

Synthesis and Characterization of Polyimides Based on Isopropylidene-containing Bis(ether anhydride)s

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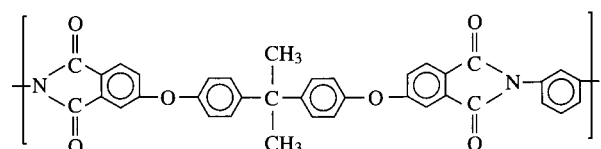
Abstract: Two bis(ether anhydride)s, 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]-diphthalic anhydride (**IV_a**) and 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalic anhydride (**IV_b**), were prepared in three steps starting from the nucleophilic nitrodisplacement reaction of 4-nitrophthalonitrile with α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**I_a**) and 4,4'-isopropylidenediphenol (**I_b**) in *N,N*-dimethylformamide (DMF) in the presence of potassium carbonate. The bis(ether anhydride)s **IV_a** and **IV_b** were polymerized with various aromatic diamines to obtain two series of poly(ether amic acid)s **VI_{a-g}** and **VII_{a-g}** with inherent viscosities in the range of 0.30~0.74 and 0.29~1.01 dL/g, respectively. The poly(ether amic acid)s were converted to poly(ether imide)s **VIII_{a-g}** and **IX_{a-g}** by thermal cyclodehydration. Most of the poly(ether imide)s could afford flexible and tough films, and they showed high solubility in polar solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide, and *m*-cresol. The obtained poly(ether imide) films had tensile strengths of 45~83 MPa, elongations-to-break of 6~27%, and initial modulus of 0.6~1.7 GPa. The T_g s of poly(ether imide)s **VIII_{a-g}** and **IX_{a-g}** were in the range of 194~210 and 204~243 °C, respectively. Thermogravimetric analysis (TG) showed that 10% weight loss temperatures of all the polymers were above 500 °C in both air and nitrogen atmospheres.

Keywords: Bis(ether anhydride), Isopropylidene, Nucleophilic nitrodisplacement reaction, Poly(ether imide)s.

Introduction

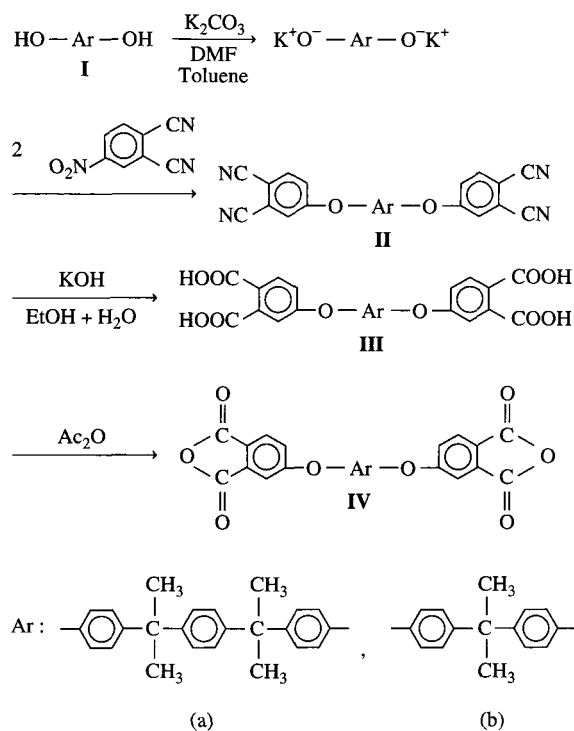
Aromatic polyimides are condensation polymers that are normally synthesized from tetracarboxylic dianhydrides and aromatic diamines. The heterocyclic imide unit imparts interchain interactions. The polymers exhibit excellent mechanical and electrical properties and outstanding thermal stability and chemical resistance [1-6]. This combination of properties, however, makes them essentially difficult to fabricate. Thus, they must be processed in the form of their soluble poly(amic acid) precursors, which are subsequently imidized in situ. However, drawbacks can arise because the poly(amic acid)s are thermally and hydrolytically unstable. The water released from imidization can create microvoids in bulk materials. Even in the production of thin films, the thermal imidization must be carefully controlled in order to minimize depolymerization and maximize the degree of imidization.

