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CRYSTALLIZATION
OF AROMATIC POLYMERS
DURING SOLUTION POLYMERIZATION

(芳香族ポリマーの溶液重合結晶化に関する研究)

1994

KUNIO KIMURA

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Introduction

Recent years have seen dramatic development in the preparation of chain extended polymer crystals as high-performance materials due to their good mechanical properties. Usually, chain extended crystals are difficult to be obtained by conventional processing methods and therefore, the special processing techniques such as gel spinning and spinning from liquid crystalline solutions have been developed thus far.[1]

There exists another stream of development for chain extended polymeric materials by means of crystallization during polymerization. The needle-like crystals of both flexible and rigid chain polymers, so called polymer whiskers, have been obtained by the solid-state polymerization of the monomers and the polymerization in the solution. Examples of the former polymerization have included (1) oxacyclobutanes such as 1,3,5-trioxane,[2,3] (2) diolefins undergoing 'four-center type' photopolymerization[4,5] and (3) monomers with conjugated triple bonds such as substituted diacetylenes.[6,7] On the other hand, the first whisker obtained by the polymerization in solution system was polyoxymethylene.[8-10] This whisker was obtained in a cationic polymerization system of 1,3,5-trioxane and it had a width of 1-2μm and a length of 10-50μm. It was brought into practical use with its unique morphology and good mechanical property.[11,12] However, polyoxymethylene whisker has a melting temperature at 180℃ and therefore the low melting temperature limits the broader commercial utilization of this whisker.

Generally, wholly aromatic polymers comprising straight and rigid-rod molecular structures have been receiving much attention as potential candidates for high-performance materials because they are expected to possess excellent thermal stability, good mechanical properties and good chemical resistance as well as many other desirable properties. But, in many cases, they are not amenable to conventional processing techniques because of their infusibility, *i.e.* they have neither meltability or solubility. These properties and the processability are usually in trade-off relationship. In order to improve such infusibility, some chemical modification to reduce their rigidity or special processing techniques are necessary. There have been numerous studies on the improvement of infusibility of aromatic polymers by chemical modification.[13-29] However, the chemical modifications of their molecular structures result in the loss of these excellent properties because of the reduction of the rigidity. Further, there have been a few studies on the processing technique of aromatic polymers.[30] In spite of the impressive developments of newer aromatic polymers and processing techniques, it has been still very hard to educe the essential properties of wholly aromatic polymers.

The first trial for obtaining needle-like crystal of wholly aromatic polymer was reported in 1977.[31] Needle-like crystals of poly(1,4-benzamide) were prepared by solid-state thermal polymerization of needle-like crystals of 4-aminobenzoyl chloride in poor solvents containing acid acceptors. Resultant needle-like crystals were highly crystalline but the polymer chains were oriented crosswise of the long axis of the needle-like crystal.

The preparation method of polymer whisker by the polymerization in solution system, which is called 'crystallization during polymerization' is of very interest for the processing of infusible aromatic polymers into the extended polymer materials. That is, even infusible polymers can be processed by building monomers into some special crystal form one by one while polymerizing.

In 1976, the crystals of poly(p-oxybenzoyl) (POB) were obtained by crystallization during high-temperature solution polymerization. The crystals obtained were unexpectedly highly crystalline but they were slab-like crystals.[32] The polymer chains aligned along the direction of the thickness of the slab-like crystals.[30,33,34] In 1983, the fibrillar crystals of POB were prepared also by crystallization during high-temperature solution polymerization. The fibrillar crystals were chain extended polymer crystals in which the polymer chains aligned along the long axis of fibrils but they were aggregates of fibrillar crystals which were not separated.[35,36]

There have been some studies on the crystallization of aromatic polymers during polymerization as described but the whisker in which the polymer chains align along the long axis of crystal has never been obtained. Furthermore, systematic study on the relationship between the crystal morphologies and the conditions of crystallization during polymerization has not reported thus far.

The aim of this work is to establish the control method of the crystal morphology of aromatic polymers, especially infusible aromatic condensation polymers by means of crystallization during solution polymerization focusing on the synthesis of the polymer whisker.

The thesis consists of four chapters. In chapter 1, the relationship between the crystal morphologies of POB and the conditions of crystallization during high-temperature solution polymerization is widely studied and the synthesis of the POB whiskers is reported. Further, the characterization and the growth mechanism of the POB whisker are discussed. In chapter 2, the control method of the size of the POB whisker is studied from the viewpoint of polymerization solvents. Preparation of the POB whisker are carried out in paraffins with different chemical structures, and the dependence of the length and the width of the whisker on the chemical structure of paraffin is investigated. In chapter 3, crystallization of copolymers of POB with m-hydroxybenzoic acid during high-temperature solution polymerization is studied and a new concept for the polymerization with the molecular recognition is proposed. In chapter 4, crystallization of other aromatic condensation polymers than POB which include poly(2-oxy-6-naphthoyl), poly(4'-oxy-4-biphenylcarbonyl), poly(p-phenylene terephthalate) and poly(4-mercaptobenzoyl) during high-temperature solution polymerization is studied, focusing on the synthesis on the polymer whiskers.

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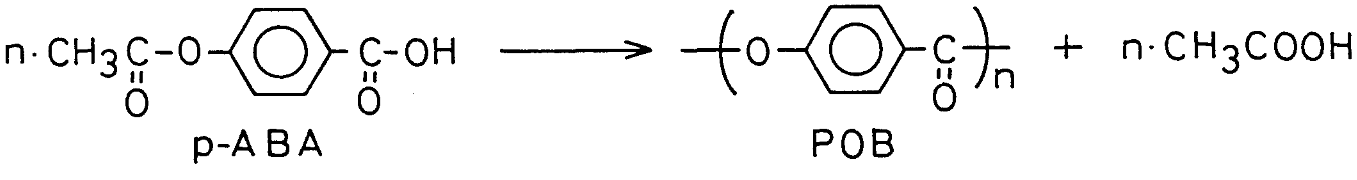
Chapter 1

Crystallization of Poly(p-oxybenzoyl) during Solution Polymerization

1-1 Introduction

Poly(p-oxybenzoyl) (POB) which is an aromatic condensation polymer of p-hydroxybenzoic acid has be expected to possess excellent mechanical properties such as modulus and strength, thermal stability and many other desirable properties due to its straight and rigid-rod molecular stracture. POB has been therefore receiving much attention as a potencial candidate for high-performan performance materials.[1-4]

First study on synthesis of POB was reported in 1954 by Hasegawa.[5] POB was tried to synthesize by bulk polycondensation of p-acetoxybenzoic acid (p-ABA) with the elimination of acetic acid at high temperature as described below.



Scheme 1-1. Synthesis of POB from p-ABA

However, POB having high molecular weight was not obtained by means of bulk polycondensation because of its infusibility. Afterwards, the studies on POB had been mainly continued to focus on the copolymerization of POB with m-acetoxybenzoic acid or other comonomers in order to improve the infusibility of POB.[6]

In 1973, Economy patented melt-processable copolymer of POB with 4,4'-biphenol and terephthalic acid.[7] This polyester surprisingly showed thermotropicity and this finding accelerated research in aromatic copolyesters. Many kinds of aromatic polyesters have been reported thus far and some of them have been commercially produced.[1,2,4]

In 1976, Economy developed a new synthetic method of POB which was a high-temperature polycondensation of p-ABA in aromatic heat exchange medium.[8-11] The polymerization reaction proceeded in a heterogeneous state, that is, POB was precipitated from the solution. The powdered POB obtained by this method had enough molecular weight and it showed extremely high thermal stability. Moreover, the powdered POB obtained was a highly crystalline slab-like crystal and they are commercially used as bearing materials from the stand point of good frictional resistance. But, the aforesaid infusibility of POB has not been overcome and high temperature compression sintering process which is normally reserved for forming ceramics is a only processing method for POB materials. The inherent properties of POB have not been educed yet. It is necessary for an eduction of the inherent properties of POB to orient polymer molecules regularly in the materials.

In 1983, Yamashita obtained the fibrillar POB crystals by high-temperature solution polycondensation of p-ABA in aromatic solvents at a low concentration of monomer under vigorous stirring.[12,13] The fibrillar crystals were chain extended polymer crystals in which the polymer chains aligned along the long axis of fibrils. However the fibrillar crystals were aggregates and not separated each other.

From the results of these studies, it seems possible to control the morphology of the POB crystal by means of the conditions of crystallization during high-temperature solution polymerization and ultimately to obtain the POB whisker which is a chain extended single crystal.

In this chapter, the relationship between the crystal morphology of POB and the conditions of crystallization during high-temperature solution polymerization are studied focusing on the synthesis of the POB whisker. Furthermore, the characterization and the growth mechanism of the POB whisker are also reported.

1-2 Synthesis of Poly(p-oxybenzoyl) Whisker

1-2-1 Experimental

Materials

Liquid paraffin (LP), diphenylsulfone (DPS), benzophenone (BP) and 4-chlorobenzophenone (CBP) were obtained from Nakarai Tesque Co. Ltd. Therm S 800 (TS800) which is a mixture of isomers of diethylbiphenyl was obtained from Nippon Steel Chemical Co. Ltd. LP, TS800 and DPS were purified by vacuum distillation. BP and CBP were used as received.

Monomer Synthesis

p-ABA

p-ABA was prepared as described in the literature.[5]

p-Propionyloxybenzoic acid (PBA)

A solution of 50g of propionyl chloride in 150ml of dichloroethane was poured into a vigorously stirred solution of 75g of p-hydroxybenzoic acid in 300ml of 3.7N-NaOH aq. at 0℃. The mixture was stirred vigorously at 0℃ for 30min, then at 25℃ for 1h. The plate-like crystals were precipitated by pouring the solution into acetone. The crystals were isolated, recrystallized from acetone twice and then dried at 60℃ under reduced pressure; Yield 63g (60%), m.p. 194℃. Chemical structure was confirmed by ^{1}H-NMR and infrared spectroscopy. Purity was checked by silica gel TLC (elution solvent; chloroform /methanol = 90/10 by volume).

p-Benzoyloxybenzoic acid (BBA)

BBA was prepared according to the procedure of PBA.

Phenyl-p-hydroxybenzoate (PHB)

PHB was prepared as described in a literature.[14]

Preparation of Poly(p-oxybenzoyl) Crystals

A typical preparation procedure of POB crystals is described in the following.

In a 200ml-cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were placed 0.9g of p-ABA and 60 ml of LP. The reaction mixture was heated with stirring under a slow stream of nitrogen unti the monomer was dissolved completely. Stirring was stopped, and then the solution was heated at 330℃ at a heating rate of 15℃/min. In a couple of minutes, the solution became turbid and then the crystals were precipitated. The solution was maintained at 330℃ for 6h. The polymer crystals / LP slurry was allowed to cool to room temperature and chloroform was added. The polymer crystals were isolated by filtration, washed several times with chloroform and acetone, and then dried at 100℃ under reduced pressure to a constant weight.

Measurements

Morphological characterization was performed on a Hitachi HU-11B scanning electron microscopy.

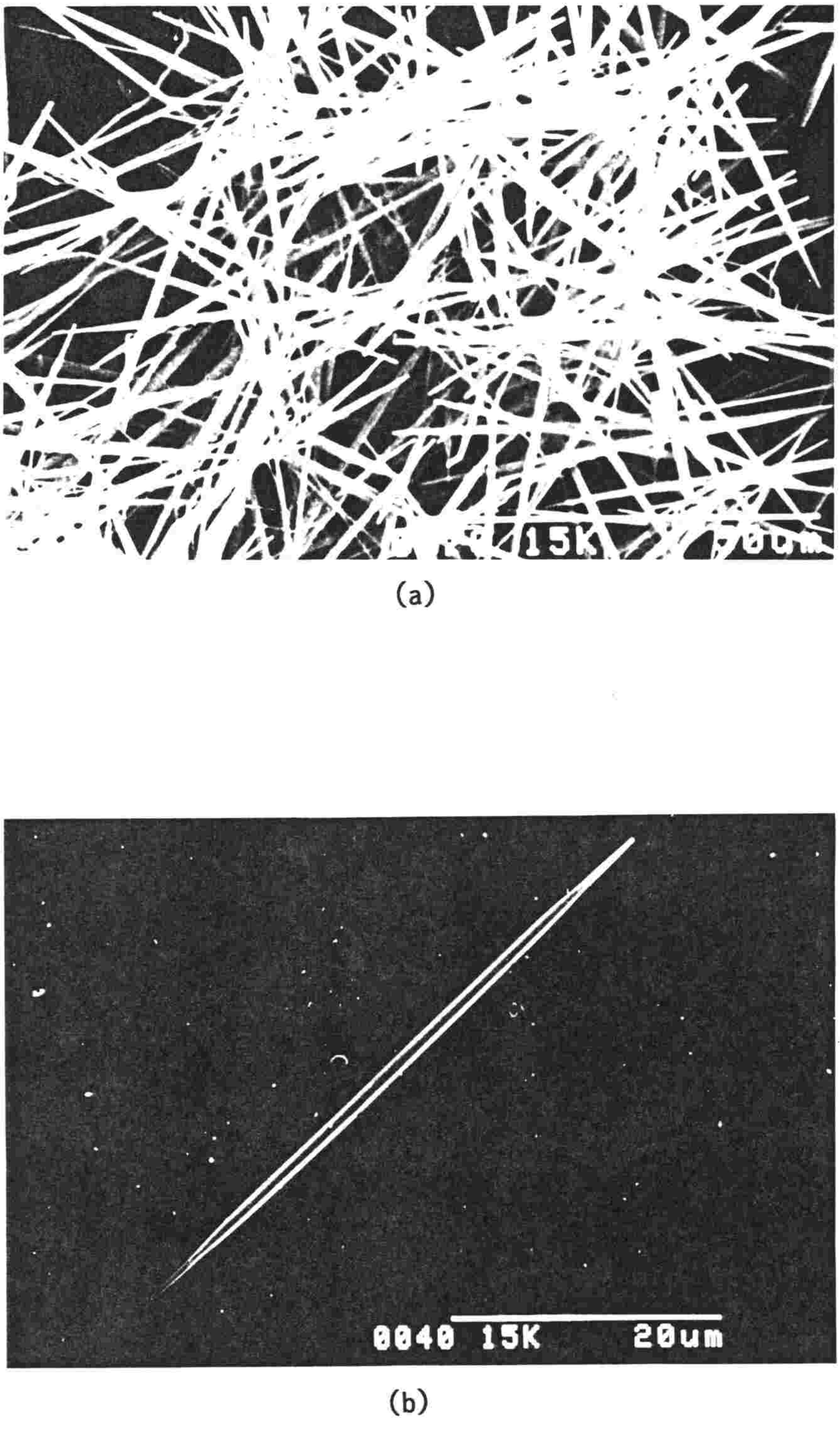
1-2-2 Results and Discussion

1-2-2-1 Synthesis of Poly(p-oxybenzoyl) Whisker

The needle-like crystals are obtained by high-temperature solution polycondensation of p-ABA in LP or TS 800 at low concentration with no stirring. They are shown in Figure 1-1 (a) and (b), respectively. These needle-like crystals have extremely high crystallinity and they can be therefore regarded as polymer whiskers. Economy *et al.* and Kricheldorf *et al.* reported the high-temperature solution polycondensation of POB previously.[8-11] The crystals which they obtained were uniform, well-oriented slab-like but not needle-like. The polymerization conditions and the crystal morphologies of POB prepared from p-ABA are listed in Table 1-1. Polymerizations were carried out at 330℃ in solvents except for BP. Polymerizations in BP were carried out at 300℃ because of the boiling temperature of BP.

Concerning the polymerization solvent, whiskers are obtained only in LP or TS 800. These whiskers have 30-70μm length and 1-2μm width. They can be easily dispersed in acetone with ultrasonic vibration. An isolated whisker which is shown in Figure 1-1(c) is very symmetrical and both tips are sharp. This characteristic feature is indicative of the crystal growth from center to both tips. This point will be discussed later. In BP, the aggregates of fibrillar crystals which are uniform and well-oriented are obtained as shown in Figure 1-1(d). The fibrillar crystals are not separated. In CBP, fine powders of slab-like crystals, of which the thickness is *ca.* 0.5μm, are obtained as shown in Figure 1-1 (e) and (f). When the polymerization is carried out in DPS, crystal is not precipitated at a concentration of 1.0%. The crystals obtained at a concentration of 3.0% are spherulites which are aggregates of plate-like crystals as shown in Figure 1-1(g).

