

# Synthesis and Properties of Fluorinated Aromatic Poly(amide imide)s Based on 4,4'-Bis(4-amino-2-trifluoromethylphenoxy)benzophenone and Various Bis(trimellitimide)s

Yu-Yang Su, Chin-Ping Yang

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan

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**ABSTRACT:** A CF<sub>3</sub>-containing diamine, 4,4'-bis(4-amino-2-trifluoromethylphenoxy)benzophenone (**2**), was synthesized from 4,4'-dihydroxybenzophenone and 2-chloro-5-nitrobenzotrifluoride. Imide-containing diacids (**3** and **5B<sub>a</sub>–5B<sub>g</sub>**) were prepared by the condensation reaction of aromatic diamines and trimellitic anhydride. Then, two series of novel soluble aromatic poly(amide imide)s (PAIs; **6A<sub>a</sub>–6A<sub>k</sub>** and **6B<sub>a</sub>–6B<sub>g</sub>**) were synthesized from a diamine (**4A<sub>a</sub>–4A<sub>k</sub>** or **2**) with the imide-containing diacids (**3** and **5B<sub>a</sub>–5B<sub>g</sub>**) via direct polycondensation with triphenyl phosphate and pyridine. The aromatic PAIs had inherent viscosities of 0.74–1.76 dL/g. All of the synthesized polymers showed excellent solubility in amide-type solvents, such as *N*-methyl-2-pyrrolidone and

*N,N*-dimethylacetamide (DMAc), and afforded transparent and tough films by DMAc solvent casting. These polymer films had tensile strengths of 90–113 MPa, elongations at break of 8–15%, and initial moduli of 2.0–2.9 GPa. The glass-transition temperatures of the aromatic PAIs were in the range 242–279°C. They had 10% weight losses at temperatures above 500°C and showed excellent thermal stabilities. The **6B** series exhibited less coloring and showed lower yellowness index values than the corresponding **6A** series. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3641–3653, 2006

**Key words:** polyamides; polycondensation; polyimides

## INTRODUCTION

Aromatic polyimides are well known for their electric insulation properties and excellent thermal stability. However, their applications are limited because rigid polyimides are insoluble and infusible in their imidization form, which leads to process difficulties.<sup>1,2</sup> Current or prior attempts concerning the solubility and processing of rigid-chain polymers have been made through the synthetic modification by the introduction of flexible linkages,<sup>3,4</sup> molecular asymmetry, or bulky side groups<sup>5,6</sup> into the backbone. These can increase the flexibility, lower the melt point or glass-transition temperature ( $T_g$ ), and improve the solubility of polymers. In addition, one of the methods is the use of copolymerization to synthesize a copolymer, such as poly(amide imide)s (PAIs), to improve the processability.<sup>7–12</sup> Wholly aromatic polyamides have been also noted for their high thermal and chemical resistance, high strength, and high modulus.<sup>13</sup> Aromatic PAI can

possess desirable characteristics with the merits of the polyamides and polyimides, such as high thermal stability, good mechanical properties, and easy processability.

Aromatic PAI can be synthesized in one of several common ways, such as an amide imide forming reaction based on trimellitic anhydride (TMA), which reacts either with diisocyanate to produce PAI or with thionyl chloride to synthesize TMA-chloride and then reacts with diamine to produce PAI,<sup>14–17</sup> an imide-forming reaction from a medium of amide-containing monomer, like polycondensation of an amide-containing diamine with dianhydride to obtain PAI,<sup>18</sup> and the amide-forming reaction from imide-containing monomers such as dicarboxylic acids or diamines.<sup>19</sup> Therefore, aromatic PAI can be prepared from imide-containing monomers and aromatic diamines or dicarboxylic acids by polycondensation like prepared polyamide. The synthesis of PAI generally involves the use of TMA as a major component, where TMA is first reacted with a specific diamine or amino acid to synthesize a diimide dicarboxylic acid (DIDA) or diacid; then, DIDA is reacted with various aromatic diamines to synthesize a series of alternative copoly(amide imide)s.<sup>20–22</sup> It was convenient to use a method in our laboratory to probe into the molecular structure and properties.

Correspondence to: C.-P. Yang (cpyang@ttu.edu.tw).

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The PAIs show color (yellow or brown) because of their conjugated aromatic structures and/or intermolecular and intramolecular charge-transfer complex (CTC) formation. It had been reported that the processability of polyimides deriving from diamine containing the  $\text{CF}_3$  group, that is, 4,4'-bis(4-amino-2-trifluoromethylphenoxy)benzophenone (**2**),<sup>23</sup> had been improved and were combined with good optical and mechanical properties and excellent thermal properties, but the solubility was still not good enough. In addition, the fluorinated PAIs were also shown to have better solubility and lighter color than common aromatic PAIs.<sup>24</sup> Lighter colored PAI films are of special importance, such as in orientation films in liquid crystal display devices.<sup>25</sup> Thus, the imide-containing, 4,4'-bis(4-trimellitimide-2-trifluoromethylphenoxy)benzophenone, a DIDA (**3**), was synthesized from the  $\text{CF}_3$ -containing diamine (**2**) and TMA in this study. Fluorinated DIDA (**3**) was reacted with various imide-containing diacids by direct polycondensation to form aromatic PAIs (the **6A** series). Moreover, the **6B** series was prepared from diamine (**2**) and DIDA (**5B<sub>a</sub>**–**5B<sub>g</sub>**). The solubility, optical properties, tensile properties, and thermal properties of the resultant polymers were investigated. The position of diamine (**2**) influenced the optical properties of the polymers. The **6B** series, based on diamine **2** in the amide segments, was much lighter in color than the **6A** series, with **2** in the imide segment.

## EXPERIMENTAL

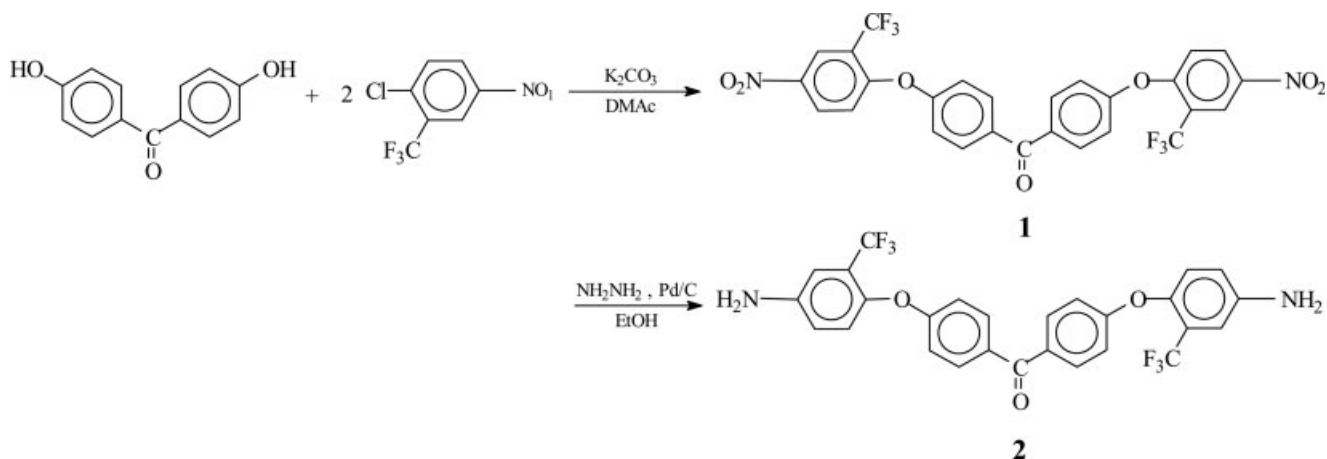
### Materials

2-Chloro-5-nitrobenzotrifluoride (Acros) and 4,4'-dihydroxybenzophenone (Acros) were used as received. TMA (Wako, Osaka, Japan) was used without previous purification. The diamines, including 4,4'-oxydianiline (**4A<sub>a</sub>**, TCI; Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), *m*-phenylenediamine (**4B<sub>a</sub>**, TCI), 4,4'-diaminodiphe-

nylmethane (**4A<sub>b</sub>**, TCI), 4,4'-diaminodiphenyl sulfide (**4A<sub>c</sub>** and **4B<sub>b</sub>**, TCI), *o*-tolidine (**4B<sub>c</sub>**, TCI), 4,4'-diaminobenzanilide (**4A<sub>d</sub>**, TCI), 3,4'-oxydianiline (**4B<sub>d</sub>**, Teijin, Ltd., Tokay), 1,4-bis(4-aminophenoxy)benzene (**4A<sub>e</sub>** and **4B<sub>e</sub>**, TCI), 1,3-bis(4-aminophenoxy)benzene (**4A<sub>f</sub>** and **4B<sub>f</sub>**, TCI), 4,4'-bis(4-aminophenoxy)biphenyl (**4A<sub>h</sub>**, Charishev), 2,2-bis[4-(4-aminophenoxy)phenyl] sulfone (**4A<sub>i</sub>**, TCI), 2,2-bis[4-(4-aminophenoxy)phenyl] propane (**4A<sub>j</sub>** and **4B<sub>g</sub>**, Charishev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**4A<sub>k</sub>**, Charishev), were used as received. 1,2-Bis(4-aminophenoxy)benzene (**4A<sub>g</sub>**) was synthesized according the literature.<sup>26</sup> Others, including *N*-methyl-2-pyrrolidone (NMP; Fluka), *N,N*-dimethylformamide (DMF; Fluka), *N,N*-dimethylacetamide (DMAc; Fluka, St. Gallen, Switzerland), pyridine (Py; Wako), triphenyl phosphite (TPP, TCI), and tetrahydrofuran (THF), were used as received.

