

# Synthesis and Properties of Fluorinated Polyimides from 1,1-Bis(4-amino-3,5-dimethylphenyl)-1-(3,4,5-trifluorophenyl)-2,2,2-trifluoroethane and Various Aromatic Dianhydrides

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Received 20 February 2008; accepted 22 August 2008

DOI 10.1002/app.29235

Published online 11 November 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A novel aromatic diamine, 1,1-bis(4-amino-3,5-dimethylphenyl)-1-(3,4,5-trifluorophenyl)-2,2,2-trifluoroethane, containing a pendant polyfluorinated phenyl group, a trifluoromethyl group, and methyl groups ortho-substituted to the amino groups in the structure was synthesized and characterized. The diamine was polymerized with several aromatic dianhydrides, including 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, and 4,4'-hexafluoroisopropylidene diphthalic anhydride, via a high-temperature one-step procedure to afford four polyimides (PIs) with inherent viscosities of 0.47–0.70 dL/g. The PIs exhibited excellent solubilities in a variety of organic solvents. They were soluble not only in polar aprotic solvents but in many common solvents, such as cyclopentanone, tetrahydrofuran, and even toluene at room temperature. The tough and flexible PI films cast from the PI solutions exhibited good thermal stabilities

and acceptable tensile properties. The glass-transition temperatures were in the range 312–365°C, and the 5% weight loss temperatures were all higher than 480°C in nitrogen. The films had tensile strengths in the range 76–99 MPa, tensile moduli of 2.2–2.8 GPa, and elongations at break of 5–8%. In addition, the PI films exhibited excellent transparency in the visible light region with cutoff wavelength as low as 302 nm and transmittance higher than 88% at the wavelength of 450 nm. The PI films showed low dielectric constants ranging from 2.50–2.68 and low moisture absorptions of less than 0.56%. The good combined properties of the PIs mainly resulted from the synergic effects of the different substituents. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2210–2219, 2009

**Key words:** fluoropolymers; polyimides; thermal properties; transparency

## INTRODUCTION

Polyimides (PIs) have been studied and developed for many years from the viewpoints of both scientific and technical interests because of their desirable physical and chemical characteristics.<sup>1–4</sup> The excellent combined properties of PIs, including good thermal stability, excellent mechanical strength, good dielectric properties, and good surface inertness, make them good candidates for many high-tech fields. For instance, PIs are widely used in microelectronic packaging as interlayer dielectrics, passivation layers, sacrificing layers, and  $\alpha$ -particle

barriers.<sup>3,5</sup> Recently, the applications of PIs in optoelectronic fabrications have been extensively investigated.<sup>6,7</sup> Although standard aromatic PIs can meet most desired properties, some requirements, such as high optical transparency, low fabricating temperature, good processability, and, in some cases, low dielectric constant, have to be addressed before their final acceptance in these fields. To overcome the bottlenecks of standard PIs, a variety of modifications have been performed, among which fluorination might be one of the most effective.<sup>3,8–19</sup> Fluoro-containing substituents, including fluorine atoms or fluoroalkyl groups (e.g.,  $-\text{CF}_3$ ), possess large electronegativities and low molar polarizations and, thus, often endow fluoropolymers with good optical transparency [both in the scope of the ultraviolet–visible (UV–vis) region and optocommunication wavelength], low humidity absorption, low refractive index, and low dielectric constant.<sup>17–19</sup> Meanwhile, the thermal properties of the polymers can often be maintained because of the outstanding thermal and thermooxidative stability of the fluoro groups.<sup>20</sup>

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50403025.

Contract grant sponsor: Beijing Municipal Science & Technology Commission; contract grant number: Z08080302110801.

*Journal of Applied Polymer Science*, Vol. 111, 2210–2219 (2009)  
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As a part of our continuous work to develop high-performance PIs for optoelectronic applications, in this study, we aimed to develop novel PIs containing both trifluoromethyl and fluorine substituents in their structure. The design was based on our previous work, in which the synergic effects of trifluoromethyl and fluorine groups often afforded PIs with good optical and dielectric properties.<sup>17,21</sup> The trifluoromethyl was designed to be attached to the main chain of the PIs, whereas the fluorine atoms were located in the lateral phenyl group. At the same time, methyl groups were introduced to the position ortho to the amino groups to increase the glass-transition temperatures ( $T_g$ 's) of the PIs via steric effects.<sup>21–23</sup> On the basis of the aforementioned considerations, a novel diamine, 1,1-bis(4-amino-3,5-dimethylphenyl)-1-(3,4,5-trifluorophenyl)-2,2,2-trifluoroethane (6FMA), which combines a trifluoromethyl group, a bulky polyfluorinated phenyl side group, and ortho-substituted methyl groups, was synthesized first. Four PIs were prepared from the diamine and several aromatic dianhydrides. The effects of the structure on the solubility and thermal, optical, mechanical, and dielectric properties of the PIs were investigated in detail.

## EXPERIMENTAL

### Materials

3,4,5-Trifluorobromobenzene (Acros, Janssen Pharmaceutica, Geel, Belgium) was purified by distillation before use. Magnesium turnings (Acros) were used as received. Anhydrous lithium trifluoroacetate was prepared in our laboratory by the reaction of lithium hydroxide and trifluoroacetic acid at 5°C for 4 h and then dried *in vacuo* at 130°C for 6 h. Tetrahydrofuran (THF) and diethyl ether were freshly distilled in nitrogen over sodium before use. Lithium hydroxide, trifluoroacetic acid, and iodine (Beijing Beihua Fine Chemicals Co., Beijing, China) were used as received. 2,6-Dimethylaniline (Acros) was purified by distillation before use. 2,6-Dimethylaniline hydrochloride was prepared by the reaction of 2,6-dimethylaniline and hydrochloric acid at 5°C for 2 h and was then filtered and dried at 120°C *in vacuo* for 8 h. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA; Acros), 4,4'-oxydiphthalic anhydride (ODPA; Beijing Pome Corp., Beijing, China), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA; Beijing Pome), and 4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA; Hoechst Celanese Corp., Chatham, NJ) were recrystallized from acetic anhydride and dried *in vacuo* at 160°C for 8 h before use. The organic solvents were commercially available and were purified by distillation before use.

