

## Organosoluble, Low-Colored Fluorinated Polyimides Based on 1,1-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane

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Received 20 January 2006; accepted in revised form 5 July 2006; published online 13 September 2006

**Key words:** fluorinated polyimides, low color, dielectric property

### Abstract

A novel trifluoromethyl-substituted bis(ether amine) monomer, 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane, was synthesized that led to a series of novel fluorinated polyimides via chemical imidization route when reacted with various commercially available aromatic tetracarboxylic dianhydrides. These polyimides were highly soluble in a variety of organic solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide, and most of them could afford transparent, low-colored, and tough films. These polyimides exhibited glass-transition temperatures ( $T_g$ s) of 227–269 °C and showed no significant decomposition below 500 °C under either nitrogen or air atmosphere. These polyimides had low dielectric constants of 2.87–3.17 at 10 kHz, low water uptake of 0.13%–0.58%, and an ultraviolet-visible absorption cutoff wavelength at 364–410 nm. For a comparative study, a series of analogous polyimides based on 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane were also prepared and characterized.

### Introduction

Aromatic polyimides are well known as one of the most important classes of high-performance polymeric materials for their outstanding thermal, mechanical and electrical properties as well as superior chemical resistance [1, 2]. However, their widespread applications are often limited because of poor solubility in organic solvents and high melting and softening temperatures, which were caused partly by the strong interchain interaction. For such drawbacks to be overcome, polymer structure modification becomes necessary [3]. Many endeavors have been made to develop new dianhydrides [4–10] and diamines [11–17] for the synthesis of soluble and/or melt processable polyimides.

A low dielectric constant is one of the most attractive properties of polyimides for microelectronic applications. In order to achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability have to be used [18]. The incorporation of aliphatic adamantane or diamantane moiety is known to result in low dielectric constants because of high hydrophobicity, low polarity, and increased free volume [19–21]. Another effective approach to decrease the dielectric constant is to introduce fluorine substituents or perfluoroalkyl side groups into polyimide materials [22–26]. The strong electronegativity of fluorine results in very low polarizability of the C–F bonds and the increase in the fractional free volume, which accompanies the replacement of methyl group by trifluoromethyl (CF<sub>3</sub>) groups.

Therefore, many fluorinated polyimides have been developed to reduce the dielectric constant [27–45]. An additional positive effect of fluorinated substituents is to enhance the solubility and optical transparency of polyimides. As part of our continuing efforts in developing tractable high-performance polymers containing fluorine substituents, the present article describes the successful synthesis of a new trifluoromethylated bis(ether amine), 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane, and its use for the preparation of soluble polyimides by the reaction of the diamine with dianhydrides. The polymers were subjected to solubility tests and thermal, optical, water uptake and dielectric property measurement and were compared to analogous counterparts prepared from a structurally similar bis(ether amine), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (BAPP3FE). The prepared polyimides were expected to exhibit enhanced solubility and optical transparency and decreased dielectric constants because of increased free volume caused by the CF<sub>3</sub> substituent and the bulky 1,1,1-triphenyl-2,2,2-trifluoroethane core.

### Experimental

#### Materials

The fluorinated bisphenol 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (**1**) was prepared from an acid-catalyzed

condensation reaction of  $\alpha,\alpha,\alpha$ -trifluoroacetophenone with phenol according to a published procedure [46, 47]. BAPP3FE (mp = 169–170 °C) was prepared in two steps starting from the aromatic substitution reaction of bisphenol **1** with *p*-chloronitrobenzene. Details of synthetic procedure and characterization data of the diamine have been described in a previous article [47]. Potassium carbonate ( $K_2CO_3$ ; from Fluka), 2-chloro-5-nitrobenzotrifluoride (**2**; from Acros), 10% palladium on charcoal (Pd/C) (from Fluka), and hydrazine monohydrate (from Acros) were used as received. Pyromellitic dianhydride (PMDA; **5a**; from Aldrich) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; **5c**; from Aldrich) were purified by recrystallization from acetic anhydride. 3,4,3',4'-Biphenyltetracarboxylic dianhydride (BPDA; **5b**; from Oxychem), 4,4'-oxydiphthalic dianhydride (ODPA; **5d**; from Oxychem), 3,4,3',4'-diphenylsulfonetetracarboxylic dianhydride (DSDA; **5e**; from New Japan Chemical Co.), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **5f**; from Hoechst Celanese) were heated at 250 °C under vacuum for 3 h prior to use. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride ( $CaH_2$ ) and stored over 4 Å molecular sieves.

#### Monomer synthesis

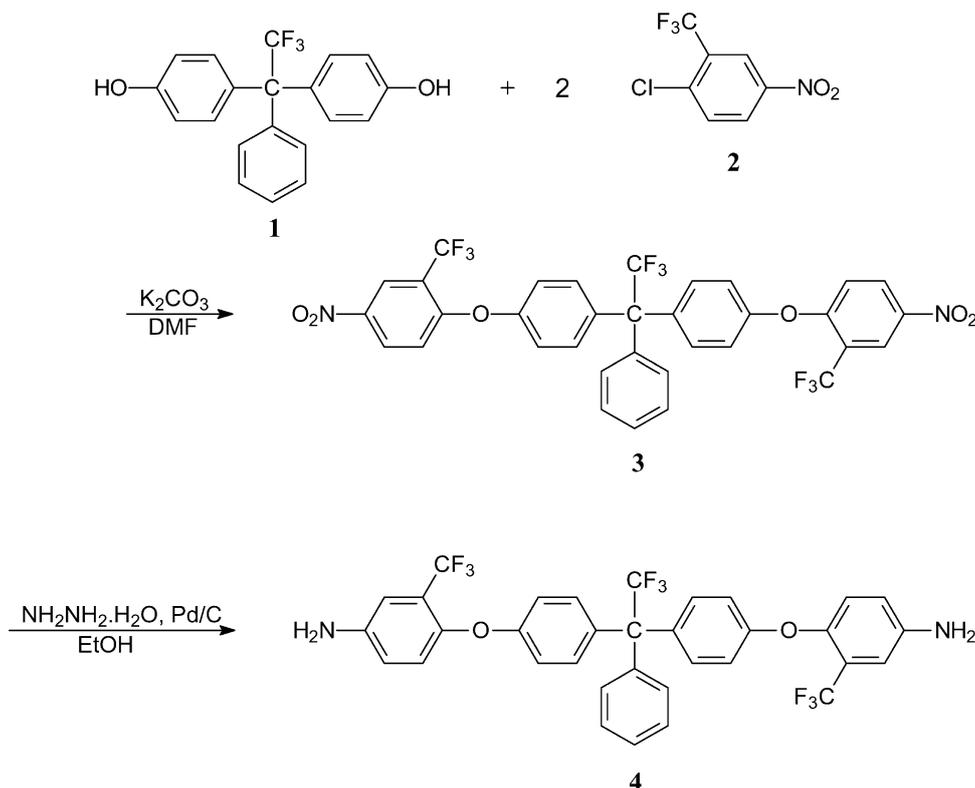
##### *1,1-Bis[4-(4-nitro-2-trifluoromethylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3)*

The bisphenol **1** (5.0 g, 0.014 mol) and 2-chloro-5-nitrobenzotrifluoride (**2**; 6.55 g, 0.029 mol) were dissolved in

