Highly Soluble and Optically Transparent Poly (ether imide)s Based on 2,6- or 2,7-Bis(3, 4-dicarboxyphenoxy)naphthalene Dianhydride and Aromatic Bis(ether amine)s Bearing Trifluoromethyl Groups

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ABSTRACT: Two series of novel fluorinated poly(ether imide)s (coded **IIIA** and **IIIB**) were prepared from 2,6-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride and 2,7-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride, respectively, with various trifluoromethyl-substituted aromatic bis(ether amine)s by a standard two-step process with thermal or chemical imidization of the poly(amic acid) precursors. These fluorinated poly(ether imide)s showed good solubility in many organic solvents and could be solution-cast into transparent, flexible, and tough films. These films were nearly colorless, with an ultraviolet–visible absorption edge of 364–386 nm. They also showed good thermal stability with glass-transition temperatures of 221–298 °C, 10% weight loss temperatures in excess of 489 °C, and char yields at 800 °C in nitrogen greater than 50%. The 2,7-substituted **IIIB** series also showed better solubility and higher transparency than the isomeric 2,6-substituted **IIIA** series. In comparison with nonfluorinated poly(ether imide)s, the fluorinated **IIIA** and **IIIB** series showed better solubility, higher transparency, and lower dielectric constants and water absorption. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 5909–5922, 2006

Keywords: dielectric properties; fluoropolymers; poly(ether imide)s; polyimides; solubility; thermal properties; transparency; trifluoromethyl group

INTRODUCTION

Aromatic polyimides are a class of high-performance polymers that have gained considerable attention in the microelectronics, aerospace, and photoelectronics industries because of their outstanding thermal, mechanical, and electrical properties and good chemical resistance.[1–3] However, their widespread applications are often limited because of their poor solubility and high processing temperature, which are caused by the rigid polymer backbones and the strong interchain interaction. Therefore, significant synthetic efforts have been made to improve the processability and solubility of polyimides with the retention of their attractive properties by the introduction of a new structure into the polymer backbone.[4,5] The light or dark-yellow color of aromatic polyimide films may hinder their applications in optical or optoelectronic materials. The coloration of aromatic polyimide films is mainly caused by the intramolecular and intermolecular charge-transfer (CT) interactions between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties.[6–8] A strategy for obtaining less colored or colorless polyimides is to use dianhydrides of lower electron acceptability and

diamines of lower electron donatability as monomers for weakening both intra- and intermolecular CT interactions.[9] Although soluble and colorless polyimides can be obtained from alicyclic dianhydride or diamine monomers,[10–13] these materials may have limited long-term thermal stability because of less stable aliphatic segments.

The incorporation of large, bulky groups into either diamine or dianhydride monomers reduces the number of chain-to-chain electronic interactions and thereby lessens CT complex formation. Recently, considerable attention has been devoted to fluorinated aromatic polyimides, especially trifluoromethyl (CF$_3$)-containing polyimides.[14–25] The bulky CF$_3$ group, introduced into polyimide backbones, results in enhanced solubility and optical transparency together with a lowered dielectric constant, which is attributed to the low polarizability of the C—F bond and the increase in the free volume. The fluorinated polyimides also provide other advantages, such as good thermal and thermooxidative stability and low moisture absorption. Besides, poly(ether imide)s have received great attention as they may provide good processability because of the presence of flexible ether links.[26,27] The development of nucleophilic displacement reactions and nitrodisplacement reactions in particular has led to the development of a large class of poly(ether imide)s from various combinations of bis(ether anhydride)s and diamines. Ultem 1000 resin is one of the important examples developed and commercialized by General Electric Co.;[28] it exhibits reasonable thermal stability and good mechanical properties together with good moldability.

We have previously reported the synthesis and properties of poly(ether imide)s derived from bis(ether anhydride)s [2,6-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**A**) and 2,7-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**B**)] based on 2,6- and 2,7-dihydroxynaphthalenes.[29,30] The reported poly(ether imide)s exhibit a good combination of properties that include excellent mechanical properties, high thermal stability, and moderate glass-transition temperatures (T_g's), but the solubility is still not satisfactory. Here we report the synthesis and characterization of two series of novel CF$_3$-containing poly(ether imide)s based on bis(ether anhydride)s **A** and **B** with various CF$_3$-substituted bis(ether amine)s. In addition to the steric effect attributed to the bulky —CF$_3$ group, the obtained poly(ether imide)s should have diminished intra- and intermolecular CT interactions not only because of the decrease in the electron-accepting property of the dianhydride components caused by the electron-donating ether linkages but also because of the decrease in the electron-donating property of the diamine components caused by the electron-withdrawing —CF$_3$ groups. Thus, the polymers would be expected to exhibit enhanced solubility in organic solvents. The mechanical, thermal, optical, and dielectric properties of thin films of the prepared poly(ether imide)s are evaluated and compared with those of analogous ones without the —CF$_3$ substituents.

EXPERIMENTAL

Materials

According to a literature process,[31] **A** (mp = 234–235 °C) and **B** (mp = 167–167 °C) were synthesized through the nitro displacement reaction of 4-nitrophthalonitrile with 2,6-dihydroxynaphthalene and 2,7-dihydroxynaphthalene, respectively, in N,N-dimethylformamide (DMF) in the presence of potassium carbonate, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile)s and the subsequent cyclodehydration of the resulting bis(ether diacid)s. The synthetic details and characterization data have been reported in our previous articles.[29,30] The CF$_3$-substituted bis(ether amine)s were prepared through the chloro-displacement reaction of 2-chloro-5-nitrobenzotrifluoride with the corresponding aromatic diols in the presence of potassium carbonate, followed by Pd/C-catalyzed hydrazine reduction; they included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (**Ia**; mp = 132–133 °C),[14] 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2-*tert*-butylbenzene (**Ib**; mp = 164–165 °C),[32] 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2,5-di-*tert*-butylbenzene (**Ic**; mp = 215–216 °C),[19] 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**Id**; mp = 155–156 °C),[15] 4,4′-bis(4-amino-2-trifluoromethylphenoxy)-3,3′, 5,5′-tetramethylbiphenyl (**Ie**; mp = 256–257 °C),[33] 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**If**; mp = 131–132 °C),[34] and 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene (**Ig**; mp = 239–240 °C).[35] N,N-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of the Poly(ether imide)s

