AFML-TR-70-250

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HIGH TEMPERATURE LAMINATING RESINS

Abraham L. Landis
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TECHNICAL REPORT AFML–TR–70–250

DECEMBER 15, 1970

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FOREWORD

This report summarizes the work performed under United States Air Force Contract F33615-69-C-1463, "Research on High Temperature Laminating Resins Having Improved Processability", Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734003, "Structure Plastics and Composites." The contract is administered by the Air Force Materials Laboratory, Nonmetallic Materials Division, with Mr. T. J. Aponyi serving as Project Engineer.

The principle investigator on the program is Dr. Abraham L. Landis. Professional assistance was furnished by Dr. Raymond J. Andres and Dr. Daniel A. Demeo. Technical assistance was provided by Mr. Raymond E. Lawrence, Mr. Auturo Castillo, Mr. Joe Madden, Mr. Herman Noji, Mr. Carl Mehrbach and Mrs. Lorraine Ryan. Professional consultation with Dr. Norman Bilow, Dr. Richard Akawie and Dr. Leroy J. Miller of Hughes Aircraft Company is gratefully acknowledged.

This report covers results of research efforts during the period of 15 May 1969 to 15 August 1970. The Hughes Internal Report Number is P70-409. The report was released by the author September 1970.

This technical report has been reviewed and is approved.

J. D. Ray

J. D. RAY, Chief
Plastics and Composites Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Nitrile-terminated polyimides were prepared by the reaction of benzophenonetetracarboxylic dianhydride (BTDA), aromatic diamines and meta- or para-aminobenzonitriles. At least two ether linkages were necessary per repeating unit to yield a fusible and soluble prepolymer provided the oligomer had no more than three repeating units. Using sulfolane as a solvent these oligomers could be A-staged with terephthalonitrile N, N'-dioxide (TPDO) to yield curable resins. A compressive strength of 7890 psi was obtained for a TPDO-cured resin made from BTDA, bis[4-(3-aminophenoxy)phenyl] ether, 2, 6-bis(3-aminophenoxy)aniline and meta-aminobenzonitrile. A flexural strength of 43.1×10^3 psi and a modulus of 2.0×10^6 psi were obtained for a glass cloth laminate using a TPDO-cured resin made by the reaction of BTDA, 1, 3-di(3-aminophenoxy)benzene, 2, 6-bis(4-aminophenoxy)aniline, and meta-aminobenzonitrile. Synthetic techniques were explored for preparing acetylene-substituted polyimides which could be cured by reaction with TPDO. The reaction between acetylene derivatives and nitrile oxides appears to proceed by an addition type reaction and can serve as the basis of curing resins containing acetylenic groups.

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SECTION I

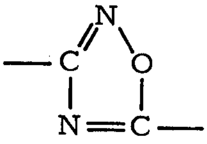
INTRODUCTION

Although many high polymers have been synthesized for high temperature application, frequently their applications are limited because of difficulties in processing them into end-use applications. Many are intractable or have limited solubility. These properties in particular limit their use in laminates. Also during the cure cycle volatile by-products may be emitted, which besides requiring high molding pressures to minimize porosity also may yield resin starved laminates.

The present study is aimed at developing high temperature stable polymers that are soluble in selected common solvents prior to cure and consequently satisfactory for use in lacquers suitable for impregnation of fiber reinforcements. Furthermore, these polymers are fusible in their prepolymer form and are curable under mild conditions into high-molecular weight thermally stable resins. Very little or no volatile material are liberated during cure; therefore curing can be accomplished with little applied pressure, and the cured composite structures will have extremely low void contents.

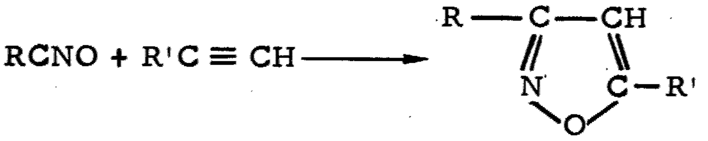
To meet these objectives, reactions of functional groups were chosen such that either linear or branched chain extensions occur by addition rather than condensation reactions. For the resin to be thermally stable the structure resulting from this addition reaction must be thermally stable as well as oxidation resistant. To best achieve these properties the structure formed should be aromatic in nature and also should have no active hydrogen. Aliphatic groups and active hydrogen tend to decrease thermal stability at elevated temperatures. For good structurally sound laminates, the prepolymers should be fluid during the initial molding so that proper flow can take place around the reinforcement.

The group of polymers which have received the greatest attention during the reporting period of this summary report are linked through the 1,2,4-oxadiazole rings formed by the reaction of the dinitrile N, N'-dioxide with dinitriles. The resulting 1,2,4-oxadiazole structure can be depicted as follows:



Polyimides have been found to posses exceptionally good thermal properties. They, therefore, have been used as films for high temperature electrical insulation. However, due to the outgasing during curing they have found limited use for laminating resins. By using nitrile terminated polymides, the cure by an addition type reaction would be possible and therefore extend its use for laminating resins. The curing of nitrile terminated polymides by such a reaction would represent a significant advancement over the present state-of-the-art. The use of polyimides as a laminating resin is based on a two stage condensation reaction between an aromatic dianhydride and an aromatic diamine. In the first step, the reactants are converted to a polyamic acid. The second stage involves conversion of the polyamic acid to the polyimide with the evolution of water. Thus, a soluble and fusible polyamic acid is converted to an insoluble infusible polyimide. Because of these properties, the nitrile-terminated polyimides must have both the molecular structure and molecular weight so that they are still soluble and fusible. To achieve these properties the nitrile-terminated prepolymers must be kept short, probably no longer than three repeating units. Also, to be fusible they must have flexibility in the main polymer chain. Fusibility at relatively low temperatures is necessary to avoid decomposing the nitrile oxide curing agent before it can add to the nitrile group. Flexibility as well as solubility was achieved by introducing ether linkages into the polymer chain.

The second group of polymers which has received some attention in the preliminary investigation includes prepolymers that have acetylenic groups present. These polymers can be cured by means of the addition reaction between nitrile oxides and acetylene. This reaction proceeds to form isoxazole rings according to the addition reaction shown below.[1]



As with the oxadiazoles, the reaction yields no volatile by-products. Polymers have been prepared by Overberger and Fujimoto[1] by treating 1,4-diethynylbenzene with terephthalonitrile N,N'-dioxide. These polymers were reported to be infusible up to 500° C (932° F) in an inert atmosphere. Thermogravimetric analysis indicated that this polymer was stable in air up to 400° C (752° F). These results suggest that such addition reactions yield bonds which have excellent thermal and oxidative stability.

Acetylene-containing monomers which can be incorporated into polyimide prepolymers have been made. The technology developed for curing the nitrile-terminated polyimide prepolymers with nitrile oxides such as terephthalonitrile N,N'-dioxide is directly applicable to the acetylene-terminated polyimide prepolymers. Also, the further possibility exists of effecting a trimerization of acetylene groups to form aromatic rings.

The two systems thus far considered, namely, the nitrile-terminated polyimides and the acetylene terminated polyimides, have thermal properties similar to those of the polyimides, while retaining the advantage of curing through an addition reaction with essentially no release of volatile by-products.

SECTION II

SUMMARY

Nitrile-terminated polyamic acids were prepared by the reaction of benzophenonetetracarboxylic dianhydride and aromatic diamines such as meta-phenylenediamine, para-phenylenediamine, benzidine, bis (4-aminophenyl) ether, 1, 3 di(3-aminophenoxy)benzene, 1, 3-di(4-aminophenoxy) benzene, and bis [4-(3-aminophenoxy)phenyl] ether. Meta- or para-aminobenzonitrile is then reacted with the anhydride-terminated polyamic acid to introduce a nitrile substituent. These polyamic acids were converted to polyimides using acetic anhydride as the dehydrating agent. At least two ether linkages were necessary per repeating unit to yield a fusible and soluble prepolymer provided the oligomer had no more than three repeating units. Using sulfolane as a solvent these oligomers could be A-staged with terephthalonitrile N, N'-dioxide to yield curable resins. A compressive strength of 7890 psi was obtained for a terephthalonitrile N, N'-dioxide cured resin made from benzophenonetetracarboxylic dianhydride, bis [4-(3-aminophenoxy)phenyl] ether, 2, 6-bis(3-aminophenoxy)aniline and meta-aminobenzonitrile. A flexural strength of 43. 1 x 10^3 psi and a modulus of 2. 0 x 10^6 psi were obtained for a glass cloth laminate using a terephthalonitrile N, N'-dioxide cured resin made from the reaction of benzophenonetetracarboxylic dianhydride; 1, 3-di(3-aminophenoxy)benzene, 2, 6-bis(4-aminophenoxy)aniline, and meta-aminobenzonitrile. Synthetic techniques were explored for preparing acetylene substituted polyimides which could be cured by reaction with terephthalonitrile N, N'-dioxide. Several approaches appear particularly promising for preparing these derivatives. The reaction between acetylene derivatives and nitrile oxides appears to proceed easily by an addition type reaction and can serve as the basis for curing resins containing acetylenic groups.

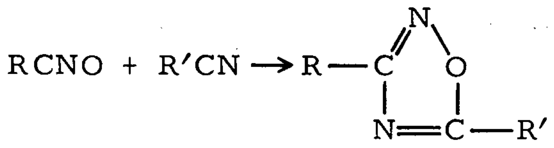
SECTION III

MATERIALS SYNTHESIS AND MOLDING STUDIES

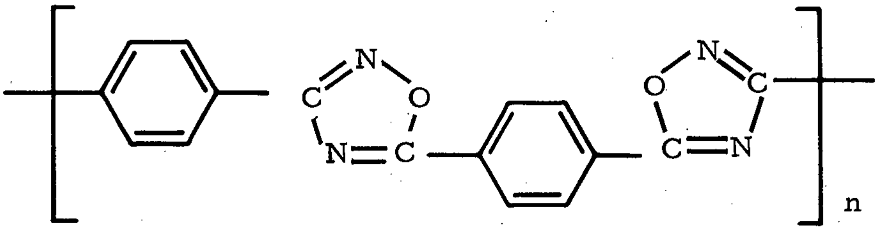
1. DISCUSSION

a. Curing of Nitrile-Substituted Polyimide Oligomers with Terephthalonitrile N,N'-Dioxide

The objective of this task was to develop a readily processable laminating resin that could cure without the use of high pressures and would yield a thermally stable resin. The approach selected was based on the formation of the 1,2,4-oxadiazole ring from the reaction of the nitrile group and the nitrile oxide. Because of the outstanding thermal and hydrolytic stability of the 1,2,4-oxadiazole ring*, this structure is an excellent candidate for high temperature polymers. This heterocyclic structure is formed by the addition reaction of nitrile oxide with nitriles according to the following equation:



Unlike many addition reactions the addition of a nitrile oxide to a nitrile group is not readily reversible. The reaction between nitrile oxides and nitrile groups has in recent years received a great deal of study. Thus, Overberger and Fujimoto[1] copolymerized terephthalonitrile N,N'-dioxide with terephthalonitrile in benzene solution to give a copolymer illustrated below.



A similar polymer was obtained by Akiyama, Iwakura, Shiraishi and Imai[2] by the solid state cycloaddition polymerization of p-cyanobenzonitrile oxide. The resulting polymer did not change on heating up to 350°C. This polymer was insoluble in common organic solvents but soluble in concentrated sulfuric acid. Also, an inherent viscosity of 0.75 was obtained for this polymer in concentrated sulfuric acid.

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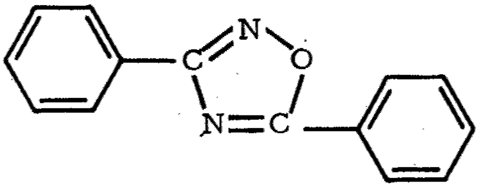
*This applies only to the aromatic substituted compounds.

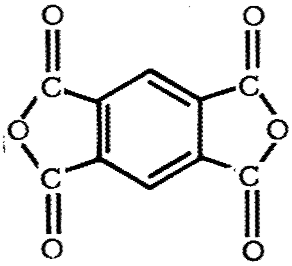
The model compound, 3,5-diphenyl-1,2,4-oxadiazole, which is illustrated below,



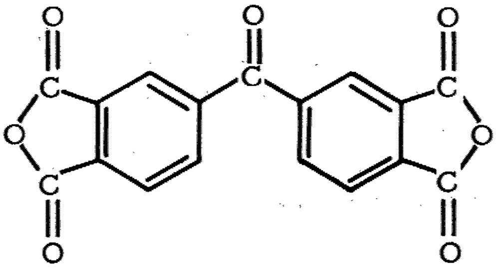
did not start to decompose until heated to 340°C. Upon further heating cleavage of the oxadiazole ring to give phenyl isocyanate and benzonitrile took place.[3]

Nitrile-terminated polyimides are good candidates as prepolymers for cure by terephthalonitrile N, N'-dioxide since polyimides have been well characterized as thermally stable polymers. The success in achieving a workable resin system using nitrile-terminated polyimide prepolymer depends upon the synthesis of a soluble, fusible nitrile terminated polyimide prepolymer. Polyimides tend to be infusible and intractable once they are formed from the polyamic acid prepolymer. Therefore, to achieve soluble and fusible nitrile terminated prepolymers, the molecular weight must be kept low.

In the present study the nitrile-terminated prepolymer was made in a several step reaction. First, an aromatic diamine is reacted with an aromatic dianhydride to yield a polyamic acid. At this point the stoichiometry of the reactants is important in determining the molecular weight of the polyamic acid; the maximum molecular weight results when the molar ratio of the diamine to the dianhydride is one. The stoichiometry is adjusted so that there are no more than three repeating units. By using an excess of a dianhydride, the initial polyamic acid is terminated by an anhydride group. The anhydride-terminated prepolymer is then capped with a nitrile group by reaction with meta-aminobenzonitrile. At this point in the preparation, the resulting polyamic acid is soluble in polar solvents such as dimethylformamide or N-methyl-2-pyrrolidinone. The polyamic acid is then converted to the polyimide by dehydration with acetic anhydride or heat. The two acid anhydrides most typically used to prepare polyimides are pyromellitic dianhydride and benzophenonetetracarboxylic dianhydride. Their structures are shown by I and II respectively.

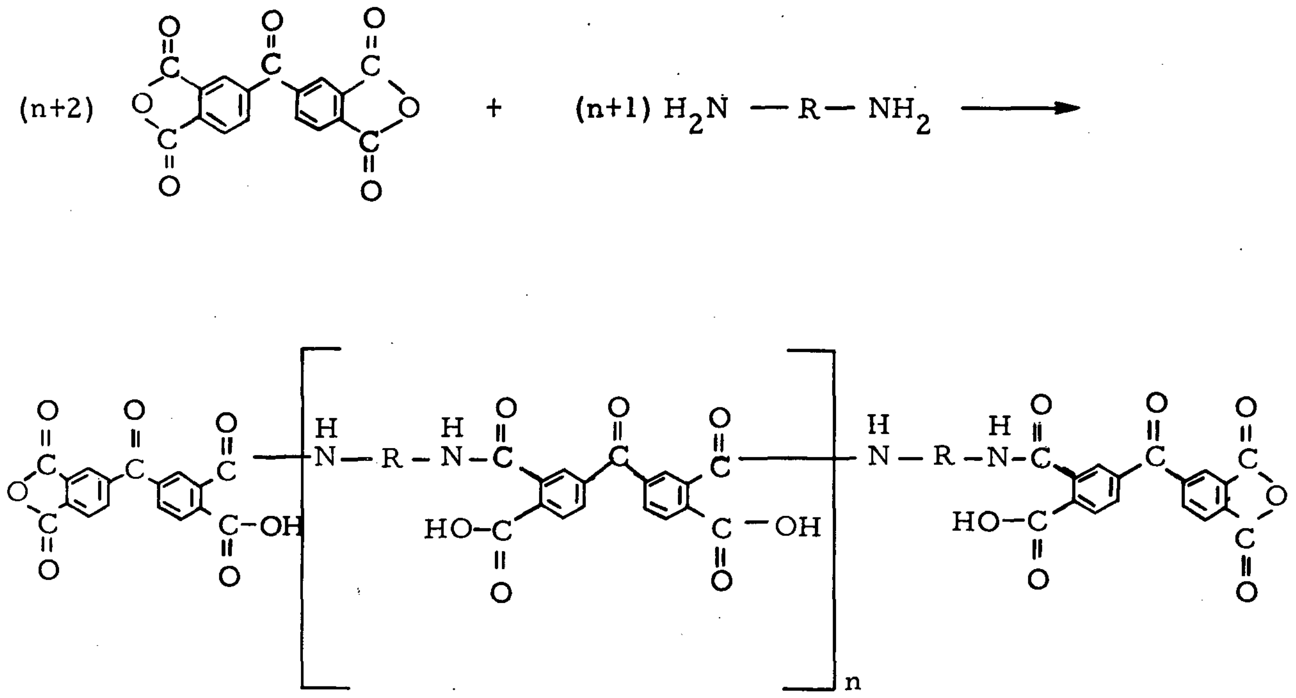


(I)

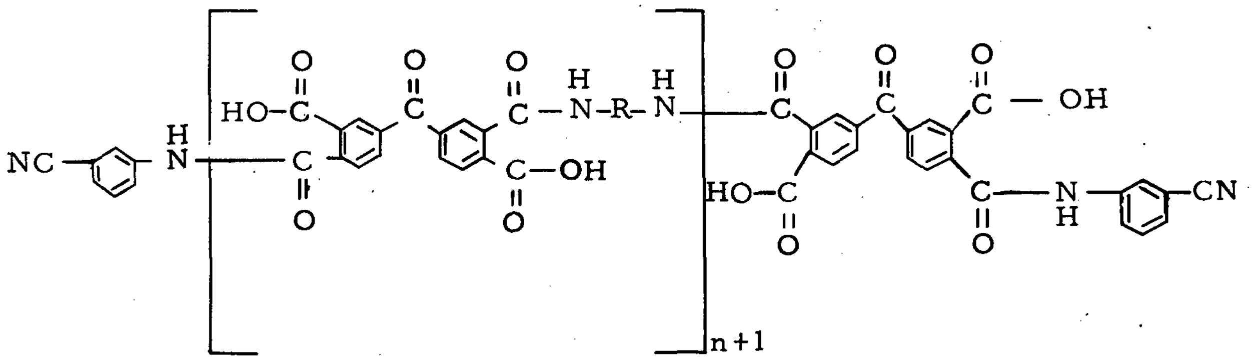


(II)

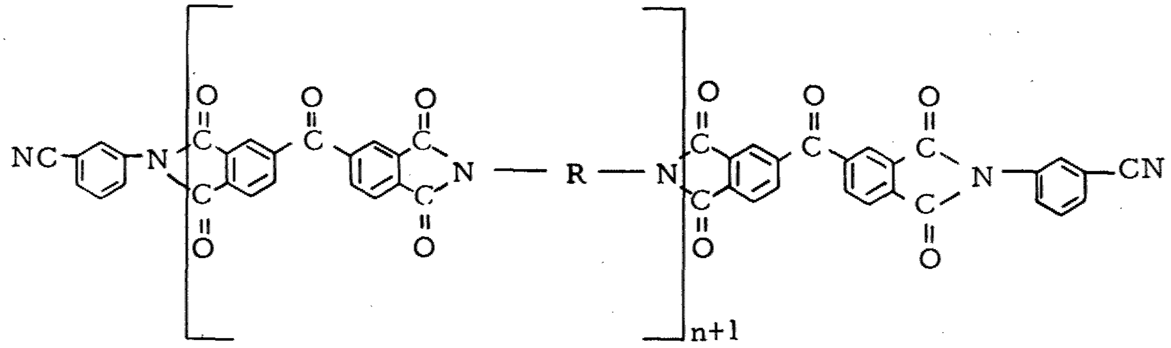
Because of the less rigid structure of the benzophenonetetracarboxylic dianhydride this compound was the anhydride employed in the present study. It is available commercially in good purity. The formation of the nitrile terminated polyamic acid is shown by the following equation.



