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16. Abstract

Fourteen ether-containing, aromatic dianhydrides have been synthesized from N-phenyl-3 or 4-nitrophthalimide and various bisphenols. The process involves nucleophilic displacement of "activated nitro groups" with bisphenolate ions. Ether-containing dianhydrides were indefinitely stable in the presence of atmospheric moisture. One-step, high temperature solution polymerization of the ether-containing dianhydrides with m-phenylene diamine, 4,4'-oxydianiline and 1,3-bis(4-aminophenoxy)benzene afforded 42 polyetherimides. The polyetherimides were all soluble in m-cresol except two which were found to be crystalline. The glass transition temperatures of the polyetherimides ranged from 178° to 277°C.

Soluble polybenzimidazopyrrolones containing ether groups were also prepared from the same ether-containing dianhydrides and aromatic tetraamines by one-step solution polymerization.

Using low molecular weight polyetherimides, various thermoset resin systems were developed and tested as matrices for fiber-reinforced composites. The curing chemistry involving reaction of the phthalonitrile group and the *o*-diaminophenyl group was found to be generally applicable to crosslinking various aromatic polymers other than polyimides.

17. Key Words (Suggested by Author(s))
polyetherimides, aromatic ethers, nitrophthalimide, dianhydride, polyetherpyrrone, composite

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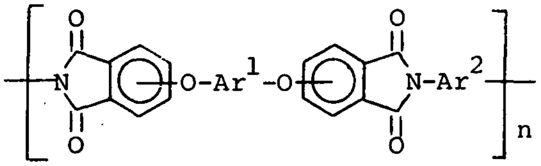
Part I. Heteroaromatic Polymers Containing Ether Groups

T. Takekoshi (Principal Investigator), J. E. Kochanowski,
J. S. Manello and M. J. Webber

SUMMARY

In Section 1 of Part I, the preparation of completely aromatic polyimides containing aromatic ether linkages is described. The structure of the polyimide which was named "Polyetherimide" is represented by the following general formula:



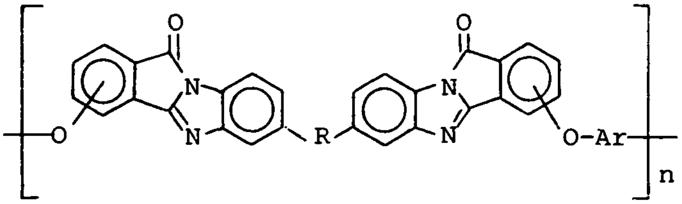
(I)

By selecting seven aromatic bisphenols (HO-Ar^1-OH) and three aromatic diamines (H_2N-Ar^2-NH_2) as starting materials, a total of 42 structurally different polyetherimides have been synthesized and their solubility and thermal properties have been screened. All of the polymers except two were soluble in m-cresol at room temperature and many of them were soluble in other solvents such as methylene chloride, chloroform, tetrachloroethane, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, and dimethylsulfoxide. The excellent solubility of polyetherimides allowed the development of a unique one-step solution polymerization involving phenolic solvents.

The lowest glass transition temperature observed was 178° and the highest was 277°, but for the majority of polyetherimides, it was between 200-240°. One percent weight loss was registered in TGA curves (in air at a heating rate of 5°/min) at a temperature in the range of 440-450°.

During the course of the synthesis, 14 ether-containing bisanhydrides were obtained. Unlike commercially available dianhydrides such as pyromellitic dianhydride, they are indefinitely stable in the presence of atmospheric moisture.

In Section 2, the preparation of polybenzimidazopyrrones containing aromatic ether links is described. The structure of the polymers which were named "Polyetherpyrrones" is represented by the following general formula:



Polyetherpyrrones have been shown to have excellent thermal stability and outstanding processability. The majority of the polyetherpyrrones prepared were soluble at room temperature in many organic solvents such as tetrachloroethane, dipolar aprotic solvents or phenolic solvents. Unlike conventional pyrrone polymers, polyetherpyrrones are fusible at temperatures above 300°C and therefore, moldable.

The complex mechanism of pyrrone ring formation was studied using a model reaction. The results led to the discovery of a unique, one-step solution polymerization to form completely cyclized polyetherpyrrones.

INTRODUCTION

Recent intensive investigation in the field of high temperature polymers has resulted in development of numerous classes of thermally and oxidatively stable polymers. Basic chemical structures of these polymers are composed of difficult-to-oxidize "electron sinks", namely, heteroaromatic rings containing nitrogen, oxygen, or sulfur atoms; for example, aromatic polyimides, polybenzimidazoles, polyoxazoles, polythiazoles, polyoxazinones, polyquinoxalines, polybenzimidazopyrrolones, etc. However, polar and rigid structure of high symmetry, which is inherent to the heteroaromatic rings, is responsible for the general lack of processability of these polymers. In general, more tractable polymeric precursors such as polyamide acids (in the case of polyimides) are formed into a desired shape and then converted in situ to the final thermally stable polymers. Because the final conversion generally involves a chemical reaction which releases a volatile product such as water, the use of these polymers is often limited to applications such as coatings, films and adhesives. A typical solution for this problem is to introduce bulky side groups of a high solvent affinity onto the polymer chain.[1] However, this type of approach generally involves exotic intermediates and cumbersome syntheses.

It has been known that flexible aromatic ether groups provide polymer chains with lower softening temperatures and improved solubility. Therefore, the combined structure of "polyether heteroaromatics" is expected to provide more balanced properties of high thermal stability and good processability. However, convenient synthetic methods to prepare such a structure have not been available.

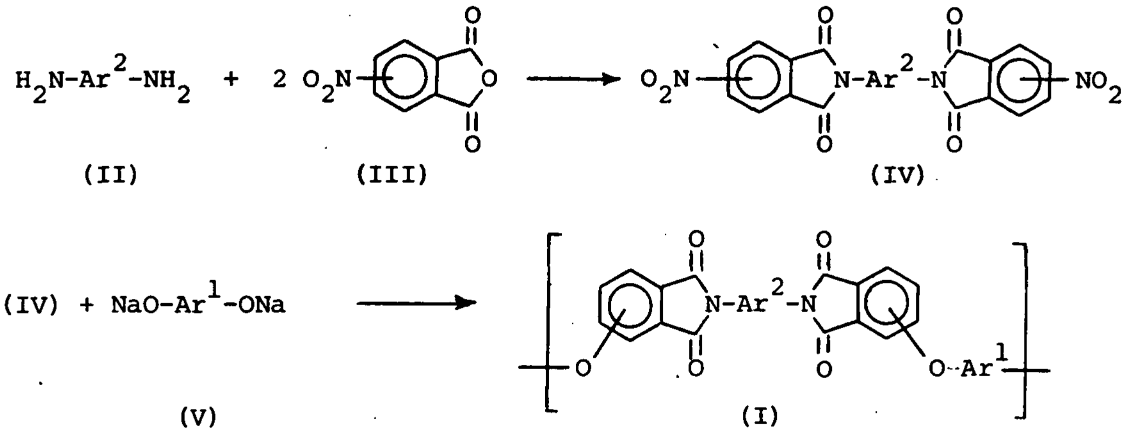
Recently, a unique chemical reaction which produces aromatic ether groups has been discovered.[2,3] The reaction involves displacement of an "activated aromatic nitro group" by a phenoxide. The reaction has made it possible to synthesize a large number of structurally different polyether heteroaromatics such as polyetherimides[4] and polyetherquinoxalines.[5]

SECTION I. AROMATIC POLYETHERIMIDES

Two synthetic routes have been considered in arriving at structure I. In Route I, imide groups are prepared first (equation 1) and ether linkages are formed in the final polymerization step (equation 2).[4]

In Route II, dianhydrides containing ether groups, namely, bis(ether anhydride)s (VIII) are prepared via nitro displacement reaction (equation 3).[3] The final imidization is carried out by the reaction of bis(ether anhydride)s and diamines, as shown by equation 5.

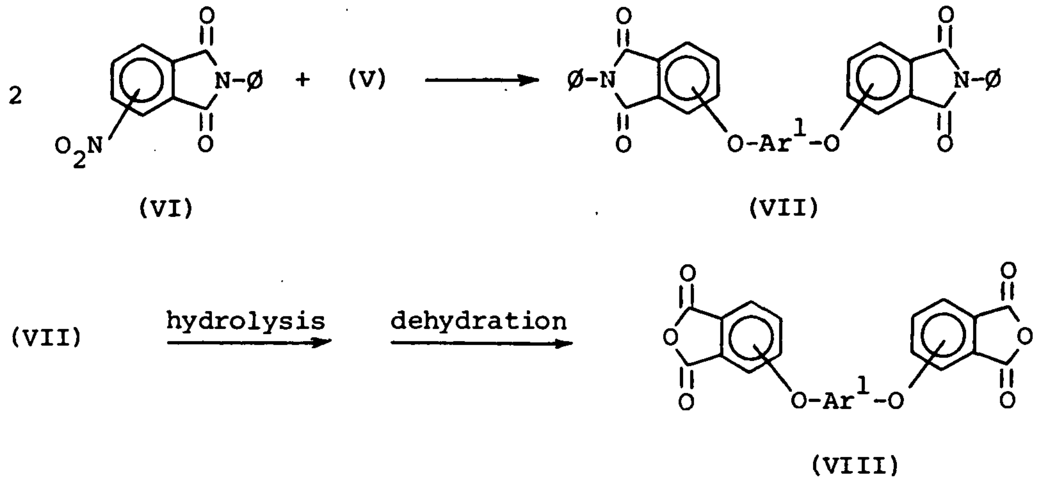
ROUTE I



(1)

(2)

ROUTE II



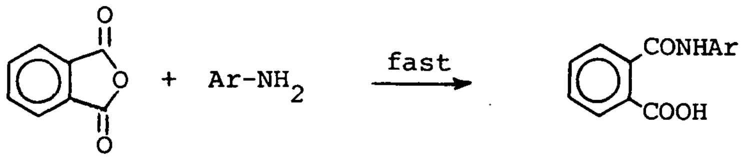
(3)

(4)

$$\text{(VIII)} + H_2N\text{-}Ar^2\text{-}NH_2 \longrightarrow \text{Polyetherimide (I)} \qquad (5)$$

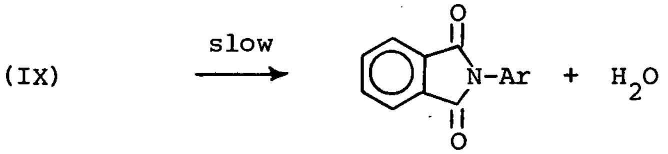
Synthesis of Polyetherimides via Route I

A. Preparation of Bisnitroimides -- The reaction of anhydrides and amines generally involves fast addition (equation 6) to form an intermediate, amide acid (IX), followed by slow intramolecular condensation (equation 7). Because amide acids are polar compounds, particularly bisamide acids, the reactions have to be carried out in a polar anhydrous solvent. In addition, the second step is an acid-catalyzed reaction. Basic aprotic dipolar solvents such as dimethylformamide are not suitable because a relatively high temperature is necessary. At higher temperatures, amines tend to be oxidized by nitro compounds. Acetic acid is a good solvent, but a long reaction time (20 hours or more) and a large quantity of this solvent are necessary because of its relatively low boiling temperature and low solubility of the products. In addition, part of the amine was converted to the corresponding acetamide which had to be eliminated by a suitable purification method. Phenolic solvents were found to be best suited. The reaction proceeded quantitatively within one hour at 130°C. The results of the preparation are tabulated in Table I.



(6)

(IX)



(7)

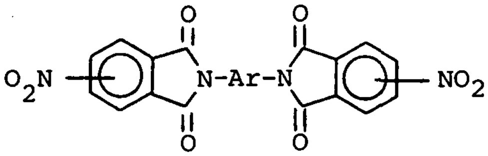
B. Disodium Salts of Bisphenols -- Although disodium salts of bisphenols can be prepared in situ in dimethylsulfoxide (DMSO) for each polymerization, anhydrous sodium salts were isolated in pure form and stocked in order to attain reproducible polymerization results.

In general, disodium salts of bisphenols tend to form a stable hydrate which can be dehydrated only with difficulty. For this reason, sodium metal and bisphenol were reacted in absolute methanol and dried under vacuum at 180-200°. The infrared spectra of the disodium salts were clean in the 3300-3600 cm^{-1} region. The absorption bands are tabulated in Table II.

C. Polymerization of Polyetherimide by Nitro Displacement -- Displacement reaction of N-substituted nitrophthalimides with phenoxide is very sensitive to water because the imide ring is hydrolyzed very fast. The polymerization was conveniently carried out in a dry box. The reaction is also affected by various other factors, control of which is very important to obtain reproducible results. Like other nucleophilic displacement reactions, it requires use of dipolar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc) and DMSO.

TABLE I

Bisnitroimides



				Analysis (%)		
-Ar-	Isomer	Yield (%)	mp (°C)	C	H	N
1,3-Benzene	3	93.4	338-342	57.4	2.3	11.7
	4	94.7	358 dec.	58.0	2.3	12.2
	3 & 4 (1:1)	91.7	278-288	58.4 (calc. 57.65	2.4 2.20	12.0 12.23)
4,4'-Diphenyl ether	3	97.8	306-308	61.5	2.7	10.2
	4	96.5	322-323	61.0	2.7	10.2
	3 & 4 (1:1)	94.3	252-272	61.3 (calc. 61.09	2.8 2.56	10.3 10.18)

Some of the results of the nitro displacement polymerization are tabulated in Table III. In general, 3-nitro isomers were more reactive than the corresponding 4-nitro isomers under identical conditions. It was also apparent that the polymerization rate is dependent on the nucleophilicity of bisphenolate ions. Thus, 4,4'-dihydroxydiphenyl ether (DDE) gave a high molecular weight polymer whereas 4,4'-dihydroxydiphenylsulfone (DSO_2) failed to yield polymer at all at 60°C. Such reactivity differences are more clearly seen in the yield of bis(N-phenylphthalimide)s described in a later section. Although hydroquinone and resorcinol salts are the most nucleophilic, high molecular weight polymers could not be obtained from these compounds. When these salts were brought in contact with bisnitroimides, an intense red color developed and brown-colored low molecular

TABLE II

IR Absorption Bands of Bisphenol Disodium Salts

Bisphenol	Absorption Bands of the Disodium Salts*
Hydroquinone	1490(w), 1470(s), 1296(w), 1269(w), 1262(s), 1191(m), 1340(w), 986(w), 842(m), 797(s).
Resorcinol	1555(s), 1312(m), 1238(m), 1196(s), 1132(m), 972(m), 838(m), 759(w), 718(w).
4,4'-Dihydroxybiphenyl	1600(m), 1490(s), 1376(m), 1270(s), 1232(w), 1184(w), 812(s).
4,4'-Dihydroxydiphenyl ether	1848(w), 1575(m), 1465(s), 1293(s), 1197(s), 1246(w), 1088(m), 850(m), 838(s), 814(s), 714(w).
4,4'-Dihydroxydiphenyl sulfide	1710(w), 1560(s), 1468(s), 1293(s), 1153(m), 1090(w), 831(s), 801(w), 719(w).
4,4'-Dihydroxydiphenyl-sulfone	1558(s), 1474(s), 1319(s), 1242(m), 1132(m), 1095(s), 990(w), 842(s), 716(m).
4,4'-Dihydroxybenzophenone	1624(w), 1580(s), 1496(m), 1322(s), 1270(s), 1160(s), 1152(s), 1108(w), 924(w), 848(m), 832(m), 820(w), 778(m).

*Spectrum was taken in mineral oil

TABLE III

Polymerization by Nitro Displacement Reaction

Polymer	Bisphenol Salt	Bisnitroimide[a]	Solvent	Yield (%)	[η] (dl/g) in DMF
1	Resorcinol	3-ODA	DMF	100	0.16
2	Resorcinol	3 & 4-ODA(1:1)	DMF	88	0.10
3	Resorcinol	4-ODA	DMF	79.1	<0.1
4	Resorcinol	3-ODA	DMSO + toluene (1:1)	100	0.14
5	Hydroquinone	3-ODA	DMF	93.4	-
6	4,4'-dihydroxy-diphenyl ether	3-ODA	DMF	100	0.80[b]
7	4,4'-dihydroxy-diphenyl ether	4-ODA	DMF	95.5	0.44[c]
8	4,4'-dihydroxy-diphenyl ether	3-mPD	DMF	94.8	0.22
9	4,4'-dihydroxy-diphenyl sulfide	3-ODA	DMAc	100	0.37[d]
10	4,4'-dihydroxy-diphenyl sulfide	4-ODA	DMAc	86.7	<0.1
11	4,4'-dihydroxy-diphenyl sulfide	3-mPD	DMAc	100	0.16
12	4,4'-dihydroxy-diphenyl sulfide	4-mPD	DMAc	80.3	<0.1
13	4,4'-dihydroxy-diphenylsulfone	4-ODA	DMAc	0	-

(a) Numbers designate the position of $-NO_2$ substituent. The diamine moieties of bisimides are shown by ODA (4,4'-oxydianiline) and m-PD (m-phenylenediamine).

(b) Measured in dimethylacetamide.

(c) Inherent viscosity in H_2SO_4 (d = 1.84) at a concentration of 0.5%.

(d) Measured in chloroform.

weight polymers were obtained. The persistent and intense color of the reaction mixture seems to indicate formation of radical ions formed by an electron transfer reaction. The final consequence would be the oxidation of bisphenols. A very large difference of oxidation potential between resorcinol or hydroquinone dianion and bisnitroimides would plausibly support the above postulation. Insolubility of some of the polyetherimides in dipolar aprotic solvents is another limitation of nitro displacement polymerization. It is very difficult to isolate the polymer in pure form from the reaction mixture. The polymer tended to be less thermally stable than the identical polymer which was obtained by Route II as shown in TGA analysis (Figure 1). From the reasons described above, it was concluded that nitro displacement polymerization is not a suitable process to synthesize a wide variety of structurally different polyetherimides.

Synthesis of Polyetherimides Via Route II

A. Preparation of Bis(N-phenylphthalimido)ethers -- N-Phenyl-3-nitrophthalimide and N-phenyl-4-nitrophthalimide were readily prepared in high yield by the reaction of aniline and the corresponding nitrophthalic anhydride in boiling acetic acid.

Anhydrous sodium salts of resorcinol (Res), hydroquinone (HQ), 4,4'-dihydroxy-biphenyl (DBP), 4,4'-dihydroxydiphenyl ether (DDE), 4,4'-dihydroxydiphenylsulfide (DDS), 4,4'-dihydroxybenzophenone (DCO) and 4,4'-dihydroxydiphenylsulfone (DSO_2) were prepared in the same manner as described previously. The displacement reaction of N-phenylnitrophthalimides with the above disodium salts was carried out in DMF. The results are tabulated in Table IV. In general, 3-nitrophthalimide is more reactive than the 4-nitro isomer and this is reflected in the yield of bis(N-phenylphthalimido)ethers. The disodium salts of DCO and DSO_2 are less reactive than other salts and somewhat higher reaction temperature was necessary. Hydroquinone and resorcinol salts, on the other hand, seem to behave differently. The reaction is fast, but a significant amount of byproduct is formed, particularly in the reaction of resorcinol salt and N-phenyl-4-nitrophthalimide. This side reaction is, from the best estimate, oxidation of dianion by the nitro compound.

In all, the reaction is very similar to the results of the nitro displacement polymerization and can be considered as the model reaction for the polymerization.

B. Hydrolysis of Bis(N-phenylphthalimido)ethers -- In general, imides are hydrolyzed by both acids and bases. Bis(N-phenylphthalimido)ethers are most conveniently hydrolyzed in aqueous sodium hydroxide. The products, tetraacid salts, are soluble in aqueous base. The byproduct, amine, is removed by azeotropic distillation or by extraction.

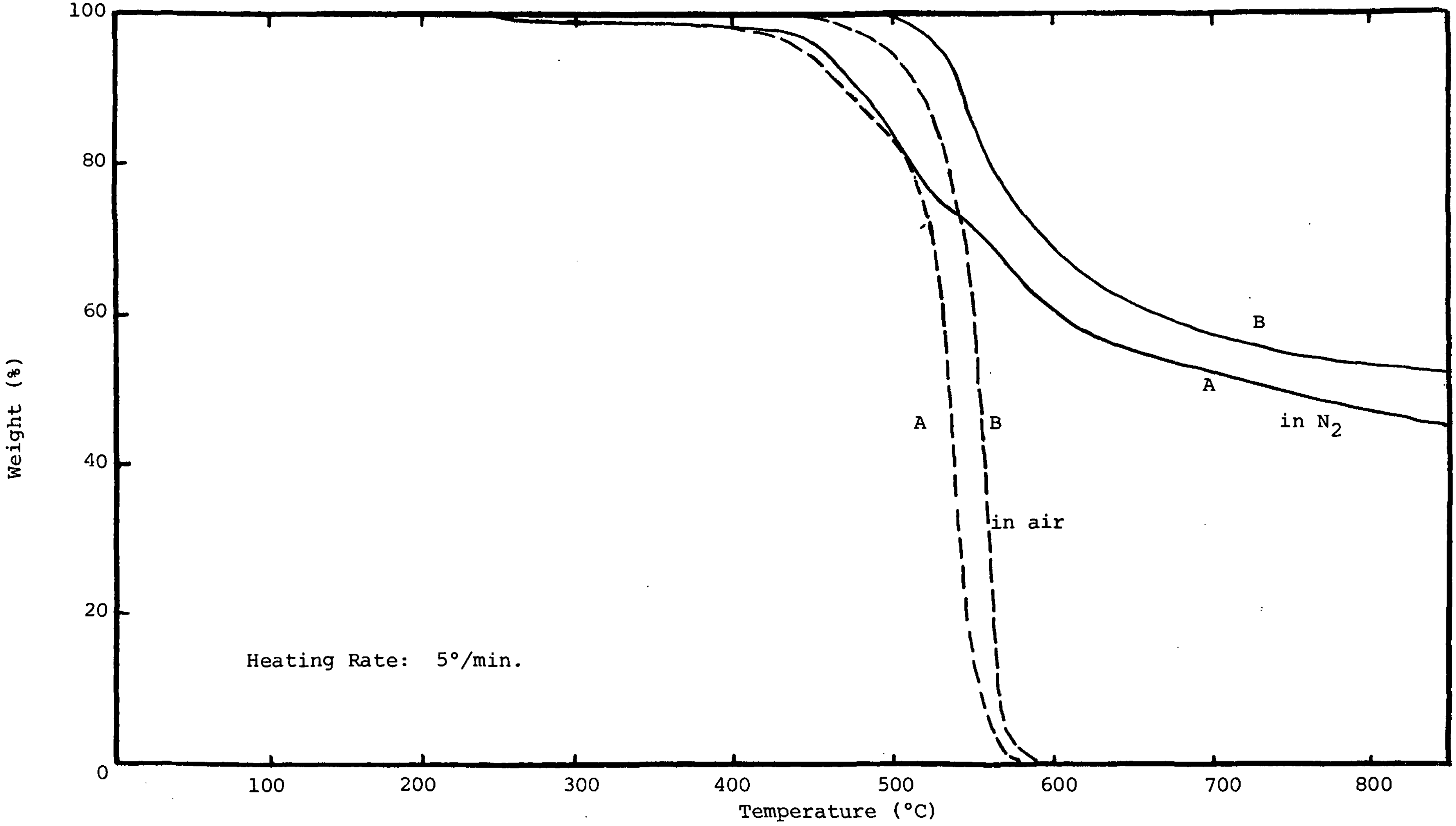
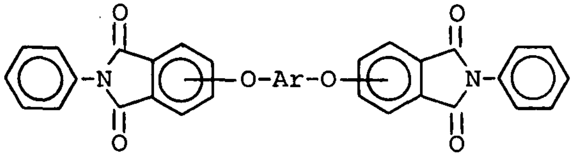


FIGURE 1. TGA of Polyetherimide 3-DDE-ODA

A -- Prepared via Route I
B -- Prepared via Route II

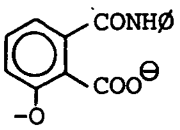
TABLE IV

Bis(N-phenylphthalimido)ethers

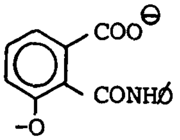


-Ar-	Isomer	Yield (%)	mp (°C)	Analysis (%)		
				C	H	N
1,3-Benzene	3	84.9	273.5-274	73.9	3.6	5.1
	4	26.7	264-266.5	73.6	3.9	5.1
				(calc. 73.91	3.65	5.08)
1,4-Benzene	3	85.9	311-312	74.3	3.9	5.0
	4	83.5	363-364	74.4	3.9	5.0
				(calc. 73.91	3.65	5.08)
4,4'-Biphenyl	3	86.7	305-306	76.4	4.0	4.4
	4	92.5	315-317	76.7	4.1	4.6
				(calc. 76.42	3.85	4.46)
4,4'-Diphenyl ether	3	99.0	239-241	74.7	4.0	4.3
	4	94.9	303-305	75.0	4.1	4.3
				(calc. 74.53	3.75	4.35)
4,4'-Diphenylsulfide	3	99.1	231-232	72.7	3.9	4.3
	4	91.5	281.5-283	72.8	3.8	4.3
				(calc. 72.71	3.66	4.24)
4,4'-Diphenylsulfone	3	85.7	200-201.5	69.0	3.8	4.0
	4	44.4	288-289.5	69.8	3.6	4.0
				(calc. 69.35	3.49	4.04)
4,4'-Benzophenone	3	91.9	237-238	75.3	4.1	4.0
	4	77.1	296-298	74.6	4.1	4.3
				(calc. 74.99	3.68	4.26)

A prominent difference in the rate of hydrolysis was observed between bis(N-phenylphthalimid-3-oxy)ethers and bis(N-phenylphthalimino-4-oxy)-ethers. The 4-oxy isomers were hydrolyzed at 100°C within 15 to 20 hours, while the 3-oxy isomers had to be reacted at least at 130° or, typically, at 180° for 2 hours. When 3-oxy isomers are hydrolyzed, the following two types of intermediates (A and B) are formed:



(A)

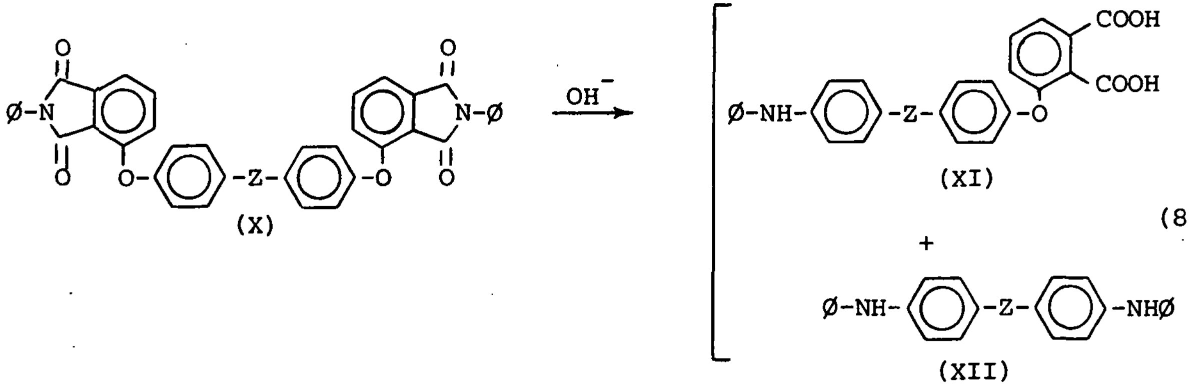


(B)

Intermediate (A) is expected to be hydrolyzed with ease, while intermediate (B) is very difficult to hydrolyze because it has a structure of 2,6-disubstituted benzoic acid derivatives.

Except for a few cases described below, pure tetraacids were isolated in nearly quantitative yield. The results are tabulated in Table V.

However, when 4,4'-bis(N-phenylphthalimid-3-oxy)diphenylsulfide (Z = S) was hydrolyzed at 130° for 13 hours, the reaction mixture contained a byproduct which was estimated to be (XI). Apparently the product was formed by the cleavage of the ether bond by nucleophilic attack of aniline. The side reaction was even more prominent when two other bisimides (Xb and Xc) were hydrolyzed. The yield of (XIIb) and (XIIc) was 41.7 and 56.1%, respectively.



(8)

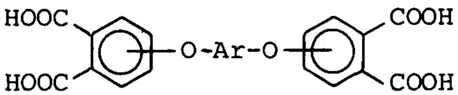
a) Z = S
b) Z = SO_2
c) Z = C=O

C. Preparation of Bis(ether anhydride)s

1) Dehydration of Tetraacids -- Dehydration of ether-containing tetraacids is attained simply by heating at approximately 200° in the presence or absence of inert high boiling solvents such as o-dichlorobenzene. However, the dehydration is conveniently carried out in a boiling acetic acid containing acetic anhydride. The method provides purification at the same time and yields bis(ether anhydride)s in quantitative yield.

