High-Pressure Synthesis and Properties of Aliphatic−Aromatic Polyimides via Nylon-Salt-Type Monomers Derived from Aliphatic Diamines with Pyromellitic Acid and Biphenyltetracarboxylic Acid

Tatsuo Inoue,[†] Yoshihiro Kumagai,[‡] Masa-aki Kakimoto,*,[‡] Yoshio Imai,[‡] and Junji Watanabe[†]

Department of Polymer Chemistry, and Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Received October 22, 1996; Revised Manuscript Received January 14, 1997[⊗]

ABSTRACT: Two aliphatic series of polyimides having well-defined structures with inherent viscosities of 0.4−2.7 dL g^{-1} were readily synthesized by the solid-state thermal polycondensation under high pressure of the salt monomers composed of aliphatic diamines having 6−12 methylene units and both pyromellitic acid (PMA) and biphenyltetracarboxylic acid (BPA) under 220 MPa at 250 °C for 5 h. It is noteworthy that the polycondensation proceeded rapidly with the elimination of water in a closed reaction vessel under high pressure, producing high molecular weight polyimides mostly within only 1 h. The thermal behavior (melting temperature and glass transition temperature) and crystallinity of the PMA- and BPA-based polyimides are also discussed in detail.

Introduction

Wholly aromatic polyimides are superengineering plastics which exhibit excellent thermal and mechanical properties and have been used widely in aerospace, electronics, and other industries over the past 3 decades.[1,2] Aliphatic−aromatic polyimides derived from aliphatic diamines (hereafter aliphatic polyimides), which were first prepared in the mid 1950s, also have great potential for superengineering plastics; however, the information on their synthesis and properties are known to a lesser extent. Some aliphatic polypyromellitimides were obtained by the melt polycondensation of the nylon-salt-type monomers composed of aliphatic diamines and pyromellitic acid (PMA) or its diester diacid[3−5] or by the high temperature solution polycondensation of aliphatic diamines with pyromellitic dianhydride (PMDA) in nitrobenzene,[6] and their properties were reported only briefly in the literature.[5−7] Koning et al.[8] reported the synthesis of several aliphatic polyimides by a conventional two-step process from aromatic dianhydrides including PMDA, 3,3′,4,4′-biphenyltetracarboxylic dianhydride, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-oxydiphthalic anhydride, and 4,4′-sulfonyldiphthalic anhydride. Although the properties of the BTDA-based polyimides were investigated in detail, less information is available on the properties of aliphatic polyimides derived from the other aromatic dianhydrides.[8]

We have found that two series of high-molecular-weight aliphatic polyimides having well-defined structures could be synthesized quite readily from aliphatic diamines bearing 6−12 methylene units and both 4,4′-oxydiphthalic acid (ODPA)[9] and 3,3″,4,4″-*p*-terphenyltetracarboxylic acid diethyl ester (TPE)[10,11] by the solid-state thermal polycondensation of the corresponding nylon-salt-type monomers under high pressure. The thermal properties of these aliphatic polyimides[9−11] and thermotropic liquid crystallinity of the TPE-based polyimides[10,11] were reported in detail. In a continuation of those studies, this article reports a successful high-pressure synthesis of the aliphatic polyimides starting from the salt monomers composed of a series of aliphatic diamines with PMA and 3,3′,4,4′-biphenyltetracarboxylic acid (BPA). The properties of the PMA- and BPA-containing polyimides are compared with those of the ODPA- and TPE-based polyimides reported previously.[9−11]

Experimental Section

Apparatus. The apparatus used for the high-pressure synthesis was the same as that described previously.[12]

Materials. Aliphatic diamines having 6−12 methylene units were purified individually by distillation under reduced pressure with potassium hydroxide pellets. Pyromellitic acid (PMA) was purified by recrystallization from water, and 3,3′,4,4′-biphenyltetracarboxylic dianhydride, by sublimation.

Preparation of Biphenyltetracarboxylic Acid (BPA). A mixture of 25 g of biphenyltetracarboxylic dianhydride in 1 L of water was refluxed until it became clear and then was cooled to room temperature. The precipitate that crystallized from water was collected and dried at 60 °C under vacuum overnight.

Preparation of Salt Monomers. Octamethylenediamine−PMA Salt (8PMA). A solution of 1.443 g (10 mmol) of octamethylenediamine in 500 mL of ethanol was added dropwise with stirring at 60 °C to a mixture of 2.542 g (10 mmol) of PMA in 200 mL of ethanol over a period of 5 h. During the addition, the resulting salt began to precipitate, and the mixture was further stirred at room temperature for 3 h. The precipitate formed was collected by filtration and dried. The yield of the salt was 3.70 g (93%). The salt was further purified by recrystallization from water, followed by thorough drying at 100 °C under vacuum overnight. The endothermic peak temperature was 274 °C (by DTA at a heating rate of 10 °C min^{-1}). IR (KBr, cm^{-1}): near 2030 (NH_3^+) and 1556 (overlapped carboxylate and NH_3^+).

Dodecamethylenediamine−BPA Salt (12BPA). A mixture of 3.303 g (10 mmol) of BPA in 200 mL of ethanol was heated to 60 °C. To the solution was added dropwise with stirring at 60 °C a mixture of 2.004 g (10 mmol) of dodecamethylenediamine in 500 mL of ethanol. After the solution was stirred at room temperature for 3 h, the precipitate formed was isolated and dried at 80 °C under vacuum overnight. The salt weighed 4.93 g (93%). This was further purified by

---

[†] Department of Polymer Chemistry.