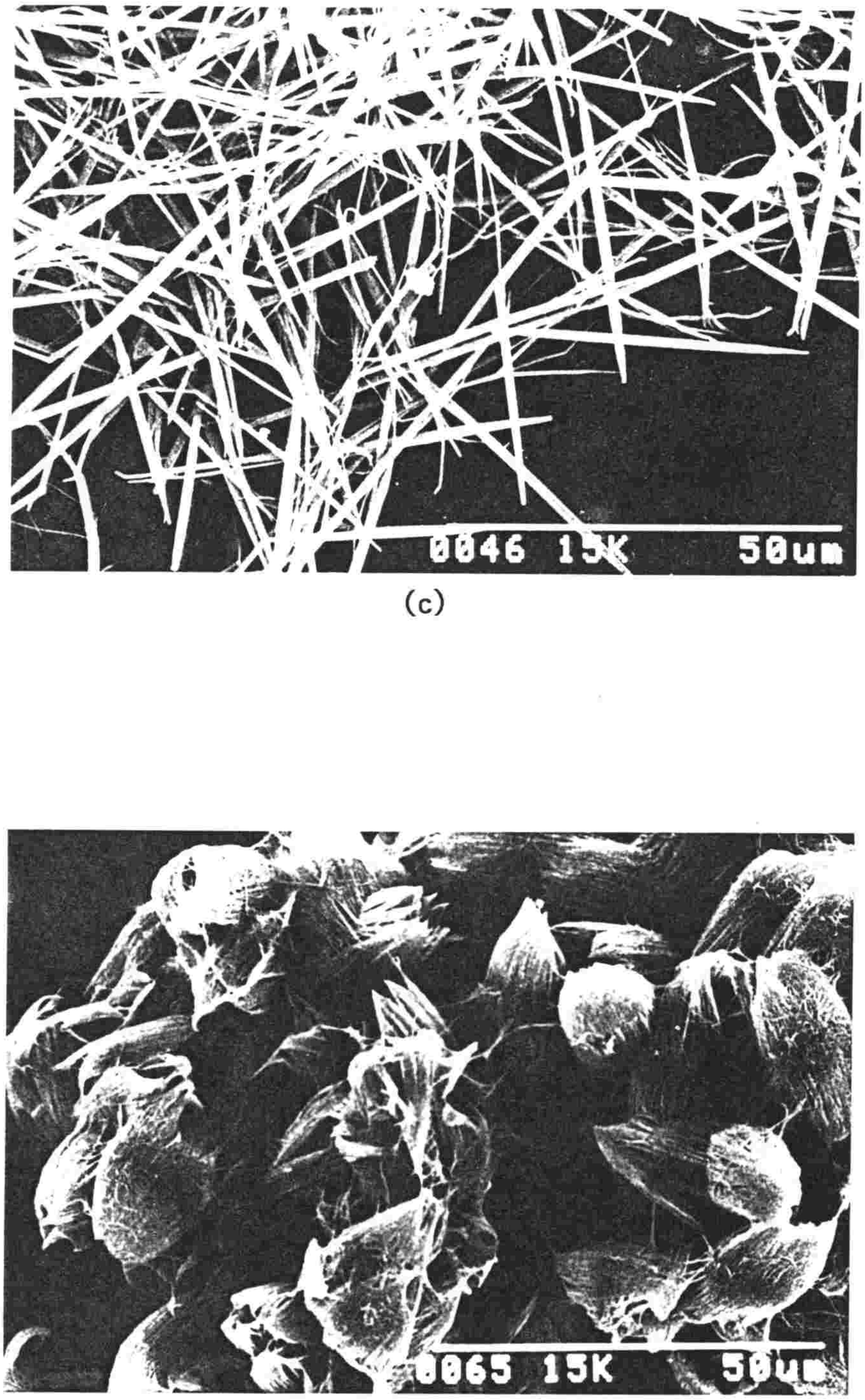
These results indicate that the crystal morphology seems to rest on polarity of the solvent, *i.e.* a less-polar solvent is preferable to obtain a whisker. These facts can be explained as follows. p-ABA is found to react initially in a homogeneous state and then the reaction continues in a heterogeneous state once precipitation has occurred. This



(a)

(b)

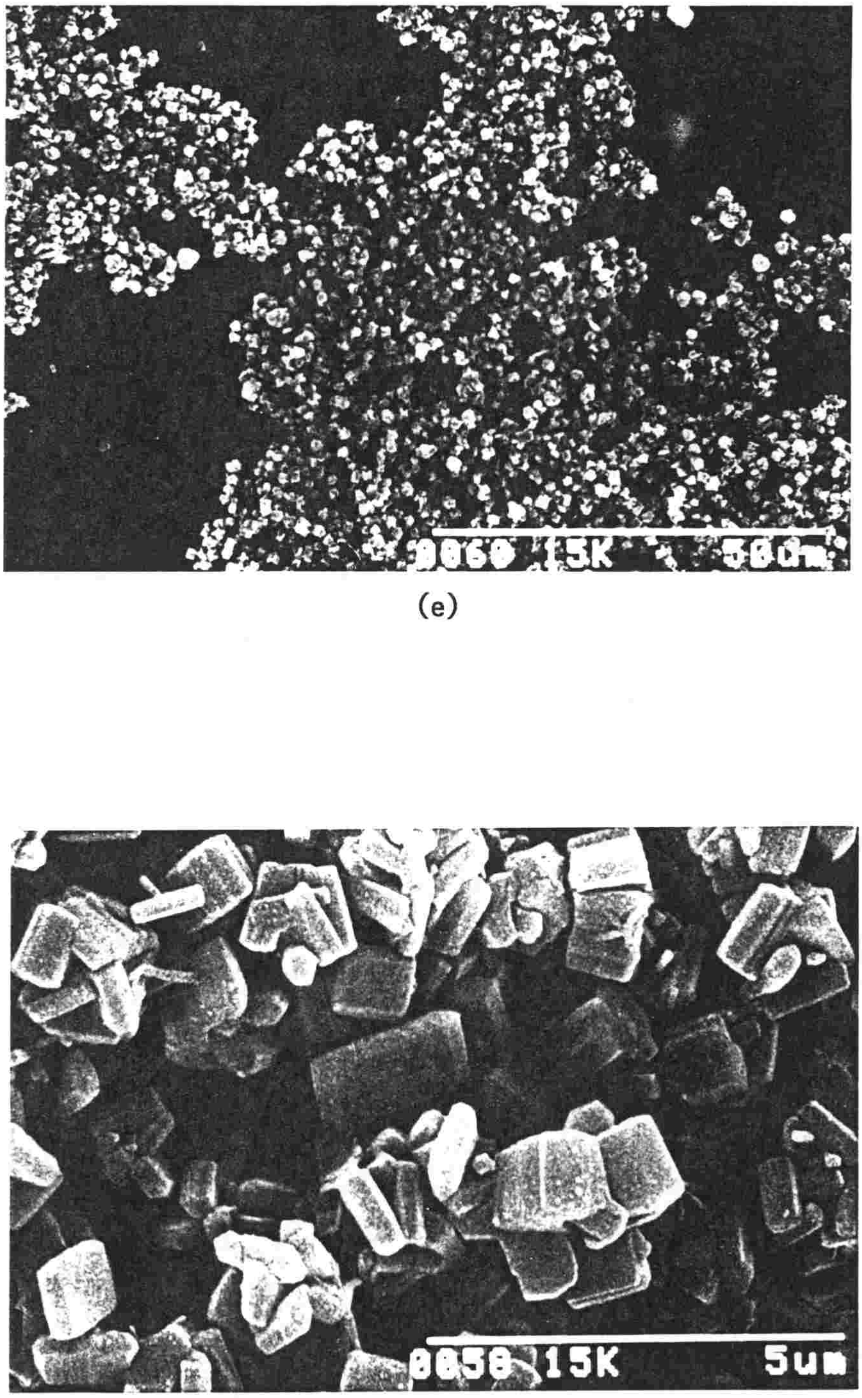
Figure 1-1. Scanning electron micrographs of POB crystals prepared (a) and (b) in LP at a concentratoion of 1.0%.



(c)

(d)

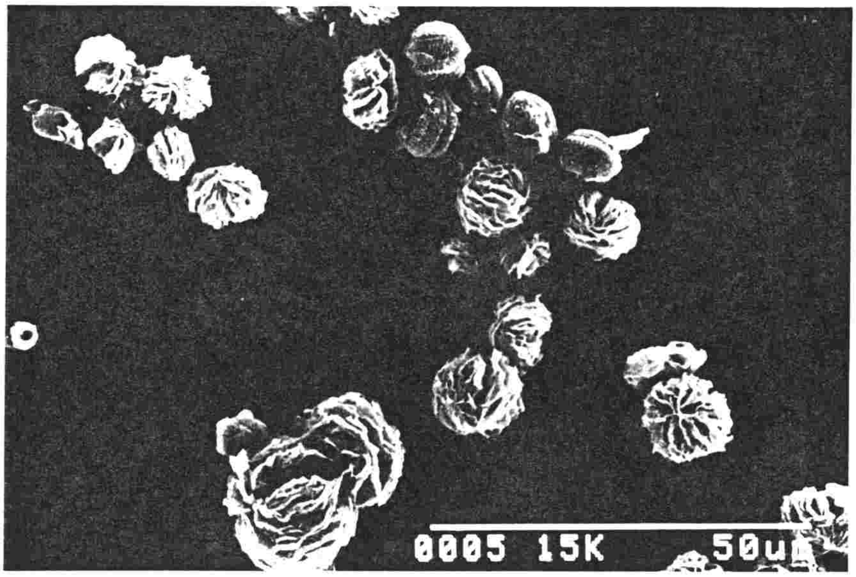
Figure 1-1. Scanning electron micrographs of POB crystals prepared (c) in TS 800 at a concentratoion of 1.0% and (d) in BP at a concentratoion of 1.0%.



(e)

(f)

Figure 1-1. Scanning electron micrographs of POB crystals prepared (e) and (f) in CBP at a concentratoion of 1.0%.



(g)

Figure 1-1. Scanning electron micrographs of POB crystals prepared (g) in DPS at a concentratoion of 3.0%.

Table 1-1. Polymerization conditions and morphological features of POB crystals

Polymer	Solvent[1]	Conc.[2] (%)	Polymerization Temperature(℃)	Time (h)	Crystal morphology
POB-1	LP	1.0	330	6	Needle-like
POB-2	LP	3.0	330	6	Needle-like
POB-3	TS 800	1.0	330	6	Needle-like
POB-4	TS 800	3.0	330	6	Needle-like
POB-5	BP	1.0	300	6	Fibrillar
POB-6	BP	3.0	300	6	Fibrillar
POB-7[3]	DPS	1.0	330	6	————
POB-8	DPS	3.0	330	6	Spherulite
POB-9	CBP	1.0	330	6	Slab-like
POB-10	CBP	3.0	330	6	Slab-like

1) Solvent: LP, liquid paraffin; TS 800, Therm S 800; BP, Benzophenone; DPS, diphenylsulphone; CBP, 4-chlorobenzophenone.

2) Conc.(%) = [Theoretical polymer yield (g) / Solvent weight (g)] x 100

3) Crystals were not obtained.

precipitation in the early stage of polymerization is because of the formation of the primary crystal nuclei, which contribute the final crystal morphology, by the crystallization of oligomers. The precipitation, which is defined as when the reaction solution becomes turbid, delays in the order of polarity of solvent except for CBP.

Order of precipitation time
early ◄————————► *late*
LP < TS 800 < BP < DPS
low ◄————————► *high*
Order of polarity of solvent

It seems reasonable to assume that the polymerization rates are nearly equal in all solvents or the rates in polar solvents are higher in a homogeneous sate. Under these situations, the degree of polymerization (DP) of oligomers precipitated are lower when the reaction is carried out in LP or TS 800 in comparison with other solvents due to lower solubility of oligomers in less-polar solvents.

The difference of the DP of the precipitated oligomers may have an influence on the crystal habits of the primary nuclei and ultimately the final crystal morphologies. Furthermore, the difference of the degree of supersaturation of the oligomers may also influence the crystal morphologies. The more detailed discussion will be described with the growth mechanism of the POB whisker in a later section.

In the case of DPS, crystal is not precipitated at a concentration of 1.0%, *i.e.* the oligomers which are formed the crystals are not precipitated. It is thought that the effective rate of polymerization decreases with the decrease of the concentration of end-group and then the polymerization actually stops before the DP of the oligomers exceeds the critical value for the precipitation because of the high solubility of the oligomers into DPS.

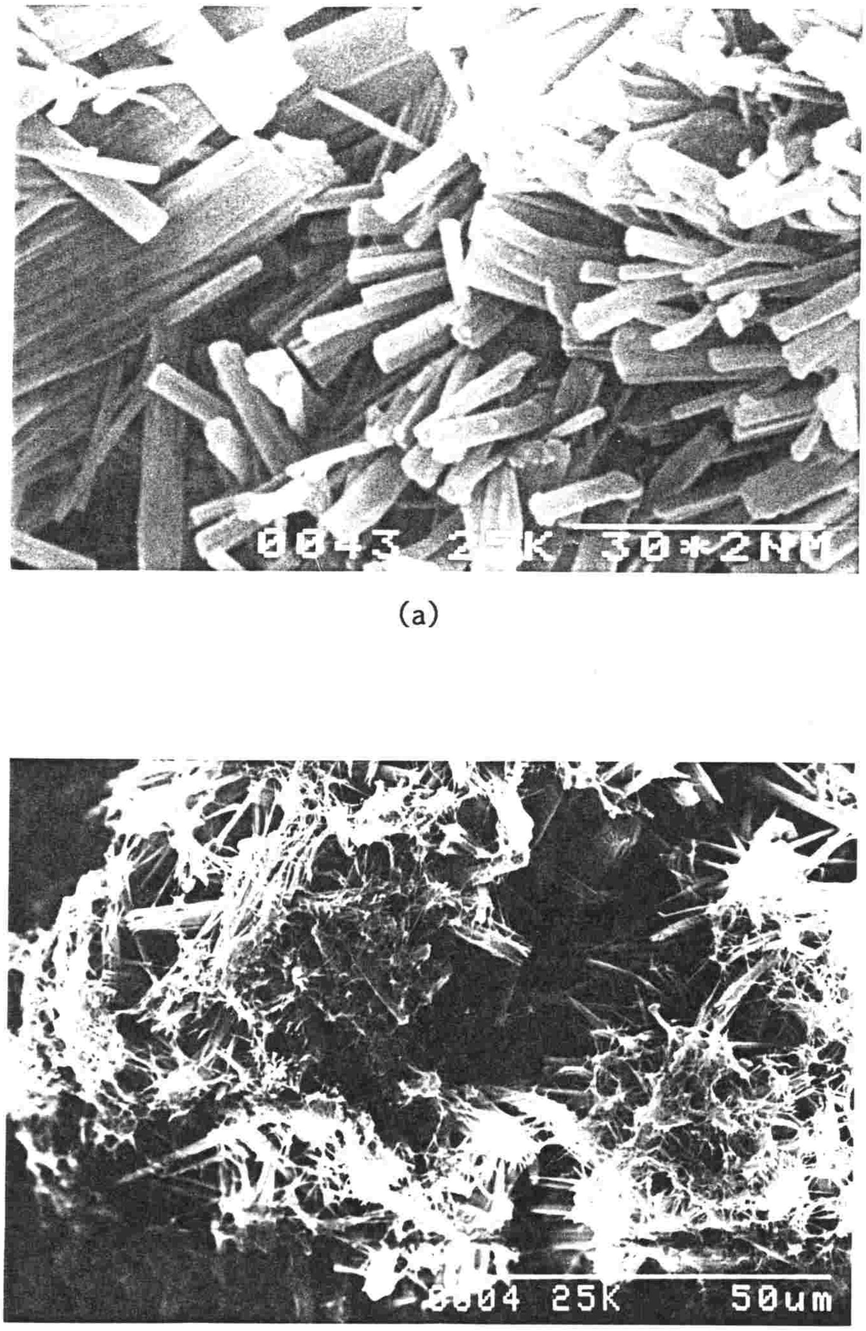
In CBP, the crystals are precipitated in as early stage of polymerization as in TS 800 in spite of the polarer solvent, whereas the obtained crystals are slab-like crystals. What occurs in CBP may be different from others. This is not understood clearly.

Concentration of polymerization and stirring are also very important factors in controlling the crystal morphologies. Higher concentration over 5% is inclined to form the fibrillated slab-like crystals as shown in Figure 1-2(a). Low concentration of 1-3% is desirable for making whiskers. With vigorous stirring, inseparable fibrillar crystals are formed as shown in Figure 1-2(b). It is necessary for making whiskers to crystallize POB during polymerization under no-stirring condition.

It is therefore concluded that the most important factors in controlling the POB crystal morphologies are the polarity of the solvent, concentration and stirring. Less-polar solvents such as LP or TS 800, low concentration of monomer and no stirring are desirable for making the POB whiskers.

1-2-2-2 Influence of Polymerization Temperature on Morphology of Poly(p-oxybenzoyl) Whisker

Polymerizations are carried out in LP at a concentration of 1.0% at various temperatures in order to know an influence of polymerization temperature on the morphology of the POB whisker. Polymerization temperatures examined here are 290℃,



(a)

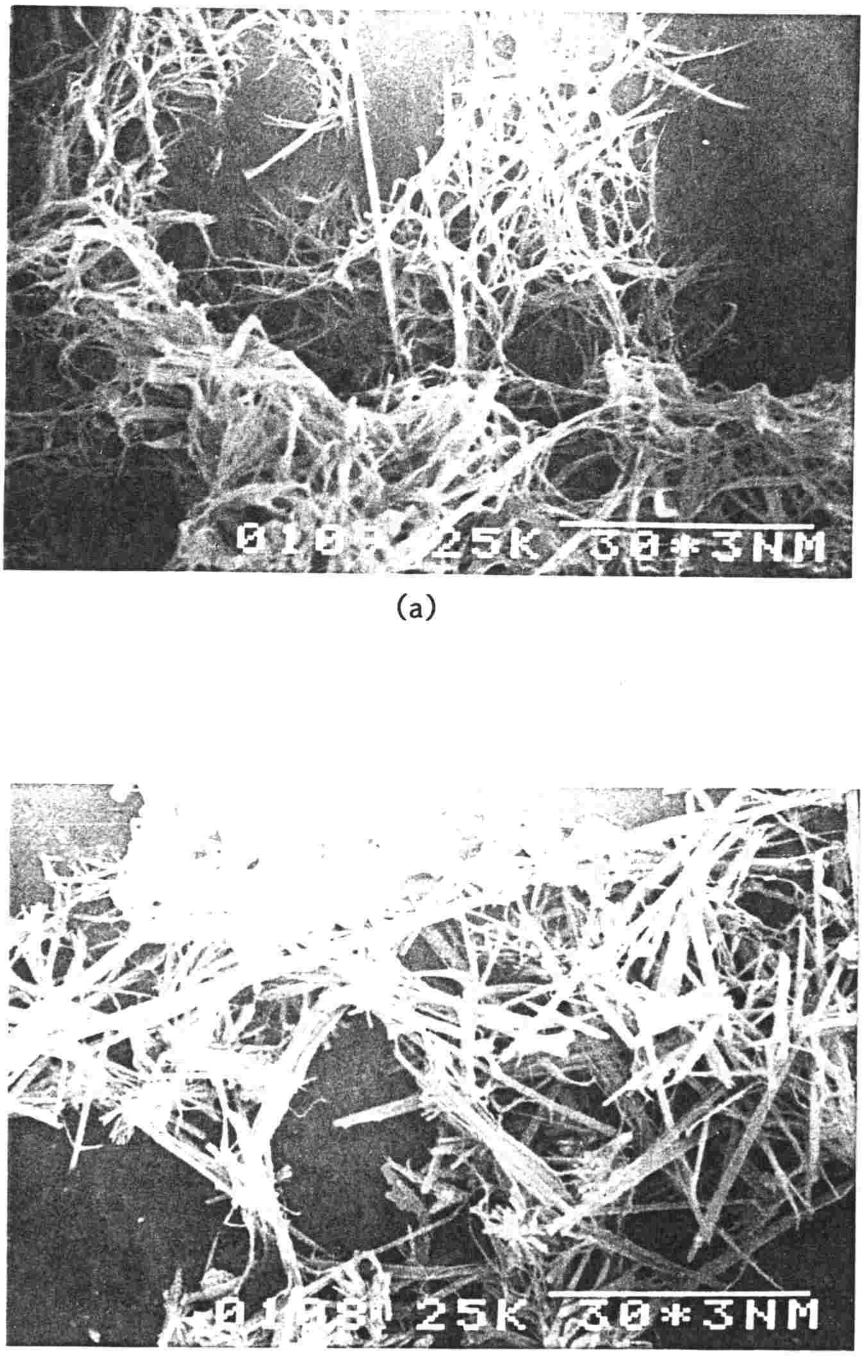
(b)

Figure 1-2. Scanning electron micrographs of POB crystals prepared in LP (a) at a concentration of 15.0% under no stirring and (b) at a concentration of 1.0% under vigorous stirring.

300℃, 310℃, 330℃, 340℃ and 350℃. Whiskers prepared at various temperatures are shown in Figure 1-3. The whiskers prepared below 330℃ do not have uniform size of the length and the width in comparison with that prepared at 330℃. Further, the whiskers do not separate and some of them show the radial growth. With increasing temperature to 330℃, the whiskers become longer with uniform size and the radial growth disappears, whereas the radial growth appears slightly with increasing temperature over 330℃.

