

Synthesis and Properties of New Adamantane-Based Poly(ether imide)s

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ABSTRACT: A new adamantane-based bis(ether anhydride), 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]adamantane dianhydride, was prepared in three steps starting from nitrodisplacement of 4-nitrophthalonitrile with the potassium phenolate of 2,2-bis(4-hydroxyphenyl)adamantane. A series of adamantane-containing poly(ether imide)s were prepared from the adamantane-based bis(ether anhydride) and aromatic diamines by a conventional two-stage synthesis in which the poly(ether amic acid)s obtained in the first stage were heated stage-by-stage at 150–270°C to give the poly(ether imide)s. The intermediate poly(ether amic acid)s had inherent viscosities between 0.56 and 1.92 dL/g. Except for those from *p*-phenylenediamine, *m*-phenylenediamine, and benzidine, all the poly(ether amic acid) films could be thermally converted into transparent, flexible, and tough poly(ether imide) films. All the poly(ether imide)s showed limited solubility in organic solvents, although they were amorphous in nature as evidenced by X-ray diffractograms. Glass transition temperatures of these poly(ether imide)s were recorded in the range of 242–317°C by differential scanning calorimetry and of 270–322°C by dynamic mechanical analysis. They exhibited high resistance to thermal degradation, with 10% weight loss temperatures being recorded between 514–538°C in nitrogen and 511–527°C in air. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 1619–1628, 1999

Keywords: adamantane; 2,2-adamantylidene unit; poly(ether imide)s

INTRODUCTION

Polyimides have found wide usage as films, coatings, adhesives and matrix resins due to their outstanding thermal behavior combined with their excellent mechanical and electrical properties.^{1,2} The ring-opening of dianhydride by a diamine yields soluble poly(amic acid)s that are capable of solution processing. However, after imidization polyimides are usually insoluble and infusible. In many cases, it may be desirable to

avoid the high cure temperature associated with curing the poly(amic acid)s to polyimides, and as such, soluble polyimides would be desirable. Therefore, there have been many attempts to prepare processable polyimides without much sacrificing the desired properties. To accomplish this goal, the incorporation of flexible bridging units as well as bulky groups into the rigid polyimide backbone, or attachment of bulky side groups has been widely used.^{3–7}

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a highly symmetrical molecule composed of three cyclohexane rings into rigid, relatively strain-free chair conformations allows no easy formation of double bond and no back-side (electrophilic or

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nucleophilic) attack. It possesses four bridgehead positions which are easily substituted using Friedel–Crafts chemistry. Substitution at the four bridgehead positions has led to formation of dendrimers and star polymers in which all arms or branches are in an enforced tetrahedral array due to the constrained geometry of adamantane.^{8–12}

Adamantane has also been inserted into the backbone of many polymers including polysulfones, polyesters, polyamides, and polyimides.^{13–19} Insertion of this thermally and oxidatively stable, bulky, and rigid tetrahedral moiety into polymers modifies and improves physical properties such as decomposition and glass transition temperatures, chain stiffness, crystallinity, and solubility. Incorporation of pendant adamantyl groups into acrylates,^{20–22} phenolics,²³ poly(phenylene)s,²⁴ poly(ether ether ketone)s,²⁵ and poly(benzyl ether)s²⁶ also results in a large increase in T_g , thermal properties, and solubility when compared to the unsubstituted polymer analog. The rigidity and bulkiness of the adamantyl moiety greatly reduces chain mobility and inhibits chain packing. This increases T_g , lowers crystallinity, and enhances solubility. In addition, thermosetting polymers based on acetylene^{27,28} or maleimide²⁹ derivatives of adamantane have been reported.

One of the main potential applications of polyimides is as membranes for gas separation. Polymers with pendant bulky groups are potential candidates for gas separation membranes. According to a model accepted widely at present,^{18,30,31} restricted mobility of chain segments in combination with the presence of bulky groups preventing tight packing of the polymer chains should lead to membrane materials with improved selectivity without loss of permeability. In this sense, the packing-disruptive adamantyl group is ideal. The increased glass transition temperatures of the polymers containing this substructure indicate restricted backbone mobility, and the bulkiness of the adamantyl unit prevents tight chain packing.

Thus, this work describes the synthesis and preliminary characterization of a new family of poly(ether imide)s based on 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]adamantane dianhydride and aromatic diamines. The incorporation of bulky 2,2-adamantylidene unit in the polymer chain is expected to increase the processability and gas permeation properties of the polymers.

