Aromatic Poly(ether imide)s Bearing Isopropylidene or Hexafluoroisopropylidene Links in the Main Chain

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ABSTRACT: Two bis(ether anhydride) monomers, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**4**) and 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (**4-F**), were synthesized from readily available compounds in three steps in high yields. Two series of poly(ether imide)s 7_{a-g} and 7_{a-g}-F based on dianhydrides **4** and **4-F**, respectively, were synthesized by a conventional two-step procedure that included a ring-opening polyaddition to give poly(amic acid)s, followed by cyclodehydration to polyimides. The intermediate poly(ether amic acid)s and the poly(ether imide)s had inherent viscosities in the range of 0.29—1.09 $dL\,g^{-1}$ and 0.21—0.98 $dL\,g^{-1}$, respectively. Except for the poly(ether imide)s derived from benzidine, the others afforded flexible and tough films. Most of the obtained poly(ether imide)s are organic-soluble. The glass transition temperatures (T_g) of these polymers ranged from 204 to 259°C. Degradation temperatures for 10% weight loss all occurred above 505°C in nitrogen and above 501°C in air. Fluorine-containing poly(ether imide)s showed higher solubility, T_gs and degradation temperatures in nitrogen, as compared to their respective nonfluorine-containing counterparts.
KEY WORDS   Poly(ether imide)s / Fluorinated Polyimides / Isopropylidene / Hexafluoroisopropylidene /

Aromatic polyimides are well known as high-performance polymer materials for their excellent mechanical and electrical properties, high thermal and thermo-oxidative stability, and outstanding solvent resistance.[1,2] A large number of polyimides with unique properties have been introduced for various industrial applications since their commercialization in the beginning of the 1960's. However, aromatic polyimides have one major disadvantage of typically being insoluble and intractable after conversion from the poly(amic acid) to the polyimide form. Most conventional processing techniques involve the fabrication of poly(amic acid) precursors followed by thermal or chemical imidization. Problems can arise because the poly(amic acid)s are thermally and hydrolytically unstable. The water evolved from imidization can also form voids in bulk materials.

Thus, many attempts have been made to improve the processing properties of aromatic polyimides, particularly their solubility and fusibility, by incorporating ether or other flexibilizing linkages into the main chain.[3-8] Considerable attention has been devoted lately to the synthesis of fluorine-containing polyimides, particularly to those with hexafluoroisopropylidene (6F) groups.[9-15] Frequently, the incorporation of 6F groups into a polymer backbone will improve the solubility and other properties such as flame retardance, thermal stability, oxidative resistance, and environmental stability, while there is often a decrease in color, crystallinity, dielectric constant, and moisture absorption.

In the present study, the synthesis and characterization of fluorine and nonfluorine-containing poly(ether imide)s are reported giving particular attention to their solubility and thermal properties. The differences in physical properties upon fluorination are investigated by using 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (**4-F** as shown in Scheme 1) and the corresonding nonfluorine-containing monomer.

EXPERIMENTAL

Materials

The reagents employed in the syntheses of bis(ether anhydride)s **4** and **4-F** including 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) (**1**) (TCI), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF) (**1-F**) (Chriskev), toluene (Alps), potassium carbonate (K_2CO_3; Fluka), *N*,*N*-dimethylformamide (DMF; Fluka), potassium hydroxide (Wako), and acetic anhydride (Janssen) were used without previous purification. *p*-Phenylenediamine (**5a**) (Wako) was purified by sublimation. *m*-Phenylenediamine (**5b**) (Janssen) was vacuum-distilled prior to use. Benzidine (**5c**) (TCI) was recrystallized from the mixture of ethanol and benzene. 4,4'-Bis(4-aminophenoxy)biphenyl (**5g**) (mp 198—199°C) was prepared by a reported method[16] that involved the nucleophilic substitution reaction of 4,4'-biphenol with *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction of the intermediate dinitro compound using hydrazine as the reducing agent and palladium as the catalyst. The other diamines such as 4,4'-diaminodiphenylmethane (**5d**) (TCI), 4,4'-diaminodiphenyl ether (**5e**) (TCI), and 1,4-bis(4-aminophenoxy)benzene (**5f**) (TCI) were used as received. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored in the presence of 4 Å molecular sieves.

