

Synthesis and Properties of Poly(ether imide)s Derived from 2,6-Bis(3,4-dicarboxyphenoxy)naphthalene Dianhydride and Aromatic Diamines

SHENG-HUEI HSIAO,¹ GUEY-SHENG LIOU,² SHIN-HUNG CHEN¹

¹ Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., Sec. 3, Taipei, Taiwan, Republic of China

² Department of Chemical Engineering, I-Shou University, 1 Hsuen-Cheng Rd., 1st Sec., Ta-Hsu Hsiang, Kaohsiung, 84008, Taiwan, Republic of China

Received 26 September 1997; accepted 2 February 1998

ABSTRACT: A new naphthalene unit-containing bis(ether anhydride), 2,6-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride, was synthesized in three steps starting from the nucleophilic nitrodisplacement reaction of 2,6-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 prepared using a conventional two-step polymerization process from the bis(ether anhydride) and various aromatic diamines. The intermediate poly(ether amic acid)s had inherent viscosities of 0.65–2.03 dL/g. The films of poly(ether imide)s derived from two rigid diamines, i.e. *p*-phenylenediamine and benzidine, crystallized 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 aromatic poly(ether imide) films had yield strengths of 104–131 MPa, tensile strengths of 102–153 MPa, elongation to break of 8–87%, and initial moduli of 1.6–3.2 GPa. The glass transition temperatures (T_g 's) of poly(ether imide)s were recorded in the range of 220–277°C depending on the nature of the diamine moiety. All polymers were stable up to 500°C, with 10% weight loss being recorded above 550°C in both air and nitrogen atmospheres. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 1657–1665, 1998

Keywords: 2,6-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride; poly(ether imide)s; thermal behavior

INTRODUCTION

Aromatic polyimides were developed in the early 1960s and since then have been of great technological importance due to their outstanding thermal and electrical properties.^{1,2} However, their applications have been limited in many fields be-

cause aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass transition or melting temperatures, which preclude melt processing. Hence one of the drawbacks in using aromatic polyimides is their poor processability, and a great deal of effort has been made to improve the processing characteristics of these intractable polyimides.^{3,4} One of the successful approaches to improve solubility and processability of polyimides with minimal detrimental effect on their high thermal stability is

Correspondence to: S.-H. Hsiao

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 36, 1657–1665 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0887-624X/98/101657-09

the introduction of bulky, pendant groups along the polymer backbone. Some organo-soluble aromatic polyimides have been demonstrated by using aromatic diamines having phenyl substituents,^{5–11} as well as phenylated aromatic tetracarboxylic dianhydrides.^{12–14}

The other effective approach to processable high-temperature polymers we developed recently is the incorporation of crank and twisted non-planar structure into the polymer backbone. For example, highly kinked and cranked bulky aromatic diamines, such as 2,2'-bis(4-aminophenoxy)biphenyl and 2,2'-bis(4-aminophenoxy)-1,1'-binaphthyl, were effectively used to prepare soluble aromatic polyamides and polyimides, with various aromatic dicarboxylic acids and tetracarboxylic dianhydrides, respectively.^{15,16} Recently, in continuation of these studies, we have been interested in the potential usefulness of the naphthyl-containing structure as a simultaneously bulky and cranked unit in the polymer main chain. We have already reported the poly(ether imide)s derived from 2,3-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride,¹⁷ 1,5-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride,¹⁸ and 2,7-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride¹⁹ with various aromatic diamines, having a compromise between good thermal stability and processability. In order to get more insight into the effect of different naphthalene linkage positions on properties of poly(ether imide)s, this article deals with the synthesis of 2,6-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**3**) and its derived poly(ether imide)s and the basic characterization of these polymers as well.