80 ml of dry DMF in a 300-ml round-bottomed flask. Then, potassium carbonate (4.5 g, 0.032 mol) was added, and the suspension mixture was heated at 100 °C for 24 h. The mixture was allowed to cool and then poured into 600 ml of water to give yellow products, which was collected, washed repeatedly with water, and dried. The crude product was recrystallized from methanol/water to give pale-yellow crystals (10.3 g, 98%) with a mp of 74–76 °C by differential scanning calorimetry (DSC) at a scan rate of 5 °C/min. IR (KBr): 1,533, 1,353 ( $-NO_2$ ), 1,268 (C–O stretching), 1146  $cm^{-1}$  (C–F stretching).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$ , ppm): 8.59 (d,  $J = 2.7$  Hz, 2H,  $H_b$ ), 8.34 (dd,  $J = 9.2, 2.7$  Hz, 2H,  $H_g$ ), 7.40 (d + t, 3H,  $H_a + H_c$ ), 7.25 (d,  $J = 8.8$  Hz, 4H,  $H_d$ ), 7.19 (br. m, 2H,  $H_b$ ), 7.12 (d,  $J = 8.8$  Hz, 4H,  $H_c$ ), 7.05 (d,  $J = 9.2$  Hz, 2H,  $H_f$ ).  $^{13}C$  NMR ( $CDCl_3$ ,  $\delta$ , ppm): 160.4 ( $C^6$ ), 153.8 ( $C^5$ ), 142.2 ( $C^9$ ), 139.3 ( $C^{12}$ ), 137.6 ( $C^2$ ), 132.2 ( $C^3$ ), 129.7 ( $C^{13}$ ), 128.9 ( $C^{14}$ ), 128.6 ( $C^8$ ), 128.3 ( $C^{15}$ ), 126.3 (quartet,  $^1J_{C-F} = 285$  Hz,  $C^{17}$ ), 123.9 (quartet,  $^3J_{C-F} = 5$  Hz,  $C^{10}$ ), 122.2 (quartet,  $^1J_{C-F} = 272$  Hz,  $C^{16}$ ), 121.0 (quartet,  $^2J_{C-F} = 33$  Hz,  $C^{11}$ ), 120.1 ( $C^4$ ), 117.6 ( $C^7$ ), 64.5 (quartet,  $^2J_{C-F} = 24$  Hz,  $C^1$ ). ANAL. Calcd for  $C_{34}H_{19}F_9N_2O_6$  (722.52): C, 56.52%; H, 2.65%; N, 3.88%. Found: C, 56.35%; H, 2.55%; N, 3.93%.

##### *1,1-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (4)*

A mixture of the dinitro compound **3** (10 g, 0.0138 mol), 10% Pd/C (0.2 g), ethanol (80 ml), and hydrazine monohydrate (5 ml) was heated at reflux temperature overnight (for about 10 h). The resultant clear, darkened solution was filtered hot to remove Pd/C, and the filtrate



Scheme 1. Synthesis of diamine monomer **4**.

was then distilled to remove the solvent. The crude product was further purified by recrystallization from ethanol/water to give 7.5 g (82%) of pure **4** with a mp of 69–70 °C (by DSC at a scan rate of 5 °C/min). IR (KBr): 3,481, 3,392 (N–H stretching), 1,232 (C–O stretching), 1,153  $\text{cm}^{-1}$  (C–F stretching).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.31 (d + t, 3H,  $\text{H}_a$  +  $\text{H}_c$ ), 7.15 (br s, 2H,  $\text{H}_b$ ), 7.04 (d,  $J = 8.7$  Hz, 4H,  $\text{H}_d$ ), 6.94 (d,  $J = 2.6$  Hz, 2H,  $\text{H}_h$ ), 6.90 (d,  $J = 8.7$  Hz, 2H,  $\text{H}_f$ ), 6.85 (d,  $J = 8.9$  Hz, 4H,  $\text{H}_e$ ), 6.77 (d,  $J = 8.6$  Hz, 2H,  $\text{H}_g$ ), 3.73 (s, 4H,  $-\text{NH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 157.8 ( $\text{C}^5$ ), 145.4 ( $\text{C}^9$ ), 142.8 ( $\text{C}^6$ ), 140.3 ( $\text{C}^{12}$ ), 134.2 ( $\text{C}^2$ ), 131.3 ( $\text{C}^3$ ), 129.8 ( $\text{C}^{13}$ ), 127.3 (quartet,  $^1J_{\text{C-F}} = 285$  Hz,  $\text{C}^{17}$ ), 128.2 ( $\text{C}^{14}$ ), 127.7 ( $\text{C}^{15}$ ), 124.5 (quartet,  $^1J_{\text{C-F}} = 271$  Hz,  $\text{C}^{16}$ ),

123.5 (quartet,  $^2J_{\text{C-F}} = 30$  Hz,  $\text{C}^{11}$ ), 122.8 ( $\text{C}^7$ ), 119.3 ( $\text{C}^8$ ), 116.7 ( $\text{C}^4$ ), 112.9 (quartet,  $^3J_{\text{C-F}} = 5$  Hz,  $\text{C}^{10}$ ), 64.1 (quartet,  $^2J_{\text{C-F}} = 24$  Hz,  $\text{C}^1$ ). ANAL. Calcd for  $\text{C}_{34}\text{H}_{23}\text{F}_9\text{N}_2\text{O}_2$  (662.55): C, 61.64%; H, 3.50%; N, 4.23%. Found: C, 61.31%; H, 3.17%; N, 4.20%.

#### Polyimide synthesis

The polyimides were synthesized by polycondensation of diamine **4** with various dianhydrides via a two-step method. The synthesis of polyimide **7a** is used as an example to illustrate the general synthetic procedure used to produce the

