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SYNTHESIS OF THERMALLY STABLE POLYMERS

Carl S. Marvel
The University of Arizona

TECHNICAL REPORT AFML-TR-72-111 Part I

July 1972

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Air Force Materials Laboratory
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Wright-Patterson Air Force Base, Ohio

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NOTICE

SYNTHESIS OF THERMALLY STABLE POLYMERS

Carl S. Marvel
The University of Arizona

FOREWORD

This report was prepared by the Department of Chemistry at The University of Arizona, Tucson, Arizona, on Air Force Contract No. F33615-71-C-1408, under Task No. 734004, "New Organic and Inorganic Polymers," of Project No. 7340, "Nonmetallic and Composite Materials." The contract efforts were accomplished under the direction of the Air Force Materials Laboratory, with the technical work directed by Mr. G. A. Loughran (LNP) as Project Scientist.

This report covers work conducted from December 1970 to April 1972. It was submitted by the author in April 1972.

The work which is reported herein was performed by Doctors R. Mortier, S. Hurley, J. Verborgt, K. P. Sivaramakrishnan, C. Marken and J. M. Vandensavel.

We are indebted to Dr. G. Ehlers of the Air Force Materials Laboratory for all the TGA curves.

This technical report has been reviewed and is approved.

R. L. Van Deusen

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

ABSTRACT

Work on the condensation of 1,5-diaminoanthraquinone and aralkyldiketones has been concluded and published.

Work on the polymer with graphitic structure obtained from 1,4,5,8-tetraaminoanthraquinone and naphthalene-1,8,4,5-diindandione has been completed and a manuscript prepared for publication.

A series of linear polymers containing aryl ether, aryl ketone and aryl sulfone units with nitrile dangling groups has been prepared. Some success has been achieved in converting the nitriles to triazine. The resulting products are promising as laminating resins.

A series of arylene polysulfides with nitrile side groups has been synthesized and show some promise as laminating resins.

Work has begun on the preparation of polymeric chains with o-dicyano substituents to test the value of phthalocyanine groups as side chains for crosslinking.

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I. INTRODUCTION

The work reported herein has been directed toward the preparation of new polymeric materials which will retain useful properties at temperatures above 500°C.

II. AREAS OF INVESTIGATION

The areas of investigation covered in this report are:

III. Polymers from 1,5-diaminoanthraquinone and p-diacetylbenzene.

IV. Thermally stable polymers with a graphitic structure.

V. Aromatic polyethers, - sulfones and -ketones as laminating resins.

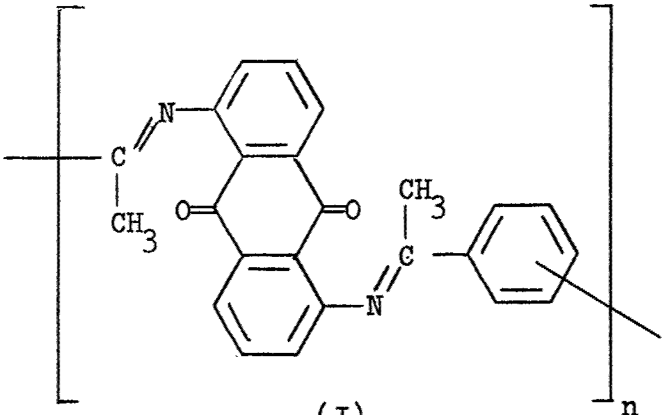
VI. Polyphenylene sulphides and related polymers for use as laminating resins.

VII. Polyphthalocyanines.

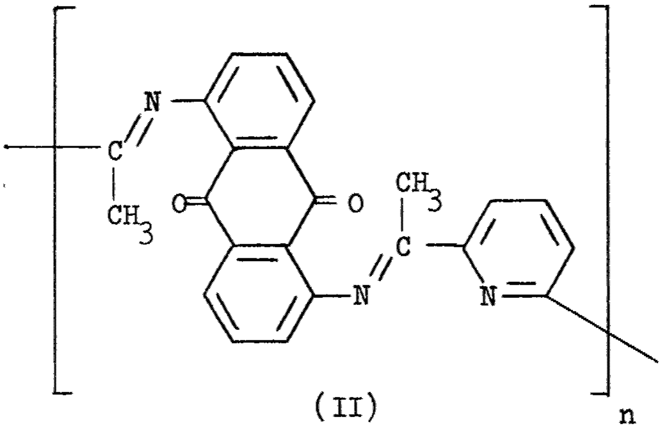
III. POLYMERS FROM 1,5-DIAMINOANTHRAQUINONE AND p-DIACETYLBENZENE

1. Introduction

As has been reported earlier[1] polymeric Schiff's bases (I, II) have been prepared from 1,5-diaminoanthraquinone and aralkyldiketones. One of these has been ring-closed to form a thermally stable polymer (III).



(I)



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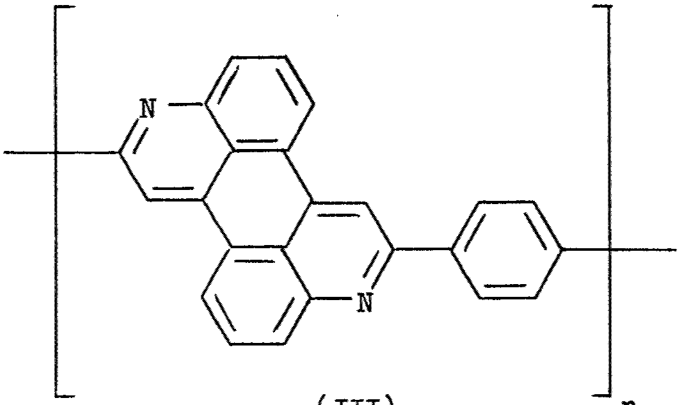


(III)

The first reaction concerned the polycondensation of 1,5-diaminoanthraquinone with 1,4-diacetylbenzene and the ring closing of the product. As the prepolymer and final product were not easily soluble in concentrated sulphuric acid, other monomers 1,3-diacetylbenzene and 2,6-diacetylpyridine were used with 1,5-diaminoanthraquinone. Difficulties were encountered in finding suitable reaction conditions in order that high molecular weight soluble polymers might be formed. The methods employed were solution, melt and sealed-tube polymerization techniques.

A polymer was formed from 1,4-diacetylbenzene and 1,5-diaminoanthraquinone in a melt polymerization. This product was successfully ring-closed to give a thermally stable polymer having a decomposition temperature in nitrogen of 900°C at a heating rate of 3°C min^{-1}. The polymer had an inherent viscosity of 0.56 dl g^{-1} in concentrated sulphuric acid (0.5% solution).

Solution polymerizations using zinc chloride catalyst gave variously no reaction or insoluble products. When either 1,3-diacetylbenzene or 2,6-diacetylpyridine were used, solution and melt polymerizations did not yield any polymeric materials. The prepolymers were obtained when the polycondensations were done in sealed tubes.

This report deals with the work undertaken to reproduce the polymer formed from 1,4-diacetylbenzene and 1,5-diaminoanthraquinone. It is hoped that during this work the reaction may be more readily understood and the reaction conditions optimised. From this groundwork it should then be possible to proceed to the synthesis of similar polymers having more desirable solubility characteristics.

2. Discussion

a. Introduction

As was reported earlier[1] attempted solution polycondensations using zinc chloride as catalyst yielded only partially condensed products. The solvent used was nitrobenzene and the reaction mixtures were heated at 140° - 170°C for 4 to 20 hr. The use of zinc chloride as the catalyst was questioned as it is able to complex with ketones:

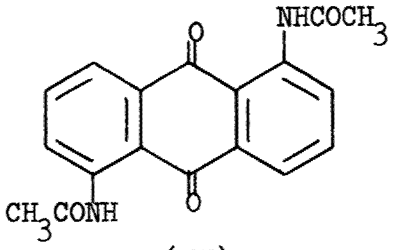
$$\mathrm{ZnCl_2} + \mathrm{O{=}C}< \longrightarrow \mathrm{ClZnO}\ \overset{+}{\mathrm{C}}<\ \mathrm{Cl^-}$$

The possibility of self-condensation of either monomer in the presence of the catalyst was also considered. Thus each monomer was heated with zinc chloride in nitrobenzene at 170°C for 23 hr. Both monomers were recovered quantitatively.

Because of the difficulties encountered using the zinc chloride/nitrobenzene system other catalysts were used in an attempt to form the Schiff's base prepolymer. Melt polycondensations were also carried out.

b. Solution polycondensations

A reaction in nitrobenzene using a mixture of glacial acetic acid and acetic anhydride as the catalyst gave a quantitative yield of 1,5-diacetamidoanthraquinone (IV) (ir, analysis, mp). As the catalyst mixture acetylated the amine an acid alone was used as the catalyst. The reaction is catalyzed by acids so a stronger acid than acetic acid was used: trichloroacetic acid. This acid also has a high bp (198°C) which minimized loss of catalyst at the reaction temperature (trifluoroacetic acid, bp 72°C).



(IV)

A reaction in nitrobenzene using trichloroacetic acid was carried out at 160°C for 22 hr. The reaction product consisted of a small amount of partially reacted diamine but the bulk of the 1,5-diaminoanthraquinone was recovered unchanged (ir, mp). This reaction was repeated under the same conditions but with a longer reaction time (40 hr). The result was the same.

Trifluoroacetic acid was then used as the catalyst with N,N-dimethylacetamide as solvent. The results of this reaction were rather ambiguous. The infrared spectrum did not show the sharp doublet (N-H) at 3305 and 3410 cm^{-1} which is characteristic of 1,5-diaminoanthraquinone thus indicating that the amino groups had reacted. The diketone carbonyl peak at 1650 cm^{-1} was also absent. However, the product was not polymeric as the inherent viscosity was < 0.02 dl g^{-1}. The microanalysis did not assist in elucidating the structure of the product.

c. Melt polycondensations

Although it was known that sublimation of both monomers, especially 1,4-diactylbenzene, took place, this reaction method was tried again. The details are given in the experimental section. After a total heating time of 15 hr a black, brittle, granular product was formed. It was insoluble in dimethylacetamide and partially soluble in methanesulphonic and concentrated sulphuric acids. The infrared spectrum indicated polymer formation by the loss of the sharp aminoanthraquinone N-H doublet and the diketone carbonyl peak. The material did not melt or soften below 500°C but at 300°C gave a small amount of a white sublimate. The inherent viscosity of the polymer in methanesulphonic acid was 0.21 dl g^{-1}.

As the previous melt condensations were carried out between 180° and 250°C, and produced a partially insoluble polymer (28%), the reaction was attempted using lower temperatures. A number of melt polycondensations were carried out using different temperature/time conditions. A reaction time of 6 hr at 150°C gave a red powder as the product. It was soluble in N,N-dimethylacetamide and had an inherent viscosity of < 0.05 dl g^{-1} (at 30°C in dimethylacetamide). A reaction carried out for 21 hr at 165°C gave a red/brown powder which was 90% soluble in dimethylacetamide. The soluble portion of the product again had an inherent viscosity of < 0.05 dl g^{-1} (at 30°C in dimethylacetamide). The dimethylacetamide insoluble part of the product was soluble in concentrated sulphuric acid.

Other reactions gave similar results i.e. products were formed which were mainly soluble in dimethylacetamide and were red to red/brown powders. It was found that the dark colored products were more insoluble in dimethylacetamide than the lighter. As noted above, the polymer having an inherent viscosity of 0.21 dl g^{-1} was black and insoluble in dimethylacetamide. Thus it would seem that repeated extraction of the Schiff's-base polymer with dimethylacetamide would not only remove any excess monomer but also low molecular weight oligomers. In general, it was found that melt condensations of 1,5-diaminoanthraquinone and 1,4-diacetylbenzene carried out for less than 24 hr at temperatures below 170°C gave red to red/brown powders mainly soluble in dimethylacetamide.

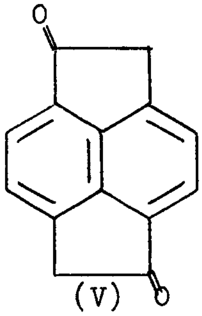
A reaction carried out between 170° and 180°C for 19 hr gave a polymeric product. The reaction was stopped after 9 hr and examination of the product (ir) showed it to contain much unchanged 1,5-diaminoanthraquinone. Continuation of the reaction for a further 10 hr gave a dark brown powder as the product. A small amount of the product (10%) was soluble in dimethylacetamide, the bulk of the product being soluble in concentrated sulphuric acid. The polymer had an inherent viscosity of 0.28 dl g^{-1}. (0.32% in concentrated sulphuric acid at 30°C).

d. Summary

Attempts have been made to polycondense 1,5-diaminoanthraquinone and 1,4-diactylbenzene by solution and melt methods. Emphasis was placed on the solution technique as this allows far greater control of the reaction and the reaction is easier to handle. However, a successful solution polycondensation has not yet been achieved. This technique, using different solvent/catalyst systems, has yielded only partially condensed products. Due to the long reaction times and high temperatures required to obtain a reaction it is possible that the solvent is interfering in the condensation. This could be by direct reaction with one of the monomers or, more likely, by a solvent decomposition product reacting.

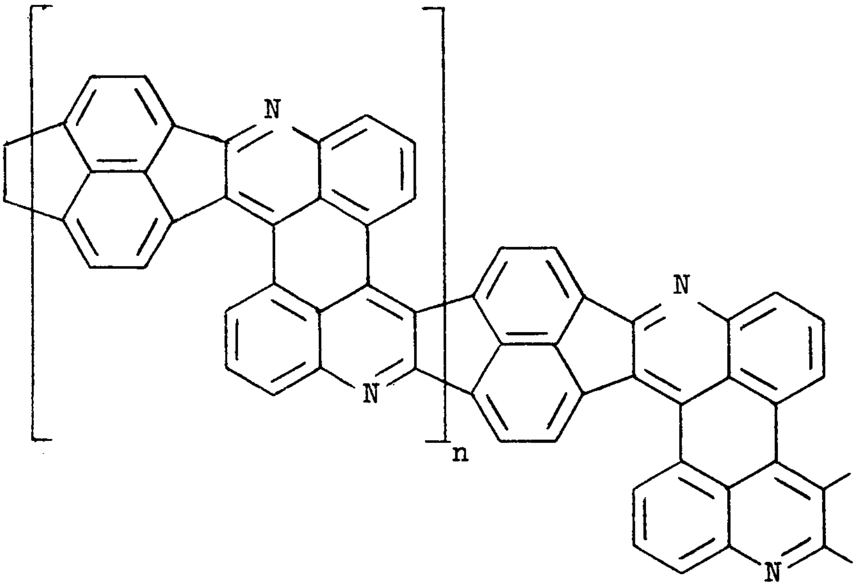
The melt polycondensation, although not going to completion, appears to have given a promising product. Improvements which are required are the use of a diketo monomer which will not sublime at the reaction temperature, and an improvement in the solubility characteristics of the polymer. The solubility of this type of polymer in more common solvents may be improved by use of other diacetyl monomers. For example, it has been shown that the Schiff's base polymer using 2,6-diacetylpyridine is soluble in dimethylacetamide, (II). This polymer was prepared by heating the reactants in a sealed tube due to the volatility of the diacetyl monomer.

The volatility of the diacetyl monomer is a problem which can be removed by using a less volatile diketo monomer. One such compound is the diketopyracene, V:



(V)

This monomer would give a Schiff's base polymer which, on treatment with polyphosphoric acid could give a complete ladder structure:



3. Experimental

a. Monomers

i) 1,5-Diaminoanthraquinone

Technical grade material was acetylated followed by hydrolysis and two crystallizations from nitrobenzene. The material was then partially freed from solvent by pumping under vacuum (10^{-1} mm Hg) at 120°C and finally purified by Soxhlet extraction with ethanol for 48 hr. The material had mp 319° - 320°C (corr.). The infrared spectrum is shown in Figure 1.

Anal. Calc. for $C_{14}H_{10}N_2O_2$: C, 70.6%; H, 4.2%; N, 11.8%.
Found: C, 70.8%; H, 4.1%; N, 11.9%.

An attempt was made to further purify the material by sublimation at 10^{-2} mm. pressure and a temperature of 200°C. This was unsuccessful as only 2% of the material sublimed in 3 days. A lower pressure is required before this technique can be used to purify 1,5-diaminoanthraquinone.

ii) 1,4-Diacetylbenzene

Commercial material was crystallized twice from ethanol and was further purified by sublimation at 0.25 mm Hg pressure and a temperature of 90°C. The material had a mp of 114° - 114.5°C. (corr.). The ir spectrum is shown in Figure 2.

Anal. Calc. for $C_{10}H_{10}O_2$: C, 74.1%; H, 6.2%.
Found: C, 73.8%; H, 6.3%.

b. Self-condensation of monomers

i) 1,5-Diaminoanthraquinone

1,5-Diaminoanthraquinone (1.0 g, 0.0042 m) and zinc chloride (0.75 g, 0.0055 m) were added to a 100 ml three-necked flask fitted with a nitrogen inlet, sealed stirrer and air condenser. Nitrobenzene (50 ml) was added and the mixture heated at 170°C for 23 hr under a slow stream of nitrogen. After cooling, the reaction mixture was added to petroleum ether (40/60; 500 ml). Water (100 ml) was added and the mixture stirred for 12 hr.

The insoluble material was filtered off and air-dried overnight. It had mp 320°C and its ir spectrum was identical with that of 1,5-diaminoanthraquinone. The yield was quantitative.

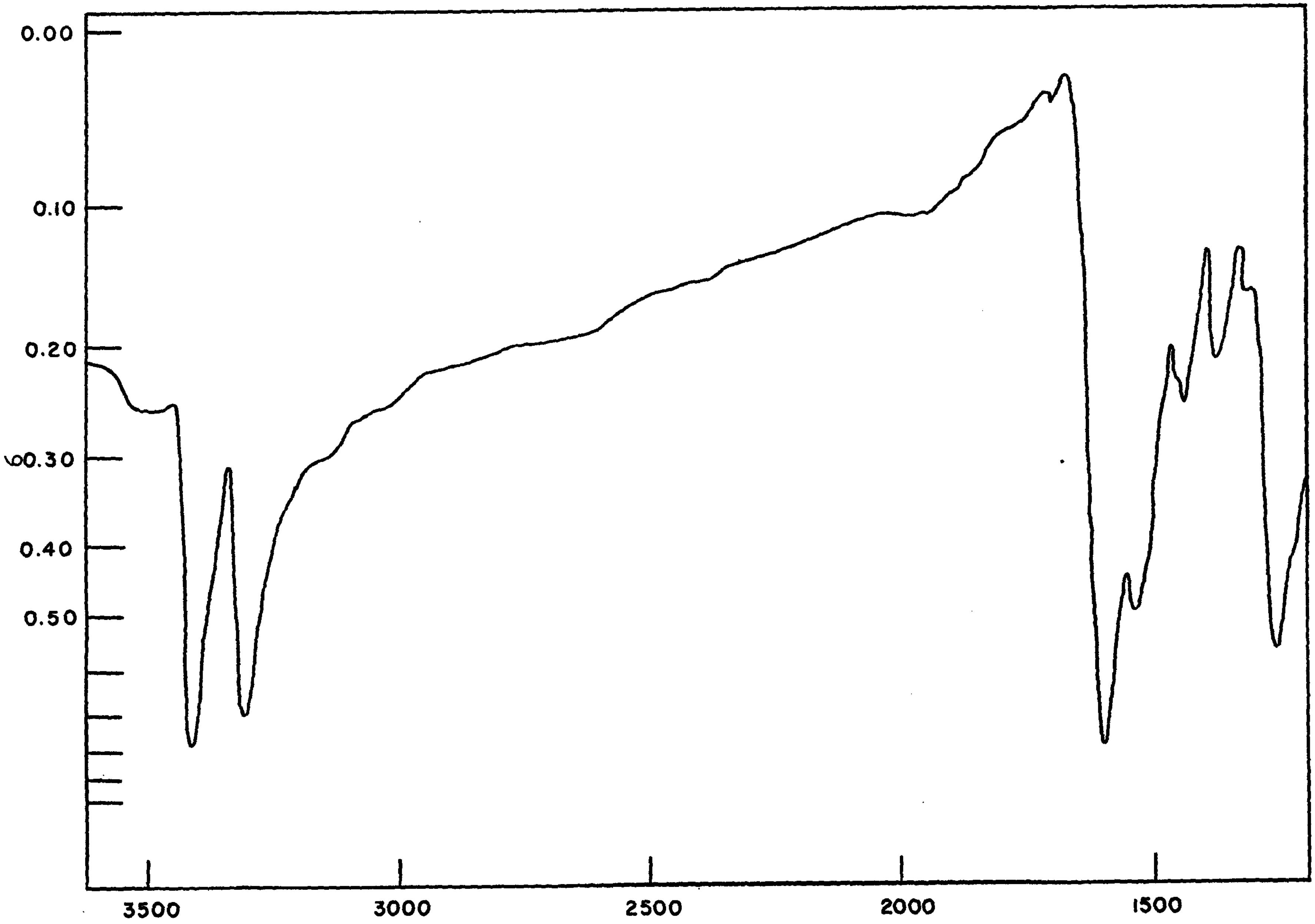


Figure 1. Infrared spectrum (KBr disc) of 1,5-diaminoanthraquinone

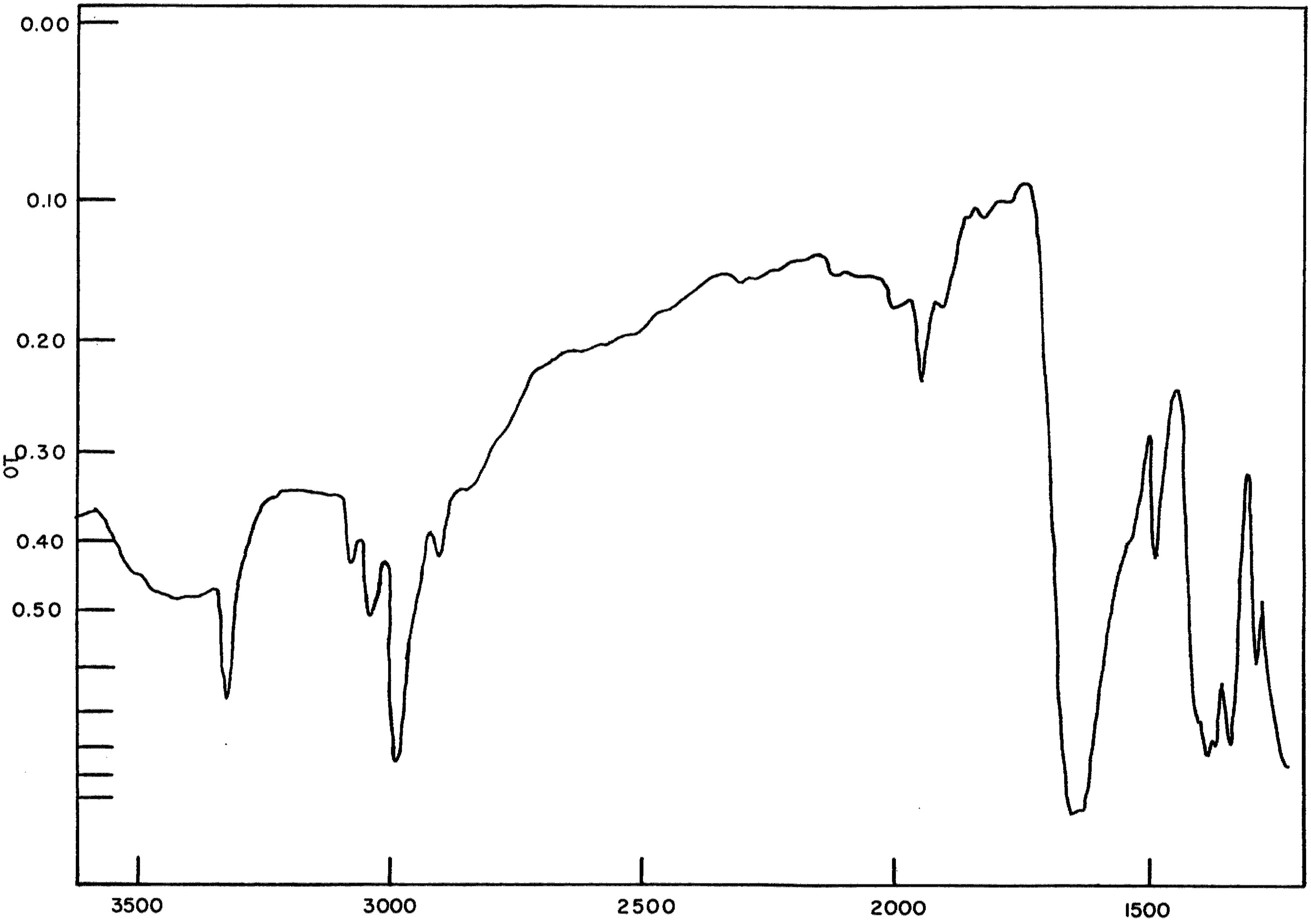


Figure 2. Infrared spectrum (KBr disc) of 1,4-diacetylbenzene

Anal. Calc. for $C_{14}H_{10}N_2O_2$: C, 70.6%; H, 4.2%; N, 11.8%.
Found: C, 69.8%; H, 4.2%; N, 11.6%.

ii) 1,4-Diacetylbenzene

Zinc chloride (0.71 g, 0.003 m) and 1,4-diacetylbenzene (0.67 g, 0.0041 m) were added to a flask fitted as above. Nitrobenzene (50 ml) was added and the mixture heated at 160°C for 22 hr. The mixture was allowed to cool and then added to a large excess of petroleum ether. A white precipitate of 1,4-diacetylbenzene was formed and the monomer (ir, mp) was recovered quantitatively.

c. Solution polymerizations

i) Acetic acid catalyzed

A mixture of 1,5-diaminoanthraquinone (2.38 g, 0.01 m), 1,4-diacetylbenzene (1.62 g, 0.01 m) glacial acetic acid (1.0 ml), acetic anhydride (4.0 ml) and nitrobenzene (50 ml) were heated at 160°C for 24 hr under nitrogen in a 100 ml three-necked flask.

After cooling, the reaction mixture was poured into petroleum ether (40/60) to yield a brown precipitate. The precipitate was filtered off and dried (3.0 g). The analysis, mp and ir spectrum showed the product to be 1,5-diacetamidoanthraquinone (93% yield). The mp was 316°C with decomposition.

Anal. Calc. for $C_{18}H_{14}N_2O_4$: C, 67.2%; H, 4.3%; N, 8.7%.
Found: C, 67.3%; H, 4.4%; N, 8.6%.

ii) Trichloroacetic acid catalyzed

1,4-Diacetylbenzene (0.81 g, 0.005 m), 1,5-diaminoanthraquinone (1.19 g, 0.005 m) and trichloroacetic acid (2.3 g) were heated with nitrobenzene (40 ml) under nitrogen at 160°C for 22 hr. The cooled reaction mixture was poured into an excess of ethanol and the red precipitate so formed was filtered off and dried. The ir spectrum and mp (318° - 319°C) of the product showed it to be 1,5-diaminoanthraquinone.

iii) Trifluoroacetic acid catalyzed

A mixture of 1,5-diaminoanthraquinone (1.19 g, 0.005 m), 1,4-diacetylbenzene (0.81 g, 0.005 m), trifluoroacetic acid (3.5 ml) and N,N-dimethylacetamide (50 ml) were heated at 170°C for 90 hr. After cooling, the reaction mixture was poured into water and the precipitate which formed was collected and extracted with methanol.

The ir spectrum of the product showed the absence of the sharp NH_2 doublet characteristic of 1,5-diaminoanthraquinone. The diketone carbonyl peak was also absent (Figure 3). The mp of the product was 290°C and the inherent viscosity (0.5% in dimethylacetamide at 30°C) was < 0.02 dl. g^{-1}.

Anal. Calc. for polymer: C, 79.1%; H, 4.4%; N, 7.7%.
Found: C, 67.1%; H, 4.5%; N, 6.7%; Res., 3.0%.

d. Melt polymerizations

As the reaction conditions were the same for all experiments, except for time and temperature, only two examples of the reaction will be given here.

1,5-Diaminoanthraquinone (1.19 g, 0.005 m) and 1,4-diacetylbenzene (0.81 g, 0.005 m) were thoroughly ground together and the mixture placed in the bottom of a pyrex tube. The tube was flushed with dry nitrogen and slowly heated to 180°C by immersing in a metal bath. The diacetylbenzene sublimed and after 4 hr heating the reaction mixture was allowed to cool. The sublimate was then washed back into the reaction zone with acetone which was evaporated by blowing nitrogen through the tube. The heating was restarted and this heating/washing cycle was repeated six times when the amount of sublimate was constant. The temperature of the reaction was slowly increased with each cycle up to a maximum of 250°C. At this temperature a small amount of the diamine also sublimed.

The product, a black brittle material, was removed from the tube, crushed and extracted with dimethylacetamide. After filtering off, the product was washed with acetone and air dried. The yield was 1.62 g (89%). The material was partially soluble in concentrated sulphuric acid and methanesulphonic acid (72%).

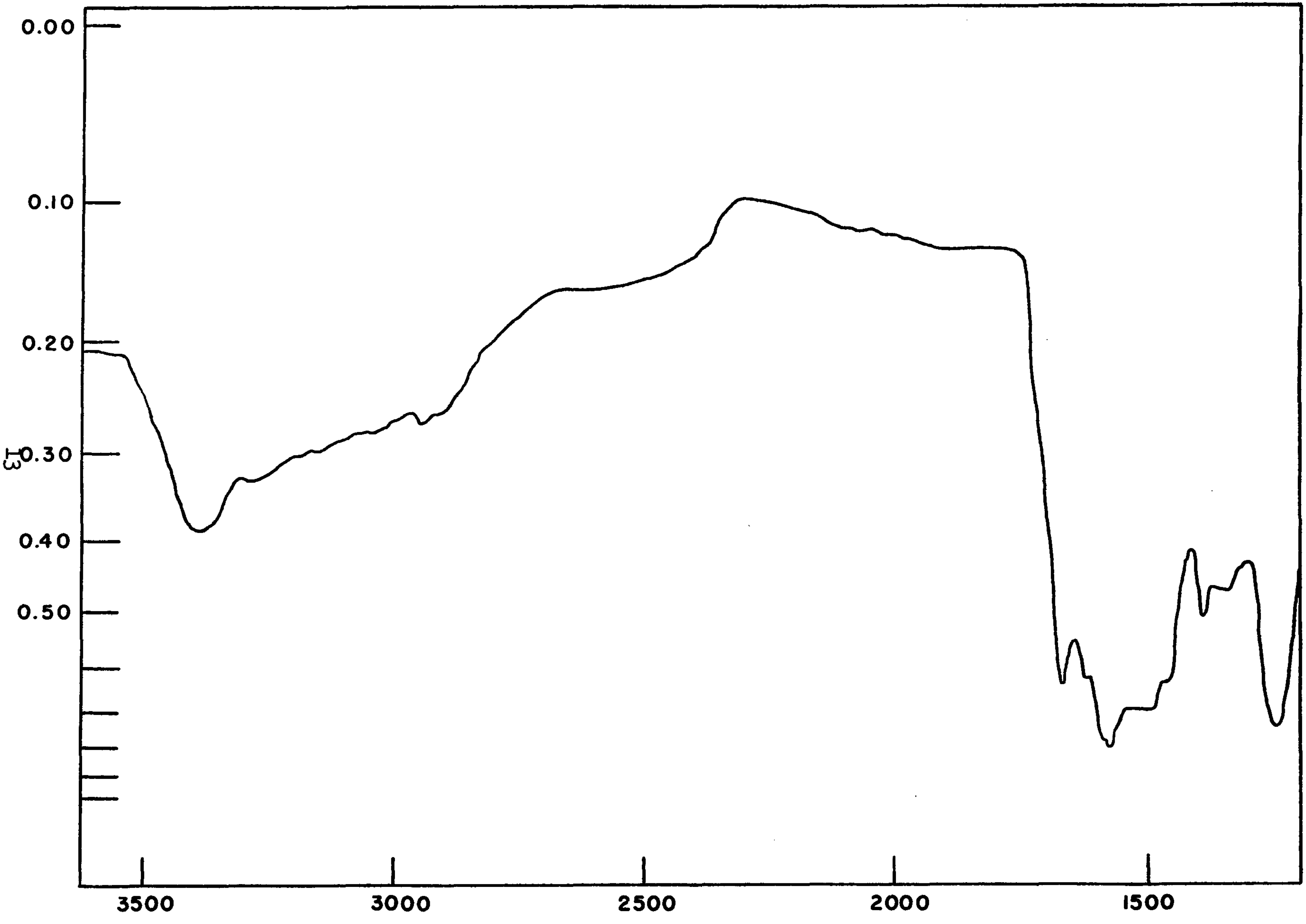


Figure 3. Infrared spectrum (Kbr disc) of product of trifluoroacetic acid catalyzed reaction

The inherent viscosity of the product (0.35% in methanesulphonic acid) was 0.21 dl. g^{-1}. The ir spectrum (Figure 4) shows the absence of the sharp NH_2 doublet characteristic of 1,5-diaminoanthraquinone at 3305 and 3410 cm^{-1}. The broad diacetylbenzene carbonyl peak at 1650 cm^{-1} is also absent. The product did not soften below 500°C but there was a small amount of white sublimate at 300°C.

Anal. Calc. for polymer (open): C, 79.1%; H, 4.4%; N, 7.7%.
(closed): C, 87.8%; H, 3.7%; N, 8.5%.
Found: C, 81.4%; H, 4.0%; N, 8.5%.

In the second example of the polymerization, the reaction was essentially as above, using the same quantities of reactants in the same polymerization tube. The tube was flushed with dry nitrogen and heated to 170°C by immersing in a metal bath. After heating for 6 hr the tube was removed from the bath and allowed to cool to room temperature. The sublimate of 1,4-diacetylbenzene was washed into the bottom of the tube with acetone and the acetone was then removed by blowing dry nitrogen through the tube overnight. Heating was then continued for 3 hr at 170°C.

After cooling, the red brittle plug of product was shaken with dimethylacetamide and found to be 100% soluble. The solution was poured into water which gave a colloidal precipitate. The product was precipitated by adding sodium chloride and heating the solution. The precipitate was collected and air-dried for 60 hr. The infrared spectrum showed the presence of much unreacted 1,5-diaminoanthraquinone and 1,4-diacetylbenzene. The dried product was reintroduced into the tube and reheated for 10 hr at 180°C.

The dark brown product was shaken with dimethylacetamide and the solution filtered. The insoluble material (90%) was found to be soluble in methanesulphonic and concentrated sulphuric acids. The polymer had an inherent viscosity of 0.28 dl. g^{-1} (0.32% solution in concentrated sulphuric acid at 30°C).

4. Future Plans

This work has been discontinued in favor of work concerning laminating resins. The work carried out on the synthesis of polymers from 1,5-diaminoanthraquinone and aralkyldiketones has been written up for publication.

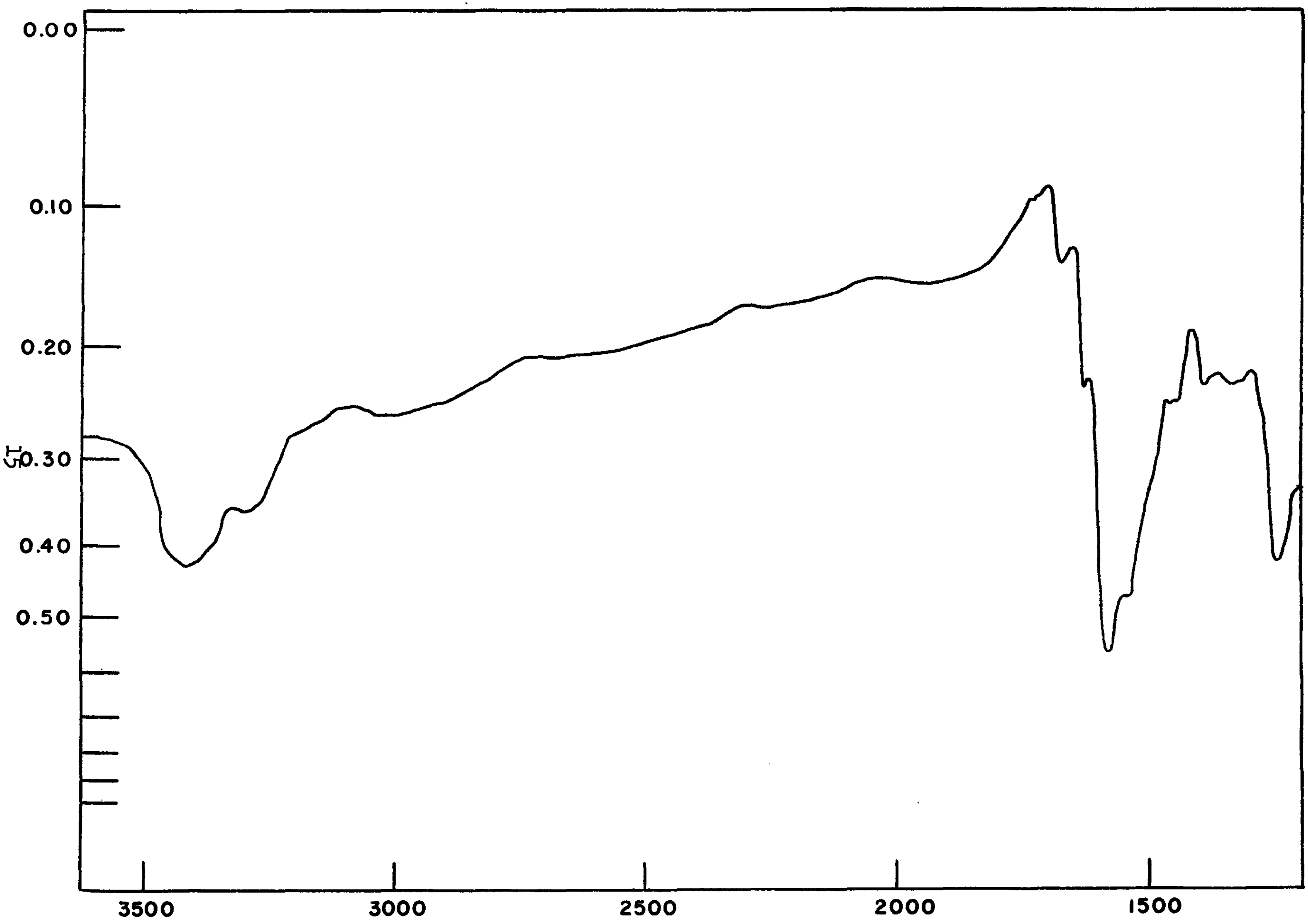


Figure 4. Infrared spectrum (KBr disc) of product of the melt polycondensation

IV. THERMALLY STABLE POLYMER WITH A GRAPHITIC STRUCTURE

1. Introduction

Some results of the work on this project, which is concerned with the preparation and properties of a thermally stable ladder polymer with a graphite-type structure, have been discussed in previous Annual Reports.[2,3]

These reports have outlined the methods used to obtain a prepolymer with an open structure from the condensation between 1,4,5,8-tetraaminoanthraquinone (TAA) and naphthalene-1,8,4,5-diindandione (TK). This polymerization has been carried out in polyphosphoric acid (PPA) and, also, in various organic solvents. Heat treatment of the isolated prepolymer can then be used to complete the ring closures and so obtain the final ladder polymer which has the graphite-type structure. It has been shown[2] that the latter polymer, which is insoluble in both organic solvents and strong acids, possesses good thermal stability. Brittle fibers have been previously obtained from prepolymers having an inherent viscosity of about 0.4.

