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Synthesis and Properties of Poly(ether imide)s Having *Ortho*-Linked Aromatic Units in the Main Chain

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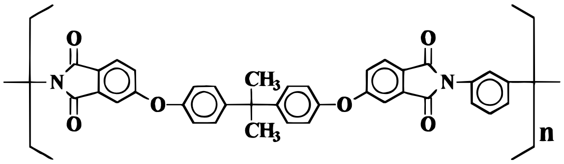
ABSTRACT: This paper demonstrates the synthesis and characterization of poly(ether imide)s with *ortho*-linked main-chain units based on the bis(ether anhydride)s derived from catechol and 2,3-dihydroxynaphthalene. The polymerization was conducted in two steps via the formation of a poly(amic acid) precursor followed by thermal cyclodehydration. The resulting polymers were characterized by inherent viscosity, solubility, film-forming ability, tensile tests, differential scanning calorimetry (DSC), thermogravimetry (TG), and wide-angle X-ray diffraction measurements. Typical poly(ether imide)s were noncrystalline and showed excellent thermal stability. The polymers had glass transition temperatures from 193 to 224 °C and exhibited excellent processability. Many poly(ether imide)s were also soluble in dipolar aprotic solvents and *m*-cresol.

Introduction

Aromatic polyimides are known for their excellent thermal stability and balanced mechanical and electric properties.[1] Polyimides are mainly used in the aerospace and electronic industries in the forms of films and moldings. Other uses for these polymers such as adhesives, gas separation membranes, composite matrices, coatings, and foams are rapidly increasing. However, aromatic polyimides are difficult to process because of high softening temperatures and limited solubility in commercially available solvents. In fact, they are usually processed via the form of their poly(amic acid) precursors.

Introduction of flexible groups, such as $-O-$ and $-C(CH_3)_2-$, in the polyimide backbone leads to a decreased glass transition temperature and an enhanced moldability. An important example is Ultem 1000 developed and commercialized by General Electric Co.,[2] which exhibits reasonable thermal stability and good mechanical properties together with good moldability. Its structure, including as it does aliphatic components, contributes to solvent and high-temperature sensitivity. The goal of better thermal stability together with retained good processability may be achieved in preparing wholly aromatic poly(ether imide)s containing unsymmetric, such as *meta*- and *ortho*-catenated, aromatic units.



Ultem 1000

Recently, we reported the synthesis of bis(ether amine)s for polyimide, polyamide, and poly(amide−imide) synthesis based on catechol or 2,3-dihydroxynaphthalene.[3−6] Catechol or 2,3-dihydroxynaphthalene readily underwent chloro displacement with *p*-chloronitrobenzene in *N*,*N*-dimethylformamide to yield the intermediate bis(*p*-nitrophenoxy) compound, which was then readily reduced to the bis(ether amine)s. There are also very recent reports of a nitro displacement reaction between catechol and 4-nitrophthalonitrile to form an *ortho*-linked bis(ether dinitrile) which was then hydrolyzed and dehydrated to the corresponding bis(ether anhydride) and used in poly(ether imide) synthesis.[7−9] Although the synthesis of the bis(ether anhydride) based on 2,3-dihydroxynaphthalene (see structure **8** in Scheme 1) and one poly(ether imide) derived from it with 4,4′-oxydianiline has also been described in the report of Eastmond and Paprotny,[8] relatively little is known about the polymers derived from bis(ether anhydride) **8**. In our continuing effort to develop high-performance polymers based on the monomers derived from naphthalenediols, the present article deals with the synthesis and basic characteriza-

