

# Synthesis and Characterization of Soluble Polyimides Derived from 2',5'-Bis(3,4-dicarboxyphenoxy)-*p*-terphenyl Dianhydride

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**ABSTRACT:** A novel bis(ether anhydride) monomer, 2',5'-bis(3,4-dicarboxyphenoxy)-*p*-terphenyl dianhydride, was synthesized from the nitro displacement of 4-nitrophthalonitrile by the phenoxide ion of 2',5'-dihydroxy-*p*-terphenyl, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) and cyclodehydration of the resulting bis(ether diacid). A series of new poly(ether imide)s bearing laterally attached *p*-terphenyl groups were prepared from the bis(ether anhydride) with various aromatic diamines via a conventional two-stage process that included ring-opening polyaddition to form the poly(amic acid)s followed by thermal or chemical imidization to the poly(ether imide)s. The inherent viscosities of the poly(amic acid) precursors were in the range of 0.62–1.26 dL/g. Most of the poly(ether imide)s obtained from both routes were soluble in polar organic solvents, such as *N,N*-dimethylacetamide. All the poly(ether imide)s could afford transparent, flexible, and strong films with high tensile strengths. The glass-transition temperatures of these poly(ether imide)s were recorded as between 214 and 276 °C by DSC. The softening temperatures of all the poly(ether imide) films stayed in the 207–265 °C range according to thermomechanical analysis. For all the polymers significant decomposition did not occur below 500 °C in nitrogen or air atmosphere. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 1008–1017, 2004  
**Keywords:** organosoluble; polyimides; poly(ether imide)s; high-performance polymers; bis(ether anhydride); thermal properties

## INTRODUCTION

Aromatic polyimides are a class of high-performance polymers that have outstanding thermal stability, chemical resistance, and mechanical properties.<sup>1,2</sup> However, their applications have been limited in some fields because aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass-transition or melting temperatures, precluding melt pro-

cessing. Consequently, the search for new polyimides that have better processability while maintaining their thermal stability should result in new materials for many applications. One approach that has been successfully applied is to incorporate ether groups or other flexibilizing linkages along the backbones, leading to a significant improvement of the solubility and/or thermoplasticity of polyimides.<sup>3–5</sup> Polyimides containing ether linkages prepared through phenoxy derivatives via nitro displacements, especially General Electric's poly(ether imide) Ultem<sup>®</sup>, have achieved great commercial success.<sup>6,7</sup> On the other hand, the introduction of bulky groups into the polymer chain<sup>8–16</sup> or the attachment of bulky

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lateral groups<sup>17–27</sup> can impart a significant increase in the glass-transition temperature ( $T_g$ ) by restricting the segmental mobility while providing good solubility from decreased packing and crystallinity. Combining these two structural modifications minimizes the trade-off between the poor processability and the improved physical properties of aromatic polyimides.

Recently, we reported on a series of poly(ether imide)s based on the bis(ether anhydride)s synthesized from hydroquinone and its derivatives.<sup>28,29</sup> It was found that the incorporation of larger side groups such as *tert*-butyl and phenyl groups on the poly(ether imide) backbone could substantially decrease their crystallinity and increase their solubility. In a continuation of these studies, the present study reports the synthesis and basic characterization of a new family of poly(ether imide)s based on 2',5'-bis(3,4-dicarboxyphenoxy)-*p*-terphenyl dianhydride. It was hoped that the incorporation of the hindered ether-linked dianhydride would decrease polymer inter-chain interactions and reduce the packing efficiency and the crystallinity, which may promote the tractability of the poly(ether imide)s.

## EXPERIMENTAL

### Materials

2,5-Diphenyl-1,4-benzoquinone (Lancaster), 4-nitrophthalonitrile (TCI), *N,N*-dimethylformamide (DMF) (Fluka), and acetic anhydride (Fluka) were used as received. *N,N*-Dimethylacetamide (DMAc; Fluka) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. *p*-Phenylenediamine (**VI<sub>a</sub>**) and benzidine (**VI<sub>c</sub>**) were purified by sublimation, and *m*-phenylenediamine (**VI<sub>b</sub>**) was purified by vacuum distillation. Some aromatic diamines such as 4,4'-oxydianiline (**VI<sub>d</sub>**; TCI), 1,4-bis(4-aminophenoxy)benzene (**VI<sub>e</sub>**; TCI), and 1,3-bis(4-aminophenoxy)benzene (**VI<sub>f</sub>**; TCI) were used without further purification. According to a well-developed technique,<sup>5,30–32</sup> 4,4'-bis(4-aminophenoxy)biphenyl (**VI<sub>g</sub>**; mp 198–199 °C), bis[4-(4-aminophenoxy)phenyl] ether (**VI<sub>h</sub>**; mp 128–129 °C), and 2',5'-bis(4-aminophenoxy)-*p*-terphenyl (**VI<sub>i</sub>**; mp 250–252 °C) were prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene with 4,4'-dihydroxybiphenyl (TCI), 4,4'-dihydroxydiphenyl ether (TCI), and 2',5'-dihydroxy-*p*-terphenyl, respectively, in the

presence of potassium carbonate, followed by the catalytic reduction of the intermediate dinitro compounds, using hydrazine monohydrate as the reducing agent and palladium on charcoal (Pd/C) as the catalyst.

