Low Dielectric Constants of Soluble Polyimides Derived from the Novel 4,9-Bis[4-(4-aminophenoxy)phenyl]diamantane

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ABSTRACT: New diamantane-based polyimides are synthesized by reacting of 4,9-bis[4-(4-aminophenoxy)phenyl]diamantane with various aromatic tetracarboxylic dianhydrides. Films of these polyimides have low dielectric constants, ranging from 2.58 to 2.74, and low moisture absorptions less than 0.3%. Four of these films have good solubilities. Three nonfluorinated polyimides were soluble in *o*-chlorophenol, *m*-cresol, *N*-methyl-2-pyrrolidone (NMP), and chloroform. The hexafluoroisopropylidene-containing polyimide was soluble in *m*-cresol, chloroform, and tetrahydrofuran (THF). The soluble polyimides have molecular weights (M_n) ranging from 33 000 to 96 000. All polyimides formed tough transparent films, with tensile strengths of 55.3−101.4 MPa, elongations to break of 6.1−22.3%, and initial moduli of 1.9−2.2 GPa. Dynamic mechanical analysis (DMA) reveals that diamantane-based polyimides have two transitions on the temperature scale between 0 and 400 °C. Their glass relaxations, characterized by DMA, occur at high temperatures, ranging from 296 to 413 °C. New diamantane-based polyimides are highly promising for electronic applications owing to their excellent physical properties, in particular an extremely low dielectric constant.

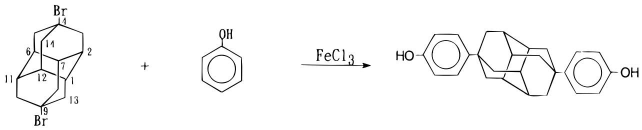
Introduction

Enhancing electric performance in a packing system has become an increasingly relevant issue in lieu of rapid advances in the microelectronic industry. Reducing the dielectric constant while maintaining thermal and mechanical properties of the thin-film interlayer dielectric material is highly desired.[1] Investigators have attempted to enhance polymer properties by incorporating trifluoromethyl or other perfluoroalkyl groups, subsequently leading to lower moisture pickup, lower dielectric constant, and better solubility.[2−12] For instance, the highly fluorinated polyimides have dielectric constants of approximately 2.5.[3,6,7]

Diamantane is a cycloaliphatic-cage hydrocarbon containing an “extended-cage” adamantane structure.[13,14] Although diamantane has been investigated for many years, only a few examples of the polymers based on diamantane are known.[15−23] Previously, the 1,4-, 4,9- and 1,6-diethynyldiamantanes were polymerized to yield clear thermoset resins that degraded between 518 and 525 °C in air or helium.[15] In that work colorless diamantane-based polybenzazoles were prepared via the established polyphosphoric acid polycondensation technique.[16] In addition, polymeric molecules based on diamantane have found specific applications in building dendritic materials.[17] Our recent work indicated that incorporating diamantyl groups into polyamides, polyesters and poly(amide−imide)s allowed these polymers to have good thermal stabilities, high glass transition temperatures, and good retention of storage moduli above their glass transition temperatures.[18−22] Regarding the incorporation of diamantane into the polyimide, only one example of the polyimide has been reported by us.[23] However, polyimide films based on diamantane have not been successfully prepared. Thus, the physical properties of diamantane-based polyimide (except for thermal stability) have not been reported.

This work concentrates primarily on synthesis of new polyimides with a low dielectric constant, for potential use as a materials for electronic applications. Herein, we successfully synthesize new polyimides involving 4,9-bis[4-(4-aminophenoxy)phenyl]diamantane (**4**) by polycondensation with aromatic dianhydrides **5**, as shown in Scheme 3. In addition, the dielectric constants, moisture absorptions, coefficient of thermal expansion (CTE), solubilities, dynamic mechanical properties, and thermal properties of polyimides are investigated as well.

Scheme 1



1 **2**

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. NMP and *m*-cresol were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. According to a previous method, 4,9-dibromodiamantane (**1**) was synthesized from norbornadiene in four steps.[21]

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 a previous method[24,25] from hydroquinone and bis(4-hydroxyphenyl) ether, respectively. The corresponding bisphenols reacted with 4-nitrophthalodinitrile in anhydrous 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.

Bis[4-(3,4-dicarboxyphenoxy)phenyl] Ether Dianhydride ($\mathbf{5_e}$): mp 238−240 °C (lit.[24] 238−239 °C); IR (KBr) 1849, 1772, 1612, 1475 cm^{-1}; MS (EI) *m/z* 494 (M$^+$, 100); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.09−7.20 (m, 12H, ArH), 7.76 (d, J = 8.3, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 116.07 (d, Ar), 118.25 (d, Ar), 120.32 (d, Ar), 121.83 (d, Ar), 125.51 (s, Ar), 131.43 (d, Ar), 136.59 (s, Ar), 150.38 (s, Ar), 153.56 (s, Ar),

