

# Organosoluble and Light-Colored Fluorinated Polyimides Based on 2,2-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane and Aromatic Dianhydrides

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**ABSTRACT:** A novel fluorinated diamine monomer, 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**2**), was prepared through the nucleophilic substitution reaction of 2-chloro-5-nitrobenzotrifluoride with 2,2-bis(4-hydroxyphenyl)propane in the presence of potassium carbonate, followed by catalytic reduction with hydrazine and Pd/C. Polyimides were synthesized from diamine **2** and various aromatic dianhydrides **3a–f** via thermal imidization. These polymers had inherent viscosities ranging from 0.73 to 1.29 dL/g. Polyimides **5a–f** were soluble in amide polar solvents and even in less polar solvents. These films had tensile strengths of 87–100 MPa, elongations to break of 8–29%, and initial moduli of 1.7–2.2 GPa. The glass transition temperatures ( $T_g$ ) of **5a–f** were in the range of 222–271°C, and the 10% weight loss temperatures

( $T_{10}$ ) of them were all above 493°C. Compared with polyimides **6** series based on 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) and polyimides **7** based on 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (6FBAPP), the **5** series showed better solubility and lower color intensity, dielectric constant, and lower moisture absorption. Their films had cutoff wavelengths between 363 and 404 nm,  $b^*$  values ranging from 8 to 62, dielectric constants of 2.68–3.16 (1 MHz), and moisture absorptions in the range of 0.04–0.35 wt %. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 922–935, 2005

**Key words:** 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane; solubility; light-colored; fluoropolymers; polyimides

## INTRODUCTION

Aromatic polyimides are well known for their excellent thermal stabilities and balanced mechanical and electric properties.<sup>1–7</sup> Optical transparency of polyimide films is of special importance in some applications, such as flexible solar radiation protectors,<sup>8,9</sup> orientation films in liquid crystal display devices,<sup>10,11</sup> optical waveguides for communication interconnects,<sup>12</sup> and optical half-waveplates for planar lightwave circuits.<sup>13</sup> However, the wholly aromatic polyimide strongly absorbs in the visible region of their UV-visible spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer complex (CTC) formation; besides, they are difficult to process because of high softening temperatures and limited solubility in commercially available solvents.

Recently, low-dielectric-constant polymers have diverse applications in the electronics industry as flexible circuitry substrates, stress buffers, interlayer dielectrics, and passivation layers; and the development of low-dielectric-constant and thermostable polymers has been quite dramatic and has drawn the attention of many polymer scientists. 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.<sup>14</sup> As is well-known, the fluorine atom has unique characteristics, such as high electronegativity and low electric polarity. These properties give fluorinated polymers 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. Fluorination is also known to enhance the solubility and optical transparency and to lower moisture absorption of polyimides.<sup>15–17</sup> Therefore, it is expected that fluorinated polyimides will be widely applied in the electro-optical and semiconductor industries.

A number of very lightly colored to colorless, transparent polyimide films have been synthesized and characterized. The optically transparent and colorless

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polyimide can be synthesized from a dianhydride and a diamine that have hexafluoroisopropylidene ( $-\text{C}(\text{CF}_3)_2-$ ) groups.<sup>18</sup> A lowering of the CTC generally between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties affords polyimide with lighter color.<sup>19</sup> For investigating CTC formations affected by the  $\text{CF}_3$  group in different substituent positions of diamine, in this study a high-purity  $\text{CF}_3$ -containing diamine, 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**2**), was synthesized and subsequently polycondensed with various commercially available aromatic dianhydrides to produce a series of fluorinated polyimides (**5a–f**). These polymers were subjected to solubility, moisture absorption, and thermal, optical, and dielectric property measurements and compared with polyimides **6a–f** and **7a–f** prepared from 6FBAPP.

## EXPERIMENTAL

### Materials

2-Chloro-5-nitrobenzotrifluoride (Acros), 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A, Acros), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP, Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (6FBAPP, Chriskev) were used as received. Aromatic dianhydrides: pyromellitic dianhydride (PMDA; **3a**) (TCI), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; **3b**) (TCI), 4,4'-oxydiphthalic anhydride (ODPA; **3e**) (TCI), and diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA; **3d**) (New Japan Chemical Co.) were recrystallized from acetic anhydride before use. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA; **3c**) (Chriskev) and 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA; **3f**) (Hoechst) were purified by sublimation. Other solvents included *N*-methyl-2-pyrrolidone (NMP; Fluka), *N,N*-diethylacetamide (DMAc; Fluka), *N,N*-dimethylformamide (DMF; Fluka), and pyridine (Py; Wako).

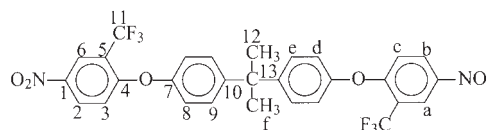
### Monomer synthesis

2,2-Bis[4-(4-nitro-2-trifluoromethylphenoxy)phenyl]propane (**1**)

2,2-Bis(4-hydroxyphenyl)propane (17.12 g, 0.075 mol) and 2-chloro-5-nitrobenzotrifluoride (34.05 g, 0.151 mol) were first dissolved in 80 mL of DMAc in a 300-mL flask with stirring. After the mixture was completely dissolved, potassium carbonate (16.6 g, 0.12 mol) was added to it in one portion. After 30 min of stirring at room temperature, the mixture was heated at 100°C for 12 h. The obtained mixture was poured into 440 mL of methanol/water (volume ratio 10/1) to give a solid, which was collected, washed thoroughly with methanol and hot water, and dried under vac-

uum at 60°C (43.84 g, 96.4%). The crude product was recrystallized from DMF/methanol to give fine, pale-cream crystals (40.95 g, 93.4%). (m.p.: 131–132°C, by DSC at a scan rate of 10°C/min).

IR (KBr): 1531, 1333 ( $-\text{NO}_2$  stretch), 1290, 1263, 1201, 1144, 1116  $\text{cm}^{-1}$  (C-F and C-O stretch). <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 8.47, 8.46 (2H, H<sub>a</sub>), 8.43–8.45 (2H, H<sub>b</sub>), 7.40, 7.39 (4H, H<sub>e</sub>), 7.16, 7.14 (4H, H<sub>d</sub>), 7.11, 7.09 (2H, H<sub>c</sub>), 1.70 (6H, H<sub>f</sub>). <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 160.2 (C<sup>4</sup>), 151.7 (C<sup>7</sup>), 147.8 (C<sup>10</sup>), 141.6 (C<sup>1</sup>), 130.0 (C<sup>2</sup>), 128.8 (C<sup>9</sup>), 123.3 (C<sup>6</sup>, quartet, <sup>3</sup>J<sub>C-F</sub> = 5 Hz), 122.3 (C<sup>11</sup>, quartet, <sup>1</sup>J<sub>C-F</sub> = 271 Hz), 119.9 (C<sup>8</sup>), 118.9 (C<sup>5</sup>, quartet, <sup>2</sup>J<sub>C-F</sub> = 32 Hz), 118.0 (C<sup>3</sup>), 42.2 (C<sup>13</sup>), 30.4 (C<sup>12</sup>).

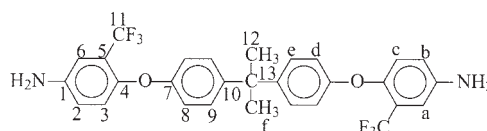


ELEM. ANAL. Calcd. For C<sub>29</sub>H<sub>20</sub>F<sub>6</sub>N<sub>2</sub>O<sub>6</sub> (606.48): C, 57.43%; H, 3.32%; N, 4.62%. Found: C, 57.46%; H, 3.25%; N, 4.68%.