TABLE V

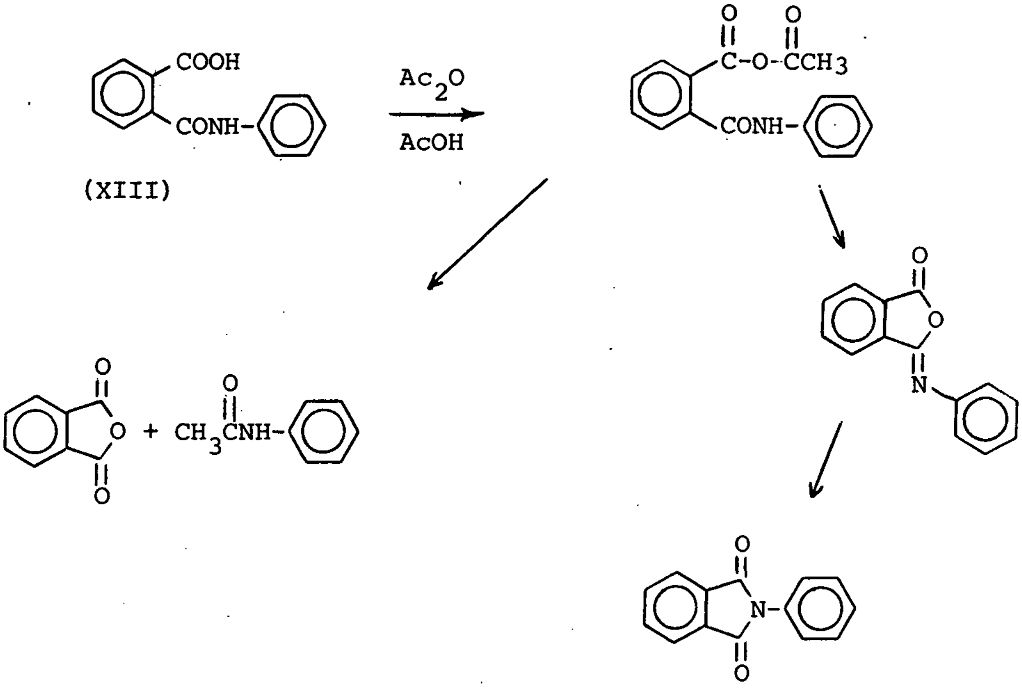
Tetracarboxylic Acids



-Ar-	Isomer	Water of Cryst.	mp (°C)	Yield (%)	Analysis (%) Calculated C	Analysis (%) Calculated H	Analysis (%) Found C	Analysis (%) Found H
1,3-Benzene	3	1 H_2O	165-170	91.0	57.90	3.56	58.6	3.8
	4	--	278-286	∿100	60.28	3.21	60.6	3.2
1,4-Benzene	3	--	305-306	86.5	60.28	3.21	60.3	3.3
	4	--	200-210 (dehyd.)	97.9	60.28	3.21	60.6	3.2
4,4'-Biphenyl	3	2 H_2O	275-280	92.7	61.09	4.03	60.3	3.7
	4	2 H_2O	284-286	94.2	61.09	4.03	61.3	3.8
4,4'-Diphenyl ether	3	--	252-254	89.8	63.40	3.42	63.7	3.6
	4	1 H_2O	167-170	94.8	61.32	3.65	61.6	3.6
4,4'-Diphenylsulfide	3	--	--[a]	∿53				
	4	2 H_2O	112-120	90.1	57.73	3.79	58.4	3.9
4,4'-Diphenylsulfone	4	1 H_2O	153-158	93.2	56.37	3.38	56.5	3.6
4,4'-Benzophenone	4	1 H_2O	200-210	96.7	62.14	3.60	62.1	3.5

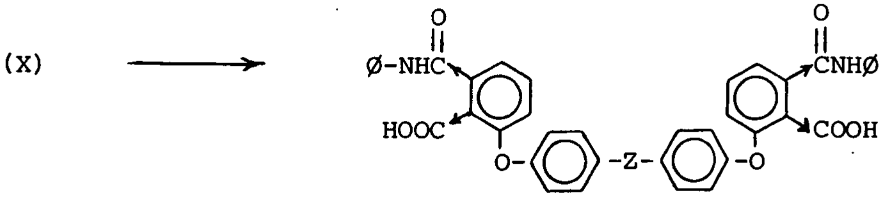
(a) Could not be obtained as pure crystals

2) Preparation from Bis(amide acid)s -- Although bis(N-phenylphthalimide)s (X) could not be hydrolyzed without side reaction, the corresponding bis(ether anhydride)s were prepared by the following different process. According to Sauer et al,[6] cyclization of N-phenylphthalimide acid (XIII) in a mixture of acetic acid and acetic anhydride gave a small amount of phthalic anhydride and acetanilide in addition to the main product, N-phenylphthalimide, as shown below.



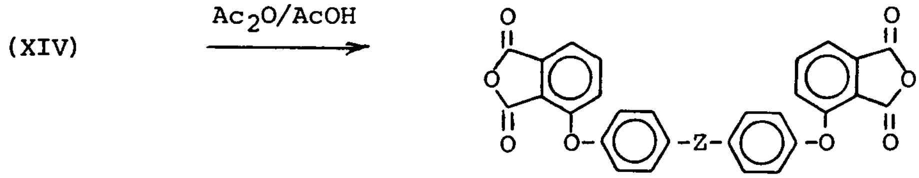
(9)

Bis(N-phenylphthalimide)s (X) were partially hydrolyzed to the corresponding bis(N-phenylamide acid)s at 40-45° in a dilute aqueous base. Surprisingly, when (XIVc) was reacted in a mixture of acetic acid and acetic anhydride, the corresponding bis(ether anhydride) (XVc) was obtained in 57.3% yield. Similarly, (XVa) and (XVb) were obtained in 40% and 57.9% yield, respectively.



(10)

(XIV) a) Z = S
b) Z = SO_2
c) Z = CO



(11)

(XV) a) Z = S
b) Z = SO_2
c) Z = CO

Bis(ether anhydride)s* are all well-defined crystalline compounds (Table VI). Interestingly, they are indefinitely stable in the presence of atmospheric moisture. Unlike pyromellitic anhydride and benzophenone tetracarboxylic dianhydride, bis(ether anhydride)s can be handled in open air without particular caution.

D. Polymerization of Polyetherimides from Bis(ether anhydride)s and Aromatic Diamines -- There are several known methods which are generally applicable to the preparation of polyimides. The most widely known method is a two-step synthesis which involves precisely controlled polymerization to prepare and isolate relatively unstable intermediates, "polyamide acids", followed by cyclo-dehydration.[7-10] In this process, it is predicted that the molecular weight control of unstable intermediates may be difficult, particularly when a large number of polymers with very different properties are involved.

Polyimides have been prepared from dianhydrides and diisocyanates by a one-step polymerization in a dipolar aprotic solvent.[11-13] The process requires diisocyanates of high purity. However, it is rather difficult to have various diisocyanates always available in pure form because of their sensitivity.

Recently we have disclosed that polyetherimides can be prepared by melt polymerization above their glass transition temperature.[14] In this process, it is essential to know beforehand the glass transition temperature of each polymer. It is, therefore, not suitable for the present work in which a large number of polymers with unknown properties are prepared.

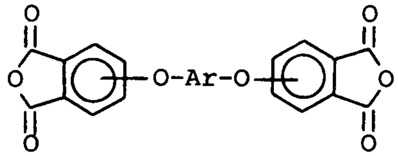
We have also discovered recently that polyetherimides are soluble in phenolic solvents and that the polymerization can be conducted in those solvents in one step.[15] The polymerization is most conveniently carried out in combination with other inert solvents such as benzene, toluene, etc., which form an azeotropic mixture with water. A mixture of a dianhydride, a diamine, a monofunctional monomer (if molecular weight control is necessary) and solvents is simply heated to reflux at 160-180° and the water formed is removed azeotropically. The polymer is then isolated by precipitation in methanol. Under the reaction conditions, oxidation of air-sensitive diamines is minimal because the solvent is acidic and also a radical inhibitor. Obviously the polymerization is insensitive to the presence of water in the starting materials. In fact, tetracarboxylic acids can be used in place of dianhydrides without any significant differences in the results.

---

*For simplicity, the following abbreviations will be used for bis(ether anhydride)s. Identification of isomer (3 or 4), bisphenol residue and DA are connected in that order. Abbreviations for bisphenol residues are: resorcinol (Res.), hydroquinone (HQ), 4,4'-dihydroxybiphenyl (DBP), 4,4'-dihydroxydiphenyl ether (DDE), 4,4'-dihydroxydiphenyl sulfide (DDS), 4,4'-dihydroxydiphenylsulfone (DSO_2), and 4,4'-dihydroxybenzophenone (DCO). For example: 3-DSO_2-DA represents 4,4'-bis(2,3-dicarboxyphenoxy)diphenylsulfone dianhydride.

TABLE VI

Bis(ether anhydride)s



-Ar-	Isomer	mp (°C)	Yield (%)	Analysis (%) C	H
1,3-Benzene	3	228-229.5	100	66.3	2.9
	4	284.4-286	89.9	65.3	2.6
				(calc.65.68	2.51)
1,4-Benzene	3	306-307	98.0	65.2	2.3
	4	265-266	91.2	66.7	2.7
				(calc.65.68	2.51)
4,4'-Biphenyl	3	280-281	88.9	70.7	3.0
	4	285-286.5	100	70.8	3.3
				(calc.70.29	2.95)
4,4'-Diphenyl ether	3	254-255.5	98.9	69.1	3.1
	4	238-239	100	68.4	3.1
				(calc.68.02	2.85)
4,4'-Diphenylsulfide	3	257-257.5	46.6	66.4	3.0
	4	189-190	97.0	66.4	3.0
				(calc.65.88	2.76)
4,4'-Diphenylsulfone	3	230.5-231.5	57.9	60.9	2.7
	4	251.5-252	99.6	62.0	3.0
				(calc.61.99	2.60)
4,4'-Benzophenone	3	278-279	59.0	69.8	3.0
	4	215-216	70.5	69.6	3.1
				(calc.68.78	2.79)

In combination with fourteen bis(ether anhydride)s described above, m-phenylene diamine (m-PD), 4,4'-diaminodiphenyl ether (ODA) and 1,3-bis(4-aminophenoxy)benzene (BAR) were used as monomers to prepare 42 polyetherimides. The results are summarized in Tables VII, VIII and IX.

In all cases, the polymerization mixture was homogeneous at the reaction temperature. Polyetherimides were all soluble in m-cresol at room temperature except two polymers, 4-HQ-BAR and 4-DBP-BAR,* which were shown to be crystalline by x-ray diffraction diagrams and differential scanning calorimetry (DSC).

E. Properties of Polyetherimides

1) Thermal Properties

a) Glass Transition Temperatures -- One of the most important properties that determines processability of a polymer is glass transition temperature (Tg). The Tg was measured by two methods, DSC and thermo-optical analysis (TOA).[16] The DSC measurement was made on the precipitated polymer samples and some of the polymers did not show sharp inflection in the DSC curve unless a dense sample, a compression molded film, was used. For this reason, Tg was confirmed by TOA measurement. A small piece of film was prepared for each polymer by compression molding and TOA was made on the film.

Usually Tg values obtained by TOA are somewhat higher than those obtained by DSC. This is the case also in the present work as shown in Tables VII, VIII and IX. The highest Tg value (DSC) was 277° for 3-DBP-ODA and the lowest was 178° for 4-DDS-BAR. The Tg could not be detected for 4-DBP-BAR by either method because the polymer was highly crystalline. The interesting trend observed in Tg values is that the Tg of the 3-isomer was without exception, significantly higher than that of the corresponding 4-isomer. The moderate Tg values of polyetherimides may be principally attributed to the flexible ether linkages in the main chains. Apparently the rotational freedom around the ether linkage of 3-isomers are sterically restricted, reflecting the higher Tg value.

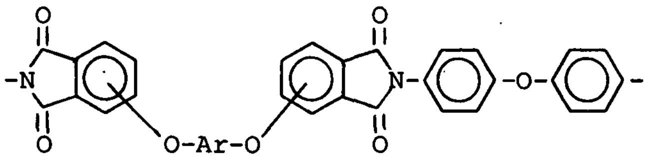
b) Thermal Stability -- TGA curves were obtained in air and in nitrogen at a heating rate of 5° per minute. As shown in Tables VII, VIII, and IX, polyetherimides are very stable. Their thermal stability is nearly comparable to that of conventional polyimides. One percent weight loss was observed at 440-500° in air and 425-550° in nitrogen, while 5% loss was registered at 470-553° in air and 477-570° in nitrogen. The most stable polymer was 4-HQ-ODA.

---

[*] The following abbreviations will be used for the names of polymers - the identity of isomer (3 or 4), bisphenol residues, diamine residues are connected in that order. The diamine residues are represented by ODA (4,4'-diaminodiphenyl ether), m-PD (m-phenylene diamine) and BAR (1,3-bis(4-aminophenoxy)benzene). For example: 3-DDS-ODA represents the polymer derived from 3-DDS-DA and 4,4'-diaminodiphenyl ether.

TABLE VII

Polyetherimides (Part 1)

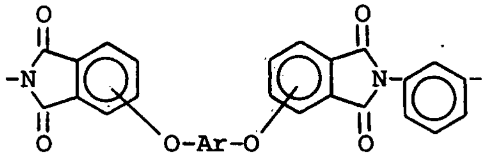


-Ar-	Isomer	Yield (%)	[η] (dl/g)[a]	Tg (°C) DSC[c]	Tg (°C) TOA[d]	TGA (°C)[e] Air(1)	TGA (°C)[e] N_2(1)	TGA (°C)[e] Air(5)	TGA (°C)[e] N_2(5)
1,3-Benzene	3	96.5	0.44	226	236	490	480	526	530
	4	98.4	0.67	209	220	480	520	537	555
1,4-Benzene	3	100	2.25	263	266	475	505	505	534
	4	100	1.71	237	242	486	553	553	570
4,4'-Biphenyl	3	100	1.70	277	N.O.	485	510	520	539
	4	96.4	0.83[b]	229	252	490	540	519	563
4,4'-Diphenyl ether	3	100	1.92	239	247	470	503	500	529
	4	100	0.97	215	221	480	510	518	552
4,4'-Diphenylsulfide	3	96.1	1.15	234	239	477	477	505	515
	4	97.8	1.02	212	219	480	485	517	535
4,4'-Benzophenone	3	95.1	2.00	252	257	480	500	522	529
	4	96.2	0.33[b]	210	222	455	510	510	546
4,4'-Diphenylsulfone	3	96.6	0.76	267	287	455	458	500	507
	4	97.5	1.13	260	262	470	470	512	536

(a) Measured in m-cresol. (b) Molecular weight was controlled by substituting 4 mole % of phthalic anhydride for 2 mole % of the dianhydride. (c) Measured at a heating rate of 40°/min. (d) Thermo-optical measurement. (e) Measured at a heating rate of 5°/min. Numbers in parentheses denote % weight loss.

TABLE VIII

Polyetherimides (Part 2)

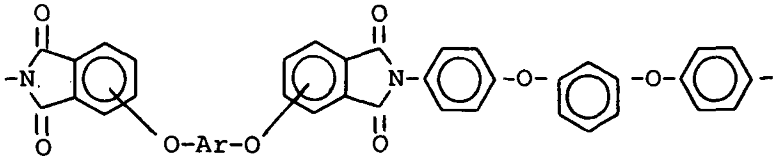


				Tg (°C)		TGA (°C)[d]			
-Ar-	Isomer	Yield (%)	[η] (dl/g)[a]	DSC[b]	TOA[c]	Air(1)	N_2(1)	Air(5)	N_2(5)
1,3-Benzene	3	93.3	0.57	241	240	460	500	510	530
	4	95.3	0.70	224	227	500	515	540	556
1,4-Benzene	3	96.2	0.45	259	N.O.	400	480	510	510
	4	95.4	0.96	255	N.O.	485	490	526	535
4,4'-Biphenyl	3	96.0	0.56	275	270	500	515	530	543
	4	97.3	0.51	247	251	480	535	525	562
4,4'-Diphenyl ether	3	99.2	0.53	238	247	480	480	513	523
	4	98.4	1.04	227	229	500	490	536	537
4,4'-Diphenylsulfide	3	95.0	0.52	231	233	470	470	504	505
	4	98.8	0.45	209	220	480	490	517	528
4,4'-Benzophenone	3	98.2	0.27	248	263	490	485	530	523
	4	96.4	1.35	239	244	480	510	523	538
4,4'-Diphenylsulfone	3	100	0.34	266	N.O.	440	425	475	477
	4	96.1	0.70	265	271	460	500	515	536

(a) Measured in m-cresol. (b) Measured at a heating rate of 40°/min. (c) Thermo-optical measurement.
(d) Measured at a heating rate of 5°/min. Numbers in parentheses denote % weight loss.

TABLE IX

Polyetherimides (Part 3)



-Ar-	Isomer	Yield (%)	[η] (dl/g)[a]	Tg (°C)		TGA (°C)[e]			
				DSC[c]	TOA[d]	Air(1)	N_2(1)	Air(5)	N_2(5)
1,3-Benzene	3	92.8	0.65	193	204	460	480	515	522
	4	89.0	1.10	188	188	450	450	535	533
1,4-Benzene	3	98.2	0.94	214	223	450	460	503	515
	4	99.1	Insol.	199	N.O.	465	520	525	554
				(T_m 330)	(T_m 349)[g]				
4,4'-Biphenyl	3	100	1.11	224	235	490	490	535	535
	4	96.0	Insol.	205	N.O.	490	500	522	555
				(T_m 343)	(T_m 328)[g]				
4,4'-Diphenyl ether	3	99.0	0.54	198	209	480	480	518	526
	4	95.7	1.10	184	191	482	530	543	557
4,4'-Diphenylsulfide	3	90.1	0.82	202	208	488	475	517	500
	4	93.6	0.60[b]	178	191	495	495	538	530
4,4'-Benzophenone	3	96.7	1.00	216	222	470	500	513	525
	4	>78.2[f]	0.93	194	204	440	500	470	525
4,4'-Diphenylsulfone	3	96.8	0.61	230	238	440	455	488	507
	4	94.4	0.88	219	226	480	460	535	529

(a) Measured in m-cresol. (b) Molecular weight was controlled by substituting 4 mole % of phthalic anhydride for 2 mole % of the anhydride. (c) Measured at a heating rate of 40°/min. (d) Thermo-optical measurement. (e) Measured at a heating rate of 5°/min. Numbers in parentheses denote % weight loss. (f) Part of the sample was lost during the work-up procedure. (g) Polymer melting points (T_m) obtained by TOA at high temperatures (>300°C) may not be accurat

2) Crystallinity -- General physical phenomena associated with crystallinity were not observed for polyetherimides except in two cases, 4-HQ-BAR and 4-DBP-BAR polymers for which crystalline melting points were 349° and 328°C, respectively, as determined by TOA. However, these melting point values were not reliable because of problems associated with temperature monitoring of the hot-stage microscope at these high temperatures. The more reliable values obtained by DSC measurement for 4-HQ-BAR and 4-DBP-BAR polymers were 330 and 343°C, respectively (see Figure 2). Crystallinity of the above two polyetherimides were also confirmed by their X-ray diffraction diagrams obtained for unoriented film samples (Figure 3).

3) Solubility -- Rigid heteroaromatic polymers such as polyetherimides have an inherently high melt viscosity. It is, therefore, essential for the polymers to be in solution when they are applied to fiber-reinforced composite systems. All polyetherimides prepared in the present work were soluble in m-cresol at room temperature except two crystalline polymers, 4-HQ-BAR and 4-DBP-BAR. In addition, many of the polyetherimides were soluble in other solvents such as DMF, DMAc, N-methylpyrrolidone, DMSO, tetrachloroethane, chloroform and methylene chloride. The results of solubility tests are tabulated in Tables X, XI and XII. According to the test results, 3-isomers are generally more soluble than the corresponding 4-isomers. This is an interesting property in contrast to the fact that the 3-isomers seem to be more rigid polymers than 4-isomers as indicated by their Tg values.

F. Polyetherimides as Base Resins for AST Composite Materials -- The following criteria have to be met for a polymer to be practically applicable to a high performance carbon fiber-reinforced composite system:

1) Good thermal stability
2) Solubility in practical solvents
3) Moderate glass transition temperature which is lower than the processing temperature
4) Readily available starting materials
5) Ease of preparation
6) Availability of curing chemistry

As discussed above in detail, polyetherimides apparently satisfy all of the criteria except (6). In Part II of this paper, the preliminary study of the curing chemistry will be discussed.

CONCLUSIONS

Nucleophilic displacement of "activated aromatic nitro groups" by bisphenolate ions was found to be a useful method to prepare aromatic ethers. Based on this reaction, fourteen ether-containing aromatic dianhydrides, namely bis(ether anhydride)s, were prepared. The combination of these bis(ether anhydride)s with m-phenylene diamine, 4,4'-diaminodiphenyl ether and 1,3-bis(4-aminophenoxy)-benzene afforded 42 structurally different polyetherimides. A unique one-step solution polymerization in m-cresol was found to be successfully applicable to the preparation of polyetherimides.

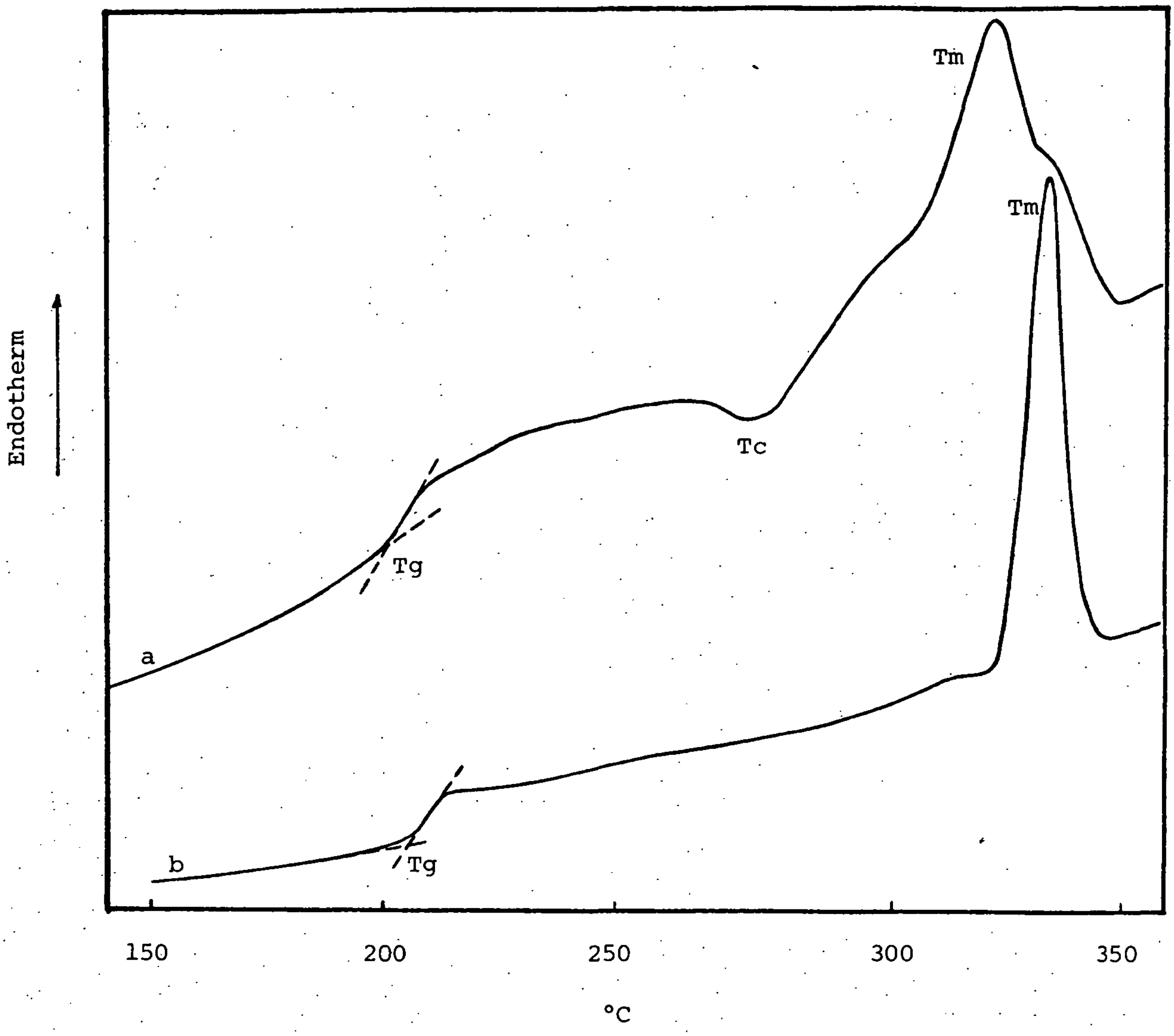
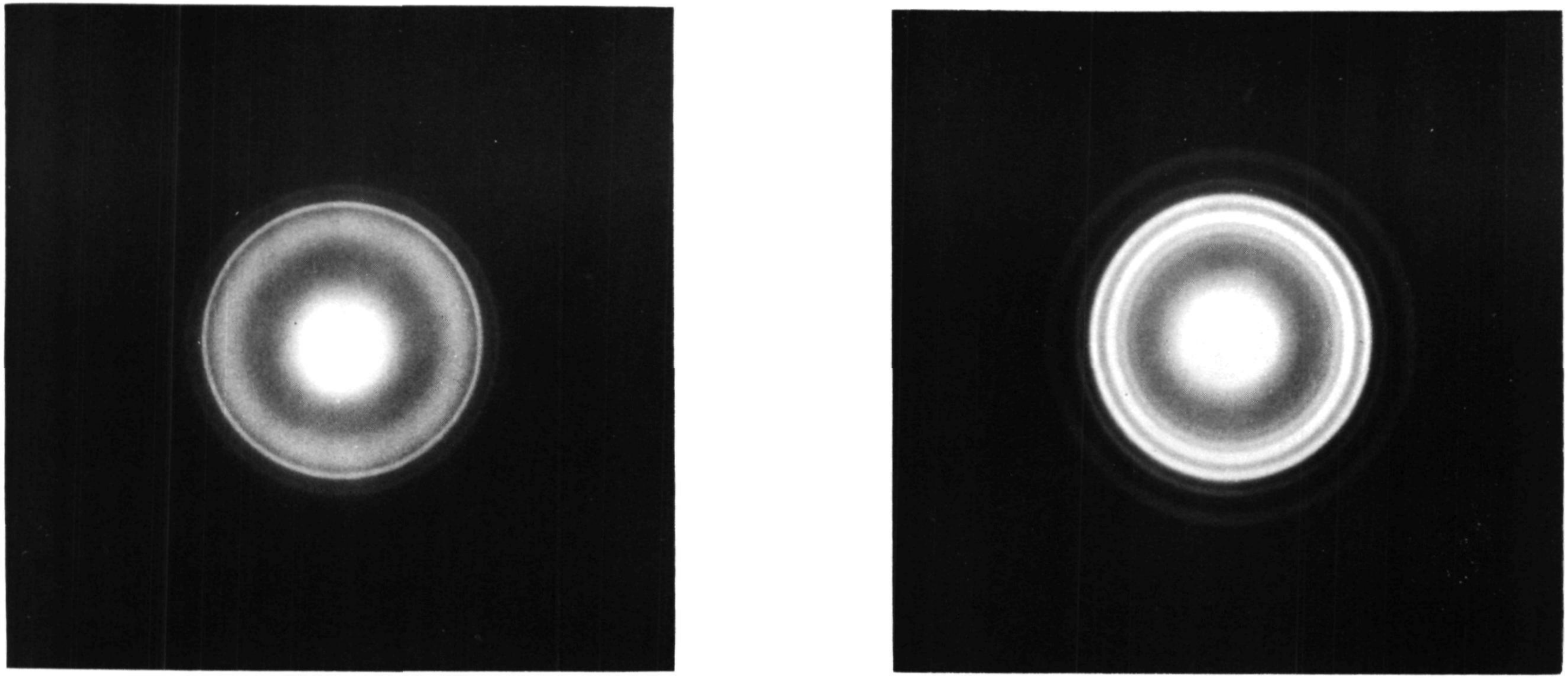


Figure 2. TGA curves of crystalline polyetherimides.
(a) 4-HQ-BAR. (b) 4-DBP-BAR (See Table IX).



a

b

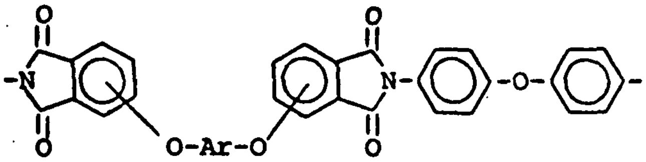
Figure 3. X-ray diffraction diagrams of crystalline polyetherimides.

