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Preparation of Aromatic Polyesters under Unstoichiometric Condition by Reaction-induced Crystallization of Oligomers. 1. Polymerization of *p*-Acetoxybenzoic Acid in the Presence of Alkyloxybenzoic Acid

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ABSTRACT: The polymerization of poly(*p*-oxybenzoyl) (POB) from *p*-acetoxybenzoic acid was examined in the presence of three kinds of aromatic monofunctional compounds such as *p*-hexyloxybenzoic acid (HOBA), *p*-decyloxybenzoic acid (DOBA) and *p*-octadecyloxybenzoic acid (OOBA) under unstoichiometric polymerization conditions. Polymerizations were carried out in liquid paraffin at 320 °C. POB crystals were obtained by reaction-induced crystallization of oligomers. The obtained POB crystals were found to be consisted of high molecular weight polymers compared with the products obtained by the melt polymerization. Polycondensation proceeded under unstoichiometric condition through following mechanisms; When DP_n of oligomers exceeds a critical value, they are crystallized to form the crystals. End-free oligomers are preferentially crystallized due to the lower solubility over end-capped oligomers. End-capped oligomers are also crystallized, and polycondensation proceeds with eliminating end-capping groups of oligomers by trans-esterification just when they are crystallized (mechanism 1). Though a part of the end-capped oligomers are contained in the crystals, end-capping groups are excluded by solid-state polycondensation (mechanism 2). The mechanism 1 is major path in the system of DOBA and OOBA due to the bulkiness of oligomer end groups, and both mechanisms 1 and 2 occur in the system of HOBA.

Introduction

Since Carothers had succeeded in preparing high molecular weight polymers by condensation reaction,[1] polymers represented by polyesters and polyamides are of fundamental importance as industrial polymeric materials for fibers, films, and so on. Among them, wholly aromatic polymers have been receiving much attention in recent years as hopeful candidates for high performance materials because of their excellent properties including thermal properties, mechanical properties, and chemical resistance.[2] Numerous types of wholly aromatic polymers have been synthesized by the polycondensation reaction thus far,[3] and they are predicted to be more valuable materials for not only superengineering plastics but also electronic-related materials in the near future.

As known, the stoichiometry between two reaction groups in monomers is of great importance for preparing high molecular weight polymers by condensation reaction. If the stoichiometric condition is out of balance by contamination of monofunctional impurities, polycondensation reaction is terminated and degree of polymerization does not increase according to eq 1 as reported previously.[4] Although this unstoichiometric condition is sometimes useful to control the molecular weight, many efforts are usually made to adjust the stoichiometric condition by the purification of monomers.

$$DP_n = \frac{1 + \frac{N_1}{N_0}}{(1 - p) + \frac{N_1}{N_0}} \tag{1}$$

DP_n: number-average degree of polymerization

N_0: number of monomers

N_1: number of monofunctional compounds

p: extent of reaction

Poly(*p*-oxybenzoyl) (POB) is a very rigid-rod aromatic polyester and has been expected as a high-performance polymer. However, POB cannot melt due to its thermal decomposition, and therefore we were unable to prepare high molecular weight polymers by melt polycondensation. Economy and co-workers carried out the precipitation polycondensation of *p*-acetoxybenzoic acid (ABA) in aromatic heat exchange media and prepared successfully high molecular weight POB, of which the crystal habit was slablike.[5,6] Kricheldorf also studied the synthesis of POB by the precipitation polycondensation of the different types of monomers and obtained high molecular weight polymers.[7,8] We have been studying this precipitation polycondensation to control the morphology of wholly aromatic polymers and obtained successfully POB whiskers and other aromatic polyesters whiskers.[9−14] The POB whiskers were prepared by the polycondensation of ABA in poor solvent such as liquid paraffin (LPF) at very low concentration with no stirring. Figure 1 is a scanning electron micrograph of the POB whiskers. The polymer chains are aligned along the long axis of the whiskers and they show single crystal nature. Formation mechanism of these whiskers had been proposed containing following three processes: (1) When the degree of polymerization of oligomers exceeds a critical value, oligomers are precipitated from the solution to form lamellae. (2) The lamellae pile up in the form of needlelike crystals with spiral growth. (3) Solid-state polymerization occurs topochemically in the needlelike crystals, and whiskers consisting of extended polymer chains are eventually formed.[10] Be-

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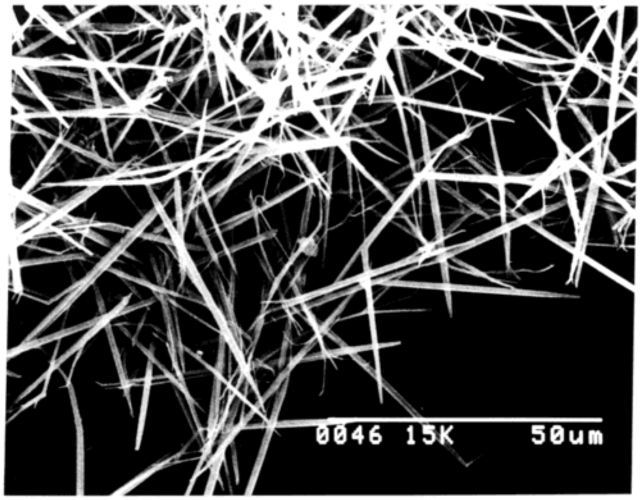


Figure 1. Scanning electron micrograph of POB whiskers.

cause the topochemical solid-state polycondensation occurs very efficiently, the resulting POB crystals consist of extremely high molecular weight polymers. Another research group also had reported the preparation of the aromatic polymer whiskers[15−19] and the reaction induced crystallization of oligomers during solution polymerization is confirmed to be a very valuable method for the morphology control of aromatic polymers.