The present report outlines the final work carried out on this project and describes some experiments directed towards the preparation of a soluble prepolymer of higher molecular weight than that previously obtained. Some experiments concerned with the reductive solubilization and the film forming properties of the prepolymers are also reported.

2. Results and Discussion

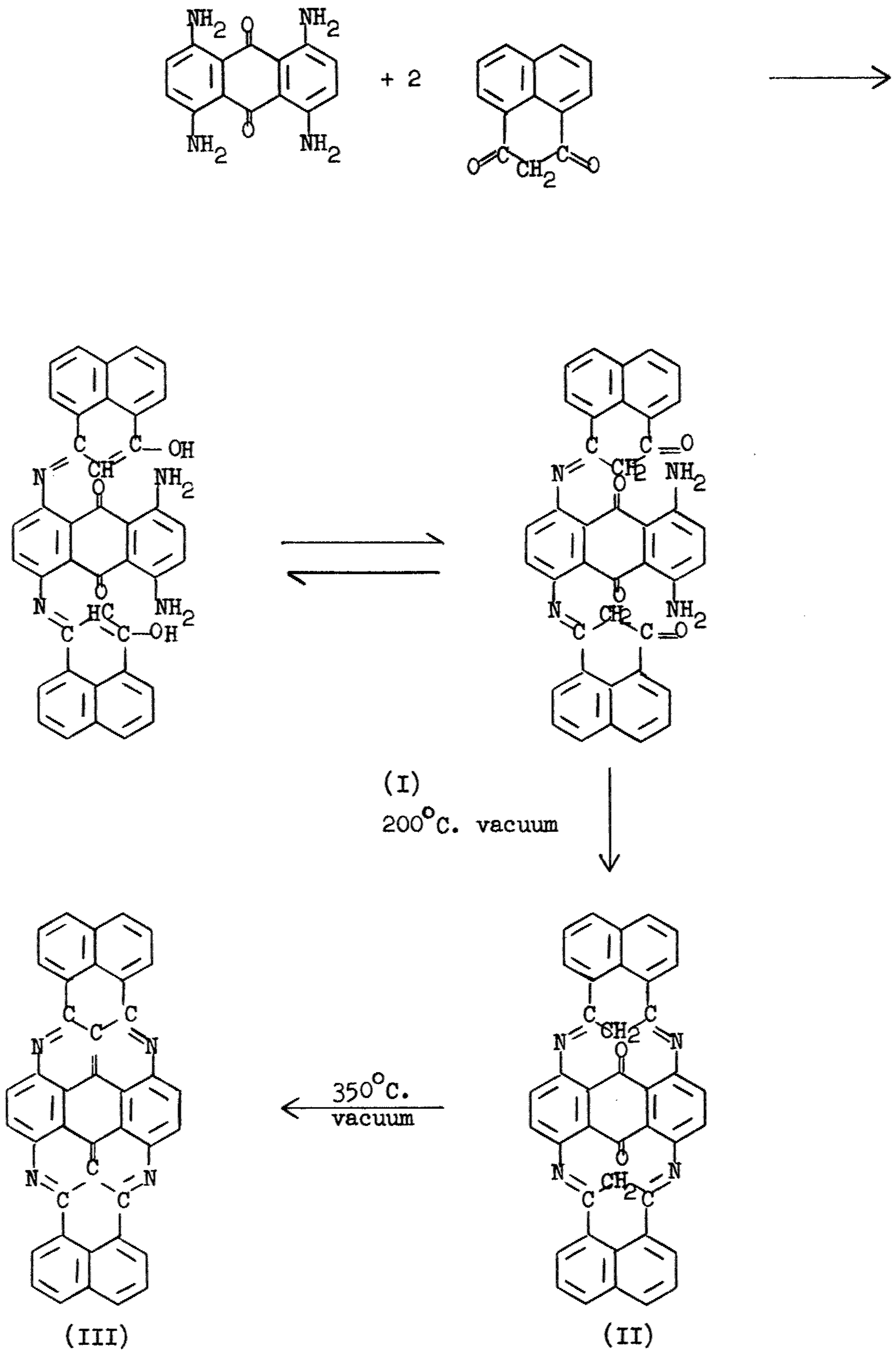
a. Model compounds

The model reaction between 1,4,5,8-tetraaminoanthraquinone and perinaphthalindandione (Equation I), carried out in DMAc containing a small amount of glacial acetic acid, has been previously reported.[2] An initial product having the structure I was obtained. Heat treatment of this isolated product led to cyclization and the formation of a compound with structure III.

When the condensation was carried out in polyphosphoric acid, the black reaction product had an elemental analysis in reasonably close agreement with the data for the open structure product (I in Equation I).

This material was easily solubilized by concentrated sulphuric acid to give a dark brown solution. Unlike the product obtained in DMAc however, the infrared spectra of this material did not show a doublet due to unreacted amine groups. The material obtained in polyphosphoric acid was heated under vacuum, but, again in contrast to the product obtained in DMAc, analysis indicated that the final ring closures had not been completed.

Equation I



b. Polymerization

The condensation of equimolar quantities of 1,4,5,8-tetraaminoanthraquinone (TAA) and naphthalene-1,8,4,5-diindandione (TK) was carried out in polyphosphoric acid (PPA) and also in various organic solvents. The conditions used in these polymerizations and the solubilities and viscosities of the resulting polymers are shown in Tables I and II. The object of these solution polymerizations was to produce a high molecular weight prepolymer with an open structure (IV in Equation II) which could be solubilized, characterized, and perhaps fabricated into a fiber or film. This open structure prepolymer can then be heated, under vacuum, to obtain an initial ladder polymer (structure V in Equation II) and, finally, a completely cyclized ladder polymer with an aromatic, graphite-type structure (VI in Equation II).

A number of polymerizations, carried out in PPA, have been previously reported.[2,3] In these earlier experiments, it was found that if drastic reaction conditions (high reaction temperature, long reaction time), were employed in an attempt to increase the molecular weight of the prepolymer, any increase in the inherent viscosity of the resulting polymer was invariably accompanied by a substantial decrease in its acid solubility.[3] An attempt was made to overcome these problems by using a two-stage polymerization in which a low molecular weight prepolymer was prepared in PPA, and then isolated and purified before being subjected to further heat treatment in this acid (Table I, experiments 1,2,3 and 4). Although not completely successful, this polymerization method did give the highest molecular weight prepolymers obtained during work on this project. However, as shown in Table I (experiments 2 and 4), the solubility of each final polymer was less than 100%. In each stage of these polymerizations a relatively low reaction temperature was employed. An attempt was made to use these conditions in a single stage polymerization (Table I, run 5). This reaction gave prepolymer with an η_{inh} comparable to the highest viscosities previously reported.[2,3] Once again however, the prepolymer was not completely soluble in methanesulphonic acid.

Equation II

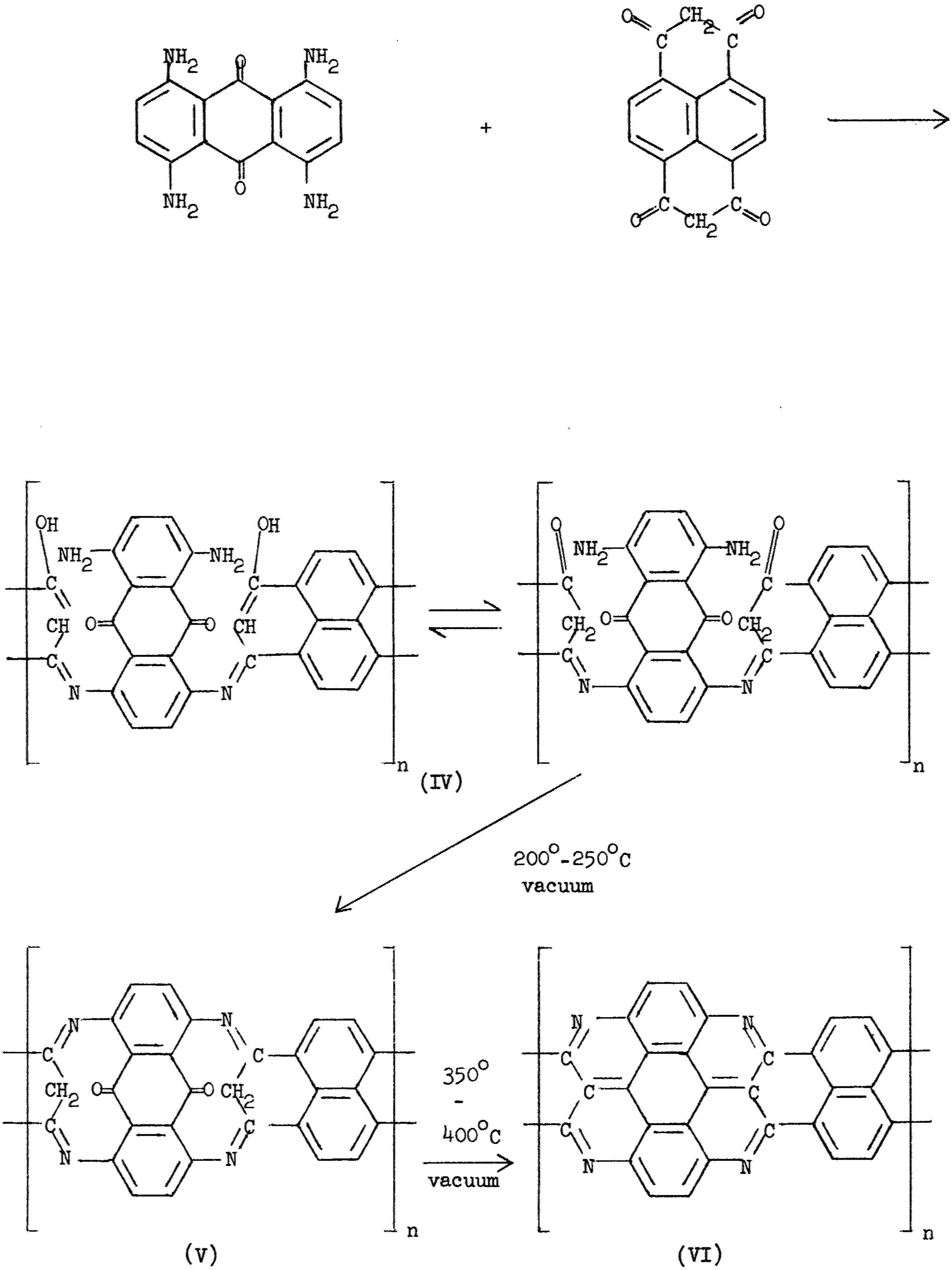


TABLE I

POLYMERIZATION IN POLYPHOSPHORIC ACID

Expt No	PPA g	TAA g	TK g	Temp °C	Time hr	Yield of Prepolymer %	Prepolymer Solubility %	η_{inh} 30°C [a]
1	16	0.268	0.264	25-120 120-145 145	3 1 45	90	100 (CH_3SO_3H)	0.11
2	12	0.244 g of polymer isolated from expt No. 1		25-160 160	2.5 24	-	68 (CH_3SO_3H) 92 (CH_3SO_3H)[b]	0.48 0.74
3	32	0.536	0.528	25-120 120-145 145	3 1 45	100	100 (CH_3SO_3H)	0.15
4	15	0.570 g of polymer isolated from expt No. 3		25-160 160	2.5 24	-	35 (CH_3SO_3H)[b] 30 (CH_3SO_3H)[b]	1.30 1.58
5	16	0.268	0.264	25-120 120-145 145 160	3 1 45 24	100	65 (CH_3SO_3H) 71 (CH_3SO_3H)	0.62 0.44

a) For the soluble fraction of a 0.5% solution.

b) Solution warmed to about 50°C to aid solubilization.

TABLE II

POLYMERIZATION IN ORGANIC SOLVENTS

Expt No	Medium	TAA g	Tk g	Temp $^{\circ}$C	Time hr	Yield of Prepolymer %	Prepolymer Solubility % in CH_3SO_3H	η_{inh}^{a} at 30°C in CH_3SO_3H
6[b]	DMAc/HAc 15 ml/ 2 ml	0.268	0.264	25-120 120-165 165	3 1-1.5 3 days	48	26	0.30
7	DMAc/CF_3COOH 15 ml/ 2 ml	0.268	0.264	25-165 165	4 24	62	100	0.18
8	CH_3SO_3H 15 ml	0.268	0.264	25-120 120-165 165	3 0.5 2 days	73	20	0.36

Solvents: DMAc, N,N,-dimethylacetamide; HAc, glacial acetic acid.

a) For the soluble fraction of a 0.5% solution.

b) The DMAc and HAc used in this experiment were purified before use. See experimental section for details.

In several runs carried out in PPA, but not those reported here, the weight of prepolymer obtained after the usual purification treatment was in considerable excess of the weight representing 100% yield. Further extraction of the finely ground polymer with water, for periods of up to one week, and treatment with a dilute aqueous solution of ammonium carbonate failed to reduce the weight of polymer significantly. Solubilization of the polymer in methanesulphonic acid and filtration of this solution showed that the high impurity content was due to silica stripped from the reaction vessel by the polyphosphoric acid during polymerization. This is most likely to occur when the flask has a scratched surface. Elemental analysis (Table III) indicated that some of the prepolymers reported here contain smaller non-combustible residues. These residues probably contain silica and small amounts of metal contaminants originally present in the polyphosphoric acid. The presence of unburned carbon and polymer in these residues could be responsible for analysis results which do not agree very closely with the calculated data (Table III). Analysis reports, indicating the presence of residues in polymers prepared in organic solvents, further suggest that combustion of these materials during analysis is incomplete.

Despite difficulties in correlating the elemental analysis data with the expected polymer structure, it was found possible to confirm that prepolymer with the open structure (IV) is formed in polymerizations carried out in PPA. Some evidence for the formation of this open-structured prepolymer was obtained by infrared spectroscopy, in particular by the presence of a doublet at 3250 cm^{-1} and 3400 cm^{-1} due to unreacted amine groups on the anthraquinone units. This doublet, which occurs at 3250 cm^{-1} and 3380 cm^{-1} in the TAA monomer,[3] was clearly observed for example in the spectra of the prepolymers obtained in experiments 3 and 5 (Table I). The other main absorption in these spectra, due to carbonyl groups, occurs at 1600 cm^{-1}. Although the doublet due to unreacted amine groups was not observed in the spectra of some prepolymers discussed here, and in a previous report,[3] it seems quite probable that the soluble fractions of these prepolymers in particular have the open structure. The infrared spectra of the prepolymers were not always well resolved due to difficulties in preparing a suitable KBr disc. However, isolation and purification of the acid (CH_3SO_3H and conc. H_2SO_4) soluble fractions from

TABLE III

ELEMENTAL ANALYSIS OF PREPOLYMERS

Calc. for $(C_{30}H_{16}N_4O_4)_n$ (prepolymer with the open structure IV):

% C, 72.58%; H, 3.23%; N, 11.29%; O, 12.90%.

Calc. for $(C_{30}H_{12}N_4O_2)n$ (intermediate ladder polymer with structure V):

% C, 78.25%; H, 2.61%; N, 12.17%; O, 6.96%.

Found:

Expt No	% C	% H	% N	% O	% res
1	67.46	3.41	8.46	12.61	5.74
2	66.67	3.14	7.80	9.66	8.31
3	65.70	3.53	7.72	9.14	8.95
3	65.05	4.22	8.03	14.15	7.58
4	70.26	2.40	8.49	13.31	0.50
5	66.09	3.22	8.76	9.01	8.99
6	70.51	2.77	2.75	21.37	1.67
7	68.08	2.82	5.48	23.10	0.59
8	66.24	2.50	6.11	16.48	0.91

a mixture of twelve different prepolymers gave material whose elemental analysis (see experimental section) was in very close agreement with the data for the open structure polymer.

A number of reasons could be responsible for the formation of insoluble prepolymer fractions: (a) the formation of high molecular weight polymer which cannot be solubilized by methanesulphonic acid; (b) the formation of crosslinked material; (c) the occurrence of side reactions; and (d) the occurrence of a second condensation during polymerization leading to the formation of polymer with a high proportion of repeat units having the ladder structure V(Equation II). It would be expected that repeat units with this structure would be less easily solubilized than those with the open structure. Furthermore, the formation of the closed structure would be most favored in polymerizations carried out at higher temperatures, particularly when relatively long reaction times are employed.

Possibility (a) is not considered to be the sole factor responsible for insolubility, as prepolymers having a soluble fraction with an inherent viscosity as high as 1.58 have been prepared. Among the possible side reactions which could lead to insoluble products, the self-condensation of the tetraamine is considered to be the most likely to occur. It was found that the tetraamine can undergo some type of self-condensation in polyphosphoric acid to give a black powder which is only partially solubilized by conc. H_2SO_4 or methanesulphonic acid, the soluble fraction having a very low inherent viscosity (< 0.1). However, it should be noted that, in contrast to many of the polymerizations reported here and in earlier reports, this reaction was carried out for a long period (24 hr) at a relatively high temperature (185°C). It is thought that the following types of unit are present in this material, although no conclusive evidence was obtained for their presence.

b. Monomers

The syntheses of 1,4,5,8-tetraaminoanthraquinone and naphthalene-1,8,4,5-diindandione will not be described here as the methods employed have been outlined in detail in previous reports.[2,3]

c. Perinaphthalindandione

This diketone was synthesized by condensing 1,8-naphthalic anhydride and diethyl malonate in the presence of fused zinc chloride according to the method described in the literature.[6] After treatment with aqueous ammonia and recovery by precipitation with HCl, the yellow-orange solid was recrystallized from aqueous acetone and then from ethanol. Glacial acetic acid can also be used for recrystallization. The dark yellow purified material starts to decompose at 245° - 250°C (lit.[6] 250°C) and melts at 261°C (uncorr), lit.[6] mp 265°C.

Anal. Calc. for $C_{13}H_8O_2$: C, 79.6%; H, 4.1%; O, 16.3%.
Found: C, 78.63%; H, 4.40%; O, 17.52%.

The 1,8-naphthalic anhydride used in this preparation was purified by a similar procedure to that described earlier for the purification of 1,4,5,8-naphthalenetetracarboxylic anhydride.[3] Pale yellow crystals were obtained after refluxing the diacid with an acetic acid-acetic anhydride mixture, mp 270°C (uncorr) lit.[7] 274°C.

Anal. Calc. for $C_{12}H_6O_3$: C, 72.73%; H, 3.03%; O, 24.24%.
Found: C, 72.91%; H, 3.00%; O, 24.67%.

d. Model reactions

A mixture of 0.268 g of 1,4,5,8-tetraaminoanthraquinone and 0.394 g of perinaphthalindandione was added to 16 g of PPA. The stirred reaction mixture was then heated as follows, under a stream of nitrogen: 25° - 120°C, 3 hr; 120° - 165°C, 1.5 hr; 165°C, 24 hr. The final reaction mixture, which was a dark reddish brown color, was added to water and, after stirring overnight, the precipitated black reaction product was filtered off, washed with water and dried. After extraction with water and ethanol, 0.33 g of product was obtained. This material was heated under vacuum for 10 hr at 240°C and then for 16 hr at 340°C.

Anal. Calc. for $C_{40}H_{24}N_4O_4$ (structure I in equation I):
C, 76.91%; H, 3.85%; N, 8.97%; O, 10.26%.

Anal. Calc. for $C_{40}H_{20}N_4O_2$ (structure II):
C, 81.62%; H, 3.40%; N, 9.52%; O, 5.44%.

Anal. Calc. for $C_{40}H_{16}N_4$ (structure III):
C, 86.96%; H, 2.90%; N, 10.15%.

Found: for initial reaction product:
C, 72.60%; H, 3.06%; N, 8.93%; O, 10.85%;
Res., 3.46%.

Found: for final product: C, 75.19%; H, 2.52%; N, 8.90%; Res., 1.92%.

The presence of a smaller non-combustible residue in the final material, as compared to the initial reaction product, cannot be accounted for.

e. Polymerization

The methods used to prepare, isolate, and purify the graphite prepolymers have been previously outlined in detail,[2,3] and will not be reported here.

The isolation and purification of the soluble fractions from twelve different prepolymers, some of which were prepared earlier,[3] was carried out as follows. The conc. H_2SO_4 soluble fractions and then the $MeSO_3H$ soluble fractions were solubilized and removed from the insoluble parts of the polymer batch by filtration through coarse and then medium porosity glass sinters. The soluble fractions were then precipitated and stirred with water for several days. Following filtration, the polymer was stirred with 10% aqueous ammonium carbonate solution, filtered, washed well with water and dried in a vacuum oven at about 80°C.

Anal. Calc. for $(C_{30}H_{16}O_4N_4)_n$ (prepolymer with the open structure IV):
C, 72.58%; H, 3.23%; N, 11.29%; O, 12.90%.
Found: C, 72.48%; H, 2.40%; N, 10.32%; O, 14.61%.

f. Self-condensation of 1,4,5,8-tetraaminoanthraquinone

The self-condensation of 1,4,5,8-tetraaminoanthraquinone was carried out in polyphosphoric acid, the finely ground tetraamine (0.345 g) being heated in this medium (15 g) at 185°C, for 24 hr, under a nitrogen atmosphere. The temperature was raised to 185°C over a period of 3.5 hr. After precipitation and extraction with water and ethanol, 0.343 g of a black material were isolated, indicating that most, if not all, of the amine had undergone some type of self-condensation reaction. The material was 39% soluble in methanesulphonic acid, the soluble fraction of a 0.5% solution having an η_{inh} of 0.07 at 30°C. Using conc. H_2SO_4 as solvent, the material was 33% soluble, the soluble fraction of a 0.5% solution having an η_{inh} of 0.04 at 30°C. The principal bands in the infrared spectrum (1200 - 4000 cm^{-1}) of this material occurred at 1250 cm^{-1}, 1600 cm^{-1} and 3400 cm^{-1} (KBr disc).

Anal. Calc. for $(C_{14}H_9N_3O_2)_n$ (polymer having units with structure VII):
C, 66.92%; H, 3.59%; N, 16.73%; O, 12.75%.
Anal. Calc. for $(C_{14}H_6N_2O_2)_n$ (polymer having units with structure VIII):
C, 71.80%; H, 2.56%; N, 11.97%; O, 13.68%.
Found: C, 60.29%; H, 3.22%; N, 11.55%; O, 17.15%;
Res., 8.21%.

g. Reductive solubilization of prepolymers

Quantitative reductive solubilization experiments were carried out at about 50°C under an atmosphere of dry, oxygen-free nitrogen. About 0.1 g of the particular prepolymer was added to a mixture of KOH (1 g) and $Na_2S_2O_4$ (1 g) in DMAc (8 ml) and water (2 ml). The mixture was magnetically stirred for one to two days and then filtered through a glass sinter attached to a side arm of the reaction flask. The soluble polymer was recovered by precipitation in water and, after filtration, it was washed well with water and dried.

h. Film formation

A small sublimator connected to an oil pump was employed in the film formation experiments. The polymer solution was placed in a small dish which was in turn placed in the sublimator. The sublimator was evacuated (0.05 - 0.25 mm Hg) and the solution was then heated at 100° - 120°C on an oil bath. Acetone, cooled to between -50°C and -70°C by solid CO_2, was passed through the cold finger of the sublimator. The methanesulphonic acid, which was removed at the rate of approximately 1 ml in 1 hr, readily collected and solidified on the cold finger. Some small pieces of the film obtained were subjected to the following heat treatment, under vacuum, in an attempt to complete the ring closures: 200° - 250°C, 24 hr; 300°C, 22 hr; 360°C, 53 hr.

Anal. Calc. for $(C_{30}H_8N_4)_n$ (final ladder polymer with structure VI):
C, 84.89%; H, 1.89%; N, 13.20%.
Found: C, 73.27%; H, 1.84%; N, 9.58%; Res., 1.38%.

4. Future Plans

Work on this project has now been terminated. The work carried out has been written up and accepted by the Journal of Polymer Science for publication.

V. AROMATIC POLYETHERS, - SULFONES AND -KETONES AS LAMINATING RESINS

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 endcapped with nitriles or having nitriles pending from the main chain can be cross-linked by a catalytic trimerization of the nitriles to thermally stable triazine rings.[9] 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 now report on the work that has been done to find a suitable backbone for such a resin. Aromatic ethers, ketones and sulfones are known to be thermally quite stable. Moieties containing these functional groups were linked together with aromatic acid chlorides in a Friedel-Crafts type polymerization.

2. Results and Discussion

a. Trimerization of benzonitrile

Many catalysts have been reported for the trimerization of perfluoroalkyl nitriles[10] and for aromatic nitriles.[11] In order to find a proper non volatile catalyst we have studied the trimerization of benzonitrile.

i) One hundred mg $FeCl_3$ and 1 g benzonitrile were heated at 190°C for 48 hr. Upon cooling some crystals separated, but the conversion was very low.

ii) One hundred mg $Cu_2(CN)_2$ + 1 g benzonitrile at 190°C for 20 hr. Some solid was formed but the conversion was low.

iii) One hundred mg active Cu powder + 1 g benzonitrile at 160°C for 20 hr. No solid was formed.

iv) One hundred mg Cu metal + 1 g benzonitrile at 160°C for 20 hr. No solid was formed.

v) One hundred mg Cu bronze + 1 g benzonitrile at 160°C for 20 hr. No solid was formed.

vi) One hundred mg barium acetylacetonate + 1 g benzonitrile at 190° for 20 hr. No solid was formed.

vii) A 1/1 complex of $ZnCl_2$ and benzonitrile was prepared by heating $ZnCl_2$ in an excess of benzonitrile. Upon cooling the complex crystallized out. It was heated at 190°C for 50 hr. It was washed with water and then with diethyl ether. The triazine crystallized out. mp 229° - 230°C. The yield was 70%.

viii) One hundred mg dibutyltinmaleate + 1 g benzonitrile were heated at 190°C for 50 hr. The catalyst went into solution. No solid was formed.

ix) One hundred mg active Cu powder and 1 g benzonitrile were heated for 60 hr at 190°C. A yield of ± 30% triazine was obtained.

x) One hundred mg Cu_2O + 1 g benzonitrile was heated at 190°C for 50 hr. Some solid was formed.

xi) One hundred mg NaH (50% in mineral oil) + 5 g benzonitrile were heated under vacuum at 250°C for 19 hr. The reaction mixture was washed with ether and gave 42% of triphenyl triazine. mp 228°C. A dark blue side product was formed. mp 200°C.

The same reaction was carried out at 130°C and gave 35% triazine.

Ten mg NaH + 5 g benzonitrile were heated at 150°C for 20 hr. Very little triazine was formed.

Five hundred mg NaH + 5 g benzonitrile were heated at 150°C for 20 hr. The yield was 75%.

Eight hundred mg of NaH and 17.5 g of benzonitrile were refluxed under nitrogen during 1 hr. The yield was 72%.

xii) One hundred mg CaH_2 + 2 g of benzonitrile were heated at 260°C during 24 hr. No visible reaction took place.

xiii) Forty mg $NaBH_4$ and 1 g of benzonitrile were heated at 260°C for 20 hr. A small amount of triazine was obtained.

It is clear from these experiments that catalysts which gave good results for the perfluoroalkyl nitriles[10] are poor catalysts for the trimerization of aromatic nitriles. Usually a much higher reaction temperature is required.

b. Model reactions

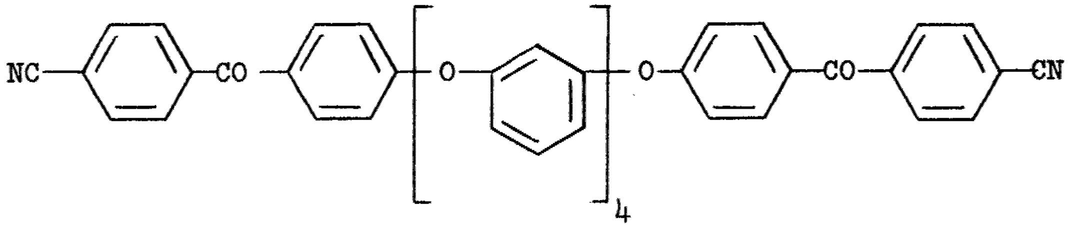
i) Benzoylation of m-hexaphenyl ether with p-cyanobenzoyl chloride

A model reaction was carried out to see if p-cyanobenzoyl chloride would give the desired endcapping. m-Hexaphenyl ether (5.3 g) and p-cyanobenzoyl chloride (3.64 g) were dissolved in 100 ml of dry 1,2-dichloroethane. $AlCl_3$ (7 g) was added and the mixture was refluxed under dry nitrogen during 4 hr. The mixture was cooled and poured into a large excess of methanol. It was reprecipitated twice from tetrahydrofuran into methanol. Yield 60%. mp 130° - 133°C. Sample JVB-18.

Anal. Calc.: C, 78.38%; H, 4.05%; N, 3.14%.

Found: C, 79.31%; H, 4.22%; N, 3.17%.

The following structure was attributed to the product, since the analysis shows clearly that only two molecules of p-cyanobenzoyl chloride reacted.



Addition of a catalyst was not required for the trimerization of the nitrile endgroups. Some residual aluminum compounds seem to catalyze this reaction. A heating period of 20 hr at 220°C under nitrogen gave a 66% yield of THF insoluble material, where the starting material was very soluble in this solvent. The infrared spectrum showed the presence of residual unreacted endgroups. (Figure 5). Since phenyl and triazine rings have a very similar absorption in infrared, we were unable to identify the triazine ring positively.

Analysis of crosslinked product: C, 79.88%; H, 4.43%; N, 3.04%.

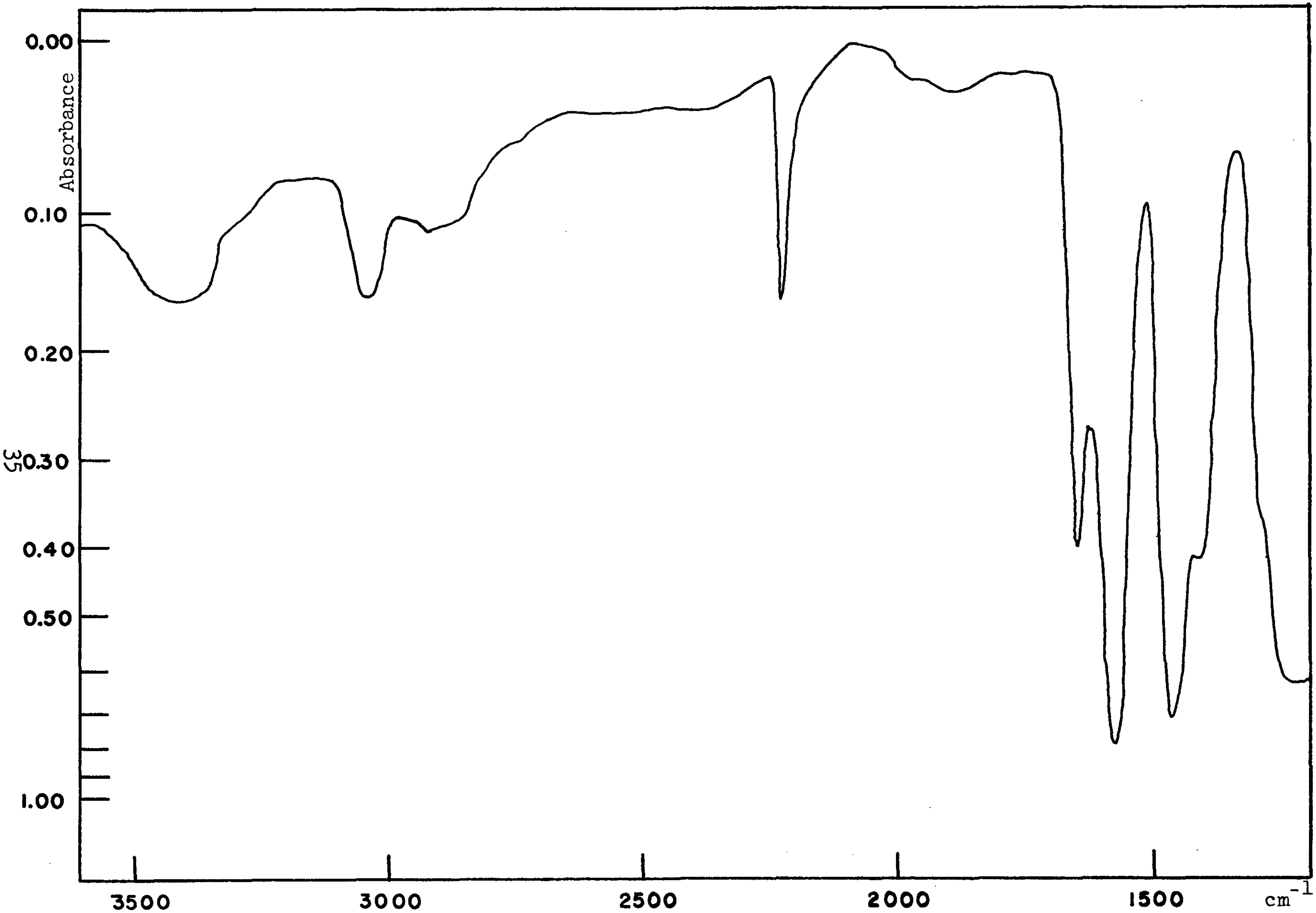
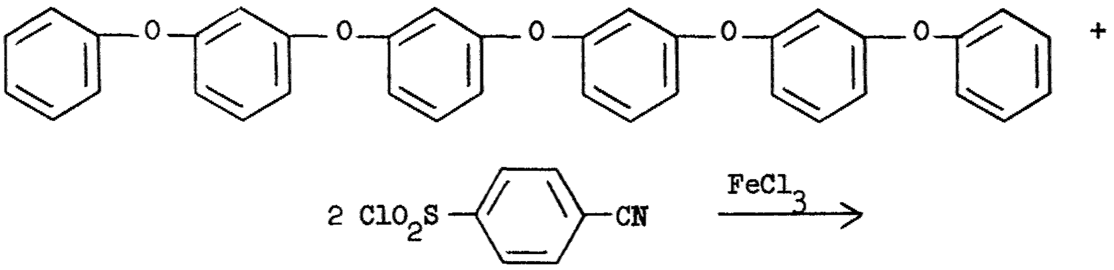


Figure 5. Infrared spectrum in KBr for model compound JVB-18

ii) Sulfonation of m-hexaphenyl ether with p-cyanobenzenesulfonyl chloride



Hexaphenyl ether (5.39 g), p-cyanobenzenesulfonyl chloride (4.03 g) and $FeCl_3$ (100 mg) were dissolved in 10 ml nitrobenzene and heated under dry nitrogen at 170°C for 20 hr. The mixture solidified upon cooling. Some of it did not dissolve in $CHCl_3$ and seemed to be cross-linked. The $CHCl_3$ solution was washed with water to remove the $FeCl_3$ after which the $CHCl_3$ was removed. We obtained a thick oil which consists of 4 products. These products have not been separated.

c. Polymerizations of m-hexaphenyl ether with isophthaloyl chloride

i) Run No. 1

Isophthaloyl chloride (4.96 g) and $AlCl_3$ (8 g) were dissolved in 100 ml of dry nitrobenzene. Hexaphenyl ether (14.93 g) was added slowly. The reaction mixture was then heated under dry nitrogen at 80°C during 15 hr. The polymer was precipitated into a large excess of methanol. It was reprecipitated twice from THF into methanol. Yield 75%. $\eta_{inh} = 0.07$ in DMF at 30°C. Sample JVB-8.

ii) Run No. 2

To a suspension of 60 millimoles of $AlCl_3$ (8 g) and 2 millimoles of p-cyanobenzoyl chloride (0.331 g) in 100 ml dichloroethane was added 25 millimoles of the hexaphenyl ether (13.465 g) in 100 ml dichloroethane. The mixture was stirred under dry nitrogen for 15 min and refluxed for 1 hr. It was cooled and 24 millimoles of isophthaloyl dichloride (4.872 g) was added in 100 ml dichloroethane. It was stirred for 30 min and refluxed for 4 hr. It was then precipitated into a large excess of methanol and reprecipitated from THF into methanol. Yield = 90%. mp 125° - 130°C. η_{inh} = 0.094 in DMAc. Infrared showed no CN band. (Figure 6). Sample submitted as JVB-14.

Anal. Calc. for $C_{44}H_{28}O_7$: C, 79.03%; H, 4.22%; O, 16.75%.

Found: C, 79.46%; H, 4.35%; O, 16.00%.

Crosslinking experiments:

Three g of the polymer were mixed with 0.5 g of $ZnCl_2$ and heated at 210°C for 20 hr. The reaction product was ground and extracted with water and dimethylacetamide. It was dried under vacuum. Sample submitted as JVB-15. The TGA curves for the prepolymer and the crosslinked polymer are given in Figure 7.

Three g of the polymer were heated without catalyst at 245°C during 20 hr. The product was ground and extracted with THF. The product was 99% insoluble in THF. Traces of aluminum compounds seem to catalyze the trimerization of the endgroups. Sample JVB-16.

Analysis of crosslinked product:

Calculated: C, 79.03%; H, 4.22%.

Found: C, 80.13%; H, 4.47%.

