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Direct Synthesis of Wholly Aromatic Polyamides by Using Reaction-Induced Crystallization

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ABSTRACT: Direct synthesis of rigid-rod aromatic polyamides was studied without condensation reagents by using reaction-induced crystallization of oligomers during solution polymerization. Polymerizations of *p*-aminobenzoic acid were carried out in an aromatic solvent at a polymerization concentration of 20% at 350 °C. High molecular weight poly(*p*-benzamide) (PBA) was obtained in the form of plate-like crystals, and the highest molecular weight was 11.6×10^3. In this polymerization, the oligomers were formed in the solution by the condensation reaction with the elimination of water. When the molecular weight of oligomers exceeded the critical value, the oligomers were precipitated by crystallization *via* supersaturated state to form the plate-like crystals. The molecular weight increased by the polymerization between the oligomers on and in the crystals. Poly(*p*-phenylene isophthalamide) (PPIA) was also obtained in the form of plate-like crystals by the polymerization of *p*-phenylene diamine (PPDA) and isophthalic acid (IPA) under the same condition as that of PBA. These results exhibited the thermally direct synthesis of infusible aromatic polyamides. Sequential addition of monomers into this heterogeneous polymerization was examined to increase the molecular weight. In the step-growth polymerization, the addition of monomers into the homogeneous polymerization could not increase the molecular weight because it was determined by the extent of reaction and reshuffled by the transamidation reaction. However, the addition of PPDA and IPA during the polymerization resulted in the increase in the molecular weight of PPIA. This result gave possibly a novel procedure for the preparation of high molecular weight condensation-type polymers.

Introduction

Wholly aromatic polyamides, so-called aramides, are representative high-performance polymers and they have been widely used as industrial materials with excellent mechanical properties, chemical resistance, thermal stability and so on.[1−3] They are usually prepared by polymerizations of aromatic diamines and aromatic diacid chlorides due to low reactivity of diamines toward diacids.[2,3] Direct synthesis of wholly aromatic polyamides from diamines and diacids is very elegant and numerous condensation reagents had been developed so far, such as *N*-phosphonium pyridine salt,[4] diphenyl and triaryl phosphite in *N*-methylpyrrolidone−pyridine,[5−7] triphenyl phosphite−lithium chloride,[8,9] triphenylphosphine−hexachloroethane,[10] and so on. Much attention has been paid to the direct synthesis without any condensation reagent as an atom economical synthesis from the viewpoint of green chemistry. Only a few studies on the direct synthesis of wholly aromatic polyamides without condensation reagents have been conducted so far to our knowledge. Bulk polymerizations of monomers containing ether group have been studied to prepare high molecular weight aromatic polyamides.[11,12] The polyamides prepared in these studies contained ether linkages to reduce their melting temperature for bulk polymerizations in a melt phase. These studies reveal that aromatic diamines can react with aromatic diacids at high temperature with eliminating water to form amide linkages. Many wholly aromatic polyamides, especially rigid-rod aromatic polyamides, do not possess melting temperatures under their thermal decomposition temperature, and therefore, high-temperature bulk polymerization is not applicable to infusible polyamides such as PBA and PPIA.

We have been studying the morphology control of intractable aromatic polymers such as polyesters, polyimides and so on by using reaction-induced crystallization of oligomers during solution polymerization.[13−16] High molecular weight polymers have been successfully prepared as crystals. This polymerization method, comprised of a formation of the oligomer crystals and a subsequent polymerization in them, is not limited by the intractability of polymers. In this paper, the direct syntheses of PBA and PPIA were examined without any condensation reagent by using the reaction-induced crystallization during solution polymerization as depicted in Scheme 1.

Experimental Section

Materials. *p*-Aminobenzoic acid (ABA) was purchased from TCI Co., Ltd., and recrystallized from ethyl acetate. IPA was purchased from Aldrich Co., Ltd., and purified by sublimation. PPDA was a gift from Taishin Chemical Co., Ltd., and used as received. An isomeric mixture of triethylbiphenyl (TEB) was purchased from Nippon Steel Chemical Co., Ltd. (trade-name Therm S 800, molecular weight 238, boiling point 340 °C), and distilled under reduced pressure (160−180 °C, 0.3 mmHg). An isomeric mixture of dibenzyltoluene (DBT) was obtained from Matsumura Oil Co., Ltd. (trade name Barrel Therm 400, molecular weight 380, boiling point 382 °C), and distilled under reduced pressure (170−175 °C, 0.3 mmHg). *N*-Methylpyrrolidone (NMP) was purchased from Aldrich Co., Ltd., and used as received.

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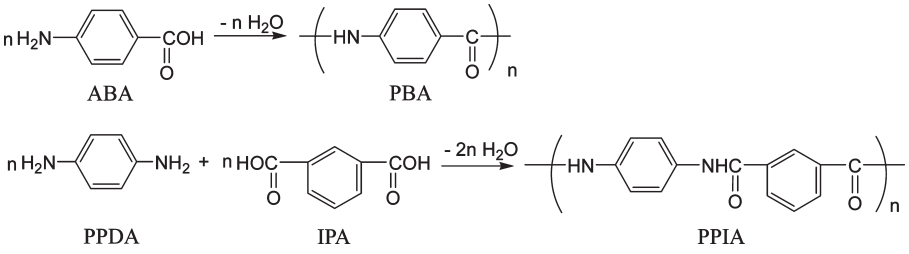
Scheme 1. Direct Syntheses of Aromatic Polyamides



