

High Subglass Transition Temperatures and Low Dielectric Constants of Polyimides Derived from 4,9-Bis(4-aminophenyl)diamantane

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This work synthesizes new diamantane-based polyimides by reacting 4,9-bis(4-aminophenyl)diamantane (**4**) with various aromatic tetracarboxylic dianhydrides. Poly(amic acid)s have high inherent viscosities of 0.74–1.36 dL/g. The polyimide **7a** can be soluble in *o*-chlorophenol, chloroform, and THF. Their cast films have a tensile strength at break up to 127 MPa, elongation to break up to 4.8%, and an initial modulus up to 2.3 GPa. These films have low dielectric constants ranging from 2.53 to 2.72, in addition to low moisture absorptions less than 0.33%. Dynamic mechanical analysis (DMA) reveals diamantane-based polyimides to have three relaxations over room temperature. The low-temperature subglass relaxations, ranging from 125 to 195 °C, are typical β relaxations for standard polyimides. Another high-temperature β_1 subglass relaxation occurs at a substantially high temperature of approximately 300 °C. The characteristic of β_1 relaxation is associated with a step decrease in G' and small transition peaks in $\tan \delta$ and G'' . Their glass relaxations occur at extremely high temperature exceeding 500 °C. Their temperatures at a 5% weight loss ranges from 491 to 536 °C in air and from 518 to 566 °C in N₂ atmosphere.

Introduction

High-performance polymers are used in applications demanding at elevated temperature while maintaining their structural integrity and an excellent combination of chemical, physical, and mechanical properties. Polyimides are certainly one of the most successful classes of high-temperature polymers, having found extensive use in the aviation, automotive, and electronic industries. However, polyimides encounter processing difficulties due to their infusibilities and poor solubilities in organic solvents. The reasons for processing difficulty are a strong interchain force, inherent macromolecular rigidity, or semicrystallinity. Many studies have attempted to enhance their processabilities and solubilities by either introducing bulky groups or flexible chains into the polymer backbones or attaching bulky side groups.^{1–7} In a similar manner, noncoplanar diamines and dianhydrides are quite effective in the improving the polyimide's solubility.^{1,6,8}

Although diamantane has been investigated for many years, only a few examples of the polymers based on

diamantane are known.^{9–17} 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.⁹ In that work colorless diamantane-based polybenzazoles were prepared via the established polyphosphoric acid polycondensation technique.¹⁰ In addition, polycules based on diamantane have found specific applications in building dendritic materials.¹¹ 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.^{12–16} Regarding the incorporation of diamantane into the polyimide, the only example of the polyimide has been reported by us.¹⁷ However, polyimide films based on diamantane have not been successfully prepared.¹⁷ Thus, the physical properties of diamantane-based polyimide (except for thermal stability) have not been reported as well.

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This work concentrates primarily on synthesizing new polyimides having a low moisture absorption and high glass transition temperature (T_g), suggesting promise as a high-temperature material for avionic applications. Herein, the successfully synthesized new polyimides involving 4,9-bis(4-aminophenyl)diamantane (**4**) by the polycondensation with aromatic tetracarboxylic dianhydrides **5**. The dielectric constants, moisture absorptions, coefficients of thermal expansion (CTE), solubilities, dynamic mechanical properties, and thermal properties of the polyimides are investigated as well. In addition, we investigated the mechanical relaxation behaviors in rigid polyimides containing **4** in order to better understand the role of polyimide backbones on the occurrence of high subglass relaxation.

Experimental Section

Materials. Pyromellitic dianhydride (**5_a**), 4,4'-carbonyldiphthalic anhydride (**5_b**), 4,4'-oxydiphthalic anhydride (**5_c**), 4,4'-hexafluoroisopropylidenediphthalic anhydride (**5_d**), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**5_e**) 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, 4,9-dibromodiamantane (**1**) was synthesized from norbornadiene in four steps.¹⁵

Herein, three steps were employed to synthesize 1,4-bis-(3,4-dicarboxyphenoxy)benzene dianhydride (**5_f**) and bis[4-(3,4-dicarboxyphenoxy)phenyl] ether dianhydride (**5_g**) by previous methods^{5,18} from hydroquinone and 4,4'-dihydroxydiphenyl ether, respectively. The corresponding bisphenols reacted with 4-nitrophthalodinitrile in dimethyl sulfoxide anhydride 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.

1,4-Bis(3,4-dicarboxyphenoxy)benzene Dianhydride (5_f): mp 263–265 °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: $\text{C}_{22}\text{H}_{10}\text{O}_8$, colorless crystal, 0.40 \times 0.50 \times 0.50 mm, monoclinic $P_{21/n}$ with $a = 6.001$ (3), $b = 10.091$ (3), $c = 14.030$ (5) Å, $\beta = 92.34^\circ$ (3) with $D_c = 1.574$ g cm^{-3} for $Z = 2$, $V = 848.9$ (6) Å³, $T = 298$ K, $\lambda = 0.7107$ Å, $\mu = 1.142$ cm^{-1} , $F(000) = 412$, $R_w = 0.032$ for 1227 observed reflections, intensity variation <1%.

