# High-Pressure Synthesis of Aliphatic Polyimides via Salt Monomers Composed of Aliphatic Diamines and Oxydiphthalic Acid

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*Received January 24, 1994; Revised Manuscript Received April 22, 1994*•

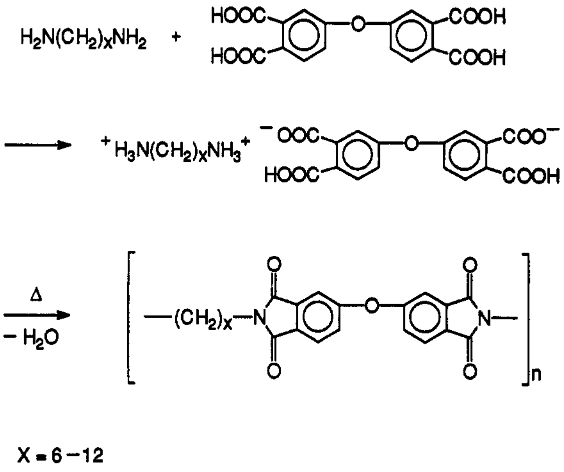
ABSTRACT: Aliphatic polyimides having inherent viscosities of 0.4–2.8 dL $g^{-1}$ were readily synthesized by the melt or solid-state polycondensation under high pressure of the salt monomers composed of aliphatic diamines having 6–12 methylene chains and 4,4′-oxydiphthalic acid at 140–330 °C under 250–650 MPa. It is notable that the high-pressure polycondensation proceeded rapidly with the elimination of water in the closed reaction vessel and was almost complete within 3 h. The polyimides having six and eight methylene units were highly crystalline yellowish white solids, whereas those with odd number carbons were amorphous pale yellow resinous products. The thermal behavior of the polyimides are also discussed.

## Introduction

Aromatic polyimides have been well known for many years as high-temperature and high-performance polymers and have found many applications in aerospace, electronics, and other industries.[1,2] Polyimide investigations have been carried out mainly with wholly aromatic polyimides, whereas relatively little detailed information is available in regard to the synthesis and properties of aliphatic diamine-based polyimides (hereafter aliphatic polyimides).[3–5] Aliphatic polyimides were first prepared in 1955 by the melt polycondensation of the salt composed of an aliphatic diamine and an aromatic tetracarboxylic acid or of a diamine and a diester diacid.[3,6,7] In addition, there is a brief indication that aromatic polyimides were also prepared via the corresponding salt monomers by thermal polycondensation.[8]

The application of high pressure is a promising methodology for the synthesis of organic compounds[9] and polymers as well. Nevertheless, although polyaddition reactions under high pressure have been investigated to give polyoxadiazole,[10] polyaminoimide,[11] polycyanurates,[12] and polyisocyanurates,[13] there is little information about high-pressure synthesis of condensation polymers. Morgan and Scott reported three decades ago the high-pressure polycondensation of the 1:1 salt of 3,3′,4,4′-tetraaminobiphenyl and pyromellitic acid under 20–70 MPa at a temperature up to 450 °C by using a hot-pressing apparatus, leading to the formation of polybenzimidazopyrrolone as a polymer molding.[14,15] Ikawa and his coworkers demonstrated the solid-state polycondensation of ω-amino acids with carbon numbers of 11 and 12 under 200–400 MPa at a temperature of 180–250 °C, giving highly crystalline aliphatic polyamides.[16,17]

These findings prompted us to study the high-pressure synthesis of aliphatic polyimides. This article deals with a successful high-pressure synthesis of aliphatic polyimides by the polycondensation of the 1:1 salts derived from a series of aliphatic diamines and 4,4′-oxydiphthalic acid (ODPA) (eq 1). The properties of the ODPA-based aliphatic polyimides are also described.



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## Experimental Section

**Apparatus.** The apparatus used for the high-pressure polymerization was the same as that described previously.[10]

**Materials.** Aliphatic diamines having 6–12 methylene units were purified individually by distillation under reduced pressure over potassium hydroxide pellets. 4,4′-Oxydiphthalic anhydride was purified by sublimation.