It is considered that the crystal morphology of the whiskers depending on the polymerization temperature is attributable to the nucleation process of primary nuclei of the whiskers. Higher polymerization temperature makes the solubility of oligomers and the oligomer formation rate higher. Lower polymerization temperature makes them lower. Therefore, the primary nuclei might be formed from a highly supersaturated state of the oligomers than that at 330℃ because of the balance between the oligomer formation rate and the solubility of oligomers at higher or lower temperatures than 330℃. The rapid nucleation from a highly supersaturated state is inclined to form the heterogeneous primary nuclei which cause the radial growth and heterogeneity of the size of the whiskers. The uniform whiskers having no radial growth might be formed from the suitably supersaturated state of the oligomers at 330℃. (see Figure 1-4)

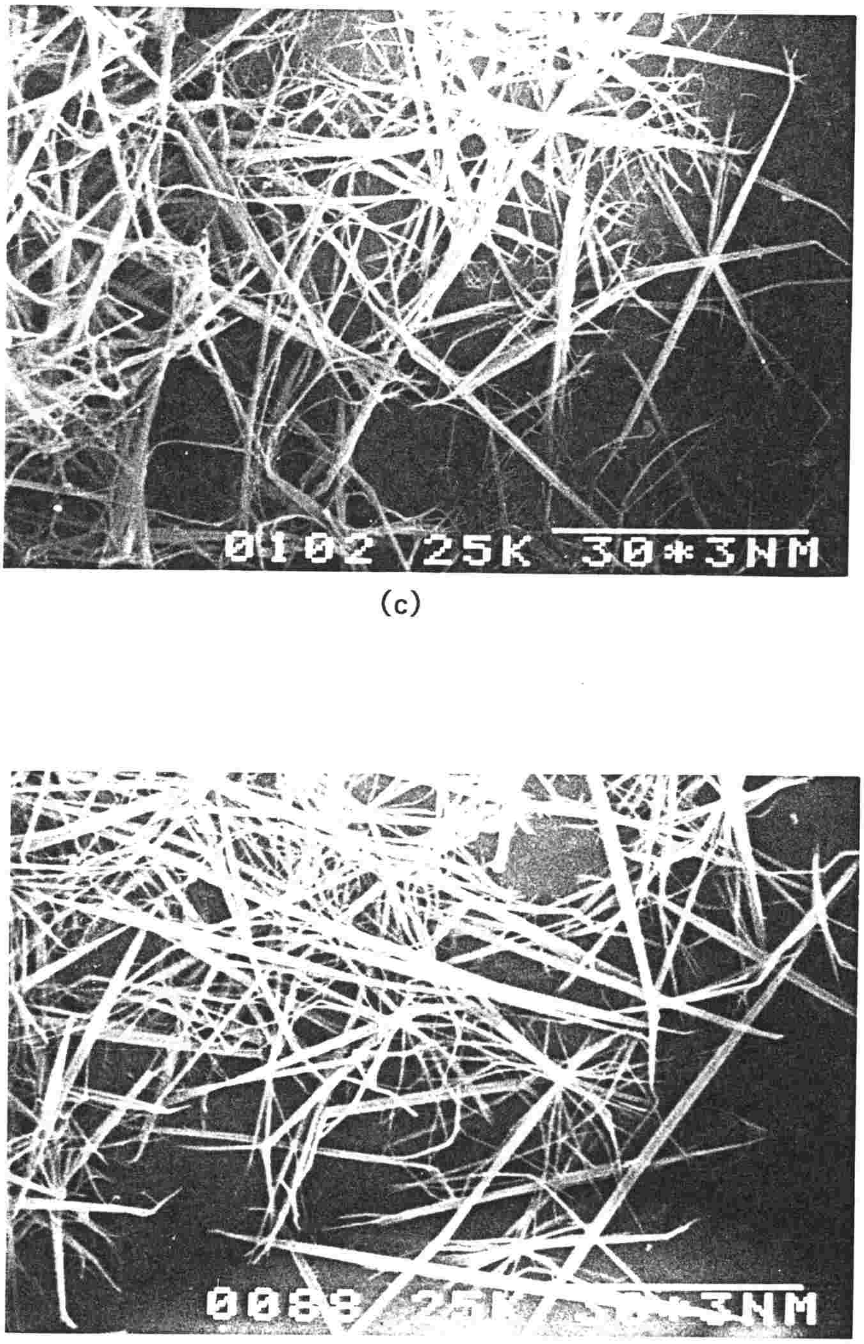
It is therefore concluded that the polymerization temperature has an influence on the morphology of the whisker and the most desirable temperature for making the whisker is *ca.* 330℃.



(a)

(b)

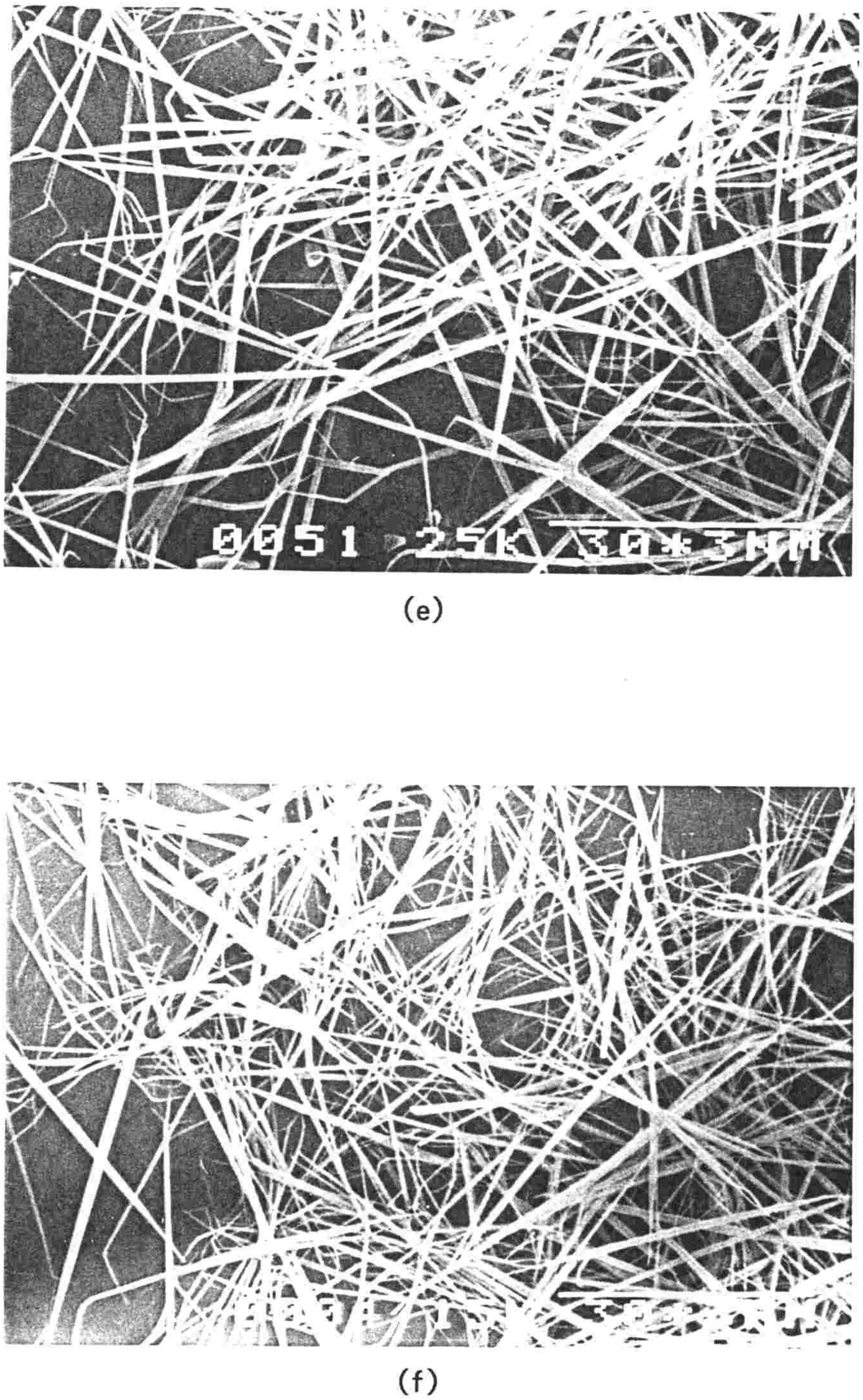
Figure 1-3. Scanning electron micrographs of POB whiskers prepared in LP at (a) 290℃ and (b) 300℃.



(c)

(d)

Figure 1-3. Scanning electron micrographs of POB whiskers prepared in LP at (c) 310℃ and (d) 320℃.



(e)

(f)

Figure 1-3. Scanning electron micrographs of POB whiskers prepared in LP at (e) 340℃ and (f) 350℃.

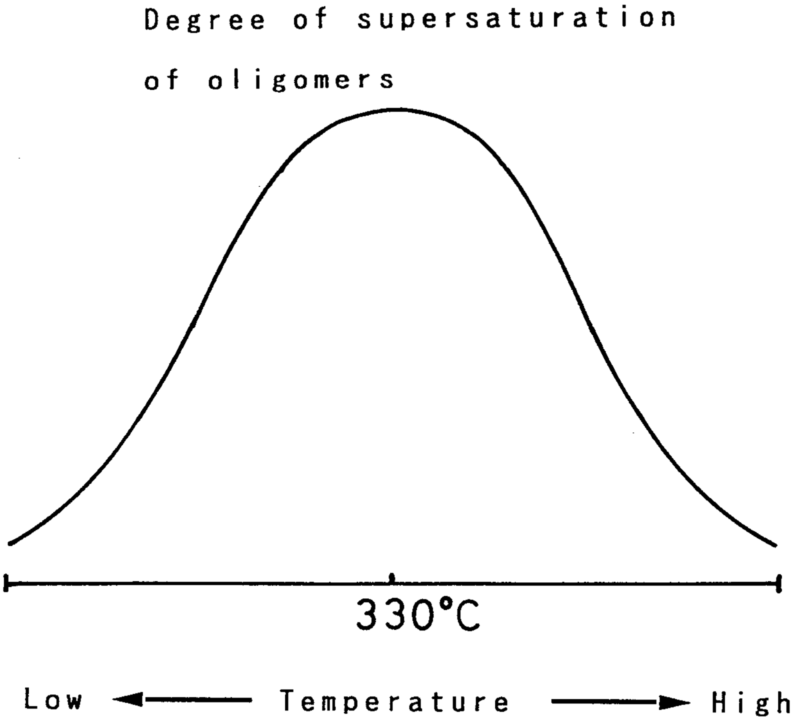
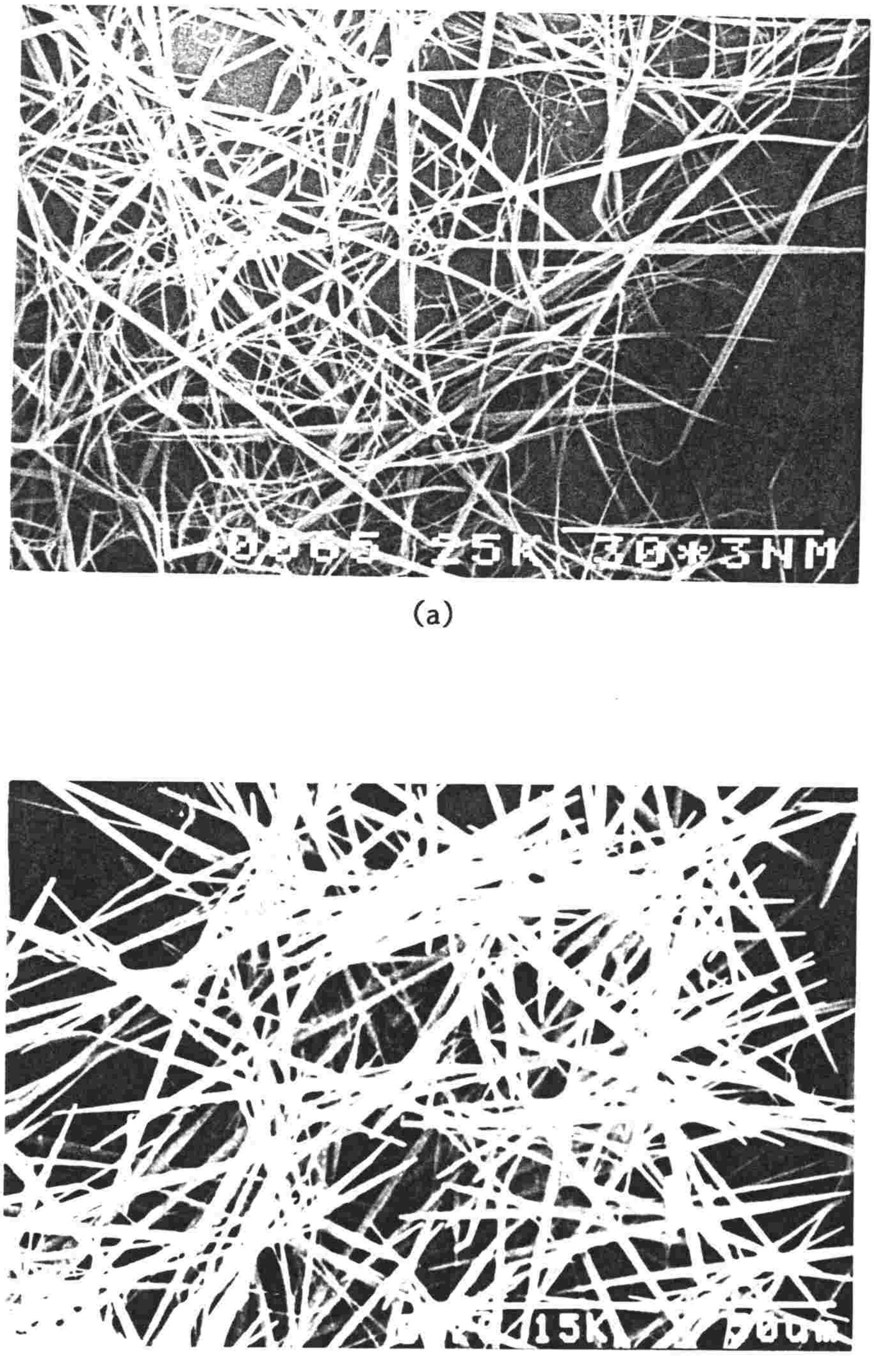


Figure 1-4. Schematic drawing of relationship between degree of supersaturation of oligomers and polymerization temperature.

1-2-2-3 Influence of Heating Rate to Polymerization Temperature on Morphology of Poly(p-oxybenzoyl) Whisker

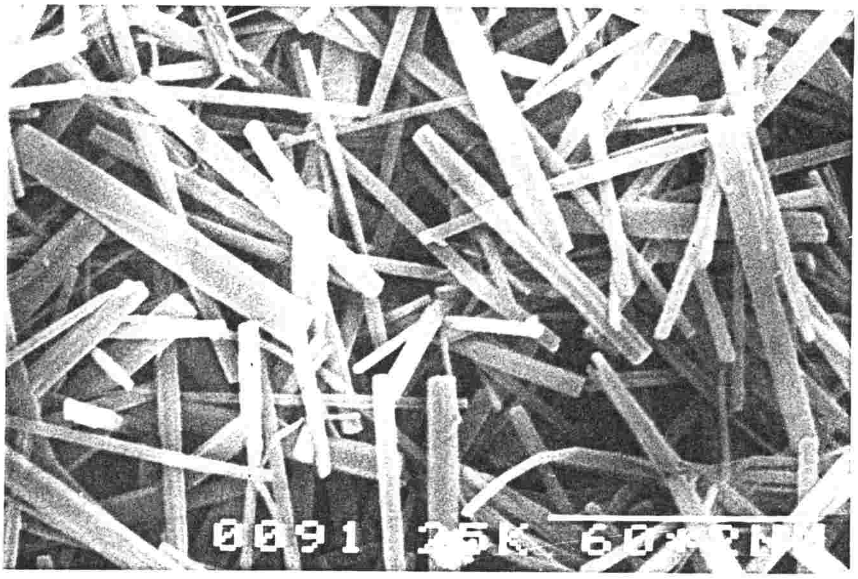
An influence of a heating rate to 330℃ on the morphology of the whisker is investigated. Polymerizations are carried out in LP at a concentration of 1.0% at 330℃. Heating rates from room temperature to 330℃ used are 5℃/min and 15℃/min. The whiskers obtained at heating rates of 5℃/min and 15℃/min are shown in Figure 1-5(a) and (b), respectively. As is seen in Figure 1-5, the whiskers obtained at a heating rate of 5℃/min do not have uniform size and show the radial growth. In this case, the precipitation of the crystals occurs on heating process at 275℃ after 49min from the beginning of heating, whereas it occurs within 3min at 330℃ in the case



(a)

(b)

Figure 1-5. Scanning electron micrographs of POB whiskers prepared in LP at a heating rate of (a) 5℃/min and (b) 15℃/min.



(c)

Figure 1-5. Scanning electron micrographs of POB whiskers prepared in LP (c) by an addition of p-ABA in one portion at 330℃.

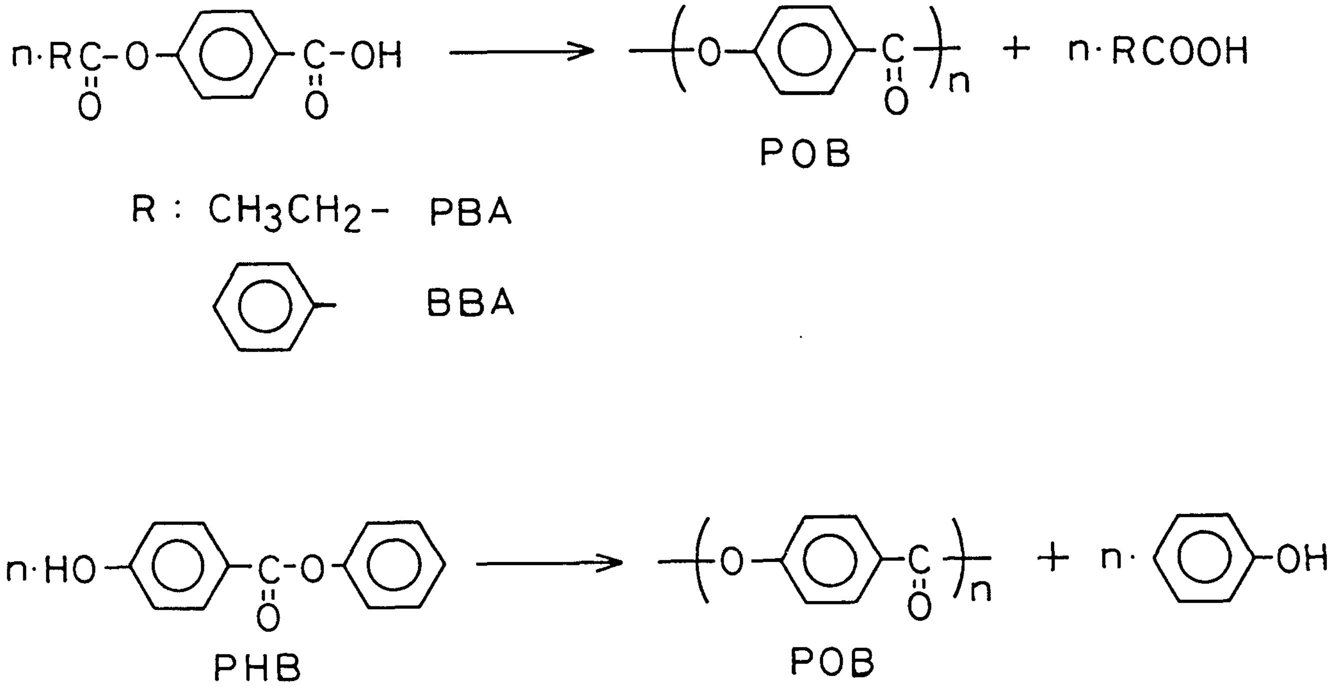
of 15℃/min, that is 25min from the beginning of heating. The difference in the heating rates leads to the difference in the precipitation temperatures which means the difference in the degree of the supersaturation of oligomers. The higher degree of the supersaturation of oligomers results in a lack of uniformity of the whisker size and the radial growth as described in the previous section.