The anhydride-capped polyamic acid is then reacted with meta-aminobenzonitrile to yield a polyamic acid of the following structure



The above prepolymer is then converted to the polyimide by treatment with acetic anhydride. The polyimide has the following structure:

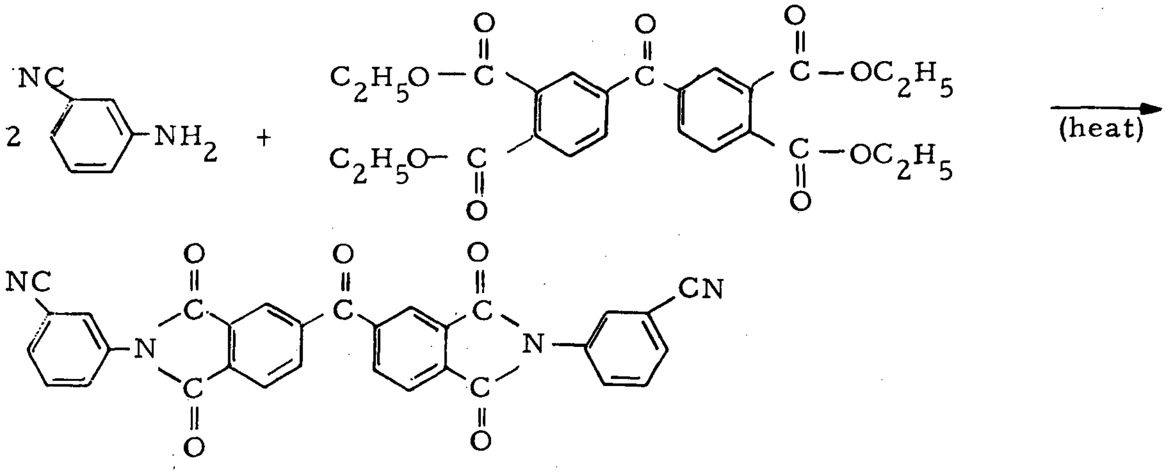


The value of n in the above nitrile-terminated polyimide prepolymer depends on the stoichiometry of the dianhydride and the diamine. This is shown in the chart below

n	Molar Ratio of Dianhydride to Diamine
0	2.00
1	1.50
2	1.33
3	1.25
$n \rightarrow \infty$	1.00

Thus, in order to keep the prepolymer short, the ratio of dianhydride to diamine should be kept close to the value of 2.

To study the feasibility of synthesizing nitrile terminated polyimides using the reaction of an ester derivative rather than the anhydride with the amine, a model compound was chosen in which tetraethyl benzophenonetetracarboxylate was reacted with meta-aminobenzonitrile (Experiment E2246-69). Ideally the reaction should take place in the manner shown on the following page.

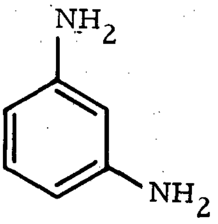


However, the reaction was only partial as indicated by the amount of ethanol recovered. This method of preparation of polyimides does not appear to offer any advantage over the reaction of dianhydrides with diamines and will not be investigated any further.

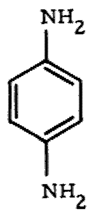
From the results of experiments F1625-01 and F1625-03 in the synthesis of polyamic acids, it appears that the order and rate of addition of reactants are critical in controlling the molecular weight. Since relatively low molecular weight telomers are desired for this study, the relatively rapid addition of the diamine to the dianhydride is used to give the low molecular weight telomers. Also, by capping the end groups of polyimides with nitrile groups, the resulting polymer is made both tractable and soluble.

The first phase of the present study involved the preparation of a soluble and fusible nitrile terminated polyimide. To learn the structural criteria necessary to obtain these properties a series of nitrile-terminated polyimides was prepared using the same dianhydride, namely benzophenone-tetracarboxylic dianhydride but varying the aromatic diamine and in some case the aminobenzonitrile used to cap the polyimide.

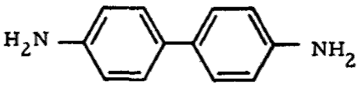
The diamines used in this study and their structure are shown below.



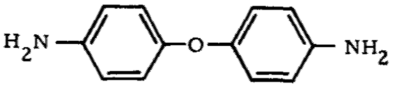
meta-phenylenediamine



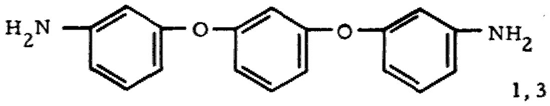
para-phenylenediamine



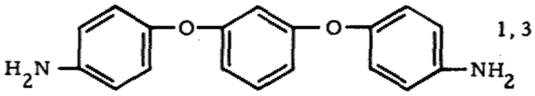
benzidine



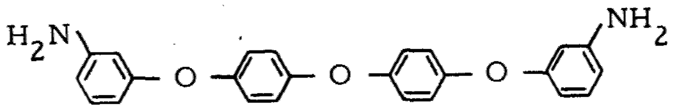
bis(4-aminophenyl) ether



1,3-di(3-aminophenoxy) benzene



1,3-di(4-aminophenoxy) benzene



bis[4-(3-aminophenoxy)phenyl] ether

Nitrile-terminated polyimides were prepared using stoichiometry such that the prepolymer contained only one repeating unit. Table I lists the nitrile-terminated polyimide prepolymers in order of solubility and fusibility, the most soluble being at the bottom of the table. In general, the fusibility increased in the same order as the solubility.

Table I points out some very significant trends. Aromatic diamines which have rigid structures, such as para-phenylenediamine, meta-phenylenediamine and benzidine, generally result in nitrile-terminated polyimides which have limited solubility in polar solvents even for 1 or 2 repeating units. Also, the high temperatures necessary for flow would involve processing difficulties for use as resins for laminates. The melting points of these prepolymers are too high for satisfactory cures with a curing agent such as terephthalonitrile N, N'-dioxide. It is only upon the introduction of ether linkages into the polymer backbone that this difficulty can be overcome. The diamino aryl ether, bis(4-aminophenyl) ether is well known and is available commercially. As the number of ether linkages is increased, both the solubility and fusibility of the polymer are also increased. Also, the introduction of such ether linkages should not compromise the thermal stability of the prepolymer. Phenylene oxides, such as Monsanto's OS-124, which is a mixed isomeric 5-ring polyphenyl ether, have excellent thermal stability.[4]

It is noteworthy that the introduction of ether linkages improves processability without compromising thermal properties in polyimide resins used to prepare glass cloth reinforced laminates.

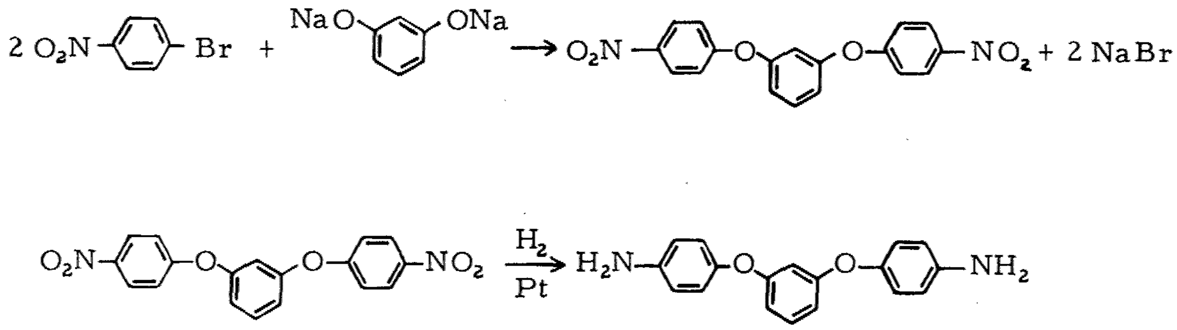
Table I. Trends in Solubility and Fusibility of Nitrile Terminated Polyimide Oligomers

Resin No.	Aromatic Diamine	Aminobenzonitrile Derivative		
		para	meta	
E2246-74a	para-phenylenediamine		X	Increase in Solubility and Fusibility ↓
F1625-23	benzidine		X	
E2246-82	meta-phenylenediamine	X	X	
F1625-14	meta-phenylenediamine	X		
E2246-71A	benzidine	X		
E2246-86	4, 4'-Diaminobiphenylether	X	X	
E2246-84	4, 4'-Diaminobiphenylether		X	
E1812-08	1, 3-di(4-aminophenoxy) benzene		X	
F1986-17	1, 3-di(3-aminophenoxy) benzene		X	
F1812-15	bis[4-(3-aminophenoxy)phenyl] ether		X	

To learn the effects of introducing an additional ether linkage into the polyimide resin, a polyamic acid was prepared by the reaction of equimolar amounts of benzophenonetetracarboxylic dianhydride and 1, 3-di(4-aminophenoxy)benzene in a solvent consisting of N-methyl-2-pyrrolidinone and N, N-dimethylacetamide (Experiment F1812-11). This resin showed better flow characteristics than that made using bis(4-aminophenyl) ether which is presently being used in polyimide resins. Also, when a glass cloth reinforced laminate was made from this resin, a relatively low molding pressure of 125 psi at 350°F to 600°F yielded a laminate which had a flexural strength of 26,120 psi and a modulus of elasticity of 1.87×10^6 psi. The molding characteristics of this resin have not been optimized, but with optimum molding parameters laminates can be fabricated with much lower void content than those prepared from the polyimides presently used because of the lower amounts of outgassing.

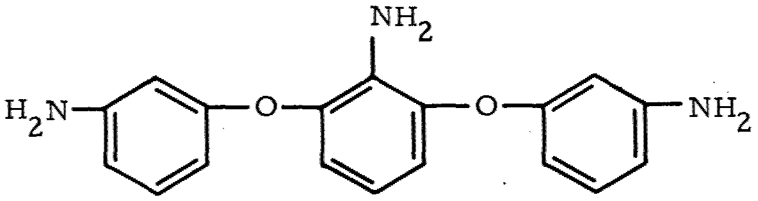
The glass-reinforced laminate did not show any weight loss when kept at 600°F for 10 hours in air. This shows that the loss of volatile products was complete during the molding operation and that the thermal stability was not sacrificed by the introduction of additional ether linkages.

The diamino aryl ethers used in the present study were prepared by a modified Ullman ether synthesis.[5] For illustrative purposes the synthesis of 1, 3-di(4-aminophenoxy)benzene is shown below.

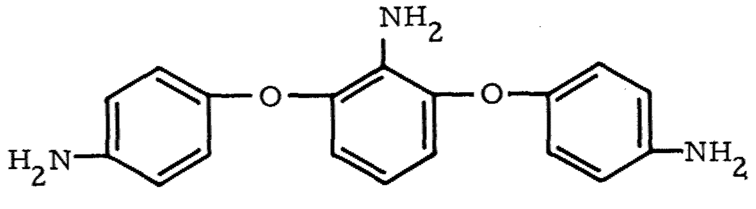


The effect of ether linkages in changing the solubility properties is shown by comparison of resin E2246-86 using bis(4-aminophenyl) ether and resin E1812-08 where 1, 3-di(4-aminophenoxy)benzene was employed. In experiment F1812-08, benzophenonetetracarboxylic dianhydride was reacted with 1, 3-di(4-aminophenoxy)benzene in a 2:1 molar ratio using dimethylformamide as the solvent. After capping the prepolymer with nitrile groups using meta-aminobenzonitrile, the polyamic acid was imidized by heating it at reflux in acetic anhydride. Unlike the resin prepared from bis(4-aminophenyl) ether this resin was appreciably more soluble in N-methyl-2-pyrrolidinone.

The most soluble and fusible nitrile terminated polyimides were those made from the aromatic diamines, 1, 3-di(3-aminophenoxy)benzene and bis[4-(3-aminophenoxy)phenyl] ether. Because of the good solubility and good flow at relatively low temperatures, higher molecular weight oligomers using these aromatic diamines are possible. This would materially increase the strength of the resins for laminates. To obtain the necessary nitrile functionality for curing sites as well as sites for crosslinking, several triamino aryl ethers were prepared using the same synthetic techniques for the preparation of the diamino aryl ethers. The compounds, 2, 6-di(3-aminophenoxy)aniline and 2, 6-di(4-aminophenoxy)aniline were prepared. Their structures are shown below.



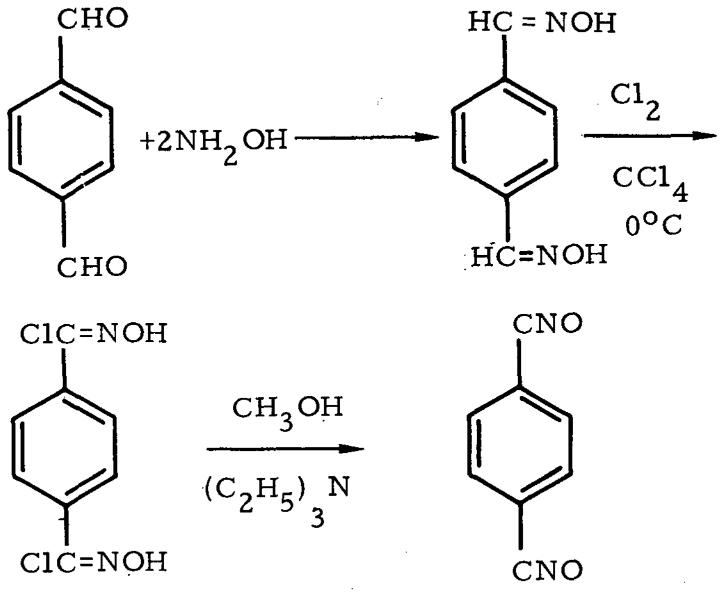
2, 6-di(3-aminophenoxy)aniline



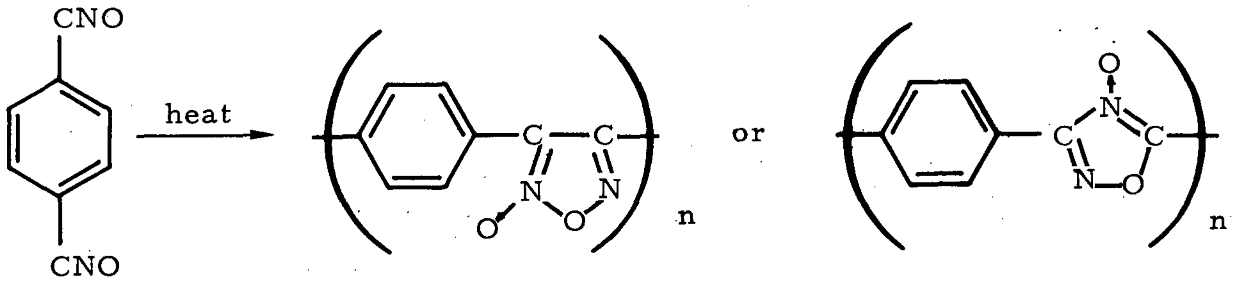
2, 6-di(4-aminophenoxy)aniline

The above amines are quite unstable as is evidenced by the fact that they darken shortly after preparation and develop an aniline like odor. The instability of these amines may be due to the presence of impurities since the nitro-derivative from which the amine is derived has not been isolated in good purity.

With the feasibility of preparing soluble and fusible nitrile terminated polyimides demonstrated, the next phase of the program was to study how the nitrile groups can most effectively be used to effect a cure by reaction with nitrile oxide to form the 1, 2, 4-oxadiazole ring. The difunctional nitrile oxide which has received the greatest amount of study in recent years is terephthalonitrile N, N'-dioxide. It is prepared by the following reaction.



At room temperature, crystalline terephthalonitrile N, N'-dioxide is relatively stable. In solution and also at elevated temperatures it homopolymerizes to the furoxan (1,2,5-oxadiazole-4-oxide) or oxazoxime (1,2,4-oxadiazole-4-oxide). This reaction is shown by the equation below.



Thus, in using this compound to cure the nitrile-terminated polyimide one has to find the conditions which promote the addition of the nitrile group to the nitrile oxide over homopolymerization. Successful additions of terephthalonitrile N, N'-dioxide with terephthalonitrile have been carried out by Overberger and Fujimoto by addition of solid terephthalonitrile N, N'-dioxide to a benzene solution of terephthalonitrile. Theoretically, two nitrile groups per prepolymer molecule should be enough to provide the necessary functionality for chain growth. Because of homopolymerization of the nitrile oxide, an excess of nitrile oxide is required to react with all the nitrile groups.

N-methylpyrrolidinone was investigated for use as a solvent for A-staging a nitrile terminated polyimide resin with terephthalonitrile N, N'-dioxide. An infrared spectrum of a resin, E2246-88 made by the copolymerization of benzophenonetetracarboxylic dianhydride, bis(4-aminophenyl) ether and meta-aminobenzonitrile in proportions chosen so that there was only one repeating unit in the polymer chain, gave the characteristic nitrile absorption band at 4.5 μ as well as other bands characteristic of this resin. The nitrile-terminated polyimide was dissolved in N-methyl-2-pyrrolidinone and a 40 percent excess of terephthalonitrile N, N'-dioxide was added. The mixture was warmed and the solvent removed using a rotary evaporator. The resulting product showed a weaker 4.5 μ band, showing the partial loss of the nitrile group. Furthermore, there was complete disappearance of a 5.4 μ band and 11.4 μ band and the emergence of a new absorption at 15.25 μ. There is no band near 15.25 μ in the spectra of either the initial prepolymer or the nitrile oxide. An examination of the product of homopolymerization of terephthalonitrile N, N'-dioxide (Experiment E2246-92) showed the presence of a 15.1 μ band. Thus, during the cure of nitrile-terminated polyimides, chain extension by the reaction of the nitrile group and nitrile oxide group proceeds at the same time as that of homopolymerization of the terephthalonitrile N, N'-dioxide.