**Preparation of Salt Monomers. Octamethylenediamine–Oxydiphthalic Acid Salt (8-ODP).** A mixture of 15.15 g (50 mmol) of oxydiphthalic anhydride in 500 mL of water was heated at 100 °C for 15 h, affording the tetracarboxylic acid solution. To this solution was added 7.21 g (50 mmol) of octamethylenediamine dropwise with stirring at 60 °C, giving a clear solution. After the solution was stirred at room temperature for 5 h, the precipitate formed was collected by filtration and dried under vacuum at room temperature. The yield of the salt was 23.5 g (96%), mp 170 and 177 °C (by DTA at a heating rate of 10 °C $min^{-1}$). IR (KBr): 1680 (carboxylic C=O) and 1568 $cm^{-1}$ (overlapped $NH_3^+$ and carboxylate C=O).

The other salts were prepared by the analogous procedure, and the IR and elemental analysis data of all the salt monomers are summarized in Table 1.

**Polymerization of Salts under High Pressure. P-8-ODP.** A 0.5-g portion of salt 8-ODP was placed into a Teflon capsule (15-mm inside diameter), and then the capsule was loaded into the cylinder. The piston–cylinder was set at the furnace and the pressure was applied at room temperature to the capsule, followed by raising temperature. The polymerization was carried out at 270 °C under 250 MPa for 15 h. The reaction time was recorded from the point where the temperature reached to 270 °C, which

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• Abstract published in *Advance ACS Abstracts,* June 1, 1994.

0024-9297/94/2227-4101$04.50/0

**Table 1. IR and Elemental Analysis Data of Salt Monomers *X*-ODP and Polyimides P-*X*-ODP**

| | elemental analysis, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | calcd | | | found | | | |
| salt or polymer | C | H | N | C | H | N | IR, cm$^{-1}$ |
| 6-ODP | 57.14 | 5.67 | 6.06 | 56.92 | 5.69 | 5.98 | 1680, 1566 |
| 7-ODP | 57.98 | 5.92 | 5.88 | 57.66 | 5.99 | 5.79 | 1675, 1566 |
| 8-ODP | 58.76 | 6.16 | 5.71 | 58.41 | 6.34 | 5.71 | 1680, 1568 |
| 9-ODP | 59.52 | 6.39 | 5.55 | 59.22 | 6.45 | 5.42 | 1698, 1570 |
| 10-ODP | 60.22 | 6.61 | 5.40 | 59.88 | 6.74 | 5.34 | 1688, 1563 |
| 11-ODP | 60.89 | 6.81 | 5.26 | 60.54 | 7.01 | 5.04 | 1692, 1568 |
| 12-ODP | 61.53 | 7.01 | 5.12 | 61.51 | 7.24 | 5.11 | 1674, 1565 |
| P-6-ODP | 67.69 | 4.65 | 7.18 | 67.89 | 4.77 | 7.18 | 1773, 1711, 1395, 747 |
| P-7-ODP | 68.31 | 4.98 | 6.93 | 67.99 | 4.81 | 6.93 | 1773, 1715, 1396, 748 |
| P-8-ODP | 68.89 | 5.30 | 6.69 | 68.74 | 5.33 | 6.75 | 1773, 1711, 1395, 747 |
| P-9-ODP | 69.43 | 5.59 | 6.48 | 69.51 | 5.57 | 6.48 | 1773, 1715, 1396, 748 |
| P-10-ODP | 69.94 | 5.87 | 6.27 | 69.75 | 5.84 | 6.23 | 1773, 1715, 1398, 748 |
| P-11-ODP | 70.42 | 6.13 | 6.08 | 70.33 | 6.09 | 6.17 | 1773, 1717, 1398, 748 |
| P-12-ODP | 70.87 | 6.37 | 5.90 | 71.20 | 6.47 | 5.99 | 1773, 1717, 1396, 748 |

required ca. 2 h. After the polymerization, the temperature was lowered to room temperature, followed by releasing the pressure to 1 atm. The polymer in the form of a flat cylindrical pellet (15-mm diameter and ca. 3-mm thick) was removed from the capsule. The pellet was then dried at room temperature under vacuum for 3 days for the complete removal of the water produced during the polymerization. The inherent viscosity of the polymer was 0.78 dL g$^{-1}$, measured at a concentration of 0.5 g dL$^{-1}$ in concentrated sulfuric acid at 30 °C. IR (KBr): 1773 and 1711 (imide C=O), 1395 (C–N), and 747 cm$^{-1}$ (imide ring).

