Formation Mechanism of Poly(4′-oxy-4-biphenylcarbonyl) Crystals Obtained by Solution Polymerization

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Received May 23, 1994; Revised Manuscript Received September 2, 1994®

ABSTRACT: Poly(4′-oxy-4-biphenylcarbonyl) (POBP) crystals are obtained from 4′-acetoxybiphenyl-4-carboxylic acid by high-temperature solution polycondensation. When the polymerization is carried out in aromatic solvents such as Therm S 800 and Therm S 900, bundlelike aggregates of fibrillar crystals are obtained. Their length and width are 5–10 and 0.1–0.2 μm. These fibrillar crystals are linked laterally to one another at the central part. The electron diffraction experiments reveal that the polymer chains align along the long axis of the fibrillar crystals. From terphenyl are obtained hexagonal slablike crystals, of which the thickness is 2–3 μm and the width is on the average 10 μm. These slablike crystals are also fibrillated in the direction of the thickness. The formation mechanism of the fibrillar crystals was followed by the observation of the crystal morphology and the polymerization time dependencies of the yield of the crystals, the crystal sizes, and the degree of polymerization (DP). Scanning electron microscopic observation of incipient crystals obtained after 1 h showed convex-lens-like shape. Transmission electron microscopic observation of them showed the lamellar steps due to spiral growth at their thin edge. The morphological observtion of the crystals obtained after 2 h showed lenslike shape but many protrusions with a width of 0.1–0.2 μm in their surfaces. This result indicates that the reorganization of crystals is accompanied by an increase of the DP by postpolymerization. From these experimental facts, it can be deduced that the formation mechanism of the bundlelike aggregates of fibrillar crystals is fundamentally similar to that in poly(oxy-1,4-benzenediylcarbonyl) whiskers and the apparent difference in crystal morphology is caused by the reorganization of crystals during slow lamellar crystallization of oligomers formed in solution polymerization.

Introduction

Wholly aromatic homopolyesters have been receiving much attention as high-performance materials because of their desirable properties such as mechanical properties, thermal stabilities, and so on. However, they usually show neither melting nor solubility. Owing to their low tractability, they are not amenable to conventional processing techniques, and therefore chemical modifications or special processing techniques must be necessary in order to use them. The chemical modifications, however, cause the polymers to lose their inherent properties.

We have been studying the crystallization of stiff polymers during solution polymerization, and it has been found that the whiskers of aromatic polyesters such as poly(oxy-1,4-benzenediylcarbonyl) (POB) and poly(oxy-2,6-naphthalenediylcarbonyl) (PON) could be prepared by high-temperature solution polycondensation.[1–7] These whiskers are prepared from the corresponding acetoxy carboxylic acids in poor solvents such as liquid paraffin or Therm S 800 or 900 at a very low concentration of monomers. The length of POB whiskers is 50–100 μm, and that of the PON whisker is 20–30 μm. Their width is 1–1.5 μm. They are expected to be brought into practical use such as polymer reinforcements with their unique morphologies, outstanding thermal stabilities, and good mechanical properties. From the viewpoint of polymer processing, we can say that crystallization during solution polymerization can be very useful especially for the poorly tractable polymers.

Poly(4′-oxy-4-biphenylcarbonyl) (POBP) is a homologue of POB. Several studies have been reported on POBP. Kricheldorf and his co-workers prepared POBP by solution polymerization of 4′-acetoxybiphenyl-4-carboxylic acid (ABPA) in Marlotherm S (Trademark of Huls AG for a mixture of isomeric dibenzylbenzenes) at 250 °C and then for several hours at 320 °C.[8,9] X-ray diffraction indicated that the obtained POBP had a very high crystallinity. They also reported on the thermal properties of POBP using DSC and TGA. However, the morphological study on POBP crystals obtained by high-temperature solution polymerization was not reported. Geil and his co-workers first described the morphology of POBP prepared by melt polymerization in constrained thin films or solution polymerization in 1-chloronaphthalene at 235 °C and the crystal structure.[10] From solution and in thin films, single crystals consisting of ca. 100-Å-thick lamellae were observed and tapered needlelike crystals were obtained by melt polymerization. In their study, solution polymerization was carried out only in 1-chloronaphthalene. No other detailed study has been reported on the morphology of POBP crystals prepared by high-temperature solution polymerization.

