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# Synthesis and Characterization of Reactive End-Capped Polymide Oligomers

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ABSTRACT

A series of reactive, end-capped, polyimide oligomers has been prepared for possible use as planarizing coatings in the electronics industry. Thus, 1,3-bis(3-aminophenoxy)benzene was treated with various excess amounts of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride in m-cresol containing toluene and isoquinoline. The resulting anhydride-terminated amic-acid oligomers were thermally imidized and then allowed to react with 3-aminophenylethyne, 1-phenyl-4-(3-aminophenyl)buta-1-ene-3-yne, 1-phenyl-4-(3-aminophenyl)-1,3-butadiyne, 2-aminobiphenylene, or 1-phenyl-2-(3-aminophenyl)ethyne. Thermal imidization of these intermediates produced the corresponding end-capped polyimide oligomers. The white oligomers were soluble in organic solvents, such as diglyme, and had glass transition temperatures ($T_g$'s) between 95 and 145°C. The $T_g$ of an ethynyl-terminated oligomer was reduced from 105 to 62°C upon the incorporation of 20 wt % of the reactive plasticizer bis[2-(3-ethynylphenoxy)ethyl]ether. The oligomers underwent exothermic polymerizations between 225 and 420°C. Their TGA thermograms showed 5% weight losses near 530°C in air.

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## INTRODUCTION

The development of very large scale integration circuits has created a need in the microelectronics industry for new dielectric insulating materials. In addition to low dielectric constants, these materials must display excellent thermal stability, low moisture uptake, and high softening temperatures. They must also effectively planarize the underlying metal surface. The leading candidates for this application are the polyimides (1-3) and the polyimide isoindoloquinazolinediones (4-6). They are applied in solution in the form of their polyamic acid precursors by a spin coating process. The thin coatings are then heated to remove residual solvent and to affect imidization. Several problems, however, are associated with this approach. For example, slight variations in the heating cycle can affect the resins' properties (2). The polymers also do not provide complete planarization (3).



Many of these problems could be solved through the development of a soluble, fully-imidized, polyimide oligomer that could be thermally cured. In fact, Thermid 600®, an ethynyl-terminated polyimide resin, has been investigated for this purpose (7). This resin, however, does not undergo sufficient flow before the initiation of the cure process. Thus, before this type of resin can be utilized, the temperature difference between the flow temperature and the cure temperature, i.e. the "processing window," must be increased. The overall goal of this research was to prepare end-capped polyimide oligomers that undergo flow at lower temperatures and/or cure at higher temperatures than the current state-of-the-art resins. Flow temperatures were to be decreased through the use of 2,2-bis(3,4-di-

carboxyphenyl)hexafluoropropane dianhydride, which is a more flexible molecule than the 3,3',4,4'-benzophenonetetracarboxylic dianhydride currently used, and by the use of a reactive plasticizer. Cure temperatures were to be increased by the use of capping agents containing enyne, 1,3-diyne, biphenylene, and phenylethynyl moieties. The specific objectives of this work were: (a) to synthesize four capping agents, i.e., 1-phenyl-4-(3-aminophenyl)buta-1-ene-3-yne, 1-phenyl-4-(3-aminophenyl)1-3-butadiyne, 2-aminobiphenylene, and 1-phenyl-2-(3-aminophenyl)ethyne; (b) to prepare polyimide oligomers of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(3-aminophenoxy)benzene end-capped with 3-aminophenylethyne and the above agents; (c) to characterize the oligomers with regard to their flow temperatures and effective curing temperatures; and (d) to synthesize bis[2-(4-ethynylphenoxy)ethyl] ether and to investigate its use as a reactive plasticizer.

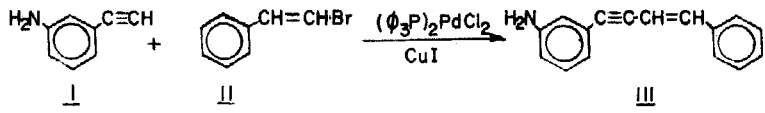


## RESULTS AND DISCUSSION

### Synthesis of End-Capping Agents

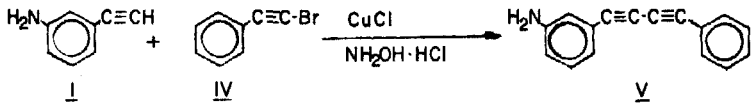
The work was initiated with the synthesis of the end-capping agent 3-aminophenylethyne (I). This material was prepared from 3-bromonitrobenzene according to the known procedure (8).

