

Synthesis and Properties of Poly(ether imide)s Based on the Bis(ether anhydride)s from Hydroquinone and Its Derivatives

SHENG-HUEI HSIAO, LIANG-RU DAI

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

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ABSTRACT: Four bis(ether anhydride)s, 4,4'-(1,4-phenylenedioxy)diphthalic anhydride (IV), 4,4'-(2,5-tolylenedioxy)-diphthalic anhydride (Me-IV), 4,4'-(2-chloro-1,4-phenylenedioxy)diphthalic anhydride (Cl-IV), and 4,4'-(2,5-biphenylenedioxy)diphthalic anhydride (Ph-IV), were prepared in three steps starting from the nucleophilic nitro-displacement reaction of 4-nitrophthalonitrile with the potassium phenoxides of hydroquinone and various substituted hydroquinones such as methylhydroquinone, chlorohydroquinone, and phenylhydroquinone in *N,N*-dimethylformamide, followed by alkaline hydrolysis and dehydration. Four series of poly(ether imide)s were prepared from bis(ether anhydride)s with various aromatic diamines by a classical two-step procedure. The inherent viscosities of the intermediate poly(amic acid)s were in the range of 0.40–2.63 dL/g. Except for those derived from *p*-phenylenediamine and benzidine, almost all the poly(amic acid)s could be solution-cast and thermally converted into transparent, flexible, and tough polyimide films. Introduction of the chloro or phenyl substituent leads to a decreased crystallinity and an increased solubility of the polymers. The glass transition temperatures (T_g) of these polyimides were recorded in the range of 204–263°C. In general, the methyl- and chloro-substituted polyimides exhibited relatively higher T_g s, whereas the phenyl-substituted ones exhibited slightly lower T_g s compared to the corresponding nonsubstituted ones. Thermogravimetric analysis (TG) showed that 10% weight loss temperatures of all the polymers were above 500°C either in nitrogen or in air. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 665–675, 1999

Keywords: hydroquinone; methylhydroquinone; chlorohydroquinone; phenylhydroquinone; bis(ether anhydride)s; poly(ether imide)s

INTRODUCTION

Aromatic polyimides are an important class of commercial polymers due to their outstanding thermal stability combined with their excellent mechanical and electrical properties.^{1,2} Polyimides are mainly used in the electronic and aerospace industries in the forms of films and mold-

ings. Other uses for these polymers, such as adhesives, gas separation membranes, composite matrices, coatings, and foams, are rapidly increasing. However, aromatic polyimides have one major disadvantage of typically being insoluble and intractable after conversion from the poly(amic acid) to the polyimide form. Most conventional processing techniques involve the fabrication of poly(amic acid) precursors followed by thermal or chemical imidization. Problems can arise because the poly(amic acid)s are thermally and hydrolytically unstable. The water evolved

Correspondence to: S.-H. Hsiao

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from imidization can also form voids in bulk materials. Therefore, much effort has been spent on synthesizing more processable, tractable polyimides without compromising the desired properties.

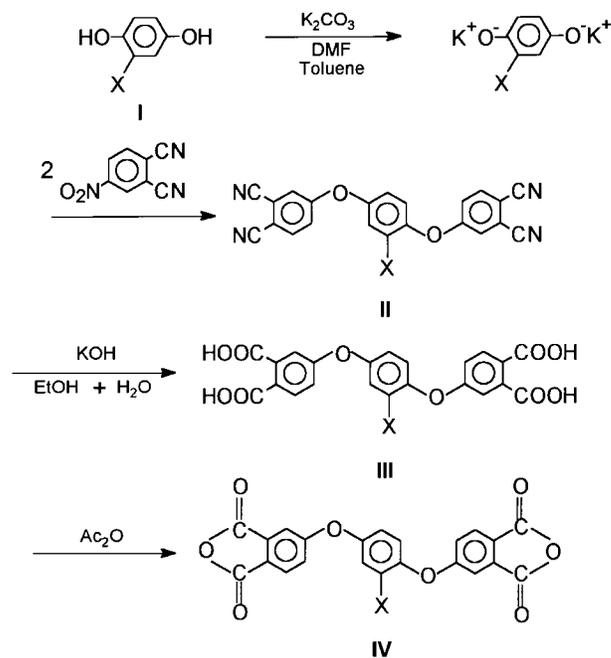
Introduction of flexible groups, such as —O— and —C(CH₃)₂—, and asymmetric aromatic units in the polyimide backbone may lead to a decreased glass transition temperature and an enhanced moldability. A successful example was the commercial Ultem 1000 resin, which was made from bisphenol A bis(ether anhydride) and *m*-phenylenediamine. The incorporation of main-chain ether linkages imparts solubility and melt processability. In order to further enhance processability and tailor properties for specific applications, many bis(ether anhydride)s and their derived poly(ether imide)s have been reported.^{6–14} The bis(ether anhydride) monomers are usually synthesized by a reaction sequence involving nitrodisplacement between an aromatic diol and a suitable nitrophthalic acid derivative, often a nitrophthalonitrile or a nitrophthalimide.

The hydroquinone-based bis(ether anhydride) such as structure IV in Scheme 1 and its derived poly(ether imide)s have been mentioned in the academic reports and patents.^{3–6,15–17} It is usually considered that *p*-phenylenedioxy units impart a certain linearity and often rigidity to polymer chains, thus leading to poor solubility of the poly(ether imide)s derived from the hydroquinone bis(ether anhydride). The present study deals with the synthesis and basic characterization of the poly(ether imide)s based on bis(ether anhydride)s derived from hydroquinone and its methyl, chloro, and phenyl derivatives. Introduction of substituents leads to a decreased regularity of the polymer chain and hinders the tight packing of the polymer chains. Thus, it is expected that the prepared poly(ether imide)s may exhibit higher solubility and lower melt viscosity. The effects of the introduction of substituents on the properties of poly(ether imide)s such as solubility, crystallinity, and thermal properties were also evaluated.

