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SYNTHESIS OF POLYIMIDES CURABLE BY INTRAMOLECULAR CYCLOADDITION

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

MARCH 1977

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This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, Work Unit No. 73400469, "Polymers for Matrix Resins and Adhesives with Improved Processibilities and Performance". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Project Scientist.

This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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


F. E. ARNOLD
Project Scientist

FOR THE COMMANDER


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

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The concept of intramolecular cycloaddition (IMC) curing of polymers for use as matrix resins, previously established for polyphenylquinoxalines, has been extended to polyimides. Two novel aromatic diamines incorporating a 2,2'-bis(phenylethynyl) diphenyl moiety were synthesized and then polymerized with various bis-anhydrides. In the optimum combination, a polyimide was obtained which was soluble in aprotic solvents, softened at 185°C, underwent a cure at 233°C wherein the 2,2'-bis(phenylethynyl) diphenyl moiety was converted to a		

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much more rigid dibenzoanthracene structure, and the resultant polymer displayed a softening point of 310-325°C after cure.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, Work Unit No. 73400469, "Polymers for Matrix Resins and Adhesives with Improved Processibilities and Performance". It was administered under the direction of Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFML Project Scientist. This report describes work conducted from September 1974 to December 1975.

The work described in this report was conducted in the Polymer Branch Laboratory by Dr. F. L. Hedberg and Dr. F. E. Arnold. The manuscript was released by the authors in September 1976 for publication as a Technical Report.

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SECTION I

INTRODUCTION

State-of-the-art matrix resins for structural composites have certain limitations. In general the aliphatic systems have limited use temperatures due to poor thermoxidative stability and their moisture sensitivity. Certain aromatic heterocyclic systems on the other hand are moisture insensitive but are limited by their poor processing parameters such as solubility, fusibility, and cure. The primary processing problem inherent to a substantial number of aromatic heterocyclic systems is the absence of an effective curing method for these systems. Limitations in high temperature mechanical performance for instance can be directly attributed to the ineffectiveness of current curing methods. Out current research has been in the area of aromatic heterocyclic resins with the objective of devising a new cure concept in an effort to resolve the processing limitations of these resins.

The state-of-the-art method of fabricating composites requires flow of linear or branched resin molecules in order to bring about wetting of the fiber reinforcement and molding. The mobility of the molecules is then arrested during the curing step in which reactive sites along the molecules are caused to react with one another to form intermolecular bonds. The result is generally a hardened, three-dimensional network structure. However, an interesting paradox results in that, while cure is meant to arrest molecular mobility, this method of cure is itself very dependent upon molecular mobility to reach completion. When molecular movement ceases, unreacted cross-linking sites become "frozen" and curing stops.

Raising the curing temperature will increase molecular movement and more reactive sites are thus "unfrozen" allowing the curing process to continue. However, what this means is that the ultimate use temperature of the resin may only be as high as the curing temperature. Aromatic and aromatic-heterocyclic resins are much more susceptible to this mobility dependence than aliphatic resins due to their inherent rigidity. Therefore, what is needed, is an entirely different method of cure which is not

dependent upon extensive molecular mobility. There are two other problems resulting from the intermolecular curing method. For one, the three-dimensional network formed tends to be brittle. Secondly, in the case of some aromatic-heterocyclic resins, condensation curing reactions are currently required to effect a crosslinked structure analogous to the backbone structure. Condensation reactions evolve gaseous by-products which result in composite-weakening voids.

In previous work (Reference 1) we proposed and verified a new concept of curing which obviated all of the drawbacks inherent in the state-of-the-art intermolecular cure. The concept is an intramolecular cycloaddition or IMC cure. This consists of starting with linear mobile polymer chains which display flow and moldability at relatively low temperatures. The molecular mobility is subsequently arrested by having pairs of pendant groups along the polymer chain undergo an intramolecular cycloaddition reaction to form a more rigid and therefore less mobile structure.

The IMC type of reaction depends upon only a rotational movement of the polymer backbone which requires substantially less molecular mobility than the translational movement needed for the intermolecular cure. Therefore, the curing reaction can continue to completion long after the resin is essentially "hard", and the resultant use temperature should be substantially higher than the cure temperature. Furthermore, because it is an intramolecular reaction, a linear polymer is obtained and the brittleness of a three-dimensional structure may be avoided. Finally, because it is a cycloaddition type of reaction no gaseous, void-producing by-products are evolved.

Polyphenylquinoxalines containing 2,2'-bis(phenylethynyl)diphenylene moieties along the polymer backbone were synthesized. As anticipated, these polymers were found to undergo an IMC curing reaction consisting of an intramolecular cycloaddition of pendant groups to a dibenzoanthracene backbone structure. The IMC reduced chain mobility and the fused ring structure increased the glass transition temperature of the polymer. The potential of this approach to curing high temperature polymers was

