Organosoluble and Light-Colored Fluorinated Polyimides from 4,4′-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl and Aromatic Dianhydrides

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ABSTRACT: A novel fluorinated diamine monomer based on 4,4′-biphenol was synthesized via a straightforward, high-yielding two-step procedure. 4,4′-Biphenol was reacted with 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate to yield the intermediate dinitro compound, which was subsequently reduced to afford the fluorinated diamine, 4,4′-bis(4-amino-3-trifluoromethylphenoxy)biphenyl. A series of organosoluble fluorinated polyimides were prepared from the diamine with various aromatic dianhydrides via a conventional two-step thermal imidization method. All polyimides were soluble in strong dipolar solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide. The polyimides showed excellent thermal and thermooxidative stability and good mechanical properties. No significant weight loss was observed below a temperature of 520 °C in nitrogen or in air, and the glass-transition temperatures ranged from 247 to 313 °C. Low dielectric constants (2.57–3.65 at 10 kHz), low moisture absorption (0.1–0.7 wt %), and low color intensity were also observed. © 2002 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 40: 524–534, 2002; DOI 10.1002/pola.10113

Keywords: fluorinated polyimides; solubility; low color intensity; low dielectric constant; fluoropolymers; polyimides

INTRODUCTION

High-performance polymer film and coating materials are increasingly being required by the electronic circuit industry. Aromatic polyimides possess many useful properties, such as high glass-transition temperatures (T_g's), excellent dimensional stability, low dielectric constants, and outstanding thermal stability.[1,2] They have diverse applications in the electronics industry as flexible circuitry substrates, stress buffers, interlayer dielectrics, and passivation layers. However, one of the problems of most polyimides is poor processability in their imidized forms due to high softening temperatures and insolubility. To extend the utility of such high-performance materials, researchers have long desired to synthesize soluble polyimides without appreciable loss in their thermomechanical properties.

A low dielectric constant is one of the most attractive properties of polyimide materials for electronic applications. One of the most effective methods to decrease the dielectric constant is to introduce fluorine atoms into polyimide materials.[3] As is well-known, the fluorine atom has unique characteristics, such as high electronegativity and low electric polarity. These properties give fluorinated polymers [e.g., poly(tetrafluoroethylene)] attractive features such as low water uptake, water and oil repellence, low permittivity,

low refractive indices, resistance to wear and abrasion, and thermal and chemical stability. In the past 2–3 decades, a number of fluorine-containing diamines and dianhydrides have been introduced for the preparation of fluorinated polyimides with low water uptake, low refractive indices, and low dielectric constants with many of the advantages of polyimides retained.[3] Fluorination is also known to enhance the solubility and optical transparency of polyimides.[4,5]

Recent studies have demonstrated that polyimides derived from ether-bridged aromatic diamines with trifluoromethyl (3F) groups, such as 1,3- and 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene, are soluble high-temperature polymer materials with low moisture uptake, low dielectric constants, high optical transparency, and low birefringence.[6–10] In this study, a new 3F-containing aromatic diamine, 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl, was synthesized and subsequently polycondensed with various commercially available aromatic dianhydrides to produce a series of fluorinated polyimides. The polymers were subjected to thermal, optical, and dielectric property measurements and compared to analogous polyimides prepared from a nonfluorinated diamine monomer, 4,4′-bis(4-aminophenoxy)-biphenyl (BAPB).

EXPERIMENTAL

Materials

4,4′-Biphenol (Tokyo Chemical Industry) and 2-chloro-5-nitrobenzotrifluoride (Acros) were used as received. As described in a previous article,[11] BAPB (mp = 198–199 °C) was prepared by the aromatic nucleophilic substitution reaction of 4-chloronitrobenzene with 4,4′-biphenol in the presence of potassium carbonate and the subsequent reduction of the intermediate dinitro compounds with hydrazine as the reducing agent and palladium as the catalyst. Pyromellitic dianhydride (PMDA or **3a**; Aldrich), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**3b**; Aldrich), diphenylsulfone-3,3′,4,4′-tetracarboxylic dianhydride (**3d**; New Japan Chemical Co.), and 4,4′-oxydiphthalic anhydride (ODPA or **3e**; Oxychem) were recrystallized from acetic anhydride before use. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (**3c**; Oxychem) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA or **3f**; Hoechst) were purified by sublimation. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Monomer Synthesis

4,4′-Bis(4-nitro-2-trifluoromethylphenoxy)biphenyl (1)

4,4′-Biphenol (14 g, 0.075 mol) and 2-chloro-5-nitrobenzotrifluoride (34 g, 0.15 mol + 0.2 g) were dissolved in 150 mL of *N,N*-dimethylformamide (DMF) in a 300-mL flask with stirring. Then, potassium carbonate (21 g, 0.15 mol) was added, and the suspension mixture was heated at 130 °C for 12 h. The mixture was allowed to cool and was poured into 600 mL of water to give a yellow solid, which was collected, washed with water, and dried (41.5 g, 98%). The crude product was recrystallized from DMF/methanol to give fine, pale-yellow needles (32 g, 76%).

mp: 215–216 °C by differential scanning calorimetry (DSC) at a scan rate of 10 °C/min. IR (KBr): 1531, 1330 (—NO_2 stretch), 1290, 1257, 1243, 1197, 1147, 1116 cm^{-1} (C—F and C—O stretch). ^{1}H NMR [dimethyl sulfoxide-d_6 (DMSO-d_6), δ, ppm]: 8.53 (d, J = 2.6 Hz, 2H, He), 8.51 (dd, J = 10.8, 2.7 Hz, 2H, Hd), 7.84 (d, J = 8.6 Hz, 4H, Ha), 7.34 (d, J = 8.6 Hz, 4H, Hb), 7.20 (d, J = 9.2 Hz, 2H, Hc). ^{13}C NMR (DMSO-d_6, δ, ppm): 159.98 (C^5), 153.69 (C^4), 141.93 (C^8), 136.85 (C^1), 130.19 (C^7), 129.01 (C^2), 123.44 (C^9), 120.87 (C^3), 118.56 (C^6).