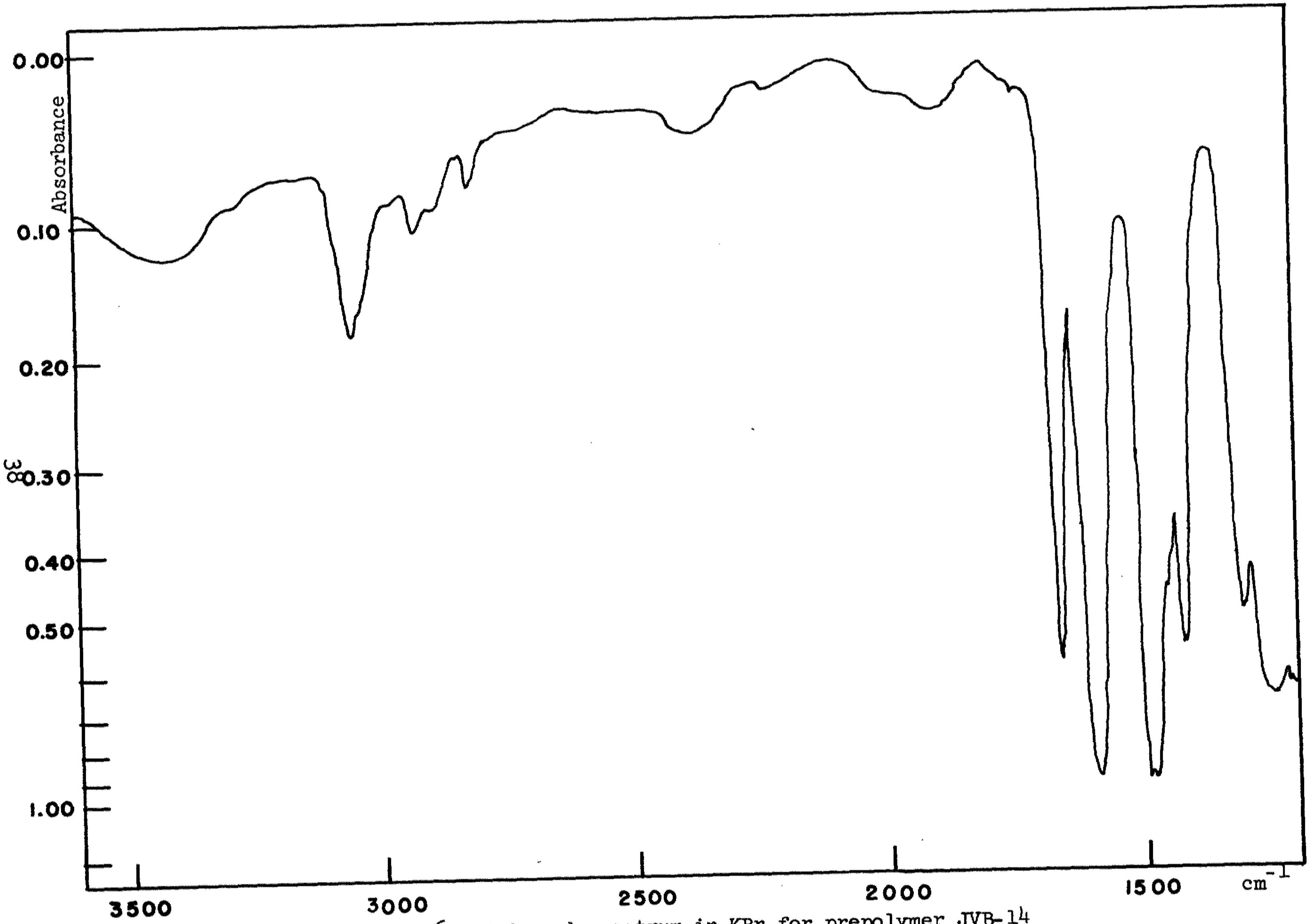


Figure 6. Infrared spectrum in KBr for prepolymer JVB-14

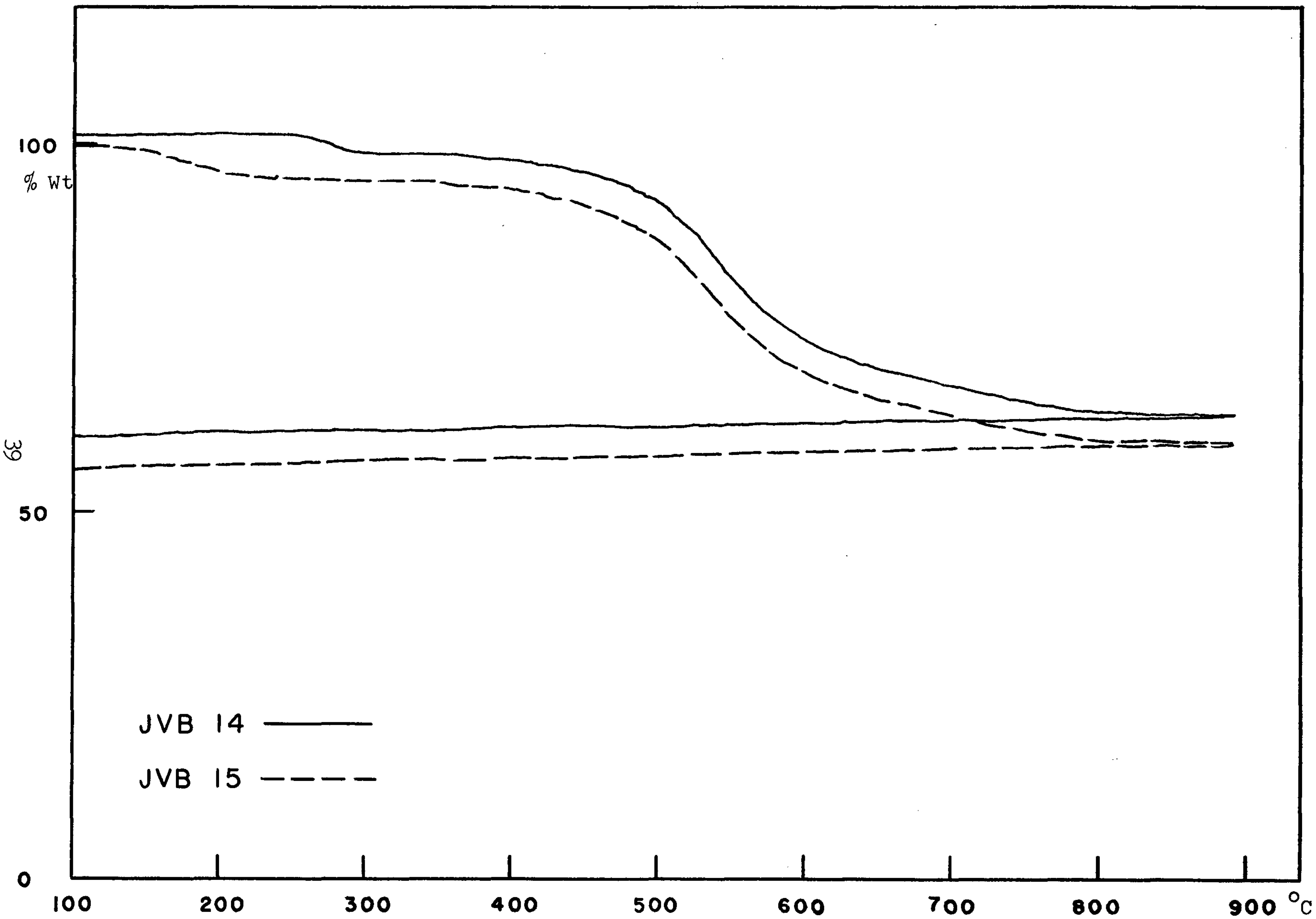


Figure 7. TGA curve for prepolymer JVB-14 and for crosslinked polymer JVB-15

iii) Run No. 3. Reaction with terephthaloyl chloride

Same reaction procedure as for Run No. 2 but with terephthaloyl chloride. The reaction product was largely crosslinked and insoluble in organic solvents. It was extracted with DMF and precipitated in methanol. The soluble product has an inherent viscosity of 0.075 in DMF at 30°C. Sample submitted as JVB-19-A.

Analysis of the soluble fraction:

Calculated for $C_{44}H_{28}O_7$: C, 79.03%; H, 4.22%.
Found: C, 79.38%; H, 4.48%.

Crosslinking experiment:

Three g of the polymer were heated at 200°C during 20 hr. The product was completely insoluble after this heating period. Sample submitted as JVB-19-B.

Analysis of the crosslinked product:

Calculated: C, 79.03%; H, 4.22%.
Found: C, 80.05%; H, 4.39%.

The TGA curves for the prepolymer and the crosslinked polymer are given in Figure 8. The crosslinking resulted in a decreased penetration in a softening test measured in a Vicat apparatus. This is shown in Figure 9.

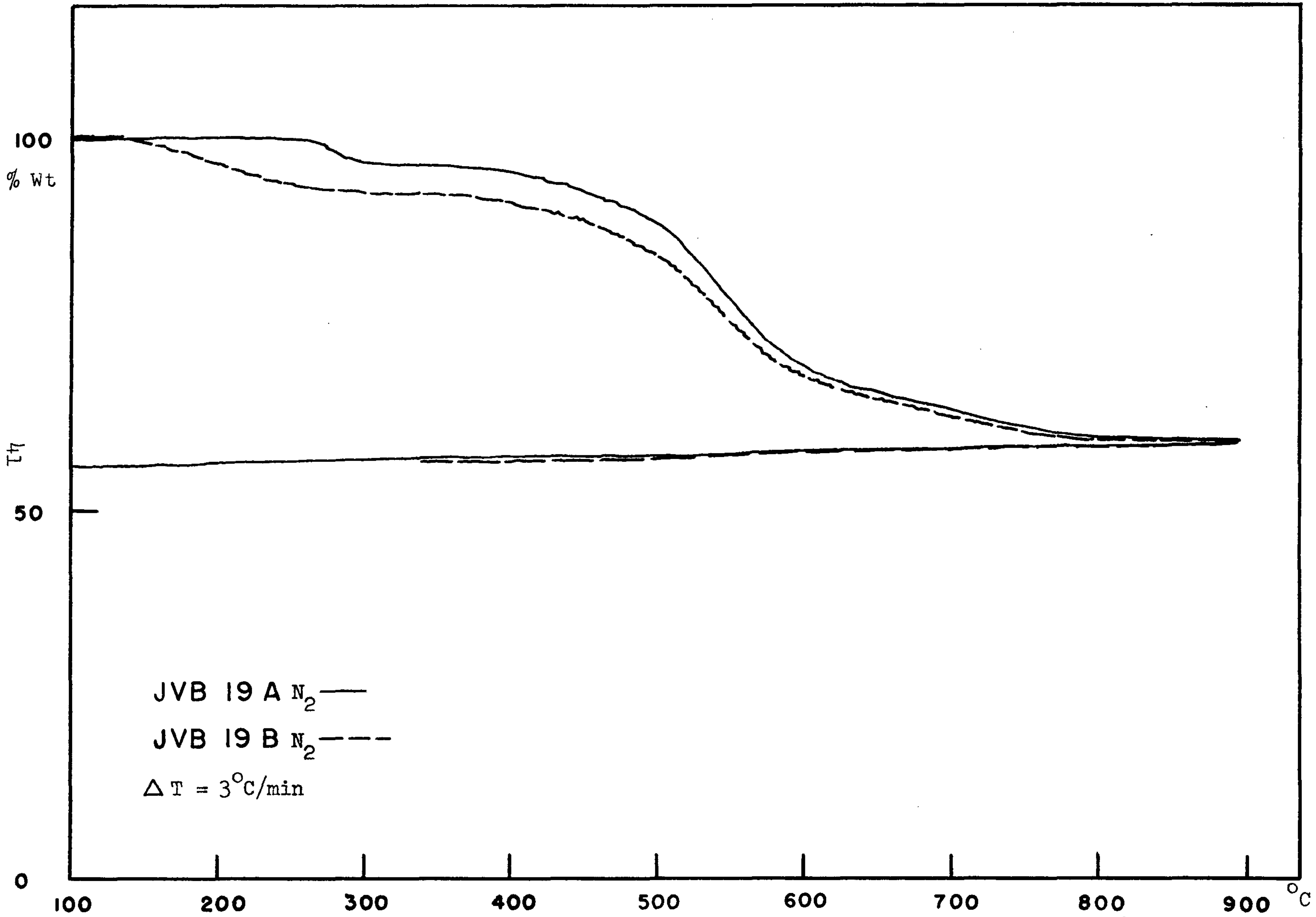


Figure 8. TGA curve for prepolymer JVB-19-A and crosslinked polymer JVB-19-B

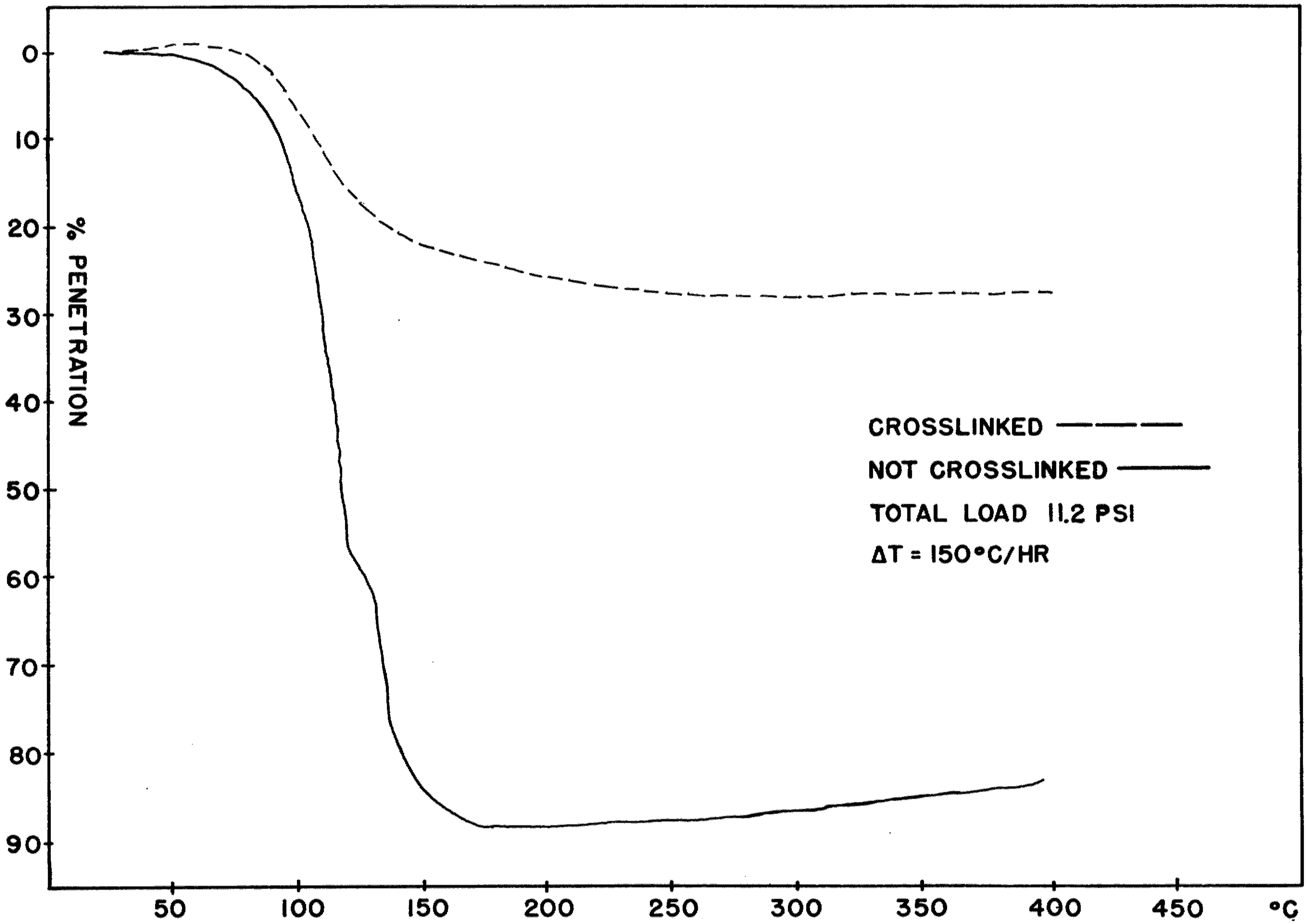


Figure 9. Softening curves for polymers JVB-19-A and JVB-19-B measured by a Vicat apparatus

iv) Run No. 4. Reaction with isophthaloyl chloride

The same procedure was used as for Run No. 2 and Run No. 3 but the amount of p-cyanobenzoyl chloride was decreased to 100 mg. The obtained product had a slightly higher viscosity. η_{inh} = 0.128 in DMF at 30°C. Sample JVB-20.

Anal. Calc. for $C_{44}H_{28}O_7$: C, 79.03%; H, 4.22%.
Found: C, 79.35%; H, 4.31%.

Crosslinking experiment:

Three g of the polymer was heated at 225°C during 25 hr. The resulting product was completely insoluble in THF, DMF and DMAc. Sample submitted as JVB-20-A.

Analysis of crosslinked polymer:

Calculated: C, 79.03%; H, 4.22%.
Found: C, 80.23%; H, 4.19%.

The TGA curve is given in Figure 10.

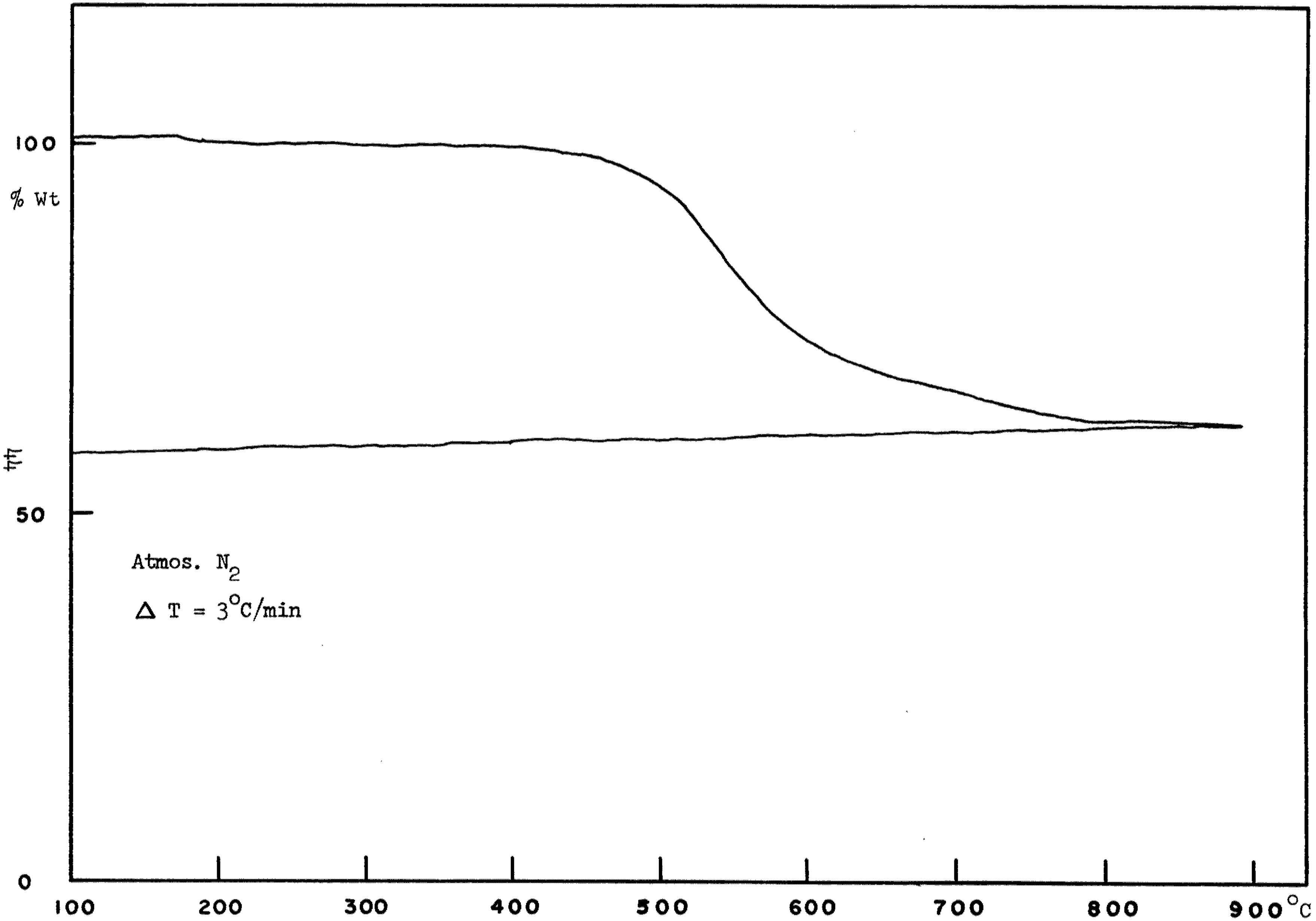


Figure 10. TGA curve for crosslinked polymer JVB-20-A

v) Run No. 5. Reaction with isophthaloyl chloride

Same reaction procedure as No. 2 but nitrobenzene was used as a solvent. The reaction temperature was kept at 65°C during 4 hr. η_{inh} = 0.03 in DMF at 30°C. Sample JVB-21.

vi) Run No. 6. Reaction with isophthaloyl chloride

Same reaction procedure as for Run No. 2 but 1 g $FeCl_3$ was used as a catalyst. η_{inh} = 0.03 in DMF at 30°C. Sample JVB-22.

Discussion: Impurities in the hexaphenyl ether made it impossible to obtain higher molecular weight prepolymers. However, it was possible to crosslink these nitrile endcapped prepolymers by heating them at temperatures of 200° - 250°C without adding catalysts. Since these polymers are low melting it was thought that polymers of m-triphenyl ether might have the same advantageous property. Since triphenyl ether can be purified more easily it was hoped to get higher molecular weight polymers from these products. It was found that dichloroethane as a solvent and $AlCl_3$ as a catalyst gave the best results in the polymerization reaction.

d. Synthesis of triphenyl ethers

i) Synthesis of m-triphenyl ether

In 300 ml toluene, 0.6 mole of phenol was dissolved. Six tenths mole of KOH (85%) was added and the water was distilled off during 2 hr. After this the toluene was distilled off and 200 mg of Cu powder and 1 g of CuCl were added. A solution of 0.3 mole of m-dibromobenzene in 100 ml of diglyme was added dropwise at 80°C. The diglyme was distilled off and the residue was kept at 180°C overnight. The mixture was cooled and extracted with ether. The product was purified by vacuum distillation and recrystallized from ether. Yield = 57%. Sample JVB-30. bp 157°C at 0.6 mm. mp 59°C. Literature 61.5°C.[12]

ii) Synthesis of linear triphenyl ether

The reaction procedure is the same but p-dibromobenzene was used. Yield = 50%. Sample JVB-31. bp 148°C at 0.06 mm. mp 77°C, Literature 77°C.[13]

e. Polymers from meta and linear triphenyl ether with isophthaloyl chloride

i) Run No. 1. Polymerization with isophthaloyl chloride

Ten millimoles of m-triphenyl ether, ten millimoles of isophthaloyl chloride and 34 mg of p-cyanobenzoyl chloride were dissolved in 100 ml of dichloroethane. Thirty millimoles of $AlCl_3$ were added and the mixture was stirred at room temperature under N_2 during 20 hr. A precipitate was formed during the reaction. It was filtered off, ground and washed with methanol. It seemed to be a cross-linked polymer and was almost completely insoluble in H_2SO_4. The filtrate was poured into methanol. The precipitated polymer had an $\eta_{inh} = 0.14$ in H_2SO_4. It melted at $165^\circ - 170^\circ C$. Only 0.5 g of this soluble material was obtained. Sample JVB-35. The infrared spectrum is given in Figure 11.

ii) Run No. 2. Polymerization with isophthaloyl chloride

Same procedure was used but no endgroups were added. The resulting polymer was again insoluble due to crosslinking. Reaction on the middle phenyl ring seemed to occur to some extent and this will cause crosslinking when high molecular weight polymers are formed. Lowering of the reaction temperature might prevent this unwanted side reaction. We have used cooling at the beginning of the reaction in Run No. 3, because the reaction mixture usually warms up when the $AlCl_3$ is added. Sample JVB-36.

iii) Run No. 3. Polymerization with isophthaloyl chloride

Same procedure as for Run No. 1 but no endgroups were added and the temperature was kept below $20^\circ C$ during the whole reaction time. This run resulted again in completely insoluble material. Sample JVB-37.

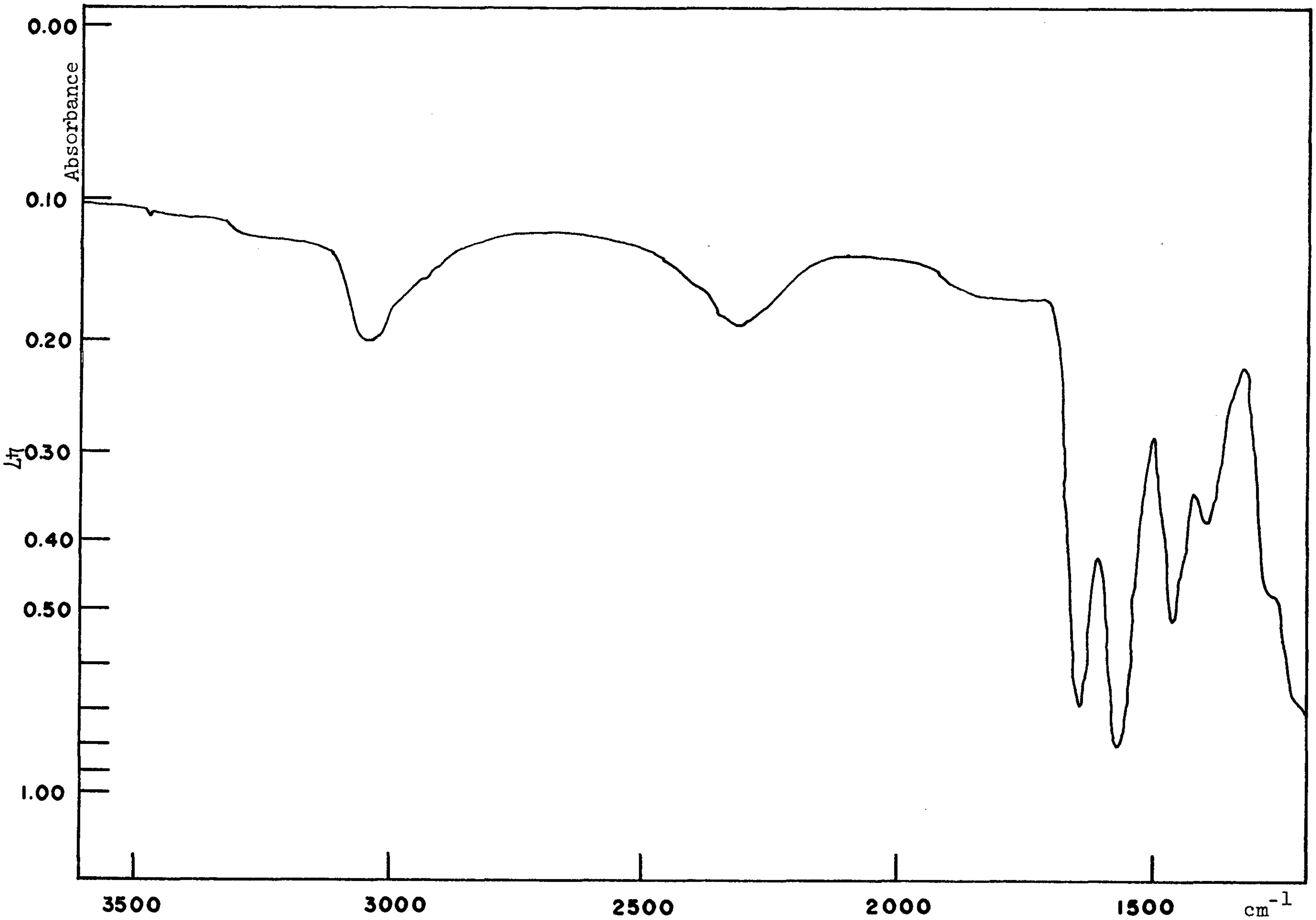


Figure 11. Infrared spectrum from a film for polymer JVB-35

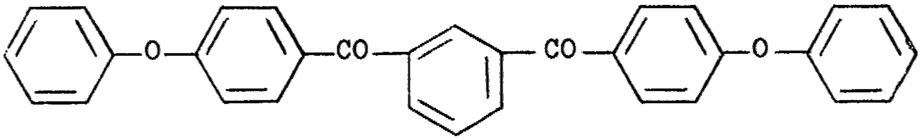
iv) Run No. 4. Polymerization with isophthaloyl chloride

Ten millimoles of linear triphenyl ether, 10 millimoles of isophthaloyl chloride and 35 mg of p-cyanobenzoyl chloride were dissolved in 100 ml dichloroethane. Thirty millimoles of $AlCl_3$ were added under cooling. The mixture is stirred at room temperature under N_2 during 20 hr. The experiment resulted again in highly cross-linked insoluble material. Sample JVB-39.

Discussion: The middle phenyl ring seems to be too reactive to prevent the formation of crosslinks. Only low molecular weight polymers of $\eta_{inh} = 0.14$ were obtained that were soluble and moldable. Higher polymerization degrees resulted in insolubility due to crosslinking. The yield of soluble and moldable material was too low to be useful.

f. Model reactions

The synthesis of the following compound was described in the 1971 annual report, AFML-TR-70-6, Part II, p. 84.

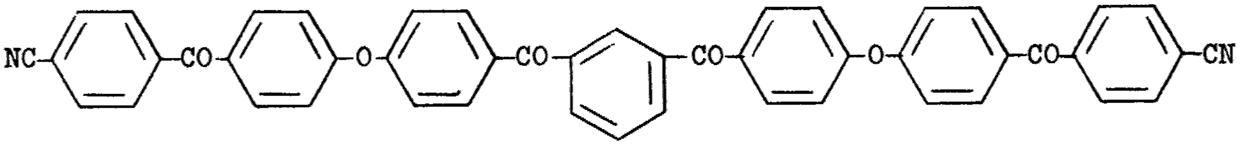


mp 110° - 111°C. Yield 66%. ir C=O at 1655 cm^{-1}

Anal. Calc.: C, 81.68%; H, 4.71%; O, 13.60%.

Found: C, 81.26%; H, 4.73%; O, 13.83%

i) Benzoylation with p-cyanobenzoyl chloride



0.031 mole of p-cyanobenzoyl chloride were dissolved in 75 ml of dichloroethane and 0.070 mole of $AlCl_3$ were added. A solution of 1,3-bis(p-phenoxybenzoyl)benzene (7.15 g or 0.015 mole) in dichloroethane was added under cooling. The mixture was stirred and allowed to stand overnight. It was then refluxed for 3 hr. The mixture was poured into 200 g of crushed ice and 100 ml of conc. HCl. The organic layer was separated and the aqueous layer was extracted twice with 100 ml of $CHCl_3$. The combined solution was dried over Na_2SO_4 and the solvent was removed. The product was recrystallized from $CHCl_3$. mp 185° - 192°C. Yield 60%. ir C≡N at 2240 cm^{-1}; C=O at 1655 cm^{-1}.

Anal. Calc.: C, 79.11%; H, 3.87%; N, 3.84%; O, 13.17%.

Found: C, 80.12%; H, 4.19%; N, 2.33%; O, 13.36%.

More $AlCl_3$ is needed for a complete reaction.

Six moles of $AlCl_3$ and a reaction time of 24 hr at room temperature gave the following analysis; after recrystallization from DMF. (Sample JVB-7).

Found: C, 79.19%; H, 4.04%; N, 4.14%. Yield 90%. mp 255° - 256°C.

The model compound was heated at 280°C during 20 hr in a sealed tube. This did not result in insolubility. Five percent of anhydrous $ZnCl_2$ was added and a similar heating period gave an 85% yield of H_2SO_4 insoluble material. The infrared spectrum showed no residual nitrile groups. The H_2SO_4 soluble fraction had an η_{inh} = 0.24 in H_2SO_4 at 30°C (0.87 g/100 ml).

ii) Synthesis of 5-Cyanoisophthalic acid

Crude 5-aminoisophthalic acid (Eastman Kodak 85%) was purified by recrystallization from water. Sixty and three-tenths g of the pure aminophthalic acid was dissolved in 85 ml of HCl_{conc} and 85 ml of water. The mixture was cooled to 0°C and 25 g of $NaNO_2$ dissolved in 50 ml of water were added dropwise under stirring. The reaction temperature was kept between 0° - 5°C.

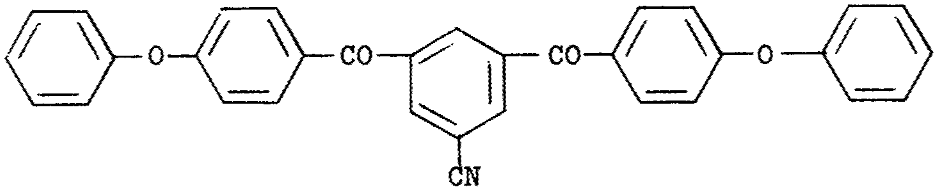
The diazonium chloride solution is then poured into the following solution:

One mole of NaCN and 33 g of CuCN were dissolved in 200 ml of water. When all was dissolved 41.3 g of $NaCO_3.H_2O$ were added. The mixture was heated to 60°C and the diazotized solution was added under stirring. A few drops of octanol were added to control excessive foaming. The mixture was cooled and HCl_{conc} was added until no more precipitate was formed. It was filtered off and treated with 200 ml conc NH_4OH to dissolve the acid. This solution was acidified again and the precipitate that was formed was recrystallized from 800 ml of water. Yield = 25 g after recrystallization. mp = 253°C. The ir spectrum gave a strong C≡N at 2230 cm^{-1}.

iii) Synthesis of 5-Cyanoisophthaloyl chloride

Twenty-five g of the acid were refluxed in 100 ml of purified thionyl chloride during 4 hr. A few drops of DMF were added. The product was purified by vacuum distillation. bp = 121°C at 0.25 mm. mp = 37° - 38°C. The ir spectrum gave a strong C≡N at 2230 cm^{-1}. (Figure 12).

iv) Reaction of 5-cyanoisophthaloyl chloride with excess diphenyl ether



Ten millimoles of 5-cyanoisophthaloyl chloride, 200 millimoles of diphenyl ether and 30 millimoles of $AlCl_3$ were stirred at room temperature under nitrogen during 24 hr. The mixture was washed with water to remove the $AlCl_3$, $CHCl_3$ was added and the solution was dried over Na_2SO_4. The chloroform was evaporated and the excess of diphenyl ether was distilled off under vacuum. Diethyl ether was added to solidify the residue. The solid residue was then recrystallized from ethanol/chloroform (1/1). Yield = 65%. mp = 167° - 168°C.

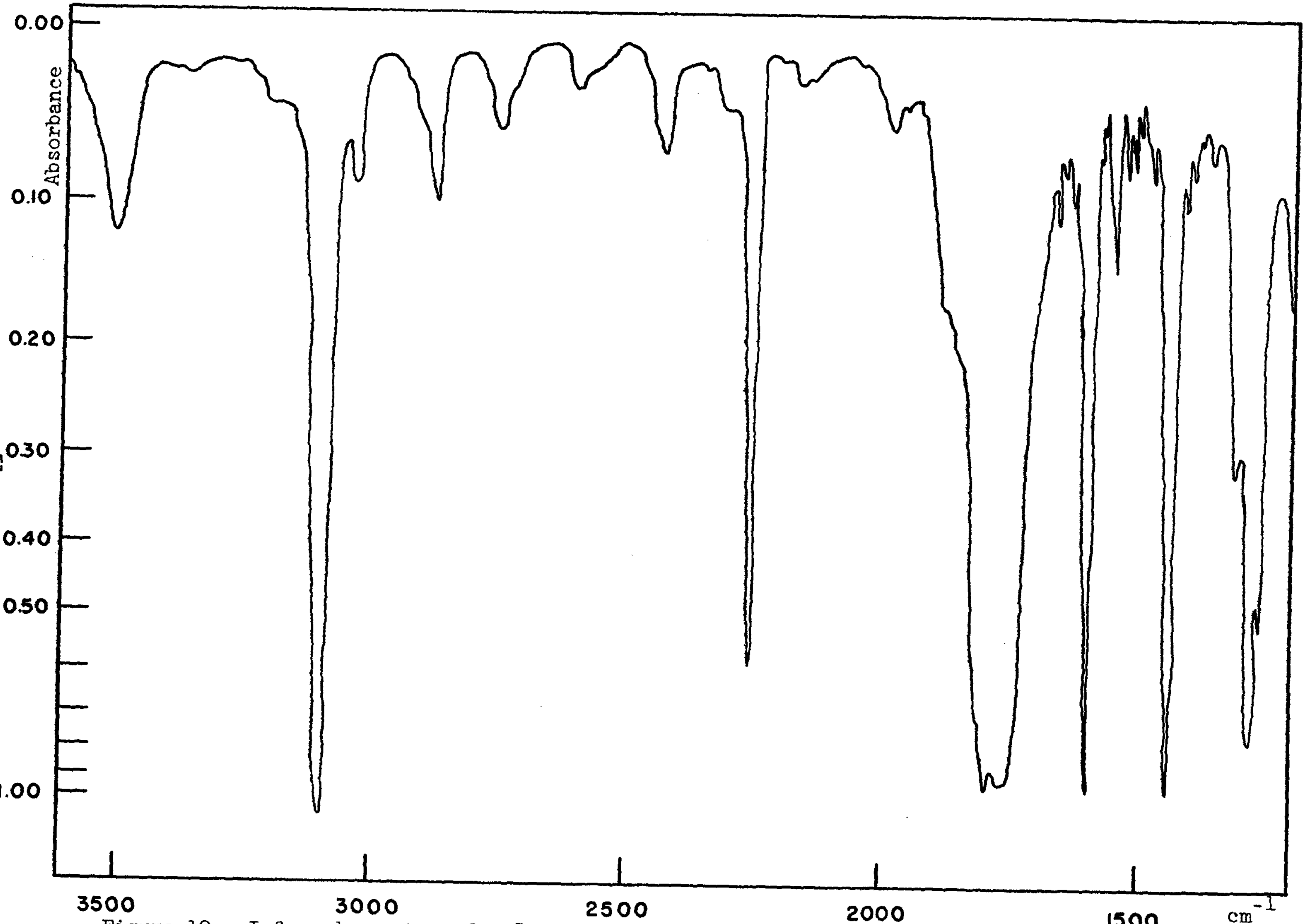


Figure 12. Infrared spectrum for 5-cyanoisophthaloyl chloride from a film between NaCl plates

Anal. Calc.: C, 79.99%; H, 4.27%; N, 2.83%; O, 12.91%.
Found: C, 78.44%, 77.40%, 77.83%.
H, 4.27%, 4.19%, 4.16%.
N, 2.63%, 2.63%, 2.58%.
O, 12.30%.

The carbon value was found to be quite low. However, the total of the four elements (as an average) did not exceed 97%. The following analysis resulted when this was taken into account.

C, 80.16%; H, 4.28%; N, 2.76%; O, 12.76%.

The ir spectrum is given in Figure 13.

g. Polymerization of diphenyl ether with iso- and terephthaloyl chloride

i) Run No. 1. Polymerization with terephthaloyl chloride

Twenty-five millimoles of diphenyl ether and 25 millimoles of terephthaloyl chloride were dissolved in 200 ml dichloroethane. Ten g of $AlCl_3$ were added and the mixture was stirred at room temperature under N_2. A precipitate was formed after 5 min. The precipitate was filtered off after 20 hr and washed with H_2O to remove the $AlCl_3$. It was dried under vacuum at 70°C. The polymer was almost completely soluble in H_2SO_4. $\eta_{inh} = 0.66$ in H_2SO_4 at 30°C. mp > 370°C. Sample submitted as JVB-24. The TGA curve is given in Figure 14.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 78.25%; H, 4.29%; Res., 1.86%
Anal. corrected for Res.: C, 79.73%; H, 4.34%.

