

Synthesis and Characterization of Polyimides Derived From Cyano-Containing 1,4-Bis(4-aminophenoxy)benzene Monomers

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Summary

A series of three new cyano-containing diamines based upon 1,4-bis(4-aminophenoxy)benzene was synthesized and polymerized with six different dianhydrides to yield 18 different polyimides. Due to the high dipole moment of the cyano group, it was believed that these polymers would display differing degrees of electroactivity depending upon the degree and position of cyano substitution. The type of dianhydride bridging group and length are also factors that affect the electroactivity of polyimides. Polyimides based upon 1,4-bis(4-aminophenoxy)benzene were used as reference materials by which the respective cyano-containing analogs were compared. As the degree of cyano group substitution increased, the glass transition temperature increased. As cyano substitution increased, the polymer chain flexibility decreased due to hindered rotation about the phenyl-ether-phenyl linkages in the diamine portion of the polymer. The tensile moduli ranged from 2.97 to 4.57 GPa and ultimate tensile strengths from 79 to 156 MPa, which are typical values of aromatic polyimides.

Keywords

polyimides, glass transition, piezoelectric, cyano, mechanical properties, thermal properties, synthesis

Introduction

In 1969 Kawai first reported that polyvinylidene fluoride (PVDF) exhibited a high piezoelectric response when drawn and poled [1]. This response is due to dipole orientation taking place in the presence of an electric field. There has been only limited study of piezoelectric polymers since this discovery, with poly(vinylidene cyanide) [2,3], polyurethanes [4,5], polyureas [4,6,7], nylons [8-10], and PVDF/trifluoroethylene copolymers [11-13] being those most frequently studied.

The use of PVDF is somewhat limited by its upper use temperature, whose piezoelectric activity starts to decrease above 80°C due to loss of polarization [14]. Nylons display higher remnant polarizations than PVDF, but the moisture absorption of nylons is detrimental to poling and the dielectric properties. Although nylons have low glass transition temperatures (T_g s) the upper use temperatures of nylons should be 150°C or higher due to orientation stabilization occurring through intermolecular hydrogen bonding [8]. Hence, the stabilization of orientation of polar groups by intermolecular forces or increased T_g may enhance the inherent electroactivity of polar polymers.

This work focuses on the synthesis of polyimides from a series of cyano-substituted 1,4-bis(4-aminophenoxy)benzene monomers. Polyimides not only display low moisture uptake, but also will have high T_g s that will enable higher use temperatures than PVDF. The cyano content and position of these polar cyano groups on the diamine monomer will allow for a determination of how much effect the dipole concentration and dipole position have on the piezoelectric properties.

Experimental

Materials

2,3-Dicyanohydroquinone, hydroquinone, 2-chlorobenzonitrile, 10% palladium on carbon, pyridinium hydrochloride, N-methyl-2-pyrrolidinone (NMP), and hydrochloric acid (HCl) (Aldrich Chemical Co.) were used as received. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) (Fisher Chemical Co.) were distilled from phosphorus pentoxide. 2,5-Dimethoxybenzonitrile (Maybridge Chemical Co.) was used as received. Potassium carbonate (Fisher Chemical Co.) was ground and dried at 100°C under reduced pressure overnight. 5-Nitro-2-chlorobenzonitrile (**1**) was prepared according to the literature [15]. 4,4'-Oxydiphthalic anhydride (**ODPA**) and isophthaloyl dianhydride (**IPDA**) (Imitech) were used as received. 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (**BTDA**) (Chriskev Co.) was recrystallized from acetic anhydride. 2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**6FDA**) (Clariant Corp.) was recrystallized from acetic anhydride. 4,4'-Bisphenol A dianhydride (**BisADA**) (GE Plastics) was recrystallized from acetic anhydride. 2,2'-Bis(3,4-dicarboxyphenyl) dimethylsilyl dianhydride (**SiDA**) was prepared according to the literature [16]. 1,4-Bis(4-aminophenoxy)benzene (**TPE-Q**) (Chriskev Co.) was used as received.

Characterization

Differential scanning calorimetric (DSC) measurements were performed under air at a heating rate of 10°C/min using a Shimadzu TA-501 Thermal Analyzer equipped with a Shimadzu DSC-50 cell. Thermogravimetric analyses (TGA) were performed in nitrogen and air at a heating rate of 2.5°C/min using a Perkin Elmer TGA. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained with a Bruker AVANCE 300 NMR spectrometer at 300 MHz. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained with a Bruker AVANCE 300 NMR spectrometer at 75 MHz. Tetramethylsilane was used as the reference for ^1H and ^{13}C NMR analyses. The reference peaks were assigned at 0 ppm. Infrared spectra (IR) were obtained with a Nicolet Magna-IR Spectrometer 750. Melting points were determined using an Electrothermal 9200 melting point apparatus and are uncorrected. Inherent viscosities

were determined using a Cannon-Ubbelohde #100 viscometer at $25.0 \pm 0.1^\circ\text{C}$. Mechanical properties were determined on thin films with a strain rate of 0.51 cm/min (0.20 in/min) according to ASTM D882 using a Sintech 2W Instron. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Syntheses