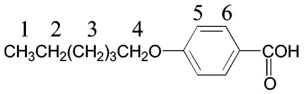
From the viewpoint of the polymerization reaction, this preparation procedure of the polymer whisker can be regarded as a new type of polycondensation reaction in which the reaction-induced phase separation, that is, crystallization of oligomers, gives two different polymerization phases, that is, liquid phase and solid phase. The change of the polymerization phase during polymerization is expected to lead to the favorable shift of the esterification equilibrium for polymer formation site. Hence, the unstiochiometric disadvantage for polycondensation reaction as mentioned above will be overcome and finally high molecular weight polymers will be obtained even under unstoichiometric condition.

In this paper, we report the preparation of high molecular weight POB under the unstoichiometric polymerization system of ABA coexisting with three different kinds of alkyloxybenzoic acids as monofunctional compounds.

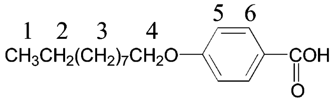
Experimental Section

Materials. ABA, *p*-hydroxybenzoic acid, *p*-hydroxybenzoic acid methyl ester, *p*-hydroxybenzoic acid ethyl ester, *p*-hydroxybenzoic acid phenyl ester, 1-bromohexane, and 1-bromodecane were purchased from Tokyo Kasei Co. Ltd. 1-Bromooctadecane was purchased from Aldrich Co. Ltd. ABA was used after recrystallization from ethyl acetate. LPF was purchased from Nacalai Tesque Co. Ltd. and purified by vacuum distillation (220−240 °C/0.3 mmHg).

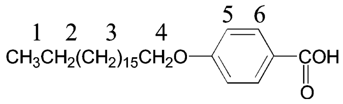
Synthesis of Monofunctional Compounds. *p*-Hexyloxybenzoic Acid (HOBA). Into a three-neck flask equipped with a thermometer and a mechanical stirrer were placed 20 g of *p*-hydroxybenzoic acid methyl ester (0.13 mol), 100 g of 1-bromohexane (0.59 mol), 89.8 g of potassium carbonate (0.65 mol) and 500 mL of acetone. This mixture was refluxed for 7 days. The excess potassium carbonate and by-product potassium bromide were filtrated off, and then acetone and excess 1-bromohexane were stripped off under reduced pressure. The obtained *p*-hexyloxybenzoic acid methyl ester was dissolved into 370 mL of water/ethanol mixed solvent, and then a solution of 25 g of potassium hydroxide (0.45 mol) in 100 mL of ethanol was added. This mixture was heated at 85 °C for 4 h. After being allowed to cool, it was acidified with dilute hydrochloric acid. The precipitates were collected and washed with water. They were dissolved into methylene chloride and dried over sodium sulfate. Evaporation of methylene chloride gave crude HOBA. Recrystallization from ethanol yielded white needlelike HOBA crystals. The yield was 15.7 g (54%). Exothermic transition temperature (°C): 72, 108 and 153. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.11. Found: C, 70.48; H, 8.05. IR (KBr; cm^{-1}): 3600−2300 (acidic O−H stretching), 2933 (aliphatic C−H stretching), 2850 (aliphatic C−H antisymmetric stretching), 1698 (acidic C=O stretching), 1602 (aromatic C=C stretching), 1259 (ether C−O−C antisymmetric stretching). ^1H NMR (DMSO-d_6; δ, ppm): 0.88 (H-1, t, 3H), 1.65−1.75 (H-2, m, 2H), 1.26−1.50 (H-3, m, 6H), 4.03 (H-4, t, 2H), 7.00 (H-5, d, 2H), 7.87 (H-6, d, 2H).



***p*-Decyloxybenzoic Acid (DOBA).** *p*-Decyloxybenzoic acid methyl ester was synthesized by a procedure similar to that for *p*-hexyloxybenzoic acid methyl ester described above. Hydrolysis of *p*-decyloxybenzoic acid methyl ester with potassium hydroxide was carried out in a mixture of water, ethanol, and 2-propanol. DOBA was obtained as white needlelike crystals by recrystallization from ethanol with a yield of 64%. Exothermic transition temperature (°C): 90, 100, 126, and 144. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.38; H, 9.35. Found: C, 73.21; H, 9.47. IR (KBr; cm^{-1}): 3600−2300 (acidic O−H stretching), 2917 (aliphatic C−H stretching), 2855 (aliphatic C−H antisymmetric stretching), 1693 (acidic C=O stretching), 1617 (aromatic C=C stretching), 1268 (ether C−O−C antisymmetric stretching). ^1H NMR (DMSO-d_6; δ, ppm): 0.83 (H-1, t, 3H), 1.60−1.75 (H-2, m, 2H), 1.22−1.40 (H-3, m, 14H), 3.99 (H-4, t, 2H), 6.97 (H-5, d, 2H), 7.88 (H-6, d, 2H).