EXPERIMENTAL

Materials

Hydroquinone (I, Janssen), methylhydroquinone (Me-I, TCI), chlorohydroquinone (Cl-I, Acros), phenylhydroquinone (Ph-I, Aldrich), acetic anhy-



	I-IV	Me-I-IV	Cl-I-IV	Ph-I-IV
X	-H	-CH ₃	-Cl	

Scheme 1.

drone (Janssen), 4-nitrophthalonitrile (TCI), and *N,N*-dimethylformamide (DMF, Fluka) were used without previous purification. *p*-Phenylenediamine (V_a, TCI) and benzidine (V_e, TCI) were purified by sublimation. *m*-Phenylenediamine (V_b, Janssen) was vacuum-distilled prior to use. 4,4'-Diaminodiphenyl ether (V_d, TCI), 4,4'-diaminodiphenylmethane (V_f, TCI), 3,4'-diaminodiphenyl ether (V_e, TCI), and 1,4-bis(*p*-aminophenoxy)benzene (V_g, TCI) were used without previous purification. According to a reported method,¹⁸ 4,4'-bis(4-aminophenoxy)biphenyl (V_h, mp 198–199°C), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (V_i, mp 123–124°C) and bis[4-(4-aminophenoxy)phenyl] sulfone (V_j, mp 185–187°C) were prepared by the nucleophilic substitution reaction of the corresponding bisphenols, i.e., 4,4'-biphenol (Fluka), 2,2-bis(4-hydroxyphenyl)propane (Wako), and 4,4'-sulfonyldiphenol (Wako) with *p*-chloronitrobenzene (TCI) in the presence of potassium carbonate and subsequent reduction of the intermediate bis(4-nitrophenoxy) compounds using hydrazine as the reducing agent and palla-

dium as the catalyst. *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

Bis(ether dinitrile)s

The bis(ether dinitrile)s were prepared from the nucleophilic nitrodisplacement reaction of 4-nitrophthalonitrile with the potassium phenoxides of corresponding hydroquinones. A detailed procedure for the preparation of 4,4'-(2,5-tolylenedioxy)diphthalonitrile (Me-II) is as follows.

In a 300 mL flask, 6.21 g (0.05 mol) of methylhydroquinone (Me-I) and 13.8 g (0.1 mol) of K_2CO_3 were suspended in a mixture of 100 mL of DMF and 70 mL of toluene. The suspension solution was heated at a reflux temperature using a Dean-Stark trap to remove the water by azeotropic distillation with toluene. After complete removal of water, the residual toluene was distilled off. Then, the reaction mixture was cooled to about 60°C, 17.3 g (0.1 mol + 0.2 g) of 4-nitrophthalonitrile was added, and heating was continued at 60°C for 24 h. On cooling, the reaction solution was poured into 500 mL of water, and the precipitated solid was collected and washed thoroughly with water. The yield of the crude product was quantitative. Recrystallization from an acetonitrile/methanol mixture (4 : 1 by volume) yields a pure brown granular crystal of bis(ether dinitrile) Me-II. The yield of the purified product was 14.4 g (85%); mp 205–208°C (DSC: 208°C). The IR spectrum (KBr) exhibited absorptions at 2234 cm^{-1} (C≡N), 1601–1481 cm^{-1} (arom. C=C), 1189 cm^{-1} (C—O—C).

Anal. Calcd for $C_{23}H_{12}N_4O_2$ (376.37): C, 73.40%; H, 3.21%; N, 14.89%. Found: C, 73.11%; H, 3.35%; N, 14.82%.

The other three bis(ether dinitrile)s, II, Cl-II, and Ph-II, were synthesized in an analogous procedure from hydroquinone (I), chlorohydroquinone (Cl-I), and phenylhydroquinone (Ph-I).

4,4'-(1,4-Phenylenedioxy)diphthalonitrile (II): Yield 81.6%; mp 257–258°C (DSC: 255°C) (lit.³ 255–257°C). IR (KBr): 2236 cm^{-1} (C≡N), 1599–1485 cm^{-1} (arom. C=C), 1191 cm^{-1} (C—O—C).

Anal. Calcd. for $C_{22}H_{10}N_4O_2$ (362.35): C, 72.92%; H, 2.78%; N, 15.46%. Found: C, 72.42%; H, 2.93%; N, 15.26%.

4,4'-(2-Chloro-1,4-phenylenedioxy)diphthalonitrile (Cl-II): Yield 84%; mp 199–201°C (DSC:

200°C) (lit.³ 204–205.5°C). IR (KBr): 2238 cm^{-1} (C≡N), 1599–1483 cm^{-1} (arom. C=C), 1191 cm^{-1} (C—O—C).

Anal. Calcd. for $C_{22}H_9N_4O_2Cl$ (376.37): C, 66.59%; H, 2.29%; N, 14.12%. Found: C, 66.88%; H, 2.46%; N, 14.08%.

4,4'-(2,5-Biphenylenedioxy)diphthalonitrile (Ph-II): Yield 74.4%; mp 222–225°C (DSC: 224°C). IR (KBr): 2238 cm^{-1} (C≡N), 1601–1481 cm^{-1} (arom. C=C), 1187 cm^{-1} (C—O—C).

Anal. Calcd. for $C_{28}H_{14}N_4O_2$ (438.44): C, 76.71%; H, 3.32%; N, 12.78%. Found: C, 76.48%; H, 3.36%; N, 13.05%.

Bis(ether diacid)s

The bis(ether diacid)s were prepared from alkaline hydrolysis of the corresponding bis(ether nitrile)s. A representative synthetic procedure for 4,4'-(2,5-tolylenedioxy)diphthalic acid (Me-III) is as follows.