Thus, there has been considerable research carried out aimed at developing aromatic polyimides that are processable in the imide form [7-12]. Most of the structural modifications that have been used to attain processability have involved an increase in chain flexibility. General Electric developed novel chemistry leading to poly(ether imide)s [13, 14]. Their research resulted in the commercial polymer designated as Ultem 1000, which was made from bisphenol A bis(ether anhydride) (see structure **IV_b** in Scheme 1) and *m*-phenylenediamine.



Ultem 1000

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The polymer, despite its lack of crystallinity, has a reasonable level of thermal stability. It has been evaluated as a composite matrix, particularly when reinforced with glass-fiber. Among Ultem's advantages are its medium-high T_g (220 °C) and its good mechanical properties.

The search for new polyimides with improved processability, for example better flow properties than Ultem 1000, has been a continuing since the commercialization of Ultem 1000. α,α' -Bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**I_a**) exhibits one more cumyl unit than bisphenol A in its molecular structure. The present article deals with the synthesis and basic characterization of poly(ether imide)s based on the bis(ether anhydride) derived from bisphenol **I_a**. For the purposes of comparative study, the analogues based on bisphenol A bis(ether anhydride) are also synthesized and characterized. It is expected that the incorporation of one more cumyl group into the recurring unit of the polymer chain will lead to better flow properties and will facilitate resin penetration into the fiber bundle during the preparation of prepregs.

Experimental

1. Materials

α,α' -Bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**I_a**) (Mitsui Petrochemical Ind.), 4,4'-

isopropylidenediphenol (bisphenol A) (**I_b**) (TCI), potassium carbonate (K_2CO_3) (Fluka), 4-nitrophthalonitrile (TCI), *N,N*-dimethylformamide (DMF) (Fluka), acetonitrile (TEDIA), acetic anhydride (Janssen) were used without previous purification. *p*-Phenylenediamine (**V_a**) (TCI) was purified by vacuum sublimation. *m*-Phenylenediamine (**V_b**) (Janssen) was purified by vacuum distillation. Benzidine (**V_c**) was recrystallized from an ethanol/benzene mixture prior to use. 4,4'-Oxydianiline (**V_e**) (TCI), 4,4'-diaminodiphenylmethane (**V_d**) (TCI), and 1,4-bis(4-aminophenoxy)benzene (**V_f**) (TCI) were used as received. According to the method described in a previous publication [15], 4,4'-bis(4-aminophenoxy)biphenyl (**V_g**) (mp 198~199 °C) was synthesized by the aromatic nucleophilic substitution reaction of 4,4'-biphenol and *p*-chloronitrobenzene in the presence of potassium carbonate, followed by hydrazine catalytic reduction of the intermediate dinitro compound.

2. Monomer synthesis

(1) Syntheses of 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalodinitrile (**II_a**) and 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalodinitrile (**II_b**)

In a 1000 mL flask, 17.3 g (0.05 mol) of α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**I_a**) and 13.8 g (0.1 mol) of K_2CO_3 were suspended in a DMF/toluene (100 mL/60 mL) mixture and heated at reflux temperature using a Dean-Stark trap to remove the water azeotropically. After the water was removed completely, 17.3 g (0.1 mol) of 4-nitrophthalonitrile was added and heating was continued at 60 °C for 24 h. Then the reaction mixture was poured into 700 mL of water, and the precipitated light brown solid was collected by filtration and dried. Yield was 14.9 g (99 %). The crude product was recrystallized from acetonitrile to afford **II_a** of light yellow needles. The yield of purified product was 13.2 g (88 %); mp. 208~211 °C.

IR (KBr): 2230 (C≡N) and 1249 (C–O) cm^{-1} .

Anal. Calcd for $C_{40}H_{30}N_4O_2$ (598.69): C, 80.24%; H, 5.05%; N, 9.35%. Found: C, 79.98%; H, 5.30%; N, 9.21%.

4,4'-[Isopropylidenebis(1,4-phenylene)dioxy]diphthalodinitrile (**II_b**) was synthesized following a similar procedure from 4,4'-isopropylidenediphenol and 4-nitrophthalodinitrile. The product was recrystallized from acetonitrile to yield light yellow crystals. Yield 67 %; mp. 185~187 °C.

