

Preparation and Properties of Melt-Processable Polyimides Based on Fluorinated Aromatic Diamines and Aromatic Dianhydrides

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ABSTRACT: Two series of melt-processable polyimides were prepared from 4,4'-bis(3-amino-5-trifluoromethylphenoxy)biphenyl (*m*-6FBAB) and 4,4'-bis(4-amino-5-trifluoromethylphenoxy)biphenyl (*p*-6FBAB) with various aromatic dianhydrides. The effects of the chemical structures of the polyimides on their properties, especially the melt processability and organic solubility, were investigated. The experimental results demonstrate that some of the fluorinated aromatic polyimides showed good melt processability at elevated temperatures (250–360°C) with relatively low melt viscosities and could be melt-molded to produce strong and tough polyimide sheets. Meanwhile, the polyimides showed excellent organic solubility in both polar aprotic solvents and common solvents to give stable polyimide solutions with high polymer concentrations and

relatively low viscosities. Thus, we prepared high-quality polyimide films by casting the polyimide solutions on glass plates followed by baking at relatively low temperatures. The polyimides derived from *m*-6FBAB showed better melt processability and solubility than the *p*-6FBAB based polymers. The melt-processable polyimides showed a good combination of thermal stability and mechanical properties, with decomposition temperatures of 547–597°C, glass-transition temperatures in the range 205–264°C, tensile strengths of 81.3–104.9 MPa, and elongations at break as high as 19.6%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2126–2135, 2008

Key words: fluoropolymers; melt; polyimides; rheology; solution properties

INTRODUCTION

Aromatic polyimides, because of their high thermal stability, excellent mechanical properties, low dielectric constant, and dissipation factor, have been used extensively in aircraft and space applications as structural and substructural materials.^{1,2} Polyimides are also used as dielectric and electrical insulation materials in microelectronic applications.^{3,4} Early versions of aromatic polyimides were usually infusible and insoluble because of their rigid chemical structures and unique interactions among their molecular chains, which resulted in difficulties in melt processing by conventional melt-injection or melt-extrusion techniques. In recent years, many researches have reported improvements in the melt processability of aromatic polyimides^{5–15} by the introduction of flexible linkages into the polymer backbones to reduce the stiffness of the polymer

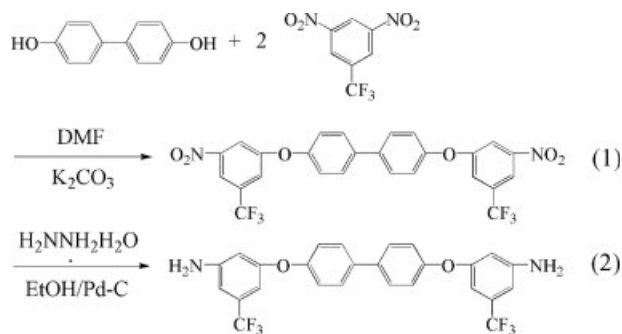
chains or the interactions among polymer chains. However, the improvements in the melt processability of aromatic polyimides have usually resulted in the sacrifice of the thermal stability and mechanical properties at elevated temperatures. Hence, there is still a big scientific and technological challenge to develop melt-processable aromatic polyimides with both outstanding thermal stability and mechanical properties.

There have also been many reports in recent years with regard to improving the solubility of aromatic polyimides with high thermal properties by the introduction of flexible linkages, fluorine-containing groups into polymer backbones,^{16–21} or pendent side-chain substituents.^{22–24} All of these efforts have been focused on the reduction of the polymer chain stiffness or the weakening of the polymer chain-chain interactions. However, few of attempts have been made to improve the melt processability of these soluble polyimides by the precise adjustment and control of the polymer molecular weight and its distribution.

In this study, two series of melt-processable aromatic polyimides were synthesized by the polycondensation of the fluorinated aromatic diamines 4,4'-

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Scheme 1 Synthesis of the fluorinated aromatic diamine *m*-6FBAB.

bis(3-amino-5-trifluoromethylphenoxy)biphenyl (*m*-6FBAB or **2**) and 4,4'-bis(4-amino-5-trifluoromethylphenoxy) biphenyl (*p*-6FBAB or **4**) with various aromatic dianhydrides in the presence of phthalic anhydride (PA) as a molecular weight-controlling and endcapping agent. The effects of the chemical structures of the fluorinated polyimides on their melt processability and solubility were systemically investigated.

EXPERIMENTAL

Materials

3,5-Dinitrobenzotrifluoride and 4,4'-biphenol (Beijing Chemical Reagents Co., Beijing, China) were used as received. 2-Chloro-5-nitrobenzotrifluoride was synthesized in our laboratory according to a method previously reported.²⁵ *N,N'*-Dimethylformamide (DMF), toluene, potassium carbonate (K_2CO_3), and *iso*-quinoline (Beijing Chemical Reagents Co.) were used as received. 1-Methyl-2-pyrrolidinone (NMP) and *m*-cresol as solvents (Beijing Chemical Reagents Co.) were vacuum-distilled and stored with 4-Å molecular sieves before use. Pyromellitic dianhydride (PMDA; Shanghai Chemspec Corp., China), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA; Ube Industries, Ltd., Honsha, Japan), and 4,4'-oxydiphthalic anhydride (ODPA; Shanghai Chemspec Corp.) were dried in a vacuum oven at 180°C for 12 h before use. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoroisopropylidene dianhydride (6FDA; 99%, Hoechst Celanese Corp., Somerville, NJ) was recrystallized from acetic anhydride, dried in a vacuum oven at 100°C for 12 h and then at 180°C for 12 h. PA (Beijing Chemical Reagents Co.) and sublimed before use.

Monomer synthesis

m-6FBAB (**2**) was synthesized with a two-step method. A dinitro compound, 4,4'-bis(3-nitro-5-trifluoromethylphenoxy)biphenyl (**1**), was first prepared by the reaction of 1 equiv of 4,4'-biphenol and 2 equiv of 3,5-dinitrobenzotrifluoride in the presence

of K_2CO_3 in DMF; the mixture was then hydrogenated by hydrazine monohydrate and Pd/C to give the fluorinated aromatic diamine (Scheme 1). The crude product of *m*-6FBAB was purified by recrystallization from ethanol to give colorless, flakelike crystals.