The quartet signals of the C^{10} and C^{11} carbons are too weak to be assigned because of the limited solubility of dinitro compound **1** in DMSO-d_6:
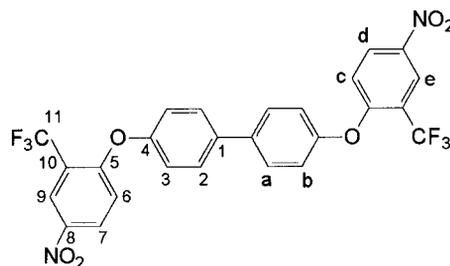
ELEM. ANAL. Calcd. For $C_{26}H_{14}F_6N_2O_6$ (564.39): C, 55.33%; H, 2.50%; N, 4.96%. Found: C, 55.40%; H, 2.39%; N, 5.05%.

For X-ray structure analysis, single crystals of **1** were grown during slow crystallization of their ethanol solutions. A crystal size of 0.55 mm × 0.20 mm × 0.10 mm was used for X-ray struc-

ture determination. Intensity data were collected on a Bruker Smart charge cover device (CCD) X-ray diffraction diffractometer at 295 K with graphite-monochromatized Mo Kα radiation (wavelength = 0.71073 Å). Compound **1** crystallized in a monoclinic system with space group P2$_1$/n [weight-average molecular weight = 546.39, a = 6.2849(2), b = 15.0424(5), c = 12.2024(4) Å; α = 90, β = 92.660(1), and γ = 90°, where D_c = 1.672 g/cm^3 for Z = 2 and V = 1152.37(7) Å^3]. Least-squares refinement based on 2649 independent reflections converged to final values of R_1 = 0.0478 and wR_2 = 0.1041.

4,4′-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl (2)

A mixture of the purified dinitro compound **1** (20 g, 0.0354 mol), 10% Pd/C (0.2 g), ethanol (150 mL), and hydrazine monohydrate (10 mL) was heated at the reflux temperature for about 6 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The crude product was purified by recrystallization from ethanol to give colorless, flakelike crystals (14.6 g, 82%).

mp: 155–156 °C by DSC (10 °C/min). IR (KBr): 3442, 3355, 3338 (N—H stretch), 1265, 1228, 1160, 1126 cm^{-1} (C—O and C—F stretch). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.54 (d, J = 8.7 Hz, 4H), 6.95 (d, J = 2.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 6H), 6.84 (dd, J = 8.7, 2.5 Hz, 2H), 5.48 (s, 4H). ^{13}C NMR (DMSO-d_6, δ, ppm): 159.45, 147.34, 143.47, 135.14, 128.95, 126.03, 124.66 (quartet, $^1J_{C—F}$ = 271 Hz), 122.69 (quartet, $^2J_{C—F}$ = 30 Hz), 119.68, 117.89, 111.60 (quartet, $^3J_{C—F}$ = 5 Hz). ELEM. ANAL. Calcd. For C$_{26}$H$_{18}$F$_6$N$_2$O$_2$ (504.43): C, 61.90%; H, 3.60%; N, 5.55%. Found: C, 62.01%; H, 3.36%; N, 5.59%.

Polymer Synthesis

The general polymerization procedure is illustrated by the following example. To a solution of 0.6981 g (1.384 mmol) of 3F-diamine **2** in 9.5 mL of dried DMAc in a 50-mL flask, 0.3019 g (1.384 mmol) of PMDA was added in one portion. The mixture was stirred at room temperature overnight (for ca. 12 h) to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) **4a** was 1.43 dL/g, as measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The polymer solution was poured into a 11-cm glass culture dish that was placed over-

night in a 90 °C oven for removal of the solvent. The semidried poly(amic acid) film was further dried and transformed into polyimide **5a** by being heated at 150 °C for 30 min, at 200 °C for 30 min, and at 250 °C for 1 h. The polyimide film was stripped from the glass substrate by being soaked in water. The inherent viscosity of the polyimide **5a** was 0.90 dL/g in *N*-methyl-2-pyrrolidone (NMP) at a concentration of 0.5 g/dL at 30 °C.