1,4-Bis(2-cyano-4-nitrophenoxy)benzene (2)

Into a 250 mL, three-neck, round bottom flask equipped with an overhead stirrer, condenser, nitrogen inlet, and nitrogen outlet were added hydroquinone (10.00 g, 0.0908 mol), 2-chloro-5-nitrobenzotrile (41.45 g, 0.2270 mol), and DMSO (75 mL). The mixture was stirred and heated at 110°C . To the solution was added potassium carbonate (50.21 g, 0.3633 mol) portion-wise to prevent excess gas evolution. The mixture was stirred for 1 h at 110°C after complete addition of potassium carbonate. The mixture was allowed to cool and poured into 500 mL of ice water causing a tan solid to precipitate. The solid was collected by filtration and stirred in 300 mL water. The light tan solid was placed into a sublimation apparatus and heated to 140°C under vacuum to sublime unreacted 2-chloro-5-nitrobenzotrile. The remaining solid was dried at 100°C under reduced pressure overnight to afford 25.97 g (71%) of a white solid. $T_m = 302\text{-}304^\circ\text{C}$ (lit [17] $T_m = 300\text{-}302^\circ\text{C}$). IR (KBr) ν (cm^{-1}) 3115, 3073 (Ar-H), 2236 (-CN), 1618, 1586 (Ar), 1174 (Ar-O). ^1H (DMSO- d_6) δ 7.10 (d, 2H), 7.35 (s, 4H), 8.30 (dd, 2H), 8.60 (d, 2H). ^{13}C (DMSO- d_6) δ 104.08, 114.07, 117.85, 122.79, 130.27, 130.53, 143.22, 151.98, 163.66.

1,4-Bis(2-cyano-4-aminophenoxy)benzene (3)

Into a Parr bottle were added 1,4-bis(2-cyano-4-nitrophenoxy)benzene (15.00 g, 0.03728 mol), 10% Pd/C (0.50 g), and DMF (75 mL). The mixture was agitated under H_2 (35 psi) for 7 h. The mixture was filtered through Celite and the solid filter cake was rinsed with DMF. The filtrate was poured into 300 mL rapidly stirring water causing a white solid to precipitate. The solid was collected by filtration and decolorized from acetone to yield a yellow powder. The powder was dried overnight at 100°C under reduced pressure to afford 12.07 g (95%) of a yellow powder. $T_m = 211\text{-}213^\circ\text{C}$. IR (KBr) ν (cm^{-1}) 3423, 3344, 3225 (- NH_2), 3110, 3070 (Ar-H), 2233 (-CN), 1642, 1629 (Ar), 1189 (Ar-O). ^1H (DMSO- d_6) δ 5.50 (s, 4H), 6.90-6.95 (m, 6H), 7.00 (d, 4H). ^{13}C (DMSO- d_6) δ 104.67, 116.68, 116.71, 119.04, 120.68, 121.62, 146.19, 148.05, 153.36. Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_6\text{O}_2$: C, 70.16; H, 4.12; N, 16.37. Found: C, 70.02; H, 4.55; N, 16.20.

2-Cyanohydroquinone (4)

Into a 250 mL, three-neck, round bottom flask equipped with a magnetic stir bar, condenser, and nitrogen inlet were added 2,5-dimethoxybenzotrile (30.05 g, 0.1842 mol) and pyridine hydrochloride (53.28 g, 0.4611 mol). The solution was heated at 200°C for 6 h. The dark solution was poured onto ice and allowed to stand at room temperature overnight. The solution was made acidic with HCl and extracted with ether. The ether layer was dried with magnesium sulfate, filtered, and evaporated under reduced pressure to afford a tan solid. The solid was placed into a sublimation

apparatus and heated to 140°C to remove any impurities. The crude solid remaining was decolorized with charcoal in acetone to yield a yellow solid. The solid was dried overnight at 60°C under vacuum to afford 18.42 g (75%) of yellow powder. $T_m = 168-169^\circ\text{C}$ (lit [18] $T_m = 169-173^\circ\text{C}$). IR (KBr) ν (cm^{-1}) 3386, 3277 (-OH), 3043 (Ar-H), 2240 (-CN), 1623, 1607 (Ar) ^1H (acetone- d_6) δ 7.05-7.15 (m, 3H), 8.50 (s, 1H), 9.20 (s, 1H). ^{13}C (acetone- d_6) δ 101.01, 117.57, 118.63, 119.15, 123.48, 151.55, 154.28.