2,2-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**2**)

To a suspension solution of the purified dinitro compound **1** (30 g, 0.0495 mol) and 10% Pd/C (0.2 g) in ethanol (150 mL), hydrazine monohydrate (10 mL) was added dropwise to the stirred mixture at 70–80°C within 30 min. After complete addition, the mixture was heated at the reflux temperature for another 2 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The obtained mixture was poured into water to precipitate white powder that was dried in vacuum at room temperature to give **2** (26.24 g, 97%). (m.p.: 131–132°C).

IR (KBr): 3421, 3400 (N-H stretch), 1263, 1230, 1159, 1128  $\text{cm}^{-1}$  (C-O and C-F stretch). <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 7.15, 7.13 (4H, H<sub>e</sub>), 6.94 (2H, H<sub>a</sub>), 6.82 (4H, H<sub>b,c</sub>), 6.78, 6.76 (4H, H<sub>d</sub>), 5.41 (4H,  $-\text{NH}_2$ ), 1.57 (6H, H<sub>f</sub>). <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 156.2 (C<sup>4</sup>), 145.6 (C<sup>7</sup>), 144.3 (C<sup>10</sup>), 142.7 (C<sup>1</sup>), 127.7 (C<sup>9</sup>), 123.6 (C<sup>11</sup>, quartet, <sup>1</sup>J<sub>C-F</sub> = 271 Hz), 123.0 (C<sup>2</sup>), 121.4 (C<sup>5</sup>, quartet, <sup>2</sup>J<sub>C-F</sub> = 30 Hz), 118.6 (C<sup>3</sup>), 116.2 (C<sup>8</sup>), 110.7 (C<sup>7</sup>, quartet, <sup>3</sup>J<sub>C-F</sub> = 5 Hz), 41.4 (C<sup>13</sup>), 30.6 (C<sup>12</sup>).



ELEM. ANAL. Calcd. For C<sub>29</sub>H<sub>24</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub> (546.51): C, 63.73%; H, 4.43%; N, 5.13%. Found: C, 63.87%; H, 4.39%; N, 4.92%.

### X-ray structure analysis

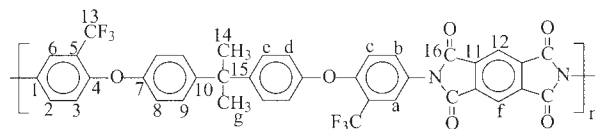
The single crystals of dinitro compound **1** were grown during slow crystallization of their DMF/methanol solution. A crystal size of  $0.50 \times 0.50 \times 0.30$  mm was used for X-ray structure determination. Intensity data were collected on a Siemens SMART CCD XRD diffractometer at 295 K with graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71,073$  E). Compound **1** crystallized in a monoclinic system with space group C2/c [ $M_w = 606.47$ ,  $a = 7.8389(2)$ ,  $b = 13.1937(4)$ ,  $c = 27.1300(8)$  Å;  $\alpha = 90^\circ$ ,  $\beta = 97.9930(10)^\circ$ ,  $\gamma = 90^\circ$  where  $D_c = 1.450$  g/cm $^3$  for  $Z = 4$  and  $V = 2778.64(14)$  Å $^3$ ]. Least-squares refinement based on 3180 independent reflections converged to final  $R_1 = 0.0400$  and  $wR_2 = 0.1176$ .

### Synthesis of polyimides

Diamine **2** (0.547 g, 1 mmol) was dissolved in 5.6 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.218 g (1 mmol) PMDA **3a** was added to it in one portion. The mixture was stirred at room temperature for 8 h to form a poly(amic acid) (PAA) solution. The PAA solution then was spread on a glass plate, which was placed in an 80°C oven for 1 h to remove the solvent. The semi-dried PAA film was further dried and imidized by sequential heating at 120°C for 10 min, 150°C for 10 min, 180°C for 10 min, 210°C for 10 min, and 250°C for 30 min. By being soaked in water, a flexible polyimide film **5a** was self-stripped off from the glass surface. The inherent viscosity of **5a** in DMAc at a 0.5 g/dL concentration at 30°C was 1.29 dL/g.

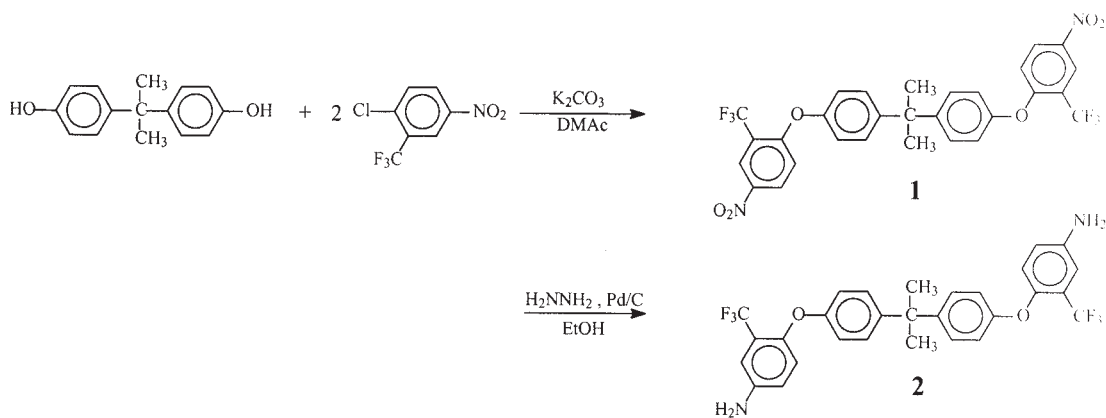
IR (film): 1780, 1728 (imide C=O), 1375 (C-N stretch), 1101, 723 cm $^{-1}$  (imide ring deformation).  $^1\text{H-NMR}$  (500 MHz, DMSO- $d_6$ ,  $\delta$ ): 8.39, 8.36 (2H,  $H_f$ ), 7.97 (2H,  $H_a$ ), 7.78, 7.76 (2H,  $H_b$ ), 7.36, 7.35 (4H,  $H_e$ ), 7.20, 7.18 (2H,  $H_c$ ), 7.11, 7.10 (4H,  $H_d$ ), 1.69 (6H,  $H_g$ ).  $^{13}\text{C-NMR}$  (125 MHz, DMSO- $d_6$ ,  $\delta$ ): 165.3 (C $^{16}$ ), 154.6 (C $^4$ ),

153.1 (C $^7$ ), 146.7 (C $^1$ ), 137.1 (C $^{10}$ ), 133.4 (C $^{11}$ ), 128.5 (C $^{12}$ , C $^9$ ), 126.3 (C $^3$ ), 123.0 (C $^{13}$ , quartet,  $^1J_{\text{C-F}} = 272$  Hz), 119.3 (C $^2$ ), 119.1 (C $^8$ , C $^5$ ), 118.0 (C $^6$ ), 42.0 (C $^{15}$ ), 30.6 (C $^{14}$ ).