Thermal Imidization Method

The general polymerization procedure is illustrated by the following example. To a solution of

bis(ether amine) **Ic** (0.270 g; 0.5 mmol) in dried DMAc (4.3 mL) in a 20-mL flask, an equimolar amount of bis(ether anhydride) **A** (0.226 g, 0.5 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to afford a highly viscous poly(amic acid) (PAA) solution. Then, the PAA solution was poured into a glass culture dish, 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 from 120 to 250 °C at a heating rate of 3 °C/min and holding at 250 °C for 1 h. The cured poly(ether imide) film was stripped from the glass substrate by immersion in water followed by drying in an oven at 100 °C. The inherent viscosity of **IIIAc** was 0.89 dL/g, as measured at a concentration of 0.5 g/dL in N-methyl-2-pyrrolidone (NMP) at 30 °C.
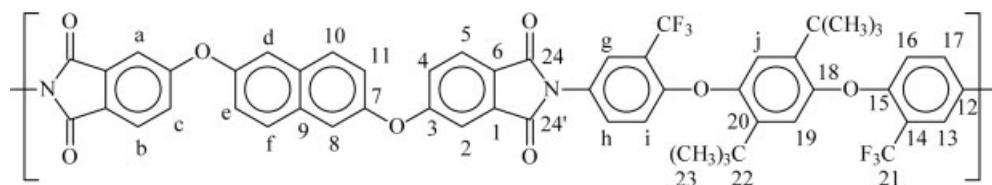
IR (film): 1781 (asymmetrical C=O stretch), 1727 (symmetrical imide C=O stretch), 1599–1479 (aromatic C=C stretch), 1376 (C—N stretch), 1252 (C—O stretch), 1054, 745 cm^{-1} (imide ring deformation). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.96 (d, J = 8.3 Hz, 2H, H$_b$), 7.92 (d, J = 8.9 Hz, 2H, H$_f$), 7.81 (s, 2H, H$_g$), 7.60 (d, J = 1.7 Hz, 2H, H$_d$), 7.55 (d, J = 8.2 Hz, 2H, H$_h$), 7.52 (d, J = 1.8 Hz, 2H, H$_a$), 7.45 (dd, J = 8.2, 1.6 Hz, 2H, H$_c$), 7.36 (dd, J = 8.8, 1.6 Hz, 2H, H$_e$), 6.97 (s, 4H, H$_i$ + H$_j$), 1.33 (s, 18H, t-butyl). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm): 166.44, 166.40 (C$^{24,24'}$), 163.80 (C^3), 155.51 (C^{15}), 152.47 (C^{18}), 150.03 (C^7), 141.64 (C^{20}), 134.17 (C^1), 131.98 (C^9), 131.19 (C^{17}), 130.26 (C^{10}), 126.03 (C^5), 125.62 (C^{13}), 125.40 (C^{12}), 125.21 (C^6), 123.31 (C^4), 122.93 (C^{21}, quartet, $^{1}J_{C-F}$ = 273 Hz), 121.37 (C^{11}), 121.01 (C^{14}), 120.63 (C^{16}), 117.65 (C^{19}), 117.11 (C^8), 112.43 (C^2), 34.47 (C^{22}), 29.96 (C^{23}).

Chemical Imidization Method

A pot of a 10 wt % PAA solution in DMAc was prepared with 0.5 mmol each of bis(ether amine) **Ic** and bis(ether anhydride) **B** by the same procedure described previously. Then, 2 mL of 2/1 (v/v) acetic anhydride/pyridine (Py) was added to the PAA solution. The mixture was heated at 80 °C for 1 h to effect a complete imidization and then poured into a glass culture dish, which was placed in an oven at 80 °C for 1 h to evaporate the solvent and form a thin, solid film. The polyimide film was then heated to 200 °C and held at that temperature for 2 h to remove the residual solvent. The inherent viscosity of **IIIBc** was 0.78 dL/g, as measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

IR (film) of **IIIBc**: 1780 (asymmetrical C=O stretch), 1732 (symmetrical imide C=O stretch), 1616–1498 (aromatic C=C stretch), 1382 (C—N stretch), 1261 (C—O stretch), 1053 and 746 cm^{-1} (imide ring deformation). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 8.00 (d, J = 8.9 Hz, 2H, H$_f$), 7.96 (d, J = 8.3 Hz, 2H, H$_b$), 7.80 (s, 2H, H$_g$), 7.53 (d, 2H, H$_h$), 7.52 (d, J = 1.9 Hz, 2H, H$_a$), 7.48 (d, J = 2.0 Hz, 2H, H$_d$), 7.45 (dd, J = 8.3, 1.9 Hz, 2H, H$_c$), 7.31 (dd, J = 8.8, 2.0 Hz, 2H, H$_e$), 6.96 (s, 4H, H$_i$ + H$_j$), 1.29 (s, 18H, H$_k$). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm): 166.42, 166.38 (C$^{25,25'}$), 163.53 (C^3), 155.53 (C^{16}), 153.56 (C^{19}), 149.99 (C^7), 141.66 (C^{21}), 135.38 (C^9), 134.12 (C^{13}), 131.19 (C^{18}), 130.82 (C^{11}), 128.77 (C^{10}), 126.03 (C^1 + C^5), 125.64 (C^{14}), 125.28 (C^6), 123.51 (C^4), 122.91 (C^{22}, quartet, $^{1}J_{C-F}$ = 273 Hz), 120.66 (C^{15} + C^{17}), 119.91 (C^{12}), 117.62 (C^{20}), 116.33 (C^8), 112.62 (C^2), 34.45 (C^{23}), 29.94 (C^{24}).
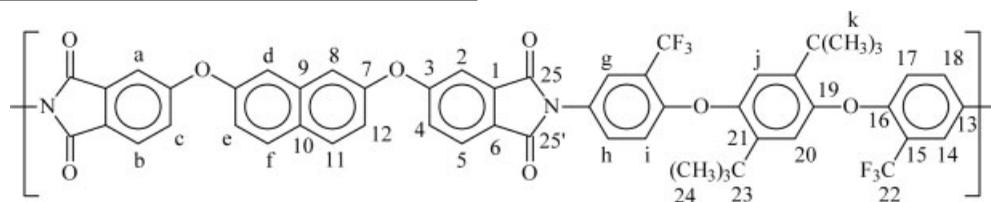
Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a Heraeus Vario EL-III CHN analyzer. ^{1}H 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. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. The tensile properties of the polymer films were measured with an Instron model 4400R tensile tester with a 5-kg load cell at a crosshead speed of 5 mm/min on strips approximately 30–50 μm thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. Differential scanning calorimetry (DSC) traces were measured on a TA Instruments DSC 2010 at a scanning rate of 15 °C/min in flowing nitrogen
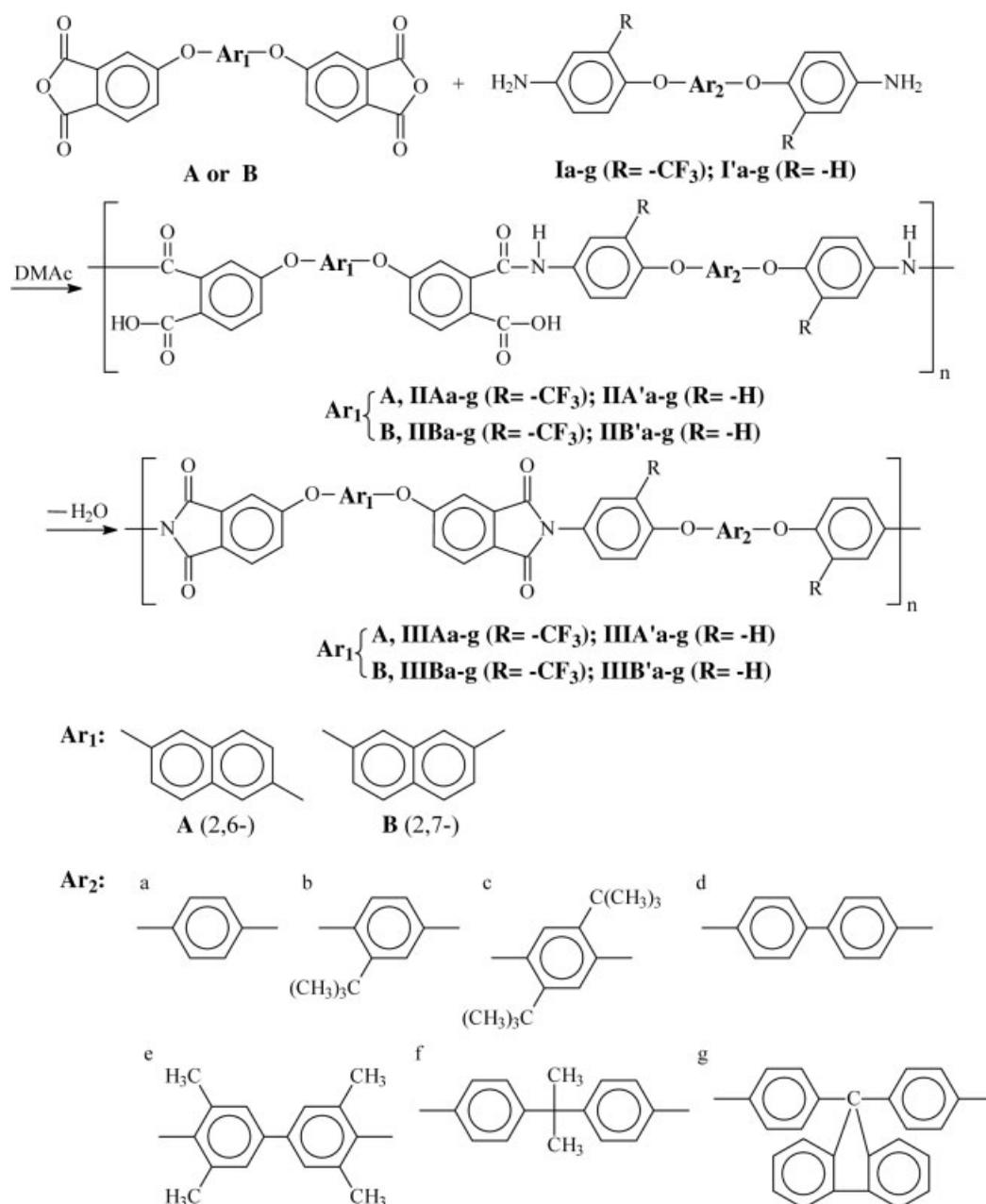
Scheme 1

