DOCTORAL DISSERTATION

Study on Synthesis of Aromatic Polyesters by Direct Polycondensation

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CONTENTS

INTRODUCTION AND THE AIM OF THIS STUDY

INTRODUCTION

Wholly aromatic polyesters have been receiving much attention as hopeful candidates for high performance polymeric materials due to their excellent properties which are derived from their rigid structure, such as thermal properties, mechanical properties, chemical resistance and so on. [1-5] However, many of them have neither good solubility nor meltability also derived from their rigid structures. Consequently, morphology control of them is very difficult by conventional processing procedures. Morphology of the polymer materials is of great importance to control the performance. [6] The relationship between good properties and poor processability is trade-off and many trials have been done to overcome this antagonistic problem.

We have been studying on the morphology control of the intractable aromatic polyesters during solution polymerization, and succeeded in the synthesis of whiskers of poly(*p*-oxybenzoyl) (POB), poly(2-oxy-6-naphthoyl) (PON) and other aromatic polyesters by polymerization in inert solvents. [7-16] These whiskers are formed by using the reaction-induced phase separation of oligomers during solution polymerization as shown in Figure 1.

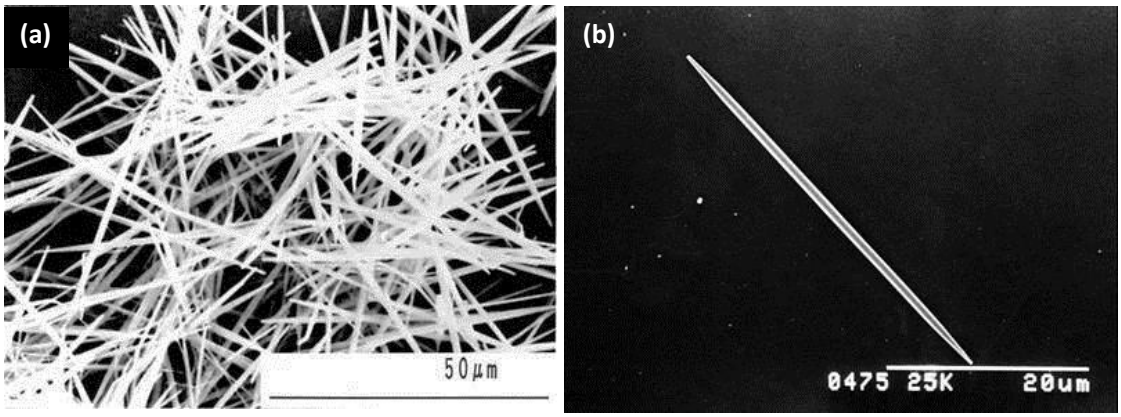

Figure 1 Scanning electron micrographs of (a) POB wiskers and (b) a single POB whisker (cited from ref no. 7)

The concept of the morphology control by using the reaction-induced phase separation of oligomers is schematically shown in Figure 2. This methodology is similar to that in Nature. The self-assembling process is combined with the polymerization process by using phase separation of oligomers, and both processes occur simultaneously and concertedly. It is like building blocks of oligomers to form the morphology with the polymerization. The polymerization is necessarily carried out in poor solvents to induce the phase separation of oligomers. The reaction-induced phase separation of oligomers in poor solvents is describable on the analogous concentration-temperature phase diagram to that of the partially miscible polymer-solvent system. [17, 18] The phase separation curve in the repulsive system, where there is no attractive interaction between oligomers and solvents, can be written as the combination of the freezing point curve of the oligomers and the upper critical solution temperature type consolution curve. Aromatic polymers discussed here are usually prepared

by the step-growth polymerization represented by polycondensation reaction. Oligomers are formed by the polymerization reaction, and the molecular weight of oligomers increases stepwise in the solution. When the molecular weight of oligomers exceeds a critical value, the oligomers are phase-separated from the super-saturation state. If the super-saturated oligomers are across the freezing point curve, they are precipitated by the crystallization to form the crystals, and the polymer crystals are finally formed by the post polymerization in the crystals. On the other hand, if they are across the consolution curve, the liquid-liquid phase separation is induced to form droplets of dense phase in dilute phase. Finally, polymer particles are formed due to the solidification of the fine droplets caused by the further polymerization in them. Miscibility between the oligomers and the solvents is a variable parameter to control the morphology.

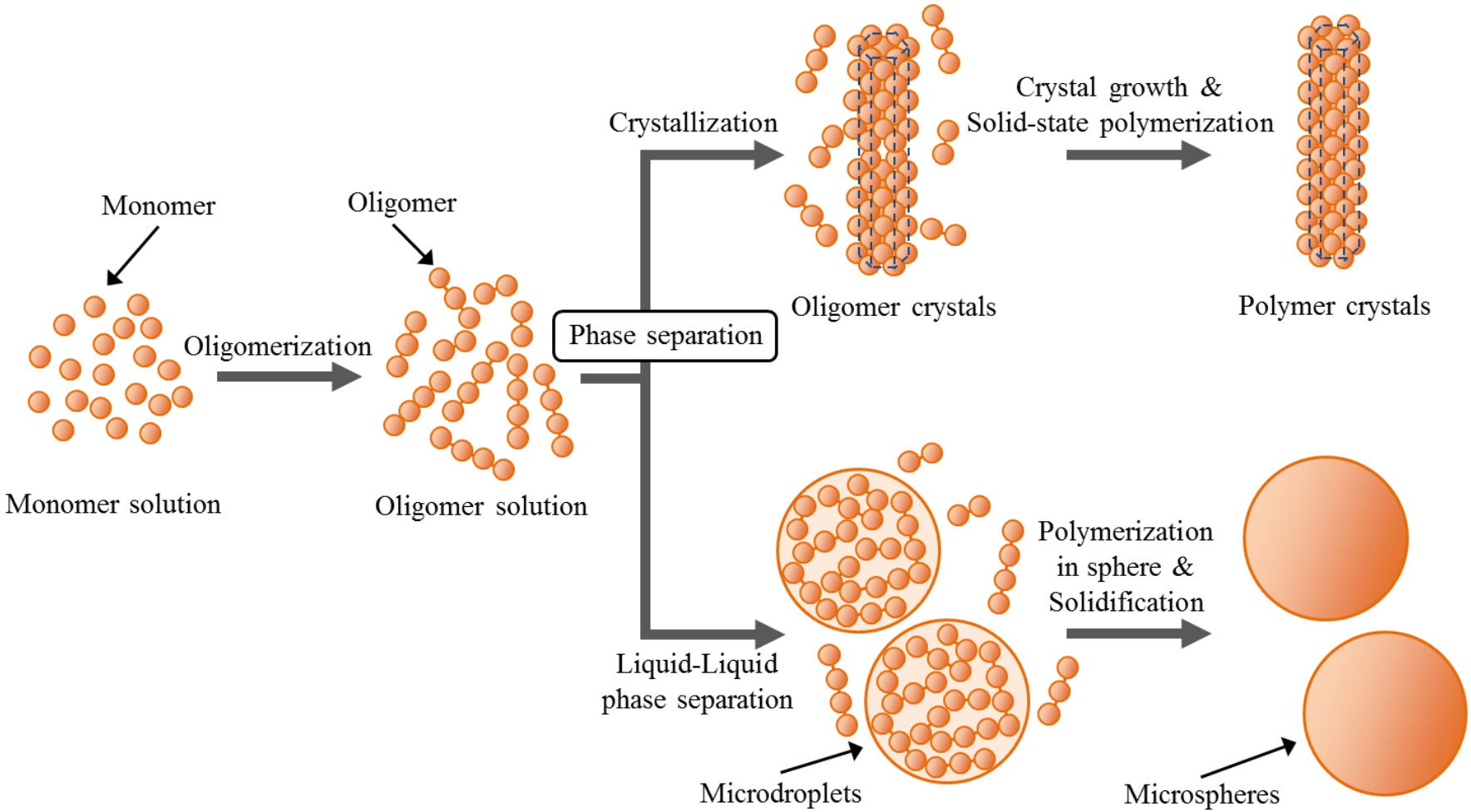

Figure 2 Schematic drawing of morphology control of aromatic polymers by using the reaction-induced phase separation of oligomers during solution polymerization.

Application of using the reaction-induced phase separation of oligomers is not only the morphology control of intractable polymers but also the preparation of high molecular weight polymers under non-stoichiometric condition. In general, the stoichiometric balance between two functional groups in monomers is of great importance for preparing high molecular weight polymers by the condensation reaction. If the stoichiometric condition is out of balance by the contamination of monofunctional impurities, the polycondensation reaction is terminated and the number-average degree of polymerization (DPn) does not increase according to eq. (1) as reported previously. [19]

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

Where, DPn: number-average degree of polymerization, N_0: number of monomers, N_1: number of monofunctional compounds, p: extent of reaction

Studies on the polymerization under non-stoichiometric condition had been reported and high molecular weight polymers were obtained. [20-27] These unique polymerizations can be categorized into two groups chemically and physically based on the mechanism, of which one is attributed to the drastic change in the reactivity of functional groups and another is attributed to the heterogeneous reaction field. The latter polymerizations incorporate the

reaction-induced crystallization of oligomers into the polymerization, and it had found that the polymerization of *p*-acetoxybenzoic acid (ABA) afforded crystals of high molecular weight POB even under non-stoichiometric conditions with an excess of aromatic monocarboxylic acid. 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 the DPn increases in the precipitates 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 by the ester-ester interchange reaction from the crystal phase to the liquid phase. The difference in the reactivity of functional groups was needless. [26] In this polymerization, the monofunctional compounds seem to be impurities to terminate the polymerization. High molecular weight POB was formed as highly crystalline precipitates by the polymerization of ABA with elimination monofunctional compounds. As mentioned above, the reaction-induced phase separation of oligomers might give a hint for the simultaneous control of the sequence regularity with the morphology.

AIM AND STRATEGY OF THIS THESIS

On the basis of the above discussion, the aim of this thesis is the development of the method to prepare wholly aromatic polyesters by direct polymerization. The aromatic monomers that have a phenolic hydroxyl group and a carboxyl group such as *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) cannot polymerize by themselves to yield POB and PON, because carboxyl groups have not enough reactivity for the condensation reaction with phenolic hydroxyl groups. Therefore, the carboxyl or the phenolic hydroxyl groups are usually converted into highly reactive groups such as alkyloxy groups or phenyl esters. Direct synthesis of aromatic polyesters from aromatic dicarboxylic acids and bisphenols has been developed as an elegant synthetic procedure, and numerous types of condensation reagents have been developed so far. [28-41] However, these methods need a large amount of condensation reagents more than equimolar to the monomer.

Recently, it has been reported that aromatic polyamides could be prepared by the direct polymerization of aromatic diamines and aromatic dicarboxylic acids in the presence of 3,4,5-trifluorophenylboronic acid (TFB). [42] In this polymerization, TFB reacts with a carboxyl group to convert a more active carboxylic boronic anhydride, and then the activated anhydride group reacts with an amino group to form the amide linkage with elimination of harmless water and TFB. This result suggests that TFB is a catalyst, not a condensation

reagent. This study implies that TFB would work for the direct polymerization of HBA and HNA to yield POB and PON. If the direct polymerization of HBA and HNA in the presence of boronic acid is used to prepare POB and PON by the reaction-induced phase separation of oligomers, this polymerization procedure will be environmentally benign because the atom efficiency of reaction improves and by-product of reaction is harmless water. From the above strategy, the new concept of the environmentally benign polymerization for aromatic polyesters by the reaction-induced phase separation of oligomers was examined in this thesis.

This thesis consists of three chapters. In Chapter 1, preparation of the POB crystals using direct polymerization of HBA in the presence of boronic anhydrides is reported. Three kinds of boronic anhydrides are used in this chapter. The control of the morphology and the molecular weight of the POB crystals is investigated from the view point of the chemical structure and the content of the boronic anhydride. It has been reported that aromatic boronic acids can generally self-condense by heating to form the cyclic trimers called boronic anhydride or triarylboroxin. [43-45] The boronic anhydrides can also activate HBA and HNA by the same mechanism as that of the boronic acid.

In Chapter 2, the preparation of PON and poly(4-oxybenzoyl-*co*-2-oxy-6-naphthoyl)s was examined by the reaction-induced phase separation during the direct polymerization in the presence of boronic anhydride. The morphology control of PON and the composition of copolymers are also reported in this chapter.

In Chapter 3, the preparation of POB and PON by direct polymerization in the presence of boronic anhydride under non-stoichiometric condition is examined, focusing on the polymerization mechanism.

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CHAPTER 1

Preparation of Poly(*p*-oxybenzoyl) Crystals Using Direct Polymerization of *p*-Hydroxybenzoic Acid in the Presence of Boronic Anhydrides

1-1 INTRODUCTION

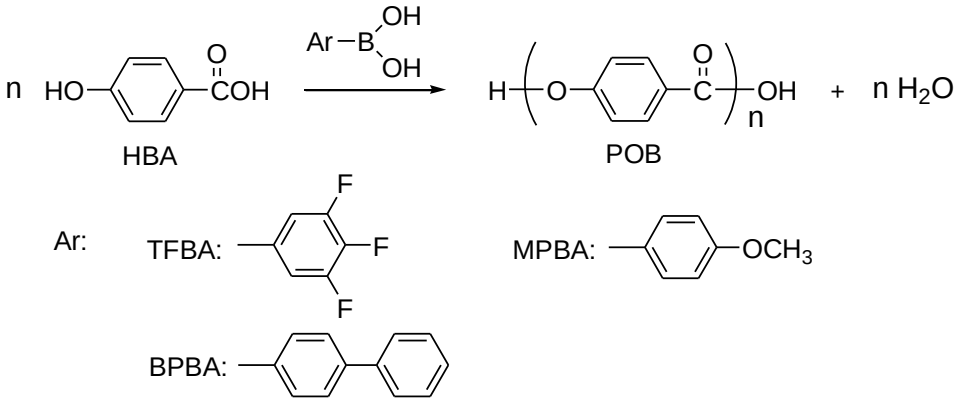
Poly(*p*-oxybenzoyl) (POB) have been expected to possess many excellent properties such as mechanical properties, including strength and modulus, thermal stability, chemical resistance and so on, and it has received great attention as high-performance materials. [1–5] Morphology of the polymer materials is of great importance to control the performance. [6] However, POB does not exhibit meltability and solubility, and the intractability makes it difficult to control the morphology by conventional processing procedures. Morphology control of the intractable aromatic polyesters has been studied by using reaction-induced phase separation of oligomers, and POB whiskers were prepared by the polymerization of *p*-acetoxybenzoic acid in poor solvents. [7–10] This whisker was formed *via* the crystallization of oligomers and the subsequent polymerization on or in the needle-like oligomer crystals. The molecular chains aligned along the long axes of the whiskers, and the

morphology with the molecular orientation is ideal to obtain the essential properties predicted from the molecular structure.

p-Hydroxybenzoic acid (HBA) does not polymerize by itself to yield POB, because a carboxyl group has not enough reactivity for the condensation reaction with a phenolic hydroxyl group. Therefore, the carboxyl or the phenolic hydroxyl group is usually converted into a highly reactive group such as an alkyloxy group or a phenyl ester. Direct synthesis of aromatic polyesters from aromatic dicarboxylic acids and bisphenols has been developed as an elegant synthetic procedure, and numerous types of condensation reagents have been developed so far. [11–24] It has been reported that aromatic polyamides could be prepared by the direct polymerization of aromatic diamines and aromatic dicarboxylic acids in the presence of 3,4,5-trifluorophenylboronic acid (TFB). [25] In this polymerization, TFB reacts with a carboxyl group to convert a more active carboxylic boronic anhydride, and then the activated anhydride group reacts with an amino group to form the amide linkage. This study implies that TFB would work for the direct polymerization of HBA to yield POB. If the crystallization of oligomers is used to prepare the POB crystals during the direct polymerization of HBA in the presence of boronic acid, the morphology of the POB crystal would be controlled by the chemical structure of boronic acid. It has been also reported that aromatic boronic acids can self-condense by heating to form cyclic trimers called boronic anhydrides or triarylboroxins. [26–28] The boronic anhydrides can also activate HBA by the

same mechanism as that of the boronic acid. Boronic anhydrides were used in this study as discussed later.

In this Chapter, the direct polymerization of HBA was examined in the presence of three kinds of anhydrides of boronic acid such as TFB, 4-methoxyphenylboronic acid (MPB) and 4-biphenylboronic acid (BPB), as shown in Scheme 1-1, not only to develop a new procedure for the POB synthesis but also to control the morphology of the POB crystals.



Scheme 1-1 Polymerization of HBA in the presence of boronic acid

1-2 EXPERIMENTAL

1-2-1 Materials

HBA was purchased from TCI (Tokyo, Japan) and recrystallized from a mixture of water

and methanol. TFB, MPB, and BPB were purchased from Sigma-Aldrich (St. Louis) and recrystallized from toluene. An isomeric mixture of dibenzyltoluene (DBT) was obtained from Matsumura Oil Co. Ltd. (Osaka, Japan, Trade name: *Barrel Therm 400*, M_W: 380, b.p.: 382^oC) and distilled under reduced pressure (170–175^oC/0.3 mmHg).

1-2-2 Measurements

Morphology was observed on a HITACHI S-3500N scanning electron microscope (Tokyo, Japan). Samples were dried, sputtered with platinum–palladium and observed at 20 kV. Average sizes of the products were determined by taking the average of more than 150 observation values. Infrared (IR) spectrum was measured on a JASCO FT/IR-410 spectrometer (Tokyo, Japan). Wide angle X-ray scattering (WAXS) was performed on a Rigaku Gaiger Flex (Matsumoto, Japan) with nickel-filtered CuKα radiation (35 kV, 20 mA). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Daltonics Auto-FLEX MALDI-TOF MS system (Billerica, MA) operating with a 337-nm N_2 laser. Spectra were obtained in the linear positive mode with accelerating potential of 20 kV. Mass was calibrated with angiotensin I (M_W 1296.69) and insulin B (M_W 3496.96) of a Sequazyme peptide mass standard kit. Samples were prepared by the evaporation-grinding method, and then measured in 3-aminoquinoline as a matrix doped

with potassium trifluoroacetate according to previously reported procedures. [29–32]

1-2-3 Determination of Number-Average Molecular Weight

Number-average molecular weight (M_n) was determined by the end group analysis. The one end group of the POB molecules was a carboxyl group or a carboxylic boronic anhydride group. The content of the carboxylic boronic anhydride end group was determined by the measurement of the content of the boronic acid on HPLC after the hydrolysis of the samples as follows: samples (2 mg) and 10 wt % KOH methanol solution (10 mL) were placed in a flask, and the mixture was completely hydrolyzed for 12 h at 100^{o}C. The solution was neutralized with dilute hydrochloric acid. The solution was analyzed by using a Waters 600E-490E system HPLC (Milford, MA) with Nova Pack HR C18 column. The eluent of HPLC was a mixture of water containing 1.0 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. The content of the carboxyl end group was estimated by calculating the absorbance ratio of carbonyl group of carboxylic acid and that of ester linkage on an IR spectrum. 4-Benzoyloxybenzoic acid and 4-(4-benzoyloxy)benzoyloxybenzoic acid, which were synthesized according to a previously reported procedure, were used to correct the absorbance ratio. [33] On the basis of these analyses, M_n was estimated by the following equation.

$$M_n = M_o / [(Abs_{acid} / 0.80\ Abs_{ester}) + (\text{boronic acid moiety in the crystals})]$$

Where, Abs_{acid}: absorbance of carbonyl group in carboxyl end group, Abs_{ester}: absorbance of carbonyl group in ester linkage, M_o: molecular weight of *p*-oxybenzoyl repeating unit, 0.80: calibration coefficient

1-2-4 Polymerization

A polymerization of HBA in the presence of TFB anhydride (TFBA) is described as a typical procedure as follows; HBA (0.23 g, 1.67 mmol) and 20 mL of DBT were placed into a cylindrical flask equipped with a mechanical stirrer and gas inlet and outlet tubes. Polymerization concentration was 1.0 %, defined as (calculated polymer weight / solvent volume) x 100. The reaction mixture was heated under a slow stream of nitrogen up to 300^{o}C with stirring. HBA was dissolved during heating. TFBA (0.26 g, 0.56 mmol) was added into the solution at 300^{o}C, and stirring was stopped after TFBA was entirely dissolved. Concentration of boronic acid residue (c_B) was 100 %, defined as (TFBA x 3/HBA) x 100. Temperature was maintained at 300^{o}C for 24 h. The solution became turbid at an initial stage of the polymerization, and then precipitates were formed with time. Precipitated POB crystals were collected by vacuum filtration at 300^{o}C and washed with *n*-hexane and acetone. A filtrate was poured into *n*-hexane, and precipitated solids, which were oligomers dissolved in

the solution at 300^{o}C, were collected by filtration. The collected oligomers were washed with *n*-hexane and dried. Polymerizations under other conditions were carried out in a similar manner.