An experiment was carried out to evaluate Resin E2246-88 as a laminating resin. Thus a lacquer containing this resin was made by dissolving the resin in N-methylpyrrolidinone. To insure the presence of an adequate amount of terephthalonitrile N, N'-dioxide a threefold excess was used (Experiment E2246-91). A 10 ply, 4" x 1" glass cloth reinforced laminate was prepared. The resulting laminate was molded at 500°F and 50 psi and had a resin content of 23.8 percent. This laminate exhibited a flexural strength of 11.0×10^3 psi. An experiment was then performed to determine the effect of increasing the molecular weight of the prepolymer on the molding characteristics. A resin synthesized with two repeating units in the polymer chain (Resin E2246-97) compared to one in the previous experiment was used to prepare a glass cloth reinforced laminate. Again a threefold excess of terephthalonitrile N, N'-dioxide was used. The laminate when molded under the same conditions as in the previous case was very poor. The resin showed practically no flow. There are several possible reasons to account for these results. First, homopolymerization of the terephthalonitrile N, N'-dioxide may be taking place in preference to the addition of the nitrile oxide group, and second, the presence of only one ether linkage in the polymer chain may be insufficient to give the resin the flow necessary during molding to yield a good laminate.

To investigate the effect of increasing ether linkages in the polymer chain on yielding a processable resin which can be cured with the terephthalonitrile N, N'-dioxide, Resin F1812-08 was prepared. This resin was similar to the resin described above with the exception that 1, 3-di(4-aminophenoxy)-benzene was used as the diamine rather than the bis(4-aminophenyl) ether used previously. This meant that there was one additional ether linkage in the polymer chain. Also, instead of the N-methyl-2-pyrrolidinone used as a solvent in the previous resin, dimethylformamide was used here. To test the ability of terephthalonitrile N, N'-dioxide to cure the resin, a solution of the resin was made in dimethylformamide using a threefold excess of terephthalonitrile N, N'-dioxide.

The solvent was removed and the resin vacuum-dried at 80° C. This resin started to soften at 140° C and at 180° C was very fluid and started to harden on the melting point block. The resin was molded into a pellet at 400° F and 200 psi. The 17 minute contact time proved to be a bit too short as evidenced by the compressive strength (600 psi).

It appeared that further advancement of the resin was necessary to obtain better physical properties. This was borne out subsequently by advancing the resin further before molding (Experiment F1812-12). Thus, a solution of the resin (Experiment F1812-08) in dimethylformamide was A staged by the gradual addition of a threefold excess of terephthalonitrile N, N'-dioxide at 65° C compared to the 50° C used after the previous experiment. After stripping off the solvent the resin was further advanced for 20 minutes at 225° F and then molded at 400° F and 200 psi. The compressive strength of this resin was 1060 psi. Undoubtedly further improvement in compressive strength can be realized from this resin through optimizing the curing and molding parameters. Examination of the pellet showed that further improvement in flow properties would be necessary for any significant improvement.

A more soluble and fusible nitrile-terminated polyimide should result from either increasing the ether linkages in the nitrile-terminated polyimide prepolymer or using an amine with meta-aminophenoxy rather than para-aminophenoxy groups. Experiment F1812-15 which used the bis[4-(3-aminophenoxy)phenyl] ether showed that this approach was fruitful. Thus, using dimethylformamide as the solvent, 2 moles of benzophenonetetracarboxylic dianhydride was reacted with one mole of bis[4-(3-aminophenoxy)-phenyl] ether and then capped with nitrile groups using 2 moles of meta-aminobenzonitrile. The resin was then imidized with acetic anhydride. The resulting resin started to soften at 80° C and was quite fluid at 100° C. In terms of fluidity and solubility a decided improvement had been made over experiment F1812-08. This resin was treated with a threefold excess of terephthalonitrile N, N'-dioxide to yield a prepolymer which started to soften at 80° C and became quite fluid at 120° C. The resin started to harden upon further heating. By 220° C the resin had set up appreciably.

Because of the good solubility and low melting point of the polymer in experiment F1812-15, it appears that good solubility and fusibility is possible not only with prepolymers having only one repeating unit but also with higher molecular weight prepolymers. This would materially increase the strength of the resin for laminates. Also, the desired amount of cross-linking can be introduced into the polymer matrix by adding a small amount of triamino aromatic ethers.

Because of the possibility of extensive homopolymerization of the terephthalonitrile N, N'-dioxide before reaction with the nitrile groups on the polymer a new solvent system for A staging the resin was investigated. The work of Klein and Fouty[6] showed that they could get almost quantitative reaction between terephthalonitrile N, N'-dioxide and aromatic dinitriles provided they employed a solvent which was inert to the dinitrile oxide and in which the dinitrile oxide was insoluble. The solvent should, however, dissolve the aromatic dinitrile. They performed these polymerizations in solvents such as diglyme, tetraglyme, veratrole, or tetramethylene sulfone. The polymerizations went quite well at room temperature. To learn if tetramethylene sulfone or sulfolane could effectively be used to A stage some nitrile-terminated polyimides, a series of experiments were performed. The sulfolane was found to be a good solvent for many of the nitrile-terminated polyimides. A typical experiment involved adding part of a three- or six-fold excess of terephthalonitrile N, N'-dioxide to a solution of the prepolymer in sulfolane and stirring at room temperature for 24 hours. At this time some undissolved terephthalonitrile N, N'-dioxide was still present. The solution was then heated to 50° C, at which time it became almost clear. The rest of the terephthalonitrile N, N'-dioxide was then added, the mixture heated at 50° C, and the prepolymer was isolated by adding the solution to ethanol. This precipitated out the polymer. The polymer was then washed with ethanol and dried.

Several experiments were performed where the nitrile-terminated prepolymer was reacted with a threefold excess of terephthalonitrile N, N'-dioxide. These reaction products showed a decided reduction in the number of nitrile groups still present as evidenced by infrared absorption. Further addition of the nitrile oxide showed a further reduction in the infrared absorption band.

Using sulfolane as a solvent, a number of A staged resins were prepared and their curing characteristic observed using a heated aluminum block. The results are tabulated in Table II. After observing the cure characteristics on a heated aluminum block, some of the more promising resins were then molded into 1/4" pellets. Their molding characteristics are shown in Table III.

The results from the experiments described in the previous table suggested that more information was required on the effect of B staging to obtain a good molded specimen. Using different B staging times, resins were prepared and then molded into 1/4" pellets. Their molding characteristics are shown in Table IV.

In the case of experiment F1986-35, the resin was molded at 400° F, and the temperature was increased slowly to 500° F and kept there. The resin flowed too much, and examination of the pellet showed some fissures. However, the resin was hard and strong. Figure 1 shows a photograph of this pellet.

Table II. Melting and Cure Characteristics of A Staged Nitrile Capped Polyimides - Terephthalonitrile N, N-dioxide Using Sulfolane as a Solvent

Experiment No.	F1986-20	F1986-23	F1986-21	F1986-22	F1986-24	F-1986-25B	F-1986-26	F1986-27	F1986-28B	F1986-32B
Moles of Reactants										
Benzophenonetetracarboxylic dianhydride, moles	1.83	1.83	2.00	1.50	2.00	1.00	1.00	2.00	1.77	1.80
1, 3-Di(3-aminophenoxy)benzene, moles	1.37	1.37	-	-	1.00	-	-	-	-	1.00
1, 3-Di(4-aminophenoxy)aniline, moles	-	-	-	-	-	0.072	0.32	-	-	0.10
Bis[4(3-aminophenoxy)phenyl]ether, moles	-	-	1.00	1.00	-	1.61	-	1.00	1.00	
meta-Aminobenzonitrile, moles	1.00	1.00	2.18	1.10	1.05	1.10	1.17	2.18	1.23	1.27
Resin Number	F1986-17	F1986-17	E1706-66	E1706-65	E1706-67	F-1986-25A	F1986-26	E1706-66	F1986-28A	F1986-32A
Molar Ratio-Curing Agent/Resin	3	2	3	3	6	6	-	6	6	6
A Staging Temperature, °C	20°	20°	20°	20°	60°	60°	-	60°	60°	50
Softening Temp. of A Staged Resin, °C	180°	160°	205°	170°	-	-	-	-		210°
Flow Temp. of A Staged Resin, °C	205°	180°	235°	190°	210°	200°	-	205°		260°
Hardening Temp. of A Staged Resin, °C	$230-40^\circ$(1)	230°(1)	275°(1)	235°(1)	240°(1)	285°(2)	-	285°(2,3)	260°(2)	280°(2)

(1) Hardens but does not set.

(2) Sets and hardens on glass slide. Apparently cross-linked as also evidenced by insolubility in concentrated sulfuric acid.

(3) To resin E1706-66 an additional 7 percent by weight of trifunctional nitrile resin F1986-26 was added.

Table III. Molding Characteristics of Resins A Staged with Terephthalonitrile N, N'-dioxide in Sulfolane

Experiment	Molding Behavior	Presence of Trifunctional Amine
F1986-21	Flowed out of mold at 550°F	No
F1986-22	Flowed out of mold at 550°F	No
F1986-25B	Cured to hard, brittle pellet at 550°F	Yes
F1986-28	Outgassed rapidly, blew out of mold at 550°F	Yes
F1986-27	Flowed out of mold at 550°F	Yes
F1986-33(1)	Cured to hard tough pellet at 550°F	Yes

(1) Resin F1986-28 "B" staged at 430°F for several hours in Argon atmosphere.

Table IV. Effect of B Staging on Molding Characteristics

Molding Experiment	Resin No.	B Staging Temp. & Time	Molding Behavior
F1986-35	F1986-28B	220°C/30 min.	Too much flow. Required additional advancing.
F1986-37	F1986-32B	220°C/60 min.	Fairly sharp molding. Less flow than in previous case.
F1986-39	F1986-28B	220°C/75 min.	Excellent pellet obtained. Did not crack on post-cure.

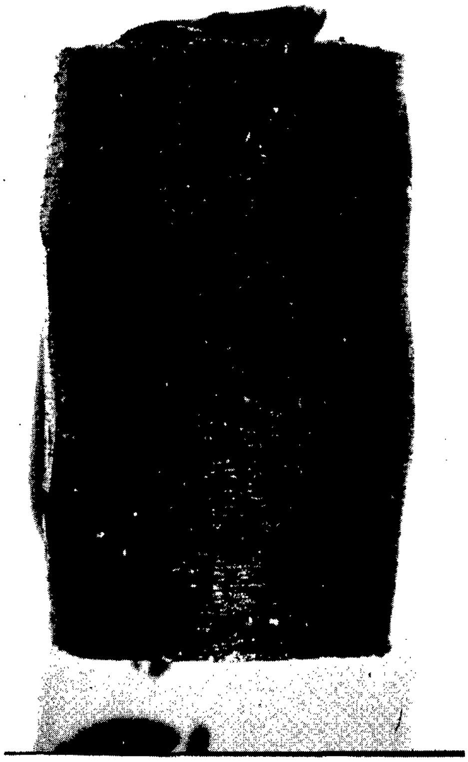


Figure 1. Pellet of Resin F1986-28B, B staged for 30 minutes at 220° C before molding.

Using similar molding parameters in molding experiment F1986-37 as in the previous experiment, except advancing the resin 60 minutes instead of 30 minutes, a much better specimen was obtained. Upon postcuring a small crack developed in the pellet. Figure 2 shows the appearance of the pellet.

Experiment F1986-39 was identical to F1986-35 except that the resin advanced for 75 minutes prior to molding, whereas Resin F1986-28B was advanced for only 30 minutes in the earlier experiment. An excellent pellet was obtained (see Figure 3).

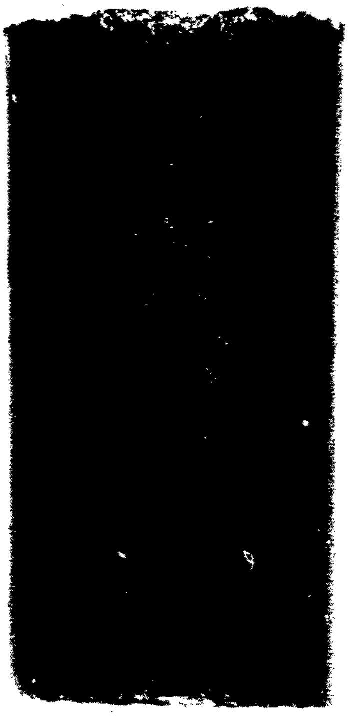


Figure 2. Pellet of
Resin F1986-32B,
B staged for 60 minutes
at 220° C before molding.

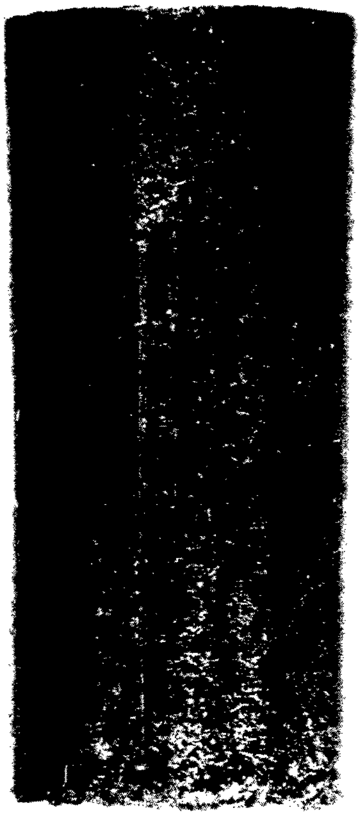


Figure 3. Pellet of
Resin F1986-28B,
B staged for 75 minutes
at 220° C before molding.

The striking difference in the molding behavior upon varying the B staging time can be seen by examining Figures 1 and 3 since the identical resin was used in both cases. Pellet F1986-39 had a density of 1.35 g/cc after postcuring at 475° F for 24 hours and then 500° F for 24 hours. Also a compressive strength of 7890 psi was obtained. These results are contrasted to compressive strengths of 500 to 900 psi that was obtained when dimethylformamide was used for A staging rather than the sulfolane used in the present group of experiments.

The oxidative stability of Pellet F1986-39 at 500° F was excellent as shown by Figure 4. In this test, the pellet was pulverized so that it passed through a 125 micron screen. The pulverized pellet was heated at 500° F in air and the weight was recorded periodically. After an initial weight loss of approximately 10 percent, probably due to moisture and volatile impurities, only about 1 percent more was lost during additional exposure at 500° F for longer than 800 hours.

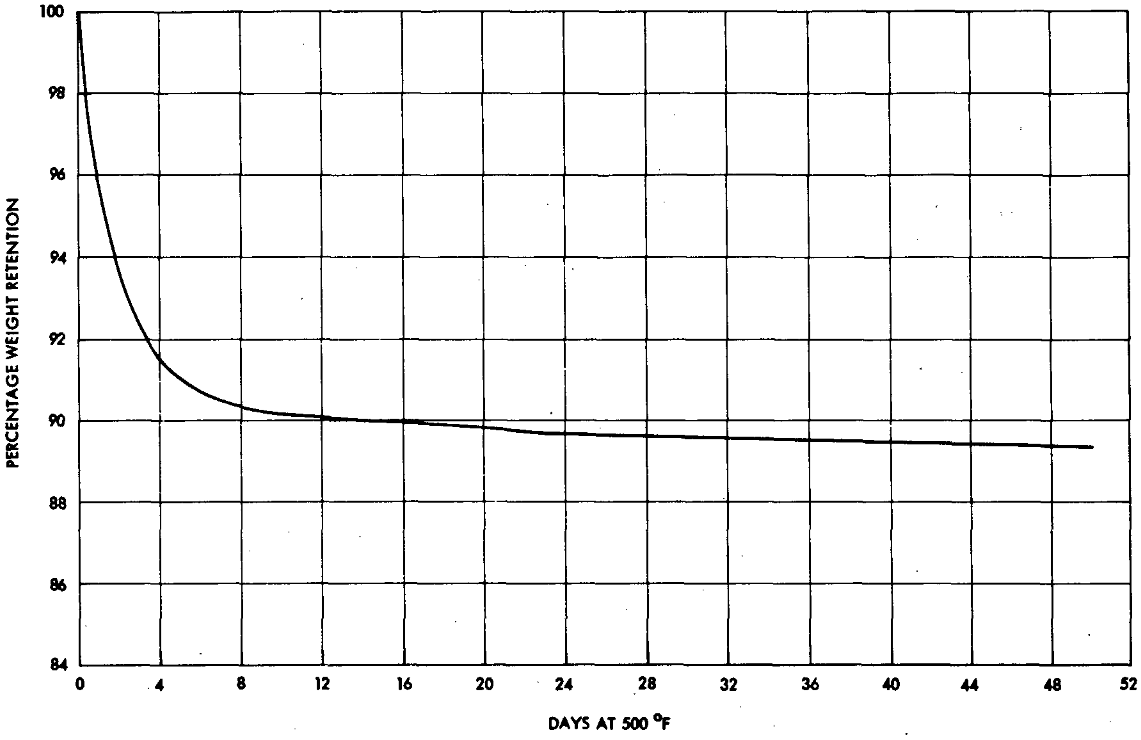


Figure 4. Weight retention in air at 500°F of pulverized pellet F1986-39.

Based on the results just described, a resin was formulated to prepare a test specimen of a glass cloth-reinforced laminate. In experiment F1986-43A a nitrile-terminated polyimide was prepared by the copolymerization of benzophenonetetracarboxylic dianhydride, 1, 3-di(3-aminophenoxy)benzene, 2, 6-bis(4-aminophenoxy)aniline and meta-aminobenzonitrile. The resin was A staged with terephthalonitrile N, N'-dioxide using sulfolane, and the resin was isolated, advanced for 1 hour at 230° C, and reconstituted in dimethylformamide. A test specimen was fabricated from this resin system. After several trial runs a 1" x 3" laminate was made with 8 plies of impregnated S glass (heat cleaned) using a molding temperature of 550°F, a molding pressure of 1000 psi and a cure time of 4 hours. The resulting specimen had a resin content of 29.5 percent and a void content of less than 7 percent. The specimen appeared very good. Without any postcuring a flexural strength of 29.7×10^3 psi and a modulus of elasticity of 0.6×10^6 psi was obtained. Postcuring of a specimen at 500°F increased the flexural strength to 43.1×10^3 psi and the modulus to 2.0×10^6 psi. Further cure at 550°F for 25 hours did not improve the flexural strength of the specimen.