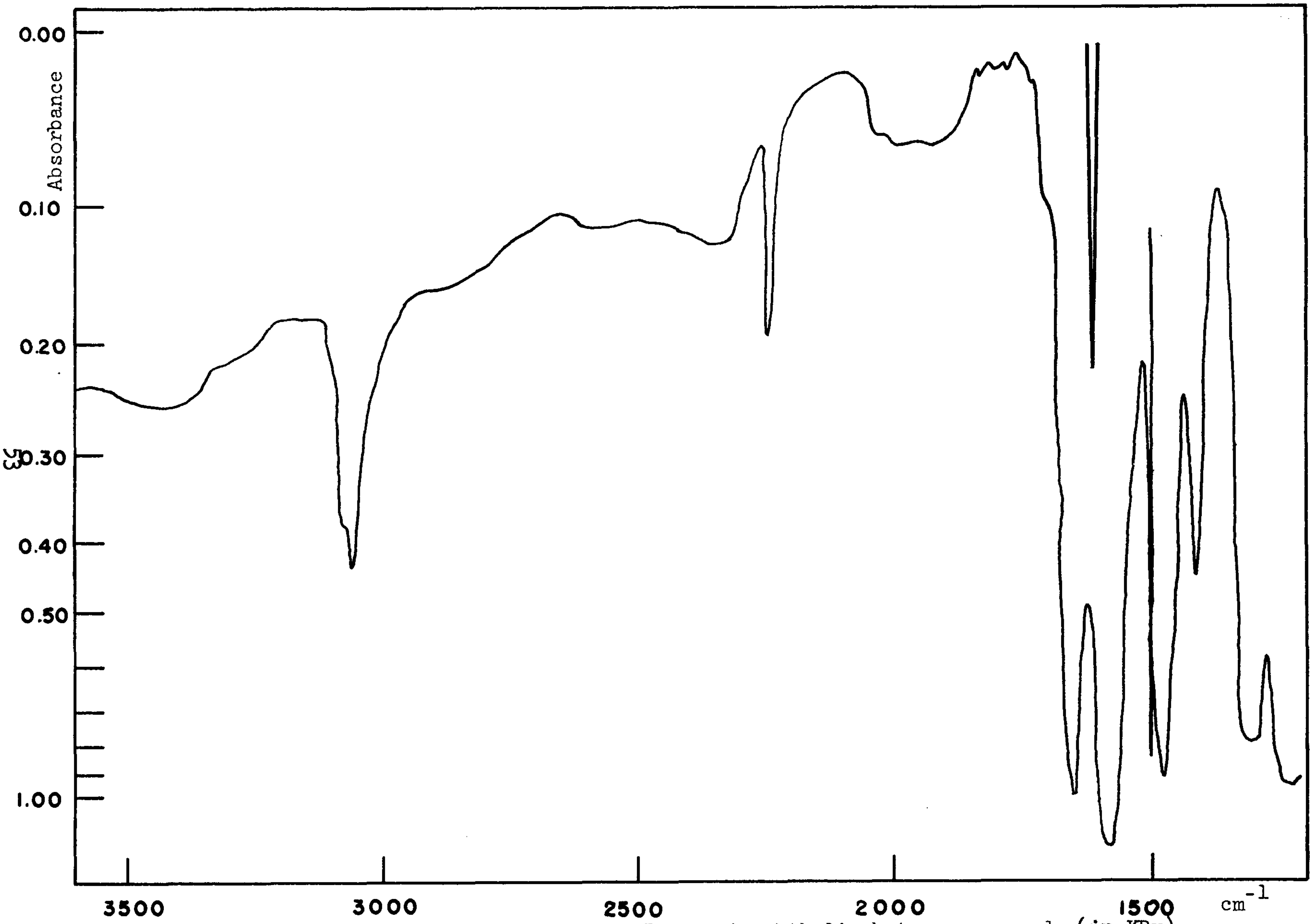


Figure 13. Infrared spectrum for the 5-cyanoisophthalic ketone compound. (in KBr)

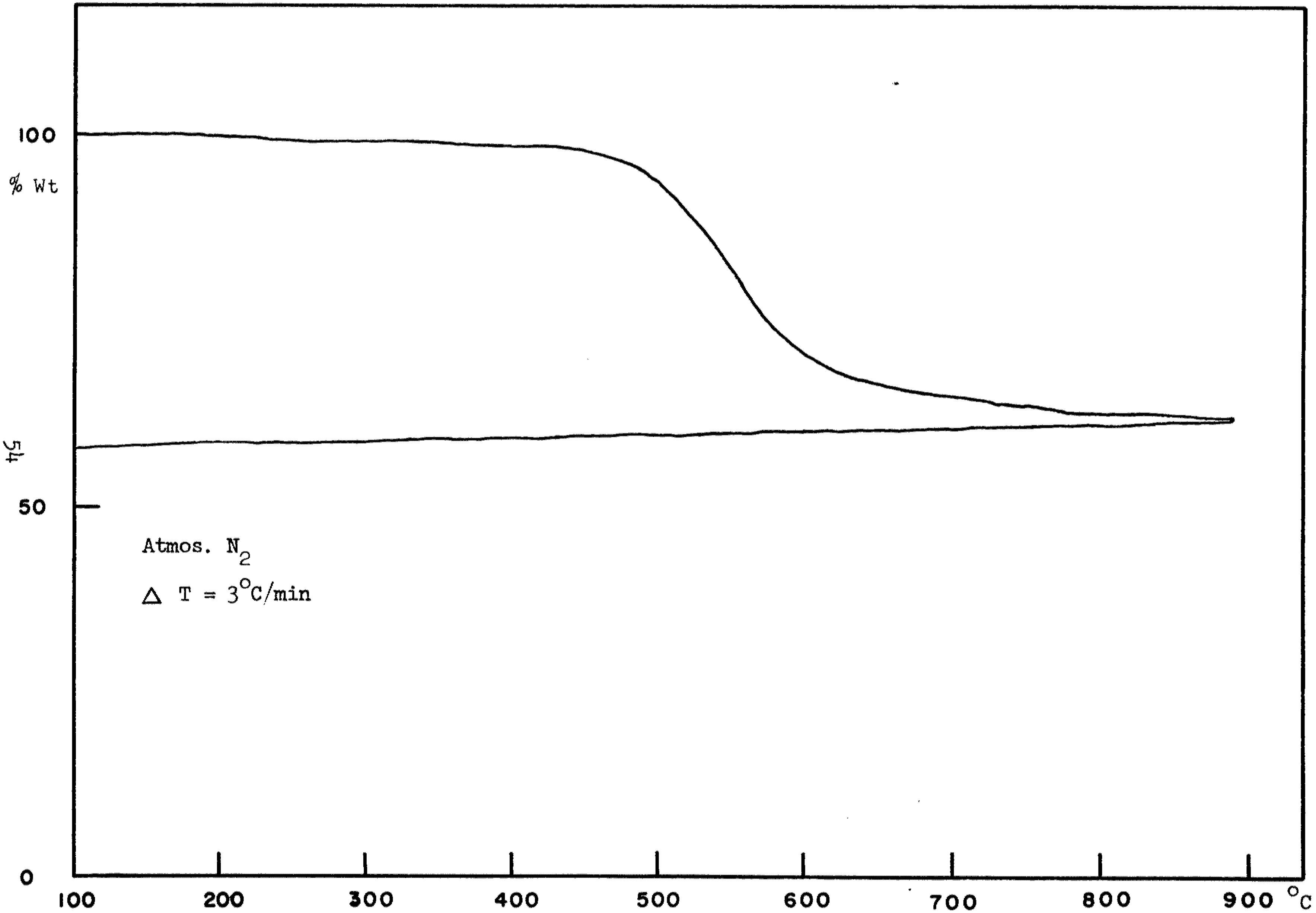


Figure 14. TGA curve for polymer JVB-24

ii) Run No. 2. Polymerization with isophthaloyl chloride

Same reaction procedure as for Run No. 1 but isophthaloyl chloride was used instead of terephthaloyl chloride. The polymer dissolved completely in H_2SO_4. $\eta_{inh} = 0.333$ in H_2SO_4 at 30°C. mp = 270° - 280°C. Sample JVB-25.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 81.24%; H, 3.98%; Res., 1.27%.
Anal. Corrected for Res.: C, 82.28%; H, 4.03%.

iii) Run No. 3. Polymerization with isophthaloyl chloride

Same reaction procedure as for Run No. 1 but isophthaloyl chloride was used and 50 mg of p-cyanobenzoyl chloride was added for endcapping. $\eta_{inh} = 0.66$ in H_2SO_4 at 30°C. mp = 280° - 300°C. Sample submitted as JVB-26.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 73.85%; H, 3.93%; Res., 2.89%.
Anal. corrected for Res.: C, 76.05%; H, 4.04%.

The TGA curve is given in Figure 15.

iv) Run No. 4. Copolymerization of iso- and terephthaloyl chloride and diphenyl ether

Twenty-five millimoles of diphenyl ether, 17 millimoles of isophthaloyl chloride, 8 millimoles of terephthaloyl chloride and 105 mg of p-cyanobenzoyl chloride were dissolved in 300 ml dichloroethane. Ten g of $AlCl_3$ were added and the mixture was stirred at room temperature under N_2 during the weekend. The precipitate was filtered off and washed with water. $\eta_{inh} = 0.314$ in H_2SO_4 at 30°C. mp 220° - 240°C.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 77.01%; H, 3.93%; Res., 1.53%.
Anal. Corrected for Res.: C, 78.26%; H, 4.03%.

Sample submitted as JVB-27. The ir spectrum is given in Figure 16. Softening curves for the prepolymer and the crosslinked polymer are given in Figure 17.

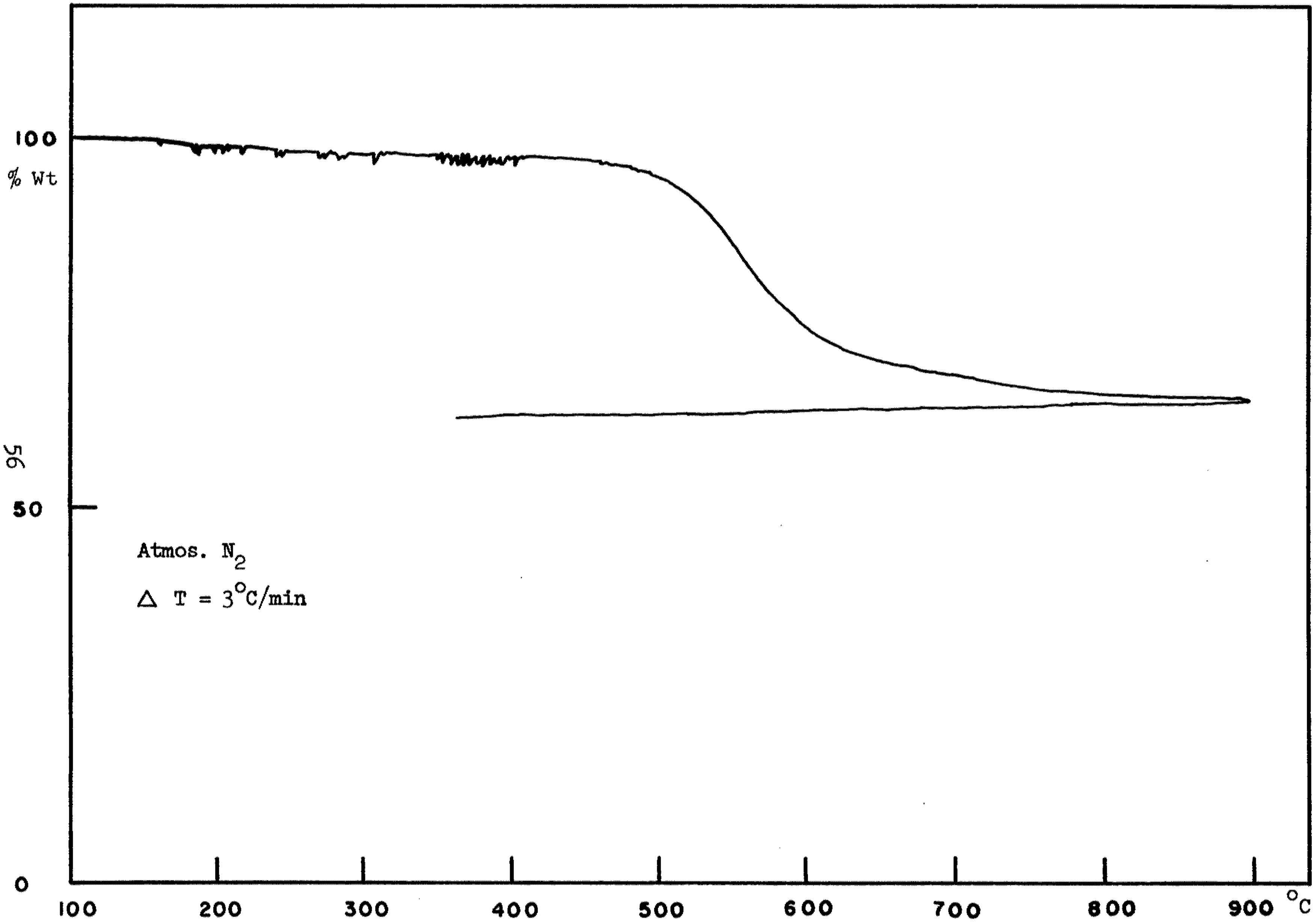


Figure 15. TGA curve for prepolymer JVB-26

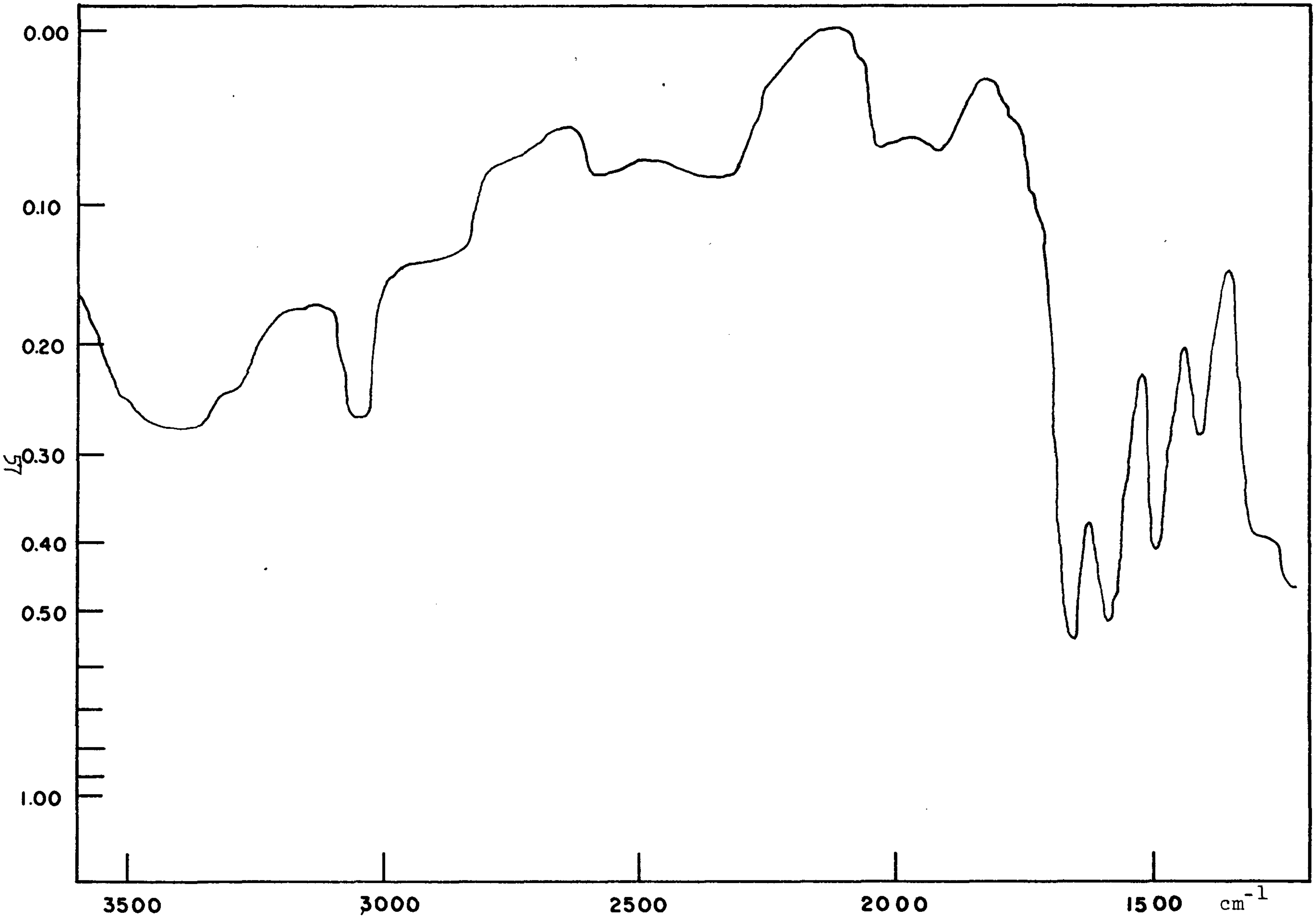


Figure 16. Infrared spectrum in KBr for prepolymer JVB-27

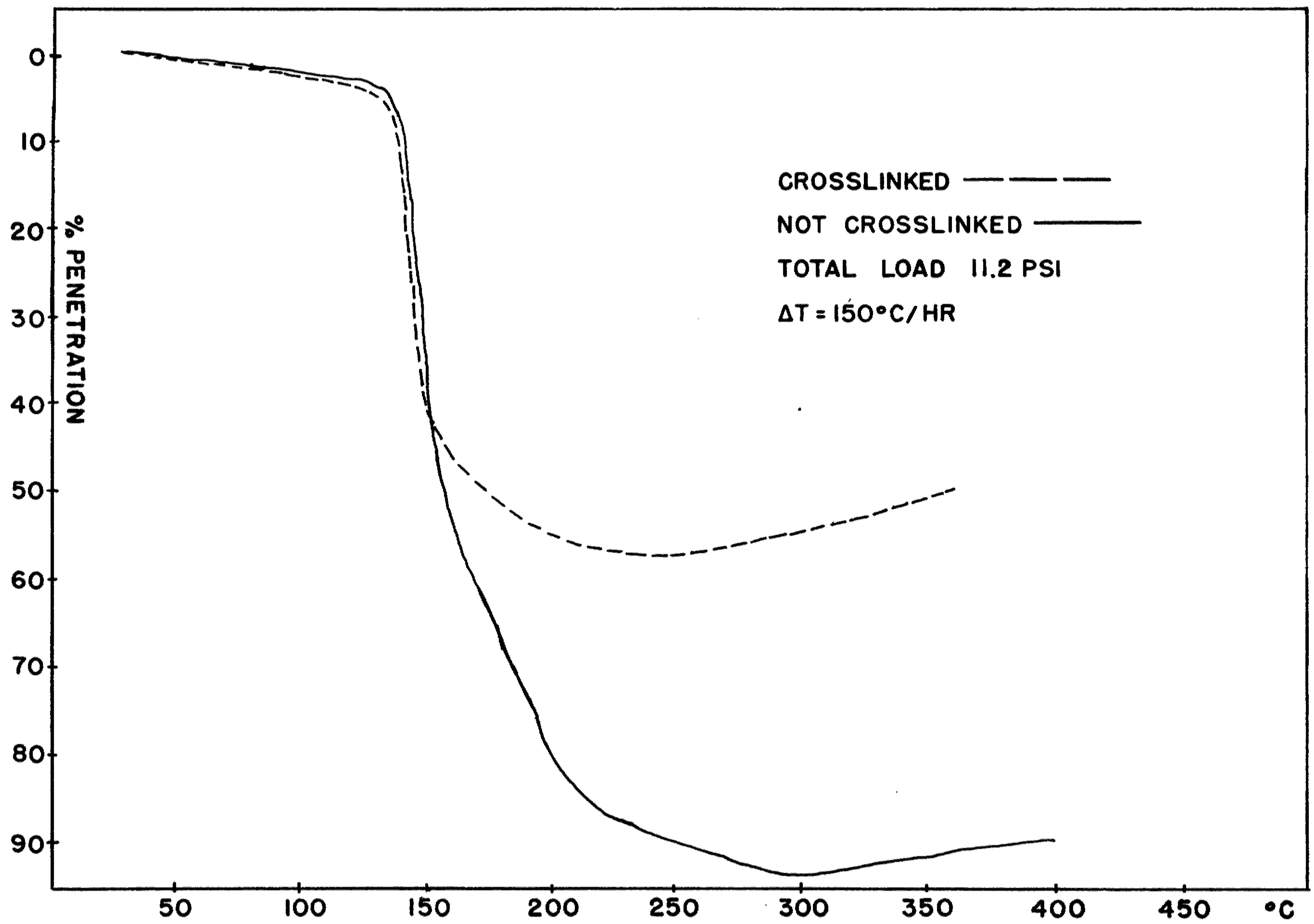


Figure 17. Softening curves for polymer JVB-27 measured by a Vicat apparatus

Crosslinking experiments on polymer JVB-27

Since the melting point of this polymer was quite low, we have tried to laminate glass fiber cloth. Strong flexible laminates were obtained by heating the polymer at 295°C under 200 psi during 20 hr. However, the cured polymer was still partially soluble in H_2SO_4. Addition of 5% dibutyltin maleate as a catalyst gave better looking and more flexible laminates. Some of these samples were sent to the Air Force Materials Laboratory in Dayton. They were labeled JVB-27-A.

Curing at 295°C during 20 hr (without catalyst) resulted in a polymer which was still 70% soluble in warm H_2SO_4. The H_2SO_4 soluble fraction had an inherent viscosity of 1.343 in H_2SO_4. The increase in viscosity from 0.314 to 1.343 indicates a fairly good trimerization of the nitriles. The polymer was probably not sufficiently endcapped to get complete crosslinking and hence insolubility.

Curing at 340°C during 18 hr resulted in a polymer which was 73% insoluble. The soluble fraction had an inherent viscosity of 0.85 in H_2SO_4. The curing of the polymer was followed by measuring its viscosity in function of the time. Sealed tubes which contained 100 mg of polymer were heated at 290°C and removed separately. The content was dissolved in 20 ml H_2SO_4 and the viscosity of the solution was measured. The results are given in the following table and in Figure 18. It is clear from these experiments that it is desirable to have more nitriles per polymer chain for a higher degree of crosslinking. 5-Cyanoisophthalic acid and derivatives were synthesized in order to be able to get nitrile pending groups.

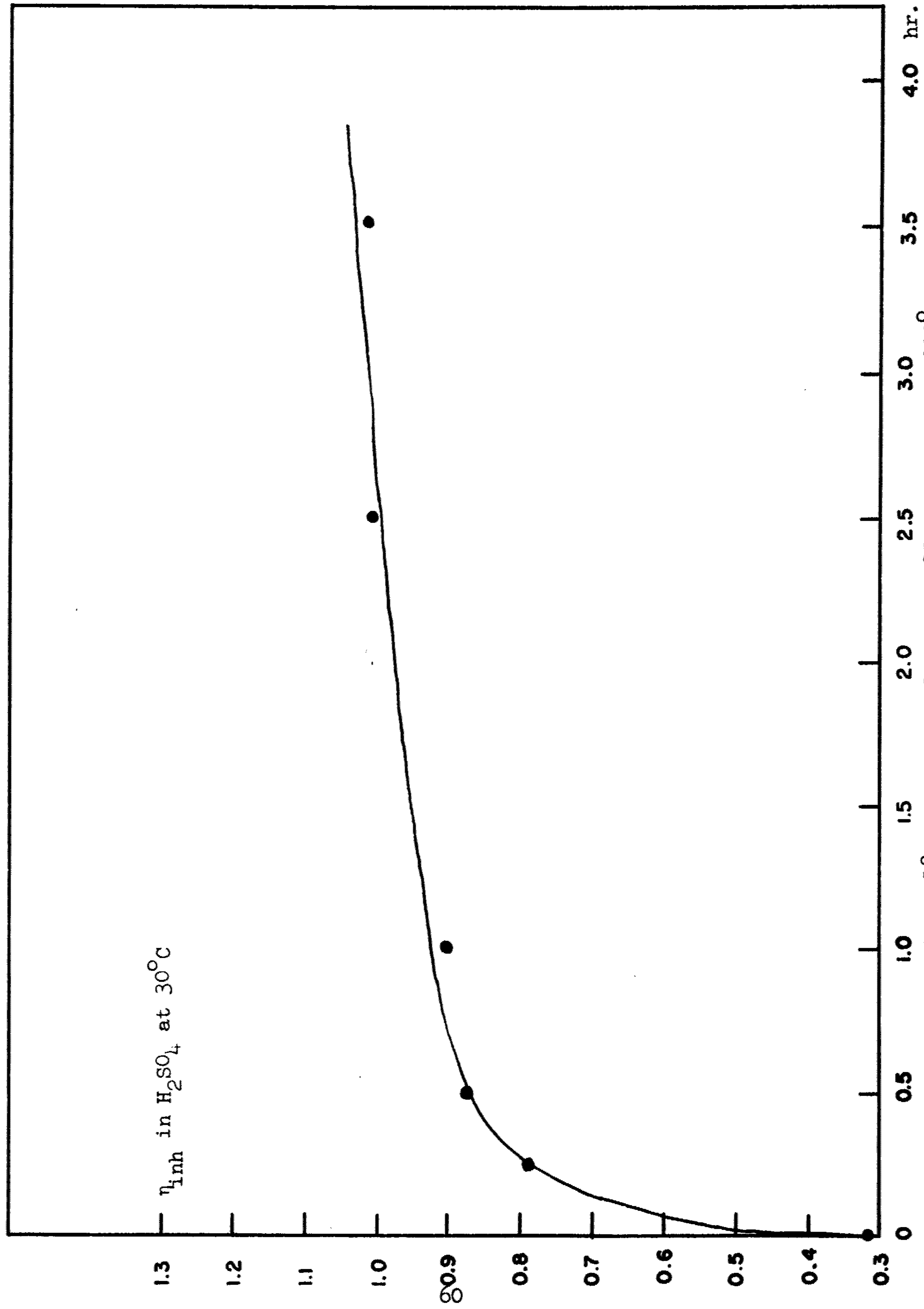


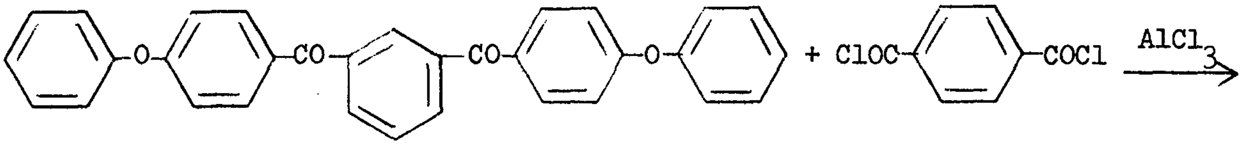
Figure 18. Curing of polymer JVB-27 by heating at 290°C

Curing of polymer JVB-27 at 290°C

time in hr	% soluble	η_{inh}
0	100	0.314
0.25	100	0.794
0.5	100	0.867
1.0	100	0.901
2.5	100	1.004
3.5	100	1.010
20	70	1.343*

*this value is corrected for the % solubility.

v) Run No. 5. Alternating copolymer of iso- and terephthaloyl chloride



Ten millimoles of 1,3-bis(p-phenoxybenzoyl)benzene, 10 millimoles of terephthaloyl chloride and 32 mgr of p-cyanobenzoyl chloride were dissolved in 200 ml of dichloroethane. Fifty millimoles of $AlCl_3$ were added and the mixture was stirred at room temperature under dry nitrogen for 20 hr. The precipitate was filtered off and washed with water. The polymer was very hardly soluble in H_2SO_4 and seems to be partially crosslinked. mp 300° - 320°C. Sample JVB-33.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 77.34%; H, 3.99%; no residue was reported.

vi) Run No. 6. Copolymerization of 5-cyanoiso-, iso- and terephthaloyl chloride with diphenyl ether

Fifty millimoles of diphenyl ether, 34 millimoles of isophthaloyl chloride, 15 millimoles of terephthaloyl chloride, 1 millimole of 5-cyanoisophthaloyl chloride and 100 mgr of p-cyanobenzoyl chloride were dissolved in 300 ml of dichloroethane. One hundred twenty millimoles of $AlCl_3$ were added under cooling and the mixture was stirred at room temperature under nitrogen for 18 hr. The precipitate was filtered off and washed with methanol in a blender. Sample submitted as JVB-41. $\eta_{inh} = 0.366$ in H_2SO_4 at 30°C. mp = 210° - 220°C.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 80.15%; H, 4.33%; no residue was reported.

No nitrile band was observed in the ir spectrum. Apparently this band is too weak to be seen. The addition of p-cyanobenzoyl chloride seems to limit the molecular weight severely. However, the treatment of the polymer with methanol in a blender seems to be very efficient to remove the $AlCl_3$, since no residue was reported. A sample cured with dibutyltin maleate at 275°C was submitted as JVB-41-A. The ir spectrum for polymer JVB-41 is given in Figure 19. The TGA curves are given in Figure 20.

vii) Copolymerization of 5-cyanoiso-, iso- and terephthaloyl chloride with diphenyl ether

Fifty millimoles of diphenyl ether, 34 millimoles of isophthaloyl chloride, 15 millimoles of terephthaloyl chloride and one millimole of 5-cyanoisophthaloyl chloride were dissolved in 200 ml of dichloroethane. One hundred twenty millimoles of $AlCl_3$ were added under cooling. The mixture was stirred at room temperature under nitrogen during 24 hr. The precipitate was filtered off and washed with methanol in a blender. $\eta_{inh} = 0.97$ in H_2SO_4 at 30°C m; = 210° - 220°C. Sample submitted as JVB-43. Very strong and flexible laminates were obtained by curing at 240°C under a pressure of less than 200 psi during 20 hr. Some of this polymer and a laminate sample were sent to the Air Force Materials Laboratories. The cured samples did not melt when heated up to 430°C.

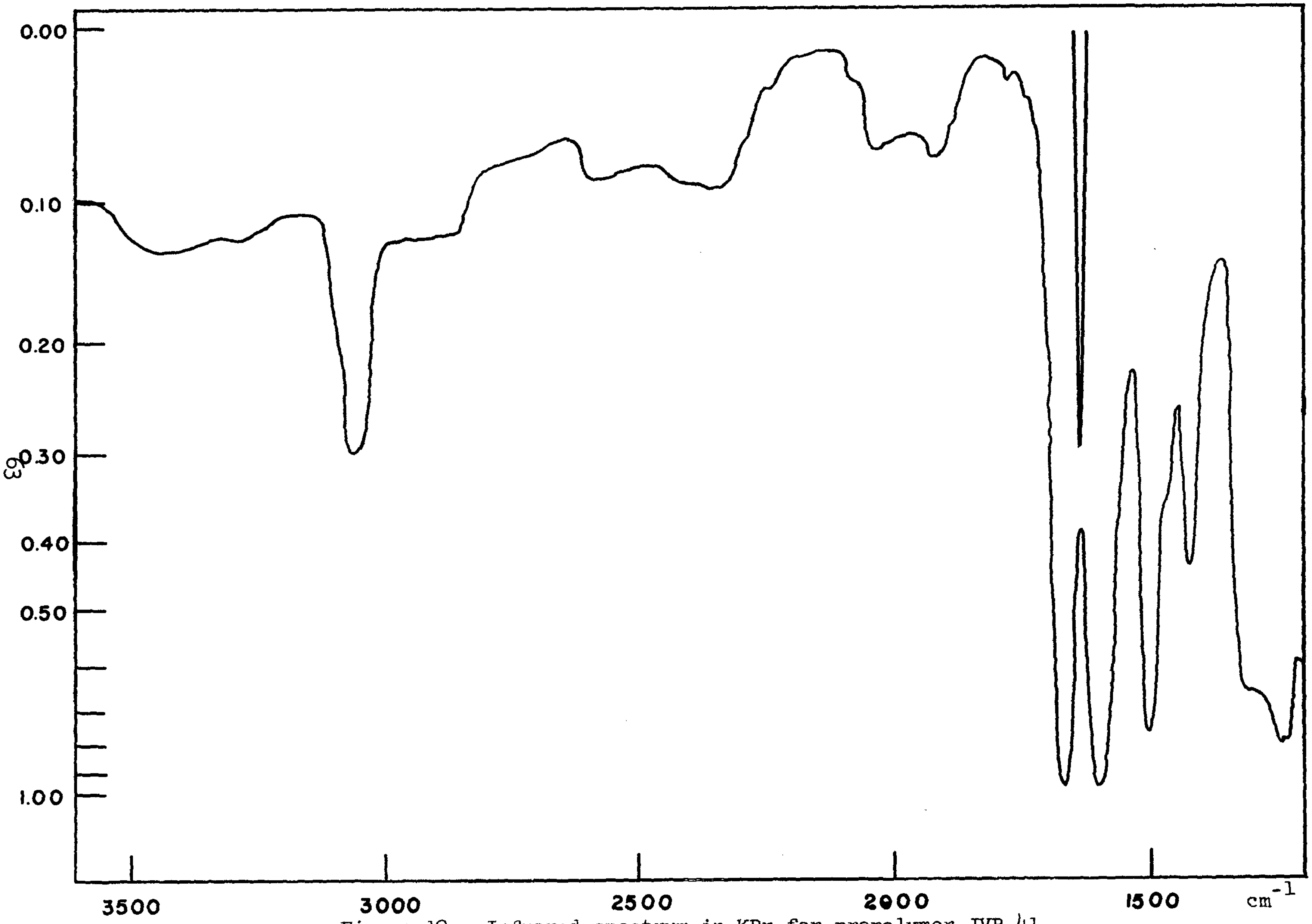


Figure 19. Infrared spectrum in KBr for prepolymer JVB-41

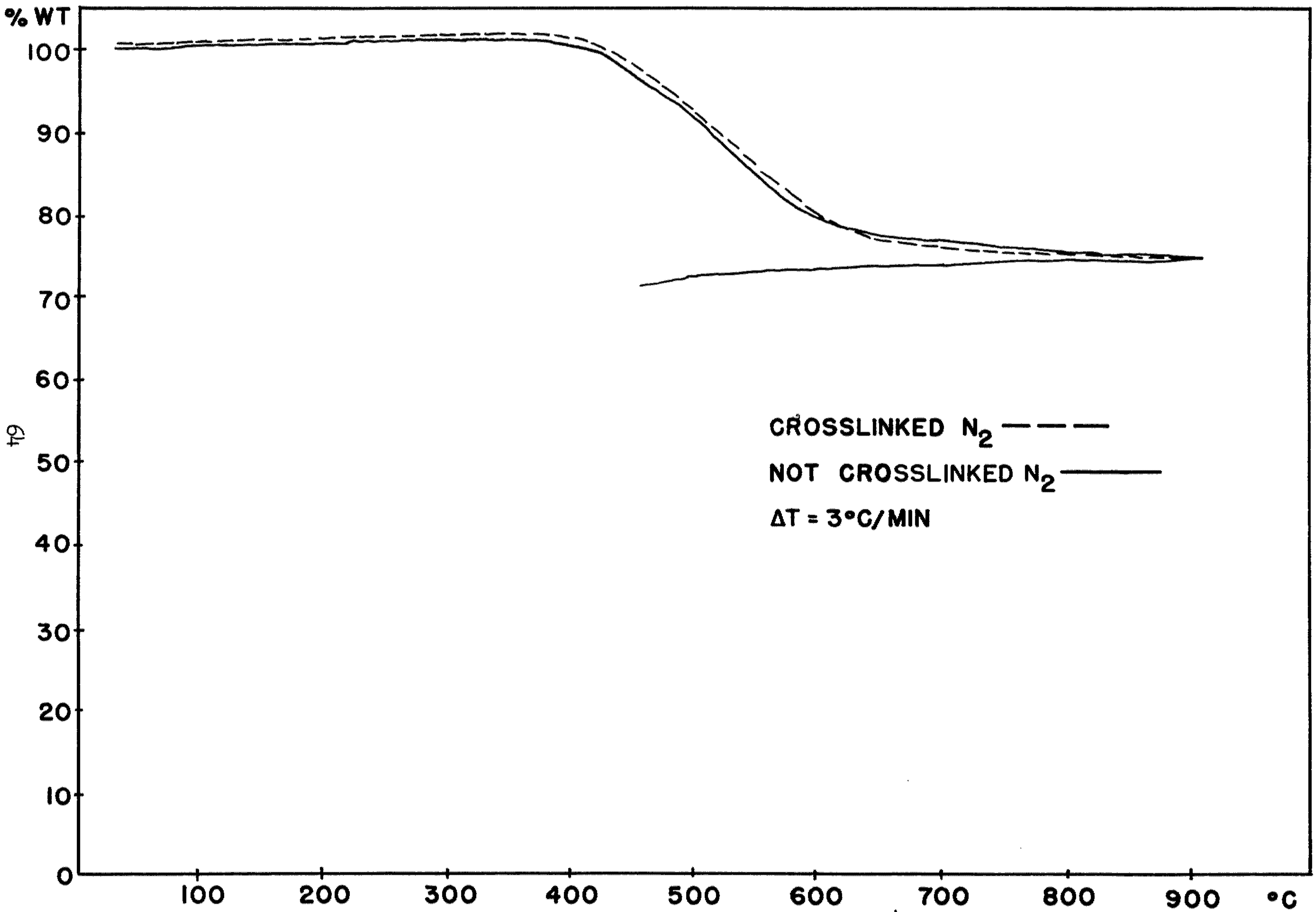


Figure 20. TGA curves for polymer JVB-41

viii) Copolymerization of 5-cyanoiso-, iso-, and terephthaloyl chloride with diphenyl ether

The same procedure as for Run No. 7 was used but on an eight times scale. However, only half the amount of solvent was used and the reaction went out of control. Overheating and excessive foaming and splattering of chemicals occurred at the beginning. $\eta_{inh} = 0.828$ in H_2SO_4 at 30°C. mp = 210° - 220°C. Submitted as JVB-45. Ninety three g of this polymer together with a laminate sample were sent to the Air Force Materials Laboratories for further testing.

ix) Run No. 9

Diphenyl ether (400 mM), 1,3-bis[p-phenoxybenzoyl]5-cyanobenzene (8mM), terephthaloyl chloride (136 mM) and isophthaloyl chloride (272 mM) were dissolved in two liter of dry 1,2-dichloroethane. $AlCl_3$ (1 M) was added cautiously and the mixture was stirred under dry nitrogen during 65 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 110 g. mp 210° - 225°C. $\eta_{inh} = 0.511$ in H_2SO_4 at 30°C. Sample submitted as JVB-46.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 78.77%; H, 4.00%; Res., 0.31%.

x) Run No. 10

The same procedure was used as for Run No. 9 but 1.2 liter of solvent were used and 150 g of $AlCl_3$ were added as fast as possible. The reaction was very exothermic at the beginning and a solid precipitate was formed almost immediately. Vigorous stirring gave a finely divided precipitate which seems to give higher viscosities. The mixture was stirred during 24 hr, filtered off and washed three times with methanol in a blender. Yield 110 g. mp 210° - 230°C. $\eta_{inh} = 1.128$ in H_2SO_4 at 30°C. Sample submitted as JVB-47.

