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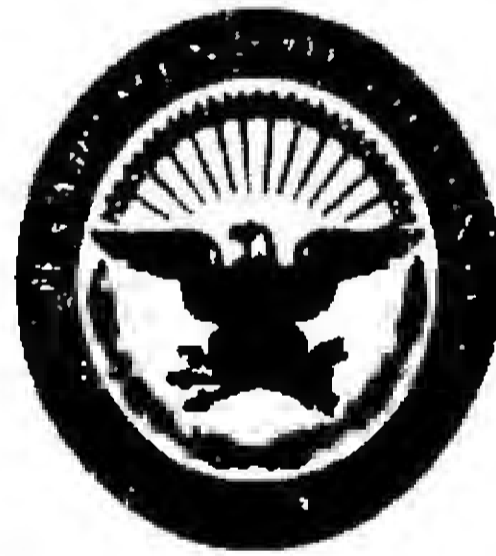
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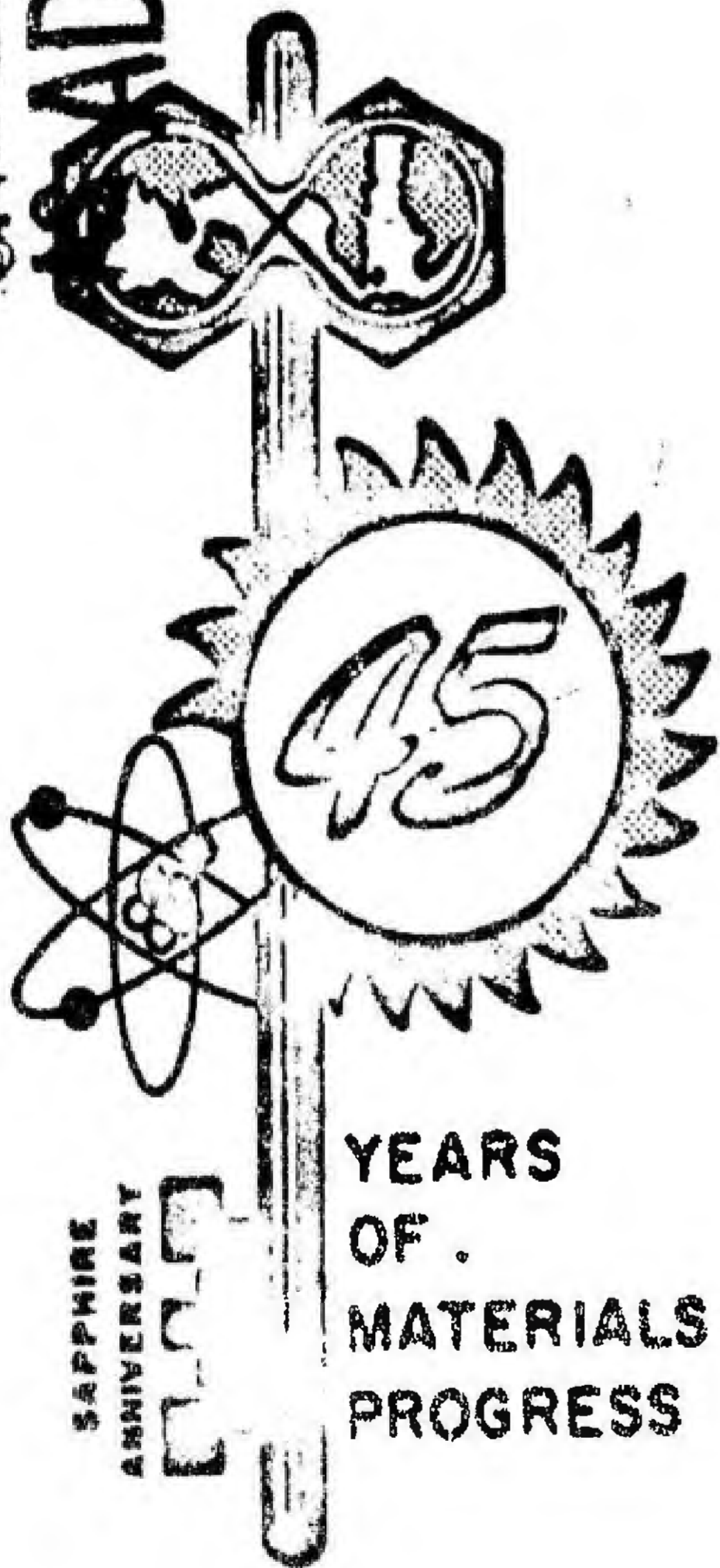
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AD NO.

RESEARCH ON AROMATIC POLYMERS FOR THERMALLY-STABLE FIBERS AND FILMS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-679
July 1962

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



Project No. 7340, Task No. 73404

(Prepared under Contract No. AF33(616)-8253 by
the E. I. du Pont de Nemours & Co., Wilmington,
Delaware; August H. Frazer, James J. Kane, and
Fred T. Wallenberger, authors.)

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ASD-TDR-62-679

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Delaware; August H. Frazer, James J. Kane, and
Fred T. Wallenberger, authors.)**

FOREWORD

This report was prepared by the E. I. du Pont de Nemours & Company, Wilmington, Delaware, on Air Force Contract No. AF33(616)-8253 under Task No. 734004, "New Organic and Inorganic Polymers," of Project No. 7340, "Nonmetallic and Composite Materials". The contract efforts were accomplished under the cognizance of the Directorate of Materials & Processes, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, with the technical work directed by Dr. W. E. Gibbs, as project engineer.

Research started on 1 June 1961 and completed 1 June 1962.

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. To test this hypothesis N-substituted polymers were prepared via the methylation of N-sodio polybenzimidazoles.

Oriented and crystalline polyhydrazide fibers can be converted by a unique cyclodehydration reaction into oriented and crystalline fibers of poly(1,3,4-oxadiazoles). Conversion of fibers (T/E/M1 = 5/24/94) of the polyhydrazide derived from equimolar amounts of isophthalic dihydrazide and terephthaloyl chloride (OIOT) gave fibers (T/E/M1 = 2.6/3.1/124) of poly(1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole), PODZ-I/T, which have excellent retention of their fiber structure even when exposed to temperatures up to 400°C. for prolonged periods of time. Such heat treatments afford a final polyoxadiazole fiber (T/E/M1 = 1.2/1.2/90). The chemical structure of model compounds containing up to 13 alternating rings consisting of 2,5-(1,3,4-oxadiazole), *m*-, and *p*-phenylene moieties was found to be stable up to 440°-500°C. This is in agreement with observed stabilities of the corresponding polymer towards thermal degradation.

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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I. Introduction and Objective

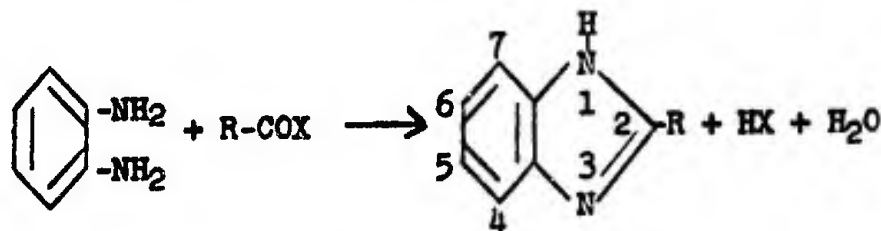
The objectives of work reported herein are the synthesis and characterization of various poly(phenylbenzimidazoles) poly(phenyloxadiazoles) and related highly aromatic compounds in order to prepare fibers and fibrous products of super thermal resistance.

II. Polybenzimidazoles - James J. Kane

Discussion

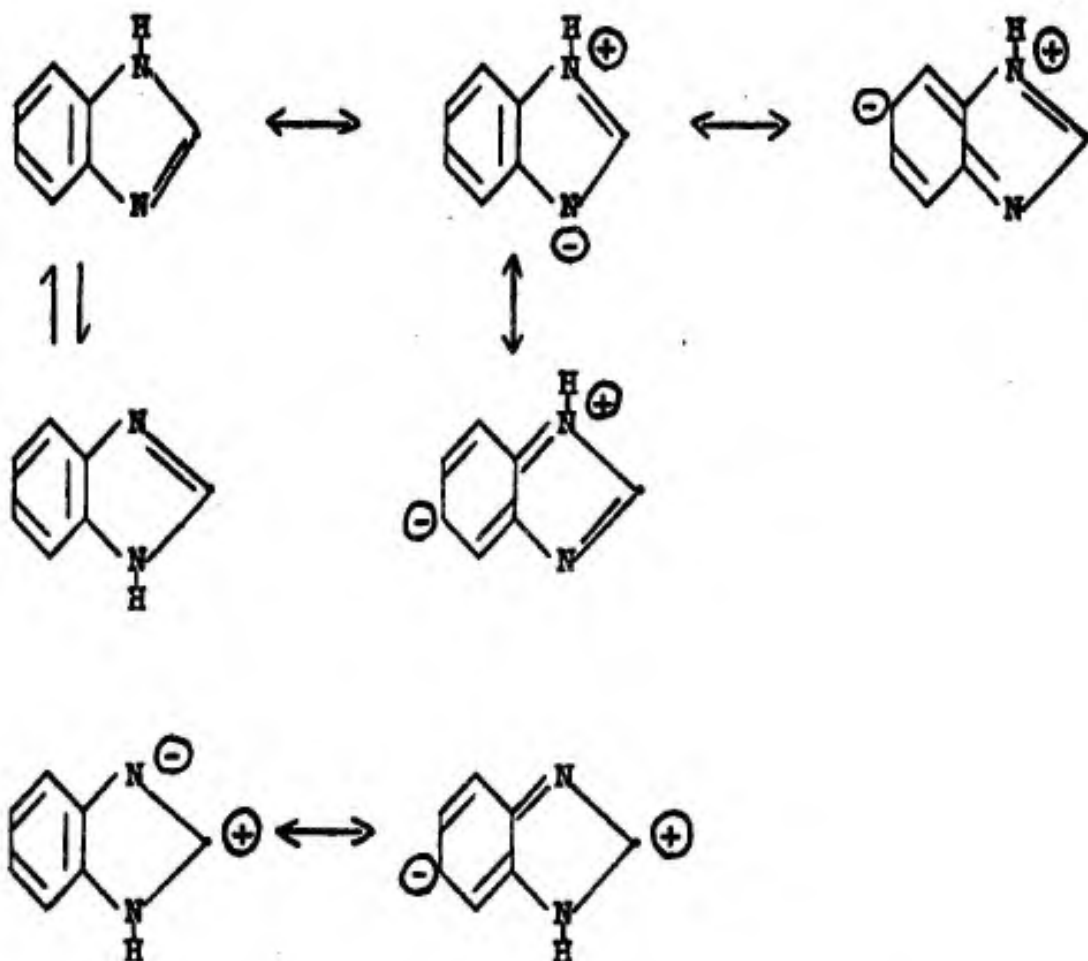
Benzimidazoles

Benzimidazole derivatives are synthesized from o-phenylenediamine and carboxylic acids or their derivatives:



The benzimidazole products are generally high melting crystalline solids possessing both acid and basic characteristics. They exhibit unusual chemical resistance to acidic, basic, and oxidizing reagents. The tautomeric nature of the benzimidazole system unsubstituted in the 1-position is a well known phenomenon rendering both nitrogens in the heterocyclic system equivalent. Similarly, hydrogen bonding in benzimidazoles 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 in the amidine-like structure. The chemical inertness of benzimidazoles is explicable in terms of the aromatic nature of the system which derives delocalization energy from overlapping of the sextet of π electrons available to both the benzene and heterocyclic rings as described by the classical structures:

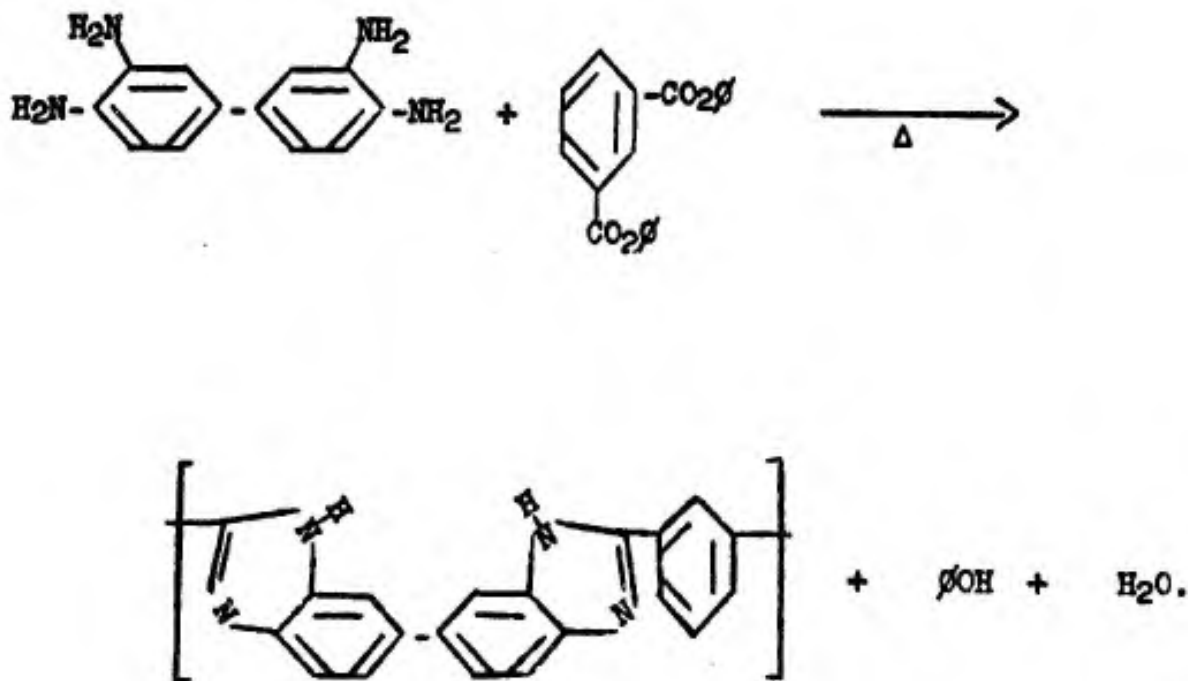
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The high melting characteristics displayed by the benzimidazoles are especially pronounced in derivatives unsubstituted in the 1-position, a prerequisite necessary for association via hydrogen bonding.

Polybenzimidazoles

Application of the general synthetic route to benzimidazoles to include bifunctional materials was first accomplished by Brinker and Robinson (1) through their discovery that bis-*o*-diamines and aliphatic dioic acids or their derivatives react to form linear condensation polymers designated as polybenzimidazoles. A modification of this procedure resulting in the preparation of polybenzimidazoles containing recurring aromatic units was developed by Marvel and Vogel (2) through the melt polymerization of bis-*o*-diamines and diphenyl esters of aromatic dicarboxylic acids:



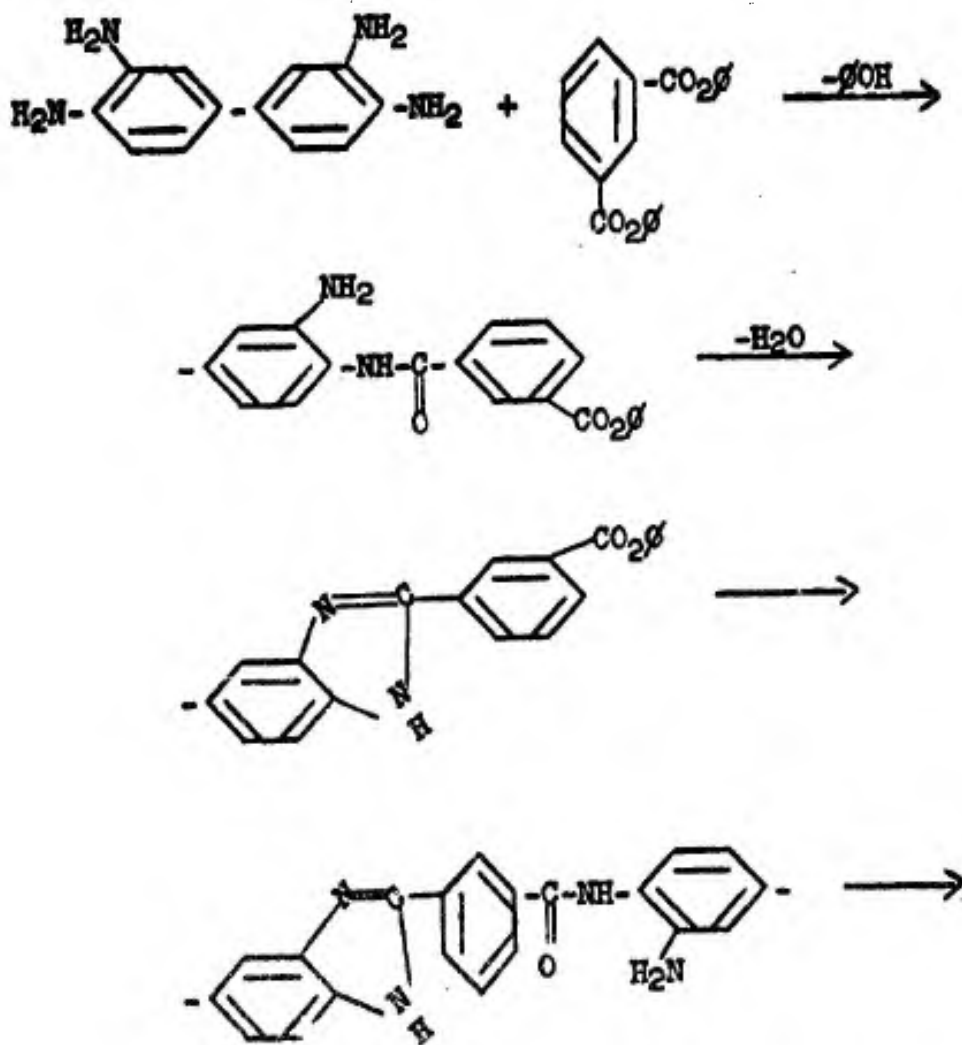
Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

The polymers prepared by Marvel and Vogel were based on the tetraamines, 3,3'-diaminobenzidine and 1,3,4,6-tetraaminobenzene and the dioic acid moieties employed were phthalic, isophthalic, terephthalic, 2,2'-biphenyl, and 3,5-pyridyl. In general, the condensation polymers have been high melting, or infusible materials exhibiting, as anticipated, high thermal and chemical resistivities.