[‡] Department of Organic and Polymeric Materials.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

S0024-9297(96)01556-2 CCC: $14.00

Table 1. Elemental Analysis Data of Salt Monomers *X*PMA and *X*BPA

	elemental anal., %					
	calcd			found		
salt	C	H	N	C	H	N
6PMA	51.89	5.99	7.56	51.50	6.01	7.47
7PMA	53.12	6.29	7.29	51.60	6.27	7.05
8PMA	54.26	6.58	7.03	53.92	6.76	7.04
9PMA	55.33	6.84	6.79	54.66	7.06	6.69
10PMA	56.33	7.09	6.57	56.07	7.06	6.59
11PMA	57.26	7.32	6.36	57.06	7.74	6.54
12PMA	58.14	7.54	6.16	57.75	7.64	6.26
6BPA	59.19	5.87	6.27	58.66	5.83	6.24
7BPA	59.99	6.13	6.08	59.85	6.12	5.91
8BPA	60.75	6.37	5.90	60.62	6.30	5.72
9BPA	61.46	6.60	5.73	61.53	6.58	5.76
10BPA	62.14	6.82	5.57	62.22	6.68	5.56
11BPA	62.78	7.02	5.42	63.06	6.82	5.44
12BPA	63.38	7.22	5.28	63.14	7.38	5.22

Table 2. Elemental Analysis Data of Polyimides P-*X*PMA and P-*X*BPA

	elemental anal., %					
	calcd			found		
polymer	C	H	N	C	H	N
P-6PMA	64.42	4.73	9.39	63.55	4.74	9.33
P-7PMA	65.38	5.16	8.97	64.81	5.08	8.88
P-8PMA	66.25	5.56	8.58	65.38	5.54	8.38
P-9PMA	67.05	5.92	8.23	66.50	6.03	8.21
P-10PMA	67.78	6.26	7.90	67.75	6.29	7.89
P-11PMA	68.46	6.57	7.60	68.36	6.68	7.61
P-12PMA	69.09	6.85	7.32	69.07	6.70	7.28
P-6BPA	70.58	4.85	7.48	69.67	4.47	7.36
P-7BPA	71.12	5.19	7.21	70.35	5.03	7.14
P-8BPA	71.63	5.51	6.96	71.79	5.60	6.75
P-9BPA	72.10	5.81	6.73	72.75	5.62	6.60
P-10BPA	72.54	6.09	6.51	71.81	6.07	6.47
P-11BPA	72.95	6.35	6.30	72.57	6.50	6.22
P-12BPA	73.34	6.59	6.11	74.33	6.85	6.05

recrystallization from water. The endothermic peak temperature was 199 °C by DTA. IR (KBr, cm^{-1}): near 2031 (NH_3^+) and 1578 (overlapped carboxylate and NH_3^+).

The other salt monomers *X*PMA and *X*BPA (*X* stands for the number of methylene unit in the aliphatic diamine) were prepared in a similar procedure as above from the combination of the aliphatic diamines and both PMA and BPA. The elemental analysis data of all the salt monomers are summarized in Table 1.

Polymerization of Salts under High Pressure, Poly(*N*,*N*′-dodecamethylenebiphenyltetracarboxdiimide) (P-12BPA). A 0.5 g portion of salt 12BPA was placed in a Teflon capsule (15-mm diameter), and the capsule was loaded into the metal cylinder. The piston-cylinder was set inside a furnace and pressure was applied at room temperature, and then the cylinder was heated. The polymerization was conducted under 220 MPa of pressure at 320 °C for 5 h. The reaction temperature was recorded from the point where the temperature reached 320 °C, which required about 1 h. After the polymerization, the temperature was lowered to room temperature, followed by release of pressure to 1 atm. The polymer, in the form of a flat cylindrical pellet (15-mm diameter and about 3-mm thick), was removed from the capsule. The pellet was then dried under vacuum at 100 °C overnight for complete removal of the water produced during the polymerization. The inherent viscosity of the polymer was 1.94 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} in concentrated sulfuric acid at 30 °C. IR (KBr, cm^{-1}): 1771 and 1707 (imide C=O), 1395 (C—N), and 743 (imide ring).

The other polyimides, P-*X*PMA and P-*X*BPA, were synthesized by a similar procedure. The elemental analysis data of all the polymers are summarized in Table 2.

Polymerization of Salt Monomers under Atmospheric Pressure. About 1 g of salt monomer *X*PMA (or *X*BPA) was charged in a 10-mL test tube. A homemade glass polymerization tube (30-mm diameter) equipped with a nitrogen inlet and a thermocouple was set in an electric heating mantle, and the inner temperature was adjusted to a temperature about 20 °C higher than the endothermic peak temperature of each salt monomer. Then the sample tube was placed in the polymerization tube, and the polymerization was carried out at the prescribed temperature for 1 h under a thin stream of nitrogen. The polymer was obtained mostly in the form of flakes but not a melt.

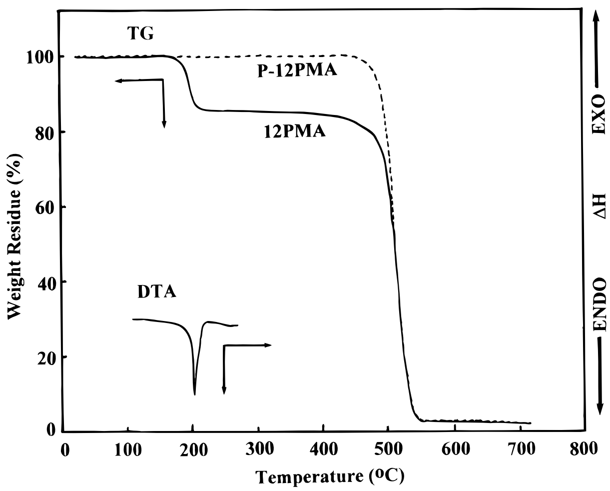


Figure 1. DTA and TG curves of salt 12BPA and polyimide P-12BPA at a heating rate of 10 °C min^{-1}.

Measurements. IR spectra were recorded on a Shimadzu FT/IR-8100 spectrophotometer. Differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-40 and TGA-40, respectively. Differential scanning calorimetry (DSC) was performed on a Seiko DSC-220C thermal analyzer. Wide-angle X-ray diffraction patterns were obtained by using a Rigaku RU-200 diffractometer with nickel-filtered Cu Kα radiation by scintillation counters at 50 kV and 180 mA.