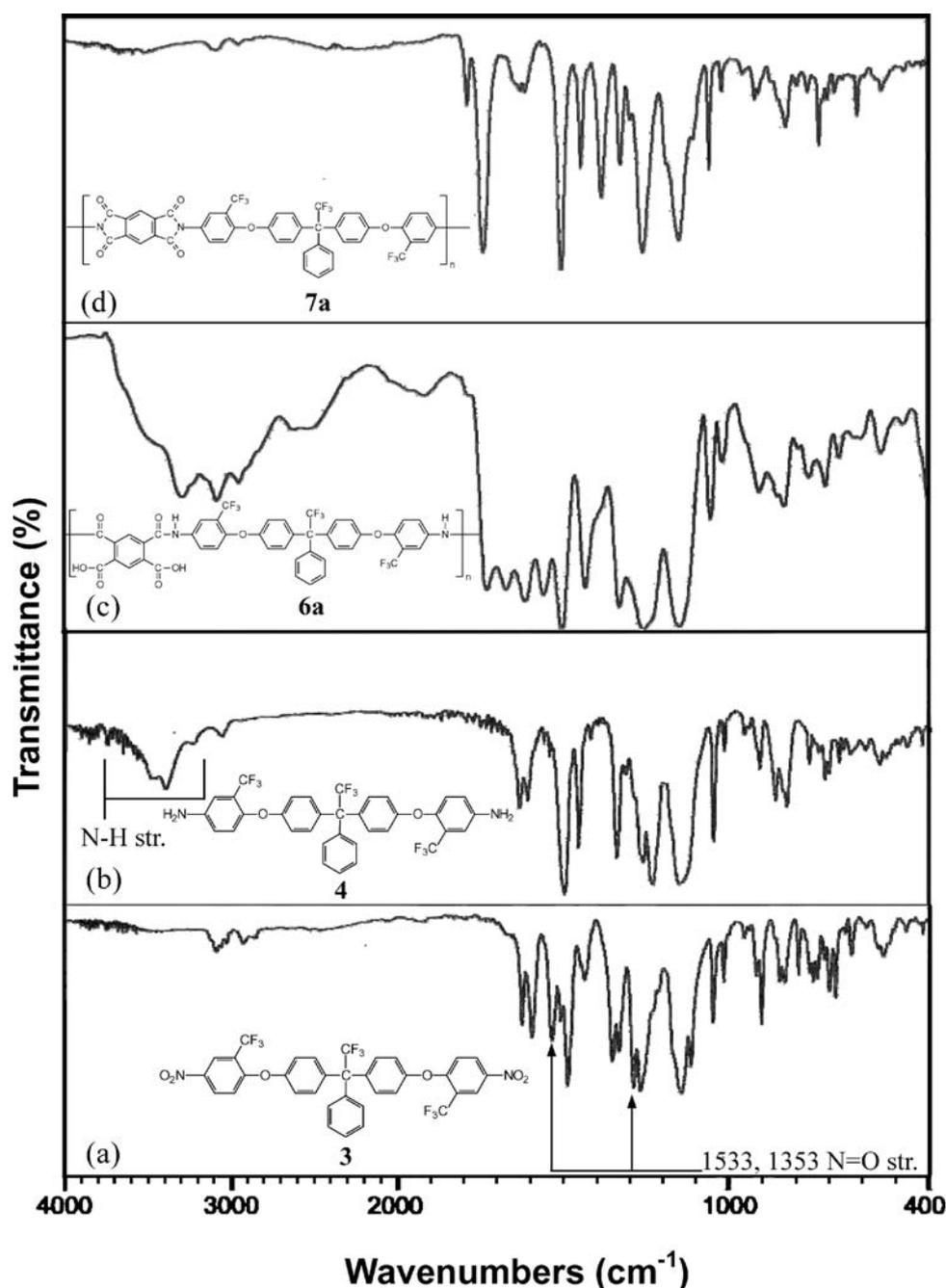


Figure 1. IR spectra of (a) dinitro compound **3**, (b) diamine **4**, (c) poly(amic acid) **6a**, and (d) polyimide **7a**.

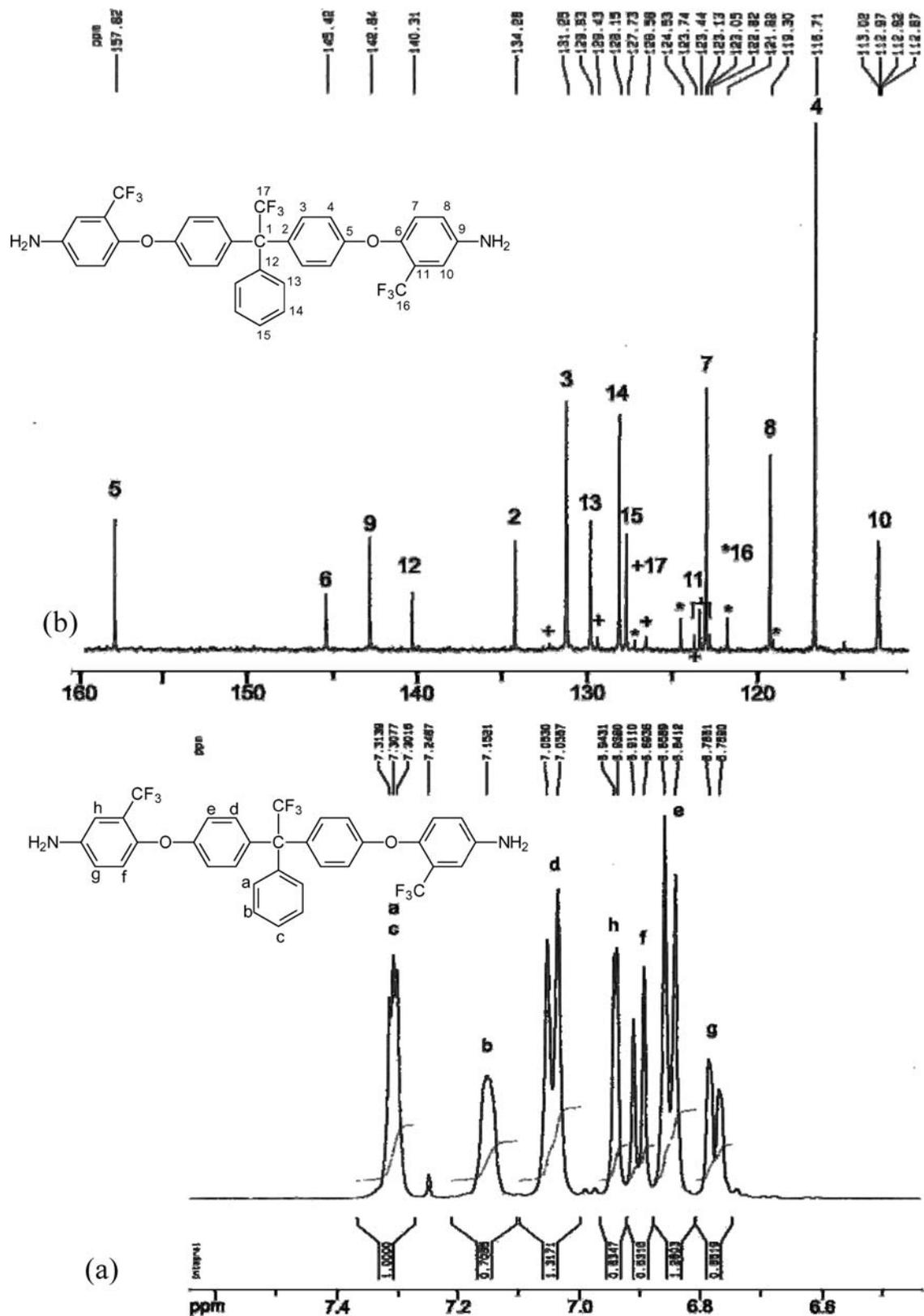
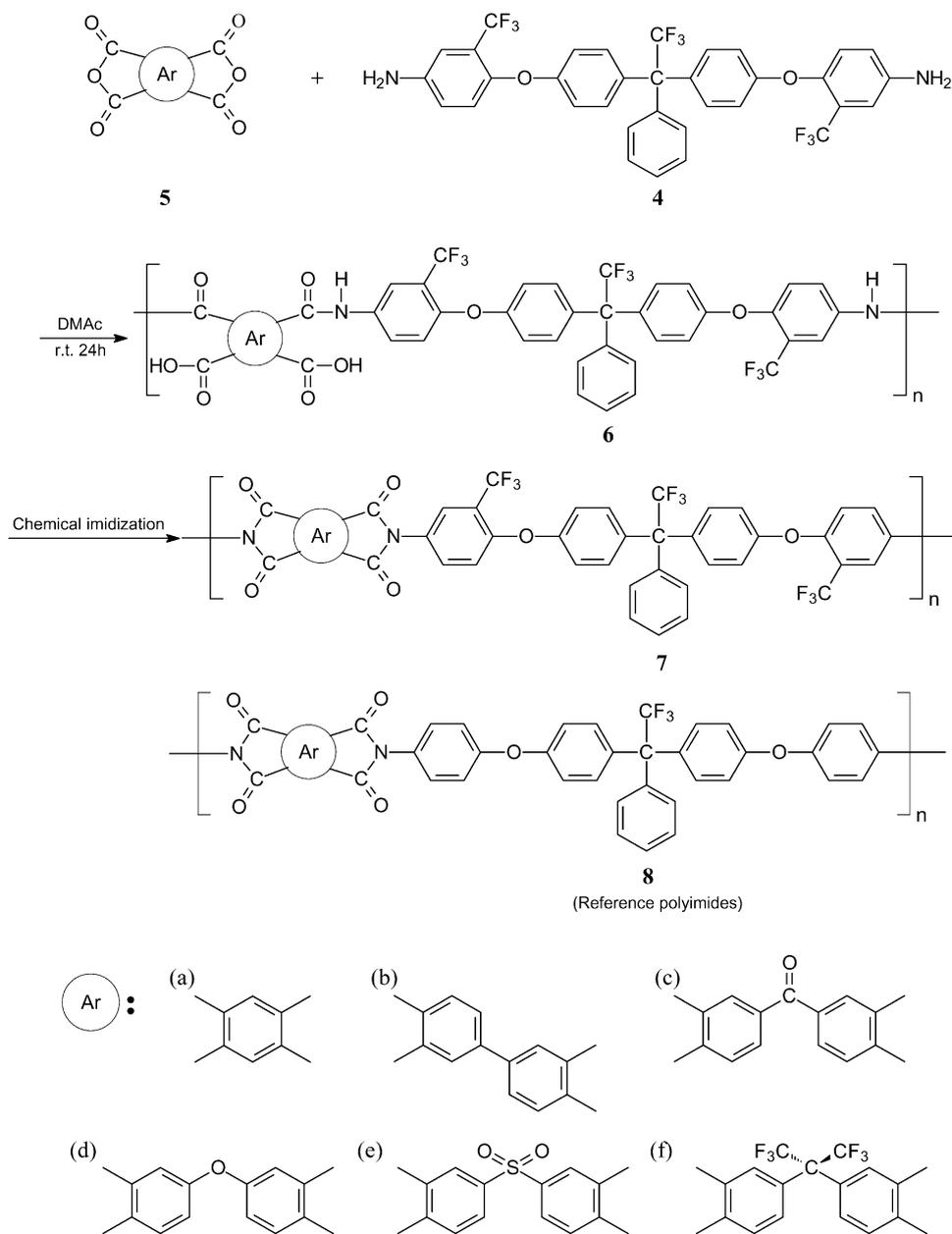


