Synthesis and Properties of New Polyamides Based on Diamantane

Yaw-Terng Chern* and Wen-Liang Wang

Institute of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106, Republic of China

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ABSTRACT: A series of new polyamides was synthesized by direct polycondensation of 1,6-diamantanedicarboxylic acid (I) with various aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) containing lithium chloride. In this process, triphenyl phosphite and pyridine were used as condensing agents. High performance of direct polycondensation with triphenyl phosphite as a catalyst to I was subsequently obtained. The polyamides had inherent viscosities of 0.43–1.48 dL/g. Dynamic mechanical analysis revealed polymers IIIc and IIId to have main melting transitions at 400 and 374 °C, respectively. Moreover, these polymers were quite temperature stable and maintained good mechanical properties ($G' \sim 10^8$ Pa) up to temperatures close to the main transition well above 350 °C. A glass transition phenomenon, in the conventional sense, was not observed. Polyamide IIIc showed a melting transition with a sharp endothermic peak appearing at 412 °C. The 5% weight loss temperature was in the range 405–420 °C in a nitrogen atmosphere. Additionally, polyamides IIIc and IIId had tensile strengths of 82.9 and 62.3 MPa, elongations to break of 13.7 and 6%, and initial moduli of 1.4 and 1.6 GPa, respectively. Interestingly, compounds I and DMF formed a single crystal bonded with a hydrogen bond. The structure of I exhibits molecular symmetry.

Introduction

Aromatic polyamides find extensive application in industry owing to their good thermal stability, good chemical resistance, and good mechanical properties. However, some aromatic polyamides contain intermolecular hydrogen bonds, and some polyamides crystallize easily. Due to these factors, some polyamides cannot be dissolved in most organic solvents and are difficult to process. Therefore, much research focuses on the modification of hard processing, i.e., attempting to maintain considerable thermal stability and improve solubility.[1–11] These studies include (1) introducing rather soft segments on the main chain (such as CH_2), (2) breaking its symmetry and regularity, thereby making crystallization impossible, (3) introducing 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.

The conventional method for synthesizing aramids begins with reacting diamine with diacid chloride monomer by low-temperature solution condensation. In another method, diamine–diacid chloride monomer pairs have also been used to prepare polyamides by interfacial condensation. In general, the molecular weight distribution of a polyamide obtained by interfacial polymerization is rather narrow and has a low product yield. In both of these methods, the diacyl chloride monomer is more unstable and has a highly corrosive property. In the 1970s, Yamazaki and coworkers reported a direct polycondensation for the synthesis of aromatic polyamides.[12,13] In this method, polyamides were synthesized by direct polycondensation of a dicarboxylic acid with aromatic diamines in NMP containing a metal salt (such as $CaCl_2$). Moreover, triphenyl or diphenyl phosphite and pyridine were used as condensing agents. According to their investigation, this procedure could produce a high yield of polymers at a high molecular weight. Furthermore, preparation of the unstable diacid chlorides would be unnecessary. Recently, aramids of modest molecular weight were synthesized by the palladium-catalyzed carbonylation and coupling reaction of diamines with aromatic dibromides or aromatic iodide.[14,15] Other investigators have used vapor-deposition polymerization to prepare a superthin membrane.[16] Meanwhile, an N-silylated diamine method was used by others to obtain a high molecular weight by focusing on diamines with low reactivity.[17]

Diamantane is a cycloaliphatic-cage hydrocarbon containing an "extended-cage" adamantane structure.[18,19] Although diamantane has been investigated for many years,[20–23] its use in polymers has only been reported once.[24] The 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 helium.[24] However, the physical properties of a diamantane-based, polymer (except for thermal stability) have not been reported. Direct polymerization can be used to prepare polymers of a high molecular weight. Moreover, in previous studies, direct polycondensation was primarily used in the polymerization reaction of aromatic acid with aromatic diamine without investigating whether such catalysts contributed to the performance of this polycyclic aliphatic diacid. Therefore, in this study, the direct polycondensation method was used to prepare polyamides.

Although Vodicka et al.[23] have reported the synthesis of 1,6-diamantanedicarboxylic acid, the synthetic route involved two extraction steps. Moreover, the formation of 1,6-diamantanedicarboxylic acid was only confirmed by elemental analysis, and the melting point was measured by DSC. In this work, a synthesis of 1,6-diamantanedicarboxylic acid (I) is performed and confirmed by NMR, elemental analysis, and X-ray diffraction analysis. Preparing a series of polyamides from I and various aromatic diamines, using triphenyl phosphite and pyridine as condensing agents, is the primary objective of this work. Furthermore, those factors affecting the molecular weight of the polymers obtained

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* Author to whom correspondence should be addressed.

