Light-Colored Fluorinated Polyimides Based on 2,5-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl and Various Aromatic Dianhydrides

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ABSTRACT: A novel trifluoromethyl-containing aromatic diamine monomer, 2,5-bis (4-amino-2-trifluoromethylphenoxy)biphenyl (**2**), was prepared through the nucleophilic substitution reaction of 2-chloro-5-nitrobenzotrifluoride and phenylhydroquinone in the presence of potassium carbonate to yield the intermediate dinitro compound (**1**), followed by catalytic reduction with hydrazine and Pd/C. A series of fluorinated polyimides (code **5a–f**) were synthesized from diamine (**2**) with six commercially available aromatic dianhydrides using a standard two-stage process with thermal or chemical imidization of poly(amic acid). Most of fluorinated polyimides showed good solubility at a concentration of 5–10 wt % and even in pyridine and dioxane. For improving solubility of **5c**, copolyimides (**5c/a–f**) were also prepared from **2** and a pair of dianhydrides (**3c/a–f**), which were mixed in the molar ratio 1:1. All the polyimide films had a tensile strength in the range from 73 to 112 MPa, an elongation at break within a range of 9–23%, and an initial modulus in the range of 1.6–2.2 GPa. These polyimides exhibited glass transition temperatures of 220–267°C and showed no significant decomposition below 500°C under either nitrogen or air atmosphere. In comparison with the analogous nonfluorinated polyimides based on 2,5-bis (4-aminophenoxy) biphenyl (**2′**), the fluorinated polyimides showed better solubility as well as reduced color intensity, lower dielectric constant, and moisture absorption. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4101–4110, 2006

Key words: polyimides; fluorinated bis(ether amine); solubility; transparency; thermal stability

INTRODUCTION

Aromatic polyimides are well known as high-performance polymers, which possess excellent thermal stability, favorable dielectric properties, and chemical resistance.[1] Polyimides are widely used as an interlayer dielectric in semiconductor devices or as substrates for flexible printed circuits. Their high optical transparency may broaden their application; for example, they can serve for optoelectric materials in flexible solar radiation protectors,[2] orientation films in liquid crystal display devices,[3] and optical waveguides for communication interconnects.[4,5] However, aromatic polyimides are difficult to process in fully imidized form because of their high softening temperatures and limited solubility. In addition, their strong absorption in the visible region of their ultraviolet-visible spectra turns them pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and intermolecular charge-transfer complex (CTC) formation.[6]

Therefore, much research has been devoted to enhancing the solubility and processability but minimizing the detrimental effect on the high thermal stability of polyimides by incorporating flexible linkages[7,8] or bulky groups[9,10] into their polymer backbone structure. Besides, to increase the optical application of polyimides, a number of very lightly colored polyimide films have been synthesized and characterized.[6,11,12] A lowering of the formation of the CTC effect between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties provides polyimide with lighter color.[13,14]

Recent studies have demonstrated that polyimides derived from bis(ether amine)s showed better solubility than the common aromatic diamines. The substituent of bis(ether amine)s will influence on the property of polyimides. For example, the symmetric and asymmetric bis(ether amine)s derived from hydroquinone or substituent-containing hydroquinone showed that the mono-*tert*-butyl substituent was more highly soluble than the mono-methyl or di-*tert*-butyl substitutes.[8,15,16] In our laboratory, continuing studies of substitute-containing bis(ether amine) turned out mono-phenyl-containing 2,5-bis(4-aminophenoxy)biphenyl (**2′**).[17] The polyimides based on **2′** still exhib-

ited good solubility and showed higher thermal stability than the mono-*tert*-butyl-containing or mono-methyl-containing ones. Besides, comparing the properties of polyimides derived from **2′** with those derived from isomeric 4,4′-bis(4-aminophenoxy)biphenyl or 2,2′-bis(4-aminophenoxy)biphenyl[18] revealed that the former (from **2′**) had far better solubility than that of the 4,4′-linked one and a far better tensile property than the 2,2′-linked one. Moreover, it had been also proved that polyimide with trifluoromethyl-substituted in the side chain can enhance the solubility and thermal stability, reduce dielectric constant and moisture absorption, and raise the optical transparency.[19–22] In this study, a new CF_3-substituted bis(ether-amine), 2,5-bis(4-amino-2-trifluoromethyl-phenoxy)biphenyl (**2**) was synthesized and polycondensed with various aromatic dianhydrides to produce a series of fluorinated polyimides (**5a–f**) or co-polyimides (**5c/a–f**). These polyimide films were subjected to solubility, thermal, optical, moisture absorption, and dielectric properties and compared with analogous nonfluorinated polyimides.

EXPERIMENTAL

Materials

Phenylhydroquinone (PHQ, TCI), 2-chloro-5-nitro-benzotrifluoride (Acros), 3,3(,4,4(-biphenyltetracarboxylic dianhydride (BPDA) (**3c**, Chriskev), 3,3(,4,4(-diphenylsulfonetetracarboxylic dianhydride (DSDA) (**3d**, New Japan Chemical Co.), and 4,4(-hexafluoroiso-propylidenediphthalic anhydride (6FDA) (**3f**, Hoechst) were used as received. Pyromellitic dianhydride (PMDA) (**3a**, Lancaster), 3,3(,4,4(-benzophenonetetracarboxylic dianhydride (BTDA) (**3b**, Acros), and 3,4,3(,4(-oxydiph-thalic anhydride (ODPA) (**3e**, Chriskev) were recrystallized from acetic anhydride before use. Other solvents including *N*-methyl-2-pyrrolidone (NMP, Fluka), *N,N*-dimethylacetamide (DMAc, Fluka), *N,N*-dimethylform-amide (DMF, Fluka), and pyridine (Py, Wako) were used as received.

Monomer syntheses

2,5-Bis(4-nitro-2-trifluoromethylphenoxy)biphenyl (1)

PHQ (13.95 g, 0.075 mmol) and 2-chloro-5-nitrobenzo-trifluoride (34.28 g, 0.152 mmol) were 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. After 30 min of stirring at room temperature, the mixture was heated at 110°C for 10 h. The obtained solution was cooled and poured into 400 mL of meth-anol–water (volume ratio: 10 : 1) to give a solid, then purified (by THF/EtOH/active carbon) to obtain a light yellow solid. The yield of the product was 37.8 g

(89% yield, mp: 60–61°C by differential scanning calorimetry (DSC) at a scan rate of 5°C/min).

