

Organosoluble and Light-Colored Fluorinated Polyimides Based on 1,1-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenylethane and Various Aromatic Dianhydrides

Chin-Ping Yang, Yung-Chung Chen

Department of Chemical Engineering, Tatung University, 40 Chungshan North Rd., Sec. 3, Taipei 104, Taiwan

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ABSTRACT: To investigate the CF₃ group affecting the coloration and solubility of polyimides (PI), a novel fluorinated diamine 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenylethane (**2**) was prepared from 1,1-bis(4-hydroxyphenyl)-1-phenylethane and 2-chloro-5-nitrobenzotrifluoride. A series of light-colored and soluble PI **5** were synthesized from **2** and various aromatic dianhydrides **3a–f** using a standard two-stage process with thermal **5a–f(H)** and chemical **5a–f(C)** imidization of poly(amic acid). The **5** series had inherent viscosities ranging from 0.55 to 0.98 dL/g. Most of **5a–f(H)** were soluble in amide-type solvents, such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF), and even soluble in less polar solvents, such as *m*-Cresol, Py, Dioxane, THF, and CH₂Cl₂, and the **5(C)** series was soluble in all solvents. The GPC data of the **5a–f(C)** indicated that the \overline{M}_n and \overline{M}_w values were in the range of 5.5–8.7 × 10⁴ and 8.5–10.6 × 10⁴, respectively, and the polydispersity index (PDI) $\overline{M}_w/\overline{M}_n$ values were 1.2–1.5. The PI **5** series had

excellent mechanical properties. The glass transition temperatures of the **5** series were in the range of 232–276 °C, and the 10% weight loss temperatures were at 505–548 °C in nitrogen and 508–532 °C in air, respectively. They left more than 56% char yield at 800 °C in nitrogen. These films had cutoff wavelengths between 356.5–411.5 nm, the b* values ranged from 5.0–71.1, the dielectric constants, were 3.11–3.43 (1MHz) and the moisture absorptions were in the range of 0.11–0.40%. Comparing **5** containing the analogous PI **6** series based on 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (BAPPE), the **5** series with the CF₃ group showed lower color intensity, dielectric constants, and better solubility. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2399–2412, 2005

Key words: light-colored; organosoluble; 1,1-bis(4-hydroxyphenyl)-1-phenylethane; fluorinated-di(ether-amine); polyimides

INTRODUCTION

Aromatic polyimides show excellent thermal stabilities and balanced mechanical and electric properties and have been used widely in the aerospace and electronics industries.^{1–7} The optical transparency of polyimide films is of 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 light-wave circuits.¹¹ And it has become a popular material. However, aromatic polyimides are difficult to process because of high softening temperatures and limited solubility in commercially available solvents and they strongly absorb in the visible region of their UV-visible spectra.

As the divers became small size gradually, lower dielectric constants have been required by the electronic circuit industry.¹² One of the most effective methods to decrease the dielectric constant is to introduce fluorine atoms into polyimide materials. As is well known, the high electronegativity of fluorine results in very low polarizability of C–F bonds and reduces the dielectric constant. Fluorination is also known to increase the space of inter-molecules so as to enhance the solubility and optical transparency and to lower the moisture absorption of polyimides.^{13,14} Therefore, it is expected that fluorinated polyimides will be widely applied in the electro-optical and semiconductor industries.

For optical applications, a number of very lightly colored to colorless transparent PI films have been synthesized and characterized. The optically transparent and colorless PI could be synthesized from a dianhydride and a diamine with the hexafluoroisopropylidene group.¹⁵ A lowering of the charge-transfer complex (CTC) between the alternating electron-donor (diamine) and the electron-acceptor (dianhydride)

Correspondence to: C.-P. Yang (cpyang@ttu.edu.tw)

moieties provides PI with a lighter color.¹⁶ We had synthesized the aromatic diamine BAPPE containing the propeller-shaped triphenylrthane and flexible ether structure to discuss the properties of the PI.¹⁷ In this study we expected to improve the solubility, increase the transparency and reduce the dielectric constants. Therefore, the BAPPE diamine containing CF₃ group, 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenylethane (2) was synthesized, and a series of fluorinated PI 5a–f was polycondensed with various commercially available aromatic dianhydride (3a–f) via thermal or chemical imidization, and compared with analogous nonfluorinated PI.

EXPERIMENTAL

Materials

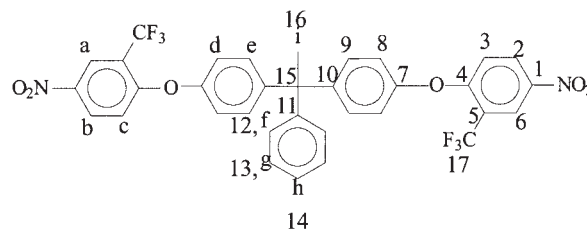
1,1-Bis(4-hydrophenyl)-1-phenylethane (Acros), 2-chloro-5-nitrobenzotrifluoride (Acros), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, 3c, Chriskev), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, 3f, Chriskev) were used as received. Pyromellitic dianhydride (PMDA, 3a, Lancaster), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, 3b, Acros), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA, 3e, New Japan Chemical Co.), and 4,4'-oxydiphthalic dianhydride (ODPA, 3d, Chriskev) were recrystallized from acetic anhydride before using. *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 4Å molecular sieves.

Monomer synthesis

1,1-Bis[4-(4-nitro-2-trifluoromethylphenoxy)phenyl]-1-phenylethane (1)

1,1-Bis(4-hydrophenyl)-1-phenylethane (22.05 g, 0.075 mole) and 2-chloro-5-nitrobenzotrifluoride (34.28 g, 0.152 mol) were first dissolved in 150 mL of DMAc 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 stirred at room temperature for 30 min, then the mixture was heated at 110°C for 10 h. The obtained mixture was poured into methanol/water (volume ratio 10/1) to give a light yellow solid, which was collected, washed thoroughly with methanol and water, and dried under vacuum at 80–100°C, then recrystallized from DMF/methanol to give a white solid (46.13 g, 92%) (m.p.: 133–134°C, by DSC at a scan rate of 5°C/min).

IR (KBr): 1533, 1334 (–NO₂ stretch), 1267, 1166, 1116 cm^{–1} (C–F and C–O stretch).



Scheme 1

¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 8.51 (d, 2H, H_a, *J* = 2.6 Hz), 8.48 (dd, 2H, H_b, *J* = 2.76 Hz), 7.37 (t, 2H, H_g, *J* = 7.4 Hz), 7.26–7.29 (6H, H_{e,f}), 7.22 (1H, H_h), 7.21–7.20 (4H, H_d), 7.19–7.17 (2H, H_c), 2.24 (–CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm): 160.23 (C⁴), 152.10 (C⁷), 148.30 (C¹¹), 146.50 (C¹), 141.74 (C¹⁰), 130.69 (C¹³), 130.15 (C¹²), 128.35 (C⁹), 128.28 (C²), 126.41 (C¹⁴), 122.37 (C¹⁷, quartet, ¹*J*_{C–F} = 273.19 Hz), 123.34 (C⁶, quartet, ³*J*_{C–F} = 5.03 Hz), 119.95 (C³), 119.11 (C⁵, quartet, ²*J*_{C–F} = 32.2 Hz), 118.19 (C⁸), 51.80 (C¹⁵), 30.29 ppm (C¹⁶).

ELEM. ANAL. Calcd. For C₃₄H₂₂F₆N₂O₆ (668.55): C, 61.08%; H 3.32%; N 4.19%. Found: C, 60.41%, H, 3.18%; N, 4.05%.

