

# Synthesis of polyamides derived from 4,9-bis(4-aminophenyl)diamantane

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A series of new polyamides were synthesized by direct polycondensation of the 4,9-bis(4-aminophenyl)diamantane with various dicarboxylic acids. The most polyamides had high inherent viscosities, ranging from 1.08 to 2.10 dl/g. Polyamides had tensile strength up to 92.8 MPa, and initial modulus reached 2.1 GPa. Although these polyamides were incorporated by the quite rigid diphenyldiamantane unit, surprisingly, all three polyamide films have tough quality. Dynamic mechanical analysis (DMA) reveals that the polyamides have three relaxations. Their  $\alpha$  relaxations occurred at high temperatures, ranging from 417 to 489°C. All three polyamide films show rather high  $G'$  values (above  $10^8$  Pa), even at temperatures exceeding 400°C. The glass transition of polyamide derived from ( $\pm$ )-1,3-cyclohexanedicarboxylic acid appeared at 417°C. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Thermally stable polymers have received extensive interest over the past decade because of increasing demands for high temperature polymers as replacements for metals or ceramics in the automotive, aerospace, and microelectronics industries. Polyamides are certainly one of the most successful classes of high-temperature polymers, and have found extensive use in the aviation, automotive, and electronic industries. However, these polyamides encounter processing difficulty due to their infusibility and poor solubility in organic solvents. Therefore, much research focuses on the modification of hard processing, i.e. attempting to maintain considerable thermal stability and improve its solubility. These studies<sup>1–11</sup> include: (1) introducing rather soft segments on the main chain (such as CH<sub>2</sub>); (2) breaking its symmetry and regularity, thereby making crystallization impossible; (3) introducing the bulky side groups to be exempt from the crystallization; (4) forming a three-dimensional structure without sharing the same surface; and (5) destroying the hydrogen-bonding by N-substitution with certain groups such as methyl.

Diamantane is a cycloaliphatic-cage hydrocarbon containing an 'extended-cage' adamantane structure<sup>12,13</sup>. Although diamantane was investigated for many years, only a few example of the polymers based on diamantane are known<sup>14–22</sup>. Regarding the incorporation of diamantane into polyamides, only we have reported that incorporation of 1,6- or 4,9-diamantane units into polyamides, had good thermal stability and good retention of storage modulus above 350°C<sup>17,20</sup>. Therefore, it is of interest to synthesize and characterize high temperature polyamides in which a diamantane nuclei are incorporated.

Herein, we successfully synthesize new polyamides involving 4,9-bis(4-aminophenyl)diamantane (**1**) by the direct polycondensation with various dicarboxylic acids **2** (Scheme 1). In addition, the solubility, dynamic mechanical properties, and thermal properties of polyamides were also investigated.

## EXPERIMENTAL

### Materials

Terephthalic acid (**2<sub>a</sub>**), isophthalic acid (**2<sub>b</sub>**), 4,4'-oxybis(benzoic acid) (**2<sub>c</sub>**), 5-*tert*-butylisophthalic acid (**2<sub>d</sub>**), *cis*-1,4-cyclohexanedicarboxylic acid (**2<sub>e</sub>**), *trans*-1,4-cyclohexanedicarboxylic acid (**2<sub>f</sub>**), and ( $\pm$ )-1,3-cyclohexanedicarboxylic acid (**2<sub>g</sub>**, mixture of *cis* and *trans*) were purified by vacuum sublimation. Anhydrous LiCl 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*-dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride, and stored over 4 Å molecular sieves. 4,9-Dibromodiamantane was prepared according to our previous study<sup>20</sup>.

4,9-Bis(4-aminophenyl)diamantane (**1**) was synthesized from 4,9-dibromodiamantane in three steps. 4,9-Dibromodiamantane reacted with benzene to generate 4,9-diphenyldiamantane. Next, 4,9-diphenyldiamantane reacted with fuming nitric acid in the presence of glacial acetic acid to generate 4,9-bis(4-nitrophenyl) diamantane, which was then hydrogenated to obtain compound **1**. Our previous studies provide a detailed procedure for preparing **1**<sup>23</sup>: m.p. 316–318°C; i.r. (KBr) 3453, 3325, 3057, 2890, 2867, 1623, 1513 cm<sup>-1</sup>; m.s. (EI) *m/z* 370 (M<sup>+</sup>, 100); <sup>1</sup>H n.m.r. (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.90 (d, 18H, hydrogen of diamantane), 3.55 (brs, 4H, NH<sub>2</sub>), 6.66 (d, *J* = 8.23, 4H, ArH), 7.18 (d, *J* = 8.64, 4H, ArH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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); Analysis calculated for C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>: 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 FTi.r. spectrophotometer was used to record i.r. spectra (KBr pellets). In a typical experiment, an average of 20 scans per sample was made. Inherent viscosities of all polymers were determined at 0.5 g/dl