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run in a PerkinElmer model 2400 CHN analyzer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX-400 spectrometer. The inherent viscosities were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 9–11-mg film samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen at a heating rate of 15 °C/min. T_g's were read as the midpoint of the heat capacity jump and were taken from the second heating scan after quick cooling from 400 °C. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 15 mA) at a scanning rate of 2°/min. Measurements were performed with film specimens 30–40 μm thick. Mechanical properties of the films were measured with an Instron model 1130 tensile tester with a 5-kg load cell at a crosshead speed of 5 cm/min on strips approximately 30–40 μm long and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a Macbeth color-eye colorimeter. Measurements were performed with films 30–40 μm thick with an observational angle of 10 ° and a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a TA Instruments DEA 2970 dielectric analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films.
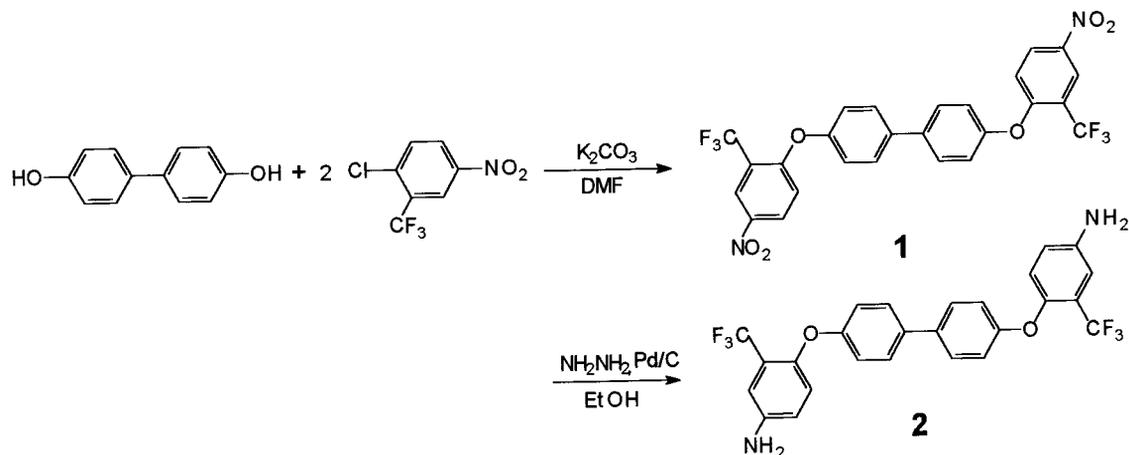
Scheme 1. Synthesis of 3F-diamine **2**.

Experiments were performed at 25 °C in a dry chamber. The equilibrium moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

RESULTS AND DISCUSSION

Monomer Synthesis

The 3F-containing bis(ether amine) **2** was prepared in two steps according to a well-developed method (Scheme 1).[11–14] The intermediate dinitro compound **1** was synthesized by the aromatic chloro-displacement reaction of 2-chloro-5-nitro-benzotrifluoride with 4,4′-biphenol in the presence of potassium carbonate in DMF. Both the para nitro group and the ortho 3F group activate the chlorine for displacement; therefore, the chloro-displacement reaction of 2-chloro-5-nitro-benzotrifluoride by the potassium phenoxide of 4,4′-biphenol can be readily carried out even at room temperature (ca. 25 °C). **2** was readily obtained in high yields by the catalytic reduction of **1** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol.

FTIR, NMR, and elemental analysis were used to confirm the structures of the intermediate **1** and the diamine monomer **2**. As shown in the Experimental section, the nitro group of compound **1** gave two characteristic bands at 1531 and 1330 cm^{-1} (NO$_2$ asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed a pair of N—H stretching

bands in the region of 3300–3500 cm^{-1}. In the ^{1}H NMR spectrum of **2**, the absorption signals of aromatic protons appear in the range of 6.83–7.55 ppm, and the resonance at 5.48 ppm is due to the primary aromatic amine protons. Figure 1 presents the ^{13}C NMR spectrum of diamine **2** in DMSO-d_6. All the carbon-13 atoms in 3F-diamine **2** resonate in the region of 110–160 ppm. The ^{13}C NMR spectrum of **2** shows three quartets because of the heteronuclear ^{13}C–^{19}F coupling. The large quartet centered at about 124.7 ppm is due to the —CF$_3$ carbon. The one-bond C—F coupling constant in this case is about 271 Hz. The 3F-attached carbon (C^{10}) also shows a clear quartet centered at about 122.7 ppm with a smaller coupling constant of about 30 Hz due to two-bond C—F coupling. Besides, the C^9 carbon (ortho to the 3F group) also has its resonance split by the three fluorines (three-bond coupling). The close quartet has an even smaller coupling constant (ca. 5 Hz) because the interaction operates over more bonds. All the spectroscopic data obtained were in good agreement with the expected structures. The molecular structure of **1** was further detailed by a single-crystal X-ray diffraction analysis. The crystal structure of **1** (Fig. 2) shows that the terminal phenylene rings are nearly orthogonal to the central biphenylene rings.