In this paper we report our observation of the crystal morphology of POBP prepared by high-temperature solution polymerization of ABPA in liquid paraffin and aromatic solvents, such as Therm S 800 and 900 (Trademark of Nippon Steel Chemical for a mixture of isomeric triethylbiphenyl and isomeric hydrogenated terphenyl, respectively) and terphenyl, at a very low concentration of ABPA without stirring. Furthermore, we refer to the formation mechanism of fibrillar POBP crystals in Therm S 800.

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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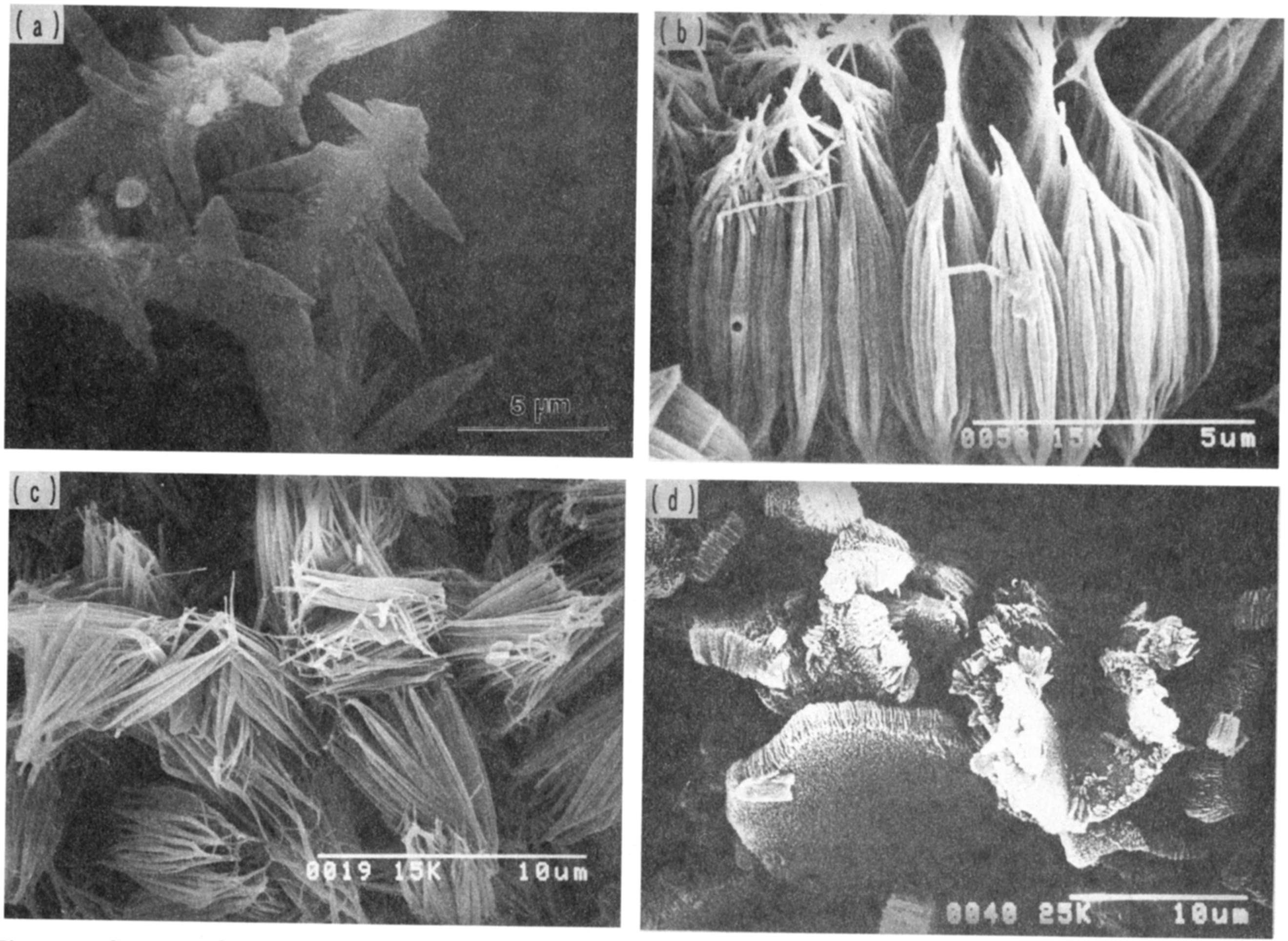

Figure 1. Scanning electron micrographs of POBP crystals prepared (a) in LP (POBP-1), (b) in TS 800 (POBP-2), (c) in TS 900 (POBP-3), and (d) in terphenyl (POBP-4).