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, based on 3,3'-diaminobenzidine and diphenylisophthalate was chosen as the most attractive polymer for large scale preparation and spinning operations because of the commercial availability of the tetra-amine salt 3,3'-diaminobenzidine tetrahydrochloride.

Details of purification of starting materials and polymerization techniques are described in the Experimental Section. The free base, 3,3'-diaminobenzidine is liberated from the hydrochloride salt with a 4% sodium hydroxide solution. Purification is accomplished by repeated recrystallizations from methanol. Polymerization of 3,3'-diaminobenzidine and diphenylisophthalate is accomplished by heating a mixture of the two reactants in the melt at 260-290° to effect the polycondensation which is accompanied by phenol and water evolution.

The reaction mechanism appears to be straightforward and is outlined below.



Since both water and phenol appear to be evolved at the same rate it is probably safe to assume that ring formation occurs as the polymer chain grows rather than by the alternative process of preliminary poly-*o*-aminoamide formation and subsequent elimination of water with ring closure to form the heterocyclic portion of the repeating unit. The driving force for ring closure would be expected to be great because of the resulting delocalization energy derived by the new aromatic system. Thus, at the temperature employed, amide formation and imidazole formation might be expected to occur at similar rates.

The polymerization reaction is carried out by immersing a flask containing the solid reactants under a nitrogen atmosphere in a 260° bath. After melting, reaction commences at about 260° as evidenced by rapid evolution of phenol and water. The reaction mass soon sets up as a glassy solid of inherent viscosity of 0.3-0.4 (DMSO) which must be removed from the flask, ground, and reheated at temperatures ranging from 260-400° over a 9-12 hour period under 0.05 mm Hg pressure. During this treatment, the remainder of the phenol is removed. The polymer obtained, a bright yellow solid, has an inherent viscosity of 0.8 (DMSO). The polybenzimidazole does not melt up to 500°C. and is soluble in DMSO, formic acid, sulfuric acid, N-methylpyrrolidone, DMAc, and DMF. Insoluble portions, apparently crosslinked polymer account for about 10% of the weight of final product. After reprecipitation from DMSO, DMAc, or DMF with water, the polymer is obtained as a tan powder. Infrared spectra of films cast from DMAc are typical of benzimidazoles.

Polybenzimidazole Fibers

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole has been dry spun from DMSO and from DMAc. Details of the spinning conditions will be found in the Experimental Section. After spinning, the yarn was extracted with water for two days and drawn 1.7X in 5 lbs. steam pressure. The yarn was then redrawn over a hot pin at the following temperatures and draw ratios: 400°, 1.1X; 350°, 1.6X; 350°, 1.3X; 350°, 1.1X; 300°, 1.2X. The redrawn fiber was highly oriented but amorphous. Treatment of the fiber with a solvent mixture of formic acid:water (50:50 by volume) induced a slight degree of crystallinity but destroyed orientation. In Table I are compiled the physical testing data for all the samples of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole. The yarn has over-all rather impressive tensile properties, being as good as or better than PODZ-I/T (T/E/M1 = 2.6/3.1/124) (see Table IX).

For comparison, data describing the tensile properties for poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole dry-spun from DMSO, drawn 1.8X in 12 lbs. steam pressure and 1.2X over a 360° hot pin are also tabulated in Table I. In general, the two yarns are comparable and the data strongly suggest that the difference in spinning solvents (DMSO and DMAc) has no effect on the tensile properties of the fibers. Dimethylacetamide, then, emerges as the more desirable of the two solvents since it does not involve

as bothersome solvent removal problems as DMSO. In addition, the yarn obtained by spinning from DMAc is lighter in color (straw-yellow) than that obtained from DMSO (dark brown).

Thermal stability and hydrolytic tests have been conducted on the fibers spun from DMSO and are tabulated in Tables II and III. These tests have not been repeated on fibers obtained from DMAc but the limits of air ageing temperatures seem to be the same for both fibers since samples of the latter material had virtually no strength after 24 hours in a 400° oven and after 15 min. in a 500° oven. Hydrolytic stability of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole is unusually good as shown by the data in Table III.

Films cast from DMAc are tough and self-supporting and when subjected to a 400° oven for a half day they are still tough but take on a purple-brown color and cannot be redissolved. This behavior strongly suggests crosslinking.

This same purple-brown coloration is observed in the fibers as they are drawn over the hot pin at 350-400°. The color disappears where the fiber is removed from the heat source suggesting a reversible thermal excitation. Samples of bulk polymer were submitted for Electron Spin Resonance studies to detect the presence of unpaired electrons and determine whether or not the process is reversible. The results obtained are qualitative but reveal an absorption band for unpaired electrons which is increased in intensity by light. The process appears not to be reversible, however.

The ability of this polymer to withstand exposure to high temperatures in the presence of air has been disappointing as indicated by the data in Table II, and this behavior has been theorized as due to the susceptibility of the N-H bond to undergo bond breaking at high temperatures and subsequent oxidation in the presence of air. Even in inert atmosphere (nitrogen) poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole subjected to temperatures up to 500°C. appears to crosslink since the resulting material, while not crystalline, is no longer soluble in the usual solvents, DMSO, DMF, DMAc, and formic acid.

Substituted Polybenzimidazoles

Thus, a long standing desire has been to obtain polybenzimidazoles substituted, preferably by an aromatic substituent in the 1-position of the heterocyclic ring. One approach to this

TABLE I

**1) POLY-2,2'-(*m*-PHENYLENE)-5,5'-BIBENZIMIDAZOLE SPUN FROM DMAc
FIBER PROPERTIES**

A. Drawn 1.65 times at 5# steam

	<u>T^a</u>	<u>E^b</u>	<u>MF</u>	<u>TR %^d</u>			<u>WR %^e</u>		
				<u>3</u>	<u>5</u>	<u>10</u>	<u>3</u>	<u>5</u>	<u>10</u>
Straight	2.19	21.4	73.6	86	66	33	57	34	13
Loop	1.53	5.1	-						
Knot	2.26	27.7	47.0						
Hot-Wet	1.27	47.8	28.0						

**B. Drawn 1.65 times at 5# steam
and redrawn 1.1 times at 400°C**

	<u>T</u>	<u>E</u>	<u>M1</u>	<u>TR %</u>			<u>WR %</u>		
				<u>3</u>	<u>5</u>	<u>10</u>	<u>3</u>	<u>5</u>	<u>10</u>
Straight	3.26	41.2	76.7	85	59	30	60	31	12
Loop	1.56	4.2	-						
Knot	2.38	24.0	50.1						
Hot-Wet	1.93	51.2	25.5						

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

	<u>T</u>	<u>E</u>	<u>M1</u>	<u>TR %</u>			<u>WR %</u>		
				<u>3</u>	<u>5</u>	<u>10</u>	<u>3</u>	<u>5</u>	<u>10</u>
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						

**D. Drawn 1.65 times at 5# steam
and redrawn 1.1 times at 350°C**

	<u>T</u>	<u>E</u>	<u>M1</u>	<u>TR %</u>			<u>WR %</u>		
				<u>3</u>	<u>5</u>	<u>10</u>	<u>3</u>	<u>5</u>	<u>10</u>
Straight	2.99	17.8	92.7	77	54	30	50	27	12
Loop	1.38	3.2	-						
Knot	1.97	8.4	5.1						
Hot-Wet	1.52	41.4	40.0						

TABLE I (CONT'D.)

**E. Drawn 1.65 times at 5# steam
and redrawn 1.2 times at 300°C**

	<u>T</u>	<u>E</u>	<u>M1</u>	<u>TR %</u>			<u>WR %</u>		
				<u>3</u>	<u>5</u>	<u>10</u>	<u>3</u>	<u>5</u>	<u>10</u>
Straight	3.43	10.0	119.7	81	57	-	52	28	-
Loop	0.40	1.6	-						
Knot	0.81	5.3	20.6						
Hot-Wet	1.70	31.2	40.3						

**2) POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE SPUN FROM DMSO
FIBER PROPERTIES**

**A. Drawn 1.8 times at 12# steam
and redrawn 1.2 times at 360°C**

	<u>T</u>	<u>E</u>	<u>M1</u>	<u>TR %</u>			<u>WR %</u>		
				<u>3</u>	<u>5</u>	<u>10</u>	<u>3</u>	<u>5</u>	<u>10</u>
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 (%) at Break
- c) - M1 = Initial Modulus (gr./denier)
- d) - TR = Tensile Recovery (%), at 3, 5, 10% Elongation
- e) - WR = Work Recovery (%), at 3, 5, 10% Elongation

TABLE II

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

<u>T (in air)</u> °C	<u>Time (hours)</u>	<u>T/E/MI^a</u>
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 ^c
450	1	2.5/2.5/27
"	3	Disintegrated
500	0.25	TWTT ^c
"	1	Disappeared

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

<u>Exposure Time^b (hours)</u>	<u>T/E/MI</u>
0	4.5/13/97
24	4.3/13/97
48	4.3/9/80
78	4.1/6/85
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 3 hours of Florida sunlight.

c) - Too weak to test.

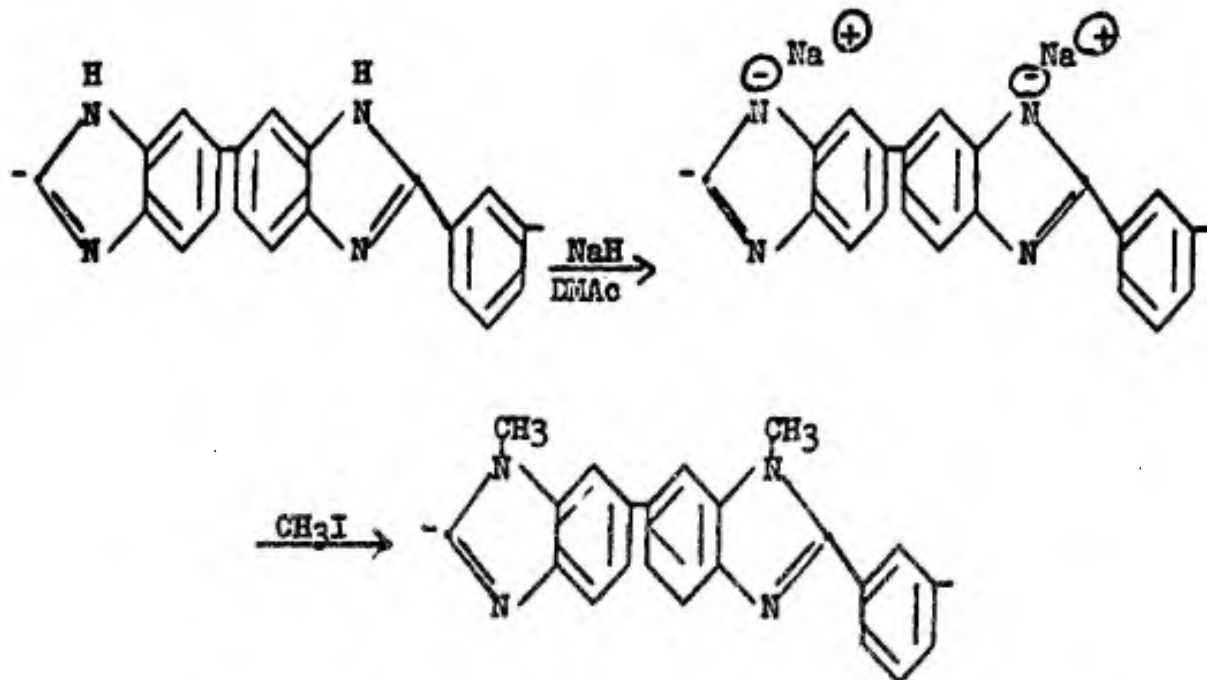
TABLE III
HYDROLYTIC STABILITIES OF POLY-2,2'-(*m*-PHENYLENE)-5,5'-
BIBENZIMIDAZOLE FIBERS

<u>Medium</u>	<u>Time (hours)</u>	<u>T/E/M^a</u>
None	-	4.5/13/97
10% NaOH	1	3.9/22/74
95-100°		
"	3	3.8/26/61
"	6	4.2/29/70
"	24	3.9/38/55
20% NaOH	1	4.4/23/75
95-100°		
"	3	4.0/23/70
"	6	3.8/25/65
"	24	3.8/25/68
40% NaOH	1	4.1/49/56
95-100°		
"	3	3.0/56/50
"	6	2.8/50/39
"	24	3.0/54/33
10% H ₂ SO ₄	1	3.6/36/50
95-100°		
"	3	3.2/35/48
"	6	3.6/42/44
"	24	3.4/38/52
20% H ₂ SO ₄	1	3.4/42/44
95-100°		
"	3	3.5/37/45
"	6	3.3/49/39
"	24	3.6/37/52
40% H ₂ SO ₄	1	3.4/36/46
95-100°		
"	3	3.6/45/53
"	6	3.4/50/44
"	24	3.1/52/43

a) - See footnotes in Table I.

type polymer is through the use of appropriately substituted tetraamines. Marvel and Vogel (2) have reported the synthesis of the polymer based on 1,3-diamino-4,6-dianilinobenzene and isophthalic acid and concluded that its ability to withstand thermal degradation is no better than the unsubstituted analog. The preparation of this polymer has been repeated in this laboratory, but only small quantities of low molecular weight polymer have been obtained.

An alternative approach to polybenzimidazoles substituted in the 1-position is by direct substitution at this position on preformed polymer. Such a reaction takes advantage of the acidic nature of the hydrogen on the heterocyclic ring and is a well known general reaction of benzimidazoles. Thus, poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole was converted to the N-methylated polymer by treatment of its sodium salt in DMAc with methyl iodide:



Infrared analysis of the methylated polymer indicated a decrease in N-H absorption intensity as well as a shift of this absorption band to a lower wave number. It is interesting to speculate that such a shift might be attributed to the decrease in hydrogen bonding which would be anticipated in the polybenzimidazole if most of the 1-positions in the polymer chain were methylated. This is analogous to the differences observed in the spectra of concentrated and dilute solutions of compounds capable

of intermolecular hydrogen bonding. The appearance of aliphatic C-H absorption bands in the infrared spectra also indicates that the desired methylation has been effected. The methylated polybenzimidazole is soluble in formic acid and has been cast into tough films from that solvent. However, unlike the starting material, it is insoluble in DMSO, DMF, and DMAc. Such a difference might be expected between the amphoteric starting material and the basic product. X-ray analysis indicates that the methylated material is amorphous. The new polymer does not melt, but it does soften at approximately 400°C. A quantitative determination of the extent of alkylation is not yet possible as no reproducible chemical analysis of the polymer has been accomplished. However, the presence of the N-H absorption in the infrared spectra is ample indication that alkylation is incomplete.

The sodium salt of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole has been treated in DMAc with iodobenzene with the hope of preparing the N-phenylated polymer. The infrared spectra of the product is identical to that of the starting material indicating that phenylation, if it occurred at all, is negligible. It may be necessary to resort to higher temperatures and sealed tubes to effect this reaction. However, even if N-arylated polybenzimidazoles may not be available by this method, it does appear to be a convenient means for the preparation of N-alkylated polymers, and possibly a method which will prove useful for the modification of polybenzimidazoles.

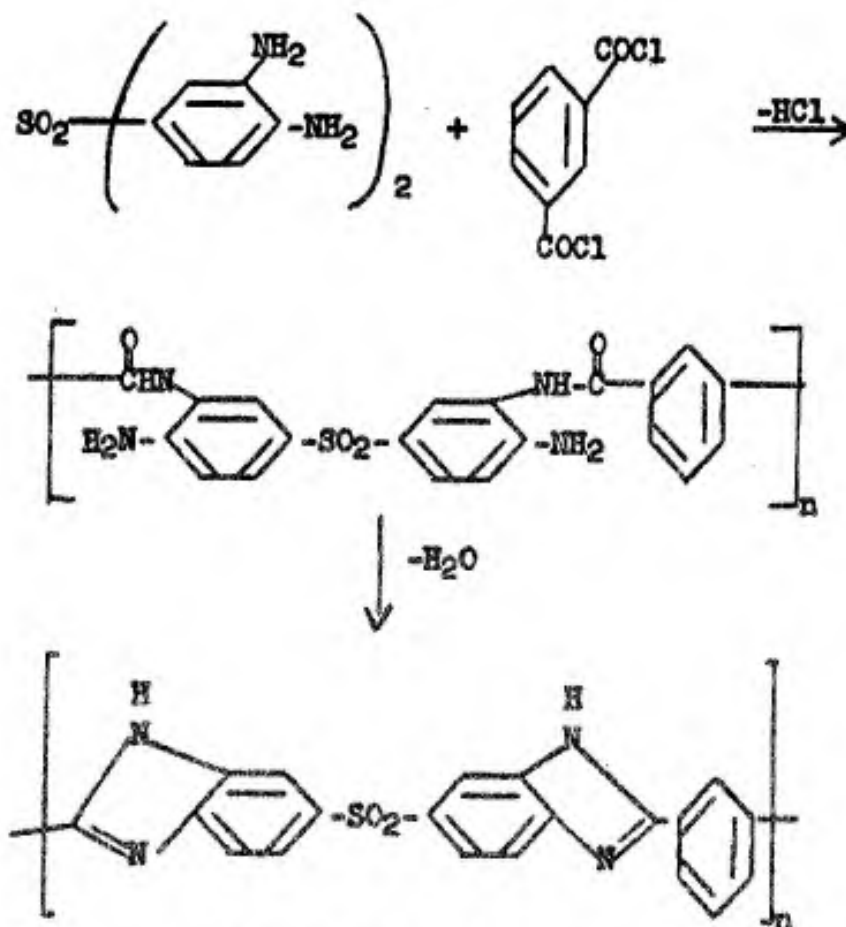
Polybenzimidazoles Containing "Insulating Groups"

Another goal sought was the preparation of polybenzimidazoles containing "insulating groups" within the polymer chain in order to relieve chain stiffness and produce a more tractable polymer. The preparation of 3,4,3',4'-tetraaminodiphenylsulfone and 3,4,3',4'-tetraaminodiphenylether was undertaken in order to provide tetraamines for possible syntheses of new polybenzimidazoles with -O- and -SO₂- "insulating groups" between the aromatic rings with the hope of imparting flexibility within the polymer chain.