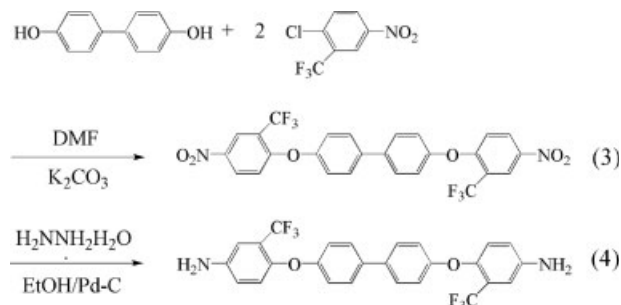
Yield: 85%. mp: 137.0–138.0°C, as determined by differential scanning calorimetry (DSC; 10°C/min). Fourier transform infrared (FTIR) spectroscopy (KBr, cm^{-1}): 3480, 3446, 3365 ($-NH_2$ stretching); 1220, 1168, 1132, 1115, 1085 (C—O—C and/or C—F stretching); 1329, 833 (C—N stretching). 1H -NMR (300 MHz, $CDCl_3$, ppm): 7.56 (d, 4H), 7.10 (d, 4H), 6.64 (s, 2H+2H), 6.46 (s, 2H), 3.88 (s, 4H). ANAL. Calcd. for $C_{26}H_{18}F_6N_2O_2$ (504.43): C, 61.90%; H, 3.60%; N, 5.55%. Found: C, 61.76%; H, 3.50%; N, 5.43%.

p-6FBAB (**4**) was prepared by the reaction of 2-chloro-5-nitrobenzotrifluoride and 4,4'-biphenol in the presence of K_2CO_3 in DMF, followed by reduction with hydrazine monohydrate and Pd/C (Scheme 2) according to the literature.²⁶ The crude product of *p*-6FBAB was purified by recrystallization from ethanol to give colorless, flakelike crystals.

Yield: 78.0%. mp: 153.0–154.0°C, as determined by DSC (10°C/min). FTIR (KBr, cm^{-1}): 3445, 3359 ($-NH_2$ stretching); 1265, 1230, 1160, 1128, 1048 (C—O—C and/or C—F stretching); 1341, 858 (C—N stretching). 1H -NMR (300 MHz, dimethyl sulfoxide- d_6 , ppm): 7.56 (d, 4H), 6.94 (s, 2H), 6.93 (d, 2H), 6.92 (d, 4H), 6.82 (d, 2H), 5.50 (s, 4H). ANAL. Calcd. for $C_{26}H_{18}F_6N_2O_2$: C, 61.90%; H, 3.60%; N, 5.55%. Found: C, 62.13%; H, 3.65%; N, 5.65%.

Synthesis of the polyimides

The polyimides were prepared with a given offset (3.0%) of aromatic dianhydride to the synthesized fluorinated diamine with the high-temperature polycondensation procedure. In a typical experiment, *m*-6FBAB–PMDA (PI-**2a**) was prepared as follows. In a 500-mL, three-necked flask equipped with a mechanical stirrer, a thermometer, and a Dean–Stark trap topped by a condenser, 20.18 g (40.0 mmol) of *m*-6FBAB, 8.46 g (38.8 mmol) of PMDA, and 0.36 g



Scheme 2 Synthesis of the fluorinated aromatic diamine *p*-6FBAB.

(2.4 mmol) of PA were placed. Then, a mixture of *m*-cresol and toluene (300 and 20 mL, respectively) and three drops of *iso*-quinoline as a catalyst were added successively. The reaction was processed at 180°C with stirring in nitrogen for 10 h. Then, the reaction solution was allowed to cool and was poured slowly into an excess of ethanol with vigorous mechanical stirring. The white precipitate was collected by filtration, washed thoroughly with ethanol and water, and dried at 100°C for 2 h. The collected precipitate was then pulverized to a powder with a pulverizer and dried in a vacuum oven at 150°C for 2 h, 180°C for 2 h, and 200°C for 1 h successively to give PI-2a. The yield was 27.90 g (98.7%).

Other polyimides, including *m*-6FBAB-BPDA (PI-2b), *m*-6FBAB-6FDA (PI-2c), and *m*-6FBAB-ODPA (PI-2d), were prepared from *m*-6FBAB with BPDA, 6FDA, and ODPA, respectively, by a similar procedure.

p-6FBAB-PMDA (PI-4a), *p*-6FBAB-BPDA (PI-4b), *p*-6FBAB-6FDA (PI-4c), and *p*-6FBAB-ODPA (PI-4d) were prepared from *p*-6FBAB with PMDA, BPDA, 6FDA, and ODPA, respectively, by a similar procedure.

Melt-molded polyimide sheets

Melt-molded polyimide sheets were prepared by hot-compressing of the polyimide powders in a mold. In a typical experiment, PI-2a powder was charged into a matched mold, which was then placed in a hot press. The mold was heated to 320°C for 15 min, and then a pressure of 5–6 MPa was applied. After it was kept at an elevated temperature for 30 min, the mold was cooled down to room temperature. A strong and tough polyimide sheet that was light brown in color was obtained, which was void-free and defect-free and translucence in appearance.

Other polyimide sheets (PI-2b, PI-2c, PI-2d, PI-4a, PI-4b, PI-4c, and PI-4d) were all prepared by a similar procedure.

Solution-cast polyimide films

Polyimide films were obtained by casting of the polyimide solution on a glass plate followed by baking to remove the residual solvent. In a typical experiment, 15.00 g of PI-2a powder was dissolved in 85.00 g of DMAc with stirring to give a homogeneous polyimide solution with 15 wt % solid content. The polyimide solution was filtered by an arenaceous funnel and then spread on a glass plate, which was then placed in an oven at 80°C for 2 h; it was then successively heated at 150°C for 2 h, 180°C for 2 h, and 200°C for 1 h. A strong, flexible, transparent film (PI-2a) was self-stripped off the glass surface by immersion of the glass plate in water. The total weight loss of the polyimide film scanned up to 350°C by thermogravimetric analysis (TGA)

was less than 0.2 wt %. Other polyimide films were prepared by a similar method.