2,5-Bis(2-cyano-4-nitrophenoxy)benzonitrile (5)

Into a 100 mL, three-neck, round bottom flask equipped with an overhead stirrer and condenser were added cyanohydroquinone (1.94 g, 0.0143 mol), 2-chloro-5-nitrobenzonitrile (6.55 g, 0.0359 mol), potassium carbonate (7.94 g, 0.0574 mol), and DMSO (25 mL). The mixture was stirred and heated at 110°C for 1 h. The mixture was allowed to cool and poured into 500 mL of ice water causing an orange solid to precipitate. The solid was collected by filtration and then transferred into a glass extraction thimble. The thimble was placed into a Soxhlet extractor and extracted with water overnight. The yellow solid was placed into a sublimation apparatus and heated to 140°C under vacuum to sublime unreacted starting materials. The remaining solid was dried at 100°C under reduced pressure overnight to afford 5.32 g (87%) of an off-white solid. $T_m = 273-275^\circ\text{C}$. IR (KBr) ν (cm^{-1}) 3110, 3072, 3045 (Ar-H), 2237 (-CN), 1615, 1585 (Ar), 1193 (Ar-O). ^1H (DMSO- d_6) δ 7.35 (d, 1H), 7.45 (d, 1H), 7.75 (d, 1H), 7.90 (d, 1H), 8.20 (s, 1H), 8.50 (dd, 2H), 8.90 (dd, 2H). ^{13}C (DMSO- d_6) δ 104.55, 104.65, 107.43, 113.58, 113.87, 113.91, 118.46, 118.51, 123.69, 126.44, 128.09, 130.29, 130.46, 130.56, 130.71, 143.72, 144.15, 151.87, 153.16, 162.04, 162.83. Anal. Calcd for $\text{C}_{21}\text{H}_9\text{N}_6\text{O}_6$: C, 59.02; H, 2.12; N, 16.39. Found: C, 58.99; H, 2.18; N, 16.29.

2,5-Bis(2-cyano-4-aminophenoxy)benzonitrile (6)

Into a 500 mL, three-neck, round bottom flask equipped with an overhead stirrer, nitrogen inlet, condenser, and nitrogen outlet were added 2,5-bis(2-cyano-4-nitrophenoxy)benzonitrile (7.53 g, 0.0176 mol) and HCl (125 mL). The mixture was stirred rapidly and cooled with an ice bath. To the mixture was added tin (29.28 g, 0.2467 mol) portion-wise to prevent excess foaming. After complete addition of tin the mixture was allowed to stir while being cooled with an ice bath for 1 h, then allowed to warm to room temperature over 1.5 h. The mixture was heated with an oil bath at 100°C for 3 h, then allowed to cool to room temperature. The mixture was poured into 400 mL ice water and basified with sodium hydroxide. The solid was collected by filtration, stirred in refluxing acetonitrile, and then filtered again. The filtrate was evaporated under reduced pressure to yield a dark yellow solid. The solid was decolorized from charcoal in acetonitrile to yield an off-white solid. The solid was dried overnight at 120°C under reduced pressure to afford 4.12 g (64%) of an off-white solid. $T_m = 207-209^\circ\text{C}$. IR (KBr) ν (cm^{-1}) 3386, 3334 (-NH₂), 3060, 3040 (Ar-H), 2233 (-CN), 1646, 1606, 1582 (Ar), 1269 (Ar-O). ^1H (DMSO- d_6) δ 5.60 (s, 2H), 5.70 (s, 2H), 6.95-7.05 (m, 6H), 7.10 (d, 2H), 7.30 (dd, 2H), 7.65 (d, 2H). ^{13}C (DMSO- d_6) δ 103.37, 104.93, 105.15, 115.33, 116.09, 116.47, 116.81, 116.86, 118.42, 120.46, 120.60, 121.97, 122.35, 124.50, 146.01, 146.78, 146.92, 147.30, 153.02, 155.21. Anal. Calcd for $\text{C}_{21}\text{H}_{13}\text{N}_6\text{O}_2$: C, 68.65; H, 3.57; N, 19.07. Found: C, 68.47; H, 3.62; N, 19.15.

3,6-Bis(2-cyano-4-nitrophenoxy)phthalonitrile (7)

Into a 300 mL, three-neck, round bottom flask equipped with an overhead stirrer, condenser, and nitrogen inlet were added 2,3-dicyanohydroquinone (13.97 g, 0.08724 mol), 5-nitro-2-chlorobenzonitrile (35.04 g, 0.1919 mol), and DMSO (100 mL). The solution was stirred and heated with an oil bath at 110°C. Potassium carbonate (48.23 g, 0.3490 mol) was added portion-wise to avoid excess gas evolution. After complete addition of potassium carbonate the deep red mixture was heated at 110°C for 1 h, then allowed to cool to room temperature. The mixture was poured into 500 mL ice water causing a lavender solid to precipitate. The solid was collected by filtration and placed into an extraction thimble. The thimble was placed into a Soxhlet extraction apparatus and extracted with water. After extraction the yellow solid was dried overnight at 120°C to yield 29.87 g (76%) of yellow powder. $T_m = 255-257^\circ\text{C}$. IR (KBr) ν (cm^{-1}) 3115, 3077 (Ar-H), 2239 (-CN), 1619, 1584 (Ar), 1253 (Ar-O). ^1H (DMSO- d_6) δ 5.60 (s, 2H), 5.70 (s, 2H), 6.95-7.05 (m, 6H), 7.10 (d, 2H), 7.30 (dd, 2H), 7.65 (d, 2H). ^{13}C (DMSO- d_6) δ 103.37, 104.93, 105.15, 115.33, 116.09, 116.47, 116.81, 116.86, 118.42, 120.46, 120.60, 121.97, 122.35, 124.50, 146.01, 146.78, 146.92, 147.30, 153.02, 155.21. Anal. Calcd for $\text{C}_{22}\text{H}_8\text{N}_6\text{O}_6$: C, 58.41; H, 1.78; N, 18.58. Found: C, 58.14; H, 1.89; N, 18.33.