IR (KBr): 1531, 1333 (—NO_2 stretch), 1250, 1167, 1117 cm^{-1} (C—F and C—O stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.50, 8.38 (s, 2H, $H_{a,a'}$), 8.48, 8.31 (d, 2H, $H_{b,b'}$, *J* = 9.2 Hz), 7.50–7.49 (3H, $H_{g,e}$), 7.45 (d, 2H, $H_{c'}$, *J* = 8.8 Hz), 7.42–7.39 (2H, $H_{c,f}$), 7.33 (t, 2H, H_h, *J* = 7.4 Hz), 7.27 (t, 1H, H_i, *J* = 7.1 Hz), 8.48 (d, 1H, H_b, *J* = 9.2 Hz), 7.10 (d, 1H, H_d, *J* = 9.2 Hz). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 160.04, 159.71 ($C^{4,4'}$), 151.98 (C^7), 147.26 (C^{10}), 141.88, 141.36 ($C^{1,1'}$), 136.35 (C^{13}), 134.80 (C^{15}), 129.99 (C^{14}), 129.77 (C^{16}), 128.76 ($C^{2,2'}$), 128.31 ($C^{6,6'}$), 134.80 (C^9), 123.28 ($C^{3,3'}$), 122.27, 122.17 ($C^{17,17'}$, quartet, $^1J_{C—F}$ = 271.3 Hz), 119.15, 118.04 ($C^{5,5'}$, quartet, $^2J_{C—F}$ = 32.5 Hz), 118.46 (C^8), 116.77 (C^{12}).
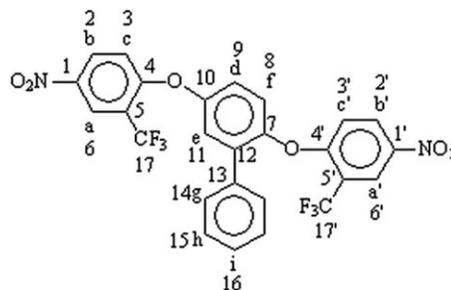
Elem. Anal. Calcd. for $C_{26}H_{14}F_6N_2O_6$ (564.07): C, 55.31%; H, 2.50%; N, 4.96%. Found: C, 55.63%; H, 3.03%; N, 5.15%.

2,5-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (2)

A mixture of the dinitro compound **1** (16.92 g, 0.03 mol), 10% Pd/C (0.2 g), and 150 mL ethanol were introduced into a 300-mL flask to which 7 mL of hydrazine monohydrate was added dropwise at 70–80°C. The mixture was heated at reflux temperature for about 2 h. The reaction solution was filtered hot to remove Pd/C, and the filtrate was concentrated, cooled to precipitate a cream crystal powder, and dried in vacuum to give **2** (13.75 g, 91%, mp: 151–152°C).

IR (KBr): 3469, 3346, 3224 (N—H stretch), 1269, 1223, 1122 cm^{-1} (C—O and C—F stretch). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.54 (d, 2H, H_g, *J* = 7.3 Hz), 7.38 (t, 2H, H_h, *J* = 7.7 Hz), 7.31 (t, 1H, H_i, *J* = 7.3 Hz), 6.98–6.96 (3H, $H_{f,a',e}$), 7.54 (d, 2H, H_a), *J* = 2.5 Hz), 6.88–6.84 (2H, $H_{b,b'}$), 6.80–6.77 (3H, $H_{c',d}$), 6.73 (d, 1H, H_c, *J* = 8.9 Hz), 5.41 (—NH_2). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 153.98 (C^7), 149.28 (C^{10}), 145.72, 145.01 ($C^{4,4'}$), 143.72, 142.82 ($C^{1,1'}$), 136.70 (C^{13}), 132.86 (C^{16}), 128.89 (C^{14}), 128.22 ($C^{3,3'}$), 127.55 (C^{15}), 123.65, 123.62 ($C^{17,17'}$, quartet, $^1J_{C—F}$ = 271.3 Hz), 122.90 (C^9), 121.35, 120.35 ($C^{5,5'}$, quartet, $^2J_{C—F}$ = 30 Hz), 120.99

(C^{11}), 119.21, 118.83 ($C^{2,2'}$), 118.70 (C^{12}), 117.22 (C^8), 110.92, 110.72 ($C^{6,6'}$, quartet, $^3J_{C-F}$ = 5.0 Hz).
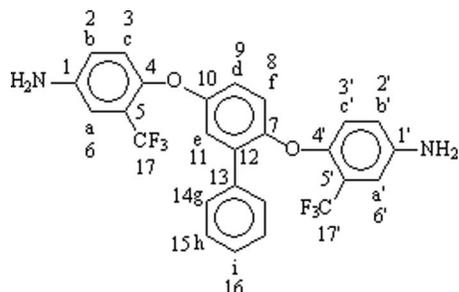
Elem. Anal. Calcd. for $C_{26}H_{18}F_6N_2O_2$ (504.43): C, 61.89%; H, 3.60%; N, 5.56%. Found: C, 62.21%; H, 4.07%; N, 5.54%.

Syntheses of polyimides

Thermal imidization: Synthesis of polyimides (H)

Diamine **2** (0.476 g, 1 mmol) was dissolved in 5.4 mL of dried DMAc in a 10-mL flask. After **2** was completely dissolved at room temperature, **3a** (0.218 g, 1 mmol) was added in one portion. The mixture was stirred at room temperature for 12 h to give a viscous poly(amic acid) (PAA) solution. The PAA solution was poured into a glass culture dish (φ = 9 cm), which was placed in an 80°C oven to remove the casting solvent. The semidried PAA films were further dried and imidized by sequentially heating from 130 to 230°C at the rate of 20°C/10 min, and 250°C for 30 min. By being soaked in water, a flexible polyimide film of **5a(H)** was released from the glass surface. The inherent viscosity (η_{inh}) in DMAc at a 0.5 g/dL concentration at 30°C was 0.79 dL/g.