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from the Yamazaki phosphorylation reaction are also studied.[12,13] Those factors include reactant concentration, the concentration of condensing agents, reaction temperature, and the amount of metal salt. In addition, the solubility, dynamic mechanical properties, and thermal properties of the polymers are also investigated.

Experimental Section

Materials. 1,4-Phenylenediamine (IIa), 1,3-phenylenediamine (IIb), 4,4'-oxydianiline (IIc), 4,4'-methylenedianiline (IId), and 4,4'-sulfonyldianiline (IIe) 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, and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Aluminum bromide was used as received. Diamantane was prepared by a previous method from norbornadiene in three steps.[25,26]

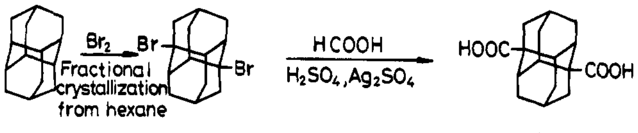
Synthesis of 1,6-Dibromodiamantane. The procedure of Tamara et al.[21,27] to synthesize dibromodiamantanes was modified as follows: diamantane (10 g, 54 mmol) was added to liquid bromine (50 mL) at ambient temperature. Next the mixture was stirred at ambient temperature for 3 h and at 63 °C for 16 h. Bromine was then removed under reduced pressure, and the residue was dissolved in CCl_4. The solution was washed with 10% aqueous $NaHSO_3$. Next the aqueous solution was extracted with CCl_4 three times. The combined CCl_4 solution was then dried under reduced pressure. The crude product (17.5 g) contained two of the likely products; these two dibromides (17.5 g) were dissolved in *n*-hexane (1000 mL) and could be separated easily by difference in solubility.[21,27] 1,6-Dibromodiamantane (7.66 g, 41% yield) crystallized preferentially from *n*-hexane. The properties were as follows: mp 272–273 °C (lit.[21] mp 272–273 °C); IR (KBr) 685, 787, 2848, 2922 cm^{-1}; EIMS *m/z* (%) 344 (M^+, 0.5), 267 (98), 265 (100), 185 (22); ^1H-NMR (300 MHz, $CDCl_3$) δ 1.67 (4H, m, J = 13.5 Hz, H-3b, 8b, 10b, 14b), 1.93 (2H, s, H-4, 9), 2.34 (4H, s, H-2, 7, 11, 12), 2.45–2.49 (8H, m, J = 13.9 Hz, H-3a, 5, 8a, 10a, 13, 14a); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.82 (C-4, 9), 34.53 (C-3, 8, 10, 14), 49.29 (C-2, 7, 11, 12), 52.47 (C-5, 13), 75.13 (C-1, 6). Anal. Calcd for $C_{14}H_{18}Br_2$: C, 48.55; H, 5.20. Found: C, 48.72; H, 5.26. IR (KBr) 783 cm^{-1} (C–Br).

Synthesis of 1,6-Diamantanedicarboxylic Acid (I) (Koch–Haaf Reaction). A flask was charged with 150 mL of 97% sulfuric acid, 3.12 g of Ag_2SO_4, and 3.54 g (0.01 mol) of 1,6-dibromodiamantane. After the mixture was cooled to 5 °C, 12 mL of 98% formic acid was added in a dropwise manner over 1 h. Stirring was continued at 5–10 °C for 6 h. The suspension was filtered, and the AgBr precipitate removed. Next the reaction mixture was poured onto 1000 g of crushed ice and stirred continuously for 15 min, and the white precipitate was subsequently filtered. The precipitate solid was washed five times with distilled water, and 2.26 g (82% yield) of I was obtained. The product was purified by recrystallization with *N,N*-dimethylformamide (DMF). The properties were as follows: mp 420 °C (measured by DSC; lit.[23] mp 410 °C); IR (KBr) 2918, 2850 (CH_2, CH), 1685 (C=O), 1420 cm^{-1} (OH); EIMS *m/z* (%) 276 (M^+, 16), 231 (100), 185 (40); ^1H-NMR (300 MHz, DMSO-d_6) δ 1.50 (4H, m, J = 11.73 Hz, H-3b, 8b, 10b, 14b), 1.62 (4H, s, H-5, 13), 1.75 (6H, m, J = 11.46 Hz, H-3a, 4, 8a, 9, 10a, 14a), 2.07 (4H, s, H-2, 7, 11, 12), 12.02 (2H, COOH); ^{13}C-NMR (75 MHz, DMSO-d_6) δ 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). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.57; H, 7.24. Found: C, 69.86; H, 7.43.

Polymerization. A typical example of the polycondensation is given below.