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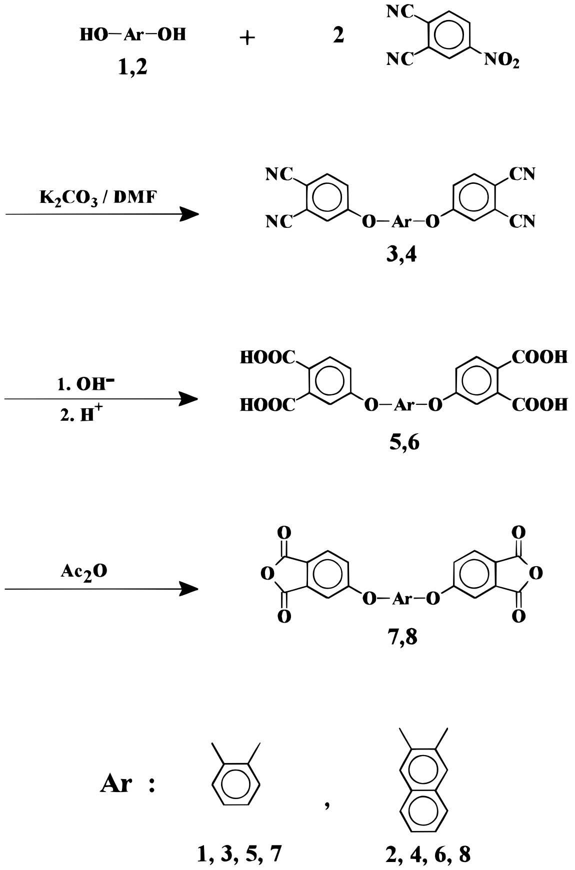
Scheme 1



tion of the poly(ether imide)s based on the bis(ether anhydride) **8** and aromatic diamines. Wholly aromatic diamines such as **9a**−**c** or the ether−diamines such as **9d**−**h** are employed in the polymer synthesis in order to produce wholly aromatic poly(ether imide) products. For the purpose of comparative study, the analogues based on the catechol bis(ether anhydride) (**7**) will also be synthesized and characterized.

Experimental Section

Materials. Catechol (or 1,2-dihydroxybenzene), 2,3-dihydroxynaphthalene (Janssen), 4-nitrophthalonitrile (TCI), *N*,*N*-dimethylformamide (DMF; Fluka), potassium carbonate (K_2CO_3; Fluka), and acetic anhydride (Janssen) were used as received. *p*-Phenylenediamine (**9a**) (Wako) and benzidine (**9c**) were purified by sublimation. *m*-Phenylenediamine (**9b**) (Janssen) was vacuum-distilled prior to use. According to the procedure described in literature,[5,6,10] 1,2-bis(4-aminophenoxy)benzene (**9f**) (mp 137−138 °C), 2,3-bis(4-aminophenoxy)naphthalene (**9g**) (mp 176−177 °C), and 4,4′-bis(4-aminophenoxy)biphenyl (**9h**) (mp 198−199 °C) were prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursors, i.e. catechol, 2,3-dihydroxynaphthalene, and 4,4′-biphenol, and *p*-chloronitrobenzene in the presence of potassium carbonate, followed by hydrazine catalytic reduction of the intermediate dinitro compounds. 4,4′-Oxydianiline (**9d**) (TCI) and 1,4-bis(4-aminophenoxy)benzene (**9e**) (TCI) were used without previous purification. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

1,2-Bis(3,4-dicyanophenoxy)benzene (3) and 2,3-Bis(3,4-dicyanophenoxy)naphthalene (4). In a 300-mL flask, 5.51 g (0.05 mol) of catechol (**1**), 17.31 g (0.1 mol) of 4-nitrophthalonitrile, and 13.8 g (0.1 mol) of K_2CO_3 were suspended in 150 mL of DMF. The suspension solution was stirred at room temperature for about 24 h. Then, the reaction mixture was poured into 700 mL of water, and the precipitated yellow solid was collected and washed thoroughly with methanol and water. The yield of the product was 16.48 g (91%). The crude product was purified by recrystallization from acetonitrile/methanol (1:1) to afford **3** as colorless needles. The yield of the purified product was 10.9 g (60%); mp 188−189 °C (lit.[7] 190.1−190.6 °C). The IR spectrum (KBr) exhibited absorptions at 2230 (C≡N) and 1250 cm^{-1}(C—O). Anal. Calcd for $C_{22}H_{10}N_4O_2$ (362.35): C, 72.92; H, 2.78; N, 15.46. Found: C, 72.90; H, 2.75; N, 15.40.