### Monomer synthesis

#### Synthesis of 3,4,5-trifluoro-2,2,2-trifluoroacetophenone (6FAP)

A mixture of magnesium (15.96 g, 0.66 mol), iodine (0.30 g, 2.36 mmol), and freshly distilled diethyl ether (300 mL) was placed into a 2000-mL, three-necked, round-bottom flask fitted with a dropping funnel, drying tube, and reflux condenser. 3,4,5-Trifluorobromobenzene (25.13 g, 0.12 mol) was added. The mixture was slowly heated at 31°C to ensure that the reaction started. Then, a mixture of 3,4,5-trifluorobromobenzene (100.88 g, 0.48 mol) in 150 mL of freshly distilled diethyl ether was added dropwise; this was followed by stirring at room temperature for 2 h. Then, a solution of anhydrous lithium trifluoroacetate (86.68 g, 0.72 mol) in freshly distilled THF (400 mL) was added to the prepared Grignard solution over a period of 2 h. The solution was then stirred overnight to give a dark brown solution. Then, a mixture of concentrated hydrochloric acid (36%, 200 mL) and distilled water (200 mL) was slowly added with agitation to give two layers. The aqueous phase was separated, and the organic phase was washed with 5% aqueous sodium bicarbonate and then distilled water until the aqueous phase was neutral. Then, the organic solution was dried over anhydrous magnesium sulfate overnight. The solution was distilled to remove the solvent, and the crude product was purified by distillation to give a colorless liquid of the compound 6FAP (91.01 g, 66.8% yield).

bp = 150–152°C. Fourier transform infrared (FTIR; KBr): 1735  $\text{cm}^{-1}$  (C=O); 1370, 1299, 1132, 1057, and 1020  $\text{cm}^{-1}$  (C–F).  $^1\text{H-NMR}$  [300 MHz, hexadeuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ ),  $\delta$ ]: 7.88 (t, 2H). Mass [m/e (relative intensity)]: 228 ( $\text{M}^+$ , 10), 159 ( $\text{M-69}^+$ , 100).

#### Synthesis of 6FMA

A mixture of 2,6-dimethylaniline (134.51 g, 1.11 mol), 2,6-dimethylaniline hydrochloride (72.53 g, 0.46 mol), and 6FAP (52.46 g, 0.23 mol) was placed in a 500-mL, three-necked, round-bottom flask fitted with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet. With stirring, the mixture was heated at 130°C until 2,6-dimethylaniline hydrochloride dissolved completely. Then, the reaction solution was heated to reflux at 180°C for 10 h. Subsequently, the mixture was cooled to room temperature, and 210 mL of a 20% aqueous solution of sodium dicarbonate was added. The excess 2,6-dimethylaniline was removed by water-vapor distillation to afford a solid. The crude product was obtained by filtration and recrystallized twice from

ethanol/water (1 : 1 v/v). This procedure afforded 74.82 g (yield = 71.9%) of white crystals.

mp = 181.1°C [by differential scanning calorimetry (DSC)]. FTIR (KBr): 3485, 3400  $\text{cm}^{-1}$  (N—H stretch); 2928  $\text{cm}^{-1}$  (C—H); 1232, 1141, 1051  $\text{cm}^{-1}$  (C—F).  $^1\text{H}$ -NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ ): 6.81 (t, 2H), 6.47 (s, 4H), 4.76 (s, 4H), 2.01 (s, 12H).  $^{13}\text{C}$ -NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ ): 149.9 (m,  $^1J_{\text{C-F}} = 253.5$  Hz), 144.2 (s), 139.4 (s), 139.3 (m,  $^1J_{\text{C-F}} = 235.3$  Hz), 129.5 (s), 128.1 (q,  $^1J_{\text{C-F}} = 286.3$  Hz), 125.7 (s), 120.7 (s), 114.5 (s), 62.2 (q,  $^2J_{\text{C-F}} = 23.2$  Hz), 18.6 (s).  $^{19}\text{F}$ -NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ ): 58.12 (s, 3F), 134.52 (s, 2F), 161.72 (s, 1F). Mass [m/e (relative intensity)]: 452 ( $\text{M}^+$ , 15), 383 ( $\text{M}-69^+$ , 100). ANAL. Calcd for  $\text{C}_{24}\text{H}_{22}\text{F}_6\text{N}_2$  (452.44): C, 63.71%; H, 4.90%; N, 6.19%. Found: C, 63.54%; H, 4.87%; N, 6.03%.

### PI synthesis

The general procedure for the preparation of the PIs can be illustrated by the synthesis of PI-1. 6FMA (9.0488 g, 0.02 mol) was added to a 250-mL, three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and thermometer. The solvent *m*-cresol (109 mL) was added, and a clear solution was obtained after stirring for 10 min at room temperature. BPDA (5.8844 g, 0.02 mol) was added in one portion. The mixture was stirred at room temperature for 3 h to yield an amber solution. Toluene (118 mL) and a catalytic amount of isoquinoline were then added, and a Dean–Stark trap was connected. The mixture was heated at 180°C and maintained at this temperature for 5 h to ensure complete imidization. The solution was then cooled to room temperature to obtain a viscous pale yellow solution. The solution was carefully poured into an excess of ethanol to yield a thin silky precipitate. The precipitate was collected and dried at 80°C *in vacuo* overnight. The yield was 14.28 g (98%). The inherent viscosity of PI-1 was 0.61 dL/g at a concentration of 0.5 g/dL in dimethylacetamide (DMAc) at 30°C.

PI-2, PI-3, and PI-4 were prepared according to a similar procedure except that BPDA was replaced by BTDA for PI-2, ODPDA for PI-3, and 6FDA for PI-4.

### Solution-cast PI films

The PI solution was first prepared by the dissolution of the PI resin in DMAc at room temperature with a solid content of 18% (w/v). After it was filtered through a 0.2- $\mu\text{m}$  Teflon syringe filter to remove any particulate, the solution was cast onto a clean glass plate and then thermally treated to produce the PI film. The treatment procedure was as follows: 80°C/2 h, 120°C/1 h, 150°C/1 h, 180°C/1 h, 200°C/1 h, and 250°C/1 h. A free-standing PI film with a very pale yellow color was obtained.

### Melt-molded PI sheets

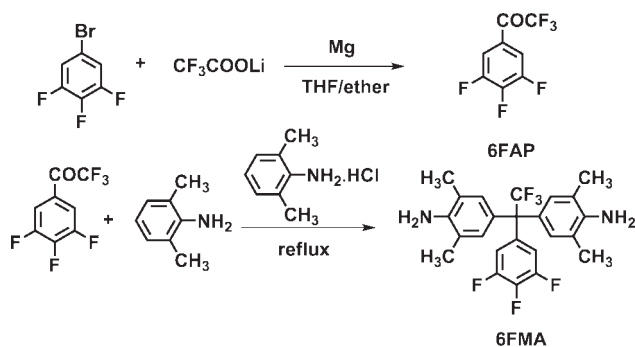
The melt-molded PI sheets for dielectric constant measurement were prepared by the melt processing of the PI resins in a mold (5 cm in diameter). In a typical experiment, the PI-1 resin was smashed to give a powder, which was charged into a matched mold. The mold was then put into a hot press. The mold was heated at 380°C for 15 min, and then a pressure of 2–3 MPa was applied. After being kept at this temperature for 30 min, the mold was cooled to room temperature. A strong and tough PI sheet, pale brown in color, was obtained; it was defect-free and transparent in appearance.