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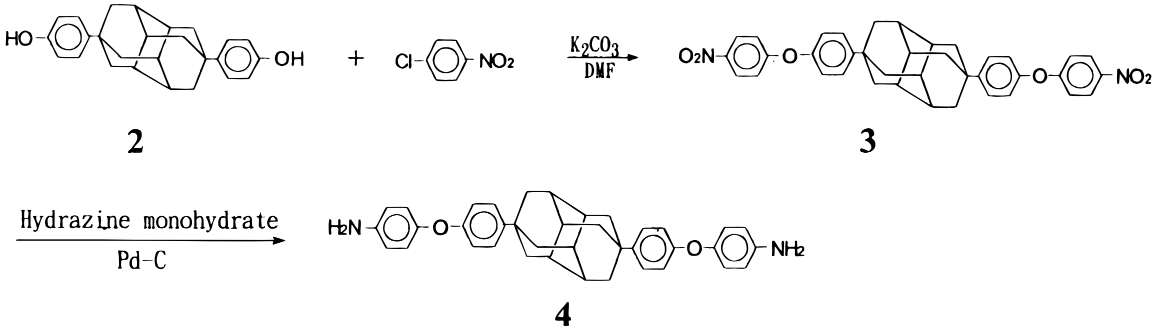
Scheme 2



159.71 (s, Ar), 167.39 (C=O), 168.50 (C=O). Crystal data: $C_{28}H_{14}O_9$, colorless crystal, 0.20 × 0.20 × 0.25 mm, triclinic $P\bar{1}$ with $a = 8.0198(16)$ Å, $b = 14.825(7)$ Å, $c = 20.016(9)$ Å, $\alpha = 109.69(3)°$, $\beta = 91.79(3)°$, and $\gamma = 94.66(3)°$ with $D_c = 1.473$ g cm^{-3} for Z = 4, V = 2228.8(14) Å^3, T = 298 K, $\lambda = 1.5418$ Å, $\mu = 8.979$ cm^{-1}, F(000) = 1020, and $R_w = 0.091$ for 3235 observed reflections, intensity variation <3%.

1,4-Bis(3,4-dicarboxyphenoxy)benzene Dianhydride (5_f): mp 263−265 °C (lit.[24] 265−266 °C); IR (KBr) 1850, 1772, 1610 cm^{-1}; MS (EI) *m/z* 402 (M$^+$, 100); ^{13}C NMR (100 MHz, DMSO-d_6) δ 116.53 (d, Ar), 118.58 (d, Ar), 121.76 (d, Ar), 125.82 (s, Ar), 131.43 (d, Ar), 136.57 (s, Ar), 151.55 (s, Ar), 159.32 (s, Ar), 167.39 (C=O), 168.39 (C=O). Crystal data: $C_{22}H_{10}O_8$, colorless crystal, 0.40 × 0.50 × 0.50 mm, monoclinic $P2_1/n$ with $a = 6.001(3)$ Å, $b = 10.091(3)$ Å, $c = 14.030(5)$ Å, and $\beta = 92.34(3)°$, with $D_c = 1.574$ g cm^{-3} for $Z = 2$, $V = 848.9(6)$ Å^3, T = 298 K, $\lambda = 0.7107$ Å, $\mu = 1.142$ cm^{-1}, $F(000) = 412$, and $R_w = 0.032$ for 1227 observed reflections, intensity variation <1%.

Synthesis of 4,9-Bis(4-hydroxyphenyl)diamantane (2). A mixture of 3.00 g (8.68 mmol) of 4,9-dibromodiamantane, 6 g of phenol and 0.500 g (3.08 mmol) of iron(III) chloride was stirred and heated at gentle reflux for 10 h. The reaction mixture was filtered and washed with methanol, and the precipitated solid was then crystallized from *N,N*-dimethylformamide (DMF) to afford 2.51 g (77.7%) of **2**: mp 362−364 °C; IR (KBr) 3246 (br), 2890, 2867, 1602, 1511 cm^{-1}; MS (EI) *m/z* 372 (M$^+$, 100); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.82 (s, 12H, H-3, 5, 8, 10, 13, 14), 1.86 (s, 6H, H-1, 2, 6, 7, 11, 12), 6.67 (d, $J = 8.6$, 4H, ArH), 7.15 (d, $J = 8.6$, 4H, ArH), 9.10 (s, 2H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 32.95 (C-4,9), 36.87 (C-1, 2, 6, 7, 11, 12), 43.21 (C-3, 5, 8, 10, 13, 14), 114.72 (d, Ar), 125.71 (d, Ar), 154.97 (s, Ar), 162.30 (s, Ar). Anal. Calcd for $C_{26}H_{28}O_2$: C, 83.87; H, 7.53. Found: C, 83.65; H, 7.47. Crystal data: $C_{32}H_{42}N_2O_4$, colorless crystal, 0.2 × 0.4 × 0.5 mm, monoclinic $P2_1/c$ with $a = 15.461(8)$ Å, $b = 6.456(3)$, Å, $c = 15.396(8)$ Å, $\beta = 117.14(4)°$ with $D_c = 1.260$ gcm^{-3} for Z = 4, V = 1367.4(11) Å^3, T = 298 K, $\lambda = 0.7107$ Å, $\mu = 1.041$ cm^{-1}, $F(000) = 560$, and intensity variation <2%.