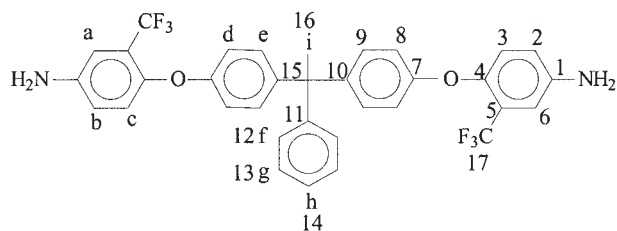
1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenylethane (2)

A suspension solution of the purified dinitro compound 1 (20 g, 0.03 mol), 10% Pd/C (0.2 g) in ethanol (150 mL), and hydrazine monohydrate (7 mL) was added to the stirred mixture at 70–80°C within 30 min. The mixture was heated at reflux temperature for 2 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The obtained mixture was poured into water to precipitate white- to cream-colored crystals that were dried in vacuum at room temperature to give 2 (17 g, 93%) (m.p.: 139–140°C).

IR (KBr): 3392, 3343 (N–H stretch), 1261, 1228, 1160, 1116 cm^{–1} (C–O and C–F stretch).

¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 7.27 (t, 2H, H_g, *J* = 7.16 Hz), 7.19 (t, H, H_h, *J* = 7.04 Hz), 7.08 (d, 2H, H_f, *J* = 7.4 Hz), 7.02 (2H, H_e), 7.00 (4H, H_a), 6.89–6.84 (4H, H_{b,c}), 6.82–6.79 (d, 2H, H_d, *J* = 8.8 Hz), 5.48 (–NH₂), 2.10 (–CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm): 156.54 (C⁷), 149.04 (C¹¹), 145.73 (C⁴), 142.90, 142.66 (C¹), 142.64 (C¹⁰), 129.65 (C¹³), 128.24 (C¹²), 127.96 (C⁹), 125.97 (C¹⁴), 123.66 (C¹⁷, quartet, ¹*J*_{C–F} = 272.69 Hz), 123.05 (C³), 121.55 (C⁵, quartet, ²*J*_{C–F} = 30.19 Hz), 118.70 (C²), 116.10 (C⁸), 110.88 (C⁶, quartet, ³*J*_{C–F} = 5.03 Hz), 51.14 (C¹⁵), 30.31 ppm (C¹⁶).

ELEM. ANAL. Calcd. For C₃₄H₂₆F₆N₂O₂ (608.58): C, 67.11%; H, 4.27%; N, 4.61%. Found: C, 66.72%; H, 4.23%; N 4.55%.



Scheme 2

Synthesis of polyimides

Thermal imidization

As polyimide 5a, the diamine 2 (0.608 g (1 mmol)) was dissolved in 6.4 mL of dried DMAc in a flask. After the diamine was completely dissolved, 0.218 g (1 mmol) of PMDA was added in one portion. The mixture was stirred at room temperature for 12 h to form a viscous poly(amic acid) (PAA) solution. Then, the obtained PAA solution was spread on a 9 cm glass culture dish, which was placed in an 80°C oven for 1 h to remove the solvents. The semidried PAA film was sequentially heated at 130°C for 10 min, 150°C for 10 min, 170°C for 10 min, 190°C for 10 min, 210°C for 10 min, 230°C for 10 min, and 250°C for 30 min. By soaking in water, a flexible PI film 5a(H) was self-stripped off from the glass surface. The inherent viscosity of 5a(H) in DMAc was 0.87 dL/g.

IR (film): 1781, 1731 (imide C=O), 1376 (C-N stretch), 1137, 725 cm^{-1} (imide ring deformation).

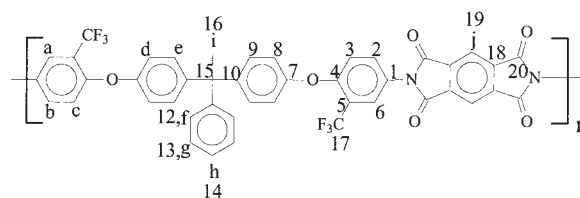
^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 8.41 (1H, H_j), 7.99 (2H, H_a), 7.79 (d, 2H, H_b , $J = 8.92$ Hz), 7.34 (t, 2H, H_g , $J = 7.36$ Hz), 7.25–7.23 (3H, $H_{f,h}$), 7.19 (d, 4H, H_e , $J = 8.64$ Hz), 7.14–7.13 (6H, H_c), 2.19 (-CH₃). ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm): 156.18 (C^{20}), 154.44 (C^7), 153.25 (C^4), 148.38 (C^{11}), 145.17 (C^{10}), 137.01 (C^{18}), 133.29 (C^1), 130.21 (C^{13}), 128.16 (C^{12}), 128.04 (C^9), 126.20 (C^{19}), 124.27 (C^{14}), 122.92 (C^{17} , quartet, $^1J_{C-F} = 272.69$ Hz), 121.56 (C^1), 119.42 (C^5 , quartet, $^2J_{C-F} = 30.19$ Hz), 119.22 (C^8), 118.95 (C^3), 117.89 (C^6), 51.42 (C^{15}), 30.16 ppm (C^{16}).

Chemical imidization

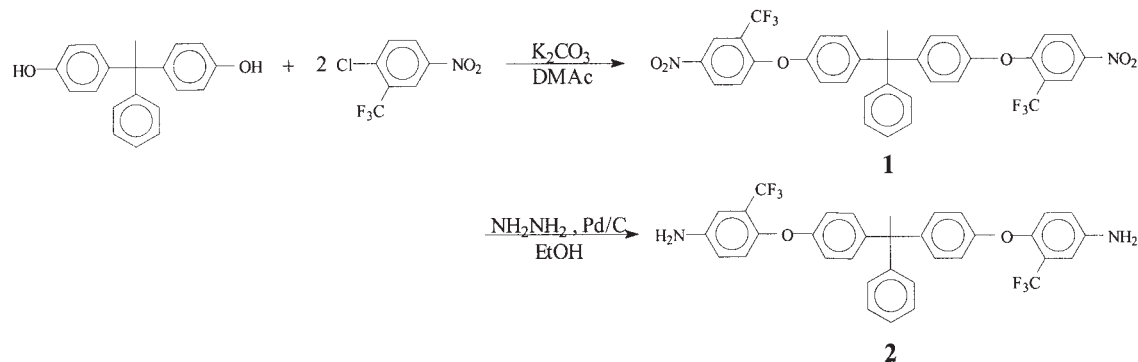
As polyimide 5a, the method of synthesizing PAA was similar to the PI(H), then was added a condensing agent (acetic anhydride/pyridine = 2/1 volume) 1 mL, and it was stirred at 80–100°C for 1 h to imidize. Then the obtained solution was poured into a glass culture dish, which was placed in a 100°C oven to evaporate the solvent and form a film. The flat PI film was sequentially heated to 200°C. By soaking in water, a flexible PI film 5a(C) was self-stripped off from the glass surface. The inherent viscosity was 0.65 dL/g.

Measurements

Melting points were measured by differential scanning calorimeter (DSC) at a heating rate of 5°C/min. Infrared spectra were recorded on a Horiba Fourier-Transform Infrared Spectrometer FTIR-720. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. ^1H and ^{13}C spectra were recorded on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer at 30°C. Weight-average molecular weight (\overline{M}_w) and number-average molecular weight (\overline{M}_n) were determined by means of a gel permeation chromatography (GPC). Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 7–10-mg film samples heated in flowing nitrogen or air (90 cm^3/min) at a heating rate of 20°C/min. The glass transition temperatures (T_g) were measured on TA Instruments DSC 2010 at the rate of 15°C/min in flowing nitrogen (40 cm^3/min). T_g was read as the midpoint of the heat capacity jump and was 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 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. The equilibrium moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25°C for 3 days.



