Synthesis and Properties of Poly(ether imide)s Based on a Benzonorbornane Bis(ether anhydride)

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ABSTRACT: A novel bis(ether anhydride) monomer, 3,6-bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride, was synthesized from the nitro displacement of 4-nitrophthalonitrile with 3,6-dihydroxybenzonorbornane in the presence of potassium carbonate, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile) and the cyclodehydration of the resulting bis(ether diacid). A series of poly(ether imide)s bearing pendant norbornane 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 imidization to the poly(ether imide)s. The inherent viscosities of the poly(amic acid) precursors were 0.81–1.81 dL/g. The poly(ether imide) with *m*-phenylenediamine as a diamine showed good organosolubility. Most of the cast poly(ether imide) films have had high tensile strengths and moduli. The glass-transition temperatures of these poly(ether imide)s, except for those from rigid *p*-phenylenediamine and benzidine, were recorded between 211 and 246 °C by differential scanning calorimetry. The softening temperatures of all the poly(ether imide) films stayed within 210–330 °C according to thermomechanical analysis. No polymers showed significant decomposition before 500 °C in a nitrogen or air atmosphere. A comparative study of the properties with the corresponding poly-(ether imide)s without pendant substituents was also made. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 1712–1725, 2002

Keywords: benzonorbornane; bis(ether anhydride); poly(ether imide); polyimides; high performance polymers; thermal properties
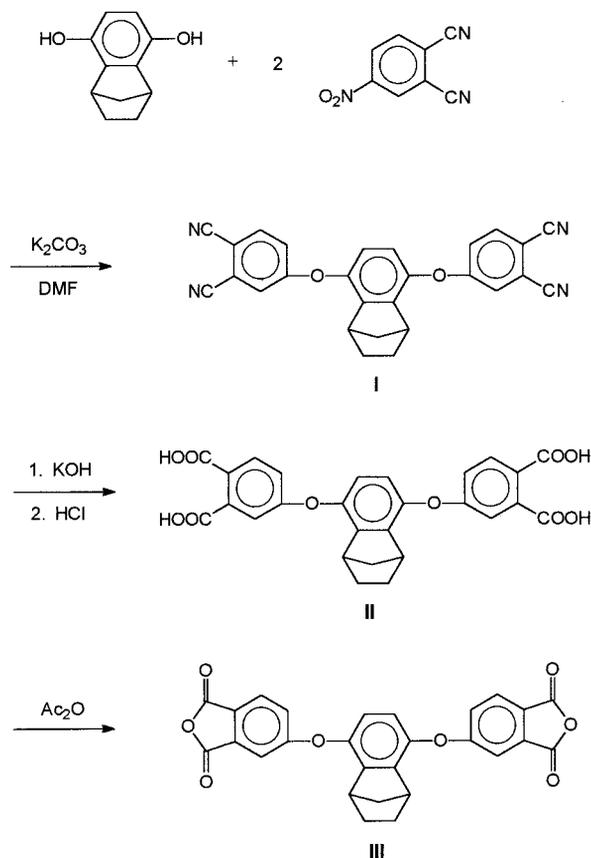
INTRODUCTION

Aromatic polyimides were developed in the early 1960s and since then have been of great technological importance because of their outstanding thermal stability and chemical resistance, together with their balanced electric and mechanical properties.[1,2] 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 temperatures (T_g's) or melting temperatures, which preclude melting processing. Consequently, the search for new polyimides with better processability but the same thermal stability should result in new materials for many applications. On the one hand, the incorporation of ether groups or other flexibilizing linkages into the main chain generally leads to a significant improvement in the solubility and/or thermoplasticity of polyimides.[3–5] On the other hand, the introduction of bulky groups into the polymer chain[6–13] or the attachment of bulky lateral groups[14–18] can impart a significant increase in T_g by restricting the segmental mobility, while

Scheme 1. Synthesis of **III**.

providing good solubility because of decreased packing and crystallinity. Combining these two structural modifications minimizes the tradeoff between the processability and positive properties of aromatic polyimides.

Recently, we reported on a series of poly(ether imide)s based on bis(ether anhydride)s synthesized from hydroquinone and its methyl, chloro, *tert*-butyl, and phenyl derivatives.[19,20] It was found that the incorporation of larger side groups such as *tert*-butyl or phenyl groups into the poly(ether imide) backbone could substantially decrease their crystallinity and increase their solubility. In a continuation of these studies, this work deals with the synthesis and basic characterization of a new family of poly(ether imide)s derived from a benzonorbornane-based bis(ether anhydride), 3,6-bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride (**III**; Scheme 1). The introduction of aryl ether linkages was expected to enhance the flexibility of the polymer chain without a significant reduction in thermal stability. Furthermore, just as with other bulky pendent groups, the fused norbornane unit tends to hinder

dense stacking of chains, which decreases crystallinity and may increase solubility. Therefore, we hoped that the poly(ether imide)s would exhibit increased tractability compared with that of conventional aromatic polyimides obtained from the hindered ether-linked dianhydride **III**.

EXPERIMENTAL

Materials

3,6-Dihydroxybenzonorbornane (Acros), 4-nitrophthalonitrile (TCI), *N,N*-dimethylformamide (Tedia), and acetic anhydride (Fluka) were used as received. *N,N*-Dimethylacetamide (Tedia) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. *p*-Phenylenediamine (**IV$_a$**) and benzidine (**IV$_c$**) were purified by sublimation, and *m*-phenylenediamine (**IV$_b$**) was purified by vacuum distillation. Some aromatic diamines such as 4,4′-oxydianiline (**IV$_d$**; TCI), 1,4-bis(4-aminophenoxy)benzene (**IV$_e$**; TCI), and 1,3-bis(4-aminophenoxy)benzene (**IV$_f$**; TCI) were used without further purification. According to a synthetic procedure described previously,[21,22] 4,4′-bis(4-aminophenoxy)biphenyl (**IV$_g$**; mp = 198–199 °C), bis[4-(4-aminophenoxy)phenyl] ether (**IV$_h$**; mp = 128–129 °C), and 3,6-bis(4-aminophenoxy)benzonorbornane (**IV$_i$**; mp = 175–176 °C) were prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene with 4,4′-dihydroxybiphenyl (TCI), 4,4′-dihydroxydiphenyl ether (TCI), and 3,6-dihydroxybenzonorbornane, respectively, in the presence of potassium carbonate, followed by catalytic reduction of the intermediate dinitro compounds with hydrazine monohydrate as the reducing agent and palladium on charcoal (Pd/C) as the catalyst.

