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Organo-Soluble Polyimides: Synthesis and Polymerization of 2,2′-Bis(trifluoromethyl)-4,4′,5,5′-Biphenyltetracarboxylic Dianhydride

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ABSTRACT: 2,2′-Bis(trifluoromethyl)-4,4′,5,5′-biphenyltetracarboxylic dianhydride (6FBPDA) was synthesized from 1-iodo-4,5-dimethyl-2-nitrobenzene via a six-step synthetic route. The dianhydride was polymerized with eight different substituted 4,4′-diaminobiphenyls in refluxing *m*-cresol containing isoquinoline to afford a series of fluorinated aromatic polyimides. The polyimides were soluble in polar aprotic, ether and ketone solvents. They had intrinsic viscosities that ranged from 1.70 to 6.72 dL/g in *N*-methyl-2-pyrrolidinone or *m*-cresol at 30 °C. The polymers underwent 5% weight losses when subjected to thermal gravimetric analysis between 440 and 570 °C in air and nitrogen atmospheres. The polymers could be solution cast into water-white, flexible, tough films which exhibited "in-plane" structural anisotropy. Their glass transition temperatures along the directions parallel to the film surface (in-plane) ranged from 327 to 345 °C (thermal mechanical analysis). Multiple relaxation processes associated with segmental and subsegmental motions were also observed with dynamic mechanical analysis. The films had in-plane coefficients of thermal expansion (CTEs) that ranged from 1.58×10^{-5} to 2.50×10^{-5} $°C^{-1}$. These films also showed linear optical anisotropy, which is characterized by the presence of larger, isotropic refractive index ($n_{\parallel}$) in-plane, and a smaller refractive index ($n_{\perp}$) perpendicular to the film surface (out-of-plane). The optical symmetry axis of the films is along the out-of-plane direction. This optical anisotropy is defined as uniaxial negative birefingence ($\mathrm{NUB} = n_{\perp} - n_{\parallel}$). Films having a thickness of 5 μm were transparent above 330 nm, and their in-plane refractive indices ($n_{\parallel}$) were 0.060 to 0.074 larger than their out-of-plane refractive indices ($n_{\perp}$). This UNB make the films candidates for use as retardation layers in liquid crystal displays.

Introduction

The overall goal of this ongoing research is to modify the structure of aromatic polyimides to attain solubility in common organic solvents without substantially decreasing the rigidity of their backbone.[1,2] Solubility is sought to allow processing in the imide form and, thus, avoid the many problems associated with handling poly(amic acid) (PAA) precursors.[3,4] This is especially important in microelectronic and optical applications where the imidization conditions for PAAs used during processing can dramatically affect the final material properties.[5,6]

It has been recognized that solution-cast aromatic polyimide films exhibit linear optical anisotropy in the directions parallel (in-plane) and perpendicular (out-of-plane) to the film surface The in-plane refractive index is isotropic, and it is larger than the out-of-plane refractive index. The optical symmetry axis of the film is along the out-of-plane direction. The film birefringence is defined as a difference in the refractive indices between the directions of out-of-plane and in-plane, and it is a negative value. In optics, this phenomenon is called as uniaxial negative birefringence (UNB). A common explanation of this phenomena is that aromatic polyimide molecules tend to randomly align parallel to the film surface during the film forming process. This leads to a larger in-plane refractive index and a smaller out-of-plane refractive index.[7] One of the applications for the optical anisotropy in polyimide films is that they may be utilized to design negative birefringent compensators for twisted and supertwisted nematic liquid crystal displays (LCDs) to improve display viewing angles.[8−11]

The maintenance of backbone rigidity and linearity not only is desirable in that it avoids or minimizes reductions in thermal and mechanical properties but also is of particular importance in uniaxial negative retardation layer applications in LCDs, where it contributes to large negative birefringence.[8−11]

One of our most successful approaches to attaining solubility without sacrificing backbone rigidity and linearity has involved the polymerization of 4,4′-diamino 2,2′-disubstituted biphenyls with aromatic dianhydrides.[1,2] The steric repulsion of the substitutents in the 2- and 2′-positions of the biphenyl moieties twists the rings dramatically out-of-plane.[12] The resulting twisted conformation inhibits chain packing and crystallization. The severe twist also breaks up the conjugation along the backbone and hinders the formation of intermolecular charge-transfer complexes. Both of these effects contribute to a dramatic reduction in color.

Recently, we investigated the effect of introducing twisted biphenyl structures in polyimide backbones through the synthesis and polymerization of appropriately substituted dianhydrides. Thus, 2,2′-dibromo-4,4′-5,5′-biphenyltetracarboxylic dianhydride (DBBPDA) and 2,2′-diphenyl-4,4′-5,5′-biphenyltetracarboxylic dianhydride (DPBPDA) were synthesized and polymerized with 4,4′-diamino 2,2′-disubstituted biphenyls in refluxing *m*-cresol containing isoquinoline.[13] Due to the groups in the 2- and 2′-positions, the solubility of the resulting polyimides was improved. One of the polymers was soluble in acetone, and several were soluble in tetrahydrofuran (THF). The acetone-soluble polymer was obtained from DBBPDA and the fluorinated di-

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amine 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl (PFMB). PFMB had also been previously polymerized with the fluorinated dianhydride 2,2′-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) to afford a polyimide that was soluble in acetone.