These results are very encouraging in demonstrating the feasibility of a nitrile-oxide-cured, nitrile-terminated polyimide system. Further improvement in the physical properties is possible. There is evidence that the trifunctional amine, 2,6-bis(4-aminophenoxy)aniline had some impurities present which could act as chain growth terminators. Upon using a purer sample of this compound for preparing resins used to fabricate laminates better physical properties should result.

b. Curing of Nitrile-Substituted Polyimide Oligomers by Catalyzing Conversion to Triazines

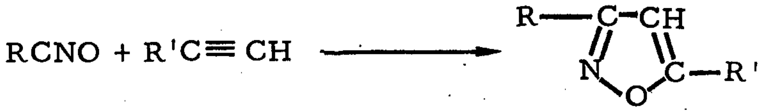
Nitriles have been trimerized to 1,3,5-triazines by various methods. Several of these include catalysis by base or acid[7] or by the use of very high pressure.[8] Some of the acid or basic catalysts are substances such as sodium hydride, sodium N-methylanilinomagnesium bromide, fuming sulfuric acid and chlorosulfonic acid. Dorfman, Emerson and Gruber[9] have made a study of materials which can be used for triazine formation from perfluoroalkanenitriles. They have screened more than 100 elements and inorganic, organometallic, and organic compounds. Several materials were found to catalyze complete conversions of the nitriles: barium metal, copper acetylacetonate, tetraphenyltin, tetraphenyllead, silver oxide, barium oxide, cadmium oxide, and two lead oxides (PbO and Pb_3O_4).

To learn if this technique was applicable for curing a nitrile-terminated polyimide, a sample of resin E2246-88 was mixed with tetraphenyltin and heated on an aluminum block. Most of the tetraphenyltin sublimed out of the sample during heating. Some hardening of the resin was noted in the range of 200-275°C but the results are inconclusive. Because of the outgassing of the catalyst and the toxicity of tetraphenyltin further work with this system will be limited to a low level of effort.

c. Curing of Acetylene-Substituted Polyimide Oligomers with Terephthalonitrile N,N'-dioxide

The objective of this task is to develop a processable high temperature stable resin based on an acetylene-substituted polyimide oligomer that can be cured with terephthalonitrile N,N'-dioxide. The approach used in this study is quite similar to that used in the curing of nitrile-substituted polyimides with terephthalonitrile N,N'-dioxide.

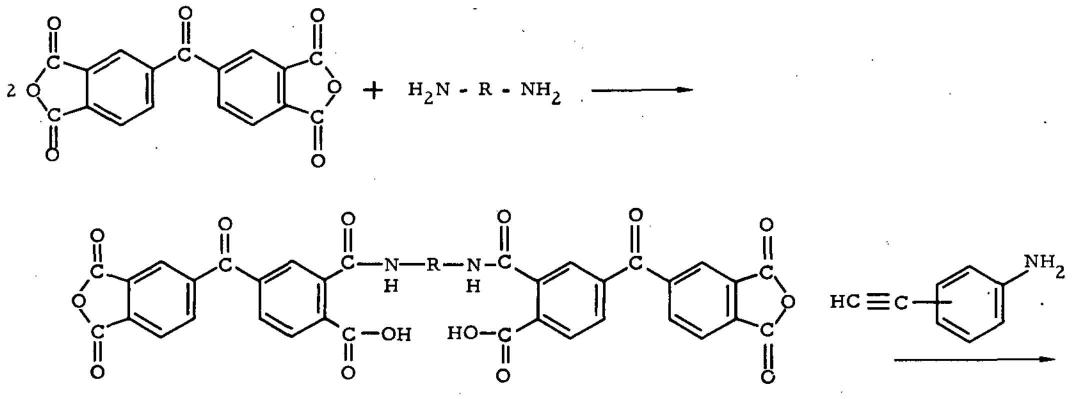
The reaction between acetylene derivatives and nitrile oxides has been carried out by Overberger and Fujimoto[1] and yields the isoxazole ring by the addition reaction shown below.

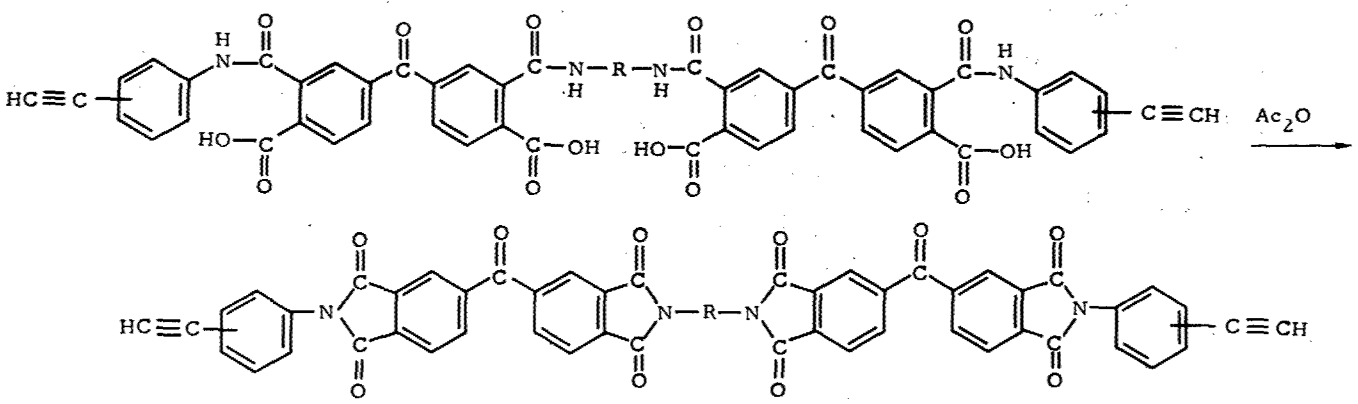


As with the oxadiazoles, the reaction yields no volatile by-products. Polymers have been prepared by Overberger and Fujimoto[1] by treating 1,4-diethynylbenzene with terephthalonitrile N,N'-dioxide. Yields of almost 100 percent were obtained in benzene solutions. The resulting polymer was infusible up to 500°C in an inert atmosphere. Thermogravimetric analysis indicated that this polymer was stable in air below 400°C. These results suggest that the oxidative and thermal stability is sufficiently high to be well in excess of the thermal requirements of a laminating resin for the objectives of this program.

The reaction of a nitrile oxide with an acetylene linkage is quite facile. An experiment was carried out in which phenylacetylene was mixed with terephthalonitrile N,N'-dioxide. When the mixture was warmed to 50° C the reaction took place immediately. D'Alelio also found that the addition reaction of acetylene derivatives and nitrile oxides proceeded quite readily.[10, 11]

The synthesis of acetylene-substituted polyimides is quite similar to that used in the preparation of nitrile-terminated polyimides. Instead of using the meta- or para-aminobenzonitrile as a means of introducing the terminating nitrile groups, the meta- or para-ethynylaniline will be used. The overall reaction can be shown as follows.

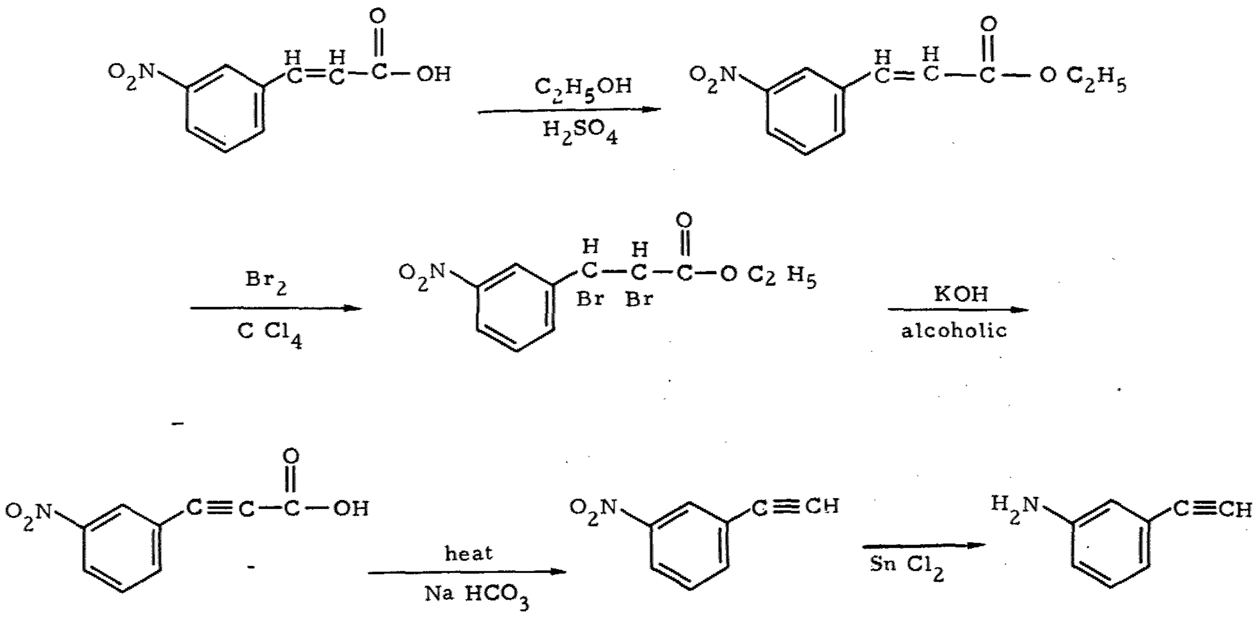




An attempt was made to prepare meta-ethynylaniline by converting meta-nitroacetophenone to the α, α'-dichloro derivative by treatment with phosphorus pentachloride and then dehydrochlorination with alcoholic potassium hydroxide. Although this reaction appears to go exceptionally well for making unsubstituted phenylacetylene, a black tarry mass resulted from attempt to make the meta-nitrophenylacetylene.

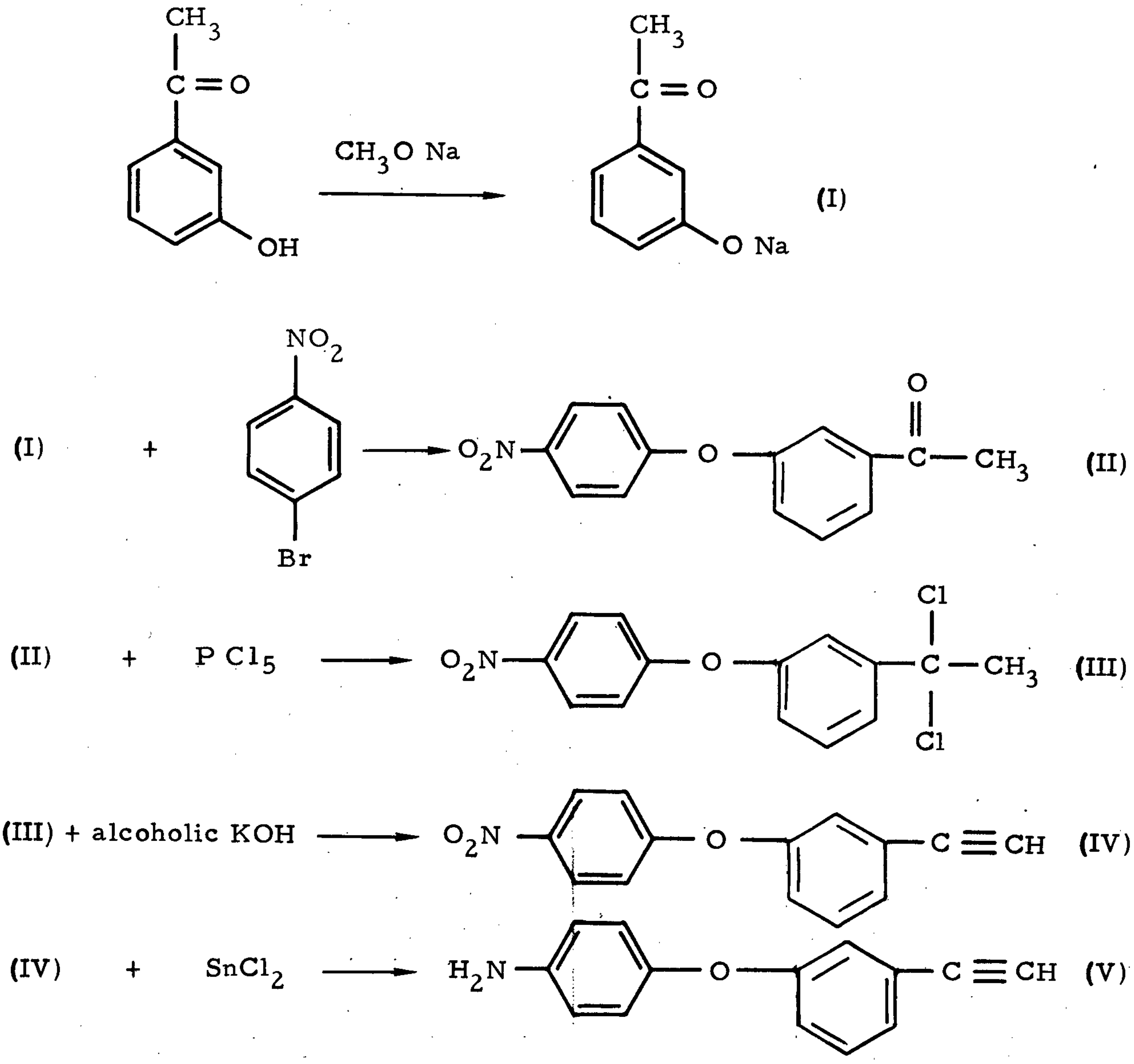
Using para-nitroacetophenone as the starting compound, chlorinating with phosphorous pentachloride and then dehydrochlorinating with alcoholic potassium hydroxide resulted in a product which was very impure and tended to oil out.

A better method involves the bromination of the appropriate nitrocinnamic acid derivative, then the dehydrobromination with alcoholic potassium hydroxide and decarboxylation with heat to yield the acetylene group. The reaction scheme can be shown as follows.



In experiment F2434-30A the ethyl 3-nitrocinnamate has been made in 90 percent yield. This was then converted to the 3-(3-nitrophenyl)-2,3-dibromopropionate (experiment F2434-30B) and dehydrobrominated to the 3-nitrophenylpropiolic acid (experiment E1706-71). This derivative will then be converted to the 3-nitrophenylacetylene and finally reduced to the 3-ethynylaniline.

Another approach that is also being investigated involves the chlorination of 3-(4-nitrophenoxy)acetophenone with phosphorus pentachloride with subsequent dehydrochlorination with alcoholic potassium hydroxide. The reaction can be shown as follows.



Although the 3-[α, α'-dichloroethyl]nitrobenzene and the 4-[α, α'-dichloroethyl]-nitrobenzene formed tars upon dehydrochlorination with alcoholic potassium hydroxide, because of the ether linkage in compound III, the effect of the nitro group should be greatly diminished. The synthesis of 3-(4-nitrophenoxy)-acetophenone has been completed (F2434-28) and is ready for conversion to compound III.

2. EXPERIMENTAL

a. Preparation of Monomers

Preparation of meta-Nitrobenzonitrile

E2246-67. Powdered potassium nitrate (101 grams, 1.00 mole) and 275 ml of concentrated sulfuric acid were added to a 1 liter three-neck round bottom flask fitted with a stirrer, addition funnel and a cooling bath. The mixture was cooled to 10°C, and benzonitrile (91.7 grams, 0.889 mole) was added dropwise to the mixture while stirring rapidly. During the addition, which took 3 hours, the temperature was kept at 20°C or below. Then the mixture was stirred for an additional hour and added to 2 liters of crushed ice. The yellow solid which precipitated was filtered, washed with water and dilute ammonia. A yield of 58 grams (44 percent of theory) was obtained after recrystallizing from aqueous ethanol (m.p. 105 to 110°C).

E1706-46. A slurry of powdered potassium nitrate (550 grams, 5.44 moles) in 1500 ml of concentrated sulfuric acid was added to a 5 liter three-neck round bottom flask and the mixture cooled to 4°C. Then benzonitrile (500 grams, 0.485 mole) was added dropwise over a 3.5 hour interval to the cold slurry, keeping the reaction mixture at about 12 to 15°C. The mixture was stirred in the ice bath for another hour, and then poured over crushed ice. The resulting precipitated product was recovered by filtration, washed repeatedly with water, then with 5 percent aqueous ammonia until the washings were practically colorless. Finally the product was washed with water and recrystallized from aqueous alcohol. The yield was 381 grams (53 percent of theoretical), melting point 112 to 114°C. A second crop of crystals which was collected from the mother liquor weighed 42 grams, giving a combined yield of 59 percent of theoretical.

Preparation of meta-Aminobenzonitrile

E2246-68. Stannous chloride (253 grams, 1.12 moles) and 338 ml of concentrated hydrochloric acid were added to a 1-liter three-neck flask fitted with a stirrer and an ice-bath. The solution was cooled to 5°C and meta-nitrobenzonitrile (55 grams, 0.371 mole from experiment E2246-67) was added all at once. Within 15 minutes the temperature rose to 94°C. Then the mixture was cooled to room temperature, and the mixture added to 1400 ml of 40 percent (weight) of sodium hydroxide solution. After cooling the resulting solution to 15°C, the amine was filtered, washed and

Experiment F1812-06-B

Adams catalyst (0.10 gram, PtO_2) was dispersed in 300 ml of absolute ethanol and the mixture was subjected to hydrogenation in the Parr hydrogenator. To the mixture, 1, 3-di(4-nitrophenoxy)benzene (16.6 grams, 0.0472 mole) was added and the mixture hydrogenated for 16 hours starting at 55 psi. The solution was then filtered to yield 13.2 grams (95.6 percent of theory) of product. This product, which had a melting point of 114° C, was recrystallized from an aqueous ethanol solution to yield 12.2 grams of purified product.

Preparation of Bis[4-(3-nitrophenoxy)phenyl] Ether

Experiment F1986-08

In a one liter round bottom flask fitted with a stirrer, distillation head, gas inlet tube and oil bath was placed 350 ml of benzene. After distilling off 25 ml of benzene to insure that the benzene was dry, sodium methoxide 13.5 grams, 0.25 mole) and 2 ml absolute methanol were added. Again, 25 ml of benzene was distilled off and then 4, 4'-oxydiphenol (25.0 grams, 0.125 mole) was added. The mixture was evaporated to dryness with stirring and cooled to room temperature. Pyridine (400 ml) that had been dried with sodium hydroxide and distilled was added, the distillation head replaced by a reflux condenser, and the mixture was heated to boiling. To this flask were added meta-bromonitrobenzene (97.0 grams, 0.48 mole) and cuprous chloride (3.8 grams) and the mixture was stirred and heated at reflux under argon for 10 hours. After cooling under argon, the mixture was poured into 600 ml of water and acidified immediately with concentrated hydrochloric acid. The solution was extracted with four 400 ml portions of benzene, and the benzene was washed twice with dilute aqueous sodium hydroxide solution, once with water, then once with dilute aqueous hydrochloric acid and finally with water. After removing the benzene on the rotary evaporator, the residue was steam-distilled to remove the unreacted 1, 3-bromonitrobenzene. The oily residue was crystallized twice from ethanol to give 26 grams (47 percent of theory) of yellow crystals having a melting point of 117-8° C. Analysis showed C, 64.97 percent; H, 3.75 percent; theoretical for $C_{24}H_{16}N_2O_7$, C, 64.82 percent; H, 3.63 percent.

