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SYNTHESIS OF THERMALLY STABLE POLYMERS

CARL S. MARVEL
THE UNIVERSITY OF ARIZONA

TECHNICAL REPORT AFML–TR–72–111, PART III

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This final report was submitted by the Department of Chemistry at The University of Arizona, Tucson, Arizona, under contract F33615-71-C-1408, job order 73400451, with the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Mr. G. A. Loughran, MBP was the laboratory project monitor.

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This technical report has been reviewed and is approved for publication.

GA Loughran

G. A. LOUGHRAN
Project Monitor

FOR THE COMMANDER

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Laminating resins, Polyarylene sulfides with dangling cyano groups, Polyarylether-ketone-sulfone polymers with dangling cyano groups, Polyarylether-ketone-sulfone polymers with dangling acetylene groups, Crosslinked acetylenic polymers, Polyarylether-ketone-sulfone polymers containing paracyclophane units, Polymers formed by Friedel-Crafts type reactions.

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Work on polyarylene sulfides with dangling cyano groups has been concluded. The polymers have good thermal stability and adhesive characteristics but crosslinking has in every case rendered them less stable.

The resins with aryl ether, ketones and sulfone units in the chain with dangling cyano groups have also been difficult to crosslink satisfactorily and the crosslinked materials are less heat stable and oxidatively stable than was the uncrosslinked material.

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BLOCK NO. 20 (continued):

Polyaryl ether, -ketone, -sulfone polymers with dangling acetylene groups have been made successfully. They give good laminates on glass fabric. They lose only a few percent of their weight at 300°C in several hours of heating. They can be crosslinked by heating at 315-320°C without a catalyst. They can be crosslinked by heating with palladium chloride and they can be crosslinked by heating with terephthalonitrile N,N'-dioxide. The polymers crosslinked by palladium catalyst oxidize excessively. The nitrile oxide crosslinked polymers have good isothermal aging properties.

Promising polyaryl ether, -ketone, -sulfone polymers with paracyclophane units have been prepared. They make good laminates on glass fabric. They crosslink well at 350°C. Samples for making large laminates for testing have been submitted.

Preliminary work on polymers with dangling cyanamide groups has been initiated.

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I. INTRODUCTION

The work reported herein has been directed toward the preparation of new polymeric materials to be used as binding resins for use in making composites to operate at high temperatures.

II. AREAS OF INVESTIGATION

The areas of investigation covered in this report are:

III. Polyphenylene sulfides and related polymers for use as laminating resins.

IV. Aromatic polyethers, -sulfones and -ketones as laminating resins (nitrile containing polymers).

V. Aromatic polyethers, -sulfones -ketone polymers with dangling acetylene groups.

VI. Polyaryl ethers, sulfones and ketones as thermally stable laminating resins.

VII. Synthesis of monomers containing aromatic cyanamide units.

VIII. Crosslinking of pendant cyano group in JVB-50 type polymers with 1,4,5,8-tetracyanonaphthalene.

III. POLYPHENYLENE SULFIDES AND RELATED POLYMERS FOR USE AS LAMINATING RESINS

1. Introduction

This work deals with the synthesis and characterization of polyphenylene sulfides containing side groups or monomer units that are capable of forming crosslinked polymers when cured by heating or otherwise. It is anticipated that the crosslinked polymers can be useful as laminating resins in high temperature work.

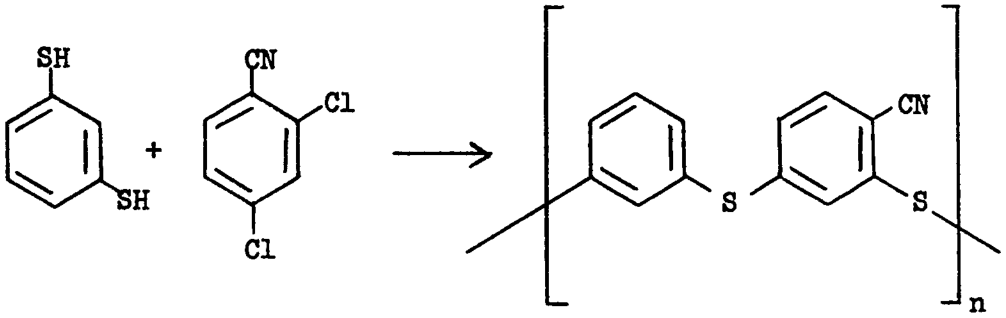
Previous work in this laboratory[1] has shown that poly(m-thiophenylenes) and poly(m,p-thiophenylenes) are quite soluble and possess low melting ranges and can therefore be practically used for laminate formation. It has also been determined that poly(m,p-thiophenylenes) containing pendant cyano groups formed insoluble products, presumed to be crosslinked polymers, when heated alone or in the presence of zinc chloride.[2] These crosslinked products were assumed to be the product of the trimerization of the nitrile groups to form s-triazines. Insoluble products were also reported when nitrile-containing poly(m,p-thiophenylenes) were heated in the presence of anthracene-9,10-bis-nitrile oxide.[2] Crosslinking in this case is believed to be the result of joining the polymer chains through the formation of 1,2,4-oxadiazole rings. It has also been reported that polymers containing [2.2]paracyclophane units in the polymer backbone formed crosslinked polymers when heated around 275°,[3] and that the cyanamide group has been successfully trimerized to form crosslinked polymers with melamine units.[4]

The curing process using the above methods proceeds without the formation of any gaseous side products. These methods can then be suitably used in the formation of hard laminates without the presence of any undesirable voids in the crosslinked polymers.

2. Results and Discussion

It has been reported by Baron and Blank[5] that potassium carbonate in dimethylformamide is a suitable medium for the reaction of an aromatic halide with an aromatic thiol to form an aromatic sulfide. Dr. Hurley[6] of this laboratory investigated this reaction further and found, after the synthesis of several model compounds, that this reaction is suitable for the formation of polyphenylene sulfides. He also found that other solvents could be used with potassium carbonate as the reacting medium and that the polymer of highest molecular weight was obtained when m-benzenedithiol and p-dibromobenzene were used as monomers and dimethylacetamide was used as the solvent.[7] He also found that the backbone of poly(m,thiophenylene) and poly(m,p-thiophenylene) would be the most suitable to use in the preparation of the nitrile-containing polyphenylene sulfides since these polymers possessed low enough melting ranges to make them convenient for use as laminating resins. In the same investigation Dr. Hurley attempted to introduce cyano groups in the polymer chains by the use of two different techniques. The first involved the reaction of polyphenylene sulfides containing thiol end groups with bromobenzonitrile thus endcapping the polymer chains with cyano groups. The second involved the bromination of the polymer chains followed by the reaction of the resulting polymers with cuprous cyanide. Both of these two methods, however, did not give the desired products and a third technique in which the nitrile groups were introduced into the polymers by the use of nitrile-containing monomers was used. The results of this work were reported earlier and involved the synthesis of nitrile-containing polyphenylene sulfides from m-benzenedithiol, p-dibromobenzene, 2,4-dichlorobenzonitrile or 3,5-dichlorobenzonitrile.

The synthesis of different poly(m-thiophenylenes) in which up to 25 molar percent of 3,5-dichlorobenzonitrile was used, was reported earlier.[2] When these polymers were heated, under nitrogen, alone at 350°C or in the presence of zinc chloride at 290°C, insoluble dark products were obtained. These products were tested for penetration under load and temperature and were found to exhibit undesirable rubbery behavior. This behavior was believed to be the result of insufficient curing sites (cyanide groups) along the polymer chains. For this reason poly(m-thiophenylene) containing pendant cyano groups in every other benzene ring was synthesized from m-benzenedithiol and 2,4-dichlorobenzonitrile in potassium carbonate and dimethylacetamide. The polymer obtained, IH-PXIII, was readily soluble in cold hexamethylphosphoric triamide in which solvent a 0.5% solution of the polymer gave an inherent viscosity of 0.06 dl/g. IH-PXIII had a melting range around 320°C and elemental analysis showed it to correspond to the desired structure.



The amounts of starting materials along with the results of the polymerization are given in Table I. Elemental analysis data are given in Table II.

Because of the low molecular weight obtained for this polymer attempts to increase the molecular weight made use of two techniques. The first involved the use of a catalytic amount of copper bronze. In this experiment the rate of the reaction seemed to increase considerably as evidenced by the disappearance of the yellow color, due to the thiophenoxide anion, within the first hour of the reaction. The second technique involved the doubling of the concentrations of the starting materials, since it was believed that the low molecular weight obtained earlier could be due to the low concentrations of the reacting species. Both of these techniques, however, failed to give the desired results as all three polymerizations gave almost identical inherent viscosities (Table III).

The failure to improve the molecular weight of the polymer obtained from 2,4-dichlorobenzonitrile and m-benzenedithiol prompted the synthesis of a similar polymer from 3,5-dichlorobenzonitrile and the same dithiol. This polymer IH-PXIX, was synthesized similarly as polymer IH-PXIII, and the polymer obtained melted at 210-220°C and was soluble in hexamethylphosphoric triamide in which solvent, a 0.5% solution of the polymer, gave an inherent viscosity of 0.38 dl/g at 24°C. The amounts of starting materials along with the results of polymerization are given in Table I.

TABLE I

POLYMERIZATION OF m-BENZENEDITHIOL AND 2,4-DICHLOROBENZONITRILE

Polymer	mBDT g(mole)	Dichloro Compound g(mole)	K_2CO_3 (g)	DMAc (ml)	Time hr	Yield (g)	η_{inh} (dl/g)	Melting Range (°C)
IH-PXIII	1.4239 (0.01)	2,4-DBN 1.7207(0.01)	3.2226	40	48	2.1	0.06	310-325
IH-PXIX	1.4230 (0.01)	3,5-DBN 1.7223(0.01)	3.2000	30	48	2.1	0.38	210-220
IH-PXX[a]	5.6896 (0.03)	DCA 6.4848(0.03)	12.7323	80	168	-	-	-
IH-PXII[a]	0.7769 (0.0055)	DBP 2.0004(0.0055)	1.8228	25	48	-	-	
IH-PXXX[b]	1.0678 (0.0075)	TBP 4.0334(0.0075)	2.4205	20	48	3.2	-	360
IH-PXXVI	0.7118 (0.01)	DCNB 0.9605(0.01)	1.7200	15	48	1.1	0.12	260-285
IH-PXVII[b]	0.5705 (0.004)	TrBP 1.7895(0.004)	1.2852	10	72	-	-	360

mBDT: m-benzenedithiol, 2,4-DBN = 2,4-dichlorobenzonitrile, 3,5-DBN = 3,5-dichlorobenzonitrile.
DCA: 2,4-dichloroaniline, TBP: tetrabromo[2.2]paracyclophane, DCNB = 2,4-dichloronitrobenzene.
TrBP: Tribromo[2.2]paracyclophane.

a. No polymer was obtained.
b. An insoluble product believed to be a crosslinked polymer was obtained.

TABLE II

ELEMENTAL ANALYSIS[a] DATA OF THE VARIOUS POLYPHENYLENE SULFIDES

Polymer	Repeating Unit	Calc. (C) Found (F)	Analysis Data % C	% H	% N	% S
IH-PXIII	$(C_{13}H_7NS_2)$	C	64.70	2.93	5.80	26.57
		F	64.67	3.07	5.80	26.50
IH-PXIX	$(C_{13}H_7NS_2)$	C	64.70	2.93	5.80	
		F	64.50	3.46	5.59	26.44
IH-PXXVI	$(C_{12}H_7NO_2S_2)$	C	55.15	2.70	5.36	24.54
		F	56.64	2.79	4.60	24.00
IH-PXIIIC	$(C_{13}H_7NS_2)$	C	64.70	2.93	5.80	26.57
		F	65.95	2.77	5.20	26.06
IH-PXIXC	$C_{13}H_7NS_2$	C	64.70	2.93	5.80	26.57
		F	64.04	2.88	4.79	26.42

a. Elemental analysis data were corrected for residue and any residual halogen.

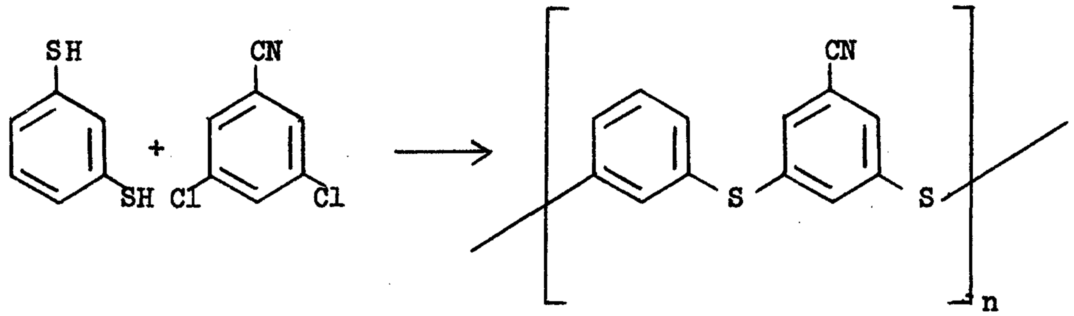
TABLE III

EFFECT OF POLYMERIZATION CONDITIONS ON THE POLYMER OBTAINED FROM m-BENZENEDITHIOL AND 2,4-DICHLOROBENZONITRILE

Polymer	MBDT g(mole)	DBN g(mole)	K_2CO_3 (g)	DMAc (ml)	Time (hr)	Yield (g)	η_{inh} (dl/g)	Melting Range
IH-PXIII	1.4239 (0.01)	1.7207 (0.01)	3.2226	40	48	2.1	0.06	310-325°
IH-PXIV	1.4233 (0.01)	1.7222 (0.01)	3.2028	25	48	2.0	0.06	295-310°
IX-PXV[1]	2.8454 (0.02)	3.4429 (0.02)	6.3535	35	24	3.7	0.06	320-330°

mBDT: m-benzenedithiol; DBN: 2,4-dichlorobenzonitrile.

1. Reaction run in the presence of a catalytic amount of copper bronze.



Two unexpected results were obtained from the above polymerizations. The first involves the high melting range of polymer IH-PXIII and the second involves the viscosities obtained for the two polymers. The very high melting range obtained for IH-PXIII as compared to that of poly(m-thiophenylene) can be rationalized by analogy to polyacrylonitrile which possesses a much higher melting point than that of polyethylene. Polymer IH-PXIII was expected to possess a higher molecular weight than that of polymer IH-PXIX since the former was prepared by the use of 2,4-dichlorobenzonitrile in which the substitution reaction is enhanced by the presence of chlorines in the more favorable ortho and para positions. No plausible explanation can be given for the fact that a lower molecular weight was obtained for IH-PXIII except to assume that the presence of the chlorines ortho to the cyano group could create a steric effect that might lead to a lower molecular weight polymer.

Isothermal aging of polymers IH-PXIII and IH-PXIX was run in an atmosphere of circulating air at 350°C. The results of this test are given in Table IV and show that in the case of IH-PXIII most of the weight loss occurred within the first 96 hours.

TABLE IV

ISOTHERMAL AGING[a] OF LINEAR AND CROSSLINKED POLYMERS

	% Weight Loss		
Polymer	96 hr	144 hr	168 hr
IH-PXIII	12.6	13.0	13.6
IH-PXIX		13.2[b]	
PS-5		14.8	
PS-9		94.7	
IH-PXIIIC	5.6	24.4	37.6
IH-PXIXC		14.0[b]	
PS-5-IH-PXIIIC		24.4	
PS-9-IH-PXIIIC		94.9	

a. All isothermal aging experiments were run in an atmosphere of circulating air.

b. Isothermal aging run for 5 days (120 hr).

Polymers IH-PXIII and IH-PXIX were cured by heating under nitrogen at 350-375° for 24 hr. The black products obtained, IH-PXIIIC and IH-PXIXC, were very brittle and could not be solubilized in hot hexamethylphosphoric triamide in which the linear polymers were quite soluble. Analysis of the crosslinked polymers by infrared analysis gave very poor spectra and therefore it could not be determined what amount of the cyanide group did react. Elemental analysis of these polymers are given in Table II and these results seem to correspond to the theoretical values calculated for the desired product. The results of the softening test of polymer IH-PXIIIC is shown in Figure 1.

Isothermal aging of IH-PXIIIC and IH-PXIXC were run in an atmosphere of circulating air at 350°C. The results of this test are given in Table IV.

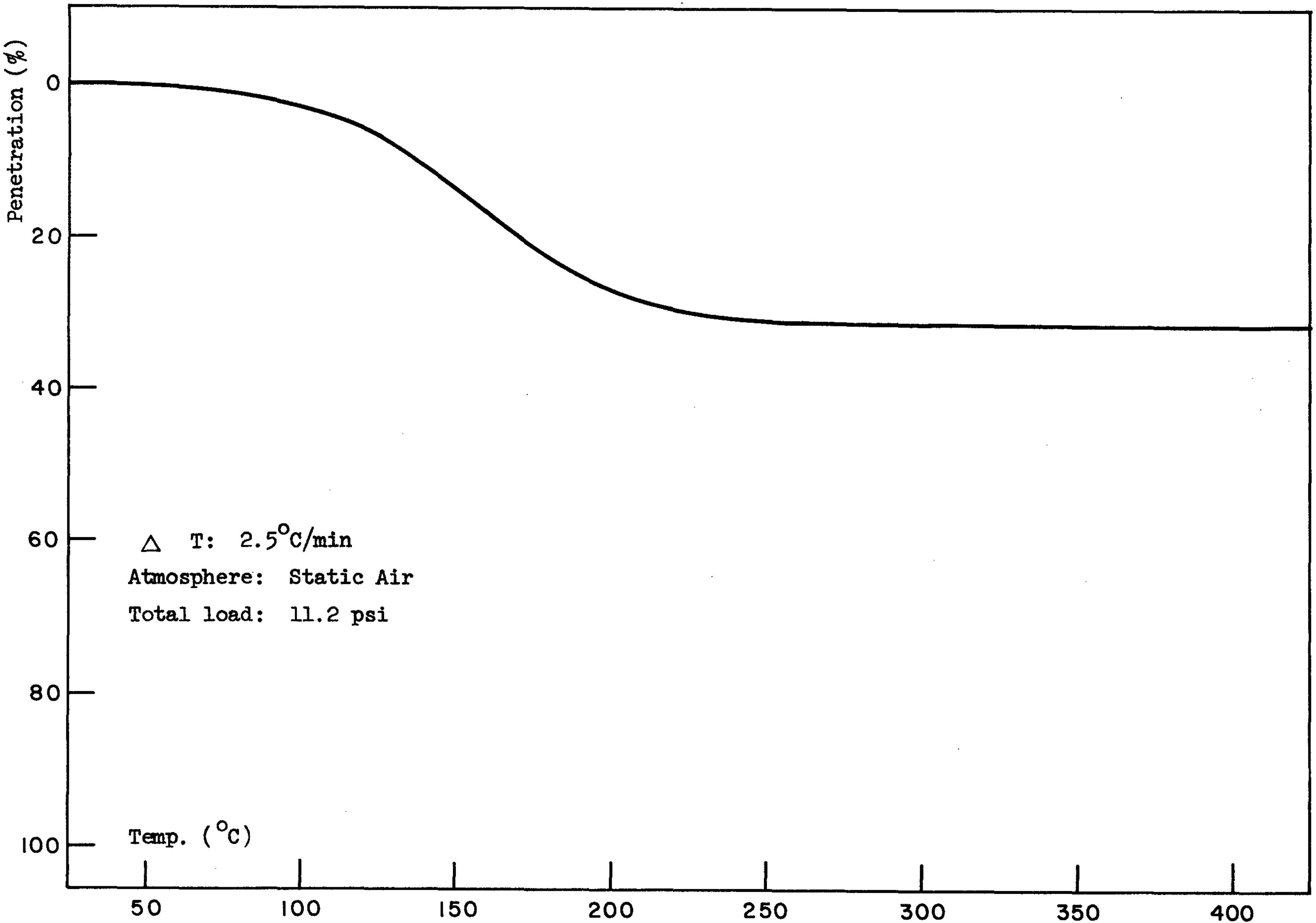


Figure 1. Softening under load of polymer IH-PXIIIC

Polymer IH-PXIII was also used as a curing agent due to its high nitrile content and low molecular weight. A sample of IH-PV prepared by the use of 5 molar percent of 3,5-dichlorobenzonitrile was mixed with 10 and 15 weight percent of IH-PXIII and the mixtures were heated under nitrogen and at 375°C for 24 hr. The crosslinked polymers IH-PVC10 and IH-PVC15 obtained did not show any improved thermal stability and the results of the softening point experiment are shown in Figures 2 and 3. Two other polymers from the ketone-sulfone-ether series synthesized by Dr. Sivaramakrishnan in this laboratory, were also crosslinked by heating with 10% by weight of IH-PXIII at 350°C and under nitrogen. Polymer JVB-50-PS-5 (made by the use of 5 wt % of nitrile-containing monomer) gave a crosslinked product (PS-5-PXIIIC) that showed a 23% wt loss when heated in an atmosphere of circulating air at 350°C for 144 hr. Polymer PS-9 (made by the use of 25 wt % of nitrile-containing monomer) was crosslinked similarly. However, the product PS-9-PXIIIC obtained showed a 94% wt loss during the same period of isothermal aging. Results of isothermal aging of the linear and crosslinked polymers are shown in Table IV.

In a previous report[2] crosslinking nitrile-containing polyphenylenesulfides by the use of anthracene-9,10-bis-nitrile oxide was described. Poly(m-thiophenylenes) containing various amounts of nitrile groups when cured in the presence of a two-fold excess of anthracene-9,10-bis-nitrile oxide gave crosslinked products that disintegrated almost completely when heated at 350°C for 5 days. Since it was believed that the reason for the rapid disintegration could be due to excess dinitrile oxide, a sample polymer, IH-PVIII, was cured with the stoichiometric amount of the dinitrile oxide and the cured polymer, IH-PVIIINOb, exhibited an improved thermal stability (Table III). The structures of the various cured polymers are given in an earlier report[2] and the results of the softening point technique are shown in Figures 4, 5, 6 and 7.

In 1972 Meyers et al[3] reported the synthesis of a linear polymer containing [2.2]paracyclophane units and the crosslinking of this linear polymer by heating at 275°C. The crosslinking was thought to occur by homolytic cleavage of the dimethylene bridges of the [2.2]paracyclophane units along one polymer chain thus forming diradicals which ultimately recombine with similar radicals along different chains thus causing them to

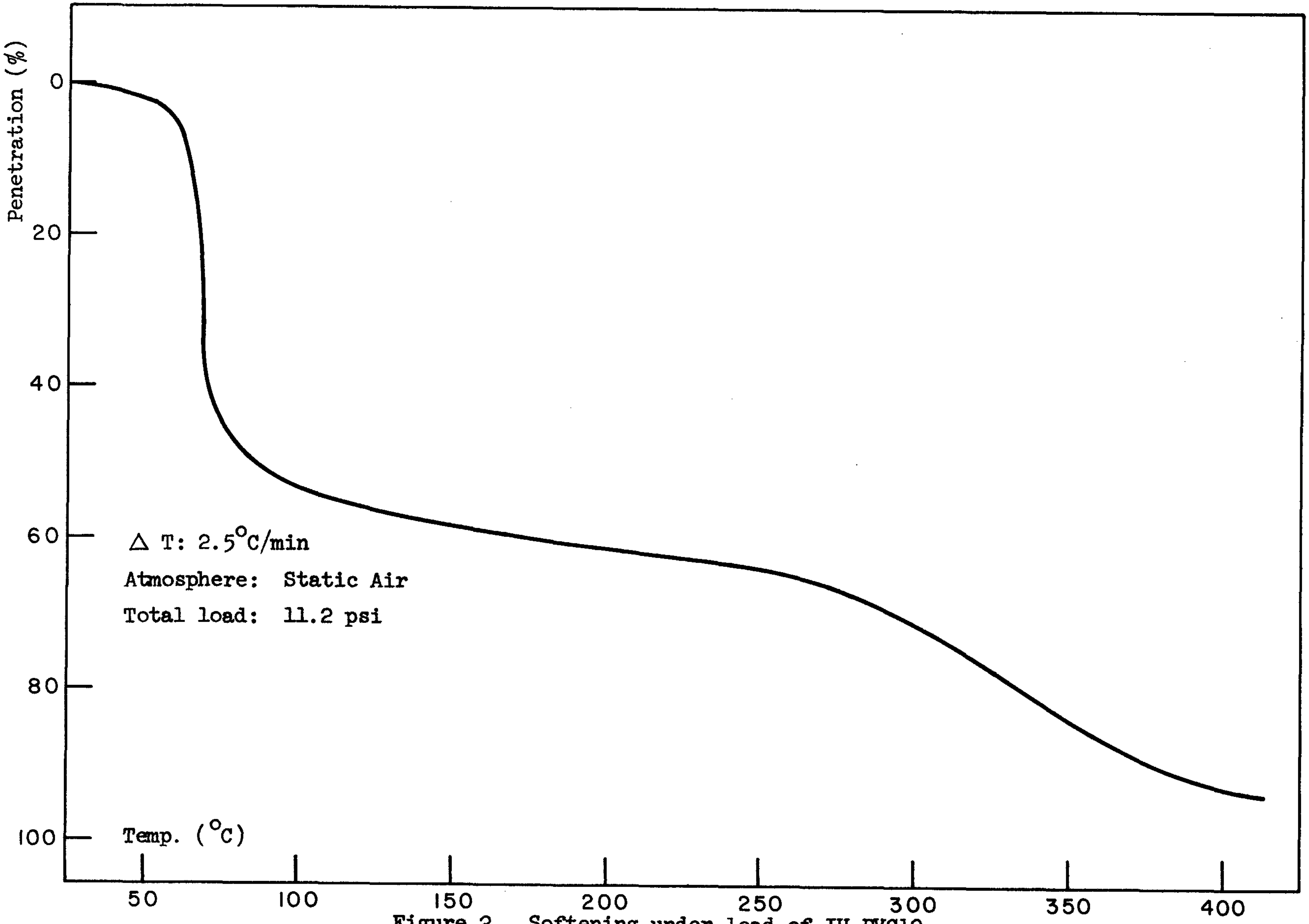


Figure 2. Softening under load of IH-PVC10

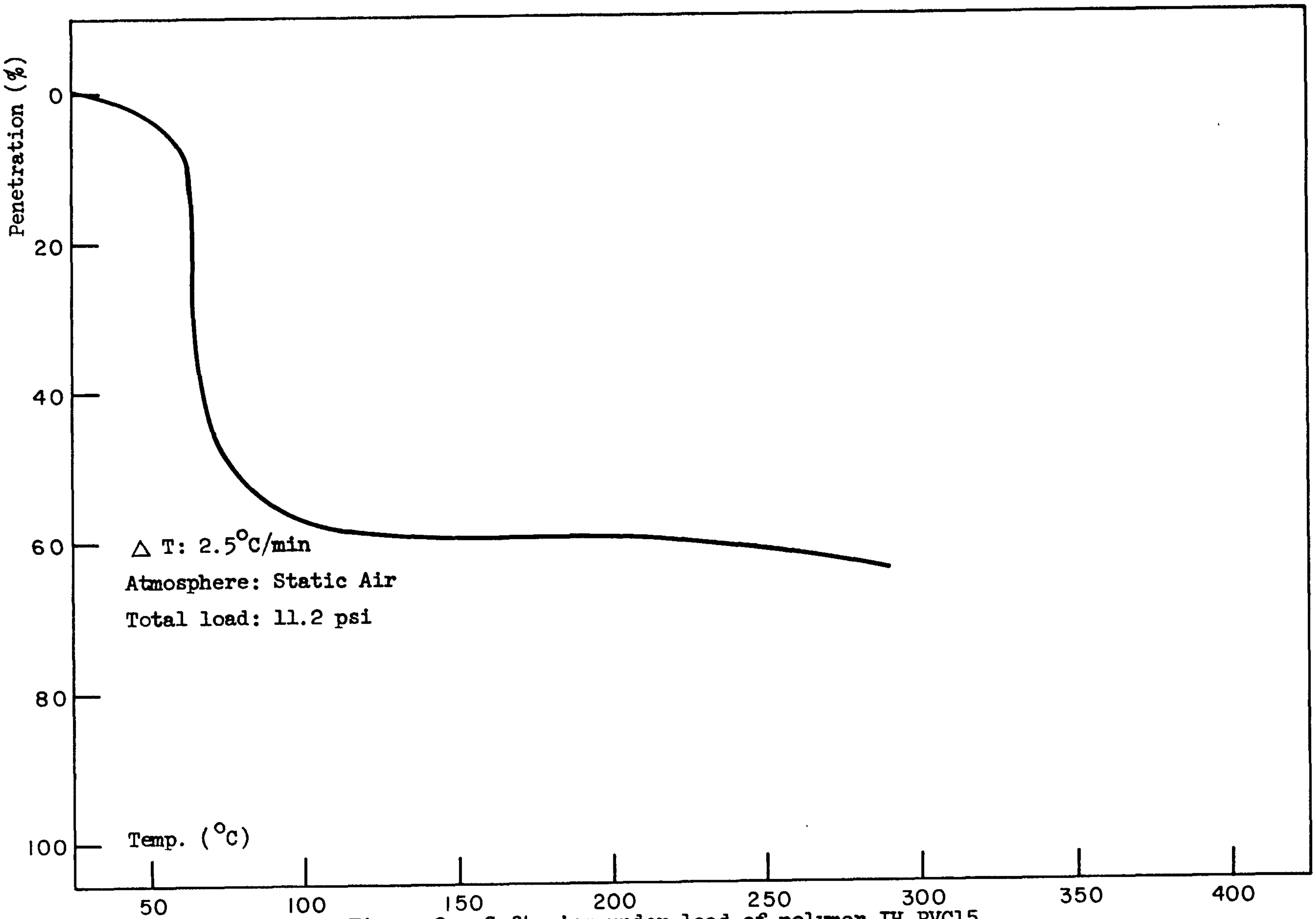


Figure 3. Softening under load of polymer IH-PVC15

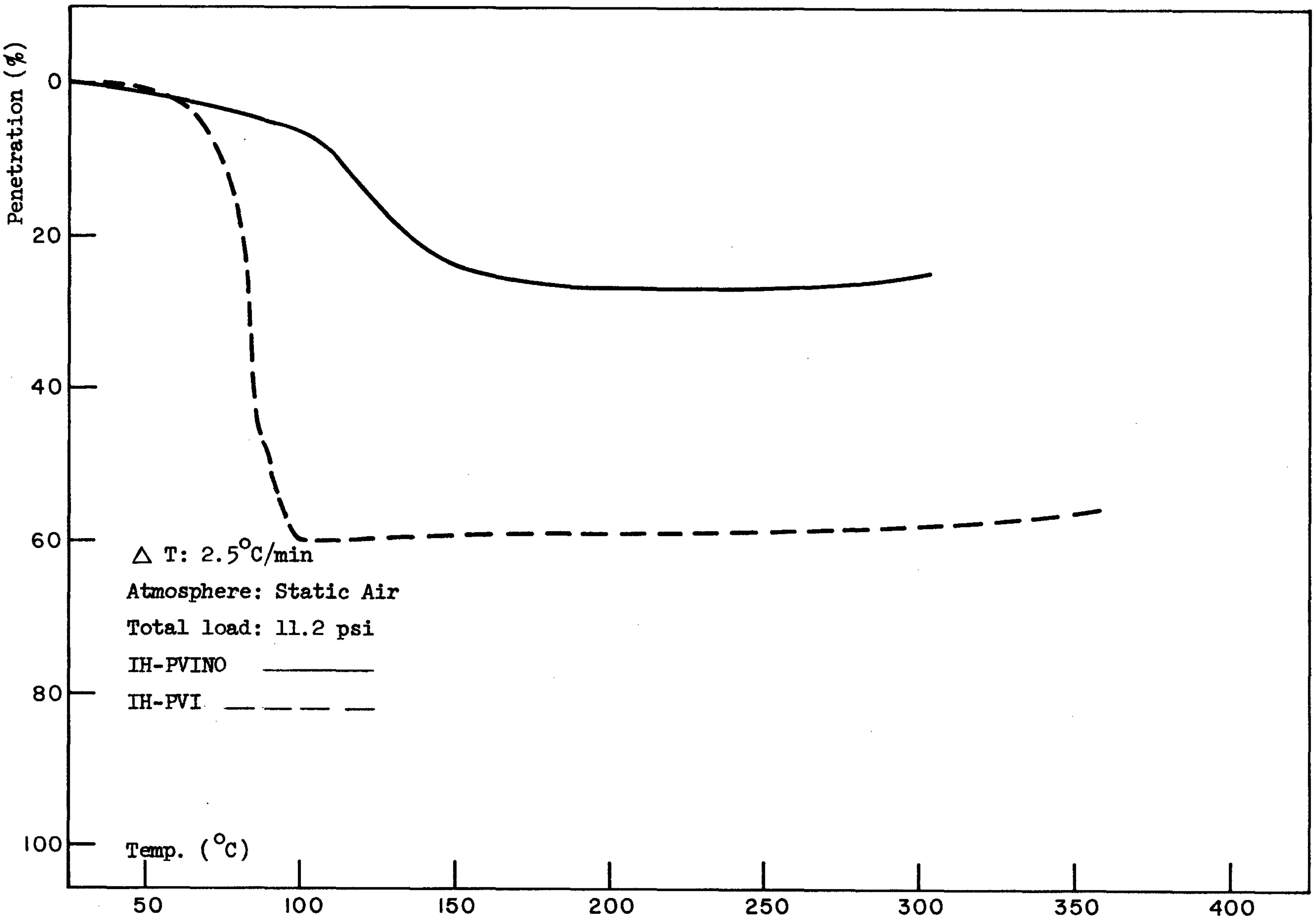


Figure 4. Softening under load of polymers IH-PVI and IH-PVINO

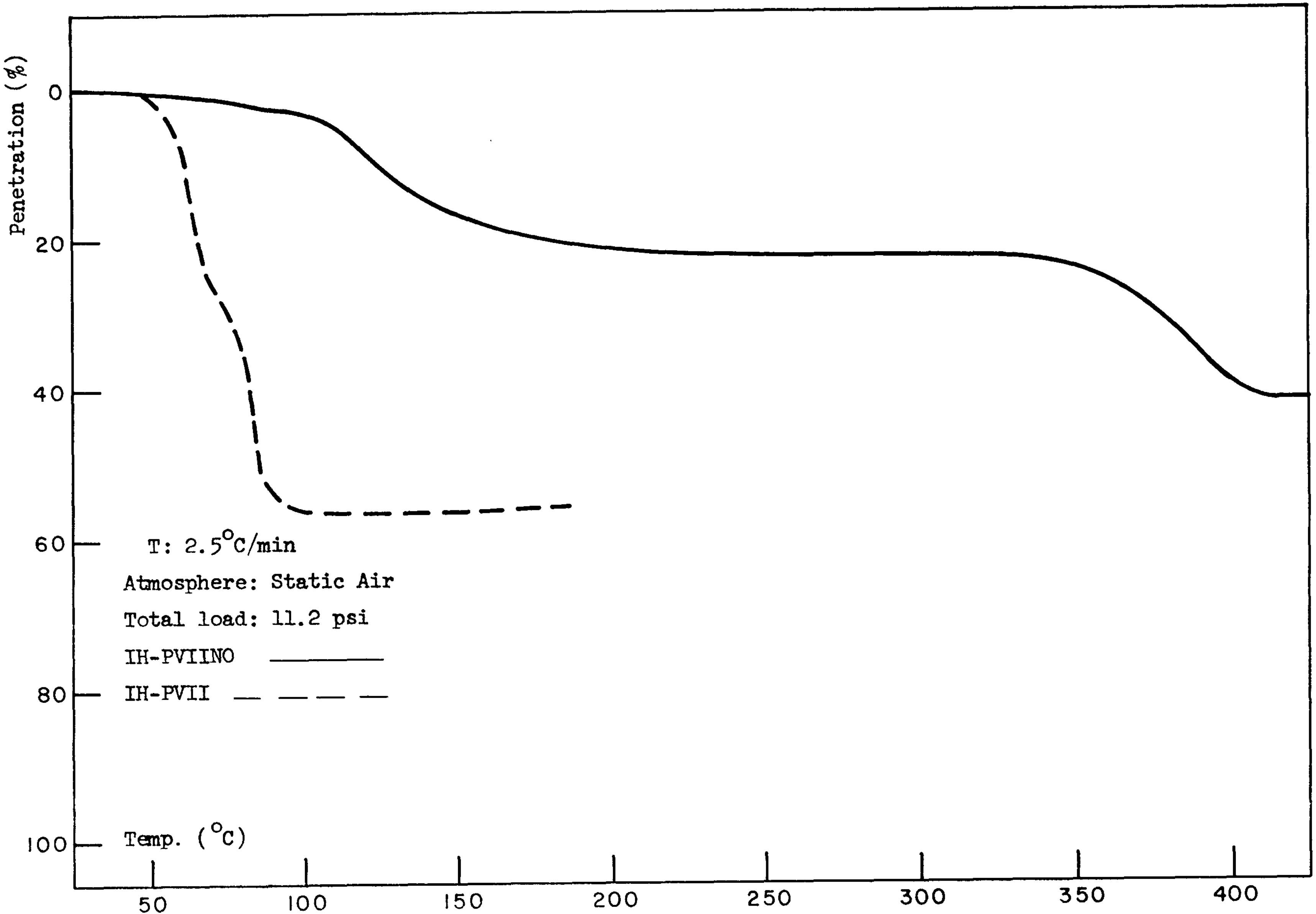


Figure 5. Softening under load of polymers IH-PVII and IH-PVIINO

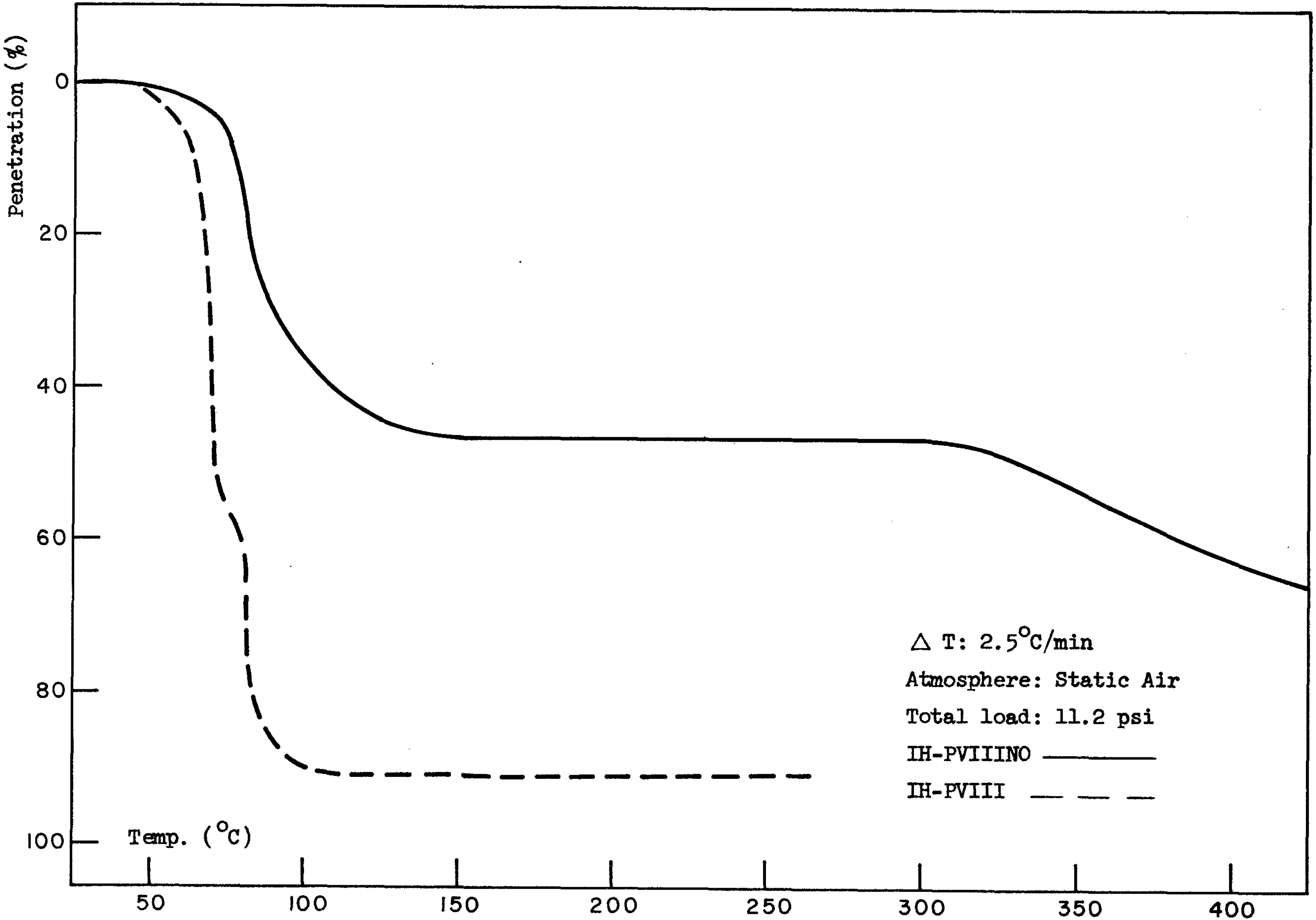


Figure 6. Softening under load of polymers IH-PVIII and IH-PVIIINO

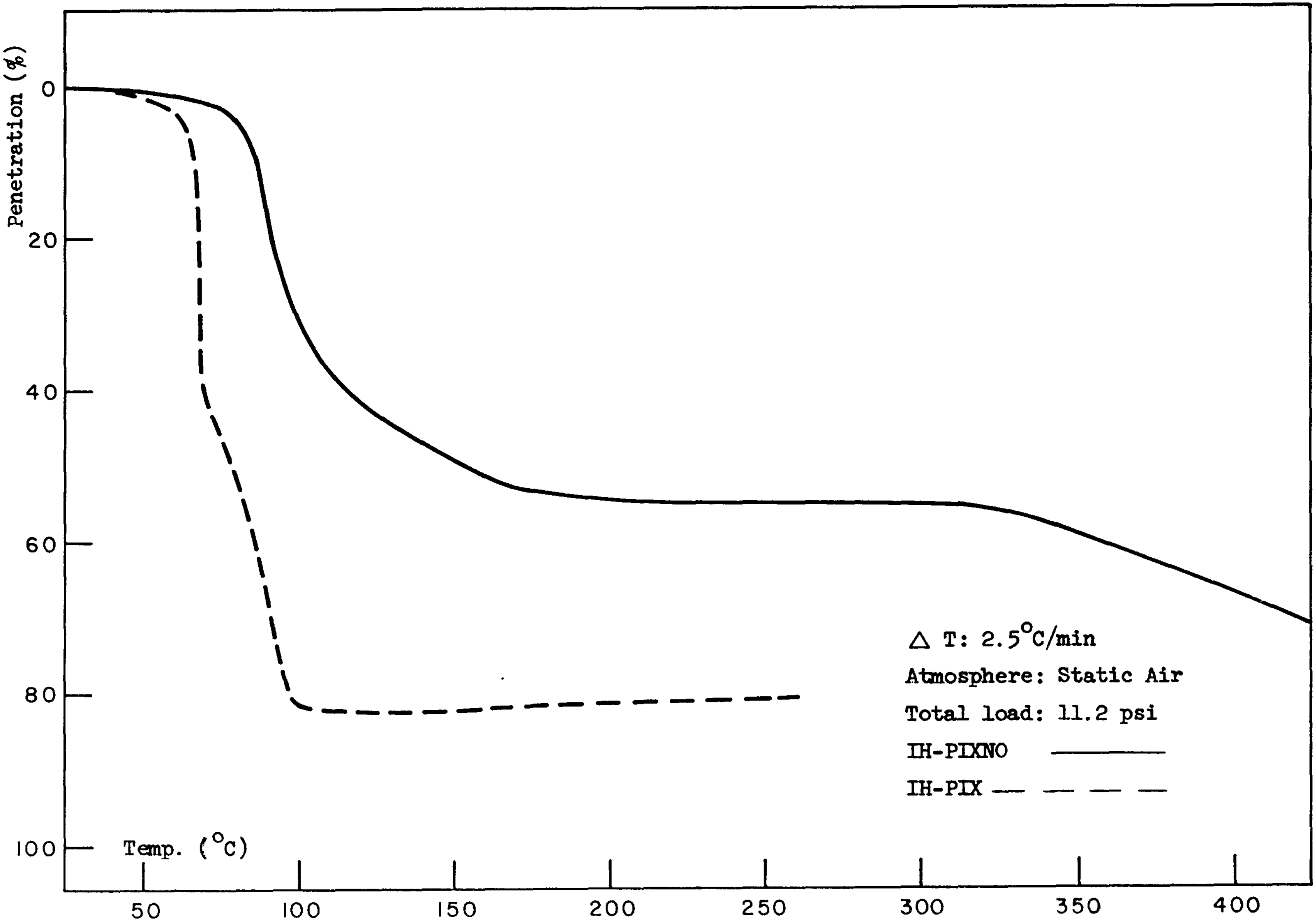
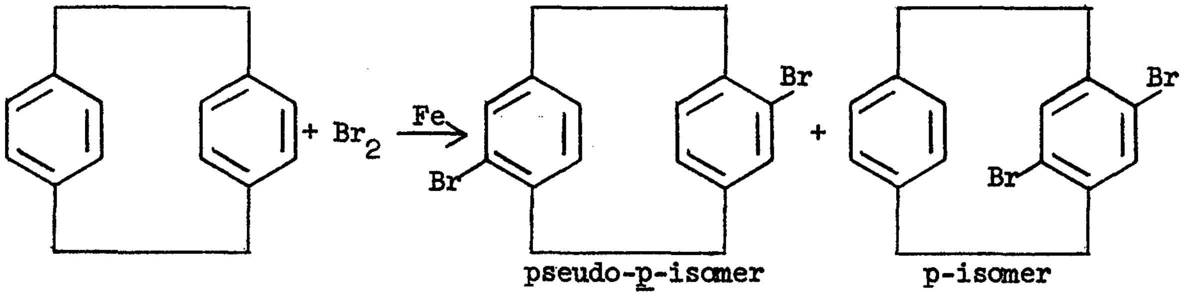


Figure 7. Softening under load of polymers IH-PIX and IH-PIXNO

crosslink. In this laboratory the synthesis of a polyphenylene sulfide containing [2.2]paracyclophane units was sought by the use of dibromo[2.2]-paracyclophane, along with p-dibromobenzene and m-benzenedithiol. Dibromo-[2.2]paracyclophane was prepared by brominating [2.2]paracyclophane in the presence of iron powder according to the procedure of Cram and Reich.[7] The dibromo compound obtained consisted mainly of the pseudo-p-dibromo isomer with a slight amount of the para isomer.



