

Synthesis and Characterization of Organosoluble Polyfluorinated Polyimides Derived from 3,3',5,5'-Tetrafluoro-4,4'-diaminodiphenylmethane and Various Aromatic Dianhydrides

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Received 16 January 2006; accepted 9 April 2006

DOI 10.1002/app.24616

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

ABSTRACT: A polyfluorinated aromatic diamine, 3,3', 5,5'-tetrafluoro-4,4'-diaminodiphenylmethane (TFDAM), was synthesized and characterized. A series of polyimides, PI-1-PI-4, were prepared by reacting the diamine with four aromatic dianhydrides via a one-step high-temperature polycondensation procedure. The obtained polyimide resin had moderate inherent viscosity (0.56–0.68 dL/g) and excellent solubility in common organic solvents. The polyimide films exhibited good thermal stability, with an initial thermal decomposition temperature of 555°C–621°C, a 10% weight loss temperature of 560°C–636°C, and a glass-transition temperature of 280°C–326°C. Flexible and tough polyimide films showed good tensile properties, with

tensile strength of 121–138 MPa, elongation at break of 9%–12%, and tensile modulus of 2.2–2.9 GPa. The polyimide films were good dielectric materials, and surface and volume resistance were on the order of a magnitude of 10^{14} and 10^{15} Ω cm, respectively. The dielectric constant of the films was below 3.0 at 1 MHz. The polyfluorinated films showed good transparency in the visible-light region, with a cutoff wavelength as low as 302 nm and transmittance higher than 70% at 450 nm. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1442–1449, 2007

Key words: polyimides; thermal properties; dielectric properties; fluoropolymers

INTRODUCTION

Polyimides have been widely used in semiconductors and integrated circuits, and many of the conventional polyimides used in these applications have been required to improve because of the developing trends of miniaturization of electronic parts, high assembly density, and high signal propagation speed. For example, the ever-smaller structures of integrated circuit chips bring many reliability problems, such as with heat releasing, capacitive resistance, and signal transmission. The signal propagation delay time, τ , between two devices in integrated circuits is proportional to the square root of the dielectric constant (ϵ) of the interlayer dielectric (ICD) and internal dielectric (IMD) materials.^{1–4} Therefore, a decrease in the ϵ of ICD or IMD materials could reduce the τ , making a low dielectric constant (low ϵ) an important issue in developing the next generation of electronic materials.⁵ Proposed new interconnect dielectrics should have an ϵ value less than 3.0.⁶ Furthermore,

new materials should have low water uptake (<1%), high thermal stability, up to 450°C, and sufficient adhesion to Si, SiO₂, Al, Cu, and other oxides or nitrides.⁶ Low- ϵ polyimides could fulfill most of these requirements and have been widely researched and developed in recent years.^{7–10}

There have been two well-established procedures reported in the literature to reduce the ϵ . Introducing substituents with low polarity or a bulky molecular volume could efficiently reduce the ϵ values of materials.¹¹ Among the substituents, fluorine-containing groups have been most sufficiently studied, and fluorination has been proved to be one of the most attractive methods for developing polyimides with good combined properties, including high solubility in common organic solvents, high transparency in the visible-light region, a low dielectric constant and dissipation factor, and in most cases, high thermal and thermooxidative stabilities.^{12–18} However, fluorination often brings many undesirable results in modifications of polyimides, such as reduction in the reactivity of diamine monomers, especially when the fluorinated groups are ortho-substituted to the amine group. The low reactivity of the monomers often causes the low molecular weights and poor mechanical properties of the polyimides obtained via conventional polymerization procedure and greatly limited

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

Journal of Applied Polymer Science, Vol. 103, 1442–1449 (2007)
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their applications. Therefore, developing polyfluorinated polyimides with high combined properties has been one of the most challenging topics in polyimide research.^{19–20}

As part of our continuous work to develop new polyimide electronic materials, the aim of the present work was to investigate the influence of fluorine substituents on the properties of the polyimides derived. Thus, a polyfluorinated diamine, 3,3',5,5'-tetrafluoro-4,4'-diaminodiphenylmethane (TFDAM), was first synthesized, and four polyimides were prepared via a high-temperature procedure. The solubility and thermal, mechanical, dielectric, and optical properties were studied.

