Low Dielectric Constants of Soluble Polyimides Based on Adamantane

Yaw-Terng Chern* and Hann-Chyan Shiue

Institute of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106, Republic of China

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ABSTRACT: This work synthesizes new adamantane-based polyimides by reacting 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane (**4**) with various aromatic tetracarboxylic dianhydrides. The poly(amic acid)s have number-average molecular weights (M_n) of 39 000−139 000. The M_n's of soluble polyimides $\mathbf{7_d}$ and $\mathbf{7_e}$ are 108 000 and 89 000, respectively. These films have low dielectric constants ranging from 2.77 to 2.91 and low moisture absorptions of less than 0.46%. Two of these polyimides have good solubilities, and even nonfluorinated polyimide $\mathbf{7_e}$ can be soluble in chloroform. All polyimides **7** formed tough and transparent films. These films have tensile strengths of 88.2−113.5 MPa, elongations to break of 5.6−12.5%, and initial moduli of 2.0−2.2 GPa. Dynamic mechanical analysis (DMA) reveals that adamantane-based polyimides have two relaxations on the temperature scale between 0 and 350 °C. The subglass relaxations of polyimides **7** do not occur at the same temperature; instead, they range from 100 to 175 °C. Differential scanning calorimetry (DSC) and DMA reveal their glass transition temperatures (T_g's) were found to be 232−330 and 262−343 °C, respectively. These T_g's lie in a manageable temperature range for processing in melt.

Introduction

Aromatic polyimides, owing to their good thermal stabilities, chemical resistance, and good mechanical and electrical properties, have been extensively applied in the aviation, automotive, and electronic industries. However, most polyimides encounter processing difficulty due to their infusibilities and poor solubilities in organic solvents. Such difficulty is due to strong interchain forces, inherent macromolecular rigidity, or semicrystallinity. Many studies have attempted to enhance their processabilities and solubilities either by introducing bulky groups or flexible chains into the polymer backbones or by attaching bulky side groups.[1−7] In a similar manner, noncoplanar diamines and dianhydrides are quite effective in improving the solubility of polyimides.[1,6,8]

Adamantane has also been incorporated into the backbones of many polymers including polyamides, polysulfones, polyesters, and polyimides, subsequently producing increased thermal stability and glass transition temperature.[9] The feasibility of incorporating adamantane as a pendant group on the polymer backbone has been examined, leading to decreased crystallinity, increased solubility, and enhanced glass transition temperature and thermal stability.[10,11] In addition, thermosetting polymers based on acetylene derivatives of adamantane have been reported.[12,13] Although the feasibility of incorporating adamantane into the backbones of the polyimides has been examined, investigations involving the relation of polyimides to physical properties based on adamantane are limited.[9] Our previous work prepared the polyimide based on adamantane.[14] However, polyimide films have not been successfully prepared due to the low inherent viscosities of poly(amic acid)s.[14] Therefore, synthesizing and characterizing polyimides, as well as incorporating adamantane into the backbones of the polyimides, are worth proceeding. In this work, we synthesized a noncoplanar and asymmetric new diamine containing flexible ether segments, 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane (**4**). The processabilities of the polyimides can be enhanced by incorporating the diamine **4** into the polyimide backbones.

This work concentrates primarily on synthesizing the new polyimides having low dielectric constants, low moisture absorptions, and easy processabilities, i.e., highly desired characteristics for a material in electronic applications. Herein, we successfully synthesized new polyimides involving the diamine **4** by polycondensation with aromatic tetracarboxylic dianhydrides **5**. The dielectric constants, moisture absorptions, solubilities, dynamic mechanical properties, and thermal properties of the polyimides were investigated.

Experimental Section

Materials. Pyromellitic dianhydride ($\mathbf{5_a}$), 4,4′-carbonyldiphthalic anhydride ($\mathbf{5_b}$), 4,4′-oxydiphthalic anhydride ($\mathbf{5_c}$), 4,4′-hexafluoroisopropylidenediphthalic anhydride ($\mathbf{5_d}$), and 3,3′, 4,4′-biphenyltetracarboxylic dianhydride ($\mathbf{5_g}$) were purified by sublimation. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. According to a previous method, 1,3-dibromoadamantane (**1**) was synthesized from adamantane.[14]

Herein, three steps were employed to synthesize 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride ($\mathbf{5_f}$) and bis[4-(3,4-dicarboxyphenoxy)phenyl] ether dianhydride ($\mathbf{5_e}$) by previous methods[5,15] from hydroquinone and 4,4′-dihydroxydiphenyl ether, respectively. The corresponding bisphenols reacted with 4-nitrophthalodinitrile in anhydride dimethyl sulfoxide in the presence of potassium carbonate as an acid acceptor to generate bis(ether dinitrile)s which, subsequently, were then hydrolyzed to bis(ether diacid)s and dehydrated to bis(ether anhydride)s: $\mathbf{5_e}$ (mp 238−240 °C, lit.[15]mp 238−239 °C); $\mathbf{5_f}$ (mp 263−265 °C, lit.[15] mp 265−266 °C).