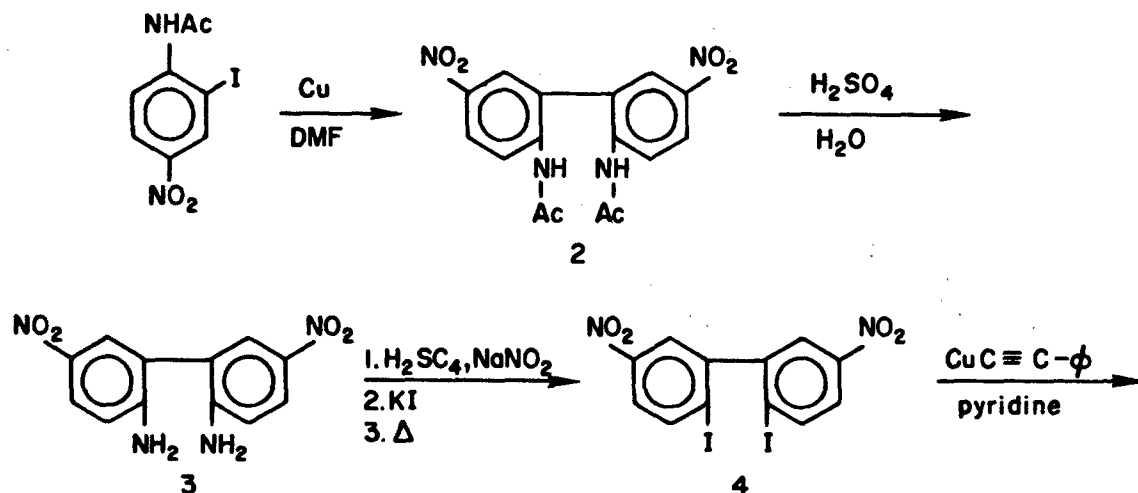
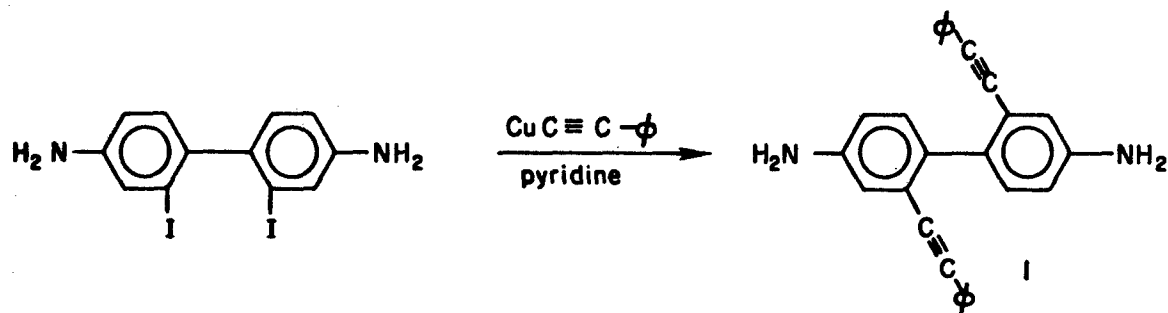
demonstrated in the processing of one such polymer having an initial Tg of 215°C. Curing at 245°C with no evolution of volatiles produced a Tg of 265°C. This very significant increase in potential use temperature via a volatile-free IMC cure provides promise for a tough phenylquinoxaline resin system which can be used to fabricate reinforced composites that have use temperatures far exceeding processing temperatures.

In the present work, we have attempted to extend the IMC curing concept to the polyimide family of high-temperature polymers.

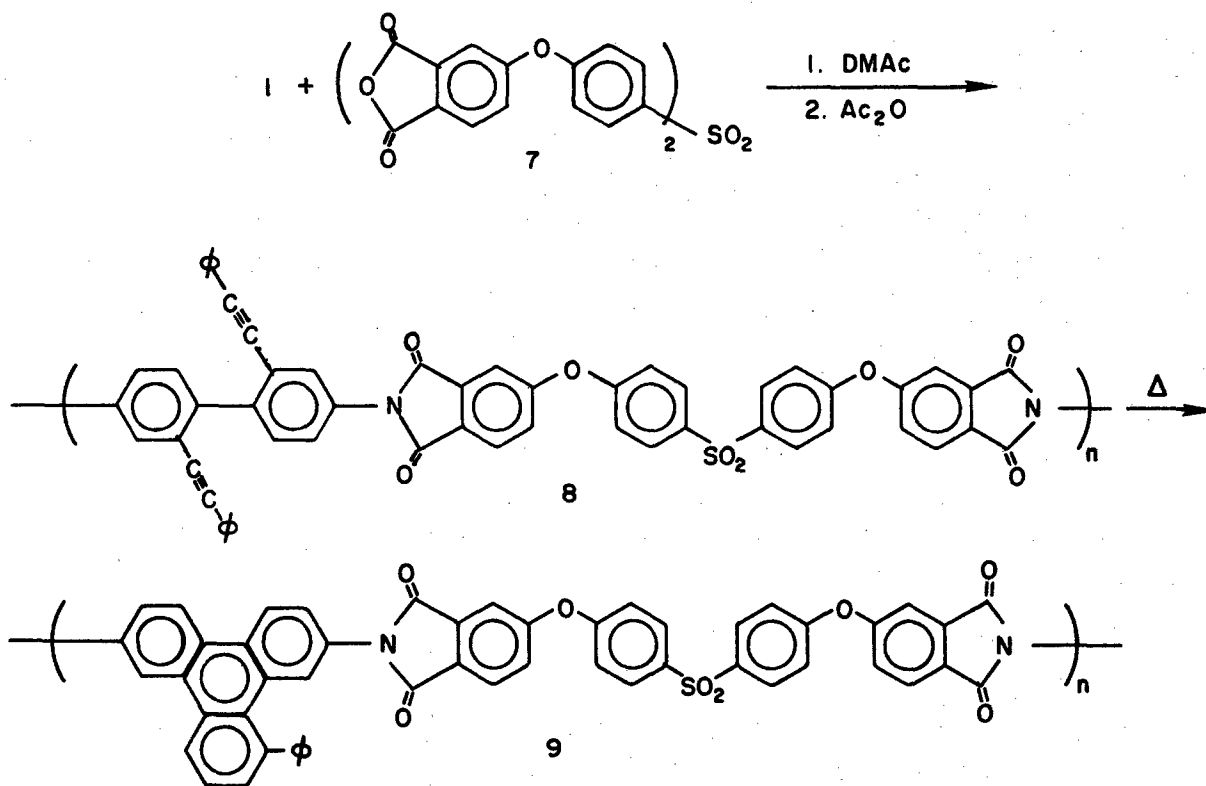
SECTION II

RESULTS AND DISCUSSION

In order to utilize an IMC reaction analogous to that used for the polyphenylquinoxaline system, i.e. based on the conversion of a 2,2'-bis(phenylethynyl) biphenyl to a dibenzoanthracene (Reference 1), the following syntheses of monomers 1 and 6 were conceived and carried out.