Monomer Synthesis

3,6-Bis(3,4-dicyanophenoxy)benzonorbornane (I)

In a 300-mL, round-bottom flask equipped with a Dean–Stark trap and a condenser were charged 25.2 g (0.143 mol) of 3,6-dihydroxybenzonorbornane and 39.5 g (0.286 mol) of anhydrous potassium carbonate with 100 mL of *N,N*-dimethylformamide and 50 mL of toluene. The mixture was heated with stirring at 140 °C for 6 h to facilitate dehydration. After most of the toluene had been removed, the mixture was cooled, and then 49.6 g (0.286 mol + 0.1 g) of 4-nitrophthalonitrile was

added. The reaction was carried out at 60 °C for about 8 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 water. The crude product was recrystallized from acetonitrile/methanol to afford off-white crystals. The yield of the purified product was 48.1 g (79%).

mp: 244–248 °C [differential scanning calorimetry (DSC), 10 °C/min]. IR (KBr): 2983, 2954, 2875 (aliphatic C—H stretching), 2231 (C≡N stretching), 1246 cm^{-1} (C—O—C stretching). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.77 (d, 2H, H$_g$), 7.32 (d, 2H, H$_e$), 7.26 (d, 2H, H$_f$), 6.88 (s, 2H, H$_a$), 3.37 (s, 2H, H$_b$), 1.91, 1.16 (d, 4H, H$_d$), 1.76, 1.53 (d, 2H, H$_c$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 161.65 (C^7), 144.34 (C^2), 142.59 (C^3), 135.55 (C^{11}), 121.04 (C^8), 120.89 (C^{12}), 120.32 (C^1), 117.83 (C^9), 115.32 (C^{14}), 114.96 (C^{13}), 109.08 (C^{10}), 49.36 (C^4), 40.63 (C^6), 26.09 (C^5).
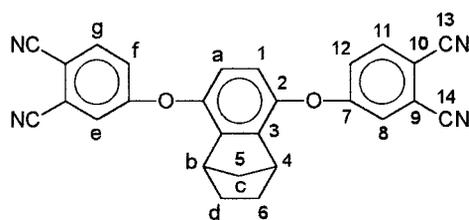
ELEM. ANAL. Calcd. for C$_{27}$H$_{16}$N$_4$O$_2$ (428.44): C, 75.69%; H, 3.76%; N, 13.07%. Found: C, 75.60%; H, 3.62%; N, 13.06%.

3,6-Bis(3,4-dicarboxyphenoxy)benzonorbornane (II)

In a 500-mL flask, a mixture of 30 g (0.07 mol) of bis(ether dinitrile) **I** and 80 g (1.4 mol) of potassium hydroxide in 200 mL of water and 200 mL of ethanol was stirred at reflux until no further ammonia was generated. The time taken to reach this stage was about 1 day. 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 by concentrated HCl to 2–3. The product phased out in the bottom of the beaker as a viscous lump, which was washed repeatedly with water and dried. The resulting bis(ether diacid) **II** was not purified or characterized in detail but was used directly in the synthesis of bis(ether anhydride) **III**.

IR (KBr): 2500–3500 (O—H stretching), 1714 (C═O stretching), 1224 cm^{-1} (C—O—C stretching).

3,6-Bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride (III)

In a 500-mL flask, bis(ether diacid) **II** was suspended in 200 mL of acetic anhydride. The suspension was boiled under reflux until it turned into a clear solution. The resulting hot, clear solution was filtered to remove any insoluble impurities. On cooling, the bis(ether anhydride) started to crystallize, and the next day the product was filtered off, washed with dry toluene, and dried *in vacuo* to give 17.8 g (54% yield based on **I**). The melting point of **III** was 212–215 °C (DSC).

IR (KBr): 1847 (asymmetric C═O stretching), 1774 (symmetric C═O stretching), 1276 cm^{-1} (C—O—C stretching). ^{1}H NMR [400 MHz, dimethyl sulfoxide-d_6 (DMSO-d_6), δ]: 8.09 (d, 2H, H$_g$), 7.56 (d, 2H, H$_f$), 7.52 (d, 2H, H$_e$), 7.05 (s, 2H, H$_a$), 3.36 (s, 2H, H$_b$), 1.92, 1.17 (d, 4H, H$_d$), 1.87, 1.76 (d, 2H, H$_c$). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 166.40 (C^7), 164.60 (C^{14}), 164.35 (C^{13}), 146.22 (C^2), 143.32 (C^3), 135.70 (C^{11}), 129.35 (C^9), 125.99 (C^{12}), 125.30 (C^{10}) 121.83 (C^8), 113.28 (C^1), 49.38 (C^4), 40.72 (C^6), 25.73 (C^5).
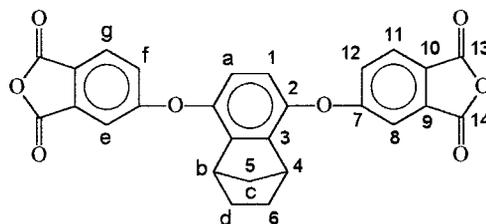
ELEM. ANAL. Calcd. for C$_{27}$H$_{16}$O$_8$ (468.41): C, 69.23%; H, 3.44%. Found: C, 68.90%; H, 3.15%.

Synthesis of Poly(ether imide)s

A typical polymerization procedure was as follows. In a 50-mL flask, 0.2995 g (1.495 mmol) of **IV$_d$** was dissolved in 9.5 mL of N,N-dimethylacetamide. After the diamine was dissolved completely, 0.7005 g (1.495 mmol) of bis(ether anhydride) **III** was added in one portion. Therefore, the solid content of the solution was approximately 10 wt %. The mixture was stirred at room temperature for about 3 h to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) (**IV$_d$**) in N,N-dimethylacetamide was 1.31 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The polymer solution was then poured into a 9-cm glass culture dish, which was placed in a 90 °C oven to

remove solvent. The semidried poly(amic acid) film was further dried and converted into the polyimide by sequential heating at 150 °C for 30 min, at 200 °C for 1 h, and at 250 °C for 1 h. A flexible poly(ether imide) film of **VI_d** self-stripped off from the glass substrate on cooling.

Measurements

Elemental analyses were made on a PerkinElmer 2400 CHN analyzer. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX 400 spectrometer with CDCl$_3$ or DMSO-d_6 as the solvent and tetramethylsilane as the internal reference. The inherent viscosities of the poly(amic acid)s were measured with an Ubbelohde viscometer at 30 °C. An Instron 1130 universal tester 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 ca. 0.08 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 (ca. 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5418 Å; operating at 40 kV and 20 mA). The scanning rate was 3 °/min over a range of 2θ = 5–45°. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 3–5-mg samples in flowing nitrogen or air (flow rate = 40 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. T_g's 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 to 300 °C at a scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s's) were taken as the onset temperatures of probe displacement on the TMA traces.

RESULTS AND DISCUSSION

Monomer Synthesis

The benzonorbornane-based bis(ether anhydride) **III** was prepared by the three-step reaction sequence shown in Scheme 1, starting from the nitro displacement of 4-nitrophthalonitrile with the potassium phenolate of 3,6-dihydroxybenzonorbornane. The yield in each step was satisfactory, and the progress of these reactions could be monitored by IR spectroscopy. Figure 1 compares the IR spectra of intermediate bis(ether dinitrile) **I** and bis(ether dicarboxylic acid) **II** and the bis(ether anhydride) monomer **III**. The IR spectrum of **I** is characterized by absorption at 2231 cm^{-1} due to the cyano group. The most characteristic bands of **II** are observed near 1714 cm^{-1} (C=O stretching) and in the region of 2500–3500 cm^{-1} (O—H stretching). The disappearance of the characteristic cyano stretching band on the IR spectrum revealed completion of hydrolysis. The spectrum of **III** shows two characteristic cyclic anhydride absorptions near 1847 and 1774 cm^{-1} attributed to the asymmetrical and symmetrical stretching vibrations of C=O. The structures of **I** and **III** were also confirmed by elemental analysis and NMR spectroscopy. As shown in Figures 2 and 3, the ^{1}H NMR and ^{13}C NMR spectra are in good agreement with the proposed structures of **I** and **III**. As indicated in the Experimental section, the elemental analysis values of **I** and **III** were in good agreement with the calculated values of their structures.