Synthesis of 1,3-Bis(4-hydroxyphenyl)adamantane (2). A 150-mL round-bottomed flask was charged with 1,3-dibromoadamantane (6.00 g, 20.4 mmol), phenol (60.0 g, 0.638 mol), and iron(III) chloride (1.10 g, 6.78 mmol). The flask was fitted with a reflux condenser and a outlet leading to a beaker with a NaOH solution to trap the HBr evolved in the reaction. The reaction was stirred at 80 °C for 16 h. The excess phenol was removed by stirring the product in 500-mL portions of hot water 3 times. The product was dried under vacuum, and

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* Author to whom correspondence should be addressed.

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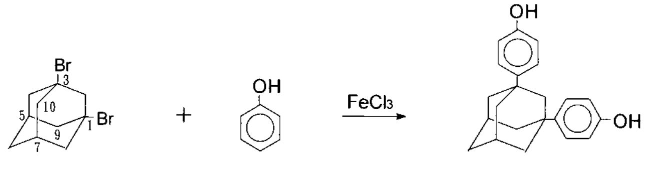
crude product was crystallized from methanol to afford 3.21 g (49.2%) of white crystals: mp 199−201 °C; IR (KBr) 3310 (br), 2890, 2865, 1606, 1512 cm^{-1}; MS (EI) m/z 320 (M$^+$, 100), 107 (50); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.66 (br s, 2H, H-6), 1.79 (m, 10 H, H-2, -4, -8, -9, -10), 2.18 (br s, 2 H, H-5, -7), 6.68 (m, 4 H, ArH), 7.15 (m, 4 H, ArH), 9.10 (s, 2 H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 29.01 (C-5, -7), 35.26 (C-6), 35.97 (C-1, -3), 41.94 (C-4, -8, -9, -10), 49.13 (C-2), 114.64 (d, Ar), 125.35 (d, Ar), 140.82 (s, Ar), 154.90 (s, Ar). Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.50; H, 7.50. Found: C, 82.32; H, 7.42. Crystal data: $C_{25}H_{32}O_3$, colorless crystal, 0.05 × 0.15 × 0.55 mm, triclinic $P1$ with $a = 6.3740(20)$ Å, $b = 13.231(5)$ Å, $c = 13.324(16)$ Å, $\alpha = 77.81(5)°$, $\beta = 76.74(6)°$, $\gamma = 79.77(3)°$ with $D_c = 1.193$ g cm^{-3} for $Z = 2$, $V = 1059.2(14)$ Å^3, $T = 298$ K, $\lambda = 1.5418$ Å, $\mu = 4.632$ cm^{-1}, $F(000) = 413$, $R_w = 0.080$ for 1965 observed reflections.

Synthesis of 1,3-Bis[4-(4-nitrophenoxy)phenyl]adamantane (3). A mixture of 1.00 g (3.13 mmol) of **2**, 1.08 g (6.85 mmol) of *p*-chloronitrobenzene, 0.950 g (6.87 mmol) of potassium carbonate, and 30 mL of dry *N*-dimethylformamide (DMF) was refluxed at 160 °C for 12 h under nitrogen. The reaction mixture was allowed to cool to room temperature, and the mixture was then poured into distilled water. The precipitate was collected by filtration and recrystallized from *N*-dimethylacetamide (DMAc) to afford 1.45 g (82.4%) of pale-yellow crystals: mp 216−218 °C; IR (KBr) 3050, 2890, 2865, 1586, 1501, 1487, 1344 cm^{-1}; MS (EI) m/z 562 (M$^+$, 100), 228 (80); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.76 (br s, 2 H, H-6), 1.91−1.99 (m, 10 H, H-2, -4, -8, -9, -10), 2.28 (br s, 2 H, H-5, -7), 7.08−7.14 (m, 8 H, ArH), 7.54 (d, $J = 8.68$ Hz, 4 H, ArH), 8.23 (d, $J = 8.68$ Hz, 4 H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 28.94 (C-5, -7), 35.03 (C-6), 36.71 (C-1, -3), 41.50 (C-4, -8, -9, -10), 48.52 (C-2), 117.12 (d, Ar), 120.01 (d, Ar), 126.13 (d, Ar), 126.93 (d, Ar), 147.95 (s, Ar), 150.97 (s, Ar), 152.35 (s, Ar), 163.31 (s, Ar). Anal. Calcd for $C_{34}H_{30}N_2O_6$: C, 72.60; H, 5.34; N, 4.98. Found: C, 72.45; H, 5.26; N, 4.91. Crystal data: $C_{34}H_{30}N_2O_6$, pale-yellow crystal, 0.20 × 0.30 × 0.30 mm, triclinic $P1$ with $a = 9.8818(15)$ Å, $b = 10.108(3)$ Å, $c = 13.988(5)$ Å, $\alpha = 91.33(3)°$, $\beta = 91.273(22)°$, $\gamma = 101.893(20)°$ with $D_c = 1.368$ g cm^{-3} for $Z = 2$, $V = 1366.3(7)$ Å^3, $T = 298$ K, $\lambda = 1.5418$ Å, $\mu = 7.277$ cm^{-1}, $F(000) = 594$, $R_w = 0.055$ for 2907 observed reflections.