IR (film): 1780, 1732 (imide C—O), 1375 (C—N stretch), 1138, 725 cm^{-1} (imide ring deformation). ^1H NMR (500 MHz, DMSO-d_6, δ, ppm): 8.41 (2H, H_j), 8.03, 7.91 (2H, $H_{a',a}$), 7.82, 7.69 (2H, $H_{b',b}$), 7.59 (2H, H_g), 7.44–7.40 (3H, $H_{h,i}$), 7.38–7.30 (2H, $H_{f,d}$), 7.31 (1H, $H_{c'}$), 7.11 (1H, H_c). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 165.25 ($C^{20,20'}$), 154.71 (C^7), 152.44 (C^{10}), 147.66 (C^{13}), 137.07 ($C^{4,4'}$), 135.79 (C^{18}), 135.45 (C^{16}), 133.43, 133.21 ($C^{1,1'}$), 128.81 (C^{15}), 128.33 (C^{14}), 128.13 (C^{19}), 126.28 ($C^{2,2'}$), 125.62 (C^9), 123.48, 122.49 ($C^{3,3'}$), 123.02, 122.97 ($C^{17,17'}$, quartet, $^1J_{C-F}$ = 271.3 Hz), 120.92 (C^{11}), 119.47 ($C^{6,6'}$), 119.35, 118.23 ($C^{5,5'}$, quartet, $^2J_{C-F}$ = 31.3 Hz), 117.94 (C^{12}), 117.24 (C^8) (as shown in Fig. 1). The results of elemental analysis were listed in Table I.

Chemical imidization: Synthesis of polyimides (C)

The method of synthesizing PAA was similar to that of polyimides (**H**). A 1-mL mixture of Ac_2O and Py (volume ratio: 2 : 1) was added to the PAA solution and stirred at 80°C for 1 h to imidize. Then, the obtained

solution was poured into a glass culture dish, which was placed in an 100°C oven for 1 h to evaporate the solvent and form a thin film. The flat polyimide film was obtained by sequentially heating at 200°C to remove the residual solvent. By being soaked in water, a flexible film was released from the glass surface.

Synthesis of copolyimide (C)

2 (1 mmol) was dissolved in 5.4 mL of dried DMAc by stirring at room temperature. After the diamine was completely dissolved, 0.50 mmol of PMDA (**3a**) was added in one portion and completely dissolved. Finally, after 0.50 mmol of BPDA (**3c**) was added, the reaction mixture was continuously stirred for 12 h to obtain viscous PAA solution. The PAA solution was imidized in the same way as to chemical imidization. The η_{inh} of the flexible film **3c/a(C)** was 0.65 dL/g. The other copolyimides were prepared from **2** and a pair of dianhydrides (**3c/a–f**) at 1 : 1M ratios.

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a HERAEUS VariouEL-III CHN analyzer. ^1H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. The inherent viscosities were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30°C. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 9–11-mg film samples heated in flowing nitrogen or air (90 cm^3/min) at a heating rate of 20°C/min. DSC analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen at a heating rate of 15°C/min. 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 mm/min on strips ~30–60 μm thick, 0.5 cm wide, and 6 cm long. 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 30–60 μm thick with an observational angle of 10 ° and a Commission International de l'Eclairage (CIE)-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 TA Instruments DEA 2970 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
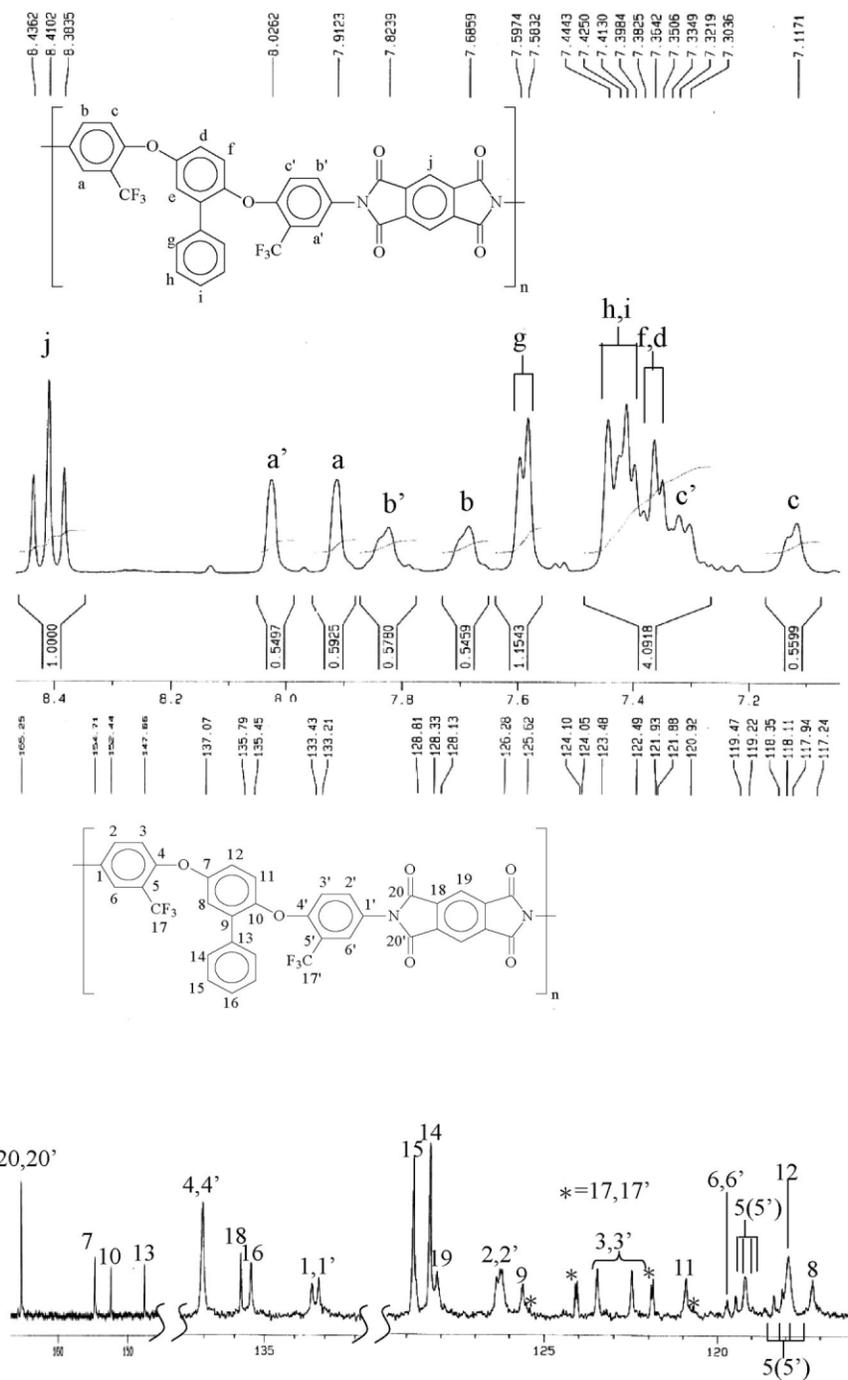
Figure 1 ^{1}H and ^{13}C NMR spectra of **5**a in DMSO-d_6.

and after immersion in deionized water at 25°C for 3 days.