In a 500-mL flask, a suspension of bis(ether dinitrile) Me-II (14 g; 0.0372 mol) in an ethanol/water mixture (150 mL/150 mL) containing dissolved 42 g (0.7439 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 4 h. Reflux was continued for about 24 h, until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and acidified by conc. HCl to pH = 1–2 to precipitate a white solid which was filtered, thoroughly washed with water, and dried to afford 15.12 g (85%) of Me-III.

4,4'-(1,4-Phenylenedioxy)diphthalic acid (III), 4,4'-(2-chloro-1,4-phenylenedioxy)diphthalic acid (Cl-III) and 4,4'-(2,5-biphenylenedioxy)diphthalic acid (Ph-III) were synthesized in an analogous procedure. The yields of these bis(ether acid)s usually above 80%. All the bis(ether diacid)s exhibited characteristic absorptions at 1700 cm^{-1} (C=O) and 2500–3500 cm^{-1} (carboxyl O—H) in their IR spectra.

Bis(ether anhydride)s

The bis(ether anhydride)s were prepared by cyclodehydration of the corresponding bis(ether diacid)s. A typical workup procedure for the preparation of 4,4'-(2,5-tolylenedioxy)diphthalic anhydride (Me-IV) is as follows.

In a 300-mL flask, bis(ether diacid) Me-III was suspended in 80 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 tiny grains of bis(ether anhydride) Me-IV started to crystallize, and next day the product was filtered off, washed with dry toluene, and dried in vacuo, to give 10.7 g (77%) yield; mp 212–214°C (DSC: 213°C). The IR spectrum (KBr) exhibited absorptions at 1852 cm^{-1} (asym. C=O str.), 1773 cm^{-1} (sym. C=O str.), 1481–1618 cm^{-1} (arom. C=C), 1187 cm^{-1} (C—O—C).

Anal. Calcd. for $\text{C}_{23}\text{H}_{12}\text{O}_8$ (416.34): C, 66.35%; H, 2.91%. Found: C, 65.86%; H, 3.02%.

Bis(ether anhydride)s IV, Cl-IV, and Ph-IV were synthesized in an analogous procedure.

4,4'-(1,4-Phenylenedioxy)diphthalic anhydride (IV): Yield 82.9%; mp 264–266°C (DSC: 264°C). IR (KBr): 1850 cm^{-1} (asym. C=O str.), 1769 cm^{-1} (sym. C=O str.), 1483–1618 cm^{-1} (arom. C=C), 1187 cm^{-1} (C—O—C).

Anal. Calcd. for $\text{C}_{22}\text{H}_{10}\text{O}_8$ (402.32): C, 65.68%; H, 2.51%. Found: C, 65.46%; H, 2.67%.

4,4'-(2-Chloro-1,4-phenylenedioxy)diphthalic anhydride (Cl-IV): Yield 65%; mp 197–200°C (DSC: 198°C). IR (KBr): 1852 cm^{-1} (asym. C=O str.), 1775 cm^{-1} (sym. C=O str.), 1477–1620 cm^{-1} (arom. C=C), 1185 cm^{-1} (C—O—C).

Anal. Calcd. for $\text{C}_{22}\text{H}_9\text{O}_8\text{Cl}$ (436.76): C, 60.50%; H, 2.08%. Found: C, 60.65%; H, 2.26%.

4,4'-(2,5-Biphenylenedioxy)diphthalic anhydride (Ph-IV): Yield 61%; mp 224–226°C (DSC: 223°C). IR (KBr): 1854 cm^{-1} (asym. C=O str.), 1773 cm^{-1} (sym. C=O str.), 1477–1599 cm^{-1} (arom. C=C), 1181 cm^{-1} (C—O—C).

Anal. Calcd. for $\text{C}_{28}\text{H}_{14}\text{O}_8$ (478.41): C, 70.30%; H, 2.95%. Found: C, 69.69%; H, 3.03%.

General Polymerization Procedure

A calculated quantity of an aromatic diamine was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, an equal molar quantity of a bis(ether anhydride) was added in one portion. The mixture was stirred at room temperature for 3 h to afford a viscous poly(ether amic acid) solution. The total amount of the diamine and the bis(ether anhydride) used was 1.0 g, and thus the obtained polymer solution had a concentration of about 10 wt %. The inherent viscosity of the resulting poly(ether amic acid) was measured in DMAc 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 an 80°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, 250°C for 20 min, and 270°C for 20 min. By soaking in hot water, a flexible poly(ether imide) film was lifted off the glass surface.

Measurements

The melting points were measured with a MEL-TEMP II apparatus or a differential scanning calorimeter (heating rate: 10°C/min). Elemental analyses were carried out on a Perkin-Elmer model 2400 C, H, N analyzer at the National Taiwan University (Taipei). IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. The inherent viscosities were measured with an Ubbelohde viscometer 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. Scans were run at 20°C/min. Glass transition temperatures (T_g s) were read at the middle of the transition in the heat capacity, and were determined on the second heating scan after quick cooling. Dynamic thermogravimetry (TG) was performed using a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyzer. Experiments were carried out on 9- to 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 K_α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$.