IR (KBr): 2232 (C≡N) and 1252 (C–O) cm^{-1} .

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) Syntheses of 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalic anhydride (**IV_a**) and 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalic anhydride (**IV_b**)

In a 500 mL flask, a suspension of bis(ether dinitrile) **II_a** (13 g; 0.02 mol) in an ethanol/water mixture (100 mL/100 mL) containing dissolved 57.7 g (1.03 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 3 h. Reflux was continued for a further 20 h until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any possible insoluble impurities. The hot filtrate was allowed to cool and acidified by concentrated HCl to pH=3. The product phased out at the bottom of the beaker as a viscous lump, which was washed repeatedly with water and dried. The resulting bis(ether diacid) **III_a** was not characterized, but was used directly in the synthesis of bis(ether anhydride) **IV_a**.

In a 300 mL flask, bis(ether diacid) **III_b** was suspended in 100 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, bis(ether anhydride) started to crystallize and the next day the product was filtered off, washed with dry toluene, and dried in vacuo, to give 9.4 g (57.5 %) of bis(ether anhydride) **IV_a**; mp. 200~202 °C (DSC, 204 °C).

IR (KBr): 1847 (asym. C=O str.), 1787 (sym. C=O str.), 1618-1481 (arom. C=C), 1274 (C-O-C) cm^{-1} .

Anal. Calcd for $\text{C}_{40}\text{H}_{30}\text{O}_8$ (638.67): C, 75.23%; H, 4.73%. Found: C, 74.07%; H, 4.68%.

4,4'-[Isopropylidenebis(1,4-phenylene)dioxy]diphthalic anhydride (**IV_b**) was prepared from the hydrolysis of bis(ether dinitrile) **II_b** and subsequent dehydration of the resulting bis(ether diacid) **III_b** in a similar work-up procedure. Yield: 33%; mp. 182-184 °C.

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

Anal. Calcd for $\text{C}_{31}\text{H}_{20}\text{O}_8$ (520.49): C, 71.54%; H, 3.87%. Found: C, 69.37%; H, 3.79%.

3. Synthesis of poly(ether imide)s

A typical polymerization was undertaken as follows. In a 50 mL flask, 0.2386 g (1.2 mmol) of 4,4'-oxydianiline (**V_e**) was dissolved in 9 g of dried DMAc. After the diamine was dissolved completely, 0.7614 g (1.2 mmol) of bis(ether anhydride) **IV_a** was added in one portion. The mixture was stirred at room temperature for 2 h. The inherent viscosity of poly(ether amic acid) **VI_e** in DMAc was 0.74 dL/g, measured at a concentration of 0.5 g/dL at 30 °C.

IR (film): 3500-3000 (O-H and N-H str.), 1716 (C=O, carboxylic acid), 1659 (C=O, amide), and 1222 (C-O-C) cm^{-1} .

The poly(ether amic acid) solution obtained was poured into a $\Phi = 9$ cm glass culture dish, which was placed in a 80 °C oven overnight to remove the solvent. The 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, 200 °C for 20 min, 220 °C for 20 min, and 250 °C for 30 min. After soaking in hot water, a flexible poly(ether imide) film of **VII_e** self-stripped off from the glass surface.

IR (film): 1778 (asym. C=O str.), 1725 (sym. C=O str.), 1602-1478 (arom. C=C str.), 1379 (C-N), and 1243 (C-O) cm^{-1} .

Other poly(ether imide)s were synthesized by an analogous procedure.

4. Measurements

IR spectra were recorded on a Jasco IR-700 infrared spectrometer. The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 30 °C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 analyzer was used to determine the thermal transitions (heating rate: 20 °C/min; flow rate of nitrogen: 30 cm^3/min). Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20 °C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25 °C) on a Rigaku Geiger-Flex D-Max III_a X-ray diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. An Instron universal tester Model 1130 with a load cell of 5 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 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.