Bis[4-(3,4-dicarboxyphenoxy)phenyl]ether Dianhydride (5_g): mp 238–240 °C; IR (KBr) 1849, 1772, 1612, 1475 cm^{-1} ; MS (EI) m/z 494 (M^+ , 100); ^1H NMR (400 MHz, DMSO- d_6) δ 7.09–7.20 (m, 12H, ArH), 7.76 (d, $J = 8.28$, 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), 159.71 (s, Ar), 167.39 (C=O), 168.50 (C=O). Crystal data: $\text{C}_{28}\text{H}_{14}\text{O}_9$, colorless crystal, 0.20 \times 0.20 \times 0.25 mm, triclinic $P\bar{1}$ with $a = 8.0198$ (16), $b = 14.825$ (7), $c = 20.016$ (9) Å, $\alpha = 109.69^\circ$ (3), $\beta = 91.79^\circ$ (3), $\gamma = 94.66^\circ$ (3) with $D_c = 1.473$ g cm^{-3} for $Z = 4$, $V = 2228.8$ (14) Å³, $T = 298$ K, $\lambda = 1.5418$ Å, $\mu = 8.979$ cm^{-1} , $F(000) = 1020$, $R_w = 0.091$ for 3235 observed reflections, intensity variation <3%.

Synthesis of 4,9-Diphenyldiamantane (2) from 1. A 150 mL, three-necked, round-bottomed flask was charged with **1** (3.00 g, 8.68 mmol), 60 mL of benzene, and iron(III) chloride (0.500 g, 3.08 mmol). The mixture was heated to reflux for 12 h. The mixture was allowed to cool to room temperature. Next, the precipitate was filtered out, and the filtrate was washed with distilled water. The filtrate was then dried under

reduced pressure. The crude product was crystallized from toluene to obtain **2** (1.54 g, 52.2%): mp 278–280 °C; IR (KBr) 3013, 2888, 2867, 1597, 1491 cm^{-1} ; MS (EI) m/z 340 (M^+ , 100); ^1H NMR (300 MHz, CDCl_3) δ 1.97 (brs, 18H, hydrogen of diamantane), 7.18–7.21 (t, 2H, ArH), 7.30–7.42 (m, 8H, ArH); ^{13}C NMR (75 MHz, CDCl_3) δ 34.23 (C-4, 9), 37.51 (C-1, 2, 6, 7, 11, 12), 43.46 (C-3, 5, 8, 10, 13, 14), 125.08 (d, Ar), 125.59 (d, Ar), 128.13 (d, Ar), 150.50 (s, Ar). Anal. Calcd for $\text{C}_{26}\text{H}_{28}$: C, 91.76; H, 8.24. Found: C, 91.65; H, 8.16. Crystal data: $\text{C}_{26}\text{H}_{28}$, colorless crystal, 0.15 \times 0.40 \times 0.40 mm, monoclinic $P_{21/n}$ with $a = 6.4218$ (20), $b = 19.619$ (4), $c = 7.9656$ (20) Å, $\beta = 113.452^\circ$ (20) with $D_c = 1.228$ g cm^{-3} for $Z = 2$, $V = 920.7$ (4) Å³, $T = 298$ K, $\lambda = 1.5418$ Å, $\mu = 4.793$ cm^{-1} , $F(000) = 369$, intensity variation <3%.