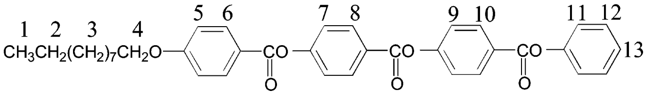
***p*-Octadecyloxybenzoic Acid (OOBA).** Into a three-neck flask equipped with a thermometer and a mechanical stirrer were placed 56 g of *p*-hydroxybenzoic acid ethyl ester (0.33 mol), 245 g of 1-bromooctadecane (0.74 mol), 16 g of sodium hydroxide (0.40 mol), and 300 mL of ethanol. This mixture was refluxed for 12 h. The by-product sodium bromide was filtrated off, and then ethanol was evaporated. The solution was poured into water and then extracted with methylene chloride. After drying over sodium sulfate, evaporation of methylene chloride gave pale brown solids. Recrystallization from *n*-hexane yielded crude *p*-octadecyloxybenzoic acid ethyl ester. Hydrolysis of *p*-octadecyloxybenzoic acid ethyl ester was carried out according to the procedure used for *p*-decyloxybenzoic acid ethyl ester. OOBA was obtained as white needlelike crystals by recrystallization from 2-propanol with a yield of 50%. Exothermic transition temperature (°C): 108 and 132. Anal. Calcd for $C_{25}H_{42}O_3$: C, 76.92; H, 10.77. Found: C, 76.83; H, 10.87. IR (KBr; cm^{-1}): 3600−2300 (acidic O−H stretching), 2918 (aliphatic C−H stretching), 2850 (aliphatic C−H antisymmetric stretching), 1687 (acidic C=O stretching), 1612 (aromatic C=C stretching), 1265 (ether C−O−C antisymmetric stretching). ^1H NMR ($CDCl_3$, CF_3COOH; δ, ppm): 0.85 (H-1, t, 3H), 1.74−1.85 (H-2, m, 2H), 1.13−1.48 (H-3, m, 30H), 4.12 (H-4, t, 2H), 7.00 (H-5, d, 2H), 8.07 (H-6, d, 2H).



Polymerization. Typical solution polymerization procedure was described as follows; Into a cylindrical vessel equipped with gas inlet and outlet tubes were placed 0.3 g of ABA (1.67×10^{-3} mol), desired amount of HOBA and 20 mL of LPF. This mixture was placed into an oil bath and heated to 320 °C under slow stream of nitrogen with stirring. When the mixture became a 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 precipitated. 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 LPF at 320 °C were precipitated by pouring the filtrate into *n*-hexane. The precipitates were collected by filtration and washed with *n*-hexane.

The melt polymerization procedure was described as follows; Into a cylindrical vessel equipped with a stirrer, gas inlet and outlet tubes were placed 2.0 g of ABA (1.11×10^{-2} mol) and 1.08 g of OOBA (2.78×10^{-3} mol). The mixture was heated to 250 °C under slow stream of nitrogen with stirring. It was kept at 250 °C for 1 h, 280 °C for 1 h, and then 300 °C for 4 h. The polymer was taken out of the vessel and washed with methanol. The polymer was obtained as pale brownish powder at a recovery yield of 2.22 g (92.0%).

Synthesis of Oligomer Model Compounds. Phenyl 4-[4-(4-Decyloxybenzoyloxy)benzoyloxy]benzoate (C10 Oligomer Model Compound). Into a flask equipped with a condenser and a gas inlet tube were placed 15.0 g of DOBA (0.054 mol) and 120 mL of thionyl chloride. Then 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 *p*-decyloxybenzoyl chloride at the yield of 14.2 g (88.9%). Into a flask equipped with a dropping funnel, a thermometer, and a gas inlet tube were placed 6.6 g of *p*-hydroxybenzoic acid (0.048 mol), 5.8 g of triethylamine (0.058 mol), and 100 mL of dried tetrahydrofuran under slow stream of nitrogen. A solution of 14.2 g of *p*-decyloxybenzoyl chloride (0.048 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. HCl−triethylamine salt was filtrated off, and tetrahydrofuran was evaporated. The obtained solids were washed with dilute hydrochloric acid and water. Recrystallization from ethyl acetate gave 8.0 g of *p*-(decyloxybenzoyloxy)benzoic acid. 4-(Decyloxybenzoyloxy)benzoyl chloride was then synthesized and reacted with *p*-hydroxybenzoic acid phenyl ester by the similar procedure described above. Phenyl 4-[4-(4-decyloxybenzoyloxy)benzoyloxy]benzoate was obtained after recrystallization from ethyl acetate. The yield was 5.9 g (24.9%). T_m (°C): 98. Anal. Calcd for $C_{37}H_{38}O_7$: C, 74.75; H, 6.40. Found: C, 75.52; H, 7.14. IR (KBr; cm^{-1}): 2927 (aliphatic C−H stretching), 2856 (aliphatic C−H antisymmetric stretching), 1747 (ester C═O stretching), 1610 (aromatic C═C stretching), 1282 (ether C−O−C antisymmetric stretching). ^{1}H NMR (CDCl$_3$; δ, ppm): 0.89 (H-1, t, 3H), 1.28−1.55 (H-3, m, 30H), 1.77−1.90 (H-2, m, 2H), 4.06 (H-4, t, 2H), 6.99 (H-5, d, 2H), 8.16 (H-6, d, 2H), 7.39−7.48 (H-7, H-9, H-12, m, 6H), 8.26−8.33 (H-8, H-10, dd, 4H), 7.20−7.28 (H-11, H-13, m, 3H).



Phenyl 4-[4-(4-Hexyloxybenzoyloxy)benzoyloxy]benzoate (C6 Oligomer Model Compound). The C6 oligomer model compound was synthesized by the above method. T_m (°C): 150. Anal. Calcd for $C_{33}H_{30}O_7$: C, 73.60; H, 5.58. Found: C, 73.52; H, 5.77. IR (KBr; cm^{-1}): 2926 (aliphatic C−H stretching), 2860 (aliphatic C−H antisymmetric stretching), 1747 (ester C═O stretching), 1606 (aromatic C═C stretching), 1273 (ether C−O−C antisymmetric stretching). ^{1}H NMR (CDCl$_3$; δ, ppm): 0.92 (H-1, t, 3H), 1.77−1.90 (H-2, m, 2H), 1.26−1.60 (H-3, m, 30H), 4.07 (H-4, t, 2H), 7.00 (H-5, d, 2H), 8.16 (H-6, d, 2H), 7.38−7.49 (H-7, H-9, H-12, m, 6H), 8.25−8.32 (H-8, H-10, dd, 4H), 7.21−7.29 (H-11, H-13, m, 3H).