Preparation of Bis[4-(3-aminophenoxy)phenyl] Ether

Experiment F1986-09

Adams catalyst (0.3 gram, PtO_2) dispersed in 50 ml of absolute ethanol was hydrogenated at 50 psi in a Parr low pressure hydrogenation apparatus. Then bis[4-(3-nitrophenoxy)phenyl] ether (5.0 grams, 0.011 mole) in 250 ml of hot absolute ethanol was added. The system was pressurized to 60 psi hydrogen and shaken for 2 hours. The pressure had dropped in 15 minutes to 54 psi, which is approximately the theoretical amount of hydrogen required to reduce the nitro groups to the amine. Then the catalyst was removed by filtration and the filtrate was concentrated by evaporation of the solvent. On cooling, fine yellowish tan crystals precipitated to yield 4.5 g (approximately theoretical) of product having a melting point of 111-2°C. Analysis showed C, 74.98 percent; H, 5.32 percent; theoretical calculated for $C_{24}H_{20}N_2O_3$, C, 74.97 percent; H, 5.25 percent.

Preparation of 2,6-Bis(3-nitrophenoxy)nitrobenzene

Experiment F2434-04; F2434-32

This experiment was patterned after that for the preparation of 1,3-bis(3-nitrophenoxy)benzene. A three neck flask was fitted with a stirrer, gas inlet and outlet tubes, distillation head and a heating mantle. To the flask was added freshly prepared sodium methoxide (6.5 grams, 0.13 moles) and 150 ml of dried benzene. Then argon was passed through the flask and 1 ml of absolute methanol added to insure that any free sodium present was converted to sodium methoxide. A total of 25 ml of solvent was then removed by distillation. To the sodium methoxide slurry was added 2-nitroresorcinol (11.0 grams, 0.07 mole) and the solvent was stripped to dryness on an oil bath, The distillate was yellow and the residue (sodium salt of 2-nitroresorcinol) was a dark purple. Pyridine (170 ml) was added to the cooled salt and the mixture heated to reflux on an oil bath under argon. To the mixture were added 3-bromonitrobenzene (50.0 grams, 0.25 mole) and cuprous chloride (2.1 gram). The mixture was heated under argon with stirring at reflux for 5 hours. After this time the cooled reaction mixture was poured into 300 ml of water and immediately acidified to Congo Red paper with concentrated hydrochloric acid (about 220 ml). The solution was extracted with 1600 ml of benzene in 5 portions; the combined portions were washed successively with two portions of 170 ml 1N sodium hydroxide, two of water, one of dilute hydrochloric acid and two of water. The benzene was removed under reduced pressure and the residue was distilled at 30 torr pressure until the bath temperature reached 190°C to remove unreacted 3-bromonitrobenzene (33 grams recovered). The residue was crystallized from ethanol to give 2.3 grams (8% yield) of 2,6 bis(3-nitrophenoxy)nitrobenzene, melting at 109-110°C.

Preparation of 2,6 Bis(3-aminophenoxy)aniline

Experiment F1986-18B

Adams catalyst (0.2g, platinum oxide) was added to 250 ml of ethanol and hydrogenated at 50 psi in a Parr low-pressure hydrogenation apparatus for 10 minutes. Then 2,6 bis(3-nitrophenoxy)nitrobenzene (1.3 grams, 0.032 mole) was added and the reaction bottle was pressurized to 60 psi. After shaking 1 hour, the pressure fell to 58 psi. The catalyst was then filtered off and the solvent stripped off under vacuum in a rotary evaporator. The residue, a greenish oil, solidified on cooling. The yield of crude material being approximately theoretical. A portion was recrystallized from a mixture of ethyl acetate toluene to give orange crystals, m.p. 100°-101°C.

In a second run the hydrogenation was lengthened to 16 hours. A white powder which melted at 184-5° C and showed no evidence of amine groups (insoluble in dilute acid), was obtained. No further study of this product was conducted, but it is possible that cyclization may have resulted.

Preparation of 2, 6 Bis(4-nitrophenoxy)nitrobenzene

Experiment F2434-26

Since in experiment F2434-04; F2434-32 the yield of 2, 6-bis(3-nitrophenoxy)nitrobenzene was low, the present preparation was repeated using 4-bromonitrobenzene replacing 3-bromonitrobenzene. Thus a three neck flask was fitted with a stirrer, gas inlet and outlet tubes, distillation head and a heating mantle. To the flask were added freshly prepared sodium methoxide (13.0 grams, 0.240 moles) and 300 ml of dried benzene. Argon was passed through the apparatus and 1 ml of absolute methanol was added to insure that any free sodium was converted to sodium methoxide. About 25 ml of solvent was removed by distillation, and to the slurry was added 2-nitroresorcinol (19.4 grams, 0.125 mole), and the solvent was stripped to dryness on an oil bath. After allowing the residue to cool, 300 ml of pyridine was added and the mixture was heated to reflux under argon on an oil bath. To the mixture were added 4-bromonitrobenzene (100 grams, 0.50 mole) and cuprous chloride (4.2 grams). After heating the mixture at reflux under argon for 5 hours, the mixture was poured into water and acidified with concentrated hydrochloric acid. The solution was then extracted with benzene and the extracts were washed with dilute sodium hydroxide solution, water, dilute hydrochloric acid and water. The benzene was removed by distillation under reduced pressure, and the residue distilled at 30 torr pressure until the bath temperature reached 190°C to remove unreacted 4-bromonitrobenzene. The residue was recrystallized from ethanol to yield 49 grams of product, m.p. 128° - 128.5°C.

Preparation of 2, 6-Bis(4-aminophenoxy)aniline

Experiment F1986-36; F1986-42, E1706-70

To a solution of 2,6-bis(4-nitrophenoxy)nitrobenzene (3.0 grams, 0.076 mole) in 250 ml of ethanol was added 0.2 gram Adams catalyst (PtO_2). The mixture was hydrogenated in a Parr low pressure apparatus at 45 psi for one hour during which time the pressure dropped 5 psi. The catalyst was filtered off and the alcohol was stripped on a rotary evaporator under vacuum. A yellow, crystalline residue remained and was used directly to cross-link polymers. The crystals appeared to be unstable and turned dark green in air within a day or two, emitting an aniline-like odor.

Preparation of Terephthalaldehyde Dioxime

Experiment F1625-20

Hydroxylamine hydrochloride (146 grams, 2.10 moles) dissolved in 700 ml of water was added to a three-neck five liter flask fitted with a stirrer and reflux condenser. Then a solution of sodium hydroxide (84 grams, 2.10 moles) in 450 ml of water was added to the flask. A solution of terephthalaldehyde (134 grams, 1.00 mole) in 1 liter of pure ethanol was added to the reaction flask. After the mixture was refluxed for 20 minutes, crystals started to separate. An additional 600 ml of ethanol was added and the solution was refluxed for 30 minutes. The contents were transferred to a 4 liter

Erlenmeyer flask and cooled to 0°C by an ice-bath. The solid residue which precipitated was recovered by filtration. Then the residue was dissolved in hot 55 percent ethanol — 45 percent water solution. Activated charcoal (10.0 grams) was added and the solution filtered and cooled. The resulting white crystals were filtered and dried. A yield of 72.0 grams (46 percent of theory) of oxime having a melting point of 221°C was obtained.

Experiment F1812-27

To a four liter Erlenmeyer flask containing a solution of terephthalaldehyde (175 grams, 1.306 moles) in ethanol (900 ml) was added a solution of hydroxylamine hydrochloride (171.4 grams, 3.263 moles) and sodium hydroxide (130.5 grams, 3.263 moles) in 1500 ml of water. The solution was held just below reflux for several hours and then allowed to stand at room temperature for several days. Upon neutralization with hydrochloric acid until neutral to litmus paper, the oxime precipitated. After filtering the oxime, the crude product was dissolved in 2 liters of 55 percent ethanol — 45 percent water, and the solution decolorized with charcoal, filtered and cooled to room temperature. The first crop of crystals were filtered to yield 92.4 grams, m.p. 222 - 223° C. The mother liquor was cooled to 6° C and allowed to stay at this temperature. A second crop, 21 grams, was obtained. Concentrating the mother liquor with the rotary evaporator yielded 52.1 grams more of product. The total yield of dioxime was 77.3 percent of theory.

Terephthalohydroxamyl Chloride

Experiment E2246-65

Terephthalaldehyde dioxime (20.0 grams, 0.123 mole) and 450 ml of absolute ether were added to a 1 liter flask fitted with a stirrer, gas inlet and outlet tube. The mixture was cooled to 0° C and nitrosyl chloride gas was passed through the mixture for 2 hours during which the oxime went into solution. After this period the ether was removed by vacuum distillation and the residue was dissolved in 1500 ml of hot benzene. Upon cooling, the terephthalohydroxamyl chloride separated out and was recovered by filtration. A yield of 10.8 grams (37.5 percent of theory) having a melting point of 173 to 175° C was obtained.

Experiment F1625-21

Terephthalaldehyde dioxime (11.2 grams, 0.068 mole) and 180 ml of carbon tetrachloride were added to a 500 ml three-neck flask fitted with a stirrer, gas inlet and outlet tube and an ice bath. A stream of chlorine gas was passed through the suspension for a period of 1.5 hours, and the temperature of the reaction mixture was held below 0°C. After passage of the chlorine gas the mixture was allowed to remain at room temperature overnight. The suspension was filtered through a fritted glass funnel, and the crude terephthalohydroxamyl chloride was dissolved in 1.5 liters of boiling benzene. Upon cooling small white crystals of the chloride separated out. These were filtered to yield 6.88 grams (43.3 percent of theory), melting point 188°C.

Experiment E1706-60A

Terephthalaldehyde dioxime (110.0 grams, 0.66 mole) was dispersed in 1200 ml of carbon tetrachloride and the dispersion was cooled to 0° C. Gaseous chlorine was bubbled through the mixture at 0° C for 3 hours, and the mixture was allowed to stand at room temperature for 24 hours. The product was recrystallized from a 10:1 mixture by volume of chloroform and ethanol. The recrystallized product weighed 48.0 grams (32 percent of theory) and melted at 180° C.

Experiment F1812-28

Terephthalaldehyde dioxime (92.4 grams, 0.563 mole) was dispersed in 1200 ml of carbon tetrachloride. The slurry was cooled to -10°C to -5°C and a vigorous stream of chlorine gas introduced below the surface of the slurry. After passing the chlorine through the mixture for several hours, the reaction mixture was allowed to stand at room temperature for 16 hours. Then the reaction mixture was filtered to yield 81.0 grams of product (62 percent yield). A 47.8 gram portion of this product was recrystallized from 2 liters of benzene to yield 24.3 grams, melting point 175° to 182°C depending upon heating rate on the melting point block.

Preparation of Terephthalonitrile N,N'-Dioxide

Experiment E2246-66

A solution of terephthalohydroxamyl chloride (10.8 grams) in 120 ml of absolute methanol was placed into a 250 ml round bottom flask fitted with a magnetic stirrer and dropping funnel. The solution was cooled to 0°C with an ice bath, and over a 1-hour period, a solution of 8.5 grams of triethylamine in 27 ml of absolute methanol was added dropwise. During the addition of the amine, a white solid separated. This solid was then filtered, washed with methanol, cold water and methanol and dried under vacuum. The yield was 6.4 grams (identification number E2246-66-A) of a white powder with a tan cast.

Experiment E1706-60B

The recrystallized terephthalohydroxamyl chloride (48.0 grams) from experiment E1706-60A was dispersed in 500 ml of absolute methanol. The dispersion was cooled to 0°C, and a solution of dry triethylamine (37.7 grams) in 130 ml anhydrous methanol was added dropwise to the stirred mixture at 0°C. After the addition of the amine, the reaction mixture was stirred at 0°C for one-half hour, allowed to warm to room temperature and stirred overnight. The product was collected by filtration, washed with methanol, then water, and finally with methanol. The dried product weighed 20.6 grams (61 percent of theory based on the dichloride) and melted at 145°C with explosive decomposition.

Experiment F1812-29

The recrystallized terephthalohydroxamyl chloride (24.3 grams) from experiment F1812-28 was dissolved in 250 ml of absolute methanol. The temperature of the solution was lowered to -5° C with a Dry Ice bath, and a solution consisting of triethylamine (26 grams, 0.257 moles) in 250 ml of absolute methanol was added dropwise over a two hour period. During the addition of the amine the temperature was kept below 0° C. After the addition the reaction mixture was allowed to stand overnight at room temperature and the light tan product was filtered, washed with methanol and then water and vacuum dried at room temperature to yield 12.1 grams (73 percent of theory) of product.

Preparation of Isophthalaldehyde

Experiment F1812-01

A 2 liter three neck round bottom flask was fitted with a stirrer, dropping funnel and a Dry Ice acetone condenser. The outlet to the atmosphere was protected with a Drierite-filled tube. To the flask was added dry ether (1000 ml) and lithium aluminum hydride (17.2 grams, 0.40 mole). Then by means of the dropping funnel, a solution containing t-butyl alcohol (89.0 grams, 1.20 moles) in 425 ml of dry ether was added over a one hour period. After the addition, the stirring was halted and the precipitate was allowed to settle. The supernatant liquid was decanted. To the wet residue was added 400 ml of bis(2-methoxyethyl) ether. Most of the residue went into solution to give 0.4 mole of lithium tri-t-butoxyaluminohydride.

Isophthaloyl chloride (40.6 grams, 0.200 mole) in 200 ml of bis(2-methoxyethyl) ether was treated dropwise with 0.4 mole of the lithium tri-t-butoxyaluminohydride at -78° C over a two hour period. The reaction product was allowed to reach room temperature and then added to crushed ice. The precipitate formed was extracted with ethanol. The solvent was stripped using the rotary evaporator. Recrystallization of the residue yielded a small amount of isophthalaldehyde (0.52 gram) having a melting point 86-87° C (literature, 90° C). It appears that much of the isophthalaldehyde was still in the water — bis(2-methoxyethyl) ether solution.

Experiment E2246-95

An attempt was made to synthesize isophthalaldehyde using a modified Reimer-Tieman reaction. To a 1 liter round bottom flask fitted with a reflux condenser, heating mantle and magnetic stirrer were added benzaldehyde (100 ml) and chloroform (80 ml). Then potassium hydroxide (300 grams) in 500 ml of water was added. Very few outward signs of reaction were apparent, but suddenly the temperature of the mixture rose so rapidly that the reflux condenser could not handle the chloroform and some undetermined amount was lost through the condenser opening. An additional 80 ml of chloroform and 100 ml of benzalaldehyde were added. The mixture was kept at 94°C for several hours. The oily layer was separated, washed with water and distilled under reduced pressure to yield 3.79 grams of a pleasant smelling yellow liquid, b.p. 174°C/<1 torr. This is probably a mixture of o-dichloromethylbenzaldehyde and m-dichloromethylbenzaldehyde. Because of the low yield and unpredictability no further effort was made to isolate the desired product.

Experiment F1706-58

To a 2 liter three neck flask fitted with a dropping funnel, reflux condenser, gas inlet and outlet tubes and heating mantle was added a slurry of lithium aluminum hydride (7.6 grams, 0.20 mole) in 500 ml of dry ether under an atmosphere of argon. Then a solution of freshly distilled t-butyl alcohol in 200 ml of dry ether was added dropwise. The reaction mixture was allowed to reflux under argon for 2 hours after the addition. The ether was then decanted from the lithium tri-t-butoxyaluminumhydride and 200 ml of dry diglyme (bis(2-methoxyethyl)ether) was added. The mixture was cooled to -78°C with a Dry Ice-acetone bath, and a solution of isophthaloyl chloride (20.3 grams, 0.10 mole) in 200 ml of dry diglyme was added slowly over a 2 hour period. The mixture was then allowed to warm slowly to room temperature and stirred overnight under argon. The diglyme was then removed using the rotary evaporator, and 600 ml of water was added to hydrolyze the product. The residue was extracted with benzene, the benzene extract washed several times with water, and the solvent was removed on the rotary evaporator. A resinous product (8.0 grams) was obtained which failed to crystallize from such solvents as alcohol, ether, and acetone.

Experiment F1986-06

To a flask fitted with a still head for vacuum distillation were added α, α, α', α'-tetrabromo-m-xylene (84.3 grams, 0.20 mole) and 200 ml of concentrated sulfuric acid. The flask was heated in an oil bath at 110°C for 3 hours while under vacuum. After the solid had all dissolved, the solution was cooled and poured over 600 grams of crushed ice. The product was filtered off and dried. Recrystallization from alcohol and water using charcoal to decolorize the solution yielded 20 grams of the isophthalaldehyde, m.p. 80-82°C (lit. value 90°C).

Preparation of α, α, α', α'-Tetrabromo-m-xylene

Experiment F1986-05

In a 1 liter three-neck flask equipped with a blade stirrer, reflux condenser and a dropping funnel was placed m-xylene (100 grams, 0.94 mole). The flask was heated in an oil bath at 140-60°C, and a 300 watt clear tungsten lamp was placed adjacent to the flask to supply the radiation energy for the photochemically induced bromination reaction. Bromine was added slowly over a 13 hour period keeping the excess bromine to a minimum. Towards the end of the addition the reaction proceeded slowly. The reaction product was then taken up with chloroform previously washed and dried to remove alcohol. The solvent was then stripped off and the residue was crystallized from hexane. The first crop (220 grams) was recrystallized to yield 120 grams of pure product.

Preparation of Isophthalaldehyde Dioxime

Experiment F1986-07

To a solution of hydroxylamine hydrochloride (22.5 grams, 0.33 mole) in 100 ml of water was added a solution of sodium hydroxide (13.2 grams, 0.33 mole) in 70 ml of water. Then a solution of isophthalaldehyde (18.0 grams, 0.13 mole) in 55 ml of ethanol was added and this solution was warmed. On cooling crystals formed. These were recrystallized from aqueous ethanol to yield 9 grams as the first crop (m.p. 186-8° C) and 7 grams second crop (m.p. 180° C, lit. value 165°).

Preparation of Isophthalohydroxamyl Chloride

Experiment F2434-15

To a 500 ml three neck flask fitted with a stirrer, gas inlet and outlet tube and Dry ice bath were added isophthalaldehyde dioxime (15.0 grams, 0.91 mole) and 200 ml of carbon tetrachloride. The temperature was maintained at less than 0° C while chlorine gas was bubbled in at a brisk rate for 1.5 hours. The mixture was allowed to stand at room temperature overnight and the solids were filtered off and crystallized from benzene to give 14 grams (67 percent of theory) of isophthalhydroxamyl chloride melting at 161 to 162°C.

