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Novel polyfluorinated polyimides derived from α,α-bis(4-amino-3,5-difluorophenyl)phenylmethane and aromatic dianhydrides: Synthesis and characterization

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Abstract

A novel aromatic diamine containing bulky lateral phenyl unit and fluorine groups *ortho*-substituted to the amino groups in the structure, α,α-bis(4-amino-3,5-difluorophenyl)phenylmethane (4FMA) was synthesized and characterized. 4FMA was polymerized with four aromatic dianhydrides to afford a series of polyimides (PIs) via a one-step high-temperature polycondensation procedure. All the PIs were amorphous and showed good solubility not only in polar aprotic solvents, but in many common solvents, such as cyclopentanone and tetrahydrofuran. The soluble polymers formed flexible, tough and transparent films. The films had a tensile strength, elongation at break, and tensile modulus in the ranges 85–107 MPa, 4–7%, 1.7–2.8 GPa, respectively. The polyimides also exhibited high-T_g (292–338 °C), good thermal stability, good dielectric strength, low dielectric constants, and low water uptakes due to the introduction of the polyfluorinated substituents in the polymer backbone. As expected, the PI films showed good transparency in the UV–Vis light region with cutoff wavelength as low as 318 nm and transmittance higher than 60% at 450 nm. PI-4 derived from 4FMA and fluorinated dianhydride 6FDA exhibited low light-absorption in the near-infrared region, especially at the optocommunication wavelength of 1310 nm and 1550 nm. The remarkable combined properties indicate their potential applications in microelectronic and optoelectronic fabrications.

Keywords: Polyimides; Fluorine; Transparency; Solubility; Thermal stability; Optoelectronics

1. Introduction

Polyimides (PIs) have been intensively studied since the 1960s because of their excellent thermal stabilities, mechanical properties and electric properties. In recent years, interest in PIs exhibiting a favorable combination of properties including high optical transparency, low refractive index (low-*n*), low dielectric constant (low-*k*), high glass transition temperature (T_g), and good mechanical properties has increased in the fields of optoelectronic and microelectronic fabrications [1,2]. However, the relatively poor processability of the standard

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wholly-aromatic PIs caused by their limited solubility in organic solvents and high melting and softening temperatures, greatly prohibit their wide applications. On the other hand, the standard PI films often exhibit deep colors because of the intra- and inter-molecular charge transfer (CT) interactions between the alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [3–5]. A strategy for obtaining less-colored or colorless PIs is to use dianhydrides with lower electron-acceptability or diamines with lower electron-donatability as monomers for weakening the CT interactions [5]. Hence, considerable efforts have been made to develop organo-soluble and colorless PIs by introducing flexible linkages, unsymmetrical units or bulky pendant groups into the PIs [6–9]. Among the modifications, fluorination might be one of the most promising procedures to achieve the compromise among the desired properties. As is well-known, the high electronegativity and low molar polarization of the fluoro-containing groups often endow the obtained PIs with many attractive features, such as good solubility in common solvents, high transparency in the visible region, low dielectric constant, and low water uptake [10–12].

In our previous work, a series of trifluoromethyl-modified PIs have been proposed and developed [13–18]. As a beneficial complementarity to our continuous work to develop high performance PIs for micro or optoelectronic fabrications, recently, we focused our work on polyfluorinated PIs [12]. Compared with fluorocarbon groups, such as $-CF_3$ and $-CF_2(CF_2)_xCF_3$, fluorine atoms exhibit much lower molar volume and can be directly linked to the main chain of the PIs so as to reduce the absorptions of C–H bonds at the optocommunication wavelength. Thus, the polyfluorinated PIs have been proposed to be used as coatings for optical waveguide fabrication [19].

One of the unavoidable problems to develop polyfluorinated PIs is the reactivity reduction of the diamine due to the steric and electronic characteristics of the fluorine groups. Recent studies show that high-molecular-weight, high-T_g, low-k, and high transparent PIs could be obtained by the high-temperature polycondensation procedure of polyfluorinated diamines [12,20]. As a part of our continuous work, a new *ortho*-fluorine-substituted aromatic diamine monomer, α,α-bis(4-amino-3,5-difluorophenyl)phenylmethane was synthesized and polymerized. Due to the presence of the bulky pendent phenyl unit and the *ortho*-substituted fluorine groups in the PI backbone, the obtained polymers are expected to show increased solubility, thermal stability and reduced dielectric constant. The effects of the structures on the properties of the PIs were investigated.

2. Experimental

2.1. Materials

2,6-Difluoroaniline and trifluoromethanesulfonic acid were purchased from Acros Corp. and were used as received. Commercial available benzaldehyde was used as received. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA, **1**, Acros), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **2**, Acros), 4,4′-oxydiphthalic anhydride (ODPA, **3**, TCI), and 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA, **4**, Hoechst Celanese Corp.) were recrystallized from acetic anhydride and dried in vacuum at 160 °C overnight prior to use. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, *N,N*-dimethylformamide (DMF), *N,N*-dimethyl-acetamide (DMAc), and other solvents were purified by distillation prior to use.