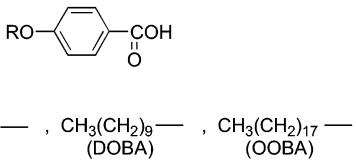
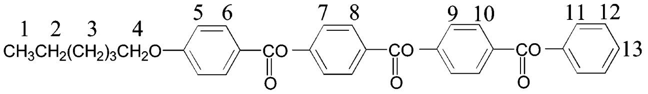


Figure 2. Structure formula of monofunctional compounds.



Measurements. Morphology of the polymer crystals was observed by scanning electron microscope (S-2150, Hitachi Co. Ltd.) at 20 kV. FT-IR spectra were measured on FT-IR spectrometer (FT/IR-410, JASCO Co. Ltd). WAXS pattern was measured by diffractometer (Cu Kα, $\lambda = 1.5418$ Å Gaiger flex, Rigaku Co. Ltd.).

Determination of Number Average Degree of Polymerization of Polymers and Content of Monofunctional Compound. A 10 mg amount of sample and 1 mL of 7.0 wt % potassium hydroxide methanol solution were placed in a test tube and kept at 25 °C until the sample was completely hydrolyzed. The solution was neutralized with dilute hydrochloric acid and then analyzed by using gas chromatography (GC-14B Shimadzu Co. Ltd.) with FID equipped with a Thermon-3000 (60−80 mesh) packed column. Number average degree of polymerization (DP$_n$) of the polymer was calculated by the molar ratio of *p*-hydroxybenzoic acid and end group.

Preparation of Phase Diagrams of Oligomer Model Compounds. Oligomer model compounds and LPF were put into glass tubes at different concentrations. They were placed into oil bath and heated until the oligomer model compounds were completely dissolved. Then temperature was lowered gradually at a rate of 5 °C/60 min, and the cloud point temperatures were determined. The phases and conjugate line between the liquid and solid phases were confirmed by microscope equipped with heating stage (MP-500D, Yanaco Co. Ltd.) under crossed polarization.

Measurement of Reaction Rate. Reaction kinetics was measured by the modified procedure reported previously.[20] Into the 40 mL cylindrical vessel equipped with gas inlet and outlet tubes were placed 0.30 g of ABA (1.67×10^{-3} mol) and 20 mL of LPF. In the cases of monofunctional compounds, the desired amount of the monofunctional compound (1.67×10^{-3} mol) and 0.43 g of phenyl 4-acetoxybenzoate (1.67×10^{-3} mol) were placed into the vessel instead of ABA. Initial concentration of functional groups was 8.35×10^{-2} mol·L^{-1} in the both cases. The mixtures were placed into an oil bath and heated to 320 °C under a slow stream of nitrogen with stirring. The progress of the polymerizations was followed by measuring the concentration of evolved acetic acid trapped in the water at different time. In the case of ABA, the concentration of evolved acetic acid was monitored until 7 min, when the precipitation of the crystals began. In the cases of monofunctional compounds, precipitation did not occurred, and it was monitored until 20 min. The amount of acetic acid produced at a given time was determined by titration with 0.1 mol·L^{-1} sodium hydroxide solution. The reactions obeyed second-order kinetics and the rate constants (k_2) were estimated from the plots of evolved acetic acid as a function polymerization time.

Results and Discussion

Polymerization of ABA under Unstoichiometric Conditions. Three kinds of *p*-alkyloxybenzoic acids such as HOBA, DOBA, and OOBA were used as monofunctional compound illustrated in Figure 2. They

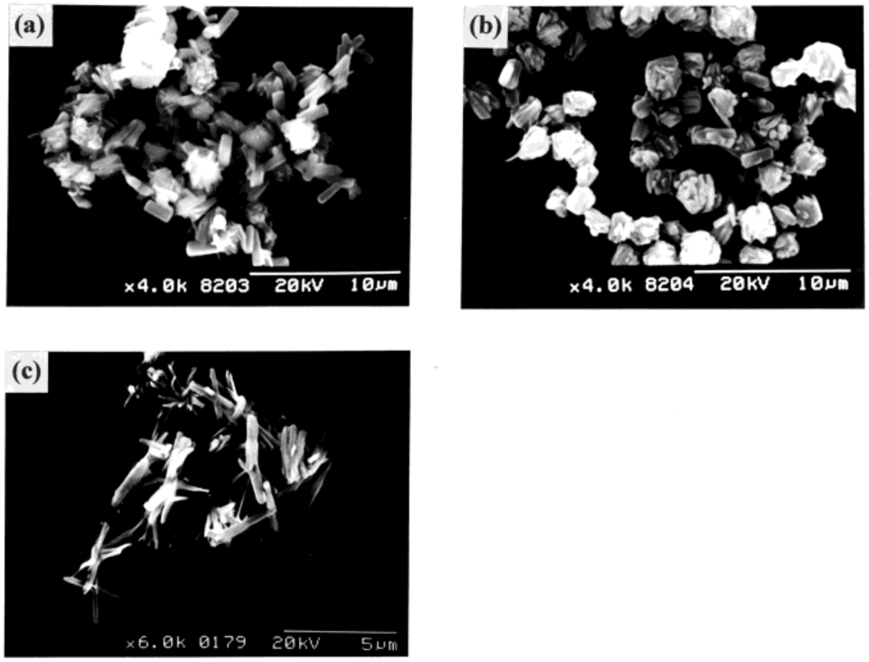


Figure 3. Scanning electron micrographs of POB crystals obtained in the systems of (a) HOBA, (b) DOBA, and (c) OOBA at χ of 20 mol % for 6 h.