1-Phenyl-4-(3-aminophenyl)buta-1-ene-3-yne (III) was obtained from the coupling reaction of β-bromostyrene (II) with I in the presence of a palladium catalyst mixture. The light yellow product was purified by several recrystallizations from aqueous ethanol.



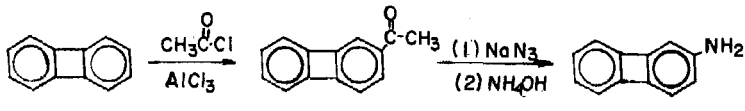

I II III

Treatment of I with phenylbromoacetylene (IV) in the presence of a copper catalyst gave 1-phenyl-4-(3-aminophenyl)-1,3-butadiyne (V). Compound IV was obtained from the reaction of phenylacetylene with bromine in the presence of base (9).



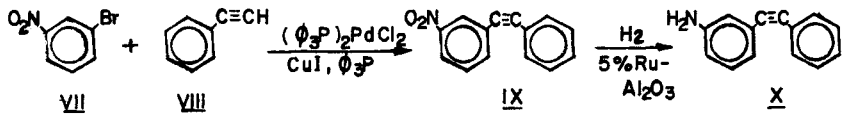

I IV V

2-Aminobiphenylene (VI) was synthesized from biphenylene according to the previously reported procedure (10). Biphenylene was prepared by diazotization of anthranilic acid followed by pyrolysis of the resultant diazonium carboxylate intermediate (11).




VI

Hydrogenation of 1-phenyl-2-(3-nitrophenyl)ethyne (IX) over a ruthenium catalyst afforded 1-phenyl-2-(3-aminophenyl)ethyne (X). Compound IX was obtained from the reaction of 3-bromonitrobenzene (VII) with phenylacetylene (VIII) in the presence of a palladium catalyst mixture. Compound X was also synthesized by treatment of 3-iodoacetanilide with cuprous phenylacetylide followed by hydrolysis. This procedure, however, gave lower yields.




VII VIII IX X

Monomers

1,3-Bis(3-aminophenoxy)benzene (XI) was prepared by the reaction of the disodium salt of resorcinol with VII followed by hydrogenation of the resulting dinitro intermediate (12). The white diamine was recrystallized from aqueous ethanol immediately prior to use.

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (XII) was extracted from DuPont's NR-150-B2.® (This complex mixture of monomers is no longer commercially available).

Synthesis of Polyimide Oligomers

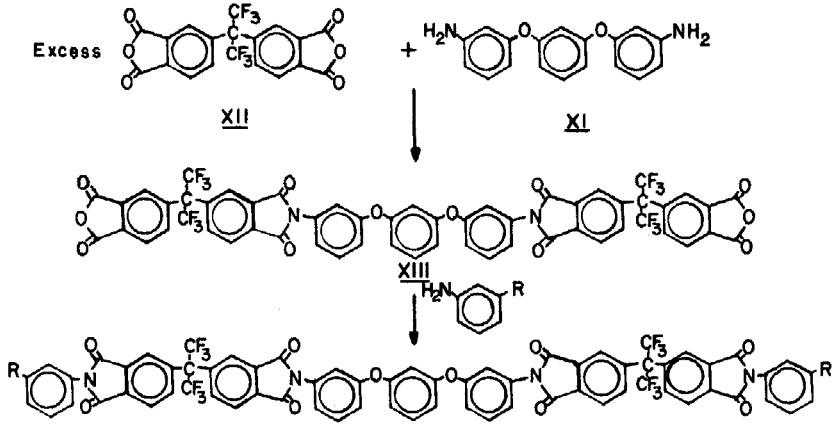
Anhydride-terminated oligomers (XIII) were prepared by allowing an excess of XII to react with XI. A 2 to 1 molar excess was normally used. One reaction was carried out with a 4 to 3 molar ratio in order to obtain an oligomer (XIVb) with a higher molecular weight. The reactions were carried out in a heated mixture of m-cresol and toluene containing isoquinoline. The water that formed during imidization was distilled from the reaction vessel as a water-toluene azeotrope. Oligomer XIII was then treated with I, III, V, VI, and X under the above conditions to afford a new series of reactive oligomers (XIV-XVIII).