Figure 2. (a) Expansions of the aromatic ring proton resonance from the 400-MHz  $^1\text{H}$  NMR spectra of diamine monomer **4** in  $\text{CDCl}_3$  (the accompanying amino group resonance at 3.73 ppm of **4** is not shown). (b)  $^{13}\text{C}$  NMR spectra of diamine **4** in  $\text{CDCl}_3$ . The quartet peaks of  $\text{C}^1$  centered at around 64 ppm are not shown.



Scheme 2. Synthesis of polyimides.

polyimides. To a solution of 0.7523 g (1.136 mmol) of 4 in 9.5 ml of CaH<sub>2</sub>-dried DMAc in a 50-ml flask, 0.2477 g (1.136 mmol) of dianhydride PMDA was added in one portion. Therefore, the solid content of the solution was approximately 10 wt.%. The mixture was stirred at room temperature overnight (for ca. 24 h) to afford a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 0.83 dl/g, measured in DMAc at a concentration of 0.5 g/dl at 30 °C. The poly(amic acid) was subsequently converted into polyimide by chemical imidization process. It was carried out by the addition of 2 ml of pyridine and 5 ml of acetic anhydride into the poly(amic acid) solution with stirring at room temperature for 1 h, and then the mixture was heated to 100 °C and held at 100 °C for 3 h. The resulting homogeneous polyimide solution was poured into methanol to give a light yellow,

fibrous precipitate, which was washed thoroughly with methanol and dried. The inherent viscosity of the **7a** in DMAc was 0.64 dl/g, measured at a concentration of 0.5 g/dl at 30 °C.

Table 1. Inherent viscosities and average molecular weights of the polyimides.

| Polyimide | $\eta_{inh}^a$ (dl/g) | $\overline{Mn}^b$ | $\overline{Mw}^b$ | $\overline{Mw}/\overline{Mn}$ |
|-----------|-----------------------|-------------------|-------------------|-------------------------------|
| 7a        | 0.64                  | 23,000            | 41,500            | 1.80                          |
| 7b        | 0.52                  | 17,000            | 30,500            | 1.80                          |
| 7c        | 0.54                  | 22,000            | 38,500            | 1.75                          |
| 7d        | 0.61                  | 18,000            | 35,500            | 1.97                          |
| 7e        | 0.57                  | 20,500            | 39,500            | 1.93                          |
| 7f        | 0.64                  | 25,500            | 52,500            | 2.06                          |

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

<sup>b</sup>Measured by GPC in THF, relative to polystyrene standards.

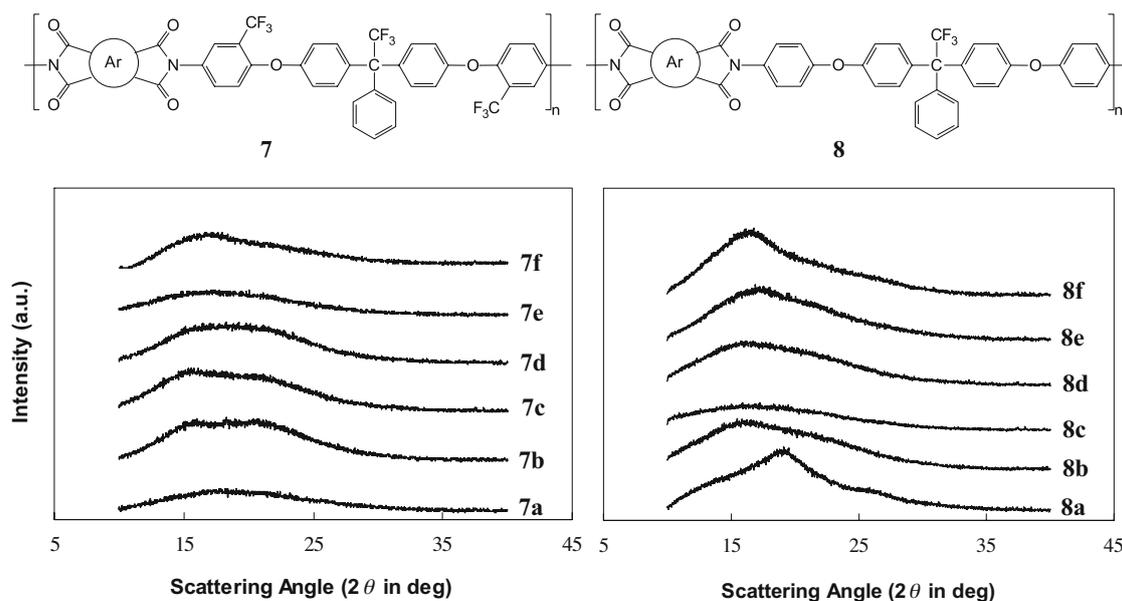


Figure 3. WAXD patterns of the polyimides.