**Table 1** Effect of reaction conditions on polymerization<sup>a</sup>

Part	Reaction conditions			Polymer	
	Monomer <sup>b</sup> (mol/l)	Reaction temp. (°C)	Reaction time (h)	Yield (%)	$\eta_{inh}^c$ (dl/g)
I	0.08	125	3	94	0.99
	0.10	125	3	95	1.04
	0.15	125	3	96	0.89
II	0.10	125	3	95	1.04
	0.10	125	5	96	1.60
	0.10	125	7	94	1.52
III	0.10	105	5	95	0.98
	0.10	115	5	97	1.66
	0.10	125	5	96	1.60
	0.10	135	5	95	1.20

<sup>a</sup> The reaction conditions are at a pyridine/NMP ratio of 0.25, P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>/I ratio at 2 and concentration of LiCl at 5 (w/v)%

<sup>b</sup> [1] = [2<sub>d</sub>]

<sup>c</sup> Measured at 30°C at concentration of 0.5 g/dl in NMP containing 5% w/v LiCl

concentration using an Ubbelohde viscometer. Gel permeation chromatography (GPC) on soluble polyamides was performed on an Applied Biosystem at 70°C with two PLgel 5  $\mu$ m 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 analyser were then 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/min and a heating rate of 20°C/min. The thermogravimetric analysis (t.g.a.) was determined under a nitrogen flow of 50 cc/min with a heating rate of 20°C/min. Dynamic mechanical analysis (d.m.a.) was performed on a Du Pont 9900 thermal analyser system. A sample of 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 $\alpha$  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.

#### Polymerization

A typical example of the polycondensation is given later.

Polyamide 3<sub>d</sub> was synthesized from 1 and 2<sub>d</sub>. A mixture of 0.740 g (2 mmol) of 1, 0.444 g (2 mmol) of 2<sub>d</sub>, 1.0 g of LiCl, 1.23 g (4 mmol) of triphenylphosphite, 4 ml pyridine, and 16 ml of NMP was heated and stirred at 115°C for 5 h. The obtained polymer solution was trickled into 500 ml of methanol, giving rise to a fibrous white precipitate that was thoroughly washed with methanol and hot water, collected by filtration, and dried. The yield was nearly quantitative. The inherent viscosity of the polyamide 3<sub>d</sub> was 1.66 dl/g, measured at 0.5 g/dl concentration in NMP containing dissolved 5 (w/v)% LiCl at 30°C. The IR

spectrum contained absorption peaks at 3306 cm<sup>-1</sup> (N-H str) and 1665 cm<sup>-1</sup> (C=O str), characteristic of the amide group. Analysis calculated for C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>: C, 82.01; H, 7.19; N, 5.04. Found: C, 81.65; H, 7.25; N, 4.68 (The values were corrected for moisture content according to previous method<sup>17</sup>).