Polyamide IIIc from I and IIc. A mixture of 0.522 g (2 mmol) of **I**, 0.4 g (2 mmol) of IIc, 0.8 g of LiCl, 1.23 g (4 mmol) of triphenyl phosphite, 4 mL of pyridine, and 16 mL of NMP was heated with stirring at 125 °C for 9 h. The obtained polymer solution was trickled into 500 mL of methanol, thereby giving rise to a fibrous white precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was almost quantitative. The inherent viscosity of the polymer was 1.48 dL/g, measured at 0.5 g/dL concentration in NMP containing dissolved 5% (w/v) LiCl at 30 °C. The IR spectrum exhibited absorptions at 3332 (NH) and 1662 cm^{-1} (C=O), characteristic of the amide group. The elemental analysis values of polymer IIIc are listed in Table 5.

Scheme 1



I

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. MS spectra were obtained by using a JEOL JMS-D300 mass spectrometer. ^1H- and ^{13}C-NMR spectra were recorded on a Bruker AM-300WB Fourier transform nuclear magnetic resonance spectrometer 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 BEC station 3500 computer using NRCC SDP software.[28] Inherent viscosities of all polymers were determined at 0.5 g/dL concentration in NMP containing dissolved 5% (w/v) LiCl at 30 °C using an Ubbelohde viscometer. Next 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 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 and a heating rate of 20 °C/min. The thermogravimetric analysis (TG) was determined under a nitrogen flow of 50 cm^3/min with a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was carried out with a Du Pont 9900 thermal analyzer system. TMA was recorded under a fixed load (2 g) at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) was performed on a Du Pont 9900 thermal analyzer system. A sample 10 mm in length, 2 mm in width, and approximately 0.8 mm in thickness was used. The dynamic shear modulus was measured at a frequency of 1 Hz 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 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. 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.

Results and Discussion

Monomer Synthesis. 1,6-Diamantanedicarboxylic acid (I) was prepared from diamantane in two steps (Scheme 1). Diamantane was reacted with dry bromine to yield a mixture of 1,6-dibromodiamantane with 1,4-dibromodiamantane. These two dibromides could be separated easily by the difference in solubility.[21,27] 1,6-Diamantanedicarboxylic acid (I) was prepared easily by Koch–Haaf carboxylation of 1,6-dibromodiamantane with 82% yield. On the basis of the shielding effect of carbon, the position of chemical shifts for carbons was readily assigned from a DEPT experiment in Figure 1. The 2D ^1H–^{13}C COSY spectrum of I is available as supporting information (see paragraph at end of paper). With the aid of carbon spectrum assignments, the position of chemical shifts for protons was readily assigned as shown in Figure 2. The structure of I was

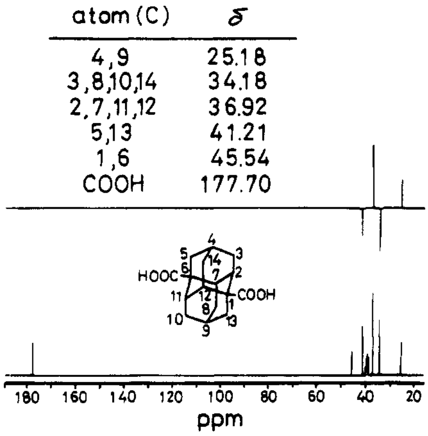


Figure 1. ^{13}C 135° DEPT and ^{13}C-NMR (75 MHz, DMSO-d_6) spectra of I.

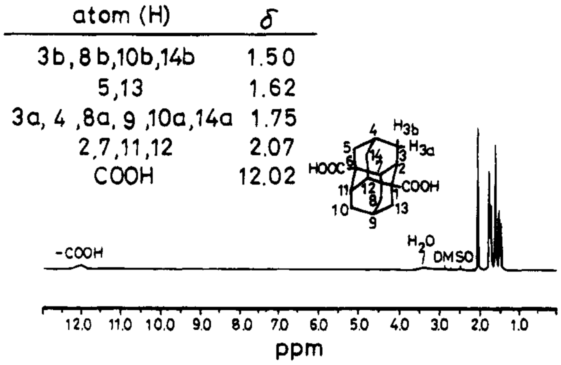


Figure 2. ^1H-NMR (300 MHz, DMSO-d_6) spectrum of I.

also confirmed by X-ray diffraction analysis. X-ray crystal data for I were acquired from a single crystal, as obtained by slow crystallization of a DMF solution of I. Interestingly, compound I and DMF formed a single crystal consisting of I and two DMF (Figure 3). The structure of I exhibits molecular symmetry. The hydrogen bond is formed between O3 of the DMF and H of the acid group in I. The intensity decay is 20% in three standard reflections owing to the evaporation of DMF at room temperature. The complete X-ray structure determinations are available as supporting information. The elemental analysis, characteristic peaks in the NMR spectra, characteristic bands in the IR spectrum, and X-ray crystallography correlate sufficiently with 1,6-diamantanedicarboxylic acid (I).