### Measurements

IR spectra were recorded on a Horiba Fourier-Transform Infrared Spectrometer FTIR-720. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer at 30°C. The color intensity of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films, using an observational angle of 10° and a CIE (Commission International de l'Eclairage)-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. 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 40–50  $\mu\text{m}$  thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 9–11-mg film samples heated in flowing nitrogen or air (90 cm $^3$ /min) at a heating rate of 20°C/min. Differential scanning calorimeter (DSC) traces were measured on a TA Instruments DSC 2010 at the rate of 15°C/min in flowing nitrogen (40 cm $^3$ /



Scheme 1

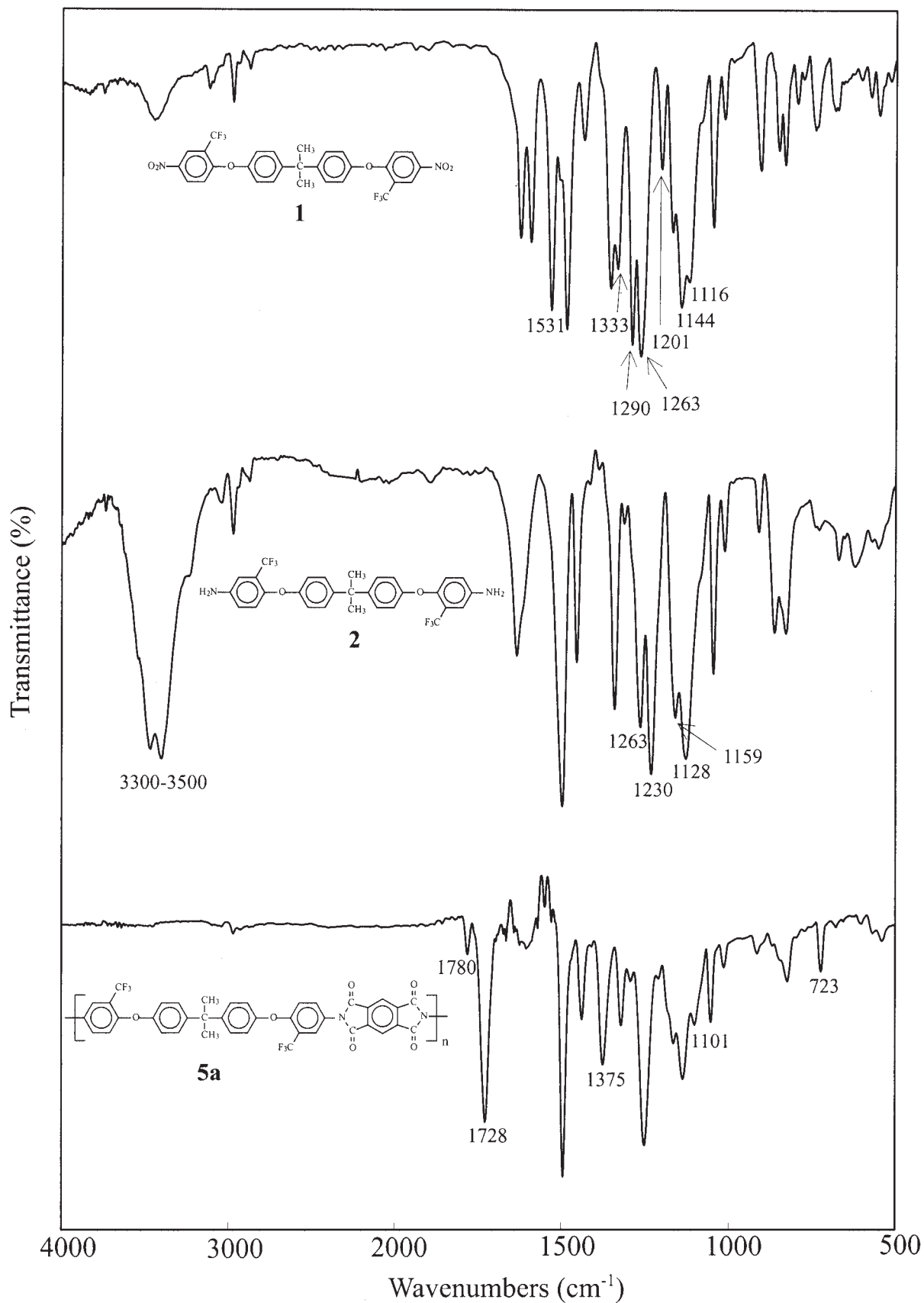


Figure 1 FTIR spectra of 3F-dinitro compound **1**, 3F-diamine **2**, and polyimide **5a**.

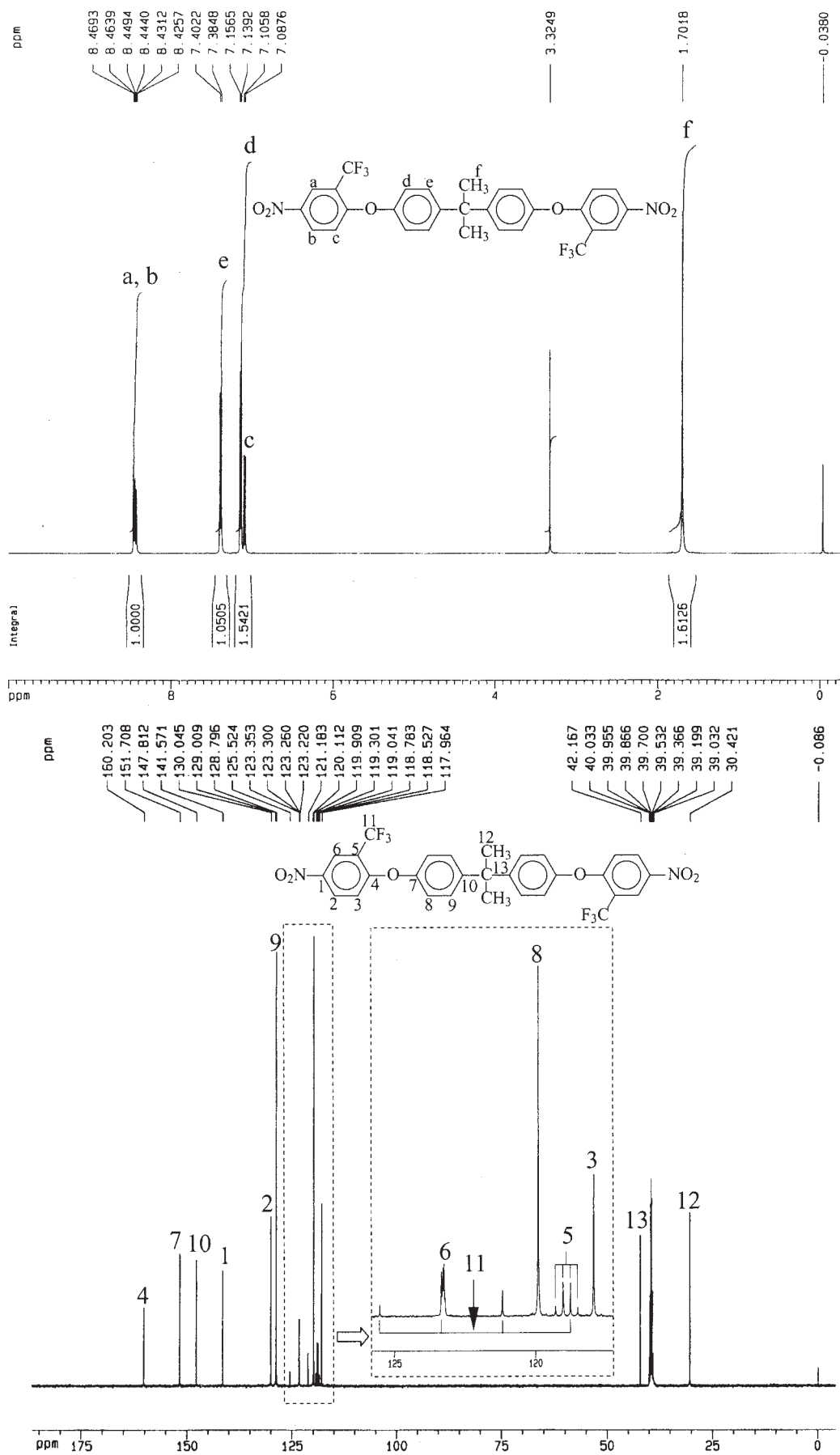


Figure 2 The <sup>1</sup>H and <sup>13</sup>C-NMR spectrum of 3F-dinitro compound 1 in DMSO-d<sub>6</sub>.