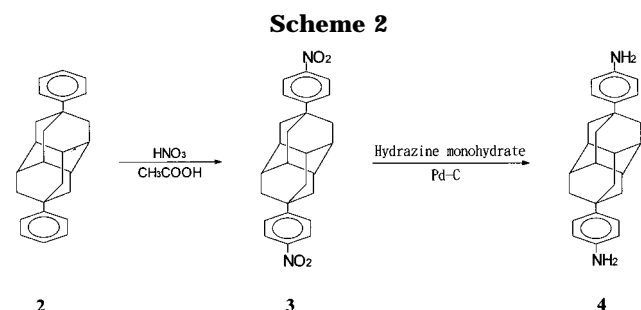
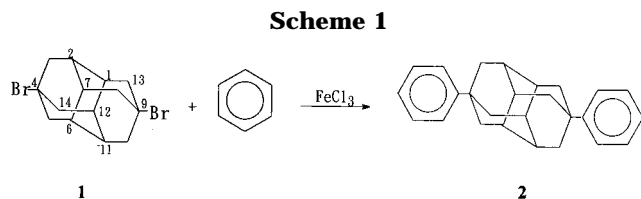
Synthesis of 4,9-Bis(4-nitrophenyl)diamantane (3). The procedure of Chapman et al.¹⁹ to synthesize **3** was modified as follows: **2** (2.00 g, 5.88 mmol) was suspended in 40 mL of glacial acetic acid, and 25 mL of fuming nitric acid was added dropwise. The resulting yellow solution was stirred for 5 days and then poured onto ice. The precipitated solid was collected by filtration yielding 2.05 g (81.1%) of **3**: mp 318–320 °C; IR (KBr) 2888, 2867, 1591, 1512, 1341, 751 cm^{-1} ; MS (EI) m/z 430 (M^+ , 100); ^1H NMR (300 MHz, CDCl_3) δ 1.98–2.01 (d, 18H, hydrogen of diamantane), 7.53 (d, $J = 9.05$, 4H, ArH), 8.16 (d, $J = 9.05$, 4H, ArH); ^{13}C NMR (75 MHz, CDCl_3) δ 35.04 (C-4, 9), 36.92 (C-1, 2, 6, 7, 11, 12), 42.97 (C-3, 5, 8, 10, 13, 14), 123.46 (d, Ar), 126.09 (d, Ar), 146.06 (s, Ar), 157.81 (s, Ar). Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4$: C, 72.56; H, 6.05; N, 6.51. Found: C, 72.38; H, 5.95; N, 6.43.

Synthesis of 4. A 150 mL, three-necked, round-bottomed flask was charged with **3** (1.00 g, 2.33 mmol), 10 mL of hydrazine monohydrate, 60 mL of ethanol and 0.02 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 *N*-dimethylacetamide (DMAc) to afford 0.751 g (87.1%) of white crystals (**4**): mp 316–318 °C; IR (KBr) 3453, 3325, 3057, 2890, 2867, 1623, 1513 cm^{-1} ; MS (EI) m/z 370 (M^+ , 100); ^1H NMR (400 MHz, CDCl_3) δ 1.90 (d, 18H, hydrogen of diamantane), 3.55 (br s, 4H, NH₂), 6.66 (d, $J = 8.23$, 4H, ArH), 7.18 (d, $J = 8.64$, 4H, ArH); ^{13}C NMR (100 MHz, CDCl_3) δ 33.42 (C-4, 9), 37.58 (C-1, 2, 6, 7, 11, 12), 43.70 (C-3, 5, 8, 10, 13, 14), 115.03 (d, Ar), 125.87 (d, Ar), 141.02 (s, Ar), 143.94 (s, Ar). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{N}_2$: C, 84.32; H, 8.11; N, 5.05. Found: C, 84.15; H, 8.06; N, 4.96.

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/sample was made. MS spectra were obtained by using a JEOL JMS-D300 mass spectrometer. ^1H 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 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. 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

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a heating rate of 20 °C/min. The thermogravimetric analysis (TG) was determined under a nitrogen flow of 50 cm³/min and a heating rate of 10 °C/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 K α 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. Next, 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, cool). 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 by Two-Step Method. Dianhydride **5_d** (0.444 g, 1.00 mmol) was added to a stirred solution of **4** (0.370 g, 1.00 mmol) in NMP (solid content 10% w/v) under N₂ at an ambient temperature for 6 h. The inherent viscosity of the poly(amic acid) **6_d** in NMP was 0.74 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum exhibited absorptions of **6_d** at 3345 (N-H and O-H str), and 1720, 1650 (C=O str) cm⁻¹, i.e., characteristic of the amic acid. The poly(amic acid) solution was then cast onto a glass plate. The poly(amic acid) **6_d** was converted to polyimide **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 of **7_d** was 0.49 dL/g, measured at a concentration of 0.5 g/dL in 1,1,2,2-tetrachloroethane at 30 °C. The symmetric and asymmetric carbonyl stretches occur at 1780 and 1720 cm⁻¹ in the FTIR spectrum of **7_d**. In other associated bands appear the C-N stretch at 1367 cm⁻¹ and the band at 712 cm⁻¹, i.e., the deformation of the imide ring to imide carbonyls. The other polyimides were prepared in a similar manner according to **4** and aromatic tetracarboxylic dianhydrides **5**.