Measurements. Morphology of products was observed on a Hitachi S-3500N scanning electron microscope (SEM). Samples were dried, sputtered with platinum−palladium and observed at 20 kV. A selected-area electron diffraction (SAED) was observed on a JEOL 2000EX II transmission electron microscope (TEM) at 200 kV. Atomic force microscopy (AFM) was performed on a Digital Instruments Inc. Nanoscope IIIa in air. Infrared (IR) spectrum was measured on a JASCO FT/IR-410 spectrometer. Wide angle X-ray scattering (WAXS) was performed on a Rigaku Gaiger Flex with nickel-filtered Cu Kα radiation (35 kV, 20 mA). Average crystallite sizes (D_{hkl}) were estimated from half widths of corresponding diffraction peaks in a WAXS intensity profile according to Scherrer's equation. The half width of the diffraction peak was corrected with that of hexamethylenetetramine. Matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectrometry was performed on a Bruker Daltonics AutoFLEX MALDI−TOF MS system operating with a 337-nm N_2 laser. Spectra were obtained in the linear positive mode with accelerating potential of 20 kV. Mass was calibrated with angiotensin I (MW 1296.69) and insulin B (MW 3496.96) of a Sequazyme peptide mass standard kit. Samples were prepared by the evaporation-grinding method, and then measured in 3-aminoquinoline as a matrix doped with potassium trifluoroacetate according to previously reported procedures.[17,18] Intrinsic viscosity [η] was measured in 97% sulfuric acid at 30 °C. The weight-average molecular weight (M_w) of PAB was calculated according to the following equation.[19] $[\eta] = 1.9 \times 10^{-7} M_w^{1.7}$. The molecular weight of PPIA was determined on a size-exclusion chromatography (SEC) HLC-8120GPC, TOSOH after *N*-methylation of PPIA according to the previously reported procedure.[20] The used columns were guard column G0003, super AWM-H X2 and Super Aw 2500(TOSOH). The outlet of the column set was connected to a UV detector. The eluent was *N*,*N*-dimethylformamide dissolving 0.01 mol·L^{-1} lithium bromide. The flow rate of the eluent was 0.6 mL·min^{-1}, and the temperature of the column was 40 °C. Molecular weight was relatively calculated by using polystyrene standards.

Polymer Synthesis. *Polymerization of ABA.* ABA (4.6 g, 3.36×10^{-2} mol) and 20 mL of DBT were placed into a cylindrical flask equipped with a mechanical stirrer and gas inlet and outlet tubes. Polymerization concentration, defined as (calculated polymer weight 4.0 g/solvent volume 20 mL) × 100, was 20%. The reaction mixture was heated under a slow stream of nitrogen up to 350 °C with stirring. Stirring was stopped after ABA was entirely dissolved during heating and temperature was maintained at 350 °C for 15 h. Precipitated PBA crystals were collected by filtration at 350 °C, and washed with *n*-hexane and acetone. A filtrate was poured into *n*-hexane, and precipitates which were oligomers dissolved in the solution at 350 °C were collected by filtration. The recovered oligomers were washed with *n*-hexane and dried. Polymerizations of ABA under other conditions were carried out in a similar manner.

Polymerization of PPDA and IPA. IPA (2.78 g, 1.68×10^{-2} mol) and 20 mL of DBT were placed into a cylindrical flask equipped with a mechanical stirrer and gas inlet and outlet tubes. The reaction mixture was heated under a slow stream of nitrogen up to 350 °C with stirring. PPDA (2.55 g, 2.35×10^{-2} mol) was added into the solution at 350 °C. Polymerization concentration was 20% and the molar ratio of PPDA and IPA in feed (χ_f) was 1.4. Stirring was stopped after the monomers were entirely dissolved and temperature was maintained at 350 °C for 15 h. Precipitated PPIA crystals were collected by filtration at 350 °C, and washed with *n*-hexane and acetone. A filtrate was poured into *n*-hexane, and precipitates were collected by filtration. The recovered oligomers were washed with *n*-hexane and dried. Polymerizations of PPDA and IPA under other conditions were carried out in a similar manner.

Table 1. Results of Polymerization of PAB

	polymerization conditions					
run no.	solvent	concn (%)	temp. (°C)	time (h)	yield (%)	M_w[a] ($\times 10^3$)
1	TEB	1	300	6	0	
2	TEB	5	300	6	4	[b]
3	TEB	20	300	15	30	5.1
4	DBT	5	330	15	15	7.6
5	DBT	10	330	15	18	5.3
6	DBT	20	330	15	30	7.3
7	DBT	20	350	15	30	11.6
8	NMP	20	200	15	0[c]	
9	none	[d]	350	15	16	3.7

[a] Determined by the viscosity measurement. [b] Not measured because of low yield. [c] Recovery yield after pouring the solution into methanol. [d] Bulk polymerization was carried out in the scale of 4.6 g.

Results and Discussion

Synthesis of PBA. Less polar solvents, which are poor to PBA and good to ABA, are necessary to induce the crystallization of oligomers during solution polymerization. Polymerizations were carried out in aromatic solvents of TEB and DBT by varying polymerization concentration and temperature. The polymerization concentration is defined as a percentage based on polymer weight and solvent volume as described in the experimental section. Polymerization results are presented in Table 1. ABA was insoluble in these solvents at room temperature, but it became dissolved during heating. First, polymerizations were carried out at 300 °C. Polymer precipitates were hardly obtained in TEB at a polymerization concentration of 1−5% at 300 °C. When the polymerization was carried out at a polymerization concentration of 20%, the solution became turbid with time and plate-like crystals were obtained after 15 h with the yield of 30% (run no. 3). The M_w of the plate-like crystals was 5.1×10^3. Since the polymerization temperature could not be raised due to a boiling temperature of TEB, the polymerizations were carried out in DBT at higher temperature of 330 and 350 °C. In these polymerizations, rectangular plate-like crystals were also obtained with the yield of 30% as typically shown in Figure 1a. The width of the plate-like crystals was in the range 200−900 nm. Chemical structure of the obtained crystals (run no. 7) was analyzed by IR spectroscopy. As shown in Figure 2a, bands of amide linkage are clearly observed at 3338 cm^{-1} (N−H) and 1656 cm^{-1} (C=O).