EXPERIMENTAL

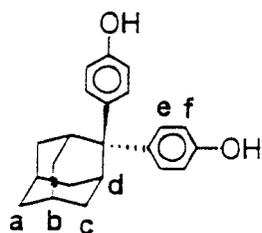
Materials

2-Adamantanone (Aldrich), phenol (Wako), zinc chloride (ZnCl_2 ; Wako), 4-nitrophthalonitrile (TCI), *N,N*-dimethylformamide (DMF; Fluka), potassium carbonate (K_2CO_3 ; Fluka), and acetic anhydride (Janssen) were used as received. *p*-Phenylenediamine (**5a**) was purified by sublimation. *m*-Phenylenediamine (**5b**) (Janssen) was vacuum-distilled prior to use. Benzidine (**5c**) (TCI) was purified by recrystallization from a benzene/ethanol mixture. 4,4'-Diaminodiphenylmethane (**5d**) (TCI), 4,4'-oxydianiline (**5e**) (TCI), and 1,4-bis(4-aminophenoxy)benzene (**5f**) (TCI) were used without further purification. According to reported methods,^{32,33} 4,4'-bis(4-aminophenoxy)biphenyl (**5g**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**5h**), and α,α' -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**5i**) were prepared by the nucleophilic substitution reaction of *p*-chloronitrobenzene with the corresponding bisphenol precursors, i.e. 4,4'-biphenol (Fluka), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) (Wako), and α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene, in DMF in the presence of potassium carbonate, followed by hydrazine catalytic reduction of the intermediate dinitro compounds. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Monomer Synthesis

2,2-Bis(4-hydroxyphenyl)adamantane (1)

In a 500-mL flask, 50.0 g (0.3328 mol) of 2-adamantanone, and 6 g of ZnCl_2 were stirred in 94 g (0.1 mol) of molten phenol. The mixture was heated at approximately 60°C on an oil bath, and then dry hydrogen chloride was bubbled in for about 4 h. The reaction system became dark brown. The reaction solution was diluted with 100 mL of ethanol, and then 150 mL of water was added to precipitate a white solid. The crude product was recrystallized from ethanol to afford colorless needle crystals of pure diol **1**. Yield, 20.6 g (19.3%); mp, 316°C (lit.¹⁸ 316–318°C). IR (KBr): 3356 cm^{-1} (O–H). ¹H-NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.26 (s, -OH, 2H), 7.13 (d, H_e , 2H), 6.56 (d, H_f , 2H), 3.17 (d, H_d , 2H), 1.89 (d, H_c , 4H), 1.71 (d, H_b , 2H), 1.62 ppm (lump, $\text{H}_a + \text{H}_c$, 6H). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_2$ (320.43): C, 82.46%; H, 7.55%. Found: C, 81.78%; H, 7.53%.



2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]adamantane (**2**)

In a 500-mL flask equipped with a Dean-Stark trap and a condenser, 10.0 g (0.0312 mol) of diol **1** and 9 g of K_2CO_3 were suspended in the mixture of 30 mL of toluene and 200 mL of DMF. The suspension solution was heated to reflux to remove water by azeotropic distillation with toluene. After the water was removed completely, the residual toluene was distilled off. Then, the solution was cooled to 60°C, and 4-nitrophthalonitrile (11 g, 0.0635 mol) was added. The mixture was allowed to stir at 60°C for 25 h. The solution was then poured into 500 mL of water to precipitate a light purple solid. The crude product was recrystallized from acetonitrile to afford pure tetranitrile **2** as a colorless needle crystal. Yield, 12.69 g (71%); mp, 242°C. IR (KBr): 2230 cm^{-1} (C≡N str.), 1592–1419 cm^{-1} (arom. C=C str.), 1249 cm^{-1} (C—O—C str.). Anal. Calcd for $C_{38}H_{28}N_4O_2$ (572.66): C, 79.70%; H, 4.93%; N, 9.78%. Found: C, 79.36%; H, 4.86%; N, 9.72%.