The tetraaminodiphenylsulfone has been prepared by conversion of 3,3'-dinitro-4,4'-dichlorodiphenylsulfone to the corresponding 4,4'-diamino- derivative with alcoholic ammonia and subsequent reduction to the tetraamine with alcoholic sodium

sulfide. Attempts to prepare the polybenzimidazole based on this tetraamine and isophthalic acid by the usual methods were unsuccessful. When tetraaminodiphenylsulfone is heated with diphenylisophthalate or dibiphenylisophthalate under the usual conditions for polybenzimidazole formation, the reaction commences with evolution of water and phenol or *p*-phenylphenol at 290° to produce only low yields of low molecular weight polymer. This result apparently is due to the immiscibility of the two reactants in the melt even at temperatures up to 300°. Thus, polymerization occurs only at the interface of the two layers. In order to promote polymerization, several reactions have been attempted in solvents. Those tested were "Aroclor"* and *p*-phenylphenol. No polymerizations have been successful in these solvents even at temperatures up to 250°.

An alternative method for preparation of this polybenzimidazole involves synthesis first of the polyamino-amide followed by cyclic dehydration to form the polybenzimidazole:



*Trademark for Monsanto's chlorinated aromatic hydrocarbon.

An attempt to prepare the polyamino-amide was made by reaction of tetraaminodiphenylsulfone with isophthaloyl chloride in hexamethylphosphoramide. The product, a white solid which does not melt up to 400° appears to be highly crosslinked and exhibits typical amide absorption in the infrared region.

Tetraaminodiphenylether was obtained by nitration of 4,4'-diacetylamino-diphenylether followed by hydrolysis and reduction to the desired tetraamine. Nitration of the diacetylamino-diphenylether by the known method (3) with 70% nitric acid in glacial acetic acid could not be repeated. However, the method of Marvel (private communication) using acetyl nitrate was successful. Hydrolysis and catalytic hydrogenation afforded the desired tetraamine.

The polybenzimidazole based on 3,4,3',4'-tetraaminodiphenylether and isophthalic acid has not yet been successfully prepared. The tetraamine, prepared only in small amounts, is extremely sensitive and has never yet been maintained as a colorless material for more than a few minutes. The product obtained by heating this tetraamine with diphenylisophthalate appeared to be decomposition products.

The polybenzimidazole based on 3,3'-diaminobenzidine and diphenylsulfone-4,4'-dicarboxylic acid has been prepared by the melt condensation of the tetraamine and the diphenylester of the dibasic acid. The polymer, which does not melt up to 400°, has been prepared in small quantities and cast into small films from formic acid, but otherwise is not yet characterized.

Experimental

Purification of 3,3'-Diaminobenzidine

3,3'-Diaminobenzidine tetrahydrochloride (Burdick and Jackson Labs, Muskegon, Michigan) is dissolved in deoxygenated water and poured into a 4% solution of aqueous sodium hydroxide to liberate free base. Crude diaminobenzidine is filtered under nitrogen, washed with cold water and finally washed with cold methanol to remove most of the color from the solid. The crude diaminobenzidine is immediately dissolved in boiling methanol (approx. 10 gr. per 1.5 liter methanol). The methanolic solution is treated with decolorizing charcoal which has been washed with hot methanol and dried in a nitrogen atmosphere. After

filtering under nitrogen to remove charcoal, the solution is immediately cooled to -10°C . in a flask purged with nitrogen, stoppered tightly and placed in the freezer. After three crystallizations the 3,3'-diaminobenzidine, m.p. $179-180^{\circ}$, is suitable for polymerization. The diaminobenzidine, once purified by the above procedure has been stored in the vacuum oven with nitrogen bleed-in for several weeks without any noticeable decomposition.

Dry Spinning of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole was prepared according to the method of Marvel and Vogel (2) and reprecipitated from DMAc. The bulk polymer, a yellow powder of inherent viscosity 0.62 (0.5% in DMSO) was dissolved in DMAc to make a solution containing 27.5% solids by weight. Yarn was spun from this viscous solution through a spinning column at approximately 200°C . After drawing 1.6 times in 3 to 5 lbs. steam, samples of the yarn were redrawn at ratios varying from 1.1 to 1.6 times over a hot pin varying in temperature from 300 to 400°C . as indicated in Table I. Dry spinning data is tabulated below.

DRY SPINNING DATA

Spun on Column A
Adaptor 20% Steam $\cong 126^{\circ}\text{C}$.
Heat Temperature 94°C .
Pressure 145 psi
Solution Delivery 1.75 ml./min.
Spinneret Holes 5
Size .005
Temperature $123^{\circ}-125^{\circ}-120^{\circ}\text{C}$.
Temperature of Incoming N_2 $206-215^{\circ}\text{C}$.
Temperature of Column Top 186°C .
Bottom 206°C .
Rate N_2 Flow 5 cu. ft./min.
Wind-up Speed 115 yd./min.

Preparation of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

The polymerization of 3,3'-diaminobenzidine and di-phenylisophthalate was carried out according to the directions of C. S. Marvel and H. Vogel (1). The polymer was obtained in

93% yield, and after reprecipitation from dimethylsulfoxide, polymer with an inherent viscosity of 1.78 (0.5% in formic acid) was obtained. Films cast from DMF and dimethylacetamide were amorphous.

Preparation of 1,3-Dianilino-4,6-dinitrobenzene

1,3-Dinitro-4,6-dichlorobenzene (50 gr., 0.21 mole) was dissolved in 100 ml. of aniline and heated to a gentle reflux for four hours. The reaction mixture was then cooled, diluted with 400 ml. of water and filtered. The black filtrate was taken up in acetone, reprecipitated with water, filtered, and washed with cold ethanol. The remaining orange solid was dissolved in benzene and reprecipitated with ethanol to yield 47 gr. (60% yield) of orange-red 1,3-dianilino-4,6-dinitrobenzene, m.p. 185-186°.

Preparation of 1,3-Diamino-4,6-dianilinobenzene

1,3-Dianilino-4,6-dinitrobenzene (7.0 gr., 0.02 mole) was suspended in 200 ml. of absolute ethanol saturated with dry HCl. To this was added 0.9 g. of 10% palladized charcoal. The reaction mixture was subjected to an initial hydrogen pressure of 40 psi. After 30 minutes the calculated amount of hydrogen was consumed and the reaction mixture was filtered to remove the catalyst. The filtrate was poured into 200 ml. of 4% sodium hydroxide solution. The free amine precipitated and was immediately filtered off under nitrogen and recrystallized from benzene to yield 2.9 g. (50% yield) of 1,3-diamino-4,6-dianilinobenzene, white needles, melting at 250-206° after recrystallization from methylene chloride.

Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.5; H, 6.25; N, 19.3.
Found: C, 74.5; H, 6.30; N, 19.3.

Preparation of Poly-3,5-diphenyl-2,2'-diimidazobenzene

1,3-Diamino-4,6-dianilinobenzene (1.45 g., 0.005 mole) and diphenylisophthalate (1.59 g., 0.005 mole) were placed in a 50 ml. flask, purged with nitrogen and heated to 250° under nitrogen. After 30 minutes, vacuum was applied (0.1 mm.) and the mixture heated to 300° for one hour. After cooling, the reaction mixture (a solid plug) was removed, finely ground, returned to the reaction flask and heated at 350° for eight hours. The

polymer was then cooled and ground to a green brown powder, m.p. 300-310° (hot bar). This material was insoluble in DMSO and DMF. Films cast from formic acid were extremely brittle.

Preparation of 3,3'-Dinitro-4,4'-diaminodiphenylsulfone

3,3'-Dinitro-4,4'-dichlorodiphenylsulfone (75 g., 0.2 mole) and 200 ml. of absolute alcohol were placed in a bomb and charged with ammonia (23 g.). After sealing the bomb, it was heated at 150° for 8 hours. After cooling, the reaction mixture was poured into 200 ml. water, filtered and washed to yield 63 g. (94%) of 3,3'-dinitro-4,4'-diaminodiphenylsulfone, m.p. 290°. After recrystallization from ethanol it melted at 305°.

Preparation of 3,4,3',4'-Tetraaminodiphenylsulfone

3,3'-Dinitro-4,4'-diaminodiphenylsulfone (36.1 g., 0.11 mole), was added to a solution containing sodium sulfide nonahydrate (307 g., 0.86 mole) in 625 ml. of ethanol and 60 ml. of water. After refluxing for 16 hrs. with stirring, most of the ethanol was distilled off. Water (200 ml.) was added to the residue and the mass was filtered and washed with cold water until neutral to yield 27 g. (91% yield) of 3,4,3',4'-tetraaminodiphenylsulfone m.p. 170-175°. After recrystallization from oxygen-free water, it melted at 180-181°.

Anal. Calcd. for $C_{12}H_{14}N_4SO_2$: C, 51.79; N, 20.13.
Found: C, 51.8; N, 20.0.

Preparation of Dibiphenylisophthalate

p-Phenylphenol (114 g., 0.56 mole) and isophthalyl chloride (191 g., 0.12 mole) were heated as a melt with stirring for 5 hrs. at 260°. After recrystallization from toluene the crude product amounted to 250 g. (94% yield). After two additional crystallizations from toluene, the p-phenylphenol melted at 230-232°.

Reaction of 3,4,3',4'-Tetraaminodiphenylsulfone with Diphenylisophthalate

In a small distillation apparatus a mixture of tetraaminodiphenylsulfone (2.783 g., 0.01 mole) and diphenylisophthalate (3.183 g., 0.01 mole) was heated one hour under nitrogen at temperatures from 270° to 310°C. The black, glassy material was powdered and heated for an additional hour at temperatures from 290° to 325°C. The resulting black product was intractable.

Reaction of 3,4,3',4'-Tetraaminodiphenylsulfone with Dibiphenylisophthalate

Tetraaminodiphenylsulfone (2.783 g., 0.01 mole) and dibiphenylisophthalate (4.705 g., 0.01 mole) was treated exactly as above. The resulting product appeared to be the same material as obtained in the above reaction.

Polymerization of 3,4,3',4'-Tetraaminodiphenylsulfone and Diphenylisophthalate in Solution

1. "Aroclor"-1254

Diphenylisophthalate (3.18 g., 0.01 mole) and tetraaminodiphenylsulfone (2.78 g., 0.01 mole) were dissolved in 50 g. of "Aroclor"-1254 and heated to 260° under nitrogen for four hours. The solution darkened and after cooling was diluted with 100 ml. of benzene and filtered. The brown solid obtained proved to be impure 3,4,3',4'-tetraaminodiphenylsulfone starting material. No polymeric materials were isolated.

2. p-Phenylphenol

The reaction described above was repeated except that 25 g. of p-phenylphenol were used in place of "Aroclor". Heating was maintained at 250° for 4 hours under nitrogen. The deposit of water droplets on the condenser walls indicated that some reaction was taking place but, after cooling, the entire reaction mixture dissolved in methanol and no polymeric materials were isolated.

Reaction of 3,4,3',4'-Tetraaminodiphenylsulfone and Isophthaloyl Chloride in Hexamethylphosphoramide

Tetraaminodiphenylsulfone (2.783 g., 0.01 mole) and isophthaloyl chloride (2.030 g., 0.01 mole) was dissolved in HMFA (35 ml.) with rapid stirring. After 15-30 minutes the solution viscosity increased and gel formation was apparent. After one hour the reaction mixture was poured into 300 ml. of methanol, filtered and washed with additional methanol. The resulting off-white solid did not melt up to 400°C. and exhibited characteristic amide absorption in the infrared region.

Methylation of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole (3.1 g., 0.01 mole) was dissolved in DMAc (80 ml.). To this solution was added a 47% dispersion of sodium hydride in mineral oil (7.0 g.). The reaction flask was then fitted with a drying tube and the mixture stirred for 1.5 hours in an ice bath before the dropwise addition of methyl iodide (total 30 g.) was begun. After this addition was complete, stirring was continued until the reaction mixture and ice bath warmed to room temperature. After addition of water (150 ml.) the brown solid polymer was filtered, washed several times with water, methanol, and ethyl ether and dried in the vacuum oven at 165°. The polymer had an inherent viscosity of 1.44 in formic acid. Infrared absorption bands at 2.90 μ (free N-H) and 3.40 μ (C-H stretching) suggest that the polymer is highly methylated. The N-methylpolybenzimidazole was obtained in 85% yield (3.0 g.). It does not melt but does soften slightly at 400°.

Phenylation of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

The procedure described above was followed using iodobenzene in place of methyl iodide. Infrared absorption band at 3.1 to 3.3 μ (N-H) indicates that phenylation was negligible.

Preparation of N,N'-Diacetyl-4,4'-diaminodiphenyl Ether

4,4'-Diaminodiphenylether (50 g., 0.25 mole) was dissolved in pyridine (450 ml.) and the mixture was cooled to 5°. Acetic anhydride (50 ml.) was added to the mixture dropwise with stirring. After addition was complete, the reaction mixture was warmed to room temperature and allowed to stand overnight. The white solid which separated was filtered, washed with water, and dried to yield 35 g. (50% yield) of N,N'-diacetyl-4,4'-diaminodiphenylether, m.p. 242°.

The preparation of this tetraamine was carried out according to directions received by private communication from the laboratory of C. S. Marvel. 4,4'-Diacetylamino-diphenylether was nitrated with acetylnitrate to yield 3,3'-dinitro-4,4'-diacetylamino-diphenylether which after hydrolysis in alcoholic potassium hydroxide and subsequent hydrogenation with Raney nickel catalyst afforded the desired 3,3',4,4'-tetraaminodiphenylether, m.p. 123-124°C.

Polymerization of 3,3',4,4'-Tetraaminodiphenylether and Diphenylisophthalate

Diphenylisophthalate (3.18 g., 0.01 mole) and 3,3',4,4'-tetraaminodiphenylether (2.30 g., 0.01 mole) were placed in a 240° bath under nitrogen. The resulting melt turned black almost immediately. Heating was continued for several hours and the temperature was gradually raised to 310°. There was never any indication of phenol or water evolution.

Hydrolysis of 4,4'-Dicarbomethoxydiphenylsulfone

To 80 ml. of a 10% aqueous KOH solution was added 4,4'-dicarbomethoxydiphenylsulfone (10 g.). The reaction mixture was refluxed for 2 hours before cooling and diluting with 100 ml. of water. After filtering the reaction mixture was acidified with conc. HCl. The resulting white precipitate was filtered and washed with water until neutral washings were obtained to yield after drying 9.0 g. (quant.) of 4,4'-dicarboxydiphenylsulfone, m.p. 370°.

Preparation of 4,4'-Dicarbophenoxydiphenylsulfone

Three grams of 4,4'-dicarboxydiphenylsulfone were dissolved in dry pyridine (35 ml.). To this mixture was added phenylsulfite (11.5 g.) (3) and the mixture heated 2 hours on the steam plate. After standing overnight, the reaction mixture was diluted with 35 ml. of water and acidified with conc. HCl. The resulting gum-like solid was filtered and washed repeatedly with ethyl ether to yield 3.0 g. (65% yield) of 4,4'-dicarbophenoxydiphenylsulfone m.p. 220-223° after recrystallization from ether-benzene.

Polymerization of 4,4'-Dicarbophenoxydiphenylsulfone and 3,3'-Diaminobenzidine

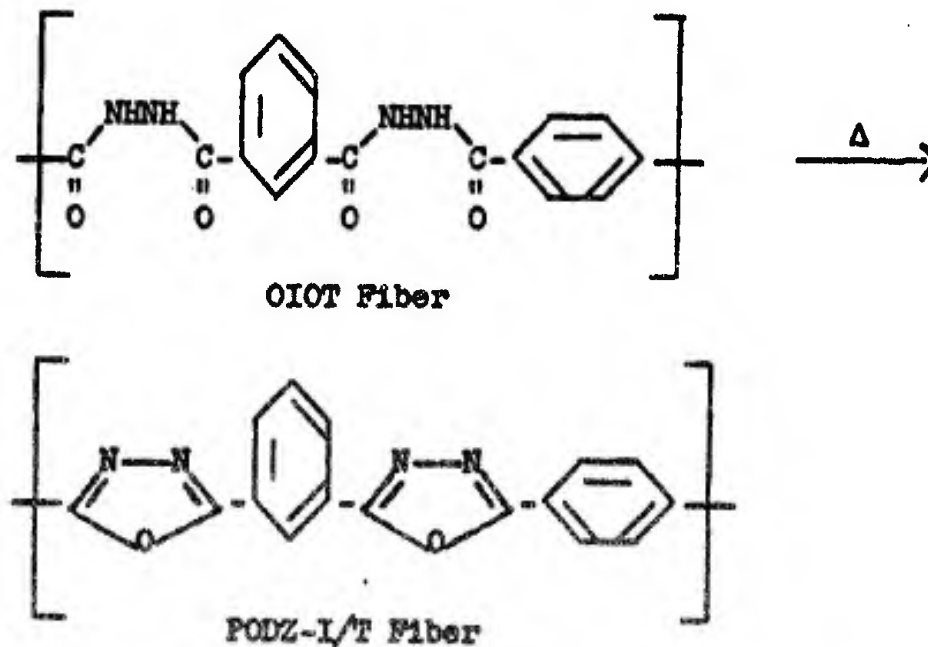
3,3'-Diaminobenzidine (1.07 g., 0.005 mole) and 4,4'-dicarbophenoxydiphenylsulfone (2.29 g., 0.005 mole) were melted in a 250° bath under nitrogen. Polymerization commenced at about 250-260° with evolution of water and phenol. The temperature was raised to 290° and heating continued until the melt set up to a solid glassy mass. The glass was broken up and reheated at temperatures ranging from 290-380° for 3 hours under vacuum (0.05 mm Hg). The yield of polymer was 1.54 g. (70%) of yellow-brown material which does not melt up to 400° and is soluble in formic acid.

III. Poly-1,3,4-oxadiazoles - F. T. Wallenberger

Background

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 (2) and the subsequent fabrication of this polymer into tough fibers by Frazer and Kane.

The other development was that Frazer discovered that aromatic poly[2,5-(1,3,4-oxadiazole)] fibers had superior high temperature-resistant properties as well as excellent fiber properties. The fabrication of these fibers was accomplished by a unique cyclodehydration of polyhydrazides in fiber form at elevated temperatures. This fiber conversion is presently the only route to poly(1,3,4-oxadiazole) fiber. There are two other synthetic routes that lead to bulk polymer (4a, b), but lack of appropriate polymer solvents and infusibility of most poly(oxadiazoles) precludes fabrication of films and fibers.