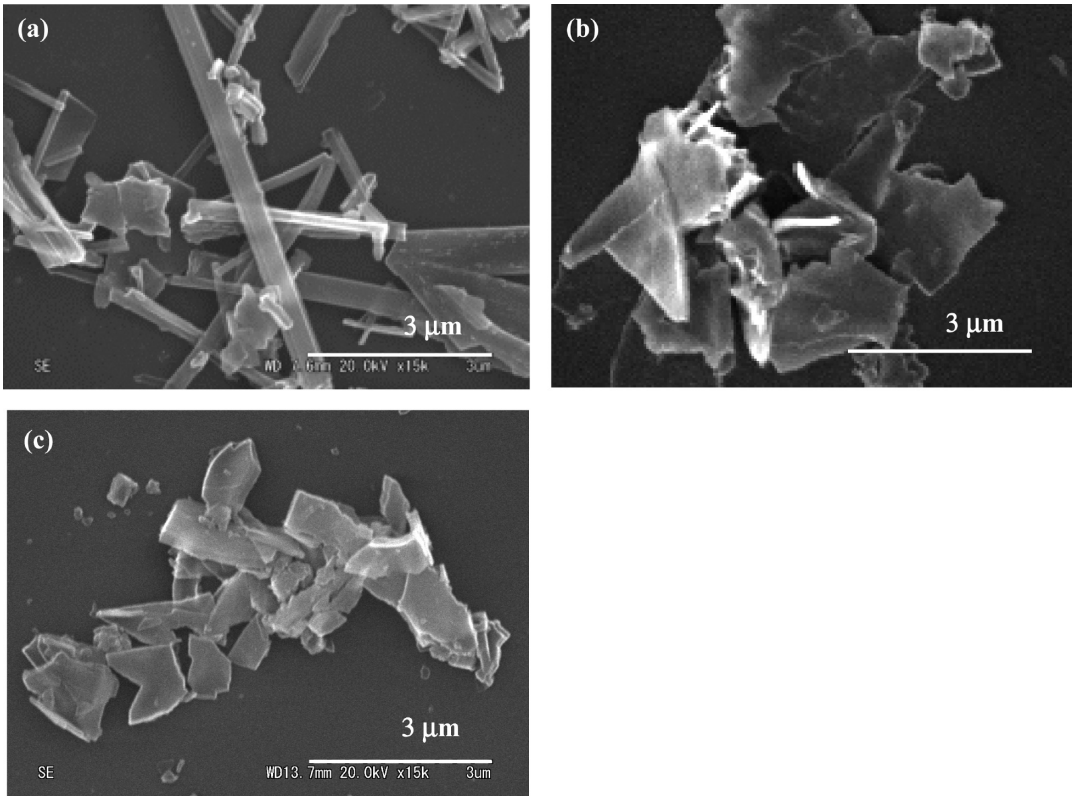


Figure 1. SEM images of (a) PBA crystals (run. no. 7), (b) PPIA crystals (run no. 10) prepared in DBT at a polymerization concentration of 20% at 350 °C, and (c) PPIA prepared by sequential monomer addition (run no. 18).

Bands of carboxyl group and amino group characterized as end-groups were not detected. This spectrum shows the formation of high molecular weight PBA. The M_w of the crystals prepared at a polymerization concentration of 20% at 330 °C (run no. 6) and at 350 °C (run no. 7) were 7.3×10^3 and 11.6×10^3, respectively. Higher polymerization temperature gave higher molecular weight. These results reveal that the direct polymerization of ABA occurs thermally with elimination of water. Polar aprotic solvent is usually adapted for the direct synthesis of polyamides with condensation reagents. For the comparison with the direct polymerization by using crystallization, the polymerization of ABA was carried out without condensation reagents in NMP at a polymerization concentration of 20% at 200 °C for 15 h. PBA was not precipitated after pouring the polymerization solution into methanol. Further, the bulk polymerization of ABA was also carried out at 350 °C for 15 h under a slow stream of nitrogen. The polymerization occurred in melt phase of ABA with elimination of water at an early stage in the polymerization and then in solid phase after a middle stage in the polymerization due to the solidification. Finally, PBA was obtained as fine powders, of which the M_w was 3.7×10^3. They were lower than those prepared by the crystallization. This might be attributed to the difficulty of the polymerization in the solid state.

A WAXS profile of the PBA crystals (run no. 7) was shown in Figure 3a. Diffraction peaks were quite sharp and diffuse hallo contributed from amorphous regions was hardly observed. Two sharp peaks at 2θ of 20.47 and 23.67° could be indexed as 110 and 200 Bragg reflections of the orthorhombic crystal unit cell of PBA, respectively.[21−23] A TEM image with a SAED pattern was shown in Figure 4. Although Debye rings of aluminum spattered on the PBA sample were superimposed to estimate *d*-spacing, the spots

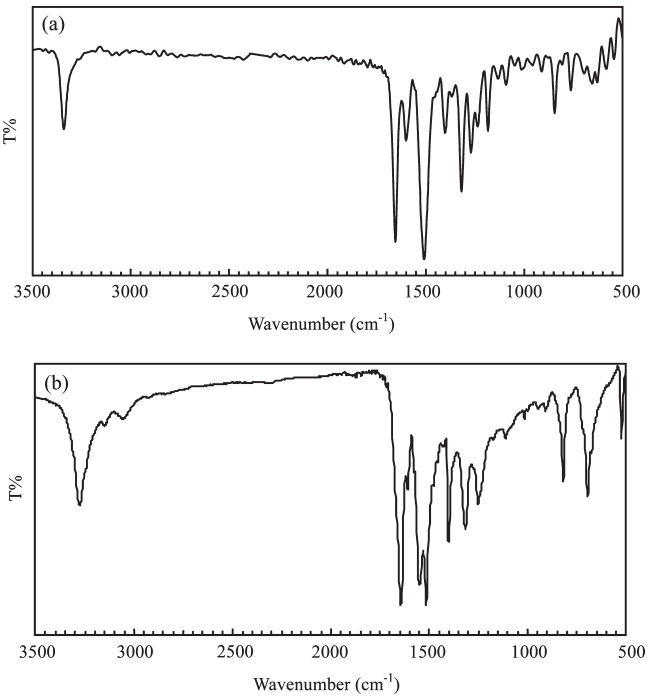


Figure 2. IR spectrum of (a) PBA crystals (run. no. 7) and (b) PPIA crystals (run no. 10) prepared in DBT at a polymerization concentration of 20% at 350 °C.

