

Synthesis and Properties of Poly(ether imide)s Derived from 2,7-Bis(3,4-dicarboxyphenoxy)naphthalene Dianhydride and Various Aromatic Diamines

SHENG-HUEI HSIAO, KUAN-YU CHU

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., 3rd Sec., Taipei, Taiwan, Republic of China

Received 1 November 1996; accepted 28 January 1997

ABSTRACT: A naphthalene unit-containing bis(ether anhydride), 2,7-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride, was prepared in three steps starting from the nucleophilic nitrodisplacement reaction of 2,7-dihydroxynaphthalene and 4-nitrophthalonitrile in *N,N*-dimethylformamide (DMF) solution in the presence of potassium carbonate followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) and subsequent dehydration of the resulting bis(ether diacid). High-molar-mass aromatic poly(ether imide)s were synthesized using a conventional two-stage polymerization process from the bis(ether anhydride) and ten aromatic diamines. The intermediate poly(ether amic acid)s had inherent viscosities of 0.95–2.67 dL/g. The films of poly(ether imide)s derived from two rigid diamines, that is, *p*-phenylenediamine and benzidine, crystallized and embrittled during the thermal imidization process. The other poly(ether imide)s belonged to amorphous materials and could be fabricated into transparent, flexible, and tough films. These poly(ether imide) films had yield strengths of 91–115 MPa, tensile strengths of 89–136 MPa, elongation to break of 11–45%, and initial moduli of 1.7–2.2 GPa. The T_g s of poly(ether imide)s were recorded in the range of 222–256°C depending on the nature of the diamine moiety. All polymers were thermally stable up to 500°C, with 10% weight loss being recorded above 540°C in air and nitrogen atmospheres. © 1997 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* **35**: 2281–2287, 1997

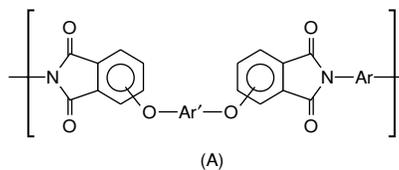
Keywords: 2,7-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride; poly(ether imide)s

INTRODUCTION

Aromatic polyimides are known for their excellent thermal stability and chemical resistance, together with balanced electric and mechanical 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, 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 followed by chemical or thermal imidization.

Poly(ether imide)s, with the following general structure (A):

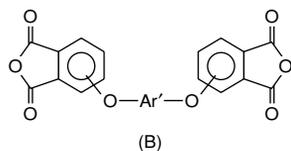


have been receiving much attention because they

Correspondence to: S.-H. Hsiao

© 1997 John Wiley & Sons, Inc. CCC 0887-624X/97/112281-07

can provide a compromise between good thermal stability and processability when compared to polyimides. The poly(ether imide)s with the general structure of (A) are usually prepared by the widely utilized two-stage process for the manufacturing of polyimides via poly(amic acid)s from bis(ether anhydride)s with general structure (B) and aromatic diamines. The large number of commercially or



synthetically available aromatic diols (the source of the Ar' moieties) and diamines (the source of the Ar units) indicates that hundreds of structurally different poly(ether imide)s may be synthesized.

Bis(ether anhydride)s having the structure (B) can be easily prepared using a nucleophilic displacement of a nitro or halide group from a phthalic acid derivative, for example, 3- or 4-nitrophthalic derivative and 3- or 4-fluorophthalic acid derivative, by reaction with the alkali metal salt of an aromatic diol. The literature depicts two major routes suitable for the synthesis of bis(ether anhydride)s derived from phthalic acid derivatives and various diols; these procedures have been reviewed by Takekoshi² and Eastmond et al.³ The most popularly used displacement reactions are those between *N*-phenyl or *N*-alkyl nitrophthalimides and bisphenolates.^{4–6} The bis(ether phthalimide)s so formed are hydrolyzed to bis(ether diacid)s and then dehydrated to yield the bis(ether anhydride)s. The alternative nitrodisplacement reaction is that between nitrophthalonitrile and bisphenolates.^{7–9} This reaction produces a tetranitrile, which is then converted to the corresponding tetracarboxylic acid and hence to the bis(ether anhydride). In principle, these techniques can be used to synthesize bis(ether anhydride)s from bisphenols (e.g., bisphenol A), benzenediols (e.g., hydroquinone, resorcinol, and catechol), or naphthalenediols. A number of bis(ether anhydride)s have been prepared from bisphenols and benzenediols.^{2–9} However, the bis(ether anhydride)s of naphthalenediols are scarcely known. In our continuing effort to develop high-performance polymers containing naphthalene moieties, this article deals with the synthesis of 2,7-

bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (4) and its derived poly(ether imide)s and the basic characterization of these polymers as well.