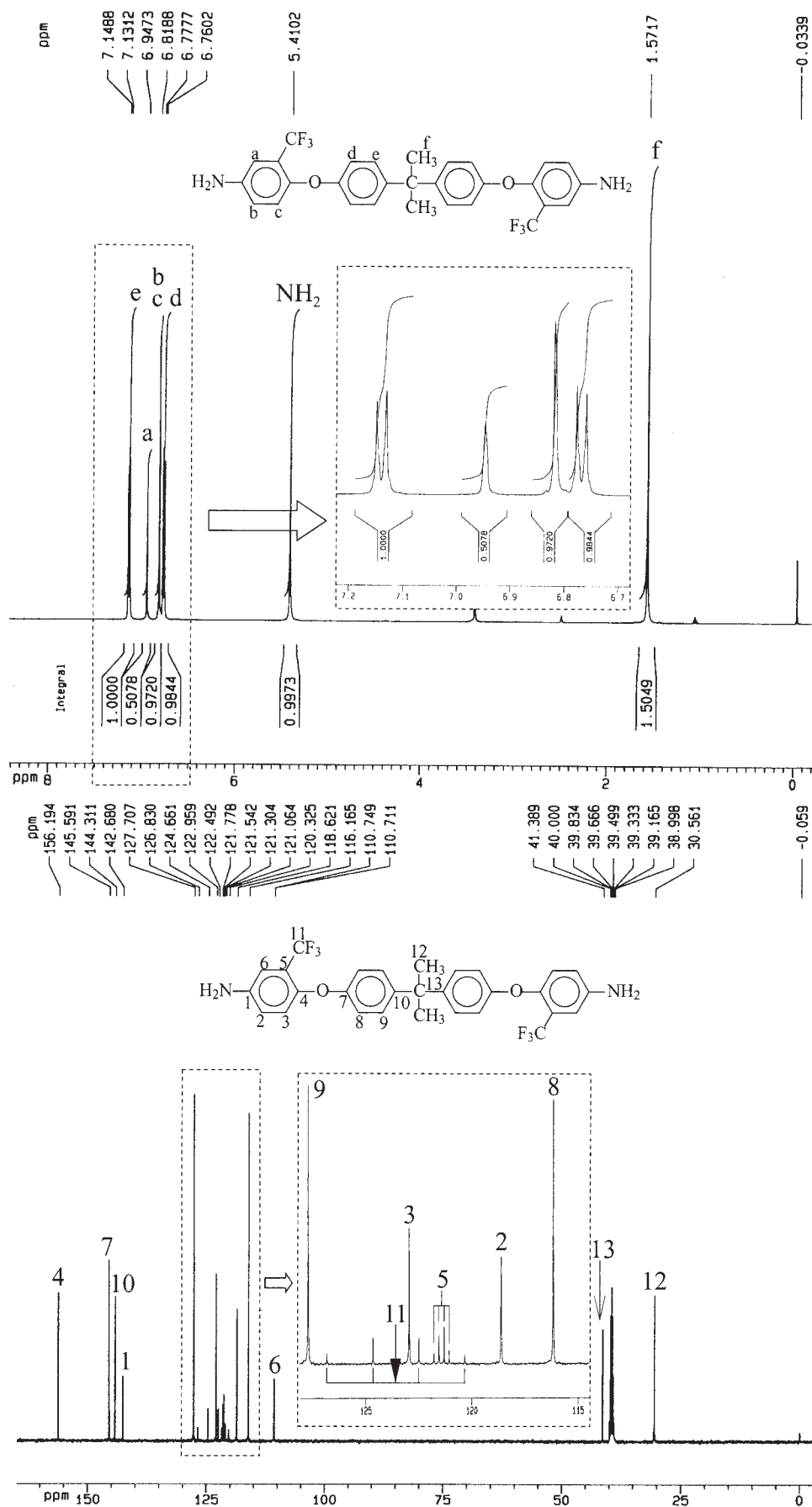


Figure 3 The <sup>1</sup>H and <sup>13</sup>C-NMR spectrum of 3F-diamine 2 in DMSO-d<sub>6</sub>.

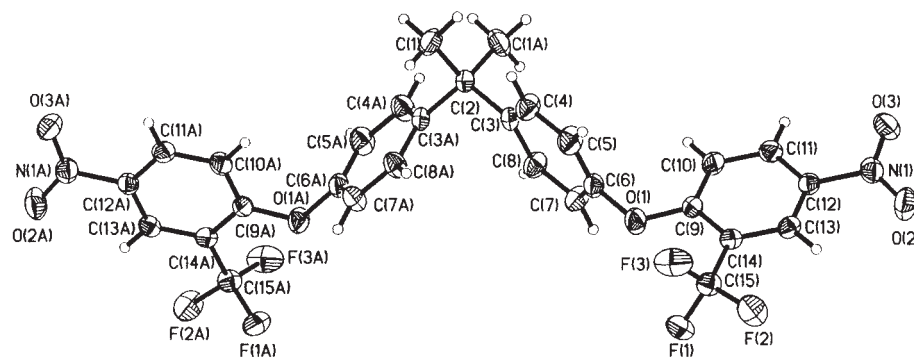
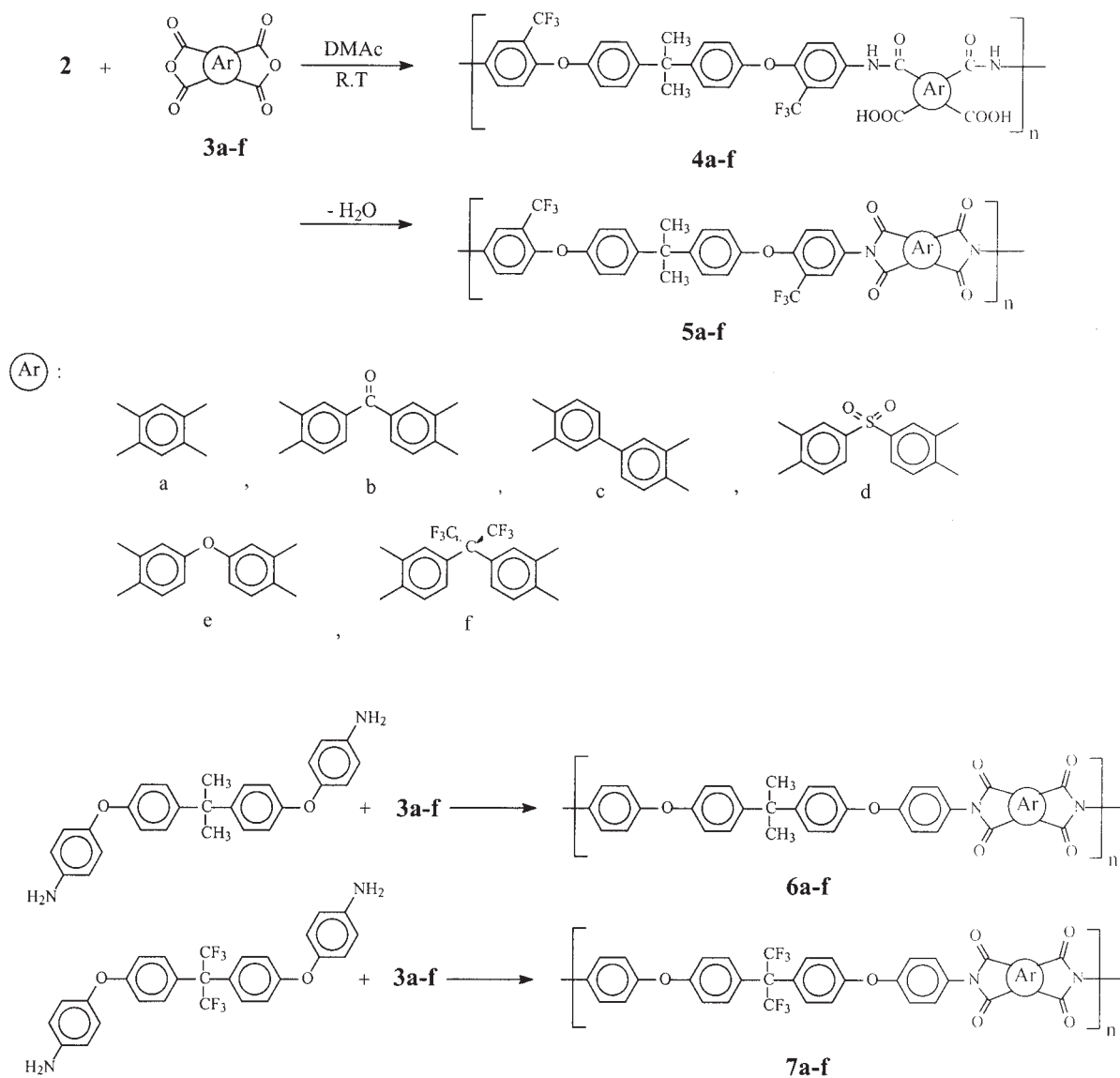