Experimental Section

Materials. ABPA was prepared as described in the literature.[11-15] Liquid paraffin (LP) and terphenyl were purchased from Nakarai Tesqu Co., Ltd. Therm S 800 (TS 800) and Therm S 900 (TS 900), which are aromatic heat exchange mediums, were purchased from Nippon Steel Chemical Co., Ltd. LP, TS 800, and TS 900 were used after the purification described in our previous report.[2] Terphenyl was used as received.

Measurements. Morphological characterization was performed by scanning electron microscopy and transmission electron microscopy. Instruments used were Hitachi 530-S and Hitachi HU-11B, respectively.

The degree of polymerization (DP) of the crystal was determined by ^{1}H-NMR end-group analysis of the acetyl group after hydrolysis with concentrated sulfuric acid in an NMR tube with a Varian Gemini-200 spectrometer, as described in the literature.[6,16]

Preparation of POBP Crystals. A typical preparation procedure for POBP crystals is described in the following. Other crystals were also obtained in a similar manner.

In a 200-mL cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were placed 0.78 g of ABPA and 60 g of TS 800. This reaction mixture was heated with stirring under a slow stream of nitrogen. When the monomer dissolved completely at around 240 °C, stirring was stopped. Heating was continued up to 330 °C and maintained at this temperature. After 20 min at 330 °C, the reaction solution became turbid and then the crystals precipitated gradually. The reaction was continued at 330 °C for 20 h in an atmosphere of nitrogen. The reaction mixture was allowed to cool to room temperature, and chloroform was added. The polymer crystals were collected by filtration, washed several times with chloroform and acetone, and dried at 100 °C under reduced pressure to a constant weight.

Table 1. Synthesis of POBP Crystals from ABPA

		polymerization				
polymer	solvent	conc[b] (%)	temp (°C)	time (h)	yield (%)	crystal morphology
POBP-1	LP	1.0	330	6	55.3	dendritic
POBP-2	TS 800	1.0	330	20	55.0	fibrillar
POBP-3	TS 900	1.0	330	20	55.6	fibrillar
POBP-4	terphenyl	1.0	330	20	54.0	slablike

[a] Solvents LP, liquid paraffin; TS 800, Therm S 800; TS 900, Therm S 900. TS 800 and TS 900 are aromatic heat-exchange media of Nippon Steel Chemical Co., Ltd. The main components of TS 800 and TS 900 are Triethylbiphenyl and hydrogenated terphenyl, respectively. [b] Conc (%) = [theoretical polymer yield (g)/solvent weight (g)] × 100.

Results and Discussion

Crystal Morphology of POBP Obtained by Solution Polymerization. POBP crystals are prepared by solution polycondensation of ABPA at 330 °C in various solvents. Morphological features of the obtained crystals are summarized in Table 1. The yields of the crystals are around 55% in all solvents. The low yields seem to be mainly due to sublimation of ABPA at 330 °C. When the polymerization is carried out in LP, dendritic crystals with irregular shape are formed as shown in Figure 1a. In TS 800 and TS 900 are obtained the bundlelike aggregates of fibrillar crystals as shown in parts b and c of Figure 1, respectively. The length