EXPERIMENTAL

Materials

Reagent-grade 2,6-dihydroxynaphthalene (TCI), 4-nitrophthalonitrile (TCI), potassium carbonate, *N,N*-dimethylformamide (DMF; Fluka), potassium hydroxide (Wako), and acetic anhydride (Janssen) were used as received. Aromatic diamines such as *p*-phenylenediamine (**4a**) and benzidine (**4c**) were purified by sublimation. *m*-Phenylenediamine (**4b**) was purified by vacuum distillation. The other reagent-grade diamines such as 4,4'-methylenedianiline (**4d**), 4,4'-oxydianiline (**4e**), 3,4'-oxydianiline (**4f**), and 1,4-bis(*p*-aminophenoxy)benzene (**4g**) were used as

received. 4,4'-Bis(*p*-aminophenoxy)biphenyl (**4h**), 2,2-bis[*p*-(*p*-aminophenoxy)phenyl]propane (**4i**), 1,1-bis[*p*-(*p*-aminophenoxy)phenyl]-1-phenylethane (**4j**), bis[*p*-(*p*-aminophenoxy)phenyl]sulfone (**4k**), 2,2-bis[*p*-(*p*-aminophenoxy)phenyl]hexafluoropropane (**4l**), and α,α' -bis[*p*-(*p*-aminophenoxy)-1,4-diisopropyl]benzene (**4m**) were prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursors 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.^{20,21} *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride. Potassium carbonate was dried at 150°C under vacuum.

Monomer Synthesis

2,6-Bis(3,4-dicyanophenoxy)naphthalene (**1**)

In a three-necked flask equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser were placed 10.0 g (62.43 mmol) of 2,6-dihydroxynaphthalene and 17.31 g (100 mmol) of dried potassium carbonate with 100 mL of DMF and 70 mL of toluene. The mixture was heated with stirring at 140°C for 6 h under nitrogen to facilitate dehydration. After the toluene had been removed, the mixture was cooled and then 22.1 g (127.60 mmol) of 4-nitrophthalonitrile was added. The reaction was carried out with stirring at 60°C for 8 h, and then the reaction mixture was precipitated into 1 L of cold water. The precipitated brown solid was filtered out and washed thoroughly with methanol. The yield of the product was 24.5 g (95%), mp 253–254°C [lit.²² 267–268°C]. The IR spectrum (KBr) exhibited absorptions at 2236 (C≡N) and 1253 cm^{−1} (C—O—C).

Anal. Calcd for C₂₆H₁₂N₄O₂ (412.41): C, 75.72%; H, 2.93%; N, 13.58%. Found: C, 75.77%; H, 2.86%; N, 13.50%.

2,6-Bis(3,4-dicarboxyphenoxy)naphthalene (**2**)

A mixture of 64.8 g (1.154 mol) of potassium hydroxide and 23.8 g (0.058 mmol) of bis(ether dinitrile) **1** in 200 mL of ethanol and 200 mL of distilled water was stirred at reflux until no further ammonia was generated. The time taken to reach this stage was about 3 days. The resulting hot, clear solution was filtered to remove any insoluble

impurities. The hot filtrate was allowed to cool, and the pH value was adjusted by dilute hydrochloric acid to near 3. The precipitate formed was collected by filtration, washed repeatedly with water, and dried under vacuum. The yield was 25.0 g (89%) of brown powder, mp 211–212°C. The IR spectrum (KBr) showed absorptions at 2500–3500 (O—H), 1694 (C=O), and 1228, 1284 cm^{-1} (C—O—C).

2,6-Bis(3,4-dicarboxyphenoxy)naphthalene Dianhydride (**3**)

A mixture of bis(ether diacid) **2** (24.5 g; 0.05 mol), acetic acid (200 mL), and acetic anhydride (200 mL) was stirred 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 needles were collected, washed with dry toluene, and dried under vacuum. The yield was 19.8 g (87%), mp 233–234°C [lit.²² 237–238°C]. The IR spectrum (KBr) exhibited absorptions at 1852 and 1769 (C=O) and 1284 cm^{-1} (C—O—C).