Monomer 1 was prepared in one step from 2,2'-diiodobenzidine. The simplicity of this preparation is somewhat offset, however, by the current expensive and low-yield preparative routes to 2,2'-diiodobenzidine (References 2, 3, 4). Reaction of monomer 1 with bis(4-(3,4-dicarboxyphenoxy)-phenyl) sulfone dianhydride (7) afforded polymer 8. It was hoped that, by analogy with previous work in the polyphenylquinoxaline area (Reference 1), polymer 8 would undergo softening below 215°-220°C to provide the desired fusibility and would subsequently undergo an IMC reaction upon heating to 245°-250°C to afford polymer 9 the softening point (T_g) of which should be >350°C.

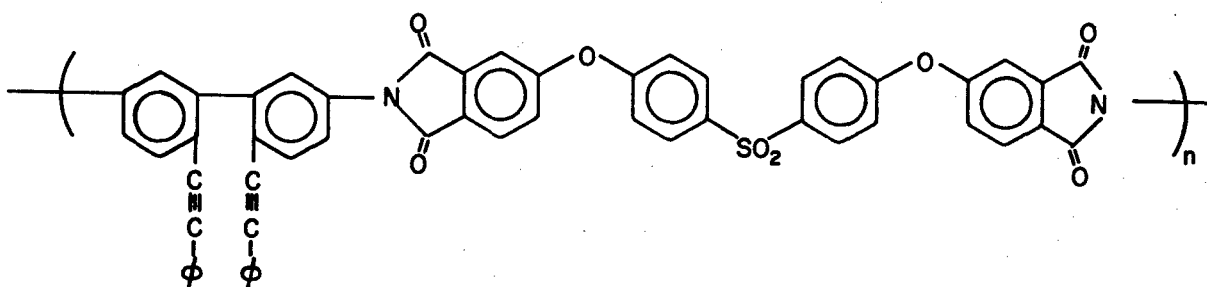
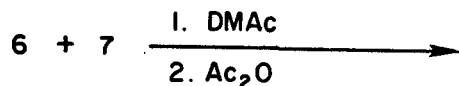


Analysis of polymer 8 by differential scanning calorimetry (DSC) showed a broad exotherm maximizing at 246°C, characteristic of an IMC reaction of the pendant phenylethynyl groups. However, no softening of polymer 8 prior to the IMC reaction was observed by either DSC or torsion braid analysis (TBA). A Tg observed at 380°C by DSC and at 400°C by TBA may be attributed by analogy with previous work to polymer 9 (Reference 1). This conclusion was further substantiated by the disappearance of the infrared acetylene absorbance of polymer 8 at 2210 cm^{-1} after heating to 300°C. While the absence of any softening prior to the IMC reaction eliminated polymer 8 as a useful candidate material, the fact that the IMC reaction proceeded in the solid state was encouraging.

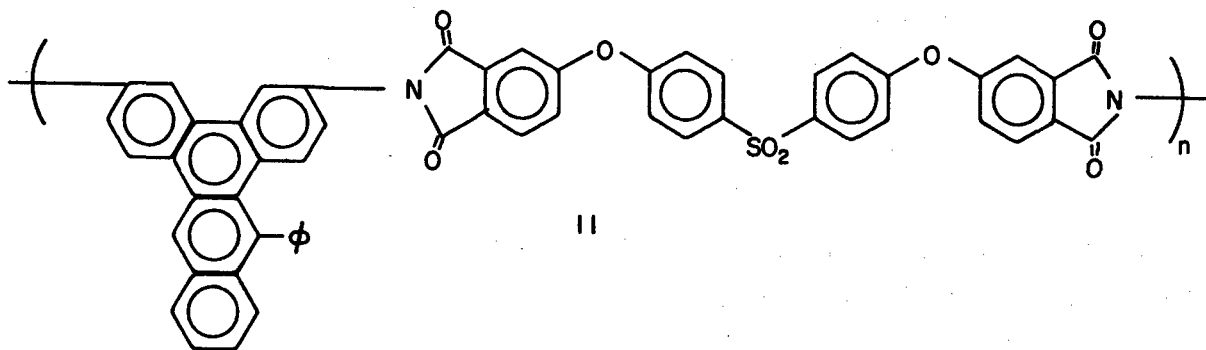
High Tg's in monomer 1- based polymers may be attributed to a large extent to the linearity inherent in monomer 1. The inclusion of monomer 1 in an IMC polymer such as structure 8 would cause a high Tg in both the initial polymer 8 and the IMC-cured polymer 9. Furthermore, because the elimination of rotational movement around the biphenyl carbon-carbon bond has only a small restrictive effect on movement along the polymer backbone, the Tg differential between polymer 8 and polymer 9 will be based mainly upon differential packing effects between the 4,4'-substituted 2,2'-bis(phenylethynyl) biphenyl and 2,7,9-trisubstituted dibenzoanthracene moieties.

Monomer 6 - based polymers analogous to polymers 8 and 9 might be expected to display both a lower initial Tg versus polymer 8 in the polymer 8 analog and a greater Tg differential between the polymer 8 and polymer 9 analogs, due to the effect of meta orientation of the nitrogen atoms versus the biphenyl linkage. The major effect is the necessitation of transitional movement of the nitrogen atoms along with their substituents in the polymer 8 analog concurrently with any rotational movement around the biphenyl carbon-carbon bond. The elimination of this rotational movement would have a severely restrictive effect upon the mobility of the polymer backbone and thus the Tg of this polymer would not be expected to be much lower than polymer 9. Therefore, monomer 6 was reacted with compound 7 to afford polymer 10. One effect of changing from a para orientation of nitrogen versus biphenyl in polymer 8 to the