Results and Discussion

Salt Monomers. Salt monomers *X*PMA and *X*BPA composed of the aliphatic diamines having 6—12 methylene units and aromatic tetracarboxylic acids PMA and BPA, respectively, with 1:1 composition were obtained readily as white precipitates in high yields (over 90%) by adding an ethanol solution of the individual diamines to a hot ethanol solution of an equimolar amount of the tetracarboxylic acid. This is interesting in view of the fact that two carboxylic acid functions correspond to one amine group forming the salt. The reverse addition of a tetracarboxylic acid to a diamine in hot ethanol resulted in the formation of a salt having an ill-defined structure something like a mixture of 1:1 and 2:1 compositions with respect to the diaminetetraacid component. The purification of the salts by recrystallization from water was essential for the preparation of the pure monomers having 1:1 diamine—tetraacid composition.

The IR spectra of these salt monomers supported the proposed salt formation, with the appearance of characteristic absorption bands due to ammonium ion at about 2030 cm^{-1} and overlapped carboxylate and ammonium ions at the 1650—1500 cm^{-1} region. The elemental analysis also supported the formation of the 1:1 salts from the aliphatic diamines and PMA and BPA (Table 1).

Figure 1 shows that DTA and TG curves of 12BPA, which are typical for the salt monomers. The DTA curve exhibited a sharp endotherm at 199 °C, and in the same temperature range, the TG curve recorded

Table 3. High-Pressure Synthesis and Thermal Properties of Aliphatic Polyimides P-*X*PMA and P-*X*BPA

salt monomer		polyimide[a]		
code	ept,[b] °C	η_{inh},[c] dL g^{-1}	T_{m},[d] °C	T_{g},[d] °C
6PMA	258	0.62		
7PMA	216	1.63	348	
8PMA	274	0.39	374	
9PMA	271	1.28	318	
10PMA	245	1.08	347	
11PMA	245	2.23	299	
12PMA	248	1.17	321	
6BPA	219	0.70	350	145
7BPA	224	1.53	260	131
8BPA	226	0.76	301	121
9BPA	209	1.75	231	108
10BPA	229	1.14	253	102
11BPA	202	2.72	222	91
12BPA	199	1.94	237	84

[a] The polymerization was carried out under 220 MPa of pressure at 320 °C for 15 h. [b] Endothermic peak temperature determined by DTA at a heating rate of 10 °C min^{-1}. [c] Measured at a concentration of 0.5 g dL^{-1} in concentrated sulfuric acid at 30 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}.

13.5% of weight loss. The weight loss value observed was very close to the calculated value (13.6%) based on the loss of 4 molar equiv of water through the imide formation from the salt. This clearly indicated that the endotherm in the DTA curve was accompanied by rapid polycondensation with the elimination of water producing polyimide. That is, the polycondensation of the salt monomer was considered to proceed so rapidly at the temperature range by a one-step direct imide-forming reaction rather than by the usual two-step process via polyamic acid precursor.

The endothermic peak temperatures of salt monomers *X*PMA and *X*BPA were in the range of 216−274 and 199−229 °C, respectively (Table 3), with little correspondence to the number of methylene unit. The peak temperatures lowered in the order of *X*PMA > *X*BPA > *X*-ODPA salts.[9] The order is probably related to the decreasing order of linearity and rigidity of molecular structures for the salt monomers.

High-Pressure Synthesis of Polyimides. The high-pressure polycondensation of the salt monomers was carried out by using a piston-cylinder type hot-pressing apparatus with use of a Teflon capsule as a reaction vessel as reported previously.[12] In practice, the polycondensations of the salts *X*PMA and *X*BPA were conducted under 220 MPa of pressure at 200−320 °C for 0.5−5 h, producing linear polyimides P-*X*PMA and P-*X*BPA as yellowish white pellets.

Figure 2 shows the time dependence of the inherent viscosity of polyimide P-12PMA formed by the high pressure polycondensation of salt 12PMA under 220 MPa of pressure at 320 °C. The melting temperature (T_{m}) of the resulting polyimide was 320 °C and the T_{m} under the high pressure should well exceed 320 °C. It is noteworthy that the polycondensation proceeded rapidly and was almost complete within only 1 h, giving the polyimide with high inherent viscosity above 1.0 dL g^{-1}, which was indicative of high molecular weight, contrary to the expectation that the polycondensation would be retarded by the application of high pressure coupled with the solid state reaction system due to restriction of mobility of the salt monomer and the growing polymer chain ends. Nevertheless, the ease of the high-pressure polycondensation is presumably attributable to the fact that the reactive ion pairs are adjacently arranged in the salt monomer crystals and the growing polymer chain ends.

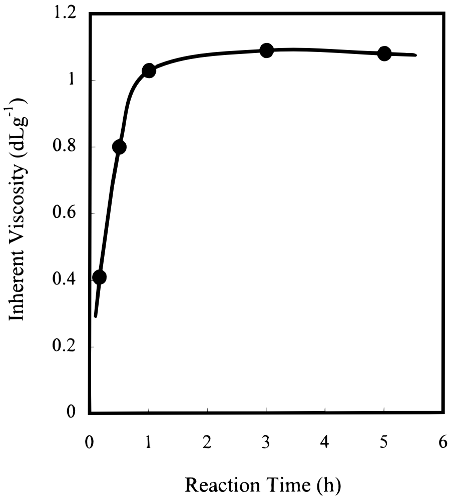


Figure 2. Time dependence of inherent viscosity of polyimide P-12PMA formed by polycondensation under 220 MPa of pressure at 320 °C.