Table 1. Inherent Viscosities and Elemental Analysis of the Poly(ether imide) Films

Polymer[a]	Inherent Viscosity (dL/g)[b]	Formula (Formula Weight)		Elemental Analysis (%)		
				C	H	N
IIIAa[d]	—	$(C_{46}H_{22}N_2O_8F_6)_n$ $[(844.68)_n]$	Calcd.	65.41	2.63	3.32
			Found	64.85	2.79	3.17
IIIAb[d]	—	$(C_{50}H_{30}N_2O_8F_6)_n$ $[(900.79)_n]$	Calcd.	66.67	3.36	3.11
			Found	66.61	3.58	3.01
IIIAc	0.89[c]	$(C_{54}H_{38}N_2O_8F_6)_n$ $[(956.89)_n]$	Calcd.	67.78	4.00	2.93
			Found	67.70	4.18	2.82
IIIAd	1.22[c]	$(C_{52}H_{26}N_2O_8F_6)_n$ $[(920.78)_n]$	Calcd.	67.83	2.85	3.24
			Found	67.72	2.99	3.13
IIIAe	0.71	$(C_{56}H_{34}N_2O_8F_6)_n$ $[(976.88)_n]$	Calcd.	68.85	3.51	2.87
			Found	68.44	3.66	2.82
IIIAf	0.95	$(C_{55}H_{32}N_2O_8F_6)_n$ $[(962.86)_n]$	Calcd.	68.81	3.35	2.91
			Found	68.63	3.42	2.88
IIIAg	0.74	$(C_{65}H_{34}N_2O_8F_6)_n$ $[(1084.98)_n]$	Calcd.	71.69	3.16	2.58
			Found	71.74	3.30	2.64
IIIBa	1.66	$(C_{46}H_{22}O_8N_2F_6)_n$ $[(844.68)_n]$	Calcd.	65.41	2.63	3.32
			Found	64.81	2.77	3.24
IIIBb	1.61	$(C_{50}H_{30}O_8N_2F_6)_n$ $[(900.79)_n]$	Calcd.	66.67	3.36	3.11
			Found	66.21	3.37	3.22
IIIBc	1.32	$(C_{54}H_{38}O_8N_2F_6)_n$ $[(956.89)_n]$	Calcd.	67.78	4.00	2.93
			Found	67.33	4.01	3.01
IIIBd	1.53	$(C_{52}H_{26}O_8N_2F_6)_n$ $[(920.78)_n]$	Calcd.	67.83	2.85	3.04
			Found	67.21	2.85	2.97
IIIBe	1.06	$(C_{56}H_{34}O_8N_2F_6)_n$ $[(976.88)_n]$	Calcd.	68.85	3.51	2.87
			Found	68.26	3.44	2.95
IIIBf	1.23	$(C_{55}H_{32}O_8N_2F_6)_n$ $[(962.86)_n]$	Calcd.	68.61	3.35	2.91
			Found	68.29	3.22	2.92
IIIBg	1.37	$(C_{65}H_{34}O_8N_2F_6)_n$ $[(1084.98)_n]$	Calcd.	71.96	3.16	2.58
			Found	71.36	3.20	2.61

[a] The poly(ether imide)s were obtained by thermal imidization.
[b] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[c] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.
[d] **IIIAa** and **IIIAb** were insoluble in the solvents NMP and DMAc.

(40 cm^3/min). T_g's were read as the midpoint temperature of the heat capacity jump and were taken from the second heating scan after quick cooling from 400 °C to room temperature. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. The experiments were carried out on 13–15-mg film samples heated in flowing nitrogen or air (90 cm^3/min) at a heating rate of 20 °C/min. 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. The experiments were performed at 25 °C in a dry chamber. The equilibrium moisture absorption was determined by the weighing of the changes in the vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 5 days.