2.2. Measurements

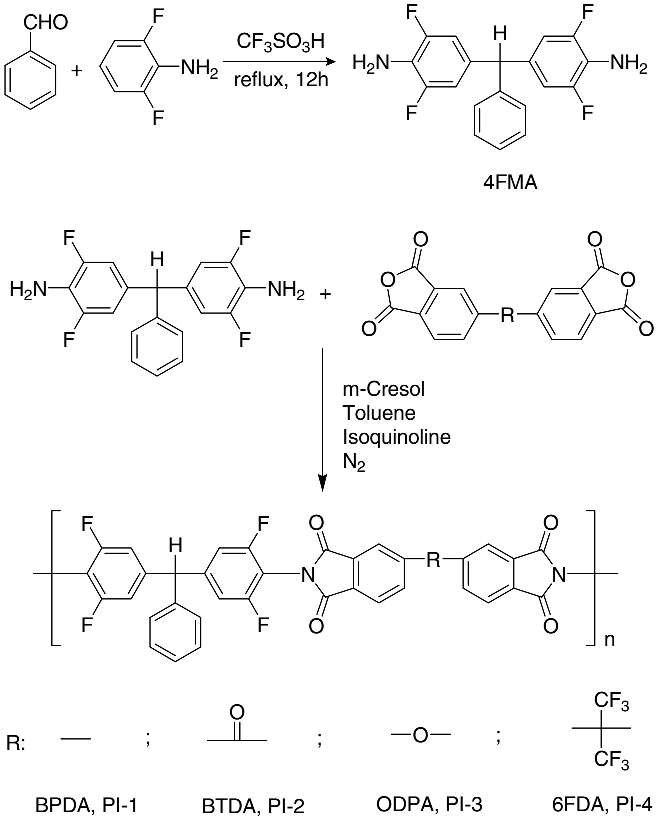
Inherent viscosity was measured by using an Ubbelohde viscometer with a 0.5 g/dL DMAc solution at 30 °C. FT-IR spectra were obtained with a Perkin–Elmer 782 Fourier transform spectrometer. UV–Vis spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. Prior to test, PI film samples were dried at 100 °C for 1 h to remove the absorbed moisture. Near-infrared spectra were measured by a Shimadzu UV-3100 UV/Vis/NIR spectrophotometer. Refractive indices of the PI films formed on a 3-in. silicon wafer were measured at the wavelength of 1310 nm at room temperature with a SaironTech Model SPA-4000 prism coupler. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices were determined by using a linearly polarized laser light parallel (transverse electric, TE) and perpendicular (transverse magnetic, TM) polarizations to the film plane, respectively. ^1H NMR and ^{13}C NMR were performed on a Varian Unity 200 spectrometer operating at 300 MHz and 400 MHz in DMSO-d_6, respectively. DSC and TGA were recorded on a Perkin–Elmer 7 series thermal analysis system at a heating rate of 20 °C/min in nitrogen at a flow rate of 200 mL/

min. Wide-angle X-ray diffraction measurements were performed at room temperature on a Siemens kristalloflex D5000 X-ray diffractometer. The tensile properties were performed on an Instron 3365 Tensile Apparatus with $80 \times 10 \times 0.05\ \mathrm{mm}^3$ specimens in accordance with GB1447-83 at a drawing rate of 2.0 mm/min. The electrical properties were measured on a Hewlett–Packard 4284A Presion LCR meter at room temperature. The surface and volume resistances were measured with film specimens with a diameter of 50 mm and a thickness of 50 μm. The dielectric constants were measured at 1 MHz with melt-molded PI sheets with a diameter of 50 mm and a thickness of approximately 120 μm. Water uptake was determined by immersing the PI film ($3.0 \times 1.0 \times 0.005\ \mathrm{cm}^3$) in water at 25 °C for 24 h, which was then dried immediately with blotting paper and weighted to determine the water uptake value.

Solubility was determined as follows: 1.5 g of PI resin was mixed with 8.5 g of a tested solvent at room temperature (15 wt% solid content), which was then mechanically stirred in nitrogen for 24 h. The solubility was determined visually as three grades: completely soluble (++), partially soluble (+), and insoluble (−). The complete solubility (++) is defined as a homogenous and clean solution is obtained, in which no phase separation, precipitation or gel formation is detected.

2.3. Monomer synthesis

The synthetic route for the diamine 4FMA is shown in Scheme 1. A mixture of 2,6-difluoroaniline (52.94 g, 0.41 mol) and benzaldehyde (10.61 g, 0.10 mol) was placed in a 250-mL three-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a dropping funnel. Then, trifluoromethanesulfonic acid (14.74 g, 0.10 mol) was added dropwise over 1 h at room temperature. After the addition, the reaction mixture was heated to reflux for 12 h. Then, the solution was cooled to room temperature, followed by neutralization with a solution of 5% sodium dicarbonate (330 mL). The pale pink precipitate was filtered and dried under vacuo at 80 °C overnight. The crude 4FMA



Scheme 1. Synthesis of 4FMA and PIs.

was purified by recrystallization twice from absolute ethanol and the yield was 24.94 g (total yield: 72.0%), m.p.: 120.9 °C (determined by DSC as peak temperature).

FT-IR (KBr, cm^{-1}): 3430, 3337, 3247, 3203, 1648, 1591, 1519, 1444, 1325, 1159, 975, 868, 836, 729, 701 and 662. ^1H NMR (300 MHz, DMSO-d_6, ppm): 7.33–7.28 (m, 2H), 7.24–7.22 (t, 1H), 7.10–7.08 (d, 2H), 6.61–6.57 (d, 4H), 5.34 (s, 1H), and 5.13(s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 152.5, 143.7, 131.1, 129.2, 128.8, 126.8, 124.2, 111.9, and 53.9. MS (EI, *m*/*e*, percentage of relative intensity): 346 (M^+, 100). Elemental analysis: Calculated for $C_{19}H_{14}F_4N_2$: C, 65.89%, H, 4.07%, N, 8.09%. Found: C, 65.88%, H, 4.12%, N, 8.14%.