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]adamantane Dianhydride (**4**)

In a 500 mL flask, a suspension solution of bis(ether dinitrile) **2** (7.3 g, 0.0127 mol) in a 1:1 volume mixture of water–methanol (100 mL/100 mL) containing dissolved 18 g of KOH was boiled under reflux. Reflux was continued until the evolution of ammonia had ceased. The total reaction time was about 24 h. The resulting hot, clear solution was filtered to remove any possible impurities. The hot filtrate was allowed to cool and acidified by conc. HCl to pH = 2–3. The white precipitate was filtered off, washed repeatedly with water, and dried to afford 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]adamantane (**3**) with a yield of 8.0 g (92%). The bis(ether diacid) **3** was then suspended in 25 mL of acetic anhydride. The suspension was boiled under reflux until turning into a clear solution. The solution was filtered to remove insoluble impurities. On cooling, the tiny

grains of bis(ether anhydride) **4** started to crystallize and next day the product was collected, washed with dry toluene, and dried in vacuo, to yield 6.25 g (88.3% on the basis of bis(ether dinitrile) **2**); mp, 227°C. IR (KBr): 1854, 1784 cm^{-1} (C=O str.), 1601–1444 cm^{-1} (arom. C=C str.), 1267, 1228 cm^{-1} (C—O—C str.). Anal. Calcd for $C_{38}H_{28}O_8$ (612.63): C, 74.50%; H, 4.61%. Found: C, 73.38%; H, 4.58%.

Synthesis of Poly(ether imide)s

A typical polymerization procedure is as follows. *p*-Phenylenediamine (**5a**) (0.1200 g, 1.100 mmol) was dissolved in 7.6 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.6799 g (1.100 mmol) of bis(ether anhydride) **4** was added in one portion. The mixture was stirred at room temperature for 2 h. The inherent viscosity of the resulting poly(ether amic acid) **6a** was 0.73 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C. The polymer solution obtained was poured into a $\varnothing = 9$ -cm glass culture dish, which was placed in an 80°C oven overnight to remove the solvent. The semi-dried 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 of **7a** self-stripped off from the glass surface. IR of **6a** (film): 3000–3500 cm^{-1} (O—H, N—H str.), 1715 cm^{-1} (C=O, carboxylic acid), 1599 cm^{-1} (C=O, amide), 1231 cm^{-1} (C—O str.). IR of **7a** (film): 1778 cm^{-1} (asym. C=O), 1726 cm^{-1} (sym. C=O) 1514, 1601 cm^{-1} (arom. C=C), 1360 cm^{-1} (C—N), 1240 cm^{-1} (C—O), 1175 and 745 cm^{-1} (imide ring deformation).

Characterization

IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. 1H -NMR spectra was measured at 30°C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO- d_6) as an external reference. Elemental analyses were run in a Perkin–Elmer Model 2400 C, H, N analyzer. Inherent viscosities of the polymers were measured in DMAc at 30°C using an Ubbelohde viscometer. The X-ray crystallographic data were collected on a CAD-4 diffractometer. The analyses were carried out on a DEC station

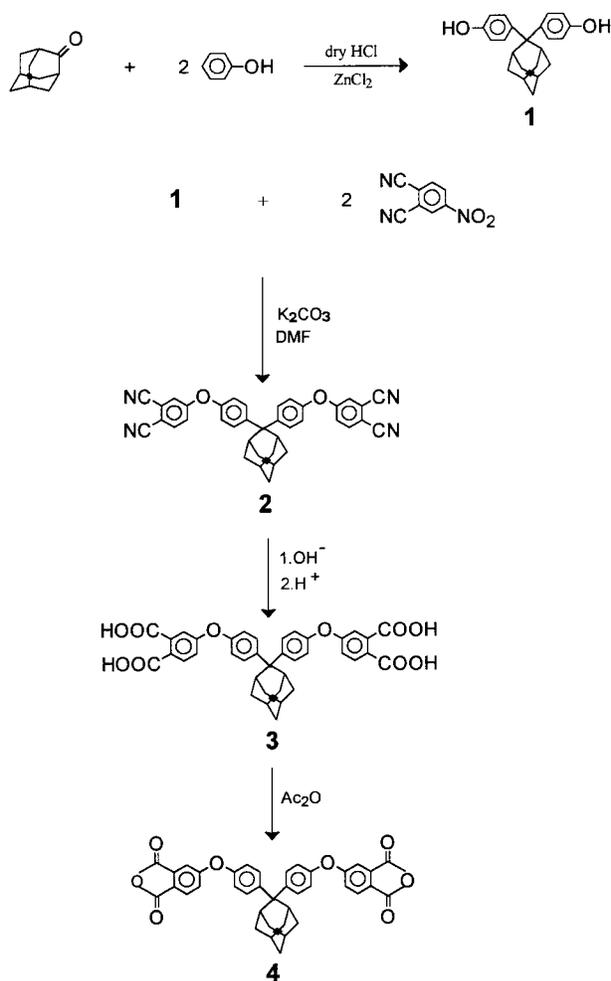
Table I. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement

Formula	C ₂₈ H ₂₈ O ₈
Formula weight	612.63
Space group	Orthorhombic <i>Pnma</i>
<i>a</i> (Å)	14.9190 (21)
<i>b</i> (Å)	30.731 (4)
<i>c</i> (Å)	6.3667 (16)
<i>V</i> (Å ³)	2919.0 (9)
<i>Z</i>	4
<i>D</i> _{calc.} (g/cm ³)	1.394
λ (Å)	1.5418
<i>F</i> (000)	1284
Unit cell detn: #; (2 θ range)	25; (32.52–0.00°)
Scan type	$\theta/2\theta$
Scan width (deg)	2(0.65 + 0.15 tan θ)
Scan speed (deg/min)	1.64–5.50
(2 θ) _{max.}	140.0
<i>hkl</i> ranges	(0; 18) (0; 37) (0; 7)
μ (cm ⁻¹)	7.618
Crystal size (mm)	0.13 × 0.15 × 0.70
Temperature (K)	298
No. of measd. reflns.	2770
No. of obsd reflns. (<i>I</i> > 2.0 σ (<i>I</i>))	2240
No. of unique reflns.	2770
<i>R</i> _f ; <i>R</i> _w ^a	0.045; 0.043
<i>G</i> ₀ <i>F</i>	1.45
Refinement program	NRCVAX
No of atoms	41
No. of refined params.	275 (2240 out of 2770 reflns.)
Minimize function	$\Sigma[w(F_o - F_c)^2]$
(Δ/σ) max.	0.0033
Residual in final D map (e/Å ³)	-0.270 → 0.270

^a $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$. $R_w = \Sigma w^{1/2}(F_o - F_c)/\Sigma w^{1/2}F_o$. $G_0F = [\Sigma w(F_o - F_c)^2]/(\text{No. of reflns} - \text{No. of params.})$; 3 standard reflections (5, 0, -1; 1, -7, 2; -2, -10, -1) monitored every 3600 s, intensity variation <1%.

3500 computer using NRCC SDP software. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 analyzer was used to determine the thermal transitions. The heating rate was 20°C/min. Glass transition temperatures (*T_g*'s) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling. Dynamic mechanical analysis (DMA) was performed on a Du Pont 9900 thermal analyzer system. A sample 10 mm in length, 2 mm in width, and approximately 0.1 mm in thickness was used. Thermo-mechanical analysis was conducted with a Rigaku TMA 8140 coupled to a Rigaku TAS-100 thermal analysis station at a heating rate of 10°/min. Thermogravimetry (TG) was performed using a Du Pont 951 thermogravimetric analyzer cou-

pled to a Du Pont 2000 thermal analyzer. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu K α radiation (40 kV, 15 mA). Scans were run at 2°/min over a range of 2 θ = 5–40°. A Toyo Baldwin Instron UTM-III 500 with a load cell of 10 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a crosshead speed of 5 cm/min were used. Measurements were performed at room temperature (about 25°C) with film specimens (about 0.1 mm thick, 1.0 cm wide, and 5 cm long), and an average of at least five individual determinations was used.



Scheme 1.

RESULTS AND DISCUSSION

Monomer Synthesis

According to a common bisphenol synthesis method,³⁴ 2,2-bis(4-hydroxyphenyl)adamantane (1) was prepared by the condensation of 2-adamantanone with excess phenol in the presence of an acidic catalyst. The structure of diol 1 was confirmed by IR, ¹H-NMR spectroscopy, and elemental analysis, and the results were in good agreement with the proposed structure.

According to a literature method,^{35–37} the adamantane unit-containing bis(ether anhydride) 4 was prepared by a three-stage synthetic procedure as shown in Scheme 1 starting from the nucleophilic nitro-displacement reaction of diol 1 and 4-nitrophthalonitrile in DMF in the presence of potassium carbonate. The resulting bis(ether dinitrile) 2 was hydrolyzed in an alkaline solution

to yield 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]adamantane (3), which was then cyclodehydrated to the bis(ether anhydride) 4. The structure of bis(ether anhydride) 4 was confirmed by elemental analysis, IR spectroscopy, and X-ray crystallographic analysis. The IR spectrum of 4 shows characteristic cyclic anhydride absorption near 1850 and 1780 cm⁻¹ attributed to the asymmetrical and symmetrical stretching vibrations of C=O. X-ray crystal data for 4 shown in Table I were acquired from a colorless crystal obtained by slow evaporation of an acetic anhydride solution of 4 in air. Refinement results in the structure shown in Figure 1. Selected bond distances and bond angles are summarized in Table II, in which the atom labeling used is the same as in Figure 1. The structure is coincident with the proposed one.