The other PI sheets (PI-2, PI-3, and PI-4) were prepared by a similar procedure.

### Measurements

$^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and  $^{19}\text{F}$ -NMR spectra were obtained on a Varian Unity 300 spectrometer (Palo Alto, CA) operating at 300 or 400 MHz in DMSO- $d_6$ . FTIR spectra were recorded on a PerkinElmer 782 Fourier transform spectrophotometer (Waltham, MA). UV–vis spectra were recorded on a Hitachi U-3210 spectrophotometer (Tokyo, Japan) at room temperature. Before testing, the PI film samples were dried at 120°C for 1 h to remove the absorbed moisture. Mass spectra were recorded on an AEI MS-50 mass spectrometer (Elmsford, NY). Wide-angle X-ray diffraction (WAXD) was conducted on a Rigaku D/max-2500 X-ray diffractometer (Tokyo, Japan) with Cu  $K\alpha_1$  radiation operated at 40 kV and 200 mA. The tensile properties were examined on an Instron 3365 tensile apparatus (Norwood, MA) with PI film specimens (50–60  $\mu\text{m}$  thick, 10 mm wide, and 80 mm long) in accordance with GB1447-83 at a drawing rate of 2.0 mm/min. An average of six individual determinations was used. DSC and thermogravimetric analysis (TGA) were recorded on a PerkinElmer 7 series thermal analysis system in nitrogen. The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of the PIs were obtained at 35°C by a size exclusion chromatograph equipped with a Waters 515 pump, a Waters 2414 refractive-index detector (Milford, MA), and a combination of Styragel HT-2, HT-3, and HT-4; the effective molecular weight ranges were 100–10,000, 500–30,000, and 5000–600,000 Da, respectively. Linear polystyrene standards were applied for the calibration. The eluent was THF at a rate of 1.0 mL/min. Inherent viscosities were measured with an Ubbelohde viscometer (Beijing Glass Instruments Factory, Beijing, China) with a 0.5 g/dL DMAc solution at 30°C. Refractive indices of the PI films formed on 3-in. silicon wafers were measured at the wavelength 1310 nm at room temperature.





**Scheme 1** Synthesis of fluorinated diamine 6FMA.

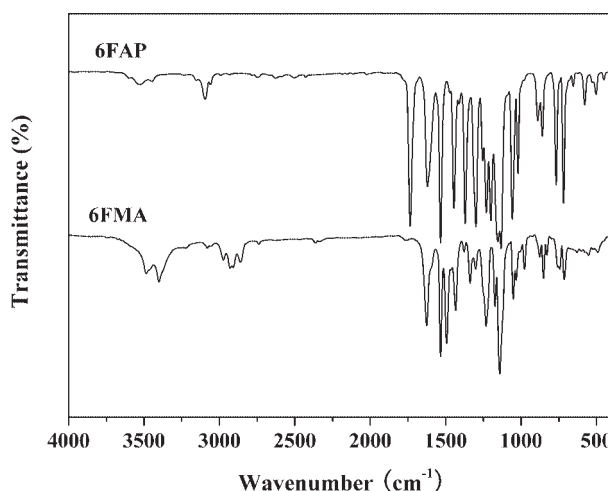
with a SaironTech model SPA-4000 prism coupler (Gwangju, Korea). The in-plane ( $n_{TE}$ ) and out-of-plane ( $n_{TM}$ ) refractive indices were determined by linearly polarized laser light parallel (transverse electric) and perpendicular (transverse magnetic) polarizations to the film plane, respectively.

The solubility was determined as follows: 1.5 g of the PI resin was mixed with 8.5 g of the tested solvent at room temperature (15 wt % solid content); the mixture was then mechanically stirred in nitrogen for 24 h. The solubility was determined visually as one of three grades: completely soluble, partially soluble, and insoluble. Complete solubility was determined when a homogeneous and clean solution was obtained, in which no phase separation, precipitation, or gel formation was detected. Water uptakes were determined by weighing the changes in the PI film ( $50 \times 50 \times 0.05 \text{ mm}^3$ ) before and after immersion in water at  $25^\circ\text{C}$  for 24 h. The surface and volume resistivities were measured with film specimens with a diameter of 50 mm and a thickness of about 50  $\mu\text{m}$ . The dielectric constants were measured at 1 MHz with melt-molded PI sheets with a diameter of 50 mm and a thickness of approximately 1.35 mm.

## RESULTS AND DISCUSSION

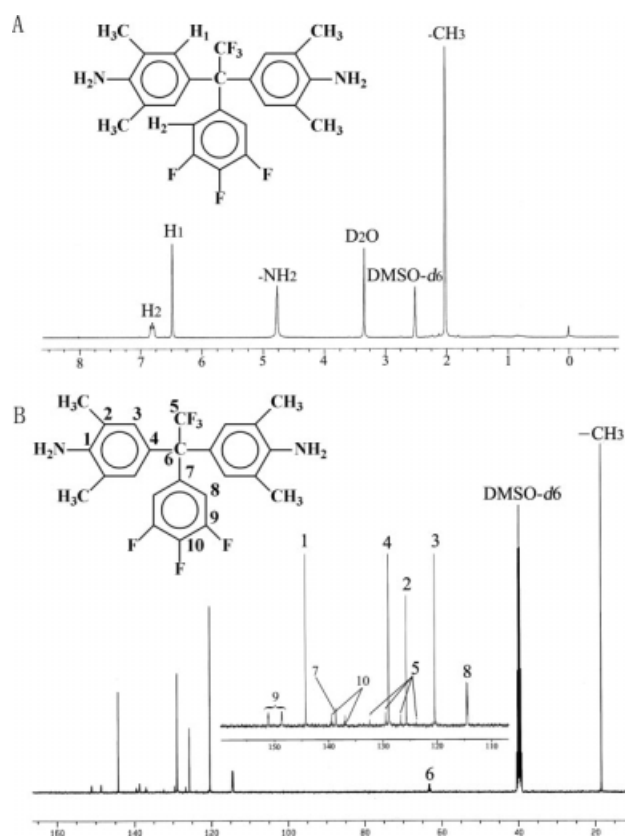
### Monomer synthesis

As shown in Scheme 1, 6FMA was synthesized via a two-step reaction. First, the intermediate compound 6FAP was synthesized by the Grignard reaction between anhydrous lithium trifluoroacetate and fluorinated bromobenzene in the presence of magnesium in THF/diethyl ether. Then, the diamine 6FMA was obtained by the coupling reaction of 6FAP and 2,6-dimethylaniline catalyzed by 2,6-dimethylaniline hydrochloride at  $180^\circ\text{C}$  with a yield of 72%.<sup>17,23</sup> A polymer-grade diamine was easily obtained by recrystallization twice from ethanol/water as white crystals. Figure 1 compares the FTIR spectra of the diamine 6FMA and the intermediate compound 6FAP. The characteristic absorption of C=O at  $1731 \text{ cm}^{-1}$