In addition to enhancing solubility, pendent trifluoromethyl groups contribute to lower polyimide dielectric constants and reduced water absorption. For example, polymers prepared from trifluoromethyl-substituted pyromellitic dianhydrides have dielectric constants of 2.6 and water absorptions of 0.38%.[14] The 6FDA−PFMB polyimide has dielectric constants of 2.7 at 1 MHz.[15]

Perfluoromethyl groups have also been shown to reduce the refractive indices of and enhance other optical properties of polyimides.[16] For example, the out-of-plane ($n_{\perp}$) and in-plane ($n_{\|}$) refractive indices of thin films of polyimides based on PFMB are lower than those of thin films of analogous polymers prepared from other 4,4′-diamino 2,2′-disubstituted biphenyls. Due to their excellent visible light transparency and low optical losses, 6FDA-based polymers have been investigated for use as optical waveguide materials.[17]

The objective of this research was to investigate the effects of introducing pendent trifluoromethyl groups along the polyimide backbone through the use of 2,2′-bis(trifluoromethyl)-4,4′,5,5′-biphenyltetracarboxylic dianhydride (6FBPDA). Thus, the new dianhydride was to be synthesized and polymerized with a series of substituted 4,4′-diaminobiphenyls. The resulting polyimides were to be thoroughly characterized. In particular, the effects of the trifluoromethyl groups on the solubility of the polymers and the optical properties of their films were to be carefully determined. The properties of the polymers were also to be compared to those of analogous polyimides prepared from the more flexible 6FDA dianhydride.

Experimental Section

Instrumentation. Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra for monomers and polymers were measured at 200 and 50 MHz on a Varian Gemini-200 spectrometer. Infrared (IR) spectra were obtained with a Beckman FT-2100 Fourier transform spectrophotometer or with a Mattson Galaxy Series FTIR 5000 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All of the melting points (mp) of the monomers were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 100 and 200 viscometers. Flow times were recorded for *N*-methyl-2-pyrrolidinone (NMP) or *m*-cresol solutions with polymer concentrations of approximately 0.50−0.25 g/dL at 30.0 ± 0.1 °C. Thermogravimetric analyses (TGA) on the polymers were obtained in nitrogen and air with a TA 2950 thermogravimetric analyzer using a heating rate of 10 °C/min. The polyimide samples prepared for TGA measurements were heated to 300 °C and retained there for 20 min before being cooled to 30 °C prior to the measurements. Glass transition temperatures (T_gs) and coefficients of thermal expansion (CTEs) of polyimide films were determined with thermal mechanical analysis (TMA) using a TA TMA 2940 thermomechanical analyzer with a tension mode. To precisely measure the CTEs, polyimide films with thicknesses between 10 and 30 μm were heated to 300 °C under nitrogen at 1.0 MPa and held at this temperature for 20 min. After cooling to 30 °C, the films were subjected to different stresses with a heating rate of 10 °C/min. The T_g was taken as the temperature at which a change in slope of a plot of film dimensional change versus temperature occurred. The T_gs obtained at each stress level were then extrapolated to zero stress. The CTE value was taken as the mean of the dimensional change between 50 °C and 150 °C. The CTEs obtained at each stress level were then extrapolated to zero stress.[11] Dynamic mechanical analysis (DMA) experiments were carried out on a Seiko DMS-200. The frequency range was between 0.01 and 10 Hz, and the heating rate was 1 °C/min. The activation energies of the subglass β relaxation were calculated using the Arrhenius equation. For the α relaxation, in principle, this equation cannot be applied since it only represents a single frequency relaxation process. However, in a narrow frequency range, this Arrhenius calculation may be used to obtain apparent activation energies as a first approximation. Transmission UV−visible spectra were measured with a Perkin-Elmer Lambda 4B spectrometer in the transmittance mode.

The linear optical refractive indices of the polyimide films were measured using a prism coupling waveguide technique. An incident laser beam having a 632.8 nm wavelength and transverse electric (TE) polarization was used. Changes in the reflected radiation intensities of the films were detected at different incident angles (θ). Changes of the intensity at different incident angle (θ) for the transverse magnetic (TM) polarization can also be obtained. The radiation angles of the resonance at which the light can be coupled into the film depend on the thickness and refractive indices of the films. Each of the sharp resonant peaks, which corresponds to a waveguide mode, were used to calculate the refractive indices in both the TE and TM polarization modes. On the basis of the multiple resonance peak positions (θ) in each mode, the refractive indices of the films along the in-plane (TE) and the out-of plane directions (TM), as well as the film thickness, could be deduced. To ensure the linear optical isotropy within the film plane, the in-plane refractive indices along different light propagation directions were also determined by rotating the film with respect to the incident beam in the waveguide coupling experiments. The in-plane refractive indices were to be constant along all of the directions in the same polyimide film. Film thickness could be determined with an accuracy of ±0.10 μm and refractive index with an accuracy of ±0.0001.

Reagents and Solvents. Copper powder (99%) (Aldrich) was activated with an aqueous solution of the dipotassium salt of ethylenediaminetetraacetic acid (EDTA) prior to use. Isoquinoline (Aldrich) was distilled under reduced pressure. *m*-Cresol, *N*,*N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) (Aldrich) were distilled from phosphorus pentoxide under reduced pressure. All of the other reagents and solvents were used as received.

