

# Synthesis and Characterization of New Polyamides Derived from 1,3-Bis[4-(4-aminophenoxy)phenyl]adamantane

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**ABSTRACT:** Several new polyamides were synthesized by direct polycondensation of the 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane (**I**) with various dicarboxylic acids. The polyamides had inherent viscosities and number-average molecular weights ( $M_n$ ) of 0.46–0.96 dL/g and 28,000–109,000, respectively. All polyamides **III** had good solubilities and were soluble in *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and pyridine. Polyamides had tensile strengths of up to 72.3 MPa, elongation to breakage values of up to 10.2%, and initial modulus of up to 2.1 GPa. Their glass transition temperatures were found to be 228–269°C and 252–307°C using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively. The melting temperature of **III<sub>f</sub>** was observed at 318°C using DSC. The temperatures of polyamides **III** at a 5% weight loss ranged from 395 to 435°C in air and from 400 to 450°C in a N<sub>2</sub> atmosphere. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 315–321, 1998

**Key words:** polyamides; adamantane; synthesis

## INTRODUCTION

High-performance polymers are used in applications demanding service at elevated temperature while maintaining their structural integrity and an excellent combination of chemical, physical, and mechanical properties. Polyamides are certainly one of the most successful classes of high-temperature polymers and have found extensive use in the aviation and automotive industries. However, these polyamides are difficult to process due to their infusibility and poor solubility in organic solvents. The reasons for processing difficulty are strong interchain forces, inherent mac-

romolecular rigidity, or semicrystallinity. Many studies<sup>1–10</sup> have attempted to enhance their processability and solubility by introducing bulky side groups or flexible chains into the polyamide backbone, by attaching bulky side groups, by breaking its symmetry and regularity, or by destroying the hydrogen bonding by *N*-substitution with certain groups such as methyl. In a similar manner, noncoplanar diamines are quite effective in the improvement of solubilities.<sup>11</sup>

Adamantane has also been incorporated into the backbone of many polymers including polyamides, polysulfones, polyesters, and polyimides, subsequently producing increased thermal stability and glass transition temperature.<sup>12</sup> The feasibility of incorporating adamantane as a pendant group on the polymer backbone has been examined, leading to decreased crystallinity, increased solubility, and enhanced glass transition temperature and thermal stability.<sup>13,14</sup> In addition, ther-

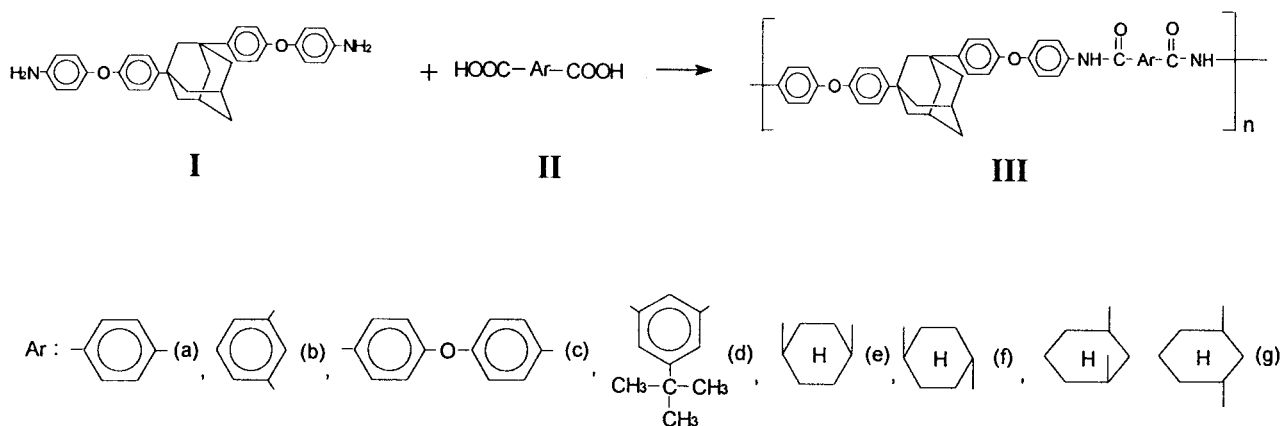
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Scheme 1

mosetting polymers based on acetylene derivatives of adamantane have been reported as well.<sup>15,16</sup> Although the feasibility of incorporating adamantane into the polyamide backbone has been examined, investigations involving the relation to the physical properties of polyamides based on adamantane are limited. Our previous work described the preparation of polyamides based on adamantane.<sup>17</sup> However, the polyamide films have not been successfully prepared due to the low inherent viscosities of the polymers.