2.4. Synthesis of polyimides

The general procedure for the preparation of the PIs could be illustrated by the synthesis of PI-1 (Scheme 1). 4FMA (6.9264 g, 0.02 mol) and *m*-cresol (94 mL) were added to a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a thermometer. After stirring at room temperature for 20 min, a clear solution was obtained. BPDA (5.8844 g, 0.02 mol) was added in one portion. The mixture was stirred at room temperature for 4 h to yield a viscous amber solution. Toluene (50 mL) and a catalytic amount of isoquinoline were then added and a Dean–Stark trap was connected. The mixture was heated to 180 °C and maintained at this temperature for 12 h to ensure the complete imidization. During the heating, the water produced by the imidization reaction was continuously removed by the azeotrope with toluene. 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 silky precipitate. The precipitate was collected and dried at 80 °C under vacuum overnight. The yield was 11.73 g (97%).

PI-2, PI-3, and PI-4 were prepared according to the same procedure as PI-1 except that BPDA was replaced by BTDA for PI-2, ODPA for PI-3 and 6FDA for PI-4, respectively.

2.5. Film preparation

First, the PI solution was prepared by dissolving the above mentioned PI resin in DMAc at room temperature with a solid content of 20% (w/w). After filtering through a 0.45 μm Teflon syringe filter to remove any particulate, the purified PI solution was spin-coated on a silicon wafer, and the thickness was controlled by the spinning rate. For example, the thickness of a specimen for FT-IR and UV–Vis measurements was controlled to be about 10 μm, and the specimen for thermal and dielectric properties measurement was adjusted to be 30–50 μm. The PI films were obtained by thermally curing the PI solution in an oven for 1 h each at 80 °C, 120 °C, 150 °C, and 250 °C, respectively. The PI film was obtained by immersing the silicone wafer in warm water.

2.6. Melt-molded PI sheets

The melt-molded PI sheets for dielectric constant measurement were prepared by the melt processing of the PI powders in a mold (5 cm in diameter). In a typical experiment, PI-1 powder was charged into a matched mold, which was then put in a hot press. The mold was heated at 360 °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, light brown in color, was obtained, which was defect-free and transparent in appearance.

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

3. Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, the fluorinated diamine 4FMA was prepared by reacting the 2,6-difluoroaniline with benzaldehyde according to a well-established procedure [21–23]. The polymerization-grade 4FMA was attained by recrystallization twice from ethanol as a needle-like pale-yellow crystal. The diamine exhibited a sharp melting point at 120.9 °C, determined by DSC. The structure of 4FMA was confirmed by ^1H NMR, ^{13}C NMR, elemental analysis and MS spectrometry. As shown in Fig. 1, the FT-IR spectrum of the diamine showed strong absorption at around 3430.7 and 3336.6 cm^{-1} owning to the primary amino groups, and the strong absorptions at 1159.0 cm^{-1} assigned to the stretching vibration of C–F bond. In Fig. 2, the ^1H NMR signal at around 5.13 ppm was assigned to the protons in the amino groups. The proton in the methylene bridge (H_a) appeared at the highest field in the spectrum except that of

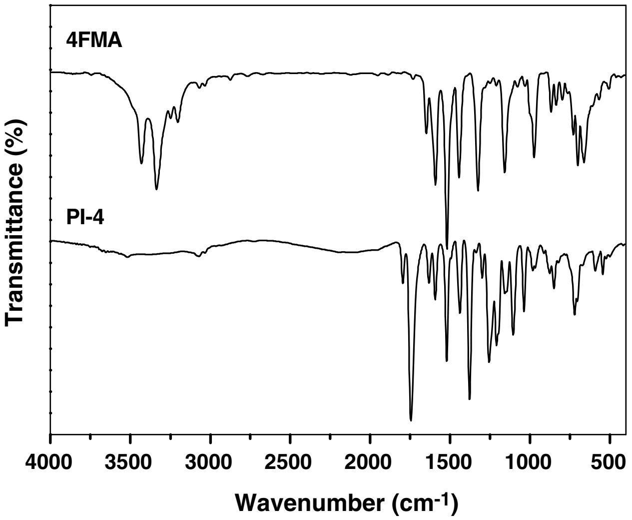


Fig. 1. FT-IR spectra of 4FMA and PI-4.

–NH_2. On the contrary, the protons in the lateral phenyl (H_c, H_d, and H_e) appeared at the lowest field in the spectrum. Although H_b was located at the *ortho* position to the electron-withdrawing fluorine group, its signal appeared in the middle part of the spectrum, indicating the synergetic effects of the electron-withdrawing fluorine group and *ortho*-substituted electron-donating hydrocarbon group. The ^{13}C NMR spectrum of 4FMA exhibited 13 peaks in the range of 54–153 ppm due to the symmetry of the molecular structure. According to Fig. 2, C_2, C_2', C_3, C_3', C_4, C_4', C_5 and C_5' all showed clear doublets because of the C–F coupling. The coupling effect decreased with the increase of the distance between C and F atoms. For instance, C_4 (coupling constant $J_{C–F}$: 239 Hz) showed a much stronger coupling effect with F than that of C_5 ($J_{C–F}$: 12 Hz). Furthermore, the elemental analysis values were in good agreement with the calculated ones and the molecular weight determined by mass spectrometry was the same with the expected value (346). All the above characterizations indicated the successful preparation of the fluorinated diamine monomer.