Synthesis of 4,9-Bis[4-(4-nitrophenoxy)phenyl]diamantane (3). A mixture of 1.00 g (2.69 mmol) of **2**, 0.938 g (5.95 mmol) of *p*-chloronitrobenzene, 0.830 g (6.00 mmol) of potassium carbonate, and 50 mL of dry *N,N*-dimethylacetamide (DMAc) was refluxed at 160 °C for 12 h under nitrogen. The reaction mixture was allowed to cool to room temperature and then poured into distilled water. The precipitate was collected by filtration and recrystallized from DMAc to afford 1.23 g (74.5%) of pale yellow crystals: mp 314−316 °C; IR (KBr) 3110, 2890, 2865, 1588, 1512, 1344 cm^{-1}; MS (EI) *m/z* 614 (M$^+$, 100), 228 (42); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (brs, 18H, hydrogen of diamantane), 6.98−7.05 (m, 8H, ArH), 7.42 (d, $J = 9.21$, 4H, ArH), 8.17 (d, $J = 9.33$, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.09 (C-4,9), 37.33 (C-1, 2, 6, 7, 11, 12), 43.49 (C-3, 5, 8, 10, 13, 14), 116.92 (d, Ar), 120.12 (d, Ar), 125.91 (d, Ar), 126.96 (d, Ar), 142.66 (s, Ar), 147.75 (s, Ar), 152.38 (s, Ar), 163.67 (s, Ar). Anal. Calcd for $C_{38}H_{34}N_2O_6$: C, 74.27; H, 5.54; N, 4.56. Found: C, 74.08; H, 5.45; N, 4.49. Crystal data: $C_{38}H_{34}N_2O_6$, very pale yellow crystal, 0.25 × 0.25 × 0.30 mm, monoclinic $P2_1/c$ with $a = 9.9526(15)$ Å, $b = 11.299(4)$ Å, $c = 13.564(5)$ Å, and $\beta = 102.740$ (22)° with $D_c = 1.372$ g cm^{-3} for Z = 2, $V = 1487.8(8)$ Å^3, $T = 298$ K, $\lambda = 1.5418$ Å, $\mu = 7.135$ cm^{-1}, $F(000) = 650$, intensity variation <2%.

Synthesis of 4,9-Bis[4-(4-aminophenoxy)phenyl]diamantane (4). A 150 mL, three-necked, round-bottomed flask was charged with **3** (1.00 g, 1.63 mmol), 10 mL of hydrazine monohydrate, 80 mL of ethanol, and 0.03 g of 10% palladium on carbon (Pd−C). The mixture was heated at reflux for 16 h and then filtered to remove the Pd−C, and the crude solid was recrystallized from DMAc to afford 0.840 g (93.0%) of white crystals: mp 314−316 °C; IR (KBr) 3431, 3355, 3076, 2890, 2867, 1622, 1500 cm^{-1}; MS (EI) *m/z* 554 (M$^+$, 100), 277 (47); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.85 (s, 12H, H-3, 5, 8, 10, 13, 14), 1.89 (s, 6H, H-1, 2, 6, 7, 11, 12), 4.94 (s, 4H, NH_2), 6.55 (d, $J = 8.76$, 4H, ArH), 6.72 (d, $J = 8.81$, 4H, ArH), 6.79 (d, $J = 8.75$, 4H, ArH), 7.29 (d, $J = 8.83$, 4H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 34.65 (C-4, 9), 36.71 (C-1, 2, 6, 7, 11, 12), 43.00 (C-3, 5, 8, 10, 13, 14), 114.79 (d, Ar). 116.06 (d, Ar), 120.66 (d, Ar), 126.04 (d, Ar), 143.56 (s, Ar), 145.20 (s, Ar), 145.66 (s, Ar), 156.63 (s, Ar). Anal. Calcd for $C_{38}H_{38}N_2O_2$: C, 82.31; H, 6.86; N, 5.05. Found: C, 82.18; H, 6.79; N, 4.97. Crystal data: $C_{46}H_{56}N_4O_4$, colorless crystal, 0.40 × 0.50 × 0.50 mm, monoclinic $P2_1/n$ with $a = 6.6322(20)$ Å, $b = 39.308$ (8) Å, $c = 8.0466$ (23) Å, and $\beta = 110.35°$ (3), with $D_c = 1.231$ g cm^{-3} for $Z = 2$, $V = 1966.9(9)$ Å^3, $T = 298$ K, $\lambda = 1.5418$ Å, $\mu = 4.210$ cm^{-1}, $F(000) = 786$, and intensity variation <3%.

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 was performed on an Applied Biosystem at 70 °C with two PLgel 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. Light scattering measurements as well as differential refractometry measurements were performed at 25 °C and $\lambda_0 = 633$ nm using an He−Ne ion laser (Photal Otsuka Model DLS-7000HL,DRM-1021). 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 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 0.05 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. The in-plane, linear coefficient of thermal expansion (CTE) was obtained from a TA TMA-2940 thermomechanical analyzer (5 °C/min, from 30 to 250 °C, 10 mN). The CTE value on the temperature scale between 50 and 200 °C was recorded after an initial conditioning step (heat to 250 °C, hold 5 min, and cool). Moisture absorption measurements were made with an ultramicrobalance of Sartorius model S3D-P on thin films (~40 μm). Measurements were taken at 30 °C for 90 h at 85% relative humidity. Dielectric constants were 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 chamber at 0% relative humidity.

Polymerization. Two typical examples of polycondensation are given below.