EXPERIMENTAL

Materials

2,7-Dihydroxynaphthalene (Acros), 4-nitrophthalonitrile (TCI), potassium carbonate (K₂CO₃, Fluka), *N,N*-dimethylformamide (DMF, Fluka), potassium hydroxide (Wako), and acetic anhydride (Janssen) were used as received. *p*-Phenylenediamine (5a) (Wako) and benzidine (5c) were purified by sublimation. *m*-Phenylenediamine (5b) (Janssen) was vacuum-distilled prior to use. 4,4'-Bis(4-aminophenoxy)biphenyl (5h) (mp 198–199°C), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (5i) (mp 126°C), and bis[4-(4-aminophenoxy)phenyl] sulfone (5j) (mp 185–187°C) were prepared by the nucleophilic substitution reaction of the corresponding bisphenols, that is, 4,4'-biphenol, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), and bis(4-hydroxyphenyl) sulfone, and *p*-chloronitrobenzene in the presence of potassium carbonate, giving the bis(*p*-nitrophenoxy) compounds, and subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst.^{10–11} The other diamines, 4,4'-methylenedianiline (5d) (TCI), 4,4'-oxydianiline (5e) (TCI), 3,4'-oxydianiline (5f), and 1,4-bis(4-aminophenoxy)benzene (5g) (TCI), were also used without purification. *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

2,7-Bis(3,4-Dicyanophenoxy)naphthalene (2)

In a 300-mL flask, 5.6 g (0.035 mol) of 2,7-dihydroxynaphthalene (1), 12.2 g (0.07 mol) of 4-nitrophthalonitrile, and 10.1 g (0.073 mol) of K₂CO₃ were suspended in 80 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 brown solid was collected and washed thoroughly with methanol and water. The yield of the product was 13.6 g (94%); mp 204–205°C [207°C (DSC)] [lit.¹² 203.5–204.5°C]. The IR spectrum (KBr) ex-

hibited absorptions at 2230 (C≡N) and 1250 cm⁻¹ (C—O—C).

ANAL. Calcd for C₂₆H₁₂N₄O₂ (412.41): C, 75.72%; H, 2.93%; N, 13.58%. Found: C, 75.67%; H, 2.95%; N, 13.50%.

2,7-Bis(3,4-Dicarboxyphenoxy)naphthalene (3)

In a 500-mL flask, a suspension of bis(ether dinitrile) **2** (11.2 g; 0.027 mol) in an ethanol/water mixture (150 mL/150 mL) containing dissolved 58.9 g (1.08 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 4 days. Reflux was continued for an additional day 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 = 3. The brown precipitated product was filtered off, washed repeatedly with water, and dried in vacuum, to give 15.6 g (100%) of bis(ether diacid) **3**; mp 207–209°C [214°C (DSC)]. IR (KBr): 2400–3600 (O—H), 1690 (C=O), and 1220 cm⁻¹ (C—O—C).

2,7-Bis(3,4-Dicarboxyphenoxy)naphthalene Dianhydride (4)

In a 500-mL flask, bis(ether diacid) **3** (12.9 g; 0.026 mol) was suspended in 120 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 brown crystals were collected, washed with dry toluene, and dried *in vacuo*, to give 8.6 g (72%) of bis(ether anhydride) **4**; mp 158–160°C [166°C (DSC)] [lit.¹² 165–167°C]. IR (KBr): 1850 (asym. C=O), 1770 (sym. C=O), 1440–1530 (arom. C=C), and 1280 cm⁻¹ (C—O—C).

ANAL. Calcd for C₂₆H₁₂O₈ (452.37): C, 69.03%; H, 2.67%. Found: C, 69.00%; H, 2.65%.