EXPERIMENTAL

Materials

2,6-Difluoroaniline was purchased from Acros (Acros, Janssen Pharmaceutica, Geel, Belgium) and was used as received. Commercially available formaldehyde (37%) and hydrochloric acid (37%) (Beijing YILI Fine Chemical Co., Ltd., Beijing, China) were used as received. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (s-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., Chatham, NJ) were recrystallized from acetic anhydride and dried in a vacuum at 160°C for 10 h prior to use. Commercially available *N*-methyl-2-pyrrolidinone (NMP), *m*-cresol, *N,N'*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMAc, Beijing Chemical Reagents Co., Beijing, China), and other reagents were purified by distillation prior to use.

Monomer synthesis

To synthesize 3,3',5,5'-tetrafluoro-4,4'-diaminodiphenylmethane (TFDAM), a mixture of 25.82 g (0.2 mol) of 2,6-difluoroaniline and 50 mL of deionized water was placed in a 500-mL three-necked flask fitted with a mechanical stirrer, a thermometer, a nitrogen inlet, and a dropping funnel, and then 23.68 g of 37% hydrochloric acid was added gradually. With vigorous stirring, 8.52 g (0.105 mol) of formaldehyde was added dropwise over 1 h after the temperature of the reaction mixture had risen to 50°C. After standing for another 0.5 h, the reaction mixture was heated to reflux for 10 h. Then the solution was cooled to room temperature followed by neutralization with a solution of 5% sodium hydroxide (200 mL). The pale yellow precipitate was filtered and dried under a vacuum at 80°C overnight. The TFDAM product was purified by recrystallization twice from absolute ethanol, and the yield was 20.53 g (76.0%).

The mp was 136.9°C determined by differential scanning calorimetry (DSC) at a scan rate of 10°C/min.

IR (KBr): 3454, 3427 (N—H stretch), 1294, 1151 cm⁻¹ (C—F stretch). ¹H-NMR (300 MHz, DMSO-*d*₆, δ): 3.48 (2H, —CH₂—), 5.01 (4H, —NH₂), 6.78 (4H, H₁). ¹³C-NMR (300 MHz, DMSO-*d*₆, δ): 39.8 (C⁵), 108.2 (C³), 123.8 (C¹), 127.9 (C⁴), 150.3, 150.4 (C², double, ¹J_{C-F} = 60 Hz). Mass [*m/e* (relative intensity)]: 270 (M⁺, 100).

ELEM. ANAL. Calcd for C₁₃H₁₀F₄N₂ (270.23): C, 57.78%; H, 3.73%; N, 10.37%. Found: C, 57.72%; H, 3.76%; N, 10.32%.

SYNTHESIS OF POLYIMIDES

The general synthesis of the polyimides can be illustrated by the synthesis of PI-4.

To a solution of 2.7023 g (10 mmol) of TFDAM in 30 mL of *m*-cresol placed in a 250-mL three-necked flask fitted with a mechanical stirrer, a nitrogen inlet, and a Dean–Stark trap, 4.4424 g (10 mmol) of 6FDA was added in three portions. After the reaction mixture was stirred in nitrogen for 0.5 h, a mixture of toluene (32 mL) and isoquinoline (catalytic amount) was added. The reaction mixture was heated to 180°C and maintained for 5 h. During the reaction, the toluene–water azeotrope was distilled out of the system. After being cooled to room temperature, the viscous solution was poured slowly into excess ethanol to yield a silky precipitate. The precipitate was collected and dried at 80°C under vacuum overnight. The yield was 7.00 g (98%). The inherent viscosity of PI-4 in DMAc was 0.56 dL/g at a concentration of 0.5 g/dL at 30°C.

