

NOTES

Organosoluble and Light-Colored Fluorinated Polyimides Based on 1,2-Bis(4-amino-2-trifluoromethylphenoxy)benzene and Aromatic Dianhydrides

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Aromatic polyimides are well known as polymer materials of high performance for their excellent thermal stabilities and balanced mechanical and electric properties.^{1–7} Polyimides are mainly used in the aerospace and electronics industries in the form of films and moldings. Optical transparency of polyimide films is special importance in some applications such as flexible solar radiation protectors,⁸ orientation films in liquid crystal display devices,⁹ optical waveguides for communication interconnects,¹⁰ and optical half-waveplates for planar lightwave circuits.¹¹ However, the wholly aromatic polyimides strongly absorb in the visible region of their UV-Vis spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer complex (CTC) formation; besides, they are difficult to process because of high softening temperatures and limited solubility in commercially available solvents.

Aromatic polyimides possess many useful properties and are increasingly being required by the electronic circuit industry.^{5,12} A low dielectric constant is one of the most attractive properties of polyimide materials for electronic applications. One of the most effective methods to decrease the dielectric constant is to introduce fluorine atoms into polyimide materials.¹² Fluorination is also known to enhance the solubility and optical transparency of polyimides.^{13–15} Therefore, it is expected that fluorinated polyimides will be widely applied in electro-optical and semiconductor industries.

Recent studies demonstrated that polyimides derived from ether-bridged aromatic diamines with trifluoromethyl (3F) groups, such as 1,3- or 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene, are soluble and high temperature polymer materials with low dielectric constant, high optical transparency,

and low birefringence.^{16,17} In this study, a high-purity CF₃-containing diamine, 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene **II**, was synthesized by modificatory method and subsequently polycondensed with various commercially available aromatic dianhydrides to produce a series of fluorinated polyimides **V_{a–f}**. These polymers were subjected to solubility, thermal, optical, dielectric property measurements and compared to analogous polyimides **VI_{a–f}**¹⁸ prepared from a nonfluorinated diamine monomer, 1,2-bis(4-aminophenoxy)benzene.

EXPERIMENTAL

Materials

Catechol (Acros) and 2-chloro-5-nitrobenzotrifluoride (Acros) were used as received. Pyromellitic dianhydride (PMDA or **III_a**; Lancaster), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA or **III_b**; Acros), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA or **III_d**; New Japan Chemical Co.) and 4,4'-oxydiphthalic dianhydride (ODPA or **III_e**; Chriskev) were recrystallized from acetic anhydride before use. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA or **III_c**; Chriskev) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA or **III_f**; Chriskev) were purified by sublimation. *N*-Methyl-2-pyrrolidone (NMP; Fluka), *N,N*-dimethylacetamide (DMAc; Fluka), *N,N*-dimethylformamide (DMF; Fluka), and pyridine (Py; Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

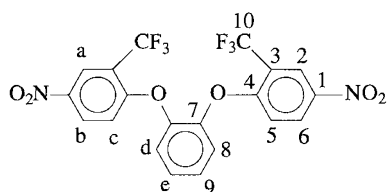
Synthesis of Monomer

1,2-Bis(4-nitro-2-trifluoromethylphenoxy)benzene I. Catechol (8.26 g, 0.075 mol) and 2-chloro-5-nitro-

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benzotrifluoride (34.28 g, 0.152 mol) were first dissolved in 150 mL of DMF in a 300 mL flask with stirring. After the mixture was completely dissolved, potassium carbonate (16.56 g, 0.12 mol) was added to it in one portion, and the mixture was heated at 110 °C for 12 h. The obtained mixture was poured into 600 mL of methanol/water (volume ratio 1/1) to give a yellow solid, which was collected, washed with water, and dried under vacuum. The crude product was recrystallized from DMF/methanol to give fine, pale-cream crystals (40 g, 95%).

mp: 209–210 °C by DSC at a scan rate of 10 °C min⁻¹. Infrared (IR, KBr): 1530, 1350 (–NO₂ stretch), 1286, 1180, 1145, 1133 cm⁻¹ (C–F and C–O stretch). Proton nuclear magnetic resonance (¹H NMR, DMSO-*d*₆, δ): 8.42 (dd, *J* = 9.11, 2.68 Hz, 2 H, H_b), 8.40 (d, *J* = 2.58 Hz, 2 H, H_a), 7.55 (s, 4 H, H_{d,e}), 7.12 (d, *J* = 9.15 Hz, 2 H, H_c). ¹³C NMR (DMSO-*d*₆, δ): 159.2 (C⁴), 144.2 (C⁷), 141.8 (C¹), 130.0 (C⁶), 128.6 (C⁹), 123.6 (C⁸), 123.2 (C², quartet, ³*J*_{C–F} = 5 Hz), 121.9 (C¹⁰, quartet, ¹*J*_{C–F} = 271 Hz), 118.0 (C³, quartet, ²*J*_{C–F} = 32 Hz), 116.8 (C⁵).