in the SAED irradiated through the plate plane of the crystal were quite sharp and they were consisted of lower to higher order diffractions. These diffraction spots can be assigned according to the PAB orthorhombic crystal unit

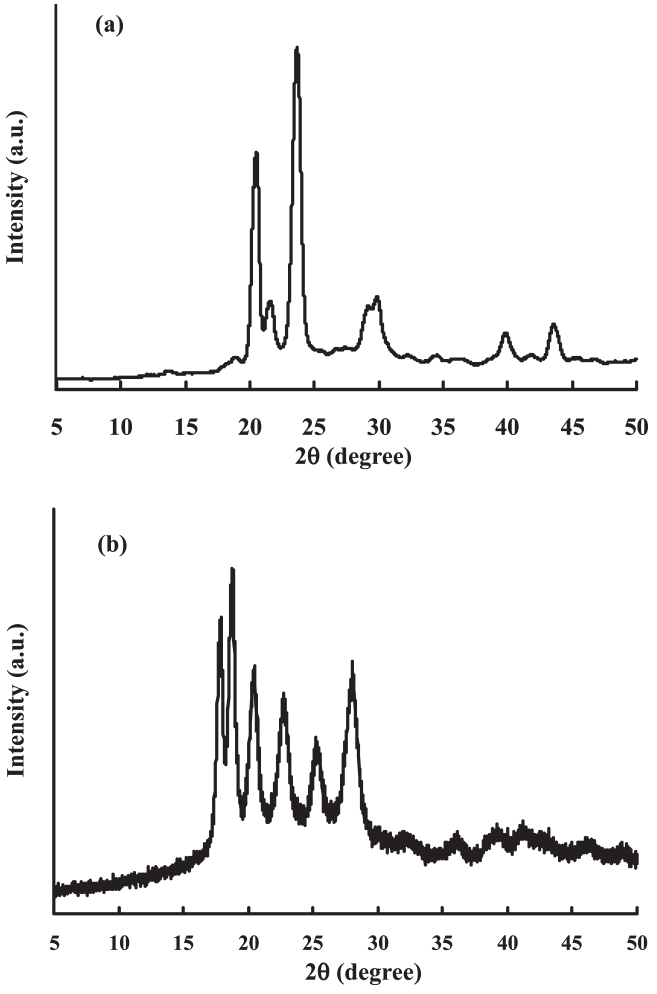


Figure 3. WAXS profiles of (a) PBA crystals (run. no. 7) and (b) PPIA crystals (run no. 10) prepared in DBT at a polymerization concentration of 20% at 350 °C.

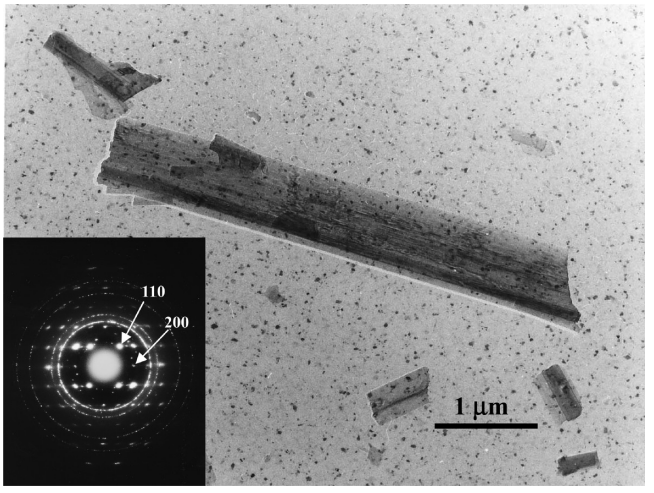


Figure 4. TEM image and a SAED pattern of PBA crystals (run no. 7). Electron beam was incident through the plate plane.

cell. This indicates that the plate-like PBA crystals possess high crystallinity and the polymer molecules are oriented perpendicular to the plate plane. The thickness of the plate crystal was evaluated by AFM measurement, and it was 65−110 nm as shown in Figure 5. The average length of the molecules estimated from M_w of 11.6×10^3 is 59.1 nm assuming the *trans* conformation as previously reported[21] and the crystal thickness is approximately twice larger than the estimated average molecular length.

In order to clarify the polymerization mechanism, the yield and the M_w of the crystals were examined in the course of polymerization in DBT at a polymerization concentration of 20% at 350 °C. Results were plotted in Figure 6 as a function of time after the temperature reached 350 °C. Recovery yields of oligomers from the solution were also plotted in Figure 6. Oligomer precipitation started after 0.5 min. The yield of the crystal increased very rapidly at an early stage in the polymerization until 3 h, and then it became constant at 30%. The morphology of the crystals was plate-like throughout the polymerization. WAXS profiles of the crystals prepared for 0.5 and 3 h were shown in Figure 7. The average crystallite sizes estimated from the 200 and 110 reflections by using Scherrer's equation and the *d*-spacing were plotted in Figure 8 as a function of time. Diffraction peaks of the crystals prepared for 0.5 h were quite sharp and diffuse hallo was hardly observed. Crystallinity of the crystals prepared for 0.5 h was as quite high as that for 15 h. The average crystallite sizes were almost constant though the polymerization. D_{110} and D_{200} after 0.5 h were 11.5 and 9.6 nm respectively, and they after 15 h were 12.4 and 9.5 nm. D_{200} tends to increase slightly with time. The values of *d*-spacing were almost constant throughout the polymerization. Highly crystalline PBA crystals were formed by the crystallization of oligomers at an early stage in the polymerization and then they grew with maintaining high crystallinity during the polymerization. The recovery yield of the oligomers decreased correspondingly, and it became ca. 2% after 6 h. The oligomers were not left in the solution after thee polymerization. This result indicates that the polymer yield of ca. 30% might be attributed to thee sublimation of ABA. The fact that the recovery yield of the oligomers decreased corresponding to the increase in the yield of the crystal reveals that the plate-like crystals are formed by the consecutive supply of oligomers from the solution. The value of M_w of the crystal also increased rapidly with the yield within 3 h. Then it increased gradually with time after the yield was leveled off, suggesting the solid-state polymerization in the precipitated crystals. The oligomers collected from the solution after 0.5 h were analyzed by MALDI−TOF mass spectrometry. The spectrum and the peak assignments are shown in Figure 9 and Table 2. The oligomers dissolved in the solution were low molecular weight and the largest oligomer in them was a nonamer. This fact indicates that the oligomers larger than the nonamers would be mainly precipitated to form the crystals. These results imply the polymerization feature as follows; the oligomers are formed in the solution by the condensation reaction of ABA with eliminating water. When the M_w of the oligomers exceeds a critical value, the oligomers are precipitated *via* supersaturated state to form the plate-like crystals in which the oligomers are aligned perpendicular to the plate plane. Further polymerization of the oligomers occurs on or in the crystal, and the high molecular weight PBA is finally synthesized in the form of the plate-like crystals.