Synthesis of Poly(ether imide)s

Poly(ether imide)s were prepared by the standard room temperature synthesis of the poly(amic acid) from dianhydride and diamine monomers with subsequent coating and thermal cure to polyimide. The synthetic route and the structures of polymers are illustrated in Scheme 2. As shown in Table III, the inherent viscosities of the intermediate poly(ether amic acid)s 6a–i ranged from 0.57 to 1.92 dL/g, indicating the formation of medium to high molecular weight polymers. The polymerization results also indicate that the monomer synthesis is successful. The casting films of poly(ether amic acid)s 6a and derived from rigid diamines, such as *p*-phenylenediamine

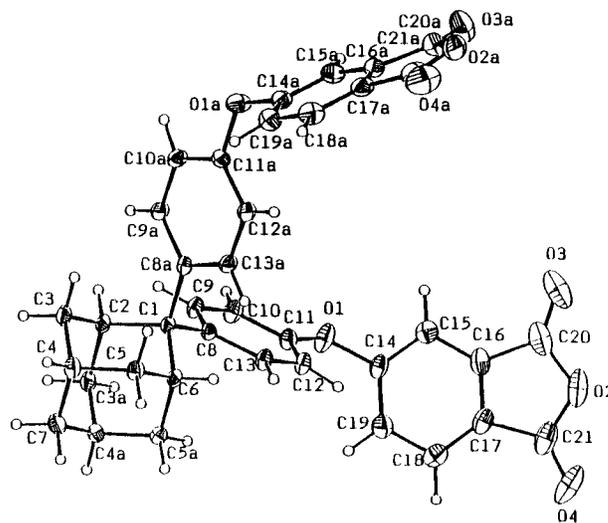


Figure 1. X-ray structure of 4.

Table II. Selected Bond Distance (Å) and Bond Angles (deg) of Bis(ether anhydride) **4**^a

C1–C2	1.565 (4)	C11–C12	1.376 (3)
C1–C6	1.558 (4)	C11–O1	1.387 (3)
C1–C8	1.544 (3)	C12–C13	1.382 (3)
C1–C8a	1.544 (3)	C14–C15	1.368 (3)
C2–C3	1.538 (3)	C14–C19	1.382 (3)
C2–C3a	1.538 (3)	C14–O1	1.392 (3)
C3–C4	1.531 (3)	C15–C16	1.402 (4)
C4–C5	1.539 (3)	C16–C17	1.365 (4)
C4–C7	1.525 (3)	C16–C20	1.469 (4)
C5–C6	1.535 (3)	C7–C18	1.364 (4)
C6–C5a	1.535 (3)	C17–C21	1.491 (4)
C7–C4a	1.525 (3)	C18–C19	1.391 (4)
C8–C9	1.396 (3)	C20–O2	1.399 (4)
C8–C13	1.397 (3)	C20–O3	1.184 (4)
C9–C10	1.377 (3)	C21–O2	1.379 (4)
C10–C11	1.388 (3)	C21–O4	1.184 (4)
C2–C1–C6	105.50 (22)	C10–C1–O1	115.62 (18)
C2–C1–C8	111.66 (14)	C12–C11–O1	124.76 (18)
C2–C1–C8a	111.66 (14)	C11–C12–C13	119.65 (19)
C6–C1–C8	111.36 (14)	C8–C13–C12	122.72 (18)
C6–C1–C8a	111.36 (14)	C15–C14–C19	122.84 (21)
C8–C1–C8a	105.43 (19)	C15–C14–O1	117.07 (21)
C1–C2–C3	110.27 (14)	C19–C14–O1	120.00 (21)
C1–C2–C3a	110.27 (14)	C14–C15–C16	115.85 (22)
C3–C2–C3a	109.13 (20)	C15–C16–C17	121.09 (22)
C2–C3–C4	109.92 (18)	C15–C16–C20	130.10 (3)
C3–C4–C5	108.56 (17)	C17–C16–C20	108.83 (24)
C3–C4–C7	109.65 (19)	C16–C17–C18	123.10 (23)
C5–C4–C7	109.81 (19)	C16–C17–C21	107.10 (24)
C4–C5–C6	109.48 (17)	C18–C17–C21	129.80 (3)
C1–C6–C5	111.22 (15)	C17–C18–C19	116.42 (23)
C1–C6–C5a	111.22 (15)	C14–C19–C18	120.70 (23)
C5–C6–C5a	108.36 (20)	C16–C20–O2	106.60 (3)
C4–C7–C4a	109.65 (22)	C16–C20–O3	131.50 (3)
C1–C8–C9	122.57 (18)	O2–C20–O3	121.90 (3)
C1–C8–C13	121.64 (18)	C17–C21–O2	107.14 (24)
C9–C8–C13	115.73 (18)	C17–C21–O4	131.30 (3)
C8–C9–C10	122.52 (19)	O2–C21–O4	121.50 (3)
C9–C10–C11	119.81 (19)	C11–O1–C14	119.21 (17)
C10–C11–C12	119.56 (19)	C20–O2–C21	110.24 (21)

