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Communications to the Editor

Novel Direct Polycondensation of 4-Hydroxybenzoic Acid by Means of Reaction-Induced Crystallization of Oligomers under Nonstoichiometric Condition

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Introduction. Direct polycondensation of polyester and polyamide is a very attractive polymerization method, and numerous types of condensation reagents have been developed so far.^{1–13} The previous direct polycondensations were carried out in homogeneous solution, and stoichiometry between two functional groups in the polymerization system is of great importance to prepare high molecular weight polymers. We had been studying the morphology control of aromatic polyesters by reaction-induced crystallization of oligomers during solution polymerization and prepared successfully poly(p-oxybenzoyl) (POB) whiskers from 4-acetoxybenzoic acid (ABA) in liquid paraffin at 320 °C.14-19 In the series of these studies, it has been found that high molecular weight POB could be prepared from ABA in liquid paraffin even under nonstoichiometric condition between acetoxy and carboxyl groups coexisting 4-alkyloxybenzoic acid.²⁰ The polycondensation proceeds under nonstoichiometric condition through following mechanisms; when DPn of oligomers exceeds a critical value, they are crystallized to form the crystals. Endfree oligomers are preferentially crystallized due to the lower solubility. Though end-capped oligomers are also crystallized, polycondensation proceeds with eliminating



end-capping groups by trans-esterification just when they are crystallized. On the basis of the above polymerization mechanisms, direct polycondensation of 4-hydroxybenzoic acid (HBA) with aromatic acid anhydride will work well to yield POB.

This paper describes our new finding of direct polycondensation of HBA in the presence of 4-alkyloxybenzoic anhydride such as 4-ethoxybenzoic anhydride (EOBA anhydride) and 4-hexyloxybenzoic anhydride (HOBA anhydride) by means of the reaction-induced crystallization of oligomers.

Experimental Section. Typical solution polymerization procedure was described as follows: Into a cylindrical vessel equipped with gas inlet and outlet tubes were placed 0.23 g of HBA (1.67 \times 10⁻³ mol), 0.52 g of EOBA anhydride (1.67 \times 10⁻³ mol), and 20 mL of liquid paraffin. This mixture was placed into an oil bath and heated to 320 °C under a slow stream of nitrogen with stirring. When the mixture became clear solution, the stirring was stopped. The solution became turbid after several minutes at 320 °C due to the crystallization, and then the polymer crystals were formed. The solution temperature was kept at 320 °C for 6 h. Afterward, the crystal suspension was filtrated at 320 °C. The obtained polymer crystals were washed with *n*-hexane and acetone and then dried. After the filtrate was allowed to cool, the compounds dissolved in liquid

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| Table 1. Polymerization of HBA in the Presence | e of 4-Alkyloxybenzoic Anhydride in Liquid Paraffin ^a | |
|--|--|--|
| | | |

| | | content of 4-alkyloxybenzoic acid unit ^c (mol %) | | | | DSC^{e} | |
|--|----------------------|---|------------------------|------------------|----------------------------|------------------------|------------------|
| concn of 4-alkyloxybenzoic anhydride in feed ^b (mol %) | polymer yield (%) | polymer | dissolved compounds | DPn ^d | morphology of the crystals | $T_{c}^{f}(^{\circ}C)$ | ΔH (J/g) |
| χEa | | | | | | | |
| 0 | 0 | | | | | | |
| 10 | 0 | | | | | | |
| 20 | 0 | | | | | | |
| 30 | 18 | 2.00 | 75.7 | 49 | slab | 324 | 34.8 |
| 40 | 30 | 1.45 | 73.3 | 68 | slab | 323 | 32.2 |
| 50 | 37 | 1.30 | 83.2 | 76 | fibril, pillar | 326 | 32.6 |
| 60 | 39 | 2.56 | 80.9 | 38 | fibril, pillar | 320 | 38.4 |
| χна | | | | | | | |
| 0-60 | 0 | | | | | | |

^{*a*} Polymerizations were carried out at 320 °C for 6 h. ^{*b*} χ is defined as {[4-alkyloxybenzoic anhydride]/([HBA] + [4-alkyloxybenzoic achydride])} × 100 (mol %). ^{*c*} Content of 4-alkyloxybenzoic acid unit is defined as {[4-alkyloxybenzoic acid unit]/([4-oxybenzoyl unit] + [4-alkyloxybenzoic acid unit])} × 100 (mol %). ^{*d*} DPn was estimated by the molar ratio of 4-hydroxybenzoic acid and 4-alkyloxybenzoic acid by quantitative analysis of end groups based on the assumption that hydroxyl and other end groups were negligible in this polymerization. ^{*e*} DSC was measured with a scanning rate of 10 °C min⁻¹. ^{*f*} Crystal–crystal transition temperature.



