicone oil. The compound for which R = C_6H_5 hydrolyzes after only several minutes of boiling in water forming phenylphosphonic acid and a white solid silicone.

P-C-N-P Polymers

As a model compound for this new type of polymer based on the P-C-N-P-backbone, the following ester has been synthesized according to a procedure in the literature[7]:

$$CH_3NH_2 + 2CH_2O + 2HPO(OEt)_2 \longrightarrow CH_3N[CH_2PO(OEt)_2]_2 + 2H_2O \qquad (18)$$

Hydrolysis of the ester with concentrated hydrobromic acid gave the acid $(HO)_2OP\text{-}CH_2\text{-}N(CH_3)\text{-}CH_2\text{-}PO(OH)_2$ which was tested for thermal stability.

A similar approach was used in a preparation of a material containing -P-C-N-C structures:

$$\begin{matrix} O \\ H\text{-}P\text{-}H \\ O \\ H \end{matrix} + CH_2O + \begin{matrix} H\text{-}N\text{-}H \\ Ph \end{matrix} + CH_2O \longrightarrow \frac{1}{n} \left[\begin{matrix} O & & \\ P\text{-}CH_2\text{-}N\text{-}CH_2 \\ O & Ph \\ H \end{matrix}\right]_n + 2H_2O \qquad (19)$$

The above reaction product separated as yellow jellylike material which on drying at 120°C turns into a brown solid in-

soluble in all common solvents. The thermal stability of this material was lower than expected, with decomposition occurring at about 200-250°C. Apparently, substitution of a N for every second P atom in a P-C-P chain does not favorably influence the thermal stability of the material.

Phosphorus-Boron Polymers

In 1891 Moissan reported[8] that the reaction between white phosphorus and boron triiodide in carbon disulfide gives a product of the composition BPI_2. This material might be considered as a fortuitous mixture except for the fact that it is slightly volatile at its melting point and gives a crystalline sublimate. Moissan also reported that BPI_2 can be reduced in hydrogen to BPI. Unfortunately, he gave very sparse experimental details, and no additional work on these compounds has been reported in the literature.

Moissan's preparation of BPI_2 was repeated using carefully purified reagents and with the strict exclusion of oxygen and moisture. The reported color changes were observed, but the red solid product was not volatile in high vacuum at 225°C, which is well above Moissan's reported sublimation temperatures. The small amount of orange sublimate which did collect was reacted with phenyllithium to convert it to a more easily handled derivative, but biphenyl was the only product which could be isolated from this reaction.

Alkylation and Arylation Reactions

The reactions of a number of halogen compounds with organometal compounds were followed by means of n.m.r. analysis. The results are summarized in the following tables.

Table 1.

Alkylation of Phosphorus Compounds with $Pb(CH_3)_4$, Dissolved in Toluene (85% Solution)

P-Compound	Ratio P-Comp. :$Pb(CH_3)_4$	Heating Time at 125°C in hours	Products	Yield%
PCl_3	2.1:1	20	CH_3PCl_2	100[a]
CH_3PCl_2	2.2:1	20	$(CH_3)_2PCl$	[b]
CH_3PBr_2	2.5:1	1(22°C)	$(CH_3)_2PBr$	13[c]
$C_6H_5PSCl_2$	2.3:1	120	$C_6H_5(CH_3)PSCl$	90
CH_3PSCl_2	2.5:1	200	$(CH_3)_2PSCl$	81

Table I (Contd.)

P-Compound	Ratio P-Comp. :$Pb(CH_3)_4$	Heating Time at 125°C in hours	Products	Yield %
$(CH_3)_2PSCl$	2.5:1	200	$(CH_3)_3PS$	12
$C_6H_5POCl_2$	2.3:1	200	$C_6H_5(CH_3)POCl$	19

[a]After 4 hours heating at 122°C, 86% CH_3PCl_2 had formed.

[b]N.m.r. peak intensity decreased strongly (indication of extensive decomposition of phosphorus-compound). After 4 hours heating at 122°C, 12% of the expected $(CH_3)_2PCl$ had formed and the n.m.r. peak intensity was strong.

[c]The content of the tube turned solid after one hour standing at room temperature, probably caused by formation of phosphonium type $(R_3PBr^+)Br^-$ compounds.

Table 2.

Alkylation of Phosphorus Compounds with $Pb(C_2H_5)_4$

P-Compound	Ratio P-Comp. :$Pb(C_2H_5)_4$	Heating Time at 125°C in hours	Products	Yield%
PBr_3	2.79:1	19 (22°C)	$C_2H_5PBr_2$	60[a]
CH_3PBr_2	2.71:1	2	$CH_3C_2H_5PBr$	100[a]
PCl_3	2.56:1	4	$C_2H_5PCl_2$	100
PCl_3	1.87:1	4	$C_2H_5PCl_2$ $(C_2H_5)_2PCl$	89 11
CH_3PCl_2	1.84:1	4[b]	$CH_3C_2H_5PCL$	100
$C_6H_5PCl_2$	1.96:1	4	$C_2H_5(C_6H_5)PCl$	100
$(CH_3)_2PCl$	1.85:1	66	$(CH_3)_2C_2H_5P$ $(CH_3)(C_2H_5)_2P$ $(CH_3)_3P$	83.5 8.5[c] 8.5[c]
$(C_6H_5)_2PCl$	2.07:1	66	$(C_6H_5)_2C_2H_5P$ $C_6H_5(C_2H_5)_2P$ $(C_6H_5)3P$	90 5[d] 5[d]

Table 2. (Contd.)

P-Compound	Ratio P-Comp. :$Pb(C_2H_5)_4$	Heating Time at 125°C in hours	Products	Yield%
$PSCl_3$	2.734:1	39	$C_2H_5PSCl_2$ $(C_2H_5)_2PSCl$	92 8
CH_3PSCl_2	1.84:1	66(115°C)	$CH_3C_2H_5PSCL$	77[e]
$C_6H_5PSCL_2$	1.92:1	66(115°C)	$C_2H_5(C_6H_5)PSCl$ $(C_2H_5)_2(C_6H_5)PS$	70[f] 20
$(CH_3)_2PSCl$	1.89:1	130	$(CH_3)_2C_2H_5PS$	84
$POCl_3$	2.64:1	90	$C_2H_5POCl_2$ $(C_2H_5)_2POCl$	40 20
$ClCH_2POCl_2$	1.87:1	160	$C_2H_5(ClCH_2)POCl$	42
$C_6H_5POCl_2$	1.77:1	120	$C_2H_5(C_6H_5)POCl$	50

[a] It is better to carry out this reaction in an open flask, since the formation of phosphonium salts can be avoided in this way.

[b] Further heating of the tube for 17 hours at 125°C caused strong decomposition of the product.

[c] Products formed by reorganization of $(CH_3)_2C_2H_5P$ to give $CH_3(C_2H_5)_2P$ plus $(CH_3)_3P$. Additional heating for 117 hours at 125°C gave 67% of $(CH_3)_2C_2H_5P$, 16.5% of $CH_3(C_2H_5)_2P$ and 16.5% of $(CH_3)_3P$. $PbCl_2$ might act as a catalyst in this reorganization reaction.

[d] Products formed by reorganization of $(C_6H_5)_2C_2H_5P$ to give $C_6H_5(C_2H_5)_2P$ plus $(C_6H_5)_3P$ (see c).

[e] Additional heating of the tube for 70 hours at 125°C gave 58% of $CH_3C_2H_5PSCl$ and 35% of $CH_3(C_2H_5)_2PS$.

[f] Additional heating of the tube for 70 hours at 125°C gave 47% of $C_2H_5(C_6H_5)_2PSCl$ and 44% of $(C_2H_5)_2C_6H_5PS$.

Table 3.

Arylation of Phosphorus Compounds with $Pb(C_6H_5)_4$

P-Compound	Ratio P-Comp.: $Pb(C_6H_5)_4$	Heating Time at 180°C in hours	Products	Yield%
PBr_3	3.01:1	180	$C_6H_5PBr_2$ $(C_6H_5)_2PBr$	68 21
CH_3PBr_2	4.63:1	180	$C_6H_5PBr_2$ $CH_3C_6H_5PBr$	54[a] 7
PCl_3	3.03:1	180	$C_6H_5PCl_2$ $(C_6H_5)_2PCl$	93 2
CH_3PCl_2	2.01:1	39(165°C)	$C_6H_5PCl_2$ $CH_3(C_6H_5)PCl$	55[b] 20
$C_6H_5PCl_2$	3.0:1	83	$(C_6H_5)_2PCl$	90
$(CH_3)_2PCl$	2.03:1	39(165°C)	$CH_3(C_6H_5)_2P$ $(CH_3)_2C_6H_5P$	50[c] 50
$(C_6H_5)_2PCl$	2.98:1	180	$(C_6H_5)_3P$	95
$PSCl_3$	3.0:1	180	$C_6H_5PSCl_2$ $(C_6H_5)_2PSCl$	35 32
CH_3PSCl_2	1.9:1	66	$CH_3C_6H_5PSCl$	100
$C_6H_5PSCl_2$	2.1:1	136	$(C_6H_5)_2PSCl$ $(C_6H_5)_3PS$	94 6
$ClCH_2PSCl_2$	1.9:1	180	$ClCH_2(C_6H_5)PSCl$	46
$POCl_3$	3.01:1	180	$C_6H_5POCl_2$ $(C_6H_5)_2POCl$	29 15.5
$C_6H_5POCl_2$	1.93:1	66	$(C_6H_5)_2POCl$	68
$ClCH_2POCl_2$	2.0:1	180	$ClCH_2(C_6H_5)POCl$	11

[a] CH_3PBr_2 decomposes partly at this temperature to give PBr_3 and other products. PBr_3 then reacts with $Pb(C_6H_5)_4$ to give $C_6H_5PBr_2$. When a tube was kept for 18 hours at 100°C, no $C_6H_5PBr_2$ was formed, but 17% of $CH_3C_6H_5PBr$ could be detected.

[b] CH_3PCl_2 reorganizes partly at this temperature to give PCl_3 and other products. PCl_3 then reacts with $Pb(C_6H_5)_4$ to give $C_6H_5PCl_2$. When a tube was kept for 18 hours at 100°C, no reaction occurred.

[c] Could have been formed from CH_3PCl_2, a reorganization product of $(CH_3)_2PCl$.

Table 4.

Alkylation of Alkylhaloarsines with Tetraalkyllead Compounds

R in PbR_4	Arsenic Compound	Product	Yield %	B.P. °C	n_D^{20}
CH_3	CH_3AsBr_2	$(CH_3)_2AsBr$	90	126-129	1.5703^{26}
C_2H_5	CH_3AsBr_2	$CH_3(C_2H_5)AsBr$	80	154-155	1.5732
$CH_2=CH$	CH_3AsBr_2	$CH_3(CH_2=CH)AsBr$	60.5	144-145	
C_5H_9	CH_3AsBr_2	$CH_3(C_4H_9)AsBr$	57	172-178	1.6368
C_2H_5	$(CH_3)_2AsBr$	$(CH_3)_2(C_2H_5)As$	56	83-84	

d. Tetraphenyltin as Arylating Agent. Two experiments with tetraphenyltin demonstrated that it can also be used as an arylating reagent. Tetraethyltin was shown earlier[9] to give excellent yields of $C_2H_5PBr_2$ when reacted with PBr_3.

The results are summarized in Table 5.

Table 5.

Arylation of PCl_3 and $PSCl_3$ with Tetraphenyltin

P-Compound	Ratio P-Comp. :$Sn(C_6H_5)_4$	Heating Time at 180°C in Hours	Products	Yield %
PCl_3	3.1:1	350	$C_6H_5PCl_2$	65
$PSCl_3$	3.09:1	130	$C_6H_5PSCl_2$ $(C_6H_5)_2PSCl$	58 36

Contrary to tetraphenyllead, tetraphenyltin reacted much faster with $PSCl_3$ than with PCl_3, e.g., while no product had been formed with PCl_3 after 40 hours heating with $Sn(C_6H_5)_4$ at 180°C, $PSCl_3$ gave under the same conditions 22% $C_6H_5PSCl_2$ and 36% $(C_6H_5)_2PSCl$. Since the content of the tube containing PCl_3 and $Sn(C_6H_5)_4$ in ratio 3.1:1 became nearly completely solid when cooled to room temperature after heating for 40 hours at 180°C, it is assumed that a complex of the type $(PCl_2)_2^{++}$ $[Sn(C_6H_5)_4Cl_2]^{--}$ is first formed which is subsequently decomposed, after long heating, to give $C_6H_5PCl_2$ and $(C_6H_5)_2SnCl_2$.

Proof of Structure by Means of Nuclear Magnetic Resonance

Methyl Phosphine Confirmation of the synthesis of methyl phosphine, H_2PCH_3, was provided by a proof of structure, utilizing

P^{31} n.m.r. at 24.3 Mc, H' n.m.r. at 40 and 60 Mc, and double resonance techniques. The compound provides an elegant example of the utilization of these techniques for structure proof.

The 24.3 Mc P^{31} n.m.r. spectrum of methyl phosphine exhibited three major peaks of relative intensity 1:2:1, separated by 187 cps. The chemical shift is +164.0 ppm relative to 85% H_3PO_4. The over-all triplet structure is consistent with two hydrogen atoms bonded directly to phosphorus. For a first order spectrum, one would also expect each peak of this triplet to be split into a smaller 1:3:3:1 quartet by the three hydrogens of the methyl group, which should be less strongly coupled to the phosphorus nucleus. The spectrum showed that each peak of the triplet was actually composed of up to 10 peaks each in an asymmetrical pattern. This suggested that there was appreciable interaction between the methyl hydrogens and the phosphine hydrogens, and that the spectrum could not be explained by a simple first order analysis.

Additional information was provided by the H' n.m.r. spectrum at 60 Mc. It contained two bands separated by 190 cps. Moreover, the integrated spectrum showed that the band at lower field, a symmetrical quartet, accounted for only one hydrogen atom out of five. The complex band at higher field resulted from the four other hydrogen atoms. The symmetrical quartet arises from the splitting of 1/2 the phosphine hydrogen resonance by the three methyl hydrogens. The other 1/2 of the phosphine hydrogen resonance fell at the same energy level as the methyl hydrogen resonance, resulting in mixing of states and a complex spectrum. This provided an explanation for the unusual splitting in the 24.3 Mc phosphorus spectrum.

The H' spectrum was then taken at 40 Mc. Since the coupling (expressed in cps) between the hydrogens is independent, while the chemical shift is dependent on the radiofrequency used, overlapping bands were shifted, although it did not completely separate them. Double resonance experiments were then used to decouple phosphorus from hydrogen by irradiating with a second radiofrequency at 16.2 Mc and high power, while observing H' at 40 Mc and low power. This effectively removes the spin-spin coupling between hydrogen and phosphorus. The 187 cps splitting of the phosphine hydrogen signal was collapsed and the methyl and phosphine hydrogen resonance bands appeared separately. The resulting decoupled spectrum approximates first order hydrogen splitting and provides unequivocal confirmation of the structure of methyl phosphine. The small residual peaks that remain in the decoupled spectrum are due to a combination of insufficient power from the decoupler output and second order splitting due to the proximity of the decoupled bands.

Dimethyl Methylphosphonate Phosphonate esters ordinarily give poorly resolved broad resonances in P^{31} n.m.r. due to strong coupling to phosphorus of the protons on the carbon atoms nearest

to phosphorus, merged with weaker coupling of protons on the next nearest carbon atoms. Dimethyl methylphosphonate provides a special case in which there are only two kinds of protons (CH_3-P- and CH_3OP-), and in which the coupling constants, J_{PH_3} = 10.9 cps and J_{PH_3} = 17.3 cps, can be accurately measured from proton n.m.r. spectra. Fortuitously, there is no overlap of the lines, and all twenty-eight of the lines predicted by simple first-order theory can be resolved in the P^{31} spectrum. The small molar volume of the compound is helpful in increasing the signal strength and thereby increasing the resolving power. The ninth and tenth lines from either end of the spectrum, having a separation of only 2.2 cps, provide a good measure of the resolving power of the instrument, and have proved useful in focusing the magnet for maximum resolving power.

CONCLUSIONS

Experimental results show that phosphorus-containing polymers of the type

$$\left[\begin{array}{c} Y \\ | \\ CH_2\text{-}P \\ | \\ X \end{array}\right]_n$$

where Y = oxygen or sulfur and X = an alkyl, aryl, alkoxy or aryloxy group, can be expected to be stable at temperatures of 400°C or higher. Although model compounds have been made the thermal stability of which support this conclusion, the preparation of pure polymeric molecules of this type has not been achieved.

After two years of effort, the most promising reaction found was the polymerization of methyl,chloromethylphosphonic chloride with zinc or magnesium:

$$n\ ClCH_2\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{|}{P}}}\text{-}Cl + nZn \longrightarrow \left[\begin{array}{c} O \\ | \\ CH_2\text{-}P\text{-} \\ | \\ CH_3 \end{array}\right]_n + nZnCl \qquad (173)$$

The presence of the desired P-CH_2-P structure in the product thus obtained has been shown by n.m.r. spectroscopy. However, repeated attempts to separate out the polymeric material thus obtained, free from the strongly complexed zinc or magnesium chloride and free from undesirable by-products (such as phosphonium structures) have not succeeded.

The other approaches for the preparation of such polymers have either been giving extremely low yield of products which were difficult to identify or a completely different reaction occurred, sometimes producing a complicated mixture of unidentified compounds.

Since long-chain P-C-P polymers have not been produced, it is not possible to predict exactly which physical properties can be

expected from the finished polymer. Tensile strength, flexibility, elasticity, etc., are all properties which are specific for polymers exhibiting more than a certain minimum molecular weight and cannot be obtained by extrapolation of properties of shorter molecules.

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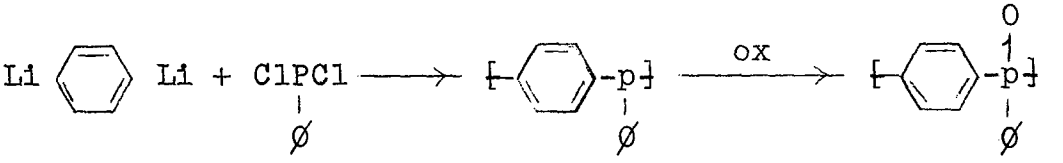
PART III. ORGANO-PHOSPHORUS POLYMERS

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INTRODUCTION

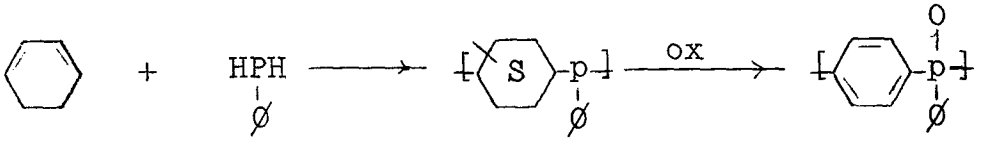
The work reported here was directed primarily to the preparation of poly phenyl p-phenylene phosphine oxide, since there was reason to believe that such a polymer would have a high level of thermal stability. Prior to undertaking this project we had attempted a "direct" synthesis of this structure via the reaction of p-dilithio benzene and phenyl dichlorophosphine.



This reaction was never successful in our hands because the dilithiobenzene preparation cannot be made pure and the "polymer" precipitated from the non-polar reaction solvent before any appreciable molecular weight was obtained.

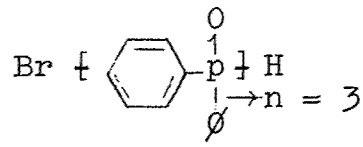
RESULTS AND DISCUSSION

We proposed to attempt the synthesis of the desired poly phenyl phenylene phosphine oxide by making use of the well-known addition of P-H bonds to carbon-carbon double bonds. The reaction proposed is shown below:



The reaction of 1,3-cyclohexadiene and phenyl phosphine did result in a polymer. However, the reaction is not as clear cut as represented since cyclohexene and some distillable phosphorus-containing compounds were also produced. The polymer contained a higher phosphorus content than expected and could not be dehydrogenated to any identifiable product.

During the course of this work we had occasion to repeat the reaction of bromobenzene, phosphorus trichloride and aluminum chloride reported by Davies and Mann[1]. This reaction gives only a poor yield of p-bromophenyl dichlorophosphine of uncertain purity. We found by hydrolysis of the pot residue that the major product was actually a low polymer analyzing for the following structure:



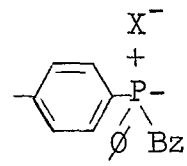
This material when examined by thermogravimetric analysis appeared to give two levels of decomposition; the higher one occurring at about 550°C.

It was evident, however, that we still did not have in our hands suitable methods of synthesis of the desired polymer. We decided to establish the level of thermal stability inherent in the p-phenylene phosphine oxide structure by synthesizing and testing suitable model compounds. To this end we prepared p-phenylene bis(diphenyl phosphine oxide) essentially by the methods reported by Baranauckas, Carlson, Harris and Lisanke[2]. Using differential thermal analysis we found that this material decomposed at 450°C. This result is in agreement with the data obtained on the thermal stability of this compound by the previous workers[2]. Furthermore, an examination of alkylene bis(diphenyl phosphine oxides) showed that they decomposed somewhat lower in the 400-445°C range.

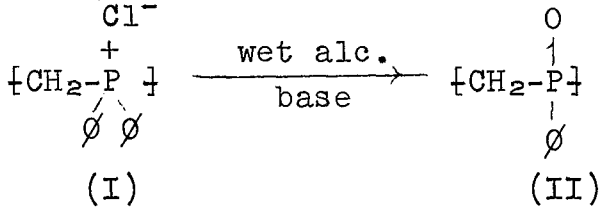
CONCLUSIONS

We conclude from this work that poly p-phenylene phosphine oxides would not be stable above 450°C and would not, therefore, fulfill the requirements of stability to 1000°F.

Two other points of interest should be mentioned although they do not relate directly to the objective of this work. The first of these concerns the elimination of phosphonium salts under basic conditions. We have found that the action of wet-alcoholic base on p-phenylene bis(triphenyl phosphonium iodide) gave at least a 75% yield of triphenyl phosphine oxide. This indicated that the phosphorus to phenylene linkage was broken preferentially in the reaction. Base cleavage of p-phenylene bis(diphenyl benzyl phosphonium iodide), however, gave p-phenylene bis(diphenyl phosphine oxide) as the isolable product. This may indicate that basic cleavage of a polymer of the following structure



would be an attractive method of preparing the desired poly phenyl p-phenylene phosphine oxide. Also, we observed that the action of base on an impure polymer (believed to have structure I below) gave a polymeric water soluble product whose infrared spectrum was compatible with that which might be expected of poly phenyl methylene phosphine oxide (II).



Product (II) was not "pure" and did not show stability above 300°C.

The second point of interest involves an unexpected reaction which we observed. Phosphorus halides and active metals such as magnesium or lithium are not known to react at ordinary temperatures. We have observed, however, that diphenyl chlorophosphine, magnesium (or lithium) and tetrahydrofuran react exothermally to give a good yield of diphenyl-4-hydroxybutyl phosphine. When the reaction is carried out on phenyl dichlorophosphine the product is phosphobenzene (ø-P=P-ø). All phosphorus halides give a reaction with active metals and tetrahydrofuran but in many cases, such as with phosphorus trichloride or phosphorus oxychloride, the products are complicated and have not been identified. We feel that this reaction deserves more attention and can be developed into another route to the preparation of compounds having phosphorus-carbon bonds.

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POLYMERIC PHOSPHORUS-NITROGEN COMPOUNDS

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SYNTHESIS OF CHLORIDES, ESPECIALLY OF POLYMERIC PHOSPHORUS NITRILIC CHLORIDES

We were able to elucidate completely the mechanism of formation of polymeric phosphorus nitrilic chlorides.

Phosphorus pentachloride has a well known structure.[1] In the vapor state the molecule is in the form of a trigonal bipyramid. Pure liquid PCl_5 exhibits a Raman spectrum which has been interpreted on the basis of a trigonal bipyramid structure. In the crystal, however, phosphorus pentachloride has an ionic structure corresponding to $[PCl_4]^+ [PCl_6]^-$. When phosphorus pentachloride is dissolved in polar solvents, it acts as an electrolyte and is present in ionic form. Transference number experiments indicate that $[PCl_4]^+$ and $[PCl_6]^-$ are formed when phosphorus pentachloride is dissolved in nitrobenzene.

We suggested that with ammonia and derivatives of ammonia respectively phosphorus pentachloride may react as a salt $[PCl_4]^+ [PCl_6]^-$. An ionic mechanism should be especially observed when a polar solvent is employed.

Sulfuryl amide reacts with phosphorus pentachloride:

$$H_2N\text{-}SO_2\text{-}NH_2 + 2\ PCl_5 \rightarrow Cl_3P{=}N\text{-}SO_2\text{-}N{=}PCl_3 + 4\ HCl \qquad (1)$$

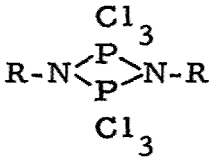
Urea reacts in an analogous manner. From the monoamide of sulfuric acid $Cl_3P{=}N\text{-}SO_2Cl$ is formed. The H-atoms located on the nitrogen atom are substituted by PCl_3. The reaction of phosphorus pentachloride which was first studied by Kirsanov presumably proceeds such that the $[PCl_4]^+$ reacts as a Lewis acid with the amide:[2]

$$R\text{-}\underset{H}{\overset{H}{N}}\rightarrow \overset{+}{P}Cl_4\ Cl^- \xrightarrow{-HCl} R\text{-}\underset{H}{\overset{Cl}{N}}\text{-}PCl_3 \xrightarrow{-HCl} \underset{I}{R\text{-}N{=}PCl_3} \qquad (2)$$

With amines in an analogous manner reaction is observed:[3]

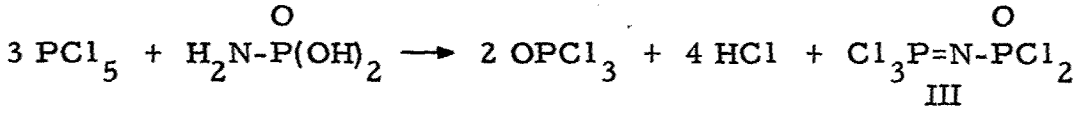
$$R\text{-}NH_2 + PCl_5 \rightarrow RN{=}PCl_3 + 2\ HCl \qquad (2a)$$

Strong bases (amines) and phosphorus pentachloride, however, are producing dimeric substances:[4]



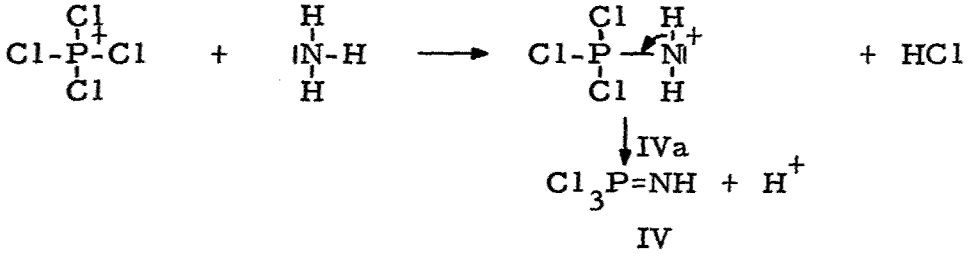
II

Accordingly, monoamido phosphoric acid reacts in tetrachloroethane solution rapidly and almost quantitatively in accordance with the equation:[5]



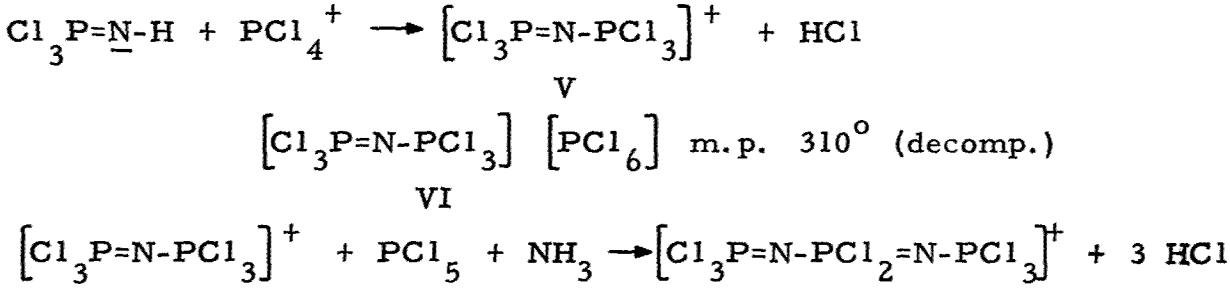
III

We were able to show that ammonia or ammonium chloride and phosphorus pentachloride may react in an analogous manner:



IV

The intermediate Product IV reacts with further PCl_4^+ to form the cation V, which combines with the anion $[PCl_6]^-$ to give the stable salt VI. This reaction occurs already at 40-60° C in polar solvents in almost quantitative yield. The salt VI easily reacts with further NH_4Cl, giving a cation VII under P-N-chain lengthening. VII was isolated in the form of a salt represented by VIII.[6]

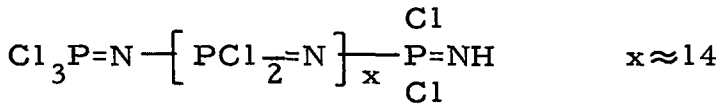


VII

VIII: $[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3]^+ [PCl_6]^-$ m.p. 161°

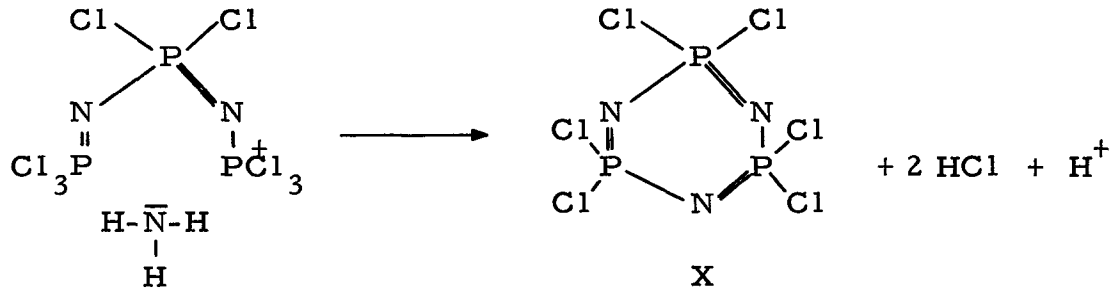
This reaction could be carried out with about 80% yield. The reaction of further ammonium chloride with VIII can now take two courses. In the one

instance the chain-lengthening reaction can occur in accordance with the scheme described above, leading to the formation of oily phosphorus nitrilic chlorides. This is particularly the case, when temperatures from 160-200° C are employed and when HCl is not removed. The chains are terminally saturated with the ions of hydrogen chloride and have the following structure IX:[7]



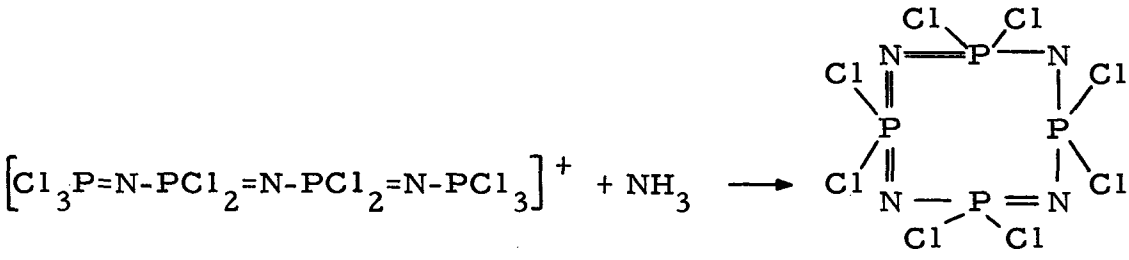
IX

In the other instance, reaction between the cation VII and NH_4Cl can lead to trimeric phosphorus nitrilic chloride X.



X

A further chain-lengthening reaction produces finally tetrameric phosphorus nitrilic chloride XI, in that a cation XII if formed which reacts further with NH_4Cl under ring closure. The yield of the tetramer is of course not high, since XII is only a by-product.



XII XI

The constitution of all mentioned products was established by nuclear magnetic resonance spectra. Furthermore, VI was reacted with SO_2 whereby XIII was formed as expected product. XIV was obtained when the salt VIII was treated with SO_2. The constitution of products arising from the reaction with SO_2 were

likewise determined with the aid of nuclear magnetic resonance spectroscopy.

$$[Cl_3P{=}N{-}PCl_3]\ [PCl_6] + 2\ SO_2 \rightarrow Cl_3P{=}N{-}\overset{O}{P}Cl_2 + 2OSCl_2 + OPCl_3 \qquad (3)$$

XIII m.p. 35.7°

$$[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3]\ [PCl_6] + 2\ SO_2 \rightarrow 2\ OSCl_2 + OPCl_3 +$$

$$Cl_3P{=}N{-}PCl_2{=}N{-}PCl_2$$

XIV m.p. 37°

XIII is found to be formed in numerous reactions in phosphorus chemistry.

First, we were able to obtain this compound in the reaction between PCl_5 and the amides of orthophosphoric acid.[5] The second method of preparing this acid chloride XIII proceeds from hydroxyl ammonium chloride, which is reacted with equimolar quantities of PCl_5 and PCl_3 at elevated temperatures:

$$[H_3NOH]\ Cl + PCl_5 + PCl_3 \rightarrow XIII + 4\ HCl$$

A third method is given in equation (3).

A further method consists of the reaction of PCl_3 with N_2O_4. PCl_3 reacts with N_2O_4 such that the tetrachloride of diphosphoric acid (XV) is formed. Furthermore, according to Klement a compound $P_4O_4Cl_{10}$ was thought to be produced.[8] This compound has been widely investigated, since it is interesting in that it cannot be explicitely formulated. Hence, several theories concerning its constitution were proposed; these dealt especially with the examination of the molecular spectra. We found, however, that the compound "$P_4O_4Cl_{10}$" contains nitrogen and that the product has the formula P_2NOCl_5 and the constitution XIII. $P_4O_4Cl_{10}$ does not exist.[9] XIV has not been found to have been formed in any other reactions.

$$Cl_2P{-}O{-}PCl_2$$
$$\begin{matrix} O & O \end{matrix}$$

XV

The intermediate products of the synthesis of phosphorus nitrilic chlorides, e.g. VI and VIII, may be obtained by other reactions too. VI may be obtained when NCl_3 and PCl_3 is allowed to react in an inert solvent:

$$NCl_3 + 3PCl_3 \rightarrow [Cl_3P{=}N{-}PCl_3]\ [PCl_6] \qquad (4)$$

VIII is formed when S_4N_4 and PCl_3 is reacted.[10] NMR measurements established

formula VIII. The older formulations are not in agreement with these measurements:[11]

$[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3]\ [PCl_6]$ VIII right

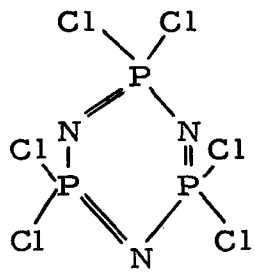
$[PCl_4]\ [NPCl_3]$ false

SYNTHESIS OF SOME POLYMERIC DERIVATIVES OF THESE CHLORIDES

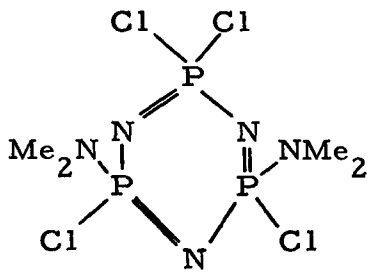
All phosphorus nitrogen chlorides are useful as starting materials for the research on phosphorus nitrogen polymers.

At first, the reactions of phosphorus nitrilic chlorides X and XI were studied. We studied the effect of nucleophilic reagents on these quasiaromatic ring systems.

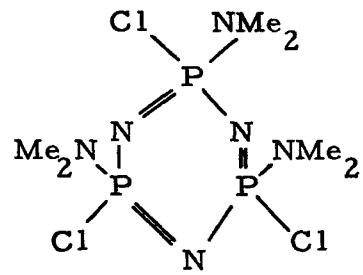
It was found: 2, 3, 4, or 6 Cl-atoms of $[NPCl_2]_3$ (X) are easily substituted by nucleophilic ligands. Strongly nucleophilic reagents attack in 1 and 3 position. Further substitution follows in 5 position of the six membered ring system.[12]



X



XVI

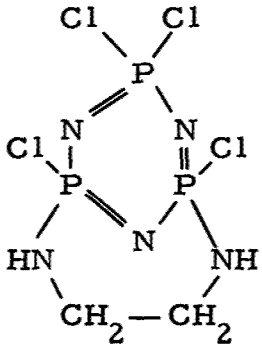


XVII

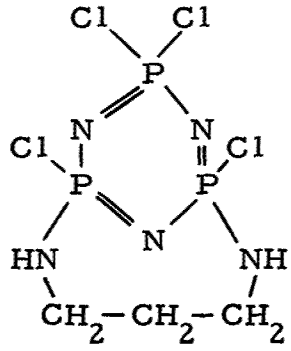
Substitution rules were derived from the behavior of trimeric and tetrameric phosphorus nitrilic chlorides.[12] The rules were checked by the synthesis of isomers and by nuclear magnetic resonance spectra of the products. After we knew these rules of substitution of chloride atoms by strong nucleophilic reagents, it was possible to think out a reasonable way of preparing polymers.

We investigated the reaction of X with polymethylenediamines. According to the rules of substitution, we found the reaction products XVIII, XIX and XX. With hexamethylenediamine, however, (or octamethylenediamine or $H_2N{-}C_6H_{10}{-}CH_2{-}C_6H_{10}{-}NH_2$) a polymeric substance was obtained. Two

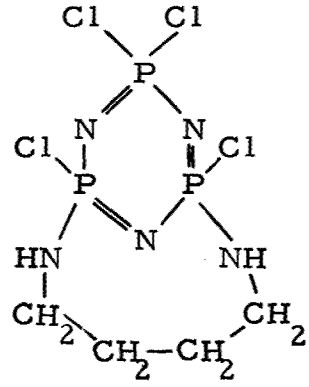
substances XXI and XXII were obtained, and their structures were elucidated.



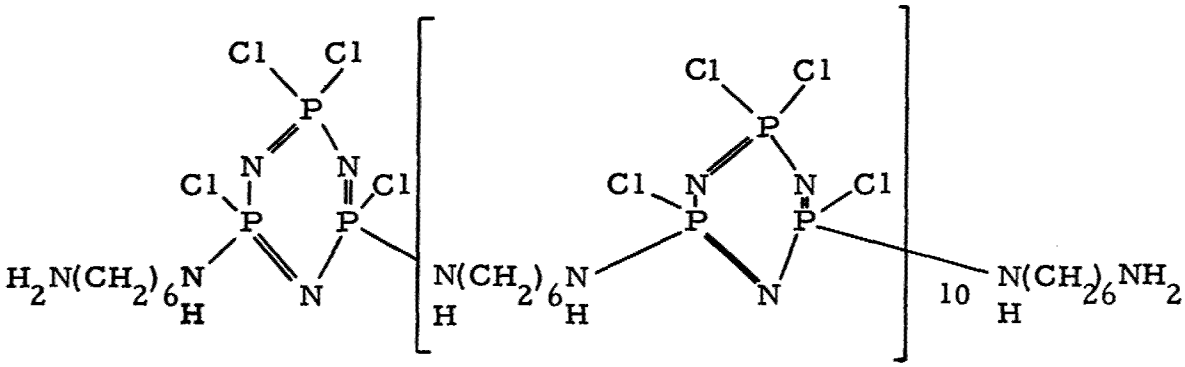
XVIII



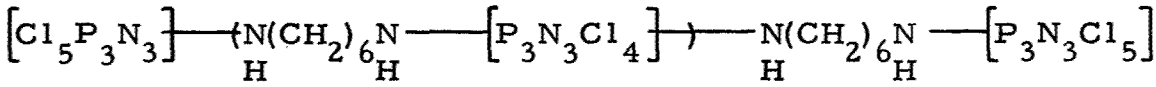
XIX



XX

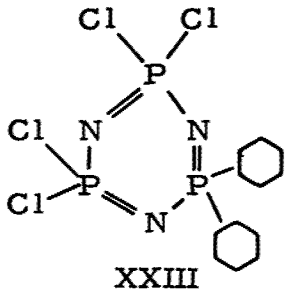


XXI

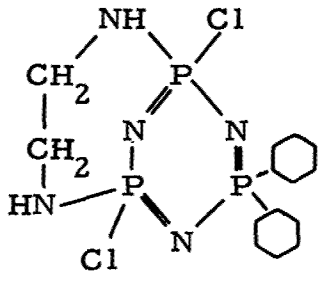


XXII

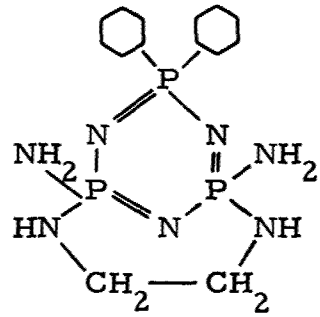
A variety of derivatives of such compounds was obtained. With diphenyl phosphorus nitrilic tetrachloride (XXIII) analogous reactions were observed. Monomers (XXIV), (XXV) are obtained with ethylenediamine; polymers are obtained with diamines which contain a longer chain $(CH_2)_n$.