Synthesis of 1,3-Bis[4-(4-aminophenoxy)phenyl]adamantane (4). A 150-mL, three-necked, round-bottomed flask was charged with **3** (1.50 g, 2.67 mmol), 15 mL of hydrazine monohydrate, 50 mL of ethanol, and 0.03 g of 10% palladium on carbon (Pd−C). The mixture was heated to reflux for 16 h. The mixture was then filtered to remove the Pd−C, and the crude solid was recrystallized from benzene to yield 0.872 g (65.1%) of white crystals: mp 191−193 °C; IR (KBr) 3428, 3341, 3060, 2890, 2870, 1618, 1505 cm^{-1}; MS (EI) m/z 502 (M$^+$, 77), 108 (100); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.69 (br s, 2 H, H-6), 1.84 (m, 10 H, H-2, -4, -8, -9, -10), 2.20 (br s, 2 H, H-5, -7), 4.93 (s, 4 H, NH$_2$), 6.56 (d, $J = 8.65$ Hz, 4 H, ArH), 6.70−6.77 (m, 8 H, ArH), 7.28 (d, $J = 8.72$ Hz, 4 H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 28.89 (C-5, -7), 35.09 (C-6), 36.19 (C-1, -3), 41.68 (C-4, -8, -9, -10), 48.71 (C-2), 114.74 (d, Ar), 116.06 (d, Ar), 120.43 (d, Ar), 125.74 (d, Ar), 143.79 (s, Ar), 144.98 (s, Ar), 145.97 (s, Ar), 156.52 (s, Ar). Anal. Calcd for $C_{34}H_{34}N_2O_2$: C, 81.27; H, 6.77; N, 5.58. Found: C, 81.06; H, 6.81; N, 5.61.

Scheme 1



1 **2**

Characterization. A Bio-Rad FTS-40 FTIR spectrophotometer was used to record IR spectra (KBr pellets). In a typical experiment, an average of 20 scans per sample was made. MS spectra were obtained by using a JEOL JMS-D300 mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300WB or AM-400 Fourier transform nuclear magnetic resonance spectrometers using tetramethylsilane (TMS) as the internal standard. A Perkin-Elmer 240C elemental analyzer was used for elemental analysis. The X-ray crystallographic data were collected on a CAD-4 diffractometer. The analyses were carried out on a DEC station 3500 computer using NRCC SDP software. The melting points were obtained by a standard capillary melting point apparatus. Inherent viscosities of all polymers were determined at 0.5 g/dL using an Ubbelohde viscometer. Gel permeation chromatography (GPC) on soluble polymers were performed on an Applied Biosystem at 70 °C with two PL gel 5-μm mixed-C columns in the NMP/LiBr (0.06 mol/L) solvent system. The flow rate was 0.5 mL/min, detection was by UV, and calibration was based on polystyrene standards. Qualitative solubility was determined using 0.01 g of polymer in 2 mL of solvent. A Du Pont 9900 differential scanning calorimeter and a Du Pont 9900 thermogravimetric analyzer were then employed to study the transition data and thermal decomposition temperature of all the polymers. The differential scanning calorimeter (DSC) was run under a nitrogen stream at a flow rate of 30 cm^3/min and a heating rate of 20 °C/min. The thermogravimetric analysis (TG) was determined under a nitrogen flow of 50 cm^3/min. 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 0.08 mm in thickness was used. The dynamic shear modulus was measured at a resonance mode. The wide-angle X-ray diffraction measurements were performed on a Philips PW 1730−10 X-ray diffractometer using Cu Kα radiation.

Tensile properties were determined from stress−strain curves with a Toyo Baldwin Instron UTM-III-500 with a load cell of 10 kg at a drawing speed of 5 cm/min. Measurements were performed at 28 °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. Moisture absorption measurements were made with an ultramicrobalance of Sartorius Model S3D-P on thin film (~40 μm). Measurements were taken at 30 °C for 90 h at 85% relative humidity. The dielectric constant was measured by the parallel-plate capacitor method using a dielectric analyzer (TA Instruments DEA 2970) on thin films. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by measuring at 25 °C in a sealed humidity chamber at 0% relative humidity.