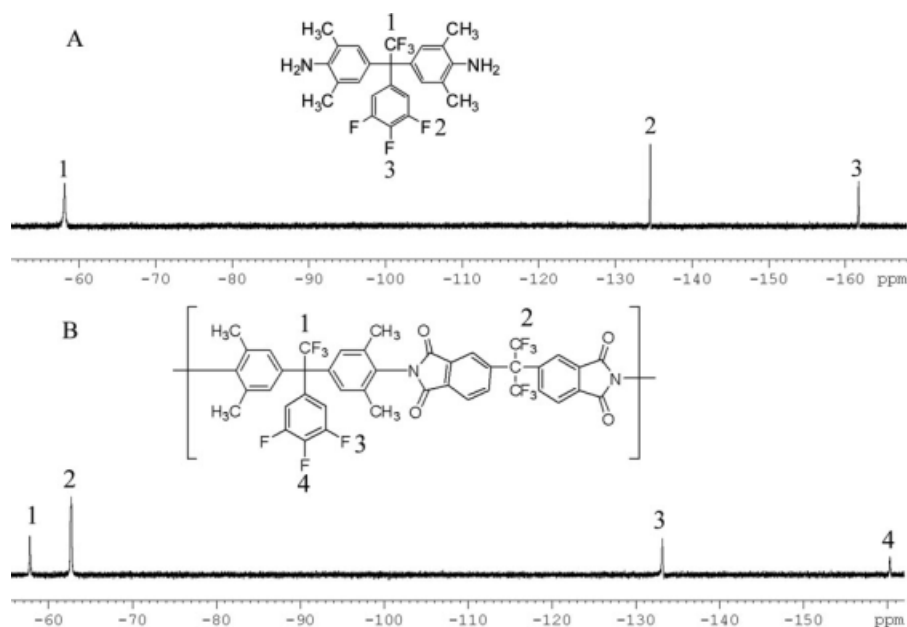


**Figure 1** FTIR spectra of the intermediate 6FAP and the diamine 6FMA.

$\text{cm}^{-1}$  in 6FAP disappeared in 6FMA, which indicated the successful coupling reaction between 6FAP and 2,6-dimethylaniline. Moreover, the characteristic absorptions of amino groups at  $3493$  and  $3396 \text{ cm}^{-1}$  and the methyl group absorption at  $2925 \text{ cm}^{-1}$  appeared in 6FMA. The strong absorptions at  $1137$  and  $1233 \text{ cm}^{-1}$ , assigned to the stretching vibration of C—F bond, also existed in the spectrum. Figure 2



**Figure 2** (A)  $^1\text{H}$ -NMR and (B)  $^{13}\text{C}$ -NMR spectra of 6FMA in  $\text{DMSO-}d_6$ .



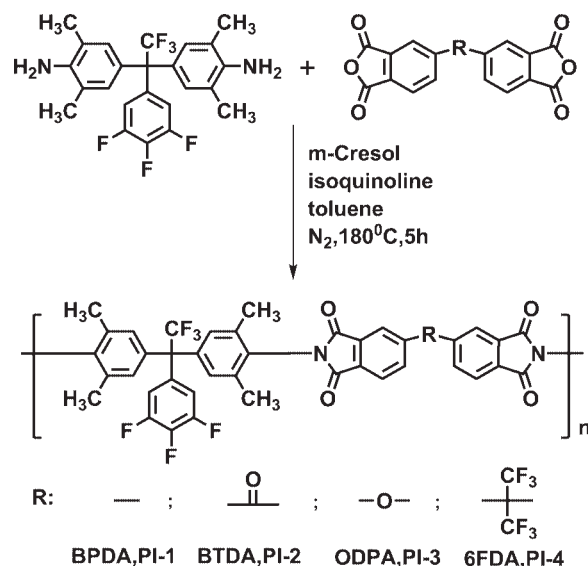
**Figure 3**  $^{19}\text{F}$ -NMR spectra of (A) the diamine 6FMA and (B) PI-4.

shows the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of 6FMA. All peaks clearly corresponded to the proposed structure. In the  $^1\text{H}$ -NMR spectra, the amine proton signal at 4.76 ppm was observed, and the proton ortho to the electron-withdrawing F atoms ( $\text{H}_2$ ) was observed in the downfield of the spectrum. In the  $^{13}\text{C}$ -NMR spectra, the quartet centered at about 128 ppm was due to the  $\text{CF}_3$  ( $\text{C}^5$ ); the one-bond  $\text{C}-\text{F}$  coupling constant in this case was about 286 Hz. The  $\text{CF}_3$ -attached carbon ( $\text{C}^6$ ) also showed a clear quartet centered at 63 ppm with a smaller coupling constant of about 23 Hz due to the two-bond  $\text{C}-\text{F}$  coupling because the interaction operated over more bonds. As for the fluoro-attached carbons, the large quartet centered at about 149.9 ppm was due to carbon  $\text{C}^9$ ; the one-bond  $\text{C}-\text{F}$  coupling constant in this case was about 253 Hz. In addition, the  $\text{C}^{10}$  carbon also had its resonance split by three fluorine atoms (one-bond coupling and two-bond coupling). The one-bond coupling constant was about 235 Hz, and the two-bond coupling constant was about 16 Hz. In the  $^{19}\text{F}$ -NMR spectrum [Fig. 3(A)], the signals at  $-58.12$ ,  $-134.52$ , and  $-161.72$  ppm were ascribed to the fluorine atoms located in  $-\text{CF}_3$  group and the pendent phenyl group, respectively. Elemental analysis also verified the chemical composition of the diamine.