^a Symmetry code: $a = (x, \frac{3}{2} - y, z)$.

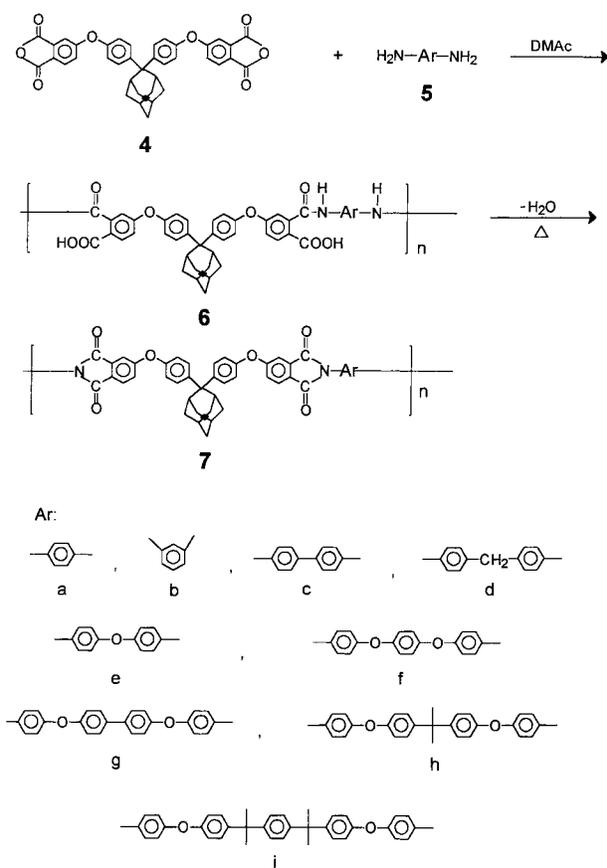
and benzidine, embrittled during the thermal imidization process. This may be attributable to the structural rigidity associated with poly(ether imide)s **7a** and **7c**. Possibly due to lower molecular weight, the film of poly(ether imide) **7b** cracked upon creasing. The other films were tough and flexible and could be creased without cracking.

The structures of poly(ether amic acid)s and poly(ether imide)s were characterized by IR spectroscopy. When the poly(ether amic acid) was cyclodehydrated to poly(ether imide), strong absorp-

tions around 1780 and 1725 cm^{-1} due to the imide carbonyl appeared, while the absorption in the regions of 2500–3500 and 1550–1650 cm^{-1} due to carboxyl and amide groups that were initially observed disappeared entirely.

Properties of Poly(ether imide)s

The solubility of poly(ether imide)s was studied qualitatively. All the poly(ether imide)s were insoluble in all the organic solvents tested that included *N*-methyl-2-pyrrolidone (NMP), DMAc,



DMF, dimethyl sulfoxide (DMSO), *m*-cresol, and tetrahydrofuran. However, the poly(ether imide)s (such as **7h** and **7i**) derived from long chain diamines bearing flexible linkages between benzene rings (such as **5h** and **5i**) swelled in NMP. These results unfortunately indicated that the incorporation of 2,2-adamantylidene unit in the poly(ether imide) backbone gave limited improvement in solubility. Unless proper diamines were selected, the poly(ether imide)s based on bis(ether anhydride) **4** and conventional diamines usually exhibited poor solubility. These unexpected results may be due to the high stiffness of the macromolecular backbones of these poly(ether imide)s caused in part by the presence of bulky, rigid 2,2-diphenyladamantane segment, in which rotation of the phenylene units is restricted by the bulky 2,2-adamantylidene group.