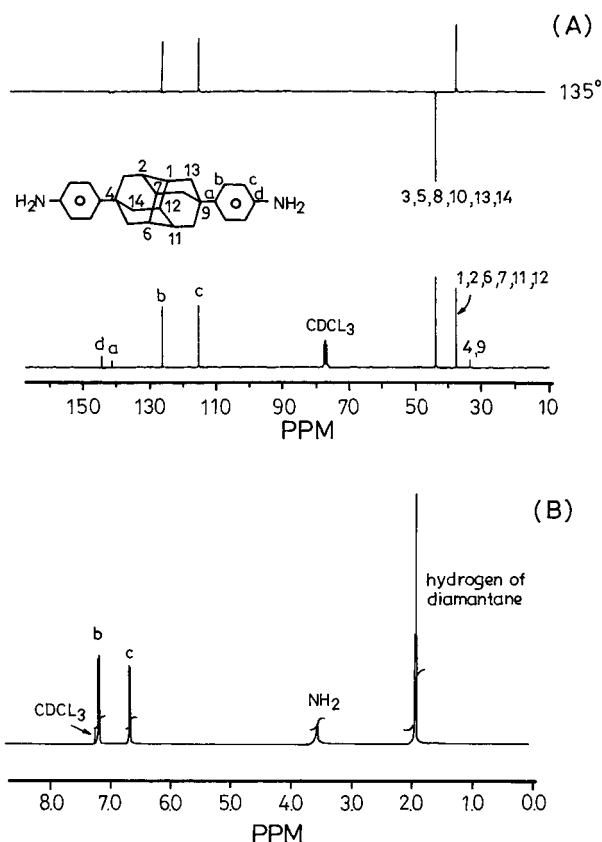


Figure 1. NMR (CDCl₃) spectra of **4**. (A) ¹³C 135° DEPT and ¹³C NMR (100 MHz); (B) ¹H NMR (400 MHz).

Results and Discussion

Monomer Synthesis. Compound **4** was synthesized from **1** in three steps as shown in Schemes 1 and 2. **1** reacted with benzene in the presence of iron(III) chloride as a catalyst to generate **2** as shown in Scheme 1. Also, Chapman et al. have effectively synthesized **2** from diamantane in the presence of aluminum chloride and *tert*-butyl bromide.¹⁹ **2** reacted with fuming nitric acid in the presence of glacial acetic acid to generate **3** in high yield. According to our results, the aromatic region of **3** displayed evidence of overnitration when in the presence of a higher concentration of fuming nitric acid. **3** was then hydrogenated to obtain compound **4**. On the basis of the shielding effect of carbon and proton, the positions of chemical shifts for carbons and protons of compound **4** was assigned in Figure 1. The signal at 3.55 ppm is typical of the amino group. When the **3** was converted into the diamine **4**, the resonances of protons Hc was found further upfield from 8.16 to 6.66 ppm (see Experimental Section). X-ray diffraction detected the structure of **2**. X-ray crystal data for **2** were acquired from a single crystal, as obtained by slowly crystallizing from a toluene solution of it. In addition, the elemental analysis data, the NMR spectra and the IR spectra, verified all of the synthesized compounds.

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, 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

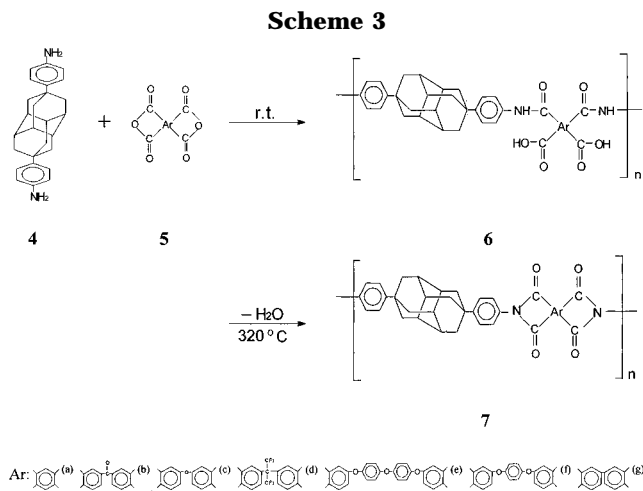


Table 1. Inherent Viscosities of Poly(amic acids) and Soluble Polyimides

dianhydride	$\eta_{inh}(\text{dL/g})$	
	poly(amic acids)	polyimides
5 _a	1.36	<i>c</i>
5 _b	0.81	
5 _c	1.02	
5 _d	0.74	0.49 ^b
5 _e	0.95	
5 _f	1.02	
5 _g	1.29	

^a Measured in NMP on 0.5 g/dL at 30 °C. ^b Measured in 1,1,2,2-tetrachloroethane on 0.5 g/dL at 30 °C. ^c Could not be measured.

between 0.74 and 1.36 dL/g. IR spectroscopy confirmed the poly(amic acids) **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 acids) **6** to 320 °C in a vacuum. The soluble polyimide **7_a** had an inherent viscosity of 0.49 dL/g. 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 2 reveals, NMR spectra confirmed the presence of polyimide **7_a**. In the proton, *i* and *j* were assigned while assuming that the *j* proton ortho to the C=O had shifted farther downfield. Also, the *i* proton signal was broadened through interaction with the nearby CF₃ groups and, possibly, by unresolved meta coupling with the *g* proton. Herein, the ¹³C NMR spectrum of **7_a** was assigned using a combination of DEPT, 2D ¹H–¹³C COSY, and the results for carbon assignments in compound **3**. In the carbon, the *e* and *f* assignments were made while assuming that the *e* carbon para to the C(CF₃)₂(Ph) had shifted farther downfield. Splitting of the *k* carbon absorption was observed due to long-range effects by the CF₃ fluorine. Similarly, the *l* carbon absorption was split into the quartet by the fluorine.