### Synthesis of diamine **2**

Diamine **2** was prepared according the literature, as shown in Scheme 1.<sup>23</sup> 4,4'-Dihydroxybenzophenone (32 g, 0.15 mol) and 2-chloro-5-nitrobenzotrifluoride (67 g, 0.3 mol) were first dissolved in 80 mL of DMAc in a 300-mL flask with stirring. After the mixture was completely dissolved, potassium carbonate (0.15 mol) was added to it in one portion, and the mixture was stirred at room temperature for 30 min and then heated at 100°C for 12 h. The obtained mixture was poured into 400 mL of methanol–water (volume ratio = 10 : 1) to give a solid, which was collected, washed thoroughly with methanol and hot water, and dried *in vacuo* at 60°C. The crude product was recrystallized from DMF–methanol to give fine, pale cream crystals of dinitro compound **1** (87 g, 98%). Then, to a suspension solution of the purified compound **1** (60 g, 0.10 mol) and 10% Pd/C (0.2 g) in ethanol (150 mL), hydrazine monohydrate (10 mL) was added at 70°C within 30 min. After this addition, the mixture was

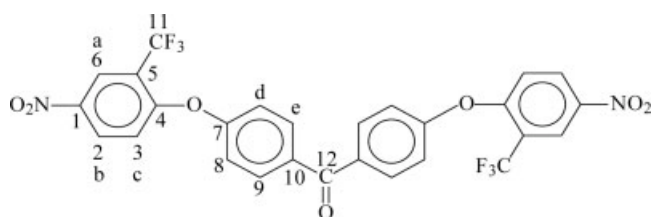


Scheme 1

heated at reflux temperature for 6 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- to cream-colored crystals, which were dried *in vacuo* at room temperature to give diamine **2** (46 g, 87%; mp = 152–153°C).

#### Dinitro compound **1**

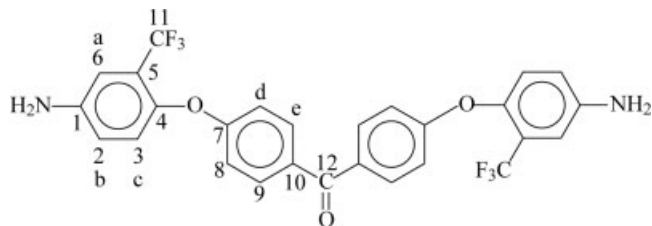
$^1\text{H-NMR}$  [500 MHz, dimethyl sulfoxide (DMSO)- $d_6$ ,  $\delta$ ]: 8.57, 8.56 (2H, d,  $\text{H}_a$ ); 8.51–8.54 (2H, dd,  $\text{H}_b$ ); 7.92–7.95 (4H, dt,  $\text{H}_c$ ); 7.39–7.42 (4H, dt,  $\text{H}_d$ ); 7.38, 7.34 (2H, d,  $\text{H}_e$ ).  $^{13}\text{C-NMR}$  (125 MHz, DMSO- $d_6$ ,  $\delta$ ): 193.3 ( $\text{C}^{12}$ ), 158.8 ( $\text{C}^4$ ), 157.7 ( $\text{C}^7$ ), 142.6 ( $\text{C}^1$ ), 134.1 ( $\text{C}^{10}$ ), 132.4 ( $\text{C}^9$ ), 130.1 ( $\text{C}^2$ ), 123.4 ( $\text{C}^6$ , quartet,  $^3J_{\text{C-F}} = 5$  Hz), 122.15 ( $\text{C}^{11}$ , quartet,  $^1J_{\text{C-F}} = 273$  Hz), 120 ( $\text{C}^5$ , quartet,  $^2J_{\text{C-F}} = 32$  Hz), 119.9 ( $\text{C}^3$ ), 119.7 ppm ( $\text{C}^8$ ).



**Dinitro Compound 1**

#### Diamine compound **2**

$^1\text{H-NMR}$  (500 MHz, DMSO- $d_6$ ,  $\delta$ ): 7.74–7.77 (4H, dt,  $\text{H}_e$ ); 7.03, 7.01 (2H, d,  $\text{H}_c$ ); 7.01, 6.99 (4H, d,  $\text{H}_d$ ); 7.00 (2H, d,  $\text{H}_a$ ); 6.89–6.91 (2H, dd,  $\text{H}_b$ ).  $^{13}\text{C-NMR}$  (125 MHz, DMSO- $d_6$ ,  $\delta$ ): 193.1 ( $\text{C}^{12}$ ), 162.0 ( $\text{C}^7$ ), 146.6 ( $\text{C}^4$ ), 140.8 ( $\text{C}^1$ ), 132.0 ( $\text{C}^9$ ), 131.3 ( $\text{C}^{10}$ ), 124.0 ( $\text{C}^3$ ), 123.4 ( $\text{C}^{11}$ , quartet,  $^1J_{\text{C-F}} = 272$  Hz), 121.9 ( $\text{C}^5$ , quartet,  $^2J_{\text{C-F}} = 30$  Hz), 120.1 ( $\text{C}^2$ ), 115.8 ( $\text{C}^8$ ), 110.8 ( $\text{C}^6$ , quartet,  $^3J_{\text{C-F}} = 5$  Hz).



**Diamine Compound 2**

#### Synthesis of DIDA

DIDA, 4,4'-bis(4-trimellitamide-2-trifluoromethyl-phenoxy)benzophenone (**3**) was obtained from TMA, and other DIDAs (**5B<sub>a</sub>**–**5B<sub>g</sub>**) were synthesized in an analogous procedure, as shown in Scheme 2. For example, the synthesis of DIDA (**3**) was performed

as following: 10.65 g (20 mmol) of fluorinated diamine **2** was dissolved in 60 mL of NMP, and 7.69 g (40 mmol) of TMA was added with stirring at room temperature for 1 h. Then, 20 mL of toluene was added, and the mixture was heated with reflux for 6 h until 0.72 mL of water was distilled azeotropically. After the complete removal of water, the residual toluene was distilled off under reduced pressure. The mixture was left to cool by filtration and 40 mL of methanol was added for one night to induce crystallization. Then, methanol was used to wash the products; the products were dried at 120°C and heated at 200°C for 1 h *in vacuo* to give 16.90 g of pale yellow powder (yield = 96%, mp = 302–303°C):

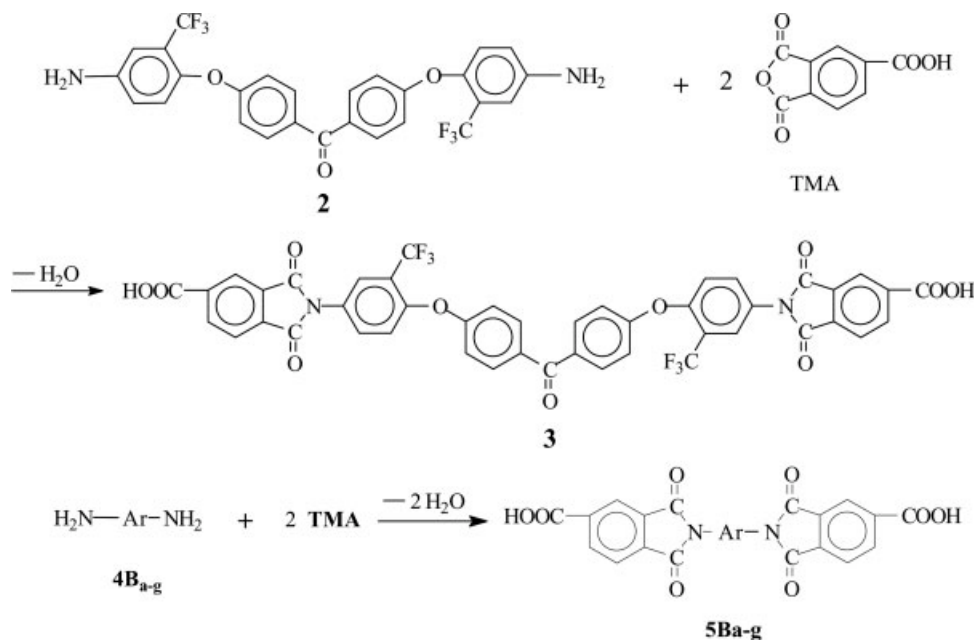
IR (KBr,  $\text{cm}^{-1}$ ): 3500–2500 (carboxylic acid —OH); 1781, 1729 (imide C=O); 1097, 727  $\text{cm}^{-1}$  (imide ring C—N).  $^1\text{H-NMR}$  (500 MHz, DMSO- $d_6$ ,  $\delta$ ): 8.44, 8.43 (1H,  $\text{H}_b$ ); 8.32 (1H,  $\text{H}_a$ ); 8.11, 8.10 (1H,  $\text{H}_c$ ); 8.04 (1H,  $\text{H}_d$ ); 7.90, 7.89 (1H,  $\text{H}_h$ ); 7.86–7.88 (1H,  $\text{H}_e$ ); 7.48, 7.46 (1H,  $\text{H}_i$ ); 7.31, 7.29 (1H,  $\text{H}_g$ ).  $^{13}\text{C-NMR}$  (125 MHz, DMSO- $d_6$ ,  $\delta$ ): 193.2 ( $\text{C}^{19}$ ), 173.9 ( $\text{C}^1$ ), 165.8–166.1 ( $\text{C}^{2,2'}$ ), 159.6 ( $\text{C}^{15}$ ), 152.7 ( $\text{C}^{12}$ ), 136.7 ( $\text{C}^6$ ), 135.6 ( $\text{C}^3$ ), 134.8 ( $\text{C}^8$ ), 133.4 ( $\text{C}^5$ ), 133.0 ( $\text{C}^9$ ), 132.4 ( $\text{C}^{17}$ ), 132.0 ( $\text{C}^{18}$ ), 127.9 ( $\text{C}^4$ ), 126.3 ( $\text{C}^{10}$ , quartet,  $^3J_{\text{C-F}} = 5$  Hz), 123.9 ( $\text{C}^7$ ), 23.5 ( $\text{C}^{14}$ ), 121.8 ( $\text{C}^{20}$ , quartet,  $^1J_{\text{C-F}} = 271$  Hz), 121.5 ( $\text{C}^{13}$ ), 120.8 ( $\text{C}^{11}$ , quartet,  $^2J_{\text{C-F}} = 31$  Hz), 118.3 ( $\text{C}^{16}$ ). ANAL. Calcd for  $\text{C}_{45}\text{H}_{22}\text{N}_2\text{O}_{11}\text{F}_6$  (880.67): C, 61.37%; H, 2.52%; N, 3.18%. Found: C, 60.50%; H, 2.61%; N, 3.74%.