### Polymer synthesis

Fluorinated PIs were prepared via a one-step high temperature polycondensation procedure, as shown in Scheme 2. The polymerization proceeded smoothly at a temperature of  $180^\circ\text{C}$ , and homogene-

ously, transparent viscous PI solutions were produced. We obtained solid, pale yellow PI resins by pouring the polymer solutions into excess ethanol. As shown in Table I, the inherent viscosities of the PI resins were measured in the range 0.47–0.70 dL/g, which were high enough to cast flexible and tough films. The molecular weights of the fluorinated PIs determined by gel permeation chromatography (GPC) in THF with linear polystyrene as a standard were in the range  $5.7\text{--}8.3 \times 10^4$  for  $M_n$  and  $10.1\text{--}13.0 \times 10^4$  for  $M_w$  with  $M_w/M_n$  values of 1.48–1.77, which showed a similar trend to that determined by the inherent viscosity measurements. Flexible and tough PI films were obtained by removal of the solvent



**Scheme 2** Synthesis of 6FMA PIs.

TABLE I  
Characteristics of Fluorinated PIs

PI	Inherent viscosity (dL/g) <sup>a</sup>	GPC data <sup>b</sup>			Formula	Elemental analysis (%)			
		$M_n (\times 10^{-4})$	$M_w (\times 10^{-4})$	$M_w/M_n$		C	H	N	
PI-1	0.61	— <sup>c</sup>	— <sup>c</sup>	— <sup>c</sup>	$C_{40}H_{24}F_6N_2O_4$	Calcd.	67.61	3.40	3.94
						Found	66.65	3.91	3.47
PI-2	0.70	7.49	13.00	1.74	$C_{41}H_{24}F_6N_2O_5$	Calcd.	66.67	3.28	3.79
						Found	66.26	3.57	4.02
PI-3	0.53	5.73	10.13	1.77	$C_{40}H_{24}F_6N_2O_5$	Calcd.	66.12	3.33	3.86
						Found	65.47	3.41	4.02
PI-4	0.47	8.34	12.31	1.48	$C_{43}H_{24}F_{12}N_2O_4$	Calcd.	60.01	2.81	3.25
						Found	59.81	2.97	3.17

All the samples were thermally baked at 250°C for 3 h before testing.

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

<sup>b</sup> Measured by GPC in THF with polystyrene as the standard.

<sup>c</sup> The polymer was partially soluble in THF.

DMAc in the PI solution by heating. The chemical compositions of the films were confirmed by the elemental analysis results listed in Table I, which were in accordance with the anticipated structures.

Figure 4 depicts the FTIR spectra of the PI films. The characteristic absorption peaks around 1783  $\text{cm}^{-1}$  (asymmetric stretching vibration of C=O), 1731  $\text{cm}^{-1}$  (symmetric stretching vibration of C=O), 1375  $\text{cm}^{-1}$  (stretching vibration of C–N), and 721  $\text{cm}^{-1}$  (imide ring deformation) were observed in all of the polymers, as were the strong C–F absorptions between 1000 and 1200  $\text{cm}^{-1}$  and the methyl group absorption at 2981 and 2930  $\text{cm}^{-1}$ . The typical <sup>1</sup>H-NMR spectrum of PI-3, shown in Figure 5, revealed that all of the hydrogen protons agreed well with the proposed polymer structure. The H<sub>1</sub> ortho to the C=O appeared the farthest downfield because of the resonance. H<sub>2</sub> and H<sub>3</sub> shifted to higher field because of the electron-donating properties of aromatic ether. In Figure 3(B), another peak appeared around –62.61 ppm compared with the <sup>19</sup>F-NMR spectrum of the monomer 6FMA, which was

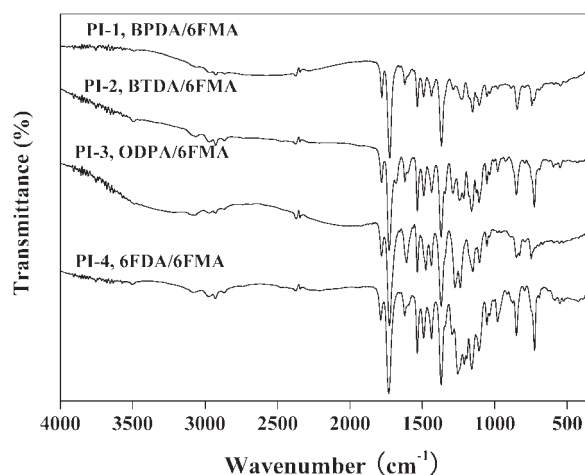


Figure 4 FTIR spectra of the PIs.

ascribed to the fluorine atoms of the 6FDA residues. These phenomena confirmed that polymerization of the monomer 6FMA with the aromatic dianhydrides was successfully achieved. The WAXD patterns are shown in Figure 6, in which no crystalline peaks were observed, which indicated the amorphous nature of the polymers. This might be interpreted by the presence of the bulky fluorinated phenyl group and the trifluoromethyl groups, which decreased the intramolecular and intermolecular interactions and resulted in loose polymer packing.

### Properties of the polymers

The solubility of the fluorinated PIs was quantitatively tested in various organic solvents, and the results are summarized in Table II. The PIs showed excellent solubility in aprotic polar solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylformamide and were also soluble in less polar solvents like *m*-cresol, THF, cyclopentanone, and even in toluene. None of the PIs were soluble in methanol. PI-4, containing a hexafluoroisopropylidene linkage, showed better solubility compared with the PIs from

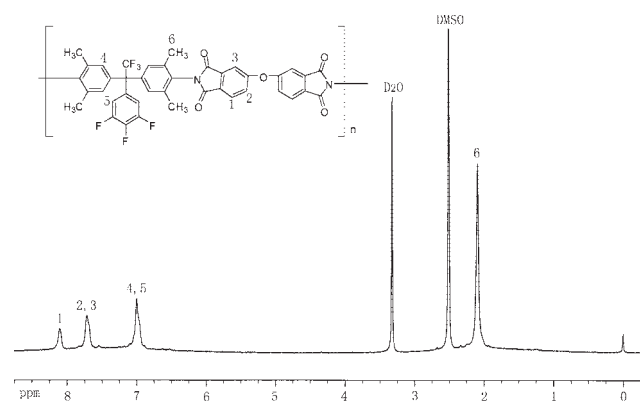


Figure 5 <sup>1</sup>H-NMR spectrum of PI-3 in DMSO-*d*<sub>6</sub>.