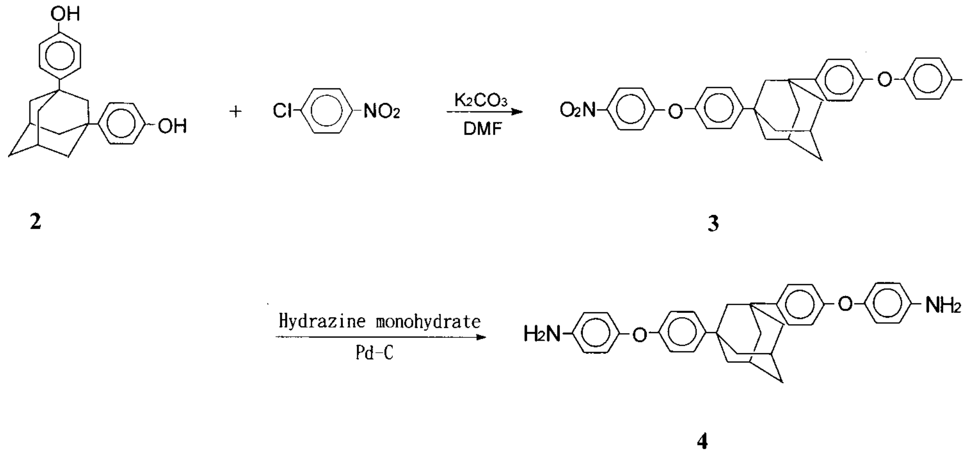
Polymer Synthesis. Dianhydride $\mathbf{5_d}$ (0.444 g, 1.00 mmol) was added to a stirred solution of **4** (0.502 g, 1.00 mmol) in NMP (solid content 10% w/v) under N_2 at ambient temperature for 6 h. The inherent viscosity and number-average molecular weight (M_n) of the poly(amic acid) $\mathbf{6_d}$ was 1.17 dL/g and 1.39 × 10^5, respectively. The IR spectrum exhibited absorptions at 3345 (N−H and O−H str) and 1720, 1650 cm^{-1} (C=O str), i.e., characteristic of the amic acid. The poly(amic acid) solution was then cast into a glass plate. The poly(amic acid) $\mathbf{6_d}$ was converted to polyimide $\mathbf{7_d}$ by successive heating in a vacuum at 80 °C for 3 h, at 200 °C for 8 h, and then at 320 °C for 6 h. The inherent viscosity and M_n of polyimide $\mathbf{7_d}$ was 0.77 dL/g and 1.08 × 10^5, respectively. The symmetric and asymmetric carbonyl stretches occurred at 1775 and 1725 cm^{-1} in the FTIR spectrum of $\mathbf{7_d}$. In the associated bands are the C−N stretch at 1370 cm^{-1} and the band at 715 cm^{-1}, i.e., deformation of the imide ring to imide carbonyls.

The other polyimides were prepared in a similar manner from **4** and aromatic tetracarboxylic dianhydrides **5**.

Results and Discussion

Monomer Synthesis. Three steps were employed to synthesize 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane (**4**) from **1** as shown in Schemes 1 and 2. **1** reacted with phenol in the presence of iron(III) chloride as a catalyst to generate **2** as shown in Scheme 1. The corresponding bisphenol **2** reacted with *p*-chloronitrobenzene in anhydride DMF in the presence of potas-

Scheme 2



sium carbonate as an acid acceptor to generate new **3**, which was hydrogenated to generate new monomer **4**. The yield of **3** was high at 82.4% by condensation of *p*-chloronitrobenzene with the dipotassium salt of **2**. This high yield can be attributed to the fact that the dipotassium salt of **2** is a good nucleophilic compound owing to the adamantyl group's electrodonating effect. On the basis of the carbon's shielding effect, the positions of the chemical shifts for the carbons of **4** were assigned in Figure 1A. With the aid of 2D ^{1}H—^{13}C cosy spectrum, the positions of the chemical shifts for protons of **4** were readily assigned as shown in Figure 1B. When **3** was converted into the diamine **4**, the reasonances of the protons Hg were found further upfield from 8.23 to 6.56 ppm (see Experimental Section). The signal appearing at 4.93 ppm is peculiar to the amino group. In addition, X-ray diffraction analysis confirmed the structures of **2** and **3**. X-ray crystal data for **2** and **3** were acquired from an individual single crystal, as obtained by slowly crystallizing from individual isopropyl alcohol and DMAc solutions, respectively. Interestingly, **2** and isopropyl alcohol formed a single-crystal bond with a hydrogen bond. Figure 2 presents the X-ray structure of **3**. Elemental analysis data, the NMR spectra, and the IR spectra confirmed all monomers reported herein.