Reaction of Phenylacetylene with Terephthalonitrile N,N'-Dioxide

Experiment F1812-21

To 25 ml of 1,3-di(trifluoromethyl)benzene were added phenylacetylene (0.429 gram, 0.00420 mole) and terephthalonitrile N,N'-dioxide (0.672 gram, 0.00420 mole). After stirring the mixture for 72 hours, the mixture was filtered. An infrared spectrum of the filtrate showed the absence of peaks at 3.2 microns and 4.8 microns as well as the absence of a broad band at 14.5-16 microns. The dried, filtered precipitate weighed 0.978 gram.

Preparation of Ethyl 3-Nitrocinnamate

Experiment F2434-30A

To a round bottom flask were added m-nitrocinnamic acid (50 grams, 0.259 mole), 420 ml of ethanol and 10 ml of concentrated sulfuric acid. The mixture was refluxed for 5 hours and allowed to stand overnight at room temperature. After this time water was added and the white product was filtered. The product was recrystallized from ethanol to yield 51.5 grams of the ester (90 percent yield), m.p. 75-76° C.

Preparation of Ethyl 3-(3-Nitrophenyl)-2, 3-dibromopropionate

Experiment F2434-30B

A 1 liter round bottom flask was fitted with a stirrer and addition funnel. To the flask were added 200 ml of carbon tetrachloride and ethyl 3-nitrocinnamate (51.5 grams, 0.233 mole). Then 11.8 ml of bromine was added dropwise with stirring. After the addition, the reaction product was placed in a large Petri dish and the carbon tetrachloride and excess bromine allowed to evaporate over a 48 hour period. The yield was 60.7 grams (72.6 percent of theory), m.p. 88-89° C.

Preparation of 3-Nitrophenylpropiolic acid

Experiment E1706-71

To a solution of potassium hydroxide (40.2 grams, 0.716 mole) in 200 ml of ethanol was added solid ethyl 3-(3-nitrophenyl-2, 3-dibromopropionate (60.7 grams, 0.159 mole). The resulting reaction mixture had a flocculent solid which made stirring difficult. The mixture was heated at reflux for 5 hours, then cooled in an ice-bath, and the brown solid was filtered. The filtrate was neutralized with concentrated hydrochloric acid and the resulting precipitate filtered. The filtrate was concentrated by distillation until the head temperature reached 95° C. At this time the solids formed were filtered and combined with previously collected precipitates. The precipitate was dispersed in 300 ml of water and 20 percent aqueous sulfuric acid added. The product was collected by filtration and dispersed in 200 ml of 5 percent sodium carbonate solution and heated. Upon cooling no precipitate formed. The solution was acidified with 10 percent aqueous sulfuric acid and the brown product was collected by filtration. After drying this product weighed 14 grams, m.p. 194-196° C.

Preparation of 3-(4-Nitrophenoxy)acetophenone

Experiment F2434-28

In a 3 necked, one liter flask set for an argon atmosphere were placed sodium methoxide (19.5 grams, 0.36 mole) and 150 ml of dry benzene. Then one ml of absolute methanol was added and a total of 25 ml of solvent was distilled off. To the mixture was added 3-hydroxyacetophenone (50 grams, 0.38 mole) and the solvent was stripped under an argon atmosphere. After allowing the residue to cool, 500 ml of dry pyridine was added and the mixture was heated at reflux. Then 4-bromonitrobenzene (71 grams, 0.35 mole) along with 6 grams of cuprous chloride was added. The mixture was stirred under argon at reflux for 5 hours. After cooling the reaction product was poured into 300 ml of water and made acidic to Congo red paper with approximately 300 ml of concentrated hydrochloric acid. The tarry mass was filtered off and washed with benzene and the filtrate was washed with six portions of benzene (total, 1750 ml). The combined extracts were washed successively with two portions of 500 ml each of 1N sodium hydroxide solution, water, dilute hydrochloric acid and water. The benzene was stripped by means of the rotary evaporator and the residue was recrystallized from alcohol containing decolorizing charcoal to yield 19 grams (22 percent of theory), melting point 82-84° C.

b. Preparation and Curing of Polymers

Copolymerization of Benzophenonetetracarboxylic Dianhydride with meta-Phenylenediamine in Molar Ratios of 2.0/1.0

Experiment F1625-01

A solution consisting of benzophenonetetracarboxylic dianhydride (8.00 grams, 0.0248 mole) dissolved in 125 ml of dimethylformamide was placed in a 500 ml three-neck round bottom flask fitted with a thermometer, a dropping funnel, and a Drierite-filled tube. Then a solution of meta-phenylenediamine (1.304 grams, 0.0124 mole) in 50 ml of dimethylformamide was added dropwise over a 2-hour period, while the solution was stirred vigorously with a magnetic stirrer. The reaction mixture was allowed to stand at room temperature for 63 hours, and the solvent was then stripped with a rotary evaporator. The residue was dried in a vacuum desiccator for 22 hours at 100° C. A yield of 12.6 grams was obtained which shows that some impurity, probably solvent, is still present. Judging from the relatively tacky nature of a solution of this resin and the viscosity of the solution, the degree of polymerization was considerably greater than the one to three which would be required to yield tractable polyimides for this study.

Experiment F1625-03

This experiment is identical to that of F1625-01 except that benzophenonetetracarboxylic dianhydride was added to the meta-phenylenediamine. Here again the tacky nature of the solution as well as the relatively high viscosity indicated that the degree of polymerization was considerably greater than the one to three which would be required to yield tractable resins.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Benzidine and meta-Aminobenzonitrile in Molar Ratios of 2.0/1.0/2.0

Experiment F1625-23

A solution consisting of benzophenonetetracarboxylic dianhydride (10.92 grams, 0.0339 mole) in 125 ml of dimethylformamide was placed in a blender. Then, with the blender running at moderate speed, a solution of benzidine (3.11 grams, 0.0169 mole) in 125 ml of dimethylformamide was added all at once. A small exotherm was noted upon this addition. After stirring vigorously in the blender for 5 minutes, the mixture was transferred to a 500 ml round bottom flask and heated at 50° C for 1.5 hours. Then meta-aminobenzonitrile (4.00 grams, 0.0339 mole) in 60 ml of dimethylformamide was added to the solution and the mixture was heated for 1.5 hours at 70° C. After allowing the solution to reach room temperature, it was transferred to a 2 liter beaker and 1 liter of ethyl acetate was added while stirring very rapidly, precipitating a small amount of light yellow product. The precipitate was recovered by filtering through a Buchner funnel, yielding 2.0 grams of solids. The filtrate was stripped of solvent with the rotary evaporator. The residue was dried under vacuum for 100 hours at 100° C to yield 12.00 grams of a yellow solid, identification number F1625-23. This solid started to soften at 197° C. Upon further heating on the Fisher-Johns melting point apparatus, the resin resolidified. No residual anhydride was noted when a portion of the resin was dissolved in a basic methanolic solution of morpholine and titrated with methanolic hydrochloric acid, using methyl yellow-methylene blue as indicator.

A portion of the above resin, F1625-23 (5.015 grams), and 100 ml of acetic anhydride was refluxed for 20 hours. Then the solvent was stripped using a rotary evaporator, and the residue was dried in a vacuum desiccator at 100° C for 20 hours yielding a resin, F1625-26, that weighed 4.464 grams. In contrast to the amine-salt form of the resin, the imidized form started to soften at 166° C and did not resolidify upon further heating.

In Situ Imidization by Acetic Anhydride of the Reaction Product of Benzophenonetetracarboxylic Dianhydride and meta-Phenylenediamine

Experiment F1625-16

meta-Phenylenediamine (1.341 grams, 0.0124 mole) in 50 ml of dimethylformamide was added dropwise to a solution of benzophenonetetracarboxylic dianhydride (8.00 grams, 0.0247 mole) in 125 ml of dimethylformamide over a 2-hour period. The mixture was then heated for 1 hour at 60° C and allowed to cool. Then 50 ml of acetic anhydride was added and the solution was allowed to reflux. After about 1 hour, precipitation of the imide took place. The imide was filtered through a fritted glass funnel, washed with dimethylformamide, and dried under vacuum for 4 days. The product identified as F1625-16 did not show any signs of melting even at temperatures as high as 390° C.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, meta-Phenylenediamine and para-Aminobenzonitrile in Molar Ratios of 2.0/1.0/2.0

Experiment E2246-71-A

A solution of benzophenonetetracarboxylic dianhydride (20.0 grams, 0.0621 mole) in 200 ml of dimethylformamide was placed into a blender. With the blender running at moderate speed, a solution of meta-phenylenediamine (3.35 grams, 0.03105 mole) in 100 ml of dimethylformamide was added. The solution was stirred in the blender for about 5 minutes; a solution of p-aminobenzonitrile (7.33 grams, 0.0621 mole) in 100 ml of dimethylformamide was added and the solution was stirred in the blender for an additional 5 minutes. At the end of this time the solution was clear and straw colored. Using vacuum distillation the solvent was stripped at 45 to 65° C. The residue was dried at 140 to 160° C in the vacuum desiccator for 24 hours yielding 28.2 grams of a golden solid, identification number E2246-72-A. This solid started to soften at 162° C.

Reaction of Resin E2246-71-A with Terephthalonitrile N, N'-Dioxide

Experiment E2246-71-B

An adduct between polymer from experiment E2246-71-A and terephthalonitrile N, N'-dioxide was made by dissolving the polymer (5.00 grams, 0.00545 mole) in 200 ml of dimethylformamide. It was necessary to warm the solution to 100° C to get the prepolymer into solution. The solution was cooled and terephthalonitrile N, N'-dioxide (1.31 grams, 0.00819 mole) in 150 ml of dimethylformamide was added. Then the mixture was immediately subjected to a vacuum drying operation in the rotary evaporator at 1 torr and 50° C. The resulting product, E2246-78-A, was placed in a cold mold and immediately transferred to a 325° F hot press and molded at 5000 psi for 60 minutes. Although a fair molding was obtained, evidence showed that insufficient flow took place.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, meta-Phenylenediamine and meta-Aminobenzonitrile in Molar Ratios of 2.0/1.0/2.0

Experiment E2246-74-A

A solution of benzophenonetetracarboxylic dianhydride (10.0 grams, 0.03106 mole) in 100 ml of dimethylformamide was placed in a blender. With the blender running at moderate speed, a solution consisting of meta-phenylenediamine (1.68 grams, 0.01503 mole) in 50 ml of dimethylformamide was added rapidly. After allowing the blender to run for about 5 minutes, a solution of meta-aminobenzonitrile (3.67 grams, 0.03106 mole) in 50 ml of dimethylformamide was added and the blender was run for an additional 5 minutes. The solution was allowed to stand for 1 hour, then subjected to vacuum distillation to remove the solvent.

The temperature was not allowed to go above 80°C during the distillation. The product was then placed in a vacuum oven at 140°C for 18 hours. Identified by number E2246-76-1, the dried product, which weighed 13.4 grams, showed the following analysis: C, 65.59 percent; H, 3.24 percent; N, 8.50 percent. This analysis is consistent with a partially imidized structure. The product had a softening point of 174°C, and when it was heated further to 200°C, it underwent a substantial decrease in viscosity.

Reaction of Resin E2246-74-A with Terephthalonitrile N,N'-Dioxide

Experiment E2246-74-B

An adduct between polymer E2246-74-A and terephthalonitrile N,N'-dioxide was made by dissolving 5.0 grams of this resin in 135 ml of hot dimethylformamide. The solution was cooled to room temperature. Then to a suspension consisting of 1.31 grams terephthalonitrile N,N'-dioxide in 20 ml of 1,3-di(trifluoromethyl)benzene was added 100 ml of ethyl acetate to disperse the nitrile oxide. This dispersion was then added to the solution of the resin, and the solvent was removed immediately by the rotary evaporator. The product softened at less than 150°C and upon further heating rehardened. The resulting product, E2246-79-A, was placed in a cold mold and immediately transferred to a 325°F hot press and molded at 5000 psi for 60 minutes. A fair amount of flow continued during this molding process indicating that insufficient curing took place. The resultant specimen had a surprisingly good appearance considering that it was only partially cured.

Reaction of Resin F1625-01 with para-Aminobenzonitrile

Experiment F1625-14

Some resin from experiment F1625-01 was imidized as follows: 3.09 grams of resin and 75 ml of acetic anhydride were placed in a round bottom flask and refluxed for 70 hours. The reaction product was recovered by removing the solvent with a rotary evaporator and then drying in vacuum at 80°C for 3 hours; 2.69 grams of product resulted. At this point, the product was insoluble in dimethylformamide; this indicates that the polyamic acid form had been imidized. A portion of this imidized resin (2.00 grams) was dispersed in 30 ml of dimethylformamide. p-Aminobenzonitrile (0.665 gram) dissolved in 25 ml of dimethylformamide was added to the suspension. The reaction mixture was stirred for 16 hours at 60°C by a magnetic stirrer. At the end of this time the reaction product was completely soluble. The solid reaction product (F1625-14) was recovered by removing the solvent with a rotary evaporator and dried at 100°C under vacuum yielding 2.59 grams of resin. The resin showed signs of flow at 198°C. When the temperature reached 306°C, the reaction product was a viscous liquid. It is interesting to note that the intractable polyimide was converted to a fusible tractable solid by capping the anhydride end groups with nitrile groups.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis (4-aminophenyl) ether and meta-Aminobenzonitrile in 2.0/1.0/2.0 Molar Ratio

Experiment E2246-84

To a 300 ml round bottom flask fitted with a heating mantle, magnetic stirrer and condenser protected from atmospheric moisture with a Drierite filled drying tube were added benzophenonetetracarboxylic dianhydride (10.0 grams, 0.03106 mole) and 70 ml of dry dimethylformamide. Then a solution of bis(4-aminophenyl) ether (3.11 grams, 0.01553 moles) in 50 ml of dimethylformamide was added. The solution was heated at 100°C for 40 minutes. Then a solution of meta-aminobenzonitrile (3.66 grams, 0.3106 mole) in dimethylformamide was added and the resulting reaction mixture was heated for 16 hours at 86°C. The solvent was then stripped using the rotary evaporator and the residue was then dried in a vacuum oven for 3 hours at 80°C to yield 16.61 grams of resin. This resin started to soften at 125°C with rehardening. Upon further heating it resoftened at 220°C. At 2.00 gram portion of this resin was imidized by refluxing with 25 ml of acetic anhydride for several hours. The acetic anhydride was stripped using the rotary evaporator to yield 1.53 grams of resin. This product started to melt at 145°C and appeared to be almost completely molten at 180°C. No outgassing was noted during melting.

Experiment E2246-88

To a 1 liter round bottom flask fitted with a magnetic stirrer, condenser protected from atmospheric moisture with a Drierite-filled tube, and heating mantle were placed benzophenonetetracarboxylic dianhydride (32.47 grams, 0.1008 mole) and 260 ml of dimethylformamide. The mixture was heated to 50°C and a solution consisting of bis(4-aminophenyl) ether (10.08 grams, 0.05042 mole) in 100 ml of dimethylformamide was added all at once. The mixture was heated at 119°C for two hours. Then was added a solution of meta-aminobenzonitrile (11.90 grams, 0.1008 mole) in 50 ml of dimethylformamide. After heating the mixture at 81°C for 1.5 hours the solvent was stripped using the rotary evaporator, and the resin was dried in a vacuum oven at 60°C for 16 hours to yield 56.4 grams. This resin was imidized by refluxing for 1.5 hours with 250 ml of acetic anhydride. An additional 100 ml of acetic anhydride was added and refluxing was continued for another 2 hours. The acetic anhydride was stripped using the rotary evaporator, and the solid was dried in a vacuum oven at 135°C for 1 hour to yield 48.6 grams of resin. This resin started to soften at 170°C and was fairly fluid when heated up to 220°C.

Reaction of Resin E2246-88 with Terephthalonitrile N,N'-Dioxide

Experiment E2246-91

To a 1 liter flask were added the resin from experiment E2246-88 (20.16 grams, 0.020 mole) and 250 ml of dry N-methyl-2-pyrrolidinone. Upon heating the mixture, the resin went into solution. When the solution cooled to room temperature, some gelation was noted. A 75 ml portion of p-xylene was added to the mixture. Then a solution was made up of terephthalonitrile N,N'-dioxide (9.60 grams, 0.060 mole) in 150 ml of N-methyl-2-pyrrolidinone. It was necessary to warm the mixture solution to 56°C to effect solution. This solution was immediately added to the solution of the resin. The resulting solution was concentrated by means of the rotary evaporator to a total weight of 160 grams. This lacquer was then identified as E2246-91-A and used to prepare glass-cloth reinforced laminates.

Molding of Glass-Cloth Reinforced Laminate from Lacquer E2246-91A

A laminate was prepared using 10 plies of glass cloth reinforcement 4" x 1". After 5 seconds contact time, the laminate was molded at 1.5 hours at 500°F, 50 psi. The resulting laminate had a resin content of 23.8 percent and an average thickness of 0.0881 inches. This laminate generally had a good appearance and had a flexural strength of 11.0×10^3 psi.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis(4-aminophenyl) Ether and meta-Aminobenzonitrile in 1.50/1.00/1.00 Molar Ratio

Experiment E2246-97

This copolymerization is similar to that of experiment E2246-88 except that the stoichiometry of the reactants was changed to yield a higher molecular weight prepolymer. Thus, benzophenonetetracarboxylic dianhydride (50.0 grams, 0.1552 mole) was dissolved in 250 ml of dimethylformamide. This solution was then warmed to 60°C and placed in a blender. To this solution was added a solution of bis(4-aminophenyl) ether (20.72 grams, 0.1035 mole) in 200 ml of dimethylformamide. The blender was stirring at medium speed during the addition to minimize concentration gradients. Then the reaction mixture was transferred to a 1 liter round bottom flask fitted with a reflux condenser, heating mantle and magnetic stirrer, and the solution was heated to 110°C. A solution consisting of meta-aminobenzonitrile (12.22 grams, 0.1035 mole) was added and the mixture was kept at 110°C for approximately 1 hour. The solvent was stripped using the rotary evaporator. Drying the resin at 80°C in a vacuum oven overnight yielded 91.1 grams of resin. This resin was then imidized by refluxing with 350 ml of acetic anhydride for several hours. The yellow imide was then filtered and dried in a vacuum oven at 120°C for 3 hours to yield 70.8 grams of resin. This resin had a softening temperature of 215°C.