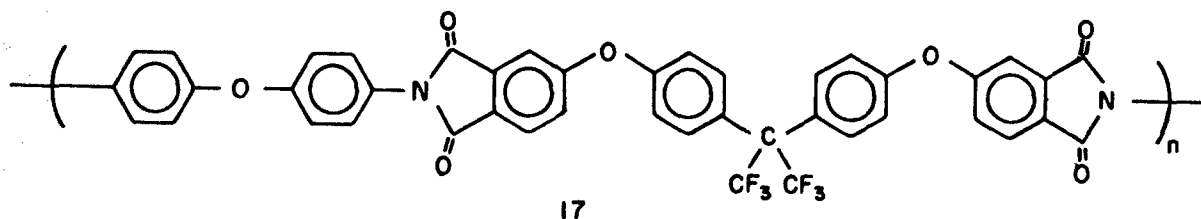
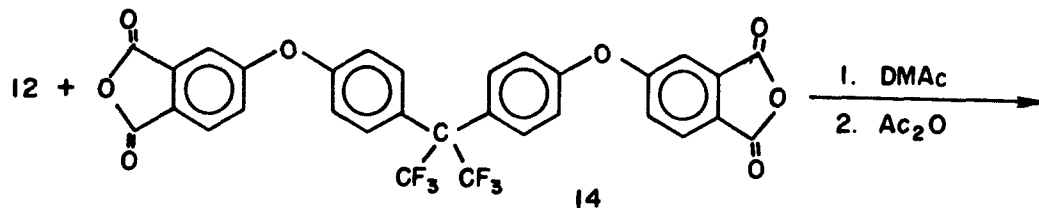
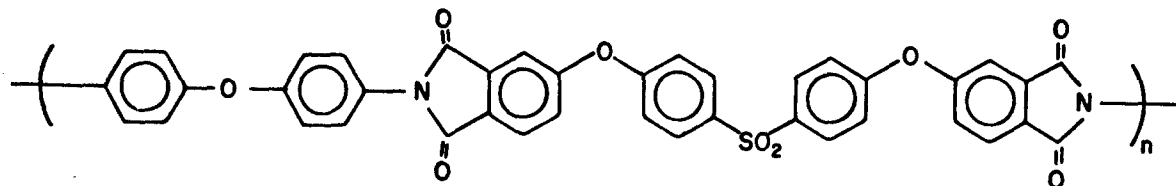
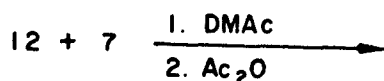
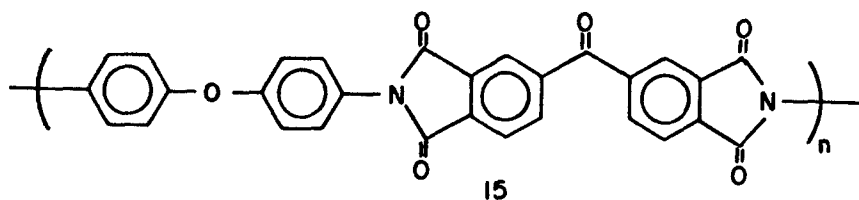
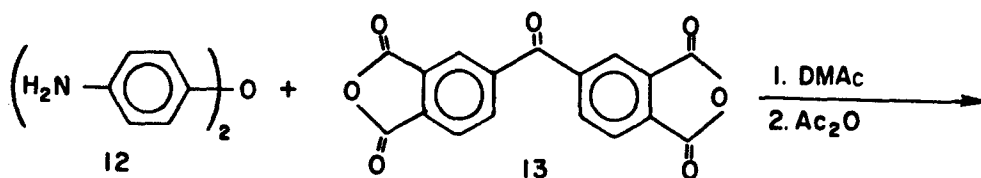
meta orientation in polymer 10 which became immediately apparent was on solubility behavior. Whereas the only aprotic solvents in which polymer 8 was soluble were N,N-dimethylacetamide (DMAc) and N,N'-dimethylformamide (DMF), polymer 10 was also soluble in tetrahydrofuran (THF) and chloroform.



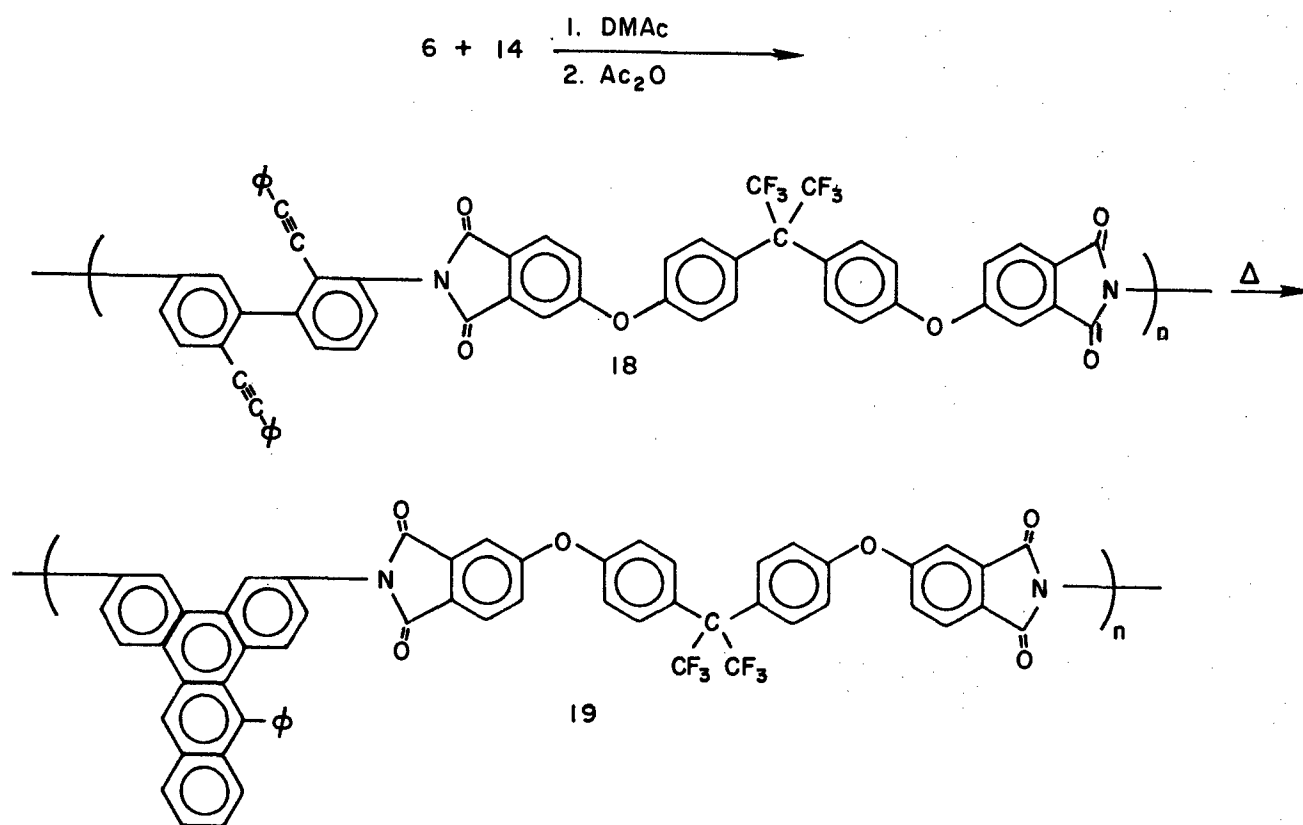
Thermomechanical analysis (TMA) of polymer 10 showed a T_g at 225°C. Analysis by DSC revealed that the exotherm corresponding to the IMC reaction maximized at 237°C. The location of the T_g for the cured system (polymer 11) was somewhat ambiguous, with one weak transition appearing at 258°C in the DSC and two transitions at 308°C and 363°C present by TMA.