Syntheses of Poly(ether imide)s

A typical polymerization procedure is as follows. *p*-Phenylenediamine (**5a**) (0.1929 g; 1.78 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.8071 g (1.78 mmol) of bis(ether anhydride) **4** 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) (**6a**) in DMAc was 1.28 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The polymer solution was

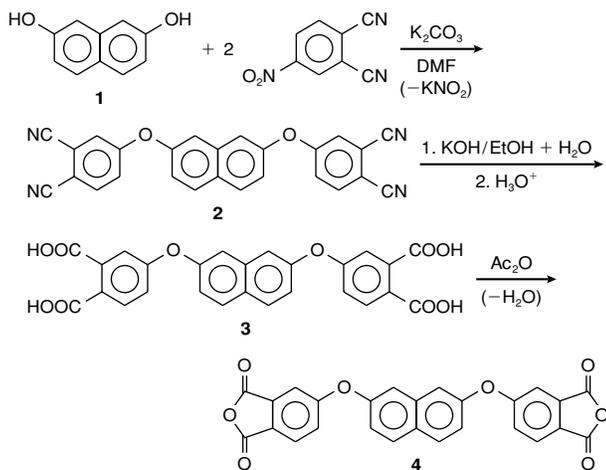
poured into a 9-cm glass culture dish, which was placed in a 90°C oven overnight to remove the solvent. The semidried poly(ether amic acid) film was further dried and transformed into poly(ether imide) by sequential heating at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min, and 250°C for 30 min. By soaking in hot water, a flexible poly(ether imide) film of **7a** lifted off from the glass surface.

IR of **6a** (film): 2400–3500 (N—H and O—H str.), 1500–1730 (broad, arom. C=C str. + C=O str. + N—H, O—H bending), and 1200–1300 cm⁻¹ (C—O). IR of **7a** (film): 1780 (asym. C=O), 1725 (sym. C=O), 1430–1620 (arom. C=C), 1365 (C—N), 1240 (C—O), 1080, and 745 cm⁻¹ (imide ring deformation).

All other poly(ether imide)s were prepared by a similar method.

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. 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 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 rapid cooling. Thermogravimetry analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 9 to 11-mg samples heated in flowing nitrogen or air (50 cm³/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 CuK_α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of 2θ = 5–40°. An Instron universal tester Model 1130 with a load cell 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), and an average of at least five individual determinations was reported.



Scheme 1.

RESULTS AND DISCUSSION

Monomer Synthesis

According to a reported method,⁷⁻⁹ the naphthalene unit-containing bis(ether anhydride) **4** was prepared using a three-stage reaction from 2,7-dihydroxynaphthalene (**1**) and 4-nitrophthalonitrile as outlined in Scheme 1. In the first step, the nitrodisplacement reaction between 2,7-dihydroxynaphthalene and 4-nitrophthalonitrile underwent satisfactorily in DMF at room temperature, in which potassium carbonate was used as the base to form the phenolate *in situ*. A 94% yield of bis(ether dinitrile) **2** was obtained in this step. Although the bis(ether dinitrile) was not further purified, it is clear that the purity was high as the purity of anhydride prepared from it was high. Then, the bis(ether dinitrile) was readily hydrolyzed to bis(ether diacid) **3** by ethanolic potassium hydroxide. The yield of the bis(ether diacid) is quantitative. Finally, the bis(ether diacid) was cyclodehydrated to bis(ether anhydride) **4** in good yield (72%); the C and H analytical data agreed well with the desired structure. The progress of these reactions could be monitored by IR spectroscopy. The IR spectrum of bis(ether dinitrile) **2** is characterized by a sharp absorption near 2230 cm^{-1} . The most characteristic bands of bis(ether diacid) **3** are observed near 1690 cm^{-1} (C=O stretching) and in the region of 2400–3600 cm^{-1} (O—H stretching). The spectrum of bis(ether anhydride) **4** show characteristic cyclic anhydride absorption near 1850 and 1770 cm^{-1} attributed to the asymmetrical and symmetrical stretching vibrations of C=O.