Monomer Synthesis

2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane (**2-F**). In a 300-mL flask, 25 g (0.074 mol) of bisphenol AF (**1-F**) and 20.55 g (0.148 mol) of K_2CO_3 were suspended in a mixture of 200 mL of DMF and 70 mL of toluene. The suspension solution was heated at a reflux temperature using a Dean-Stark trap to remove the water azeotropically. After complete removal of water, the residual toluene was distilled off. Then, the reaction mixture was cooled to about 60°C, and 26.5 g

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(0.15 mol) of 4-nitrophthalonitrile was added and heating was continued at 60°C for 24 h. After cooling, the reaction mixture was poured into 700 mL of water, and the precipitated light yellow solid was collected and washed thoroughly with methanol and water. The yield of the crude product was quantitative. The crude product was purified by recrystallization from acetonitrile. The yield of the purified product was 31 g (71%); mp 230°C. The IR spectrum (KBr) exhibited absorptions at 2238 ($C\equiv N$ str.), 1591—1487 (arom. $C=C$ str.), 1249 (C–O–C str.) and 1210 cm^{-1} (C–F str.).

Anal. Calcd for $C_{31}H_{14}N_4O_2F_6$ (588.47): C, 63.27%; H, 2.40%; N, 9.52%. Found: C, 62.90%; H, 2.52%; N, 9.44%.

2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]propane (**2**) was synthesized starting from bisphenol A (**1**) and 4-nitrophthalonitrile in an analogous procedure. Yield (after recrystallization): 28.57 g (67%); mp 185—187°C.

IR (KBr): 2232 ($C\equiv N$ str.), 1591—1486 (arom. $C=C$ str.) and 1252 cm^{-1} (C–O–C str.).

Anal. Calcd for $C_{31}H_{20}N_4O_2$ (483.55): C, 74.52%; H, 4.17%; N, 11.59%. Found: C, 74.47%; H, 4.35%; N, 11.65%.

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane (**3-F**). In a 1000-mL flask, a suspension of bis(ether dinitrile) **2-F** (30 g; 0.051 mol) in an ethanol–water mixture (200 : 200 mL) containing dissolved 57.2 g (1.02 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 2 h. Reflux was continued for about 24 h until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and acidified by conc HCl to pH = 1–2 while stirred. The product phased out in the bottom of the beaker as a viscous lump, which was washed repeatedly with water and dried. The resulting bis(ether acid) **3-F** was not purified and not characterized in detail but was used directly in the synthesis of bis(ether anhydride) **4-F**.

IR (KBr): 2400—3600 (O–H str.), 1717 (C=O str.), 1244 cm^{-1} (C–O–C str.).

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane (**3**) was prepared from the alkaline hydrolysis of corresponding bis(ether dinitrile) **2** in a similar procedure. The bis(ether diacid) **3** was not characterized and were used directly in the synthesis of bis(ether anhydride) **4**.

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (**4-F**). In a 1000-mL flask, bis(ether diacid) **3-F** was suspended in 300 mL of acetic anhydride. The suspension was boiled under reflux until turning into a clear solution. The resulting hot, clear solution was filtered to remove any insoluble impurities. On cooling, the bis(ether anhydride) started to crystallize and next day the product was filtered off, washed with dry toluene, and dried *in vacuo*, to give 16.9 g yield. The filtrate was concentrated to about 1/3 its original volume, and another 12.5 g of the product was collected. Thus, a total yield was about 92% theoretically. The mp of **4-F** was 228°C.

IR (KBr): 1854 (asym. C=O str.), 1783 (sym. C=O str.), 1595—1483 (arom. $C=C$ str.), 1288 (C–O–C str.), and 1207 cm^{-1} (C–F str.).