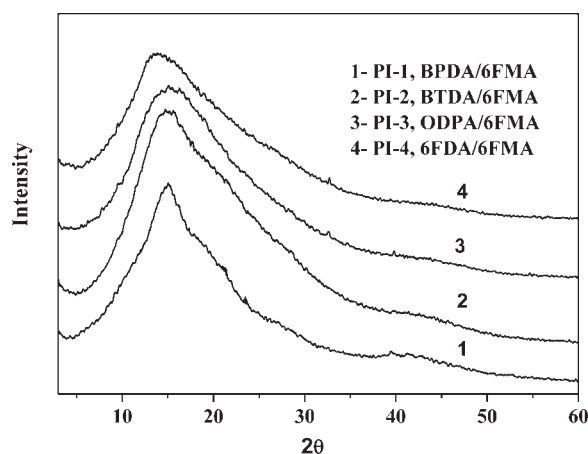


Figure 6 WAXD patterns of the PIs.

the other dianhydrides. Compared with the non-fluorinated PI derived from  $\alpha,\alpha$ -(4-amino-3,5-dimethylphenyl)phenylmethane (BADP) and BTDA, PI-2 was completely soluble in toluene at room temperature, whereas BADP–BTDA could not dissolve completely until it was heated at 80°C.<sup>24</sup> The good solubility of the PIs might have been due to the presence of the bulky polyfluorinated phenyl and trifluoromethyl groups, which increased the disorder of the chains, hindered the dense chain stacking, and thus reduced the intermolecular interactions. The excellent solubility in cyclopentanone and  $\gamma$ -butyrolactone would be of great benefit because both solvents are widely used in microelectronic assembly, such as the solvent or developer for photosensitive PIs.<sup>25,26</sup> Therefore, these PIs might find applications in semiconductor fabrications.

The thermal behaviors of the PIs were evaluated by DSC and TGA, and the results are tabulated in Table III. The  $T_g$ 's of the polymers were in the range 312–365°C and were recorded as the second-heating trace of the DSC measurement. No melting endothermic peaks were observed in the DSC traces (Fig. 7), which revealed the amorphous nature of the polymers. This agreed well with the results from the WAXD measurements. As shown in Table III, the PIs exhibited  $T_g$ 's higher than 310°C. The high

values were mainly attributed to the methyl groups ortho-substituted to the imide ring, which restricted the rotation of nitrogen atoms along the phenyl ring at elevated temperatures, which resulted in more rigid polymer chains. The same phenomena have been well observed in these kinds of PIs.<sup>21–23</sup> In addition, no notable weight loss was observed below 450°C for any of the PIs from the TGA curves shown in Figure 8. The PIs exhibited good thermal stability with initial thermal decomposition temperatures in the range 519–531°C, temperatures at 10% weight loss in the range 540–550°C, and residual weight retentions at 700°C in the range 57–64%. The good thermal stability of the PIs was attributed to the presence of the bulky phenyl group in the polymer backbone, which enhanced the thermal stability of these polymers. The TGA data indicated that the fluorinated PIs had fairly high thermal stability regardless of the introduction of fluorinated groups.

The tensile properties of the flexible films are summarized in Table IV. All of the fluorinated PIs afforded good-quality films. They showed tensile strengths of 76–99 MPa, elongations at break of 5–8%, and tensile moduli of 2.2–2.8 GPa, which confirmed the successful preparation of high-molecular-weight PIs via the high-temperature, one-step procedure.

The PI films exhibited excellent electrical properties with surface and volume resistances on the order of magnitude of  $10^{15} \Omega$  and  $10^{17} \Omega$  cm, respectively (Table IV). The dielectric constants measured from the molding PI sheets at 1 MHz were in the range 2.62–2.93, which were much lower than those of the standard PIs, such as Kapton, derived from pyromellitic dianhydride and 4,4'-oxydianiline (dielectric constant = 3.5 at 1 KHz).<sup>8</sup> The decreased dielectric constants might have been due to the bulky fluorinated phenyl and trifluoromethyl groups, which resulted in less efficient chain packing and increased the molecular free volumes.<sup>27,28</sup> In addition, the strong electronegativity of fluorine results in the very low polarizability of C–F bonds, which also decreases the dielectric constant. As expected, PI-4 from 6FMA and 6FDA had the lowest

TABLE II  
Solubility of the PIs

PI	Solvents							
	NMP	DMF	<i>m</i> -cresol	toluene	$\gamma$ -BL	THF	CPA	Methanol
PI-1	++	++	++	++	+	+	+	–
PI-2	++	++	++	++	++	++	++	–
PI-3	++	++	++	++	++	++	++	–
PI-4	++	++	++	++	++	++	++	–

– = insoluble; + = partially soluble; ++ = soluble at room temperature;  $\gamma$ -BL =  $\gamma$ -butyrolactone; CPA = cyclopentanone; DMF = *N,N*-dimethylformamide; NMP = *N*-methyl-2-pyrrolidone.



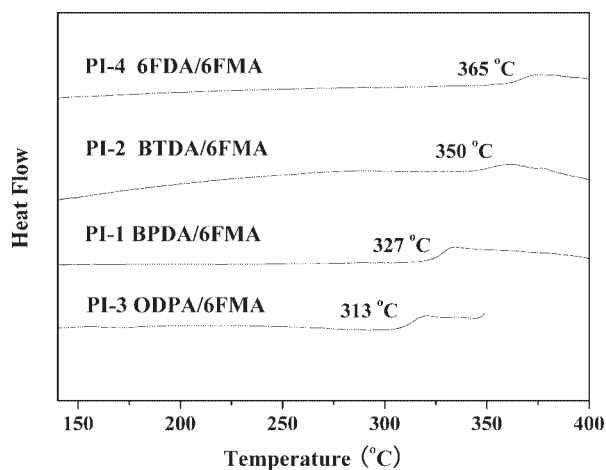
**TABLE III**  
Thermal Properties of the PI Films

PI	$T_g$ (°C)	$T_d$ (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$R_w$ (%)
PI-1	327	527	508	543	57
PI-2	350	522	501	550	63
PI-3	313	520	503	546	64
PI-4	365	532	484	540	65