### Monomer Synthesis

#### 2',5'-Dihydroxy-*p*-terphenyl (II)

2,5-Diphenyl-1,4-benzoquinone (25 g, 96 mmol) was added to a mixture of zinc powder (12 g) in acetic acid (500 mL), and this mixture was refluxed for 6 h. The mixture solution was filtered when hot, and filtrate was then diluted with hot water (600 mL). The filtrate was allowed to cool to room temperature. The resulting precipitate was filtered, collected, and dried under vacuum as a light yellow solid (21.6 g, 86%; mp 224–225 °C).

IR (KBr): 3539, 3438 (O—H stretching), 1182, 1140  $\text{cm}^{-1}$  (C—O—C stretching). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.95 (s, 2H, —OH), 7.57 (dd,  $J = 8.0, 0.9$  Hz, 4H), 7.41 (dd,  $J = 7.5, 7.8$  Hz, 4H), 7.29 (dd,  $J = 7.4, 7.4$  Hz, 2H), 6.88 (s, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 147.0, 138.3, 128.8, 127.9, 126.4, 125.2, 117.4. ELEM. ANAL. Calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> (262.31): C, 82.42%; H, 5.38%. Found: C, 82.78%; H, 5.28%.

#### 2',5'-Bis(3,4-dicyanophenoxy)-*p*-terphenyl (III)

In a 300-mL round-bottom flask equipped with a Dean–Stark trap and a condenser 9.6 g (0.0366 mol) of diol **II** and 10.1 g (0.073 mol) of anhydrous potassium carbonate were charged with 100 mL of DMF and 50 mL of toluene. The mixture was heated with stirring at 140 °C for 6 h to facilitate dehydration. After most toluene had been removed, the mixture was cooled, and then 12.7 g (0.073 mol) of 4-nitrophthalonitrile was added. The reaction was carried out at 80 °C for about 12 h, and then the reaction mixture was precipitated into 500 mL of cold water. The precipitated light yellow solid was filtered out and washed thoroughly with methanol and water. The yield of the product was 18.3 g (97%), mp 226–227 °C.

IR (KBr): 2235 (C≡N stretching), 1244  $\text{cm}^{-1}$  (C—O—C stretching). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 8.04 (d,  $J = 8.7$  Hz, 2H), 7.84 (d,  $J = 2.2$  Hz, 2H), 7.51 (d,  $J = 7.6$  Hz, 4H), 7.50 (dd,  $J = 8.7, 2.2$  Hz, 2H), 7.49 (s, 2H), 7.38 (dd,  $J = 7.6, 7.3$  Hz, 4H), 7.32 (dd,  $J = 7.3, 7.2$  Hz, 2H). ELEM. ANAL. Calcd. for C<sub>34</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> (514.54): C, 79.37%; H, 3.53%; N, 10.89%. Found: C, 78.78%; H, 3.37%; N, 10.92%.

**2',5'-Bis(3,4-dicarboxyphenoxy)-p-terphenyl (IV)**

In a 500-mL flask, a mixture of 18 g (0.035 mol) of bis(ether dinitrile) **III** and 40 g (1.4 mol) of potassium hydroxide in 200 mL of water and 200 mL of ethanol was stirred at a reflux temperature until no further ammonia was generated. It took about 1 day to reach this stage. The resulting clear solution was filtered hot to remove any insoluble impurities. The hot filtrate was allowed to cool, and the pH value was adjusted to 2–3 using concentrated HCl. The precipitated white solid was collected by filtration, washed repeatedly with water, and dried. The yield of the product was 20.3 g. The product, bis(ether diacid) **IV**, was not further purified and not characterized in detail but was used directly in the synthesis of bis(ether anhydride) **V**. IR (KBr): 2500–3500 (O—H stretching), 1689 (C=O stretching), 1226  $\text{cm}^{-1}$  (C—O—C stretching).

**2',5'-Bis(3,4-dicarboxyphenoxy)-p-terphenyl Dianhydride (V)**

In a 500-mL flask, 20 g of bis(ether diacid) **IV** was suspended in 100 mL of acetic anhydride and 100 mL of acetic acid. The suspension was boiled under reflux for 3 h. After the solution was cooled to room temperature, the product was filtered and dried at 250 °C under vacuum. Yield of **V**: 16.5 g (87%); mp 305–308 °C. IR (KBr): 1849 (asymmetric C=O stretching), 1772 (symmetric C=O stretching), 1270  $\text{cm}^{-1}$  (C—O—C stretching). ELEM. ANAL. Calcd. for  $\text{C}_{34}\text{H}_{18}\text{O}_8$  (554.51): C, 73.64%; H, 3.27%. Found: C, 73.28%; H, 3.33%.

**Synthesis of Poly(ether imide)s**

A typical polymerization procedure is as follows. In a 50-mL flask, 0.5988 g (1.625 mmol) of diamine **VI<sub>g</sub>** was dissolved in 14.2 mL of DMAc. After the diamine was dissolved completely, 0.9012 g (1.625 mmol) of bis(ether anhydride) **V** was added in one portion. Thus, the solid content of the solution is approximately 10 wt %. The mixture was stirred at room temperature for about 24 h to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) (**VII<sub>g</sub>**) in DMAc was 1.26 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The poly(amic acid) was subsequently converted into polyimide by either a thermal or a chemical imidization process. For the thermal imidization process, about 10 g of the obtained poly(amic acid) solution was poured into a 9-cm

glass culture dish, which was placed in a 80 °C oven for the slow release of the casting solvent. The semidried poly(amic acid) film was further dried and converted to polyimide by sequential heating at 150 °C for 30 min, 200 °C for 1 h, and 250 °C for 1 h. A flexible poly(ether imide) film of **VIII<sub>g</sub>** self-stripped off from the glass substrate upon cooling. Chemical imidization was performed by adding 2 mL of pyridine and 5 mL of acetic anhydride into the remaining poly(amic acid) solution and stirring the mixture at room temperature overnight. The reaction solution was then poured into methanol to give a pale yellow precipitate, which was collected and dried.