Following the synthesis of the dibromo compound, a polymer containing paracyclophane units was sought from m-benzenedithiol, 90% p-dibromobenzene and 10% dibromo[2.2]paracyclophane. The polymer obtained (IH-PXII) gave a low inherent viscosity and was shown by elemental analysis not to correspond to the desired structure presumably due to the failure of paracyclophane to get incorporated in the polymer backbone. In order to investigate this further, a polyphenylene sulfide prepared from the use of m-benzenedithiol and dibromo[2.2]paracyclophane was attempted twice. In both cases no polymer was obtained as only starting materials were recovered when the reaction mixture was neutralized in a dilute methanolic hydrochloric acid solution. It is believed that two factors are involved in the inability to form the polymer. First, the inductive effect of the two methylene groups causes the benzene rings to be less positively charged and consequently decreases the rate of attack by the thiophenoxide anion. Second, the presence of the two methylene groups on carbons ortho to the carbons being attacked by the bulky sulfide ion causes a steric hindrance which could prevent the reaction from taking place.

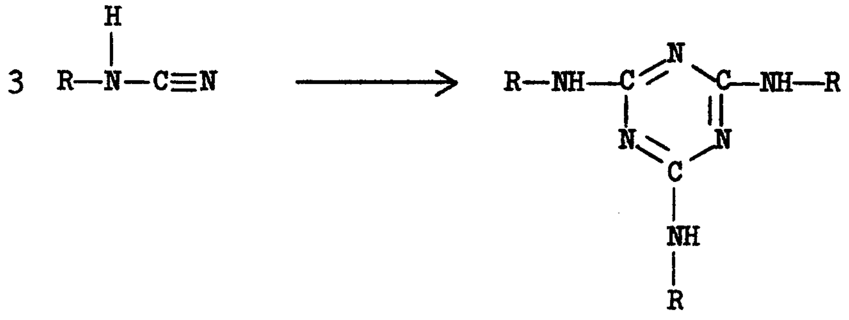
A polyphenylene sulfide containing [2.2]paracyclophane units was then attempted by the use of a paracyclophane monomer which contains more than one bromine in each benzene ring. The presence of the additional bromines was thought to facilitate the nucleophilic substitution reaction by increasing the formal positive charge of the benzene ring. Tetrabromo-[2.2]paracyclophane was therefore prepared from [2.2]paracyclophane and bromine in the presence of iron powder. The product obtained was a mixture of isomers as evidenced by the melting range exhibited by this product, and no attempt to isolate the individual isomers was made since any one of the isomers can be used in the polymerization reaction. No recrystallization solvent for the tetrabromo compound could be found and the final product was obtained by repeated precipitation from chloroform with ether. This technique was however adequate since elemental analysis gave results that were within the required limits of the theoretical values.

The polymerization of m-benzenedithiol and tetrabromo[2.2]paracyclophane in a medium of potassium carbonate/dimethylacetamide produced a creamish polymer that did not melt below 360°C and that could not be dissolved in several organic solvents including dimethylacetamide, hexamethylphosphoric triamide and sulfolane and in concentrated sulfuric acid. It is possible that crosslinking occurred via the additional bromines and so a tribromo[2.2]paracyclophane in which the lonely bromine in one of the benzene rings would be unreactive enough to eliminate crosslinking via this route was sought.

Several reactions to prepare tribomo[2.2]paracyclophane produced only the monobromo compound as evidenced by elemental analysis. The tribromo product was finally obtained from the reaction of the monobromo compound with bromine in the presence of iron powder. As in the case of the tetrabromo compound the tribromo product was hard to recrystallize and an analytical sample was obtained by repeated precipitation from chloroform with ligroin.

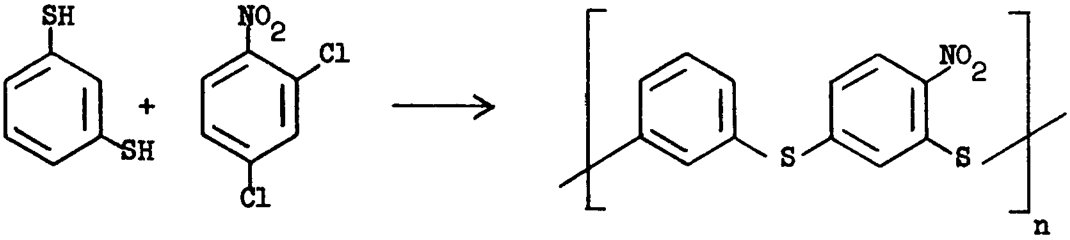
Polymerization of tribromo[2.2]paracyclophane with m-benzenedithiol in a medium of potassium carbonate in dimethylacetamide gave after hydrolysis a product that could not be solubilized in either hexamethylphosphoric triamide or in sulfuric acid. This seems to indicate that if a polymer was obtained, it must have been crosslinked. No efforts to identify the product further were attempted.

The most recent method used to crosslink polyphenylene sulfides makes use of the cyanamide group as the crosslinking site. It has been reported[4] recently that cyanamide-containing monomers were reacted to form crosslinked polymers and that the crosslinking occurred by the trimerization of the cyanamide group to give substituted melamines.



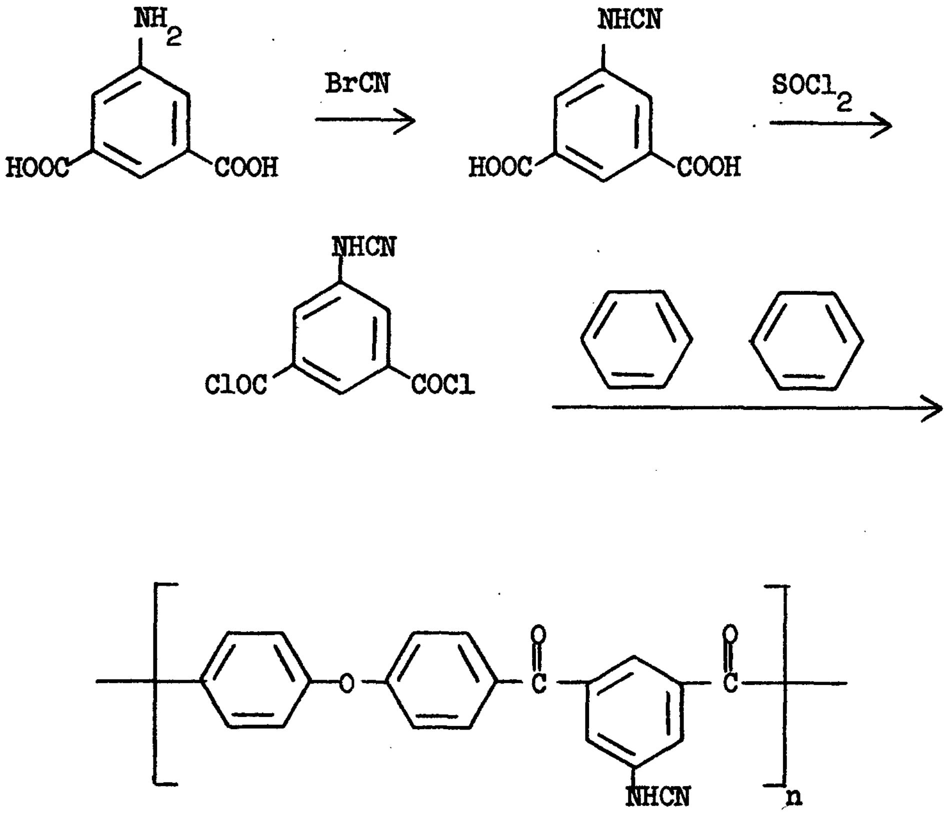
Two methods were followed to produce polymers that contain the cyanamide groups. In the first, introduction of cyanamide group into the polymer chain was sought by the use of a cyanamide-containing monomer. For this purpose, the synthesis of 2,4-dichlorophenylcyanamide was attempted from 2,4-dichloroaniline and cyanogenbromide in ethanol. The product obtained was extremely hard to recrystallize and could only be obtained by repeated precipitation from ether with ligroin at dry ice/acetone temperature ($\sim$ - 78°C). The product obtained looked pure, gave a cyanide absorption in the infrared spectrum but analyzed slightly higher than expected for nitrogen by elemental analysis. Since a purer product could not be obtained, this compound was nevertheless used in the polymerization with m-benzenedithiol. The polymer obtained was soluble in cold hexamethylphosphoric triamide in which solvent a 0.5% solution gave an inherent viscosity of 0.12 dl/g.

It was originally thought that the synthesis of a cyanamide-containing polyphenylene sulfide could not be obtained by the above method since the cyanamide group was not expected to withstand the severe reaction conditions (basic medium at 160-170°C). Therefore a different method to prepare a cyanamide-containing polymer was sought from preparing an amino-containing polyphenylene sulfide which could be later reacted with cyanogen bromide to give cyanamide-containing polymer. The reaction of 2,4-dichloroaniline with m-benzenedithiol by the usual procedure gave a yellow solution that remained unchanged after a reaction time of one week. Hydrolysis of the reaction mixture did not result in a solid polymer precipitate but a milky suspension which turned clear when ether was added. A polymer did not form here since it is believed that the amino group is a strong deactivating agent in the nucleophilic substitution reaction. Due to the failure in preparing an amino-containing polyphenylene sulfide by the above method, a similar polymer was sought from 2,4-dichloronitrobenzene and m-benzenedithiol followed by reduction of the resultant polymer with hydrogen in the presence of palladium on carbon as the catalyst. The polymer containing nitro groups was prepared in the same manner as the previous polymers. The product obtained was yellow-green in color, melted between 260-285°C and was soluble in hexamethylphosphoric triamide in which solvent it gave an inherent viscosity of 0.12 dl/g.



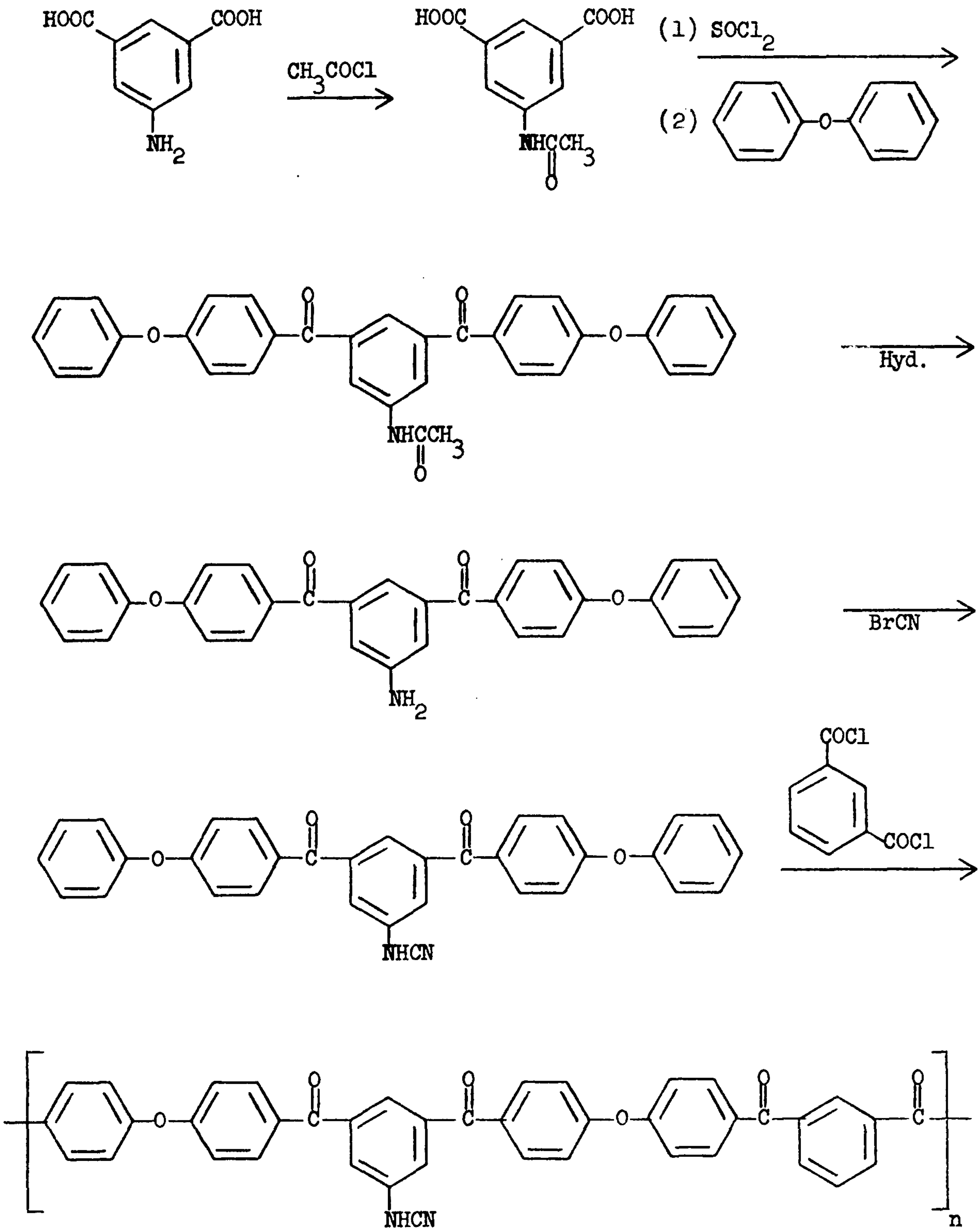
Reduction of this polymer with hydrogen and palladium on carbon has not been completed yet.

Another part of this project involved the synthesis of a polymer, other than a polyphenylene sulfide, containing the cyanamide group. This was initiated since it was thought that the reaction conditions, under which the polyphenylene sulfides are prepared, are too severe to leave the cyanamide groups intact where they can be later used in crosslinking reactions. The polymer sought involved the use of 5-aminoisophthalic acid to prepare a cyanamide containing monomer which can be later polymerized with diphenyl ether as follows:



Because the starting diacid is insoluble on common organic solvents and in most of the exotic ones, the reaction with cyanogen bromide was run in dimethylsulfoxide. The products obtained did not yield the desired compound and so this procedure was abandoned.

Another process to form a cyanamide-containing polymer was attempted as follows:


HOOC
COOH
NH2
CH3COCl
HOOC
COOH
NHCCH3
O
(1) SOCl2
(2)
O
O
C
O
C
O
O
NHCCH3
O
Hyd.
O
O
C
O
C
O
O
NH2
BrCN
COCl
COCl
O
O
C
O
C
O
O
NHCN
O
O
C
O
C
O
O
C
O
C
NHCN
n

3. Experimental

a. 2,4-Dichlorobenzonitrile

The synthesis of this compound was described in an earlier report.[2] It was recrystallized three times before use.

b. 3,5-Dichlorobenzonitrile

This compound was purchased from Aldrich Chemicals and was used as obtained.

c. m-Benzenedithiol

The synthesis of this compound was described in an earlier report.[2]

d. Dibromo[2.2]paracyclophane

This compound was synthesized according to the procedures of Cram and Reich[7] with the exact amounts of starting materials used. The procedure was followed only for the preparation of the pseudo-p-dibromo isomer, however, the product obtained melted with about a 10° range and infrared showed it to contain a small amount of the para isomer.

Anal. Calc. for $C_{16}H_{14}Br$: C, 52.00%; H, 3.74%.
Found: C, 52.49%; H, 3.85%.

e. Tribromo[2.2]paracyclophane

The attempts to synthesize this compound from [2.2]paracyclophane and three moles of bromine in chloroform in the presence of iron powder and the use of a magnetic stirrer gave the monobromo compound even after a reaction time of three days. The tribromo compound was obtained by the reaction of the monobromo compound (5.74 g; 0.02 mole) with 6.5 g (0.041 mole) of bromine in the presence of iron powder and with mechanical stirring. The procedure used was that of Cram[7] for the preparation of the tetrabromo compound and the product was obtained in 25% yield by precipitation from chloroform with ligroin.

Anal. Calc. for $C_{16}H_{13}Br_3$: C, 43.14%; H, 2.92%; Br, 53.93%.
Found: C, 43.36%; H, 2.78%; Br, 53.75%.

f. Tetrabromo[2.2]paracyclophane

This compound was prepared according to the procedure of Cram and Reich.[7] [2.2]Paracyclophane (10.4 g; 0.05 mole) and 32.0 g (0.2 mole) of bromine gave 21.2 g of tetrabromo[2.2]paracyclophane (82% yield).

Anal. Calc. for $C_{16}H_{12}Br_4$: C, 36.68%; H, 2.31%; Br, 61.00%.
Found: C, 36.82%; H, 2.20%; Br, 60.65%.

g. 2,4-Dichlorophenylcyanamide

A solution-suspension of 8.1 g (0.05 mole) of 2,4-dichloroaniline, 5.3 g (0.05 mole) of cyanogen bromide, 5.2 g of potassium bicarbonate in 200 ml of ethanol was stirred at room temperature overnight followed by heating at 60° for 30 hr. The solvent was later distilled and the residue triturated with 10% potassium hydroxide solution. Ether was later added and the organic layer separated, washed with water and dried over magnesium sulfate. Ether was later removed by rotatory evaporation to give a greenish gummy product. After several attempts to recrystallize the residue, it was obtained as a white powdery solid by repeated precipitation from ether with ligroin at dry ice/acetone temperature ($\sim$ -78°). The product obtained weighed 3.6 g (39% yield) and melted at 160-162°C.

Anal. Calc. for $C_7H_4N_2Cl_2$: C, 44.95%; H, 2.15%; Cl, 37.91%; N, 14.98%.
Found: C, 45.06%; H, 2.28%; Cl, 34.86%; N, 16.97%.

h. Polymerizations

All polymerizations were run in a basic medium of potassium carbonate in dimethylacetamide. The procedure has been reported earlier[2] and the amounts of starting materials, reaction conditions and results of polymerizations are given in Table I.

i. Crosslinking

All crosslinking reactions were run in a test tube with a side outlet equipped with aluminum foil lining of the inside walls and were run at $\sim$ 350°C under nitrogen for 24 hr.

j. 5-Acetamidoisophthalic acid

Into a 250 ml round-bottomed flask equipped with a magnetic stirrer, a reflux condenser and a drying tube were placed 10.0 g (0.045 mole) of 5-aminoisophthalic acid and 100 ml of acetyl chloride. The reaction mixture, which stayed milky during the reaction time, was refluxed for three days. After cooling it was poured into 200 ml of ice and the solid filtered and washed with water. Recrystallization of this solid from 50:50 methanol/water gave 8.1 g of the acetanilide after drying. Infrared spectrum of the product gave carbonyl absorptions at 1720 (carboxyl) and 1655 (amide carbonyl)

cm^{-1}. Proton nmr spectrum showed absorptions at $\delta = 8.45$ (2 aromatic protons ortho to amide group), $\delta = 8.18$ (1 aromatic proton ortho to the two carboxyl groups), $\delta = 3.20$ (1 N-H proton) and $\delta = 2.14$ (3 methyl protons).

Anal. Calc. for $C_{10}H_9NO_5$: C, 53.81%; H, 4.06%; N, 6.28%.
Found: C, 52.63%; H, 4.11%; N, 6.13%.

4. Future Plans

This work is essentially complete. No further work on sulfides is planned at the present time.

IV. AROMATIC POLYETHERS, -SULFONES AND -KETONES AS LAMINATING RESINS (NITRILE CONTAINING POLYMERS)

1. Introduction

Thermally stable laminating resins are needed which are low melting in the prepolymer stage and which can be cured without giving off any volatiles.[8] It is anticipated that polymers having nitriles from the main chain can be crosslinked by catalytic trimerization to thermally stable triazine rings.[9] These polymers having nitriles in the backbone of the polymers can also be crosslinked through 1,3-dipolar addition reaction with bis-nitrile oxides to give thermally stable 1,2,4,-oxadiazoles.[10] Alternatively these pendant nitriles can be crosslinked by treating with a difunctional monomer, where the reaction proceeds without the evolution of any volatile byproducts. To be useful these polymers should melt at a temperature not much higher than 200°C, they should flow easily and adhere to glass fibers. We reported in our previous two Annual Reports[11] the synthesis of such type of resins and various catalysts screened to effect the curing reaction. Aromatic ethers, ketones and sulfones are known to be thermally stable. Moieties containing these functional groups were linked with aromatic acid chlorides in a Friedel Crafts type polymerization.

Alternate approach to crosslink polyaromatic ethers, -ketones was undertaken. This was achieved by incorporating [2.2]paracyclophane moieties in the polymer backbone. These polymers on thermal treatment give ethylenic crosslinks. Polymers containing [2.2]paracyclophane units in the backbone on thermal treatment have been reported to afford crosslinked polymers.[12]

a. Polymers from 4,4′-bis(p-phenoxybenzenesulfonyl)diphenyl ether

i) Results and discussion

A terpolymer (PS-3 type) obtained from the Friedel-Crafts type polymerization of 4,4′-bis(p-phenoxybenzenesulfonyl)diphenyl ether, 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene and isophthaloyl chloride, had good thermal properties. The softening point curve of crosslinked PS-3 (using triphenyltin hydroxide as catalyst) appeared to approach that of JVB-50 type resins [made from 1,3-bis(p-phenoxybenzenesulfonyl)benzene] cured with $ZnCl_2$. The polymer PS-3 contains 5 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene.

To get comparisons of thermal and physical properties of polymers with varying cyano content, new products of PS-3 type which contain 3 wt%, 8 wt %, 15 wt % and 25 wt % of 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene were prepared for softening point curve determination and thermogravimetric analysis. These polymers were crosslinked using triphenyltin hydroxide and zinc chloride as catalysts and the isothermal aging of the cured and uncured polymers were studied.

The softening curve of all polymer samples as well as their crosslinked varieties are shown in Figures 8-13. Very little crosslinking has been achieved by using triphenyltin hydroxide and zinc chloride catalysts.

ii) Isothermal aging of terpolymers and crosslinked terpolymers from 4,4′-bis(p-phenoxybenzenesulfonyl)diphenyl ether

The results from the isothermal weight loss studies of PS-3 polymer and its crosslinked products obtained by using zinc chloride and triphenyltin hydroxide as catalysts are given in Table V. It can be seen from the Table V that these polymers possess good thermal stability at 300°C but losses are considerable at 350°C. Isothermal aging was studied in an atmosphere of circulating air.

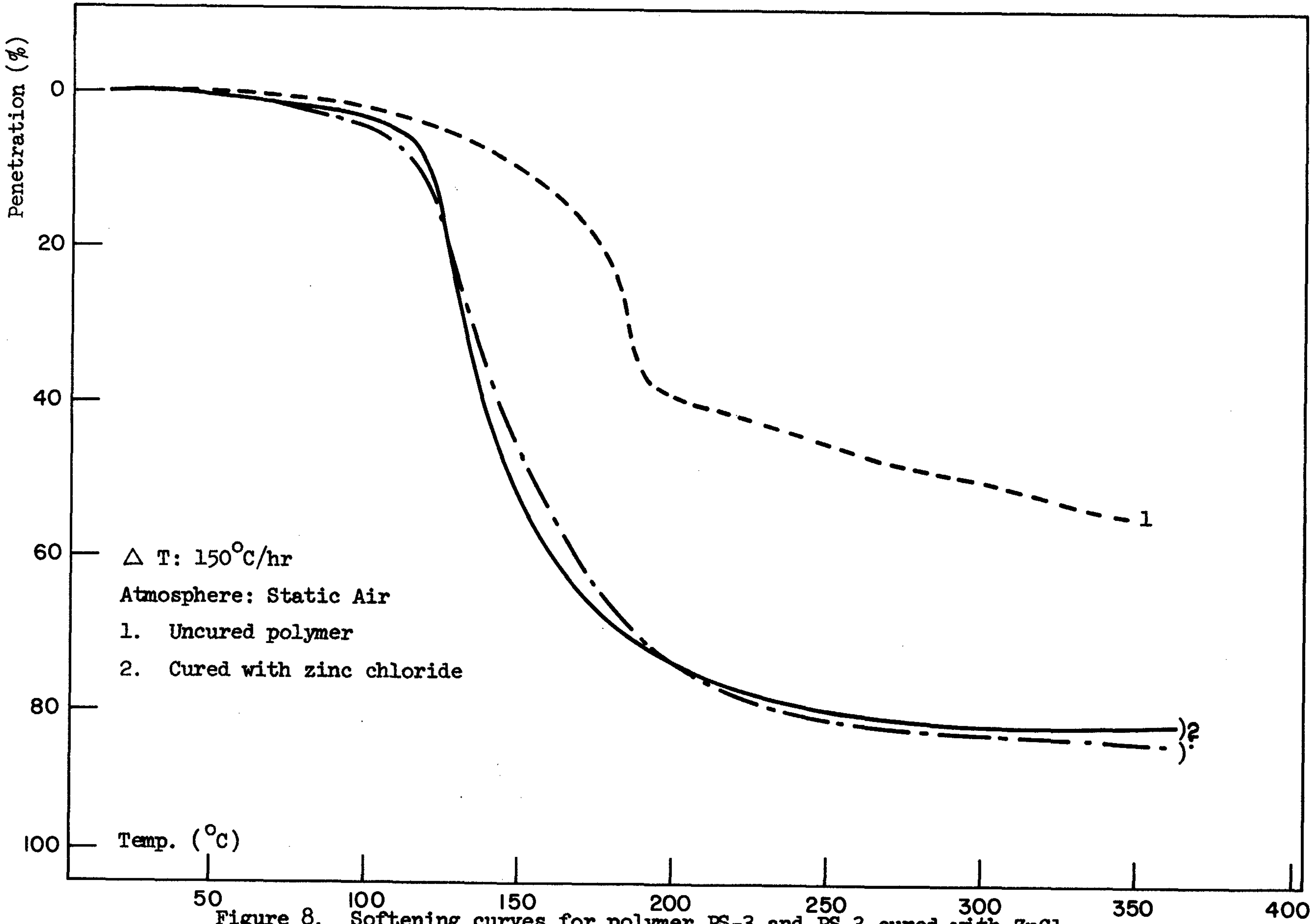


Figure 8. Softening curves for polymer PS-3 and PS-3 cured with $ZnCl_2$.
Measured by Vicat Apparatus.

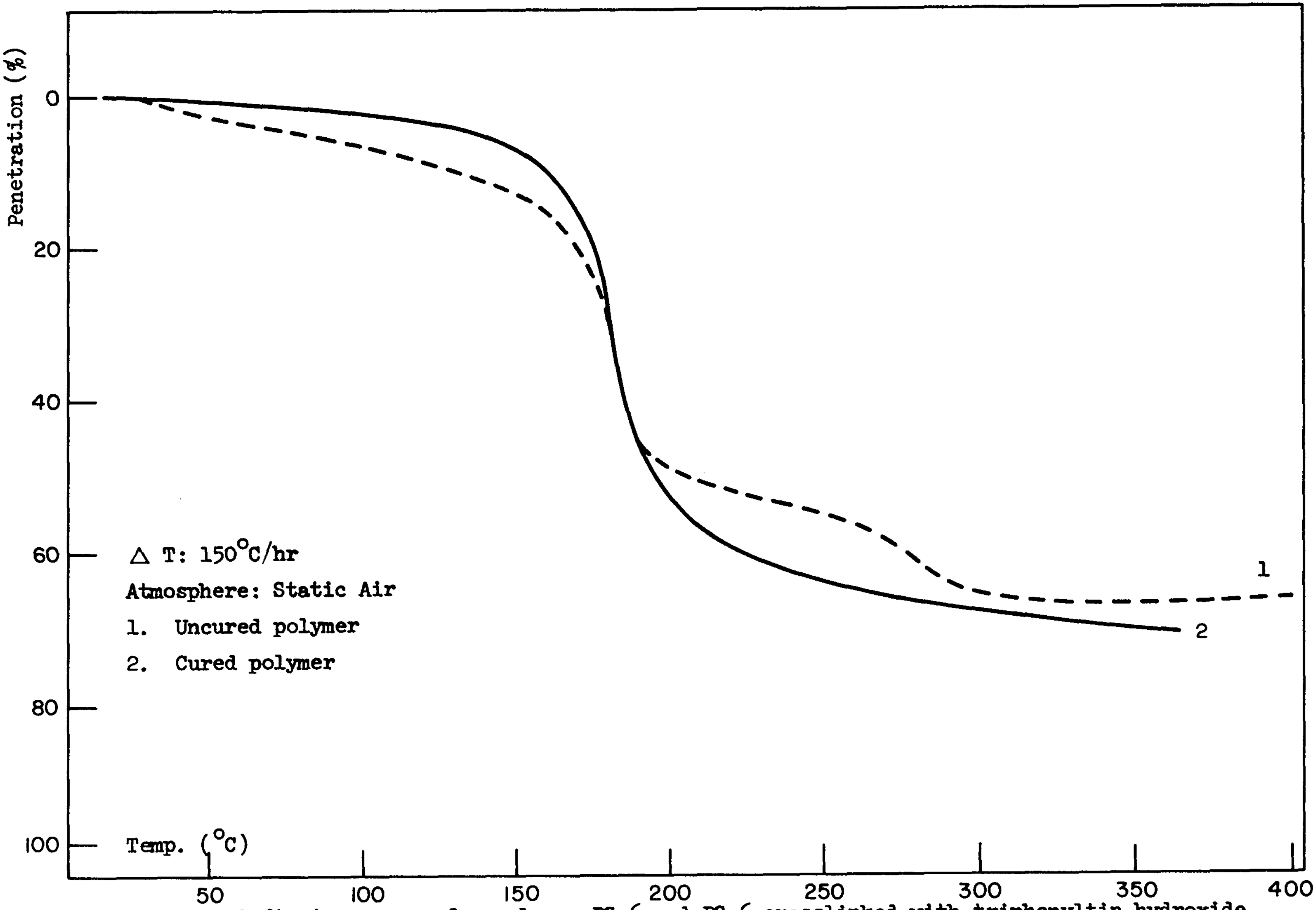


Figure 9. Softening curves for polymer PS-6 and PS-6 crosslinked with triphenyltin hydroxide

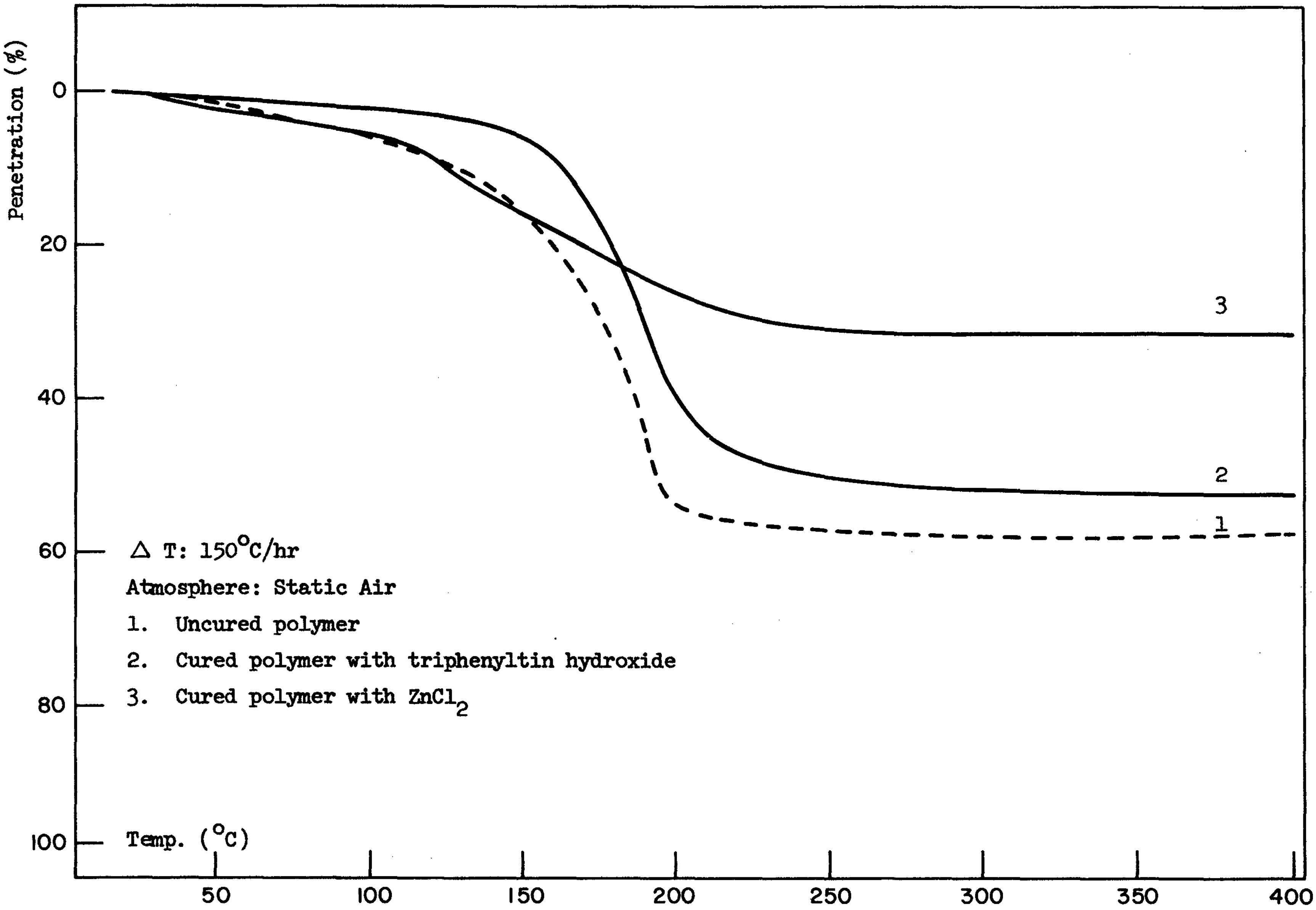


Figure 10. Softening curves for polymer PS-7 and PS-7 crosslinked with triphenyltin hydroxide and zinc chloride. Measured by Vicat Apparatus.

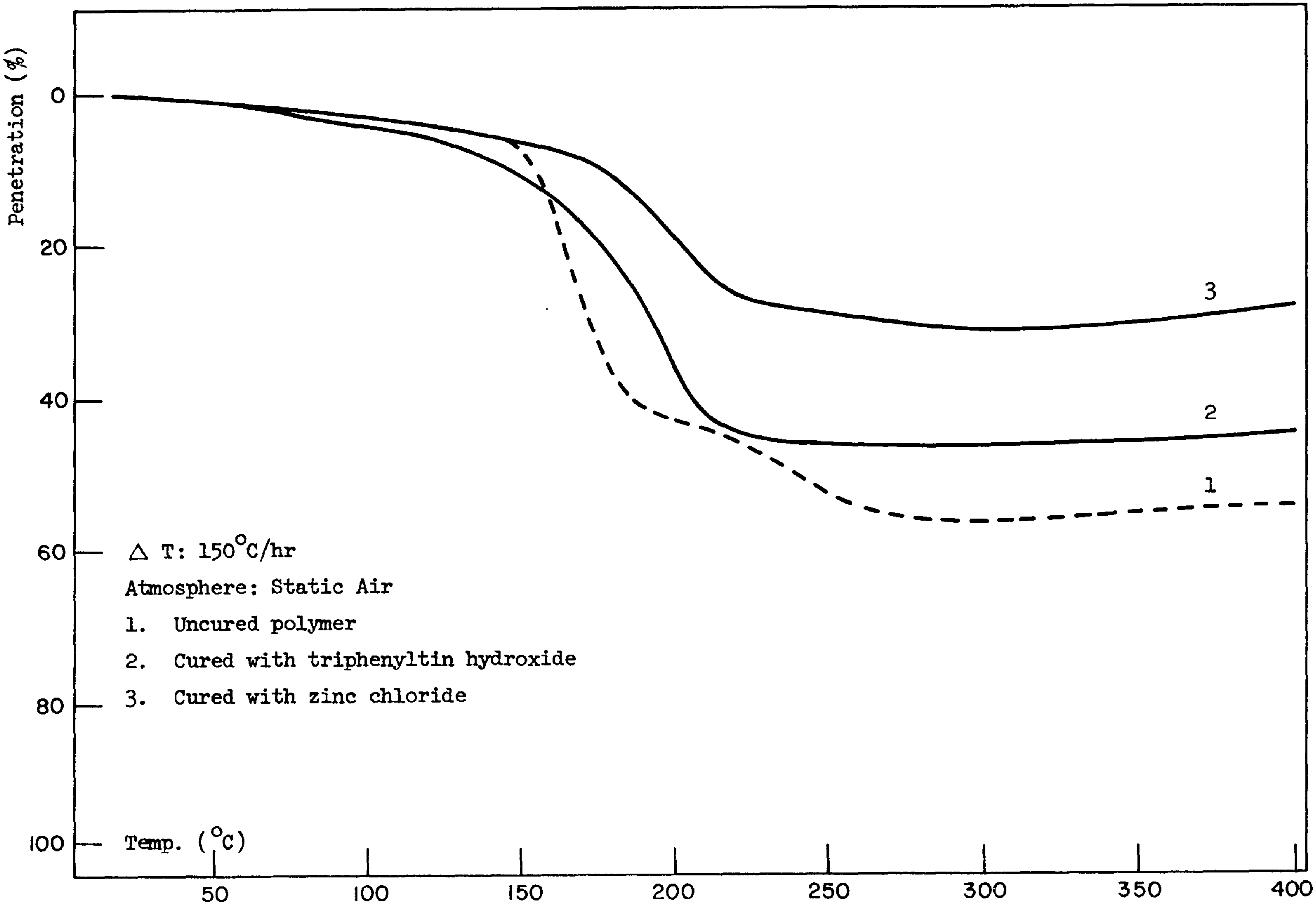


Figure 11. Softening curves for polymer PS-8 and PS-8 crosslinked with triphenyltin hydroxide and zinc chloride. Measured by Vicat Apparatus.

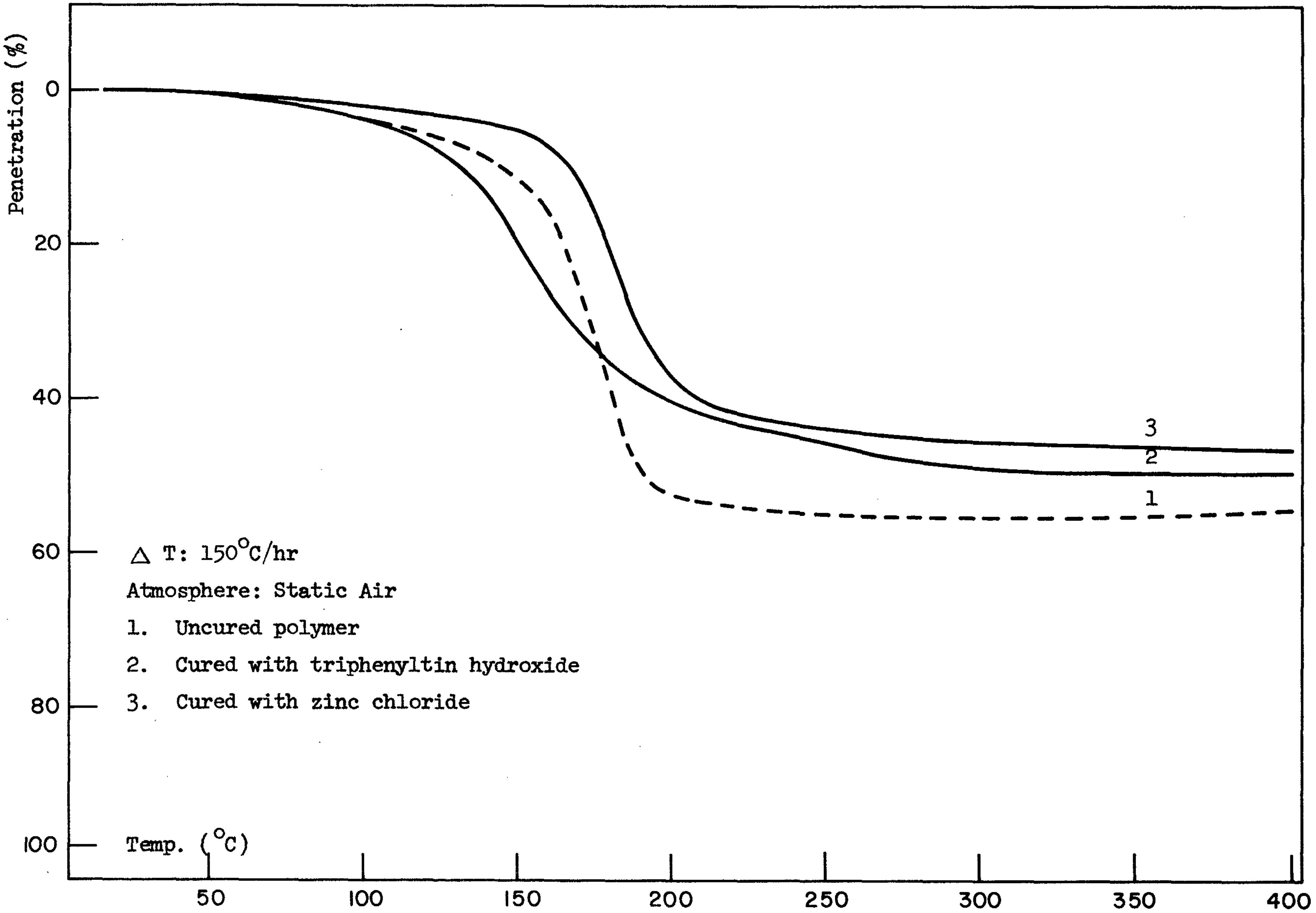


Figure 12. Softening curves for polymer PS-9 and PS-9 crosslinked with triphenyltin hydroxide and zinc chloride. Measured by Vicat Apparatus.

