

Synthesis and characterization of new polyimides derived from 4,9-diaminodiamantane

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(Received 20 June 1997; revised 27 September 1997; accepted 19 November 1997)

This work reports the synthesis of new diamantane-based polyimides by the reaction of 4,9-diaminodiamantane (**I**) with various aromatic tetracarboxylic dianhydrides. The polyimide film **IV_a** has a low dielectric constant of 2.7 and a low moisture absorption of 0.205%. The number-average molecular weight (\bar{M}_n) of polyimide **IV_a** is 37 kg/mol. Dynamic mechanical analysis (DMA) reveals that polyimide **IV_a** has only a glass transition at 308°C on the temperature scale between 0 and 350°C. The glass transition temperatures of the polyimides were also found to be 295–325°C by means of a differential scanning calorimetry (d.s.c.). The polyimide **IV_a** had tensile strength at breakage of 68.4 MPa and initial modulus of 2.0 GPa. The temperatures of polyimides at a 5% weight loss ranged from 432 to 488°C in air and from 489 to 530°C in N₂ atmosphere. The polyimide **IV_a** is soluble *m*-cresol. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyimides; diamantane; dielectric constant)

INTRODUCTION

Thermally stable polymers have received extensive interest over the past decade due to increasing demands for high-temperature polymers as replacements for metals or ceramics in automotive, aerospace, and microelectronic industries. Polyimides are certainly one of the most successful class of high-temperature polymers, and have found extensive application in the aviation, automotive, and electronic industries. However, they are frequently insoluble and unable to melt below their decomposition temperatures. Therefore, processing in melt or solution is generally impossible. Many investigators have attempted to enhance their processability and solubility by introducing either 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 improving the solubility of polyimides^{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, 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 helium⁹. In that work colorless diamantane-based polybenzazoles were prepared via the established polyphosphoric acid polycondensation technique¹⁰. In addition, polycules based on diamantane have found specific applications in building dendritic materials¹¹. Our recent work indicated that incorporating diamantane units 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, only a example of the polyimide has been reported by us¹⁷. However, polyimide films based on diamantane have not been successfully prepared¹⁷. Thus, the physical properties of diamantane-based polyimide (except for thermal stability) have not been reported as well.

Blaney *et al.* have reported the synthesis of 4,9-diaminodiamantane¹⁸. A Ritter reaction of 4,9-dihydroxydiamantane and acetonitrile in sulphuric acid gave the diamide, which could be hydrolysed to 4,9-diaminodiamantane using hydrochloric acid in methanol. However, the formation of 4,9-diaminodiamantane was only confirmed by the melting point. A different method for synthesis of 4,9-diaminodiamantane (**I**) in this work: the reaction of 4,9-dibromodiamantane and acetonitrile in sulphuric acid gave the diamide and the diamide was hydrolysed to 4,9-diaminodiamantane using sodium hydroxide in diethylene glycol. Moreover, 4,9-diacetamidodiamantane and diamine **I** were completely confirmed by n.m.r., i.r., elemental analysis, and X-ray diffraction analysis.

Owing to the low hydrophilicity and polarity of diamantane, the polymers based on diamantane offer advantages over the fully aromatic materials in long term thermal and environmental stability, by possessing a low dielectric constant and having a low moisture absorption. Therefore, synthesizing and characterizing polyimides, as well as incorporating diamantane nucleus into the polyimide backbones are worthwhile proceeding. This article describes the preparation and characterization of polyimides derived from 4,9-diaminodiamantane (**I**) and various aromatic tetracarboxylic dianhydrides, as shown in *Scheme 2*. In addition, the dielectric constants, moisture absorptions, coefficients of thermal expansion (CTE),

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solubility, dynamic mechanical properties, and thermal properties of the polyimides were also investigated.

EXPERIMENTAL

Materials

4,4'-Oxydiphthalic anhydride (**II_c**), 4,4'-carbonyldiphthalic anhydride (**II_d**) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**II_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 was synthesized from norbornadiene in four steps¹⁹.