Figure 4 X-ray structure of the 3F-dinitro compound 1.



Scheme 2

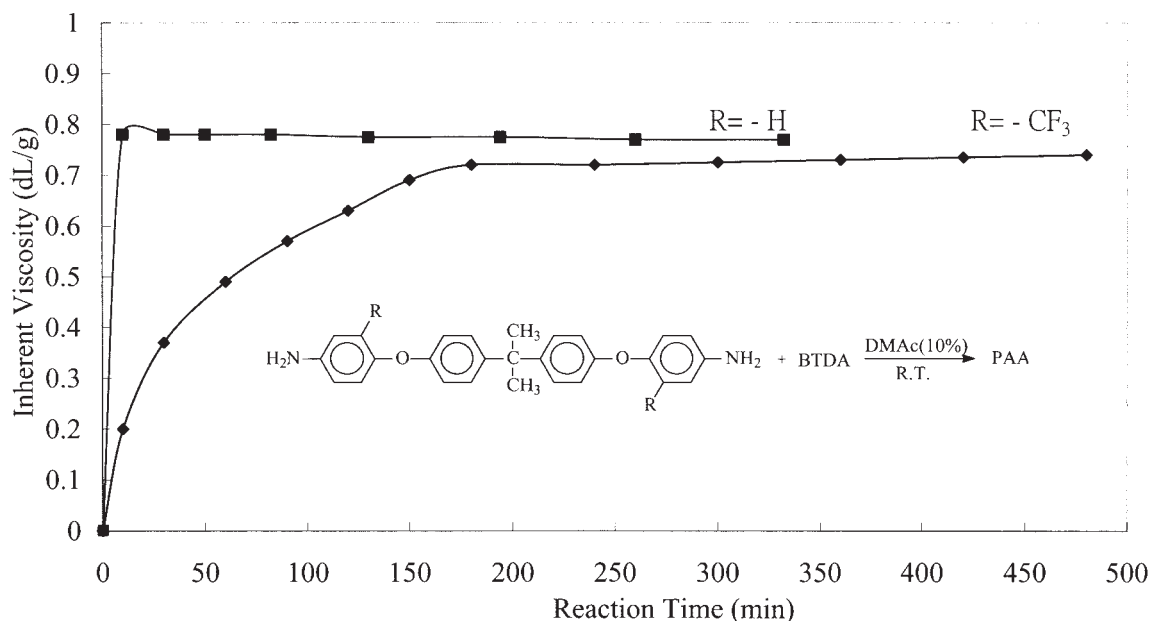


Figure 5 Viscosity change of poly(amic acid)s prepared in DMAc at 10% solid content at room temperature.

min). Glass transition temperatures were read as the midpoint of the heat capacity jump and were taken from the second heating scan after a quick cooling down from 400°C. The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a Hewlett-Packard 4194A dielectric analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. 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 CF<sub>3</sub>-containing diamine **2** was prepared in two steps according to a well-developed method (Scheme 1). The intermediate dinitro compound **1** was synthesized from the aromatic nucleophilic substitution of 2-chloro-5-nitrobenzotrifluoride with 2,2-bis(4-hydroxyphenyl)propane in the presence of potassium carbonate. Diamine **2** was readily obtained in high yields by the catalytic reduction of **1** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. Compared with 1-chloro-4-nitrobenzene, 2-chloro-5-nitrobenzotrifluoride had higher activity reacting with bisphenol, so the temperature and the amount of K<sub>2</sub>CO<sub>3</sub> in the substitution reaction were reduced to avoid coloring of the dinitro compound. In this study, the substitution reaction under 100°C for 12 h had better results. FTIR, NMR, and elemental analysis were used

to confirm the structures of the intermediate **1** and the diamine monomer **2**. Figure 1 shows the FTIR spectra of dinitro compound **1** and diamine **2**. The nitro group of compound **1** gave two characteristic bands at 1531 and 1333 cm<sup>-1</sup> (NO<sub>2</sub> 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<sup>-1</sup>.

Figures 2 and 3 present the <sup>1</sup>H and <sup>13</sup>C-NMR spectra of dinitro compound **1** and diamine **2**. The absorption signals of aromatic protons of **1** appeared in the region of 7.09–8.47 ppm, and those of **2** shifted to a higher field between 6.76–7.15 ppm. In the <sup>1</sup>H-NMR spectrum of **1**, the protons H<sub>a</sub> and H<sub>b</sub> resonated at the farthest downfield due to the inductive effect of the electron withdrawing -NO<sub>2</sub> and -CF<sub>3</sub> groups; the protons H<sub>c</sub> and H<sub>d</sub> *ortho*-oriented to aromatic ether appeared in the upfield due to the conjugation effect. After reduction, the protons H<sub>a</sub> and H<sub>b</sub> of **2** shifted to the upfield due to the electron donating property of the amino groups.

In <sup>13</sup>C-NMR spectra, all the carbon-13 atoms in **1** and **2** showed thirteen main signals, which resonated in the region of 30.4–160.2 and 30.6–156.2 ppm, respectively. The <sup>13</sup>C-NMR spectrum of **1** shows three quartets because of the heteronuclear <sup>13</sup>C–<sup>19</sup>F coupling. The large quartet centered at about 122 ppm was due to the CF<sub>3</sub> carbon. The one-bond C–F coupling constant in this case was about 271 Hz. The CF<sub>3</sub>-attached carbon (C<sup>5</sup>) also showed a clear quartet centered at about 119 ppm with a smaller coupling constant of about 32 Hz due to the two-bond C–F



