# Preparation of Poly(*p*-oxybenzoyl) Microspheres Having Needlelike Crystals on the Surface

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ABSTRACT: Polymerization of 4-acetoxybenzoic acid (ABA) with 3,5-diacetoxybenzoic acid (DABA) was examined to create a novel morphology of poly(*p*-oxybenzoyl) (POB) by means of the phase separation of oligomers during polymerization. Polymerizations were carried out at a concentration of 1.0% in liquid paraffin at 320 °C. Polymerization of ABA yielded the POB whiskers. On the other hand, the polymerization of ABA with DABA of which the concentration in the feed ($\chi_f$) was 0.05−0.20 yielded the microspheres having needlelike crystals on the surface. The average diameter of the microspheres was in the range of 3.4−1.6 $\mu$m and the average length of the needlelike crystals was 3.2−0.3 $\mu$m. The diameter and length decreased with $\chi_f$. DABA acted as a liquid−liquid phase separation inducer and the liquid−liquid phase separation of co-oligomers comprising 4-oxybenzoyl units and 3,5-dioxybenzoyl units was induced in the beginning of polymerization to form the core microspheres. Then the phase separation mode was changed to the crystallization of the homooligomers of the 4-oxybenzoyl unit and the homooligomers were crystallized as needlelike crystals on the surface of microspheres already precipitated. Solid-state polymerization occurred in the precipitates. The microspheres having needlelike crystals were prepared by the combination of liquid−liquid phase separation and the crystallization of oligomers during solution polymerization. The obtained microspheres having needlelike crystals possessed very high crystallinity and exhibited good thermal stability.

## Introduction

Morphology of the polymeric materials is of great importance to create the functional and high performance materials as well as the polymer chain orientation. In particular, wholly aromatic polymers have been paid much attention as hopeful candidates for the aforesaid materials due to excellent properties derived from their rigid structures, such as thermal stability, mechanical properties, chemical resistance, optical properties, and so on.[1,2] However, they exhibit neither solubility or fusibility, and the intractability makes them inaccessible for preparing the morphology by conventional techniques.

We have been studying the morphology control of rigid polymers by means of the oligomer phase-separation during solution polymerization, and prepared successfully poly(*p*-oxybenzoyl) (POB) whisker[3−5] and poly(*p*-oxycinnamoyl) (POC) microspheres[6,7] by polymerization in liquid paraffin (LPF). The POB whiskers, in which the polymer chains are aligned along the long axis of the whiskers, are formed by the reaction-induced crystallization of oligomers with the spiral growth of oligomer lamellae and the following solid-state polymerization in the crystals. Many other aromatic polymer whiskers have been prepared by this method.[8−17] In contrast to the POB whisker, the POC microspheres are prepared through the formation of microdroplets by the liquid−liquid phase separation and the further polymerization in them. Although the POB and POC are totally insoluble aromatic polyesters, the reaction-induced crystallization of oligomers is very workable to control the morphology. Recently, it becomes more desired to establish the methodology for the morphology control.

This article describes our finding on the preparation of POB microspheres having needlelike crystals on the surface.

## Experimental Section

**Materials.** 4-Acetoxybenzoic acid (ABA) was purchased from TCI Co. Ltd. and purified by recrystallization from ethyl acetate. 3,5-Diacetoxybenzoic acid (DABA) was prepared according to the previous papers.[18,19] The melting points of ABA and DABA are 193 and 162 °C, respectively. LPF was purchased from Nacalai Tesque Co., Ltd., and purified by vacuum distillation (220−240 °C/0.3 mmHg).

**Polymer Synthesis.** Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed ABA (0.30 g, 1.67 mmol), DABA (0.044 g, 0.185 mmol), and 20 mL of LPF. The reaction mixture was heated under slow stream of nitrogen up to 320 °C with stirring. The stirring was stopped after ABA and DABA were completely dissolved. The temperature was maintained at 320 °C for 6 h. The products were collected by vacuum filtration at 320 °C and washed with *n*-hexane and acetone. The filtrate was poured into *n*-hexane, and the precipitated oligomers which were dissolved in LPF at 320 °C were collected by filtration. Characteristics of the polymer products were as follows. FT-IR (KBr) ($cm^{-1}$): 3074, 2925, 1738, 1598, 1509, 1445, 1415, 1258, 1200, 1156, 1050, 1012, 885, 753.