RESULTS AND DISCUSSION

Monomer Synthesis

The bis(ether anhydride)s IV, Me-IV, Cl-IV, and Ph-IV were prepared by a three-step reaction sequence, shown in Scheme 1. First, the intermediate bis(ether dinitrile)s were obtained from the nucleophilic nitrodisplacement of 4-nitrophthalonitrile with the phenoxide ions of hydroquinones in DMF. The purified bis(ether dinitrile)s were readily hydrolyzed to bis(ether diacid)s by ethanolic potassium hydroxide, and then the generated bis(ether diacid)s were cyclodehydrated to yield the final bis(ether anhydride)s. The structures of the intermediate bis(ether dinitrile)s and

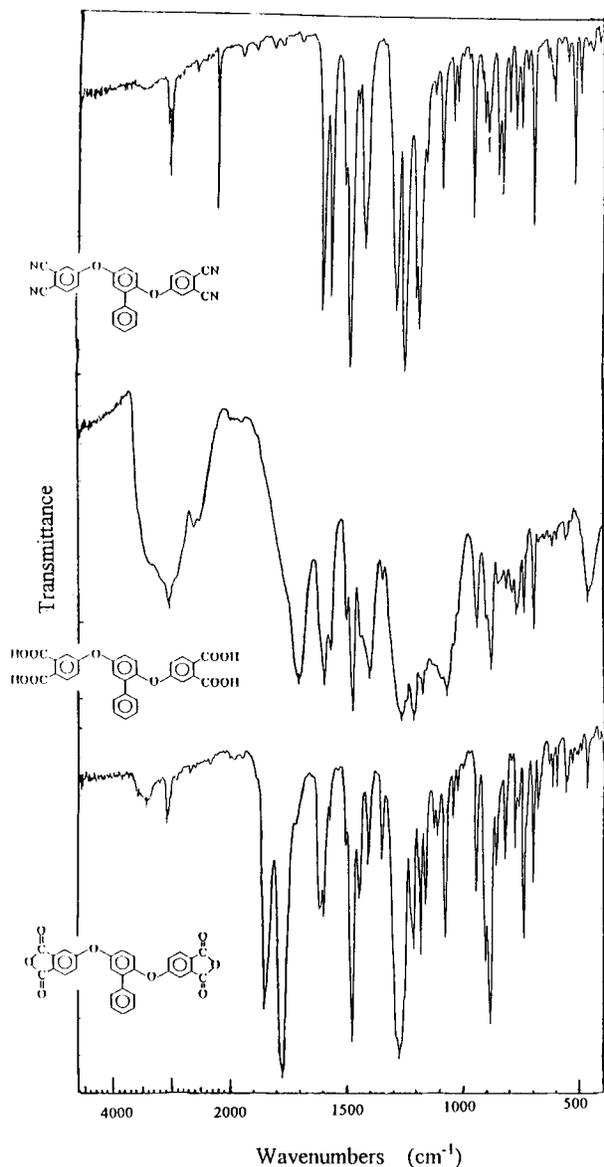


Figure 1. Infrared spectra of 4,4'-(2,5-biphenylenedioxy)diphthalonitrile (Ph-II), 4,4'-(2,5-biphenylenedioxy)diphthalic acid (Ph-III), 4,4'-(2,5-biphenylenedioxy)diphthalic anhydride (Ph-IV).

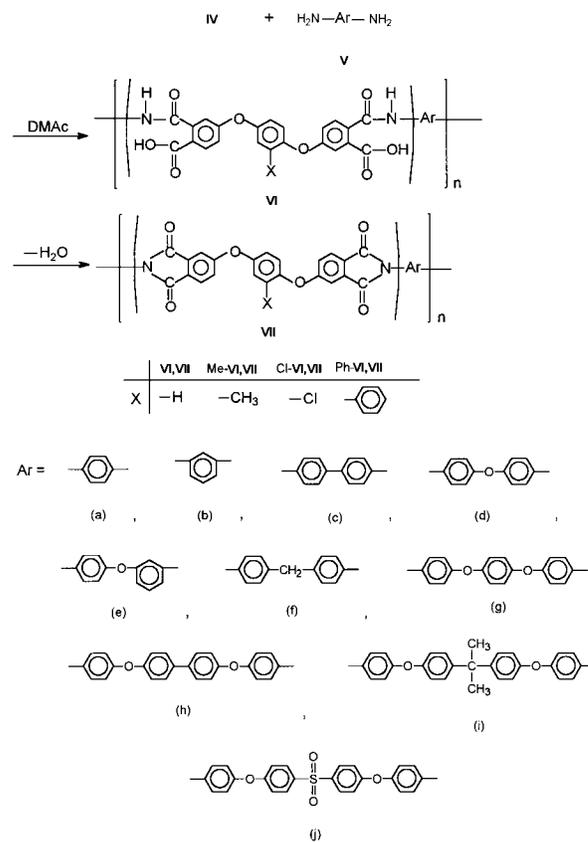
the bis(ether anhydride) products were confirmed by elemental analysis and infrared spectroscopy, and the intermediate bis(ether diacid)s were only checked by infrared spectroscopy.

As a typical example, Figure 1 summarizes the IR spectra of bis(ether dinitrile) Ph-II, bis(ether diacid) Ph-III, and bis(ether anhydride) Ph-IV. After the cyano group was hydrolyzed to the carboxyl group, the sharp absorption near 2238 cm^{-1} characteristic to the cyano group disappeared, and the carbonyl stretching absorption around

1711 cm^{-1} and the broad O—H absorption in the region between 2500 and 3500 cm^{-1} appeared. After the bis(ether diacid) was cyclodehydrated to the bis(ether anhydride), the broad O—H absorption disappeared, and the spectrum showed characteristic cyclic anhydride absorbances near 1854 and 1773 cm^{-1} , suggesting the asymmetric and symmetric stretching vibrations of C=O.

Polymer Synthesis

All poly(ether imide)s were prepared from the bis(ether anhydride)s with various aromatic diamines by a conventional two-stage process as outlined in Scheme 2. The parentheses in the formulas of polymers VI and VII indicate that the asymmetric dianhydride moiety may appear in the polymer chain, as shown or in the reverse head and tail direction. This convention is needed since the simple order of dianhydride repeating units cannot be assumed. As shown in Table I, the inherent viscosities of the resulting four series of poly(ether amic acid)s, VI_{a-j}, Me-VI_{a-j}, Cl-VI_{a-j}, and Ph-VI_{a-j}, are in the ranges of 0.68–1.71 dL/g,



Scheme 2.