Characterization

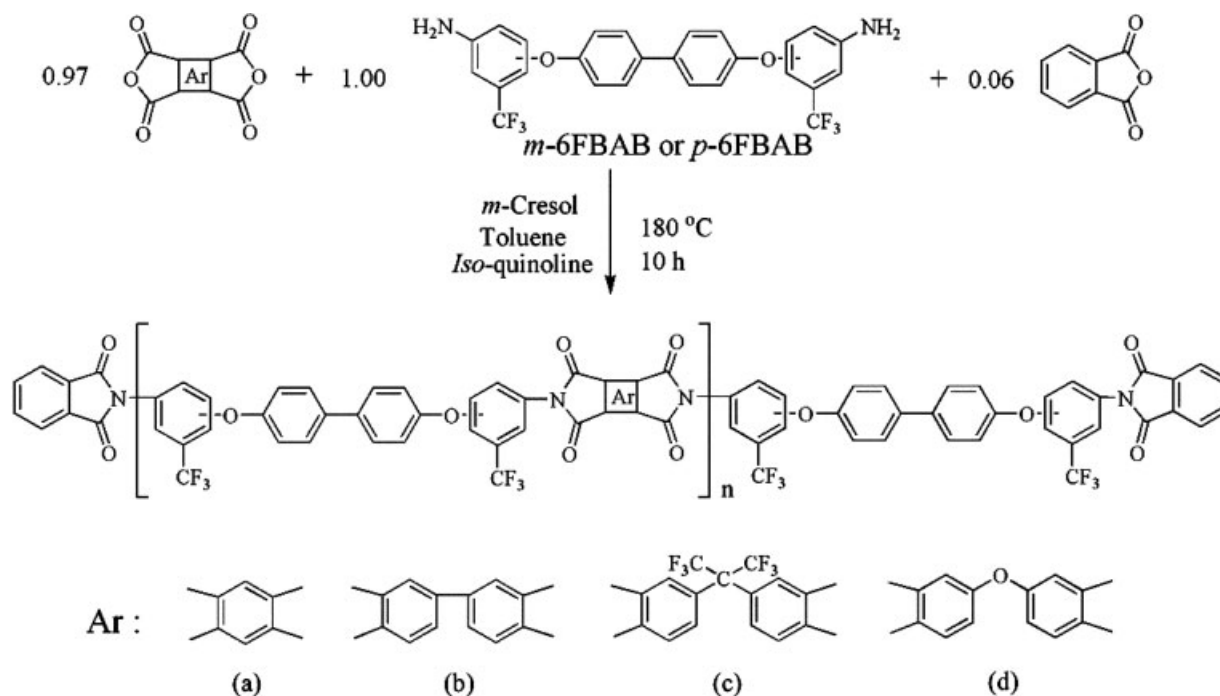
FTIR spectra were obtained from a PerkinElmer 782 FTIR spectrophotometer (PerkinElmer Corp. Norwalk, CT). ¹H-NMR spectra were obtained from a Varian Unity 300 spectrometer (Varian Ltd., Palo Alto, CA) operating at 300 MHz in CDCl₃ or dimethyl sulfoxide-*d*₆.

Inherent viscosities (η_{inh} 's) were measured with an Ubbelohde viscometer (Shanghai Liang Jing Glass Instrument Factory, Shanghai, China) in NMP at 30°C (0.5 g/dL). Number-average molecular weights (M_n 's) and weight-average molecular weights (M_w 's) were obtained via gel permeation chromatography (GPC) performed with a set of a Waters 515 high-performance liquid chromatography pump, a Waters 2414 differential refractometer (Waters Co., Milford, MA), and a combination of Styragel HT-2, HT-3, and HT-4, (Waters Co., Milford, MA) the effective molecular weight ranges of which were 100–10,000, 500–30,000, and 5000–600,000, respectively. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min at 35°C. Polystyrene standards were used for calibration.

DSC measurements were conducted on a PerkinElmer DSC-7 on 6–7 mg of the sample under a nitrogen purge at a heating rate of 20°C/min. Temperature and heat flow were calibrated with indium and zinc standards. The glass-transition temperature (T_g) value was taken at the inflection point of the DSC curve. TGA was conducted on a PerkinElmer 7 series thermal analysis system in nitrogen. The onset decomposition temperature (T_d), 5% weight loss temperature (T_5), 10% weight loss temperature (T_{10}), and residual weight (R_w) at 700°C were determined by TGA at a heating rate of 20°C/min.

Rheological experiments were carried out on a TA Instruments AD2000 rheometer with a parallel plate fixture with a diameter of 25 mm. The temperature was controlled with environmental test chamber (ETC) of the AD2000 rheometer (TA Instruments Corp., New Castle, DE). Sample specimen discs, 25 mm in diameter and 1–1.5 mm thick, were prepared by press-molding of about 0.80 g of powder at room temperature. The test chamber was preheated to the desired temperature before the specimen was loaded. Melt viscosity was measured with the flow mode with a constant stress (10^4 Pa) or a constant shear rate (1.0 s^{-1}) and about 5 Pa of normal force.

The mechanical properties of the solution-cast films were measured according to GB/T 13022-1991: the test specimens were prepared by the cutting of the films into 10 mm wide strips with a thickness of 0.3–0.4 mm and a total length of 120 mm. The ten-



Scheme 3 Synthetic pathways of the fluorinated aromatic polyimides.

sion properties of the melt-molded polyimide sheets were measured according to GB/T 16421-1996: the sheets were cut into dumbbell-shaped specimens with a thickness of 2 mm, a total length greater than 75 mm, a minimum width of 5 mm, and a maximum width of 10 mm. The test specimens for the flexural strength and modulus were measured according to GB/T 16419-1996, and the size of the test specimens was $2 \times 3 \times 40$ mm.

Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Hitachi U-3210 spectrophotometer (Hitachi, Tokyo, Japan).

RESULTS AND DISCUSSION

Polymer synthesis

The aromatic polyimides were prepared by the polymerization of the fluorinated aromatic diamines *m*-6FBAB or *p*-6FBAB with four different aromatic dianhydrides (PMDA, BPDA, 6FDA, and ODPA) in the presence of PA as an endcapping agent with a one-pot method (Scheme 3). The polycondensation was carried out at $180\text{ }^\circ\text{C}$ for 10 h in a homogeneous solution with *m*-cresol as the solvent and *iso*-quinoline as the catalyst. Meanwhile, toluene was used as an azeotropic reagent to carry out the byproduct, water, to compel the polymerization to be processed completely. Thus, fully imidized polymer powders with controlled molecular weights were obtained. The formations of the polyimides were confirmed with FTIR and $^1\text{H-NMR}$. Figure 1 shows the FTIR spectra of the polyimides derived from *m*-6FBAB and *p*-6FBAB

and ODPA, with PA as the molecular weight-controlling and endcapping agent. All polyimides exhibited characteristic imide group absorptions around 1780 and 1720 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretching), 1380 cm^{-1} (C–N stretching), and 1100 and 725 cm^{-1} (imide ring deformation). Figure 2 shows two typical $^1\text{H-NMR}$ spectra of PI-2c, PI-2d, PI-4c, and PI-4d. The proton signals attributed to the polyimide backbones derived from the fluorinated aromatic diamines and aromatic dianhydrides were all detected.

The molecular weights of the polyimides were determined by GPC and η_{inh} , as shown in Table I.

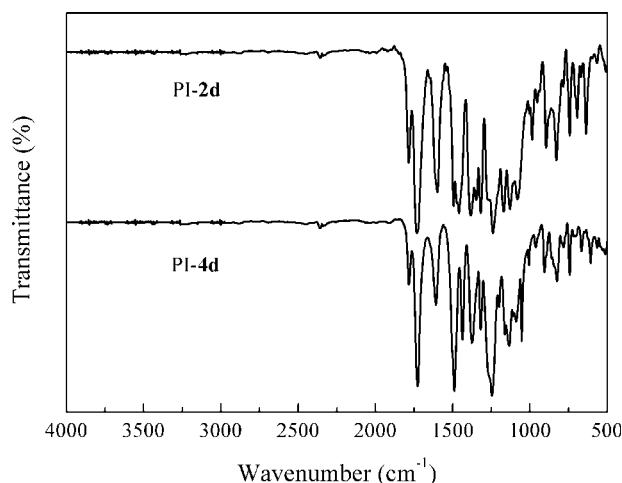


Figure 1 FTIR spectra of the fluorinated aromatic polyimides (PI-2d and PI-4d).