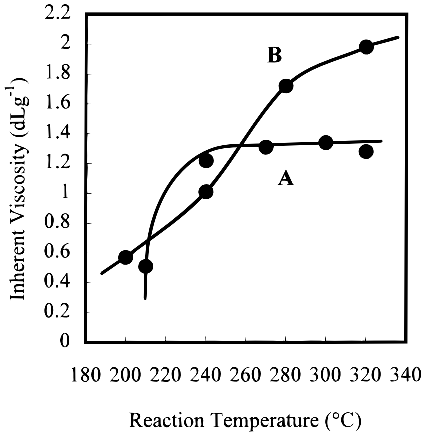


Figure 3. Effect of reaction temperature on inherent viscosity of polyimides (A) P-9PMA and (B) P-12BPA formed by polycondensation under 220 MPa of pressure for 5 h.

The most striking aspect of the high-pressure polycondensation of the salt monomer was that the salt directly afforded a high molecular weight polyimide within such a short reaction time, despite of fact that the byproduct, water, produced during the polycondensation, co-existed in the closed reaction vessel. In fact, some moisture was detected on the surface of the polyimide pellet taken out of the closed reaction vessel just after the high-pressure polycondensation. Therefore, it is thought that the water produced is excluded effectively from the solid polymer mass throughout the reaction; namely, the polycondensation proceeds rapidly under unequilibrium state.

The reaction temperature was also an important factor for the high pressure synthesis of polyimides with high molecular weights. Figure 3 exhibits the effect of reaction temperature on the inherent viscosities of polyimides P-9PMA and P-12BPA formed by the high-pressure polycondensation of salts 9PMA and 12BPA under 220 MPA of pressure for 5 h. In the preceding section, it was shown that the polycondensation of the salts took place at around the endothermic peak temperature (determined by DTA) of the salt monomers; however, no information was available on the molecular weight of the resulting polyimides by the thermal analysis (DTA and TG). The peak temperature of salt 9PMA was 271 °C, and the polyimide could not be obtained below 200 °C as can be seen from Figure 3.

Similarly, the peak temperature of salt 12BPA was 199 °C, and no polyimide was obtainable below 160 °C. Thus, the polycondensation were found to occur at temperatures as much as 40−70 °C lower than the peak temperatures of the salts under high pressure. However, these low reaction temperatures gave polyimides of quite low molecular weights. In both cases, the inherent viscosities of the resulting polyimides increased with increasing reaction temperature. The suitable reaction temperatures to attain high inherent viscosities over 1.0 dL g^{-1}, indicative of high molecular weights, were the temperatures close to the T_m's of P-9PMA and P-12BPA under high pressure that were much higher than the T_m's under 1 atm.

Table 3 summarizes the results of the high-pressure synthesis of polyimides P-*X*PMA and P-*X*BPA from the salt monomers *X*PMA and *X*BPA, respectively. From these results, all the salt monomers readily afforded the corresponding polyimides having high inherent viscosities of 0.4−2.7 dL g^{-1}. It is interesting to note that the inherent viscosity values exhibited an odd−even alteration with the higher values for the odd-numbered polyimides. This tendency was in contrast to the odd−even effect of melting temperatures for these polyimides. That is, the polyimides with comparatively lower melting temperatures seemingly had higher molecular weights, when they were prepared by the high-pressure polycondensation of the corresponding salt monomers.

The polymers thus formed were confirmed to be polyimides by means of IR spectroscopy and elemental analysis. All the polymers exhibited characteristic absorption bands due to imide ring at 1771−1769, 1719−1693, 1397−1391, and 745−727 cm^{-1}, with disappearance of characteristic ammonium salt absorptions ca. 2030 and 1560 cm^{-1} for the salt monomers. The elemental analysis values of the polymers were in close agreement with the values for the proposed polyimide structures (Table 2). These results clearly supported the formation of polyimides.

The polycondensation of the salt monomers *X*PMA and *X*BPA also proceeded by heating under atmospheric pressure, yielding polyimides. However, the polycondensation even at about 20 °C higher temperatures than the peak temperatures of the salts very often produced polyimides insoluble in any solvents including methanesulfonic acid and concentrated sulfuric acid, indicating the formation of cross-linked polyimides. This is probably caused by intermolecular amidation as a side reaction in addition to the main imide-forming reaction during the solid-state thermal or melt polycondensation under atmospheric pressure. Therefore, polycondensation under high pressure was found to be very useful for the synthesis of the aliphatic polyimides having well-defined structures.

Thermal Behavior of Polyimides. The thermal behavior of the polyimides was evaluated by DTA, DSC, and TG. Table 3 also lists the T_m's and glass transition temperatures (T_g) of the high-pressure synthesized polyimides. As to the even-numbered aliphatic polypyromellitimides, Korshak et al.[6] showed that polyimide P-12PMA had a T_m of 297 °C, while the T_m's of polyimides P-8PMA, P-10PMA, and P-12PMA were reported to be 383, 323, and 305 °C, respectively, by Evans et al.[5] The odd-numbered P-9PMA was reported to have a T_m of 271 °C by Koning et al.[8] They also presented that the BPA-based polyimide P-6BPA had a T_m of 336 °C and a T_g of 150 °C.[8] These T_m values reported were mostly some 20 °C lower than those of this study with one exception (P-8PMA), and the results are attributable to the higher crystallinity of the high-pressure synthesized polyimides having well-defined structures.