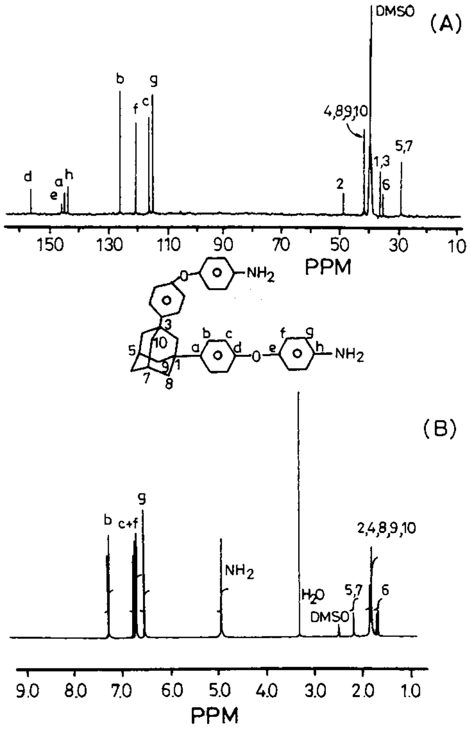


Figure 1. NMR (DMSO-d_6) spectra of **4**. (A) ^{13}C NMR (100 MHz); (B) ^{1}H NMR (400 MHz).

Synthesis of Polymers. New adamantane-based polyimides were synthesized by a conventional two-step procedure starting from **4** and aromatic tetracarboxylic dianhydrides **5** through ring-opening polyaddition and subsequent thermal cyclodehydration, as shown in Scheme 3. Table 1 summarizes those results. The ring-opening polyaddition in NMP at room temperature yielded poly(amic acid)s **6** with high inherent viscosities ranging between 0.91 and 1.36 dL/g. According to the GPC data, the high molecular weights of **6** were usually attainable (Table 1). In fact, all M_w/M_n values were lower than those of the commercial materials, which may be due to the somewhat low reactivity of **4** containing rigid and bulky adamantyl groups. IR spectroscopy confirmed the formation of poly(amic acid)s **6**. The characteristic absorption bands of the amic acid appeared near 3345 (N—H and O—H str), 1720 (acid, C=O str), 1650 (amide, C=O str), and 1540 cm^{-1} (N—H bending). Next, the thermal conversion to polyimides **7** was performed by successively heating the poly(amic acid)s **6** to 320 °C in a vacuum. The soluble polyimides $\mathbf{7_d}$ and $\mathbf{7_e}$ had high inherent viscosities of 0.77 and 0.73 dL/g, respectively. Table 1 also indicates that the M_n's of polyimides $\mathbf{7_d}$ and $\mathbf{7_e}$ are 108 000 and 89 000, respectively. IR spectroscopy confirmed the formation of polyimides **7**. The characteristic absorption bands of the imide ring appeared near 1780 (asym C=O str), 1720 (sym C=O str), 1390 (C—N str), and 745 cm^{-1} (imide ring deformation). In addition, as Figure 3 reveals, NMR spectra confirmed the polyimide $\mathbf{7_d}$. In the proton, f and g were assigned while assuming that the g proton ortho to the C=O had shifted farther downfield. Also, the f proton signal was broadened through interaction with the nearby CF$_3$ groups and, possibly, by unresolved meta coupling with the e proton.

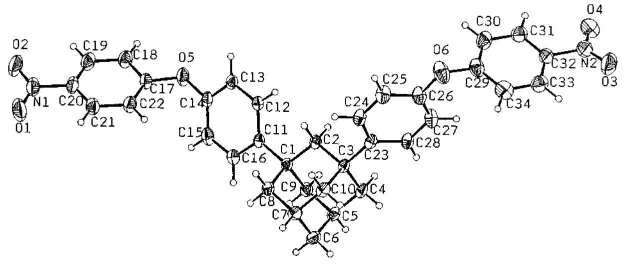


Figure 2. X-ray structure of **3**.