RESULTS AND DISUSSION

Monomer syntheses

The CF$_3$-containing bis(ether amine) **2** and the analogous nonfluorinated diamine (**2′**) were prepared in two steps as shown in Scheme 1. The intermediate dinitro compounds **1** and **1′** were synthesized using a nucleophilic aromatic substitution reaction between PHQ with 2-chloro-5-nitrobenzotrifluoride and 4-chlornitrobenzene respectively, in the presence of potassium carbonate in DMF. The diamines **2** and **2′** were readily obtained in high yields by the Pd/C-catalyzed reduction of dinitro compounds with hydrazine hydrate in refluxing ethanol. However, there was an interesting change in monomers as R being CF$_3$ (**1** and **2**) or being H (**1′** and **2′**) (as shown in Scheme 1). The monomer **1** was amorphous, soluble, and low melting

TABLE I
Elemental Analysis of the Polyimides

Polymer[a]	Formula[b]		Elemental analysis (%)		
			C	H	N
5a	$C_{36}H_{16}F_6O_6N_2$ (686.52)$_n$	Calcd	62.97	2.35	4.08
		Found	62.40	2.66	3.82
5b	$C_{43}H_{20}F_6O_7N_2$ (790.63)$_n$	Calcd	65.32	2.55	3.54
		Found	65.18	2.40	3.31
5c	$C_{42}H_{20}F_6O_6N_2$ (762.62)$_n$	Calcd	66.13	2.64	3.67
		Found	65.98	3.00	3.41
5d	$C_{42}H_{20}F_6O_8N_2S$ (826.68)$_n$	Calcd	61.02	2.44	3.39
		Found	61.05	2.38	3.38
5e	$C_{42}H_{20}F_6O_7N_2$ (778.62)$_n$	Calcd	64.79	2.59	3.60
		Found	64.46	2.34	3.22
5f	$C_{44}H_{20}F_{12}O_6N_2$ (900.63)$_n$	Calcd	58.68	2.24	3.11
		Found	59.28	2.26	2.85

[a] **5c** was obtained by the thermal imidization; others were obtained by the chemical imidization.
[b] Values in parentheses indicate formula weight.

(mp 61°C); **1′** was crystalline (mp 160°C) and easily purified. On the contrary, as these two (**1** and **1′**) were reduced to diamines (**2** and **2′**), the monomer **2** was crystalline (mp 152°C) but **2′** showed low melting point (mp 60°C) and was amorphous. These might concern with the particular molecular structure. FTIR, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis described in experimental part were used to confirm the structure of the intermediate dinitro compound **1** and the diamine compound **2**.

Polymer syntheses

All the fluorinated polyimides (**5a–f**) were synthesized from diamine (**2**) and six commercially available dianhydrides (**3a–f**) by a conventional two-step procedure of ring-opening polyaddition at room temperature to poly(amic acid)s (**4a–f**), followed by sequential heating to 250°C or treatment with a mixture of Ac_2O/Py to obtain the corresponding polyimides. Moreover, the analogous nonfluorinated polyimides (**6a-f**) were prepared via thermal imidization as shown in Scheme 2. **5c** showed poor solubility because of the biphenyl structure of BPDA and the diamine **2**. The possibilities of preparing soluble copolyimides were investigated by carrying out the polymerization of soluble **5a–f** and insoluble **5c**. First, the diamine **2** reacted with one of the dianhydrides (**3a–f**) to form oligomeric PAA with amine groups as the chain ends, and then another dianhydride (**3c**) was added to form co-PAA, which was then transformed to copolyimides. The elemental analysis results of the fluorinated polyimides are listed in Table I and were in good agreement with the calculated values of the proposed structures. The inherent viscosities of the **5(H)** and **5(C)** were recorded in the range of 0.60–0.87 and 0.60–0.71 dL/g, respectively, as measured in DMAc. Most of polyimide prepared through thermal imidization had the higher inherent viscosity than those prepared by chemical imidization.
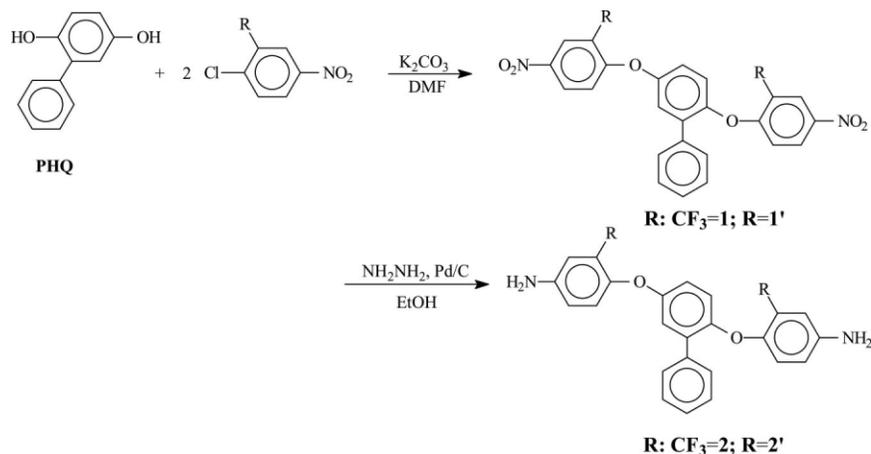
Scheme 1 Synthesis of diamine **2** and **2′**.
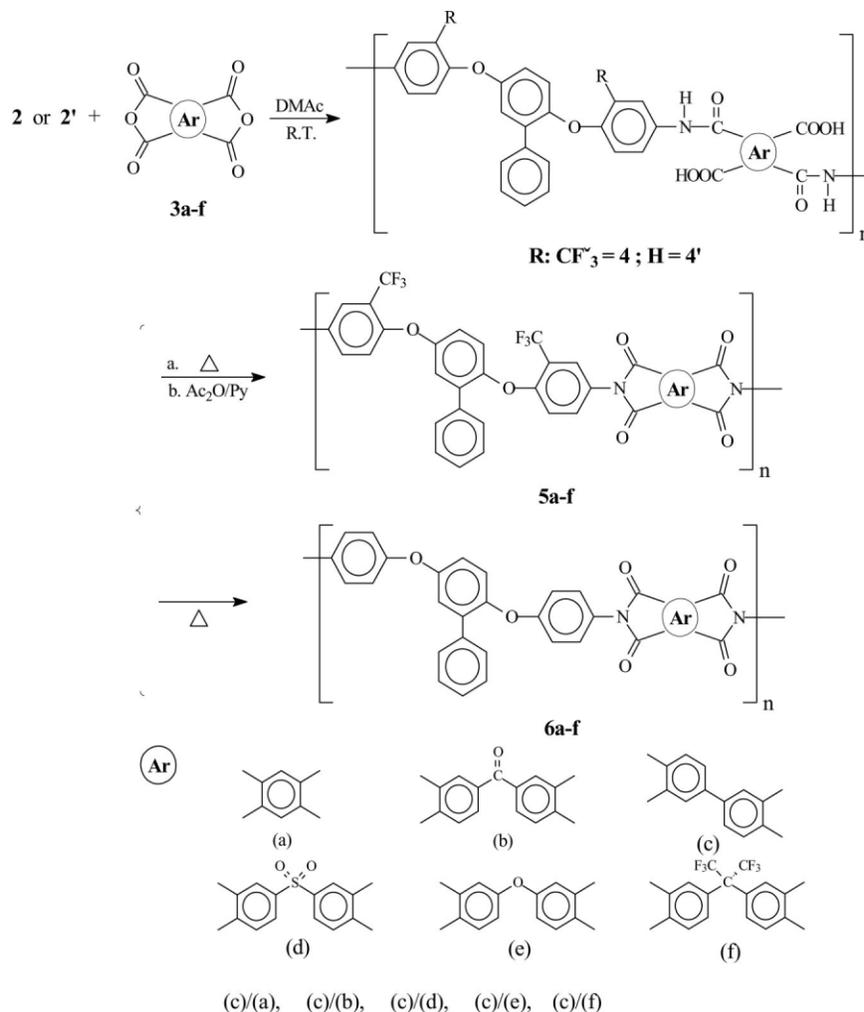
Scheme 2 Synthesis of polyimides and copolyimides.