Other DIDAs (**5B<sub>a</sub>**–**5B<sub>g</sub>**) were synthesized in an analogous procedure.

#### Synthesis of PAIs (**6A<sub>a</sub>**–**6A<sub>k</sub>** and **6B<sub>a</sub>**–**6B<sub>g</sub>**)

The synthesis of **6A<sub>c</sub>** was a typical procedure. A mixture of 0.216 g (1.000 mmol) of **4A<sub>c</sub>**, 0.880 g (1 mmol) of diacid **3**, 0.24 g of  $\text{CaCl}_2$ , 1.4 mL of Py, 0.6 mL of TPP, and 3 mL of NMP was heated with stirring at 100°C for 4 h. At the end of the reaction, the obtained polymer solution was trickled into stirred methanol. The yellow stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C under reduced pressure. The inherent viscosity ( $\eta_{\text{inh}}$ ) of **6A<sub>c</sub>** was 1.37 dL/g. All of the other PAIs were synthesized with similar methods:

IR (film): 1779 (asymmetric C=O stretch); 1724 (symmetric imide C=O stretch); 1654 (amide N—H); 1145, 723  $\text{cm}^{-1}$  (imide ring deformation).  $^1\text{H-NMR}$  (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 10.75 (2H, d,  $\text{H}_k$ ); 8.55 (2H, s,  $\text{H}_i$ ); 8.47, 8.45 (2H, d,  $\text{H}_h$ ); 8.15, 8.13 (2H, d,  $\text{H}_g$ ); 8.03 (1H, s,  $\text{H}_a$ ); 7.88 (4H, s,  $\text{H}_e$ ); 7.86 (2H, s,  $\text{H}_b$ ); 7.85 (4H, d,  $\text{H}_j$ ); 7.47, 7.45 (2H, d,  $\text{H}_c$ ); 7.36 (4H, d,  $\text{H}_l$ ); 7.28, 7.26 (4H, d,  $\text{H}_d$ ).  $^{13}\text{C-NMR}$  (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 193.2 ( $\text{C}^{11}$ ), 166.2, 166.1 ( $\text{C}^{24,24'}$ ), 163.5 ( $\text{C}^{19}$ ), 159.4 ( $\text{C}^7$ ), 152.5 ( $\text{C}^4$ ), 140.1 ( $\text{C}^{15}$ ), 138.1 ( $\text{C}^{18}$ ), 134.4 ( $\text{C}^{20}$ ), 133.8 ( $\text{C}^{10}$ ), 133.5 ( $\text{C}^{13}$ ), 132.9 ( $\text{C}^{23}$ ), 132.3 ( $\text{C}^{22}$ ), 131.7 ( $\text{C}^{16}$ ),



Scheme 2

131.3 (C<sup>21</sup>), 129.9 (C<sup>17</sup>), 127.9 (C<sup>1</sup>), 126.3 (C<sup>14</sup>), 123.7 (C<sup>2</sup>), 122.3 (C<sup>3</sup>), 121.5 (C<sup>6</sup>), 121.7 (C<sup>12</sup>, quartet, <sup>1</sup>J<sub>C-F</sub> = 270 Hz), 121.4 (C<sup>9</sup>), 120.7 (C<sup>5</sup>, quartet, <sup>2</sup>J<sub>C-F</sub> = 31 Hz), 118.1 (C<sup>8</sup>; shown later in Fig. 3).

Others were prepared by a similar method, and the condition of PAIs synthesis are listed in Table I.

TABLE I  
Synthesis of PAIs

Polymer	Reagent <sup>a</sup>					$\eta_{\text{inh}}$ (dL/g) <sup>b</sup>
	NMP (mL)	CaCl <sub>2</sub> (g)	Py (mL)	TPP (mL)	Additional NMP (mL)	
6A <sub>a</sub>	1.4	0.22	1.4	0.6	0	0.78
6A <sub>b</sub>	1.1	0.22	1.4	0.6	2.2	0.94
6A <sub>c</sub>	1.2	0.24	1.4	0.6	1.8	1.37
6A <sub>d</sub>	1.1	0.22	1.3	0.6	2.8	0.96
6A <sub>e</sub>	2.8	0.25	1.4	0.6	0	0.78
6A <sub>f</sub>	1.2	0.24	1.4	0.6	2.4	1.00
6A <sub>g</sub>	1.2	0.24	1.5	0.6	0	0.74
6A <sub>h</sub>	1.2	0.25	1.5	0.6	1.2	0.82
6A <sub>i</sub>	1.2	0.23	1.4	0.6	2.3	0.79
6A <sub>j</sub>	1.2	0.25	1.3	0.6	0.6	0.83
6A <sub>k</sub>	1.4	0.24	1.5	0.6	2.0	0.99
6B <sub>a</sub>	4	0.3	1	0.6	8	0.88
6B <sub>b</sub>	4	0.27	1	0.6	8	1.06
6B <sub>c</sub>	4	0.27	1	0.6	6	1.16
6B <sub>d</sub>	4	0.24	1	0.6	6	1.29
6B <sub>e</sub>	4	0.24	1	0.6	6	1.76
6B <sub>f</sub>	3.7	0.25	1	0.6	1.3	1.09
6B <sub>g</sub>	4	0.26	1	0.6	4	1.08

<sup>a</sup> The polymerizations were carried out with 1 mmol of each monomer at 100°C.

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

### Film preparation

A solution of the polymer was made by the dissolution of about 0.45 g of the PAI in 5 mL of DMAc to afford an approximate 10 wt % solution. The homogeneous solution was poured into a glass culture dish 9 cm in diameter, which was placed in a 110°C oven overnight to evaporate the solvent and to form a solid film and was then sequentially heated to 200°C and held at that temperature for 1 h. Polymer films were self-stripped off from the glass surface by soaking in water. The polymer films were further dried *in vacuo* at 160°C for 12 h.

### Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a Heraeus VarioEL-III CHN analyzer. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were measured on a Bruker AV-500 Fourier transform NMR spectrometer.  $\eta_{\text{inh}}$ 's were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30°C. Weight-average molecular weights ( $M_w$ 's) and number-average molecular weights ( $M_n$ 's) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration with a Waters 2410 apparatus and with THF as the eluent. The color intensity of the polymers was evaluated on a Macbeth color-eye colorimeter. Measurements were performed for the films at an observational angle of 10° and with a Commission Internationale de l'clairage (CIE)-D illuminant. A CIE  $L^*a^*b^*$  color difference



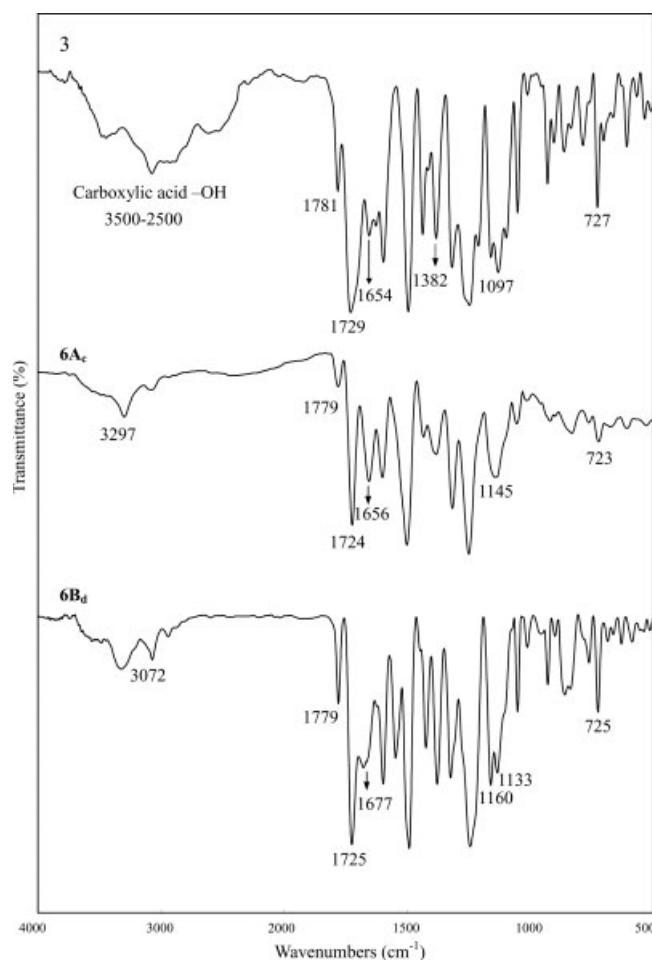
equation was used. Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV-vis spectrophotometer.  $T_g$  of the polymer were measured on TA Instruments DSC 2010 in flowing nitrogen  $40\text{ cm}^3/\text{min}$  at a heating rate of  $15^\circ\text{C}/\text{min}$ . 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 ( $90\text{ cm}^3/\text{min}$ ) at a heating rate of  $20^\circ\text{C}/\text{min}$ . The mechanical properties of the films were measured on an Instron model 1130 tensile tester with a 5-kg load cell at a crosshead speed of  $5\text{ cm}/\text{min}$  on strips approximately  $30\text{--}60\ \mu\text{m}$  thick and  $0.5\text{ cm}$  wide with a 2-cm gauge length. An average of at least five individual determinations was used.

## RESULTS AND DISCUSSION

### Synthesis of DIDA

Fluorinated DIDA **3** was synthesized as shown in Scheme 2. DIDA **3** was synthesized by the ring-opening addition of fluorinated diamine **2** and TMA at a 1 : 2 molar rate at room temperature in NMP to yield the intermediate diamide tetraacid; this was followed by intramolecular cyclodehydration by toluene–water azeotropic distillation. After distillation of toluene, the DIDA/NMP solution was obtained, and this was then cooled, washed with methanol, and vacuum-dried at  $200^\circ\text{C}$  for 2 h to give the yellow crystalline products.

DIDA **3** was confirmed by elemental analysis, IR,  $^1\text{H}$ , and  $^{13}\text{C}$ -NMR spectroscopy. The FTIR characteristic absorptions of DIDA **3** are shown in Figure 1. As the diacid was prepared, the characteristic absorption bands of carboxylic acid were observed at  $2500\text{--}3500$  and  $1654\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  of carboxylic acid), and imide rings were observed at  $1781$ ,  $1729$ ,  $1382$ ,  $1097$ , and  $727\text{ cm}^{-1}$ . In the  $^1\text{H}$ -NMR spectrum (Fig. 2),  $\text{H}_b$  and  $\text{H}_a$  adjacent to carboxylic acid and the imide ring resonated at farthest downfield because of the inductive effect and resonance;  $\text{H}_f$  and  $\text{H}_g$  ortho-oriented to aromatic ether shifted to the upfield. All of the  $^{13}\text{C}$  atoms of DIDA **3** showed 20 main signals (Fig. 2), and there were three quartets because of the heteronuclear  $^{13}\text{C}\text{--}^{19}\text{F}$  coupling. The large quartet centered at about 121 ppm was due to the one-bond  $\text{C}\text{--}\text{F}$  ( $\text{C}^{20}$ ); its coupling constant was 271 Hz. The  $\text{CF}_3$ -attached carbon ( $\text{C}^{11}$ ) also showed a clear quartet centered at about 119.8 ppm with a smaller coupling constant of 31 Hz due to two-bond  $\text{C}\text{--}\text{F}$  coupling. In addition,  $\text{C}^{10}$  (ortho to the  $\text{CF}_3$  group) also had its resonance split by the three fluorines (three-bond coupling); its coupling constant was 5 Hz. The previous results show that DIDA **3** was synthesized successfully.



**Figure 1** FTIR spectra of diimide-diacid **3** and PAIs **6A<sub>c</sub>** and **6B<sub>a</sub>**.

### Synthesis of the polymers

Aromatic PAIs (**6A<sub>a</sub>**–**6A<sub>k</sub>** and **6B<sub>a</sub>**–**6B<sub>g</sub>**) containing trifluoromethyl groups were synthesized from diamine (**4A<sub>a</sub>**–**4A<sub>k</sub>** or **2**) and the imide-containing diacids (**3** or **5B<sub>a</sub>**–**5B<sub>g</sub>**) by the direct polycondensation procedure with TPP/Py as condensing agents (Scheme 3). To understand the influence on the physical properties of the position of diamine **2** in PAIs, diamine (**2**) was also synthesized with TMA to produce DIDA (**3**). Isomeric PAI **6A<sub>a</sub>**, which has diamine **2** in the imide segments, were synthesized by **3** and aromatic diamines **4A<sub>a</sub>**–**4A<sub>k</sub>** (Scheme 3).

The synthesis conditions and  $\eta_{\text{inh}}$ 's of these aromatic PAIs (**6A<sub>a</sub>**–**6A<sub>k</sub>** and **6B<sub>a</sub>**–**6B<sub>g</sub>**) are summarized in Table I.  $\eta_{\text{inh}}$  values of the polymers could be obtained with a higher initial reaction concentration and added an additional amount of NMP to the highly viscous reaction medium before the formation of swollen gel.  $\eta_{\text{inh}}$  values for **6A<sub>a</sub>**–**6A<sub>k</sub>** and **6B<sub>a</sub>**–**6B<sub>g</sub>** ranged from 0.78–1.76 dL/g, indicating a moderate-to-high-molecular-weight polymer.

A typical IR spectrum is shown in Figure 1. The IR spectrum of **6A<sub>c</sub>** showed characteristic absorptions for