### Measurements

Elemental analyses were run in a PerkinElmer model 2400 C, H, N analyzer. Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a JEOL EX 400 spectrometer with  $\text{CDCl}_3$  as the solvent and tetramethylsilane as the internal reference. The inherent viscosities of the polymers were measured with an Ubbelohde viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD 6000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized  $\text{Cu-K}\alpha$  radiation. Gel permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5  $\mu\text{m}$  Styragel HR-2 and HR-4 columns (7.8 mm I.D.  $\times$  300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow polystyrene standards. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress-strain behavior of the polyimide film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.09 mm thick), and an average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a GretagMacbeth Color-Eye 3100 colorimeter. Measurements were performed with films (56–89  $\mu\text{m}$  thick) with an observational angle 10° and a Commission International de l'Éclairage (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–visible spectrophotometer UV-1601. Dielectric property of the polymer films was tested by the parallel-plate capacitor

method using a HP-4194A Impedance/Gain Phase Analyzer. Gold electrodes were vacuum deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate 30  $\text{cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20  $\text{cm}^3/\text{min}$ ). Glass transition temperatures ( $T_g$ ) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400 °C at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7

Table 2. Solubility behavior of the polyimides<sup>a</sup>.

| Solvents <sup>b</sup> | Polyimides |    |    |    |    |    |
|-----------------------|------------|----|----|----|----|----|
|                       | 7a         | 7b | 7c | 7d | 7e | 7f |
| NMP                   | +          | +  | +  | +  | +  | +  |
| DMAc                  | +          | +  | +  | +  | +  | +  |
| DMF                   | +          | +  | +  | +  | +  | +  |
| DMSO                  | +          | +h | +  | +  | +  | +  |
| <i>m</i> -Cresol      | +          | +  | +h | +  | +  | +  |
| THF                   | +          | +  | +  | +  | +  | +  |
| $\text{CHCl}_3$       | +          | +  | +  | +  | +  | +  |
| Acetone               | –          | +  | +  | +  | +  | +  |
| Ethanol               | –          | –  | –  | –  | –  | –  |

+ = soluble at room temperature; +h = soluble on heating at 100 °C or boiling temperature; – = insoluble even on heating.

<sup>a</sup>The solubility was determined by using 10 mg sample in 1 ml of stirred solvent.

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

instrument with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. The TMA experiments were conducted from 50 °C to 300 °C at a scan rate of 10 °C/min, and softening temperatures ( $T_s$ ) were taken as the onset temperatures of probe displacement on the TMA traces. The equilibrium water uptake was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for three days.

## Results and discussion

### Synthesis of monomer

The new CF<sub>3</sub>-containing bis(ether amine) **4** was prepared by a two-step reaction sequence as shown in Scheme 1. The first step is an aromatic etherification of the bisphenol **1** with 2-chloro-5-nitrobenzotrifluoride (**2**) in the presence of potassium carbonate in DMF to form the dinitro compound **3**. The diamine **4** was readily obtained in high yields by the catalytic reduction of the intermediate dinitro compound **3** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. The structures of the dinitro compound **3** and the targeted diamine monomer **4** were confirmed by FTIR, NMR, and elemental analysis. Figure 1 (a) and (b) show the FTIR spectra of the synthesized compounds **3** and **4**, respectively. The nitro groups of compound **3** gave two characteristic bands at 1,533 and 1,353 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 the typical N–H stretching bands in the region of 3,300–3,500 cm<sup>-1</sup>. Figure 2 illustrates the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of diamine

monomer **4** in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectra [Figure 2(a)] confirm that the nitro groups have been completely converted into amino groups by the high field shift of the aromatic proton signals and by the signal at 3.73 ppm corresponding to the primary aromatic amine protons. As shown in Figure 2(b), except C<sup>1</sup> all the carbon-13 atoms in compounds **3** and **4** resonate in the region of 112–160 ppm, and C<sup>1</sup>, C<sup>11</sup>, C<sup>16</sup>, and C<sup>17</sup> show clean quartet peaks because of the heteronuclear <sup>13</sup>C–<sup>19</sup>F coupling. Thus, all the spectroscopic data obtained were in good agreement with the expected structures.

### Synthesis of polymers

As shown in Scheme 2, all the polyimides were prepared in conventional two-step method by the reaction of diamine **4** with six commercially available dianhydrides (**5a–5f**) to form the poly(amic acid)s, followed by chemical imidization. All the **7** series polyimides exhibited excellent solubility in polar solvents such as NMP and DMAc. Therefore, the characterization of inherent viscosity was carried out without any difficulty, and the inherent viscosities of these polyimides were in the range of 0.52–0.64 dl/g, as measured in DMAc at 30 °C. GPC analysis revealed that the weight-average (Mw) and number-average (Mn) molecular weights of these polyimides were in the range of 30,500–52,500 and 17,000–25,500, respectively (Table 1). For a comparative study, a series of referenced polyimides (**8a–8f**) were also synthesized from BAPP3FE and dianhydrides **5a–5f**. The inherent viscosities of the precursor poly(amic acid)s of **8a–8f** were in the range of 0.94–1.70 dl/g, indicating the formation of high molecular weight polymers. Polyimides **8a–8d** were obtained by the thermal

Table 3. Thin film tensile properties and thermal behavior data of polyimides.

| Polymer code | Tensile properties of the polyimide films |                         |                       | $T_g^a$ (°C)           | $T_s^b$ (°C) | $T_d^c$ (°C)      |        | Char yield <sup>d</sup> (%) |
|--------------|-------------------------------------------|-------------------------|-----------------------|------------------------|--------------|-------------------|--------|-----------------------------|
|              | Tensile strength (MPa)                    | Elongation to break (%) | Initial modulus (GPa) |                        |              | In N <sub>2</sub> | In air |                             |
| 7a           | 73                                        | 7                       | 1.94                  | 269                    | 267          | 572               | 567    | 57                          |
| 7b           | 103                                       | 10                      | 1.87                  | 245                    | 241          | 588               | 568    | 60                          |
| 7c           | 111                                       | 10                      | 2.15                  | 234                    | 227          | 582               | 557    | 60                          |
| 7d           | 76                                        | 9                       | 1.79                  | 227                    | 218          | 580               | 562    | 60                          |
| 7e           | 76                                        | 9                       | 1.68                  | 248                    | 247          | 535               | 541    | 55                          |
| 7f           | 91                                        | 9                       | 1.93                  | 242                    | 236          | 569               | 559    | 55                          |
| 8a           | 87                                        | 11                      | 1.96                  | 324 (472) <sup>e</sup> | 322          | 616               | 587    | 64                          |
| 8b           | 108                                       | 15                      | 1.89                  | 270                    | 272          | 628               | 602    | 68                          |
| 8c           | 115                                       | 10                      | 2.00                  | 257                    | 257          | 616               | 597    | 60                          |
| 8d           | 103                                       | 14                      | 1.85                  | 252                    | 254          | 616               | 593    | 65                          |
| 8e           | 107                                       | 11                      | 1.92                  | 279                    | 282          | 584               | 569    | 60                          |
| 8f           | 105                                       | 11                      | 1.98                  | 271                    | 272          | 599               | 576    | 61                          |

<sup>a</sup>Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C.