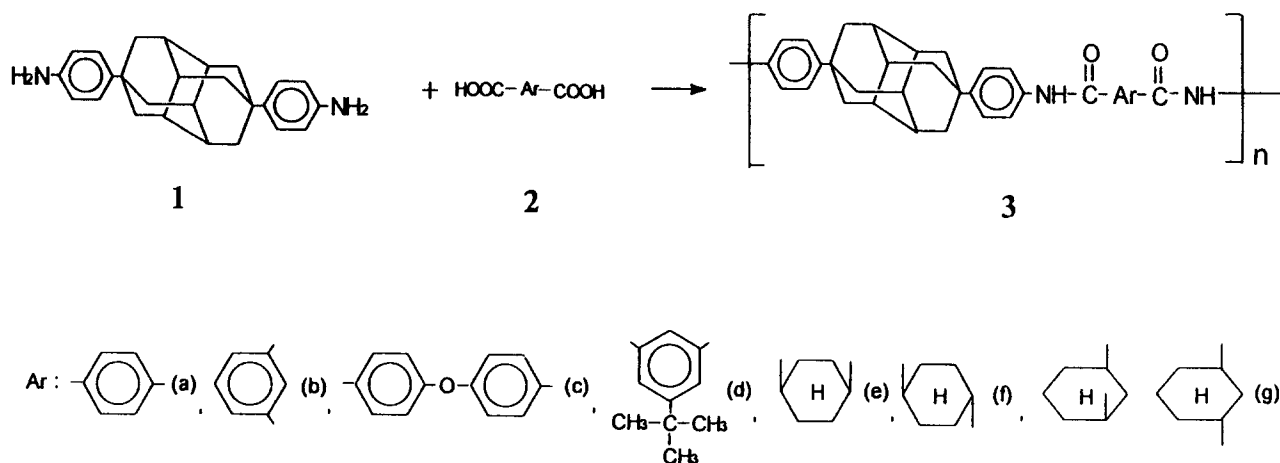
## RESULTS AND DISCUSSION

### Effect of the reaction parameters on the inherent viscosities of 3<sub>d</sub>

Part I in Table 1 reveals that the inherent viscosities of polyamide 3<sub>d</sub> increased with an increasing monomer concentration up to 0.10 M. A higher concentration of monomer led to an adverse effect in the solubility of polyamide. This caused a decrease of the inherent viscosity of polyamide. Part II in Table 1 also indicates that the inherent viscosity of polyamide 3<sub>d</sub> markedly increased with an increasing reaction time. However, a decreased inherent viscosity of 1.52 dl/g was obtained when the reaction time was 7 h. According to Part III in Table 1, the inherent viscosities of polyamide 3<sub>d</sub> increased with increasing reaction temperature up to 115°C. However, a decreased inherent viscosity was obtained when the reaction temperature exceeded 115°C. This decrease in viscosity might cause an adverse effect on the complex form derived from LiCl and phenol at an excessively high temperature, subsequently causing side reactions to increase<sup>24</sup>. Therefore, in this work the inherent viscosity of the polyamide 3<sub>d</sub> decreased. From these results, we infer that the most favorable conditions for this system are a monomer concentration of 0.10 M, reaction temperature of 115°C, and reaction time of 5 h.

### Synthesis of polyamides

Various new polyamides were prepared from compound 1 with the corresponding dicarboxylic acids 2 by using the most favorable conditions for the reaction with 5-tert-butylisophthalic acid (2<sub>d</sub>), as shown in Scheme 1. Polycondensation results are listed in Table 2. All polyamides were obtained with nearly quantitative yield. Most of the polyamides, except 3<sub>a</sub> and 3<sub>f</sub>, had high inherent viscosities, ranging from 1.08 to 2.10 dl/g. The unsatisfactory results obtained from terephthalic acid (2<sub>a</sub>) and



Scheme 1

Table 2 Synthesis of polyamides<sup>a</sup>

Polymer	Yield (%)	$\eta_{inh}^b$ (dL/g)	Remark <sup>c</sup>	$\bar{M}_n^f \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
<b>3<sub>a</sub></b>	98	0.23 <sup>c</sup>	P	— <sup>g</sup>	—
<b>3<sub>b</sub></b>	98	2.10 <sup>d</sup>	G	11.9	1.6
<b>3<sub>c</sub></b>	91	1.29	P	7.8	2.0
<b>3<sub>d</sub></b>	97	1.66	S	11.5	1.8
<b>3<sub>e</sub></b>	98	1.08 <sup>d</sup>	S	5.4	1.5
<b>3<sub>f</sub></b>	94	0.50 <sup>c</sup>	P	—	—
<b>3<sub>g</sub></b>	95	1.94	S	14	3.9

<sup>a</sup> [I] = [dicarboxylic acid] = 0.10 M; Pyridine/NMP = 0.25; P(OC6H5)<sub>3</sub>/I = 2.0; LiCl = 5 (w/v)%; temperature = 115°C; time = 5 h

<sup>b</sup> Measured at 30°C at a concentration of 0.5 g/dl in NMP containing 3 (w/v)% LiCl

<sup>c</sup> Measured at 30°C at a concentration of 0.5 g/dl in H<sub>2</sub>SO<sub>4</sub>

