Synthesis and characterization of tough polyamides derived from 4,9-bis[4-(4-aminophenoxy)phenyl]diamantane

Yaw-Terng Chern* and Wen-Liang Wang
Institute of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

A series of new polyamides was synthesized by direct polycondensation of the 4,9-bis[4-(4-aminophenoxy)-phenyl]diamantane (**I**) with various dicarboxylic acids. The polyamides had high inherent viscosities and number-average molecular weights ($\bar{M}_n$) of 0.65–1.65 dl g^{-1} and 32 000–140 000, respectively. Although the symmetrical and rigid 4,9-diphenyldiamantane units were incorporated into polyamide **III**, especially, most polyamides **III** were extremely tough. Their elongation value at break was up to 60.5%. These films had tensile strength up to 116.1 MPa, and initial modulus reached 2.1 GPa. Two relaxations occurred on the temperature scale between 0 and 400°C in these polyamides. Their α relaxations arose at high temperatures, ranging from 342 to 381°C. Moreover, these polyamides remained quite stable at high temperatures and maintained good mechanical properties ($G' \approx ca.~10^8$ Pa) up to temperatures close to the main transition markedly exceeding 330°C. Furthermore, incorporating bulky diamantane units and the flexible ether linkages into the polyamides **III**, contributes toward the good solubility of most polyamides. In addition, their temperatures at a 5% weight loss ranged from 384 to 433°C in air and from 387 to 436°C in N$_2$ atmosphere. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyamides; diamantane; toughness)

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 the automotive, aerospace, and microelectronics industries. Polyamides, which are certainly one of the most successful classes of high-temperature polymers, have found extensive use in the aviation, automotive and electronic industries. The conventional method for the synthesis of aramids begins with having diamine react with a diacid chloride monomer by low-temperature solution polycondensation. In another method, Yamazaki and co-workers reported a direct polycondensation for the synthesis of aromatic polyamides[1,2]. According to their investigation, this procedure could obtain a high yield of polymers at a high molecular weight. Recently, aramids of modest molecular weight were synthesized by the palladium-catalysed carbonylation and coupling reaction of diamines with aromatic dibromides or aromatic iodide[3,4]. Meanwhile, a *N*-silylated diamine method was used by others to obtain a high molecular weight by focusing on the diamine with low reactivity[5].

Diamantane is a cycloaliphatic-cage hydrocarbon containing an 'extended-cage' adamantane structured[6,7]. Although diamantane has been investigated for many years, only a few examples of the polymers based on diamantane are known[8–16]. Recently, we reported that incorporation of 1,6- or 4,9-diamantylene groups into polyamides afforded good thermal stability and good

retention of storage modulus above 350°C[11,13,14]. However, it was necessary for LiCl to be added into the polymer solution for casting polyamide films, due to the symmetric and rigid 1,6- or 4,9-diamantylene groups. It has been generally recognized that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to significant improvements in solubility and other process characteristics of the polymers, without greatly sacrificing thermal stability. To improve their processability, the flexible ether linkages were incorporated into the diamantane-based polyamides in this work.

Preparing diamantane-based polymers has received considerable attention owing to their unique combination of stiffness, chemical and solvent resistance, high glass transition temperature, and retention of physical properties at high temperature. Herein, we successfully synthesize new polyamides involving 4,9-bis[4-(4-aminophenoxy)phenyl]diamantane (**I**) by the direct polycondensation with various dicarboxylic acids **II**. The solubility, dynamic mechanical properties, and thermal properties of polyamides are investigated as well.

EXPERIMENTAL

Materials

Terephthalic acid (**II$_a$**), isophthalic acid (**II$_b$**), 4,4′-oxybis(benzoic acid) (**II$_c$**), 5-*tert*-butylisophthalic acid (**II$_d$**), *cis*-1,4-cyclohexanedicarboxylic acid (**II$_e$**), *trans*-1,4-cyclohexanedicarboxylic acid (**II$_f$**), and (±)1,3-cyclohexanedicarboxylic acid (**II$_g$**, mixture of *cis* and *trans*) were

---

purified by vacuum sublimation. Anhydrous LiCl (Merck) was dried in a vacuum oven at 150°C for 6 h and at 180°C for 10 h. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethyla-cetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride, and stored over 4 Å molecular sieves. According to our previous method, 4,9-dibromodiamantane was prepared[14].