The proximity of the T_g for polymer 10 to the IMC reaction temperature was too close for substantial softening to occur before cure. In order to attain a lower T_g , a study was made of the effect of various dianhydrides on the T_g of polyimides derived from p,p'-oxydianiline (12). Reaction of monomer 12 was carried out with benzophenone-3,3',4,4'-tetracarboxylic dianhydride (13), monomer 7, and 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]-hexafluoropropane dianhydride (BFDA) (14) to afford polymers 15, 16 and 17, respectively.



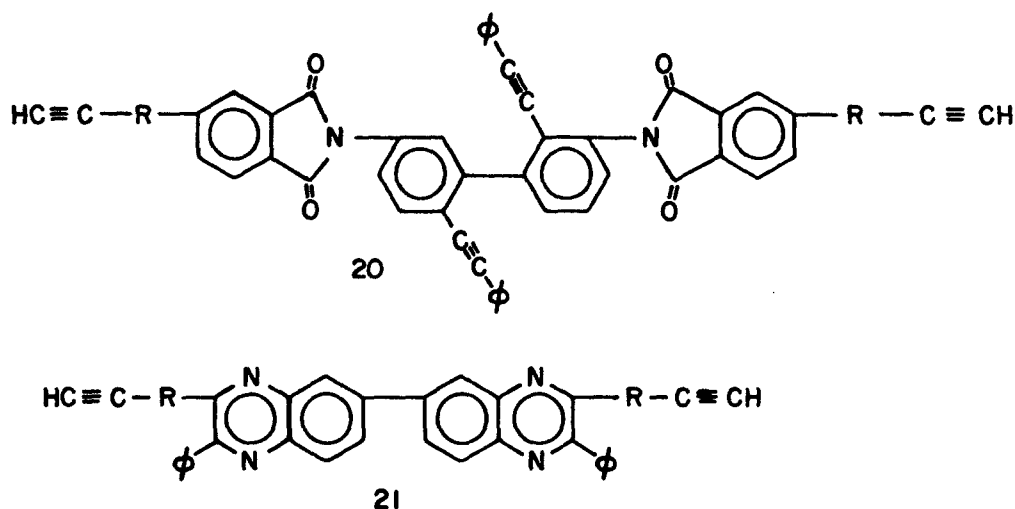
The Tg's of polymers 15, 16, and 17 (all determined by DSC) were 268°, 247°, and 220°C, respectively. On the basis of these results, the optimal combination of monomers appeared to be 6 and 14 which were reacted together to give polymer 18. Analysis of this polymer showed a Tg by TMA of 185°C. The IMC reaction exotherm began around 165°C but did not show a significant rate of increase until above 200°C with a maximum at 233°C. The Tg of the cured polymer (19) after the IMC reaction appeared at 310°C by TMA and 325°C by DSC.



SECTION III CONCLUSIONS

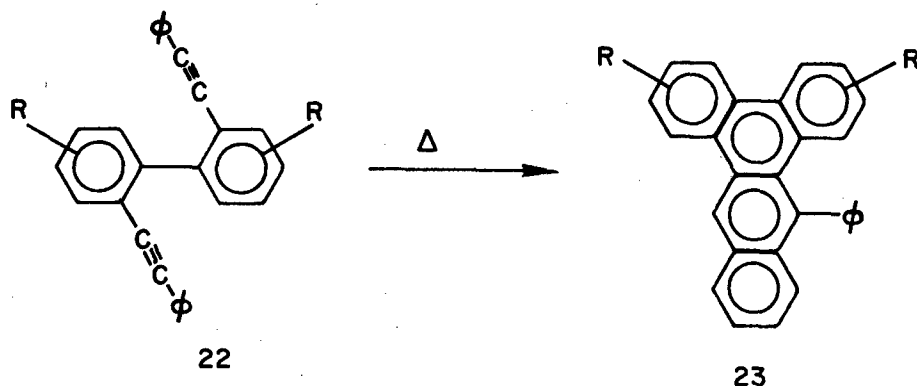
The thermomechanical properties for polymer 18 satisfy the original goals of this research effort supplementing and further confirming the proof of the IMC concept offered in Reference 1. In theory, polymer 18 could be softened and molded at 185°C and cured at 215°C, and the cured polymer (19) would be usable at temperatures up to 300°C. In practice, polymer 18 suffers from a problem which has been found to be common to all high molecular weight thermoplastic polymers, specifically that the extent of flow at the T_g is insufficient for satisfactory processing.