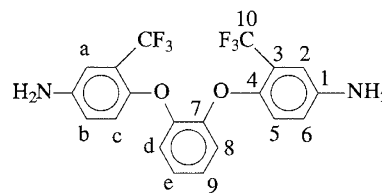


C ₂₀ H ₁₀ F ₆ O ₆ N ₂ (488.30)	Calcd.	C 49.20	H 2.06	N 5.74
	Found	C 49.18	H 2.07	N 5.74

1,2-Bis(4-amino-2-trifluoromethylphenoxy)benzene

II. To a suspension solution of the purified dinitro compound **I** (20 g, 0.04 mol) and 10% Pd/C (0.2 g) in ethanol (150 mL), hydrazine monohydrate (7 mL) was added dropwise to the stirred mixture at 70–80 °C within 30 min. After complete addition, the mixture was heated at reflux temperature for another 2 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was poured into water to precipitate white powder that was dried in vacuum at room temperature to give **II** (19.2 g, 96%). The crude product was purified by recrystallization from MeOH/H₂O.

mp: 116–117 °C by DSC (10 °C min⁻¹). IR (KBr): 3450, 3357, 3327 (N–H stretch), 1265, 1222, 1164, 1123 cm⁻¹ (C–O and C–F stretch). ¹H NMR (DMSO-*d*₆, δ): 7.03 (m, 2 H, H_e), 6.89 (d, 2 H, H_d), 6.83 (m, 2 H, H_a), 6.74–6.79 (m, 4 H, H_{b,c}), 5.33 (s, 4 H, –NH₂). ¹³C NMR (DMSO-*d*₆, δ): 147.9 (C⁷), 145.2 (C⁴), 143.7 (C¹), 124.0 (C⁹), 123.7 (C¹⁰, quartet, ¹*J*_{C–F} = 271 Hz), 121.1 (C⁸), 120.5 (C³, quartet, ²*J*_{C–F} = 30 Hz), 119.1 (C⁵), 118.6 (C⁶), 111.0 (C², quartet, ³*J*_{C–F} = 5 Hz).

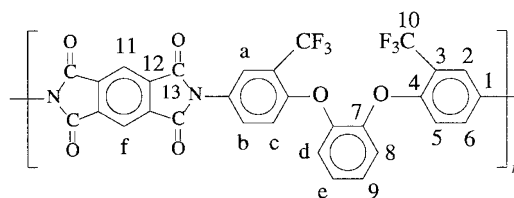


C ₂₀ H ₁₄ F ₆ O ₆ N ₂ (428.33)	Calcd.	C 56.08	H 3.29	N 6.54
	Found	C 56.09	H 3.30	N 6.54

Synthesis of Polyimides

The general polymerization procedure is illustrated by the following example. Diamine **II** (0.428 g, 1 mmol) was dissolved in 5.7 mL of dried DMAc in a 50 mL flask. After the diamine was dissolved completely, 0.218 g (1 mmol) of PMDA **III_a** was added to it in one portion. The mixture was stirred at room temperature for 12 h to form a poly(amic acid) (PAA) solution. PAA solution then was poured into a glass culture dish (ϕ = 9 cm), which was placed in an 80 °C oven for 1 h to remove the solvent. The semidried PAA film was further dried and imidized by sequential heating at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min, and 250 °C for 30 min. By being soaked in water, a flexible polyimide film of **V_a** was self-stripped off from the glass surface. The inherent viscosity of **V_a** in DMAc at a 0.5 g dL⁻¹ concentration at 30 °C was 0.76 dL g⁻¹ (Table I).

IR (film): 1781, 1730 (imide C=O), 1380 (C–N stretch), 1103, 726 cm⁻¹ (imide ring deformation). ¹H NMR (DMSO-*d*₆, δ): 8.38 (s, 2 H, H_f), 7.91 (s, 2 H, H_a), 7.75 (d, *J* = 9.55 Hz, 2 H, H_b), 7.46 (s, 4 H, H_{d,e}), 7.15 (d, *J* = 9.0 Hz, 2 H, H_c). ¹³C NMR (DMSO-*d*₆, δ): 165.2 (C¹³), 154.3 (C⁴), 145.4 (C⁷), 137.0 (C¹²), 133.1 (C¹), 127.3 (C¹¹), 126.0 (C^{6,9}), 122.9 (C⁵), 122.8 (C¹⁰, quartet, ¹*J*_{C–F} = 271 Hz), 118.5 (C³, quartet, ²*J*_{C–F} = 32 Hz), 117.8 (C⁸), 117.1 (C²).



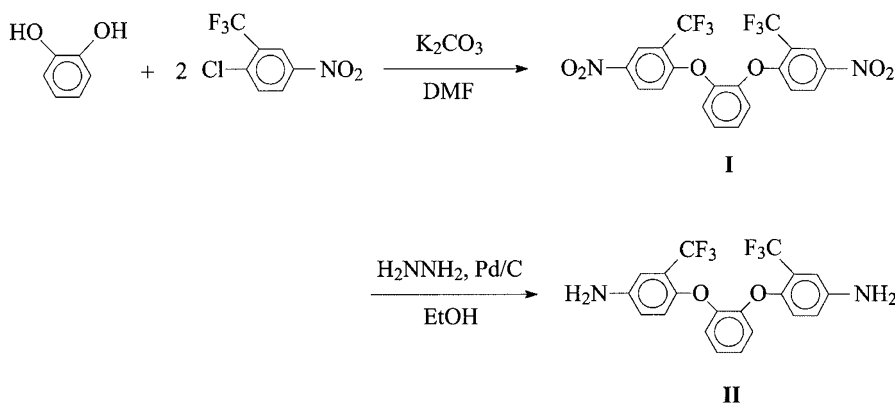
Measurements

IR spectra were recorded on a Horiba Fourier-Transform Infrared Spectrometer FT-720. Elemental analyses were run in a PerkinElmer Model 2400 C, H, N analyzer. ¹H and ¹³C spectra were recorded on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at 0.5 g dL⁻¹ concentration using a Cannon-Fenske viscometer at 30 °C. Thermogravimetry analysis (TGA) was conducted with a TA Instruments TGA 2050. Experiments were carried out