Monomers. 1-Iodo-4,5-dimethyl-2-nitrobenzene (1). The compound was prepared from 3,4-dimethylaniline by the described procedure:[18,19] mp 68−70 °C (Lit.[19] mp 69−70 °C).

1,2-Dimethyl-4-nitro-5-(trifluoromethyl)benzene (2). A mixture of 50.00 g (18.05 mmol) of **1**, 98.00 g (72.06 mmol) of sodium trifluoroacetate, 75.00 g (39.38 mmol) of copper(I) iodide, 400 mL of DMF, and 80 mL of toluene in a three-necked, 1 L, round-bottom flask fitted with a nitrogen inlet pipet, a Dean−Stark trap, and a mechanical stirrer was heated to reflux (oil bath temperature = 130 °C) under nitrogen. After 75 mL of toluene was removed from the Dean−Stark trap, the bath was heated to 170 °C and maintained at this temperature for 6 h. The mixture was cooled to room temperature and poured into an excess amount of water. The precipitate that formed was collected by filtration and extracted with ether. The solvent was removed under reduced pressure to afford 35.02 g (94.5%) of a crude, dark brown, liquid. The product, which contained some 4-nitro-1,2-dimethylbenzene, was used directly in the next step without further purification: IR (neat) 1522, 1347 (NO_2), 1151, and 1136 cm^{-1} (CF_3); ^{1}H NMR ($CDCl_3$) δ 7.66 (s, 1H, aromatic), 7.53 (s, 1H, aromatic), and 2.36 ppm (s, 6H, CH_3). Anal. Calcd for $C_9H_8F_3NO_2$: C, 49.32; H, 3.68. Found: C, 49.60; H, 3.82.

1-Amino-4,5-dimethyl-2-trifluoromethylbenzene (3). A mixture of 35.02 g of crude **2**, 4.50 g of activated carbon, 0.20 g of ferric chloride hexahydrate, and 100 mL of methanol was heated at reflux for 15 min. Hydrazine monohydrate (11.7 mL, 12.1 g, 241 mmol) was then added dropwise over 1 h. The mixture was stirred and heated at reflux overnight. After the mixture was allowed to cool to room temperature, the carbon black was removed by filtration. After the solvent was removed on a rotary evaporator, the residue was distilled at 75−80 °C/3 mmHg to yield 17.26 g (53.4%) of a colorless liquid: IR (neat) 3502, 3407 (NH_2), 1277, 1154, 1124, and 1109 cm^{-1} (CF_3); ^1H NMR ($CDCl_3$) δ 7.14 (s, 1H, aromatic), 6.53 (s, 1H, aromatic), 3.69 (s, 2H, NH_2), and 2.17 ppm (s, 3H, CH_3). Anal. Calcd for $C_9H_{10}F_3N$: C, 57.14; H, 5.33. Found: C, 57.39; H, 5.23.

1-Iodo-4,5-dimethyl-2-(trifluoromethyl)benzene (4). The intermediate **3** (34.02 g, 0.1798 mol) was dissolved in a warm mixture of 100 mL of concentrated hydrochloric acid and 100 mL of water. After the solution was cooled to 0 °C, a cool solution of 12.74 g (0.1846 mol) of sodium nitrite in 30 mL of water was added dropwise so that the solution remained below 10 °C. The insoluble material was removed by filtration to give a clear diazonium salt solution, which was then added dropwise to a solution of 40.00 g (0.2409 mol) of potassium iodide in 400 mL of water at 10 °C. The mixture was stirred for 30 min and then warmed to room temperature. The precipitate was collected by filtration, washed with a sodium bisulfite aqueous solution, and recrystallized from ethanol/water by dissolving in hot ethanol and adding water to cloudiness to obtain 37.80 g (70%) of white crystals: mp 51−53 °C; IR (KBr) 1298, 1151, 1121, and 1106 cm^{-1} (CF_3); ^1H NMR ($CDCl_3$) δ 7.75 (s, 1H, aromatic), 7.36 (s, 1H, aromatic), and 2.23 ppm (s, 6H, CH_3). Anal. Calcd for $C_9H_8F_3I$: C, 36.03; H, 2.69. Found: C, 35.98; H, 2.71.

4,4′,5,5′-Tetramethyl-2,2′-bis(trifluoromethyl)biphenyl (5). A mixture of 30.00 g (100 mmol) of intermediate **4**, 25.00 g of activated copper, and 85 mL of DMF was heated at reflux for 36 h. After the mixture was allowed to cool to room temperature, it was filtered to remove copper. The filtrate was poured into an excess amount of water. The precipitate that formed was collected by filtration and recrystallized from ethanol to give 12.61 g (73%) of light yellow crystals: mp 114−116 °C; IR (KBr) 1258, 1164, 1146, and 1131 cm^{-1} (CF_3); ^1H NMR ($CDCl_3$) δ 7.00 (s, 2H, aromatic), 7.45 (s, 2H, aromatic), 2.33 (s, 6H, CH_3), and 2.29 ppm (s, 6H, CH_3). Anal. Calcd for $C_{18}H_{16}F_6$: C, 62.43; H, 4.66. Found: C, 62.53; H, 4.74.