When p-ABA is added in one portion at 330℃ in LP, the precipitation of the crystals occurs within 5min after the addition. This condition corresponds to an infinitely fast heating rate. The whiskers obtained have very short length: 7-8μm with the various widths as shown in Figure 1-5(c) and both tips of the whiskers are flat. In this case, these crystal morphologies might be attributable to the significantly rapid nuclear formation.

It is therefore concluded that the heating rate has an influence on the morphology of the whisker and 15℃/min is a desirable heating rate for the preparation of the uniform whiskers.

1-2-2-4 Influence of Chemical Structure of Monomer on Morphology of Poly(p-oxybenzoyl) Whisker

The derivatives of p·hydroxybenzoic acid such as PBA, BBA and PHB are used as monomers for the preparation of the POB whiskers. The reactions of PBA or BBA are acidolysis reactions with the elimination of propionic acid or benzoic acid, and the reaction of PHB is a transesterification reaction with the elimination of phenol as shown below.



Scheme 1-2. Synthesis of POB from PBA, BBA and PHB

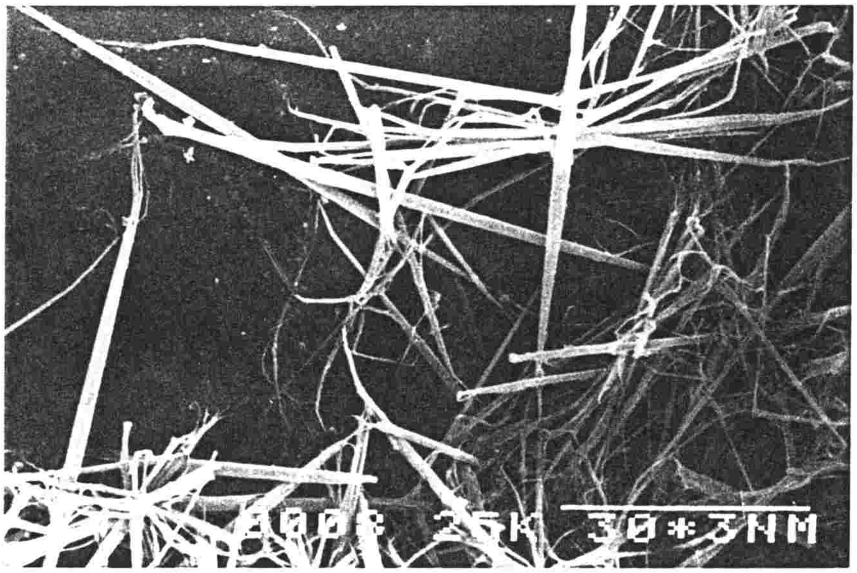
Polymerizations are carried out in LP at a concentration of

1.0% at 330℃ for 6h at a heating rate of 15℃/min.

PBA and BBA give the whiskers which slightly show the radial growth as shown in Figure 1-6(a) and (b), respectively. PHB gives needle-like crystals which grow radially from the central point as shown in Figure 1-6(c). The yield of the crystals from PHB is 18% which is one-third of those from other monomers.

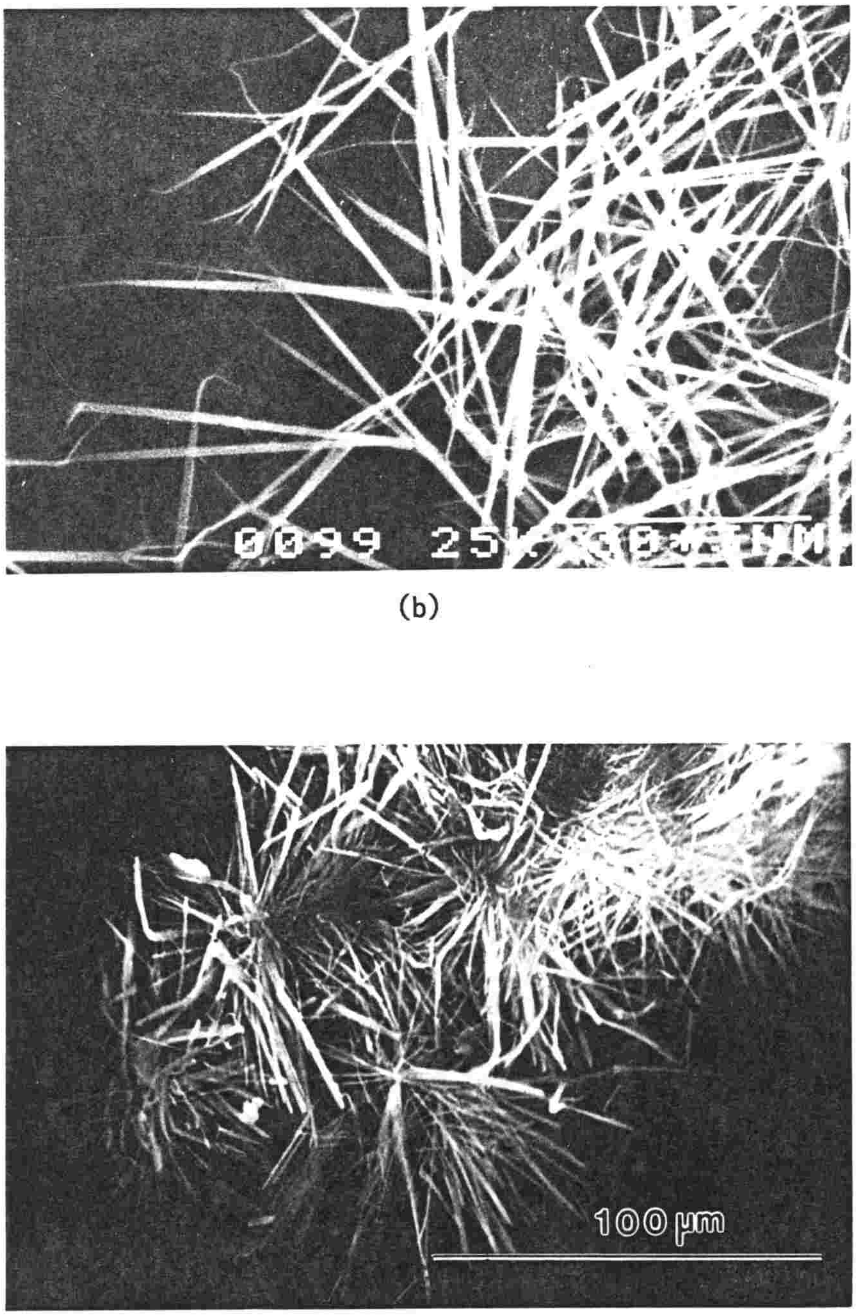
On the basis of the uniformity of the whisker shape, p-ABA is preferred as a monomer compared with PBA, BBA and PHB. The difference of formation rates of oligomers, solubility of oligomers and crystallizability of oligomers having different end-groups might mainly influence the uniformity of the whisker shape.

It is summarized that the derivatives of p-hydroxybenzoic acid essentially give the POB whiskers and p-ABA is a desirable monomer for the preparation of the uniform whiskers.



(a)

Figure 1-6. Scanning electron micrographs of POB whiskers prepared from (a) PBA.



(b)

(c)

Figure 1-6. Scanning electron micrographs of POB whiskers prepared from (b) BBA and (c) PHB.

1-3 Characterization of Poly(p-oxybenzoyl) Whisker

1-3-1 Experimental

Materials

POB whiskers were prepared as described in the previous section.

Measurements

Wide-angle X-ray scattering was conducted on a Rigaku 2028 X-ray diffractometer with nickel-filtered CuKα radiation. Selected-area electron diffraction was carried out in a Hitachi HU-11B transmission electron microscope.

The densities of the obtained crystals were measured by the floating method using *n*-butyl bromide and carbon tetrachloride at 25℃.

Thermal properties were evaluated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Perkin-Elmer DSC-7 at a heating rate of 10℃/min in nitrogen. TGA was performed on a Shimazu TG-30 at a heating rate of 10℃/min on a 5mg sample in air.

1-3-2 Results and Discussion

1-3-2-1 Crystal Structure of Poly(p-oxybenzoyl) Whiskers

The X-ray diffraction pattern of the POB whiskers prepared in LP is shown in Figure 1-7. As is seen in Figure 1-7, the diffraction from amorphous parts is not observed at

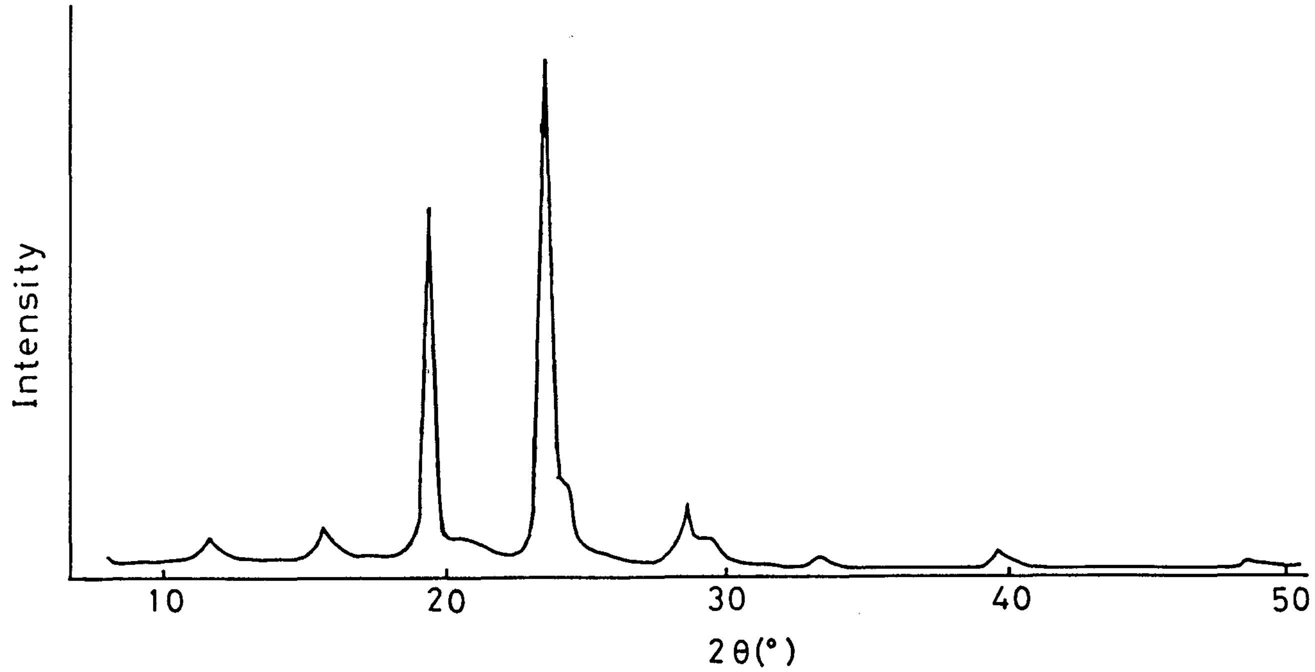


Figure 1-7. X-ray diffraction pattern of POB whiskers.

all and the diffraction peaks are very sharp. It suggests that the POB whiskers have extremely high degree of crystallinity.

Figure 1-8 shows a selected-area electron diffraction pattern of a POB whisker prepared in LP. The diffraction pattern does not show the true fiber pattern of cylindrical symmetry and it consists of sharp spots of lower to higher order reflections as clearly observed. This is due to the single crystal nature of the whisker. The meridian of this pattern corresponds to the long axis of the crystal, and this fact reveals that the polymer chains align along the long axis of the whisker. The calculated fibre identity period of *cis*-

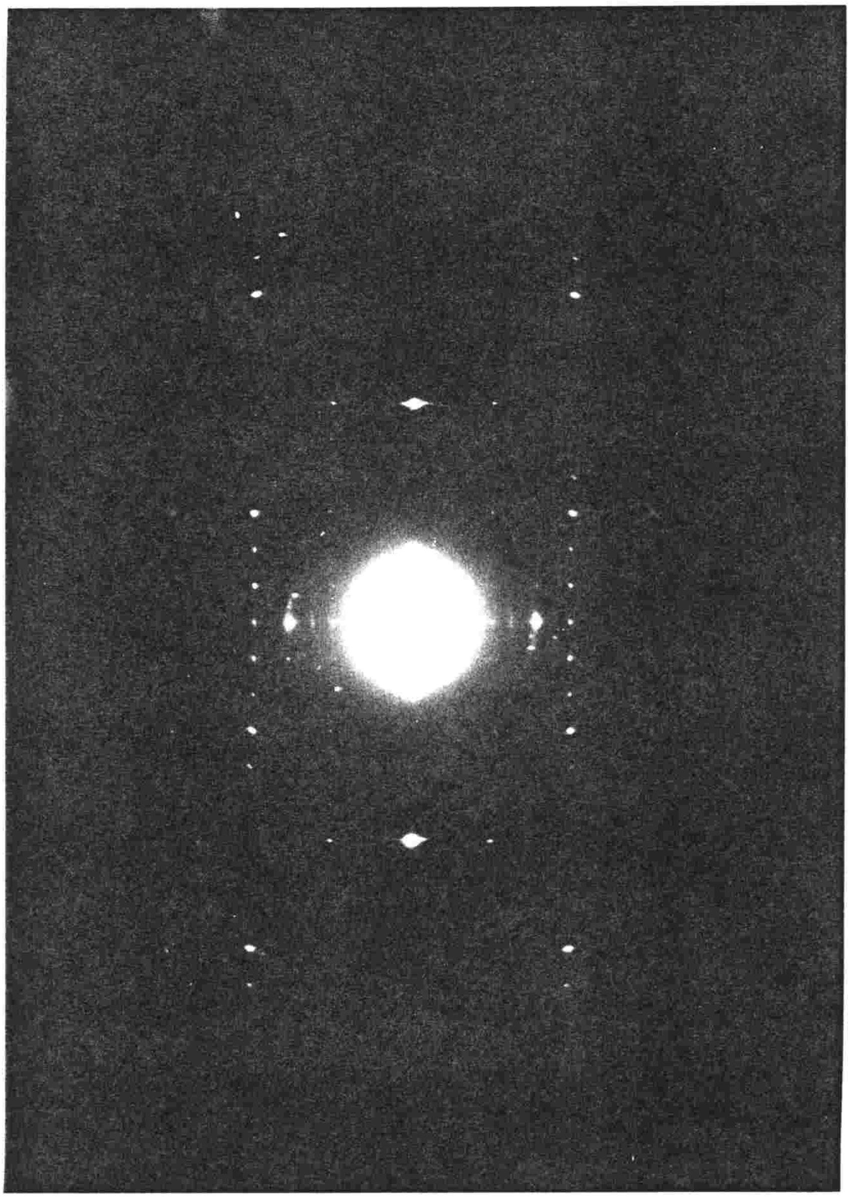


Figure 1-8. Electron diffraction pattern of POB whiskers.

conformation is 12.49Å and that of *trans*-conformation is 6.35Å. The observed fibre identity period is 12.54Å which is corresponding to two chemical residues and it is implied that the the conformation of polymer molecules in the crystal may be *cis*- conformation or torsional conformation.

The observed densities of the POB crystals are listed in Table 1-2. The observed densities of the POB whiskers are higher than those of crystals with other morphologies and they are very close to the theoretical density: 1.52g/cm³. It is suggested that the higher densities of the whiskers are due to the closer packing of polymer chains, and this result substantiates the consideration from the diffraction results.

Table 1-2. Densities and thermal properties of POB crystals

Polymer	Density (g/cm³)	Solid-solid transition tempareture (℃)[1] Heating	Cooling	Temperature of 5wt% loss[2] (℃)
POB-1	1.51	370.0	335.5	524
POB-2	1.50	346.5	322.4	512
POB-3	1.51	360.9	330.7	496
POB-4	1.50	349.7	327.6	492
POB-5	1.48	347.2	316.3	446
POB-6	1.48	325.3	321.3	488
POB-7	———	———	———	——
POB-8	1.43	325.0	310.8	331
POB-9	1.50	348.6	319.6	432
POB-10	1.49	349.4	321.0	463

1) measured by DSC at a heating rate of 10℃/min in nitrogen.

2) measured by TGA at a heating rate of 10℃/min in air.

1-3-2-2 Thermal Properties of Poly(p-oxybenzoyl) Whiskers

Thermal properties of the POB crystals are summarized in Table 1-2. The whiskers display significantly higher thermal stability than the other crystals on the basis of TGA. The temperature of 5wt% loss of the whiskers prepared in LP at a concentration of 1.0% is 524℃, which is the highest in the POB crystals. The temperatures of 5wt% loss are roughly correlated with the densities of the crystals as shown in Figure 1-9, *i.e.* the crystals in which the polymer chains pack more densely show higher thermal stability.