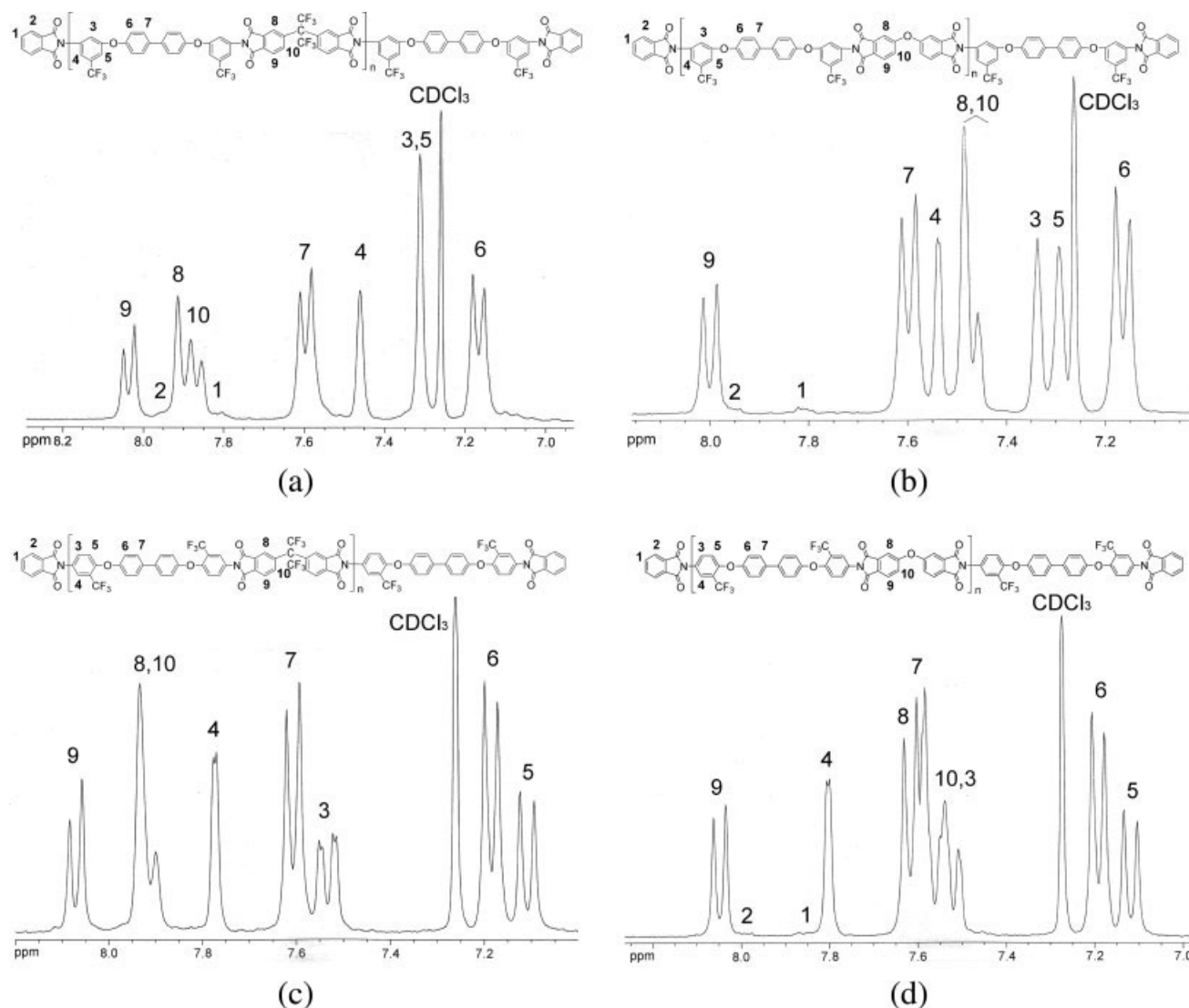


Figure 2 ^1H -NMR spectra of typical fluorinated aromatic polyimides in CDCl_3 : (a) PI-2c, (b) PI-2d, (c) PI-4c, and (d) PI-4d.

The theoretical number-average molecular weights ($M_n^{T_r}$'s) of the aromatic polyimides depended obviously on the aromatic dianhydrides that were used. The aromatic polyimides derived from PMDA and BPDA (PI-2a, PI-2b, PI-4a, and PI-4b) could not give

molecular weight data by GPC due to the difficulty of dissolving the polyimides in GPC solvents (THF); however, the polyimides derived from 6FDA and ODA (PI-2c, PI-2d, PI-4c, and PI-4d) gave good GPC results. For instance, the polyimides based on

TABLE I
Molecular Weights and η_{inh} Values of the Fluorinated Aromatic Polyimides

PI	η_{inh} (dL/g) ^a	M_n^T (g/mol)	M_n (g/mol) ^b	M_w (g/mol) ^b	PDI (M_w/M_n) ^b
PI-2a	0.36	2.3×10^4	— ^c	—	—
PI-2b	0.48	2.5×10^4	—	—	—
PI-2c	0.16	3.0×10^4	1.0×10^4	2.7×10^4	2.6
PI-2d	0.35	2.6×10^4	4.5×10^4	7.1×10^4	1.9
PI-4a	—	2.3×10^4	—	—	—
PI-4b	0.99	2.5×10^4	—	—	—
PI-4c	0.57	3.0×10^4	6.4×10^4	9.6×10^4	1.5
PI-4d	0.71	2.6×10^4	6.4×10^4	9.3×10^4	1.5

^a Measured at 30°C.

^b Determined by GPC.

^c Not detected.

TABLE II
Solubility of the Fluorinated Aromatic Polyimides

PI	NMP	DMAc	DMF	<i>m</i> -Cresol	THF	CHCl ₃	Toluene	Acetone	EtOH
PI-2a	++	++	++	+	++	-	-	-	-
PI-2b	+	+	+	++	+-	+-	-	-	-
PI-2c	++	++	++	++	++	++	++	+-	-
PI-2d	++	++	++	++	++	++	++	+-	-
PI-4a	-	-	-	-	-	-	-	-	-
PI-4b	+	+	+	+	+-	-	-	-	-
PI-4c	++	++	++	++	++	++	+	+-	-
PI-4d	++	++	++	++	++	+	+-	+-	-

The qualitative solubility was determined by the dissolution of 1.0 g of polymer in 9.0 g of solvent. ++: soluble at room temperature; +: soluble on heating; +-: swelling; -: insoluble even with heating.

ODPA (PI-2d and PI-4d) showed M_n values in the range $4.5\text{--}6.4 \times 10^4$ and M_w values in the range $7.1\text{--}9.3 \times 10^4$, respectively. The η_{inh} 's of the polyimides were measured in the range 0.16–0.48 dL/g for the PI-2 series, compared to 0.57–0.99 dL/g for the PI-4 series. Clearly, the differences in GPC molecular weights and η_{inh} 's of the polyimides were due to the chemical structures of the fluorinated aromatic diamines. The polydispersity indices (PDIs; $PDI = M_w/M_n$) of the polyimides ranged from 1.5 to 1.9, except for that of PI-2c, which showed very low molecular weights ($M_n = 1.0 \times 10^4$ g/mol and $M_w = 2.7 \times 10^4$ g/mol) and a low η_{inh} ($\eta_{inh} = 0.16$ dL/g). The molecular weights of the PI-2 series were less than that of the PI-4 series because the reactivity of *m*-6FBAB was lower than that of *p*-6FBAB. For PI-2d, PI-4c, and PI-4d, the M_n^T 's were much lower than the measured M_n 's, probably because of the difference in the solution properties between the polyimides and the standard polystyrene.

Polyimide solubility

The molecular-weight-controlled polyimides showed good solubility in organic solvents (Table II). The

polyimides derived from 6FDA and ODPA (PI-2c, PI-2d, PI-4c, and PI-4d) showed better solubilities than those derived from PMDA and BPDA (PI-2a, PI-2b, PI-4a, and PI-4b). For instance, PI-2c and PI-4c showed good solubilities not only in strong aprotic solvents such as NMP and DMAc but also in common organic solvents such as THF and chloroform. The polyimide solubility decreased in the order of the following solvents: NMP, DMAc, DMF > *m*-Cresol > THF and chloroform > Toluene, acetone, and ethanol. Figure 3 shows the dependence of the polyimide solution viscosity ($\log \eta$) on the polymer solid concentrations, in which it can be seen that $\log \eta$ values linearly increased with increasing polymer solid concentrations from 5 to 50% for PI-2d and 5 to 35% for PI-4d. PI-2d (*m*-6FBAB–ODPA) exhibited a much lower viscosity than PI-4d at the same solid concentration. For instance, the viscosity of PI-2d at 30 wt % solid concentration was 4×10^4 mPa s, compared to 1×10^5 mPa s for PI-4d.