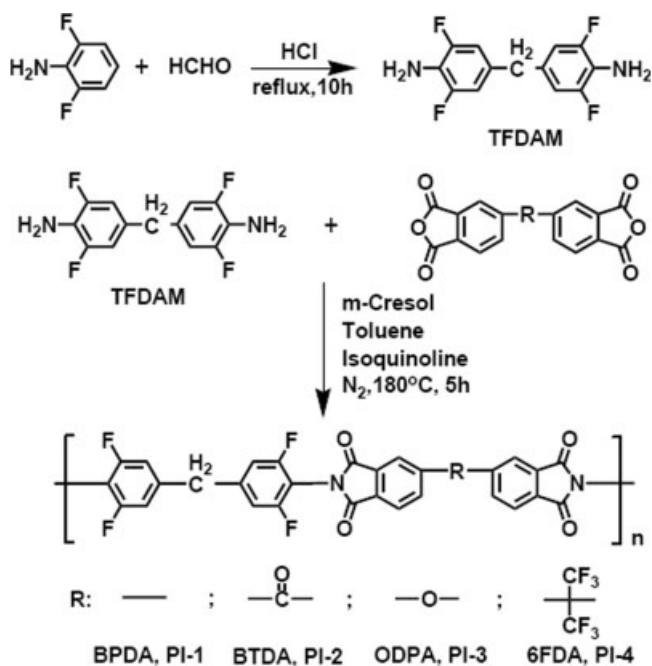
IR (film): 1775, 1726 (imide C=O), 1380 (C—N stretch), 1105, 721 cm⁻¹ (imide ring deformation). ¹H-NMR (300 MHz, DMSO-*d*₆, δ): 4.07 (2H, —CH₂—), 7.43 (4H, H₁), 7.92 (2H, H₂), 7.98 (2H, H₄), 8.17 (2H, H₃).

In a 100-mL three-necked round-bottomed flask, 6.00 g of PI-4 resin was dissolved in 34 g of DMAc. The mixture was stirred at room temperature for 24 h to afford a viscous and homogeneous polyimide solution with a solids content of 15 wt %. The solution was filtered via a 0.2-μm Teflon syringe in order to remove any undissolved impurities. The filtrate was cast onto a glass plate, and the solvent was removed at 80°C for 1 h, 120°C for 1 h, 150°C for 1 h, and 180°C for 1 h. Freestanding polyimide film that was a very pale yellow in color was obtained.

PI-1–PI-3 resins and films were prepared in the same manner as PI-4 except that 6FDA was replaced by BPDA for PI-1, BTDA for PI-2, and ODPA for PI-3.

Measurements

Inherent viscosity was measured using an Ubbelohde viscometer with 0.5 g/dL DMAc solution at



Scheme 1 Synthesis of diamine TFDAM and polyimides PI-1-PI-4.

30°C. FTIR 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 the test, polyimide film samples were dried at 100°C for 1 h in order to remove the absorbed moisture. The refractive indices of the PI films formed on a 3-inch silicon wafer were measured at a wavelength of 1.550 μm 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 linearly polarized laser light polarizations parallel (transverse electric, TE) and perpendicular (transverse magnetic, TM) to the film plane. ^1H - and ^{13}C -NMR were performed on a Varian Unity 200 spectrometer operating at 300 MHz in $\text{DMSO-}d_6$ or CDCl_3 , respectively. DSC and thermogravimetric analysis (TGA) were performed on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer.

Solubility was determined as follows: 1.5 g of polyimide resin was mixed with 8.5 g of solvent at room temperature (15% solids content), which was then mechanically stirred in nitrogen for 24 h. Solubility was determined visually as three grades: completely soluble (++) , partially soluble (+) , and insoluble (-) . Complete solubility (++) was defined as obtaining a homogenous and clean solution, in which no phase separation, precipitation, or gel formation was detected. Tensile properties were deter-

mined on an Instron 3365 tensile apparatus with specimens $80 \times 10 \times 0.05$ mm in size in accordance with GB1447-83 at a drawing rate of 5.0 mm/min. The electrical properties were measured on a Hewlett-Packard 4284A Precision LCR meter at room temperature. Surface and volume resistances were measured with film specimens 50 mm in diameter and 50 μm thick. The dielectric constants were measured at 1 MHz with film specimens 25 mm in diameter and 50 μm thick. Water uptake was determined by immersing the polyimide film ($3.0 \times 1.0 \times 0.005$ cm^3) in water at 25°C for 24 h. The polyimide film was then immediately dried with blotting paper and weighed to determine water uptake.