4,9-Bis[4-(4-aminophenoxy)phenyl]diamantane (**I**) was synthesized from 4,9-dibromodiamantane in three steps. 4,9-Dibromodiamantane reacted with phenol to generate 4,9-bis(4-hydroxyphenyl)diamantane. Next, the corre-sponding bisphenol reacted with *p*-chloronitrobenzene in the presence of potassium carbonate to generate new 4,9-bis[4-(4-nitrophenoxy)phenyl]diamantane, which was hydrogenated to generate the new diamine **I**. Our previous studies provide a detailed procedure for the preparation of **I**[17]. Its properties are as follows: 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 n.m.r. (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 n.m.r. (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$_2$O$_2$: 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$_4$O$_4$, colorless crystal, 0.40 × 0.50 × 0.50 mm, monoclinic P^{21}/n with a = 6.6322 (20), b = 39.308 (8), c = 8.0466 (23) Å, β = 110.35 (3), with Dc = 1.231 g cm^{-3} for Z = 2, V = 1966.9 (9) Å^3, T = 298 K, λ = 1.5418 Å, μ = 4.210 cm^{-1}, F(000) = 786, 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 were made. Inherent viscosities of all polymers were determined at 0.5 g dl^{-1} concentration in a NMP containing dissolved 3% (w/v) LiCl at 30°C using an Ubbelohde viscometer.

Gel permeation chromatography (GPC) on soluble polyamides was performed on an Applied Biosystem at 70°C with two PL gel 5 μm mixed-C columns in the NMP/LiBr (0.06 mol l^{-1}) solvent system. The flow rate was 0.5 ml min^{-1}, detection was made by UV, 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 analyser 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^{-1} and a heating rate of 20°C min^{-1}. The thermogravimetric analysis (T_g) was determined under a nitro-gen flow of 50 cm^3 min^{-1} with a heating rate of 20°C min^{-1}. 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 0.05 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^{-1}. 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. Minimized energy conformations were constructed and analyzed using 'cvff' force field on the Insight II, BIOSYM's 3D molecular modelling program.

Polymerization

A typical example of the polycondensation is given below.

Polyamide **III$_c$** was synthesized from **I** and **II$_c$**. A mixture of 1.662 g (3 mmol) of **I**, 0.606 g (3 mmol) of **II$_c$**, 1.0 g of LiCl, 1.845 g (6 mmol) of triphenyl phosphite, 4 ml of pyridine, and 16 ml of NMP was heated and stirred at 130°C for 5 h. The obtained polymer solution was trickled into 500 ml methanol, giving rise to a fibrous white preci-pitate that was thoroughly washed with methanol and hot water, collected by filtration, and dried. The yield was nearly quantitative. The inherent viscosity of polyamide **III$_c$** was 1.65 dl g^{-1}, measured at 0.5 g dl^{-1} concentration in NMP containing dissolved 5% (w/v) LiCl at 30°C. The IR spectrum contained absorption peaks at 3317 cm^{-1} (N–H) and 1668 cm^{-1} (C=O), i.e. characteristic of the amide group.

RESULTS AND DISCUSSION

Effect of the reaction parameters on the inherent viscosities of III$_c$

Part I in *Table 1* reveals that the inherent viscosities of polyamide **III$_c$** increased with an increasing monomer concentration up to 0.20 M. However, the inherent viscosity of **III$_c$** slightly increased when the monomer concentration exceeded 0.15 M. Part II in *Table 1* also indicates that the inherent viscosities of polyamide **III$_c$** increased with an increase in reaction time. However, a decreased inherent viscosity of 1.32 dl g^{-1} was obtained when the reaction time was 7 h. Such a decrease is possibly attributed to the increase in side reactions, i.e. quite similar to those derived in previous literature[18]. According to Part III in *Table 1*, the inherent viscosities of polyamide **III$_c$** increased with an

Table 1 Effect of reaction conditions on polymerization^a

Part	Reaction conditions			Polymer		
	Monomer^b (mol l^{-1})	Reaction temp. (°C)	Reaction time (h)	Yield (%)	η^c_{inh} (dl g^{-1})	Remark^d
I	0.10	120	3	97	0.94	S
	0.15	120	3	98	1.05	S
	0.20	120	3	96	1.08	S
II	0.15	120	3	98	1.05	S
	0.15	120	5	97	1.43	S
	0.15	120	7	94	1.32	S
III	0.15	110	5	95	1.39	S
	0.15	120	5	97	1.43	S
	0.15	130	5	97	1.65	S
	0.15	140	5	94	1.02	S

^{a}The reaction conditions are pyridine/NMP ratio at 0.25, P(OC$_6$H$_5$)$_3$/**I** ratio at 2 and concentration of LiCl at 5% (w/v).
^{b}[**I**] = [**II$_c$**].
^{c}Measured at 30°C at a concentration of 0.5 g dl^{-1} in NMP containing 5% w/v LiCl.
^{d}Appearance of the polymerization system: S, homogeneous solution.