Figure 4 depicts the effect of storage time on the viscosities of PI-2d and PI-4d in NMP solutions with different solid concentrations. The polymer solutions with lower polyimide concentrations (<30 wt % for

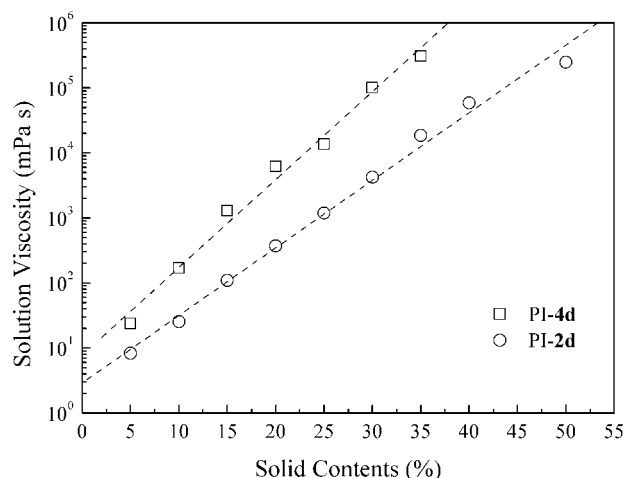


Figure 3 Relationship between $\log \eta$ of the polyimides in NMP and the polymer solid content.

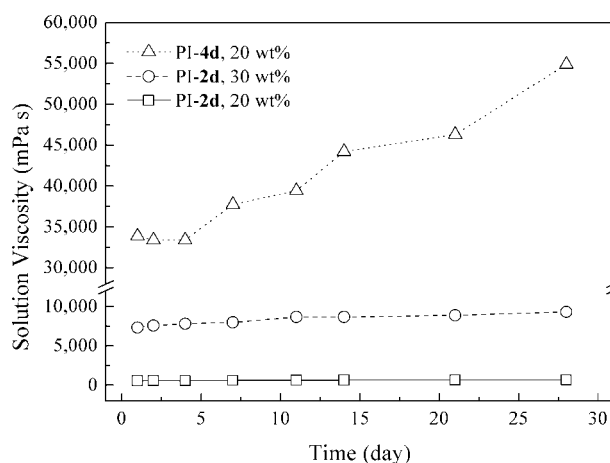


Figure 4 Effect of storage time on the viscosity of the polyimides in NMP.

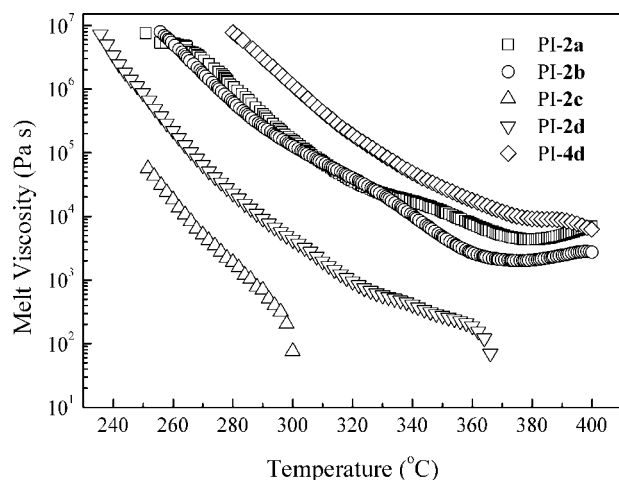


Figure 5 Melt viscosities of the fluorinated aromatic polyimides as a function of temperature.

PI-2d and <15 wt % for PI-4d) were very stable in storage at room temperature, in which no precipitation, gelation, or phase separation occurred during a storage period of more than 4 weeks. However, the polyimide solution with a higher polyimide concentration (20 wt % for PI-4d) showed an obvious increase in $\log \eta$ after storage for more than 3 weeks, which implies that polymer aggregation might have occurred due to the closed distance of the polymer chains in the concentrated solution. All of these results indicated that the solubilities of polyimides based on *m*-6FBAB were better than those of *p*-6FBAB based polyimides.

Melt processability

The melt processabilities of the fluorinated aromatic polyimides were investigated by rheology. Figure 5 shows the melt viscosities of the fluorinated aromatic polyimides as a function of heating temperature. The melt rheological behaviors of the PI-2 series depended greatly on the chemical structures of the polymer backbones. The melt viscosity of PI-2c (*m*-6FBAB-6FDA) decreased abruptly with increasing temperature greater than 250°C and reached 10^2 Pa s at 300°C, which was probably due to the very low molecular weight. PI-2d (*m*-6FBAB-ODPA) exhibited similar melt rheological behavior to PI-2c, with a drop in melt viscosity at 360°C. PI-2a (*m*-6FBAB-PMDA) and PI-2b (*m*-6FBAB-BPDA) showed the highest melt viscosities of $0.3\text{--}0.8 \times 10^4$ Pa s at temperatures above 360°C. In comparison, PI-4d showed much a higher melt viscosity than PI-2d. Meanwhile, PI-4a, PI-4b, and PI-4c were not fusible in the same conditions, probably due to the para-substituted aromatic diamine.

The melt stabilities of the fluorinated aromatic polyimides were also investigated by rheology at a

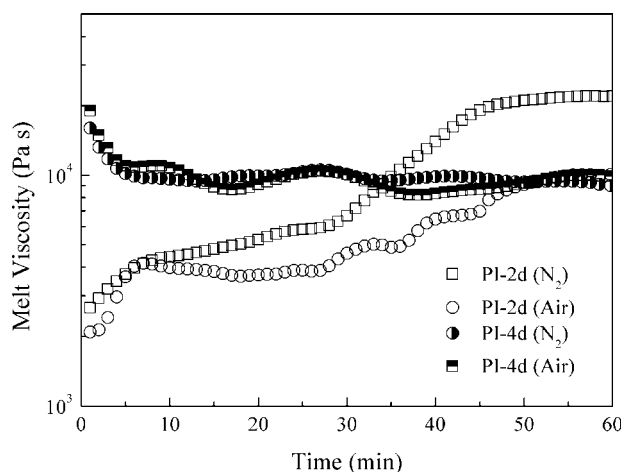


Figure 6 Melt viscosities of PI-2d and PI-4d in air and N₂ as a function of time at 330°C.

suitable shear rate at 330°C. Figure 6 shows the melt viscosities of PI-2d and PI-4d as a function of time in air and N₂, respectively. It was clear that PI-4d possessed good melt stability in both air and N₂. However, the melt viscosity of PI-2d increased gradually during the measurement.