**Characterization.** The morphology of the products was observed on scanning electron microscope (SEM Hitachi S-3500N). Samples were dried, sputtered with gold and

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observed at 20 kV. The size parameters of the product, which were diameter of the microspheres, number of needlelike crystals in unit area of the surface and length, and the width and tip angle of needlelike crystals, were determined by the average of over 100 observation values. The density of the products was measured by the flotation method using bromoform and toluene at 25 °C. Number of the microspheres having needlelike crystals ($N$) was calculated with yield, density and shape parameters according to eq 1 assuming that the cross section of the needlelike crystals was hexagonal like the POB whisker.[3]

$$N = Y/[\pi\rho d^2/2\{d/3 + \sqrt{3}\, W^2 n(3L - \mathrm{W/tan(q/2)}\}] \quad (1)$$

where $N$ is the number of microsphere having needlelike crystals on surface, $Y$ is the yield, $\rho$ is the density of microsphere having needlelike crystals on surface, $d$ is the average diameter of microspheres, $n$ is the number of needlelike crystal in unit area of the surface, $W$ is the average width of needlelike crystal, $L$ is the average length of needlelike crystal, and $\theta$ is the tip angle of needlelike crystals.

The FT-IR spectrum was measured on a microscopic FT-IR spectrometer (FT-IR-410, Itron IRT30, JASCO, Co., Ltd). Aperture size was 30 $\mu$m. Solid-state $^{13}$C NMR was measured on Bruker AVANCE300WB operating at 75 MHz. Wide-angle X-ray scattering (WAXS) was conducted on a Rigaku 4012K2 with nickel-filtered Cu K$\alpha$ radiation (35 kV, 20 mA). Thermal transition was evaluated by differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) with a scanning rate of 10 °C·min$^{-1}$ in nitrogen atmosphere. Thermal stabilities were evaluated by a thermogravimetric analyzer (TGA) (Perkin-Elmer TGA-7) with a scanning rate of 10 °C·min$^{-1}$ in nitrogen atmosphere.

**Composition Analysis.** The products or the recovered oligomers (ca. 10 mg) and 1 mL of 7.0 wt % potassium hydroxide methanol solution were placed in a test tube and kept at 25 °C for 24 h to be completely hydrolyzed. Then they are neutralized with aqueous HCl. The composition was determined on the basis of the concentration of 4-hydroxybenzoic acid and 3,5-dihydroxybenzoic acid measured by HPLC (Waters 600E) with a Nova Pack HR C18 column. The eluent was the mixture of water containing 2.0 wt % acetic acid and acetonitrile, and the mixing volume ratio of these two solvents was changed linearly from 90/10 to 0/100 for 40 min.

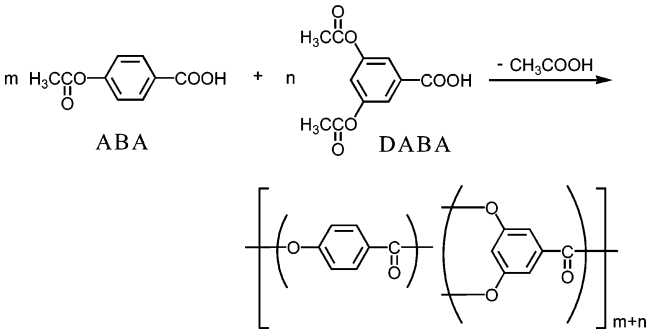
## Results and Discussion

**Concept for Making Microspheres Having Needlelike Crystals on Surface.** The reaction-induced phase separation of oligomers during solution polymerization in poor solvent is a favorable procedure for the morphology control of intractable polymers such as POB. The behaviors of the reaction-induced phase separation of oligomers during solution polymerization can be described as an analogy for the partially miscible polymer−solvent systems as already reported.[20,21] On a concentration−temperature phase diagram ($C-T$ phase diagram), the phase separation curve in the repulsive system, in which there is no attractive force like hydrogen bonding between oligomer and solvent, can be written as the combination of a freezing point curve of oligomers and an upper critical solution temperature (UCST) type consolute curve. The oligomers are formed in homogeneous phases at the beginning of the polymerization. When the molecular weight of the oligomers exceeds the critical value, the oligomers are phase-separated through a supersaturated state. If the oligomers cross the freezing point curve, the oligomer crystals are formed in the solution and polymer crystals like whiskers are finally obtained by solid-state polymerization in the oligomer crystals. On the other hand, if they cross the consolute curve, microdroplets are formed and the microspheres are finally obtained by further polymerization in them leading to solidification with maintaining the spherical morphology. To create a novel morphology of the microspheres having needlelike crystals on the surface, these two phase separation modes should be combined in the course of the polymerization. The liquid−liquid phase separation is initially induced to form the core microspheres, and then the phase separation mode is changed to the crystallization to form the needlelike crystals. It is necessary to form the needlelike crystals on the surface of the microspheres that the crystallization is started after the solidification of microspheres. In this study, DABA is used as a liquid−liquid phase separation inducer, and the polymerization of ABA is carried out with the addition of a small amount of DABA in LPF. Incorporation of the 3,5-dioxybenzoyl unit into the oligomers of the 4-oxybenzoyl unit must lower not only the crystallizability of oligomers but also the freezing point curve due to the entropic contribution, and the co-oligomers containing 3,5-dioxybenzoyl unit are precipitated through the liquid−liquid phase separation. After completion of phase separation of co-oligomers, homooligomers of 4-oxybenzoyl unit are phase separated by the crystallization to form the needlelike crystals on the surface of the microspheres already formed.