The other polymers were synthesized by similar procedures, and the IR and elemental analysis data of all the polymers are given in Table 1.

**Polymerization of Salts under Reduced Pressure. P-8-ODP.** The polymerization of 0.5 g of salt 8-ODP was carried out by using a Shibata glass tube oven GTO-350 at 150–200 °C under 2.6 kPa (20 Torr) for 1–3 h. The polymer formed was insoluble in any solvent. The IR spectrum was the same as that of the polymer described above.

The other polymers were prepared by the analogous procedure.

**Measurements.** IR spectra were recorded on a Shimadzu FT/IR-8100 spectrophotometer. Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DTA-40, DSC-41, and TGA-40, respectively. The peak temperature of the DTA or DSC endotherm was taken as the melting point of each sample. Wide-angle X-ray diffraction patterns were obtained by using a Rigakudenki RU-200 diffractometer with nickel-filtered Cu K$\alpha$ radiation by scintillation counters at 50 kV and 180 mA.

## Results and Discussion

**Salt Monomers.** The 1:1 salts *X*-ODP composed of the aliphatic diamines having 6–12 methylene units (*X* stands for the number of methylene units in the aliphatic diamine) and ODPA were prepared as white precipitates by dissolving the individual aliphatic diamine with an equimolar amount of ODPA in a hot water solution, followed by cooling.[5–8]

The IR spectrum of salt 8-ODP is shown in curve A in Figure 1. The IR spectra of all the salt monomers supported the proposed salt formation, with the appearance of a characteristic absorption band due to overlapped carboxylate and ammonium ions at the 1563–1570-cm$^{-1}$ region, while with retention of the carboxylic absorption at 1674–1698 cm$^{-1}$. The elemental analysis of the products also supported the formation of the 1:1 salts from the aliphatic diamines and ODPA (Table 1).

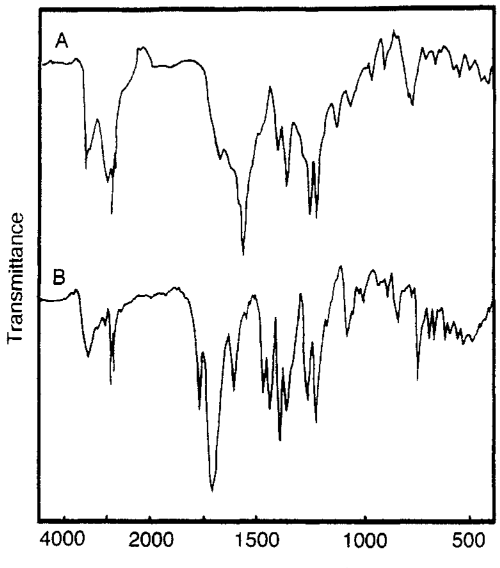

**Figure 1.** IR spectra of (A) salt 8-ODP and (B) polymer P-8-ODP.

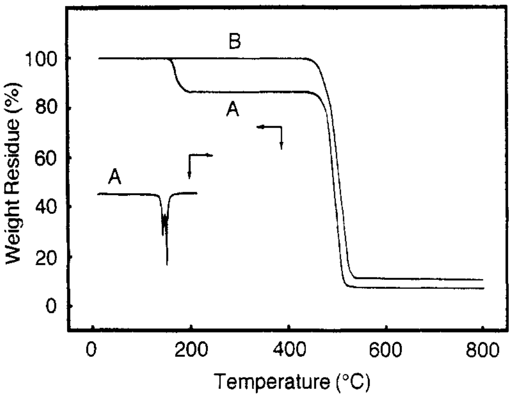

**Figure 2.** DTA and TG curves of (A) salt 8-ODP and (B) polymer P-8-ODP.

Figure 2 shows the DTA and TG curves of salt 8-ODP. As can be seen from the DTA curve, salt 8-ODP exhibited sharp endothermic peaks at around 170 °C due to melting at a fast heating rate of 10 °C min$^{-1}$. The weight loss of the salt commenced at its melting point, ending at around 200 °C as observed on the TG curve (curve A in Figure 2). Thus the melting was accompanied by vigorous evolution of water with rapid solidification of the melt, giving directly the solid polyimide. The weight loss value observed at the temperature range between 170 and 200 °C was 13.8%, which was in close agreement with the calculated value of 14.7% based on the loss of four molar equivalent of water through imide formation from the salt. These results strongly suggested that the imide-forming reaction from the salt monomer proceeded so rapidly at the temperature range and apparently by the one-step reaction rather than the two-step reaction via polyamic acid precursor.