Table 1. Reaction Rate Constants of ABA and Monofunctional Compounds[a]

reaction	k_2 ($\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$)[b]	r[c]
self-condensation of ABA	0.33	
HOBA + PAB[d]	0.39	1.18
DOBA + PAB	0.33	1.00
OOBA + PAB	0.32	0.97

[a] Reactions were carried out at 320 °C in LPF. Initial concentration of acetoxy group and carboxyl group was 0.083 $\text{mol}\cdot\text{L}^{-1}$. [b] Secondary order reaction constant. [c] Relative reactivity ratio of monofunctional compounds to ABA defined as k_2 of monofunctional compounds/k_2 of ABA. [d] PAB stands for phenyl 4-acetoxybenzoate.

possess long alkyloxy groups to enhance the solubility into LPF, as well as to avoid the sublimation during high-temperature polymerization. Polymerizations of ABA were carried out in LPF at 320 °C for 6 h with coexisting monofunctional compound to break the stoichiometric balance between the acetoxy group and the carboxyl group. First, the reactivity of ABA is examined, compared with those of monofunctional compounds. ABA has an acetoxy group which is an electron-withdrawing group. On the other hand, the monofunctional compound has an alkyloxy group which is an electron-donating group. If the activity of these compounds to ester−acid exchange reactions are quite different, eq 1 should be compensated by a correction factor r as shown in eq 2.

$$\mathrm{DP_n} = \frac{1 + r\dfrac{N_1}{N_0}}{(1 - p) + r\dfrac{N_1}{N_0}} \tag{2}$$

r: reactivity ratio of monofunctional compounds to ABA

The reactivity of monofunctional compounds was estimated by the reaction with phenyl 4-acetoxybenzoate. The reactions were followed by the measuring the concentration of evolved acetic acid. These reactions obeyed the second-order kinetics, and k_2s were obtained as shown in Table 1. k_2 of the self-condensation reaction of ABA at 320 °C in LPF is 0.33 $\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$, and those of HOBA, DOBA, and OOBA with phenyl 4-acetoxybenzoate are in the range 0.39−0.32 $\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$. The correction factor rs defined as k_2 of monofunctional compound/k_2 of ABA are 0.97−1.18, which are close to 1. This reveals that compensation by a factor r is negligible in this polymerization condition.

Table 2 summarizes the results of polymerization. The molar percent of monofunctional compounds (χ) is defined as follows:

$$\chi = \{[\text{monofunctional compounds}]/([\text{ABA}] + [\text{monofunctional compounds}])\} \times 100$$

χ_H, χ_D, and χ_O stand for the molar percent of HOBA, DOBA, and OOBA, respectively.

POB crystals were obtained at $\chi_H \leq 60$ mol %, $\chi_D \leq 30$ mol %, and $\chi_O \leq 30$ mol %. Any crystals were not precipitated at all out of these ranges of χ. The obtained crystals exhibit very clear crystal habits such as needle, pillar, slab, or plate as shown in Figure 3. The crystal morphology is highly related to χ. FT-IR spectra of the polymer crystals and the compound dissolved in LPF are illustrated in Figure 4. The ν peak of carbonyl group in ester linkage appears at 1747 cm^{-1} in both spectra. However, the ν peaks of hydroxyl and carbonyl group in carboxyl group, which are clearly found at 3300−2500 and 1693 cm^{-1} in the spectrum of the dissolved compound disappear in the spectrum of the polymer crystals. The ν peak of aliphatic C−H of alkyloxybenzoic acid is strongly found at 2926 and 2860 cm^{-1} only in the spectrum of the dissolved compound. These results reveal that the high molecular weight polymer is formed as crystals, and most of the monofunctional compound moiety remains in liquid phase. WAXS patterns of the obtained POB crystals show very sharp diffraction peaks as shown in Figure 5. The polymer crystals possess

Table 2. Polymerization of ABA in the Presence of Alkyloxybenzoic Acid[a]

concn of alkyloxybenzoic acid in feed[b] (mol %)	polymerization method[c]	polymer yield (%)	content of alkyloxybenzoic acid unit in polymer[d] (mol %)	DP$_n$		morphology of crystals
				calcd[e]	obsd[f]	
			χ_H: HOBA			
10	Sp	36	1.63	10.0	60	pillar
20	Sp	51	2.44	5.0	40	pillar
30	Sp	53	1.72	3.3	57	pillar
40	Sp	39	2.17	2.5	45	slab
50	Sp	42	2.33	2.0	42	plate
60	Sp	38	2.86	1.7	34	plate
			χ_D: DOBA			
10	Sp	48	0.36	10.0	277	needle
20	Sp	50	0.62	5.0	161	pillar
30	Sp	53	0.43	3.3	232	pillar
			χ_O: OOBA			
10	Sp	27	0.17	10.0	489	needle
20	Sp	38	0.29	5.0	344	needle
30	Sp	39	0.35	3.3	283	pillar
20	Mp		14.3	5.0	6	

[a] Polymerizations were carried out at 320 °C for 6 h. [b] χ_H is defined as {[HOBA]/([ABA] + [HOBA])} × 100. χ_D is defined as {[DOBA]/([ABA] + [DOBA])} × 100. χ_O is defined as {[OOBA]/([ABA] + [OOBA])} × 100. [c] Sp and Mp show solution polymerization and melt polymerization, respectively. [d] Content of alkyloxybenzoic acid unit in polymer is defined as {[alkyloxybenzoic acid unit]/([*p*-oxybenzoyl unit] + [alkyloxybenzoic acid unit])} × 100. [e] Calcd: DP$_n$ was calculated according to the eq 1 with *p* of 1. [f] Obsd: DP$_n$ was estimated by the molar ratio of *p*-hydroxybenzoic acid and alkyloxybenzoic acid by quantitative analysis of end-groups based on the assumption that hydroxy and other end groups were negligible in this polymerization.