1-3 RESULTS AND DISCUSSION

1-3-1 Boronic Anhydrides

As described above, it is well known that boronic acids undergo dehydration on simple heating to convert anhydrides. [31–33] Boronic acids used in this study were recrystallized from toluene, and they might possibly change anhydrides during the procedure of recrystallization. In an IR spectrum of the recrystallized TFB, a band of B-O linkage of a boronic anhydride was clearly observed at 1360 cm^{-1}, but that of the hydroxyl group was totally absent. This spectrum is identical with that of the 2,4,6-tris(3,4,5-trifluorophenyl)-1,3,5,2,4,6-trioxatriborinane, which is the TFBA, and TFB was completely converted into TFBA by heating during the recrystallization procedure. Other boronic acids were also converted to anhydrides confirmed with IR, and therefore boronic anhydrides were unintentionally used instead of boronic acids.

1-3-2 Morphology of Precipitated POB Crystals

Polymerizations were carried out in DBT at a concentration of 1.0 % at 300°C for 24 h in the presence of three different boronic anhydrides. HBA was insoluble in DBT at 25°C, but it became dissolved during heating. Table 1-1 presents results of the polymerization. Concentration of boronic acid residue (c_B) was defined as the molar ratio of boronic acid residue to the HBA defined as (TFBA x 3/HBA) x 100. Nothing was precipitated at c_B of 1 mol %, but crystals were obtained as precipitates at c_B from 5 to 100 mol % with the yields from 21 to 32 %. Some amounts of oligomers were left in the solution because of the solubility, and therefore the yield of the precipitated crystals was not so high. The obtained crystals were insoluble in organic solvents, and therefore their chemical structures were analyzed by the IR spectroscopy. Figure 1-1 shows an IR spectrum of the crystals prepared with TFBA at c_B of 10 mol % (run no. T-3) as a representative.

Carbonyl and ether band of ester linkage are clearly observed at 1738 and 1190 cm^{-1}, and this spectrum is identical with that of POB. HBA polymerized to yield POB in the presence of the boronic anhydride. M_n of the crystals determined by the end group analysis ranged from 3.8×10^3 to 5.4×10^3, which is discussed later. Morphology of the crystals is influenced by not only the structure of boronic anhydrides but also the value of c_B. In the polymerization with TFBA, needle-like crystals were obtained at c_Bs of 5 and 10 mol % as shown in Figure

Table 1-1 Polymerization of HBA in the presence of boronic anhydride

Run no.	Polymerization condition [a]		Yield (%)	M_n (x10^3)	Morphology of products [c]
	Boronic anhydride	c_B (mol%) [b]			
T-1	TFBA	1	0		
T-2	TFBA	5	21	4.7	needle
T-3	TFBA	10	25	3.8	needle
T-4	TFBA	50	28	4.4	SAS
T-5	TFBA	100	32	5.4	SAS
M-1	MPBA	1	0		
M-2	MPBA	5	13	3.5	slab
M-3	MPBA	10	15	1.9	fibrillated slab
M-4	MPBA	50	30	5.8	needle
M-5	MPBA	100	19	6.9	SAS
B-1	BPBA	1	0		
B-2	BPBA	5	42	1.8	needle, slab
B-3	BPBA	10	33	2.9	fibrillated slab
B-4	BPBA	50	44	14.4	fibrillated slab
B-5	BPBA	100	48	14.7	fibril, SAS

[a] Polymerizations were carried out in DBT at a concentration of 1.0% at 300°C for 24 h. [b] Content of boronic acid (c_B mol%) = ([Boronic anhydride] x 3 / [HBA]) x 100 [c] SAS stands for spherical aggregates of slab-like crystals.

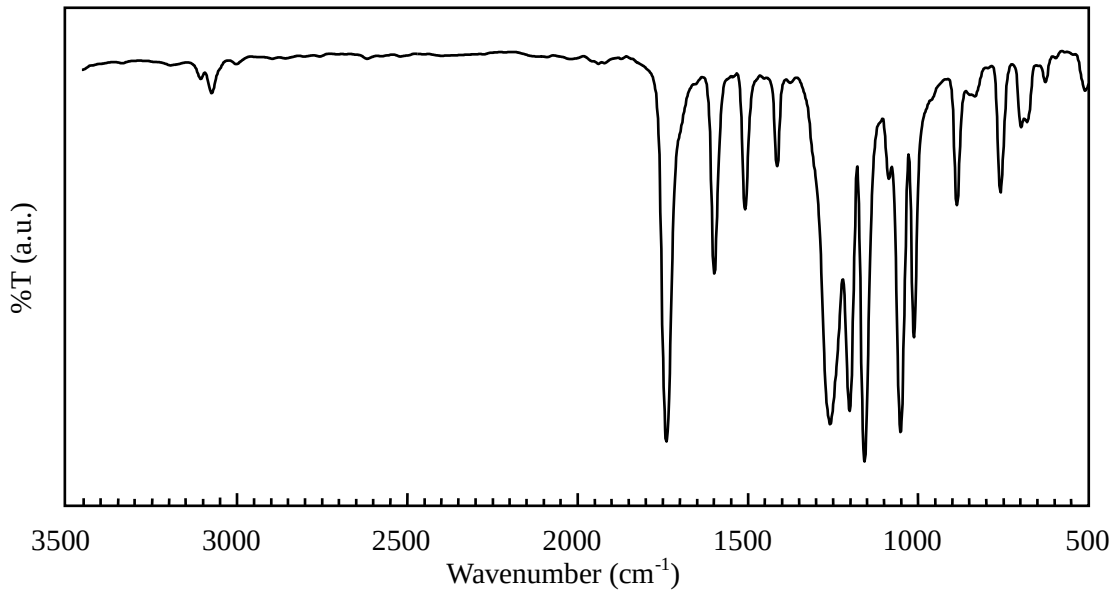


Figure 1-1 IR spectrum of needle-like crystals prepared in the presence of TFBA at c_B of 10 mol% (run no. T-3).

1-2(a). The average length and width of the needle-like crystals prepared at c_B of 5 mol % (run no. T-2) were 3.9 and 0.2 μm, respectively. Those prepared at c_B of 10 mol % (run no. T-3) were 5.0 and 0.3 μm, respectively. Figure 1-3 shows a WAXS intensity profile of the needle-like crystals. Diffuse halo attributed to amorphous regions was hardly detected, and the needle-like crystal possessed high crystallinity. Diffraction peaks at 15.6, 17.0, 19.3, 19.8, 23.5, 28.6, 37.9, and 42.9^o were observed at 2h, which could be assigned according to the orthorhombic unit cell of the POB crystal; phase I (a = 0.745, b = 0.564, and c = 1.247 nm) and phase II (a = 1.115, b = 0.380, and c = 1.256 nm). [34] To discuss the formation mechanism of the needle-like crystals, morphological change of the crystals was examined during polymerization as presented in Figure 1-4. Lamellae, fine slab-like, and rod-like crystals were formed after 6 h. It notes that a trace of screw dislocation was observed on the surface of some lamella as marked by an arrow in Figure 1-4(a). Then, rod-like crystals were seen after 12 h, suggesting that the lamellae served as the nuclei for the rod-like crystals. Many streaks run perpendicular to the long axis of the rod-like crystal as also marked by an arrow in Figure 1-4(b), indicating that these rod-like crystals were formed by spiral growth of the lamellae from the screw dislocation. After 24 h, the length of the needle-like crystal increased to 5.0 μm. The piling-up lamellae structure was slightly seen in these needle-like crystals, but many of them had smooth surface. After 36 h, the piling-up lamellae structure disappeared and the needle-like crystals with smooth surface were formed as shown in Figure

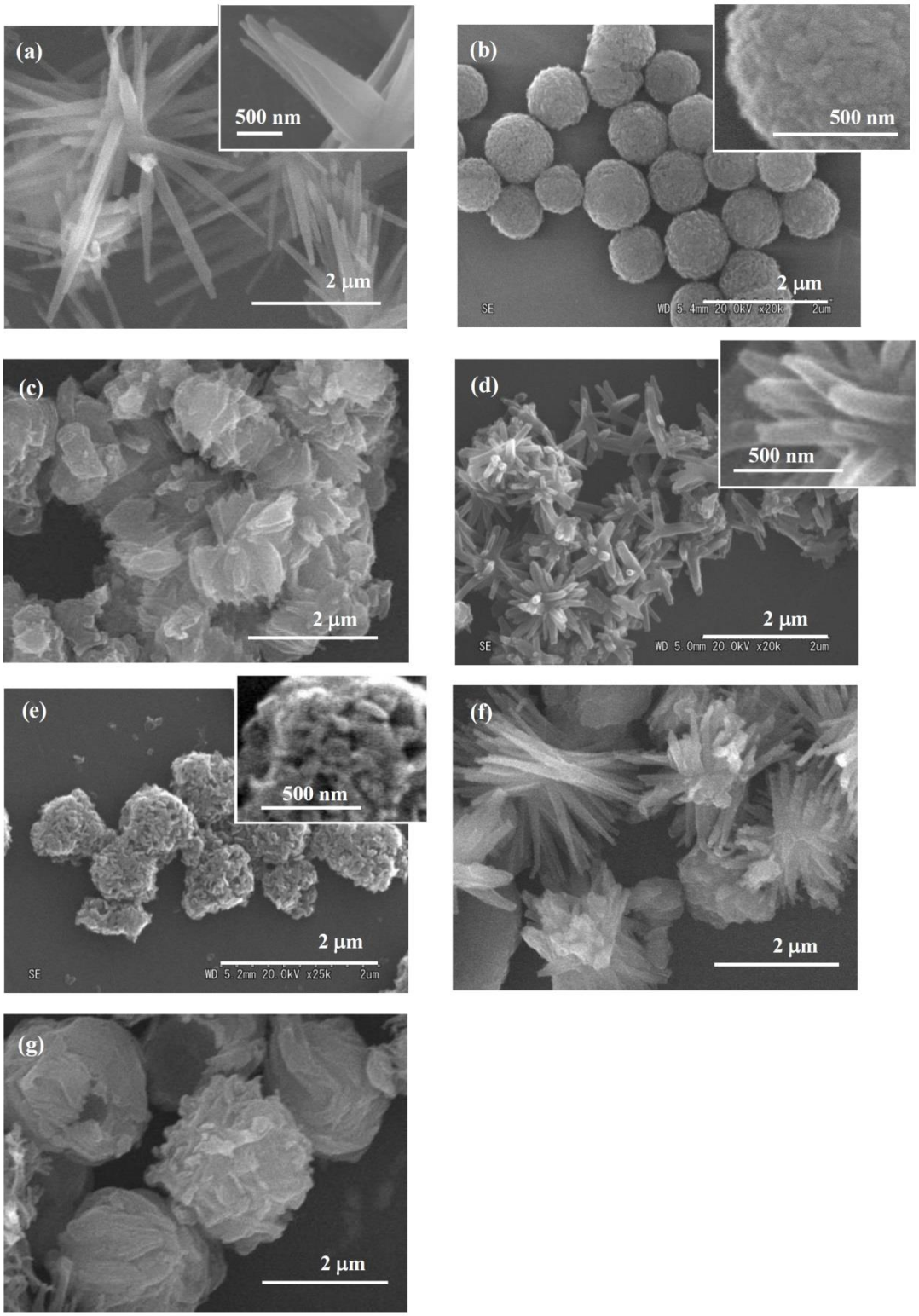


Figure 1-2 POB crystals prepared in the presence of TFBA at c_Bs of (a) 10 mol% (run no. T-3), (b) 100 mol% (run no. T-5), MPBA at c_Bs of (c) 10 mol% (run no. M-3), (d) 50 mol% (run no. M-4), (e) 100 mol% (run no. M-5), and BPBA at c_Bs of (f) 5 mol% (run no. B-2), (g) 100 mol% (run no. B-5).

1-4(c). This morphological change resembles that of the POB whiskers prepared from *p*-acetoxybenzoic acid as previously reported. [7, 8] The resemblance of morphological development implies the formation mechanism of the needle-like crystal as follows; when the molecular weight of the oligomers exceeds a critical value, the oligomers are phase-separated by crystallization *via* the super-saturated state to form the lamellae. The screw dislocation occurs on the lamellae, and then the needle-like crystals are formed by the spiral growth of the lamellae. Molecular weight increases by the polymerization on and in the crystals.

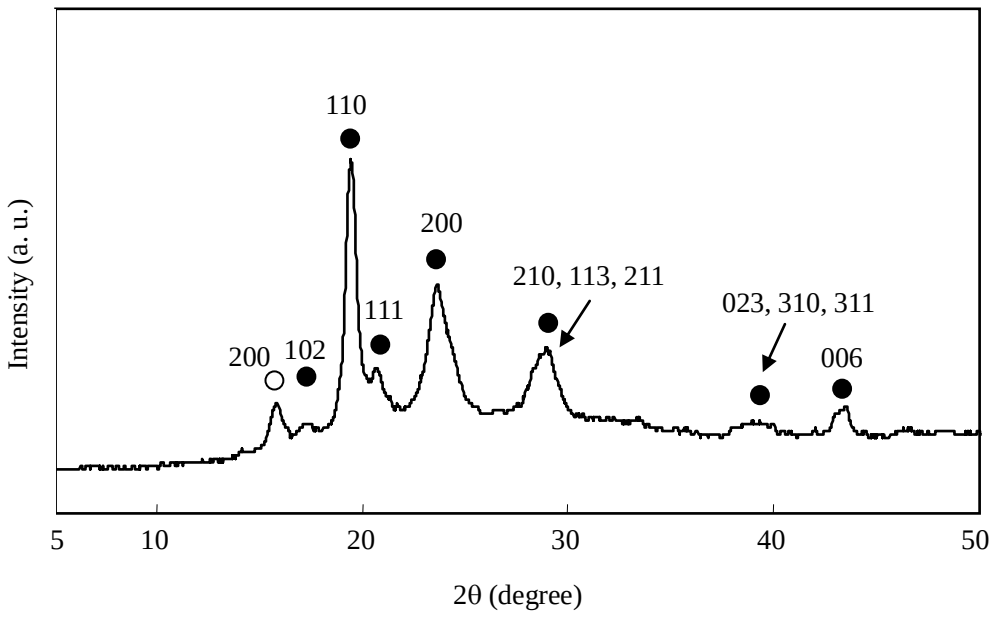


Figure 1-3 WAXS intensity profiles of POB needle-like crystals prepared with TFBA at c_B of 10 mol% for 24 h (run no. T-3). Diffraction peaks marked by ● and ○ are attributed to orthorhombic phase I and II, respectively.

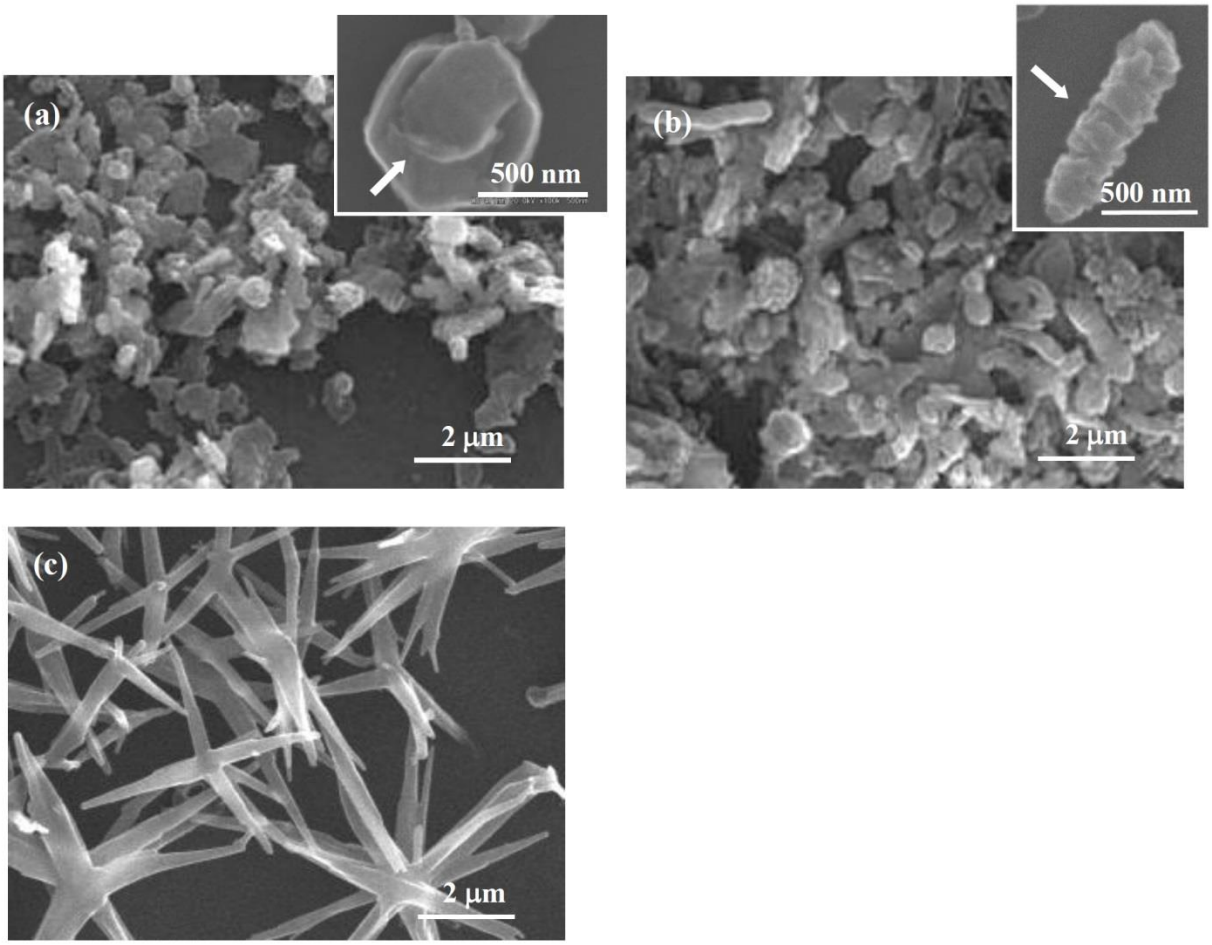


Figure 1-4 POB crystals prepared in the presence of TFBA at c_B of 10 mol% for (a) 6, (b) 12 and (c) 36 h.

Morphology was drastically changed at higher c_B. Microspheres, which were aggregates of slab-like crystals, were formed at c_Bs of 50 mol % (run no. T-4) and 100 mol % (run no. T-5) as shown in Figure 1-2(b). The average diameter of these spheres was 0.9 μm. It has been reported that the structure of the oligomer end groups influenced the morphology of POB crystals. [35] When the value of c_B increased, the ratio of the carboxylic boronic anhydride end group in the precipitated oligomers increased as discussed later. The bulkiness of the

carboxylic boronic anhydride end group prevents forming the crystal with clear habit. Lower c_B is favorable for the needle-like crystals, and higher c_B is favorable for the microspheres.

With respect to MPB anhydride (MPBA), the POB crystals were obtained at c_B from 5 to 100 mol % with the yields from 13 to 30 %. Fine slab-like crystals were formed at c_Bs of 5 and 10 mol % (run no. M-2 and -3), and they were fibrillated along the direction of the thickness as shown in Figure 1-2(c). Needle-like crystals were obtained at c_B of 50 mol % (run no. M-4) as shown in Figure 1-2(d). The needlelike crystal prepared with MPBA was averagely 0.9 μm in length and 250 nm in width. The size was smaller than that of the needle-like crystals prepared with TFBA. The tips were not sharp comparing with those prepared with TFBA. Microspheres, which were aggregates of fine slab-like crystals, were also formed at c_B of 100 mol % (run no. M-5) as shown in Figure 1-2(e), and the average diameter of these spheres was 0.8 μm. With respect to BPB anhydride (BPBA), the POB crystals were also obtained at c_B from 5 to 100 mol % with the yields from 33 to 48 %. The needle-like crystals were formed only at c_B of 5 mol % as shown in Figure 1-2(f), and they were averagely 2.2 μm in length and 150 nm in width. Fibrillated crystals were formed with slab-like crystals at c_Bs from 10 to 50 mol % and microspheres, which were also aggregates of the slab-like crystals, were obtained at c_B of 100 mol % as shown in Figure 1-2(f). According to the value of c_B, lower c_B is approximately desirable for the needle-like crystal in the polymerization with MPBA and BPBA. According to the structure of the boronic anhydride,

TFBA is more favorable to prepare the needle-like crystal than MPBA and BPBA. This tendency for the preparation of the needlelike crystal might be attributed to the bulkiness of the carboxylic boronic anhydride end group.

1-3-3 Molecular Weight of POB Crystals

As described, morphology of POB is strongly influenced by not only the structure of the boronic anhydrides but also its c_B. M_n of the precipitated POB crystals also depends on them as presented in Table 1-1. M_n of the crystals prepared in the presence of TFBA and MPBA ranged from 3.8×10^3 to 6.3×10^3 and from 1.9×10^3 to 6.9×10^3, respectively. With respect to BPBA, M_n of the crystals ranged from 1.8×10^3 to 14.7×10^3. It notes that M_n increased with c_B, and BPBA gave the highest M_n among the boronic anhydrides used in this study. When the value of c_B is 100 mol %, all the carboxylic end group of the precipitated oligomers must be converted to a carboxylic boronic anhydride end group. Phenolic hydroxyl end group nucleophilically attacks the activated end group of the oligomer in the crystals, and the polymerization proceeds more efficiently at c_B of 100 mol % to yield the highest M_n. In contrast to this, when the value of c_B is lower than 100 mol %, some oligomers having nonactivated carboxyl end group are precipitated to form the crystals, and the carboxyl end group terminates the polymerization in the crystals.