Anal. Calcd for $\text{C}_{26}\text{H}_{12}\text{O}_8$ (452.37): C, 69.03%; H, 2.67%. Found: C, 68.97%; H, 2.70%.

Polymer Synthesis

A typical polymerization procedure is as follows: To a solution of 0.3069 g (1.533 mmol) of 4,4'-oxydianiline (**4e**) in 9.5 mL of DMAc was added 0.6931 g (1.533 mmol) of bis(ether anhydride) **3** at once at 0–5°C under nitrogen. The solution was stirred at that temperature for 1 h and then at room temperature for 3 h. The inherent viscosity of the resulting poly(amic acid) (**5e**) in DMAc was 2.03 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

The poly(amic acid) film was obtained by casting from the reaction solution onto a 9-cm glass culture dish and drying in a 90°C oven overnight to remove the solvent. The semidried poly(ether amic acid) (**5e**) in the form of film was further dried and converted to poly(ether imide) (**6e**) by successive heating at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min, and then 250°C for 1 h. By being soaked in hot water, a flexible poly(ether imide) film of **6e** lifted off from the glass surface. The infrared (IR) spectrum of **5e** (film) exhibited absorptions at 2300–3500 (N—H and O—H str.), 1500–1800 (broad, arom. C=C str. + C=O str. + N—H, O—H bending), and 1200–1300

cm^{-1} (C—O). IR of **6e** (film): 1779 (asym. C=O), 1725 (sym. C=O), 1379 (C—N), and 745 cm^{-1} (imide ring deformation).

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

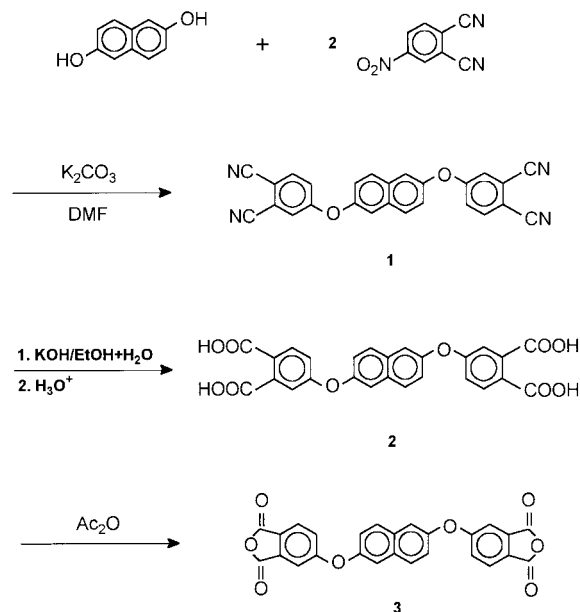
Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform spectrophotometer. 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. Differential scanning calorimetry (DSC) was performed with a Sinku Riko DSC-7000 coupled to a Sinku Riko TA-7000 analyzer. 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 (TG) was conducted with a DuPont 951 thermogravimetric analyzer equipped with a DuPont 2000 thermal analyst. Experiments were carried out on 9–11-mg samples heating in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20°C/min. Wide-angle X-ray diffraction patterns were obtained at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered $\text{Cu K}\alpha$ radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. An Instron model 1130 universal tester 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), and an average of at least five individual determinations was reported.

RESULTS AND DISCUSSION

Monomer Synthesis

According to a reported method,^{22–24} a polymer-forming aromatic tetracarboxylic dianhydride, 2,6-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**3**), was prepared in three steps as shown in Scheme 1. The aromatic tetranitrile containing ether linkage (**1**) was synthesized readily starting from 4-nitrophthalonitrile and 2,6-dihydroxynaphthalene in a high yield of 95%, according to



a slight modification of the procedure of Takekoshi et al.²³ using potassium carbonate as a base in DMF–toluene mixture. Although the bis(ether dinitrile) was not further purified, it is clear that the purity was high enough as the purity of anhydride prepared from it was high. Then, the bis(ether dinitrile) was readily hydrolyzed to bis(ether diacid) **2** by ethanolic potassium hydroxide. The yield of the bis(ether diacid) is quantitative. Finally, the bis(ether diacid) was cyclodehydrated to bis(ether anhydride) **3** in good yield (87%).