**Measurements**

Elemental analysis was made on a Heraeus VarioEL-III 2400 CHN analyzer. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. The inherent viscosities of the poly(amic acid)s were measured with an Ubbelohde viscometer at 30 °C. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress–strain behavior of the polyimide film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.6 mm thick), and an average of at least five individual determinations was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer, using graphite-monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , operating at 40 kV and 20 mA). The scanning rate was 3°/min over a range of  $2\theta = 10^\circ\text{--}40^\circ$ . Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on samples approximately 5–7 mg in size in flowing nitrogen (flow rate of 40  $\text{cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20  $\text{cm}^3/\text{min}$ ). Glass-transition temperatures ( $T_g$ ) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick-cooling from 400 °C at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 40 °C to 300 °C at a scan rate of 10 °C/min

using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures ( $T_s$ ) were taken as the onset temperature of probe displacement on the TMA traces.

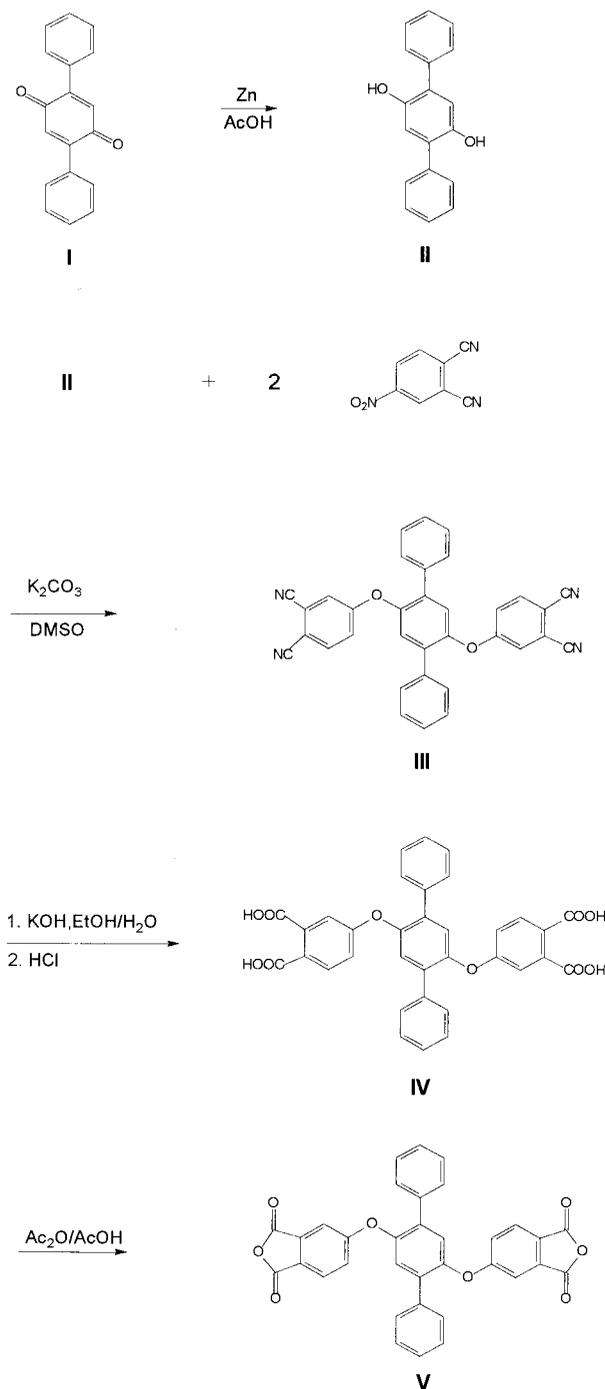
## RESULTS AND DISCUSSION

### Monomer Synthesis

The new bis(ether anhydride) **V** was prepared by a three-step reaction sequence starting from 2',5'-dihydroxy-*p*-terphenyl (**II**), as shown in Scheme 1. According to a reported method,<sup>32</sup> diol **II** was prepared by the reduction of 2,5-diphenyl-1,4-benzoquinone (**I**) using Zn in refluxing acetic acid. Nucleophilic nitro displacement of 4-nitrophthalonitrile with the potassium phenolate of diol **II** gave 2',5'-bis(3,4-dicyanophenoxy)-*p*-terphenyl (**III**). Alkaline hydrolysis of the bis(ether dinitrile) **III** with aqueous potassium hydroxide in ethanol afforded 2',5'-bis(3,4-dicarboxyphenoxy)-*p*-terphenyl (**IV**), which was subsequently dehydrated with acetic anhydride to generate the desired monomer **V**. The yield in each step was satisfactory, and the obtained product in each step was confirmed by IR spectroscopy. Figure 1 shows the IR spectra of intermediate compounds **III** and **IV** and of bis(ether anhydride) monomer **V**. The IR spectrum of bis(ether dinitrile) **III** is characterized by absorption at  $2235\text{ cm}^{-1}$  because of the cyano group. The most characteristic bands of bis(ether diacid) **IV** can be observed near  $1689\text{ cm}^{-1}$  (C=O stretching) and in the region of  $2500\text{--}3500\text{ cm}^{-1}$  (O—H stretching). The disappearance of the characteristic cyano stretching band on the IR spectrum revealed completion of hydrolysis. The spectrum of bis(ether anhydride) **V** shows two characteristic cyclic anhydride absorptions near  $1849$  and  $1772\text{ cm}^{-1}$ , attributed to the asymmetrical and symmetrical stretching vibrations of C=O. The structures of bis(ether dinitrile) **III** and bis(ether anhydride) **V** were also confirmed by elemental analysis. The elemental analyses of these two compounds were in good agreement with the calculated values for the proposed structures, as reported in the Experimental section.