2,2′-Bis(trifluoromethyl)-4,4′5,5′-biphenyltetracarboxylic dianhydride(7). A solution of 6.92 g (20.0 mmol) of **5**, 240 mL of pyridine, and 40 mL of water in a three-necked, 500 mL, round-bottom flask fitted with a mechanical stirrer and a condenser was heated to 90 °C. Potassium permanganate (28.44 g, 180.0 mmol) was added in several portions. Each portion was added after the solution changed from purple to brown. After the mixture was stirred at 90 °C for 6 h, it was filtered while still hot to remove manganese dioxide (MnO_2). The MnO_2 was washed with hot water several times. After the combined filtrates were evaporated to dryness under reduced pressure, the white residue was dissolved in a solution of 8.00 g of sodium hydroxide in 200 mL of water. Potassium permanganate (13.60 g, 86.05 mmol) was added to the solution at 90 °C. After the mixture was heated at 90 °C for 8 h, the excess potassium permanganate was destroyed by adding ethanol. The MnO_2 was removed from the hot mixture by filtration and washed with hot water. The combined filtrates were concentrated to 80 mL and acidified to pH = 2.0 with concentrated hydrocholoric acid. The white precipitate that formed was collected by filtration and air-dried to give 2,2′ bis(trifluoromethyl)-4,4′5,5′-biphenyltetracarboxylic acid (**6**). The tetraacid was heated to 200 °C under reduced pressure overnight and then sublimed at 240 °C under reduced pressure to give 5.80 g (67%) of a white solid. The product was recrystallized from toluene to afford a white powder: mp 209−211 °C; IR (KBr) 1860, 1791 (anhydride), 1251, 1172, 1146, and 1126 cm^{-1} (CF_3); ^1H NMR (acetone-d_6) δ 8.66 (s, 2H, aromatic) and 8.29 ppm (s, 2H, aromatic); ^{13}C NMR (acetone-d_6) δ 121.2 (q, CF_3), 125.1, 129.5, 134.3, 135.7, 135.9 (q, $C_{aromatic}$-CF_3), 143.9, 162.7 and 162.9 ppm. Anal. Calcd for $C_{18}H_4F_6O_6$: C, 50.25; H, 0.94. Found: C, 49.93; H, 0.91.

4,4′-Diamino-2,2′-dichlorobiphenyl (8a). The compound was prepared from 3-chloro-1-nitrobenzene by the described procedure.[20] Its mp was 164−166 °C (Lit.[20] mp 165−166 °C).

4,4′-Diamino-2,2′-dibromobiphenyl (8b). The compound was prepared from 3-bromo-1-nitrobenzene by the described procedure.[21] Its mp was 150−152 °C (Lit.[12] mp 150−151.5 °C).

4,4′-Diamino-2,2′-diiodobiphenyl (8c). The compound was prepared from 1-iodo-3-nitrobenzene by the described procedure [22] with a mp of 170−171 °C (Lit.[21] mp 169−170 °C).

4,4′- Diamino-2,2′- bis(trifluoromethyl)biphenyl (8d). The compound was prepared from 2-bromo-5-nitrobenzotrifloride or 2-iodobenzotrifluoride by the described procedures.[12,23] Its mp was 180−182 °C (Lit.[23] mp 181−182 °C).

4,4′-Diamino-2,2′-dimethylbiphenyl (8e). The compound was prepared from 3-nitrotoluene by the described procedure.[24] Its mp was 104−106 °C (Lit.[24] mp 105−106 °C).

4,4′-Diamino-3,3′-dimethylbiphenyl (8f). The compound, which was obtained from Aldrich, was recrystallized twice from ethanol after neutralization with sodium hydroxide. Its mp was 131−132 °C.

4,4′-Diamino-2,2′-dichloro-6,6′-dimethylbiphenyl (8g). The compound was prepared from 2-methyl-5-nitroaniline by the described procedure.[25] Its mp was 166−168 °C (Lit.[25] mp 167−168 °C).

4,4′-Diamino-2,2′-dichloro-5,5′-dimethoxybiphenyl (8h). The compound, which was obtained from Eastman, was recrystallized from THF/hexane and sublimed. Its mp was 182−184 °C.

Polymerizations. The dianhydride (1.70 mmol) was added to a stirred solution of 1.70 mmol of the diamine in the appropriate amount of *m*-cresol containing five drops of isoquinoline under nitrogen at ambient temperature. After the solution was stirred for 3 h, it was heated to reflux and maintained at that temperature for 3 h. During this time, the water of imidization was allowed to distill from the reaction mixture along with 1−2 mL of *m*-cresol. The *m*-cresol was continually replaced so as to keep the total volume of the solution constant. After the solution was allowed to cool to ambient temperature, it was diluted with 30 mL of *m*-cresol and then slowly added to vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150 °C for 24 h. The polymers were isolated in 91−95% yields. All of the IR spectra of film samples contained characteristic polyimide absorption bands at 1780 cm^{-1} (C=O, symmetrical stretch), 1727 cm^{-1} (C=O, asymmetric stretch), and 742 cm^{-1} (C=O, bending).[26,27] The spectra also contained a band near 1126 cm^{-1}, characteristic of the trifluoromethyl group.[28]