To clarify the difference in the polymerization behavior between TFBA and BPBA, the yield and M_n of the crystals were investigated in the course of polymerization at c_B of 100 mol %. Figure 1-5(a,b) plots them as a function of time. In the polymerization with TFBA, the yield increased until 18 h and then it became constant at 41%. M_n of the crystals also increased with time, but it increased continuously after the yield was leveled off and it reached to 8.4 x 10^3 after 36 h. In the polymerization with BPBA, the yield increased until 24

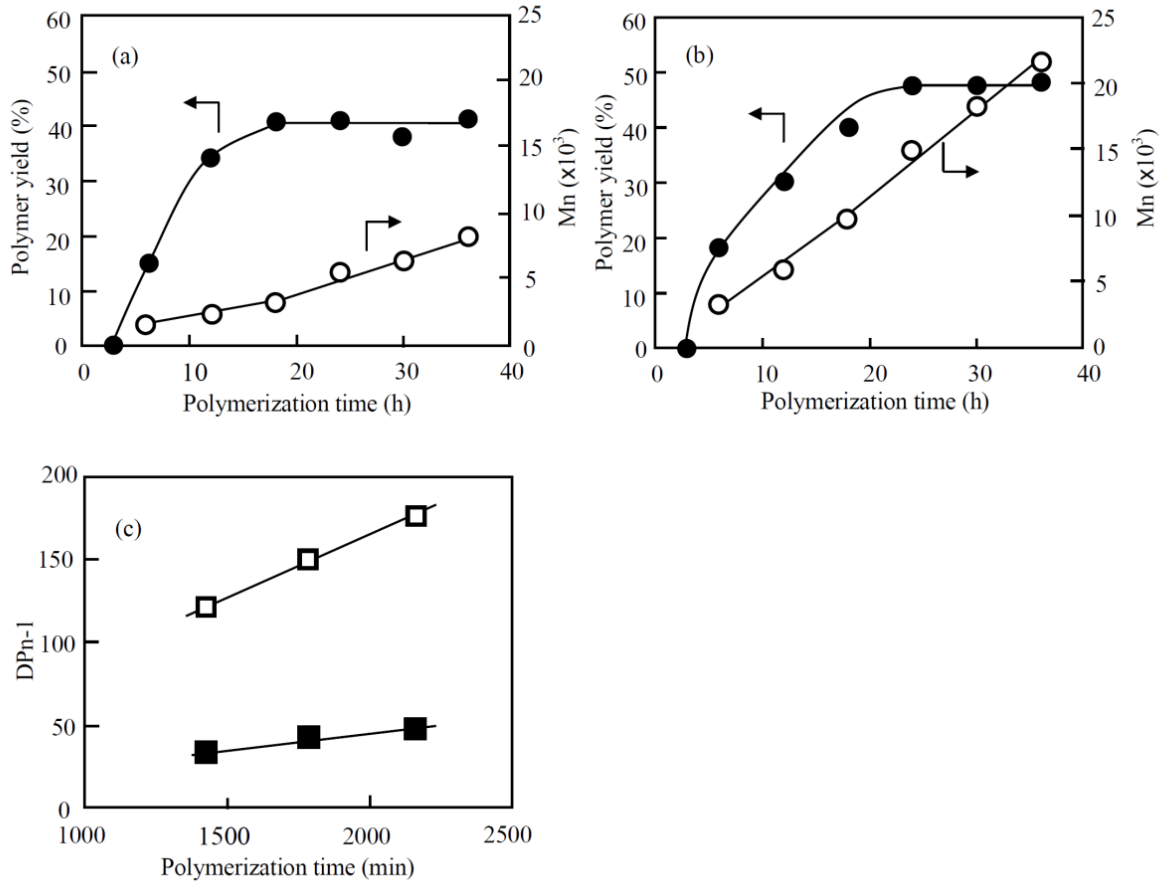


Figure 1-5 Plots of yield (●) and M_n (○) of POB crystals as a function of time in the polymerizations at c_B of 100 mol% in the presence of (a) TFBA and (b) BPBA. Plots of DPn-1 as a function of time (c) in the polymerizations at c_B of 100 mol% in the presence of (■) TFBA and (□) BPBA.

h and then it became constant at 48%. M_n of the crystals also increased linearly with time even after the yield was leveled off and it reached to 21.4 x 10^3 after 36 h. The fact that M_n increased after the yield became constant proves the polymerization in the crystals. Number-average degree of the polymerization (DPn) was calculated from M_n, and Figure 1-5(c) plots DPn-1 as a function of time after the yield of the crystals was constant. Linear relationships between DPn-1 and time are observed in both the polymerization systems, and this linearity shows that the polymerization in the crystals apparently obeys the second-order kinetics. Rate constants of the second-order kinetics (k_2) for the polymerization with TFBA and BPBA were estimated from the slope as 76.1 and 1.12 x 10^3 g mol^{-1} min^{-1}, respectively. The value of k_2 of BPBA is 14.7 times larger than that of TFBA. It can be expected that the acidity of TFBA might be higher than that of BPBA because of electro-withdrawability of fluorine atoms and, hereby, TFBA accelerates the polymerization. However, BPBA gave higher M_n and the reason for this is not the acidity. The oligomers recovered from the solution after 12 and 24 h were analyzed by MALDI-TOF mass spectrometry. Spectra and peak assignments were also shown in Figure 1-6 and Table 1-2, respectively. In the polymerization with TFBA, oligomers up to heptamers were detected after 12 and 24 h, and these results indicate that octamers were mainly precipitated to form the crystals. Further polymerization occurred between the oligomers on and in the crystals. In the polymerization with BPBA, oligomers up to nonamers were detected and decamers were mainly precipitated. The critical

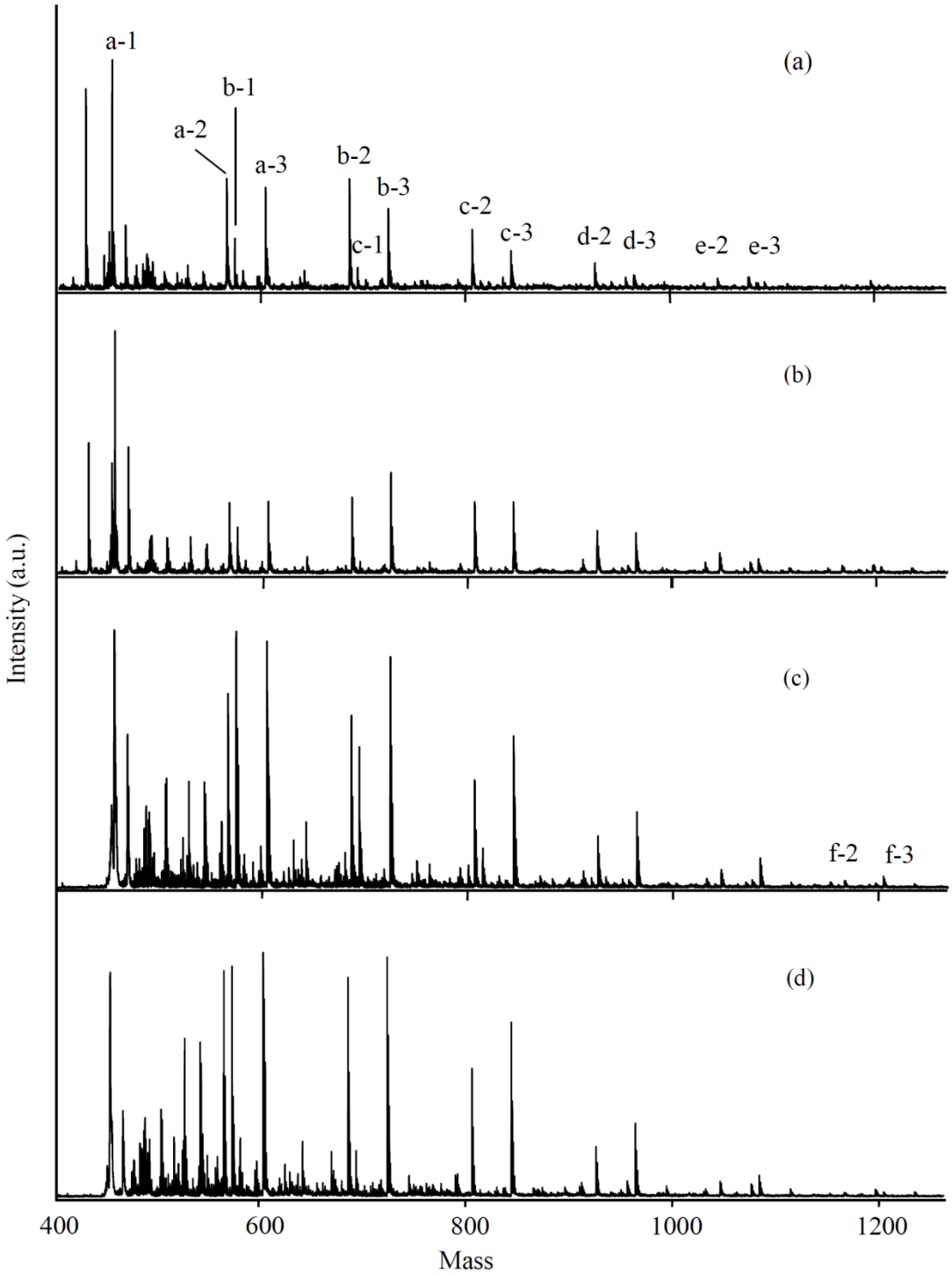
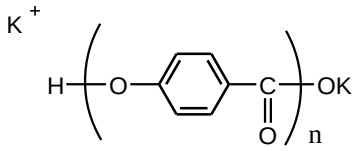
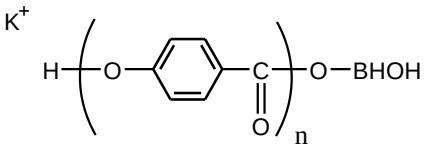
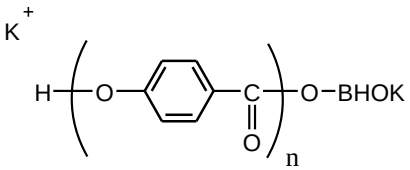


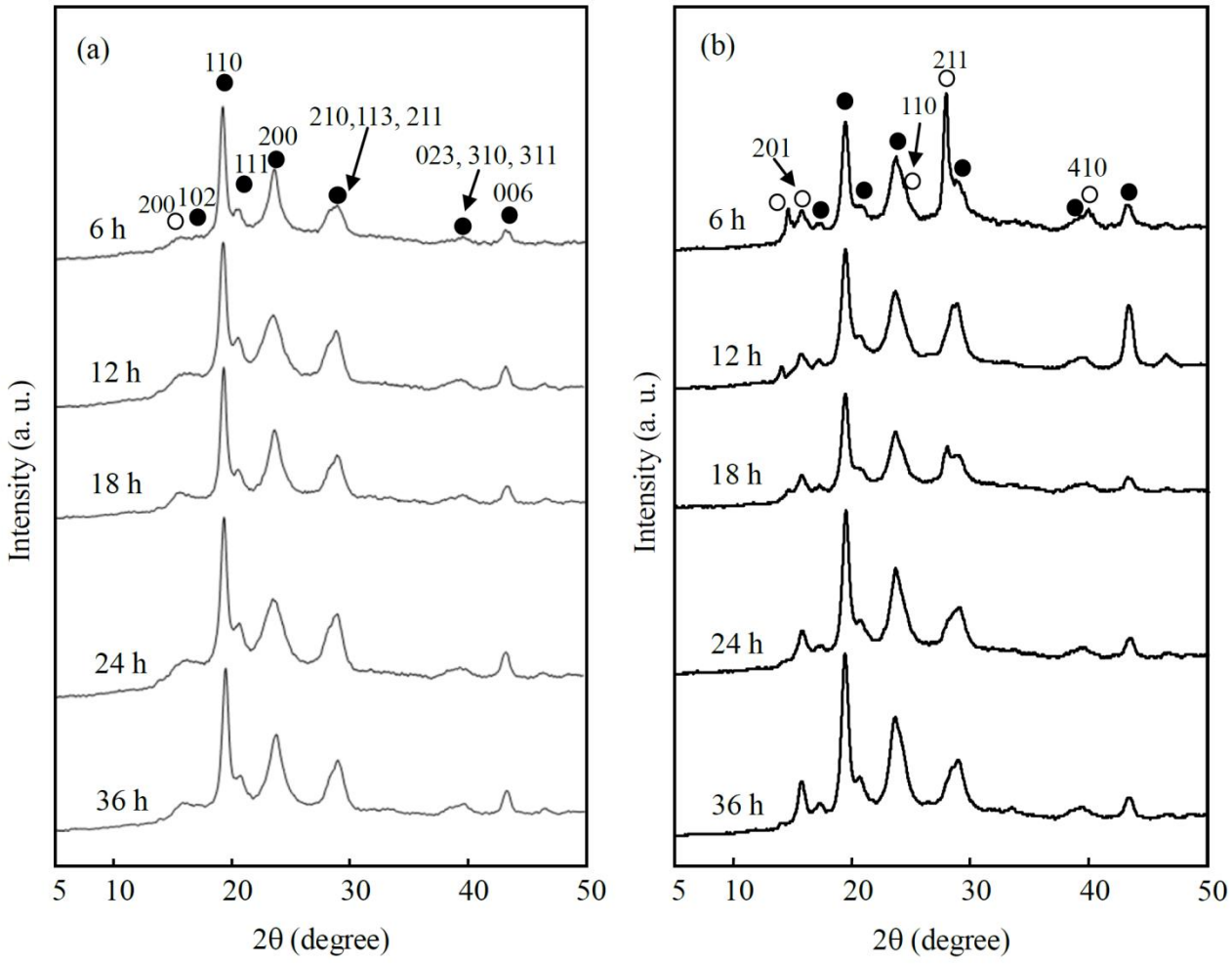
Figure 1-6 MALDI-TOF mass spectra of oligomers collected from solution. Polymerizations were carried out at c_B of 100 mol% in the presence of TFBA for (a) 12 h, (b) 24 h and BPBA for (c) 12 h, (d) 24 h.

Table 1-2 Structural assignment of peaks in the MALDI-TOF mass spectra reported in Figure 1-6

Structure	n	Calc. mass	Peak code	Obs. mass	
				TFBA	BPBA
	3	455.51	a-1	454.24	456.33
	4	575.62	b-1	574.26	574.85
	5	695.73	c-1	- [a]	694.93
	4	565.36	a-2	566.34	566.99
	5	685.46	b-2	686.36	686.98
	6	805.57	c-2	806.33	806.96
	7	925.68	d-2	926.27	926.97
	8	1045.79	e-2	- [a]	1046.90
	9	1165.90	f-2	- [a]	1166.95
	4	603.44	a-3	604.33	604.94
	5	723.54	b-3	724.35	724.92
	6	843.65	c-3	844.33	844.92
	7	963.76	d-3	964.22	964.9
	8	1083.87	e-3	- [a]	1081.98
	9	1203.98	f-3	- [a]	1204.90

[a] not detected.

M_n of the oligomers prepared with BPBA was higher than that with TPBA, suggesting that the end groups of anhydride between carboxyl group and BPBA enhance the solubility of oligomers. As aforementioned, it has been previously reported that two orthorhombic phases, phase I and II, coexist in the POB crystal at room temperature, and orthorhombic (pseudohexagonal) phase III exists at high temperature above 340 ^{o}C. [34, 36] The *a*-axis and the *b*-axis of the unit cell of phase II are 0.370 nm longer and 0.184 nm shorter that those of phase I, respectively. The *c*-axis of these phases is almost the same. The structures of phase I and II easily change another phase in high temperature condition above 200 ^{o}C. [37] Phase II



is

Figure 1-7 WAXS intensity profiles of POB crystals prepared with (a) TFBA and (b) BPBA at c_B of 100 mol% for 6, 12, 18, 24 and 36 h. Diffraction peaks marked by ● and ○ are attributed to orthorhombic phase I and II, respectively.

proposed to be most prevalent in low-molecular weight oligomers, and the relative amount of phase I increases with polymerization time and temperature. Figure 1-7 shows WAXS intensity profiles of the crystals prepared at c_B of 100 mol % for different time. Diffuse halo attributed to amorphous regions was hardly observed, therefore, the polymerization proceeded

with maintaining high crystallinity. The crystal prepared with TFBA for 6 h mainly consisted of the phase I as similar as those prepared for 36 h, even though the M_n was only 5.0 x 10^2. Although M_n of the crystals prepared for 6 h was 1.7 x 10^3 in the polymerization with BPBA, which was higher than that prepared with TFBA, the crystal consisted of the phase I and II. Then, the relative amount of the phase I increased with polymerization time. The appearance of phase II in the crystals prepared with BPBA is attributed to bulkiness of carboxylic boronic anhydride end group of the oligomers. It can be speculated that the loose packing of the molecules in the phase II prepared with BPBA makes the polymerization more efficiently in the crystals, resulting in the higher molecular weight than that with TFBA.

1-4 CONCLUSIONS

The POB crystals were obtained *via* the crystallization during the polymerization of HBA with the boronic anhydrides. The morphology was considerably influenced by not only the structure of the boronic anhydride but also its concentration. Needle-like crystals were obtained in the presence of TFBA at c_Bs of 5 and 10 mol %. They were formed by the spiral growth of lamellae caused by the screw dislocation. Spherical aggregates of slab-like crystals were formed at c_B from 50 to 100 mol %. The polymerization with MPBA also yielded the needle-like crystals at c_B of 50 mol %, and the spherical aggregates of slab-like crystals at c_B

of 100 mol %. Slab-like crystals were formed at c_B from 5 to 10 mol %. In the polymerization with BPBA, the needle-like crystals were obtained at c_B of 5 mol % with a small amount of slab-like crystals. Fibrillar crystals were formed with the spherical aggregates of slab-like crystals at c_B from 10 to 100 mol %. The morphology of the POB crystals could be controlled by the structure of the boronic anhydrides and its content c_B, and the polymerization with TFBA at lower c_B was favorable to prepare the needle-like crystal. These tendencies are attributed to the bulkiness of the activated end group, and the smaller size is desirable not to prevent the crystallization. Molecular weight was also influenced by them. M_n of the crystals prepared in the presence of TFBA and MPBA ranged from 1.9×10^3 to 6.9×10^3. That of the crystals prepared in the presence of BPBA ranged from 1.8×10^3 to 14.7×10^3. M_n increased generally with c_B, and BPBA gave the highest M_n among the boronic anhydrides used in this study. When the value of c_B was 100 mol %, all the carboxylic end group of the precipitated oligomers were activated by the boronic anhydrides to form a carboxylic boronic anhydride group, and the polymerization proceeds more efficiently. Rate constant of the second-order kinetics of the polymerization with BPBA in the crystals was 14.7 times larger than that with TFBA. Loose packing of the molecules in the crystal prepared with BPBA was caused by the bulkiness of the end groups, and this makes the polymerization in the crystals more efficiently. Morphology and molecular weight of the POB crystals could be controlled by the chemical structure and the content of boronic anhydride.

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CHAPTER 2

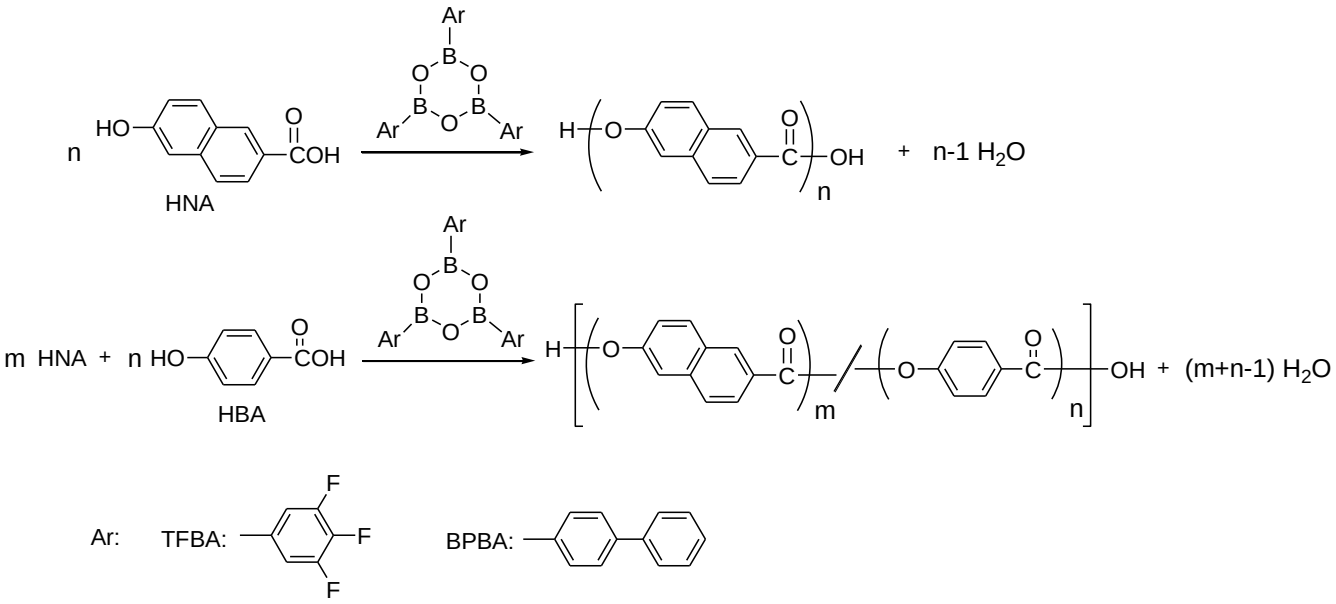
Preparation of Poly(2-oxy-6-naphthoyl) and Poly(4-oxybenzoyl-*co*-2-oxy-6-naphthoyl) Copolymers Using Reaction-Induced Phase Separation during Direct Polymerization in the Presence of Boronic Anhydride

2-1 INTRODUCTION

Poly(2-oxy-6-naphthoyl) (PON) possesses many excellent properties such as mechanical strength, thermal stability, chemical resistance and so on as well as poly(*p*-oxybenzoyl) (POB), and it has been received great attention as high performance materials. [1–3] These properties are influenced by the morphology of the polymers, and therefore the morphology control is of great importance to control the performance. PON does not exhibit solubility and fusibility, and this intractability makes PON difficult to process. Morphology control of PON had been studied by using reaction-induced phase separation of oligomers and PON whiskers were prepared by the polymerization of 2-acetoxy-6-naphthoic acid in an inert solvent. [2, 3] Copolymerization is also useful to improve the intractability of the polymers with maintaining

the properties, and 2-oxy-6-naphthoyl (ON) moiety has been often used as a component for thermotropic liquid crystalline aromatic polyesters. Various types of copolyesters comprising of ON moiety had been prepared so far. [4–11] Among them, copolymers of ON moiety and *p*-oxybenzoyl (OB) moiety are industrially important as super engineering plastics, and some of these copolymers are commercially available under the trade name of Vectra.