Scheme 3



Scheme 4

RESULTS AND DISCUSSION

Monomer synthesis

The new CF_3 -containing diamine 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenylethane (**2**) was prepared in two steps according to a well-developed method, as shown in Scheme 4. The intermediate dinitro compound **1** was synthesized by a nucleophilic aromatic substitution reaction between 2-chloro-5-nitrobenzotrifluoride with 1,1-bis(4-hydroxyphenyl)-1-phenylethane in the presence of potassium carbonate in DMAc. The diamine **2** was readily obtained in high yields by the Pd/C-catalyzed reduction of **1** with hydrazine hydrate in refluxing ethanol.

FTIR, NMR, and elemental analysis were used to confirm the structures of the dinitro compound **1** and the diamine **2**. Figure 1 shows the FTIR spectra of **1** and **2**. The **1** gave two characteristic bands at 1533 and 1334 cm^{-1} . After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical N-H stretching bands in the region of 3300–3500 cm^{-1} .

Figures 2 and 3 present the ^1H and ^{13}C NMR spectra of **1** and **2**. In the ^1H NMR spectrum, the absorption signals of the aromatic protons of **1** appear in the range of 7.2–8.5 ppm, and the proton of the methyl group appears in 2.24 ppm. The protons H_a and H_b resonated at the farthest downfield, caused by the inductive effect of the electron withdrawing $-\text{NO}_2$ and $-\text{CF}_3$ groups. And the protons H_c and H_d ortho-oriented to aromatic ether appeared in the upfield. After reduction, the aromatic proton and the protons of the methyl group shifted to the upfield region due to the electron donating property of the amine groups. The H_a and H_b of diamine **2** shifted to the upfield region due to the amino groups. In the ^{13}C NMR spectra, the carbon-13 atoms in **1** showed 2 aliphatic signals in the region of 30–52 ppm and 15 aromatic signals in 118–160 ppm, and **2** also showed 2 aliphatic signals in 30–51 ppm and 15 aromatic signals in 111–157 ppm; the number of C were conformed to **1** and **2**. In Figure 2, the dinitro compound showed three quartets be-

cause of the heteronuclear ^{13}C - ^{19}F coupling. The large quartet centered at about 123 ppm is due to the $-\text{CF}_3$ carbon. The one-bond C-F(C^{17}) coupling constant in this case is 273 Hz. The 3F-attached carbon (C^5) also shows a clear quartet, and its coupling constant is 32 Hz due to two-bond C-F coupling. Besides, the C^6 carbon, ortho to the 3F group, also has its resonance split by the three fluorines (three-bond coupling). The close quartet has an even smaller coupling constant, about 5 Hz. As above, the 3F-diamine has similar splitting patterns ($^1J_{\text{C-F}} = 273$ Hz, $^2J_{\text{C-F}} = 30$ Hz, and $^3J_{\text{C-F}} = 5$ Hz), also found in Figure 3. All the spectroscopic data obtained were in good agreement with the expected structures.

Polymer synthesis

Polyimides **5a–f** were synthesized in two steps by the polymerization reactions of CF_3 -containing diamine **2** with commercially available dianhydrides **3a–f** to form PAA **4a–f**, followed by thermal or chemical imidization as shown in Scheme 5. The synthesis of the polymer was as follows: the diamine was dissolved in DMAc, then was added an equivalent dianhydride by the ring-opening polyaddition to form PAA at room temperature. The PAA solution was then poured into a glass culture or a plate glass to form the PI(H) film through cyclodehydration by heating to 250°C sequentially or by adding an equivalent condensing agent ($\text{Ac}_2\text{O}/\text{Py}$) to imidize and cast the film directly.

The GPC data of the PI **5a–f**(C) are shown in Table II, \overline{M}_n and \overline{M}_w values available in the range of $5.5\text{--}8.7 \times 10^4$ and $8.5\text{--}10.6 \times 10^4$, respectively. PDI values were from 1.2 to 1.5. The measured values of elemental analysis of **5a–f** are close to the calculated ones in Table I. **5a–f**(H) and **5a–f**(C) had inherent viscosities ranging from 0.60 to 0.98 dL/g and 0.55 to 0.78 dL/g. Figure 4 presents the variation curves of inherent viscosities of the PAA obtained from BPDA with **2** and BAPPE diamine at various times. From the curve, the fluorinated **2** proceeded relatively slowly, and its inherent viscosity reached 0.79 dL/g after 5 hr. Then, the

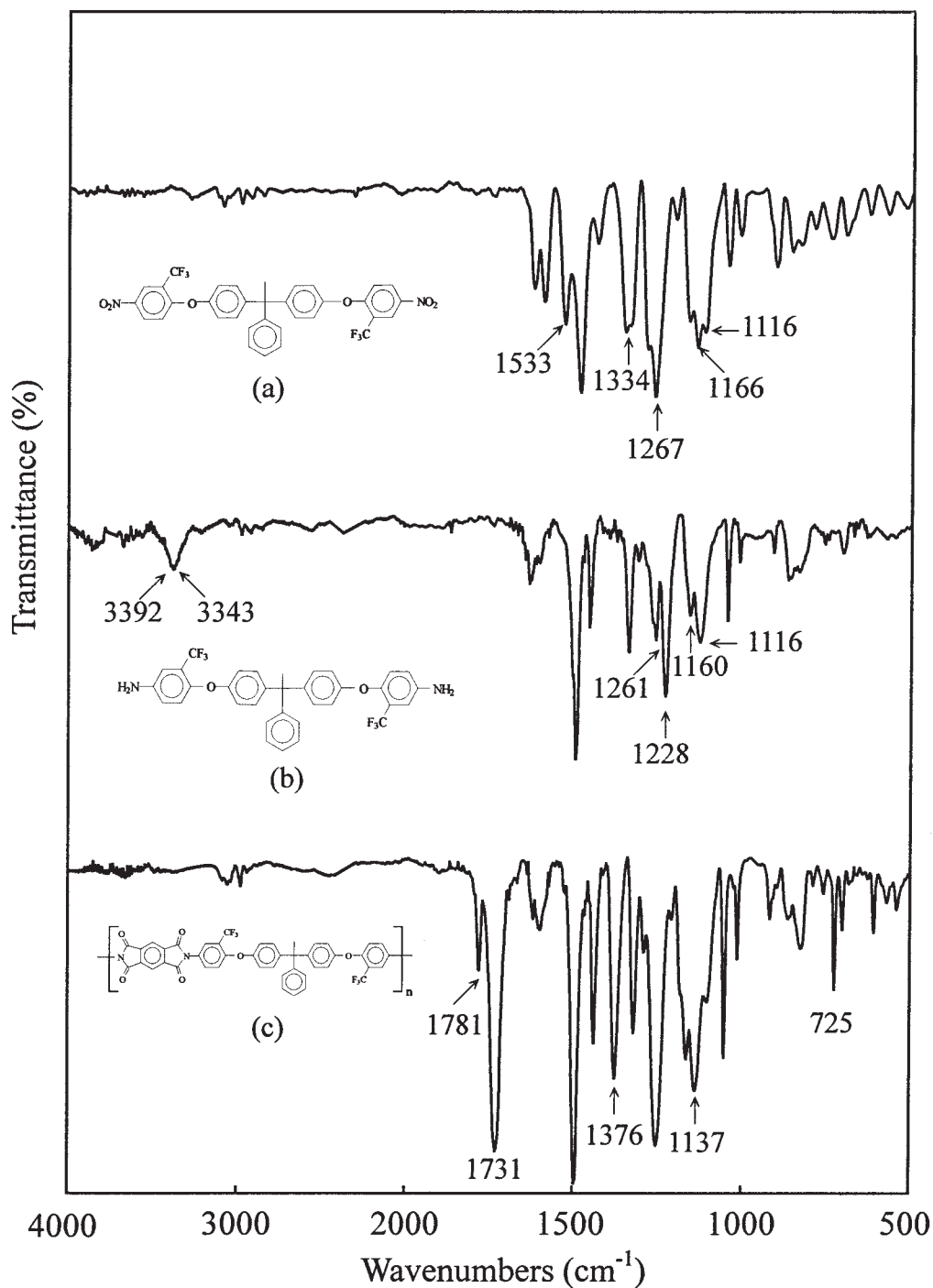


Figure 1 FT-IR spectra of (a) 3F-dinitro compound, (b) 3F-diamine, (c) polyimide by PMDA (5a).

inherent viscosity increased slowly and reached 1.12 dL/g in 12 hr. But the BAPPE diamine proceeded relatively fast, and its inherent viscosity increased quickly within 10 min, with the inherent viscosity reaching 1.72 dL/g after 30 min.