<sup>b</sup>Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min. The film samples were heated at 300 °C for 30 min prior to the TMA experiment.

<sup>c</sup>Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

<sup>d</sup>Residual wt.% at 800 °C in nitrogen.

<sup>e</sup>Peak top temperature of the melting endotherm on the first DSC heating trace.

imidization method due to their insolubility in organic solvents, whereas polyimides **8e** and **8f** were prepared via the chemical imidization route.

The complete imidization of polymers was confirmed by IR spectra. A typical set of IR spectra for poly(amic acid) **6a** and polyimide **7a** are shown in Figure 1(c) and (d). All polyimides exhibited characteristic absorption bands of the imide group near  $1,780$  and  $1,730\text{ cm}^{-1}$  (typical of imide carbonyl asymmetrical and symmetrical stretch),  $1,375$  (C–N stretch), and  $1,100$  and  $725$  (imide ring deformation), together with some strong absorption bands in the region of  $1,100$ – $1,300\text{ cm}^{-1}$  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 **7** series polyimides generally agreed well with the calculated values for the proposed structures.

### Properties of polymers

#### X-ray diffraction data

The morphology of the polyimide films was characterized by WAXD measurements using nickel-filtered Cu  $K\alpha$  radiation. As presented in Figure 3, all the **7** and **8** series polyimides showed almost completely amorphous diffraction patterns. This is reasonable because of the presence of non-coplanar 1,1,1-triphenyl-2,2,2-trifluoroethylidene core (for both series) and the bulky  $\text{CF}_3$  substituents on the benzene ring (for the **8** series) that will inhibit close chain packing and decrease chain–chain interactions.

#### Solubility

The solubility of the polyimides was determined qualitatively in various common organic solvents, and the data are listed in Table 2. All the polyimides **7a–f** showed an excellent solubility might be due mainly to the presence of

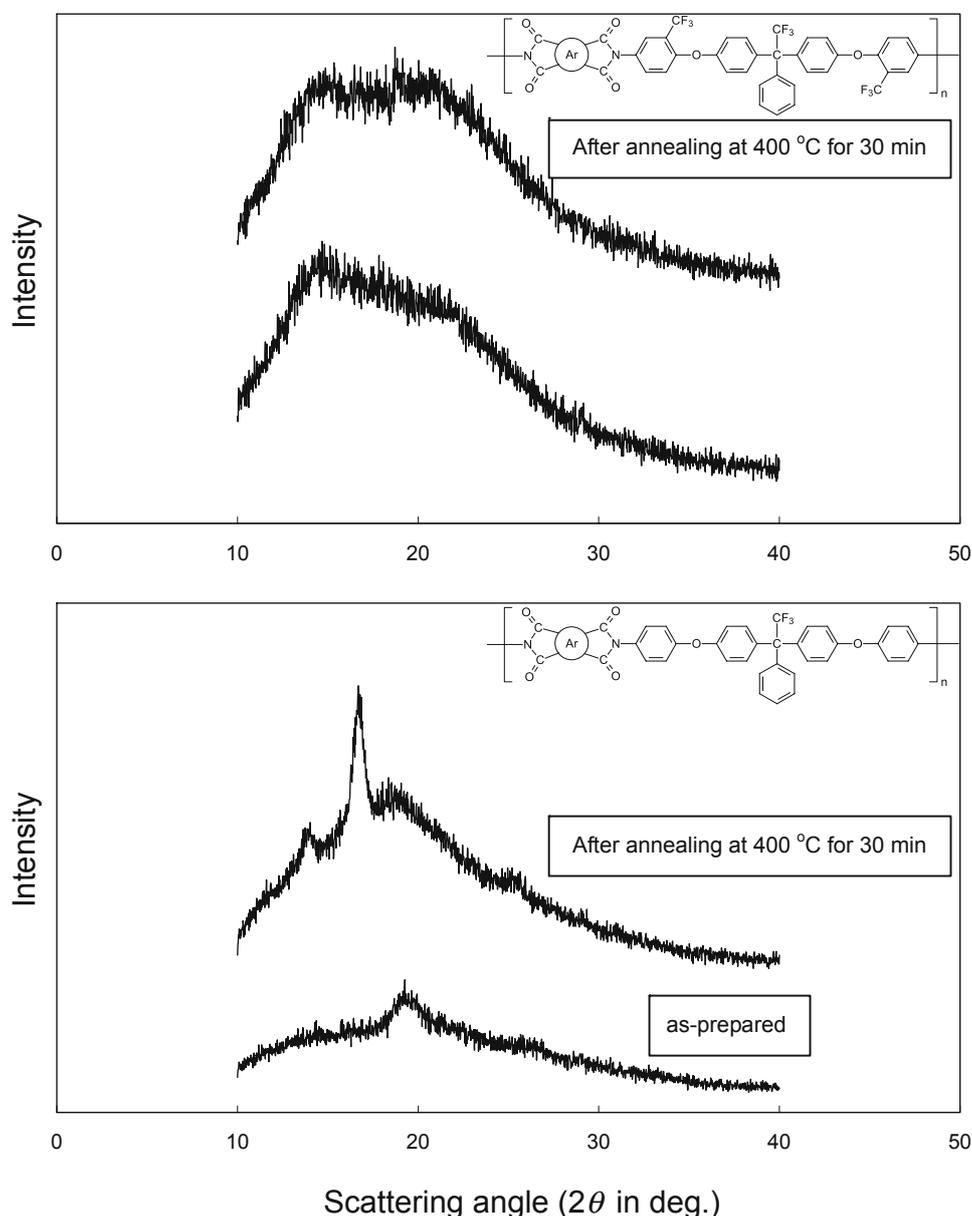


Figure 4. WAXD patterns of the as-prepared films of polyimides **7a** and **8a** and those after isothermal annealing at  $400\text{ °C}$  for 30 min.