3.2. Synthesis of polyimides

The fluorinated PIs were prepared from 4FMA with four aromatic dianhydrides via a one-step high-temperature polycondensation procedure (Scheme 1) in *m*-cresol. Due to the effect of the *ortho*-substituted electron-withdrawing fluorine substituents, the amino in 4FMA has much lower reactivity as compared with their non-fluorinated analogues [12,20]. On the other hand, the fluorine substituents hinder the attack reaction of diamine with the dianhydride by their steric hindrance. The steric hindrance increased with the increase of the numbers of fluorine substituents. From this point of view, it would be very difficult to obtain PAA with high-molecular-weights from 4FMA, which containing both two *ortho*-substituted-fluorine atoms to amine groups, by conventional two-step procedure. One-step high-temperature polycondensation procedure provides enough energy to promote the polymerization reaction and is widely utilized to develop fluorinated PIs [24–27]. Thus, in this work, a series of PIs were prepared via this procedure and the inherent viscosity was tested as a criterion for the estimation of the molecular weight. As shown in Table 1, the inherent viscosity of the polymers measured at a concentration of 0.5 g/dL in DMAc at 30 °C was in the range of 0.52–0.75 dL/g, indicating moderate molecular weights. According to GPC analysis, their weight-average molecular weights (M_w) and number-average molecular weights (M_n) were recorded in the range of 2.6×10^4–3.8×10^4 and 4.4×10^4–6.4×10^4, respectively, indicating the similar trend with that of the inherent viscosity data. Fig. 1 depicts the FT-IR spectrum of PI-4 in which the absorption at 1796 and 1745 cm^{-1} were related to the asymmetric and symmetric stretching vibrations of the imide carbonyl group. The band at 721 cm^{-1} was due to the vibrations of the imide group and the band

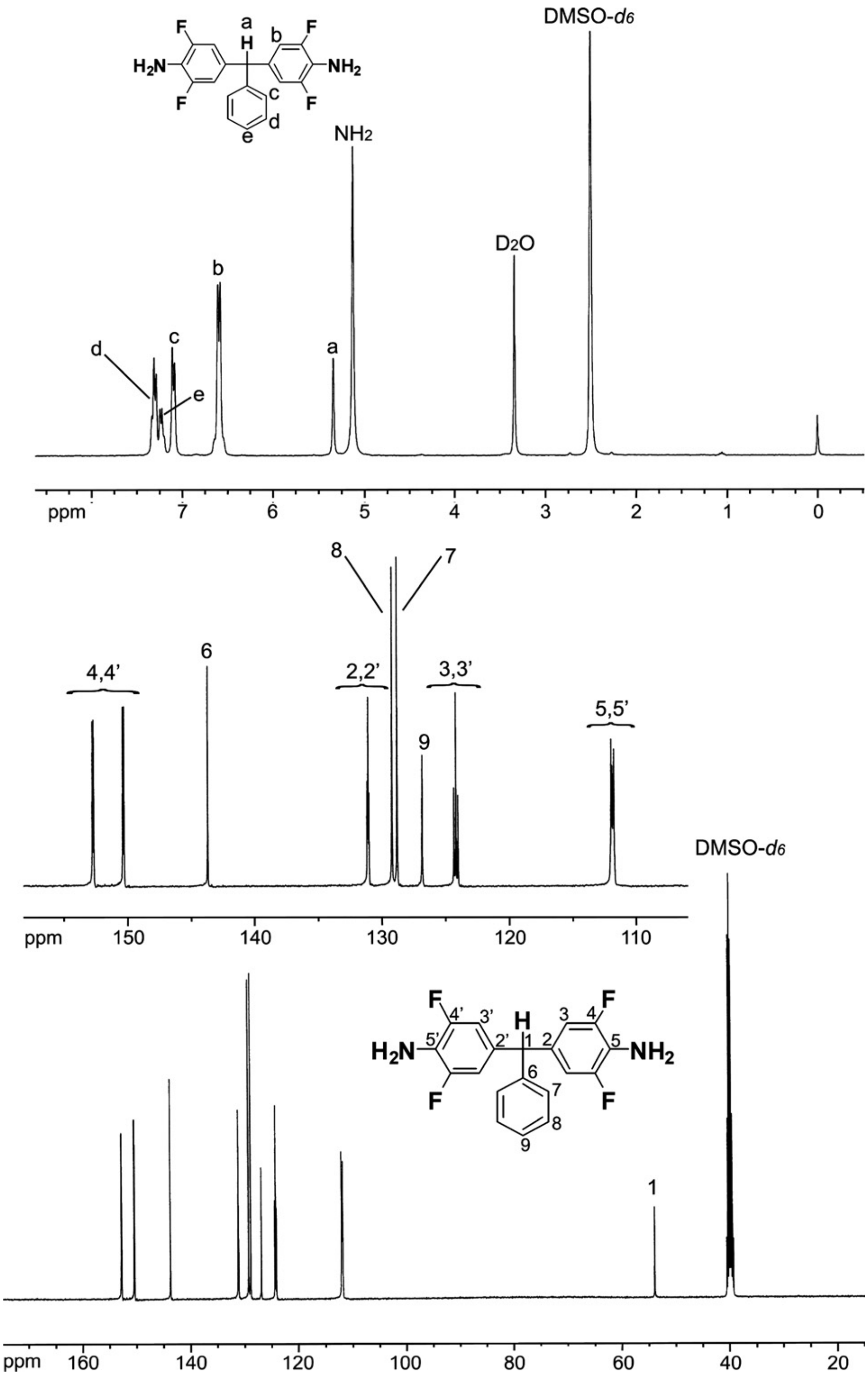


Fig. 2. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of 4FMA.