2,3-Bis(3,4-dicyanophenoxy)naphthalene (**4**) was synthesized in an analogous procedure from 2,3-hydroxynaphthalene and 4-nitrophthalonitrile. The product was recystallized from acetonitrile to yield white crystals. Yield 72%; mp 264−265 °C (lit.[8] 265−266 °C). IR (KBr): 2230 (C≡N), 1255 cm^{-1} (C—O—C). Anal. Calcd for $C_{26}H_{12}N_4O_2$ (412.41): C, 75.72; H, 2.93; N, 13.58. Found: C, 75.68; H, 2.90; N, 13.49.

1,2-Bis(3,4-dicarboxyphenoxy)benzene (5) and 2,3-Bis(3,4-dicarboxyphenoxy)naphthalene (6). In a 500-mL flask, a suspension of bis(ether dinitrile) **3** (10.5 g; 0.036 mol) in an ethanol/water mixture (100 mL/100 mL) containing dissolved 32.5 g (0.58 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 5 h. Reflux was continued for about 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 white precipitated product was filtered off, washed with water until neutral, and dried in vacuum, to give 11.8 g (93%) of bis(ether diacid) **5**. IR (KBr): 2500−3600 (O—H), 1700 (C=O), 1250 cm^{-1} (C—O—C).

2,3-Bis(3,4-dicarboxyphenoxy)naphthalene (**6**) was prepared in a similar procedure from the alkaline hydrolysis of bis(ether dinitrile) **4**. Yield: 92%. IR (KBr): 2500−3600 (O—H), 1700 (C=O), 1215 cm^{-1} (C—O—C).

1,2-Bis(3,4-dicarboxyphenoxy)benzene Dianhydride (7) and 2,3-Bis(3,4-dicarboxyphenoxy)naphthalene Dianhydride (8). In a 500-mL flask, bis(ether diacid) **5** (11.8 g; 0.027 mol) was suspended in 70 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 crystallized white needles were collected, washed with dry toluene, and dried *in vacuo*, to give 9.4 g (87%) of bis(ether anhydride) **7**; mp 187−188 °C (lit.[7] 187.1−187.6 °C). IR (KBr): 1850 (asym C=O), 1780 (sym C=O), 1450−1615 (arom C=C), 1270 cm^{-1} (C—O—C). Anal. Calcd for $C_{22}H_{10}O_8$ (402.32): C, 65.68; H, 2.51. Found: C, 65.32; H, 2.38.

2,3-Bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**8**) was prepared from bis(ether diacid) **6** in a similar method. Yield: 86%. Mp: 264−265 °C (lit.[8] 264.6−265.4 °C). IR (KBr): 1855 (asym C=O), 1785 (sym C=O), 1440−1620 (arom C=C), 1250 cm^{-1} (C—O—C). Anal. Calcd for $C_{26}H_{12}O_8$ (452.37): C, 69.09; H, 2.67. Found: C, 68.65; H, 2.64.

Synthesis of Poly(ether imide)s. A typical polymerization procedure is as follows. 4,4′-Oxydianiline (**9d**) (0.3069 g, 1.53 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely 0.6931 g (1.53 mmol) of 2,3-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**8**) was added in one portion. The mixture was stirred at room temperature for 2.5 h. The inherent viscosity of the resulting poly(ether amic acid) (**11d**) in DMAc was 1.15 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The polymer solution obtained was poured into a ∅ = 9-cm glass culture dish, which was placed in a 90 °C oven overnight to remove the solvent. The semidried 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 **13d** self-stripped off from the glass surface.

IR of **11d** (film): 2700−3600 (N—H and O—H str), 1500−1780 (broad, arom C=C str + C=O str + N—H, O—H bending), 1200−1300 cm^{-1} (C—O). IR of **13d** (film): 1780 (asym C=O), 1720 (sym C=O), 1500−1620 (arom C=C); 1390 (C—N), 1240 (C—O), 1100 and 720 cm^{-1} (imide ring deformation).

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

Characterization. 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. 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. The heating rate was 20 °C/min. Glass transition temperatures (T_g's) 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) at a heating rate of 20 °C/min. 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 Kα radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5-40°$. 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

There are now many reports[11−16] of the synthesis of bis(ether anhydride)s and poly(ether imide)s derived from various aromatic diols. The diols are usually incorporated into the bis(ether anhydride) monomers by a nitro displacement reaction with a phthalic acid derivative or a phthalodinitrile followed by alkaline hydrolysis of the intermediate bis(ether phthalimide) or bis(ether dinitrile) and subsequent dehydration of the resulting tetraacid.