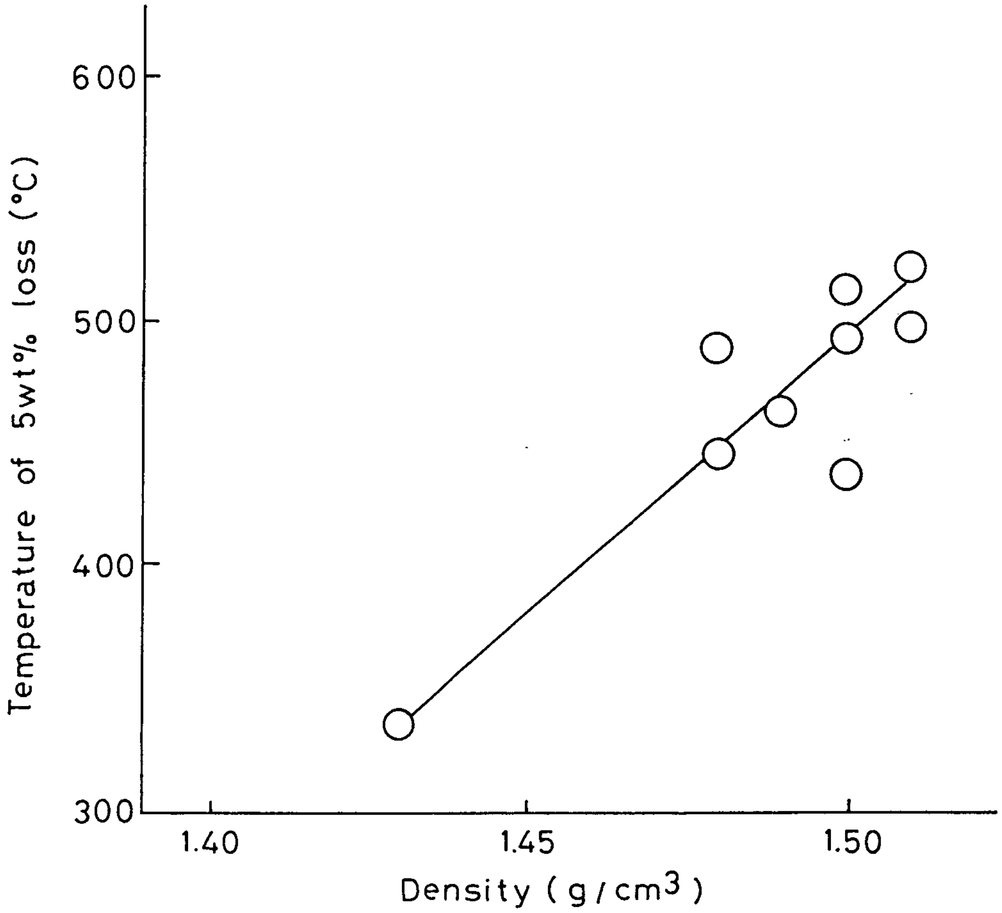


Figure 1-10. Relationship between transition temperatures and densities of POB crystals.

It is known that POB crystal shows a reversible first-order solid-solid transition at around 350℃ differing from the melting process and it is regarded as a transition to a pseudohexagonal packing of polymer molecules by a rotation of 1,4-phenylene ring around σ-bonds in the *para* position.[8,9,15-17] DSC analysis of the prepared POB crystals confirms the presence of the reversible transition and the transition temperatures are also tabulated in Table 1-2. The fact that the transition temperatures of the whiskers are higher than those of the crystals with other morphologies would be understood due to the closer packing of polymer chains in the whiskers. The transition temperatures are highly related to the densities of the crystals as plotted in Figure 1-10, *i.e.* the crystals having higher densities show higher transition temperatures.

Thermal properties such as thermal stabilities and thermal transition behaviors depend on the degree of perfection of the crystal, and the crystals with higher degree of perfection display, of course, better thermal properties. In the POB crystals, the whiskers exhibit outstanding thermal properties.

1-4 Growth Mechanism of Poly(p-oxybenzoyl) Whisker

1-4-1 Experimental

Materials

LP was used after the purification as described in the previous section. p-ABA was prepared as described in the

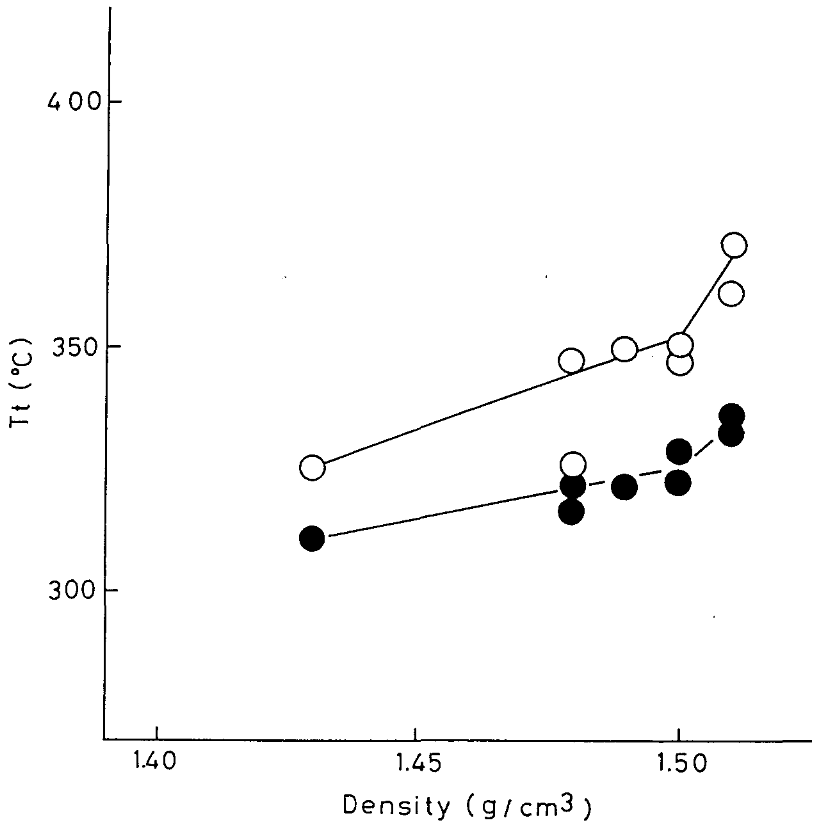


Figure 1-10. Relationship between transition temperatures (T_t) and densities of POB crystals; (○) T_t detected on heating scan, (●) T_t detected on cooling scan.

literature.[5]

Preparation of Poly(p-oxybenzoyl) Whiskers

In a 500 ml round-bottomed flask equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were placed 4.5g of p-ABA and 300g of LP. The reaction mixture was heated with stirring until the monomer was dissolved completely. Stirring was stopped, and then the solution was heated up to 330℃ at a heating rate of 15℃/min. The solution was maintained at 330℃ for the predetermined time under a slow stream of nitrogen. The polymer crystals / LP slurry was quenched to room temperature and chloroform was added. The polymer crystals were isolated by filtration, washed several times with chloroform and acetone, and then dried at 100℃ under reduced pressure to a constant weight.

Measurements

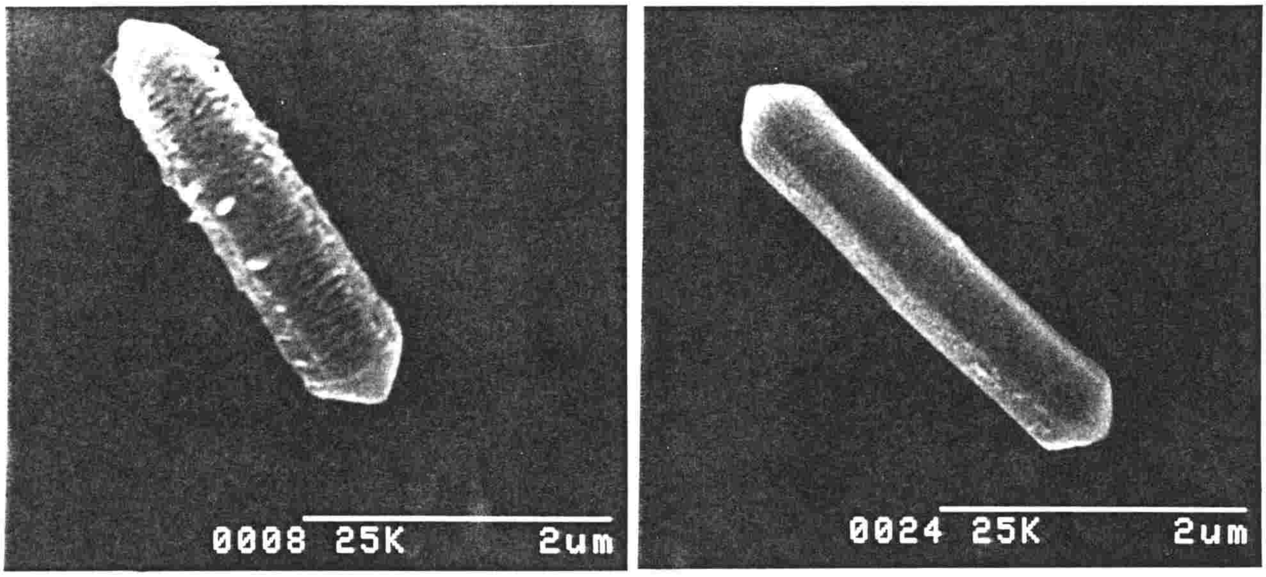
Morphological observations were carried out by using a Hitachi 530-S scanning electron microscope and a Hitachi HU-11B transmission electron microscope.

The degree of polymerization (DP) of oligomers was evaluated by reversed phase chromatography with the technique of gradient elution. Developing solvent was changed continuously from the mixture of 2% acetic acid aq. / acetonitrile (90/10 by volume) to acetonitrile with 40min. The DP of polymers was measured by ^{1}H-NMR end-group analysis of the acetyl group after hydrolysis of the crystal with conc. sulfuric acid in an NMR tube with a Varian Gemini-200 spectrometer according to the procedure described in a literature.[18]

1-4-2 Results and Discussion

1-4-2-1 Morphology of Incipient Crystal of Poly(p-oxybenzoyl) Whisker

An incipient crystals polymerized in LP at 330℃ for 3min are shown in Figure 1-11(a). It is observed that the oligomeric materials adhere on the surface of the crystal because of the precipitation of oligomers during quenching process from 330℃ to room temperature. The obtained crystals were washed in 1N-KOH aq. at 30℃ for 30min to remove the



(a) (b)

Figure 1-11. Scanning electron micrographs of an incipient crystal (a) prepared in LP at 330℃ for 3min (b) washed in 1N-KOH solution.

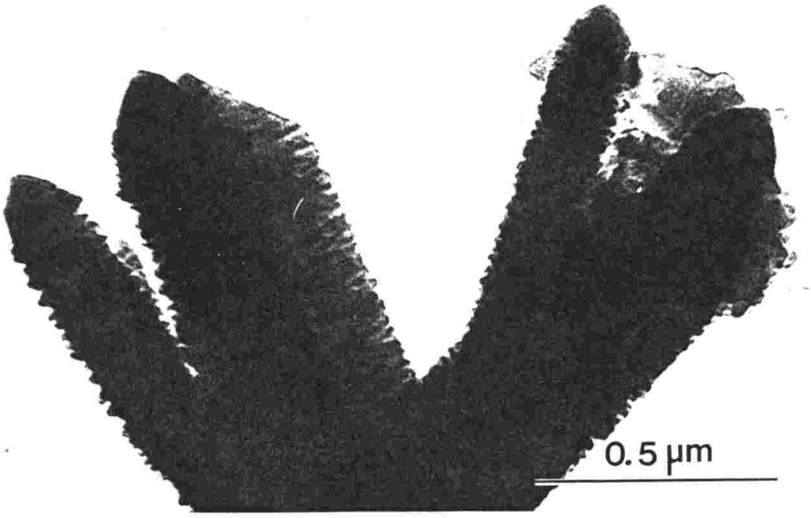


Figure 1-12. Transmission electron micrographs of incipient crystals washed in 1N-KOH solution.

adhered materials. The scanning and transmission electron micrographs of the washed crystals are Figure 1-11(b) and 1-12. The incipient crystal is found to be a needle-like hexagonal pillar and both tips are sharp. Further, a protuberance is observed at the center of the crystal. In Figure 1-12, the lamellar structure, of which the thickness is *ca.* 50Å, pilling up along the long axis of the crystal is clearly observed and the 'shish' as in 'shish-kebab' fibrous crystals does not exist. On the other hand, the eventual whiskers do not have any lamellar structures but a smooth surface as shown in Figure 1-13. These morphological features strongly imply that the needle-like crystals formed with a spiral growth of lamellar from the central protuberance to both tips.

The width of the incipient crystal is *ca.* 0.6μm and it is smaller than that of the eventual whiskers. This fact indicates that the crystal growth occurs not only on the spiral steps of both tips which are of great advantage for secondary nucleation (A in Figure 1-14) but also on the lateral plane (B in Figure 1-14).

1-4-2-2 Morphological Development of Poly(p-oxybenzoyl) Whisker with Polymerization Time

The scanning electron micrographs of the whiskers prepared at 330℃ for 10min and 30min are shown in Figure 1-15. The increase not only in the length but also in the width is observed within 10min, whereas the subsequent increase in the width is not observed after 10min. Moreover, the angle of both pointed ends of the whisker prepared for 30min becomes sharper.

The changes of the length, the width and the tip angle

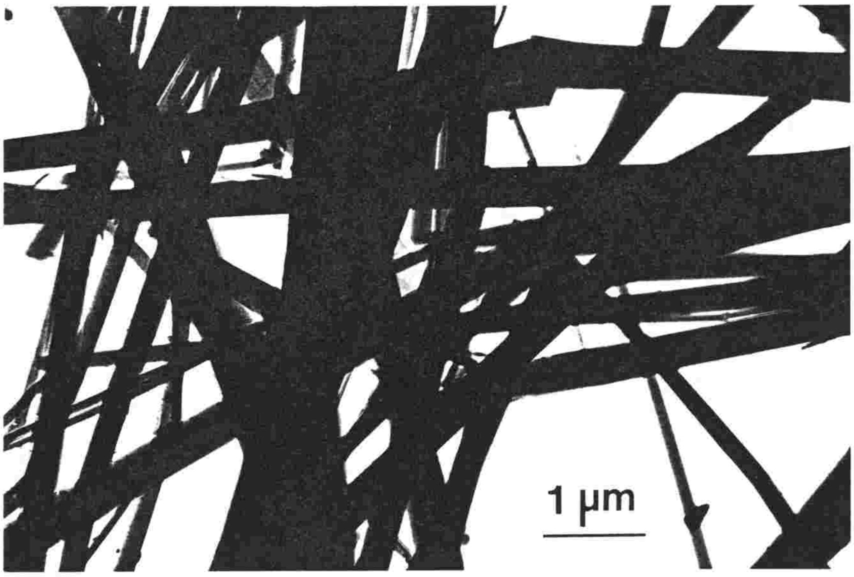


Figure 1-13. Transmission electron micrograph of POB whiskers polymerized in LP at 330℃ for 6h.

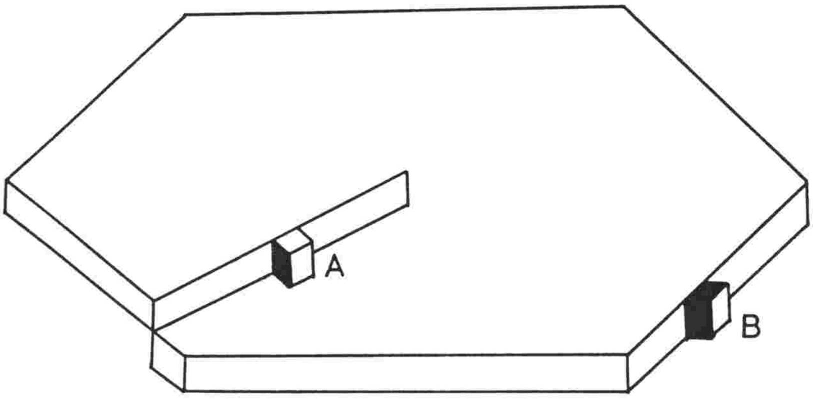
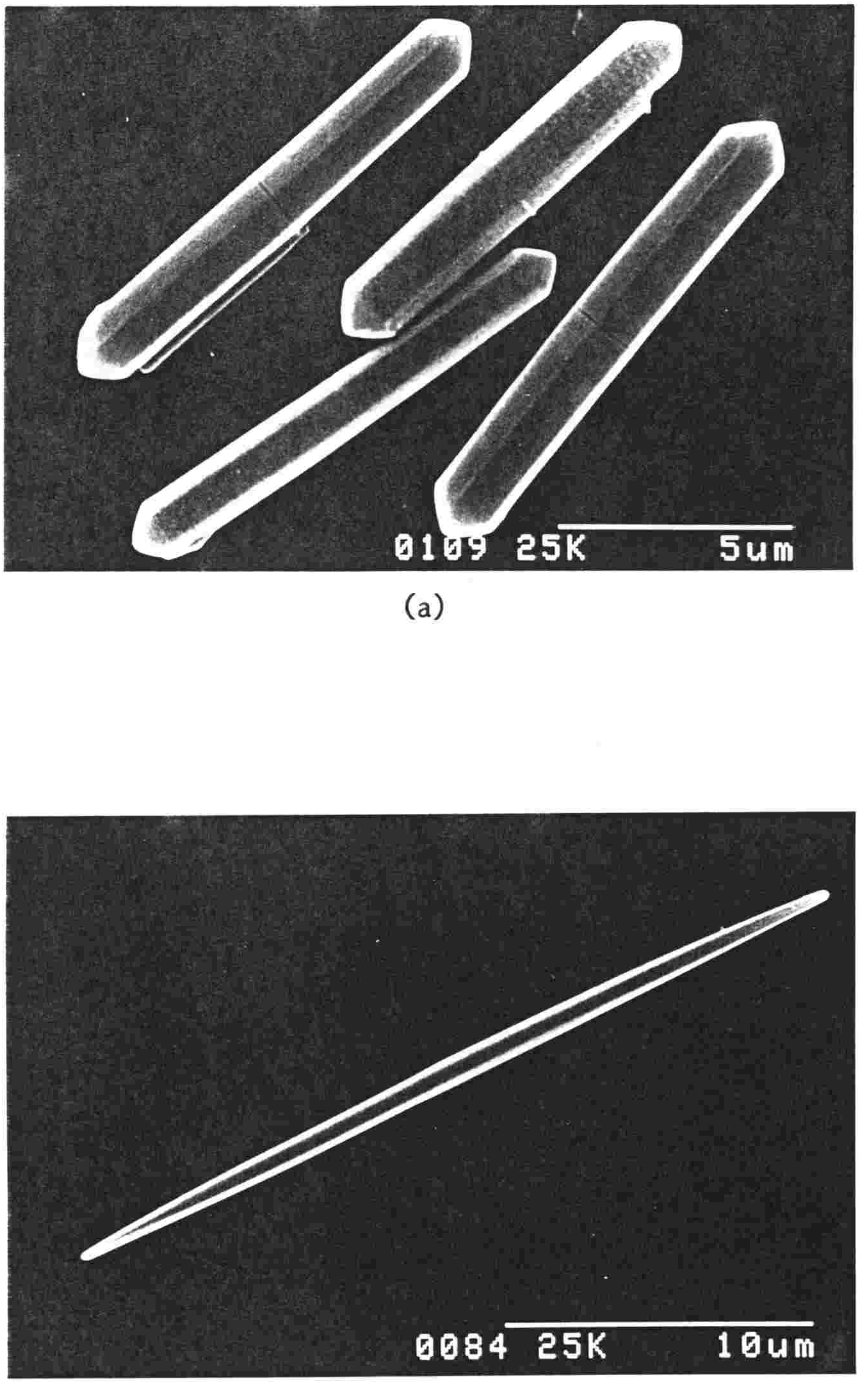


Figure 1-14. Schematic drawing of secondary nucleation. A, favorable nucleus; B, unfavorable nucleus.