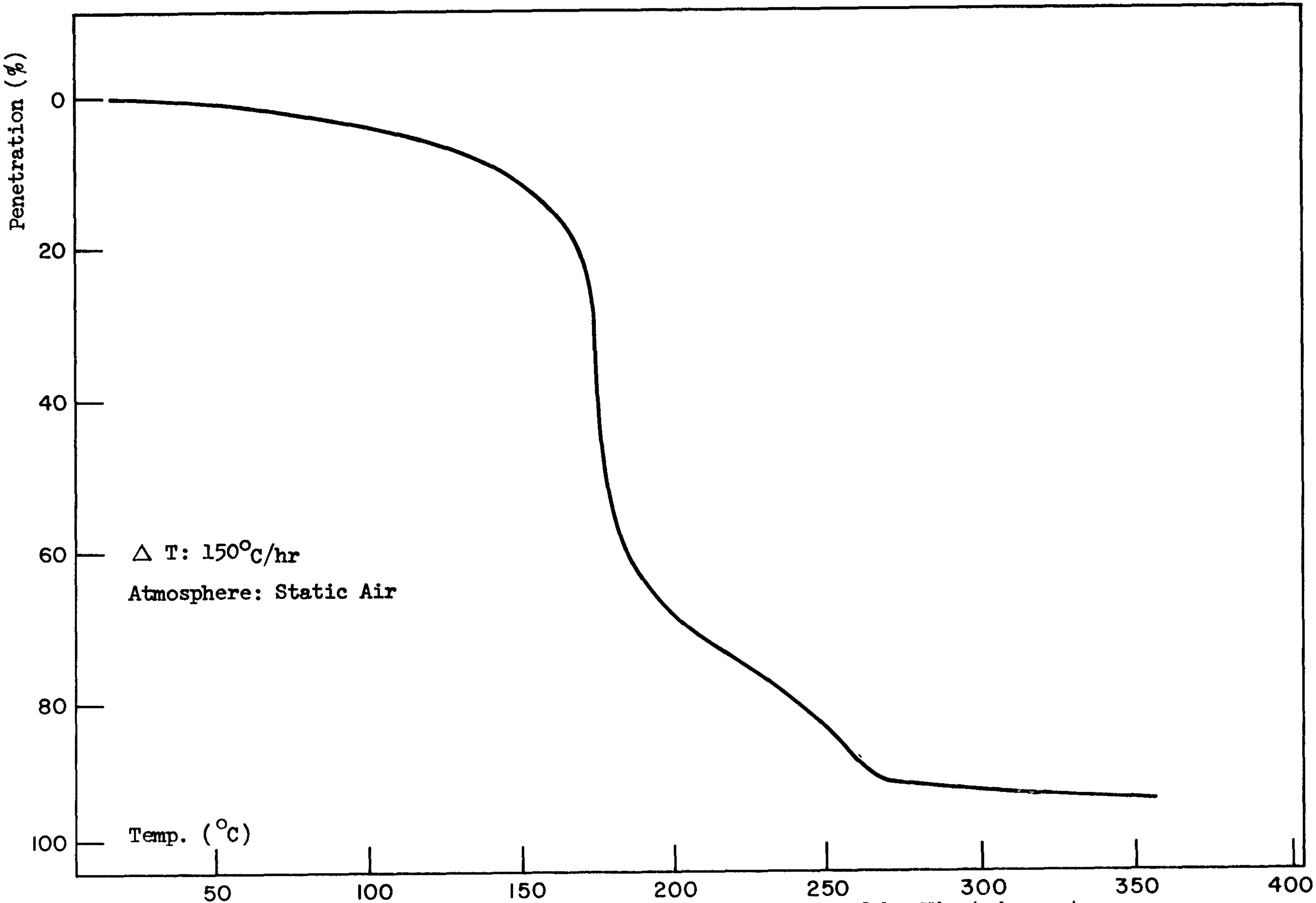


Figure 13. Softening curve for polymer PS-10. Measured by Vicat Apparatus.

TABLE V

ISOTHERMAL WEIGHT LOSSES (% wt) OF TERPOLYMERS FROM 4,4′-bis(p-PHENOXYBENZENESULFONYL)DIPHENYL ETHER

Time	PS-3	PS-3**	PS-6	PS-6**	PS-7	PS-7*	PS-7**	PS-8	PS-8*	PS-8**	PS-9	PS-9*	PS-9**
<u>Temp. 300°C</u>													
24	2.46	2.2	1.32	3.97	1.41	1.87	7.0	.6	4.0	2.92	1.5	1.71	7.3
48	2.78	9.5	2.04	4.30	1.68	1.68	7.5	.6	4.0	3.71	2.1	2.24	9.0
96	6.75	10.7	4.79	6.61	4.5	3.5	10.6	1.8	5.9	7.25	4.5	4.88	12.4
168	6.75	10.7	4.80	6.61	4.5	3.5	11.1	1.8	5.9	7.30	4.5	4.88	12.5
<u>Temp. 350°C</u>													
24	18.0	27.0	15.03	12.10	15.6	9.53	22.5	4.6	12.62	18.35	14.2	5.0	12.9
48	41.35	50.3	30.55	14.70	33.4	12.15	31.8	19.4	17.82	29.0	28.1	22.7	35.4
72	74.82	57.4	60.40	22.80	65.9	20.75	52.24	39.67	33.3	50.96	57.6	46.2	54.8
168	98.4	91.4	96.10	76.74	99.0	71.9	95.5	89.5	81.85	95.8	99.5	95.94	90.22

* Crosslinked using triphenyltin hydroxide as catalyst.

** Crosslinked using zinc chloride as catalyst.

PS-3 (crosslinked using triphenyltin hydroxide) at 300°C (12.9% wt loss) at 350°C (78.0% wt loss).

iii) Experimental

a) Preparation of 3 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene content in PS-3 type polymer

4,4′-Bis(p-phenoxybenzenesulfonyl)diphenyl ether (19.65 g; 31 mM), 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (0.75 g; 1.5 mM) and isophthaloyl chloride (6.60 g; 32.5 mM) were dissolved in 250 ml of dry dichloroethane. $AlCl_3$ (27 g) was added and the mixture was stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 21.5 g; mp 235-240°C. $\eta_{inh} = 0.595$ in H_2SO_4 at 30°C. Sample submitted as PS-6. See Figure 9.

Anal. Calc.: C, 69.20%; H, 3.93%; S, 8.02%.
Found: C, 67.55%; H, 3.57%; S, 8.20%.

b) Preparation of 8 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene content in PS-3 type polymer

4,4′-Bis(p-phenoxybenzenesulfonyl)diphenyl ether (18.1 g; 28.5 mM), 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (1.98 g; 4 mM) and isophthaloyl chloride (6.60 g) were dissolved in 250 ml of dry dichloroethane. $AlCl_3$ (27 g) was added and the mixture was stirred under dry nitrogen at room temperature during 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 22.0 g mp 225-235°C. $\eta_{inh} = 0.645$ in H_2SO_4 at 30°C. Sample submitted as PS-7. See Figure 10.

Anal. Calc.: C, 69.82%; H, 3.94%; S, 7.54%; N, 0.22%.
Found: C, 68.50%; H, 3.62%; S, 6.98%; N, 0.21%; Res., 0.47%.

c) Preparation of 15 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene content in PS-3 type polymer

4,4′-Bis[p-phenoxybenzenesulfonyl]diphenyl ether (15.85 g; 25 mM); 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (3.71 g; 7.5 mM) and isophthaloyl chloride (6.60 g; 32.5 mM) were dissolved in 250 ml of dry dichloroethane. $AlCl_3$ (27 g) was added and the mixture was stirred under dry nitrogen at room temperature during 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 21.8 g mp 225-235°C. $\eta_{inh} = 0.594$ in H_2SO_4 at 30°C. Sample submitted as PS-8. See Figure 11. Anal. Calc.: C,71.10%; H, 3.95%; S, 6.73%; N, 0.44%.
Found: C,69.34%; H, 3.61%; S, 6.20%; N, 0.44%; Res.,0.51%.

d) Preparation of 25 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene in PS-3 type polymer

4,4′-Bis[p-phenoxybenzenesulfonyl]diphenyl ether (13.15 g; 20.75 mM); 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (5.82 g; 11.75 mM) and isophthaloyl chloride (6.60 g; 32.5 mM) were dissolved in 250 ml of dry dichloroethane. $AlCl_3$ (27 g) was added and the mixture was stirred under dry nitrogen during 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 22 g; mp 225-230°C. $\eta_{inh} = 0.655$ in H_2SO_4 at 30°C. Sample submitted as PS-9. See Figure 12.

Anal. Calc.: C, 71.94%; H, 3.99%; S, 5.72%; N, 0.70%.
Found: C, 70.51%; H, 3.64%; S, 5.91%; N, 0.61%; Res., 0.75%.

e) Preparation of 5 wt % of 5-cyanoisophthaloyl unit in terpolymer (JVB-57 type polymer)

4,4′-Bis[p-phenoxybenzenesulfonyl]diphenyl ether (9.51 g; 15 mM), 5-cyanoisophthaloyl chloride (0.57 g; 2.5 mM) and isophthaloyl chloride (2.54 g; 12.5 mM) were dissolved in 100 ml of dichloroethane. $AlCl_3$ (10 g) was added and the mixture was stirred under dry nitrogen at room temperature during 24 hr. The precipitate was filtered and washed three times with methanol in a blender. Yield 9.2 g; mp 225-230°C. $\eta_{inh} = 0.594$ in H_2SO_4 at 30°C. Sample submitted as PS-10. See Figure 13.

Anal. Calc.: C, 69.11%; H, 3.66%; S, 8.38%.
Found: C, 66.83%; H, 3.57%; S, 7.97%; Res., 0.94%.

f) Attempted crosslinking of PS-5 and PS-8 polymer using chlorosulfonic acid

A solution of 1 g of the polymer in 6 g of chlorosulfonic acid were kept at 0° for 24 hr. The solution was poured over ice and the product was filtered, washed with water, and dried. No crosslinking could be effected under this condition as the polymer was found to be soluble in dimethylacetamide.

b. Polymers from 1,3-bis(p-phenoxybenzenesulfonyl)benzene

i) Results and discussion

In earlier reports the preparation of JVB-50 type polymers having 3 to 25 wt % of 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene was reported. When these polymers were heated alone or in the presence of zinc chloride under nitrogen and at 300°C insoluble dark products were obtained. These products showed Vicat softening point around 150-200°C. This lower softening point for a crosslinked polymer was believed to be the result of insufficient crosslinking sites (cyanide groups) along the polymer chains. For this reason a polymer having higher cyano content was obtained from the Friedel-Crafts polymerization of 1,3-bis(p-phenoxybenzenesulfonyl)benzene and 5-cyanoisophthaloyl chloride. The reaction was found to be very slow and afforded a polymer having an inherent viscosity of 0.36 in H_2SO_4. Crosslinking of this polymer was effected by heating it at 360°C for 24 hr in nitrogen atmosphere. Softening curves for non-crosslinked as well as crosslinked polymers are given in Figures 14 and 15.

Approach to crosslink polymers containing pendant aromatic nitriles in the polymer chain through the 1,3-dipolar addition reaction with bis-nitrile oxide was studied. For this purpose terephthalonitrile oxide was prepared and crosslinking reaction with JVB-50 type polymer having 25 wt % of 1,3-bis(p-phenoxybenzoyl)-5-cyano benzene was studied. No crosslinking could be effected.

ii) Experimental

a) Preparation of PS-12 (25 wt % cyano component)

1,3-Bis(p-phenoxybenzenesulfonyl)benzene (5.1496 g; 10 mM), 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (2.9680 g; 5.98 mM) isophthaloyl chloride (2.1407 g; 10.66 mM) and terephthaloyl chloride (1.0705 g, 5.33 mM) were dissolved in dry dichloroethane (75 ml). Aluminum chloride (7.5 g; 56.25 mM) was added, and the mixture was stirred under nitrogen at room temperature for 24 hr. The mixture was diluted with methanol and filtered. The polymer was washed with methanol three times in a blender. mp 160-180°C $\eta_{inh} = 0.594$ in H_2SO_4 at 30°C.

Anal. Calc.: C, 71.49%; H, 3.96%; N, 0.80%; S, 6.09%.

Found: C, 70.20%; H, 3.70%; N, 0.64%; S, 5.99%; Res., 0.1%.

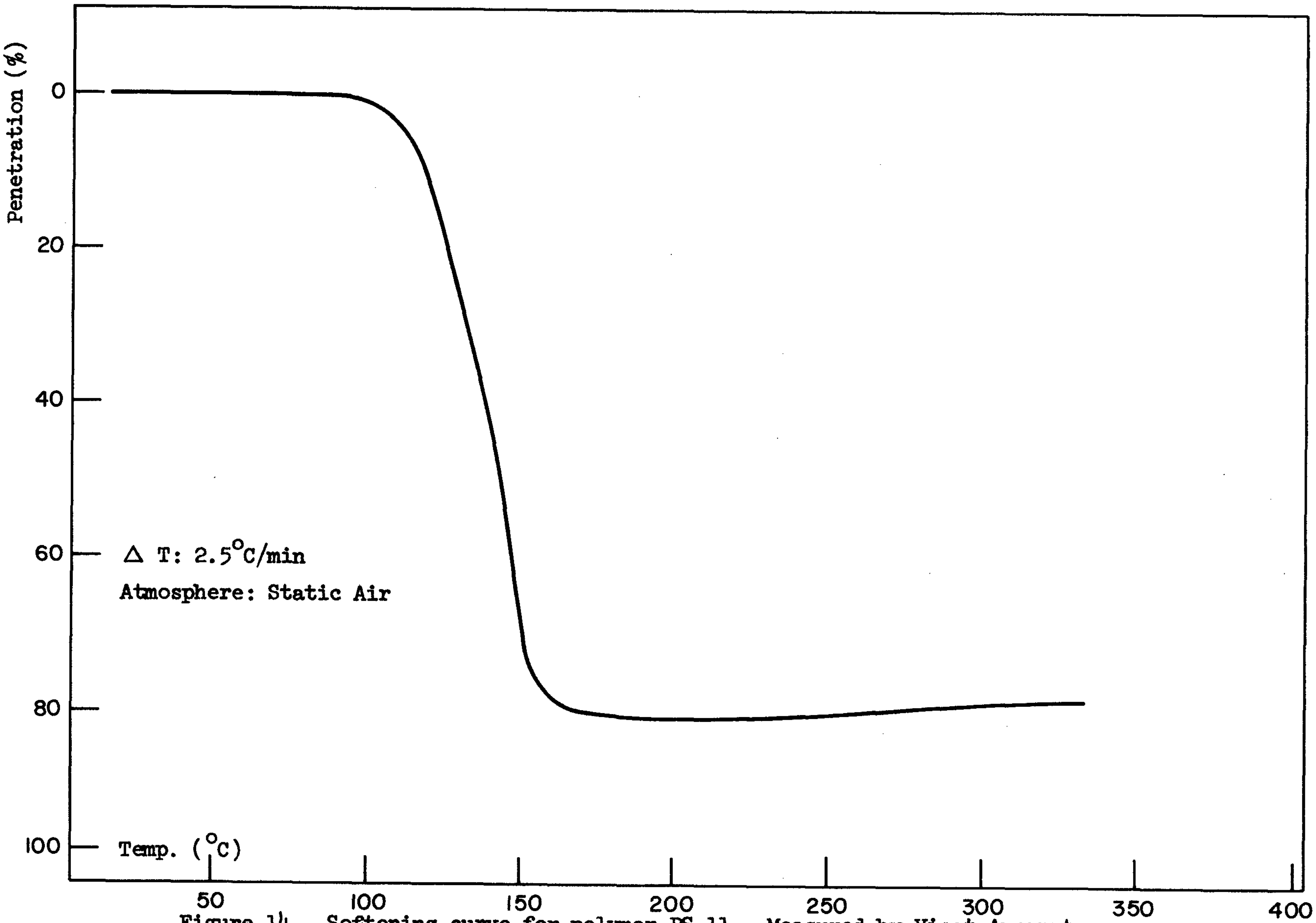


Figure 14. Softening curve for polymer PS-11. Measured by Vicat Apparatus.

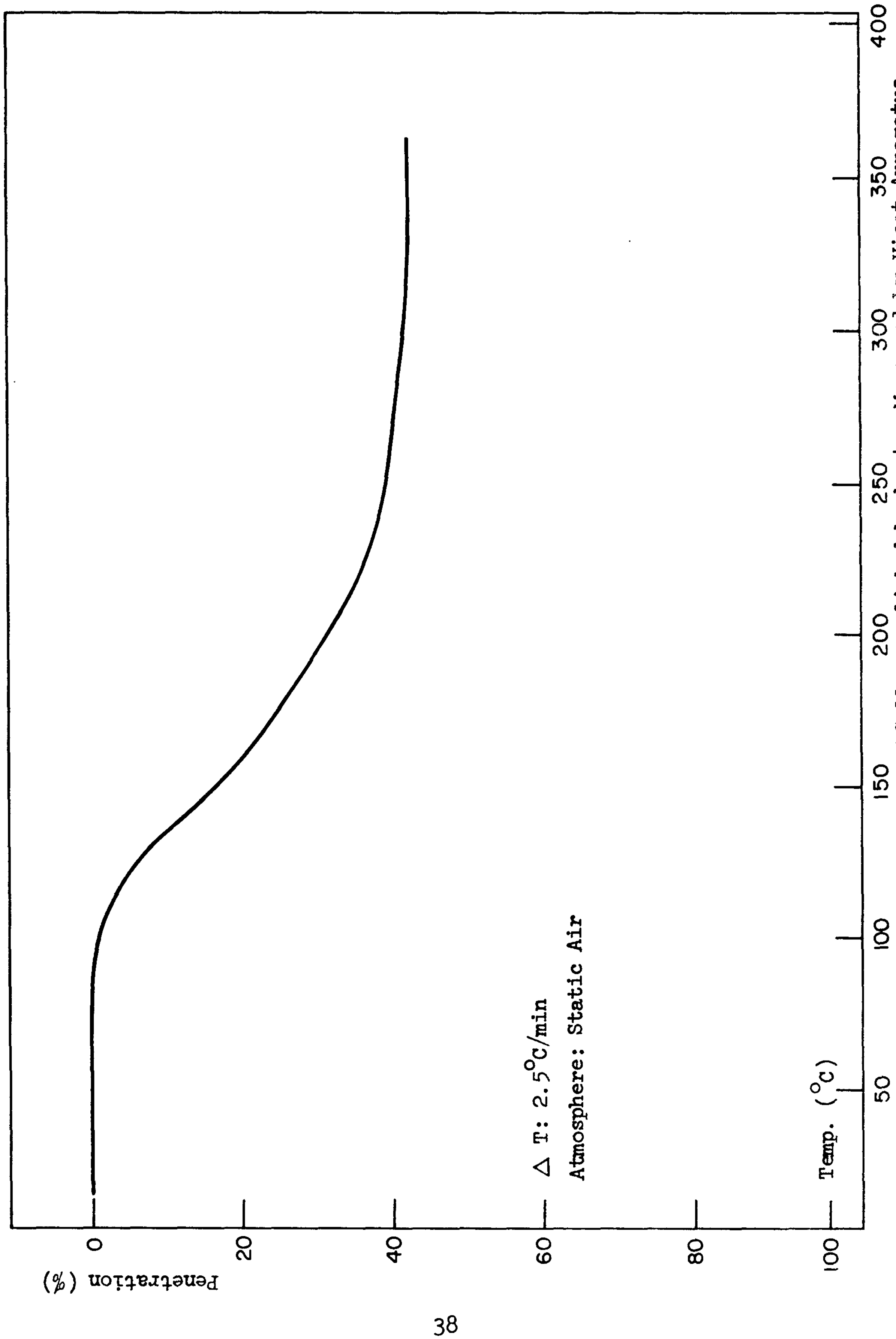


Figure 15. Softening curve for polymer PS-11 crosslinked by heat. Measured by Vicat Apparatus.

b) Polymer from 1,3-bis(p-phenoxybenzenesulfonyl)benzene and 5-cyanoisophthaloyl chloride

1,3-Bis(p-phenoxybenzenesulfonyl)benzene (2.71 g; 5.0 mM) and 5-cyanoisophthaloyl chloride (1.14 g; 5.0 mM) were dissolved in 50 ml of dry dichloroethane. $AlCl_3$ (6.75 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed three times with methanol in a blender and dried. Yield = 3.4 g. mp 175-190°C η_{inh} = 0.358 in H_2SO_4 at 30°C. Sample submitted to Materials Laboratory as PS-11. See Figure 14.

Anal. Calc.: C, 66.95%; H, 3.58%; S, 9.15%; N, 2.00%.

Found: C, 65.24%; H, 3.85%; S, 8.65%; N, 1.34%; Res., 1.39%.

Heating PS-11 at 360°C for 24 hr in nitrogen atmosphere yielded 90% crosslinked polymer (insoluble in dimethylacetamide). This insoluble product was labelled as PS-11-C. See Figure 15.

Anal. Calc.: C, 66.95%; H, 3.85%; S, 9.15%; N, 2.00%.

Found: C, 66.41%; H, 4.26%; S, 7.74%; N, 2.64%; Res., 1.15%.

c) Attempted crosslinking reaction of JVB-50 type polymers with terephthalonitrile oxide

i) Preparation of terephthaldehyde dioxime

Terephthaldehyde (29.8 g; 0.222 mole) was dissolved in 250 ml of absolute ethanol. A solution of free hydroxylamine was then prepared by adding a solution of sodium hydroxide (19.6 g; 0.4895 mole) in 38 ml of water to hydroxylamine hydrochloride (34.0 g; 0.4895 mole) in 178 ml of water. This solution was then added to the solution of terephthaldehyde in ethanol. The resulting reaction mixture was heated at reflux for one hr and cooled to room temperature. The oxime which separated, was recovered by filtration. The filtrate was concentrated to about one half its volume and the oxime isolated by filtration. The combined yield of oxime was 39 g or 98.5 percent of theory and it had a melting point of 222°C. Recrystallization from a 1:1 ethanol-water mixture yielded white crystals having a mp of 224°C.

d) Preparation of terephthalhydroximoyl chloride

A one-liter, three-necked flask was equipped with a stirrer, gas inlet and outlet tube and a thermometer. To the reaction flask was added terephthalaldehydedioxime (33.3 g; 0.203 mole) and nitrobenzene (330 ml). While the slurry was stirred vigorously a stream of chlorine gas was bubbled through for 6 hr at room temperature (∼ 30°C). The product was filtered and washed with fresh carbon tetrachloride. No attempt was made at this time to work up the nitrobenzene mother liquor which undoubtedly contained terephthalhydroximoyl chloride. After drying the crude product in a vacuum oven at 40°C, it was recrystallized from benzene to yield 22 g of product (44 percent of theory, mp 187-189°C).

e) Preparation of terephthalonitrile N,N′-oxide

To a one-liter, three-necked flask fitted with a dropping funnel, thermometer, stirrer and a dry-ice-water-acetone bath was added absolute methanol (340 ml). The solution was cooled to 2°C and terephthalhydroximoyl chloride (8.0 g, 0.0344 mole) was added. The solution was kept at 0°C and a solution of triethylamine (10 g; 0.089 mole) in absolute methanol (200 ml) was added dropwise over a 15 min period. A light tan colored product came out of solution during the addition. After the addition the mixture was stirred for 15 min and the product was recovered by filtration. The product was washed with methanol, distilled water, and again with methanol. After drying the product under vacuum overnight, it was stored in the refrigerator. A yield of 5.0 g (90 percent of theory) was obtained.

f) Attempted reaction of polymer sample PS-12 with terephthalonitrile N,N′-dioxide

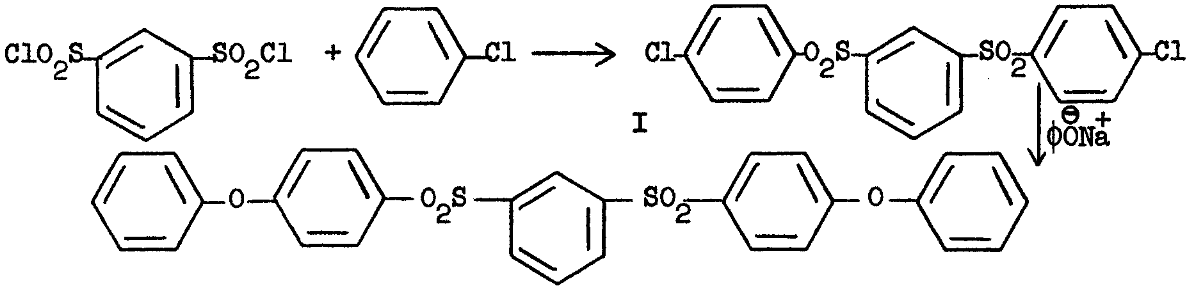
PS-12 (1.0 g) was dissolved in 15 ml of dry sulfolane. The mixture was warmed whereupon the polymer dissolved to yield a clear straw-colored solution. The solution was cooled to room temperature and freshly prepared terephthalonitrile N,N′-oxide (0.2 g) was added and the mixture stirred for 24 hr at room temperature. No crosslinking was effected under these conditions as no gel formation was observed.

c. Alternate method to prepare 1,3-bis(p-phenoxybenzenesulfonyl)benzene

i) Results and discussion

So far the synthesis of 1,3-bis(p-phenoxybenzenesulfonyl)benzene was accomplished by the condensation of m-benzene disulfonyl chloride with diphenyl ether. Purification of the crude product from this reaction has to be done with cumbersome vacuum distillation as this product distills around 500°C/0.25 mm. So, alternate synthesis was devised.

Reaction of meta benzene disulfonyl chloride with chlorobenzene in presence of ferric chloride gave 1,3-bis(p-chlorobenzenesulfonyl)benzene which on subsequent reaction with sodium phenoxide gave (II).



I

II

ii) Experimental

a) 1,3-Bis(p-chlorobenzenesulfonyl)benzene (I)

Chlorobenzene (22.50 g; 0.2 mole) and meta benzene disulfonyl chloride (27.5 g; 0.1 mole) were taken in a 250 ml beaker and heated to 100°C. A spatula full of anhydrous ferric chloride was added. Immediate evolution of hydrogen chloride was observed and the reaction mixture exothermed to 180-190°C. The reaction mixture was cooled and added 50 ml of isopropanol followed by 5 ml of acetylacetone. The solid separated was filtered and crystallized from methanol to fine tan-colored crystals. mp 146-148°C.

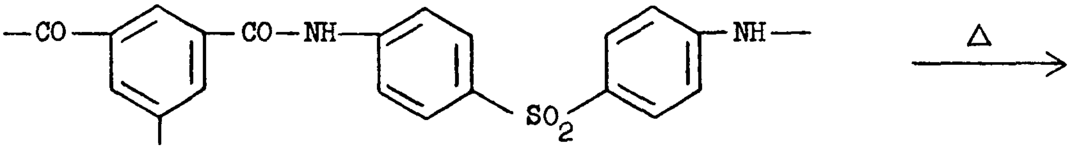
Anal. Calc. for $C_{18}H_{12}S_2O_4Cl_2$: C, 50.40%; H, 2.80%; S, 15.0%; Cl, 16.63%.
Found: C, 50.39%; H, 2.85%; S, 14.97%; Cl, 16.61%.

b) 1,3-Bis(p-phenoxybenzenesulfonyl)benzene

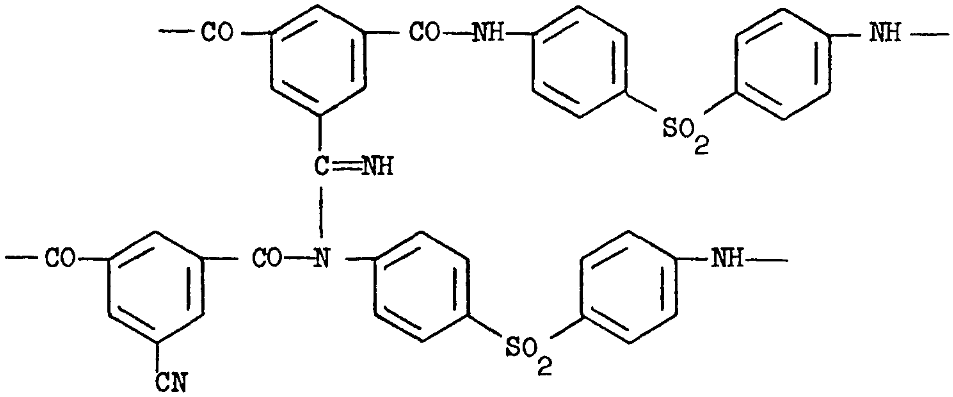
1,3-Bis(p-chlorobenzenesulfonyl)benzene (1.46 g; 3.3 mmole) sodium phenoxide (0.83 g; 7.2 mole) and dimethylsulfoxide (25 ml) were stirred at 100°C in nitrogen atmosphere for 30 hr. After cooling the reaction mixture to room temperature, it was poured into 500 ml of water and the product separated was filtered, washed with water and dried. Yield 1.32 g (80%). mp 70-75°C. The infrared spectrum of this product was identical with that of spectrum of 1,3-bis(p-phenoxybenzenesulfonyl)benzene prepared by condensation of meta benzene disulfonyl chloride and diphenyl ether.

d. Attempted crosslinking of JVB-50 type polymer having 25 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene with isophthalamide

A German patent[12] described a crosslinking reaction from a polymer containing pendant cyano groups and amide linkage in the polymer. The polymer having structure (III) when heated at 350°C for 5 hr gave cross-linked polymer (IV) The crosslinking reaction is being thought to give poly(imino imide amide linkage).



III



IV

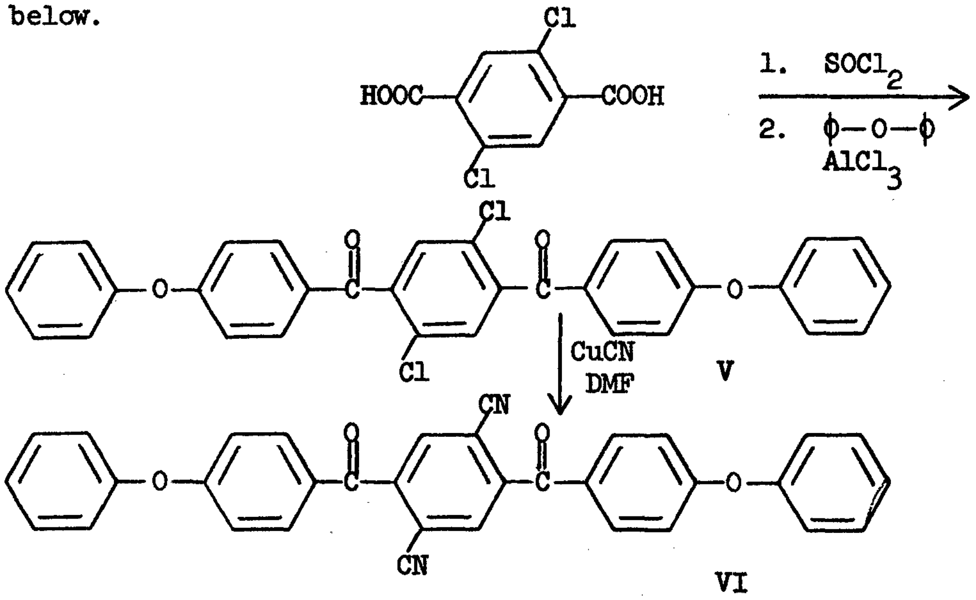
Reaction of JVB-50 type polymer having 25 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene with isophthalamide at 350° for 24 hr was attempted but did not afford the desired poly(imino imide amide) crosslinks.

e. Terpolymer containing 1,4-bis(p-phenoxybenzoyl)-2,5-dicyanobenzene

i) Results and discussion

In earlier reports the preparation of JVB-50 polymers having 3 to 25 wt % of 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene was reported.[11] When these polymers were heated alone or in the presence of zinc chloride under nitrogen and at 300°C, insoluble dark products (insoluble in dimethylacetamide) were obtained. These products showed vicat softening point around 150-200°C. This lower softening point for a crosslinked polymer was believed to be the result of insufficient crosslinking sites (nitrile groups) along the polymer chains. For this reason a polymer (PS-11) having higher cyano content (22 wt % of 5-cyanoisophthaloyl unit) was obtained from the Friedel-Crafts polymerization of 1,3-bis(p-phenoxybenzenesulfonyl)-benzene and 5-cyanoisophthaloyl chloride. Crosslinking was effected to some extent by heating the polymer at 360°C for 24 hr. See Figures 14 and 15.

Another approach to incorporate higher weight percent of nitrile in the polymer was using 1,4-bis(p-phenoxybenzoyl)-2,5-dicyanobenzene (VI) as monomer. Synthesis of (VI) was performed according to the scheme outlined below.



A terpolymer was prepared from 1,3-bis(p-phenoxybenzenesulfonyl)benzene and (VI) (25 wt % in the final polymer) and isophthaloyl chloride. This polymer on heating at 350°C for 24 hr gave crosslinked product (insoluble in dimethylacetamide). This polymer as well as the crosslinked product will be sent to Materials Laboratory for TGA and softening point determination.

ii) Experimental

a) 1,4-Bis[p-phenoxybenzoyl]-2,5-dichlorobenzene

2,5-Dichloroterephthalic acid (0.2 mole), thionyl chloride (200 ml) were refluxed for 6 hr. Removal of thionyl chloride afforded 2,5-dichloroterephthaloyl chloride.

2,5-Dichloroterephthaloyl chloride (50 g) was dissolved in one liter of diphenyl ether. Anhydrous aluminum chloride (55 g) was added and the mixture was stirred under nitrogen atmosphere during 24 hr. The reaction mixture was poured into water (two liter). The solids precipitated upon dilution of the reaction mixture in water with ether, was filtered and washed with water. The product was crystallized from dimethylformamide to afford white shiny crystals, 39.5 g; mp 266-268°C. Infrared spectrum of this compound in Nujol exhibited carbonyl absorption at 1745 cm^{-1}.

Anal. Calc. for $C_{32}H_{20}Cl_2O_4$: C, 71.25%; H, 3.71%; Cl, 13.18%.
Found: C, 70.38%; H, 3.98%; Cl, 13.06%.

b) 1,4-Bis[p-phenoxybenzoyl]-2,5-dicyanobenzene

1,4-Bis[p-phenoxybenzoyl]-2,5-dichlorobenzene (10.78 g; 0.02 mole) and cuprous cyanide (5 g) were taken in dimethylformamide (100 ml) and the solution was refluxed for 6 hr. The resulting solution was poured into a solution containing ferric chloride (10 g), hydrochloric acid (50 ml) in water and the whole mixture kept 60°C for 1 hr, then filtered, washed with water and crystallized from benzene to give 7.5 g of green colored product. mp 157-158°C. Infrared spectrum of this product in Nujol exhibited absorption at 2230 cm^{-1} due to cyano group.

Anal. Calc. for $C_{34}H_{20}N_2O_4$: C, 78.50%; H, 3.85%; N, 5.39%.
Found: C, 76.99%; H, 4.33%; N, 5.24%; Res., 1.00%.

Three hundred mg of 1,4-bis[p-phenoxybenzoyl]-2,5-dicyanobenzene was heated at 350°C in nitrogen atmosphere for 24 hr and the dark black colored insoluble product (in dimethylacetamide) was dried.

Anal. Calc. for $C_{34}H_{20}N_2O_4$: C, 78.5%; H, 3.85%; N, 5.39%.
Found: C, 76.05%; H, 3.73%; N, 5.46%; Res., 0.98%.

c) Polymer from 1,4-bis[p-phenoxybenzoyl]-2,5-dicyanobenzene, 1,3-bis[p-phenoxybenzenesulfonyl]benzene and isophthaloyl chloride

1,3-Bis[p-phenoxybenzenesulfonyl]benzene (1.85 g; 34 mM) 1,4-bis[p-phenoxybenzoyl]-2,5-dicyanobenzene (0.83 g; 16 mM) and isophthaloyl chloride (1.015 g; 50 mM) were dissolved in 50 ml of dry dichloroethane. $AlCl_3$ (4 g; 30 mM) was added and the mixture was stirred at room temperature ($\sim 30^{\circ}C$) for 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 2.24 g; softening point 220-240°C, $\eta_{inh} = 0.272$ in sulfuric acid at 30°C. This polymer is soluble in dimethylacetamide.

Anal. Calc.: C, 72.78%; H, 3.92%; S, 6.72%; N, 1.38%.
Found: C, 67.27%; H, 4.04%; S, 7.21%; N, 1.37%; Res., 1.50%.

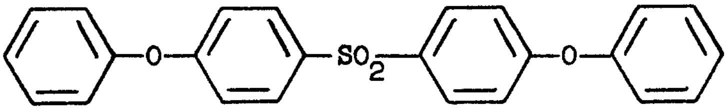
Three hundred mgm of the polymer was heated at 350°C for 24 hr in nitrogen atmosphere. The resultant product was refluxed with 100 ml of dimethylacetamide for 4 hr and the insoluble product was filtered, washed with water and dried.

Anal. Calc.: C, 72.78%; H, 3.92%; S, 6.72%; N, 1.38%.
Found: C, 67.43%; H, 3.84%; S, 6.83%; N, 0.79%; Res., 3.62%.

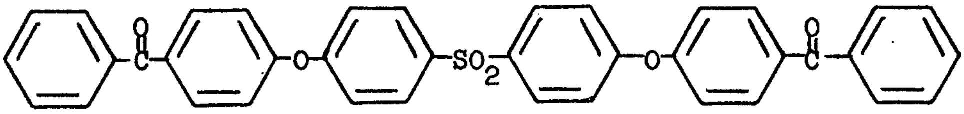
f. Polymers from 4,4′-diphenoxydiphenylsulfone

i) Results and discussion

Previously terpolymers from 1,3-bis(p-phenoxybenzenesulfonyl)-benzene as well as from 4,4′-bis(p-phenoxybenzenesulfonyl)diphenyl ether were described. A new sulfone monomer 4,4′-diphenoxydiphenylsulfone (VII), which can be readily obtained from the reaction of 4-chlorophenylsulfone and sodium phenoxide. Model reaction of (VII) with benzoyl chloride gave disubstituted product (VIII).



VII



VIII

Compound VII was polymerized with isophthaloyl chloride and 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene. These polymers in general possessed higher softening points and higher inherent viscosities compared to the polymers obtained from 1,3-bis[p-phenoxybenzenesulfonyl]benzene and 4,4′-bis(p-phenoxybenzenesulfonyl)diphenyl ether, having the same wt % of 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene. These polymers were then crosslinked using zinc chloride as well as triphenyltin hydroxide as catalysts. All polymers as well as crosslinked variety have been submitted to Air Force Materials Laboratory for TGA and softening point determination.

ii) Isothermal aging of polymers containing 4,4′-diphenoxydiphenylsulfone units

Isothermal aging of all these polymers were run in an atmosphere of circulating air at temperatures of 300 and 350°C. The results of this test are given in Tables VI and VII. Both the crosslinked as well as the noncrosslinked polymers exhibited good thermal stability around 300°C for 7 days but showed considerable weight losses at 350°C. Crosslinked polymers in general possessed inferior thermal stability compared to the noncrosslinked polymers.

TABLE VI

ISOTHERMAL AGING DATA OF POLYMERS FROM 4,4′-DIPHENOXYDIPHENYLSULFONE

	% weight losses	
Polymer	at 300°C for*	at 350°C for* (7 days)*
PS-13	3.51	74.60
PS-14	5.08	92.72
PS-15	9.03	98.26
PS-16	6.43	97.95
PS-17	7.05	99.08

TABLE VII

ISOTHERMAL AGING DATA
OF CROSSLINKED POLYMERS FROM 4,4′-DIPHENOXYDIPHENYLSULFONE

Derived from Polymer	Catalyst used for Crosslinking	% weight losses	
		at 300°C for 7 days	at 350°C for 7 days
PS-13	ϕ_3 SnOH	10.80	72.02
PS-14	ϕ_3 SnOH	6.62	62.95
PS-15	ϕ_3 SnOH	12.48	83.37
PS-14	$ZnCl_2$	10.80	72.02
PS-15	$ZnCl_2$	17.96	94.41
PS-16	$ZnCl_2$	19.28	99.31
PS-17	Heat	10.30	99.29

iii) Experimental

a) 4,4′-Diphenoxydiphenylsulfone

To a one-liter, three-necked, round bottom flask fitted with mechanical stirrer, thermometer and nitrogen gas inlet/outlet was added 5.74 g (0.2 mole) of twice crystallized bis(4-chlorophenyl) sulfone, and sodium phenoxide (51.04 g; 0.44 mole), 300 ml of dimethylsulfoxide and 20 ml of chlorobenzene. A positive stream of nitrogen gas was maintained over the mixture during the reaction. The mixture was stirred and heated at temperature 110°C for a period of approximately 90 hr. After the reaction, the reaction mixture was poured into two liter of water and the resultant product separated was filtered, recrystallized from isopropanol-chloroform to give white crystals in 85% yield. mp 141-142°C.

Anal. Calc. for $C_{24}H_{18}O_4S$: C, 71.62%; H, 4.51%; S, 7.97%.
Found: C, 71.40%; H, 4.42%; S, 8.18%.

b) Benzoylation of 4,4′-diphenoxydiphenylsulfone

To a stirred suspension of aluminum chloride (0.025 mole) in 50 ml of 1,2-dichloroethane was added a solution of benzoyl chloride (1.52 g; 0.01 mole) and 4,4′-diphenoxydiphenylsulfone (2.01 g; 0.005 mole) in 50 ml of 1,2-dichloroethane. The mixture was stirred at room temperature for 24 hr. At the end of reaction, the reaction mixture was poured into one liter of methanol and the product separated was filtered and crystallized from chloroform-methanol. Yield 3.74 g (90%) mp 228-230°C.

Anal. Calc. for $C_{38}H_{26}SO_6$: C, 74.82%; H, 4.27%; S, 5.25%.
Found: C, 74.56%; H, 4.24%; S, 5.22%.

c) Polymer from 4,4′-diphenoxydiphenylsulfone and isophthaloyl chloride

4,4′-Diphenoxydiphenylsulfone (4.02 g; 10 mM) and isophthaloyl chloride (2.03 g; 10 mM) were dissolved in 100 ml of dry dichloroethane. $AlCl_3$ (6.675 g; 50 mM) was added and the mixture was stirred under nitrogen ($\sim$30°C) for 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 5.10 g (labelled as PS-18) softening point 200-210°C. η_{inh} = 0.562 in H_2SO_4 at 30°C. This polymer is soluble in dimethylacetamide.

Anal. Calc.: C, 72.18%; H, 3.76%; S, 6.01%
Found: C, 71.00%; H, 3.70%; S, 6.00%; Res., 1.47%.

d) Polymer from 4,4′-diphenoxydiphenylsulfone and terephthaloyl chloride

4,4′-Diphenoxydiphenylsulfone (4.02 g; 10 mM) and terephthaloyl chloride (2.03 g; 10 mM) were dissolved in 100 ml of dry dichloroethane. $AlCl_3$ (6.675 g; 50 mM) was added and the mixture was stirred under nitrogen ($\sim$ 30°C) for 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 5.00 g (labelled as PS-19). Softening point 235-245°C, η_{inh} = 0.675 in H_2SO_4 at 30°C. This polymer is soluble in dimethylacetamide.

Anal. Calc.: C, 72.18%; H, 3.76%; S, 6.01%.
Found: C, 71.94%; H, 3.87%; S, 5.90%.

e) Preparation of 5 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene in the terpolymer

4,4′-Diphenoxydiphenylsulfone (1.90 g; 4.725 mM); 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (0.138 g; .275 mM) and isophthaloyl chloride (1.015 g; 5 mM) were dissolved in 50 ml of dry 1,2-dichloroethane. $AlCl_3$ (2.7 g; 20 mM) was added and the mixture was stirred under nitrogen (~ 30°C) for 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 2.85 g (labelled as PS-13). See Figure 16. Softening point 215-235°C. η_{inh} = 0.616 in H_2SO_4 at 30°C. This polymer is soluble in dimethylformamide and dimethylacetamide.