The oligomers were white powders that could be cast into water-white films from diglyme solutions. The IR spectra of the oligomers exhibited peaks at 1720 $cm^{-1}$ and 1600 $cm^{-1}$, characteristic of car-

bonyl and ether absorptions. The number-average molecular weights, which were determined by vapor pressure osmometry, corresponded closely to the theoretical values. The oligomers DSC thermograms showed baseline shifts characteristic of glass transitions between 105 and 145°C followed by polymerization exotherms with maxima between 285 and 440°C (Table 1, Figure 1).

The oligomer's $T_g$'s were dependent on molecular weight as witnessed by the fact that the $T_g$ of oligomer XIV increased from 95 to 105°C when the molecular weight was increased from 1,320 to 2,450. The exotherm maxima for the oligomers increased in the following order:

XIV (ethynyl) < XV (enyne) ≈ XVII (1,3-diyne)
< XVIII (phenylethynyl) ≈ XVII (biphenylene)




| OLIGOMER | R |
|---|---|
| XIV | -C≡CH |
| XV | -C≡C-CH=CH-C$_6$H$_5$ |
| XVI | -C≡C-C≡C-C$_6$H$_5$ |
| XVII |  |
| XVIII | -C≡C-C$_6$H$_5$ |

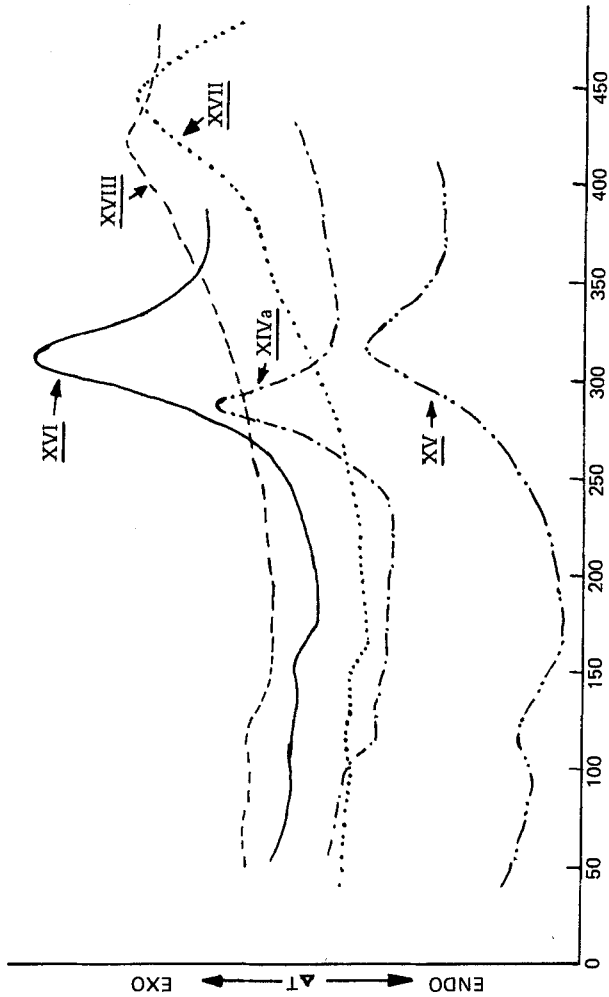



Figure 1: DSC Spectra of End-Capped Polyimide Oligomers

Oligomers XVII and XVIII displayed broad exotherms, which made the determination of the onset temperature difficult. As can be seen in Table 1, all of the oligomers displayed broad processing windows. Visual observations made on a hot-stage microscope revealed that the oligomers were completely liquid at temperatures 40-50°C above their $T_g$'s, which should further facilitate processing. They were soluble in diglyme, chlorinated hydrocarbons, and aliphatic ketones, which should allow them to be applied by spin coating techniques.

The oligomers displayed excellent thermal stability. Their TGA thermograms showed 5% weight losses between 518 and 540°C in air. Although these thermograms were nearly identical, an isothermal aging study conducted at 316°C in circulating air showed that the 1,3-diyne-terminated oligomer XVI was less stable than oligomers



TABLE 1

Characterization of End-Capped, Polyimide Oligomers

| | | DSC[a] | | | TGA[b] | |
|---|---|---|---|---|---|---|
| | | | Exotherm | | Weight Loss | |
| Oligomer | $\bar{M}_n$[c] | $T_g$[d] | Onset | Maxima | Processing Window | 5% | 50% |
| XIVa | 1329 | 95 | 225 | 285 | 120 | 535 | 608 |
| XIVb | 2450 | 105 | 225 | 265 | 80 | | |
| XV | 1428 | 115 | 230 | 315 | 115 | 527 | 606 |
| XVI | 1455 | 145 | 235 | 310 | 90 | 540 | 608 |
| XVII | 1379 | 145 | 250-300 | 440 | 105-155 | 522 | 600 |
| XVIII | 1481 | 120 | 225-250 | 420 | 105-130 | 518 | 607 |

[a] Heating rate 20°C/min in nitrogen. All temperatures in °C.