at 1379 cm^{-1} is due to the C–N stretching vibration. The FT-IR spectra of all the other prepared PIs were almost identical, indicating the successful formation of imide structure. The ^{1}H NMR spectra of the representative PIs (PI-1 and PI-4) are shown in Fig. 3. All the protons were in good

Table 1
Synthesis and characterization of the PIs[a]

PI	$[\eta]_{inh}$[b] (dL/g)	GPC[c]			Formula	Elemental analysis (%)			
		M_n	M_w	M_w/M_n			C	H	N
PI-1	0.75	27,200	60,100	2.21	$C_{35}H_{16}F_4N_2O_4$	Calcd.	69.54	2.67	4.63
						Found	68.15	2.91	4.64
PI-2	0.58	26,300	48,000	1.83	$C_{36}H_{16}F_4N_2O_5$	Calcd.	68.36	2.55	4.43
						Found	67.20	2.73	4.56
PI-3	0.60	25,900	44,400	1.72	$C_{35}H_{16}F_4N_2O_5$	Calcd.	67.75	2.60	4.51
						Found	66.68	2.71	4.61
PI-4	0.52	38,000	63,700	1.68	$C_{38}H_{16}F_{10}N_2O_4$	Calcd.	60.49	2.14	3.71
						Found	59.71	2.33	3.82

[a] All the samples were thermally baked at 250 °C for 3 h prior to test.
[b] Measured in DMAc at a concentration of 0.5 g/dL at 30 °C.
[c] Measured by GPC in THF; polystyrene was used as standard.

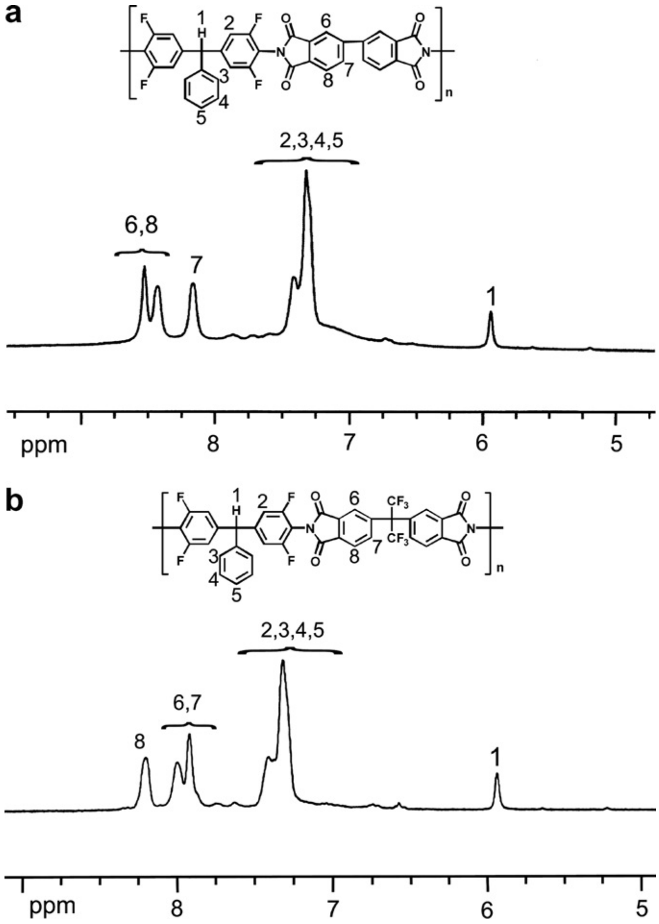


Fig. 3. ^1H NMR spectra of (a) PI-1 and (b) PI-4 in DMSO-d_6.

agreement with the proposed structure. In both of the circumstances, the proton in the –CH– linkage appeared farthest upfield of the spectra, whereas the protons in the dianhydride moiety resonated farthest downfield of the spectra. In addition, the elemental analysis of the PIs also agreed well

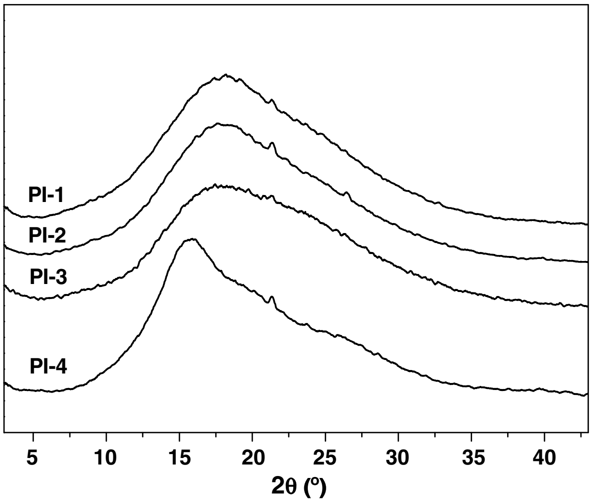


Fig. 4. Wide-angle X-ray diffraction patterns of PI films.

with the calculated values from the proposed structures. The WAXD patterns of the PIs are shown in Fig. 4, in which no crystalline peaks were observed, indicating the amorphous nature of the polymers. This might be interpreted by the presence of the bulky phenyl group and the fluorinated substituents, which decreased the intra- and inter-molecular interactions, resulting in loose polymer packaging and aggregates.