Effects of the Reaction Conditions on the Inherent Viscosity of IIIc. Effect of Monomer Concentration. Figure 4 indicates that the inherent viscosity of IIIc increased with increasing monomer concentration. For a reaction between reactants, the greater the number of molecules of each reactant in a given volume, the more collisions there will be in a given time, and therefore the faster the reaction will occur. Moreover, the inherent viscosity of IIIc increased slightly when the concentration of the monomer exceeded 0.10 M. The concentration range for the monomer did not reach an excess to the point that the solubility would be reduced.

Effect of Pyridine/NMP Ratio. Part I in Table 1 reveals that the inherent viscosity of IIIc increased with the addition of pyridine. Perhaps because of the pyridine, the triphenyl phosphite and the monomer produce a complex form. As a result, the process of polycondensation would be promoted. Experimental results also indicated that the inherent viscosity of IIIc would reach a maximum when the volume ratio of NMP to pyridine was 4.

Effect of LiCl. Part II in Table 1 reveals that adding LiCl may improve the solubility of polyamide IIIc by weakening the hydrogen bond between the molecules. Moreover, LiCl may form a complex with the generated phenol to reduce the side reaction and thus obtain a higher inherent viscosity.[13] If the quantity added is excessive, however, the solubility of polyamide IIIc may have an adverse effect. Table 1 also shows that the most suitable quantity of LiCl to be added is 5% (w/v). When LiCl was added excessively, a highly viscous swollen gel was generated during the reaction. A subsequent decrease in the inherent viscosity of the formed polymer IIIc would occur. This result is quite similar to that in previous literature.[13]

Effect of Reaction Temperature. Part III in Table 1 indicates that if the temperature of reaction was lower than 75 °C, the reactants could not dissolve completely; in addition, it would be difficult for the polycondensation reaction to proceed. The inherent viscosity of polyamide IIIc increased markedly with increasing reaction temperature. According to kinetic theory, the higher the temperature, the faster molecules move and the greater their kinetic energy. So the number of collisions that occur in a given time and the energy involved in each collision increase with increasing temperature. However, a decreased inherent viscosity of 0.88 dL/g was obtained when the reaction was carried out at 134 °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 reaction.[13] Therefore, the inherent viscosity of the formed polymer IIIc decreased.

Effect of $P(OC_6H_5)_3$/Monomer Ratio. Part IV in Table 1 reveals that when the mole ratio of $P(OC_6H_5)_3$ to I equals 2, the inherent viscosity of IIIc reaches a maximum. Moreover, all of the polymers IIIc had a high inherent viscosity when the mole ratio of $P(OC_6H_5)_3$ to I exceeded 2. However, when the ratio of $P(OC_6H_5)_3$ to I was less than 2, the inherent viscosity of IIIc was small. This was probably because I and $P(OC_6H_5)_3$ formed a complex during polycondensation. When the mole ratio of $P(OC_6H_5)_3$ to I was 2, I could completely form a complex. This result is the same as that in previous literature.[29]

Effect of Reaction Time. Figure 5 indicates that the effect of reaction time on the inherent viscosity of IIIc is rather small when the reaction time exceeds 6 h. Notably, around 9 h is the proper reaction time. However, if the reaction time is too long, the inherent viscosity of IIIc decreases, perhaps as a result of the increase in side reaction; this result is similar to those derived in previous literature.[13]

Optimum Reaction Conditions for IIIc. From the above results, we can infer that direct polycondensation with triphenyl phosphite as a catalyst to I is of high performance. The most favorable conditions for this system are the concentration of monomer at 0.1 M, pyridine/NMP ratio at 0.25, $P(OC_6H_5)_3$/I ratio at 2, the quantity of LiCl to be added at 5% w/v the reaction temperature at 125 °C, and the reaction time at 9 h.

Synthesis of Polymers. Various polyamides were prepared from I with the corresponding aromatic diamines by using the most favorable conditions for the reaction with 4,4′-oxydianiline (IIc) (Scheme 2). Polycondensation results are listed in Table 2. All polyamides were obtained with almost quantitative yield. The polyamides had medium and high inherent viscosities (0.43–1.48 dL/g). The inherent viscosities of the polya-