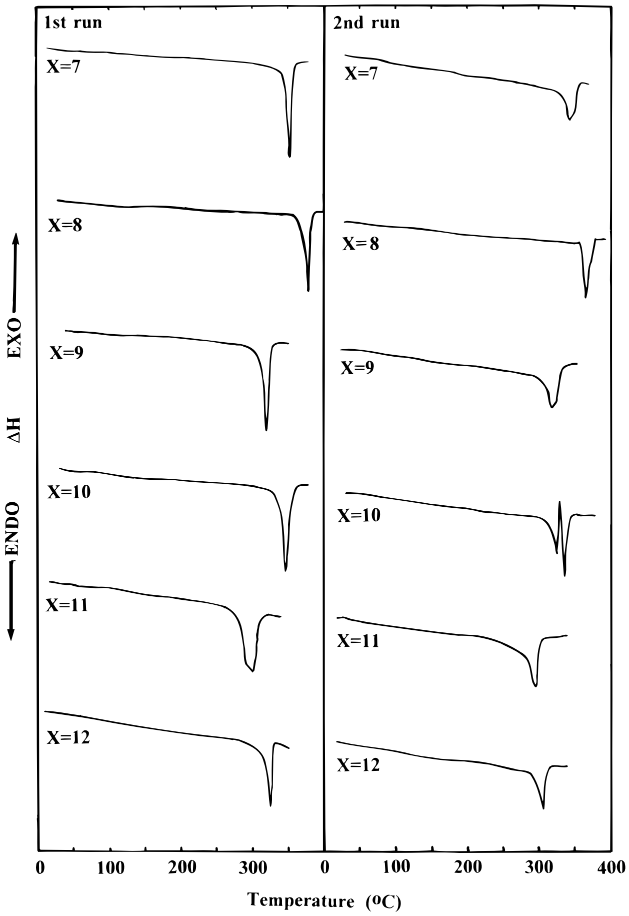


Figure 4. DSC curves of polyimides P-*X*PMA ($X = 7-12$) at a heating rate of 10 °C min^{-1}.

A typical TG curve of the polyimide is shown in curve B in Figure 1. All the aliphatic polyimides exhibited no weight loss below 400 °C and hence were stable up to this temperature in the melt state under nitrogen.

The thermal behavior of the aliphatic polyimides is discussed in more detail below. Figure 4 shows the DSC curves of polyimides P-*X*PMA ($X = 7-12$) at a heating rate of 10 °C min^{-1}. P-6PMA exhibited no T_m below its decomposition temperature around 430 °C, and the DSC trace of the polymer was not included in this figure. The DSC curve of each polyimide on the first heating run, which reflects the property of the as-synthesized polymer under high pressure, exhibited only one melting endothermic peak. Each curve on the second heating run shows the property of the polymer independent of the method of preparation. Here all the second heating thermogram were measured in the same conditions that after the first cooling from the melted state to room temperature at the rate of 10 °C min^{-1}. The second runs exhibited one melting endothermic peak with a shoulder or two melting transitions. The behavior obtained at the second heating run was reproducable upon the third or fourth heating run. Although Figure 4 excluded the DSC traces of the first and second cooling runs, all the polyimides exhibited one exothermic peak due to crystallization on every cooling run. No T_g was detected for the P-*X*PMA series because of their inherently high crystalline nature as evidenced by the DSC traces on the second heating run as well as the first.

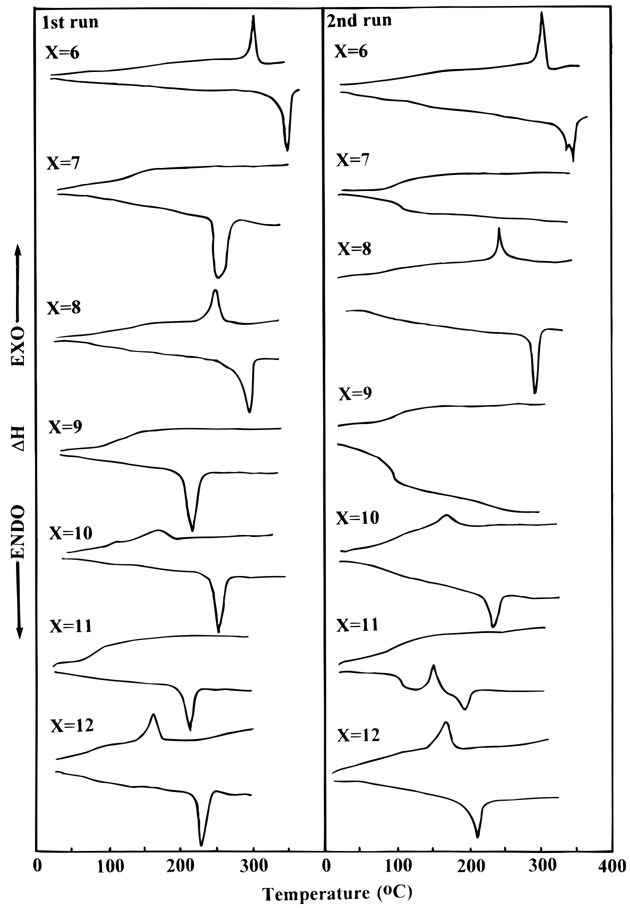


Figure 5. DSC curves of polyimides P-*X*BPA ($X = 6-12$) at a heating rate of 10 °C min^{-1}.

From these results, it can be said that some of the P-*X*PMA polyimides, which were formed after melting and subsequent crystallization melted twice at the second heating run due to the presence of two types of crystals or exhibited a crystal−crystal transition or a recrystallization just before melting. On the contrary, the as-polymerized polyimides under high pressure melted just once at higher temperature with a larger enthalpy change on the first heating run, suggesting that the high-pressure polycondensation of the salt monomers affords a stable crystal of the polyimides.

Figure 5 illustrates the DSC curves of polyimides P-*X*BPA ($X = 6-12$). Similar to P-*X*PMA mentioned just above, the enthalpy changes for melting of the even-numbered P-*X*BPA on the first heating run were also higher than those on the second run. The T_m's of the first run were, of course, higher than those on the second run. Therefore, the high pressure polycondensation of the salt monomers influenced the crystal formation of the even-numbered P-*X*BPA as well as P-*X*PMA. The odd-numbered P-*X*BPA were less crystallizable than the even-numbered ones. Polyimides P-7PBA and P-9BPA were so difficult to crystallize that their DSC curves on the first cooling run showed no crystallization exothermic peak and those on the second heating exhibited no T_m but a clear T_g. Nevertheless, their DSC traces on the first heating run showed large and sharp melting peaks. As for P-11BPA, the rate of crystallization was higher than those of P-7BPA and P-9BPA, and the DSC curve on the second heating run showed a crystallization exothermic peak at 148 °C, followed by a melting endothermic peak at 197 °C with a small enthalpy change. These results suggest that, although the odd-numbered polyimides P-XBPA preferred an amorphous structure, they could be crystallized during the high pressure polycondensation.