Synthesis of PPIA. Polymerizations of PPDA and IPA were also carried out in DBT at a polymerization concentration of 20% at 350 °C for 15 h, which were the best polymerization condition for high molecular weight PBA. IPA was less soluble in DBT than PPDA, and therefore PPDA was added as a solid to the solution after IPA was entirely dissolved during heating. Although it has been reported that the polymerization with oligomer crystallization was not so strongly susceptible to the stoichiometric balance in two

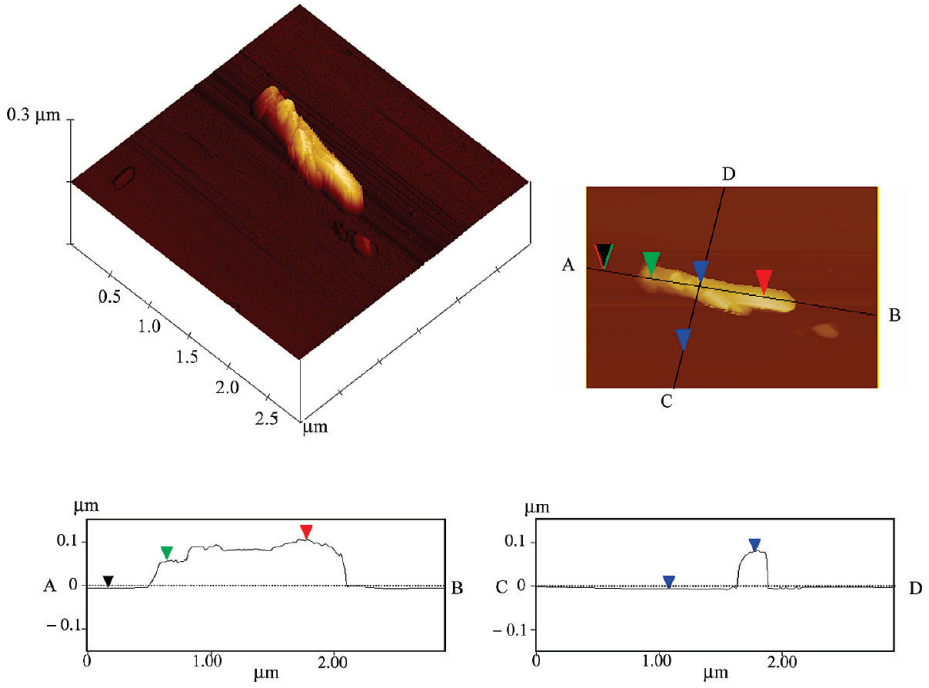


Figure 5. AFM images and height profiles of PBA crystals (run. no. 7) prepared in DBT at a polymerization concentration of 20% and 350 °C.

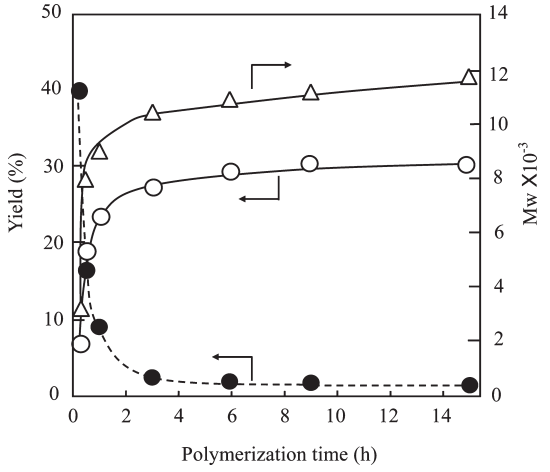


Figure 6. Plots of yield (○) and M_w (△) of PBA crystals and recovery yield of oligomers (●) as a function of polymerization time. Polymerization of ABA was carried out in DBT at a polymerization concentration of 20% at 350 °C.

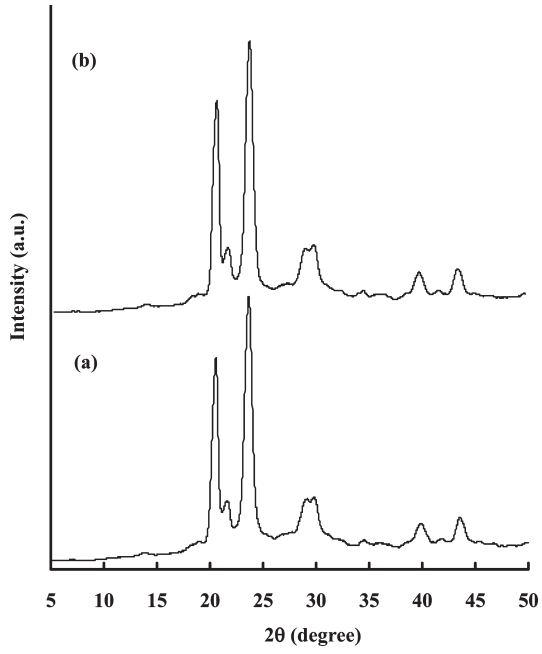


Figure 7. WAXS profiles of PBA crystals prepared in DBT at a polymerization concentration of 20% and 350 °C for (a) 0.5 and (b) 9 h.