Synthesis of Poly(ether imide)s

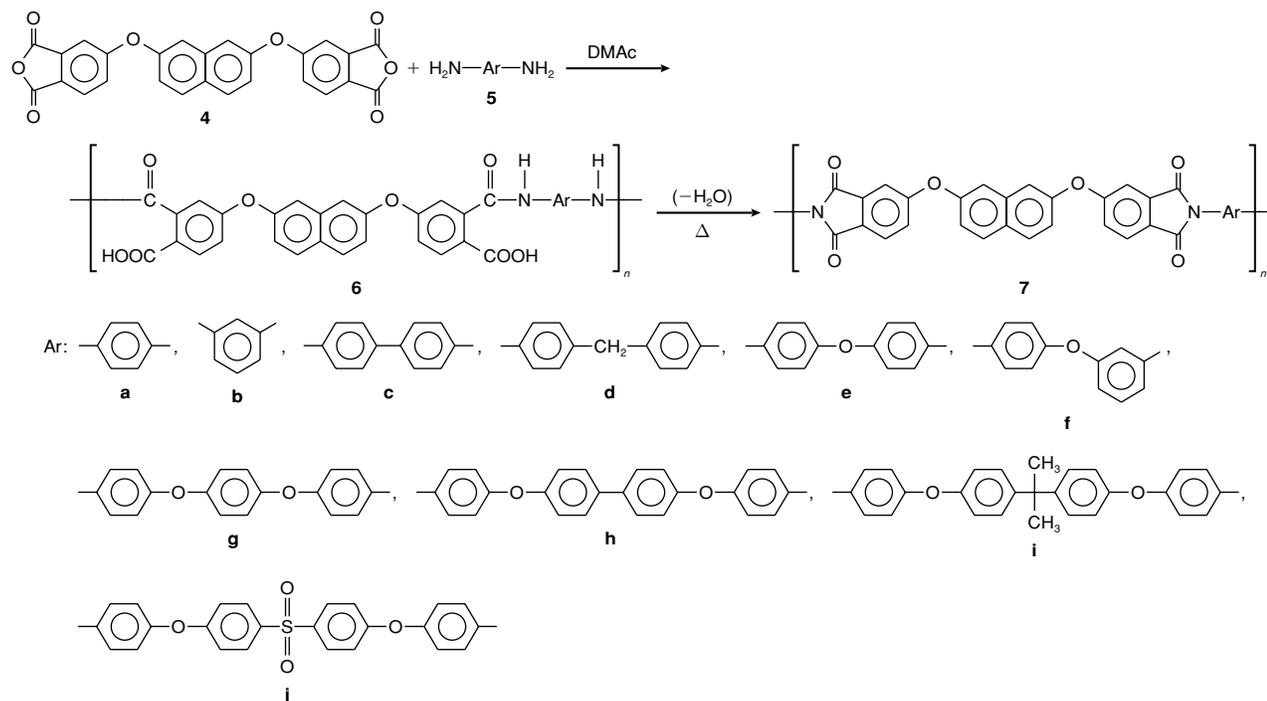
Bis(ether anhydride) **4** was converted to poly(ether imide)s by reaction with aromatic diamines by a conventional two-stage process in DMAc. The viscosities of the reaction mixtures become very high as poly(ether amic acid)s were formed, indicating the formation of high-molecular-weight polymer. As shown in Table I, the inherent viscosities of the intermediate poly(ether amic acid)s are in the 0.95 to 2.67 dL/g range. The polymerization results also indicate that the monomer synthesis is successful. The casting films of poly(ether imide)s **7a** and **7c** derived from rigid diamines, such as *p*-phenylenediamine and benzidine, embrittled during the thermal imidization process. This may be due to a high degree of crystallinity developed within these poly(ether imide)s. The other films were tough and flexible and could be creased without cracking.

IR spectroscopy allows monitoring of the imide ring formation during thermal cyclodehydration. 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 2400–3500 cm^{-1} and 1500–1730 cm^{-1} disappeared, and those of the imide ring occurred near 1780 (asym. C=O str.), 1725 (sym. C=O str.), 1365 (C—N str.), 1080, and 745 cm^{-1} (imide ring deformation). The strong absorption around 1240 cm^{-1} was assigned to the aryl ether stretching.

Among the poly(ether imide)s prepared, **7b** and **7e–h** were reported in a recent publication,¹³ where imidization was carried out chemically. The other five poly(ether imide)s **7a**, **7c**, **7d**, **7i**, and **7j** are first synthesized. Some basic properties of these polymers, such as the glass transition temperatures, solubility behavior, and thermal stability, are compared with the reported data. The inherent viscosity data of the poly(amic acid) precursors and more thermogravimetric data, some mechanical property data, and some X-ray data, which were not reported previously are included in the present study.