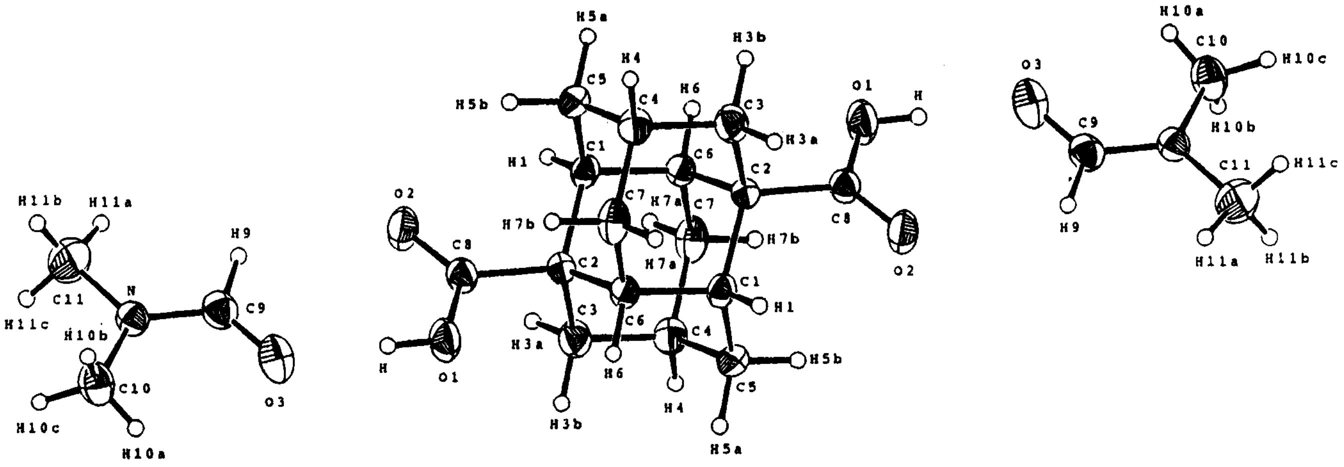


Figure 3. X-ray structures of I containing two DMF.

Table 1. Effect of Reaction Conditions on Polyamidation[a]

	reactn conditions				polymer		
part	pyridine/NMP (v/v)	LiCl (w/v %)	reacn temp (°C)	$P(OC_6H_5)_3/I$ (mol/mol)	yield (%)	η_{inh}[b] (dL/g)	remark[c]
I	0	5	125	2.5	88.7	0.58	S
	1/4	5	125	2.5	98.4	1.11	S
	2/3	5	125	2.5	98.3	0.93	S
	1	5	125	2.5	98.2	0.89	S
	3/2	5	125	2.5	96.7	0.97	S
	7/3	5	125	2.5	97.3	0.95	S
	4	5	125	2.5	95.9	0.99	S
II	1/4	0	125	2.5	20.4	0.20	S
	1/4	2	125	2.5	94.2	0.98	S
	1/4	5	125	2.5	98.4	1.11	S
	1/4	8	125	2.5	95.3	0.84	S
	1/4	10	125	2.5	95.8	0.83	S
	1/4	15	125	2.5	93.4	0.78	G
	1/4	20	125	2.5	94.7	0.62	G
III	1/4	5	75	2.5	0	0	P
	1/4	5	83	2.5	32.8	0.29	S
	1/4	5	94	2.5	50.7	0.68	S
	1/4	5	102	2.5	90.5	0.65	S
	1/4	5	113	2.5	98.5	0.82	S
	1/4	5	125	2.5	98.4	1.11	S
	1/4	5	134	2.5	98.3	0.88	S
IV	1/4	5	125	1.5	98.7	0.51	S
	1/4	5	125	2.0	97.5	1.48	S
	1/4	5	125	2.5	98.4	1.11	S
	1/4	5	125	2.8	98.2	0.92	S
	1/4	5	125	3.6	95.4	1.03	S

[a] (I) = (IIc) = 0.1 M, reaction time = 9 h. [b] Measured at 30 °C at a concentratin of 0.5 g/dL in NMP containign 5 w/v % LiCl. [c] Appearance of the polymerization system: S, homogeneous solution; G, viscous swollen gel; P, monomer is not completely soluble.

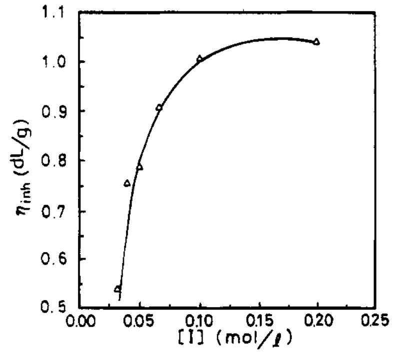


Figure 4. Plot of η_{inh} (dL/g) vs monomer concentration [I].

mides increased with decreasing rigidity of the polymer backbone, depending on the diamines used. This result is the same as those found in previous literature.[28] The

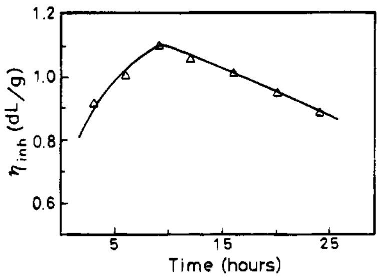


Figure 5. Plot of η_{inh} (dL/g) vs reaction time.