Anal. Calc. for $C_{20}H_{12}O_3$: C, 79.97%; H, 4.03%.
Found: C, 77.65%; H, 3.93%; Res., 0.51%.

Conclusions

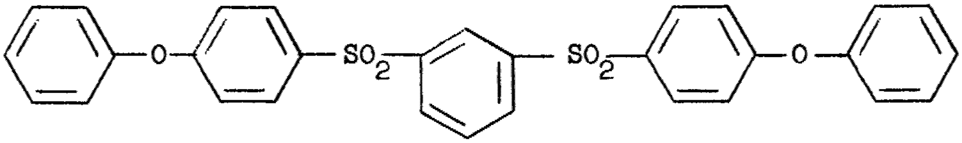
The large deviations from the calculated composition of some polymers are more likely due to difficulties in burning this type of polymer than to impurities. However, washing the polymers with methanol in a blender seems to be a proper way to remove most of the aluminum compounds.

It was shown that copolymers of iso- and terephthaloyl chloride with diphenyl ether can provide low melting prepolymers. It seems to be more advantageous to use 5-cyanoisophthalic acid derivatives as the reactive group than using the p-cyanobenzoyl chloride since only partially crosslinked samples were obtained in this latter case. This way we can control the number of nitriles per chain and hence the degree of crosslinking. The incorporation of this 5-cyanoisophthalic group seems to lower the melting point of the prepolymer further and seems to be more reactive towards trimerization than is the p-cyanobenzoyl group.

h. Model reactions

i) 1,3-bis(p-phenoxy benzenesulfonyl) benzene

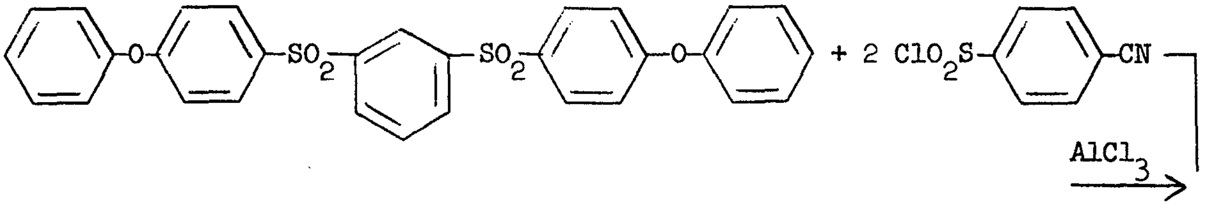
The synthesis of 1,3-bis(p-phenoxybenzenesulfonyl) benzene was described in the 1971 annual report, AFML-TR-70-6, Part II, p. 83.



The analysis gave the following results:

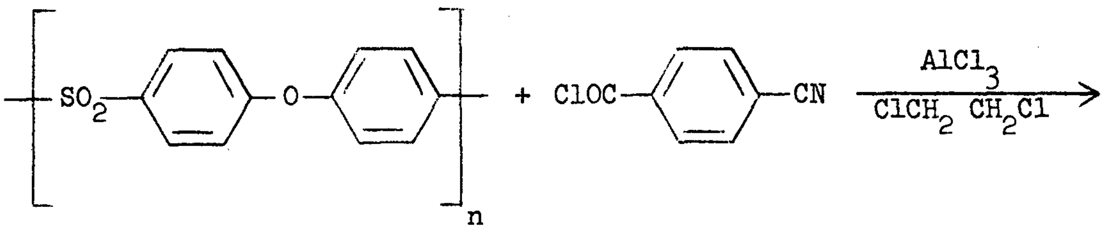
	% calculated	% found
C:	66.40%	66.28%
H:	4.09%	4.31%
O:	17.69%	17.48%
S:	11.82%	11.55%

ii) Sulfonation with p-cyanobenzenesulfonyl chloride



20 millimoles of the model compound (10.85 g), 40 millimoles of the sulfonyl chloride (8.06 g) and 100 millimoles of $AlCl_3$ (13.3 g) were dissolved in 50 ml of nitrobenzene and heated slowly to 160°C for 20 hr. An almost insoluble black product was obtained, probably due to crosslinking by trimerization of the nitrile groups.

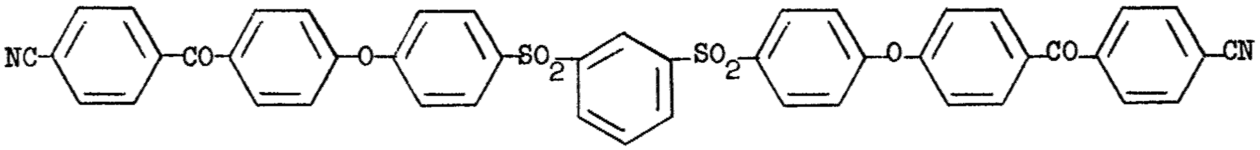
iii) Benzoylation of a polysulfone polymer



Ten g of the polysulfone polymer (η_{inh} = 0.41) were dissolved in 250 ml of dry nitrobenzene. Ten g of $AlCl_3$ were added and the mixture was stirred. One g of p-cyanobenzoyl chloride in 50 ml nitrobenzene was added and the mixture was allowed to stand overnight. It was then heated at 90°C for 3 hr. It was cooled and precipitated into a large excess of methanol and reprecipitated from DMAc into methanol.

Infrared shows a CO stretching at 1650 cm^{-1}, but no CN band. This band was probably too weak to be seen. The product melted at ± 300°C.

iv) Benzoylation of 1,3-bis(p-phenoxybenzenesulfonyl) benzene with p-cyanobenzoyl chloride



To a stirred suspension of $AlCl_3$ (0.05 mole, 6.67 g) in 50 ml of ethylene chloride was added a solution of p-cyanobenzoyl chloride (0.025 mole, 4.4 g) and 0.012 mole of the sulfone compound (6.5 g) in 50 ml of ethylene chloride. The mixture was allowed to stand at room temperature for 1 hr and was then refluxed for 2 hr. The mixture was poured into 100 ml of conc. HCl and 100 g of crushed ice. The organic layer was separated and the aqueous layer extracted with 2 x 50 ml of ethylene chloride. The combined extracts were washed with water, 10% sodium carbonate and again with water. The solution was concentrated under reduced pressure and poured into a large excess of methanol/water (9/1).mp ± 75°C yield 80%. Infrared shows C≡N at 2240 cm^{-1}; C=O at 1665 cm^{-1}.

Anal. Calc.: C, 68.98%; H, 3.52%; N, 3.49%; S, 8.00%.
Found: C, 66.99%; H, 3.64%; N, 2.65%; S, 9.47%.

The same procedure was used with the following amounts of starting material and a reflux time of 4 hr:

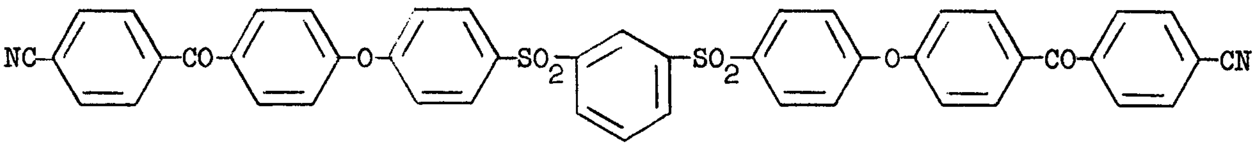
(0.020 mole of sulfone compound
:(0.040 mole of p-cyanobenzoyl chloride
(0.120 mole of $AlCl_3$

The product was recrystallized from ethanol/THF and dried under vacuum. mp ± 110°C. Yield 80%.

Anal. Calc.: C, 68.98%; H, 3.52%; N, 3.49%; S, 8.00%.
Found: C, 69.35%; H, 3.77%; N, 3.49%; S, 7.80%.

v) Trimerization of the nitrile model compound

a) Run No. 1



One and five tenths g of the model compound and 0.5 g $ZnCl_2$ were heated in a sealed tube at 295°C for 22 hr. The tube was broken and the ground contents were washed several times with water and then with THF. It was dried under vacuum at 100°C. A one-gram (66%) black insoluble material was obtained. The infrared indicated complete trimerization since the C≡N band disappeared completely. The infrared also indicated that a certain amount of amide was formed by hydrolysis of the nitrile. (See Figure 21).

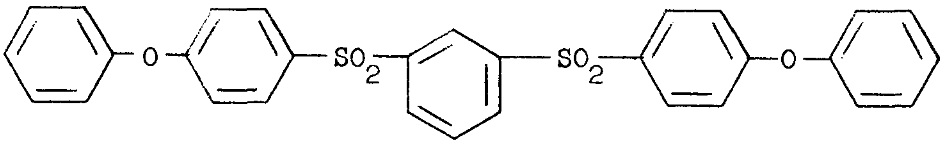
b) Run No. 2

One and five-tenths g of the nitrile model compound and 150 mg active Cu powder were heated at 295°C in a sealed tube for 22 hr. The tube was broken and the content ground and washed with THF. The THF insoluble product was very small.

c) Run No. 3

One and one-tenth g of the nitrile model compound and 120 mg NaH were mixed and heated under N_2 at 220°C for 45 hr. The mixture is still soluble in THF and ir shows that the C≡N is still there.

i. Polymers from 1,3-bis(p-phenoxybenzenesulfonyl) benzene and iso- and terephthaloyl chloride



Copolymerization with iso- and terephthaloyl chloride will very likely produce low melting terpolymers.

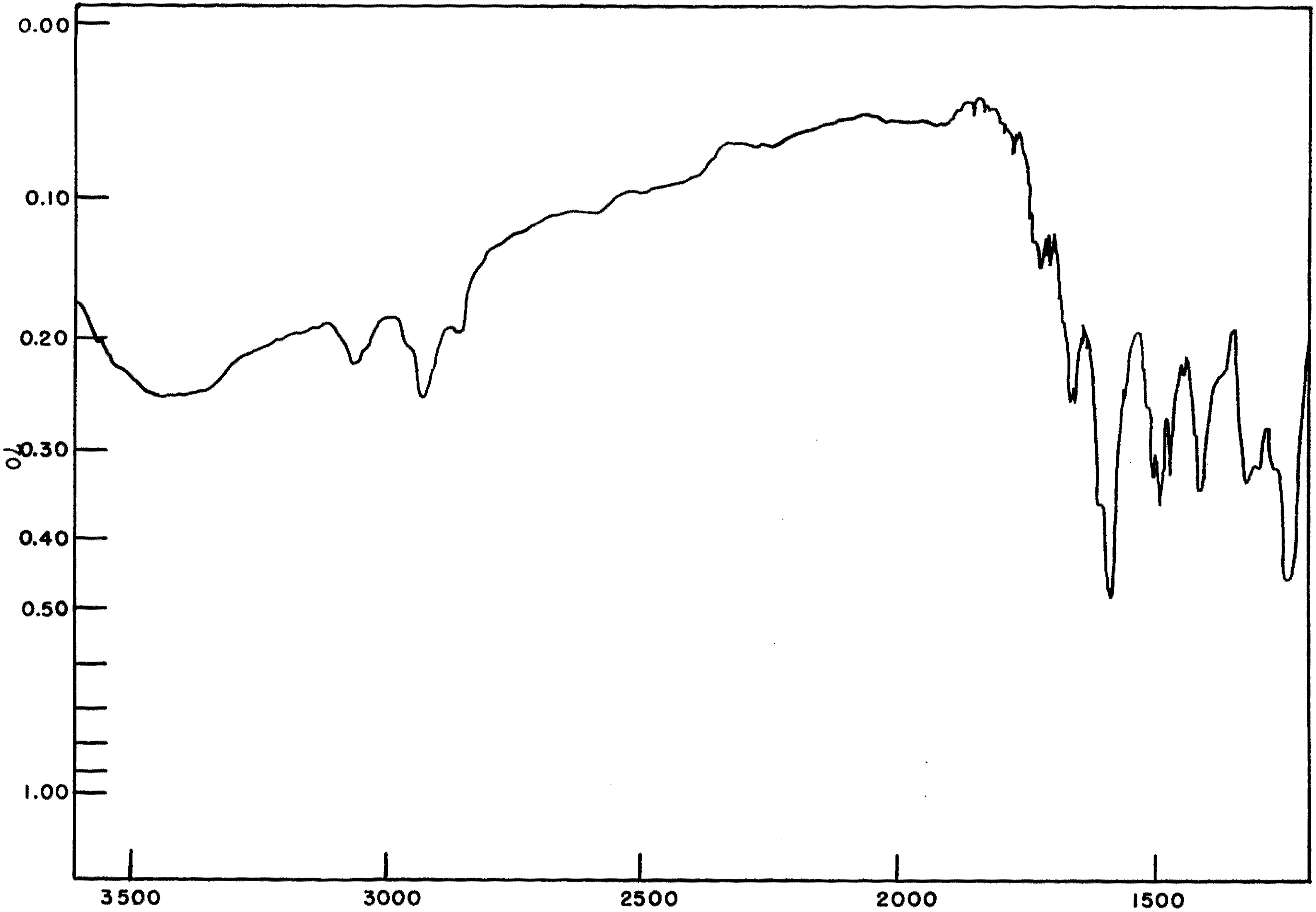


Figure 21. Infrared spectrum of the zinc chloride trimerized model compound

i) Run No. 1. Polymerization with isophthaloyl chloride

Ten millimoles of the sulfone compound, 10 millimoles of isophthaloyl chloride and 28 mgr of p-cyanobenzoyl chloride were dissolved in 100 ml of dichloroethane. Fifty millimoles of $AlCl_3$ were added under cooling and the mixture was stirred at room temperature during 20 hr. The precipitate was filtered off and washed with water. $\eta_{inh} = 0.65$ in H_2SO_4 at 30°C. mp = 185° - 190°C. Sample JVB-34-A.

Anal. Calc. for $C_{38}H_{26}O_8S_2$: C, 67.64%; H, 3.88%.
Found: C, 67.31%; H, 3.57%.

Several attempts to laminate glass fiber cloth resulted in very brittle material. Addition of 5% dibutyltin maleate as a catalyst for the trimerization did not improve these results. Apparently not enough nitriles are present in this polymer.

ii) Run No. 2. Polymerization with isophthaloyl chloride

Same reaction procedure as for Run No. 1 but 43 mgr of p-cyanobenzoyl chloride were added. $\eta_{inh} = 0.33$ in H_2SO_4 at 30°C. mp = 180° - 200°C. Sample submitted as JVB-38.

Catalysis by 5% dibutyltin maleate gave very flexible and strong laminates. A sample was sent to the Air Force Materials Laboratory. Sample submitted as JVB-38-A. The TGA curves are given in Figure 22.

iii) Run No. 3. Copolymerization of iso- and terephthaloyl chloride

Ten millimoles of the sulfone compound, 7 millimoles of isophthaloyl chloride, 3 millimoles of terephthaloyl chloride and 38 mgr of p-cyanobenzoyl chloride were dissolved in 100 ml dichloroethane. Fifty millimoles of $AlCl_3$ were added under cooling and the resulting mixture was stirred at room temperature under nitrogen during 20 hr. $\eta_{inh} = 0.585$ in H_2SO_4 at 30°C. mp = 190° - 200°C. Sample submitted as JVB-40. Catalysis by dibutyltin maleate gave very good laminates. The infrared spectrum is given in Figure 23.

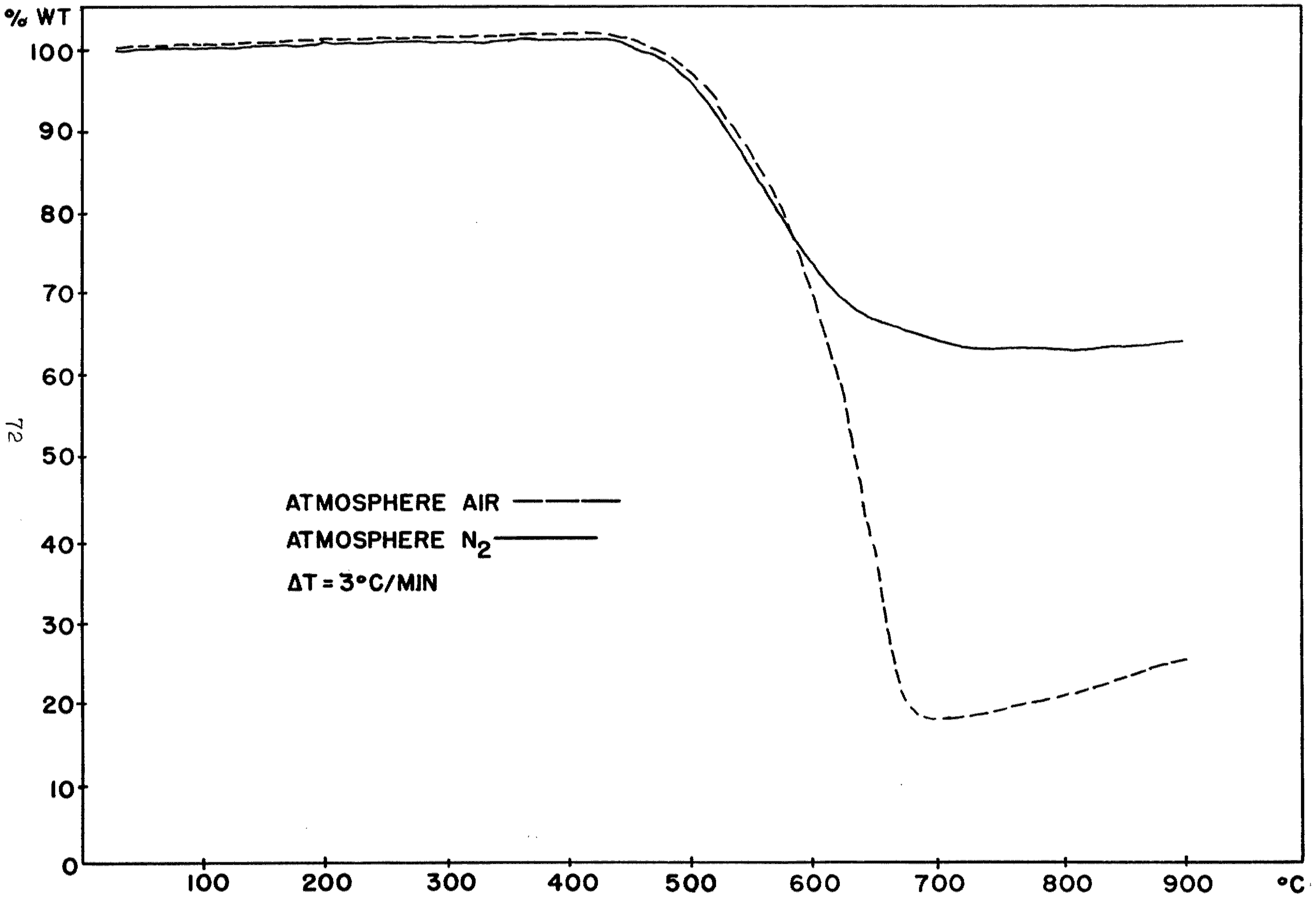


Figure 22. TGA curves for polymers JVB-38 and JVB-38-A

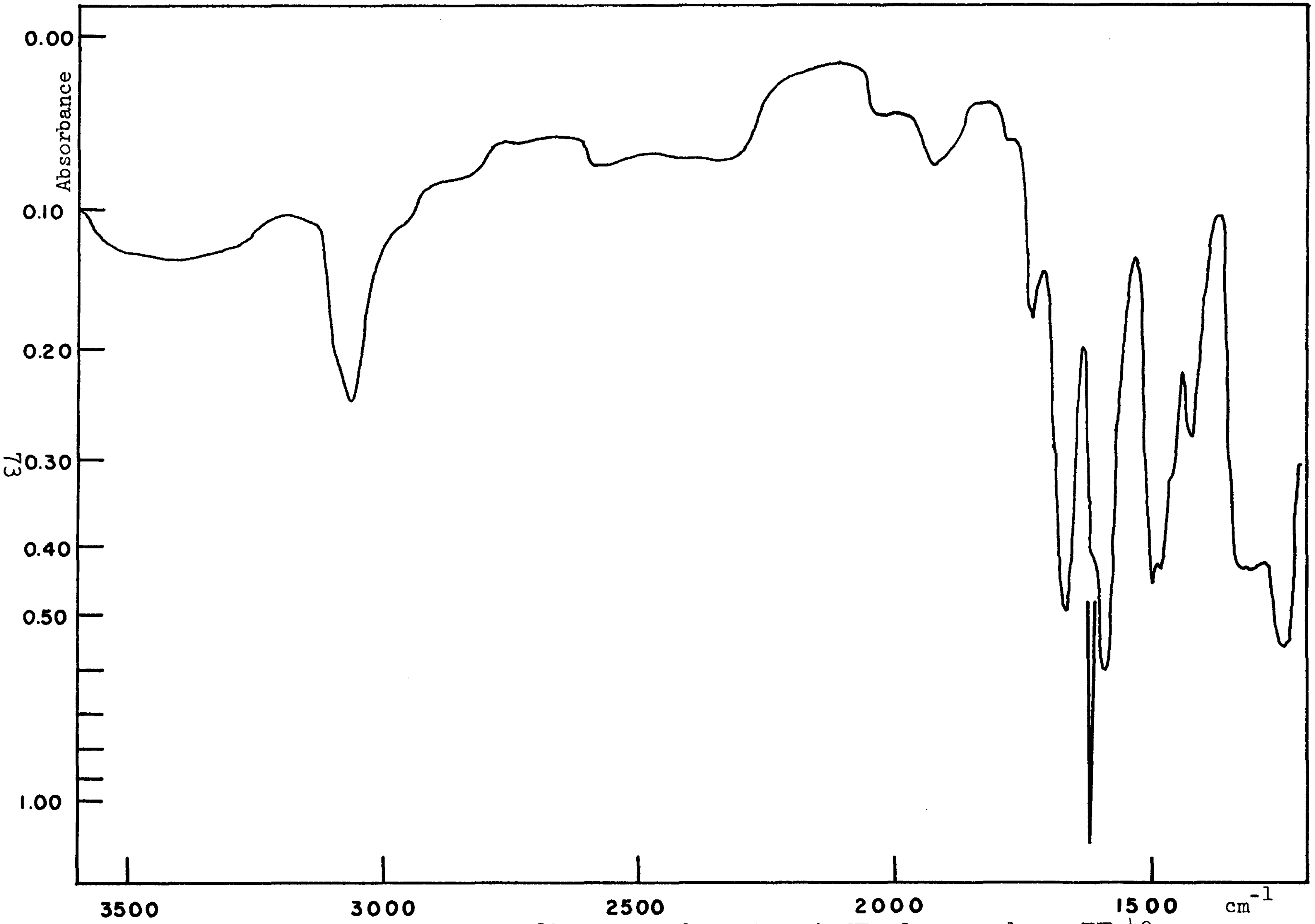


Figure 23. Infrared spectrum in KBr for prepolymer JVB-40

iv) Run No. 4. Copolymerization with 5-cyanoiso-, iso- and terephthaloyl chloride

Twenty millimoles of the sulfone compound and 1 millimole of the 5-cyano-isophthalic ketone compound were dissolved in 200 ml dichloroethane. Fourteen millimoles of isophthaloyl chloride and 7 millimoles of terephthaloyl chloride were added. One hundred millimoles of $AlCl_3$ were added under cooling. The mixture was stirred at room temperature under nitrogen during 20 hr. Sample JVB-44. $\eta_{inh} = 0.432$ in H_2SO_4 at 30°C. mp = 180°C.

Conclusions:

The sulfone compound gave low melting prepolymers that might be useful. This compound has to be purified further in order to get higher molecular weight polymers. The polymers could be crosslinked but the addition of a catalyst was necessary for these polymers. Strong, flexible laminates were obtained when more p-cyanobenzoyl chloride was used. This suggests the use of 5-cyanoisophthalic acid to get bigger prepolymers. As it was the case for the polymers of diphenyl ether, the ir spectrum shows no nitrile band since this band is too weak to be seen. Only in very concentrated samples can one find a small peak which might be attributed to the nitriles.

v) Run No. 5

1,3-bis[p-phenoxybenzenesulfonyl]benzene (111.36 mM), 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene (10 mM), terephthaloyl chloride (26.36 mM) and isophthaloyl chloride (95 mM) were dissolved in one liter of dry dichloroethane. One mole of $AlCl_3$ was added cautiously and the mixture was stirred under nitrogen at room temperature during 24 hr. Only highly crosslinked material was obtained. Thin layer chromatography showed the presence of a small fraction of a side product in the sulfone compound. It was removed by vacuum distillation. The first fraction (up to 320°C) was recrystallized several times from diethyl ether and gave a compound that melted at 105°C. The ir showed no SO_2 band while the -C-O-C- band was present. The mass spectrum gave a molecular weight of 370.

Anal. Found for the unknown compound: (C, 79.65%; H, 5.14%; S, 6.42%.
(C, 79.09%; H, 4.89%; S, 6.64%.

vi) Run No. 6

1,3-bis[p-phenoxybenzenesulfonyl]benzene (150 mM), 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene (10 mM), terephthaloyl chloride (50 mM) and isophthaloyl chloride (110 mM) were dissolved in one liter of dry dichloroethane. $AlCl_3$ (800 mM) was added and the mixture was stirred under nitrogen at room temperature during 18 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 103 g. mp 200° - 215°C. $\eta_{inh} = 0.693$ in H_2SO_4 at 30°C. Sample submitted as JVB-50. The infrared spectrum is given in Figure 24.

Anal. Calc. for $C_{38}H_{26}S_2O_8$: C, 67.64%; H, 3.88%; S, 9.50%.
Found: C, 67.48%; H, 3.73%; S, 9.27%; Res., 3.52%.

Sample JVB-50 had the best physical properties, on evaluation by Air Force Materials Laboratory. Additional sample of JVB-50 was required for further evaluation. A series of experiments were performed to see whether a reproducible polymer with same inherent viscosity could be obtained. Results of these experiments are given in Table IV. Infrared spectrum of JVB-50-PS-1 is given in Figure 25.

vii) Run No. 7

1,3-bis[p-phenoxybenzenesulfonyl]benzene (179.62 mM), 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene (10 mM) and isophthaloyl chloride (169.62 mM) were dissolved in one liter of dry dichloroethane. $AlCl_3$ (800 mM) was added and the mixture was stirred under nitrogen at room temperature during 16 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 104 g. mp 190° - 200°C. $\eta_{inh} = 0.512$ in H_2SO_4 at 30°C. Sample submitted as JVB-55.

Anal. Calc. for $C_{38}H_{26}S_2O_8$: C, 67.64%; H, 3.88%; S, 9.50%.
Found: C, 66.30%; H, 3.58%; S, 9.38%; Res., 0.49%.

Isothermal aging data of samples JVB-50 and JVB-50-PS-1 are given in Table V.

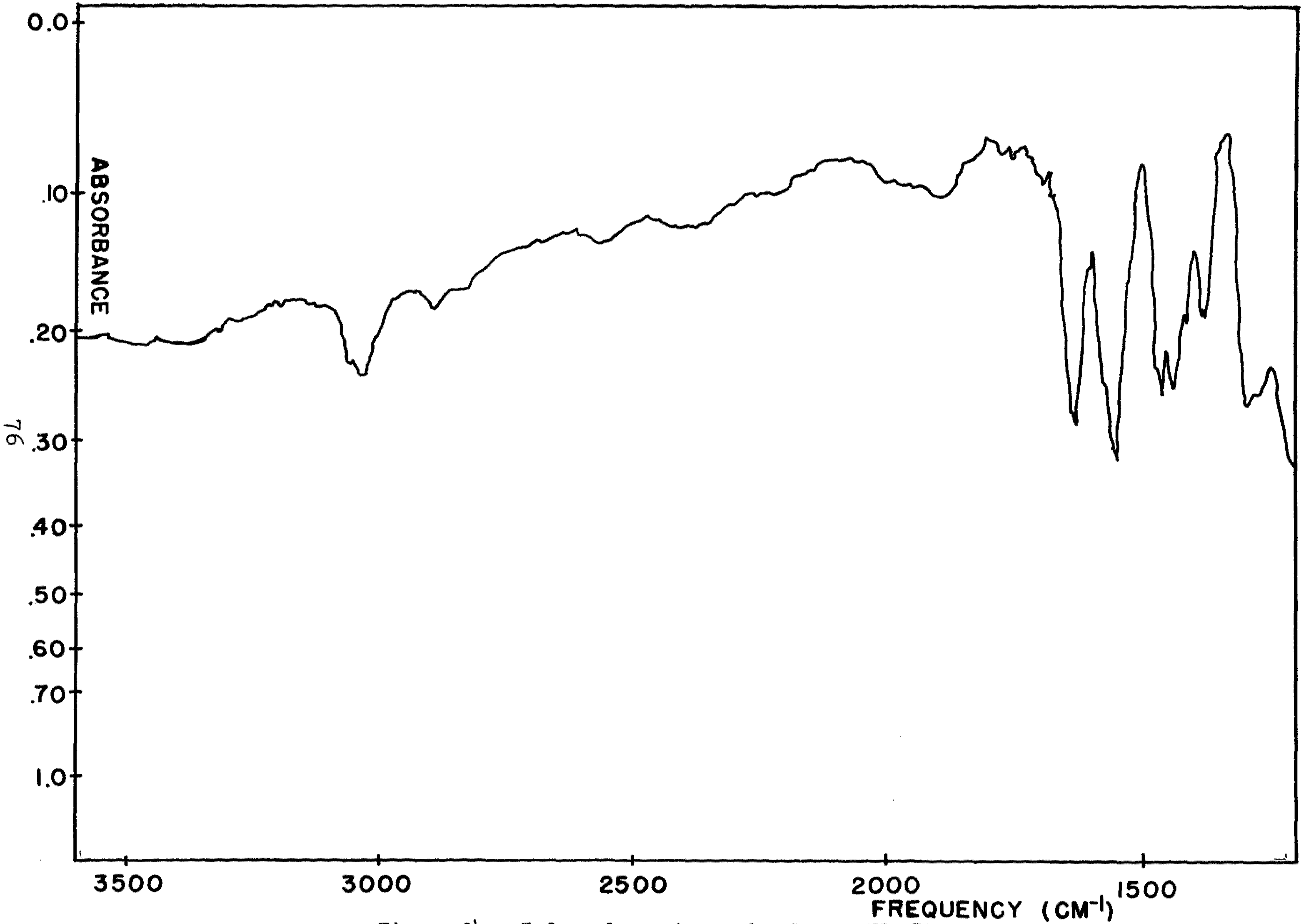


Figure 24. Infrared spectrum of polymer JVB-50

TABLE IV

RESULTS OF EXPERIMENTS TO REPRODUCE POLYMER JVB-50 of η_{inh} 0.693

Polymer Sample No.	Millimoles of monomer					
	1,3-bis [p-phenoxy-benzenesulfonyl] benzene	1,3-bis [p-phenoxy-benzoyl] benzene	Isophthaloyl chloride	Terephthaloyl chloride	η_{inh}[a]	mp°C
JVB-50-PS-1	112.5	7.5	82.5	37.5	0.35	190-205
JVB-50-PS-2	18.75	1.25	13.75[b]	6.25[c]	0.33	190-205
JVB-50-PS-3	18.75	1.25	13.75[b]	6.25[c]	0.52	210-225
JVB-50-PS-4	18.75	1.25	13.75[b]	6.25[b]	0.42	185-210
JVB-50-PS-5	18.75	1.25	13.75[b]	6.25[b]	0.47	190-205

a) 0.5 g/100 ml sulphuric acid at 30°C.

b) Purified by distillation.

c) Purified by recrystallization from ligroin.

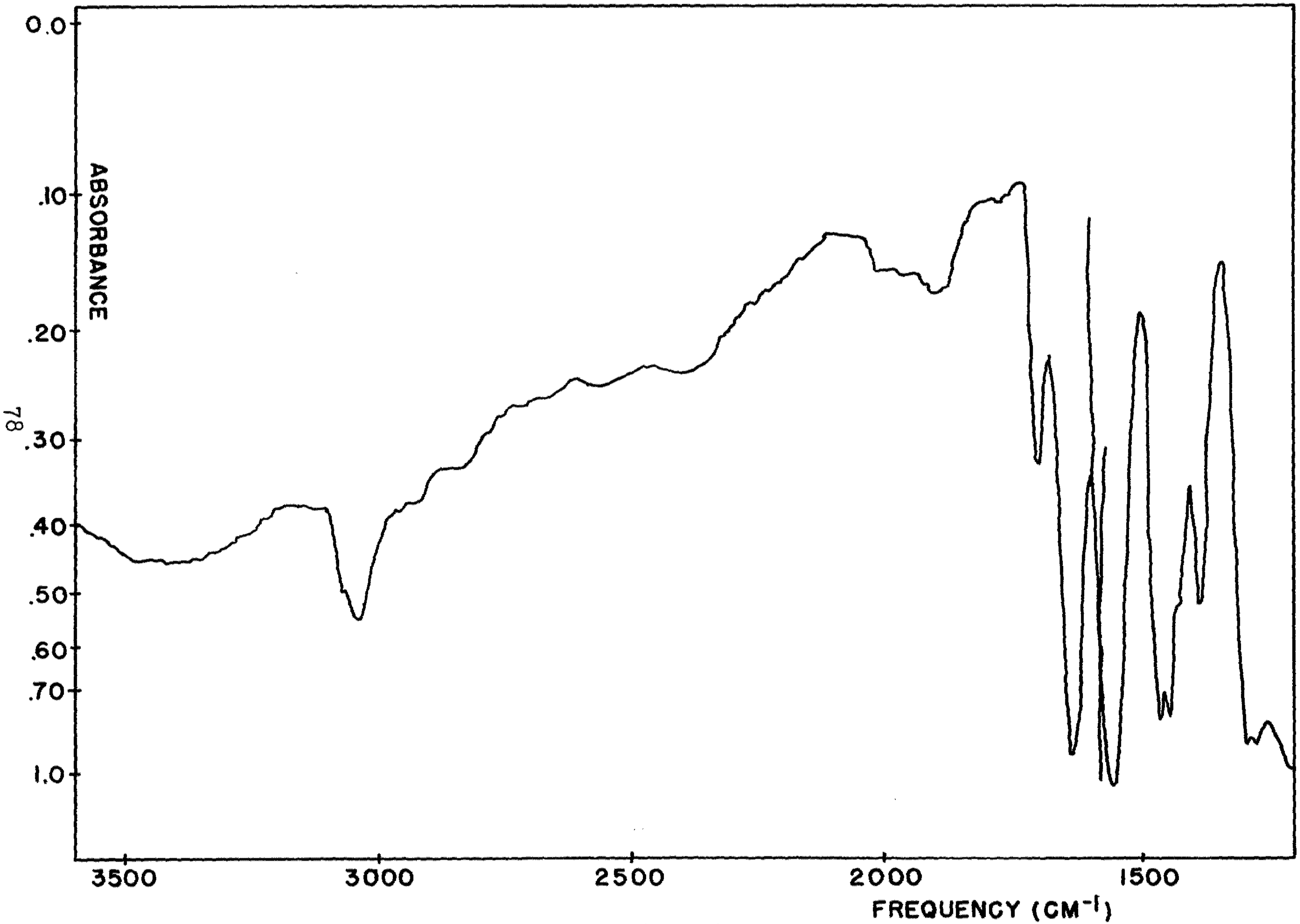


Figure 25. Infrared spectrum of polymer JVB-50-PS-1

TABLE V

ISOTHERMAL WEIGHT LOSSES OF POLYMERS JVB-50 AND JVB-50-PS-1

Sample	Temperature °C	Time (hr)	% weight loss
JVB-50	200	144	1.044
	300	192	1.393
	350	144	5.866
	400	24	9.450
	400	48	14.91
	400	120	50.94
	400	168	63.30
	400	216	66.68
JVB-50-PS-1	200	144	1.498
	300	192	1.947
	350	144	7.444

viii) Run No. 8

1,3-bis[p-phenoxybenzenesulfonyl]benzene (170 mM), 5-cyanoisophthaloyl chloride (5 mM) and isophthaloyl chloride (165 mM) were dissolved in one liter of dichloroethane. $AlCl_3$ (800 mM) was added and the mixture was stirred under nitrogen at room temperature during 45 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 109 g. mp 190° - 210°C. $\eta_{inh} = 0.599$ in H_2SO_4 at 30°C. Sample submitted as JVB-56.

Anal. Calc. for $C_{38}H_{26}S_2O_8$: C, 67.46%; H, 3.88%; S, 9.50%.
Found: C, 66.96%; H, 3.58%; S, 9.55%; Res., 0.52%.

ix) Run No. 9

1,3-bis[p-phenoxybenzenesulfonyl]benzene (166.75 mM), 5-cyanoisophthaloyl chloride (20 mM) and isophthaloyl chloride (146.75 mM) were dissolved in 1 liter of dichloroethane. $AlCl_3$ (800 mM) was added and the mixture was stirred under nitrogen at room temperature during 45 hr. The precipitate was filtered off and washed three times with methanol in a blender. Yield 106 g. mp 190° - 210°C. $\eta_{inh} = 0.955$ in H_2SO_4 at 30°C. Sample submitted as JVB-57.

Anal. Calc. for $C_{38}H_{26}S_2O_8$: C, 67.64%; H, 3.88%; S, 9.50%.
Found: C, 66.61%; H, 3.54%; S, 9.18%; Res., 0.86%.

Sample JVB-57 was not completely soluble in dimethylacetamide (7.94 wt % insoluble). The soluble portion in dimethylacetamide had an inherent viscosity of 0.660 (in dimethylacetamide at 30°C). Preparation of sample JVB-57 was repeated to see whether a polymer completely soluble in dimethylacetamide could be obtained. In all experiments lower molecular weight polymers (of inherent viscosity 0.2 - 0.4), soluble in dimethylacetamide was obtained. The results are summarized in Table VI.

It was found that polymers JVB-50, JVB-55, JVB-56 and JVB-57 do not crosslink upon heating without adding catalysts. They were dissolved in dimethyl formamide and 5-7% of anhydrous $ZnCl_2$ was added. Glass fiber cloth was then impregnated with the viscous solution and the solvent was evaporated under vacuum at 90°C. Quite brittle laminates were obtained this way. They were then heated at 230°C under a pressure of ± 200 psi during 16 to 20 hr.