Anal. Calc.: C, 72.35%; H, 4.12%; S, 5.64%; N, 0.09%.
Found: C, 72.20%; H, 4.01%; S, 5.33%; N, 0.21%.

f) Preparation of 8 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene in the terpolymer

4,4′-Diphenoxydiphenylsulfone (1.829 g; 4.55 mM); 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene (0.225 g; .45 mM) and isophthaloyl chloride (1.015 g; 5 mM) were dissolved in dry dichloroethane. $AlCl_3$ (2.75 g; 20 mM) was added and the mixture was stirred at room temperature (~ 30°C) in nitrogen atmosphere for 24 hr. The precipitate was filtered and washed three times with methanol in a blender and dried. Yield = 2.80 g (labelled as PS-14). See Figures 17 and 18. Softening point 195-210°C. η_{inh} = 0.693 in H_2SO_4 at 30°C. This polymer is soluble in dimethylformamide and dimethylacetamide.

Anal. Calc.: C, 72.63%; H, 4.10%; S, 5.36%; N, 0.25%.
Found: C, 71.40%; H, 3.95%; S, 5.52%; N, 0.18%; Res., 0.69%.

g) Preparation of 15 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene in the terpolymer

4,4′-Diphenoxydiphenylsulfone (1.17 g; 4.15 mM), 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (0.43 g; 0.85 mM) and isophthaloyl chloride (1.015 g; 5.0 mM) were dissolved in 50 ml of dry dichloroethane. $AlCl_3$ (2.75 g; 20 mM) was added and the mixture stirred at room temperature (~ 30°C) in nitrogen atmosphere for 24 hr. The precipitate was filtered and washed three times with methanol in a blender and dried. Yield = 2.80 g (labelled as PS-15). See Figure 19. Softening point 190-205°C. This polymer is soluble in dimethylacetamide. η_{inh}=0.820 in H_2SO_4 at 30°C.

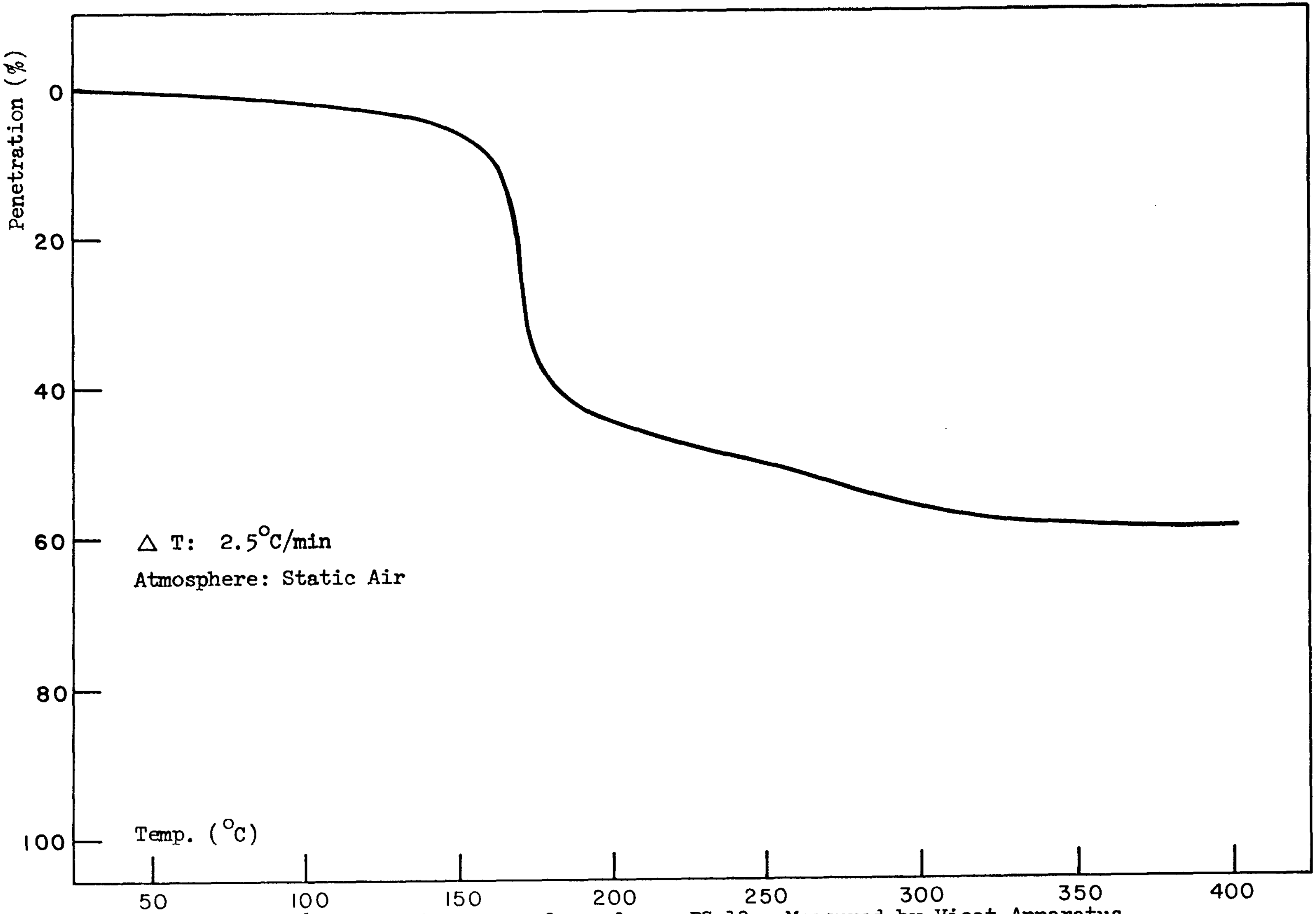


Figure 16. Softening curve for polymer PS-13. Measured by Vicat Apparatus.

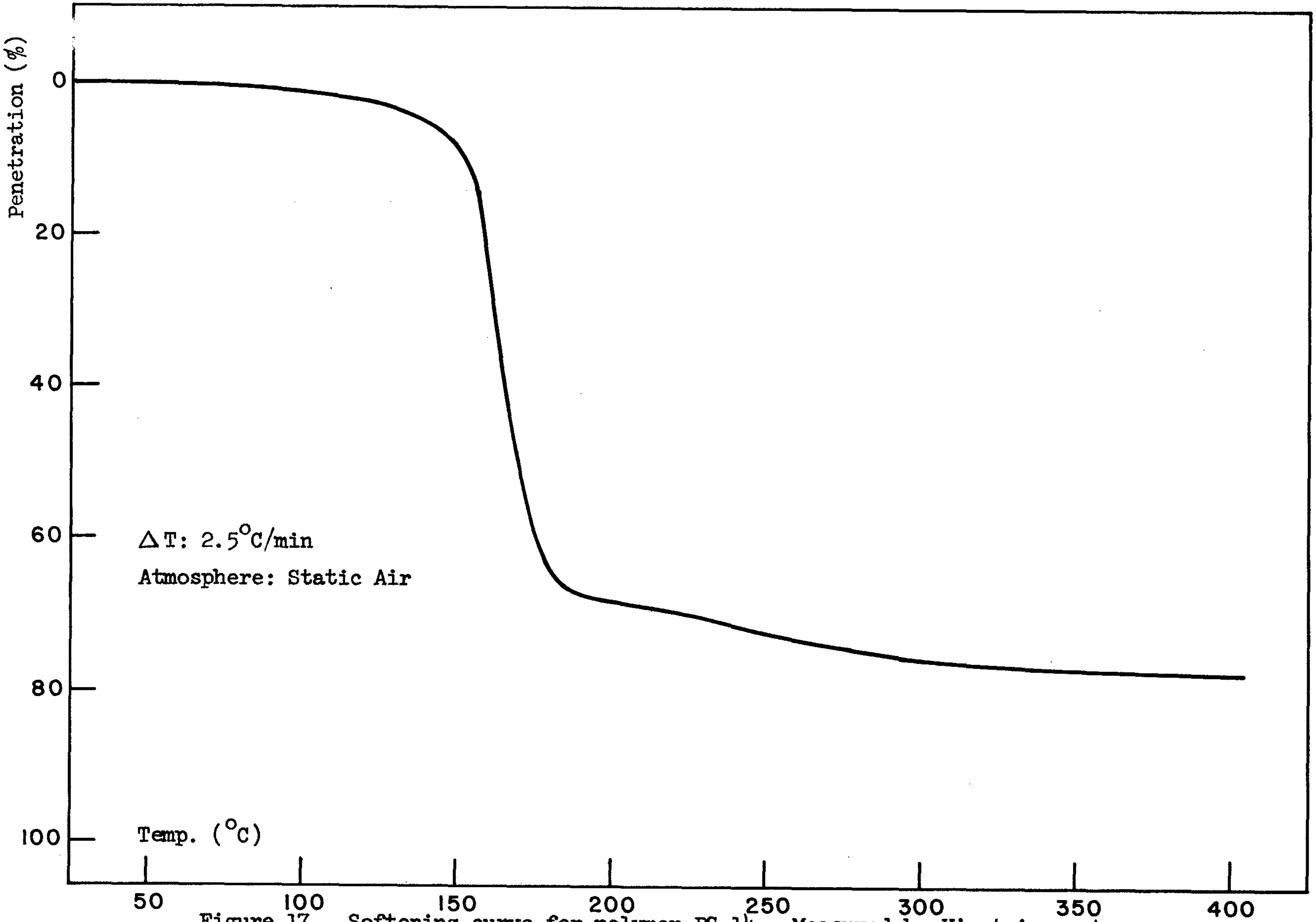


Figure 17. Softening curve for polymer PS-14. Measured by Vicat Apparatus.

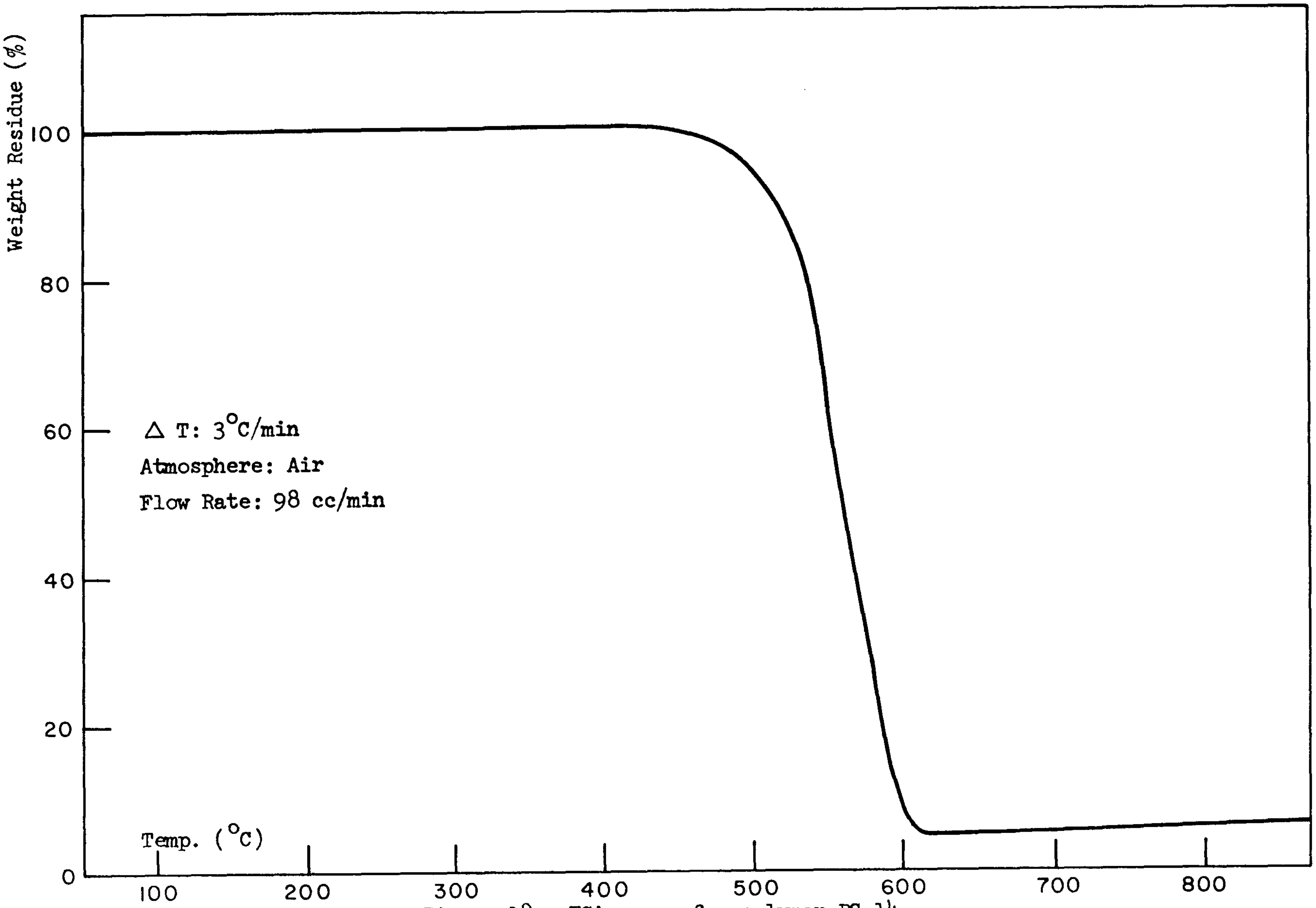


Figure 18. TGA curve for polymer PS-14

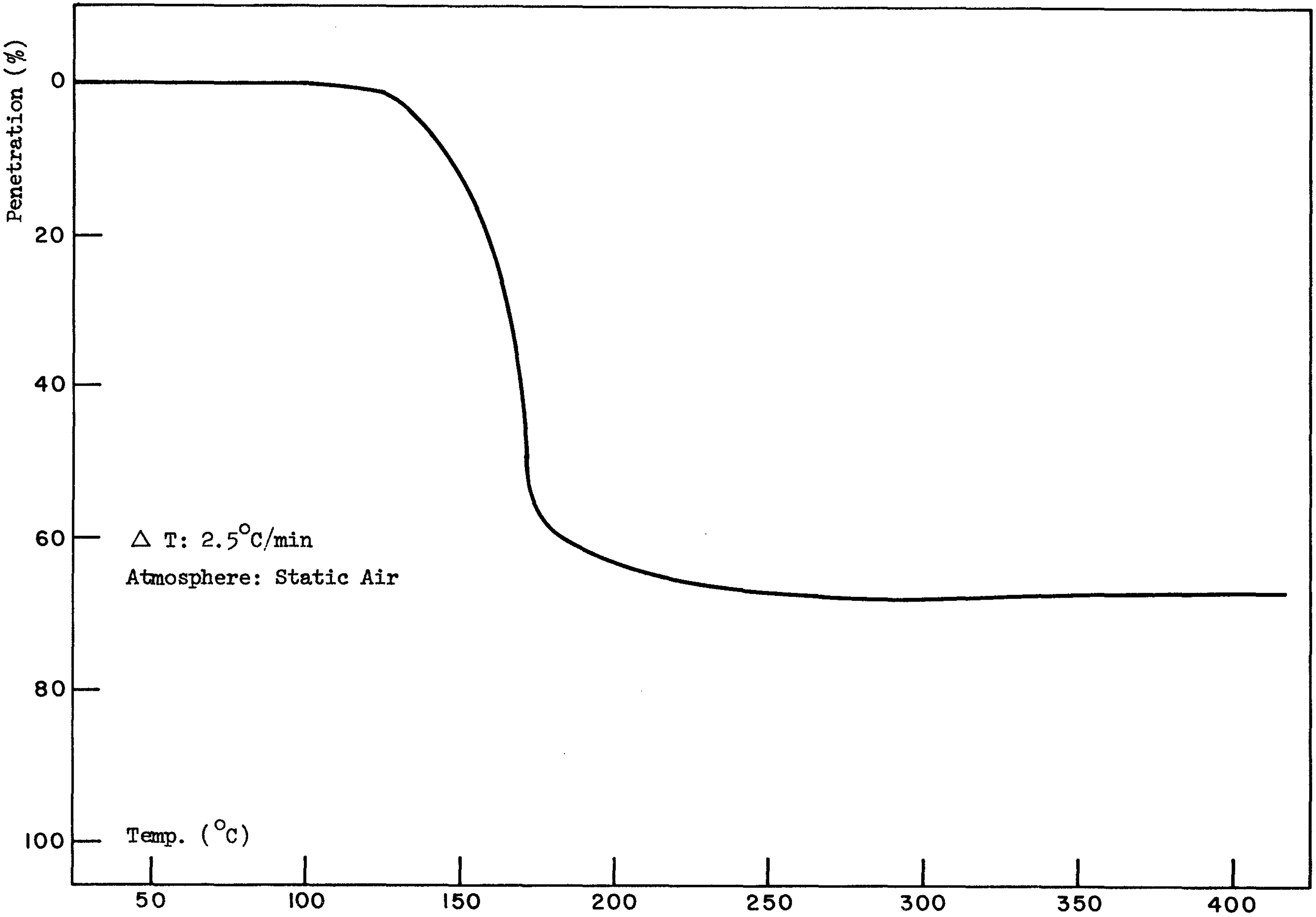


Figure 19. Softening curve for polymer PS-15. Measured by Vicat Apparatus.

Anal. Calc.: C, 73.14%; H, 4.09%; N, 0.43%; S, 4.83%.

Found: C, 72.10%; H, 3.99%; N, 0.24%; S, 4.50%; Res., 0.99%.

h) Preparation of 25 wt % of 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene in the terpolymer

4,4′-Diphenoxydiphenylsulfone (1.407 g; 3.5 mM), 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene (0.743 g; 1.5 mM) and isophthaloyl chloride were dissolved in 50 ml of dry dichloroethane. $AlCl_3$ (2.75 g; 20 mM) was added and the mixture was stirred at room temperature (~ 30°C) in nitrogen atmosphere for 24 hr. The precipitate was filtered and washed three times with methanol in a blender and dried. Yield = 2.85 g (labelled as PS-16). See Figure 20. Softening point 200-225°C. η_{inh} = 0.923 in H_2SO_4 at 30°C. This polymer is soluble in dimethylacetamide.

Anal. Calc.: C, 74.10%; H, 4.07%; S, 3.99%; N, 0.75%.

Found: C, 74.01%; H, 3.99%; S, 4.15%; N, 0.56%.

i) Polymer from 4,4′-diphenoxydiphenylsulfone and 5-cyanoisophthaloyl chloride

4,4′-Diphenoxydiphenylsulfone (2.01 g; 5 mM) and 5-cyanoisophthaloyl chloride (1.14 g; 5 mM) were dissolved in 50 ml of dry dichloroethane. $AlCl_3$ (3.99 g; 30 mM) was added and the mixture was stirred at room temperature (~ 30°C) in nitrogen atmosphere for 24 hr. The precipitate was filtered and washed three times with methanol in a blender and dried. Yield = 4.5 g (labelled as PS-17). See Figures 21 and 22. Softening point 180-200°C. η_{inh} = 0.342 in H_2SO_4 at 30°C. The polymer is soluble in dimethylacetamide.

Anal. Calc.: C, 70.84%; H, 3.76%; S, 5.72%; N, 2.51%.

Found: C, 69.98%; H, 3.67%; S, 5.47%; N, 2.42%; Res., 0.56%.

Five hundred mg of this polymer was heated at 350°C for 24 hr in nitrogen atmosphere. The resultant black colored mass after grinding in a mortar and pestle was boiled up with 100 ml of dimethylacetamide, filtered, washed with water and dried.

Anal. Calc.: C, 70.84%; H, 3.76%; S, 5.72%; N, 2.51%.

Found: C, 69.63%; H, 4.05%; S, 4.35%; N, 2.87%; Res. 1.11%.

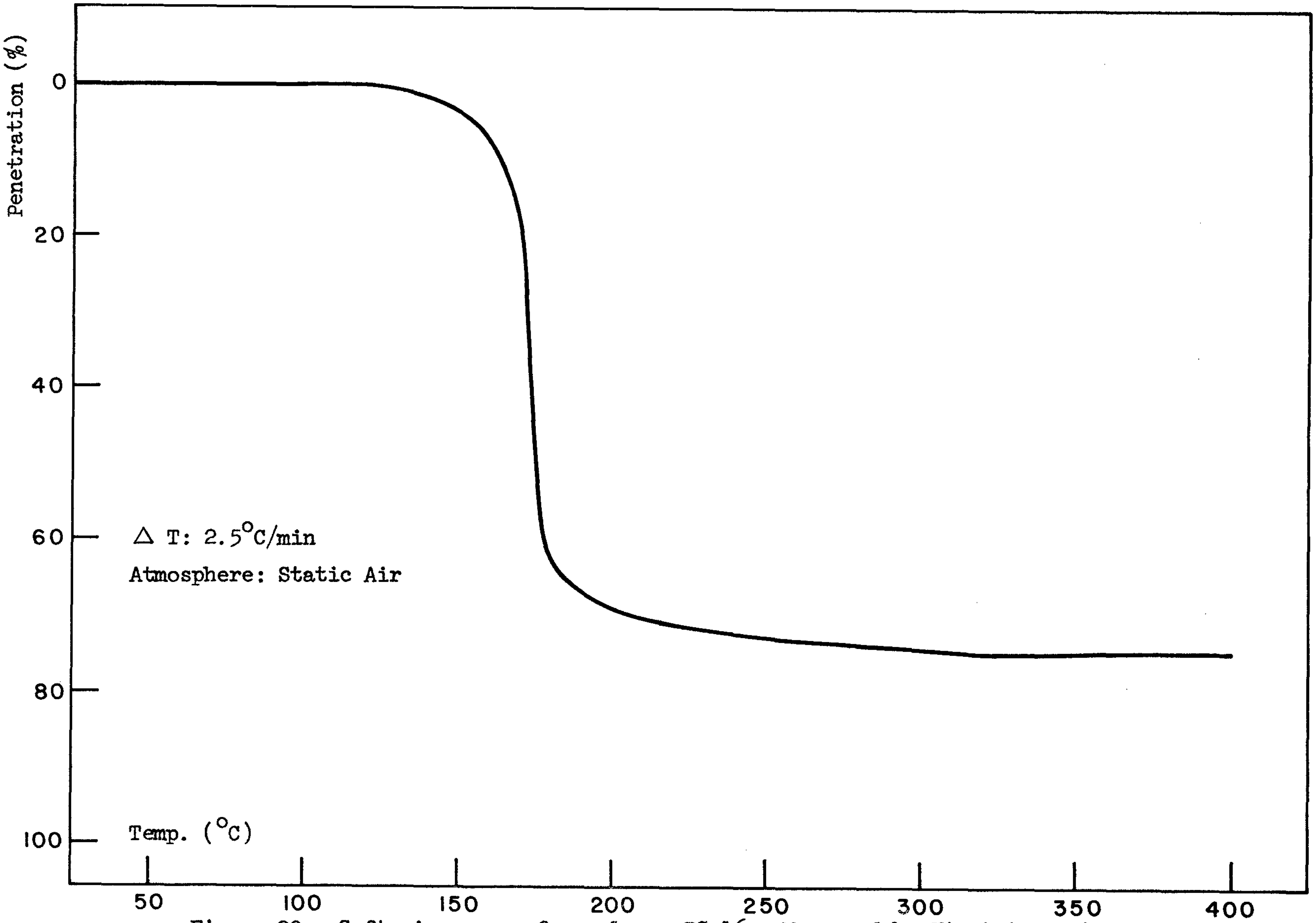


Figure 20. Softening curve for polymer PS-16. Measured by Vicat Apparatus.

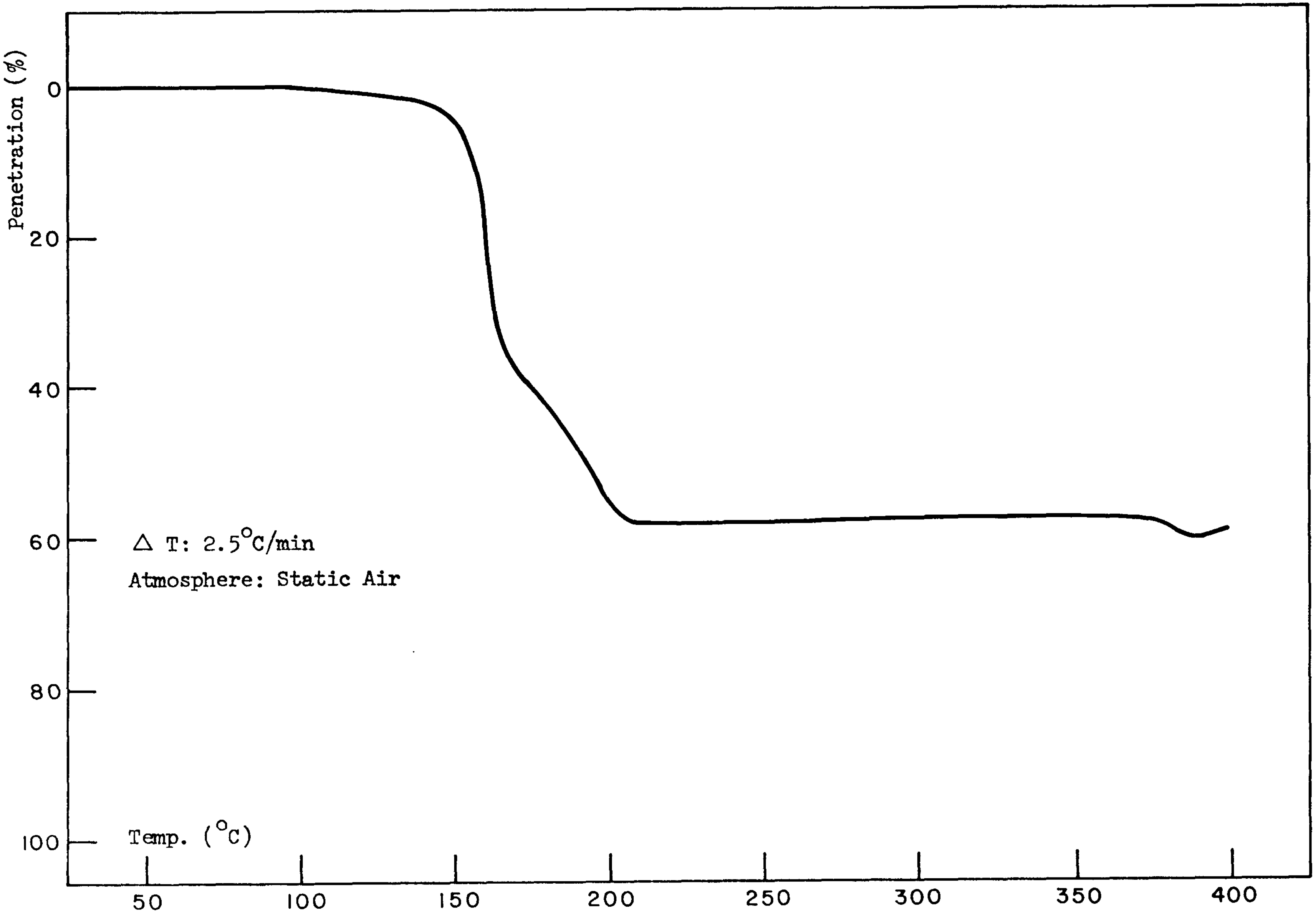


Figure 21. Softening curve for polymer PS-17. Measured by Vicat Apparatus.

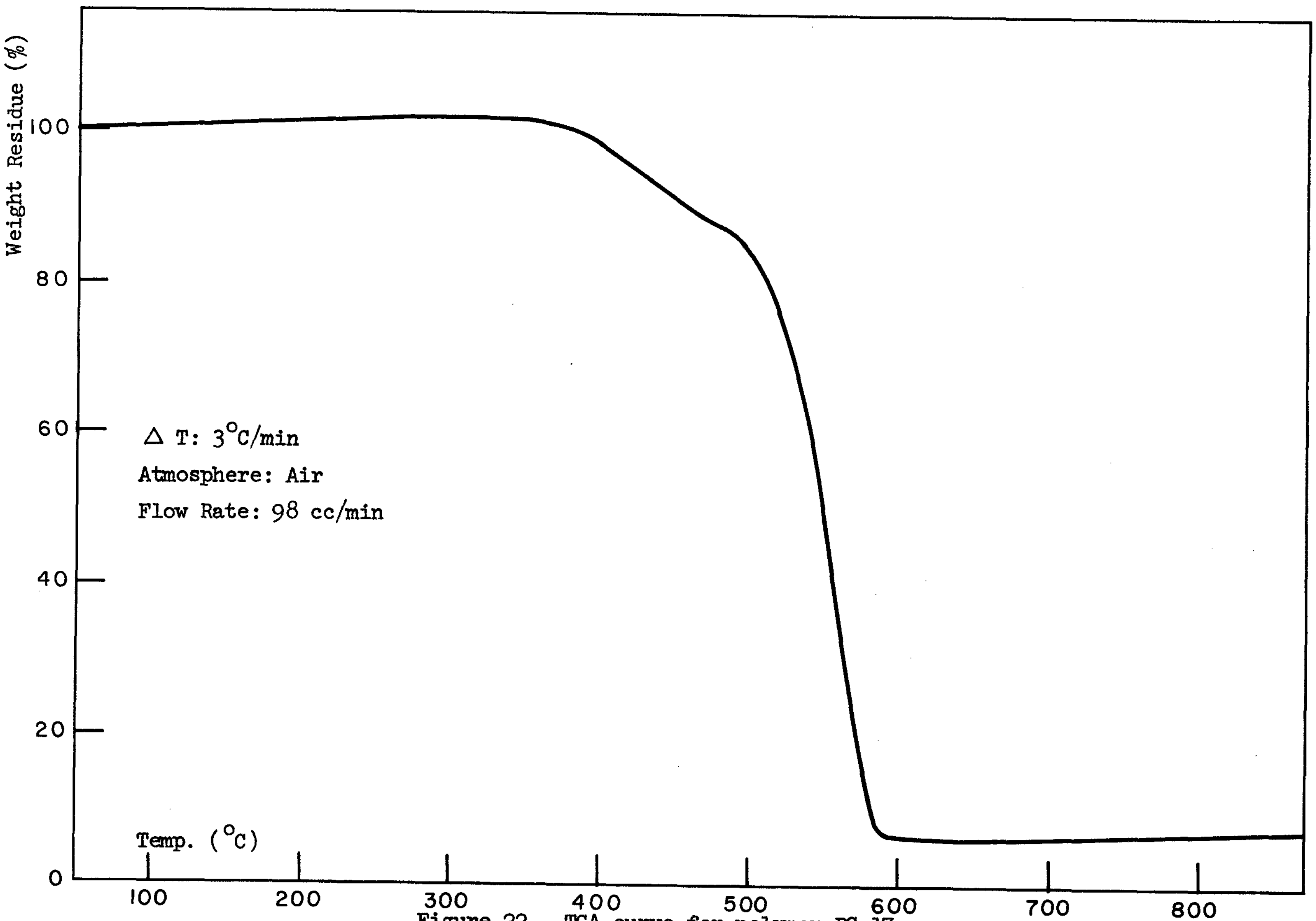


Figure 22. TGA curve for polymer PS-17

j) Crosslinking reactions

Crosslinking reactions were run in test tube whose inside walls were coated with aluminum foil and equipped with a nitrogen inlet and a side outlet. The crosslinked material was removed from the aluminum foil by dissolving the latter in dilute hydrochloric acid followed by filtration, washing and drying.

2. Future Plans

It is not anticipated further work will be done on nitrile substituted polymers of this particular type.

V. AROMATIC POLYETHERS -SULFONES -KETONE POLYMERS WITH DANGLING ACETYLENE GROUPS

1. Introduction

Thermally stable laminating resins are needed which are low melting in the prepolymer stage and which can be cured without giving off any volatiles. It is known that acetylene compounds give catalytic trimerization with formation of benzene rings and they also can be crosslinked by cycloaddition with bis-nitrile oxides to yield the isoxazole ring. To be useful, the polymers should melt at a temperature not much higher than 200°C, they should flow easily and adhere to glass fibers. Aromatic ethers, ketones and sulfones are known to be thermally stable. Moieties containing these functional groups were copolymerized with acetyl containing monomers and linked together with aromatic acid chlorides in a Friedel-Crafts type polymerization. The acetyl polymers were then converted into polymers with dangling acetylene groups by the Vilsmeyer reaction.

2. Substitution Reactions

a. Discussion

Substitution reactions of 4,4′-dibromodiphenylacetylene and 4,4′-thiodiphenol or bisphenol S in basic medium failed as a preparation method for acetylene polymers.

The reason why these attempts failed, is probably because there are no electron-withdrawing groups in the halogen compounds which could make the substitution easier.

For this reason reactions were done with activated halogen compounds.

Compounds with a substituted acetyl group were reacted and then on these polymers, a transformation reaction to obtain the acetylene polymers was done.

These reactions of 2,4-dihydroxyacetophenone with 4,4′-dichlorodiphenylsulfone and 2,4-dichloroacetophenone with 4,4′-dihydroxydiphenylsulfone did not give any polymers.

The reason there is no polymer formation in the reaction of these acetophenone derivatives is probably due to condensation of the acetyl function in basic medium.

An attempt to prepare 2,4-diphenoxyacetophenone from 2,4-dichloroacetophenone and sodium phenolate in DMSO did not give the expected product. The reaction product remained in the water phase and no product was extracted with ether. This means that 2,4-dichloroacetophenone gives condensation products in reaction with phenolate.

b. Experimental

i) Substitution reactions

a) Reaction of 4,4′-thiodiphenol and 4,4′-dibromodiphenylacetylene, KOH as base

The reaction of 4,4′-thiodiphenol, 2.183 g (0.01 mole) and 4,4′-dibromodiphenylacetylene, 3.36 g (0.01 mole) in the presence of 1.375 g of KOH (0.025 mole) and DMAc (40 ml) as solvent was carried out. The reaction was run at 165°C under nitrogen for 48 hr. The reaction mixture was then precipitated in water/MeOH, and the isolated product washed with ether. Only 350 mgr (5%) of insoluble product in ether could be isolated. The softening point was about 230°C.

b) Reaction of 4,4′-thiodiphenol and 4,4′-dibromodiphenylacetylene, K_2CO_3 as base

The reaction of 4,4′-thiodiphenol (0.01 mole) and 4,4′-dibromodiphenylacetylene (0.01 mole) in the presence of K_2CO_3 (0.023 mole) and DMAc (25 ml) as solvent was carried out. The reaction conditions were the same as for the previous reaction and the reaction was worked up in the same way. In this case only 200 mgr of insoluble product in ether could be isolated. The softening point was about 240°C.

c) Reaction of bisphenol S and 4,4′-dibromodiphenylacetylene

The reaction of bisphenol-S (4,4′-dihydroxydiphenylsulfone) (2.50 g, 0.01 mole) and 4,4′-dibromodiphenylacetylene (3.36 g, 0.01 mole) in the presence of 3.18 g K_2CO_3 (0.023 mole) and DMAc (40 ml) as solvent was carried out. The reaction conditions were the same as in the previous reactions and the reaction was worked up in the same way. Only 200 mgr of insoluble product in ether could be isolated.

d) Reaction of 2,4-dihydroxyacetophenone and 4,4′-dichlorodiphenylsulfone

The reaction of 2,4-dihydroxyacetophenone (3.42 g, 0.0225 mole) and 4,4′-dichlorodiphenylsulfone (6.457 g, 0.0225 mole) was carried out. First, the 2,4-dihydroxyacetophenone was dissolved in 11 g DMSO and 33 g of chlorobenzene was reacted with 0.045 mole of NaOH (50%) by flushing with nitrogen and with good stirring. The water was removed from the system while the temperature was raised to about 140°C. Then the temperature was raised to 155°C and the chlorobenzene remaining in the reaction flask distilled while raising the temperature.

Then, a 50% solution of 4,4′-dichlorodiphenylsulfone in dry chlorobenzene, maintained at 110°C was added over a period of 10 min. The excess solvent was allowed to distill at a rate sufficient to hold the material temperature at about 160°C. The reaction was continued at 160°C for 16 hr. The reaction mixture was then precipitated in $MeOH/H_2O$. The precipitate was taken up in ether and then in acetone. The remaining product 0.850 g (∼ 10%) had a softening point of about 235°C.

e) Reaction of 2,4-dichloroacetophenone and bisphenol S

i) K_2CO_3 as base

The reaction of 2,4-dichloroacetophenone (1.89 g, 0.01 mole) and bisphenol S (2.50 g, 0.01 mole) in the presence of K_2CO_3 (2.764 g, 0.02 mole) in 40 ml DMAc as solvent was carried out under nitrogen at 160°C for 48 hr. The reaction mixture was poured into $MeOH/H_2O$. The reaction product melted at about 165-175°C and was completely soluble in acetone.

ii) KOH as base

4,4′-Dihydroxydiphenylsulfone (0.01 mole) was dissolved in 20 ml DMSO and 40 ml benzene, and to this solution was added a solution of 0.02 mole KOH (50% in H_2O). The water was distilled out of the reaction vessel and the temperature raised at that time to 175°C. When the temperature was dropped to 80°C, a solution of 0.01 mole, 2,4-dichloroacetophenone in 10 ml DMSO was added. The temperature was raised to 110-120°C and the reaction was continued for a further four hr under nitrogen and stirring. The reaction mixture was poured out in $MeOH/H_2O$. The isolated product melted at 140-142°C and was completely soluble in acetone.

3. Acetylene dangling Polymers by Friedel-Crafts Polymerization

a. Results and discussion

Various aromatic polyethers -sulfones -ketone polymers with dangling acetylene groups with different composition were synthesized. As the conversion of an acetyl group into an acetylene group is a known reaction for simple molecules, we did these reactions on the respective acetyl containing polymers. Terpolymers of type A were obtained from a Friedel-Crafts type polymerization of 4,4′-diphenoxydiphenylsulfone (I), 2,4-diphenoxyacetophenone (II), isophthaloyl chloride and terephthaloyl chloride using $AlCl_3$ as catalyst. The composition and properties of the polymers are given in Table VIII. The viscosity was expected to be higher which is the case when sulfuric acid is used as solvent. Polymer A-I-1 gives η_{inh} 0.391 and A-IV-1 gives η_{inh} 0.479 at 30°C in H_2SO_4, instead of 0.234 and 0.264 respectively in DMF. The only explanation for this phenomenon could be a dissociation effect in DMF which does not occur in H_2SO_4. The melting point is in the range of 200°C which would make their properties useful for laminating glass fibers.

TABLE VIII

POLYMERS FROM 2,4-DIPHENOXYACETOPHENONE AND 4,4′-DIPHENOXYDIPHENYLSULFONE

							Analyses[e]					
							Calc. %			Found %		
Polymer	IPC[a]	TPC[b]	Compound I[c]	Compound II[d]	η_{inh}[f]	mp°C	C	H	S	C	H	S
A-I-1	5.5	-	2.75	2.75	0.234	205-225	74.53	3.92	3.31	73.57	4.03	3.92
A-II-1	3.43	-	1.44	2.88	0.179	195-215	73.69	3.87	4.27	73.01	4.07	4.52
A-III-1	6.20	-	1.55	4.65	0.244	200-220	73.30	3.84	4.73	71.67	3.76	5.03
A-IV-1	4.33	-	0.866	3.46	0.264	200-220	73.06	3.82	4.99	71.79	3.88	5.26
A-V-1	3.40	1.70	1.29	3.81	0.216	195-215	73.30	3.84	4.73	72.48	3.99	4.58

a) Millimoles of isophthaloyl chloride.

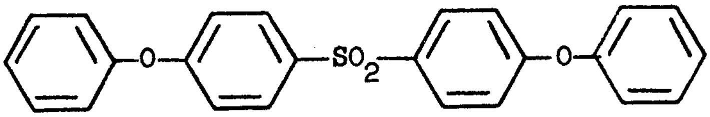
b) Millimoles of terephthaloyl chloride.

c) Millimoles of 2,4-diphenoxyacetophenone.

d) Millimoles of 4,4′-diphenoxydiphenylsulfone.

e) The analysis is corrected for the residues.

f) In DMF (0.5 g/100 ml) at 30°C.



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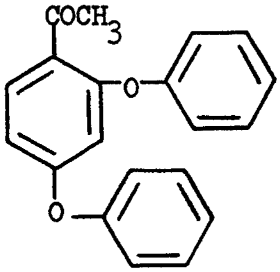
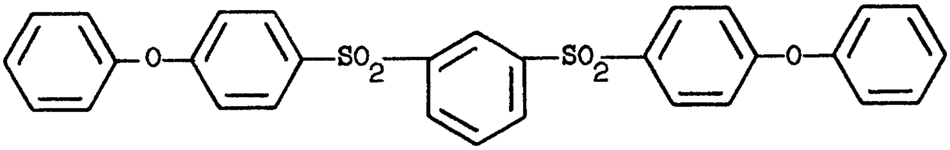


II

Terpolymers from type B were obtained from a Friedel-Crafts polymerization of 1,3-bis[p-phenoxybenzenesulfonyl]-benzene (III), 2,4-diphenoxyacetophenone (II), isophthaloyl chloride and terephthaloyl chloride using $AlCl_3$ as catalyst. The composition and properties of the polymers are given in Table IX.



III

These polymers with acetyl groups in the backbone were then converted into β-chloro unsaturated aldehydes by the Vilsmeyer reaction. This reaction gives 90% yield and above. The scheme of the reaction is as follows:

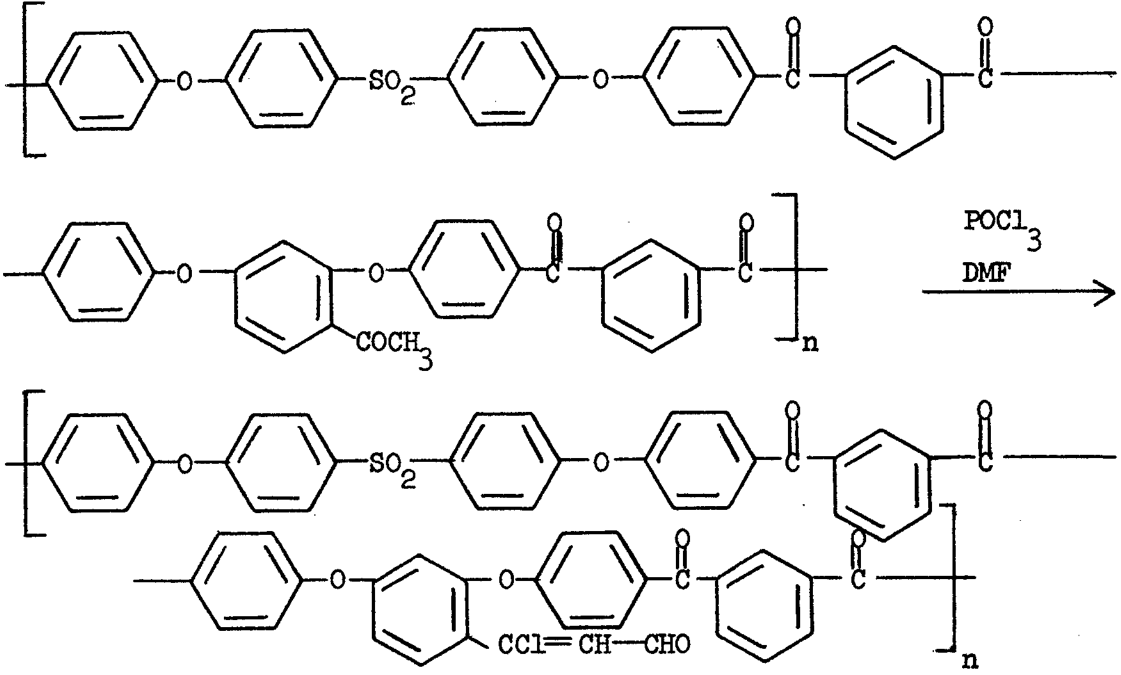


TABLE IX

POLYMERS FROM 2,4-DIPHENOXYACETOPHENONE AND 1,3-bis-[p-PHENOXYBENZENESULFONYL]-BENZENE

							Analyses[e]					
							Calc. %			Found %		
Polymer	IPC[a]	TPC[b]	Com-pound I[c]	Com-pound III[d]	η_{inh}[f]	mp°C	C	H	S	C	H	S
B-I-1	4.22	-	2.11	2.11	0.165	190-210	71.61	3.79	5.78	70.93	4.09	6.30
B-II-1	3.87	-	1.29	2.58	0.14	195-215	70.19	3.71	7.20	68.87	3.85	7.36
B-III-1	5.60	-	1.40	4.20	0.182	210-225	69.55	3.67	7.83	68.90	3.72	8.15
B-IV-1	4.75	-	0.95	3.80	0.171	210-225	69.18	3.65	8.20	68.41	3.76	7.91
B-V-1	2.96	1.48	2.22	2.22	0.165	190-210	71.61	3.79	5.78	70.17	3.97	5.78
B-VI-1	3.0	1.50	1.12	3.37	0.176	200-220	69.55	3.67	7.83	68.43	3.84	7.69

a) Millimoles of isophthaloyl chloride.

b) Millimoles of terephthaloyl chloride.