The melting points of salt monomers 6-ODP to 12-ODP, as shown in Table 1, were in the range between 170 and 225 °C. When salt 8-ODP was heated at a temperature of 150–200 °C under a reduced pressure of 2.6 kPa for 1–3 h, it afforded polyimide. Nevertheless, the polyimide produced was quite insoluble in any solvents including methanesulfonic acid and concentrated sulfuric acid, indicating that the polyimide had cross-linked through some side reactions such as probable intermolecular

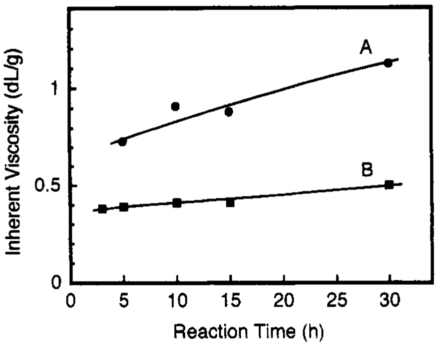

**Figure 3.** Time dependence of inherent viscosity of polymer P-8-ODP formed (A) by the polymerization at 290 °C under 250 MPa and (B) by the reaction at 270 °C under 450 MPa.

amidation. The cross-linked polyimide was amorphous (discussed later again), as evidenced by the X-ray diffraction study, and showed no melting temperature ($T_m$) with glass transition temperature ($T_g$) of 100 °C. In addition, the other salt monomers afforded the corresponding polyimides, which were insoluble in any solvents, by the solid state or melt polycondensations under the reduced pressure conditions.

**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.[10] The polycondensation was conducted at 140–330 °C under 250–600 MPa for 3–30 h, affording readily linear polyimides as pale yellow pellets. The reaction time was recorded from the point where the temperature reached to a constant reaction temperature, which usually required around 2 h.

Figure 3 shows the time dependence of the inherent viscosity of polyimide P-8-ODP formed by the high-pressure polycondensation of salt 8-ODP. Both curves revealed that the polycondensation proceeded rapidly and almost completely within 3 h, giving the polyimide with high inherent viscosities above 0.4 dL g$^{-1}$. It is notable that the polycondensation progressed even under these high-pressure conditions which usually restricted molecular motion of the salt monomer as well as the growing polymer chain ends. The most striking aspect of the present results was that the high-pressure polycondensation proceeded smoothly giving high molecular weight polyimide, despite the fact that the polymerization was accompanied by the elimination of water, which stayed in the closed reaction vessel. Such an ease of the high-pressure polycondensation is probably attributable to the fact that the reactive ion pairs are adjacently arranged in the salt monomer crystals and the growing polymer chain ends. Naturally, a higher pressure of 450 MPa further restricted the molecular motion necessary for the polymer formation, and hence gave the polyimide having lower viscosity value, compared with the polycondensation under a lower pressure of 250 MPa.

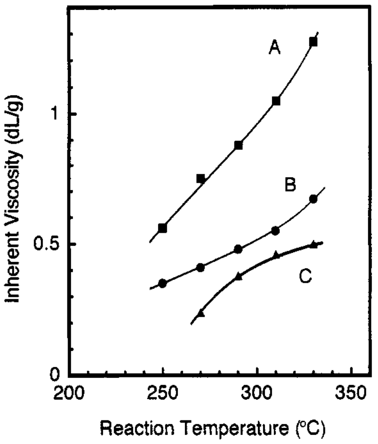

**Figure 4.** Temperature dependence of inherent viscosity of polymer P-8-ODP formed by the polymerization for 15 h (A) under 250 MPa, (B) under 450 MPa, and (C) under 620 MPa.