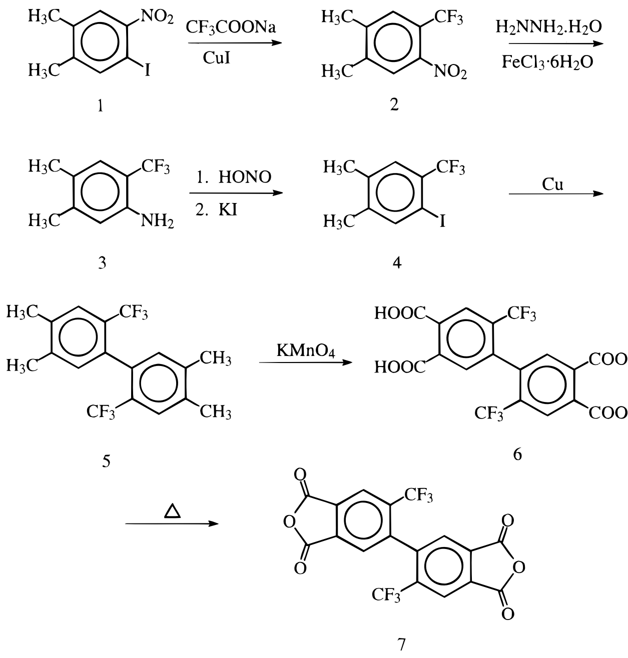
Preparation of Films for Optical Studies. Solutions of the polyimides in cyclopentanone and/or DMAc (8% w/w) were filtered through 1 μm Whatman Teflon syringe filters and ejected onto silicon wafers. The thickness of the films were controlled using metering rods. The wafers were placed on a hot plate at 60 °C to gently evaporate the solvent. After 1 h, the samples were placed in a vacuum oven and dried at 150 °C for 24 h. The film thickness ranged from 1.0 to 10 μm.

Results and Discussion

Monomer Syntheses. Several attempts to synthesize 6FBPDA from DBBPDA and its derivatives were unsuccessful. For example, the brominated dianhydride was treated with a mixture of dibromodifluoromethane, cadmium powder, copper(I) chloride, and DMF. Although these reagents have been shown to generate trifluoromethylcopper that can couple with aryl halides,[29,30] no product could be isolated from the reaction mixture. The same result was obtained when the dianhydride was converted to an *N*-phenylimide derivative with excess aniline and then treated with the reagent mixture. An attempt to trifluoromethylate tetra-*n*-butyl-2,2′-dibromo-4,4′,5,5′-biphenyltetracarboxylate with sodium trifluoroacetate and copper(I) iodide[31] was also unsuccessful.

Since DBBPDA could not be converted to 6FBPDA, a six-step synthetic route to the monomer was devised

Scheme 1



(Scheme 1). Thus, 1-iodo-4,5-dimethyl-2-nitrobenzene (**1**) was converted to 1,2-dimethyl-4-nitro-5-trifluoromethylbenzene (**2**) by a treatment with sodium trifluoroacetate (CF_3COONa) and copper(I) iodide in DMF. The crude trifluoromethylated product, which was used without purification, was reduced to 1-amino-4,5-dimethyl-2-trifluoromethylbenzene (**3**) with hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$). 1-Iodo-4,5-dimethyl-2-trifluoromethylbenzene (**4**) was obtained by the Sandmeyer reaction of the diazonium salt of **3** with potassium iodide (KI). Compound **4** was dimerized by a treatment with copper (Cu) power to afford 4,4′,5,5′-tetramethyl-2,2′-bis(trifluoromethyl)biphenyl (**5**), which was oxidized with potassium permanganate ($KMnO_4$). The tetraacid intermediate **6** was dehydrated to 6FBPDA (**7**) by heating at 200 °C under reduced pressure. The new dianhydride was purified by sublimation and recrystallization from toluene.

Polymer Syntheses. 6FBPDA (**7**) was polymerized with eight different di- or tetrasubstituted 4,4′-diaminobiphenyls (**8**) in *m*-cresol containing a catalytic amount of isoquinoline (Scheme 2). The diamines used were 4,4′-diamino-2,2′-dichlorobiphenyl (**8a**), 4,4′-diamino-2,2′-dibromobiphenyl (**8b**), 4,4′-diamino-2,2′-diiodobiphenyl (**8c**), 4,4′- diamino-2,2′- bis(trifluoromethyl)-biphenyl (**8d**), 4,4′-diamino-2,2′-dimethylbiphenyl (**8e**), 4,4′-diamino-3,3′-dimethylbiphenyl (**8f**), 4,4′-diamino-2,2′-dichloro-6,6′-dimethylbiphenyl (**8g**) and 4,4′-diamino-2,2′-dichloro-5,5′-dimethoxybiphenyl (**8h**). The polymerizations, which were carried out with 10% (w/v) solids concentrations, were initially run at ambient temperature for 3 h. The reaction mixtures were then heated at reflux for another 3−7 h, so that the PAAs cyclized to the corresponding polyimides. The water of imidization was allowed to distill from the reaction mixtures. The polyimides (**9**), which remained in solution throughout the polymerization, were isolated by precipitation in ethanol.