RESULTS AND DISCUSSION

Monomer synthesis

The fluorinated diamine TFDAM was prepared according to a well-known procedure for developing diaminodiphenylmethane and its analogs.²¹⁻²³ 2,6-Difluoroaniline was reacted with formaldehyde under the catalysis of hydrochloric acid, followed by neutralization with sodium hydroxide to produce diamine at a yield of 76% (Scheme 1). To have polymer-grade monomer, TFDAM was purified by recrystallization twice from ethanol to be obtained as white crystals. The diamine exhibited a sharp melting point, at 136.9°C, determined by DSC. In the FTIR spectrum shown in Figure 1, the characteristic absorption bands of the primary amino in the region of 3500–3000 cm^{-1} appeared. The strong absorption bands between 1200 and 1100 cm^{-1} , assigned to the stretching vibration of the C–F bond, also were observed in the spectrum. Figure 2 presents the ^1H - and ^{13}C -NMR spectra of TFDAM. An amine proton

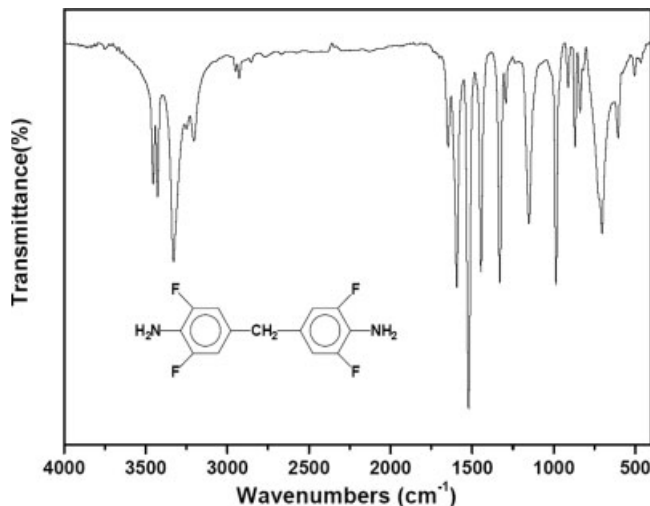


Figure 1 FTIR spectrum of TFDAM.

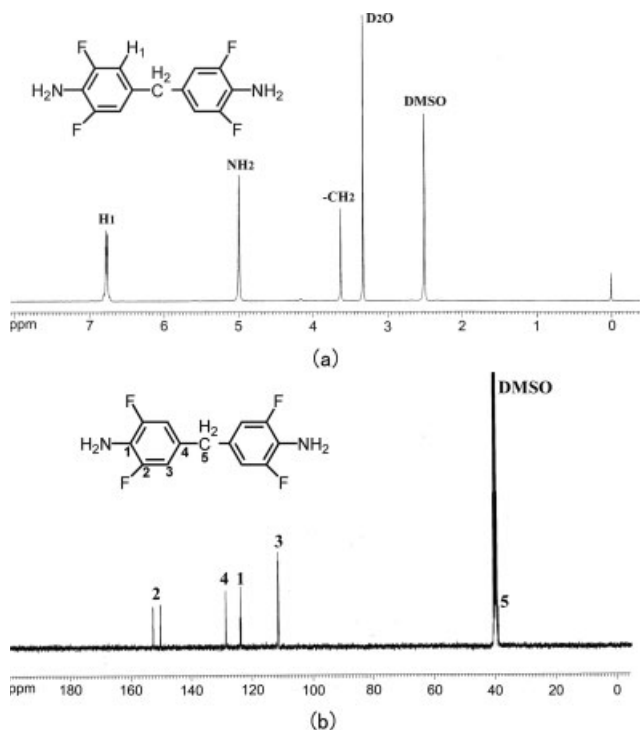


Figure 2 ^1H - and ^{13}C -NMR spectra of TFDAM in $\text{DMSO-}d_6$.

signal at 5.01 ppm was observed, and a proton ortho to the electron-withdrawing F atoms (H_1) was observed in the downfield of the spectrum. In ^{13}C -NMR, C^2 showed clear double absorptions, at 150 and 152 ppm, probably because of the $^2\text{J}_{\text{C-F}}$ coupling of the carbon with the fluorine atom in the diamine. It can be seen that the coupling effect between C and F atoms decreased with an increase in the distance between C and F. For instance, C^2 showed a stronger coupling effect (coupling constant: 60 Hz) with F than did C^1 and C^3 (coupling constant: 3 Hz). Elemental analysis also verified the chemical composition of the diamine.