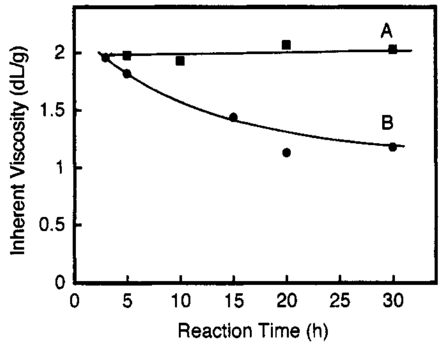

**Figure 5.** Time dependence of inherent viscosity of polymer P-12-ODP formed by the polymerization under 250 MPa (A) at 200 °C and (B) at 280 °C.

Figure 4 depicts the influences of reaction temperature and pressure on the inherent viscosity of polyimide P-8-ODP by the polymerization of the salt. Under a constant pressure, the inherent viscosity of the resultant polyimide increased with increasing reaction temperature. At a constant reaction temperature, in contrast, the viscosity values decreased obviously with the increase of reaction pressure; the results corresponded well with those discussed above. Hence the application of pressure to the polycondensation could not accelerate but actually retard this type of polyimide formation; nevertheless the fact that the polymerization could proceed readily is again remarkable.

In the case of the high-pressure polycondensation of salt 12-ODP, a different polymerization behavior was observed. Figure 5 exhibits the time dependence of the viscosity value of polyimide P-12-ODP formed by the polymerization of salt 12-ODP. The course of the high-pressure polycondensation at 200 °C under 250 MPa was as usual as that for salt 8-ODP discussed above. When the polycondensation was carried out at 280 °C under the same pressure, the viscosity value decreased with increasing reaction time after reaching a maximum at an early stage of the polycondensation. The viscosity decrease is probably related to the melting behavior of both the salt monomer and the polymer. In this case, the melting point of salt 12-ODP was 225 °C, while the resultant polyimide had $T_m$ of 160 °C, which was 65 °C lower than the salt monomer. Therefore it is thought that the polymerization at such a higher temperature of 280 °C probably proceeded in a melt state, even though taking into account a considerable increase in the $T_m$ of the polyimide by the application of pressure. The molten polymer once formed presumably suffered hydrolysis more easily in the closed reaction vessel by the water produced during the polyimide formation, and hence resulted in lowering of the viscosity value of the polyimide. This was evidenced by the following experimental fact: when polyimide P-12-ODP, having inherent viscosity of 1.98 dL g$^{-1}$ formed by the polycondensation at 200 °C under 250 MPa for 5 h, was subjected to further reaction at 280 °C under the same pressure for 15 and 30 h, the viscosity values apparently reduced to 1.50 and 1.25 dL g$^{-1}$, respectively.

Figure 6 shows the influences of reaction temperature and pressure on the inherent viscosity of polyimide P-12-

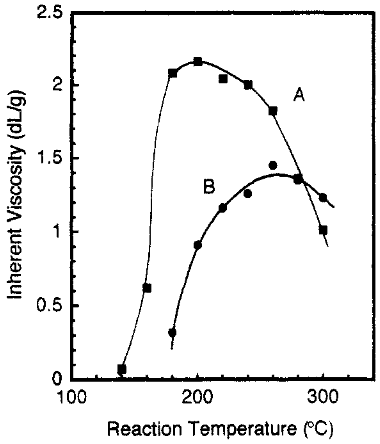

**Figure 6.** Temperature dependence of inherent viscosity of polymer P-12-ODP formed by the polymerization for 15 h (A) under 220 MPa and (B) under 580 MPa.