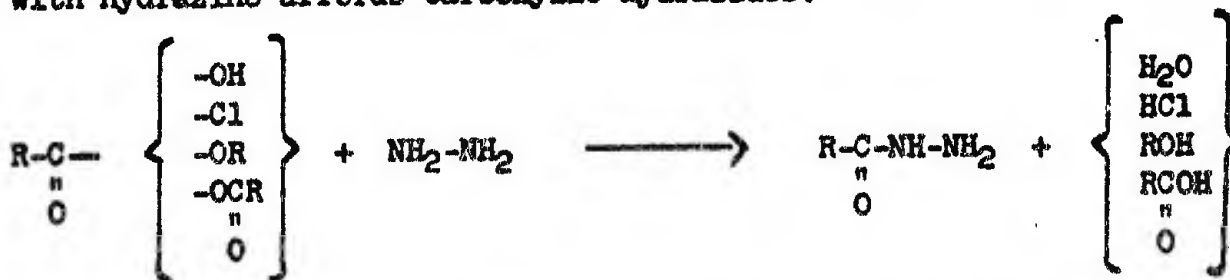
One polyoxadiazole fiber, namely, poly[1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole)] (50:50), PODZ-I/T, showed most promising thermal stabilities. It is obtained by cyclodehydration of the alternating polyhydrazide derived from terephthaloyl chloride and isophthalic dihydrazide.

This fiber conversion should be quantitative from the chemical standpoint in order to afford the desired high-temperature properties, and it 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 still unconverted polyhydrazide links. Finally, possible side reactions, as noticed by Stolle (5a) and Pellizzare (5c), for the thermal cyclodehydration of dibenzoylhydrazine may also prove to be detrimental in attaining polyoxadiazole fibers with optimum fiber properties and optimum thermal stabilities.

Thus, it was not unexpected that reproducibility of this unique polymer reaction (in fiber form) was extremely difficult and required research under most accurately defined reaction conditions, and this report summarizes our present knowledge of polyoxadiazoles, polyhydrazides, polyhydrazide chelates, and of model compounds.

Polyhydrazides

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

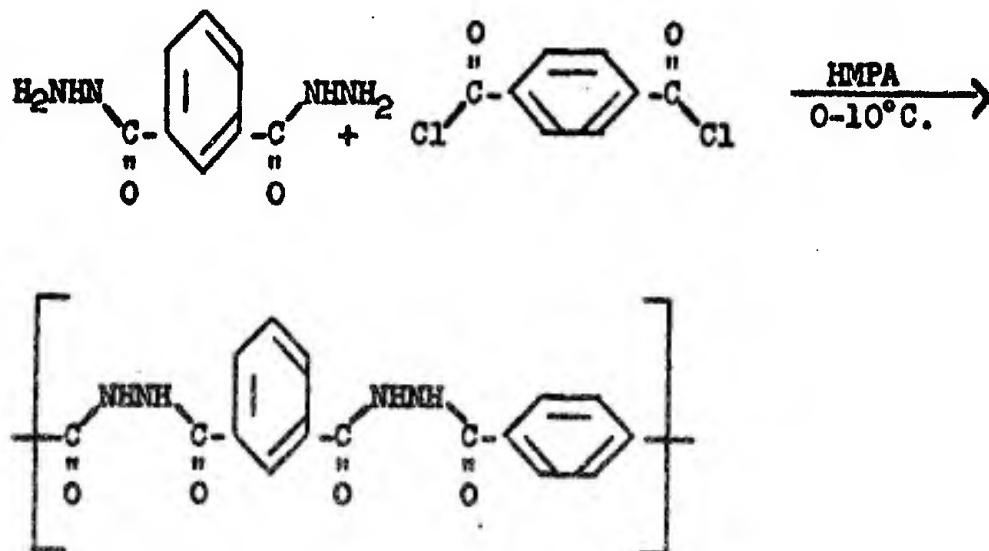


The reaction of esters with hydrazine or 85-100% hydrazine hydrate is regarded to be quantitative while the other acid derivatives frequently lead to undesirable mixtures of mono-, di-, tri-, and tetraacyl hydrazines. Diesters, when treated with hydrazine hydrate in alcohol, yield nearly quantitatively the desired dihydrazides which are polymer intermediates (8).

1. Preparation of Bulk Polymer

Low temperature polymerization of equimolar amounts of dihydrazide and carbonyl chloride in amide solvents, such as hexamethylphosphoramide (HMPA), N-methylpyrrolidone (NMP), containing 2-5% lithium chloride was found to be the only preparative method (6) that consistently yielded high molecular weight polyhydrazides. Preparative methods (7) found in the patent literature did not yield high molecular weight polyhydrazides which could be fabricated into films and fiber.

Thus, OIOT was prepared from equimolar amounts of isophthalic dihydrazide and terephthaloyl chloride in amide solvents, such as hexamethylphosphoramide (HMPA) or N-methylpyrrolidone (NMP). The reaction proceeds at room temperature (or below) and high molecular weight polymer is attained after 4-16 hours of reaction. The polymer, precipitated with water or methanol, has inherent viscosities (η_{inh}) in dimethyl sulfoxide (DMSO) ranging from 0.5-1.50. The preferred preparative solvent is hexamethylphosphoramide.



Since the resulting polyhydrazides often contain small amounts of ash after combustion, it is advisable to carry out the polymerization in polyethylene flasks and with "Teflon"*

*Trademark for Du Pont's TFE-fluorocarbon fiber.

stirrers. Further washings with distilled and deionized water are in order to prevent facile chelation of hydrazide links with metal ions.

2. Fabrication of Fibers

Two spinning solvents have been used during this study, dimethyl sulfoxide (DMSO) and dimethyl acetamide (DMAc). The latter solvent allows spinning at lower temperatures, hence provides for milder operating conditions.

One batch of OIOT, $\eta_{inh} = 1.03$ (DMSO), was spun from DMSO (25% solids) and drawn 2X at 10 lbs. of steam, dried and redrawn 1.2X at 310°C. over a hot plate. As-spun yarn (T/E/M₁ = 1.8/117/41) was thus oriented (T/E/M₁ = 3.2/27/61) and finally crystallized (T/E/M₁ = 5.2/24/80). A one-year old sample ($\eta_{inh} = 1.6$) of an oriented yarn (T/E/M₁ = 3.5/38/69) would not allow redrawing and was not further investigated. A further batch, prepared in HMPA and spun from DMSO has been more thoroughly evaluated with respect to fiber properties, which are given in Table IV.

Alternatively, DMAc may be used as spinning solvent. Results are also contained in Table IV. Use of this solvent allows higher draw ratios, and lower spinning temperatures. When preparing DMAc solutions, excessive heating should be avoided since the polymer precipitates at about 120-130°C.

A number of spins were carried out with DMAc containing 2 or 5% LiCl as solvent. The advantage of this modified solvent is that solution commences more smoothly than in straight DMAc and that yarn with high moduli can be obtained. Results are also listed in Table IV.

Spinning of OIOT from DMSO customarily affords fiber with a dark yellow color, particularly after redrawing at 300°C. This may be attributable to the onset of conversion or to degradation. Even yarn obtained from DMAc was slightly yellow colored. To avoid this discoloration altogether, it was necessary to carry out the spinning operation with DMSO under nitrogen. Perfectly white yarn resulted after drawing at 100°C. and redrawing at 320°C.

TABLE IV
POLYHYDRAZIDE (OIOT) FIBER PROPERTIES

Spinning solvent/additives % Solids Spinning & column temp. °C. Draw ratio/°C. Redrawn/°C.	DMSO*/none 25 125/214 2X; 10# steam -	DMAc**/none 25 105/220 2X; 10# steam -	1.2X; 310	4.9/24/94 5.4 1.9/6.3 4.7 2.9/10/56 7.4	3.3/20/76 6.2 1.6/5.5 5.5 2.3/9/52 7.1	34/33/36 27/35/39 65/64/78 55/62/67 140	33/17/18 31/18/16 63/35/35 62/38/34 130	39/23/24 42/29/31 68/45/47 71/56/58 145	low/low med. 305° >370°
Ten. (T), % Elong. (E), Mod. (MI) Denier Loop T/E/MI Denier Knot T/E/MI Denier Elevated T/E/MI (90°C. air) Denier Work Recovery, WR, 3% [RT/RT wet/90°C. wet] Work Recovery WR, 5% Ten. Recovery TR, 3% [RT/RT wet/90°C. wet] Tensile Recovery TR, 5% Wash-Set Recovery Angle X-ray crystal. (amt./perf.) X-ray orient. (degrees) Fiber Stick Temperature, FST, °C. Melting Point °C.									

TABLE IV (CONT'D.)

POLYHYDRAZIDE (OIOF) FIBER PROPERTIES

Spinning solvent/additives % Solids Spinning & column temp. °C. Draw ratio/°C. Redrawn/°C.	DMAC/5% LiCl		DMAC/2% LiCl	
	20	2.25X; 10# steam	21	2.25X; 10# steam
Ten. (T), % Elong. (E) Mod. (MI) Denier	1.3/89/44 8.8	4.1/12/106 4.3	3.7/8.6/112 3.7	4.7/4.4/169 2.6
Loop T/E/MI Denier	1.1/78/35 9.8	0.3/0.8/52 4.4	0.7/0.7/64 3.5	0.3/0.6/50 2.6
Knot T/E/MI Denier	1.3/96/16 9.7	1.4/2.2/68 4.0	1.1/3.0/45 4.6	0.5/4.2/94 2.4
Elevated T/E/MI (90°C. air) Denier	1.8/90/38 8.7	4.8/19/92 4.3	4.9/13/78 3.8	
Work Recovery, WR, 3% [RT/RT wet/ 90°C. wet]	32/11/6 17/8/4	42/23/17 40/28/18	41/36/33 43/41/43	49/38/38 50/49/50
Work Recovery, WR, 5% Tensile Recovery, TR, 3% [RT/RT wet/90°C. wet]	66/29/17 44/20/12 85	75/48/39 72/59/45 90	72/67/50 72/72/72 185	78/68/64 78/77/76 195
Tensile Recovery, TR, 5% Wash-Set Recovery Angle X-Ray Crystal. (amt./perf.) X-Ray Orientation Density (fiber) Fiber Stick Temperature FST, °C.	trace - -	low/low 61° - 305°C.	low/low 56° -	med./med. 40° (med.) 1.4529

To even further broaden the scope of attainable OIOT properties prior to conversion, it was of interest to study the effects of heat setting on tenacity and x-ray crystallinity. The results are tabulated in Table V.

TABLE V
HEAT SETTING OF OIOT YARNS

<u>Fiber</u>	<u>T/E/M₁ Before</u>	<u>T/E/M₁ After</u>
1) Drawn (oriented)	3.2/27/61	3.7/19/85
2) Redrawn (oriented and crystalline)	6.0/8/151	6.8/10/147

This treatment enhanced crystallinity and tenacity of the two fibers to high levels.

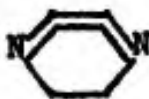
It may be seen that proper choice of spinning, drawing and heat setting conditions [Tables IV and V] makes it possible to obtain OIOT with tenacities ranging from 3 to 7 gpd., with elongations ranging from 4-27% and with moduli ranging from 60-169.

This study, therefore, affords a great variety of yarns with various combinations of properties, each of which may be critical in attaining optimum properties of PODZ-I/T fiber after conversion.

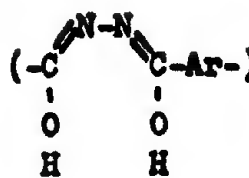
3. Stabilization of Polyhydrazide Enolates

Polyhydrazides, in basic solution, exhibit an intensely yellow color (presumably due to conjugation in the enol form) as has been discussed already (6). When films or fibers are exposed to tertiary amines, similar color changes occur. As the amine evaporates (on drying or prolonged exposure to air) the color disappears and the sample becomes colorless. "Dabco"*, a tert. amine, was added to polyhydrazide films and fibers, accomplishing a permanent and irreversible color change to yellow. Fibers in this form were studied to see if the enol form is easier converted into PODZ than the normal structure.

*Trademark for Houdry Processing Corp.'s catalyst.



"Dabco", Diazabicyclooctane



Enol Form

4. Ultraviolet Stability

Polyhydrazide films cast from DMAc or from HMPA showed no color break up to 1000 hours in the Fade-Ometer.

Samples of OIOT in its yellow form, stabilized by "Dabco" were exposed to the Fade-Ometer. While no color break occurred, the sample became brittle in less than 200 hrs. of exposure.

5. Solvent Retention

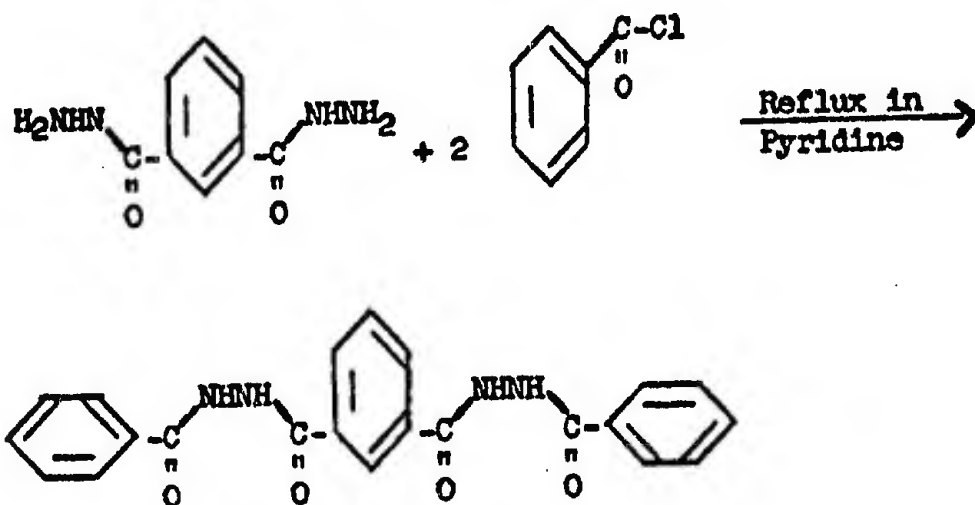
OIOT films have been cast from various solvents. Films cast from DMSO produced large amounts of odors attributable to DMS, DMSO₂ and DMSO when heated to 180-350°. In order to remove the solvent, the films were soaked in boiling water for one week and dried at 80°C. (vac.) for one week. After this treatment, up to 5% sulfur was still contained in the film samples as evidenced by microanalysis. Such solvent retention in OIOT fibers may cause degradation when the fiber is redrawn and crystallized at 300°C. prior to conversion into polyoxadiazole fiber.

OIOT films, cast from hexamethylphosphoramide (HMPA), which is the preferred preparative solvent, occasionally contained up to 1% solvent (as calculated from phosphorous analysis) even after drying for 72 hrs. at 80°C. (vac.). Films cast from DMAc did not show such drastic solvent retention.

6. Model Compounds

The delicate balance of reaction conditions by which polyhydrazides are converted into polyoxadiazoles made it necessary to prepare a number of pertinent model compounds which contain the hydrazide link for evaluation.

These model compounds are reproduced in Table VI. Examples H-1 and H-2 are dihydrazides. Examples H-3, H-4 and H-5 are oligohydrazides (in analogy to polyhydrazides) which are ready to undergo cyclodehydration and yield oligooxadiazoles. Dihydrazides are prepared by refluxing the appropriate dialkylester with hydrazine hydrate in ethylalcohol (8). The series of oligohydrazides, which are di-sec. hydrazides, is prepared (9,10) in pyridine solution by reaction of a dihydrazide with a suitable carbonyl chloride.

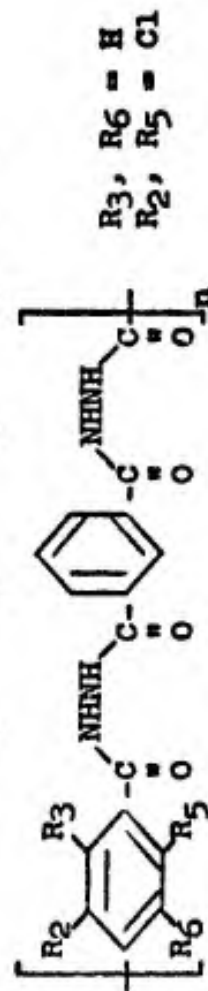
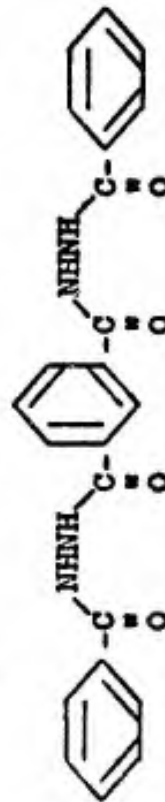
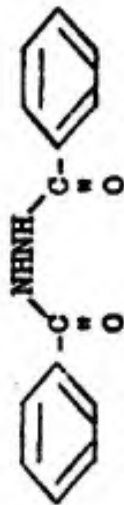
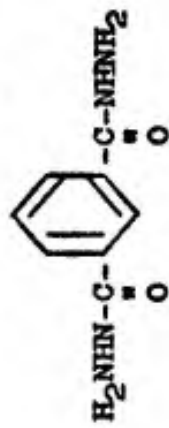


The substituted polyhydrazide, H-6, thought capable of sterically facilitating cyclodehydration, was obtained from 2,5-dichloroterephthaloyl chloride and isophthalic dihydrazide in equimolar amounts. Hexamethylphosphoramide was the solvent without addition of inorganic salts.

Chelating Properties of Polyhydrazides

Polyhydrazides, in analogy to simple monomeric hydrazides (11), readily undergo chelation with a host of inorganic salts. When it was noticed that even carefully prepared polyhydrazides contained 0.2 to 2.0% ash after combustion, it was apparent that such salts might be detrimental and prevent complete cyclodehydration into polyoxadiazoles. A study designed to eliminate this trace chelation simultaneously led to experiments described here, which might possibly open up a new area of investigation, if utility for OIOT/chelate films or fibers can be found.

TABLE VI
OLIGOHYDRAZIDES



1. Preparation of Chelate Films

Initial chelating studies of OIOT polymer were carried out with film because of greater ease of handling. A OIOT/HgCl₂ chelate film which was prepared was completely transparent, colorless and could be dried in vacuum at 80° over the week-end without change of appearance. When heated at 80° in an air atmosphere, this film turned brown. The original HgCl₂/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.

Other metal salt chelate polymers of OIOT were prepared but films could not be cast, owing to their insolubility in various solvents.