The ^{1}H and ^{13}C NMR spectra of **5a** are shown in Figure 1. In the ^{1}H NMR spectrum, all the protons resonated in the region of 7.1–8.4 ppm. The H$_j$ close to the imide ring appeared at the farthest downfield owing to the resonance; the H$_{a,a'}$ *ortho*-oriented to the CF$_3$ group shifted to the upfield, owing to the shielding effect. The H$_{c,c'}$ shifted to higher filed owing to the electron-donating property of aromatic ether. In the ^{13}C NMR spectrum, **5a** showed 28 signals owing to the different environments of two phenoxy groups. However, it showed only 25 peaks because of the overlapping of C^{20}-C$^{20'}$, C^4-C$^{4'}$, and C^6-C$^{6'}$. The aromatic carbons C$^{20,20'}$ were of the carbonyl groups and evidenced in the downfield. The large quartet centered at about 123 ppm was due to the CF$_3$ carbon (C^{17}). The one-carbon C—F coupling constant in this case was about 273 Hz. The CF$_3$-attached carbon (C^5) also showed a quartet centered with a smaller coupling constant of about 31 Hz because of two-bond C—F coupling.

Properties of polymer

The solubility of these polymers was tested in various organic solvents, with the results summarized in Table II. The polymers **5d–f** showed an excellent solubility in the amide-type solvents such as NMP, DMAc, DMF, but **5b(H)** and **5c** were insoluble and **5a** slightly dissolved. In contrast, the **5(C)** series prepared via chemical imidization had better solubility than those prepared thermally, especially in chlorinated and ether-type solvents. In addition, **5b(C)** dissolved more easily in all the tested solvents than did **5b(H)**. This might be attributed to the formation of some intermolecular links of the C=O group of BTDA during the thermal imidization[23] and due to the higher percentage of imidization through thermal imidization. However, the biphenyl rigid group of **5c** prepared via thermal or chemical imidization still showed poor solubility. Therefore, copolyimides were synthesized from **5c** and **5a–f** at 1:1M ratios, and their solubilities were compared. The solubility of copolyimides could

TABLE II
Inherent Viscosity and Solubility Properties of Polyimide Films in Various Solvents[a]

Polymer[b]	NMP	DMAc	DMF	DMSO	m-Cresol	Py	Dioxane	THF	CH$_2$Cl$_2$	CHCl$_3$	η_{inh} (dL/g)[c]
5a(H)	+	+	+	+ (h)	+ (h)	+	+ (h)	+	−	−	0.79
5b(H)	−	−	−	−	−	−	−	−	−	−	—
5c(H)	−	−	−	−	−	−	−	−	−	−	0.65[d]
5d(H)	++	++	+++	++ (h)	+	++	++ (h)	+	+	++	0.82
5e(H)	++	++	+++	++ (h)	+	++	++ (h)	+	+	+	0.87
5f(H)	++	++	+++	++	++	+++	++	++	++	++	0.60
5a(C)	+	+	+	+	+ (h)	+	+	+	−	−	0.60
5b(C)	++	+++	+++	+	+	+++	++	+++	−	−	0.60
5c(C)	−	−	−	−	−	−	−	−	−	−	0.65[d]
5d(C)	++	+++	+++	+++	++	+++	+++	+++	++	+++	0.66
5e(C)	++	+++	+++	++ (h)	++	+++	++ (h)	+++	++	+++	0.71
5f(C)	++	+++	+++	++	++	+++	+++	+++	++	+++	0.67
5c/a(C)	+	+	+ (h)	−	+ (h)	+	+++	+	−	−	0.65
5c/b(C)	+	+	+ (h)	+ (h)	+ (h)	+	+++	+	−	+	0.64
5c/d(C)	+	+	+ (h)	+ (h)	+ (h)	+	+++	+	−	−	0.64
5c/e(C)	+	+	+ (h)	−	+ (h)	+	+	+	−	+	0.79
5c/f(C)	++	+++	++	+ (h)	+ (h)	+++	+++	++	+	++	0.56
6a(H)	−	−	−	−	−	−	−	−	−	−	
6b(H)	−	−	−	−	−	−	−	−	−	−	
6c(H)	−	−	−	−	−	−	−	−	−	−	
6d(H)	+	+	+	+	+	+	−	−	−	−	
6e(H)	−	−	−	−	−	−	−	−	−	−	
6f(H)	++	++	+++	++	++	+++	++	+	+	+	