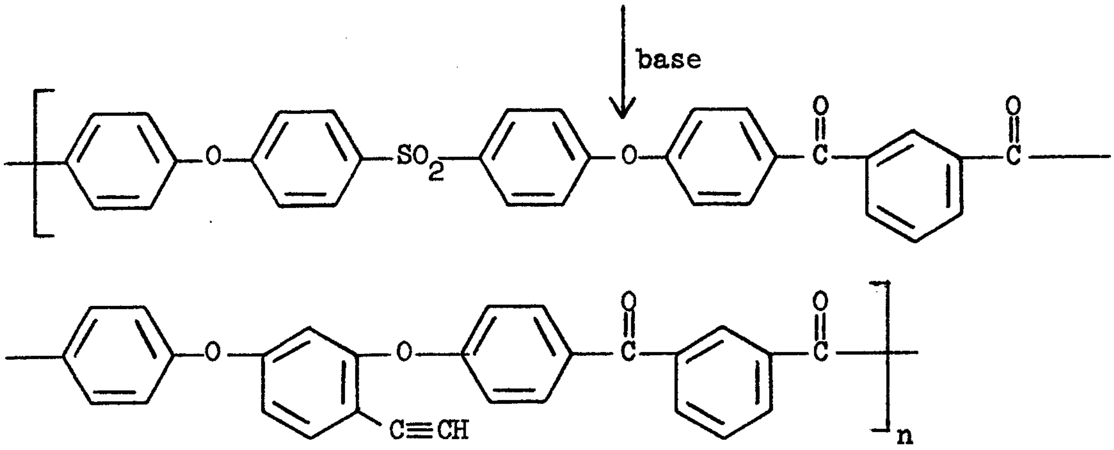
c) Millimoles of 2,4-diphenoxyacetophenone.

d) Millimoles of 1,3-bis-[p-phenoxybenzenesulfonyl]-benzene.

e) The analysis is corrected for the residues.

f) In DMF (0.5 g/100 ml) at 30°C

By treating the β-chloroaldehyde polymers with a base the respective acetylene polymers could be prepared (90% conversion and above).



Several bases were tested for the conversion, NaOH in dioxane/H_2O/DMF, ∅ONa in DMF, $LiNH_2$ in DMF and KOH in DMF/EtOH. We obtained the best results for the analysis with KOH in DMF/EtOH. No chlorine is retained in the final acetylene polymer so that this reaction is complete.

The composition and properties of the acetylene dangling polymers from type A are given in Table X, from type B in Table XI. All of these polymers were soluble in DMF. Samples for thermogravimetric analysis and softening point determinations were sent to the Air Force Materials Laboratory. The following samples were sent: A-I-2 (CS-1-A), B-I-2 (CS-1-B), B-III-2 (CS-3-B) and B-IV-2 (CS-4-B). An attempt for making a laminate gave excellent adhesive properties to glass fiber to make a homogenious laminate, this test was done with polymer A-III-2 in 33 wt % ratio to glass fiber (3 plates were pressed with 33% of their weight on polymer, one hr at 260°C and 16,000 psi). This laminate was sent to the Air Force Materials Laboratory for testing.

Crosslinking experiments were done of polymers A-I-2, B-I-2, B-III-2, with $PdCl_2$ (8 wt %) as catalyst (the cured polymers are CS-1-A-CP, CS-1-B-CP, CS-3-B-CP) and A-I-2, A-III-1, B-IV-2 with TPNO (terephthalonitrileoxide which gave CS-1-A-CT, CS-3-A-CT and CS-4-B-CT as cured polymers. The yield of crosslinked polymer insoluble in DMF is given in Table XII. Samples for thermogravimetric analysis and softening point determinations were sent to the Air Force Materials Laboratory.

TABLE X

ACETYLENE POLYMERS A

			Analyses[a]					
			Calc. %			Found %		
Polymer	η_{inh}^{b}	mp$^{\circ}$C	C	H	S	C	H	S
A-I-2	0.168	195-210	75.94	3.79	3.37	74.05	3.88	3.45
A-II-2	0.161	180-195	74.59	3.78	4.32	73.40	3.70	4.61
A-III-2	0.168	180-195	73.95	3.77	4.77	72.28	3.89	5.05
A-IV-2	0.176	185-200	73.58	3.77	5.03	72.43	3.98	5.01
A-V-2	0.183	185-205	73.95	3.77	4.77	72.39	3.82	5.14

a) The analysis is corrected for the residues.

b) In DMF (0.5 g/100 ml) at 30°C.

TABLE XI

ACETYLENE POLYMERS B

			Analyses[a]					
			Calc. %			Found %		
Polymer	η_{inh}^{b}	mp$^{\circ}$C	C	H	S	C	H	S
B-I-2	0.132	185-205	72.79	3.67	5.88	71.18	3.73	5.77
B-II-2	0.124	175-190	70.90	3.63	7.26	68.78	3.83	7.14
B-III-2	0.143	195-210	70.06	3.61	7.89	68.59	3.65	7.54
B-IV-2	0.150	195-210	69.58	3.60	8.24	69.29	3.77	8.02
B-V-2	0.143	180-195	72.79	3.67	5.88	70.89	3.72	6.02
B-VI-2	0.146	185-205	70.06	3.61	7.89	68.65	3.73	7.61

a) The analysis is corrected for the residues.

b) In DMF (0.5 g/100 ml) at 30°C.

The polymers crosslinked with $PdCl_2$ were heated 24 hr at 210°C and 48 hr at 285°C under nitrogen. The polymers crosslinked with TPNO were first A-staged in solution (sulfolane), after precipitation and drying the residue was heated 24 hr at 210°C and 48 hr at 285°C. A-III-2 was crosslinked by heating 24 hr at 210°C, 24 hr at 250°C and 24 hr at 285°C and less TPNO was used for crosslinking. The cured product ($PdCl_2$ catalyst) was stirred overnight with diluted HCl.

TABLE XII

CROSSLINKING EXPERIMENTS

Polymer	Crosslinked Polymer	Catalyst	% Crosslinked Pol. (insoluble product)
A-I-2	CS-1-A-CP	$PdCl_2$	95.9
A-I-2	CS-1-A-CT	TPNO	100
A-III-2	CS-3-A-CT	TPNO	88.9
B-I-2	CS-1-B-CP	$PdCl_2$	98.2
B-III-2	CS-3-B-CP	$PdCl_2$	90.5
B-IV-2	CS-4-B-CT	TPNO	97.3

Isothermal aging experiments were done in air. The results (loss of weight) are given in Table XIII. Most of the non-cured polymers show complete stability up to 300°C. Even at 350°C the thermal stability of polymers A-III-2 (14 wt % acetylene component), A-IV-2 (11 wt % acetylene component) and A-V-2 (14 wt % acetylene component, 33% terephthaloyl chloride) is very good. The lower the concentration of the acetylenic component the higher the thermal stability will be in the acetylene dangling polymers from type A. The polymers from type B (non-crosslinked) are less stable at 350°C but at 300°C most of them show complete thermal stability.

The polymers crosslinked with $PdCl_2$ are not thermally stable at all and give a serious loss of weight at 250°C. The reason could be that there was an oxidation rather than a trimerization. For this reason we shall try to find another catalyst to avoid this problem. The acetylene polymers crosslinked by TPNO on the other hand are thermally stable at 250°C and show

TABLE XIII

ISOTHERMAL AGING OF NON-CURED AND CURED ACETYLENE POLYMERS

	Percent loss of weight		
Polymer	7 days at 250°C	7 days at 300°C	4 days at 350°C
A-I-2	no	2	42.7
A-II-2	no	no	10.3
A-III-2	no	0.7	4.9
A-IV-2	no	no	2.1
A-V-2	no	no	5.8
B-I-2	no	no	23.3
B-II-2	no	5.2	46.4
B-III-2	no	no	8.1
B-IV-2	no	no	10.4
B-V-2	no	2.7	19.4
B-VI-2	no	no	11.6
CS-1-A-CP	16.4	38.8	85
CS-1-A-CT	no	7.2	64
CS-1-B-CP	11.7	40	83
CS-3-B-CP	24.6	---	88
CS-4-B-CT	no	6	58

a fairly high thermal stability at 300°C. Above this temperature (350°C) however they show an enormous loss in weight.

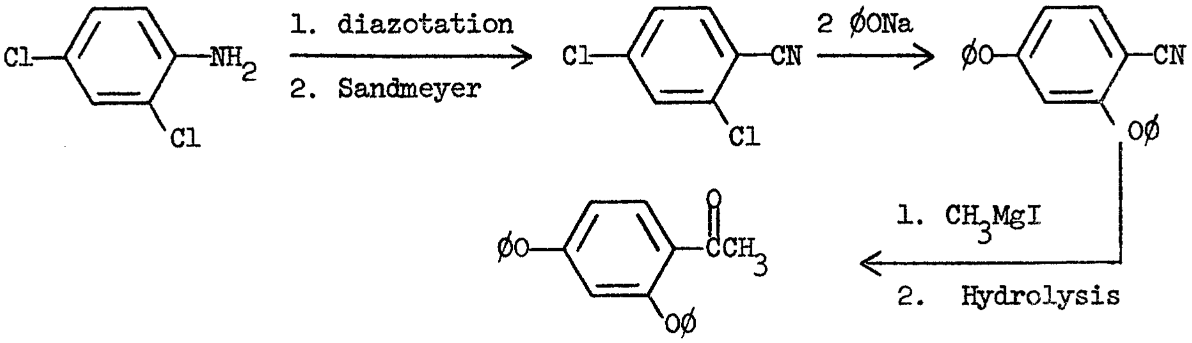
b. Experimental

i) Polymers from 4,4′-diphenoxydiphenylsulfone and 2,4-diphenoxyacetophenone

a) Monomer synthesis

i) 2,4-diphenoxyacetophenone

2,4-Diphenoxyacetophenone was prepared from 2,4-dichloroaniline by diazotation and Sandmeyer reaction with cuprous cyanide. On the reaction product was done a substitution of the chlorine with sodium phenolate and then a Grignard reaction with MeMgI which results in the formation of 2,4-diphenoxyacetophenone.



a) 2,4-Dichlorobenzonitrile[13]

2,4-Dichloroaniline (42.5 g, 0.25 mole) was treated with 85 ml concentrated HCl and 85 ml H_2O. Under cooling 0-5°C and stirring was added dropwise a solution of 24 g $NaNO_2$ in 50 ml H_2O. The diazonium chloride solution was then poured in small quantities to a solution of 40 g NaCN and 33 g CuCn in 200 ml H_2O at 60°C. The temperature was kept between 60-70°C while adding the diazonium salt solution. Then the 2,4-dichlorobenzonitrile was steam distilled. Recrystallization from MeOH. mp 59°C. Yield 22.5 g.

b) 2,4-Diphenoxybenzonitrile[14]

2,4-Dichlorobenzonitrile (12.04 g, 0.07 mole) was treated with 17.8 g sodium phenolate (0.155 mole) in 100 ml DMSO at 100-110°C during 48 hr under nitrogen and stirring. Then, the DMSO was evaporated and the residue was dissolved in ether. The ether solution was then washed with water. After evaporation of the ether, the product was recrystallized from MeOH. Yield 11.5 g. mp 85-86°C.

c) 2,4-Diphenoxyacetophenone

To a Grignard solution of CH_3MgI (0.14 mole) in 50 ml of anhydrous ether, was added a solution of 38.5 g, 2,4-diphenoxybenzonitrile in 350 ml dry benzene. After 48 hr reflux the complex was hydrolyzed. The ether solution was then washed out with water and dried over Na_2SO_4. After evaporation of the solvent, the product was distilled at 170°C under 0.025 mm pressure, yield 20 g.

Anal. Calc.: C, 78.94%; H, 5.26%.
Found: C, 78.79%; H, 5.37%.

ii) 4,4′-Diphenoxydiphenylsulfone

Bis-[4-chlorophenylsulfone] (57.4 g), (0.2 mole) was reacted with 51 g sodiumphenolate (0.44 mole) in 350 ml DMSO, under stirring and flushing with nitrogen for 90 hr at 110°C. The reaction mixture was then poured into 2 liter of water. The isolated product was then recrystallized from isopropanol-chloroform. Yield 33 g, mp 141-142°C.

b) Polymers from 4,4′-diphenoxydiphenylsulfone and 2,4-diphenoxyacetophenone

i) Preparation of polymer A-I-2 (30 wt% acetylene component

a) Preparation of polymer A-I-1

2,4-Diphenoxyacetophenone (0.8362 g, 2.75 mM), 4,4′-diphenoxydiphenylsulfone (1.1055 g, 2.75 mM) and isophthaloyl chloride (1.1165 g, 5.5 mM) were dissolved in 40 ml dichloroethane. $AlCl_3$ (3.29 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was then filtered off, washed several times with methanol in a blender and dried. Yield 2.42 g mp 205-225°C. η_{inh} 0.234 at 30°C in DMF.

Anal. Calc.: C, 74.53%; H, 3.92%; S, 3.31%.
Found: C, 73.57%; H, 4.03%; S, 3.92%.

b) Preparation of β-chloroaldehyde A-I-C

A solution of 2.168 g acetyl polymer A-I-1 in 110 ml DMF (Dry) was added to a freshly prepared solution of Vilsmeyer reagent. [The Vilsmeyer reagent was made by adding $PdCl_3$ to cold DMF and this solution was stirred for a further two hr under cooling. For 1 mM of acetyl component there is used three ml Vilsmeyer reagent (1 ml $POCl_3$ in 2 ml DMF)].

The reaction mixture was then stirred one day at room temperature and one night at 40°C. After cooling, the polymer was precipitated in water which contains some sodium acetate. The polymer was filtered, washed out with water and dried. Yield 2.11 g mp 185-205°C.

Anal. Calc.: C, 72.29%; H, 3.65%; S, 3.16%; Cl, 3.50%.
Found: C, 71.02%; H, 3.67%; S, 3.34%; Cl, 3.68%.

c) Preparation of polymer A-I-2

To a solution of 0.252 g KOH in 10 ml ethanol and 20 ml of DMF at 80°C was added a solution of the previous β-chloroaldehyde (1.876 g in 90 ml DMF). After complete addition the reaction mixture was stirred for a complete reaction time of 75 min at 80°C. The polymer was then precipitated in distilled water which contained some acetic acid. Yield 1.66 g mp 195-210°C η_{inh} 0.168 at 30°C in DMF.

Anal. Calc.: C, 75.94%; H, 3.79%; S, 3.37%.
Found: C, 74.05%; H, 3.38%; S, 3.45%.

ii) Preparation of polymer A-II-2 (19 wt % acetylene component

a) Preparation of polymer A-II-1

2,4-Diphenoxyacetophenone (0.3954 g, 1.3 mM), 4,4′-diphenoxydiphenylsulfone (1.0452 g, 2.6 mM) and isophthaloyl chloride (0.7917 g, 3.9 mM) were dissolved in 30 ml dichloroethane. $AlCl_3$ (2.26 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was then filtered off and washed several times with MeOH in a blender and dried. Yield 1.82 g mp 195-215°C η_{inh} 0.179 in DMF at 30°C.

Anal. Calc.: C, 73.69%; H, 3.87%; S, 4.27%.

Found: C, 73.01%; H, 4.07%; S, 4.52%.

b) Preparation of β-chloroaldehyde A-II-C

A solution of 1.534 g acetyl polymer A-II-1 in 75 ml DMF was added to three ml Vilsmeyer reagent (1 ml $POCl_3$ in 2 ml DMF). The reaction was then continued and worked up as for polymer A-I-C. mp 185-200°C. Yield 1.400 g.

Anal. Calc.: C, 72.25%; H, 3.69%; S, 4.14%; Cl, 2.29%.

Found: C, 72.00%; H, 3.78%; S, 4.24%; Cl, 2.30%.

c) Preparation of polymer A-II-2

To a solution of 70 mg KOH in 5 ml ethanol and 10 ml of DMF at 80°C was added a solution of the previous β-chloroaldehyde (0.769 g in 40 ml DMF). The reaction was continued and worked up as for polymer A-I-2. Yield 0.67 g mp 185-200°C η_{inh} 0.161 at 30°C in DMF.

Anal. Calc.: C, 74.59%; H, 3.78%; S, 4.32%.

Found: C, 73.40%; H, 3.70%; S, 4.61%.

iii) Preparation of polymer A-III-2 (14 wt % acetylene component)

a) Preparation of polymer A-III-1

2,4-diphenoxyacetophenone (0.4729 g, 1.55 mM) 4,4′-diphenoxydiphenylsulfone (1.8693, 4.65 mM) and isophthaloyl chloride (1.2586 g, 6.2 mM) were dissolved in 50 ml dichloroethane. $AlCl_3$ (3.60 g) was added and the reaction worked up as for polymer A-I-1. Yield 2.70 g mp 200-220°C η_{inh} 0.244 at 30°C in DMF.

Anal. Calc.: C, 73.30%; H, 3.84%; S, 4.73%.

Found: C, 71.67%; H, 3.76%; S, 5.03%.

b) Preparation of β-chloroaldehyde A-III-C

A solution of polymer A-III-1 (2.400 g in 120 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 2.250 g. mp 175-195°C.

Anal. Calc.: C, 72.23%; H, 3.71%; S, 4.62%; Cl, 1.71%.

Found: C, 71.58%; H, 3.81%; S, 4.70%; Cl, 1.35%.

c) Preparation of polymer A-III-2

To a solution of 0.150 g KOH in 10 ml ethanol and 20 ml DMF at 80°C is added a solution of the previous β-chloroaldehyde (2.212 g in 120 ml DMF). The reaction was then worked up as for polymer A-I-2. Yield 1.956 g mp 180-195°C η_{inh} 0.168

Anal. Calc.: C, 73.95%; H, 3.77%; S, 4.77%.
Found: C, 72.28%; H, 3.89%; S, 5.05%.

iv) Preparation of polymer A-IV-2 (11 wt % acetylene component

a) Preparation of polymer A-IV-1

2,4-Diphenoxyacetophenone (0.2633 g, 0.866 mM), 4,4′-diphenoxydiphenylsulfone (1.3925 g, 3.46 mM) and isophthaloyl chloride (0.8789 g, 4.33 mM) were dissolved in 35 ml dichloroethane. $AlCl_3$ (2.54 g) was added and the reaction worked up as for polymer A-I-1. Yield 2 g mp 200-220°C η_{inh} 0.264 at 30°C in DMF.

Anal. Calc.: C, 73.06%; H, 3.82%; S, 4.99%.
Found: C, 71.97%; H, 3.88%; S, 5.26%.

b) Preparation of β-chloroaldehyde A-IV-C

A solution of 1.800 g polymer A-IV-1 in 90 ml DMF was added to the freshly prepared Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 1.700 g mp 175-190°C.

Anal. Calc.: C, 72.22%; H, 3.72%; S, 4.91%; Cl, 1.36%.
Found: C, 71.94%; H, 3.79%; S, 4.99%; Cl, 1.42%.

c) Preparation of polymer A-IV-2

To a solution of 0.090 g KOH in 5 ml ethanol and 10 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (1.664 g in 80 ml DMF). The reaction was then worked up as for polymer A-I-2. Yield 1.449 g mp 185-200°C η_{inh} 0.176 at 30°C in DMF.

Anal. Calc.: C, 73.58%; H, 3.77%; S, 5.03%.
Found: C, 72.43%; H, 3.98%; S, 5.01%.

v) Preparation of polymer A-V-2 (14 wt % acetylene component)

a) Preparation of polymer A-V-1

2,4-Diphenoxyacetophenone (0.3926 g, 1.291 mM), 4,4′-diphenoxydiphenylsulfone (1.5569 g, 3.813 mM), isophthaloyl chloride

(0.6906 g, 2.402 mM) and terephthaloyl chloride (0.3453 g, 1.701 mM) were dissolved in 80 ml dichloroethane. $AlCl_3$ (3.04 g) was added and worked up as for polymer A-I-1. Yield 2.228 g mp 195-215°C. η_{inh} 0.216 at 30°C in DMF.

Anal. Calc.: C, 73.30%; H, 3.84%; S, 4.73%.

Found: C, 72.48%; H, 3.99%; S, 4.58%.

b) Preparation of β-chloroaldehyde A-V-C

A solution of polymer A-V-1 (2.020 g in 100 ml DMF was added to the freshly prepared Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 1.86 g mp 185-205°C.

Anal. Calc.: C, 72.23%; H, 3.71%; S, 4.62%; Cl, 1.71%.

Found: C, 72.33%; H, 3.86%; S, 5.20%; Cl, 1.87%.

c) Preparation of polymer A-V-2

To a solution of 0.118 g KOH in 5 ml ethanol and 10 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (1.740 g in 85 ml DMF). The reaction was then worked up as for polymer A-I-2. Yield 1.418 g mp 185-205°C η_{inh} 0.183 at 30°C in DMF.

Anal. Calc.: C, 73.95%; H, 3.77%; S, 4.77%.

Found: C, 72.39%; H, 3.82%; S, 5.14%.

ii) Polymers from 1,3-bis[p-phenoxybenzenesulfonyl]-benzene and 2,4-diphenoxyacetophenone

a) Synthesis of monomers

i) 2,4-Diphenoxyacetophenone

The preparation of this monomer is given on page 69.

ii) 1,3-Bis-[p-phenoxybenzenesulfonyl]-benzene

1,3-m-Benzenedisulfonyl chloride (65 g) was dissolved in 750 ml of dry diphenyl ether. A portion of 2.5 g sublimed $FeCl_3$ was added, and the mixture was stirred under nitrogen at 140°C for 15 hr. The mixture was washed with water and then dried over Na_2SO_4. The excess of diphenyl ether was distilled off under vacuum and the residue was distilled via a short path (bp 400-420°C/0.06 mm). The glassy solid was dissolved in 100 ml of $CHCl_3$ and precipitated as a white powder in one liter of diethyl ether. mp 142-143°C.

b) Polymers from 1,3-bis[p-phenoxybenzenesulfonyl]-benzene

i) Preparation of polymer B-I-2 (26 wt % acetylene component)

a) Preparation of polymer B-I-1

2,4-Diphenoxyacetophenone (0.900 g, 2.96 mM), 1,3-bis-[p-phenoxybenzenesulfonyl]-benzene (1.640 g, 2.96 mM) and isophthaloyl chloride (1.201 g, 5.92 mM) were dissolved in 50 ml dichloroethane. $AlCl_3$ (3.99 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was then filtered off, washed several times with methanol in a blender and dried. Yield 3.025 g mp 190-210°C η_{inh} 0.165 at 30°C in DMF.

Anal. Calc.: C, 71.61%; H, 3.79%; S, 5.78%.
Found: C, 70.93%; H, 4.09%; S, 6.30%.

b) Preparation of β-chloroaldehyde B-I-C

A solution of polymer B-I-1 (1.815 g in 90 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 1.710 g mp 180-195°C.

Anal. Calc.: C, 69.76%; H, 3.55%; S, 5.55%; Cl, 3.08%.
Found: C, 69.36%; H, 3.74%; S, 5.01%; Cl, 2.78%.

c) Preparation of polymer B-I-2

To a solution of 0.210 g KOH in 10 ml ethanol and 20 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (1.612 g in 75 ml DMF). The reaction was then worked up as for polymer A-I-2. Yield 1.33 g mp 185-205°C η_{inh} 0.132 at 30°C in DMF.

Anal. Calc.: C, 72.79%; H, 3.67%; S, 5.88%.
Found: C, 71.18%; H, 3.73%; S, 5.77%.

ii) Preparation of polymer B-II-2 (16 wt % acetylene component)

a) Preparation of polymer B-II-1

2,4-Diphenoxyacetophenone (0.3945 g, 1.29 mM), 1,3-bis-[p-phenoxybenzenesulfonyl]-benzene (1.398 g, 2.58 mM) and isophthaloyl chloride (0.7856 g, 3.87 mM) were dissolved in 35 ml dichloroethane. $AlCl_3$ (2.58 g) was added and the reaction worked up as for polymer B-I-1. Yield 1.94 g mp 195-215°C η_{inh} 0.14 at 30°C in DMF.

Anal. Calc.: C, 70.19%; H, 3.71%; S, 7.20%.

Found: C, 68.87%; H, 3.85%; S, 7.36%.

b) Preparation of β-chloroaldehyde B-II-C

A solution of polymer B-II-1 (1.600 g in 70 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 1.470 g mp 170-190°C.

Anal. Calc.: C, 69.06%; H, 3.56%; S, 7.01%; Cl, 1.94%.

Found: C, 69.22%; H, 4.07%; S, 6.74%; Cl, 2.00%.

c) Preparation of polymer B-II-2

To a solution of 0.091 g KOH in 5 ml ethanol and 10 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (1.184 g in 60 ml DMF). The reaction was worked up as for polymer A-I-2. Yield 1.058 g mp 175-190°C η_{inh} 0.124 at 30° in DMF.

Anal. Calc.: C, 70.90%; H, 3.63%; S, 7.26%.

Found: C, 68.78%; H, 3.83%; S, 7.14%.

iii) Preparation of polymer B-III-2 (11 wt % acetylene component

a) Preparation of polymer B-III-1

2,4-Diphenoxydiphenylsulfone (0.4363 g, 1,4 mM), 1,3-bis[p-phenoxybenzenesulfonyl]-benzene (2.2764 g, 4.2 mM) and isophthaloyl chloride (1.1368 g, 5.6 mM) were dissolved in 80 ml dichloroethane. $AlCl_3$ (3.72 g) was added and the reaction worked up as for polymer B-I-1. Yield 3.235 g mp 210-225°C η_{inh} 0.182 at 30°C in DMF.

Anal. Calc.: C, 69.55%; H, 3.67%; S, 7.83%.

Found: C, 68.90%; H, 3.72%; S, 8.15%.

b) Preparation of β-chloroaldehyde B-III-C

A solution of polymer B-III-1 (2.800 g in 130 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 2.65 g mp 185-205°C.

Anal. Calc.: C, 68.73%; H, 3.56%; S, 7.69%; Cl, 1.42%.

Found: C, 68.20%; H, 3.65%; S, 7.44%; Cl, 0.61%.

c) Preparation of polymer B-III-2

To a solution of 0.145 g KOH in 10 ml ethanol and 20 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (2.519 g in 120 ml DMF). The reaction was worked up as for polymer A-I-2.

Yield 2.09 g mp 195-210°C η_{inh} 0.143 at 30°C in DMF.

Anal. Calc.: C, 70.06%; H, 3.61%; S, 7.89%.

Found: C, 68.59%; H, 3.65%; S, 7.54%.

iv) Preparation of polymer B-IV-2 (9 wt % acetylene component

a) Preparation of polymer B-IV-1

2,4-Diphenoxyacetophenone (0.2895 g, 0.95 mM), 1,3-bis-[p-phenoxybenzenesulfonyl]-benzene (2.0596 g, 3.8 mM) and isophthaloyl-chloride (0.9642 g, 4.75 mM) were dissolved in 40 ml dichloroethane. $AlCl_3$ (3.15 g) was added and the reaction worked up as for polymer B-I-1. Yield 2.80 g mp 210-225°C η_{inh} 0.171 at 30°C in DMF.

Anal. Calc.: C, 69.18%; H, 3.65%; S, 8.20%.

Found: C, 68.41%; H, 3.76%; S, 7.91%.

b) Preparation of β-chloroaldehyde B-IV-C

A solution of polymer B-IV-1 (2.600 g in 130 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 2.42 g mp 195-210°C.

Anal. Calc.: C, 68.54%; H, 3.56%; S, 8.07%; Cl, 1.12%.

Found: C, 68.94%; H, 3.69%; S, 7.35%; Cl, 0.46%.

c) Preparation of polymer B-IV-2

To a solution of 0.105 g KOH in 5 ml ethanol and 10 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (2.247 g in 120 ml DMF). The reaction was worked up as for polymer A-I-2. Yield 1.82 g mp 195-210°C. η_{inh} 0.15 at 30°C in DMF.

Anal. Calc.: C, 69.58%; H, 3.60%; S, 8.24%.

Found: C, 69.29%; H, 3.77%; S, 8.02%.

v) Preparation of polymer B-V-2 (26 wt % acetylene component

a) Preparation of polymer B-V-1

2,4-Diphenoxyacetophenone (0.6768 g, 2.22 mM), 1,3-bis-[p-phenoxybenzenesulfonyl]-benzene (1.203 g, 2.22 mM), isophthaloyl chloride (0.6008 g, 2.96 mM), and terephthaloyl chloride (0.3004 g, 1.48 mM) were dissolved in 40 ml dichloroethane. $AlCl_3$ (2.95 g) was added and the reaction worked up as for polymer B-I-1. Yield 2.157 g mp 190-210°C η_{inh} 0.165 at 30°C in DMF.

Anal. Calc.: C, 71.61%; H, 3.79%; S, 5.78%.

Found: C, 70.17%; H, 3.97%; S, 6.06%.

b) Preparation of β-chloroaldehyde B-V-C

A solution of polymer B-V-1 (1.835 g in 75 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 1.650 g mp 175-195°C.

Anal. Calc.: C, 69.76%; H, 3.55%; S, 5.55%; Cl, 3.08%.

Found: C, 69.62%; H, 3.58%; S, 5.87%; Cl, 2.61%.

c) Preparation of polymer B-V-2

To a solution of 0.057 g KOH in 5 ml ethanol and 5 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (0.780 g in 40 ml DMF). The reaction was worked up as for polymer A-I-2. Yield 0.703 g mp 180-195°C η_{inh} 0.143 at 30°C in DMF.

Anal. Calc.: C, 72.79%; H, 3.67%; S, 5.88%.

Found: C, 70.89%; H, 3.72%; S, 6.02%.

vi) Preparation of polymer B-VI-2 (11 wt % acetylene component

a) Preparation of polymer B-VI-1

2,4-Diphenoxyacetophenone (0.3421 g, 1.125 mM), 1,3-bis-[p-phenoxybenzenesulfonyl]-benzene (1.829 g, 3.375 mM), isophthaloyl chloride (0.609 g, 3 mM) and terephthaloyl chloride (0.3045 g, 1.5 mM) were dissolved in 40 ml dichloroethane. $AlCl_3$ (2.99 g) was added and the reaction worked up as for polymer B-I-1. Yield 2.184 g mp 200-220°C. η_{inh} 0.176 at 30°C in DMF.

Anal. Calc.: C, 69.55%; H, 3.67%; S, 7.83%.

Found: C, 68.43%; H, 3.84%; S, 7.69%.

b) Preparation of β-chloroaldehyde B-VI-C

A solution of polymer B-VI-1 (2 g in 100 ml DMF) was added to a freshly prepared solution of Vilsmeyer reagent and worked up as for polymer A-I-C. Yield 1.9 g mp 185-200°C.

Anal. Calc.: C, 68.73%; H, 3.56%; S, 7.69%; Cl, 1.42%.

Found: C, 68.13%; H, 3.66%; S, 7.19%; Cl, 1.22%.

c) Preparation of polymer B-VI-2

To a solution of 0.098 g KOH in 5 ml ethanol and 10 ml DMF at 80°C was added a solution of the previous β-chloroaldehyde (1.758 g in 80 ml DMF). The reaction was worked up as for polymer A-I-2. Yield 1.6 g mp 185-205°C η_{inh} 0.146 at 30°C in DMF.

Anal. Calc.: C, 70.06%; H, 3.61%; S, 7.89%.

Found: C, 68.65%; H, 3.73%; S, 7.61%.

iii) Crosslinking reactions

a) Curing of polymer A-I-2 with TPNO[15] (terephthalonitrile oxide

Acetylene dangling polymer A-I-2 (0.650 g) was dissolved in 25 ml sulfolane (dry) by heating at 60-70°C. Then 0.160 g TPNO was added and the reaction mixture stirred for 1 hr at room temperature. Another 0.160 g TPNO was then added and stirring was continued for a further two hr at 60°C. The reaction was then poured into methanol and the precipitate was filtered off and washed out with MeOH, then dried. The dry product (0.830 g) was then cured in an aluminum foil under nitrogen, 24 hr at 210°C and 48 hr at 285°C. The residue was then taken up in DMF and stirred overnight. After filtration and drying the same weight of product was recovered so that the cured product was 100% insoluble in DMF.

b) Curing of polymer A-I-2 with 8 wt % $PdCl_2$

A well ground mixture of 0.842 g polymer A-I-2 and 8 wt % $PdCl_2$ was heated 24 hr at 210°C and 48 hr at 285°C, in an aluminum foil under nitrogen. The black-brown residue was then treated with diluted HCl for 24 hr. After filtration and washing out with water it was dried. Then, it was taken up in DMF and stirred overnight; 4.1% was soluble and 95.9% insoluble.

c) Curing of polymer A-I-3 with TPNO

Acetylene dangling polymer A-I-3 (0.600 g) was dissolved in 25 ml sulfolane (dry) by heating at 60-70°C. Then 30 mg TPNO was added and the reaction mixture stirred for one hr at room temperature. Another 30 mg TPNO was then added and stirring was continued for a further two hr at 50°C. The reaction was then worked up as for polymer A-I-2. The isolated product (0.535 g) was then heated under nitrogen, 24 hr at 210°C, 24 hr at 250°C and 24 hour at 285°C. The residue was then treated with DMF overnight, filtered and dried. There remained 88.9% product insoluble in DMF.

d) Curing of polymer B-I-2 with 8 wt % $PdCl_2$

A well ground mixture of polymer B-I-2 (0.6935 g and 8 wt % $PdCl_2$) was heated 24 hr at 210°C and 48 hr at 285°C, in an aluminum foil under nitrogen. The residue was then treated with diluted HCl for 24 hr, it was then filtered, washed out and dried. 98.2% was insoluble in DMF.

e) Curing of polymer B-III-2 with 8 wt % $PdCl_2$

A well ground mixture of polymer B-III-2 (0.6711 g and 8 wt % $PdCl_2$) was heated and treated in the same circumstances as previous sample. There was 90.5% insoluble material left after stirring up the residue overnight with DMF.

f) Curing of polymer B-IV-2 with TPNO

Acetylene dangling polymer B-IV-2 (0.776 g) was dissolved in 25 ml sulfolane (dry) by heating at 60-70°C. Then 0.180 g TPNO was added and the reaction mixture stirred for one hr at room temperature. Another 0.180 g TPNO was then added and the reaction continued and worked up as for polymer A-I-2. After treating the residue with DMF there remained 97.3% insoluble material.

4. Future Plans

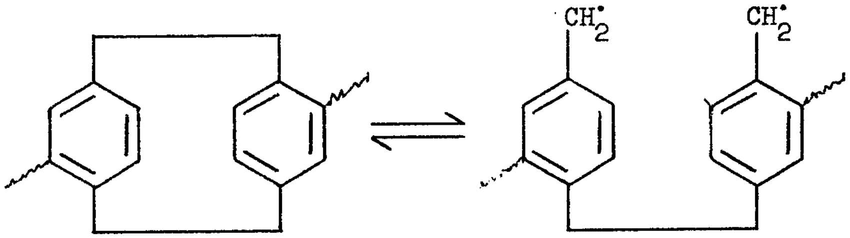
This work will be continued when the results of the Vicat and the TGA curves are received from the Materials Laboratory. Samples of sufficient size to make test laminates will be prepared.

VI. POLYARYL ETHERS, SULFONES AND KETONES AS THERMALLY STABLE LAMINATING RESINS

1. Introduction

Crosslinking processes which liberate gaseous side products have the deleterious effect of producing voids which weaken laminates. Hence, thermally stable laminating resins are needed which are not only low melting prior to crosslinking, but also can be cured without giving off volatiles. Particularly promising in this respect are polymers containing the [2.2] paracyclophane unit.

In 1972 Meyers et al[16] reported the synthesis of a linear polymer containing [2.2] paracyclophane units and the crosslinking of this polymer by heating at 275°C. Crosslinking in such polymers is based upon the thermal homolysis of the [2.2] paracyclophane dimethylene bridge to produce a substituted p,p′-dimethylbibenzyl diradical. In the absence of reactive hydrogens or free radical traps, these radicals may either 1) recombine intramolecularly, leading to no change or 2) combine intermolecularly, giving rise to ethylenic polymer crosslinks.



Aromatic ethers, ketones and sulfones are known to be thermally quite stable.[17] Consequently, polymers containing these functional groups and incorporating paracyclophane units would appear to be materials of great potential as high-temperature resistant laminating resins.

In this section varying amounts of a [2.2] paracyclophane derivative have been introduced into polymers prepared from either of two diphenyl ether sulfones, 1,3-bis(p-phenoxybenzenesulfonyl)benzene or 4,4′-bis(p-phenoxybenzenesulfonyl) diphenyl ether, with isophthaloyl chloride or terephthaloyl chloride.

2. Results and Discussion

a. Polymers from 1,3-bis(p-phenoxybenzenesulfonyl)benzene

Polymers incorporating between five and 29% by weight of 3,9-bis-

(p-phenoxybenzoyl)[2.2]paracyclophane have been prepared by Friedel-Crafts polymerization with 1,3-bis(p-phenoxybenzenesulfonyl)benzene and isophthaloyl chloride. The polymers investigated and the weight contributions of each component are listed in Table XIV. In addition a polymer employing a mixed acid chloride (2:1 ratio of isophthaloyl and terephthaloyl chloride) and one using terephthaloyl chloride have been prepared, each containing 15 wt % of the [2.2] paracyclophane unit.

i) Physical and thermal properties

A comparison of the melting points of these polymers has revealed several general trends. First, the replacement of isophthaloyl by terephthaloyl units in the polymer raises the melting point. In the case of PS-CP-1 (isophthaloyl units) and PS-CP-5 (terephthaloyl units) which contain identical amounts of the [2.2] paracyclophane component, the melting point was increased by 30-35°C. Secondly, increasing amounts of the [2.2] paracyclophane unit raise the melting points of the resultant polymer. For example, polymers containing 5-15 wt % of the [2.2] paracyclophane monomer melt in the range of 180-210°C; whereas, the polymers possessing larger amounts (22-29 wt %) of this component apparently crosslink before the melting point is reached.

The solubilities parallel the melting points: polymers containing a larger number of [2.2] paracyclophane units exhibit lower solubilities than those possessing smaller amounts of the [2.2] paracyclophane monomer. All of these polymers are insoluble in dioxane. Although 30% solutions have not proven possible, these polymers are somewhat soluble in dimethylacetamide and sulfolane.

The low solubility of these polymers in H_2SO_4 has necessitated heating the sample to get solution. Under such conditions degradation and sulfonation may occur. This may account for the moderately low inherent viscosities observed in H_2SO_4 and for the larger values obtained with hexamethylphosphoric triamide (HMPA) as the solvent.

The crosslinked terpolymers obtained by heating PS-CP-1 (containing 15 wt % of the [2.2] paracyclophane derivative) at 350°C for 24 hr exhibited distinct crosslinking. A shorter crosslinking reaction time of 4 hr gave crosslinked product in 85% yield. The vicat softening point curves of PS-CP-1 and the crosslinked polymer PS-CP-1-C are given

TABLE XIV

WEIGHT PERCENTAGES FOR POLYMERS OF 1,3-BIS(p-PHENOXYBENZENESULFONYL)BENZENE AND 3,9-BIS[p-PHENOXYBENZOYL][2.2]PARACYCLOPHANE WITH ISOPHTHALOYL CHLORIDE

Polymer	Wt % of Paracyclophane	Wt % of Disulfone	Wt % of Isophthaloyl Chloride
DTW-5	5.5	75.0	19.5
DTW-1	8.8	71.7	19.5
PS-CP-3	8.8	71.7	19.5
PS-CP-1	15.8	64.8	19.4
DTW-3	16.6	64.1	19.3
PS-CP-6	20.2	60.5	19.3
DTW-4	22.0	58.8	19.2
PS-CP-7	26.1	54.8	19.1
DTW-2	28.7	52.2	19.1

in Figure 23. The crosslinked PS-CP-1-C polymer sintered very slightly whereas the uncured sample fused and melted readily. Thermogravimetric analysis (TGA) of PS-CP-1 before and after crosslinking is given in Figure 24. Both the polymer and crosslinked polymer exhibited a TGA break at approximately 475°C in nitrogen.

Polymer PS-CP-3 having only 9 wt % of 3,9-bis(p-phenoxybenzoyl)-[2.2]paracyclophane showed no substantial crosslinking on heating at 350°C. for 24 hr (see Figures 25 and 26). Cured polymers from PS-CP-4 and PS-CP-5 showed crosslinking to some degree but not to the extent of PS-CP-1 (see Figures 27, 28, 29, 30).

To investigate the effect of a higher degree of crosslinking in the thermal and softening properties, terpolymers of the PS-CP-1 type (isophthaloyl units) having 20, 26 and 29 wt % of 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane were prepared and have been submitted to the Air Force Materials Laboratory for softening point and thermogravimetric analyses. In addition polymer DTW-1 (9 wt % of the [2.2] paracyclophane component) has been cured at different temperatures (250-350°C) and for various periods (24-48 hr) to determine maximum crosslinking procedures. Identical experiments have been performed for sample DTW-2 (29 wt % of the [2.2]paracyclophane); however, the results of these analyses are not yet available.

ii) Isothermal aging experiments

Isothermal aging experiments were run in circulating air. The isothermal weight losses of these polymers at different temperatures are compiled in Table XV. All of these polymers as well as the crosslinked materials exhibited good thermal stability at 250°C with weight losses around 5% in 200 hr and fair thermal stability at 275°C with weight losses around 6-7% but showed considerable weight losses around 15-20% at 300°C. Polymer PS-CP-5 having terephthaloyl units exhibited better isothermal stability than polymers containing the isophthaloyl unit. Considerable weight losses exhibited at 300°C by these polymers may be due to the oxidation of benzylic C-H bonds. Work to improve the thermal stability of these polymers by substituting benzylic C-H with alkyl groups or fluorine will be in our future plans.