Table I. Inherent viscosity of poly(amic acid)s and polyimides and elemental analysis of the polyimides

Poly(amic acid)		Polyimide		Formula	Elemental analysis (%)			
Code	η_{inh} (dL g ⁻¹) ^a	Code	η_{inh} (dL g ⁻¹) ^a		M_w	C	H	N
IV _a	0.80	V _a	0.76	(C ₃₀ H ₁₂ O ₆ N ₂ F ₆) _n	Calcd.	59.03	1.98	4.59
				(610.43) _n	Found	59.04	2.00	4.59
IV _b	0.78	V _b	0.75	(C ₃₇ H ₁₆ O ₇ N ₂ F ₆) _n	Calcd.	62.20	2.26	3.92
				(714.53) _n	Found	62.19	2.25	3.93
IV _c	0.79	V _c	0.76	(C ₃₆ H ₁₆ O ₆ N ₂ F ₆) _n	Calcd.	62.98	2.35	4.08
				(686.52) _n	Found	63.00	2.36	4.08
IV _d	0.72	V _d	0.68	(C ₃₆ H ₁₆ O ₈ N ₂ F ₆ S ₁) _n	Calcd.	57.61	2.15	3.73
				(750.58) _n	Found	57.62	2.14	3.72
IV _e	0.75	V _e	0.70	(C ₃₆ H ₁₆ O ₇ N ₂ F ₆) _n	Calcd.	61.55	2.30	3.99
				(702.52) _n	Found	61.56	2.30	3.98
IV _f	0.70	V _f	0.68	(C ₃₉ H ₁₆ O ₆ N ₂ F ₁₂) _n	Calcd.	56.00	1.93	3.35
				(836.55) _n	Found	55.98	1.92	3.36

^aMeasured at a polymer concentration of 0.5 g dL⁻¹ in DMAc at 30 °C.

**Scheme 1.** Synthesis of 3F-diamine **II**.

on 9–11 mg film samples heated in flowing nitrogen or air (100 cm³ min⁻¹) at a heating rate of 20 °C min⁻¹. Differential scanning calorimeter (DSC) traces were measured on TA Instruments DSC 2010 at the rate of 15 °C min⁻¹ in flowing nitrogen (40 cm³ min⁻¹). Glass transition temperatures were read as the midpoint of the heat capacity jump and were taken from the second heating scan after a quick cooling down from 400 °C. Mechanical properties of the films were measured with an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 cm min⁻¹ on strips approximately 40–50 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films, using an observational angle of 10° and a CIE (Commission International de l'Eclairage)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV-vis spectrophotometer. The dielectric property of the polymer films was tested by the parallel-plate capacitor

method with a Hewlett Packard 4194A dielectric analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber.

RESULTS AND DISCUSSION

Monomer Synthesis

The CF₃-containing diamine **II** was prepared in two steps according to a well-developed method (Scheme 1). The intermediate dinitro compound **I** was synthesized from the aromatic nucleophilic substitution of 2-chloro-5-nitrobenzotrifluoride with catechol in the presence of potassium carbonate. Diamine **II** was readily obtained in high yields by the catalytic reduction of **I** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. FT-IR, NMR, and elemental analysis were used to confirm the structures of the intermediate **I** and the diamine monomer **II**. In FT-IR spectra, the nitro group of compound **I** gave two characteristic bands at 1530 and 1350 cm⁻¹ (NO₂ asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino

group showed the pair of N–H stretching bands in the region of 3300–3500 cm^{-1} (As Exp. Part and Figure 1).

The ^1H NMR spectra absorption signals of aromatic protons of **I** appeared in the region of 7.1–8.5 ppm, and those of **II** shifted to higher field between 6.7–7.1 ppm as Figure 2. In the ^1H NMR spectrum of **I**, the protons H_b and H_a resonated at the farthest downfield region due to the inductive effect of electron withdrawing $-\text{NO}_2$ and $-\text{CF}_3$ groups; the H_c *ortho*-oriented to aromatic ether shifted to the upfield region due to the greater shielding caused by the resonance effect. After reduction, the H_a of **II** still resonated at the more downfield region due to the inductive effect of CF_3 group, but the H_b of **II** shifted to the upfield region due to the electron donating effect of the amino group.

In ^{13}C NMR spectra, all the carbon-13 atoms in **I** and

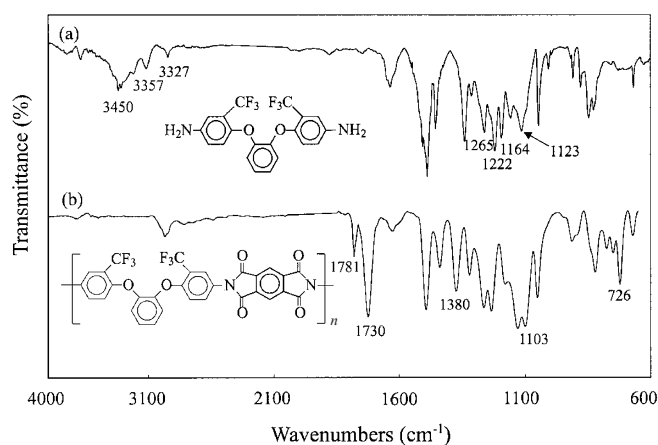


Figure 1. FT-IR spectra of (a) 3F-diamine **II** and (b) a representative polyimide **V_a**.