TABLE I
Elemental Analysis of PI Films^a

PI	Formula and molecular weight		Elemental analysis (%)		
			C	H	N
1	$(\text{C}_{41}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_4)_n$ (724) _n	Calcd.	65.92	2.29	5.30
		Found	65.56	2.42	5.27
2	$(\text{C}_{42}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_5)_n$ (752) _n	Calcd.	64.76	2.17	5.03
		Found	64.16	2.43	5.12
3	$(\text{C}_{41}\text{H}_{26}\text{F}_6\text{N}_2\text{O}_5)_n$ (740) _n	Calcd.	63.98	2.22	5.15
		Found	63.77	2.46	5.33
4	$(\text{C}_{44}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4)_n$ (874) _n	Calcd.	56.65	1.78	4.13
		Found	56.64	1.84	4.16

^a All samples were thermally baked at 250°C for 3 h prior to testing.

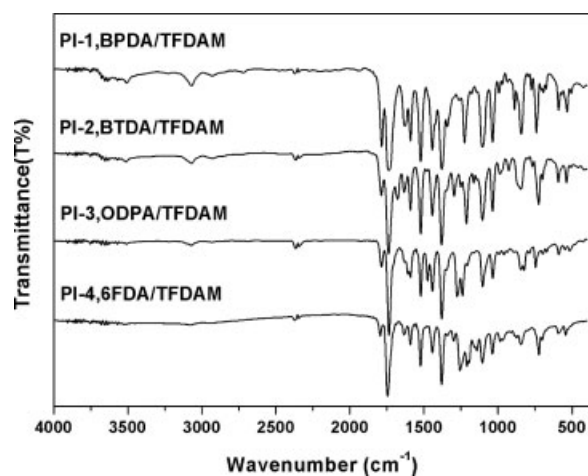


Figure 3 FTIR spectra of polyimides.

Polymer synthesis

Four polyimides were prepared via the one-step high-temperature polycondensation procedure. Poly(amic acid) (PAA) was first formed by the nucleophilic attack of the amine ($-\text{NH}_2$) in the diamine to the carbonyl ($\text{C}=\text{O}$) in the dianhydride, followed by *in situ* thermal-dehydration reaction to afford a polyimide solution. The PAA reaction was strongly influenced by the nucleophilicity of the amine and the

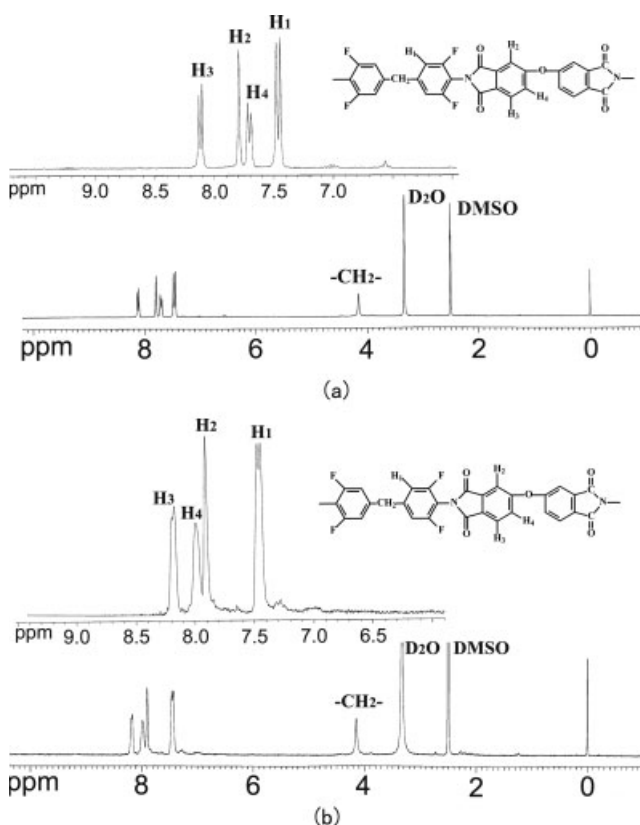


Figure 4 ^1H -NMR spectra of (a) PI-3 and PI-4 (b) in $\text{DMSO-}d_6$.