Results and Discussion

1. Monomer synthesis

There are now many reports in the literature of bis(ether anhydride)s as precursors to high-molecular-weight poly(ether imide)s synthesized starting from nitrodisplacement reactions between aromatic

diols or their sodium salts, and nitrophthalic acid derivatives or nitrophthalonitrile [13, 16-22]. According to one reported method [22], the bis(ether anhydride) **IV_a** and **IV_b** were prepared using the three-stage route shown in Scheme 1. The synthesis started from the nitrodisplacement reaction of 4-nitrophthalonitrile with α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**I_a**) or 4,4'-isopropylidenediphenol (**I_b**) to yield the bis(ether dinitrile)s 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalodinitrile (**II_a**) or 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalodinitrile (**II_b**). The bis(ether dinitrile)s were then hydrolyzed and dehydrated to yield bis(ether anhydride)s **IV_a** and **IV_b**. The structures of the intermediate bis(ether dinitrile)s and bis(ether anhydride)s were confirmed by elemental analysis and infrared spectroscopy. Figure 1 shows the IR spectra of bis(ether dinitrile) **II_a** and bis(ether anhydride) **IV_a**. The sharp absorption near 2230 cm^{-1} is peculiar to the $\text{C}\equiv\text{N}$ group in **II_a**, and the characteristic $\text{C}=\text{O}$ stretching absorptions of dianhydride **IV_a** appear around 1850 and 1780 cm^{-1} . The IR spectra of bis(ether dinitrile) **II_b** and bis(ether anhydride) **IV_b** are reproduced in Figure 2. The change of spectra due to the transformation of functional groups is very similar

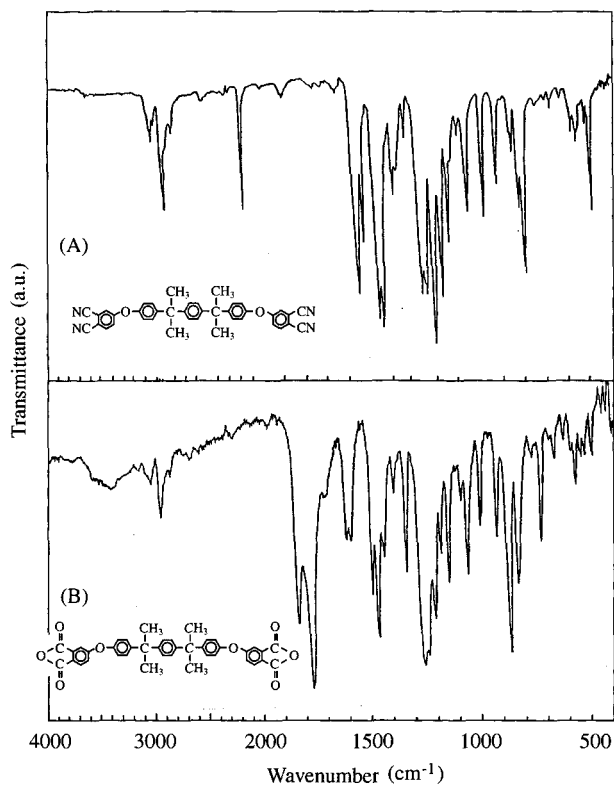


Figure 1. The IR spectra of 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalodinitrile (A) and 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalic anhydride (B).