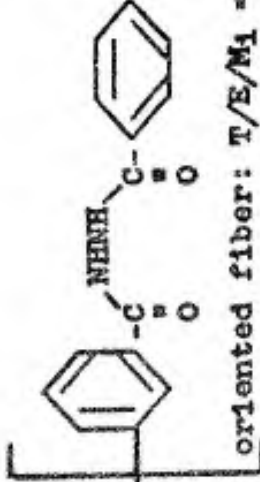
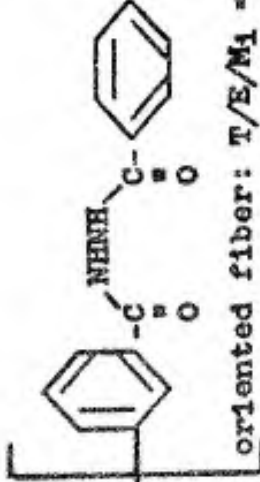
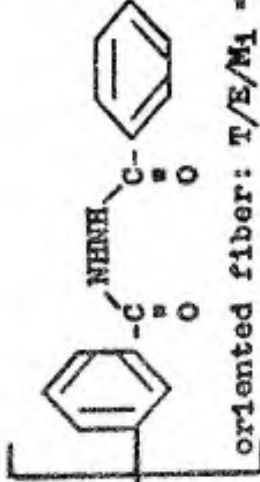
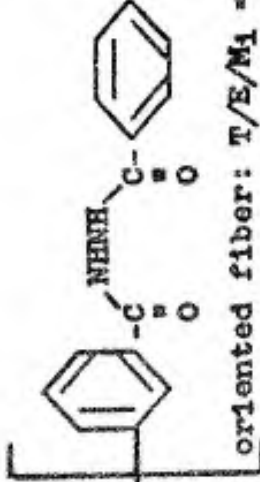
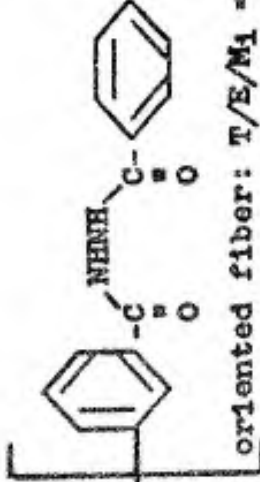
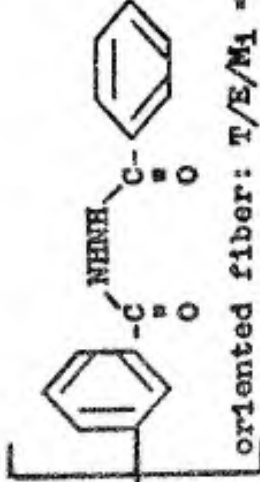
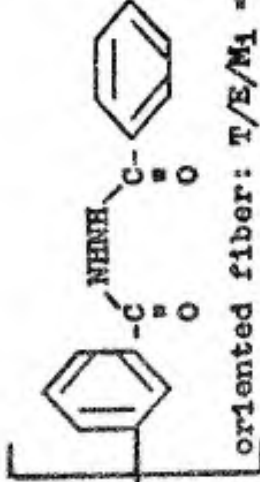
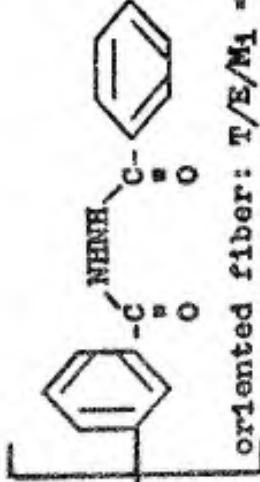
Chelation of OIOT films occurred, however, readily on aluminum plates or on brass plates. The film cast on brass adhered well for 4 hours in boiling water. Discoloration of the OIOT occurred simultaneously which is indicative of a picking up of metal ions. A film of OIOT cast on aluminum could not be 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 in water. This interesting adhesion is possibly due to a polymer-to-metal self-bonding.

2. Fabrication of Chelate Fibers

Such chelate properties of films and fibers may lead to interesting applications in the field of high temperature materials. Chelated OIOT fibers might possibly afford a new class of high temperature-resistant fibers. Such fibers which carry metal salts could be further treated by reducing the metal salts to Me⁰.

OIOT fibers were, therefore, chelated in a DMF bath containing about 10-15% of metal salt. In some cases, a small amount of tertiary amine, e.g., N,N'-dimethyl aniline, was added to make the salt bath more basic. This generally resulted in less extensive chelation.

TABLE VII
POLYHYDRAZIDE/CHELATE FIBER PROPERTIES

Sample	Chemical Structure		Metal Salt	Color of Dry Yarn	T/E/M ₁ ***	Crystallinity of Yarn/Additive
	DMP Bath (I)	Bath II				
3		-	oriented fiber: T/E/M ₁ = 3.2/27/61	Dk. green	0.5/16/22	Amorphous/Amorphous
4		-		Lemon	1.1/96/38	Amorphous/Crystalline
6		-		Straw	0.7/5/32	Amorphous/Cryst. (random)
7-I		DMA*		Black [Ag°]	0.9/65/34	Amorphous/Crystalline
7-II		DMA*		Dk. grey [Ag°]	1.3/99/36	Amorphous/Crystalline
9		DMA*		Silvery [Ag°]	1.3/101/36	Amorphous/Trace Cryst.
10		-		Olive	1.2/82/37	Amorphous/Amorphous
11		-		Green	1.2/90/38	Amorphous/Trace Cryst.

* N,N'-Dimethylaniline

** Short contact time

*** Reference: T/E/M₁ = 1.8/118/41, undrawn, amorphous OIOT

When oriented (drawn) fiber (T/E/M₁ = 3.2/27/61) was used, the fiber properties, after chelation, as shown in Table VII appeared to correspond to those characteristic of unoriented (as-spun) OIOT fiber (T/E/M₁ = 1.8/118/41) with no indication of x-ray orientation.

Ions such as cobalt, chromium, silver, tin, and copper have been used in this exploratory investigation. A special case, however, seemed to result when AgNO₃ was used as metal salt. In DMF, chelation results in a straw colored OIOT/AgNO₃ fiber. When this fiber is run through a subsequent N,N'-dimethyl aniline bath, the tert. amine, surprisingly, will reduce AgNO₃ on OIOT to give Ag⁰/OIOT, with fibers having a silvery, grey, or black appearance depending upon conditions, such as temperature, exposure time and concentration of solutions.

The change in yarn properties and the reversion of oriented to amorphous yarn (Table VII) was paralleled by a similar property change when crystalline and oriented (drawn and redrawn) OIOT fiber was chelated (Table VIII; 27, 28). The chelated yarn, in this instance, had lost its original crystallinity, and appeared to correspond to oriented (drawn) OIOT fiber (T/E/M₁ = 3.2/27/61) with respect to fiber properties.

TABLE VIII

HIGH TENACITY CHELATE FIBERS

	<u>CoCl₂-Bath</u>	<u>OIOT Fiber</u> <u>T/E/M₁</u>	<u>Chelate Fiber</u> <u>T/E/M₁</u>	<u>Crystallinity</u> <u>of Additive</u>	<u>Color</u> <u>of Fiber</u>
27	DMF	5.2/24/80	2.3/15/55	+	Green
28	DMF + DMA*	5.2/24/80	3.4/27/59	trace	Olive
29	DMF + DMA*	1.0/96/39	0.8/100/39	+	Green

*DMA, N,N'-dimethyl aniline.

A sample of as-spun (amorphous) OIOT fiber was also chelated (Table VIII, 29). It retained all its fiber properties.

High temperature stability might result if these high tenacity chelate fibers were reduced to OIOT/Me⁺ fibers.

3. Reaction with Alkoxides

During the course of investigations on polyhydrazides, it was noticed that OIOT gave highly viscous and partly swellable solutions when treated with alkoxy derivatives such as sodium methoxide or aluminum isopropoxide. When a 1% solution of OIOT in dimethyl sulfoxide was warmed to 70°, an unusual viscous gel-like mass resulted. No change in appearance resulted on standing for over 2 days at room temperature. Evaporation on a steam bath resulted in a continuous film which was yellow in appearance and did not melt below 400°C. After drying in a drying oven overnight, it was analyzed and shown to contain 30% ash.

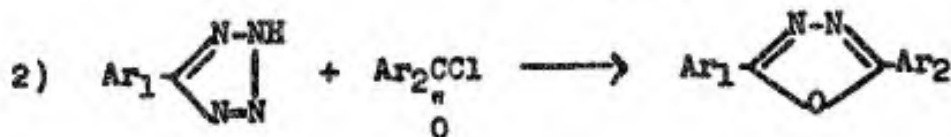
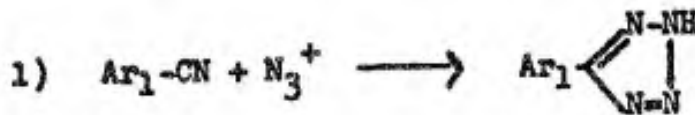
A similarly viscous solution resulted by treating a 1% solution of polyhydrazide in dimethyl sulfoxide with sodium methoxide. However, in this instance, a brown solid precipitated. It was washed with ethanol and dried. Microanalytical analysis showed it to contain 20.2% ash.

A structural analysis of both metal alkoxide derivatives of OIOT has not yet been successful.

Poly(1,3,4-oxadiazoles) and Fiber

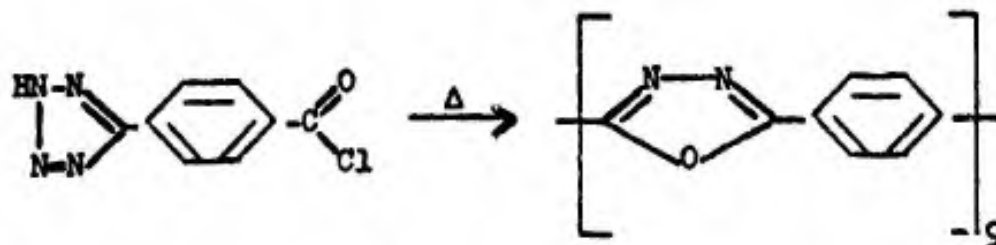
1. Synthetic Routes to Bulk Polymer

Huisgen and coworkers have reported extensively (12,13) on the reaction of tetrazoles with acid chlorides. It gives 1,3,4-oxadiazoles. He successfully



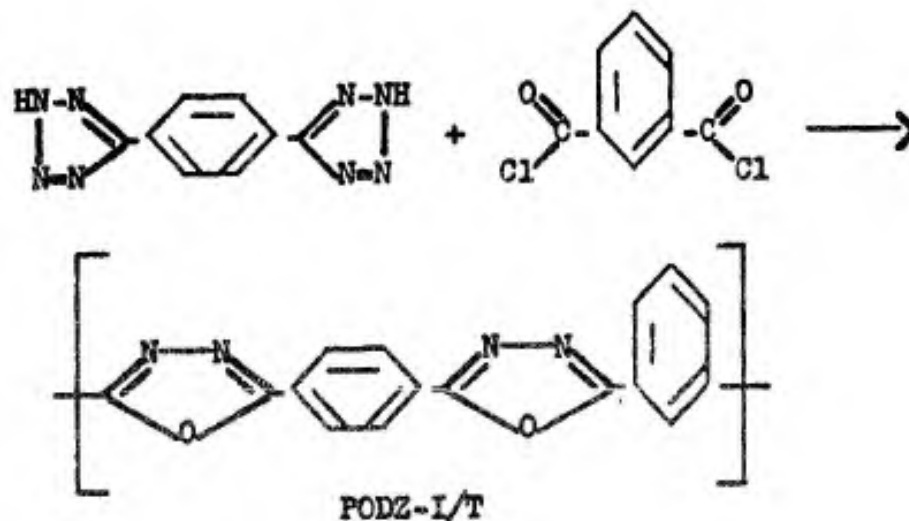
made oligocyclic oxadiazoles, including one consisting of a nine-membered ring system with alternating p-phenylene rings and oxadiazole rings. This reaction has been used to prepare a number of model compounds for PODZ-I/T as described in a later section.

Huisgen and coworkers attempted preparation of polyoxadiazoles (13) by the following variation of the initially explored reaction.



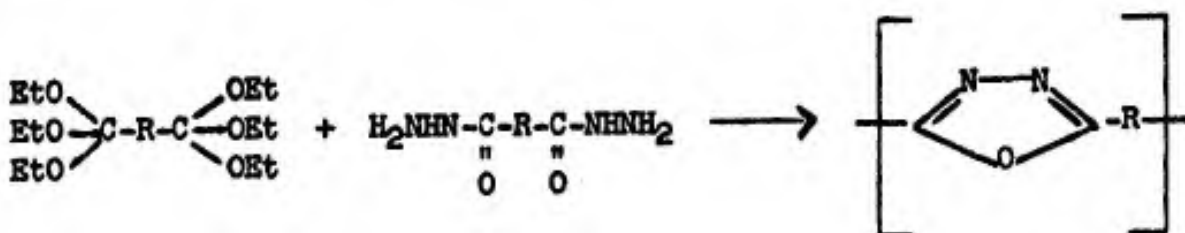
The resulting product resembled the 9-membered oligo-oxadiazole but could not be recrystallized. This polymerization was, therefore, not further pursued.

Abshire and Marvel (4) have reported the preparation of several aromatic polyoxadiazoles from ditetrazoles and diacid chlorides in inert solvents. This type of preparation was repeated



using amide solvents such as hexamethylphosphoramide in the hope that higher molecular weight polymer would result. A few experiments using this route yielded polyoxadiazole with viscosities lower than 0.3 (in sulfuric acid).

Another method for preparing polyoxadiazoles was briefly studied. It involves reaction of bis-ortho esters and dihydrazides in accordance with the monomeric model reaction reported by Ainsworth (14).



The preparation of bis-ortho esters can be carried out by treating diiminoesters with absolute alkanols according to monomeric model reactions (15). Three diiminoester hydrochlorides (16,17) have been prepared. They are: dimethyl iminosuccinate, diethyl iminosuccinate, and diethyl iminoisophthalate. The diethyl ortho-succinate has been prepared with great difficulty in reasonably pure form and reacted with isophthalic dihydrazide. No high polymer resulted.

2. Polyoxadiazole Bulk Polymer from OIOT

The inaccessibility of high molecular weight polyoxadiazoles by above routes, the lack of solvents for such polymers and the excellent synthesis of high molecular weight polyhydrazides discovered by Frazer made OIOT and its fibers the potential intermediate for PODZ-I/T.

The cyclodehydration of monomeric model reactions 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.



Hence, several types of conversions were studied and are described in the following paragraphs. Thermal conversion of polyhydrazide fibers is described in a later chapter.

Conversion of polyhydrazide bulk polymer at elevated temperatures was studied by heating a finely ground (40 mesh) sample of OIOT for 48 hrs. at 283° (0.4 mm.). The resulting PODZ-I/T bulk polymer analyzed correctly 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. Steam at this temperature did not effect cyclization and 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 (19) had reported that symmetrical aromatic dihydrazides could be converted into 2,5-disubstituted 1,3,4-oxadiazoles by the reaction of phosphoazo-derivatives of cyclohexylamine $[C_6H_{11}N=PNHC_6H_{11}]$. Thus, a 2.5% solution of OIOT in a mixture of dimethyl sulfoxide 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, washed and dried. The analytical results 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 above solution and bulk conversions was not soluble in conventional polymer solvents including trifluoroacetic acid, hence could not be fabricated into films and fibers. For this reason, it was necessary to convert polyhydrazide fibers by thermal conversion into polyoxadiazole fibers.

3. Conversion of Fiber in Vacuum

This study was designed to furnish information about the dehydration-cyclization mechanism in conjunction with fiber properties. The goal was to find optimum conversion conditions. Such conversions were carried out with polyhydrazide (OIOT) fibers at 222°, 242°, 265° and 283°C., whereby the fiber samples were wound around small perforated metal bobbins. These bobbins were placed in a tube which was evacuated and then heated in solvent vapors corresponding to above boiling points. A sample of bulk polymer (40 mesh) was likewise converted at 283° (vac.).

For fiber conversions, OIOT yarn (T/E/M₁ = 5/24/80) was used. Samples of individual runs, comprising 3-6 bobbins, were periodically withdrawn in order to follow the conversion with time.

The withdrawn samples were analyzed (T/E/M₁, ϵ_0 , IR) and showed the following results which are typical for this type of conversion.

No conversion occurred at 222° within 72 hrs. as evidenced by virtually unchanged oxygen analyses. However, the yarn properties changed from T/E = 5.2/20 to 2.6/9.

At 242° there was a slow conversion, estimated by oxygen analysis to be 50% in about 48 hrs. The yarn properties gradually changed from T/E = 5.2/20 to 1.9/5.

At 265° the yarn conversion proceeded with noticeable rate but within 30 hrs. the yarn properties had changed from T/E = 5.2/20 to 0.7/0.6. After 72 hrs. at 283° the same result (T/E = 1.0/1.0) was observed with nearly complete conversion to PODZ.

Conversion studies in vacuum were cumbersome and gave inhomogeneous fiber samples after conversion.

4. Conversion of Fiber in Solvent Vapors

It was believed that conversion in solvent vapors at temperatures ranging from 270-290°C. would provide better conversion conditions because of better heat transfer. Thus, a number of conversions were carried out in refluxing diphenylmethane, 265°C., and diphenylethane, 283°C. Because of the known chelating tendency of polyhydrazides, the conversion of skeins of OIOT was carried out on "Teflon" bars, thus avoiding glass rods or metal bobbins. A larger sample of OIOT, after conversion at 265°, was used for thermal stability studies which provided a second heating cycle. The initial polyoxadiazole properties are given in Table IX.

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

Ten. (T), % Elong. (E), Mod. (M ₁)	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°
Oxygen Analysis (Theor. 11.10%)	12.1%

Throughout the investigation it was noticed that micro-analytical data are not as reliable as would be desirable. Incomplete combustion or actual presence of ash of unknown origin would require a detailed analytical study.

When microanalytical results begin to indicate completion of conversion (with consistently high oxygen values) data such as those shown in Table IX are characteristic for initial

polyoxadiazole fiber properties. Further heating of such initial polyoxadiazole fibers at 280° or, more efficiently, at 300-400°C. slightly changes initial properties, T/E/M₁ = 2.6/3.1/124 to final properties, T/E/M₁ = 1.0/1.0/109 which then no longer change on continued heating, but still show high oxygen values and occasionally ash of undetermined origin.

5. Conversion of Fibers in Nitrogen

In order to obtain large samples and to circumvent the cumbersome procedure of exposing fibers to solvent vapors (whereby solvents quite often show signs of degradation), it was decided to use muffle furnaces (with N₂ leads) for conversion of OIOT fibers at 280°C.