Figure 1. Scanning electron micrographs of POB crystals in the system of EOBA anhydride at χ_{Ea} of (a) 30, (b) 40, (c) 50, and (d) 60 mol %.

paraffin at 320 °C were precipitated by pouring the filtrate into *n*-hexane. The precipitates were collected by filtration and washed with *n*-hexane.

Results and Discussion. EOBA anhydride²¹ and HOBA anhydride²¹ were used as condensation reagents as shown in Scheme 1. Polymerizations of HBA were carried out in liquid paraffin at 320 °C with coexisting 4-alkyloxybenzoic anhydride. These anhydrides possess alkyloxy group to avoid the sublimation during high-temperature polymerization. Table 1 summarizes the results of polymerization. The molar ratio of 4-alkyloxybenzoic anhydrides in feed (χ) is described as follows:

$$\chi \text{ (mol \%)} = \frac{[4\text{-alkyloxybenzoic anhydride}]}{[HBA] + [4\text{-alkyloxybenzoic anhydride}]} \times 100$$

 χ_{Ea} and χ_{Ha} stand for the molar ratio of EOBA anhydride and HOBA anhydride in feed, respectively.

When EOBA anhydride was added, the crystals were formed during polymerization at χ_{Ea} of 30–60 mol %with the yield of 18-39%. Any crystals were not precipitated at χ_{Ea} of less than 30 mol % and more than 70 mol %. Scanning electron micrographs of the obtained crystals are shown in Figure 1. They exhibit very clear crystal habits such as slab, fibril, and pillar. As we had reported previously, there exist two major modes for phase separation of oligomers during solution polymerization, of which one is the crystallization of oligomers and another is liquid-liquid phase separation of oligomers.²²⁻²⁴ If the oligomers are precipitated by the crystallization, the oligomer crystals are formed in the solution, and then the polymer crystals having clear crystal habit are finally formed. In contrast to this, if the oligomers are phase-separated by the liquid-liquid phase separation, the microspheres are obtained through the formation of the microdroplets. In this case, the crystal habit completely disappeared and the spherical morphology appeared. In this study, the products ex-



Figure 2. Plots of (a) DPn and yield of polymers and (b) number of polymer chains (Np) in crystals prepared at χ_{Ea} of 50 mol % as a function of polymerization time.

hibit the clear crystal habit, and therefore, it can be thought that they are formed by the crystallization of oligomers. On the other hand, crystals were not formed in the presence of HOBA anhydride at any χ_{Ha} 's. FT-IR spectra of the crystals and the dissolved compounds in liquid paraffin prepared at χ_{Ea} of 50 mol % for 6 h were measured to confirm the chemical structure. The characteristic peaks of POB such as ester carbonyl group appear clearly at 1739 and 1261 cm⁻¹, and the hydroxyl group is not detected in the spectrum of the crystals. The spectra of the crystals are identical with that of POB. The result of the elemental analysis result of the crystal is in good agreement with the calculated value. These confirm the formation of POB as the crystals.²⁵ The peaks of carboxylic anhydride appearing at 1773 and 1706 cm^{-1} disappear completely, and the ester group is clearly observed in the spectrum of the dissolved compounds in liquid paraffin. The hydroxy group in HBA is not detected. This result shows that HBA is completely converted into 4-(4-ethoxybenzoyloxy)benzoic acid (EBBA), and oligomer is formed by the ester-acid exchange reaction with eliminating EOBA. POB is insoluble in any solvents, and hence DPn cannot be directly measured by NMR and GPC. In this study, DPn of the obtained polymer in the crystals was determined by the molar ratio of HBA and EOBA after hydrolysis of polymers, assuming that hydroxyl end group did not exist in the polymer chains, which was consistent with the results of FT-IR spectra.²⁰ DPns are also shown in Table 1. DPns of the obtained polymers are from 38 to 76. It increases with increasing χ_{Ea} up to 50 mol % and then decreases over 50 mol %. Polymerization at χ_{Ea} of 50 mol % gives the highest DPn of 76. The influence of χ_{Ea} on DPn can be explained as follows. At χ_{Ea} of 50 mol %, all HBAs are completely converted into the EBBA, and the molar ratio of two functional groups, which are the 4-ethoxybenzoyloxy group in EBBA and the carboxyl group, is the highest value of 0.5. In other words, χ_{Ea} of 50 mol % gives the least nonstoichiometric condition among χ_{Ea} 's. When χ_{Ea} is less than 20 mol %, the stoichiometry is largely out of balance, and oligomers are not formed enough to be phase-separated because of the low concentration of activated monomers. Therefore, the crystals are not precipitated at χ_{Ea} of less than 20 mol %. On the other hand, the crystals were not obtained at χ_{Ea} of more than 70 mol %. In this case, excess EOBA anhydride reacts with the carboxyl end group of oligomers to form the anhydride end group, and the oligomers cannot be phase-separated due to the increase of miscibility into liquid paraffin. Figure 2 plots DPn and the yield of the polymer crystals as a function of polymerization time at χ_{Ea} of 50 mol %. DPn increases from 18 for 1 h to 76 for 6 h with increasing the yield of