XXIII



XXIV

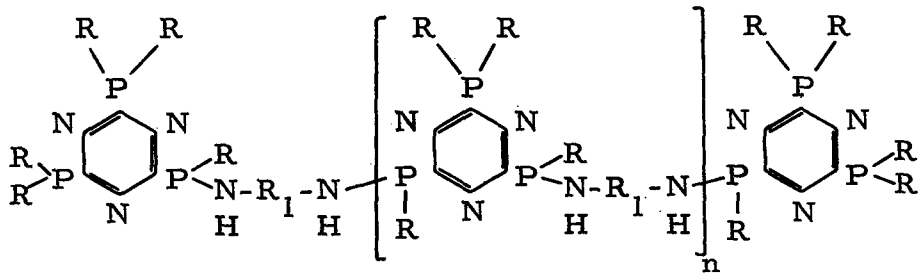


XXV

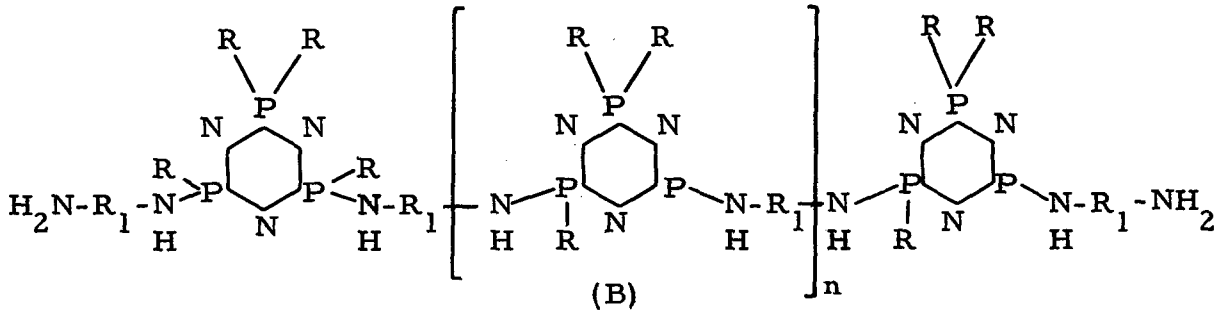
Some of the polymers are resins. When heated to about 150° the polymers become

thermoplastic. Of course, the behaviour depends largely upon the substituents.

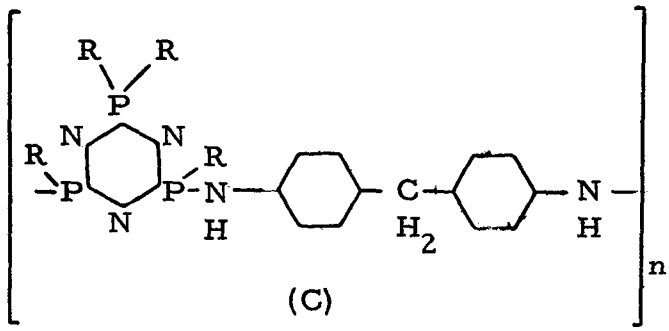
Types of polymers which could be obtained with phosphorus nitrilic chlorides as starting material:



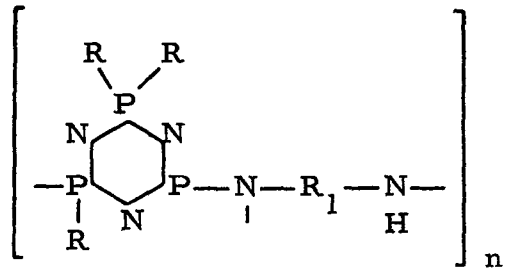
(A)



(B)

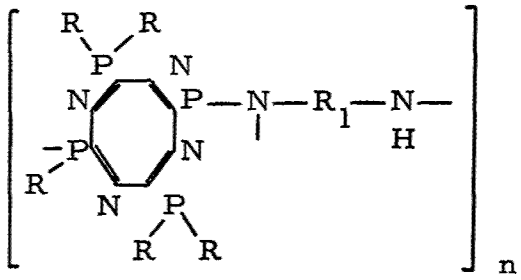


(C)



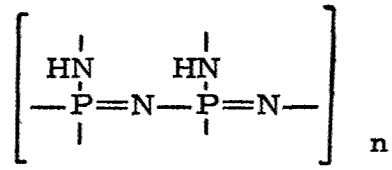
(D)

A, B, C, D are derivatives of trimeric phosphorus nitrilic chloride.



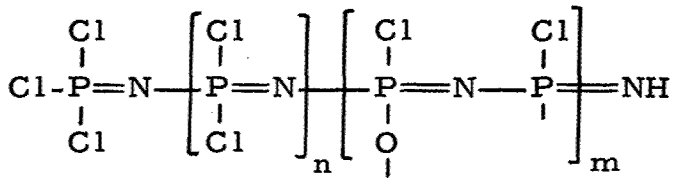
(E)

E is a derivative of tetrameric phosphorus nitrilic chloride.



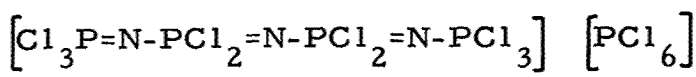
(F)

F may be obtained starting with the trimer or the tetramer respectively.

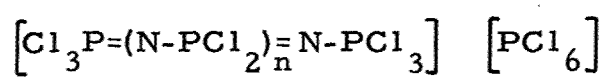


(G)

G is a derivative of the linear phosphorus nitrilic chloride. With traces of water, IX is polymerized producing G.



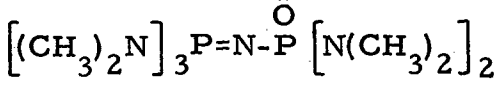
(H)



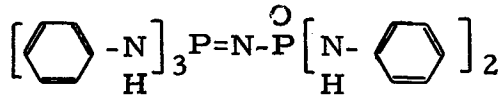
(I)

H and I are products of the reaction of NH_4Cl and PCl_5. Further, it can be shown by NMR spectroscopy that when trimeric phosphorus nitrilic chloride is reacted with PCl_5 by heating the two substances in a closed tube at about 220°, the salts I are formed.

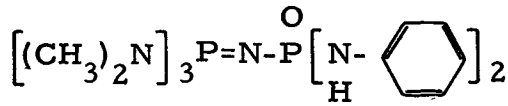
Other polymers could be obtained with $Cl_3P{=}N{-}\overset{O}{P}Cl_2$ (XIII) as starting material. Each chlorine atom in this compound can be substituted by an amino group (XXVI). It became apparent in the preparation of the anilide (XXVIb) that polymers are easily formed if the procedure of preparation is carried out at temperatures in excess of 0° C. The amides XXVII are condensated to polymeric substances when heated to 150-200° C (XXVIII).



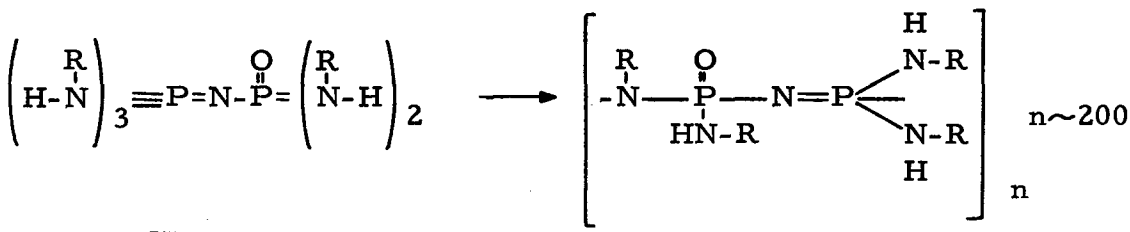
XXVIa



XXVIb

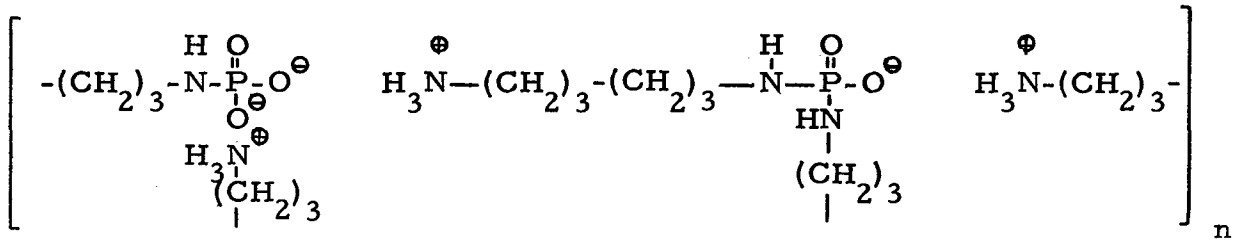


XXVIc



XXVII XXVIII

With hexamethylenediamine a pentamide was formed. This amide was sensitive towards water, and with water a stable polymeric substance XXIX was formed.



Another polymeric material is formed when $Cl_3P{=}N{-}P(O)Cl_2$ is brought to reaction with urea or with $K\left[OCN\right]$. However, $(Cl)_2(C_6H_5)P{=}N{-}P(Cl)(C_6H_5)$ which was prepared just recently may be a better starting material for such polymers.

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PREPARATION AND REACTIONS OF ISOCYANATES OF SULFURIC AND PHOSPHORIC ACID

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Institute of Inorganic Chemistry
University of Heidelberg

Abstract

Various syntheses of the diisocyanate of sulfuric acid will be described. Its properties and reactions with proton-active materials will be discussed. Reaction with glycols and with diamines leads to the formation of polymeric sulfo-urethanes and sulfo-ureas which, however, are only slightly stable towards hydrolysis. Further, a new synthesis of phosphorus oxytriisocyanate will be mentioned.

Organic diisocyanates have long served as important starting materials for the preparation of polymers, of which the polyurethanes especially have attained significance in technical fields. Inorganic poly-isocyanates on the other hand were until recent times only seldom described in the literature and relatively little was known about their reactions.

We thus commenced three years ago with a program of research directed primarily towards the preparation of the isocyanates of sulfuric acid for the purpose of studying their poly-addition reactions with lower alcohols and with amines. In this manner, we hoped to gain access to polymeric sulfo-urethanes and sulfo-ureas.

The preparation of sulfuryl diisocyanate was accomplished with the assistance of chlorosulfonylisocyanate. This compound can be easily prepared in the reaction between cyanogen chloride and sulfur trioxide according to R. Graf [1]:

$$ClCN + SO_3 \longrightarrow ClSO_2NCO$$

We found that a further convenient procedure consists in the reaction of urea with chlorosulfonic acid. Isocyanic acid then reacts in the sense of a sulfonation to form chlorosulfonylisocyanate:

$$H_2N\text{-}CO\text{-}NH_2 + ClSO_3H \longrightarrow HNCO + \left[NH_4\right]^+ \left[ClSO_3\right]^-$$

$$ClSO_2\text{-}\boxed{OH + H}\text{-}N{=}C{=}O \xrightarrow{ClSO_3H} ClSO_2NCO + HCl\uparrow + H_2SO_4$$

Sulfuryldiisocyanate could be prepared for the first time in good yield and purity by employing silver cyanate in accordance with

$$OCNSO_2Cl + AgNCO \longrightarrow O_2S(NCO)_2 + AgCl.$$

Sulfurydiisocyanate is a colourless liquid of low viscosity which boils at 139° C/760 mm and solidifies at -5° C.

This reaction employing the silver salt is, however, too expensive for the preparation of larger quantities of the compound. A further convenient method of synthesis of the diisocyanate of sulfuric acid consists of reacting sulfur trioxide with potassium cyanate. This leads to the formation of potassium disulfate together with disulfuryldiisocyanate and this latter compound splits off sulfur trioxide upon being heated for longer periods of time at 140° C to yield sulfuryldiisocyanate

$$2\,KOCN + 4\,SO_3 \longrightarrow K_2S_2O_7 + S_2O_5(NCO)_2$$

$$S_2O_5(NCO)_2 \xrightarrow{\Delta} SO_2(NCO)_2 + SO_3$$

However, the reaction of sulfur trioxide with cyanogen bromide represents the most expedient method of preparation of $SO_2(NCO)_2$. In this case, elementary bromine and sulfur dioxide are formed together with disulfuryldiisocyanate, whereupon pyrolytic fission can be carried out in the manner just described to produce, as before, sulfur trioxide and the diisocyanate of sulfuric acid:

$$2\,BrCN + 3\,SO_3 \longrightarrow S_2O_5(NCO)_2 + Br_2 + SO_2$$

$$S_2O_5(NCO)_2 \xrightarrow{\Delta} SO_2(NCO)_2 + SO_3$$

The reactive behaviour of the diisocyanate is determined by the two isocyanate groups, which, as would be expected, react with all proton-active materials. With excess water, liberation of CO_2 occurs and sulfamide is formed in quantitative yield:

$$O_2S\begin{<}{N{=}C{=}O \\ N{=}C{=}O} + 2\,H_2O \longrightarrow O_2S\begin{<}{NH\text{-}CO\text{-}OH \\ NH\text{-}CO\text{-}OH} \xrightarrow{-2CO_2} O_2S\begin{<}{NH_2 \\ NH_2}$$

If, however, only 1 mole of water in acetonitrile is allowed to act upon the diisocyanate, amidosulfuric acid isocyanate is first formed. This substance is not very stable and it slowly undergoes a head-to-tail polymerization to form a sulfuryl urea polymer possessing a terminal isocyanate group:

$$OCN\text{-}SO_2\text{-}NCO + H_2O \longrightarrow HO\text{-}CO\text{-}NH\text{-}SO_2\text{-}NCO \xrightarrow{-CO_2} H_2N\text{-}SO_2\text{-}NCO$$

$$H_2N\text{-}SO_2\text{-}NCO + n\ H_2N\text{-}SO_2\text{-}NCO \rightleftharpoons H_2N\text{-}SO_2\text{-}(NH\text{-}CO\text{-}NH\text{-}SO_2)_n\text{-}NCO$$

The course of polymerization was measured kinetically and a result for the half life of amidosulfonic acid isocyanate of $T_{25}o = 623$ minutes was found.

In the reaction of sulfuryldiisocyanate and of amidosulfonic acid isocyanate with alcohols and with amines, a large number of sulfo-urethanes and sulfo-ureas could be prepared. Further details in this respect cannot be included in this report.

The activation of the isocyanate group by the neighbouring SO_2-group is so great that both sulfuryldiisocyanate and amidosulfonic acid isocyanate react with acid amides, although in general these amides are characterized by low proton activity. In this way, the reaction with sulfamide led to the formation of the following compounds:

Urea disulfonic acid amide:

$$H_2NSO_2NH\text{-}CO\text{-}NH\text{-}SO_2NH_2$$

Sulfuryl-di-urea sulfuryl amide:

$$H_2NSO_2NH\text{-}CO\text{-}NHSO_2NH\text{-}CO\text{-}NHSO_2NH_2$$

Polysulfuryl ureas:

$$H_2NSO_2\text{-}(NH\text{-}CO\text{-}NHSO_2\text{-})_n\text{-}NH_2$$

In a similar manner, urea and thio-urea react very readily with both starting compounds. Unfortunately, however, polymers of this type are not very stable. As a result of the numerous SO_2 groups with their acidifying influence in the chain, all the compounds just mentioned hydrolyze rather easily.

Further experiments were conducted with the aim of increasing the stability towards hydrolysis by incorporating organic groups in the molecule. By reacting sulfuryldiisocyanate with ethylene glycol, we were able to obtain polymeric horn-like materials which were readily soluble in dimethylformamide and from which films could be prepared. However, the polymers are not resistant to prolonged treatment with boiling water and hydrolysis occurs in this case also. The course of synthesis is as follows:

$$\ldots OCN\text{-}B\text{-}NCO + HO\text{-}R\text{-}OH + OCN\text{-}B\text{-}NCO + HO\text{-}R\text{-}OH\ldots$$

$$\downarrow$$

$$-CONH\text{-}B\text{-}NHCO\text{-}O\text{-}R\text{-}O\text{-}CO\text{-}NH\text{-}B\text{-}NH\text{-}CO\text{-}O\text{-}R\text{-}O\text{-}CO\ldots\ldots$$

$B = SO_2$; $R = -CH_2\text{-}CH_2-$

Example: $HO\text{-}CH_2\text{-}CH_2O\text{-}CO\text{-}NH\text{-}(SO_2NHCO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}NH)_3\text{-}$

$$-SO_2NH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2OH$$

M.p. 169°

We hope now to encounter superior properties in the corresponding phosphorus compounds. Phosphorus oxytriisocyanate will serve as starting material in these studies. This compound can be obtained in the reaction of phosphorus oxytrichloride with monomeric isocyanic acid in the presence of weak bases, although yields are poor.

$$OPCl_3 + 3\ HNCO \longrightarrow OP(NCO)_3 + 3\ HCl$$

Further research will be conducted with dichlorophosphorus oxyisocyanate, $OPCl_2(NCO)$, which can be obtained in good yield from the reaction of phosphorus pentachloride with urethane according to A. V. Kirsanov:[2]

$$PCl_5 + H_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}C_2H_5 \longrightarrow Cl_2\underset{\underset{O}{\|}}{P}\text{-}N{=}C{=}O + 2\ HCl + C_2H_5Cl$$

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1. R. Graf, Chem. Ber. 89. 1071 (1956).

2. A. V. Kirsanov, Zhur. Obschei. Khim. 24. 1033 (1954); C. A. 49. 8787a (1955).

METAL-SILOXY CONDENSATION REACTIONS

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Abstract

In search for a prototype inorganic condensation reaction that could be used later for study of inorganic polycondensation reactions, it was found that the reaction of $NaOSi\phi_3$ with ϕ_3SnCl, $(\underline{n}\text{-}C_4H_9)_2SnCl_2$, and $(CH_3)_2SnCl_2$ in an aprotic solvent is consistent with the overall equations:

$$\phi_3SnCl + NaOSi\phi_3 \rightarrow \phi_3SiOSn\phi_3 + NaCl$$

$$(\underline{n}\text{-}C_4H_9)_2SnCl_2 + 2NaOSi\phi_3 \rightarrow (\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2 + 2NaCl$$

$$(CH_3)_2SnCl_2 + 2NaOSi\phi_3 \rightarrow (CH_3)_2Sn(OSi\phi_3)_2 + 2NaCl$$

with no evidence that significant side reactions occur. These reactions appear to go to completion as shown by quantitative determination of NaCl and the stannosiloxane product. The sodium chloride by-product forms immediately, indicating that these reactions at room temperature in benzene are extremely rapid. Quantitative rate measurements could not be made but the stoichiometry of the reaction was established. In the course of the study, several new stannosiloxanes were prepared and characterized by infrared spectroscopy and elemental analysis.

The preparation, characterization, and some properties are reported for siloxy derivatives of bis(cyclopentadienyl)titanium(IV). Monosiloxy derivatives were prepared by the reaction of the appropriate sodium silanolate with bis(cyclopentadienyl)titanium dichloride in toluene at 75-90°C under anhydrous conditions. The compounds prepared and characterized were trimethylsiloxybis(cyclopentadienyl)-titanium chloride, methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, and triphenylsiloxybis(cyclopentadienyl)titanium chloride. These Ti-O-Si compounds are orange crystalline substances; the triphenylsiloxy derivative melts at 201-204°C. Replacement of C_6H_5 by CH_3 groups markedly lowers the melting points and thermal stabilities.

Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was prepared in toluene at 75-90°C from bis(cyclopentadienyl)titanium dihalide and sodium triphenylsilanolate or triphenylsilanol. $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$ is a white crystalline substance melting at 202-204°C.

An orange crystalline substance identified as 1,3-dichloro-1,1,3,3-tetrakis-(cyclopentadienyl)dititoxane was isolated from reactions of bis(cyclopentadienyl)-titanium dichloride with sodium trimethylsilanolate or sodium dimethylphenyl-silanolate.

The stabilities of the siloxy derivatives of bis(cyclopentadienyl)titanium(IV) and the yields of these compounds are directly related to the basicity or electron-donating properties of the siloxy group: the greater the basicity of the siloxy group, the more unstable is the silicon-titanium compound. Reaction paths are

postulated for the formation of these compounds.

The preparation and some properties are reported for a series of compounds containing the Si–O–Cr^{VI} linkage. A series of bis(triorganosilyl) chromates was obtained by the reaction $CrO_3 + 2R_3SiOH \rightarrow (R_3Si)_2CrO_4 + H_2O$ in methylene chloride. The silyl chromates prepared and characterized were bis(p-tolyldiphenylsilyl) chromate, bis(tricyclohexylsilyl) chromate, bis(cyclohexyldiphenylsilyl) chromate, and bis(triphenylsilyl) chromate. These compounds are light-sensitive and decompose when heated above their melting points. The most stable is bis(triphenylsilyl) chromate; aliphatic groups reduce the thermal stability.

Reaction of either chromium(VI) oxide or chromyl chloride with diphenylsilanediol gives a mixture of two siloxy-chromium compounds which are difficult to separate. Compound I is believed to have the linear structure:

$$HO[Si(C_6H_5)_2O]_3Cr(O)_2[OSi(C_6H_5)_2]_3OH$$

whereas compound II is apparently the cyclic structure:

$$\left[Cr(O)_2[OSi(C_6H_5)_2]_2OCr(O)_2[OSi(C_6H_5)_2]O\right]$$

Compound I is a yellow-orange oil and compound II is a yellow-orange crystalline solid with a sharp decomposition point at 169°C. Elemental analysis, infrared and ultraviolet spectra, molecular weight data, and chemical behavior support the postulated structures. Reaction schemes for the formation of these compounds are suggested.

INTRODUCTION

Within the past decade many attempts have been made to synthesize high molecular weight organometallic oxide polymers containing a metal-oxygen-metal backbone to which are attached "plasticizing" organic groups. The only high molecular weight polymers of this type which have been prepared are the organosiloxane compounds. Various workers claim to have made stannosiloxane, borosiloxane, arsenosiloxane, antimonosiloxane, aluminosiloxane, titanosiloxane, and aluminoxane compounds. However in all cases where molecular weights have been determined such "polymers" were found to be telomers with less than fifty repeating units in the chain. Little effort has been made to establish the nature and mechanism of even simple inorganic condensation reactions, and in too many cases the reactants and reaction products have not even been precisely characterized. Because high molecular weight organometallic oxide polymers have not been obtained, a careful study has been undertaken of the nature of the reactions involved in two siloxane-transition metal systems, and a kinetic and stoichiometric study of the mechanism of the formation of stannosiloxanes has been initiated.

Siloxy-Titanium Chemistry

James S. Skelcey

Because titanium alkoxides are polymeric and give rise to polymeric hydrolysis products which are heat resistant[1] and because of the well-known thermal stability of organosiloxanes, it is of interest to attempt to combine the structures of these two and compare the properties of the Ti–O–Si system with those of the Ti–O–C and Si–O–Si systems. Known siloxy-titanium compounds, their properties, and methods of preparation which are recorded in the literature have been reviewed in a WADD Technical Report[2]. Bradley[3] reviewed the physical and chemical properties of the tetrakis(trialkylsiloxy)titanium compounds; all are liquids except tetrakis(triethylsiloxy)titanium and tetrakis(dibutylmethylsiloxy)titanium. The siloxy-titanium compounds are perceptibly more resistant to hydrolysis and show greater thermal stability than the titanium alkoxides.

Prior to the start of this investigation in December 1959, no reactions of bis(cyclopentadienyl)titanium dichloride and siloxy compounds were reported in the literature, but in 1960 Gutmann and Meller[4] described the isolation of tetrakis(triphenylsiloxy)titanium from the reaction of bis(cyclopentadienyl)-titanium dichloride and sodium triphenylsilanolate in toluene at reflux temperature. The isolation of this product, rather than bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, was explained on the basis that the extreme stability of tetrakis(triphenylsiloxy)titanium favors its formation even though this involves the cleavage of the cyclopentadienyl rings from the titanium atom. Thus, the formation of compounds with less than four triphenylsiloxy groups bonded to titanium was believed to be unlikely. Although their reaction was carried out at a higher temperature than was used in this investigation, it has been shown that both mono- and di-substituted triphenylsiloxy compounds of bis(cyclopentadienyl)titanium(IV) can be prepared along with tetrakis(triphenylsiloxy)titanium.

Van der Kerk and Noltes[5,6] have reported the synthesis of bis(triphenylsiloxy)-bis(cyclopentadienyl)titanium by the reaction of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate in toluene at 90°C. The product was described as orange-yellow crystals which melt at 203-205°C. Identification of this compound was based solely on the percentage of combined titanium and silicon oxides after ignition of a sample. Our investigation has shown that the orange-yellow crystals which are isolated in this reaction are actually triphenylsiloxybis(cyclopentadienyl)titanium chloride and not bis(triphenylsiloxy)bis-(cyclopentadienyl)titanium. Since the percentage of combined metal oxides in triphenylsiloxybis(cyclopentadienyl)titanium chloride is 28.75 and that in bis(triphenylsiloxy)bis(cyclopentadienyl)titanium is 27.32, conclusive identification cannot be based on this information.

In this laboratory the preparation, characterization, and some properties have been studied in detail for trimethylsiloxybis(cyclopentadienyl)titanium chloride, methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, triphenylsiloxybis-(cyclopentadienyl)titanium chloride, and bis(triphenylsiloxy)bis(cyclopentadienyl)-titanium. In addition 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dititoxane was isolated and characterized as a side product in the reactions of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate.

Experimental

The monosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) were prepared by the treatment of bis(cyclopentadienyl)titanium dichloride with the appropriate sodium silanolate in toluene or benzene solutions at 75-90°C or at room temperature. The triphenylsiloxy derivative was also obtained by the reaction of bis(cyclopentadienyl)titanium dichloride and triphenylsilanol in the presence of triethylamine. Bis(triphenylsiloxy)bis(cyclopentadienyl)titanium was prepared by the reaction of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate, as well as by the reaction of bis(cyclopentadienyl)titanium diiodide and triphenylsilanol in the presence of triethylamine.

Trimethylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl[OSi(CH_3)_3]$; methyldiphenylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl[OSi(CH_3)-(C_6H_5)_2]$; triphenylsiloxybis(cyclopentadienyl)titanium chloride, $(C_5H_5)_2TiCl[OSi-(C_6H_5)_3]$; and 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dititoxane, $[(C_5H_5)_2-ClTi]_2O$, are crystalline orange solids, while bis(triphenylsiloxy)bis(cyclopentadienyl)titanium, $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$, is a white crystalline solid.

The siloxy compounds are all soluble in benzene, toluene, chlorobenzene, nitrobenzene, acetone, chloroform, and carbon tetrachloride. They are slightly soluble in ether, petroleum ether, and aliphatic hydrocarbons. The dititoxane has a lower solubility in all of these solvents but is moderately soluble in toluene, nitrobenzene, and 1,4-dioxane.

All of these compounds are decomposed by concentrated sulfuric acid. When acetone solutions of the siloxy derivatives are treated with hydrogen chloride gas a red solution results, presumably with the formation of $(C_5H_5)_2TiCl_2$. All of the compounds are hydrolyzed by sodium hydroxide dissolved in an acetone-water

mixture; however $[(C_5H_5)_2ClTi]_2O$ appears to be much more stable towards alkaline hydrolysis than the siloxy compounds. Solutions of all compounds decompose with formation of titanium dioxide when exposed to atmospheric moisture for long periods of time.

Differential thermal analyses of $(C_5H_5)_2TiCl[OSi(CH_3)(C_6H_5)_2]$, $(C_5H_5)_2TiCl[OSi(C_6H_5)_3]$, and $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$ show that these compounds soon start to decompose above their melting points. Decomposition is essentially complete for $(C_5H_5)_2TiCl[OSi(CH_3)(C_6H_5)_2]$ and $(C_5H_5)_2TiCl[OSi(C_6H_5)_3]$ at 500°C., while for $(C_5H_5)_2Ti[OSi(C_6H_5)_3]_2$ this occurs at approximately 425°C. The dititoxane slowly turns dark above 200°C. and rapidly decomposes above 225°C. The overall stability of $(C_5H_5)_2TiCl[OSi(CH_3)_3]$ is much lower than that of the phenylsiloxy derivatives.

Infrared, visible, and ultraviolet spectra as well as molecular weight, x-ray diffraction, and complete elemental analytical data are reported and discussed in a thesis by J. S. Skelcey[7].

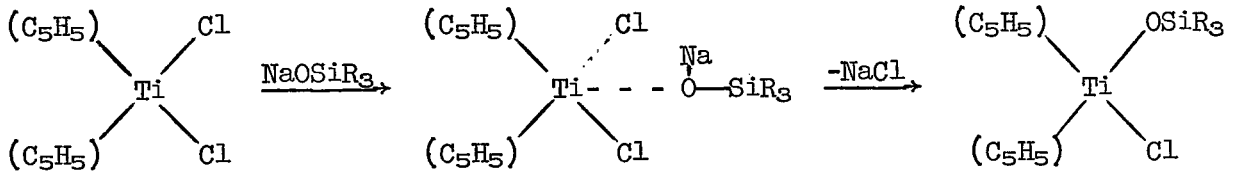
Discussion

The formation of these siloxy compounds can be visualized as occurring either by a dissociation process or a bimolecular displacement reaction. A dissociation reaction involving one of the following processes seems unlikely in a solvent such as toluene.

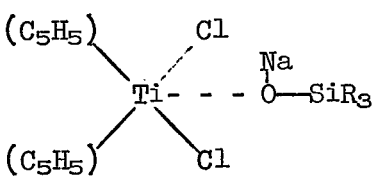
$$(C_5H_5)_2TiCl_2 \rightleftharpoons (C_5H_5)_2TiCl^+ + Cl^-$$

$$NaOSiR_3 \rightleftharpoons Na^+ + R_3SiO^-$$

A bimolecular displacement process seems more probable:

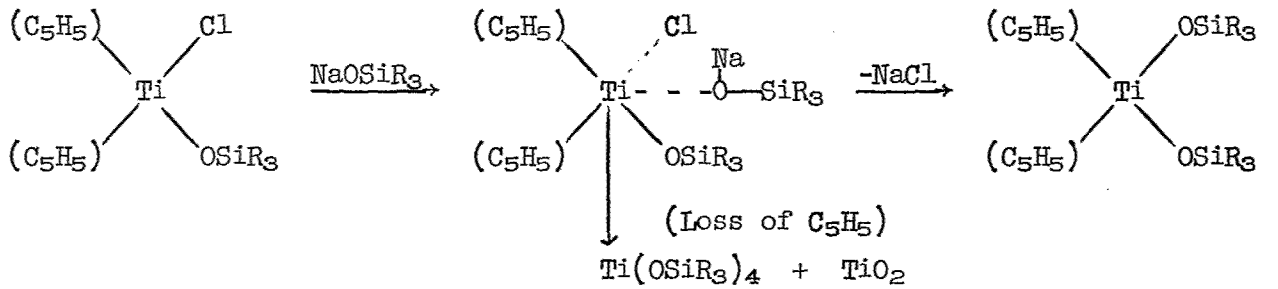


Bis(cyclopentadienyl)titanium dichloride has an essentially tetrahedral arrangement of cyclopentadienyl rings and chlorine atoms about the titanium atom. The primary bonding involves a set of tetrahedral orbitals of the titanium atom derived by a mixing of the $3d^34s$ and $4s4p^3$ hybrids. π-Bonding to the cyclopentadienyl rings then occurs through the d_{z^2} and $d_{x^2-y^2}$ orbitals of titanium. Since there is a mixing of the $3d^34s$ and $4s4p^3$ hybrids, 3d and 4p orbitals are still available to accept an electron pair from the oxygen of the silanolate and form the activated complex:



The coordination of the oxygen electron-pair to the titanium would favor the use of the titanium 3d orbitals since they are at a lower energy level than the 4p orbitals. Because of the steric hindrance of the cyclopentadienyl groups, attack by the silanolate should occur on the chlorine side of the molecule and simultaneous weakening of a titanium-chlorine bond may be expected to lead to formation of the siloxy-titanium compound and sodium chloride. The increase in electron density about the titanium atom in the activated complex is expected to weaken the bonding between titanium and the cyclopentadienyl rings and to make them more susceptible to cleavage.

The initial step in the formation of the monosubstituted compound is probably quickly followed by an attack by the silanolate on the second chlorine according to the following scheme; the reaction is driven by the formation of the less soluble sodium chloride.



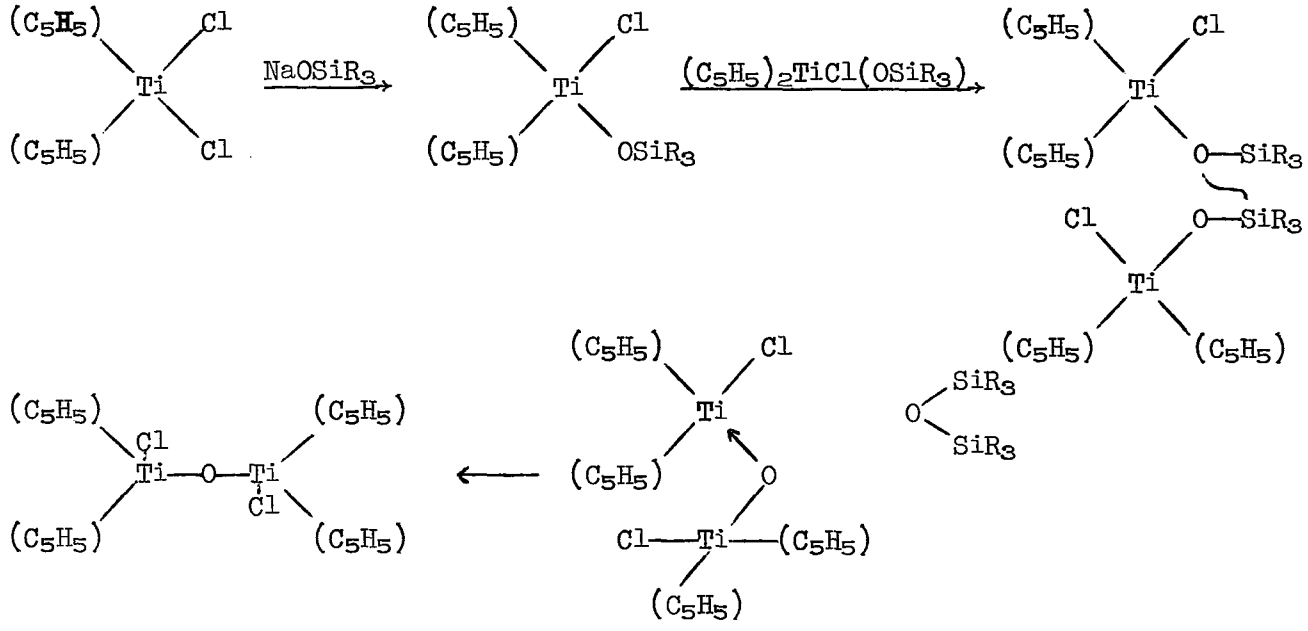
Formation of the activated complex in this case is a critical step in the reaction since either the disubstituted product is formed or ring removal occurs with formation of the tetrasubstituted compound or titanium dioxide. The penta-coordination of titanium in the complex weakens the bonds between titanium and the cyclopentadienyl rings because the increased electron density about the metal should decrease the π-bonding. Coupled to this may be a steric factor. The presence of two bulky triorganosiloxy groups as well as a chlorine atom around the bis(cyclopentadienyl)titanium(IV) moity may put an additional strain on the titanium-carbon bonds because of a crowding of these large groups about the metal atom. The formation of titanium dioxide is not completely understood; it may be the result of moisture in the reaction or an effect of the self-condensation of silanolates which would furnish the oxygen necessary for titanium dioxide formation.

On this basis it is easy to visualize why such low yields of the monosiloxy derivatives of bis(cyclopentadienyl)titanium(IV) have been obtained. Consideration of the fact that the only disubstituted compound isolated was bis(triphenylsiloxy)bis(cyclopentadienyl)titanium and that only very small amounts of trimethylsiloxybis(cyclopentadienyl)titanium chloride were isolated leads to the belief that the basicity or electron-pair donating properties of the siloxy group is a very important factor determining the stability of these compounds. If this is so, the greater basicity of the trimethylsiloxy group in comparison to the triphenylsiloxy group should further weaken the titanium-carbon bonds in the activated complex and increase the tendency for loss of cyclopentadienyl groups to occur. This is observed to be the case. Differences in the steric effects between the cyclopentadienyl rings and trimethylsiloxy or triphenylsiloxy

groups apparently is not significant; basicity of the siloxy groups appears to be the deciding factor which determines the stability of the activated complex and controls the subsequent formation of the siloxybis(cyclopentadienyl)-titanium(IV) compound.

Moisture in the reaction mixture also enhances the cleavage of titanium-carbon bonds. The reactions of bis(cyclopentadienyl)titanium dichloride and sodium triphenylsilanolate which were carried out in the open produced only titanium dioxide and tetrakis(triphenylsiloxy)titanium. The reactions involving sodium trimethylsilanolate yielded large amounts of titanium dioxide, but the presence of tetrakis(trimethylsiloxy)titanium in the reaction products was not confirmed. Sodium silanolates are hygroscopic solids which easily hydrolyze to the silanol and sodium hydroxide, and their handling in the open must be kept to a minimum. Reactions of bis(cyclopentadienyl)titanium dichloride with sodium silanolates in the presence of moisture probably proceed by base-induced hydrolysis of the titanium compound which yields titanium dioxide as the main product.

The isolation of 1,3-dichloro-1,1,3,3-tetrakis(cyclopentadienyl)dititoxane in the reaction of bis(cyclopentadienyl)titanium dichloride with sodium trimethylsilanolate and sodium dimethylphenylsilanolate is not at first easily understood. However, consideration of the greater stabilities of hexamethyldisiloxane and tetramethyldiphenyldisiloxane in comparison to the respective silanols suggests a plausible mechanism for the formation of the dititoxane. This is illustrated by the following scheme:



The first step of such a reaction might be the formation of the monosubstituted siloxy compound of bis(cyclopentadienyl)titanium(IV). Release of electrons by the trimethylsilyl or dimethylphenylsilyl group should make the electrons of the oxygen atom more available for coordination and also should oppose the $d_{\pi} - p_{\pi}$ bonding between silicon and oxygen atoms in which an oxygen electron pair interacts with the empty d orbitals of silicon. Therefore, the d orbitals of silicon are more available to accept an electron pair. Two molecules of the

monosubstituted compound can react by coordination of the oxygen atom of one siloxy compound to the silicon atom of the other compound. This might then be followed by the formation of the stable disiloxane and the titanium-oxygen-titanium bond of the dititoxane.

The siloxy derivatives of bis(cyclopentadienyl)titanium(IV) were in general difficult to purify. The solubilities of these compounds in organic solvents are similar to those of bis(cyclopentadienyl)titanium dichloride and organosilicon compounds. Thus, in many cases repeated recrystallizations were necessary for purification.