TABLE II
Inherent Viscosity and Solubility of the Polyimides^a

PI	η_{inh} (dL/g)	Solvents ^b							
		NMP	DMF	<i>m</i> -cresol	CPA	γ -BL	THF	Toluene	Methanol
PI-1	0.64	++	++	++	++	+	++	–	–
PI-2	0.62	++	++	++	++	++	++	–	–
PI-3	0.68	++	++	++	++	++	++	+	–
PI-4	0.56	++	++	++	++	++	++	++	–

^a (++) Soluble at room temperature; (+) partially soluble; (–) insoluble.

^b NMP: *N*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; CPA: cyclopentanone; γ -BL: γ -butyrolactone.

electrophilicity of the anhydride. It is well known that high electronegative substituents, such as fluorine or trifluoromethyl, would reduce the nucleophilicity (or reactivity) of the amine, especially when the substituents are ortho to the amine group. On the other hand, the fluorine substituents on the ring hinder the reactivity of the diamine by their steric hindrance, which increased with the increase in the number of fluorine substituents. From this point, it would be very difficult to obtain high-molecular-weight PAA by a conventional two-step procedure from TFDAM, which contained two ortho-substituted-fluorine atoms to the amine groups.²⁴ The one-step high-temperature polycondensation procedure provides enough energy to promote the polymerization reaction and is widely used to develop fluorinated polyimides.^{25–26} In the present work, a series of polyimides were successfully prepared via this procedure, and the inherent viscosity ranged from 0.56 to 0.68 dL/g, indicating high-molecular-weight resins were obtained. Flexible and tough polyimide films were obtained by removing DMAc from the polyimide solution by heating. The chemical compositions of the films were confirmed by elemental analysis, and the results are listed in Table I, which were in good agreement with the anticipated structures.

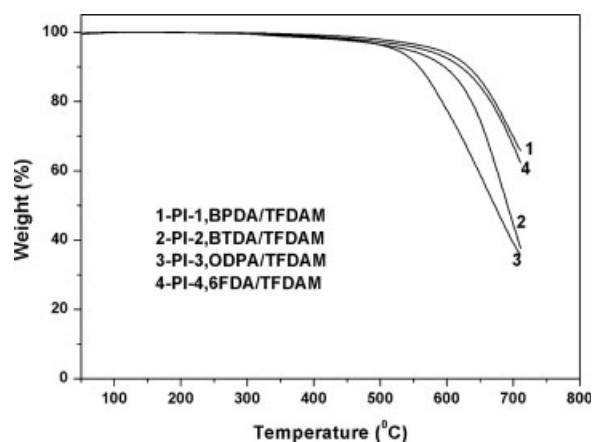


Figure 5 TGA curves of polyimides (in nitrogen; heating rate: 20°C/min).

Figure 3 depicts the FTIR spectra of the polyimide films. The characteristic absorption peaks around 1780 cm^{-1} (asymmetric stretching vibration of C=O), 1720 cm^{-1} (symmetric stretching vibration of C=O), and 1380 cm^{-1} (stretching vibration of C–N) were observed in all the polymers. In addition, strong absorption of C–F around 1200–1000 cm^{-1} was found in the spectra. Typical ¹H-NMR spectra of PI-3 and PI-4, shown in Figure 4, revealed that all the hydrogen protons agreed well with the proposed polymer structures.

The crystallinity of the polyimide films was evaluated by X-ray diffraction analysis with 2θ ranging from 3° to 40°. All the polymers showed an amorphous nature, which was further confirmed by DSC measurement discussed below.

Properties of polymers

The solubility of the polyimide resins was qualitatively evaluated in eight typical solvents with different polarities and boiling points. Solubility was classified according to the procedure mentioned in the Measurements section. As presented in Table II, the polyimides were soluble in most of the solvents tested. Differences in solubility could only be identified in toluene and methanol. For example, among the four polyimides, PI-4 was the only one soluble in toluene, and PI-3 was partially soluble in toluene. All the polyimides were not soluble in methanol. PI-4,

TABLE III
Thermal Properties of the Polyimide Films

PI	T_g (°C)	T_d^a (°C)	$T_{5\%}^a$ (°C)	$T_{10\%}^a$ (°C)	R_w^b (%)
PI-1	326.8	621.6	574.8	626.2	62
PI-2	295.5	594.2	546.8	597.4	39
PI-3	280.3	555.5	526.4	560.7	37
PI-4	300.3	617.3	591.0	636.1	66

^a T_d , Onset decomposition temperature; $T_{5\%}$, $T_{10\%}$, temperatures at 5% and 10% weight loss, respectively.