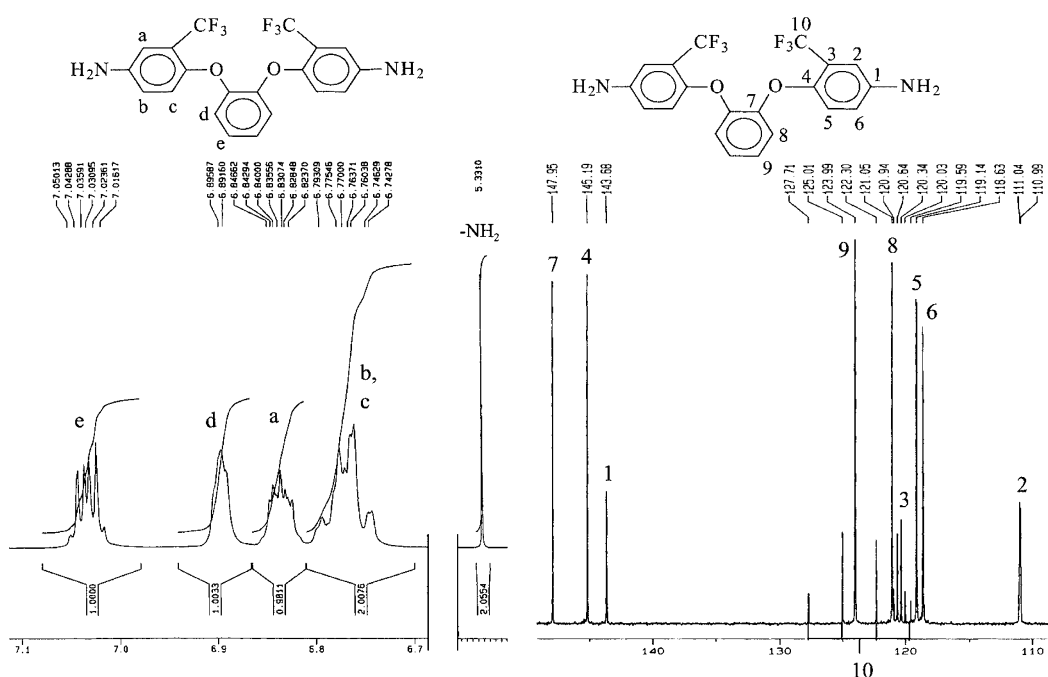


Figure 2. The ^1H and ^{13}C NMR spectra of 3F-diamine **II** in $\text{DMSO-}d_6$.

II showed ten main signals, which resonated in the region of 116–160 and 110–148 ppm, respectively. The ^{13}C NMR spectrum of **I** shows three quartets because of the heteronuclear ^{13}C – ^{19}F coupling. The large quartet centered at about 122 ppm was due to the CF_3 carbon and the one-bond C–F coupling constant was about 271 Hz. The CF_3 -attached carbon (C^3) also showed a clear quartet centered at about 118 ppm with a smaller coupling constant of about 32 Hz due to two-bond C–F coupling. Besides, the C^2 carbon (*ortho* to the CF_3 group) also had its resonance split by the three fluorines (three-bond coupling). The close quartet had an even smaller coupling constant (*ca.* 5 Hz) because the interaction operated over more bonds. Similar splitting patterns (with $^1J_{\text{C-F}} = 271$ Hz, $^2J_{\text{C-F}} = 30$ Hz, and $^3J_{\text{C-F}} = 5$ Hz) were also found in the ^{13}C NMR spectrum of **II** (Figure 2). All the spectroscopic data obtained were in good agreement with the expected structures.

Polymer Synthesis

All the polymers **V** were synthesized from diamine **II** and dianhydrides **III_{a-f}**, by a conventional two-step procedure ring-opening polyaddition at room temperature to poly(amic acid)s **IV**, followed by sequential heating to 250 °C to obtain the corresponding polyimides, as shown in Scheme 2. Figure 3 presents the variation curves of inherent viscosities of the poly(amic acid)s obtained from PMDA with CF_3 -containing diamine **II** or nonfluorinated **II'** at various times. The reaction of PMDA with fluorinated **II** proceeded relatively slow and its inherent viscosity