Recently, high molecular weight POB was directly synthesized from *p*-hydroxybenzoic acid (HBA) in the presence of boronic anhydride with eliminating water, and unique morphologies such as a needle and a sphere were successfully obtained as precipitates by using the reaction-induced phase separation of oligomers. [12] In this polymerization, boronic anhydride and boronic acid acted as a catalyst. The morphology of the POB precipitates was influenced by the structure of the boronic anhydride. This polymerization is of interest from the viewpoint of not only the morphology control but also in view of the environmental benign procedure. In this chapter, the direct polymerization of 2-hydroxy-6-naphthoic acid (HNA) was examined in the presence of two boronic anhydrides such as 2,4,6-tris(3,4,5-trifluorophenyl)-1,3,5,2,4,6-trioxatriborinane (TFBA) and 2,4,6-tri(biphenyl-4-yl)-1,3,5,2,4,6-trioxatriborinane (BPBA) by using reaction-induced phase separation of oligomers to control the morphology of PON. Based on this result, copolymerization of HNA and HBA was also examined as shown in Scheme 2-1.



Scheme 2-1 Polymerization of HNA and copolymerization with HBA in the presence of boronic anhydride.

2-2 EXPERIMENTAL

2-2-1 Materials

HNA and HBA were purchased from TCI (Tokyo, Japan), and recrystallized from a mixture of water and methanol. 3,4,5-Trifluorophenylboronic acid (TFB) and 4-biphenylboronic acid (BPB) were prepared as described in Chapter 1. These two boronic acids were converted into boronic anhydride during the purification by recrystallization confirmed by IR spectroscopy. [13–15] An isomeric mixture of dibenzyltoluene (DBT) was purified by the same manner described in Chapter 1.

2-2-2 Measurements

Morphology was observed on a HITACHI S-3500N scanning electron microscope (SEM) (Tokyo, Japan). The details are shown in Chapter 1. Infrared (IR) spectrum was measured on a JASCO FT/IR-410 spectrometer (Tokyo, Japan). Wide angle X-ray scattering (WAXS) was performed on a Rigaku Gaiger Flex (Matsumoto, Japan) with nickel-filtered CuKα radiation (35 kV, 20 mA). Transition temperatures from crystal phase to anisotropic melt phase (T_{KN}) of copolymers were measured on a Perkin-Elmer DSC 8000 (Waltham, USA) with a scanning rate of 20^{o}C min^{-1} in nitrogen atmosphere.

2-2-3 Determination of number-average molecular weight

Number-average molecular weight (M_n) was determined by the end group analysis. The one end group of PON molecules was a carboxyl group or a carboxylic boronic anhydride group. The content of the carboxylic boronic anhydride end group was determined by the measurement of the content of the boronic acid on HPLC after the hydrolysis of the samples as follows: samples (2 mg) and 10 wt% KOH methanol solution (5 mL) were placed in a flask, and the mixture was completely hydrolyzed for 12 h at 100^{o}C. The solution was neutralized with dilute hydrochloric acid. The solution was analyzed by using a HITACHI D-2000 Elite

HPLC (Tokyo, Japan) with Nova Pack HR C18 column. The eluent of HPLC was a mixture of water containing 1.0 vol% acetic acid and acetonitrile, and the mixing volume ratio of these two solvents was changed linearly from 90/10 to 73/27 for 8 min. On the other hand, the content of the carboxyl end group was estimated by calculating the absorbance ratio of carbonyl group of carboxylic acid and that of ester linkage based on an IR spectroscopy. 6-(2-Naphthoyloxy)-2-naphthoic acid and 6-(6-(2-naphthoyloxy)-2-naphthoyloxy) -2-naphthoic acid, which were synthesized according to a previously reported procedure, [16] were used to correct the absorbance ratio.

On the basis of these analyses, M_n was estimated by the following equation.

$$M_n = M_{ON} / [(Abs_{acid} / 1.04\ Abs_{ester}) + (\text{molar fraction of boronic acid residue in the crystals})]$$

Where, Abs_{acid} : absorbance of carbonyl group in carboxyl end group, Abs_{ester} : absorbance of carbonyl group in ester linkage, M_{ON}: molar weight of ON moiety, 1.04: calibration coefficient for ON moiety.

M_n of copolymers was estimated by the following equation.

$$M_n = [M_{OB}\, r_p/100 + M_{ON}(1 - r_p)/100] \times [1 + 1/\{(Abs_{acid} /(0.80 r_p/ 100 + 1.04(1 - r_p/100)Abs_{ester}) + (\text{molar fraction of boronic acid moiety in the crystals})\}]$$

Where, M_{OB}: molar weight of OB moiety, r_p (mol%): content of OB moiety in copolymers, 0.80: calibration coefficient for OB moiety.

2-2-4 Composition analysis of copolymers

Samples were hydrolyzed and the molar ratios of HBA and HNA were determined by HPLC according to the similar procedure for the determination of M_n as described above. Composition of copolymers (r_p) was expressed as the content of OB moiety according to the following equation.

$$r_p \text{ (mol\%)} = [OB] \times 100/([OB]+[ON]).$$

2-2-5 Polymerization

2-2-5-1 Polymerization of HNA

HNA (0.22 g, 1.18 mmol) and 20 mL of DBT were placed into a cylindrical flask equipped with a mechanical stirrer and gas inlet and outlet tubes. Polymerization concentration was 1.0%, defined as (calculated polymer weight/solvent volume) x 100. The reaction mixture was heated under a slow stream of nitrogen up to 300^{o}C with stirring. HNA was dissolved during heating. BPBA (0.21 g, 0.39 mmol) was added into the solution at 300^{o}C and stirring was stopped after BPBA was entirely dissolved. Concentration of boronic anhydride (c_B) was 100 mol%, defined as (3[boronic anhydride]/[HNA]) x 100 based on the

concentration of a boronic acid residue. Temperature was maintained at 300°C for 24 h. The solution became turbid at an initial stage of the polymerization and then precipitates were formed with time. Precipitated PON crystals were collected by vacuum filtration at 300°C, and washed with *n*-hexane and acetone. Polymerizations under other conditions were carried out in a similar manner.

2-2-5-2 Copolymerization of HNA and HBA

Copolymerizations of HNA and HBA were carried out with varying the content of HBA in feed (r_f) in DBT at 300°C for 24 h in the presence of BPBA at c_B of 100 mol% according to the procedure similar to the polymerization of HNA. Concentration of polymerization was 1.0%.

$$r_f \text{ (mol\%)} = [\text{HBA}] \times 100/([\text{HBA}]+[\text{HNA}]).$$

2-3 Results and discussion

2-3-1 Polymerization of HNA

Polymerizations of HNA were carried out in DBT at a concentration of 1.0% at 300°C for

24 h in the presence of two different boronic anhydrides with varying the value of c_B. HNA was insoluble in DBT at 25°C, but it became dissolved during heating. Table 2-1 presents results of the polymerization. In the polymerization with TFBA, precipitates were obtained with the yields of 34 to 80%. The precipitates were insoluble in common organic solvents, and therefore their chemical structures were analyzed by the IR spectroscopy. Figure 2-1(a) shows an IR spectrum of the precipitates formed with TFBA at c_B of 50 mol% (run no. 2) as a representative. Bands of carbonyl groups and ether groups in ester linkages are clearly observed at 1736 and 1180 cm^{-1}, and this spectrum is identical with that of PON. Further, bands of hydroxyl end groups and carboxyl end groups are hardly visible, suggesting high molecular weight. The M_n determined by the end group analysis increased with the value of c_B and it ranged from 2.7×10^3 to 9.0×10^3. The precipitates did not exhibit clear morphology at c_B of 10 mol%, whereas those prepared at c_B of 50–100 mol% exhibited clear morphology as shown in Figure 2-2(a) and (b). Spheres with needles on their surface were formed at c_B of 50–70 mol%. The average diameters of the spheres prepared at c_B of 50 and 70 mol% were 2.22 and 1.94 μm, respectively. The average length and width of the needles on the surface prepared at c_B of 50 mol% were 540 and 130 nm, respectively. And those at c_B of 70 mol% were 290 and 140 nm. In contrast to these, spheres having smooth surface were formed at c_B of 100 mol%. The average diameter and its coefficient of variation (*cv*) of the spheres were 1.76 μm and 18%, respectively. Figure 2-3(a) and (b) show WAXS intensity profiles of the

Table 2-1 Results of polymerization of HNA in the presence of boronic anhydride

Run no.	Polymerization condition [a]		Polymer yield (%)	M_n (x10^3)	Morphology
	Boronic anhydride	c_B [b] (mol%)			
1	TFBA	10	34	2.7	Unclear
2	TFBA	50	80	4.9	SN [d]
3	TFBA	70	77	6.6	SN
4	TFBA	100	62	9.0	Sphere
5	BPBA	10	40	5.4	Cone
6	BPBA	30	71	8.3	Cone
7	BPBA	50	55	9.9	Sphere
8	BPBA	70	66	12.1	Sphere
9	BPBA	100	58	12.9	Sphere

[a] Polymerizations were carried out in DBT at 300°C at a concentration of 1.0% at 300°C for 24 h. [b] c_B (mol%) = ([boronic anhydride] x 3 / [HNA]) x 100. [c] Temperature of 5 wt% loss measured on TGA at a scanning rate of 10 °Cmin^{-1} in N_2. [d] SN stands for spheres with needles on their surface.

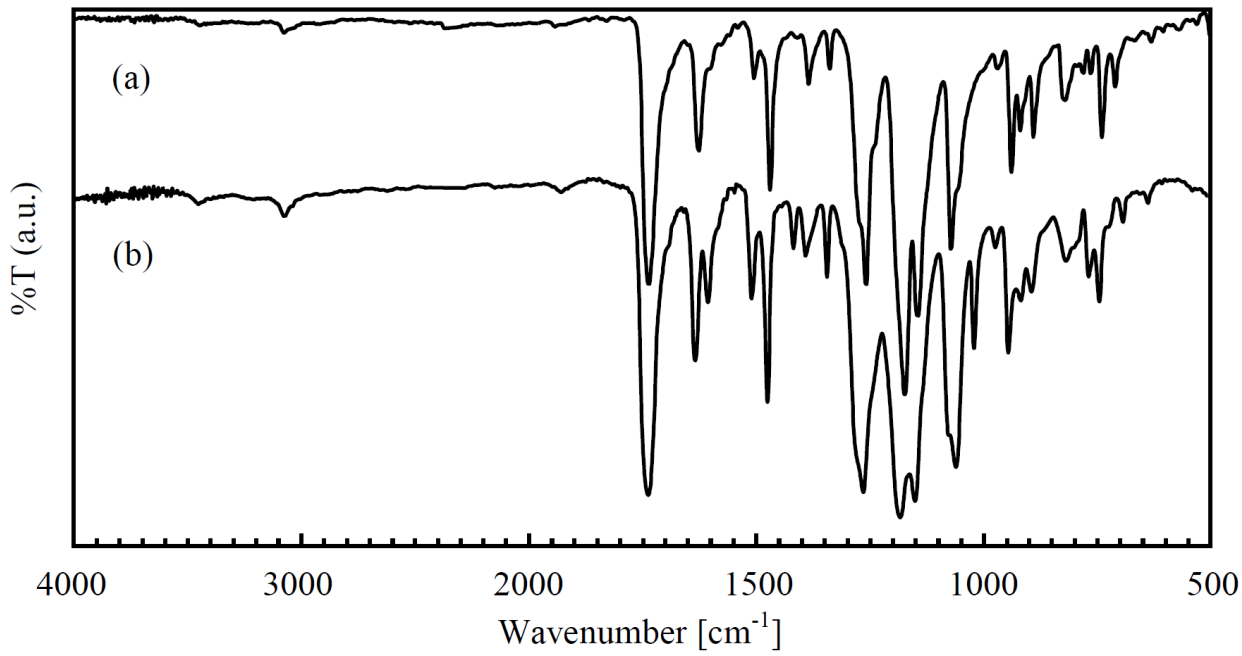


Figure 2-1 IR spectra of (a) PON prepared in the presence of TFBA at c_B of 50 mol% and (b) copolymer of HBA and HNA (r_f = 50 mol%) prepared in the presence of BPBA at c_B of 100 mol%.

spheres with needles on their surface (run no. 2) and the spheres having smooth surface (run no. 4), respectively. In spite of the morphology, diffuse halo attributed to amorphous region was hardly detected in these profiles, indicating that these precipitates possessed high crystallinity. Diffraction peaks were observed at 2θ of 10.4, 15.4, 18.7, 23.0, 27.8, 38.2 and 42.6°, which could be assigned according to the orthorhombic unit cell of the PON crystal with a = 0.766, b = 0.598, and c = 1.712 nm. [17]

With respect to the polymerization with BPBA, the PON precipitates were formed with the yields of 40 to 71%. The M_n also increased with the value of c_B in the range from 5.4×10^3 to 12.9×10^3. The M_n prepared with BPBA was higher than that with TFBA at the same c_B value. The morphology of the precipitates changed drastically with the value of c_B. Aggregates of cone-like crystals were formed at c_B of 10 and 30 mol% as shown in Figure 2-2(c). The cone-like crystals grew radially from the centre part. The average length from the centre part and the width of the cone-like crystals prepared at c_B of 10 mol% were 690 and 280 nm, respectively. And those at c_B of 30 mol% were 610 and 170 nm, respectively. The size of the corn-like crystals prepared at c_B of 30 mol% was slightly smaller than that at c_B of 10 mol%. Morphology was drastically changed at c_B of 50–100 mol% from cone-like crystal to spheres as shown in Figure 2-2(d). The average diameter and the cv value of these spheres were 620–670 nm and 13–16%, respectively. These spheres did not possess smooth surface and many protuberances were observed on the surface. The spheres have rugged surface

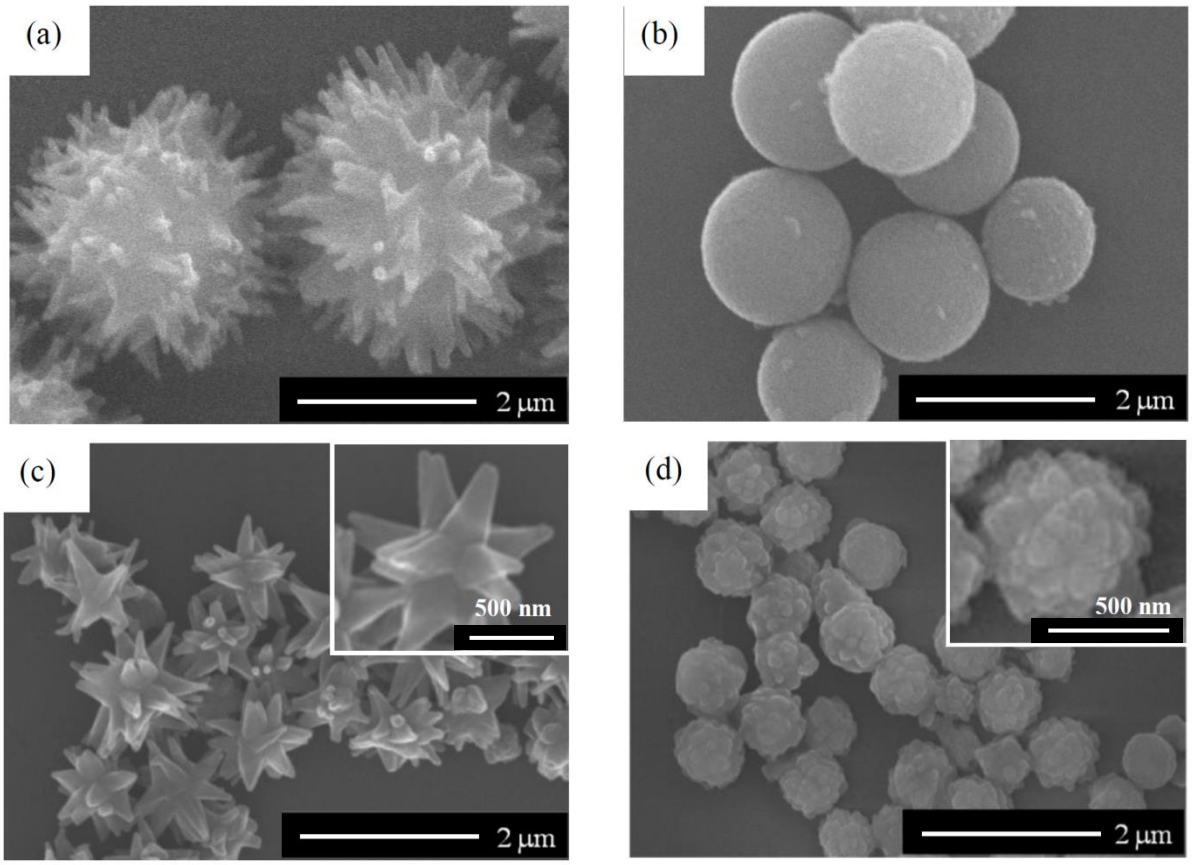


Figure 2-2 PON precipitates prepared in the presence of TFBA at c_B of (a) 50 mol% and (b) 100 mol%, and those prepared in the presence of BPBA at c_B of (c) 30 mol% and (d) 100 mol%.

which are different from those prepared with TFBA. Figure 2-3(c) and (d) show WAXS intensity profiles of the aggregates of the cone-like crystals (run no. 6) and the spheres (run no. 9). They also possessed high crystallinity as well as the precipitates obtained with TFBA.

The polymerization mechanism is explainable as follows: the boronic anhydride reacts with phenolic hydroxyl group of HNA to form a boronate. Then the carboxylic acid in HNA is activated by an isomerization of the boronate to form a carboxylic boronic anhydride. Then phenolic hydroxyl group of HNA attacks the carboxylic boronic anhydride to form an ester

linkage with eliminating boronic acid. This boronic acid reacts with carboxylic acid directly to form the carboxylic boronic anhydride or with another boronic acid to form boronic anhydride with elimination of water. This reaction continues to form the oligomers. When the molecular weight of the oligomers exceeds a critical value, the oligomers are precipitated to form the products *via* super-saturated state. If the crystallization is induced, the oligomer crystals having clear habit are formed. The polymerization between the oligomers occurs in or on the crystals. On the other hand, if the liquid–liquid phase separation is induced, the spheres are formed *via* the formation of droplets. In the droplets, the concentration of the oligomers becomes high and the polymerization proceeds to increase the M_n, leading the solidification with maintaining the spherical morphology. The morphology of the precipitates is significantly influenced by the value of c_B. The crystals are formed at a low value of c_B and the spheres are done at a high value of c_B. The oligomers having carboxyl end group are precipitated at a low value of c_B and those having carboxylic boronic anhydride end group are precipitated at a high value of c_B. The oligomers having carboxylic boronic anhydride end group exhibit lower freezing point than those having carboxyl end group, bringing about the liquid–liquid phase separation rather than crystallization. Further the oligomers having anhydride end group possess lower crystallizability due to the bulkiness of end group. Due to these effects, the spheres are naturally formed at a high value of c_B. In contrast, the crystals having clear habit are formed at a low value of c_B.