<sup>d</sup> Measured at 30°C at a concentration of 0.25 g/dl in NMP containing 3 (w/v)% LiCl

<sup>e</sup> Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation; G, swollen gel

<sup>f</sup> By g.p.c. (relative to polystyrene)

<sup>g</sup> Could not be measured

Table 3 Solubility of polyamides<sup>a</sup>

Solvent	Polymer						
	<b>3<sub>a</sub></b>	<b>3<sub>b</sub></b>	<b>3<sub>c</sub></b>	<b>3<sub>d</sub></b>	<b>3<sub>e</sub></b>	<b>3<sub>f</sub></b>	<b>3<sub>g</sub></b>
NMP	+ -	+ -	+ -	++	+ -	-	+
DMAc	-	-	+ -	+ -	+ -	-	-
DMF	-	-	-	-	-	-	-
Pyridine	+ -	+ -	+ -	+ -	+ -	-	+ -
DMAc/LiCl <sup>b</sup>	+ -	+	+	++	+	+ -	++
NMP/LiCl <sup>b</sup>	+ -	+	+	++	+	+ -	++

<sup>a</sup> 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

<sup>b</sup> Concentration of LiCl is 3 (w/v)%

*trans*-1,4-cyclohexanedicarboxylic acid (**2<sub>f</sub>**) were caused by the poor solubility of both polyamides (**3<sub>a</sub>** and **3<sub>f</sub>**). Although the reaction medium of **3<sub>c</sub>** also formed a polymer precipitation during the reaction, the inherent viscosity of **3<sub>c</sub>** remained high. In addition, although the reaction medium of **3<sub>b</sub>** formed a swollen gel during the reaction, the inherent viscosity of **3<sub>b</sub>** also remained high. Interestingly, polyamides **3<sub>b</sub>** and **3<sub>e</sub>** displayed the most interesting solution behaviour. At the 5.0% solid level, the viscous polymerization mixture of **3<sub>b</sub>** and **3<sub>e</sub>** remained clear and stirrable until they were allowed to cool to 120 and 80°C, respectively. The individual mixture then slowly set to a gel-like mass.

The process was reversible as the gel could be dissolved by heating or formed by cooling. According to g.p.c. data, polyamides **3** had medium and high number-average molecular weight ( $\bar{M}_n$ ) of 54 000~140 000. FTi.r. spectroscopy confirmed the formation of polyamides **3**. FTi.r. spectra of the polyamides detected characteristic amide bands appearing at 3289~3333 cm<sup>-1</sup> (N-H str) and 1655~1670 cm<sup>-1</sup> (C=O str).

#### Characterization of polyamides

The solubility of polyamides were tested in various solvents. Table 3 summarizes those results. As a result of the

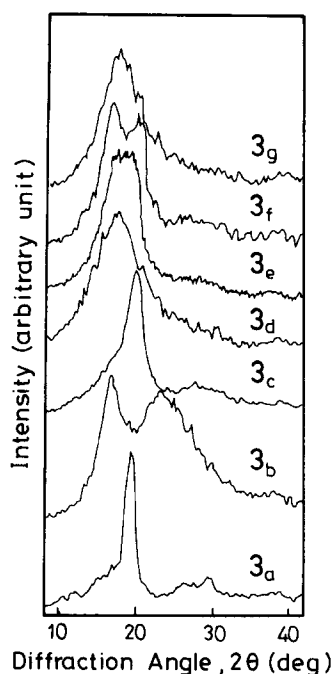


Figure 1 Wide-angle X-ray diffraction curves of polyamides

Table 4 Mechanical properties of polyamide films

Polymer	Strength to break (MPa)	Elongation to break (5)	Initial modulus (GPa)
3 <sub>d</sub>	90.9 (78.6) <sup>a</sup>	17.3 (8.5)	2.1 (2.1)
3 <sub>e</sub>	68.6 (67.5)	26.7 (4.3)	1.9 (2.0)
3 <sub>g</sub>	92.8 (87.8)	25.3 (6.3)	2.0 (2.0)

<sup>a</sup> The values in parentheses are those of the polyamides derived from 1,6-bis(4-aminophenyl)diamantane<sup>25</sup>