**Table 2. High-Pressure Synthesis and Properties of Polyimides P-*X*-ODP**

| monomer | | polymzn conditions$^a$ | | polymer | | |
|---|---|---|---|---|---|---|
| *X* | mp,$^b$ °C | temp, °C | press, MPa | $\eta_{inh}$,$^c$ dL g$^{-1}$ | $T_m$,$^d$ °C | $T_g$,$^d$ °C |
| 6 | 204 | 280 | 250 | 0.47 | 230 | 118 |
| 7 | 221 | 240 | 290 | 1.56 | | 110 |
| 8 | 170, 177 | 270 | 250 | 0.78 | 220 | 100 |
| 9 | 190 | 240 | 300 | 1.12 | | 89 |
| 10 | 202, 217 | 240 | 260 | 2.89 | 175 | 83 |
| 11 | 193 | 220 | 260 | 1.77 | | 74 |
| 12 | 225 | 240 | 220 | 2.00 | 160 | 70 |

[a] The polymerization was carried out for 15 h. [b] Determined by DTA at a heating rate of 10 °C min$^{-1}$ in nitrogen. [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 20 °C min$^{-1}$ in nitrogen ($T_m$, 1st scan; $T_g$, 2nd scan).

ODP by the polymerization of the salt. The polymerization under a lower pressure of 220 MPa afforded the polyimide with higher viscosity values, and this was consistent with the results of Figure 4. But each curve had a maximum with respect to the inherent viscosity. This behavior was presumably related to the results of Figure 5 that a higher reaction temperature more readily enhanced the hydrolysis of the polyimide formed.

Table 2 summarizes the results of the high-pressure synthesis of polyimides P-*X*-ODP from salt monomers *X*-ODP. From these results, it was concluded that all the salt monomers readily afforded the corresponding polyimides having inherent viscosities of 0.4–2.8 dL g$^{-1}$, indicative of high molecular weights, by the high-pressure polycondensation under these reaction conditions.

The polymers thus formed by the high-pressure synthesis were confirmed to be polyimides by means of IR spectroscopy and elemental analysis (Table 1). A typical IR spectrum of polyimide P-8-ODP is shown in curve B in Figure 1. All the polymers exhibited characteristic absorption bands due to imide ring at ca. 1773, 1711–1717, 1395–1398, and 747–748 cm$^{-1}$, indicative of the formation of polyimides. The elemental analysis values of the polymers were in close agreement with the values for the proposed polyimide structures.

**Properties of Polyimides.** Figure 7 shows the wide-angle X-ray diffraction patterns of salt 8-ODP and the corresponding polyimide by both reduced-pressure and high-pressure polycondensations. The polyimide prepared under reduced pressure (curve B) was completely amorphous, whereas the polymer obtained under high pressure (curve C) was highly crystalline. Thus it is obvious that the high-pressure polycondensation readily afforded highly crystalline polyimide. Curve D represents the polyimide after the amorphous polymer, which was obtained by melting and quenching the high-pressure-polymerized polymer, was annealed under the high pressure. The crystallinity of the annealed polyimide was somewhat lower than that of the high-pressure-synthesized polyimide. The results suggested that the high-pressure polycondensation induced crystallization of the growing polyimide.

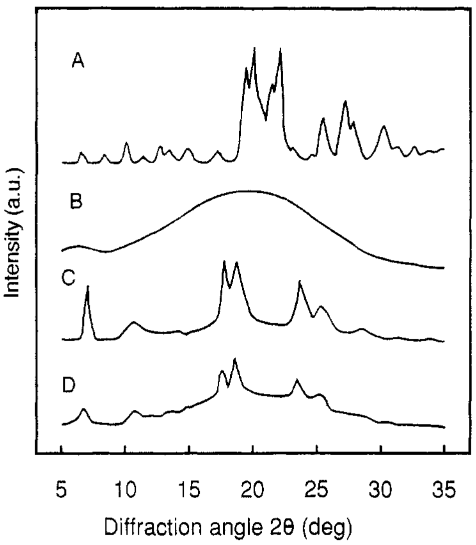

**Figure 7.** Wide-angle X-ray diffraction patterns of (A) salt 8-ODP and polymer P-8-ODP obtained (B) by the polymerization under reduced pressure, (C) by the high-pressure polymerization, and (D) by the high-pressure annealing of amorphous polyimide.

The thermal behavior of the polyimides was evaluated by means of DTA, DSC, and TG. Table 2 also lists the $T_m$s and $T_g$s of the high-pressure-synthesized polyimides. The polyimides having an even number of methylene chains had crystalline $T_m$s, which decrease from 230 to 160 °C with increasing number of methylene units, whereas those with odd number carbons had no $T_m$. All the polyimides had $T_g$s of 70–118 °C which lowered monotonically with the increase of number of methylene units. A typical TG curve of the high-pressure-synthesized polyimide is shown in curve B in Figure 2. All the polyimides were stable up to 400 °C in nitrogen in the melt state.