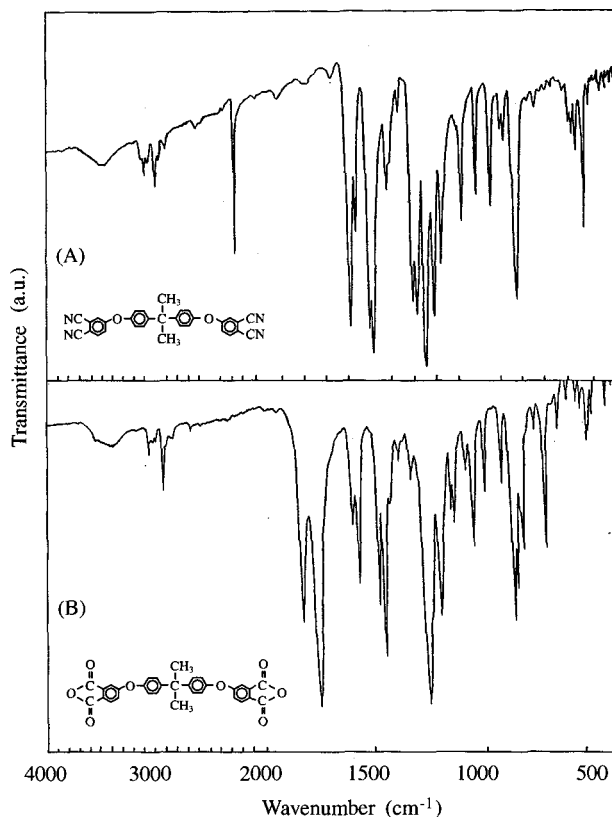
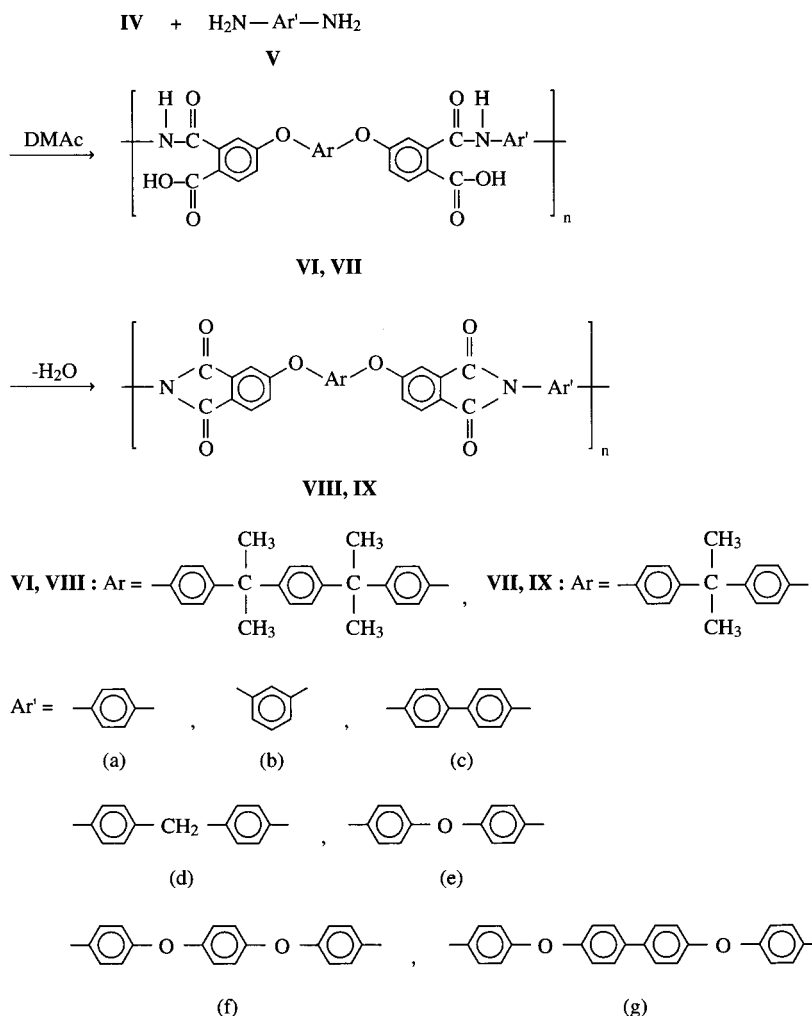


Figure 2. The IR spectra of 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalodinitrile (A) and 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalic anhydride (B).

to that observed in Figure 1.

2. Synthesis of poly(ether imide)s

All poly(ether imide)s **VIII_{a-g}** and **IX_{a-g}** were prepared from the synthesized bis(ether anhydride)s **IV_a** and **IV_b** with various aromatic diamines (**V_{a-g}**) by a conventional two-stage process as outlined in Scheme 2. The bis(ether anhydride) was first reacted with a diamine at room temperature in dry DMAc to form a viscous poly(ether amic acid) solution. As shown in Table I, the inherent viscosities of the resulting two series of poly(ether amic acid)s, **VI_{a-g}** and **VII_{a-g}**, are in the range of 0.34~0.74 dL/g and 0.29~1.09 dL/g, respectively. The molecular weights of these poly(ether amic acid)s are high enough to permit the casting of tough and flexible films. All the poly(ether amic acid) films were transformed to the poly(ether imide) films by sequential heating to 250 °C, and the film properties of these poly(ether imide)s are also listed in Table I. Except for the films obtained from poly(ether imide)s **VIII_c** and **IX_c** derived from benzidine (**V_c**) which embrittled during cure, the others afforded flexible films. Figure 3 shows the IR spectra of the representative poly(ether amic acid) **VI_c** and poly(ether



Scheme 2

Table I. Preparation of poly(ether imide)s.