Table 2 Synthesis of polyamides[a]

Polymer	Yield (%)	η_{inh}^b (dl g⁻¹)	Remark[c]	$\bar{M}_n^d \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
III_a	98	0.65	S	3.2	2.1
III_b	96	0.96	S	7.7	1.7
III_c	97	1.65	S	14	3.3
III_d	97	0.77	S	8.7	2.2
III_e	95	1.19	S	9.6	3.9
III_f	98	—[e]	P	—	—
III_g	94	1.03	S	9.7	3.5

[a][I] = [dicarboxylic acid] = 0.15 M; Pyridine/NMP = 0.25; P(OC₆H₅)₃/I = 2.0; LiCl = 5% (w/v); temperature = 130°C; time = 5 h.
[b]Measured at 30°C at a concentration of 0.5 g dl⁻¹ in NMP containing 3% (w/v) LiCl.
[c]Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation.
[d]By GPC (relative to polystyrene).
[e]Could not be measured.

Table 3 Solubility of polyamides[a]

Solvent	Polymer						
	III_a	**III_b**	**III_c**	**III_d**	**III_e**	**III_f**	**III_g**
NMP	+ −	+ +	+	+ +	+ −	+ −	+ +
DMAc	+ −	+ −	+ −	+ −	+ −	+ −	+
DMF	−	−	−	+ −	−	+ −	+ −
Pyridine	−	+ −	+ −	+	+	+ −	+
DMAc/LiCl[b]	+ +	+ +	+ +	+ +	+ +	+ −	+ +
NMP/LiCl[b]	+ +	+ +	+ +	+ +	+ +	+ −	+ +

[a]Solubility: + +, soluble at room temperature; +, soluble on heating at 60°C; + −, partially soluble on heating at 60°C; −, insoluble on heating at 60°C. Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide.
[b]Concentration of LiCl is 3% (w/v).

Table 4 Mechanical properties of polyamide films

Polyamide	Strength to break (MPa)	Elongation to break (%)	Initial modulus (GPa)
III_a	40.0	7.3	2.1
III_b	63.3 (76.6)[a]	46.1 (9.3)	1.8 (2.1)
III_c	65.6 (66.0)	60.5 (27.7)	1.8 (1.8)
III_d	116.1	7.3	2.0
III_e	51.0	35.2	1.9
III_g	74.3 (77.7)	27.7 (10.0)	1.9 (1.9)

[a]The values in parentheses are those of the polyamides derived from 1,6-bis[4-(4-aminophenoxy)phenyl]diamantane.

increasing in reaction temperature. However, a decreased inherent viscosity of 1.02 dl g⁻¹ was obtained when the reaction was performed at 140°C. This might cause an adverse effect on the complex form derived from LiCl and phenol at an excessively high temperature, thereby leading to an increase in side reactions[18]. Therefore, in this work the inherent viscosity of polyamide **III_c** decreased. From the above results, we can infer that the most favourable conditions for this system are the monomer concentration at 0.15 M, reaction temperature at 130°C, and reaction time at 5 h.

Synthesis of polyamide **III**

Various new polyamides were prepared from **I** with the corresponding dicarboxylic acids by using the most favourable conditions for the reaction with 4,4′-oxybis-(benzoic acid) (**II_c**), as shown in *Scheme 1*. *Table 2* presents the polycondensation results. All polyamides were obtained with nearly quantitative yield. The polyamides **III** had high inherent viscosities, ranging from 0.65 to 1.65 dl g⁻¹. However, the reaction solution of **III_f** was quite viscous but turbid during the polycondensation. Unfortunately, the inherent viscosity of **III_f** could not be measured due to its poor solubility. According to GPC data, $\bar{M}_n$ of polyamides **III** also had high molecular weights, ranging from 32 000 to 140 000. IR spectroscopy confirmed the formation of polyamides **III**. FTIR spectra of the polyamides **III** detected characteristic amide bands appearing at 3292–3318 cm⁻¹ (N–H str), and 1654–1665 cm⁻¹ (C=O str).