The chemical structures of all synthesized compounds were confirmed by means of elemental analysis and IR spectroscopy. Concerning the synthesis of the bis(ether diacid) (**2**), the disappearance of a characteristic cyano stretching band at around 2236 cm^{-1} on the IR spectrum revealed completion of the hydrolysis of the bis(ether dinitrile) compound (**1**), and the most characteristic bands of bis(ether diacid) **2** are observed near 1690 cm^{-1} (C=O stretching) and in the region of $2500\text{--}3500\text{ cm}^{-1}$ (O—H stretching). The spectrum of bis(ether anhydride) **3** shows characteristic cyclic anhydride absorptions near 1850 and 1770 cm^{-1} attributed to the asymmetrical and symmetrical stretching vibrations of C=O. The elemental analyses of all of these compounds were also in good agreement with the calculated values for the proposed structures.

Polymer Synthesis

The conventional two-step procedure starting from aromatic diamines and tetracarboxylic dianhydrides is a convenient method for the preparation of polyimides.^{1,2} New poly(ether imide)s (**6**) were synthesized by the two-step method starting from aromatic bis(ether anhydride) (**3**) with aromatic diamines (**4a–m**) through the ring-opening polyaddition and subsequent thermal cyclodehydration (Scheme 2), and the results are summarized in Table I. The ring-opening polyaddition in DMAc at room temperature afforded poly(ether amic acid)s (**5**) with inherent viscosities of $0.65\text{--}2.03\text{ dL/g}$, suggesting the formation of high-molecular-weight polymers. The polymerization results also indicate that the monomer synthesis is successful. The casting film of poly(ether imide) **6a** derived from rigid *p*-phenylenediamine em-

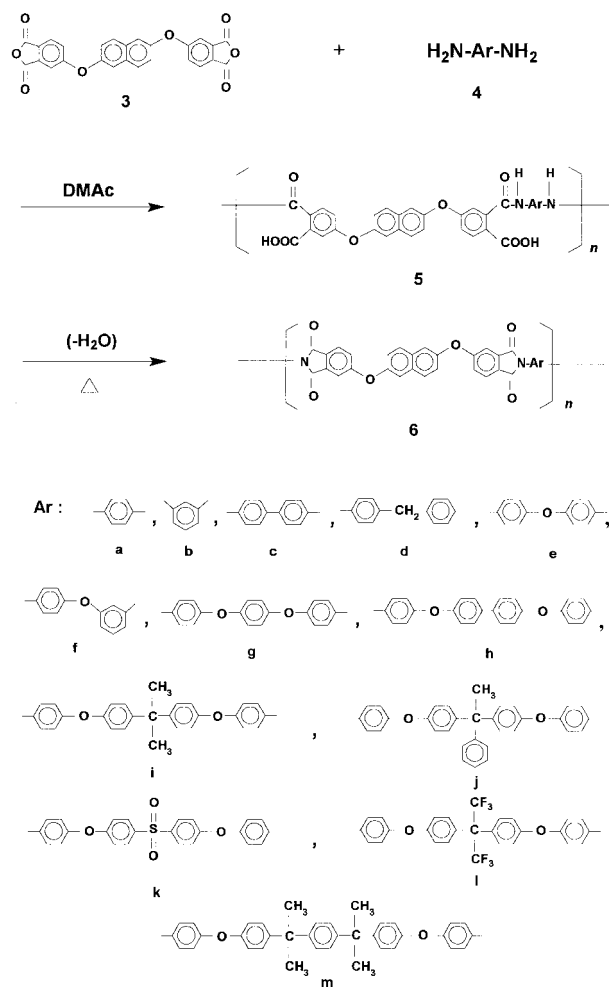


Table I. Inherent Viscosities of Poly(ether amic acid)s and Quality of Poly(ether imide) Films^a