Anal. Calcd for $C_{31}H_{14}O_8F_6$ (628.44): C, 59.25%; H,

2.25%. Found: C, 58.02%; H, 2.29%.

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**4**) was prepared from the dehydration of corresponding bis(ether diacid) **3** in a similar method. Yield, 20.06 g (66%); mp 182—184°C.

IR (KBr): 1849 (asym. C=O str.), 1781 (sym. C=O str.), 1619—1479 (arom. $C=C$ str.), and 1285 cm^{-1} (C–O–C str.).

Anal. Calcd for $C_{31}H_{20}O_8$ (520.49): C, 71.54%; H, 3.87%. Found: C, 70.37%; H, 3.79%.

Synthesis of Poly(ether imide)s

A typical polymerization procedure is as follows. 4,4′-Diaminophenyl ether (**5$_e$**) (0.2417 g; 1.21 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.7583 g (1.21 mmol) of bis(ether anhydride) **4-F** was added in one portion. The mixture was stirred at room temperature for 3 h. The inherent viscosity of the resulting poly(ether amic acid) (**6$_e$-F**) was 0.50 dL g^{-1}, as measured in DMAc at a concentration of 0.5 g dL^{-1} at 30°C. The polymer solution was poured into a 9-cm glass culture dish, which was placed in a 90°C oven overnight to remove the solvent. The semi-dried poly(ether amic acid) film was further dried and transformed into poly(ether imide) by sequential heating at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min, and 250°C for 30 min. By soaking in hot water, a flexible poly(ether imide) film of **7$_a$-F** self-stripped off from the glass surface.

All other poly(ether imide)s were prepared by an analogous procedure.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer at the National Taiwan University (Taipei). The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 30°C. A Sinku Riko DSC-7000 thermal differential scanning calorimeter equipped with a Sinku Riko TA-7000 analyzer was used to determine the thermal transitions. Heating rate was 20°C min^{-1}. Glass transition temperatures (T_gs) were read at the middle of the change in the heat capacity, and were taken from the second heating scan after quick cooling. Thermogravimetry (TG) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 9—11 mg samples heated in flowing nitrogen or air (50 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu-K_α radiation (40 kV, 15 mA). The scanning rate was 2° min^{-1} over a range of 2θ = 5—40°. An Instron universal tester Model HT-9102 (Hung Ta Instrument Co., Taiwan) with a load cell 100 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a crosshead speed of 5 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.1 mm thick). An average of at least five individual determinations was used.
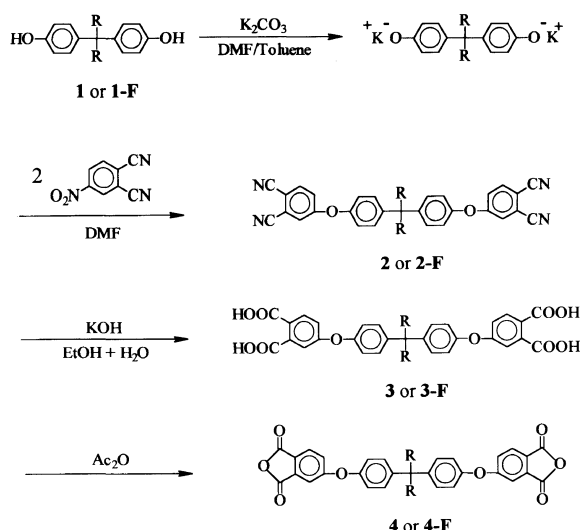
1, 2, 3, 4: R= —CH$_3$

1-F, 2-F, 3-F, 4-F: R= —CF$_3$

Scheme 1. Preparation of bis(ether anhydride)s.