TABLE VI

RESULTS OF EXPERIMENTS TO OBTAIN JVB-57

Polymer Sample No.	Millimoles of monomer			η_{inh}^{a}	mp °C
	1,3-bis [p-phenoxy-benzenesulfonyl] benzene	Isophthaloyl chloride	5-cyano-isophthaloyl chloride		
JVB-57-PS-1	16.675	14.675	2.0	0.221	185-205
JVB-57-PS-2	16.675	14.675	2.0	0.22	185-200
JVB-57-PS-3	16.675	14.675	2.0	0.36	185-210

Strong and flexible laminates were obtained. A strong three-ply laminate was made this way from polymer JVB-44. Crosslinking tests are given in the following table. Two g of the polymer were dissolved in 10 ml of dimethyl formamide and the $ZnCl_2$ was added. The solvent was then evaporated under vacuum at 90°C, and the polymer was then heated at 230°C during 16 hr. The polymers were stirred in 50 ml of H_2SO_4 during 45 hr, filtered off, washed and dried under vacuum.

CROSSLINKING EXPERIMENT

Polymer	Amount of $ZnCl_2$	% insolubility
JVB-55	108 mg	100%
JVB-56	130 mg	100%
JVB-57	140 mg	100%

It is clear from these experiments that such a long heating period is not required to get complete crosslinking. Experiments are currently underway to find out more about the curing time.

It was found that these polymers are film forming materials. JVB-57 (η_{inh} = 0.955) gave a strong film with some flexibility. Fibers were spun from a melt of polymer JVB-50 (η_{inh} = 0.693) without adding a catalyst.

j. Polymers from diphenyl sulfide

It was hoped that diphenyl sulfide would react in the same manner as diphenyl ether. The sulfide group could then be oxidized to a sulfone group. This might be another way to get low melting p-linked polysulfones. The sulfide polymer itself might have good thermal stability and good adhesive properties.

i) Run No. 1

Redistilled diphenyl sulfide (100 mM), terephthaloyl chloride (30 mM) and isophthaloyl chloride (70 mM) were dissolved in 200 ml of dry dichloroethane. $AlCl_3$ (300 mM) was added slowly and the mixture was stirred under nitrogen at room temperature during 24 hr. It was poured into a large excess of methanol and washed twice with methanol in a blender. Yield = 60%.

mp 180° - 200°C. η_{inh} = 0.270 in H_2SO_4 at 30°C. Sample JVB-51.
Anal. Calc. for $C_{20}H_{12}SO_2$: C, 75.93%; H, 3.82%; S, 10.32%.
Found: C, 75.17%; H, 3.88%; S, 10.55%.

ii) Run No. 2

The same procedure was used as for Run No. 1 but only isophthaloyl chloride was used. η_{inh} = 0.265 in H_2SO_4 at 30°C. Sample JVB-51-B.

iii) Run No. 3

The same procedure was used as for Run No. 1 but only isophthaloyl chloride was used. The amount of solvent was reduced to 50 ml of dichloroethane. η_{inh} = 0.240 in H_2SO_4 at 30°C. Sample JVB-51-C.

iv) Run No. 4

Isophthaloyl chloride (20 mM) was dissolved in 100 ml of dry dichloroethane. $AlCl_3$ (50 mM) was added and the reaction mixture was cooled in an ice bath. Diphenyl sulfide (20 mM) was then added dropwise under nitrogen. The mixture was allowed to come to room temperature after three hr and was then stirred for another 21 hr. η_{inh} = 0.257 in H_2SO_4 at 30°C. Sample JVB-51-C.

A side reaction seems to occur in this polymerization. The purity of the diphenyl sulfide was checked by gas chromatography and no impurities were found.

v) Run No. 5

Isophthaloyl chloride (20 mM) and phenyl sulfide (21 mM) were dissolved in 150 ml of dry dichloroethane. $AlCl_3$ (50 mM) was added and the mixture was stirred under nitrogen during 20 hr. η_{inh} = 0.364 in H_2SO_4 at 30°C. Sample JVB-51-d.

vi) Run No. 6

Isophthaloyl chloride (20 mM) and phenyl sulfide (20 mM) were dissolved in 150 ml of dry heptane. $AlCl_3$ (42 mM) were added and the mixture was stirred under nitrogen during 20 hr. The precipitate was filtered off and washed twice with methanol in a blender. η_{inh} = 0.314 in H_2SO_4 at 30°C. Sample JVB-51-e.

vii) Run No. 7

Isophthaloyl chloride (20 mM), 1,3-bis(p-phenoxybenzoyl)-5-cyanobenzene (1 mM) and phenyl sulfide (20 mM) were dissolved in 150 ml of dry dichloroethane. $AlCl_3$ (45 mM) was added and the mixture was stirred under nitrogen during 20 hr. The precipitate was filtered off and washed twice with methanol in a blender. $\eta_{inh} = 0.518$ in H_2SO_4 at 30°C. Sample JVB-51-f.

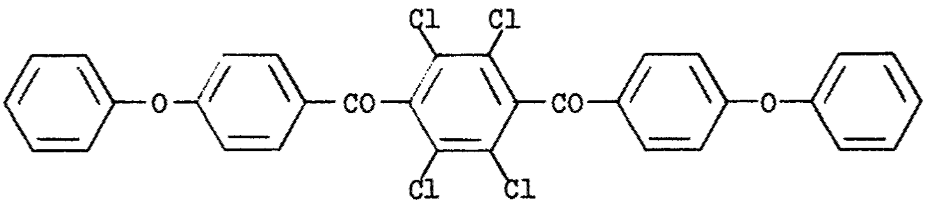
Conclusions

It looks like a slight excess of phenyl sulfide compared to the amount of acid chloride gives higher viscosities. This can be seen in run No. 5 and run No. 7. However, a side reaction occurred in all runs. A deep red color developed when the polymers were dissolved in sulphuric acid. This indicates the formation of triphenyl carbinol groups in the Friedel Crafts reaction. The same phenomenon did not happen in the other polymerizations.

k. Polymer from 1,4-bis[p-phenoxybenzoyl]2,3,5,6-tetrachlorobenzene

i) Synthesis of 1,4-bis[p-phenoxybenzoyl]2,3,5,6-tetrachlorobenzene

Tetrachloroterephthaloyl chloride (50 g) was dissolved in one liter of dry diphenyl ether. $AlCl_3$ (50 g) was added and the mixture was stirred under nitrogen at room temperature during 24 hr. The precipitate was filtered off and washed several times with water. The product was recrystallized twice from dimethyl formamide. Yield 90%. mp 256° - 257°C. Sample JVB-52.



Anal. Calc. for $C_{32}H_{18}Cl_4O_4$: C, 63.19%; H, 2.98%; Cl, 23.30%.
Found: C, 63.02%; H, 2.92%; Cl, 23.51%.

ii) Polymerization. Run No. 1

1,4-bis[p-phenoxybenzoyl]2,3,5,6-tetrachlorobenzene (25 mM) was dissolved in 300 ml of dichloroethane and 100 ml of nitrobenzene. Diphenyl ether (50 mM), 1,3-bis[p-phenoxybenzoyl]-5-cyanobenzene (2 mM) and isophthaloyl chloride (77 mM) were added. $AlCl_3$ (300 mM) was then added and the mixture was stirred under nitrogen during 20 hr. The mixture was poured into a large excess of methanol and the precipitate was washed once with methanol in a blender. $\eta_{inh} = 0.219$ in H_2SO_4 at 30°C. Sample JVB-53.

iii) Polymerization. Run No. 2

1,4-bis[p-phenoxybenzoyl]2,3,5,6-tetrachlorobenzene (20 mM) and isophthaloyl chloride (20 mM) were dissolved in 200 ml of nitrobenzene. $AlCl_3$ (100 mM) was added and the mixture was stirred under nitrogen at room temperature during 24 hr. It was precipitated into a large excess of methanol and washed once more with methanol in a blender. $\eta_{inh} = 0.227$ in H_2SO_4 at 30°C. It was noted that these polymers are soluble in organic solvents such as dimethyl formamide and nitrobenzene. The polyketones which are not substituted with halogens were completely insoluble in these solvents. This increased solubility would be advantageous for laminating purposes.

1. Replacement of the halogens of 1,4-bis[p-phenoxybenzoyl]2,3,5,6-tetrachlorobenzene with nitrile groups

The replacement of the adjacent halogens by nitrile groups would give us a way to make an ortho dinitrile compound which could be incorporated in a polymer chain. The polymer could then be crosslinked by heating it with copper bronze to form copper phthalocyanine crosslinks.

i) Run No. 1

Twenty millimoles of the tetrachloro compound were refluxed in 100 ml of dimethyl formamide with 100 millimoles of CuCN during 24 hr. Five ml of pyridine was added after one hr of refluxing. The mixture was poured in a large excess of water, the precipitate was filtered off and recrystallized from dimethyl formamide. Most of the starting material was recovered this way.

ii) Run No. 2

Ten millimoles of the tetrachloro compound and 100 millimoles of KCN were refluxed during 50 hr in 500 ml of dimethyl formamide. One gram of KI was added to facilitate the replacement. The mixture was cooled and poured into a large excess of water. The precipitate was filtered off and recrystallized twice from dimethyl formamide. mp 210°C. Yield 3 g.

No CN or -C-Cl absorption was found in the infrared spectrum. A Beilstein test for halogens was also negative. The mass spectrum gave a molecular weight of 470. This corresponds to a replacement of all the halogens by hydrogen. Sample JVB-52-A.

4. Future Plans

Work will continue along the lines indicated here especially on the search for new catalysts for the trimerization of nitriles.

VI. POLYPHENYLENE SULPHIDES AND RELATED POLYMERS FOR USE AS LAMINATING RESINS

1. Introduction

This investigation is directed towards the synthesis of polyphenylene sulphides and related polymers for use as laminating resins. It is anticipated that, like aromatic polyethers, these polymers will be thermally stable with relatively low melting points below their decomposition temperatures.[14]

Substitution of these polyphenylene sulphides, with suitable functional groups that could be used to crosslink them, may provide materials that could be useful laminating resins for high temperature uses. This application depends upon crosslinking the polymer chains to give an insoluble, high melting, and thermally stable network with no evolution of volatiles, or side-products, which would cause voids and resulting weak points in the laminate matrix. Previous work in this[15], and other laboratories[16], indicated that nitrile groups could be appropriate substituents since they can be converted to triazines without forming side-products. The formation of voids in the cured polymer could, therefore, be avoided.

The results of previous work on this project have been reported[17] by Drs. D. A. McCombs and J. Wilbur. In these earlier investigations, some low molecular weight ($\eta_{inh} \sim 0.1$) polyphenylene sulphides were prepared from the reaction of salts of m-benzenedithiol and meta- and para- dibromobenzene. This report deals with the continuation of work on this project.

2. Results and Discussion

a. Model compounds

It has been reported[18] that potassium carbonate in N,N-dimethylformamide (DMF) provides a suitable medium for the reaction between an aromatic dithiol and an aromatic dihalide, to give linear polymers with sulphide linkages. However, the polymerizations which are of immediate interest to us were not reported. Model reactions were, therefore, carried out between thiophenol and various aromatic dibromides, in order to evaluate the feasibility of using K_2CO_3/DMF as the reaction medium for the corresponding polymerizations, in which m-benzenedithiol is reacted with the dibromo compound.

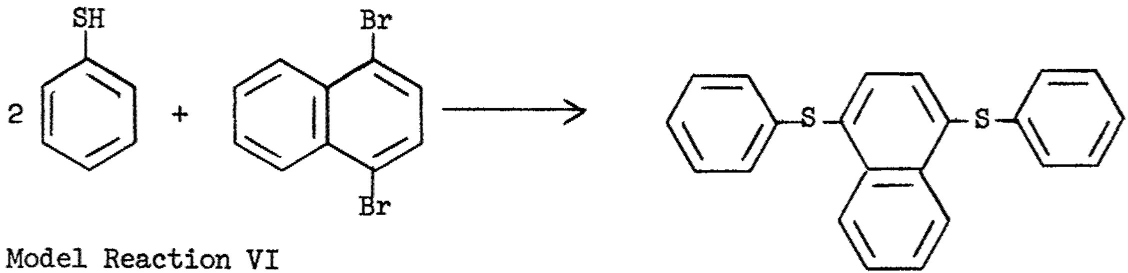
Potassium carbonate in DMF may also be a suitable medium for the reaction between polyphenylene sulphides containing thiol endgroups and 4-bromobenzonitrile. This reaction would give nitrile endcapped polymers which would be suitable for trimerization experiments. Model reactions have, therefore, been carried out between 4-bromobenzonitrile and thiophenol, and m-benzenedithiol.

The model reactions, referred to above, are shown schematically in Scheme I, together with the yields of the respective model compounds. These reactions were generally carried out in DMF, at 150° - 155°C for 24 hr, and in each case a 15% excess (based on the thiol group concentration) of K_2CO_3 was used. Further experimental details for these reactions are given in a later section.

A bright yellow color, due to the thiophenoxy anion, was rapidly formed in these reactions during the period in which the temperature was raised to 150° - 155°C. The intensity of this yellow color usually decreased in the later stages of the reactions. These observations apply also to the polymerizations carried out in DMF which are discussed below.

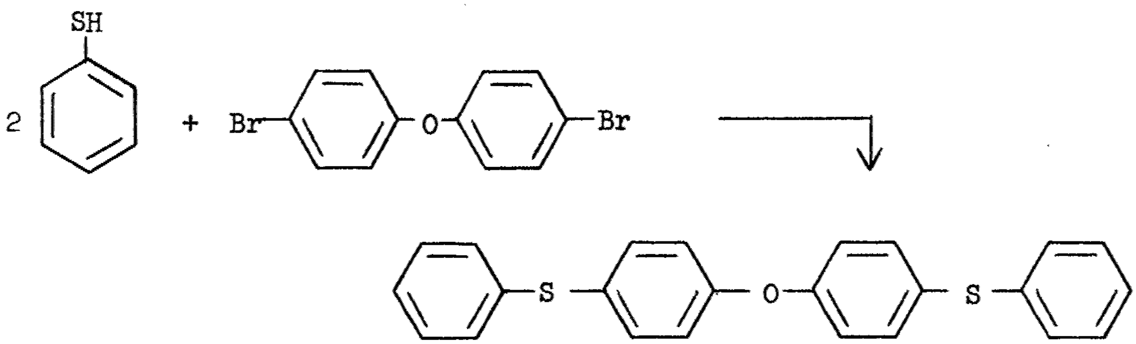
As indicated in Scheme I, the yield of each model compound [except diphenyl sulphide and 4,4′-bis(phenylthio)diphenyl ether] is reasonably high, suggesting that K_2CO_3/DMF should provide a suitable medium for the polymerization of an aromatic dithiol and an aromatic dibromo compound, and, also, for the endcapping reaction. Furthermore, it appears that these reactions proceed by the expected nucleophilic displacement mechanism as, in each case, products with a rearranged structure were not isolated. The corresponding polymerizations should, therefore, also proceed without positional isomerization, thus giving polymers of the desired structure. The structure of each model compound was confirmed by elemental analysis, infrared spectroscopy and, also, where possible, by comparison of the physical properties with the corresponding literature values (see experimental section).

Model Reaction V



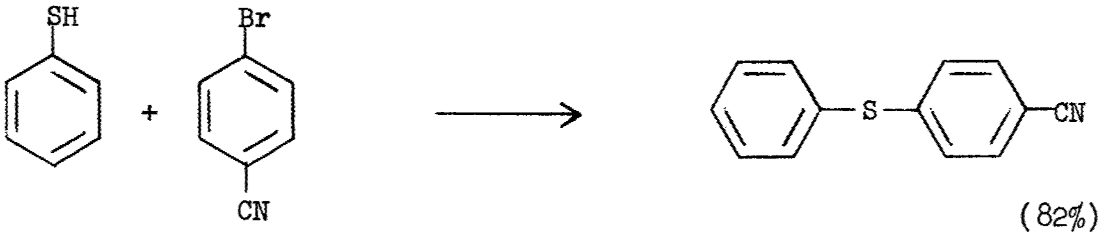
(90%)

Model Reaction VI



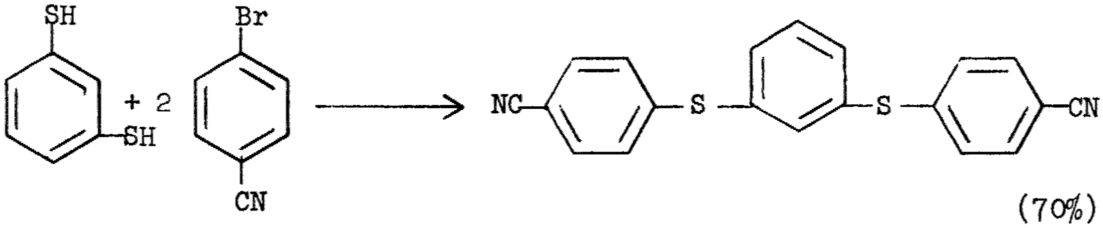
(41%)

Model Reaction VII



(82%)

Model Reaction VIII



(70%)

The products of model reactions VII and VIII will be used during future investigations of the catalyzed trimerization of nitrile groups to triazines. The triazines formed in this way may then serve as model compounds for trimerized polymers. It should also be noted that the other model compounds shown in Scheme I could be used as monomers in future polymerization work. Friedel-Crafts polymerization employing these compounds and aromatic disulphonyl chlorides, or diacid chlorides, could be used to obtain polymers with a variety of structures. The sulphones, obtained by oxidation of these model compounds, could also be used in similar polymerizations.

b. Polymerization

i) General

Work involving the polyphenylene sulphides and related polymers has been carried out, and is proceeding, in three areas.

Polymers with various structures have been prepared and some of their physical properties have been determined. It is hoped that these investigations will indicate the most suitable backbone structures for polymers which will eventually be substituted with nitrile groups and then crosslinked to give the laminating resins.

The polymerization between p-dibromobenzene and m-benzenedithiol has been investigated further, in order to determine the most suitable reaction conditions (solvent, metal carbonate, time and temperature) for the synthesis of a high molecular weight polyphenylene sulphide. It was decided to use p-dibromobenzene in this investigation as poly(m,p-thiophenylene) is easily solubilized in several organic solvents.

Work has also been directed towards the preparation of polymers having nitrile groups, both in the main chain and as endgroups. Initially, attention was devoted solely to the preparation of a poly(m,p-thiophenylene) having nitrile endgroups. However, it is now thought, as a result of work carried out by Dr. J. Verborgt in this laboratory, that crosslinking of polymers containing nitrile groups in the main chain will be more advantageous than the crosslinking of nitrile endcapped polymers. Work involving the preparation of polyphenylene sulphides containing nitrile groups in the main chain has, therefore, been recently commenced. Two approaches are being used in this investigation, i.e., direct bromination of poly(m,p-thiophenylene) and subsequent replacement of the bromine groups by nitrile groups using cuprous cyanide, and the use of 2,4- and 3,5-dichlorobenzonitrile as polymerization monomers.

ii) The preparation of polymers with various structures

The results of polymerizations carried out, using m-benzenedithiol and various aromatic dibromo compounds as monomers, are shown in Table VII, together with the reaction conditions employed. Structures of the various polymers are shown in Scheme II, and elemental analysis data for these polymers is given in Table VIII. Analysis data for polymer sample SH-P14 is not yet available. One other polymer has also been obtained by using 4,4′-biphenyldithiol and bis(p-bromophenyl) ether as monomers. However, this polymer is contaminated with a gel, formed from the silicone oil used to lubricate the mechanical stirrer shaft, and purification has not yet been carried out.

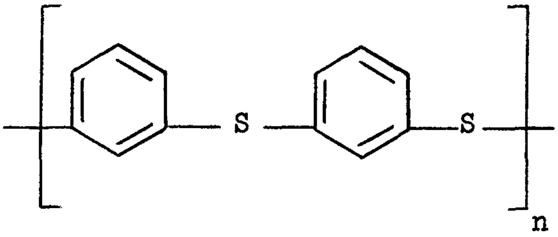
Several of the polymer structures shown in Scheme II do not indicate the type of endgroups present. In these cases, either bromine, or thiol, endgroups may be present. The structure of SH-P7 may differ from that shown in Scheme II, as m-dibromobenzene and 4,4′-dibromobiphenyl may not alternate regularly in the polymer chain. The analysis data given for this polymer in Table VIII was calculated for the ideal structure.

Sample SH-P1 was isolated by precipitation and was then washed well with water and methanol before drying. This polymer was then stirred for several hours with diethyl ether, in order to remove any residual monomer and, also, the very low molecular weight material. The resulting sample is SH-P1a. As shown in Tables VII and VIII, the treatment with ether has a negligible effect on the melting point range, viscosity, and elemental analysis of the polymer. With the exceptions of SH-P13 and SH-P14, all other polymers reported in Table VII were stirred with ether, filtered, and then dried in the final purification stage. In each case, this treatment appeared to remove a small amount of very low molecular weight material. In some cases, very small amounts of residual monomers were also removed.

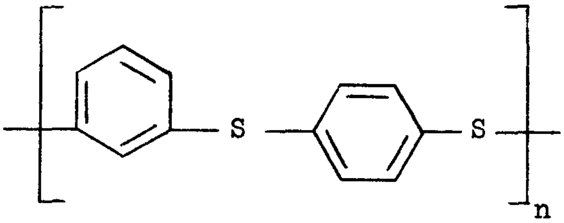
Scheme II

Polymer Structures

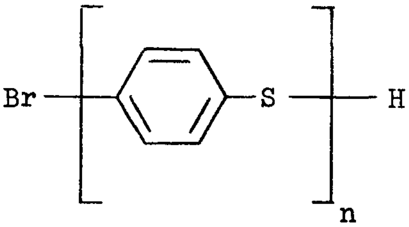
Sample Nos. SH-P1 and SH-P1a



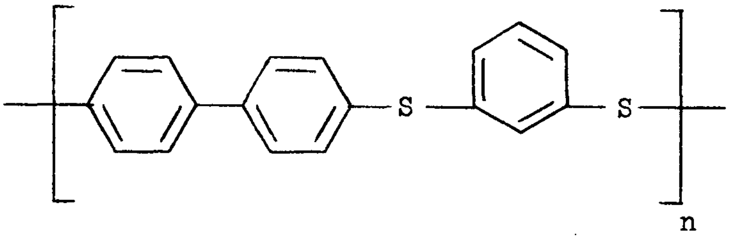
Sample No. SH-P2



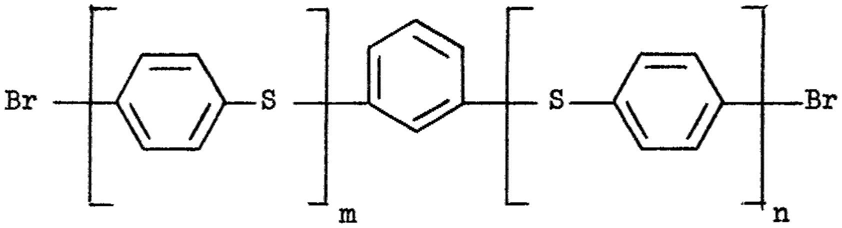
Sample No. SH-P3



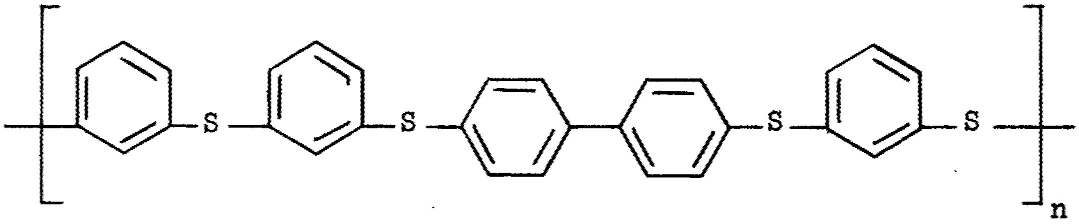
Sample No. SH-P4



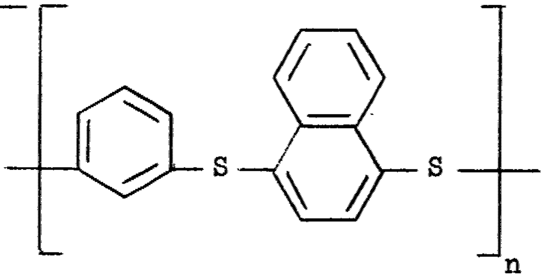
Sample No. SH-P5



Sample No. SH-P7



Sample No. SH-P10



Sample Nos. SH-P13 and SH-P14

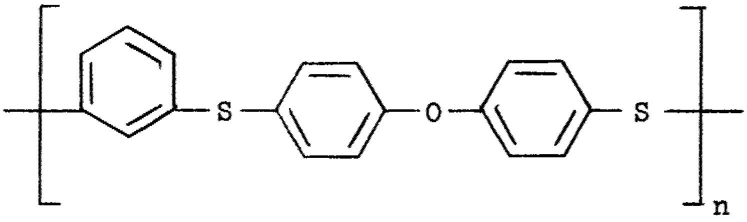


TABLE VII

PREPARATION AND PROPERTIES OF POLYPHENYLENE SULPHIDES AND RELATED POLYMERS

Polymerization (Sample No.)	MBDT g(moles)	dibromo compound g(moles)	DMF ml	K_2CO_3 g(moles)	Temp °C	Time hr	Polymer yield g	mpt[a] °C	η_{inh} 0.5% solution in HMP at 30°C
1. (SH-P1 and SH-P1a)[b]	5.6077 (0.04)	MDBB 9.4341 (0.04)	80	12.70 (0.092)	120-150 150-155	1 24	8.7	105-115 110-120	0.1 0.08
2. (SH-P2)	5.6060 (0.04)	pDBB 9.4290 (0.04)	80	12.70 (0.092)	50-150 150-155	2 24	7.7	110-140	0.15
3. (SH-P3)	4.725 g (0.025 mole) of 4-bromothiophenol		50	3.97 (0.029)	25-150 150-155	1-1/4 23-3/4	2.5	240-250	---[c]
4. (SH-P4)	4.4114 (0.031)	DBBP 9.6721 (0.031)	70	9.84 (0.071)	25-150 150-155	1 24	8.81	160-190	---
5. (SH-P5)	4-bromo-thiophenol 4.725(0.025)	MDBB 0.566 (0.0024)	50	3.97 (0.029)	25-150 150-155	2 24	2.65	210-230	---
6. (SH-P7)	2.8410 (0.02)	MDBB 2.3633(0.01) DBBP 3.1200(0.01)	40	6.35 (0.046)	25-150 150-155	1-1/2 24	4.25	85-105	0.11
7. (SH-P10)	2.8392 (0.02)	DBN 5.7199 (0.02)	40	6.35 (0.046)	25-150 150-155	1-1/4 25	4.67	155-195	---
8. (SH-P13)	2.8440 (0.02)	DBE 6.5692 (0.02)	40	6.35 (0.046)	25-150 150-155	1-1/4 24	1.72	only oligomeric gum isolated.	
9. (SH-P14)	2.8442 (0.02)	DBE 6.5698 (0.02)	40	6.35 (0.046)	25-150 150-155	1-1/4 96	4.41[d]	55-70	0.07

TABLE VII (CONCLUDED)

Footnotes:

HMP = Hexamethylphosphoramide
MDBB = m-dibromobenzene
DBBP = 4,4′-dibromobiphenyl
DBE = bis(p-bromophenyl) ether
MBDT = m-benzenedithiol
pDBB = p-dibromobenzene
DBN = 1,4-dibromonaphthalene

The polymers, whose viscosities are given, were 100% soluble in HMP.

a) The melting range of the polymers was determined, in open capillaries, using a standard melting point determination apparatus. The figures given, which are uncorrected, are, therefore, approximate.

b) Differences between the two samples SH-P1 and SH-P1a are explained in the text.

c) $\overline{M}_n$ calculated from bromine endgroup analysis $= \sim 1500$ (one bromine group per chain).

d) Mechanical losses during workup were greater than usual.

TABLE VIII

ELEMENTAL ANALYSIS OF POLYMERS

Sample No.	Formula of Polymer Repeat Unit	Calc. (C) Found (F)	Analysis Data				
			% C	% H	% S	% Br	Total %
SH-P1	$(C_6H_4S)_n$	C	66.67	3.70	29.63	---	---
		F	63.08	3.58	26.75	6.24	99.65
SH-P1a	$(C_6H_4S)_n$	C	66.67	3.70	29.63	---	---
		F	63.42	3.54	27.28	5.51	99.75
SH-P2	$(C_6H_4S)_n$	C	66.67	3.70	29.63	---	---
		F	66.21	3.73	28.45	1.75	100.14
SH-P3	$(C_6H_4S)_n$	C	66.67	3.70	29.63	---	---
		F	63.88	3.56	26.91	5.24	99.59
SH-P4	$(C_{18}H_{12}S_2)_n$	C	73.97	4.11	21.92	---	---
		F	70.85	4.12	19.98	5.00	99.85
SH-P5	predominantly $(C_6H_4S)_n$	C	66.67	3.70	29.63	---	---
		F	61.33	3.41	25.34	9.76	99.84
SH-P7	$(C_{30}H_{20}S_4)_n$	C	70.87	3.94	25.20	---	---
		F	69.13	3.92	24.16	2.28	99.49
SH-P10	$(C_{16}H_{10}S_2)_n$	C	72.18	3.76	24.06	---	---
		F	71.95	3.80	23.85	$<$ 0.3	99.60

Except for samples SH-P13 and SH-P14, the yields given in Table VII refer to the amount of ether insoluble polymer which was isolated. As indicated in this table, the polymers were generally obtained in high yield. The isolation of only a small amount of oligomeric material in polymerization 8 was not unexpected as the corresponding model reaction (VI) involving thiophenol and bis(p-bromophenyl) ether gave only a 41% yield of 4,4′-bis(phenylthio)diphenyl ether after a reaction time of 24-1/4 hr at 150° - 155°C. The use, in polymerization 9, of a much longer reaction time (96 hr) did result in the formation of polymer although, even in this case, the polymer isolated had only a very low molecular weight. Polymerization 9 actually gave a higher polymer yield than indicated in Table VII, as about 6 g of fairly pure polymer were initially isolated. However, accidental losses during subsequent reprecipitation of the polymer reduced the yield to 4.41 g. Polymerizations 8 and 9, and model reaction VI, indicate that the bromine groups in bis(p-bromophenyl) ether are displaced by the thiophenoxy anion only with difficulty. Polymer with the structure of SH-P14 can probably be prepared more successfully by using m-dibromobenzene and 4,4′-biphenyletherdithiol as monomers. The latter dithiol has now been prepared by reducing the corresponding disulphonyl chloride and, following purification, this polymerization will be carried out.

The structures of the polymers reported in Table VII were confirmed by elemental analysis (See Table VIII) and, also, by infrared spectroscopy. Absorption in the 600-900 cm^{-1} region is very characteristic of the benzene ring substitution pattern and, for each of the polymers reported, the absorption in this region corresponded to the expected polymer structure. As in the case of the model reactions, there appears to be no positional isomerization on the aromatic ring, the polymerizations taking place by the expected nucleophilic displacement mechanism.

As would be expected, the melting range of the polyphenylene sulphides and related polymers, reported in Table VII, is very dependent upon their structure. The poly(p-thiophenylene), prepared in polymerization 3, has the most regular structure and, therefore, as expected, this polymer has the highest melting point. The melting range, infrared spectrum, and solubility (see below) of SH-P3 are in good agreement with the corresponding data reported by other workers[19-21] for poly(p-thiophenylene).

In polymerization 5, 4-bromothiophenol was polymerized in the presence of a small amount of m-dibromobenzene, so that a meta-thiophenylene group would become incorporated in each predominantly para-linked polymer chain. It was hoped that incorporation of this unit would lower the melting point and increase the solubility of poly(p-thiophenylene). Although the melting range was lowered slightly (cf SH-P3), the solubility of the polymer does not appear to have been significantly increased. The small lowering of the melting range could be due to the formation of lower molecular weight polymer. A more efficient method of changing a polymer's properties involves the use of two different dibromo compounds, as illustrated in polymerization 6. In this reaction both m-dibromobenzene and 4,4′-dibromobiphenyl were polymerized with m-benzenedithiol. Comparison of the solubility (see below) and melting range of the polymers SH-P4 and SH-P7 indicates that the incorporation of further meta-thiophenylene units has a great effect on the physical characteristics of the polymer. By varying the proportion of the two dibromo compounds, a variety of polymers, having different ratios of meta- and biphenyl-linkages, could be prepared. Some control over the melting point of the polyphenylene sulphides can, therefore, be achieved.

The softening behavior of samples SH-P1a, SH-P2, SH-P3 and SH-P4 has also been studied by Dr. G. F. L. Ehlers and Mr. K. R. Fisch of the AFML. They report[22] that each of these polymers showed distinct melting and display a two-step penetration on the softening apparatus. Generally, these penetrations occurred close to, or at somewhat lower temperatures, than the melting range temperatures given in Table VII. In the case of SH-P1a, DTA showed two distinct endotherms (at 85° - 90°C and 120°C) which are apparently crystalline melting points. Dr. Ehlers and Mr. Fisch suggest[22] that two different crystalline forms are present, and report that the same behavior has been observed previously with poly(p-thiophenylene) samples from Dow Chemical Company and from Ryton. The softening point curve of SH-P3 showed much similarity to the curve for Ryton polyphenylene sulphide, although SH-P3 seems to have a lower average molecular weight and a wide molecular weight distribution.[22]

TGA of the four samples referred to above was not carried out in the AFML, as Dr. Ehlers and Mr. Fisch report[22] that past experience has shown that polyphenylene sulphides have thermograms lying close to that of the Ryton polyphenylene sulphide. However, isothermal aging of several of the polymers reported in Table VII has been carried out in this laboratory. Samples(0.16 - 0.38 g) of the polymers were weighed into small pyrex tubes and were then aged in a small furnace in an atmosphere of non-circulating air. After aging at 200°C, the resulting material was further aged at 300°C, 350°C and 400°C. The aging times and temperatures are shown in Table IX, together with the cumulative weight loss for each polymer.

As shown in Table IX, all of the polymers, apart from SH-P3, showed small and similar weight losses at 200°C and 300°C. However, at 350°C, and particularly at 400°C, significant weight loss occurs from all of the polymers. The weight losses at the higher temperatures may not reflect the properties of the initial material, as the original polymer structure may have been changed by the prior aging at 200°C and 300°C. All of the polymers, apart from SH-P3, melted and darkened at 200°C. This behavior occurred at 300°C for SH-P3. The darkening was even more pronounced at 350°C and 400°C. At the completion of the isothermal aging experiments, all of the polymers had turned to black solids (possibly non-melting materials) having a charcoal-like appearance. In some cases, a white sublimate seemed to be formed at 400°C. The good glass adhesion shown by these polymers, and also their pyrolyzed products, was most noticeable during these experiments. When the polymers were removed from the furnace to be weighed, the resulting contraction caused small pieces of glass to be pulled from the walls of the pyrex tubes. In most cases, there still appeared to be good glass adhesion after the aging at 400°C. No analysis of the polymer residues has been carried out.

The solubility of the polymers reported in Table VII varied considerably with structure, as might be expected. The polymers (except SH-P7 and SH-P14) were not swollen, or completely solubilized, by cold organic solvents. Polymer SH-P1a was partially solubilized by conc.H_2SO_4 and methanesulphonic acid, giving pinkish-brown solutions. Polymer SH-P3 appeared to be partially soluble in conc.H_2SO_4 giving a green solution.

TABLE IX

ISOTHERMAL AGING OF POLYPHENYLENE SULPHIDES AND RELATED POLYMERS

Polymer Sample (Initial wt., g)	Cumulative wt loss(%). After 6 days at 200°C	Cumulative wt loss(%). After 8 days at 300°C	Cumulative wt loss(%). After 7 days at 350°C	Cumulative wt loss(%). After 9 days at 400°C
SH-P1a (0.2952)	0.34	4.5	21.8	67.8
SH-P2 (0.1952)	0.41	1.95	7.07	77
SH-P3 (0.1664)	6.65	13.3	16.0	84.4
SH-P4 (0.2236	1.48	4.96	8.8	49.3
SH-P7 (0.3733)	1.53	3.08	9.6	66
SH-P10 (0.3147)	1.56	2.32	17.2[a]	--

Footnotes:

a) After 5 days at 350°C. This experiment was terminated when the pyrex tube cracked and polymer was lost.

It has been previously reported[23] that conc. H_2SO_4 reacts with poly(p-thiophenylene). Several of the polymers did dissolve completely in warm, or boiling, organic solvents to give clear, colorless solutions. However, in a number of cases, precipitation of the polymer often took place as the solution cooled to room temperature. The occurrence and the time taken for this precipitation was dependent upon the particular polymer/solvent combination. It has been previously reported,[24] that both poly(2,6-dimethyl-phenylene oxide) and poly(2,6-diphenyl-phenylene oxide) crystallize from various organic solvents. Similar behavior has been reported[23] for poly(p-thiophenylene).

The meta linked polymer (SH-Pla) was completely soluble in most common organic solvents, when these were either warmed or boiled, e.g., DMAc, DMF, DMSO, C_6H_6, THF, HMP, $CHCl_3$, CCl_4, chlorobenzene, toluene, N-methylpyrrolidone etc. However, in the majority of the solvents examined, the polymer precipitated fairly rapidly as the solution cooled to room temperature. In the case of THF and N-methylpyrrolidone, precipitation occurred after 2-3 days, and, in the case of HMP, precipitation did not commence until approximately one week after solubilization.

Poly(m,p-thiophenylene) (SH-P2) was also soluble in a wide variety of common organic solvents when these were either warmed or boiled. However, in the majority of solvents examined, precipitation again occurred rapidly as the solutions cooled to room temperature. However, this polymer does not precipitate from either HMP, or N-methylpyrrolidone, even after many weeks. Precipitation from THF occurred after a period of 1-2 days and from CCl_4 and $CHCl_3$ only after several hours.

A sample of poly(p-thiophenylene) (SHP3) was extracted successively, with boiling toluene and diphenyl ether. Seventeen percent of the polymer was soluble in toluene and, of the remaining polymer, 53% was soluble in diphenyl ether. These data are in agreement with the solubility data reported by Handlovits[21] for poly(p-thiophenylene).

The solubility of polymers SH-P4 and SH-P10 has not been fully investigated. Polymer SH-P4 did dissolve in N-methylpyrrolidone, but precipitation occurred as the solution cooled. It must also be noted that polymer SH-P7 is readily soluble in THF and HMP at room temperature.

The incorporation of further meta-thiophenylene linkages into the polymer prepared from m-benzenedithiol and 4,4′-dibromobiphenyl, therefore, has a very significant effect on the polymer solubility. Polymer SH-P14 is readily soluble, at room temperature, in benzene, THF, and HMP.

Polymers SH-P1a, SH-P2, SH-P3, and SH-P4 all showed good glass-glass adhesion.

iii) Effect of polymerization conditions on the molecular weight of poly(m,p-thiophenylene)

The results of the experiments which have been carried out to determine the effect of polymerization conditions on the molecular weight of poly(m,p-thiophenylene) are collected in Table X. Analysis data for the polymers, where this is available, is given in Table XI. Polymerization 2, previously reported in Table VII is given for the purposes of comparison. Elemental analysis and, in all cases, infrared spectroscopy, indicated that the polymers had the expected structure. The complete absence of polymerization in diphenyl ether was unexpected. Polymer has also been obtained from a reaction carried out in N-methylpyrrolidone, but workup of this material is not yet complete.