Polymer Synthesis by the Two-Step Method. Dianhydride $\mathbf{5_d}$ (0.444 g, 1.00 mmol) was added to a stirred solution of **4** (0.554 g, 1.00 mmol) in NMP (solid content 11% w/v) under N_2 and reacted at 5 °C for 6 h. The inherent viscosity of the poly(amic acid) $\mathbf{6_d}$ in NMP was 1.01 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum exhibited absorptions at 3345 (N—H and O—H str), and 1720, 1650 (C=O str) cm^{-1}, characteristic of the amic acid. The poly(amic acid) solution was then cast onto a glass plate. The poly(amic acid) $\mathbf{6_d}$ was converted to polyimide $\mathbf{7_d}$ by successive heating in vacuum at 80 °C for 3 h, at 200 °C for 8 h, and, then, at 320 °C for 6 h. The inherent viscosity of $\mathbf{7_d}$ was 0.63 dL/g, measured at a concentration of 0.5 g/dL in chloroform at 10 °C. The symmetric and asymmetric carbonyl stretches occur at 1784 and 1733 cm^{-1} in the FTIR spectrum of $\mathbf{7_d}$. In other associated bands are the C—N stretch at 1377 cm^{-1} and the band at 717 cm^{-1} which is deformation of the imide ring to imide carbonyls.

Polymer Synthesis by the One-Step Method. Dianhydride $\mathbf{5_d}$ (0.444 g, 1.00 mmol) was added to a stirred solution of **4** (0.554 g, 1.00 mmol) in *m*-cresol (solid content 5% w/v) containing 2% isoquinoline at 50 °C in N_2 atmosphere. The solution, after being stirred for 3 h, was heated at reflux (200 °C) for 5 h. During this time, the water of imidization was allowed to distill from the reaction mixture. The *m*-cresol was continually replaced to maintain the total volume of the solution. The solution, after cooling to ambient temperature, was diluted with 10 mL of *m*-cresol and then slowly added to 500 mL of vigorously stirred ethanol. The polymer that precipitated was collected, filtered, washed with ethanol and water, and dried under reduced pressure at 150 °C for 8 h. The inherent viscosity of $\mathbf{7_d}$ was 1.05 dL/g, as measured at a concentration of 0.5 g/dL in NMP at 30 °C.

Results and Discussion

Monomer Synthesis. [4,9-Bis[4-(4-aminophenoxy)-phenyl]diamantane (**4**) was synthesized from 4,9-dibromodiamantane (**1**) in three steps as shown in Schemes 1 and 2. According to Scheme 1, **1** reacted with phenol in the presence of iron(III) chloride as a catalyst to generate new **2**. The corresponding bisphenol **2** reacted with *p*-chloronitrobenzene in anhydrous DMAc in the presence of potassium carbonate as an acid acceptor to generate new **3**, which was hydrogenated to generate new monomer **4**. The yield of **3** was high (74.5%) by condensation of *p*-chloronitrobenzene with the dipotassium salt of **2**. Such a high yield can be attributed to the fact that the dipotassium salt of **2** is a good nucleophilic compound owing to the diamantyl group's electrodonating effect. On the basis of the carbon's shielding effect, the positions of chemical shifts for carbons of **4** were readily assigned in Figure 1A, due to the symmetric structure of **4**. The positions of chemical shifts for protons of **4** were also assigned in Figure 1B. The signal at 4.94 ppm is peculiar to the amino group. When **3** was converted into the diamine **4**, the resonances of protons Hg were found to be further high field from 8.17 to 6.55 ppm (see Experimental Section). Also, X-ray diffraction analysis confirmed the structures of **4**, **2**, and **3**. X-ray crystal data for **2** and **3** were acquired from single crystals by slowly crystallizing from individual DMF solutions, respectively. Interestingly, one **2** in association with two DMFs formed a single crystal complex via a hydrogen bond. A single crystal of **4** was also obtained by slowly crystallizing it from a DMAc solution of **4**. **4** and DMAc (molecular ratio = 1:2) subsequently formed a single crystal complex via a hydrogen bond. The structures of all three compounds exhibited molecular symmetry. Figure 2 illustrates X-ray structures of compound **4**. On the other hand, elemental analysis, NMR spectra, and IR spectra confirmed all synthesized new compounds.

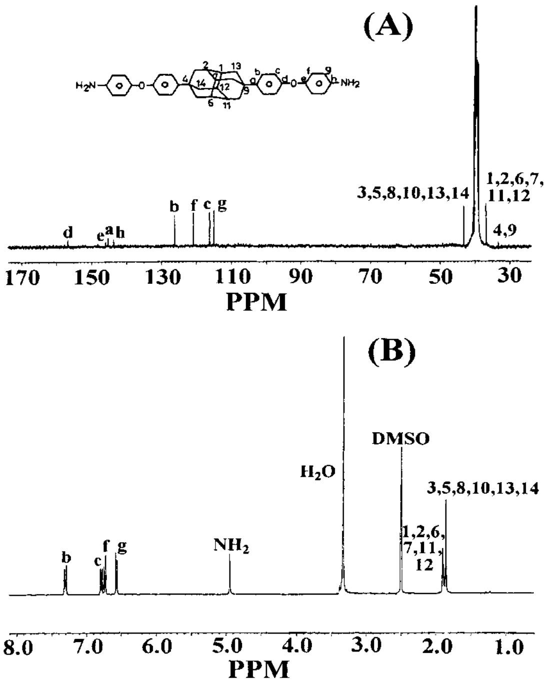


Figure 1. NMR (DMSO-d_6) spectra of **4**: (A) ^{13}C NMR (100 MHz); (B) ^1H NMR (400 MHz).