Therefore, it is of interest to synthesize and characterize polyamides in which adamantane is incorporated into the backbone. To improve their processability, a noncoplanar and asymmetric new diamine containing flexible ether segments, 1,3-bis[4-(4-aminophenoxy)phenyl]adamantane (**I**), was incorporated into the backbone of polyamide **III**. Herein, we successfully synthesized new polyamides involving the diamine **I** by the direct polycondensation with various dicarboxylic acids **II** (Scheme 1). In addition, the solubilities, dynamic mechanical properties, and thermal properties of the polyamides were also investigated.

## EXPERIMENTAL

### Materials

Terephthalic acid (**II<sub>a</sub>**), isophthalic acid (**II<sub>b</sub>**), 4,4'-oxybis(benzoic acid) (**II<sub>c</sub>**), 5-tertbutylisophthalic acid (**II<sub>d</sub>**), *cis*-1,4-cyclohexanedicarboxylic acid (**II<sub>e</sub>**), *trans*-1,4-cyclohexanedicarboxylic acid (**II<sub>f</sub>**), and ( $\pm$ )-1,3-cyclohexanedicarboxylic acid (**II<sub>g</sub>**, 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*-dimethylacetamide (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, 1,3-dibromoadamantane was prepared.<sup>17</sup>

1,3-Bis[4-(4-aminophenoxy)phenyl]adamantane (**I**) was synthesized from 1,3-dibromoadamantane in three steps: First, 1,3-dibromoadamantane was reacted with phenol to generate 1,3-bis(4-hydroxyphenyl)adamantane. Next, the corresponding bisphenol was reacted with *p*-chloronitrobenzene in the presence of potassium carbonate to generate new 1,3-bis[4-(4-nitrophenoxy)phenyl]adamantane which was hydrogenated to generate the new diamine **I**. Our previous studies provided a detailed procedure for preparing **I**.<sup>18</sup> Its (**I**) properties are as follows: mp 191–193°C; IR (KBr) 3428, 3341, 3060, 2890, 2870, 1618, 1505  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  502 ( $M^+$ , 77), 108 (100); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  1.69 (brs, 2H, H-6), 1.84 (m, 10H, H-2, 4, 8, 9, 10), 2.20 (brs, 2H, H-5, 7), 4.93 (s, 4H, NH<sub>2</sub>), 6.56 (d,  $J$  = 8.65, 4H, ArH), 6.70–6.77 (m, 8H, ArH), 7.28 (d,  $J$  = 8.72, 4H, ArH); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  28.89 (C-5, 7), 35.09 (C-6), 36.19 (C-1, 3), 41.68 (C-4, 8, 9, 10), 48.71 (C-2), 114.74 (d, Ar), 116.06 (d, Ar), 120.43 (d, Ar), 125.74 (d, Ar), 143.79 (s, Ar), 144.98 (s, Ar), 145.97 (s, Ar), 156.52 (s, Ar).

ANAL. Calcd. for C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>: C, 81.27%; H, 6.77%; N, 5.58%. Found: C, 81.06%; H, 6.81%; N, 5.61%.