[a] +++ = soluble at concentration of 10% (100 mg sample in 1 mL of the solvent); ++ = soluble at 5%; + = soluble at 1%; − = insoluble; h = heating. NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethyl acetamide; DMF, N,N-dimethyl formamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.
[b] (H): polyimides were obtained by the thermal imidization; (C): polyimides were obtained by the chemical imidization.
[c] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.
[d] The inherent viscosity of 5c was obtained from poly(amic acid).

be improved because the polymer destroyed. Besides, the introduction of the alternate soluble chain could also enhance the solubility. The copolyimide derived from BPDA/6FDA had better solubility than other copolyimides and dissolved easily in amide-type, Py, and dioxane solvents.

Comparing with the fluorinated polyimides, the analogous nonfluorinated polyimides presented a relatively decreased solubility. 5e based on ODPA showed an excellent solubility in amide-type solvents, Py but was dissolved slightly in THF, CH$_2$Cl$_2$, and CHCl$_3$ solvents. However, 6e exhibited poor solubility in all the tested solvents. The large differences between the 5 and 6 series could be attributed to the presence of bulky CF$_3$ groups in the former. The CF$_3$ groups inhibited close packing, thus reducing the chain–chain interactions to enhance solubility.

The color intensities of the polyimide films are given in Table III. As for the influence on color by the chemical or thermal imidization method, the former can avoid oxidization in the air and thus reduce b* value, such that the b* values of 5(C) is in the range of 8.3–66.2 and is lower than that of 5(H). For comparison, nonfluorinated polyimides and copolyimides were also prepared and characterized by its color in-

tensity. Figure 2 indicates that the fluorinated polyimide films had a lower b* value than that of the corresponding nonfluorinated films. Table III also shows that the color intensity of the polyimides was affected by dianhydride moieties, which decreased in the following order: PMDA > BTDA > BPDA > DSDA. The ODPA and 6FDA produced light-colored polymer films in contrast to other dianhydrides. In addition, the b* value of copolyimides ranged from 17.3 to 55.9, with the highest b* value in PMDA-containing one.

The color intensities of the 5 series could also be elucidated from the cutoff wavelength (λ_0) observed in UV–vis absorption spectra. Figure 3 portrays UV–visible spectra and the λ_0 values are listed in Table III. Consistent with the results obtained from the colorimeter, the fluorinated polyimides revealed a shorter λ_0 than their respective nonfluorinated analogues. A comparison of the two different imidization methods showed that the λ_0 values of 5(C) were lower than those of 5(H). Besides, the λ_0 values of copolyimide (5c/a–f(C)) ranged from 392 to 414 nm, with the ODPA or 6FDA-containing ones exhibiting lower λ_0.

To summarize, all the polyimide containing pendant CF$_3$ group manifested shorter λ_0 and higher optical transparency than their corresponding nonfluori-

TABLE III
Color Coordinates and the Cutoff Wavelength (λ_0) from UV–Visible Spectra for the 5 and 6 Series Polyimide and Copolyimide Films

Polymer	Film thickness (μm)	Color coordinates[a]				λ_0 (nm)
		b^*	Δb^*	a^*	L^*	
Blank	—	1.0		−0.4	96.2	—
5a(H)	55	72.5		−8.7	89.3	423.0
5b(H)	56	69.9		−10.9	91.0	420.5
5c(H)	40	25.3		−5.9	92.6	397.0
5d(H)	57	39.5		−7.5	90.4	401.5
5e(H)	57	21.1		−5.1	92.1	375.0
5f(H)	46	12.2		−3.5	94.4	369.5
5a(C)	61	66.2	−6.3	−11.4	91.2	416.5
5b(C)	87	42.4	−27.5	−9.2	91.6	407.0
5c(C)	—	—	—	—	—	—
5d(C)	63	32.6	−6.9	−8.7	93.2	399.0
5e(C)	44	8.3	−12.8	−2.7	95.4	364.0
5f(C)	56	11.9	−0.3	−3.1	94.8	366.0
5c/a(C)	77	55.9		−12.3	92.5	414.0
5c/b(C)	58	28.8		−9.5	94.5	401.5
5c/d(C)	54	27.0		−6.8	92.2	398.0
5c/e(C)	73	21.6		−6.5	94.1	397.0
5c/f(C)	59	17.3		−6.2	95.1	392.0
6a(H)	50	79.9	7.4	5.7	83.1	442.0
6b(H)	43	79.8	9.9	0.6	85.3	434.0
6c(H)	83	49.7	24.4	5.0	74.3	425.5
6d(H)	67	61.5	22.0	−0.2	80.9	426.5
6e(H)	56	30.7	9.6	−2.1	86.3	385.5
6f(H)	44	22.7	10.5	−7.2	94.6	377.5
Kapton	41	83.8		−5.0	88.1	444.0

[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.

nated polyimides. The electron-withdrawing CF_3 group in diamine moieties was presumably effective in decreasing CTC between polymer chains through steric hindrance and the inductive effect. Moreover, 6FDA and ODPA produced fairly transparent and almost colorless polyimide films in contrast with other dianhydrides. The results were attributed to the ether chain of ODPA and the hexafluoroisopropylidene group of 6FDA, which led to a reduction of the intermolecular CTC formation and electro-acceptor moieties.

The mechanical properties of flexible polyimide films are summarized in Table IV. The fluorinated polyimides had strengths at break of 73–112 MPa, elongations to break of 9–23%, and initial moduli of 1.6–2.2 GPa. Most of these polymers showed distinct yield points on stress–strain curves, which had strength from 81 to 113 MPa. **5c** showed the best strength because of the rigid biphenyl group. Polyimide film prepared through thermal imidization with better strength is concerning to the polymer molecular weight (inherent viscosity). Moreover, **5c/a–f** showed strengths at break of 99–132 MPa, elongations to break of 10–14%, and initial moduli of 1.8–2.2 GPa. Copolyimides also had good mechanical properties as compared to the properties of their corresponding polyimides, indicating that the strength and toughness of these films were not affected by copolymerization. As compared with the nonfluorinated polyimides, though the strengths of fluorinated polyimides were reduced, the other properties like solubility and the color intensity improved.