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

Poly(ether amic acid)s			Poly(ether imide)s		
Polymer Code	η_{inh}^a (dL/g)	Film ^b Quality	Polymer Code	η_{inh}^c (dL/g)	Film ^d Quality
VI _a	1.00	Flexible	VII _a	0.26	Brittle
VI _b	0.68	Flexible	VII _b	0.54	Flexible
VI _c	1.25	Flexible	VII _c	— ^e	Brittle
VI _d	1.20	Flexible	VII _d	0.87	Flexible
VI _e	0.90	Flexible	VII _e	0.39	Flexible
VI _f	0.86	Flexible	VII _f	1.40	Flexible
VI _g	0.94	Flexible	VII _g	0.81	Brittle
VI _h	1.71	Flexible	VII _h	1.51	Flexible
VI _i	0.74	Flexible	VII _i	0.64 ^a	Flexible
VI _j	0.71	Flexible	VII _j	0.53 ^a	Flexible
Me-VI _a	0.93	Flexible	Me-VII _a	0.50	Brittle
Me-VI _b	0.78	Flexible	Me-VII _b	0.90	Flexible
Me-VI _c	1.70	Flexible	Me-VII _c	0.73	Brittle
Me-VI _d	1.49	Flexible	Me-VII _d	1.33	Flexible
Me-VI _e	0.73	Flexible	Me-VII _e	0.49	Flexible
Me-VI _f	1.16	Flexible	Me-VII _f	— ^e	Flexible
Me-VI _g	1.29	Flexible	Me-VII _g	1.37	Flexible
Me-VI _h	2.63	Flexible	Me-VII _h	— ^e	Flexible
Me-VI _i	1.55	Flexible	Me-VII _i	1.18 ^a	Flexible
Me-VI _j	1.04	Flexible	Me-VII _j	0.81 ^a	Flexible
Cl-VI _a	0.91	Flexible	Cl-VII _a	0.47	Brittle
Cl-VI _b	0.56	Flexible	Cl-VII _b	0.94	Flexible
Cl-VI _c	1.26	Flexible	Cl-VII _c	— ^e	Brittle
Cl-VI _d	1.13	Flexible	Cl-VII _d	0.62	Flexible
Cl-VI _e	0.53	Flexible	Cl-VII _e	0.34 ^a	Flexible
Cl-VI _f	0.90	Flexible	Cl-VII _f	0.87	Flexible
Cl-VI _g	1.19	Flexible	Cl-VII _g	0.82	Flexible
Cl-VI _h	1.56	Flexible	Cl-VII _h	0.61	Flexible
Cl-VI _i	1.07	Flexible	Cl-VII _i	0.66 ^a	Flexible
Cl-VI _j	1.01	Flexible	Cl-VII _j	0.62 ^a	Flexible
Ph-VI _a	0.52	Flexible	Ph-VII _a	0.48	Brittle
Ph-VI _b	0.44	Flexible	Ph-VII _b	0.41 ^a	Flexible
Ph-VI _c	0.40	Brittle	Ph-VII _c	0.24	Brittle
Ph-VI _d	0.57	Flexible	Ph-VII _d	0.52 ^a	Flexible
Ph-VI _e	0.52	Flexible	Ph-VII _e	0.43 ^a	Flexible
Ph-VI _f	0.58	Flexible	Ph-VII _f	0.47 ^a	Flexible
Ph-VI _g	0.79	Flexible	Ph-VII _g	0.70 ^a	Flexible
Ph-VI _h	0.97	Flexible	Ph-VII _h	0.58 ^a	Flexible
Ph-VI _i	0.78	Flexible	Ph-VII _i	0.62 ^a	Flexible
Ph-VI _j	0.64	Flexible	Ph-VII _j	0.57 ^a	Flexible

^a Measured at a concentration of 0.5 g/dL in DMAc at 30°C.^b Films were cast by slow evaporation of polymer solutions in DMAc.^c Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.^d Poly(ether imide)s films were obtained by sequential heating the poly(ether amic acid)s films at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min, 250°C for 20 min, and 270°C for 20 min.^e Insoluble in sulfuric acid.

0.73–2.63 dL/g, 0.53–1.56 dL/g, and 0.40–0.97 dL/g, respectively. Except for Ph-VI_c, all the other poly(ether amic acid)s could be cast into tough

and flexible films. The poly(ether amic acid) films were subsequently converted to the poly(ether imide) films by means of thermal imidization. The

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

Polymers	Solvents ^b						
	NMP	DMSO	DMF	<i>m</i> -Cresol	THF	DMAc	Conc. H ₂ SO ₄
VII _a	—	—	—	—	—	—	+
VII _b	+h	—	—	+h	—	—	+
VII _c	—	—	—	—	—	—	—
VII _d	+h	—	—	+h	—	—	+
VII _e	+h	+h	+	+h	—	—	+
VII _f	—	—	—	+h	—	—	+
VII _g	—	—	—	—	—	—	+
VII _h	—	—	—	—	—	—	+
VII _i	+h	+h	+	+h	+	+	+
VII _j	+h	+h	+h	+h	—	+	+
Me-VII _a	—	—	—	—	—	—	+
Me-VII _b	—	—	—	—	—	—	+
Me-VII _c	—	—	—	—	—	—	+
Me-VII _d	—	—	—	+h	—	—	+
Me-VII _e	—	—	—	—	—	—	+
Me-VII _f	—	—	—	—	—	—	—
Me-VII _g	—	—	—	—	—	—	+
Me-VII _h	—	—	—	—	—	—	—
Me-VII _i	—	—	+h	+	+	+	+
Me-VII _j	—	+h	+h	+	—	+	+
Cl-VII _a	—	—	—	—	—	—	+
Cl-VII _b	—	—	—	—	—	—	+
Cl-VII _c	—	—	—	—	—	—	—
Cl-VII _d	+h	+h	+h	+h	—	—	+
Cl-VII _e	+h	+h	+h	+h	—	+	+
Cl-VII _f	+h	+h	+h	+h	—	—	+
Cl-VII _g	+h	—	—	+h	—	—	+
Cl-VII _h	+h	—	—	+h	—	—	+
Cl-VII _i	+	+h	+	+h	+	+	+
Cl-VII _j	+	+h	+	+h	+h	+	+
Ph-VII _a	—	—	—	—	—	—	+
Ph-VII _b	+h	+h	+h	+h	—	+h	+
Ph-VII _c	+h	—	—	+h	—	—	+
Ph-VII _d	+h	+h	+h	+h	—	+h	+
Ph-VII _e	+h	+h	+	+h	—	+	+
Ph-VII _f	+	+h	+	+h	—	+	+
Ph-VII _g	+h	+h	+h	+h	—	—	+
Ph-VII _h	+	+h	+h	+h	—	+	+
Ph-VII _i	+	+h	+	+h	—	+	+
Ph-VII _j	+h	+h	+	+h	—	+	+