Herein, three steps were employed to synthesize 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (**II_b**) and bis[4-(3,4-dicarboxyphenoxy)phenyl] ether dianhydride (**II_a**) by a previous method^{5,20} from hydroquinone and 4,4'-dihydroxydiphenyl ether, respectively. The corresponding bisphenols reacted with 4-nitrophthalodinitrile in anhydrous dimethylsulfoxide in the presence of potassium carbonate as an acid acceptor to generate the bis(ether dinitrile)s which, subsequently, is where it is then hydrolyzed to the bis(ether diacid)s and dehydrated to the bis(ether anhydride)s.

1,4-Bis(3,4-dicarboxyphenoxy)benzene dianhydride (**II_b**): mp 263–265°C (lit.²⁰ 263–265°C); i.r. (KBr) 1850, 1772, 1610 cm⁻¹; MS (EI) *m/z* 402 (M⁺, 100); ¹³C n.m.r. (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: C₂₂H₁₀O₈, colorless crystal, 0.40 × 0.50 × 0.50 mm, monoclinic P₂¹/n with *a* = 6.001 (3), *b* = 10.091 (3), *c* = 14.030 (5) Å, β = 92.34° (3) with *Dc* = 1.574 g cm⁻³ for *Z* = 2, *V* = 848.9 (6) Å³, *T* = 298 K, λ = 0.7107 Å, μ = 1.142 cm⁻¹, *F*(000) = 412, *Rw* = 0.032 for 1227 observed reflections, intensity variation < 1%.

Bis[4-(3,4-dicarboxyphenoxy)phenyl] ether dianhydride (**II_a**): mp 238–240°C (lit.²⁰ 238–239°C); i.r. (KBr) 1849, 1772, 1612, 1475 cm⁻¹; MS (EI) *m/z* 494 (M⁺, 100); ¹H n.m.r. (400 MHz, DMSO-*d*₆) δ 7.09–7.20 (m, 12H, ArH), 7.76 (d, *J* = 8.28, 2H, ArH); ¹³C n.m.r. (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: C₂₈H₁₄O₉, colorless crystal, 0.20 × 0.20 × 0.25 mm, triclinic P-1 with *a* = 8.0198 (16), *b* = 14.825 (7), *c* = 20.016 (9) Å, α = 109.69° (3), β = 91.79° (3), γ = 94.66° (3) with *Dc* = 1.473 g cm⁻³ for *Z* = 4, *V* = 2228.8 (14) Å³, *T* = 298 K, λ = 1.5418 Å, μ = 8.979 cm⁻¹, *F*(000) = 1020, *Rw* = 0.091 for 3235 observed reflections, intensity variation < 3%.

Synthesis 4,9-diacetamidodiamantane

4,9-Dibromodiamantane (14.88 g, 43 mmol) was dissolved in a mixture of cyclohexane (100 ml) and acetonitrile (132 ml), and H₂SO₄ (6 ml, 97%) was added with stirring. Stirring was continued at 38°C. After 16 h, water and ice were added to the stirred mixture (a thick orange suspension). The white precipitate formed, was filtered and washed, and 11.5 g of white powder was obtained after recrystallization from *N*-dimethylacetamide (DMAc) to give 4,9-diacetamidodiamantane in 70% yield: mp 395.3°C (measured by d.s.c., lit.¹⁸ 399°C), MS (EI) *m/z* 302 (M⁺, 100); ¹H n.m.r. (300 MHz, DMSO-*d*₆) δ 1.72 (s, 6H, CH₃), 1.77 (brs, 6H, H-1, 2, 6, 7, 11, 12), 1.88 (brs, 12H,

H-3, 5, 8, 10, 13, 14), 7.27 (brs, 2H, NH); ¹³C n.m.r. (75 MHz, DMSO-*d*₆) δ 23.76 (CH₃), 37.12 (C-1, 2, 6, 7, 11, 12), 40.75 (C-3, 5, 8, 10, 13, 14), 49.09 (C-4, 9), 168.75 (C=O); Anal. Calc. for C₁₈H₂₆N₂O₂: C, 71.52; H, 8.61; N, 9.27. Found: C, 71.37; H, 8.54; N, 9.21.