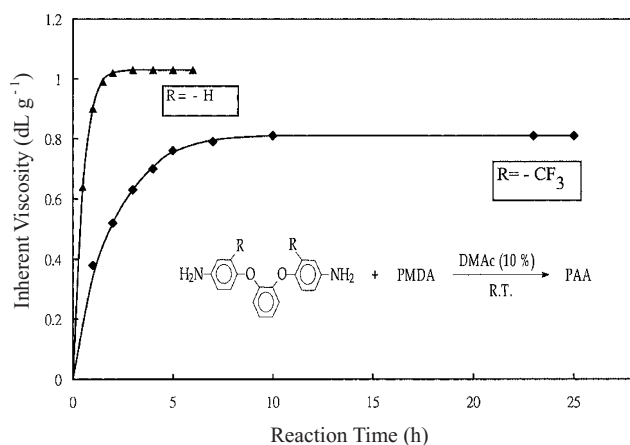
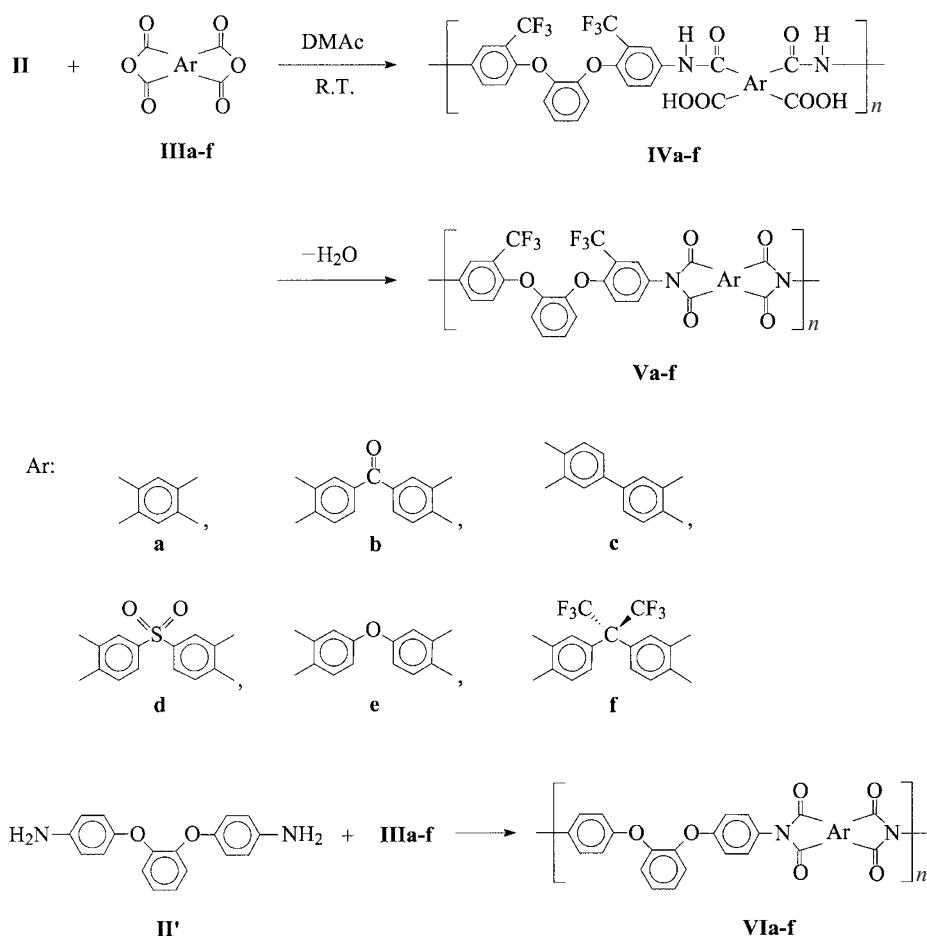


Figure 3. Viscosity change of poly(amic acid)s prepared in DMAc at 10% solid content at room temperature.

reached 0.76 dL g^{-1} after 5 h. After this point, inherent viscosity increased slowly; polymerization nearly ceased at 0.8 dL g^{-1} after 10 h. The reaction of PMDA with **II'** proceeded relatively fast and its inherent viscosity increased fast within 50 min; inherent viscosity reached 1.03 dL g^{-1} after 80 min and then decreased gradually.

IR spectroscopy allows monitoring of the imide ring formation during thermal curing. The typical set of

FT-IR spectra of polyimide **V_a** are shown in Figure 1. As the poly(amic acid) was converted into the polyimide, the characteristic absorption bands of the imide ring were observed near 1781 and 1730 (asymmetrical and symmetrical C=O stretching vibration), 1380 (C–N stretching vibration), and 1103 and 726 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm^{-1} due to the C–O and C–F stretching. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the poly(amic acid) precursor into polyimide.

In general, structure identification of standard aromatic polyimides by the NMR spectroscopy is difficult due to poor solubility. In this study, polyimides **V** had good solubility in organic solvent and could be identified by NMR spectra easily. The typical NMR spectra of soluble polypyromellitimide **V_a** are shown in Figure 4. In the ^1H NMR spectrum, all the protons resonated in the region of 7.1–8.4 ppm. The protons H_f on the pyromellitimide unit resonated at the farthest downfield, owing to the inductive effect and resonance. H_a and H_b also resonated at lower fields because of close to the electron withdrawing CF_3 group and imide ring. The H_c shifted to higher field due to the electron donat-