Polymer Synthesis

In general, polyimide can be synthesized from the polycondensation of a diamine and a dianhydride through either a two-step polymerization, that is, the formation of a poly(amic acid) and subsequent
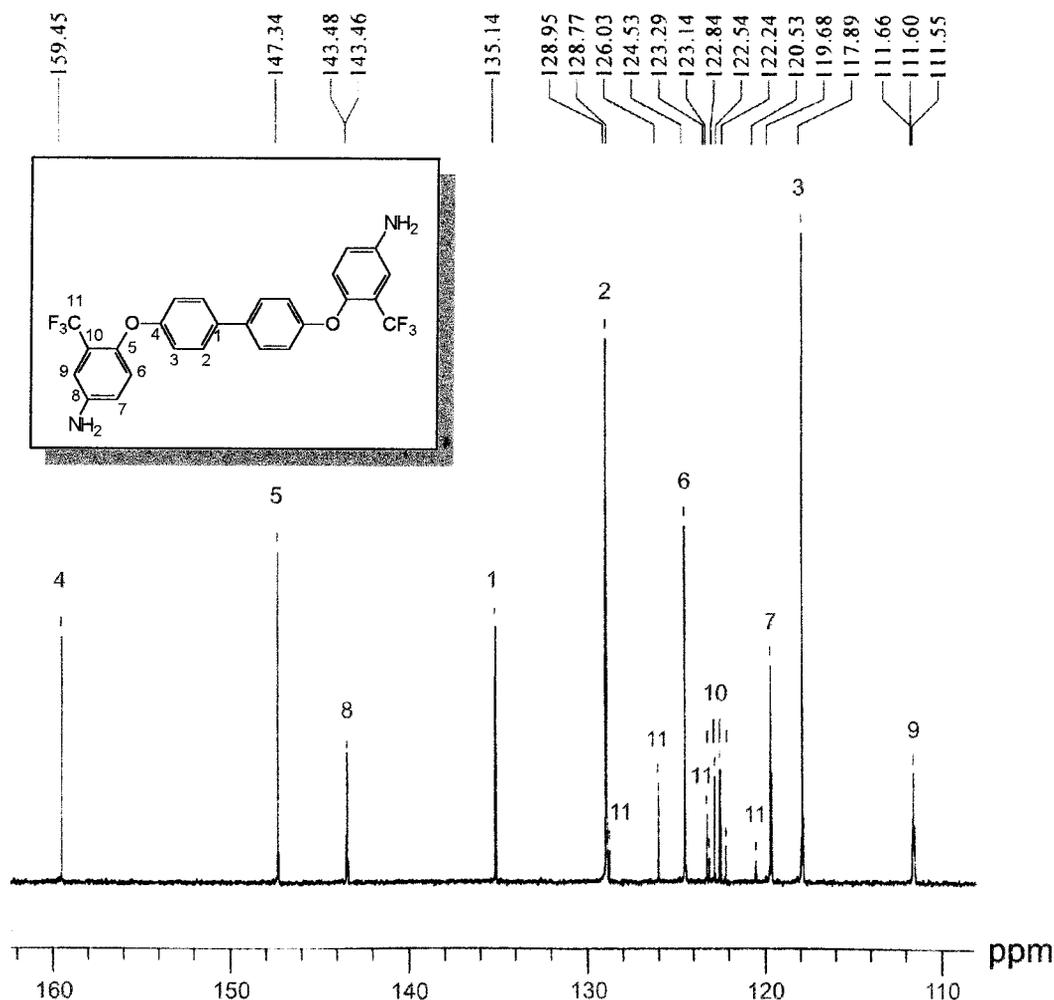
Figure 1. ^{13}C NMR spectrum of 3F-diamine **2** in DMSO-d_6.

thermal or chemical imidization, or a direct one-step solution polycondensation at high temperatures. The former approach was adopted to synthesize polyimides in this study. The reaction scheme for the synthesis of fluorinated polyimides **5a–5f** is shown in Scheme 2. No difficulty was encountered in obtaining high molecular weight poly(amic acid)s from the reactions of 3F-diamine **2** with aromatic dianhydrides **3a–3f**. Although the amino groups in diamine **2** were less basic than a normal aromatic amine because of the inductive deactivation of the 3F group, a result confirmed by the slow polymerization rate inferred from the data in Figure 3, such 3F-diamine was still sufficiently reactive to give high molecular weight poly(amic acid)s when they were allowed to polymerize for a sufficient length of time. As shown in Table I, the inherent viscosities of the intermediate poly(amic acid)s were 0.83–1.43

dL/g. The molecular weights of all the poly(amic acid)s were sufficiently high to permit the casting of flexible and tough poly(amic acid) films, which were subsequently converted into tough polyimide films by extended heating at elevated temperatures. These polyimides exhibited excellent solubility in polar solvents such as NMP and DMAc. Therefore, the characterization of solution viscosity was carried out without any difficulty, and the inherent viscosities of the polyimides were recorded to be 0.78–1.31 dL/g, as measured in NMP or DMAc.