The ^1H and ^{13}C NMR spectra of PI 5a in DMSO-*d*₆ are shown in Figure 5. In ^1H NMR spectrum, all the protons resonated in the region of 7.1–8.4 ppm and the proton of the methyl group resonated in the region

of 2.2 ppm. The H_j closed to the imide ring appeared farthest downfield owing to the resonance; the H_a ortho-oriented to the CF_3 group shifted to the upfield, owing to the shielding effect. The $\text{H}_{d,c}$ shifted to higher field owing to the electron-donating of the aromatic ether group. In the ^{13}C NMR spectrum, 5a showed 2 aliphatic signals in 30–51 ppm and 18 aromatic signals in 118–165 ppm; the number of C conformed to 5a. The carbon C^{20} with the carbonyl group

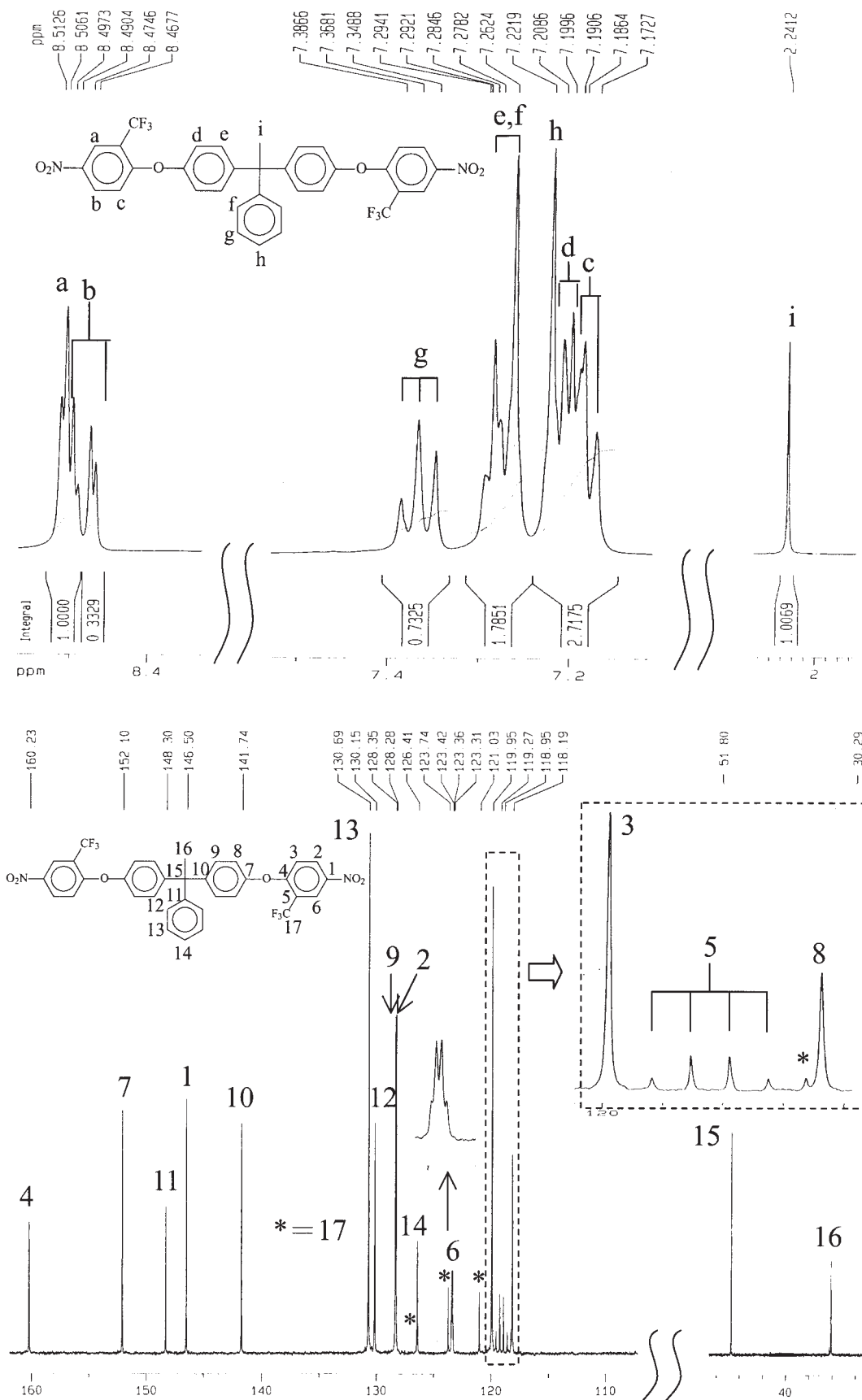


Figure 2 The ^1H and ^{13}C NMR spectrum of 3F-dinitro 1 in $\text{DMSO-}d_6$.