3.3. Solubility

The solubility of the PIs was determined by dissolving 1.5 g of PI resin in 8.5 g of solvent at room temperature or upon heating, as shown in Table 2. As can be seen, all the PIs, except PI-1, showed good solubility not only in polar aprotic solvents such as NMP and DMAc, but in some less polar solvents, such as THF, $CHCl_3$, and CPA. None of the PIs was soluble in methanol. PI-4, with bulky hexafluoroisopropylidene linkage in the backbone, could be easily dissolved in NMP or DMAc at a solid content as high as 25–30%. The PI solution was very stable at room temperature, in which no precipitation, gelation or phase separation occurred during storage of more than one month. The good solubility of the present PIs was due to the synergetic effects of the bulky lateral phenyl and the fluorine groups in the backbones, which disrupted the regularity of the molecular chains and hindered the dense chain stacking, thus increased the solubility. Compared with PI-4, PI-1 possessed inferior solubility, which needed heating to get completely dissolved solution in DMSO and γ-butyrolactone. It was mainly due to the rigidity of the polymer chain resulted from the rigid biphenyl backbone in the dianhydride moiety.

Comparing PI-4 with the similar PI derived from another polyfluorinated diamine, 3,3′,5,5′-tetrafluoro-4,4′-diaminodiphenylmethane (TFDAM) and 6FDA [12], the former showed improved solubility in comparison with the corresponding TFDAM-6FDA PI. For instance, PI-4 dissolved in chloroform within 40 min at a solid content of 20% (w/w), whereas TFDAM-6FDA required 16 h. This improvement in solubility behavior could probably be attributed to the presence of phenyl group in the polymer backbone.

3.4. Thermal stabilities

The thermal properties of the PIs, which were evaluated by DSC and TGA measurements, are summarized in Table 3. The DSC plots (Fig. 5) revealed the clear glass transitions of the PIs in the range of 291–338 °C, recorded as the second-heating trace of DSC, depending on the structure of the dianhydride component. The high-T_gs of the PIs are mainly due to the substitution of fluorine groups in the position *ortho* to an imide ring, which restrict the rotation of nitrogen atom along the phenyl ring, resulting in more rigid polymer chains,

Table 2
Solubility of the PIs[a]

PI	Solvent[b]								
	m-cresol	NMP	DMAc	CPA	$CHCl_3$	THF	γ-BL	DMSO	Methanol
PI-1	++	++	++	++	++	++	+	+	−
PI-2	++	++	++	++	++	++	++	++	−
PI-3	++	++	++	++	++	++	++	++	−
PI-4	++	++	++	++	++	++	++	++	−

[a] ++: Soluble at room temperature; +: partially soluble; −: insoluble.

[b] CPA: cyclopentanone; γ-BL: γ-butyrolactone; DMSO: dimethylsulfoxide.

Table 3
Thermal properties of the PIs[a]

PI	T_g (°C)	T_d[a] (°C)	T_5[b] (°C)	T_{10}[c] (°C)	Char at 700 °C (%)
PI-1	338	590	589	628	74
PI-2	312	577	568	607	71
PI-3	292	596	575	619	71
PI-4	316	565	551	578	55

[a] T_d: onset decomposition temperature.
[b,c] T_5, T_{10}: temperatures at 5% and 10% weight loss.

which in turn increase the T_g values of the polymers. The same tendency had been observed in this kind of PIs [28]. Compared with the PIs from TFDAM [12], the PIs from 4FMA revealed slightly higher T_g values than their TFDAM counterparts. This might be attributed to the steric hindrance of the molecular segment mobility caused by the lateral phenyl group, although it might result in higher free volume and weaken the inter-molecular interactions, which should reduce T_g [29,30]. PI-1, derived from the rigid BPDA, showed the highest T_g due to the rigid biphenyl unit; and PI-3 obtained from ODPA showed a lowest T_g because of the presence of a flexible ether linkage between the phthalimide units.

Fig. 6 depicts the TGA curves of the PIs. All the PIs showed single-stage decomposition with 5% weight loss in the range of 551–589 °C in nitrogen, and they left more than 55% char yield at 700 °C in nitrogen. The good thermal stability of the PIs can be attributed to the presence of a bulky phenyl group in the polymer backbone, which enhances the thermal stability of these polymers. The TGA data indicates that the fluorinated PIs had fairly high thermal stability regardless of the introduction of fluorine groups.

3.5. Mechanical and electrical properties

All the fluorinated PIs afforded flexible, transparent and tough films, and the mechanical and electrical properties are given in Table 4. The PIs showed acceptable tensile strength (84–106 MPa), elongations at break (4–7%) and tensile modulus (1.7–2.8 GPa), enhancing their utility in semiconductor applications. In addition, the PIs films showed good dielectric properties. The surface and volume resistivities were recorded at the order of magnitude of 10^{17} Ω and 10^{18} Ω cm, respectively (Table 4). The dielectric constants of the PI films were in the range of 2.75–2.98, which were much lower than that of the standard aromatic PI (PMDA/ODA = 3.5) [31]. The decreased dielectric constant values might be due to the presence of the bulky phenyl group in the polymer chain which decreased the chain packing and increased the free volume, thus decreasing the dielectric constant [32]. The low molar-polarizable fluorine substitution further decreased the dielectric constant [33]. For example, PI-4, derived from 6FDA and 4FMA, with the highest fluorine content (25.18%), exhibited the lowest dielectric constant of 2.75. Moreover, the low dielectric constant of PI-4 may also be affected by the