The collected aqueous filtrates were combined and acidified with HCl causing a yellow precipitate to form, which was the monosubstituted product 3-(2-cyano-4-nitrophenoxy)-6-hydroxyphthalonitrile. This product could be reacted with 5-nitro-2-chlorobenzonitrile to synthesize **7**. $T_m = 265-266^\circ\text{C}$. IR (KBr) ν (cm^{-1}) 3260 (-OH), 3069 (Ar-H), 2256, 2237 (-CN), 1615, 1591 (Ar), 1264 (Ar-O). ^1H (DMSO- d_6) δ 7.30 (d, 1H), 7.50 (s, 1H), 7.75 (s, 1H), 8.45 (dd, 1H), 8.90 (d, 1H), 12.10 (s, 1H). ^{13}C (DMSO- d_6) δ 102.11, 103.24, 109.04, 112.84, 113.95, 114.00, 116.87, 124.29, 129.01, 130.74, 130.98, 143.21, 147.51, 159.99, 162.73.

3,6-Bis(2-cyano-4-aminophenoxy)phthalonitrile (8)

Into a 300 mL, three-neck, round bottom flask equipped with an overhead stirrer, nitrogen inlet, condenser, and nitrogen outlet were added 3,6-bis(2-cyano-4-nitrophenoxy)phthalonitrile (5.00 g, 0.0111 mol) and HCl (50 mL). The mixture was stirred rapidly and cooled with an ice bath. To the mixture was added tin (20.00 g, 0.1685 mol) portion-wise to prevent excess foaming. After complete addition of tin, the mixture was allowed to stir while being cooled with an ice bath for 1 h, then allowed to warm to room temperature over 1.5 h. The mixture was heated with an oil bath at 100°C for 3 h, then allowed to cool to room temperature. The mixture was poured into 400 mL ice water and basified with sodium hydroxide. The solid was collected by filtration. The solid was stirred in refluxing acetonitrile, then the mixture was filtered. The filtrate was evaporated under reduced pressure to afford a dark yellow solid. The solid was decolorized from charcoal in acetonitrile to afford a bright yellow solid. The solid was dried overnight at 120°C under vacuum to afford 3.58 g (83%) of a bright yellow solid. $T_m = 257-259^\circ\text{C}$. IR (KBr) ν (cm^{-1}) 3450, 3359 (-NH₂), 3068, 3018 (Ar-H), 2239 (-CN), 1619, 1584 (Ar), 1254 (Ar-O). ^1H (DMSO- d_6) δ 7.55 (d, 2H), 8.10 (s, 2H), 8.6 (dd, 2H), 9.0 (d, 2H). ^{13}C (DMSO- d_6) δ 101.41, 109.44, 110.98, 112.52, 116.57, 127.90, 129.46, 129.70, 142.45, 152.02, 160.48. Anal. Calcd for $\text{C}_{22}\text{H}_{12}\text{N}_6\text{O}_2$: C, 67.34; H, 2.06; N, 21.42. Found: C, 67.29; H, 1.89; N, 21.48.

General Polymerization

Into a 100 mL, three-neck, round bottom flask equipped with an overhead stirrer, nitrogen inlet, and nitrogen outlet were added the required diamine and NMP. After the diamine dissolved an equimolar amount of dianhydride was added with an NMP rinse to ensure total addition of dianhydride. The concentration of the solution was 20% (wt/V). The solution was allowed to stir at room temperature overnight. The poly(amic acid) was pressure filtered through 0.22 to 1.00 μm filter paper, depending upon polymer viscosity. The solution was doctored onto a glass plate in a clean room. The poly(amic acid) film was thermally imidized to the polyimide under nitrogen at a temperature 15-20°C above the polyimide T_g . The resulting films were removed from the glass by soaking overnight in warm water. Complete imidization was indicated through IR analyses of the films.