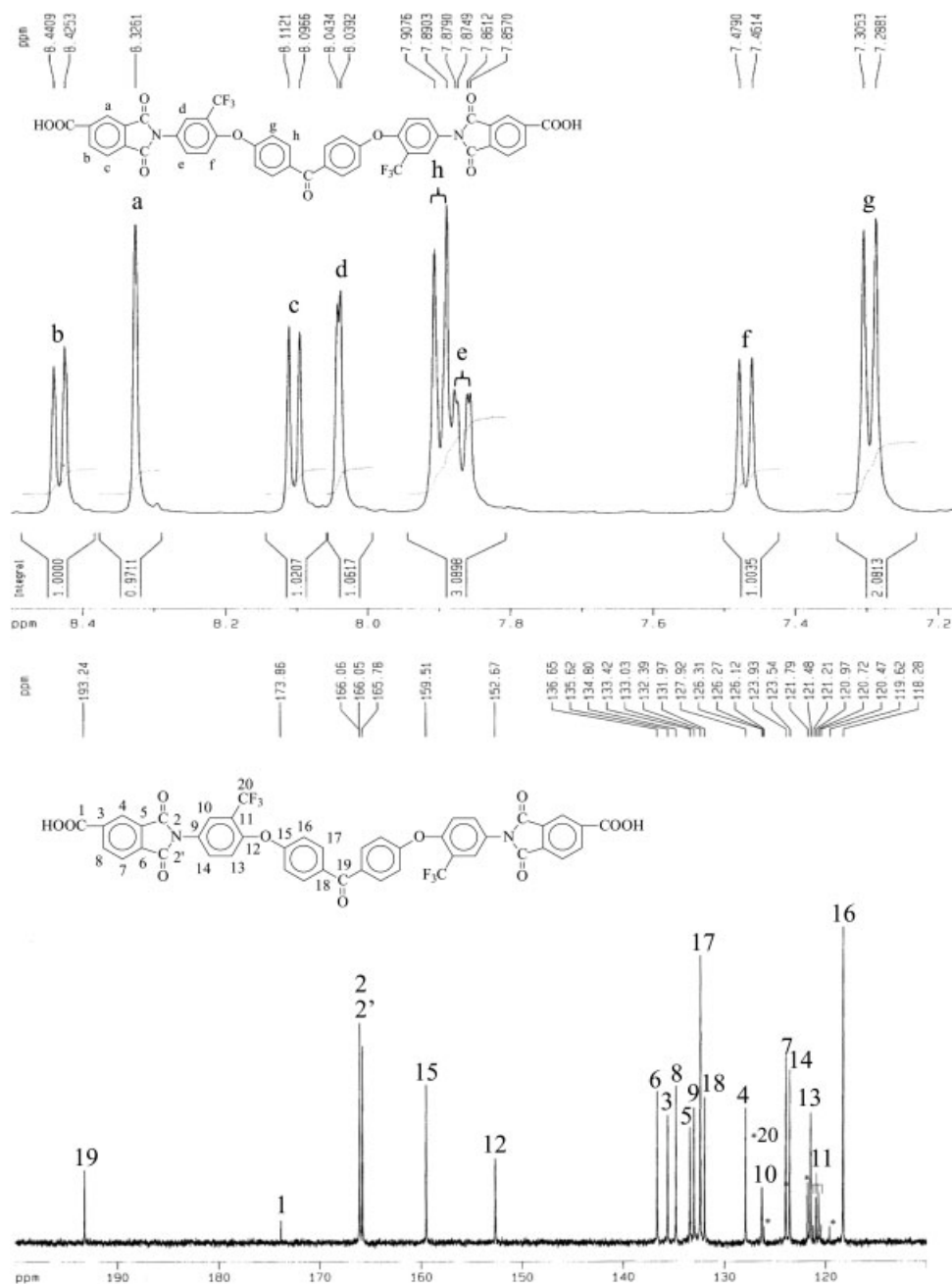


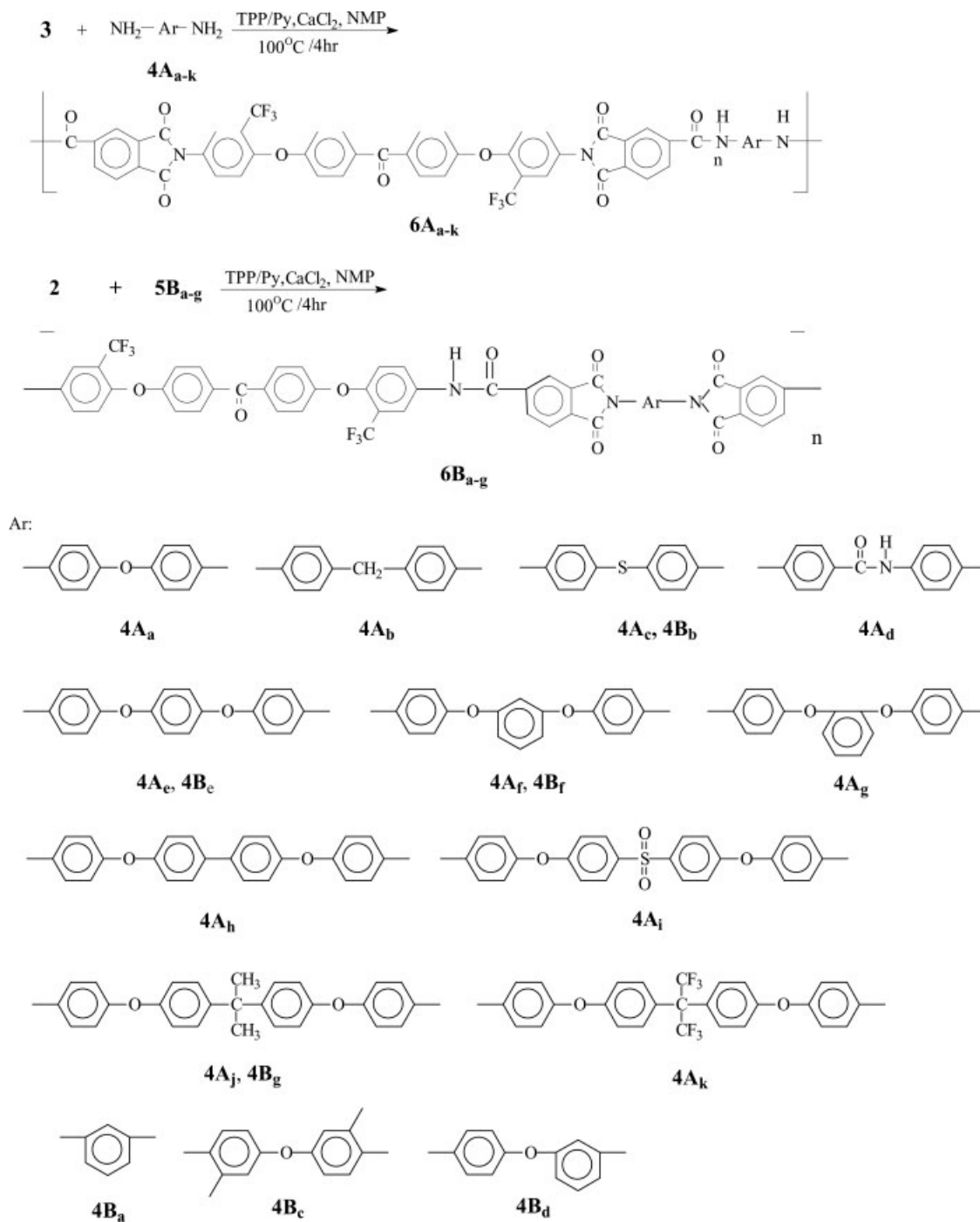
Figure 2 <sup>1</sup>H and <sup>13</sup>C spectra of diimide-diacid **3** in DMSO-*d*<sub>6</sub>.

the imide ring at 1779 and 1724 cm<sup>-1</sup> due to the asymmetrical and symmetrical carbonyl stretching vibration and at 1145 and 723 cm<sup>-1</sup>, due to ring deformation, and the amide ring at 3297 and 1656 cm<sup>-1</sup>. The IR spectrum for **6B<sub>d</sub>**, which exhibited characteristic absorptions for the imide ring at 1779 and 1725 cm<sup>-1</sup>, ring deformation at 1133 and 725 cm<sup>-1</sup>, and the absorption of an amide group, appeared at 3072 (N—H stretch) and 1677 (C=O stretch) cm<sup>-1</sup>.

The typical <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of **6A<sub>c</sub>** are shown in Figure 3. The aromatic protons of **6A<sub>c</sub>** were in the region 7.28–8.44 ppm. H<sub>d</sub> shifted to a higher field due to the electron-donating property of

the ether group, and H<sub>f</sub> close to the imide ring appeared at the farthest downfield. The <sup>13</sup>C-NMR of **6A<sub>c</sub>** showed 24 main signals, and the number of C was still consistent with the structure. The large quartet centered at about 122 ppm was due to the one-bond C—F (C<sup>12</sup>); its coupling constant was 270 Hz. The CF<sub>3</sub>-attached carbon (C<sup>5</sup>) also showed a clear quartet centered at about 121 ppm with a smaller coupling constant of 31 Hz due to two-bond C—F coupling. C<sup>11</sup> of the ketone group and C<sup>24,24'</sup> of the carbonyl group were evidenced in the downfield.

The results of the elemental analysis are listed in Table II, which shows that the PAIs had slight



Scheme 3

moisture absorption because of their amide groups. The observed values were corrected by the elimination of the amount of absorbed water, and the corrected values were in good agreement with the calculated ones. From the GPC data (Table II), the  $M_w$  and  $M_n$  values of polymer dissolving in THF were available in the ranges  $4.0 \times 10^4$  to  $7.5 \times 10^4$  and  $6.4 \times 10^4$  to  $10.0 \times 10^4$ , respectively, relative to standard polystyrene, and one of the GPC curve is shown in Figure 4. The polydispersity indices (PDIs) of these polymers were in the range 1.30–1.61. The aforemen-

tioned results, including FTIR, elemental analysis, and NMR spectra (see the Experimental section), show that the **6A** and **6B** series were synthesized successfully.

### Properties of the polymers

The solubility of the aromatic PAIs (**6A<sub>a</sub>–6A<sub>k</sub>** and **6B<sub>a</sub>–6B<sub>g</sub>**) polymers is shown in Table III. Polymers (**6A<sub>a</sub>–6A<sub>k</sub>** and **6B<sub>a</sub>–6B<sub>g</sub>**) could be dissolved at room temperature in amide type solvents, such as NMP,