The development of crystallinity for these polymers was not expected because of the kinked, bulky adamantane-2,2-diyl structure, and this was confirmed by their wide-angle X-ray diffraction patterns. Most of the poly(ether imide)s af-

forded good-quality, creasable films. These films were subjected to tensile test. A typical film of **7d** showed a tensile strength of 109 MPa, elongation to break of 8%, and initial modulus of 2.53 GPa.

Thermal properties of all the poly(ether imide)s were evaluated by thermogravimetry (TG), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA). The thermal behavior data of all the polymers are summarized in Table IV. The representative TG diagrams of poly(ether imide) **7a** measured in air and in nitrogen are shown in Figure 2. All the other poly(ether imide)s showed a similar pattern of decomposition and did not show significant weight loss below 450°C in air or nitrogen, but with more than 41% residue remaining when heated to 800°C in nitrogen. The 10% weight loss temperatures of these polymers vary in the ranges of 511–527°C in air and 514–538°C in nitrogen.

DSC measurements were carried out at a heating rate of 20°C/min in nitrogen. Rapid cooling from an elevated temperature of approximately 350°C to room temperature yielded predominantly amorphous samples so that in all cases distinct baseline shifts could be observed in the subsequent second heating traces of DSC. The midpoint of the baseline shift is defined as T_g of the polymer. In the DMA measurement, the peak temperature of $\tan \delta$ was defined as T_g because a drastic decrease in storage modulus (G') occurred

Table III. Inherent Viscosities of poly(ether amic acid)s and film quality of poly(ether imide)s

Poly(ether amic acid)s		Poly(ether imide)s ^b	
Code	η_{inh}^a (dL/g)	Code	Film Quality
6a	0.73	7a	Brittle
6b	0.56	7b	Brittle
6c	1.29	7c	Brittle
6d	0.82	7d	Flexible
6e	1.92	7e	Flexible
6f	1.08	7f	Flexible
6g	1.56	7g	Flexible
6h	1.37	7h	Flexible
6i	1.78	7i	Flexible

^a Measured on 0.5 g/dL in DMAc at 30°C.

^b All the poly(ether imide) films were obtained by sequential heating of the poly(ether amic acid) 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.

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

Polymer Code	T_g (°C)	T_s^c (°C)	Decomposition Temperature ^d (°C)		Char Yield ^e (%)
			In N ₂	In Air	
7a	304 ^a (294) ^b	281	524	516	47
7b	286 (— ^f)	276	514	511	51
7c	317 (322)	311	531	522	58
7d	278 (300)	265	527	514	53
7e	285 (283)	289	529	520	48
7f	252 (273)	257	531	522	49
7g	273 (283)	267	538	527	53
7h	252 (270)	238	534	521	43
7i	242 (265)	237	529	513	41

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

^b Maximum of tan δ , measured by DMA using shear mode at a heating rate of 5°C/min.

^c Softening temperatures measured by TMA (penetration method) with a load of 5 g at a heating rate of 10°C/min.

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

^e Residual weight (%) when heated to 800°C in nitrogen.

^f No available specimens could be obtained.

at this point. As shown in Table IV, the T_g values of these poly(ether imide)s stay in the range of 242–317°C by DSC and 265–322°C by DMA. The softening temperatures (T_s , which may be considered as apparent T_g) are also included in Table IV, and they are recorded between 237 and 311°C. The order in T_g or T_s is quite comparable to the increasing order of rigidity of the polymer chain.

Introduction of flexible ether or isopropylidene linkage into the polymer backbone generally leads to a decreased T_g or T_s , e.g., poly(ether imide)s **7f**, **7h**, and **7i** exhibited a relatively lower T_g or T_s . Figure 3 shows the typical DMA curves of representative poly(ether imide) **7g** film at a heating rate of 5°C/min. All the poly(ether imide)s revealed similar DMA curves and still main-