Results and Discussion

Monomer Synthesis

Three new cyano-containing diamines were synthesized to determine the influence of cyano group position and number on the physical and mechanical properties of polyimides. The synthetic routes to monomers **3**, **6**, and **8** (Figure 1) are shown in Scheme 1. Cyanohydroquinone (**3**) was synthesized through demethylation of 2,5-dimethoxybenzonitrile. Each hydroquinone was treated with 5-nitro-2-chlorobenzonitrile in the presence of potassium carbonate in DMSO to afford dinitro compounds **2**, **5**, and **7**. Monosubstituted products complicated the synthesis of pure cyano-containing dinitro compounds (Scheme 2). The ease of removal of monosubstituted product from the desired disubstituted product was in the order of $2 > 5 > 7$. Due to the limited solubility of the monosubstituted and disubstituted products in common organic solvents, liquid-liquid extraction and column chromatography were not an option for purification. For **2** and **5**, stirring the products in water removed the monosubstituted products that were still in the respective phenoxide forms. This procedure was not as effective for **7**, but extraction in a Soxhlet extraction apparatus with water removed the remaining phenoxide. Increasing reaction temperatures and times led to black, gummy products.

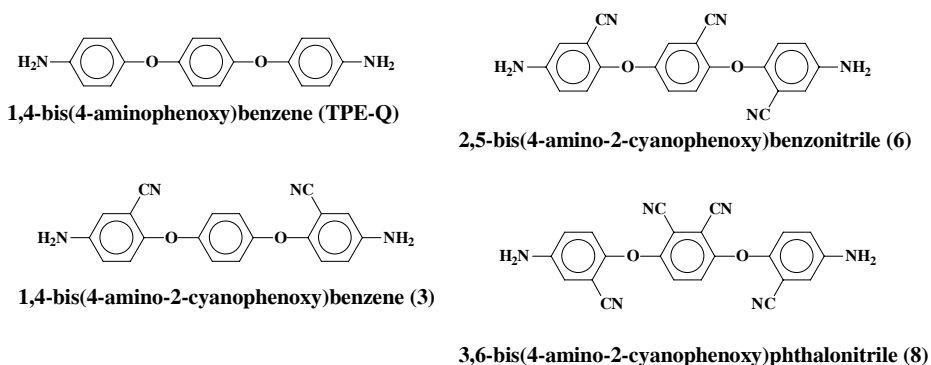
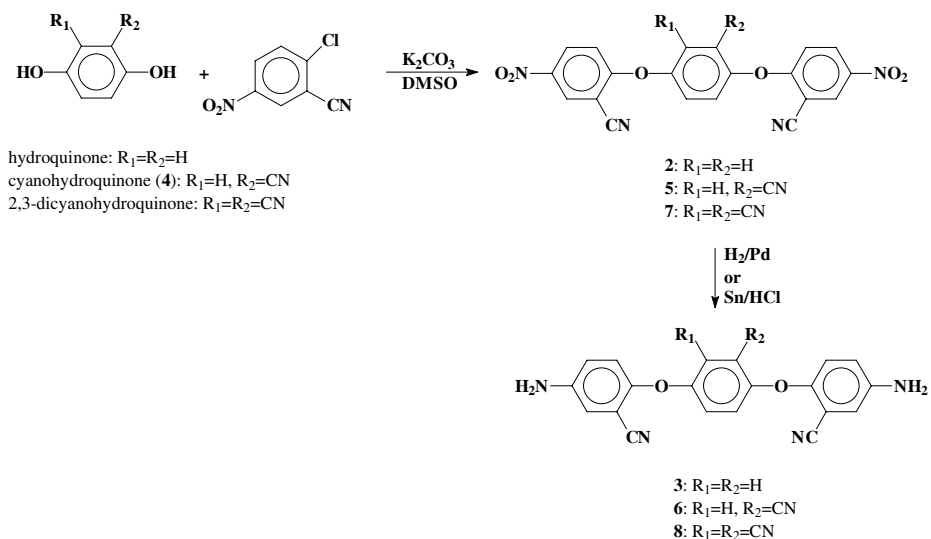
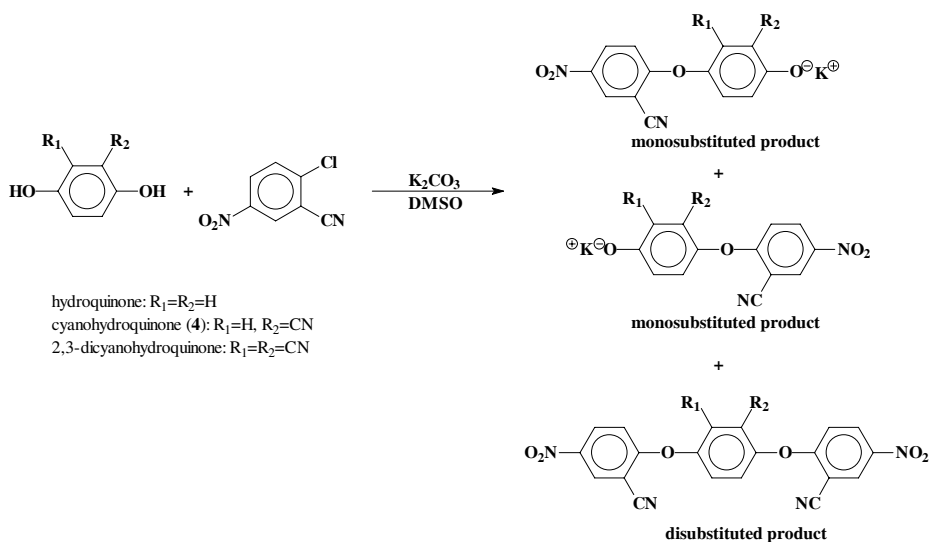