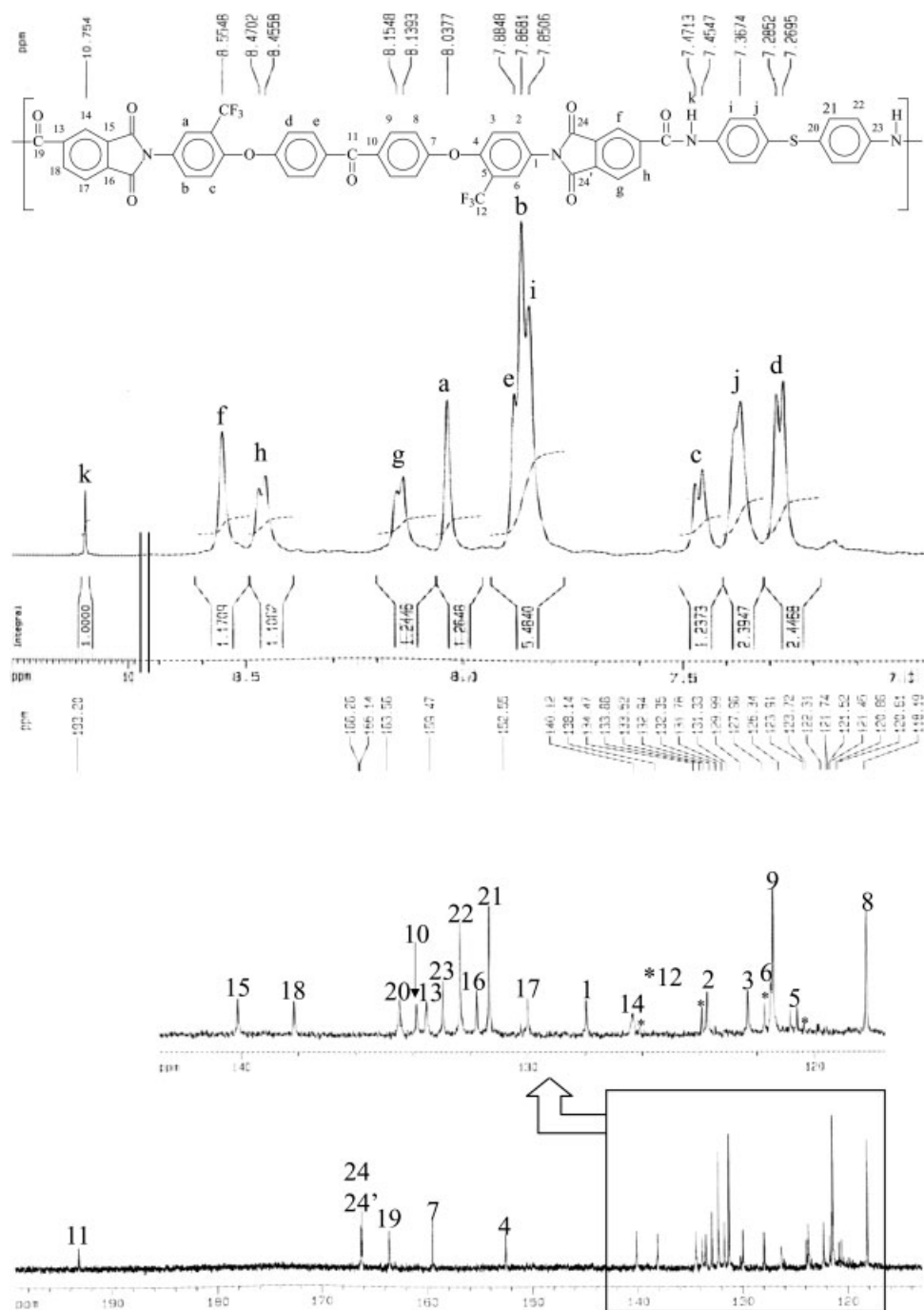


Figure 3 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of PAI 6A<sub>c</sub> in DMSO-*d*<sub>6</sub>.

DMAc, and DMF. Thus, these polymers could be solution (DMAc) cast into polymer films easily. Most of the polymers were also soluble in *m*-cresol, Py, and THF except 6A<sub>d</sub>. Because 6A<sub>d</sub> contained more amide groups, they made the hydrogen bond between polymer chains stronger. The solubility of polymers was very different in dioxane and was based on the polymer's structure. Aromatic PAIs, such as 6A<sub>h</sub>, 6B<sub>a</sub> and 6B<sub>c</sub>, with more rigid structures were insoluble in dioxane. 6A<sub>j</sub>–6A<sub>k</sub> and 6B<sub>g</sub> revealed good solubility in diox-

ane due to the bulky substituent group in the side chain or backbone, which could reduce the interaction between the polymer chains to enhance solubility. However, all polymers were not soluble in CH<sub>2</sub>Cl<sub>2</sub>. When the 6A and the 6B series were compared, there were only slightly different solubilities in dioxane and CH<sub>2</sub>Cl<sub>2</sub>.

The color intensities of the polymer were determined by the polymer structure. If a monomer has color or colored byproducts that are not eliminated



TABLE II  
Elemental Analysis and GPC Data for PAIs

Polymer	Formula ( $M_w$ )		Elemental analysis (%) <sup>a</sup>			GPC data <sup>a</sup>		
			C	H	N	$M_n \times 10^4$	$M_w \times 10^4$	$M_w/M_n$
<b>6A<sub>a</sub></b>	(C <sub>57</sub> H <sub>30</sub> N <sub>4</sub> O <sub>10</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	65.52	2.89	5.36	3.97	6.39	1.61
		Found	63.67	2.90	5.37			
<b>6A<sub>b</sub></b>	(C <sub>58</sub> H <sub>32</sub> N <sub>4</sub> O <sub>9</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.80	3.09	5.37	7.01	9.79	1.40
		Found	64.59	3.0	5.44			
<b>6A<sub>c</sub></b>	(C <sub>57</sub> H <sub>30</sub> N <sub>4</sub> O <sub>9</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.54	2.94	5.45	7.25	9.66	1.33
		Found	65.68	2.95	5.46			
<b>6A<sub>d</sub></b>	(C <sub>58</sub> H <sub>31</sub> N <sub>5</sub> O <sub>10</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.99	2.92	6.53	—	—	—
		Found	64.59	2.82	6.62			
<b>6A<sub>e</sub></b>	(C <sub>63</sub> H <sub>34</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.55	3.01	4.93	5.00	7.45	1.50
		Found	65.02	2.90	4.93			
<b>6A<sub>f</sub></b>	(C <sub>63</sub> H <sub>34</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.55	3.01	4.93	5.55	7.88	1.42
		Found	65.10	3.03	4.95			
<b>6A<sub>g</sub></b>	(C <sub>63</sub> H <sub>34</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.55	3.01	4.93	6.80	9.34	1.37
		Found	64.80	3.05	4.98			
<b>6A<sub>h</sub></b>	(C <sub>69</sub> H <sub>38</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	68.32	3.16	4.62	—	—	—
		Found	67.58	3.09	4.67			
<b>6A<sub>i</sub></b>	(C <sub>69</sub> H <sub>38</sub> N <sub>4</sub> O <sub>13</sub> F <sub>6</sub> S) <sub>n</sub>	Calcd	64.89	3.00	4.39	5.01	7.22	1.44
		Found	63.02	3.07	4.27			
<b>6A<sub>j</sub></b>	(C <sub>72</sub> H <sub>44</sub> N <sub>4</sub> O <sub>13</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	67.19	3.45	4.35	4.91	7.17	1.46
		Found	67.13	3.46	4.42			
<b>6A<sub>k</sub></b>	(C <sub>71</sub> H <sub>38</sub> N <sub>4</sub> O <sub>11</sub> F <sub>12</sub> ) <sub>n</sub>	Calcd	63.12	2.83	4.15	5.32	8.14	1.53
		Found	64.26	2.90	4.32			
<b>6B<sub>a</sub></b>	(C <sub>51</sub> H <sub>26</sub> N <sub>4</sub> O <sub>9</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	64.29	2.75	5.88	—	—	—
		Found	63.46	2.77	5.91			
<b>6B<sub>b</sub></b>	(C <sub>57</sub> H <sub>30</sub> N <sub>4</sub> O <sub>9</sub> F <sub>6</sub> S <sub>1</sub> ) <sub>n</sub>	Calcd	64.53	2.85	5.28	6.00	9.61	1.60
		Found	62.51	2.90	5.31			
<b>6B<sub>c</sub></b>	(C <sub>59</sub> H <sub>34</sub> N <sub>4</sub> O <sub>9</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	67.05	3.24	5.30	6.52	9.20	1.41
		Found	67.75	3.26	5.18			
<b>6B<sub>d</sub></b>	(C <sub>57</sub> H <sub>30</sub> N <sub>4</sub> O <sub>10</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	65.52	2.89	5.36	7.58	9.96	1.31
		Found	64.04	3.12	5.48			
<b>6B<sub>e</sub></b>	(C <sub>63</sub> H <sub>34</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.55	3.01	4.93	5.24	7.78	1.48
		Found	64.98	3.06	4.94			
<b>6B<sub>f</sub></b>	(C <sub>63</sub> H <sub>34</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	65.55	3.01	4.93	5.42	7.76	1.43
		Found	65.07	3.10	4.98			
<b>6B<sub>g</sub></b>	(C <sub>72</sub> H <sub>44</sub> N <sub>4</sub> O <sub>11</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	68.93	3.53	4.46	4.65	7.30	1.57
		Found	67.51	3.55	4.52			

<sup>a</sup> With respect to a polystyrene standard and with THF as the eluent (**6A<sub>d</sub>**, **6A<sub>h</sub>**, and **6B<sub>a</sub>** were insoluble in THF).

fully, the polymers show color. The CTC formation between polymer chains through steric hindrance also influences the color intensities of the polymer. A lowering of the formation of the CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties provides polyimides with lighter colors.<sup>27,28</sup> The color coordinates of these polymers are given in Table IV. In this case, we based our judgment of the degree of yellowness on the yellowness index ( $b^*$ ) value.