Characterization of Polymers. The solubilities of these polyimides were tested in various solvents. Table 2 summarizes those results. The hexafluoroisopropylidene-containing polyimide **7_a** exhibited an excellent solubility toward test solvents. The polyimide **7_a** was soluble in *o*-chlorophenol, chloroform, and THF. How-

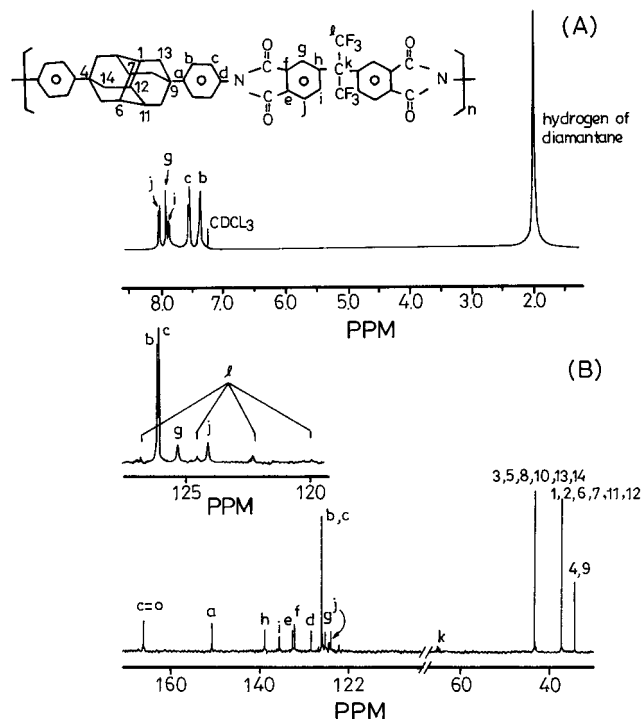


Figure 2. NMR (CDCl₃) spectra of polyimide **7_a**. (A) ¹H NMR (400 MHz); ¹³C NMR (125 MHz).

Table 2. Solubilities of Polyimide^a

solvent	polymer						
	7 _a	7 _b	7 _c	7 _d	7 _e	7 _f	7 _g
<i>o</i> -chlorophenol	–	–	–	+	–	–	–
<i>m</i> -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.

ever, the other polyimides **7**, except **7_a**, were insoluble in the test solvents due to the presence of extremely rigid 4,9-diphenyldiamantyl elements. Transparency and pale yellowish colors of all polyimide films **7** were obtained by successively heating the corresponding poly(amic acids) **6**. Unexpectedly, during the imidization process, the polyimide film **7_e** cracked in a vacuum. Notably, the brittle behavior of **7_e** is possibly attributed to the fact that the polyimide **7_e** has a greater tendency to form a crystal than the other polyimides **7** (in Figure 3). Initially, polyimide films **7** were structurally characterized by X-ray methods. Figure 3 indicates that all polyimides **7** had nearly the same amorphous patterns and contained a broad peaks appearing (2 θ) at around 18°. However, the polyimide **7_e** had an obviously higher orientation than the other polyimides **7**. Additional work is required to characterize the structure more accurately.

Table 3 summarizes the dielectric constants, moisture absorptions, CTEs, and mechanical properties of polyimides **7**. The mechanical properties were determined via an instron machine. All polyimides **7**, except **7_a** and **7_e**, exhibited high tensile strengths of 84.1–127 MPa.