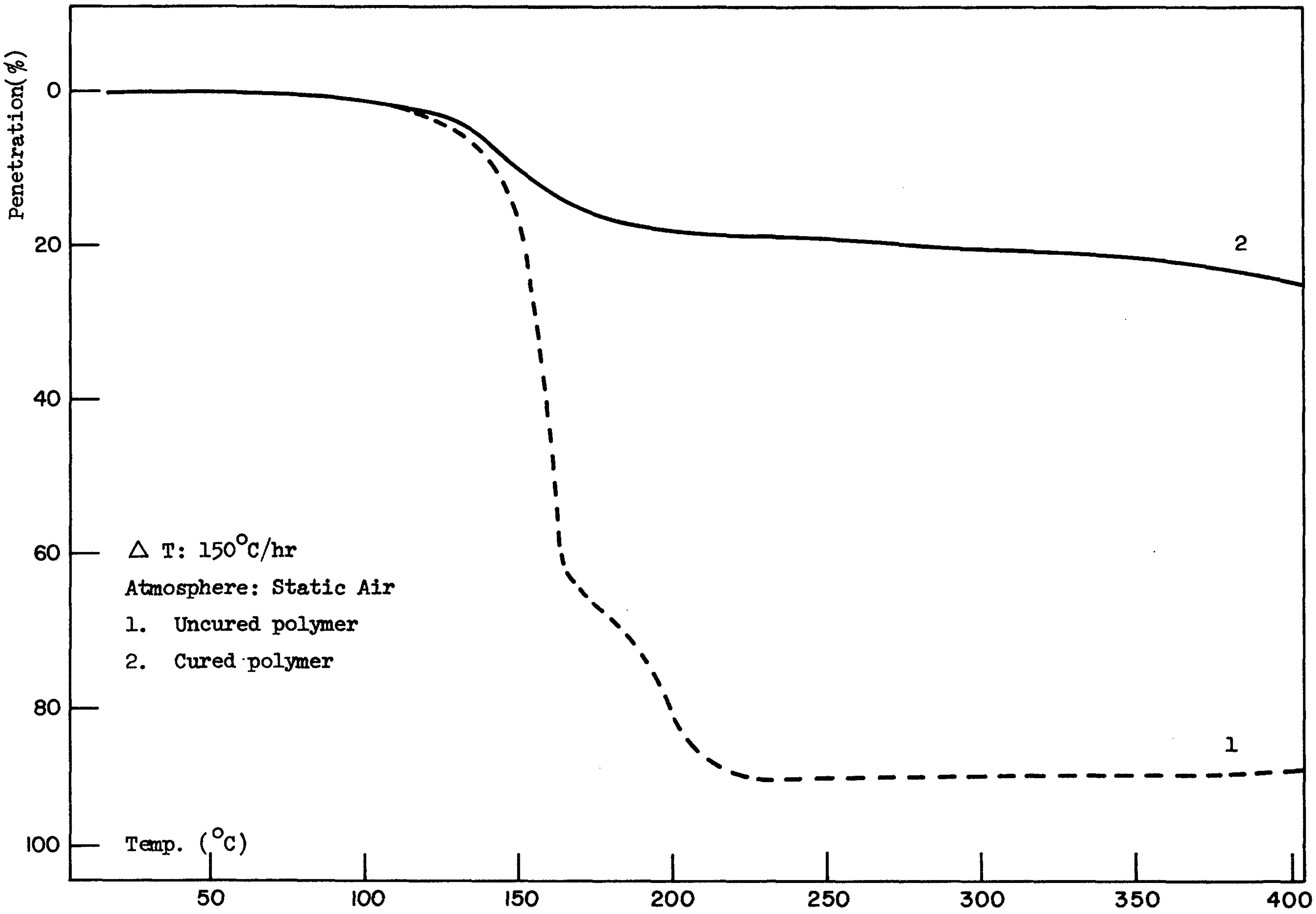


Figure 23. Softening curve for PS-CP-1 and PS-CP-1-C. Measured by Vicat Apparatus.

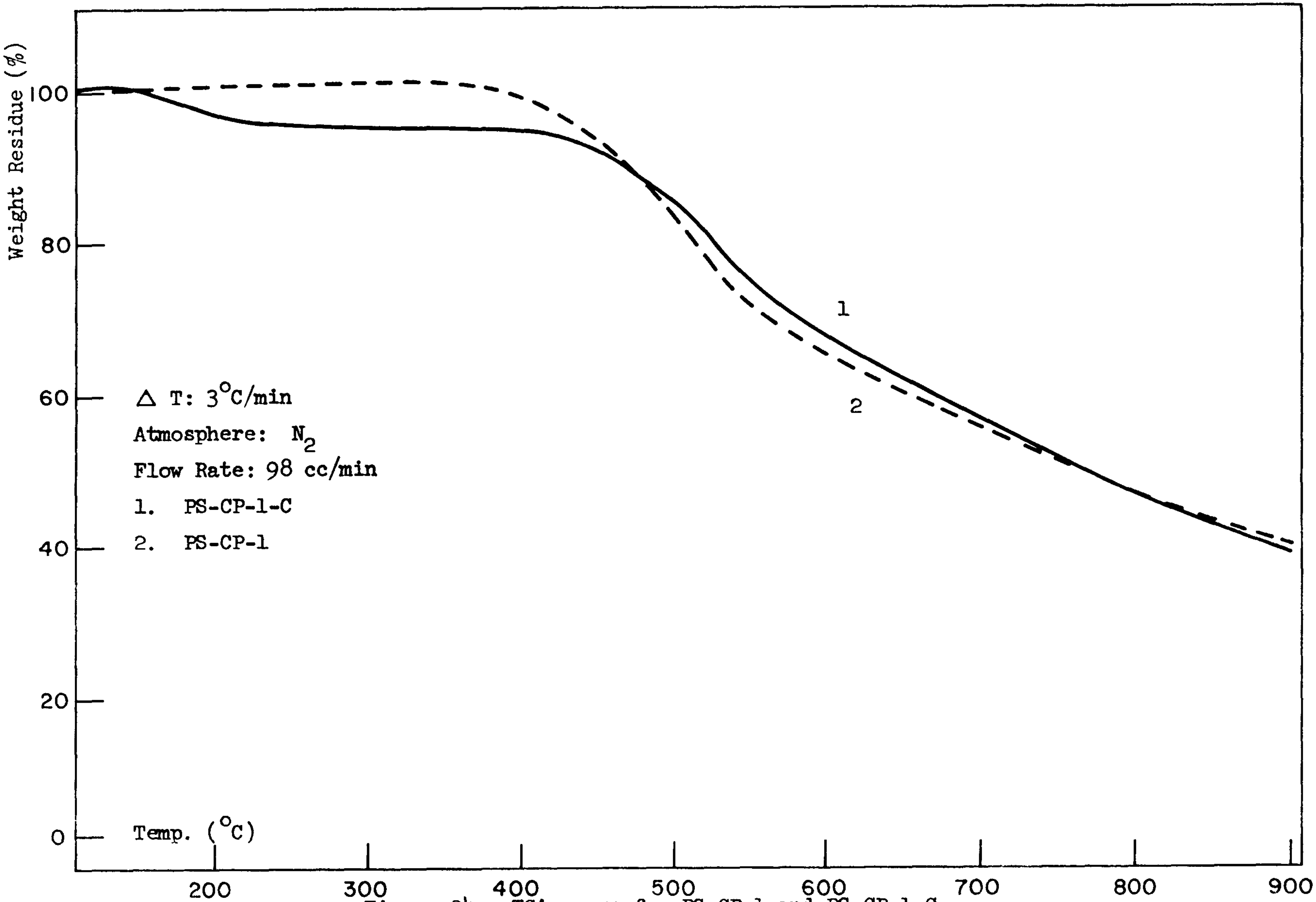


Figure 24. TGA curve for PS-CP-1 and PS-CP-1-C

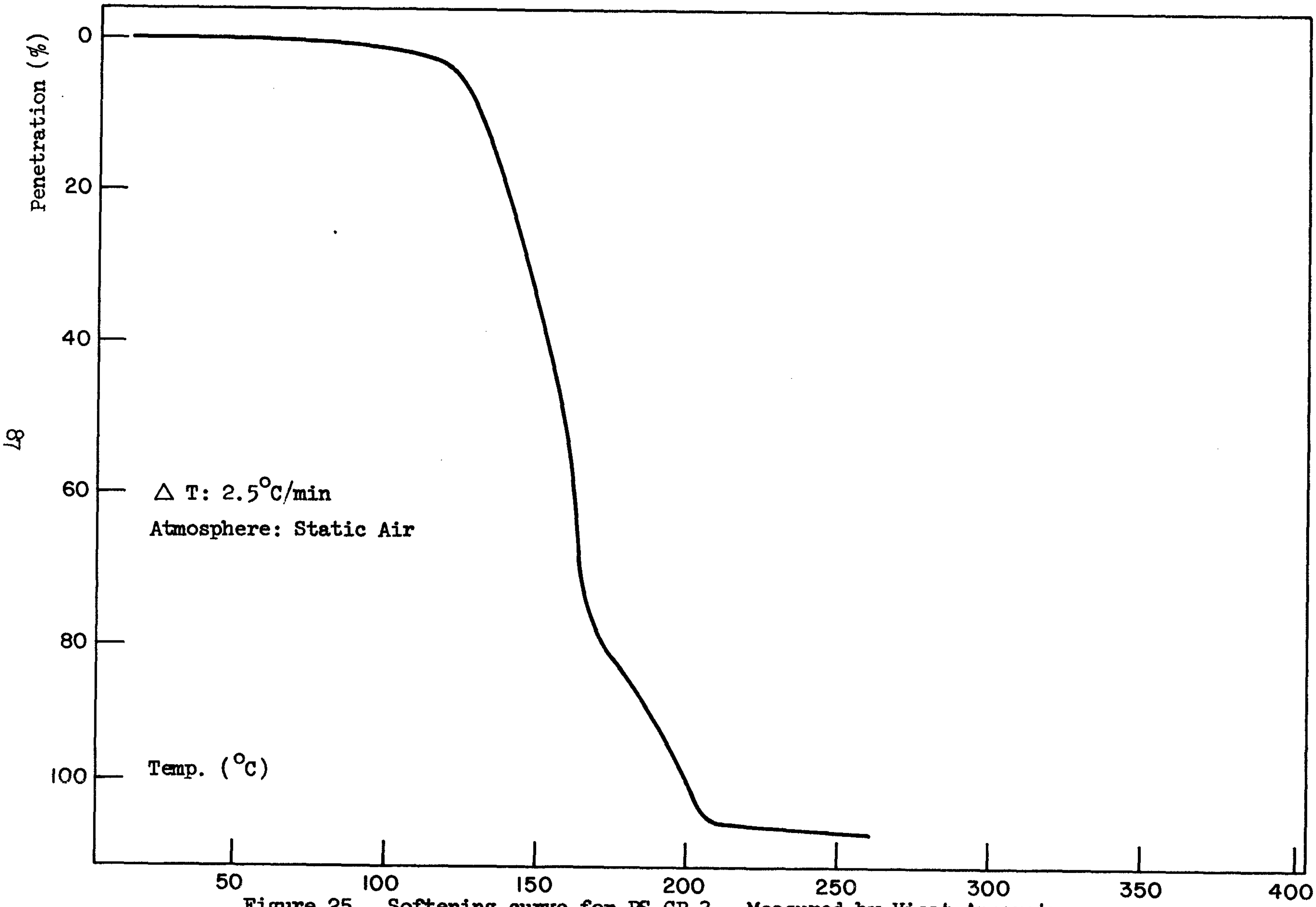


Figure 25. Softening curve for PS-CP-3. Measured by Vicat Apparatus.

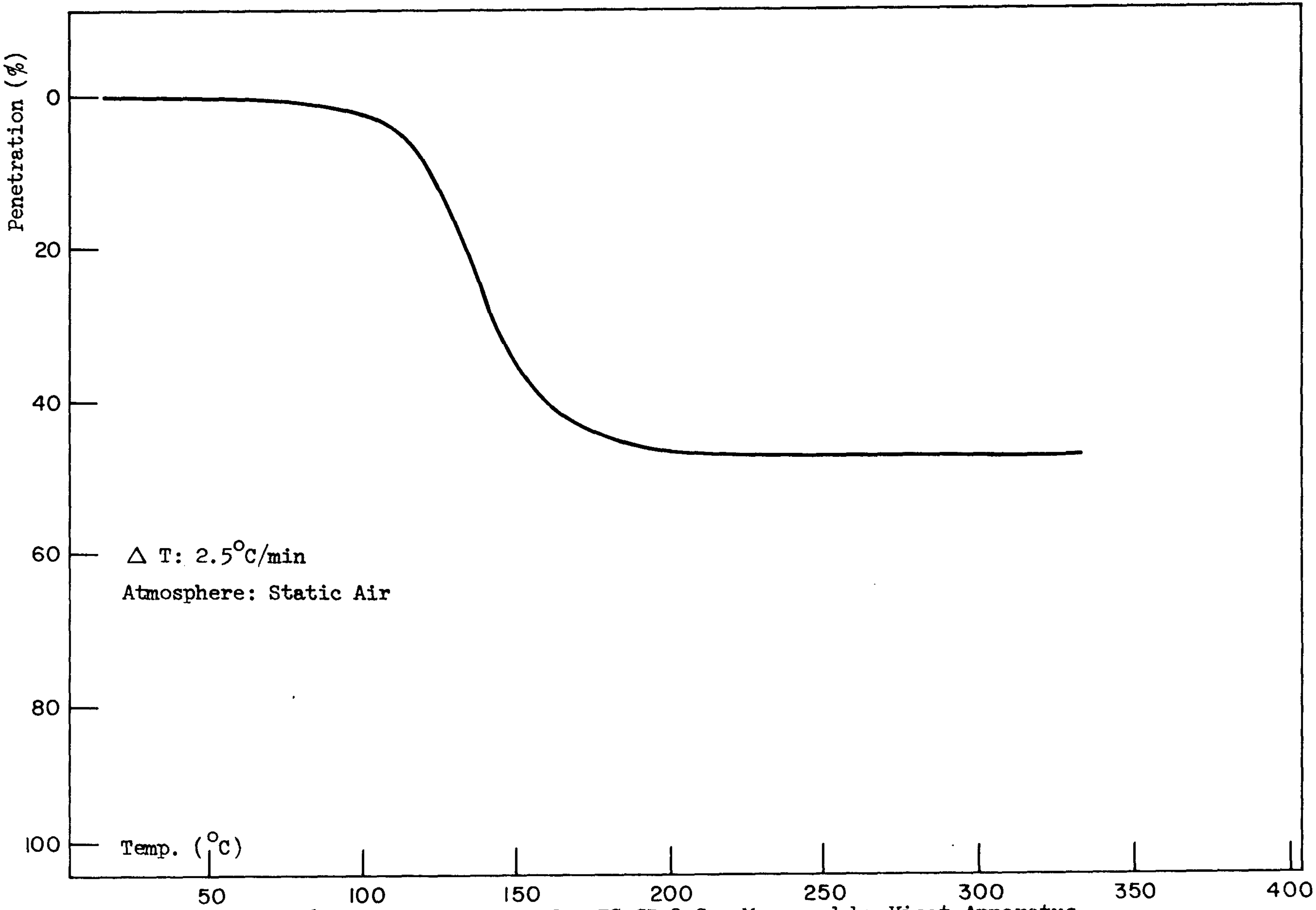


Figure 26. Softening curve for PS-CP-3-C. Measured by Vicat Apparatus.

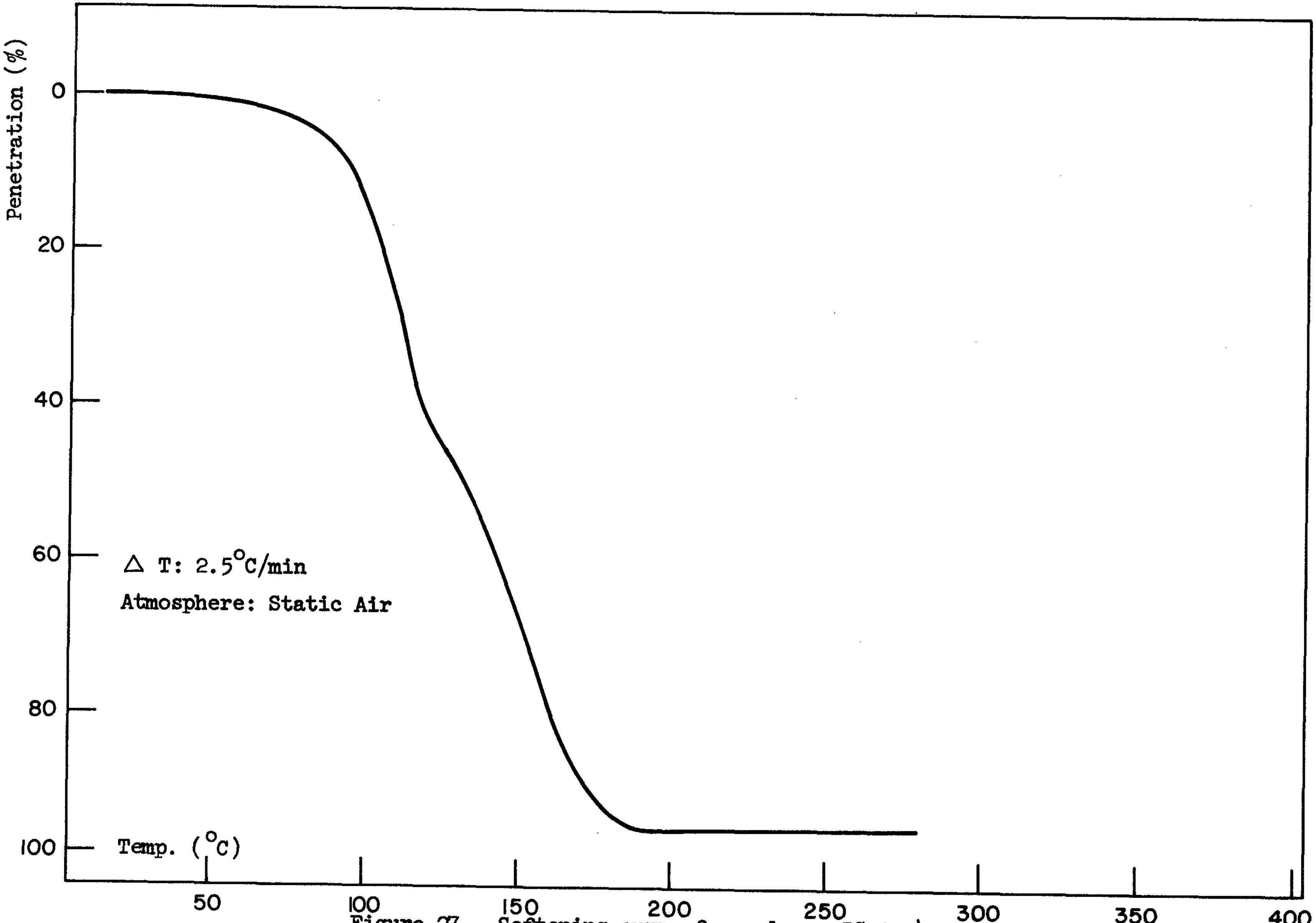


Figure 27. Softening curve for polymer PS-CP-4

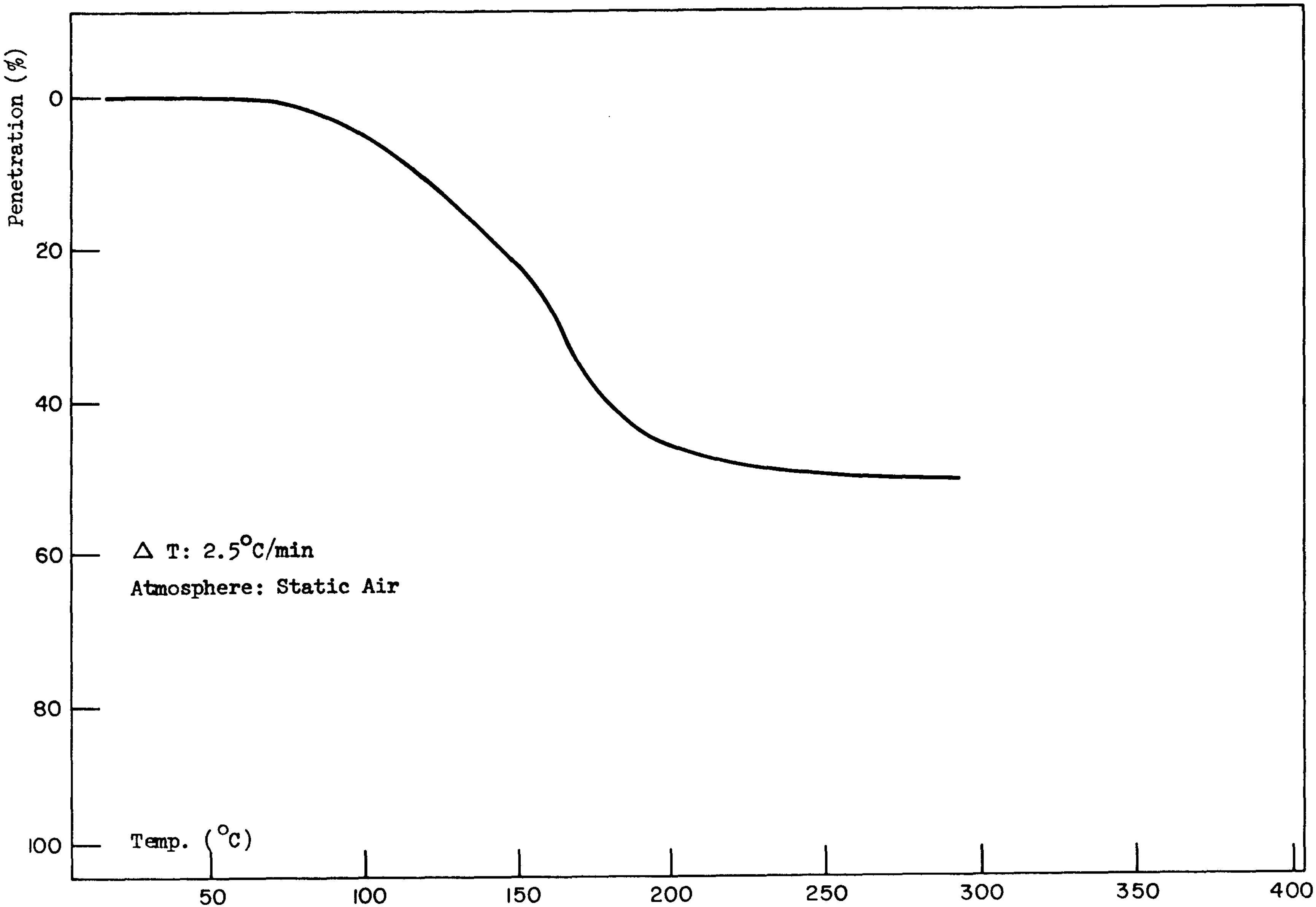


Figure 28. Softening curve for PS-CP-4-C. Measured by Vicat Apparatus.

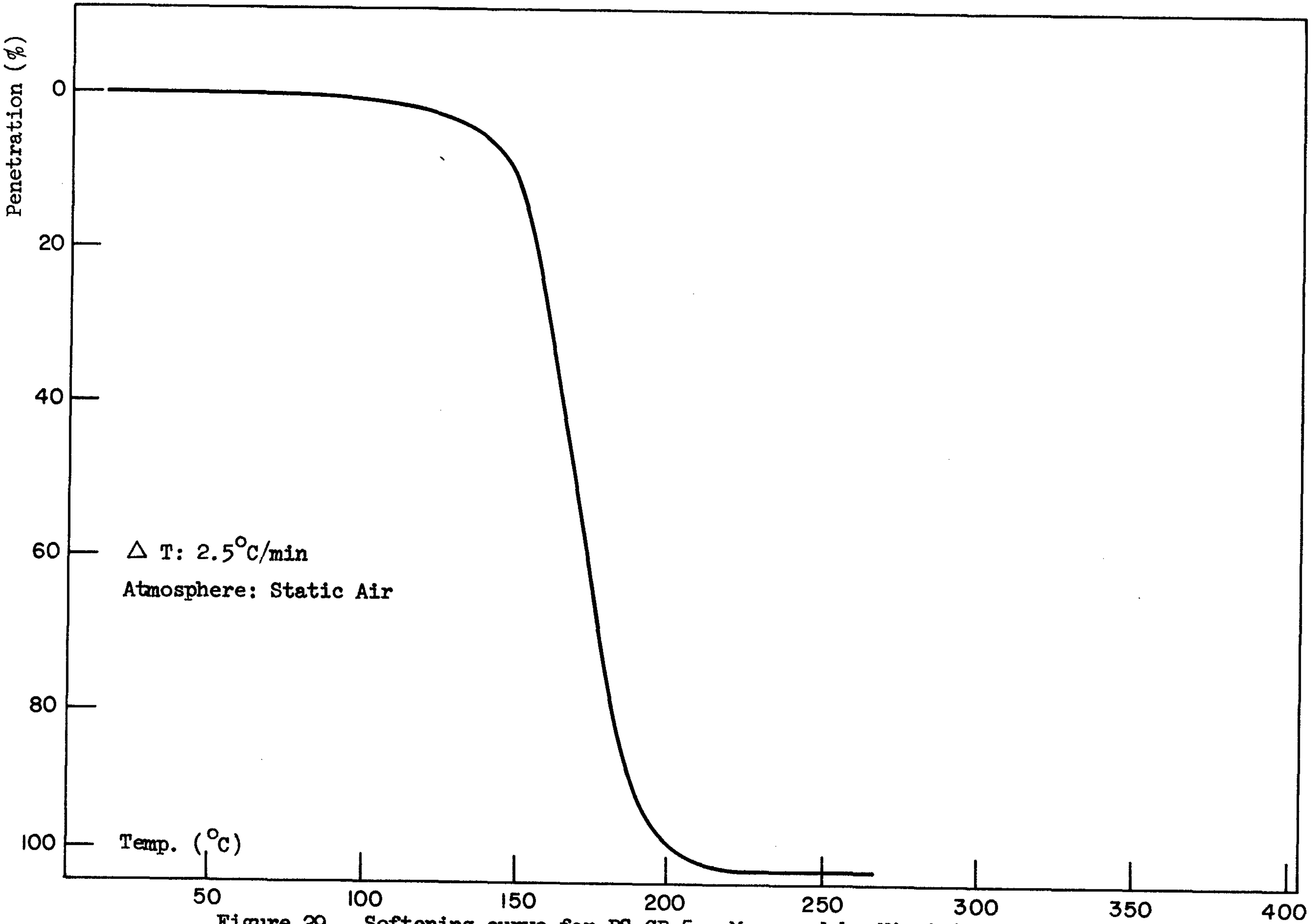


Figure 29. Softening curve for PS-CP-5. Measured by Vicat Apparatus.

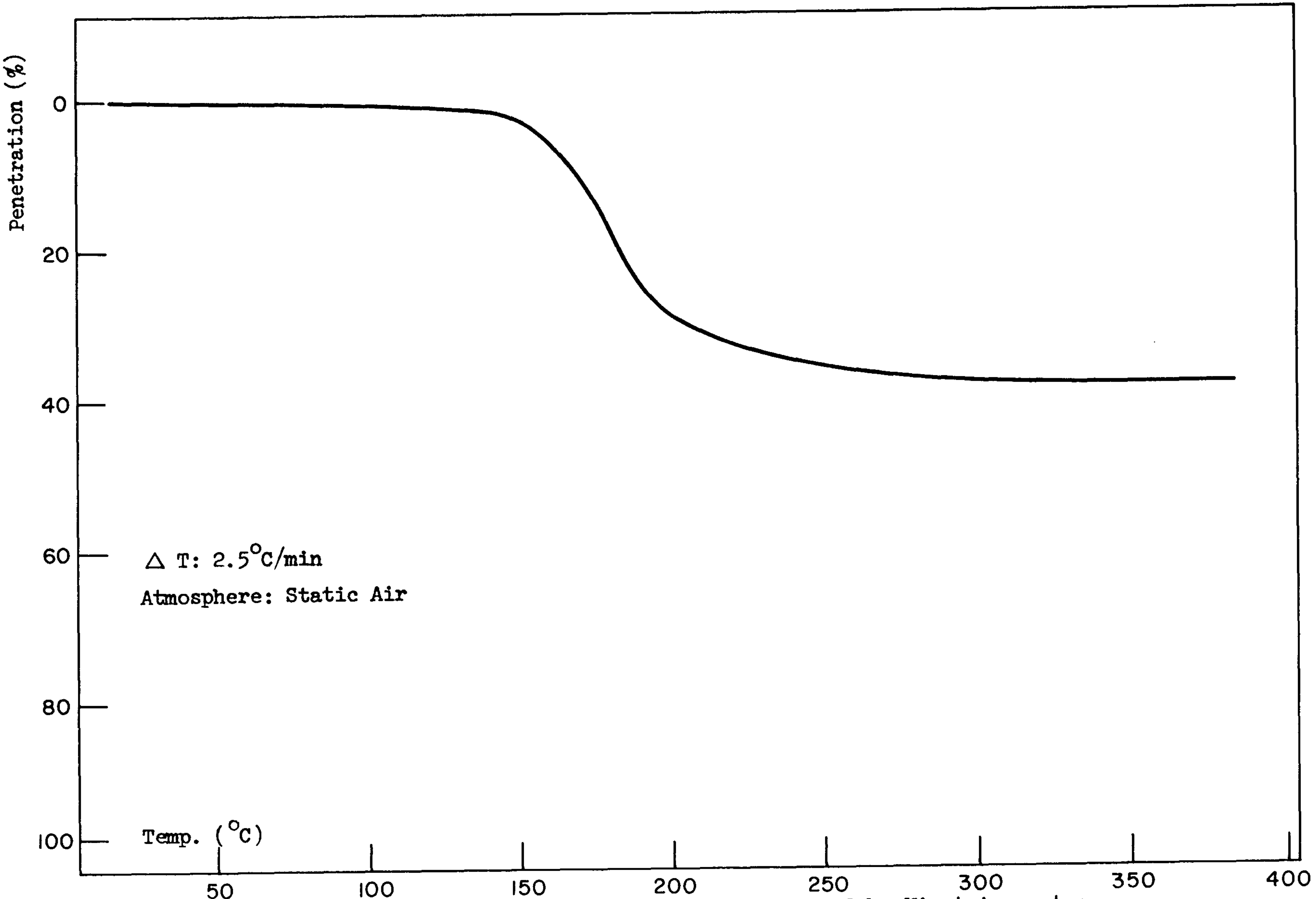


Figure 30. Softening curve for PS-CP-5-C. Measured by Vicat Apparatus.

TABLE XV

ISOTHERMAL WEIGHT LOSSES FOR POLYMERS CONTAINING [2.2]PARACYCLOPHANE UNITS

Polymer	Percent loss of weight 7 days at 250°C	7 days at 275°C	7 days at 300°C
PS-CP-3	4.1	6.5	16.9
PS-CP-3-C	4.2	6.8	18.5
PS-CP-1	8.0	13.3	15.0
PS-CP-1-C	11.1	15.5	21.0
PS-CP-6	3.4	4.8	17.4
PS-CP-6-C	10.4	10.9	14.6
PS-CP-7	10.4	11.8	13.8
PS-CP-7-C	14.2	15.2	21.5
PS-CP-2	5.0	10.3	22.0
PS-CP-2-C	17.7	19.2	24.0
PS-CP-4	5.8	7.0	11.3
PS-CP-4-C	5.3	7.9	19.6
PS-CP-5	3.3	5.1	12.7
PS-CP-5-C	1.2	2.5	10.6

iii) Laminates

Laminates were formed from three pieces of E-181 glass fiber fabric (67 wt %) and a polymer (33 wt %) by heating at 250°C under 15,000 psi on a Carver press. The polymers employed were DTW-5, DTW-1, DTW-3 and DTW-2 which contain 6, 9, 17 and 25 wt % respectively of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane. Preliminary results indicate that polymers with low (6-17 wt %) paracyclophane content produce laminates with potentially useful properties. On the other hand polymers with higher (29 wt %) paracyclophane content are too high melting and insufficiently soluble to adhere adequately to the fiber. All laminates have been submitted for evaluation.

b. Polymers from 4,4′-bis(p-phenoxybenzenesulfonyl) diphenyl ether

Polymers incorporating 5, 8 and 15 wt % of 3,9-bis[p-phenoxybenzoyl]-[2.2]paracyclophane have been prepared by Friedel-Crafts polymerization with 4,4′-bis(p-phenoxybenzenesulfonyl) diphenyl ether and isophthaloyl chloride.

i) Physical and thermal properties

Polymers from 4,4′-bis(p-phenoxybenzenesulfonyl) diphenyl ether exhibited higher melting points and lower solubilities than did the corresponding polymers from 1,3-bis(p-phenoxybenzenesulfonyl)benzene. For example, polymers JW-P1 and JW-P2 with only 8 and 5 wt % respectively of the [2.2] paracyclophane derivative crosslinked at temperatures below their melting points. In addition to being insoluble in dioxane polymer JW-P1 exhibited extremely low solubilities in dimethylacetamide (0.1 g/liter) and sulfolane (0.4 g/ liter).

The low solubilities of these polymers in concentrated H_2SO_4 has required heating to effect solution. Since the measured inherent viscosities were highly dependent upon the concentration and degree of heating applied, degradation and sulfonation probably occur under such conditions.

ii) Laminates

Laminates were formed from three pieces of E-181 glass fiber fabric and a polymer (33 wt %) by heating at 250°C under 15,000 psi on a Carver press. The polymers employed were JW-P2 and JW-P1, containing 5 and 8 wt % respectively of 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane. In both cases the polymer has proven too high melting and insufficiently soluble to adequately penetrate and adhere to the fabric. Consequently, preliminary results indicate that these laminates do not possess useful properties.

3. Experimental

a. Synthetic route to the [2.2] paracyclophane monomer

i) Dibromination of [2.2] paracyclophane

This procedure is that of Cram et al.[19] A solution of 46.2 g (0.288 mole) of bromine in 400 ml of carbon tetrachloride was prepared and 30 ml of this solution was stirred with 0.4 g of iron filings and 300 ml of dichloromethane for 1 hr. Dichloromethane (500 ml) was added, the solution was brought to reflux, and 30 g (0.144 mole) of [2.2] paracyclophane was added. The remainder of the bromine solution was added over a period of 3 hr. After completion of the bromine addition, the mixture was refluxed for 0.5 hr. The reaction mixture was washed several times with 10% sodium bisulfite solution, then with saturated sodium chloride solution and dried. After removal of solvent the crude product was dissolved in 500 ml of hot chloroform, 300 ml of ether was added and it was allowed to crystallize. Yield 16.5 g (31%); mp 245-249°C.

ii) Dicarboxy[2.2]paracyclophane

A mixture of 350 ml of ether and 200 ml of 2 N. n-butyllithium in hexane was stirred under nitrogen for 15 min and 12.3 g (32.9 m mole) of pseudo-p-dibromo[2.2]paracyclophane was added. After the solution had stirred at room temperature for 20 hr, it was dumped into dry ice (solid carbon dioxide). Water (500 ml) was added and the aqueous layer separated was collected. Ether layer was washed with additional 50 ml of water. The combined aqueous layer was neutralized with hydrochloric acid. The precipitated acid was filtered and washed with large volume of water to remove valeric acid (formed by reaction of excess n-butyllithium with CO_2). The crude acid 8.5 g (88% yield) was dried at 100°C. The infrared spectrum showed a carbonyl absorption at 1675 cm^{-1} (in Nujol) or at 1650 cm^{-1} (in KBr). Crystallization from dimethylformamide-water (4:1 ratio) afforded a white powder, mp > 500°C.

Anal. Calc. for $C_{18}H_{16}O_4$: C, 72.96%; H, 5.44%.
Found: C, 74.09%; H, 5.65%.

iii) [2.2] paracyclophane bis acid chloride

Dicarboxy[2.2]paracyclophane (6.0 g) was refluxed with 120 ml of thionyl chloride for 3 hr. Removal of excess thionyl chloride under aspirator pressure gave 6.1 g of [2.2] paracyclophane bis acid chloride.

This was washed with petroleum ether to give yellow colored powder 5.8 g (78%), mp 213-218°C. The infrared spectrum showed a carbonyl absorption at 1665 cm^{-1} (Nujol).

Anal. Calc. for $C_{18}H_{14}O_2Cl_2$: C, 64.88%; H, 4.21%; Cl, 21.33%.
Found: C, 65.01%; H, 4.57%; Cl, 21.67%.

iv) 3,9-Bis[p-phenoxybenzoyl]-[2.2]paracyclophane

To a solution of 12.0 g (32.8 mM) of [2.2]paracyclophane bis acid chloride in 600 ml of diphenyl ether was added 60 g of $AlCl_3$. After the suspension had been stirred at room temperature for 24 hr, the mixture was washed with water and then dried over sodium sulfate. The distillation of 400 ml of diphenyl ether under reduced pressure and the addition of 500 ml of petroleum ether to the residual solution precipitated 15.5 g (79%) of a white solid, mp 244-246°C. The product showed a carbonyl absorption at 1645 cm^{-1} (KBr).

Anal. Calc. for $C_{42}H_{32}O_4$: C, 84.00%; H, 5.33%.
Found: C, 83.76%; H, 5.37%.

b. Preparation of disulfone monomers

i) 1,3-Bis(p-phenoxybenzenesulfonyl)benzene

To a solution of 137.0 g (0.498 mole) of <u>m</u>-benzenesulfonyl chloride in 170 g of diphenyl ether was added 1.0 g of ferric chloride. The reaction was stirred at 170°C for 24 hr. After the reaction had cooled to room temperature, ethyl ether was added and the mixture was washed with water. The ether layer was separated, filtered, and dried over Na_2SO_4. Evaporation of the ether and distillation of diphenyl ether under reduced pressure afforded a crude solid. The crude product then was distilled under high vacuum (0.1 mm) with an open flame. The distillate solidified upon cooling and was dissolved in 40 ml of chloroform and 800 ml of ethyl ether. A small amount of insoluble black residue was filtered from the solution. The addition of 800 ml of petroleum ether precipitated 160 g (63%) of a white powder, mp 70-75°C.

ii) 4,4′-Bis(p-phenoxybenzenesulfonyl) diphenyl ether

To a solution of phenoxybenzene-4,4′-disulfonyl chloride (60 g, 0.163 mole) in 400 ml of dry diphenyl ether (429.2 g, 2.52 mole) was added 3.0 g of ferric chloride. The mixture was stirred under nitrogen and heated to 160-165°C for 48 hr. The cooled suspension was filtered free of ferric chloride and petroleum ether (500 ml) was added to precipitate a brown solid. The resultant precipitate was filtered and then extracted in a Soxhlet for 10 hr with 800 ml of methanol. The material not extracted by methanol was dissolved in chloroform and then passed through a short (25 cm) alumina column. Concentration of the chloroform and the addition of petroleum ether precipitated 53.4 g (52%) of a white solid, mp 196-200°C [lit[18] 185-187°C; ir spectra in KBr identical].

c. Polymers from 1,3-bis(p-phenoxybenzenesulfonyl)benzene containing varying amounts of the [2.2] paracyclophane unit in the backbone

i) Preparation of 6 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (3.394 g, 6.25 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.250 g, 0.42 mM), and isophthaloyl chloride (1.356 g, 6.68 mM) in 125 ml of dry dichloroethane was added 4.5 g of $AlCl_3$. The suspension was stirred under nitrogen atmosphere at room temperature for 24 hr. The precipitate was filtered off and washed four times with methanol in a blender. Yield 3.0 g (67%); mp 185-210°C. The sample was labelled as DTW-5.

Anal. Calc.: C, 68.38%; H, 3.73%; S, 10.05%.

Found: Analysis not yet available.

ii) Preparation of 9 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

1,3-Bis(p-phenoxybenzenesulfonyl)benzene (2.439 g, 4.5 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.30 g, 0.5 mM) and isophthaloyl chloride (1.015 g, 5.0 mM) were dissolved in 75 ml of dry dichloroethane. $AlCl_3$ (3.33 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed four times with methanol in a blender. Yield 3.08 g mp 190-210°C. η_{inh} = 0.659 in H_2SO_4 at 30°C. Sample submitted to the Materials Laboratory as PS-CP-3.

Anal. Calc.: C, 69.50%; H, 3.81%; S, 8.44%.

Found: C, 67.79%; H, 4.14%; S, 7.52%; Res., 1.74%.

Three hundred mg of PS-CP-3 was heated at 360°C in nitrogen atmosphere for 24 hr. The dark black colored product was refluxed in 100 ml of dimethylacetamide, filtered, washed with water and dried. Quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. This crosslinked polymer was labelled as PS-CP-3-C and submitted to Air Force Materials Laboratory for TGA and softening point determination.

Anal. (for PS-CP-3-C). Calc.: C, 69.21%; H, 3.97%; S, 8.47%.

Found: C, 67.79%; H, 4.14%; S, 7.52%; Res., 1.74%.

iii) Large scale preparation of 9 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer) for curing and laminate formation

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (45.47 g, 83.80 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (5.60 g, 9.32 mM), and isophthaloyl chloride (18.926 g, 93.22 mM) in 1400 ml of dry dichloroethane was added 63 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature. The mixture was filtered and the precipitate was washed four times with methanol in a blender. Yield 52 g (83%); mp 190-215°C. $\eta_{inh} = 0.42$ in H_2SO_4 at 30°C (required heating to effect solution). The sample was labelled as DTW-1.

Anal. Calc. for DTW-1: C, 69.21%; H, 3.97%; S, 8.47%.

Found: C, 69.03%; H, 3.64%; S, 8.53%.

A 0.488 g sample of DTW-1 was cured at 250°C for 48 hr and then was boiled with 20 ml of dimethylacetamide for 1 hr. After the solvent was filtered the polymer was washed with water and dried under vacuum at 160°C. Yield 0.415 g (85%). Other samples were cured at 350°C for 24 and 48 hr and at 300°C for 36 and 48 hr.

A laminate was formed from DTW-1 (300 mg) sandwiched between three pieces of glass fiber fabric (600 mg). Eight drops of dimethylacetamide were added to the fabric on each side. The sample was folded within aluminum foil and pressed under 15,000 psi at 250°C for 0.5 hr.

iv) Preparation of 16 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

1,3-Bis(p-phenoxybenzenesulfonyl)benzene (2.22 g, 4.1 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.54 g, 0.9 mM) and isophthaloyl chloride (1.015 g, 5.0 mM) were dissolved in 75 ml of dry dichloroethane. $AlCl_3$ (3.33 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed four times with methanol in a blender. Yield 3.23 g (88%) mp 185-210°C. η_{inh} = 0.38 in H_2SO_4 at 30°C. Sample submitted to the Materials Laboratory as PS-CP-1.

Anal. Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 69.98%; H, 3.85%; S, 7.55%.

A 300 mg sample of PS-CP-1 was heated at 360°C in nitrogen atmosphere for 24 hr. The resultant dark colored product was boiled with 100 ml of dimethylacetamide and filtered, washed with water and dried. Almost quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. This crosslinked polymer was labelled as PS-CP-1-C and submitted to the Air Force Materials Laboratory for TGA and softening point determination.

Anal. for PS-CP-1-C Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 70.90%; H, 4.04%; S, 7.17%; Res., 0.84%.

Crosslinking reaction was also effected in 85% yield by heating PS-CP-1 at 360°C for four hr.

v) Preparation of 17 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (2.907 g, 5.36 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.750 g, 1.25 mM), and isophthaloyl chloride (1.343 g, 6.61 mM) in 125 ml of dry dichloroethane was added 4.5 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature. The mixture was filtered and the precipitate was washed four times with methanol in a blender. Yield 3.0 g (66%); mp 180-210°C. The sample was labelled as DTW-3.

Anal. Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: Analysis not yet available.

vi) Preparation of 20 wt % of 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (2.08 g, 3.83 mM), 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane (0.69 g, 1.15 mM), and isophthaloyl chloride (1.015 g, 5.0 mM) in 75 ml of dry dichloroethane was added 3.3 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature. The precipitate was filtered from the mixture and washed four times with methanol in a blender. Yield 3.2 g (94%); mp 210-225°C η_{inh} = 0.34 H_2SO_4 at 30°C. The sample was submitted to the Materials Laboratory as PS-CP-6.

Anal. Calc.: C, 71.29%; H, 3.98%; S, 7.18%.

Found: C, 69.09%; H, 4.12%; S, 6.73%; Res., 2.67%.

A sample (300 mg) of PS-CP-6 was heated at 350°C in a nitrogen atmosphere for 24 hr. The resultant black product was boiled with 100 ml of dimethylacetamide and then filtered, washed with water and dried. An almost quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. This crosslinked product was labelled as PS-CP-6-C and submitted to the Air Force Materials Laboratory for TGA and softening point determinations. (See Figures 31 and 32).

Anal. for PS-CP-6-C Calc.: C, 71.29%; H, 3.98%; S, 7.18%.