Poly(ether amic acid)		Poly(ether imide)		
Code	$\eta_{inh}^{(a)}$ (dL/g)	Code	$\eta_{inh}^{(a)}$ (dL/g)	Film quality
VI _a	0.49	VIII _a	— ^(b)	Flexible
VI _b	0.30	VIII _b	—	Flexible
VI _c	0.45	VIII _c	—	Brittle
VI _d	0.40	VIII _d	0.37	Flexible
VI _e	0.74	VIII _e	0.56	Flexible
VI _f	0.50	VIII _f	0.57	Flexible
VI _g	0.55	VIII _g	0.90	Flexible
VII _a	0.51	IX _a	—	Flexible
VII _b	0.29	IX _b	—	Flexible
VII _c	0.79	IX _c	—	Brittle
VII _d	0.36	IX _d	0.60	Flexible
VII _e	0.73	IX _e	0.56	Flexible
VII _f	0.84	IX _f	0.87	Flexible
VII _g	1.09	IX _g	0.98	Flexible

(a) Measured at concentration of 0.5 g/dL in DMAc at 30 °C.

(b) Insoluble in DMAc.

imide) VIII_e. When the poly(ether amic acid) was converted into the poly(ether imide), the characteristic absorption bands of N–H, O–H, and the carbonyl groups in the regions of 3000–3500 and 1657–1717 cm⁻¹ disappeared, while those of the imide ring were observed near 1778 (asym. C=O str.), 1725 (sym. C=O str.), 1379 cm⁻¹ (C–N str.); the characteristic absorption of ring deformation was found near 725 cm⁻¹.

3. Properties of poly(ether imide)s

The solubility of the poly(ether imide)s synthesized in this study was determined for the film samples in excess solvents, and the results are listed in Table II. Poly(ether imide)s derived from wholly aromatic diamines such as *p*-phenylenediamine (V_a), *m*-phenylenediamine (V_b), and benzidine (V_c) revealed poor solubility; they were insoluble in all the solvents tested. The poly(ether imide)s derived from

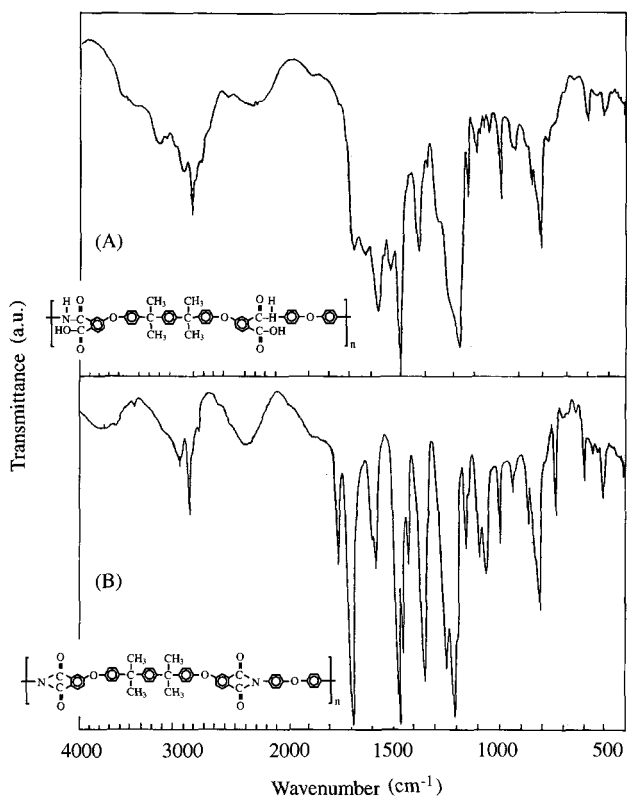


Figure 3. The IR spectra of poly(ether amic acid) VI_c (A) and poly(ether imide) VIII_c (B).