^a Solubility: (+) soluble at room temperature, (+h) soluble on heating, (—) insoluble even on heating.

^b NMP: *N*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; DMAc: *N,N*-dimethylacetamide.

films of poly(ether imide)s derived from rigid diamines such as *p*-phenylenediamine (V_a) and benzidine (V_c) seriously cracked during the thermal imidization process, possibly because a high degree of crystallinity developed within those poly(ether imide)s. This was confirmed by X-ray diffractometry. The films of poly(ether imide)s de-

rived from the other diamines are flexible and exhibit high strengths. The results indicated that the polymers had high molecular weights, and the synthesis of the bis(ether anhydride) monomers was successful.

IR spectroscopy allows monitoring of the imide ring formation during thermal cure. The charac-

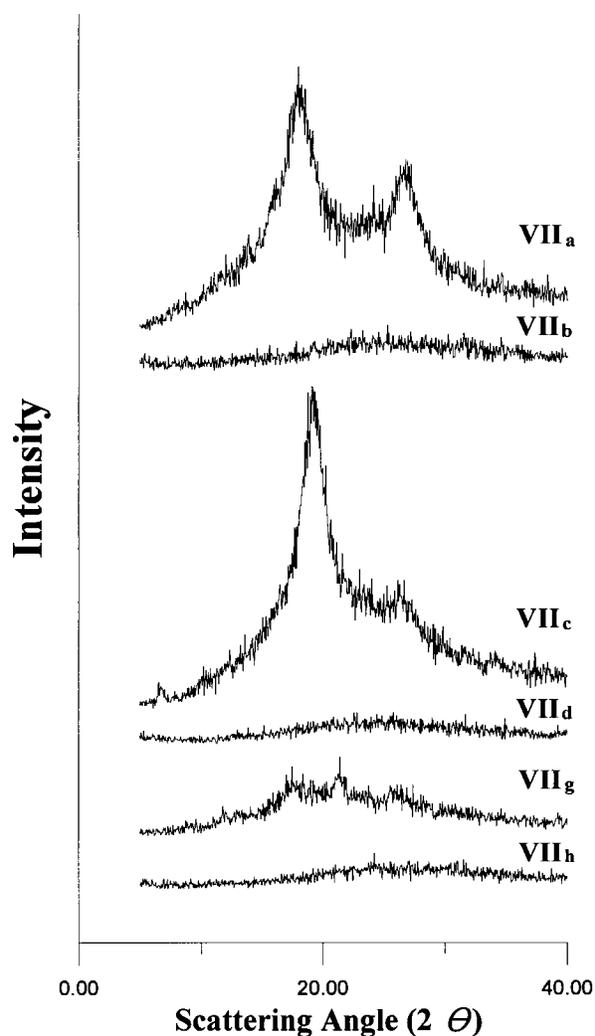


Figure 2. Wide-angle X-ray diffractograms of some poly(ether imide)s derived from 4,4'-(1,4-phenylene-dioxy)diphthalic anhydride (IV).

teristic absorption bands of the imide ring were observed near 1780 (asym. C=O str.), 1720 (sym. C=O str.), 1380 (C—N str.), 1110 and 745 cm^{-1} (imide ring deformation). The aryl ether stretching absorbed near 1250 cm^{-1} .

Properties of Poly(ether imide)s

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. In the series of poly(ether imide)s derived from hydroquinone bis(ether anhydride) IV, about one-half of the polymers could be dissolved in hot NMP and *m*-cresol. The poly(ether imide)s VII_e, VII_i, and VII_j derived from 3,4'-diaminodiphenyl

ether (V_e), and long-chain diamines bearing flexible linkages such as V_i and V_j showed higher solubility. They were soluble in most of the tested solvents. The introduction of methyl substituent on the phenylene unit of bis(ether anhydride) did not lead to an improved solubility. In some cases, such as Me-VII_b, Me-VII_d, and Me-VII_e, the introduction of methyl groups resulted in a decreased solubility. This may be explained by the fact that the introduction of methyl group decreased the rotational freedom of ether linkage. However, the introduction of chloro or phenyl group could inhibit close chain packing and increase polymer fractional free volume that increases polymer chain rotational and flexural mobility, thus leading to a slight increase in solubility. Moreover,