Figure 1



Scheme 1



Scheme 2

Reduction of the dinitro products varied depending upon structure. Compound **2** was reduced using catalytic hydrogenation to yield **3**. Catalytic hydrogenation using hydrogen and palladium led to two products when reducing **7**, as shown by thin layer chromatography (silica gel plates with ethyl acetate as eluent). The major spot was the desired diamine **8**. A second faint spot appears just below the diamine spot, which was not identified, but was determined not to be unreacted **7**. This impurity was not able to be removed using standard purification techniques such as sublimation and recrystallization. Due to the limited solubility of **8**, column chromatography was not

possible. However, reduction of **7** to **8** was accomplished using tin/HCl. No impurities were produced using this route. Reduction of **5** was also accomplished using tin/HCl.

Polymer Synthesis

Each diamine readily reacted with **ODPA**, **6FDA**, **BTDA**, **IPDA**, **BisADA**, and **SiDA** (Figure 2) to yield viscous poly(amic acid) solutions (Scheme 3, Table 1). Inherent viscosities of the poly(amic acid)s were measured to determine the pore size of the filter paper for pressure filtration. The solutions were pressure filtered to remove dust and/or small particles in the solution. This was necessary since the polymer films were to be characterized for electromechanical response under high electric fields. Attempted chemical imidization using acetic anhydride and pyridine led to precipitation of the polymer from solution in most cases. Hence, each poly(amic acid) was thermally imidized to the respective polyimide. Thermal imidization was carried out under a nitrogen atmosphere 15-20°C above the polyimide T_g to ensure complete cyclodehydration from the amic acid to the imide without causing the cyano groups to react with each other, or other thermal processes to occur.

Table 1. Physical properties of polyimides

Diamine	Dianhydride	η_{inh} (dL/g) ¹	T_g (°C)	T_d, N_2 (°C) ²	T_d, air (°C) ²
TPE-Q	ODPA	0.54	244	518	495
	6FDA	1.03	264	488	500
	BTDA	0.89	252	488	467
	IPDA	0.68	224	502	472
	BisADA	0.61	195	469	502
	SiDA	1.08	238	468	495
3	ODPA	0.79	250	473	468
	6FDA	0.67	269	483	471
	BTDA	0.27	261	466	458
	IPDA	0.70	244	492	467
	BisADA	0.48	207	436	419
	SiDA	0.44	230	478	442
6	ODPA	0.36	235	480	432
	6FDA	0.46	273	476	490
	BTDA	0.58	261	484	482
	IPDA	0.46	239	464	465
	BisADA	0.37	207	436	422
	SiDA	0.47	242	484	487
8	ODPA	0.83	250	493	475
	6FDA	0.67	269	465	498
	BTDA	0.27	261	483	479
	IPDA	0.70	244	485	488
	BisADA	0.48	229	439	463
	SiDA	0.41	265	486	485

¹Inherent viscosity of poly(amic acid) in NMP at a concentration of approximately 0.5 g/dL at 25.0°C

²Temperature at which polymer underwent a 5% weight loss when subjected to TGA with a heating rate of 2.5°C/min