Polymer Code	η_{inh} (dL/g)	Polymer Code	Film Quality
5a	2.02	6a	Slightly brittle ^b
5b	0.65	6b	Flexible
5c	1.55	6c	Flexible
5d	1.06	6d	Flexible
5e	2.03	6e	Flexible
5f	0.80	6f	Flexible
5g	1.53	6g	Flexible
5h	1.92	6h	Flexible
5i	1.50	6i	Flexible
5j	1.55	6j	Flexible
5k	1.20	6k	Flexible
5l	1.00	6l	Flexible
5m	1.26	6m	Flexible

^a Imidization was achieved thermally by stepwise increase of the temperature, with a maximum temperature of 250°C for 1 h.

^b Cracked upon creasing.

brittled during the thermal imidization process. This may be due to a high degree of crystallinity developed within the polymer. The other films were tough and flexible and could be creased without cracking.

The thermal conversion to poly(ether imide)s was carried out by successive heating of the poly(amic acid) films to 250°C. The formation of polyimides was confirmed by IR spectroscopy. The characteristic absorption bands of amide and carboxyl groups in the ranges of 2500–3500 and 1500–1750 cm^{-1} disappeared, and those of the imide ring occurred near 1780 (asym. C=O str.), 1725 (sym. C=O str.), 1379 (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, **6b,e–h** were reported in a recent publication,²³ where imidization was carried out chemically. The other eight poly(ether imide)s **6a,c,d,i–m** have not been previously reported. Some basic properties of these polymers, such as the glass transitions, 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.

Polymer Characterization

The solubility of the polyimides was studied qualitatively. Poly(ether imide)s **6i,j,l,m** were highly swollen in 1,3-dimethyl-2-imidazolidone (DMI), and the results may be attributable to the introduction of flexible ether linkages and other flexible bridging groups, such as isopropylidene, hexafluoroisopropylidene, and phenylethylidene, coupling the aromatic portions of the polymer chain, which hinder close packing of the polymer chain. All the poly(ether imide)s were insoluble in all the dipolar aprotic organic solvents tested that included *N*-methyl-2-pyrrolidone (NMP), DMAc, DMF, and dimethyl sulfoxide. Thus, these results implied that the incorporation of 2,6-naphthalenedioxy unit into the poly(ether imide) main chain gave limited improvement in solubility. The results are similar to those of the previously published 1,5- and 2,7-analogues and are less favorable when compared to the 2,3-polymers.^{17–19}

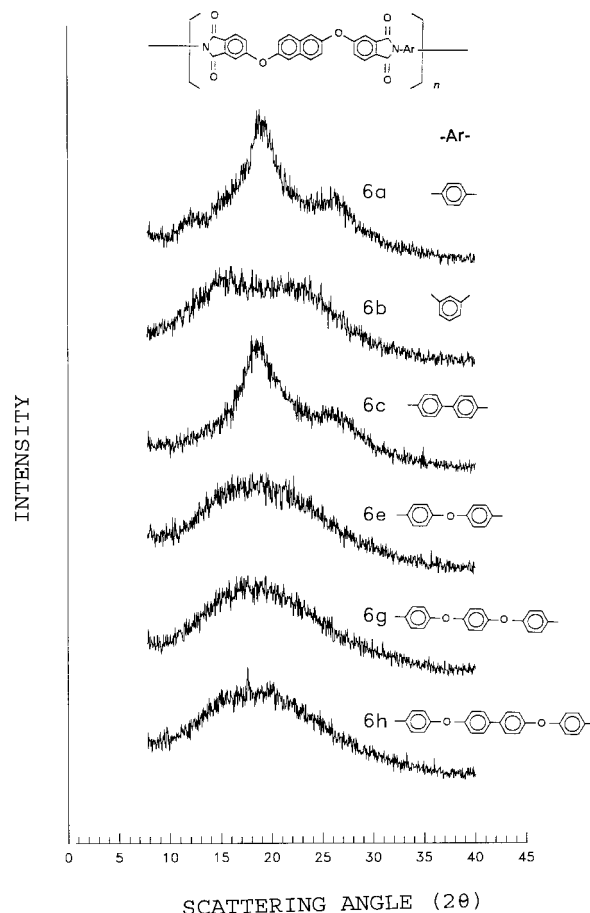
**Figure 1.** Wide-angle X-ray diffraction patterns of poly(ether imide)s.