Reaction of Resin E2246-97 with Terephthalonitrile N,N'-Dioxide

Experiment E2246-98

A solution of the resin described in E2246-97 (20.0 grams) was dissolved in 400 ml of dry N-methyl-2-pyrrolidinone to yield a relatively thick solution. Just prior to impregnation, the terephthalonitrile N,N'-dioxide (6.49 grams, 0.04050 mole) was dissolved in 100 ml of N-methyl-2-pyrrolidinone and mixed with the solution of the resin. This lacquer was used to impregnate style 181 S glass cloth reinforcement. Two laminates, one with a contact time of 1 minute at 550°F and the other with 5 minutes at 550°F, were both molded at 550°F and 50 psi for 1 hour. The resin showed very poor flow under these conditions as was evidenced by the lack of flash and ease of delamination.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, meta-Phenylenediamine, meta-Aminobenzonitrile and para-Aminobenzonitrile in a 2.0/1.0/1.0/1.0 Molar Ratio

Experiment E2246-82

The objective of this experiment was the preparation of low melting nitrile-terminated polyimides. To a 250 ml round bottom flask fitted with a heating mantle, magnetic stirrer, condenser and Drierite-filled drying tube were added benzophenonetetracarboxylic dianhydride (10.0 grams, 0.03116 mole) and 60 ml of dry dimethylformamide. Then a solution of meta-phenylenediamine (1.68 grams, 0.0155 mole) in 25 ml of dry dimethylformamide was added all at once. The solution was stirred vigorously with the magnetic stirrer and heated to 50°C for 30 minutes. A solution of meta-aminobenzonitrile (1.83 grams, 0.0155 mole) and para-aminobenzonitrile (1.83 grams, 0.0155 mole) in 25 ml of dimethylformide was added, and the solution was heated to 106°C for 1 hour. The solvent was then stripped using the rotary evaporator yielding 20.2 grams of resin. Further heating of the resin in vacuum for several hours at 80°C reduced the weight to 17.5 grams showing that some solvent was present. This solid started to melt at 112°C. By the time the temperature reached 145°C, the solid became quite fluid and showed bubbles in the liquid phase indicative of outgassing. When the temperature reached 172°C, the resin started to harden. Upon further heating the resin resoftened at 290°C. The resin was imidized by placing 2.0 grams of resin and 25 ml of acetic anhydride in a 50 ml round bottom flask and heating the mixture under reflux for 16 hours. After stripping the acetic anhydride using the rotary evaporator, the imidized resin was heated in a vacuum oven at 80°C for three hours to yield 1.50 grams of a golden yellow product which started to melt at 216°C.

Reaction of meta-Aminobenzonitrile with Benzophenonetetracarboxylic Dianhydride

Experiment E2246-80

To a 100 ml flask was added a solution of benzophenonetetracarboxylic dianhydride (5.00 grams, 0.01553 moles) in 25 ml of dry dimethylformamide. Then a solution of meta-aminobenzonitrile (3.67 grams, 0.03106 moles) in 25 ml of dry dimethylformamide was added. The solution was heated at 85°C for several hours. After this time the solvent was removed using the rotary evaporator and the resulting solid was dispersed in 150 ml of a acetic anhydride. The mixture was heated at reflux for several hours. Then the acetic anhydride was stripped using the rotary evaporator. The resulting product, (7.80 grams) had a melting point of 280-305°C.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis (4-aminophenyl) Ether, para-Aminobenzonitrile and meta-Aminobenzonitrile in 2.0/1.0/1.0/1.0 Molar Ratios

Experiment E2246-86

To a 300 ml round bottom flask fitted with a magnetic stirrer, heating mantle and condenser protected from atmospheric moisture with a Drierite-filled tube were added benzophenonetetracarboxylic dianhydride (10.0 grams, 0.03106 mole) and 50 ml of dry dimethylformamide. The solution was warmed to 50°C and then all at once was added a solution of bis(4-aminophenyl) ether (3.11 grams, 0.01553 mole) in 50 ml of dimethylformamide. The solution was then kept at 65°C for 1 hour. After this time a solution of meta-aminobenzonitrile (1.83 grams, 0.01553 mole) and para-aminobenzonitrile (1.83 grams, 0.01553 mole) in 40 ml of dimethylformamide was added. After keeping the solution at 95°C for 1.5 hours, the solvent was stripped using the rotary evaporator. The solid was dried in the vacuum oven at 80°C for 16 hours to yield 16.3 grams of resin having a softening point greater than 175°C. A 2.00 gram portion of this resin was imidized by refluxing with 25 ml of acetic anhydride for 2 hours. The acetic anhydride was then stripped using the rotary evaporator. The solid was dried in the vacuum oven at 65°C for 72 hours. This resin started to melt at 153°C and had to be heated to 200°C to obtain any appreciable flow.

Copolymerization of Isophthalonitrile and Terephthalonitrile N,N'-Dioxide

Experiment E2246-93

Two prepolymers from the copolymerization of isophthalonitrile and terephthalonitrile N,N'-dioxide were made so that the stoichiometry of the reactants yielded in one case a nitrile-terminated prepolymer, and in the second case a nitrile oxide-terminated prepolymer. The nitrile oxide-terminated prepolymer was prepared by dissolving terephthalonitrile N,N'-dioxide (1.60 grams, 0.010 mole) in 50 ml of dimethylformamide. It was necessary to warm to 55°C to effect solution. As soon as the reactants were in solution, this solution was added immediately to a solution of isophthalonitrile (0.64 gram, 0.005 mole) in 25 ml of dimethylformamide. The solution was cooled immediately to 0°C and allowed to stand overnight, after which time it was concentrated to a total weight of 19.7 grams on the rotary evaporator. The nitrile terminated prepolymer was prepared by dissolving terephthalonitrile N,N'-dioxide (0.80 gram, 0.005 mole) in 50 ml of dimethylformamide. It was necessary to warm to 55°C to get complete solution. This solution was then added to a solution of isophthalonitrile (1.28 grams, 0.01 mole) in 25 ml of dimethylformamide. The solution was cooled to 0°C and allowed to stand overnight after which time it was concentrated to a total weight of 24.6 grams using the rotary evaporator. This two part lacquer system was mixed just prior to use using it to impregnate glass cloth reinforcement. A laminate was then made with this resin using molding temperature of 500°F and pressures of 50 psi for 1.5 hours. The resulting laminate had a relatively low resin content (14.0 percent) and appeared to be cured. However, due to poor flow characteristics, the laminate lacked flexural strength and tended to delaminate easily.

Homopolymerization of Terephthalonitrile N,N'-Dioxide

Experiment E2246-92

To a 50 ml flask were added terephthalonitrile N,N'-dioxide (2.0 grams) and dry dimethylformamide (25 ml). The solution was warmed to 70°C to effect solution and then kept at 90°C for approximately 1 hour. Then the dimethylformamide was stripped using the rotary evaporator, and the solid was dried at 35°C overnight to yield 2.01 grams of product. This polymer started to soften at 140 to 175°C and upon further heating resolidified.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, 1,3-Di(4-aminophenoxy)benzene, and meta-Aminobenzonitrile in 2.0/1.0/2.0 Molar Ratio

Experiment F1812-08

To a solution of benzophenonetetracarboxylic dianhydride (11.02 grams, 0.03424 mole) in 75 ml of dimethylformamide was added a solution of 1,3-di(4-aminophenoxy)benzene (5.00 grams, 0.01712 mole) in 25 ml of dimethylformamide. The solution was then heated at 80°C for 30 minutes and a solution of meta-aminobenzonitrile (3.93 grams, 0.034 mole) in 25 ml of dimethylformamide was added. After heating the mixture for 16 hours at 50°C the solvent was stripped off with the rotary evaporator. The solid was then imidized by heating it at reflux for two hours with 150 ml of acetic anhydride. The resin turned bright yellow. The resin was filtered and dried in vacuum for 16 hours at 80°C to yield 10.4 grams of nitrile-terminated imide. This resin started to soften at 163°C and was quite fluid by 190°C.

Reaction of Terephthalonitrile N,N'-Dioxide with Resin F1812-08

Experiment F1812-09

To a 250 ml round bottomed flask were added resin F1812-08 (5.0 grams) and 100 ml of dimethylformamide. The mixture was stirred under gentle reflux for a couple of hours. The small amount of insolubles (less than 0.1 gram) was removed by centrifugation, and to the solution was added solid terephthalonitrile N,N'-dioxide, portion by portion, until a total of 2.91 grams (0.01265 mole) had been added. The mixture was heated at 50°C for several hours. After stripping off the solvent in a rotary evaporator, the solid resin was vacuum-dried at 80°C to yield 7.39 grams of product. This resin started to soften at 140°C and at 180°C was quite fluid. Upon further heating the resin started to reharden on the melting point block.

Experiment F1812-12

To a 150 ml round bottom flask were added resin F1812-08 (2.0 grams) and 40 ml of dimethylformamide. The mixture was stirred at 70°C overnight. After cooling, the solution was centrifuged to remove any insoluble resin (less than 0.2 gram). The solution was warmed to 65°C and terephthalonitrile N, N'-dioxide (0.582 gram, 0.00364 mole) was added portion by portion over a half-hour period. After the addition the solution was warmed for an additional hour at this temperature. An additional portion of terephthalonitrile N,N'-dioxide (0.29 gram, 0.00182 mole) was added and the mixture was warmed for 20 minutes more. The solution was cooled to room temperature, and the solvent was stripped off in a rotary evaporator and vacuum-dried at 30°C to yield 2.88 grams of prepolymer. This resin had an apparent softening point of 80°C. At 140°C it was quite fluid and upon further heating started to harden. By 200°C the resin had set up to a hard intractable solid.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis[4(3-aminophenoxy)phenyl] Ether, and meta-Aminobenzonitrile in 2.0/1.0/2.0 Molar Ratios

Experiment F1812-15

To a 50 ml round bottom flask fitted with a condenser, heating mantle and magnetic stirrer were added 10 ml of dimethylformamide and benzophenonetetracarboxylic dianhydride (1.68 grams, 0.005202 mole). Then a solution of bis[4-(3-aminophenoxy)phenyl] ether (1.00 gram, 0.002601 mole) in 10 ml of dimethylformamide was added. The solution was warmed to 65°C and stirred for 1 hour. Then meta-aminobenzonitrile (0.612 gram, 0.005202 mole) was added, and the solution was stirred for 16 hours at 75°C. The solvent was then stripped off with a rotary evaporator and 25 ml of acetic anhydride was added to the residue. After heating the mixture at reflux for 2 hours the acetic anhydride was stripped using the rotary evaporator. The solid started to soften at 80°C and was quite fluid at 100°C.

Reaction of Terephthalonitrile N,N'-Dioxide with Resin F1812-15

Experiment F1812-16

The resin from experiment F1812-15 was dissolved in 30 ml of dimethylformamide. To this solution was added portion by portion over a 30 minute period a total of 1.25 grams (0.007803 mole) of terephthalonitrile N,N'-dioxide. The solution was warmed to 70°C for about 45 minutes and the solvent was stripped off with the rotary evaporator. Then the solid residue was dried for three days at 50°C in vacuum to yield 3.9 grams. This solid started to soften at around 80°C, becoming quite fluid at 120°C. The resin started to harden upon further heating. By 220°C the resin had hardened considerably.

Copolymerization of 4,4'-Oxydibenzonitrile and Terephthalonitrile N,N'-Dioxide

Experiment F1812-13

To a 250 ml round bottom flask were added 50 ml of dry dimethylformamide and 4,4'-oxydibenzonitrile (5.00 grams, 0.0225 mole).

Terephthalonitrile N,N'-dioxide (5.40 grams, 0.0225 mole) was added portion by portion over a 45 minute period. After the addition the solution was stripped of solvent in the rotary evaporator and the solid was dried at 65°C for 16 hours (9.02 grams). This solid melted to a clear amber liquid at 120°C and as still fluid at 225°C. Upon cooling a transparent glass resulted. It should be noted that the melting point of 4,4'-oxydibenzonitrile is 182°C.

Preparation of a Polyamic Acid Resin from 1,3-Di(4-aminophenoxy)-benzene and Benzophenonetetracarboxylic Dianhydride

Experiment F1812-11

Benzophenonetetracarboxylic dianhydride (8.24 grams, 0.02555 mole) dissolved in 38 ml of N-methyl-2-pyrrolidinone was placed in a three necked 300 ml flask fitted with a stirrer, a condenser protected from the atmosphere with a Drierite-filled tube, thermometer and heating mantle. To the flask was added a solution of 1,3-di(4-aminophenoxy)benzene (10.0 grams, 0.03425 mole) in 38 ml of N,N-dimethylacetamide. The solution was kept at 55°C for 16 hours. This resin when isolated by stripping the solvent showed better flow characteristics when heated on a melting point block than the resin made from bis(4-aminophenyl) ether. A glass cloth-reinforced laminate made from this resin could be molded at 125 psi at 350°F to 600°F to yield a laminate which had a flexural strength of 26,120 psi and a flexural modulus of 1.87×10^6 psi. It was noteworthy that this glass-reinforced laminate did not show any weight loss when heated at 600°F for 10 hours in air.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, 1,3-Di(3-aminophenoxy)benzene and meta-Aminobenzonitrile in Molar Ratios of 1.83/1.37/1.00

Experiment F1986-17

To a 100 ml flask fitted with a magnetic stirrer and heating mantle were added benzophenonetetracarboxylic dianhydride (2.062 grams, 0.0064 mole) and 50 ml of dimethylformamide. The solution was warmed to 50°C, and 25 ml of a dimethylformamide solution containing 1,3-di(3-aminophenoxy) benzene (1.401 grams, 0.00479 mole) was added all at once. The solution was kept at 65°C for 1 hour. After this time meta-aminobenzonitrile (0.42 gram, 0.0035 mole) was added. The solution was stirred at reflux for several hours. Then the solvent was removed by means of the rotary evaporator and imidized by treatment with 75 ml of acetic anhydride. After refluxing for about 1 hour the mixture was filtered and washed with hexane. The golden yellow product was dried at 40°C in vacuum. The resin started to melt at 120°C and was quite fluid at 140°C. It should be noted that the stoichiometry was adjusted so that the polymer backbone had on the average three repeating units and therefore had a theoretical average molecular weight of about 2258.

Reaction of Resin F1986-17 with Terephthalonitrile N,N'-Dioxide

Experiment F1986-20

To a 50 ml round bottom flask were added 0.5 gram of resin F1986-17 (approximately 2 x 10^{-5} mole) and 20 ml of dry sulfolane. Then 0.010 g of terephthalonitrile N, N'-dioxide was added. After stirring the mixture for several hours at room temperature an additional amount of nitrile oxide was added bringing the total to 0.0532 grams. The mixture was stirred for several days after which time solution was complete. Addition of this solution to ethanol caused the resin to precipitate out. This resin was filtered and dried in vacuum.

Experiment F1986-23

Resin F1986-17 (1.200 grams, 0.00531 mole) was dissolved in 20 ml of sulfolane. Then a total of 0.170 grams (0.00106 mole) of terephthalonitrile N, N'-dioxide was added portion by portion at room temperature. The mixture was stirred for 21 hours, and the resin was isolated by precipitation with ethanol. After washing with ethanol the resin was dried in vacuum. The resulting resin when heated on the melting point block started to soften at 160°C and was fluid at 180°C. Upon further heating at 230°C the resin started to resolidify.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis[4-(3-aminophenoxy)phenyl] Ether and meta-Aminobenzonitrile in Molar Ratios of 2.00/1.00/2.18

Experiment E1706-66

To a 100 ml round bottom flask fitted with a Drierite-protected reflux condenser, magnetic stirrer and heating mantle was added a solution of benzophenonetetracarboxylic dianhydride (2.095 grams, 0.00650 mole) in 30 ml of dimethylformamide. The solution was heated to 60°C and a solution of bis[4-(3-aminophenoxy)phenyl] ether (1.250 grams, 0.00325 mole) in 25 ml of dimethylformamide was added. After the addition, the solution was refluxed for 2 hours, solid meta-aminobenzonitrile (0.839 gram, 0.0071 mole) was added, and the mixture was heated at reflux for 2 hours. The solvent was stripped using the rotary evaporator, and the polyamic acid was imidized by heating at reflux for 2-1/2 hours with 30 ml of acetic anhydride. The imidized product was recovered by filtration and washed with hexane. After drying under vacuum the resin started to melt at 180°C when heated on the melting point block. It should be noted that the stoichiometry in this reaction was such that the polymer chain had only one unit.

Reaction of Resin E1706-66 with Terephthalonitrile N,N'-Dioxide

Experiment F1986-21

Resin E1706-66 (1.2 grams, 0.0010 mole) was dissolved in 20 ml of sulfolane. Then a total of 0.484 gram (0.00302 mole) of terephthalonitrile N,N'-dioxide was added portion by portion, and the mixture was stirred for

24 hours. After this time the resin was isolated by precipitating with ethanol, filtering, washing with alcohol and finally drying in vacuum. This resin started to soften at 205°C and upon further heating cured at 235°C. A test molding of a 1/4" pellet at 275°C, 30 minute cure yielded a pellet which showed poor strength.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis[4(3-aminophenoxy)phenyl] Ether and meta-Aminobenzonitrile in Molar Ratios of 1.50/1.00/1.10

Experiment E1706-65

To a 100 ml round bottom flask fitted with a reflux condenser protected from atmospheric moisture with a Drierite-filled tube, magnetic stirrer and heating mantle was added a solution of benzophenonetetracarboxylic dianhydride (1.885 grams, 0.00585 mole) in 30 ml of dimethylformamide. The solution was warmed to 60°C and a solution of bis[4-(3-aminophenoxy)phenyl] ether (1.500 grams, 0.00390 mole) in 25 ml of dimethylformamide was added. The solution was heated at reflux for 2 hours, solid meta-aminobenzonitrile (0.507, 0.0043 mole) was added, and the mixture was refluxed for another two hours. The product was then concentrated to dryness on a rotary evaporator to form a thick resin. Acetic anhydride was then added to bring the volume up to 75 ml and the reaction mixture was refluxed for 2 hours. The product was recovered by filtration and washed repeatedly with hexane. This resin started to soften at 190°C when heated on the melting point block. It should be noted that the stoichiometry of reactants was adjusted so that the polymer chain consisted of two repeating units.