Monomer Synthesis. According to the reported method,[7,8] the *ortho*-linked bis(ether anhydride)s **7** and **8** were prepared by a three-stage route starting from the nitro displacement reaction of 4-nitrophthalonitrile with catechol or 2,3-dihydroxynaphthalene (Scheme 1). The yield in each step was satisfactory, and the structure of bis(ether anhydride)s was confirmed by element analysis and infrared spectroscopy. The satisfactory synthesis of high-molecular-weight polymers is also a good proof that pure bis(ether anhydride)s have been prepared.

Scheme 2

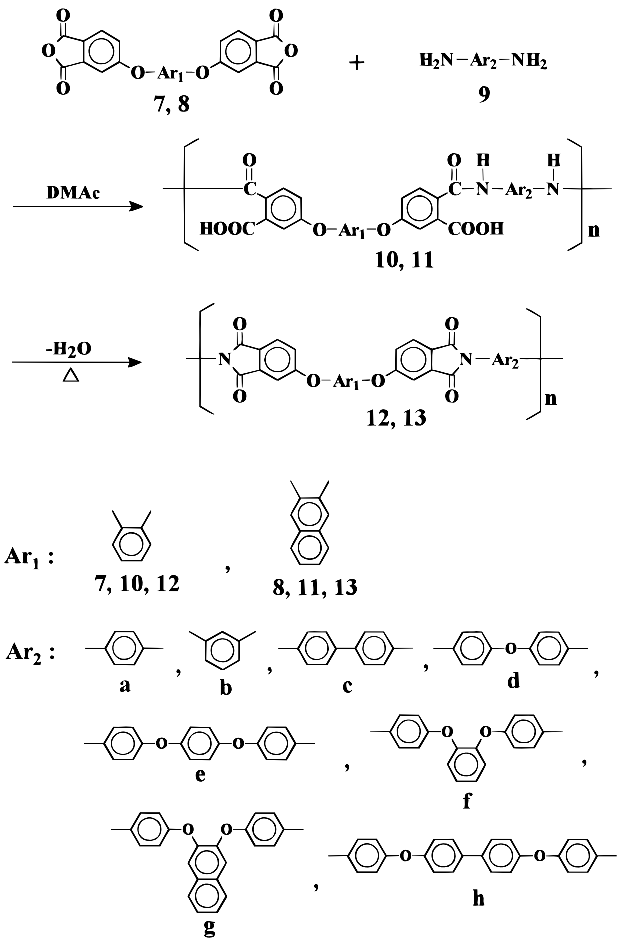


Table 1. Inherent Viscosities and Film Quality of Poly(ether amic acid)s and Poly(ether imide)s

poly(ether amic acid)			poly(ether imide)		
code	η_{inh}[a] (dL/g)	film quality[b]	code	η_{inh}[a] (dL/g)	film quality[c]
10a	1.13	flexible	**12a**	*d*	highly brittle
10b	0.93	flexible	**12b**	0.58	slightly brittle
10c	1.37	flexible	**12c**	*d*	highly brittle
10d	1.25	flexible	**12d**	0.83	flexible
10e	1.63	flexible	**12e**	*d*	flexible
10f	0.94	flexible	**12f**	0.72	flexible
10g	1.10	flexible	**12g**	0.60	flexible
10h	1.91	flexible	**12h**	0.83	flexible
11a	0.92	flexible	**13a**	*d*	highly brittle
11b	0.80	flexible	**13b**	0.53	slightly brittle
11c	1.20	flexible	**13c**	*d*	highly brittle
11d	1.15	flexible	**13d**	0.73	flexible
11e	1.52	flexible	**13e**	0.75	flexible
11f	0.78	flexible	**13f**	0.60	flexible
11g	0.84	flexible	**13g**	0.49	flexible
11h	1.13	flexible	**13h**	0.94	slightly brittle

[a] Measured in DMAc on 0.5 g/dL at 30 °C. [b] Films were cast by slow evaporation of polymer solutions in DMAc. [c] Films were obtained by sequential heating of the poly(ether amic acid) films at 150 °C for 20 min, 180 °C for 20 min, 200 °C for 20 min, 220 °C for 20 min, 250 °C for 30 min. [d] Insoluble in DMAc.