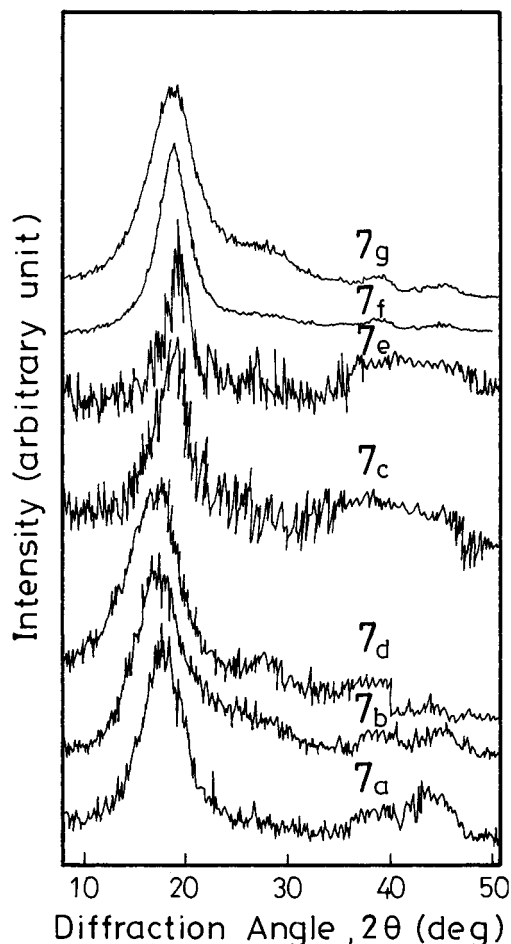


Figure 3. Wide-angle X-ray diffraction curves of polyimides. All polyimides **7** were fractured in a brittle manner under the tensile test. Thus, the elongation to break values of polyimides **7** were low. This phenomenon is attributed to the fact that the polyimides **7** contain extremely rigid and bulky 4,9-diphenyldiamantyl elements. In addition, the polyimide **7a** has a relatively low tensile strength primarily because **7a** has a low inherent viscosity.

The moisture absorptions of polyimides **7** are very small, i.e., less than 0.33%, because of the water proofing effect of the diamantane elements. The polymer's absorbed moisture heavily influences its dielectric constant. Table 3 also indicates that the dielectric constants of diamantane-based polyimides **7** are quite low: ranging from 2.53 to 2.72. Even the nonfluorinated polyimides **7** also had low dielectric constants. A comparison of the moisture absorption and dielectric constant of polyimides **7** with the corresponding polyimide derived from **5e** and 4,4'-oxydianiline shows that polyimides **7** have lower moisture absorptions and dielectric constants. Such low dielectric constants are due to the fact that diamantane are the fully aliphatic hydrocarbon, subsequently leading to low hydrophobicity and polarity. We speculate that this event is due to the "dilution" effect of the polar imide groups by the diamantyl groups (on a weight basis based on polymer).

Table 3 indicates that the CTEs of polyimides **7** resemble those of flexible polyimides.²⁰ Such a resem-

blance is due to the fact that the main chains of polyimides **7** have rather bulky 4,9-diphenyldiamantyl elements. These bulky groups loosen the molecular packing in the films. In addition, producing a polyimide film from polyimide solution generally leads to lower CTE than from the corresponding poly(amic acid).⁷ The polyimide films **7** using for measuring CTE were obtained by casting from the corresponding poly(amic acid). Thus, the CTEs of polyimides **7** are moderate.

Thermal analysis was performed according to DSC, DMA, and TGA. Table 4 summarizes those results. The polyimides **7** did not decompose until 400 °C in air and nitrogen atmosphere. Their temperatures at a 5% weight loss ranged from 491 to 536 °C in air and from 518 to 566 °C in N₂ atmosphere. Isothermal gravimetric analysis is a more significant measure of the thermal stability of a polymer. Polyimide **7a** was run in isothermal experiment at 200 °C, and it did not decompose until 14 h in air and nitrogen 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. All polyimides **7** did not show typical glass transitions. This absence is attributed to that the bulky and rigid diphenyldiamantyl element increases the polymers **7** chains' rigidity which, subsequently, produce high glass transition temperatures of **7** exceeding 500 °C.

More detailed information can be obtained from the dynamic mechanical behavior measurements taken of the films as a function of temperature. Films of about 50 μm thickness were examined on the temperature scale between 0 and 500 °C. Figure 4 present the mechanical relaxation spectra of polyimide **7c**. On the basis of tan δ and *G''* peaks, three relaxations were observed at ca. 146, 300, and ~500 °C. The low-temperature transition named β₂ (ca. 146 °C) is a typical β relaxation for standard polyimides. This relaxation is associated with approximately a quarter of 1 order of magnitude step decrease in *G'*. Such a transition has generally been accounted for rotation or oscillations of the phenyl groups within the polyimide's diamine moiety.^{21,22} The second transition named β₁, at 300 °C, is associated with a step decrease in *G'*. Small transition peaks in tan δ and *G''* also appeared during β₁ transition. The reason for this transition still remains uncertain. Coburn et al. also reported that high subglass relaxation at 300 °C were observed in the rigid rodlike polyimides based on a variety of 2,2'-disubstituted benzidines and rigid dianhydrides.²³ From above results, we can infer that this high subglass relaxation (approximately 300 °C) seems to occur in the extremely rigid polyimide. With an increasing temperature, *G'* decreases steadily from 325 to 450 °C, without showing either abrupt changes or a marked relaxation. The temperature of the last relaxation from a glass state to a rubbery plateau cannot be determined precisely from the mechanical relaxation spectra currently available. This inability is attributed to that the *T_g* of **7c** exceeds

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Table 3. Physical Properties of Polyimide Films