The thermal stabilities of the siloxy derivatives of bis(cyclopentadienyl)titanium-(IV) are lower than the tetrasubstituted siloxy compounds of titanium(IV). This is especially noted in the comparison of triphenylsiloxybis(cyclopentadienyl)-titanium chloride and bis(triphenylsiloxy)bis(cyclopentadienyl)titanium with tetrakis(triphenylsiloxy)titanium. Furthermore, these bis(cyclopentadienyl)-titanium(IV) compounds have titanium-carbon bonds which are more susceptible to hydrolytic cleavage than the titanium-oxygen-silicon bonds of tetrasubstituted siloxy compounds of titanium.

Inorganic Condensation Reactions. I. Preparation of Some Stannosiloxanes

Curt Thies

Within the past decade many workers have attempted to synthesize polymers with elements other than carbon in the chain backbone. A majority have followed the simple and classical route to polymer formation by mixing bifunctional reactants which polycondense. While there is ample information on the products formed from a large variety of different elemental systems, little effort has been made to establish the nature and mechanism of simple inorganic condensation reactions. Because of their commercial interest, the only inorganic polycondensation process studied quantitatively is the polymerization of difunctional silanols. Thus a prototype condensation reaction, carefully characterized in stoichiometry and rate, is needed to understand the details of inorganic condensation reactions. Once a prototype system is established, variations with respect to the influence of pendant substituents and other elements on the condensation reaction can be evaluated. In addition it will be possible to determine whether or not the theory of polycondensation as developed by Flory, Carrothers and others for simple organic condensation reactions can be applied to inorganic systems as well.

Since the silanediol system has been studied in detail, a prototype copolycondensation reaction with difunctional siloxy compounds was chosen for investigation. For the other comonomer, difunctional compounds of tin were chosen because of the availability of commercially pure monomers and the reported stability of Sn–O–Si bonds. As the first step in this study, the preparation and characterization of dimeric and trimeric species was undertaken.

Experimental

Sodium triphenylsilanolate ($NaOSi\phi_3$) was prepared by the cleavage of $\phi_3SiOSi\phi_3$ with a stoichiometric amount of sodium hydroxide.[8] The equilibrium is forced to the right by removing the water formed from the reaction mixture.

All organotin chlorides were obtained from commercial sources. Triphenyltin chloride (ϕ_3SnCl), diphenyltin dichloride (ϕ_2SnCl_2), and dimethyltin dichloride [$(CH_3)_2SnCl_2$] were recrystallized from toluene at -14°C. Dibenzyltin dichloride [$(\phi CH_2)_2SnCl_2$] was recrystallized from toluene at -4°C while dibutyltin dichloride [$(n\text{-}C_4H_9)_2SnCl_2$] was recrystallized from 30-60° petroleum ether at -4°C.

Preparation of stannosiloxane compounds. Several stannosiloxane compounds were prepared by dissolving $NaOSi\phi_3$ in dry benzene and adding to this solution a stoichiometric amount of the appropriate organotin chloride also dissolved in benzene. After mixing, the reaction mixture was allowed to stand five to fifteen minutes at room temperature before the sodium chloride precipitate was removed by filtration. The clear filtrate was taken to dryness *in vacuo* and the product recrystallized.

Stoichiometry. Stoichiometry of the reaction of $NaOSi\phi_3$ with ϕ_3SnCl, $(CH_3)_2SnCl_2$, and $(n\text{-}C_4H_9)_2SnCl_2$ in benzene was established by obtaining closed material balances about reaction systems involving semi-micro quantities of reactants. In

order to obtain sufficient material for analysis, 5 ml. aliquots of the reactant solutions were pipetted into the reactor, a 50 ml. Erlenmeyer. The solutions ranged in concentration from 0.007 to 0.05 M. After mixing, the reaction mixture was kept in the reactor for a known period at room temperature before being filtered into a tared 50 or 125 ml. filter flask. The clear filtrate was temporarily set aside.

All traces of benzene in the reactor and filter were removed by drying at 90°C. Upon cooling, the reactor was extracted with 10 ml. of distilled water. This solution was transferred to the filter and drawn into a clean 125 ml. filter flask. A second extraction with 5 ml. of water was used to insure complete removal of sodium chloride from the reactor and filter. Chloride present in the combined water extract (15 ml.) was determined by titration with 0.0200 N standard silver nitrate using dichlorofluorescein as the indicator.

Several standard chloride analyses were carried out to establish the effectiveness of the above extraction and titration method. The results indicate that in the presence of $\phi_3SiOSn\phi_3$ the average recovery is 99.0% with a standard deviation (σ) of ± 0.21%. The presence of organotin chlorides did not appear to affect chloride recovery significantly except in the case of $(CH_3)_2SnCl_2$ where the effect is small.

After the water extraction, the reactor and filter were dried at 105°C. Upon cooling, the reactor was extracted with 10 ml. benzene. The extract was transferred to the filter and drawn into the tared 125 ml. filter flask containing the original benzene filtrate. A second 10 ml. benzene extraction was used to assure complete removal of solids from the walls of the reactor and filter. The combined benzene filtrate was taken to constant weight in vacuo and the weight of the solid residue determined by difference. The amount of stannosiloxane compound present in this residue was measured spectrophotometrically using the characteristic Si–O–Sn peak for identification. Examination of infrared spectra of the reactants and products established that only the intense Si–O–Sn peak in the various stannosiloxane compounds absorbed significantly in the 10.40 to 10.60μ region.

In order to carry out spectrophotometric determinations of various stannosiloxanes, it was first necessary to prepare calibration plots for each compound. Solutions of known concentrations ranging from 0.0055 to 0.0091 M were prepared using purified $\phi_3SiOSn\phi_3$, $(n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, and $(CH_3)_2Sn(OSi\phi_3)_2$ samples. Cyclohexane was used as a solvent for $\phi_3SiOSn\phi_3$ and $(n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$, while carbon disulfide was employed for $(CH_3)_2Sn(OSi\phi_3)_2$. Eight and one-half microns was selected as the 100% transmission reference point. In all cases, Beer's Law was obeyed over the concentration range investigated.

The yield of a stannosiloxane compound in a given reaction mixture was determined by preparing a solution (cyclohexane or carbon disulfide) of the solid residue with a known concentration (c_o, M). Absorbancy of the Si–O–Sn peak was then measured as outlined above, and the concentration (c, M) of the stannosiloxane compound actually present in the solution taken from the appropriate Beer's Law calibration plot. The yield (%) was calculated from the relation:

$$Y = (c/c_o) \times 10^2$$

Results

A. Stannosiloxane formation. A series of stannosiloxane compounds was synthesized by the procedure outlined above. Pertinent data are listed in Table I. Only carbon-hydrogen data are reported here. Combined Si-Sn oxides, determined by the method of Gilman and King, were within ± 1.0% of the theoretical value.[9]

TABLE I

Stannosiloxane Compounds Prepared by Silanolate Condensation Reaction in Benzene

Compound	Moles of $NaOSi\phi_3$ Used	M.P., °C	Yield, %	Analytical Calculated C,%	Calculated H,%	Found C,%	Found H,%
$\phi_3SiOSn\phi_3$	0.00612	139-140	59.7	69.15	4.80	69.33	4.84
$(CH_3)_2Sn(OSi\phi_3)_2$	0.00708	155-156	64.9	65.26	6.01	65.44	5.9
$(n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$	0.00677	69-70	79.5	67.46	6.90	67.61	6.57
$\phi_2Sn(OSi\phi_3)_2$	0.00758	148.5-149.5	40.2	70.01	5.83	70.05	5.64
$(\phi CH_3)_2Sn(OSi\phi_3)_2$	0.00958	122-123	78.3	70.36	5.39	70.41	5.31

B. Stoichiometry and rate of stannosiloxane formation. Representative stoichiometric results for the reaction of $NaOSi\phi_3$ with ϕ_3SnCl, $(CH_3)_2SnCl_2$, and $(n\text{-}C_4H_9)_2SnCl_2$ in benzene are presented in Table II. The NaCl, $\phi_3SiOSn\phi_3$, $(CH_3)_2Sn(OSi\phi_3)_2$, and $(n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ yields are consistent with the overall equations:

$$NaOSi\phi_3 + \phi_3SnCl \rightarrow \phi_3SiOSn\phi_3 + NaCl$$

$$2NaOSi\phi_3 + (n\text{-}C_4H_9)_2SnCl_2 \rightarrow (n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2 + 2NaCl$$

$$2NaOSi\phi_3 + (CH_3)_2SnCl_2 \rightarrow (CH_3)_2Sn(OSi\phi_3)_2 + 2NaCl$$

There is no evidence that significant side reactions occurred. Although a few relatively low $(n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$ and $(CH_3)_2Sn(OSi\phi_3)_2$ yields were observed, a frequency plot of data from 42 runs shows the results cluster about a central value of 96%. Since the $NaOSi\phi_3$ used was only 96-98% pure, this is the expected range for total consumption of reactants.

TABLE II

Representative Stoichiometric Data for Stannosiloxane Formation

Initial Reactant Concn. (g. equiv./l)	Sodium Chloride Yield (%)	Stannosiloxane Yield (%)
$\phi_3SiOSn\phi_3$:		
0.0127	96.2	96.7

continued

Table II - continued

Initial Reactant Concn. (g. equiv./l)	Sodium Chloride Yield (%)	Stannosiloxane Yield (%)
$\phi_3SiOSn\phi_3$:		
0.0127	99.6	100.2
0.0127	98.0	103.2
0.0345	97.4	99.4
0.0345	97.6	98.5
0.0345	96.0	98.7
$(n\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$:		
0.026	96.8	89.3
0.026	96.7	93.6
0.026	95.8	89.5
0.049	96.8	89.3
0.049	98.3	97.5
0.049	97.9	100.0
0.049	97.3	97.1
$(CH_3)_2Sn(OSi\phi_3)_2$:		
0.0127	--	88.5
0.0136	98.6	98.7
0.0136	90.9	97.8
0.0136	99.0	87.1
0.049	94.7	97.0
0.026	97.2	96.4

Sodium chloride formation is rapid when stoichiometric amounts of $NaOSi\phi_3$ are mixed in benzene with ϕ_3SnCl, $(CH_3)_2SnCl_2$, $(n\text{-}C_4H_9)_2SnCl_2$, or ϕ_2SnCl_2. Representative data are shown in Table III. Since the $NaOSi\phi_3$ used in this study was 96-98% pure, the observed sodium chloride recoveries correspond to total $NaOSi\phi_3$ consumption. Variation in the sodium chloride yields is within experimental error.

TABLE III

Representative Sodium Chloride Recovery Data

Initial Reactant Concn. (g. equiv./l)	Reaction Time (minutes)	Sodium Chloride Recovery (% theoretical)
$\phi_3SiOSn\phi_3$:		
0.0127	1.1	96.2
0.0127	51.3	99.6
0.0127	2796.0	98.0
0.0345	0.9	96.0
0.0345	27.8	97.4
0.0345	2994.0	97.6
$(\underline{n}\text{-}C_4H_9)_2Sn(OSi\phi_3)_2$:		
0.0147	4.0	95.2
0.0147	9.0	100.9
0.0147	148.1	99.8
0.0147	1207.0	99.7
0.0490	0.8	94.6
0.0490	50.4	95.1
0.0490	1560.0	94.9
$(CH_3)_2Sn(OSi\phi_3)_2$:		
0.0136	3.8	98.4
0.0136	12.5	99.0
0.0136	61.8	98.6
0.0136	682.0	90.9
0.0490	1.0	95.0
0.0490	50.2	95.5
0.0490	2190.0	94.7

The rapid rate of sodium chloride formation found in this study indicates that $NaOSi\phi_3$-organotin chloride condensation processes carried out at room temperature in benzene are extremely fast. Such reactions are complete in less than a minute, so quantitative rate data could not be obtained.

Since quantitative rate measurements were not made, elucidation of a reaction mechanism for the $NaOSi\phi_3$-organotin chloride condensation process in benzene is not possible. However, certain inferences may be drawn from the stoichiometric and qualitative rate data which were obtained. One of these is that pure $NaOSi\phi_3$ will react in benzene with a stoichiometric amount of R_3SnCl or R_2SnCl_2 to give quantitative yields of the corresponding stannosiloxane compound. Side reactions do not occur under the mild reaction conditions employed in this study

This is significant since conventional polycondensation processes must utilize reactions which are free of undesirable side reactions. Extrapolation of the above results to bifunctional systems which are capable of polymer formation might seem precarious, but syntheses of organic condensation polymers are based on simple reactions of multifunctional groups. The fact that these reactions were free of secondary processes was established from studies of the corresponding monofunctional systems. The lack of such knowledge has been one of the handicaps in syntheses of organometallosiloxane polymers. Results of the present investigation indicate the reaction of pure $(NaO)_2Si\phi_2$ with R_2SnCl_2 in an aprotic solvent should yield stannosiloxane polymers having a regular alternating (–Si–O–Sn–O–) structure. If cyclic compounds are formed, it should be possible to isolate and identify these. The important point is Si–O–Si or Sn–O–Sn bonds should not be formed by various side reactions under normal reaction conditions if pure reactants are employed.

It is significant that the reaction of $NaOSi\phi_3$ with organotin chlorides in benzene is extremely fast and irreversible. The sodium chloride byproduct precipitates immediately thereby forcing the reaction to completion. This distinguishes such reactions from those commonly employed to synthesize organic condensation polymers. Organic polycondensation processes, in general, have utilized slow, reversible organic reactions which require elevated temperatures and reduced pressure for high polymer formation. A notable exception is the interfacial polycondensation technique which has recently been developed. In this method a fast, irreversible polymerization of two fast-reacting intermediates occurs near the interface between phases of a heterogeneous liquid system.[10,11] Characteristic features of ordinary melt and interfacial polycondensation processes are compared in Table IV.[10] The interfacial method is obviously the simplest since impurities, stoichiometric imbalance of reactants, and even side reactions do not necessarily limit polymer formation. All of these factors drastically limit the molecular weight of polymers formed by the melt condensation process.

Since reactions ordinarily used in interfacial polycondensations are similar to the $NaOSi\phi_3$-organotin chloride reaction (fast and irreversible), it appears that regular alternating stannosiloxane polymers could be prepared by the interfacial method. The only difficulty seems to be lack of a suitable heterogeneous solvent system since relatively pure $(NaO)_2Si\phi_2$ has already been isolated.

TABLE IV

Comparison of Interfacial and Melt Polycondensation

	Interfacial	Melt
Intermediates		
Purity	moderate to high (90%)	high (98%)
Balance	unnecessary	necessary
Stability to heat	unnecessary	necessary

continued

Table IV - continued

	Interfacial	Melt
Polymerization conditions		
Time	several minutes	several hours
Temperature	0-40°C	>200°C
Pressure	atmospheric	high and low
Equipment	simple, open	special, sealed
Products		
Yield	low to high	high
Structure	unlimited	limited by stability to heat and fusibility

C. Polymer formation. Several stannosiloxane polymers were synthesized by the in situ condensation of $(NaO)_2Si\phi_2$ with $(n\text{-}C_4H_9)_2SnCl_2$. The polymers have not been fully characterized as to their hydrolytic and thermal stability, molecular weight, or various other physical properties. Attention was focused on determining if the silanolate-organotin chloride reaction involving bifunctional reactants proceeded in the same manner as the monofunctional systems. The polymerizations were carried out under a variety of reaction conditions. Complete material balances were established about each reaction system and the sodium chloride recovery data taken as a measure of the extent of reaction.

The results (Table V) show there is essentially no difference in the extent of reaction of each polymerization process. Similar sodium chloride recoveries were obtained for the polymerization carried out at -14°C for two hours and that carried out at reflux temperature for 24 hours.

TABLE V

Material Balance Data for In Situ Preparation of Stannosiloxane Polymers

Sample	$(n\text{-}C_4H_9)_2SnCl_2$ Added, Mole	Reaction Time, Min.	Reaction Temperature, °C.	Sodium Chloride Recovery, %	Total Bulk Polymer Recovered, %
ϕ-Bu I	0.0250	108	-4	98.0	99.2
ϕ-Bu II	0.0226	30	reflux	97.4	98.2
ϕ-Bu III	0.0249	3042	-14	97.7	--
ϕ-Bu IV	0.2026	1440	reflux	97.1	87.4

Undesirable side reactions in the *in situ* $(NaO)_2Si\phi_2$-$(n\text{-}C_4H_9)_2SnCl_2$ polycondensation process were detected by fractionating the bulk stannosiloxane polymers into a methanol-soluble and methanol-insoluble fractions as outlined previously. Carbon, hydrogen, and chlorine analyses for each methanol-insoluble fraction are shown in Table VI. Calculated carbon-hydrogen values are for the [O–Siϕ_2–O–Sn-(n-C_4H_9)$_2$] unit.

Although none of the fractions had carbon-hydrogen analyses which agreed well with the calculated values, carbon-hydrogen analyses for the ϕ-Bu I and ϕ-Bu II fractions are extremely close. This indicates, but does not prove, the ϕ-Bu I and ϕ-Bu II polymerizations were relatively free of side reactions. In contrast, carbon-hydrogen analyses for the ϕ-Bu III and ϕ-Bu IV fractions differ significantly from the calculated values. In these cases the Si–Sn ratio is 1 indicating significant side reactions have occurred. It is interesting to note reaction times for ϕ-Bu III and ϕ-Bu IV are much greater than those for ϕ-Bu I and ϕ-Bu II. Infrared spectra for all methanol-soluble fractions were essentially identical.

TABLE VI

Analytical Data for Methanol-Insoluble Stannosiloxane Polymer Fractions

Polymer	Analytical				
	Calculated		Found		
	C (%)	H (%)	C (%)	H (%)	Cl (%)
ϕ-Bu I	53.73	6.27	53.33 53.22	6.20 2.24	0.0
ϕ-Bu II	53.73	6.27	53.43 53.37	6.36 6.25	0.0
ϕ-Bu III	53.73	6.27	48.42 48.62	6.60 6.52	0.0
ϕ-Bu IV	53.73	6.27	44.64 44.72	6.86 6.92	0.0

The above results show the *in situ* $(NaO)_2Si\phi_2$-$(n\text{-}C_4H_9)_2SnCl_2$ polymerization process is rapid and yields polymers which contain Si–O–Sn bonds. However, further conclusions about these polymers cannot be made at present since they have not been properly characterized. Such characterization will be the subject of a future study. In addition it will be necessary to perform the polymerization with highly purified monomers under conditions more conducive to high polymer formation than those attempted to date.

Summary

A series of stannosiloxane compounds has been prepared by the condensation of sodium triphenylsilanolate with various organotin chlorides in benzene. Infrared and elemental analyses were employed to characterize the reaction products.

The stoichiometry of the reaction of sodium triphenylsilanolate with triphenyltin chloride, dimethyltin dichloride, and dibutyltin dichloride in benzene has been established. Sodium chloride byproduct yields were obtained by standard silver nitrate titration. Stannosiloxane yields were determined spectrophotometrically using the characteristic Si–O–Sn peak for identification. Results obtained using these techniques show the sodium chloride-organotin chloride condensation reaction in benzene goes to completion and is free of significant side reactions.

Sodium chloride formation has been found to be rapid when sodium triphenylsilanolate is caused to react at room temperature in benzene with a stoichiometric amount of an organotin chloride. Such reactions are complete in less than a minute, so quantitative rate data could not be obtained. For this reason, a mechanism cannot be postulated for the sodium triphenylsilanolate-organotin chloride condensation process in benzene. However, the lack of side reactions in such processes is significant since this implies the reaction of pure $(NaO)_2Si\phi_2$ with organotin dichlorides in an aprotic solvent will yield high molecular weight stannosiloxane polymers having a regular alternating (–Si–O–Sn–) structure.

Several stannosiloxane polymers have been prepared under a wide range of reaction conditions by the in situ condensation of $(NaO)_2Si\phi_2$ with dibutyltin dichloride. The polymers were not fully characterized, but it has been established that the polymerization process is rapid. Highly purified $(NaO)_2Si\phi_2$, which is soluble in absolute ethanol, has been isolated and will be used in future stannosiloxane polymerizations.

Infrared spectra and complete analytical data of some eighty preparations and additional experimental detail are available in the dissertation of C. Thies, Department of Chemistry, Michigan State University.

Silyl Chromates

Curtis R. Hare

Recent interest in polymeric inorganic molecules has lead to consideration of the possibility of incorporating the difunctional and approximately tetrahedral chromyl group into siloxy compounds. In this laboratory an investigation has been undertaken of the synthesis and properties of compounds in the general class $(R_3Si)_2CrO_4$. The methods developed for the preparation, isolation, purification, and characterization of these compounds were then used in studying the more complex reactions of chromium(VI) compounds with the silanediols. Simple $(R_3Si)_2CrO_4$ compounds also were used to observe the effects of different organic groups (R) on the properties of silylchromates.

When this investigation was undertaken in 1958, no information was available on the chemistry of the Cr^{VI}–O–Si linkage. Schmidt and Schmidbaur[12] recently reported the preparation of bis(trimethylsilyl)chromate from hexamethyldisiloxane and chromium(VI) oxide. This compound also was prepared as a part of this investigation. Granchelli and Walker[13] have patented a method of preparation for bis(triphenylsilyl) chromate by the reaction of triphenylsilanol with chromium(VI) oxide in glacial acetic acid or xylene. Preparation of the compound was carried out independently in this investigation.

Bis(triorganosilyl)chromates were synthesized by condensation of the appropriate silanol with chromium(VI) oxide in chlorinated-methane solutions in which the silanols are soluble but chromium(VI) oxide is not.

$$2R_3SiOH + CrO_3 \xrightarrow[\text{heat}]{CH_2Cl_2} (R_3Si)_2CrO_4 + H_2O$$

Solutions of the silanol immediately took on a yellow-orange color when chromium(VI) oxide was added, and in all cases the reaction mixtures were highly colored within thirty minutes. After 0.5-3.0 hours of refluxing, the reaction mixture was filtered to remove excess chromium(VI) oxide and the solvent was removed with a rotary evaporator. The crude product, obtained in 94-97% yield (based on the silanol), was then purified by recrystallization from an appropriate solvent. Characterization of the products was based upon analytical and spectrophotometric data. Complete experimental details, including infrared, visible, and ultraviolet spectra as well as molecular weight, x-ray diffraction, and complete elemental analytical data are reported and discussed in a thesis by Curtis R. Hare[14].

Experimental

Bis(triphenylsilyl) chromate. Three types of reactions were used under varying conditions to prepare bis(triphenylsilyl) chromate: (a) the reaction of triphenylsilanol with chromium(VI) oxide, (b) the reaction of triphenylsilanol with chromyl chloride, and (c) cohydrolysis of triphenylchlorosilane and chromyl chloride. The first general reaction was studied most extensively because any excess chromium(VI) oxide is easily removed by filtration and a high yield (96-97%) of crude product is obtained regardless of the solvent used or the

presence of base.

Crude bis(triphenylsilyl) chromate from reactions (a) and (b) was recrystallized from methylene chloride and an 85% yield of orange-colored crystals (m.p. 153.5-154°C) was obtained. This compound decomposes above its melting point. Analytical data are recorded in Table I.

Bis(p-tolyldiphenylsilyl) chromate. This compound was prepared by the general method. After removal of the solvent, a red, uncrystallizable oil was obtained. It was dissolved in methylene chloride, hexane was added, and the solution was boiled to remove methylene chloride. A yellow crystalline product was obtained from the cooled solution. After recrystallization from hexane, the melting point was 98.5-99°C; decomposition occurs above the melting point. Analytical data are recorded in Table I.

Bis(cyclohexyldiphenylsilyl) chromate. The preparation of bis(cyclohexyldiphenylsilyl) chromate was effected by the general method. Purified material is an orange solid melting at 84-85°C. Solid bis(cyclohexyldiphenylsilyl) chromate does not appear to decompose at its melting point but it is unstable at 100°C. Analytical data are recorded in Table I. The purity of the silyl chromate is 96% based on chromium content and 107% based on silicon content. These data, along with the low molecular weight, indicate that separation of the silanol from the silyl chromate was not complete. Since this product is highly soluble in common organic solvents and a good recrystallization technique for its purification could not be developed, further effort did not seem justified.

TABLE I

Some Properties of Silyl Chromates

Compound	Composition (%)				Molecular Weight	Melting Point (°C)
	Cr	Si	C	H		
bis(triphenylsilyl) chromate						153.5-154
Calculated	8.19	8.84	68.11	4.76	634	
Found	8.20	8.91	68.04	4.80	626 ± 10	
bis(p-tolyldiphenylsilyl) chromate						98.5-99
Calculated	7.85	8.47	68.50	5.17	664	
Found	7.76	8.55	68.51	5.22	644 ± 10	
bis(cyclohexyldiphenylsilyl) chromate						84-85
Calculated	8.04	8.68	66.84	6.55	647	
Found	7.72	9.25	66.56	6.52	633 ± 10	
bis(tricyclohexylsilyl) chromate						125-126
Calculated	7.76	8.37	64.43	9.91	671	
Found	7.68	8.40	64.22	9.78	643 ± 10	

Bis(tricyclohexylsilyl) chromate. This compound was also prepared by the general method previously described. The recrystallized red-orange solid had a melting point of 125-6°C. It is unstable above its melting point and has a different absorption spectrum from the other compounds in this series.

Bis(trimethylsilyl) chromate. Hexamethyldisiloxane was refluxed with chromium(VI) oxide in methylene chloride, and after 12 hours the mixture was filtered and solvent removed. The resulting red oil was not distilled owing to its explosive character. Vacuum evaporation into a bath at -78°C was used to isolate the compound. The product is stable when stored at -78°C in the dark, but at room temperature and in the absence of light it shows appreciable decomposition within three hours. The infrared, visible, and ultraviolet spectra of this compound were recorded without isolation of the substance from solution. An attempt to determine the molecular weight of bis(trimethylsilyl) chromate in benzene failed because of reaction of the silyl chromate with benzene.

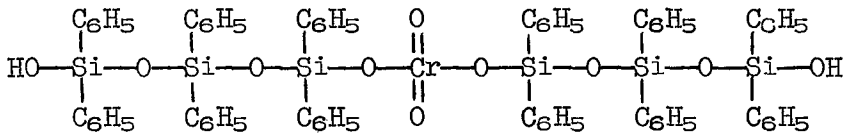
Properties of silyl chromates. All of the silyl chromates described in the previous section decompose into a black amorphous solid on prolonged exposure to light. Bis(tricyclohexylsilyl) chromate is less light sensitive than the other silyl chromates, while bis(trimethylsilyl) chromate decomposes most rapidly on exposure to light. All except the aliphatic silyl chromates may be safely stored in the dark at room temperature.

The aliphatic silyl chromates and bis(cyclohexyldiphenylsilyl) chromate are decomposed by concentrated nitric acid, and all are decomposed by a mixture of concentrated sulfuric and nitric acids. Both bis(trimethylsilyl) chromate and bis(methyldiphenylsilyl) chromate are decomposed by water. In the case of bis(trimethylsilyl) chromate, the disiloxane is formed on hydrolysis. All the silyl chromates are decomposed by homogeneous hydrolysis in an acetone-water solution. Homogeneous hydrolysis of bis(triphenylsilyl) chromate by addition of water to an acetone solution gives the silanol in a nearly quantitative yield, and about half of the chromium remains in the hexavalent state, most likely as chromic acid.

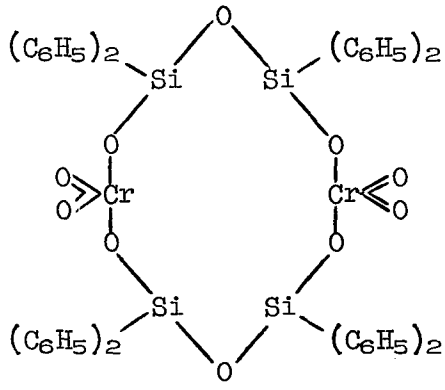
The silyl chromates are very soluble in methylene chloride, carbon tetrachloride, chloroform, acetone, and ethanol. With the exception of bis(cyclohexyldiphenylsilyl) chromate and the aliphatic silyl chromates, they are all only slightly soluble in cyclohexane and aliphatic hydrocarbons.

Of the compounds prepared, thermal stability is greatest for bis(triphenylsilyl) chromate which decomposes above its melting point of 153.5-154°C. All of the organosilyl chromates decompose above their melting points except for bis(cyclohexyldiphenylsilyl) chromate which is stable to about 15° above its melting point of 84-85°C.

Condensation products of diphenylsilanediol with chromium(VI) compounds. The reaction of diphenylsilanediol with chromium(VI) oxide or chromyl chloride in methylene chloride or carbon tetrachloride has been carried out under various conditions. Two compounds tentatively believed to be represented by the structures I and II below are obtained, but compound I is very difficult to separate in pure form.



Compound I



Compound II

Characterization of compounds I and II. Numerous determinations of molecular weight and elemental analysis of compound I have been made. Although complete removal of impurities (hexaphenylcyclotrisiloxane, compound II, and solvent) is difficult, the most nearly pure product has a silicon-chromium ratio approaching six to one and a molecular weight of about 1300. These data are consistent with structure I. The infrared spectrum of this compound shows weak OH, strong Si–O–Si, and strong Cr=O absorptions. The product repels cold water but is slowly attacked by hot water; it is rapidly hydrolyzed with acetone-water solution. In the latter case, the only product isolated was hexaphenylcyclotrisiloxane. Compound I is sticky when freshly prepared, but on standing it hardens into a yellow-brown glassy substance. It is quite stable at room temperature in the dark, but in light it slowly decomposes to a black mass from which hexaphenylcyclotrisiloxane has been isolated. Even in the glassy state compound I is easily melted with the heat of the hand. Differential thermal analysis shows that it begins to decompose at about 275°C; the thermal effect reaches a maximum at 460°C.

Compound II has the following elemental analysis: carbon, 58.15% (calcd. 58.05%); hydrogen, 4.23% (calcd. 4.06%); chromium, 10.46% (calcd. 10.48%); and silicon, 11.47% (calcd. 11.30%). The molecular weight of compound II (calcd. 993) was found to be 1168 ± 100 using diphenyl as a cryoscopic solvent and 1030 ± 100 in benzene. The low precision of these determinations is due to the low solubility of compound II in these and all other solvents tried. Compound II is hydrolyzed by acetone-water to give tetraphenyldisiloxane-1,3-diol; this information suggests that the disiloxy group exists in compound II. The infrared spectrum shows no OH absorption, medium Si–O–Si absorption characteristic of strain-free siloxanes, and Cr=O absorptions A model using bond angles and distance of strain-free cyclic siloxanes indicates that structure II is plausible in a crown conformation.

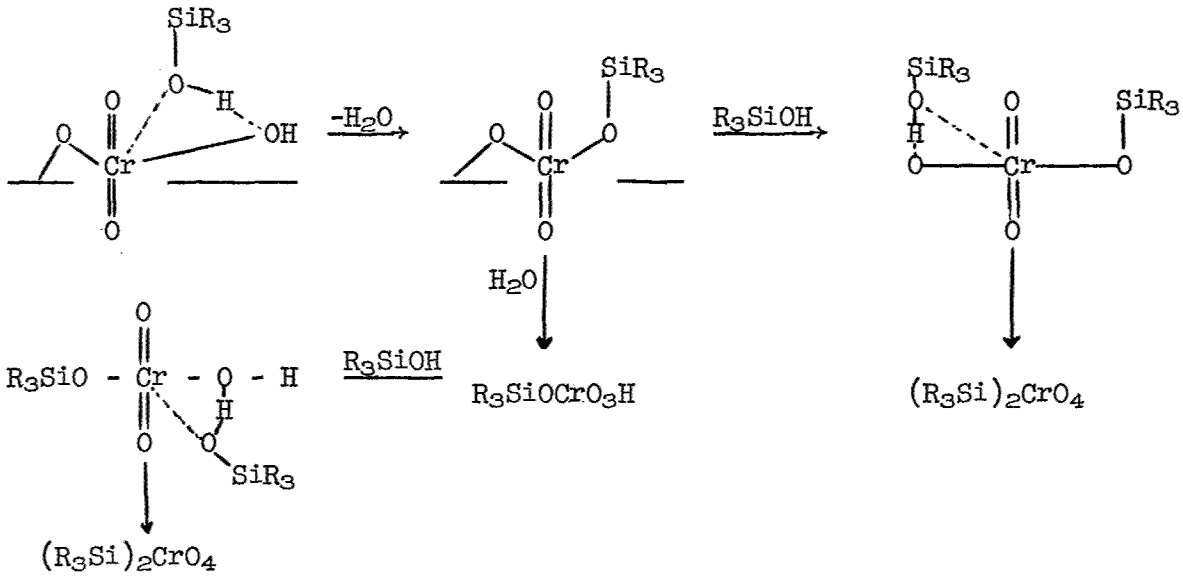
Compound II has a sharp decomposition point at 169°C which is unchanged by recrystallization. It slowly decomposes to a brown solid when exposed to light and is decomposed in hot acetone, ethanol, and benzene. It is sparingly soluble in cold methylene chloride, chloroform, carbon tetrachloride, carbon disulfide,

benzene, and acetonitrile.

Discussion

Since chromium(VI) oxide is insoluble in the solvent, the initial step of the reaction for the formation of the silylchromate is probably adsorption of the silanol on the surface of chromium(VI) oxide. Surface reaction sites probably are defects which contain chemisorbed water--that is, sites containing chromic acid. The adsorption complex may be attacked by the silanol to give the silylchromate or by water to form the half chromate ester. The half chromate ester ($R_3SiOCrO_3H$) may be freed from the surface by the solvent and react immediately with a second silanol molecule to form the silylchromate:

Reaction Scheme A



The proposed formation of a half ester is based on a similar proposal in the oxidation of alcohols by chromic acid[15], and retention of oxygen by the silicon atom is based on studies involving organochromate esters[16,17] and the silicon-oxygen bond strength. Chromic acid or hydrated chromium(VI) oxide is justified by the observed enhancement of the reaction when slightly moist chromium(VI) oxide is used as a reactant. The homogeneous reaction of triphenylsilanol and chromyl chloride probably proceeds by a similar two-step mechanism in solution with elimination of hydrogen chloride.

The rapid reaction of diphenylsilanediol with either chromium(VI) oxide or chromyl chloride is surprising. Formation of a mixture of compounds I and II in each case was accomplished within thirty minutes, whereas longer reaction times (10-30 hours) reduced the yields of products and increased the yield of decomposition products. No decomposition products were obtained from the thirty-minute reaction.

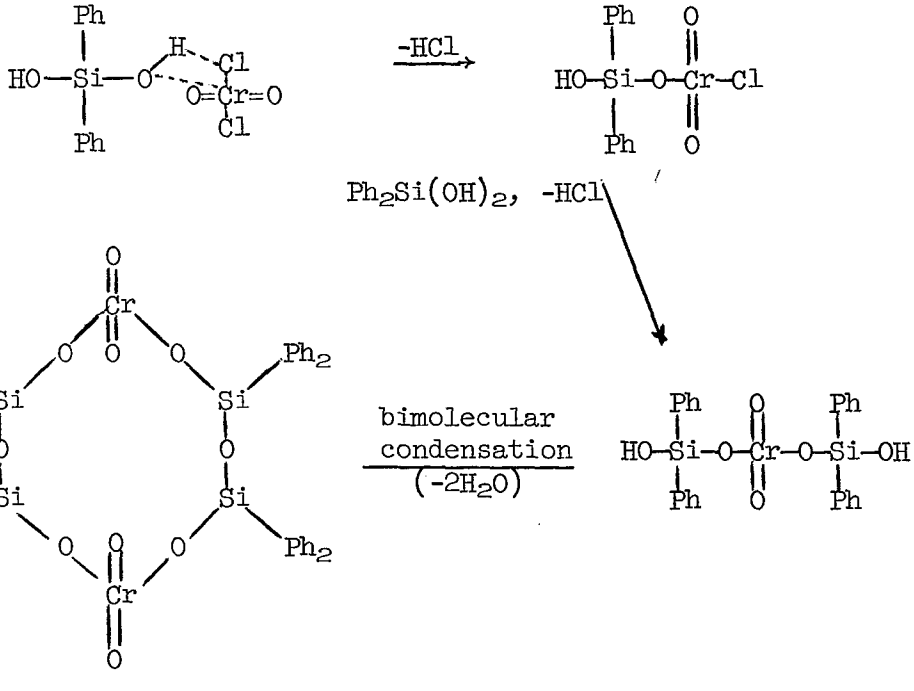
Failure to obtain an A-B silylchromate with alternate chromium-oxygen-silicon-oxygen bonds from the reaction of diphenylsilanediol and chromium(VI) oxide or

chromyl chloride is attributed to the tendency of the diol to undergo rapid self-condensation which is either acid or base catalyzed. This is illustrated by the observation that diphenylsilanediol is not soluble in pure methylene chloride, but in the presence of a trace of chromyl chloride it dissolves and forms hexaphenylcyclotrisiloxane and higher siloxanes. The condensation of diphenylsilanediol to form hexaphenylcyclotrisiloxane apparently does not participate in the overall formation of compound I. Compound I is produced only in poor yield by the reaction of hexaphenylcyclotrisiloxane and chromyl chloride or by the reaction of chromium(VI) oxide or chromyl chloride with hexaphenyltrisiloxane-1,5-diol. Compound II is not obtained at all from these reactions but is produced in good yield by the reaction of tetraphenyldisiloxane-1,3-diol and chromium(VI) oxide. Also, compound II undergoes a rapid reaction (15 minutes) with diphenylsilanediol in methylene chloride to give a product with the characteristics of compound I.

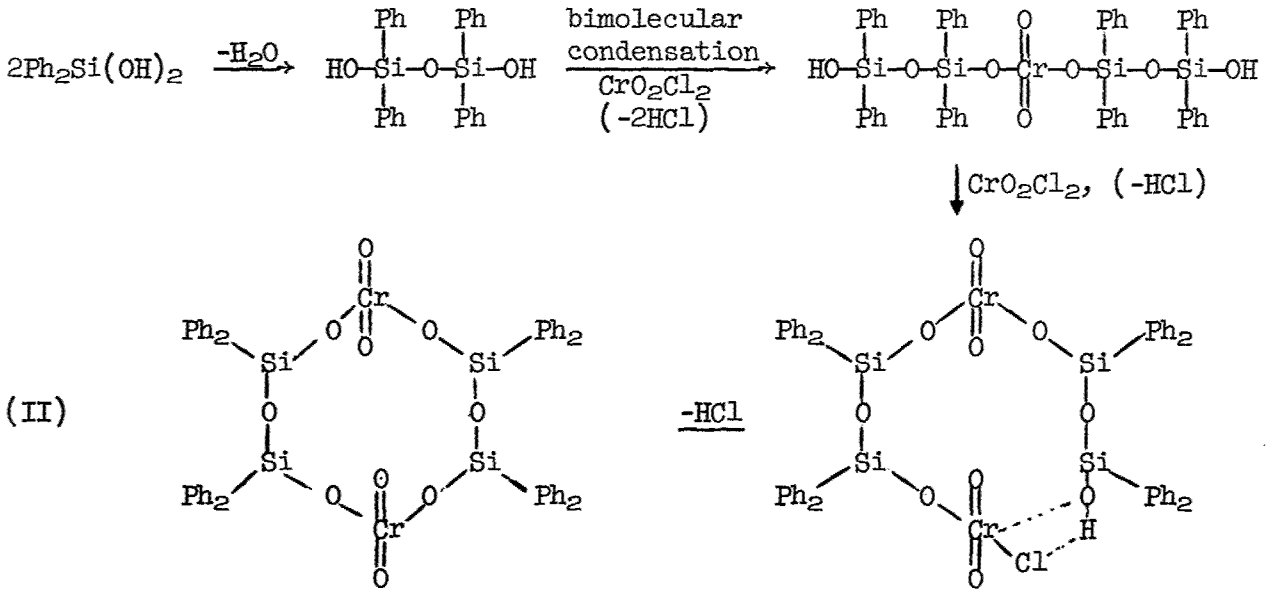
A possible mechanism for the formation of compound II from the reaction of diphenylsilanediol with chromyl chloride in methylene chloride is a reaction of the diol with chromyl chloride by elimination of hydrogen chloride to form $Ph_2(OH)SiOCr(O_2)Cl$. This intermediate may react with a second molecule of the diol to form $Ph_2(OH)SiOCr(O_2)OSi(OH)Ph_2$, which may in turn undergo condensation with a similar molecule to form compound II. Compound II could also be produced by the formation of tetraphenyldisiloxane-1,3-diol by self-condensation of the diol, followed by successive reactions with chromyl chloride.

