

# Preparation and Properties of New Polycyclic Aliphatic Polyamides Base on Diamantane

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## SYNOPSIS

A series of novel polycyclic aliphatic polyamides was synthesized by direct polycondensation of the 1,6-diamantane dicarboxylic acid with various alicyclic diamines in *N*-methyl-2-pyrrolidone (NMP) containing lithium chloride, using triphenyl phosphite and pyridine as a condensing agent. The polyamides had inherent viscosities of 0.33–0.49 dL/g. The glass transition temperatures of these polyamides were in the range of 200–220°C, and the 5% weight loss temperatures were in the range were 290–319°C in nitrogen. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It is well known that aromatic polyamides have good thermal stability, chemical resistance, and good mechanical properties, and are therefore applied in many industries. Polyamides can be prepared in several ways. The most popular method for synthesis of polyamides is low-temperature solution condensation starting from diamine–diacid chloride monomer pairs. Some methods use diamine–diacid chloride pairs to prepare polyamides by interfacial condensation. In general, the molecular weight distribution of polyamides obtained by interfacial condensation is rather narrow and low yield of product. In both methods, the monomer in using diacyl chloride is more unstable, and has the defect of being highly corrosive. In the 1970s, Yamazaki et al. reported a direct polycondensation for the synthesis of aromatic polyamides.<sup>1,2</sup> In this method, polyamides were synthesized by direction polycondensation of dicarboxylic acid with aromatic diamines in a polar solvent (such as NMP) containing a metal salt (such as LiCl, CaCl<sub>2</sub>), and using triphenyl or diphenyl phosphite and pyridine as condensing agents. A high yield of high-molecular-weight polymers can be obtained. Furthermore, it

makes the preparation of unstable diacid chlorides unnecessary. Recently, a report appeared on the synthesis of aramids of modest molecular weight by the palladium-catalyzed carbonylation and coupling reaction of diamines and aromatic dibromides or aromatic iodide.<sup>3,4</sup> Some methods used vapor-deposition polymerization to prepare a super thin film;<sup>5,6</sup> others used an *N*-silylated diamine method to obtain polyamides of high molecular weight of focusing on the diamine with low reactivity.<sup>7,8</sup>

An increasing need for polymers with various specific properties such as high glass transition temperature, improved processability, and long-term thermal stability is still a major driving force in the development of new monomers. With the development of microelectronic engineering, especially with the development of integrated circuit (IC) technology, many new polymers with low dielectric constants have been synthesized as thin films for multilayer boards and other materials for electronics. In preparing polyimides, some methods introduce alicyclic diamines<sup>9,10</sup> or polyalicyclic dianhydride<sup>11–13</sup> into the main chains of polyimides to restrain the formation of intermolecular charge-transfer complex, to improve the transparency, and to lower the dielectric constant. We tried to prepare polycyclic aliphatic polyamides in this research. Diamantane is a cycloaliphatic cage hydrocarbon containing an “extended cage” adamantane structure.<sup>14,15</sup> Although diamantane has been of interest to synthetic

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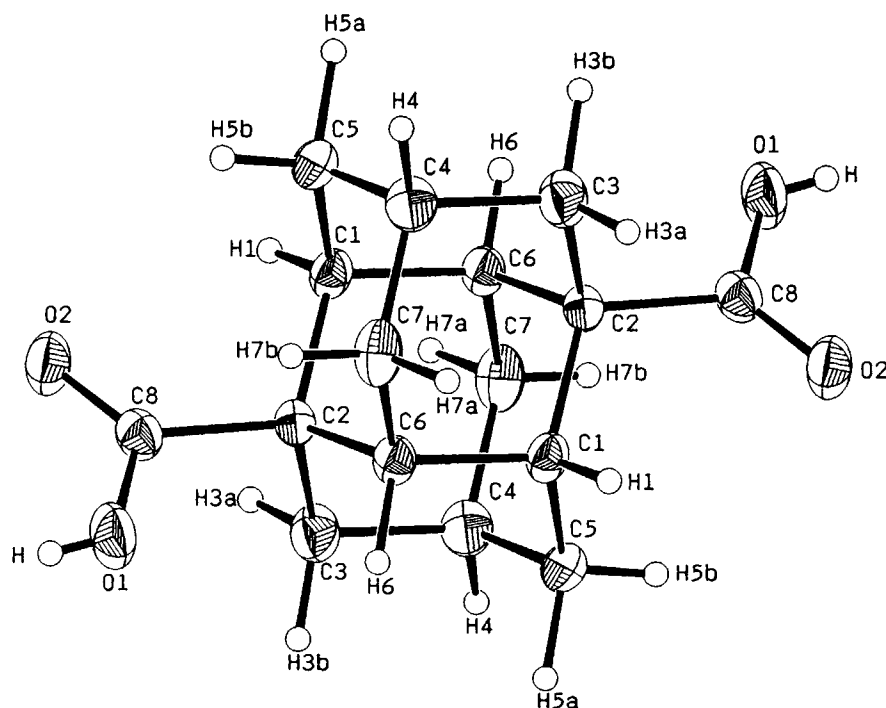