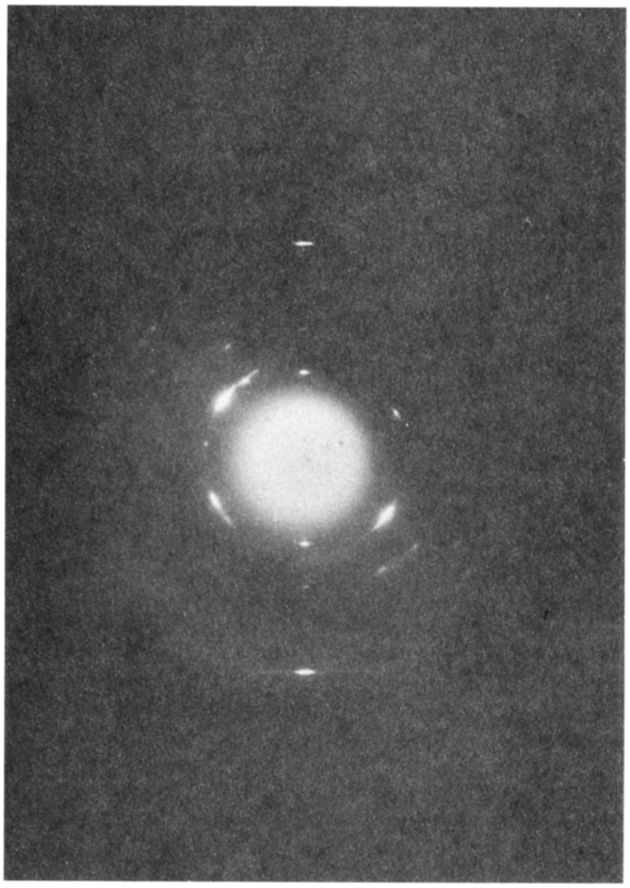

Figure 2. Electron diffraction pattern of POBP fibrillar crystals prepared in TS 800.

of each fibrillar crystal is 5−10 μm and the width is 0.1−0.2 μm. These fibrils are linked laterally to one another at the central part. In terphenyl are formed hexagonal slablike crystals, of which the thickness is 2−3 μm and the width is on the average 10 μm, as shown in Figure 1d. They are also fibrillated in the direction of the thickness. These results show that the crystal morphologies of POBP are quite different with the kinds of solvents. Especially in LP, the resultant crystals have irregular shape. Their formation mechanism seems to be different from that in the case of aromatic solvents, in which the formed crystals have regular shape, and it seems to be concerned with liquid−liquid phase separation of oligomers. This formation mechanism will be described at length elsewhere. Here, the crystals obtained by polycondensation in aromatic solvents will be mainly treated.

Structural Features of Fibrillar Crystals. An electron diffraction pattern of a fibril of the bundlelike aggregates of fibrillar crystals is shown in Figure 2. This electron diffraction pattern consists of sharp spots of lower to higher order reflections as observed clearly. This is due to the single-crystal nature of the fibrillar crystals. The meridian of this pattern corresponds to the long axis of the fibrillar crystal. The fiber identity period is 10.44 Å, corresponding to one chemical residue. The unit cell parameters tentatively determined using the electron diffraction pattern of stacked lamellae are shown in Table 2, which may correspond to that of phase I type crystal structure reported by Geil.[10] From the electron diffraction experiments, it is concluded that the fibrillar crystals are chain-extended single crystals and that the polymer chains align along the long axis of the fibrillar crystals.

Table 2. Unit Cell Dimensions for POBP Crystals

crystal system	orthorhombic
lattice constants (Å)	
a	7.32
b	5.35
c (fiber axis)	10.44

Table 3. Thermal Stabilities of POBP Fibrillar Crystals[a]

	temp of 5 wt % loss (°C)		temp of 10 wt % loss (°C)	
polymer	air	nitrogen	air	nitrogen
POBP-2	496	526	512	546
POBP-3	497	528	513	555
POBP-4	438	503	462	532

[a] Thermal stabilities were measured by TGA at a heating rate of 10 °C/min.

Thermal Properties of POBP Crystals Obtained by Polymerization in Aromatic Solvents. Thermal properties of POBP fibrillar crystals obtained by polymerization in aromatic solvents were evaluated by DSC and TGA. The results are summarized in Table 3. The fibrillar crystals exhibit excellent thermal stabilities. Losses of 5 wt % of POBP-2 and POBP-3 are found at around 496 °C in air and at around 527 °C in nitrogen. The temperatures of 5 wt % loss of POBP-4 are lower.

Thermal transition behaviors of POBP crystals were measured by DSC analysis. Kricheldorf et al. reported previously that DSC traces of POBP displayed only one endotherm between 550 and 600 °C, which represented simultaneous melting and decomposition.[8,9] Geil et al. found other transitions at ca. 350 and 530 °C, which were supported by the changes in electron diffraction patterns.[10] The POBP crystals prepared here, however, did not show any detectable peaks until 500 °C, being consistent with the result described in the literature.[8,9] They were not run above 500 °C.