RESULTS AND DISCUSSION

Polymer Synthesis

Two series of novel fluorinated poly(ether imide)s, **IIIA** and **IIIB**, with an isomeric repeat unit were synthesized by a two-step procedure in which PAAs were first prepared by the ring-opening polyaddition of bis(ether anhydride)s **A** and **B**, respectively, with various CF$_3$-bearing bis(ether amine)s (**Ia–Ig**) in DMAc, followed by the thermal and chemical imidization of PAA (Scheme 1). No difficulty was encountered in obtaining high-molecular-weight PAAs from the reactions of
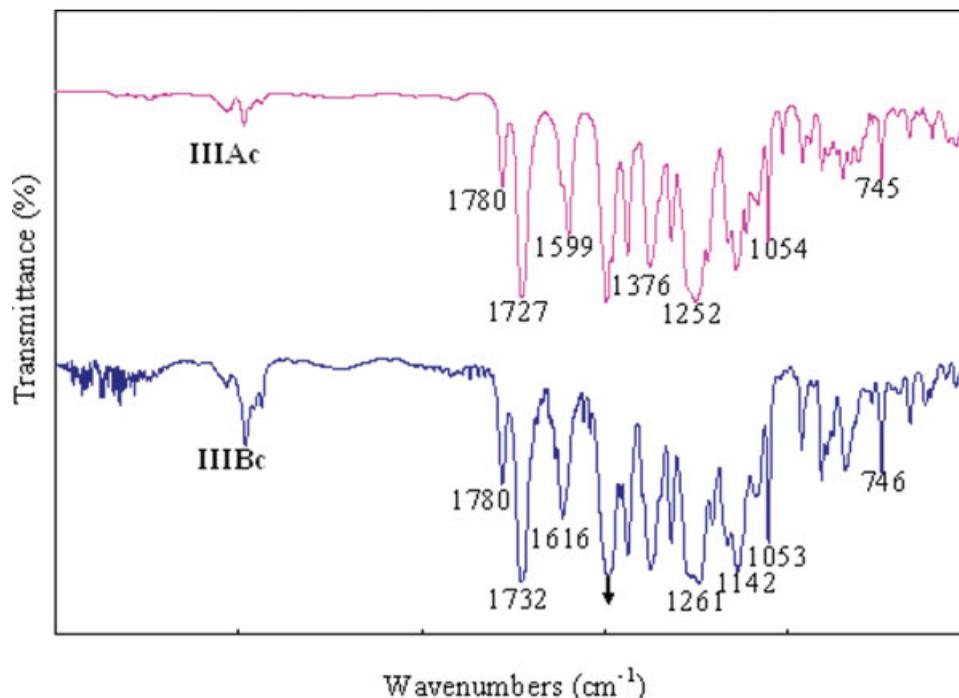
Figure 1. FTIR spectra of thin films of poly(ether imide)s **IIIAc** and **IIIBc**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Ia–Ig with **A** or **B**. Even though the amino groups in these bis(ether amine)s were less basic than a normal dramatic amine because of the inductive deactivation of the $-CF_3$ group, these CF_3-substituted bis(ether amine)s were still sufficiently reactive to give high-molecular-weight PAAs when they were allowed to polymerize for an extended period of time (ca. 10 h). The maintained reactivity of these bis(ether amine)s is most likely based on the meta substitution to the amino group. Tough and flexible poly(ether imide) films were obtained via the casting of the PAA solution onto a glass substrate, followed by a thermal curing process at 250 °C. Most poly(ether imide)s exhibited good solubility in organic solvents; therefore, the characterization of the solution viscosity was carried out without any difficulty. As shown in Table 1, the inherent viscosities of soluble poly(ether imide)s were in the range of 0.71–1.66 dL/g, as measured in NMP or DMAc.

The chemical structures of the polymers were confirmed with FTIR, NMR, and elemental analysis. All the poly(ether imide)s showed characteristic imide absorption bands around 1780 and 1730 (imide carbonyl asymmetrical and symmetrical stretching), 1380 (C—N stretching), and 1050 and 750 cm^{-1} (imide ring deformation), together with the C—O and C—F multiple stretching

absorptions in the region of 1100–1300 cm^{-1} (Figure 1). The ^{1}H NMR and ^{13}C NMR chemical-shift data and assignments of two representative poly(ether imide)s, **IIIAc** and **IIIBc**, are described in the Experimental section. The assignments of each carbon and proton were assisted by the two-dimensional NMR spectra illustrated in Figures 2 and 3, and these spectra are in complete agreement with the proposed molecular structures. In addition to IR and NMR spectra, the elemental analysis results of poly(ether imide)s also generally agreed with the calculated values for the proposed structures.