Current and future work on IMC is directed toward solving this problem. One approach is the use of oligomers such as structures 20 or 21. Thermal addition polymerization of terminal acetylene end-groups



has been shown in recent years to afford resin systems with either imide (Reference 5) or quinoxaline (Reference 6) backbones. The incorporation of an IMC site in such resins should substantially lower the current high curing temperatures for these resins without lowering their excellent use temperature.

A second approach to increased initial flow is the use of plasticizers. The major drawback to this approach is that the amount of plasticizer necessary to cause a sufficient lowering of the Tg of an IMC polymer such as 18 will also lower the Tg of polymer 19 to such an extent that there will be no significant gain in use temperature versus cure temperature. A method which might circumvent this dilemma is to incorporate the IMC site into the plasticizer as in structure 22. The R-groups would be varied to accommodate both a low melting point and compatibility with the specific thermoplastic polymer to be plasticized. In this case, it is the plasticizer which would undergo "cure" to give the higher melting derivative 23. By virtue of its increased melting point, its inertness, and its probable lesser compatibility with the polymer, compound 23 would remain in the resin system as an inert filler while allowing the system to reassume the original Tg (and use temperature) of the pure thermoplastic resin.



SECTION IV EXPERIMENTAL

1. GENERAL

All DSC and TDA measurements were carried out under nitrogen at 20°C per minute by Drs. G. F. L. Ehlers and K. R. Fish of the Polymer Branch, Nonmetallic Materials Division, Wright-Patterson Air Force Base, Ohio 45433. All viscosity measurements were carried out at 30°C.

2. MONOMERS

a. 2,2' Diiodobenzidine

2,2'-Diiodobenzidine was prepared in two steps from 3-iodonitrobenzene by reported procedures (References 2 and 3).

b. 2,2'-Bis(phenylethynyl)benzidine (1)

A mixture of 2,2'-diiodobenzidine (8.8 g, 0.020 mole) and copper phenylacetylide (6.5 g, 0.040 mole) was stirred under a flow of dry nitrogen for 15 minutes, and then 250 ml of pyridine which had been simultaneously deaerated with dry nitrogen for 15 minutes was added. The reaction mixture was stirred and refluxed under nitrogen for 48 hours, during which time three 1.0 g (0.001 mole) portions of copper phenylacetylide were added at 8-, 24-, and 32-hour intervals, respectively. The pyridine was then vacuum-distilled from the reaction mixture at 1.0 mm pressure. The residue was extracted 3x200 ml with methylene chloride, and the combined methylene chloride extracts were filtered. The filtrate was concentrated to 100 ml and chromatographed on a column of dry alumina. The column was eluted with methylene chloride followed by 1:1 methylene chloride-tetrahydrofuran (THF). The progress of the 2,2'-bis-(phenylethynyl)benzidine was followed by means of a 254 mm fluorescent lamp upon irradiation with which the substance afforded an intense blue fluorescence. The portion of eluate containing the 2,2'-bis(phenylethynyl)benzidine was concentrated to dryness and the residue was dissolved in 250 ml of THF. The substance was precipitated as its bis-HCL salt by the addition of 10 ml of concentrated HCL. The salt was collected by filtration, washed with THF, and suspended in 50 ml of methanol. Addition of 10 ml of

concentrated NH_4OH regenerated the free diamine which was precipitated by the addition of the methanolic solution to 500 ml of water. The product from the final precipitation was drier under vacuum for 16 hours at 23°C and 1 mm and dissolved in 100 ml of dry benzene. The benzene solution was concentrated to dryness by freeze-drying at two microns to give 3.6 g (48%). The 2,2'-bis(phenylethynyl)benzidine softened above 70°C to a very viscous melt and darkened above 150°C . Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{N}_2$: C, 87.50; H, 5.21; N, 7.29 mol. wt., 384. Found: C, 87.46, 87.12; H, 5.05, 5.17; N, 6.90; mol. wt., 384 (by mass spectrometry).

c. 2'-Iodo-4'-nitroacetanilide

2'-Iodo-4'-acetanilide has been previously prepared in two steps starting from 2-iodoaniline (Reference 7). For the present work, we used a different two-step route starting from the more readily available 4-nitroaniline. The first step was a modification of a reported procedure for iodination of 4-nitroaniline which utilized acetic acid as the reaction solvent and was found by TLC analysis to give a less pure product in our hands (Reference 8).

(1) 2-Iodo-4-nitroaniline

A solution of p-nitroaniline (91.0 g, .66 mole) in dry N,N-dimethylacetamide (450 ml) was stirred at 0° with ice-bath cooling. To this was added a solution in methanol (200 ml) at a rate such that the temperature of the reaction mixture did not exceed 40°C . After completion of the addition, the reaction mixture was stirred an additional one hour at 23°C and poured, with stirring, into three liters of water. The precipitate which formed was stirred for one hour, filtered, washed with water, and dried overnight at 60°C and 1 mm. The crude product (168.6 g) contained a very small amount of higher R_f impurity by TLC (probably diiodinated material) and was used without further purification or drying for the next step in the reaction sequence.