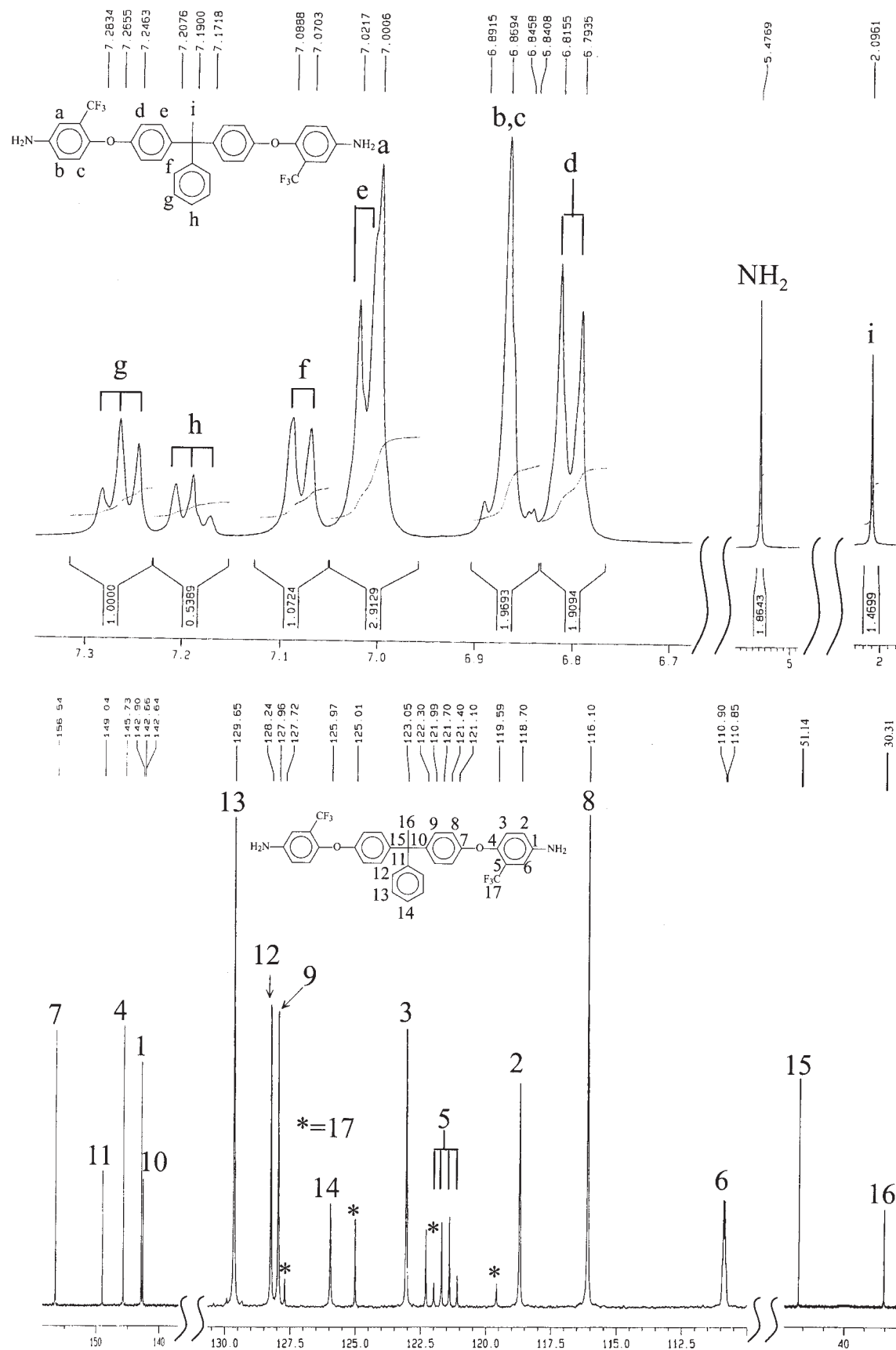
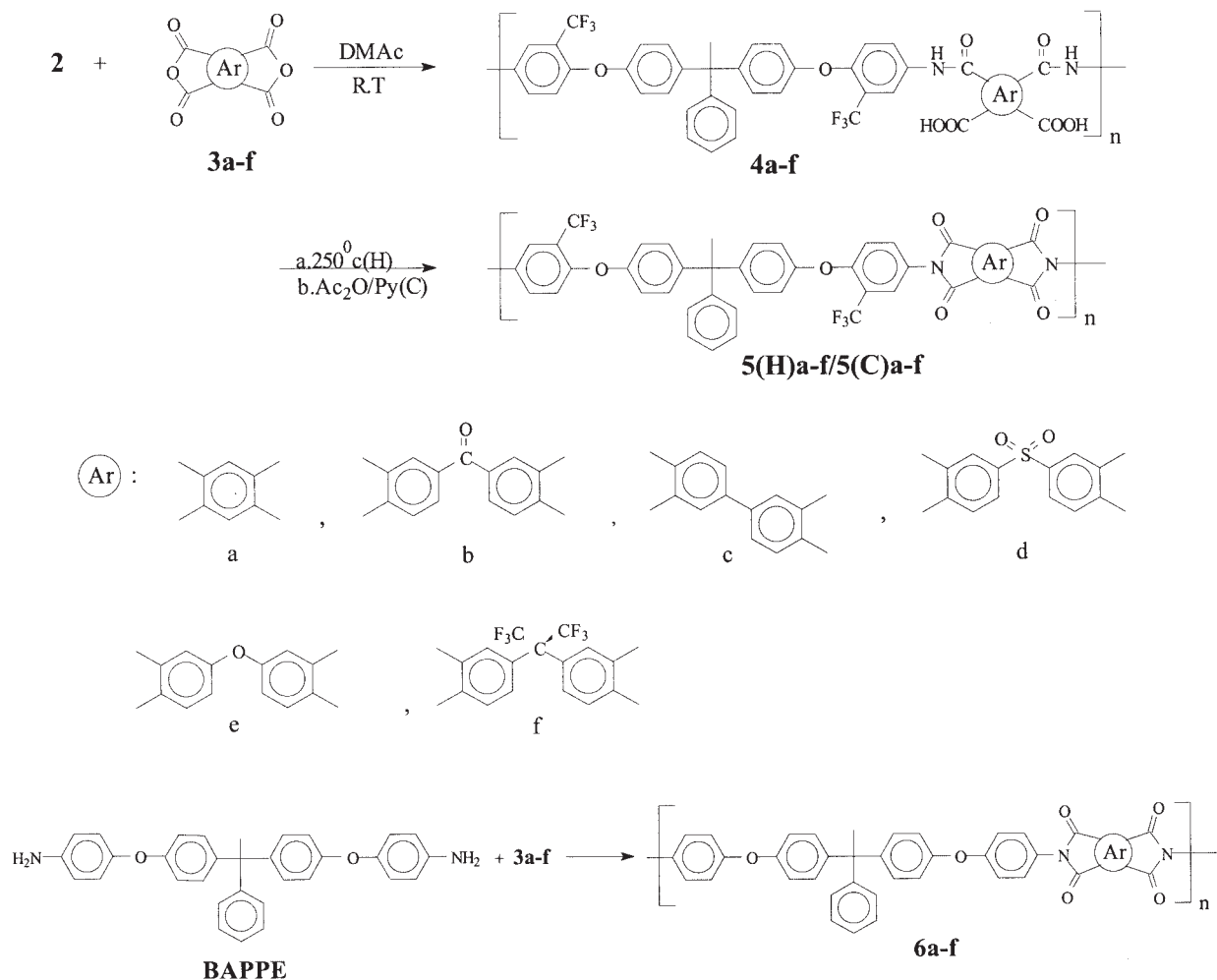


Figure 3 The ^1H and ^{13}C NMR spectrum of 3F-diamine 2 in $\text{DMSO-}d_6$.



Scheme 5

was evidenced in the downfield. The large quartet centered at about 123 ppm was due to the CF_3 carbon. The one-carbon C^{17} C-F coupling constant in this case

was about 273 Hz. The CF_3 -attached carbon (C^5) with a smaller coupling constant, about 30 Hz, was due to two-bond C-F coupling.

TABLE I
Inherent Viscosity and Elemental Analysis of the Polyimides

Polyimides				Formula	Elemental analysis (%)			
Code	η_{inh} (dL/g) ^a	Code	η_{inh} (dL/g) ^a	M_w		C	H	N
5a(H)	0.87	5a(C)	0.65	$(\text{C}_{44}\text{H}_{24}\text{O}_6\text{N}_2\text{F}_6)_n$ (790.67) _n	Calcd	66.84	3.06	3.54
					Found	66.76	2.96	3.51
5b(H)	0.78 ^b	5b(C)	0.64	$(\text{C}_{51}\text{H}_{28}\text{O}_7\text{N}_2\text{F}_6)_n$ (894.78) _n	Calcd	68.46	3.15	3.13
					Found	68.15	2.89	2.92
5c(H)	0.98	5c(C)	0.78	$(\text{C}_{50}\text{H}_{28}\text{O}_6\text{N}_2\text{F}_6)_n$ (866.77) _n	Calcd	69.29	3.26	3.23
					Found	70.60	3.12	3.18
5d(H)	0.75	5d(C)	0.68	$(\text{C}_{50}\text{H}_{28}\text{O}_8\text{N}_2\text{F}_6\text{S}_1)_n$ (930.83) _n	Calcd	64.52	3.03	3.01
					Found	65.32	3.14	2.93
5e(H)	0.60	5e(C)	0.55	$(\text{C}_{50}\text{H}_{28}\text{O}_7\text{N}_2\text{F}_6)_n$ (882.77) _n	Calcd	68.03	3.20	3.17
					Found	69.08	3.37	2.99
5f(H)	0.65	5f(C)	0.65	$(\text{C}_{53}\text{H}_{28}\text{O}_6\text{N}_2\text{F}_{12})_n$ (1016.80) _n	Calcd	62.61	2.78	2.76
					Found	61.91	2.69	2.47

^a Measured at a polymer concentration of 0.5 of g/dL in DMAc at 30 °C.