Properties of the Polymers

The solubility of these polymers was tested in various organic solvents, and the results are listed in Table 2. In some cases such as **IIIAg**, **IIIBa**, and **IIIBd**, the poly(ether imide)s prepared by the chemical imidization method showed a higher solubility than the thermally cured ones. The lower solubility of the thermally cured poly(ether imide)s might be attributed to denser chain packing and aggregation during imidization at elevated temperatures. When we compared the solubility behaviors between these two isomeric fluorinated poly(ether imide)s, particularly those
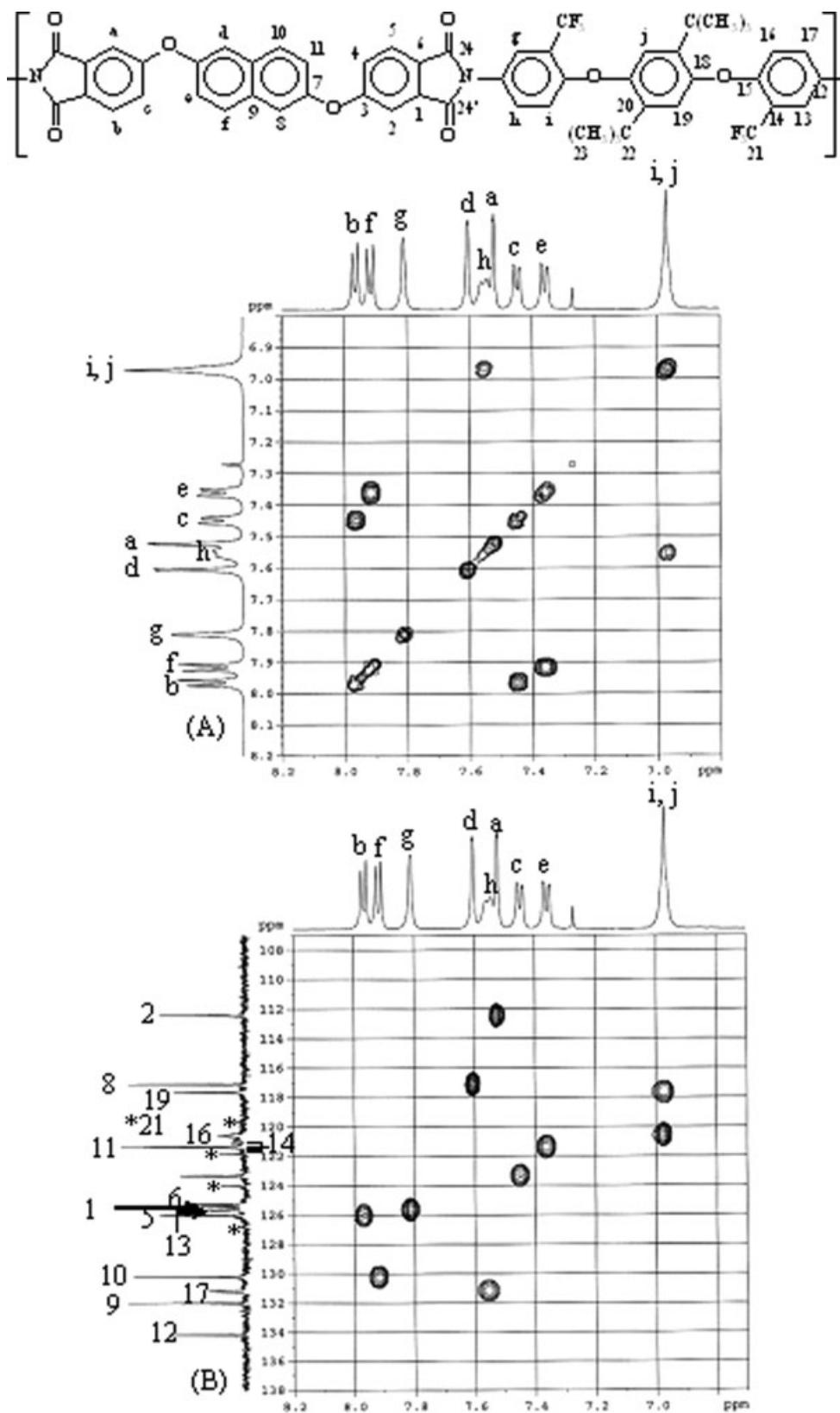
Figure 2. (A) Correlation spectroscopy spectrum and (B) heteronuclear chemical-shift correlation spectrum of poly(ether imide) **IIIAc** in CDCl$_3$.
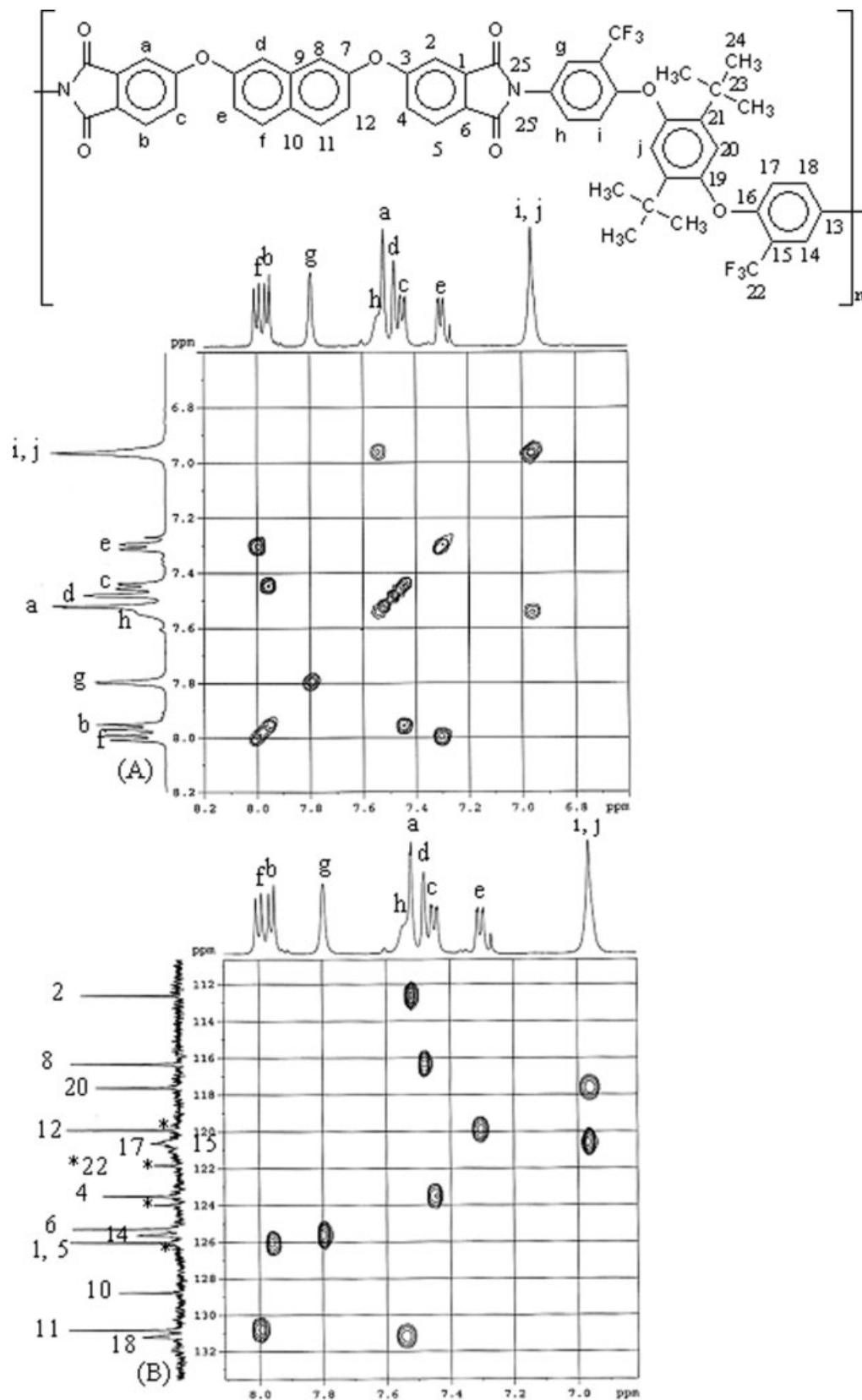
Figure 3. (A) Correlation spectroscopy spectrum and (B) heteronuclear chemical-shift correlation spectrum of poly(ether imide) **IIIBc** in CDCl₃.