(2) 2'-Iodo-4'-nitroacetanilide

The crude 2-iodo-4-nitroaniline (168.5 g) prepared as described above, was dissolved in acetic acid (900 ml) by stirring at 23°C . Acetic

anhydride (160 ml) was added and the solution was stirred and heated at 110° for one hour. The reaction mixture was cooled and poured into six liters of ice water, and the precipitate formed was stirred for one hour, filtered, washed with water, dried under suction, and recrystallized from ethanol to afford 194 g (95% based upon p-nitroaniline) of 2'-iodo-4'-nitroacetanilide. Elemental analysis, I.R. and m.p. (120°C) were in agreement with the literature (Reference 7).

d. 2,2'-Bis(acetamido)-5,5'-dinitrobiphenyl (2)

A mixture of 2'-iodo-4'-nitroacetanilide (50.02 g., 0.164 mole), copper-bronze (87.9 g) and N,N-dimethylformamide (350 ml) was stirred and heated at 150°C under nitrogen for one hour and filtered. The filter cake was washed with tetrahydrofuran, and the combined filtrate and washings were concentrated under vacuum to 100 ml and poured, with stirring, into 1200 ml of concentrated ammonium hydroxide. The resultant precipitate was filtered, washed with water, and dried at 100°C and 1 mm to yield 34.1 g (58%) of 2,2'-bis(acetamido)-5,5'-dinitrobiphenyl. An analytical sample, m.p. 263-265°C, was obtained by recrystallization from ethanol. Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 53.60; H, 3.91; N, 15.63; mol. wt., 358. Found: C, 53.60, 53.27; H, 3.78, 3.76; N, 15.82, 15.74; mol. wt., 358 (by mass spectrometry).

e. 2,2'-Diamino-5,5'-dinitrobiphenyl (3)

To a solution of 2,2'-bis(acetamido)-5,5'-dinitrobiphenyl (34.1 g, 0.0953 mole) in concentrated sulfuric acid (500 ml) was added, slowly, 250 ml of water. The reaction mixture was stirred and heated at 110°C for one hour, and then poured, with stirring, into four liters of ice water. The resultant precipitate was filtered, washed with water, and dried at 100°C and 1 mm to give 24.9 g (96%) of 2,2'-diamino-5,5'-dinitrobiphenyl. An analytical sample, m.p. 315-317°C, was obtained by recrystallization from ethanol-tetrahydrofuran. Anal. Calcd. for $C_{12}H_{10}N_4O_4$: C, 52.55; H, 3.68; N, 20.43; mol. wt., 274. Found: C, 52.31, 52.43; H, 3.75, 3.57; N, 20.53, 20.64; mol. wt., 274 (by mass spectrometry).

f. 2,2'-Bis(phenylethynyl)-5,5'-dinitrobiphenyl (5)

A mixture of 2,2'-diiodo-5,5'-dinitrobiphenyl (19.8 g, 0.040 mole), copper phenylacetylide (14.6 g, 0.089 mole) and pyridine (373 ml) was deaerated with nitrogen for 15 minutes and heated at 110°C under nitrogen for five hours. The reaction mixture was then cooled to 23°C and poured, with stirring, into 5.5 liters of 10% sulfuric acid. After one hour of stirring, the precipitate which formed was filtered, washed with water, dried under suction for 20 hours, and extracted with chloroform. Removal of chloroform and recrystallization from benzene afforded 9.3 g (52%) of 2,2'-bis(phenylethynyl)-5,5'-dinitrobiphenyl, m.p. 216°-218°C. Anal. Calcd. for $C_{28}H_{16}N_2O_4$: C, 75.66; H, 3.63; N, 6.30; mol. wt., 444. Found: C, 75.82, 75.66; H, 3.59, 3.43; N, 6.10, 6.07, mol. wt. 444 (by mass spectrometry).

g. 2,2'-Bis(phenylethynyl)-5,5'-diaminobiphenyl (6)

To a solution of calcium chloride (9.94 g, 0.0904 mole) in water (100 ml), stirred under nitrogen, was added in order absolute ethanol (200 ml), zinc dust (6.05 g, 0.0931 mole) and a solution of 2,2'-bis(phenylethynyl)-5,5'-dinitrobiphenyl (2.06 g, 0.00464 mole) in dioxane (100 ml). The resultant mixture was stirred and refluxed under nitrogen for four hours, cooled to 23°C, and filtered to remove excess zinc. The filtrate was diluted with water (1.5 liters), affording a yellow precipitate, and extracted with chloroform (3 x 200 ml). The combined chloroform extracts were concentrated to dryness by vacuum distillation. The residue was taken up in methanol (30 ml), fluoboric acid (10 ml) and diluted with 5% fluoboric acid (150 ml). The brown precipitate present was filtered and the filtrate was made basic with ammonium hydroxide. The yellow precipitate which formed was filtered, washed with water, and dried under vacuum at 60°C to give 0.84 g (47%) of 2,2'-bis(phenylethynyl)-5,5'-diaminobiphenyl, m.p. 159°-161°C after recrystallization from chloroform-cyclohexane. Anal. Calcd. for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29; mol. wt., 384 Found: C, 87.07, 87.00; H, 5.02, 4.86; N, 7.37, 7.38, mol. wt., 384 (by mass spectrometry).

3. POLYMERS

a. Poly[(1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)[2,2'-bis(phenylethynyl) [1,1'-biphenyl]-4,4'-diyl](1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl) oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy]. (8)

A mixture of 2,2'-bis(phenylethynyl)-benzidine (1.014 g, 0.263 mole) and bis(4-(3,4-dicarboxyphenoxy) sulfone dianhydride (1.430 g, 0.263 mole) was stirred under an atmosphere of dry nitrogen while N,N-dimethylacetamide (DMAC, 250 ml), which had been dried over molecular sieves and deaerated with dry nitrogen, was added. The reaction mixture was stirred at 23°C for 24 hours. Acetic anhydride (10 ml) was added to the reaction mixture and it was heated at 130°C for 1.5 hours. After cooling, the reaction mixture was poured into two liters of methanol to precipitate the polymer which was washed four times in a blender with methanol and dried at 80°C for 24 hours. A 0.5% solution in DMAC at 30°C gave an inherent viscosity of 0.45. Anal. Calcd. for $C_{56}H_{30}N_2O_8S$: C, 75.50; H, 3.39; N, 3.14; S, 3.60. Found: C, 75.16, 75.63; H, 3.13, 3.17; N, 2.69, 2.72; S, 3.63, 3.86.