Solubility. All of the polymers based on 6FBPDA were soluble in phenolic solvents. Polymers **9a−d**, **9g**, and **9h** were also soluble in polar aprotic solvents (DMSO, DMF, DMAc, NMP), an ether solvent (THF), and ketone solvents (acetone, cyclopentanone) (see Table 2). Polymer **9e** was soluble in THF and polar aprotic solvents, while polymer **9f** was only soluble in polar aprotic solvents. Only one analogous polyimide (DBBPDA−PFMB) based on DBBPDA or DPBPDA was soluble in ketone solvents.[13] Thus, 6FBPDA was considerably more effective in producing polymers soluble in these solvents. In fact, the solubility behavior of the polymers based on 6FBPDA was very similar to that of analogous polymers based on 6FDA.[32]

Relative to structural changes in the diamine component, the polymer based on 4,4′-diamino-2,2′-dimethylbiphenyl (**9e**) was soluble in more solvents than the polymer based on 4,4′-diamino-3,3′-dimethylbiphenyl (**9f**). Thus, as with the polymers based on DBBPDA and DPBPDA,[13] the effect of substituents in the 2- and 2′-positions on solubility was greater than that of substituents in the 3- and 3′- positions.

Solution Properties. The intrinsic viscosities of the polyimides ranged from 1.70 to 6.72 dL/g in NMP or *m*-cresol (see Table 1). These values are considerably higher than those displayed by analogous polymers based on 6FDA.[32] Although this could be due to differences in molecular weight, it is likely that they are to some degree an indication that the polymers possess more extended conformations in the solutions. Evidence for this hypothesis is provided by the fact that the persistence lengths of 6FBPDA−PFMB is 6.6 nm compared to 2.0 nm for 6FDA−PFMB in THF.[33,34]

Thermal Properties. The T_gs and CTEs of the polyimides were obtained from TMA measurements on 10−30 μm films, which were cast from THF or DMAc solutions. The T_gs ranged from 327 to 345 °C (Table 1). In most cases, the values are slightly higher than those of analogous polymers based on DBBPDA and comparable to those of polymers based on DPBPDA. These values are also considerably higher than those displayed by analogous polymers based on 6FDA.

The CTEs of the polyimides ranged from 1.58×10^{-5} to 2.50×10^{-5} °C^{-1} (Table 1). These values are 50−100% higher than those of the analogous polymers based on DBBPDA.[13] The values, however, are not significantly different than those of analogous polymers based on DPBPDA. CTEs are associated with the rigidity and linearity of the polymer chain, which affect the chain packing. The fact that the CTE increased as the substituents at the 2- and 2′-positions were changed from bromine to perfluoromethyl and phenyl may be due to an increase in free volume. The CTEs of the polyimides were less than half of those of analogous polymers based on 6FDA.[32] This is probably due to the major differences in chain linearity and rigidity.

DMA curves of 6FBPDA-DMB obtained at different frequencies are shown in Figure 1. Two relaxation processes can be seen above room temperature. An apparent β relaxation process occurs around 80 °C, while an α relaxation process occurs around 350 °C. The β relaxation is more frequency dependent than the α relaxation. Using the Arrhenius equation the activation energy of the β relaxation was calculated to be around 150 kJ/mol, while the α relaxation was determined to have an apparent activation energy of around 800 kJ/mol. The activation energy of process is critically dependent up on the chemical structures of polyimide. DMA curves of polyimides synthesized from 6FBPDA and the diamines DCB, DMB, and DBB obtained at 0.01

Scheme 2

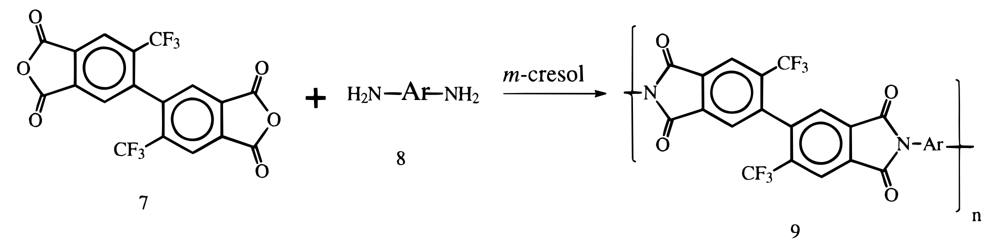
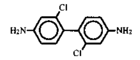
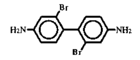
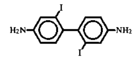
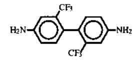
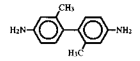
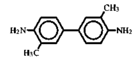
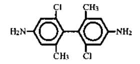
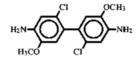


Table 1. Aromatic Polyimides Based on 6FBPDA

PI	Diamine		$[\eta]^a$	$T_g{}^b$	CTE^c	TGA^d (°C)	
No.	No.	-Ar-	(dL/g)	(°C)		N_2	Air
9a	*8a*		1.70	342	1.77	555	532
9b	*8b*		3.32	343	1.66	538	528
9c	*8c*		3.18	337	1.68	445	444
9d	*8d*		4.83	332	1.80	569	549
9e	*8e*		3.26	345	1.65	488	503
9f	*8f*		6.72^e	344	2.18	495	474
9g	*8g*		3.74	327	1.90	479	456
9h	*8h*		2.13	340	2.01	462	442

[a] Intrinsic viscosity determined in NMP at 30 ± 0.1 °C. [b] Temperature at which a change in slope occurred on a plot of film dimensional change vs temperature obtained by TMA with a heating rate of 10 °C/min. Films were subjected to initial stresses of 2.0–7.0 MPa, and the T_gs at each stress level were extrapolated to zero stress. [c] The CTE ($\times 10^{-5}$ °C^{-1}) values was taken as the mean between 50 and 150 °C and extrapolated to zero stress. [d] Temperature at which a 5% weight loss occurred when the polymers were subjected to TGA with a heating rate of 10 °C/min. [e] Intrinsic viscosity determined in *m*-cresol at 30 ± 0.1 °C.