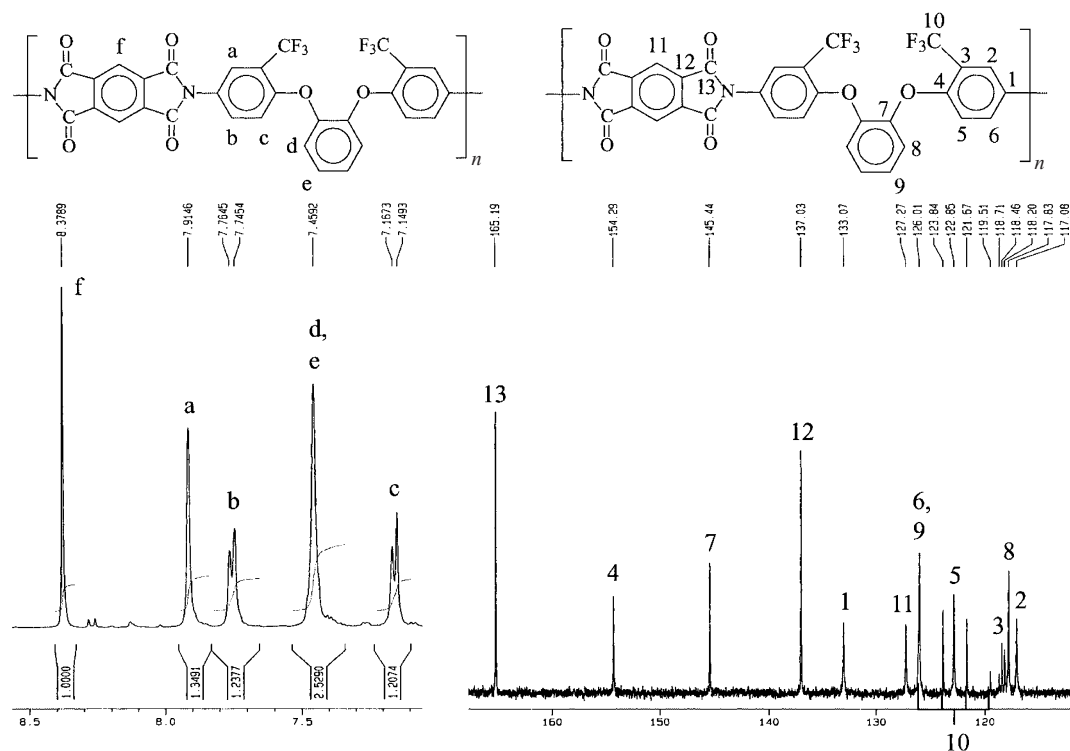


Figure 4. The ^1H and ^{13}C NMR spectra of polyimide V_a in $\text{DMSO}-d_6$.

ing property of aromatic ether. In ^{13}C NMR spectrum, all the carbon-13 atoms in V_a showed 13 signals, which were in good agreement with the expected structures. Carbon C^{13} of the carbonyl group was evidenced in the downfield region. Furthermore, the splitting of the ^{13}C signals caused by couplings between carbon and fluorine also could be observed in the spectrum. The magnitudes of $^1J_{\text{C-F}}$ and $^2J_{\text{C-F}}$ are 271 Hz and 32 Hz, respectively. The results of elemental analysis of V_{a-f} are listed in Table I. Above-cited results evidenced that series **V** had been synthesized successfully.

Properties of Polymer

The solubility of these polyimides was tested in various organic solvents, and the results are summarized in Table II. Polymers $\text{V}_{a,c-f}$ had excellent solubilities in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO and were also soluble in less polar solvents like pyridine, and dioxane. In general, almost all polypyromellitimides on the basis of various diamines were insoluble in organic solvents. Unlike previous reports, in this study polypyromellitimide V_a based on special diamine **II** showed good solubility. However, after heating, V_b can be dissolved in tested solvents. This might be attributable to the formation of some intermolecular links of the $\text{C}=\text{O}$ group of BTDA during the thermal imidization. On the contrary, V_b (**C**) synthesized *via* chemical imidization did not possess crosslinks and exhibited better solubility. Compared with polyimides **VI**, polyimides **V** showed better solubility. Poor sol-

ubility for the **VI** series indicates either strong intermolecular interactions or good packing ability. Therefore, the large differences in solubility between the **V** and **VI** series are attributed to the presence of bulky trifluoromethyl group, which inhibited close packing, thereby reducing the interchain interactions to enhance solubility.

The color intensities of the polyimides were elucidated from the yellowness or redness indices observed by a Macbeth color-eye colorimeter. For comparison, the corresponding polyimides **VI** without the CF_3 groups were also prepared and characterized by their color intensity. The color coordinates of these polyimides are given in Table III. The color intensity of polyimides was affected by dianhydride moieties with decreased in the following decreasing order: PMDA > BTDA > DSDA > BPDA > ODPDA > 6FDA as showed in Figure 5. V_{c-f} displayed lighter color than the others. As compared **V** series with **VI** series, the results indicate that the **V** series showed a lower b^* value (a yellowness index) in contrast with the corresponding polyimides **VI**. The color intensities of the polyimides could also be elucidated from the cutoff wavelength observed in the UV-vis absorption spectra. Figure 6 shows the UV-vis spectra of the polyimide films, and the cutoff wavelengths (λ_0) from these spectra are listed in Table III.

Polyimides **V** had λ_0 in the range of 365–421 nm. V_{c-f} were lightly colored and exhibited λ_0 lower than 395 nm. In particular, 6FDA and ODPDA produced

Table II. Solubility behavior of the polyimides^a

Polymer	Solvent ^d						
	NMP	DMAC ^b	DMF	DMSO	Py	<i>m</i> -Cresol	Dioxane
V _a	++	++	++	++	++	+	+
V _b	+	+	+	+	+	+	S
V _c	++	++	++	++	++	+	+
V _d	++	++	++	++	++	+	+
V _e	++	++	++	++	++	+	+
V _f	++	++	++	++	++	++	++
V _b (C) ^c	++	++	++	++	++	+	+
VI _a	-	-	-	-	-	-	-
VI _b	S	-	-	-	-	S	-
VI _c	++	-	-	-	-	+	-
VI _d	-	-	-	-	-	-	-
VI _e	-	-	-	-	-	-	-
VI _f	++	++	++	++	++	++	++

^aQualitative solubility was determined with 10 mg of polymer in 1 mL of solvent: ++, soluble at room temperature; +, soluble on heating; S, swelling or partially soluble; -, insoluble even on heating. ^bThe solubility was determined at 10% solid content. ^cPolyimides were obtained by the chemical imidization method with NMP as solvent. ^dNMP: *N*-methyl-2-pyrrolidone; DMAC: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine.