### Characterization

A Bio-Rad FTS-40 FTIR spectrophotometer was used to record the 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 a 0.5 g/dL concentration using an Ubbelohde viscometer at 30°C. 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 by UV (254 nm), and calibration was based on polystyrene standards (Shodex). Qualitative solubility was determined using 0.01 g of the polymer in 2 mL of the solvent. A DuPont 9900 differential scanning calorimeter (DSC) and a DuPont 9900 thermogravimetric analyzer were then employed to study the thermal transitions and thermal decomposition temperature of all the polymers. The DSC was run under a nitrogen stream at a flow rate of 30 mL/min and a heating rate of 20°C/min. The thermogravimetric analysis (TG) was determined under a nitrogen flow of 50 mL/min with a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) was performed on a DuPont 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 and an amplitude of 0.2 mm. The wide-angle X-ray diffraction measurements were performed on a Philips PW 1730-10 X-ray diffractometer using CuK $\alpha$  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. 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 below: Polyamide **III<sub>c</sub>** was synthesized from **I** and **II<sub>c</sub>**. A mixture of 0.803 g (1.6 mmol) of **I**, 0.323 g (1.6 mmol) of **II<sub>c</sub>**, 1.0 g of LiCl, 0.984 g (3.2 mmol) of triphenyl phosphite, 4 mL of pyridine, and 16 mL of NMP was heated and stirred in a flask fitted with a magnetic stirbar at 125°C for 5 h under nitrogen. The obtained polymer solution was trickled into 500 mL of methanol, giving rise to a fibrous white precipitate that was thoroughly washed individually with methanol and hot water, collected by filtration, and dried under a vacuum. The yield was nearly quantitative. The in-

herent viscosity of polyamide **III<sub>c</sub>** was 0.96 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 3310 cm<sup>-1</sup> (N—H str) and 1665 cm<sup>-1</sup> (C=O str), which are characteristic of the amide group.

## RESULTS AND DISCUSSION

### Effect of the Reaction Parameters on the Inherent Viscosities of **III<sub>c</sub>**

Part I of Table I reveals that the inherent viscosities of polyamide **III<sub>c</sub>** increased with an increasing monomer concentration of up to 0.08 M. However, a higher concentration of the monomer appeared to have an adverse effect on the solubility of the reaction mixture. This caused a decrease of the inherent viscosities of polyamide **III<sub>c</sub>**. Part II of Table I also indicates that the inherent viscosities of polyamide **III<sub>c</sub>** increased with an increase in the reaction temperature up to 125°C. However, a decreased inherent viscosity of 0.59 dL/g was obtained when the reaction was performed at 135°C. This decreased viscosity 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 the side reactions.<sup>19</sup> Therefore, in this work, the inherent viscosity of the formed polyamide decreased. Part III of Table I shows that the inherent viscosities of polyamide **III<sub>c</sub>** increased with increasing reaction time. However, a decreased inherent viscosity of 0.75 dL/g was obtained when the reaction time was 7 h. Such a decrease is probably attributed to a result of the increase in side reactions, that is, quite similar to those derived in the previous literature.<sup>19,20</sup> The side reactions still remain uncertain. From the above results, we can infer that the most favorable conditions for this system are the monomer concentration at 0.08 M, reaction temperature of 125°C, and reaction time at 5 h.

### Synthesis of Polyamides **III**

Various new polyamides were prepared from **I** with the corresponding dicarboxylic acid **II** (Scheme 1) by using the most favorable conditions for the reaction with *cis*-1,4-cyclohexanedicarboxylic acid (**II<sub>c</sub>**). Polycondensation results are listed in Table II. All polyamides were obtained in a nearly quantitative yield. Polyamides **III** had medium and high inherent viscosities, ranging from 0.46 to 0.96 dL/g. Ac-

**Table I Effect of Reaction Conditions on Polymerization for Polyamide III.**

Part	Reaction Conditions			Polymer		
	Monomer <sup>a</sup> (mol L)	Reaction Temp (°C)	Reaction Time (h)	Yield (%)	$\eta_{inh}^b$ (dL/g)	Remark <sup>c</sup>
I	0.06	125	5	90	0.69	S
	0.08	125	5	98	0.91	S
	0.10	125	5	97	0.62	S
	0.12	125	5	98	0.51	S
	0.15	125	5	96	0.45	S
II	0.08	115	5	97	0.86	S
	0.08	125	5	98	0.91	S
	0.08	135	5	93	0.59	S
III	0.08	125	3	92	0.56	S
	0.08	125	5	98	0.91	S
	0.08	125	7	96	0.74	S

The reaction conditions are a pyridine/NMP ratio of 0.25, a  $P(OC_6H_5)_3/I$  ratio of 2, and the concentration of LiCl of 5 (w/v) %.