Synthesis of Polymers. New diamantane-based polyimides were synthesized by a conventional two-step procedure starting from **4** and aromatic tetracarboxylic dianhydrides **5** through the ring-opening polyaddition and subsequent thermal cyclodehydration (Scheme 3). Table 1 summarizes those results. Compound **4** almost did not react with aromatic tetracarboxylic dianhydrides **5** at room temperature (25 °C), likely due to that the rigid and bulky diamantyl element which increases the polymer chain rigidity. The more rigid polymer chain necessitates more activation energy to produce high inherent viscosity. Thus, the ring-opening polycondensation proceeded at 50 °C. Viscosity buildup, however, was noticeably slower than for standard diamines like 4,4′-oxydianiline. The subsequent poly(amic acid)s **6** had high inherent viscosities of 0.75—1.25 dL/g. IR spectroscopy confirmed the poly(amic acid)s **6**. The characteristic absorption bands of the amic acid ap-

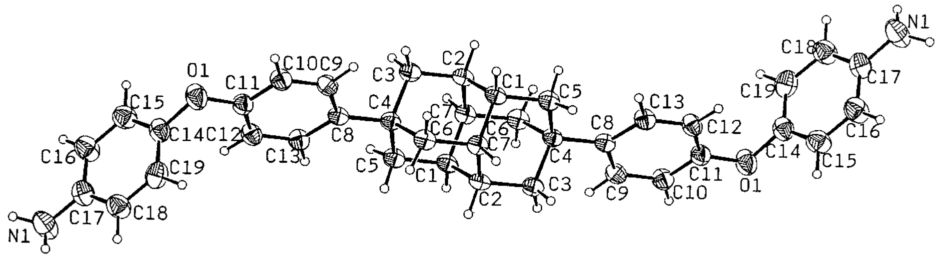


Figure 2. X-ray structure of **4**.

Scheme 3

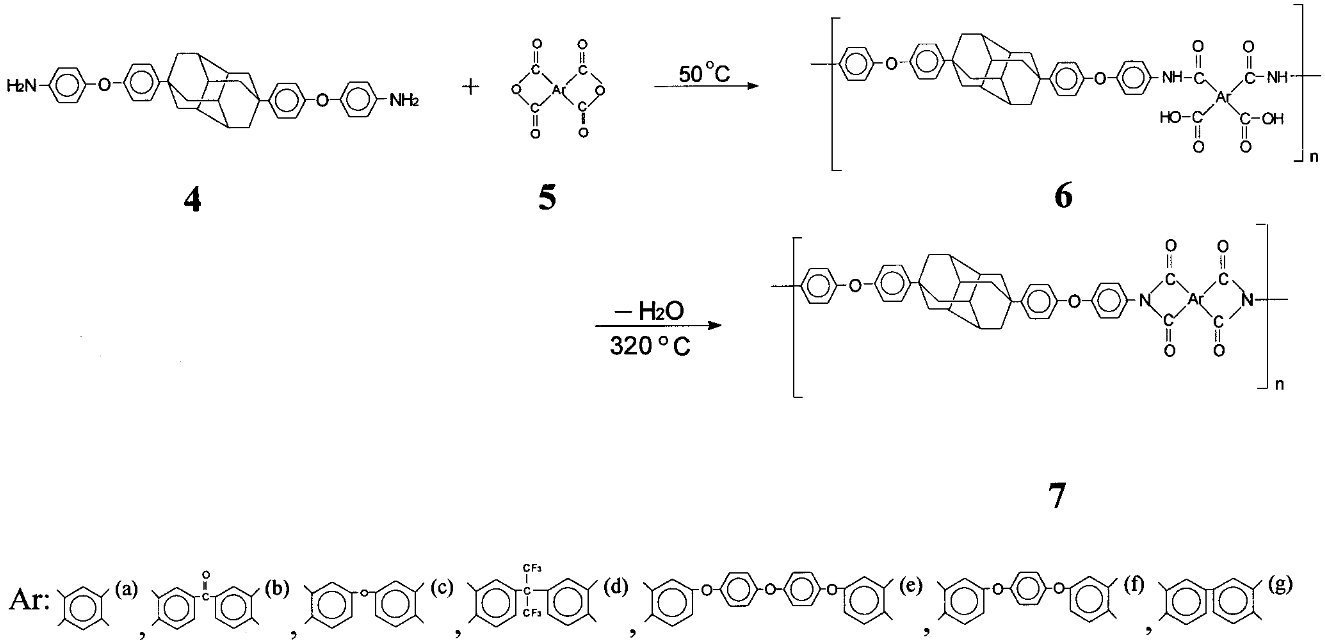


Table 1. Inherent Viscosities and GPC Molecular Weights of Poly(amic acid)s and Soluble Polyimides

	poly(amic acid)s	polyimides		
Dianhydride	η_{inh} (dL/g)[a]	M_n[e] × 10^{-4}	M_w/M_n	η_{inh} (dL/*g*)[a]
5_a	0.91	[f]		
5_b	1.01			
5_c	1.25	6.0	1.5	0.52[b]
5_b	1.01	3.3	1.6	0.63[c]
5_e	1.01	6.2	2.1	0.80[c]
5_f	0.75			0.43[b]
5_g	0.79			
5_d[d]		9.6	1.5	1.05
5_e[d]		8.7	1.4	1.04
5_f[d]		7.1	1.4	0.83