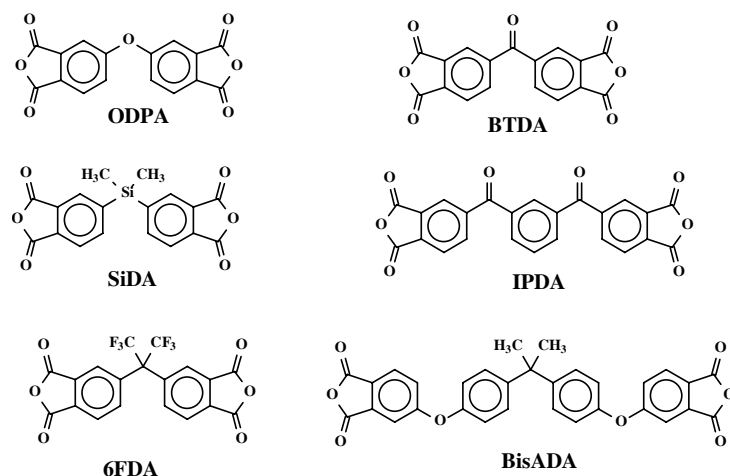
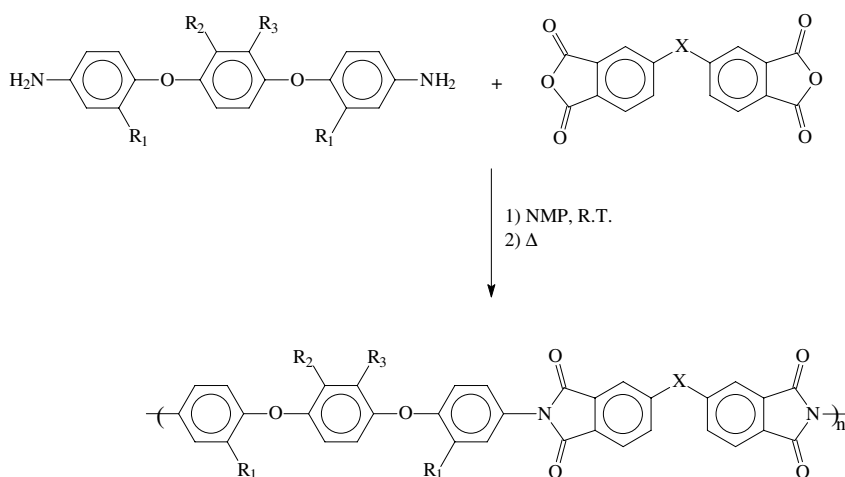
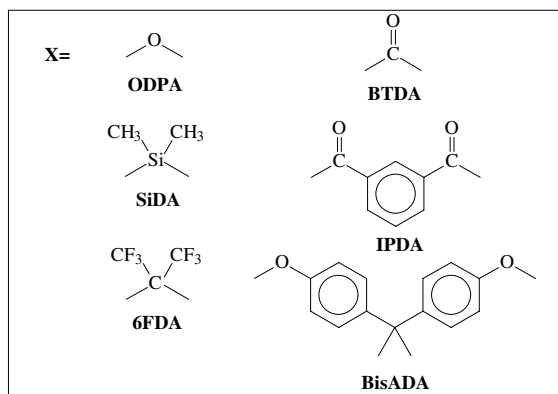


Figure 2



TPE-Q: $R_1=R_2=R_3=H$
3: $R_1=CN$, $R_2=R_3=H$
6: $R_1=R_2=CN$, $R_3=H$
8: $R_1=R_2=R_3=CN$



Scheme 3

In an attempt to do a systematic variation of polymer structure for each diamine, a series of six different dianhydrides were chosen as comonomers. Factors considered included length, dipole density, type of dipole, and flexibility of dianhydride. This study was pursued in the belief that the electromechanical response is dependant upon a combination of dipole density, location, and polymer flexibility. A polymer with high dipole density but low flexibility would not have the ability to align well in an electric field. Therefore, a balance between position of dipoles, type of dipoles, number of dipoles, and polymer backbone flexibility are critical factors in designing electroactive polymers.

Preliminary studies have indicated that the polyimides derived from **8** displayed the highest remanent polarizations (P_r) [19]. Specifically, the polyimide **8/SiDA** had the highest P_r (42 mC/m^2), indicating that a highly polar bridge is not required in the dianhydride in order to maximize P_r . In contrast, the well-known piezoelectric polymers nylon 7 (86 mC/m^2) [20], nylon 11 (51 mC/m^2) [20], and PVDF (51 mC/m^2) [21] displayed higher P_r values than the polyimides in this work. The orientation of dipoles in nylons can be disrupted by the ability of polyamides to absorb water. Water can act as a plasticizer to allow dipoles to relax. Water can also interrupt the hydrogen bonding, allowing the dipoles to relax. Polyimides do not absorb water to the extent of polyamides, which offers an advantage over the odd-numbered nylons. Polyimides also offer the advantage of higher use temperatures over PVDF due to the high T_g s. PVDF only has an upper use temperature of about 80°C . The amorphous polyimides in this work will start to lose dipole orientation as the glass transition temperature is approached.

Thermal Properties

The thermal properties of the polyimides are listed in Table 1. In general, polyimides from **8** had the highest T_g values throughout the dianhydride series compared to those from **TPE-Q**, **3**, and **6**. Polyimides from **3** and **6** had very similar T_g values. Polyimides from **TPE-Q** had among the lowest T_g s in each dianhydride series. Since T_g values are dependent upon ease of polymer motion, the increase in cyano group content apparently causes the polymer chain mobility to decrease. This may be due to the cyano groups hindering phenyl-ether-phenyl ring rotation.

Polyimides based upon BisADA had the lowest decomposition temperatures due to the isopropylidene linkage. The decomposition temperature values obtained in this work are typical of polyimides.

Both PVDF and nylons have low T_g s and are semi-crystalline. The T_g of PVDF is -40°C [22] and nylon 11 is 42°C [23]. The polymer decomposition temperatures of PVDF and nylon 11 are much lower than the polyimides in this work due to the high aliphatic nature of the polymers. Polymer decomposition values are typically in the 350 to 400°C range for PVDF and nylon 11.