4, 6, 7: R= —CH$_3$

4-F, 6-F, 7-F: R= —CF$_3$

Ar :

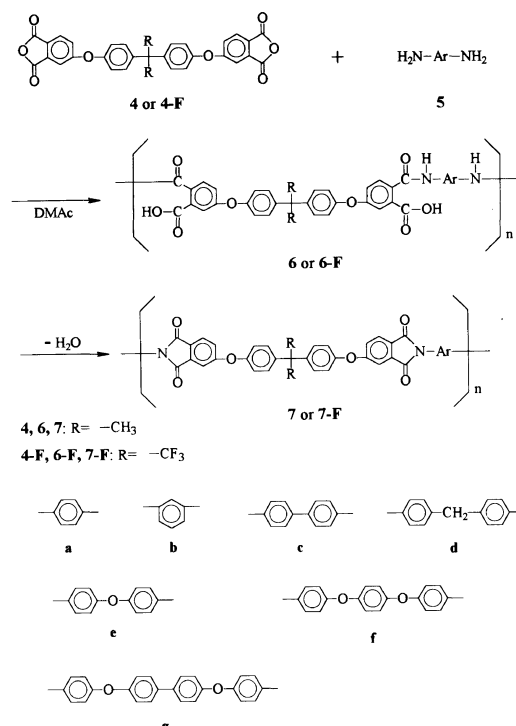**Scheme 2.** Preparation of poly(ether imide)s.

RESULTS AND DISCUSSION

Monomer Synthesis

According to a reported method,[4] bis(ether anhydride)s **4** and **4-F** were prepared using a three-stage route starting from the nitro displacement reaction of the dipotassium phenolates of diols **1** or **1-F** with 4-nitrophthalonitrile (Scheme 1). The yields in each step were high, and the structure of bis(ether anhydride)s was confirmed by elemental analysis and infrared spectroscopy. The IR spectra of bis(ether dinitrile)s **2** and **2-F** were characterized by a sharp absorption near 2240 cm^{-1} due to the cyano group. The most characteristic bands of bis(ether anhydride)s **4** and **4-F** were observed near 1850 and 1780 cm^{-1}, pointing at the asymmetrical and symmetrical stretching vibrations of the cyclic anhydride carbonyl groups.
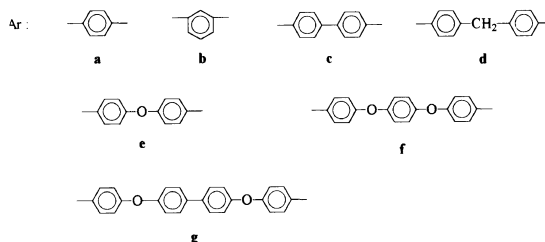
Synthesis of Poly(ether imide)s

Poly(ether imide)s **7$_{a-g}$** and **7$_{a-g}$-F** were synthesized from bis(ether anhydride)s **4** and **4-F**, respectively, with various aromatic diamines **5$_{a-g}$** by the conventional two-stage process, involving a ring-opening polyaddition and subsequent thermal cyclodehydration. The bis(ether anhydride)s were added to a solution of the diamines in DMAc at room temperature (Scheme 2). The solid content was maintained at 10 wt%. High molecular weight poly(ether amic acid) solution with inherent viscosities of 0.29—1.09 dL g^{-1} were obtained in 3 h. Transparent and flexible films of the poly(ether amic acid)s could be obtained by casting the resulting polymer DMAc solutions at 90°C for 24 h. Even those polymers having the lower viscosities (0.29 dL g^{-1}) gave quite flexible films, which can be explained by the presence of the isopropylidene or hexafluoroisopropylidene (6F) units and other flexible groups, such as ether, in the main chain. The thermal conversion to poly(ether imide)s was carried out by heating the poly(ether amic acid) films at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min,