[a] Measured in NMP on 0.5 g/dL at 30 °C. [b] Measured in *o*-chlorophenol on 0.5 g/dL at 30 °C. [c] Measured in chloroform on 0.5 g/dL at 10 °C. [d] Prepared in *m*-cresol containing 2% isoquinoline at 200 °C. [e] By GPC (relative to polystyrene). [f] Could not be measured.

peared near 3350 (N—H and O—H str), 1720 (C=O str, acid), 1650 (C=O str, amide) 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**. The soluble polyimides **7** had inherent viscosities of 0.43—1.05 dL/g. Table 1 also indicates that the inherent viscosities of polyimides **7** prepared by the one-step method exceeded those of polyimides **7** prepared by a two-step method. This finding closely resembles that in the previous literature.[26] According to GPC data, medium and high molecular weights were generally attainable (Table 1). In fact, all M_w/M_{ns} were lower than those of the commercial materials, which may be a merit of the somewhat low reactivity of **4** containing the rigid and bulky diamantyl group. 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, NMR spectra also confirmed the polyimide **7_d**, as shown in Figure 3. In the proton spectrum, m and n were assigned while assuming that the n proton ortho to the C=O had shifted farther downfield. Also, the m proton signal was broadened through interaction with the nearby CF_3 groups and, possibly, by unresolved meta coupling with the k proton. Herein, the ^{13}C NMR spectrum of **7_d** was assigned using a combination of DEPT, 2D $^1H-^{13}C$ COSY, and the results for carbon assignments in compound **3**. In the carbon spectrum, the i and j assignments were made while assuming that the i carbon para to the $C(CF_3)_2(Ph)$ had shifted farther downfield. In addition, splitting of the o carbon absorption was observed due to long-range effects by the CF_3 fluorine. Similarly, the p carbon absorption was split into a quartet by the fluorine.

If we consider that polyimides **7** contain bulky and rigid diamantyl groups, the polymer backbone seems to have an appreciable rigid conformation. Light scattering measurements of **7_d** were taken to estimate the polyimide chain flexibility in a solution. From a Zimm plot, the weight-average molecular weight (M_w) and the *Z*-average root-mean-square radius of gyration (R_g) were determined; and the M_w and R_g values are 150 000 and 101 nm, respectively.

Characterization of Polymers. The polyimide solubilities were tested in various solvents. Table 2

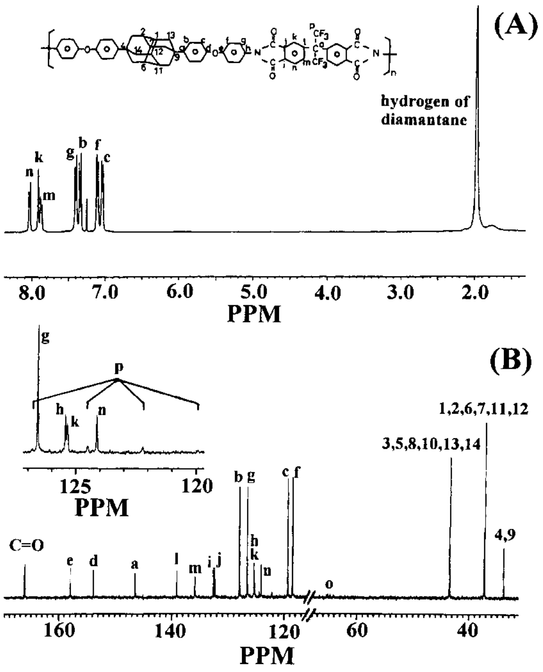


Figure 3. NMR ($CDCl_3$) spectra of polyimide $\mathbf{7_d}$: (A) ^1H NMR (400 MHz); (B) ^{13}C NMR (125 MHz).

Table 2. Solubilities of Polyimide[a]

	polymer							
solvent	$\mathbf{7_a}$	$\mathbf{7_b}$	$\mathbf{7_c}$	$\mathbf{7_d}$	$\mathbf{7_e}$	$\mathbf{7_f}$	$\mathbf{7_g}$	ref[b]
o-chlorophenol	−	−	+	+ −	+ −	+ +	−	+ −
m-cresol	+ −	+ −	+ −	+	+	+	+ −	+ −
chloroform	−	−	+ +	+ +	+ +	+ −	−	−
THF	−	−	−	+	−	−	−	−
NMP	−	−	+	+ −	+ −	−	−	+ −
DMAc	−	−	+ −	+ −	+ −	−	−	+ −

[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. [b] The aromatic polyimide was synthesized from $\mathbf{5_e}$ and 4,4′-oxydianiline in our laboratory.

summarizes those results. Owing to the bulky diamantyl elements and flexible ether segments, polyimides **7** were amorphous and soluble in a number of common organic solvents, e.g., chloroform, *m*-cresol, *o*-chlorophenol, or THF. Even the nonfluorinated polyimides ($\mathbf{7_c}$, $\mathbf{7_e}$, and $\mathbf{7_f}$) were soluble in *o*-chlorophenol, *m*-cresol, NMP, and chloroform. A comparison of the solubility of $\mathbf{7_e}$ with the corresponding polyimide derived from $\mathbf{5_e}$ and 4,4′-oxydianiline shows that polyimide $\mathbf{7_e}$ has better solubility. We believe that, for the polymers considered herein, perhaps the bulky diamantyl groups that prevent spontaneous parallel alignment of the rodlike molecules significantly weaken these forces of attraction. The hexafluoroisopropylidene-containing polyimide $\mathbf{7_d}$ exhibited slightly better solubility than the other soluble polyimides **7**. The polyimide $\mathbf{7_d}$ was soluble in *m*-cresol, THF, and chloroform. However, the polyimides $\mathbf{7_a}$, $\mathbf{7_b}$, and $\mathbf{7_g}$ were insoluble in the test solvent owing to their relatively rigid anhydride moieties.