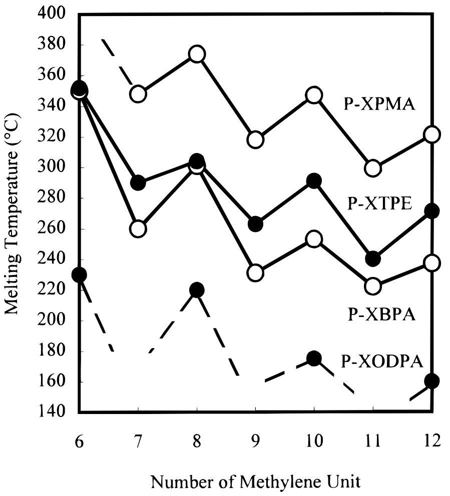


Figure 6. Plots of T_m's of polyimides P-*X*PMA, P-*X*BPA, P-*X*-ODPA, and P-*X*TPE vs number of methylene unit.

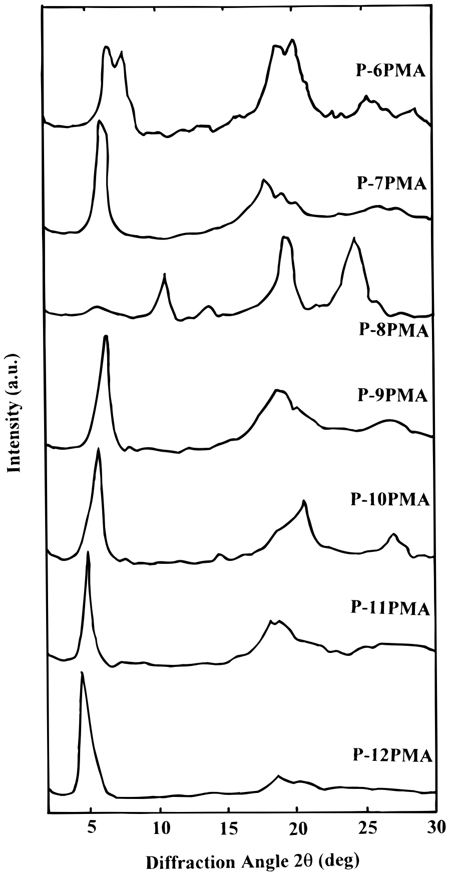


Figure 7. Wide-angle X-ray diffraction of polyimides P-*X*PMA ($X = 6-12$).

Figure 6 shows the dependence of the number of methylene units for the T_m's of the series of aliphatic polyimides including P-*X*PMA and P-*X*BPA obtained here and the previously reported P-*X*-OPDA[9] and P-*X*TPE.[11] The T_m's of polyimides P-*X*PMA and P-*X*BPA were in the ranges 374−299 and 350−222 °C, respectively. In each series of the polyimides, the T_m's exhibited a remarkable odd−even effect with the higher values for the even-numbered polyimides. The T_m's of P-*X*PMA were highest among the four kinds of the polyimides because of the linear and highly symmetric

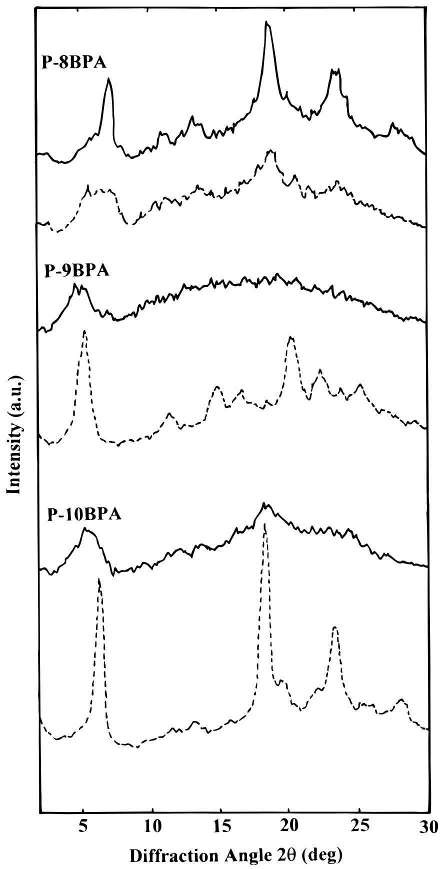


Figure 8. Wide-angle X-ray diffraction diagrams of polyimides P-XBPA ($X = 8, 9, 10$): solid line is that of atmospheric-pressure-polymerized polyimide and broken line is that of high-pressure-synthesized polyimide.

molecular structure, and the T_m's of these polyimides were lowered in the order of P-XPMA > P-XTPE (352−240 °C) > P-XBPA > P-X-ODPA (230−160 °C).

Although P-XPMA had no T_g due to high crystallinity, the T_g's ofP-XBPA were in the range 145−84 °C, which was lowered monotonically with an increasing number of methylene units. The results reflect a lowering in the rigidity of polyimide backbone with an increase in the methylene spacer length. The T_g values of the series of aliphatic polyimides decreased in the following order: P-XTPE (141−86 °C) ≈ P-XBPA > P-X-ODPA (118−70 °C), and the decreasing order was the same as that of the T_m's.

Crystallinity of Polyimides. Figure 7 shows the wide-angle X-ray diffraction diagrams of a series of polyimides P-XPMA synthesized under high pressure. This indicated that all the polyimides had a high level of crystallinity. Little difference was observed between the high-pressure-sythesized polyimides and the atmospheric-pressure-polymerized polyimides, which were also highly crystalline despite having less defined structure.