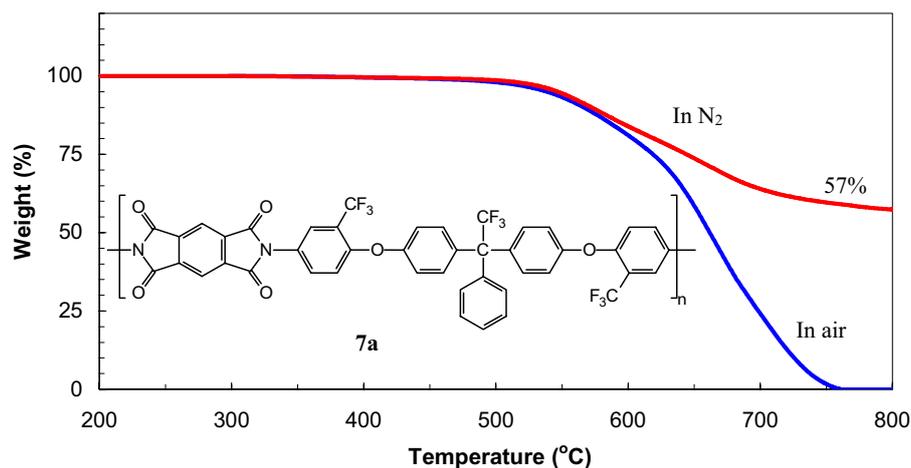


Figure 5. TGA thermograms of polyimide **7a** at a heating rate of 20 °C/min.

the bulky CF<sub>3</sub> substituents. All the polyimides were soluble both in aprotic polar solvents and in common organic solvents such as NMP, DMAc, DMF, DMSO, *m*-cresol, chloroform, and THF. Most of them were also soluble in acetone. Conversely, most of the **8** series polyimides (**8a–8d**) were insoluble in the above solvents at room temperature or heated. The large differences in solubility between the **7** and **8** series could be attributable to the bulky CF<sub>3</sub> substituents on the benzene ring, which increased the disorder in the chains and inhibited dense chain packing, thus reducing the chain–chain interactions to enhance solubility. The solubility properties of the present series polyimides (**7**) are comparable to those of structurally related fluorine-containing polyimides (derived from an isomeric diamine of **4**) recently reported by the Yang's group [17].

#### Tensile properties

The tensile properties of films cast from the resulting polyimides are also summarized in Table 3. The polymer films had tensile strengths of 73–115 MPa, elongations to

break of 7%–15%, and tensile moduli of 1.68–2.15 GPa. All the polymers behaved as ductile materials with good tensile strengths and moderate elongations to break. The casting films of the **7a–7f** series generally exhibited slightly lower strengths and moduli than those of the **8a–8f** series, possibly due to increased free volume and decreased cohesive force caused by the CF<sub>3</sub> group on the benzene ring.

#### Thermal properties

The thermal properties of the polyimides were investigated by DSC, TMA, and TGA. The corresponding data of thermal analysis are summarized in Table 3. DSC experiments were conducted at a heating rate of 20 °C/min in nitrogen. Rapid cooling from 400 to 50 °C produced predominantly amorphous samples, so the glass-transition temperature ( $T_g$ ) of all the polyimides could be observed on the subsequent heating DSC traces. The  $T_g$  values of the fluorinated polyimides **7a–f** were in the range from 227 to 269 °C. The decreasing order of  $T_g$  generally correlated with that of chain flexibility. As expected, the polyimide **7d** obtained from ODPDA showed the lowest  $T_g$  due to the presence of a flexible ether linkage between the phthalimide units, and the polyimide **7a** derived from PMDA exhibited the highest  $T_g$  due to the rigid pyromellitimide unit. The range of  $T_g$  values for the polyimides **8a–f** were in the range from 252 to 324 °C. Although polyimide **8a** showed an amorphous X-ray diffraction pattern, but it revealed a broad, medium-intensity melting endotherm around 472 °C. This result indicates that polymer **8a** may have a higher crystallization tendency upon heating. As can be seen from Figure 4, a slight increase in crystallinity was observed if the film sample of **8a** was annealed at elevated temperatures such as 400 °C for 30 min. In contrast, the polyimide **7a** failed to show any crystallinity even after annealing at the similar condition. This can be attributable to the effect of the large volume of CF<sub>3</sub> on regularity of the polyimides obtained.

The softening temperatures ( $T_s$ ; may be referred as apparent  $T_g$ ) of the polyimide films were determined by

Table 4. Color coordinates and cutoff wavelength ( $\lambda_o$ ) from UV–Vis absorption spectra of the polyimide films<sup>a</sup>.

| Polymer | Film thickness ( $\mu\text{m}$ ) | $a^*$ | $b^*$ | $L^*$ | $\lambda_o$ (nm) |
|---------|----------------------------------|-------|-------|-------|------------------|
| paper   |                                  | −0.5  | 1.1   | 94.6  |                  |
| 7a      | 59                               | −8.8  | 48.5  | 87.7  | 410              |
| 7b      | 89                               | −5.4  | 25.8  | 87.9  | 399              |
| 7c      | 65                               | −4.7  | 40.1  | 86.6  | 400              |
| 7d      | 56                               | −4.3  | 19.9  | 88.5  | 372              |
| 7e      | 63                               | −6.8  | 32.5  | 89.4  | 391              |
| 7f      | 73                               | −5.6  | 22.0  | 89.1  | 364              |
| 8a      | 61                               | −5.5  | 96.0  | 80.1  | 435              |
| 8b      | 52                               | −5.7  | 47.9  | 80.2  | 413              |
| 8c      | 60                               | −6.3  | 84.4  | 82.2  | 423              |
| 8d      | 68                               | −5.6  | 63.7  | 81.9  | 384              |
| 8e      | 78                               | −5.9  | 28.8  | 86.5  | 417              |
| 8f      | 67                               | −5.7  | 22.8  | 90.4  | 383              |

<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  $a^*$  indicated green color. A positive  $b^*$  means yellow color, while a negative  $b^*$  implies blue color.