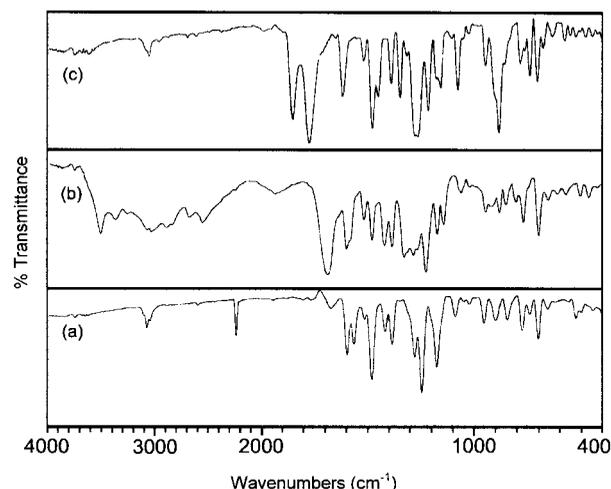
### Polymer Synthesis

A series of novel poly(ether imide)s **VIII<sub>a</sub>–VIII<sub>i</sub>** containing the laterally attached *p*-terphenyl unit



Scheme 1

were prepared from bis(ether anhydride) **V** with various aromatic diamines (**VI<sub>a</sub>–VI<sub>i</sub>**) by a conventional two-stage process, as outlined in Scheme 2, first forming the poly(amic acid)s (**VII**) at room temperature in an aprotic solvent such as DMAc (about 10 wt % solids), followed by thermal or chemical imidization to yield poly(ether imide)s



**Figure 1.** IR spectra of (a) bis(ether dinitrile) **III**, (b) bis(ether diacid) **IV**, and (c) bis(ether anhydride) **V**.

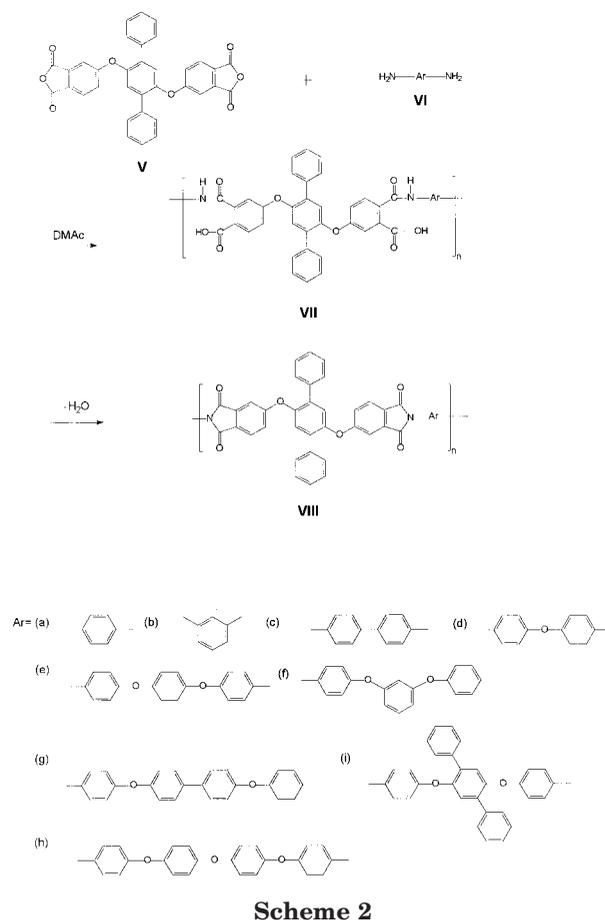
(**VIII**). In the first step, the viscosities of the reaction mixtures became very high as poly(amic acid)s were formed, indicating the formation of high-molecular-weight polymers. As shown in Table 1, the inherent viscosities of the intermediate poly(amic acid)s are in the 0.62–1.26 dL/g range. The polymerization results also indicate that monomer synthesis was successful. The thermal conversion to poly(ether imide)s was carried out by successive heating of the poly(amic acid) films to 250 °C. All poly(ether imide)s, including those derived from rigid *p*-phenylenediamine and benzidine, could afford good, free-standing films. The poly(amic acid)s also could be chemically imidized to poly(ether imide)s by treatment with a mixture of pyridine and acetic anhydride.