The formation of polyimides was confirmed with elemental analysis and IR spectroscopy. FTIR spectroscopic characterization was performed on thin films. All polyimides exhibited characteristic imide group absorptions around 1780 and 1725 (typical of imide carbonyl asymmetrical and symmetrical stretching), 1380
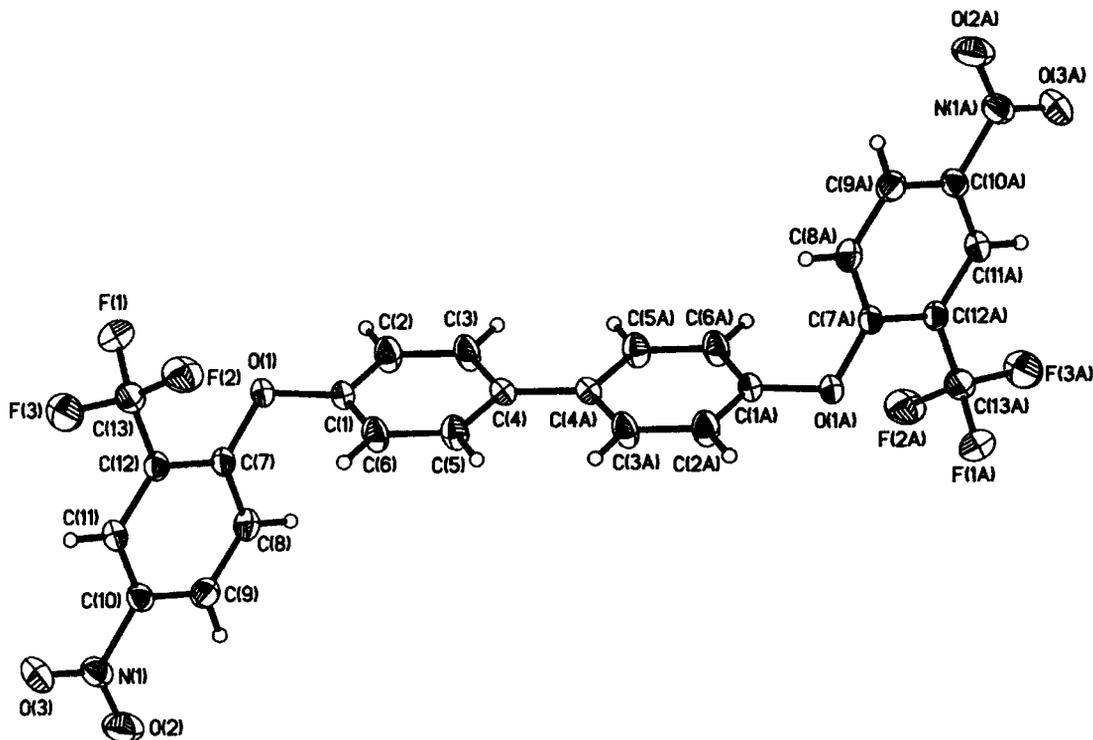
**Figure 2.** X-ray structure of the 3F-dinitro compound **1**.

(C—N stretching), and 1100 and 725 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C—O and C—F stretching. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the poly(amic acid) precursor into polyimide. The results of the elemental analyses of all the polyimides are listed in Table I. The values found were in good agreement with the calculated ones of the proposed structures.

Properties of the Polyimides

All the fluorinated polyimides (**5a–5f**) revealed an amorphous nature, as evidenced by the X-ray diffraction patterns. The solubility of the polyimides was tested qualitatively in various organic solvents, and the results are summarized in Table II. In addition, the solubility behaviors for the analogous nonfluorinated polyimides **5a–5f'** reported previously[11] are listed for comparison. Because of the introduction of the bulky 3F group, most polyimides were readily soluble in polar solvents such as NMP and DMAc at room temperature or upon heating. Conversely, for the **5a–5f'** series, only the polyimide (**5f'**) derived from 6FDA was solu-

ble in the solvents tested. Poor solubility for the other **5'** polyimides indicates either strong intermolecular interactions or good packing ability. As described previously,[11] polyimides **5a'** and **5b'** showed semicrystalline X-ray diffraction patterns. Therefore, the large differences in solubility between the **5** and **5'** series are attributed to the molecular asymmetry and the presence of bulky 3F groups. The backbone asymmetry and 3F group inhibited close packing, thereby reducing the interchain interactions to enhance solubility.

The color intensities of the polyimides were elucidated from the yellowness or redness indices observed by a Macbeth color-eye colorimeter. For comparison, the corresponding polyimides (**5'**) without the 3F groups were also prepared and characterized by their color intensity. The color coordinates of these polyimides are given in Table III. The results shown in Table III indicate that all the **5** series fluorinated polyimides showed a lower b^* value (a yellowness index) in contrast with the corresponding nonfluorinated polyimides (the **5'** series). Moreover, the color intensities of the polyimides could also be elucidated from the cutoff wavelength observed in the UV–vis absorption spectra. Figure 4 shows the UV–vis spectra of
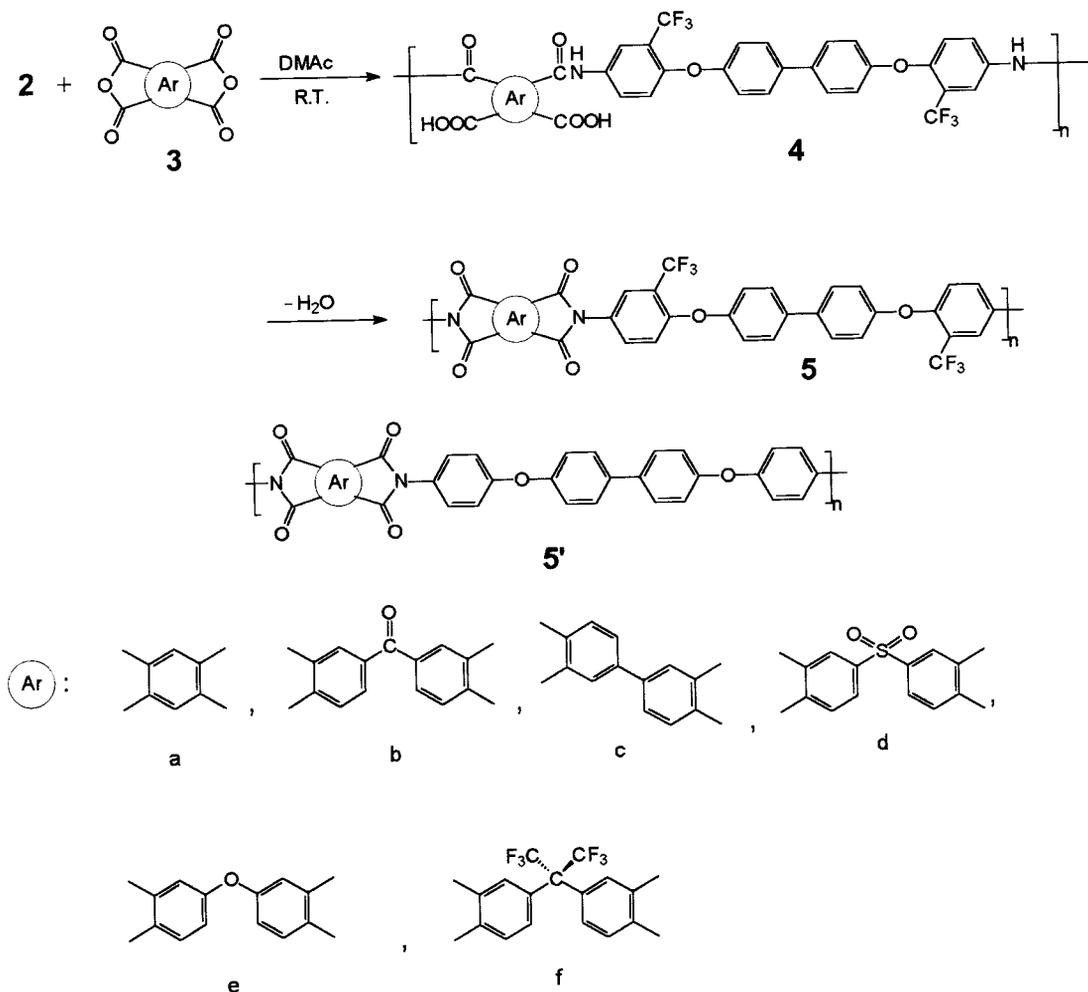
Scheme 2. Synthesis of the polyimides.