Hence, a great variety of polyhydrazides was converted. Small or large samples were placed in furnaces and allowed to react for periods usually in excess of 2 days, until microanalytical data showed constant values as sign of complete conversion.

Only a few representative samples, as shown in Table X, indicate that conversion proceeds to the initial polyoxadiazole fiber.

TABLE X
INITIAL POLYOXADIAZOLE PROPERTIES

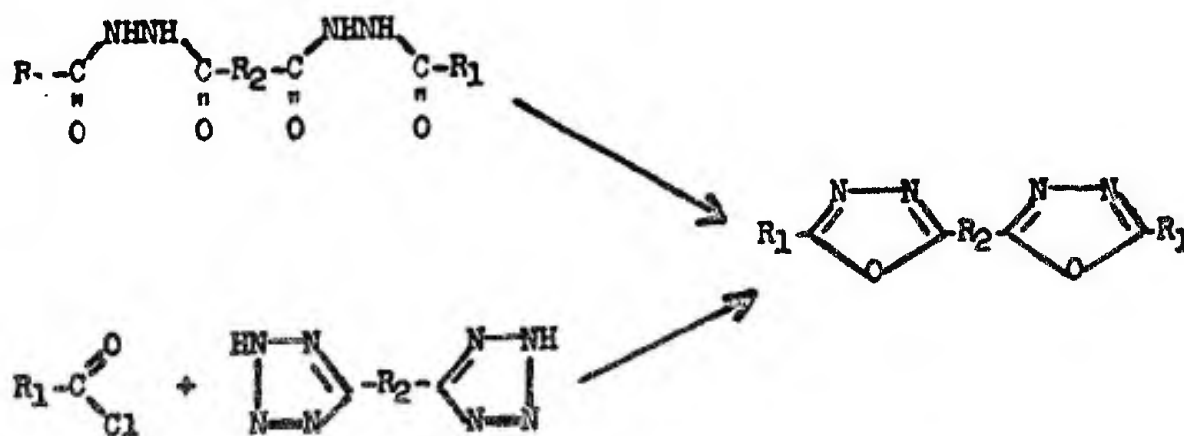
	<u>T/E/M₁/Den.</u>	<u>O%</u>	<u>Note</u>
29	2.6/3.1/124	12.10	Converted in boiling diphenylmethane 273°C.
49-1	2.8/3.6/104/3.9	13.38	Converted in nitrogen at 280°C. (furnace).
49-3	2.4/6.6/102/3.5	12.40	Converted in N ₂ at 280°C.
49-4	3.0/3.2/149/2.8	11.89	Cyclized in furnace (N ₂ , 280°C.). Sample contained ash.
70-2	3.2/7.4/140/3.5	12.20	Courtesy W. Sweeney and C. Smullen. Sample contained ash.

Further heating at 300-400°C., in analogy with above-mentioned cases, produces final polyoxadiazole properties ($T/E/M_1 \sim 1.0/1.0/90$) as will be discussed in conjunction with thermostability studies in a later section.

Thus, conversions in muffle furnaces at 280°C. represent the most suitable means of converting polyhydrazide fibers into polyoxadiazole fibers. While some improvements can be visualized, such as better conversion control with standardized analytical methods, there appears to be much reason to believe that these properties are representative of polyoxadiazole fibers derived from all-aromatic polyhydrazide fibers. Since PODZ-I/T effectively represents a polyphenyl analogue, its fibers are expected to possess high chain stiffness, as expressed by low elongations and high moduli.

6. Model Compounds









Oligo-oxadiazoles have been prepared as model compounds for thermal stability studies of PODZ-I/T. Generally there are two possible synthetic approaches. One utilizes the ring closure of hydrazides to give oxadiazoles, the other makes use of the Huisgen reaction (12,13), i.e., the reaction of tetrazoles with acid chlorides.



Thus, unsubstituted model compounds for PODZ-I/T (coded O-1 to O-8) were prepared accordingly (Table XI). The lower members (3 to 5 rings) were conveniently prepared from

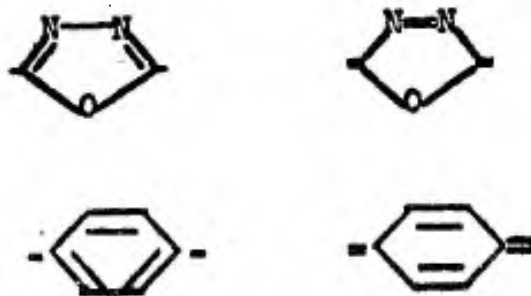
TABLE II

UNSUBSTITUTED OLIGO-CHLADIAZOLES

Olefin	Structure	Formula and Mol. Wt.	Analysis					UV Spectra			Fluorescence Spectra	
			C, %	H, %	N, %	O, %	M.P., °C	λ_{max} , m μ	log ϵ	Solvent	Fl. λ	Int. Solvent
0-1		$C_6H_6N_2$ 106.12	Calcd: 65.74	4.14	19.17	10.95	(37) ¹² 247.5	4.27	EtOH ¹²			
			Found: ref. 12									
0-2		$C_{14}H_{10}N_2O$ 222.24	Calcd: 75.67	4.54	12.61	7.20	144	280.0	4.45	DW	360	332 1.50 DW
			Found: 74.98	4.58	12.39	7.38	(136) ¹³ 280.0	4.44	EtOH ¹³			
0-3		$C_{16}H_{12}N_2O_2$ 290.28	Calcd: 66.20	3.47	19.31	11.02	(270) ¹² 298.0	4.54	dioxane ¹³			
			Found: ref.									
0-4		$C_{22}H_{14}N_2O_2$ 336.40	Calcd: 72.12	3.85	15.29	8.74	310	312.0	4.69	DW	390	365 1.05 DW
			Found: 71.60	4.10			(308) ¹³ 312.5	4.69	DW ¹³			
							383.0		Et_2O_4			
0-5		$C_{22}H_{14}N_2O_2$ 336.40	Calcd: 72.12	3.85	15.29	8.74	285.0	4.70	DW	360	340 0.80 DW	
			Found: 71.70	3.90	15.10	9.00	297.5		Et_2O_4			
0-6		$C_{24}H_{16}N_2O_4$ 404.66	Calcd: 69.72	3.39	17.11	9.78	(395) ¹³ 367.5		DW ¹³			
			Found: ref. 13									
0-7		$C_{24}H_{16}N_2O_4$ 404.66	Calcd: 69.72	3.39	17.11	9.78	303.0	4.98	Et_2O_4			
			Found: 68.90	3.38	9.42							
0-8		$C_{24}H_{16}N_2O_6$ 482.90	Calcd: 68.78	3.21	17.83	10.18	395.0	5.00	Et_2O_4			
			Found: 68.30	3.20								

oligo-hydrazides H-3, H-4, and H-5 by converting them into the corresponding oligo-oxadiazoles. The higher numbered oxadiazoles (5 to 9 rings) were prepared by the Huisgen reaction (Table XII) because synthesis and purification of the precursor-hydrazides would present a forbidding problem. Model compound O-5, a five-membered oxadiazole, was prepared by both methods with identical properties. Oxadiazoles O-7, a 9-membered model compound, and O-8, a 13-membered polyphenyl analogue (molecular weight ~ 1000) are most useful for a comparative evaluation of thermal stabilities of polyoxadiazoles and oligo-oxadiazoles (as discussed later) and for a spectral analysis (Figure 1).

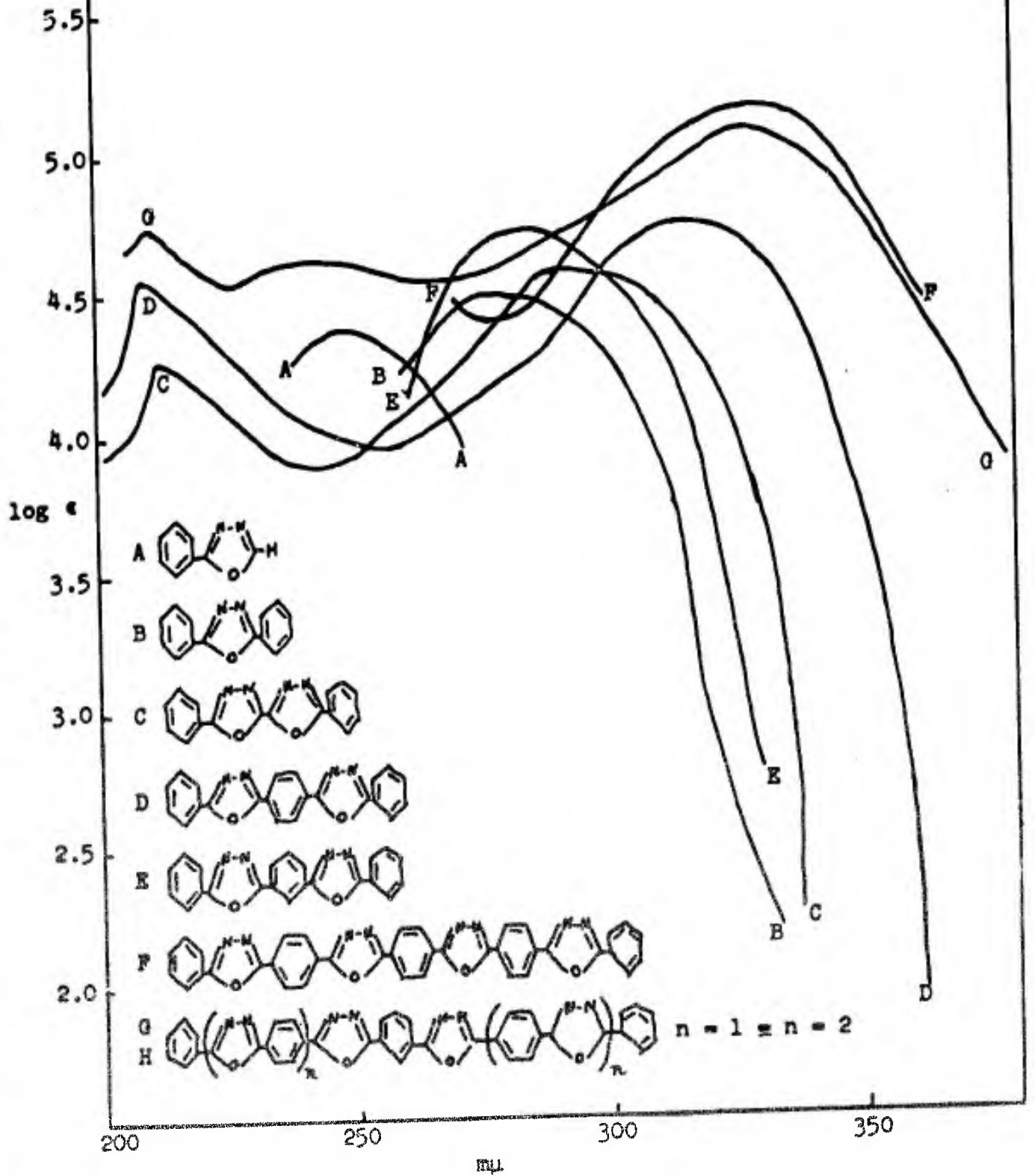
Huisgen (13) has shown that the oxadiazole moiety is spectrally equivalent to a *p*-phenylene moiety as evidenced by identical bathochromic shifts in going from biphenyl (2 rings) to terphenyl (3 rings) to noviphenyl (9 *p*-phenylene rings) and in going from 2-phenyl-1,3,4-oxadiazole (O-2, 2 rings) to 2,5-diphenyl-1,3,4-oxadiazole (O-3, 3 rings) to O-4 (5 rings) and O-6 (9 rings). This nine-membered noviphenyl analogue was the highest member he was able to prepare.



The conjugation in *p*-polyphenylene and *p*-polyoxadiazoles should be different from that observed in *m*-polyphenyls and oxadiazoles containing *m*-phenylene rings. Gillam and Key (20) found that the long-wave absorption maxima in *m*-polyphenyls are constant in their position for $n = 2-16$ and that the extinction consists additively of biphenyl extinctions.

Since PODZ-I/T is not a *p*-polyphenyl analogue, conjugation in its spectrum would be limited. The same should be true of PODZ-I/T model compounds such as O-5 (5 rings), O-7 (9 rings), and O-8 (13 rings).

FIGURE 1
OXADIAZOLE SPECTRA



This is borne out by inspection of the UV spectra of unsubstituted oxadiazoles contained in Table XI (Figure 1). However, since the oxadiazole structure is equivalent to *p*-phenylene, the only *m*-structures in oligo-oxadiazoles 0-5, 0-7, and 0-8 originate from meta-phenylene moiety.


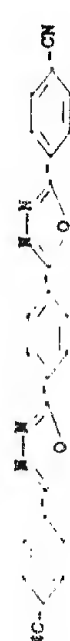

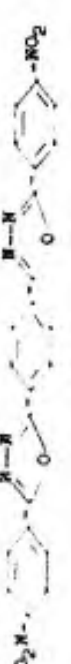

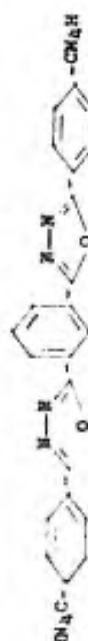
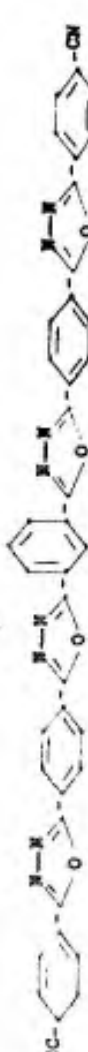
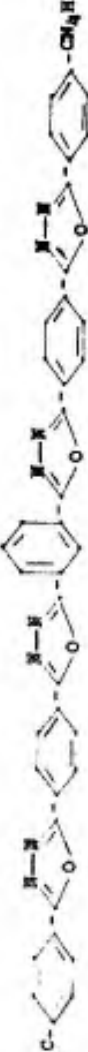
The light absorption of oxadiazoles prepared for this study should, therefore, be representative of the following polyphenyls (Table XIII):

TABLE XIII
OXADIAZOLES AND *m*-POLYPHENYLS

<u>Oxadiazole</u>	<u>Equivalent <i>m</i>-Polyphenyl</u>	
0-5	n = 1	
0-7	n = 2	
0-8	n = 3	

The analyses of various substituted oxadiazoles, as prepared for this study as intermediates, are tabulated in Table XIV, together with physical properties of a few similar compounds as reported by Huisgen (12,13). These compounds have not been evaluated further.

TABLE XIV
SUBSTITUTED OLIGO-OXADIAZOLES

Code	Structure	Formula and Mol. Wt.	Analyses					M.P., °C.
			C %	H %	N %	O %		
0-9		C ₂₄ H ₁₆ N ₈ 214.21	Calc'd: 44.85 Found: 45.20	2.82 2.92	52.32 52.00	10.01	250	
0-10		C ₂₄ H ₁₂ N ₆ O ₂ 416.39	Calc'd: 69.22 Found: ref. 13	2.90	20.19	7.69	(395) 13	
0-11		C ₂₄ H ₁₄ N ₁₂ O ₂ 502.45	Calc'd: 57.37 Found: ref. 13	2.80	33.46	6.37	(390) 13	
0-12		C ₂₂ H ₁₂ N ₆ O ₆ 456.38	Calc'd: 57.89 Found: ref. 13	2.65	18.42	21.04	405	
0-13		C ₂₄ H ₁₂ O ₂ N ₆ 416.39	Calc'd: 69.39 Found: 68.92	2.66 3.07	20.23 20.20	7.76	345	
0-14		C ₂₄ H ₁₄ O ₂ N ₁₂ 502.45	Calc'd: 57.37 Found: 56.62	2.80 3.25	33.46 27.5	6.37	260	
0-15		C ₄₀ H ₂₂ N ₁₀ O ₄ 706.66	Calc'd: 67.98 Found: 67.30	3.14 3.20	19.59	9.06	>400	
0-16		C ₄₀ H ₂₄ N ₁₆ O ₄ 792.74	Calc'd: 60.60 Found: -	3.04	28.28	8.08	>320	

Thermal Stabilities of Polymers

1. Thermal Stability of the Oxadiazole Structure

The thermal stability of poly(1,3,4-oxadiazole) fibers was investigated in order to assess accurately their possible utility at elevated temperatures. This study was carried out on thermogravimetric balances, and the programmed thermogravimetric analyses (TGA) are reproduced in Figures 2 and 3.

Curve 1 (Fig. 2) is reproduced from a programmed TGA run (N_2) using PODZ-I/T fiber with fiber properties (T/E/M₁ = 2.6/3.1/124) as shown in Table IX.

Curve 2 (Fig. 2) is reproduced from a paper of Abshire and Marvel for PODZ-I/T bulk polymer with an inherent viscosity of $\eta = 0.01$ (2%, H_2SO_4).

Curve 3 (Fig. 2) is a record of a TGA run using a 9-membered oligo-oxadiazole (mol. weight ~ 600).