extremely high crystallinity. Consequently, they seem to be formed by the crystallization of oligomers followed by the solid-state polymerization. The range of χ in which the crystals can be formed becomes wider in the system of HOBA than DOBA and OOBA. POB is insoluble into solvents. DP$_n$ of the obtained polymer crystals could not be directly determined by the conventional methods such as GPC, viscosity measurement and NMR. In this study, DP$_n$s were estimated by end-group analysis after hydrolysis of polymers on GC as reported,[21] which is the only method for intractable polymers. Alkyloxybenzoic acid was detected, but acetic acid was not detected in all samples. This indicates that the end group of polymers is the alkyloxybenzoyl unit besides hydroxy and other end groups formed by the side reaction. The hydroxy end group might be generated by the reaction of ester and acid as reported.[22] But the rate constant of this reaction was one order smaller than that of the ester formation reaction between acetoxy group and acid. Then DP$_n$s were calculated by the molar ratio of *p*-hydroxybenzoic acid and alkyloxybenzoic acid by assuming that the contribution of hydroxy and other end groups to DP$_n$ could be neglected. Surprisingly, it is much higher than that calculated according to the eq 1. DP$_n$ is 34 even at χ_H of 60 mol % which means 1.5 times the molar content of HOBA to ABA. DP$_n$s of POB obtained in the system of DOBA and OOBA are higher than that in the system of HOBA, and they are 232 and 283 at χ of 30 mol %, respectively. The difference of DP$_n$ in the structure of monofunctional compounds is discussed in the following section. In contrast to these results, DP$_n$ of the products prepared by melt polymerization at χ_O of 20 mol % is 6, and the melt polycondensation of ABA in the presence of monofunctional compound obeys eq 1.

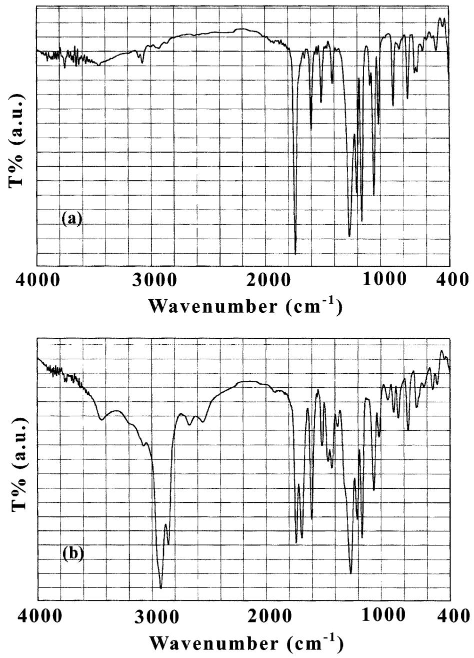


Figure 4. FT-IR spectra of (a) POB crystals and (b) compounds dissolved in LPF prepared for 6 h in the system of HOBA at χ_H of 50 mol %.

The composition of the polymer crystals and the compounds dissolved in LPF was analyzed by GC after hydrolysis. Figure 6 plots the compositions of monofunctional compound moiety in the crystals and the dissolved compounds against those in feed in the system of HOBA and DOBA. In both systems, monofunctional compound moieties are scarcely contained in polymer crystals, and they are almost concentrated in the liquid phase. This result is in good agreement with the result of FT-IR described above. This fact suggests that the oligomers which are not end-capped by monofunctional compounds are selectively phase-separated to form the crystals on the basis of the difference in the solubility derived from end groups, and DP$_n$ increases by the solid-state polymerization. The oligomers end-capped by monofunctional compounds are also phase-separated to form the crystals, and then monofunctional compound moiety contained in the crystals are excluded by the solid-state polymerization from the crystal phase to the liquid phase. The content of monofunctional compound moiety in the polymer crystals prepared in the system

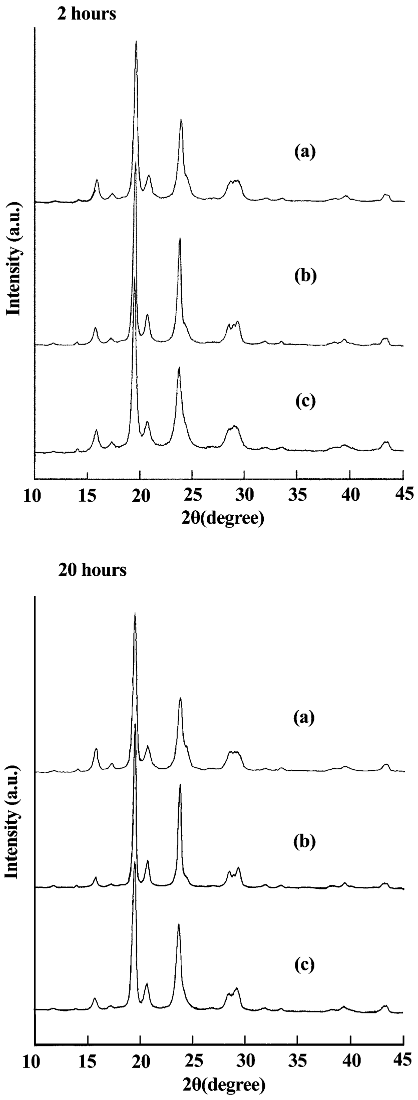


Figure 5. WAXS intensity profiles of POB crystals obtained in the systems of (a) HOBA, (b) DOBA, and (c) OOBA at χ of 30 mol % for 2 and 20 h.