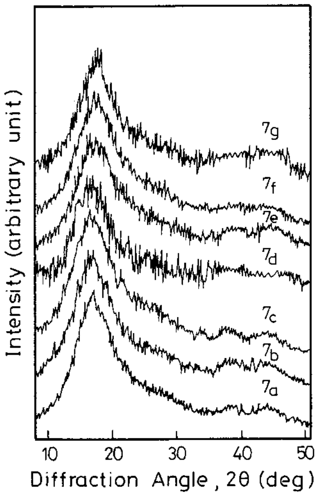


Figure 4. Wide-angle X-ray diffraction curves of polyimides.

Transparent and pale yellow polyimide films **7** were obtained by successively heating the corresponding poly(amic acid)s **6**. All polyimide films **7** were tough. Initially, the polyimide films **7** were structurally characterized by the wide angle X-ray method. As Figure 4 indicates, all polyimides **7** had nearly the same amorphous patterns, with exhibited a broad peak appearing at around 16° (2θ).

Table 3 summarizes the dielectric constants, moisture absorptions, CTEs, and mechanical properties. The mechanical properties were determined via an Instron machine. The mechanical properties of polyimides **7**, in general, were satisfactory. When compared to the polyimide based on the more flexible anhydride, i.e., $\mathbf{5_e}$, the polyimide $\mathbf{7_e}$ gave fairly high values of elongation to break. This higher elongation likely result from the more flexible nature of the backbone due to the presence of the flexible anhydride $\mathbf{5_e}$.

The moisture absorptions of polyimides **7** are extremely small, <0.3% (Table 3), because of the water proofing effect of the fluorine atoms and diamantane elements. The absorbed moisture of polymers heavily influences their dielectric constants.[3] Table 3 also indicates that the dielectric constants of diamantane-based polyimides **7** are low, ranging from 2.58 to 2.74. Even the nonfluorinated polyimides **7** also had low dielectric constants. Such low dielectric constants result from the fact that diamantane is a fully aliphatic hydrocarbon, subsequently leading to low hydrophobicity and polarity. We speculate that this causes a “dilution” effect of the polar imide groups by the diamantyl groups (on a weight basis based on polymer).

The CTEs of polyimides **7** resemble those of flexible polyimides[9] (see Table 3). This similarity is because polyimides **7** have bent ether units and bulky diamantyl groups. These bent units and bulky groups loosen the films’ molecular packing. In addition, producing a polyimide film from polyimide solution generally yields a lower CTE than from the corresponding poly(amic acid).[7] Herein, the polyimide films **7** using for measuring CTE were obtained by casting from the corresponding poly(amic acid). Thus, the CTEs of polyimides **7** were moderate.

Thermal analysis was performed by means of DSC, DMA, and TGA. Table 4 summarizes those results The polyimides **7** did not decompose until 400 °C in air and nitrogen atmosphere. Their temperature at a 5% weight loss ranged from 475 to 517 °C in air and from 483 to 530 °C in N_2 atmosphere. The influences of residual water or solvent and history of thermal annealing were occasionally observed in the initial DSC heating run. Therefore, the first heating of the samples was curtailed at 400 °C. In addition, T_g and other thermal properties were assessed according to the DSC charts of the second heating. The glass transition

Table 3. Physical Properties of Polyimide Films

polymer	strength to break (MPa)	elongation to break (%)	initial modulus (GPa)	CTE (ppm/°C)	% H_2O absorption[a] 85% RH	dielectric constant (dry, 1 kHz)
$\mathbf{7_a}$	55.3	8.1	2.2	67.8	0.133	2.66
$\mathbf{7_b}$	91.7	9.6	2.0	41.6	0.264	2.74
$\mathbf{7_c}$	101.4	14.8	1.9	56.5	0.137	2.69
$\mathbf{7_d}$	86.8	6.1	2.2	57.5	0.122	2.58
$\mathbf{7_e}$	78.2	22.3	1.9	74.9	0.163	2.67
$\mathbf{7_f}$	100.6	12.7	1.9	67.1	0.171	2.65
$\mathbf{7_g}$	89.9	8.5	2.2	72.4	0.149	2.66

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

Table 4. Thermal Properties of Polyimides

polymer	DSC[a]	DMA[b]		dec[c] Temp (°C)	
	T_g (°C)	T_g (°C)	T_β (°C)	in air	in n2
$\mathbf{7_a}$	394	413	150	508	517
$\mathbf{7_b}$	341	337	150	511	512
$\mathbf{7_c}$	319	348	150	495	508
$\mathbf{7_d}$	349	372	150	475	505
$\mathbf{7_e}$	267	296	100	487	483
$\mathbf{7_f}$	292	298	125	489	505
$\mathbf{7_g}$	[d]	366	150	517	530

[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 10 °C/min. [d] Not be found.