**Table 1. Results of Polymerization of ABA and DABA[a]**

| run no. | $\chi_f$[b] | yield (%) | morphology | $\chi_p$[c] |
|---|---|---|---|---|
| 1 | 0.00 | 46 | needlelike crystal | 0.00 |
| 2 | 0.05 | 56 | microsphere having needlelike crystals | 0.06 |
| 3 | 0.10 | 48 | microsphere having needlelike crystals | 0.10 |
| 4 | 0.15 | 48 | microsphere having needlelike crystals | 0.18 |
| 5 | 0.20 | 43 | microsphere having needlelike crystals | 0.19 |

[a] Polymerizations were carried out in LPF at 320 °C for 6 h. [b] $\chi_f$ = [DABA]/{[ABA]+[DABA]}. [c] $\chi_p$ = [3,5-dioxybenzoyl unit]/{[4-oxybenzoyl unit] + [3,5-dioxybenzoyl unit]}.




**Morphology of Product.** Polymerizations of ABA were carried out with the molar ratios of DABA in feed ($\chi_f$ = [DABA]/{[ABA] + [DABA]}) varying from 0.05 to 0.25 in LPF at 320 °C. Table 1 summarizes the results of polymerization, and Figure 1 shows the morphology of products. In all polymerizations, the solutions became turbid within 9 min due to the precipitation of oligomers and the products were obtained as precipitates after 6 h. As aforesaid, the polymerization of ABA in LPF yielded the POB whiskers, of which average lengths and widths were 46.0 $\mu$m and 1.5 $\mu$m, respectively. In contrast to this, the copolymerizations at $\chi_f$ of 0.05−0.20 afforded microspheres having needlelike crystals on the surface with a yield of 56−43%. The product prepared by the copolymerization at $\chi_f$ of 0.25 did not exhibit a clear morphology. Size parameters are sum-