Found: C, 70.60%; H, 4.30%; S, 5.92%; Res., 2.29%.

vii) Preparation of 22 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (2.663 g, 4.91 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (1.00 g, 1.66 mM), and isophthaloyl chloride (1.337 g, 6.59 mM) in 125 ml of dry dichloroethane was added 4.5 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature. The mixture was filtered and the precipitate was washed four times with methanol in a blender. Yield 3.3 g (73%); mp > 360°C (crosslinked prior to melting). The sample was labelled as DTW-5.

Anal. Calc.: C, 71.29%; H, 3.98%; S, 7.18%.

Found: Analysis not yet available.

viii) Preparation of 26 wt % of 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane (using isophthaloyl chloride as acid monomer)

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (1.895 g, 3.5 mM), 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane (0.90 g, 1.5 mM), and isophthaloyl chloride (1.015 g, 5.0 mM) in 75 ml of dry dichloroethane was added 3.3 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature. The precipitate was filtered from the mixture and washed four times with methanol in a blender. Yield 3.1 g (90%); mp 210-225°C; η_{inh} = 0.411 in H_2SO_4 at 30°C. The sample was submitted

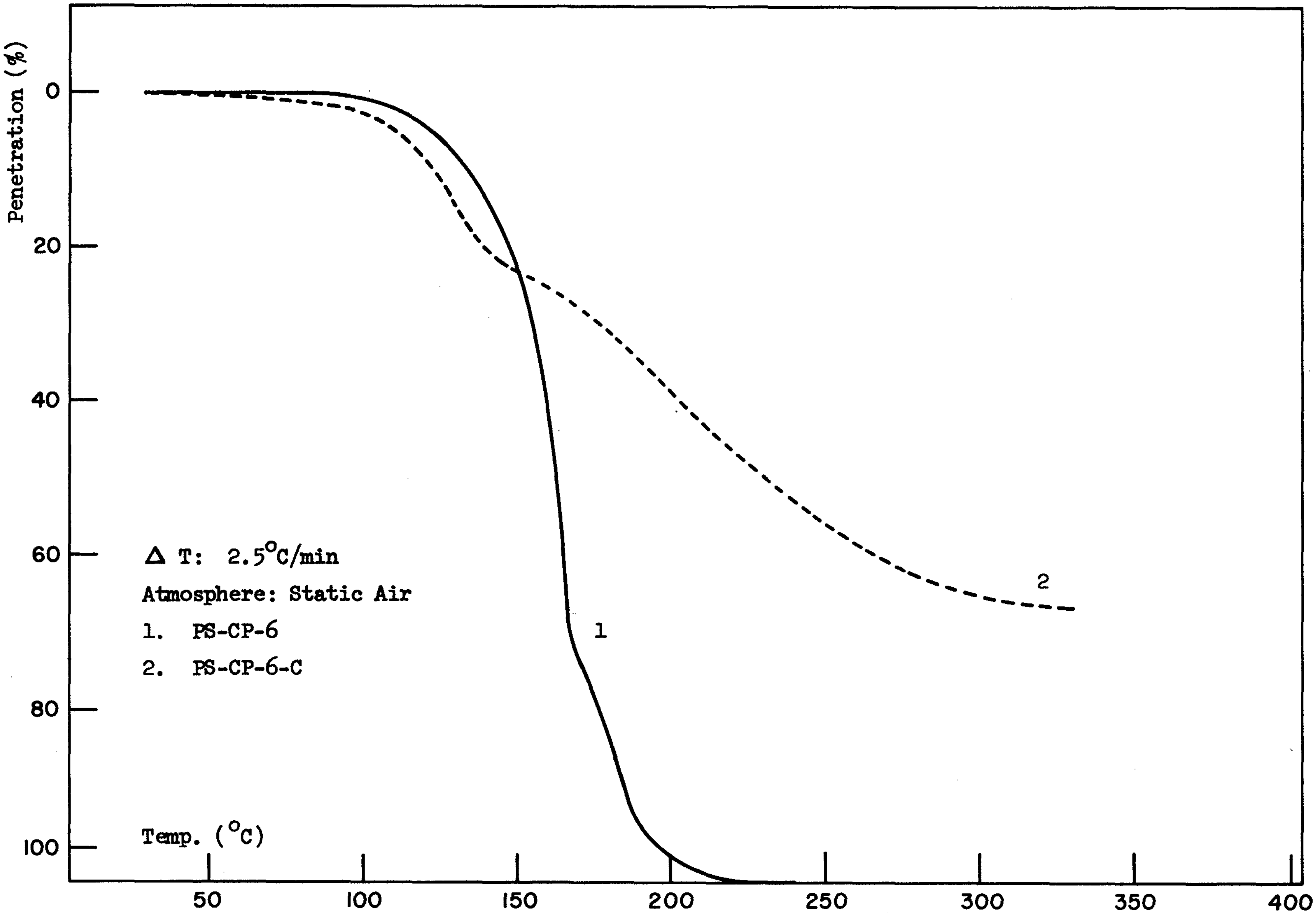


Figure 31. Softening under load of polymers PS-CP-6 and PS-CP-6-C

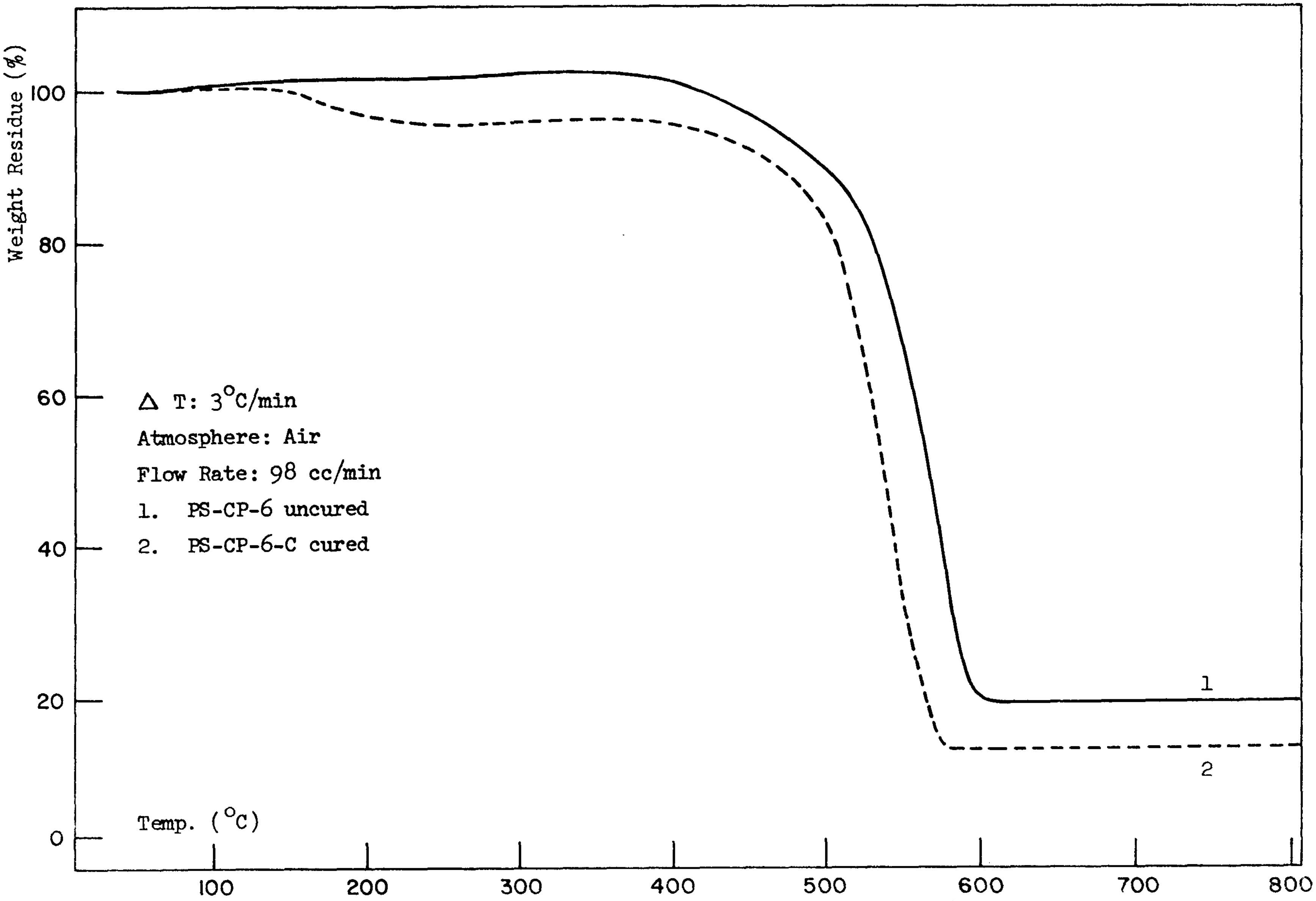


Figure 32. TGA curve for polymers PS-CP-6 and PS-CP-6-C

to the Materials Laboratory as PS-CP-7.

Anal. Calc.: C, 71.07%; H, 4.24%; S, 6.78%.

Found: C, 69.28%; H, 3.83%; S, 5.66%; Res., 4.48%.

A 300 mg sample of PS-CP-7 was heated under nitrogen at 350°C for 24 hr. The resultant black solid was boiled with 100 ml of dimethylacetamide and then filtered, washed with water and dried. An almost quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. The crosslinked product was labelled as PS-CP-7C and submitted to the Air Force Laboratory for TGA and softening point determinations. (See Figs. 33, 34).

Anal. for PS-CP-6-C Calc.: C, 71.07%; H, 4.24%; S, 6.78%.

Found: C, 69.67%; H, 4.26%; S, 5.42%; Res., 5.10%.

ix) Preparation of 29 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

To a solution of 1,3-bis(p-phenoxybenzenesulfonyl)benzene (33.21 g, 61.2 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (18.20 g, 30.3 mM), and isophthaloyl chloride (18.59 g, 91.6 mM) in 1400 ml of dry dichloroethane was added 63 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature and for 2 hr at 40°C. The mixture was filtered and the precipitate was washed five times with methanol in a blender. Yield 55 g (87%); mp > 360°C (crosslinked prior to melting). η_{inh} = 0.79 in HMPA at 30°C (required heating to effect solution). The sample was labelled as DTW-2.

Anal. Calc.: C, 72.73%; H, 4.17%; S, 6.17%.

Found: C, 71.34%; H, 4.13%; S, 5.65%.

x) Preparation of 15 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride and terephthaloyl chloride in the ratio of 2:1 as the acid chloride monomers)

1,3-bis(p-phenoxybenzenesulfonyl)benzene (2.22 g, 4.1 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.54 g, 0.9 mM), isophthaloyl chloride (0.645 g, 3.18 mM) and terephthaloyl chloride (0.372 g, 1.83 mM) were dissolved in 75 ml of dry dichloroethane. $AlCl_3$ (3.33 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed four times with methanol in a blender. Yield 3.15 g (92%); mp 195-210°C. η_{inh} = 0.36 in H_2SO_4 at 30°C. Sample submitted to the Materials Laboratory as PS-CP-4.

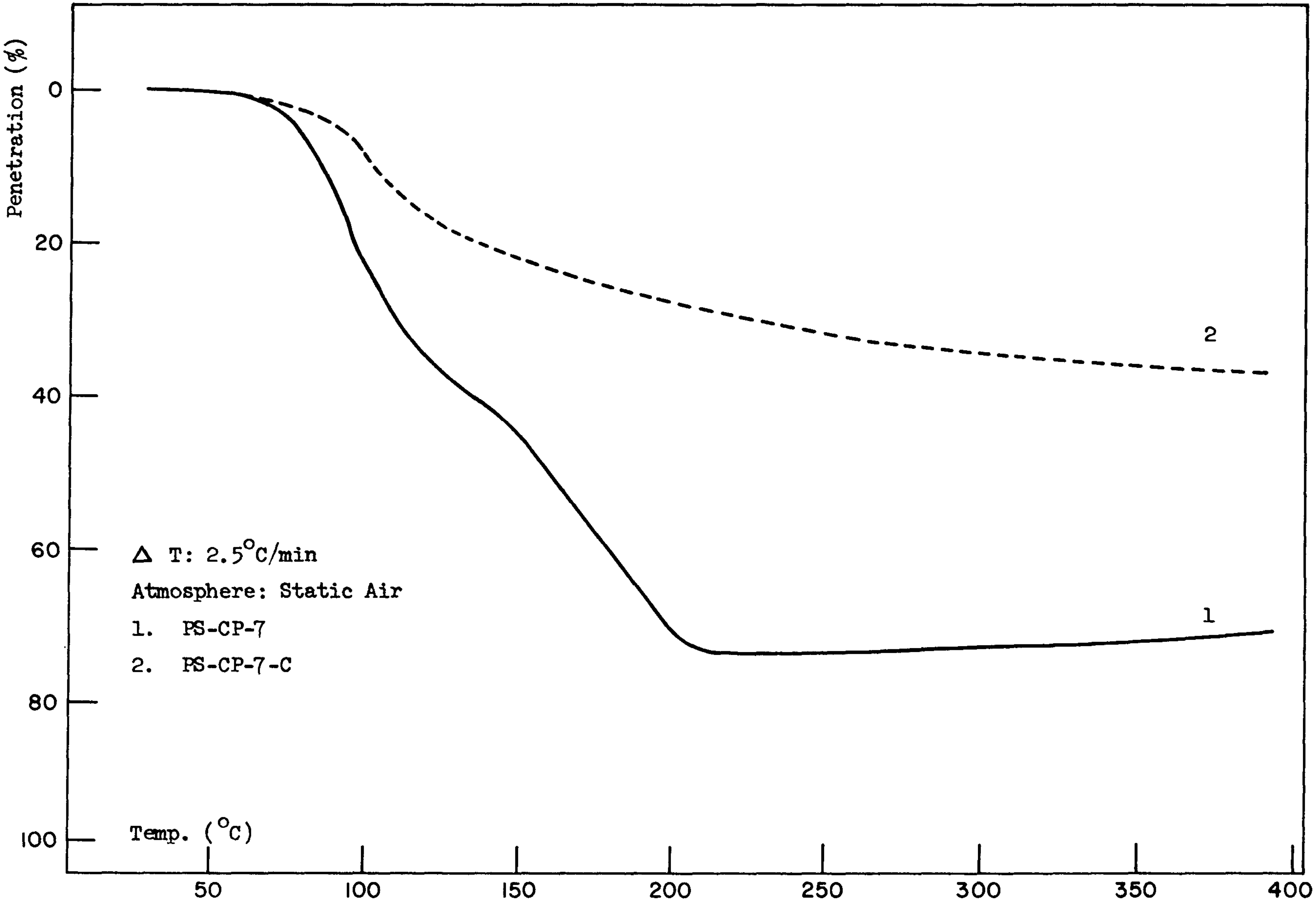


Figure 33. Softening under load of polymers PS-CP-7 and PS-CP-7-C

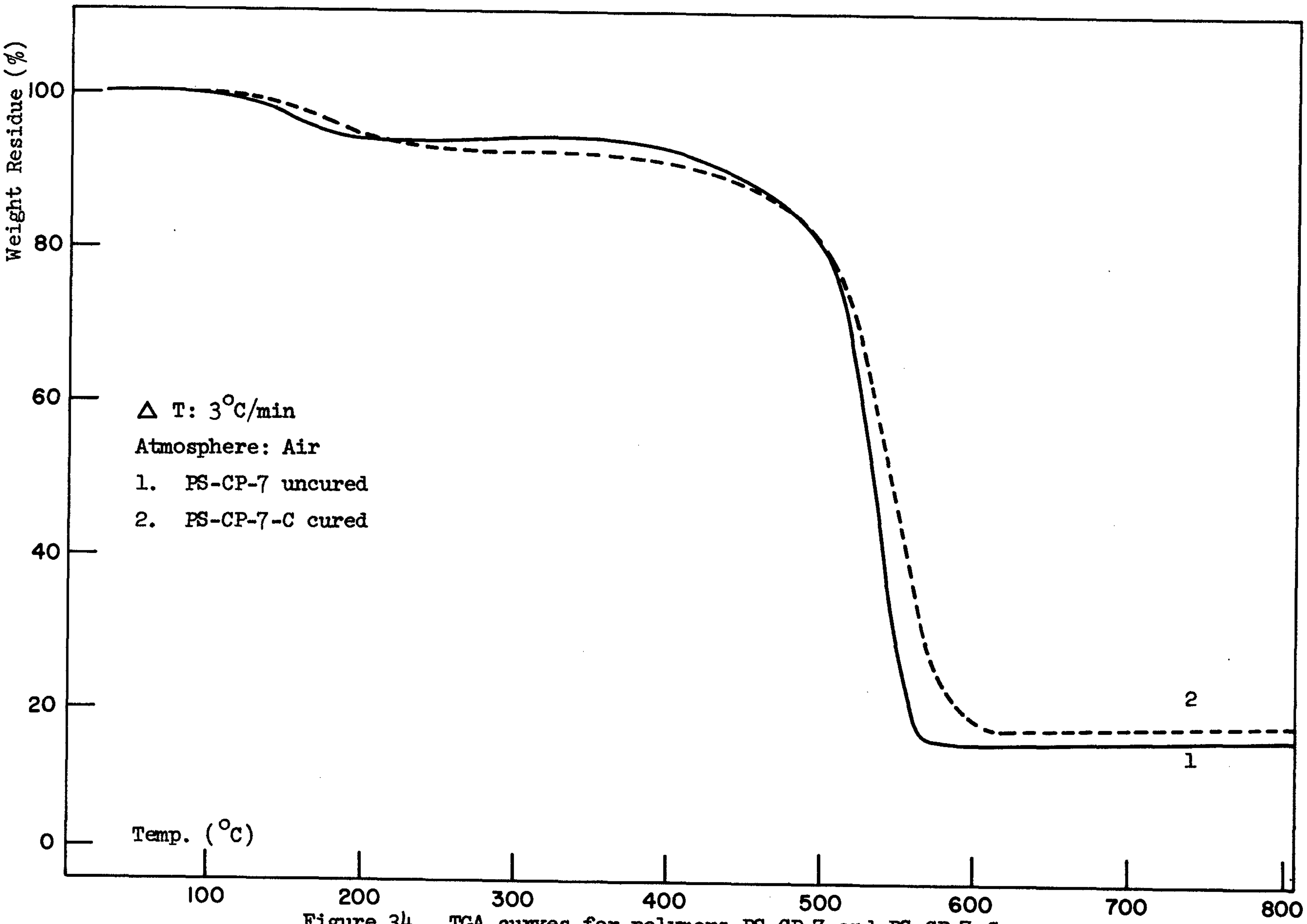


Figure 34. TGA curves for polymers PS-CP-7 and PS-CP-7-C

Anal. Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 69.66%; H, 4.22%; S, 6.38%; Res., 2.10%.

A 300 mg sample of PS-CP-4 was heated at 360°C in nitrogen atmosphere for 24 hr. The dark product was boiled with 100 ml of dimethylacetamide, filtered, washed with water and dried. Almost quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. This crosslinked polymer was labelled as PS-CP-4-C and submitted to Air Force Materials Laboratory for TGA and softening point determination.

Anal. (for PS-CP-4-C) Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 68.73%; H, 4.18%; S, 6.16%; Res., 4.25%.

xi) Preparation of 15 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using terephthaloyl chloride as the acid chloride monomer

1,3-Bis(p-phenoxybenzenesulfonyl)benzene (2.22 g, 4.1 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.54 g, 0.9 mM) and terephthaloyl chloride (1.015 g, 5.0 mM) were dissolved in 75 ml of dry dichloroethane. $AlCl_3$ (3.33 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 3.20 g (94%) mp 225-240°C. $\eta_{inh} = 0.38$ in H_2SO_4 at 30°C. Sample submitted to the Materials Laboratory as PS-CP-5.

Anal. Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 69.70%; H, 4.01%; S, 6.90%; Res., 2.32%.

A 300 mg sample of PS-CP-5 was heated at 360°C in nitrogen atmosphere for 24 hr. The dark black colored product was boiled with 100 ml dimethylacetamide, filtered, washed with water and dried. A quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. This crosslinked polymer was labelled as PS-CP-5-C and submitted to Air Force Materials Laboratory for TGA and softening point determination.

Anal. (for PS-CP-5-C). Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 68.73%; H, 4.18%; S, 6.16%; Res., 4.25%.

d. Polymers from 4,4′-bis[p-phenoxybenzenesulfonyl]diphenyl ether containing varying amounts of the [2.2] paracyclophane unit

i) Preparation of 5 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

To a solution of 4,4′-bis[p-phenoxybenzenesulfonyl] diphenyl ether (7.81 g, 12.3 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.50 g, 0.8 mM), and isophthaloyl chloride (2.66 g, 13.1 mM) in 400 ml of dry dichloroethane was added 13.3 g of $AlCl_3$. The suspension was stirred under nitrogen for 24 hr at room temperature. The mixture was filtered and the precipitate was washed three times with methanol and twice with chloroform in a blender. Yield 8.2 g (82%); mp > 360°C (crosslinked prior to melting). The sample was labelled as JW-P2.

Anal. Calc.: C, 69.90%; H, 3.75%; S, 7.88%.

Found: C, 69.15%; H, 3.88%; S, 7.49%.

ii) Preparation of 8 wt % of 3,9-bis(p-phenoxybenzoyl)[2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

To a solution of 4,4′-bis[p-phenoxybenzenesulfonyl] diphenyl ether (52.7 g, 83.0 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (5.6 g, 9.3 mM), and isophthaloyl chloride (18.7 g, 92.3 mM) in 1400 ml of dry 1,2-dichloroethane was added $AlCl_3$ (98.9 g, 744 mM). The suspension was stirred under nitrogen at room temperature for 48 hr. The mixture was filtered and the precipitate was washed twice with methanol in a blender. Another washing was performed with chloroform. [Upon pouring this chloroform wash into methanol a precipitate was obtained, mp 223-260°C.] The bulk of the polymer was washed again in methanol. Yield 59.9 g (85%); mp > 360°C (crosslinked prior to melting). The sample was labelled as JW-P1.

Anal. Calc.: C, 70.42%; H, 3.79%; S, 7.58%.

Found: C, 69.85%; H, 3.95%; S, 7.10%.

iii) Preparation of 15 wt % of 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (using isophthaloyl chloride as acid chloride monomer)

4,4′-Bis(p-phenoxybenzenesulfonyl) diphenyl ether (2.536 g, 4.0 mM), 3,9-bis[p-phenoxybenzoyl][2.2]paracyclophane (0.6 g, 1.0 mM) and isophthaloyl chloride (1.015 g, 5.0 mM) were dissolved in 75 ml of dry dichloroethane. $AlCl_3$ (3.5 g) was added and the mixture stirred under nitrogen atmosphere at room temperature during 24 hr. The precipitate was filtered off and washed four times with methanol in a blender. Yield 3.52 g (93%); mp 225-235°C. $\eta_{inh} = 0.575$ in H_2SO_4 at 30°C. Sample submitted to Materials Laboratory as PS-CP-2. (See Figures 35 and 36).

Anal. Calc.: C, 71.12%; H, 4.04%; S, 6.86%.

Found: C, 68.66%; H, 3.92%; S, 6.24%; Res., 2.10%.

A 300 mg sample of PS-CP-2 was heated at 360°C in nitrogen atmosphere for 24 hr. The resultant dark colored product was refluxed in 100 ml of dimethylacetamide, filtered, washed with water and dried. Quantitative yield of crosslinked polymer (insoluble in dimethylacetamide) was obtained. This crosslinked polymer was labelled as PS-CP-2-C and submitted to Air Force Materials Laboratory for TGA and softening point determination.

Anal. (for PS-CP-2-C). Calc.: C, 71.12%; H, 4.04%; S, 6.86%.

Found: C, 71.12%; H, 3.92%; S, 6.24%; Res., 2.10%.

4. Future Plans

This work on paracyclophane crosslinking will be continued. It is hoped to prepare new paracyclophanes without benzyl hydrogens which will have greater oxidative stability.

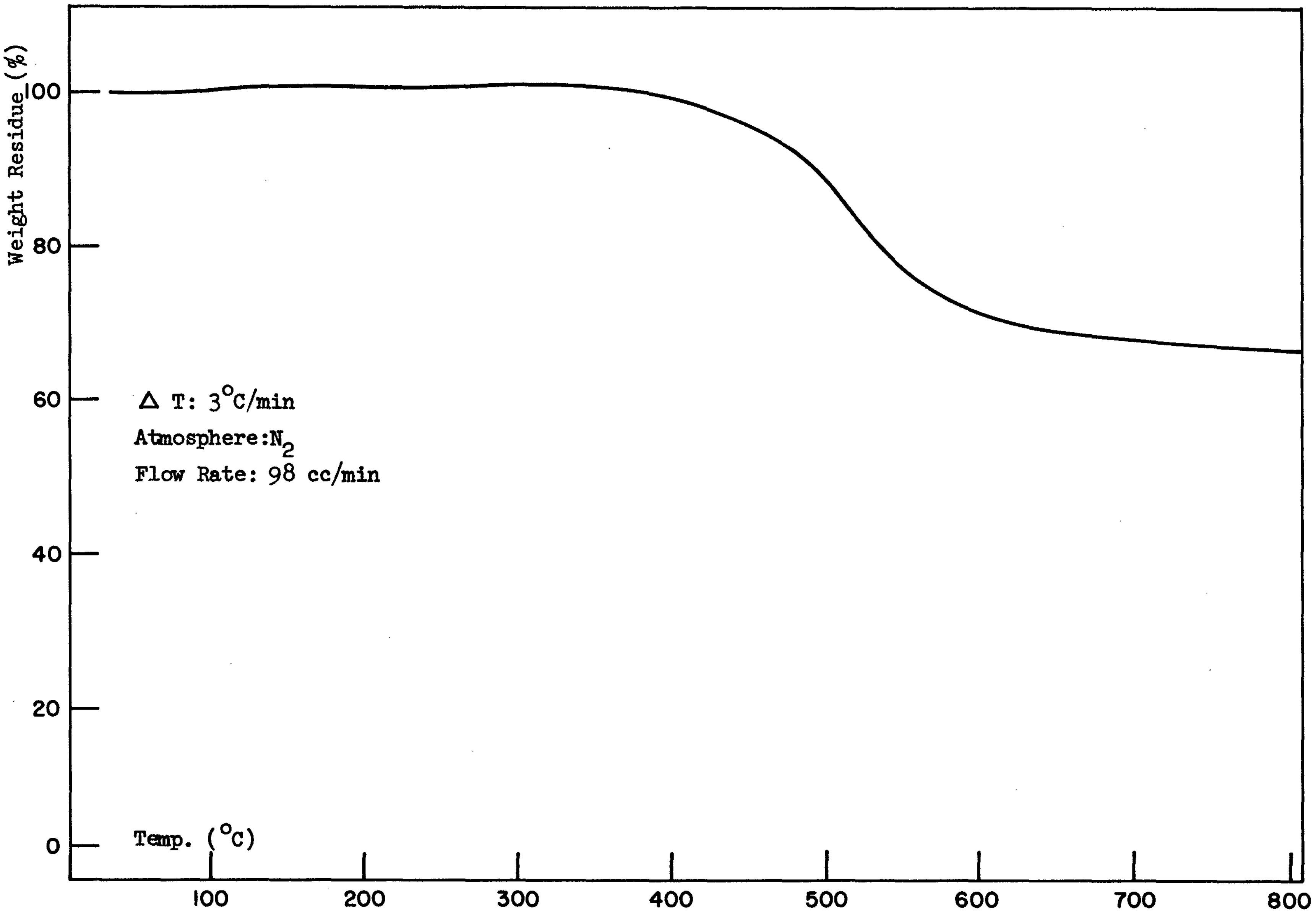


Figure 35. TGA curve for polymer PS-CP-2

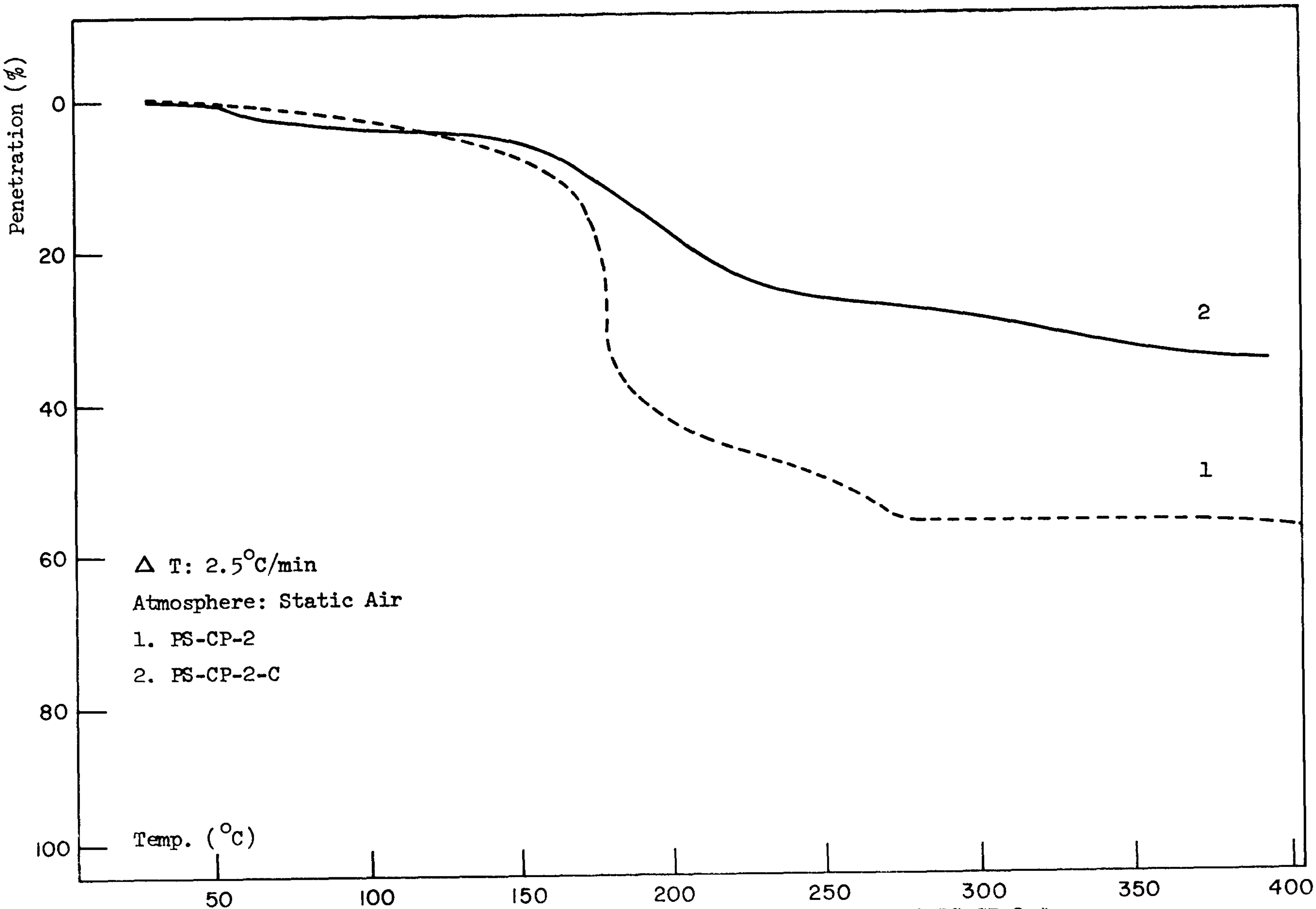
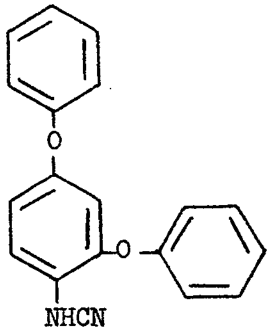


Figure 36. Softening under load of polymers PS-CP-2 and PS-CP-2-C

VII. SYNTHESIS OF MONOMERS CONTAINING AROMATIC CYANAMIDE UNITS

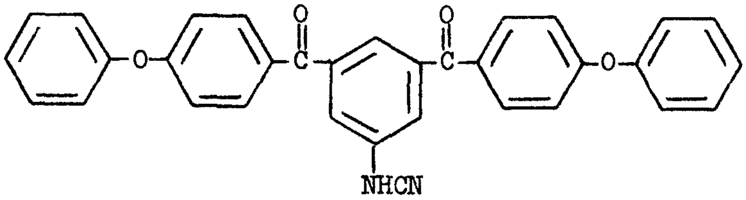
1. Results and Discussion

Polymers containing pendant cyanamide groups which on trimerization either by heat or catalyst should afford melamine type crosslinks which possess fair thermal stability. Hence the synthesis of monomers containing cyanamide groups to be incorporated into the aromatic polyethers, polyketones, polysulfones was undertaken. For this purpose 2,4-diphenoxy phenyl cyanamide (XIII)



XIII

and

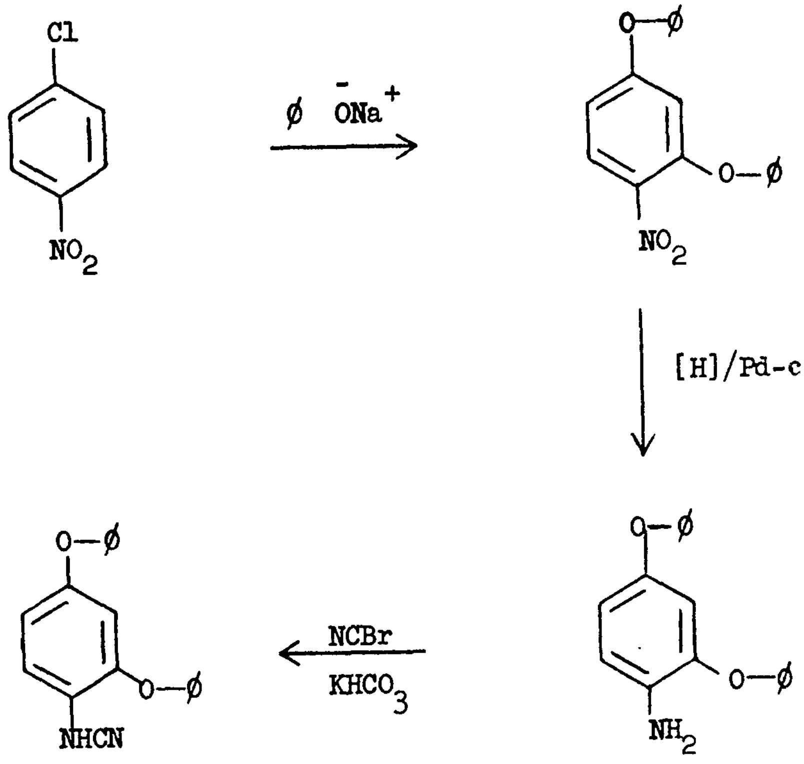


XIV

and 1,3-bis(p-phenoxybenzoyl)-5-cyanamidobenzene (XIV) was prepared according to Schemes I and II.

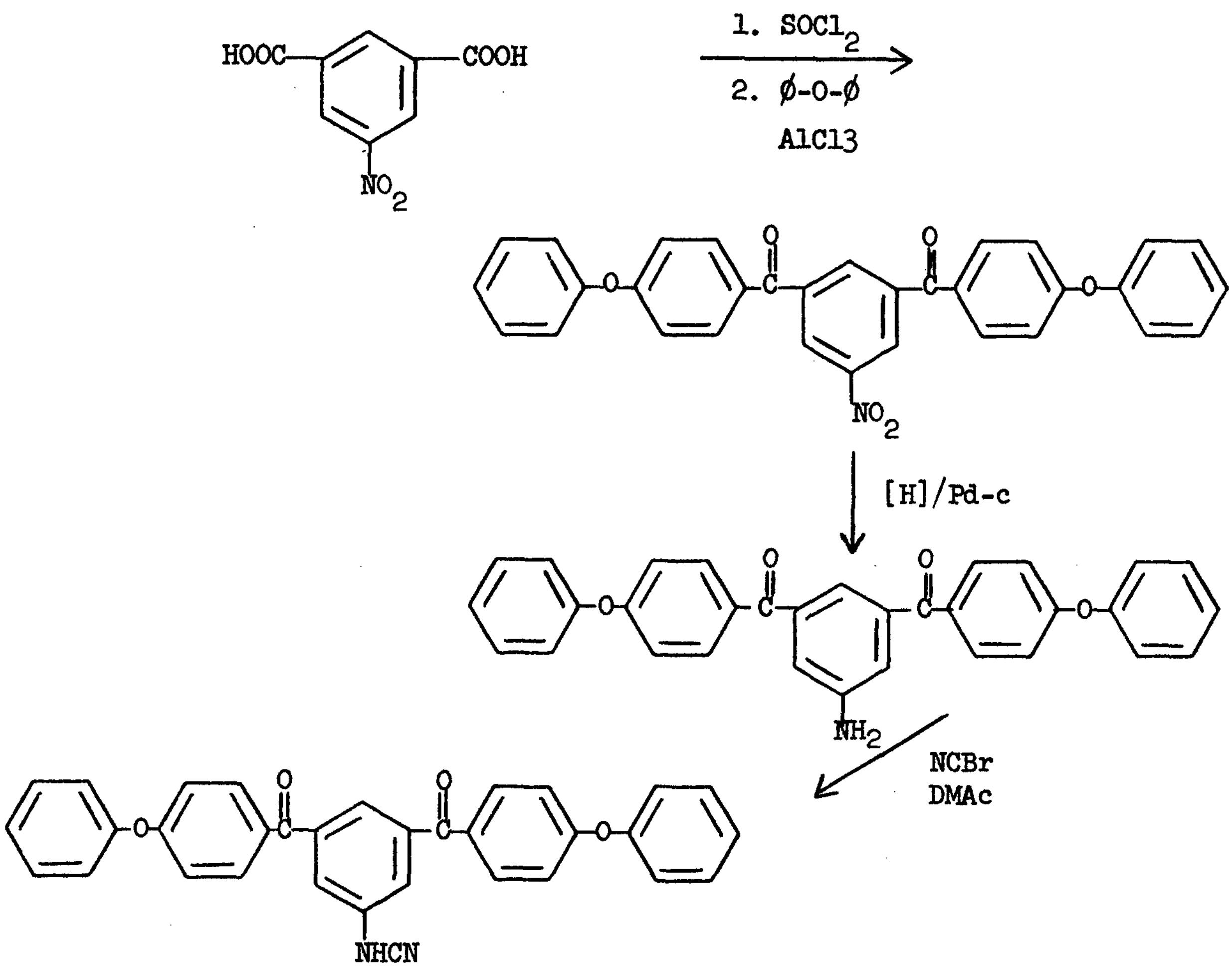
Trimerization condition of (XIII) and (XIV) will be studied further. (XIII) and (XIV) will be polymerized with sulfone monomer and aromatic diacid chlorides.

Scheme I



XIII

Scheme II



XIV

2. Experimental

a. 2,4-Diphenoxynitrobenzene

2,4-Dichloronitrobenzene (19.2 g, 0.1 mole) and sodium phenoxide were taken in 100 ml of dimethyl sulfoxide and the mixture was stirred at 120°C in nitrogen atmosphere for 24 hr. After cooling the reaction mixture to room temperature, the reaction mixture poured into 500 ml of water and the precipitate separated out was filtered and crystallized from methanol to give 2,4-diphenoxynitrobenzene as pale yellow needles (25.1 g, 80% yield) mp 60°C. The infrared spectrum of this compound in Nujol exhibited absorptions due to NO_2 group at 1575 cm^{-1} and 1455 cm^{-1} and absorption due to C-O-C stretching at 1080 cm^{-1}.

Anal. Calc. for $C_{18}H_{15}NO_4$: C, 70.38%; H, 4.23%; N, 4.56%.
Found: C, 70.29%; H, 4.40%; N, 4.35%.

b. 2,4-Diphenoxyaniline

2,4-Diphenoxynitrobenzene (9.2 g, 0.03 mole) was dissolved in 75 ml of absolute ethanol and 0.5 g of 5% Palladium on charcoal catalyst was added and the mixture was shaken in a Paar hydrogenator at 50 psi pressure of hydrogen for 24 hr. The catalyst was filtered and removal of ethanol afforded 8.1 g (98%) of 2,4-diphenoxyaniline. Crystallization from alcohol-water afforded light tan crystals. mp 86°C. The infrared spectrum in Nujol exhibited a doublet at 3450 cm^{-1} and 3355 cm^{-1} due to amine absorption.

Anal. Calc. for $C_{18}H_{15}NO_2$: C, 77.97%; H, 5.42%; N, 5.05%.
Found: C, 78.11%; H, 5.51%; N, 4.95%.

c. 2,4-Diphenoxy phenyl cyanamide

2,4-Diphenoxyaniline (2.77 g, 0.01 mole), cyanogen bromide (1.06 g, 0.01 mole) and potassium bicarbonate (1.01 g, 0.01 mole) and 100 ml of absolute ethanol were stirred at room temperature for 24 hr and then refluxed for three hr. After removing ethanol the residue was taken in ether (100 ml). The ether layer was washed with 5% sodium hydroxide solution and then washed free of base and dried over anhydrous sodium sulfate. Removal of ether gave 1.85 g of off-gray powder. This was crystallized from ether-petroleum ether mixture. mp 97-98°C. The infrared spectrum of this product exhibited absorption at 2225 cm^{-1} due CN group.

Anal. Calc. for $C_{19}H_{14}N_2O_2$: C, 75.51%; H, 4.64%; N, 9.27%.
Found: C, 76.53%; H, 4.51%; N, 10.32%.

Higher nitrogen and lower carbon analyses observed could be due to contaminants like N,N′-dicyano-2,4-diphenoxyaniline.

d. 5-Nitroisophthaloyl chloride

5-Nitroisophthalic acid (21.1 g, 0.1 mole) and thionyl chloride (100 ml) and dimethylformamide (1 ml) were refluxed for four hr. Excess of thionyl chloride was removed under vacuum and the residue was distilled. 5-Nitroisophthaloyl chloride (21.7 g) a yellow colored liquid bp 135-140°C/ 2.5 mm was collected.

Anal. Calc. for $C_8H_3NCl_2O_2$: C, 38.73%; H, 1.21%; N, 5.64%; Cl, 28.60%.
Found: C, 38.81%; H, 1.32%; N, 5.46%; Cl, 28.76%.

e. 1,3-Bis(p-phenoxybenzoyl)-5-nitrobenzene

5-Nitroisophthaloyl chloride (24.8 g, 0.1 mole), diphenyl ether (340 g, 2.0 mole) and aluminum chloride (0.6 mole) were stirred under nitrogen atmosphere at room temperature for 24 hr. The reaction mixture was kept at 50°C for one hr, then cooled to room temperature and poured into one liter of 5% hydrochloric acid. The organic layer was set aside and the aqueous layer was extracted with ether. The organic layer and the ether extracts were combined, washed with water and dried over anhydrous sodium sulfate. Removal of ether and distillation of excess of diphenyl ether under vacuum afforded yellow colored product. This was purified by passing through a column of neutral alumina using benzene as eluent. Light yellow crystals, 34 g, mp 125-126°C were obtained. Removal of benzene followed by crystallization from benzene-ethyl ether solution, i.e. small amount of benzene was added to dissolve the product, then ethyl ether was added to crystallize the product. Infrared spectrum of this compound in Nujol exhibited absorptions due to carbonyl group at 1640 cm^{-1} and due to NO_2 group at 1450 cm^{-1}.

Anal. Calc. for $C_{32}H_{21}NO_6$: C, 74.56%; H, 4.08%; N, 2.72%.
Found: C, 75.26%; H, 4.32%; N, 2.75%.

f. 1,3-Bis(p-phenoxybenzoyl)-5-aminobenzene

1,3-Bis(p-phenoxybenzoyl)-5-nitrobenzene (5 g) was dissolved in 100 ml of benzene. Ethanol (1 ml) and 0.5 g of 10% Palladium-Charcoal catalyst were added and the mixture was shaken in a Paar hydrogenator at

50 psi pressure for 24 hr. After removing the catalyst and removing benzene afforded 4.1 g of yellow powder mp 163-164°C. Recrystallization from ethanol afforded 3.5 g of yellow crystals mp 167-168°C. Infrared spectrum of this product in Nujol exhibited a triplet at 3400 cm^{-1}, 3360 cm^{-1} and 3325 cm^{-1}, due to $-NH_2$ group.