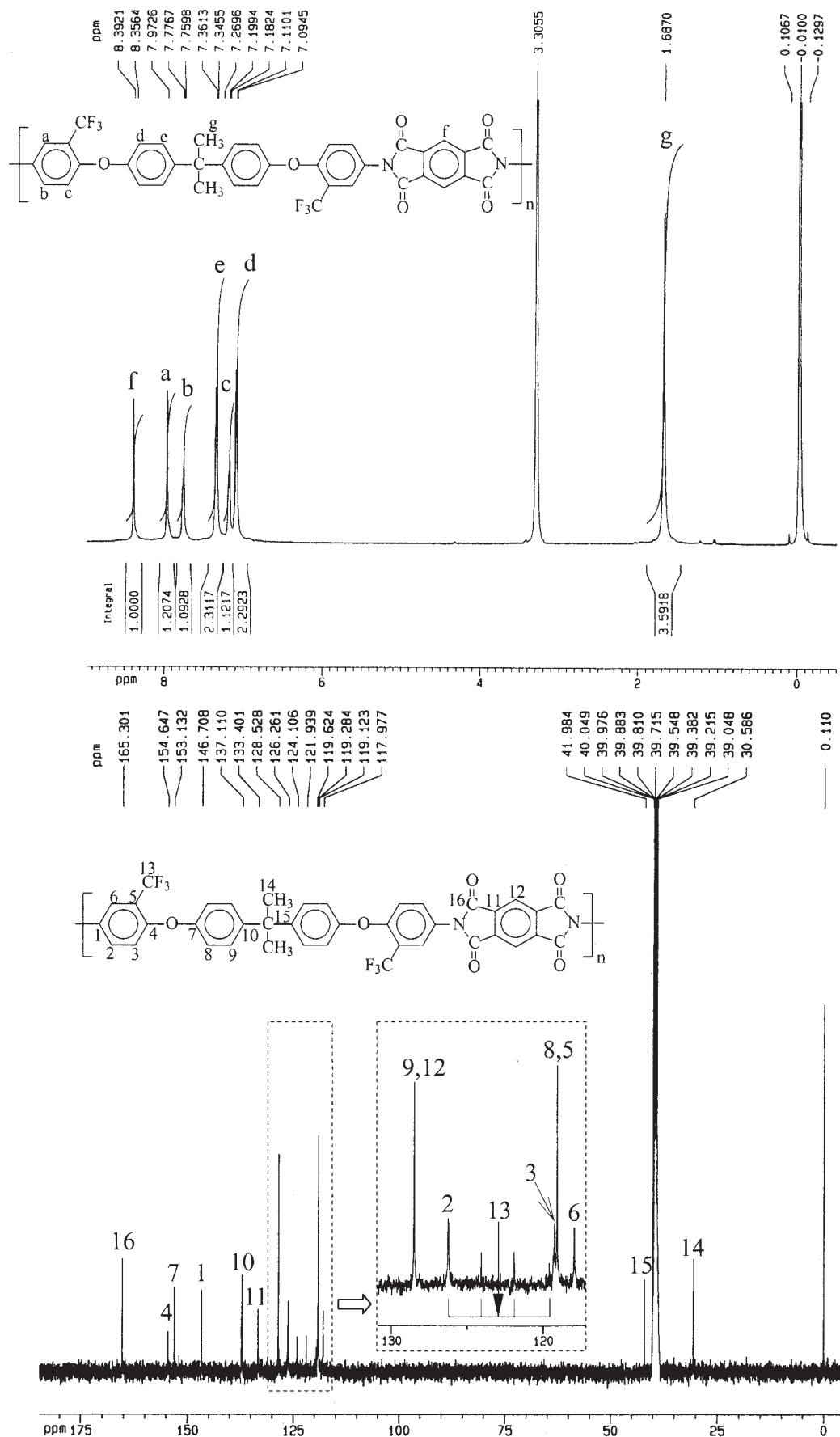


Figure 6 The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectrum of polyimide 5a in  $\text{DMSO}-d_6$ .

TABLE I  
Inherent Viscosity and Elemental Analysis

Code	Poly (amic acid)	Code	Polyimide	Formula (formula weight)		Elemental analysis of polyimide (%)		
	$\eta_{inh}^a$ (dL/g)		$\eta_{inh}^a$ (dL/g)			C	H	N
4a	0.82	5a	1.29	(C <sub>39</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub> (728.60) <sub>n</sub>	Calcd Found	64.29 63.83	3.04 2.96	3.84 3.89
4b	0.77	5b	0.73	(C <sub>46</sub> H <sub>26</sub> N <sub>2</sub> O <sub>7</sub> F <sub>6</sub> ) <sub>n</sub> (832.71) <sub>n</sub>	Calcd Found	66.35 66.16	3.15 3.03	3.36 3.42
4c	0.71	5c	1.04	(C <sub>45</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub> (804.70) <sub>n</sub>	Calcd Found	67.17 66.86	3.26 3.14	3.48 3.55
4d	0.79	5d	0.80	(C <sub>45</sub> H <sub>26</sub> N <sub>2</sub> O <sub>8</sub> S <sub>1</sub> F <sub>6</sub> ) <sub>n</sub> (868.76) <sub>n</sub>	Calcd Found	62.21 61.90	3.02 2.85	3.22 3.33
4e	1.08	5e	1.15	(C <sub>45</sub> H <sub>26</sub> N <sub>2</sub> O <sub>7</sub> F <sub>6</sub> ) <sub>n</sub> (820.70) <sub>n</sub>	Calcd Found	65.86 65.40	3.19 3.02	3.41 3.48
4f	0.79	5f	1.11	(C <sub>48</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> F <sub>12</sub> ) <sub>n</sub> (954.73) <sub>n</sub>	Calcd Found	60.39 60.09	2.74 2.58	2.93 3.00

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

coupling. Besides, the C<sup>6</sup> carbon (ortho to the CF<sub>3</sub> group) also had its resonance split by the three fluorines (three-bond coupling). The close quartet had an even smaller coupling constant (~ 5 Hz) because the interaction operated over more bonds. Similar splitting patterns (<sup>1</sup>J<sub>C-F</sub> = 271 Hz, <sup>2</sup>J<sub>C-F</sub> = 30 Hz, and <sup>3</sup>J<sub>C-F</sub> = 5 Hz) were also found in the <sup>13</sup>C-NMR spectrum of **2** (Fig. 3). All the spectroscopic data obtained were in good agreement with the expected structures. The crystal structure of **1** (Fig. 4) shows that the four phenylene rings cannot be all in the same plane because of steric hindrance. This will disturb the coplanarity of the aromatic unit to enhance the solubility of the formed polyimide.

### Polymer synthesis

All the polymers **5** were synthesized from diamine **2** and dianhydrides **3a–f**, by a conventional two-step procedure ring-opening polyaddition at room temperature to PAA **4**, followed by sequential heating to 250°C to obtain the corresponding polyimides, as shown in Scheme 2. Figure 5 presents the variation curves of inherent viscosities of the PAA obtained from BTDA with CF<sub>3</sub>-containing diamine **2** or BAPP at various times. The reaction of BTDA with fluorinated **2** proceeded relatively slowly, and its inherent viscosity reached 0.69 dL/g after 150 min. After this point, inherent viscosity increased slowly and reached 0.72 dL/g in 180 min; polymerization nearly ceased and no increase in inherent viscosity was observed after 200 min. The reaction of BTDA with BAPP proceeded relatively fast and its inherent viscosity increased fast within 10 min; inherent viscosity reached 0.78 dL/g after 30 min and then decreased gradually.

The typical IR spectrum of **5a** is shown in Figure 1. All polyimides exhibited characteristic imide group

absorptions around 1780 and 1728 cm<sup>-1</sup> (typical of imide carbonyl asymmetrical and symmetrical stretch), 1375 cm<sup>-1</sup> (C-N stretch), and 1101 and 723 cm<sup>-1</sup> (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm<sup>-1</sup> due to the C-O and C-F stretching. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the PAA precursor into polyimides.