[b] Heating rate 10°C/min in moist air.

[c] Determined by membrane osmometry.

[d] Extrapolated change in slope.

XIII, XVII and XIII (Table 2). This oligomer lost approximately 40% of its weight in 723 hours, as compared to the 20% weight losses experienced by the other materials.

Study of Thermal Cure Conditions

In order to determine the conditions necessary to cure the oligomers, they were subjected to several different thermal treatments (Table 3). Thus, oligomer XIVa was heated at 275°C for 20 min. Although the resin's $T_g$ was increased from 95 to 205°C and the material became insoluble, these conditions did not result in a complete cure. The treated oligomer's DSC thermogram still showed a slight exotherm above its $T_g$. The $T_g$ also continued to increase when the curing time or temperature was increased. Curing did appear to be essentially complete after heating at 275°C for 120 min. The $T_g$ of the resin treated in this manner (270°C) was not significantly different from that of a sample heated at 300°C for 75 min.

The $T_g$ of the 1,3-diyne-terminated oligomer XVI could not be detected after heating at 275°C for 20 min. The sample did show a weak exotherm above 300°C indicating that curing was not complete. The exotherm was reduced but still present after a sample was heated at 325°C for 20 min. A slight baseline shift also appeared near 250°C.

TABLE 2
Isothermal Aging at 316°C in Circulating Air

| Oligimer[a] | % WEIGHT LOSS AFTER INDICATED HOURS | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | 21 | 43 | 67 | 138 | 309 | 529 | 673 | 723 |
| XIVa | 2.2 | 2.7 | 3.9 | 4.1 | 4.5 | 8.8 | 15.2 | 19.6 | 21.6 |
| XVI | 3.1 | 4.0 | 5.1 | 6.6 | 9.8 | 18.8 | 30.7 | 36.4 | 38.8 |
| XVII | 3.3 | 4.0 | 5.1 | 5.2 | 6.2 | 8.4 | 13.3 | 16.7 | 17.9 |
| XVIII | 5.8 | 5.5 | 6.7 | 6.5 | 7.6 | 11.0 | 17.8 | 21.8 | 23.5 |

a The thermal characterization of oligomer XV is currently in progress.

TABLE 3

Effect of Curing Conditions on Oligomers' $T_g$'s

| Oligomer | $T_g$(°C)[a] | Cure Conditions: Temp. (°C) | Time (Min) | $T_g$(°C) |
|---|---|---|---|---|
| XIVa | 95 | 275 | 20 | 195 |
| | | 250 | 120 | 260 |
| | | 275 | 120 | 270 |
| | | 300 | 75 | 275 |
| XIVb | 105 | 275 | 20 | 220 |
| XVI | 145 | 275 | 20 | None[b] |
| | | 325 | 20 | 250 |
| XVII | 145 | 350 | 20 | 195 |
| XVIII | 120 | 350 | 20 | 190 |

[a] Extrapolated change in slope on DSC thermogram obtained under nitrogen with a heating rate of 20°C/min.

[b] Could not be detected by DSC analysis.

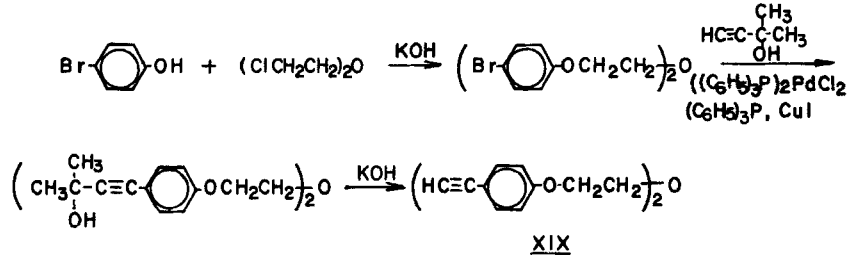
Heating the biphenylene-terminated oligomer XVII at 275°C for 20 min increased the $T_g$ from 145 to 170°C. The $T_g$ was raised to nea 200°C by heating at 350°C for 20 min. The DSC thermogram of this material still showed a weak exotherm above 375°C.