Reaction of Resin E1706-65 with Terephthalonitrile N,N'-Dioxide

Experiment F1986-22

Resin E1706-65 (1.200 grams, 0.00065 mole) was dissolved in 20 ml of sulfolane. Then a total of 0.207 gram (0.0013 mole) of terephthalonitrile N,N'-dioxide was added portion by portion. The mixture was stirred for 24 hours and the resin was isolated by precipitation with ethanol. After washing with ethanol the resin was dried in vacuum. Upon heating on the melting point block the resin started to soften at 170°C and flowed freely at 190°C. When it was held at 235°C for 5 minutes, the resin partially cured. An attempt to mold a pellet of this resin keeping the mold at 325°C for 120 minutes gave a partially cured product.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, 1,3-Bis(3-aminophenoxy)benzene and meta-Aminobenzonitrile in a Molar Ratio of 2.00/1.00/1.05

Experiment E1706-67

To a 100 ml round bottom flask fitted with a reflux condenser protected from atmospheric moisture with a Drierite-filled tube, magnetic stirrer and heating mantle was added a solution of benzophenonetetracarboxylic dianhydride (4.408 grams, 0.0137 mole) in 30 ml of dimethylformamide. The solution was heated to 60°C and a solution of 1,3-bis(3-aminophenoxy) benzene (2.000 grams, 0.00684 mole) in 15 ml of dimethylformamide was added. After refluxing the solution for 2 hours, a solution of meta-aminobenzonitrile (1.697 grams, 0.01437 mole) in 15 ml of dimethylformamide was added. The solution was further refluxed for 2 hours. After stripping the dimethylformamide solvent with the rotary evaporator, 60 ml of acetic anhydride was added and the mixture was refluxed for 2-1/2 hours to imidize the polyamic acid. The product was recovered by filtration and washed repeatedly with hexane and dried in vacuum. This product started to melt at 175°C when heated on the melting point block. It should be noted that the stoichiometry of this reaction was adjusted so that theoretically the polymer had a degree of polymerization of one.

Reaction of Resin E1706-67 with Terephthalonitrile N,N'-Dioxide

Experiment F1986-24

Resin E1706-67 (1.200 grams, 0.00109 mole) was dissolved in 20 ml of sulfolane. After dissolving the resin, terephthalonitrile N,N'-dioxide (0.349 gram, 0.00218 mole) was added portion by portion, and the mixture was stirred at room temperature for 22 hours. Then the resin was isolated by precipitation with methanol, washed with methanol and dried under vacuum. This resin melted rather sharply at 210°C and cured to a brittle solid at 240°C.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis[4-(3-aminophenoxy)phenyl] Ether; 2,6-Bis(3-aminophenoxy) aniline and meta-Aminobenzonitrile in Molar Ratios of 1.61/1.00/ 0.072/1.10

Experiment F1986-25A

The stoichiometry of the experiment was adjusted so that there were on the average two repeating units in the main polymer chain. Thus, benzophenonetetracarboxylic dianhydride (1.507 grams, 0.00461 mole) was dissolved in 10 ml of dimethylformamide. Then a solution containing bis[4(3-aminophenoxy)pheny] ether (1.100 grams, 0.00286 mole) and 2,6-bis(3-aminophenoxy)aniline (0.0600 gram, 0.000205 mole) in 10 ml of dimethylformamide was added. The solution was stirred under reflux for 2 hours, and then a solution containing meta-aminobenzonitrile (0.378 gram, 0.00320 mole) in 5 ml of dimethylformamide added and the solution was heated at reflux for 2 hours. After stripping the solvent with a rotary evaporator the solid resin was heated at reflux with 75 ml of acetic anhydride. The resin was recovered as a fine precipitate by addition of methanol, filtered, washed with methanol and dried under vacuum.

Reaction of Resin F1986-25A with Terephthalonitrile N,N'-Dioxide

Experiment F1986-25B

Resin F1986-25A (2.07 grams, 0.00111 mole) was dissolved in 30 ml of sulfolane. Then terephthalonitrile N,N'-dioxide (1.06 grams, 0.0066 mole) was added and the solution was kept at room temperature for 24 hours. It was then heated to 55 to 60°C and an additional 0.40 grams of terephthalonitrile N,N'-dioxide was added. The mixture was kept at 55 to 60°C for 6 hours, and the resin was recovered by pouring into ethanol to precipitate the resin. The resin was washed and dried under vacuum. This resin started to melt at 200°C and cured at 285°C. The cured resin was insoluble in concentrated sulfuric acid.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, 2,6-Bis(3-aminophenoxy)aniline and meta-Aminobenzonitrile in Molar Ratios of 1.00/0.32/1.17

Experiment F1986-26

Benzophenonetetracarboxylic dianhydride (1.000 gram, 0.0030 mole) was dissolved in 10 ml of dimethylformamide. Then 2,6-bis-(3-aminophenoxy)aniline (0.273 gram, 0.000932 mole) in 10 ml of dimethylformamide was added and the solution was heated at reflux for 1 hour. After this time, meta-aminobenzonitrile (0.414 gram, 0.0035 mole) in 5 ml of dimethylformamide was added and the solution was heated at reflux for an additional hour. The dimethylformamide was removed by means of the rotary evaporator, and the resin was then heated at reflux with 25 ml of acetic anhydride. The reaction mixture was added to methanol, and the precipitate was washed with methanol and dried to yield 0.45 grams. The mother liquors when evaporated yielded a yellow oil as a residue.

Reaction of Resin E1706-66 with the Trifunctional Nitrile of Experiment E1986-26 and Terephthalonitrile N,N'-Dioxide

Experiment F1986-27

This experiment was performed to learn the effects of additional crosslinking achieved by using a trifunctional nitrile as shown in experiment F1986-26. Thus, Resin E1706-66 (1.0 grams, 0.00084 mole) and the trifunctional nitrile (F1986-26, 0.0730 gram, 4.6×10^{-5} mole) were dissolved in 15 ml of sulfolane. Then terephthalonitrile N,N'-dioxide (0.40 gram, 0.0025 mole) was added and the mixture was stirred for 26 hours at room temperature. After this time an additional amount of terephthalonitrile N,N'-dioxide (0.40 gram, 0.0025 mole) added and the mixture heated at 60°C for 26 hours and the resin isolated by precipitation with ethanol, washing with ethanol and vacuum drying. The resulting resin starts to melt at 205° to 215°C and cures at 280 to 290°C.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, Bis[4-(3-aminophenoxy)phenyl] Ether, 2,6-Bis(3-aminophenoxy) aniline, and meta-Aminobenzonitrile in Molar Ratios of 1.77/1.00/0.12/1.23

Experiment F1986-28A

The ratio of reactants used in this experiment should yield a polymer which on the average has two repeating units in the main polymer chain. To a solution of benzophenonetetracarboxylic dianhydride (1.507 grams, 0.00461 mole) in 10 ml of dimethylformamide was added a solution of bis-[4-(3-aminophenoxy)phenyl] ether (1.000 gram, 0.00260 mole) and 2,6-bis-(3-aminophenoxy)aniline (0.0895 gram, 0.000305 mole) in 10 ml of dimethylformamide. The solution was heated at reflux for 1 hour and meta-aminobenzonitrile (0.378 gram, 0.00320 mole) in 5 ml of dimethylformamide was added. After heating at reflux for 30 minutes the mixture was kept at room temperature for an additional 16 hours and heated for an additional hour at reflux. The dimethylformamide solvent was stripped using the rotary evaporator, and the resin was added to 20 ml of acetic anhydride and heated at reflux for 3 hours. The slurry was then added to ethanol, and the precipitated resin was washed with alcohol and dried in vacuum.

Reaction of Resin F1986-28A with Terephthalonitrile N,N'-Dioxide

Experiment F1986-28B

Resin F1986-28A (1.70 grams) was dissolved in 30 ml of sulfolane. Then 0.77 gram of terephthalonitrile N,N'-dioxide was added and the mixture was heated at 55 to 60°C for 2 hours. An additional 0.32 gram of terephthalonitrile N,N'-dioxide was added and the solution was heated 3 more hours. After this time the resin was isolated by pouring the solution into ethanol, filtering and washing the precipitated resin. After drying the resin weighed 3.0 grams. This resin started to melt at 210°C and flowed at 240°C. At 260°C the resin cured with evolution of some gas. An attempt to mold the resin as a pellet at 260°C was unsuccessful because of loss of resin due to violent gas evolution.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, 1,3-Di(3-aminophenoxy)benzene, 2,6-Bis(3-aminophenoxy)aniline and meta-Aminobenzonitrile in Molar Ratios of 1.80/1.00/0.10/1.27

Experiment F1986-32A

To a warm solution of benzophenonetetracarboxylic dianhydride (1.091 grams, 0.00339 mole) in 10 ml of dimethylformamide was added a solution of 1,3-di(3-aminophenoxy)benzene (0.550 gram, 0.00188 mole) and 2,6-bis(3-aminophenoxy)aniline (0.055 gram, 0.000188 mole) in 10 ml of dimethylformamide. The solution was heated at reflux for 1 hour, and then meta-aminobenzonitrile (0.284 gram, 0.0024 mole) in 5 ml of dimethylformamide was added. The solution was refluxed for an additional 45 minutes when additional meta-aminobenzonitrile was added (0.028 gram). The solution was refluxed overnight and the solvent was stripped with the rotary evaporator. The residue was heated at reflux with 25 ml of acetic anhydride, and the resin was recovered by addition of the reaction product to ethanol, filtration, washing with ethanol and vacuum drying.

Reaction of Resin F1986-32A with Terephthalonitrile N,N'-Dioxide

Experiment F1986-32B

Resin F1986-32A (1.41 grams, 0.000838 mole) was dissolved in 30 ml of sulfolane. To the solution was added terephthalonitrile N,N'-dioxide (0.48 gram, 0.00335 mole). The mixture was stirred at room temperature for 16 hours, after which time an additional 0.15 gram of terephthalonitrile N,N'-dioxide was added. The mixture was heated at 50°C for 3 hours and the resin was isolated by precipitation with ethanol, filtration, washing the precipitate with ethanol and vacuum drying. The resin started to soften at 210 to 215°C, flowed at 260°C and cured at 280°C.

Copolymerization of Benzophenonetetracarboxylic Dianhydride, 1,3-Di(3-aminophenoxy)benzene, 2,6-Bis(4-aminophenoxy)aniline, and meta-Aminobenzonitrile in Molar Ratios of 1.80/1.00/0.10/1.28

Experiment F1986-43A

A solution containing 1,3-di(3-aminophenoxy)benzene (2.75 grams, 9.41 mmols) and 2,6-bis(4-aminophenoxy)aniline (0.27 gram, 0.94 mmol) in 15 ml of dry dimethylformamide was added to a solution of benzophenonetetracarboxylic dianhydride (5.46 grams, 16.94 mmols) in 25 ml of dry dimethylformamide. After heating at reflux for several hours the solution was kept at room temperature for an additional 16 hours. Then meta-aminobenzonitrile (1.42 grams, 12.0 mmols) was added and the solution was heated at reflux for several hours. The solvent was then stripped using the rotary evaporator, and the resin was imidized by refluxing in acetic anhydride. To isolate the resin the acetic anhydride-resin slurry was added to ethanol. After repeated washing with ethanol the resin was vacuum dried to yield 7.45 grams of resin.

Reaction of Resin F1986-43 with Terephthalonitrile N,N'-Dioxide

Experiment F1986-43B

The resin (7.45 grams) from experiment F1986-43A just described was dissolved in 70 ml of sulfolane. Then a total of 3.20 grams of terephthalonitrile N, N'-dioxide was added in two portions: first, 2.45 grams; second, after 16 hours at room temperature, 0.75 gram. The dispersion was then heated at 50°C for several hours. To isolate the resin the solution was added to ethanol which precipitated the resin. After filtration and thorough washing with ethanol the resin was advanced at 230°C for 1 hour in an inert atmosphere. The treatment served to remove most of the volatile constituents as well as to A-stage the resin. The resin readily dissolved in dimethylformamide.

Addition of Terephthalonitrile N, N'-Dioxide to a Polyimide Made by Copolymerization of Benzophenonetetracarboxylic dianhydride, Bis[4-(3-aminophenoxy)phenyl] ether and meta-aminobenzonitrile in Molar Ratios of 2.10/1.00/2.60

Experiment F1986-52; F-1986-16; E2236-60

The purpose of these experiments was to demonstrate the addition of nitrile oxide groups to nitrile groups in promoting chain growth. This was done by observing changes in solution viscosity. Benzophenonetetracarboxylic dianhydride (2.32 grams, 0.00718 mole) was dissolved in 20 ml of dimethylformamide, and a solution of bis[4-(3-aminophenoxy)phenyl] ether (1.31 grams, 0.00342 mole) in 10 ml of dimethylformamide was added. The solution was heated at reflux for several hours, and then meta-aminobenzonitrile (1.05 grams, 0.00890 mole) was added and heating at reflux was continued for an additional hour. Then the solvent was stripped using the rotary evaporator and the residue was heated with 25 ml of acetic anhydride at reflux for several hours. The imidized resin was isolated by pouring the acetic anhydride into ethanol, filtering and washing the precipitate and finally drying in vacuum. The dried resin (1.000 gram, 0.0084 mole) was dissolved in 20 ml of sulfolane and terephthalonitrile N, N'-dioxide (0.54 gram, 0.00336 mole) was added portion by portion at room temperature, and the solution was stirred for 16 hours. Additional terephthalonitrile N, N'-dioxide (0.20 gram, 0.0013 mole) was added and the mixture was stirred 4 hours at 50° C. The resin was isolated by pouring the solution into ethanol, filtering and washing the resin. After drying the resin at 40° C for 30 minutes in vacuum the product was heated 1 hour under argon at 230° C and cooled and 0.25 gram (Sample I) was removed. The remainder was heated under argon for 4 hours at 280° C (Sample II).

Solution viscosities were measured by dissolving each sample in dimethylformamide, using approximately 0.25 gram for 10 ml of solution. Only 25 percent of Sample II dissolved, the remainder being filtered off and the viscosity being measured on the filtrate. The results were as follows:

	wt. g/ml	Efflux Time for Solution (sec)	Efflux Time for Solvent (sec)	η_{inh}	$[\eta]$
Sample I	0.0244	340.9	266.3	0.101	
	0.0122	302.4	263.7	0.114	0.125
Sample II	0.048	295.6	266.3	0.217	
	0.024	279.0	263.7	0.242	0.26

Reaction of Tetraethyl Benzophenonetetracarboxylate with meta-Aminobenzonitrile

Experiment E2246-69

Into a 50 ml round bottom flask fitted with an oil bath, Vigreux distillation column and magnetic stirrer was placed tetraethyl benzophenonetetracarboxylate (14.3 grams, 0.0304 mole). The ester was warmed to 80° C and meta-aminobenzonitrile (6.4 grams, 0.0542 mole) was added. The mixture was gradually heated from 136 to 190° C over a 16-hour period. Several droplets of distillate that were collected proved to be ethanol as evidenced by infrared spectroscopy. Continued heating at this temperature yielded about 1 to 2 ml of an oily distillate. Vacuum drying the residue at 50° C for 20 hours yielded a brittle brown solid, 14.9 grams, identification number E2246-70-1.

SECTION IV

RECOMMENDATIONS FOR FUTURE WORK

Since it has been demonstrated that soluble and fusible nitrile-terminated polymide prepolymers can be made and cured with terephthalonitrile N, N'-dioxide,, it is recommended that one obtain the highest possible molecular weight, fusible, thermosetting polyimide prepolymer having sufficient nitrile groups to allow complete cure with terephthalonitrile N, N'-dioxide. The effect of properly utilizing a solvent system for A-staging the resin should be investigated so that the physical properties of laminates made from this resin can be optimized. Optimum molding parameters should also be developed for these resins. The use of catalysts in controlling the mode of addition and the curing rate of the addition polymerization process should be looked into. There is evidence that a catalyst such as boron trifluoride etherate would accelerate the addition polymerization process.

The use of a resin system based on polyfunctional nitrile substituted polyphenylene oxide and terephthalonitrile N, N'-dioxide should be studied. Experimental results show that such a system is feasible but that the cure is extremely rapid. The major task of this investigation is to slow down the addition reaction and make it proceed smoothly. Possibly this can be accomplished by the introduction of trace solvents and impurities.

Addition polymers based on the formation of 1,3,5-triazines should be investigated. The proper choice of a catalyst is the main task involved. The triazine ring has been shown to be thermally stable, and its formation during cure will contribute to the thermal properties of the polymers.

Addition polymers based on the reaction of terephthalonitrile N, N-dioxide with acetylene terminated polymers should be studied. Based on the technology developed in making soluble and fusible nitrile-terminated polyimides, similar prepolymers could be made which are acetylene-terminated. The chief task is the synthesis of pure ethynylaniline derivatives which can be used to make these prepolymers. The resulting resin system should be optimized by varying the stoichiometry so that one can obtain fusible polyimides with molecular weights as high as possible without sacrificing the necessary fusibility. The desired rigidity in the polymer can be obtained by incorporating a small amount of triamino aryl ether into the polymer structure. A-staging can be accomplished with the same solvent system used for advancing the nitrile-terminated polyimide and terephthalonitrile N, N'-dioxide. The literature reports that the addition of a nitrile oxide to an acetylenic group is much more facile than its addition to a nitrile group and therefore this type of cure offers much promise as a relatively low temperature curing system.

As in the other system, one should study the effect of both acid and basic catalysts on the cure rate of this resin system.

Addition polymers based on the trimerization of acetylene groups present another fruitful approach and should be studied. The trimerization of acetylenes to form benzenes has been known for a long time. In recent years, this reaction has been simplified by the discovery that a Ziegler-type catalyst causes it to proceed very effectively and rapidly at ordinary temperatures. Catalysts such as tri(isobutyl)aluminum-titanium tetrachloride and triethylaluminum-titanium tetrachloride have been effectively used to trimerize mono- and dialkylacetylenes to substituted benzenes. The Ziegler-type catalyst, therefore, should be investigated for curing, by trimerization the acetylene-terminated polyimide prepolymers discussed above.

SECTION V

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13. ABSTRACT

Nitrile-terminated polyimides were prepared by the reaction of benzophenonetetracarboxylic dianhydride (BTDA), aromatic diamines and meta- or para-aminobenzonitriles. At least two ether linkages were necessary per repeating unit to yield a fusible and soluble prepolymer provided the oligomer had no more than three repeating units. Using sulfolane as a solvent these oligomers could be A-staged with terephthalonitrile N, N'-dioxide (TPDO) to yield curable resins. A compressive strength of 7890 psi was obtained for a TPDO cured resin made from BTDA, bis[4-(3-aminophenoxy)phenyl] ether, 2,6-bis(3-aminophenoxy)aniline and meta-aminobenzonitrile. A flexural strength of 43.1×10^3 psi and a modulus of 2.0×10^6 psi were obtained for a glass cloth laminate using a TPDO-cured resin made by the reaction of BTDA, 1, 2-di(3-aminophenoxy)-benzene, 2, 6-bis(4-aminophenoxy)aniline, and meta-aminobenzonitrile. Synthetic techniques were explored for preparing acetylene-substituted polyimides which could be cured by reaction with TPDO. The reaction between acetylene derivatives and nitrile oxides appears to proceed by an addition type reaction and can serve as the basis of curing resins containing acetylenic groups.

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Thermosetting Addition Polymers						
Polyimides						
Polyoxadiazoles						
Terephthalononitrile N, N'-dioxide						