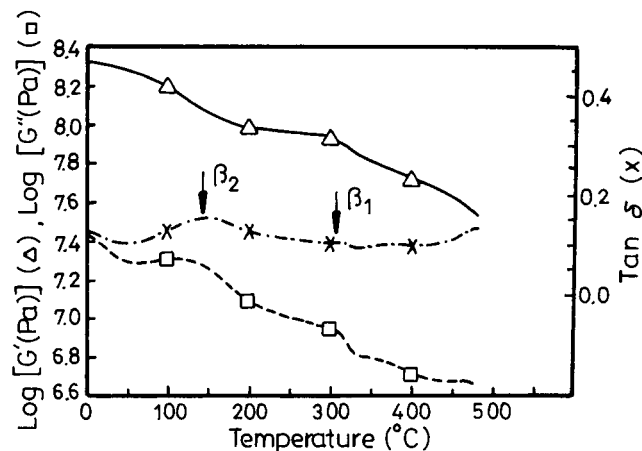
polymer	strength to break (MPa)	elongation to break (%)	initial modulus (GPa)	CTE (ppm/°C)	% H ₂ O absorption ^a 85% RH	dielectric constant (dry, 1 kHz)
7 _a	87.0	3.0	2.3	97	0.243	2.64
7 _b	123.5	4.8	2.2	92	0.324	2.72
7 _c	84.1	4.5	2.2	69	0.284	2.68
7 _d	26.9	0.74	2.3	61	0.168	2.53
7 _f	73.9	3.0	2.1	76	0.275	2.65
7 _g	127	4.2	2.3	86	0.268	2.64
ref ^b	90.5	12.5	2.0	c	0.406	3.25

^aMoisture absorption of polyimide films were measured at 30 °C for 90 h. ^bA poly(ether imide) was synthesized from 4,4'-oxydianiline and 5_a in our laboratory. The inherent viscosity of its poly(amic acid) precursor was 0.85 dL/g. ^c Not measured.

Table 4. Thermal Properties of Polyimides

polymer	DMA ^a			decomposition ^b temp (°C)	
	T _g (°C)	T _{β1} (°C)	T _{β2} (°C)	in air	in N ₂
7 _a	>500	300	150	515	548
7 _b	>500	300	175	520	536
7 _c	>500	300	146	508	537
7 _d	>500	300	171	491	518
7 _f	>500	320	125	498	542
7 _g	>500	300	195	536	566

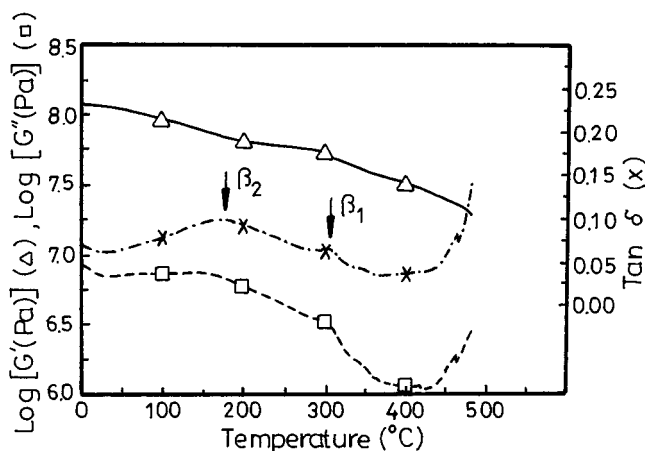
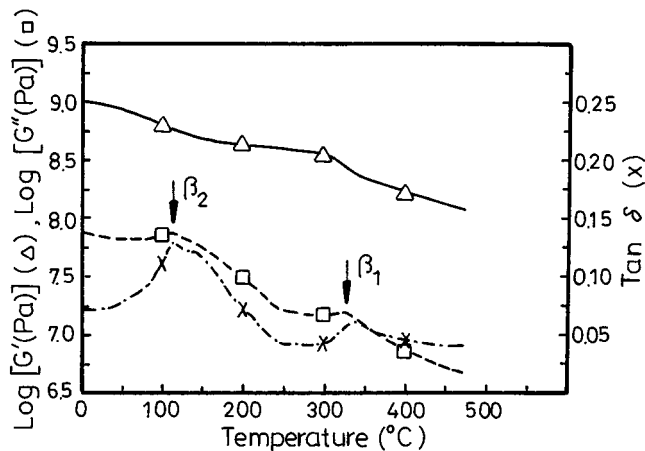
^a The glass and subglass transitions measured by DMA using shear mode at a heating rate of 5 °C/min. ^b Temperature at which 5% weight loss recorded by TG at a heating rate of 10 °C/min.

**Figure 4.** Dynamic mechanical analysis curves for 7_c at a heating rate of 5 °C/min.

500 °C due to that the extremely rigid and bulky 4,9-diphenyldiamantyl elements are incorporated into polyimide 7_c backbone.