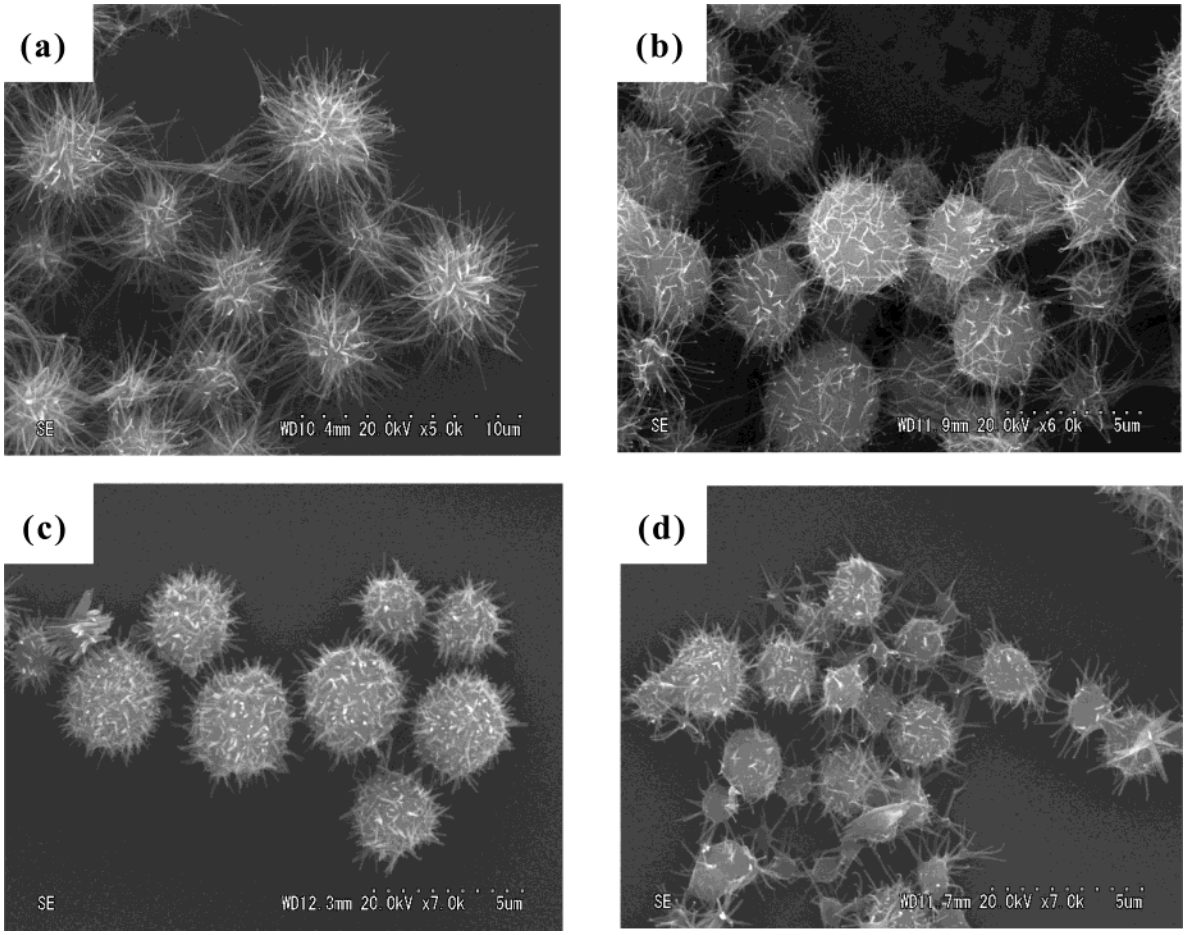



**Figure 1.** Morphology of the products prepared at $\chi_f$ of (a) 0.05, (b) 0.10, (c) 0.15, and (d) 0.20.

**Table 2. Size Parameters and Thermal Stability of Products**

| run no. | diam of sphere ($\mu$m) | length of needle ($\mu$m) | width of needle ($\mu$m) | no. of needles on surface ($\mu m^{-2}$) | no. of spheres ($\times 10^9$)[a] | 5% wt loss temp (°C)[b] |
|---|---|---|---|---|---|---|
| 1 | | 46.0 | 1.5 | | | 524 |
| 2 | 3.4 | 3.2 | 0.2 | 5 | 3.1 | 485 |
| 3 | 3.0 | 0.9 | 0.2 | 7 | 3.9 | 440 |
| 4 | 2.4 | 0.3 | 0.1 | 10 | 11.1 | 437 |
| 5 | 1.6 | 0.5 | 0.1 | 11 | 35.3 | 422 |

[a] Number of microsphere having needlelike crystals in polymerization system calculated with eq 1. [b] TGA was measured with a heating rate of 10 °C·min$^{-1}$ in $N_2$.

marized in Table 2. The diameter of the core microspheres ranges from 3.4 to 1.6 $\mu$m and the length of the needlelike crystals ranges from 3.2 to 0.3 $\mu$m. They exhibit the broad and unimodal distributions of which the coefficient of variation for the diameter and the length are in the range of 23−55% and 37−41%, respectively. They are related to the content of DABA and tend to decrease with $\chi_f$. Number of needlelike crystal in unit area of the surface ($n$) increases from 5 to 11 $\mu m^{-2}$ with $\chi_f$. The needlelike crystals are densely formed on the surface of the microspheres prepared at higher $\chi_f$. The number of microspheres ($N$) is also dependent on $\chi_f$ and it increases with $\chi_f$. The formation of microspheres via the liquid−liquid phase separation of