Characterization of polyamides

The solubility of the polymers was tested in various solvents. *Table 3* summarizes those results. Incorporating of bulky diamantane units and flexible ether linkages into polyamides **III** allowed most of the polyamides **III**, except **III_a** and **III_f**, to be soluble in NMP, DMAc and pyridine. Notably the polyamides **III_a** and **III_f** had the worst solubility among the polyamides **III**. This inferiority is attributed to the fact that the polyamides **III_a** and **III_f** contained relatively rigid and symmetrical structures in the diacid moiety of polyamides **III_a** and **III_f**, respectively. When NMP and DMAc were added with 3% (w/v) LiCl, the solubility of polyamide **III_a** was markedly enhanced. The polyamide films **III** were structurally characterized by X-ray methods. Due to the largely bulky of diamantane structure, the polyamides **III** had nearly the same amorphous patterns with broad peaks appearing (2θ) at around 18°.
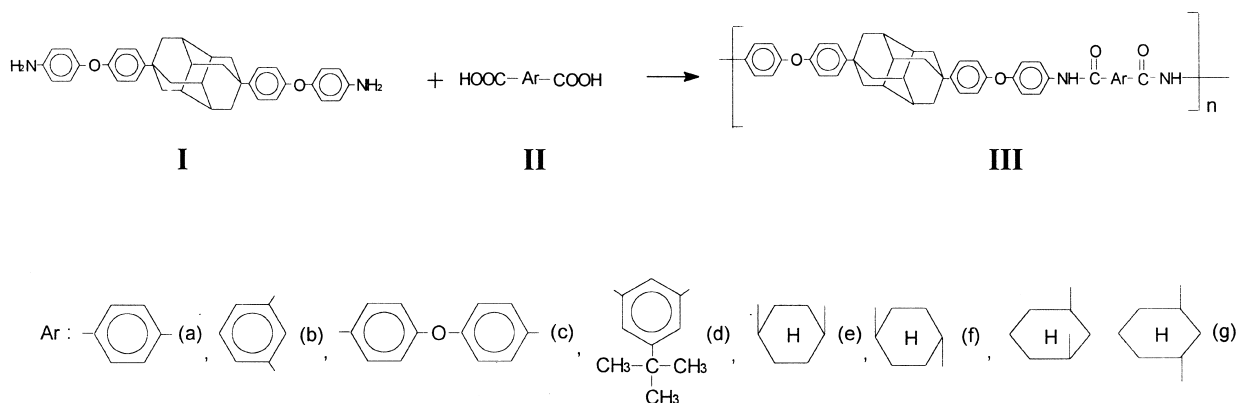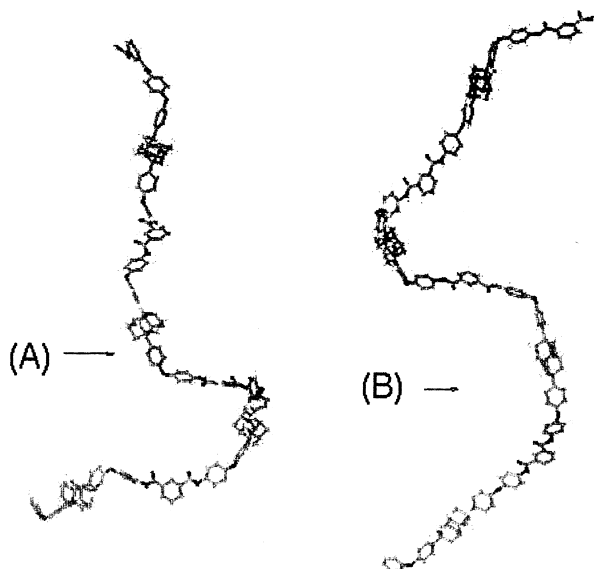

Scheme 1

Figure 1 Minimized energy conformations of models for polyamide **III**$_b$ with 4,9-diamantylene moieties in the main chain. (A) Before calculation; (B) after calculation.