and 250°C for 30 min. Completion of the imidization by the heating program was confirmed by dynamic thermogravimetry of a sample of the poly(ether amic acid). It was found that the weight loss was complete around 230°C, and the thermogravimetry curve of a sample showed no difference from the curve of a sample imidized as a film on a glass substrate. More rapid temperature elevation resulted in cracked or brittle films. The films of poly(ether imide)s **7$_c$** and **7$_c$-F** embrittled during thermal imidization, probably due to the presence of the rigid 4,4'-bis(phthalimido)biphenylene moiety in their macromolecular backbones. The other poly(ether imide) films were transparent, flexible, and tough. Poly(ether imide)s **7$_{d-g}$** and **7$_{e-f}$-F** were readily soluble in polar solvents like DMAc, and **7$_{a-d}$-F** were soluble in concentrated sulfuric acid. Therefore, the characterization of inherent viscosity was carried out without any difficulty, and the inherent viscosities of these poly(ether imide)s were in the range of 0.29—0.98 dL g^{-1}. Poly(ether imide)s **7$_{a-c}$** were insoluble in organic solvents, and they readily decomposed in concentrated sulfuric acid due to the presence of isopropylidene groups. Therefore, no attempts was made to characterize their inherent viscosities.

IR spectroscopy allows monitoring of the imide ring formation during curing. As the poly(ether amic acid) was converted into the poly(ether imide), the characteristic absorption bands of the imide ring were observed near 1780 (asym. C=O str.), 1720 (sym. C=O str.), 1390 (C–N str.), 1100 and 720 cm^{-1} (imide ring deformation), and those of amide and carboxyl groups in the regions of 2500—3500 cm^{-1} and 1500—1730 cm^{-1} disappeared.

Properties of Poly(ether imide)s

Solubility of poly(ether imide)s was studied qualitatively, and the results are listed in Table II. The solubilities

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Table I. The inherent viscosities and film quality of poly(ether amic acid)s and poly(ether imide)s

Poly(ether amic acid)			Poly(ether imide)		
Code	η_{inh}[a] /dL g^{-1}	Film quality[b]	Code	η_{inh} /dL g^{-1}	Film quality[e]
6_a	0.51	F	7_a	—[c]	F
6_b	0.29	F	7_b	—[c]	F
6_c	0.79	F	7_c	—[c]	B
6_d	0.36	F	7_d	0.60[a]	F
6_e	0.73	F	7_e	0.56[a]	F
6_f	0.84	F	7_f	0.87[a]	F
6_g	1.09	F	7_g	0.98[a]	F
6_a-F	0.29	F	7_a-F	0.29[d]	F
6_b-F	0.29	F	7_b-F	0.28[d]	F
6_c-F	0.42	F	7_c-F	0.21[d]	B
6_d-F	0.42	F	7_d-F	0.63[d]	F
6_e-F	0.50	F	7_e-F	0.68[a]	F
6_f-F	0.36	F	7_f-F	0.72[a]	F
6_g-F	0.45	F	7_g-F	0.92[a]	F

[a] Measured in DMAc on $0.5\,\text{g}\,\text{dL}^{-1}$ at 30°C. [b] Films were cast by slow evaporation of polymer solutios in DMAc. [c] Insoluble in DMAc and decomposed in H_2SO_4. [d] Measured in concentrated H_2SO_4 on $0.5\,\text{g}\,\text{dL}^{-1}$ at 30°C. [e] Films were obtained by sequential heating of the poly(ether amic acid) films at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min, and 250°C for 30 min. B, brittle; F, flexible.

Table II. Solubility of poly(ether imide)s[a]

Polymer code	Solvent[b]					
	NMP	DMAc	DMF	DMSO	m-Cresol	THF
7_a	—	—	—	—	—	—
7_b	—	S	—	—	—	—
7_c	—	—	—	—	—	—
7_d	+	+h	—	—	+	—
7_e	+	+	—	—	+	—
7_f	+	+h	S	—	+	S
7_g	+	+	S	—	+	S
7_a-F	S	—	S	S	S	S
7_b-F	S	S	S	S	S	S
7_c-F	+h	—	—	—	+h	—
7_d-F	+	+h	+	+h	+h	+
7_e-F	+	+	+	—	+h	+
7_f-F	+	+	+	+h	+h	+
7_g-F	+	+	+	—	—	+

[a] +, soluble at room temperature; +h, 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; THF, tetrahydrofuran.