These two plausible mechanisms for the formation of compound II are illustrated by the following schemes B and C:

Reaction Scheme B

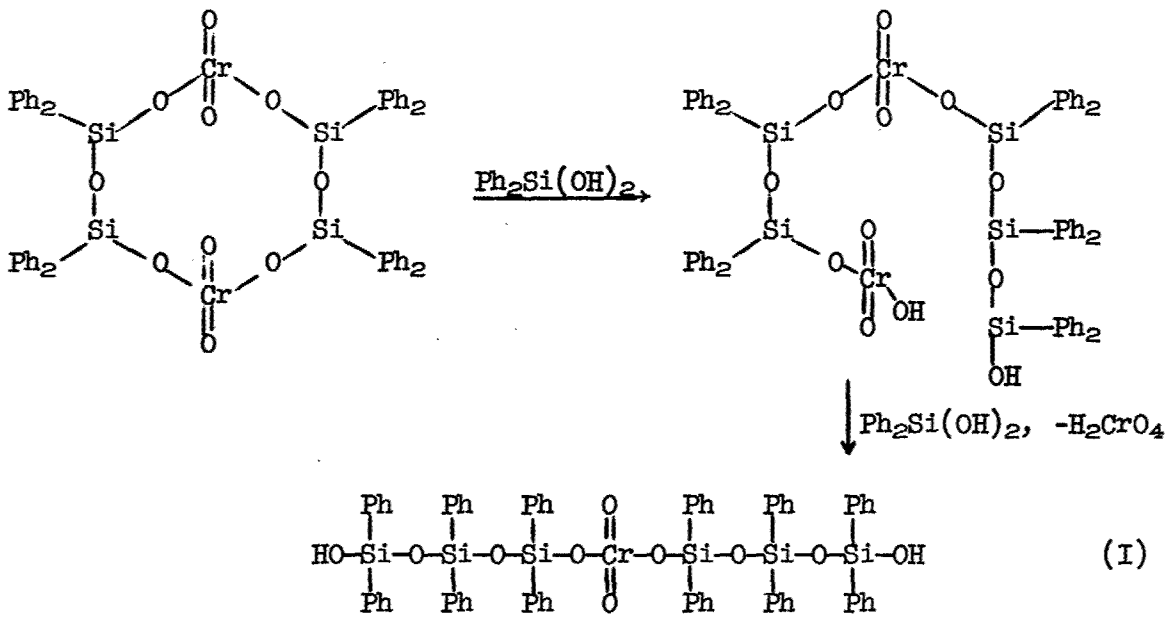


Reaction Scheme C

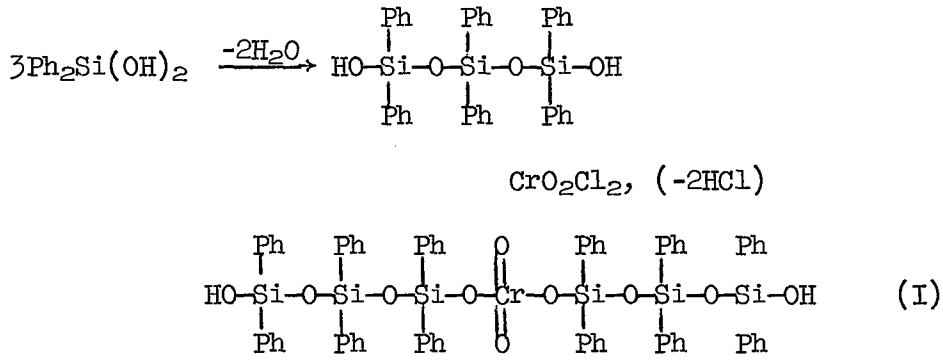


Compound I may be formed from the reaction of 2 molecules of diphenylsilanediol with compound II (Reaction Scheme D), hexaphenylcyclotrisiloxane with chromyl chloride, or hexaphenyltrisiloxane-1,5-diol with chromyl chloride (Reaction Scheme E). Only the first and last reactions seem plausible.

Reaction Scheme D



Reaction Scheme E



The reaction of diphenylsilanediol with chromium(VI) oxide probably proceeds in a manner similar to Scheme A. Intermediates analogous to those of Schemes B and C may give compound II. Reaction Scheme D is favored over a reaction scheme analogous to E since combination of hexaphenyltrisiloxane-1,5-diol with chromium(VI) oxide failed to give compound I. The higher yield of compound II over compound I in the reaction of diphenylsilanediol with chromium(VI) oxide may be due to the fact that reactions of Scheme E do not occur with chromium(VI) oxide, or to a slower reaction due to the insolubility of chromium(VI) oxide in methylene chloride.

The thermal stability of the bis(triorganosilyl)chromates follows a definite pattern. The least stable is bis(trimethylsilyl)chromate which explodes when heated to about 80°C; the most stable is bis(triphenylsilyl)chromate which decomposes as it melts at 153.5-154°C. The effect of the presence of donor groups on the stability of the silylchromate is illustrated by the reduced stability of bis(p-tolyldiphenylsilyl)chromate (m.p. 98.5-99°C, decomp.) or bis(methyldiphenylsilyl)chromate (decomp. 85°C) compared to bis(triphenylsilyl)chromate. Of the solid silylchromates prepared, only bis(cyclohexyldiphenylsilyl)chromate was stable above its melting point.

Compound I is the most thermally stable compound prepared in this investigation. It has no definite melting point but passes from a brittle glass into a viscous fluid by the heat of the hand. Differential thermal analysis of this material shows it begins to decompose at 275°C. Compound II decomposes very sharply at 169°C without melting. Its lower stability may be due to thermal cracking of the cyclic structure.

The toxicity of all known hexavalent chromium compounds warrants a word of caution concerning the silylchromates. The physiological properties of these compounds have not been investigated and more than normal care should be observed in handling them.

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RESEARCH ON ORGANIC CHEMISTRY OF FERROCENE

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(I) GENERAL METHODS

(1) Surface-(Thin layer)-Chromatography of Ferrocene-derivatives

(Together with H. Pelousek and A. Mohar (1))

Abstract: Surface-chromatography on Silica-jelly (Kieselgel-G) using benzene-ethanol-mixtures or hexane as solvents has proved to be a very useful analytical method for rapid separation and identification of ferrocene-derivatives.

So far no simple and reliable analytical method has been known for the qualitative separation and rapid identification of ferrocene-derivatives though it is needless to say that such a method would be of great value. Paperchromatography is limited to hydrophilic compounds like ferrocene-carboxylic acids (2) (3); otherwise a rather tedious impregnation-procedure and use of an uncommon solvent (dimethylsulfoxide) are necessary, as has been shown for the case of ferrocene and four of its derivatives (4).

Use has been now made of surface-chromatography (thin-layer-chromatography, Dunnschichtchromatographie (5)), a method already used for the separation of hydrophobic compounds. Chromatography of more than 100 ferrocene-derivatives has proved that we now have a very useful analytical method at hand which in short time (10 - 20 minutes) allows in most cases a clear separation of even complex mixtures. Many examples shown later on in this paper may demonstrate the applicability of this method.

Although its possibilities have not been fully investigated, it has already been of great help for the rapid identification of reaction-mixtures (i.e. Friedel-Crafts acylations) and in checking the purity of products and starting-materials. Moreover many reactions (oxidations with MnO_2, rearrangements, dehydrations and Friedel-Crafts acylations) may be followed easily by withdrawing samples in certain intervals and analyzing them by the described method. In certain cases surface-chromatography may be extended to a preparative scale thereby allowing the separation of otherwise inseparable isomers. Fractions obtained by chromatography on alumina-columns too can easily be checked for their purity.

No details of the procedure will be given here. In preparing the plates we followed the instructions of Brenner and Niederweiser (6) using "Kieselgel-G Merck" as adsorbent as they did.

The following solvent-systems were the most suitable for ferrocene-derivatives bearing functional groups:

A: benzene; B: benzene-ethanol(30:1, v/v); C: benzene-ethanol(15:1).
For ferrocene and alkyl-(aralkyl)-ferrocenes, n-hexane has given the best results.

Ten to 20 minutes are required to develop the chromatogram using these solvents. A good separation, showing distinct spots, is attained along a solvent front 8 cm from the starting point.

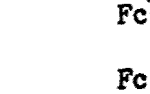
As ferrocene-derivatives are coloured, it is a great advantage that no special colour-tests are necessary. In some cases spraying with an oxidizing agent (bromine, $NaIO_4$-solution) deepens the original orange colour by production of deeply coloured ferrocinium-compounds thereby increasing the sensitivity of the method.

According to our experience optimal amounts are 50-100μg for every component present in a mixture. 2-5μg, however, may still be detected and on the other hand as much as 1 mg gives somewhat big, but nevertheless distinct spots without tailing. Therefore an impurity of 2-5 °/oo may be detected in some cases.

Fig. 1 shows only a few examples out of many so far tested in order to show the range of applicability. Most of them have been chosen because of their interest in connection with out work on ferrocene-acetylenic-compounds (part III of this paper) and bridged ferrocenes (part II). A number of alkyl-ferrocenes are discussed under I-2. The R_F-values of many others are to be found in the original paper (1).

Table 1

Ferrocene-derivatives.
Fc = ferrocenyl = $C_{10}H_9Fe$ and ferrocenylene($C_{10}H_8Fe$)

Number	Compound
1	Ferrocene (Fc.H)
2	1,1'-Trimethylen-ferrocene
3	1,1'-(α-ketotrimethylene)-ferroc.
4	Fc.CHO
5	Fc.$COCH_3$
6	Fc$(COCH_3)_2$ (1,1'-)
7	Fc.CH_2OH
8	Fc.CHOH.Fc
9	Fc.CH_2.Fc
10	Fc$(CHOH.CH_3)_2$ (1,1'-)
11	
12	Fc.CHOH.C≡CH
13	Fc.COH(CH_3)C≡CH
14	Fc.C_3H_7
15	Fc.CH$(CH_3)C_2H_5$

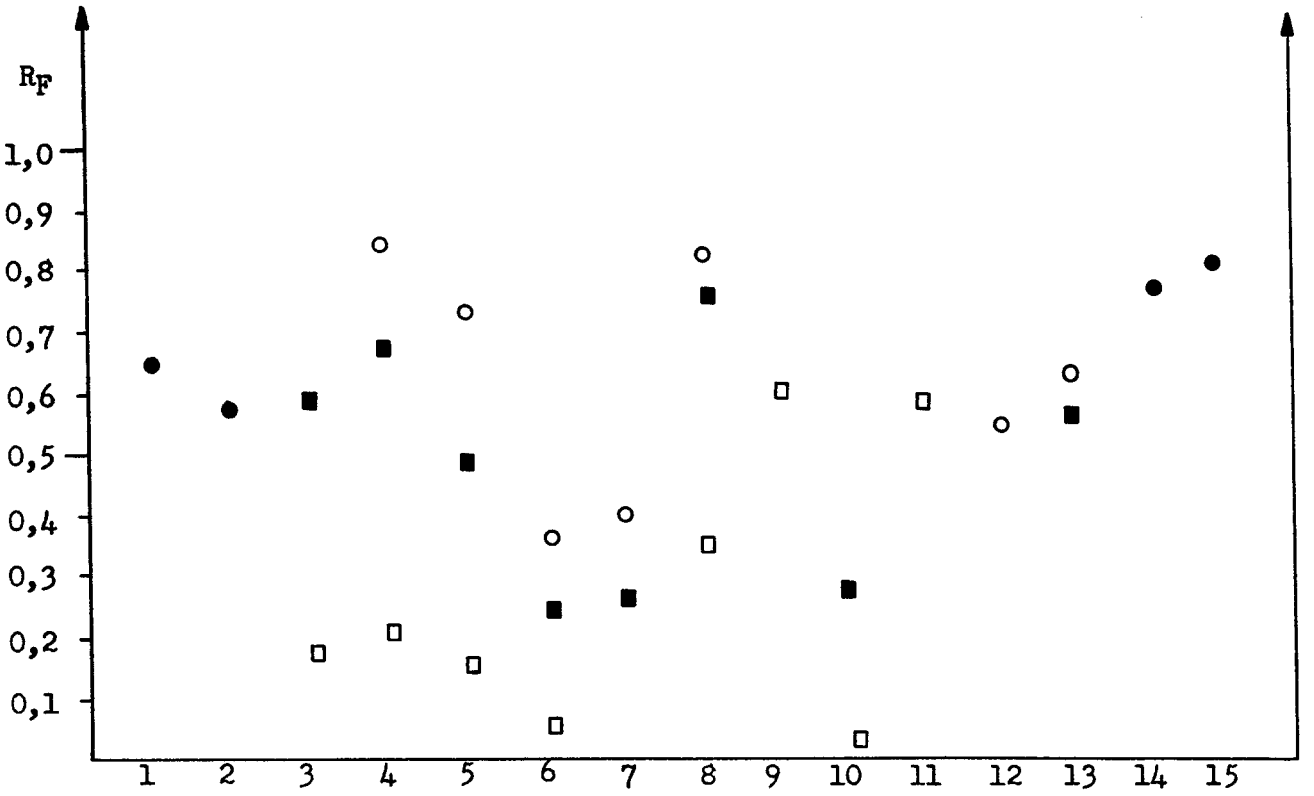


Fig. 1: R_F-values of ferrocene-derivatives
The numbers refer to the compounds
of table 1. Solvents A : □ ; B : ■
C : o ; hexane : ●

(2) Preparation of alkylferrocenes from acylferrocenes by reduction with $LiAlH_4/AlCl_3$ (Together with A. Mohar and M. Peterlik (7)).

Abstract: Acylferrocenes, ferrocenyl-carbinols and ethers of ferrocene, which contain the grouping Fc-C<, may smoothly be reduced to the corresponding alkyl-(aralkyl)-ferrocenes by means of $LiAlH_4/AlCl_3$. This reduction method makes alkyl-and bis-alkyl-ferrocenes easily accessible.

Reduction of ferrocenyl-ketones (Fc.CO.R) to the corresponding alkyl-compounds($Fc.CH_2R$) is an important problem in ferrocene-chemistry as it offers the most important possibility of arriving at alkyl- and dialkyl-ferrocenes, the acylferrocenes being easily accessible by Friedel-Crafts-synthesis. This problem has not yet been solved satisfactory. Both methods applied so far, namely either hydrogenation or Clemmensen-reduction offered some disadvantages being time consuming and/or giving impure products. Na-ethanol reduction may be employed only in certain cases like diferrocenyl-ketone (8), benzoyl-ferrocene (9) or thenoyl-ferrocene (10).

Brown and White (11) and Nystrom and Berger (12) have recently suggested a reduction method for certain aryl-ketones, using $LiAlH_4$-$AlCl_3$ as reducing

agent. As the reduction, however, seems to take its course via an intermediate carbonium-ion and therefore is accelerated by electrondonating groups, only those carbonyl-groups are reducable with are flanked either by two phenyl-groups or at least one bearing electrondonating groups in o-and/or p-position. Simple compounds like acetophenone or benzaldehyde are not at all or only in small yields accessible to $LiAlH_4/AlCl_3$-reduction.

If the ferrocenyl-residue is a stronger electron donator than phenyl(8), then, in contrast to benzene compounds, even simple acylferrocenes should be reducible. Diferrocenyl-ketone(13) and thenoyl-ferrocene(10) have been reduced by $LiAlH_4/AlCl_3$, but this was not surprising as these compounds are rather similar to benzophenone which is easily reducible to diphenylmethane.

All the compounds investigated so far, including ferrocene carboxaldehyde (Fc.CHO), bridged ferrocenes, 1, 1' (α-ketotrimethylene)-ferrocene (Table 2) and mono and diacylferrocenes could be reduced in almost quantitative yields to the corresponding oxygen free derivative by a simple procedure in a very short time - in most cases within a few minutes.

Not only acyl-ferrocenes, but also alcohols and ethers may smoothly be reduced to the corresponding alkyl-(aralkyl) compounds. (Table 3 contains some examples). The only structural requirement being the grouping Fc-C-O-.

Therefore the $LiAlH_4/AlCl_3$-reduction represents a method by which alkyl- and aralkyl-ferrocenes are easily accessible, as the Friedel-Crafts-acylation yielding the required starting compounds is one of the best investigated reactions in ferrocene-chemistry(14).

Alkyl-ferrocenes may easily be separated and thereby distinguished from starting materials (ketones, alcohols, ethers) by surface-chromatography (part I-1) using hexane as solvent. Thereby the time may be established after which reduction is complete. Figure 2 shows Rf-values of some mono- and dialkyl-ferrocenes obtained during this investigation.

Table 2 gives the refractive indices of oily alkyl-ferrocenes. It can be observed that the n_D-values decrease regularily with the increasing number of C-atoms in the side-chain(s). Therefore the nature of substitution of an unknown alkyl-ferrocene may be estimated from its refractive-index.

Table 2

n-Alkylferrocenes prepared by $LiAlH_4/AlCl_3$-reduction of acylferrocenes
All di-substituted products are heteroannular

Acylferrocene	Alkylferrocene			
	Nr.	Formula	mp.	n_D^{20}
Fc.CHO	1	Fc.Me	35°	--
Fc.COMe	2	Fc.Et	--	1.6007
Fc.COEt	3	Fc.C_3H_7	--	1.5900
Fc.COC_3H_7	4	Fc.C_4H_9	--	1.5795
Fc.COC_4H_9	5	Fc.C_5H_{11}	--	1.5711
Fc.COC_6H_5	6	Fc.$CH_2C_6H_5$	74-75°	--

Table 2 (Cont'd)

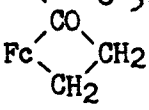
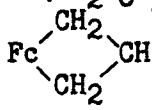
Acylferrocene	Alkylferrocene			
	Nr.	Formula	mp.	n_D^{20}
$Fc(COMe)_2$	7	$Fc(Et)_2$	--	1.5807
$Fc(COEt)_2$	8	$Fc(C_3H_7)_2$	--	1.5603
$Fc(COC_3H_7)_2$	9	$Fc(C_4H_9)_2$	--	1.5530
$Fc(COC_4H_9)_2$	10	$Fc(C_5H_{11})_2$	--	1.5428
$Fc(COC_6H_5)_2$	11	$Fc(CH_2C_6H_5)_2$	103-05°	--
	12		105-06°	--

Table 3

Alkylferrocenes from alcohols and ethers by reduction with $LiAlH_4/AlCl_3$

Compound reduced	Alkylferrocene obtained	
	Nr.	Formula
$Fc.CH_2OH$	1	Fc.Me
Fc.CHOH.Me	2	Fc.Et
$Fc.CHOH.C_6H_5$	6	$Fc.CH_2C_6H_5$
$Fc(CHOH.C_6H_5)_2$	11	$Fc(CH_2C_6H_5)_2$
$Fc.CHOH.C\equiv CH$	13	$Fc.CH_2C\equiv CH$
$Fc.CH_2OCH_2.Fc$	1	Fc.Me
	7	$Fc(ET)_2$

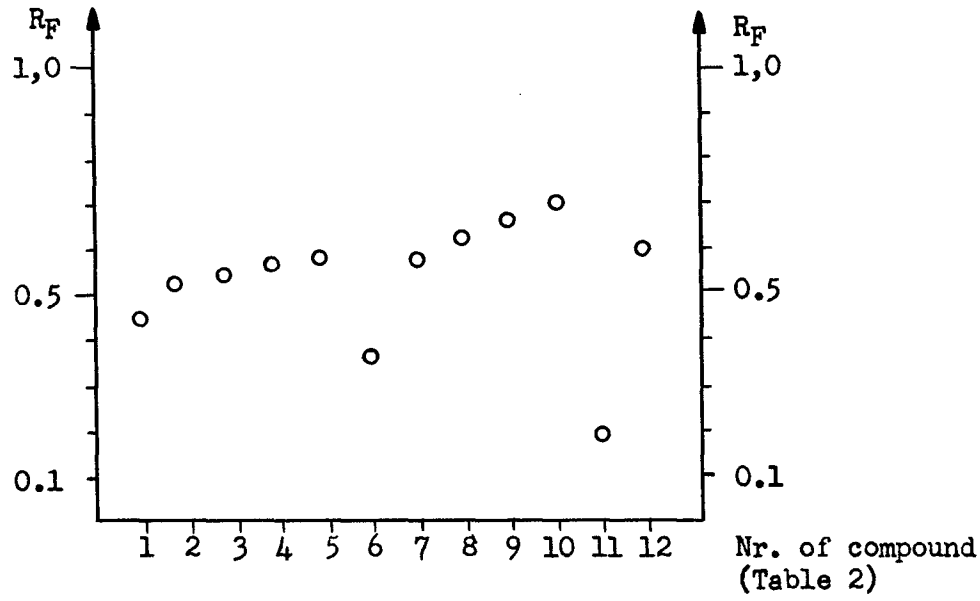


Fig. 2: R_F-values of alkyl- and dialkyl-ferrocenes. Kieselgel-G "Merck", solvent: n-hexane

(II) BRIDGED FERROCENES

(Together with H. Seiler and M. Peterlik)(3)

Abstract: The following bridged ferrocenes were prepared from the appropriate ferrocene derivatives: bis-(trimethylene)- and diethyl-bis (trimethylene)-ferrocene (twofold bridged) and tris-(trimethylene) -ferrocene (threefold bridged). The ultimate aim was the preparation of a penta-bridged ferrocene and therefore, deca-ethylferrocene was prepared, for comparison purposes, by successive acetylation and reduction. These latter three compounds are the highest known substituted ferrocenes which can be obtained by substitution of the ferrocene-nucleus.

The stereochemistry of bridged ferrocenes has been investigated by acetylation of 1,1'-(trimethylene)-ferrocene and separation of stereoisomeric de-acetyl-derivatives. The diethylcompounds derived therefrom could be synthesized in an independent way.

The stereochemical possibilities of bridged ferrocenes is discussed.

(1) Introduction.

Bridged ferrocenes, in which two cyclopentadiene-moieties are heteroannularily linked by a suitable chain, seem to be fitting compounds for studying stereochemical problems in the ferrocene-field. Moreover from the preparation of such bridged compounds some interesting contributions to the chemistry of ferrocene could be expected.

At the start of the present investigation only ferrocenes with one bridge in the molecule were known:

(a) 1,1'-(α-ketotrimethylene)-ferrocene (I) has been obtained by intramolecular acetylation of ferrocene-propionicacid (15). This ketone (I) could be reduced to the oxygen free 1,1'-(trimethylene-ferrocene(II). (2,7).

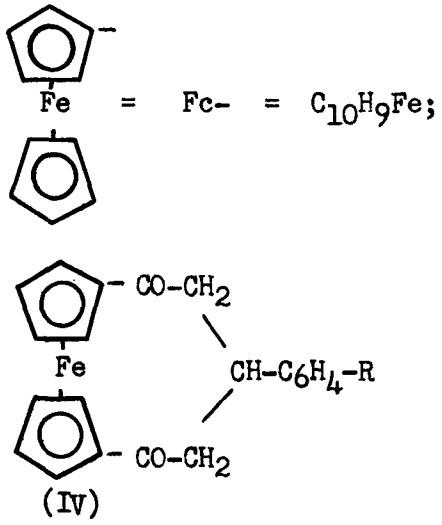
(b) II and similar compounds with a four or five-membered bridge have been obtained in small yields (0,02 - 2,5 %) from α,ω-bis-cyclopentadienyl-alkanes(16).

(c) 1,1'-(tetramethylethylene)-ferrocene, a compound bridged by an unusual two carbon-bridge has been reported recently(17).

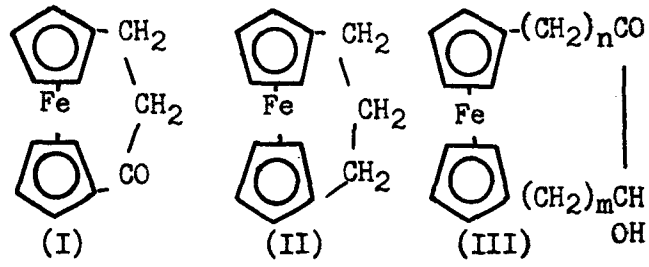
(d) Ferrocene-acyloins (III), containing bridges from 4 to 10 C atoms in length, have been obtained by intramolecular condensation of appropriate ferrocene-1,1'-diesters.(2)

(e) Cyclic ethers, such as 1,1'-(dimethyleneoxy) ferrocene (17) and derivatives thereof, as described in part III of this paper, can be obtained from heteroannular glycols by dehydration (8).

(f) Furdik et al. recently described a new class of bridged ferrocenes (IV) derived from diacetyl-ferrocene by alkalicatalyzed condensation with aldehydes (benzaldehyde and derivatives) (18).



(IV)



(I) (II) (III)

(2) Discussion.

A. Two- (3) and threefold bridged ferrocenes. Starting from β-ferrocenylmethylpropionate(V), from ferrocene-1,1'-dipropionic-acid (VI), the preparation of which could much be imrpoved(2), or from the above mentioned monobridged compound(II) we could synthesize the two- and threefold bridged compounds: bis- or tris (trimethylene)-ferrocene (XVIII, XXIII) arriving in every case at the same intermediate, the bridged ketone (XVII). The best way, however, is to cyclize VI by intramolecular Friedel-Crafts-reaction to the diketone (XVI). Both ketones (XVI and XVII) on reduction gave the bis-bridged ferrocene XVIII. In the latter case (via the dibridged diketone XVI) the overall yield based on ferrocene being 15%. From bis-trimethylene-ferrocene(XVIII) a simple route led to the threefold bridged ferrocene: tris-trimethyleneferrocene (XXIII).

In all cases investigated so far, four types of reactions proved to be useful:

(a) Formylation with N-methyl-formanilide and $POCl_3$ (Vielsmeyer-reaction).
(b) Knoevenagel-condensation of the aldehydes, obtained by the above method, with malonic acid and hydrogenation of the acrylic acids to the corresponding propionic acids.
(c) Ringclosure of the propionicacids with trifluoroacetic-anhydride (TFAA) or intramolecular Friedel-Crafts-cyclization.
(d) Catalytic hydrogenation over PtO_2 or reduction with $LiAlH_4/AlCl_3$ of the ketones, obtained according to (c), yielded the desired trimethylene-compounds (XIII, XVIII, XXIII).

Formylation of monosubstituted ferrocenes (as electrophilic substitution process) occurs at the ring which is activated by a substituent and thus leads to homoannular disubstituted aldehydes (e.g. VII). This compound exhibits in the IR spectrum a rather strong absorption band at 1105 cm^{-1} and a somewhat weaker band at 1000 cm^{-1} proving homoannular disubstitution in accordance with the so called 9, 10 μ rule(19). Similar behavior is exhibited by formyl-ethylferrocene, obtained by the formylation of ethylferrocene and its reduction prodect ethyl-hydroxymethyl ferrocene. A further proof for this type of substitution is that the dipropionic acid (X) obtained from the monopropionate (V) differs in many respects from the heteroannular dipropionic acid (VI)(2).

Ring closure of VI or X with TFAA gave only the monoacylated products (XIV, XV) in accordance with the deactivating effects of the CO-group towards a second (heteroannular) acylation. After hydrogenation to the bridged ferrocene propionic acid (XIII), a second ring closure could be achieved yielding the ring ketone (XVII). (XVII) could also be obtained from trimethylene-ferrocene via the aldehyde (XI). The ketone (XVII) could be hydrogenated over PtO_2 or preferably by $LiAlH_3/AlCl_3$ (Part I-2) and smoothly converted into the desired bis-bridged ferrocene (VIII).

Friedel-Crafts cyclization of the dipropionic-acid (VI) (after conversion into the dichloride with PCl_3) in high dilution gave in a single step the diketone (XVI) in good yields. Reduction of this diketone provides a convenient route to the compound XVIII.

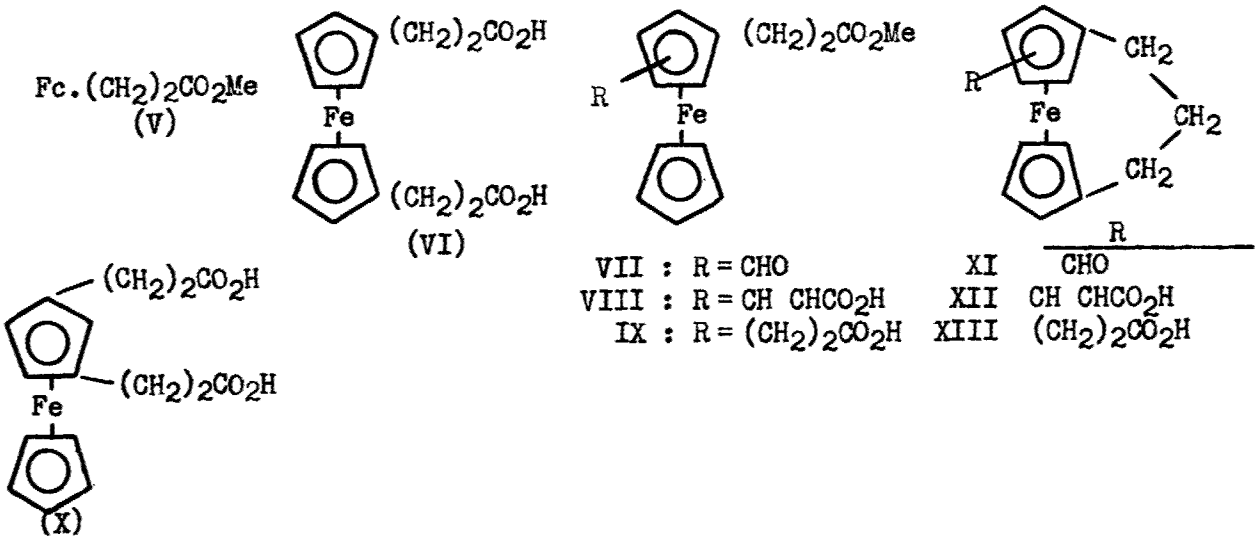
Further formylation (XIX), Knoevenagel-condensation (XX), hydrogenation (XXI), cyclization (TFAA, XXII) and final reduction of the three bridged monoketone (XXII) led to the tris-trimethylene-ferrocene (XXIII). This can be used as a precursor for the synthesis of higher bridged ferrocenes and, as a first step towards this goal, the aldehyde XXIV has been obtained in good yields.

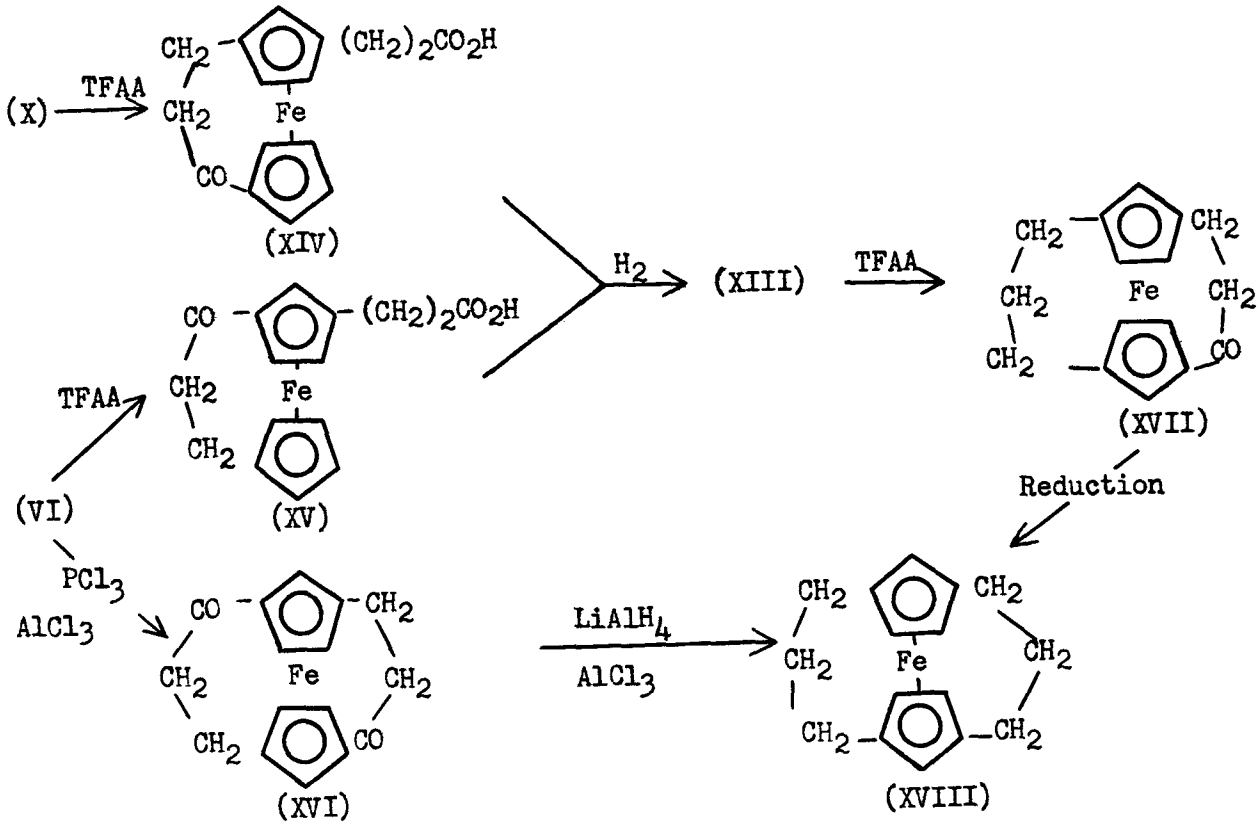
Most of the intermediates have been purified by chromatography on alumina and checked for their purity on thin-layer-chromatograms. Some of the aldehydes could be characterized as semicarbazones and the acids have been identified by paperchromatography.

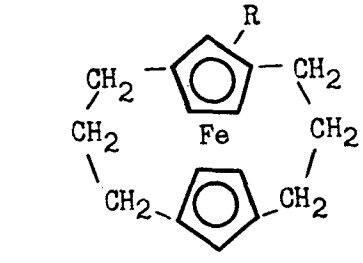
For R_F-values see table 4.

Most of the bridged compounds are crystalline and can easily be purified by chromatography and/or sublimation.

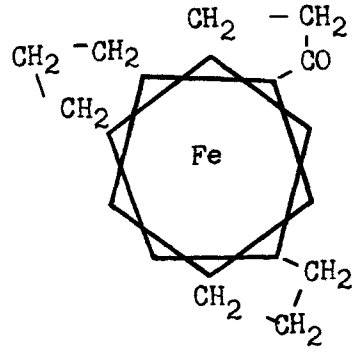
The relative positions of the bridges (very probably 1,3 for XVIII and 1,2,4 for XXIII) will be discussed under (3). The formulae have been formulated according to this assumption, although sometimes a mixture of isomeric 1,2 -and 1,3- compounds may be possible.



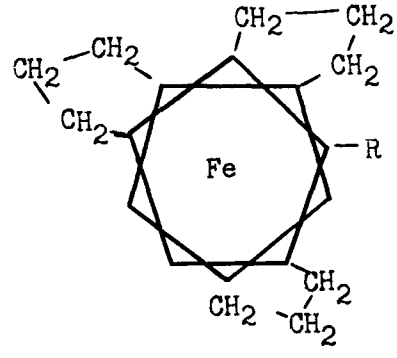




XVIII : R H
XIX : R CHO
XX : R CH CHCO2H
XXI : R (CH2)2CO2H



(XXII)



XXIII : R H
XXIV : R CHO

Table 4

R_F-values of ferrocene-carboxylicacids. Descending technique. Solvent: n-butanol-ethanol-aqu.ammonia-water: 4:4:1:1. Paper: Schleicher & Schull 2043 a.

Compound Nr.	R_F	Compound Nr.	R_F
VI	0.38	XXVIII	0.71
VII (corresp. acid)	0.62	XXVIII (corresp. malonic-acid	0.28
VIII(" diacid)	0.35	XXIX	0.60
X	0.38	XXIX " "	0.25
XII	0.71		

Table 4 (Cont'd)

Compound Nr.	R_F	Compound Nr.	R_F
XIII	0.70	XXXI (corr. acid)	0.53
XIV	0.56	XXXII(corr. mal. acid)	0.18
XV	0.56	XXXIII	0.55
		XXXIII(corr. mal. acid)	0.21

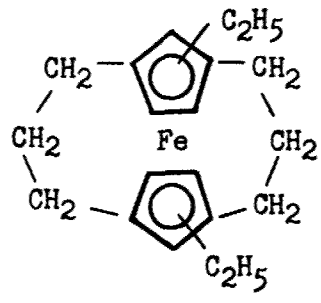
B. Diethyl-bis (trimethylene) ferrocene. In connection with the work on manifoldbridged ferrocenes, also a diethyl-bisbridged compound (XXV) has been prepared.

The synthesis has been accomplished making use of the same reactions as mentioned above under A. (Reactions a-d) Starting from 1,1'-diethylferrocene (XXVI), via the aldehyde (XXVII) and the acrylic-acid (XXVIII) the propionic acid (XXIX) has been obtained in good overall yield. After conversion into its methylester (XXX), it could be formylated to give the aldehyde (XXXI). Knoevenagel-condensation (and simultaneous saponification) led to the acrylic acid (XXXII), which over Pd/C could be hydrogenated to the diethyl-dipropionic-acid (XXXIII). In this and other cases the crude Knoevenagel-condensation-products according to paperchromatograms are mixtures of the desired acrylic acids and corresponding malonicacids (i.g. $Fc\text{-}CH=C(COOH)_2$). Accordingly the propionicacids too are mixtures, which, however, after distillation in vacuo are pure, as during the distillation malonic-acids are decarboxylated. In table 4 the malonic-acids in question are included.

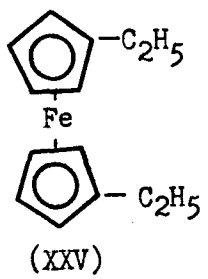
In analogy to the above mentioned di-propionicacids (VI, X), the diethyl-ferrocene-dipropionic acid (XXXIII) after twofold ringclosure with TFAA (and subsequent hydrogenation after each cyclization) yielded the desired twofold bridged compound XXV.

It has not been established whether the formyl group enters the mono-or disubstituted cyclopentadiene-ring of diethylferrocenyl- methylpropionate (XXX) to give a "symmetrically" or unsymmetrically substituted compound. In the formula (below), XXXI tentatively has been assigned a sym. bis-heteroannular structure. In regard to the final bisbridged compound, however, the course of substitution is of no significance, as each of the two possible isomers (sym. or unsym.) will give the same final product XXV.

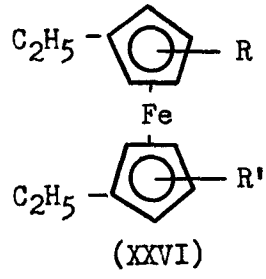
The relative positions of the three substituents in each cyclopentadiene-moiety will be discussed under (3).