unsatisfactory results obtained from *p*-phenylenediamine (IIa) were caused by the poor solubility of IIIa. The formation of polyamides III was confirmed by IR spectroscopy and elemental analyses. Elemental analysis results for these polyamides are listed in Table 2. In all cases, the carbon values were found to be lower

Scheme 2

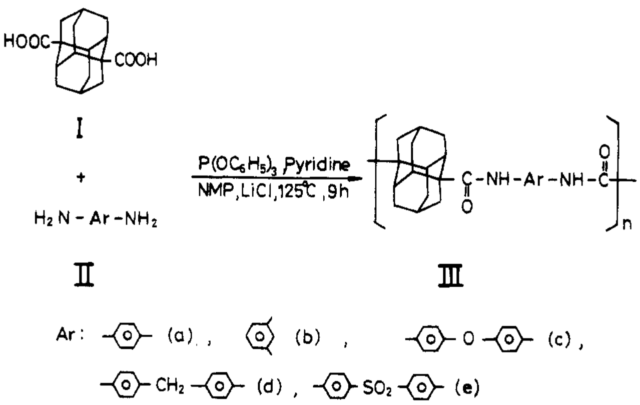


Table 2. Synthesis and Characterization of Polyamides[a]

polymer	yield (%)	η_{inh}[b] (dL/g)	remark[c]	elem anal.				H_2O[d] (%)
					% C	% H	% N	
IIIa	95.4	0.43	P	calcd	75.86	6.90	8.05	
				found	74.25	7.22	7.60	2.4
				cor	76.08	7.12	7.79	
IIb	95.3	0.57	S	calcd	75.86	6.90	8.05	
				found	73.34	7.46	7.33	3.4
				cor	75.92	7.33	7.59	
IIIc	97.5	1.48	S	calcd	76.36	6.36	6.36	
				found	73.95	6.91	6.83	3.0
				cor	76.24	6.78	7.04	
IIId	96.2	0.78	S	calcd	79.45	6.85	6.39	
				found	75.23	7.07	5.83	4.0
				cor	78.36	6.90	6.07	
IIIe	96.5	0.70	S	calcd	68.85	5.74	5.74	
				found	65.59	6.08	5.16	4.0
				cor	68.32	5.87	5.38	

[a] (I) = (aromatic diamine) = 0.1 M; pyridine/NMP = 1/4; $P(OC_6H_5)/I = 2.0$; LiCl = 5% w/v; temperature = 125 °C, time = 9 h. [b] Measured at 30 °C at a concentration of 0.5 g/dL in NMP containing 5% w/v LiCl. [c] Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation. [d] % H_2O = $(W - W_0)/W_0 \times 100\%$; W = weight of polymer sample after standing at room temperature; W_0 = weight of polymer sample after drying in vacuo at 100 °C for 12 h; corrected value = found value/(1 − % H_2O) for C and N, corrected value = (found value − % H_2O/9)/(1 − % H_2O) for H.

than those calculated for the expected structures. The moisture uptake per polymer was in the range of 2.4–4.0 wt % at room temperature, which could be calculated by the weight change of vacuum-dried polymer samples after exposure to air. The values, corrected for moisture content, correlated well with the proposed structures. FTIR spectra of the polyamides showed characteristic amide bands at 3300–3340 and 1650–1670 cm^{-1}.

Characterization of Polymers. The solubility of these polymers was tested in various solvents, and those results are summarized in Table 3. IIId and IIIe were readily soluble in NMP. Polyamide IIIc was also completely dissolved in NMP on heating to 60 °C. Polyamide IIIa had poor solubility. X-ray diffraction results, as discussed below, revealed that IIIa had the highest crystallization tendency among the other polyamides III. Therefore, its solubility was particularly poor. This solubility behavior was consistent with the results of X-ray diffraction studies. However, when NMP, DMAc, and DMF were added with 5% w/v LiCl, solubility was enhanced markedly. For instance, polymers IIIc, IIId, and IIIe were soluble at 15% w/v.