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)
6b		153	10	2.26
6c		137	8	3.15
6d	120	129	25	1.83
6e	131	128	31	1.98
6f		130	10	1.99
6g	128	135	87	1.94
6h	117	134	80	1.83
6i	104	114	22	1.76
6j		121	26	1.85
6k		110	11	1.82
6l	105	102	48	1.64
6m		111	11	1.90

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 **6a,c** showed a fair degree of crystallinity. This can be attributed to the existence of rigid planar imide segments in their polymer backbones which led to a better packing of polymer chain. On the contrary, insertion of one or two additional phenoxy groups into the recurring units of **6a,c** resulted in a significant decrease in crystallinity. For example, polymers **6e,h** showed almost completely amorphous diffraction patterns. This is reasonable because the presence of more kinked ether groups induces

looser chain packing. The incorporation of a *m*-phenylene unit (polymer **6b**) also revealed a large decrease in crystallinity. In general, these X-ray diffraction patterns are very similar to those of 1,5-, 2,7-, and 2,3-isomeric poly(ether imide)s reported previously.¹⁷⁻¹⁹

Except for polymer **6a**, all the poly(ether im-

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

Polymer Code	T_g^a (°C)	Decomposition Temperature ^b (°C)		Char Yield ^c (%)
		In Air	In N ₂	
6a	^d	592	595	57.3
6b	272	595	600	54.5
6c		606	619	63.3
6d	277	577	584	65.1
6e	260	598	600	66.1
6f	240	589	590	71.3
6g	240	593	584	61.5
6h	252	593	595	65.3
6i	231	559	562	59.3
6j	242	574	558	52.1
6k	259	565	566	47.1
6l	240	574	575	54.0
6m	220	547	559	57.4

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

^b Temperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 20°C/min.

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

^d No discernible transitions were observed.