Table III shows the rheological data of the fluorinated aromatic polyimides. According to the melt viscosity suitable for injection molding (<1000 Pa s),^{27,28} PI-2c and PI-2d might be suited for melt injection molding [melt viscosity at 360°C (η_{360}) < 189 Pa s]. The melt viscosity ratio (MVR) calculated by eq. (1) is usually used to describe melt stability.²⁹

$$\text{MVR} = \text{MV}_{30} / \text{MV}_5 \quad (1)$$

where MV_5 and MV_{30} are the melt viscosities (Pa s) one determines by melting a sample and maintaining it at a certain temperature for 5 and 30 min, respectively. PI-2a and PI-2b exhibited poor melt stabilities but PI-2c, PI-2d, and PI-4d showed good melt stabilities. The MVR data measured in air were

TABLE III
Rheological Behavior Data of the Fluorinated Aromatic Polyimides

PI	η_{280} (Pa s) ^a	η_{360} (Pa s)	$T_{0.5 \text{ MPa s}}$ (°C) ^b	MVR_1^c	MVR_2^d
2a	107×10^4	0.8×10^4	290	8.4	9.6
2b	63×10^4	0.3×10^4	280	6.1	10.3
2c	0.2×10^4	very low	≤ 240	1.1	1.1
2d	2.3×10^4	0.02×10^4	250	1.3	1.8
4d	775×10^4	1.8×10^4	310	1.0	1.0

^a Melt viscosity at 280°C.

^b Temperatures at which the melt viscosity was 5×10^5 Pa s.

^c Melt viscosity ratio measured in N₂.

^d Melt viscosity ratio measured in air.

TABLE IV
Thermal Properties of the Fluorinated Aromatic Polyimides

PI	T_g (°C) ^a	Thermal stability ^b			
		T_d (°C)	T_5 (°C)	T_{10} (°C)	R_w (%) ^c
PI-2a	250	597	568	605	56.7
PI-2b	230	582	581	605	60.6
PI-2c	217	554	540	569	53.9
PI-2d	205	587	586	609	63.7
PI-4a	— ^d	550	560	601	51.7
PI-4b	264	592	578	619	63.1
PI-4c	263	547	546	563	46.5
PI-4d	236	593	577	612	65.1

^a Measured from DSC under nitrogen at a heating rate of 20°C/min.

^b Measured from TGA under nitrogen at a heating rate of 20°C/min.

^c R_w retention at 700°C.

^d Not detected.

higher than those measured in nitrogen, which implies that air also had a negative effect on the melt stability.

Thermal properties

The thermal properties of the fluorinated aromatic polyimides are presented in Table IV. The T_g 's of the polyimides, determined by DSC in the second run, were in the range 205–250°C for the PI-2 series and 236–264°C for the PI-4 series. Clearly, T_g decreased with increasing polyimide backbone flexibility. In the PI-2 series, T_g decreased in the order of the aromatic dianhydrides used: PI-2a > PI-2b > PI-2c > PI-2d. PI-2d had a T_g of 205°C, 45°C lower than that of PI-2a. Moreover, the PI-4 series had higher T_g values than the PI-2 series. For instance, PI-4c (*p*-6FBAB-6FDA) had a T_g of 263°C, 46°C higher than PI-2c (*m*-6FBAB-6FDA). This could be interpreted by the difference in imide linkages in the polymer

chains, in which the PI-4 series were para-linked imides, compared to meta-linked ones in PI-2 series. The para-linked PI-4 series had more well-packed structures than the meta-linked PI-2 series.^{30,31}

The thermal stabilities of the polyimides were evaluated by dynamic TGA at a heating rate of 20°C/min in nitrogen. The polyimides did not lose appreciable weight until the temperature was scanned to 500°C. For the PI-2 series, the T_d 's of PI-2a, PI-2b, and PI-2d ranged from 582 to 597°C, 28–43°C higher than that of PI-2c. T_5 and T_{10} increased in the order: PI-2c < PI-2a < PI-2b ≈ PI-2d. The PI-4 series exhibited similar thermal properties to the PI-2 series.

The thermal properties of the polyimide films were also measured. The results indicate that the thermal properties of the films were almost the same with the relative powders.

Mechanical properties

Table V summarizes the mechanical properties of the solution-cast polyimide-films and melt-molded polyimide sheets. Except for PI-2c (*m*-6FBAB-6FDA), all of the other fusible polyimides could be melt-molded at 260–310°C to give a tough and transparency polymer sheets with thicknesses of 1.0–4.0 mm. The tensile strengths were measured in the range 84.3–102.8 MPa, and the tensile moduli were measured in the range 1.81–1.98 GPa. The flexural strengths were determined in the range 126.5–127.6 MPa, and the flexural moduli were determined in the range 2.60–2.98 GPa. PI-2c was melt-processed to give a brittle material that could not be prepared for test samples, probably due to its limited molecular weight. PI-2d showed excellent mechanical properties with a tensile strength of 92.7 MPa, a tensile modulus of 1.95 GPa, a flexural strength of 127.0 MPa, a flexural modulus of 2.98 GPa, and an elongation at break of 7.5%. In comparison, PI-4d showed

TABLE V
Mechanical Properties of the Solution-cast Polyimide Films and Melt-Molded Sheets

PI	Solution-cast films			Melt-pressed sheets				
	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Flexural strength (MPa)	Flexural modulus (GPa)
2a	81.3	2.79	4.8	85.1	1.81	8.4	127.6	2.75
2b	92.5	2.74	7.0	84.3	1.98	5.1	127.9	2.65
2c	88.9	2.90	4.8	— ^a	—	—	—	—
2d	95.5	2.72	5.1	92.7	1.95	7.5	127.0	2.98
4a	— ^a	—	—	—	—	—	—	—
4b	103.2	2.35	11.4	—	—	—	—	—
4c	102.1	2.42	7.8	—	—	—	—	—
4d	104.9	2.38	10.5	102.8	1.81	19.6	126.5	2.60

^a Not detected.

much better mechanical properties; it had a tensile strength of 102.8 MPa and an elongation at break of 19.56%. Table V shows the mechanical properties of all of the solution-cast polyimide films except PI-4a due to its difficulty being dissolved in common solvents. The tensile strengths and elongations at break for the PI-2 series ranged from 81.3 to 95.5 MPa and 4.8 to 7.0%, respectively, lower than those for the PI-4 series (102.1–104.9 MPa and 7.8–11.4%).