(XXV)



(XXV)



(XXVI)

	R	R'
XXVII :	CHO	H
XXVIII:	$CH=CHCO_2H$	H
XXIX :	$(CH_2)_2CO_2H$	H
XXX :	$(CH_2)_2CO_2Me$	H
XXXI :	$(CH_2)_2CO_2Me$	CHO
XXXII :	$(CH_2)_2CO_2H$	$CH=CH.CO_2H$
XXXIII:	$(CH_2)_2CO_2H$	$(CH_2)_2CO_2H$

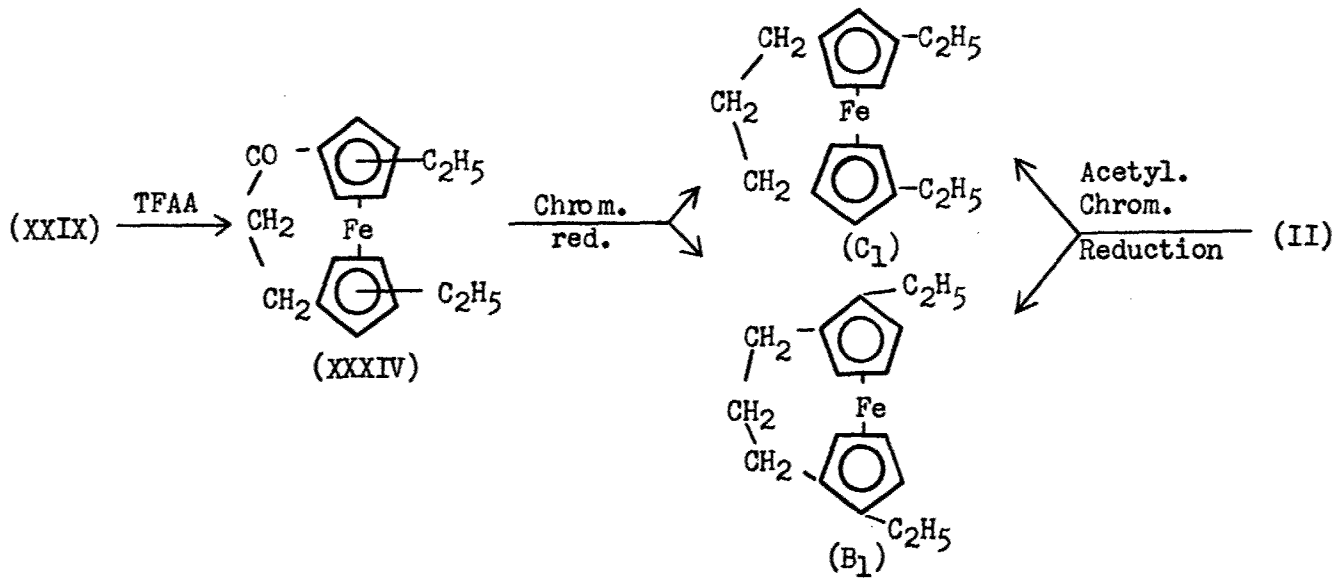
(3) Stereochemistry of bridged ferrocenes.

A. Isomeric diacetyl-1,1'-(trimethylene)-ferrocenes. Rinehart et al. have carried out systematic studies on the acetylation of alkylferrocenes in regard to the steric possibilities(20) and they were able to isolate isomeric diacetyl-dimethyl-ferrocenes (21). For similar work on phenyl-ferrocene see Rosenblum (22).

By exhaustive Friedel-Crafts-acetylation of the monobridged compound II and after careful chromatography on alumina using benzene-ether(4:1) as eluant, we could separate three isomeric diacetyl-1,1'-(trimethylene)-ferrocenes: (A) mp.139-146°, (B) mp.111-115° and (C) mp.132-136°, A being the fastest, C the slowest moving compound. The same three derivatives (and a trace of a fourth isomer) could be detected on thin-layer-chromatograms, moving in the same order. The approximate amounts of the three isomers were A : B : C (1:40:60). For IR-identification purposes and in order to obtain compounds which could be independently synthesized, B and C were reduced to the corresponding diethyl-trimethylene-ferrocenes B_1 and C_1 resp.

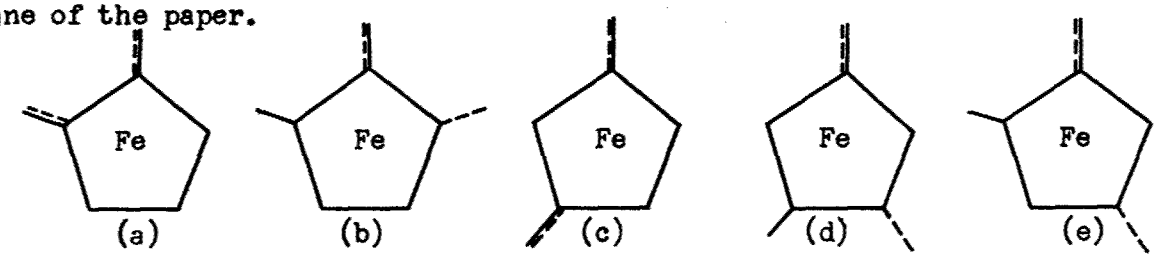
The synthesis of these diethyl-(trimethylene) ferrocenes could be accomplished as follows: the above mentioned 1,1'-diethylferrocene-propionicacid (XXIX) which represents doubtlessly a mixture of isomers has been cyclized with TFAA to get (a mixture of isomeric) ring-ketones (XXIV). This mixture by chromatography on alumina could be separated in two isomers (amounts appr. 1:7). One of these ketones (the main product) on reduction (either catalytically or with $LiAlH_4/AlCl_3$) gave a diethylderivative, which, according to its IR-absorption-spectrum is identical with C_1. The second isomer (obtained in lower yields) on reduction gave a product identical with B_1.

IR-data (absorption in the 900-1000 cm^{-1} region; for previous discussions of relation between IR-data and substitution cf.inter alia 20, 21, 22, 23) as well as steric considerations seem strongly to indicate, that C_1 (and therefor C) represents the 1,3-(β-)disubstitution-type, whilst B_1 (and B) belong to 1,2-(α-) disubstituted ferrocene-compounds. Cf. the formulation below.



B. Discussion of steric possibilities. To count the number of possible stereoisomers of a given, especially higher substituted ferrocene-derivative, ball and stick-models proved to be very useful.

Of a tetrasubstituted ferrocene with two pairs of equal substituents (diacetyl-dialkylferrocenes, diacetyl-monobridged and diethyl-monobridged ferrocene) five isomers (a-e) are possible, which are shown below. A full line represents a substituent (or half of a bridge) above the plane of the paper, a dotted line a substituent (half a bridge) below the plane. Iron lies in the plane of the paper.

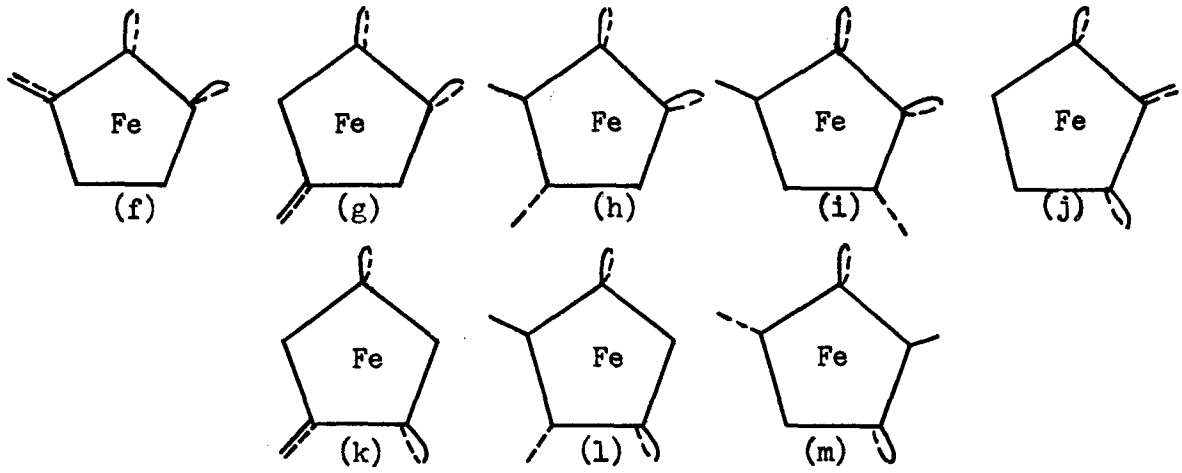


α,α' (2,2')- (a): cis- ; (b) : trans- ; (a) and (c) are mesoforms
β,β' (3,3')- (c): cis- ; (d) : trans- ; (b), (d) and (e) racemic
α,β' (2,3')- equal to α',β (2',3) = (e) (DL)

As already mentioned, Rinehart and Motz (21) could isolate four stereoisomeric diacetyl-dimethyl-ferrocenes, to which - mainly according to IR-date - they assigned configurations a - d.

As further shown by models, a dibridged ferrocene (i.g. XVIII) can only exist in two stereoisomeric forms (a) and (c), as in (b), (d) and (e) the distances are too far to allow a second three-carbon-bridge.

Of a dibridged-diethyl-ferrocene (XXV) eight positional isomers are possible, four of which are mesoforms and four being racemates.



Meso : (f), (g), (j), (k) DL : (h), (i), (l), (m)

For a threefold-bridged ferrocene as XXIII, there remain only four possibilities, namely (f), (g), (j) and (k), but as (f) = (j), and (g) = (k), if the three bridges are identical (XXIII), for such a compound only two stereoisomeric forms are left.

In higher substituted ferrocenes, the situation gets even more complicated. Thus in the synthesis of a decaethyl-ferrocene, as described below under II-4, in some steps we were dealing with rather complex mixtures of positional isomers. The following scheme 1 gives the number of possible polyethyl- and diacetyl-polyethyl-ferrocenes from diethyl- to decaethyl-ferrocene. (FC : Friedel-Crafts-acetylation; Red : reduction with $LiAlH_4/AlCl_3$).

Scheme 1.

ONE Diethyl —1.FC→ FIVE Diacetyl-diethyl —1.Red→ THREE Tetraethyl

—2.FC→ THIRTEEN Diacetyl-tetraethyl (5 meso- . 8 DL-forms) —2.Red.→ THREE Hexaethyl

—3.FC→ FIVE Diacetyl-hexaethyl —3.Red.→ ONE Octaethyl —4.FC→

ONE Diacetyl-octaethyl —4.Red.→ ONE Decaethyl-ferrocene.

Regarding all these possibilities, it can be assumed, however, that there need not be an equal distribution of all possible isomers. Homoannular substitution of alkyl-ferrocenes is governed by electronic and/or steric effects. Whilst for electronic reasons position 2 (α) will be preferred, steric effects - especially if bulky substituents are present - will make position 3 (β) more accessible to electrophilic attack (20, 22).

Therefor the following assumptions in regard to the compounds described in this paper may be made:

(a) As the twofold bridged compounds (XVI-XVIII) are sharp melting and obviously seem to be pure and as only two isomeric forms are possible (see

previous page), for steric as well for reasons given above (IR-data !) we assume the two bridges to be in 1,3 (β-). (Configuration c).

(b) Similar considerations in the case of the threefold bridged ferrocenes (XXII-XXIV) make it very probable that the three bridges are in the positions 1,2,4 (configuration g = k) where a more equal distribution is possible than in the highly crowded configurations f = j. The same consideration is valid for the diethyl-dibridged compound (XXV). Here, of course, (g) and (k) are not identical and both isomers may be possible.

(c) Of the three isomeric diacetyl-trimethylene-ferrocenes A, B and C (mentioned above: II-3-A), the main product (C) which on reduction gave the diethyl-bridged ferrocene C_1 (which on the other hand could be obtained on an independent way), very probably corresponds to the 1,3-substitution-type (c and/or d). Consequently B (and B_1) will be a 1,2-disubstituted product (a and/or b). In most cases (20)β-disubstituted products are obtained in larger amounts than the corresponding 1,2-isomers. A, finally which has been obtained in very small amounts could be the 2,3'-isomer (e).

Confirmation of these assumptions has been obtained from IR-absorptions-spectra, as already has been mentioned in some cases. All spectra were in good agreement with previous observations (20-23).

(4) The stepwise ethylation of ferrocene: Deca(?)ethyl-ferrocene.

Although scale-models show that from a steric point of view a fivefold-bridged ferrocene should be possible, it seemed to be advisable to prepare first a fully alkylated ferrocene. So far only an unidentified polyethylferrocene has been described, obtained from ferrocene by reaction with ethylene and $AlCl_3$ (24). We have now obtained a highly ethylated (decaethyl-?) ferrocene by step-wise acetylation and subsequent reduction starting from 1,1'-diethylferrocene.

After four Friedel-Crafts acetylations (acetylchloride/$AlCl_3$ in CH_2Cl_2) and subsequent reductions with $AlCl_3/LiAlH_4$ (cf. part I-2 of this paper) a liquid polyethylferrocene was obtained. After two further acetylation and reduction steps we arrived at a compound melting from 40-50° (10% overall yield) which according to analysis, however, still was not fully ethylated (octaethyl !). Moreover, after a continuous decrease from diethylferrocene, our product in the IR-absorption-spectrum exhibited a weak band at 3080cm^{-1}, characteristic for nuclear bonded hydrogen (Fc-H), while in the aliphatic C-H region (2800-2900cm^{-1}) an increase from diethyl to the octaethylferrocene was observed. As we had not achieved full ethylation, two further acetylation and reduction steps were carried out. Thus, a product was obtained which had a melting range from 50 to 230°. It was "purified" by spreading it on a porous plate kept at 180° for five minutes. This product melted from 200-230° after sintering at 180°.

Analysis cannot be used to distinguish between a nona and decaethylferrocene ($C_{28}H_{46}Fe$, Calcd. C 76.7, H 10.5; $C_{30}H_{50}Fc$, Calcd. C 77.2, H 10.7). However, our product represents at least a nona-ethylferrocene (Found, C 76.9, H 10.5).

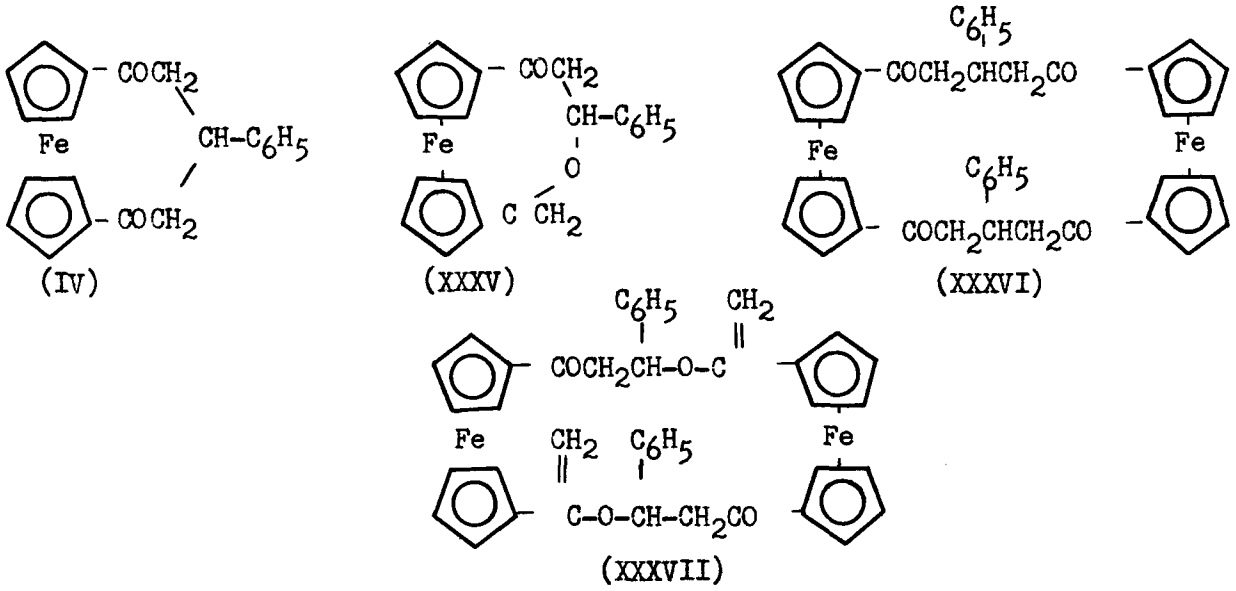
Furthermore, the weak Fc-H band had almost completely disappeared. Final proof may be gained by NMR. We may assume that we have achieved practically complete ethylation and the product is the highest substituted ferrocene derivative

known.

All diacetylated polyethylferrocenes were purified by chromatography on alumina and checked on thin-layer-chromatograms. According to theory (cf. II-3-B) most of them proved to be mixtures of positional isomers. The liquid polyethylferrocenes were purified by distillation in high vacuum. The refractive indices decrease from diethylferrocene ($n_D = 1.5807$) towards a final value: 1.5460. In a similar regular fashion the R_F-values (thin-layer chromatograms, Kieselgel-G, hexane) increased from diethylferrocene (0.60) to decaethyl-ferrocene (0.85).

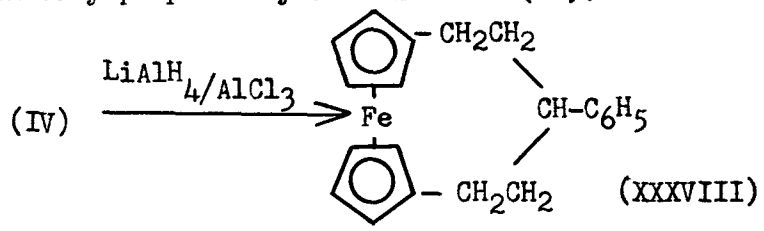
(5) Elucidation of the structure of a bridged ferrocene, obtained from 1,1' diacetylferrocene.

Both C. R. Hauser and coworkers (25) and M. Furdik et al. (18) by alkali-catalyzed reaction of diacetylferrocene with benzaldehyde have obtained a high melting compound (mp.$>300^\circ$), to which Furdik tentatively assigned the structure (IV) whilst Hauser discusses three further possible structures (XXXV - XXXVII).



On account of some IR-data and formation of a mono-phenylhydrazone Hauser prefers XXXV or XXXVII rather than IV or XXXVI. To clarify this matter and to establish the structure of the compound in question we have reduced it with $LiAlH_4/AlCl_3$ to the corresponding O-free ring: $C_{21}H_{22}Fe$, mp. 110-112°. This compound according to IR-data and hydrogenation - results lacks a $C=CH_2$ group and is monomolecular, as has been proved by cryoscopic and ebullioscopic molecular-weight determinations (Calcd. for XXXVIII 330, found 320-326).

It has been established therefore that the bridged-ferrocene in question has the structure IV as already proposed by Furdik et al (18).



(III) FERROCENE ACETYLENIC COMPOUNDS
(Together with A.Mohar) (8,26)

Abstract: Ferrocenyl-ethynyl-carbinols and -acetylenic-glycols were obtained from Fc.CHO (and $Fc.COCH_3$) by appropriate synthetic methods. Reactions carried out with these novel compounds included:
(a) Oxidative coupling which led to diacetylenic-glycols.
(b) Oxidation with MnO_2 yielding acetylenic-mono-and di-ketones, which served as starting materials for heterocyclics containing the ferrocene-nucleus.
(c) Catalytic hydrogenation of sec. carbinols which gave saturated ferrocenyl-carbinols whilst tert, carbinols underwent simultaneous hydrogenolysis to give ferrocenyl-alkanes.
(d) Saturated ferrocenyl-carbinols and -glycols can easily be dehydrated with acid alumina thereby yielding ferrocenyl-alkenes. Compounds of suitable structure give ethers.
(e) Reduction of ferrocenyl-acetylenic-carbinols and -glycols with $LiAlH_4/AlCl_3$ leading to oxgen-free acetylenic compounds containing the grouping $Fc.CH(R)C\equiv C-$ (R = H, Me).
(f) $LiAlH_4$-treatment of ferrocenyl-acetylenic-glycols (Whiting-reaction) which gave diferrocenyl-butadiene and -hexatriene.
Some rearrangements of unsaturated systems were observed.

(1) Introduction.

The manifold preparative possibilities offered by acetylenic compounds prompted us, to introduce acetylenic-groups into suitable ferrocene-derivatives.

For comparison with phenyl-and thienyl-ethynyl-carbinols (28, 29), we have prepared ferrocenyl-ethynyl-carbinols (XXXIX) and acetylenic glycols (XL). These compounds were easily synthesi ed from ferrocene-carboxaldehyde or acetyl - ferrocene.

$Fc.\underset{R}{C}OH.C\equiv CH$
(XXXIX)

	R
a:	H
b:	Me

$FcCHOHC\equiv CC_6H_5$
(XLI)

$Fc.\underset{R}{C}OH(C\equiv C)_n\underset{R}{C}OH.R'$
(XL)

	R	R'	n
a:	H	Fc	1
b:	Me	Fc	1
c:	H	C_6H_5	1
d:	H	Me	1
e:	H	Fc	2
f:	Me	Fc	2

(2) Discussion.

A. Synthesis. Synthesis of the simple carbinols XXXIX a and b was achieved by reaction of FcCHO or $FcCOCH_3$ with Na-acetylide in liquid ammonia and both compounds were obtained in a crystalline form. The ferrocenyl-ethynyl carbinol (XXXIXa) was obtained in a much higher yield, 70%, than its methyl homologue, the tertiory carbinol XXXIXb, 16%. Because of steric factors, the lower yield might be attributed to a higher reactivity of the aldehyde as compared with the ketone. The IR-absorption spectrum of XXXIXa nicely exhibited four different

-H-bands: OH : 3600, C≡C-H : 3300, Fc-H 3090 and C-H (aliph.) 2880 cm^{-1}. A characteristic band at 1106 cm^{-1} in both cases (XXXIX a and b) proved monosubstituted ferrocenes.

Some difficulties have been encountered during the preparation of simple glycols of type XL(n=1), as Fc.CHO neither reacted with acetylene-di-magnesiumbromide nor with XXXIX a (as the Na-salt in liquid ammonia). These reactions should have given XL a. 1,4-diphenyl-but-2-yn-diol-1,4, however, can be obtained from benzaldehyde without difficulty. This is another case of ferrocene-aldehyde reacting more slowly than benzaldehyde, especially in carbonyl-addition-reactions (30), which is in contrast, to the electrondonating behaviour of the ferrocenyl-group, which should make the CO-group in Fc.CHO more strongly polarized than in benzaldehyde, as also shown by IR-data (30).

Ferrocene reacts with substituted acetylenes as well as with acetylene itself. Thus, the phenyl acetylene XLI was obtained in good yields.

According to the literature, Li-salts of acetylenes should give better yields in reactions with carbonyl groups and should be more soluble (31). Therefore, in the preparation of the desired glycols XL (n=1), Li-salts instead of Na-salts (again in liquid ammonia) were used. Indeed from methyl-ethynyl-carbinol with Fc.CHO and XXXIXa with benzaldehyde (where Na-salts had given no results) by using Li-salts, the desired glycols XL d and c could be obtained. Equally diferrocenyl-acetylene-glycol (XLa) could be prepared via Li-salts (reaction of Fc.CHO in liquid ammonia with either di-Li-acetylide or the Li-salt of XXXIX a). Di-Li-acetylide is rather easily accessible from phenyl-Li and acetylene. (32)

From the reaction of dilithio-acetylide with FcCHO, the glycol and small amounts of the carbinol XXXIX were obtained and these two products were easily separated.

On the other hand, di-Li-acetylide with $Fc.COCH_3$ in tetrahydrofurane gave only the carbinol XXXIX b in even better yields than in the reaction of $Fc.COCH_3$ with Na-acetylide, whilst the expected glycol XL b could not be isolated.

With the unsymmetrical glycols (XL, R' not Fc) two racemates are possible. The symmetrical compounds (R'=Fc) contain two equivalent asymmetric C-atoms and therefore may be present as a mixture of the meso and DL-form. Indeed, all crude glycols had a considerable melting-range whilst on analysis they gave correct values. In some cases separation of the diastereomers could be achieved by crystallization, but not by chromatography. In the case of XL a only the higher melting form could be obtained in a pure state. In analogy to the corresponding diphenyl-compound it may be assumed that this isomer corresponds to the racemate, the lower melting diastereomer would be the meso-form.

B. Reactions.

a) Oxidative coupling. Coupling of ethynyl-compounds with Cu_2Cl_2 in NH_3/NH_4Cl with oxygen (31) which gives diacetylenic-derivatives, in our case (ferrocenyl-compounds) led to extensive oxidation of the ferrocene-moiety. Eglinton's modification (33), however, using Cu-II-acetate in pyridine-ether as coupling-agent, gave the diacetylenic-glycols XLe and f (from the carbinols

XXXIX a and b) in good yields.

b) Oxidation with MnO_2. For oxidation of ferrocenyl-acetylenic-carbinols and -glycols to corresponding ketones, oxidizing agents, as usually applied to acetylenic compounds (chromic acid, (31)) of course were out of question. MnO_2 seemed to be a much more promising oxidant (13,34). Indeed, by treating the following ferrocenyl-carbinols and glycols with MnO_2 in chloroform, the corresponding ketones could be obtained in excellent yields (table 5). The optimal conditions (time and temperature) could be determined easily by analyzing the reaction-mixtures with the aid of thin-layer-chromatography. Thereby the deeply coloured ketones can be distinguished from the yellow to orange starting materials, which are more strongly adsorbed and therefore exhibit lower R_F-values.

Table 5

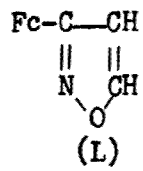
Ferrocenyl-(acetylenic)-mono and diketones.

Hydroxy-compounds		Keto-compounds		
Formula	Nr.	Formula	Nr.	mp.
Fc.CHOH.C≡CH	XXXIX a	Fc.CO.C≡CH	XLII	78-80°
Fc.CHOH.C≡C.C_6H_5	XLI	Fc.CO.C≡C.C_6H_5	XLIII	103-06°
Fc.CHOH.CH = CH.C_6H_5	XLIV	Fc.CO.CH = CH.C_6H_5	XLV	
cis	XLIV a	cis	XLV a	129-30°
trans	XLIV b	trans	XLV b	139-40°
Fc.CHOH.$CH_2CH_2C_6H_5$	XLVI	Fc.CO.$CH_2CH_2C_6H_5$	XLVII	84-86°
Fc.CHOH.C≡C.CHOH.Fc	XL a	Fc.CO.C≡C.CO.Fc	XLVIII	158-61°
(Fc.CHOH.C≡C-)$_2$	XL e	(Fc.CO.C≡C-)$_2$	XLIX	charring until 200

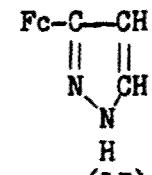
XLII: Ferrocenyl-ethynyl-ketone (XLII) on treatment with hydroxylamine or hydrazine gave the heterocyclic compounds 3-ferrocenyl-isoxazole (L) and 3-ferrocenyl-pyrazole (LI). For similar reactions in benzene-chemistry cf. Bowden and Jones (35).

XLIII, XLV: XLI could be smoothly oxidized with MnO_2 to give the ketone XLIII.

The two geometrical isomers a and b of the ketone XLV were obtained on oxidation of the corresponding cis and trans ethylenic carbinols XLIV a and b. These were prepared by stereospecific reduction of the acetylenic compound XLI. See under (c) below. The trans-compound XLV b was identical with a cinnamoyl-ferrocene formerly obtained by Knoevenagel-condensation of benzaldehyde with acetylferrocene (36, 37) or from ferrocene and cinnamoylchloride (38).



(L)



(LI)

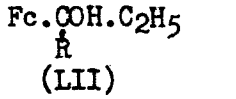
XLVII: The saturated ketone XLVII obtained by MnO_2-oxidation of the corresponding carbinole (XLVI) which, on the other hand was prepared by hydrogenation

of either XLI or XLIV, proved to be identical with a product already obtained formerly (25, 36, 38). The same ketone was accessible by prototropic rearrangement of the unsaturated carbinols XLIV a and b after treatment with alkali in ethanol, albeit in rather poor yields.

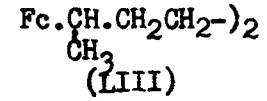
XLVIII, XLIX: Containing two asymmetric C-atoms, both (crude) glycols (XLa and XLe) are mixtures of two possible diastereomers (meso-and racemic form), the separation of which sometimes is rather tedious.

As expected, both stereoisomeric forms of XL, a or e, and the crude mixture thereof gave uniform diketones upon oxidation. Product XLVIII, from XLa, was sharp melting while XLIX, from XLe, had no melting point.

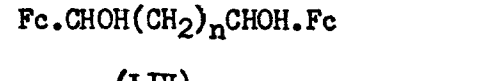
c) Hydrogenation - Hydrogenolysis. Catalytic hydrogenation of ferrocenyl-ethynyl-carbinol (XXXIX a) over Pd/C in ethanol gave the saturated compound ferrocenyl-ethyl-carbinol (LII a) which, on the other hand, could be obtained by a Grignard-reaction of ferrocene-carboxaldehyde with ethylmagnesium bromide, or by $LiAlH_4$- reduction of propionyl-ferrocene (Fc.COEt). The methyl-compound (XXXIX b), however, showed a different behaviour. After a rapid uptake of two moles hydrogen a third mole was consumed more sluggishly and a oxygen-free compound could be isolated which proved to be sec. butyl-ferrocene: Fc.CH(Me)Et. This alkyl-ferrocene was also obtained by hydrogenation of ferrocenyl-methyl-ethyl-carbinol (LIIb) which in turn could be prepared from acetyl-ferrocene and ethylmagnesium bromide. Such a hydrogenolytic cleavage of a C-O-bond is well known in benzene-chemistry, where benzylalcohol as well as substituted benzyl-alcohols under similar conditions (Pd-catalysts in alcohol) of hydrogenation give rise to alkyl-benzenes (39). In the ferrocene-field apparently only tertiary carbinols are subject to hydrogenolysis to give O-free compounds and therefore this is a further example of a reaction where a distinct difference in reactivity between benzene-and ferrocene-chemistry exists. As expected, also the tertiary glycol XL f could be hydrogenated to the parent "hydrocarbon" 2,7-diferrocenyl-n-octane (LIII) whilst the secondary glycols XL a and e yielded the saturated glycols LIV a and b.



(LII)
a : R = H
b : R = Me



(LIII)



(LIV)
a : n = 2
b : n = 4

For a further study of hydrogenolysis, diferrocenyl-carbinol (LVI) was prepared from diferrocenyl-ketone (LV) with $LiAlH_4$. Hydrogenation of this carbinol using Pd/C in ethanol gave - albeit only in 33% yield - diferrocenyl-methane (LVII) which in turn could be obtained from the ketone (LV) by reduction with $LiAlH_4/AlCl_3$ (13). The low yield of LVII in the hydrogenolysis-reaction certainly is due to the bad solubility of the OH-free compound (LVII) in ethanol.

Partial hydrogenation of some of the acetylenic compounds, mentioned in this paper, over Lindlar's catalyst (31) gave the corresponding ethylenic compounds (i.g.LVIII a and b), which undergo rearrangements rather easily. These and similar rearrangements are still under investigation. In the case of the ferrocenyl-phenyl-compound XLI (cf. table 5), by partial catalytic hydrogenation the cis-isomer (XLIV a) was obtained whilst chemical reduction ($LiAlH_4$) gave the

trans-isomer (XLIV b, table 5).

Fc.CO.Fc	Fc.CHOH.Fc	$Fc.CH_2.Fc$	$Fc.\underset{\underset{R}{|}}{C}OH.CH=CH_2$
(LV)	(LVI)	(LVII)	(LVIII) a : R = H b : R = Me

d) Dehydration. After chromatography of the above mentioned saturated carbinols (LII a and b) on acid alumina ("Woelm", activity grade I) in benzene, products were obtained which according to their IR-spectra had no more OH-groups but possessed a C=C-double-bond (LIX a, b). In both cases on hydrogenation over Pd/C in ethanol one mole hydrogen was consumed rapidly. Thereby from LIX b the same sec. butyl-ferrocene was obtained which has been mentioned above (hydrogenolysis of LII b). The unsaturated compound derived from LIIa (= LIXa) gave n-propyl-ferrocene (cf. part I-2, table 2). LIX a and b represent therefore propenyl-ferrocene (a) and sec. butenyl-ferrocene (b) respectively.

$Fc.C=\underset{\underset{R}{|}}{C}H.CH_3$ (LIX)
a : R = H
b : R = Me

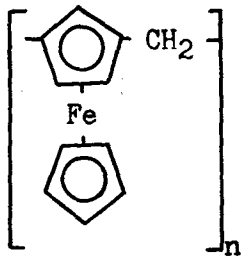
To our knowledge, this mild method of dehydration has no parallel in benzene or even in ferrocene chemistry. Up to now, dehydrations have been run under rather drastic conditions such as with alumina at 200° (40) or by heating with $KHSO_4$ (41). This new method has been applied to other examples.

For preparative purposes it is preferable to carry out the dehydration by short shaking (15-30 min.) of a benzene-solution of the appropriate carbinol or glycol together with a five-tenfold amount of acid alumina at room temperature. Short heating is not advisable since sidereactions sometimes occur, as shown below.

Ferrocenyl-methyl-carbinol (Fc.CHOH.Me), easily accessible from acetyl-ferrocene and $LiAlH_4$, gave vinyl-ferrocene ($Fc.CH=CH_2$) in 50% yield. Under similar conditions neither phenyl-methyl-carbinol nor phenyl-ethyl-carbinol gave unsaturated products. With regard to preparative simplicity the new synthesis of this interesting vinyl compound certainly is superior to the hitherto described methods: pyrolysis of the carbinol (Fc.CHOH.Me) or its acetate with alumia at 200° (yields 21 and 56% resp. (40) or treatment of $FcCH_2CH_2NMe_3^+ I^-$ with OH^- (yield: 3% (42)).

The facility with which ferrocenyl-carbinols can be dehydrated, doubtlessly is in close connection with the stability of ferrocenyl-carbonium-ions of the following type: Fc-C$\lessgtr$, which has been observed by many authors. According to the E_1-mechanism these ions have to be postulated as intermediates in a dehydration-reaction. A further proof for this assumption was gained by the following reactions: when $Fc.CH_2OH$ (36) was treated with acid alumina in refluxing benzene, polymeric ferrocenes such as LX could be isolated (IR, CH-analysis). Very probably they have been formed by an electrophilic substitution in which the cation $Fc.CH_2^+$ took part.

At room-temperature, however, intermolecular attack of this cation on an oxygen-atom of unchanged carbinol ($Fc.CH_2CH$) takes place, thereby yielding diferrocenyl-di-methylether (LXI) which could be isolated in high yields. This



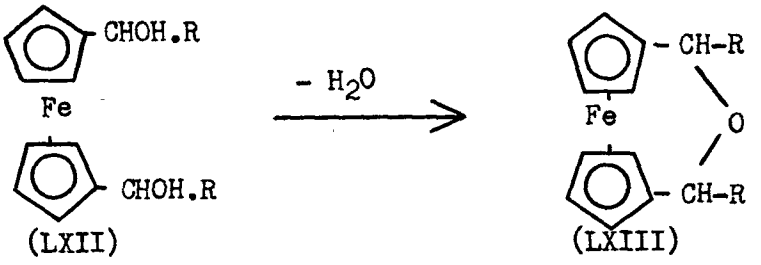
(LX)

$Fc.CH_2OCH_2Fc$
(LXI)

ether formerly has been prepared under conditions where also formation of $Fc.CH_2^+$ might be expected (36).

Similar results were observed when the glycols LXII a and b ($LiAlH_4$-reduction-products of 1.1'-diacetyl and dibenzoylferrocene) were subjected to dehydration with acid alumina in benzene. At room-temperature the intermediate carbonium-ion attacks a neighbouring OH-group and cyclic (bridged) ethers LXIII a and b are formed. Recently a simple compound of this type : 1,1'-(dimethylenoxy) ferrocene has been obtained by Rinehart et al. (17) by treatment of 1,1'-di-hydroxy-methylferrocene with p-toluenesulfochloride in refluxing benzene. LXII a on treatment with acid alumina in refluxing benzene gave appreciable amounts of instable 1,1'-divinylferrocene which, after hydrogenation, has been identified as 1,1'-diethyl-ferrocene. Is it obvious therefor that at more drastic conditions bis-dehydration had occured to a larger extend.

LXIII a and b contain two asymmetric C-atoms and therefor have to occur as racem- and meso-forms. Thin-layer-chromatograms showed indeed, that at least in the case of the dimethyl-compound (LXIIIa) two spots were present which both corresponded to compounds of similar melting point and gave the same analytic values.



(LXII) (LXIII)

a : R = Me
b : R = phenyl

a : R = Me
b : R = phenyl

The glycol LIV b could be dehydrated to give a hexadiene (LXIV) which after hydrogenation afforded 1,6-differrocenyl-n-hexane (LXV). Dehydration of LIV a should have given 1,4-diferrocenyl-butadiene (LXVI) but no distinct product could be isolated. LXVI, however, could be prepared by the Whiting-reaction from XL a (cf. discussion below, under (f)).

$(Fc.CH=CH.CH_2-)_2$ (LXIV)

$Fc.(CH_2)_6Fc$ (LXV)

$Fc.CH=CH.CH=CH.Fc$ (LXVI)

e) Reduction with $LiAlH_4/AlCl_3$. Rather surprisingly, the new reduction-method (part I-2 of this paper) offered a convenient possibility for the preparation of oxygen free ferrocenyl-acetylenic compounds containing the structural element Fc-CH-C≡C-.

Both ferrocenyl-ethynyl-ketone (XLII) and its precursor, the easily accessible ferrocenyl-ethynyl-carbinol (XXXIX a) on reduction with the complex hydride

gave propargyl-ferrocene (LXVII a), identified by its IR-absorption-spectrum, its Hg-compound (mp. 175-178°), its R_F-value (thin-layer-chromatography), and by hydrogenation which gave n-propyl-ferrocene. Similarily, the tert, carbinol XXXIX b yielded secondary butynl ferrocene (LXVII b), which was characterized in the same way as the propargyl-compound (Hg-compound, mp. 169-172°).

Both alkynes are distillable liquids and are rather unstable. After some time, even when kept at 0°, insoluble products are deposited from the liquid. Propargyl ferrocene turns red and by chromatographing the tar, a ketone could be separated which in every respect was identical with ferrocenyl ethynyl ketone (XLII). Since the carbinol XXXIX a is quite stable, it can be excluded as an intermediate in this autoxidation reaction.

From $Fc.CHOH.C\equiv C.C_6H_5$ (XLI) and its corresponding ketone (XLIII) with $LiAlH_4/AlCl_3$ 1-ferrocenyl-3-phenyl-propyn-2 (LXVII c) was obtained which could be hydrogenated (Pd/C) to give 1-ferrocenyl-3-phenyl-n-propane (LXVIII). The propyne again was susceptible to oxidation and by MnO_2 could be easily converted into the ketone XLIII. In this reaction, as a by-product, a yellow oil could be isolated which could be catalytically reduced to the above mentioned ferrocenyl-phenyl-propane (LXVIII). For this substance, rather tentatively, the preliminary structure of an allene (LXIX) is proposed.

The glycols XL a and e, as well as their corresponding di-ketones (XLVIII and XLIX, table 5) could be reduced to the desired acetylenic "hydrocarbons" LXX a and b, which in turn could be hydrogenated to give the corresponding saturated compounds diferrocenyl-butane (LXXI) and -hexane (LXV) respectively. LXX b containing the diacetylenic-moiety, is very unstable and after short time is contaminated with the di-ketone XLIX and therefore its purification is rather difficult.

$Fc.\underset{R}{C}H.C\equiv C.R'$ (LXVII)

a : R = R' = H
b : R = Me, R' = H
c : R = H, R' = C_6H_5

$Fc.CH_2CH_2CH_2C_6H_5$ (LXVIII)

$Fc.CH=C=CH.C_6H_5$ (LXIX)

$Fc.CH_2(C\equiv C)_nCH_2Fc$ (LXIX)

a : n = 1
b : n = 2

$Fc.CH_2CH_2CH_2CH_2Fc$ (LXXI)

f) $LiAlH_4$-treatment of acetylenic-glycols: diferrocenyl-polyenes. As previously mentioned (under d), the socalled Whiting-reaction (treating alkyn-diols with $LiAlH_4$ to obtain butadienes (43) offered the possibility of preparing 1,4-diferrocenyl-butadiene (LXVI) from the corresponding glycol (XLa). Thereby the higher melting (DL-) form yielded a product which decomposed at appr. 230°, whilst the lower melting isomer (meso-) gave a diferrocenyl-butadiene, melting range 130-230°. Both products analyzed correctly for $C_{24}H_{22}Fe_2$ (LXVI), could not be distinguished on thin-layer chromatograms and on hydrogenation gave the same diferrocenyl-butane (LXXI). It had to be assumed, that they might represent geometrical isomers: namely trans-trans from the DL- and a possible mixture of cis-cis and trans-cis from the meso-form.