When polymerization was carried out in DMF, the inherent viscosity of the resulting polymer increased, as expected, as the reaction time was raised from 24 to 72 hr (polymerizations 2, 10 and 11). However, when the polymerization was carried out for 96 hr (polymerizations 12 and 13),an unexpected lowering of the molecular weight occurred. No explanation for this result can be given at present. Polymer was observed to precipitate from the reaction mixture, and then to coagulate, during polymerizations 2, 10, 11, 12 and 13. It was thought that this behavior might limit the attainable molecular weight and, therefore, an attempt was made to keep the polymer in solution by using a greater volume of DMF (polymerizations 14 and 15). Less precipitation, and no coagulation, occurred during these polymerizations, but this dilution of the reaction mixture caused a very significant decrease in the viscosity of the polymer obtained. Both DMAc and HMP appear to be good solvents for this polymerization, a reasonably high molecular weight polymer being produced in both polymerizations 16 and 17.

TABLE X

EFFECT OF POLYMERIZATION CONDITIONS ON THE MOLECULAR WEIGHT OF POLY(m,p-THIOPHENYLENE)

Polymerization (Sample No.)	MBDT g(moles)	pDBB g(moles)	Solvent vol., ml	K_2CO_3 g(moles)	Temp °C	Time hr	Polymer yield g	mpt[a] °C	ηinh[b] 0.5% solution in HMP at 30°C
2. (SH-P2)	5.6060 (0.04)	9.4290 (0.04)	DMF 80	12.70 (0.092)	50-150 150-155	2 24	7.7	110-140	0.15
10. (SH-P6)	2.8434 (0.02)	4.7197 (0.02)	DMF 40	6.35 (0.046)	80-150 150-155	3/4 48	2.90	110-130	0.26
11. (SH-P9)	2.8416 (0.02)	4.7230 (0.02)	DMF 40	6.35 (0.046)	25-150 150-155	2-1/4 72	3.53	105-125	0.40
12. (SH-P16)	2.8435 (0.02)	4.7271 (0.02)	DMF 40	6.35 (0.046)	25-150 150-155	1-1/4 96	3.53	100-125	0.24
13. (SH-P16a)	2.8383 (0.02)	4.7200 (0.02)	DMF 40	6.35 (0.046)	25-150 150-155	1 96-1/2	3.64	105-120	0.18
14. (SH-P11)	2.8425 (0.02)	4.7249 (0.02)	DMF 80	6.35 (0.046)	25-150 150-155	1-1/4 48	3.53	110-125	0.13
15. (SH-P12)	2.8452 (0.02)	4.7294 (0.02)	DMF 80	6.35 (0.046)	25-150 150-155	1-1/4 72	3.51	100-120	0.15
16. (SH-P18)	2.8401 (0.02)	4.7201 (0.02)	DMAc 40	6.35 (0.046)	25-165 165-170	1-3/4 48	3.73	100-120	0.41
17. (SH-P19)	2.8414 (0.02)	4.7224 (0.02)	HMP 40	6.35 (0.046)	25-170 170-175	3/4 48	3.86	115-135	0.27
18.	2.8413 (0.02)	4.7218 (0.02)	Ph_2O 40	6.35 (0.046)	25-170 170-175	1-1/4 72	no polymer or oligomer isolated.		

Footnotes:

MBDT = m-benzenedithiol
DMF = N,N-dimethylformamide
DMAc = N,N-dimethylacetamide
pDBB = p-dibromobenzene
HMP = Hexamethylphosphoramide
Ph_2O = Diphenyl ether

a) The melting range of the polymers was determined, in open capillaries, using a standard melting point determination apparatus. The figures given, which are uncorrected, are, therefore, approximate.

b) All polymers were 100% soluble when heated in HMP.

TABLE XI

ELEMENTAL ANALYSIS OF POLY(m,p-THIOPHENYLENE) SAMPLES

Sample No.	Found Analysis Data[a]				Total %[b]
	% C	% H	% S	% Br	
SH-P2	66.21	3.73	28.45	1.75	100.14
SH-P6	65.89	3.63	29.12	< 0.3	99.82[c]
SH-P9	66.32	3.75	29.35	0.93	100.35
SH-P16	66.10	3.75	29.85	< 0.3	99.70
SH-P11	66.02	3.72	29.70	< 0.3	99.44
SH-P12	66.09	3.66	29.58	< 0.3	99.33

Footnotes:

a) Anal. calc. for $(C_6H_4S)_n$: C, 66.67%; H, 3.70%; S, 29.63%.

b) Total does not include %Br where this is less than 0.3%.

c) Includes a residue of 1.18%.

Further polymerizations will be carried out in DMAc and HMP, using longer reaction times and higher temperatures. The use of pyridine, quinoline and tetramethylene sulphone, as polymerization solvents, will also be investigated. The effect of using other metal carbonates will also be determined.

Isothermal aging of polymer SH-P9 resulted in the following cumulative weight losses after 6 days at 200°C, 8 days at 300°C, 7 days at 350°C, and then 9 days at 400°C: 0.29%; 1.75%; 9.1%; 93%. Weight losses at the lower temperatures are similar to those observed for the poly(m,p-thiophenylene) sample SH-P2 (Table IX). However, at the completion of the aging at 400°C, SH-P9 had lost 16% more weight than SH-P2.

iv) Substitution of polyphenylene sulphides with nitrile groups

Initial experiments in this area were concerned with the preparation of poly(m,p-thiophenylene) containing nitrile endgroups. In polymerization 19 (Table XII), the initial stage was carried out to obtain a polymer with bromine and thiol endgroups. The reaction mixture was then cooled slightly and further dithiol, DMF, and K_2CO_3 were added. The reaction was then continued. The object of this two-stage reaction was to obtain a polymer having only thiol endgroups. However, analysis indicated that the polymer obtained (SH-P8) still contained some bromine endgroups (See Table XII), although these are present in low concentration. This polymerization was then repeated (polymerization 20, Table XII) with the addition of a third stage, in which 4-bromobenzonitrile and further DMF were added. Both elemental analysis and infrared spectroscopy indicated that this approach had met with some success, and that the polymer obtained (SH-P15) contained some nitrile endgroups. When the infrared spectrum of this polymer was obtained from a "slow scan", a clear nitrile group absorption was observed at 2225 cm^{-1}. This band was not observed when the spectrum was taken using a "fast scan." Also, the polymer was stirred with ether during the final purification stage and, therefore, does not contain residual 4-bromobenzonitrile.

TABLE XII

TWO- AND THREE-STAGE POLYMERIZATION

Polymerization (Sample No.)	MBDT g(moles)	pDBB g(moles)	DMF ml	K_2CO_3 g(moles)	Temp $^\circ$C	Time hr	Polymer yield g[a]	mpt[b] $^\circ$C	η_{inh} 0.5% solution in HMP at 30°C
19. 1st stage	2.8409 (0.02)	4.7200 (0.02)	40	6.35 (0.046)	25-150 150-155	2 24	---	---	---
2nd stage (SH-P8)[c]	1.1630 (0.008)	---	20	2.5 (0.018)	150-155	6	4.05	95-125	0.27 (solubility= 95.6%)
20. 1st stage	2.8456 (0.02)	4.7294 (0.02)	40	6.35 (0.046)	50-150 150-155	1-1/4 24	---	---	---
2nd stage	1.9145 (0.014)	---	20	4.3 (0.031)	150-155	16	---	---	---
3rd stage (SH-P15)[c]	3.7235 g (0.021 moles) of 4-bromobenzonitrile added		10	---	150-155	24	3.58	95-110	0.18 (solubility= 100%)

Footnotes: MBDT = m-benzenedithiol pDBB = p-dibromobenzene

a) Diethyl ether insoluble polymer.

b) Determined in open capillaries on a melting point determination apparatus.

c) Anal. calc. for $(C_6H_4S)_n$: C, 66.67%; H, 3.70%; S, 29.63%.
Anal. found for SH-P8: C, 66.09%; H, 3.87%; S, 29.35%; Br, 0.83%.
Anal. found for SH-P15: C, 66.88%; H, 3.58%; S, 28.80%; Br, < 0.3%; N, 0.52%.

The success of this method of introducing nitrile endgroups is probably limited by the fact that, particularly in DMF, polymer precipitates during the early stages of reaction, and then coagulates into a soft mass. DMAc, or hexamethylphosphoramide, may be better solvents for this type of reaction. Also, if suitable reaction conditions can be found, it may be possible to carry out this reaction in one stage, using an intial mixture of a dibromo compound, an excess of the dithiol, and 4-bromobenzonitrile. It may also be noted that a number of the polymers reported in Table X have very low bromine contents, i.e., a high concentration of thiol endgroups. Attempts will be made to endcap these polymers by reacting them with 4-bromobenzonitrile, in the presence of K_2CO_3.

The introduction of nitrile groups, as substituents on the main chain, is being approached in two ways. The first of these involves the use of 3,5- and 2,4-dichlorobenzonitrile as monomers. The preparation of 3,5-dichlorobenzonitrile has now been carried out and, following purification, this compound will be used in polymerizations. The preparation of 2,4-dichlorobenzamide has been completed, but this amide requires further purification before conversion to the corresponding nitrile. By employing mixtures of one of these nitriles and an aromatic dihalide, it should be possible to exert some control over the number of nitrile groups present as substituents on the polymer backbone.

The second method of introducing of nitrile groups into the polymer backbone involves bromination of the aromatic rings, followed by treatment with cuprous cyanide. A similar method of introducing nitrile groups into an oligomeric phenylene oxide has been reported.[25] In this work, a Br_2/Fe mixture, in CCl_4, was used as the brominating agent. An attempt was made to brominate polymer SH-P11 (Table X) using this method. This polymer could be partially dissolved in the volume of CCl_4 employed by boiling the mixture. The bromination was then carried out at room temperature. The resulting crude polymer was very high melting, and could not be completely dissolved in boiling HMP. The part that did dissolve was reprecipitated as a dark-brown/black material. It should be noted that a large excess of bromine was employed in this experiment. This method may be more applicable for introducing smaller amounts of bromine into the polymer, as the resulting crude material may then be lower melting and more easily solubilized and could, therefore, be purified more easily.

Allowing a mixture of SH-P11 and bromine to stand overnight was found to be a better method of brominating the polymer, as the HBr and unreacted bromine can be easily removed from the crude product. After reacting a sample of SH-P11 with excess bromine, the weight increase indicated that an average of 1-2 bromine groups had been introduced into each aromatic ring of the polymer chain. The melting range of the polymer (SH-P11B) had increased from 110° - 125°C to 205° - 225°C. Infrared spectroscopy indicated that a change in the ring substitution pattern had occurred. These observations are similar to results reported by other workers.[23] Analysis data for the brominated polymer is not yet available. A sample of SH-P12 was reacted with a smaller amount of bromine and, in this case, the weight increase indicated that an average of one bromine group for every 2-3 aromatic rings had been introduced. This polymer (SH-P12A) melted at 120° - 135°C (SH-P12 melts at 100° - 120°C). Elemental analysis of this polymer is not yet available.

A sample of SH-P11B was reacted with cuprous cyanide in refluxing DMF, in an attempt to replace the bromine groups with nitrile groups. N-methylpyrrolidone may be a better solvent for this reaction,[26,27] as it would dissolve the cuprous cyanide, and may also partially solubilize the brominated polymer. After workup, the weight loss from SH-P11B indicated that some bromine groups had been replaced by nitrile groups. This was confirmed by infrared spectroscopy which clearly showed an absorption at 2225 cm^{-1} due to nitrile groups. The resulting bright yellow polymer (SH-P11C) turned to a dark-brown color at about 200°C, but did not melt below 500°C. The structure of these materials is presently being investigated.

Further attempts will be made to introduce nitrile groups into the polymer chain by the methods described above. In particular, the low molecular weight polymer (SH-P14, Table VII) containing ether and sulphide linkages will be employed, as this may yield substituted polymers with a relatively low melting point and better solubility than the substituted poly(m,p-thiophenylenes).

3. Experimental

a. Thiols

i) Thiophenol

Thiophenol was dried over anhydrous $MgSO_4$ and was then purified by distillation at reduced pressure, using a column packed with glass helices. A middle fraction of bp 56° - 57°C (10 mm Hg) was collected; lit[28] bp 46.4°C (10 mm Hg). The cause of this boiling point difference of 10°C is not known.

ii) 4-Bromothiophenol

This compound was purified by crystallization from ethanol. mp 73° - 75°C (uncorr.); lit[28] 75°C.

iii) m-Benzenedithiol

m-Benzenedithiol was obtained by the reduction of m-benzenedisulphonyl chloride with zinc amalgam in sulphuric acid. Experimental details of this preparation will not be given here, as the methods employed, for both the amalgam preparation and the reduction, have been reported by Caesar.[29] The only modifications made to the reported procedure were concerned with the workup. The reaction mixture was filtered under gravity and the solid material was washed with distilled water and then ether. The dithiol was extracted from the slightly cloudy aqueous filtrate, using diethyl ether. The ether extracts were then combined and dried over $MgSO_4$. Removal of the ether, after filtration, gave the crude dithiol. This was purified by distillation, under reduced pressure, using a small Vigreux column fitted with a partial take-off head. A clear colorless middle fraction was collected of bp 122° - 129°C (5-11 mm Hg). Distillation of a second batch of crude dithiol gave a clear colorless middle fraction of bp 127° - 132°C (14-18 mmHg); lit[28] bp 123°C (17 mm Hg). The reason for the discrepancy between the boiling points of these fractions and the literature boiling point is not clear. The presence of impurities could not be detected in the infrared spectrum of either batch of dithiol. Analysis data for the second batch is given below.

Anal. Calc. for $C_6H_6S_2$: C, 50.70%; H, 4.23%; S, 45.07%.
Found: C, 50.61%; H, 4.28%; S, 44.88%.

Four dithiol preparations have been carried out giving crude yields of 63%, 94%, 92.5% and 91% respectively. The combined yield of purified dithiol from the first two preparations was 61% and from the second two preparations, 79%. The m-benzenedisulphonyl chloride was supplied by Koppers (99.5%, mp 58° - 61°C; lit[30] mp 61° - 61.5°C). This material was used as received. The zinc dust was supplied by J. T. Baker (C. P. powder, 99.5%).

iv) 4,4′-Biphenyldithiol

This dithiol was prepared according to a procedure outlined in the literature.[18] After sublimation (160° - 165°C at ~ 0.05 mm Hg), a 77% yield of the white dithiol was obtained. mp 177.5° - 179°C (uncorr); lit[18] 178° - 180°C.

Anal. Calc. for $C_{12}H_{10}S_2$: C, 66.06%; H, 4.59%; S, 29.36%.
Found: C, 66.26%; H, 4.58%; S, 29.19%.

The 4,4′-biphenyldisulphonyl chloride (Aldrich Chemical Co.) was used as received.

v) 4,4′-Biphenyletherdithiol

A reported procedure[18] was also used for the preparation of this dithiol. After sublimation (96° - 98°C at 0.05 mm Hg), the product was contaminated with a small amount of a yellow impurity. This dithiol will be resublimed before use.

b. Bromides

i) Bromobenzene

Bromobenzene was dried over anhydrous $MgSO_4$ and then distilled, at atmospheric pressure, using a Vigreux column. A middle fraction was collected, bp 155°C (756 mm Hg); lit[28] bp 156°C (760 mm Hg).

ii) m-Dibromobenzene

This material was dried over anhydrous $MgSO_4$ and then distilled, at atmospheric pressure, using a column packed with glass helices. A middle fraction of bp 217.5° - 218.5°C (758-760 mm Hg) was collected; lit[28] bp 218°C (760 mm Hg).

iii) p-Dibromobenzene

This compound was purified by recrystallization from ethanol, after treatment of the hot solution with decolorizing charcoal. mp 85° - 87°C (uncorr); lit[28] 87.3°C.

iv) 4,4′-Dibromobiphenyl

This material was purified by recrystallization from methanol. mp 163° - 164°C (uncorr); lit[28] 164°C.

v) 1,4-Dibromonaphthalene

This material was recrystallized twice from ethanol, using decolorizing charcoal. mp 79° - 80°C (uncorr); lit[31] 81° - 82°C.

vi) Bis(p-bromophenyl) ether

This compound was purified by crystallization from a mixture (4:1) of glacial acetic acid and distilled water. mp 58.5° - 59.5°C (uncorr); lit[28] 60.5°C.

c. Nitriles

i) 4-Bromobenzonitrile

This compound was purified by crystallization from ethanol. mp 110° - 111°C (uncorr); lit[28] 114°C.

ii) 3,5-Dichlorobenzonitrile

This nitrile has been obtained from the corresponding benzoic acid compound via the acid chloride and the amide. The 3,5-dichlorobenzoic acid (Aldrich Chemical Co.) was used as received.

The acid (38.2 g, 0.2 mole) was mixed with excess thionyl chloride (44 g, 0.37 mole) in a round-bottomed flask. This mixture was magnetically stirred and refluxed for 1-3/4 hr. The initially paste-like reaction mixture turned to a dark colored liquid as the acid chloride was formed. A distillation head and a condenser were then fitted to the flask and the unreacted thionyl chloride ($\sim$ 10.5 g) was slowly distilled from the reaction mixture to leave $\sim$43 g of the crude, dark-brown acid chloride.

The crude acid chloride was added dropwise to 100 ml of concentrated aqueous ammonia which was magnetically stirred and cooled with an ice/salt bath. This addition took about one hour. The resulting mixture was left to stand overnight and the crude 3,5-dichlorobenzamide (35.5 g, 93.5% yield) was then filtered off. Recrystallization from distilled water yielded four crops of combined weight 28 g. The melting points of these crops ranged from 156.5° - 159°C (uncorr). Infrared spectroscopy indicated that this material still contained some impurities. Further crystallization of the amide from water yielded amide of mp 156° - 157°C (uncorr).

Anal. calc. for $C_7H_5Cl_2NO$: C, 44.21%; H, 2.63%; Cl, 37.37%; N, 7.37%.
Found: C, 44.43%; H, 2.57%; Cl, 37.23%; N, 7.39%.

This amide has been converted to the corresponding nitrile using a recently reported procedure which employs HMP as the dehydrating agent.[32] Workup of this product is not yet complete. However, the dehydration reaction has been carried out on a small scale using 3 g (0.016 mole) of amide and 11 ml of HMP. This mixture was refluxed for 2 hr and, after initial workup as described in the literature[32] and also sublimation, 2.05 g (74.5%) of 3,5-dichlorobenzonitrile were obtained. Infrared spectroscopy confirmed that the nitrile, free of amide, had been obtained. However, the mp of the nitrile (~ 45° - 62°C; lit[33] 65°C) indicates that further purification is required.

The thionyl chloride, used to convert the acid to the acid chloride, was fractionated, using a Vigreux column, from quinoline and then from boiled linseed oil. A middle fraction was collected in each case. The HMP (Dow tech. grade), used to dehydrate the amide, was dried and clarified by passage through a column of activated alumina. It was then further dried over calcium hydride before use.

iii) 2,4-Dichlorobenzonitrile

This nitrile is being obtained from the corresponding benzoic acid compound using the methods described above. The amide has been obtained, and following purification, which is presently being carried out, this compound will be converted to the nitrile.

d. Solvents

"SpectrAR" grade DMF was used in the polymerizations and model reactions and was dried over anhydrous $MgSO_4$ before use.

The DMAc, HMP and diphenyl ether were stirred with and then refluxed over calcium hydride. These solvents were then fractionally distilled using a Vigreux column and a partial take-off head, a middle fraction being collected in each case. The DMAc boiled at 58°C (11 mm Hg); lit[34] 58.0° - 58.5°C (11.4 mm Hg). The HMP boiled at 69.5°C (1 mm Hg); lit[35] 68° - 70°C (1 mm Hg). The diphenyl ether boiled at 74° - 76°C (0.5 - 0.6 mm Hg); lit[28] 121°C (10 mm Hg), i.e., 74°C (0.5 mm Hg).

e. Model Reactions

All model reactions were carried out under dry nitrogen in a three-necked flask equipped with a condenser. The reaction mixtures were magnetically stirred and heated on an oil bath. At the completion of each reaction, the yellow solution usually contained some solid material. Each reaction mixture was initially worked up in a similar manner. The DMF was removed under reduced pressure, and dilute HCl was then slowly added to the remaining solid/liquid mixture. In each case carbon dioxide was evolved and, usually, the odor of thiophenol was regenerated, indicating that reaction was not complete. The aqueous mixture was then extracted with benzene. The benzene extracts were combined, washed with water, and dried over $MgSO_4$. Following filtration, the benzene was removed under reduced pressure leaving either a yellowish liquid, or a yellowish-white solid. The conditions employed in each reaction, and the isolation of each model compound, are described below:

Model Reaction I

Thiophenol (10.83 g, 0.098 mole) and bromobenzene (15.39 g, 0.098 mole) were reacted together in 200 ml of DMF containing 15.55 g (0.113 mole) of K_2CO_3. The mixture was heated between 25° and 150°C for 2 hr, and then at 150° - 155°C for 48 hr. Diphenyl sulphide was isolated by distillation after the initial workup described above. 6.41 g (35%) of diphenyl sulphide were obtained; bp 147° - 152°C (8-9 mm Hg) lit[28] 145°C (8 mm Hg).

Model Reaction II

Thiophenol (11.12 g, 0.101 mole) and p-dibromobenzene (11.92 g, 0.0505 mole) were reacted together in 100 ml of DMF containing 16.03 g (0.116 mole) of K_2CO_3. The mixture was heated between 25°C and 150°C for 2 hr and then at 150° - 155°C for 24 hr. The residue remaining after the initial workup was distilled under reduced pressure. A small amount of thiophenol, but no p-dibromobenzene, was collected. The solid pot-residue was recrystallized from absolute ethanol. Three crops were obtained whose combined weight was 12.77 g [86% yield of p-bis(phenylthio)benzene]. mp 77° - 82°C (uncorr); lit[36] 82° - 83°C. Further recrystallization from absolute ethanol gave a pure sample of p-bis(phenylthio)benzene. mp 79° - 81°C (uncorr).

Anal. Calc. for $C_{18}H_{14}S_2$: C, 73.48%; H, 4.76%; S, 21.78%.
Found: C, 73.32%; H, 4.78%; S, 21.74%.

Model Reaction III

Thiophenol (10.44 g, 0.095 mole) and m-dibromobenzene (11.21 g, 0.0475 mole) were reacted together in 100 ml of DMF containing 15.08 g (0.109 mole) of K_2CO_3. The mixture was heated between 25°C and 150°C for 2-1/2 hr and then at 150° - 155°C for 26 hr. The mixture remaining after the initial workup was distilled under reduced pressure. A small initial fraction (~1 ml) boiling at 150° - 164°C (0.1 - 0.2 mm Hg) was discarded. The fraction boiling at 164° - 170°C (0.1 - 0.2 mm Hg) was collected. This was slightly cloudy and was, therefore, filtered through a small glass sinter containing a small plug of cotton-wool to give 9.7 g [69-70% yield of m-bis(phenylthio) benzene] of a clear, colorless oil. The boiling point of m-bis(phenylthio) benzene is reported[36] to be 180° - 185°C (0.35 mm Hg), i.e. ~ 160°C (0.1 mm Hg).

Anal. Calc. for $C_{18}H_{14}S_2$: C, 73.48%; H, 4.76%; S, 21.78%.
Found: C, 73.35%; H, 4.90%; S, 21.78%.

Model Reaction IV

Thiophenol (10.79 g, 0.098 mole) and 4,4′-dibromobiphenyl (15.288 g, 0.049 mole) were reacted together in 100 ml of DMF containing

15.55 g (0.113 mole) of K_2CO_3. The mixture was heated from 25° to 150°C over 3/4 hr and then at 150° - 155°C for 24 hr. The white solid remaining after the initial workup was distilled under reduced pressure, using a very short path distillation head. A small amount of thiophenol, but no 4,4'-dibromobiphenyl, was recovered. The remaining yellowish-white solid was recrystallized from ^{i}PrOH. Two crops having a combined weight of 15.5 g [85.5% yield of 4,4'-bis(phenylthio)biphenyl] were obtained. mp 113° - 118°C. A third crop of very low mp was discarded. A small amount of material was also spilled. The yield of this reaction is therefore greater than 85%. Further recrystallization from ^{i}PrOH gave a pure sample of 4,4'-bis(phenylthio)benzene. mp 115° - 116°C (uncorr); lit[36] 119° - 120°C.

Anal. Calc. for $C_{24}H_{18}S_2$: C, 77.84%; H, 4.87%; S, 17.30%.
Found: C, 77.95%; H, 5.14%; S, 17.13%.

Model Reaction V

Thiophenol (5.51 g, 0.05 mole) and 1,4-dibromonaphthalene (7.16 g, 0.025 mole) were reacted together in 50 ml of DMF containing 7.95 g (0.058 mole) of anhydrous K_2CO_3. The mixture was heated from 25° to 150°C over 1 hr and 20 min and then at 150° - 155°C for 24 hr. After removal of the DMF and acidification the crude product was extracted with ether. After drying, the ether was evaporated to leave a yellowish-white solid. The material was recrystallized from ^{i}PrOH, after treating the hot solution with decolorizing charcoal. Two crops having a combined weight of 7.74 g [90% yield of 1,4-bis(phenylthio)naphthalene] were obtained. mp 95° - 103°C. Further recrystallization from ^{i}PrOH gave a pure sample of 1,4-bis(phenylthio)naphthalene. mp 101° - 103°C (uncorr).

Anal. Calc. for $C_{22}H_{16}S_2$: C, 76.76%; H, 4.65%; S, 18.61%.
Found: C, 76.91%; H, 4.62%; S, 18.77%.

Model Reaction VI

Thiophenol (5.55 g, 0.05 mole) and bis(p-bromophenyl)ether (8.28 g, 0.025 mole) were reacted together in 50 ml of DMF containing 8.0 g (0.058 mole) of K_2CO_3. The mixture was heated from 25° to 150°C over 1-1/2 hr and then at 150° - 155°C for 24-1/4 hr. The brown liquid remaining after the initial workup was distilled under reduced pressure, using a very short path distillation head. A small amount of thiophenol was recovered. The remaining brown oily liquid crystallized when the flask was scratched with a glass rod. This solid was recrystallized from ^{i}PrOH using a small amount of decolorizing charcoal. One crop of white crystals was obtained, weighing 4.0 g [41% yield of 4,4′-bis(phenylthio) diphenyl ether]. mp ~ 64° - 74°C. A small second crop of paste-like solid was discarded. Further crystallization from ^{i}PrOH gave a pure sample of 4,4′-bis(phenylthio)diphenyl ether. mp 86° - 88°C (uncorr); lit[36] 82° - 84°C. Analysis data for this compound is not yet available.

Model Reaction VII

Thiophenol (3.104 g, 0.028 mole) and 4-bromobenzonitrile (5.096 g, 0.028 mole) were reacted together in 60 ml of DMF containing 4.5 g (0.033 mole) of K_2CO_3. The mixture was heated between 25° and 150°C for 1-1/2 hr and then at 150° - 155°C for 23-1/2 hr. The yellow oil remaining after the initial workup was distilled under reduced pressure, using a very short path distillation head. A small amount of white sublimate (4-bromobenzonitrile), together with a small amount of thiophenol, was first collected. A clear, colorless oil (4.84 g, 82% yield of 4-cyanodiphenyl sulphide) was then collected. bp 132° - 135°C (0.2 - 0.25 mm Hg).

Anal. Calc. for $C_{13}H_9NS$: C, 73.93%; H, 4.27%; N, 6.64%; S, 15.17%.
Found: C, 74.18%; H, 4.50%; N, 6.79%; S, 15.25%.

Model Reaction VIII

m-Benzenedithiol (2.847 g, 0.02 mole) and 4-bromobenzonitrile (7.298 g, 0.04 mole) were reacted together in 40 ml of DMF containing 6.35 g (0.046 mole) of K_2CO_3. The mixture was heated from 25° to 150°C for 1-1/4 hr and then at 150° - 155°C for 24 hr. After the initial workup, a thick yellow oil, which solidified at room temperature, was obtained. This material was distilled under reduced pressure, using a very short path distillation head. A small amount of white sublimate (4-bromobenzonitrile) was obtained and a black residue remained. This residue was dissolved in ether to give a dark yellow solution. After extraction with 20% aqueous NaOH, 20% HCl and 10% aqueous $NaHCO_3$, this

solution (light yellow color) was dried over anhydrous sodium sulphate. The ether was then removed leaving a yellow viscous oil which solidified at room temperature. This solid was recrystallized from ethanol after treatment with a small amount of decolorizing charcoal. Two crops of combined weight 4.79 g [70% yield of m-bis(4-cyanophenylthio)benzene] were obtained. mp 74° - 78°C. Further recrystallization from ethanol gave pure white crystals of this model compound. mp 85° - 87°C (uncorr).
Anal. Calc. for $C_{20}H_{12}N_2S_2$: C, 69.77%; H, 3.49%; N, 8.14%; S, 18.61%.
Found: C, 69.99%; H, 3.49%; N, 8.21%; S, 18.27%.

Two preparations of m-bis(4-cyanophenylthio)benzene have been previously reported.[17] One preparation gave white crystals (mp 86.5° - 87.5°C) and the other yellow crystals (mp 79° - 80.5°C). Analysis of these materials agreed quite closely, and was similar to the analysis reported above. Comparison of the infrared spectra and melting points of the various products seems to indicate that the yellow compound reported earlier contains some impurity.

f. Polymerizations

Polymerizations were carried out using the conditions indicated in Tables VII, X and XII. The reactions were carried out, under dry nitrogen, in a three-necked flask fitted with a condenser. Some polymerizations were stirred magnetically, but mechanical stirring, which was used in most cases, is preferable. At the completion of many of the polymerizations, the yellow reaction mixture contained some precipitated polymer. The polymers were isolated by precipitation in a cold mixture of methanol and dilute HCl. The reaction mixture was slowly added to the precipitant which was rapidly stirred. A thick white precipitate of polymer was formed. This mixture was stirred overnight. The polymer was filtered off and then stirred successively with water and methanol for several hours. After filtration, it was dried and then stirred with diethyl ether for several hours. Following filtration, the polymers were dried in a vacuum oven. The diethyl ether soluble material was recovered and, in each case, appeared to be very low molecular weight material. As noted earlier, the treatment with ether was omitted when polymer SH-P14 was worked up. This polymer was reprecipitated from benzene. After the completion of some polymerizations, the solid mass of polymer formed in the reaction mixture could not be broken up by stirring with precipitant. When possible, these polymers were reprecipitated from benzene, or THF. In the case of the insoluble polymers, a blender was used to obtain the polymer in a finely divided form. The polyphenylene sulphides, and the other polymers reported, are white, or off-white, powdery solids.

g. Substitution of nitrile groups in the polymer chain

i) Bromination

Some discussion of the results of the bromination of several polymers has been given above and, therefore, only experimental procedures will be reported here.

Three ml of bromine were added to 1.086 g of SH-P11 (melting range 110° - 125°C) contained in a small flask. The flask was stoppered and the bromination was allowed to proceed at room temperature for about 18 hr. The reaction mixture was then added to a water/methanol mixture and stirred for several hours. The polymer was filtered off, stirred with water and then methanol and, following filtration, was dried in a vacuum oven. The polymer obtained (2.490 g; melting range, 205° - 225°C) was white (SH-P11B).

Polymer SH-P12 (1.05 g) (melting range 100° - 120°C) was reacted for 20 hr with 0.3 ml of bromine in the manner described above. The polymer obtained (1.31 g; melting range 120° - 135°C) was off-white (SH-P12A). Analysis data for these polymers is not yet available.

ii) Reaction of brominated polymer with cuprous cyanide

Some discussion of the results of this reaction has been given above and experimental details only will be given here.

A 1.026 g sample of SH-P11B was mixed with 0.8 g of CuCN and 50 ml of dry SpectrAR grade DMF in a small round-bottomed flask. The flask was fitted with a condenser and the mixture was then refluxed for 20-1/2 hr. Initially, the reaction mixture has a greenish tinge but after a short period of heating this becomes a brownish color. At the completion of the reaction, the red-brown mixture was allowed to cool slightly and was then added to 60 g of $FeCl_3.6H_2O$ dissolved in a mixture of conc. HCl (20 ml) and water (120 ml). This mixture was stirred at 60° - 70°C for about 1/2 hr and the polymer was then filtered off. The polymer was washed successively with 5 portions (~ 50 ml) of dilute HCl and dilute aqueous ammonia. It was then stirred with water and methanol, filtered off and dried in a vacuum oven. The bright yellow polymer (0.82 g, SH-P11C) which was obtained did not melt below 500°C, but darkened to a brown color at ~ 200°C. Analysis data for the polymer is not yet available.

4. Future Plans

Work will be continued in the areas discussed in this report. Also, trimerization of the model compounds and polymer which are nitrile endcapped will be investigated.

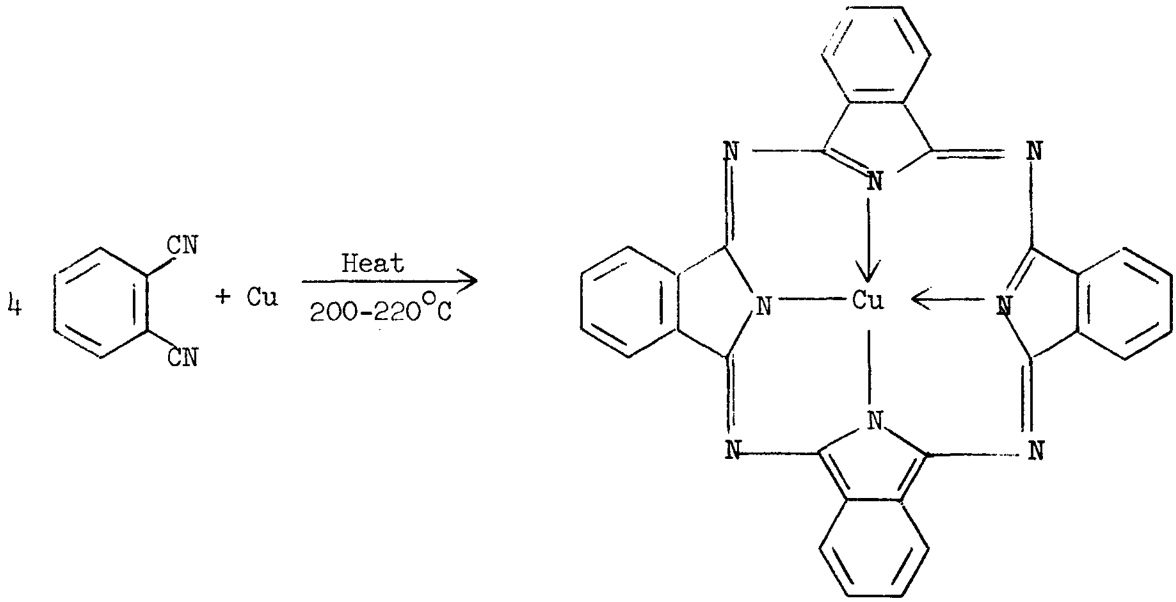
. VII. POLYPHTHALOCYANINES

1. Introduction

Much work has been done on the synthesis of materials useful for the making of thermally stable laminates. The majority of the materials in use are crosslinked by a heat curing method to produce the laminate. However, these laminates, although they may be thermally stable, suffer from a lack of strength due to the incorporation of gas bubbles in the matrix of the final product. This is a consequence of the type of crosslinking agent used. Work is being done in this laboratory designed to produce laminating resins which on curing do not have this defect. The approach used has been to investigate the conversion of aromatic nitriles to triazines and to thus use this method to crosslink thermally stable polymers such as polyethers and polysulphones. Some of the work done on the crosslinking of nitriles by the formation of triazines has been reported in the literature.[37-39]

Another possible method of achieving strong, thermally stable laminates also uses nitriles. This is by the use of the phthalocyanine synthesis. This synthetic method has been known for the synthesis of dyes and has been applied to the synthesis of polymers.[40-42] It is known that the fusion of phthalonitrile with copper bronze gives a nearly quantitative yield of copper phthalocyanine. (See Scheme 1).

Scheme 1



It is known that copper phthalocyanine has great thermal stability since it can be sublimed under nitrogen at 560°C without decomposition.[43] Thus it would appear that phthalocyanine units could be used to crosslink polymers with the absence of gas voids and with no loss in thermal stability.

2. Discussion

a. Introduction

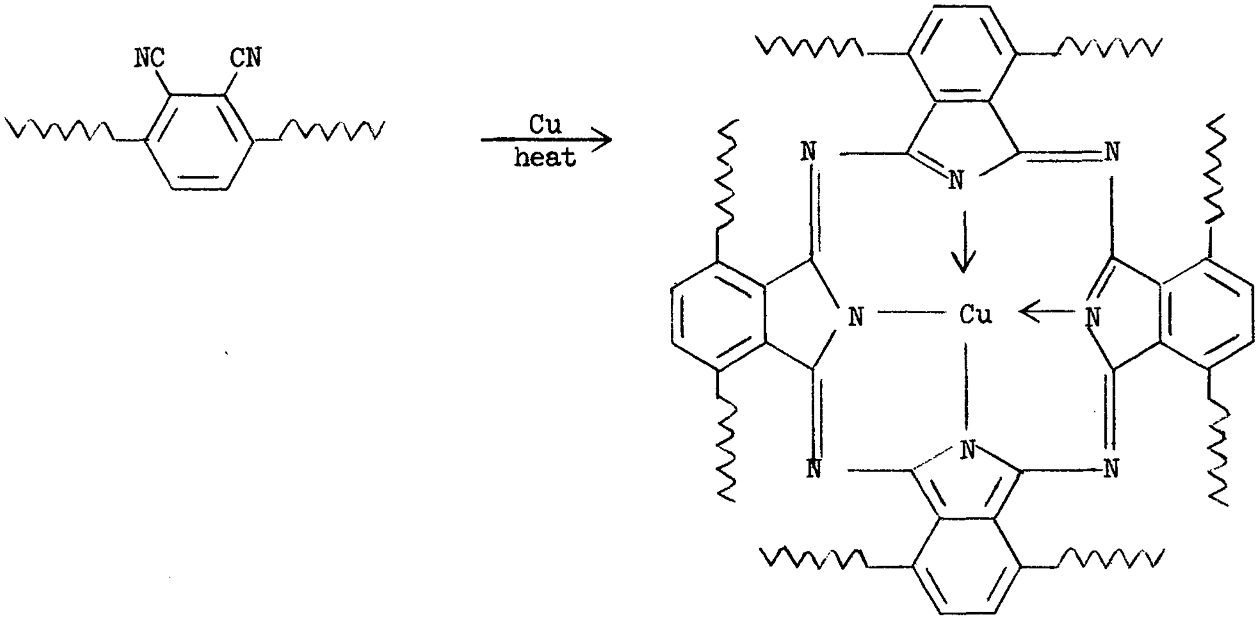
To achieve the desired thermally stable laminates the phthalocyanine units are to be used to crosslink polyethers, polysulfones, polyketones and polysulfides by either of two methods. The first being the incorporation of an ortho-dicyano aromatic system into the polymer backbone for the formation of the phthalocyanine crosslink. (See Scheme 2). The second being the endcapping of a polymer chain with an ortho-dicyano aromatic unit for formation of the phthalocyanine crosslink. (See Scheme 3).