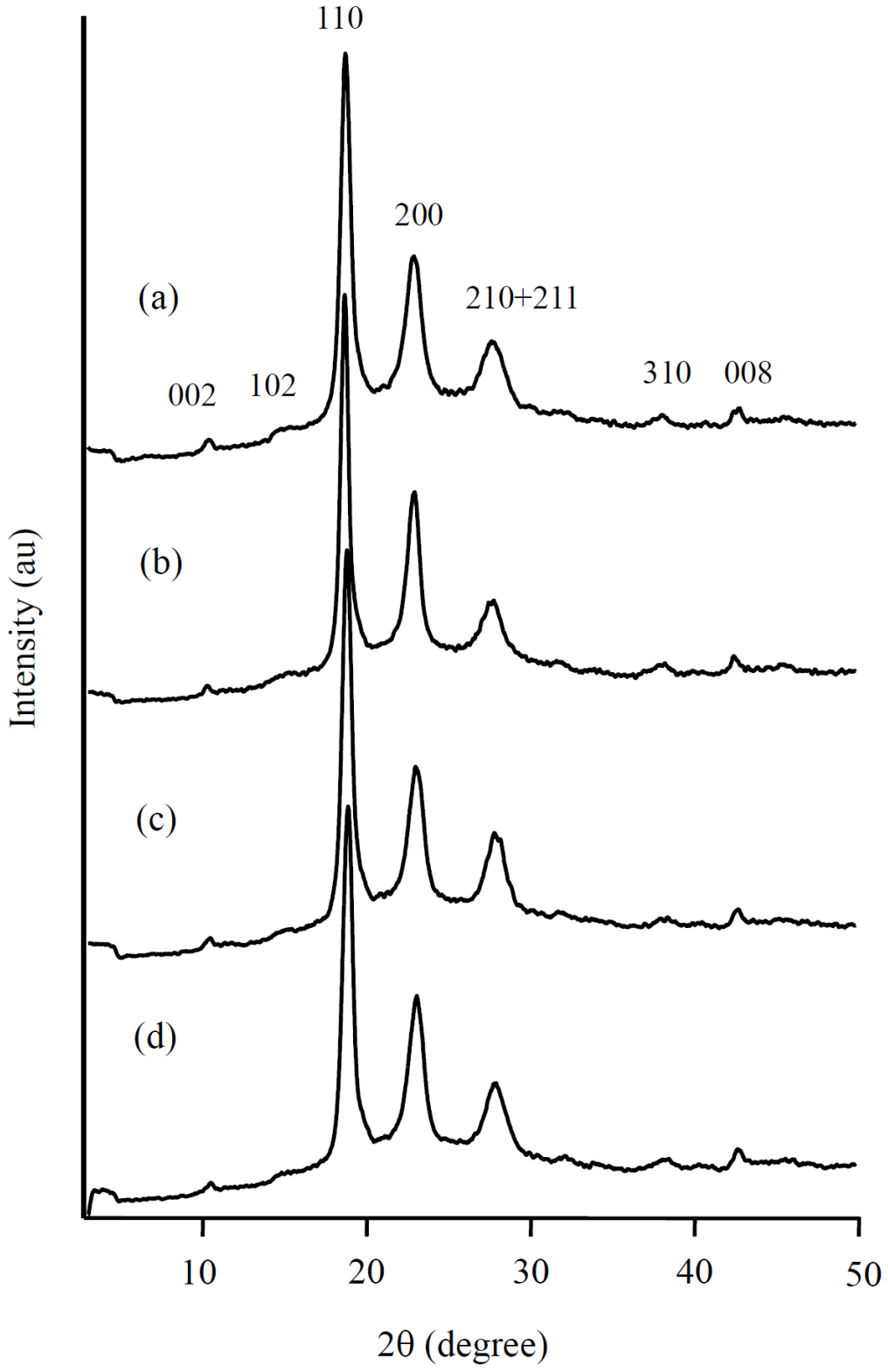


Figure 2-3 WAXS intensity profiles of the PON prepared in the presence of TFBA at c_B of (a) 50 mol% and (b) 100 mol%, and those prepared in the presence of BPBA at c_B of (c) 30 mol% and (d) 100 mol%.

The M_n increased with c_B and it became the highest at c_B of 100 mol%. Further, BPBA gave the higher M_n than TFBA as described. When the value of c_B is 100 mol%, all carboxylic end groups of the precipitated oligomers must be converted to carboxylic boronic anhydride end groups. Phenolic hydroxyl end group attacks the activated end group of the oligomer in or on the crystals, and the polymerization proceeds efficiently to yield the highest M_n. On the other hand, when the value of c_B is lower than 100 mol%, some oligomers having carboxyl end group are precipitated to form the crystals and the carboxyl end group terminates the polymerization. With respect to the structure of boronic anhydride, the tendency that BPBA afforded the higher molecular weight was also observed in the polymerization of HBA due to the size effect of carboxylic and boronic anhydride end group as previously reported. [12] The yield and the M_n of the PON precipitates prepared in the presence of TFBA and BPBA at c_B of

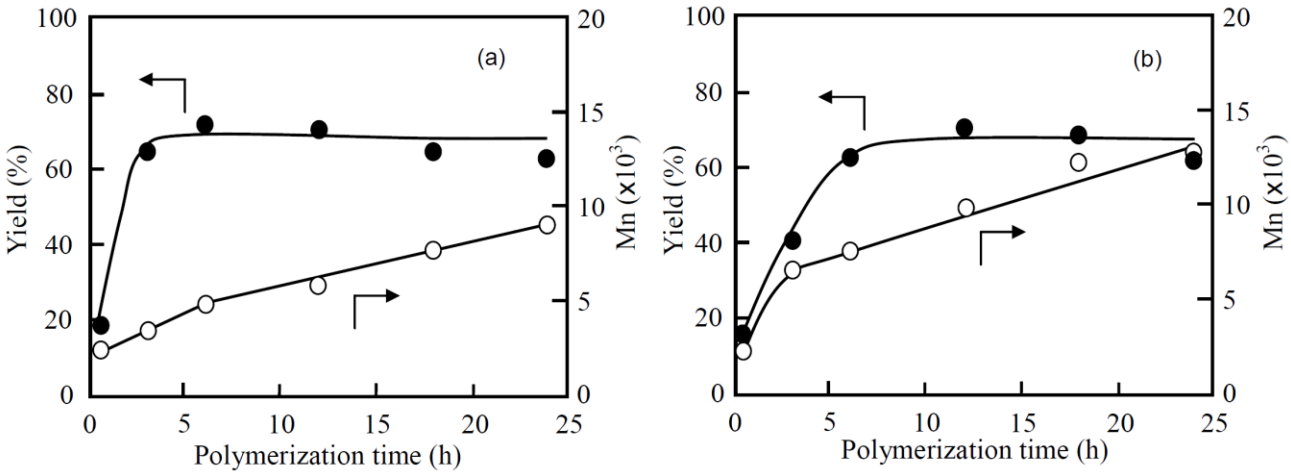


Figure 2-4 Plots of yield (●) and M_n (○) of PON precipitates prepared in the presence of (a) TFBA and (b) BPBA at c_B of 100 mol% as a function of time.

100 mol% were plotted as a function of time in Figure 2-4. In both polymerizations, they increased with time in the initial stage of the polymerization. The M_n increased continuously after the yield was leveled off. This fact suggests the efficient polymerization in the precipitates. The linearity between the M_n and the time after the yield was leveled off indicates that the polymerization in the precipitates apparently obeys second-order kinetics. The polymerization rate in the precipitates could not be accurately determined because the initial concentration of the end group was not determined. Therefore, the polymerization rate was compared using the slope (*R*). The values of *R* of the polymerization with TFBA and BPBA were calculated as 3.92 and 5.06 min^{-1}, respectively. The value of *R* in the polymerization with BPBA is slightly larger, but there is not so large difference between TFBA and BPBA. The PON did not exhibit a melting temperature under the decomposition and the polymerization proceeded in the solid state. [2, 3, 7, 18] It had been reported that *a* axis of the PON crystal unit cell slowly increased with temperature up to the transition at 330^{o}C, and *b* and *c* remained almost constant. [18] The volume of the crystal unit cell increased *ca*. 10% at 330^{o}C. The crystal structure changed from an orthorhombic structure to a new orthorhombic one which was almost pseudohexagonal. The polymerization temperature 300^{o}C was closed to the transition temperature, suggesting that the polymerization in the precipitates might occur in a new orthorhombic structure rather than an orthorhombic structure. This structural change is one possibility for the efficient polymerization in the

Table 2-2 Results of polymerization of HNA in the presence of BPBA with additions of HNA

Run no.	Polymerization condition [a]				Polymer Yield			M_n ($\times 10^3$)
	Initial conc. (wt%)	Time for monomer addition (h)	Total conc. (wt%)	Total polymerization time (h)	Calc. (mg)	Obs. (mg)	Yield (%)	
10	1.0	no	1.0	24	0.20	0.12	60	12.9
11	1.0	no	1.0	48	0.20	0.15	75	26.5
12	1.0	24 [b]	2.0	48	0.40	0.26	65	35.1
13	1.0	24, 48 [c]	3.0	72	0.60	0.45	75	24.6
14	3.0	no	3.0	24	0.60	0.45	75	17.0

[a] Polymerizations were carried out in DBT at 300°C in the presence of BPBA at c_B of 100 mol% for initial HNA at 300°C. [b] HNA of 1.0 wt% was added once after 24 h and the polymerization was carried out for another 24h. [c] HNA of 1.0 wt% was added twice after 24 h and 48 h, and the polymerization was carried out for another 24 h.

precipitates. The polymerization reaction proceeded more rapidly at the initial stage of the polymerization until the yield was leveled off than that at the middle stage of polymerization in the both polymerization systems. When the oligomers precipitate to form the crystals, they polymerized not only in the crystals but also on the crystallization site. The contribution of the polymerization on the crystals makes the total polymerization rate higher. At the initial stage of the polymerization, the yield increased more rapidly in the polymerization with TFBA than BPBA, but oppositely the M_n increased more slowly. In the polymerization with TFBA, the rapid precipitation of the oligomers in the polymerization with TFBA makes the polymerization on the crystals slower than that with BPBA.

According to the reaction mechanism, by-produced boronic acid activates a carboxyl group directly or converts to anhydride with elimination of water. The c_B value of 100 mol% is desirable to prepare high molecular weight PON precipitates. If the value of c_B in the

solution keeps more than 100 mol% in the solution, the polymerization will proceed efficiently to afford high molecular weight PON precipitates even after the addition of HNA. In order to prove this, HNA was added after 24 and 48 h into the polymerization system. The results were presented in Table 2-2. The concentration of HNA for the addition was fixed as 1.0% to maintain the c_B value of 100 mol% in the solution phase. The M_n and the yield of the PON precipitates after adding HNA once were 3.5×10^4 and 65%, respectively. Those after adding twice were 2.5×10^4 and 75%, respectively. The total c_B value became lower to 50 mol% and 33.3 mol% after adding HNA once and twice. The M_n increased naturally with the polymerization time and those prepared without the addition of HNA for 24 h and 48 h were 1.3×10^4 and 2.7×10^4. Although molecular weight distribution could not be measured due to the insolubility of PON, the M_n prepared with the addition of HNA was not lower than that without the addition. This result reveals that the boronic anhydride acts as a catalyst even in the heterogeneous polymerization system.

2-3-2 Copolymerization of HBA and HNA

Poly(4-oxybenzoyl-*co*-2-oxy-6-naphthoyl) is usually prepared by the melt polymerization of *p*-acetoxybenzoic acid and 2-acetoxy-6-naphthoic acid. The viscosity of the melt polycondensation limits the molecular weight, and the efficient elimination of acetic acid

from the polymerization phase is of importance to gain high molecular weight copolymers. Further, copolymers usually show high melting temperature and this makes difficult to extrude the polymers from a reaction vessel. To overcome these problems, one procedure has been to prepare oligomers by the melt polycondensation, followed by a subsequent solid-state polymerization. [19] Another procedure has been to prepare the copolymers in an inert solvent. The polymerization proceeded in dispersion and coarse granules consisting of small particles are ultimately obtained in this procedure. [20, 21] In this polymerization, the small particle size and high surface area of droplets allow rapid removal of the by-product, leading to higher molecular weight than that prepared by the melt polycondensation. [22] Based on these previous studies, the copolymerization of HBA and HNA was also examined in the presence of BPBA at c_B of 100 mol% with varying the value of r_f. The results are presented in Figures 2-5 and 2-6. The value of r_p was determined by the HPLC analysis after hydrolysis. Their chemical structures were also analyzed by the IR spectroscopy. Figure 2-1(b) shows an IR spectrum of the precipitates formed with BPBA at c_B of 100 mol% at r_f of 50 mol% as a representative. Carbonyl and ether bands of ester linkage are clearly observed at 1734 and 1179 cm^{-1}. In addition, bands of 1,4-phenylene group and 2,6-naphthylene group are visible at 1599 cm^{-1} and 1629 cm^{-1}, respectively. Additionally, the bands corresponding to the end groups are hardly visible. This spectrum indicates the formation of a high molecular weight copolymer. In all copolymerizations, the value of r_p was lower than that of r_f, indicating that

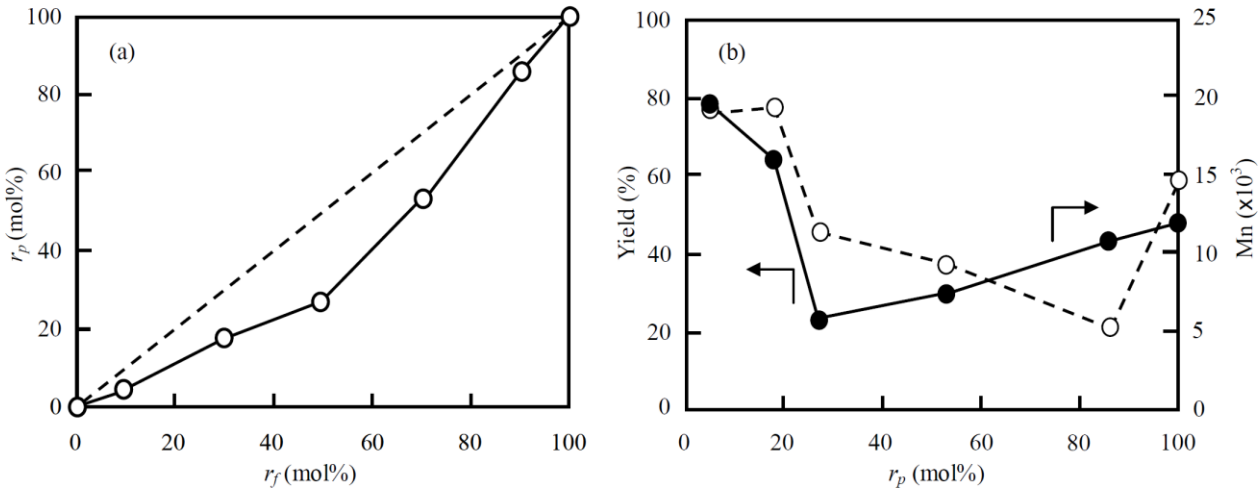


Figure 2-5 Plots of (a) relation between r_f and r_p, and (b) yield (●) and M_n (○) as a function of r_p of precipitates prepared in the presence of BPBA at c_B of 100 mol% for 24 h.

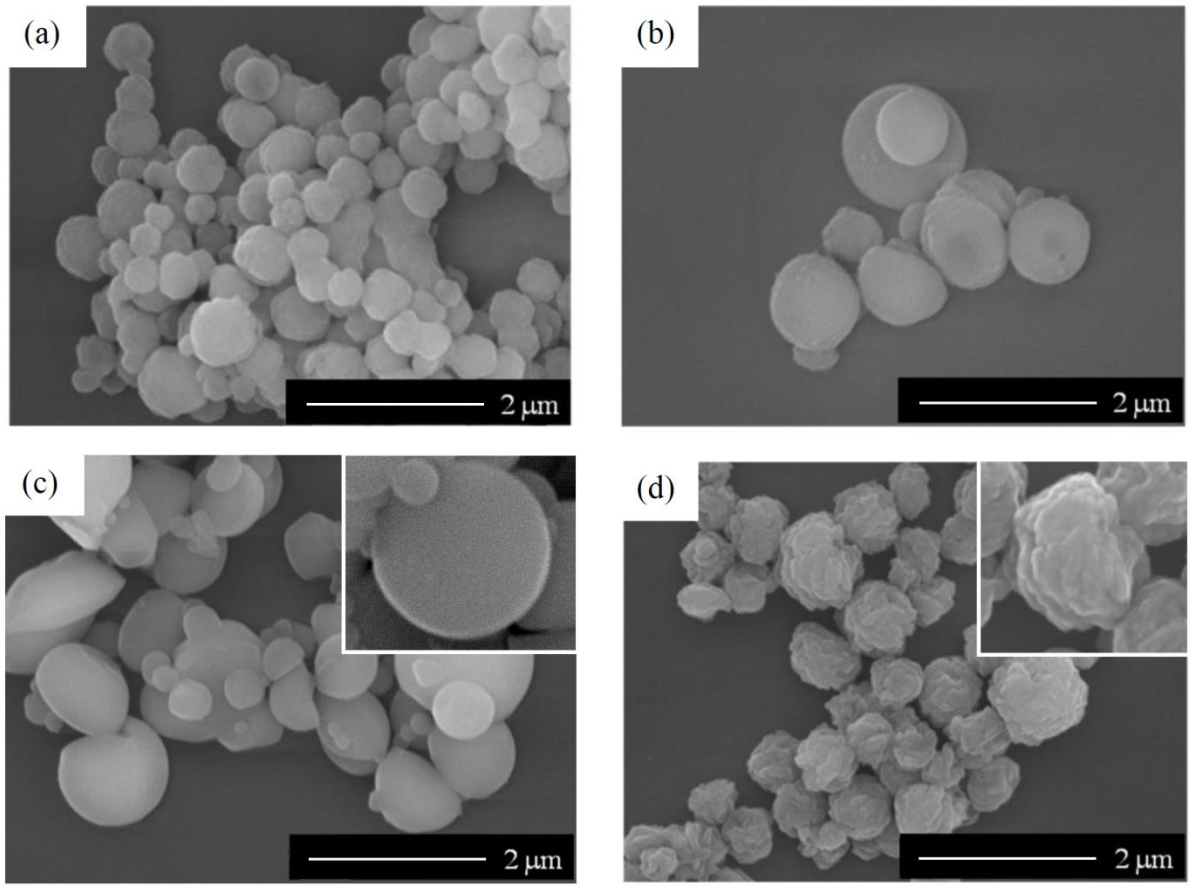


Figure 2-6 Copolymer precipitates prepared in the presence of BPBA at c_B of 100 mol% at r_f of (a) 10, (b) 50, (c) 70 and (d) 90 mol%.

the oligomers rich in ON moiety were precipitated more rapidly than those rich in OB moiety due to lower solubility. The spheres were formed as precipitates, as shown in Figure 2-6. Although the spheres having rugged surface were formed at r_f of 90 mol%, those prepared at r_f of 10–70 mol% possessed smooth surface. The diameter of the spheres was approximately 0.4–1.7 μm. Transition temperatures from crystal phase to anisotropic melt phase (T_{KN}) of copolymers highly relates to the value of r_p, and it becomes lower than 300 ^oC when the value of r_p is in the range from 30 to 78 mol%. [7, 18] The copolymerization makes the freezing point of the oligomers lower, leading to the liquid–liquid phase separation rather than crystallization. The spherical morphology was formed *via* the liquid–liquid phase separation at r_f of 50–90 mol%, and the polymerization occurred in the discontinuous dense phase. Further, the copolymerization generally lowers the crystallizability of the oligomers bringing about to extinguish clear crystal habit. These tendencies caused the formation of the spherical morphology in copolymerization system. The yield of the precipitates decreased with the decrease in the value of r_f until 50 mol% and then increased. The r_f of 50 mol% gave the minimum yield of 23%. The solubility of the oligomers also relates to the value of r_f and generally it becomes maximum at the middle range of the composition, leading to the minimum yield of the precipitates at r_f of 50 mol%. The M_n also became lower with the copolymerization. Figure 2-7 shows the WAXS intensity profiles of the spheres of the copolymers. Crystalline peaks became broader and disappeared in the middle range of r_f and

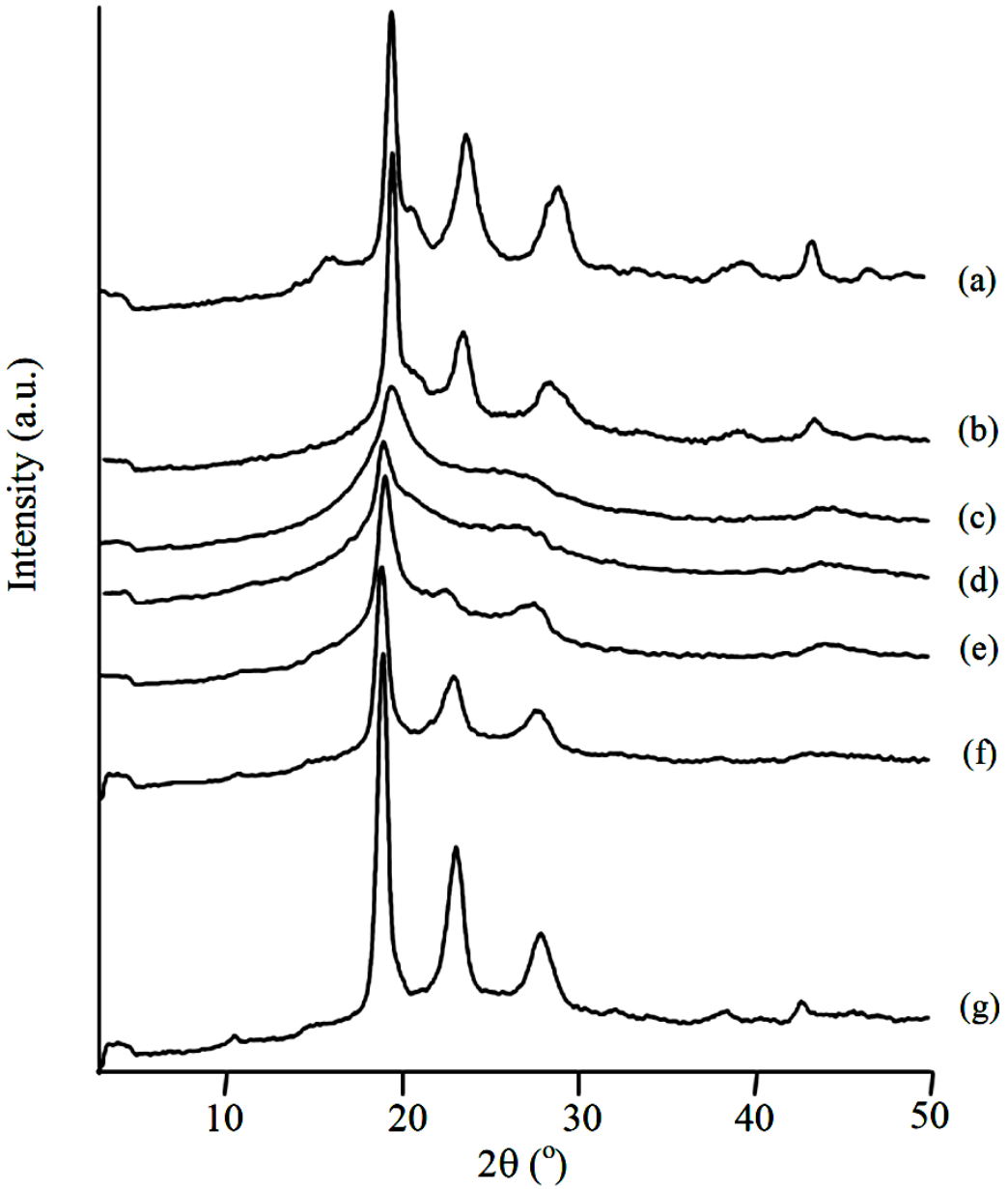


Figure 2-7 WAXS intensity profiles of copolymers at c_B of 100 mol% at r_f of (a) 100, (b) 90, (c) 70, (d) 50, (e) 30, (f) 10 and (g) 0 mol%.

the crystallinity of the spheres prepared in the middle range of r_f became lower. The spheres prepared at r_f of 90 mol% possessed relatively high crystallinity, being attributed to the rugged surface.