^b Measured at a polymer concentration of 0.5 g/dL in conc. H_2SO_4 at 30 °C.

TABLE II
GPC Data of Polyimides^a

PI	$\overline{M}_n \times 10^4$	$\overline{M}_w \times 10^4$	$\overline{M}_w/\overline{M}_n$
5a(C)	5.5	8.5	1.5
5b(C)	7.2	9.5	1.3
5c(C)	7.1	9.3	1.3
5d(C)	8.0	10.1	1.3
5e(C)	7.9	9.9	1.3
5f(C)	8.7	10.6	1.2

^a Relative to polystyrene standard, using THF as the eluent.

Properties of polymers

The solubility of the fluorinated PI 5 series and the analogous nonfluorinated 6 series was tested in various organic solvents, and the results are summarized in Table III. The 5a–f obtained via thermal and chemical cyclodehydration were soluble in all test solvents except for 5b(H). In aprotic polar solvents, such as NMP, DMAc, DMF, and DMSO, they showed excellent solubility; and even in less polar solvents, like *m*-cresol, Py, Dioxane, THF, CH₂Cl₂, they were also soluble. The excellent solubility of the 5 series might

be due to the presence of the propeller-shaped triphenylethane, flexible ether structure, and the bulky CF₃ substitutes. Otherwise, the solubility of 5b(C) was better than 5b(H). It might be because the ketone group of BTDA was easy to form crosslinking with the amine group, which was produced in the intercondensation of amic acid during the thermal imidization. Comparing the solubility of the 5 series with the 6 series, the 5 series showed better solubility than the 6 series. It could be because the diamines with triphenylethane and ether structure showed little effects; however, the CF₃ group showed great effects. It also could be because the CF₃ group could inhibit close packing and reduced the interchain interactions to enhance solubility.

The color intensities of the PIs were elucidated from the lightness (L*), yellowness (b*), and redness (a*) indices observed by a colorimeter. The difference in a* values and L* values were small, and were affected by the thickness and surface of films. But the b* values were much different. We depend on the b* values to estimate the degree of yellow. The results are listed in Table IV and Figure 6. 5a(H) derived from PMDA had the maximum b* value. Then were BTDA, BPDA, and

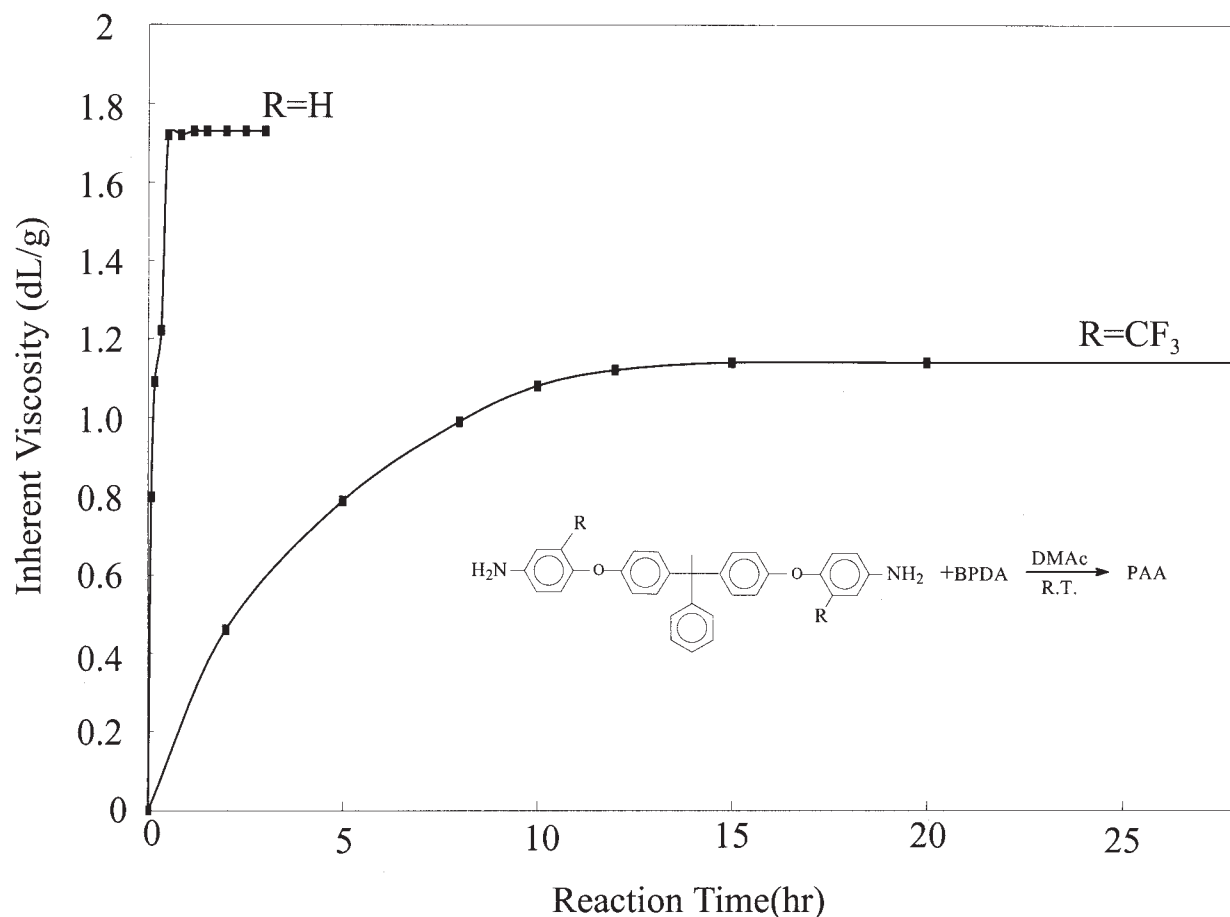


Figure 4 Viscosity change of poly(amic acid)s prepared in DMAc at 15% solid content at room temperature.