Table 5 Thermal properties of polyamides

Polymer	DMA[a] T_α(°C)	Decomposition temperature (°C)[b] in air	in N$_2$
III$_a$	381	433	435
III$_b$	347	432	436
III$_c$	368	415	424
III$_d$	345	401	416
III$_e$	342	384	390
III$_f$	—[c]	385	387
III$_g$	347	388	387

[a]The α transition measured by DMA using shear mode at a heating rate of 5°C min^{-1}.
[b]Temperature at which 5% weight loss recorded by TG at a heating rate of 20°C min^{-1}.
[c]Could not be measured.

Colorless films of most polyamides **III**, except **III**$_d$, **III**$_f$ and **III**$_g$, were obtained by casting from their DMAc solution containing 3% (w/v) LiCl. Polyamide films **III**$_d$ and **III**$_g$ were also obtained by casting from their DMAc solutions without LiCl. However, the polyamide film **III**$_f$ could not be obtained owing to its poor solubility. The mechanical properties were determined via an instron machine. *Table 4* summarizes the tensile properties of the polyamides. The mechanical properties of these films were, in general, satisfactory. Although the symmetrical and rigid 4,9-diphenyldiamantane units were incorporated into poly-amide **III**, especially, most polyamides **III** (except **III**$_a$ and **III**$_d$) were extremely tough. The elongation values at break of the polyamides **III** (except **III**$_a$ and **III**$_d$) ranged from 27.7 to 60.5%. A comparison of tensile properties of the systems studied herein with the corresponding polyamides derived from 1,6-bis[4-(4-aminophenoxy)phenyl]diaman-tane shows that the polyamides derived from 4,9-bis[4-(4-aminophenoxy)phenyl]diamantane are markedly tough, as shown in *Table 4*. The difference on mechanical properties may be due to the different internal structures derived from the various monomers. In general, the properties of materials depend on their internal structures. Those structures can be easily visualized by molecular models.
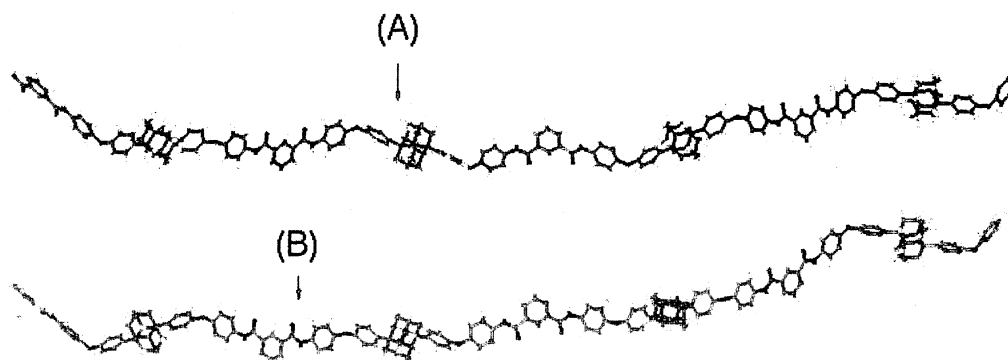
Minimized energy conformations of polyamides **III** were constructed by using 1500 steps. The values of root mean square (RMS) derivative for each conformation is less than 0.1. As *Figure 1* reveals, minimized energy conformations of models for the polyamide **III**$_b$ (i.e. four repeat units of each chain to account for nonlocal interaction) indicates that the minimized energy conformation of polyamides is helical. This finding suggests that mechanical properties of the polyamide **III**$_b$ are extremely tough in nature, whereas *Figure 2* depicts that minimized energy conforma-tion of the polyamide with 1,6-diamantylene groups are nearly linear conformation. These findings suggest that the mechanical properties of the polyamides with 4,9-diaman-tylene groups are tougher than those of the polyamides with 1,6-diamantylene groups. In addition, the polyamide with 1,6-diamantylene groups (1166.6 kcal) is larger in the total energy of conformation than the polyamide **III**$_b$ with 4,9-diamantylene groups (1088.5 kcal). The finding indicates that the thermodynamic conformation of poly-amide **III**$_b$ with 4,9-diamantylene groups is more stable than that of polyamide with 1,6-diamantylene groups.