the polyimide films, and the cutoff wavelengths from these spectra are listed in Table III. Consistent with the results obtained from the colorimeter, all the fluorinated polyimides revealed a lower cutoff wavelength than their respective nonfluorinated analogues. The 6FDA and ODPA produced fairly transparent and almost colorless polyimide films in contrast to other dianhydrides. These results were attributed to the reduction of the intermolecular charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The light colors of the polyimides with the 3F groups in their diamine moieties can be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing 3F group in diamine **2** was effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by de-

creasing the electron-donating property of diamine moieties). The low polarizability of fluorine and fluorinated groups also weakened the interchain interactions. The decrease in intermolecular CTC formation was understandable also from the significant solubility of the polyimides prepared from 3F-diamine **2**.

All the fluorinated polyimides (**5a–5f**) afforded good-quality and creasable films. These films were subjected to a tensile test, and their tensile properties are summarized in Table IV. They showed an ultimate tensile strength of 97–119 MPa, an elongation to break of 9–38%, and an initial modulus of 1.8–2.1 GPa. Some of them, such as **5a**, **5c**, and **5e**, behaved as tough materials. Their specimens necked during tensile testing and had moderate extension to break.

DSC and TGA were used to evaluate the thermal properties of the polyimides. The thermal
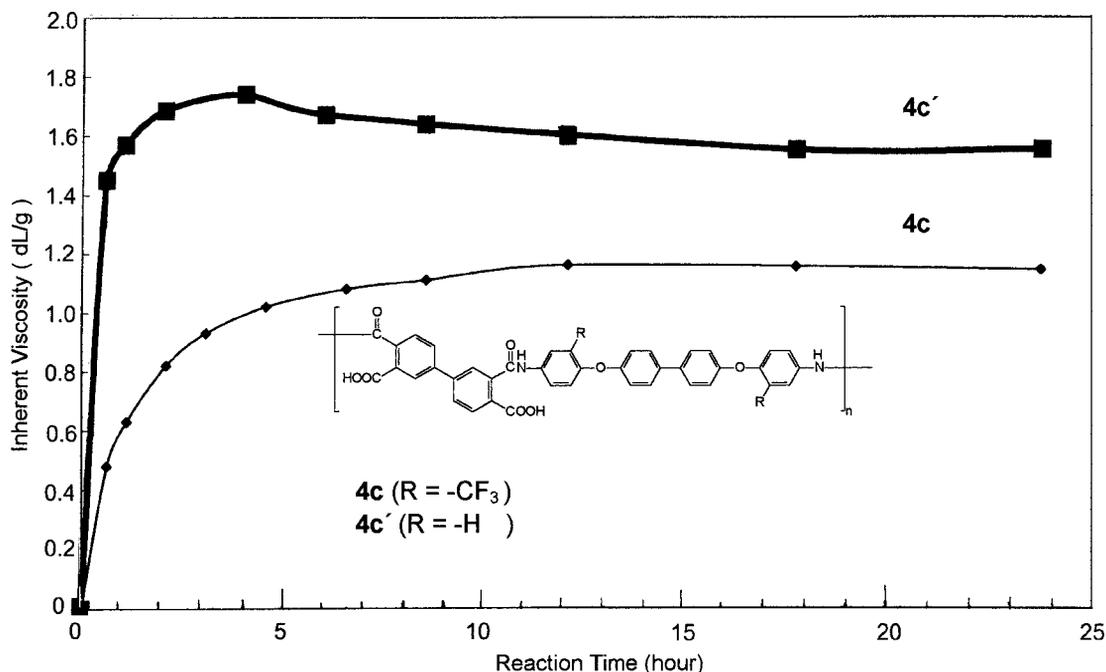
Figure 3. Viscosity change in poly(amic acid)s **4c** and **4c′** prepared in DMAc with a 10% solid content at room temperature.