The formation of poly(ether imide)s was confirmed by elemental analysis and IR spectroscopy. As can be seen from Table 1, the elemental analysis values of the poly(ether imide)s generally agreed well with the calculated value for the proposed structures. Figure 2 illustrates the IR spectra of a thin-film sample of poly(amic acid) **VII<sub>i</sub>** and fully cyclized polyimide **VIII<sub>i</sub>**. The complete conversion of *o*-carboxyl amide to the imide ring was shown by the disappearance of the amic acid bands at 1650–1700  $\text{cm}^{-1}$  and 2500–3500  $\text{cm}^{-1}$ , together with the appearance of characteristic imide absorption bands at 1778 (asymmetrical C=O stretch), 1724 (symmetrical C=O stretch), 1379 (C–N stretch), 1114, and 746  $\text{cm}^{-1}$  (imide ring deformation).

## Properties of Poly(ether imide)s

### Organosolubility

The solubility of the poly(ether imide)s was studied qualitatively in various solvents. As shown in Table 2, except for polymers **VIII<sub>a</sub>** and **VIII<sub>c</sub>**, these poly(ether imide)s were soluble in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO and in *m*-cresol at room temperature or upon heating. The poly(ether imide)s **VIII<sub>b</sub>**, **VIII<sub>d</sub>**, **VIII<sub>e</sub>**, and **VIII<sub>h</sub>** also could be dissolved in chlorinated solvents such as 2-chlorophenol and chloroform. The good solubility of these poly(ether imide)s can be attributed to the presence of laterally attached *p*-terphenyls, together with the flexible aryl ether linkages along the polymer backbone. The insolubility of poly(ether imide)s **VIII<sub>a</sub>** and **VIII<sub>c</sub>** can be explained by the rigid nature of their diamine moieties. Because of its molecular regularity, poly(ether imide) **VIII<sub>i</sub>** also showed poor solubility. For comparison, the solubility behavior data of analogous poly(ether imide)s of the **IX** series without the pendent phenyl groups that

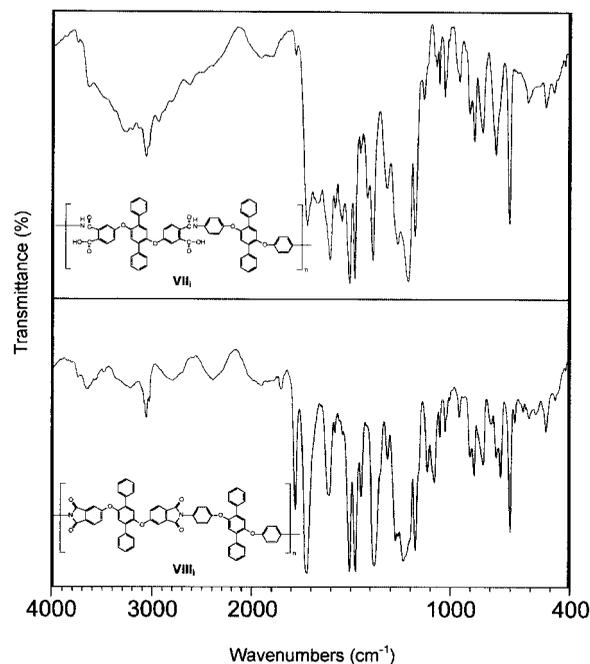


**Table 1.** Inherent Viscosity of Poly(amic acid)s and Elemental Analysis of Poly(ether imide)s

Poly(amic acid)		Elemental Analysis (%) of Poly(ether imide)s <sup>b</sup>					
Code	$\eta_{inh}^a$ (dL/g)	Code	Formula (Formula Weight)		C	H	N
<b>VII<sub>a</sub></b>	0.86	<b>VIII<sub>a</sub></b>	$(C_{40}H_{22}N_2O_6)_n$ (626.62) <sub>n</sub>	Calcd.	76.67	3.54	4.47
				Found	75.66	3.52	4.31
<b>VII<sub>b</sub></b>	0.62	<b>VIII<sub>b</sub></b>	$(C_{40}H_{22}N_2O_6)_n$ (626.62) <sub>n</sub>	Calcd.	76.67	3.54	4.47
				Found	75.77	3.48	4.17
<b>VII<sub>c</sub></b>	1.06	<b>VIII<sub>c</sub></b>	$(C_{46}H_{26}N_2O_6)_n$ (702.72) <sub>n</sub>	Calcd.	78.62	3.73	3.99
				Found	77.72	3.64	3.66
<b>VII<sub>d</sub></b>	0.84	<b>VIII<sub>d</sub></b>	$(C_{46}H_{26}N_2O_7)_n$ (718.72) <sub>n</sub>	Calcd.	76.87	3.65	3.89
				Found	76.03	3.64	3.54
<b>VII<sub>e</sub></b>	0.93	<b>VIII<sub>e</sub></b>	$(C_{52}H_{30}N_2O_8)_n$ (810.82) <sub>n</sub>	Calcd.	77.03	3.73	3.45
				Found	76.23	3.58	3.12
<b>VII<sub>f</sub></b>	1.14	<b>VIII<sub>f</sub></b>	$(C_{52}H_{30}N_2O_8)_n$ (810.82) <sub>n</sub>	Calcd.	77.03	3.73	3.45
				Found	76.48	3.59	3.29
<b>VII<sub>g</sub></b>	1.26	<b>VIII<sub>g</sub></b>	$(C_{58}H_{34}N_2O_8)_n$ (886.92) <sub>n</sub>	Calcd.	78.55	3.86	3.16
				Found	77.64	3.88	2.92
<b>VII<sub>h</sub></b>	1.05	<b>VIII<sub>h</sub></b>	$(C_{58}H_{34}N_2O_9)_n$ (968.75) <sub>n</sub>	Calcd.	77.15	3.80	3.10
				Found	76.13	3.65	2.62
<b>VII<sub>i</sub></b>	1.18	<b>VIII<sub>i</sub></b>	$(C_{64}H_{38}N_2O_8)_n$ (963.01) <sub>n</sub>	Calcd.	79.82	3.98	2.91
				Found	79.39	3.97	2.71

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

<sup>b</sup> Poly(ether imide) samples were prepared by thermal imidization.