the crystals, and then it is constant after the yield is leveled off. The number of polymer chains (Np) in the crystals was calculated according to the following equation to know the polymerization behavior.

$$Np = \frac{yield \times N}{(120.1 \times DPn + 166.2)}$$

where yield is the yield of crystals (grams) and N is the Avogadro's number.

The plot of Np as a function of time is also shown in Figure 2. Np decreases with polymerization time despite the yield increases and then becomes constant after 6 h. This decrement of Np reveals the occurrence of solidstate polymerization in the crystals. The termination of this solid-state polymerization is not clear yet, but it may be due to the defect or disordering of polymer chain ends in the crystals. Analysis of the composition of EOBA moiety in the crystals and the dissolved compounds at χ_{Ea} of 50 mol % elucidates that most of EOBAs are left in the liquid phase during polymerization. From these results, direct polycondensation of HBA in the presence of EOBA anhydride proceeds as follows. HBA reacts first with EOBA anhydride to form activated monomer EBBA. EOBA by-produced in situ breaks the stoichiometry between the 4-alkyloxybenzoyloxy group in EBBA and the carboxyl group. The ester-acid exchange reaction between the 4-ethoxybenzoyloxy group and the carboxyl group forms oligomers in the solution. When the DPn of oligomers exceeds the critical value, the oligomers are phase-separated to form the crystal. The solid-state polymerization takes place in the crystals with eliminating EOBA, and high molecular weight POB is formed even under the nonstoichiometric condition. As described above, the crystals were not precipitated in the case of HOBA anhydride. The oligomers prepared with HOBA possess a longer alkyloxy end group, and this enhances the miscibility of oligomers. Therefore, the oligomers are hardly phase-separated.

Thermal properties and crystal structure of POB are very susceptible to molecular weight, and they are examined to support the formation of high molecular weight POB. Thermal properties of the obtained crystals were measured by DSC and TGA.²⁶ It is well-known that POB crystal exhibits a reversible first-order solidsolid transition at around 350 °C differing from the melting process, and it is regarded as a transition to pseudohexagonal packing of polymer chains due to a rotation of 1,4-phenylene ring around the s-bond in the para position.²⁷⁻³¹ The obtained crystals exhibit the crystal-crystal transition temperature at 320-326 °C with ΔH of 32–38 J g⁻¹, as shown in Table 1. The temperature of 5 wt % loss for the crystals prepared at χ_{Ea} of 50 mol % for 20 h is 512 °C, which is comparable to that for POB prepared from ABA. WAXS patterns (Cu K α) of the obtained POB crystals show very sharp diffraction peaks being accounted for by the crystal unit of POB crystals. These results strongly support the formation of high molecular weight POB.

It is concluded that this study provides a new direct polycondensation of HBA with EOBA anhydride as a condensation reagent, and the phase separation of oligomers is of great importance to prepare high molecular weight POB.