(a)

(b)

Figure 1-15. Scanning electron micrographs of POB crystals polymerizad in LP at 330℃ for (a) 10min and (b) 30min.

are followed as a function of polymerization time. The distribution diagrams of the length and the width of the whisker prepared for 3min, 10min and 30min are shown in Figure 1-16 and 17, respectively. The very narrow distributions of both length and width show that the lamellar crystals with screw dislocations which serve as primary nuclei for the spiral growth of the whiskers are formed in the very early stage of the polymerization and oligomers precipitated after the formation of the primary nuclei are exhausted only in the crystal growth. The slightly broader distributions with polymerization time are due to the heterogeneous crystal growth by the crystal precipitation. The average length is 3.0μm at 3min, 12.5μm at 10min and 32.0μm at 30min. The average width is 0.6μm at 3min, 1.01μm at 10min and 0.98μm at 30min. The fact that the crystals grow as well laterally as longitudinally at the beginning of the crystal growth and after a certain time they grow only longitudinally is explicable as follows. In the very early stage of the polymerization, oligomers of low DP are formed in the homogeneous solution state, and as soon as the DP exceeds a critical value, oligomers crystallize in the form of lamellae from the solution. A screw dislocation is generated in the precipitated lamellae and subsequent crystallization occurs. At the beginning of the polymerization, crystallization occurs not only at the slip plane but also on the lateral plane because of the high degree of supersaturation of oligomers. Further polymerization and crystallization result in the lower concentration of oligomers in the homogeneous state, *i.e.* the degree of supersaturation decreases. Then, crystallization occurs preferentially at the slip plane rather than the lateral plane because of the advantage of secondary nucleation

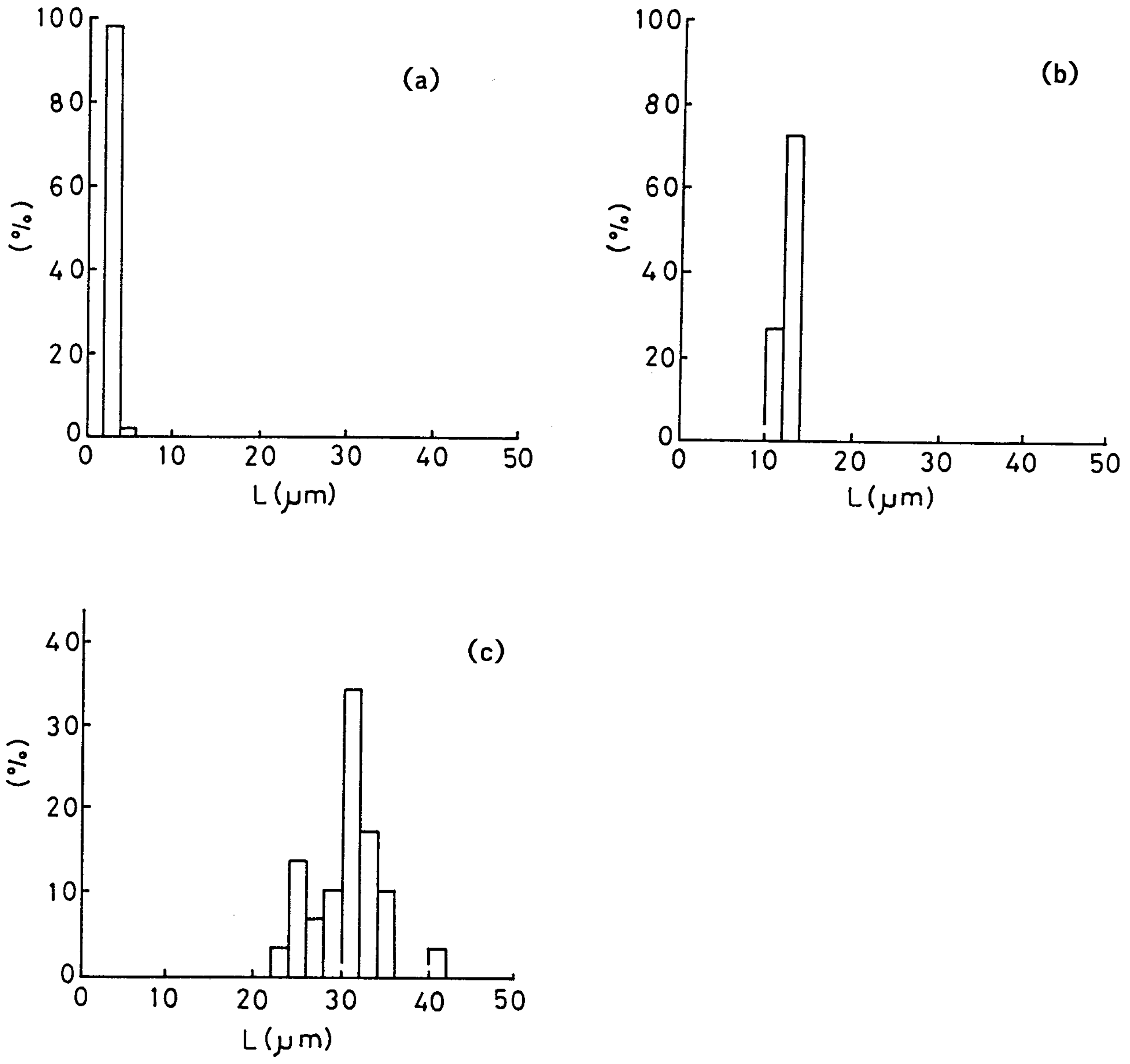


Figure 1-16. Distribution of POB whisker length (Lμm).
prepared in LP at 330℃ (a) for 3min. Average length is 3.0μm.
(b) for 10min. Average length is 12.5μm. (c) for 30min.
Average length is 32.0μm.

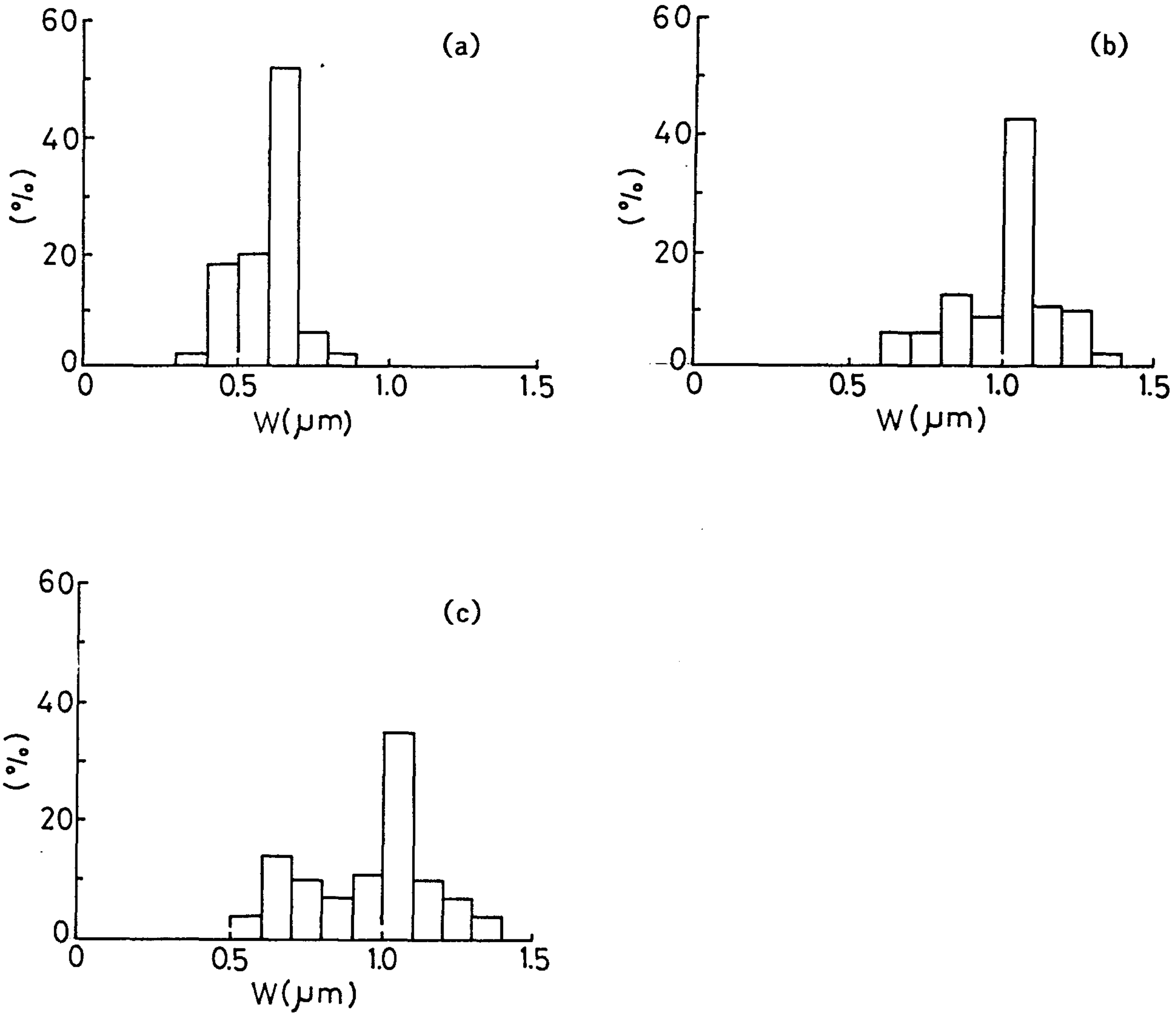


Figure 1-17. Distribution of POB whisker width (Wμm). prepared in LP at 330℃ (a) for 3min. Average width is 0.6μm. (b) for 10min. Average length is 1.01μm. (c) for 30min. Average length is 0.98μm.

for crystal growth.

Tip angle is plotted as a function of polymerization time in Figure 1-18. Tip angle is constant at 80° up to 20min, whereas it suddenly becomes significantly sharper to 7-8° at 30min. The sudden change in tip angle results from the change in the feature of the crystal growth. A spiral step produced by intersection of a screw dislocation with the surface of a crystal is developing as schematically shown in Figure 1-19. The growth rate of step at the small radius of curvature decreases due to the increase of the strain energy of secondary nucleation and therefore the spiral appears to rotate with uniform angular velocity under a steady state.[19-23] However, under the situation of the lower degree

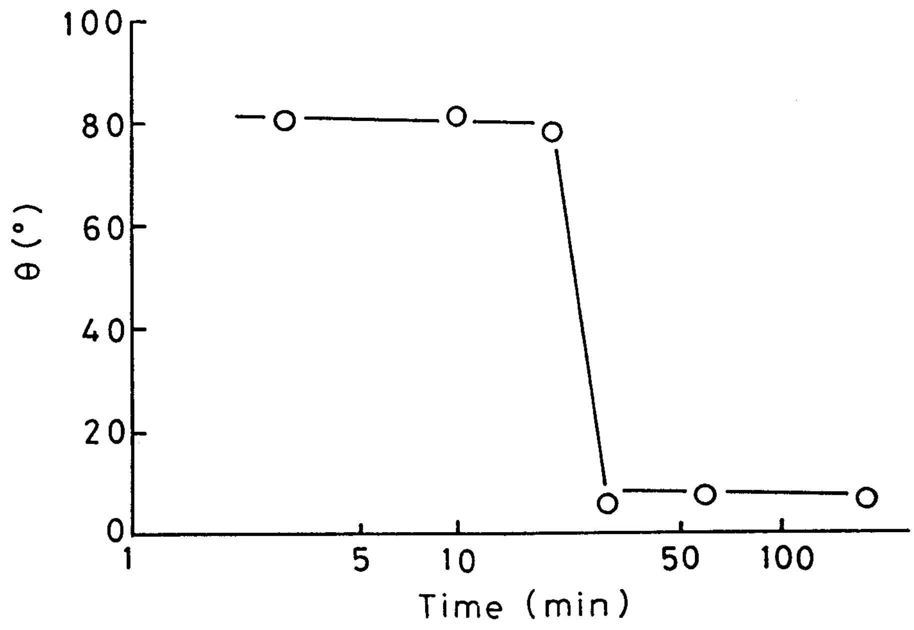


Figure 1-18. Tip angle (θ) of POB whiskers as a function of polymerization time. Prepared in LP at 330℃.

of supersaturation of oligomers the crystal growth is not determined by secondary nucleation, *i.e.* the growth rate depends on the number of oligomers which are reachable to the step, and the crystal growth is determined by the formation rate of the precipitated oligomers. The growth rate of step becomes steady at every radius of curvature and it results in the faster angular velocity at the smaller radius of curvature which leads to a sudden sharpening of tip angle. The successive stages in the development of a spiral growth starting from a screw dislocations schematically shown in Figure 1-20.

It is therefore concluded that the crystal growth of the whisker contains following steps: (1) formation of lamellae by crystallization of oligomers and successive generation of a screw dislocation on lamellae, (2) crystal development by a spiral growth and a lateral growth with increasing both length and width, (3) crystal development only by a spiral growth with increasing length, (4) crystal development by a spiral growth with increasing length along with sharpening tips.

From this mechanism, the influence of the solvent properties on the crystal morphologies as described in previous section, that fibrillar crystals or spherulites are formed in polar solvents such as BP and DPS, can be speculated more clearly. The oligomers of higher DP that are produced in polar solvents form thicker primary nuclei. Because of this thickness, it is difficult for a screw dislocation to form in the thicker lamellar, and the lamellae grow preferentially in the lateral direction. Fibrillation occurs even in the crystals that develop from thicker and wider nuclei owing to the extended chain packing along the same direction.

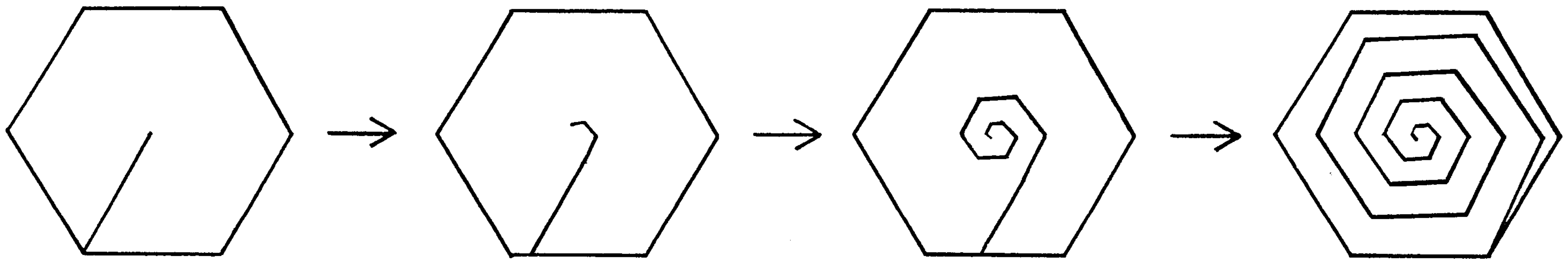


Figure 1-19. Schematic drawing of a spiral growth.

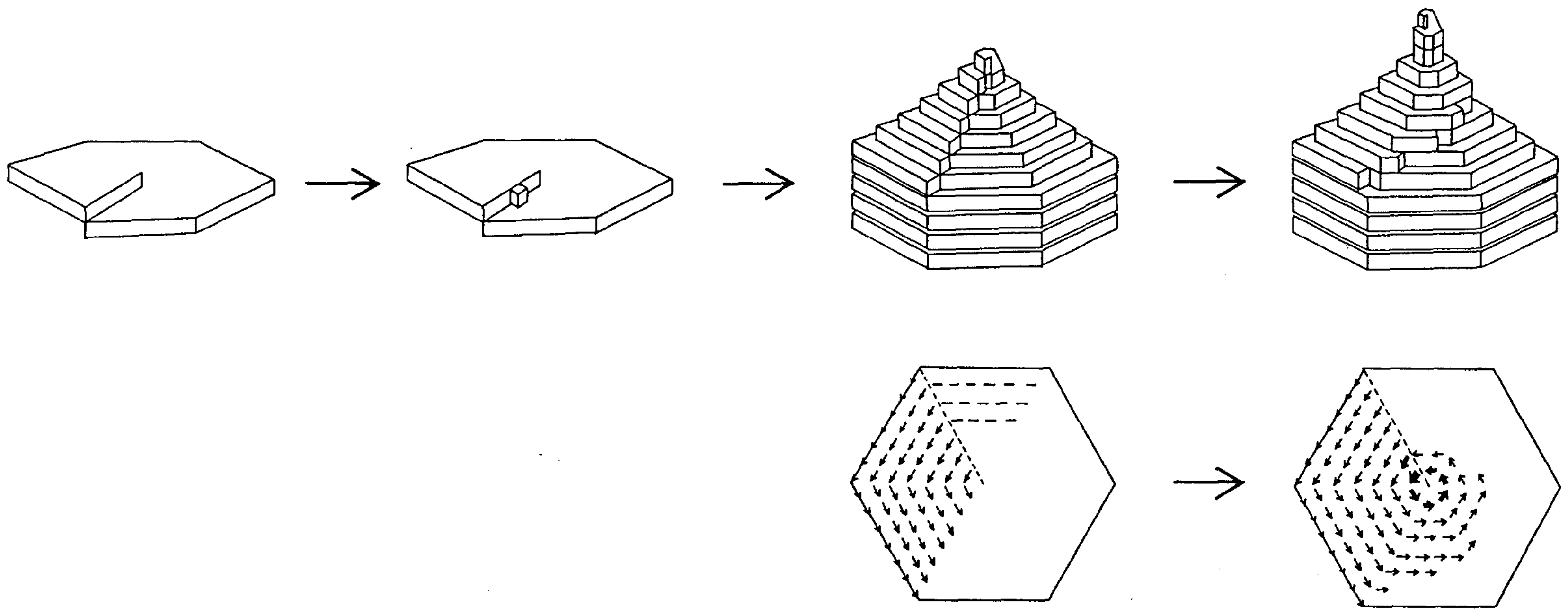


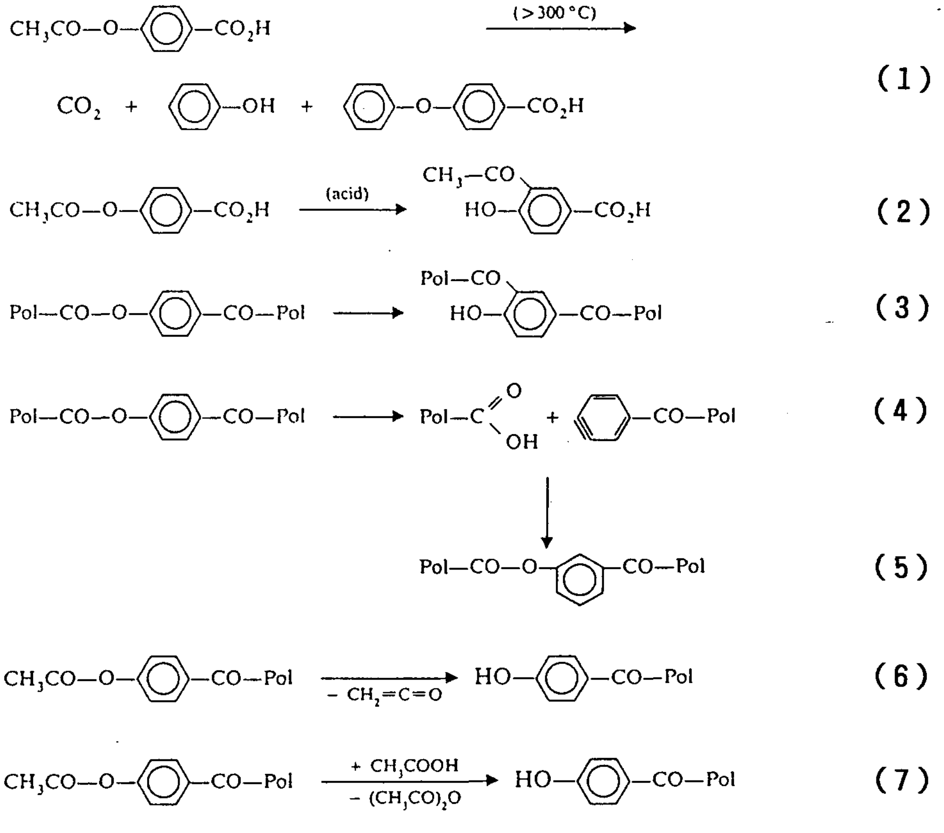
Figure 1-20. Successive stages in development of a spiral growth starting from a screw dislocation.