The $T_g$ of the phenylethynyl-terminated oligomer XVIII increased slightly from 120 to 145°C upon heating at 275°C for 20 min. Heatin at 350°C for 20 min produced a material with a $T_g$ near 190°C that continued to cure above 300°C.

Synthesis and Use of a Reactive Plasticizer

It was postulated that the oligomers' flow properties could be enhanced through the use of reactive plasticizers. Bis[2-(4-ethynyl phenoxy) ethyl] ether (XIX) was selected as a suitable plasticizer

candidate, and was synthesized by the following route:



XIX

The DSC thermogram of XIX showed a melting endotherm with a minimum at 96°C followed by a polymerization exotherm with a maximum near 240°C. The sample used to obtain this thermogram was allowed to cool to room temperature in the DSC cell and then reheated. The DSC thermogram obtained was essentially linear indicating that the polymerization of the ethynyl groups was complete.

Various amounts of XIX and XIVb were dissolved in diglyme, stirred, and then coprecipitated in methanol. Solid oligomer-plasticizer mixtures were prepared that contained from 5 to 20 wt % XIX. The fact that the mixtures displayed only one $T_g$, which ranged from 100 to 62°C, indicates that the components were compatible (Table 4).

## CONCLUSIONS

Soluble, thermally-stable, polyimide oligomers of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 1,3-bis(3-aminophenoxybenzene) that are end-capped with latent crosslinking sites can be prepared. These oligomers will soften and flow at temperatures considerably below those needed to affect their thermal cure. Their flow temperatures can be decreased through the use of a com-

TABLE 4

Effect of Plasticizer on the $T_g$ of the Ethynyl-terminated Oligomer XIVb

| Sample No. | Wt. % Plasticizer (XIX) | $T_g$[a] (°C) | Exotherm (°C) Extrapolated Onset | Exotherm (°C) Maximum |
|---|---|---|---|---|
| XIVb | 0 | 105 | 200 | 265 |
| XIVb-1 | 5 | 100 | 200 | 270 |
| XIVb-2 | 10 | 87 | 175 | 265 |
| XIVb-3 | 15 | 82 | 175 | 262 |
| XIVb-4 | 20 | 62 | 175 | 265 |

[a] Extrapolated change in slope on DSC thermogram obtained under nitrogen with a heating rate of 20°C/min.



patible, reactive plasticizer. Their cure temperatures can be varied from 250 to 350°C by employing different end-capping groups. Although brief thermal treatments result in their insolubility in organic solvents, the resins' crosslink densities continue to increase as the heating times are increased. The resins must be heated for several hours before curing is complete, and their $T_g$'s reach the cure temperature. The generated crosslinks are thermally stable and are formed without the evolution of volatile by-products.

## EXPERIMENTAL

Instrumentation. Infrared (IR) spectra were obtained with Perkin Elmer 457 and 1330 spectrometers. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian EM-360-A spectrometer. All samples were run in dueterated chloroform at approximately 10% (w/v) concentration using tetramethyl silane as an internal standard. Differential scanning calorimetric (DSC) thermograms were obtained

with a DuPont 900 thermal analyzer equipped with a differential scanning calorimetric cell. Thermogravimetric analysis (TGA) thermograms were obtained with a DuPont 990 thermal analyzer. Number average molecular weights were determined using a Perkin Elmer Model 115 vapor pressure osmometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

3-Aminophenylethyne (I). Treatment of m-bromonitrobenzene with 2-methyl-3-butyn-2-ol in the presence of a palladium catalyst mixture gave 2-methyl-4-(3-nitrophenyl)-3-butyn-2-ol. Hydrogenation of the nitro intermediate over a ruthenium catalyst followed by hydrolysis according to the known procedure (8) afforded the light-yellow viscous liquid, bp 45-50°C (0.15mm), [lit. (8) 40°C (0.06mm)].