The <sup>1</sup>H and <sup>13</sup>C-NMR spectra of **5a** are shown in Figure 6. In the <sup>1</sup>H-NMR spectrum, all the protons resonated in the region of 7.10–8.39 ppm. The H<sub>f</sub> closed to the imide ring appeared at the farthest downfield owing to the resonance. The H<sub>c,d</sub> shifted to higher field due to the electron donating property of aromatic ether. In the <sup>13</sup>C-NMR spectra, all the carbon-13 atoms in **5a** showed sixteen main signals, carbon C<sup>16</sup> of the carbonyl group was evidenced in the downfield. The quartet centered at about 123 ppm was due to the CF<sub>3</sub> carbon. The one-bond C–F coupling constant in this case was about 272 Hz. The results of elemental analysis of **5a–f** are listed in Table I. The above-cited results evidenced that series **5** had been synthesized successfully.

### Properties of polymers

The solubility of these polyimides was tested, and the results are summarized in Table II. The **5** series showed excellent solubility in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO, and were also soluble in less polar solvents like *m*-cresol, pyridine, dioxane, and THF. **5b** needed heating to be dissolved in tested solvents. This might be attributable to the formation of some intermolecular links of the C=O group of BTDA during the thermal imidization.<sup>20</sup> On the contrary, **5b(C)** synthesized via chemical imidiza-

TABLE II  
Solubility Behavior of Polyimides<sup>a</sup>

Polymer	Solvents <sup>b</sup>									
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH <sub>2</sub> Cl <sub>2</sub>	acetone
5a	++	++	++	+	+	++	+	++	++	+–
5b	+	+	+	+	–	+	–	–	–	–
5c	++	++	++	+	+	++	+	++	–	S
5d	++	++	++	+	+	++	+	++	++	+–
5e	++	++	++	++	+	++	++	++	++	++
5f	++	++	++	+	+	++	++	++	++	++
5b(C) <sup>c</sup>	++	++	++	++	++	++	++	++	++	++
6a	–	–	–	–	–	–	–	–	–	–
6b	–	–	–	–	–	–	–	–	–	–
6c	–	–	–	–	–	–	–	–	–	–
6d	+	+	+	+	+	+	+	+	–	–
6e	+	+	+	+	+	+	+	+–	–	–
6f	++	++	+	+	+	++	+	++	++	–
7a	S	S	S	–	–	S	S	S	–	–
7b	S	S	S	–	S	S	S	S	–	–
7c	+	+	+	–	+	+	+	+	–	–
7d	++	++	+	+	+	++	+	++	++	–
7e	+	+	+	+	+	+	+	+	–	–
7f	++	++	+	+	+	++	+	++	++	–

<sup>a</sup> Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent. ++ = soluble at room temperature; + = soluble on heating; +– = partially soluble on heating; S = swelling; – = insoluble even on heating.

<sup>b</sup> NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

<sup>c</sup> (C) : Polyimides were obtained by the chemical imidization method.

tion did not possess crosslinking and exhibited better solubility. In addition, the solubility of the analogous polyimides 6a–f reported previously had been listed for comparative purposes. Obviously, the differences in solubility between the 5 and 6 series are attributed to the bulky 3F groups, which increased the disorder in the chains and hindered dense chain stacking, thus reducing the interchain interactions to enhance solubility. Compared with the polyimides 7 series, the 5 series also showed better solubility. This might be the 5 series exhibited the hindered isopropylidene and CF<sub>3</sub> groups in diamine, simultaneously.

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 6 series without the CF<sub>3</sub> groups and 7 series were also prepared and characterized by their color intensity. The results shown in Table III and Figure 7 indicate that the 5 series showed a lower *b*\* value (a yellowness index) in contrast with the corresponding 6 series. Moreover, the color intensities of the polyimide could also be elucidated from the cutoff wavelength observed in the UV–Vis absorption spectra. Figure 8 shows the UV–Vis spectra of the polyimides films, and the cutoff wavelengths from these spectra are listed in Table III. Consistent with the results obtained from the colorimeter, all the fluorinated 5 series revealed a lower cutoff wavelength than

TABLE III  
Color Coordinates and the Cut-Off Wavelength ( $\lambda_0$ ) from UV-Visible Spectra for Both 5, 6, and 7 Series Polyimide Films

Polymer	Film thickness ( $\mu\text{m}$ )	Color coordinates <sup>a</sup>			$\lambda_0$ (nm)
		<i>b</i> *	<i>a</i> *	<i>L</i> *	
5a	28	62.2	–15.2	98.1	404
5b	30	48.8	–14.7	98.6	394
5c	34	19.9	–8.1	99.6	391
5d	22	22.8	–8.4	99.4	365
5e	30	8.6	–2.9	99.7	363
5f	36	11.1	–3.8	99.5	365
6a	52	86.5	–1.5	91.4	435
6b	23	79.3	–12.3	96.5	401
6c	53	49.0	–14.8	97.7	414
6d	45	58.9	–11.6	95.4	407
6e	50	20.5	–7.2	98.0	380
6f	42	24.3	–8.3	98.5	375
7a	45	81.0	–10.7	95.4	420
7b	80	70.2	–3.4	88.9	435
7c	60	37.1	–12.0	96.8	408
7d	73	49.6	–10.4	93.4	405
7e	34	15.8	–4.5	97.3	369
7f	53	17.8	–5.2	97.1	375

<sup>a</sup> The color parameters were calculated according to a CIE LAB equation, using paper as a standard. *L*\* is lightness; 100 means white, while 0 implies black. A positive *a*\* means red color, while a negative *a*\* indicates green color. A positive *b*\* means yellow color, while a negative *b*\* implies blue color.

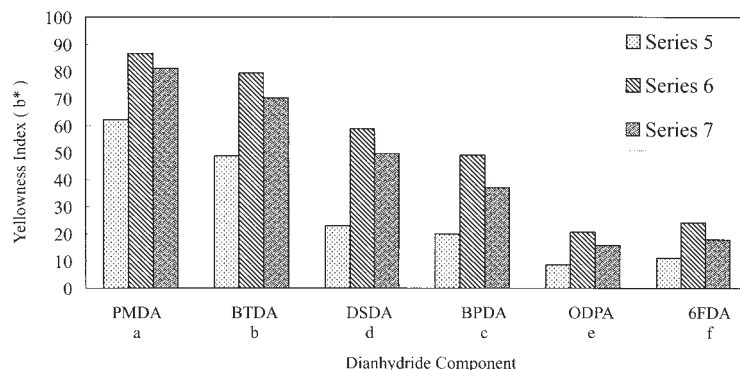


Figure 7 Comparison of the yellowness index ( $b^*$  value) between polyimides 5, 6, and 7.

their respective nonfluorinated analogues 6 series. The light colors of the polyimides with the  $\text{CF}_3$  groups in their diamine moieties could be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing  $\text{CF}_3$  group in diamine 2 was effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect. Table III, Figure 7, and Figure 8 also show that the 5 series own lower cutoff wavelength and  $b^*$  value than the 7 series. The  $\text{CF}_3$  groups of the 5 series closed to imide groups were more effective in lowering intermolecular CTC effect than those of the 7 series in hexafluoroisopropylidene. Therefore, the colorlessness as well as the transparency of the 5 series was better than that of the corresponding 7 series. Figure 7 also shows that the color intensity of the polyimide was affected by dianhydride moieties with the order from deep (PMDA) to pale (ODPA). 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 CTC between alternating electron-do-

nor (diamine) and electron-acceptor (dianhydride) moieties.