Properties of Poly(Ether imide)s

The solubility of poly(ether imide)s was studied qualitatively. Except for poly(ether imide)s **7d**, **7i**, and **7j**, the poly(ether imide)s were insoluble in all the organic solvents tested. Poly(ether imide)s **7d**, **7i**, and **7j** were soluble in *N*-methyl-2-pyrrolidone (NMP). Incorporation of isopropyl-



dene unit into the polymer backbone increased the flexibility of polymer chain; hence, poly(ether imide) **7i** could also be dissolved in chloroform. Poly(ether imide) **7j** containing polar sulfone group also dissolved in DMF. These results indicated that the incorporation of 2,7-diphenoxynaphthalene unit in the poly(ether imide) main chain gave limited improvement in solubility. Un-

less proper diamines were selected, the poly(ether imide)s based on bis(ether anhydride) **4** and conventional diamines usually exhibited poor solubility.

The crystallinity of the prepared poly(ether imide)s was measured by wide-angle X-ray diffraction scans. Typical diffraction patterns for some representative polymers are presented in Figure 1. Poly(ether imide)s **7a** and **7c**, which embrittled during thermal imidization, showed crystalline patterns. This can be attributed to the existence of the rigid planar imide segments in their polymer backbones that led to a better packing of polymer chains. On the contrary, insertion of one or two additional phenoxy groups into the recurring units of **7a** and **7c** resulted in a significant decrease in crystallinity. For example, polymers **7e** and **7h** showed almost completely amorphous diffraction patterns. This is reasonable because the presence of more kinked ether groups induces looser chain packing. The incorporation of *m*-phenylene unit (polymer **7b**) also led to a large decrease in crystallinity.

All the poly(ether imide)s which exhibited amorphous X-ray diffraction patterns could be processed into highly cohesive, good-quality, and creasable films. These flexible films were subjected to tensile test, and the results are included

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

Polymer Code	η_{inh}^a (dL/g)	Polymer Code	Film Quality ^b
6a	1.28	7a	Brittle
6b	0.95	7b	Flexible
6c	1.71	7c	Brittle
6d	0.98	7d	Flexible
6e	1.82	7e	Flexible
6f	0.95	7f	Flexible
6g	1.82	7g	Flexible
6h	2.67	7h	Flexible
6i	1.32	7i	Flexible
6j	0.98	7j	Flexible

^a Measured in DMAc at 30°C by an Ubbelohde viscometer.

^b Poly(ether imide) films obtained by sequential 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.

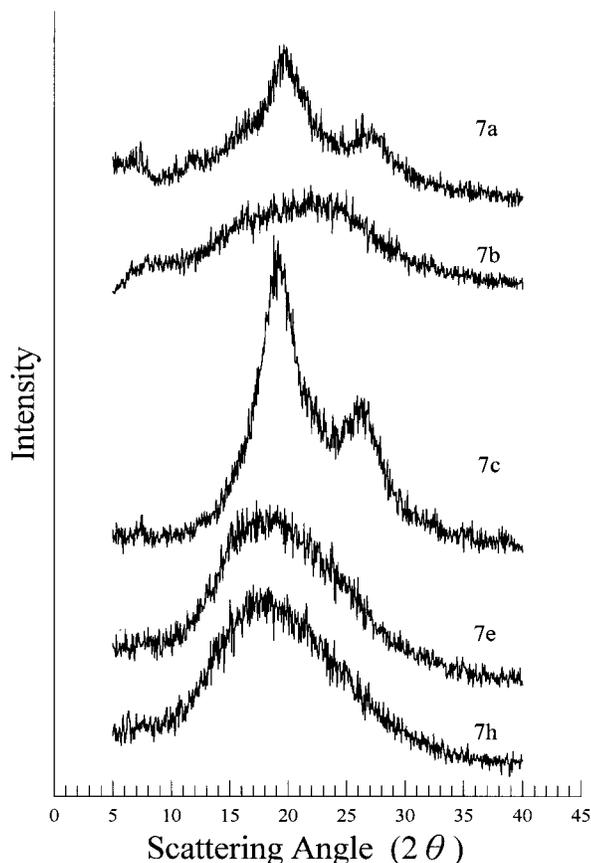


Figure 1. Wide-angle X-ray diffractograms of poly(ether imide)s **7a**, **7b**, **7c**, **7e**, and **7h**.

in Table II. All the specimens showed high tensile strengths. Their yield or tensile strengths were usually higher than 90 MPa. Except for poly(ether imide)s **7b** and **7j**, all other polymers yielded during tensile testing and had a moderate elongation to break, indicative of high toughness.