1-Phenyl-4-(3-aminophenyl)buta-1-ene-3-yne (III). A mixture of 5.8575 g (0.05 mol) 3-aminophenylethyne, 35 ml triethylamine, 9.1525 g (0.05 mol) β-bromostyrene, 0.062 g triphenylphosphine and 0.008 g bis(triphenylphosphine)palladium (II) chloride was heated to reflux under a nitrogen atmosphere with vigorous stirring. After 0.008 g of cuprous iodide was added, the reaction mixture was stirred and heated at reflux for 5 h, cooled, and filtered. The filtrate was evaporated to dryness under reduced pressure. The dark yellow residue was dissolved in toluene and then precipitated in petroleum ether. The product was recrystallized from an ethanol-water mixture to afford 9.9 g (75%) of a light yellow powder, mp 88-89°C IR (melt) 3490, 3350 (s,m, $-NH_2$), 2250 $cm^{-1}$ (w, $-C\equiv C-$); NMR δ3.5 (m, 2H,$-NH_2$), 7.5 (m, 11H, aromatic, C=CH-) Anal. Calcd for $C_{16}H_{13}N$: C,87.67; H,5.94; N,6.39. Found: C,87.96; H,6.01; N,5.97.

Phenylbromoethyne (IV). The reaction of phenylacetylene and bromine in the presence of base was carried out according to the known procedure (9) to afford the water-white liquid, bp 40-42°C (0.1mm) [(lit, (9) bp 40-41°C (0.1mm)].

1-Phenyl-4-(3-aminophenyl)-1,3-butadiyne (V). To a stirred mixture of 4.68 g (0.04 mol) 3-aminophenyl ethyne, 12 ml DMF, 16 ml 30% aqueous ethylamine, 0.012 g cuprous chloride and a few crystals of hydroxylamine hydrochloride was slowly added a solution of 7.24 g (0.04 mol) phenylbromoethyne in 12 ml of DMF. The reaction mixture was stirred for 15 min during which time hydroxylamine hydrochloride was periodically added to maintain the copper in Cu (I) state. Potassium cyanide (1.0 g) was then added, and the mixture cooled to -10°C. The solid that precipitated was recrystallized from 80% aqueous ethanol to afford 3.4 g (74%) of off-white needles, mp 91-93°C; IR (KBr) 3450, 3350 (m,s, $-NH_2$), 2200 $cm^{-1}$ (w, $-C\equiv C-$); NMR $\delta$3.4 (m, 2H, $NH_2$), 7.4 (m, 9H, aromatic). Anal. Calcd for $C_{16}H_{11}N$: C,88.48; H,5.07; N,6.45. Found: C,88.48; H,5.12; N,6.37.

2-Aminobiphenylene (VI). Treatment of 2-acetylbiphenylene with sodium azide followed by hydrolysis of the acetamide intermediate as described (10) provided a 30% yield of the yellow powder: mp 125-126°C (lit. (10) 126-128°C).

1-Phenyl-2-(3-nitrophenyl)ethyne (IX). A mixture of 40.0 g (0.2 mol) m-bromonitrobenzene, 60 ml triethylamine, 0.246 g triphenylphosphine, 30 ml phenylacetylene and 0.032 g bis(triphenylphosphine)palladium (II) chloride was heated to reflux under a nitrogen atmosphere with vigorous stirring. After 0.032 g of cuprous iodide was added, the

reaction mixture was stirred and heated at reflux for 5 h, cooled and filtered. The filtrate was evaporated to dryness under reduced pressure to afford 27.0 g (62%) of the crude product. The material was used without purification in the following synthesis. A small sample was recrystallized from 80% aqueous ethanol to yield a light yellow powder, mp 68-69°C: IR (KBr) 1520, 1360 (s,s $-NO_2$), 2250 $cm^{-1}$ (w, $-C\equiv C-$). Anal. Calcd for $C_{14}H_9NO_2$: C,75.33; H,4.04; N,6.28. Found: C,75.55; H,4.14; N,6.12.

1-Phenyl-2-(3-aminophenyl)ethyne (X). To a suspension of 18.0 g of crude 1-phenyl-2-(3-nitrophenyl)ethyne in 150 ml of isopropanol contained in a 500 ml reaction bottle was added 0.55 g of a 5% ruthenium on aluminum oxide catalysts. The reaction bottle was placed in a Parr hydrogenation apparatus and heated to 70°C under a hydrogen atmosphere (70 psi). The reaction mixture was agitated for 48 h, cooled, and filtered. The filtrate was distilled under reduced pressure to afford a yellow oil which slowly crystallized upon standing to give 8.0 g (51%) of light yellow crystals, mp (46-48°C): IR (neat) 3450, 3350, 1600 (s,s,s, $-NH_2$), and 2250 $cm^{-1}$ (w, $-C\equiv C-$); NMR $\delta$3.3 (m, 2H, $NH_2$), 7.0 (m, 9H, aromatic). Anal. Calcd for $C_{14}H_{11}N$; C,87.04; H,5.69; N,7.25. Found: C,86.94; H,5.86; N,7.28.