To settle this question, both racemic (mp. 140°) and meso-(mp. 104°) diphenylbutyn-diol ($C_6H_5CHOH.C{\equiv}C.CHOH.C_6H_5$) were treated with $LiAlH_4$ thereby giving pure trans-trans (mp. 148) and a crude diphenyl-butadiene (mp. 40-120°). Pure cis-cis should melt at 70°; cis-trans is an oil. After a few recrystallizations, the melting point reached 140° indicating that a rearrangement to the stable trans-trans isomer had taken place.

It may be concluded that in both cases (diferrocenyl and diphenyl) the DL glycols give the trans-trans butadienes, while the lower melting meso forms yield a mixture of geometrical isomers; possible, the cis-cis compounds form under the controlled conditions.

The UV-absorption-spectra of diphenyl-, phenyl-ferrocenyl and diferrocenyl-butadiene (LXVI) have been compared and the following results been obtained: (the "mixed" phenyl-ferrocenyl-butadiene was prepared from XL c and $LiAlH_4$).

In hexane-CH_2Cl_2 the three butadienes exhibited peaks at 330mμ. Besides this main-band, in the diphenyl-compound two weaker maxima could be observed at 316 and 345 mμ, respectively. In the ferrocenyl-phenyl derivative the 345mμ was present as a shoulder whilst diferrocenyl-butadiene only had one broad maximum at 330 mμ. Therefore it is obvious that with increasing number of electron-donating ferrocene-moieties at the ends of the conjugated system the fine structure of the spectra disappears.

Finally, the diacetylenic glycol XL e was treated with $LiAlH_4$ and 1,6-diferrocenyl-hexatriene (LXXII) was obtained in good yields. Only traces of the dihydroxy-diene (LXXIII) could be detected, whilst in the case of the corresponding diphenyl-compound the triene as well as the dihydroxy-diene are obtained. (Yields 30% and 27% respectively (44). The triene (LXXII) which is more stable than the diyne (LXXb) after hydrogenation have the already mentioned 1,6-diferrocenyl-hexane (LXV).

$Fc(CH=CH)_3Fc$
(LXXII)

$(Fc.\underset{\underset{OH}{|}}{CH}.CH=CH-)_2$
(LXXIII)

ACKNOWLEDGEMENT

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METALLO-ORGANIC COMPOUNDS CONTAINING METAL-NITROGEN BONDS.

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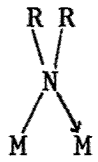
London, Ontario, Canada.

ABSTRACT

By means of reactions involving transition metal chlorides MCl_x and lithium dialkylamides a number of new dialkylamino-derivatives of titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten have been prepared. Aminolysis of some of these compounds involved considerable steric effects due to shielding of the metal atom. In the case of quinquevalent niobium and tantalum the steric effect precluded the formation of pentakis-derivatives except with dimethylamino-, N-methyl-n-butylamino-, and piperidino-groups. With higher dialkylamines the products were $Nb(NR_2)_4$ and $RN{=}Ta(NR_2)_3$. Studies on the reactions of dialkylamino-titanium compounds with primary amines showed that polymeric compounds may be obtained.

INTRODUCTION

The dialkylamino- compounds of the transition metals were of special interest since they bridge the gap between the relatively stable metal alkoxides and the generally unstable metal alkyls. In addition there was the possibility that metal-nitrogen polymers would be formed, either by coordination-polymerization (I) in which the lone-pair of electrons on the nitrogen forms an intermolecular coordinate bond, or by using the bifunctional primary amine as in (II).



(I)



(II)

In the case of the primary amino-derivatives there was the further possibility that coordination-polymerization would also take place. There were also some factors which might operate against polymerization. Thus in the dialkylamino-derivatives the intermolecular bond (I) might be prevented by steric effects or by "intramolecular coordination" involving $d\pi - p\pi$ bonds $M{=}NR_2$. In the case of primary amino-derivatives there was the further possibility that only one of the hydrogens of the NH_2- group would be replaceable by metal and this would prevent polymerization by mechanism (II). Prior to 1959 the only binary dialkylamino-compound of a transition metal or actinide element reported was the tetrakis-(diethylamino)-uranium (IV) obtained by Gilman and coworkers[1] from the reaction involving uranium tetrachloride and lithium diethylamide. Dermer and Fernelius[2] prepared $Ti[N(C_6H_5)_2]_4$ by treating titanium tetrachloride with sodium diphenylamide.

We have shown that the lithium dialkylamide- metal chloride reaction (I) is suitable for the synthesis of numerous dialkylamino-derivatives of titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.

$$MCl_x + xLiNR_2 \rightarrow M(NR_2)_x + xLiCl \qquad (1)$$

Most of the dialkylamino-derivatives may be distilled under reduced pressure although in some cases [e.g. Nb(V), Ta(V) compounds] interesting thermal decomposition occurs. The aliphatic dialkylamino- compounds were readily hydrolysed or alcoholysed but arylamino-derivatives were relatively more stable. Some interesting steric effects were observed in the dialkylamino- compounds whilst in the primary amino- compounds a number of polymeric derivatives were obtained.

Titanium and Zirconium Compounds

1. Dialkylamino-, and other secondary amino-derivatives.

Some data on tetrakis-(dialkylamino)-titanium and zirconium compounds[3] are presented in Table 1.

Table 1

Compound	Appearance	Boiling point (°C mm.Hg.)
$Ti(NMe_2)_4$	Yellow liquid	50/0.05
$Ti(NEt_2)_4$	Orange liquid	112/0.1
$Ti(NPr^n_2)_4$	Red liquid	150/0.1
$Ti(NBu^i_2)_4$	Red liquid	170/0.1
$Zr(NMe_2)_4$	White solid (mp.70°)	80/0.05
$Zr(NEt_2)_4$	Green liquid	120/0.1
$Zr(NPr^n_2)_4$	Green liquid	165/0.1
$Zr(NBu^i_2)_4$	Green solid	180/0.1 (sublimes)

Some tetrakis-(dialkylamino)-titanium and -zirconium compounds

Only in the case of $Zr(NMe_2)_4$ was there any evidence of polymerization at the boiling point of benzene and it is noteworthy that the compound is significantly less volatile than the corresponding titanium derivative. From a consideration of the steric effects demonstrated in the aminolysis of these tetrakis-(dialkylamino)-derivatives it was deduced that the absence of polymerization was a consequence of the powerful shielding of the central atom by the dialkylamino- groups. In the aminolysis reactions an excess of a higher boiling amine was added to the tetrakis-(dialkylamino)-derivative and the liberated lower boiling amine was fractionated off until it appeared that the reaction was complete. The extent of these reactions is shown in the following equations.

$$Ti(NMe_2)_4 \xrightarrow[(5\ days)]{Et_2NH} Ti(NMe_2)(NEt_2)_3,\ (bp.\ 95^\circ/0.05\ mm.) \quad (2)$$

$$Ti(NMe_2)_4 \xrightarrow[(3\ days)]{Pr^n_2NH} Ti(NMe_2)(NPr^n_2)_3,\ (bp.\ 135^\circ/0.05\ mm.) \quad (3)$$

$$Ti(NMe_2)_4 \xrightarrow[(3\ days)]{Bu^i_2NH} Ti(NMe_2)(NBu^i_2)_3,\ (bp.\ 170^\circ/0.1\ mm.) \quad (4)$$

$$Ti(NMe_2)_4 \xrightarrow[(1\ day)]{Piperidine} Ti(NC_5H_{10})_4,\ (bp.\ 180^\circ/0.1\ mm.) \quad (5)$$

$$Ti(NMe_2)_4 \xrightarrow[(5\ days)]{2\text{-Methyl piperidine}} Ti(NMe_2)(NC_5H_9Me)_3,\ (bp.\ 160^\circ/0.1\ mm.) \quad (6)$$

$$Ti(NMe_2)_4 \xrightarrow[(3\ days)]{2,6\text{-Dimethyl piperidine}} Ti(NMe_2)_3(NC_5H_8Me_2),\ (bp.\ 120^\circ/0.05) \quad (7)$$

$$Ti(NEt_2)_4 \xrightarrow[(1\frac{1}{2}\ days)]{Piperidine} Ti(NC_5H_{10})_4 \quad (8)$$

$$Zr(NMe_2)_4 \xrightarrow[(16\ hrs.)]{Et_2NH} Zr(NEt_2)_4 \quad (9)$$

$$Zr(NMe_2)_4 \xrightarrow[(3\ days)]{Pr^n_2NH} Zr(NPr^n_2)_4 \text{----------(10)}$$

$$Zr(NMe_2)_4 \xrightarrow[(7\ days)]{Pr^i_2NH} Zr(NMe_2)_2(NPr^i_2)_2, \text{ (sublimes } 100^\circ/0.05\text{)---(11)}$$

$$Zr(NMe_2)_4 \xrightarrow[(2\ days)]{\text{2-Methyl piperidine}} Zr(NC_5H_9Me)_4 \text{ (bp. } 190^\circ/0.1\text{)----------(12)}$$

$$Zr(NMe_2)_4 \xrightarrow[(6\ days)]{\text{2,6-Dimethyl piperidine}} Zr(NC_5H_8Me_2)_4, \text{ (bp. } 200^\circ/0.05 \text{ mm.)-------(13)}$$

$$Zr(NEt_2)_4 \xrightarrow[(2\ days)]{Pr^i_2NH} Zr(NEt_2)_3(NPr^i_2), \text{ (bp. } 112^\circ/0.05 \text{ mm.)-----(14)}$$

$$Zr(NEt_2)_4 \xrightarrow[(4\ days)]{Bu^i_2NH} Zr(NBu^i_2)_4, \text{ (bp. } 180^\circ/0.1 \text{ mm.)----------(15)}$$

$$Zr(NEt_2)_4 \xrightarrow[(6\ hrs.)]{\text{Piperidine}} Zr(NC_5H_{10})_4, \text{ (bp. } 190^\circ/0.2 \text{ mm.)---------(16)}$$

The above reactions are readily interpreted as controlled by steric factors. For example in the case of titanium compounds it is clear that the dimethylamino- groups in $Ti(NMe_2)_4$ are equally replaced by diethylamino-, di-n-propylamino-, or di-iso-butylamino- groups although the experimental conditions were not strictly comparable. However, when di-isopropylamine was used only a small amount of $Ti(NMe_2)_3(NPr^i_2)$ was formed in a reaction lasting 6 days. Even more striking was the behaviour of piperidine, 2-methyl piperidine, and 2,6-dimethyl piperidine. In the reaction with piperidine all of the dimethylamino-groups were replaced because piperidine exerts a smaller steric effect than the di-n-alkylamino- groups (excepting Me_2N-). When 2-methyl piperidine was used substitution was limited to the formation of $Ti(NMe_2)(NC_5H_9Me)_3$ whilst with 2,6-dimethyl piperidine steric hindrance to substitution was so powerful that only one dimethylamino- group could be replaced. Nevertheless, it was evident that the steric effect of di-isopropylamine was greater than that of 2,6-dimethyl piperidine. The behaviour of tetrakis-(dimethylamino)- zirconium was also in accordance with steric control of substitution. It would be predicted that the zirconium atom being larger than titanium would cause $Zr(NMe_2)_4$ to be more prone to nucleophilic reagents than $Ti(NMe_2)_4$. The veracity of this prediction was well established by the fact that complete substitution of dimethylamino- groups was achieved by Et_2N-, Pr^n_2N-, and Bu^i_2N- groups in the case of zirconium in contrast to trisubstitution in the case of titanium. The complete substitution of dimethylamino- groups attached to zirconium by piperidine, 2-methyl piperidine, or 2,6-dimethyl piperidine emphasizes the importance of steric effects in these reactions. Only in the reaction of di-isopropylamine with $Zr(NMe_2)_4$ which was restricted to disubstitution was there evidence of steric hindrance to substitution of tetrakis-(dimethylamino)-zirconium. On the other hand it would be expected that the greater steric effect of diethylamino- groups would lead to greater steric hindrance to substitution of $Zr(NEt_2)_4$. This was strikingly proved in the reaction with di-isopropylamine which was confined to mono-substitution.

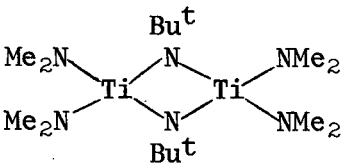
2. Derivatives of Primary amines.

When either $Ti(NMe_2)_4$ or $Ti(NEt_2)_4$ were treated with excess of the primary amine RNH_2, where R = Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, or cyclohexyl, a coloured solid approximating to the limiting formula $Ti(NR)_2$ was formed. The colours ranged from orange through red to brown and the compounds were practically insoluble and non-volatile. These properties suggested that the compounds were highly polymeric due to metal-nitrogen bridges (II). It is clear that the primary amines are behaving as bifunctional reactants in the aminolysis:-

$$Ti(NMe_2)_4 + 2RNH_2 \rightarrow [Ti(NR)_2]_x + 4Me_2NH \text{----------} (17)$$

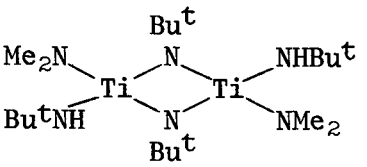
The primary amino-derivatives were all readily hydrolysed or alcoholysed.

When $Ti(NMe_2)_4$ was treated with excess tertiary butylamine only disubstitution occurred with the formation of the dimer $Ti_2(NMe_2)_4(NBu^t)_4$ which probably has the formula (III):-



(III)

Once again it appeared that steric factors controlled the extent of the reaction. Prolonged treatment of (III) with excess of tertiary butylamine failed to produce any higher polymers although some replacement of dimethylamino-groups took place. Instead the volatile (sublimes 140-160°/0.1 mm.) deep red solid dimer $Ti_2(NMe_2)_2(NBu^t)_2(NHBu^t)_2$ was obtained which may well have structure (IV)

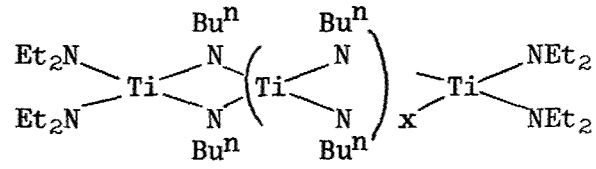


(IV)

In the reactions involving $Ti(NEt_2)_4$ and n-butylamine it was possible to isolate a number of soluble polymers of the general formula $Ti_n(NBu^n)_{2n-2}(NEt_2)_4$.

$$nTi(NEt_2)_4 + (2n-2)Bu^nNH_2 \rightarrow Ti_n(NBu^n)_{2n-2}(NEt_2)_4 + (4n-4)Et_2NH \text{-----} (18)$$

It is believed that these compounds are polymers involving tetrahedrally 4-coordinated titanium with terminal Et_2N- groups acting as chain stoppers as in (V)



(V)

These products were dark red non-volatile solids and polymers containing 6, 14, 16 and ca 100 titanium atoms per molecule were obtained.

A significant result was obtained from the reaction involving $Ti(NMe_2)_4$ and aniline. A black microcrystalline non-volatile solid corresponding in analysis to $Ti(NC_6H_5)_2$ remained after drying at 215°/0.1 mm. It was most interesting to find that this compound was noticeably less readily hydrolysed than any of the aliphatic primary amino-derivatives.

3. Tris-(diethylamino)-titanium (III).

From the reaction involving titanium trichloride and lithium diethylamide a brown liquid was obtained. From the analysis it was deduced that the compound was substantially the tervalent titanium derivative $Ti(NEt_2)_3$ containing some coordinated amine. When heated under reduced pressure the compound disproportionated to give tetrakis-(diethylamino)-titanium (IV) and left a non-volatile residue containing lower valency compounds of titanium.

Vanadium, Niobium and Tantalum Compounds

1. Vanadium Compounds.

Vanadium tetrachloride reacted with lithium dialkylamides to form tetrakis-(dialkylamino)-vanadium (IV) derivatives[4]. For example, $V(NMe_2)_4$ was obtained as a green solid (mp. 40°; bp. 65°/1.0 mm.) and $V(NEt_2)_4$ was a dark green liquid (bp. 110°/0.05 mm.). Alcoholysis of the tetrakis-(dialkylamino)-vanadium derivatives afforded the vanadium tetraalkoxides.

Vanadium trichloride reacted with lithium diethylamide to form a dark brown liquid which was substantially tris-(diethylamino)-vanadium (III) with some coordinated diethylamine. This product resembled the corresponding titanium compound by undergoing disproportionation when heated in vacuo.

2. Niobium Compounds.

Studies of the reactions of niobium pentachloride with lithium dialkylamides led to some interesting results[5]. In the case of lithium dimethylamide the product was substantially pentakis-(dimethylamino)-niobium (V) with <10% of quadrivalent niobium present. The pure $Nb(NMe_2)_5$ was isolated by vacuum sublimation. With the higher dialkylamides the amount of quadrivalent niobium in the crude products increased steadily with length of the alkyl chain (i.e. Et, 69%; Pr^n, 85%; Bu^n, 91% reduction). In each case the tetrakis-(dialkylamino)-niobium (IV) compound was obtained by vacuum distillation. Some data on niobium compounds are given in Table 2.

Table 2

Compound	Appearance	Boiling point (° C/mm.Hg)
$Nb(NMe_2)_5$	Brown solid	sublimes 100/0.1
$Nb(NMeBu^n)_5$	Red liquid	decomp. 150/0.1
$Nb(NC_5H_{10})_5$	Yellow crystals	decomp. 170/0.1
$Nb(NEt_2)_4$	Brown liquid	120/0.1
$Nb(NPr^n_2)_4$	Red liquid	155/0.1
$Nb(NBu^n_2)_4$	Red liquid	175/0.1
$Nb(NMeBu^n)_4$	Red liquid	150/0.1
$Nb(NC_5H_{10})_4$	Brown liquid	decomp. 170/0.1

Some Alkylamino-niobium Compounds.

We have interpreted the breakdown of pentakis-(dialkylamino)-niobium (V) compounds as being caused by steric compression within the molecule. Obviously the intramolecular compression will become more severe as the size of the di-n-alkylamino- group is increased. This is in accord with the increasing percentage of Nb(IV) found in the initial products from the $NbCl_5$-$LiNR_2$ reactions. This view is also supported by the additional facts that pentakis-derivatives were also obtained with N-methyl-n-butylamino- and piperidino- groups. Our work on titanium and zirconium compounds showed very clearly that the steric effect of the piperidino- group was significantly less than that of the diethylamino- and higher di-n-alkylamino- groups. Moreover, there can hardly be any doubt that the steric effect of the $MeBu^nN$- group must be less than that for diethylamino- groups because the methyl group being small allows the n-butyl group to bend away from the centre of the $Nb(NMeBu^n)_5$ molecule.

Further evidence for the existence of powerful steric effects was forthcoming from some reactions involving $Nb(NMe_2)_5$ and diethylamine. In one case the reactants were maintained at the boiling point of diethylamine for 2 hours and the liberated dimethylamine was fractionated off. No reduction of niobium occurred but aminolysis was restricted to disubstitution.

$$Nb(NMe_2)_5 + 2Et_2NH \rightarrow Nb(NMe_2)_3(NEt_2)_2 + 2Me_2NH \qquad (19)$$

In another experiment continued for 9 days the replacement of dimethylamino- groups was still incomplete and about 30% reduction of niobium occurred. Distillation of the product gave the quadrivalent compound $Nb(NMe_2)(NEt_2)_3$ as a red liquid (bp. 120°/0.1 mm.). Evidently the niobium can accommodate three dimethylamino- groups and two diethylamino- groups but the introduction of the third or fourth diethylamino- groups leads to instability.

3. Thermal decomposition of pentakis-(dialkylamino)-niobium compounds.

The formation of tetrakis-(dialkylamino)-niobium (IV) compounds by thermolysis of the pentakis-(dialkylamino)-niobium (V) is extremely interesting and raises the question of mechanisms. Although the mechanism of the thermolysis has not yet been studied some useful observations may be made. Thus it was noticed that secondary amine was also liberated in the reaction and this suggests that the dialkylamino- radical is involved in hydrogen abstraction. The following equations suggest possible mechanisms for the thermolysis.

$$Nb[N(C_2H_5)_2]_5 \rightarrow Nb[N(C_2H_5)_2]_4 + (C_2H_5)_2\dot{N} \text{----------(20)}$$

$$2(C_2H_5)_2\dot{N} \rightarrow (C_2H_5)_2NH + CH_3CH{=}NC_2H_5 \text{----------(21)}$$

An interesting feature of the thermolysis of $Nb(NMeBu^n)_5$ was the formation of $Bu^nN{=}Nb(NMeBu^n)_3$ in addition to $Nb(NMeBu^n)_4$. This was the only case in which the quinquevalent $RN{=}Nb(NRR')_3$ was found because there was no evidence for the formation of such compounds in the thermolysis of the dialkylamino-derivatives.

4. Tantalum Compounds.

The reactions of tantalum pentachloride with various lithium dialkylamides LiX, where X = NMe_2, NEt_2, NPr^n_2, $NMeBu^n$ and NC_5H_{10}, were studied. From these reactions the corresponding pentakis-derivatives were obtained, in contrast to the behaviour of niobium pentachloride. However, only the pentakis-dimethylamino-derivative $Ta(NMe_2)_5$ could be sublimed without decomposition and this calls to mind the behaviour of $Nb(NMe_2)_5$. When the higher pentakis-(dialkylamino)-compounds of tantalum were heated in vacuo thermolysis took place with the formation of substantially the interesting quinquevalent compounds $RN{=}Ta(NR_2)_3$ together with some tetrakis-(dialkylamino)-tantalum (IV). Some data on the tantalum compounds are presented in Table 3.

Table 3

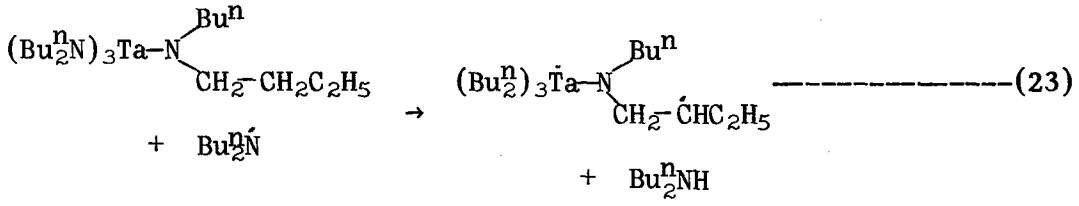
Compound	Appearance	Boiling point (°C/mm.Hg)
$Ta(NMe_2)_5$	Yellow crystals	sublimes 100/0.1
$EtN{=}Ta(NEt_2)_3$	Yellow liquid	120/0.1
$Pr^nN{=}Ta(NPr^n_2)_3$	Orange liquid	150/0.1
$Bu^nN{=}Ta(NBu^n_2)_3$	Yellow liquid	180/0.1
$Ta(NC_5H_{10})_5$	Yellow solid	-
$Ta(NMeBu^n)_5$	Orange liquid	decomp. 160/0.1
$Bu^nN{=}Ta(NMeBu^n)_3$	Orange liquid	150-155/0.1
$Ta(NMeBu^n)_4$	Red liquid	155-180/0.1

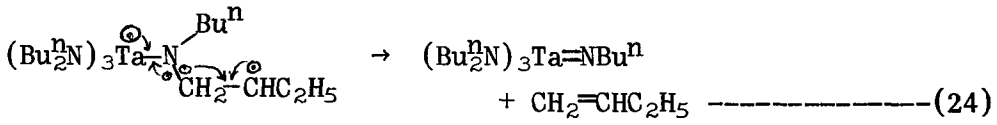
Some Alkylamino-compounds of Tantalum.

The detailed mechanism of the formation of the quinquevalent derivatives $RN{=}Ta(NR_2)_3$ is as yet obscure but from product analysis it appears that secondary amine and olefin are also produced in the thermolysis of $Ta(NR_2)_5$ compounds. We suggest as a tentative explanation that the pentakis-derivative dissociates to the tetrakis-derivative and a dialkylamino radical.

$$Ta(NR_2)_5 \rightarrow Ta(NR_2)_4 + R_2N \text{----------(22)}$$

Further it is suggested that the quadrivalent tantalum compound is so unstable that it reacts with the radical before the latter becomes "free". A possible sequence would be hydrogen abstraction by the radical followed by the elimination of olefin.

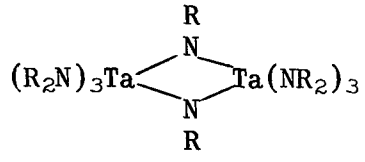




The thermolysis of $Ta(NMeBu^n)_5$ was of added interest because of the choice of alkyl groups attached to the nitrogen. The formation of $Ta(NMeBu^n)_4$ and $Bu^nN{=}Ta(NMeBu^n)_3$ but not $MeN{=}Ta(NMeBu^n)_3$ suggests that a methyl group in $Ta(NMeBu^n)_4$ is preferentially attacked by the N-methyl-n-butylamino-radical. It is pertinent to examine the evidence on which the formula for the $RN{=}Ta(NR_2)_3$ derivatives is based. Firstly there is the analytical data for tantalum and nitrogen. However, the analytical figures for $RN{=}Ta(NR_2)_3$ are fairly near to those for $Ta(NR_2)_4$. The second factor is the determination of the average valency of the tantalum by a chemical method. This ruled out the quadrivalent formula $Ta(NR_2)_4$. The third and decisive piece of evidence was forthcoming from the identification of the primary amine RNH_2 in addition to the secondary amine among the products of alcoholysis.

$$RN{=}Ta(NR_2)_3 + 5ROH \rightarrow Ta(OR)_5 + RNH_2 + 3R_2NH \qquad (25)$$

However, there remains the possibility that the compound is the dimer $Ta_2(NR)_2(NR_2)_6$ with a double primary amino-bridge as in (VI).



(VI)

The dimeric structure (VI) was ruled out by the volatility of the compounds which were close to the volatilities of the monomeric tetrakis-(dialkylamino)-niobium (IV) compounds. Consequently we assign the monomeric formula $RN{=}Ta(NR_2)_3$ which contains the metal-nitrogen π-bond.

Chromium, Molybdenum and Tungsten Compounds.

When chromium trichloride was treated with lithium diethylamide a small yield of tris-(diethylamino)-chromium (III) was ultimately obtained as a volatile (bp. 90°/0.1 mm.) green liquid.

From the reaction involving molybdenum pentachloride and lithium diethylamide a very small yield of substantially pure tetrakis-(diethylamino)-molybdenum (IV) was obtained as a volatile (bp. 110°/0.1 mm.) violet liquid.

From molybdenum trichloride an impure tris-(diethylamino)-molybdenum (III) was obtained as a non-volatile brown gum.

When tungsten hexachloride was allowed to react with lithium diethylamide some tetrakis-(diethylamino)-tungsten (IV) was obtained as a volatile (bp. 120°/0.1 mm.) red liquid. All of these chromium, molybdenum and tungsten compounds were readily hydrolysed.

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CYCLIC ORGANOSILICON COMPOUNDS

Henry Gilman
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Abstract

The studies reported at this time are concerned primarily with cyclic compounds, particularly those containing one or more silicon atoms in the ring.

Introduction

Earlier investigators had shown that some of our cyclic compounds had promising properties of potential use as high temperature lubricants and fluids. It was then observed that one of these compounds had special characteristics of a high-temperature antioxidant. The compound is 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, abbreviated later by the Air Force as "5,10,10".

It was also known that some disilanes had above-average thermal stabilities. This suggested a study of non-polymeric polysilanes which were either perphenylated or which contained a high percentage of phenyl or aryl groups. One of the more attractive approaches to the polysilanes was through the interesting cyclic-polysilanes first reported by Kipping.

I. Preparation and Structure of Compounds "A" and "B".

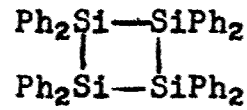
(1) Preparation

Kipping first prepared his Compound "A" and Compound "B" by the reaction of dichlorodiphenylsilane with sodium in toluene. We have found that Compound "A" is readily prepared in highly satisfactory yields by reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran. Neither lithium nor tetrahydrofuran were reasonably accessible to Kipping when he first prepared "A" and "B". Incidentally, we have shown that it is possible to go smoothly from Compound "A" to Compound "B" by the use of various reagents such as RLi compounds, and particularly a small excess of lithium metal. It should be stated that from Kipping's reaction he also obtained smaller quantities of Compound "C" and Compound "D" as well as some "polymers".

(2) Structure

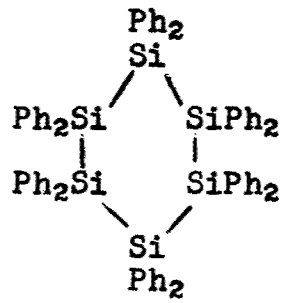
A rather large number of structures was suggested and considered by Kipping for his Compound "A", practically all of them having the diphenylsilylene, $(C_6H_5)_2Si$, unit. His choice was the structure having two terminal trivalent silicon atoms:

• • •$Si(Ph_2)Si(Ph_2)Si(Ph_2)(Ph_2)Si$• • • This was a reasonable structure then in view of the high reactivity of "A". However, we have shown that "A" is in reality octaphenylcyclotetrasilane:

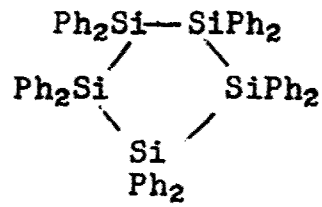


The high reactivity is due to the pronounced ease of opening this ring.

Kipping considered his Compound "B" to be isomeric with his "A" and designated it as octaphenylcyclotetrasilane. Inasmuch as we showed that "A" was octaphenylcyclotetrasilane, it seemed quite reasonable to expect that Compound "B" had some other structure. Initially we suggested that "B" was dodecaphenylcyclohexasilane:



More recent work indicates that although "A" and "B" arecycles containing different numbers of diphenylsilylene groups, that "B" is very probably decaphenylcyclopentasilane:



Some of the evidence for this is the opening of the ring by reaction with lithium in tetrahydrofuran to give the 1,5-dilithiodecaphenylpentasilane, $LiSi(Ph_2)Si(Ph_2)SiSi(Ph_2)(Ph_2)Si(Ph_2)Li$, which reacts smoothly with tri-n-butyl phosphate to give 1,5-di-n-butyl-decaphenylpentasilane, $n\text{-}C_4H_9Si(Ph_2)Si(Ph_2)Si(Ph_2)Si(Ph_2)Si(Ph_2)C_4H_9\text{-}n$. Among other supporting evidence for this structure is the NMR ratio of aryl hydrogen: alkyl hydrogen.

II. Reactions of Compound "A"

(1) With Organic Halides

As mentioned earlier "A" undergoes ready ring opening. One of these reactions first observed by Kipping (possi-

bly incidental to an examination of various solvents) was with sym.-tetrachloroethane to give 1,4-dichloro-octaphenyltetrasilane:

$$\text{"A"} + Cl_2CHCHCl_2 \longrightarrow Cl(SiPh_2)_4Cl$$

Because of the value of such compounds for the preparation of new polysilanes and new cyclic organosilicon and related types, we studied the reactions of "A" with a wide variety of organic halides, incidental to which the course of the reaction was established. It is noteworthy that C_2HCl_5 reacts with "A" in five minutes at 150° to give a 99% yield of the 1,4-dichloro-octaphenyltetrasilane. The temperature effect is significant because at 70° the yield is 82% after 10 days. Another illustration of the temperature effect is with 1,1,2-tribromoethane which after 10 days at 80° gives a 67% yield of 1,4-dibromo-octaphenyltetrasilane and after 6 minutes at 188° gives a yield of 92%. There can be appreciable effects with isomers: for example, $ClCH_2CHClCH_2Cl$ after 5 days at 150° gives a 73% yield; whereas $Cl_2CHCHClCH_3$ after 15 hours at 147° gives a 98% yield. No reaction has been observed under corresponding conditions with the following unsaturated halides: $ClCH{=}CHCl$; $Cl_2C{=}CHCl$; $Cl_2C{=}CCl_2$; C_6H_5Cl; $C_6H_5C(Cl){=}C(Cl)(C_6H_5)$.

From the study of "A" with organic halides there developed in other areas more convenient procedures not only for the quantitative estimation of R_3SiM and R_3SnM types, but also for aryllithium compounds and methyllithium which can not be analyzed by the double-titration procedure using benzyl chloride. Some of the halides found useful in these analytical procedures are allyl bromide for R_3SiM and R_3SnM types; and halides such as CCl_4, $C_6H_5CCl_3$, Br_2CHCH_2Br, C_2HCl_5, and $BrCH_2CH_2Br$ for RLi compounds having the C-Li linkage.

(2) With Halogens

The reaction with halogens takes an expected general course to give the 1,4-dihalo-octaphenyltetrasilane. However, special care must be exercised to get satisfactory yields. For example, with bromine there is formed not only the 1,4-dibromo compound, $Br(SiPh_2)_4Br$, but also dibromo compounds having a lesser number of (Ph_2Si) groups, such as 1,2-dibromotetraphenyldisilane, $BrSi(Ph_2)Si(Ph_2)Br$. Actually, the reaction of bromine with "A" or "B" can be used as one of the preferred methods for the preparation of 1,2-dibromotetraphenyldisilane.

(3) With Hydrogen Bromide and Hydrogen Chloride.

These halogen acids have been shown to cleave "A" under suitable conditions to give the corresponding $H(SiPh_2)_4X$, a type which lends itself to preferential or selective reactions to build cyclic or linear polysilanes.

(4) Phosphorus Pentachloride

The present method of choice for the formation of

1,4-dichloro-octaphenyltetrasilane is the reaction of "A" with PCl_5. The yields are in the 95% range. Phosphorus trichloride does not react with "A" under corresponding conditions. However, the 1,4-dichloro-octaphenyltetrasilane is formed by reaction of "A" with sulfuryl chloride, thionyl chloride, mercuric chloride, stannic chloride, and some other inorganic chlorides. The corresponding dibromo and di-iodo compounds are formed from mercuric bromide and mercuric iodide, respectively. In the reaction with mercuric chloride the high yield of 1,4-dichloro-octaphenyltetrasilane is accompanied by an equivalent high yield of mercurous chloride. Mercuric acetate also reacts smoothly with "A".

(5) Lithium

Depending upon experimental conditions, lithium (in very small amounts) will convert Compound "A" to Compound "B". However, equivalent amounts give the 1,4-dilithio-octaphenyltetrasilane, $Li(SiPh_2)_4Li$, in quite satisfactory yields. To obtain such yields it is necessary to observe specified conditions to avoid significant cleavages of Si-Si bonds after ring "A" has opened. These secondary cleavages can lead to the formation of a 1,3-dilithiohexaphenyltrisilane, $Li(SiPh_2)_3Li$, and other silyllithium compounds.

(6) Hydrogenolysis

The disilane bonds of various organosilicon compounds were found to be cleaved by hydrogen to give silicon hydrides when treated under conditions of relatively high temperatures and pressures in the presence of copper oxide catalysts, providing that the silicon-silicon bonds were activated by the presence of phenyl groups (as in "A"). Raney nickel was not effective as a catalyst for the hydrogenolysis reaction, nor could the aromatic rings be hydrogenated when attached to the disilane linkage.

The opening of "A" can be effected also by hydrides such as lithium aluminum hydride. Depending on reaction conditions one can not only obtain the 1,1,2,2,3,3,4,4-octaphenyltetrasilane, $H(SiPh_2)_4H$, but also other cleavage products such as sym.-tetraphenyldisilane, $H(SiPh_2)_2H$. Additionally, some hydrides such as lithium aluminum hydride can convert "A" to "B".

(7) Organometallic and Pseudo-organometallic Compounds.

Organometallic compounds such as RLi types will cleave Compound "A". For example, methyllithium gives a satisfactory yield of 4-methyloctaphenyltetrasilanyllithium:

$$\text{"A"} + CH_3Li \longrightarrow CH_3(SiPh_2)_4Li$$

Hydrolysis of this silyllithium compound yields the corresponding $CH_3(SiPh_2)_4H$; and reaction of the silyllithium compound with trimethyl phosphate gives the 1,4-dimethyloctaphenyltetrasilane,

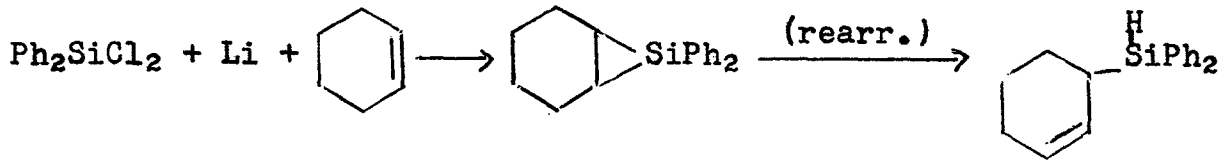
$CH_3(SiPh_2)_4CH_3$. Two other types of reactions take place with RLi compounds: one of these is cleavage to smaller polysilanes; and the other is partial conversion of "A" to "B". This latter reaction also probably involves secondary cleavages prior to the formation of "B".

In general, reactions like those just described with RLi compounds also take place with so-called pesudo-organometallic compounds such as triphenylsilyllithium, $(C_6H_5)_3SiLi$.

It is highly significant that Compound "B" after a very short period of reaction with methyllithium in tetrahydrofuran followed by reaction with trimethyl phosphate gives good yields of 1,5-dimethyldecaphenylpentasilane, $CH_3(SiPh_2)_5CH_3$. There is also formed some $CH_3(SiPh_2)_4CH_3$ and some $CH_3(SiPh_2)_2CH_3$.

III. Diphenylsilylene, $(C_6H_5)_2Si$

Incidental to the synthesis of new highly phenylated cyclic compounds containing not only silicon in the ring, but also combinations of silicon and other elements, a study was made on the possible use of a reaction species such as diphenylsilylene. This analog of diphenylcarbene, $(C_6H_5)_2C$, is possibly formed incidental to the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran. When this reaction was carried out in the presence of cyclohexene as a trapping reagent, one of the products isolated was 2-cyclohexen-1-yldiphenylsilane, which may have formed by a rearrangement of a precursory silacyclopropane type:



The structure of this compound was established by an independent synthesis. However, subsequent studies revealed that pure cyclohexene would not do this, and that the active agent was the cyclohexenehydroperoxide. Growing out of this incompleted study was the observation that a compound like allyloxytriphenylsilane can actually function to a degree as an allylating agent:

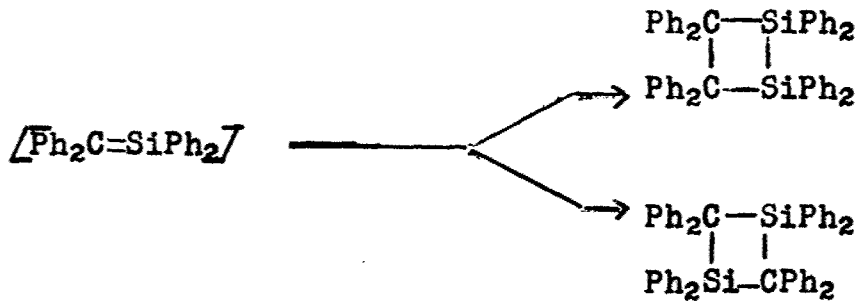
$$C_3H_5\text{-}O\text{-}SiPh_3 + Ph_3SiLi \longrightarrow C_3H_5SiPh_3$$

IV. Unsaturation Stemming from a Silicon Atom.

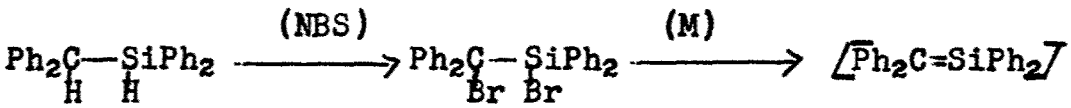
There appears to be at this time no unequivocal evidence for unsaturation stemming from a silicon atom to provide units such as Si=Si, Si=C, Si=O. It does seem possible on theoretical and other grounds to find some support for a Si=C type of bonding.