(a) 4-HQ-BAR (b) 4-DBP-BAR

(See Table IX)

TABLE X

Solubility of Polyetherimides (Part 1)



-Ar-	Isomer	Solubility					
		NMP	DMAc	DMF	DMSO	$CHCl_3$	CH_2Cl_2
1,3-Benzene	3	s	s	s	s	s	s
	4	sw	i	i	i	i	i
1,4-Benzene	3	s	s	i	s	i	i
	4	s	i	i	i	sw	i
4,4'-Biphenyl	3	s	s	s	sw	s	i
	4	s	i	i	i	i	i
4,4'-Diphenyl ether	3	s	s	s	pi	s	s
	4	s	i	i	i	s	i
4,4'-Diphenyl sulfide	3	s	s	i	i	s	s
	4	s	i	i	i	i	i
4,4'-Benzophenone	3	s	s	s	s	s	s
	4	s	sw	i	i	s	i
4,4'-Diphenylsulfone	3	s	s	s	s	sw	sw
	4	s	s	s	s	sw	s

s = soluble

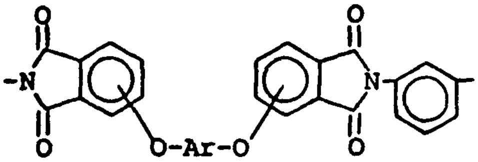
i = insoluble

pi = partially soluble

sw = swells

TABLE XI

Solubility of Polyetherimides (Part 2)



		Solubility					
-Ar-	Isomer	NMP	DMAc	DMF	DMSO	$CHCl_3$	CH_2Cl_2
1,3-Benzene	3	s	s	s	s	pi	pi
	4	s	sw	i	i	i	sw
1,4-Benzene	3	s	s	s	s	pi	pi
	4	s	i	i	i	i	i
4,4'-Biphenyl	3	s	s	s	sw	sw	sw
	4	s	i	i	i	pi	i
4,4'-Diphenyl ether	3	s	s	s	s	s	s
	4	s	pi	i	i	pi	sw
4,4'-Diphenyl sulfide	3	s	s	s	s	s	pi
	4	s	s	i	i	s	sw
4,4'-Benzophenone	3	s	s	s	s	s	s
	4	s	i	i	i	i	i
4,4'-Diphenylsulfone	3	s	s	s	s	sw	sw
	4	s	s	s	sw	sw	sw

s = soluble

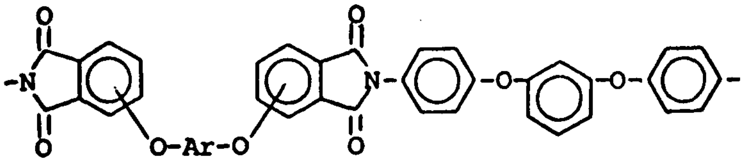
i = insoluble

pi = partially soluble

sw = swells

TABLE XII

Solubility of Polyetherimides (Part 3)



		Solubility					
-Ar-	**Isomer**	NMP	DMAc	DMF	DMSO	$CHCl_3$	CH_2Cl_2
1,3-Benzene	**3**	s	s	s	s	s	s
	4	sw	i	i	i	i	i
1,4-Benzene	**3**	pi	pi	pi	pi	pi	i
	4	i	i	i	i	i	i
4,4'-Biphenyl	**3**	s	s	pi	sw	s	i
	4	i	i	i	i	i	i
4,4'-Diphenyl ether	**3**	s	s	s	s	s	s
	4	i	i	i	i	i	i
4,4'-Diphenyl sulfide	**3**	s	s	s	s	s	s
	4	pi	i	i	i	i	i
4,4'-Benzophenone	**3**	s	s	s	s	s	s
	4	s	sw	i	i	s	i
4,4'-Diphenylsulfone	**3**	s	s	s	s	s	s
	4	s	s	s	sw	s	s

s = soluble

i = insoluble

pi = partially soluble

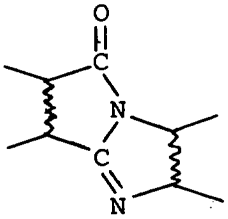
sw = swells

The polyetherimides were non-crystalline except in two cases, and their glass transition temperatures varied widely (178-277°), but well-below the decomposition temperature (440-500°). These key properties of polyetherimides seem to assure adequate process characteristics over a wide temperature range. The wide process window may be important in terms of the nature of the curing reactions which will be developed in Phase II of this project.

The polyetherimides were all soluble in m-cresol at room temperature except the two crystalline polymers described earlier. In addition, many of them are soluble in other solvents such as chloroform, tetrachloroethane, NMP, DMAc and DMF. This excellent solubility of polyetherimides is one of the most important properties in view of the practical application of the final resin formulation.

SECTION II. POLYETHERPYRRONES

Numerous types of heteroaromatic polymers have been prepared by cyclopolycondensation of aromatic dianhydrides and aromatic tetraamines since Bell et al[18] and Marvel et al[19] first reported such polymers. The repeating unit of these polymers is composed of fused heterocyclic rings commonly containing the following chemical group:

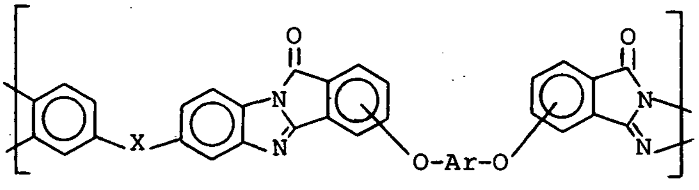


Depending on the type of heterocyclic rings (5- or 6-membered), the polymers may be called polybenzimidazopyrrolones,[18] benzimidazoisoquinolines,[20] arylenebenzimidazoles,[21] benzimidazobenzphenanthrolines,[22] etc.

These polymers, generally known as "pyrrones", possess excellent electrical properties and thermooxidative stability, as well as outstanding mechanical properties. They are also unique in terms of extraordinary resistance against the action of ionizing radiation.[18,23]

Although pyrrones are generally recognized to have outstanding overall properties, they belong to a group of the least tractable polymers. Pyrrones are infusible and generally not moldable. In only limited cases, molding has been performed in the presence of plasticizers.[24] Pyrrones are also insoluble in organic solvents, although they can be dissolved in strong acids such as polyphosphoric acid, sulfuric acid, benzenesulfonic acid and methanesulfonic acid. This intractability of pyrrones not only severely limits its polymer processing technique, but also its synthetic method. Completely cyclized polymers can be prepared by simply heating the monomer mixtures at high temperature or by high temperature solution polymerization in polyphosphoric acid.[25-27] With these methods, however, the obtained polymers can not be applied to practical end uses due to lack of processability. More recently, a careful study by Johnston[28] revealed that melt polymerization and solution polymerization in polyphosphoric acid could not be applied to the preparation of polybenzimidazopyrrolones. On the other hand, dianhydrides and diamines have been reacted at low temperatures in dipolar aprotic solvents to afford soluble polymer intermediates which have uncyclized or partially cyclized polymeric structures. The resulting solutions can be applied to the preparation of films or coatings in the manner similar to polyimide applications. However, the preparation of such solutions is extremely difficult and cumbersome primarily because of their instability. Solutions of pyrrone prepolymers tend to form gel readily.[28]

In Section I, it was shown that aromatic ether groups in the polymer chain provide polyimides with marked improvements in solubility and moldability. A similar effect has been shown with polybenzimidazopyrrolones derived from aromatic tetraamines and bis(ether anhydride)s. The general structure of the polymers is represented by (XVI) and will be called polyetherpyrrone.



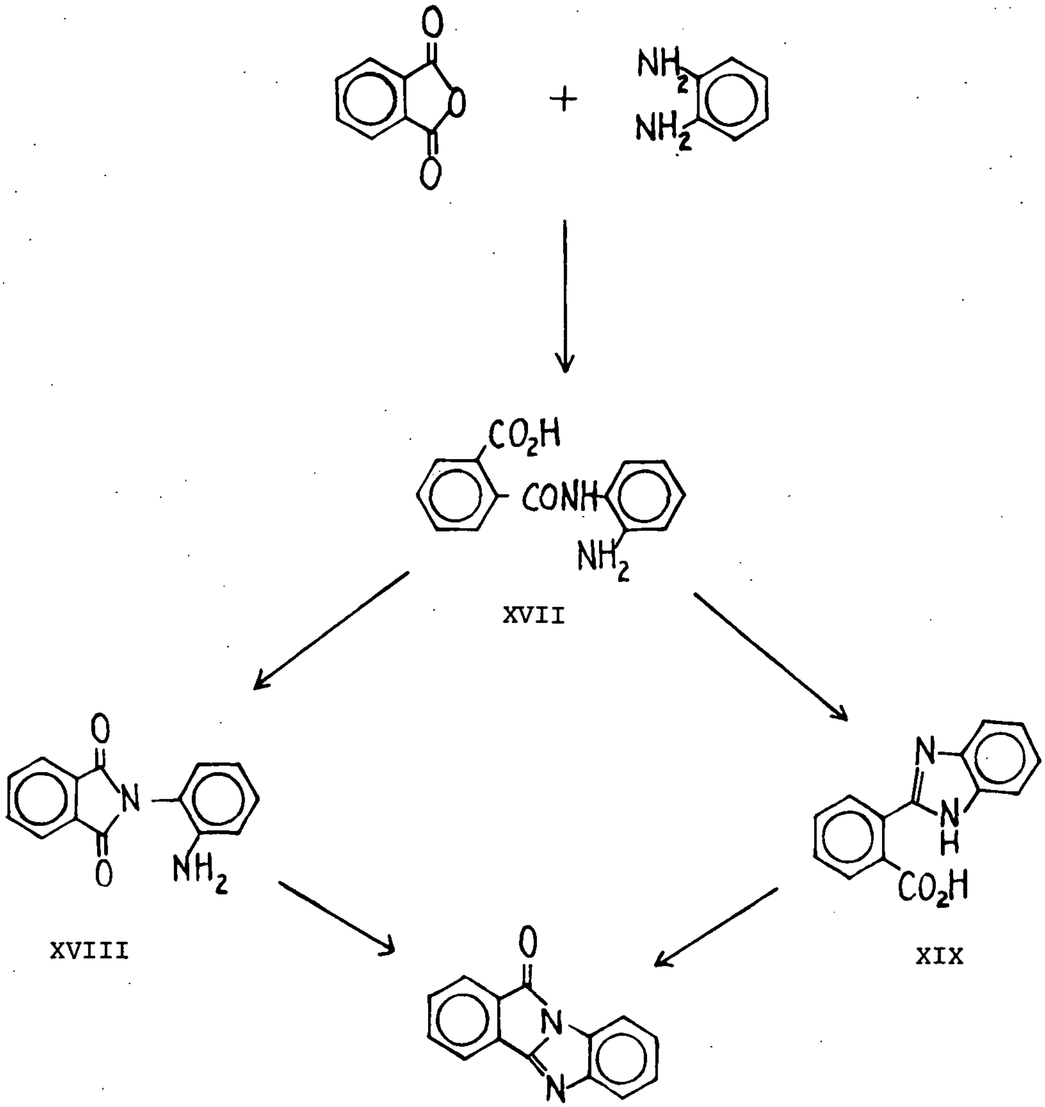
(XVI)

Model Reaction

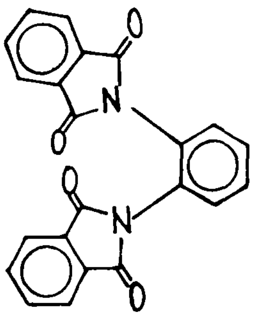
The reaction of phthalic anhydride and o-phenylenediamine has been described on numerous occasions.[18,19,21,29-32] When phthalic anhydride is added to the solution of o-phenylenediamine at ambient temperature, amide-acid-amine (XVII) is formed quantitatively. As for what happens after that is the subject of controversy and confusion. The main reason for the confusion seems to arise from the complex nature of the reaction as illustrated in Figure 4. At least seven intermediates and products have been reported. Added difficulties are analytical problems. Many of the intermediates are unstable and tend to interconvert readily. In addition, these compounds, except pyrrone (XX), are very polar, high melting and extremely insoluble, so that quantitative analysis of the complex mixture is difficult. Furthermore, entirely different results may be obtained depending upon the reaction conditions, particularly temperature and presence or absence of solvent.

Direct heating of an equimolar mixture of o-phenylenediamine and phthalic anhydride tends to give a substantial amount of o-phenylenebisbenzimidazole (XXIII).[19,29-31] Close observation indicated that in the initial stage the reaction took place in the molten liquid of o-phenylenediamine because the melting point of o-phenylenediamine is the lowest (102°C). Such a condition is obviously favorable for the formation of bisbenzimidazole (XXIII) because the reaction proceeds in the presence of an excess amount of o-phenylenediamine. Subsequently, at the final stage, the reaction may take place in the presence of an excess amount of phthalic anhydride. Some differences were observed in the product ratios when the reaction was carried out under different heating programs.[19] However, the formation of bisbenzimidazole (XXIII) could not be avoided as shown by the careful analytical work of Young.[31] After the reaction mixture was treated with acetic anhydride for the complete cyclization, approximately 16% of bisbenzimidazole (XXIII) and 22% of bisimide (XXI) were obtained in addition to 44% of pyrrone (XX). Both XXI and XIII represent models for crosslink structures of pyrrone polymers. It is understandable from these results that Marvel et al[19] obtained pyrrone polymers always containing insoluble gel by melt polymerization.

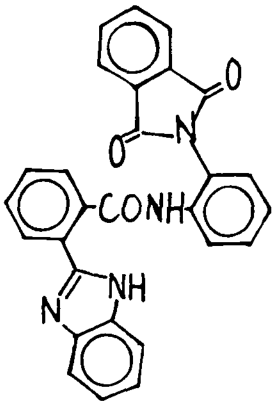
Figure 4. Reaction of Phthalic Anhydride and o-Phenylenediamine



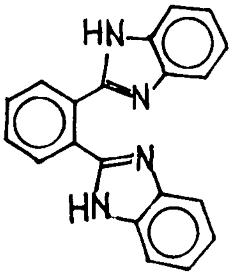
XX



XXI



XXII



XXIII

The reaction in dipolar aprotic solvents at ambient temperature was first reported by Bell et al,[18] followed by Colson et al[21] and Van Deusen.[22] With this technique, soluble intermediates, polyamide-acid-amines, were obtained and subsequently converted to pyrrones in the manner similar to polyamide-acid and polyimide systems. Colson[21] described that amide-acid-amine (XVII) was predominantly converted to aminoimide (XVIII) on heating at 160° in dimethylacetamide. Contrary to this observation, careful analytical examination by Young[32] showed that amide-acid-amine (XVII) was converted in diemthylformamide at 154° to a 2:1 mixture of aminoimide (XVIII) and benzimidazole-acid (XIX). The same reaction in the absence of solvent yielded 19% of pyrrone (XX) and 36% of benzimidazole acid (XIX). Aminoimide (XVIII) was not present in the products, indicating that pyrrone (XX) was formed from aminoimide (XVII). Interestingly, Yong[32] identified that the remainder of the products was an intermolecular reaction product, benzimidazole-amide-imide (XXII), which implied the existence of yet another crosslinking mechanism.

It has been generally known that cyclodehydration to form heterocyclic rings such as imide and benzimidazole rings is catalyzed by acid. The cyclization of aminoimide (XVIII) to form pyrrone (XX) is also expected to be accelerated in acidic solvents such as m-cresol. In addition, amino groups are strongly protonated in acidic solvents and the nucleophilic reaction of amino groups on anhydride groups is significantly retarded. Under such a condition, it is probable that acylation of amino groups become more selective reducing side reaction such as bisacylation of o-diamino groups.

Reaction of o-phenylenediamine and phthalic anhydride was studied in various solvent mixtures containing m-cresol. The results are shown in Table XIII. The initial reaction to form amide-acid-amines (XVII) was carried out at room temperature and the resulting solution was heated to reflux. The water formed was continuously removed azeotropically by the use of a Dean-Stark trap, and the reaction mixture was analyzed by gas chromatography using o-terphenyl as an internal standard.

When an amide-acid-amine solution in a benzene-m-cresol mixture (62.5: 37.5) was refluxed at 90°C, approximately 75% of the theoretical amount of water was collected in two hours and after that the dehydration was very slow. At this point, the reaction mixture consisted of essentially only pyrrone (XX) benzoimidazole acid (XIX) and aminoimide (XVIII). On raising the reflux temperature to 180°C by distilling off the benzene, the cyclization proceeded rapidly and practially quantitative yield of pyrrone (XX) was obtained. In contrast, a significant quantity of bisimide (XXI) and bisbenzimidazole (XXIII) was formed when the initial cyclization reaction was carried out above 130°C.

TABLE XIII

Reaction of Phthalic Anhydride and o-Phenylenediamine

Solvents (%)	Concentration of Reactants (%)	Reaction Conditions	Yield of Pyrrone (%)[a]
o-Dichlorobenzene (100)	25	190-194°/4.5 hrs	72.6
N-Methylpyrrolidone (62.5) Benzene (37.5)	10	107-128°/3.3 hrs 128-181°/1 hr 181°/1 hr	85.8
o-Xylene (62.5) m-Cresol (37.5)	25	138°/10 min. 161°/1.3 hrs	75.5
Toluene (62.5) m-Cresol (37.5)	25	120°/10 min. 130°/0.5 hr.	71.3[b]
Benzene (62.5) m-Cresol (37.5)	10	90-94°/4.4 hrs	98.2[b]
Benzene (62.5) m-Cresol (37.5)	10	90-94°/2.5 hrs 97-174°/48 min. 174-180°/1.5 hrs	98.7

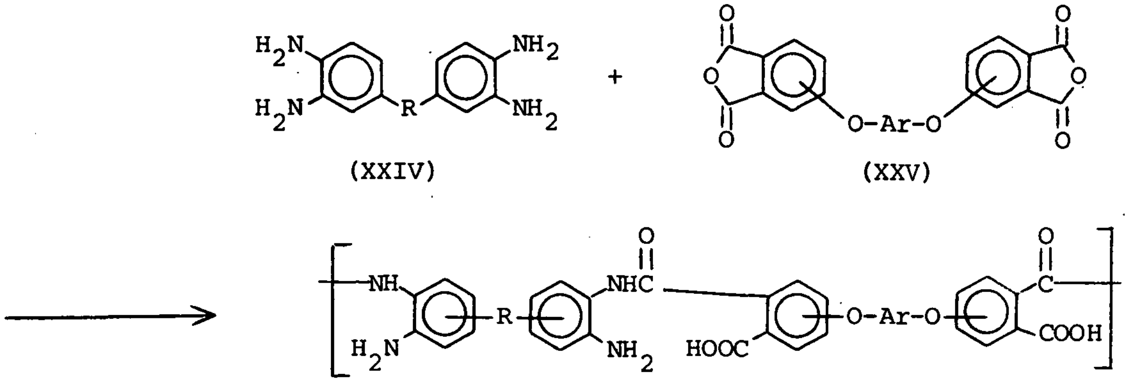
a. Determined by gas chromatography using o-terphenyl as an internal standard.

b. The cyclization was not complete. The figures show the sum of pyrrone (XX) and pyrrone-forming intermediates, benzimidazole acid (XIX) and aminoimide (XVIII) which were converted to XX in GC injection port.

Polymerization of Polyetherpyrrones

The polymerization of polyetherpyrrones was run under a carefully controlled condition based on the results of the above model reaction study.

A m-cresol solution of 4,4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride and phthalic anhydride (chain terminator) was added dropwise with stirring to a m-cresol solution of 3,3',4,4'-tetraaminobenzophenone at 30-40°C. A clear viscous solution of polyamide-acid-amine (XXVI) was obtained. The solution was heated at 80-90° and benzene was added dropwise with stirring. Too rapid addition of benzene may cause temporary precipitation of polymer and lead to gel formation.



(XXIV) (XXV)

(XXVI)

(12)

It is important that the reaction mixture remains homogeneous during each phase of the polymerization. When phase separation of the solution or precipitation of polymer intermediate occurred during the polymerization, the final polymer always contained a substantial quantity of gel. This is because the crosslinking reaction is an intermolecular reaction, and it is favored in the more condensed phase.

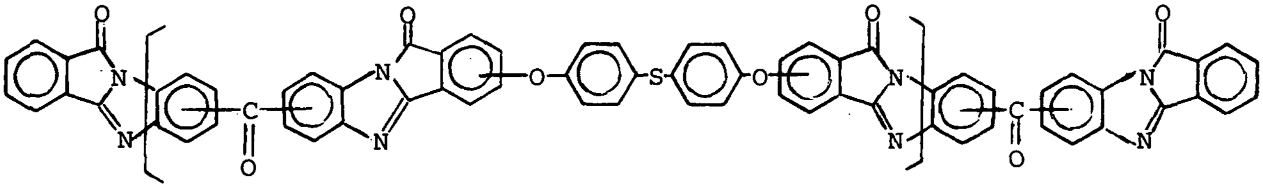
The optimum amount of benzene was approximately 50 volume percent of m-cresol. Too small an amount of benzene raised the boiling temperature of the reaction mixture too high; on the other hand, polyamide-acid-amine (XXVI) tended to precipitate at too high a concentration of benzene.

The polyamide-acid-amine solution containing benzene was then heated to reflux at 110-120°, and the water was continuously removed by the use of a Dean-Stark trap. In approximately one hour, about 75% of the theoretical amount of water was collected, and the formation of water slowed down markedly. By this time, the amide-acid-amine groups apparently had cyclized to form benzimidazole-acid and imide-amine groups which were further cyclized to pyrrone groups.

Interestingly, Colson[21] described that benzimidazole-acid (XIX) did not cyclize below 240°C. However, this observation was for the solid state reaction and did not take into account stabilization by crystalline lattice energy. In contrast, the dehydration of benzimidazole-acid moiety proceeded at 150-160°C at an appreciable rate in m-cresol. The reaction was complete at 180°C within one hour. The resulting solution of polyetherpyrrone was homogeneous at room temperature and had an intense clear yellow color characteristic of the pyrrone moiety. The polymer was isolated by precipitation. Polymerizations were carried out at various levels of phthalic anhydride which was used as a chain terminator. The results are summarized in Table XIV.

TABLE XIV

Polyetherpyrrones (Part 1)



Exp. No.	Monomers[a] DA/TA/PA (Molar Ratio)	Yield %	[η][b] (dl/g)	Tg[c] (°C)
25-235	9:10:2	97.9	0.29	252
25-236	19:20:2	97.1	0.41	264
25-240	39:40:2	93.8	0.43	264
25-238	59:60:2	95.5	0.48	267

a) DA - dianhydride, TA - 3,3',4,4'-tetraaminobenzophenone, PA - phthalic anhydride.

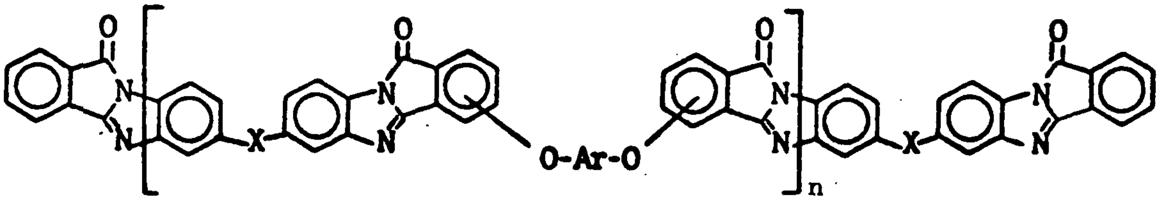
b) Measured in m-cresol at 25°C.

c) Measured by DSC at 40°/min.

Other bis(ether anhydride)s described in Section I and various tetraamines were also polymerized under similar conditions. The results are summarized in Table XV. In experiments #25-252, -253 and -269, dianhydrides were only sparsely soluble in m-cresol. Therefore, the dianhydride was added in the form of a dispersion in m-cresol. When 3,3',4,4'-tetraaminodiphenyl ether and 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide were reacted at 35°C in m-cresol, the resulting polyamide-acid-amine solution separated into two phases. The heterogeneous solution became homogeneous again on heating at 100°C, but massive gelation occurred in the final dehydration stage at 180°C. This problem was avoided when the initial reaction was run at 75°C instead of 35°C. The polyamide-acid-amine solution remained homogeneous throughout the entire polymerization stage.

TABLE XV

Polyetherpyrrones* (Part 2)



Exp. Code	X	Ar	Isomerism	Yield (%)	[η] (dl/g)	Tg (°C)
25-252	$-\overset{O}{\overset{\|}{C}}-$	1,4-Benzene	3	98.0	0.65	317
25-253	$-\overset{O}{\overset{\|}{C}}-$	4,4'-Diphenyl-sulfone	4	76.4**	0.46	303
25-261	$-SO_2-$	4,4'-Diphenyl-sulfide	4	95.8	0.58	295
25-269	$-\overset{O}{\overset{\|}{C}}-$	4,4'-Diphenyl ether	3	99.3	0.76	298
25-274	-O-	4,4'-Diphenyl-sulfide	4	98.0	1.64	264
25-238	$-\overset{O}{\overset{\|}{C}}-$	4,4'-Diphenyl-sulfide	4	95.5	0.48	267

*A 2:49:50 molar ratio of phthalic anhydride, bis(ether anhydride) and tetraamine was used.

**Yield of the soluble part; some gel was formed.

Properties of Polyetherpyrrones

A. Solubility

Pyrrone polymers reported earlier[18,19] were not soluble in conventional organic solvents. In contrast, polyetherpyrrones were soluble in organic solvents such as tetrachloroethane, m-cresol and o-chlorophenol.

B. IR Spectrum

The IR spectrum of a thin film prepared from polyetherpyrrone #25-238 is shown in Figure 5. The cyclodehydration of the polymer was shown to be complete, as evidenced by the lack of N-H and -OH absorptions in the 2800-3600 cm^{-1} region. A weak band at approximately 3500 cm^{-1} is considered to be the overtone of the major pyrrone band at 1755 cm^{-1}.

C. Thermal Properties

Thermogravimetric analysis (TGA) was performed at a heating rate of 5°/min. The excellent thermal stability of polyetherpyrrones is shown in Figure 6 for the sample obtained from tetraaminobenzophenone and 4,4'-bis(3,4-dicarboxyphenoxy)-diphenylsulfide dianhydride. Approximately 70% of the weight is retained at 800°C in nitrogen. A minor weight loss is seen at 260-280°C both in air and in nitrogen. The glass transition temperature of the polymer lies in this range (267°). The weight loss may be attributed to the loss of residual solvent, of which diffusion during the drying procedure was limited by the high glass transition temperature.

The glass transition temperature of polyetherpyrrones was obtained by differential scanning calorimetry as shown in Table XV. The values are substantially higher than those of the corresponding polyetherimides, reflecting rigid heteroaromatic structure.

CONCLUSIONS

Formation of benzimidazopyrrolone (pyrrone) from phthalic anhydride and o-phenylenediamine was studied in solutions containing m-cresol. Under a controlled condition, pyrrone could be prepared in essentially quantitative yield without forming by-products. Aromatic tetraamines and ether-containing dianhydrides described in Section 1 were polymerized in a benzene-m-cresol mixture to obtain high molecular weight polyetherpyrrones. Polyetherpyrrones were soluble in phenolic solvents and films could be cast from the m-cresol solution. The glass transition temperature of polyetherpyrrones was significantly higher than that of the corresponding polyetherimides, presumably because of the higher degree of rigidity.