Figure 1 X-Ray structure of 1,6-diamantane dicarboxylic acid (I).

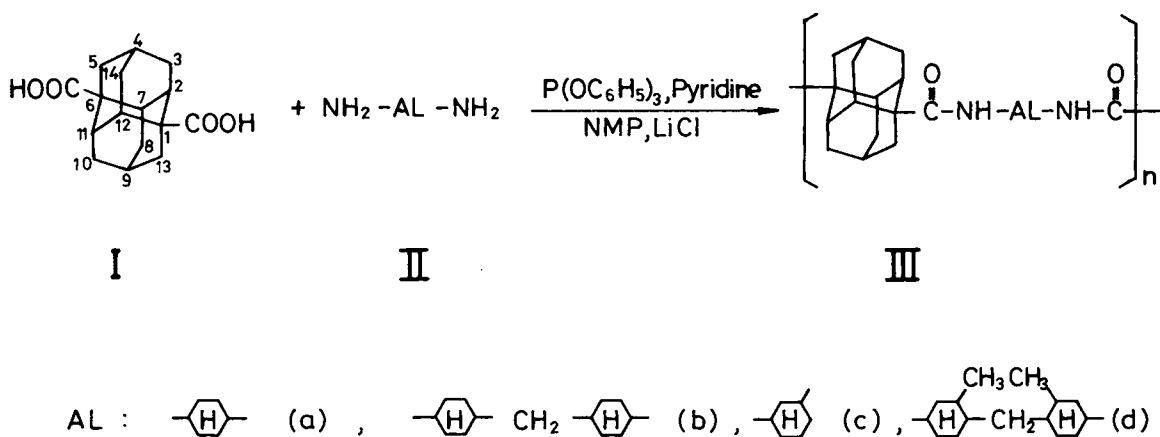
chemists for many years,<sup>16-18</sup> its use in polymers has been reported only once.<sup>19</sup> Very recently, we reported that a series of novel polyamides were synthesized by direct polycondensation of 1,6-diamantane dicarboxylic acid with various aromatic diamines in NMP containing lithium chloride, and using triphenyl phosphite and pyridine as condensing agents. Colorless polyamide film was obtained with good mechanical properties up to temperatures well above 350°C.<sup>20</sup> This study is a continuation of our recent publication on the production of new polycyclic polyamides. The main purpose of this work was to prepare a series of novel polycyclic aliphatic polyamides from 1,6-diamantane dicarboxylic acid and various alicyclic diamines by using triphenyl phosphite and pyridine as condensing agents. Solubility and thermal behaviors of the polyamides were also investigated.

## EXPERIMENTAL

### Materials

Commercially obtained anhydrous LiCl was dried in a vacuum at 150°C for 6 h and at 180°C for 10 h. *N*-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pres-