Table III. Tensile properties of poly(ether imide) films[a]

Polymer code	Strength at yield	Strength at break	Elongation at break
	MPa	MPa	%
7_a	—	90	9
7_b	—	80	6
7_d	—	83	9
7_e	—	79	6
7_f	91	76	25
7_g	80	83	24
7_a-F	—	103	11
7_b-F	—	105	7
7_d-F	—	167	12
7_e-F	—	100	10
7_f-F	97	96	11
7_g-F	83	96	12

[a] The films of 7_c and 7_c-F were too brittle to test.

Table IV. Thermal behavior data of poly(ether imide)s

Polymer code	T_g[a]	Decomposition temperature[b]/°C		Char yield[c]
	°C	In N_2	In air	%
7_a	217	522	520	58.0
7_b	212	505	501	54.5
7_c	243	522	521	62.7
7_d	211	512	517	59.0
7_e	210	527	527	52.6
7_f	204	519	524	54.1
7_g	214	526	529	56.4
7_a-F	250	525	515	54.2
7_b-F	239	512	512	51.9
7_c-F	259	536	529	58.3
7_d-F	236	516	512	56.9
7_e-F	236	521	516	51.7
7_f-F	220	527	522	56.3
7_g-F	228	526	511	56.5

[a] Midpoint of baseline shift in the second heating DSC trace, with a heating rate of $20°C\,min^{-1}$ in nitrogen. [b] Tempertures at which 10% weight loss were recorded by TG at a heating rate of $20°C\,min^{-1}$. [c] Residual weight % at 800°C in nitrogen.

of these polymers are partially dependent on the diamine components. Those derived from rigid diamines like p-phenylenediamine and benzidine, such as polymers 7_a, 7_c, 7_a-F, and 7_c-F, were almost all insoluble in all the solvents tested. This can be attributable to the existence of the rigid planar 1,4-bis(phthalimido)phenylene or 4,4'-bis(phthalimido)biphenylene units in their polymer backbones, which may lead to a higher packing density of polymer chains. The poly(ether imide)s 7_b and 7_b-F based on m-phenylenediamine also revealed poor solubility. However, introduction of flexible kinks in the diamine components led to an enhanced solubility. Almost all the polymers derived from flexible diamines were soluble in polar solvents such as NMP, DMAc, and m-cresol. As compared to the nonfluorine-containing counterparts, the 6F-containing poly(ether imide)s

revealed an increased solubility. For example, most of polymers 7_{d-g}-F were also soluble in DMF and DMSO and even in less polar solvents like tetrahydrofuran (THF). It thus appears that the presence of the bulky flexible $-C(CF_3)_2-$ groups induces loose chain packing and, consequently, the solvent molecules can penetrate easily to solubilize the polymer chains.

The crystallinity of the poly(ether imide)s was examined by wide-angle X-ray diffraction. All the polymers, even those obtained from p-phenylenediamine and benzidine, showed amorphous patterns. The amorphous nature of these polymers can be mainly explained by the presence of flexible ether and isopropylidene or 6F linkages in the polymer backbone. Except for the benzidine-derived poly(ether imide)s 7_c and 7_c-F, all the poly(ether imide)s could be processed into flexible and tough films. The tensile properties of these flexible films are given in Table III. The films of nonfluorine-containing polymers 7_{a-g} had a tensile strength of 76—90 MPa and an elongation at break of 6—25%. Polymers 7_f and 7_g, which were derived from the bisphenol A bis(ether anhydride) with 1,4-bis(4-aminophenoxy) benzene (5_f)
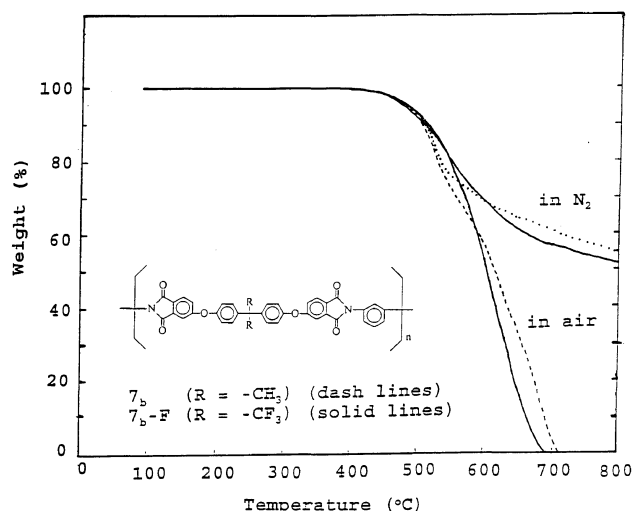
Figure 1. TG thermograms of poly(ether imide)s 7_b and 7_b-F.