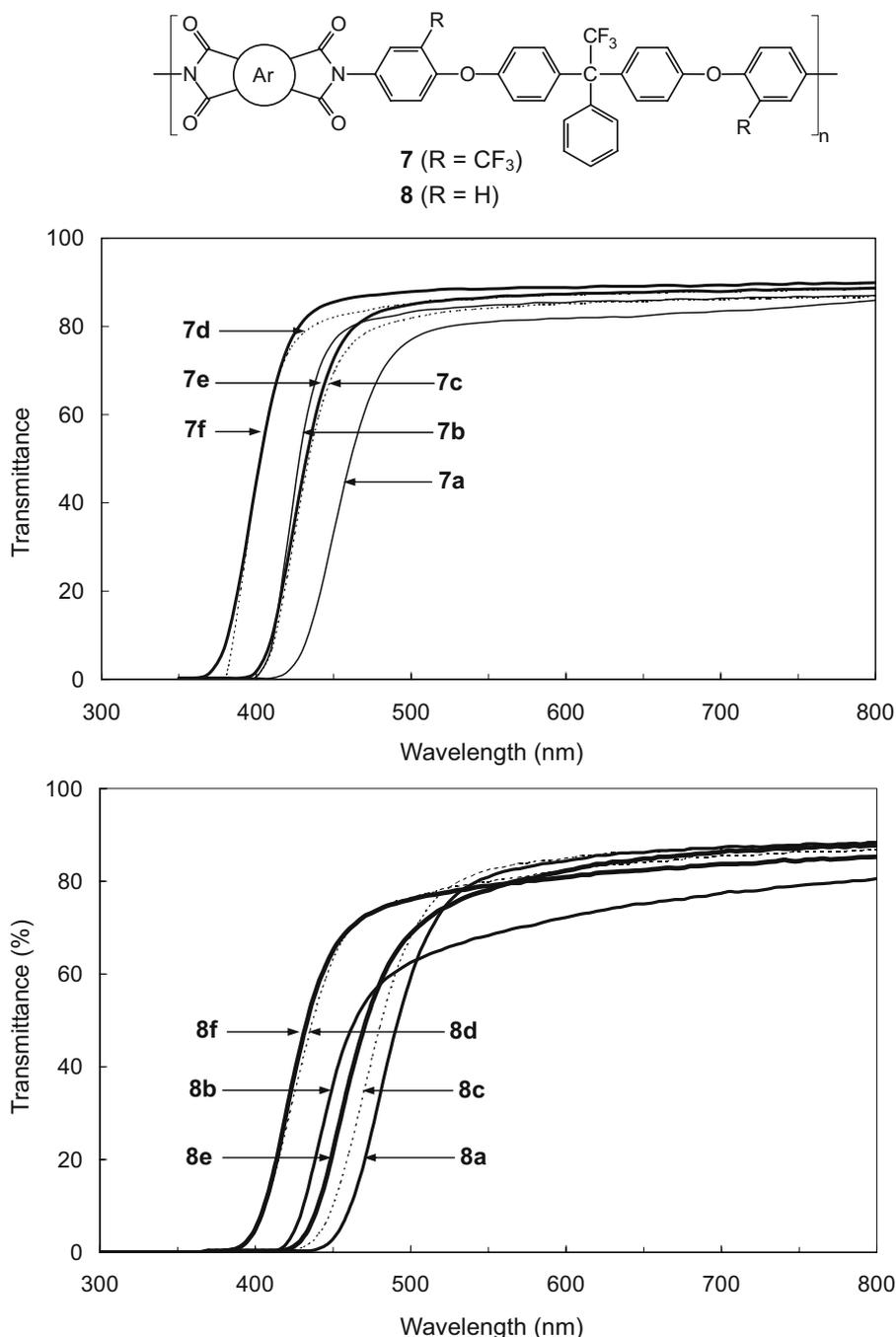


Figure 6. Transmission UV-vis spectra of some polyimide films (59–89  $\mu\text{m}$  thick).

the TMA method using a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. As can be seen from Table 3, most of the  $T_s$  values obtained by TMA are comparable to the  $T_g$  values measured by DSC experiments. The trend of  $T_s$  variation with the chain stiffness is similar to that of  $T_g$  observed in the DSC measurements. Slightly lower  $T_g$  and  $T_s$  values for the **7** series polyimides in comparison with the **8** series polyimides might be a result of decreased interchain interactions due to the bulky pendant CF<sub>3</sub> groups in the former.

The thermal stability of the polyimides was evaluated by TGA measurements in both air and nitrogen atmospheres.

Typical TGA curves of polyimide **7a** are reproduced in Figure 5. All the other polyimides showed similar patterns of degradation with no significant weight loss before 500 °C in nitrogen or air, but with more than 55 wt.% residue remaining when heated to 800 °C in nitrogen. The decomposition temperature ( $T_d$ ) at 10% weight loss of polyimides **7a–f** were recorded in the range of 535–588 °C in nitrogen and 541–568 °C in air, and those of polyimides **8a–f** were recorded in the range of 584–628 °C in nitrogen and 569–602 °C in air. All the obtained results indicated that the obtained polyimides still exhibited an excellent thermal stability regardless of the incorporation of the CF<sub>3</sub> substituents in the molecular chain.

Table 5. Moisture absorption and dielectric constants of polyimides.

| Polymer code | Film thickness ( $\mu\text{m}$ ) | Water uptake (%) | Dielectric constant (dry) |        |
|--------------|----------------------------------|------------------|---------------------------|--------|
|              |                                  |                  | 10 kHz                    | 40 MHz |
| 7a           | 59                               | 0.50             | 3.08                      | 3.04   |
| 7b           | 89                               | 0.40             | 3.04                      | 3.04   |
| 7c           | 65                               | 0.58             | 3.13                      | 3.13   |
| 7d           | 56                               | 0.20             | 2.93                      | 2.92   |
| 7e           | 63                               | 0.35             | 3.17                      | 3.35   |
| 7f           | 73                               | 0.13             | 2.87                      | 2.81   |
| 8a           | 61                               | 0.65             | 3.17                      | 3.16   |
| 8e           | 52                               | 0.58             | 3.21                      | 3.19   |
| 8c           | 60                               | 0.63             | 3.25                      | 3.20   |
| 8d           | 68                               | 0.32             | 3.15                      | 3.12   |
| 8e           | 78                               | 0.49             | 3.26                      | 3.20   |
| 8f           | 67                               | 0.28             | 3.08                      | 3.05   |

### Color intensity and optical transparency

The color intensities of the polyimides were elucidated from the yellowness or redness indices observed by a Macbeth color-eye colorimeter. The results shown in Table 4 indicate that the 7 series fluorinated polyimides generally showed a lower  $b^*$  value (a yellowness index) in comparison with the corresponding 8 polyimides. Moreover, thin films were measured for optical transparency using UV-Vis spectroscopy. Figure 6 depicts the transmittance UV-Vis spectra of the typical polyimide films, and the cutoff wavelengths (absorption edge,  $\lambda_0$ ) from the UV-Vis spectra are also listed in Table 4. Consistent with the results obtained from colorimeter, all the 7 series polyimides revealed a lower  $\lambda_0$  than their respective 8 series analogs. The films from more highly fluorinated polyimides 7a-f exhibited higher percent transmittance values (>80%) compared to those from polyimides 8a-f. The 6FDA and ODPDA produced fairly transparent and essentially colorless polyimide films in contrast to other dianhydrides, 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  $\text{CF}_3$  substituents in their diamine moieties can be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing  $\text{CF}_3$  groups on the outer benzene rings of diamine 4 were effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). The decrease in intermolecular CTC formation is understandable also from the significant solubility of the polyimides prepared from diamine 4.

### Dielectric constants and water absorption

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 polymer film. This procedure excludes any contact problems. As reported in Table 5, polyimides 7a-7f revealed lower dielectric constants (2.87-3.17 at 10 kHz) compared to analogous polyimides 8a-8f (3.08-3.26 at 10 kHz). The decreased dielectric constants

might be partly attributable to the bulky  $\text{CF}_3$  substituents, which resulted in less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine results in very low polarizability of the C-F bonds, thus decreasing the dielectric constant. Table 5 also presents the water uptake of all the polyimides, which ranges from 0.13% to 0.65%. In comparison, most of the polyimides 7a-7f exhibited lower water uptakes than the corresponding less fluorinated 8a-8f polyimides. The low water uptakes ensure that the polymers have stable dielectric performance. Polyimide 7f exhibited the lowest water uptake due to the higher fluorine content in the repeat unit. Therefore, the 6FDA-derived polyimide 7f exhibited the lowest dielectric constant of 2.87 at 10 kHz due to its higher fractional free volume and hydrophobicity.

### Conclusions

A novel fluorine-containing diamine monomer, 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-phenyl-2,2,2-trifluoroethane (4), was synthesized via a straightforward, high-yielding two-step procedure. A series of organosoluble, light-colored fluorinated polyimides have been obtained from the trifluoromethyl-substituted bis(ether amine) with various aromatic dianhydrides by the two-step chemical imidization method. The resulting polyimides were characterized by high solubility, good film-forming capability, high optical transparency, excellent thermal stability, moderate to high glass transition temperatures ( $T_g = 227\text{--}269\text{ }^\circ\text{C}$ ), and low dielectric constants. Thus, this series of polyimides exhibit a good combination of properties required for high-performance materials and demonstrate a potential for future application.

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