Figures 5–7 depict the mechanical relaxation spectra of polyimides 7_d, 7_f, and 7_g. In all three polyimides, their relaxation spectra resemble those of 7_c. Three relaxation transitions also occurred in all three polyimides on the temperature scale between 0 and 500 °C. The low-temperature subglass relaxation, termed β₂, did not occur at a same temperature in all three polyimides. The second subglass transition around 300 °C, termed β₁, is also associated with a step decrease in *G'* as well as small transition peaks in tan δ and *G''*. High *T_g*s exceeding 500 °C also appeared in all three polyimides.

The mechanical relaxation spectra of polyimides 7_a and 7_b also resemble those of 7_c. Table 4 summarizes the relaxation temperatures of polyimides 7. According to this table, the low-temperature β₂ subglass relaxation of polyimides 7 did not occur at the same temperature. The higher β₂ relaxation temperature appeared when the polyimides 7, except 7_a, were incorporated with the more rigid dianhydrides 5. In addition, the β₁ transi-

**Figure 5.** Dynamic mechanical analysis curves for 7_d at a heating rate of 5 °C/min.**Figure 6.** Dynamic mechanical analysis curves for 7_f at a heating rate of 5 °C/min.

tions (approximately 300 °C) occur at a markedly higher temperature than typically observed in most other polyimides. This relaxation's temperature resembles high subglass relaxations in the extremely rigid polyimides based on a variety of 2,2'-disubstituted benzidines and rigid dianhydride.²³ From both cases, the unusually high subglass relaxation seems to occur in the polyimides with the extremely rigid backbones. Moreover, the β₁ relaxations of the polyimides 7, except 7_f, occur at the same temperatures. Coburn et al. also reported that the subglass temperature and magnitude to change in dianhydride is insensitive.²³ Table 4 also indicates that the glass transition temperatures of polyimides 7 exceeded 500 °C. Such extremely high *T_g*s are attributed to that the rotation of these bonds are hindered by the rigid and bulky 4,9-diphenyldiamantyl

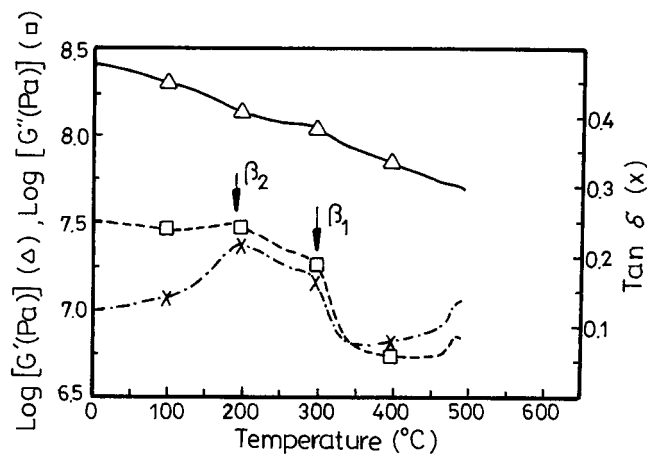


Figure 7. Dynamic mechanical analysis curves for 7_g at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$.

elements, ultimately causing an increasing chain stiffness of polyimides **7**.

Conclusion

This work has synthesized diamantane-based polyimides by a conventional two-step procedure starting from **4** and aromatic tetracarboxylic dianhydrides **5** through the ring-opening polyaddition, subsequently yielding poly(amic acid)s **6** with high inherent viscosities between 0.74 and 1.36 dL/g, and subsequent thermal

cyclodehydration. The polyimide **7_d** can be soluble in *o*-chlorophenol, chloroform, and THF. Transparency and pale yellowish color of polyimide films were obtained from the corresponding poly(amic acid)s. All polyimides **7**, except **7_d** and **7_e**, exhibit high tensile strengths of 84.1–127 MPa. Their dielectric constants are markedly low, ranging from 2.53 to 2.72. Three transitions occur in these polyimides by means of DMA. The low-temperature β_2 subglass relaxation is a typical β relaxation for standard polyimides. Another relatively high-temperature β_1 subglass relaxation occurs at a markedly higher temperature of approximately $300\text{ }^\circ\text{C}$ than typically observed in most other polyimides. The characteristic of β_1 relaxation is associated with step decrease in G' and small transition peaks appearing in $\tan \delta$ and G'' . Their glass transitions occur at extremely high temperatures exceeding $500\text{ }^\circ\text{C}$. Their temperatures at a 5% weight loss rang from 491 to $536\text{ }^\circ\text{C}$ in air and from 518 to $566\text{ }^\circ\text{C}$ in N_2 atmosphere. The CTEs of these films are moderate owing to the bulky 4,9-diphenyldiamantyl elements loosen the molecular packing in the films.

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