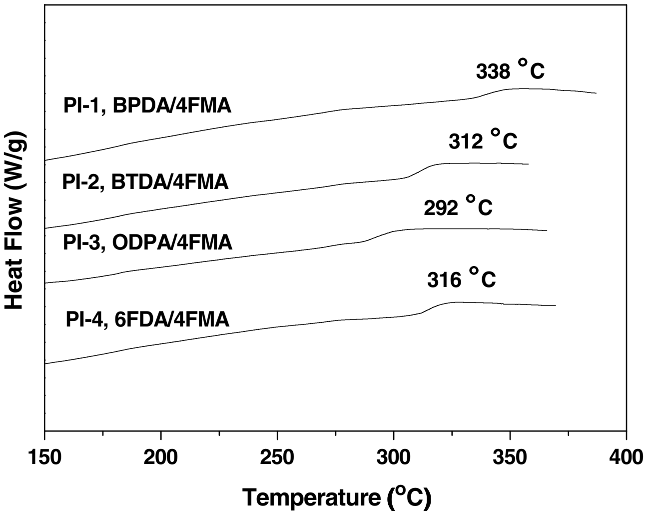


Fig. 5. DSC curves of the PIs (in nitrogen, heating rate: 20 °C/min).

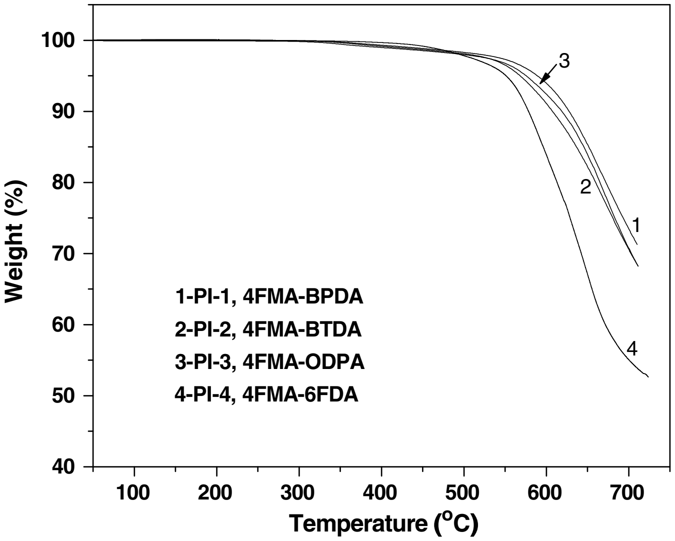


Fig. 6. TGA curves of the PIs (in nitrogen, heating rate: 20 °C/min).

Table 4
Mechanical and electrical properties of the PIs

PI	E_B[a] (%)	T_S[a] (MPa)	T_M[a] (GPa)	ρ_S[b] ($\times 10^{-17}$ Ω)	ρv[b] ($\times 10^{-18}$ Ω cm)	ε[c]
PI-1	6.77	106.6	2.8	9.79	2.80	2.98
PI-2	5.96	105.2	2.6	2.49	2.70	2.93
PI-3	6.69	85.9	1.7	3.47	7.96	2.89
PI-4	3.97	84.7	2.7	6.41	7.65	2.75

[a] E_B: Elongation at break; T_S: tensile strength; T_M: tensile modulus.

[b] ρv: Volume resistivity; ρ_S: surface resistivity.

[c] Dielectric constant measured at 1 MHz by melt-molded PI sheets.

molecular packaging efficiency of its chemical structure. The bulky hexafluoroisopropylidene group in the structure contributed to the low molecular packing order from steric hindrance, which resulted in its lowest dielectric constant in the four polyimides [34].

3.6. Optical properties

The optical properties are given in Table 5 and the UV–Vis spectra of films about 15 μm thick are shown in Fig. 7. It can be seen from Table 5 that the fluorinated PI films exhibited good transparency, the UV cutoff wavelength was in the range of 318–365 nm, and the transmittance at 450 nm was higher than 60%. Especially PI-4, with the highest fluorine content, exhibited the best transparency, with UV cutoff wavelength of 318 nm and 82% of transmittance at 450 nm. These results were attributed to the reduction of inter-molecular CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The bulky pendent phenyl group and fluorinated groups were effective in reducing the CTC formation through steric hindrance and the inductive effect (by decreasing the electron-donating property of the diamine moieties). The decrease in inter-molecular CTC

Table 5
Optical properties of the PI films[a]

PI	F_c (%)	λ_{cutoff} (nm)	T_{450} (%)	d (μm)	n_{TE}	n_{TM}	n_{av}	Δn	ε
PI-1	12.6	365	75	4.8	1.6143	1.5794	1.6027	0.0349	2.83
PI-2	12.0	360	60	7.0	1.6010	1.5801	1.5940	0.0209	2.79
PI-3	12.3	357	65	8.2	1.5985	1.5735	1.5902	0.0250	2.78
PI-4	25.2	318	82	4.7	1.5416	1.5259	1.5364	0.0157	2.60

[a] F_c: fluorine content; λ_{cutoff}: cutoff wavelength; T_{450}: transmittance at 450 nm; d: film thickness for refractive index measurement; n_{TE}: in-plane refractive index; n_{TM}: out-of-plane refractive index; n_{av}: average refractive index; Δn: birefringence; ε: optically estimated dielectric constant, $\varepsilon = 1.10 n_{\text{av}}^2$.