behavior data of all the fluorinated polyimides are presented in Table V. DSC experiments were conducted at a heating rate of 15 °C/min in nitrogen. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so the T_g's of all the polyimides could be easily read in the subsequent heating DSC traces. The T_g values of these polyimides were in the 247–313 °C range, depending on the structure of the dianhydride component and decreasing with the increasing flexibility of the polymer backbones. As expected, the polyimide (**5e**) obtained from ODPA

Table I. Inherent Viscosity (η_{inh}) of Poly(amic acid)s and Polyimides and Elemental Analysis of the Polyimides

Poly(amic acid)		Polyimide		Elemental Analysis (%) of Polyimides				
Code	η_{inh} (dL/g)[a]	Code	η_{inh} (dL/g)[a]	Formula (Formula Weight)		C	H	N
4a	1.43	**5a**	0.90[b]	$(C_{36}H_{16}N_2O_6F_6)_n$	Calcd.	62.98	2.35	4.08
				$(686.52)_n$	Found	62.62	2.32	4.07
4b	1.09	**5b**	1.31[b]	$(C_{43}H_{20}N_2O_7F_6)_n$	Calcd.	65.32	2.55	3.54
				$(790.63)_n$	Found	65.06	2.23	3.68
4c	1.19	**5c**	1.01[b]	$(C_{42}H_{20}N_2O_6F_6)_n$	Calcd.	66.15	2.64	3.67
				$(762.62)_n$	Found	66.01	2.17	3.68
4d	0.84	**5d**	0.78	$(C_{42}H_{20}N_2O_8S_1F_6)_n$	Calcd.	63.48	2.54	3.53
				$(826.68)_n$	Found	63.37	2.46	3.46
4e	0.83	**5e**	0.95	$(C_{42}H_{20}N_2O_7F_6)_n$	Calcd.	64.79	2.59	3.60
				$(778.62)_n$	Found	64.71	2.09	3.65
4f	1.27	**5f**	0.92	$(C_{45}H_{20}N_2O_6F_{12})_n$	Calcd.	59.22	2.21	3.07
				$(912.64)_n$	Found	59.16	1.98	3.17

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

Table II.   Solubility Behavior of the Polyimides[a]

					Solvent					
Polymer	NMP	DMAc	DMF	DMSO	m-Cresol	Pyridine	Dioxane	Tetrahydrofuran	CH_2Cl_2	Acetone
5a	++	+	+	−	−	−	−	−	−	−
5b	+	+	+	+	S	++	−	−	−	−
5c	+	+	−	−	+	+−	S	−	−	+−
5d	++	++	++	+	+	++	+	−	+−	+−
5e	+	+	++	+	+	++	+	−	++	+−
5f	++	++	++	+	+	++	+	++	++	+−
5a′	−	−	−	−	−	−	−	−	−	−
5b′	−	−	−	−	−	−	−	−	−	−
5c′	−	−	−	−	−	−	−	−	−	−
5d′	−	−	S	−	−	−	−	−	−	−
5e′	−	−	−	−	S	−	−	−	−	−
5f′	+	+	+	+	+	+	+	++	++	−

[a] Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent. ++ = soluble at room temperature; + = soluble on heating; S = swelling; − = insoluble even on heating.

showed the lowest T_g due to the presence of a flexible ether linkage between the phthalimide units, and the polyimide (**5a**) derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit.

The thermal stability of the polyimides was evaluated by dynamic TGA conducted at a heating rate of 20 °C/min. The temperatures of 10% weight loss (T_{10}'s) in nitrogen and air atmospheres were determined from original TGA ther-

mograms and are also tabulated in Table V. The T_{10} values of these polyimides stayed within 540–603 °C in nitrogen and within 544–583 °C in air. They left more than a 52% char yield at 800 °C in nitrogen. The TGA data indicate that these polyimides had fairly high thermal stability.

The measurements of the dielectric constants were performed between gold layers: the polyimide film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the

Table III.   Color Coordinates and Cutoff Wavelength (λ_0) from UV–vis Spectra for both **5** and **5′** Series Polyimide Films

Polymer	Film Thickness (μm)	Color Coordinates[a]			λ_0 (nm)
		b*	a*	L*	
5a	34	73.66	−8.52	93.96	413
5b	38	55.98	−12.86	96.49	407
5c	40	27.04	−8.15	98.16	400
5d	31	26.74	−9.79	99.08	378
5e	33	13.85	−3.74	98.04	368
5f	39	14.70	−4.17	98.96	364
5a′	28	84.78	3.79	89.93	436
5b′	34	87.84	3.14	90.05	443
5c′	25	48.56	−16.08	98.52	410
5d′	32	60.22	−15.82	97.96	411
5e′	31	17.69	−8.00	99.76	379
5f′	32	21.47	−9.33	99.62	375