the other diamines V_{d-g} that have kinked linkages, such as the $-O-$ and $-CH_2-$ groups between aromatic rings, exhibited higher solubility. All of them could be dissolved in *N*-methyl-2-pyrrolidone (NMP), DMAc, and *m*-cresol. On the whole, the poly(ether imide)s of the VIII series seem to be more soluble than those of the IX series. For example, most VIII_{d-g} were soluble in *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF); however, IX_{d-g} all were insoluble in these two solvents. Moreover, dimethyl sulfoxide (DMSO) is clearly not a good solvent for these poly(ether imide)s. The slightly higher solubility associated with the VIII series polymers in comparison with those of the IX series can be explained by the fact that the insertion of one more cumyl unit between the phthalimide groups leads to higher flexibility of the polymer backbone.

The crystallinity of the prepared poly(ether imide)s was evaluated by wide-angle X-ray diffraction experiments. Poly(ether imide)s VIII_c and IX_c derived from benzidine displayed a rougher X-ray diffraction pattern than the other polymers. This result could be related to their higher chain packing density due to the presence of the rigid planar 4,4'-bis(phthalimido)biphenylene segment in the polymer chain. All the poly(ether imide)s, except for VIII_c and IX_c, showed almost completely amorphous patterns.

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

Polymer code	Solvent ^(b)					
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF
VIII _a	-	-	-	-	-	-
VIII _b	-	-	-	-	-	-
VIII _c	-	-	-	-	-	-
VIII _d	+	+	+	-	+	+
VIII _e	+	+	+	-	+	+
VIII _f	+	+h	+h	-	+	+h
VIII _g	+	+	-	-	+	+
IX _a	-	-	-	-	-	-
IX _b	-	-	-	-	-	-
IX _c	-	-	-	-	-	-
IX _d	+	+h	-	-	+	-
IX _e	+	+	-	-	+	-
IX _f	+	+h	-	-	+	-
IX _g	+	+	-	-	+	-

(a) +: soluble at room temperature; +h: soluble on heating; -: 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.

Polymer code	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
VIII _a	63	52	14	0.7
VIII _b	-	57	7	1.0
VIII _d	-	45	5	0.9
VIII _e	61	50	10	0.6
VIII _f	53	49	16	0.6
VIII _g	56	50	27	0.6
IX _a	-	84	11	1.1
IX _b	-	80	6	1.4
IX _d	-	78	9	1.0
IX _e	-	88	6	1.7
IX _f	90	84	14	1.0
IX _g	80	83	24	0.8

With the exception of VIII_c and IX_c, the other poly(ether imide)s could be fabricated into good-quality, creasable films. The flexible cast films were subjected to a tensile test, and the results are given in Table III. The tensile strength, elongation at break, and initial modulus of these films were in the ranges of 45~83 MPa, 6~27 %, and 0.6~1.7 GPa, respectively. Four of the VIII series poly(ether imide)s, that is, VIII_{a, b, f, g}, and two of the IX series poly(ether imide)s, that is, IX_f and IX_g, behaved as tough materials. They necked during tensile testing and had moderate elongation-to-break. All the poly(ether imide) films of the VIII series showed lower tensile strengths and initial modulus than those of the IX series, possibly because their polymer chains were less stiff.

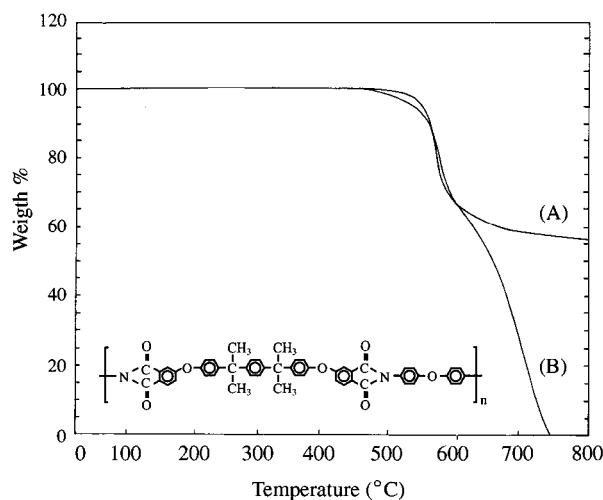
Table IV. Thermal properties of poly(ether imide)s.