The thermal behavior data of all polymers are summarized in Table V. DSC experiments showed that a rapid cooling from 400°C to room temperature pro-
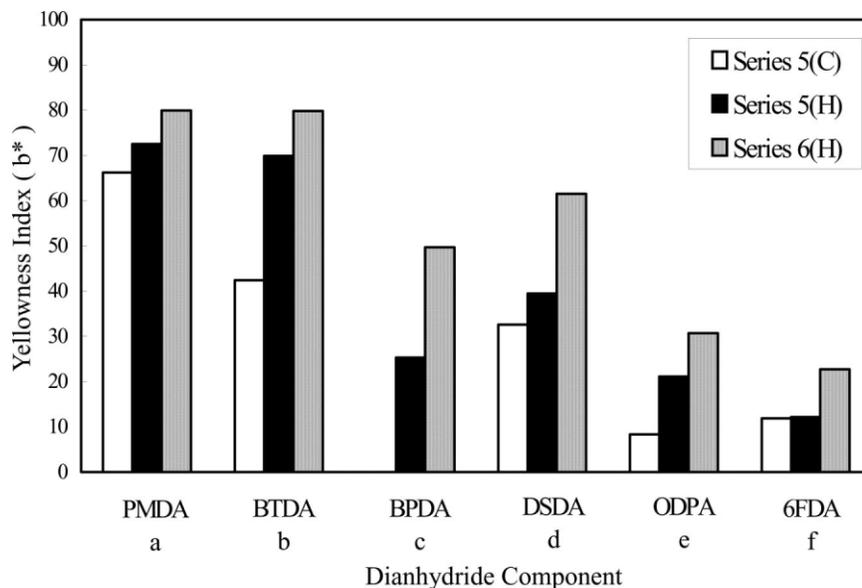
Figure 2　Comparison of the yellowness index (b^* value) for the **5(C)**, **5(H)**, and **6(H)** series.
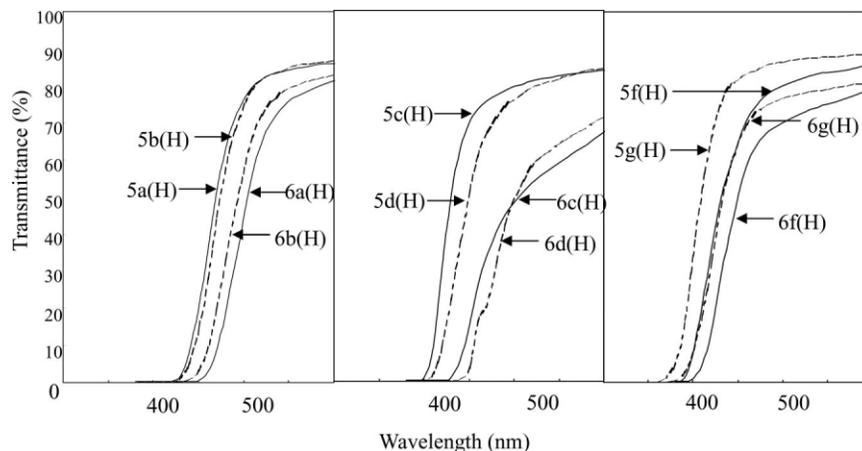
Figure 3 UV–visible spectra of polyimide films.

duced predominantly amorphous samples, rendering T_g of all the polyimides easily readable in the subsequent heating traces. The T_g values of **5a–f** were in the range of 220–267°C and **5c/a–f(C)** were between 242 and 267°C, depending on the structure of the dianhydride component, and decreasing order of T_g was generally correlated with the chain flexibility. As expected, **5a** derived from PMDA exhibited the highest T_g because of the rigid pyromellitimide unit, and **5e** obtained from ODPA showed the lowest T_g because of the presence of a flexible ether linkage between the phthalimide units. Comparing fluorinated polyimides

with nonfluorinated polyimides, T_gs for **5a–f** were relatively lower than **6a–f**; this might be a result of reduced chain–chain interaction and poor chain packing due to the bulky pendant CF_3 groups.

The temperatures for 10% weight loss (T_{10}) of the **5** series in nitrogen and air atmospheres stayed within 516–588°C and within 533–572°C, respectively. They left more than 50% char yield at 800°C in nitrogen. DSDA-bearing **5d** showed lower T_{10} values than other polyimides. This might be attributed to the weak

TABLE IV
Tensile Properties of Polyimide Films

Polymer	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
5a(H)	99	96	19	2.2
5b(H)	—	81	15	1.7
5c(H)	113	112	13	2.0
5d(H)	—	100	10	1.8
5e(H)	110	103	11	2.1
5f(H)	90	88	12	1.7
5a(C)	98	95	22	1.8
5b(C)	81	73	23	1.6
5d(C)	—	81	9	1.6
5e(C)	98	92	12	2.0
5f(C)	—	92	9	1.7
5c/a(C)	106	99	10	2.1
5c/b(C)	—	132	11	2.2
5c/d(C)	—	105	10	1.9
5c/e(C)	120	118	14	1.8
5c/f(C)	122	121	13	2.0
6a(H)	—	113	12	2.3
6b(H)	—	117	9	2.3
6c(H)	—	123	11	2.5
6d(H)	—	114	8	2.2
6e(H)	—	110	10	2.1
6f(H)	—	115	9	2.2

TABLE V
Thermal Properties of Polyimides and Copolyimides

Polymer[a]	T_g (°C)[b]	T_{10} (°C)[c] In N$_2$	T_{10} (°C)[c] In air	Char Yield (%)[d]
5a	267	580	559	56
5b	236	581	567	58
5c	246	588	572	61
5d	249	516	533	52
5e	220	581	566	58
5f	236	555	548	55
5c/a	261	584	578	44
5c/b	242	588	577	55
5c/d	251	562	556	56
5c/e	242	587	575	58
5c/f	242	567	558	57
6a[e]	286	572	569	58
6b	243	565	562	60
6c	248	568	569	60
6d	255	521	543	51
6e	230	570	570	58
6f	247	558	546	59

[a] **5c** was obtained by thermal imidization; others were obtained by chemical imidization.
[b] Baseline shift in the second heating DSC traces, with a heating rate of 15°C/min.
[c] Temperatures at which 10% weight loss were recorded by TGA at a heating rate of 20°C/min.
[d] Residual weight (%) when heated to 800°C in nitrogen.
[e] **6a–c** were according to the Ref. 17.