Synthesis of Poly(ether imide)s. All poly(ether imide)s were prepared by the two-stage process outlined in Scheme 2, described above in detail for the polymer (**13d**) derived from bis(ether anhydride) **8** and 4,4′-oxydianiline (**9d**). The diamines used are also listed in Scheme 2. Polymer preparation involved adding the bis(ether anhydride) to a diamine in dry DMAc solution to form the poly(ether amic acid), pouring the poly(ether amic acid) solution onto a glass substrate, slowly evaporizing the solvent, and then thermally dehydrating to form the poly(ether imide). Thus, all the polymers were obtained in the form of films. Completion of the imidization by the heating program as shown in Experimental Section was confirmed by dynamic thermogravimetry of a sample of the poly(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. Among the 16 polymers synthesized, polymers **12b**, **12d**, **12h**, and **13d** have appeared in literature;[7,8] the other 12 are first synthesized. As shown in Table 1, the inherent viscosities of the intermediate poly(ether amic acid)s are in the 0.80−1.91 dL/g range. The casting films of poly(ether imide)s **12a**, **13a**, **12c**, and **13c** which were derived from rigid diamines, such as *p*-phenylenediamine and benzidine, embrittled during the thermal imidization process, possibly due to a high degree of crystallinity associated with these poly(ether imide)s. The free-standing films obtained from poly(ether imide)s **12b**, **13b**, and **13h** cracked upon creasing, probably caused by the structural rigidity. The other poly(ether imide)s afforded

Table 2. Solubility Behavior of Poly(ether imide)s[a]

	solvent[b]							
polymer code	NMP	DMAc	DMF	DMSO	*m*-cresol	THF	CH_2Cl_2	$CHCl_3$
12a	−	−	−	−	−	−	−	−
12b	+	+	+	+	+	−	+	+
12c	−	−	−	−	−	−	−	−
12d	+	+	+	+h	+	−	−	+
12e	+	−	−	−	+h	−	+	+
12f	+	+	+	+h	+	−	−	+
12g	+	+	+h	−	+	−	−	−
12h	+	+	+h	−	+h	−	+	+
13a	−	−	−	−	−	−	−	−
13b	+	+	+h	−	+h	−	−	−
13c	−	−	−	−	−	−	−	−
13d	+	+	+	−	+	−	+	+
13e	+	+	+	+h	+	−	−	+
13f	+	+	+	+	+h	−	−	−
13g	+	+	+	−	+	−	−	−
13h	+	+	+	+h	+	−	+	+

[a] Solubility: +, soluble at room temperature; +h, soluble at high temperature, and −, insoluble. [b] NMP: *N*-methyl-2-pyrrolidone. DMAc: *N*,*N*-dimethylacetamide. DMF: *N*,*N*-dimethylformamide. DMSO: dimethyl sulfoxide. THF: tetrahydrofuran.

good creasable films. Most of poly(ether imide)s exhibited excellent solubility in polar solvents like DMAc. Therefore, the characterization of inherent viscosity was carried out without any difficulty, and the inherent viscosities of soluble poly(ether imide)s were in the range of 0.49−0.94 dL/g.

IR spectroscopy allows monitoring of the imide ring formation during cure. When the poly(ether amic acid) was converted into the poly(ether imide), the characteristic absorption bands of amide and carboxyl groups in the regions of 2700−3600 cm^{-1} and 1500−1730 cm^{-1} disappeared, and those of the imide ring were observed near 1780 (asym C=O str), 1720 (sym C=O str), 1390 (C−N str), 1100 and 745 cm^{-1} (imide ring deformation). The aryl ether stretching absorbed near 1240 cm^{-1}.