"As-prepared" powders and films were structurally characterized by X-ray methods. Polymer IIIa shows sharp diffraction peaks at $2\theta \sim 15°$ and $2\theta \sim 18°$, indicating the high degree of crystallinity (x-ray data available as supporting information). The other polyamides had almost the same semicrystalline patterns, exhibiting crystalline peaks (2θ) at around 15°. Additional work is required to characterize the structures more accurately. Colorless IIIc, IIId, and IIIe films were obtained by casting from their DMAc solution containing 5% w/v LiCl. The mechanical properties were determined by an Instron machine. The tensile properties of the polyamides are summarized in Table 4. The IIIc and IIId films have tensile strengths of 82.9 and 62.3 MPa, elongation to break values of 13.7 and 6%, and initial moduli of 1.4 and 1.6 GPa, respectively. The IIIc film has a higher tensile strength than IIId primarily because IIIc has a higher inherent viscosity. Also, since IIIc has a rather soft segment (−O−), the elongation at break of IIIc is also greater. Polymer IIIf could also be cast into film but is quite brittle. Polyamides IIIa and IIIb were difficult to cast into film owing to poor solubility.

The thermal behavior of these polymers was evaluated by TG, DSC, TMA, and DMA. The thermal properties of the polymers are summarized in Table 5. Representative TG curves for these polymers are made available as supporting information. Their temperatures at a 5% weight loss range from 405 to 420 °C in nitrogen and from 390 to 405 °C in air.

Since the influence of residual water or solvent and history of thermal annealing are sometimes observed in the first heating run of DSC, the first heating of the samples was curtailed at 300 °C; in addition, the T_g and other thermal properties were evaluated according to the DSC charts of the second heating. There was no evidence of a glass transition for all of the samples whose thermograms are shown in Figure 6. Polymer IIIa exhibited a featureless trace up to a temperature of around 350 °C, followed by the sawtoothed shape of the endothermic peak appearing at around 400 °C, interpreted as a melting process accompanied by decomposition. Polymers IIIb and IIId showed a rather featureless DSC trace starting from 50 to 280 °C. At around 300 °C, a small broad exothermic process started to occur in this temperature range, interpreted here as a recrystallization process. Next, a broad endothermic process at around 350 °C started to occur in this temperature range, interpreted here as the simultaneity of melting process and decomposition. Polymer IIIc showed a rather featureless DSC trace starting from 50 to 300 °C. At around 308 °C, a very broad exothermic process started to occur in this temperature range, interpreted here as a recrystallization process immediately followed by a melt transition with an endothermic peak appearing at around 390 °C. Next, thermal decomposition occurred at well above 400 °C. In polymer IIIe, the transition from an ordered solid to an isotropic melt gave rise to a rather sharp endothermic peak appearing at 412 °C.

The thermal properties of IIIc and IIId, as measured by TMA, are available as a supporting information. When the temperature reaches 370 °C, the film of IIIc softens and shows the softening transition temperature (T_s). This softening temperature of IIIc correlates well with the endothermic peak at around 390 °C, as obtained by DSC. Polymer IIId also shows a softening transition temperature at approximately 330 °C.

More detailed information can be obtained from the dynamic mechanical behavior measurements taken of the films as a function of temperature. Films of about 80 μm thickness were studied between −100 and +400

Table 3. Solubility of Polyamides

	solvent[a]							
polymer	NMP	DMSO	DMAc	DMF	pyridine	DMAc/LiCl[b]	NMP/LiCl[b]	conc H_2SO_4
IIIa	+−	+−	−	−	−	++	++	++
IIIb	+−	+−	+−	+−	−	++	++	++
IIIc	+	+−	+−	+−	+	++	++	++
IIId	++	+−	+−	+−	+−	++	++	++
IIIe	++	+−	+−	+−	+−	++	++	++

[a] Key: ++, soluble at room temperature; +, soluble on heating at 60 °C; +−, partially soluble on heating at 60 °C; −, insoluble. Abbreviations: DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone, DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide. [b] Concentration of LiCl is 5% w/v.

Table 4. Tensile Properties of Polymer Films[a]

polymer	tensile strength (MPa)	elongation at break (%)	initial modulus (GPa)
IIIc	82.9	13.7	1.4
IIId	62.3	6.0	1.6

[a] Films were cast from a polymer solution of DMAc containing 5% w/v LiCl.

Table 5. Thermal Properties of Polyamides

				decomp[d] temp (°C)	
polymer	T_m[a] (°C)	T_s[b] (°C)	T_α[c] (°C)	in air	in N_2
IIIa	*e*			405	420
IIIb				401	414
IIIc	390	370	400	390	405
IIId		330	374	396	409
IIIe	412			402	418

[a] Melting transition measured by DSC at a heating rate of 20 °C/min. [b] Softening temperature measured by TMA at a heating rate of 10 °C/min. [c] α transition measured by DMA. [d] Temperature at which 5% weight loss occurred as recorded by TG at a heating of 20 °C/min. [e] Not found.