Table 5 Thermal properties of polyamides

Polymer	d.m.a. <sup>a</sup> $T_{\alpha}$ (°C)	Decomposition temperature (°C) <sup>b</sup>	
		in air	in N <sub>2</sub>
3 <sub>a</sub>	— <sup>c</sup>	425	448
3 <sub>b</sub>	—	431	452
3 <sub>c</sub>	—	423	445
3 <sub>d</sub>	450	405	437
3 <sub>e</sub>	489	380	417
3 <sub>f</sub>	—	375	408
3 <sub>g</sub>	417	378	405

<sup>a</sup> The  $\alpha$  transition measured by d.m.a. using shear mode at a heating rate of 5°C/min

<sup>b</sup> Temperature at which 5% weight loss recorded by t.g. at a heating rate of 20°C/min

<sup>c</sup> Could not be measured

incorporation of rigid diphenyldiamantane units into polyamides **3**, their solubility were not ideal. Only polyamides **3<sub>d</sub>** and **3<sub>g</sub>** were soluble in NMP. When NMP and DMAc were added with 3 (w/v)% LiCl, the solubility of polyamides **3<sub>b</sub>**, **3<sub>c</sub>** and **3<sub>e</sub>** were markedly enhanced. However, the polyamides **3<sub>a</sub>** and **3<sub>f</sub>** were not soluble in tested solvents. This inferiority is attributed to the fact that the polyamides **3<sub>a</sub>** and **3<sub>f</sub>** contained relatively rigid and symmetrical structures in the diacid moieties of polyamides **3<sub>a</sub>** and **3<sub>f</sub>**. X-ray diffraction results, as discussed later, also revealed that **3<sub>a</sub>** and **3<sub>f</sub>** had semi-crystalline patterns.

The wide-angle X-ray diffractograms of the polyamides **3** are given in Figure 1. Polymers **3<sub>a</sub>** and **3<sub>c</sub>** showed

semicrystalline patterns, exhibiting similar crystalline peaks ( $2\theta$ ) appearing at around 19°; similarity in lattice parameters for both polymers is expected. Polymer **3<sub>b</sub>** also shows a semicrystalline pattern, exhibiting crystalline peaks ( $2\theta$ ) appearing at around 16 and 23°. The other polyamides had nearly the same amorphous patterns with broad peaks appearing ( $2\theta$ ) at around 17°. Additional work is required to characterize the structures more accurately.

Colourless films of polymers **3<sub>d</sub>** and **3<sub>g</sub>** were obtained by casting from their NMP solutions. Polyamide **3<sub>g</sub>** was cast at a high temperature of 80°C. Polyamide films **3<sub>b</sub>** and **3<sub>e</sub>** were also obtained by casting at high temperatures from their NMP solutions containing 3 (w/v)% LiCl. Polyamide **3<sub>b</sub>** was cast into a film but quite brittle. However, the other polyamide films were not obtained, because of their poor solubility. The mechanical properties were determined via an Instron machine. Table 4 summarizes the tensile properties of polyamides. In general, mechanical properties of these films were good. Surprisingly, all three films are extremely tough in nature, and their elongations to breakage values ranged from 17.3% and 26.7%. A comparison of tensile properties of the systems studied herein with the corresponding polyamides derived from 1,6-bis(4-aminophenyl)diamantane<sup>25</sup> shows that the polyamides derived from 4,9-bis(4-aminophenyl)diamantane are markedly tough as shown in Table 4. The difference on mechanical properties may be caused by the different internal structures derived from the various monomers. In general, the properties of materials depend on their internal structures. Additional work is required to characterize the structures more accurately.

Thermal analysis was performed by d.s.c., d.m.a. and t.g.a. Table 5 summarizes those results. The temperatures of polyamides **3** at 5% weight loss ranged from 375 to 431°C in air and from 405 to 452°C in an N<sub>2</sub> atmosphere. When the polyamides were derived from the alicyclic dicarboxylic acids **2<sub>e</sub>**, **2<sub>f</sub>** and **2<sub>g</sub>**, their temperatures at a 5% weight loss were lower than those of the polyamides **3** derived from the aromatic dicarboxylic acids. As for the d.s.c. experiment, initial heating of samples was curtailed at 300°C. In addition,  $T_g$  and other thermal properties were evaluated according to the d.s.c. charts of the second heating. Polyamides **3** did not display a typical glass transition between 30 and 400°C. This is attributed to the fact that these polyamides possess  $T_g$  values that exceed their thermal decomposition temperatures, as discussed later in the d.m.a. results.