Properties of Poly(ether imide)s. Solubility of the wholly aromatic poly(ether imide)s synthesized in this study was determined for the film samples in excess solvents, and the results are listed in Table 2. In general, the 2,3-dihydroxynaphthalene-based poly(ether imide)s showed a solubility behavior similar to that of the catechol-based analogues. Most of poly(ether imide)s revealed good solubility in various solvents, especially in highly polar aprotic solvents such as NMP, DMAc, and DMF, and in phenolic solvents like *m*-cresol. That is, the solubility of aromatic polyimides was remarkably improved by both incorporation of ether linkages and *ortho*-linked aromatic moieties. However, those derived from rigid diamines like *p*-phenylenediamine and benzidine, such as polymers **12a**, **12c**, **13a**, and **13c**, were insoluble in all the solvents tested. This can be attributed to their high level of crystallinity as evidenced by the wide-angle X-ray diffraction measurements later on. Thus, the solubilities of these polymers are also partially dependent on the diamine components. Moreover, only limited polymers showed solubility in DMSO and chlorinated solvents like dichloromethane and chloroform, and all prepared in this work were still insoluble in common organic solvents like THF, ethanol, or acetone.

The crystallinity of the prepared poly(ether imide)s was evaluated by wide-angle X-ray diffraction experiments. Typical diffraction patterns for some representative polymers are reproduced in Figures 1 and 2. Poly(ether imide)s **12a**, **12c**, **13a**, and **13c**, which embrittled during thermal imidization, showed a highly crystalline pattern. This can be attributed to the existence of the rigid planar 1,4-bis(phthalimido)phenylene or 4,4′-bis(phthalimido)biphenylene segments in their polymer backbones, leading to a better packing of polymer chains. The poly(ether imide)s **12b** and **13b** based on *m*-phenylenediamine also revealed some crystallinity. Insertion of one or two phenoxy groups into the recurring units of **12a**, **12c**, **13a**, and **13c** resulted in a significant decrease in crystallinity. For example, polymers **12d**, **12h**, and **13d** presented amorphous diffraction patterns. This is reasonable because the presence of a kinked ether group induces loose chain packing. However, polymer **13h** showed a stronger

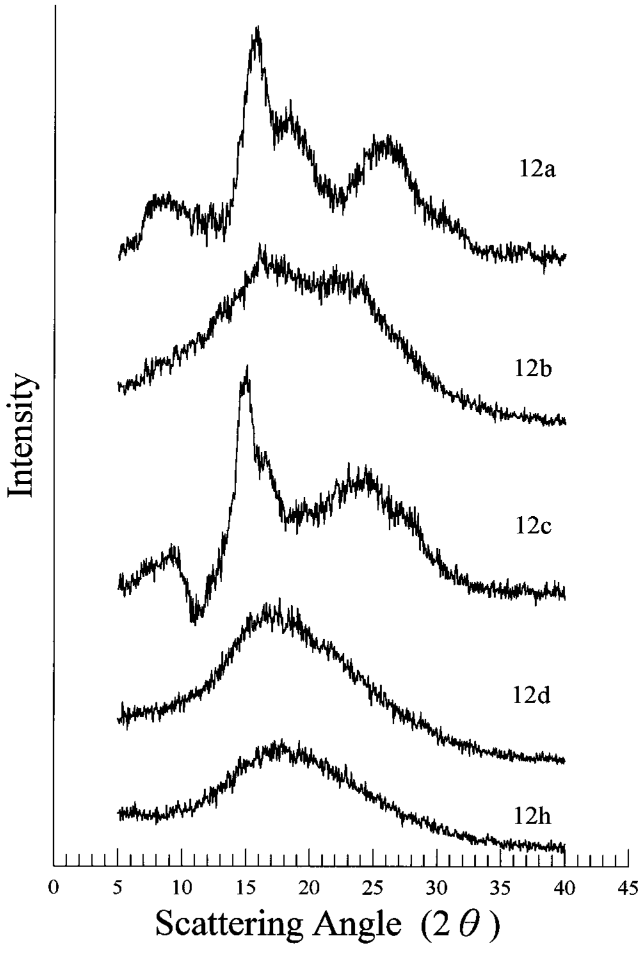


Figure 1. Wide-angle X-ray diffractograms of poly(ether imide)s based on 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**7**).