Mechanical Properties

The tensile properties of the polyimides are listed in Table 2. Tensile strengths ranged from 79 to 156 MPa and tensile moduli from 2.58 to 4.57 GPa . These values are typical of aromatic polyimides. Polyimides derived from **BisADA** typically displayed the lowest tensile strength and modulus, which is due to the isopropylidene linkage. Polyimides derived from more rigid dianhydrides, such as **IPDA** and **BTDA**, led to high tensile strength and moduli values.

Table 2. Tensile properties of polyimides

Diamine	Dianhydride	η_{inh} (dL/g) ¹	σ (MPa) ²	E (GPa)	ϵ (%) ²
TPE-Q	ODPA	0.54	96.3 ± 4.4	2.97 ± 0.07	15.2 ± 4.1
	6FDA	1.03	104.8 ± 4.9	3.05 ± 0.11	10.6 ± 1.3
	BTDA	0.89	141.6 ± 3.4	4.12 ± 0.22	6.9 ± 0.8
	IPDA	0.68	136.3 ± 3.4	4.21 ± 0.17	5.6 ± 0.8
	BisADA	0.61	79.1 ± 3.0	2.58 ± 0.04	57.6 ± 7.4
	SiDA	1.08	93.1 ± 2.3	2.70 ± 0.15	10.6 ± 1.6
3	ODPA	0.79	105.1 ± 6.9	3.17 ± 0.31	12.4 ± 2.1
	6FDA	0.67	114.4 ± 10.6	3.42 ± 0.27	11.5 ± 1.5
	BTDA	0.27	136.1 ± 6.2	4.05 ± 0.08	15.9 ± 7.2
	IPDA	0.70	156.0 ± 6.2	4.57 ± 0.11	8.2 ± 2.6
	BisADA	0.48	92.0 ± 4.5	3.10 ± 0.10	9.0 ± 1.0
	SiDA	0.44	102.7 ± 6.3	3.17 ± 0.31	6.5 ± 1.2
6	ODPA	0.36	130.7 ± 3.4	3.88 ± 0.13	2.0 ± 0.1
	6FDA	0.46	131.0 ± 5.7	3.84 ± 0.19	7.5 ± 0.3
	BTDA	0.58	133.1 ± 4.0	4.07 ± 0.12	2.8 ± 0.1
	IPDA	0.46	130.7 ± 6.8	3.94 ± 0.12	9.3 ± 2.1
	BisADA	0.37	109.6 ± 4.6	3.34 ± 0.09	6.5 ± 1.2
	SiDA	0.47	129.4 ± 2.7	3.70 ± 0.05	2.9 ± 0.1
8	ODPA	0.55	117.3 ± 3.7	3.44 ± 0.30	6.0 ± 1.8
	6FDA	0.44	129.5 ± 8.3	3.71 ± 0.06	7.5 ± 1.7
	BTDA	0.28	138.4 ± 4.1	4.30 ± 0.10	11.2 ± 0.9
	IPDA	0.52	99.8 ± 6.3	3.62 ± 0.25	4.9 ± 0.7
	BisADA	0.35	127.6 ± 2.0	3.44 ± 0.19	16.8 ± 4.8
	SiDA	0.41	118.7 ± 4.9	3.65 ± 0.15	8.8 ± 0.7

¹Inherent viscosity of poly(amic acid) in NMP at a concentration of approximately 0.5 g/dL at 25.0°C

²Tensile strength and elongation measured at break

Tensile elongation values ranged from 2 to 57%. A majority of the samples were in the 2 to 10% range, which is typical of aromatic polyimides. The flexibility of the isopropylidene linkage and length of **BisADA** are two possible reasons for higher elongation values in two cases (**TPE-Q** and **8**).

These polyimides display better mechanical properties than nylons and PVDF. PVDF has a tensile strength of 50 MPa, tensile modulus of 2.3 GPa, and an elongation of 40% [24]. Nylon 11 has a tensile strength of 60 Pa, tensile modulus of 1.0GPa, and an elongation of 110% [24]. Although the elongation values are higher for PVDF and nylon 11, the polyimides have higher tensile strength and modulus. All three classes of polymers are tough materials, capable of being used in similar applications.

Conclusions

Three new cyano-containing diamines based upon 1,4-bis(4-aminophenoxy)benzene were synthesized and polymerized with six different dianhydrides to afford electroactive polyimides. Base polymers using 1,4-bis(4-aminophenoxy)benzene were used as a reference to determine the influence of cyano group number and position on polymer properties. Polymer decompositions in air and nitrogen remained fairly

constant throughout each respective dianhydride. No real trends were observed in the tensile properties of the polyimides. These values were typical of aromatic polyimides.

T_g values of the polyimides were required in order to determine poling conditions for electromechanical testing. Due to the good mechanical properties and high T_g values, these polymers would find applications as high temperature sensors. Future publications will concentrate on electromechanical characterization of these polymers.

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