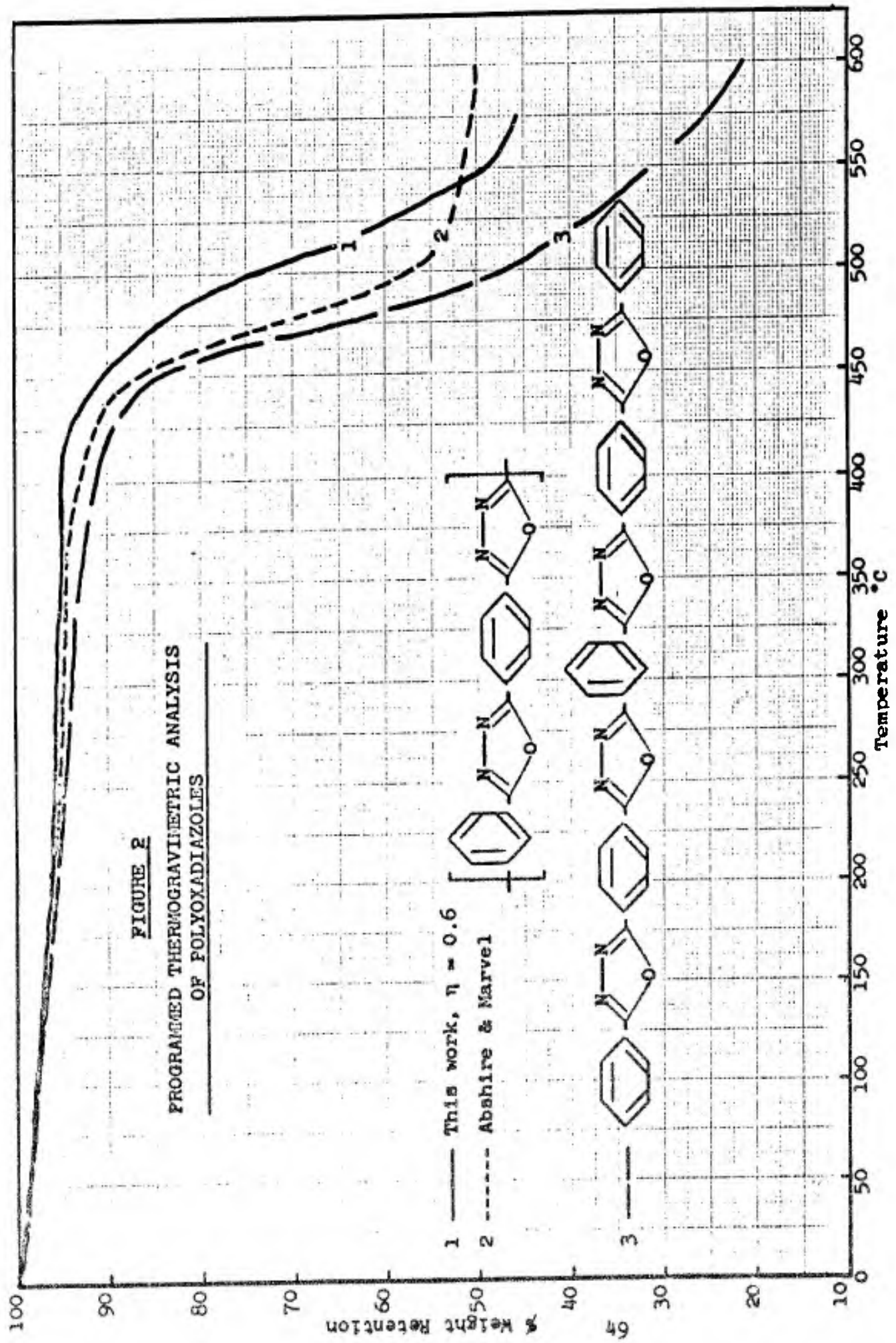
Curve 1 (Fig. 3) is reproduced from programmed TGA of the polyhydrazide OIOT, which is converted into PODZ-I/T. This reaction - although normally carried out isothermally - proceeds also with programmed temperature increase. Water loss occurs and the plateau shortly before 400-450° shows that polyoxadiazole has formed.

Curve 2 (Fig. 3) is the record of a TGA run using poly-(octamethylene dihydrazide). As in case of curve 3 (Fig. 2), conversion occurs, is completed at about 350°C., and PODZ-(CH₂)₈ gives evidence as stable species at temperatures above 350°C.

Thus, aromatic poly-1,3,4-oxadiazoles (examples 1 and 2; Fig. 2) are thermally stable and decompose between 450 and 500°C. Aliphatic polyoxadiazoles (example 5) degrades between 400-450°C. Such differences between aliphatic and aromatic species, which are reflected also in melting points, are expected. The aliphatic example has, therefore, been included only for reference.

2. Fiber Properties at Elevated Temperatures

Polyoxadiazole fibers, PODZ-I/T were investigated carefully by a study concerned with the thermal stability with respect to fiber properties.



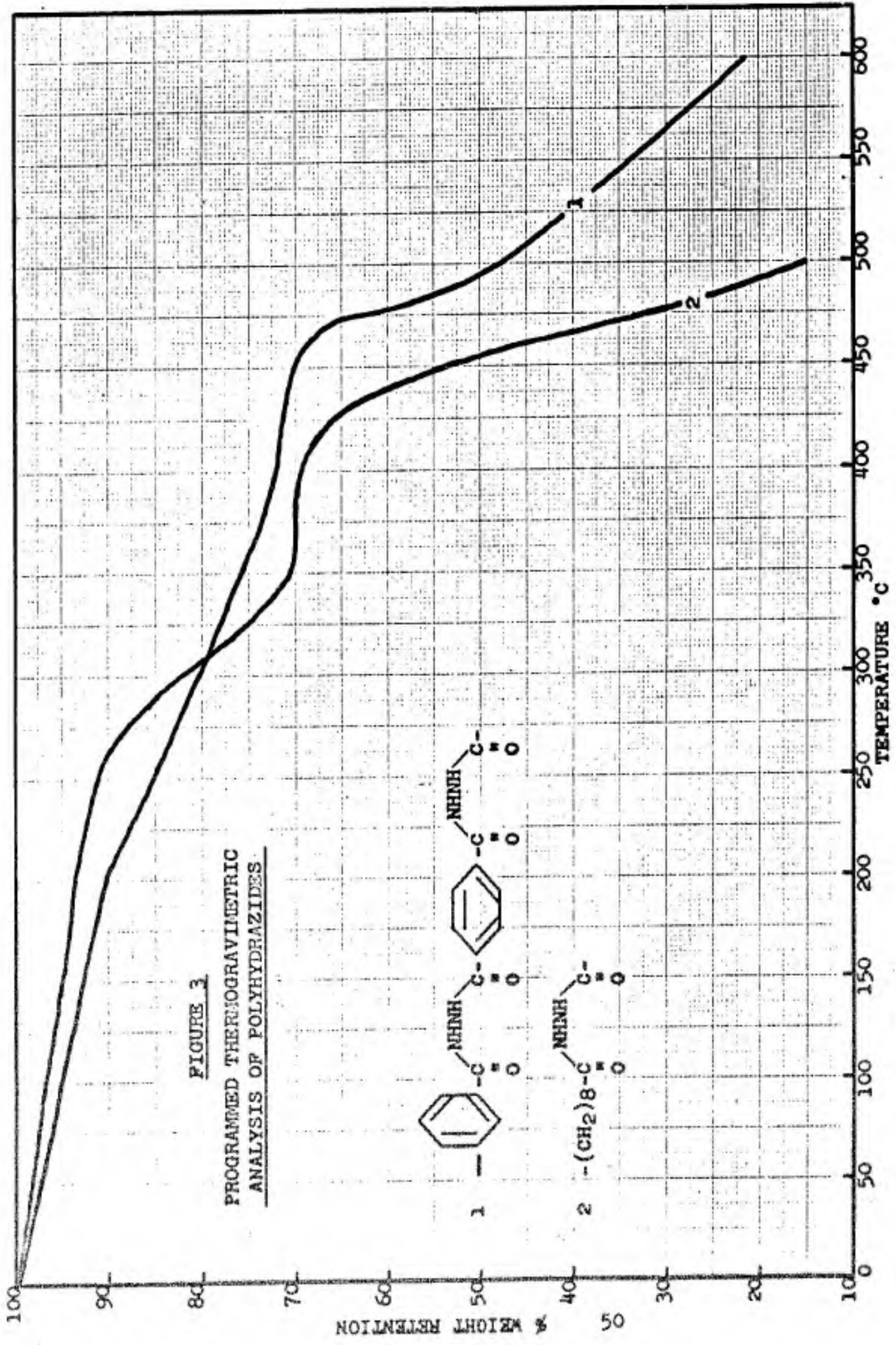


TABLE XV
THERMAL STABILITY OF PODZ-I/T FIBER (300-400°C.)
 Initial Fiber Properties T/E/Mi/den. = 2.6/3.1/124/3.0

Hours	300°C., Air (b.o.)		300°C., Nitrogen (b.o.)	
	T/E/Mi/Den.	WT/%/MI	T/E/Mi/Den.	WT/%/MI
2	2.5/4.8/102/3.2	96.5/>100/50.0	2 2.7/4.2/104/3.3	>100/>100/84.0
4	--	--	4 2.8/3.6/91/2.8	>100/>100/74.5
6	2.6/3.2/102/3.0	100.0/>100/81.2	6 2.3/2.2/104/2.7	92.5/71.5/84.0
24	1.3/1.4/114/2.9	50.0/45.2/90.0	24 2.3/2.4/107/2.9	92.5/77.5/86.5
52	1.1/1.1/93/3.2	42.4/35.2/75.0	150 1.7/1.6/87/2.9	65.4/51.6/70.0
72	--	--	325°C., Nitrogen (b.o.)	
96	1.2/1.2/87/2.7	46.2/38.1/70.0	2 2.6/2.7/145/2.5	100.0/87.1/>100
120	1.7/1.6/87/3.0	65.4/51.6/70.0	4 2.8/3.9/139/2.9	>100/>100/>100
144	2.0/1.8/105/3.1	76.9/58.1/84.7	6 2.4/2.0/136/2.9	92.3/64.5/>100
168**	1.2/1.2/112/2.7	46.2/38.7/90.3	24 2.0/1.8/149/2.8	76.9/58.1/>100
			48 Not tested	--
	350°C., Air (b.o.)		350°C., Nitrogen (b.o.)	
			1 2.8/3.9/102/2.8	>100/>100/82.5
			2 2.4/2.8/101/3.2	92.5/90.5/81.5
			6 2.7/3.4/118/2.8	>100/>100/69.0
			12 1.9/1.9/105/2.9	73.2/61.2/84.5
24	2.1/2.2/103/2.7	80.8/71.0/83.1	24 2.3/2.2/132/2.9	88.5/71.0/>100
48	2.1/2.2/113/2.9	80.8/67.7/91.1	48 2.5/2.6/128/2.8	96.2/83.9/>100
72	1.7/1.6/110/3.0	65.4/51.6/88.7	72 1.7/1.4/164/2.9	65.4/45.2/>100
96*	1.1/1.1/102/3.3	42.3/32.3/82.3	96* 1.2/1.2/83/2.7	46.2/38.7/66.9
	375°C., Air*** (b.o.)		375°C., Nitrogen (b.o.)	
2	1.8/1.8/81/2.9	69.2/58.1/65.3	2 1.5/1.3/118/2.9	57.7/42.9/95.2
4	1.9/2.2/72/2.8	73.1/71.0/58.1		
6	1.7/1.7/66/2.7	65.4/54.89/53.2	6 1.2/1.2/97/3.3	46.2/38.7/78.2
			24 1.6/1.4/112/2.7	61.5/45.2/90.3
48*	1.6/1.3/100/2.7	61.5/41.9/80.6	48* 1.3/1.1/92/3.0	50.0/35.5/74.2
	400°C., Air (b.o.)		400°C., Nitrogen (b.o.)	
1	2.0/2.3/77/2.6	76.9/74.2/62.1		
2	2.4/2.7/64/3.1	92.3/87.1/51.6		
4	2.1/1.9/81/2.5	80.8/61.3/65.3	4 1.7/1.8/100/3.0	65.8/58.1/80.6
24	2.5/2.6/67/2.6	96.2/83.9/54.0	6 1.6/1.5/89/2.9	59.6/48.4/71.8
40*	1.8/1.8/84/2.8	69.2/58.1/67.7	24* 1.3/1.2/102/2.8	50.4/38.7/82.3
	450°C., Air		450°C., Nitrogen	
1	Samples partly burnt and degraded		Samples partly burnt and degraded	

*Longer exposure times produced fiber which was too brittle to test.
 **Fiber was too brittle to test in duplicate experiment.
 ***Fiber samples partially degraded >4 hrs. in duplicate runs due to uneven heating.

A number of PODZ-I/T fiber samples, on perforated metal bobbins, were placed into muffle furnaces, the temperature of which was accurately controlled by Pyrovans. By this procedure, samples - in air or in nitrogen atmosphere - were kept at constant temperatures between 300° and 450°C. for prolonged periods of time. At given time intervals, samples were withdrawn and fibers were tested (T/E/M₁/den./%O).

The results of this study are contained in Table XV. Polyoxadiazole, PODZ-I/T, with initial fiber properties (T/E/M₁/den. = 2.6/3.1/124/3.0) were heated and attained final PODZ-I/T fiber properties [T/E/M₁/den. ~ 1.1/1.1/90] after a certain time at temperatures between 300° and 400°C. (in air or nitrogen).

In agreement with the TGA curve 1 on Figure 2 the PODZ-I/T fibers disintegrated at temperatures between 400° and 450°C.

Data reported in Table XV refer to b.o. (boiled-off) fiber properties.

3. Final Oxadiazole Fiber Properties after HT-exposure

As becomes evident from Table XV, polyoxadiazole properties change upon exposure to high temperatures. Thus, Table XVI was compiled to elucidate final and constant fiber properties of PODZ-I/T.

TABLE XVI
FINAL POLYOXADIAZOLE PROPERTIES

	<u>T/E/M₁/Den.</u>	<u>O%</u>	<u>Note</u>
44-9	1.1/1.1/93/3.2	11.57	After 52 hrs. at 300° (air).
39-4	1.2/1.2/112/2.7	11.80	After 168 hrs. at 300°C. (air).
48-4	2.1/1.8/136/3.6	*	After 48 hrs. at 400°C. (air).
54-4	1.3/1.1/92/3.0	*	After 48 hrs. at 375°C. (N ₂).
43-4A	1.1/1.1/102/3.3	*	After 96 hrs. at 350°C. (air).
43-5	1.2/1.2/83/2.7	*	After 96 hrs. at 350° (N ₂).

* Not yet available.

Thus, it appears that the initial PODZ-I/T fiber (Table X) obtained by complete cyclization of OIOT possesses a fiber structure which gradually changes into a thermally more stable but stiffer structure. Thus, the final polyoxadiazole structure has lower elongations and higher moduli and is, therefore, most characteristic of a polymer consisting exclusively of intralinear aromatic rings.

Summary

1. Poly(1,3,4-oxadiazole Fiber Properties

Poly(1,3,4-oxadiazole) fiber, PODZ-I/T, with high thermal stabilities has been prepared by cyclodehydration of polyhydrazide fiber, OIOT.

OIOT fiber for this study was prepared with various levels of properties and with various degrees of crystallinity. In general, tenacities (T) ranged from 3 to 7 gpd., elongations (%E) from 10-24% and moduli (M_1) ranged from 80-169.

Optimum conversion of OIOT fiber proceeds at 280°C. in a muffle furnace under positive nitrogen pressure and is completed in 48-72 hrs., as evidenced by analyses.

PODZ-I/T fiber obtained in this manner had the following typical fiber properties: T/E/ M_1 /den. = 2.6/3.1/124/3.1 and was thermally stable when exposed to prolonged periods of time to temperatures of 400°C.

During heat treatment between 300 and 400°C. the initial polyoxadiazole fiber apparently undergoes a structural change and final and reproducible polyoxadiazole fiber properties are: T/E/ M_1 /den. ~ 1.3/1.1/92/3.0.

Chemically, the polyoxadiazole structure was found to degrade severely between 450-500°C.

2. Conclusions

The preparation of poly(1,3,4-oxadiazole) fiber represents a major breakthrough in modern polymer technology. While reactions on polymers are usually not very efficient, poly(1,3,4-oxadiazoles)

readily result by thermal cyclodehydration of polyhydrazides. The reaction goes to completion even in fiber form, and the resulting poly(1,3,4-oxadiazole) fibers have measurable fiber properties even after prolonged exposure to 400°C. in air or nitrogen.

Experimental

Preparation of OIOT in NMP and HMPA

A solution of 48.5 g. isophthalic dihydrazide in 325 ml. N-methylpyrrolidone containing 15 g. lithium chloride is cooled in an ice bath. To this stirred solution are added 50.75 g. terephthaloyl chloride, and the reaction mixture is stirred overnight prior to isolation which affords a polymer with a melt temperature of 370°C. and an inherent viscosity of 0.84.

In a similar experiment in which only 10 g. lithium chloride are used and the diacid chloride added in 5 equal portions at 5-minute intervals, the inherent viscosity is 1.50.

The most useful solvent is hexamethylphosphoramide (HMPA). Polymer prepared in HMPA at room temperature is washed three times with distilled and deionized water and three times with dry methanol. It is then dried at 83°C. (vac.). The polymer prepared in this manner had a polymer melt temperature in excess of 370°C. and inherent viscosities of at least 0.90 to 1.00.

Dimethyl acetamide (DMAc), although a good solvent for prepared polyhydrazide OIOT, cannot be used to prepare high molecular weight polymer from the intermediate. The best η_{inh} was 0.3 to 0.4.

Preparation of OIOT in hexamethyl phosphoramide did not require the addition of lithium chloride to the preparative solution, as was necessary when using N-methylpyrrolidone (NMP) as solvent.

OIOT solutions up to 25% in concentration were found to be stable in NMP, DMSO, DMAc, and in DMAc containing 2 to 5% LiCl for periods exceeding one month. Even an original preparative solution containing OIOT/HMPA/HCl was rather stable. The inherent viscosity changed from 0.90 (day of OIOT preparation) to 0.67 (after four weeks of being in HMPA/HCl solution).

OIOT/HgCl₂ Chelate Film

OIOT, 0.75 g. (0.0046 moles) in 3 ml. DMAc was diluted to 10 ml. To this solution was added 1.3 g. (0.0048 moles) mercuric chloride which dissolves. The faint yellow color, of the solution, disappears simultaneously. Through an eyedropper were added 0.3 ml. of triethylamine which turned the solution very viscous and gave it an intense yellow color. It was diluted with stirring to a final volume of 40 ml. A film was cast from this rather dilute solution. This film was dried in a vacuum oven at 80°C. over a period of a week-end. A tough film of the chelate resulted. When this film was dried in air instead of in vacuum, it turned brown and discolored. A similar discoloration was noticed when this film was heated to 250°C.

2,5-Dichloroterephthaloyl Chloride

2,5-Dichloroterephthalic acid, 160 g., was refluxed overnight with 50 ml. of thionyl chloride. The yellow suspension gradually became a yellow solution after a few drops of DMF was added. It was filtered through glass wool to remove black solid particles from the acid chloride solution. Excess thionyl chloride was removed by vacuum distillation. The oily residue was taken up in n-hexane, stirred with charcoal and filtered hot. Crystallization produced colorless 2,5-dichloroterephthaloyl chloride, m.p. 81°C.

Anal. Calcd. for C₈H₂O₂Cl₄: C, 35.33; H, 0.74; Cl, 52.16;
Found: C, 35.53; H, 0.76; Cl, 52.87; C, 35.45; H, 0.76; Cl, 52.87;
C, 35.45; H, 0.90; Cl, 52.95.

Dibenzoylhydrazine (10)

The preparation of this compound has been carried out in two ways. The first reaction was that of benzoyl chloride in DMAc reacted with hydrazine hydrate in DMAc. The product of this reaction was identical with that of a preparation which is described in Organic Synthesis. This preparation involved reaction of hydrazine sulfate (0.5 moles) with freshly distilled benzoyl chloride (1.0 mole) and sodium hydroxide. The yield of the recrystallized product, m.p. 238°C., was 80 g. (66%).