reactive groups comparing with homogeneous solution polymerization,[24−26] this stoichiometric balance might slightly influence the yield and the molecular weight of PPIA crystals. Both IPA and PPDA sublimated during polymerization, while PPDA sublimed faster than IPA bringing about the stoichiometric imbalance. Polymerizations were carried out by varying the value of χ_f in the range 1.0−1.6. Yields and intrinsic viscosities [η] of the crystals are plotted in Figure 10 as a function of χ_f. The correlation between the value of [η] and the molecular weight of PPIA has not been determined, and therefore the value of [η] was used to discuss the molecular weight. PPIA crystals were obtained with a yield of 83−95%. The yield was related to the value of χ_f, and it had a maximum value at χ_f of 1.4−1.5. The value of [η] was also related to χ_f and the highest [η] was 0.40 dL·g^{-1} at χ_f of 1.4. On the basis of these results, χ_f of 1.4 is the most preferable to adjust the stoichiometric balance between the two reactive groups. IR spectrum of the plate-like crystals obtained at χ_f of 1.4 was shown in Figure 2b. Bands of amide linkage are clearly observed at 3283 cm^{-1} (N−H) and 1653 cm^{-1} (C═O), and those of carboxyl group and amino group characterized as end-groups were not detected. The spectrum reveals the formation of high molecular weight PPIA. Although the obtained crystals were plate-like as also shown in Figure 1b, the crystal was not rectangular like the PBA crystal. A WAXS profile of the PPIA crystals prepared at χ_f of 1.4 (run no. 10) was shown in Figure 3b. Sharp diffraction peaks were detected at 2θ of 17.84, 18.76, 20.44, 22.76, 25.29, and 28.06°. Diffuse hallo contributed from amorphous regions was hardly observed. The plate-like crystals possessed quite high crystallinity, and this also implies

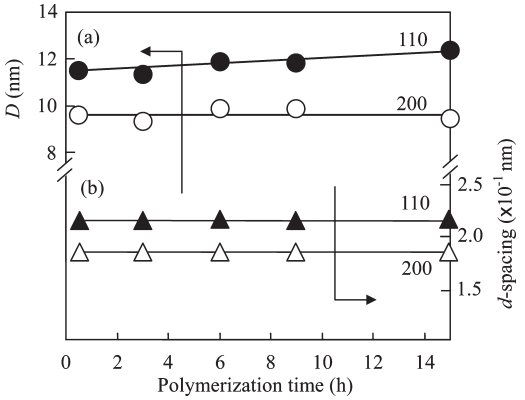


Figure 8. Plots of (a) crystallite size (D) and (b) d-spacing of 110 and 200 reflections of PBA crystals as a function of polymerization time. Polymerization of ABA was carried out in DBT at a polymerization concentration of 20% at 350 °C.

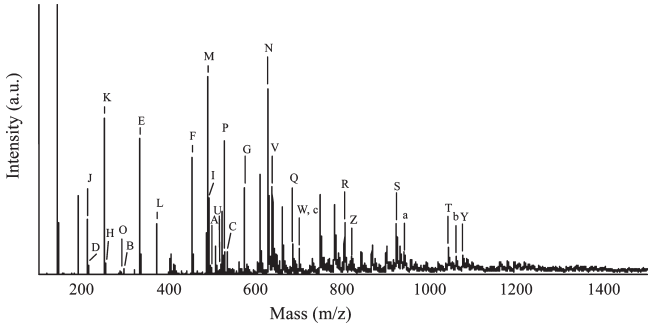


Figure 9. A MALDI−TOF mass spectrum of oligomers recovered from the solution after 0.5 h of polymerization of ABA in DBT at a polymerization concentration of 20% at 350 °C.

Table 2. Structural Assignments of Peaks in the MALDI−TOF Mass Spectrum in Figure 9

peak code	mass (m/z) measured	mass (m/z) calculated	n[a]	oligomer structure[b]
A	495.3	495.5	4	H^+ H–(pBA)$_n$–OH
B	294.8	295.4	2	K^+ H–(pBA)$_n$–OH
C	533.8	533.6	4	
D	214.6	214.3	1	
E	333.0	333.4	2	K^+ K–(pBA)$_n$–OH
F	452.4	452.6	3	
G	571.9	571.7	4	
H	252.7	252.4	1	K^+ K–(pBA)$_n$–OK
I	490.5	490.7	3	
J	213.4	213.3	1	H^+ H–(pBA)$_n$–NH–
K	250.6	251.3	1	
L	370.2	370.5	2	K^+ H–(pBA)$_n$–NH–
M	489.6	489.6	3	
N	609.0	608.7	4	
O	288.9	289.4	1	K^+ K–(pBA)$_n$–NH–
P	527.8	527.7	3	
Q	684.1	684.9	4	
R	803.5	804.0	5	K^+ K–(pBA)$_n$–NK–
S	922.8	923.1	6	
T	1042.1	1042.3	7	
U	518.4	518.6	3	K^+ –C(=O)–(pBA)$_n$–OH
V	637.8	637.7	4	
W	698.2	697.8	4	K^+ K–(pBA)$_n$–NH–
X	487.4	487.5	2	H^+ –C(=O)–(pBA)$_n$–NH–
Y	1075.2	1075.1	9	H^+ H–(pBA)$_n$–H
Z	821.6	821.8	6	H^+ –C(=O)–(pBA)$_n$–H
a	940.9	941.0	7	
b	1060.1	1060.1	8	
c	698.2	697.9	4	K^+ K–C(=O)–(pBA)$_n$–K

[a] number of *p*-benzamide unit in oligomer structure. [b] pBA: –HN–C(=O)–

that the crystals were formed by the crystallization of oligomers, as well as the PBA crystals.

The yields and the value of $[\eta]$ of both PPIA crystals and oligomers collected from the solution were examined in the course of the polymerization at χ_f of 1.4. They were plotted in Figure 11 as a function of time. The yield of the crystals increased rapidly to 91% up to 2 h, and then it increased gradually until 6 h. Afterward, it became constant at 95%. Correspondingly, the yield of the oligomers recovered from the solution decreased rapidly until 2 h and then it became constant at 3%. This fact indicates that the crystals were formed by the consecutive supply of the oligomers from the solution. With respect to the viscosity, it increased until 6 h, and then became constant at 0.40 $dL \cdot g^{-1}$. The value of $[\eta]$ of the collected oligomers was constant at 0.07 $dL \cdot g^{-1}$ throughout the polymerization. These results reveal that high molecular weight PPIA was formed as plate-like crystals by the similar mechanism to PBA crystals. The fact that the value of $[\eta]$ became constant after the yield was leveled off indicated that the solid-state polymerization did not occur efficiently as compared to the polymerization of PBA.