Polymer code	$T_g^{(a)}$ (°C)	$T_d^{(b)}$ (°C)		Residue ^(c) wt (%)
		in N ₂	in air	
VIII _a	210	509	507	49.4
VIII _b	200	515	513	50.4
VIII _c	227 (358) ^(d)	533	514	59.3
VIII _d	201	516	518	57.9
VIII _e	202	539	527	56.8
VIII _f	194	531	527	48.3
VIII _g	200	540	540	55.3
IX _a	217	522	520	58.0
IX _b	212	505	501	54.5
IX _c	243 (340) ^(d)	522	521	62.7
IX _d	211	512	517	59.0
IX _e	210	527	527	52.6
IX _f	204	519	524	54.1
IX _g	214	526	529	56.4

- (a) From the second DSC heating traces with a heating rate of 10 °C/min in nitrogen.
 (b) Decomposition temperatures at which 10 % weight loss were recorded by TG, with a heating rate of 20 °C/min.
 (c) At 800 °C in nitrogen.
 (d) Values in parentheses were the endotherm peak temperatures observed on the first heating DSC trace, with a heating rate of 20 °C/min.

The thermal properties of all the poly(ether imide)s were evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TG). Some experimental data, such as the glass transition temperature (T_g), 10 % weight loss temperature (T_d), and residual wt% at 800 °C in nitrogen, are included in Table IV. All the poly(ether imide)s were heated to 400 °C, then cooled rapidly to room temperature to form more amorphous samples; thus, all of them showed a distinct glass transition on the subsequent DSC heating curve. The temperature at the middle point of baseline shift is defined as T_g . Poly(ether imide)s VIII_{a-g} revealed lower T_g s than the respective IX_{a-g} by about 7~16 °C. This is reasonable because polymers VIII_{a-g} have a more flexible macromolecular backbone. The T_g values of these two series of poly(ether imide)s were recorded in the ranges of 194~210 °C and 204~243 °C, respectively. Polymers VIII_c and IX_c showed a sharp melting endotherm peak at 358 and 340 °C, respectively. However, rapidly cooling and reheating showed a strong glass transition around 227 and 243 °C, respectively, pointing to a low crystallization rate. As expected, these two poly(ether imide)s exhibited the highest T_g value among the polymers of their individual series due to the presence of rigid biphenylene moiety.

As a representative example, the TG curves of poly(ether imide) VIII_e are illustrated in Figure 4. All the other poly(ether imide)s showed similar patterns of degradation with no significant weight loss

**Figure 4.** TG curves of poly(ether imide) VIII_e in N₂ (A) and in air (B) at a heating rate of 20 °C/min.

before 480 °C in air or nitrogen, but with near or more than 50 wt% residue remaining when heated to 800 °C in nitrogen. The 10% weight loss temperatures (T_d) of these two series of poly(ether imide)s VIII_{a-g} and IX_{a-g} were recorded respectively in the range of 507~540 and 501~529 °C in air, and 509~540 and 505~527 °C in nitrogen.

Conclusions

The nitrodisplacement reactions between 4-nitrophthalonitrile with α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (I_a) and 4,4'-isopropylidenediphenol (I_b) were successfully carried out to form the corresponding bis(ether dinitrile)s, which were subsequently hydrolyzed and dehydrated to the desired bis(ether anhydride)s, 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalic anhydride (IV_a) and 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]diphthalic anhydride (IV_b). Their structures could be confirmed by IR and elemental analysis. Using the traditional two-step method, the bis(ether anhydride)s IV_a and IV_b were polymerized with various aromatic diamines to form two series of fourteen poly(ether imide)s which had moderate to high molecular weights to permit the casting of strong and tough films.

Most of the poly(ether imide)s belong to amorphous materials with glass transition temperatures between 194~243 °C and they are readily soluble in a variety of organic solvents such as NMP, DMAc, and *m*-cresol. The poly(ether imide)s of the VIII_{a-g} series exhibited slightly higher solubility, but lower tensile strength, tensile modulus, and T_g when compared to their corresponding IX_{a-g} counterparts, due

to the presence of one more cumyl segment in the repeated unit of the polymer chain.

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