Synthesis of 4,9-diaminodiamantane

4,9-Diacetamidodiamantane (11.0 g, 36.4 mmol) was refluxed for 24 h in a diethylene glycol (220 ml) solution of sodium hydroxide (23.5 g). The mixture changed to yellow and then to orange-brown, and was then extracted with chloroform. The normal work up of the product produced white crystals of compound **I** in a 45% yield after vacuum sublimation. Compound **I**: mp 220.4°C (measured by d.s.c., lit.¹⁸ 238–240°C); MS (EI) *m/z* 218 (M⁺, 100); ¹H n.m.r. (300 MHz, C₆D₆) δ 0.644 (br, 2H, NH₂), 1.42 (brs, 12H, H-3, 5, 8, 10, 13, 14), 1.57 (brs, 6H, H-1, 2, 6, 7, 11, 12); ¹³C n.m.r. (75 MHz, C₆D₆) δ 38.43 (C-1, 2, 6, 7, 11, 12), 45.63 (C-4, 9), 46.39 (C-3, 5, 8, 10, 13, 14); Anal. Calc. for C₁₄H₂₂N₂: C, 77.06; H, 10.09; N, 12.84. Found: C, 76.78; H, 10.18; N, 12.75. Crystal data: C₁₄H₂₄N₂O, colorless crystal, 0.05 × 0.40 × 0.50 mm, monoclinic C₂/c with *a* = 10.956 (4), *b* = 6.554 (3), *c* = 17.581 (7) Å, β = 103.04° (3) with *Dc* = 1.277 g cm⁻³ for *Z* = 4, *V* = 1229.7 (9) Å³, *T* = 298 K, λ = 0.7107 Å, μ = 0.666 cm⁻¹, *F*(000) = 520, intensity variation < 1%.

Polymer synthesis

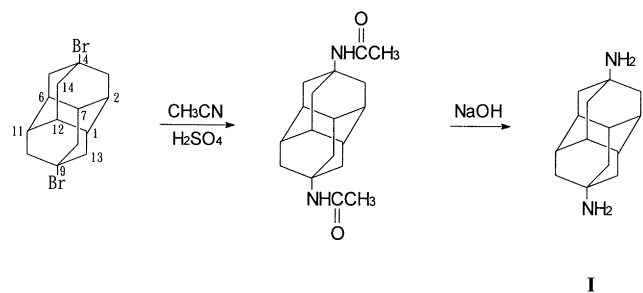
Dianhydride **II_a** (0.494 g, 1.00 mmol) was added to a stirred solution of **I** (0.218 g, 1.00 mol) in NMP (solid content, 10%, w/v) under N₂ and reacted at ambient temperature for 6 h, and then at 60°C for 3 h. The inherent viscosity of poly(amic acid) **III_a** in NMP was 0.65 dl/g, measured at a concentration of 0.5 g/dl at 30°C. The i.r. spectrum exhibited absorptions at 3345 (N–H and O–H stretching), and 1715, 1647 cm⁻¹ (C=O stretching), characteristic of the amic acid. The poly(amic acid) **III_a** was converted to polyimide **IV_a** by successive heating in vacuum at 80°C for 3 h, at 200°C for 8 h, and then at 250°C for 6 h. *M_n* of polyimide **IV_a** is 37 000. The symmetric and asymmetric carbonyl stretches occurred at 1762 and 1703 cm⁻¹ in the FT-i.r. spectrum of **IV_a**. Other associated bands are the C–N stretch at 1350 cm⁻¹ and the band at 747 cm⁻¹, which is deformation of the imide ring to imide carbonyls. The other polyimides were prepared in a similar manner from **I** and aromatic tetracarboxylic dianhydrides.

Characterization

A Bio-Rad FTS-40 FT-i.r. spectrophotometer was used to record i.r. 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. ¹H and ¹³C n.m.r. 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 (g.p.c.) 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 made by u.v., 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 employed to study the transition data and thermal decomposition temperature of all the polymers. The differential scanning calorimeter (d.s.c.) was run under a nitrogen stream at a flow rate of 30 cc/mm and a heating rate of 20°C/min. The thermogravimetric analysis (TG) was determined under a nitrogen flow of 50 cc/mm. Dynamic mechanical analysis (DMA) was performed on a Du Pont 9900 thermal analyzer system. A sample with 10 mm in length, 2 mm in width and approximately 0.04 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 Istron UTM-III-500 with a load cell of 10 kg at a drawing speed of 5 cm/mm. Measurements were performed at 28°C with film specimens (about 0.1 mm