Scheme 3

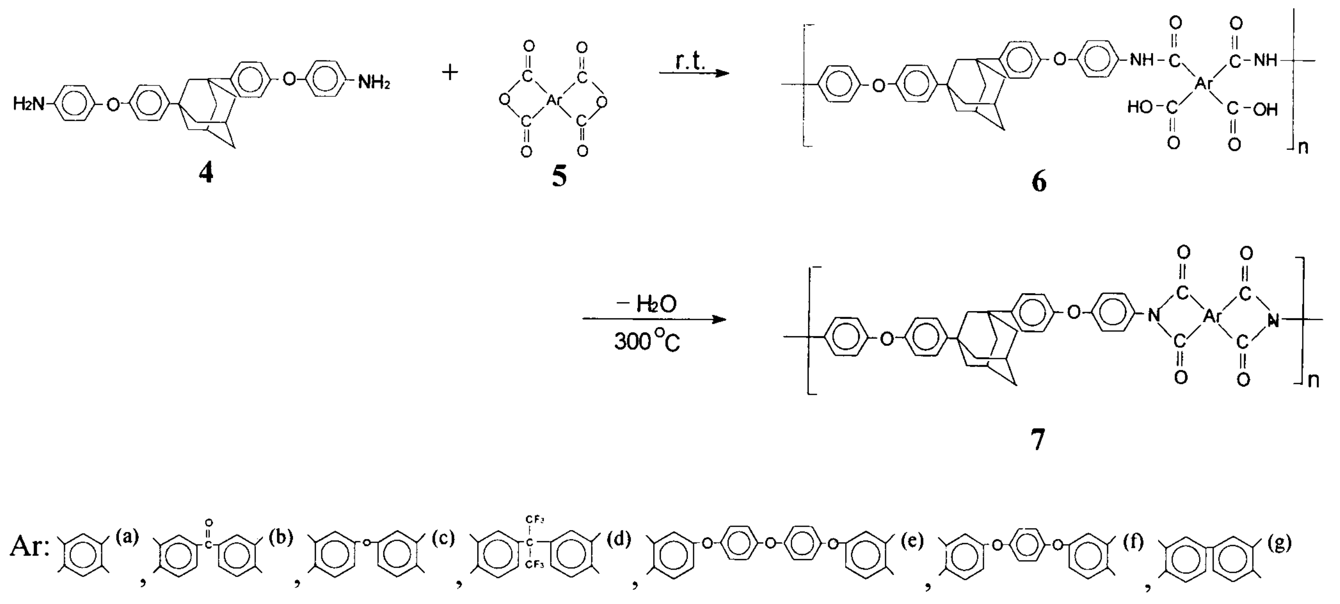


Table 1. Inherent Viscosities and GPC Molecular Weights of Poly(amic acid)s and Soluble Polyimides

dian-hydride	poly(amic acid)s			polyimides		
	$10^{-4}M_n$[a]	M_w/M_n	η_{inh},[b] dL/g	$10^{-4}M_n$[a]	M_w/M_n	η_{inh},[c] dL/g
5a	6.4	1.5	1.06	d		
5b	8.1	1.6	0.94			
5c	6.6	1.3	1.36			
5d	13.9	1.7	1.17	10.8	1.7	0.77
5e	6.5	1.2	1.05	8.9	2.2	0.73
5f	7.9	1.8	0.91			
5g	3.9	1.2	1.27			

[a] By GPC (relative to polystyrene). [b] Measured in NMP on 0.5 g/dL at 30 °C. [c] Measured in chloroform on 0.5 g/dL at 10 °C. [d] Could not be measured.

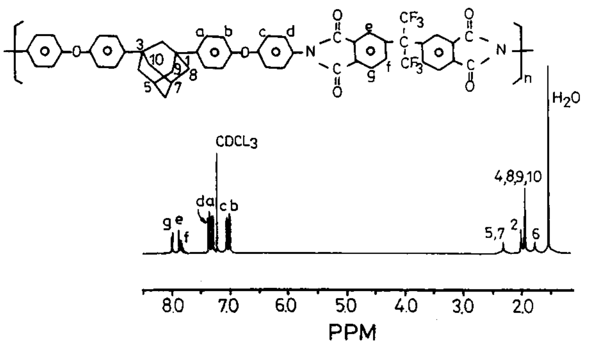


Figure 3. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of polyimide 7_d.

Table 2. Solubilities of Polyimides[a]

solvent	polymer						
	7_a	7_b	7_c	7_d	7_e	7_f	7_g
o-chlorophenol	+−	+−	+−	+−	+−	+−	+−
m-cresol	−	+−	+−	+−	+−	−	−
chloroform	−	−	−	+	+	+−	−
THF	−	−	−	+	−	−	−
NMP	−	−	−	−	−	−	−
DMAc	−	−	−	+−	+−	−	−
cyclohexanone	−	−	−	+	−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble on heating at 60 °C; + −, partial soluble on heating at 60 °C; −, insoluble on heating at 60 °C. Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; THF, tetrahydrofuran.

Table 3. Physical Properties of Polyimide Films

polymer	strength to break, MPa	elongation to break, %	initial modulus, GPa	dielectric const, dry, 1 KHz	% H_2O absorption[a], 85% RH
7a	96.1	10.5	2.2	2.85	0.267
7b	113.5	11.2	2.1	2.91	0.459
7c	104.9	12.5	2.1	2.88	0.254
7d	99.68	5.6	2.2	2.77	0.167
7e	88.2	11.8	2.0	2.87	0.245
7f	87.2	10.2	2.0	2.87	0.261
7g	100.8	11.5	2.2	2.86	0.283

[a] Moisture absorptions of polyimide films were measured at 30 °C for 90 h.