Table 2. Solubility of Polyimides Based on 6FBPDA

polymer	acetone	THF	DMF	DMSO	DMAc	NMP
9a	+[a]	+[b]	+	+	+	+
9b	+	+	+	+	+	+
9c	+	+	+	+	+	+
9d	+	+	+	+	+	+
9e	+	+	+	+	+	+
9f	−	−	+	+	+	+
9g	+	+	+	+	+	+
9h	+	+	+	+	+	+

[a] Key: − = Solubility less than 2–3 g/L at room temperature. [b] Key: + = Minimum solubility of 2–3 g/L at room temperature.

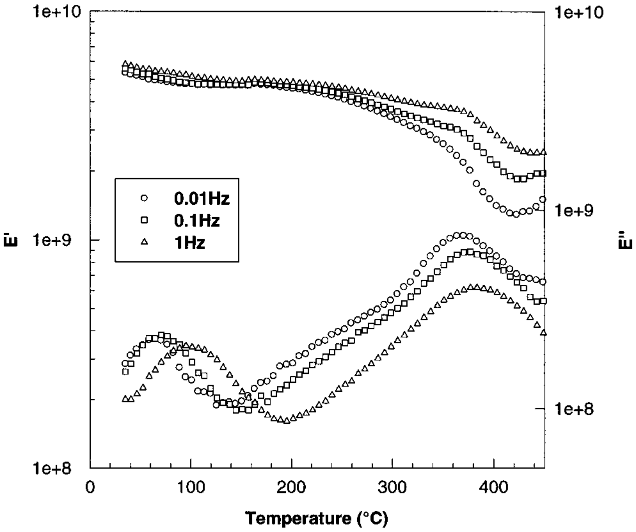


Figure 1. DMA curves of 6FBPDA–DMB at different frequencies.

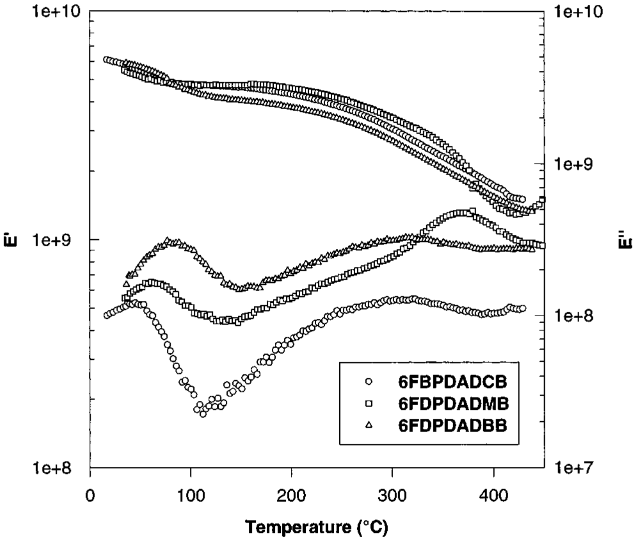


Figure 2. DMA curves of polyimides synthesized from 6FBPDA and different diamines.

Hz are shown in Figure 2. The β relaxation temperature increases as the size of the group in the 2,2′-positions of the diamines increases. This β relaxation process has been shown to be associated with the biphenyl diamine component.[35] Figures 1 and 2 reveal another less apparent process between the β relaxation and the α relaxation. This relaxation process has a relaxation temperature of around 250 °C, which is independent of the type of diamines. This may indicate that the origin of this relaxation is associated with the trifluoromethyl groups in the 6FBPDA. This multiple β relaxation behavior will be discussed in detail in other publications.[32,36]

Film samples of the polyimides underwent 5% weight losses at 460 to 570 °C in nitrogen and at 440 to 550 °C in air when subjected to TGA with a heating rate of 10 °C/min (Table 1). Thus, the polymers based on 6FBPDA dianhydride displayed better thermal and thermooxidative stability than analogous polymers based on DBBPDA and analogous polymers based on 6FDA.[32] This is most likely due to the strong carbon–fluorine bonds in the polymers and the strong electron-withdrawing effects of the trifluoromethyl groups. The bond energies of carbon–bromine, carbon–hydrogen, and

Table 3. Optical Properties of Films of Polyimides Based on 6FBPDA

PI	transparency onset (nm)	80% transmission (nm)	$n_{\|}$	$n_{\perp}$	Δn^a
9a	346	428	1.6133	1.5445	−0.0688
9b	342	424	1.6210	1.5548	−0.0662
9c	339	422	1.6341	1.5807	−0.0534
9d	324	383	1.5605	1.4939	−0.0666
9e	332	428	1.6010	1.5276	−0.0734
9f	348	430	1.6053	1.5270	−0.0783
9g	335	414	1.5870	1.5270	−0.0600
9h	325	400	1.5820	1.5224	−0.0576

[a] UNB: $\Delta n = n_{\perp} - n_{\|}$.

carbon−fluorine bonds are 276, 413, and 441 kJ mol^{-1}, respectively.[37]

The 5% weight loss temperatures for the polymers were similar to those of analogous polyimides based on DPBPDA.[13] However, isothermal aging studies on the BPDA−PFMB polyimides showed that polyimides containing pendent trifluoromethyl groups are more thermally and thermooxidatively stable than analogous polymers containing pendant phenyl groups.[38]

Relative to changes in structure in the diamine component, polymers containing electron-withdrawing, deactivating groups were more thermally and thermooxidatively stable than those containing electron-donating, activating groups. Diamines in a polyimide are presumed to be the site of the greatest electron density and is thus a likely point of oxidation. Hence, the electron-deficient diamines afford more oxidatively stable polyimides than electron-rich diamines. The effect of replacing carbon−hydrogen bonds with carbon−fluorine bonds can be seen by comparing the 5% weight loss temperature of the polymers based on 4,4′-diamino-2,2′-dimethylbiphenyl (**9e**) with those of the polymer based on PFMB (**9d**).