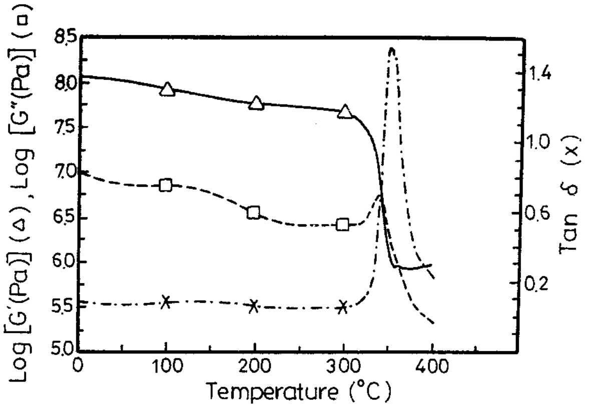


Figure 5. Dynamic mechanical analysis curves for $\mathbf{7_c}$ at a heating rate of 5 °C/min.

temperatures of **7**, except $\mathbf{7_g}$, were found to be 267−394 °C. The rigid and bulky diamantyl ring increases the polymer chain rigidity which, in turn, gives high glass transition temperatures. When the polyimides containing the more flexible ether segments, i.e., $\mathbf{7_c}$, $\mathbf{7_e}$, and $\mathbf{7_f}$, their T_gs were lower. Moreover, the T_gs of polyimides **7** decreases markedly with an increasing content of ether segment. In addition, T_gs of polyimides $\mathbf{7_c}$, $\mathbf{7_e}$, and $\mathbf{7_f}$ lie in a manageable temperature range for processing in the melt.

More detailed information can be obtained from the dynamic mechanical behavior measurements taken of the films as a function of temperature. Herein, films of around 50 μm thickness were studied between 0 and 450 °C. Figure 5 presents the mechanical relaxation spectra of polyimide $\mathbf{7_c}$. Two relaxations appeared at ca. 150 and 348 °C, based on tan δ and G'' peaks. The subglass transition (ca. 150) is a typical β relaxation for standard polyimides. This relaxation is associated with approximately a quarter of one order of magnitude decrease in G'. Moreover, the subglass relaxation is markedly less prominent than the glass relaxation. Such a transition has generally been attributed to the rotation or oscillations of the phenyl groups within the polyimide's diamine moiety.[27,28] In addition, the glass transition at around 348 °C is associated with approximately a mid 1 order of magnitude step decrease in G'.

The mechanical relaxation spectra of polyimides $\mathbf{7_d}$ and $\mathbf{7_g}$ resembles those of $\mathbf{7_c}$. Two relaxation transitions also occurred in both cases on the temperature scale between 0 and 400 °C. The subglass transitions also appeared at around 150 °C. The glass transitions of $\mathbf{7_d}$ and $\mathbf{7_g}$ appeared at 372 and 366 °C, respectively. However, the hump of tan δ for $\mathbf{7_g}$ is obviously smaller in the glass relaxation than that of tan δ for $\mathbf{7_d}$. The small hump is attributed to the fact that the more rigid anhydride $\mathbf{5_g}$ was incorporated into the polyimide $\mathbf{7_g}$. In addition, the mechanical relaxation spectra of polyimides $\mathbf{7_e}$ and $\mathbf{7_f}$ resemble those of the previous discussed polyimides. However, the subglass relaxations of polyimides $\mathbf{7_e}$ and $\mathbf{7_f}$ shifted to lower temperatures of 100 and 125 °C, respectively. Such a shift is possibly attributed to the fact that the ether segments relatively high content were incorporated in $\mathbf{7_e}$ and $\mathbf{7_f}$. Owing to the same reasons, the T_gs of both polyimides ($\mathbf{7_e}$ and $\mathbf{7_f}$) were obviously lower than the T_gs of the other values reported herein for polyimides **7**. Table 4 also summarizes the glass and β relaxation temperatures of polyimides **7**. The glass transition temperatures of polyimides **7** ranged from 296 to 413 °C. The high T_g is attributed to that the rotation of these bonds were hindered by the rigid and bulky diamantyl groups, causing chain stiffness to increase.

Conclusion

Due to the low hydrophobicity and polarity of the rigid and bulky diamantane, the new diamantane-based polyimides exhibit high solubilities, low dielectric constants, low moisture absorptions, and high T_gs. Interestingly, three nonfluorinated polyimides, i.e., $\mathbf{7_c}$, $\mathbf{7_e}$ and $\mathbf{7_f}$, are soluble in *o*-chlorophenol, *m*-cresol, NMP, and chloroform. Transparent pale yellowish polyimide films were obtained. These films display good mechanical properties and good thermal stabilities. Their dielectric constants are extremely low, ranging from 2.58 to 2.74. Two relaxations were observed in these polyimides by means of DMA. The subglass relaxation is a typical β relaxation for standard polyimides. Their glass relaxations occurred at high temperatures by DMA, ranging from 296 to 413 °C. Due to the bent ether units and bulky diamantyl group, the CTEs of these films are moderate. In addition, the polyimides prepared by a one-step method have a higher molecular weight than those prepared by a two-step method. Due to good physical properties of polyimides reported herein, particularly extremely low dielectric constants, these materials are highly promising for electronic applications such as interlayer dielectrics.

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