oligomers, which is binodal decomposition process, is a nucleation and growth mechanism. It is well-known that the critical radius of nucleus and nucleation rate depend on the degree of super-saturation and the higher degree of supersaturation afforded a larger number of nuclei having smaller radius.[22,23] Because of this, a larger number of smaller microspheres having needlelike crystals are formed at higher $\chi_f$. The composition of 3,5-dioxybenzoyl unit in the products ($\chi_p$) was estimated by HPLC after hydrolysis of the products. The $\chi_p$s tabulated in Table 1 are in good agreement with the $\chi_f$s. The chemical structure of the microspheres having needlelike crystals prepared at $\chi_f$ of 0.10 is analyzed by FT-IR and solid-state $^{13}$C NMR. The spectra are shown in Figure 2. The C═O band for the ester linkage is clearly observed at 1738 cm$^{-1}$. The bands characterized to carboxylic acid and acetoxy group are hardly detected. The characteristic aromatic band of 3,5-dioxybenzoyl unit is observed at 1445 cm$^{-1}$. With respect to $^{13}$C NMR, the spectrum of the microspheres having needlelike crystals is shown together with that of POB as a reference. The sharp peaks assigned as 4-oxybenzoyl unit are clearly observed at 163, 155, 133, 126, and 124 ppm in the spectrum of POB. On the other hand, the peaks of 3,5-dioxybenzoyl unit are clearly observed as shoulders beside the characteristic peaks of POB in the spectrum of the microspheres having needlelike crystals. These results confirm that the product comprises high molecular weight POB containing the 3,5-dioxybenzoyl unit.