Glass transition temperatures (T_g) of the sev-

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

Polymer Code	T_g^a (°C)	Decomposition Temperature ^d (°C)		Char Yield ^e (%)
		In N ₂	In Air	
7a	— ^b (444) ^c	551	557	59.6
7b	256	582	582	62.8
7c	— ^b	591	583	64.1
7d	251	546	545	64.5
7e	250	580	579	60.0
7f	229	545	545	61.3
7g	228	572	573	60.1
7h	237	578	578	65.0
7i	222	543	543	59.0
7j	246	559	543	55.8

^a From DSC measurement conducted at a heating rate 20°C/min; T_g s were read at the middle of the base line shift on the second DSC heating traces.

^b No discernible glass transitions was observed.

^c The peak temperature of endotherm on the first DSC heating trace.

^d Temperatures at which 10% weight loss were recorded by thermogravimetry at a heating rate of 20°C/min.

^e Residual weight % at 800°C in nitrogen.

eral poly(ether imide)s were determined by differential scanning calorimetry (DSC). They were in the range of 222 to 256°C as shown in Table III. The T_g values of five poly(ether imide)s **7b** and **7e–h** are virtually identical with those reported by Eastmond and Paprotny.¹³ According to well-established principles, T_g of poly(ether imide)s vary with molecular structure. Incorporation of flexible hinges like ether group or unsymmetrical aromatic unit leads to a decrease in T_g . For example, 4,4'-oxydianiline-based poly(ether imide) **7e** had a T_g of 250°C, while the 3,4'-oxydianiline- and 1,4-bis(4-aminophenoxy)benzene-de-

Table II. 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)
7b	—	136	11	2.2
7d	109	100	23	2.2
7e	102	102	45	1.8
7f	115	104	36	1.9
7g	99	97	42	1.9
7h	91	90	28	1.8
7i	95	89	32	1.7
7j	—	101	11	1.8

rived polymers **7f** and **7g** showed a relatively lower T_g of 229 and 228°C, respectively. As shown by the T_g values of polymers **7h–j**, the introduction of rigid biphenylene unit or polar sulfonyl group resulted in higher T_g values. Poly(ether imide)s **7a** and **7c** exhibited no discernible T_g possibly due to high crystallinity. In general, observed T_g s for the polymers prepared in this study are not unusually low and the polymers are potentially useful for some practical purposes; the commercial polymer Ultem® has a T_g of about 215–220°C. The temperatures of 10% weight loss in nitrogen and air atmospheres were determined by TGA and tabulated in Table III. In general, all the polymers exhibited good thermal stability with no significant weight loss up to approximately 500°C in air and nitrogen, and the temperatures at 10% weight loss were above 540°C. The amount of carbonized residue (char yield) of poly(ether imide)s in nitrogen atmosphere was in the range of 55.8 to 65.0% weight even at 800°C, showing high intrinsic fire-retardant characteristics.

CONCLUSIONS

A series of high-molar-mass poly(ether imide)s based on 2,7-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride and various aromatic diamines have been prepared as films. Typical poly(ether imide)s were noncrystalline. The incorporation of 2,7-diphenoxynaphthalene units into the poly(ether imide) backbone did not lead to a signifi-

cant increase in solubility. However, several of these polymers exhibited a desired combination of properties that included excellent mechanical properties, high thermal stability, and moderate T_g s.

REFERENCES AND NOTES

1. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., *Polyimides*, Chapman and Hall, New York, 1990.
2. T. Takekoshi, *Polymer J.*, **19**, 191 (1987).
3. G. C. Eastmond, P. C. B. Page, J. Paprotny, R. E. Richards, and R. Shaunak, *Polymer*, **35**, 4215 (1994).
4. T. Takekoshi, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1759 (1985).
5. G. C. Eastmond, J. Paprotny, and I. Webster, *Polymer*, **34**, 2865 (1993).
6. H. S.-I. Chao and E. Barren, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 1675 (1993).
7. D. R. Heath and J. G. Wirth, U.S. Pat. 3,787,475 (1974) (to General Electric Co.).
8. G. C. Eastmond and J. Paprotny, *Polymer*, **35**, 5148 (1994).
9. G. C. Eastmond and J. Paprotny, *Macromolecules*, **28**, 2140 (1995).
10. K. Suematsu, *Macromolecules*, **18**, 2083 (1985).
11. S.-H. Hsiao, C.-P. Yang, and C.-K. Lin, *J. Polym. Res.*, **2**, 1 (1995); *Chem. Abstr.*, **123**, 287811g (1995).
12. G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, **6**, 1455 (1996).
13. G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, **6**, 1459 (1996).