Changes in the yield, the M_n and the value of r_p were examined during the polymerization at r_f of 70 mol%. Figure 2-8 plots the results as a function of polymerization time. The yield increased very slowly with time until 18 h and then it became constant. The M_n increased linearly with time and it reached 13.5×10^3 after 36 h. In the polymerization of HNA, the M_n also increased with time as aforesaid. However, the M_n did not increase linearly throughout the polymerization. It increased gradually after the yield was leveled off, being attributed to the solid-state polymerization. In the copolymerization at r_f of 70 mol%, the polymerization occurred in the dense phase and the oligomers were supplied very slowly from the dilute solution phase to the dense phase. Because of these, the polymerization rate apparently obeys the second-order kinetics throughout the polymerization. With respect to the composition, the value of r_p was not constant throughout the polymerization. The value of r_p was 66 mol% for 6 h, and afterward it decreased gradually to 54 mol% with the increase in the yield until 18 h. In the initial stage of the polymerization, the oligomers rich in OB moiety were precipitated and then the oligomers rich in ON moiety started to be gradually precipitated with time. This fact provides a possibility that the copolymers have sequence gradations or the spheres are comprised of a mixture of copolymers having different composition. The sequence of the

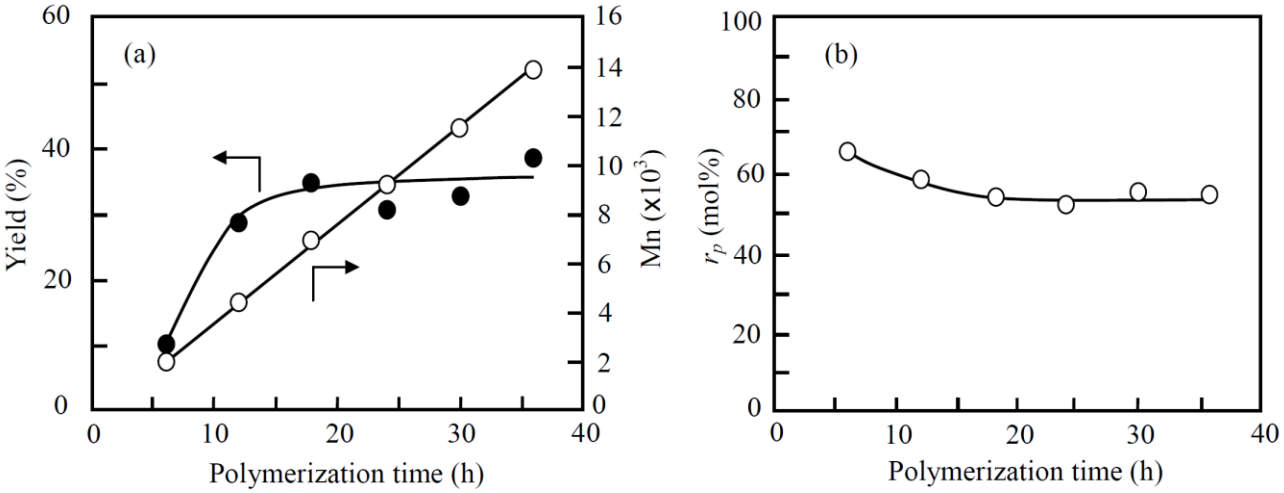


Figure 2-8 Plots of (a) yield (●) and M_n (○), and (b) r_p of copolymer prepared r_f of 70 mol% as a function of polymerization time. Polymerizations were carried out in the presence of BPBA at c_B of 100 mol%.

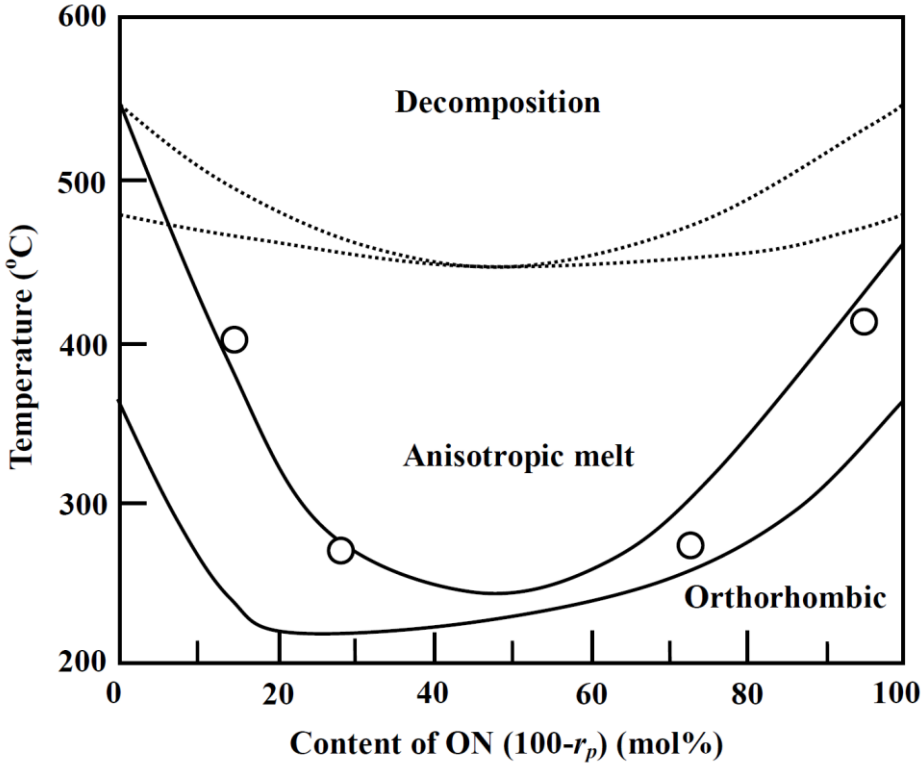


Figure 2-9 Plot of T_{KN} (○) as a function of content of ON on a phase-diagram previously reported in ref. 18.

prepared copolymers could not be directly analyzed by NMR because of insolubility. It is well known that T_{KN} is significantly influenced by not only the composition but also the sequence of copolymer even at the same composition. [23] T_{KN}s of the copolymers measured on a DSC were plotted as a function of the content of ON moiety (100-r_p mol%) on the phase-diagram previously prepared with the copolymers produced by the melt polymerization. [17] Figure 2-9 shows the plot. T_{KN}s of the copolymers prepared in this study are on the phase line between the crystal and the anisotropic phase, and they are in good agreement with the previous results. This good conformity indicates that the copolymers prepared in this study have not sequence gradation and they are random copolymers. The reshuffling reaction such as trans-esterification reaction takes place in the dense droplets at high temperature, leading to the randomization of the sequence.

2-4 CONCLUSIONS

The morphology of the PON precipitates was influenced by not only the structure of the boronic anhydride but also the value of c_B. Spheres with needles on their surface were obtained in the polymerization with TFBA at c_B of 50–70 mol%, and those having smooth surface were formed at c_B of 100 mol%. These precipitates possessed high crystallinity and the M_n increased with the value of c_B in the range from 2.7×10^3 to 9.0×10^3. With respect to

the polymerization with BPBA, the aggregates of conelike crystals were formed at c_B of 10–30 mol% and spheres having rugged surface were formed at c_B of 50–100 mol%. The M_n also increased with the value of c_B in the range from 5.4×10^3 to 12.9×10^3 and it became the highest at c_B of 100 mol%. The M_n prepared with BPBA was higher than that with TFBA at the same c_B value. When the value of c_B was 100 mol%, all carboxylic end groups of the precipitated oligomers were converted to carboxylic boronic anhydride end groups which reacted with the phenolic hydroxyl end group in or on the crystals to afford high molecular weight. The copolymerization of HBA and HNA was also examined in the presence of BPBA at c_B of 100 mol% with varying the value of r_f. Polymerization proceeded in the droplet formed by the liquid–liquid phase separation in the middle range of r_f. Spheres were formed with high molecular weight, of which the value of r_p was lower than that of r_f. This indicates that the oligomers rich in ON moiety were precipitated more rapidly than those rich in OB moiety due to lower solubility.

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CHAPTER 3

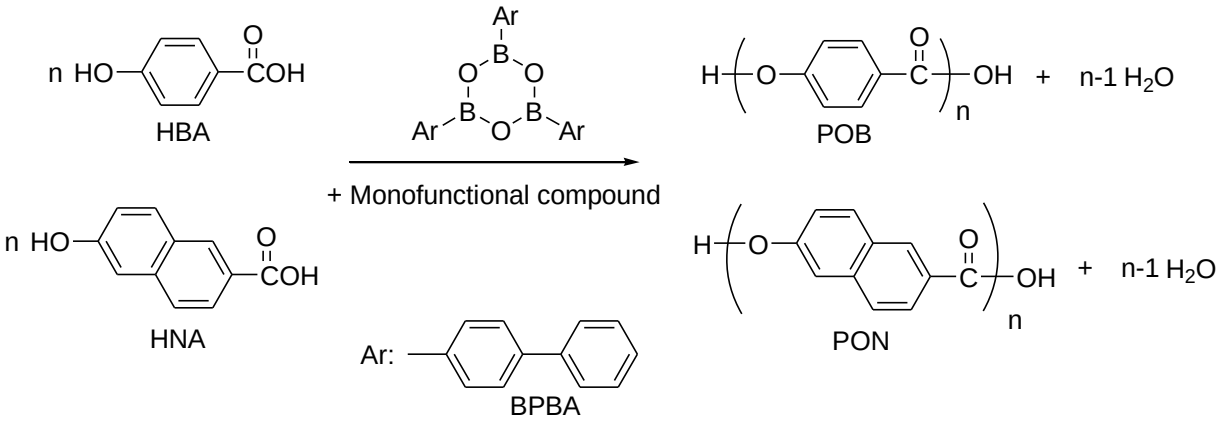
Preparation of Aromatic Polyesters by Direct Polymerization in the Presence of Boronic Anhydride under Non-stoichiometric Condition

3-1 INTRODUCTION

Poly(*p*-oxybenzoyl) (POB) and poly(2-oxy-6-naphthoyl) (PON) attract a great deal of attention as high-performance polymers possessing many excellent properties such as mechanical property, thermal stability, chemical resistance and so on. [1-5] These aromatic polyesters are usually synthesized by the polymerization of the corresponding acetoxy aromatic acids with elimination of acetic acids. Although these polyesters are expected to be high-performance materials, they show neither fusibility nor solubility owing to their rigid structure, and the intractability makes them difficult to process by conventional procedures. In general, copolymerization is applied to give them the fusibility, and the aromatic copolyesters are well known as thermotropic liquid crystalline polymers. The whiskers of POB and PON had been prepared by using reaction-induced crystallization of oligomers, and they are expected as to be high-performance fillers. [6-8] This reaction-induced crystallization of

oligomers during polymerization is a unique method to control the morphology of intractable polymers, because it cannot be limited by the intractability of polymers.

Direct synthesis of aromatic polyesters had also been developed as an elegant synthetic procedure, and numerous types of condensation reagents were developed so far. [9] These polymerizations are regarded as atom-economical syntheses and they will be widely accepted as environmental benign syntheses. It has been reported that the direct polymerization of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) in the presence of anhydride of boronic acid such as 2,4,6-tri(biphenyl-4-yl)-1,3,5,2,4,6-trioxatriborinane (BPBA) shown in Scheme 3-1, gave the precipitates of POB and PON crystals having unique morphology. [10, 11] In these polymerizations, BPBA activates the carboxyl group to react with the phenolic hydroxyl group in liquid phase. Even though the oligomers were precipitated from the solution to form the crystals, the polymerization occurred in the precipitated crystals to yield high molecular weight polymers.



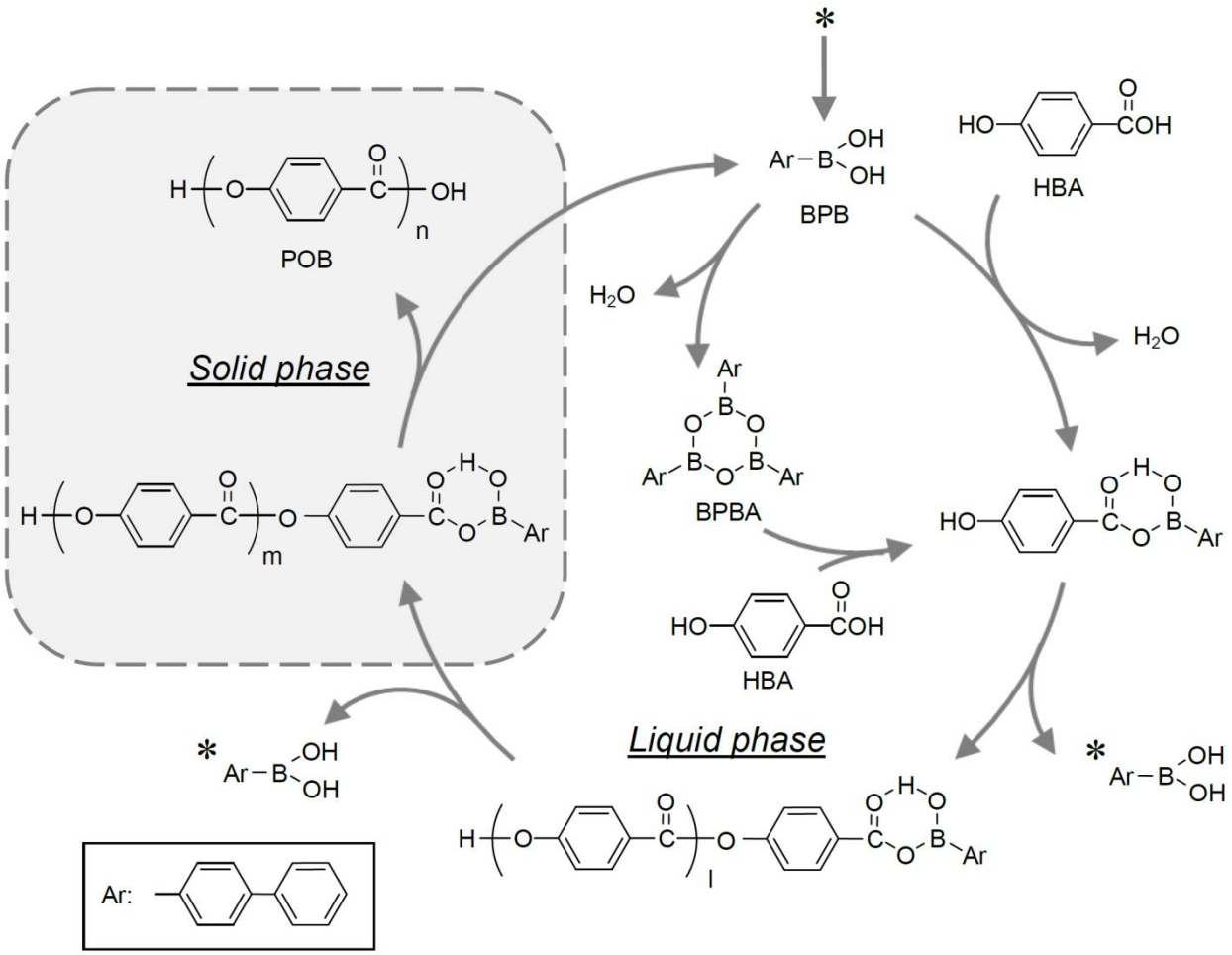
Scheme 3-1 Synthesis of POB and PON by direct polymerization of HBA and HNA in the presence of BPBA

It is well known that stoichiometric balance between two reactive groups is of the greatest importance to synthesize high molecular weight polymers by the step-growth polymerization. [12] If the polymerization is carried out in homogeneous system under non-stoichiometric condition, it is usually terminated and the molecular weight becomes lowered according to the following eq. (1).

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

Where, DPn: number-average degree of polymerization, N_0: number of monomers, N_1: number of monofunctional compounds, p: extent of reaction

Several unusual polymerizations which did not obey the equation (1) had been reported and high molecular weight polymers were obtained even under non-stoichiometric condition. [13-20] These unique polymerizations can be categorized into two groups chemically and physically based on the mechanism, of which one is attributed to the drastic change in the reactivity of functional groups and another is attributed to the heterogeneous reaction field. In the latter case, heterogeneous polymerization in which the polymerization proceeds with precipitation yields polymers having higher molecular weights than the theoretically calculated values even though the reactivity of functional groups does not change during



Scheme 3-2 Polymerization mechanism of HBA in the presence of BPBA

polymerization. The direct polymerizations of HBA and HNA in the presence of boronic anhydride are heterogeneous polymerizations as aforesaid, and they will be expected to afford high molecular weight polymers even under non-stoichiometric condition.

In this Chapter, the polymerizations of HBA and HNA in the presence of boronic anhydride were examined with the addition of monofunctional compounds such as an aromatic carboxylic acid and a phenol to clarify the influence of stoichiometric imbalance on molecular weight of POB and PON.

3-2 Experimental

3-2-1 Materials

HBA and HNA were prepared as described in Chapter 2. 4-Biphenylboronic acid (BPB) was prepared as previously mentioned in Chapter 1. BPB was converted into BPBA during the purification by recrystallization as confirmed by IR spectroscopy. [21-23] *p*-Hexyloxybenzoic acid (HOBA), 4-(4-hexyloxybenzoyloxy)benzoic acid (HBBA) and *p*-hexyloxyphenol (HOPH) were synthesized according to the previously reported procedures. [16, 19] 4-(4-Hexyloxyphenoxycarbonyl) phenol (HPCP) was synthesized according to the previously reported procedure. [24] An isomeric mixture of dibenzyltoluene (DBT) was purified by the same procedure as that described in Chapter 1.

3-2-2 Measurements

Morphology was observed on a HITACHI S-3500N scanning electron microscope (SEM). The details are described in Chapter 1. Infrared (IR) spectrum was measured on a JASCO FT/IR-410 spectrometer. Wide angle X-ray scattering (WAXS) was performed on a Rigaku Geigerflex with nickel-filtered CuKα radiation (35 kV, 20 mA). Number-average degree of

polymerization (DPn) was determined by the end group analysis using FT-IR and HPLC after hydrolysis according to the previous procedures. [6, 12, 15]

3-2-3 Polymerization

A polymerization of HBA with HOBA in the presence of BPBA at χ_{HOBA} of 20 mol% is described as a typical procedure.