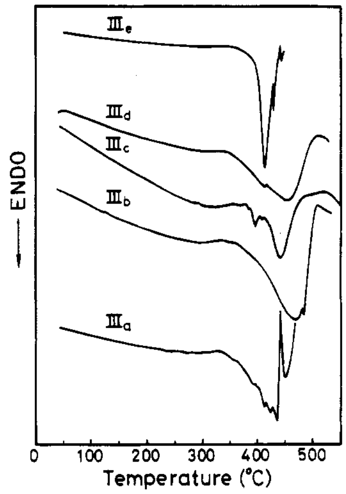


Figure 6. DSC thermograms of the studied polymers at a heating rate of 20 °C/min in nitrogen.

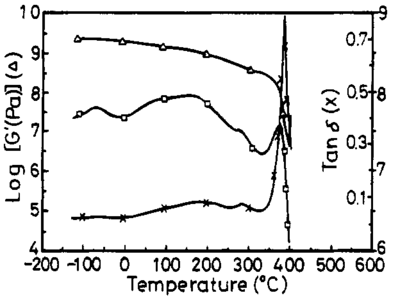


Figure 7. Dynamic mechanical analysis curves for IIId film at a heating rate 2.5 °C/min at 1 Hz.

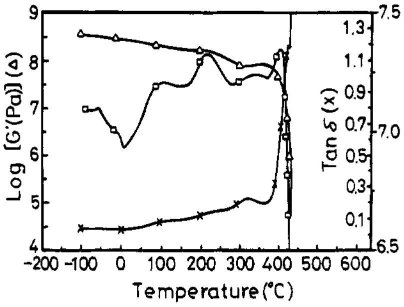


Figure 8. Dynamic mechanical analysis curves for IIIc film at a heating rate 5 °C/min at 1 Hz.

°C. The mechanical relaxation spectra of IIId are shown in Figure 7. Three profound relaxations based on tan δ and G'' peaks are observed, i.e., at −68 °C, at approximately 185 °C, and at 374 °C. The relaxation process can be approached by verifying results obtained with other related polymers.[30−32] The low temperature of −68 °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 temperature, at approximately 185 °C, is very broad in G'' and tan δ. The transition 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. Such a transition was also observed in other related polymers.[31−33] With increasing temperature, G' decreases steadily from −100 to +320 °C, without showing either abrupt changes or a marked relaxation. Small transition peaks in tan δ and G'' at about 280 °C were also observed. The reason for this transition still remains uncertain. We believe that possible recrystallization is taken into account in the relaxation process, as discussed below with polymer IIIc. The main transition, at around 374 °C, could be indicative of either a glass or a melting transition. Such transitions correlated well with the melting endothermic peaks obtained by DSC. Moreover, the polymer particles softened and coalesced at these temperatures. Thus, this transition is attributed to the melting transition.

The mechanical relaxation spectra of polymer IIIc are shown in Figure 8. Four relaxations were observed, at −50, +213, +315, and +400 °C, based on tan δ and G'' peaks. Two lower relaxations were observed in G'' but not found in tan δ. In both, transition of IIIc is similar to that of IIId. A shoulder peak was observed at 100 °C in G''. The third, 315 °C, is associated with a slight increase in G'. Moreover, this temperature correlates well with the recrystallization temperature obtained by DSC. Thus, such a transition is attributed to the recrystallization process. The main transition at 400 °C in G'' could be indicative of a melting transition. The melting transition that appears at 400 °C correlates well with the values obtained by DSC. Again, the onset of thermal decomposition was above 400 °C. In both cases, polyamides IIIc and IIId show rather high G' values (about 10^8 Pa), even at temperatures higher than 350 °C.

Conclusion

1,6-Diamantanedicarboxylic acid (I) was prepared by Koch−Haaf carboxylation of 1,6-dibromodiamantane in 82% yield. Interestingly, compound I and DMF formed a single crystal, bonded by a hydrogen bond. Diamantane-containing polyamides with high inherent viscosities could easily be obtained by direct polycondensation of I and aromatic diamines by means of triphenyl phosphite in NMP−pyridine solution in the presence of LiCl. Colorless IIIc and IIId films had tensile strengths of 82.9 and 62.3 MPa, elongation to break values of 13.7 and 6%, and initial moduli of 1.4 and 1.6 GPa, respectively.

Diamantane-containing polyamides IIIc and IIId show main melting transitions at 400 and 374 °C, respectively. In both cases, these polyamides show rather high G' values (about 10^8 Pa), even at temperatures higher than 350 °C. A glass transition was not observed. The crystallinities of polyamides III vary significantly, depending on the main chain moiety from the diamines. Polyamide IIIc shows a melting transition with a sharp endothermic peak at 412 °C by DSC measurement.

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Supporting Information Available: X-ray data of monomer I, 2D ^{1}H−^{13}C NMR (COSY) spectra of I, wide-angle X-ray diffraction curves of polyamides, and TMA curves of polyamides (8 pages). Ordering information is given on any current masthead page.

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