Characterization of Polymers. These polyimides solubilities were tested in various solvents. Table 2 summarizes those results. Due to the incorporation of an asymmetric 1,3-adamantyl structure and flexible ether segments into the polyimides **7**, the nonfluorinated polyimide $\mathbf{7_e}$ is soluble in chloroform. The hexafluoroisopropylidene-containing polyimide $\mathbf{7_d}$ exhibited an excellent solubility toward test solvents; it was soluble in chloroform, cyclohexanone, and THF. However, the other polyimides **7**, except $\mathbf{7_d}$ and $\mathbf{7_e}$, were insoluble in the test solvents due to the relatively rigid structures in the dianhydride moieties. Transparent and pale-yellow polyimide films **7** were obtained by successively heating the corresponding poly(amic acid)s **6**. Initially, the polyimide films **7** were structurally characterized by X-ray methods. All polyimides **7** had nearly the same amorphous patterns, with a broad peak appearing (2θ) at around 18°.

Table 3 summarizes the dielectric constants, moisture absorptions, and mechanical properties of the films. The mechanical properties were determined via an instron machine. The mechanical properties of these films were, in general, satisfactory. Elongation to break values of all the polyimides **7**, except $\mathbf{7_d}$, were moderate due to the incorporation of the flexible ether segments into polyimides **7**. The moisture absorptions of the polyimides are small, i.e., less than 0.46%, owing to the waterproofing effect of the fluorine atoms and adamantane elements. Table 3 also indicates that the dielectric constants of adamantane-based polyimides **7** were low, ranging from 2.77 to 2.91. Such low dielectric constants are owed to the fact that adamantane is a fully aliphatic hydrocarbon, subsequently leading to low hydrophobic-

Table 4. Thermal Properties of Polyimides

	DSC[a]	DMA[b]		dec[c] temp, °C	
polymer	T_g, °C	T_g, °C	T_β, °C	in air	in N$_2$
7a	330	343	100	501	500
7b	272	295	170	500	496
7c	268	309	137	495	506
7d	284	317	170	470	485
7e	232	262	121	445	491
7f	250	284	111	485	492
7g	292	319	175	487	515

[a] Glass transition temperature (T_g) measured by DSC at a heating rate of 20 °C/min in nitrogen. [b] The glass and subglass transitions measured by DMA using shear mode at a heating rate of 5 °C/min. [c] Temperature at which 5% weight loss recorded by TG at a heating rate of 20 °C/min.

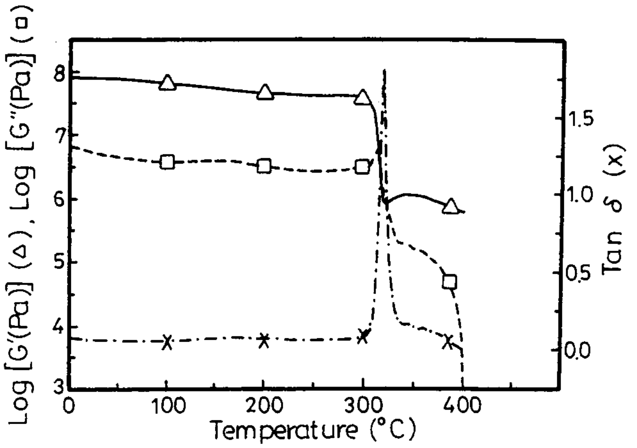


Figure 4. Dynamic mechanical analysis curves for $\mathbf{7_d}$ at a heating rate of 5 °C/min.

ity and polarity. We speculate that this event is due to the "dilution" effect of the polar imide groups by the adamantyl groups (on a weight basis based on polymer).

Thermal analysis was performed by means of DSC, DMA, and TGA. Table 4 summarizes those results. The temperatures of polyimides **7** at a 5% weight loss ranged from 445 to 501 °C in air and from 485 to 515 °C in N$_2$ atmosphere. The initial DSC heating run occasionally detected the influences of residual water or solvents and the history of thermal annealing. Therefore, the first heating of the samples was curtailed at 350 °C. In addition, T_g and other thermal properties were evaluated according to the DSC charts of the second heating. Table 4 also indicates that the glass transitions of polyimides **7** range from 232 to 330 °C. Regarding the higher number of flexible ether-containing polyimides **7**, i.e., $\mathbf{7_c}$, $\mathbf{7_e}$, and $\mathbf{7_f}$, their T_g values were lower than the other polyimides **7**. Moreover, the T_g's of polyimides **7** markedly decreased with an increasing content of ether segment. The higher T_g, i.e., $\mathbf{7_a}$ and $\mathbf{7_g}$, is attributed to the fact that the rotations of these bonds are hindered by the rigid structures within the dianhydride moieties of the polyimides, causing chain stiffness to increase. According to the DSC analysis, the dianhydride was varied for a given diamine, in which the T_g roughly followed the order $\mathbf{7_a} > \mathbf{7_g} > \mathbf{7_d} > \mathbf{7_b} > \mathbf{7_c} > \mathbf{7_f} > \mathbf{7_e}$. In addition, their T_g's lie in a manageable temperature range for processing in melt.