The imide-containing isomeric PAIs (the **6A** and **6B** series) were deeper colored (a larger  $b^*$  value) due to the intermolecular CTC formation. The values of the parameter  $b^*$  of the **6B** series was between 33.9 and 51.4, whereas the value of the parameter  $b^*$  of the **6A** series was between 54.5 and 85.4. By comparing the  $b^*$  value of the **6B** polymers with their analogous **6A** series, the  $b^*$  values of the **6B**

polymers was apparently lower than those of the corresponding **6A** polymers. Polymers such as **6A<sub>e</sub>**–**6A<sub>f</sub>** and isomeric **6B<sub>e</sub>**–**6B<sub>f</sub>** were synthesized by the same monomer but via a different process (as shown in Scheme 3) and exhibited different coloration. The polymer structure of **6B** had a lower intermolecular CTC effect than the isomeric **6A**; this led to the polymers of **6B** showing a lighter color than the polymers of **6A** (as shown in Fig. 5).

Moreover, the color intensities of the polymers could also be elucidated from the cutoff wave number ( $\lambda_0$ ) observed in the UV–vis absorption spectra. When the  $\lambda_0$  value was close to UV regions (200–400 nm), the color of the polymers was lighter. Although the  $\lambda_0$  values of the **6A** and **6B** series were higher than 400 nm, the results conformed to the  $b^*$  values. The **6B** series showed lower  $\lambda_0$  values and higher transmittance than the **6A** series; this showed that

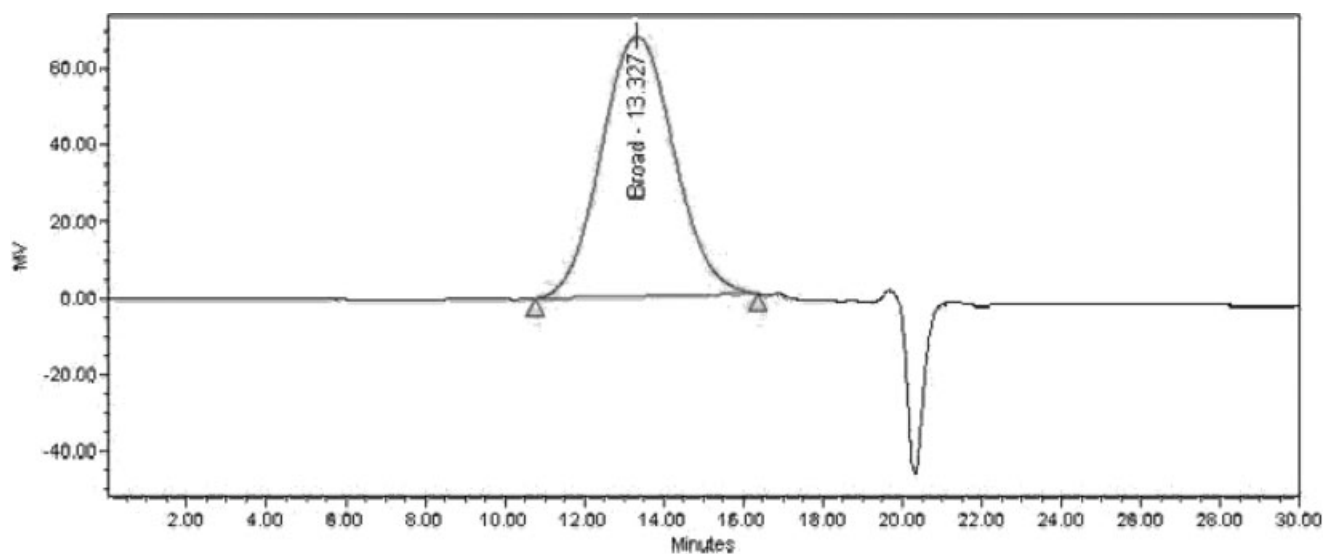


Figure 4 GPC curve of the PAI 6A<sub>c</sub>.

the 6B series was indeed lighter colored than the 6A series. Moreover, 6B<sub>f</sub> had better optical properties than 6B<sub>e</sub> because the metastructure reduced the CTC formation (as shown in Fig. 6).

The thermal properties of all of the polymers was evaluated by TGA and differential scanning calorimetry (DSC) measurements. The results are summarized in Table IV. Quenching from an elevated temperature of about 400°C to room temperature in air gave predominantly amorphous samples so that the  $T_g$  values of all the polymers could be easily

revealed in the subsequent DSC scans. The  $T_g$  values of aromatic PAIs (6A<sub>a</sub>–6A<sub>k</sub> and 6B<sub>a</sub>–6B<sub>g</sub>) were in the range 242–279°C, which followed the decreasing order of the chain flexibility and steric hindrance of the polymers backbones. In general, the incorporation of a less symmetric *m*-phenylene unit leads to a decrease in  $T_g$ . For example, the polymers of 6A<sub>e</sub> and 6B<sub>e</sub>, which contained parasubstituted phenylene rings, had higher  $T_g$  values than did the analogous polymers of 6A<sub>f</sub> and 6B<sub>f</sub>, which contained metasubstituted phenylene rings units, respectively.

TABLE III  
Solubility of PAIs<sup>a</sup>

Polymer	Solvent						
	Amide-type solvent (NMP, DMAc, and DMF)	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH <sub>2</sub> Cl <sub>2</sub>
6A <sub>a</sub>	++	++	++	++	–	++	–
6A <sub>b</sub>	++	++	++	++	–	++	–
6A <sub>c</sub>	++	++	++	++	–	++	–
6A <sub>d</sub>	++	++	–	–	–	–	–
6A <sub>e</sub>	++	++	++	++	++	++	–
6A <sub>f</sub>	++	++	++	++	++	++	–
6A <sub>g</sub>	++	++	++	++	++	++	+
6A <sub>h</sub>	++	++	++	++	–	–	–
6A <sub>i</sub>	++	++	++	++	–	++	–
6A <sub>j</sub>	++	++	++	++	++	++	++
6A <sub>k</sub>	++	++	++	++	++	++	++
6B <sub>a</sub>	++	+	++	++	–	–	–
6B <sub>b</sub>	++	++	++	++	–	++	–
6B <sub>c</sub>	++	++	++	++	–	++	–
6B <sub>d</sub>	++	++	++	++	–	++	–
6B <sub>e</sub>	++	++	++	++	S	++	–
6B <sub>f</sub>	++	++	++	++	+	++	–
6B <sub>g</sub>	++	++	++	++	++	++	–

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

TABLE IV  
Color Coordinates of the PAIs

Polymer	Film thickness (μm)	$b^*$	$a^*$	$L^*$	Cutoff wavelength (nm)
6A <sub>a</sub>	69	71.5	-9.4	93.2	445
6A <sub>b</sub>	55	58.1	-7.4	92.3	424
6A <sub>c</sub>	55	84.4	7.2	86.5	460
6A <sub>d</sub>	47	77.5	4.0	85.2	448
6A <sub>e</sub>	45	72.8	-0.5	85.8	437
6A <sub>f</sub>	58	65.7	2.5	82.6	434
6A <sub>g</sub>	49	69.5	2.7	83.5	438
6A <sub>h</sub>	49	71.9	-4.0	89.4	436
6A <sub>i</sub>	64	54.5	-7.1	92.0	420
6A <sub>j</sub>	41	72.4	-9.0	92.5	433
6A <sub>k</sub>	45	62.8	-9.3	93.3	423
6B <sub>a</sub>	63	51.4	-2.5	86.0	418
6B <sub>b</sub>	52	33.9	-4.5	92.4	420
6B <sub>c</sub>	52	50.1	-0.2	86.4	407
6B <sub>d</sub>	73	37.9	-6.1	93.0	411
6B <sub>e</sub>	63	43.3	-8.1	94.1	409
6B <sub>f</sub>	58	36.3	-8.3	93.9	409
6B <sub>g</sub>	53	35.5	-8.6	95.1	408

The color parameters were calculated according to a CIE  $L^*a^*b^*$  color equation, with paper as the standard.  $L^*$  is lightness: 100 means white, whereas 0 implies black. A positive  $a^*$  value means a red color, whereas a negative  $a^*$  indicates a green color. A positive  $b^*$  value means a yellow color, whereas a negative  $b^*$  value implies a blue color.

The thermal stability of the polymers was characterized by TGA. The temperatures at 10% weight loss ( $T_{10}$ 's) in nitrogen and air atmospheres were determined from the original thermograms and are also tabulated in Table V. The  $T_{10}$  of PAIs (6A<sub>a</sub>-6A<sub>k</sub> and 6B<sub>a</sub>-6B<sub>g</sub>) stayed in the range 517-550°C in nitrogen and 486-533°C in air, respectively. These imide-containing polymers had higher  $T_{10}$  values due to the incorporation of the thermally stable imide group in the main chain. Compared the isomers of 6A and 6B, the  $T_{10}$  values of 6B were higher than 6A, such as 6B<sub>b</sub> > 6A<sub>c</sub> and 6B<sub>g</sub> > 6A<sub>j</sub>, as shown in

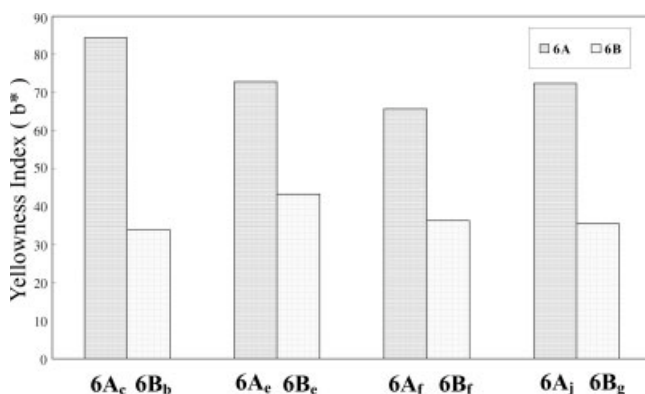


Figure 5 Comparison of the  $b^*$  value between PAIs in the 6A and 6B series.