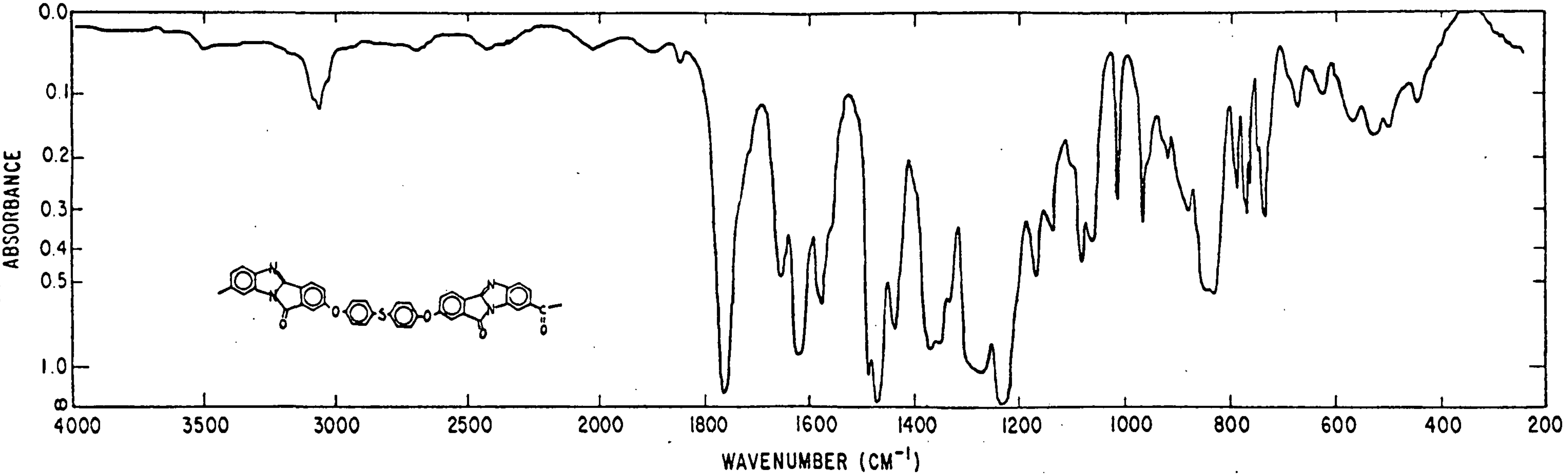


FIGURE 5. IR SPECTRUM OF POLYETHERPYRRONE

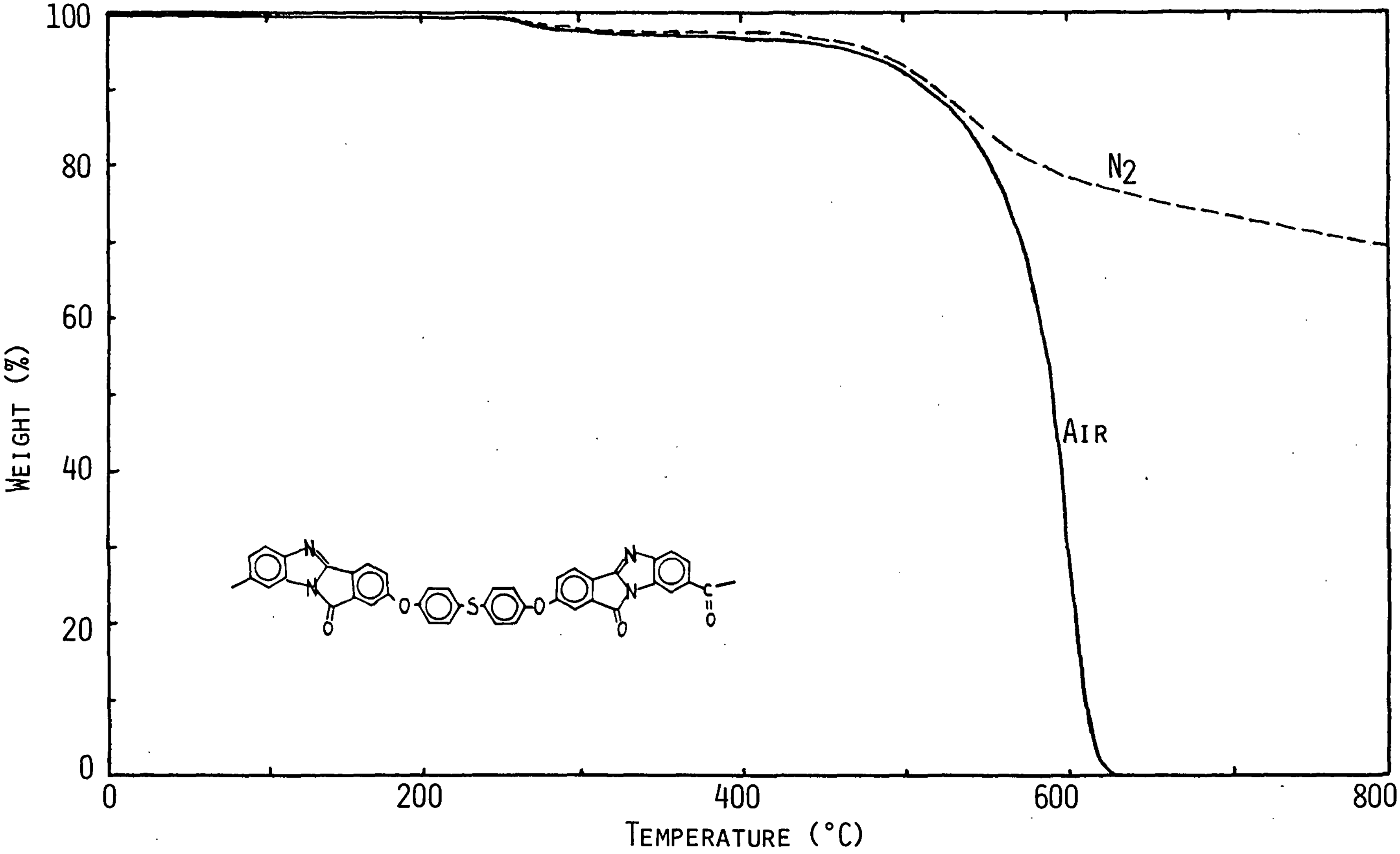


FIGURE 6. TGA CURVES OF POLYETHERPYRRONE - 5°C/MIN

EXPERIMENTAL

Hydroquinone and resorcinol were purified by vacuum distillation. 4,4'-Dihydroxydiphenyl ether and 4,4'-dihydroxybenzophenone were sublimed under vacuum. 4,4'-Dihydroxydiphenylsulfide and 4,4'-dihydroxydiphenylsulfone were recrystallized from toluene and water, respectively. Both m-phenylene diamine and 4,4'-diaminodiphenyl ether were purified by vacuum distillation. 3- and 4-Nitrophthalic anhydrides were purified and separated by fractional distillation under vacuum.

1) Bis(nitroimide)s (IV)

The preparation of 4,4'-bis(3-nitrophthalimido)diphenyl ether is described below as a typical example.

In a one liter, three-neck flask equipped with a stirrer, thermometer and a Dean-Stark condenser were placed 3-nitrophthalic anhydride (140.0 g, 0.725 mole), 4,4'-diaminodiphenyl ether (72.58 g, 0.3625 mole), phenol (250 g) and toluene (200 ml). The flask was placed in an oil bath maintained at 180° and the reaction mixture was allowed to reflux with stirring. The toluene was continuously withdrawn from the Dean-Stark condenser until the boiling temperature of the reaction mixture reached 140°C. The heating was continued at 140° for 0.5 hour during which time most of the water formed was removed. The Dean-Stark condenser was replaced by a recirculating trap (Figure 7) filled with molecular sieve (4A). The reflux at 140° was continued for an additional hour to insure the complete dehydration. The reaction mixture was diluted with 450 ml of toluene and cooled. The resulting mixture was poured into 3.5 liters of methanol and the yellow crystalline precipitate was collected by filtration. The precipitate was slurried in 2 liters of an acetone-methanol mixture (1:1). The slurry was boiled for 15 minutes and filtered. The resulting pure product was dried at 100°/0.5 mm Hg overnight. The yield of the bisnitroimide was 195.1 g (97.8%). The melting point was 306-308°.

Anal. Calcd. for $C_{28}H_{14}N_4O_9$: C, 61.09; H, 2.56; N, 10.18. Found: C, 61.5; H, 2.7; N, 10.2.

2) Anhydrous Bisphenol Disodium Salts (V)

The preparation of 4,4'-dihydroxydiphenylsulfide disodium salt is given below as an example.

Reagent grade absolute methanol was stirred under nitrogen in the presence of calcium hydride (5-10 g per liter) for several hours and distilled. The following procedure was carried out in a dry box. Freshly cut, clean sodium (14.239 g, 0.6194 mole) was added to about 200 ml of dry methanol. After the sodium had reacted completely, 4,4'-dihydroxydiphenylsulfide (67.597 g, 0.3087 mole) was added. The resulting mixture was magnetically stirred and heated to reflux until a homogeneous solution resulted. About 100 ml of dry toluene (treated with CaH_2 and distilled) was added and the solution was distilled to remove the methanol. When most of the methanol was distilled off, an additional 150 ml of dry toluene was added. The distillation was continued until the vapor temperature rose to 100°C. The reaction

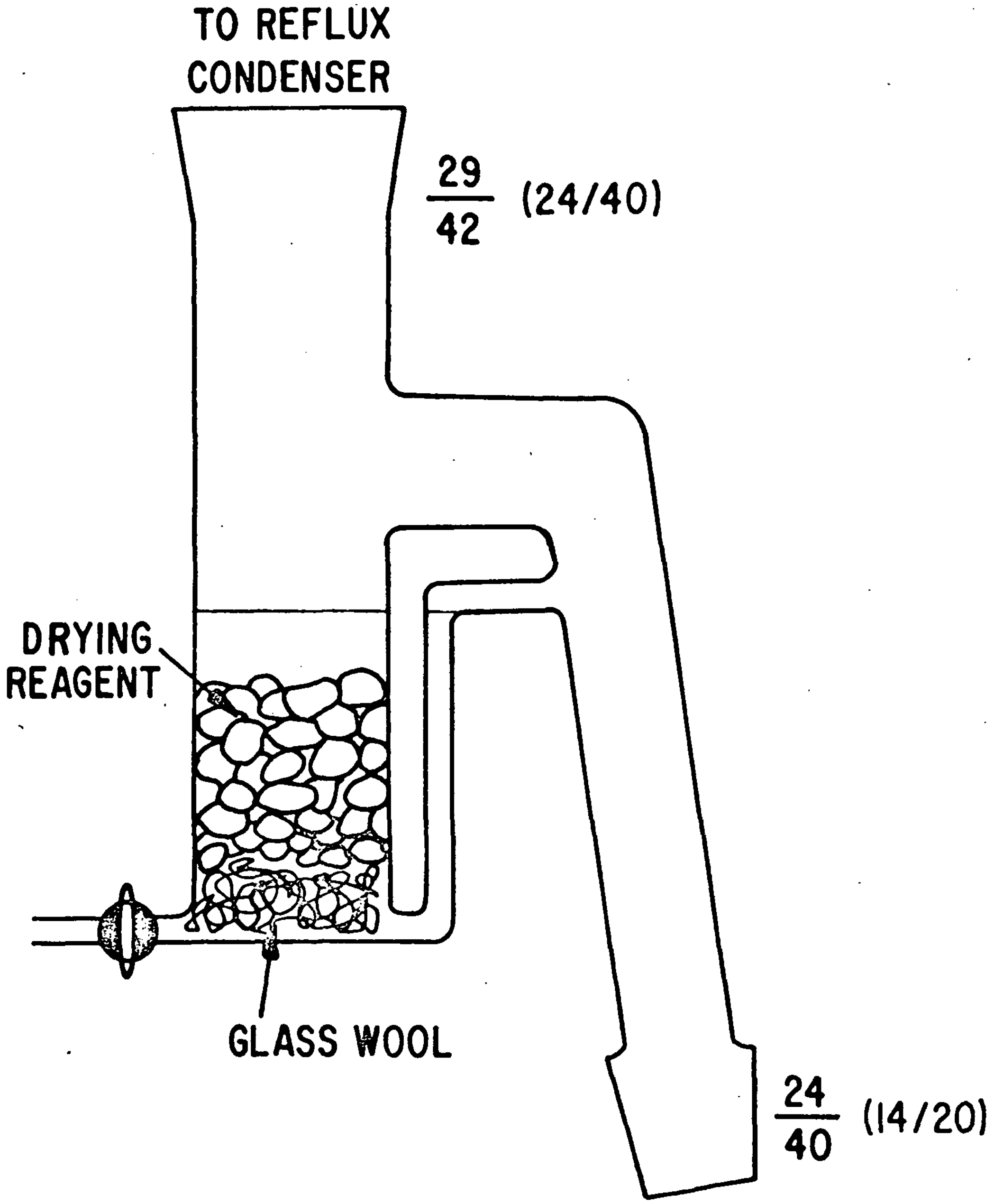


FIG. 7 RECIRCULATING TRAP

mixture was cooled and the white precipitate of the disodium salt was filtered. The salt was transferred into a 400 ml drying tube (Figure 8). The tube was taken out of the dry box and brought under vacuum. The tube was gradually heated in an oil bath up to 200°C. Drying at 200° was continued until a vacuum of 0.02 mm Hg was attained. The yield of the disodium salt was 79.97 g (97.7%).

3) Polymerization by Nitro Displacement Reaction

A typical polymerization is described below. The polymerization was carried out in a dry box.

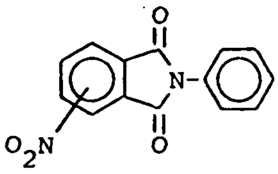
Disodium salt of 4,4'-dihydroxydiphenylsulfide (3.5020 g, 0.013355 mole) was added in portions into a mixture of 4,4'-bis(3-nitrophthalimido)diphenyl ether (7.3507 g, 0.013355 mole) and 40 ml of anhydrous N,N-dimethylacetamide at 60°C. The mixture was stirred at 60°C for 60 minutes and poured into methanol stirred in a blender. The polymer was filtered, washed with methanol and dried under vacuum. The yield of the polymer was 9.14 g. The intrinsic viscosity in chloroform was 0.37 dl/g.

The reaction conditions may be slightly modified depending on the solubility of the polymers, reactivity of monomers and nucleophilicity of bisphenolates.

4) 1,3-Bis(4-aminophenoxy)benzene

A mixture of p-chloronitrobenzene (68.71 g, 0.436 mole), anhydrous resorcinol disodium salt (32.63 g, 0.2118 mole), cuprous chloride (1 g) and 350 ml of DMF was stirred and heated at 100 ± 10°C under nitrogen for 5 hours. The reaction mixture was cooled and poured into 4 liters of water. The precipitate was isolated by filtration and recrystallized from an isopropanol-acetic acid mixture (75:1). The yield of 1,3-bis(4-nitrophenoxy)benzene was 59.72 g (80.1%). The melting point was 110-111°C. The above dinitro compound (57.5 g, 0.1632 mole), 10% Pt on carbon (2 g) and DMF (100 ml) were placed in a 500 ml Parr pressure bottle and hydrogenated at 3.3 atm. of pressure. Only 0.2 moles of hydrogen was absorbed in 8 hours. An additional 200 ml of DMF and 0.5 g of platinum oxide were added and the hydrogenation was resumed. The reaction was fast and a total of 0.83 moles of hydrogen (85% of theory) was taken up over a period of 4 hours. The reaction mixture was filtered and the filtrate was distilled under vacuum. The fraction boiling at 250-260°C/0.15 mm Hg was collected. The yield was 35.0 g (73.4%) and the melting point was 115-117°C; Lit. 114.6-115.1°.[17]

5) N-phenylnitrophthalimide (VI)



In a 5 liter, three-neck flask equipped with a Dean-Stark trap and a stirrer were placed 4-nitrophthalic anhydride (393.0 g, 2.035 moles), glacial acetic acid (3.3 liters) and cyclohexane (300 ml). To this was added aniline (198.64 g, 2.133 moles) and the resulting mixture was heated to reflux under nitrogen for 11 hours. During this time, 500 ml of azeotropic mixture were removed by the aid of the D-S

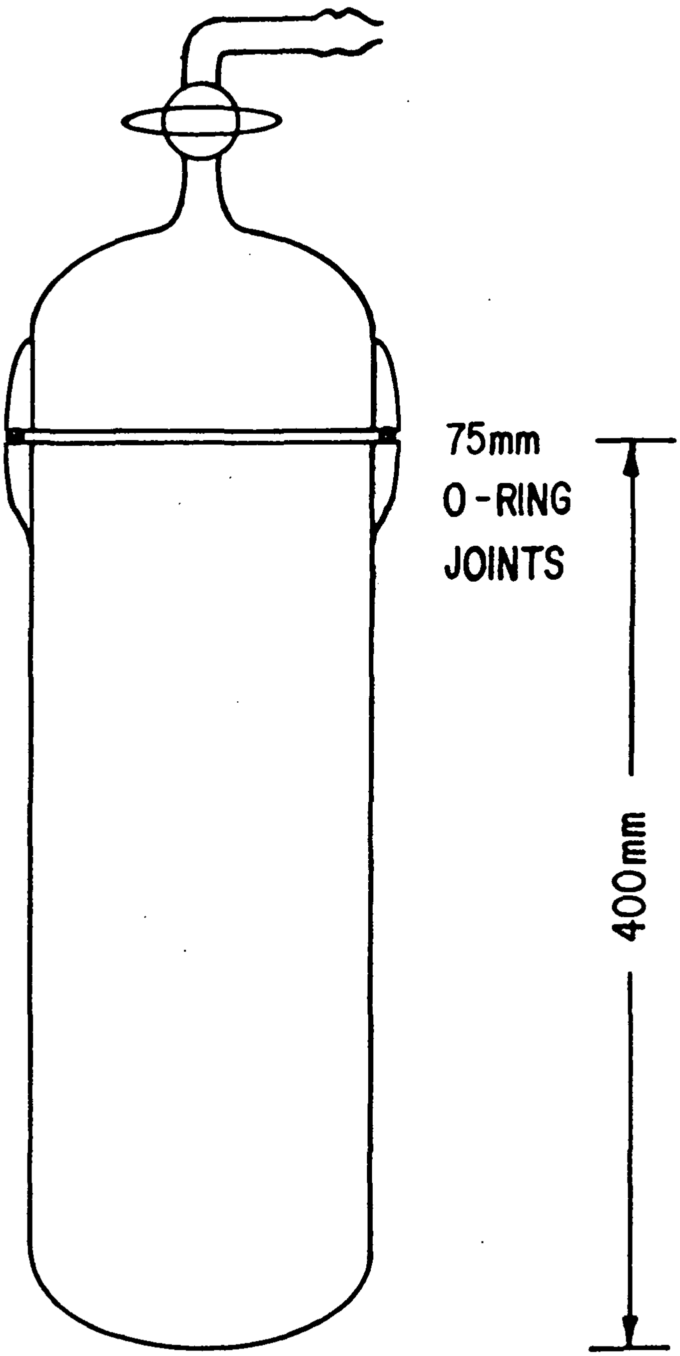


FIG. 8 DRYING TUBE

trap. Upon cooling the reaction mixture was filtered. The bright yellow crystals were washed with water and dried under vacuum. The yield was 512.6 g. The filtrate was diluted with water and the precipitate was filtered (22.7 g). The material was recrystallized from toluene to give an additional 18.5 g of pure N-phenyl-4-nitrophthalimide. Total yield was 531.1 g (97.3%). The 3-nitro isomer was prepared by the identical procedure.

6) Bis(N-phenylphthalimido)ethers (VII)

The preparation of 4,4'-bis(N-phenylphthalimid-3-oxy)diphenylsulfide is given below as a typical example.

A mixture of N-phenyl-3-nitrophthalimide (61.06 g, 0.2276 mole) and 200 ml of DMF was stirred under a nitrogen atmosphere. Anhydrous disodium salt of 4,4'-dihydroxydiphenylsulfide (29.85 g, 0.1138 mole) was added at once to the above solution. The reaction mixture was heated at 65° for one hour, during which time the initial dark brown color faded to yellow and crystalline product precipitated. The reaction mixture was cooled and added to 600 ml of water. The precipitate was filtered, washed with water, and then with methanol. The precipitate was slurried in 500 ml of boiling methanol. The slurry was heated to a boil for 10 minutes and filtered while it was hot. The yield of the bisimide was 74.52 g (99.1%). The melting point was 231-232°.

Other bisimides were prepared in a similar manner. In general, N-phenyl-4-nitrophthalimide was less reactive and a higher reaction temperature (70-80°C) was necessary. For poorly nucleophilic bisphenol salts such as salts of 4,4'-dihydroxybenzophenone and 4,4'-dihydroxydiphenylsulfone, reactions were carried out at 80-100°C.

7) Tetracarboxylic Acids

a) 4-Isomer -- 4,4'-Bis(N-phenylphthalimid-4-oxy)diphenylsulfide (70.0 g, 0.1060 mole), sodium hydroxide (34 g) and 250 ml of water were placed in a 500 ml flask equipped with a Dean-Stark trap and a stirrer. The mixture was stirred under nitrogen and heated to reflux for 20 hours during which time the aniline formed was azeotropically removed by use of the D-S trap. The reaction mixture was filtered and poured into a dilute hydrochloric acid. The white precipitate was filtered, washed with cold water and dried under vacuum at 60°C. The yield of the tetraacid was 55.59 g (96.0%).

b) 3-Isomer -- Because of steric hindrance, the 3-isomers had to be hydrolyzed at higher temperatures. 1,4-Bis(N-phenylphthalimid-3-oxy)benzene (109.52 g, 0.1982 mole), 128.5 g of 50% aqueous sodium hydroxide and 600 ml of water were placed in a 2 liter pressure reactor. The mixture was stirred and heated at 180° for 2.5 hours. The reaction mixture was cooled and extracted with ether to remove the aniline. The aqueous solution was added to dilute hydrochloric acid. The crystalline precipitate was filtered, washed with cold water and dried under vacuum. The yield of the tetraacid was 75.12 g (86.5%).

8) Bis(amide acid)s (XIV)

4,4'-Bis[2(or 3)-carboanilino-3(or 2)-carboxyphenoxy]diphenylsulfone -- 4,4'-Bis(N-phenylphthalimid-3-oxy)diphenylsulfone (63.65 g, 0.0919 mole) was added to a mixture of sodium hydroxide (11 g, 0.275 mole), tetrahydrofuran (60 ml) and water (300 ml). The mixture was stirred and heated at 40-44° for 4 hours. The reaction mixture was filtered and the filtrate was added dropwise into a mixture of 35% hydrochloric acid (30 ml) and water (130 ml). The bis(amide acid) precipitated wasfiltered, washed with water and dried under vacuum at 50°. The yield was 67.5 g.

Anal. Calcd. for $C_{40}H_{28}N_2SO_{10}$: C, 65.93; H, 3.87; N, 3.84. Found: C, 65.0; H, 4.1; N, 3.4.

Similarly, 4,4'-bis[2(or 3)-carboanilino-3(or 2)-carboxyphenoxy]diphenylsulfone was obtained in 99.6% yield.

9) Bis(ether anhydride)s (VIII), (XV)

a) From Tetraacids -- A mixture of 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether (27.00 g, 0.0509 mole) and glacial acetic acid (300 ml) was stirred and heated to reflux. Acetic anhydride (15 ml) was added and the resulting mixture was heated to reflux for about 20 minutes. After cooling, yellow crystals of bisanhydride were filtered, washed with acetic acid and dried. The yield was 24.90 g (98.9%) and the melting point was 254-255.5°C.

b) From Bis(amide acid)s -- A mixture of acetic anhydride (39 g, 0.38 mole) and glacial acetic acid (200 ml) was stirred and heated to 90°. A bis(amide acid), 4,4'-bis(2-carboanilino-3-carboxyphenoxy)diphenylsulfone (65.50 g, 0.0899 mole), was added to the above solution. The resulting mixture was heated to a boil for ca. 10 minutes during which time crystals of the dianhydride precipitated. The precipitate was filtered, washed with acetic acid and dried. The yield was 28.21 g (57.9%). The melting point was 230.5-231.5°C.

Anal. Calcd. for $C_{28}H_{14}SO_{10}$: C, 61.99; H, 2.60. Found: C, 60.9; H, 2.7.

Similarly, 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride was obtained in 59.0% yield from the corresponding bis(amide acid).

10) One-Step Solution Polymerization

a) 4,4'-Bis(2,3-dicarboxyphenoxy)diphenyl Ether Dianhydride and 4,4'-Diaminophenyl Ether -- In a 100 ml, three-neck flask fitted with a Dean-Stark condenser were placed 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether (4.4495 g, 9.000 mmoles), 4,4'-diaminodiphenyl ether (1.8021 g, 9.000 mmoles), m-cresol (32 ml) and toluene (8 ml). The mixture was magnetically stirred under nitrogen and heated to reflux. The amount of the refluxing toluene was adjusted in such a way that the temperature of the solution was maintained at 160°. The heating was continued for one hour during which time most of the water was removed. The D-S condenser was then replaced with a recirculating trap (Figure 7) filled with dry Molecular Sieve 4A. The reaction mixture was further heated to reflux at 160° for an additional 2.5 hours and diluted with approximately 30 ml of m-cresol. The resulting solution was cooled and poured into methanol with stirring in a blender. The polymer precipitate was filtered, washed with methanol and dried under vacuum at 100°C. The yield of the polymer was 6.03 g. The intrinsic viscosity was 1.92 dl/g in m-cresol.

Anal. Calcd. for $C_{40}H_{22}N_2O_8$: C, 72.94; H, 3.37; N, 4.25. Found: C, 73.8; H, 3.6; N, 4.1.

b) 4,4'-Bis(3,4-dicarboxyphenoxy)diphenylsulfone Dianhydride and 1,3-Bis(4-aminophenoxy)benzene -- A mixture of 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfone dianhydride (3.2252 g, 5.9455 mmoles), 1,3-bis(4-aminophenoxy)benzene (1.7380 g, 5.9455 mmoles), m-cresol (23 ml) and toluene (7 ml) was heated to reflux in the same manner as experiment (a). The heating was continued for 1.75 hours and the Dean-Stark condenser was replaced with a recirculating trap filled with Molecular Sieve 4A. The reaction mixture was further heated to reflux at 160° for an additional 4 hours. The resulting viscous solution was diluted with approximately 25 ml of m-cresol and the polymer was precipitated in methanol. The yield of the polymer was 4.52 g. The intrinsic viscosity was 0.88 dl/g in m-cresol.

Anal. Calcd. for $C_{46}H_{26}N_2SO_{10}$: C, 69.17; H, 3.28; N, 3.51. Found: C, 69.4; H. 3.4; N, 3.3.

c) 1,4-Bis(2,3-dicarboxyphenoxy)benzene Dianhydride and m-Phenylenediamine -- 1,4-Bis(2,3-dicarboxyphenoxy)benzene (5.8358 g, 14.506 mmoles), m-phenylenediamine (1.5687 g, 14.506 mmoles), m-cresol (35 ml) and toluene (5 ml) were placed in a flask set up exactly the same as in experiment (a). The mixture was heated to reflux at 160° for 0.5 hour, during which time most of the water was removed. The Dean-Stark condenser was replaced by a recirculating trap filled with Molecular Sieve 4A. The reaction mixture was further heated to reflux for an additional 4 hours at 160° and cooled. The resulting viscous solution was diluted with 20 ml of m-cresol and the solution was poured into methanol stirred in a blender. The white polymer precipitate was filtered, washed with hot methanol and dried at 150° under vacuum. The yield of the polymer was 6.62 g. The intrinsic viscosity was 0.45 dl/g in m-cresol.

Anal. Calcd. for $C_{28}H_{14}N_2O_6$: C, 70.88; H, 2.97; N, 5.91. Found: C, 70.8; H, 3.0; N, 5.8.

d) 1,4-Bis(3,4-dicarboxyphenoxy)diphenyl Sulfide Dianhydride and 1,3-Bis(4-aminophenoxy)benzene with 4% Phthalic Anhydride -- A mixture of 1,4-bis(3,4-dicarboxyphenoxy)diphenyl sulfide (2.985 g, 5.848 mmoles), 1,3-bis(4-aminophenoxy)benzene (1.744 g, 5.967 mmoles), phthalic anhydride (0.0354 g, 0.239 mmoles), m-cresol (24 ml) and toluene (8 ml) was stirred and heated to reflux. The reaction was carried out in the same manner as in the previous experiments at 160° for 3.25 hours. The reaction mixture was cooled and diluted with about 20 ml of a 7:3 mixture of phenol and toluene. The solution was poured into methanol. The polymer precipitate was filtered, washed and dried. The yield was 4.26 g (93.0%). The intrinsic viscosity was 0.60 dl/g in m-cresol. The glass transition temperature was 178° (DSC).

11) Reaction of o-Phenylenediamine and Phthalic Anhydride

Phthalic anhydride was purified by sublimation. o-Phenylenediamine was distilled under vacuum. m-Cresol was dehydrated with Molecular Sieve (4Å) and distilled under vacuum. Other solvents were dried over calcium hydride. Phthalic anhydride and o-phenylenediamine were added to a particular solvent mixture under nitrogen at room temperature and then heated to reflux. The water formed was continuously removed by use of a recirculating trap filled with Molecular Sieve 4A. Analysis was carried out by gas chromatography using o-terphenyl as an internal standard.

12) Preparation of Polyetherpyrrones (XVI)

Two typical examples are given below.

1) Phthalic anhydride (0.0452 g, 0.305 mmoles) and 4,4'-bis(3,4-dicarboxyphenoxy)-diphenyl sulfide dianhydride (3.040 g, 5.955 mmoles) were dissolved in 40 ml of m-cresol. The solution was added dropwise at 35-40°C to a mixture of 3,3',4,4'-tetraaminobenzophenone (1.480 g, 6.108 mmoles) and 20 ml of m-cresol over a period of 45 minutes. The resulting homogeneous solution was heated at 90° and 30 ml of benzene was added dropwise. The reaction mixture was then allowed to reflux at 105-115°C for one hour during which time the water was continuously removed by recirculating the refluxing solvent through a trap filled with Molecular Sieve. Part of the benzene was removed and the reaction mixture was further heated to reflux at 140° for 0.5 hour. The benzene was distilled off and about 5 ml of toluene was added. The solvent was further distilled until the solution temperature reached 185°C. The solution was refluxed at 185°C for 2 hours and then poured into methanol. The yellow precipitate of polyetherpyrrone was filtered, washed with methanol and dried at 200° under vacuum. The yield of the polymer was 3.87 g (93.8%). The intrinsic viscosity was 0.43 dl/g in m-cresol. The glass transition temperature was 264°C as measured by DSC.