Our interest in this problem was focused on the possibility of using compounds having such linkages for the synthesis of new

cyclic organosilicon compounds. For example, the following simple dimerization might give a four-membered ring analogous to Compound "A"



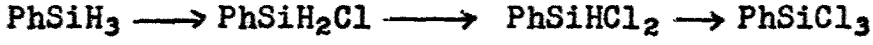
One of the approaches to the preparation of the starting compound is as follows:



Among products isolated from this particular reaction was tetraphenylethylene, $Ph_2C{=}CPh_2$. When the reaction was carried out in the presence of dry air, good yields of benzophenone were obtained. Other related studies involved (1) dehydrohalogenation, and (2) dehydration for the possible introduction of an unsaturated-like system.

V. Stepwise Conversion of Si-H to Si-Cl

Preferential reactions involving polyfunctional groups are helpful in arriving at new types, cyclic or linear. With this in mind, we have developed some procedures for the stepwise replacement of hydrogen attached to silicon by chlorine. The reagent currently used for this purpose is phosphorus pentachloride, and a selected illustration is the following:



VI. Cyclic Organosilicon Compounds Containing both Silicon and Carbon in the Ring.

(1) 2,5,8-Trimethyl-5,10-Dihydrophenazasiline Derivatives

The successful application of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline ("5,10,10") as a high-temperature antioxidant suggested the synthesis of related types. An earlier procedure developed by us suffers because the required 2,2'-dibromodiarylamines are difficult to prepare and because N-alkylation was only accomplished by reacting the corresponding N-lithio intermediate with alkyl sulfates in refluxing tetrahydrofuran. A simple procedure

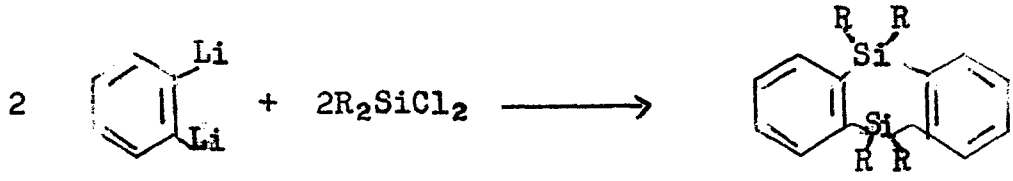
for the homologous and more accessible di-p-tolylamine derivatives involves treatment of a glacial acetic acid solution of N-methyldi-p-tolylamine with two molar equivalents of bromine to give N-methyl-2,2'-dibromodi-p-tolylamine. This compound was then converted by the halogen-metal interconversion reaction to the corresponding dilithio compound, which on treatment with dichlorodiphenylsilane gave 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline. Thus, a 5,10-dihydrophenazasiline derivative has been synthesized quite straightforwardly by a simple bromination reaction and cyclization reaction.

(2) Bromination of "5,10,10".

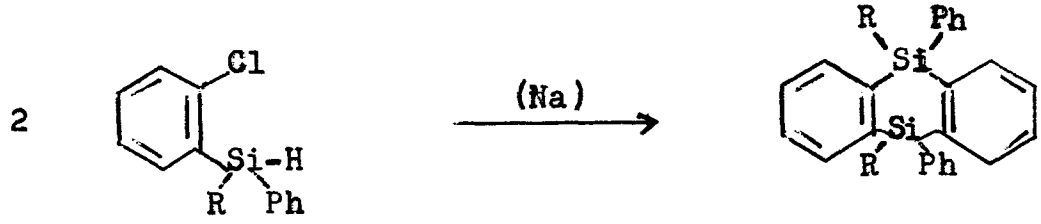
A somewhat direct approach to new derivatives of "5,10,10" would be the introduction of functional and reactive nuclear substituents. Despite the generally ready cleavage of a C-Si bond by bromine, it was possible to brominate "5,10,10" and introduce two nuclear bromines symmetrically to give 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline.

(3) 5,10-Dihydrosilanthrene Derivatives.

The 5,10-dihydrosilanthrene compounds, a new cyclic organosilicon system chosen from several to be included in this report, are silicon analogs of 9,10-dihydroanthracene. They were first prepared by us by the following general procedure:



A new sequence has been developed which involves intermolecular Wurtz-type coupling reactions

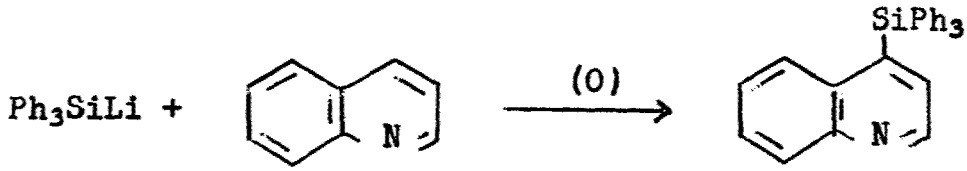


This expands significantly the versatility of the synthesis to permit the introduction of a wide variety of groups which generally impart added thermal stability to organosilicon compounds.

VII. Triphenyl-4-quinolylsilane.

Among the radicals which might be expected to improve

thermal stabilities of organosilicon compounds are heterocycles containing nitrogen, such as the pyridyl and quinolyl groups. We earlier reported the synthesis of triphenyl-4-pyridylsilane, and at that time had no success in the preparation of the quinoline analog. We have now succeeded in synthesizing triphenyl-4-quinolylsilane. The reaction used was the addition of triphenylsilyllithium to quinoline followed by nitrobenzene oxidation of the intermediate dihydro compound.



It is interesting to note that addition involves the 4-position and not the 2-position.

SYNTHESIS OF ORGANOTIN POLYMERS BY POLY-ADDITION

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The results of a synthetic program directed towards the preparation of IVth main group organometallic polymers are presented.

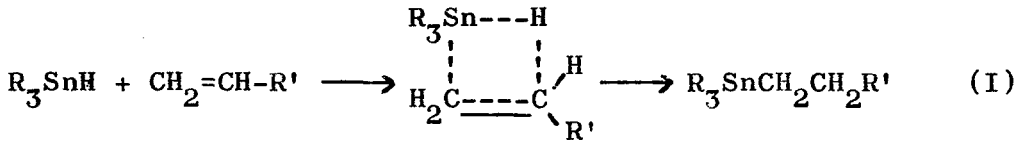
The main body of the report is concerned with the synthesis of linear polymers having a carbon chain regularly interrupted by tin (and in some cases other IVth group) atoms. Such polymers have been obtained by means of true poly-addition reactions (hydrogen transfer polymerization) involving an organotin dihydride and either a dienic or a diynic or a monoynic coumpound.

The synthesis of IVth group organometal-substituted polystyrenes -carbon chain polymers containing the organometallic moiety as a substituent group -as well as of a series of poly-p-phenylenesilanes—polymers consisting of chains of p-phenylene groups connected by dialkyl(aryl) silane groups- are dealt with briefly.

I. ORGANOTIN POLY-ADDITION POLYMERS

In recent years at our Institute much attention had been paid to the formation of tin-carbon bonds by the reaction of organotin hydrides with carbon-carbon unsaturated compounds[1-4]. When our organometallic polymer program was initiated it was decided to apply this reaction principle to the synthesis of organotin polymers. Aspects of the chemistry of organotin hydrides related to the possibility of preparing polymers have been discussed at the 1959 Polymer Branch Contractors' Conference[5]. Some points will be recalled briefly as this will lead to a better appreciation of the scope of the polymer-forming reaction.

Adducts are formed upon reaction of triorganotin monohydrides with a variety of monosubstituted terminal olefins[2,3]:



$$R_3SnH + CH_2{=}CH{-}R' \longrightarrow \begin{matrix} R_3Sn\text{---}H \\ \vdots \quad\quad \vdots \\ H_2C\text{----}C \end{matrix}\begin{matrix} H \\ \diagup \\ \\ \diagdown \\ R' \end{matrix} \longrightarrow R_3SnCH_2CH_2R' \qquad (I)$$

Reactions involving triphenyltin hydride proceed smoothly at moderate temperatures (70-100°). Both the reaction time (usually a few hours, sometimes as short as few minutes) and the yield (generally high, in some cases quantitative) depend on the substituent R'. Trialkyltin hydrides react slower and only if the olefinic bond is activated sufficiently by R' (e.g. when R' represents an aryl group).

Where investigated (e.g. n-octene, acrylonitrile, styrene) the organotin group was found to have added to the terminal olefinic carbon atom. Whereas polar effects influence the rate of the reaction, steric factors mainly determine its course. Terminal addition seems to be the rule.

With the exception of certain reactions of alkyltin hydrides for which very recently peroxide catalysis has been applied[6], these reactions proceed in the absence of any added catalyst. Similar reactions of carbon or silicon hydrides require among others peroxide catalysts or U.V.light or high temperatures. These circumstances promote homopolymerization of reactive olefins. Owing to the much greater reactivity of organotin hydrides reaction conditions minimizing this unwanted reaction may be selected. It can be eliminated completely by using an inhibitor like hydroquinone. This is clearly of importance for the realization of the reaction on a polymeric level.

Similar reactions have been realized using acetylenic derivatives as the unsaturated partner[3]:

$$R_3SnH + HC{\equiv}C\text{-}R' \longrightarrow \begin{matrix} R_3Sn & & H \\ & C{=}C & \\ H & & R' \end{matrix} \xrightarrow{R_3SnH} R_3SnCH_2CHR'SnR_3 \qquad \text{(II)}$$

However, the reactivity of organotin hydrides towards carbon-carbon triple bonds is much higher than towards olefinic double bonds. Mostly, these reactions proceed exothermally in the absence of any added catalyst. Consequently, when applying one mole of a monohydride per mole of a monoacetylenic compound, only the olefinic adduct is being formed. Similarly, when applying two moles of a monohydride, two separate reaction steps can be distinguished, the second one requiring more severe conditions.

Considering the foregoing, the possibility of applying this reaction principle to the synthesis of polymers is evident.

A. Upon reaction of an organotin dihydride with an appropriate diolefine (preferably an α,ω-diene) linear polymers are being formed under incorporation of organotin groups in the main chain[7]:

$$\begin{matrix} R \\ | \\ H\text{-}Sn\text{-}H \\ | \\ R \end{matrix} + CH_2{=}CH\text{-}R'\text{-}CH{=}CH_2 \longrightarrow \left[\begin{matrix} R \\ | \\ -Sn-CH_2CH_2-R'-CH_2CH_2- \\ | \\ R \end{matrix} \right]_n \qquad \text{(III)}$$

Optimal conditions for polymer-formation have been determined for each combination of R and R' by studying both the model reactions, viz. between dihydride and mono-olefine and between monohydride and diolefine (see e.g. ref.[7]):

$$R'\text{-}CH{=}CH_2 + \begin{matrix} R \\ | \\ H\text{-}Sn\text{-}H \\ | \\ R \end{matrix} + CH_2{=}CH\text{-}R' \longrightarrow R'CH_2CH_2\overset{\overset{R}{|}}{Sn}CH_2CH_2R' \qquad \text{(IV)}$$

$$R_3SnH + CH_2{=}CH\text{-}R'\text{-}CH{=}CH_2 + HSnR_3 \longrightarrow R_3SnCH_2CH_2R'CH_2CH_2SnR_3 \qquad (V)$$

B. Starting from acetylenic compounds as the unsaturated reaction partner, and making use of the earlier mentioned marked difference in reactivity of the organotin hydride towards double and triple bonds, two different routes leading to polymers can be followed[8]:

1. Reaction of an α,ω-diyne with an organotin dihydride in a 1:1 ratio under very mild conditions will result in the formation of a linear polymer. In this case the reaction ends after conversion of the triple bonds into double bonds:

$$\begin{matrix} R \\ | \\ H\text{-}Sn\text{-}H \\ | \\ R \end{matrix} + HC{\equiv}C\text{-}R'\text{-}C{\equiv}CH \longrightarrow \left[\begin{matrix} R \\ | \\ -Sn\text{-}CH{=}CH\text{-}R'\text{-}CH{=}CH- \\ | \\ R \end{matrix} \right]_n \qquad (VI)$$

2. Reaction of a monoacetylenic compound with an organotin dihydride again in an exactly 1:1 ratio will proceed in two steps, viz. formation of an olefinic organotin monohydride and subsequently, at higher temperature, homopoly-addition of this monomer:

$$\begin{matrix} R \\ | \\ H\text{-}Sn\text{-}H \\ | \\ R \end{matrix} + HC{\equiv}C\text{-}R' \longrightarrow \begin{matrix} R \\ | \\ H\text{-}Sn\text{-}CH{=}CH\text{-}R' \\ | \\ R \end{matrix} \longrightarrow \left[\begin{matrix} R & R' \\ | & | \\ -SnCH_2CH- \\ | \\ R \end{matrix} \right]_n \qquad (VII)$$

Two molecules of the 1:1 addition intermediate can form a six-membered cyclic dimer with the two tin atoms in 1,4-position. As appears from an absorption peak at 988 cm^{-1}, originating from the C-H bending vibration of trans-disubstituted ethylene groups, the olefinic intermediate has the trans structure, its formation presumably being promoted by steric factors. The trans structure, in its turn, favours the formation of the distannacyclohexane system. This reaction course has been observed upon reaction of diphenyltin dihydride with phenylacetylene[9].

Dienic or diynic compounds having the two unsaturated groups in a sterically favourable position have also been found to yield cyclic oligomers in addition to linear polymers:
Reaction of diphenyltin dihydride with divinyl organometallic derivatives yields the bimetallic cyclohexane analogues (cyclic monomers) as the main product[9]:

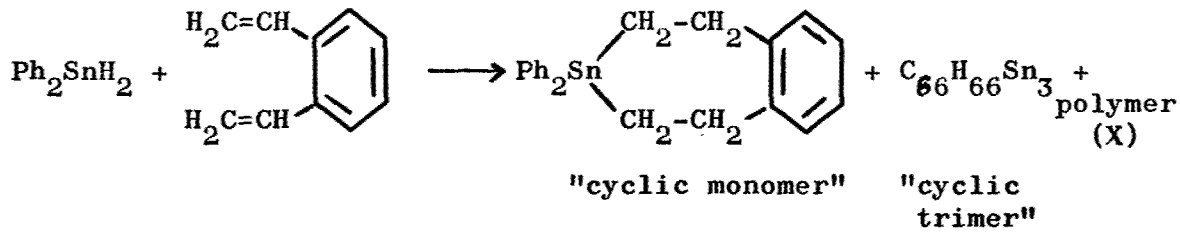
$$Ph_2SnH_2 + \begin{matrix} H_2C{=}CH \\ \diagdown \\ M^{IV}Ph_2 \\ \diagup \\ H_2C{=}CH \end{matrix} \longrightarrow Ph_2Sn \begin{matrix} \diagup CH_2\text{-}CH_2 \diagdown \\ \\ \diagdown CH_2\text{-}CH_2 \diagup \end{matrix} M^{IV}Ph_2 \qquad (VIII)$$

Reaction of organotin dihydrides with hexadiyne-1,5 in addition to the expected polymers yields 1-stannacycloheptadiene-2,5 derivatives (cyclic monomers) in 12-28% yield[8]:

$$R_2SnH_2 + \begin{matrix} HC{\equiv}C \\ \diagdown \\ (CH_2)_2 \\ \diagup \\ HC{\equiv}C \end{matrix} \longrightarrow R_2Sn \begin{matrix} \diagup CH{=}CH \diagdown \\ \\ \diagdown CH{=}CH \diagup \end{matrix} (CH_2)_2 \qquad (IX)$$

(R = Ph, Me, Et, Pr, Bu)

Reaction of diphenyltin dihydride with o-divinyl benzene in addition to polymer (70%) affords the cyclic monomer (M.p. 98-100°C; 16% yield) and the 21-membered cyclic trimer (M.p. 277-280°; 14% yield), both having been characterized by analysis, infrared spectrum and molecular weight:



The basic reaction underlying the polymer-forming interactions just discussed is an example of a true poly-addition reaction (hydrogen transfer polymerization). The close resemblance to the formation of polyurethane from diols and diisocyanates is evident. In our case an active hydrogen atom bound to tin reacts with a carbon-carbon double or triple bond; in the other process an active hydrogen of a hydroxyl group reacts with a carbon-nitrogen double bond of an isocyanate.

The polymer-forming reactions were carried out under nitrogen in order to eliminate oxidative degradation of the organotin hydrides. Low reaction temperatures (60-110°) were employed in order to prevent disproportionation of the dihydrides leading to mono- and trifunctional hydrides which would act as chain-stopping and cross-linking agents respectively. In reactions involving acetylenic reactants a solvent was applied in the first stage in order to warrant its smooth course. Ultimately, the resulting polymeric products were heated in vacuo.

The progress of the reaction can be determined very easily by I.R. absorption measurements. The disappearance of the characteristic Sn-H stretching vibration in the 1800-1840 cm^{-1} region (5.5μ)[10], together, of course, with the disappearance of vibrations connected with the presence of olefinic or acetylenic unsaturation, is the most clear-cut indication that the reaction has gone to completion. Absence of these vibrations in the I.R.spectra of low molecular weight products reveals their cyclic nature. The phenyl-substituted compounds and polymers, containing both germanium and tin, or both lead and tin, display in their infrared spectra distinctive perturbed phenyl vibrational absorptions[11], the relative intensities of which are indicative of the ratio in which these elements are present[7].

The polymers obtained have been characterized by analysis, infrared spectroscopy, solubility, polymer melt temperature and in some cases by weight-average molecular weight (ultracentrifuge measurements[12]) or thermogravimetric analysis.

A survey of the combinations of reaction partners investigated is presented below.

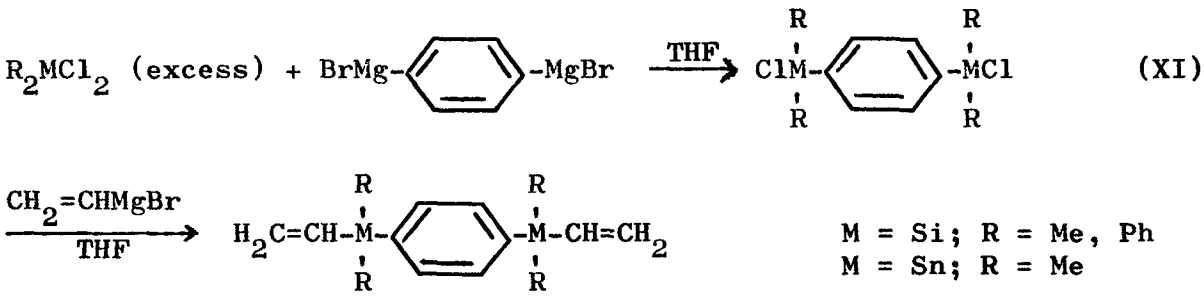
A. Polymers from reactions of organotin dihydrides and dienic compounds

A number of reactive aliphatic dienic compounds (glycol diacrylate, glycol dimethacrylate, methacrylic anhydride and allyl methacrylate)

yielded polymeric products ranging from hard, brittle or tough solids to viscous oils. These products which are likely to contain cyclic oligomers have not been characterized in any detail. Some were slightly cross-linked as a result of the occurrence of vinyl-type polymerization.

Reactions with cyclopentadiene afforded the 1:1 adducts only, the reactivity of its double bond apparently being insufficient for poly--addition to occur.

Reactions with divinyl organometallics resulted mainly in cyclization reactions[9]. With this in mind, we synthesized some divinyl derivatives of a novel type:

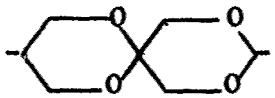
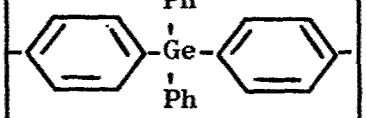
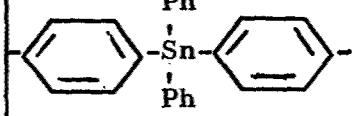
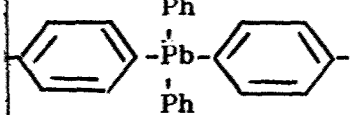


These, owing to the presence of the 1,4-phenylene group, were expected to yield linear polymers upon reaction with organotin dihydrides. However, reaction of these compounds with triphenyltin hydride, although affording the expected products, was attended by some decomposition. Reaction with diphenyltin dihydride did not produce products with any appreciable molecular weight, considerable evolution of gas and formation of metallic tin being observed. Apparently the p-phenylene divinyl derivatives are susceptible to the reducing action of the organotin hydrides.

In Table I poly-addition polymers are summarized which have been obtained from 1,4-divinylbenzene, 3,9-divinylspirobi (meta-dioxane) as well as from di-p-styrenyl-substituted derivatives of germanium, tin and lead[7]. The position of the vinyl groups in these dienes sterically disfavors ring-formation.

TABLE I

Polymers from R_2SnH_2 and $CH_2=CHR'CH=CH_2$ (Equation III)

R	R'	Appearance of polymer	T melt (^oC)	Solubility	$\bar{M}_w$
Ph		glasslike	75	C_6H_6, $CHCl_3$	33,000[a]
Pr	id.	rubbery, tacky		id.	
Ph		glasslike	90	id.	19,000
Ph		hard, brittle	110	id.	27,000
Pr	id.	tough solid	240	C_6H_6 (slightly)	
Ph,Pr[b]	id.	hard $\xrightarrow{120^o}$ rubbery		id.	
Ph		hard, brittle	100	C_6H_6, $CHCl_3$	48,000
Pr	id.	tough $\xrightarrow{130^o}$ rubbery		swells in C_6H_6	
Bu	id.	hard, tough		id.	
Ph,Pr[b]	id.	glasslike	130	C_6H_6	
Ph		glasslike	70	C_6H_6, $CHCl_3$	14,000
Pr	id.	tough $\xrightarrow{90^o}$ rubbery		C_6H_6 (slightly)	

[a] Osmometric measurement ($\bar{M}_n$)

[b] Equimolar mixture of Ph_2SnH_2 and Pr_2SnH_2

These polymers after reprecipitation from benzene showed the correct analysis indicating that these were indeed true 1:1 poly-addition products and that vinyl-type polymerization was negligible under the reaction conditions employed.

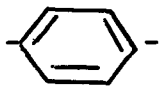
In general polymer melt temperatures are quite low. Interchain forces will be rather weak, because of lack of hydrogen bonding. Moreover, the relatively large metal atoms and their bulky substituents will hamper Van der Waals interaction and crystallization.

B. Polymers from organotin dihydrides and acetylenic compounds

1. Organotin dihydrides have been reacted with hexadiyne-1,5, nonadiyne-1,8 and 1,4-diethynylbenzene. The resulting polymers, ranging from rubberlike, elastic solids to viscous oils, are summarized in Table II.

TABLE II

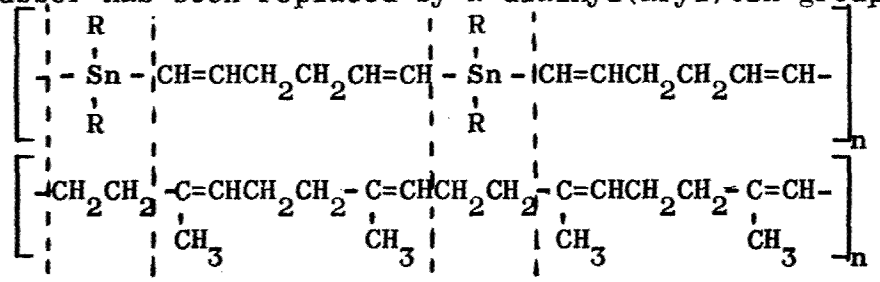
Polymers from R_2SnH_2 and $HC{\equiv}CR'C{\equiv}CH$ (Equation VI)

R	R'	Appearance of polymer[a]	Soluble in[a]	$\bar{M}_w$	Cyclic monomer formed
Ph	$-(CH_2)_2-$	rubberlike, completely resilient	C_6H_6 (partly)	75,000	yes
Me	id.	rubbery solid	crosslinked swells in C_6H_6	-	id.
Et	id.	id.	id.	-	id.
Pr	id.	soft, slightly elastic, viscous flow	C_6H_6	50,000	id.
Bu	id.	id.	id.	50,000	id.
Ph	$-(CH_2)_5-$	soft, tacky viscous flow	C_6H_6, $CHCl_3$	100,000	no
Bu	id.	viscous oil	id.	45,000	id.
Ph		solid $\xrightarrow{160^\circ}$ rubbery	C_6H_6	65,000	id.

[a] After heating in vacuo

No well-defined polymers could be isolated from the reaction of organotin dihydrides and certain pentadiyne-1,4 derivatives (R' = -CHOH- and -CPhOH-).

Polymers obtained from hexadiyne-1,5 were freed from the cyclic monomer by heating in high vacuum (150-250° at 10^{-3} mm.Hg). These polymers show some structural resemblance to natural rubber. Apart from the presence of methyl groups, every second $-CH_2CH_2-$ group in natural rubber has been replaced by a dialkyl(aryl)tin group:



(XII)

Replacement of the ethylene group in this type of organotin polymer by the pentamethylene group results in the loss of the rubberlike properties. The polymer derived from 1,4-diethynylbenzene, having much greater chain rigidity, is solid.

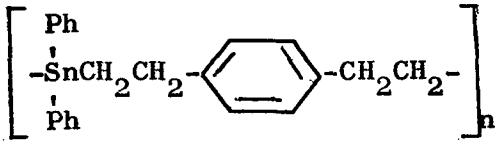
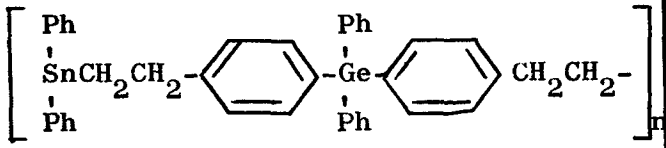
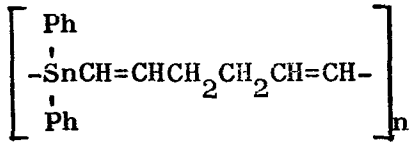
As might be expected, the molecular weights of the poly-addition polymers obtained from diynes are appreciably higher than those of the polymers obtained from dienes.

2. Organotin dihydrides (R = Pr, Bu, Ph) have been reacted with phenylacetylene (R' = Ph) (Equation VII)[8]. Benzene-soluble polymeric products with the expected composition were formed, these products ranging from very viscous oils (R = Pr, Bu) to a hard, brittle solid with m.p. ca. 80° (R = Ph). In the latter case isolation of the cyclic dimer in crystalline form was successfully carried out[9]. No attempts have been made to separate cyclic oligomers from the two liquid polymers which were found to have a rather low average molecular weight (R = Pr, $\bar{M}_w$ = 3,400, n = 11).

The results of thermogravimetric tests on some poly-addition polymers (Chevenard thermobalance, N_2 atmosphere, heating rate 2.5° per min.) are presented in Table III. Temperature at which 5 and 50% weight-loss has occurred ($T_{5\%}$ and $T_{50\%}$), residual weight at 900° (RW) and the percentage of inorganic elements in the original polymer are given.

TABLE III

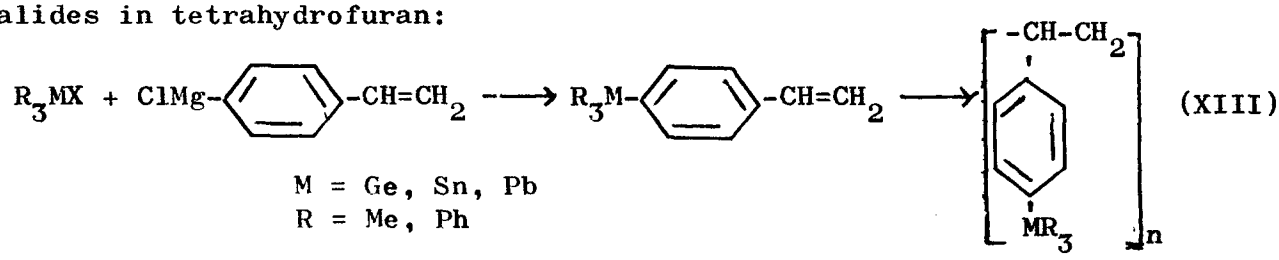
Thermogravimetric analysis of some IVth group metal polymers

Polymer	$T_{5\%}$	$T_{50\%}$	RW %	% inorg. elements
	300	385	28	29.3
	325	460	30	27.1
	280	355	27	33.6

II. IVth GROUP ORGANOMETALLIC DERIVATIVES OF STYRENE AND α-METHYLSTYRENE

Current interest in organometallic monomers suitable for vinyl-type polymerization led us to synthesize a number of IVth group organometallic derivatives of styrene and α-methylstyrene and to study their polymerization[13,14].

The triphenylmono-, diphenyldi- and the trimethylmono-p-styrenyl derivatives of germanium, tin, and lead were obtained by interaction of p-vinylphenylmagnesium chloride[15] with the appropriate organometallic halides in tetrahydrofuran:



(XIII)

M = Ge, Sn, Pb
R = Me, Ph

Whereas triphenyl-p-styrenylsilane, due to steric factors cannot be obtained in this way, the trimethylsilyl derivative was readily formed.

Similar reactions involving p-isopropenylmagnesiumchloride afforded organometal-substituted α-methyl-styrenes[14].

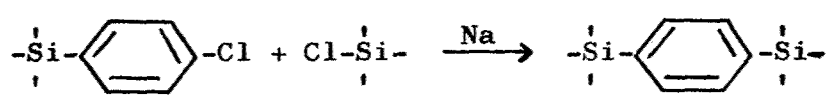
The styrene monomers are readily polymerized, thermally or using peroxide catalysis, to afford solid, transparent products with an appreciable metal content (e.g. poly-trimethyl-p-styrenyllead contains 58.2% by weight of lead).

A rather interesting dependency was found to exist between the nature of the metal atom and the polymerization velocity. A quantitative study (including the carbon analogue p.tert.butylstyrene) revealed the sequence Pb > Si > C > Ge > Sn[14]. Homolytic cleavage of lead-carbon bonds during polymerization, providing a source of extra chain-initiating radicals and resulting in a crosslinked product, is probably responsible for the greater rate of polymerization of the styrenyllead monomer. The sequence Si > C > Ge > Sn is best related to a decreasing electron-attracting effect of the organometallic substituents. It might be that for silicon electron--attraction as a result of d_{π}-p_{π} interaction with the styrenyl group surpasses the effect of electronegativity which decreases in the order C, Si, Ge, Sn. Korshak et al.[16] have found a similar sequence Si > C > Ge > Sn for the polymerization of vinyl-substituted organometallics. The thermal stability of these carbon chain polymers is determined by the temperature at which the depolymerization reaction starts, e.g. for poly--p-trimethylgermylstyrene (when heated at a rate of 2.5° per min.) at 325°, zero residual weight being attained at 440°.

III. POLY-p-PHENYLENESILANES

Silicon-aryl bonds are quite stable towards heat and oxidation. Polymers consisting of chains of p-phenylene groups, connected by organosilyl groups might be expected to have good thermal stability. Moreover, these polymers because of their inherent chain rigidity may be expected to have better crystalline properties than the poly-addition polymers mentioned in Section I. The latter have an amorphous structure as appeared from X-ray data and this was reflected in their low melting temperatures.

The feasibility of obtaining poly-p-phenylene silanes by Wurtz-type condensation reactions involving appropriate combinations of p-chlorophenyl- and chlorosilanes has been studied:



(XIV)

Model reactions involving combinations of monofunctional with mono- or difunctional reactants were carried out in order to find suitable reaction conditions. Using refluxing toluene as the solvent and sodium sand as the condensing agent, products with the expected composition were isolated in satisfactory yields. Some oligomeric compounds obtained analytically pure are summarized in Table IV.

TABLE IV

Synthesis of some oligomeric p-phenylenesilanes

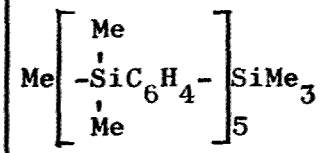
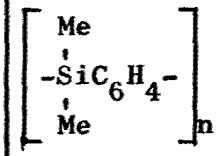
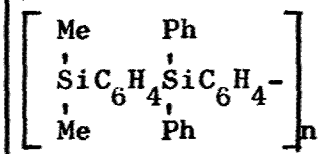
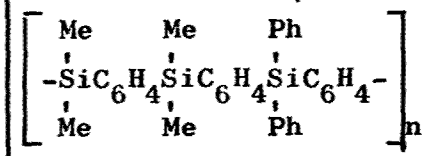
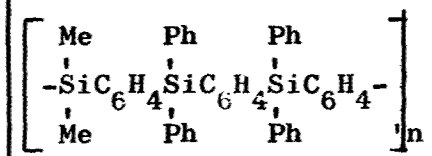
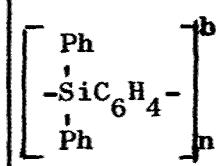
Reaction	Product	M.p.
$Me_3SiCl + Me_3SiC_6H_4Cl$	$Me_3SiC_6H_4SiMe_3$	94-96
$Me_2SiCl_2 + 2\ Me_3SiC_6H_4Cl$	$Me_3Si(C_6H_4SiMe_2)_2Me$	78-81
$ClMe_2SiC_6H_4SiMe_2Cl + 2\ Me_3SiC_6H_4Cl$	$Me_3Si(C_6H_4SiMe_2)_3Me$	131-133
$Me_2SiCl_2 + 2\ Me_3SiC_6H_4SiMe_2C_6H_4Cl$[a]	$Me_3Si(C_6H_4SiMe_2)_4Me$	170-173
$ClMe_2SiC_6H_4SiMe_2Cl +$ $2\ Me_3SiC_6H_4SiMe_2C_6H_4Cl$[a]	$Me_3Si(C_6H_4SiMe_2)_5Me$	187-191
$Ph_3SiCl + Ph_3SiC_6H_4Cl$	$Ph_3SiC_6H_4SiPh_3$	337-341
$Ph_2SiCl_2 + 2\ Ph_3SiC_6H_4Cl$	$Ph_3Si(C_6H_4SiPh_2)_2Ph$	365-368
$ClMe_2SiC_6H_4SiMe_2Cl + 2\ Ph_3SiC_6H_4Cl$	$Ph_3Si(C_6H_4SiMe_2)_2C_6H_4SiPh_3$	220-222

[a] Obtained via: $Me_3SiC_6H_4MgCl + ClSiMe_2C_6H_4Cl$

Similar reactions involving difunctional reactants afforded polymeric products identified by analysis and infrared spectrum (comparison with model compounds) as poly-p-phenylenesilanes. Solubility of these polymers in aromatic solvents allowed removal of the lowest molecular weight products by fractional precipitation. In Table V melting point (temperature at which softening starts and at which a clear melt is obtained), number average molecular weight (ebullioscopic in benzene) and the results of thermogravimetric analyses for some of the poly-p-phenylene silanes isolated are presented.

TABLE V

Synthesis of some poly-p.phenylene silanes

Polymer	M.p.(°C)	$\bar{M}_n$	Weight loss (%) at (°C)				
			400	450	500	600	900
	187-191	759[a]	15	55	80	85	86
	200-225	3800	-	2	22	56	58
	155-170	2400	2	9	16	49	53
	190-210	2900	1	7	30	47	47
	215-245	2600	-	-	1	44	46
	>360	-	2	5	20	30	35
id.[c]	235-260	2100	5	7	30	58	59

[a] Theoretical value; [b] benzene-insoluble fraction;

[c] benzene-soluble fraction

Molecular weight determination by means of end-group analysis (determination of residual chlorine by Parr bomb fusion followed by electrometric titration) gave values five to ten times those found by the ebullioscopic method, the chlorine contents being unexpectedly low. The poly-p-phenylene silanes prepared so far contain on the average only 10-30 p-phenylene groups per molecule. The attainment of high molecular weights is hampered by the limited solubility of this type of polymer in the common organic solvents causing its precipitation from the reaction medium. The choice of toluene -one of the best solvents for this type of

polymer- as the reaction solvent has the disadvantage that it cannot be considered inert with respect to the polymer-forming reactions. It is known that toluene undergoes metallation by reactive organosodium compounds with the formation of benzylsodium. When it is assumed that the polycondensation involves the intermediate formation of organosodium derivatives, reaction with the solvent, i.c. toluene, instead of with a chlorosilyl group will result in chain termination by each of the two following reactions:

$$-\overset{|}{\underset{|}{Si}}C_6H_4Cl \xrightarrow{Na} \left[-\overset{|}{\underset{|}{Si}}C_6H_4Na\right] + PhCH_3 \longrightarrow -\overset{|}{\underset{|}{Si}}C_6H_5 + PhCH_2Na$$

$$-\overset{|}{\underset{|}{Si}}Cl + PhCH_2Na \longrightarrow -\overset{|}{\underset{|}{Si}}CH_2Ph + NaCl \qquad (XV)$$

Thus, instead of p-chlorophenyl and chlorosilyl end-groups the polymer would contain phenyl- and benzyl-silicon end-groups. This mechanism of termination which would seem to prevent the attainment of appreciable molecular weights finds support in the actually observed low residual chlorine content of the fractions isolated.

The high thermal stability of fully alkylated or arylated silanes is reflected in that of the polymeric silanes. All polymer samples investigated remain perfectly stable during the initial heating period, then undergo rapid degradation over a narrow temperature range to give a stabilized residue of high thermal stability still containing an appreciable percentage of residual carbon.

ACKNOWLEDGMENT

Our thanks are due to Mr.H.A.Budding for his skillful contribution to this program.

The cooperation of Dr.G.F.L.Ehlers (WADD Nonmetallic Materials Laboratory) who made the TGA curves available to us, is gratefully acknowledged.

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ORGANOMETALLIC COMPOUNDS OF GROUP III, IV, AND V

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ABSTRACT

The preparation and reactions of a number of organometallic compounds has been studied. The organolithium compounds under investigation are Ph_2CHLi, Ph_3CLi, Ph_3SnLi, Ph_3GeLi, Ph_3PbLi, Ph_2PLi and Ph_2NLi. Also included in this series is Ph_2NNa. The reactions of these organometallics with various compounds as carbon dioxide, water, alkyl halides, aryl halides, aralkyl halides, metallic halides and esters has been studied.

A research program has recently been initiated on organometallic chemistry of certain elements of group III, IV and V of the periodic table. This program has two objectives; the first is the synthesis and evaluation of physical and chemical properties of a class of perarylated compounds indicated by the general structure RnMM'Rn. In most cases, R is a phenyl group (Ph); M or M' is either B, Al, C, Si, Ge, Sn, Pb, P and N; M = or $\neq$ M' and n is either 2 or 3 depending on the valence of M. The second objective, which is the subject of this report, is the study of the synthesis and reactions of the intermediate organometallics (R_nM-metal) necessary for the preparation of the perarylated $R_nMM'R_n$ compounds.

A series of compounds possessing various combinations of elements, $R_nMM'R_n$, will offer a convenient manner of studying some chemical reactions as, for example, hydrolysis and oxidation on simple structures. The preparation of compounds containing M-M' bonds can be accomplished by various means. The following examples illustrate a few of the various methods which have been reported in the literature.