sure over calcium hydride and stored over 4 Å molecular sieves. 1,4-Diaminocyclohexane (mixed isomer) (**IIa**) was distilled at reduced pressure and stored in the dark before use. 4,4'-Methylene bis(cyclohexylamine) (mixed isomer) (**IIb**), 1,3-cyclohexane diamine (mixed isomer) (**IIc**), and 4,4'-methylene bis(2-methyl cyclohexylamine) (**IId**) were received and used without any further purification. Diamantane was prepared by a literature procedure from norbornadiene in three steps.<sup>21,22</sup> 1,6-Diamantane dicarboxylic acid (**I**) was prepared from diamantane in two steps.<sup>20</sup> Diamantane was reacted with dry bromine to give 1,6-dibromodiamantane, and then by Koch-Waaf carboxylation of 1,6-dibromodiamantane to obtain 1,6-diamantane dicarboxylic acid (**I**). The properties are as follows: mp: 439°C (measured by DSC); IR (KBr)  $\text{cm}^{-1}$ : 2918, 2850 ( $\text{CH}_2, \text{CH}$ ); 1685 ( $\text{C}=\text{O}$ ); 1420 (OH);  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ )  $\delta$  1.50 (4H, m,  $J = 11.73$  Hz, H-3a, 8a, 10a, 14a), 16.2 (4H, s, H-5, 13), 1.75 (6H, m,  $J = 11.46$  Hz, H-3b, 4, 8b, 9, 10b, 14b), 2.07 (4H, s, H-2, 7, 11, 12), 12.02 (2H, COOH);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{DMSO-}d_6$ )  $\delta$  25.18 (C-4, 9), 34.18 (C-3, 8, 10, 14), 36.92 (C-2, 7, 11, 12), 41.21 (C-5, 13), 45.54 (C-1, 6), 177.70 (COOH). The x-ray structure of **I** is shown in Figure 1.



Scheme 1

### Polymerization

We have sought the most favorable conditions for polycondensation with the 4,4'-methylene bis-(cyclohexylamine) (**IIb**) system. A typical example of polycondensation is given below.

### Polyamide IIIb from I and IIb

A mixture of 0.522 g (2 mmol) of **I**, 0.42 g (2 mmol) of **IIb**, 0.8 g of LiCl, 1.353 g (4.4 mmol) of triphenyl phosphite, 4 mL of pyridine, and 16 mL of NMP was heated with stirring at 110°C for 10 h. The obtained polymer solution was trickled on 500 mL distilled water giving rise to a white precipitate which was washed thoroughly with hot water, collected by filtration, and dried. The yield was 91%. The inherent viscosity of the polyamide was 0.49 dL/g, measured at 0.5 g/dL concentration in NMP containing dissolved 4 (w/v)% LiCl at 30°C. The IR spectrum exhibited absorptions at 3353  $\text{cm}^{-1}$  (N—H) and 1633  $\text{cm}^{-1}$  (C=O), characteristic of amide groups.

### Characterization

A Bio-Rad FTS-40 FTIR spectrophotometer was used to record spectra of the 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 concentration in NMP containing 4 (w/v)% LiCl at 30°C using an Ubbelohde viscometer. Qualitative solubility was determined using about 0.01 g of polymer in 2 mL of solvent. A Du Pont 9900 differential scanning calorimeter (DSC) and Du Pont 9900 thermogravimetric analyzer (TG) were employed to study the transition

data and thermal decomposition temperature. Wide-angle x-ray diffraction (WAXD) measurements were performed on a Philips PW 1730-10 X-ray diffractometer using  $\text{CuK}\alpha$  radiation.

A solomat TSC/RMA Model 91000 (Solomat Instruments, Stamford, CT) TSC spectrometer was used. The standard TSC depolarization spectrum, which is in many ways similar to a low frequency (ca.  $10^{-3}$  Hz) dielectric loss spectrum, is referred to as a "global" spectrum. Global TSC spectra were obtained by polarizing the film from 270°C (generally above  $T_g$ ) and polarizing while quenching at 30°C to the freezing temperature. Depolarization spectra were then measured upon reheating at 7°C/min to above  $T_g$ . To prepare the sample film for TSC, 50 mg of polymer was ground with a mortar and pestle. The finely ground sample was then pressed in a special die (used in preparing KBr pellet for IR analysis) at 20,000 pounds per square inch under vacuum to yield a transparent disk.