Polymer Synthesis

A series of novel poly(ether imide)s containing the benzonorbornane unit were prepared from the benzonorbornane bis(ether anhydride) with various aromatic diamines by a conventional two-stage process, outlined in Scheme 2, first forming the poly(amic acid) (**V**) at room temperature in an aprotic solvent such as *N,N*-dimethylacetamide (ca. 10 wt % solids) and then thermally imidizing to give poly(ether imide)s (**VI**). 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 were 0.81–1.81 dL/g. The polymerization results also indicate that the monomer synthesis was successful. The thermal conversion to poly(ether imide)s
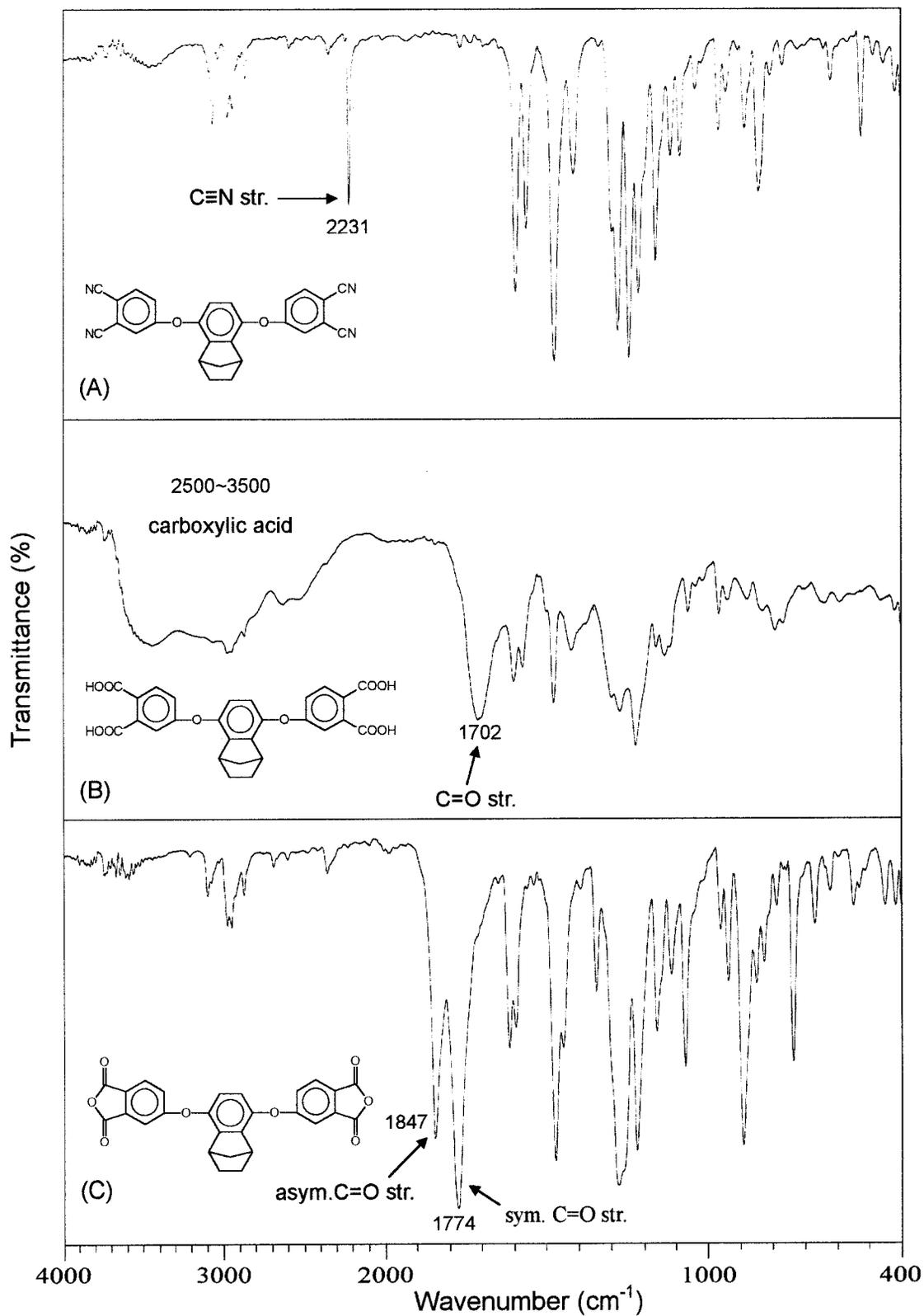
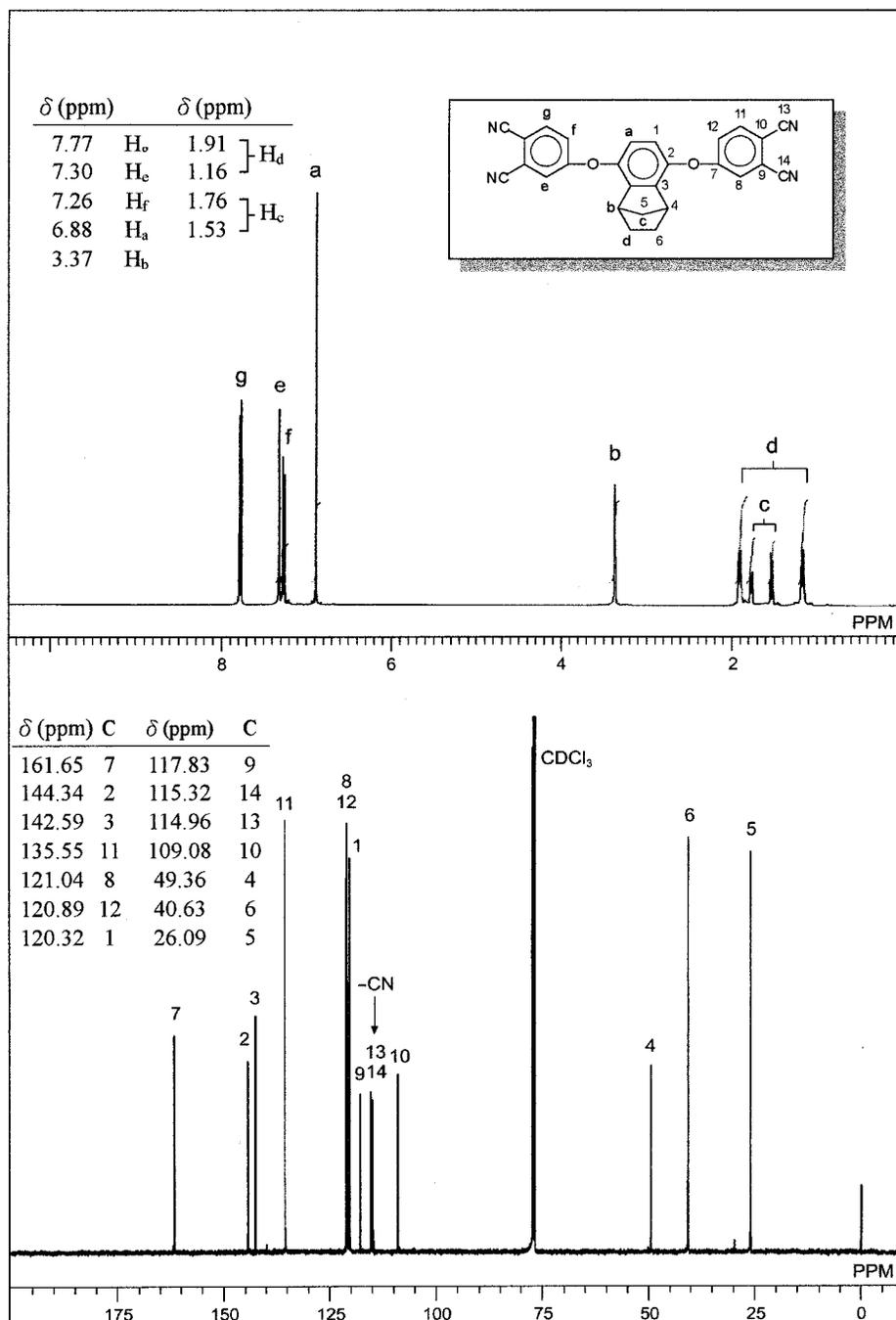**Figure 1.** IR spectra of (A) **I**, (B) **II**, and (C) **III**.