HBA (0.55 g, 3.99 mmol), HOBA (0.22 g, 0.99 mmol) and 20 mL of DBT were placed into a cylindrical flask equipped with gas inlet and outlet tubes. Polymerization concentration was 3.0%, defined as (calculated polymer weight/solvent volume) x 100. The reaction mixture was heated under a slow stream of nitrogen up to 300^{o}C with stirring. HBA was dissolved during heating. Then, BPBA (0.90 g, 1.66 mmol) was added into the solution at 300^{o}C and stirring was stopped after BPBA was entirely dissolved. The mixture was heated at 300^{o}C for 24 h. The solution became turbid at an initial stage of the polymerization and precipitates were formed with time. Precipitated POB crystals were collected by vacuum filtration at 300^{o}C, and washed with *n*-hexane and acetone. The yield of the POB precipitates was 29%. The filtrate was poured into *n*-hexane and precipitated oligomers which were dissolved in the solution at 300^{o}C were collected by filtration. The recovered oligomers were washed with *n*-hexane and dried.

Polymerizations of HBA under other conditions and those of HNA were carried out in the similar manner.

3-3 RESULTS AND DISCUSSION

3-3-1 Polymerization under non-stoichiometric condition

The most suitable polymerization condition for the preparation of high molecular weight polymers was determined on the basis of the previous studies. [10, 11] The polymerizations of HBA or HNA were performed in a mixture of dibenzyltoluene at a concentration of 3.0% at 300^{o}C for 24 h in the presence of BPBA. The amount of BPBA was one third of the total amount of the carboxylic acid that was the equimolar amount of BPB moiety to the total amount of the carboxyl group. HOBA and HOPH, which were monofunctional compounds, were added to break the stoichiometric balance between the carboxyl group and the phenolic hydroxyl group in the polymerization system. These monofunctional compounds were not lost from the solution by sublimation and evaporation at the polymerization temperature owing to *p*-hexyloxy groups. Monomers and monofunctional compounds were insoluble in the solvent at 25^{o}C, but they became dissolved during heating. The molar ratios of HOBA and HOPH (χ_{HOBA} and χ_{HOPH}) were defined as the following equation to express the stoichiometric

imbalance.

$$\chi_{HOBA}\ (mol\%) = \{[HOBA] / ([HBA\ or\ HNA] + [HOBA])\} \times 100$$

$$\chi_{HOPH}\ (mol\%) = \{[HOPH] / ([HBA\ or\ HNA] + [HOPH])\} \times 100$$

The yields and the DPn values of POB and PON were plotted as a function of the χ values as shown in Figure 3-1. The polymerization of HBA under stoichiometric condition afforded the POB crystals having DPn of 79 with the yield of 38%. At the initial stage of polymerization, oligomers were formed in the solution by the polymerization. When the molecular weight of oligomers exceeded the critical values, the oligomers were precipitated *via* super-saturated state to form the crystals. In the precipitated crystals, further polymerization occurred simultaneously with the growth of the crystals by the consecutive supply of oligomers from the solution. BPBA activated the carboxylic acid to convert the carboxyl-boronic anhydride, [10, 11] and the anhydride group reacted with the phenolic hydroxyl group to form ester linkage with eliminating BPB. By-produced BPB was then reclaimed as BPBA with eliminating water and the reclaimed BPBA activated another carboxylic group as shown in Scheme 3-2. Concentration of oligomers in the solution phase decreased by the precipitation and the polymerization was practically terminated by the low concentration. Therefore, a certain amount of oligomers were left in the solution, resulting in

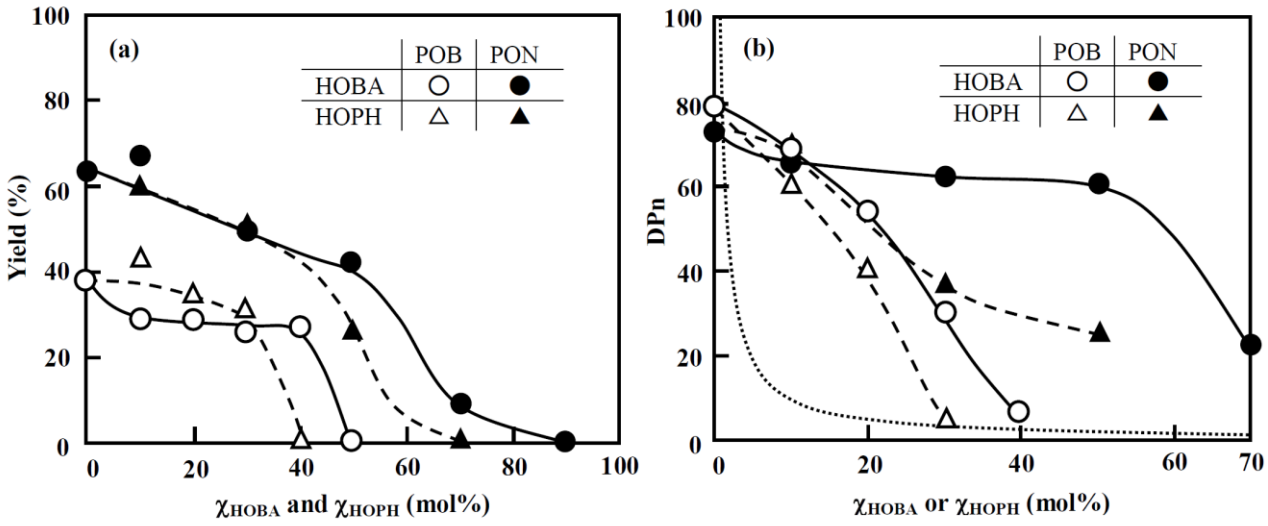


Figure 3-1 Plots of (a) yield and (b) DPn of precipitated POB and PON as a function of χ_{HOBA} (○, ●) and χ_{HOPH} (△, ▲). Polymerizations were carried out for 24 h. Dashed line in (b) is a curve calculated by eq. (1).

a lowering of the yield. In the polymerization of HBA with HOBA, the POB precipitates were obtained up to χ_{HOBA} of 40 mol% and χ_{HOPH} of 30 mol% with the yield of 28-44% as shown in Figure 3-1(a). The yields of the precipitates were not so high owing to the remaining of oligomers in the solution. IR spectra of the POB precipitates prepared at χ_{HOBA} of 20 mol% and the oligomers recovered from the solution were shown in Figure 3-2 as representatives. The characteristic band of ester C=O was clearly seen at 1739 cm^{-1}, and the bands of carboxyl C=O, carboxylic OH and phenolic OH were not visualized. The spectrum of the precipitates is identical with that of POB, suggesting the formation of high molecular weight. On the other hand, the bands of carboxyl C=O, carboxylic OH and phenolic OH were seen in the spectrum of the recovered oligomers, besides that of ester C=O. Additionally, the C-H band of

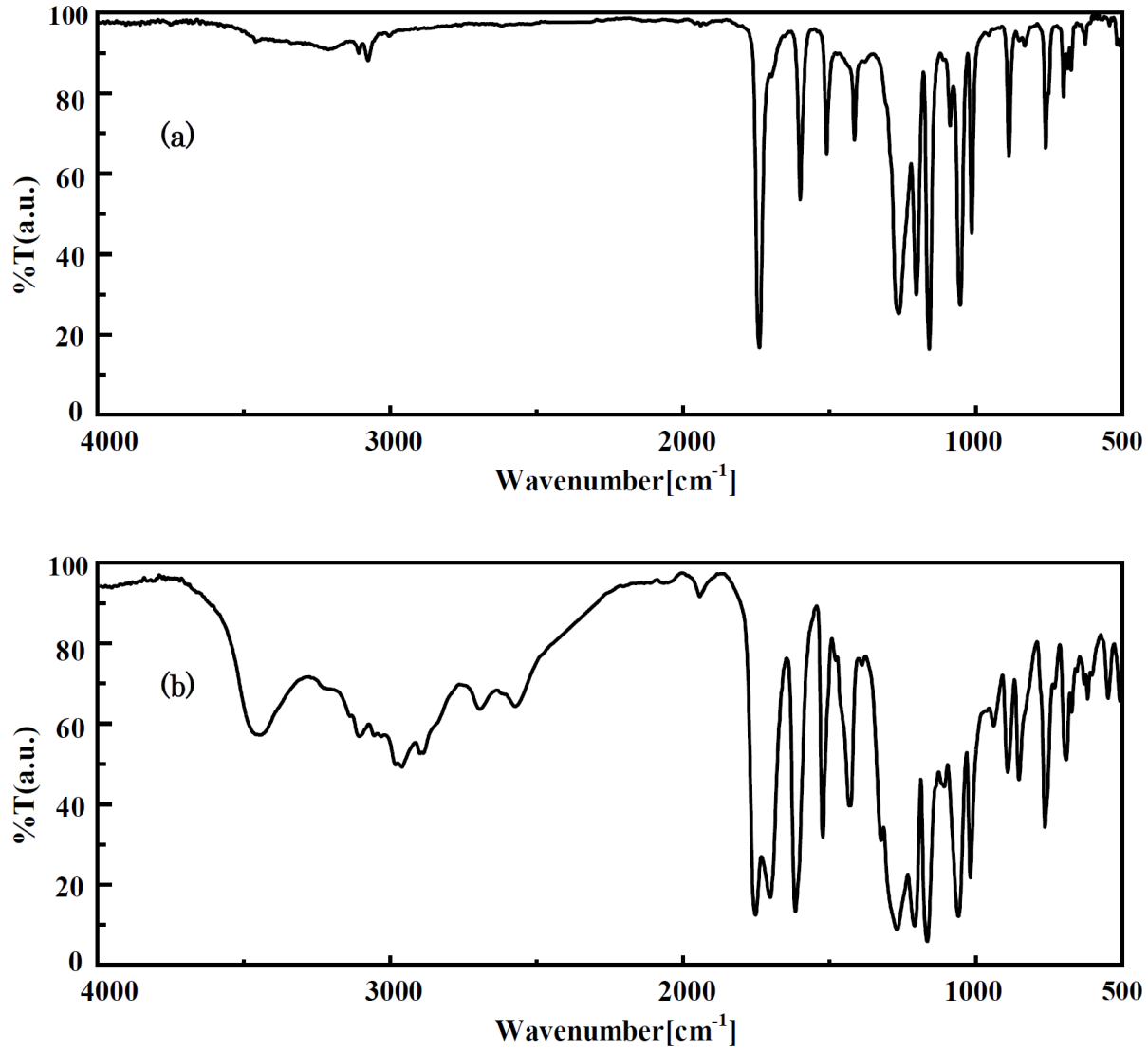


Figure 3-2 IR spectra of (a) precipitated POB and (b) oligomers recovered from solution. Polymerization was carried out at χ_{HOBA} of 20 mol% for 24 h.

p-hexyloxy group was observed at 2866-2938 cm^{-1}. It is noteworthy that the DPn of the precipitates is much higher than the DPn calculated according to the eq. (1). Even though the calculated DPn at χ of 20 mol% is only 5, the DPn values of the POB precipitates prepared at χ_{HOBA} of 20 mol% and at χ_{HOPH} of 20 mol% were 54 and 40, corresponding to the number-average molecular weight (M_n) of 6.7 x 10^3 and 5.0 x 10^3, respectively. The critical χ

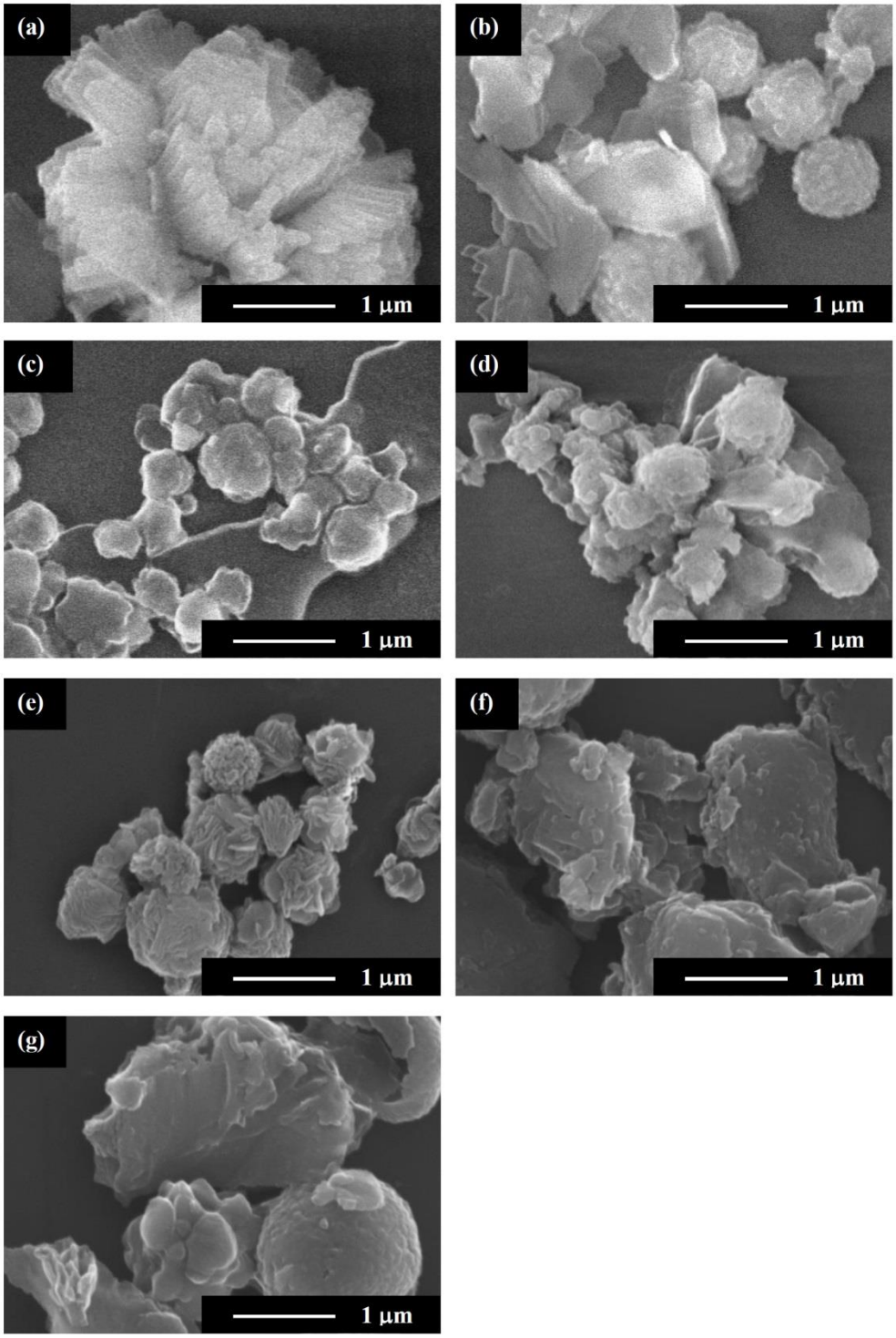


Figure 3-3 POB precipitates prepared for 24 h at χ_{HOBA} of (a) 0 mol%, (b) 10 mol%, (c) 20 mol% (d) 30 mol%, and at χ_{HOPH} of (e) 10 mol%, (f) 20 mol% and (g) 30 mol%.

value of the POB precipitates and the DPn values obtained with HOBA are higher than those with HOPH. This difference will be discussed later. The morphology of the POB precipitates prepared with HOBA and HOPH were shown in Figure 3-3. Fibrillated slab-like or pillar-like POB crystals were formed by the polymerization without monofunctional compounds, but the crystal habit disappeared gradually with the value of χ_{HOBA} and χ_{HOPH}.WAXS intensity profiles of the POB precipitates were shown in Figure 3-4. X-ray powder intensity profiles were measured by the reflection mode, and all samples were measured under the same conditions. Diffuse halo attributed to amorphous regions was hardly detected and the crystals possessed high crystallinity. Diffraction peaks were observed at 2θ of 15.6, 17.0, 19.3, 19.8, 23.5, 28.6, 37.9 and 42.9^{o} assignable with two different orthorhombic unit cells of the POB crystal; phase I (a = 0.745, b = 0.564, c = 1.247 nm) and phase II (a = 1.115, b = 0.380, c = 1.256 nm) marked in Figure 3-4. [25] Crystallinity became lower with the χ as well as the morphology. These precipitates contained both crystal structure of the phase I and II, and the relative amount of the phase II increased with the χ values. It is well known that the appearance of the phase II was attributed to the bulkiness of oligomer end group. [10, 24, 26] Therefore, the increase in the relative amount of the phase II and the decrease in the crystallinity can be explained by the increase in the amount of the bulky end groups derived from HOBA, being good agreement with the change in the DPn with the χ value.

In the polymerization of HNA, PON was formed as precipitates in the presence of

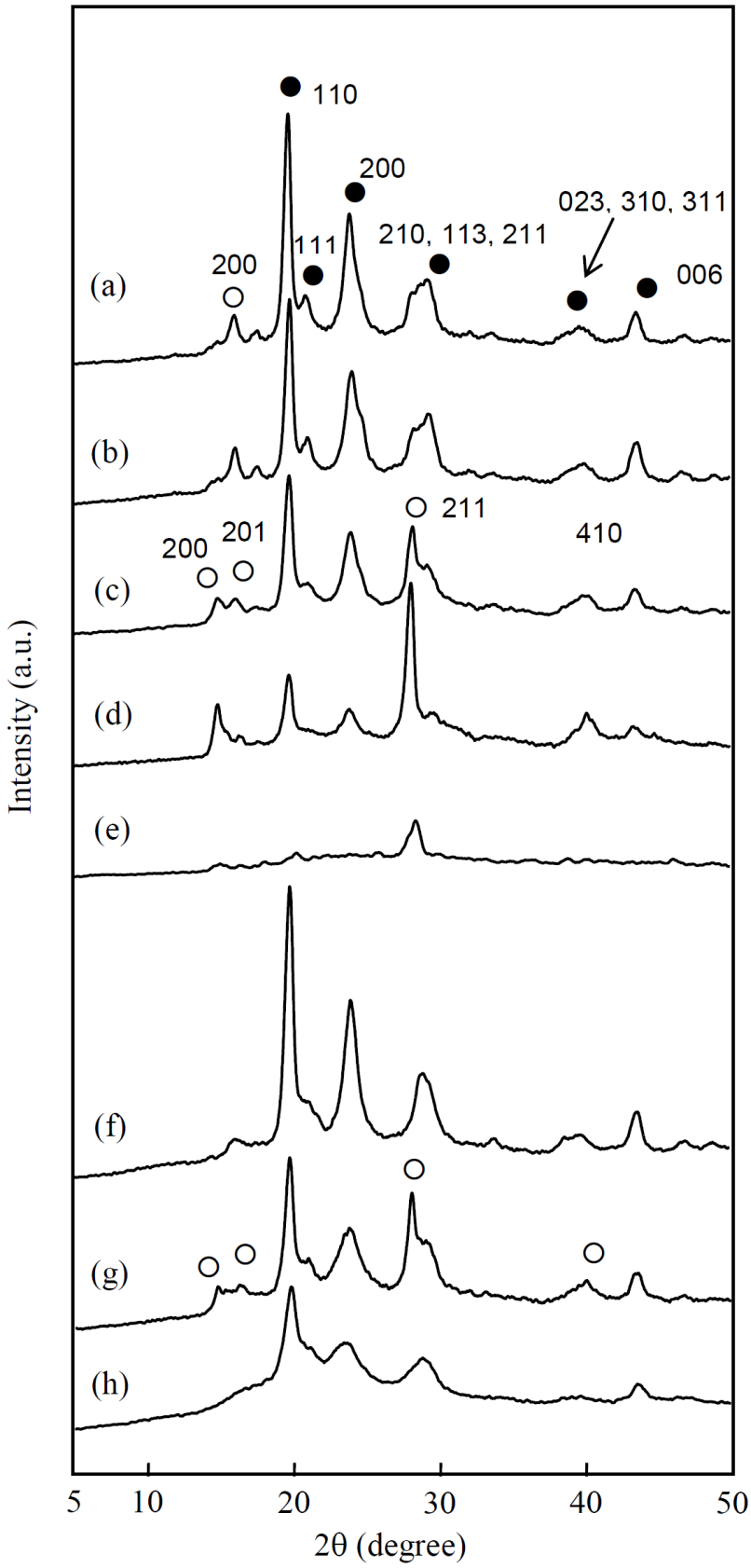


Figure. 3-4 WAXS intensity profiles of POB crystals prepared for 24 h at χ_{HOBA} of (a) 0 mol%, (b) 10 mol%, (c) 20 mol%, (d) 30 mol%, (e) 40 mol%, and at χ_{HOPH} of (f) 10 mol%, (g) 20 mol% and (h) 30 mol%. Diffraction peaks of phase I and phase II are marked by ● and ○, respectively.