TABLE VI
Moisture Absorption and Dielectric Constants of Polyimides

Polymer[a]	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (dry)			
			1 kHz	10 kHz	1 MHz	40 MHz
5a	46	0.39	3.65	3.63	3.48	3.45
5b	137	0.18	3.45	3.41	3.37	3.39
5c	50	0.32	3.35	3.35	3.27	3.30
5d	119	0.40	3.40	3.43	3.40	3.41
5e	79	0.28	3.30	3.28	3.20	3.18
5f	83	0.13	3.24	3.23	3.14	3.11
6a	38	0.56	3.67	3.64	3.57	3.60
6b	28	0.99	3.78	3.78	3.66	3.68
6c	45	0.78	3.86	3.80	3.65	3.67
6d	49	0.69	3.73	3.71	3.58	3.59
6e	39	0.57	3.73	3.68	3.60	3.65
6f	42	0.47	3.72	3.62	3.53	3.57
Kapton	28	0.52	3.89	3.85	3.67	3.69

[a] **5a,b,d–f** were obtained by the chemical imidization. **5c** and the **6** series were obtained by the thermal imidization.

bonding of C—S and the degradation in the heating process. However, **5d** showed higher T_{10} values in air than in nitrogen, also indicating excellent antioxidation. For copolymer, they also had outstanding thermal stability like homopolyimides, without affecting the copolymerization. These TGA data indicated that these polyimides have excellent thermal stability and are comparable to or higher than that of nonfluorinated polyimides.

Dielectric constants and moisture absorption of all polyimides are presented in Table VI. **5a–f** had lower dielectric constants (3.14–3.48 at 1 MHz) than those of **6a–f** (3.55–3.66 at 1 MHz). The decreased dielectric constants might be attributed to the presence of the bulky CF_3 group, which resulted in less efficient chain packing. In addition, the strong electronegativity of fluorine resulted in very low polarizability of the C—F bonds, reducing the dielectric constants. Thus, the 6FDA-derived **5f** and **6f** exhibited the lowest dielectric constants in the two series. The moisture absorption of **5a–f** exhibited lower data (0.13–0.40%) than their analogous **6a–f** (0.47–0.99%) because of the hydrophobicity of the CF_3 group. Besides, the moisture absorption might be influenced by imide and ether groups, and films' thickness. The nonfluorinated polyimides contained more ether group than kapton-type polyimide; thus they showed slightly high moisture absorption. Moreover, **5f** and **6f** exhibited the lowest moisture absorption in the two series because of the higher fluorine content in the repeat unit.

CONCLUSIONS

A new fluorinated bis(ether amine) (**2**) was prepared through the nucleophilic substitution reaction of 2-chloro-5-nitrobenzotrifluoride and phenylhydroquinone, followed by hydrazine catalytic reduction of the dinitro intermediate. A series of light-colored fluorinated polyimides and copolyimides have been synthesized from **2** with various dianhydrides. The ODPA-derived and 6FDA-derived polyimides (**5e, 5f**) were characterized by good solubility and light color. Moreover, fluorinated polyimides exhibited lighter color, better solubility, lower dielectric constants, and moisture absorption than those of the corresponding nonfluorinated polyimides. For improving solubility of **5c**, copolyimide was prepared via chemical imidization. The resulting copolyimide series showed good solubility and tensile properties.

References

1. Ghosh, M. K.; Mittal, K. L. Eds.; Marcel Dekker: New York, 1996.
2. Landis, A. L.; Naselow, A. B. U.S. Pat. 4,645,824 (1987).
3. Higashi, K.; Noda, Y. Eur. Pat. 240,249 (1986).
4. Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. Electron Lett 1993, 29, 2107.
5. Ando, S.; Sawada, T.; Inoue, Y. Electron Lett 1993, 29, 2143.
6. Ando, S.; Matsuura, T.; Sasaki, S. Polym J 1997, 29, 69.
7. Hsiao, S. H.; Yang, C. P.; Lin, W. L. Macromol Chem Phys 1999, 200, 1428.
8. Yang, C. P.; Yang, H. W. J Appl Polym Sci 2000, 75, 87.
9. Hsiao, S. H.; Yang, C. P. Macromol Chem Phys 1997, 198, 211.
10. Yang, C. P.; Chen, R. S. J Polym Sci Part A: Polym Chem 2000, 38, 1428.
11. Xu, S. G.; Yang, M. J.; Bai, F. L. Synth Met 2003, 137, 1097.
12. Yang, C. P.; Hsiao, S. H.; Chen, K. H. Polymer 2002, 43, 5094.
13. Rogers, F. E. U.S. Pat. 3,356,648 (1964).
14. Dine-Hart, R. A.; Wright, W. W.; Makromol Chem 1971, 143, 189.
15. Liaw, D. J.; Liaw, B. Y. Polym J 1996, 28, 970.
16. Liaw, D. J.; Liaw, B. Y. J Polym Sci Part A: Polym Chem 1999, 35, 1527.
17. Yang, C. P.; Chen, R. S. J Polym Sci Part A: Polym Chem 2002, 40, 429.
18. Hsiao, S. H.; Yang, C. P.; Lin, C. K. J Polym Res 1995, 2, 1.
19. Takashi, K.; Atsushi, S.; Shoji T. (to Mitsui Chem Industry Co., Japan) Jpn. Kokai Tokkyo Koho JP 297,067 (2002).
20. Xie, K.; Liu, J. G.; Hhou, H. W.; Zhang, S. Y.; He, M. H.; Yang, S. Y. Polymer 2001, 42, 7267.
21. Banerjee, S.; Madhra, M. K.; Salunke, A. K.; Maier, G. J Polym Sci Part A: Polym Chem 2002, 40, 1016.
22. Myung, B. Y.; Kim, J. J.; Yoon, T. H. J Polym Sci Part A: Polym Chem 2002, 40, 4217.
23. Yang, C. P.; Chen, R. S.; Hsu, M. F. J Polym Res 2002, 9, 245.