Figure 2. ^1H NMR and ^{13}C NMR spectra of bis(ether dinitrile) **I** in $CDCl_3$.

was carried out by successive heating of the poly-(amic acid) films to 250 °C. All poly(ether imide)s could afford good, free-standing films, although the films of **VI_a** and **VI_c** might crack on fingernail cracking because of structural rigidity.

To provide comparisons, we have included in Table 1 previously determined data for some analogous poly(ether imide)s (**VI′**) without the

norbornane group. As noted previously,[19] the casting films of **VI_a′**, **VI_c′**, and **VI′_e** became brittle during the thermal imidization process because of a three-dimensional crystalline order developed within the polymers.

Figure 4 shows the IR spectra of a thin-film sample of poly(amic acid) **V_a** and fully cyclized polyimide **VI_a**. The complete conversion of *o*-car-
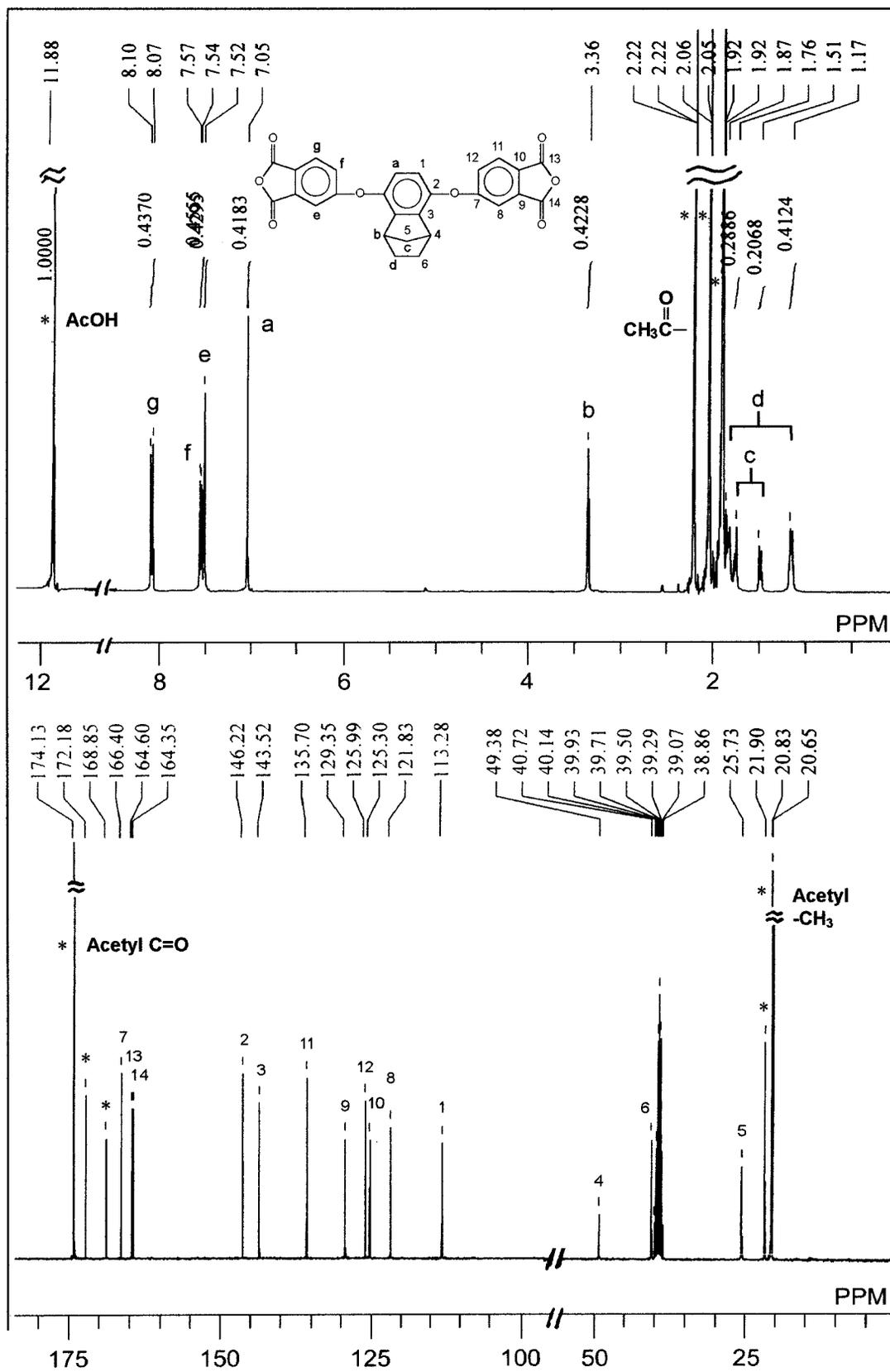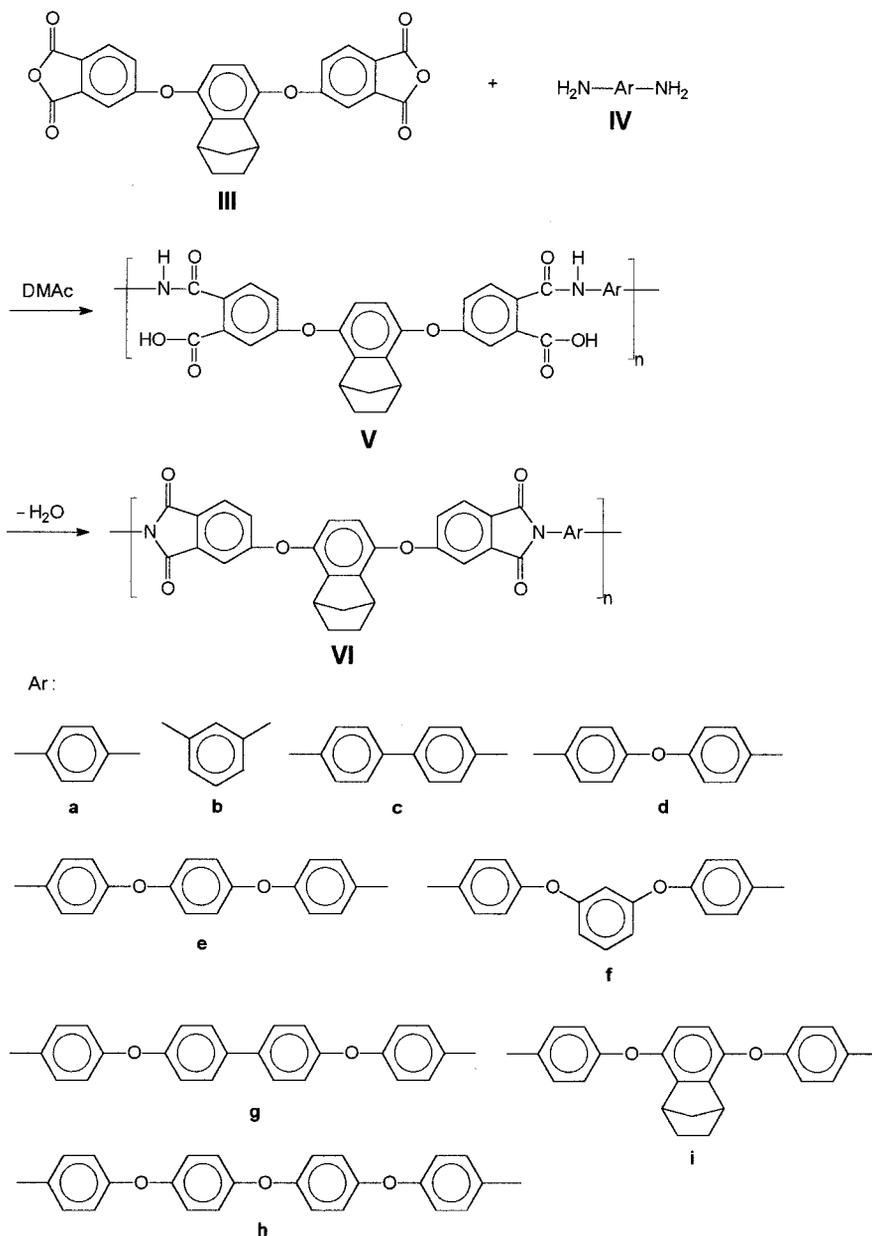
Figure 3. ¹H NMR and ¹³C NMR spectra of bis(ether anhydride) **III** in DMSO-d_6 in the presence of some drops of acetic anhydride.