^b Residual weight retention (R_w %) at 700°C.

TABLE IV
Mechanical and Electrical Properties of Polyimide Films

PI	E_B^a (%)	T_S^a (MPa)	T_M^a (GPa)	$R_S^b \times 10^{-14}$ (Ω)	$R_V^b \times 10^{-15}$ (Ω cm)	S_D^c (KV/mm)	ϵ^d
PI-1	12	137.8	2.9	3.6	3.4	126	2.94
PI-2	11	138.1	2.9	2.1	6.1	108	2.96
PI-3	9	124.2	2.6	4.3	7.2	114	2.87
PI-4	12	129.1	2.6	3.9	5.4	122	2.79

^a E_B , Elongation at break; T_S , tensile strength; T_M , tensile modulus.

^b R_V , Volume resistance; R_S , surface resistance.

^c S_D , Dielectric strength.

^d Dielectric constant measured at 1 MHz.

which contained a hexafluoroisopropylidene linkage, showed better solubility than that obtained by the other dianhydrides. The good solubility of the polyfluorinated polyimides might have been due to the reduced crystallinity that resulted from the fluorine substituents. It was very beneficial that the polyimides were soluble in cyclopentanone and γ -butyrolactone. Both these solvents are widely used in microelectronic assembly as solvents or developers for photosensitive polyimides.^{27–28} Therefore, the present polyimides might find applications in the field of semiconductor manufacture.

The thermal decomposition behavior of the polyimides is shown in Figure 5 (TGA), and the thermal data are presented in Table III. Interestingly, the polyimides unexpectedly exhibited thermal stability, with a initial decomposition temperature (T_d) ranging from 555°C–621°C, a 10% weight loss temperature of 560°C–636°C, and a residual weight ratio of 37%–66% at 700°C. The high T_d values were mainly attributed to the steric hindrance of the molecular chains resulting from the multifluorine substituents around the imide moiety. In contrast, the strong C–F bond contributed to the high thermal resistance of the polymers.

The glass-transition temperature of the polyimides ranged from 280.3°C to 326.8°C, decreasing in the order BPDA > 6FDA > BTDA > ODPDA. As can be seen from Table III, PI-1, derived from BPDA, exhibited a higher T_g than those of those prepared from

the other three dianhydrides. The rigidity of BPDA restricted the glass transition of PI-1, hence increasing the T_g . The high T_g values might be attributed to the substitution of fluorine groups in the position ortho to an imide ring, which restricted the rotation of the nitrogen atom along the phenyl ring, resulting in more rigid polymer chains that in turn increased the T_g values of the polymers. The same tendency has been widely observed in this kind of polyimide.²⁹

The polyimide films exhibited acceptable mechanical properties, with tensile strength of 124–138 MPa, elongations at break of 9%–12%, and tensile modulus of 2.6–2.9 GPa (Table IV). The tensile properties from another point confirmed the successful preparation of high-molecular-weight polyimide via a high-temperature one-step procedure from “inactive” TFDAM and aromatic dianhydrides.

The polyimide films showed good dielectric properties, and surface and volume resistance were recorded in the magnitude of 10^{14} Ω and 10^{15} Ω cm, respectively (Table IV). The dielectric strength of the films was greater than 108 KV/mm. There was some relationship between the dielectric constant and fluorine content in the polyimides. For example, PI-4, which had the highest fluorine content, 17.58%,

TABLE V
Optical Properties and Water Uptake of Polyimide Films

PI	d^a (μ m)	F_c^b (%)	T_{450}^c (%)	λ^d (nm)	W_u^e (%)
PI-1	20	3.13	72	351	0.39
PI-2	21	2.99	71	323	0.54
PI-3	22	3.05	81	317	0.47
PI-4	21	17.58	76	302	0.36

^a Film thickness.

^b Fluorine content.

^c Transmittance at 450 nm.

^d UV cutoff wavelength.

^e Water uptake.