Anal. Calc. for $C_{1628}H_{794}N_{160}O_{195}S_{39}$: C, 72.52; H, 2.94; N, 8.31. Found: C, 71.9; H, 3.2; N, 8.4.

2) Finely pulverized 4,4'-Bis(2,3-dicarboxyphenoxy)benzene (2.573 g, 6.396 mmoles) was dispersed in 30 ml of m-cresol solution containing phthalic anhydride (0.0321 g, 0.217 mmole). The dispersion was added in portions to a mixture of 3,3',4,4'-tetraaminobenzophenone (1.576g, 6.505 mmoles) and 30 ml of m-cresol. The addition took one hour, during which time the reaction temperature was maintained at 35-40°C. The last trace of the dispersion was washed in with an additional 10 ml of m-cresol. The resulting solution was further stirred at room temperature for one hour. It was then heated to 110° and about 35 ml of benzene was added dropwise. The reaction mixture was heated to reflux at 115°C for one hour, during which time the water was continuously removed by recirculating the refluxing solvent through a trap filled with Molecular Sieve. The benzene was distilled off and about 5 ml of toluene was added. The toluene was partially distilled off until the pot temperature rose to 185°C. The reaction mixture was then heated to reflux at 180-185°C for 2 hours. The polymer was precipitated in methanol and dried at 240°C under vacuum. The yield was 3.64 g (98.0%). The intrinsic viscosity in m-cresol was 0.65 dl/g. The glass transition temperature was 317°C.

Anal. Calc. for $C_{2094}H_{958}N_{240}O_{298}$: C, 73.44; H, 2.82; N, 9.82. Found: C, 71.7; H, 3.4; N, 9.4.

REFERENCES

1. P. Darmory and M. Debenedetto, French Patent 2,173,923.
2. D. R. Heath and J. G. Wirth, US Patent 3,763,210 (1973); Ibid., 3,787,375 (1974).
3. D. R. Heath and T. Takekoshi, US Patent 3,879,428 (1975).
4. D. R. Heath and J. G. Wirth, US Patent 3,838,079 (1974).
5. J. G. Wirth and D. R. Heath, US Patent 3,852,244 (1974).
6. C. K. Sauers et al, J. Org. Chem., 36, 1941 (1971); Ibid, J. Am. Chem. Soc., 94, 8156 (1972).
7. J. I. Jones, F. W. Ochinski and F. A. Rackley, Chem. Ind. (London), 1962, 1686.
8. G. M. Bower and L. W. Frost, J. Polymer Sci., A1(10), 3135 (1963).
9. L. W. Frost and I. Kesse, J. Appl. Polymer Sci., 8(3), 1039 (1964).
10. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, J. Polymer Sci., A3(4), 1373 (1965).
11. W. J. Farrissey, J. S. Rose and P. S. Carleton, Polymer Preprints, 9, No. 2, 1581 (1968).
12. R. A. Meyers, J. Polymer Sci., A1(7), 2757 (1969).
13. J. Sabeth, French Patent 1,498,015.
14. T. Takekoshi and J. E. Kochanowski, US Patent 3,803,085 (1974).
15. T. Takekoshi and J. E. Kochanowski, US Patent 3,420,697 (1975).
16. A. R. Schultz and B. M. Gendron, J. Applied Polymer Sci., 16, 461 (1972).
17. A. L. Williams, R. E. Kinney and R. F. Bridger, J. Org. Chem., 32, 2501 (1967).
18. V. L. Bell and G. F. Pezdirtz, J. Polymer Sci., B-3, 977 (1965).
19. F. Dawns and C. S. Marvel, J. Polymer Sci., A-3, 3549 (1965).
20. F. E. Arnold and R. L. Van Deusen, J. Appl. Polymer Sci., 15, 2035 (1971)
21. J. G. Colson, R. H. Michel and R. M. Paufler, J. Polymer Sci., A-1, 4, 59 (1966).
22. R. L. Van Deusen, J. Polymer Sci., B-4, 211 (1966).

23. V. L. Bell and R. A. Jewell, J. Polymer Sci., A-1, 5, 3043 (1967).

24. B. I. Liogn'kii, A. A. Berlin, G. M. Shamraev, P. P. Misevichyas, and A. N. Mochyulis, Trudy Akad. Nauk Lit. SSR (1971).

25. A. A. Berlin, B. I. Liogn'kii, G. M. Shamraev and G. V. Belova, Izv. Akad. Nauk USSR, Ser. Khim., 945 (1966).

26. W. E. Gibbs, J. Macromol. Sci., Chem., A2, 1291 (1968).

27. A. A. Berlin, B. I. Liogn'kii, G. M. Shamraev and G. V. Belova, Vyskomol. Soed., 9A, 1936 (1967).

28. N. J. Johnston, J. Polymer Sci., A-1, 10, 2727 (1972).

29. H. Vogel and C. S. Marvel, J. Polymer Sci., A-1, 1531 (1963).

30. A. Bistizycki and A. Lecco, Helv. Chim. Acta, 4, 425 (1921).

31 H. Lieb, Monatsh. Chem., 39, 873 (1918).

32. P. R. Young, J. Heterocyclic Chem., 9, 371 (1972).

STUDY OF IMPROVED RESINS FOR ADVANCED SUPERSONIC TECHNOLOGY COMPOSITES

Part II. Curing Chemistry of Aromatic Polymers and Composite Studies

W. B. Hillig, G. A. Mellinger, T. Takekoshi (Principal Investigators),
R. W. Bulson, J. W. Nehrich and M. J. Webber

I. INTRODUCTION

Although great numbers of thermally stable polymers have been investigated in recent years, their poor process characteristics, particularly flow properties, hampered their practical applications to the area of high performance fiber-reinforced composite systems. In such applications, the more tractable low molecular weight "prepolymers" could be used provided that the prepolymers could be "cured" to produce a three-dimensionally crosslinked infinite network structure. However, such crosslinking reactions must meet the following conditions:

1) The chemical structure of crosslink moieties must be at least as thermally stable as the prepolymer chain itself.

2) The crosslinking reaction should be very slow below processing temperature and should not take place at ambient temperature.

3) The rate of the crosslinking reaction should be reasonably fast around the processing temperature.

4) The crosslinking reaction should not form volatile byproducts.

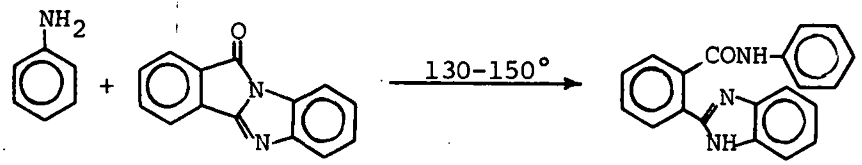
5) If a byproduct is formed by the crosslinking reaction, it should be non-volatile and thermally stable.

Commonly used crosslinking reactions based on olefinic unsaturation, epoxide, isocyanate, etc. are not suitable according to the above criteria. It has been known that aromatic nitriles cyclotrimerize on heating to form sym-triazines. The reaction is generally very slow even at 300°C. It can be catalyzed in the presence of Friedel-Crafts-type catalysts or certain organometallic compounds. Some degree of success was reported by Marvel et al[1] on the crosslinking of polysulfone ether resins containing nitrile groups. However, the curing rate was slow and a high level of catalyst concentration was necessary. Possible undesirable effect of the residual catalyst in the cured resin is an unanswered question. In addition, it is inherently difficult to achieve a high crosslink density by trimerization reactions. As the curing reaction proceeds, the rate may slow down drastically. A high degree of viscosity effect on the reaction rate is expected since three reacting nitrile groups are attached to constrained polymer chains.

We have investigated the chemistry of several crosslinking reactions based on different principles, and subsequently applied some of the reactions to glass and carbon fiber-reinforced composite systems.

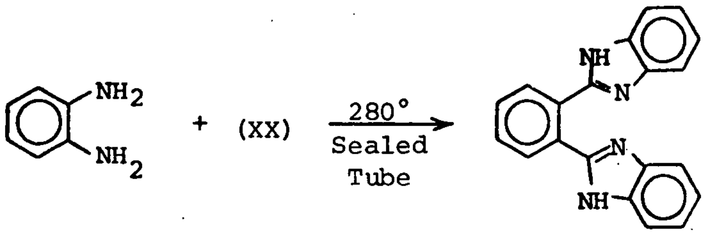
II. POLYETHERIMIDE-TETRAAMINE CURING SYSTEM

During the course of the study on pyrrone model reaction (Part I; Section II), it was found that pyrrone (XX) reacted with aniline and formed o-benzimidazobenzanilide (XXVII). It was also found that pyrrone (XX) reacted with o-phenylenediamine to form bisbenzimidazole (XXIII) when heated in a sealed tube. These reactions indicate that low molecular weight polymers containing more than two pyrrone groups could be cured by reacting with diamines or tetraamines. Based on this principle, various low molecular weight polyetherpyrrones and pyrroneimide copolymers were prepared as shown in Table XVI and XVII.



(XX) (XXVII)

(13)



(XXIII)

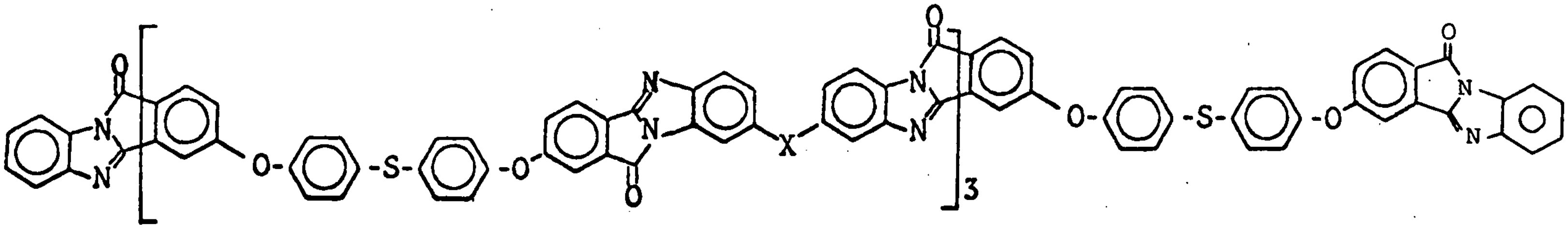
(14)

Several curing formulations were made by dissolving these pyrrone-containing oligomers with various aromatic diamines and tetraamines. Preparation of composites from these formulations were attempted. However, uniform and consistent composite samples could not be obtained. The resin seemed to cure prematurely at an initial stage of composite preparation resulting in poor flow of the resin and significant solvent entrapment. Further development of the pyrrone addition system was abandoned.

Interestingly, we have found that o-benzimidazobenzanilide (XXVII) is also formed by the reaction of N-phenylphthalimide and o-phenylenediamine as shown in Equation 15. However, the reactivities of the two systems are significantly different. Reaction (13) proceeds at 130-150°C, while reaction

TABLE XVI

Oligoetherpyrrones



Exp.* Code	X	Tg (°C)	Analysis (calc.) C	H	N	S
25-232	nil	217	73.3 (73.55	3.4 3.16	8.2 8.58	4.7 4.91)
25-231	-O-	187	71.9 (72.22	3.5 3.11	7.8 8.42	4.5 4.82)
25-233	$-\underset{\underset{O}{\|}}{C}-$	206	71.2 (72.59	3.3 3.07	7.6 8.31	5.1 4.76)
25-228	$-SO_2-$	225	69.4 (68.51	3.3 2.95	7.8 7.99	8.2 8.00)

* A 2:3:4 molar ratio of o-phenylenediamine, tetraamine and 4,4'-bis(3,4-dicarboxyphenoxy)-diphenyl sulfide dianhydride was employed.

TABLE XVII

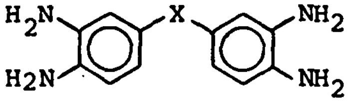
Preparation of Pyrrone-Imide Copolymers

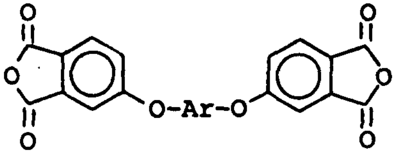
Tetraamine[a] -X-[c]	Diamines[a,b]	Bis(ether anhydride)[a] -Ar-[d]	Yield (%)	Formula	Analysis (%) C	H	N
$-SO_2-$ (1)	ODA (2) o-PDA (2)	4,4-Diphenylsulfide (4)	99.2	$C_{160}H_{86}N_{12}S_5O_{24}$	70.6 (70.6	3.5 3.2	5.8 6.2)
$-SO_2-$ (2)	ODA (1) o-PDA (2)	"	100	$C_{160}H_{84}N_{14}S_6O_{29}$	68.6 (69.6	3.4 3.1	6.7 7.1)
-O- (2)	m-PDA (1) o-PDA (2)	"	99.7	$C_{154}H_{80}N_{14}S_4O_{20}$	70.7 (71.8	3.6 3.1	8.0 7.6)

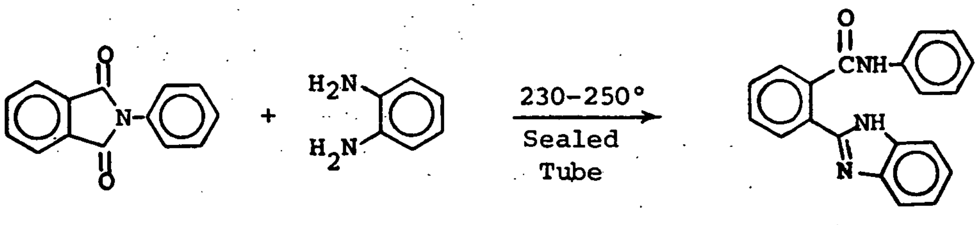
(calc. value) given in parentheses under Analysis.

(a) Numbers in parentheses denote molar ratio.

(b) ODA = Oxydianiline; o-PDA = o-Phenylenediamine; m-PDA = m-Phenylenediamine.

(c) Substituent in 

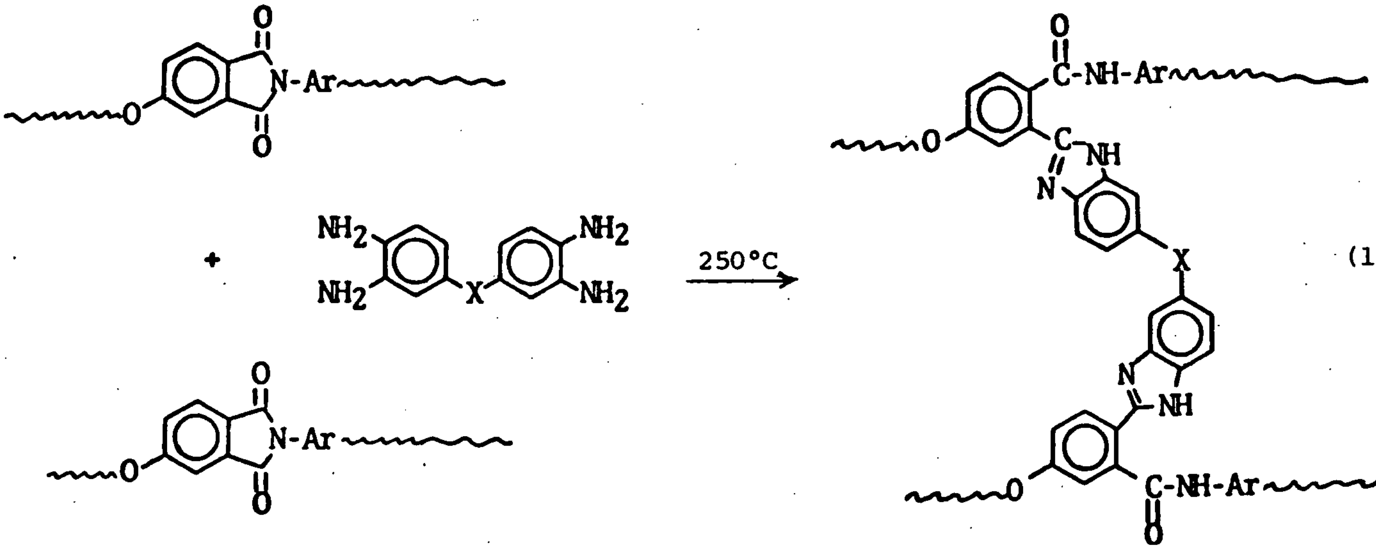
(d) Substituent in 



(XXVII)

(15)

(15) occurs at 230-250°C. Based on reaction (15), it was anticipated that polyimides should be crosslinked by heating with tetraamines as illustrated in Equation 16. Because the reaction proceeds only above 230-250°C, such a curing system was expected to have a reasonably wide processing window.

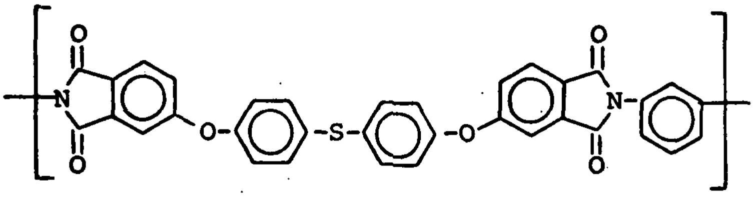


(16)

Polyetherimide ([η] = 0.28) prepared from m-phenylenediamine and 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride was formulated with tetraaminobenzophenone in m-cresol as shown in Table XVIII.

TABLE XVIII

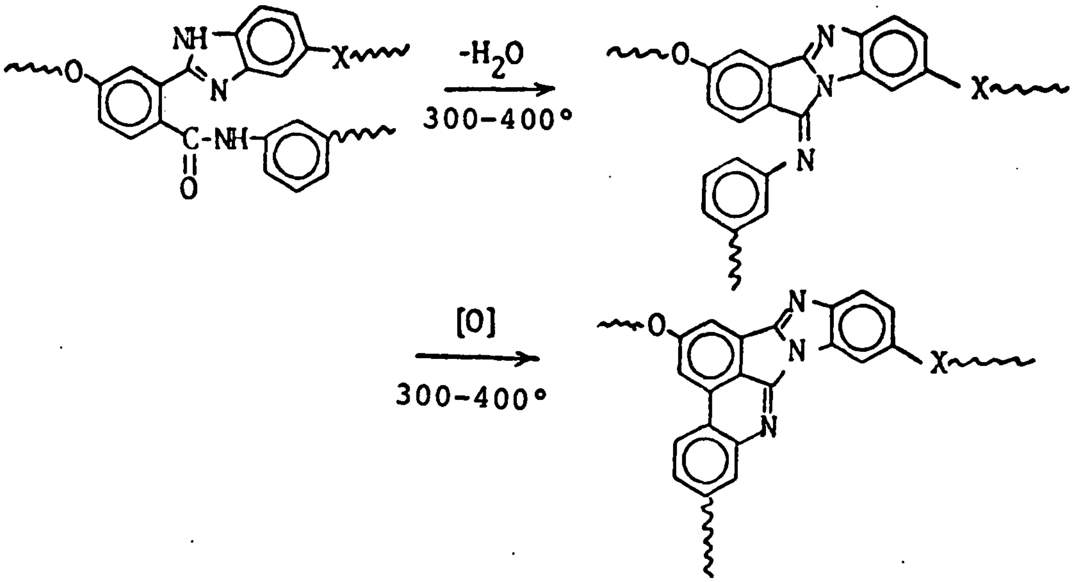
Formulation of Polyetherimide-Tetraamine Curing Resin #25-293

 [η] = 0.28 (*m*-cresol)	2.00 g
3,3',4,4'-Tetraaminobenzophenone	0.200 g
m-Cresol	7.8 g
TOTAL SOLID CONTENT	22.0 %

Glass Fiber Composites

Mini-bars of unidirectional S-glass fiber composites were prepared using Formulation #25-293 under various conditions. Because the resin cured at 230-260° as predicted by the model reaction, process characteristics were excellent and good reproducible results were obtained. A typical composite had a dimension of 0.05" x 0.08" x 1.5" and a fiber content of 45-60%. Flexural modulus and strength were measured after samples were post-cured at 300°C in air for 16 hours. The results are shown in Figure 9. The values are normalized at 60% fiber volume. Both modulus and strength dropped rapidly above 200°C indicating an under-cured state. However, it was found that the result could be markedly improved by increasing the post-cure temperature. Flexural modulus and strength obtained after 16 hours of post-cure at 400°C in air are shown in Figure 10. The values are also normalized at 60% fiber volume. Strengths at 400°C of over 100,000 psi are considered excellent. The improvement may be attributed to further cyclocondensations postulated below as well as cross-linking by air oxidation.

II



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(18)

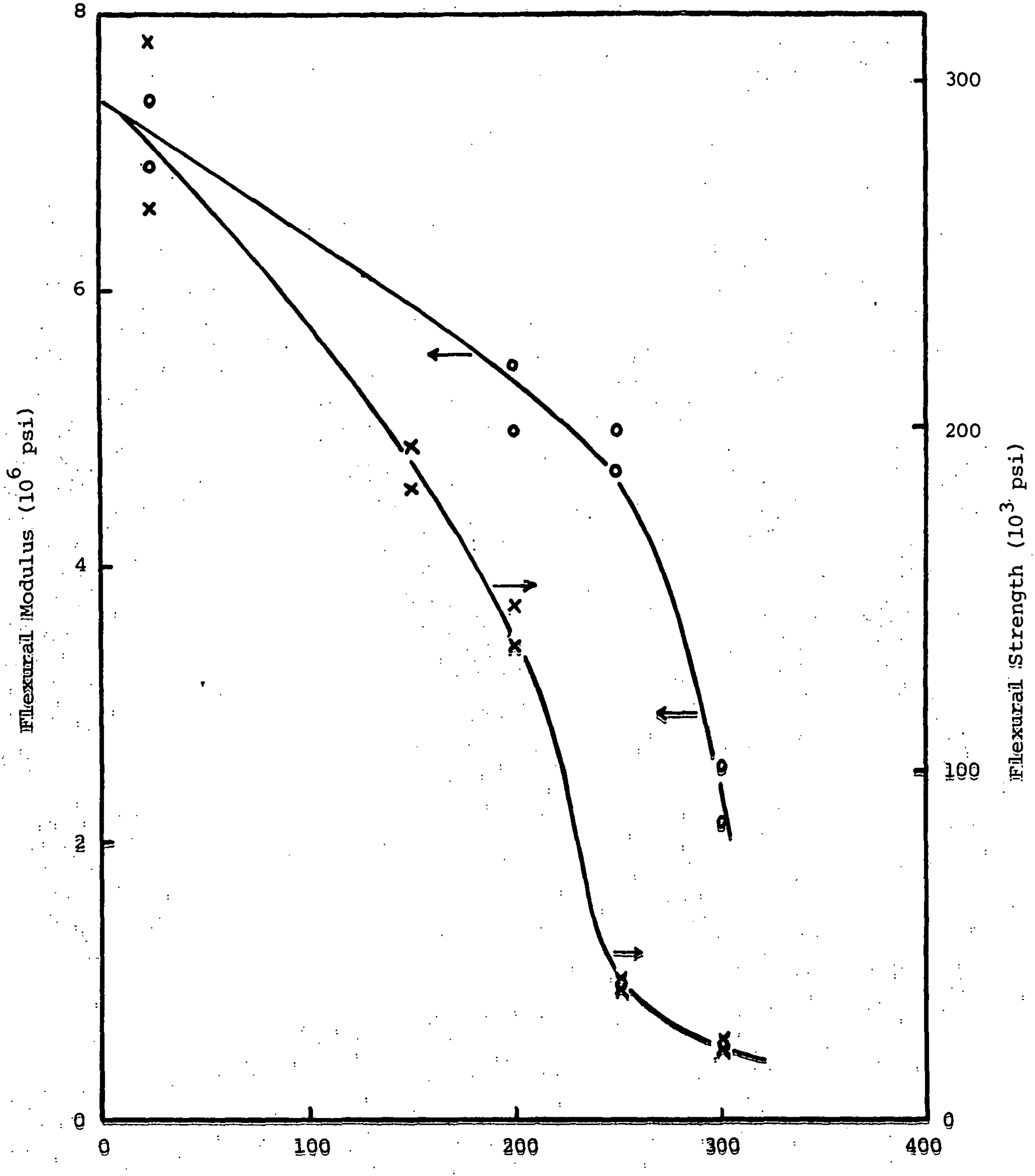
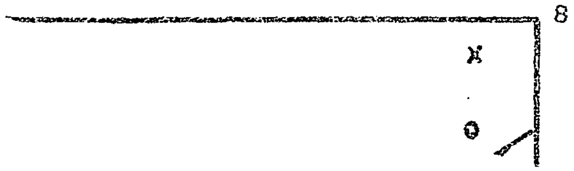


Figure 9. Mechanical Properties of S-Glass Fiber Composites Prepared from Resin Formulation #25-293 (Table XVIII) and Post-Cured at 300°C for 16 hours. The values are normalized to 60 volume % fiber content.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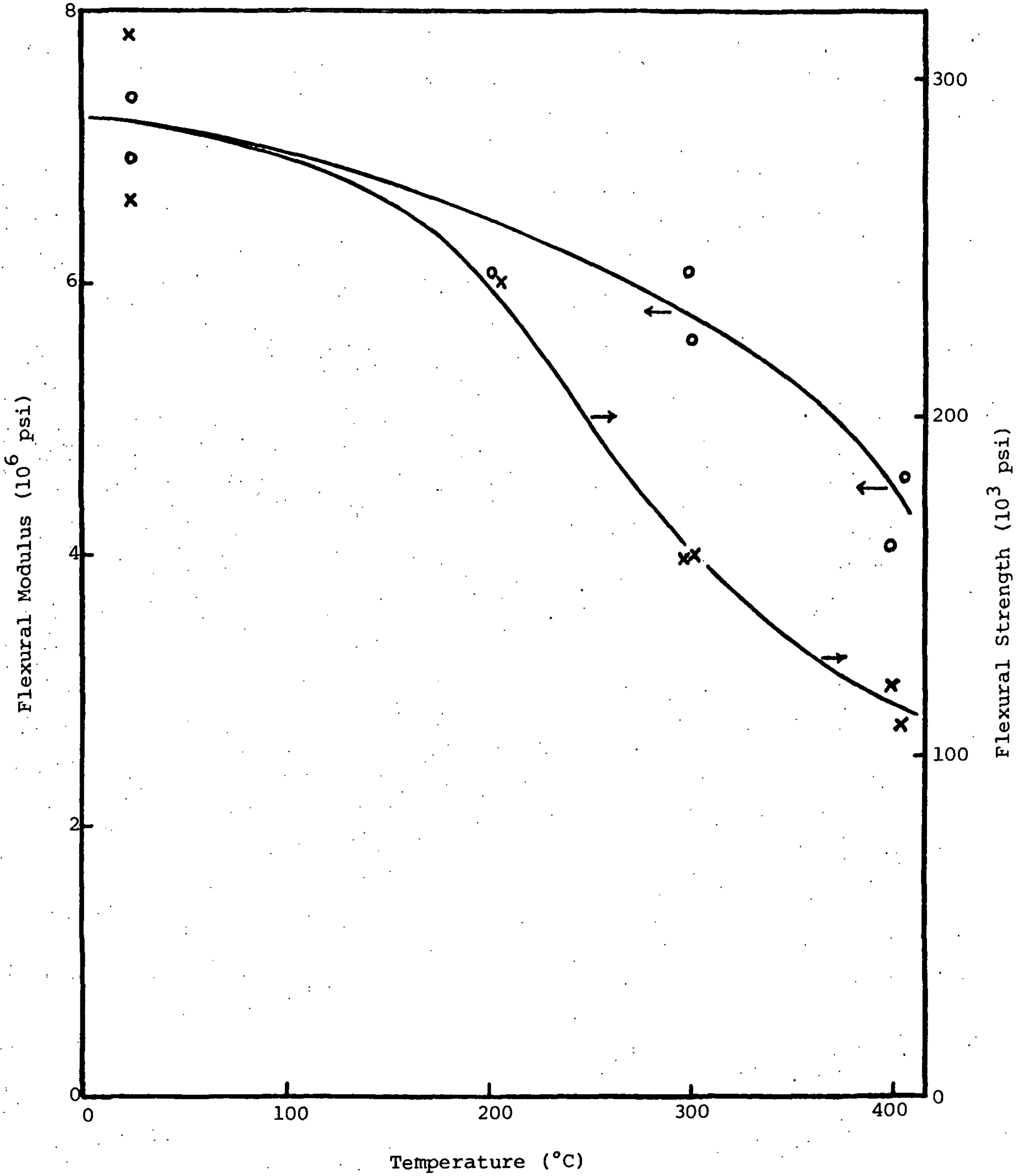


Figure 10. Mechanical Properties of S-Glass Fiber Composites Prepared from Resin Formulation #25-293 (Table SVIII) and Post-Cured at 400°C for 16 hours.
The values are normalized to 60 volume % fiber content.