Thermal analysis was performed by DSC, DMA and TGA. *Table 5* summarizes those results. The temperatures of polyamides **III** at a 5% weight loss ranged from 384 to 433°C in air and from 387 to 436°C in N$_2$ atmosphere. When the polyamides were derived from the alicyclic dicarboxylic acids **II**$_e$, **II**$_f$ and **II**$_g$, their temperatures at a 5% weight loss were lower than those of the polyamides derived from the aromatic dicarboxylic acids. With respect to the DSC experiment, initial heating of the samples was curtailed at 300°C. In addition, T_g and other thermal properties were evaluated according to the DSC charts of the second heating. All polyamides **III** did not display a typical glass
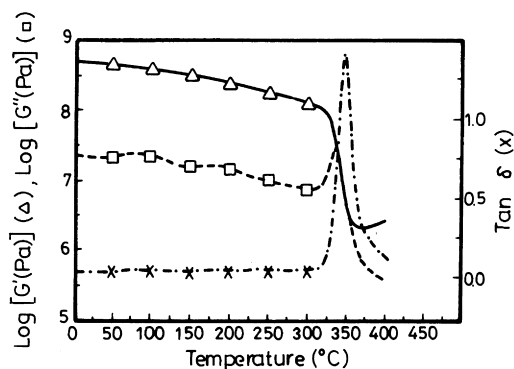

Figure 2 Minimized energy conformations of models for polyamide derived from 1,6-bis[4-(4-aminophenoxy)phenyl]diamantane and **II**$_b$. (A) Before calculation; (B) after calculation.

Figure 3 Dynamic mechanical analysis curves for III_d at a heating rate $5°C\ min^{-1}$.

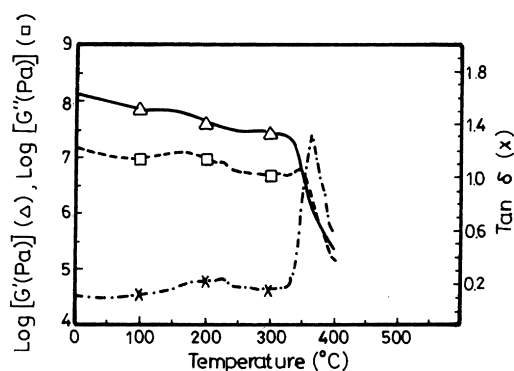**Figure 4** Dynamic mechanical analysis curves for III_e at a heating rate $5°C\ min^{-1}$.

transition on the temperature scale between 30 and 400°C. This is attributed to the fact that T_g values of the polyamides **III** exceed their thermal decomposition temperatures, as discussed below in the DMA results.

More detailed information can be obtained from the dynamic mechanical behaviour measurements taken of the films as a function of temperature. Films of about 50 μm thickness were studied between 0 and 400°C. *Figure 3* depicts the mechanical relaxation spectra of III_d. Based on tan δ and G'' peaks, two profound relaxations appeared at *ca.* 100 and 345°C. The relaxation process can be approached by verifying results obtained with other related polymers[19–21]. The low temperature transition, i.e. around 100°C, arose in G'' and tan δ. The relaxation in polyamides was probably related to the rotation of rigid segments of the *p*-phenylene and amide groups around 'hinges' such as –O– and –CH$_2$– in diamines[19–21]. Such a transition also appeared in other related polymers. With an increasing temperature, G' steadily decreases from 0 to 320°C, without showing either abrupt changes or a marked relaxation. The main relaxation of III_d, at around 345°C, was possibly due to the glass relaxation process. However, the main relaxation of polyamide III_d nearly approached their thermal decomposition, thereby accounting for why precisely determining the main relaxation is difficult. *Figure 3* also indicates that the polyamide III_d exhibited good retention of storage modulus at a temperature exceeding 320°C.

Figure 4 depicts the mechanical relaxation spectra of polyamide III_e. Two relaxations also occurred in polyamide III_e on the temperature scale between 0 and 400°C. The low temperature, at around 200°C, is extremely broad in G'' and

tan δ. Moreover, the relaxation is associated with a step decrease in G''. The reason for this relaxation resembles that of III_d. The main relaxation at around 342°C is probably due to thermal decomposition. The mechanical relaxation spectra of the other polyamides **III** resembles those of III_d. *Table 5* summarizes the α relaxation temperatures of polyamides **III**. This table indicates that the α relaxation temperatures of polyamides **III** are generally high, ranging from 342 to 381°C. The high α relaxation is attributed to that the rotation of these bonds were hindered by the bulky and rigid 4,9-diphenyldiamantylene units, resulting in an increasing chain stiffness. This same table also reveals that the α relaxation temperatures of the polyamides III_e, III_f and III_g derived from the alicyclic dicarboxylic acids resemble those of the polyamides derived from the aromatic dicarboxylic acids.