Anal. Calcd. for C₁₄H₁₂N₂O₂: C, 70.00; H, 5.04; N, 11.66;
C, 69.90; H, 5.10; N, 11.64; C, 69.70; H, 4.95.

β,β',N,N' -Dibenzoylterephthalic Dihydrazide

Dibenzoylterephthalic dihydrazide was prepared in DMAc solution with added acid acceptor. In a 250 ml. round bottom three-necked flask adapted with stirrer, condenser, and dropping funnel was placed 75 ml. of DMAc and 9.7 g. (0.05 moles) of terephthalic dihydrazide which previously had been rigorously dried. To the stirred 2.0 ml. of triethylamine solution was added a mixture of 50 ml. of DMAc containing 21.0 g. (0.15 moles) of benzoyl chloride. The addition was complete after one-half hour. The resulting solution was stirred and heated for one hour. It was poured into a large volume of water. The resulting product was filtered and washed with hot methanol, hot water, and acetic acid. The white solid was dried in vacuum at 100°C. It was recrystallized and the final pure product (16.0 g.; 84%) had a sharp melting point of 360°C.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.93;
Found: C, 65.44; H, 4.68; N, 13.80; C, 65.43; H, 4.60; N, 13.80.

β,β',N,N' -Dibenzoylisophthalic Dihydrazide

This solution was prepared in a similar fashion as the para-phenylene analog above. The solution was washed with water, and the precipitate was recrystallized from glacial acetic acid. The pure white product (13.6 g.; 66%) had a melting point of 318-320°C.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.93;
Found: C, 65.70; H, 4.59; N, 13.80.

2,5-Diphenyl-1,3,4-oxadiazole

Dibenzoylhydrazine, 7.20 g. (0.03 moles) was dissolved and refluxed in phosphorus oxychloride (80 ml.) for four hours. Excess phosphorus oxychloride was completely removed by distillation and the residue was carefully treated with water (in the hood). It was then washed with water and filtered. The white solid was recrystallized from alcohol to yield a total of 6.0 g. (94%) of 2,5-diphenyl-1,3,4-oxadiazole, m.p. 144°C. (lit. 138°).

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.67; H, 4.54; N, 12.61;
Found: C, 74.98; H, 4.58; N, 12.39; C, 74.92; H, 4.38.

1,4-D1-[2-phenyl-5-(1,3,4-oxadiazolyl)]benzene

Dibenzoylterephthalic dihydrazide, 8.04 g. (0.02 moles) was refluxed in suspension with 18 ml. of phosphorus oxychloride for 12 hours. There was a noticeable change in appearance and crystal structure of the suspended solid in going from material to the product. Neither material was soluble in phosphorous oxychloride. Excess phosphorous oxychloride was distilled off under vacuum. Water was dropwise (and carefully) added to the residue. It was filtered and recrystallized from dimethylformamide (50 ml./1 g.) to give white shiny plates of the oligo-oxadiazole, m.p. 310°C. (lit. 308°C.) (4,6).

Anal. Calcd. for $C_{22}H_{14}N_4O_2$: C, 72.12; H, 3.85;
Found: C, 71.60; H, 4.01.

1,3-D1-[2-phenyl-5-(1,3,4-oxadiazolyl)]benzene

This compound was prepared from the corresponding dihydrazide as described above for the para-phenylene analog. It was refluxed for 24 hours. The only difference noted was that starting material and product were soluble. The final solution was filtered (glass wool) to remove small amounts of foreign particles. A large amount of the product crystallized out (Fraction I) over the week-end. It was filtered and the mother liquor was evaporated to dryness (Fraction II). After complete removal of the excess phosphorous oxychloride the residue of the mother liquor from the distillation was treated carefully with water and the additional precipitate was filtered. Both fractions, the original precipitate and the additional amount of oxadiazole recovered from the mother liquor, were separately recrystallized from dimethylformamide (20 ml./1 g.). The melting point of the products was 250°C. This product is not described in the literature.

Anal. Calcd. for $C_{22}H_{14}N_4O_2$: C, 72.12; H, 3.85;
O, 8.74; Found: C, 71.70; H, 3.90; O, 9.00.

This compound was prepared by alternate methods, namely, those described by Huisgen (12,13), who discovered that the reaction of tetrazoles with acid chlorides gives high yields of 1,3,4-oxadiazoles. His method was adapted in the following manner:

6.40 g. of m-phenylene ditetrazole in 150 ml. of dry pyridine was treated with 17.0 ml. of benzoyl chloride and refluxed for 1-1/2 hrs. To insure completion of reaction, the reflux was cut back to 80°C., a temperature which was maintained for the reaction overnight. It was cooled and a few drops of water were added to destroy excess acid chloride. It was then poured into 500 ml. of water. The precipitate was filtered and washed with water. An amount of 14.0 g. of dry, crude material was obtained. It was recrystallized from dimethylformamide (charcoal) and filtered. The filtrate was placed in the refrigerator. The first crop was washed with 10 ml. of DMF and then with 100 ml. of water. The white needles (6.6 g.) were dried, m.p. 250°C. Only a very small amount of additional crop (1.5 g.) could be obtained from the filtrate, m.p. 250°C. The total yield was 83.5% of the theory.

Anal. Calcd. for $C_{22}H_{14}N_4O_2$: C, 72.12; H, 3.85;
Found: C, 71.60; H, 4.10.

p-Cyanobenzoyl Chloride

A sample of 50 g. of p-cyanobenzoic acid (Genessee Research Corporation) was treated with 250 ml. of thionyl chloride under mild reflux (60°C.). Two drops of DMF were added which noticeably reduced the reaction time. Complete solution (with brown color) occurred after two hours. Excess thionyl chloride was distilled off, initially under aspirator vacuum, later under high vacuum. A brown residue remained. This residue was taken up in 50 ml. of dry benzene, filtered from a small amount of brown material which was possibly the anhydride. The solution was treated with charcoal, filtered and precipitated with 250 ml. of hexane. Three fractions were obtained. Fraction I consisted of 21 g. of slightly yellow leaflets. Fraction II was obtained on cooling to 0°C. and consisted of 18 g. of slightly yellow leaflets. Fraction III was obtained on cooling to -40°C., and consisted of 10 g. of a yellow to orange colored powder which awaits further purification. The melting points of Fractions I and II are in agreement with the literature (13,18), m.p. 65-67°.

Anal. Calcd. for C_8H_4ONCl : N, 9.24%; Found: N, 9.20%.

1,3-Di-[2-(p-cyanophenyl)-5-(1,3,4-oxadiazolyl)]benzene

A mixture of 21.4 g. (0.1 mole) of m-phenylene ditetrazole and 33.1 g. of p-cyanobenzoyl chloride (0.2 moles) was placed in 150 ml. of dry pyridine. The reaction vessel was gently heated. After the bulk of the reaction had occurred, the reaction was refluxed for two hours. The reaction was then poured into two liters of distilled water with good stirring, and was filtered and washed three times with water. It was dried overnight in a vacuum oven at 80°C. The crude yield 30.0 g. of brown solid. It was recrystallized from large amounts of dimethylformamide (30 g./1500 ml./130°C.) using charcoal to give a white powdery product, m.p. 345-347°C. The final yield of pure product was 25.5 g. (60%). A second crop has not been purified.

m-Phenyleneditetrazole

This material was generously supplied by Dr. A. H. Frazer in pure form. It was not further purified prior to its use in preparations described in this report.

Anal. Calcd. for C₈H₆N₈: C, 44.85; H, 2.82; N, 52.32;
Found: C, 45.20; H, 2.92; N, 52.00.

1,3-Di-[2-(p-[tetrazoyl-(5)]-phenyl)-1,3,4-oxadiazolyl-(5)]-benzene (0-14)

A mixture of 24.09 g. (0.0575) of 1,3-di-[2-(p-cyanophenyl)-1,3,4-oxadiazolyl-(5)]-benzene (which had previously been prepared from m-phenyleneditetrazole and p-cyanobenzoyl chloride) and 13.0 g. (0.20) sodium azide, 8.48 g. (0.20) lithium chloride and 600 ml. dimethylformamide was gently heated to reflux. The reflux was maintained for 1 week. After the first day a slightly pink solution resulted with a white precipitate which increased in amount as the reaction proceeded. The mixture was poured onto 2 liters of distilled water, it was acidified with a small volume of 1/2 conc. hydrochloric acid and filtered. Water and DMF are difficult to remove (very slow filtration). The solid was twice boiled with water after filtration and then dried at 150/25 ml. It was 2X recrystallized from dimethylacetamide (DMAc) to remove a tenaciously adhering brown impurity. The product, ready for further reaction, analyzed correctly and had a m.p. = 200°C.

Anal. Calcd. for C₂₄H₁₄N₁₂O₂(502.5): C, 57.36; H, 2.80.
Found: C, 56.62; H, 3.25.

1,3-D1-[2-(p-(phenyl-1,3,4-oxadiazolyl-(5))-phenyl)-1,3,4-oxadiazolyl-(5)]-benzene (0-7)

Above prepared ditetrazole, 21.0 g. (0.04) was suspended in 250 ml. boiling pyridine and reacted with 15.0 ml. (0.12) benzoyl chloride for a period of 8 hours. The white crystalline product was extracted with pyridine and DMF.

β-Membered Oligo-oxadiazole (0-8)

The preparation of this compound proceeded in analogy to the lower membered oligo-oxadiazoles. 4.02 g. (0.004 moles) of the ditetrazole, 0-14, were reacted with 4.28 g. of p-cyano-benzoyl chloride (0.025 moles) in pyridine for 24 hrs. Precipitation with water and recrystallization from DMF yielded 5.00 g. pure of dicyano derivative, 0-15, m.p. > 320° (degr.). Reaction with LiN₃ in analogy to previously described methods and subsequent treatment with benzoyl chloride gave 0-8, which was extracted with pyridine and DMF since no recrystallizing solvents were found. M.p. > 400°C.; UV spectrum virtually superimposable with that of 0-7.

Dimethyl Iminosuccinate

A solution of 100 g. (1.25 moles) of succinonitrile in 80.1 g. (2.5 moles) of dry methanol and 100 ml. of dry dioxane was saturated with dry HCl gas. The white solid precipitated while the solution cooled in an ice water bath warmed up gradually. The addition of HCl gas was discontinued and the solution was stirred for 1 hr. The solid, being the dihydrochloride of dimethyl iminosuccinate, was filtered, washed twice with dry ethyl ether, and stored in a desiccator.

Diethyl Iminosuccinate

Forty grams succinonitrile were dissolved in 240 ml. of dry ether and 46.0 g. of absolute ethanol in a 500 ml. Erlenmeyer flask adapted with calcium chloride tube, thermometer, magnetic stirrer, and ice water bath. Dry hydrogen chloride was added to the stirred solution. After about one-half hour of HCl addition, two layers appeared, the dihydrochloride of diethyl iminosuccinate crystallized from the lower layer with noticeable increase in temperature. The solid which resulted was washed twice with ether to remove excess HCl and dried in a desiccator.

Anal. Calcd. for $C_8H_8O_2N_2Cl$: C, 39.19; H, 7.40;
Cl, 28.94; Found: C, 38.63, 38.27; H, 7.35, 7.41; Cl, 26.9, 27.1.

Diethyl Iminoisophthalate

12.8 g. of isophthalonitrile (0.1 mole), m.p. 158-160, was placed in 135 ml. of ethyl acetate and 20 ml. of benzene in an Erlenmeyer flask. The mixture was stirred and 9.2 g. of absolute alcohol (0.2 moles) was added. With continued stirring in an ice water bath, the solution was saturated with dry HCl gas, stoppered and allowed to stand for 24 hrs. The solution was turbid after one hour and crystals appeared after 15 hrs. The solid was filtered, washed with ether and dried in a desiccator.

Anal. Calcd. for $C_{12}H_{18}N_2O_2Cl_2$: C, 49.15; H, 6.14;
Cl, 24. Found: C, 46.70; H, 6.20; Cl, 25.4.

72 g. of dry diethyl iminoisophthalate were placed portion-wise into a double-layered solution of saturated potassium carbonate and ether with rapid stirring. The ether layer was several times decanted and replaced. The final ether layer (350 ml.) containing free diethyl iminoisophthalate was dried over anhydrous sodium sulfate overnight. The ether was then evaporated on a Rinco Rotovac with gentle warming. The solid was recovered without exposure to air and moisture and stored in a desiccator. The total dry weight of the pure product was 9.4 g.

Diethyl Orthosuccinate

Diethyl iminosuccinate dihydrochloride, 95 g., were dissolved in 600 ml. of absolute alcohol in a 3-necked flask adapted with nitrogen inlet calcium chloride tube and stirrer. The solution was stirred for 3 days at room temperature. It was then made alkaline with a 10% solution of sodium ethoxide (phenolphthalein). Excess ethanol was distilled off and 200 ml. of ether were added. Solid which had precipitated was filtered and washed with ether. The ether was evaporated in a Rinco Rotovac. The solid which again precipitated was washed once more with a small amount of ether and the diethyl orthosuccinate in ether was distilled. Three fractions were obtained: (1) Room temperature (0.8 ml.) consisting of ether and alcohol; (2) boiling point 68-78°C. (0.8 mm.); and (3) 78°C. (1.0 mm.).

Chelating of OIOT Yarns

OIOT yarn was passed through a DMF bath containing ~10% salt metal in 750 ml. DMF at $100^{\circ} \pm 5^{\circ}\text{C.}$, with a 12" contact in bath. The windup speed was uniformly 15 FPM. Samples of yarn thus obtained were dried in a vac oven at 85°C.

Occasionally it was desired to chelate the yarn in more basic solutions to study the difference in chelation with the basicity of the bath. In these cases a small amount of N,N'-dimethylaniline was added.

The addition of dimethylaniline to the DMF bath of AgNO_3 proved disadvantageous because of Ag° plating with simultaneous and vigorous reaction. In case where the effect of N,N'-dimethylaniline in connection with AgNO_3 chelating was studied, the following arrangement proved useful.

The yarn was passed through a DMF/ AgNO_3 bath at $100^{\circ}\text{C.} \pm 5^{\circ}\text{C.}$ and then through a subsequent DMF-N,N'-dimethylaniline bath. In these cases Ag° was directly plated on the fiber [color of the yarn grey, silvery or black] while omission of the second bath yielded AgNO_3 -chelate fiber with straw color and different x-ray diffraction.

IV. References

1. K. C. Brinker and I. M. Robinson, U.S. 2,895,948, 7/1/59 to E. I. du Pont de Nemours & Company, Preparation of Polybenzimidazoles.
2. C. S. Marvel and H. Vogel, J. Polymer Sci., 50, 511 (1961).
3. Swiss Patent 212,641, 3/3/41 to Soc. pour l'end. Chim. d Bale, 3,3'-Dinitro-4,4'-diaminodiphenyl Ether.
4. (a) J. Sauer, R. Huisgen, and H. J. Sturm, Tetrahedron, 11, 241 (1960). (b) E. J. Abshire and C. S. Marvel, Makromol. Chem., 44-46, 388 (1961).
5. (a) R. Stolle, J. Pr. Chem. (2), 68, 30 (1903); (b) *ibid.*, 69, 155 (1904); (c) N. Pellizzare, Atti. della Reale Acad. dei Lincei (Reconditi) 8, I, 328 (1900).
6. A. H. Frazer and F. T. Wallenberger, in preparation.
7. F.P. 870,259 (3/6/42); U.S. 2,349,979 (5/30/44); U.S. 2,476,968 (7/26/49); U.S. 2,512,891 (6/27/50); U.S. 2,615,862 (10/28/52).
8. W. Borsche, W. Müller and C. A. Bodenstein, Ann. 475, 120 (1929).
9. F. N. Hayes, B. S. Rogers, and D. G. Ott; J. Am. Chem. Soc., 77, 1850 (1955).
10. H. A. Hatt, Org. Synth., 16, 18 (1936).
11. R. Stolle and A. Benrath, J. Pr. Chem., 70, 263 (1904), A. Benrath, P. Giesler and O. Gartner, *ibid.*, 107, 211 (1924).
12. R. Huisgen, J. Sauer, H. J. Sturm, and J. H. Markgraf, Chem. Ber., 93, 2106 (1960).
13. J. Sauer, R. Huisgen, and H. J. Sturm, Tetrahedron, 11, 214 (1960).
14. C. Ainsworth, J. Am. Chem. Soc., 77, 1148 (1955).
15. S. M. McElvain and J. W. Nelson, J. Am. Chem. Soc., 64, 1825 (1942).
16. A. Pinner, Chem. Ber., 16, 352 (1885).

IV. References (Continued)

17. G. Luckenbach, Chem. Ber., 17, 1428 (1884).
18. J. N. Ashley, H. J. Barber, A. J. Eioins, G. Newberry,
and A. D. H. Self, J. Chem. Soc., 115 (1942).
19. E. Klingsberg, J. Org. Chem., 23, 1086 (1958).
20. A. E. Gillam and D. H. Hey, J. Chem. Soc. 1170 (1939).

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Unclassified Report

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. 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. To test this hypothesis N-substituted polymers were

prepared via the methylation of N-sodio polybenzimidazoles. Oriented and crystalline polyhydrazide fibers can be converted by a unique cyclodehydration reaction into oriented and crystalline fibers of poly(1,3,4-oxadiazoles). Conversion of fibers (T/E/M1 = 5/24/94) of the polyhydrazide derived from equimolar amounts of isophthalic dihydrazide and terephthaloyl chloride (OIOT) gave fibers (T/E/M1 = 2.6/3.1/124) of poly(1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole), POIZ-I/T, which have excellent retention of their fiber structure even when exposed to temperatures up to 400°C. for prolonged periods of time. Such heat treatments afford a final polyoxadiazole fiber (T/E/M1 = 1.2/1.2/90). The chemical structure of model compounds containing up to 13 alternating rings consisting of 2,5-(1,3,4-oxadiazole), m-, and p-phenylene moieties was found to be stable up to 440°-500°C. This is in agreement with observed stabilities of the corresponding polymer towards thermal degradation.

1. Polymers
2. Organic solvents
3. Deterioration
- I. AFSC Project 7340, Task 73404
- II. Contract AF 33(616)-8253
- III. E. I. du Pont de Nemours & Co., Wilmington, Delaware
- IV. August H. Frazer, et al
- V. Not aval fr OTS
- VI. In ASTIA collection

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