<sup>a</sup>  $[I] = [II_e]$ .

<sup>b</sup> Measured at 30°C at a concentration of 0.5 g/dL in NMP containing 5% w/v LiCl.

<sup>c</sup> Appearance of the polymerization system: S, homogeneous solution.

According to the GPC data, the  $M_n$ 's of polyamides **III** had medium and high molecular weights, ranging from 28,000 to 109,000. IR spectroscopy confirmed the formation of polyamides **III**. FTIR spectra of the polyamides detected characteristic amide bands appearing at  $3290\text{--}3320\text{ cm}^{-1}$  (N—H str),  $1665\text{--}1670\text{ cm}^{-1}$  (C=O str), and  $1526\text{--}1541\text{ cm}^{-1}$  (N—H bending).

### Characterization of Polyamides

The polyamides solubilities were tested in various solvents. Table III summarizes those results. Due to the bulky and asymmetrical 1,3-adamantyl structure and flexible ether segment, polyamides

**III** had good solubilities, and they could be dissolved in NMP, DMAc, *N,N*-dimethylformamide (DMF), and pyridine. The polyamide films **III** were structurally characterized by X-ray methods. Due to the bulky and asymmetrical 1,3-adamantyl element, these polyamides **III** had nearly the same amorphous pattern with broad peaks appearing ( $2\theta$ ) at around  $17^\circ$ , as shown in Figure 1. However, polyamide **III<sub>f</sub>** had a greater tendency to form crystal than did the other polyamides **III**, due to the incorporation of symmetrical dicarboxylic acid **II<sub>f</sub>** into polyamide **III<sub>f</sub>**. Additional work is required to characterize the structures more accurately.

Colorless films of all polyamides **III** were ob-

**Table II Synthesis of Polyamides**

Polymer	Yield (%)	$\eta_{inh}^a$ (dL/g)	$M_n^b \times 10^{-4}$	$M_w/M_n$	Remark <sup>c</sup>
<b>III<sub>a</sub></b>	98	0.59	4.5	1.6	S
<b>III<sub>b</sub></b>	97	0.46	3.9	1.6	S
<b>III<sub>c</sub></b>	98	0.96	5.8	1.7	S
<b>III<sub>d</sub></b>	93	0.61	3.3	1.6	S
<b>III<sub>e</sub></b>	98	0.91	10.9	1.7	S
<b>III<sub>f</sub></b>	96	0.72	4.2	1.6	S
<b>III<sub>g</sub></b>	91	0.62	2.8	2.6	S

$[I] = [\text{dicarboxylic acid}] = 0.08M$ ; pyridine/NMP = 0.25;  $P(OC_6H_5)_3/I = 2.0$ ; LiCl = 5 (w/v) %; temperature =  $125^\circ\text{C}$ ; time = 5 h.

<sup>a</sup> Measured at  $30^\circ\text{C}$  at a concentration of 0.5 g/dL in NMP containing 3 (w/v) % LiCl.

<sup>b</sup> By GPC (relative to polystyrene).

<sup>c</sup> Appearance of the polymerization system: S, homogeneous solution.