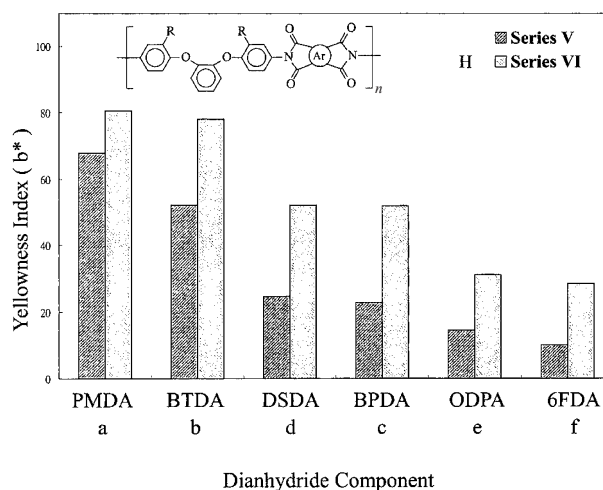
Table III. Color coordinates and cutoff wavelength (λ_0) from UV-vis spectra for both V and VI series polyimides films

Polymer	Color Coordinates ^a			λ_0 (nm) ^b	Film thickness (μm)
	b*	a*	L*		
Paper	0.97	-0.43	96.20	-	-
V _a	67.9	-10.9	91.5	421	62
V _b	52.2	-3.3	93.2	405	48
V _c	22.8	-7.2	95.1	394	43
V _d	24.6	-9.3	94.2	395	53
V _e	14.5	-5.6	95.5	369	40
V _f	10.1	-3.5	95.6	365	46
VI _a	80.5	-10.1	82.2	455	63
VI _b	78.1	-2.9	87.3	434	50
VI _c	52.0	-8.6	89.3	416	58
VI _d	52.2	-3.7	84.3	415	50
VI _e	31.1	-6.3	91.2	386	45
VI _f	28.4	-7.1	92.6	383	68
Kapton	85.1	-0.3	90.1	443	38

^aThe color parameters were calculated according to a CIE LAB equation, using paper as a standard. L* is lightness; 100 means white, while 0 implies black. A positive a* means red color, while a negative a* indicated green color. A positive b* means yellow color, while a negative b* implies blue color.

^bTransparency cut-off wavelength in nm.

fairly transparent and almost colorless polyimide films in contrast to other dianhydrides. Consistent with the results obtained from the colorimeter, all the fluorinated polyimides revealed a shorter λ_0 than their respective nonfluorinated analogues. The light color of the polyimides with the CF₃ groups in their diamine

**Figure 5.** Comparison of the yellowness index (b* value) between polyimides V and VI.

moieties could be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing CF₃ group in diamine II was effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). The good optical transparency and lighter color of the ODPA- and 6FDA-derived polyimide films result from the decrease in the intermolecular CTC interaction and electron conjugation by the aromatic ether and the bulky CF₃ group.

The tensile properties are summarized in Table IV. These films had strengths at break of 92–123 MPa,

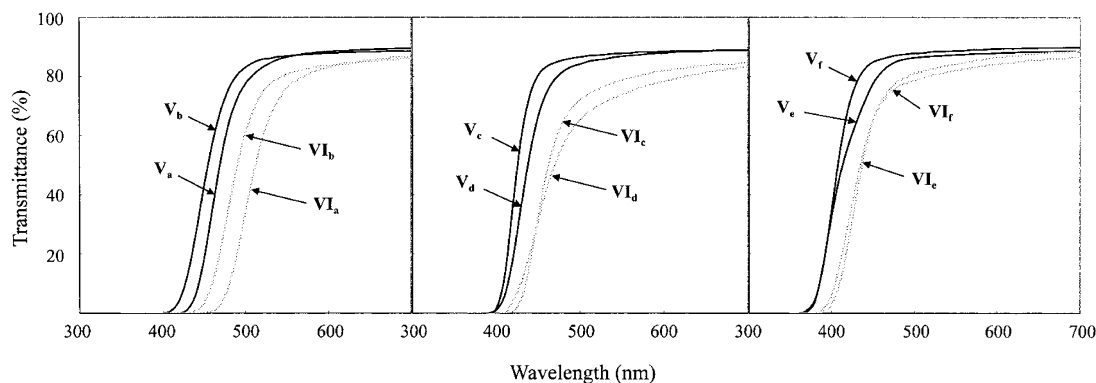


Figure 6. UV-vis spectra of polyimide films.

Table IV. Tensile properties of polyimide films

Polymer	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
V _a	101	92	20	2.0
V _b	–	123	11	2.3
V _c	123	117	42	2.4
V _d	–	108	8	2.2
V _e	–	112	17	2.2
V _f	–	105	9	2.1

Table V. Thermal behavior data for the polyimides

Polymer	DSC T_g^a (°C)	TGA		Char Yield ^d (wt%)
		Decomposition Temp. ^b (°C)		
		In Air	In Nitrogen	
V _a	277	582	592	51
V _b	236	570	585	50
V _c	249	592	602	59
V _d	255	547	541	53
V _e	223	582	590	55
V _f	247	550	560	52

^aMidpoint of baseline shift in the second heating DSC trace with a heating rate of 15 °C min⁻¹ under a nitrogen atmosphere.

^bTemperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C min⁻¹. ^cResidual weight % at 800 °C under a nitrogen atmosphere.

elongations at break of 8–42%, and initial modulus of 2.0–2.4 GPa, respectively. V_a and V_c showed a clear yield point on their stress–strain curves (yield strength: 101 and 123 MPa) and had higher elongation at break, indicating high toughness. Combining rigid dianhydride with tortuous diamine, the capability of polymer backbone to assume a range of conformations while retaining considerable rigidity character may be responsible for this toughness.

The thermal behavior data of all the fluorinated polymers are presented in Table V. DSC experiments were conducted at a heating rate of 15 °C min⁻¹ in nitrogen. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so the glass transition temperatures (T_g) of all the polyimides could

be easily read in the subsequent heating DSC traces. The T_g values of polyimides V_{a–f} were in the range of 223–277 °C, depending on the structure of the dianhydride component and decreasing with the increasing flexibility of the polymer backbones. As expected, the polyimide V_a derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit. However, the polyimide V_e obtained from ODPA showed the lowest T_g of 223 °C. This is reasonable because its dianhydride moiety has a flexible ether linkage.

The thermal stability of the polyimides was evaluated by TGA conducted at a heating rate of 20 °C min⁻¹. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA thermograms and are also tabulated in Table V. The T_{10} values of polyimides V_{a–f} stayed in the range of 541–602 °C in nitrogen and in the range of 547–592 °C in air, respectively. They left more than 50% char yield at 800 °C in nitrogen. BPDA-derived V_c had the highest T_{10} and char yield. Polyimide V_d bearing a sulfonyl group in dianhydride DSDA exhibited lower values than the other polymers. This may be attributed to the weak bonding of C–S bond and easily degradation on the heating process. VI_d also showed lower thermal stability, as shown in Figure 7.

The measurements of the dielectric constants were performed between gold layers: the polyimide film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the polymer film. This procedure excludes any contact problems. Table VI shows the results. Fluorinated polyimides V_{a–f} had lower dielectric constants (2.70–3.62 at 1 MHz) than commercial polyimides such as Kapton films and non-fluorinated polyimide VI_a. The decreased dielectric constants might be attributable to the presence of bulky CF₃ groups, which resulted in less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine resulted in very low polarizability of the C–F bonds, thereby decreasing the dielectric constant. Hence, the 6FDA-derived polyimide

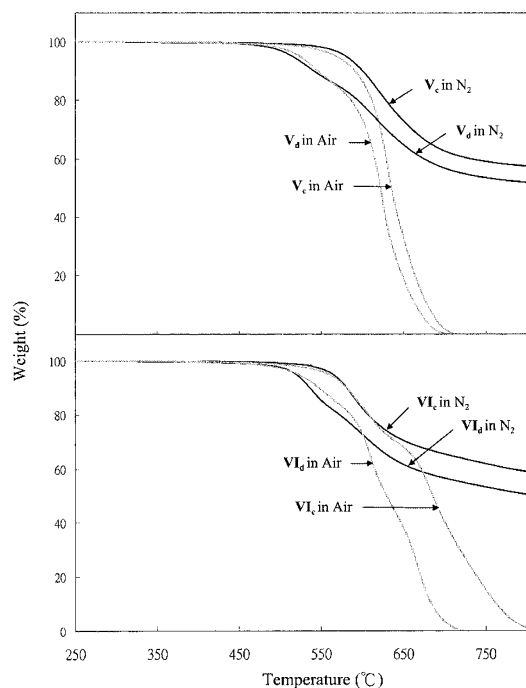


Figure 7. Typical TGA curves of polyimides $V_{c,d}$ and $VI_{c,d}$ with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

Table VI. Moisture absorption and dielectric constants of the polyimides

Polyimide	Film thickness (μm)	Dielectric Constant			
		1 kHz	10 kHz	1 MHz	40 MHz
V_a	85	3.64	3.63	3.62	3.60
V_b	62	3.57	3.56	3.54	3.52
V_c	53	3.31	3.28	3.25	3.22
V_d	55	3.53	3.51	3.47	3.45
V_e	73	3.02	2.97	2.93	2.90
V_f	56	2.73	2.72	2.70	2.67
VI_a	50	3.96	3.93	3.91	3.89
Kapton ^b	40	3.89	3.85	3.80	3.75

^aData in parentheses are those of the VI series polyimides. ^bA reference polyimide prepared from PMDA and 4,4'-oxydianiline (η_{inh} of the poly(amic acid) precursor 1.9 dL g^{-1}).

V_f exhibited the lowest dielectric constant than those prepared from the other dianhydrides of polyimides V_{a-e} .

CONCLUSIONS

A high-purity, almost colorless fluorinated diamine **II**, 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene, was prepared through nucleophilic substitution reaction of catechol and 2-chloro-5-nitrobenzotrifluoride, followed by catalytic reduction with hydrazine. A series of light-colored and organosoluble polyimides **V** have been obtained from the trifluoromethyl-substituted diamine with different aromatic dianhydrides. These polyimides were char-

acterized by excellent thermal stability and good mechanical property. They exhibit better solubility, lighter color and lower dielectric constant than corresponding nonfluorinated polyimides.

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