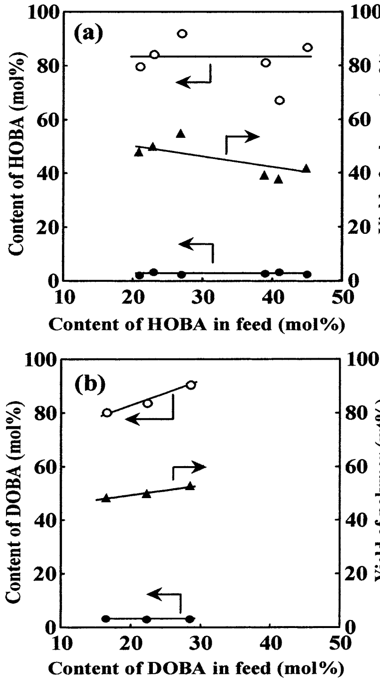


Figure 6. Plots of content of (a) HOBA and (b) DOBA in polymer (●), compounds recovered from solution (○), and yield of polymer (▲) vs content of alkyloxybenzoic acid in feed. Polymerization time was 6 h.

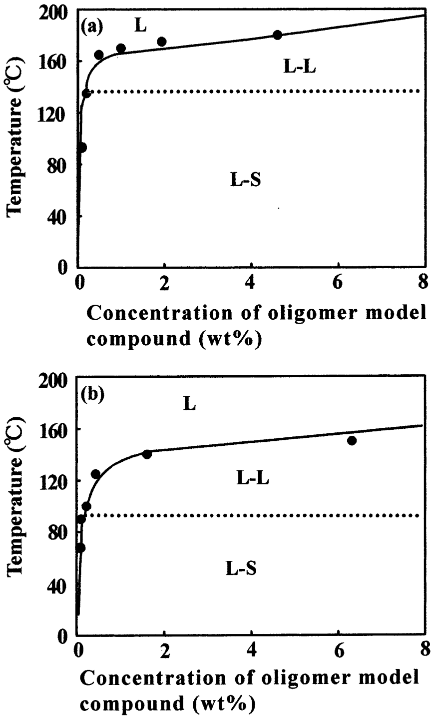


Figure 7. *C*−*T* phase separation diagrams of (a) C6 and (b) C10 oligomer model and LPF. L: liquid phase. L−L: two immiscible liquid phases. L−S: liquid and solid phases.

of OOBA is less than that in the system of HOBA. This implies that the oligomers end-capped by OOBA are harder to contain in the crystals than HOBA due to the bulkiness of the end groups. The wider range of χ_H to form the polymer crystals seems to be attributable to the lower solubility of end-capped oligomers by HOBA than others. To confirm this speculation, we examined the phase separation behavior of end-capped oligomers. The oligomers phase-separated in the actual polymerization system cannot be isolated. Hence, C6 and C10 oligomer model compounds were synthesized as models for the oligomers end-capped by HOBA and DOBA, respectively. *C*−*T* phase diagrams of oligomer model compounds and LPF were made to infer phase separation behavior of oligomers influenced by alkyloxy end groups. The obtained phase diagrams are shown in Figure 7. The phase separation curves appear as a combination of UCST consolution curve and the freezing point curve of model compounds in analogy to those reported previously for partially miscible polymer−solvent systems.[23−26] An important characteristic of these diagrams is that both the phase separation curve and the conjugate line between liquid−solid of C10 shift toward lower temperature compared with those of C6. The longer alkyloxy end group enhances the solubility of oligomer into LPF and this makes oligomer to be hardly phase-separated leading to the narrower range of χ_D and χ_O.

Polymerization Mechanism under Unstoichiometric Conditions. Polymerization of ABA in the presence of monofunctional compound in LPF reveals that most of monofunctional compounds are not contained in the polymer crystals and the POB of high DP_n

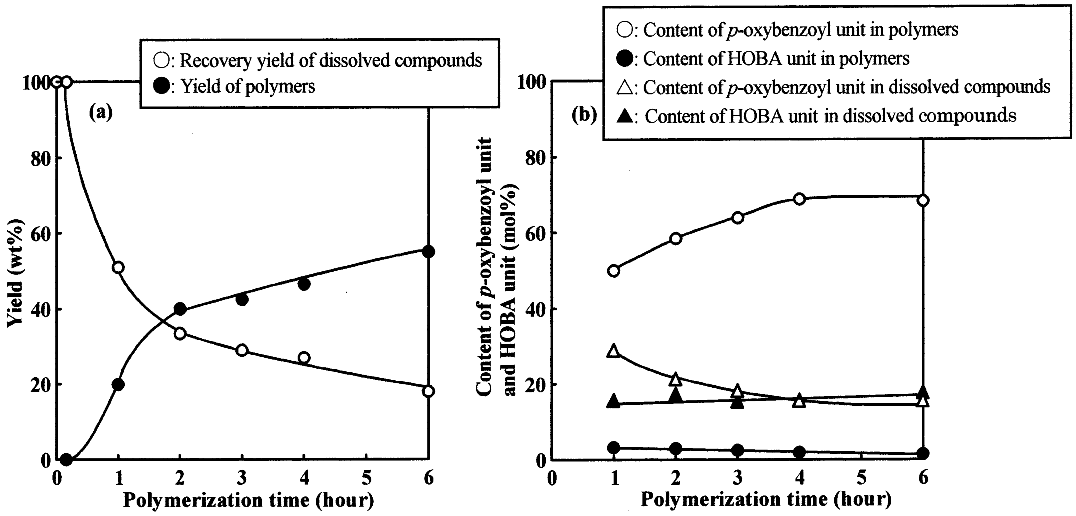


Figure 8. Polymerization time dependencies of (a) yield of polymers and recovery yield of dissolved compounds and (b) content of *p*-oxybenzoyl unit and HOBA unit compared to the whole units prepared at χ_H of 30 mol %.