Table 2. Solubility of the Poly(ether imide)s

Polymer[a]	Solvent[b]								
	NMP	DMAc	DMF	DMSO	*m*-Cresol	Py	Dioxane	THF	CHCl$_3$
IIIAa(H)	−−	−−	−−	−−	−−	−−	−−	−−	−−
IIIAb(H)	−−	−−	+−	−−	−−	++	−−	−−	−−
IIIAc(H)	+	−−	+	−−	+++	+++	++	+++	+++
IIIAd(H)	+	−−	−−	−−	−−	−−	−−	−−	−−
IIIAe(H)	+++	+++	+++	−−	+++	+++	++	+++	+++
IIIAf(H)	+++	+++	+++	−−	+++	+++	++	+++	+
IIIAg(H)	++	+	+	+	++	+++	+	+	+
IIIAa(C)	−−	−−	−−	−−	−−	+−	−−	+−	−−
IIIAb(C)	−−	−−	+++	−−	+	+++	+++	+++	+
IIIAc(C)	−−	−−	+	−−	−−	+++	++	+++	−−
IIIAd(C)	++	+++	+++	−−	−−	+++	+	+++	−−
IIIAe(C)	+++	+++	−−	−−	++	+++	+++	+++	+
IIIAf(C)	+++	+++	+++	−−	++	+++	+++	+++	+++
IIIAg(C)	+++	+++	+++	++	++	+++	+++	+++	+++
IIIA′a(H)–IIIA′g(H)	−−	−−	−−	−−	−−	−−	−−	−−	−−
IIIBa(H)	++	++	++	−−	−−	++	−−	−−	−−
IIIBb(H)	+++	++	−−	−−	−−	+++	−−	−−	+++
IIIBc(H)	+++	++	++	−−	−−	+++	−−	+++	+++
IIIBd(H)	+	+	+	−−	−−	−−	−−	−−	−−
IIIBe(H)	+++	+++	+++	−−	−−	+++	−−	+++	+++
IIIBf(H)	+++	+++	+++	−−	−−	+++	−−	+++	+++
IIIBg(H)	+++	+++	+++	−−	−−	+++	−−	−−	+++
IIIBa(C)	+++	+++	+++	+++	−−	+++	−−	+++	++
IIIBb(C)	+++	+++	+++	−−	−−	+++	−−	+++	+++
IIIBc(C)	+++	+++	+++	−−	+++	+++	+++	+++	+++
IIIBd(C)	+++	+++	+++	−−	++	+++	−−	+++	+++
IIIBe(C)	+++	+++	+++	−−	+++	+++	+++	+++	+++
IIIBf(C)	+++	+++	+++	−−	++	+++	+++	+++	+++
IIIBg(C)	+++	+++	+++	+−	+−	+++	+++	+++	+++
IIIB′a(H)	−−	−−	−−	−−	−−	−−	−−	−−	−−
IIIB′b(H)	−−	++	−−	−−	−−	−−	−−	−−	+++
IIIB′c(H)	−−	−−	−−	−−	−−	−−	−−	−−	+++
IIIB′d(H)	−−	−−	−−	−−	−−	−−	−−	−−	−−
IIIB′e(H)	−−	−−	−−	−−	−−	−−	−−	−−	+++
IIIB′f(H)	+++	++	−−	−−	−−	−−	−−	−−	+++
IIIB′g(H)	−−	−−	−−	−−	−−	−−	−−	−−	−−

^{a} The polyimides were obtained by thermal imidization (H) or chemical imidization (C).
^{b} The solubility was determined at room temperature. +++ = soluble at 10 wt % solid; ++ = soluble at 5 wt % solid; + = soluble at 1 wt % solid; +− = partially soluble; −− = insoluble.

derived from bis(ether amine)s **Ia–Ic**, the 2,7-naphthalenedioxy-containing polymers displayed solubility superior to that of 2,6-analogues because of less symmetric catenation on the naphthalene ring. All the chemically treated **IIIB** series poly(ether imide)s could easily be dissolved both in polar solvents, such as NMP, DMAc, and DMF, and in common organic solvents, such as Py, tetrahydrofuran (THF), and chloroform. Good solubility in low-boiling-point solvents is beneficial for the preparation of polymer films or coatings at low processing temperatures. These fluorinated poly(ether imide)s, **IIIAa(H)–IIIAg(H)** and **IIIBa(H)–IIIBg(H)**, obviously showed better solubility in the testing solvents than the corresponding nonfluorinated poly(ether imide)s, **IIIA′a(H)–IIIA′g(H)** and **IIIB′a(H)–IIIB′g(H)**. This can be mainly attributed to the effect of the large volume of CF$_3$ groups, which increased the disorder along the polymer chain, decreased interchain interactions, and reduced the efficiency of chain packing, leading to significantly enhanced solubility.

Table 3. Mechanical Properties of the Poly(ether imide) Films

Polymer[a]	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
IIIAa	—	109	8	1.7
IIIAb	—	140	12	2.2
IIIAc	—	127	9	2.1
IIIAd	—	135	15	2.3
IIIAe	138	136	12	2.5
IIIAf	—	123	10	2.3
IIIAg	—	130	10	3.2
IIIA′a	—	105	10	1.9
IIIA′b	—	117	33	1.7
IIIA′c	—	102	10	1.7
IIIA′d	90	89	11	1.7
IIIA′e	—	106	19	1.7
IIIA′f	—	102	10	2.1
IIIA′g	—	128	11	2.2
IIIBa	115	100	12	2.2
IIIBb	—	117	11	2.0
IIIBc	117	115	10	2.0
IIIBd	132	123	19	2.6
IIIBe	—	78	11	1.8
IIIBf	103	99	13	1.8
IIIBg	—	91	7	1.8
IIIB′a	97	96	17	1.7
IIIB′b	—	100	11	2.0
IIIB′c	108	106	11	2.1
IIIB′d	—	98	16	2.0
IIIB′e	95	94	17	1.9
IIIB′f	—	80	9	1.6
IIIB′g	—	132	11	2.1

[a] The poly(ether imide) samples were obtained by the thermal imidization method.

All the fluorinated poly(ether imide)s could be processed into good-quality, creasable films with low color. These films were subjected to tensile tests, and the results are shown in Table 3. They had strengths at break of 78–140 MPa, elongations at break of 7–19%, and initial moduli of 1.7–3.2 GPa, which indicated that they were tough and strong materials. In all cases, the **IIIB** series polymers revealed a lower tensile strength than the corresponding **IIIA** series, probably because of the increase in the chain flexibility with the existence of 2,7-catenated naphthalene units in the backbones. For comparison, the tensile properties of the nonfluorinated poly(ether imide)s, **IIIA′** and **IIIB′**, are also included in Table 3. The results indicate that these CF_3-containing poly(ether imide)s not only had good solubility but

also retained good tensile properties comparable to those of the nonfluorinated ones.

The thermal behavior data of all poly(ether imide)s are tabulated in Table 4. The T_g values of the **IIIA** and **IIIB** series poly(ether imide)s, determined by DSC, were in the ranges of 223–298 and 221–286 °C, respectively. The decreasing order of T_g generally correlated with that of the chain flexibility. As expected, the *tert*-butyl-substituted poly(ether imide)s exhibited higher T_g values than the corresponding unsubstituted ones because of the hindrance effect of the chain

Table 4. Thermal Properties of the Poly(ether imide)s

Polymer[a]	T_g (°C)[b]	T_5 (°C)[c] In N_2	T_5 (°C)[c] In Air	T_{10} (°C)[d] In N_2	T_{10} (°C)[d] In Air	Char Yield (%)[e]
IIIAa	232	549	516	581	549	50
IIIAb	244	499	479	522	518	61
IIIAc	258	492	450	508	478	57
IIIAd	244	551	521	585	550	57
IIIAe	298	452	453	491	489	66
IIIAf	223	402	494	528	527	65
IIIAg	272	545	526	582	560	60
IIIA′a	247	508	500	523	523	58
IIIA′b	239	532	530	555	561	60
IIIA′c	259	492	462	505	506	44
IIIA′d	251	542	535	565	566	64
IIIA′e	297	505	495	553	528	64
IIIA′f	235	517	514	533	542	60
IIIA′g	288	547	527	569	561	67
IIIBa	227	568	531	590	562	60
IIIBb	237	527	472	539	507	56
IIIBc	252	493	445	509	465	54
IIIBd	238	563	505	591	569	62
IIIBe	286	466	445	503	483	50
IIIBf	221	531	484	549	515	61
IIIBg	264	564	537	591	568	66
IIIB′a	224	524	524	554	548	63
IIIB′b	236	514	511	524	530	43
IIIB′c	249	491	481	515	509	31
IIIB′d	237	528	535	565	563	56
IIIB′e	286	495	496	512	527	61
IIIB′f	227	524	502	539	540	56
IIIB′g	279	547	539	571	566	62
Ultem 1000	227	506	505	532	532	58