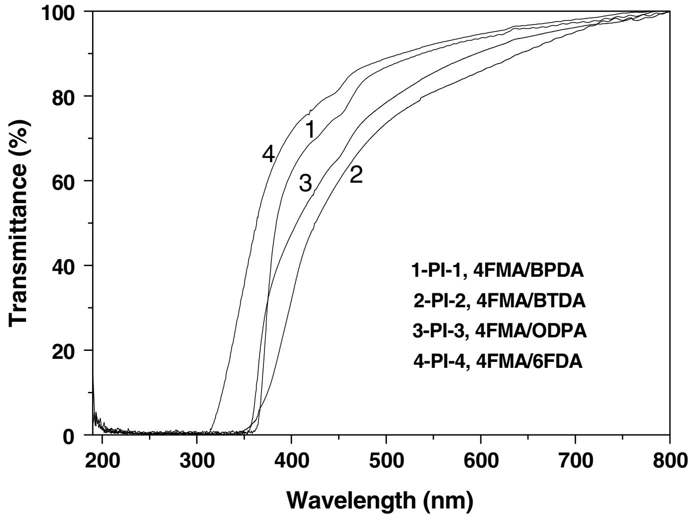


Fig. 7. UV–Vis spectra of PI films (film thickness: ~10 μm).

formation could be evidenced by the significant solubility of the polyimides prepared from the diamine. The water uptakes of the PI films decrease according to the sequence of PI-2 (0.58%) > PI-3 (0.48%) ≈ PI-1 (0.45%) > PI-4 (0.35%). Generally, a structurally flexible polymer with bulky chemical groups in its structure shows more water uptake than a linear, rigid polymer. Although the polyimides had bulky pendent phenyl in the structure, their water uptake was still very low, compared with the standard aromatic polyimide PMDA–ODA (3.19%) [34], which could be attributed to the hydrophobic fluorinated substituents in the molecular structures of the PIs. In addition, it is obvious that the water uptake of the PI films decreased with the increase of the fluorine content.

The refractive indices of the PI films were determined by a prism coupler method, and the results are listed in Table 5. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of the PI films range from 1.5416 to 1.6143 and 1.5259 to 1.5801, respectively. The fact that the n_{TE} values of the PI films are slightly higher than the n_{TM} ones implies that the chain orientation parallel to the film plane

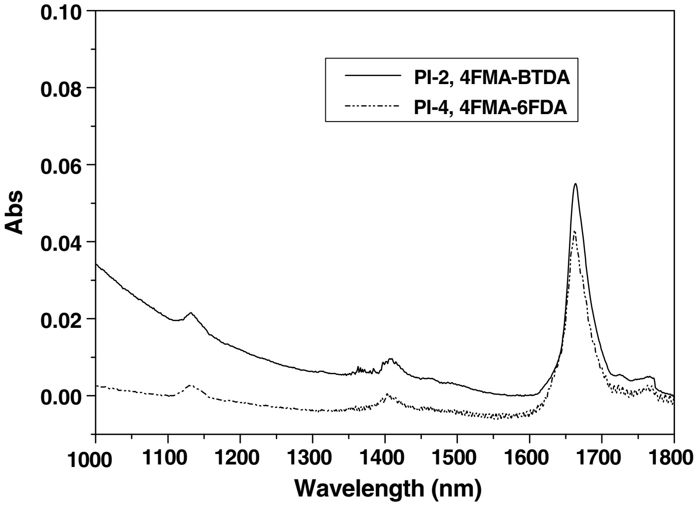


Fig. 8. Near-infrared spectra of the PI-2 and PI-4 (film thickness: ~150 μm).

is more dominant than that perpendicular to the plane. The average refractive indices (n_{av}) estimated from the n_{TE} and n_{TM} values are in the range between 1.5364 and 1.6027 in the following order: PI-4 (1.5364) < PI-3 (1.5902) < PI-2 (1.5940) < PI-1 (1.6027). This trend is consistent with their chemical structures. For instance, PI-4, with the highest fluorine content exhibited the lowest n_{av}, whereas PI-1 showed the highest one. The high n_{av} of PI-1 can be ascribed to the more dense packing of the molecular chains caused by the planar biphenyl structure in the BPDA moiety. The same reason resulted in the highest in-plane/out-of-plane birefringences (Δn) value of the PI (0.0349).

The dielectric constant (ε) of the materials at around 1 MHz can be estimated from the refractive index (n_{av}) according to a modified Maxwell′s equation, $\varepsilon = 1.10n^2$ [35]. Thus, the dielectric constants were in the range of 2.60–2.83, a little lower than the values measured by melt-molded sheets, but the trend of variation were similar.

It is known that the carbon–hydrogen (C–H) and oxygen–hydrogen (O–H) bonds strongly affect the absorptions in the near-infrared region [36]. The low absorption at the wavelengths of both 1310 and 1550 nm, which are often used in optical communications, is an important consideration in designing polymer components for optical devices. It is reported that the absorption due to C–H bonds can be obviously reduced by the replacement of hydrogen moiety in the C–H bonds to halogen atoms such as fluorine (F) and chlorine (Cl), or deuterium atom (D) [37,38]. Fig. 8 shows the near-infrared absorption of PI-2 and PI-4. As expected, the absorption of PI-4 was weaker than that of PI-2. However, at the key telecommunication wavelengths of 1310 and 1550 nm, both polymer films show low light absorption. The smaller absorption of PI-4 than those of the other PIs might be attributed to the decreased C–H and increased C–F proportion in this material [39].

4. Conclusions

A series of polyfluorinated PIs were developed from a newly-synthesized aromatic diamine 4FMA and various aromatic dianhydrides. The high-molecular-weight PIs obtained by the one-step high-temperature procedure showed good solubility in common organic solvents. Flexible and tough PI films exhibited high-T_gs and good thermal stability, and they also exhibited good transparency in UV–Vis region and low absorption in the near-infrared region. Thus, this series of PIs demonstrated a good combination of properties and might be of interest for microelectronics or optoelectronics applications.

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