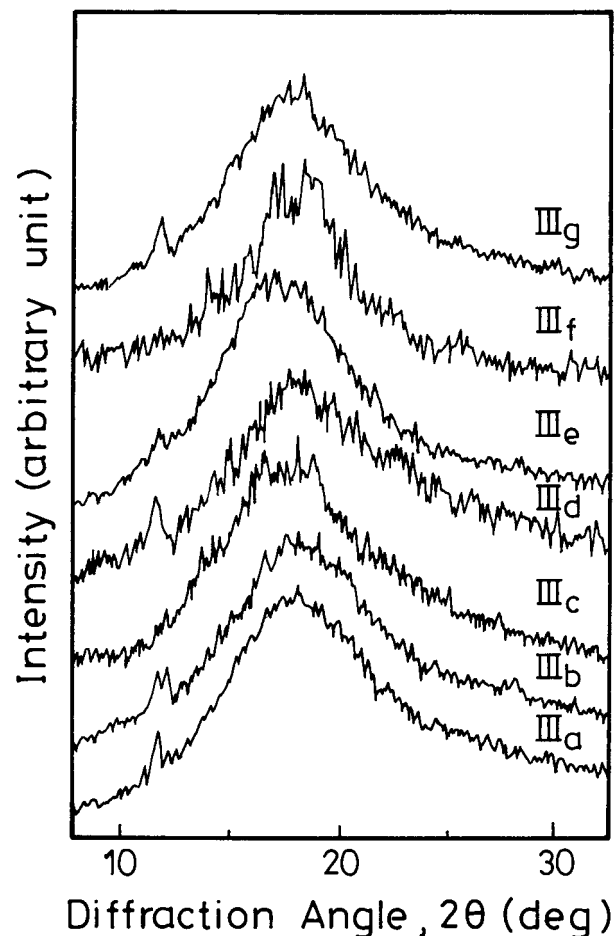
**Table III Solubility of Polyamides**

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

Solubility: ++, soluble at room temperature; +, soluble on heating at 60°C; +–, partial soluble on heating at 60°C; –, insoluble on heating at 60°C. NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide.

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

tained. However, polyamide III<sub>f</sub> was cast into a film that was quite brittle. Such a brittle behavior is possibly attributed to the greater tendency of polyamide III<sub>f</sub> to form crystal compared to the



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

other polyamides III. The mechanical properties were determined via an Instron machine. The tensile properties of the polyamides are summarized in Table IV. The mechanical properties of these films were, on the whole, medium. Polyamides III had tensile strengths of 49.5–72.3 MPa, elongation-to-breakage values of 3.6–10.2%, and initial moduli of 2.0–2.1 GPa.

Thermal analysis was performed using DSC, DMA, and TGA. Table V summarizes those results. The temperatures of polyamides III at a 5% weight loss ranged from 395 to 435°C in air and from 400 to 450°C in an N<sub>2</sub> atmosphere. When the polyamides III were derived from the alicyclic dicarboxylic acids III<sub>e</sub>, III<sub>f</sub>, and III<sub>g</sub>, their temperatures at a 5% weight loss were lower than those of the polyamides derived from the aromatic dicarboxylic acids. As for the DSC experiment, initial heating of the samples was curtailed at 300°C. In addition, the *T<sub>g</sub>* and other thermal properties were evaluated according to the DSC charts of the second heating. Figure 2 indicates that almost all polyamides III, except III<sub>f</sub>, showed typical glass transitions ranging from 228 to 269°C. In polymer

**Table IV Mechanical Properties of Polyamide Films**

Polymer	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
III <sub>a</sub>	56.2	6.9	2.1
III <sub>b</sub>	49.5	10.2	2.1
III <sub>c</sub>	60.2	3.6	2.0
III <sub>d</sub>	64.1	3.6	2.1
III <sub>e</sub>	72.3	4.3	2.0
III <sub>g</sub>	58.4	6.3	2.0

**Table V** Thermal Properties of Polyamides

Polymer	DSC <sup>a</sup>		DMA <sup>b</sup>	Decomposition <sup>c</sup> Temperature (°C)	
	$T_g$ (°C)	$T_m$ (°C)	$T_g$ (°C)	In Air	In N <sub>2</sub>
III <sub>a</sub>	269		299	426	440
III <sub>b</sub>	245		283	435	450
III <sub>c</sub>	228		253	430	443
III <sub>d</sub>	259		307	419	442
III <sub>e</sub>	229		252	408	420
III <sub>f</sub>	— <sup>d</sup>	318	— <sup>e</sup>	395	400
III <sub>g</sub>	234		263	401	417

<sup>a</sup> Glass transition temperature ( $T_g$ ) and melting transition temperature measured by DSC at a heating rate of 10°C/min in nitrogen.

<sup>b</sup> Glass transitions measured by DMA using shear mode at a heating rate of 5°C/min.