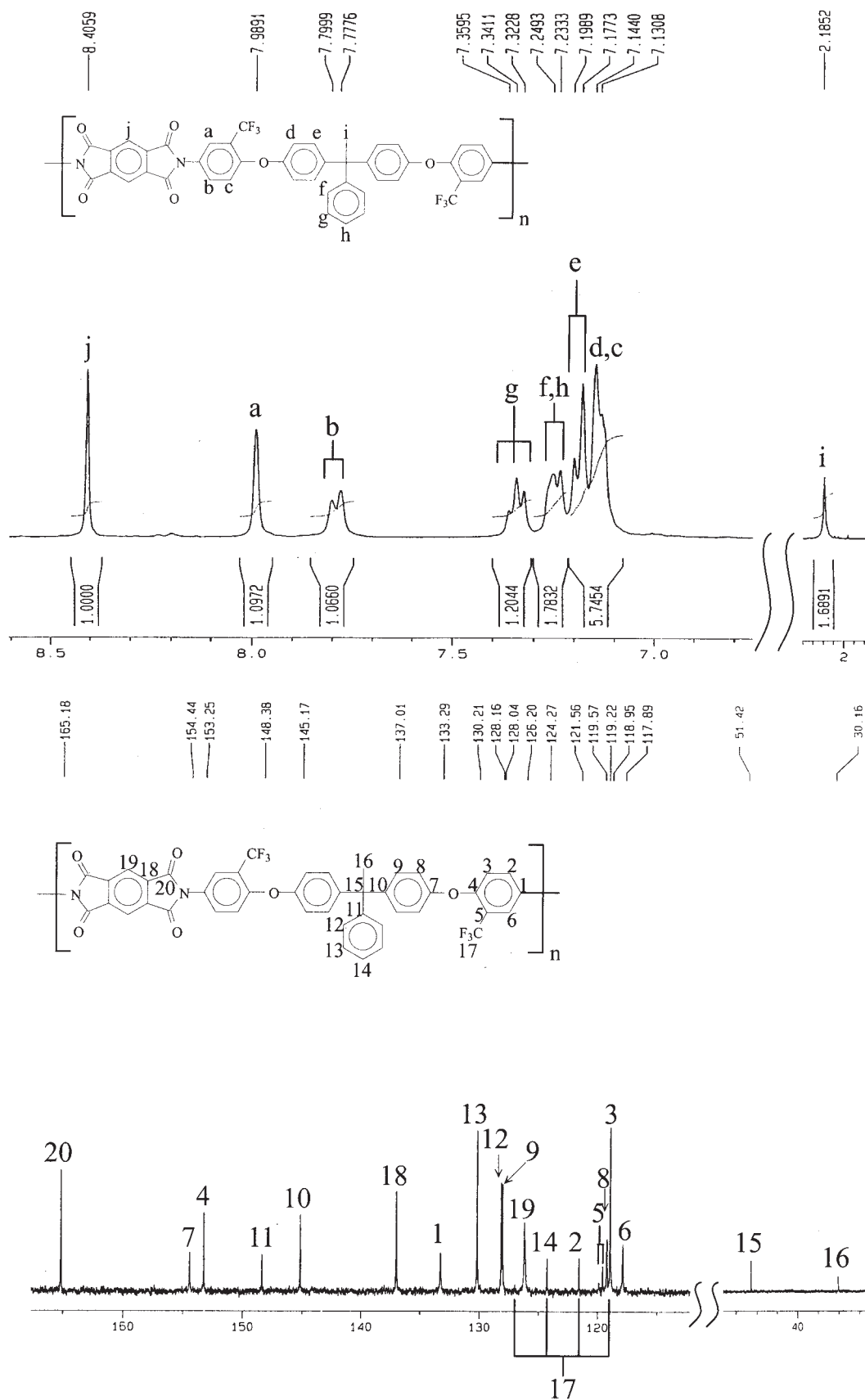


Figure 5 The ^1H and ^{13}C NMR spectra of polyimide 5_a in $\text{DMSO-}d_6$.

TABLE III
Solubility Behavior of Polyimides^a and Inherent Viscosity of Polyimides

Polymer code ^c	Solvent ^b								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CHCl ₃
5a(H)	++	++	++	+	–	++	+	++	++
5b(H)	–	–	–	–	–	–	–	–	–
5c(H)	+	+	++	S	+	++	+	++	+
5d(H)	++	++	++	++	+	++	+	++	++
5e(H)	++	++	++	+	+	++	+	++	++
5f(H)	++	++	++	+	+	++	++	++	++
5a(C)	++	++	++	++	++	++	+	++	++
5b(C)	++	++	++	++	+	++	++	++	++
5c(C)	++	++	++	+	++	++	++	++	++
5d(C)	++	++	++	++	+	++	++	++	++
5e(C)	++	++	++	++	++	++	++	++	++
5f(C)	++	++	++	++	++	++	++	++	++
6a	–	–	–	–	–	–	–	–	–
6b	–	–	–	–	–	–	–	–	–
6c	+	–	–	–	+	+	–	–	–
6d	+	+	+	–	+	+	+	–	–
6e	+	–	–	–	+	+	+	–	++
6f	++	++	++	+	++	++	++	++	++

^a Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent. ++ = soluble at room temperature; + = soluble on heating; S = swelling; – = insoluble even on heating.

^b NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

^c (H) : Polyimides were obtained by the thermal imidization method. (C) : Polyimides were obtained by the chemical imidization method.

TABLE IV
Color Coordinates and the Cut-off Wavelength (λ_0) from UV-Visible Spectra for 5(H), 5(C), and 6 Series Polyimide Films

Polymer code ^b	Film thickness (μm)	Color coordinates ^a				λ_0 (nm)
		b* 0.006	Δb^*	a* 0.009	L* 100.006	
5a(H)	49	71.1		–12.9	96.1	411.5
5b(H)	39	55.1		–13.4	96.9	401.0
5c(H)	48	22.5		–7.8	99.0	394.5
5d(H)	46	20.1		–8.8	99.3	385.5
5e(H)	27	5.0		–1.9	100.0	357.0
5f(H)	54	9.6		–3.8	99.5	365.0
5a(C)	63	63.2	–7.9	–15.8	97.5	409.5
5b(C)	50	27.9	–27.2	–11.4	99.5	395.5
5c(C)	44	22.4	–0.1	–9.6	99.5	393.5
5d(C)	48	17.7	–2.4	–8.1	99.5	384.5
5e(C)	68	5.0	–0.0	–2.2	99.9	356.5
5f(C)	55	6.6	–3.0	–3.1	100.0	363.0
6a(H)	70	85.6	14.5	–3.3	90.1	436.0
6b(H)	45	81.0	25.9	–7.9	93.5	423.0
6c(H)	67	56.9	34.4	–12.4	94.9	416.5
6d(H)	32	50.0	29.9	–13.1	96.4	401.0
6e(H)	60	32.3	27.0	–7.0	96.7	385.0
6f(H)	37	28.8	19.2	–9.0	98.0	380.0

^a The 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* indicates green color. A positive b* means yellow color, while a negative b* implies blue color.

^b (H) : Polyimides were obtained by the thermal imidization method. (C) : Polyimides were obtained by the chemical imidization method.

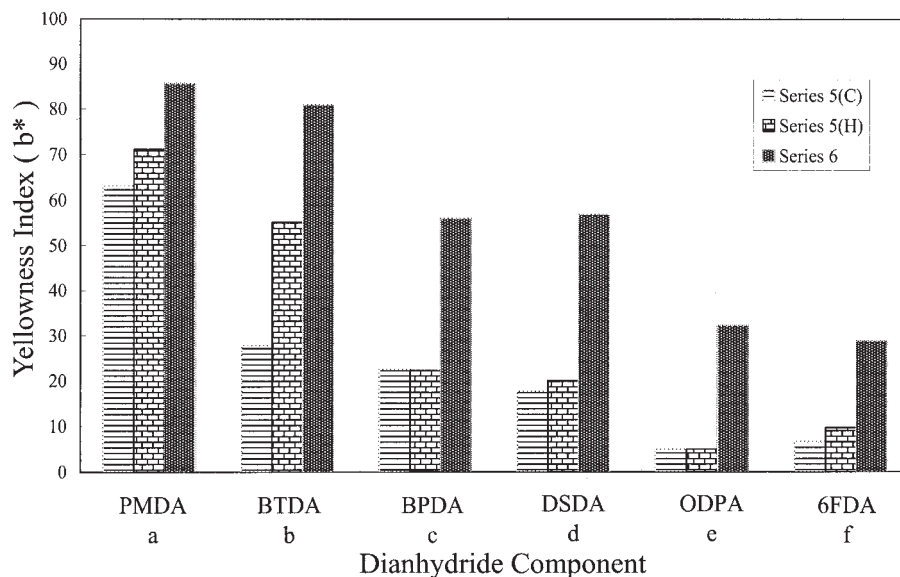


Figure 6 Comparison of the yellowness index (b^* value) between polyimides 5(C), 5(H), and 6.

DSDA in order. Moreover, 6FDA and ODPA were lighter than above. Compare 5(H) and 5(C): 5(C) showed a lower b^* value than 5(H), the Δb^* of 5a and 5b had maximum values. And the 5 series showed a lower b^* value in comparison with the analogous non-fluorinated 6 series, the PI 6b and 6c with the maximum Δb^* , and 6a with the minimum Δb^* .