## RESULTS AND DISCUSSION

### Synthesis of Polymers

Novel polycyclic aliphatic polyamides were synthesized from **I** with the corresponding alicyclic diamines by direct polycondensation procedure (Scheme 1). The results of the polycondensation are listed in Table I. All the polyamides were obtained with almost quantitative yield. The polyamides had inherent viscosities of between 0.33 and 0.49 dL/g. FTIR spectra of the polyamides showed characteristic amide bands at 3353–3362 and 1633–1650  $\text{cm}^{-1}$ . A representative FTIR spectrum of **IIIId** is shown in

**Table I** Synthesis of Polycyclic Aliphatic Polyamides<sup>a</sup>

Polymer	$\eta_{inh}^b$ (dL/g)	Remark <sup>c</sup>
<b>IIIa</b>	0.33	S
<b>IIIb</b>	0.49	S
<b>IIIc</b>	0.42	S
<b>IIId</b>	0.48	S

<sup>a</sup> Polymerization was carried out with 0.1M of each monomer in NMP using triphenylphosphite and pyridine as condensing agents at 110°C for 10 h.

<sup>b</sup> Measured at 30°C at a concentration of 0.5 g/dL in NMP containing 4 (w/v)% LiCl.

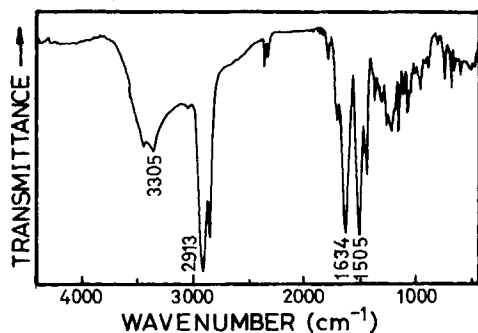
<sup>c</sup> Appearance of the polymerization system: S, turbid suspension solution.

Figure 2. The IR spectrum exhibits characteristic amide bands at 3305–3430 and 1634  $\text{cm}^{-1}$ .

### Characterization of Polyamides

The solubility of these polymers was tested in various solvents and the results are summarized in Table II. The polyamides **IIIb**, **IIIc**, and **IIId** were soluble in NMP and DMAc on heating to 60°C. But when NMP, DMAc, DMF, and pyridine were added with 4 (w/v)% LiCl, all the polyamides were soluble in these solvents. X-Ray diffraction patterns are shown in Figure 3. The diffractograms indicate that polyamides **III** are essentially amorphous, but at small angles diffraction maxima are observed at positions indicating a periodicity in the structure.

The thermal behavior of these polyamides was evaluated by DSC, TSC, and TG techniques. The thermal properties of the polyamides are summarized in Table III. The representative DSC and TG curves for these polymers are shown in Figure 4. Their temperatures at 5% weight loss ranged from 290 to 319°C in nitrogen and 273 to 297°C in air.

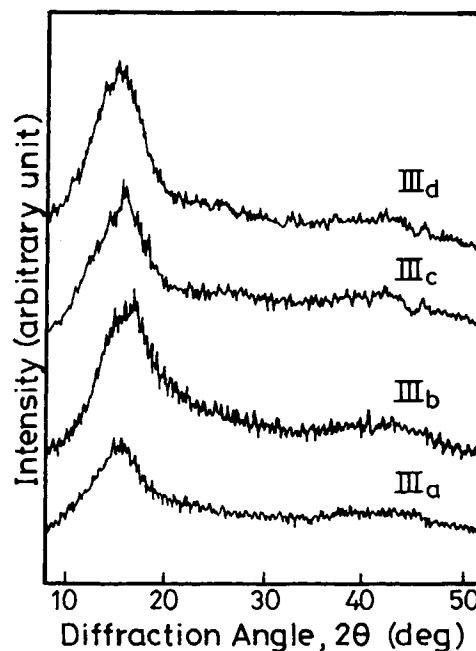
**Figure 2** FTIR spectrum of polyamide **IIId**.**Table II** Solubility of Polycyclic Aliphatic Polyamides<sup>a</sup>

Polymer	Solubility <sup>b</sup>			
	NMP	DMAc	DMF	Pyridine
<b>IIIa</b>	+	+	+	+
<b>IIIb</b>	++	++	+	+
<b>IIIc</b>	++	++	+	+
<b>IIId</b>	++	++	+	+

<sup>a</sup> NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide.

<sup>b</sup> Solubility: ++, soluble on heating at 60°C; +, soluble in solvent containing 4 (w/v)% LiCl; -, insoluble.