Figure 8 exhibits the wide-angle X-ray diffraction patterns of representative BPA-series polyimides P-8BPA, P-9BPA, and P-10BPA prepared both under high pressure and atmospheric pressure. The high-pressure effect is generally observed on the promotion of crystal growth of the polyimides. Most of the high-pressure-synthesized polyimides, with two exceptions (P-6BPA and P-8BPA), were highly crystalline due to having a well-defined structure, while the atmospheric-pressure-polymerized polyimides were less crystalline but not completely amorphous. One of the exceptions is seen in the X-ray diffraction patterns of P-8BPA in Figure 8. The crystallinity of the high-pressure-synthesized P-8BPA was lower than that of the atmospheric-pressure-polymerized polyimide. This is probably related to the melting temperature of polyimides. Since both P-6BPA and P-8BPA have high melting temperatures above 300 °C, they were obtained in linear structure without cross-linking by the atmospheric pressure polycondensation, and hence they are easy to crystallize during the polycondensation at around 240 °C, while the corresponding high-pressure-synthesized polyimides are far less mobile for the crystal growth under a high pressure of 220 MPa at 250 °C. As shown above, the high-pressure effect can be seen clearly only in the P-XPBA system. This is ascribed to the ability of the cis−trans conformational change as illustrated in Figure 9.

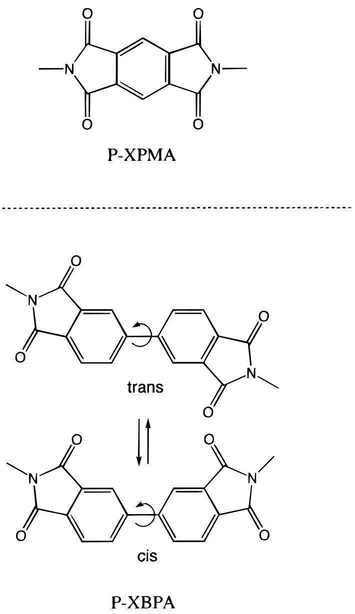


Figure 9. Possible conformations of the diimide moiety for P-XPMA and P-XBPA.

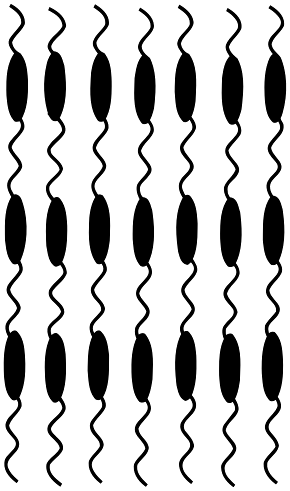


Figure 10. Layer structure proposed for polyimides P-XPMA and P-XBPA.

In addition, the high-pressure-synthesized polyimides of both P-XPMA and P-XBPA series generally exhibited a sharp and large diffraction peak at the small-angle side near 5−6° in 2θ (θ = diffraction angle), as seen in Figures 7 and 8 again. The results suggest that these aliphatic polyimides presumably have a smectic-like

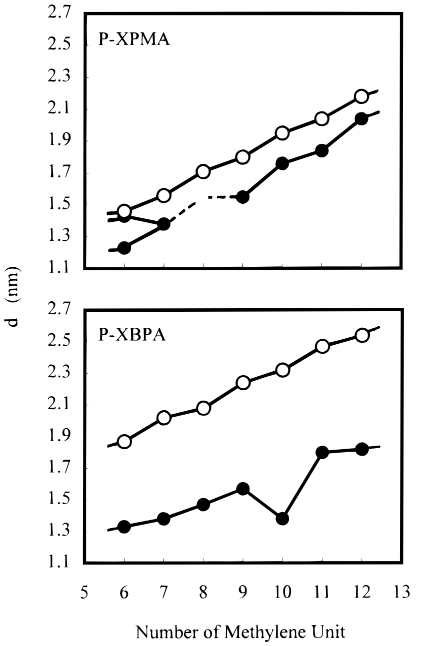


Figure 11. Plots of layer spacing of polyimides P-*X*PMA and P-*X*BPA vs number of methylene unit: closed circle is the layer spacing measured from the wide-angle X-ray diffraction diagram and open circle is from the molecular model.

ordered layer structure, as shown in Figure 10. The only one exception is the case of P-6PMA, which exhibited two layer diffraction peaks, showing the existence of two types of crystals, on the small angle side of the X-ray diffraction diagram. This phenomenon may be ascribed to the crystalline structure influenced by the fit between the length of six methylene units (0.74 nm) and that of pyromellitimide group (0.75 nm).

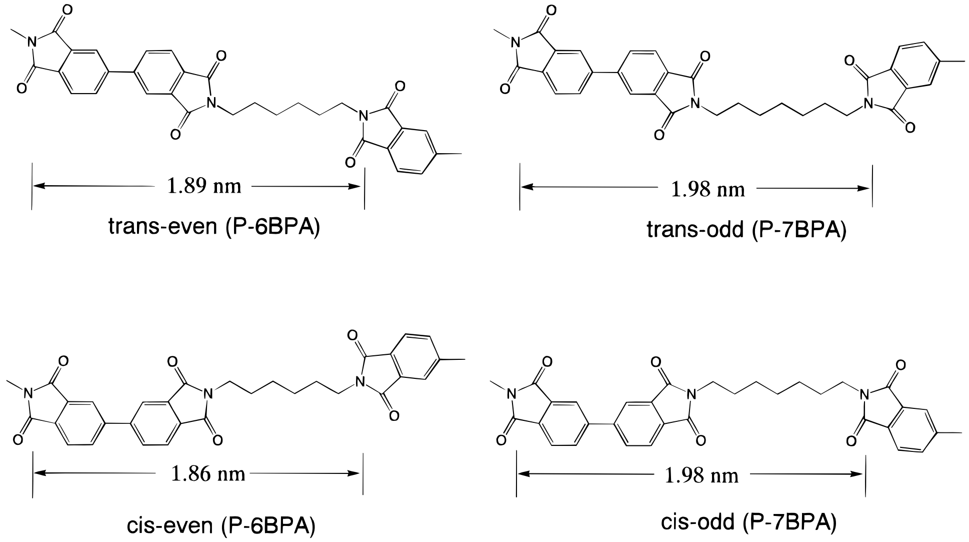
Figure 11 illustrates the layer spacing of both polyimides P-*X*PMA and P-*X*BPA (closed circles), calculated from the angle of the small angle diffraction peak by adapting the following well-known Bragg's equation, as a function of the number of methylene units

$$2d \sin \theta = n\lambda$$

where d is the layer spacing, θ is the angle of scatter, n is the order of reflection, and λ is the wavelength of the X-ray used. In the present case, n is 1 and λ is 0.1542 nm for nickel-filtered Cu Kα radiation. The open circles in this figure exhibit the unit lengths of the polyimides measured by the molecular model.