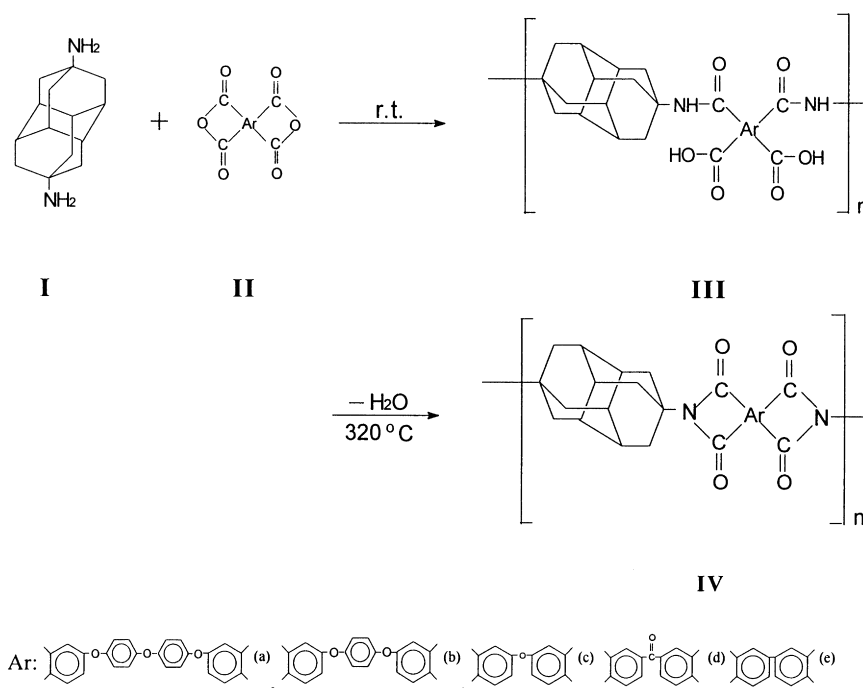
Scheme 1

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 30 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. Dielectric constant was measured by the parallel-plate capacitor method and 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.

RESULTS AND DISCUSSION

Monomer synthesis

The reaction of 4,9-dibromodiamantane with acetonitrile in the presence of H₂SO₄ afforded 4,9-diacetamidodiamantane in 70% yield. Although Blaney *et al.* have reported the synthesis of 4,9-diacetamidodiamantane, the synthetic route from 4,9-dichlorodiamantane involved two steps. Herein, 4,9-diacetamidodiamantane was prepared easily by Ritter reaction of 4,9-dibromodiamantane in one step. Then the reaction of 4,9-diacetamidodiamantane with sodium hydroxide afforded compound **I** in 45% yield, as shown in *Scheme 1*. On the basis of the shielding effect of carbon and proton, the positions of chemical shifts for carbons and protons of compound **I** were assigned in *Figure 1*. The signal at 0.644 ppm is peculiar to the amino group. The structure of **I** was confirmed unambiguously by X-ray diffraction analysis. The ORTEP diagram of **I** is shown in *Figure 2*. X-ray crystal data for **I** was acquired from a single crystal obtained by slowly crystallizing from a chloroform solution of **I**. Interestingly, compound **I** and H₂O (absorbed in



Scheme 2

chloroform) formed a single crystal with a hydrogen bond. In addition, the elemental analysis, the n.m.r. spectra, and the n.m.r. spectra also verified the formation of 4,9-diacetamidodiamantane.

Synthesis of polymers

New diamantane-based polyimides **IV** were synthesized by a conventional two-step procedure starting from **I** and aromatic tetracarboxylic dianhydrides **II** through the ring-opening polyaddition and subsequent thermal cyclodehydration, as shown in Scheme 2. Table 1 summarizes those results. The ring-opening polyaddition in NMP at room temperature afforded poly(amic acid)s **III** with medium inherent viscosities between 0.41 and 0.65 dl/g, but the result for viscosities was unsatisfactory. These medium viscosities were probably due to the fact that the bulky and rigid diamantane ring increases the rigidity of the polymer chain. The more rigid the polymer chain is, the more energy is needed to form high inherent viscosity of polymer by polymerization. In addition, we also attempted to synthesize polyimides by a one-step method. However, in the reaction solutions occurred precipitation during the imidization of the poly(amic acid)s **III**. I.r. spectroscopy confirmed the formation of poly(amic acid)s **III**. The characteristic absorption bands of the amic acid appeared near 3345 (N-H and O-H stretching), 1720 (acid, C=O stretching), 1650 (amide, C=O stretching), and 1540 cm⁻¹ (N-H