Scheme 2. Synthesis of poly(ether imide)s.

boxyl amide into the imide ring was supported by the disappearance of the amic acid bands at 1650–1700 and 2500–3500 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 cm^{-1} (imide ring deformation).

Properties of Poly(ether imide)s

The solubility of the poly(ether imide)s was studied qualitatively. As shown in Table 1, except for polymers VI_b and VI_i, the poly(ether imide)s were insoluble in aprotic polar solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, and dimethyl sulfoxide. However, poly(ether imide)s VI_e to VI_h, with multiring ether-bridged diamine moieties, could be dissolved in hot m-cresol and 2-chlorophenol. These results indicated that the incorporation of the benzonorbornane unit into the poly(ether imide) main chain gave limited improvement in solubility. Unless proper diamines were selected, the poly(ether imide)s based on bis(ether anhydride)

Table 1. Inherent Viscosity of Poly(amic acid)s and Film Quality and Solubility Behavior of Poly(ether imide)s
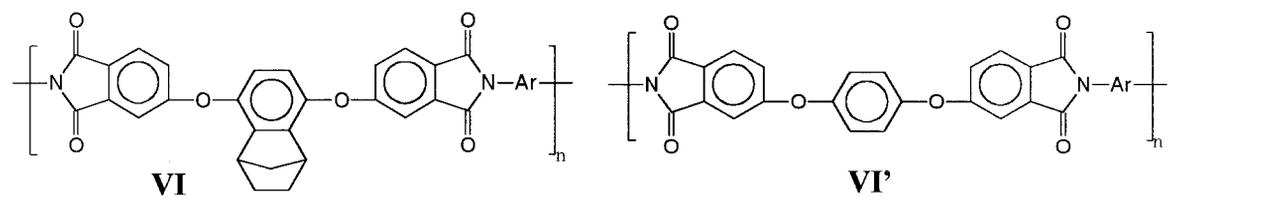
Polymer Code	η_{inh} (dL/g)[a]	Film Quality[b]	Solubility[c]						
			NMP	DMAc	DMF	DMSO	m-Cresol	2-Chlorophenol	THF
VI$_a$	1.28	F	−	−	−	−	−	−	−
VI$_b$	0.82	F	+	+	−	−	+	+	−
VI$_c$	1.53	F	−	−	−	−	−	−	−
VI$_d$	1.31	F	−	−	−	−	−	−	−
VI$_e$	1.39	F	−	−	−	−	+h	+h	−
VI$_f$	1.76	F	−	−	−	−	s	+h	−
VI$_g$	1.53	F	−	−	−	−	+h	+h	−
VI$_h$	0.94	F	s	−	−	−	+h	+h	−
VI$_i$	1.81	F	+h	+h	−	−	−	+	+
VI′$_a$	1.00	B	−	−	−	−	−	−	−
VI′$_b$	0.68	F	+h	−	−	−	+h	+h	−
VI′$_c$	1.25	B	−	−	−	−	−	−	−
VI′$_d$	1.20	F	+h	−	−	−	+h	+h	−
VI′$_e$	0.94	B	−	−	−	−	−	−	−
VI′$_g$	1.71	F	−	−	−	−	−	−	−

[a] Inherent viscosity of the poly(amic acid) precursor measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

[b] Imidization was achieved thermally by a stepwise increase of the temperature, with a maximum temperature of 250 °C for 1 h. F = flexible; B = brittle (cracked upon creasing).

[c] Qualitative solubility was tested with 10 mg of a sample in 1 mL of the solvent. + = soluble at room temperature; s = swelling; +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.

III and conventional diamines usually exhibited poor solubility in organic solvents.