Formation Mechanism of Bundlelike Aggregates of Fibrillar Crystals. In order to clarify the formation mechanism of the bundlelike aggregates of the fibrillar crystals, morphological features of the crystals prepared in TS 800 were followed with the polymerization time. The crystals were collected by vacuum filtration at 330 °C to avoid the crystallization of dissolved oligomers onto the surface of the crystals during cooling. The scanning electron microscopic observation of crystals obtained in the early stage of polymerization shows a convex-lens-like shape, different from the final crystals as shown in Figure 3. The lenslike incipient crystals polymerized for 2 h are 2−3 μm in diameter and 0.1−0.2 μm in thickness, which are apparently smaller than that of the final crystals polymerized for 20 h.

Crystals polymerized for 1 h are observed by transmission electron microscopy to know the formation mechanism of these lenslike crystals. A micrograph of the crystals is shown in Figure 4. As the remarkable result, the stacking of lamellae due to the spiral growth can be clearly observed at the thin edge of the crystal (see arrow in Figure 4). This fact supports that the formation of the incipient lenslike crystals is similar to that of the POB whiskers in the growth mechanism, which is consisted of the following steps: crystallization of oligomers with a critical length as lamellae from solution and stacking of lamellae along a long axis of a whisker with a spiral growth caused by a screw dislocation, as reported previously.[3−5]

As can be seen in the enlarged micrograph of Figure 3, many protrusions exist clearly on the surface of the

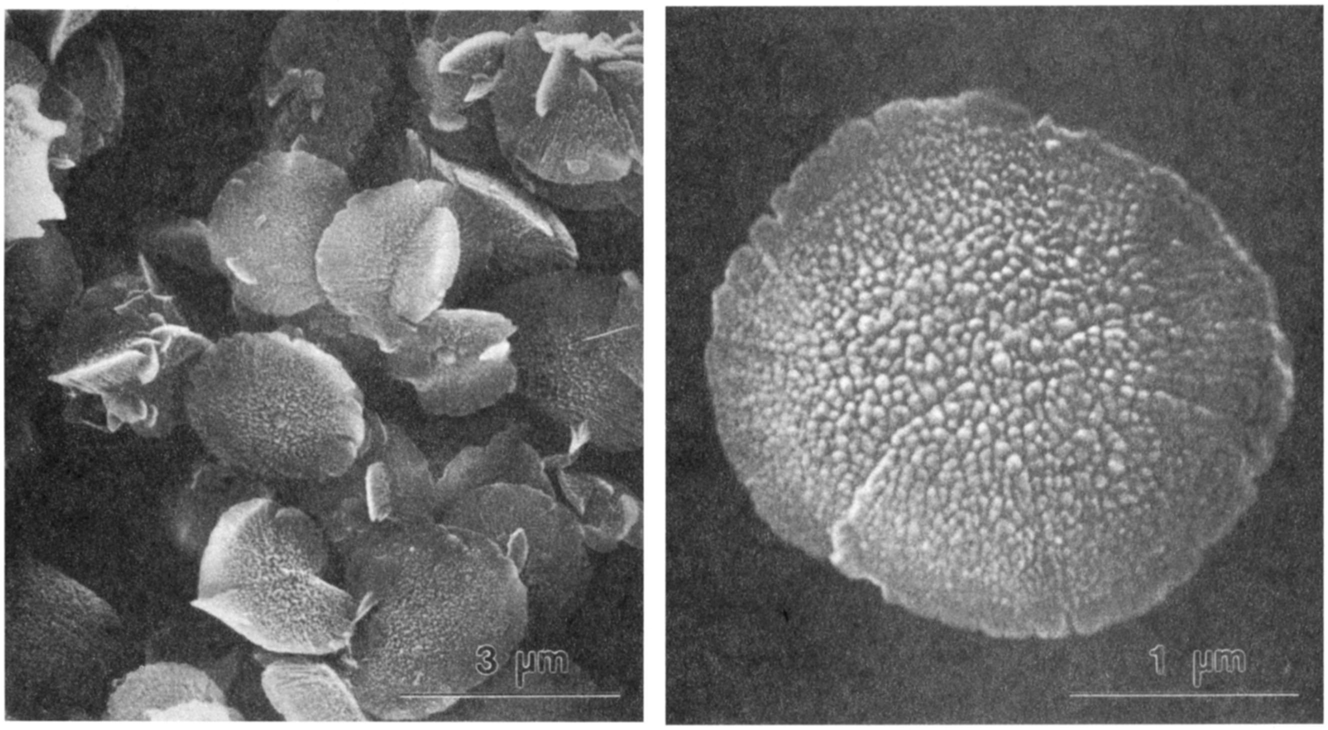

Figure 3. Scanning electron micrograph of POBP crystals prepared in TS 800 at 330 °C for 2 h.