Anal. Calc. for $C_{32}H_{23}NO_4$: C, 79.20%; H, 4.74%; N, 2.89%.
Found: C, 78.25%; H, 4.79%; N, 2.81%.

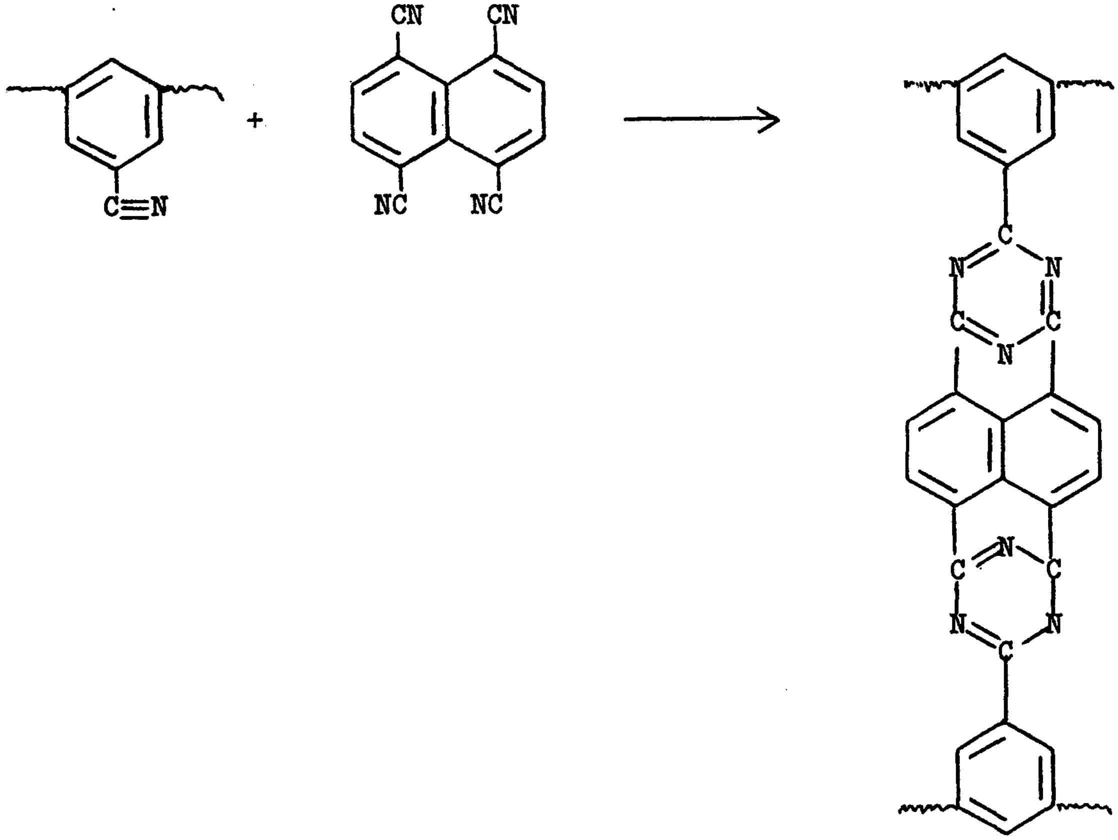
3. Future Plans

This work will be completed at a later date.

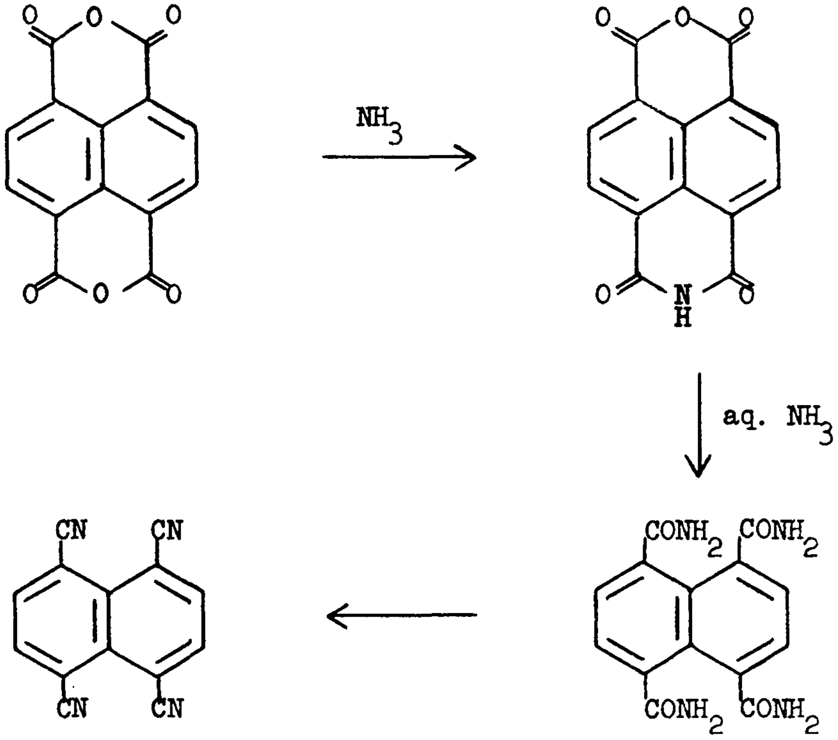
VIII. CROSSLINKING OF PENDANT CYANO GROUP IN JVB-50 TYPE POLYMERS WITH 1,4,5,8-TETRACYANONAPHTHALENE

1. Results and Discussion

A new approach to crosslinking of JVB-50 type polymers by the reaction with a tetranitrile like 1,4,5,8-tetracyanonaphthalene was undertaken. It is hoped that each pair of nitriles in the naphthalene compound will react with one nitrile of the polymer chain to give a triazine crosslink. For this purpose the unknown compound 1,4,5,8-tetracyanonaphthalene had to be synthesized.



Reaction of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride with ammonia at 300°C gave the diimide (XV) which on further treatment with ammonia gave the tetramide (XVI) Because of very sparing solubility of the tetramide in the reaction medium the attempted dehydrations using thionyl chloride and DMF have not produced the desired 1,4,5,8-tetracyanonaphthalene (XVII). Dehydration with polyphosphoric acid, phosphorous pentoxide and with oleum will be attempted.



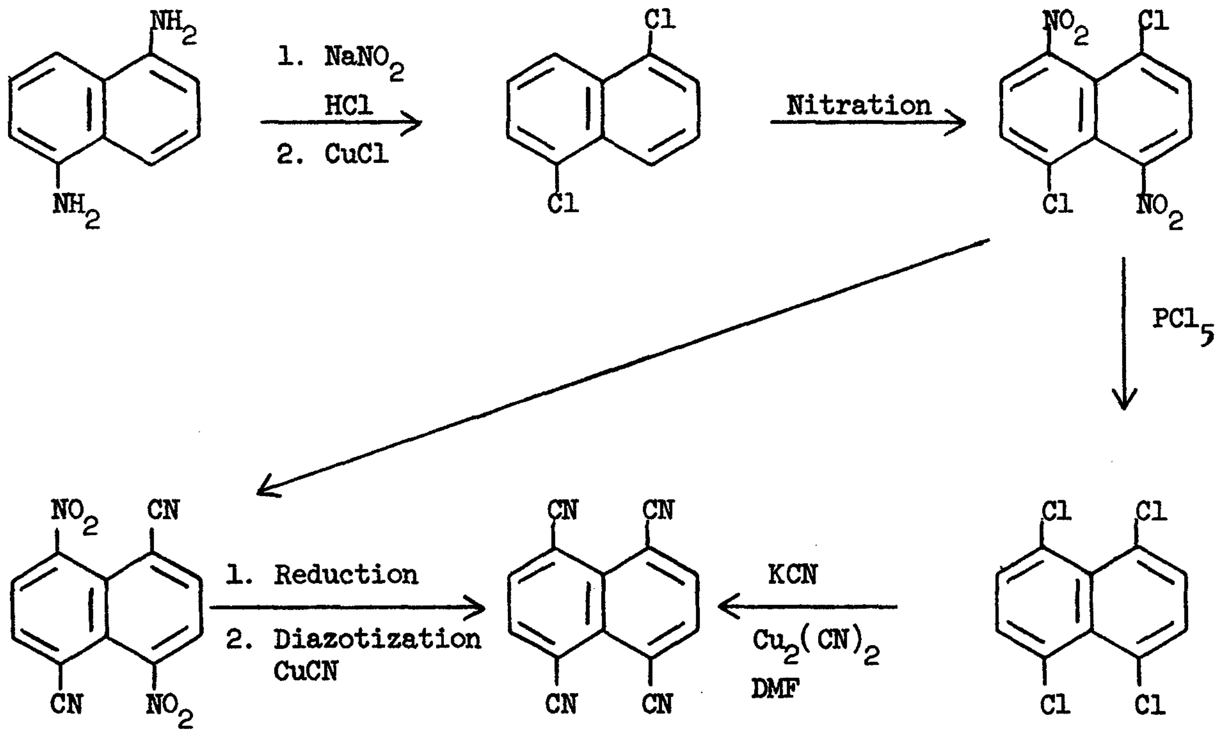
XV

XVI

XVII

Alternate approach to the synthesis of 1,4,5,8-tetracyanonaphthalene can be tried according to the following Scheme III:

Scheme III



2. Experimental

a. 1,4,5,8-Naphthalene tetramide

A mixture of 26.8 g (0.1 mole) of 1,4,5,8-naphthalene tetracarboxylic dianhydride and 50 ml of concentrated aqueous ammonia was placed in a 500 cc round-bottom flask and was heated at 300°C overnight, yielding 24.1 g of the diimide and this diimide was stirred with 80 cc of concentrated aqueous ammonia solution at room temperature for 24 hr. The mixture was, filtered, the filter cake washed with water and dried under reduced pressure at 80°C yielding 26.1 g of tetramide. mp> 360°C.

b. Attempted dehydration of 1,4,5,8-naphthalene tetramide to 1,4,5,8-tetracyanonaphthalene

i) With thionyl chloride in dimethylformamide

To a mixture of 32 g of tetramide in 200 ml of DMF was added rapidly 45 ml of thionyl chloride and the mixture was stirred overnight. Then another 35 cc of thionyl chloride was added and the mixture was stirred for another 24 hr. The solution was then poured onto two liters of crushed ice and after filtration the filter cake was suspended in 150 cc of NaOH aq (5%)and filtered. The solid was washed with water and dried. Infrared spectrum did not exhibit any nitrile absorption and the spectrum was almost identical with that of the starting material.

ii) With thionyl chloride

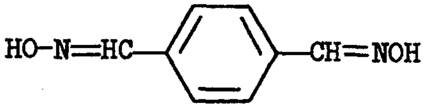
A mixture of 10 g of tetramide was refluxed with 150 ml of thionyl chloride. After removing thionyl chloride and washing the product with sodium hydroxide solution (5%) and then with water gave back starting material as shown by the infrared spectrum.

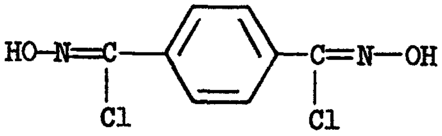
3. Future Plans

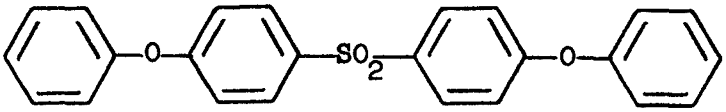
We may do some further work on this next year.

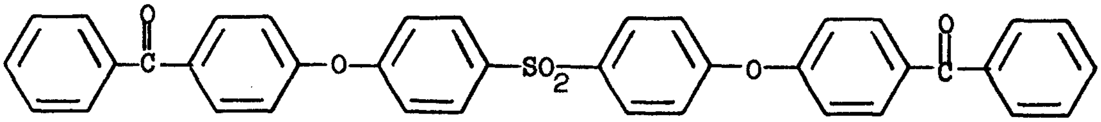
APPENDIX I

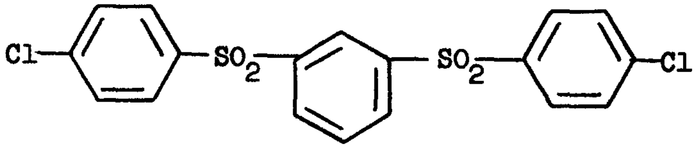
NEW COMPOUNDS

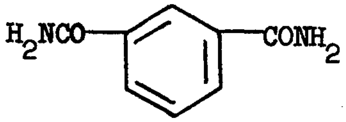


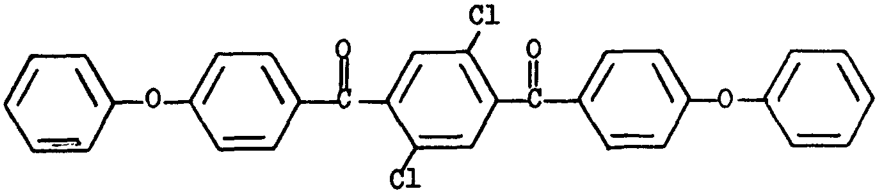








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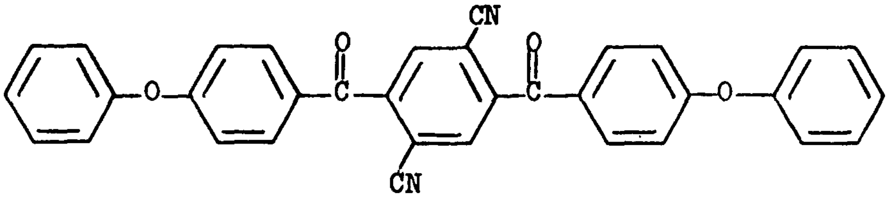
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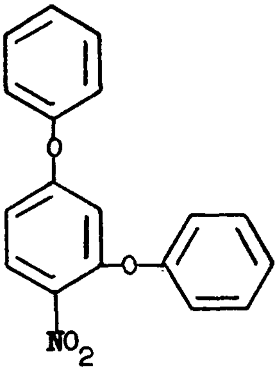
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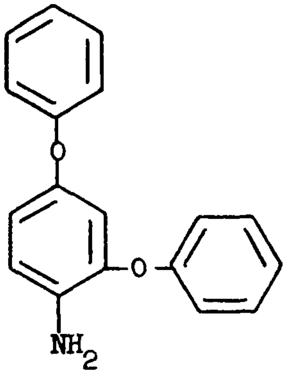
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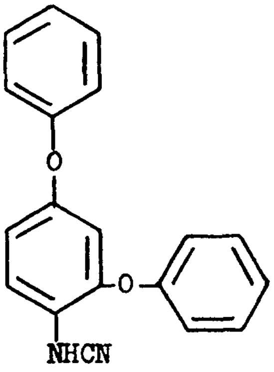
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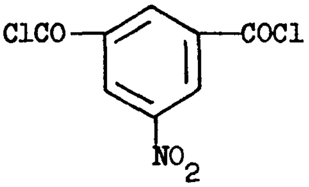
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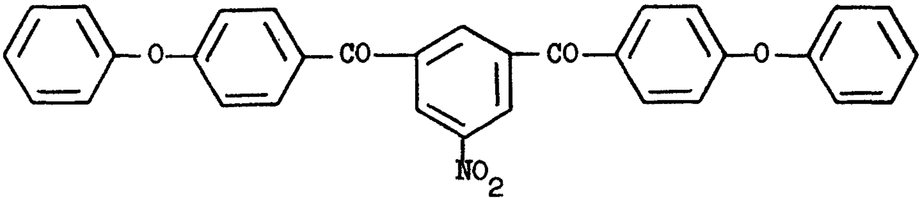
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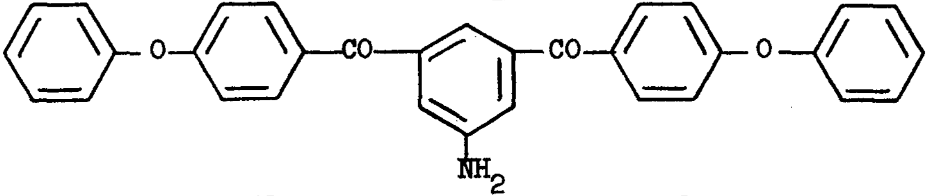
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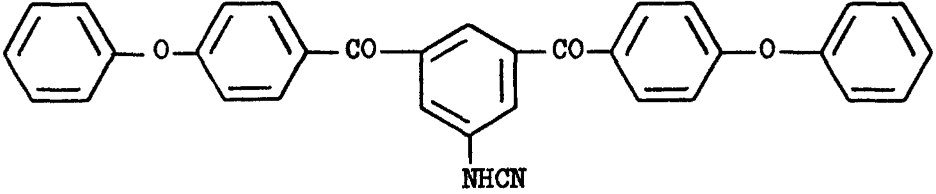
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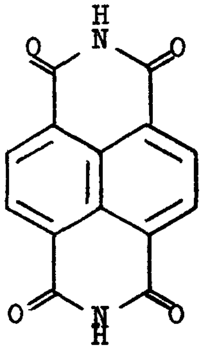
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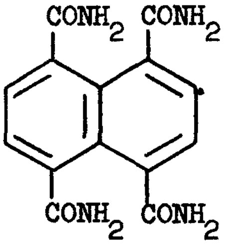
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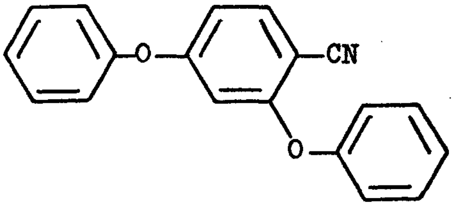
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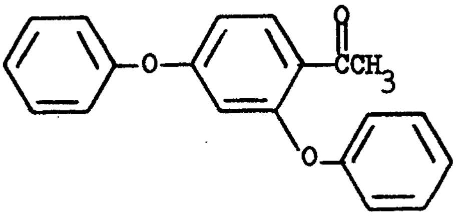
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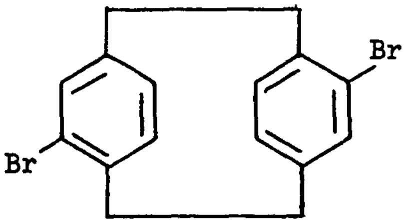
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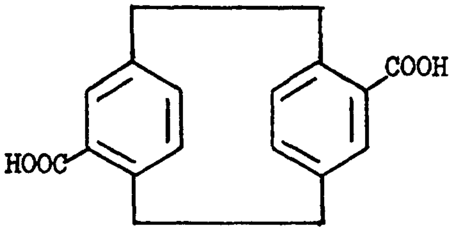
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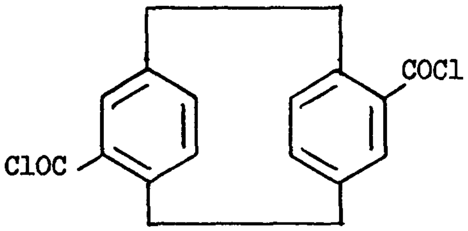
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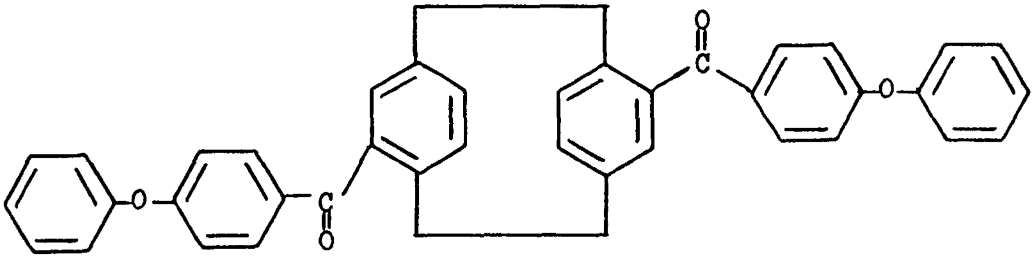
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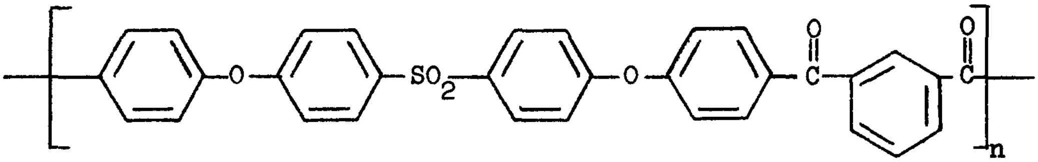
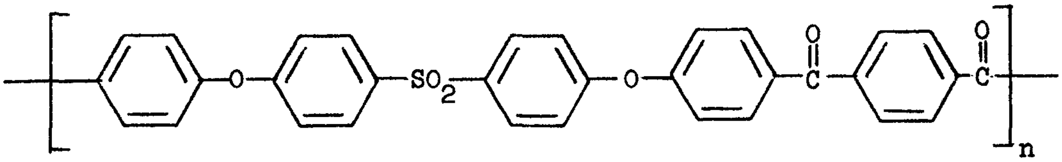
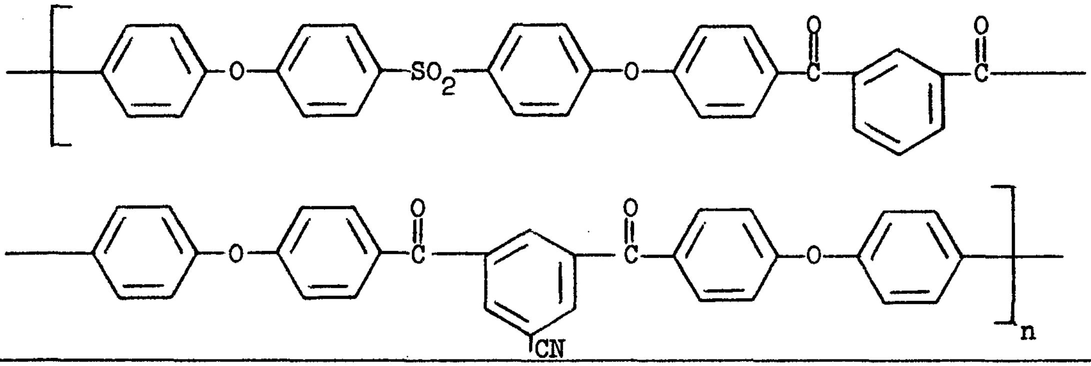
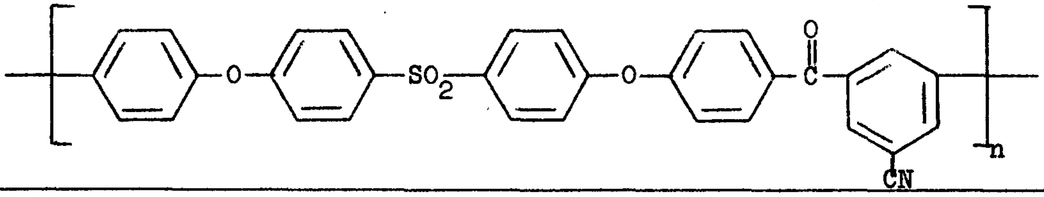
APPENDIX II

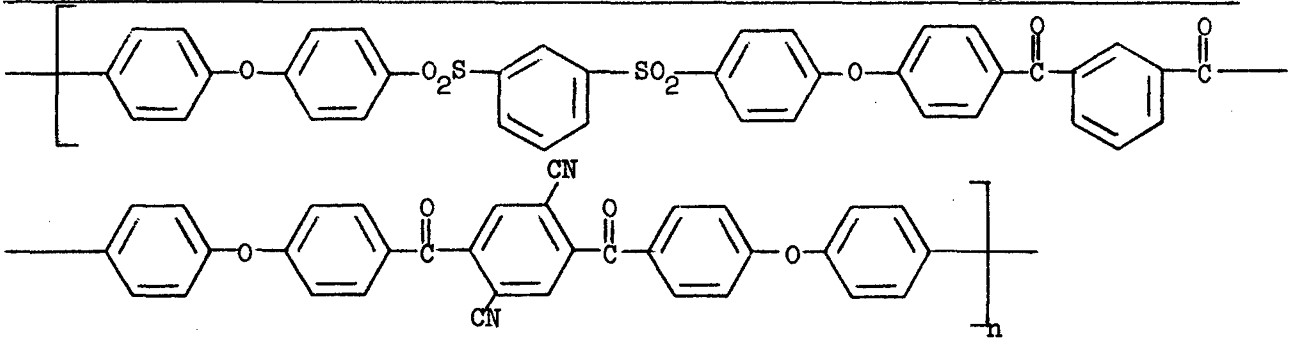
NEW POLYMERS

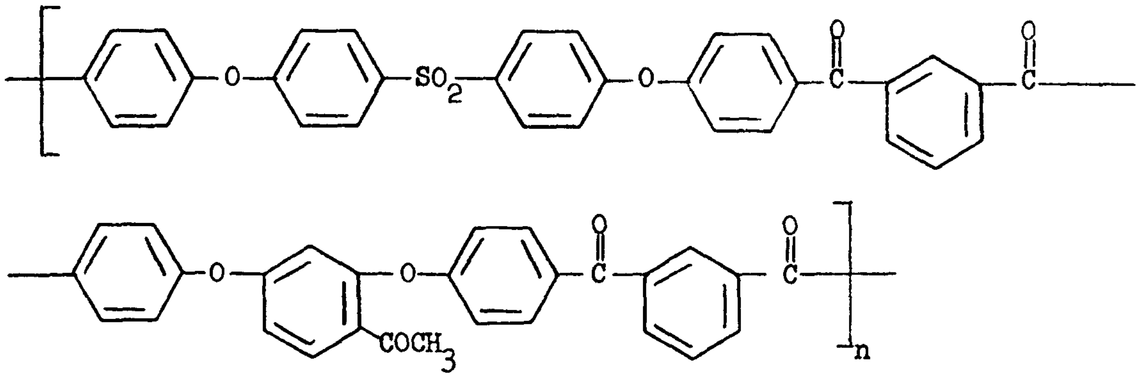








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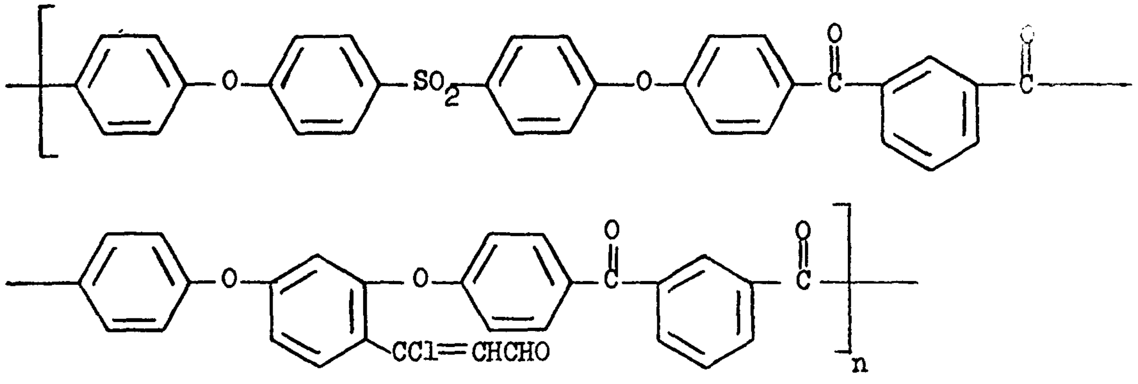
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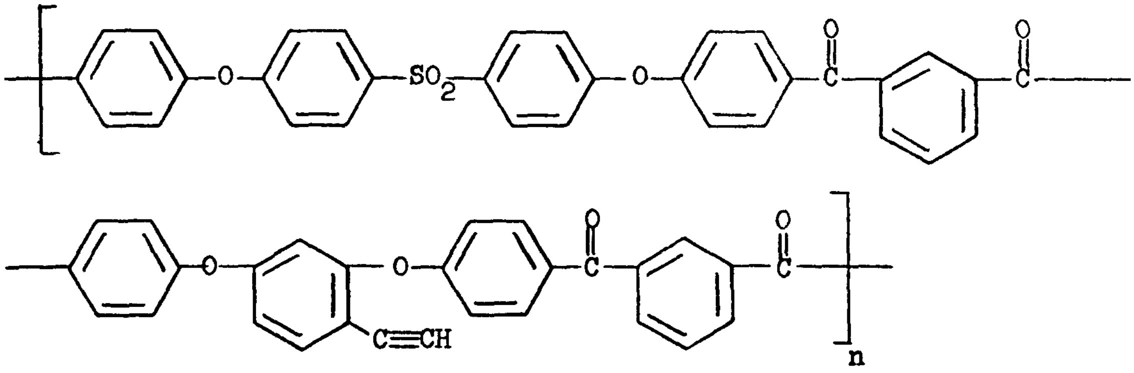
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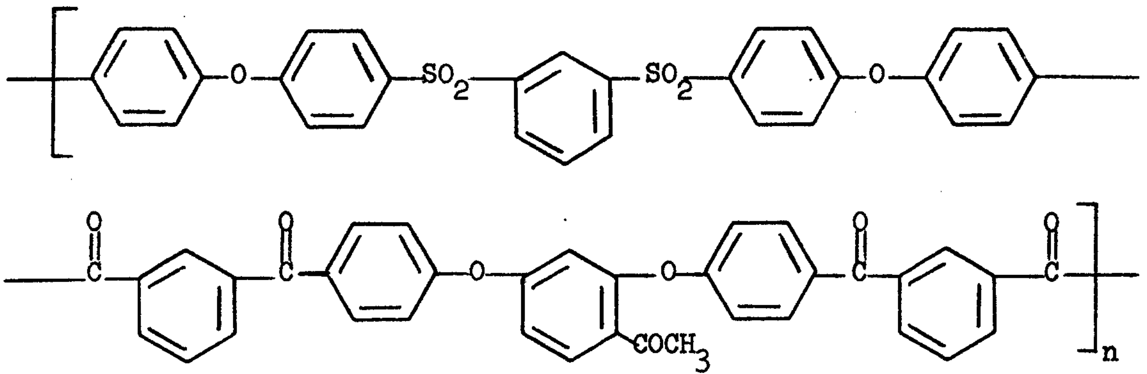
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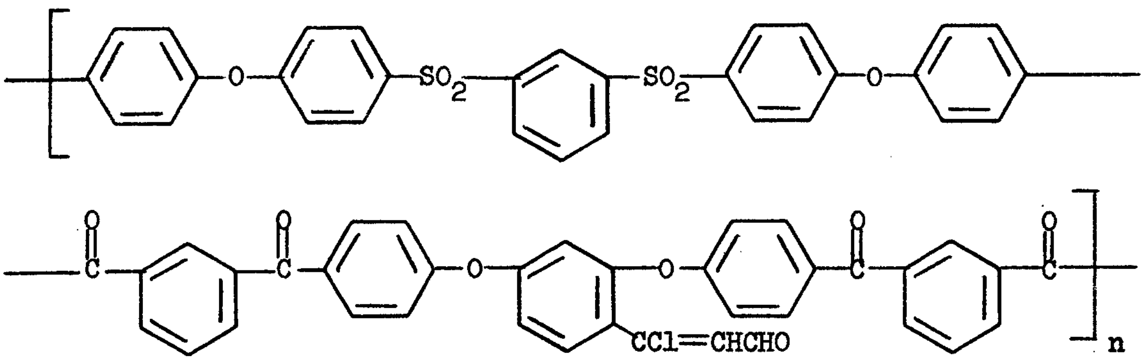
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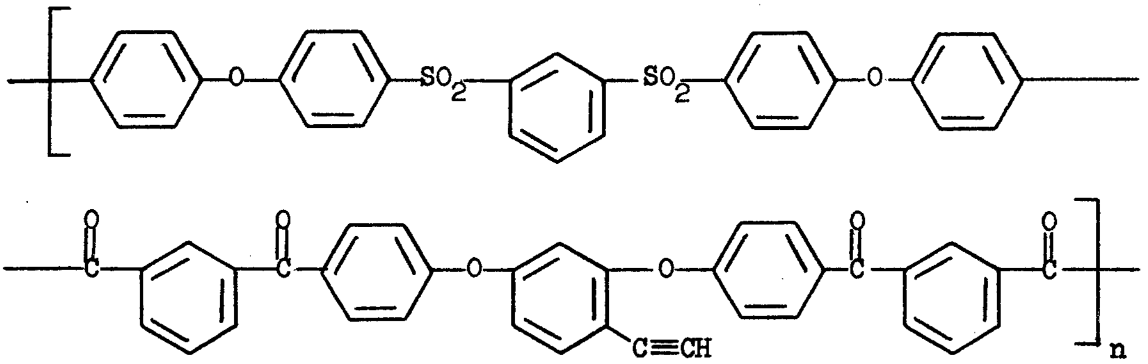
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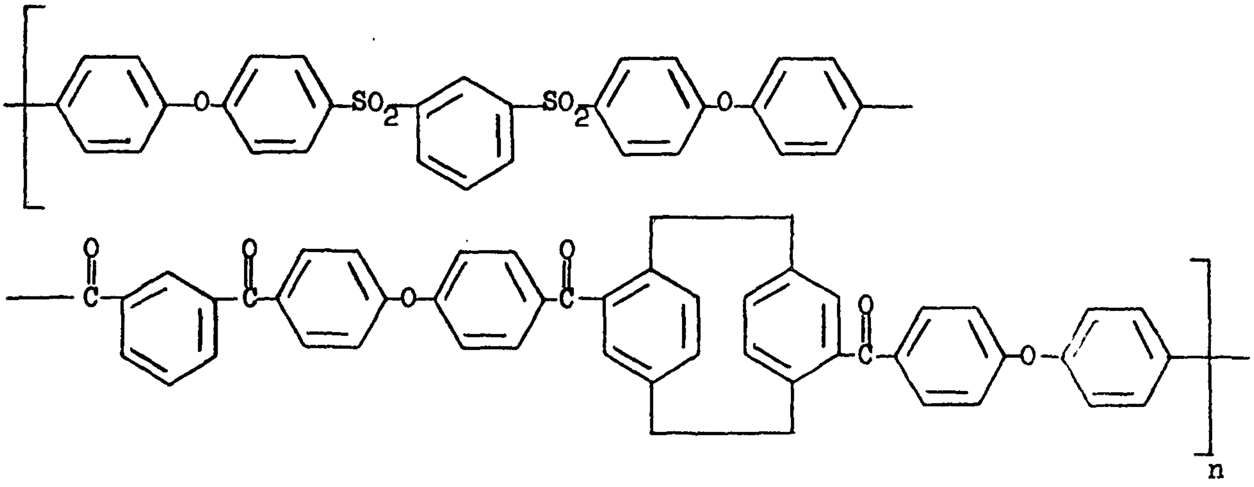
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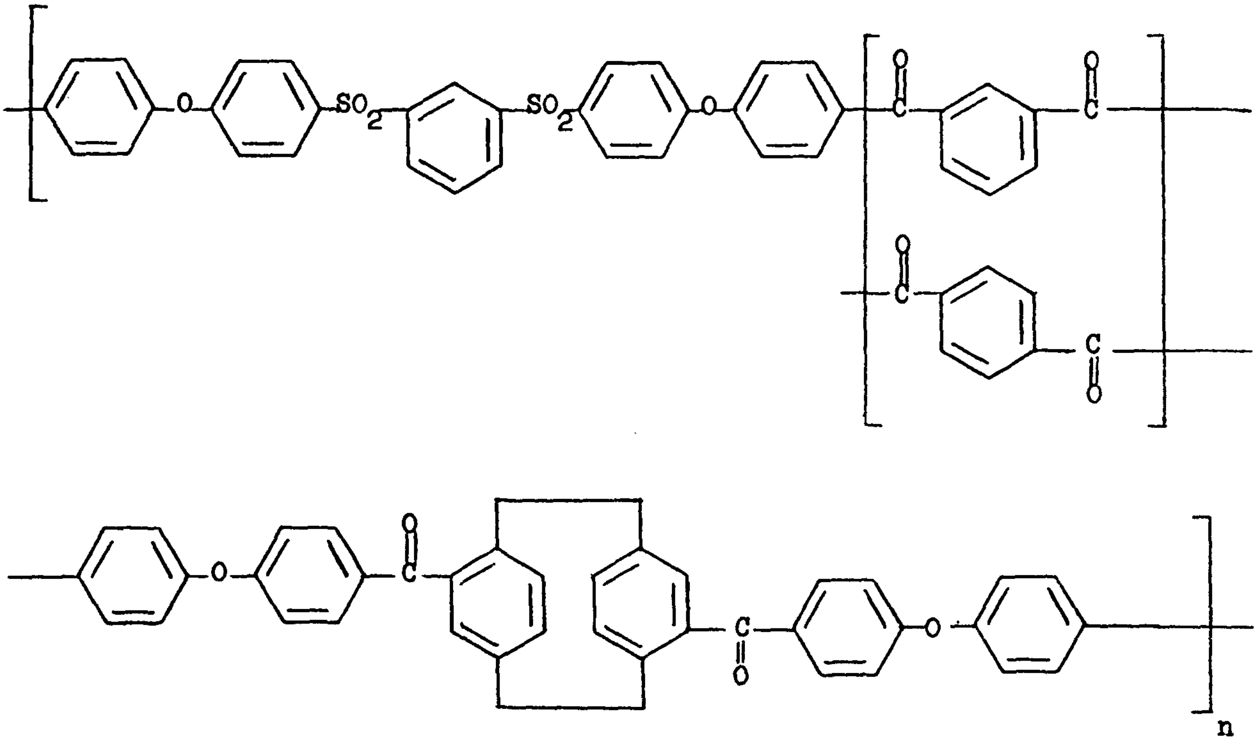
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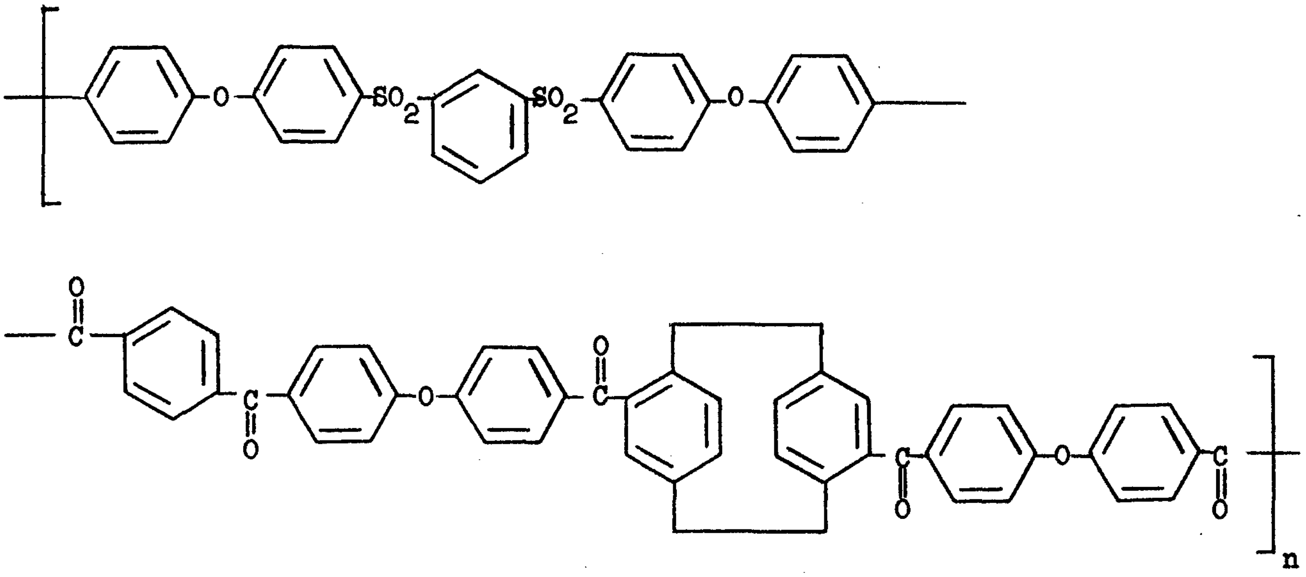
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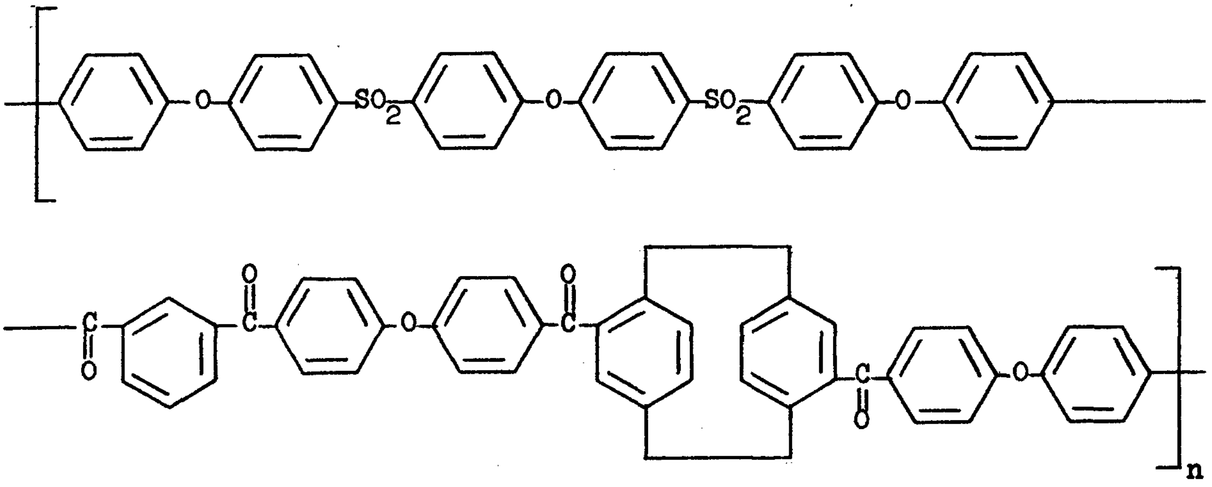
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APPENDIX III

RESULTS OF ANALYSIS - SECTION VI

Page No.

95 3,9-Dibromo[2.2]paracyclophane. mp 245-249°C.

Anal. Calc. for $C_{16}H_{14}Br_2$: C, 52.45%; H, 3.82%.

Found: C, 52.43%; H, 3.87%.

99 Polymer DTW-3, containing 17 wt % of 3,9-bis[p-phenoxybenzoyl][2.2] paracyclophane

Anal. Calc.: C, 70.15%; H, 3.90%; S, 7.66%.

Found: C, 68.63%; H, 3.87%; S, 7.25%.

100 Polymer DTW-4, containing 22 wt% of 3,9-bis[p-phenoxybenzoyl][2.2] paracyclophane

Anal. Calc.: C, 71.29%; H, 3.98%; S, 7.18%.

Found: C, 71.45%; H, 4.03%; S, 6.65%.

97 Polymer DTW-5, containing 6 wt % of 3,9-bis[p-phenoxybenzoyl][2.2] paracyclophane

Anal. Calc.: C, 68.38%; H, 3.73%; S, 10.05%.

Found: C, 68.62%; H, 3.72%; S, 8.60%.

96 1,3-Bis(p-phenoxybenzenesulfonyl)benzene

Anal. Calc. for $C_{30}H_{22}O_6S_2$: C, 66.40%; H, 4.09%; S, 11.82%.

For the sample (A), mp 183-193°C, white in color

Found: C, 66.35%; H, 4.20%; S, 11.58%.

For the sample (B), mp 70-75°C, white in color

Found: C, 66.28%; H, 4.13%; S, 11.71%.

Since we isolated about 4% of the sample A (mp 183-193°C) from the gross product as shown as sample B (mp 70-75°C), and the results of elementary analysis of these two samples have no significant difference, it is assumed that sample A would probably be the pure 1,3-bis(p-phenoxybenzenesulfonyl)benzene, and that the sample would be a mixture of 1,3-bis(p-phenoxybenzenesulfonyl)benzene and 1,3-bis(o-phenoxybenzenesulfonyl)benzene. The gross product, i.e. sample B, was used to make polymers in this report.

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