Carbon Fiber Composites

Polyetherimide-tetraamine formulation #25-293 was found to be too viscous to apply to carbon fiber tows, which were finer and more brittle than glass fiber. The molecular weight of the polyetherimide used in this formulation is apparently too high. The resin did not flow adequately during the molding process.

In order to improve the flow properties of the resin, polyetherimide of a lower molecular weight (#25-304) was prepared as shown in Table XIX from 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride and m-phenylenediamine. o-Phenylenediamine was used as a capping agent which formed pyrrone end groups. Curing resin formulation #25-307 was prepared from this oligoetherimide and tetraaminobenzophenone as shown in Table XIX. Small composite samples were made from #25-307 resin as shown in Table XX. While the process characteristics of this resin were better than #25-293, the resin exhibited severe weight loss at high post-cure temperatures.

Another polyetherimide-tetraamine curing resin (#25-330) was prepared from slightly modified oligomer (#25-328) as shown in Table XXI. It contained a lower concentration of curing agent.

Small composite samples were prepared from #25-330 resin and post-cured under various conditions. Although #25-330 resin showed good processability. it tended to give high void content in the final composite. Accordingly, the mechanical properties at 300°C were not satisfactory (Table XXII). Further study on modification of the resin formulation and process conditions will be needed in order to obtain satisfactory results from these resin systems.

TABLE XIX

Composition of Formulation 25-307, Pyrrone-capped PEI and Tetraamine

	Composition	Molar Ratio	
Base Resin 25-304			
	4-SDA*	5	
	m-Phenylenediamine	4	
	o-Phenylenediamine	2	3.00 g
Curing Agent			
	Tetraaminobenzophenone		0.500 g
Solvent			
	m-Cresol		8.00 g
Solid Content			30.4%

*4,4'-Bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride

TABLE XX

Properties of Carbon Fiber Composites from Formulation 25-307

Type of Fiber[a]	Molding Conditions Under Pressure (°C/hr)	Post Cure (°C/hr)	Fiber Vol %	Void Vol %	Mechanical Properties at 300°C in air: Flex. Mod. 10^6 psi	Mechanical Properties at 300°C in air: Flex. Str. 10^3 psi
M-II	235/1	400/16	52	7.4	7.2	80.7
M-II	235/1	400/16	Resin burned out		-	-

M-II = Modmor® Type II Graphite Fiber

TABLE XXI

Composition of Formulation 25-330

	Composition	Molar Ratio	
Base Resin 25-328			
	4-SDA*	5	
	m-Phenylenediamine	4	
	o-Phenylenediamine	1	15.00 g
Curing Agent			
	Tetraaminobenzophenone		1.500 g
Solvent			
	m-Cresol		38.5 g
Solid Content			30.0%

*4,4'-Bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride

TABLE XXII

Properties of Carbon Fiber Composites from Formulation 25-330

					Mechanical Properties at 300°C in air	
Type of Fiber[a]	Molding Conditions Under Pressure (°C/hr)	Post Cure[b] (°C/hr)	Fiber Vol %	Void Vol %	Flex. Mod. 10^6 psi	Flex. Str. 10^3 psi
M-I	235/1	225/1.5-350/14	59	6.0	6.5	50.0
AU	260/1	300/1(N_2)-350/15	50	27.4	3.8	36.6
AU	260/1	300/1(N_2)-375/15(N_2)	42	31.4	4.3	53.5
AU	260/1	300/1(N_2)-400/15(N_2)	53	20.4	5.2	45.9
AU	260/1	300/1-400/16	57	19.1	7.1	71.8
AU	260/1	300/1-400/15(N_2)	46	27.0	6.6	59.0

(a) M-I = Modmor® high modulus carbon fiber, Type I, Grade C, #G143.

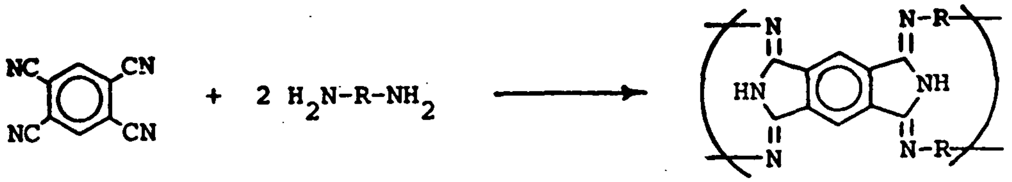
AU = Hercules AU untreated carbon fiber.

(b) All samples were post-cured under atmospheric pressure in air unless otherwise indicated.

III. POLYMERS CONTAINING PHTHALONITRILE GROUPS

Phthalonitrile-Terminated Polyetherimides and Diamines

Recent literature[2-5] has indicated that 1,2-dicyano compounds such as succinonitrile and phthalonitrile derivatives undergo cyclopolymerization to form thermally stable resins:



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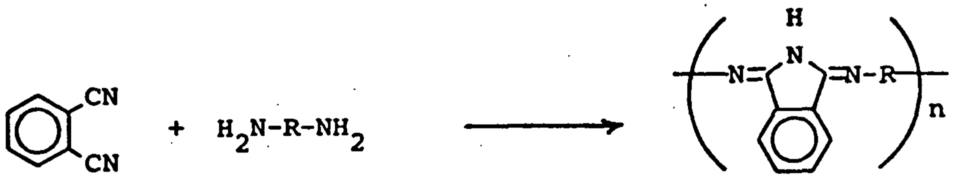

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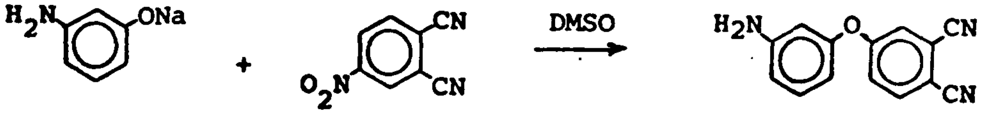
(21)

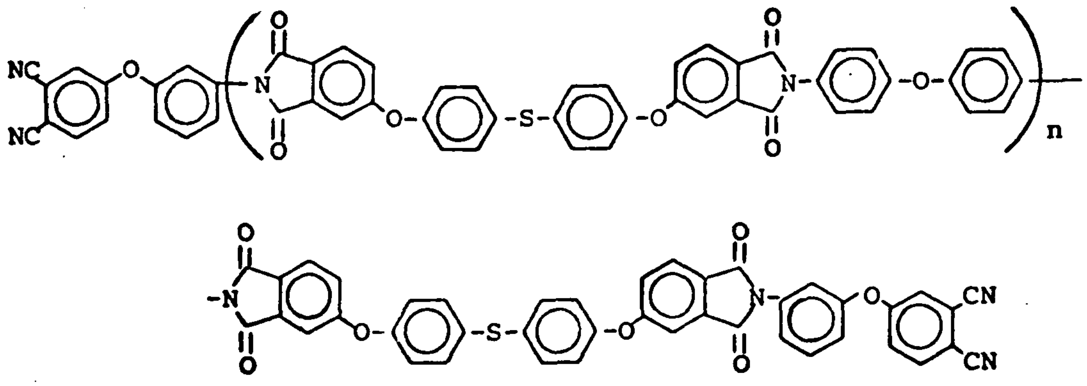
In order to introduce phthalonitrile groups to polyetherimide chains, 4-(3-aminophenoxy)phthalonitrile (XXVII) was prepared according to the following scheme:



(22)

(XXVIII)

Using (XXVIII) as a chain stopper, low molecular weight polyetherimides of the following structure (XXIX) were prepared in m-cresol by the same polymerization method described in Part I. Prepolymer (XXIX, n = 4) was designated



(XXIX)

as PEI-5CN resin. The resin was dissolved in m-cresol to form approximately 30% solutions. One molar equivalent of diamine or 2/3 molar equivalent of melamine per mole of PEI-5CN resin was added to the above resin solutions. The compositions of the resulting PEI-5CN resin formulations are listed in Table XXIII. The solutions had an adequate fluidity despite relatively high solid contents.

TABLE XXIII

Formulation of PEI-5CN Resin Solutions

Exp. Code	115-A	115-B	115-C	115-D
PEI-5CN Prepolymer (wt. %)	32.5	31.3	32.0	31.5
Amines	None	DAB[a]	Melamine	ODA[b]
Conc. (wt. %)	--	3.65	1.51	3.45
m-Cresol (wt. %)	67.5	65.0	66.5	65.1
Total Solid (wt. %)	32.5	35.0	33.5	34.9

a) 3,3-Diaminobenzophenone

b) 4,4'-Diaminodiphenyl Ether

A few drops of each PEI-5CN resin solution were applied on aluminum foil and heated at 280° in air. All resins except 115-A were cured within 2-3 hours to a rubbery gum. The cured resins were insoluble but seemed to be under-cured.

Formulation 115-C was subsequently scaled up to obtain 46.3 g of a m-cresol solution (32.8% solid). Carbon fiber composites were made from the solution and preliminary tests were performed as shown in Table XXIV. The results indicated that more efficient curing and higher crosslink density are required for this system.

TABLE XXIV

Carbon Fiber Composites from PEI-5CN Resin Cured with Melamine

Composition (%)	Curing Conditions (°C)	Post Baking (°C)	Test Temperature (°C)	Flexural Strength (psi)	Flexural Modulus (psi)
Fiber* 36.0 Resin 63.3	285 1 hr	None	25	117,000	8.58×10^6
Fiber* 45.5 Resin 56.7	285 1 hr	350 4 hrs	215	65,000	4.8×10^6

* Morganite II carbon fiber

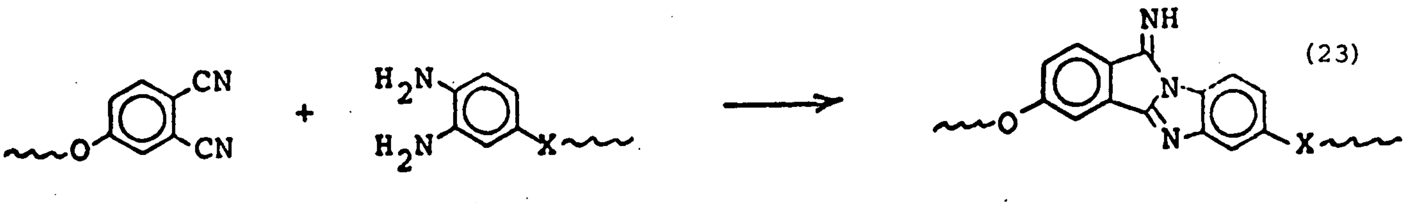
Phthalonitrile-Terminated Polyetherimides and Tetraamines

A. Preliminary Study

It was found that a quantitative amount of o-phenylene-bisbenzimidazole was formed when a 1:2 molar mixture of phthalonitrile and o-phenylenediamine was heated at 250°C. When larger amounts of phthalonitrile were used over the above ratio, the excess phthalonitrile was left unreacted except for a minor part which was converted to a blue pigment, possibly phthalocyanine. A plausible reaction mechanism is illustrated in Figure 11.

Based on the above model reaction, phthalonitrile-terminated oligomers (XXX) are expected to form crosslinked network on heating with proper tetraamine, as illustrated below.

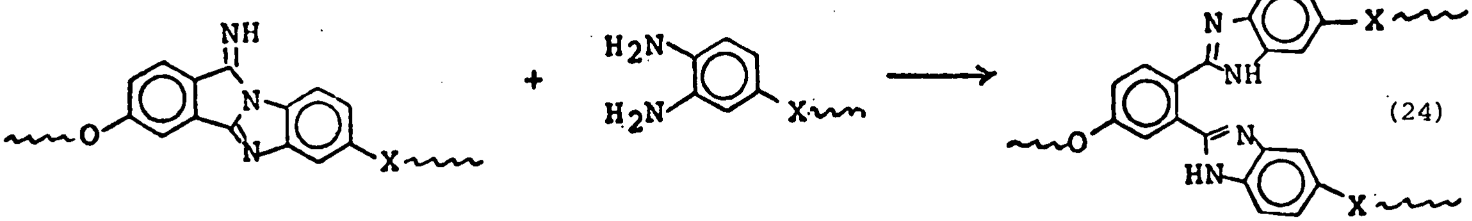
a) Chain Extension



(23)

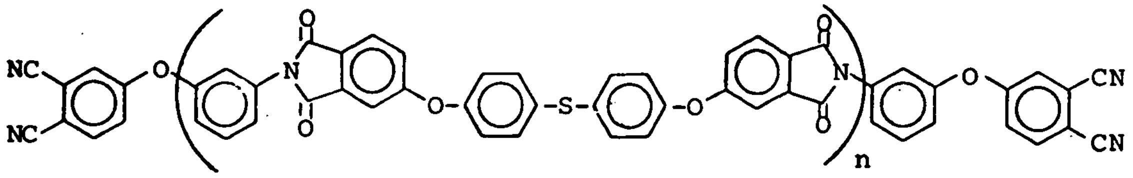
(XXX) (XXXI)

b) Crosslinking



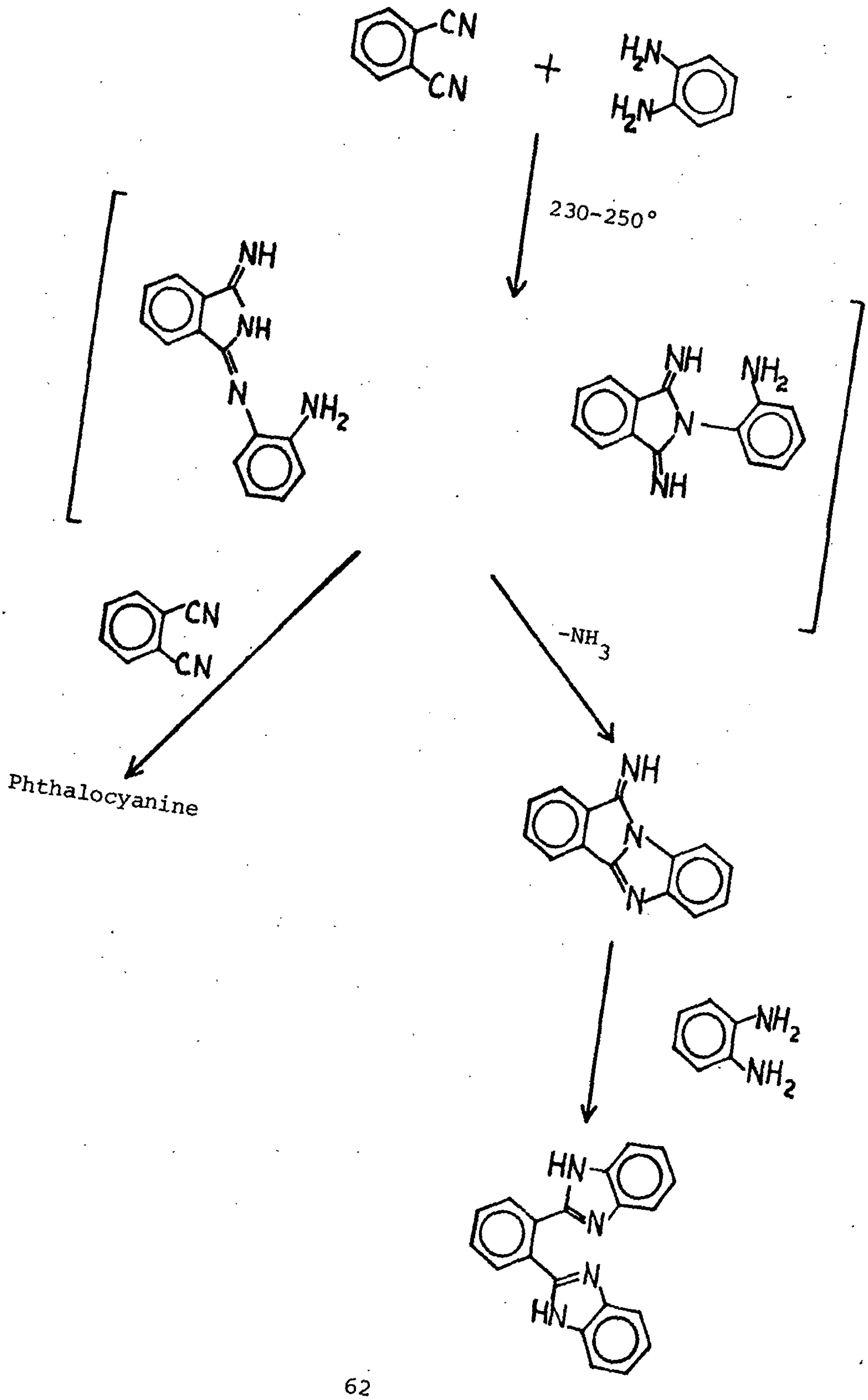
(24)

Oligoetherimide containing phthalonitrile end groups (XXXII) was prepared from a 3:2:4 molar mixture of m-phenylenediamine, 4-(3-aminophenoxy) phthalonitrile and 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride.



(XXXII) $\bar{n} = 4$

Figure 11. Reaction of Phthalonitrile and *o*-Phenylenediamine



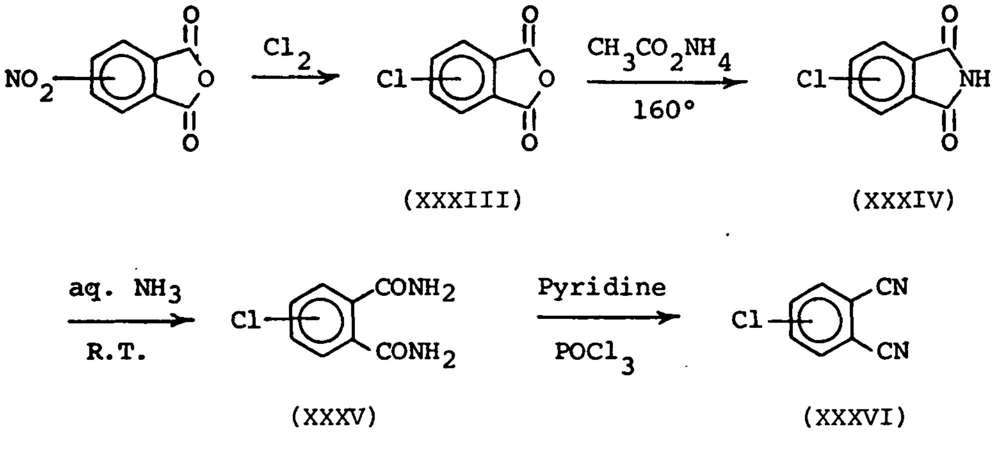
Formulations containing a 1:2 molar ratio of oligoetherimide (XXXII) and 3,3',4,4'-tetraaminobenzophenone were prepared in m-cresol. The solution was spread on a glass plate, and the solvent was evaporated to leave a yellow liquid. It was then gradually heated from 120°C to 320°C over a period of 50 minutes to form a well-cured yellow film. The IR spectrum of the film (Figure 12) indicated that the curing was nearly complete. The nitrile absorption at 2230 cm^{-1} is very weak and a broad band at 3400 cm^{-1} is attributed to the formation of bisbenzimidazole moieties.

Based on the above curing test, formulation #10543-8 was prepared as shown in Table XXV. 1,3-Bis-(3,4-dicyanophenoxy)benzene was added with the expectation of increasing the crosslinking efficiency.

Mini-bars of unidirectional carbon fiber composites were prepared from formulation #10543-8 as shown in Table XXVI. Respectable values of modulus and strength were obtained at 300°C.

B. Scale-up Study

In order to scale-up the preparation of phthalonitrile-terminated oligoetherimide, the synthesis of 4-(3-aminophenoxy)phthalonitrile (XXVIII) had to be improved. In reaction (22), an electron-transfer reaction between extremely electron deficient 4-nitrophthalonitrile and aminophenoxide tended to occur, giving a significant amount of resinous byproducts. This problem could be avoided by using 4-chlorophthalonitrile in place of 4-nitrophthalonitrile. 4-Chlorophthalonitrile was prepared according to the following scheme:



(XXXIII)

(XXXIV)

(XXXV)

(XXXVI)

3-Chlorophthalonitrile was also prepared by the identical procedure.

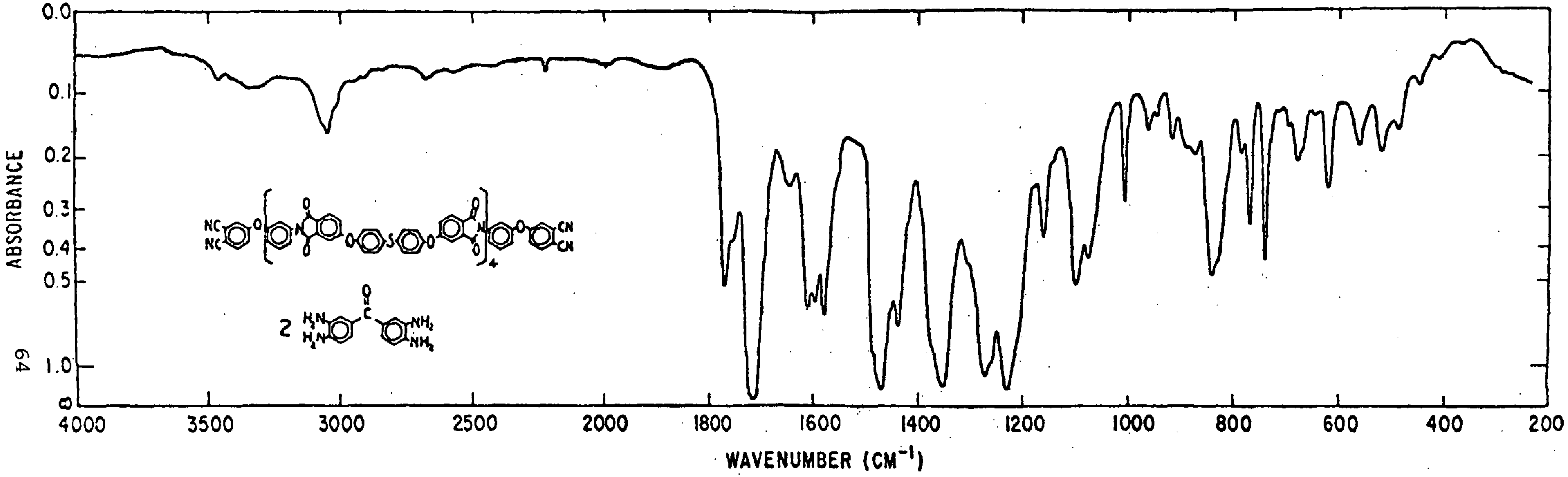


FIGURE 12. IR SPECTRUM OF PHTHALONITRILE-TERMINATED PEI CURED WITH TETRAAMINOBENZOPHENONE

TABLE XXV

Composition of Formulation #10543-8

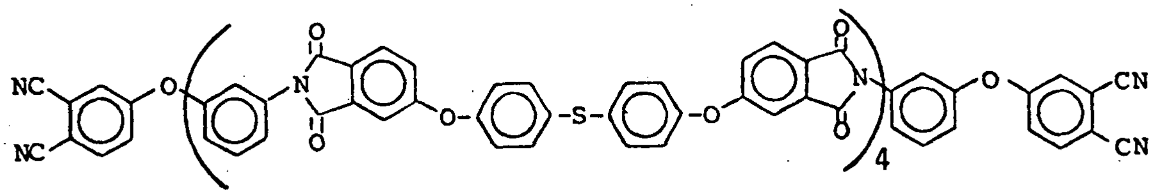
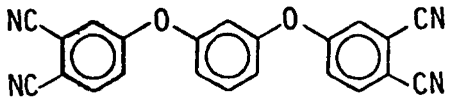
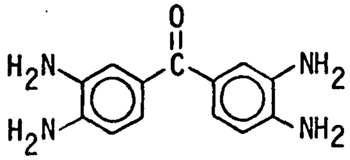
Monomers		Molar Ratio
	2.00 g	1
	0.100 g	0.37
	0.361 g	2
m-Cresol	5.30 g	-
Solids Content	31.7 wt %	

TABLE XXVI

Properties of Carbon Fiber Composites from Formulation #10543-8

					Mechanical Properties at 300°C in air	
Type of Fiber[a]	Molding Conditions Under Pressure (°C/hr)	Post Cure[b] (°C/hr)	Fiber Vol %	Void Vol %	Flex. Mod. 10^6 psi	Flex. Str. 10^3 psi
AU	285/2	300/2-375/16	43.9	15.8	6.2	92
AU	285/1	320/112	46.8	16.4	7.7	99
AU	285/1	320/112	48.5	9.5	9.1	104

(a) AU = Hercules AU untreated carbon fiber.

(b) All samples were post-cured under atmospheric pressure in air

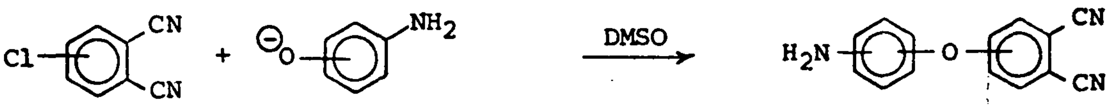
TABLE XXVII

Preparation of Aminophenoxyphthalonitriles

Starting Materials			
Aminophenol	Chlorophthalonitrile	Yield (%)	mp (°C)
p-[a]	3-chloro-	96.5	198-199
p-[a]	4-chloro-	91.4	132-133
m-[a]	3-chloro-	94.6	134.5-135.5
m-[a]	4-chloro	97.7	170-171
o-[b]	3-chloro-	84.1	135-136
o-[b]	4-chloro-	90.9	119.5-120

(a) Anhydrous sodium salt was preformed and reacted with chlorophthalonitriles.
(b) Free phenol was directly reacted in the presence of anhydrous potassium carbonate.

Nucleophilic displacement of chlorophthalonitrile by various isomeric aminophenoxides proceeded at 50-60° in DMSO and gave nearly quantitative yield of aminophenoxyphthalonitriles.

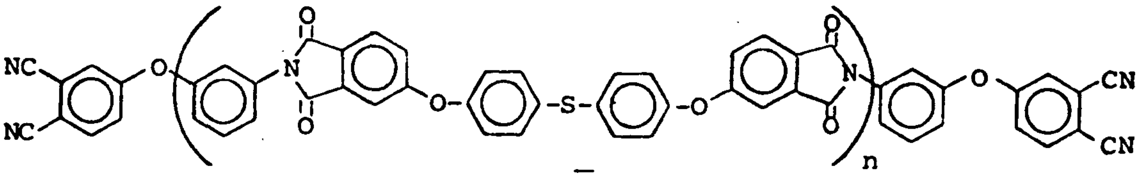


(25)

(XXXVII)

In reaction (25), aminophenoxide could be formed in situ from aminophenol and anhydrous potassium carbonate. The results are summarized in Table XXVII.

A total of approximately 200 g of phthalonitrile-terminated oligoetherimide (XXXVIII) was prepared in three batches. The material was designated PEI-3CN, indicating its degree of polymerization was 3. The glass transition temperature of this material was 144°C.



(XXXVIII) $\bar{n} = 3$

Subsequently, oligomer PEI-3CN was formulated with 1.5 molar equivalents of tetraaminobenzophenone as shown in Table XXVIII.

TABLE XXVIII

Composition of Formulation #10543-24

		Molar Ratio
PEI-3CN, Oligomer (XXXVIII)	40.64 g	1
3,3',4,4'-Tetraaminobenzophenone	7.00 g	1.5
m-Cresol	110.1 g	
	Solid Content	30.2 wt %

After diluting to an appropriate concentration level (22%), the resin solution was applied to Hercules type A.U. continuous carbon fiber roving. The impregnation was carried out in a continuous manner as illustrated in Figure 13. Ten layers of 2" x 3" prepreg were placed in a mold and cured under various conditions as summarized in Table XXIX. In general, the process characteristics were very good. The maximum pressure required was around 300 psi or below except in one case.