**Figure 2.** Typical IR spectra of poly(amic acid) **VII<sub>i</sub>**, poly(ether imide) **VIII<sub>i</sub>**.

were reported previously<sup>28</sup> are also included in Table 2. As can be seen, polymers **VIII<sub>b</sub>**, **VIII<sub>d</sub>**, **VIII<sub>e</sub>**, and **VIII<sub>g</sub>** revealed enhanced solubility compared with the corresponding **IX** counterparts. This could be explained by the reason explained above.

### Crystallinity

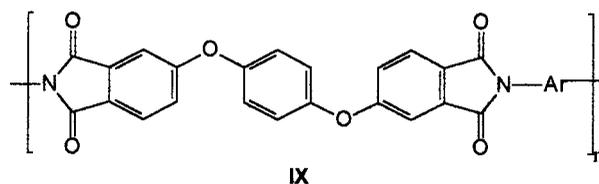
The crystallinity of the prepared poly(ether imide)s was determined by wide-angle X-ray diffraction (WAXD) scans. All the **VIII** series polymers showed almost completely amorphous diffraction patterns. This is reasonable because the presence of bulky pendent phenyl groups (laterally attached *p*-terphenyl) induces looser chain packing. Figure 3 compares the WAXD patterns of polymers **VIII<sub>a</sub>** and **VIII<sub>c</sub>** with their analogous **IX<sub>a</sub>** and **IX<sub>c</sub>**. As reported previously,<sup>28</sup> poly(ether imide)s **IX<sub>a</sub>** and **IX<sub>c</sub>**, which became brittle during thermal imidization, revealed semicrystalline patterns. From this comparison, an obvious effect on the crystallinity of these poly(ether imide)s from the introduction of pendent phenyl groups can be confirmed.

**Table 2.** Solubility Behavior of Poly(ether imide)s Prepared by Thermal or Chemical Imidization

Polymer Code	Solubility <sup>a</sup>								
	NMP	DMAc	DMF	DMSO	m-Cresol	2-Chlorophenol	THF	1,4-Dioxane	Chloroform
VIII <sub>a</sub>	-/- (-) <sup>b</sup>	-/- (-)	-/- (-)	-/- (-)	-/- (-)	-/- (-)	-/-	-/-	-/-
VIII <sub>b</sub>	+h/+ (+h)	+h/+ (-)	-/+ (-)	-/+h (-)	+h/+ (+h)	+/+ (+h)	-/-	-/-	+/+
VIII <sub>c</sub>	-/- (-)	-/- (-)	-/- (-)	-/- (-)	-/- (-)	-/- (-)	-/-	-/-	-/-
VIII <sub>d</sub>	+/+ (+h)	+/+ (-)	-/+h (-)	-/- (-)	+h/+h (+h)	+/+ (+h)	-/-	-/-	+h/+h
VIII <sub>e</sub>	+h/+h (-)	+h/+h (-)	+h/+h (-)	-/- (-)	+h/+h (-)	-/- (-)	-/-	-/-	-/-
VIII <sub>f</sub>	+/+	+/+	+/+	+h/+h	+h/+h	+/+	-/-	-/-	+/+
VIII <sub>g</sub>	+h/+h (-)	+h/+h (-)	-/- (-)	+h/+h (-)	+h/+h (-)	-/- (-)	-/-	-/-	-/-
VIII <sub>h</sub>	+/+	+/+	+/+	+h/+h	+/+	-/-	-/-	+h/+h	+/+
VIII <sub>i</sub>	-/+h	-/-	-/-	-/+h	-/+h	-/-	-/-	-/-	-/-

<sup>a</sup> Qualitative solubility tested with 10 mg of sample in 1 mL of the solvent. +: soluble at room temperature; +h: soluble on heating at 100 °C; -: insoluble even on heating; NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

<sup>b</sup> Data in parentheses are those of the IX counterparts prepared by thermal imidization:

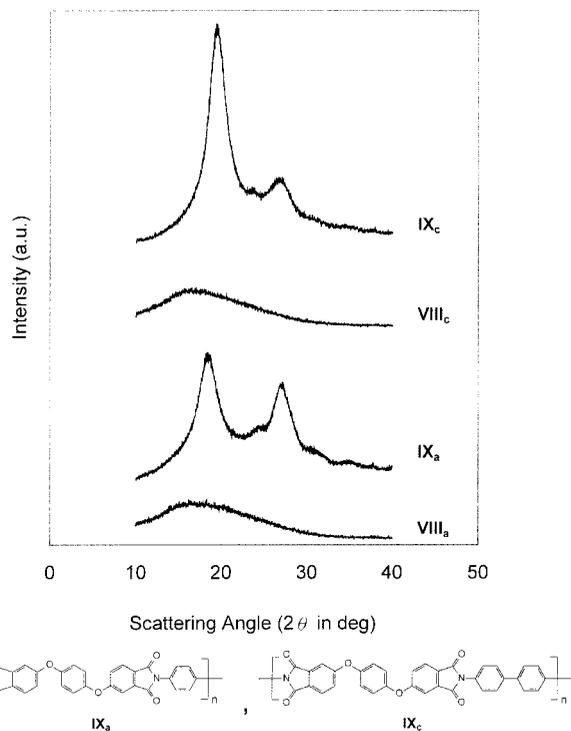


### Tensile Properties

All the poly(ether imide)s could be processed into good quality, free-standing films. These films were subjected to tensile tests, and the results are included in Table 3. They show an ultimate tensile strength of 71–129 MPa, an elongation to break of 10%–35%, and an initial modulus of 1.71–2.17 GPa, indicating they are strong and tough polymeric materials.

### Thermal Properties

DSC, TMA, and TGA were used to evaluate the thermal properties of the poly(ether imide)s. To ensure completion of ring closure and removal of residual solvent, all the poly(ether imide) samples were heated at 300 °C for 1 h prior to all thermal analysis experiments. DSC was used to determine the  $T_g$  values of the poly(ether imide)s with a heating rate of 20 °C/min under nitrogen. All polymers showed a well-defined baseline shift in the heating traces, and their  $T_g$  values were recorded as in the range of 214–276 °C (Table 4). No melting endothermic peak was observed from DSC curves before decomposition of the polymers. Thus, DSC measurements also revealed the amorphous nature of the poly(ether imide)s. The



**Figure 3.** Comparison of the WAXD patterns of poly(ether imide)s VIII<sub>a</sub> and VIII<sub>c</sub> with their structurally similar counterparts IX<sub>a</sub> and IX<sub>c</sub>.

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

Polymer Code	Strength at Break Point (MPa)	Elongation at Break Point (%)	Initial Modulus (GPa)
VIII <sub>a</sub>	129	15	2.17
VIII <sub>b</sub>	71	10	1.71
VIII <sub>c</sub>	122	14	2.06
VIII <sub>d</sub>	123	17	2.06
VIII <sub>e</sub>	90	16	1.92
VIII <sub>f</sub>	95	16	2.09
VIII <sub>g</sub>	111	35	1.90
VIII <sub>h</sub>	107	14	1.83
VIII <sub>i</sub>	103	13	1.97

softening temperatures ( $T_s$ , or apparent  $T_g$ ) of these poly(ether imide)s were also measured by TMA using a loaded penetration probe. The  $T_s$

value was defined as the onset temperature of the probe displacement on the TMA trace. A typical TMA thermogram for poly(ether imide) VIII<sub>e</sub> is illustrated in Figure 4. The  $T_s$  values of VIII<sub>a</sub>–VIII<sub>i</sub> ranged from 201 to 265 °C. Insertion of flexible ether linkages or a less symmetrical *m*-phenylene unit increased the overall flexibility of the polymer chain and, thus, generally resulted in a decrease in  $T_g$  or  $T_s$ , as shown by some  $T_g$  orders observed in Table 4: VIII<sub>a</sub> (258 °C) > VIII<sub>b</sub> (248 °C), VIII<sub>a</sub> (258 °C) > VIII<sub>d</sub> (240 °C) > VIII<sub>e</sub> (232 °C) > VIII<sub>f</sub> (215 °C), and VIII<sub>c</sub> (276 °C) > VIII<sub>g</sub> (243 °C). Previously reported  $T_g$  values<sup>28</sup> of the corresponding poly(ether imide)s (IX) without the pendent phenyl groups are also listed in Table 4. When the two sets of poly(ether imide)s are compared, the VIII series poly(ether imide)s generally showed slightly higher  $T_g$  values. Thus, the increased rotational barrier of the pendent phenyl groups may overcome the effects of increased free

**Table 4.** Thermal Behavior Data of Poly(ether imide)s<sup>a</sup>

Polymer Code	$T_g^b$ (°C)	$T_s^c$ (°C)	$T_d$ (°C) <sup>d</sup>		Char Yield <sup>e</sup> (%)
			In N <sub>2</sub>	In Air	
VIII <sub>a</sub>	258 (–) <sup>f</sup>	241	500 (604)	495	54 (58)
VIII <sub>b</sub>	248 (234)	240	557 (573)	565	56 (56)
VIII <sub>c</sub>	276 (–)	267	589 (600)	583	67 (63)
VIII <sub>d</sub>	240 (236)	230	560 (572)	560	57 (55)
VIII <sub>e</sub>	232 (217)	213	541 (589)	538	52 (58)
VIII <sub>f</sub>	215	207	564	576	59
VIII <sub>g</sub>	243 (224)	234	565 (581)	568	63 (54)
VIII <sub>h</sub>	214	201	564	564	54
VIII <sub>i</sub>	233	226	555	570	55

<sup>a</sup> All poly(ether imide)s were heated at 300 °C for 1 h prior to thermal analysis.