The layer spacing of P-*X*PMA except for P-8PMA exhibited an odd−even alteration with the higher values for the even-numbered polyimides, which strongly suggests a difference in the crystalline structure between the odd-numbered and even-numbered P-*X*PMA polymers. Each layer spacing of P-*X*PMA was almost the same as the extended unit length of the respective polyimides measured by the molecular model. On the other hand, the layer spacing for P-*X*BPA increased almost monotonically with increasing the number of methylene unit except for P-10BPA. It is rather surprising that the layer spacing of P-*X*BPA was much shorter than the spacing of the corresponding P-*X*PMA, because the biphenyltetracarboxdiimide group should have a longer unit length than the pyromellitimide group. Moreover, each layer spacing of P-*X*BPA was over 0.5 nm shorter than the modeled extended unit length of the respective polyimides as shown in Figure 11.

There are three probable reasons for these findings. The first reason is the conformational effect based on the rotation around the σ-bond connecting biphenyl group which generates cis and trans conformation as shown in Figure 9. The second one is gauche conformational effect of the methylene unit. The third one is that the polymer chain is tilted against the normal of the layer. Figure 12 shows the unit lengths of P-6BPA and P-7BPA having cis or trans biphenyl and gauche-free extended methylene conformation. This figure indicates that there is little difference between the unit lengths of cis and trans P-*X*BPA. Thus, since the cis−trans conformational change does not influence the unit lengths of P-*X*BPA, the first reason cannot result in this discussed phenomenon. Figure 11 also indicates that the unit lengths of the P-*X*BPA system prepared under high pressure do not exhibit an odd−even alteration. This finding suggests that the methylene chain of P-*X*BPA has the gauche conformation to some extent. Therefore, we can say that the second reason is suitable and the shorter layer spacing of P-*X*BPA is mainly due to the gauche methylene conformational effect. However, the suitability of the third reason cannot be confirmed because the unit length is not proportional to the number of methylene units.



trans-even (P-6BPA)

trans-odd (P-7BPA)

cis-even (P-6BPA)

cis-odd (P-7BPA)

Figure 12. Unit lengths of P-6BPA and P-7BPA taking cis or trans conformation.

The layer spacing of P-10BPA is smaller than expected because the length of the ten methylene units is almost the same as that of the biphenyltetracarboxdiimide group, and hence this may affect the crystalline layer structure, similar to the case of P-6PMA discussed above.

Conclusions

The high-pressure thermal polycondensation of the salt monomers composed of aliphatic diamines with 6−12 methylene units and pyromellitic acid and biphenyltetracarboxylic acid readily afforded the aliphatic−aromatic polyimides P-*X*PMA and P-*X*BPA, respectively, having high inherent viscosities and well-defined structures. Surprisingly, the polycondensation progressed rapidly in the solid state, directly affording polyimides with high molecular weights in one step mostly within only 1 h, despite the fact that the byproduct water condensed during the high-pressure polymerization coexisted in a closed reaction vessel. The melt polycondensation of these salt monomers under atmospheric pressure very often yielded undesirable cross-linked polyimides. Therefore, the solid-state thermal polycondensation under high pressure is advantageous for a simple, efficient, and rapid synthetic method of polyimides having higher purity and higher crystallinity compared with the polyimides prepared by other synthetic methods.

Acknowledgment. The authors gratefully acknowledge the support for this work by a Grant-in-Aid for Scientific Research B from the Ministry of Education, Science, and Culture of Japan (No. 05453142).

References and Notes

(1) Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. *Polyimides: Thermally Stable Polymers*; Consultants Bureau: New York, 1987.
(2) Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Blakie: New York, 1990.
(3) Edwards, W. M.; Robinson, I. M. *U.S. Pat.* 2,710,853, 1955.
(4) Sorenson, W. R.; Campbell, T. W. *Preparative Methods of Polymers Chemistry*, 2nd ed.; Interscience : New York, 1968; p 88.
(5) Evans, J. R.; Orwoll, R. A.; Tang, S. S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 971.
(6) Korshak, V. V.; Babchinitser, T. M.; Kazaryan, L. G.; Vasilyev, V. A.; Genin, Ya. V.; Azriel, A. Ye.; Vygodsky, Ya. S.; Churochkina, N. A.; Vinogradova, S. V.; Tsvankin, D. Ya. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 247.
(7) Sroog, C. E. *Encycl. Polym. Sci. Tech.* **1969**, *11*, 247.
(8) Koning, C.; Teuwen, L.; Meijer, E. W.; Moonen, J. *Polymer* **1994**, *35*, 4889.
(9) Itoya, K.; Kumagai, Y.; Kakimoto, M.; Imai, Y. *Macromolecules* **1994**, *27*, 4101.
(10) Inoue, T.; Kakimoto, M.; Imai, Y.; Watanabe, J. *Macromolecules* **1995**, *28*, 6368.
(11) Inoue, T.; Kakimoto, M.; Imai, Y.; Watanabe, J. *Macromol. Chem. Phys.* in press.
(12) Itoya, K.; Kakimoto, M.; Imai, Y.; Fukunaga, O. *Polym. J.* **1992**, *24*, 979.

MA9615563