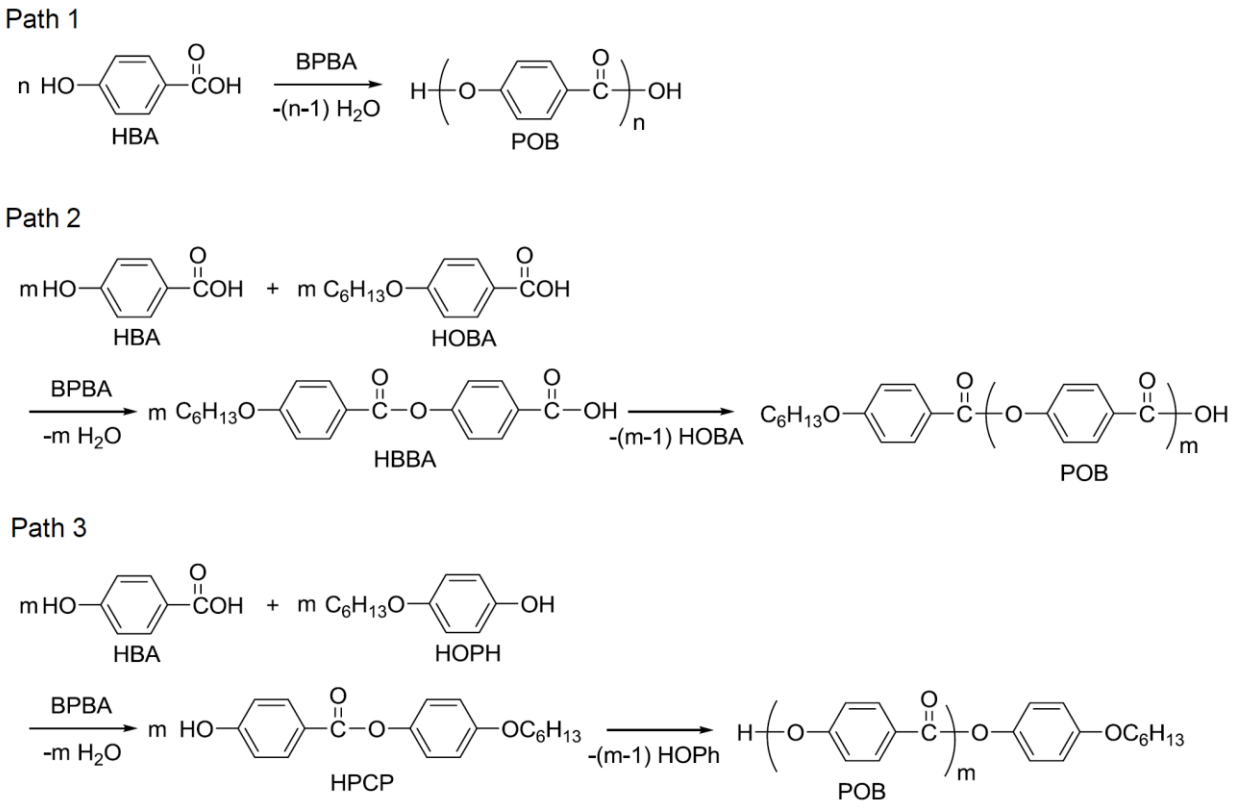
monofunctional compounds as well as POB as shown in Figure 3-1. While the morphology of the precipitates became unclear with increase in the χ values, they were spherical precipitates. WAXS intensity profiles of the PON precipitates were measured and the precipitates possessed higher crystallinity at lower χ values as well as POB. The yield decreased with the χ values, but the yields at χ_{HOBA} and χ_{HOPH} of 50 mol% were 42 and 26%, respectively. The yield of PON was higher than that of POB throughout the χ values, and the χ values critical to precipitate PON was larger than those of POB. In terms of DPn, the DPn values of the PON precipitates prepared at χ_{HOBA} and χ_{HOPH} of 50 mol% were 61 and 26, corresponding to M_n of 1.06×10^4 and 4.6×10^3 respectively. The DPn values of the PON precipitates prepared under non-stoichiometric condition were much higher than those calculated by eq. (1) as well as POB. In this study, the yields and the DPn values of the PON precipitates were larger than those of POB precipitates, being attributed to the lower solubility of the PON oligomers than the POB oligomers.

3-3-2 Polymerization behavior under non-stoichiometric condition

Based on the previous studies, [16, 19] it might be expected that oligomers end-capped by monofunctional compounds are precipitated to form the crystals, but the molecular weight increases by further polymerization in the crystals with the elimination of monofunctional

compounds by ester exchange reaction as shown in Scheme 3-3. In order to prove the mechanism for the increase in the molecular weight under non-stoichiometric condition, the change in the yield and the DPn of the POB precipitates were examined in the course of the polymerization at χ of 20 mol%. The results were plotted as a function of polymerization time as shown in Figure 3-5 with those prepared under stoichiometric condition (χ = 0 mol%). The yield and the DPn increased with time continuously within 24 h and then they increased slowly in the polymerization under stoichiometric condition. On the other hand, they also increased with time in the presence of HOBA, but the behaviors were quite different. The increase in the yield and the DPn was divided into four periods as shown in Figure 3-5 (a).

Both increased with time until 6 h (Period I), and then became constant until 12 h (Period II). Afterward, they increased again with time until 24 h (Period III), and finally became constant (Period IV). This unique behavior can be explained as follows; the oligomers were formed in the solution by direct polymerization, and then oligomers were precipitated *via* the super-saturation state as aforesaid. Owing to this, the yield and the DPn increased with time in Period I. The carboxyl group of HOBA was also activated by BPBA as well as that of HBA, and HOBA reacted with phenolic hydroxyl group, resulting in the formation of oligomers end-capped by HOBA. Hence, the plateau region of the yield and the DPn appeared in Period II. Oligomers end-capped by HOBA also polymerized with the elimination of HOBA by the ester exchange reaction in the solution, [16] and then oligomers started to precipitate in Period



Scheme 3-3 Possible polymerization reactions under non-stoichiometric condition

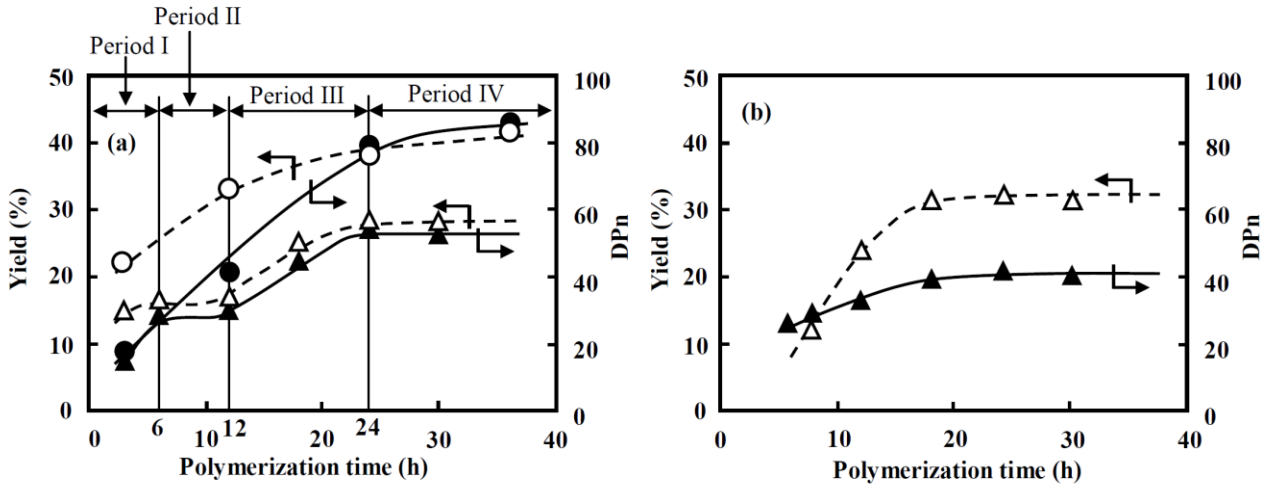


Figure 3-5 Plots of yield and DPn of precipitated POB prepared under stoichiometric condition (○, ●) and non-stoichiometric condition (△, ▲) at (a) χ_{HOBA} and (b) χ_{HOPH} of 20 mol% as a function of polymerization time.

III. After 24 h, the precipitation of oligomers stopped and the polymerization in the crystals finished in Period IV. The kinetics of HBA and HBBA were examined by the end group analysis to bear out the above mechanism. The kinetics in the solution and those in the precipitates were plotted in Figure 3-6 (a) and (b), respectively. DPn increased linearly with time, and hence it clearly shows that these reactions obeyed the second-order kinetics. The second-order rate constants (k_2) estimated by the slopes of these plots were presented in Table 3-1. The k_2 value of the polymerization of HBA with BPBA was 1.4×10^{-1} L mol^{-1} min^{-1} (Path 1 in Scheme 3-3). The k_2 value of the polymerization of HBBA, which was a model compound of a oligomers end-capped by HOBA, without BPBA was 1.0 L mol^{-1} min^{-1}, and it was 7 times larger than that of HBA. However, the k_2 value of the polymerization of HBBA with BPBA was 1.6×10^{-1} L mol^{-1} min^{-1} which was almost equal to that of HBA (Path 2 in Scheme 3-3). The ester exchange reaction between *p*-hexyloxybenzoyl group and carboxyl-boronic anhydride group proceeds more slowly. Based on this, the both polymerizations which were the direct polymerization and the ester exchange polymerization occurred in the solution. However, the solubility of the oligomers end-capped by HOBA must be much higher than that of end-free oligomers which were not end-capped, and the end-capped oligomers were not precipitated in Period II. In Period III, the molecular weight of the end-capped oligomers increased with elimination of HOBA by the ester exchange reaction and end-capped oligomers began to precipitate *via* the super-saturated state, resulting

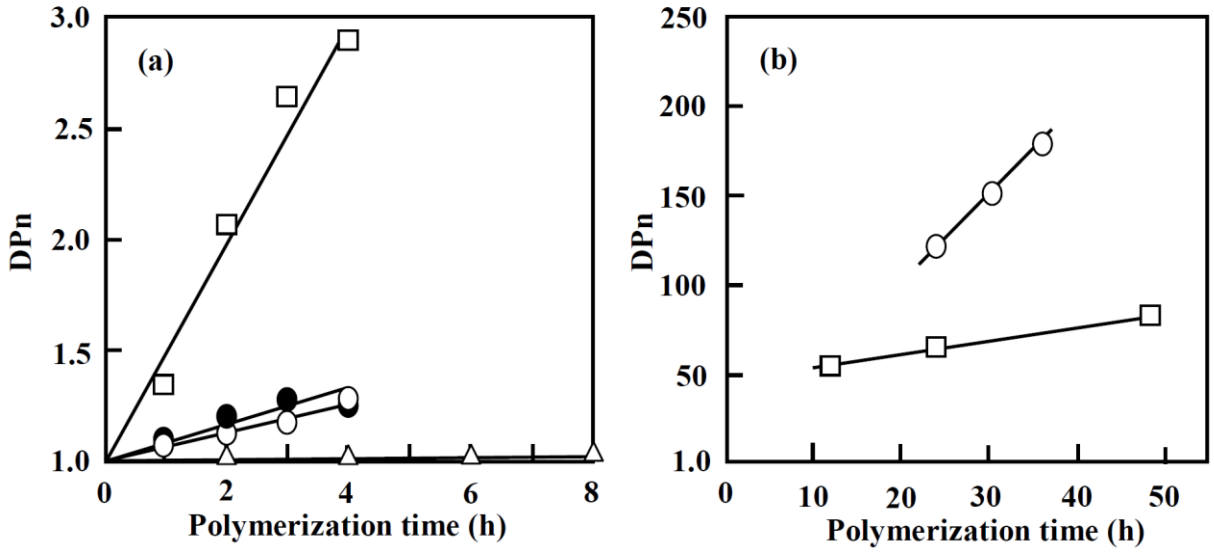


Figure 3-6 Kinetic plots of polymerization carried out at a concentration of 8.3×10^{-2} mol·L^{-1} at 300°C in (a) solution and (b) solid. □: HBBA without BPBA, ●: HBBA with BPBA, ○: HBA with BPBA, and △: HPCP without BPBA

Table 3-1 Second-order kinetic constants of polymerization of HBA and HBBA in solution and solid phase [a]

Phase	Monomer	Concentration of BPBA [b] (mol%)	k_2
Solution	HBA	100	1.4×10^{-1} L·mol^{-1}·min^{-1}
Solution	HBBA	0	1.0 L·mol^{-1}·min^{-1}
Solution	HBBA	100	1.6×10^{-1} L·mol^{-1}·min^{-1}
Solution	HPCP	0	3.0×10^{-3} L·mol^{-1}·min^{-1}
Solid	HBA	100	1.1 kg·mol^{-1}·min^{-1}
Solid	HBBA	0	8.2×10^{-2} kg·mol^{-1}·min^{-1}

[a] Polymerizations were carried out at a concentration of 8.3×10^{-3} mol·L^{-1} at 300°C. [b] [BPBA] × 3 / [Carboxylic Acid] ×100

in the increase in the yield. The k_2 values of the polymerization of HBA and HBBA in the precipitates were 1.1 and 8.2 x 10^{-2} kg mol^{-1} min^{-1}, respectively. Precipitation did not occur in the polymerization of HBBA with BPBA owing to the higher solubility of oligomers, and hence the k_2 value could not be estimated. The polymerization of end-free oligomers proceeded much faster than that of end-capped oligomers in the precipitates, but the end-capped oligomers were also polymerized gradually with elimination of HOBA. When the crystal grew by the precipitation of oligomers, bringing about the increase in the yield, the polymerization occurred not only in the crystals but also at the crystal growth step during the registration of oligomers into the crystals. Therefore, the DPn increased again with the yield in Period III. In contrast to this, the DPn increased monotonously with the yield in the polymerization of HBA in the presence of HOPH as shown in Figure 3-5(b). In this polymerization, oligomers end-capped by HOPH can also polymerize with the elimination of HOPH by the ester exchange reaction in the solution. [19] The k_2 value of the polymerization of HPCP, which was a model compound of a oligomer end-capped by HOPH, in the solution was 3.0 x 10^{-3} L mol^{-1} min^{-1} (Path 3 in Scheme 3-3), and it was 46 times lower than that of HBA. Additionally, the oligomers end-capped by HOPH must have higher solubility than end-free oligomers, resulting in the inhabitation of the precipitation. Owing to these, the yields and the DPn increased monotonously with time.

3-4 CONCLUSIONS

The polymerizations of HBA and HNA in the presence of BPBA afforded high molecular weight POB and PON in the form of the precipitate under non-stoichiometric condition. The calculated DPn at χ of 20 mol% was only 5 but, nevertheless, the DPn values of the POB precipitates prepared at χ_{HOBA} of 20mol% and at χ_{HOPH} of 20mol % were 54 and 40, corresponding to M_n of 6.7×10^3 and 5.0×10^3, respectively. In the case of PON, those prepared at χ_{HOBA} and χ_{HOPH} of 50 mol% were 61 and 26, corresponding to the M_n of 1.06×10^4 and 4.6×10^3 respectively, which were much higher than the calculated DPn values. The polymerization mechanism was considered as follows; oligomers were prepared by the direct polymerization of HBA with eliminating water in the solution, and then they were precipitated to form the crystals at the initial stage of the polymerization. Oligomers end-capped by monofunctional compounds were also formed in the solution, but the polymerization was not terminated. It continued with the elimination of monofunctional compounds by the ester exchange polymerization, and therefore the end-capped oligomers were precipitated in the middle of the polymerization. The polymerization occurred even in the precipitated crystals by not only the direct polymerization but also the ester exchange polymerization, resulting in the increase in molecular weight. The direct polymerizations of HBA and HNA by using the reaction-induced crystallization of oligomers were not significantly susceptible to the

stoichiometric imbalance between two functional groups.

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CONCLUDING REMARKS

In general, *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) cannot polymerize by themselves to yield poly(*p*-oxybenzoyl) (POB) and poly(2-oxy-6-naphthoyl) (PON), because carboxyl groups have not enough reactivity for the condensation reaction with phenolic hydroxyl groups. Accordingly, it has been developed that using numerous types of condensation reagents and converting the carboxyl or the phenolic hydroxyl group into highly reactive groups such as phenyl esters or alkyloxy groups so far.

In this thesis, direct polycondensations of HBA and HNA proceed in the presence of boronic anhydrides by using the reaction-induced phase separation of oligomers. In this polymerization, boronic anhydrides or boronic acids react with carboxyl groups to convert more active carboxylic boronic anhydrides, and then the activated anhydride groups react with phenolic hydroxyl groups to form the ester linkages with elimination of harmless water and boronic acids. It suggests that boronic anhydrides and boronic acids are catalysts, not condensation reagents. It is an environmentally benign polymerization procedure because the atom efficiency of reaction improves and by-product of reaction is harmless water.

In Chapter 1, POB crystals were prepared by the reaction-induced crystallization during direct polymerization of HBA in the presence of boronic anhydrides. Polymerizations were carried out at 300^{o}C in dibenzyltoluene at a concentration of 1% with three kinds of

anhydrides of boronic acid such as 3,4,5-trifluorophenylboronic acid (TFB), 4-methoxyphenylboronic acid (MPB) and 4-biphenylboronic acid (BPB). The POB crystals were formed as precipitates in the solution and the morphology was considerably influenced by both the structure of the boronic anhydride and its concentration (c_B). Needle-like crystals were firmed in the presence of TFB anhydride (TFBA) at c_Bs of 5 and 10 mol % by the spiral growth of lamellae. Spherical aggregates of slab-like crystals were formed at c_Bs from 50 to 100 mol %. The polymerization with MPB anhydride and BPB anhydride (BPBA) also yielded the needle-like crystals at c_Bs of 50 and 5 mol %, respectively. The polymerization with TFBA at lower c_B was favorable to prepare the needle-like crystal. Molecular weight was also influenced by the structure of the boronic anhydride and c_B. M_n increased generally with c_B and BPBA gave the highest M_n of 14.7×10^3 at c_B of 100 mol %. The loose packing of the molecules in the crystal caused by the bulkiness of the end-groups made the polymerization in the crystals more efficiently. Morphology and molecular weight of the POB crystals could be controlled by the chemical structure and the content of boronic anhydride.

In Chapter 2, PON was obtained as precipitates by direct polymerization of HNA in the presence of boronic anhydrides such as TFBA and BPBA. The polymerizations were carried out in dibenzyltoluene at 300 ^oC for 24 h. Both morphology and molecular weight of the PON precipitates were considerably influenced by not only the structure of the boronic anhydride but also the value of c_B. Spheres with needles on their surface were formed in the

polymerization with TFBA at c_B of 50–70 mol%, and those having smooth surface were obtained at c_B of 100 mol%. The M_n increased with the value of c_B in the range from 2.7 x 10^3 to 9.0 x 10^3. Aggregates of cone-like crystals were prepared in the polymerization with BPBA at c_B of 10–30 mol%, and spheres having rugged surface were formed at c_B of 50–100 mol%. The M_n also increased with the value of c_B in the range from 5.4 x 10^3 to 12.9 x 10^3. These PON precipitates possessed high crystallinity in spite of the morphology. The copolymerizations of HNA and HBA were also examined in the presence of BPBA at c_B of 100 mol% with varying the content of HBA in feed (r_f). Copolymers were obtained as spheres of which the content of *p*-oxybenzoyl moiety was lower than the value of r_f due to the difference in the solubility of the oligomers.

In Chapter 3, direct polymerizations of HBA and HNA in the presence of boronic anhydride were examined by using crystallization under non-stoichiometric condition. The polymerizations were carried out with the addition of monofunctional compounds such as an aromatic carboxylic acid and a phenol. High molecular weight POB and PON were obtained in the form of precipitates, and their molecular weights were much higher than those calculated according to the stoichiometric imbalance. Oligomers were formed by the direct polymerization with eliminating water in the solution, and then they were precipitated to form the crystals at the initial stage of the polymerization. Oligomers end-capped by monofunctional compounds were also formed in the solution, but the polymerization

continued with the elimination of monofunctional compounds by the ester exchange reaction. The end-capped oligomers were precipitated in the middle of the polymerization, and the polymerization proceeded efficiently even in the precipitated crystals by not only the direct polymerization but also the ester exchange polymerization, resulting in the increase in molecular weight.

This research for the doctoral dissertation has afforded the new methodology to control the morphology and to prepare the high molecular weight of the wholly aromatic polyesters during direct polymerization in the presence of boronic anhydrides as catalyst by means of using the reaction-induced phase separation of oligomers.

LIST OF PUBLICATIONS

[1] Preparation of Poly(*p*-oxybenzoyl) Crystals using Direct Polymerization of *p*-Hydroxybenzoic Acid in the Presence of Boronic Anhydrides, Masahiro Kihara, Shin-ichiro Kohama, Shota Umezono, Kanji Wakabayashi, Shinichi Yamazaki and Kunio Kimura, *Journal of Polymer Science Part A:Polymer Chemistry,* 2011, **49**, 1088-1096

[2] Preparation of Poly(2-oxy-6-naphthoyl) and Copolymers using Reaction-induced Phase Separation during Direct Polymerization in the Presence of Boronic Anhydride, Masahiro Kihara, Shinichi Yamazaki and Kunio Kimura, *Polymer Chemistry*, 2011, **2**, 1195-1202,

[3] Preparation of Aromatic Polyesters by Direct Polymerization in the Presence of Boronic Anhydride under Non-stoichiometric Condition, Masahiro Kihara, Yuma Sakakiyama, Shinichi Yamazaki and Kunio Kimura, *Polymer*, 2015, **66**, 222-229

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