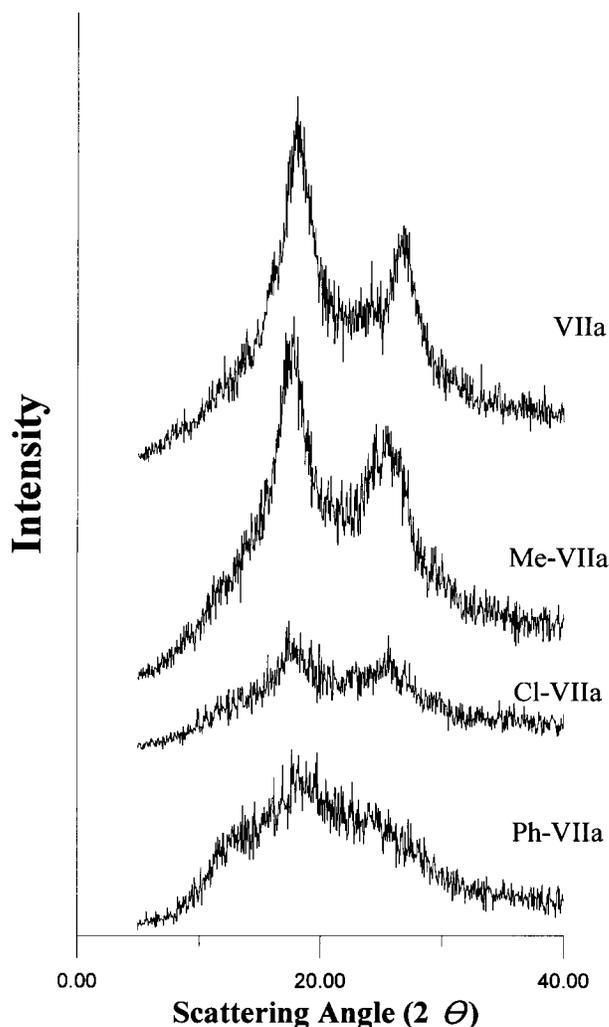


Figure 3. Wide-angle X-ray diffractograms of poly(ether imide)s derived from *p*-phenylenediamine and various bis(ether anhydride)s.

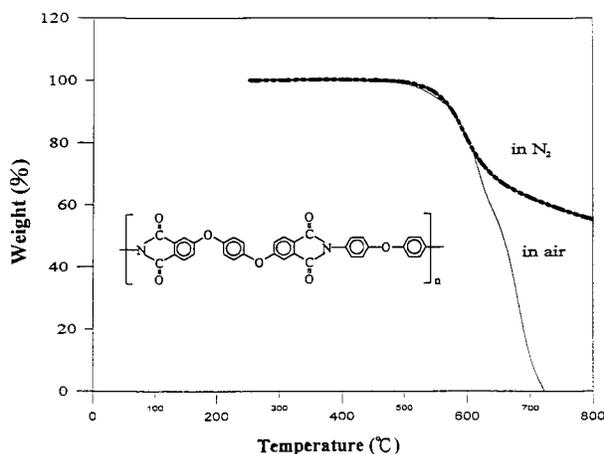


Figure 4. TG curves of poly(ether imide) VII_d, with a heating rate of 20°C/min.

most of the poly(ether imide)s were soluble in concentrated sulfuric acid.

The X-ray diffraction patterns of some poly(ether imide)s over the 2θ range of 5–40° are shown in Figures 2 and 3. As shown in Figure 2, the poly(ether imide)s (VII_a and VII_c) derived from symmetric and rigid diamines such as *p*-phenylenediamine (V_a) and benzidine (V_c) showed a crystalline diffraction pattern. This also explained the reason why all the poly(ether imide)s derived from diamines V_a and V_c embrittled during thermal imidization, as mentioned earlier. The high level of crystallinity associated with these polymers may be attributable to the existence of the rigid, nearly planar 1,4-bis(phthalimido)phenylene or 4,4'-bis(phthalimido)biphenylene units in their polymer backbone, leading to a better packing of polymer chains. Changing the *p*-phenylene group to *m*-phenylene or inserting one or two additional phenoxy groups into the polymer's recurring unit, for example, VII_b, VII_d, VII_g, and VII_h, reduced the polymer crystallinity drastically. However, poly(ether imide) VII_g still seems to reveal some degree of crystallinity. This result also corresponds to the formation of brittle, noncreasable, and opaque film of VII_g during the imidization of its poly(ether amic acid)s film. The effect of introducing pendent groups on the polymer crystallinity can be seen from Figure 3. Methyl substitution results in little influence. However, the attachment of chloro or phenyl group causes a significant decrease in crystallinity.

The thermal stability of the polymers was evaluated by thermogravimetry (TG). As a represen-

tative example, the TG curves of poly(ether imide) VII_d are shown in Figure 4. The poly(ether imide) showed no significant weight loss before 500°C in air or nitrogen. The polymer remained more than 52.2% residue when heated to 800°C in nitrogen. But in air, oxidative degradation continued above 600°C, and the polymer decomposed completely at about 720°C. A comparison of the TG curves of poly(ether imide)s having different substituents, VII_d, Me-VII_d, Cl-VII_d, and Ph-VII_d, in nitrogen is shown in Figure 5. The introduction of chloro and methyl groups slightly lowered the initial decomposition temperature of polymers, and the effect of the phenyl group did not seem significant. Some TG data of all the poly(ether imide)s are summarized in Table III. The 10% weight loss temperatures (T_{10}) of these four series poly(ether imide)s were recorded in the ranges of 554–604°C, 511–663°C, 555–586°C, and 573–638°C, respectively. The char residues of these polymers when heated to 800°C at 20°C/min in nitrogen were all above 50%.