There have been a few studies on the formation mechanism of POB crystals during high-temperature solution polymerization. Economy *et. al* had reported that the crystal growth proceeded by the crystallization of monomers into the growing plane of the crystal surface which was similar to the molecular spinning mechanism and then polymerization occurred in the crystal.[8,15] Kricheldorf *et. al* had reported another mechanism that the POB crystal was formed by both lateral crystal growth of the seed crystals by adding oligomers onto its surface and longitudinal crystal growth by sandwiching lamellar oligomer crystals on top of each other, and then polymerization also occurred in the crystal.[24] However, these previous mechanism of POB crystal formation can be excluded by morphological observations in the case of the formation of the POB whiskers.

1-4-2-3 Increase of Molecular Weight of Poly(p-oxybenzoyl) during Whisker Formation

Electron microscopic observations suggest that the lamellae observed in the incipient crystal of the whisker have *ca.* 50Å thickness, which is corresponding to the octamer of p-ABA. In order to clarify this point, the oligomers which are dissolved in a homogeneous solution state at 330℃ are analyzed by a reversed phase chromatography. Polymerization was carried out at a concentration of 1.0% in LP at a heating rate of 15℃/min. The oligomers which were dissolved in solution at 330℃ were isolated from the filtrate after the vacuum filtration at 330℃ to separate the precipitated crystals.

The chromatogram of the oligomers prepared for 30min is shown in Figure 1-21. The peaks detected were assigned on the basis of the model compounds and the results of other polyester oligomers. It had reported by several authors that thermal polycondensation of p-ABA involved decarboxylation along with formation of phenol and 4-phenoxybenzoic acid. In addition, the fries-rearrengement yielded trifunctional comonomers during thermal polycondensation as described below.[16,24]



Scheme 1-3. Side reactions during thermal polycondensation

Nonassignable peaks in Figure 1-21 might correspond to the by-products produced during polymerization. The oligomers which have higher DP than 7 do not exist in the homogeneous solution state. The chromatogram of the oligomers prepared

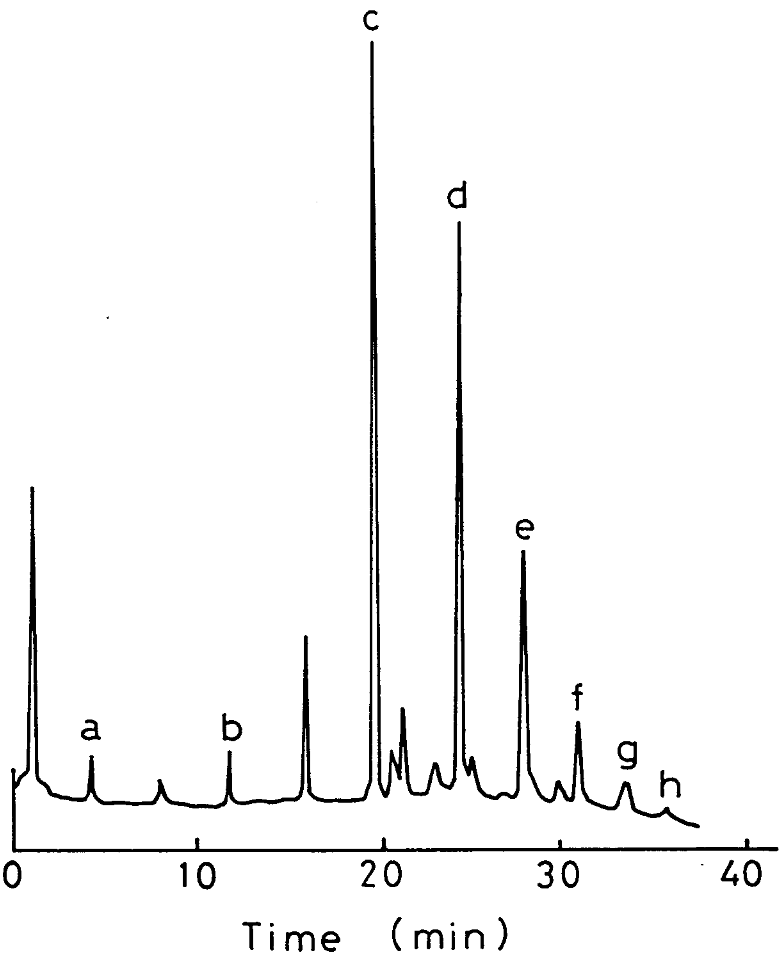


Figure 1-21. Chromatogram of oligomers dissolved in LP.
Prepared at 330℃ for 30min. (a) p-hydroxybenzoic acid;
(b) p-ABA; (c) dimer; (d) trimer; (e) tetramer; (f) pentamer; (g) hexamer;
(h) heptamer.

for 10min is very close to that in Figure 1-21 and the oligomer having the highest DP in solution is also heptamer. It is therefore concluded that the oligomers which are precipitated and crystallize in the form of lamellae are oligomers larger than heptamer. The results of the chromatography supports the result of the electron microscopic observation experimentally.

Polymerization time dependencies of the yield and the DP of the whisker are shown in Figure 1-22. While the yield does not increase after 16h, the DP continues to increase with polymerization time even after the yield levels off. This fact reveals that the post-polymerization between lamellae occurs in the crystal region and extended chain crystals are formed. Table 1-3 lists the DP and the calculated polymer chain length. The DP reaches 1800-1900 after 60h and the polymer chains extend to 1.17μm. Condensation polymers which have high DP like the POB whisker have never been reported thus far. In the growth of the whisker, the post-polymerization proceeds very effectively between lamellae due to the regular arrangements of the polymer chain ends.

The whiskers are etched by 1N-KOH aq. at 30℃ for 72h to observe the inner structure. Figure 1-23 shows the electron

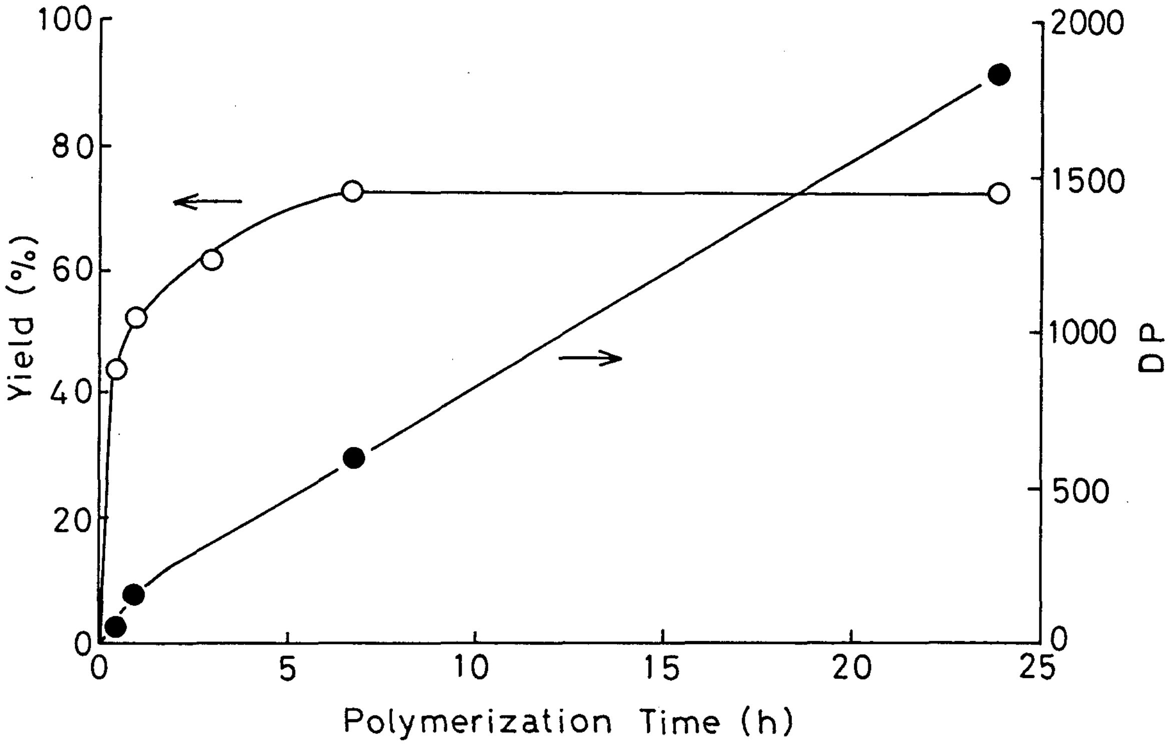
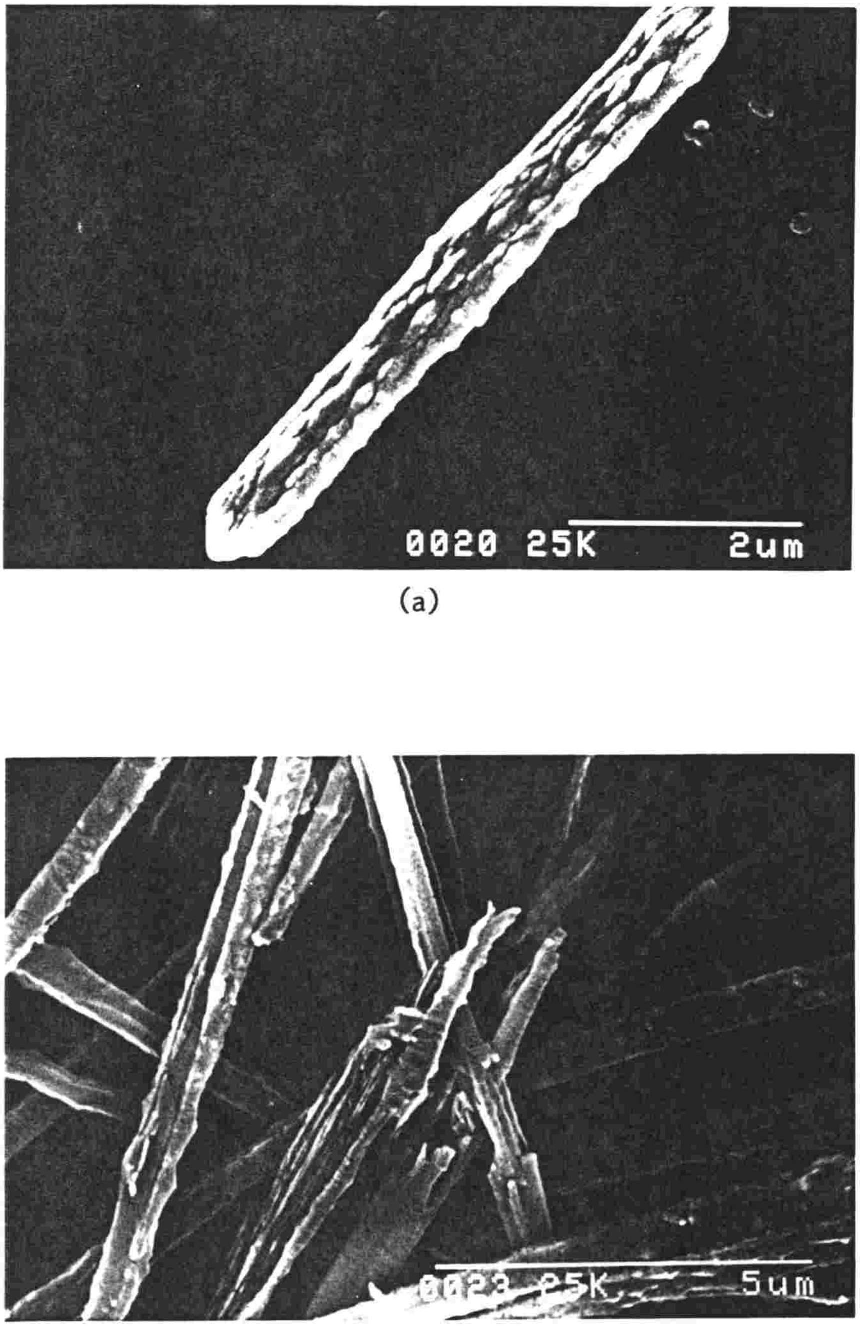


Figure 1-22. Variation of yield (○) and degree of polymerization (●) of POB whiskers with polymerization time.



(a)

(b)

Figure 1-23. Scanning electron micrograph of POB whiskers etched with 1N-KOH solution at 30℃ for 72h. Prepared in LP at 330℃ for (a) 3min and (b) 24h.

Table 1-3. Degree of polymerization and molecular chain length with polymerization time

Polymerization time (min)	Degree of polymerization	Molecular chain length (μm)
3	48	0.03
60	135	0.09
400	566	0.36
1440	1863	1.17

scanning micrographs of the etched whiskers prepared for 3min and 24h. As is seen in Figure 1-23, the twisted bundle structures are clearly observed along to the long axis of the incipient crystal, whereas the twisted bundle structure disappears and well oriented fibrillar structure appears after 24h. The change of the inner structure suggests that the reorganization into extended chain crystals occurs accompanying the post-polymerization.

1-5 Conclusion

The synthesis and characterization of the POB whiskers are studies. The most important factors in controlling the POB crystal morphologies during high-temperature solution polymerization are polarity of solvent, concentration of monomer and stirring. Less-polar solvents such as LP or TS 800, low concentration of monomer and no stirring are desirable for making whiskers. These conditions give the whiskers of which the length is 30-70μm and the width is 1-2μm. The POB whisker is the first polymer whisker obtained by condensation reaction.

It is found from the diffraction examinations that the whiskers exhibit single-crystal nature and the polymer chains align along the long axis of the whisker.

Owing to the closest packing of polymer chains in the crystal, the whiskers prepared in LP display the highest thermal stability in TGA, *i.e.* the temperature of 5wt% loss in air is over 500℃, and the highest first-order solid-solid transition temperature in DSC compared with the crystals with other morphologies.

The formation mechanism of the whisker is studied along their morphological features and it is found that the formation mechanism contains following steps as schematically illustrated in Figure 1-24.

(1) Oligomers of low DP are formed in a homogeneous solution state. As soon as the DP exceeds 7, oligomers are precipitated in the form of lamellae.
(2) The lamellae pile up along the long axis of needle-like crystals with a spiral growth caused by a screw dislocation.
(3) After that, DP increases by the transesterification in the interlamellae region and the reorganization of the crystal occurs.

Furthermore, it is particularly noteworthy that the synthetic method of the POB whisker provides a new concept for morphological processing of infusible polymers. That is, infusible polymers can be processed into some crystal form by the combination of crystallization with solution polymerization of monomers.

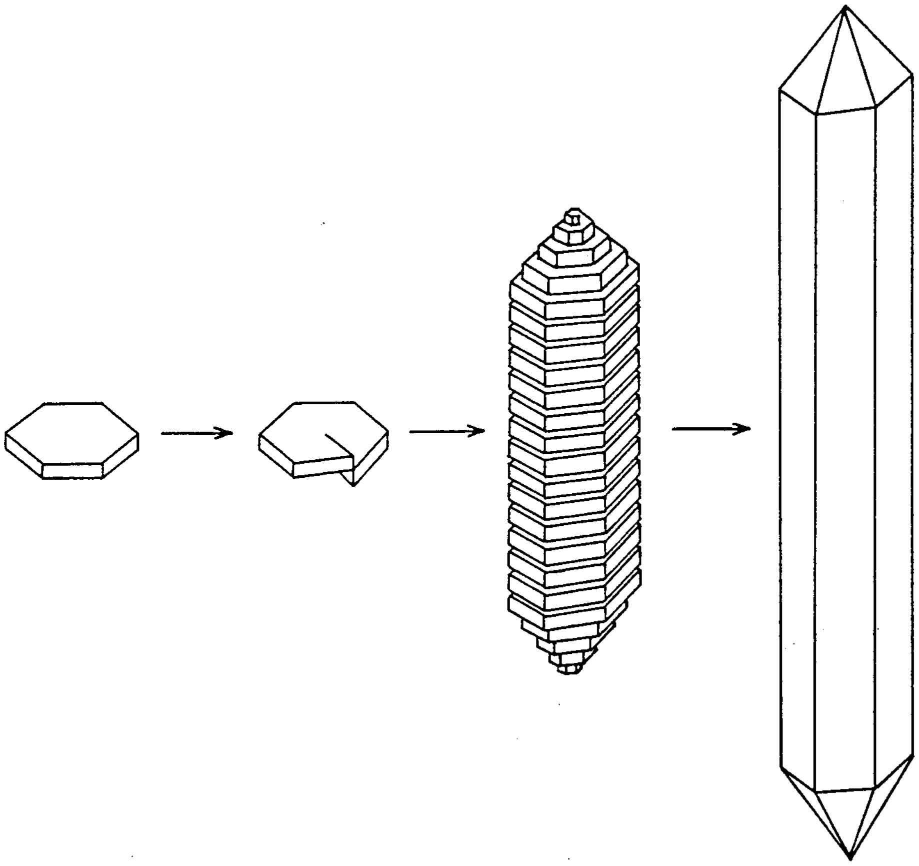


Figure 1-24. Schematic drawing of growth mechanism of POB whisker.

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Chapter 2

Control of Size of Poly(p-oxybenzoyl) Whisker

2-1 Introduction

Poly(p-oxybenzoyl) (POB) whiskers were prepared by crystallization during high-temperature solution polymerization of p-acetoxybenzoic acid (p-ABA). The POB whisker which is a chain extended polymer crystal exhibits outstanding thermal stability and moreover, it is expected to show the good mechanical properties because of its straight and rigid-rod structure. The POB whisker will be therefore brought into practical use, *e.g.* an organic reinforcement in composites and so forth.