bending). Next, the thermal conversion to polyimides **IV** was performed by successively heating the poly(amic acid)s **III** to 250°C in a vacuum. Table 4 indicates that the soluble polyimide **IV_a** has \bar{M}_n and \bar{M}_w/\bar{M}_n of 37 000 and 1.6, respectively. In fact the \bar{M}_w/\bar{M}_n is lower than those of the commercial materials, which may be due to the somewhat low reactivity of **I**, containing the rigid and bulky diamantane units. I.r. spectroscopy confirmed the polyimides **IV**. The characteristic absorption bands of the imide ring appeared near 1780 (asym C=O stretching), 1720 (sym C=O stretching), 1390 (C-N stretching), and 745 cm⁻¹ (imide ring deformation).

Characterization of polymers

The solubility of polyimides was tested in various solvents. Table 2 summarizes those results. The polyimide **IV_a** was soluble in *m*-cresol. However, the other polyimides **IV**, except **IV_a**, were insoluble in the test solvents, due to the containment of extremely rigid backbones. A transparent and very pale yellow film of polyimide **IV_a** was obtained by successively heating the corresponding poly(amic acid) **III_a**. However, the other polyimide films **IV**, except **IV_a**, cracked during the imidization process, due to their low inherent viscosities. Initially, the polyimide films **IV** were structurally characterized by X-ray methods. All polyimides **IV** had nearly the same amorphous patterns with broad peaks appearing at around 18° (2θ), as shown in Figure 3. However, the polyimide **IV_e** had obviously a higher chain

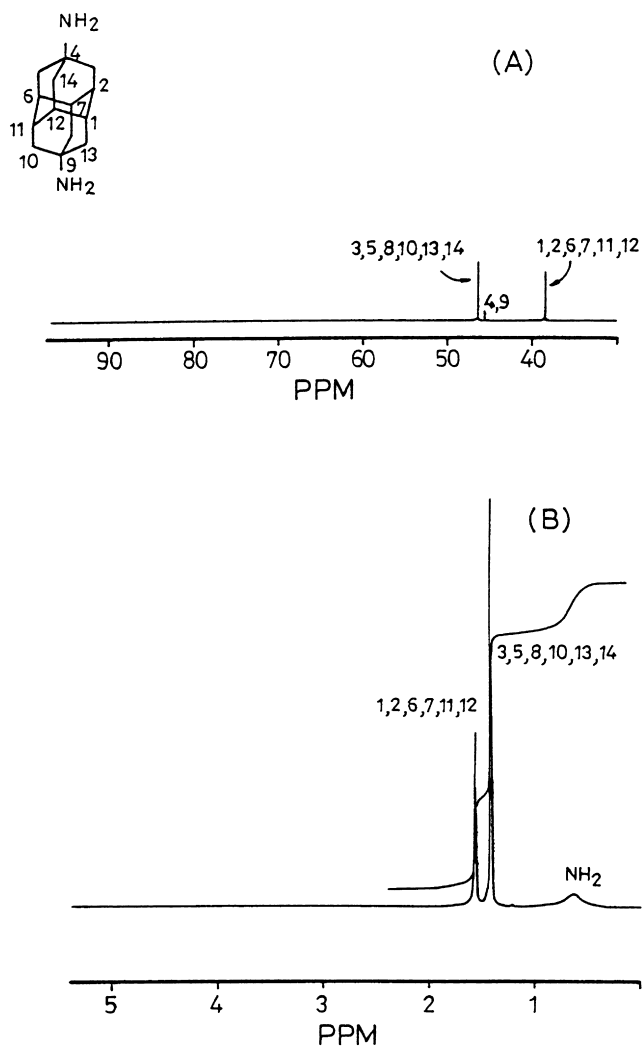


Figure 1 N.m.r. (C₆D₆) spectra of I: (A) ¹³C n.m.r. (100 MHz); (B) ¹H n.m.r. (400 MHz)