Figure 8 exhibits the X-ray diffraction diagrams of a series of polyimides P-*X*-ODP prepared by the high-pressure polycondensation. The polyimides having even number of methylene chains such as P-6-ODP and P-8-ODP were highly crystalline and yellowish white brittle solids. This is because the $T_m$s of the polyimides (230 and 220 °C) were higher than the melting points of the corresponding salt monomers (204 and 170 °C), and hence the high-pressure polymerization proceeded in a solid state. In the case of the other polyimides with even number carbons like P-10-ODP and P-12-ODP, they had the $T_m$s (175 and 160 °C) lower than the melting points of the corresponding salts (202 and 225 °C), and the high-pressure polymerization probably progressed in a melt state, thereby affording semicrystalline yellowish white tough moldings. The polyimides having an odd number of methylene units such as P-7-ODP, P-9-ODP, and P-11-ODP were pale yellow resinous products, which were formed by the high-pressure polycondensation in a melt state. These odd-numbered polyimides were not completely amorphous but had some smectic-like structures as evidenced by the broad low-angle peak observed at 3–7° (2*θ*), which was probably

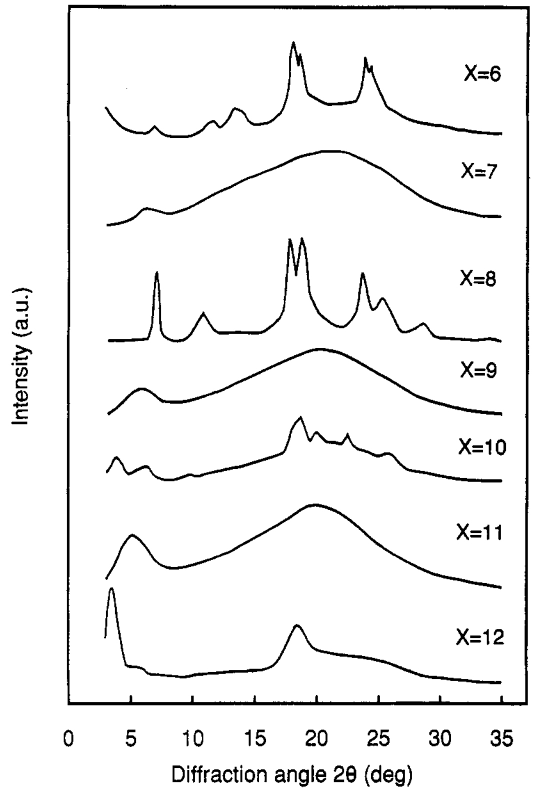

**Figure 8.** Wide-angle X-ray diffraction patterns of polymers P-*X*-ODP obtained by the high-pressure polymerization.

arising from the periodicity of the repeat unit distance along the chain axis of the polyimides.

The crystallinity and thermal behavior of these polyimides P-*X*-ODP were almost comparable to those of the polyimides having the same structures reported earlier, which were synthesized by the high-temperature solution polycondensation.[4]

## Conclusions

The polycondensation of salt monomers composed of aliphatic diamines having 6–12 methylene units and oxydiphthalic acid under high pressure at high temperature was found to afford readily aliphatic polyimides of high molecular weights. It is interesting to note that the polycondensation proceeded rapidly in one step with the elimination of water in the closed reaction vessel under high pressure and was almost complete within 3 h. When the $T_m$s of the resultant polyimides are higher than the melting points of the corresponding salt monomers, the high-pressure polycondensation resulted in the formation of highly crystalline polyimides. Thus, the high-pressure polycondensation provides a simple and efficient method for the synthesis of aliphatic polyimides compared with other known methods and should become more and more important for the preparation of other polyimides and many condensation polymers as well.

**Acknowledgment.** The authors gratefully acknowledge the support for this work by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials, Design, Preparation, and Control from the Ministry of Education, Science, and Culture of Japan (no. 3205039). The authors are also indebted to Mr. Tatsuo Inoue for part of this work.

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