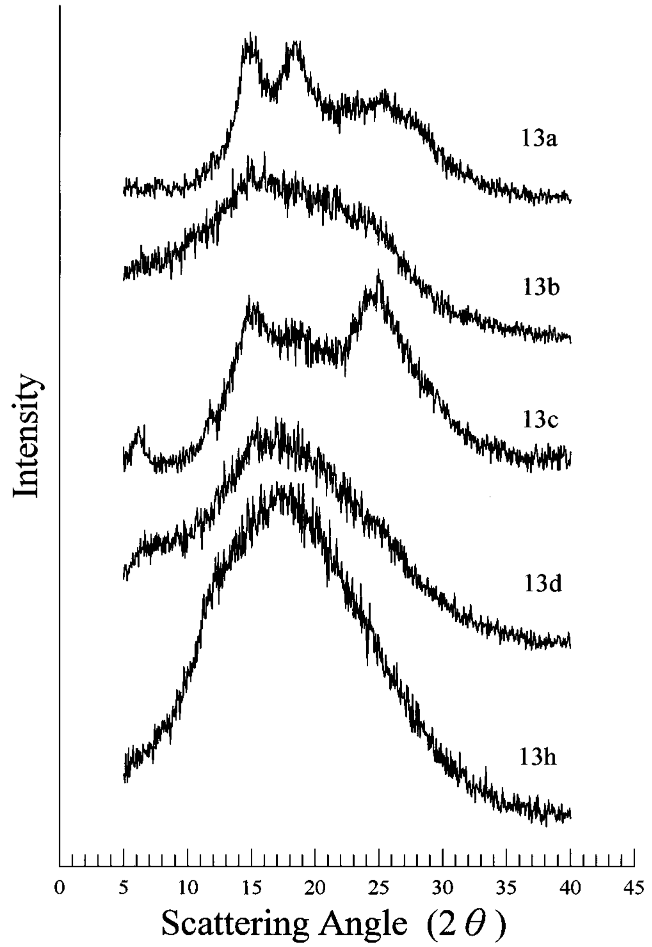


Figure 2. Wide-angle X-ray diffractograms of poly(ether imide)s based on 2,3-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**8**).

Table 3. Tensile Properties of Poly(ether imide) Films

polymer code	strength at yield point (MPa)	strength at break point (MPa)	elongation at break point (%)	initial modulus (GPa)
12b		47	3	1.9
12d		84	8	1.4
12e	107	84	32	1.6
12f		66	4	1.8
12g		66	7	1.5
12h	103	91	63	1.3
13b		72	3	1.9
13d		108	8	1.8
13e		65	4	1.8
13f		67	4	1.9
13g		74	4	2.0
ref[a]		80	6	1.4

[a] A poly(ether imide) with the same structure as Ultem 1000, synthesized from Bisphenol A bis(ether anhydride) and *m*-phenylenediamine in our laboratory. The inherent viscosity of its poly(amic acid) precursor was 0.40 dL/g.

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

polymer code	T_g[a] (°C)	decomposition temp[b] (°C) in N_2	decomposition temp[b] (°C) in air	char yield[c] (%)
12a		557	575	52.2
12b	224	533	557	48.9
12c		568	580	60.3
12d	212	558	579	52.1
12e	202	561	568	51.5
12f	193	553	572	52.2
12g	216	535	542	55.9
12h	204	557	581	59.8
13a		553	561	55.7
13b	219	548	559	54.9
13c		570	583	65.8
12d	206	556	560	57.6
13e	220	560	570	56.5
13f	204	554	575	57.8
13g	222	540	551	60.8
13h	218	563	569	60.0
ref[d]	212	505	501	54.5

[a] From the second DSC heating scan after quick cooling; heating rate, 20 °C/min. [b] Temperature at which 10% weight loss recorded by thermogravimetry at a heating rate of 20 °C/min. [c] Residual weight % at 800 °C in nitrogen. [d] See footnote of Table 3.