CONCLUSION

According to the results presented herein, introducing a diamantane unit into the polyamide backbone yielded polyamides **III** with good thermal stability, high α relaxation temperature, and good retention of storage modulus approaching thermal decomposition temperature. The polyamides had high inherent viscosities, ranging from 0.65 to 1.65 dl g^{-1}. Their $\bar{M}_n$ values ranged from 32 000 to 140 000. In addition, incorporating bulky diamantane units and flexible ether linkages into the polyamides **III** allowed most of the polyamides **III**, except III_a and III_f, to have good solubility, and most of the polyamides **III** were soluble in NMP, DMAc and pyridine. Colorless polyamide films were obtained. Polyamides had a tensile strength up to 116.1 MPa, elongation value at break up to 60.5%, and initial modulus up to 2.1 GPa. DMA reveals two relaxations arose on the temperature scale between 0 and 400°C in the polyamides **III**. Their α relaxations occurred at high temperatures, ranging from 342 to 381°C. Their temperatures at a 5% weight loss ranged from 384 to 433°C in air and from 387 to 436°C in N$_2$ atmosphere. Further, introducing alicyclic dicarboxylic acid into the polyamide backbone allowed polyamides III_e, III_f and III_g to maintain high α relaxations but lower thermal stabilities.

REFERENCES

1. Yamazaki, N., Higashi, F. and Kawabata, J. J., *Polym. Sci. Polym. Chem. Ed.*, 1974, **12**, 2149.
2. Yamazaki, N., Matsumoto, M. and Higashi, F. J., *Polym. Sci. Polym. Chem. Ed.*, 1975, **13**, 1373.
3. Perry, P. J. and Wilson, B. D., *Macromolecules*, 1993, **26**, 1503.
4. Perry, P. J., Tuner, S. R. and Blevins, R. W., *Macromolecules*, 1993, **26**, 1509.
5. Oishi, Y., Kakimoto, M. and Imai, Y., *Macromolecules*, 1988, **21**, 547.
6. Olah, G. A., Prakash, G. K. S., Shin, J. G., Krishnamurthy, V. V., Mateescu, G. D., Liang, G., Sipos, G., Buss, V., Gund, T. M. and Schleyer, P. v. R., *J. Am. Chem. Soc.*, 1985, **107**, 2764.
7. Vogel, O., Anderson, B. C. and Simons, D. M., *Tetrahedron Lett.*, 1966, **4**, 415.
8. Malik, A. A., Archibald, T. G. and Baum, K., *Macromolecules*, 1991, **24**, 5266.
9. Dang, T. D., Archibald, T. G., Malik, A. A., Bonsu, F. O., Baum, K., Tan, L. S. and Arnold, F. E., *Polymer Prepr.*, 1991, **32**(3), 199.
10. Chapman, O. L. and Ortiz, R., *Polym. Prepr.*, 1995, **36**(1), 739.
11. Chern, Y. T. and Wang, W. L., *Macromolecules*, 1995, **28**, 5554.
12. Chern, Y. T., *Macromolecules*, 1995, **28**, 5561.
13. Chern, Y. T., Fang, J. S. and Kao, S. C., *J. Polym. Sci. Polym. Chem. Ed.*, 1995, **58**, 1417.

14. Chern, Y. T. and Wang, W. L., *J. Polym. Sci. Polym. Chem.*, 1996, **34**, 1501.
15. Chern, Y. T. and Chung, W. H., *Makromol. Chem. Phys.*, 1996, **197**, 1171.
16. Chern, Y. T. and Lin, M. C., *Polym. Bull.*, 1995, **35**, 41.
17. Chern, Y. T. and Shiue, H. C., *Macromolecules*, 1997, **30**, 5766.
18. Yamazaki, N., Matsumoto, M. and Higashi, F. J., *Polym. Sci. Polym. Chem. Ed.*, 1975, **13**, 1373.
19. Steeman, P. A. M. and Maurer, F. H., *J. Polymer*, 1992, **33**, 4236.
20. Frosini, V. and Butta, E., *J. Polym. Sci. Polym. Lett.*, 1971, **9**, 253.
21. Sun, Z., Dong, L., Zhuang, Y., Cao, L., Ding, M. and Feng, Z., *Polymer*, 1992, **33**, 4728.