[a] The color parameters were calculated according to a CIE LAB equation with paper as a standard. L* is lightness: 100 means white and 0 implies black. A positive a* means red, and a negative a* indicates green. A positive b* means yellow, and a negative b* implies blue.
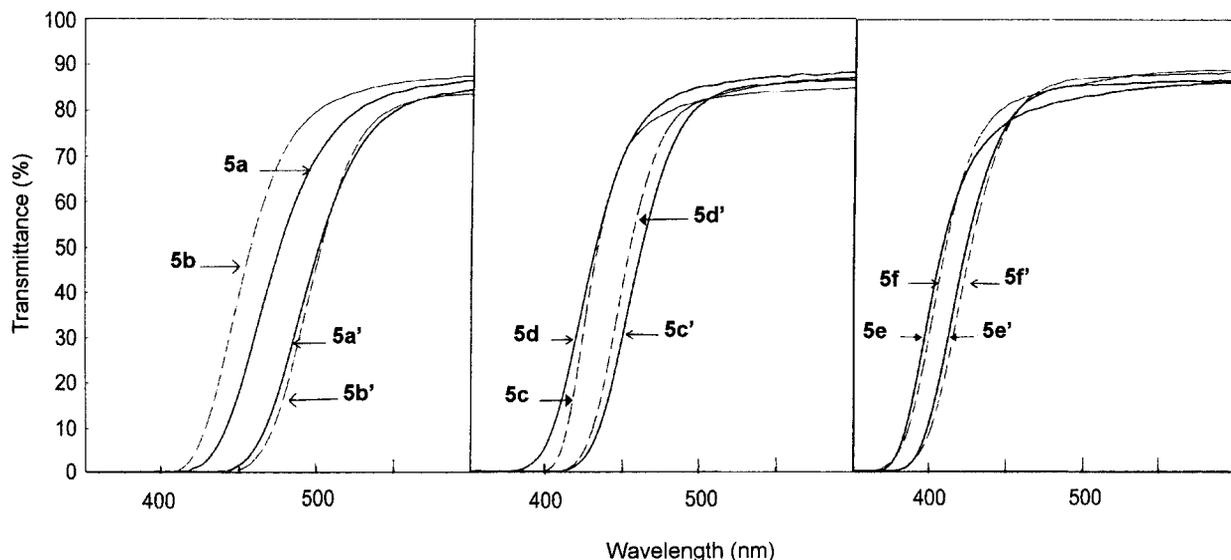
Figure 4. UV–vis spectra of the polyimide films.

polymer film. This procedure excluded any contact problems. Table VI shows the results. Polyimides **5a–5f** had lower dielectric constants (2.57–3.65 at 10 kHz) than commercial polyimides such as Kapton films (3.94). The decreased dielectric constants might be attributable to the presence of bulky 3F groups, which resulted in less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine resulted in very low polarizability of the C—F bonds, thereby decreasing the dielectric constant. Therefore, the 6FDA-derived polyimide **5f** exhibited the lowest dielectric constant of 2.57 at 10 kHz due to the higher free volume and hydrophobicity. Table VI also presents the moisture absorption of the polyimides, which ranged from 0.1 to 0.7%. In comparison, polyimides **5a–5f** exhibited lower moisture absorptions than the corresponding nonfluorinated homologues **5a–5f′**

and Kapton film. Polyimide **5f** exhibited the lowest moisture absorption due to the higher fluorine content in the repeat unit.

CONCLUSIONS

A series of novel fluorinated polyimides were obtained from 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl and aromatic dianhydrides. These polyimides were characterized by high solubility, good film-forming ability, high optical transparency, excellent thermal stability, and good mechanical properties together with low dielectric constants. Therefore, this series of poly-

Table IV. Tensile Properties of the Polyimide Films

Polymer	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
5a	97	26	1.8
5b	108	11	2.0
5c	119	33	1.9
5d	98	9	2.1
5e	114	38	1.8
5f	101	10	2.1

Table V. Thermal Behavior Data for the Polyimides

Polymer	T_g (°C)[a]	T_{10} (°C)[b]		Char Yield (%)[c]
		In N$_2$	In Air	
5a	313	600	573	55
5b	260	592	567	55
5c	276	603	581	60
5d	279	540	554	55
5e	247	601	583	54
5f	274	599	540	52

[a] Baseline shift in the second heating DSC traces with a heating rate of 15 °C/min.
[b] Temperatures at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.
[c] Residual weight (%) at 800 °C in nitrogen.

Table VI.   Moisture Absorption and Dielectric Constants of the Polyimides

Polyimide	Film Thickness (μm)	Moisture Absorption (%)	Dielectric Constant (Dry)		
			1 Hz	100 Hz	10 kHz
5a	36	0.7 (0.9)[a]	3.89	3.72	3.65
5b	37	0.4 (0.4)	3.59	3.29	3.24
5c	35	0.5 (0.8)	3.32	3.14	3.09
5d	35	0.6 (0.7)	2.94	2.77	2.73
5e	31	0.4 (0.7)	3.58	3.43	3.39
5f	39	0.1 (0.2)	2.70	2.59	2.57
Kapton[b]	29	2.1	4.35	4.05	3.94

[a] Data in parentheses are those of the **5′** series polyimides.
[b] A reference polyimide prepared from PMDA and 4,4′-oxydianiline (η_{inh} of the poly(amic acid) precursor = 2.90 dL/g).

imides demonstrated a good combination of properties and processability.

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