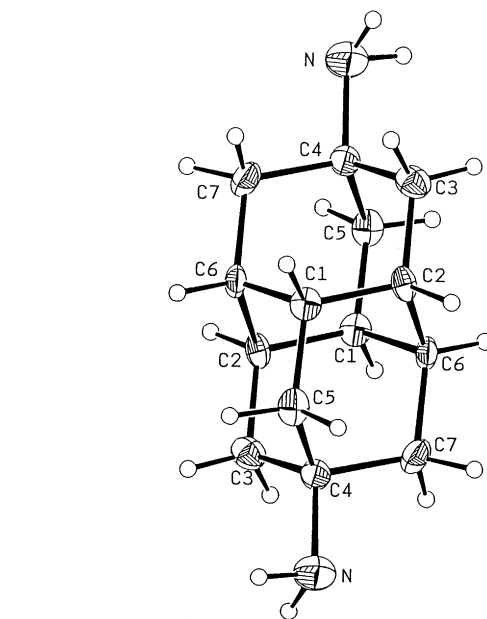


Figure 2 X-ray structure of I

Table 1 Inherent viscosities of poly(amic acid)^a

Polymer	Inherent viscosity (dl/g)	Remark ^b
III _a	0.65	S
III _b	0.45	S
III _c	0.50	S
III _d	0.41	S
III _e	0.46	S

^aPolymerization was carried out with 1 mmol of each monomer in NMP (solid content, 10%, w/v) at ambient temperature for 6 h, and then at 60°C for 3 h

^bAppearance of the polymerization system: S, homogeneous solution

packing density. This higher chain packing density is attributed to that the relatively rigid dianhydride **II_e** was incorporated into the polyimide **IV_e**.

Thermal analysis was performed by means of d.s.c., DMA, and t.g.a. *Table 3* summarizes those results. Since the influences of residual water or solvent and the history of thermal annealing are occasionally observed in the initial heating run of d.s.c. Therefore, samples were at first heated to 350°C. In addition, T_g was determined by the second heating run of d.s.c.. All polyimides **IV**, except **IV_e**, displayed typical glass transitions ranging from 295 to 325°C. The bulky and rigid diamantane unit increases the rigidity of the polymer **IV** chain which, in turn, gives high glass transition temperatures. The temperatures of polyimides **IV** at a 5% weight loss ranged from 432 to 488°C in air and from 489 to 530°C in N₂ atmosphere.

More detailed information can be obtained from the dynamic mechanical behavior measurements taken from the films, as a function of temperature. A film of ~40 μm thickness, was studied on the temperature scale between 0 and 350°C. *Figure 4* depicts the mechanical relaxation spectra of polyimide **IV_a**. With an increasing temperature, G' decreases steadily from 0 to 275°C, without showing either abrupt changes or a marked relaxation. Similarly, a marked relaxation in G'' and $\tan \delta$ was not observed in the meantime. The glass transition at around 308°C is associated with an approximately two orders of magnitude step decrease in G' . Its T_g lies in a manageable temperature range for processing in melt. A comparison of the mechanical behavior of the system studied here with that

of typical polyimides^{21,22} shows that the main difference was not the observation of subglass transition in the 50–200°C range in this work. This absence is attributed to the fact that the diamine moiety of the polyimide **IV_a** did not contain the phenyl group. This also suggests that the subglass relaxation of a typical polyimide has a close relationship with the phenyl groups within the diamine moiety of polyimide.

Properties of polyimide **IV_a** are summarized in *Table 4*. Polyimide exhibited tensile strength at breakage of