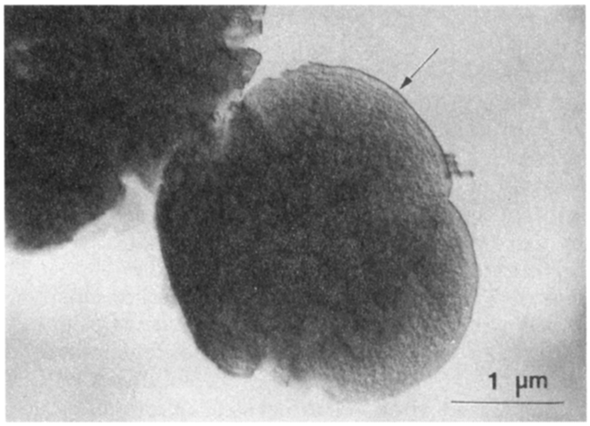

Figure 4. Transmission electron micrograph of incipient POBP crystals prepared in TS 800 at 330 °C for 1 h.

lenslike crystal. These protrusions may be formed by the reorganization of crystals accompanying the increase of DP by postpolymerization.

A scanning electron micrograph of crystals polymerized for 4 h is shown in Figure 5. Many fibrillar crystals develop into bundlelike aggregates. These fibrillar crystals have sharp tips and almost the same length in the aggregate. The width of each fibrillar crystal is consistent with that of protrusion on the lenslike crystals. This fact suggests that the fibrillar crystals grow independently from the protrusions and become longer.

Polymerization time dependencies of the yield, the thickness, and the width of the crystals are shown in Figure 6. Here, the thickness is defined as the central thickness of lenslike crystals in the early stage of polymerization and thereafter the length of fibrillar crystals. The width is defined as the diameter of the lenslike crystals and the bundlelike aggregates of fibrillar crystals. The yield of crystals increases slowly compared with that in the case of polymerization of *p*-acetoxybenzoic acid in LP as described in the literature.[6] The thickness of the crystals increases until 10 h with the yield of the crystals, but the width does not increase after 6 h.

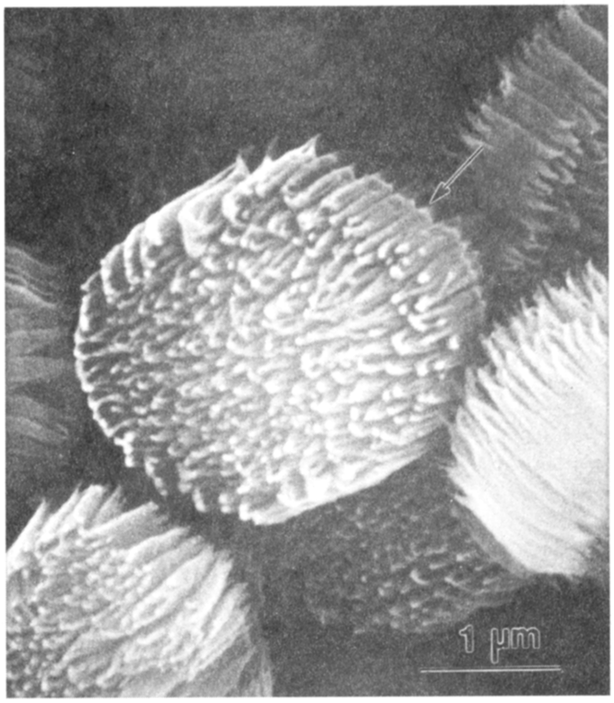

Figure 5. Scanning electron micrograph of POBP crystals prepared in TS 800 at 330 °C for 4 h.

The variation of the DP with the polymerization time is shown in Figure 7. The DP increases rapidly until 4 h. Thereafter, the DP continues to increase steadily with the polymerization time even after the yield levels off. This fact shows that chain growth continues in the crystals by transesterification and the condensation process, without incorporation of monomers or oligomers from the solution.