Moreover, the color intensities of the PIs could also be elucidated from the cutoff wavelength (λ_0) observed in the UV-Vis absorption spectra. Figure 7 shows the UV-Vis spectra of the PI 5a–f and 6a–f films, and the λ_0 from these spectra are listed in Table IV. 5(H) had the λ_0 in the range of 357–411.5 nm and shorter than 6(H) did. Moreover, the λ_0 of 5(C) was lowest. The measurement of UV-Vis spectra was the same with the colorimeter: the fluorinated PI 5 series had shorter λ_0 and higher transparency.

Therefore, the light-colored 5 series could be explained by the bulky and strong electron withdrawing CF_3 group in the diamine, which can decrease the CTC formation between inter- or intra-molecular and inductive effect. Moreover, ODPA and 6FDA produce fairly transparent and almost colorless PI films in contrast to the other dianhydrides. These results were attributed to the ether-chain of ODPA and the hexafluoroisopropylidene group of 6FDA, which could inhibit the formation of the CTC effect.

The mechanical properties of PI 5a–f are summarized in Table V. 5a–f(H) had strengths at break of 101–123 MPa, elongations at break of 10–21%, and initial moduli of 1.9–2.3 GPa. 5a–f(C) had similar properties. Whether 5(H) or 5(C), 5b,c, and e showed distinct yield points on stress–strain curves and had strengths of 92–139 MPa. In this case, the PI from the diamine 2 with BTDA, BPDA, or ODPA had high toughness.

The thermal properties of PI 5(H) were measured by TGA and DSC. The thermal behavior data of all polymers are listed in Table VI.

The DSC experiment of rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so that the T_g of PIs could be easily measured in the second heating traces of DSC. The T_g values of 5a–f(H) were in the range of 232 to 276 °C. The PI 5a derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit, and 5e derived from ODPA showed the lowest T_g due to the presence of a flexible ether linkage between the phthalimide units.

The temperatures of 10% weight loss (T_{10}) values of PI 5a–f in nitrogen and air atmospheres stayed within

TABLE V
Tensile Properties of Polyimide Films

Polymer code ^a	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
5a(H)	-	102	14	2.0
5b(H)	115	111	13	2.3
5c(H)	104	101	18	1.9
5d(H)	-	108	10	2.2
5e(H)	120	113	21	2.2
5f(H)	-	123	12	2.2
5a(C)	84	83	13	1.7
5b(C)	105	103	12	2.0
5c(C)	139	134	11	2.8
5d(C)	-	108	12	2.0
5e(C)	92	82	19	1.8
5f(C)	-	96	11	1.8

^a (H) : Polyimides were obtained by the thermal imidization method. (C) : Polyimides were obtained by the chemical imidization method.

TABLE VI
Thermal Properties Data of Polyimides

Polymer	T_g (°C) ^a	T_{10} (°C) ^b		Char yield (%) ^c
		In N ₂	In air	
5a(H)	276	544	522	60
5b(H)	242	546	525	61
5c(H)	246	548	529	62
5d(H)	255	505	508	56
5e(H)	232	545	532	60
5f(H)	251	536	525	57

^a Baseline shift in the second heating DSC traces, with a heating rate of 15 °C/min.

^b Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20°C/min.

^c Residual weight (%) when heated to 800°C in nitrogen.

505–548°C and within 508–532°C, respectively. They left more than 55% char yield at 800°C in nitrogen. The 5d derived from DSDA showed the lowest T_{10} and

char yield. It caused weak bonding of the C-S bond, which easily degraded in the heating process.

The measurements of the dielectric constants were performed between gold layers. The polymer film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the film. This procedure excluded any contact problems. The dielectric constants of 5a–f and 6a–f are shown in Table VII. The 5 series showed lower dielectric constants (3.11–3.43 at 1M Hz) than the non-flourinated PI 6 series (3.34–4.18 at 1M Hz) did. The decreased dielectric constants might be attributed to the presence of the bulky CF₃ group. The strong electronegativity of fluorine resulted in very low polarizability of the C-F bonds, thus decreasing the dielectric constants. Otherwise, the 6FDA-derived PI 5f and 6f exhibited the lowest dielectric constants in the two series.

The moisture absorption of PI was shown in Table VII. In comparison, 5a–f exhibited lower moisture ab-

TABLE VII
Moisture Absorption and Dielectric Constants of Polyimides

Polymer ^a	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (dry)			
			1k Hz	10k Hz	1M Hz	40M Hz
5a	73	0.30	3.35	3.34	3.29	3.26
5b	36	0.40	3.48	3.47	3.43	3.41
5c	46	0.27	3.38	3.37	3.33	3.26
5d	60	0.32	3.40	3.38	3.36	3.28
5e	65	0.11	3.36	3.33	3.30	3.24
5f	53	0.11	3.20	3.14	3.11	3.05
6a	68	0.74	4.24	4.23	4.18	4.15
6b	43	0.99	3.54	3.53	3.49	3.48
6c	68	0.67	3.63	3.62	3.60	3.56
6d	50	0.93	3.69	3.68	3.65	3.63
6e	36	0.58	3.57	3.49	3.42	3.38
6f	41	0.40	3.40	3.39	3.34	3.26
Kapton	28	0.52	3.89	3.85	3.67	3.69

^a Polyimides were obtained by the thermal imidization method.

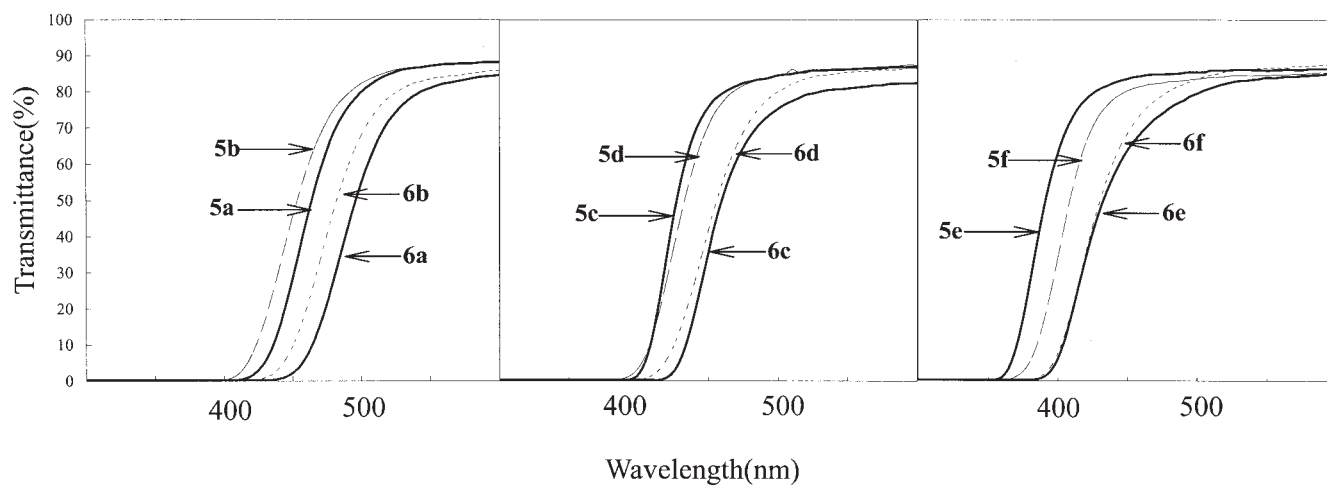


Figure 7 UV-visible spectra of polyimide films.

sorption (0.11–0.40%) than the corresponding analogous non-fluorinated 6a-f (0.40–0.99%) owing to the hydrophobicity of the CF₃ group.

CONCLUSION

A series of novel PI was obtained from the new fluorinated diamine 1,1-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1-phenylethane (2) and various aromatic dianhydrides using a standard two-stage process with thermal and chemical imidization of poly(amic acid). The 5 series exhibited lighter color than the corresponding non-fluorinated 6 series. The 5 series showed excellent solubility and lower dielectric constants and moisture absorption than the 6 series.

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