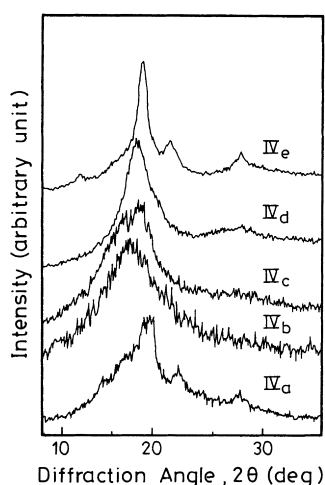


Figure 3 Wide-angle X-ray diffraction curves of polyimides

Table 2 Solubility of polyimides^a

Solvent	Polymer				
	IV_a	IV_b	IV_c	IV_d	IV_e
<i>o</i> -Chlorophenol	+ -	+ -	+ -	+ -	+ -
<i>m</i> -Cresol	+	+	+	+	+
Chloroform	+ -	+ -	+ -	-	-
DMAC	+ -	+ -	+ -	-	-
NMP	+ -	+ -	+ -	-	-
THF	-	-	-	-	-

^aSolubility: + +, soluble at room temperature; +, soluble on heating at 60°C; + -, partially soluble on heating at 60°C; -, insoluble on heating at 60°C

Abbreviation: NMP, *N*-methyl-2-pyrrolidone; DMAC, *N,N*-dimethylacetamide; THF, tetrahydrofuran

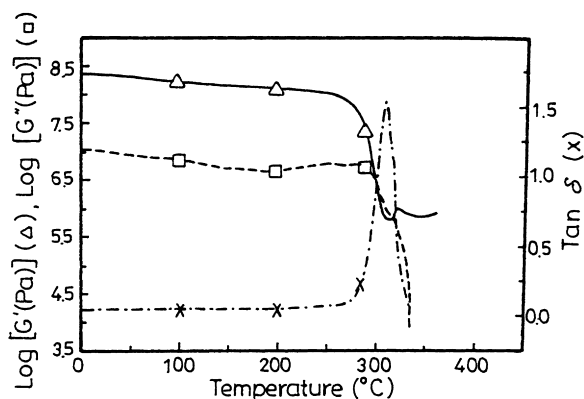


Figure 4 Dynamic mechanical analysis curves for **IV_a** at a heating rate of 5°C/min

Table 3 Thermal properties of polyimides

Polymer	T_g (°C)	Decomposition ^c temperature (°C)		
		D.s.c. ^a	DMA ^b	In air
IV_a	295	308	432	489
IV_b	310		440	495
IV_c	320		457	499
IV_d	325		438	515
IV_e	— ^d		488	530

^aGlass transition temperature (T_g) measured by d.s.c. at a heating rate of 20°C/min in nitrogen

^bThe glass transition measured by DMA using shear mode at a heating rate of 5°C/min

^cTemperature at which 5% weight loss recorded by t.g.a. at a heating rate of 10°C/min

^dNot found

Table 4 Characteristics of polyimide

Properties	IV_a
\bar{M}_n ^a	37 000
\bar{M}_w	59 000
\bar{M}_w/\bar{M}_n	1.6
Glass transition temp. ^b (°C)	308
Decomp. temp. ^c (°C)	
In air	432
In N ₂	489
Tensile strength (MPa)	68.4
Initial modulus (GPa)	2.0
Elongation to break (%)	4.8
% H ₂ O absorption ^d , 85% RH	0.205
Dielectric constant (dry, 1 KHz)	2.7
CTE (ppm/°C)	74

^aBy g.p.c. (relative to polystyrene)

^bBy DMA

^cTemperature at which 5% weight loss recorded by t.g.a. at a heating rate of 10°C/min

^dMoisture absorption of polyimide film was measured at 30°C for 90 h

68.4 MPa, elongation to breakage of 4.8%, and initial modulus of 2.0 GPa. This table also indicates that the introduction of the diamantane unit into the polyimide backbone resulted in a polyimide with a low dielectric constant and low moisture absorption. Such low moisture absorption and dielectric constant result from the fact that diamantane is a fully aliphatic hydrocarbon structure leading to low hydrophilicity and polarity. We speculate that this causes a 'dilution' effect of the polar imide groups by the diamantane units (on a weight basis based on polymer). The CTE of polyimide **IV_a** resembles those of flexible polyimides²³. This similarity is because the main chains of polyimide **IV_a** contain bulky diamantane units. These bulky units loosen the molecular packing in the film. Thus, the CTE of polyimide **IV_a** is moderate.