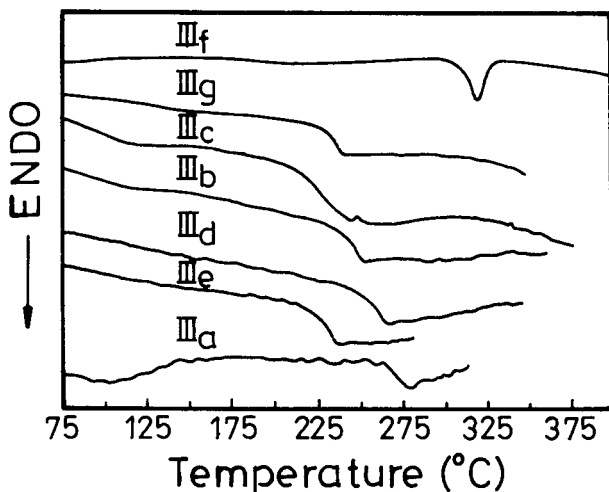
<sup>c</sup> Temperature at which 5% weight loss recorded by TG at a heating rate of 20°C/min.

<sup>d</sup> Not found.

<sup>e</sup> Could not be measured.

III<sub>f</sub>, the transition from an ordered solid to an isotropic melt gave rise to sharp endothermic peaks appearing around 318°C.

The mechanical relaxation spectra of polyamide III<sub>d</sub> is shown in Figure 3. A film of about 60 μm thickness was studied on the temperature scale between -100 and 350°C. Based on tan δ and  $G''$  peaks, two profound relaxations were observed at -60 and 307°C. The relaxation process can be approached by verifying results obtained with other related polymers.<sup>21,22</sup> The low-temperature relaxation, at around -60°C, was observed in  $G''$  and tan δ. The relaxation had very little effect on the values of the real part of the modulus  $G'$ . This

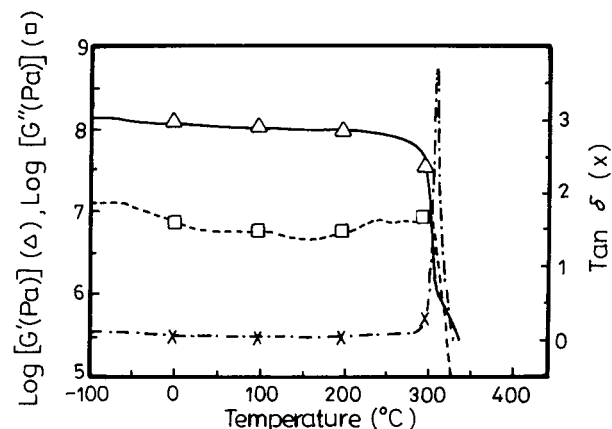


**Figure 2** DSC thermograms of the studied polymers at a heating rate of 20°C/min in a nitrogen atmosphere.

relaxation is attributed to a mechanism of motion (rotation) of the amide bonds together with water molecules that are bonded to them.<sup>21,22</sup> A shoulder peak was observed at 250°C in  $G''$ . The glass relaxation at around 307°C is associated with approximately a two orders of magnitude decrease in  $G'$ . Table V summarizes the glass transition temperatures of polyamides III. Polyamides III had high glass transition temperatures, ranging from 252 to 307°C.

## CONCLUSIONS

According to the results presented herein, introducing the bulky and asymmetric 1,3-adamantyl



**Figure 3** Dynamic mechanical analysis curves for III<sub>d</sub> at a heating rate of 5°C/min.

segment into the polyamide backbone yielded polyamides with good solubilities and high glass transition temperatures. The polyamides had medium and high inherent viscosities, ranging from 0.46 to 0.96 dL/g, and their molecular weight ranged from 28,000 to 109,000. All polyamides had good solubilities and could be soluble in NMP, DMAc, DMF, and pyridine. Polyamides had tensile strengths of 49.5–72.3 MPa, elongation-to-breakage values of 3.6–10.2%, and initial moduli of 2.0–2.1 GPa. Their glass transition temperatures were found to be 228–269°C and 252–307°C using DSC and DMA, respectively. The melting temperature of **III<sub>f</sub>** was observed at 318°C using DSC. The temperatures of polyamides **III** at a 5% weight loss ranged from 395 to 435°C in air and from 400 to 450°C in a N<sub>2</sub> atmosphere.

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