The crystallinity of the prepared poly(ether imide)s were determined by WAXD scans. The WAXD patterns of all the **VI** series poly(ether imide)s together with some **VI′** analogues are depicted in Figure 5. All the **VI** series polymers showed almost completely amorphous diffraction patterns. This is reasonable because the presence of bulky pendent norbornane groups induces looser chain packing. Poly(ether imide)s **VI′$_a$** and **VI′$_c$**, which became brittle during thermal imidization, revealed semicrystalline patterns. Polymer **VI′$_e$** also seems to reveal some degree of crystallinity. This result corresponds to the formation of a brittle, noncreasable, and opaque film of **VI′$_e$** during thermal imidization of its poly(amic acid) film. In contrast to these semicrystalline poly(ether imide)s, the corresponding polymers **VI$_a$**, **VI$_c$**, and **VI$_e$** showed almost completely amorphous WAXD patterns because of the norbornane units.

All the poly(ether imide)s could be fabricated into good-quality and free-standing films. These films were subjected to tensile tests, and the results are included in Table 2. Most of the specimens showed high tensile strengths. Their tensile strengths were usually higher than 100 MPa. The relatively lower strength of **VI$_a$** with respect to the other poly(ether imide)s may be due to stress buildup caused by the rigid diamine residue. The film of **VI$_a$** was somewhat brittle; it cracked on creasing. As can be seen in Table 2, most polymers revealed low elongations to break, indicative of brittle fracture.

DSC was used to determine the T_g values of the poly(ether imide)s at a heating rate of 20 °C/min under nitrogen. Because the absorbed moisture or the residual solvent may sometimes influence the first heating run of DSC, all the samples were at first heated to 400 °C (20 °C/min) and then rapidly cooled to 40 °C at a programmed cooling rate of 200 °C/min. All polymers except for **VI$_a$** and **VI$_c$**
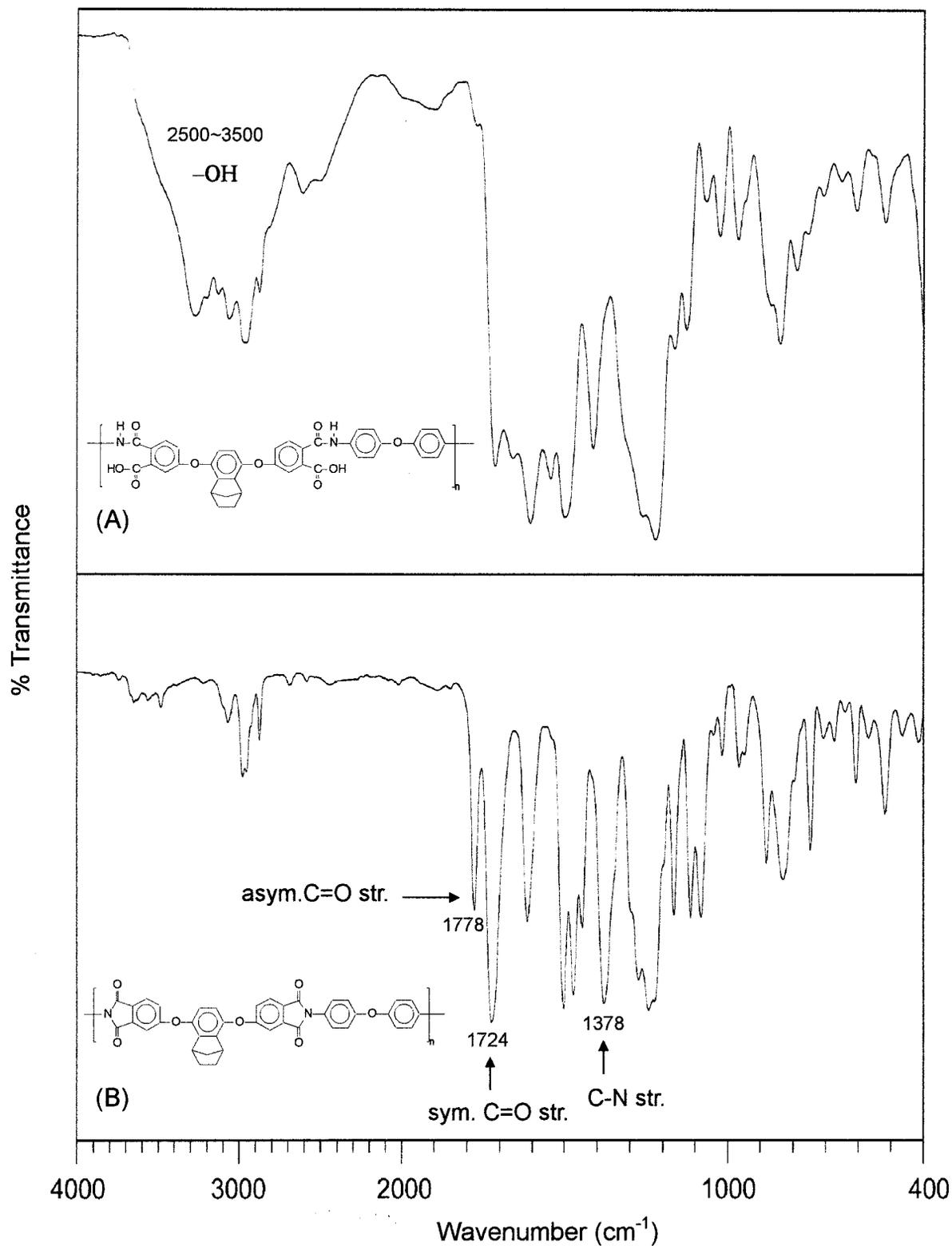
Figure 4.   IR spectra of (A) poly(amic acid) $\mathbf{V_d}$ and (B) polyimide $\mathbf{VI_d}$.
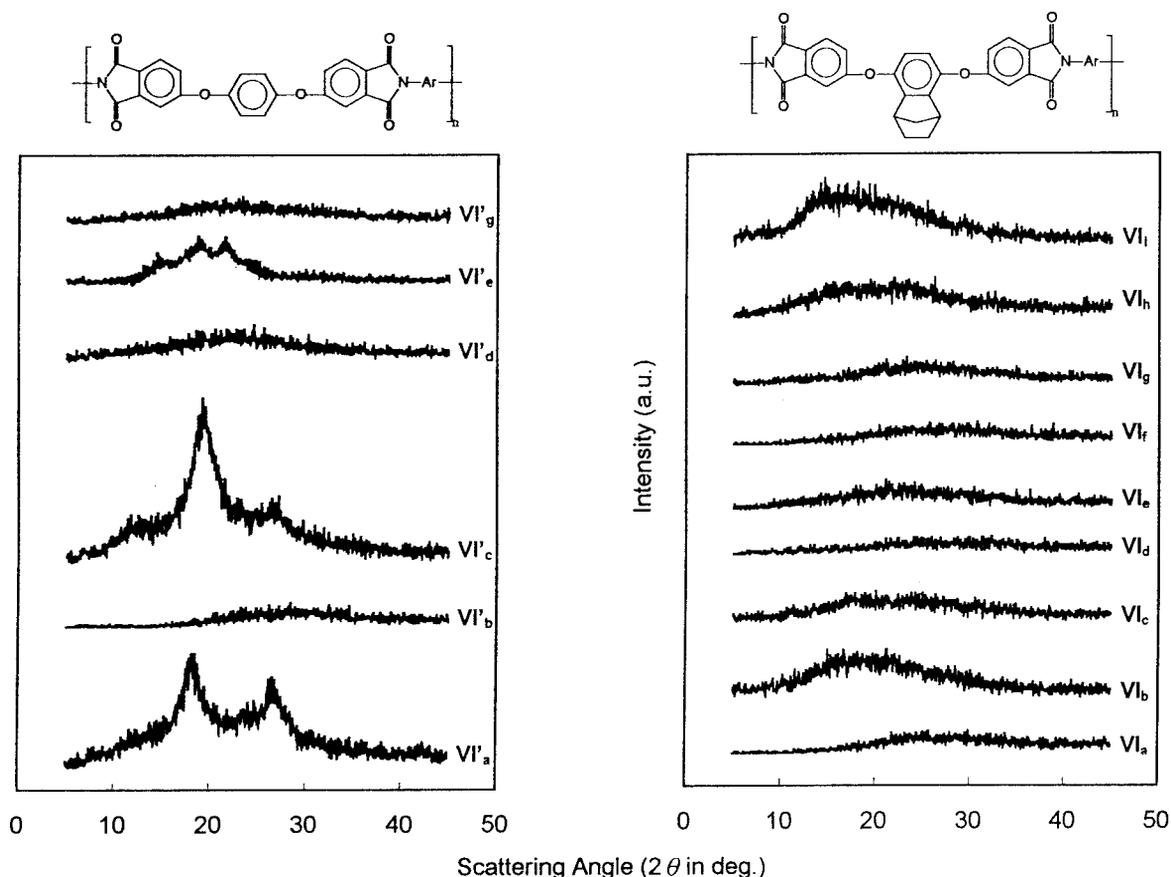
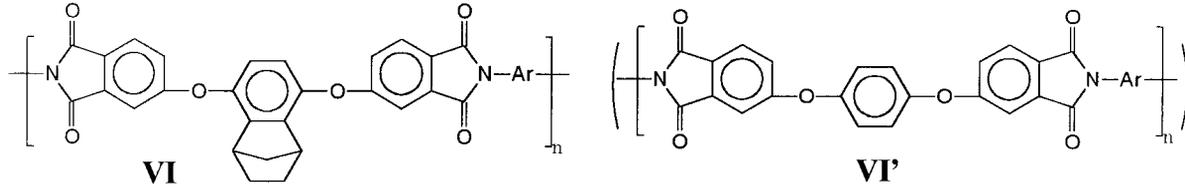**Figure 5.** Wide-angle X-ray diffractograms of poly(ether imide)s.