1,3-Bis(3-aminophenoxy)benzene (XI). Treatment of 3-nitrobromobenzene with the disodium salt of resorcinol followed by hydrogenation according to the known procedure (12) gave the off-white powder, mp 102-104°C (lit. (12) 102-104°C).

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (XII). The dianhydride was extracted from DuPont's NR-150-B2® resin by the following general procedure (13). The polyimide resin solution was

treated with 10% excess alcoholic sodium hydroxide and then heated at 60°C for a minimum of 20 min. The tetrasodium salt of 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane that precipitated was collected by filtration, washed with ethanol, air dried, and then dissolved in water. The water solution was added to 15% HCl to precipitate the corresponding tetraacid, which was washed with water and dried under reduced pressure at 60°C. The tetraacid was converted to the dianhydride by stirring in refluxing acetic anhydride for 2 h. The anhydride was recrystallized from glacial acetic acid immediately prior to use.



Synthesis of end-capped oligomers. The following is the general procedure for the preparation of the oligomers. To a suspension of 7.8 g (0.018 mol) of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride in 20 ml of m-cresol was added 10 drops of isoquinoline. The suspension was gently heated to affect solution of the dianhydride and then cooled to ambient temperature. After a solution of 2.63 g (0.009 mol) of 1,3-bis(3-aminophenoxy)benzene in 15 ml of m-cresol was added, the mixture was heated to 120°C. Toluene (15 ml) was slowly added to the heated solution. The toluene-water azeotrope was immediately started to reflux was removed by distillation. After the toluene addition-distillation cycle was repeated twice, 0.018 mol of the appropriate end-capping agent was added. Toluene (15 ml) was again added, and the resulting toluene-water azeotrope distilled from the reaction mixture. After this toluene addition-distillation cycle was repeated 4 times, the reaction mixture was cooled to ambient temperature and slowly added to ethanol. The

precipitate was reprecipitated from diglyme with ethanol to afford a 70 to 80% yield of the white oligomer.

Bis[2-(4-bromophenoxy)ethyl]ether. A mixture of 69.2 g (0.4 mol) p-bromophenol and 22.4 g (0.4 mol) potassium hydroxide in 120 ml of ethanol was placed in a 500-ml flask equipped with an overhead stirrer and a condenser. After 20.02 g (0.14 mol) of bis(2-chloroethyl)ether was added, the mixture was stirred and heated at reflux for 14 h. The white solid that formed upon cooling was collected by filtration and recrystallized from ethanol to yield 42.0 g (55%) of product, mp 106-107°C.

Bis[2-(4-ethynylphenoxy)ethyl]ether (XIX). A mixture of 15.0 g (0.036 mol) of bis[2-(4-bromophenoxy)ethyl]ether, 9.1 g (0.018 mol) of 2-methyl-3-butyn-2-ol, and 180 ml of triethylamine was degassed by bubbling nitrogen through it for 20 min. After 0.24 g of triphenylphosphine, 0.06 g of bis(triphenylphosphine)palladium (II) chloride, and 0.06 g of cuprous iodide were added, the mixture was stirred and heated at reflux for 20 h, cooled, and filtered. The residue was washed with triethylamine and ether until the ether washings were clear. The combined filtrates were reduced to dryness under reduced pressure. The residue was dissolved in 100 ml of methylene chloride and extracted 3 times with 100 ml of 5% sulfuric acid and twice with 100 ml of water. The methylene chloride was removed under reduced pressure to afford 13.0 g (84%) of the yellow-brown bisbutynol adduct, mp 73-74 °C. To a solution of 8.0 g (0.018 mol) of the crude adduct in 250 ml of toluene under nitrogen was added 12.0 g of potassium hydroxide in 100 ml of methanol. The

mixture was stirred and heated to reflux. After approximately 100 ml of the solution was slowly removed by distillation, an additional 50 ml of toluene was added. The majority of the solvent was then removed by distillation. The yellow precipitate that formed was washed several times with water and then recrystallized from toluene to afford 3.8 g (67%) of white crystals, mp 96-97°C.

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