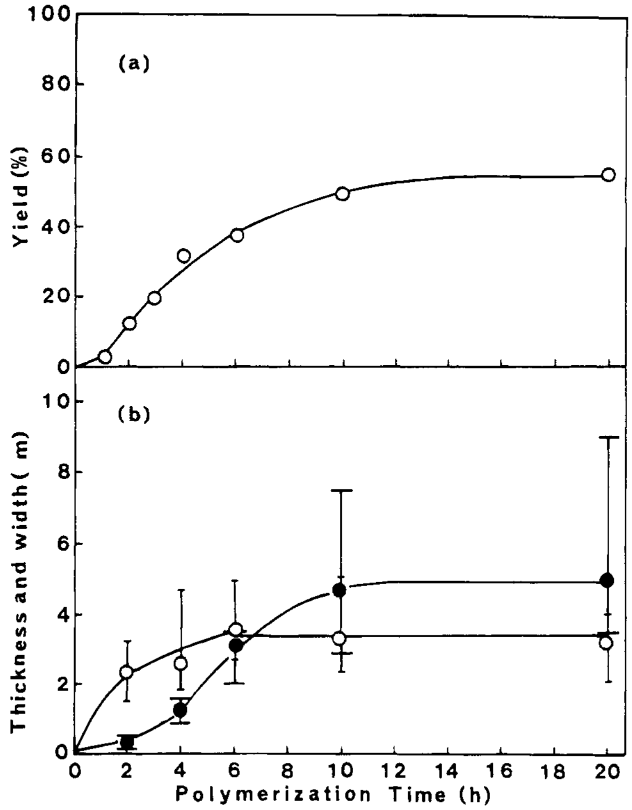

Figure 6. Polymerization time dependencies of (a) yield and (b) thickness (●) and width (○) of crystals obtained in TS 800.

The results described above lead to a conclusion for the most suitable formation mechanism of the bundlelike aggregates of fibrillar crystals as schematically described in Figure 8. The oligomers are formed in a homogeneous state and then crystallized in the form of lamellae from the solution as soon as the DP exceeds a critical value. The lamella grows to the lateral direction preferentially prior to the occurrence of a screw dislocation. Once the screw dislocation is formed in the precipitated lamellae, the step of the screw dislocation becomes a more favored attachment site for subsequent crystallization than the usual growth step because of the advantage of the secondary nucleation for crystal growth, and the convex-lens-like crystals are formed. On the other hand, reorganization of the lenslike crystals occurs accompanying the postpolymerization, and many protrusions are formed on the surface of the lenslike crystals. Subsequently, many fibrillar crystals develop from the incipient protrusions. In conclusion, it can be suggested that the formation mechanism of the bundlelike aggregates of fibrillar crystals is fundamentally similar to that in POB whiskers and reorganization of crystals during slow lamellar crystallization makes the morphology of the final crystals different from whiskers.

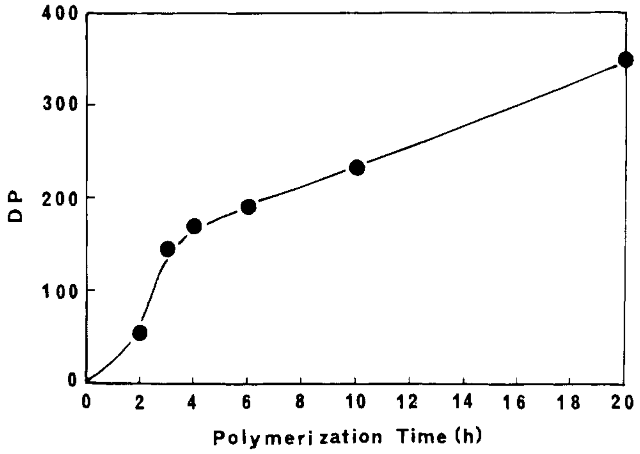

Figure 7. Variation of DP of POBP in crystals with polymerization time.

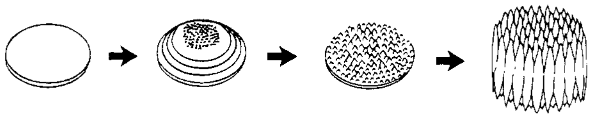

Figure 8. Schematic drawing of the formation mechanism of bundlelike aggregates of fibrillar crystals.

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