The mechanical relaxation spectra of **3<sub>e</sub>** are shown in Figure 2. Films of about 40  $\mu$ m thickness were studied. Based on  $\tan \delta$  and  $G''$  peaks, three relaxations appeared at ca. -40, 240 and 489°C. The relaxation process can be compared to results obtained with other related polymers<sup>26-28</sup>. The low temperature transition of -40°C is a typical relaxation for polyamides. This relaxation is attributed to a mechanism of motion (rotation) of the amide bonds together with water molecules that are bonded to them. The second transition, i.e. around 240°C, was observed in  $G''$  and  $\tan \delta$ , and this relaxation is associated with a step decrease in  $G''$ . The relaxation in polyamides is probably related to the rotation or oscillation of the phenyl groups within the diamine moiety of the polyamide. Such a transition was also seen in related polymers<sup>26-28</sup>. The main relaxation, at around 489°C, is probably caused by thermal decomposition. It is noted that polyamide **3<sub>e</sub>** exhibited good retention of storage modulus at a temperature exceeding 420°C.

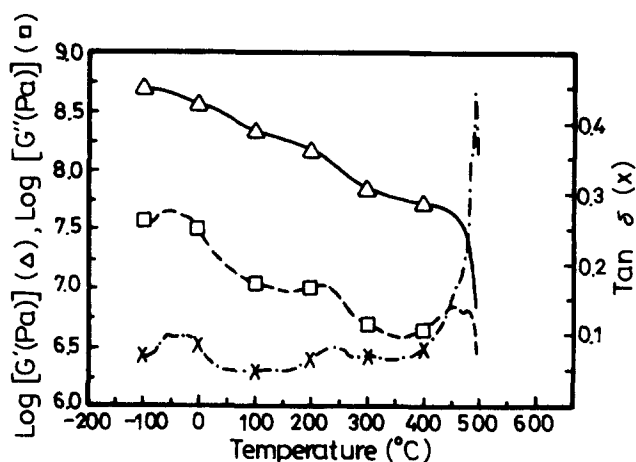


Figure 2 Dynamic mechanical analysis curves for  $3_e$  at a heating rate of  $5^\circ\text{C}/\text{min}$

The mechanical relaxation spectra of polyamide  $3_d$  resembles those of  $3_e$ . Three relaxations were also observed in polyamide  $3_d$  on the temperature scale between  $-100$  and  $400^\circ\text{C}$ . The low-temperature transition shifted to  $-75^\circ\text{C}$ . The second relaxation appeared at  $200^\circ\text{C}$ . In addition, the main transition appeared at  $450^\circ\text{C}$ . The reason for all three relaxations resemble that for polyamide  $3_e$ . In addition, the mechanical relaxation spectra of polyamide  $3_g$  resembles those of the previous discussed polyamides. Two relaxations were observed in polyamide  $3_g$  on the temperature scale between  $0$  and  $400^\circ\text{C}$ . The subglass relaxation appeared at about  $125^\circ\text{C}$ . The reason for the relaxation (at  $125^\circ\text{C}$ ) is similar to that of polyamide  $3_e$ . The main transition, at around  $417^\circ\text{C}$ , was observed in  $G''$  and  $\tan \delta$ , and the main relaxation is associated with an order of magnitude step decrease of approximately  $0.8$  in  $G'$ . The main relaxation ( $417^\circ\text{C}$ ) was interpreted as a glass relaxation process followed by a thermal decomposition well above  $425^\circ\text{C}$ . In all three cases, polyamides show rather high  $G''$  values (above  $10^8$  Pa) even at temperatures exceeding  $400^\circ\text{C}$ .

## CONCLUSION

According to the results presented herein, introducing the diamantyl unit into the polyamide backbone gave polymers with good thermal stability, high  $\alpha$  relaxation temperatures, and good retention of storage moduli approaching the thermal decomposition temperature. In addition, the diamantane unit can readily be incorporated into polyamides through the extended monomer method to obtain high molecular weight materials. However, the rigid

4,9-diphenyldiamantane unit does decrease solubility and processability but without diminishing thermoproperties. Overall, such a rigid cycloaliphatic unit can provide routes to new materials with improved optical properties without sacrificing thermal behavior.

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