Figure 4 presents the mechanical relaxation spectra of polyimide $\mathbf{7_d}$. Two relaxations appeared at ca. 170 and 317 °C, based on tan δ and G'' peaks. The subglass relaxations (ca. 170) are a typical β relaxation for standard polyimides. This relaxation is associated with approximately a quarter of 1 order of magnitude decrease in G'. Moreover, the subglass relaxation is much less prominent than the glass relaxation. Such a transition has generally been accounted for by the rotation or oscillations of the phenyl groups within the diamine moieties of the polyimides.[16,17] The glass transition at around 317 °C is associated with approximately a mid-1 order of magnitude step decrease in G'.

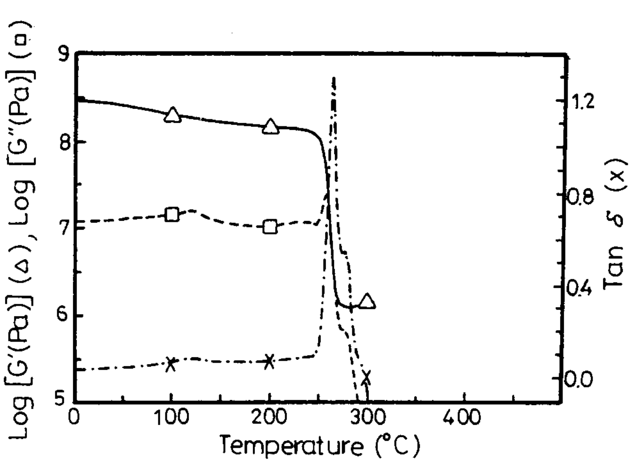


Figure 5. Dynamic mechanical analysis curves for **7e** at a heating rate of 5 °C/min.

Figure 5 depicts the mechanical relaxation spectra of polyimide $\mathbf{7_e}$. In polyimide $\mathbf{7_e}$, its relaxation spectra resemble those of $\mathbf{7_d}$. Two relaxation transitions also occurred in polyimide $\mathbf{7_e}$ on the temperature scale between 0 and 350 °C. However, the subglass relaxation did not occur at the same temperature in both polyimides ($\mathbf{7_d}$ and $\mathbf{7_e}$). Table 4 lists the glass and β relaxation temperatures of polyimides **7**. The glass transition temperatures of polyimides **7** ranged from 262 to 343 °C. Although the flexible ether segments were incorporated into the polyimides **7**, the glass transition temperatures of the polyimides **7** were generally high. Such high T_g's are attributed to the rigid and bulky adamantyl groups, resulting in increasing chain stiffness. However, the T_g's of polyimides $\mathbf{7_e}$ and $\mathbf{7_f}$ were obviously lower than the other polyimides **7**. This lower T_g is attributed to the fact that the relatively higher content of ether segments was incorporated in $\mathbf{7_e}$ and $\mathbf{7_f}$. In addition, the subglass relaxation of polyimides **7** did not occur at the same temperature, rather ranging from 100 to 175 °C.

Conclusions

Due to the low hydrophobicity and polarity of the rigid and bulky adamantane, the new adamantane-based polyimides exhibit low dielectric constants, low moisture absorptions, and high T_g's. Nonfluorinated polyimide $\mathbf{7_e}$ can be soluble in *o*-chlorophenol. Similarly, fluorinated polyimides $\mathbf{7_d}$ can be soluble in chloroform, cyclohexanone, and THF. In this work, transparent and pale-yellow polyimide films were obtained by casting from the corresponding poly(amic acid)s. These films display good mechanical properties and good thermal stabilities. Their dielectric constants are low, ranging from 2.77 to 2.91. Two relaxations were observed in these polyimides by means of DMA. The subglass relaxation is a typical β relaxation for standard polyimides. However, the subglass relaxations of polyimides **7** do not occur at the same temperature, rather ranging from 100 to 175 °C. DSC and DMA indicate that their glass transition temperatures are 232–330 and 262–

343 °C, respectively. These T_g's lie in a manageable temperature range for processing in melt.

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