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- (21) EOBA anhydride was synthesized according to following procedure. Into a flask equipped with a condenser and a gas inlet tube were placed 15.0 g of EOBA purchased from Aldrich Co. Ltd. (0.090 mol) and 120 mL of thionyl chloride. Several drops of N,N-dimethylformamide were added into this solution under a nitrogen atmosphere. The mixture was stirred at 25 °C for 12 h. Excessive thionyl chloride was evaporated. Extraction with hot *n*-hexane gave crude 4-ethoxybenzoyl chloride at a yield of 12.4 g (74.4%). Into a flask equipped with a dropping funnel, a thermometer, and a gas inlet tube were placed 11.2 g of EOBA (0.067 mol), 10.2 g of triethylamine (0.101 mol), and 100 mL of dried tetrahydrofuran under a slow stream of nitrogen. A solution of 12.4 g of 4-ethoxybenzoyl chloride (0.067 mol) in 50 mL of dried tetrahydrofuran was added dropwise through a dropping funnel to the mixture at 5 °C for 20 min. The mixture was

stirred at 5 °C for 2 h and then at 25 °C for 6 h. HCltriethylamine salt was filtrated and tetrahydrofuran was evaporated. The obtained solids were washed with water. Washed solids were dissolved in ethyl acetate and dried over sodium sulfate. Recrystallization from ethyl acetate gave 18.1 g of 4-ethoxybenzoic anhydride. The yield was 85.5%. $T_{\rm m}$ (°C): 114. IR (KBr; cm⁻¹): 2980 (aliphatic C–H stretching), 2856 (aliphatic C-H antisymmetric stretching), 1773 (anhydride C=O antisymmetric stretching), 1706 (anhydride C=O symmetric stretching), 1604 (aromatic C=C stretching), 1026 (anhydride C–O stretching). ¹H NMR (CDCl₃; δ, ppm): 1.40 (CH₃CH₂O, t, 6H), 4.03–4.10 (CH₃CH₂O, m, 4H), 6.90 (phenyl, d, 4H), 8.03 (phenyl, d, 4H). HOBA anhydride was synthesized as the similar procedure to EOBA anhydride was synthesized above. The yield of HOBA anhydride was 83.0%. $T_{\rm m}$ (°C): 49. IR (KBr; cm⁻¹): 2931 (aliphatic C–H stretching), 2858 (aliphatic C–H antisymmetric stretching), 1778 (anhydride antisymmetric stretching), 1719 (anhydride C=O symmetric stretching), 1604 (aromatic C=C stretching), 1031 (anhydride C–O stretching), 1001 (diolattice C C Stretching), 1031 (anhydride C–O stretching). ¹H NMR (CDCl₃; δ , ppm): 0.90 (CH₃CH₂(CH₂)₃CH₂O, t, 6H), 1.75–1.85 (CH₃CH₂CH₂) (CH₂)₃CH₂O, m, 4H), 1.26-1.52 (CH₃CH₂(CH₂)₃CH₂O, m, 12H), 4.03 (CH₃CH₂(CH₂)₃CH₂O, t, 4H), 6.95 (phenyl, d, 4H), 8.07 (phenyl, d, 4H).

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- (25) Anal. Calcd for $C_{352}H_{206}O_{101}$ at χ_{Ea} of 30 mol %: C, 69.87%; H, 3.43%. Found: C, 69.73%; H, 3.62%. Anal. Calcd for $C_{485}H_{282}O_{139}$ at χ_{Ea} of 40 mol %: C, 69.90%; H, 3.41%. Found: C, 69.96%; H, 3.55%. Anal. Calcd for $C_{541}H_{314}O_{155}$ To that $T_{\chi_{Ea}}$ of 50 mol %: C, 69.91%; H, 3.41%. Found: C, 69.81%; H, 3.53%. Anal. Calcd for $C_{275}H_{162}O_{79}$ at χ_{Ea} of 60 mol %: C, 69.83%; H, 3.45%. Found: C, 69.82%; H, 3.61%.
- (26) DSC were performed on Perkin-Elmer DSC-7 with a scanning rate of 10 °C min⁻¹ in a nitrogen atmosphere. TGA were performed on Perkin-Elmer TGA-7 with a scanning rate of 10 $^\circ C$ min^{-1} in a nitrogen atmosphere.
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