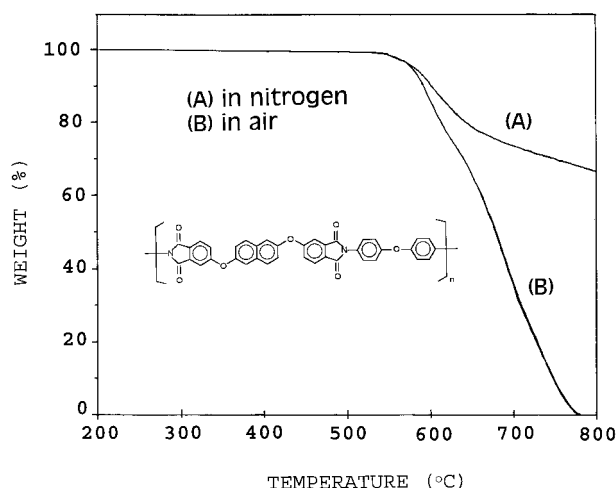
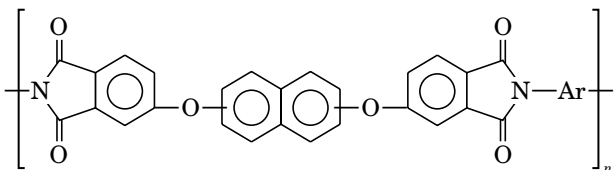
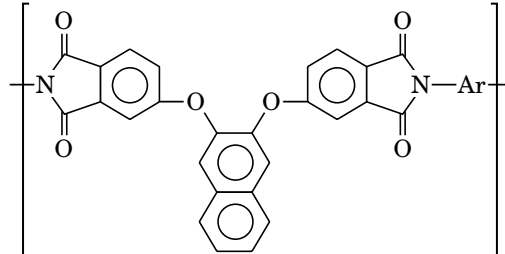
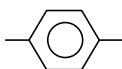
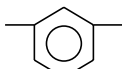
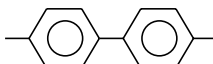
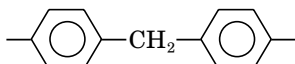
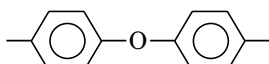
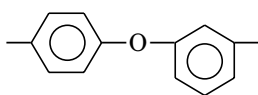
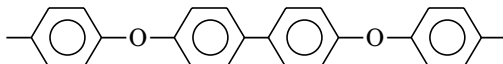
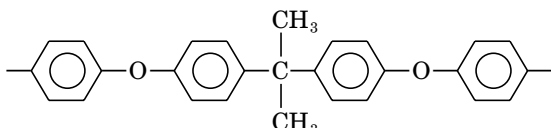
**Figure 2.** TG thermograms of poly(ether imide) **6e** at a heating rate of 20°C/min.

Table IV. Glass Transition Temperatures of Isomeric Poly(ether imide)s

	and			
T_g^a (°C) of Poly(ether imide)s Having Different Disubstituted Naphthalene Units				
—Ar—	2,6	1,5	2,7	2,3
	b			
	272	265	256	219
				
	277	250	251	no ^c
	260	262	250	206
	240	239	229	no
	240	250	228	220
	252	256	237	218
	231	226	222	no

^a The samples were first heated to 400°C at a heating rate of 20°C/min in nitrogen and then rapidly cooled to room temperature in flowing air. T_g s were read at the middle of the change in the baseline shift on the second DSC heating trace.

^b No discernible T_g was observed.

^c The polymers were not prepared.

ide)s could be processed into highly cohesive, good-quality, and creasable films. These flexible films were subjected to tensile test, and the results are summarized in Table II. All the specimens showed high tensile strengths. Their yield

or tensile strengths were usually higher than 110 MPa. Except for poly(ether imide)s **6b,e,f,j,k,m**, all other polymers yielded during tensile testing and had fairly high elongation to break, indicative of high toughness.

Thermal behavior of all the poly(ether imide)s was evaluated by DSC and TG. The representative TG diagrams of poly(ether imide) **6e** measured in air and nitrogen atmosphere are shown in Figure 2. All the other poly(ether imide)s showed similar patterns of decomposition with no significant weight loss below 500°C in air or nitrogen. Besides sulfone-containing poly(ether imide) **6k**, which has lower dissociation energy, all the other polymer exhibited more than 52 wt % residue remaining when heated to 800°C in nitrogen. The data reported in Table III show that the 10% weight loss temperatures of these poly(ether imide)s were recorded in the range of 550–605°C in air and 560–620°C in nitrogen. The amount of carbonized residue (char yield) of poly(ether imide)s in nitrogen atmosphere was in the range of 47.1–66.1% weight even at 800°C, showing high intrinsic fire-retardant characteristics. The glass transition temperatures (T_g), defined by the midpoint of baseline shift, of these poly(ether imide)s were observed in the range of 220–277°C as shown in Table III, depending on the structure of diamine component and decreasing with decreasing rigidity of the polymer backbone. The T_g values of five poly(ether imide)s **6b,e–h** are higher by 15–40°C than those reported by Eastmond and Paprotny,²⁴ where the polymers were imidized chemically. The difference in T_g may be attributable to different imidization methods, characterization techniques, and instruments. Poly(ether imide)s **6a,c** exhibited no discernible T_g possibly due to high crystallinity. Poly(ether imide) **6m** has the lowest T_g , 220°C, which is due to the highest amount of flexible bridges, isopropylidene and ether groups, per repeat unit of the macromolecule. The large window between T_g and the decomposition temperature makes these polymers attractive for practical processing comparing with the commercial polymer Ultem resin that has a T_g of about 215–220°C. The effect of isomeric attachment in the naphthalene unit on glass transition is shown in Table IV. In most cases, the T_g 's of the 2,6-polymers are similar to those of the 1,5-polymers and are higher than those of the 2,7- and 2,3-polymers. The explanation is that an overall decrease in T_g for the 2,7- and 2,3-poly(ether imide)s correlates with backbone flexibility due to their less symmetric backbones when compared to 2,6- and 1,5-systems.