Figure 13. PREPARATION OF CARBON FIBER PREPREG

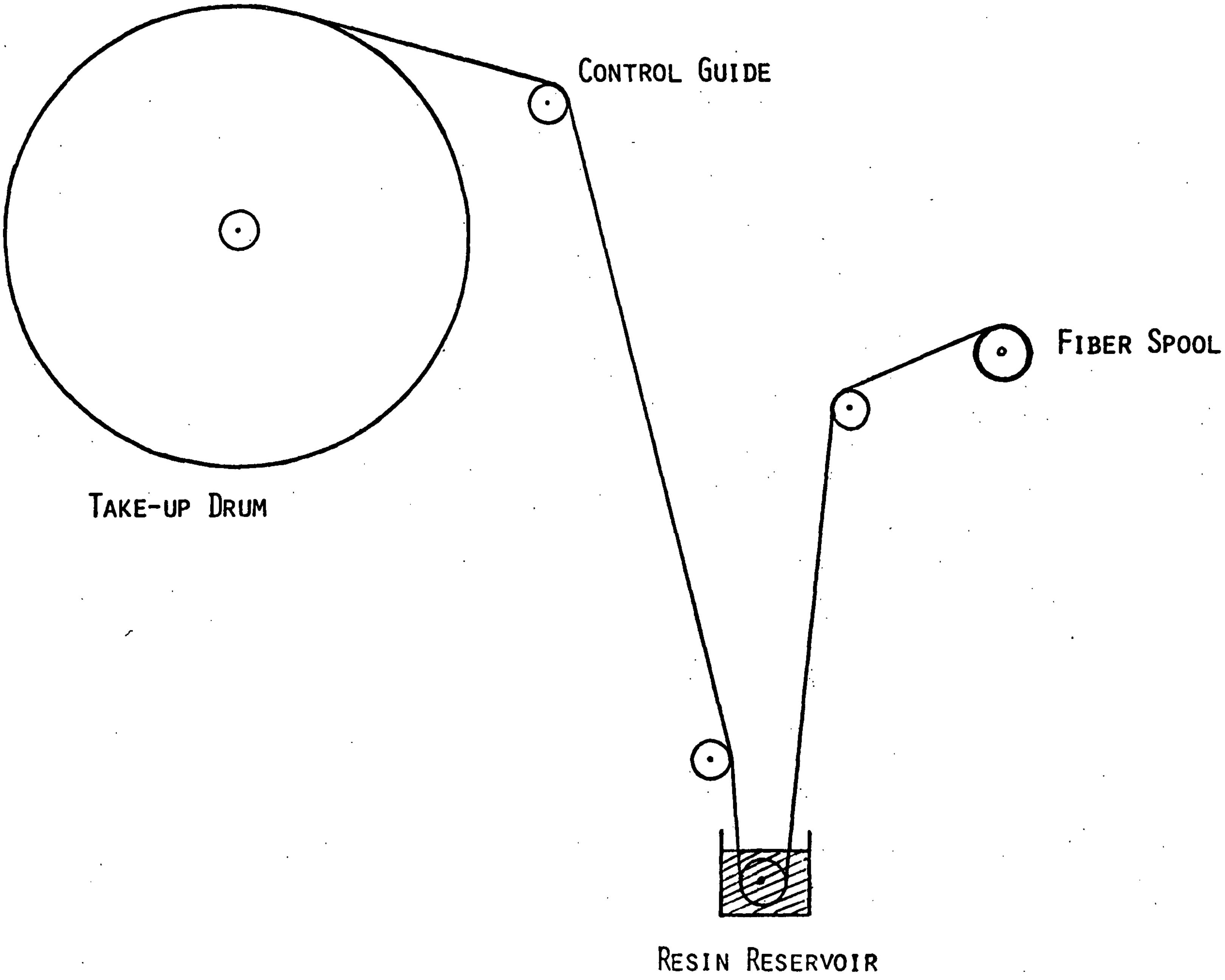


TABLE XXIX

Preparation of Carbon Fiber Composites from Formulation #10543-24

Plaque Ident.	1	2	3	4	5	6	7	8	9
Resin	Formulation #10543-24	→	→	→	→	→	→	→	→
Bath									
% Solids	16	22	→	→	→	→	→	→	→
Temp.	R.T.	→	→	→	→	→	→	→	→
Prepreg									
Pre Dry on drum	1 hr with 2-250 watt heat lamps								
Oven Dry									
Time (min)	15	30	→	→	→	→	→	→	→
Temp (°C)	150	185	→	→	→	→	→	→	→
w/o Res + Solvent	45	46	55	51	51	55	54	50	50
w/o m-cresol remaining	15	3.5	→	→	→	→	→	→	→
Molding									
Preheat									
Duration (min)	23	30	→	→	→	→	→	→	→
Temp. (°C)	200	200	→	→	→	→	→	→	→
Cure									
Total time (min) to reach curing press.	25	33	44	37	34	36	37	35	36
Pressure (psi)	10	55	8650	215	160	270	325	55	325
Duration (hr)	16	16	16	16	6	16	6	16	16
Temp. (°C)	285	→	→	→	→	→	→	→	→
Composition									
V/o voids	1.3	8	8.8	4.7	4.9	3.7	3.4	8.6	4.3
V/o fiber	63.2	51.5	51.8	49.5	57.6	50.4	51.4	58.9	49.2
V/o resin	35.4	40.5	39.4	45.8	37.4	45.8	45.2	32.5	46.5
ρ (g/cc)	1.63	1.48	1.55	1.52	1.55	1.54	1.54	1.51	1.52

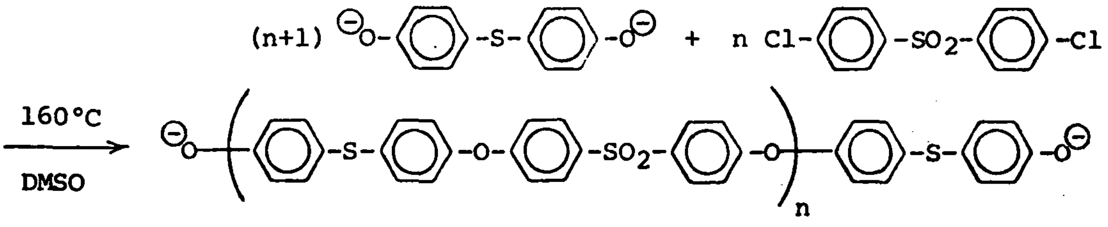
The resulting 2" x 3" x 0.1" plaques were cut into 0.15" wide test specimens and subjected to post-cure at 320°C in air. The results are summarized in Table XXX.

Phthalonitrile-Terminated Polyethersulfones

Polyethersulfones have been prepared commercially by nucleophilic displacement of 4,4'-dihalodiphenylsulfones with bisphenol salts[6] in dipolar aprotic solvents or by Friedel-Crafts reaction of aromatic ethers and sulfonyl chlorides.[7] The polymers are known as excellent engineering thermoplastics with good high temperature stability. However, polyethersulfones are generally not useful as structural materials above 250°C because their glass transition temperatures are below 300°. Creep and yield of polymers at high temperature can be prevented by crosslinking the polymer chains. Marvel et al[1] introduced nitrile groups into polysulfones and attempted to trimerize them and form sym-triazine crosslinks. The trimerization reaction was extremely slow and inefficient even at 300°C. It is a statistically inherent problem that a high degree of crosslink density cannot be attained by trimerization of functional groups constrained onto polymer chains.

We have found that phthalonitrile-terminated oligoethersulfones can be effectively crosslinked by the same method as described in the preceding chapter for phthalonitrile-terminated polyetherimides, namely, with tetraamines.

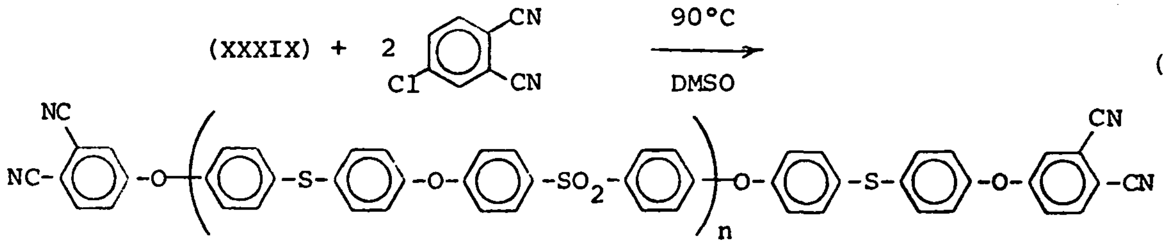
Phenoxide-terminated low molecular weight polyethersulfone (XXXIX) was prepared by the known procedure[8] in the presence of an excess amount of bisphenol salt:



(26)

(XXXIX)

The oligomer (XXXIX) was subsequently in situ capped with 4-chlorophthalonitrile to form phthalonitrile-terminated polyethersulfone (XL):



(27)

(XL)

TABLE XXX

Properties of Carbon Fiber Composites from Formulation #10543-24 at 300°C in Air

Postbake	As Molded		4 hr @ 320°C			8 hr @ 320°C			12 hr @ 320°C		
	Flexural		Flexural		Shear	Flexural		Shear	Flexural		Shear
Plaque Ident.	Strength	Mod.	Strength	Mod.	Strength	Strength	Mod.	Strength	Strength	Mod.	Strength
	psix10^3	psix10^6	psix10^3	psix10^6	psix10^3	psix10^3	psix10^6	psix10^3	psix10^3	psix10^6	psix10^3
1	14.9	2.1	32.7	4.3	2.6	56.0	8.8	3.1	*	*	*
2	12.2	1.2	59.9	7.8	2.4	76.7	9.5	3.1	90.0	11.7	3.4
4	7.2	.97	45.4	6.7	2.5	45.9	9.3	2.7	44.3	9.3	4.0
6	10.5	.97	55.5	8.4	2.8	53.1	9.0	2.6	49.4	7.8	2.7
7	7.9	.98	38.8	4.3	2.4	21.7**	2.0	1.8	29.3	4.1	2.4
9	7.1	.94	24.9	3.4	2.5	35.0	4.0	3.0	24.8	4.1	2.6
9*									28.2	5.3	2.8

Note:

*Tested at room temperature.

**Large void in test specimen.

***Sample delaminated in test fixture.

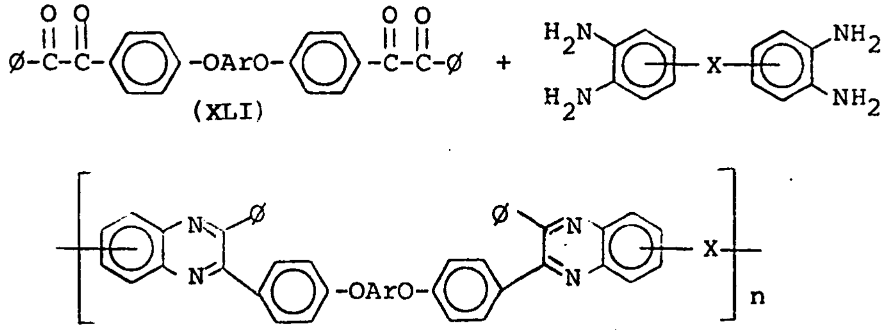
Oligomer (XL), with an average n of 2, had a glass transition of 100°C, was apparently non-crystalline and was soluble in conventional solvents such as methylene chloride and chloroform. The infrared spectrum of the thin film cast from the chloroform solution is shown in Figure 14. The characteristic nitrile absorption at 2230 cm^{-1} and the absence of hydroxy absorption around 2600 cm^{-1} are clearly seen.

The above phthalonitrile-terminated oligoethersulfone (XL, n = 2) and 3,3',4,4'-tetraaminobenzophenone were dissolved in m-cresol at a molar ratio of 1:2. The solution was spread on a glass plate and heated to evaporate the solvent. The residual liquid had excellent flow above 200°C and cured efficiently at 250-300°C to form a tough film. The infrared spectrum of the cured film is shown in Figure 15. Only a small amount of nitrile was left unreacted as shown by the intensity of absorption at 2230 cm^{-1} and a benzimidazole group was formed as characterized by the broad band at 2800-3500 cm^{-1}. The DSC curve obtained for the cured film exhibited a weak transition at 240°C.

Phthalonitrile-capped polyethersulfone was not tested as a matrix in fiber-reinforced composites. However, excellent flow and efficient curing properties seem to promise good processability.

Polyquinoxaline Curing System

The synthesis of phenylated polyquinoxalines has received considerable attention.[9] These polymers possess improved thermo-oxidative stability and solubility compared with polyquinoxalines reported earlier.[10] More recently Heath and Wirth[11] prepared even more readily processable phenylated polyetherquinoxalines (XLII) from bis(1,2-diketoether)s (XLI) and bis(1,2-diaminophenyl)compounds:



(XLI)

(XLII)

(28)

Polyetherquinoxalines (XLII) possess relatively low glass transition temperatures and therefore can be readily molded. However, they are not useful as structural materials at elevated temperatures and an efficient crosslinking reaction for polyquinoxalines has not been available. In a recent investigation, Hergenrother[12] described the synthesis of polyquinoxalines containing pendant reacting groups such as -CN, -OCN, -CNO and -C≡CH.

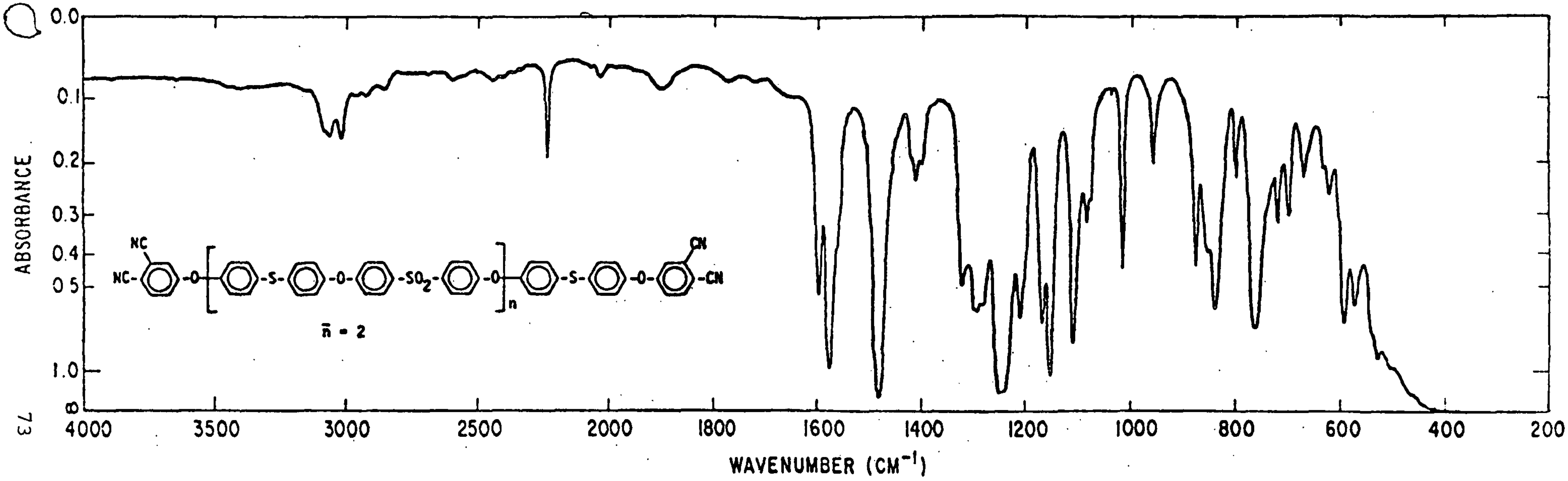


FIGURE 14. IR SPECTRUM OF PHTHALONITRILE-TERMINATED POLYETHERSULFONE

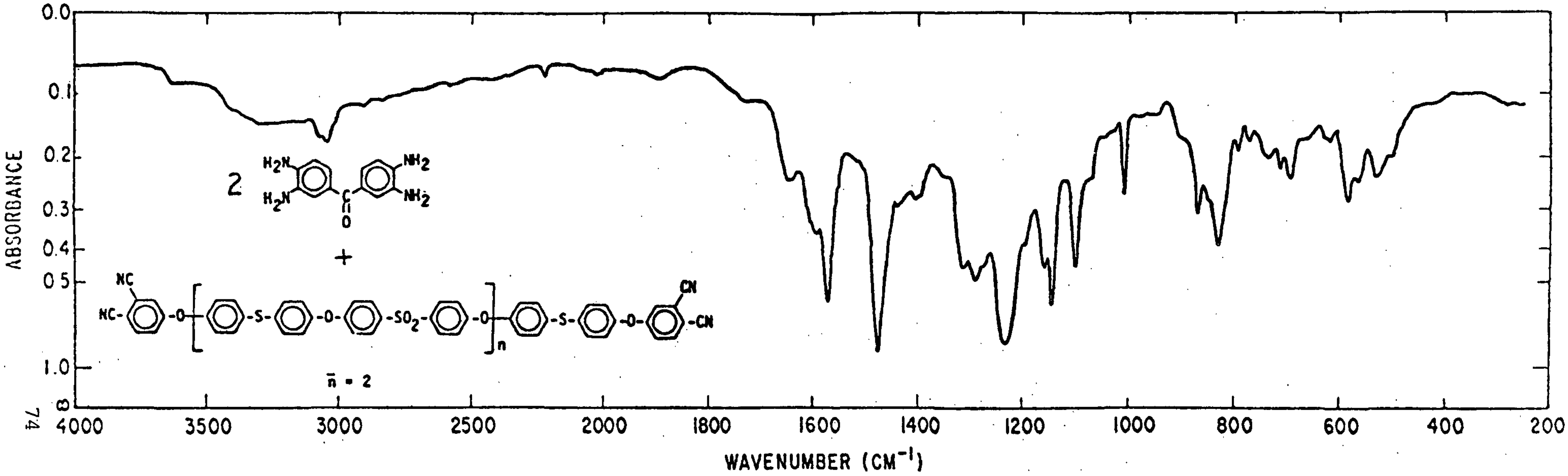
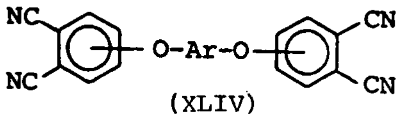


FIGURE 15. IR SPECTRUM OF PHTHALONITRILE-TERMINATED POLYETHERSULFONE CURED WITH TETRAAMINOBENZOPHENONE

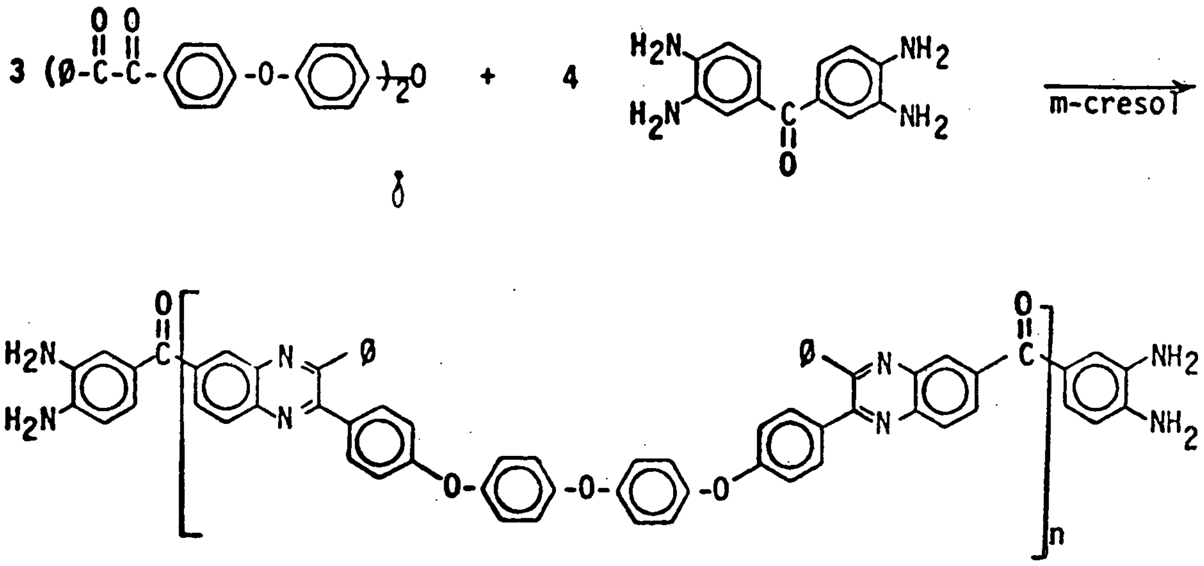
However, the synthesis involves rather esoteric intermediates and cumbersome preparations. In addition, use of high molecular weight polymers rather than low molecular weight oligomers may cause process difficulties in applications such as carbon fiber composites.

We have found that low molecular weight polyetherquinoxalines with o-diaminophenyl end groups (XLIII) can be efficiently cured by heating with bis(phthalonitrile)ethers of the following structure (XLIV):



(XLIV)

Oligomer (XLIII) can be readily prepared by simply polymerizing in the presence of an excess amount of tetraamine, as shown by the following example:



(29)

(XLIII) n = 3

The infrared spectrum of oligomer (XLIII) is shown in Figure 16.

Bis(phthalonitrile)ethers (XLIV) were prepared by nucleophilic displacement of chlorophthalonitriles with bisphenolate salts in DMSO. In an alternate method, bisphenols were directly reacted in the presence of potassium carbonate. The results are summarized in Table XXXI.

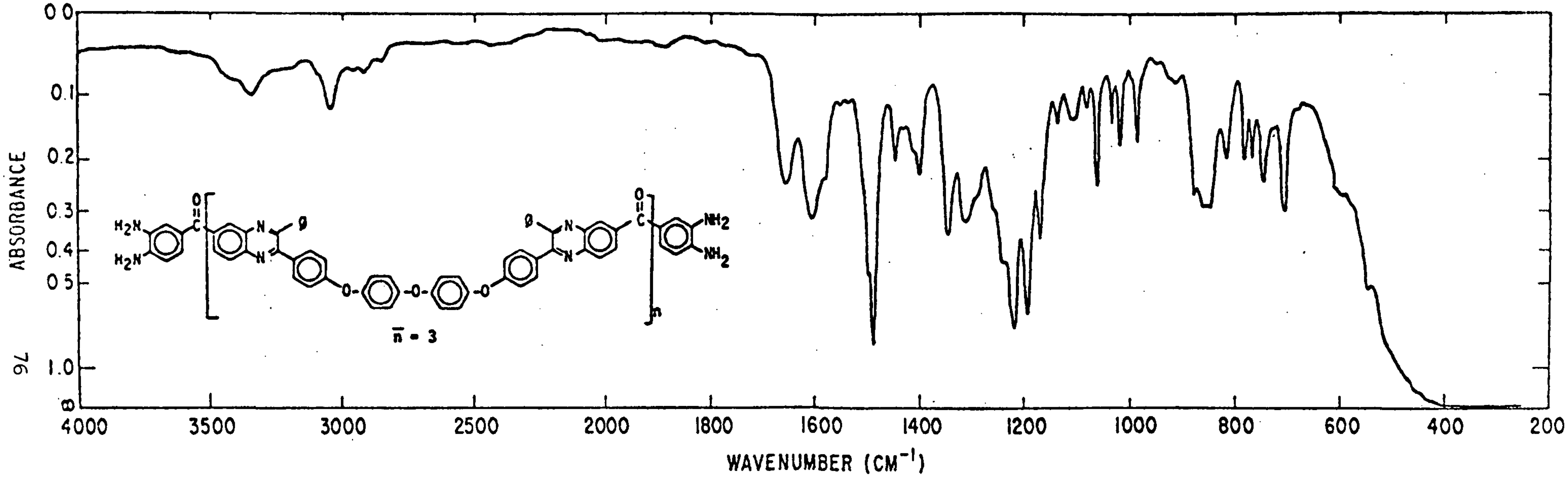
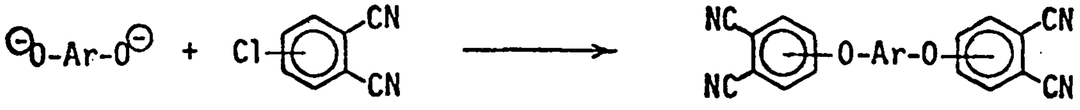


FIGURE 16. IR SPECTRUM OF POLYETHERQUINOXALINE WITH o-DIAMINO TERMINAL GROUPS

TABLE XXXI

Preparation of Phthalonitrile Ethers



Ar(OH)$_n$	Chlorophthalonitrile	Phthalonitrile Ethers Yield (%)	mp (°C)
Hydroquinone[a]	3-isomer	96.9	316-317
	4-isomer	96.5	253-255
Resorcinol[a]	3-isomer	85.5	191-192
	4-isomer	94.6	180.5-181.5
Catechol[b]	3-isomer	82.8	154.5-155.5
	4-isomer	77.7	187.5-188.5
4,4'-Dihydroxydiphenylsulfide[a]	3-isomer	95.2	247.5-248.5
	4-isomer	75.1	175-177
Phloroglucinol[b]	3-isomer	92.8	358-359
	4-isomer	84.4	271-272

(a) Anhydrous sodium salt was preformed and reacted with chlorophthalonitrile.

(b) Free phenols were directly reacted in the presence of potassium carbonate.

Some of the compounds listed in Table XXXI have been prepared by Heath and Wirth.[13]

A methylene chloride solution (30 wt %) containing a 1:1.6 molar ratio of 4,4'-bis(3,4-dicyanophenyl)diphenyl sulfide; (XLIV; Ar = diphenyl sulfide) and quinoxaline oligomer (XLIII) was spread on a glass plate and dried. When the residue was heated it softened at 150-160° and became a very fluid yellow liquid above 220-230°C. Rapid curing occurred at 270-280°C and a tough amber-colored film was obtained. The cured film was isothermally aged at 330°C in air. In the initial few hours, approximately 2.7% weight loss was observed, perhaps because of the residual curing reaction. In the following 170 hours, virtually no weight loss occurred (Figure 17). The glass transition temperature of the cured film was 220°C.

In Figure 18 is shown the infrared spectrum of the cured film prepared from a 1:2 molar mixture of bisphthalonitrile ether (XLIV; Ar = diphenyl sulfide) and quinoxaline oligomer (XLIII). The crosslinking reaction was nearly complete as seen by the absence of nitrile absorption at 2230 cm^{-1} and amino absorption at 3300-3500 cm^{-1}.

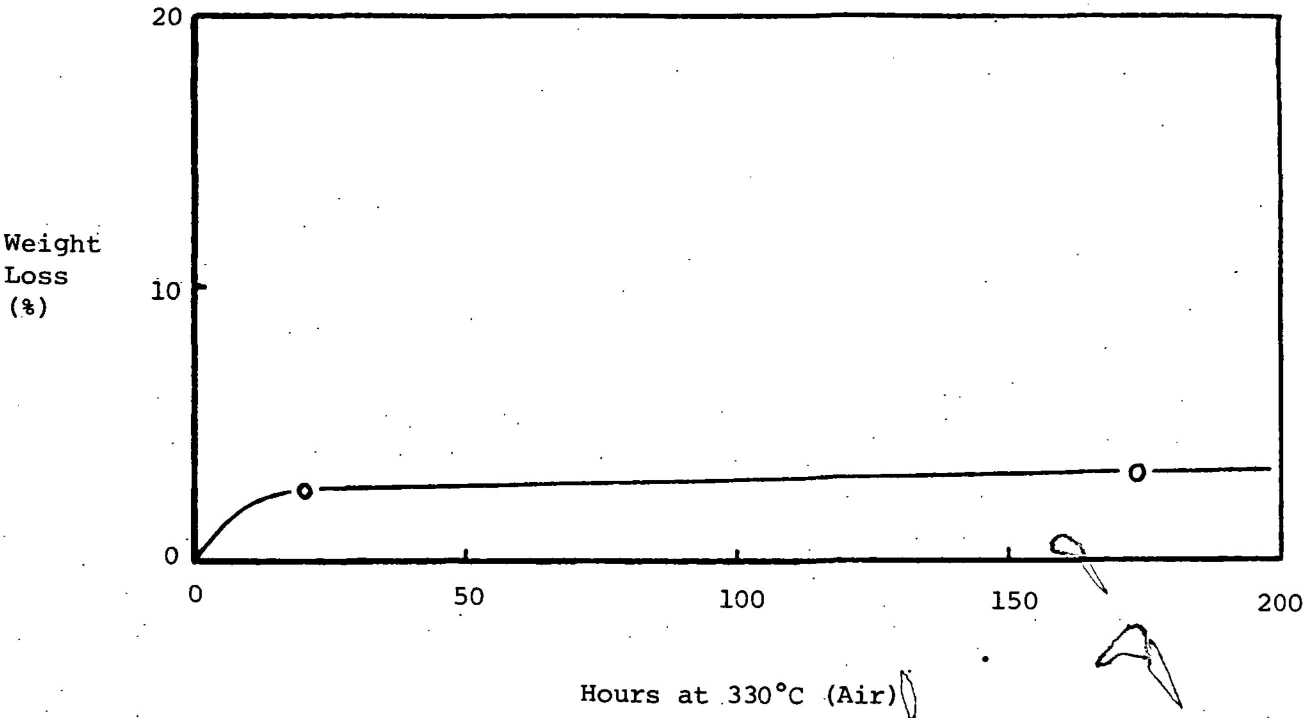


Figure 17. Isothermal Weight Loss of Polyetherquinoxaline Cured with Bisphthalonitrile Ether.