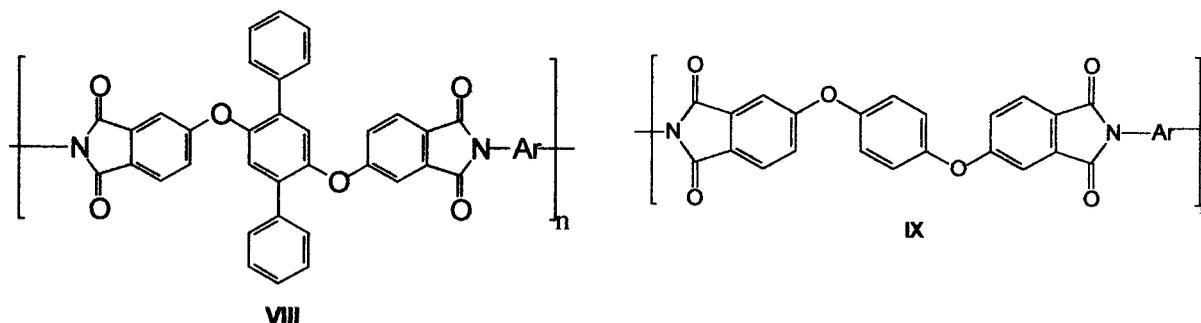
<sup>b</sup> Midpoint temperature of baseline shift on the DSC heating trace at a rate of 20 °C/min.

<sup>c</sup> Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min.

<sup>d</sup> Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

<sup>e</sup> Residual weight percent at 800 °C in nitrogen.

<sup>f</sup> Values indicated in the parentheses are those of the IX counterparts.

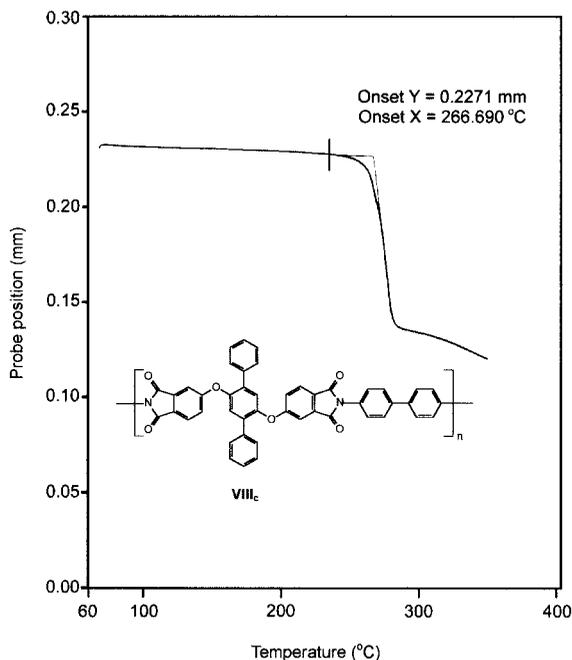


volume and decreased interchain interactions introduced with the pendent groups.

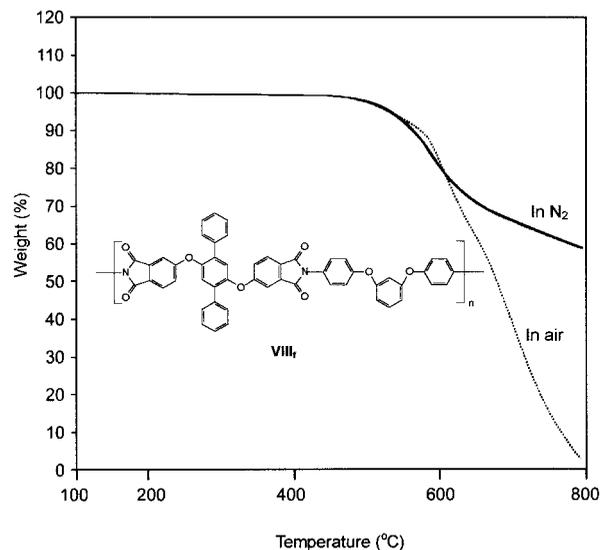
Thermal and thermooxidative stability was investigated by TGA. Typical TGA curves for poly(ether imide) **VIII<sub>f</sub>** are reproduced in Figure 5. Decomposition temperatures ( $T_d$ ) at a 10% weight loss were recorded in the range of 500–589 °C in nitrogen and 495–583 °C in air. They left more than a 52% char yield at 800 °C in nitrogen. Although the  $T_d$  values for the **VIII** series were slightly lower than those of the corresponding **IX** series, the TGA data indicated that these poly(ether imide)s had fairly high thermal and thermooxidative stability that was comparable to standard polyimides.

## CONCLUSIONS

The new bis(ether anhydride) **V** was prepared from diol **II** and 4-nitrophthalonitrile by a well-established synthetic route. A series of high-molecular-weight poly(ether imide)s containing laterally attached *p*-terphenyl were prepared by conventional two-step polycondensation of **V** with various aromatic diamines. These poly(ether imide)s were essentially amorphous and generally showed a higher solubility in common



**Figure 4.** TMA thermogram of poly(ether imide) **VIII<sub>c</sub>**.



**Figure 5.** TGA thermogram of poly(ether imide) **VIII<sub>f</sub>** at a heating rate of 20 °C/min.

organic solvents compared with conventional aromatic polyimides. In addition, the newly obtained poly(ether imide)s displayed high thermal and thermooxidative stability with moderately high  $T_g$  and  $T_s$  values and good mechanical properties. Thus, these poly(ether imide)s could be considered as newly processable high-performance polymeric materials.

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