Synthesis of PPIA by Addition of Monomers. It is well-known that the average molecular weight of condensation type polymers do not increase by the addition of monomers during the homogeneous polymerization because the average molecular weight is determined by the extent of reaction (p) as follows;[27]

$$M_n = M_o/(1-p)$$

M_n is the number-average molecular weight; M_o is the molecular weight of structural unit. Additionally, exchange reaction such as transamidation reaction reshuffles the sequence of polymers leading to the decrease in molecular weight of polymers after addition of monomers. These are serious drawbacks to prepare high molecular weight of polyamide. However, the polymerization accompanied by the crystallization of oligomers, which is a heterogeneous polymerization, gives possibly an answer to dissolve these drawbacks. Even though the value of p is lowered by the addition of monomers in the solution phase, it is not done directly in the solid state. If the crystals would grow continuously by the addition of monomers with the polymerization on the crystal surface, the molecular weight would increase with the amount of the additional monomers. The oligomers are continuously formed in the solution and they crystallize with polymerizing on the surface of the crystals with end-groups of the polymers registered in the crystals. The formation of the oligomers follows the step-growth manner, whereas the polymerization with crystallization is recognized as the chain-growth manner. Both polymerizations of PBA and PPIA occur on the surface of the crystal to increase molecular weight, but the molecular weight of PBA increased gradually by the polymerization in the crystals. On the other hand, the molecular weight of PPIA does not increase by the polymerization in the crystals as aforesaid, and the contribution of the polymerization in the crystals to the increase in the molecular weight is negligible. Therefore, the polymerization of PPIA is more preferable than that of PBA in order to clarify the effect of the monomer addition on the molecular weight.

There are two important factors for the steady crystal growth after the addition of monomers, of which one is the concentration of monomers for addition (C_{ad}) and another is the time when the monomers are added at 350 °C (t_{ad}). If C_{ad} were too high, the crystallization on the side surface of the plate-like crystal and the formation of new nuclei (primary nucleation) would be induced because of the high degree of supersaturation, resulting in lowering the average molecular weight due to the increase in the number of polymer molecules. Regarding t_{ad}, if the monomers will be added in the late stage of polymerization, the step for crystal growth will be damaged by the thermal roughening and so on, leading to primary nucleation to form new nuclei. IPA and PPDA were added to the polymerization of PPIA in DBT at a polymerization concentration of 20% at 350 °C by varying the value of C_{ad} and t_{ad}. Polymerizations were carried for 18 h after the final addition of monomers. Polymerization results are presented in Table 3. First, the monomers were added at C_{ad} of 2.5, 5 and 10% after 15 min (t_{ad} = 15 min). The value of χ_f was fixed at 1.4. The values of [η] of the obtained polymers were 0.42 (run no. 11), 0.43 (run no. 12), and 0.44 dL·g^{-1} (run no. 13), and the molecular weight increased by the addition of monomers. With respect to t_{ad}, the values of [η] of the polymers obtained at C_{ad} of 5% after 60 and 360 min were 0.42 (run no. 14) and 0.40 dL·g^{-1} (run no. 15), and they became lower than that after 15 min. The values of [η] of the polymers obtained at C_{ad} of 10% exhibited the similar tendency (run no. 13 and 16). Although the molecular weight increased by the addition of monomers, it decreased with the increasing in t_{ad}. On the basis of these results, the desirable C_{ad} and t_{ad} were determined as 2.5% and 15 min, respectively. The monomers were sequentially added at C_{ad} of 5.0 and 2.5% after 15 min with the interval of 15 min (run no. 17 and 18) until the total concentration became 40%. After 18 h, the values of [η] of the polymers increased and that for the polymer prepared at C_{ad} of 2.5% reached 0.51 dL·g^{-1} while maintaining the plate-like morphology as shown in Figure 1c. The number-average molecular weight (M_n) and its distribution (M_w/M_n) were evaluated by SEC after *N*-methylation according to a previously reported procedure.[20] The values of [η], M_n, and M_w/M_n were plotted as a function of total concentration in Figure 12, and SEC profiles were shown in Figure 13. The M_n and the value of [η] increased linearly with the total concentration, and this strongly indicates that the molecular weight of PPIA in the crystals increased by the addition of monomers as expected. However, M_n is not exactly proportional to total concentration, and it is much lower than the theoretical value (dashed line in Figure 12a) assuming that the precipitated oligomers after the monomer addition are consumed to increase the molecular weight, in other words the number of polymer molecules is constant. M_w/M_n increased slightly from 1.96 to 2.06 by the addition of monomers. The possibility of the crystallization on the side surface of the crystal or the primary nucleation cannot be completely excluded and it reminds faintly in this polymerization system. SEC curves exhibit unimodality and the curve shifts to higher molecular weight with increasing the number of the addition. It notes that the curve became broader toward the higher molecular weight with

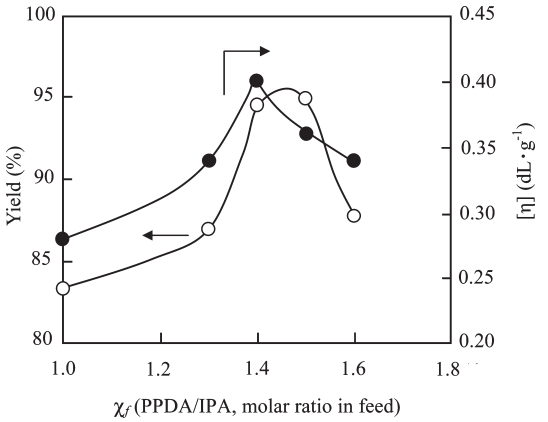


Figure 10. Plots of yield (○) and intrintsic viscosity [η] (●) of PPIA crystals as a function of χ_f. Polymerization was carried out in DBT at a polymerization concentration of 20% at 350 °C for 15 h.