All the fluorinated polyimides afforded good-quality films. The tensile properties of flexible films are summarized in Table IV. They showed an ultimate tensile strength of 87–100 MPa, an elongation to break of 8–29%, and an initial modulus of 1.7–2.2 GPa. 5a showed a distinct yield point in the stress-strain curve and had the largest elongation to break among this series, indicative of high toughness. This might have concern with the structure (diamine and PMDA moieties) and the highest inherent viscosity (1.29 dL/g). The thermal properties of all the fluorinated polyimides are presented in Table V. DSC experiments with rapid cooling from 400°C to room temperature produced predominantly amorphous samples, so the  $T_g$  of all the polymers could be easily read in the subsequent heating DSC traces. The  $T_g$  values of 5a–f were in the 222–271°C range, depending on the structure of the dianhydride component and decreasing with the increasing flexibility of the polymer backbones. The 5e obtained from ODPA showed the lowest  $T_g$  due to the

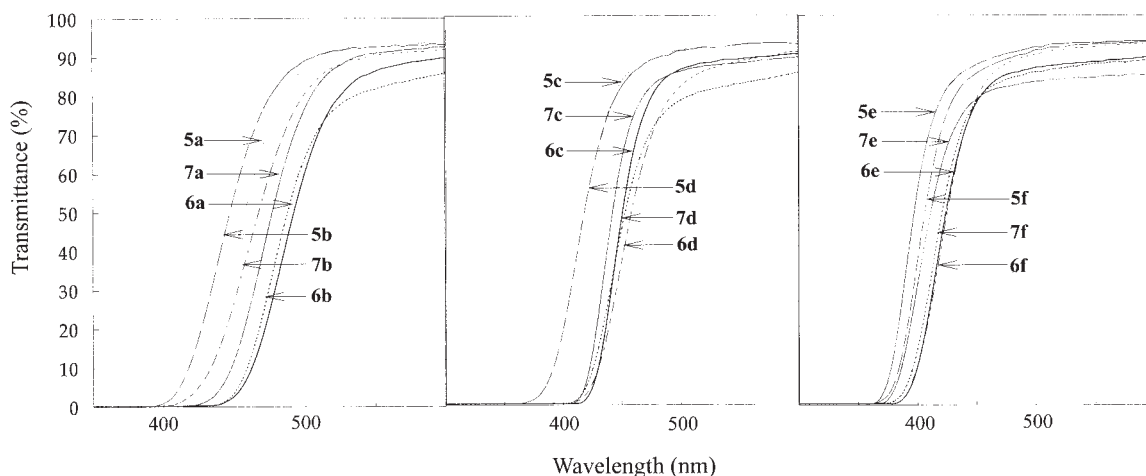


Figure 8 UV-visible spectra of polyimide films.

**TABLE IV**  
Mechanical Properties of Polyimide Films

Code	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
5a	91	87	29	1.7
5b	—	99	9	2.1
5c	—	95	12	2.1
5d	—	99	8	2.2
5e	—	99	11	2.0
5f	—	100	11	2.0

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

The  $T_{10}$  in nitrogen and air atmospheres were determined from original TGA thermograms and are also tabulated in Table V. The  $T_{10}$  values of **5a–f** stayed within 493–552°C in nitrogen and within 496–543°C in air. They left more than a 50% char yield at 800°C in nitrogen. **5d** having a sulfonyl group in dianhydride DSDA exhibited lower  $T_{10}$  values than the other polyimides. This might be attributed to the weak bonding of the C–S bond and easy degradation on the heating process. According to the data, these fluorinated polyimides showed an outstanding thermal stability.

Table VI shows the results of the measurements of the dielectric constants. Fluorinated polyimides **5a–f** had lower dielectric constants (2.68–3.16 at 1M Hz) than nonfluorinated polyimides **6a–f** (3.05–3.43 at 1M Hz). The decreased dielectric constants might be attributable to the presence of bulky  $CF_3$  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.

**TABLE V**  
Thermal Properties of Polyimides

Code	TGA			Char yield (%) <sup>c</sup>
	DSC $T_g$ (°C) <sup>a</sup>	Decomposition temperature (°C) <sup>b</sup>		
		In nitrogen	In air	
5a	271	542	535	55
5b	234	543	532	58
5c	243	552	529	59
5d	246	493	496	49
5e	222	546	543	54
5f	244	544	530	55

<sup>a</sup> Midpoint of baseline shift in the second heating DSC trace with a heating rate of 15°C/min under a nitrogen atmosphere.

<sup>b</sup> Temperatures at which 10% weight loss were recorded by TGA at a heating rate of 20°C/min.

<sup>c</sup> Residual weight % at 800°C under a nitrogen atmosphere.

**TABLE VI**  
Moisture Absorption and Dielectric Constants of Polyimides

Polymer	Film thickness ( $\mu\text{m}$ )	Moisture absorption (%)	Dielectric constant (Dry)			
			1k Hz	10k Hz	1M Hz	40M Hz
5a	38	0.06	3.19	3.09	3.05	3.03
5b	36	0.16	3.16	3.13	3.09	3.08
5c	29	0.04	3.21	3.19	3.16	3.14
5d	33	0.35	3.15	3.11	3.08	3.05
5e	30	0.04	3.14	3.08	2.99	2.95
5f	43	0.04	2.8	2.71	2.68	2.66
6a	55	0.78	3.53	3.50	3.43	3.39
6b	22	0.71	3.47	3.41	3.38	3.35
6c	43	0.56	3.49	3.40	3.35	3.31
6d	26	0.69	3.50	3.47	3.42	3.43
6e	34	0.55	3.43	3.38	3.35	3.38
6f	36	0.23	3.20	3.11	3.05	2.99
7a	50	0.35	3.24	3.15	3.11	3.07
7b	70	0.50	3.27	3.21	3.18	3.19
7c	55	0.37	3.31	3.25	3.21	3.17
7d	38	0.43	3.30	3.21	3.19	3.15
7e	40	0.51	3.25	3.14	3.09	3.05
7f	41	0.11	2.98	2.86	2.80	2.77
Kapton	28	0.52	3.89	3.85	3.67	3.69

Otherwise, **5a–f** had lower dielectric constants than polyimides **7a–f** (2.80–3.21 at 1M Hz). The **5** series with the  $CF_3$  group closing imide group have lower dielectric constants than the **7** series with the hexafluoroisopropylidene group. **5a–f** had lower dielectric constants than commercial polyimides such as Kapton films (3.67 at 1M Hz). Besides, the 6FDA-derived polyimides **5f**, **6f**, and **7f** exhibited the lowest dielectric constant in the three series due to the higher free volume and hydrophobicity. Table VI also presents the moisture absorption of the polyimides. **5a–f** exhibited lower moisture absorptions (0.04–0.35%) than the corresponding nonfluorinated homologues **6a–f** (0.23–0.78%) and Kapton film (0.52%) did, owing to the hydrophobicity of the  $CF_3$  group. Otherwise, **5a–f** had lower moisture absorptions than **7a–f** (0.11–0.51%), as the above-cited reason in dielectric constants. Moreover, polyimides **5f**, **6f**, and **7f** exhibited the lowest moisture absorption in the three series due to the higher fluorine content in the repeat unit.

## CONCLUSIONS

A novel fluorinated diamine monomer **2** was synthesized via a straightforward, high-yielding two-step procedure. 2,2-Bis(4-hydroxyphenyl)propane was reacted with 2-chloro-5-nitrobenzotrifluoride to yield the intermediate dinitro compound, which was subsequently reduced to afford the diamine. A series of novel fluorinated polyimides **5** have been obtained from the trifluoromethyl-substituted diamine with different aromatic dianhydrides. The resulting polyimides exhibit lighter color, better solubility, and lower dielectric constants and moisture absorption

than the corresponding BAPP-derived polyimides **6** and 6FBAPP-derived polyimides **7** series. Although the degree of polymerization of PAA based on fluorinated diamine **2** was somewhat lower than that of the BAPP-derived one, the formed **5** series was characterized by good mechanical properties as well as thermal properties.

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