Thermal properties of the resulting microspheres are examined. It is known that the POB crystal shows a reversible first-order solid−solid transition at around 350 °C differing from the melting process, and it is regarded as a transition to pseudohexagonal packing of polymer molecule by a rotation of 1,4-phenylene ring

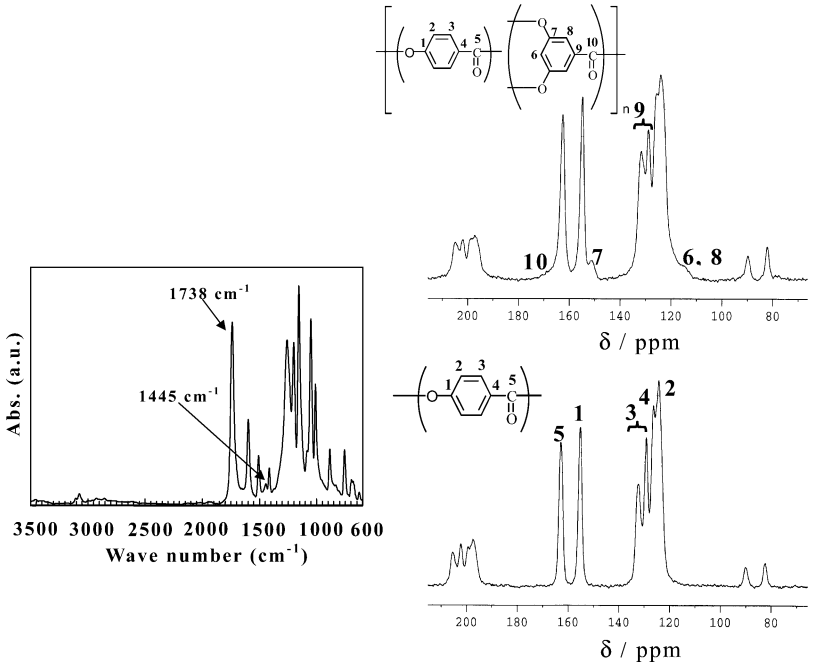



**Figure 2.** IR and $^{13}C-CP/MASS$ NMR spectra of microspheres having needlelike crystals on surface prepared at $\chi_f$ of 0.10.

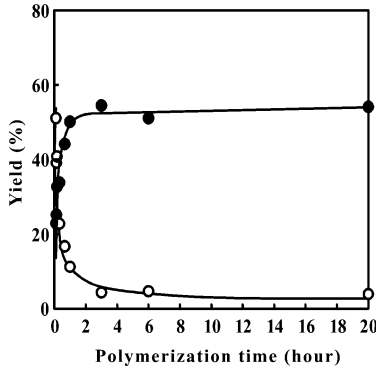



**Figure 3.** Plot of the yield of the product (●) prepared at $\chi_f$ of 0.10 and the oligomers dissolved in LPF (○).

around $\sigma$-bonds in the para position.[24−28] The microspheres having needlelike crystals do not show any thermal transitions on DSC scanning including solid−solid transition, melting, and crystallization. With respect to the thermal stability, the micropheres having needlelike crystals exhibit a 5 wt % loss temperature of 485−422 °C, which becomes lower with increase of $\chi_f$ as shown in Table 2. The 3,5-dioxybenzoyl unit lowers thermal stability but the microspheres having needlelike crystals are still in the highest class of thermally stable polymers.

**Formation Mechanism of Microspheres Having Needlelike Crystals on the Surface.** To understand the formation mechanism of the microsphere having needlelike crystal on the surface, the yield, density, morphology, size parameters, and content of 3,5-dioxybenzoyl unit were followed in the course of the polymerization at $\chi_f$ of 0.10. Figure 3 is a plot of the yield of the microspheres and the oligomers dissolved in LPF. The yield of the microspheres increases rapidly within 1 h and afterward it increases gradually with polymerization time. On the contrary, that of the oligomers decreases correspondingly. This result reveals that the products are formed by the consecutive supply of oligomers from the homogeneous phase. Figure 4 shows the morphology of the products prepared at the early stage of polymerization. The products prepared for 10 min after the precipitation are spheres having smooth surface. This morphological feature indicates that they are formed through the liquid−liquid phase separation. The products prepared for 20 min are also spheres, but many thorns appeared on the surface of the spheres. Then these thorns grow into the needlelike crystals. Figure 5 is a plot of size parameters and *N* as a function of polymerization time. The diameter of microsphere increases rapidly at the initial stage of polymerization and then decreases after 1 h. Elimination of the 3,5-dioxybenzoyl unit from the product by segregation, discussed later, is likely one of the reason for the diameter decrease. However, this diameter decrease is mainly attributed to the closer packing of inner structure of the microspheres with increasing crystallinity as also discussed later. The length of needlelike crystals also increases rapidly after 20 min to 1 h and then continues to increase gradually with the yield. The size of the microspheres having needlelike crystals, which is the sum of the diameter of the core microspheres and the 2-fold length of needlelike crystals, is almost constant after 1 h. This fact suggests that the needlelike crystals are formed from the inside of the microspheres and the apparent increase of the length of needlelike crystals after 1 h is brought about by the decrease of the diameter of core microspheres. *N* decreases rapidly within 20 min, and then it becomes constant. This initial drop of *N* indicates that the microspheres grow by not only the consecutive supply of oligomers but also the coalescence of microdroplets within 20 min, and it is a characteristic phenomenon for the formation of microdroplets through liquid−liquid phase separation. Figure 6 is a plot of the composition and the content of the 3,5-dioxybenzoyl unit in the microspheres as a function of polymerization time. The composition of 3,5-dioxybenzoyl unit in the product prepared for 8 min is 23 mol %, which is quite a bit higher than $\chi_f$, and it decreases rapidly until 20 min. In particular, that of the spheres prepared within 20 min is much higher than $\chi_f$. Then it decreases slowly approaching closely to a $\chi_f$ of 0.10. The content of 3,5-dioxybenzoyl unit increases within 1 h