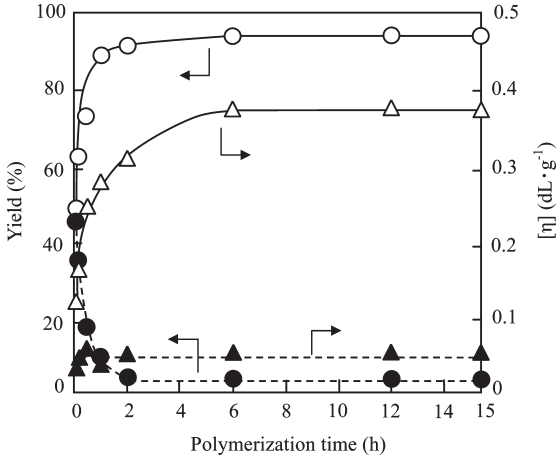


Figure 11. Plots of yield (○) and [η] (△) of crystals, and yield (●) and [η] (▲) of oligomers collected from solution as a function of polymerization time. Polymerization of PPDA and IPA was carried out in DBT at a polymerization concentration of 20% and χ_f of 1.4 at 350 °C.

Table 3. Results of Polymerization of PPIA with Sequential Monomer Addition

	condition of monomer addition [a]						
run no.	C_{ad} (%)[b]	number of addition	total concn (%)	t_{ad} (min)[c]	interval time (min)[d]	yield (%)	[η] (dL·g^{-1})[e]
10	0	0	20.0	0		95	0.40
11	2.5	1	22.5	15		89	0.42
12	5	1	25.0	15		91	0.43
13	10	1	30.0	15		96	0.44
14	5	1	25.0	60		90	0.42
15	5	1	25.0	360		92	0.40
16	10	1	30.0	60		94	0.39
17	5	4	40.0	15	15	96	0.48
18	2.5	8	40.0	15	15	86	0.51

[a] Polymerizations were carried out in DBT for 18 h after the final addition at an initial polymerization concentration of 20% at 350 °C. [b] C_{ad} is the concentration of added monomers. The molar ratio of PPDA/IPA was 1.4. [c] t_{ad} is the time when monomers were added. [d] Interval time of monomer addition. [e] Measured in 97% sulfuric acid at 30 °C.

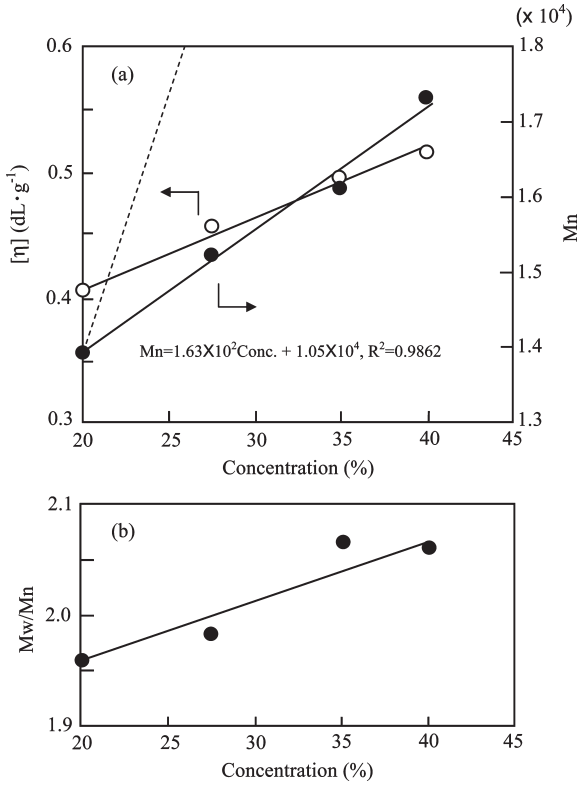


Figure 12. Plots of (a) intrinsic viscosity [η] and Mn, and (b) M_w/M_n as a function of total concentration. C_{ad} and t_{ad} were 2.5% and 15 min, respectively. Polymerization was carried out in DBT at χ_f of 1.4 at 350 °C.

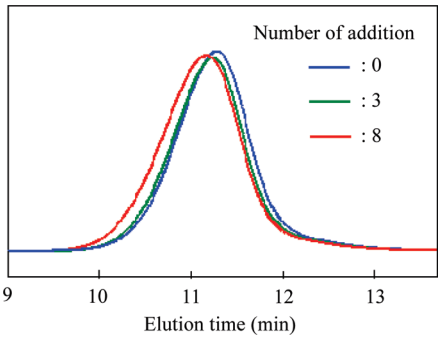


Figure 13. SEC profiles of *N*-methylated PPIA prepared with sequential monomer addition. C_{ad} and t_{ad} were 2.5% and 15 min, respectively. Polymerization was carried out in DBT at χ_f of 1.4 at 350 °C.

increasing the number of the addition and low molecular weight polymers still existed after the addition. This change in the profiles supports the above discussion.

Conclusions

High molecular weight PBA and PPIA were prepared as plate-like crystals by the direct polymerization without any condensation reagent. The obtained crystals possessed quite high crystallinity. The polymerization proceeded as follows; the oligomers were formed in the solution by the condensation reaction with the elimination of water. When the molecular weight of the oligomers exceeded the critical value, they were precipitated by crystallization to form the plate-like crystals due to the low miscibility between the oligomer and the solvent. The molecular weight increased by the polymerization between the oligomers on or in the crystals. These results provide the thermally direct synthetic procedure of infusible aromatic polyamides. In the step-growth polymerization, the addition of monomers into the homogeneous polymerization could not increase the average molecular weight because it was determined by the extent of reaction and reshuffled by the transamidation reaction. However, the sequential addition of monomers into this heterogeneous polymerization resulted in the increase in the molecular weight of PPIA, possibly providing a novel procedure for the preparation of high molecular weight condensation-type polymers.

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