CONCLUSIONS

A series of high-molecular-weight poly(ether imide)s based on 2,6-bis(3,4-dicarboxyphenoxy-

)naphthalene dianhydride were prepared by conventional two-step polycondensation with various aromatic diamines. Typical poly(ether imide)s were noncrystalline. The introduction of a bulky and cranked 2,6-diphenoxynaphthalene unit into the polymer backbone did not lead to significantly improved solubility of the polymers in various organic solvents. However, several of these polymers exhibited a desired combination of properties requiring for high-performance materials that include excellent mechanical properties, high thermal stability, and moderate T_g 's.

The authors wish to thank the National Science Council of the Republic of China for financial support (Grant number NSC-86-2815-C-036-024-E).

REFERENCES AND NOTES

1. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., *Polyimides*, Chapman and Hall, New York, 1990.
2. M. K. Ghosh and K. L. Mittal, Eds., *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.
3. Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).
4. Y. Imai, *React. Funct. Polym.*, **30**, 3 (1996).
5. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2189 (1984).
6. F. W. Harris and Y. Sakaguchi, *Proc. Polym. Mater. Sci. Eng.*, **60**, 187 (1989).
7. H.-J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 39 (1991).
8. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 1691 (1991).
9. Y. Oishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1027 (1992).
10. H.-J. Jeong, A. Kobayashi, M. Kakimoto, and Y. Imai, *Polym. J.*, **26**, 373 (1994).
11. F. Akutsu, T. Kataoka, H. Shimizu, Naruchi, and M. Miura, *Macromol. Chem., Rapid Commun.*, **15**, 411 (1994).
12. F. W. Harris, W. A. Feld, and L. H. Lanier, *Appl. Polym. Symp.*, **26**, 421 (1975).
13. F. W. Harris and S. L.-C. Hsu, *High Perform. Polym.*, **1**, 1 (1989).
14. R. Giesa, U. Keller, P. Eiselt, and H.-W. Schmidt, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 141 (1993).
15. G.-S. Liou, M. Maruyama, M. Kakimoto, and Y.

- Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2499 (1993).
16. G.-S. Liou, M. Maruyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 3273 (1993).
17. S.-H. Hsiao, C.-P. Yang, and K.-Y. Chu, *Macromolecules*, **30**, 165 (1997).
18. S.-H. Hsiao, C.-P. Yang, and K.-Y. Chu, *Macromol. Chem. Phys.*, **198**, 2153 (1997).
19. S.-H. Hsiao and K.-Y. Chu, *J. Polym. Sci., Part A: Polym. Chem.*, **35**, 2281 (1997).
20. K. Suematsu, *Macromolecules*, **18**, 2083 (1985).
21. S.-H. Hsiao, C.-P. Yang, and C.-K. Lin, *J. Polym. Res.*, **2**, 1 (1995); *Chem. Abstr.*, **123**, 287811g (1995).
22. G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, **6**, 1455 (1996).
23. T. Takekoshi, J. W. Wirth, D. R. Heath, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3069 (1980).
24. G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, **6**, 1459 (1996).