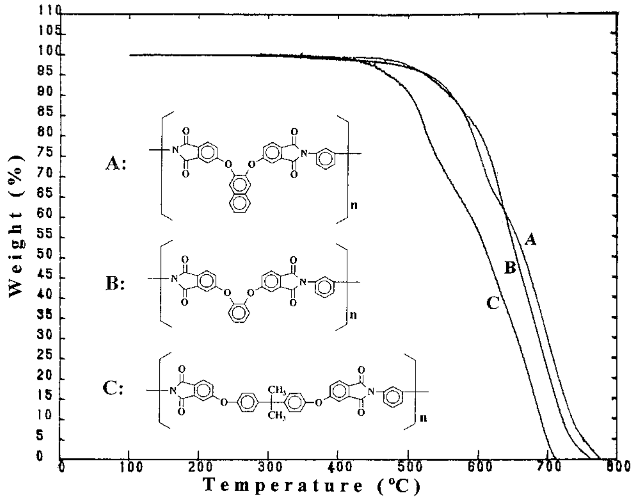


Figure 3. TG curves of poly(ether imide)s **12b**, **13b**, and Ultem at a heating rate of 20 °C/min in air.

reflection hump between $2\theta = 10$ and 30°, pointing to a higher packing density. Therefore, its cast film exhibited a brittle nature.

The flexible cast films were subjected to a tensile test, and the results are given in Table 3. The tensile strength, elongation at break, and initial modulus of these films were in the ranges 47–108 MPa, 3–63%, and 1.3–1.9 GPa, respectively. The strengths of some films were superior to those of the poly(ether imide) having the same structure at Ultem which was prepared in our laboratory. The poly(ether imide) **12h** derived from the catechol bis(ether anhydride) and 4,4′-bis(*p*-aminophenoxy)biphenyl exhibited the largest extension to break (63%). This result corresponds to that discovered by Eastmond et al.,[9] although they reported a much higher value of 170%. The difference may be owing to different testing machines, measurement conditions, and even sampling methods. In contrast to polymer **12h**, the film made from the 2,3-dihydroxynaphthalene-based polymer **13h** showed a slightly brittle nature, and even no available specimens could be produced.

Thermal properties of all the poly(ether imide)s were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). All the poly(ether imide)s showed a similar pattern of decomposition with no significant weight loss below 520 °C in air or nitrogen, but with more than 52 wt % residue remaining when heated to 800 °C in nitrogen. The data reported in Table 4 show that the 10% weight loss temperatures of these poly(ether imide)s were recorded in the range of 542–581 °C in air and 533–568 °C in nitrogen. By comparing the TG thermograms shown in Figure 3, it is apparent that the wholly aromatic poly(ether imide)s **12b** and **13b** are more heat resistant than Ultem due to the lack of aliphatic groups. Except for the highly crystalline poly(ether imide)s **12a**, **12c**, **13a**, and **13c**, all the other polymers showed distinct baseline shifts on their DSC heating traces. Glass transition temperatures (T_g's), defined as the temperature at the midpoint of the baseline shift, of the two series poly(ether imide)s **12a**−**h** and **13a**−**h** were recorded in the ranges 193−224 and 204−220 °C, respectively. These values are similar to those reported for Ultem 1000. In addition, some T_g data, such as those of polymers **12b**, **12d**, and **12h**, are similar to those reported in literature.[7] In general, the **13** series of poly(ether imide)s had slightly higher T_g's than the analogous **12** series. This result can be explained by the fact that the bulky, pendent 2,3-disubstituted naphthalene unit may increase intermolecular barriers to segment movement. The moderate T_g values of these poly(ether imide)s are apparently attributed to the low rotational energy barrier around ether linkages and to the unsymmetrical *ortho*-linked aromatic units in the main chain.

Conclusions

Several novel *ortho*-linked aromatic poly(ether imide)s having high molecular weights have been synthesized from aromatic diamines with the bis(ether anhydride)s based on catechol and 2,3-dihydroxynaphthalene. The poly(ether imide)s were amorphous except in some cases. The T_g of poly(ether imide)s ranged from 193 to 224 °C, which is comparable to that of Ultem, but they showed a higher thermal stability than Ultem due to the lack of aliphatic segments. These poly(ether imide)s generally exhibited good thermal processabilities because of the presence of large windows between T_g and the decomposition temperature (above 500 °C). The polymers were also soluble in various solvents, and strong flexible films could be cast from solution. These properties make these poly(ether imide)s attractive for practical applications such as high-performance engineering plastics.

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