showed a well-defined baseline shift in the second heating trace, and their T_g values were recorded from 211 to 246 °C. No discernible glass transitions were detected for VI_a and VI_c by DSC, probably because of the structural rigidity of their polymer chains. However, T_s of these rigid poly-

Table 2. Tensile Properties of Poly(ether imide) Films

Polymer Code	Strength at Break Point (MPa)	Elongation at Break Point (%)	Initial Modulus (GPa)
VI_a	53	3	3.08
VI_b	106	11	1.97
VI_c	105	5	3.01
VI_d	132	16	2.53
VI_e	114	12	2.18
VI_f	107	12	2.19
VI_g	141	9	2.56
VI_h	107	12	2.05
VI_i	118	10	2.22

(ether imide)s, which may be considered the apparent T_g, could be readily determined in the TMA experiments. The T_s values of the other benzonorbornane poly(ether imide)s were also measured with TMA. In most cases, the T_s values obtained by TMA were comparable to the T_g values measured by the DSC experiments. The insertion of flexible ether linkages or a less symmetrical m-phenylene unit increased the overall flexibility of the polymer chain and, therefore, generally resulted in a decrease in T_g or T_s, as shown by some T_s orders observed in Table 3: VI_a (330 °C) > VI_b (210 °C), VI_e (232 °C) > VI_f (210 °C), VI_a (330 °C) > VI_d (248 °C) > VI_e (232 °C) > VI_h (213 °C), and VI_c (310 °C) > VI_g (239 °C).

For comparison, the T_g values of some VI' analogues are also included in Table 3. For the poly(ether imide)s containing flexible diamine residues, the VI series polymers, such as VI_d, VI_e, and VI_g, showed a slightly higher T_g than their VI' counterparts. This may be a result of increased rotational barriers and steric hindrance of segmental movement caused by the norbornane

Table 3. Thermal Behavior Data for Poly(ether imide)s

Polymer Code	T_g (°C)[a]	T_s (°C)[b]	T_d (°C)[c] N₂	Air	Char Yield (%)[d]
VI$_a$	—[e]	330	551 (604)	548	59 (58)
VI$_b$	212 (243)[f]	210	547 (573)	554	60 (56)
VI$_c$	—	310	570 (600)	572	68 (63)
VI$_d$	246 (236)	248	559 (572)	569	66 (55)
VI$_e$	230 (217)	232	549 (589)	566	63 (58)
VI$_f$	211	210	543	571	64
VI$_g$	237 (224)	239	553 (581)	580	65 (54)
VI$_h$	215	213	528	552	65
VI$_i$	230	230	533	531	68

[a] Midpoint temperature of baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400°C.
[b] Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min. The film samples were heated at 300 °C for 30 min before the TMA experiment.
[c] Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.
[d] Residual weight percentage at 800 °C in nitrogen.
[e] No discernible transition.
[f] Values in parentheses are those of the **VI′** counterparts.

groups. However, poly(ether imide) **VI$_b$** revealed a lower T_g than **VI′$_b$** by 31 °C. This may indicate that in this case the effect of increased free volume prevailed over the steric hindrance effect. Although polymers **VI′$_a$** and **VI′$_c$** revealed crystalline WAXD patterns, well-defined melting endotherms were not observed on the DSC traces before 450 °C, possibly because of high melting points. The less stiff poly(ether imide) **VI′$_e$** revealed a broad medium-intensity endotherm around 389 °C, and the melting peak shifted to a lower temperature (ca. 372 °C) and became more sharp after annealing at elevated temperatures (Fig. 6). The results indicate that polymer **IV′$_e$** may have a higher crystallization tendency on heating. In contrast, the benzonorbornane-based counterpart **IV$_e$** showed no clear melting endotherms from T_g to 400 °C on the DSC thermograms because of its amorphous nature.

Thermal and thermooxidative stability was investigated by TGA. Typical TGA curves for poly(ether imide) **VI$_a$** are reproduced in Figure 7. Decomposition temperatures (T_d's) at 10% weight losses were recorded from 531 to 580 °C in nitrogen; they were slightly lower than those of anal-

ogous **VI′** counterparts. This is reasonable if we consider the aliphatic content of these poly(ether imide)s. Most of these poly(ether imide)s showed good thermal stability in air that was comparable with that in a nitrogen atmosphere before 600 °C, indicating that these benzonorbornane-based poly(ether imide)s had good thermooxidative stability. In some cases, the T_d values were higher in air than in nitrogen, possibly because of oxidative crosslinking or an early weight-gained oxidation of the aliphatic groups with thermal degradation in air. These poly(ether imide)s showed great residues (59–68%) on heating to 800 °C in nitrogen, even though they contained the aliphatic substituents. Moreover, char yields of **VI** polymers were slightly higher than those of corresponding **VI′** polymers, probably because of interchain crosslinking between some aliphatic segments during thermal pyrolysis.