and 4,4'-bis(4-aminophenoxy)biphenyl (5_g), respectively, behaved as a ductile material; they necked during testing and had a moderate elongation at break. The films of 6F-containing polymers 7_{a-g}-F exhibited a higher strength compared to those of nonfluoro polymers. They had tensile strengths in the range of 96—167 MPa and elongations at break between 7—12%. The poly(ether imide)s 7_f-F and 7_g-F obtained from diamines 5_f and 5_g also necked under tension; however, they showed a lower elongation at break than the corresponding nonfluoro polymers.

The thermal properties of the obtained poly(ether imide)s were investigated by differential scanning calorimetry (DSC) and dynamic TG. The results are summarized in Table IV. All the polymers were rapidly cooled from elevated temperatures at approximately 400°C to room temperature to form predominantly amorphous samples, and thus, distinct glass transitions could be observed on the subsequent heating DSC traces. The 7 series and 7-F series poly(ether imide)s exhibited T_gs in linkages into the polymer chain resulted in a decrease in T_g. Poly(ether imide)s 7_{a-g}-F revealed higher T_gs than the corresponding nonfluorinated 7_{a-g} by about 14—23°C, which may be due to the bulky structure of the 6F group which retards the segmental mobility and hence leads to a higher T_g. For example, the 6F-containing poly(ether imide) 7_b-F ($T_g = 239°C$) showed higher T_g by 17°C than the corresponding 7_b ($T_g = 212°C$), a poly(ether imide) with the same structure as Ultem®1000.

As a representative example, the TG thermograms of poly(ether imide)s 7_b and 7_b-F are reproduced in Figure 1. All the other poly(ether imide)s showed similar patterns of degradation with no significant weight loss before 500°C in air or nitrogen, but with more than 50 wt% residue remaining when heated to 800°C in nitrogen. The data reported in Table IV show that the 10% weight loss temperatures of poly(ether imide)s 7_{a-g}-F were recorded in the range of 512—536°C in nitrogen and 512—529°C in air, and those of poly(ether imide)s 7_{a-g} were recorded in the range of 505—527°C in nitrogen and 501—529°C in air. In nitrogen atmosphere, all the

fluorine-containing poly(ether imide)s showed a slightly higher 10% weight loss temperature than their non-fluorine-containing counterparts, possibly due to the high C–F and C–CF$_3$ bond strengths. However, in air atmosphere, most of the isopropylidene-containing poly(ether imide)s showed a slightly higher value compared to their respective 6F-based counterparts. This may be explained by the fact that the polymers with aliphatic segments gain weight as they are oxidized, then rapidly lose weight as they degrade. Furthermore, it can also be noticed that there is a large window between the T_g and the decomposition temperature, which could be advantageous in the processing of these polymers.

CONCLUSIONS

Two series of poly(ether imide)s have been synthesized from the bis(ether anhydride)s containing the isopropylidene or hexafluoroisopropylidene group with aromatic diamines *via* a conventional two-step polymerization. Most of the poly(ether imide)s afforded flexible and tough films, even though some of them had low inherent viscosities. The obtained fluorine and nonfluorine-containing poly(ether imide)s had T_g values higher than 200°C and were thermally stable, with 10% weight loss temperatures being recorded above 500°C. The fluoro poly(ether imide)s showed a higher T_g and an increased solubility compared to the corresponding nonfluoro polymers.

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