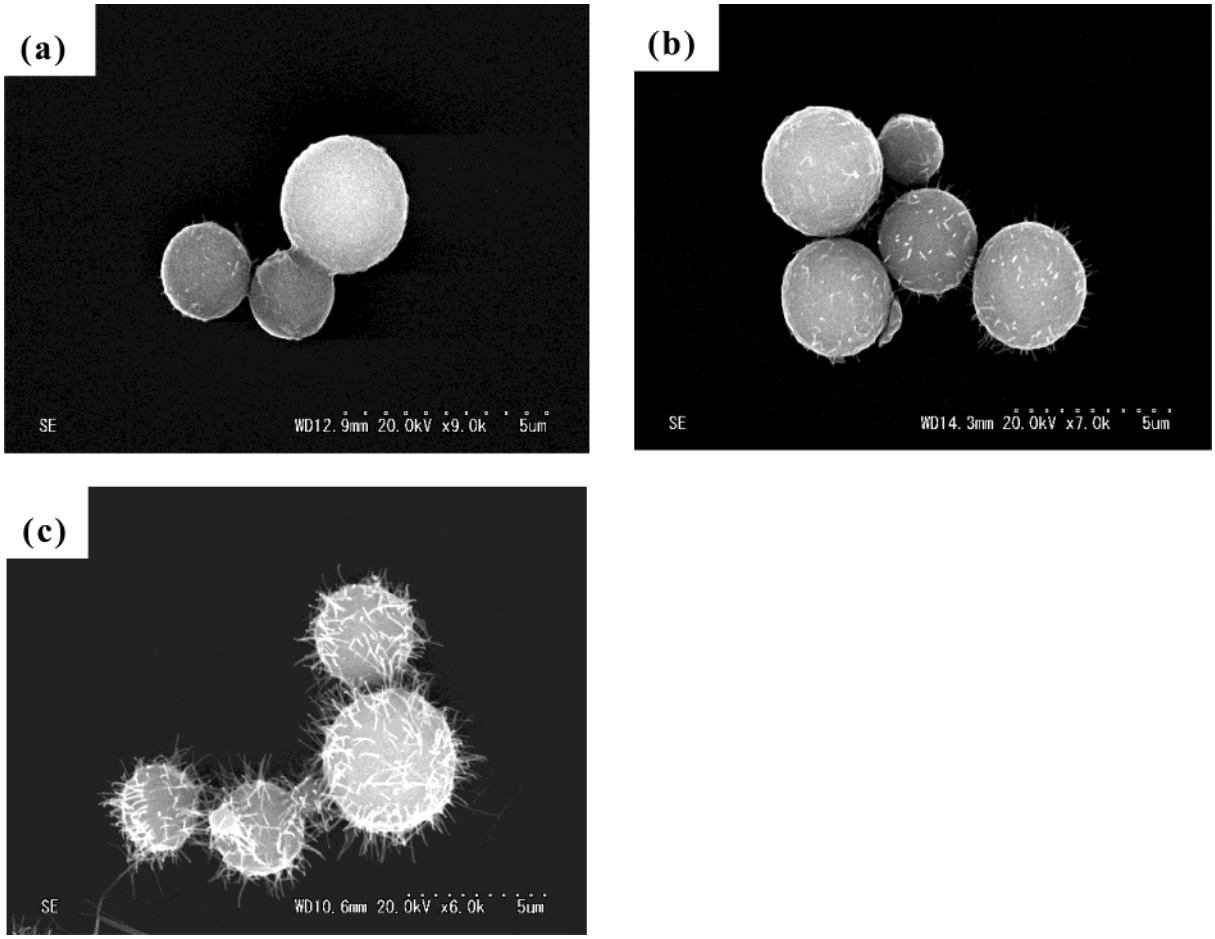



**Figure 4.** Morphology of the products prepared at $\chi_f$ of 0.10 for (a) 10, (b) 20, and (c) 40 min.

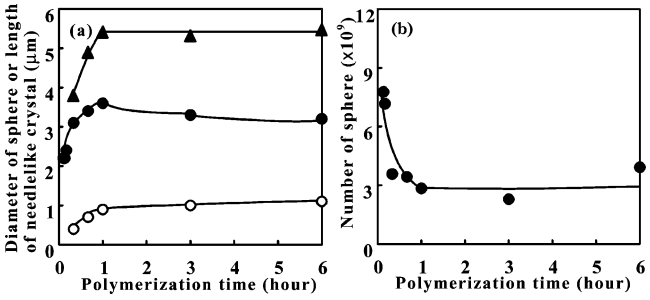



**Figure 5.** Plots of (a) diameter of sphere (●), length of needlelike crystal (○), and size of microspheres having needlelike crystals (▲) and (b) number of the microsphere prepared at $\chi_f$ of 0.10 as a function of polymerization time. The size of a microsphere having needlelike crystals is defined as the sum of the diameter of the microsphere and the 2-fold length of the needlelike crystal.

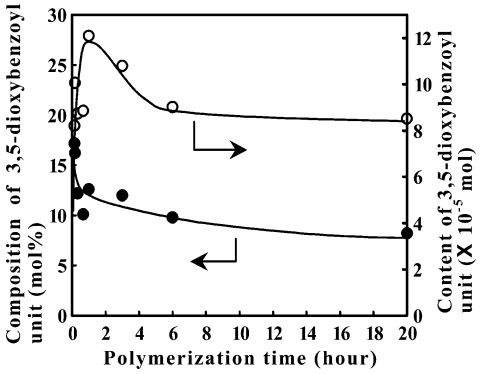



**Figure 6.** Plot of composition (●) and content (○) of the 3,5-dioxybenzoyl unit in the product prepared at $\chi_f$ of 0.10 as a function of polymerization time.

and then decreases with polymerization time. These results reveal that the co-oligomers containing 3,5-dioxybenzoyl unit are preferentially precipitated by liquid−liquid phase separation in the beginning of polymerization and form the microspheres having smooth surface. The homooligomers comprised of 4-oxybenzoyl unit are also phase-separated but they become incorporated into microdroplets. The microdroplets formed by liquid−liquid phase separation are solidified by the further polymerization of oligomers in them, leading to the increase in molecular weight. This solidification, which is crystallization in the microdroplets, prevents the coalescence from occuring any longer, due to the stable surface resulting in constant $N$ after ca. 20 min. After 20 min, some of the co-oligomers containing the 3,5-dioxybenzoyl unit or the 3,5-dioxybenzoyl unit are eliminated from the microspheres by the segregation or ester−ester exchange reaction during the solidification, and hereby the diameter decreases slightly. Afterward, the homooligomers are mainly phase-separated by the crystallization to form the needlelike crystals on the solid surface of the microspheres, so-called heterogeneous nucleation. The microspheres are etched by aqueous KOH solution to examine the inner structure. Figure 7 shows the etched microspheres prepared at the initial stage of polymerization and for 6 h at $\chi_f$ of 0.1. Coagulated needlelike crystals are found in the microspheres prepared for 6 h. These microspheres are solid and not hollow. The short needlelike crystals of which