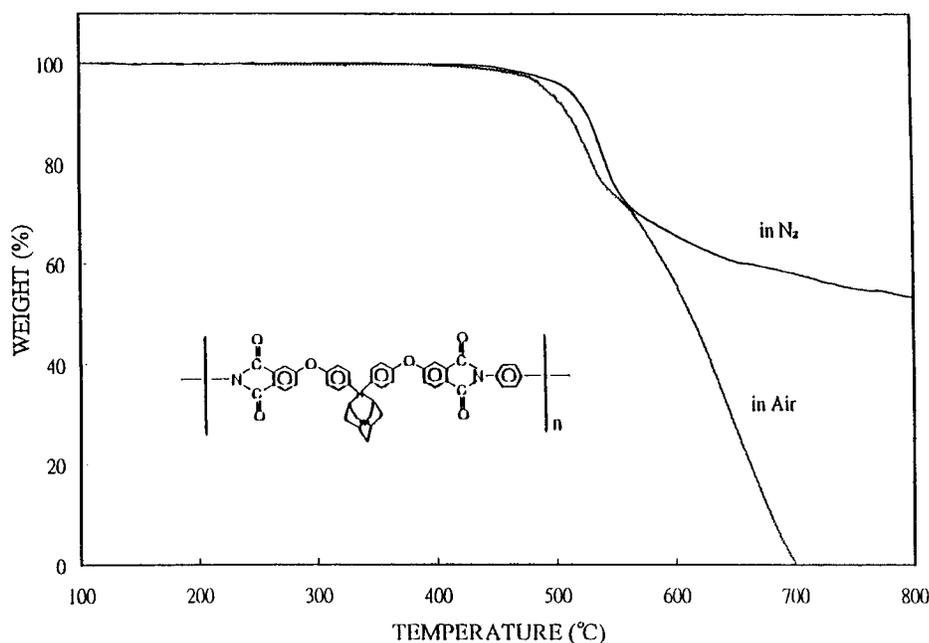


Figure 2. TG curves of poly(ether imide) **7a** at a heating rate of 20°C/min.

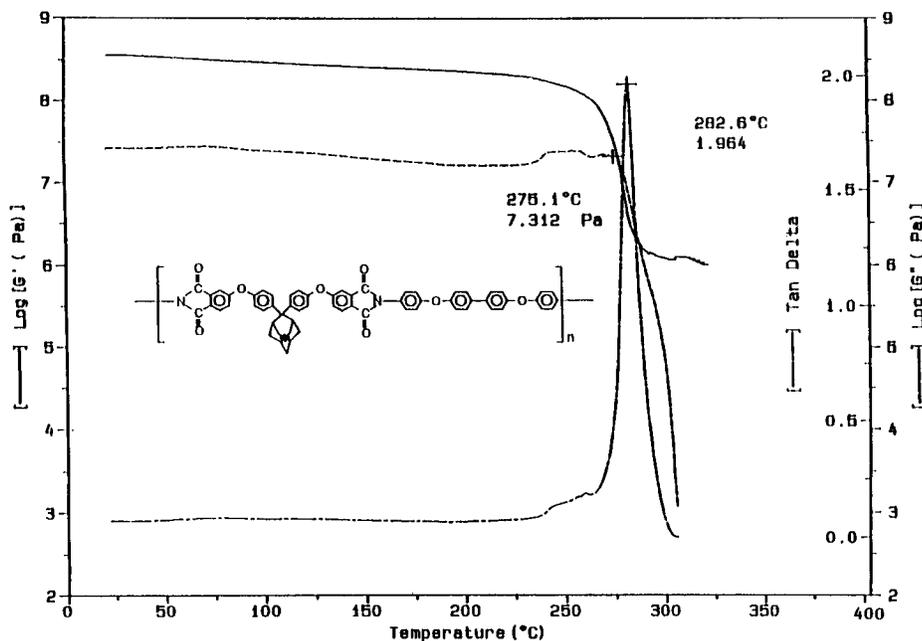


Figure 3. DMA curves for **7g** at a heating rate of 5°C/min.

tained high mechanical properties ($G' \sim 10^8$ Pa) even at 200–250°C. Although not studied as part of this work, these poly(ether imide)s may have high selectivity/permeability due to the presence of bulky adamantylidene units and therefore may prove useful in gas separation membrane application.

CONCLUSIONS

A new adamantane-based bis(ether anhydride), 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]adamantane dianhydride, was synthesized from readily available compounds in four main steps. A series of high-molar-mass poly(ether imide)s have been synthesized from this dianhydride monomer and aromatic diamines. All the poly(ether imide)s were noncrystalline. The incorporation of adamantane-2,2-diyl units into the poly(ether imide) backbone did not lead to an increase in solubility. However, several of these polymers exhibited a desired combination of properties that included good mechanical properties, high thermal stability, and moderate to high T_g 's.

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