[a] The poly(ether imides) were obtained by the thermal imidization method.
[b] Baseline shift in the second-heating DSC traces at a heating rate of 15 °C/min.
[c] Temperature of 5% weight loss recorded by thermogravimetry at a heating rate of 20 °C/min.
[d] Temperature of 10% weight loss recorded by thermogravimetry at a heating rate of 20 °C/min.
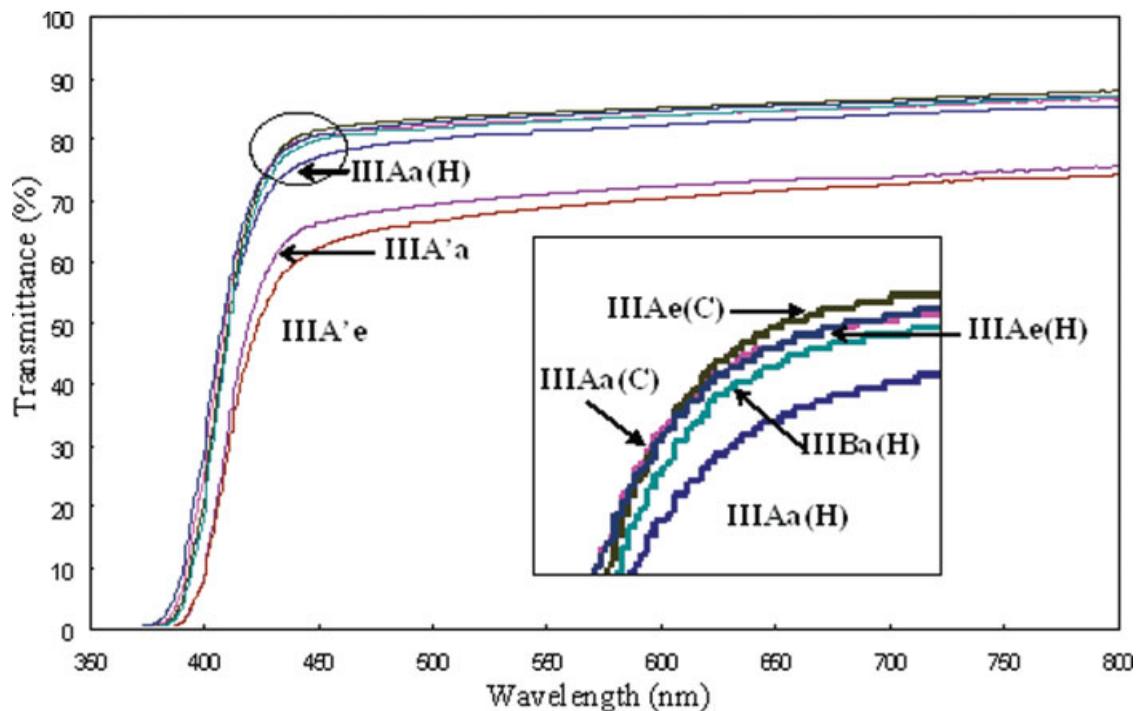[e] Residual weight (%) with heating to 800 °C in nitrogen.

Figure 4. TGA curves of poly(ether imide)s **IIIAg** and **IIIBg** and Ultem 1000 at a heating rate of 20 °C/min.

rotation in the substituted polymers. Hence, the T_g order was as follows: **IIIAc** (**IIIBc**) > **IIIAb** (**IIIBb**) > **IIIAa** (**IIIBa**). In these fluorinated poly-

mers, **IIIAf** and **IIIBf**, derived from bis(ether amine) **If**, showed the lowest T_g values because of the presence of a flexible isopropylidene linkage,
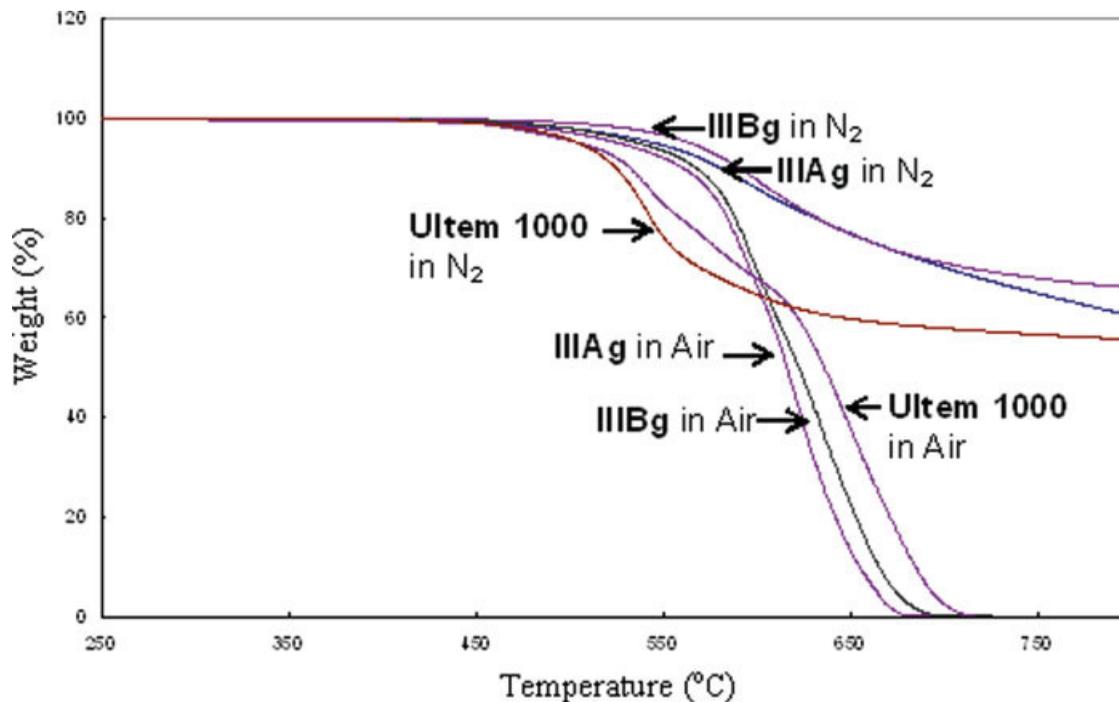

Figure 5. UV–vis spectra of some poly(ether imide) films.