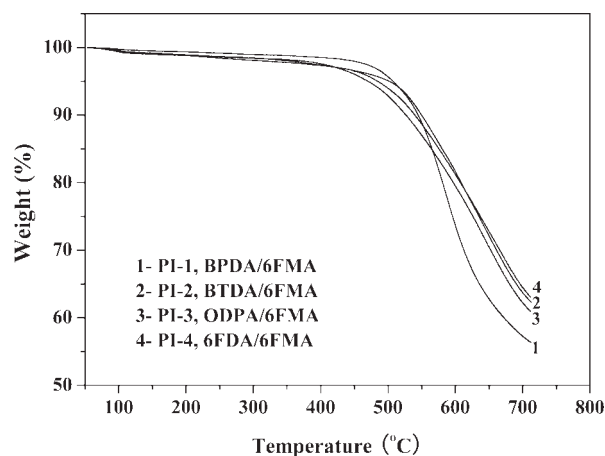
$R_w$  = residual weight retention at 700°C in nitrogen;  $T_{5\%}$  = temperature at 5% weight loss;  $T_{10\%}$  = temperature at 10% weight loss;  $T_d$  = onset decomposition temperature.

dielectric constant in the series, and this might have been due to the higher fluorine content of the PI. Moreover, the bulky hexafluoroisopropylidene group in the dianhydride moiety also contributed to the low dielectric constant of the PI.<sup>29</sup>

Table V summarizes the optical properties of the PI films evaluated by UV-vis measurements with the 10- $\mu\text{m}$ -thick films. The cutoff wavelength ( $\lambda_{\text{cutoff}}$ ) values ranged from 302 (PI-4) to 348 nm (PI-1), and the optical transmittance values at the wavelength of 450 nm ( $T_{450\text{nm}}$ ) were all higher than 88%. Figure 9 shows the UV-vis spectra of the fluorinated PI films. The  $\lambda_{\text{cutoff}}$  value decreased and the  $T_{450\text{nm}}$  value increased with increasing fluorine content of the PIs. For example, PI-4, with the highest fluorine content of 26.49%, showed  $\lambda_{\text{cutoff}}$  and  $T_{450\text{nm}}$  values of 302 nm and 96%, respectively. The good optical transparency was mainly due to the reduction of the intermolecular and intramolecular charge-transfer complexes (CTCs) between the electron-donor (diamine) and electron-acceptor (dianhydride) moieties.<sup>30</sup> The bulky pendent phenyl group and fluorinated groups were effective in reducing the CTC formation through steric hindrance and the inductive effect.<sup>31</sup> The three fluorine atoms substituted in the pendent phenyl group also inhibited the for-



**Figure 7** DSC curves of the fluorinated PIs.



**Figure 8** TGA curves of the fluorinated PIs.

mation of CTCs, and similar results have been reported in the literature.<sup>32</sup>

The refractive indices of the PIs measured at 1310 nm are summarized in Table V. All of the PI films exhibited much lower average refractive index ( $n_{\text{av}}$ ) values than the standard pyromellitic dianhydride/4,4'-oxydianiline film.<sup>33</sup> The PI films with higher fluorine contents had lower refractive indices, presumably because of the low molar refraction of the fluorine atoms. On the other hand, the pendent phenyl and methyl groups increased the molecular volume of the PIs, which, in turn, decreased the refractive indices of the PIs according to Lorentz-Lorenz equation.<sup>34</sup> All of the PI films had higher  $n_{\text{TE}}$  values than  $n_{\text{TM}}$  values, which indicated that they had positive birefringences and the molecular chains were preferentially aligned in the film plane.<sup>35</sup> The values of in-plane/out-of-plane birefringence of the PI films ranged from 0.0099 to 0.0210. The low birefringences of the PIs may have arisen from the twisted structure of the diamine containing methyl, trifluoromethyl, and fluorinated phenyl groups, which interrupted the efficient packing of the PI molecular chains and destroyed the ordered structures of the PIs. The relatively small birefringence of PI-4 implied that the PI chain was randomly oriented in the film.

The optical dielectric constants of the fluorinated PIs, estimated from  $n_{\text{av}}$  according to a modified form of Maxwell's equation (dielectric constant =  $1.10n^2$ )<sup>36</sup> to be 2.50–2.68, agreed well with the measured ones (Table IV). For example, PI-3 exhibited an estimated dielectric constant of 2.65, which was a little lower than the measured value of 2.68.

The PI films showed low water uptakes of 0.30–0.56%; this was due to the hydrophobic nature of the fluorine substituents. With the increase of fluorine content, the water uptakes of the PI films decreased from 0.56% (PI-2) to 0.30% (PI-4). The low



**TABLE IV**  
Mechanical and Electrical Properties of the PI Films

PI	$E_B$ (%)	$T_S$ (MPa)	$T_M$ (GPa)	$\rho_s \times 10^{-15}$ ( $\Omega$ )	$\rho_v \times 10^{-17}$ ( $\Omega$ cm)	$\epsilon$
PI-1	8	90.3	2.4	3.7	1.3	2.93
PI-2	5	76.5	2.3	1.5	2.1	2.79
PI-3	6	83.9	2.2	2.4	2.5	2.68
PI-4	8	99.2	2.8	3.2	2.2	2.62

$\epsilon$  = dielectric constant measured at 1 MHz with melt-molded PI sheets;  $\rho_s$  = surface resistivity;  $\rho_v$  = volume resistivity;  $E_B$  = elongation at break;  $T_M$  = tensile modulus;  $T_S$  = tensile strength.

**TABLE V**  
Optical Properties and Water Uptake of the PI Films

PI	$F_c$ (%)	$\lambda_{\text{cutoff}}$ (nm)	$T_{450\text{nm}}$ (%) <sup>c</sup>	$W_u$ (%)	Refractive indices at 1310 nm <sup>a</sup>				$\epsilon$
					$n_{\text{TE}}$	$n_{\text{TM}}$	$n_{\text{av}}$	Birefringence	
PI-1	16.04	348	95	0.46	1.5684	1.5474	1.5614	0.0210	2.68
PI-2	15.43	331	91	0.56	1.5613	1.5475	1.5567	0.0138	2.67
PI-3	15.69	346	88	0.35	1.5558	1.5421	1.5512	0.0137	2.65
PI-4	26.49	302	96	0.30	1.5120	1.5021	1.5087	0.0099	2.50

$\epsilon$  = dielectric constant estimated from the modified form of Maxwell's equation ( $\epsilon = 1.10n_{\text{av}}^2$ );<sup>36</sup>  $F_c$  = fluoro content;  $W_u$  = water uptake.

<sup>a</sup> See the Measurements section.

water uptakes ensured that the PIs had stable dielectric constants.