We observed that when alicyclic diamine was used, the temperature of the polyamides at 5% weight loss was more than 120°C lower than that of the polyamides with aromatic diamines.<sup>20</sup> The glass-transition temperatures of the polyamides were found to be 200–220°C by DSC. The global TSC spectrum of polyamides **IIId** taken at a heating rate of 7°C/min is shown in Figure 5. There was a prominent glass transition at 204°C, consistent with the DSC determination at a comparable heating rate. At lower temperatures, two transitions were observed at –50°C ( $\beta$ -transition) and –69°C ( $\gamma$ -transition). The  $\beta$ -transition is typical for polyamides. This re-

**Figure 3** X-Ray diffraction diagrams for polyamides **III**.

**Table III Thermal Behavior Data of Polycyclic Aliphatic Polyamides**

Polymer	Glass Transition Temperature (°C) <sup>a</sup>	Decomposition Temperature (°C) <sup>b</sup>	
		In N <sub>2</sub>	In Air
IIIa	212	319	297
IIIb	217	313	292
IIIc	200	290	273
IIIId	220	303	281

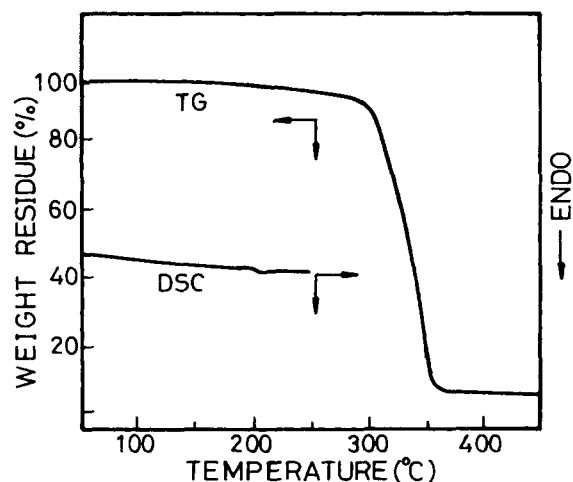
<sup>a</sup> Determined by DSC at a heating rate of 20°C/min in nitrogen.

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

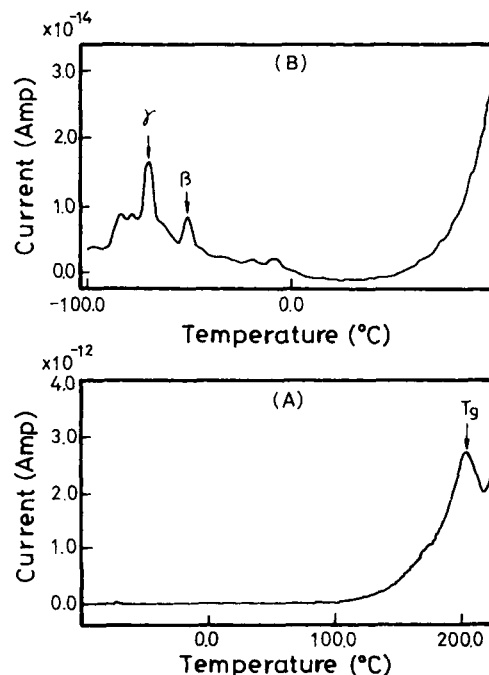
laxation are attributed to a mechanism of motion (rotation) of the amide bond together with water molecules that are bonded to them.<sup>23</sup> We do not know what mechanism of motion is related to the  $\gamma$ -transition. It is recognized that additional work is needed to characterize the mechanisms of motion. The chemical thermal stability versus degradation of the polyamides composed of aliphatic diamines was largely reduced, but by using the alicyclic diamine, the glass transition temperature of the polyamides did not decrease very much.

## CONCLUSIONS

The polycyclic aliphatic polyamides with medium inherent viscosity could be obtained by direct po-



**Figure 4** DSC and TG curves for polyamide IIIc at a heating rate of 20°C/min in nitrogen.



**Figure 5** Global TSC spectrum for polyamides IIIId: (A) above 0°C, (B) below 0°C.

lycondensation of I and alicyclic diamines by means of triphenyl phosphite in NMP-pyridine solution in the presence of LiCl. The high-molecular-weight polyamides could not be obtained because of their poor solubility. On introduction of alicyclic diamines into the polyamide backbone results in polyamides with high  $T_g$  and low thermal stability. The glass-transition temperature of the polyamides was found to be 200–220°C by DSC.

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