Table 5. Water Absorption, Dielectric Constants, and λ_0 Values of the Poly(ether imide) Films

Polymer[a]	Film Thickness (μm)	Water Absorption (%)	Dielectric Constant (Dry)			λ_0 (nm)[b]
			1 kHz	10 kHz	1 MHz	
IIIAa	27	0.52	3.37	3.32	3.20	385 (376)
IIIAb	26	0.39	3.47	3.44	3.37	383 (381)
IIIAc	32	0.33	3.43	3.40	3.32	386 (383)
IIIAd	33	0.48	3.78	3.75	3.70	384 (384)
IIIAe	34	0.53	3.68	3.66	3.62	386 (376)
IIIAf	48	0.47	3.48	3.39	3.28	379 (385)
IIIAg	35	0.61	3.17	3.13	3.09	381 (378)
IIIA′a	44	0.87	3.72	3.69	3.64	389
IIIA′b	52	0.74	3.86	3.83	3.66	387
IIIA′c	68	0.63	4.01	3.97	3.82	396
IIIA′d	32	0.58	4.01	3.96	3.82	385
IIIA′e	71	0.57	4.14	4.07	3.95	387
IIIA′f	43	0.70	3.87	3.84	3.73	383
IIIA′g	38	0.82	3.96	3.93	3.78	384
IIIBa	44	0.39	3.29	3.22	3.08	377 (374)
IIIBb	52	0.38	3.13	3.09	2.94	368 (376)
IIIBc	55	0.51	3.28	3.25	3.13	368 (373)
IIIBd	75	0.14	3.47	3.38	3.14	372 (375)
IIIBe	68	0.48	3.59	3.51	3.35	374 (370)
IIIBf	48	0.55	3.69	3.63	3.49	368 (371)
IIIBg	35	0.49	3.59	3.55	3.44	364 (371)
IIIB′a	54	0.79	3.56	3.50	3.32	363
IIIB′b	41	0.74	3.70	3.65	3.51	375
IIIB′c	48	0.94	3.84	3.80	3.67	369
IIIB′d	58	0.38	4.13	4.07	3.88	380
IIIB′e	45	0.48	4.10	4.04	3.91	372
IIIB′f	36	0.61	3.76	3.72	3.59	375
IIIB′g	42	0.64	3.87	3.82	3.68	370
PMDA–ODA	31	0.67	4.28	4.23	4.04	443

[a] The poly(ether imide)s were obtained by the thermal imidization method.
[b] Taken from the UV–vis spectra of the poly(ether imide) films. The data in parentheses are for the poly(ether imide) films prepared by the chemical imidization method.

whereas **IIIAe** and **IIIBe** exhibited the highest T_g values in each series because of the presence of a rigid tetramethylbiphenyl unit in the diamine moiety. Moreover, **IIIAg** and **IIIBg** also showed moderately high T_g values because of the presence of rigid 9,9-diphenylfluorene moieties in the main chains. In addition, the 2,7-naphthalenediyl **IIIB** series polymers showed a slightly lower T_g value than the respective isomeric 2,6-naphthalenediyl **IIIA** series polymers, and this is possibly attributable to a higher chain flexibility in the former. In comparison with the analogous nonfluorinated poly(ether imide)s, some fluorinated poly(ether imide)s, such as **IIIAa**, **IIIAd**, **IIIAf**, **IIIAg**, and **IIIBg**, exhibited a lower T_g, which might have been a result of reduced interchain interactions and poor chain packing due to the bulky pendant CF_3 groups. For comparison, a

poly(ether imide) with a structure similar to that of commercial Ultem 1000 was prepared from bisphenol A bis(ether anhydride) and m-phenylenediamine, and its thermal properties were characterized. As shown in Table 4, most of the poly(ether imide)s prepared in this work showed T_g values higher than that of Ultem 1000.

The temperatures of 10% weight loss in nitrogen and air atmospheres were determined from original TGA thermograms. Typical TGA curves of polymers **IIIAg** and **IIIBg**, together with Ultem 1000, are illustrated in Figure 4. Polymers **IIIAg** and **IIIBg** showed better stability than Ultem. The temperatures of 10% weight loss of the **IIIA** series in nitrogen and air stayed within 491–585 and 489–560 °C, and for the **IIIB** series, they remained within 503–591 and 483–568 °C. They all left more than 50% char yield at 800 °C

in nitrogen. It is quite reasonable that methyl- or *tert*-butyl-substituted poly(ether imide)s such as **IIIAc**, **IIIAe**, **IIIBc**, and **IIIBe** began to decompose at lower temperatures than the unsubstituted ones. The TGA data indicated that these fluorinated poly(ether imide)s had fairly high thermal stability, regardless of the introduction of CF_3 groups. These poly(ether imide)s were highly thermostable and exhibited a large interval between the decomposition temperatures and T_g's, which may be useful for their thermal processing.

The transmission UV–vis spectra were measured for tough and flexible films of all the poly(ether imide)s. Typical UV–vis spectra of some representative polymer films are illustrated in Figure 5. All the fluorinated poly(ether imide) films exhibited a cutoff (absorption-edge) wavelength (λ_0) shorter than 400 nm and were entirely transparent and nearly colorless. Almost all the CF_3-containing poly(ether imide)s revealed a lower λ_0 value and higher optical transparency than the CF_3-free analogues. The λ_0 values of the **IIIA** and **IIIB** series polymers were in the ranges of 376–386 and 364–377 nm, respectively (Table 5). The slightly higher λ_0 values of the thermally imidized poly(ether imide) films might be a result of thermal oxidation of chain-end amino groups. The bulky and electron-withdrawing CF_3 group in the bis(ether amine) moieties was presumably effective in decreasing CT complexes between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). The electron-donating ether groups in the dianhydride component also contributed toward decreasing the overall electron affinity of the phthalimide units and subsequently lowering the intra- and intermolecular CT interactions. It also can be seen from Table 5 that the 2,7-catenated **IIIB** series poly(ether imide)s showed a lower λ_0 value and slightly higher optical transparency than their 2,6-catenated **IIIA** counterparts. This can be attributable to the fact that 2,7-catenation may reduce the conjugation length and chain packing efficiency, leading to a further decrease in the color intensity.

The dielectric constants and water absorption of all the poly(ether imide) films are also reported in Table 5. For comparison, the data of a standard polyimide film from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) are also given in Table 5. The **IIIA** and **IIIB** series poly(ether imide)s exhibited dielectric constants at 1 MHz in the ranges of 3.09–3.70 and 2.94–3.49, respectively, which are lower than those of the corresponding nonfluorinated poly(ether imide)s and the standard PMDA–ODA polyimide. The decreased dielectric constants could be explained by the attribution of the bulky $—CF_3$ substituents in the polymer backbone, which has low polarizability and can increase the free volume of the polymer chain. As expected, the fluorinated poly(ether imide)s exhibited lower water absorption (0.14–0.61%) than the corresponding nonfluorinated analogues (0.38–0.94%) because of the hydrophobic nature of the CF_3 group. The low water absorptions ensured that these polymers had stable dielectric performance.

CONCLUSIONS

Two series of novel fluorine-containing poly(ether imide)s, **IIIA** and **IIIB**, were prepared from **A** and **B**, respectively, with various fluorinated aromatic bis(ether amine)s via the thermal and chemical imidization method. These poly(ether imide)s were characterized by high solubility, good film-forming capability, low color, high optical transparency, high thermal stability, and low dielectric constants and water absorption. Thus, these poly(ether imide)s demonstrated a good combination of properties and may be of interest for optical or optoelectronic applications.

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