All of these results imply that the polyimide with *para*-imide units in the polymer backbone possessed better mechanical properties than that with the *meta*-imide polymer chain. The difference between the mechanical properties of the melt-molded sheets and solution-cast films might have been due to the difference in the sample preparation procedures. Although the polyimides were melt processable, the mechanical properties were lower than those of the respective solution-cast analogs. Perhaps there were some high-molecular-weight compositions that melted incompletely during melt-molding.

Moisture absorption and optical properties

Figure 7 depicts the moisture uptakes of the polyimide films, as measured by two different methods. In method A, the test polyimide samples were immersed in water at $30 \pm 0.5^\circ\text{C}$ for 24 or 72 h; then, the water uptakes were determined by the weight changes. In method B, the test polyimide samples were treated in boiling water at 100°C for 6 or 24 h; the water uptakes were then determined by weighing. The PI-2 series showed water uptakes in the range of 0.38–0.56% by method A and 0.38–0.58% by method B, respectively; these values were lower than those of the PI-4 series, which had water uptakes of 0.48–0.92% by method A and 0.63–1.16% by method B. PI-2d exhibited the lowest water uptake of 0.38% by both methods. The moisture

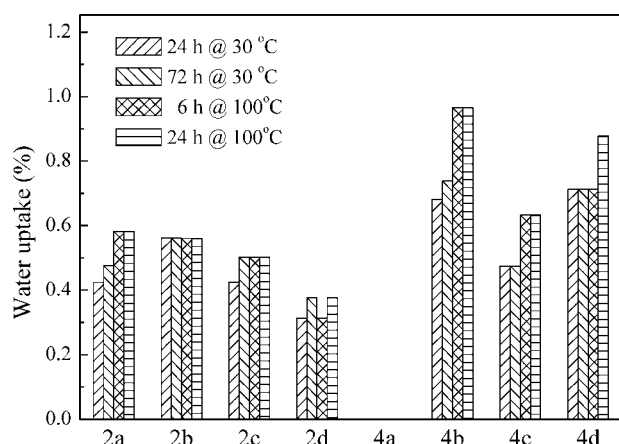


Figure 7 Water uptakes of the fluorinated aromatic polyimide films as determined by two methods.

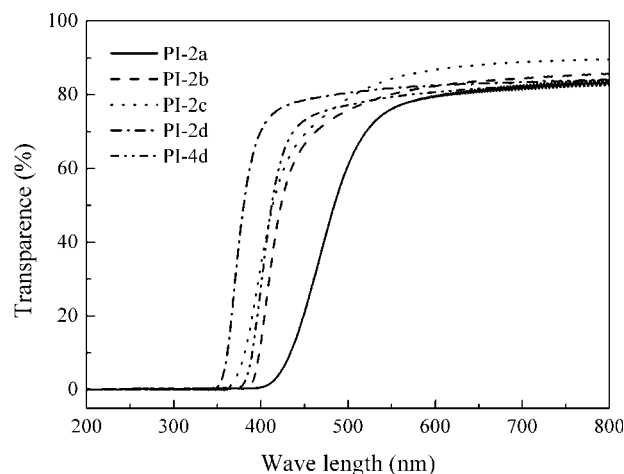


Figure 8 UV-vis spectra of the fluorinated aromatic polyimide films.

uptakes of polyimide films based on *m*-6FBAB were lower than those of films based on *p*-6FBAB. This may have been due to the films based on *m*-6FBAB being compacter in their thicknesses.

Figure 8 shows the UV-vis spectra of the fluorinated aromatic polyimides PI-2a–PI-2d and PI-4d films. The cutoff wavelengths (λ_0 's) observed in UV-vis spectra were used to elucidate the colors of the polyimide films. It was clear that the values of λ_0 decreased in the order: PI-2a (428 nm) > PI-2b (394 nm) > PI-2c (378 nm) > PI-2d (358 nm). The polyimide films based on 6FDA and ODPa were fairly transparent and almost colorless, probably due to the reduction of the intermolecular charge-transfer complex between imide moieties.^{32,33} All polymer films of the PI-2 series showed lower λ_0 values than the films of the corresponding PI-4 series. For instance, the cutoff wave length of PI-2d was 358 nm, 26 nm lower than that of PI-4d (386 nm), which implies that the meta-linked diamine was effective in decreasing charge-transfer complex formation among the polymer chains.

CONCLUSIONS

Two series of fluorinated aromatic polyimides were synthesized from *m*-6FBAB and *p*-6FBAB with aromatic dianhydrides. The experimental results indicate that polyimides derived from *m*-6FBAB showed better melt processabilities than the *p*-6FBAB based polymers. The polyimides based on *m*-6FBAB also possessed better solubilities, lower water uptakes, and lower λ_0 's. The fluorinated polyimide (PI-2d) derived from *m*-6FBAB and ODPa showed an excellent solubility, a low melt viscosity of 200 Pa s, a good melt stability at 360°C , a good thermal stability with a thermal decomposition temperature of 587°C , good mechanical properties with a tensile strength

of 92.7 MPa, and an elongation at break of 7.5%; polyimide (PI-4d) derived from *p*-6FBAB and ODPA had a melt viscosity of 1.8×10^4 Pa s at 360°C, a thermal decomposition temperature of 593°C, and mechanical properties with a tensile strength of 102.8 MPa and elongation at break of 19.6%.

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