CONCLUSIONS

New diamantane-based polyimides were synthesized by a conventional two-step procedure starting from **I** and aromatic tetracarboxylic dianhydrides through the ring-opening polyaddition, afforded poly(amic acid) **III** with medium inherent viscosities between 0.41 and 0.65 dl/g, and subsequent thermal cyclodehydration. The polyimide **IV_a** had \bar{M}_n of 37 000. The polyimide **IV_a** was soluble in *m*-cresol. A transparent and very pale yellow polyimide film **IV_a** was obtained by casting from the corresponding poly(amic acid). The polyimide **IV_a** had tensile strength at breakage of 68.4 MPa and initial modulus of 2.0 GPa. DMA reveals that only a glass transition appeared in the polyimide **IV_a** on the temperature scale between 0 and 350°C. Its glass relaxation process occurred at 308°C. This T_g lies in a manageable temperature range for processing in melt. The subglass relaxation of polyimide **IV_a** was not observed. This suggests that the subglass relaxations of typical polyimides have a close relationship with the phenyl groups within the diamine moieties of the polyimides. Due to the low hydrophilicity and polarity of diamantane, the polyimide **IV_a** exhibits low dielectric constant and low moisture absorption. Their temperatures at a 5% weight loss ranged from 432 to 488°C in air and from 489 to 530°C in N₂ atmosphere.

ACKNOWLEDGEMENTS

We are grateful to the National Science Council of the Republic of China for the support of this work.

REFERENCES

- Harris, F.W. and Hsu, S.L.-C., *High Perform. Polym.*, 1989, **1**, 1.
- Oishi, Y., Ishida, M., Kakimoto, M.A. and Imai, Y., *J. Polym. Sci., Polym. Chem.*, 1992, **30**, 1027.
- Misra, A.C., Tesoro, G., Hougham, G. and Pendharkar, S.M., *Polymer*, 1992, **33**, 1078.
- Kim, W.G. and Hay, A.S., *Macromolecules*, 1993, **26**, 5275.
- Eastmond, G.C. and Paprotny, J., *Macromolecules*, 1995, **28**, 2140.
- Falcigno, P.A., Jasne, S. and King, M., *J. Polym. Sci., Polym. Chem.*, 1992, **30**, 1433.
- Trofimenko, S. and Auman, B.C., *Macromolecules*, 1994, **27**, 1136.
- Feiring, A.E., Auman, B.C. and Wonchoba, E.R., *Macromolecules*, 1993, **26**, 2779.
- Malik, A.A., Archibald, T.G. and Baum, K., *Macromolecules*, 1991, **24**, 5266.
- Dang, T.D., Archibald, T.G., Malik, A.A., Bonsu, F.O., Baum, K., Tan, L.S. and Arnold, F.E., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1991, **32**(3), 199.
- Chapman, O.L. and Ortiz, R., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1995, **36**(1), 739.
- Chern, Y.T. and Wang, W.L., *Macromolecules*, 1995, **28**, 5554.
- Chern, Y.T., *Macromolecules*, 1995, **28**, 5561.
- Chern, Y.T., Fang, J.S. and Kao, S.C., *J. Polym. Sci., Polym. Chem. Ed.*, 1995, **58**, 1417.
- Chern, Y.T. and Wang, W.L., *J. Polym. Sci., Polym. Chem.*, 1996, **34**, 1501.
- Chern, Y.T. and Chung, W.L., *Makromol. Chem. Phys.*, 1996, **197**, 1171.
- Chern, Y.T., *J. Polym. Sci., Polym. Chem.*, 1996, **34**, 125.
- Blaney, F., Johnston, D. E., Mckervey, M. A., Rooney, J. J., *Tetrahedron Lett.*, 1975, **99**.
- Gund, T.M., Schleyer, P.v.R., Unruh, G.D. and Gleicher, G.J., *J. Org. Chem.*, 1974, **39**, 2995.
- Takekoshi, T., Kochanowski, J.E., Manello, J.S. and Webber, M.J., *J. Polym. Sci., Polym. Chem.*, 1985, **23**, 1759.
- Bernier, G.A. and Kline, D.E., *J. Appl. Polym. Sci.*, 1968, **12**, 593.
- Perena, J.M., *Angew. Makromol. Chem.*, 1982, **106**, 61.
- Matsuura, T., Hasuda, Y., Nishi, S. and Yamada, N., *Macromolecules*, 1991, **24**, 5001.