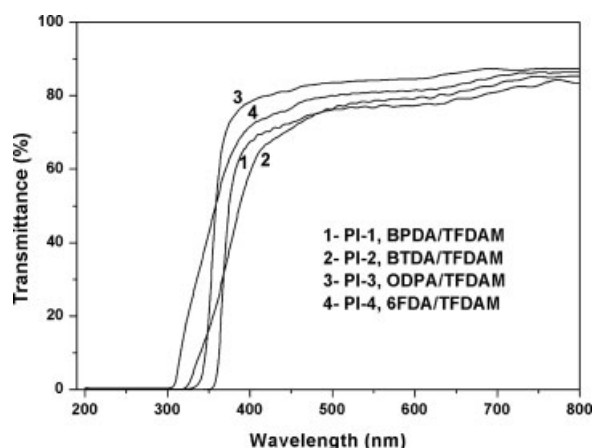


Figure 6 UV-vis spectra of polyimide films.

TABLE VI
Refractive Indices and Birefringence of PI Films

PI	d (μm) ^a	n_{TE} ^b	n_{TM} ^c	n_{AV} ^d	Δn ^e
PI-1	3.4	1.6037	1.5989	1.6021	0.0048
PI-2	3.3	1.6104	1.6032	1.6080	0.0072
PI-3	3.3	1.5933	1.5866	1.5911	0.0067
PI-4	3.2	1.5765	1.5722	1.5751	0.0043

^a Film thickness.

^b In-plane refractive index.

^c Out-of-plane refractive index.

^d Average refractive index.

^e Birefringence.

exhibited the lowest dielectric constant (2.79 at 1 MHz). The other three polyimides, which had similar fluorine contents, showed similar dielectric constants (2.87–2.94). The low dielectric constants could be explained as the low electronic polarizability of the fluorine substituents.

The optical data of the polyimide films are summarized in Table V, and the UV–vis spectra of films about 20 μm thick are shown in Figure 6. It can be seen from the data that the cutoff UV wavelength and transmittance at 450 nm decreased with an increase in the fluorine content of the films. For example, PI-4, which had the highest fluorine content, showed the best transparency with a cutoff UV wavelength of 302 nm and 76% of transmittance at 450 nm. The good transparency of the polyimide films might be interpreted as the prevention of formation of an intermolecular or intramolecular charge transition complex (CTC) resulting from the strong electronegativity of fluorine substituents.³⁰

The polyimide films exhibited low water uptake, 0.36%–0.54% (Table V). The decreasing tendency (PI-2 > PI-3 > PI-1 > PI-4) indicated that high fluorine content was conducive to reducing the water uptake of the polymers, which was attributed to the hydrophobic nature of fluorine substituents.

The refractive indices, n_{TE} and n_{TM} , average refractive indices, n_{AV} , calculated by the equation $(2n_{TE} + n_{TM})/3$, and birefringence, Δn , calculated as the difference between the n_{TE} and the n_{TM} of the PI films, are listed in Table VI. PI-4, derived from 6FDA and TFDAM, showed the lowest refractive index and birefringence values, which was mainly ascribed to the higher fluorine content of PI-4, and the low polarizability of fluorine substituents. It is well known that the dielectric constant (ϵ) of polymer materials at about 1 MHz could be estimated from the refractive index (n) according to a modified Maxwell's equation, $\epsilon = 1.10n^2$.³¹ With respect to the present PIs, the estimated ϵ values agreed well with the measured ones. For example, for PI-4, the esti-

mated ϵ value was 2.73, and the measured value was 2.79 (Table IV).

CONCLUSIONS

A series of organosoluble low- ϵ polyimides have been prepared from a polyfluorinated diamine, TFDAM, and various aromatic dianhydrides. The polyimide films exhibited good combined properties, including high thermal stability, high solubility, acceptable mechanical and optical properties, and good dielectric properties. The good properties of the present polyimides were mainly attributed to the ortho-substituted fluorine groups, which can cause an increase in the dihedral angle between the aromatic ring in the diamine moiety and the five-membered imide ring. The easy processability and prominent properties of the present polyimides would make them good candidates for protecting or insulating materials for microelectronic assembly and other high-tech fields. The detailed applications of the polyimides will be discussed in forthcoming articles.

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