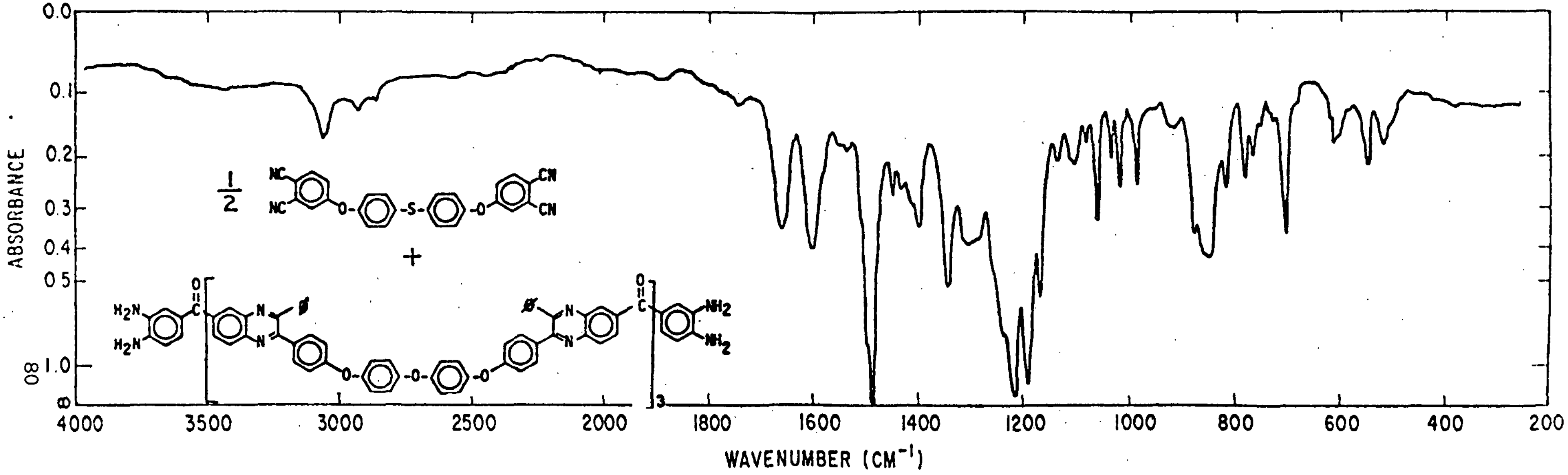


FIGURE 18. IR SPECTRUM OF POLYETHERQUINOXALINE CURED WITH BISPHTHALONITRILE ETHER

CONCLUSIONS

Exploratory investigation has been carried out on the chemistry of several crosslinking reactions. Among these the reaction of phthalonitrile group and o-diaminophenyl group to form bisbenzimidazole crosslink moiety was found to be the most versatile and effective system. Using the key intermediate, 4-chlorophthalonitrile, phthalonitrile groups were introduced to low molecular weight polyetherimide and polyethersulfone. The phthalonitrile-capped oligomers were effectively cured with 3,3',4,4'-tetraaminobenzophenone. Similarly, low molecular weight polyetherquinoxaline having o-diaminophenyl end groups was found to be cured with bisphthalonitrile derivatives which were also prepared from 4-chlorophthalonitrile.

Preliminary study was made on fabrication of small carbon fiber composites using resin matrix composed of phthalonitrile-capped polyetherimide and 3,3'-tetraaminobenzophenone. The result indicated that the resin system had good processability and efficient curing property.

EXPERIMENTAL, PART II

Reaction of Benzimidazopyrrolone (XX) and Aniline

A mixture of benzimidazopyrrolone (0.510 g, 2.32 mmoles), aniline (0.216 g, 2.32 mmoles) and 3 ml of dry N,N'-dimethylacetamide was stirred at 140-144°C under nitrogen. Within 5 minutes crystalline precipitate of o-benzimidazo-2-ylbenzanilide (XXVII) began to appear. The reaction was terminated in 25 minutes and the reaction mixture was poured into methanol. The colorless precipitate was filtered, washed with toluene and dried under vacuum. The yield of XXVII was 0.347 g (47.8%), mp. 347-348°C (decomp.). The mass spectrum of XXVII showed significant peaks at 313 (M/e), 310, 309, 295 (M-18), 221 and 93.

Preparation of 1,2-Bis(2-benzimidazolyl)benzene (XXIII) from Benzimidazopyrrolone (XX)

An equal molar mixture of benzimidazopyrrolone (XX) and o-phenylenediamine was placed in a glass tube and the tube was sealed under vacuum. On heating at 280°C for 2 hours, white crystalline material was obtained in quantitative yield, mp. 424-426°C.

Preparation of Oligoetherpyrrones (Table XVI)

Two experiments are described below as typical examples.

(1) A mixture of 3,3',4,4'-tetraaminodiphenylsulfone (2.2347 g, 8.289 mmoles), o-phenylenediamine (0.5788 g, 5.352 mmoles), 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (5.4646 g, 10.705 mmoles) and 40 ml of m-cresol was stirred at 40-45°C under nitrogen for approximately 1.5 hours. To the resulting homogeneous solution was added 35 ml of benzene, and the mixture was stirred and heated to reflux at 110° for one hour. During this period the majority of the water was removed azeotropically by use of a Dean-Stark trap. About 10 ml of the benzene was distilled off and the reaction mixture was heated to reflux at 130° for 15 minutes. The benzene was further removed and the reaction mixture was refluxed at 160° for 0.5 hour. During this period the water was continuously removed by recirculating the refluxing solvent through a trap filled with Molecular Sieve. Finally, it was heated to reflux at 185-190°C for an additional 0.5 hour. The polymer was precipitated in methanol, washed with methanol and dried at 100° under vacuum. The bright yellow powder was further dried at 200°C under vacuum. The yield of pyrrone polymer was 7.06 g (94.1%).

Anal. Calc. for $C_{160}H_{82}N_{16}S_7O_{22}$: C, 68.51; H, 2.95; N, 7.99; S, 8.00.

Found: C, 69.4; H, 3.3; N, 7.8; S, 8.2.

(2) 4,4'-Bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (4.4102 g, 8.640 mmoles) was dissolved in 25 ml of dry m-cresol. The solution was added dropwise with stirring to a mixture of 3,3'-diaminobenzidine (1.3884 g, 6.480 mmoles), o-phenylenediamine (0.4671 g, 4.320 mmoles) and 40 ml of m-cresol at 40°C. When approximately 90% of the solution was added, phase separation occurred and the stirring was difficult because of the sticky bottom phase. The rest of the dianhydride solution was added at 50°C. The total addition took one hour. The resulting mixture was heated to 85-90° when it became homogeneous. About 20 ml of benzene was added and the reaction mixture was heated to reflux at 105-110° for 0.5 hour, during which time the water was removed azeotropically. The benzene was gradually distilled off to allow the pot temperature to rise to 185° over a period of 15 minutes. It was further refluxed at 185-190° for one hour, recirculating the solvent through a trap filled with Molecular Sieve. The product was isolated in a manner similar to that in the previous experiment. The yield of bright yellow powdery oligomer was 5.47 g (96.9%).

Anal. Calc. for $C_{160}H_{82}N_{16}S_4O_{16}$: C, 73.55; H, 3.16; N, 8.58; S, 4.91.
Found: C, 73.3; H, 3.4; N, 8.2; S, 4.7.

Preparation of Pyrrone-Imide Copolymer (Table XVII)

A typical example is given below.

A mixture of 3,3',4,4'-tetraaminodiphenyl ether (1.2557 g, 5.453 mmoles) m-phenylenediamine (0.2949 g, 2.726 mmoles), o-phenylenediamine (0.5897 g, 5.453 mmoles) and 30 ml of m-cresol was stirred under nitrogen. 4,4'-Bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (5.5674 g, 10.906 mmoles) was added in portions to the above mixture at 40°C. When approximately 25% of the dianhydride was added, the reaction mixture was very viscous. The rest of the dianhydride was dissolved in hot m-cresol (20 ml) and cooled. The dianhydride solution was then added dropwise to the above mixture over a period of 15 minutes at 40-45°C. Approximately 20 ml of benzene was added and the reaction mixture was heated to reflux at 105-110° for one hour. During this period the water was removed by the use of a recirculating trap filled with Molecular Sieve. The benzene was distilled off until the temperature reached 180°. The reaction mixture was then further heated to reflux at 175-180°. The reaction was then further heated to reflux at 175-180°C for one hour to complete the dehydration. The product was precipitated in methanol, washed with methanol and dried under vacuum. The yield of yellow copolymer was 7.00 g (99.7%). The material was soluble in sym-tetrachloroethane, dimethylacetamide and m-cresol. The glass transition temperature was 184°C.

Anal. Calc. for $C_{154}H_{80}N_{14}S_4O_{20}$: C, 71.82; H, 3.13; N, 7.61.
Found: C, 70.7; H, 3.6; N, 8.0.

Reaction of N-Phenylphthalimide and o-Phenylenediamine

N-phenylphthalimide(0.670 g, 3.00 mmoles) and o-phenylenediamine (0.108 g, 1.00 mmole) were heated at 245°C for 30 minutes in a sealed tube. The tube was open and the crystalline solid was extracted twice with 10 ml of boiling chloroform to remove the unreacted N-phenylphthalimide. White crystalline solid insoluble in chloroform was o-benzimidazoylbenzamide (XXVII). The yield of XXVII was 0.243 g (77.6%).

Preparation of Mini-Composite Bars

A small tow (1.5 inch long) of S-glass fiber was dipped in the resin solution and the wet fiber tow was dried at 135° in an oven for 4 minutes. The dried tow was placed in a vacuum mold. It was maintained at 200° under vacuum for 15 minutes and then at 250° for 10 minutes before closing the mold. Finally, it was cured at appropriate temperatures for 16 hours under pressure. The dimension of composites was 0.05" x 0.08" x 1.5".

Preparation of Oligoetherimides #25-304 (Table XIX) and #25-328 (Table XXI)

#25-304 -- m-Phenylenediamine (1.7302 g, 16.00 mmoles) and o-phenylenediamine (0.8651 g, 8.00 mmoles) were dissolved in 30 ml of m-cresol. To this solution was added in portions 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (10.2092 g, 20.00 mmoles) over a period of 15 minutes. The viscous mixture was stirred and heated to 60°C and about 20 ml of benzene was added dropwise. The reaction mixture was stirred and heated to reflux at 105-110°C for 0.5 hour, during which time the water was removed azeotropically. Part of the benzene was distilled off over a period of 0.5 hour to raise the reaction temperature to 160°C. Approximately 10 ml of toluene was added and the distillation was continued until the pot temperature reached 180°C. The reaction mixture was then heated to reflux at 180°C for 1.5 hours to complete the dehydrocyclization by use of a recirculating trap filled with Molecular Sieve. The product was precipitated in methanol and dried under vacuum. The yield of yellow powdery oligomer was 12.0 g (100%). The intrinsic viscosity in m-cresol was 0.22 dl/g. The glass transition temperature was 180°C.

Anal. Calc. for $C_{176}H_{94}N_{12}O_{28}S_5$: C, 70.81; H, 3.17; N, 5.63.
Found: C, 71.0; H, 3.5; N, 5.7.

#25-328 -- The polymerization was carried out under the same conditions as in #25-304 except that the molar ratio of the dianhydride, m-phenylenediamine and o-phenylenediamine was 5:4:1. The yield of the oligomer was 100%.

Anal. Calc. for $C_{170}H_{90}N_{10}O_{30}S_5$: C, 70.09; H, 3.11; N, 4.81.
Found: C, 69.9; H, 3.4; N, 4.8.

Reaction of Phthalonitrile and o-Phenylenediamine

Phthalonitrile (0.0303 g, 0.236 mmole) and o-phenylenediamine (0.0518 g, 0.479 mmole) were placed in a 1 cc glass ampoule and the ampoule was sealed under vacuum. It was heated at 250° for 2 hours and cooled. White crystals of bisbenzimidazole (XXIII) was obtained in quantitative yield.

Preparation of 4-(3-Aminophenoxy)phthalonitrile (XXVIII) from 4-Nitrophthalonitrile

A mixture of m-aminophenol (23.27 g, 0.2132 mole), 50% aqueous sodium hydroxide (17.06 g, 0.2132 mole), DMSO (100 ml) and benzene (50 ml) was placed in a 300 ml, three-neck flask fitted with a Dean-Stark trap. The mixture was heated to reflux to remove the water azeotropically. After most of the water had been removed, the D-S trap was replaced with a recirculating trap filled with calcium hydride. The heating at reflux was continued for 4 hours and the resulting mixture was cooled to room temperature. 4-Nitrophthalonitrile (36.92 g, 0.2132 mole) was added at once and the resulting mixture was stirred for 30 minutes at room temperature. The dark colored reaction mixture was poured into cold water. The dark brown precipitate was filtered, washed with water and dried under vacuum. The yield of the crude product was 41.9 g (83.5%). The material was recrystallized from toluene under nitrogen using activated carbon. The material was recrystallized from acetic acid and once more from ethanol. The pure 4-(3-aminophenoxy)phthalonitrile was yellow, needle-shaped crystals, mp 172-173°. The yield of the pure material was 13.5 g.

Anal. Calc. for $C_{14}H_9N_3O$: C, 71.48; H, 3.86; N, 17.86.

Found: C, 71.3; H, 4.2; N, 17.9.

Phthalonitrile-Terminated Polyetherimide (XXIX, n = 4) PEI-5CN Resin)

A mixture of 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (5.1046 g, 10.000 mmoles), 4,4'-diaminodiphenyl ether (1.6018 g, 8.000 mmoles), 4-(3-aminophenoxy)phthalonitrile (0.9410 g, 4.000 mmoles), m-cresol (24 ml) and toluene (7 ml) was heated to reflux for 30 minutes during which time the water was removed by the use of a Dean-Stark trap. The D-S trap was replaced with a recirculating trap filled with Molecular Sieve 4A and the amount of toluene was adjusted in such a way that the reaction mixture boiled constantly at 160°. The heating was continued for 2 hours and cooled. The reaction mixture was concentrated by vacuum evaporation. The resulting 5CN resin solution weighed 18.21 g (32.5% solids). Part of the solution was added to toluene. The precipitated prepolymer was filtered, washed with toluene and dried. The glass transition temperature of this polymer was 150°C.

Anal. Calc. for $C_{216}H_{116}N_{14}S_5O_{36}$: C, 71.21; H. 3.21; N, 5.38; S, 4.40.
Found: C, 72.5; H, 3.7; N, 5.8; S, 4.5.

Phthalonitrile-Terminated Polyetherimide (XXXII)

A mixture of 4-(3-aminophenoxy)phthalonitrile (1.1762 g, 5 mmoles), *m*-phenylenediamine (0.8111 g, 7.5 mmoles), 4,4'-bis(3,4-dicarboxyphenoxy) diphenylsulfide dianhydride (5.1046 g, 10 mmoles), 20 ml of *m*-cresol and 10 ml of toluene was stirred and heated to reflux at 140-145°. The water was continuously removed by recirculating the refluxing solvent through a trap filled with Molecular Sieve. After heating for 3 hours the solution was cooled and poured into methanol stirred with a blender. The precipitate was filtered, washed with methanol and dried. The yield was 6.45 g (95.8%). The intrinsic viscosity was 0.17 in *m*-cresol. The glass transition was observed at 152° by DSC.

Preparation of 3- and 4-Chlorophthalic Anhydrides (XXXIII)

3-Nitrophthalic anhydride (102.4 g, 0.530 mole) was melted by heating at 200-220° and chlorine gas was bubbled through the melt. The reaction was complete after continuously bubbling the chlorine for 4 hours at 200-227°C. The product was distilled under vacuum, 189°/24 mm Hg. The yield of pure 3-chlorophthalic anhydride was 74.7 g (77.2%), mp 123.5-124.5°C.

Similarly, 4-nitrophthalic anhydride was reacted with Cl_2 at 230-250°. The product was distilled at 145-154°/6-8 mm Hg. The yield was 75%.

Preparation of 3- and 4-Chlorophthalimide (XXXIV)

A mixture of 3-chlorophthalic anhydride (72.3 g, 0.396 mole) and ammonium acetate (159.8 g) was heated at 145° for one hour. The solution was further heated and volatiles were evaporated until the boiling point of the reaction mixture reached 160°C. The resulting mixture was cooled and allowed to solidify. The solid was washed with water and dried. The yield was 69.05 g (96.7%), mp 234.5-235.5°C.

4-Chlorophthalimide was prepared by the identical method. The yield was 86.2%; mp 209.5-210.5°C.

Preparation of 3- and 4-Chlorophthalamide (XXXV)

Finely pulverized 3-chlorophthalimide (68.6 g, 0.378 mole) was added in portions into 400 ml of 30% ammonium hydroxide solution at 15-20°C. The addition took 0.5 hour. The reaction mixture was stirred at room temperature for one hour and filtered. The white crystalline precipitate of the diamide was washed with 700 ml of water and dried under vacuum at room temperature. The yield was 48.3 g (64.3%).

4-Chlorophthalamide was prepared under identical conditions. The yield was 91.0%.

Preparation of 3- and 4-Chlorophthalonitrile (XXXVI)

A mixture of 3-chlorophthalamide (109.0 g, 0.549 mole), 520.4 g of anhydrous pyridine (dried with CaH_2) and 1220 ml of dry methylene chloride was stirred and cooled at 8-15°C. A mixture of 168.0 g of phosphorous oxychloride and 200 ml of dry methylene chloride was added dropwise to the above mixture over a period of 50 minutes. The resulting mixture was further stirred at room temperature for 25 minutes and poured into water. The organic layer was extracted with methylene chloride. The methylene chloride solution was washed with water and evaporated under vacuum. The tan crystal of 4-chlorophthalonitrile was obtained as a residue. The yield was 76.4 g (85.6%). The crude material contained approximately 5% of imide (XXXIV). This was purified by the following procedure. The crude nitrile (153.8 g) was dispersed in a mixture of toluene (1.2 l) and 30% aqueous ammonia (50 ml) and the mixture was stirred for 15 minutes at room temperature. The precipitate of bisamide (XXXV) was removed by filtration. The toluene solution was separated, washed with water and evaporated under vacuum. The crystalline residue weighed 133.06 g. The material was finally purified by vacuum sublimation. The melting point of the pure 4-chlorophthalonitrile was 129-130°C.

Similarly, 3-chlorophthalonitrile was obtained in a crude yield of 88.1%, which contained about 10% of the corresponding imide (XXXIV). After purification under the same conditions described for the 4-isomer, the yield was 62.2%, mp 109-110°C.

Preparation of Aminophenoxyphthalonitriles (Table XXVII)

Method A -- m-Aminophenol sodium salt (1.6425 g, 12.5 mmoles) was dissolved in 10 ml of dry DMSO and maintained at 49°C. 3-Chlorophthalonitrile (2.0367 g, 12.5 mmoles) was added in portions with stirring over a period of 10 minutes. The temperature rose to 60°C. The reaction mixture was further stirred at 56-59°C for 0.5 hour and poured into 50 ml of water. The precipitate was filtered, redispersed in 200 ml of fresh water, filtered, and dried under vacuum. The crude 3-(3-aminophenoxy)phthalonitrile weighed 2.79 g (94.6%). The material was recrystallized from toluene with the aid of decolorizing carbon. The melting point of the pure material was 134.5-135.5°.

Anal. Calc. for $C_{14}H_9N_3O$: C, 71.48; H, 3.85; N, 17.87.

Found: C, 72.3; H, 4.4; N, 17.8.

Method B -- A mixture of o-aminophenol (2.705 g, 24.8 mmoles), 4-chlorophthalonitrile (4.031 g, 24.8 mmoles) and 20 ml of DMSO was stirred and heated at 55°C under nitrogen until a clear homogeneous solution resulted. Finely pulverized anhydrous potassium carbonate (13.56 g, 98.1 mmoles) was added in portions over a period of 5 minutes. The resulting mixture was stirred and heated at 74-78°C for 2 hours. It was cooled and poured into 60-70 ml of water with stirring. The precipitate was filtered, redispersed in fresh water, filtered and dried. The yield of crude 4-(2-aminophenoxy)phthalonitrile was 5.30 g (90.9%). The material was recrystallized from toluene with the aid of activated carbon. The pure material melted at 119.5-120°C.

Anal. Calc. for $C_{14}H_9N_3O$: C, 71.48; H, 3.85; N, 17.87.

Found: C, 70.5; H, 3.9; N, 17.8.

Preparation of Phthalonitrile-Terminated Oligoetherimide (XXXVIII) (PEI-3CN)

4,4'-Bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (51.046 g, 0.1000 mole) was dispersed in 60 ml of m-cresol and the mixture was heated at 90°C. To this mixture was added 4-(3-aminophenoxy)phthalonitrile (15.683 g, 0.06667 mole) in portions over a period of 0.5 hour. A m-cresol solution (20 ml) containing m-phenylenediamine (7.209 g, 0.06667 mole) and toluene (60 ml) were added to the above reaction mixture. The resulting mixture was stirred and heated to reflux for 0.5 hour during which time the water was removed by use of a Dean-Stark trap. Further dehydration was carried out at 140° for one hour by recirculating the refluxing solvent through a trap filled with Molecular Sieve. The product was precipitated in methanol and dried under vacuum. The yield of light yellow powder was 67.91 g (91.8%). The glass transition temperature was 144°C as measured by DSC. The intrinsic viscosity in chloroform was 0.098 dl/g.

Anal. Calc. for $C_{124}H_{64}N_{10}O_{20}S_3$: C, 70.58; H, 3.06; N, 6.64.

Found: C, 70.3; H, 3.3; N, 6.9.

Impregnation of Carbon Fiber Tow

Resin formulation #10543-24 (Table XXVIII) was diluted with m-cresol to a total solid concentration of 22 weight percent. Hercules type A.U. continuous carbon fiber tow (10,000 filaments) was continuously dipped at a speed of 5.5 ft/min through the above resin solution at room temperature. The wet tow was then taken up onto a drum, which was covered with Teflon coated aluminum foil in order to facilitate removal of the prepreg (Figure 13). Uniform distribution of the impregnated tow was achieved with the aid of a controlled guide pulley synchronized with take-up speed. The two-inch wide wet prepreg was dried on the drum by heating with two infrared lamps for one hour. It was then cut into three-inch long pieces.

Preparation of Carbon Fiber Composites

Two pieces of the above 2" x 3" prepreg were loaded unidirectionally in a mold and processed under various conditions as described in Table XXIX.

Post-Cure

The 2" x 3" composite plaque was cut along the fiber into 0.150 inch wide test specimens and subjected to post-curing in an oven in air.

Preparation of phthalonitrile-Terminated Polyethersulfone (XL)

A mixture of 4,4'-dihydroxydiphenylsulfide disodium salt (5.790 g, 22.08 mmoles), 4,4'-dichlorodiphenylsulfone (4.227 g, 14.72 mmoles), DMSO (40 ml) and benzene (20 ml) was stirred under nitrogen and heated to reflux at 125-130° for one hour. During this period the reaction mixture was thoroughly dried by recirculating the refluxing benzene through a trap filled with calcium hydride. The benzene was distilled off and the reaction mixture was heated at 160°C for 0.5 hour. The resulting reaction mixture was cooled to 90°C and 4-chlorophthalonitrile (2.393 g, 14.72 mmoles) was added. It was then heated at 100°C for 25 minutes, cooled to room temperature and poured into 300 ml of methanol. The white precipitate of the polymer was filtered, washed with water and dried under vacuum. The yield was 9.04 g (92.0%). The glass transition temperature was 100°C and the intrinsic viscosity in chloroform was 0.144 dl/g.

Anal. Calc. for $C_{76}H_{46}N_4S_5O_{10}$: C, 68.34; H, 3.47; N, 4.20.
Found: C, 68.1; H, 3.7; N, 4.0.

Preparation of o-Diaminophenyl-Terminated Polyetherquinoxaline (XLIII)

3,3',4,4'-Tetraaminobenzophenone (1.938 g, 8 mmoles) was dissolved in 15 ml of m-cresol at 140°C under nitrogen. The solution was cooled to 50°C and 4,4'-bis(phenylglyoxaloylphenoxy)diphenyl ether (3.712 g, 6 mmoles) was added over a period of 10 minutes. About 10 ml of toluene was added and the mixture was heated to reflux for 0.5 hour. The water was removed by recirculating the refluxing toluene through a trap filled with Molecular Sieve. The reaction mixture was then poured into 400 ml of methanol stirred in a blender. The precipitated oligomer was filtered, washed with methanol and dried under vacuum. The yield was 5.03 g (96.4%). The glass transition temperature was 203°C. The intrinsic viscosity measured in chloroform was 0.182 dl/g.

Anal. Calc. for $C_{172}H_{110}N_{16}O_{13}$: C, 79.18; H, 4.25; N, 8.59.
Found: C, 77.9; H, 4.5; N, 8.1.

Preparation of Phthalonitrile Ethers (XLIV)

Two typical examples are given below:

1) 3-Chlorophthalonitrile (2.00 g, 0.0123 mole) was dissolved in dry DMSO (10 ml). 4,4'-Dihydroxydiphenylsulfide disodium salt (1.61 g, 0.00614 mole) was added in portions to the above solution over a period of 20 minutes. The resulting reaction mixture was stirred at 42-44°C for 2 hours, and then poured into 30 ml of water. The precipitate was filtered, washed with water and dried under vacuum at 80°C. The yield of 4,4'-bis(2,3-dicyanophenoxy)diphenylsulfide was 2.75 g (95.2%). The product was recrystallized from 25 ml of *o*-dichlorobenzene with the aid of activated carbon. The pure material melted at 247.5-248.5°C.

Anal. Calc. for $C_{28}H_{14}N_4SO_2$: C, 71.47; H, 3.00; N, 11.91.
Found: C, 70.9; H, 3.1; N, 11.7.

2) 4-Chlorophthalonitrile (19.512 g, 0.1200 mole) and phloroglucinol (5.049 g, 0.0400 mole) were dissolved in 50 ml of dry DMSO under nitrogen. Finely pulverized potassium carbonate (68.25 g, 0.4935 mole) was added in portions with stirring at 85°C. The addition took 15 minutes and the temperature rose to 134°C. The reaction mixture was cooled and then stirred at 104-109°C for 0.5 hour. The mixture was poured into 150 ml of water. The crystalline precipitate of 1,3,5-tris(2,3-dicyanophenoxy)benzene was filtered, washed with water and dried. The yield was 15.53 g (77.0%). The material was recrystallized from cyclohexanone and triturated with ethanol. The yield of pure product was 11.92 g, mp 271-272°C.

Anal. Calc. for $C_{30}H_{12}N_6O_3$: C, 71.43; H, 2.40; N, 16.66.
Found: C, 72.2; H, 2.7; N, 16.7.

REFERENCES

1. J. Verborgt and C. S. Marvel, J. Polymer Sci., A-1, 11, 261 (1973).

2. D. I. Packham and F. A. Rackley, Polymer, London, 1969, 10, 559.

3. D. I. Packham and J. C. Haydon, Polymer, London, 1970, 11, 385.

4. R. J. Gaymans, K. A. Hodd and W. A. Holmes-Walker, Polymer, London, 1971, 12, 400.

5. E. Woehrle, Makromol. Chem., 160, 83 (1972); ibid., 99 (1972).

6. a) R. N. Johnson et al, J. Polymer Sci., A-1, 5, 2375 (1967).
   b) W. F. Hale et al, ibid., 2399 (1967).
   c) R. N. Johnson et al, ibid., 2415 (1967).

7. M. E. A. Cudby et al, Polymer, London, 6, 589 (1965).

8. J. B. Rose, Polymer, London, 15, 456 (1974).

9. a) P. M. Hergenrother and H. H. Levine, J. Polymer Sci., A-1, 5, 1453 (1967).
   b) P. M. Hergenrother, J. Polymer Sci., A-1, 6, 3170 (1968).
   c) W. Wrasidlo and J. M. Augl, J. Polymer Sci., B, 7, 281 (1969).
   d) Ibid., A-1, 7, 3393 (1969).
   e) P. M. Hergenrother and D. E. Kiyohara, Macromolecules, 3, 387 (1970).
   f) P. M. Hergenrother, J. Macromol. Sci., C6, 1 (1961).
   g) F. L. Hedberg and F. E. Arnold, J. Polymer Sci., A-1, 12, 1925 (1974).

10. a) G. P. DeGaudemaris and B. J. Sillion, J. Polymer Sci., B, 2, 203 (1964).
    b) J. K. Stille and J. R. Williamson, J. Polymer Sci., B, 2, 209 (1964).
    c) Ibid., A, 2, 3867 (1964).
    d) J. K. Stille, J. R. Williamson, and F. E. Arnold, J. Polymer Sci., A, 3, 1013 (1965).
    e) J. K. Stille and F. E. Arnold, J. Polymer Sci., A, 3, 551 (1966).

11. D. R. Heath and J. G. Wirth, U.S. Patent 3,852,244 (1975).

12. P. M. Hergenrother, U.S. Patent 3,852,243 (1974).

13. D. R. Heath and J. G. Wirth, U.S. Patent 3,869,499 (1975).

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