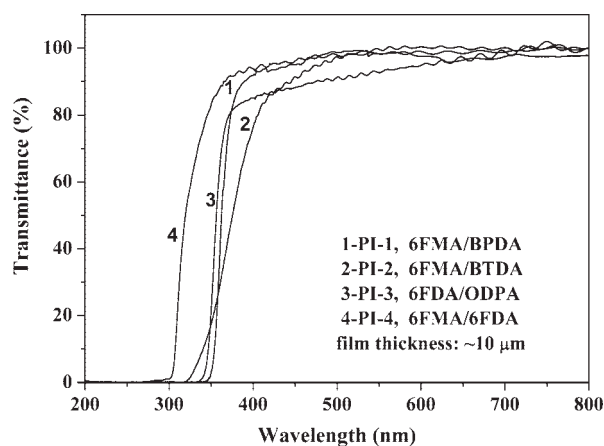
## CONCLUSIONS

The synergetic effects of the trifluoromethyl group and pendent multifluorinated phenyl and ortho-substituted methyl groups on the properties of the PIs were investigated. Good solubilities in common solvents, high thermal stabilities and  $T_g$ 's, good mechanical strengths, low dielectric constants, low refractive indices, and low birefringences were achieved with the PIs derived from an aromatic diamine 6FMA and various dianhydrides. In particular, PI-4, derived from 6FDA and 6FMA demonstrated good combined properties, including a 10% weight

loss temperature of 540°C, a  $T_g$  value of 365°C, a  $T_{450\text{nm}}$  value of 96%, an  $n_{\text{av}}$  value of 1.5087, and a birefringence of 0.0099. The superior properties indicate their potential use in the fields of microelectronics and optoelectronics.

## References

- Polyimides: Fundamentals and Applications; Malay, K. G.; Mittal, K. L., Eds.; Marcel Dekker: New York, 1996.
- Polyimides; Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds.; Chapman & Hall: New York, 1990.
- Maier, G. Prog Polym Sci 2001, 26, 3.
- Feger, C. In Multichip Module Technologies and Alternatives: The Basics; Doane, D. A.; Franzon, P. D., Eds.; Van Nostrand Reinhold: New York, 1993; p 311.
- Abadie, M. J. M.; Sillion, B. Polyimides and Other High Temperature Polymers; Elsevier: Amsterdam, 1991; p 6.
- Ma, H.; Jen, A. K. Y. L.; Dalton, R. Adv Mater 2002, 14, 1339.
- Chang, C. C.; Chen, C. P.; Chou, C. C.; Kuo, W. J.; Jeng, R. J. J Macromol Sci Part C: Polym Rev 2005, 45, 125.
- Banerjee, S.; Madhra, M. K.; Salunke, A. K.; Jaiswal, D. K. Polymer 2003, 44, 613.
- Al-Masri, M.; Kricheldorf, H. R.; Fritsch, D. Macromolecules 1999, 32, 7853.
- Chung, I. S.; Kim, S. Y. Macromolecules 2000, 33, 3190.
- Dang, T. D.; Mather, P. T.; Alexander, M. D.; Grayson, C. J.; Houtz, M. D.; Spry, R. J.; Arnold, F. E. J Polym Sci Part A: Polym Chem 2000, 38, 1991.
- Xie, K.; Liu, J. G.; Zhou, H. W.; Zhang, S. Y.; He, M. H.; Yang, S. Y. Polymer 2001, 42, 7267.
- Lee, C. W.; Kwak, S. M.; Yoon, T. H. Polymer 2006, 47, 4140.
- Bes, L.; Rousseau, A.; Boutevin, B.; Mercier, R.; Kerboua, R. Macromol Chem Phys 2001, 202, 2954.



**Figure 9** UV-vis spectra of the fluorinated PIs.

15. Li, H. S.; Liu, J. G.; Wang, K.; Fan, L.; Yang, S. Y. *Polymer* 2006, 47, 1443.
16. Liu, B. J.; Hu, W.; Matsumoto, T.; Jiang, Z. H.; Ando, S. *J Polym Sci Part A: Polym Chem* 2005, 43, 3018.
17. Li, H. S.; Liu, J. G.; Rui, J. M.; Fan, L.; Yang, S. Y. *J Polym Sci Part A: Polym Chem* 2006, 44, 2665.
18. Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Macromolecules* 1994, 27, 6665.
19. Banerjee, S.; Madhra, M. K.; Kashinath, S. A.; Maier, G. *J Polym Sci Part A: Polym Chem* 2002, 40, 1016.
20. Hu, A. J.; Hao, J. Y.; He, T.; Yang, S. Y. *Macromolecules* 1999, 32, 8046.
21. Zhao, X. J.; Liu, J. G.; Rui, J. M.; Fan, L.; Yang, S. Y. *J Appl Polym Sci* 2007, 103, 1442.
22. Qiu, Z. M.; Wang, J. H.; Zhang, Q. Y.; Zhang, S. B.; Ding, M. X.; Gao, L. X. *Polymer* 2006, 47, 8444.
23. Langsam, M.; Burgoyne, W. F. *J Polym Sci Part A: Polym Chem* 1993, 31, 909.
24. Qian, Z. G.; Pang, Z. Z.; Li, Z. X.; He, M. H.; Liu, J. G.; Fan, L.; Yang, S. Y. *J Polym Sci Part A: Polym Chem* 2002, 40, 3012.
25. Goff, P. L.; Yuan, E. L.; Proskow, S. E. P. Pat. 047,184 (1981).
26. Naiini, A.; Racicot, D.; Roza, A. J.; Weber, W. D.; Waterson, P. J. U.S. Pat. 0,025,494 (2002).
27. Hougham, G.; Tesoro, G.; Viehbeck, A.; Chapple-Sokol, J. D. *Macromolecules* 1994, 27, 5964.
28. Hougham, G.; Tesoro, G.; Viehbeck, A. *Macromolecules* 1996, 29, 3453.
29. Lee, C.; Shul, Y.; Han, H. *J Polym Sci Part B: Polym Phys* 2002, 40, 2190.
30. Ando, S. *J Photopolym Sci Technol* 2004, 17, 219.
31. Hasegawa, M.; Horie, K. *Prog Polym Sci* 2001, 26, 259.
32. Ando, S.; Matsuura, T.; Sasaki, S. *Polym J* 1997, 29, 69.
33. Russel, T. P.; Guggen, H.; Swalen, J. D. *J Polym Sci Polym Phys Ed* 1983, 21, 1745.
34. Chang, E. P.; Holguin, D. *J Adhes* 2005, 81, 925.
35. Arnold, F. E.; Shen, D. X.; Lee, C. J.; Harris, F. W.; Cheng, S. Z. D.; Lau, S. F. *J Mater Chem* 1993, 3, 353.
36. Oishi, Y.; Onodera, S.; Oravec, J.; Mori, K.; Ando, S.; Terui, Y.; Maeda, K. *J Photopolym Sci Technol* 2003, 16, 263.