Analysis of the polymer by DSC showed an exothermic reaction maximizing at 246°C, corresponding to the intramolecular cycloaddition of the acetylenes to form polymer 9. No glass transition temperature (T_g) was observed for the polymer below the 246°C cycloaddition temperature either by DSC, TMA or TBA. The T_g of the cured polymer 9 was 380°C by DSC and 400°C by TBA.

b. Poly[(1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)[2,2'-bis(phenylethynyl)[1,1'-biphenyl]-5,5'-diyl](1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl)oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy] (10)

A mixture of 2,2'-bis(phenylethynyl)-5,5'-diaminobiphenyl (0.292 g, 0.000760 mole) and bis(4-(3,4-dicarboxyphenoxy)phenyl)sulfone dianhydride (0.412 g, 0.000760 mole) in DMAC (20 ml) was reacted according to the same procedure described previously for polymer 8 to afford polymer 10 with an inherent viscosity 0.11 (0.5% solution in DMAC). Anal. Calcd. for $C_{56}H_{30}N_2O_8S$: C, 75.50; H, 3.39; N, 3.14; S, 3.60. Found: C, 75.55, 75.85; H, 2.96, 3.25; N, 3.05, 3.32; S, 3.38, 3.40.

Analysis of polymer 10 by DSC showed an exothermic reaction maximizing at 237°C. Prior softening of the polymer at 225°C was indicated by TMA. After curing the polymer at 240-250°C for 24 hours, a Tg of 358°C was measured by DSC for polymer 11. TMA of polymer 11 showed transitions at 308°C and 362°C.

c. Poly[(1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)[1,4-phenyleneoxy-1,4-phenylene](1,3-dihydro-1,3-dioxo-2H-isoindole-2,5--diyl) carbonyl] (15)

A mixture of p,p'-oxydianiline (1,378 g, 0.00689 mole) and benzophenone-3,3',4,4'-tetracarboxylic dianhydride (2.217 g, 0.00689 mole) in DMAC (50 ml) was reacted according to the same procedure described above for polymer 8. Before addition of the acetic anhydride, a 10 ml aliquot was removed for a viscosity determination on the intermediate amide-acid: $\eta_{inh}=1.38$. Polymer 15 precipitated during the heating period with acetic anhydride. The polymer was only soluble in strong acids. Anal. Calcd. for $C_{29}H_{14}N_2O_6$: C, 71.60; H, 2.88; N, 5.76. Found: C, 70.35, 70.52; H, 2.68, 2.70; N, 4.87, 5.10.

Analysis of polymer 15 by DSC showed a Tg of 268°C and Tm of 392°C.

d. Poly[1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl][1,4-phenyleneoxy-1,4-phenylene] (1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl) oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy] (16)

A mixture of p,p'-oxydianiline (0.500 g, 0.00250 mole) and bis (4-(3,4-dicarboxyphenoxy)phenyl) sulfone dianhydride (1.35 g, 0.00250 mole) in DMAC (100 ml) was reacted according to the same procedure described previously for polymer 8 to afford polymer 16 with an inherent viscosity of 0.74 (0.5% solution in DMAC). Anal. Calcd. for $C_{40}H_{22}N_2O_9S$: C, 67.98; H, 3.14; N, 3.97; S, 4.54. Found: C, 68.28, 68.02; H, 3.10, 3.13; N, 3.88, 4.02; S, 4.38, 4.47.

Analysis of polymer 16 by DSC showed a Tg of 247°C.

e. Poly[(1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)[1,4-phenyleneoxy-1,4-phenylene](1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl)oxy-1,4-phenylene [bis (trifluoromethyl) methylene]-1,4-phenyleneoxy] (17)

A mixture of p,p'-oxydianiline (0.137 g, 0.000684 mole) and 2,2'-bis [4-(3,4-dicarboxyphenoxy) phenyl]hexafluoropropane dianhydride (0.430 g, 0.000684 mole) in DMAC (20 ml) was reacted according to the same procedure described above for polymer 8 to afford polymer 17 with an inherent viscosity of 0.28 (0.5% solution in DMAC). Anal. Calcd. for $C_{43}H_{22}F_6N_2O_7$: C, 65.15; H, 2.80; F, 14.38; N, 3.54. Found: C, 64.54, 64.52; H, 2.69, 2.61; F, 14.48, 14.49; N, 3.46, 3.62.

Analysis of polymer 17 by DSC showed a Tg of 220°C.

f. Poly[(1,3-dihydro-1,3-dioxo-2H-isoindole-5,2-diyl)[2,2'-bis (phenylethynyl) [1,1'-biphenyl]-5,5'-diyl] (1,3-dihydro-1,3-dioxo-2H-isoindole-2,5-diyl) oxy-1,4-phenylene [bis (trifluoromethyl) methylene]-1,4-phenyleneoxy] (18)

A mixture of 2,2'-bis(phenylethynyl)-5,5'-diaminobiphenyl (0.172 g, 0.000448 mole) and 2,2'-bis[4-(3,4-dicarboxyphenoxy) phenyl]hexafluoropropane dianhydride (0.282 g, 0.000448 mole) in DMAC (20 ml) was reacted according to the same procedure described above for polymer 8 to afford polymer 18 with an inherent viscosity of 0.30 (0.5% solution in DMAC). Anal. Calcd. for $C_{59}H_{30}F_6N_2O_6$: C, 72.54; H, 3.10; N, 2.87. Found: C, 71.52; H, 3.13; N, 2.93.

Analysis of polymer 18 by DSC showed an exotherm beginning around 165°C, increasing rapidly above 200°C and maximizing at 233°C. A Tg for the cured polymer (19) occurred at 325°C by DSC. TMA showed a Tg for polymer 18 of 185°C and a Tg of 310°C for polymer 19.

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