CONCLUSIONS

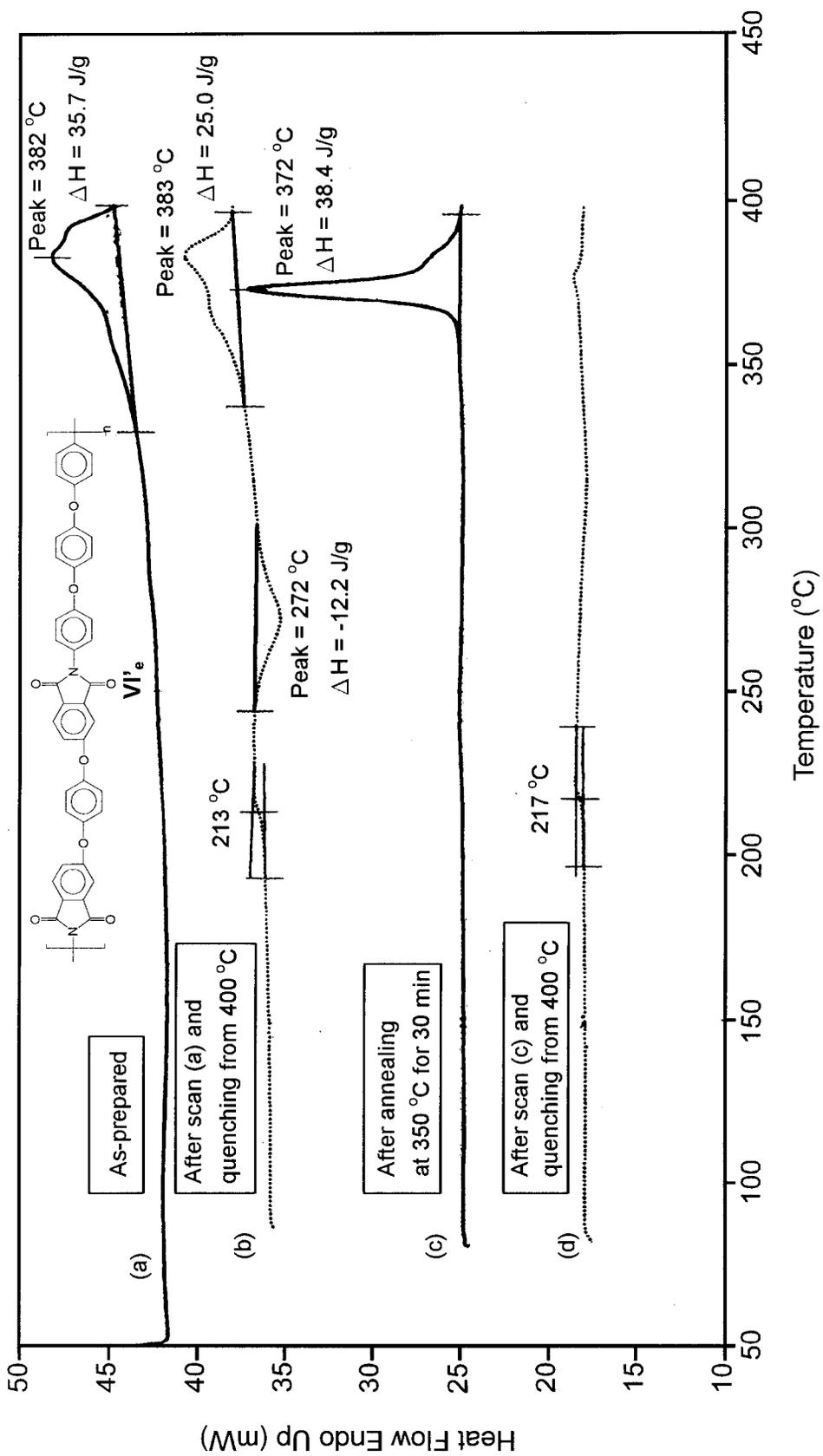A series of high molecular weight poly(ether imide)s based on benzonorbornane bis(ether anhy-

Figure 6. DSC thermograms of the as-prepared film sample of **VI′**$_e$ and the film sample after isothermal annealing and quenching.
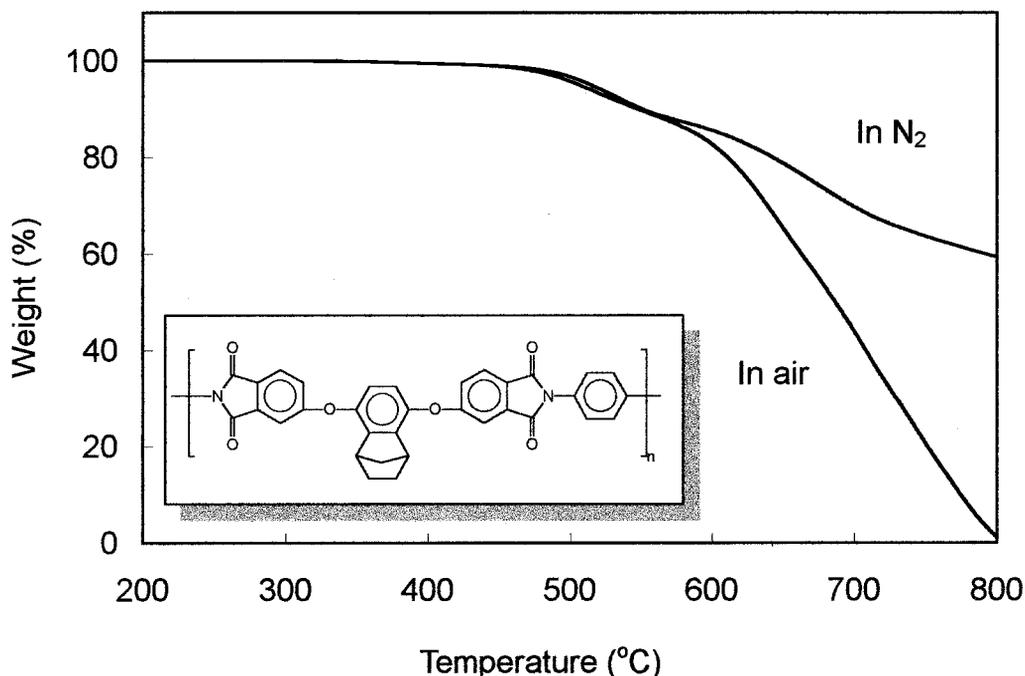
Figure 7. TGA curves of poly(ether imide) **VI_a** (heating rate = 20 °C/min).

dride) **III** were prepared by conventional two-step polycondensation with various aromatic diamines. These poly(ether imide)s were noncrystalline. The introduction of a bulky pendent norbornane unit onto the polymer backbone did not lead to significantly improved solubility of the polymers in organic solvents. However, several of these polymers exhibited a desired combination of properties required for high-performance materials, including excellent mechanical properties, high thermal and thermooxidative stability, and moderate T_g's and T_s's.

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