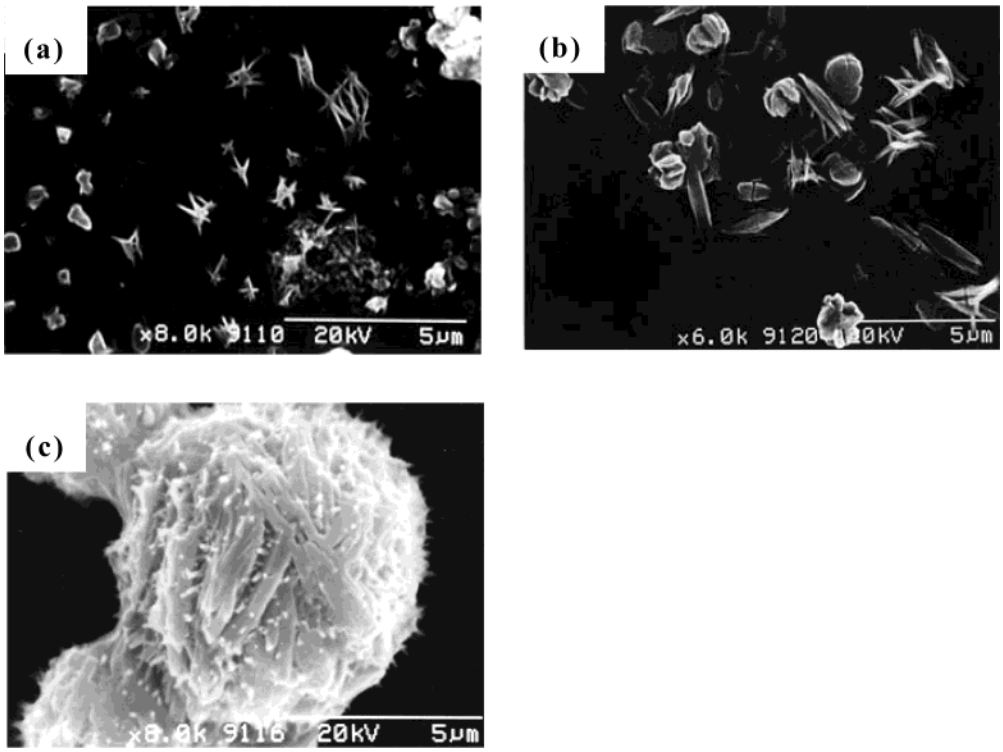



**Figure 7.** Inner structure of microspheres prepared at $\chi_f$ of 0.10 for (a) 10 min, (b) 20 min, and (c) 6 h. The microspheres were etched by a 0.7% KOH methanol solution.

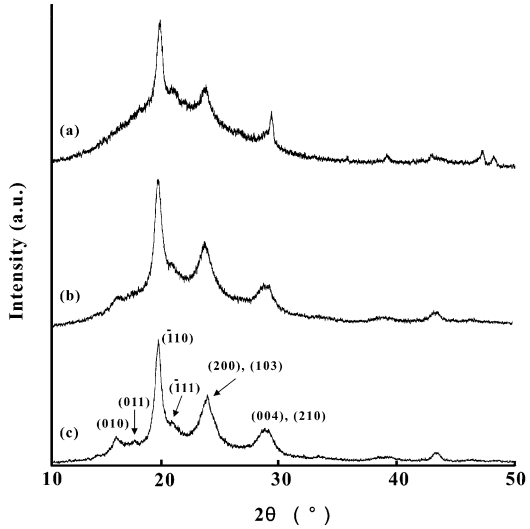



**Figure 8.** WAXS profiles of the products prepared at $\chi_f$ of 0.10 for (a) 8 min, (b) 20 min, and (c) 6 h.

the average length is 0.6 $\mu$m are observed in the microspheres having smooth surface prepared for 10 min. These crystals are formed by the crystallization in the microdroplets caused by the increase of the molecular weight of the oligomers. In the microspheres having many thorns on the surface prepared for 20 min are found the grown needlelike crystals of which the average length is 2.1 $\mu$m. The tips of these needlelike crystals appeared on the surface of the microspheres seems to serve as the nuclei for the needlelike crystals on the surface of the microspheres. Figure 8 shows the WAXS profiles of the products prepared at $\chi_f$ of 0.10. The characteristic peaks of the POB crystal are clearly observed at $2\theta$ of 19, 21, 24, 28, and 29°, and they can be indexed according to the POB unit cell.[29] The profile of the microspheres having smooth surfaces prepared for 8 min comprises POB crystal diffraction peaks and the diffuse halo of the amorphous region. However, the diffuse halo decreases and the peaks become sharper in the profile of the microspheres having many thorns on the surface prepared for 20 min. The diffuse halo is hardly observed and the crystal diffraction peaks become much sharper in the profile of the microspheres having needlelike crystals on the surface prepared for 6 h. It is obvious that the crystallinity of the microspheres enhances with time, and the microspheres having needlelike crystals prepared for 6 h possess extremely high crystallinity. This change in the profile shows the development of the crystalline structure with time, resulting in the decrease of the diameter of core microspheres, and it is consistent with the above discussion.

## Conclusions

POB microspheres having needlelike crystals on the surface are prepared by the polymerization of ABA with an addition of DABA at $\chi_f$ of 0.05−0.20 in LPF. The diameter and the length of the needlelike crystals are highly related to $\chi_f$ and they decrease with $\chi_f$. They possess high crystallinity and exhibit good thermal stability. The formation mechanism is as follows. The co-oligomers of 4-oxybenzoyl unit and 3,5-dioxybenzoyl unit are preferentially precipitated at the beginning of the polymerization by liquid−liquid phase separation to form the microdroplets. They grow by not only the consecutive supply of oligomers from the solution but also the coalescence. Then they are solidified by the crystallization which is induced by the increase of molecular weight by the further polymerization in them. Afterward, the homooligomers of 4-oxybenzoyl unit are precipitated by the crystallization on the solid surface of the microspheres as heterogeneous nucleation and the needlelike crystals are formed on the surface.

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