Optical Properties. Most of the polymers could be cast into flexible, tough, colorless films from cyclopentanone and THF solutions at ambient temperature and atmospheric pressure. Polymers **9e** and **9f**, which were not soluble in these solvents, could be cast into similar films from DMAc solutions. However, the films were usually heated at 60 °C to facilitate solvent evaporation and then dried at 150 °C under reduced pressure.

Films that were 5 μm thick began to transmit light at 324−346 nm. The films transmitted 80% of light above 383−428 nm (Table 3). Thus, they were slightly more transparent than analogous polymers based on DBBPDA and DPBPDA.[13] Their transparencies were very similar to those of analogous polymers based on 6FDA.[32]

The in-plane ($n_{\|}$) and out-of-plane ($n_{\perp}$) refractive indices of the films of **9** ranged from 1.557 to 1.634 and from 1.505 to 1.584, respectively (Table 3). Thus, the refractive indices were lower than those of analogous DBBPDA- and DPBPDA-based polyimides and similar to those of analogous 6FDA-based polymers.[32] Refractive index is related to the ratio of the induced dipole moment to the molar volume and is known to decrease as the polarizability of chemical bonds decreases.[16] Relative to structural changes in the diamine component, the refractive indices increased in the order of **9d** < **9e** < **9a** < **9b** < **9c** for the 4,4′-diamino 2,2′-disubstituted biphenyl-based polyimides. This is consistent with an increase in polarizability due to the incorporation of more polarizable bonds.

The UNBs ($\Delta n = n_{\perp} - n_{\|}$) of the films ranged from −0.051 to −0.073 (Table 3). Thus, the UNB values of the films of **9** were less than those of analogous films of DBBPDA-based polyimides. This may reflect the differences in the abilities of the polymer chains to pack in the plane of the film.[10,11] This is consistent with the fact that the in-plane CTEs of the films of **9** were considerably larger than those of the films of the DBBPDA polymers.

The UNBs of the films of **9** were larger than that of films of analogous 6FDA-based polymers.[32] For example, the Δn of the 6FBPDA−PFMB film was −0.0534 while that of the 6FDA−PFMB polymer was −0.0462. Once again, this is most likely a reflection of differences in the chain linearity and rigidity, which affect in-plane chain orientation. The in-plane CTE of the 6FBPDA−PFMB film was less than half that of a 6FDA−PFMB film.[32]

Even though the UNBs of the films of **9** were lower than those of BPDA-based polymers, the new polymers should be extremely useful as retardation layers in LCDs.[8−11] The solubility of most of the polymers in ketone solvents is a major advantage since it greatly facilitates their use in commercial film casting operations.

Conclusions

2,2′-Bis(trifluoromethyl)-4,4′,5,5′-biphenyltetracarboxylic dianhydride (6FBPDA) can be prepared from 1-iodo-4,5-dimethyl-2-nitrobenzene and polymerized with aromatic diamines to afford polyimides with intrinsic viscosities as high as 6.72 dL/g. The introduction of trifluoromethyl groups in the 2- and 2′-positions of the dianhydride component of BPDA-based polymers results in dramatic changes in their properties. For, example, polymers that are only soluble in phenolic solvents can be made soluble in ketone, ether and polar aprotic solvents. Trifluoromethyl groups are more effective in increasing solubility than bromine atoms or phenyl groups in the same positions. The fluorinated substituents also increase the polymer T_gs and CTEs.

The incorporation of fluorine in the polymers results in a reduction in the refractive indices of their films. The wavelength range over which thin films transmit light is also increased. Films can be prepared that transmit light below 350 nm. However, the fluorinated substituents decrease the in-plane orientation of the polymer chains in the films. Thus, the difference in their out-of-plane refractive index and their in-plane refractive index, i.e., the optical UNB, is not as large as that of films of nonsubstituted analogues. The trifluoromethyl groups result in a larger reduction in UNB than do bromine substituents.

Interesting comparisons can be made between analogous polymers prepared from 6FBPDA and the more flexible 6FDA. Although polymers prepared from both dianhydrides display similar solubilities, the intrinsic viscosities of 6FBPDA polymers are more than twice as high. The CTEs of films of 6FBPDA polymers are less than half those of films of 6FDA polymers, while their absolute UNB values are approximately 50% higher.

The dramatic difference in properties and solution behavior can be attributed to differences in backbone rigidity. The comparisons suggest that our goal of enhancing polyimide solubility without decreasing backbone rigidity has been achieved. In fact, the T_gs of the 6FBPDA polymers indicate that the backbones are more rigid than those of considerably less-soluble, BPDA-based polyimides.

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