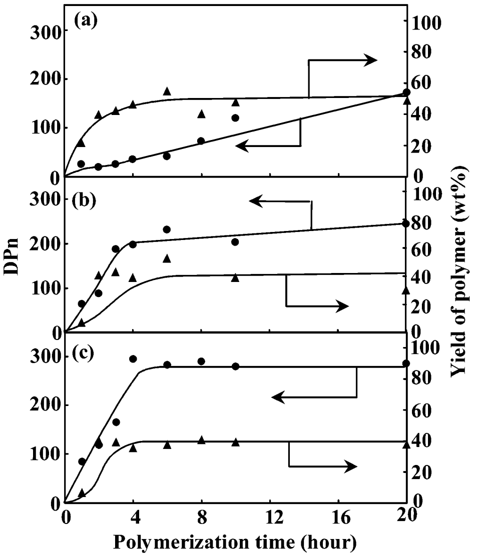


Figure 9. Increase of DP_n (●) and yield (▲) of polymer in the systems of (a) HOBA, (b) DOBA, and (c) OOBA at χ of 30 mol %.

is obtained. It is in interest that the polycondensation is not terminated by monofunctional compound. To clarify the polymerization mechanism were examined the change of the content of monofunctional compound moiety and *p*-oxybenzoyl unit in the polymer crystals and the dissolved compounds, and the polymerization time dependency of DP_n. The results are shown in Figures 8 and 9. Figure 8 shows that the yield of the polymer crystals increases and the recovery yield of the dissolved compounds decreases with polymerization time. This shows that the polymer crystals are grown by consecutive supply of oligomers from the liquid phase. It is noteworthy that the content of HOBA moiety decreases gradually in the crystal and that of *p*-oxybenzoyl unit increases with polymerization time. In contrast, the content of HOBA moiety increases in liquid phase and that of *p*-oxybenzoyl unit decreases with polymerization time. These results indicate that small amount of oligomers end-capped by HOBA are contained in the polymer crystals and HOBAs are excluded by the solid-state polymerization from the crystal phase to the liquid phase. WAXS profiles of the crystals prepared for 2 and 20 h are shown in Figure 5. The crystallinity of the crystals prepared for 2 h is as high as that prepared for 20 h. The change of the unit cell dimension during polycondensation is now under detailed investigation and will be reported elsewhere. Figure 9 shows the increases of DP_n and yield of the polymer crystals during polycondensation at χ of 30 mol %. DP_n increases from 20 for 2 h to 173 for 20 h in the system of HOBA. DP_n is kept on increasing even after 4 h when the yield of the polymer crystals is leveled off. This is an evidence for the occurrence of solid-state polymerization. On the other hand, DP_n increases from 65 to 245 in the system of DOBA and from 84 to 286 in the system of OOBA. DP_n of polymers prepared for 20 h increases in order of the length of alkyloxy groups at the same χ. It is characteristic in both systems of DOBA and OOBA compared with HOBA that DP_n increases more rapidly with increasing the yield of the polymer crystals at early stage of polymerization, and then the increase of DP_n becomes slower after the yields are leveled off. The increase of DP_n after the yield is leveled off is brought about the solid-state polycondensation reaction which obeys second-order kinetics. The rate constants (k_2) in the system of HOBA and DOBA are estimated from the slope in Figure 9 after 4 h, and they are obtained as 7.04×10^{-1} and 4.22×10^{-1} kg·mol^{-1}·min^{-1}, respectively. The concentrations of end groups at 4 h are used for calculation as initial concentrations in these systems. The difference in rate constant of the solid-state polycondensation is not significant. From these results, polycondensation under unstoichiometric condition proceeds according to the following mechanisms: Oligomers are formed in the solution. When DP_n of oligomers exceeds a critical value, they are crystallized to form the crystals. Oligomers which are not end-capped by monofunctional compound are preferentially crystallized due to the lower solubility. Oligomers end-capped by ester−acid exchange reaction between acetoxy group and alkyloxybenzoic acid are also phase-separated but most of them are excluded by segregation. If some of the end-capped oligomers are partially contained into crystals, polycondensation proceeds with eliminating end-capping groups of oligomers by an ester−acid exchange type trans-esterification reaction just when they are crystallized (mechanism 1). Though a small amount of end-capped oligomers are possible to be contained in the crystals, end-capping groups are excluded by the solid-state polycondensation of ester−ester or ester−acid exchange reaction (mechanism 2). In the systems of DOBA and OOBA, end-capped oligomers are hard to contain in the crystals due to the bulkiness of end-capping groups, and therefore mechanism 1 is a major step. On the contrary, in the system of HOBA for which the size of the alkyloxy group is smaller, both mechanisms 1 and 2 occur to increase DP_n. It remains unclear how the phase-separable oligomers are formed in liquid phase even at high χ, and it should be clarified near future.

Conclusions

High molecular weight polymers can be prepared even under unstoichiometric conditions by reaction-induced crystallization of oligomers during solution polycondensation. Polycondensation under unstoichiometric conditions proceeds through following mechanisms; Oligomers are formed in the solution, and when the DP_n of oligomers exceeds a critical value, they are crystallized to form the crystals. End-free oligomers are preferentially crystallized due to the lower solubility than end-capped oligomers. End-capped oligomers are also crystallized and polycondensation proceeds with eliminating end-capping groups of oligomers by trans-esterification just when they are crystallized. Though a part of the end-capped oligomers are contained in the crystals, end-capping groups are excluded by solid-state polycondensation. This polycondensation induced by oligomer phase separation provides a new type of interfacial polymerization between the liquid and the solid phases.

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