Symmetrical Ph_3M-$M'Ph_3$

$$2Ph_3CCl + Zn \longrightarrow Ph_3C\text{-}CPh_3 + ZnCl_2 \quad (1)$$
$$2Ph_3SiCl + 2Na \longrightarrow Ph_3SiSiPh_3 + 2NaCl \quad (2)$$
$$2Ph_3SiCl + Mg \longrightarrow Ph_3SiSiPh_3 + MgCl \quad (3)$$
$$3PbCl_2 + 6PhMgX \longrightarrow Ph_3PbPbPh_3 + 6MgCl + Pb \quad (4)$$
$$3PbCl_2 + 6PhLi \longrightarrow Ph_3PbPbPh_3 + 6LiCl + Pb \quad (5)$$
$$PhMgX(\text{large excess}) + GeCl_4 \longrightarrow Ph_3GeGePh_3 \quad (6)$$
$$2Ph_2PCl + 2Na \longrightarrow Ph_2P\text{-}PPh_2 + NaCl \quad (7)$$

Unsymmetrical $Ph_3MM'Ph_3$

The unsymmetrical $Ph_3MM'Ph_3$ compounds require a two-step process. This involves the preparation of an intermediate organometallic, Ph_nM-metal, which is then further reacted with a $Ph_nM'X$ compound to yield the desired unsymmetrical product. The preparation of the intermediate Ph_nM-metal has been studied quite extensively. A few specific examples for its preparation reported in the literature are the following:

$$Ph_3CCl + 2Li \xrightarrow{THF} Ph_3CLi + LiCl \quad (8)$$

$$Ph_3CH + NaNH_2 \xrightarrow{NH_3} Ph_3CNa + NH_3 \quad (9)$$

$$Ph_3SiCl + 2Li \xrightarrow{THF} Ph_3SiLi + LiCl \quad (10)$$

$$Ph_3GeH + Na \xrightarrow{NH_3} Ph_3GeNa + 1/2H_2 \quad (11)$$

$$Ph_2Sn + PhLi \longrightarrow Ph_3SnLi \quad (12)$$

$$Ph_4Pb + Na \xrightarrow{NH_3} Ph_3PbNa + PhH + NaNH_2 \quad (13)$$

$$Ph_3SiSiPh_3 + 2Li \xrightarrow{THF} 2Ph_3SiLi \quad (14)$$

The subsequent reaction of the intermediate Ph_nM-metal with an arylmetallic halide $Ph_nM'X$ has been studied extensively by Gilman (1) in a series of six publications.

$$Ph_nM\text{-metal} + Ph_nM'X \quad Ph_nMM'Ph_n + \text{metal halide} \quad (15)$$

Most of the above reactions (1 through 15) are not of a general nature which can be applied to all the elements of interest in groups III, IV and V. A reaction which is successful for the tin compound may not necessarily work for the lead analog. Gilman (2) has however indicated that the reaction reported in equation 10 may be of a general nature and applicable for other metals or metalloids.

In our studies on the synthesis of M-M' compounds, essentially three different methods thus far have been used to synthesize the organometallic intermediates.

Direct Method

$$R_nMCl + 2Li \longrightarrow LiCl + R_nMLi \quad (16)$$

Cleavage Method

$$R_nMMR_n + 2Li \longrightarrow 2R_nMLi \quad (17)$$

Metal-Hydrogen Exchange

$$Ph_2NH + C_4H_9Li \longrightarrow C_4H_{10} + Ph_2NLi \quad (18)$$
$$Ph_2NH + NaH \longrightarrow H_2 + Ph_2NNa \quad (19)$$

Each method of synthesis and its reactions will be discussed in greater detail separately.

Direct Method

The direct method of preparing triphenylsilyllithium (Ph_3SiLi) from chlorotriphenylsilane and lithium metal in tetrahydrofuran (THF) was first reported by Gilman (2). Using this procedure, this reaction has now been extended to include the preparation of diphenylmethyllithium, triphenylgermyllithium,

triphenyltinlithium, triphenylleadlithium and diphenylphosphinolithium. The metallic chlorides readily react with lithium in THF to yield the desirable organolithium compounds in good yields. When subjected to Color Test I (3) all the organolithium compounds produced a positive color test indicating the presence of the M-Li bond. This Color Test I was useful in following the course of a reaction to determine the presence or absence of the organometallic reagents. An indication of the yield of organometallic reagent was obtained by derivatization with benzyl chloride. The values obtained in all cases do not indicate the true yields of the organometallic reagent since no attempt was made at maximizing yields. The benzyl derivatives as shown in Table I were characterized by mixture melting point determinations and comparison of the infrared curves with benzyl derivatives which were synthesized by an alternate route as shown in equation 20.

$$Ph_nMCl + C_6H_5CH_2MgCl \longrightarrow MgCl_2 + Ph_nMCH_2C_6H_5 \qquad (20)$$

TABLE I

$Ph_nM^{n+1}Li$	Benzyl Derivative	M.P. [e]	% Yield
Ph_3CLi [a]	Ph_3CCH_2Ph	143.5-145	67
---	Ph_3CCH_2Ph [c]	141.0-142.0	75
Ph_3SiLi [a]	Ph_3SiCH_2Ph	98.5-99.5	39
---	Ph_3SiCH_2Ph [c]	96.0-97.0	65
Ph_3GeLi [a]	Ph_3GeCH_2Ph	85.0-86.5	60
Ph_3GeLi [b]	Ph_3GeCH_2Ph	85.0-87.0	75
Ph_3SnLi [a]	Ph_3SnCH_2Ph	90.0-91.0	77
Ph_3SnLi [b]	Ph_3SnCH_2Ph	91.0-92.0	72
---	Ph_3SnCH_2Ph [c]	91.0-92.0	80
Ph_3PbLi [a]	Ph_3PbCH_2Ph	95.0-96.0	76
Ph_3PbLi [b]	Ph_3PbCH_2Ph	95.0-97.0	87
---	Ph_3PbCH_2Ph [c]	94.0-95.0	67
Ph_2PLi [a]	$Ph_2P(O)CH_2Ph$ [d]	193.0-194.0	80
Ph_2PLi [b]	$Ph_2P(O)CH_2Ph$	193-194	83
---	$Ph_2P(O)CH_2Ph$ [c]	192.0-193.5	64

(a) Prepared by the direct method. (b) Prepared by cleavage of Ph_nMMPh_n.
(c) Prepared by the reaction of the benzyl Grignard with the Ph_nMCl.
(d) Benzyl substituted phosphine compounds are easily air oxidized to the phosphine oxide. Since the purification of the benzyl phosphine derivative was done with no precaution to exclude atmospheric oxygen, the phosphine was readily converted to the phosphine oxide. (e) Melting points are uncorrected.

Some other reactions carried out on the individual organolithium compounds are shown in Table II.

TABLE II

	Ph_nMLi	Reactant	Product	% Yield
1.	Ph_3CLi	$(CH_3)_3SiCl$	$Ph_3CSi(CH_3)_3$ +	37
				12
2.	Ph_3CLi	CO_2	Ph_3CCOOH	80
3.	Ph_2CHLi	Ph_3SnCl	$Ph_2CHSnPh_3$	63
4.	Ph_2CHLi	Ph_3SiCl	$Ph_2CHSiPh_3$	81
5.	Ph_2CHLi	Ph_2SiCl_2	$(Ph_2CH)_2SiPh_2$	78
6.	Ph_2CHLi	$PhSiCl_3$	$(Ph_2CH)_3SiPh$	28
7.	Ph_2CHLi	$(CH_3)_3SiCl$	$Ph_2CHSi(CH_3)_3$	66
8.	Ph_2CHLi	CO_2	$Ph_2CHCOOH$	91
9.	Ph_3SnLi	Ph_3SiCl	$Ph_3SnSiPh_3$	ca. 20
10.	Ph_3SnLi	$(CH_3)_3SiCl$	$Ph_3SnSnPh_3$	69
11.	Ph_3SnLi	PhBr	Ph_4Sn	62
12.	Ph_3SnLi	C_2H_5I	$Ph_3SnC_2H_5$	87
13.	Ph_3SnLi	$(C_4H_9O)_3PO$	$Ph_3SnC_4H_9$	70
14.	Ph_3SnLi	CO_2	$Ph_3SnSnPh_3$	85
15.	Ph_3SnLi	H_2O	Ph_3SnH	74
16.	Ph_2PLi	CH_2Cl_2	$Ph_2PCH_2PPh_2$	59

Ph_3CLI and Ph_2CHLi

Triphenylmethyllithium was not used extensively to synthesize Ph_3CMPh_n type compounds because of difficulties encountered in the isolation of the desired product. Tomboulian (4) describes the formation of two different species of organolithium compounds in the direct method preparation of triphenylmethyllithium.

$$Ph_3CCl + 2Li \longrightarrow LiCl + Ph_3CLi \qquad (21)$$

$$2Ph_3CCl + 3Li \longrightarrow Ph_2C\underset{Li}{\langle\!\!\rangle} CPh_3 + 2LiCl \qquad (22)$$

In addition to the formation of two organometallic species, Ph_3CLi undergoes another undesirable side reaction very readily. When Ph_3CLi is derivatized with Ph_nMCl it readily undergoes a metal-halogen interchange.

$$Ph_3CLi + Ph_nMCl \longrightarrow Ph_3CCl + Ph_nMLi \qquad (23)$$

This reaction further complicates the use of Ph_3CLi as an organometallic reagent for the synthesis of M-M' compounds. The other Ph_nMLi organometallics that were studied also undergo metal-halogen interchange, however, to an apparently lesser extent. In addition, in no case was any other product formed indicative of a reaction similar to that shown in equation 22.

Since Ph_3CLi caused many undesirable by products, it was of interest to see if the analogy would be carried over to the Ph_2CHLi organometallic. The diphenylmethyl derivative Ph_3MCPh_2H could also be converted to compounds possessing a $\equiv MC(Ph_2)M' \equiv$ bonding if such structure should become of interest.

$$Ph_2CHLi + Ph_nMCl \quad Ph_nMCPh_2H + LiCl \qquad (24)$$
$$Ph_nMCPh_2H + C_4H_9Li \quad C_4H_{10} + Ph_nMCPh_2Li \qquad (25)$$
$$Ph_nMCPh_2Li + Ph_nM'Cl \quad LiCl + Ph_nMCPh_2M'Ph_n \qquad (26)$$

Diphenylmethyllithium was prepared very readily by use of the direct method. Some of its reaction products are shown in Table II. Unlike triphenylmethyllithium, diphenylmethyllithium does not appear to form side reaction as shown in equation 22 and 23.

Ph_3SnLi

Triphenyltinlithium has been prepared previously and described in literature by Wittig (5).

$$(C_6H_5)_2Sn + C_6H_5Li \longrightarrow (C_6H_5)_3SnLi \qquad (27)$$

Gilman (6) later modified the preparation according to the following reaction.

$$3C_6H_5Li + SnCl_2 \longrightarrow 2LiCl + (C_6H_5)_3SnLi \qquad (28)$$

By use of the direct method of synthesis, Ph_3SnLi can readily be prepared in high yields. It undergoes various reactions as shown in Table II. Unfortunately, it also undergoes metal-halogen interchange when used for the preparation of Ph_3SnMPh_n compounds. The degree of interchange appears to be less than in the Ph_3CLi reactions.

Cleavage Method

In the course of preparing the various organolithium compounds via the direct method, it appeared that an intermediate compound is formed prior to the formation

of the organolithium compound. This assumption is based on the following observations: (1) shortly after the clear THF solution of the chloride is added to the lithium, a white cloudiness appears with most metallic halides (7). At this stage Color Test I is negative. With further reaction the white cloudiness disappears with the formation of a dark colored solution which gives a positive Color Test I; (2) by-product of this reaction usually found in small quantities is the coupled product $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$; (3) the by-product $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ can readily be cleaved by lithium in THF to produce excellent yields of $(C_6H_5)_nM^{n+1}Li$. Gilman (8) and co-workers in the direct preparation of triphenylsilyllithium noted similar observations and proposed the following series of reactions.

$$(C_6H_5)_3SiCl + 2Li \longrightarrow (C_6H_5)_3SiLi + LiCl \quad (29)$$

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiCl \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + LiCl \quad (30)$$

$$(C_6H_5)_3SiSi(C_6H_5)_3 + 2Li \longrightarrow 2(C_6H_5)_3SiLi \quad (31)$$

To verify our observations, hexaphenylditin, hexaphenyldigermanium, hexaphenyldilead and tetraphenylbiphosphine were all subjected to lithium cleavage in THF and produced excellent yields of the organolithium compound. No attempts were made to optimize the yields of the organolithium compounds prepared either by the direct method or the cleavage of the Ph_nMMPh_n compounds. The organolithium reagent was derivatized with benzyl chloride to produce the benzyl derivatives as shown in Table I. The same benzyl derivatives were synthesized by an alternate route (see equation 20) so that mixed melting points and comparisons of their infrared spectra could be made. The various benzyl derivatives were characterized by elemental analysis, mixture melting points and comparison of the infrared curves of each benzyl derivative made by the three synthesis routes.

Of the two methods used for the preparation of the organolithium compounds, the cleavage of Ph_nMMPh_n method offers some advantage in that the starting material can be obtained in a higher degree of purity and the yields are somewhat higher (see Table I). For the preparation of the various Ph_nMLi compounds, it is felt however that either one of these two methods is preferable to those reported in literature (5,6) since only one species of organolithium compound is present and thus offers a cleaner reaction.

Metal-Halogen Exchange

The preparation and reactions of lithium and sodium diphenylamine was studied. These organometallic compounds were prepared by a metal-hydrogen exchange reaction.

$$Ph_2NH + C_4H_9Li \longrightarrow C_4H_{10} + Ph_2NLi \quad (32)$$

$$Ph_2NH + NaH \longrightarrow H_2 + Ph_2NNa \quad (33)$$

The reactions of these organometallics with various halides is shown in Table III.

TABLE III

	Ph_2N	Reactant	Product	Yield
1.	Ph_2NLi	Ph_3CCl	Ph_2NCPh_3 +	70
			Ph_3C–(C$_6$H$_4$)–NHPh	3.2
2.	Ph_2NNa	Ph_3CCl	Ph_2NCPh_3	66
3.	Ph_2NLi	Ph_3SiCl	Ph_2NSiPh_3	68
4.	Ph_2NNa	Ph_3SiCl	Ph_2NSiPh_3	56
5.	Ph_2NLi	Ph_3GeCl	Ph_2NGePh_3	23
6.	Ph_2NNa	Ph_3GeCl	Ph_2NGePh_3	40
7.	Ph_2NLi	Ph_2PCl	Ph_2NPPh_2	58
8.	Ph_2NNa	Ph_2PCl	Ph_2NPPh_2	70

$$Ph_2NNa \text{ or } (Li) + Ph_nMCl \longrightarrow NaCl + Ph_2NMPh_n \qquad (34)$$

In all cases the normal expected product was obtained. In the reaction of Ph_2NLi and Ph_3CCl, however, an additional para isomer was obtained in low yields. Some preliminary acid hydrolysis studies on Ph_3SiNPh_2 have shown that the Si-N bond in such structures is easily cleaved.

$$Ph_3SiNPh_2 + HOH \longrightarrow Ph_3SiOSiPh_3 + Ph_2NH \qquad (35)$$

The properties of the other Ph_nMNPh_2 compounds are presently being investigated.

Attempts to prepare the Ph_3SnNPh_2 compound by reaction 34 has been unsuccessful. Addition of Ph_3SnLi to azobenzene was also unsuccessful.

$$Ph_3SnLi + PhN{=}NPh \longrightarrow Ph_3SnN(Ph)-N(Ph)H \qquad (36)$$

Apparently the Sn-N bond is very hydrolytically unstable.

$$Ph_3SnNPh_2 + HOH \longrightarrow Ph_3SnOSnPh_3 + Ph_2NH \qquad (37)$$

In both reactions that failed to yield a Sn-N compound, one of the reaction products identified was $Ph_3SnOSnPh_3$. The desired product containing the Sn-N bond was apparently cleaved during the work up of the reaction. By use of extremely anhydrous conditions it is believed that the Sn-N compound can be isolated.

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7. The cloudiness which appears is probably due to the low solubility of the intermediate $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ in the quantity of solvent used.

8. D. Wittenberg and H. Gilman, Quart. Rev., 13, 121 (1959).

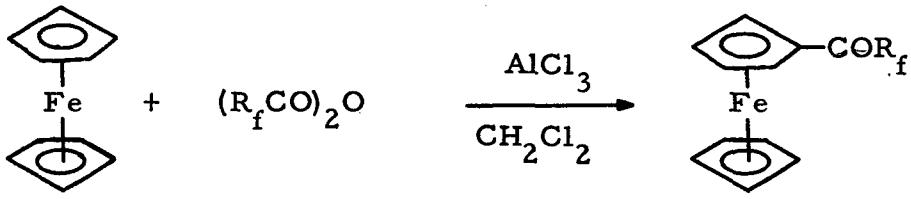
A STUDY OF THE FRIEDEL-CRAFTS ACYLATION OF FERROCENE WITH PERFLUOROCARBOXYLIC ACID DERIVATIVES

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Aeronautical Systems Division

Since the discovery of bis(cyclopentadienyl)iron or ferrocene in 1950 numerous derivatives of this unique organometallic compound have been prepared and their properties studied. In connection with a program involving the synthesis of polymeric derivatives of ferrocene, it was of interest to investigate methods for the preparation of fluorine-containing ferrocene monomers and polymers. Initially this involved the preparation and study of model compounds representative of new types of ferrocenes, such as the hitherto unknown perfluoroalkylferrocenyl ketones, 1,1-dihydroperfluoroalkylferrocenes, and perfluoroalkylferrocenes. In this paper are reported some of the preliminary results obtained in the investigation of synthetic approaches to the perfluoroalkylferrocenyl ketones, C_5H_5Fe-$C_5H_4COR_f$, as well as some observations and conclusions resulting from a study of the rather well-known Friedel-Crafts reaction with ferrocene.

Acylation of ferrocene with perfluorocarboxylic acid anhydrides was carried out to yield the desired perfluoroacylferrocenes in accordance with the following general reaction:



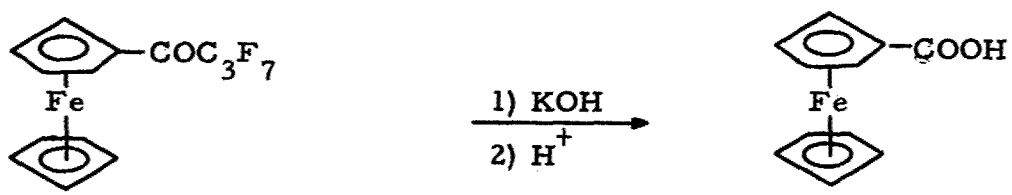
where R_f = CF_3-, C_2F_5-, and C_3F_7-

The reactions were conducted in methylene chloride using anhydrous aluminum chloride as the catalyst. In these acylations, only monosubstituted ketones were isolated (in 30-40% yield) even when conditions favoring diacylation were employed,

i.e., slow addition of ferrocene to the anhydride-aluminum chloride mixture.

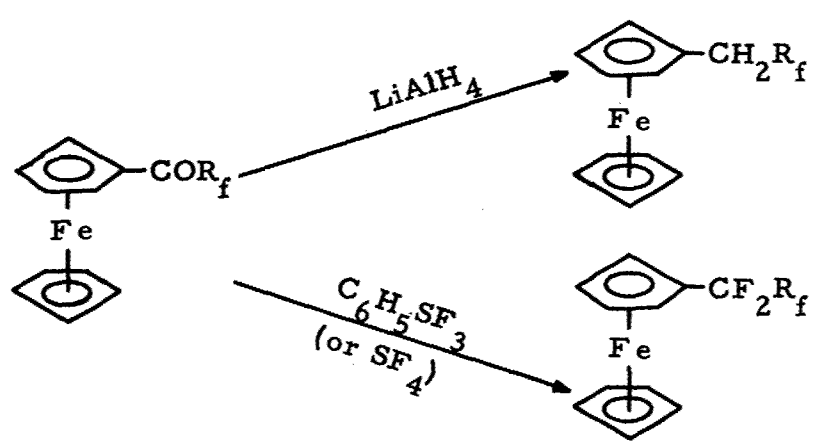
Acylations of ferrocene involving the substitution of a perfluoroacyl halide for the anhydride, in general, gave lower yields of the ketones. The yield of perfluoropropylferrocenyl ketone from the reaction of perfluorobutyryl chloride and ferrocene was found to be less than 10%.

Solid, crystalline 2, 4-dinitrophenylhydrazones were prepared from the perfluoromethyl-and perfluoroethylferrocenyl ketones, but could not be obtained from the perfluoropropyl homolog by conventional procedures. In an attempt to prepare the oxime of the latter compound, using hydroxylamine hydrochloride and excess potassium hydroxide in absolute ethanol, ferrocenemonocarboxylic acid was obtained upon acidification of the reaction mixture.



(65%)

Reduction of the ketones to 1, 1-dihydroperfluoroalkylferrocenes and conversion of the ketones to perfluoroalkylferrocenes is presently under investigation according to the following general reactions:



where R_f = CF_3-, C_2F_5-, and C_3F_7-

Acylations of ferrocene using non-fluorine-containing acyl compounds, such as acetyl chloride, are known to accur in good yields (1) and, in many cases, with additional formation of diacylferrocenes. The electron-withdrawing nature of a perfluoroalkyl group adjacent to the carbonyl carbon of the perfluoroacyl derivative gives rise to acylium intermediates of very limited stability. On the other hand, methyl (or alkyl) groups on the carbonyl carbon tend to stabilize acylium ions.

$$(\text{Stability of } CH_3CO^{\oplus} \gg CF_3CO^{\oplus})$$

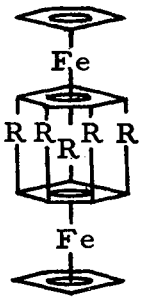
Consequently, perfluoro acid derivatives are far less reactive in Friedel-Crafts acylations than their aliphatic analogs.

Moreover, the apparent absence of bis(perfluoroacyl)ferrocenes is probably a result of the large electron-withdrawing and deactivating effect of a perfluoroacyl group attached to the ferrocene nucleus.

The sluggish reactivity of perfluoroacyl compounds in the above reactions most likely enables a considerable quantity of unacylated ferrocene to enter into concomitant reactions, possibly with the solvent or aluminum chloride. This is evidenced by the repeated isolution of non-fluorine-containing brown powders and resins as by-products.

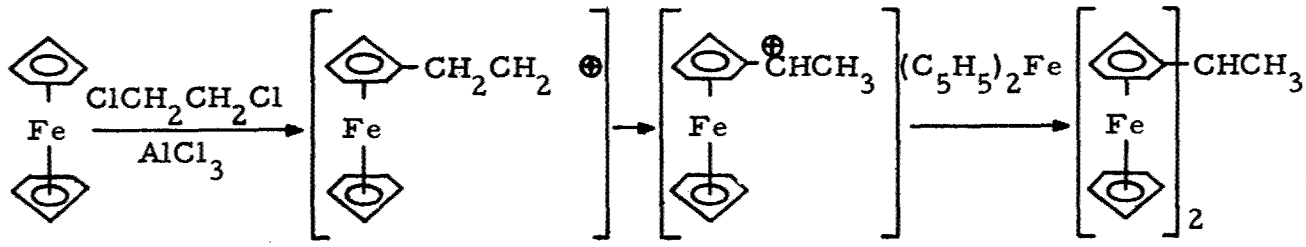
Nesmeyanov et. al. (2, 3) have studied the reactions of ferrocene and methylene and ethylene chloride in the presence of anhydrous aluminum chloride. When these reactions were carried out at or near the boiling point of the solvent involved, "polyalkanodiferrocenes" were reported as the products of the reaction.

Structure of pentaalkanodiferrocenes (Nesmeyanov)



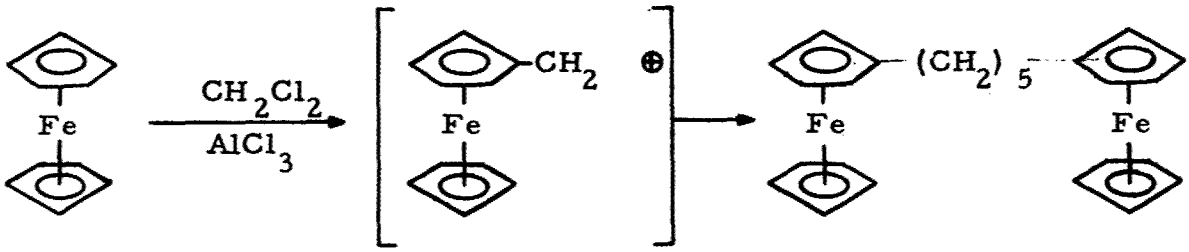
R = $-CH_2-$ or $-CH_2CH_2-$

By using different mole ratios of ferrocene to ethylene chloride a diferrocenylthane was isolated (4). Rinehart (5) proved that this compound was actually 1, 1-diferrocenylethane whose formation presumably resulted from a carbonium ion rearrangement which occurred during the course of the reaction.



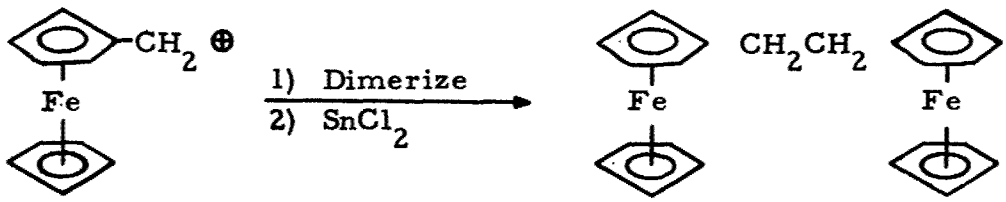
In view of this evidence it does not seem likely that 1, 2-ethane bridges would be formed in "pentaethanodiferrocene." However, the absence of methyl groups was indicated on examination of the infrared spectrum of the pentaethano compound which would disprove the presence of any $CH_3\underset{|}{C}H$-linkages.

With pentamethanodiferrocene, the formation of a methylene bridge in the presence of aluminum chloride would be expected to occur via the carbonium on:



However, evidence has been presented (6) which shows that this unique carbonium species (from formaldehyde and ferrocene in sulfuric acid) combines to give 1, 2-diferrocenylethane upon reduction:

$$C_5H_5FeC_5H_5 + CH_2O \xrightarrow{H_2SO_4} C_5H_5FeC_5H_4CH_2OH \rightarrow C_5H_5FeC_5H_4CH_2^{\oplus}$$



The present authors have studied the reaction of methylene chloride and ethylene chloride with ferrocene in the presence of aluminum chloride at room temperature or lower (in ferrocene/aluminum chloride mole ratios of 2:3).

With methylene chloride no reaction other than oxidation to ferrocinium ion occurred at temperatures of -30° or lower when the reaction mixture was hydrolyzed after 5 hours of stirring at the low temperature. However, if, after the 5 hours of stirring at the low temperature, the reaction mixture was allowed to warm to room temperature and then stirred at this temperature for an additional 18 hours, five distinct products were isolated. The separation of these products was based primarily on differences in solubilities of the materials in different solvents. These products and some of their properties are listed in Table I. With the exception of the formation of compound V, ethylene chloride with ferrocene and aluminum chloride gave the same products as when methylene chloride was used as the solvent, both by the procedure of Nesmeyanov et. al. (4) or by a procedure similiar to the above methylene chloride reaction.

TABLE I

COMPOUND	M. P.	COLOR	YIELD*	SOLUBILITY
I	78-80°	yellow	0.34g	moderately sol. in methanol
II**	138-139	yellow	0.2 g	sol. in ether, ppt. with MeOH, sol. in cyclohexane
III	178-180	yellow	3.2 g	insol. in ether, sol. in benzene, ppt. with MeOH, sol. in cyclohexane
IV	dec.> 250°	brown	1 g	insol. in cyclohexane, sol. in benzene
V	dec. 180°	yellow	0.3 g	slightly sol. in pet. ether, b.p. 30-60°; Recryst. from methanol

*Based on the use of 37.2g of ferrocene and 40g of $AlCl_3$. The yield is based on purified material.

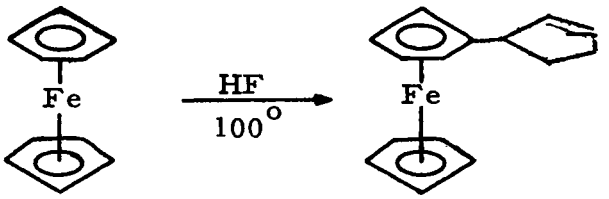
**Pentaethanodiferrocene

The separation of the materials was difficult and often required many repeated extractions. All compounds had bands in the 9-10 region of their infrared spectra. According to the separation procedure described by Nesmeyanov et. al. (4), compound II is apparently "pentaethanodiferrocene." Compound I has an infrared spectrum almost identical to that of compound III and perhaps is a lower molecular weight precursor of the latter. Compound I was originally obtained as a resinous material from a cyclohexane elution of a sample placed on an alumina column in petroleum ether (b.p. 30-60°). It was later found that a better method of purification of this compound may be effected based on its partial solubility in methanol from which it can be obtained in the form of a yellow powder, m.p. 78-80°.

Compound II (presumably pentaethanodiferrocene) is distinguished easily from the other products because in its infrared spectrum it contains a band in the 7.9u (1260cm) region which is extremely intense when the compound is pure.

The fact that all of these compounds (except V) have been isolated from either methylene chloride or ethylene chloride indicated that the reaction products were formed independent of the chemical nature of the solvent employed. This led to the question of how aluminum chloride might affect ferrocene in the presence of polar solvents but in the absence of strong alkylating agents, acylating agents, or other electrophiles.

Anhydrous hydrogen fluoride (a moderately strong Lewis acid) has been reported to catalyze the acetylation of ferrocene. However, when no acylating agent was present, anhydrous hydrogen fluoride cleaved some of the ferrocene (at 100°) and cyclopentenylferrocene was obtained as the product.



The present authors have found that shaking ferrocene and trifluoroacetic anhydride in HF for two days at room temperature did not result in acylation of the ferrocene but in the formation of cyclopentenylferrocene.

It is believed that excess aluminum chloride also causes a similar cleavage-acylation reaction in the absence of strong acylating or alkylating agents. In this connection it may be noted that the analysis of "pentaethanodiferrocene" reported by Nesmeyanov et. al. (2) is in close agreement with the calculated percentage composition of cyclopentenylferrocene (dimer) as shown in Table II.

TABLE II

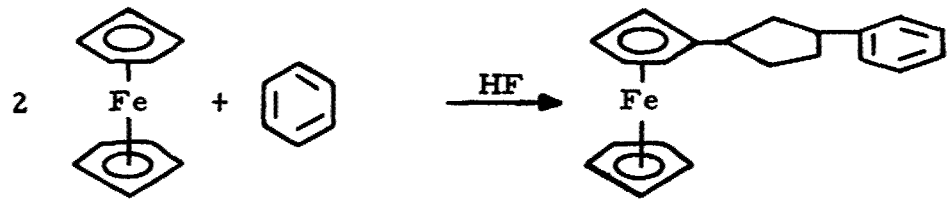
ANALYTICAL DATA ON PENTAETHANODIFERROCENE

Element	Found for (2) Pentaethanodiferrocene %	Calculated for (2) Pentaethanodiferrocene %	Calculated for Cyclopentenylferrocene %
C	71.64, 71.50	71.74	71.46
H	6.25, 6.30	6.02	6.34
Fe	21.70, 22.25	21.90	22.2

One difference between hydrogen fluoride and aluminum chloride is the greater strength of the latter as a Lewis acid. Thus it would be expected that aluminum chloride would favor further alkylation of ferrocene by "cyclopentadienyl fragments" or the formation of polymeric materials. (Hydrogen fluoride gives monomeric, aluminum chloride gives polymeric materials.)

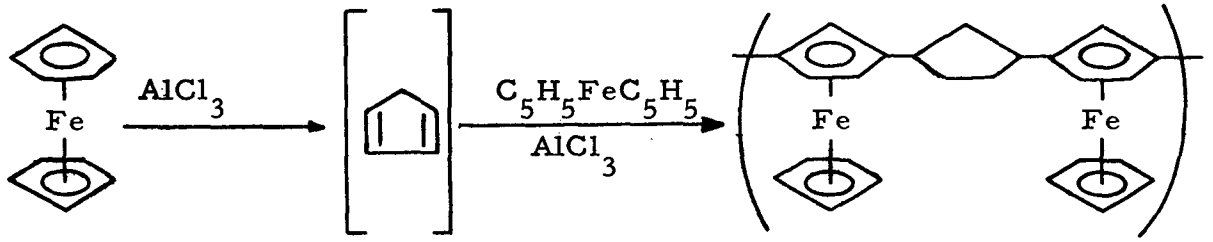
It was initially believed that in the aluminum chloride-alkylene chloride-ferrocene

reactions, cyclopentenyl ferrocene may be an intermediate in the formation of dimeric and polymeric materials made up of ferrocene and cyclopentyl residues. However, preliminary experiments in which cyclopentenyl ferrocene was treated with aluminum chloride in methylene chloride, led to recovery of most of the ferrocene starting material. There was evidence that only a trace of compound II was formed (when the reaction was carried out at room temperature for 18 hours.) Weinmayr (7) also pointed out that cyclopentenyl ferrocene did not react with benzene in the presence of hydrogen fluoride. However, when benzene, ferrocene and anhydrous hydrogen fluoride were reacted together a phenylcyclopentylferrocene was obtained.

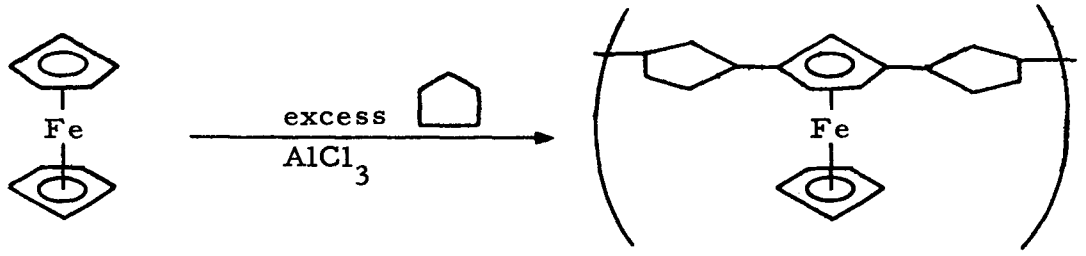


This indicated that phenylcyclopentylferrocene is not formed through a cyclopentenyl intermediate. Such evidence points to the fact that perhaps the important intermediate in all of these reactions is the "cyclopentadienyl fragment" which arises from the cleavage of ferrocene with hydrogen fluoride or aluminum chloride.

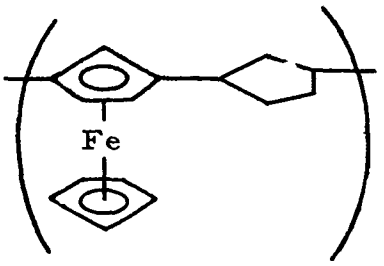
The mole ratio of aluminum chloride to ferrocene, the temperature and the relative polarity of the solvent may play a role in determining the nature of the products isolated in the reaction of ferrocene, alkylene halides and aluminum chloride. The experiment of Nesmeyanov et. al., using smaller quantities of aluminum chloride (at one time) in methylene chloride and higher temperatures, favored products possibly arising from the following reaction:



However, at lower temperatures and with higher concentrations of aluminum chloride, the ratio of cleavage products of ferrocene to unreacted ferrocene was favored. This, in turn, has apparently led to the formation of products of the type indicated in the following reaction:



Conditions intermediate to the above two cases may have led to compounds possessing the following structures:

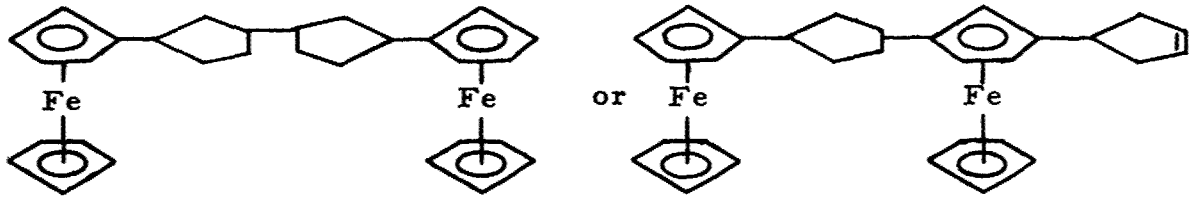


The analytical data seems to point out the fact that the materials isolated in the ferrocene-aluminum chloride-alkylene chloride reactions are made up of combinations of ferrocene and "five methylene groups" (or cyclopentyl groups.)

The available elemental analysis and molecular weight data on compounds I-V and the structures proposed for these compounds are summarized below.

1. Compound I, m.p. 78-80°

Proposed structures:



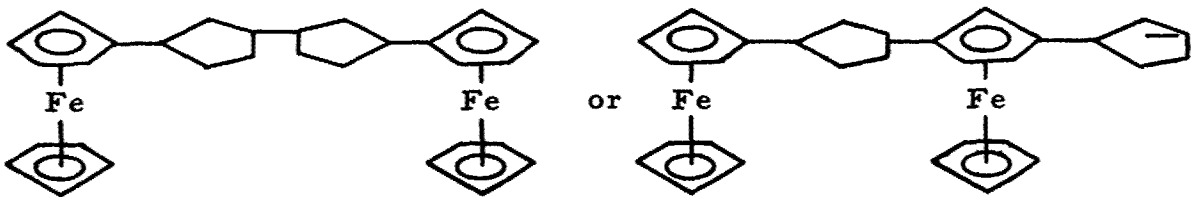
Calc. for $C_{30}H_{32}Fe_2$: C, 71.46%; H, 6.34%; Fe, 22.2%

M. W. 504

Found: C, 71.24%; H, 6.36%; Fe, 24.2%*
71.00%; H, 6.23%; Fe, 24.4%*

* The iron is suspected as being high and is being repeated. M. W. not received

2. Compound II ("pentaethanodiferrocene"), m.p. 138-139°



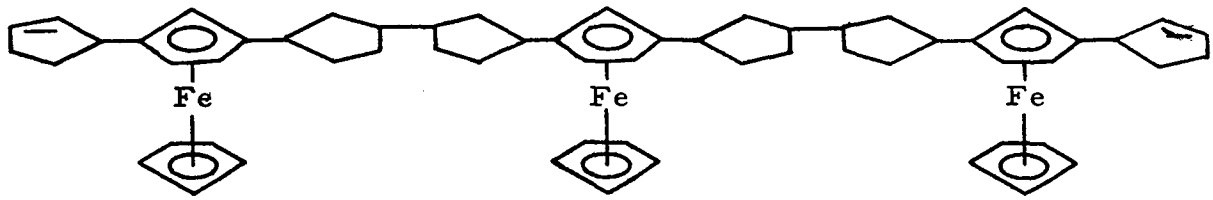
Calc. for $C_{30}H_{32}Fe_2$: C, 71.46; H, 6.34; Fe, 22.2%

M. W. 504

Found: C, 71.64; H, 6.25; Fe, 21.70
C, 71.50; H, 6.30; Fe, 21.90

M. W. 545, 568

3. Compound III, m. p. 178-180°



Calc. for $C_{60}H_{70}Fe_3$: C, 75.17; H, 7.35; Fe, 17.47

M. W. 958

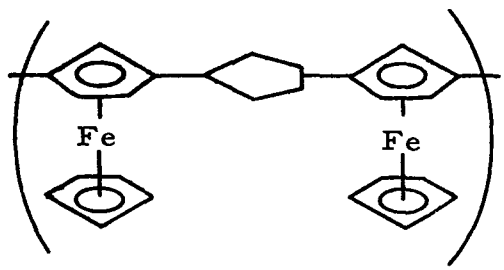
Found: C, 76.37; H, 6.89; Fe, 16.50
C, 76.39; H, 6.87; Fe, 16.83

M. W. ca. 1000

4. Compound IV.

The analysis had not been received at the time this paper was prepared. Its infrared spectrum, however, is very similar to those of Compounds I and III. From its physical properties it appears to be one of the higher molecular-weight materials reported by Nesmeyanov (2).

5. Compound V.



Calc. for $C_{22}H_{20}Fe_2$: C, 66.70%; H, 5.09%

Found: C, 67.08%; H, 5.20%
C, 67.01%; H, 5.21%

This material appears to be similar to the material isolated by Nesmeyanov et. al. (3) in the reaction of ferrocene, methylene chloride, and aluminum chloride at 40°. The latter workers state that according to their analytical data their reaction products contain 2 ferrocene units per "5 methylene" fragments. The molecular weights of two materials were reported by the Russian workers as 1000 and 2000, respectively.

On the basis of the results reported in the present work, these authors believe that in products of the ferrocene-alkylene halide-aluminum chloride reactions the "five methylene groups" described by Nesmeyanov et. al. are, in reality, a cyclopentyl group and that the "pentaethano" linkage is essentially two cyclopentyl rings, joined together or separated alternately by ferrocene.

Physico-chemical studies on these materials are now under investigation. Further work on the elucidation of the structure of these materials is also planned, along with continued studies of the preparation of the fluorine-containing compounds described at the beginning of this report.

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