In order to gain further knowledge of these systems the thermal stability and laminate properties of the phthalocyanine of tetracyano compounds are being investigated. The present investigations cover the synthesis of model nitrile compounds and the attempted preparation of their phthalocyanines.

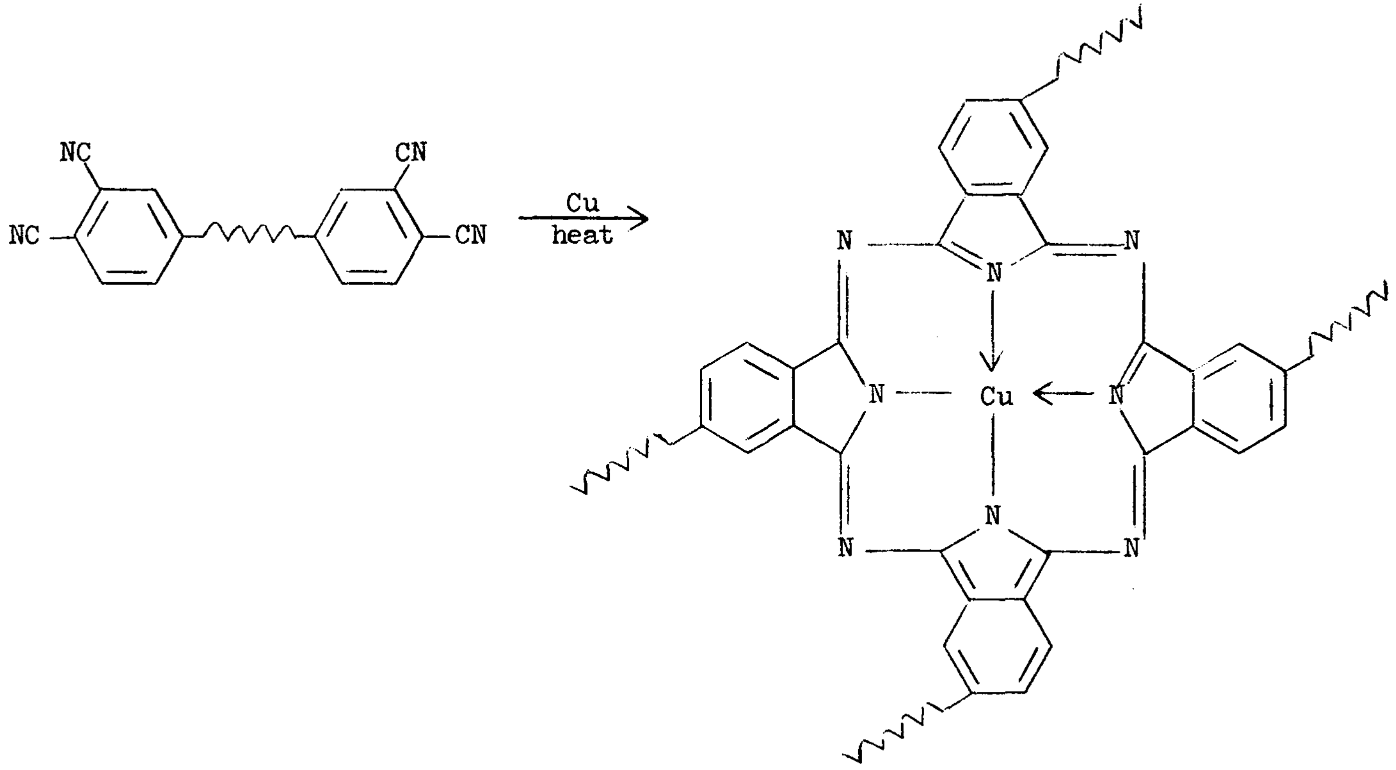
b. Results

The model nitrile compounds prepared were phthalonitrile and pyromellitonitrile. Phthalonitrile was prepared from phthalimide by a straight forward procedure. (See Scheme 4).

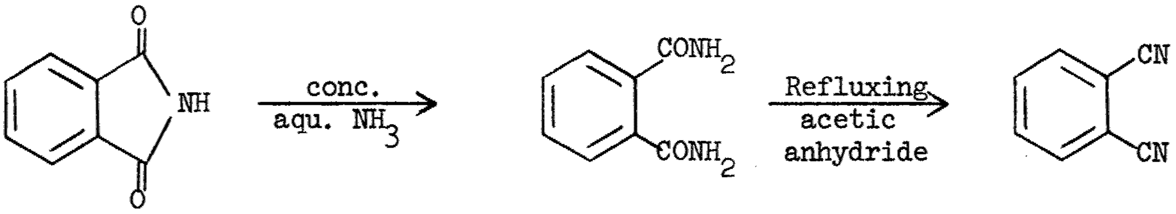
SCHEME 2



SCHEME 3

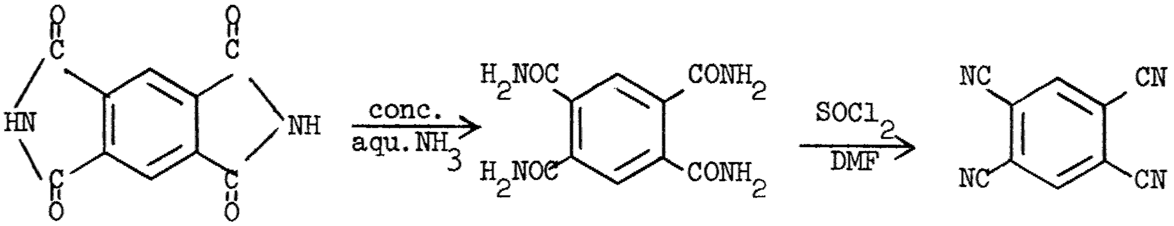


Scheme 4



The pyromellitonitrile was prepared according to the procedure of Marvel and Martin[41] with the final dehydration step as modified by Thurman.[44] (See Scheme 5). The details for both of these preparations are reported in the experimental section.

Scheme 5



An attempt was made to synthesize the monomeric copper phthalocyanine by use of the "phthalocyanine synthesis" developed by Marvel and Rassweiler.[40] The method required heating phthalic anhydride and urea in the presence of cuprous chloride. This reaction was not very successful as most of the phthalic anhydride was converted to phthalimide (mp, solubility, analysis).

The synthesis of copper phthalocyanine from phthalonitrile and copper bronze should be easily accomplished. However, when heating the phthalonitrile and copper bronze under the condition given in the experimental section, a material was isolated which had trace amounts of copper phthalocyanine in the presence of large quantities of materials which as of the present time remain unidentified. This copper phthalocyanine was detected by ir spectrum (See Table XIII) comparison with the literature values.[45]

Not all of the peaks could be detected since they were being obscured by the other material present. The infrared spectrum also revealed that there were no unreacted nitrile groups in this isolated material.

TABLE XIII

INFRARED COMPARISON OF COPPER PHTHALOCYANINES

Copper Phthalocyanine (cm^{-1})	Polymeric Copper Phthalocyanine (cm^{-1})	Polymeric Phthalocyanine Ether[41] (cm^{-1})	Copper Phthalocyanine Literature[45] (cm^{-1})
720	724		720-730
752	740	745	745-750
800	785		780-790
885	885	875	870-885
	945	950	945-950
	1045	1050	1045-1060
1090		1090	1080-1090
1120	1130	1120	1118-1123

A polymeric phthalocyanine similar to that reported by Drinkard and Bailar[42] also appeared to be elusive when the preparation was attempted from pyromellitonitrile and copper bronze in a sealed tube. The material which showed no indication of melting or decomposing up to 500°C appeared to contain a small quantity of copper phthalocyanine units by infrared spectrum (See Table XIII) in the presence of larger amounts of some unidentified substances. The infrared spectrum of this material revealed the presence of a large quantity of unreacted nitrile groups by a strong absorption at 2210 cm^{-1}. Since there appears to be a large quantity of unreacted nitrile material in this sample, it is not surprising to find only a limited quantity of copper phthalocyanine units present. The material that contains these nitrile groups is an integral part of the product since it was not removed by numerous washings in acetone and glacial acetic acid.

Similar infrared spectrum frequencies for a polymeric phthalocyanine were reported (See Table XIII) by Marvel and Martin[41] for polymers prepared from phthalonitrile, 3,3′,4,4′-tetracyanodiphenyl ether and copper bronze. They suggest that polymerization occurred to low degree and that unreacted nitrile groups also were in the product before being hydrolyzed in the final purification.

The results in the present investigation suggest that the formation of copper phthalocyanines were incomplete and were formed in the presence of competing reactions. For these reactions to be useful as crosslinking reactions for polymers the conditions need to be perfected.

3. Experimental

a. Reagents

Phthalimide and pyromellitic diimide were used as supplied by Aldrich Chemical Company. Urea (A.R. grade) was used as supplied by Matheson, Coleman and Bell. The copper bronze was supplied by Sargent-Welch. Thionyl chloride was fractionated first from quinoline and then boiled linseed oil.[46]

Phthalic anhydride was purified by crystallization from chloroform. The main impurity, phthalic acid, was removed by mixing the anhydride with cold chloroform in which the acid is insoluble. Cuprous chloride was purified by dissolving in concentrated hydrochloric acid and then diluting the resultant solution with water until crystallization began. After the solution had cooled the white granular crystals were filtered off and washed with absolute ethanol and then ether. The crystals of pure cuprous chloride were dried and stored under vacuum.

b. Preparation of phthalonitrile

Phthalimide (67 g, 0.46 mole) was added to concentrated ammonia solution (200 ml) in a 500 ml beaker. The mixture was stirred at room temperature for 24 hr when the micro-crystalline solid was filtered off and dried in a vacuum oven at 100°C overnight. The yield of phthalamide was 71 g (95%) and it had mp 222° - 223°C (lit[47] 222°C).

Phthalamide (70 g, 0.43 mole) and acetic anhydride (250 ml) were added to a 500 ml round bottom flask fitted with a stirrer and reflux condenser. The mixture was refluxed for 6 hr and the hot reaction mixture was then poured into 600 ml of boiling water in order to decompose the excess acetic anhydride. The solution was cooled in ice and made alkaline with sodium hydroxide solution. The resultant crystalline product was filtered off, washed with water and dried at 90°C. The mp of this material was found to be 215° - 220°C which is close to the mp of phthalamide. The product was therefore subjected to sublimation at 10^{-1} mm Hg and 90°C to obtain phthalonitrile as the sublimate. The aqueous reaction mixture was also extracted with ether to obtain any dissolved phthalonitrile; phthalamide being insoluble in ether. The combined sublimate and ether extract gave 31 g (57%) of phthalonitrile mp 134° - 137°C. Crystallization from benzene and sublimation gave pure phthalonitrile mp 140° - 141°C (lit[47] 141°C).

c. Preparation of pyromellitonitrile

To 55.6 g (0.257 mole) of pyromellitic diimide in a 500 ml Erlenmeyer flask was slowly added 350 ml of concentrated ammonium hydroxide. After stirring this for 22 hr the solution was filtered and evaporated under reduced pressure. After drying the solid residue for 20 hr at 60°C under vacuum 63.2 g (98.2%) of pyromellitamide was obtained, mp 460° - 463°C with decomposition.

To 950 ml of dimethyl formamide in a three liter three-necked flask was added 60.0 g (0.240 mole) of the above pyromellitamide. After purging the system with N_2 and cooling the solution to 0°C, 330 g of thionyl chloride was slowly added over a period of one hr. This material was stirred at room temperature for three days. The unreacted pyromellitamide (19.0 g) was removed by filtration and was allowed to react with 165 g of additional thionyl chloride in 350 ml of dimethyl formamide as above. The filtrates from the reactions were poured over 3.5 liter of crushed ice, respectively, and the precipitates were collected and dried. The precipitates were crystallized twice from 95% ethanol to yield 27.9 g (65.1 %) of pyromellitonitrile; mp 272° - 274°C (lit[48] 270° - 272°C);

ir (KBr) 3110 cm^{-1} (C-H), 3040 cm^{-1} (C-H), 2250 (C N) and 925 cm^{-1} (1,2,4,5 aromatic substitution (lit[49] 3120 cm^{-1}, 3030 cm^{-1}, 2220 cm^{-1} and 925 cm^{-1}).

d. <u>Attempted preparation of copper phthalocyanine</u>

Cuprous chloride (2.00 g, 0.02 mole), phthalic anhydride (5.94 g, 0.04 mole) and urea (25 g) were heated under nitrogen at 120°C. The temperature was slowly raised to 175°C and the mixture kept at this temperature for 4-1/2 hr. Further quantities of cuprous chloride (1.00 g, 0.01 mole) and urea (8 g) were added and the mixture heated at 175°C for 7 hr.

The green product was washed from the reaction flask with boiling water (300 ml). The product was then washed successively with 18% hydrochloric acid (400 ml), water (600 ml), 6% ammonium hydroxide (500 ml), water (200 ml) and 18% hydrochloric acid (200 ml). The product was completely dissolved.

The green aqueous solution of the reaction product was neutralized with ammonium hydroxide and reduced in volume until white crystalline needles were formed. These were filtered off and the evaporation of the mixture continued until no more needle crystals were formed. The crystals were dried at 100°C; yield 3.8 g (63% based on total conversion of phthalic anhydride to phthalimide), mp 234° - 235°C (lit[47] 238°C).

Anal. Calc. for $C_8H_5O_2N$: C, 65.3%; H, 3.4%; N, 9.5%.
Found: C, 65.1%; H, 3.5%; N, 9.5%.

e. <u>Copper phthalocyanine</u>

Freshly sublimed phthalonitrile (2.13 g, 0.017 mole) was ground with a mortar and pestle and introduced into a thick-walled pyrex test tube. Copper bronze (0.267 g, 0.004 mole) was then added and the reactants shaken to give as nearly a homogeneous mixture as possible. Using a Wood's metal bath, the temperature of the mixture was increased to 190°C when the mixture was too solid to stir (stirring being accomplished with a thermometer. The color of the melt was originally green but after one-half hr the semi-solid was blue. The product was finally heated for 1/4 hr at 220°C.

After cooling, the product was removed from the tube by scraping and washing with ethanol. The product was then ground with ethanol, filtered and washed with ethanol until the filtrate was colorless. Unreacted copper was removed by dissolving the product in concentrated sulphuric acid (20 ml). The solution was filtered and poured slowly onto crushed ice. The flocculent blue precipitate was allowed to coalesce overnight and then filtered off. The pure copper phthalocyanine was washed with water, air-dried overnight and finally dried at 90°C in a vacuum oven. The yield of material was 212 g and it had a mp > 380°C with some decomposition at 280°C. The ir spectrum (see Table XIII) reveals the presence of a small quantity of copper phthalocyanine in the presence of large amounts of unidentified materials.

Anal. Calc.: C, 66.73%; H, 0.27%; N, 19.46%.
Found: C, 38.14%; H, 2.85%; N, 11.27%.

f. Polymeric copper phthalocyanine

A mixture of 4.45 g (0.025 mole) of pyromellitonitrile and 0.635 g (0.010 mole) of copper bronze was intimately ground with a mortar and pestle. This mixture was sealed in a thick-walled pyrex tube under vacuum and heated in a Wood's metal bath at 290° to 310° for 11 hr. The tube was then opened and the contents removed. This reaction mixture was ground, stirred in 300 ml of acetone for 12 hr, filtered, and rinsed with acetone until the washes were colorless, to remove unreacted pyromellitonitrile. The residue was stirred in 300 ml of glacial acetic acid for 12 hr to remove unreacted copper bronze and filtered. The acetic acid washwas repeated six additional times. After the final wash the residue was rinsed with 300 ml of water followed by 300 ml of acetone and was dried. The yield of material was 1.96 g and it had a mp > 500°C with no decomposition or softening. The ir spectrum (see Table XIII) reveals the presence of a small quantity of a copper phthalocyanine material in the presence of unidentified substance.

Anal. Found: C, 42.97%; H, 0.93%; N, 20.31%.

4. Future Work

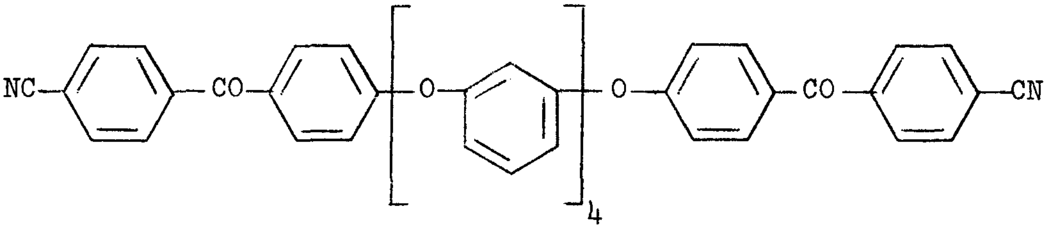
The preparation of phthalocyanines is to be pursued in order to obtain them as pure as possible with a minimal amount of purification so they can be easily and neatly applied to the crosslinking of the desired polymers. The preparation of the polymeric copper phthalocyanine will be continued in order to determine its thermal stability. The synthesis of 4-chlorophthalonitrile, 3,6-dichlorophthalonitrile, 3,4-dicyanobenzoic acid and 2,3-dicyanoterephthalic acid are to be initiated for their incorporation into the polyethers, polysulfones, polyketones or polysulfides for the formation of phthalocyanine crosslinking.

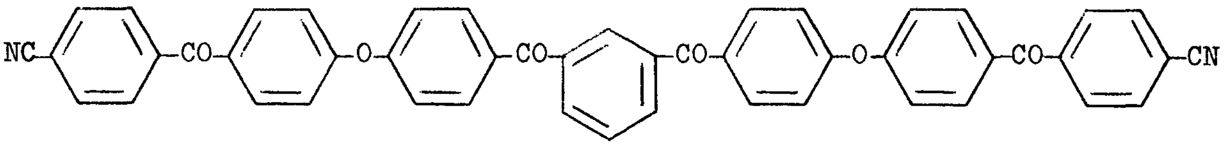
VIII. CONCLUSIONS

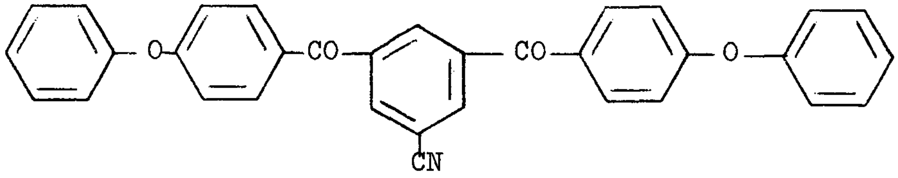
Work on the laminating-type resins needs to be continued and new backbones, as well as new methods for crosslinking, need to be developed. This is a promising area that should be pushed.

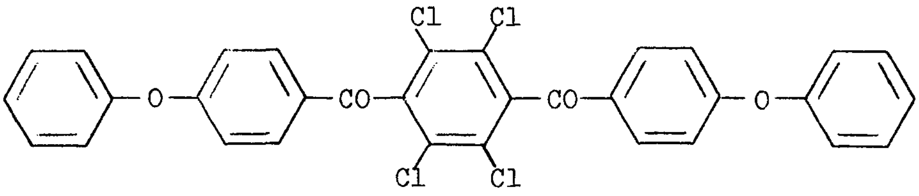
APPENDIX I

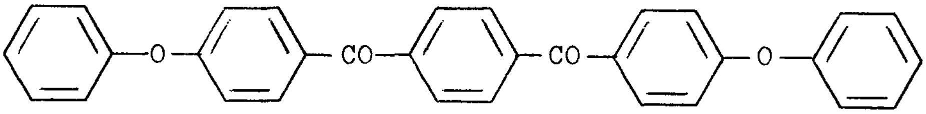
NEW COMPOUNDS

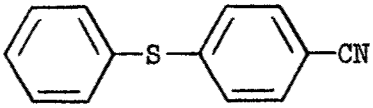


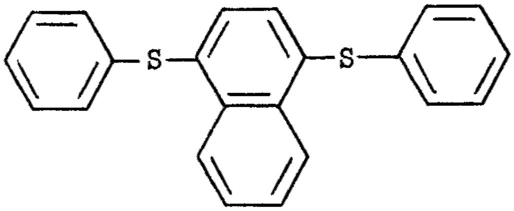












APPENDIX II

NEW POLYMERS

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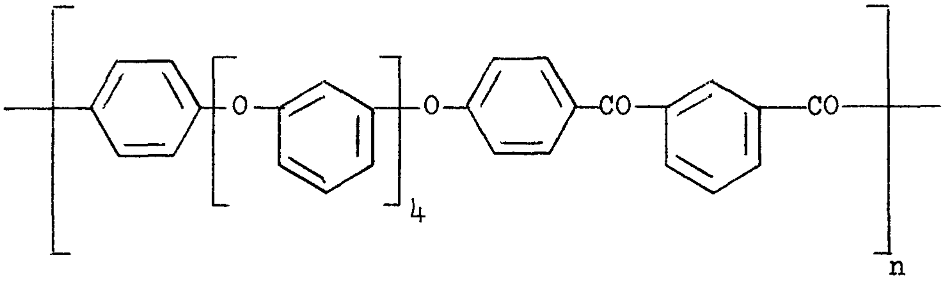

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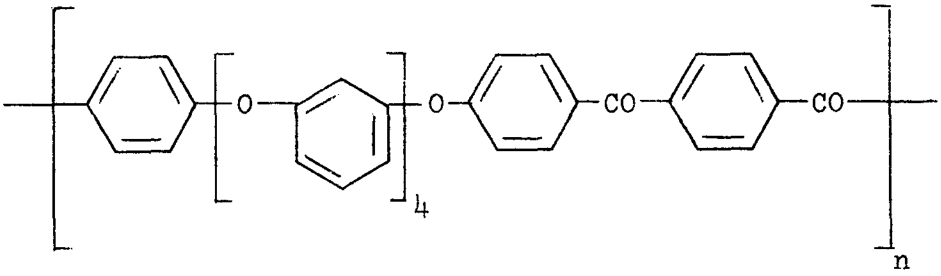

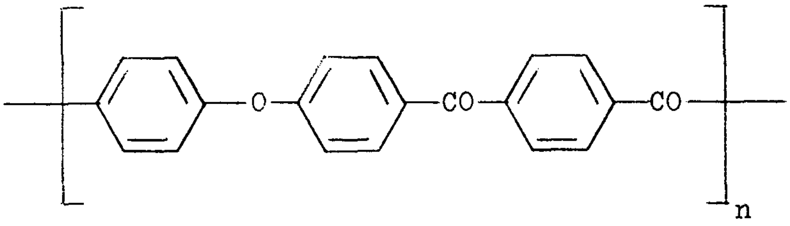

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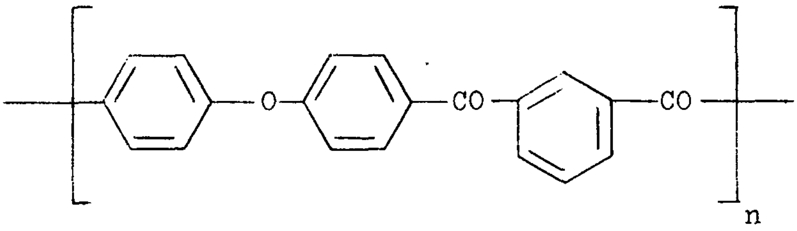

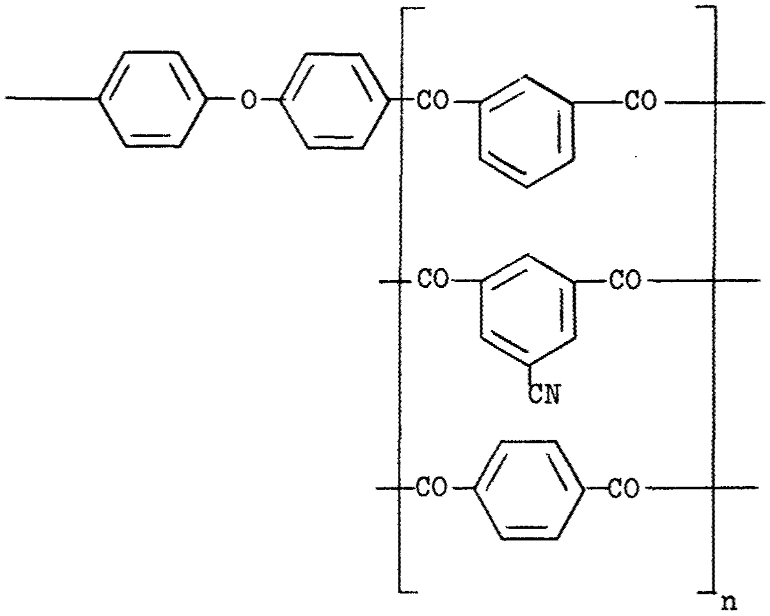

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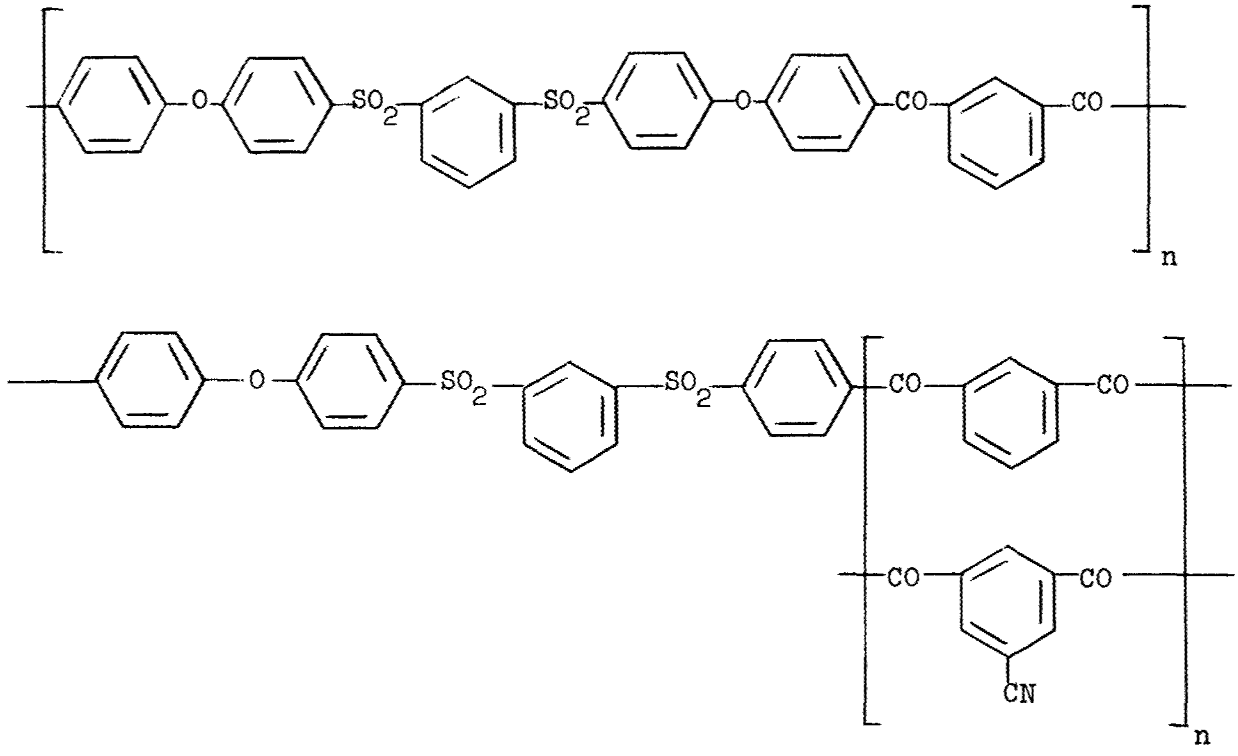

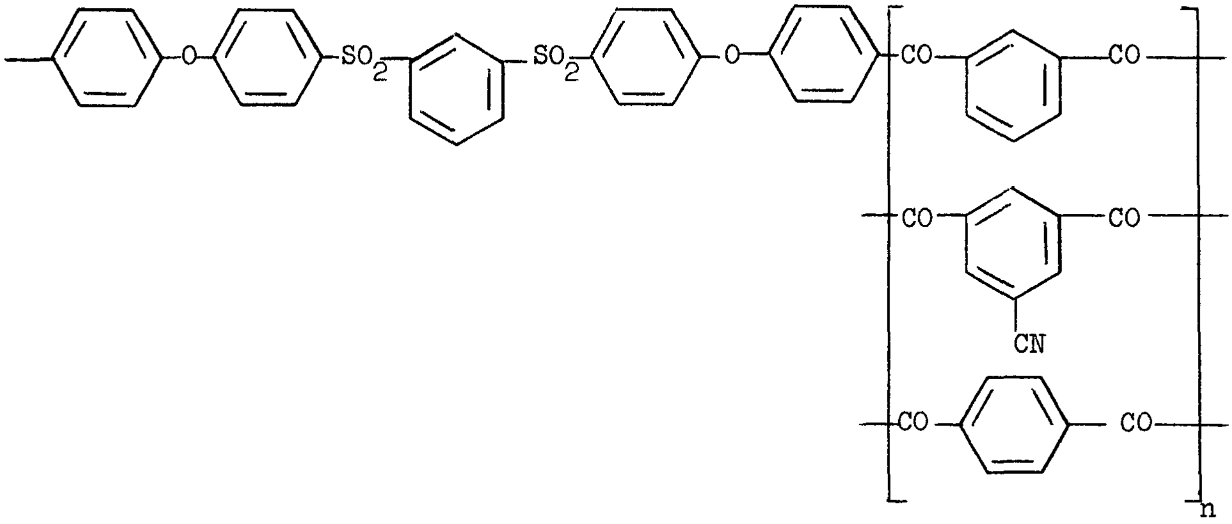
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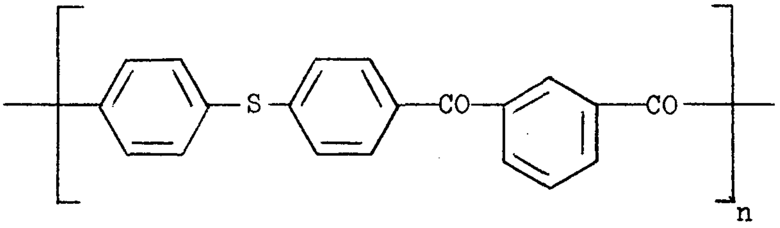
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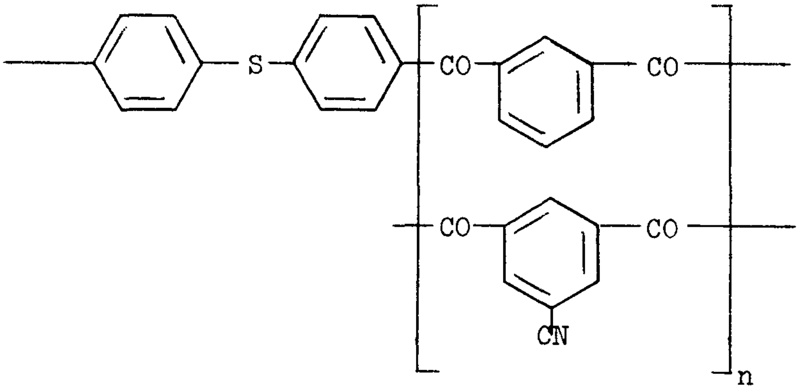
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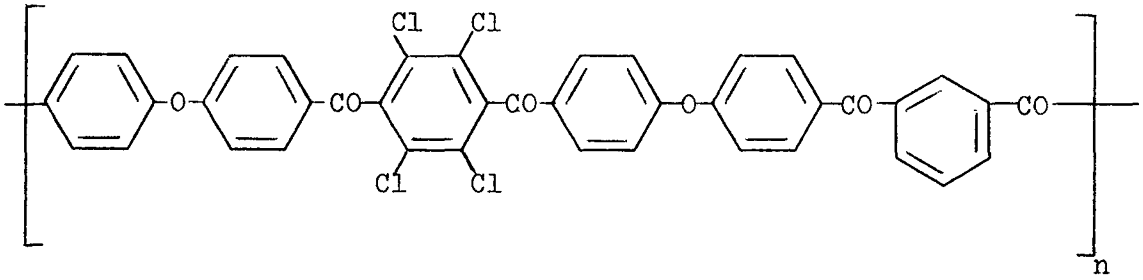
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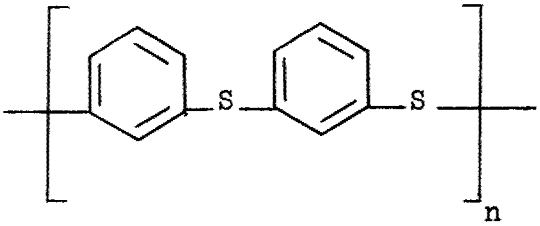

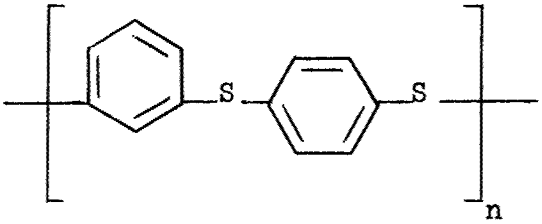

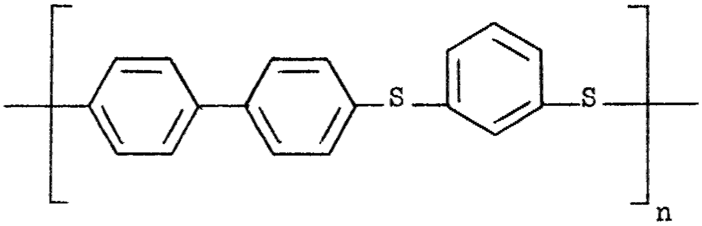

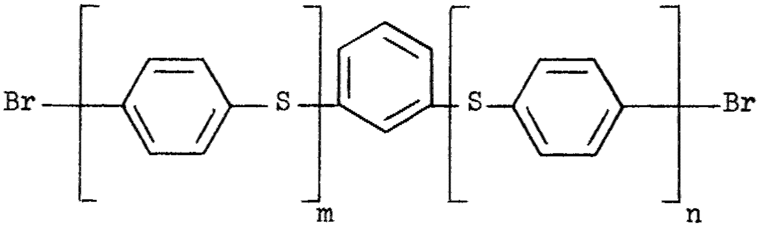

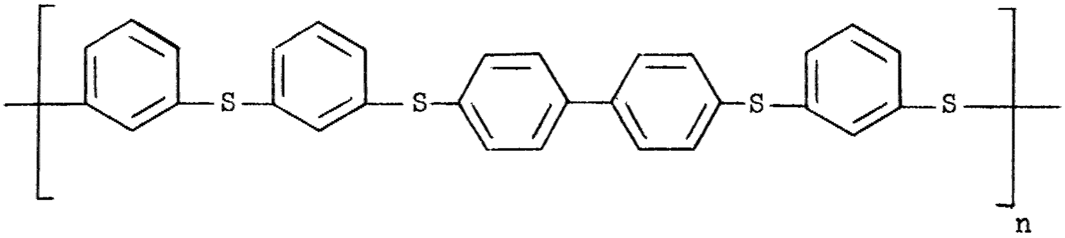

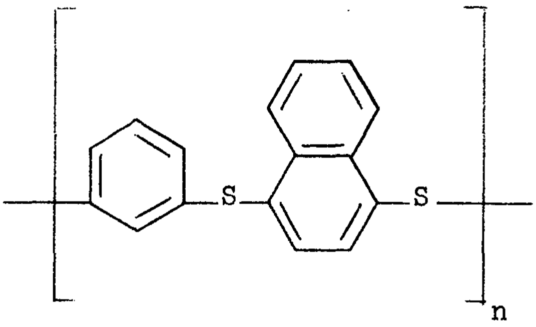
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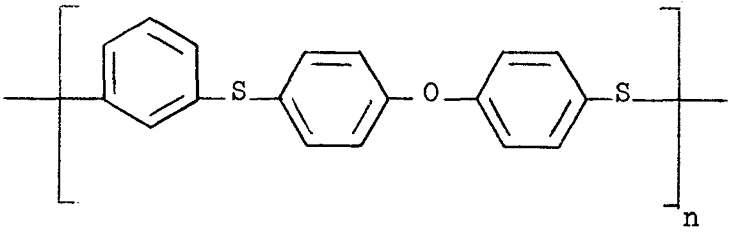
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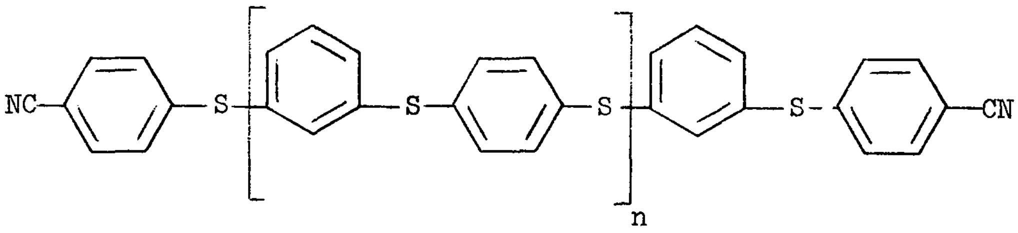
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Summary Report (December 1970 to April 1972

5. AUTHOR(S) *(First name, middle initial, last name)*

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/LNP, Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

Work on the condensation of 1,5-diaminoanthraquinone and aralkyldiketones has been concluded and published.

Work on the polymer with graphitic structure obtained from 1,4,5,8-tetraaminoanthraquinone and naphthalene-1,8,4,5-diindandione has been completed and a manuscript prepared for publication.

A series of linear polymers containing aryl ether, aryl ketone and aryl sulfone units with nitrile dangling groups has been prepared. Some success has been achieved in converting the nitriles to triazine. The resulting products are promising as laminating resins.

A series of arylene polysulfides with nitrile side groups has been synthesized and show some promise as laminating resins.

Work has begun on the preparation of polymeric chains with o-dicyano substituents to test the value of phthalocyanine groups as side chains for crosslinking.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
1,5-Diaminoanthraquinone						
Aralkyldiketones						
1,4,5,8-Tetraaminoanthraquinone						
Naphthalene-1,8,4,5-diindandione						
Ladder Polymers						
Polymers with Graphitic Structure						
Polyaryl ethers with Aryl ketone and Aryl Sulfone Units						
Nitrile side and end group on polymers						
Triazine Units						
Polyarylenesulfides with Nitrile side groups						
O-Dicyanoaryl units for phthalocyanine formation						