The poly(ether imide)s were quenched from an elevated temperature at approximately 400°C to form predominantly amorphous samples; thus, distinct glass transitions generally could be observed on the subsequent heating DSC traces. The glass transition temperatures (T_g s) of the four series of poly(ether imide)s VII_{a-g}, Me-VII_{a-g}, Cl-VII_{a-g}, and Ph-VII_{a-g} were recorded in the ranges of 204–248°C, 210–260°C, 216–254°C, and 207–263°C. Due to the chain stiffness, no discernible transitions were observed for most of the poly(ether imide)s derived from diamines V_a and V_c. In most cases, the methyl-substituted or

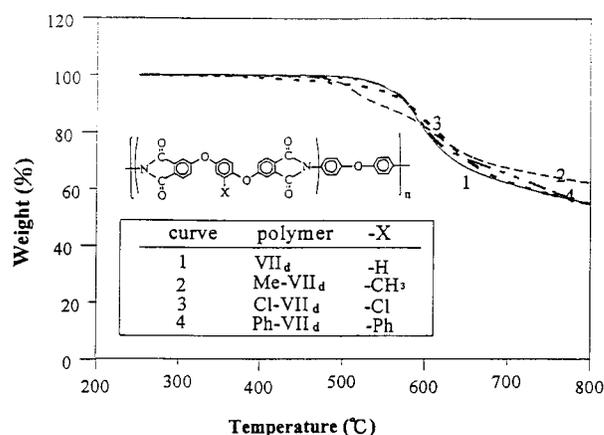


Figure 5. TG curves of poly(ether imide)s VII_d, Me-VII_d, Cl-VII_d, and Ph-VII_d, with a heating rate of 20°C/min in nitrogen.

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

Polymer Code	T_g^a (°C)	T_d^b (°C)	Char Yield ^c (%)
VII _a	—	604	58.4
VII _b	245	573	55.7
VII _c	—	600	63.3
VII _d	235	572 (575) ^d	55.3
VII _e	215 (308) ^e	572	54.8
VII _f	237	556	59.3
VII _g	215	589	57.7
VII _h	232	581	54.2
VII _i	204	554	57.6
VII _j	248	575	52.2
Me-VII _a	—	533	64.0
Me-VII _b	260	513	59.7
Me-VII _c	—	539	63.8
Me-VII _d	250	538 (564) ^d	62.5
Me-VII _e	222	539	59.4
Me-VII _f	243	541	62.2
Me-VII _g	227	522	54.7
Me-VII _h	236	563	51.9
Me-VII _i	210	520	53.3
Me-VII _j	240	511	51.6
Cl-VII _a	—	581	50.4
Cl-VII _b	254	561	52.5
Cl-VII _c	—	586	57.2
Cl-VII _d	230	572 (572) ^d	55.1
Cl-VII _e	221	584	57.9
Cl-VII _f	248	555	59.3
Cl-VII _g	225	578	57.9
Cl-VII _h	223	585	50.2
Cl-VII _i	216	556	60.9
Cl-VII _j	227	559	55.5
Ph-VII _a	263	573	60.9
Ph-VII _b	234	564	59.4
Ph-VII _c	210	564	56.9
Ph-VII _d	228	538 (572) ^d	54.3
Ph-VII _e	213	566	57.9
Ph-VII _f	222	550	54.9
Ph-VII _g	218	573	57.0
Ph-VII _h	207	569	54.2
Ph-VII _i	212	547	52.0
Ph-VII _j	234	563	55.2

^a From the second DSC heating traces with a heating rate of 20°C/min in nitrogen.

^b Decomposition temperatures at which 10% weight loss was recorded by TG at a heating rate of 20°C/min in nitrogen.

^c Residual weight % when heated to 800°C in nitrogen.

^d Values in parentheses are 10% weight loss temperatures observed in air.

^e The endotherm peak temperature observed on the first DSC trace.

chloro-substituted poly(ether imide)s exhibited higher T_g s than the corresponding unsubstituted analogs. Thus, the effect of asymmetry and irregularity introduced with the pendent group, which should lessen T_g , may be overcome by the increased rotational barrier to ether linkage due to

the presence of pendent group at the ortho position. For the chlorine-containing polymers, a dipolar effect from the C—Cl bond may be another factor causing a T_g increase. Minority of chloro-substituted polymers and most of the phenyl-substituted poly(ether imide)s showed a slightly

lower T_g than the corresponding unsubstituted ones. This may be due to the effects of chain separation, asymmetry, and irregularity caused by the large side substituents. In the same series of poly(ether imide)s, the T_g values of polymer generally decreased with increasing flexibility of the diamine moiety. The introduction of *m*-phenylene or ether linkage in the macromolecular chain led to a decreased T_g , whereas the introduction of biphenylene or sulfonyl group caused an increased T_g . Furthermore, a melting endotherm was observed at 380°C during the first heating of poly(ether imide) VII_e. Rapid cooling and reheating showed a strong T_g at 215°C and disappearance of the melting transition, pointing at a low crystallization rate. Although most of the poly(ether imide)s derived from diamines V_a and V_c exhibited crystalline X-ray diffraction patterns, well-defined melting endotherms were not observed on the DSC traces before decomposition, possibly due to high melting points.

CONCLUSIONS

The nitrodisplacement reactions between 4-nitrophthalonitrile and the potassium phenolates of hydroquinone, methylhydroquinone, chlorohydroquinone, and phenylhydroquinone 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 in high purity and high yields. Using the traditional two-step method, the bis(ether anhydride)s were polymerized with various aromatic diamines to form four series of poly(ether imide)s. The poly(ether imide)s derived from rigid diamines such as *p*-phenylenediamine (V_a) and benzidine (V_c) had high crystallinity, and their films embrittled during thermal imidization. The other poly(ether imide)s were amorphous materials and could afford strong and tough films. The introduction of larger side groups such as chloro or phenyl groups in the poly(ether imide) backbone could substantially decrease their crystallinity and increase their solubility. The introduction of methyl and chloro groups usually slightly enhanced the T_g values, but phenyl substitution

slightly decreased the T_g values. Except for the poly(ether imide)s containing methyl substituent, all the other series of poly(ether imide)s did not show significant weight loss before 500°C.

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