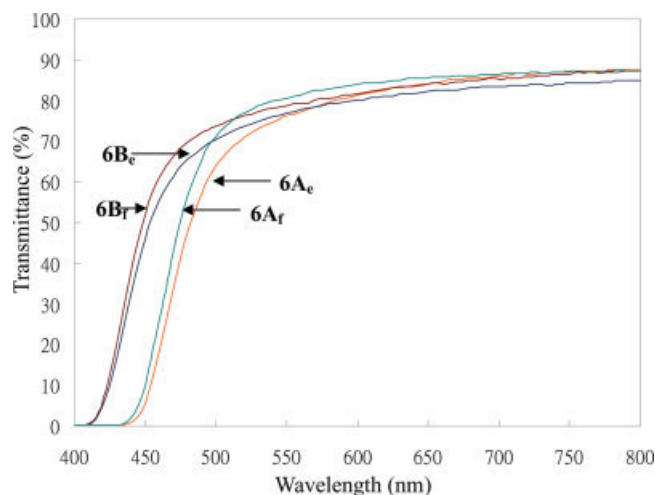


Figure 6 UV-vis spectra of the PAI films 6A<sub>e</sub>-6A<sub>f</sub> and 6B<sub>e</sub>-6B<sub>f</sub>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Figure 7. This indicated that the 6B series showed better thermal stability than the 6A series. Moreover, the chair yields of all these polymers at 800°C were above 48%.

All of the polymers were cast into transparent and flexible films from polymer solutions of DMAc. The results are summarized in Table VI. For aromatic PAIs (6A<sub>a</sub>-6A<sub>k</sub> and 6B<sub>a</sub>-6B<sub>g</sub>), these films had tensile strengths of 90-113 MPa, elongations at break of 8-

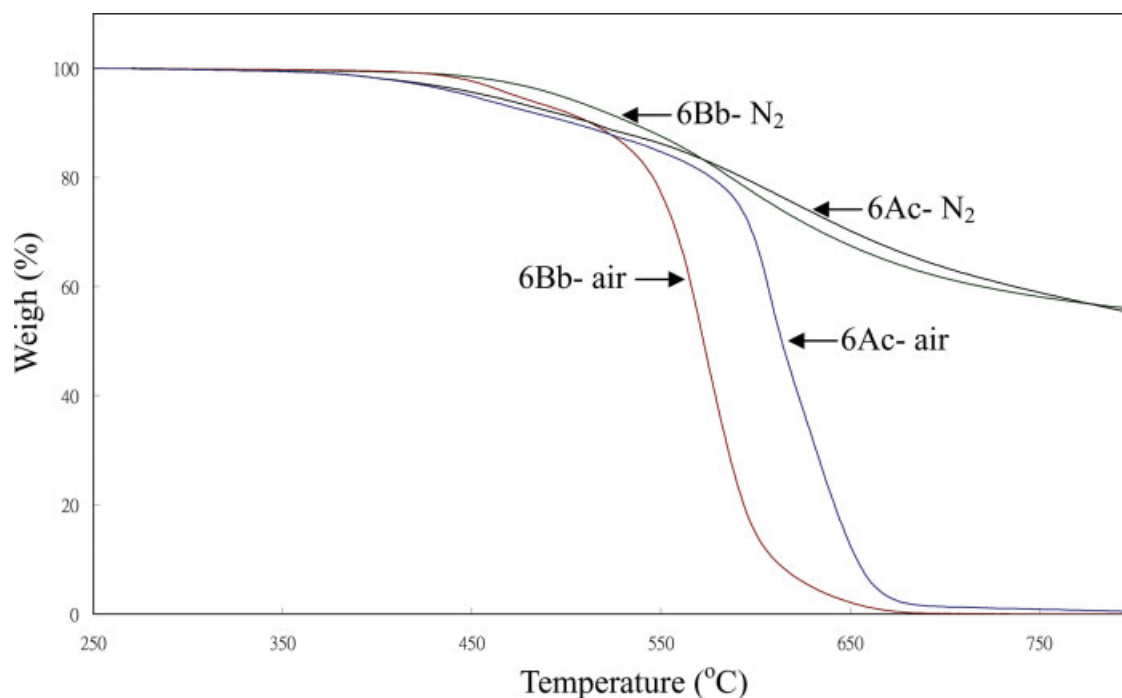
TABLE V  
Thermal Properties of PAIs

Polymer	$T_g$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>		Char yield (%) <sup>c</sup>
		In N <sub>2</sub>	In air	
6A <sub>a</sub>	266	525	515	53.2
6A <sub>b</sub>	270	527	502	54.6
6A <sub>c</sub>	268	522	508	60.4
6A <sub>d</sub>	271	513	504	59.6
6A <sub>e</sub>	252	534	522	55.8
6A <sub>f</sub>	246	543	522	58.9
6A <sub>g</sub>	246	539	509	57.5
6A <sub>h</sub>	257	550	523	61.6
6A <sub>i</sub>	264	537	512	56.0
6A <sub>j</sub>	274	517	500	55.5
6A <sub>k</sub>	258	541	533	56.3
6B <sub>a</sub>	279	531	516	56.1
6B <sub>b</sub>	254	533	516	56.9
6B <sub>c</sub>	254	518	486	60.2
6B <sub>d</sub>	260	529	534	56.8
6B <sub>e</sub>	265	536	522	57.1
6B <sub>f</sub>	242	532	532	57.9
6B <sub>g</sub>	252	527	517	55.8

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

<sup>b</sup> Recorded by thermogravimetry at a heating rate of 20°C/min under a nitrogen atmosphere.

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



**Figure 7** TGA curves of PAIs **6A<sub>c</sub>** and **6B<sub>b</sub>**. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

16%, and initial moduli of 2.1–2.9 GPa (Table VI). Most of **6A<sub>a</sub>–6A<sub>k</sub>** and **6B<sub>a</sub>–6B<sub>g</sub>** showed a clear yield point on their stress–strain curve, and they had strengths at a yield of 95–118 MPa. **6B<sub>c</sub>** had a higher tensile strength and initial modulus, which revealed good tensile properties with hard and strong characters. Also, most of the tensile strengths are increased

as the  $\eta_{inh}$ 's increased; for example, **6B<sub>e</sub>–6B<sub>f</sub>** showed higher tensile strengths than their isomers **6A<sub>e</sub>–6A<sub>f</sub>**. As shown by these results, these polymers all possessed good tensile properties with hard, strong, and tough mechanical characteristics.

## CONCLUSIONS

A series of high-molecular-weight aromatic PAIs (**6A<sub>a</sub>–6A<sub>k</sub>** and **6B<sub>a</sub>–6B<sub>g</sub>**) were obtained by the direct polycondensation reaction of a light-colored and CF<sub>3</sub>-containing diamine (**2**) and various diacids. These polymers exhibited better solubility than common aromatic PAIs through the introduction of the bulky CF<sub>3</sub> group in the polymer chains to reduce the packing efficiency. They were all soluble in the amide-type solvents. Most of the polymer films displayed yield points and had higher tensile strengths. In comparison with the isomeric **6A** series, **6B** PAIs exhibited less color together with good thermal and tensile properties.

**TABLE VI**  
Tensile Properties of the PAI Films<sup>a</sup>

Polymer	Strength at yield (MPa)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
<b>6A<sub>a</sub></b>	96	90	15	2.1
<b>6A<sub>b</sub></b>	97	93	11	2.2
<b>6A<sub>c</sub></b>	95	92	12	2.3
<b>6A<sub>d</sub></b>	106	105	16	2.5
<b>6A<sub>e</sub></b>	95	93	10	2.2
<b>6A<sub>f</sub></b>	95	94	8	2.3
<b>6A<sub>g</sub></b>	—	97	9	2.1
<b>6A<sub>h</sub></b>	—	95	8	2.2
<b>6A<sub>i</sub></b>	—	92	9	2.0
<b>6A<sub>j</sub></b>	98	94	11	2.1
<b>6A<sub>k</sub></b>	101	100	11	2.2
<b>6B<sub>a</sub></b>	—	91	8	2.2
<b>6B<sub>b</sub></b>	96	91	9	2.3
<b>6B<sub>c</sub></b>	118	113	9	2.9
<b>6B<sub>d</sub></b>	109	105	12	2.5
<b>6B<sub>e</sub></b>	107	104	14	2.2
<b>6B<sub>f</sub></b>	109	105	15	2.1
<b>6B<sub>g</sub></b>	—	112	10	2.3

<sup>a</sup> The films were cast via the slow evaporation of polymer solutions in DMAc.

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