When the whiskers are used as industrial materials, the control of the size of the whisker is of great importance from the standpoint of the reinforcing effect depending on the axial ratio and processability.

It is revealed in chapter 1 that the crystal morphologies are significantly dependent on the nature of the solvent and this fact suggests that it is possible to control the size of the whisker by the nature of the solvent.

In this chapter, the relationship between the size of the whisker and the chemical structure of paraffin as the polymerization solvent is studied for the purpose of the control of the size, *i.e.* the length and the width of the POB whisker.

2-2 Solvent Effect on Size of Poly(p-oxybenzoyl) Whisker

2-2-1 Experimental

Materials

p-ABA was prepared as described in chapter 1. Liquid paraffin (LP) was used after vacuum distillation as also described in chapter 1. Sasol wax H2 (SW) purchased from Sasol, South African Coal & Gas Co. Ltd. was used after recrystallization from benzene.

Preparation of Poly(p-oxybenzoyl) Whiskers

A typical preparation procedure for POB whiskers is described in the following. Other crystals were also obtained in a similar manner.

In a 200ml-cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes, 0.90g of p-ABA and 60g of SW were placed. This reaction mixture was heated with stirring under a slow stream of nitrogen unti the monomer dissolved completely. Stirring was stopped and heating was continued up to 330℃, and then the temperature was maintained at 330℃. In a couple of minutes, the reaction solution became turbid and then whiskers were formed. The reaction was continued at 330℃ for 6h. The reaction mixture was allowed to cool to room temperature and then benzene was added. The whiskers were collected by filtration after being washed in hot benzene several times, and they were then dried at 100℃ under reduced pressure to constant weight.

Measurements

Morphological characterization was performed on a Hitachi 530-SH scanning electron microscopy. Chemical structure of solvents was analyzed by ^{13}C-NMR at 120℃ on a Varian FT-80A spectrometer.

2-2-2 Results and Discussion

2-2-2-1 Chemical Structure of Paraffin

Two kinds of paraffin are used as solvent in this work: one is a liquid at room temperature (LP) and the other is a solid (SW) with a melting temperature of around 110℃. The chemical structures of these paraffins are analyzed by ^{13}C-NMR. The distribution of primary, secondary and tertially carbons, assigned according to previous studies[1-4], are tabulated in Table 2-1. From these results, it can be seen that SW is a totally linear paraffin containing no branches. On the other hand, the LP has many branches, *i.e.* 15.2% of total carbons are tertially.

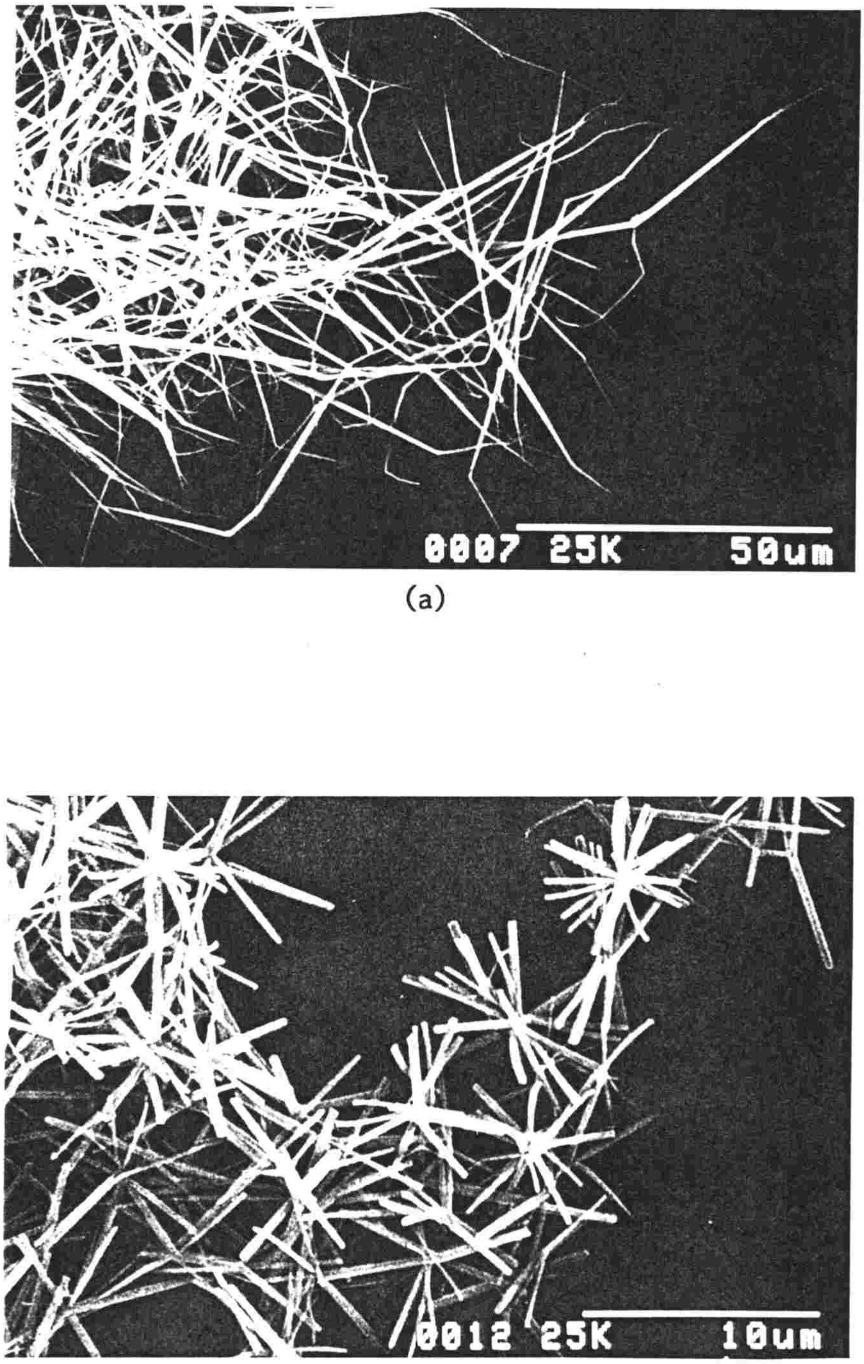
Table 2-1. Chemical structure of paraffins analyzed by ^{13}C-NMR

		Distribution of carbon atoms (number)			Molar ratio of tertially carbon
Paraffin	Mn	Primary	Secondary	Tertially	(%)
LP	928	12	44	10	15.2
SW	759	2	52	0	0.0

2-2-2-2 Morphology of Poly(p-oxybenzoyl) Whiskers

The POB whiskers prepared in LP (POB-1) and SW (POB-4) are shown in Figure 2-1. The features of the whiskers are quite different depending on the used solvents. The conspicuous differences in their crystal shapes are : (1) both length and width of POB-4 are smaller, the length and width being, respectively, a tenth and half that of POB-1; (2) the tips of POB-1 are very sharp but those of POB-4 are completely flat; and (3) POB-1 shows single, needle-like crystals but POB-4 shows radial growth from the center.

In order to clarify that these differences are attributable to the solvent effect, the shapes of crystals prepared in various mixtures of LP and SW are observed. The results are summarized in Figure 2-2, 2-3 and Table 2-2. The crystal shape is largely changed with the mixing ratio of two solvents. As the content of SW in the solvent increased, both the length (L) and width (W) of the whiskers decrease. The tip angle (θ) of the whiskers becomes broader and the trunk ratio (l/L) (see Figure 2-4), which is proportional to the tip angle, becomes higher as the content of SW increases. Furthermore, the yield of POB-4 is quite low compared with the others. The solubility test of p-ABA in these paraffins at 330℃ shows that maximum solubility of p-ABA in LP is over 15wt%, but in SW it is only 1.5wt%. Because of this low solubility, sublimation of p-ABA from the SW solution occurs more vigorously during polymerization compared with the LP solution, and this sublimation diminishes the yield of whiskers.



(a)

(b)

Figure 2-1. Scanning electron micrographs of POB whiskers prepared at 330℃ for 6h in (a) LP (POB-1) and (b) SW (POB-4).

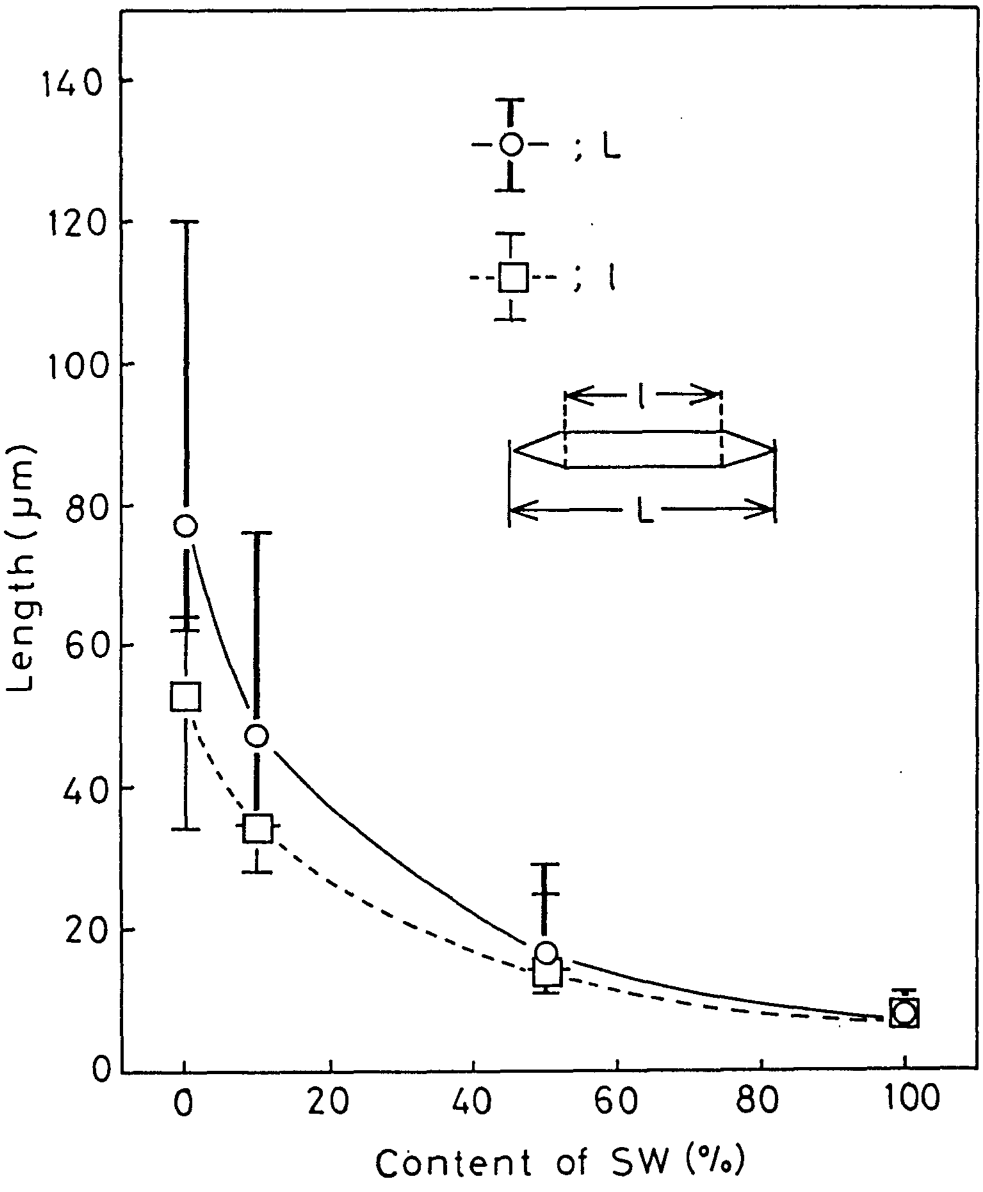


Figure 2-2. Length (L) (○) and trunk length (l) (□) of whiskers plotted as functions of content of SW in solvent.

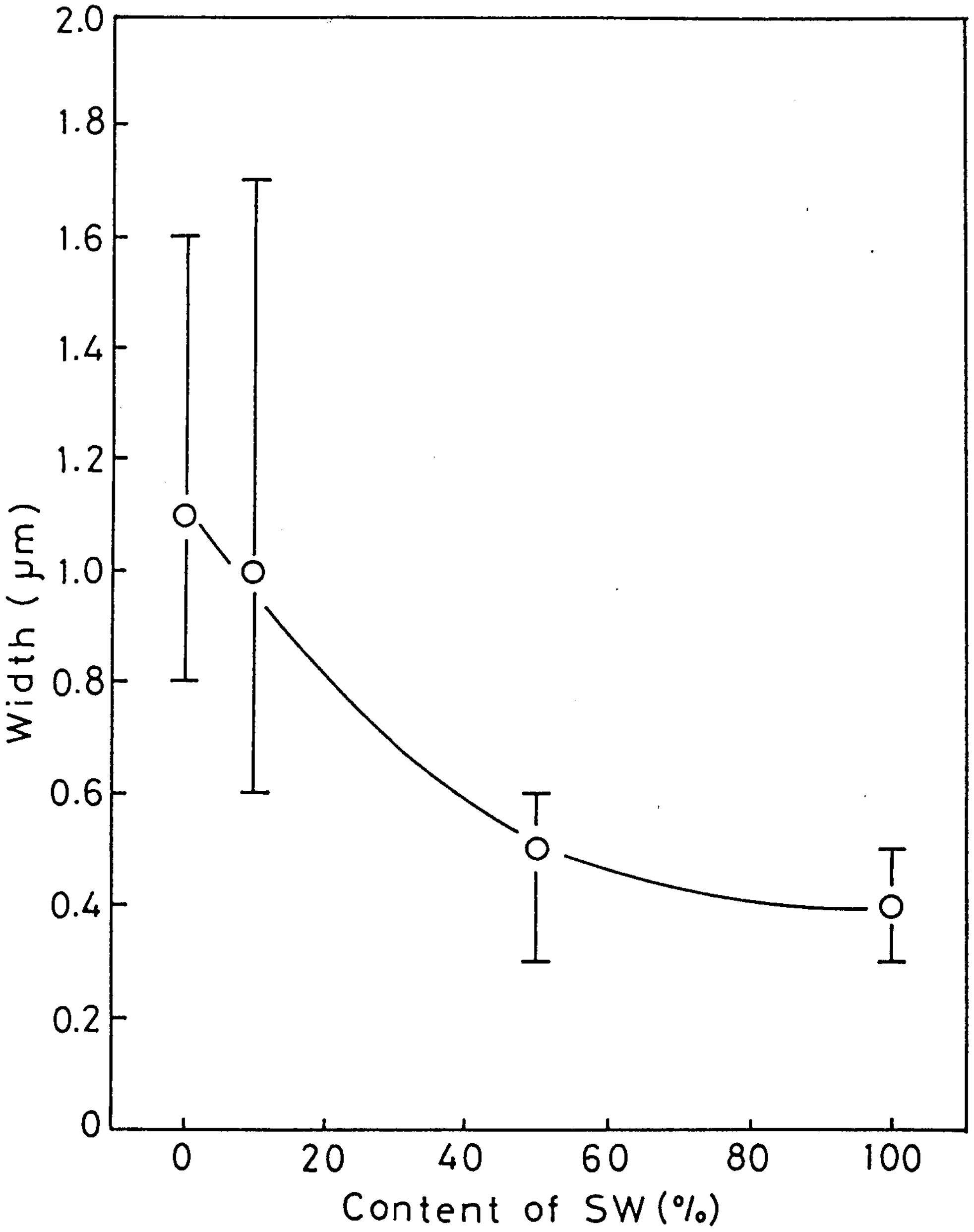


Figure 2-3. Width (W) of whiskers plotted as a function of content of SW in solvent.

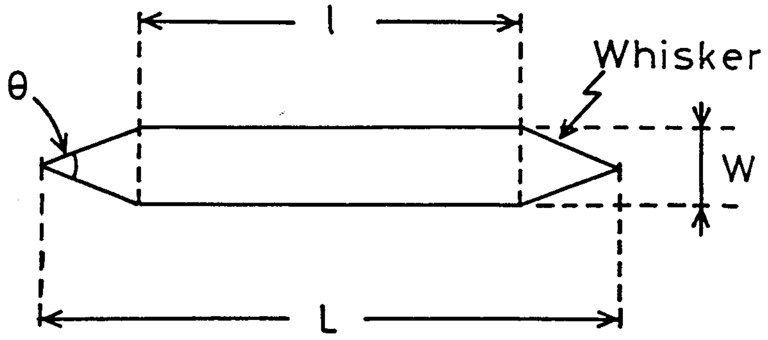


Figure 2-4. Description of parameters relating to whisker size and shape.

Table 2-2. Size of POB whiskers from p-ABA in paraffin

Polymer	Solvent[1)] LP / SW (weight ratio)	Yield (%)	Size of whisker[2)] (μm) Length (L)	Trunk length (l)	Width (W)	Trunk ratio l/L (%)	Tip angle θ (°)
POB-1	100 / 0	79	78	41	1.1	53	4
POB-2	90 / 10	79	47	34	1.0	72	9
POB-3	50 / 50	73	17	14	0.5	82	19
POB-4	0 / 100	27	8	8	0.4	100	180

1) Solvent weight ratio; LP (liquid paraffin) / SW (Sasol wax)

2) Length (L), trunk length (l), width (W) and tip angle (θ) are described in Figure 2-4.

It has already suggested in chapter 1 that the sizes of the whiskers are determined by both the number and the size of those lamellar crystals with screw dislocations formed in the early stages of polymerization. The number of lamellar crystals (N) contributing to whisker growth can be experimentally estimated from the yield of polymers and the average weight of whiskers obtained (equation (1)). Here, it is shown that these whiskers have hexagonal cross-sections as described in chapter 1.

$$N = \frac{\varepsilon \cdot M}{(\sqrt{3}/8) \cdot W^2 \cdot (L+2l) \cdot \rho} \qquad (1)$$

where, ε is the yield (%), M is the molar mass of the POB repeating unit, W is the average width of whiskers, L is the average length of the whiskers, l is the average trunk length of the whiskers and ρ is the density of the POB whisker (1.54×10^{-12} g/μm^3).

The results are plotted in Figure 2-5. N increases as the content of SW in the solvent increases and N in SW is quite large compared with N in LP. For the purpose of understanding this phenomenon, the shapes of whiskers obtained at 330℃ for 3min are also observed in LP (POB-5) and SW (POB-6). The results are summarized in Table 2-3 and the distributions of both the length and the width of crystals are shown in Figure 2-6. It is evident that many more nuclei for whisker growth with smaller width are formed in SW than in LP. The narrow distributions of both the length and width shows that lamellar crystals with dislocations serve as nuclei for whisker growth. The numbers of whiskers after 3min at 330℃ are in good agreement with those estimated from the final whiskers. This good agreement implies that there is no time

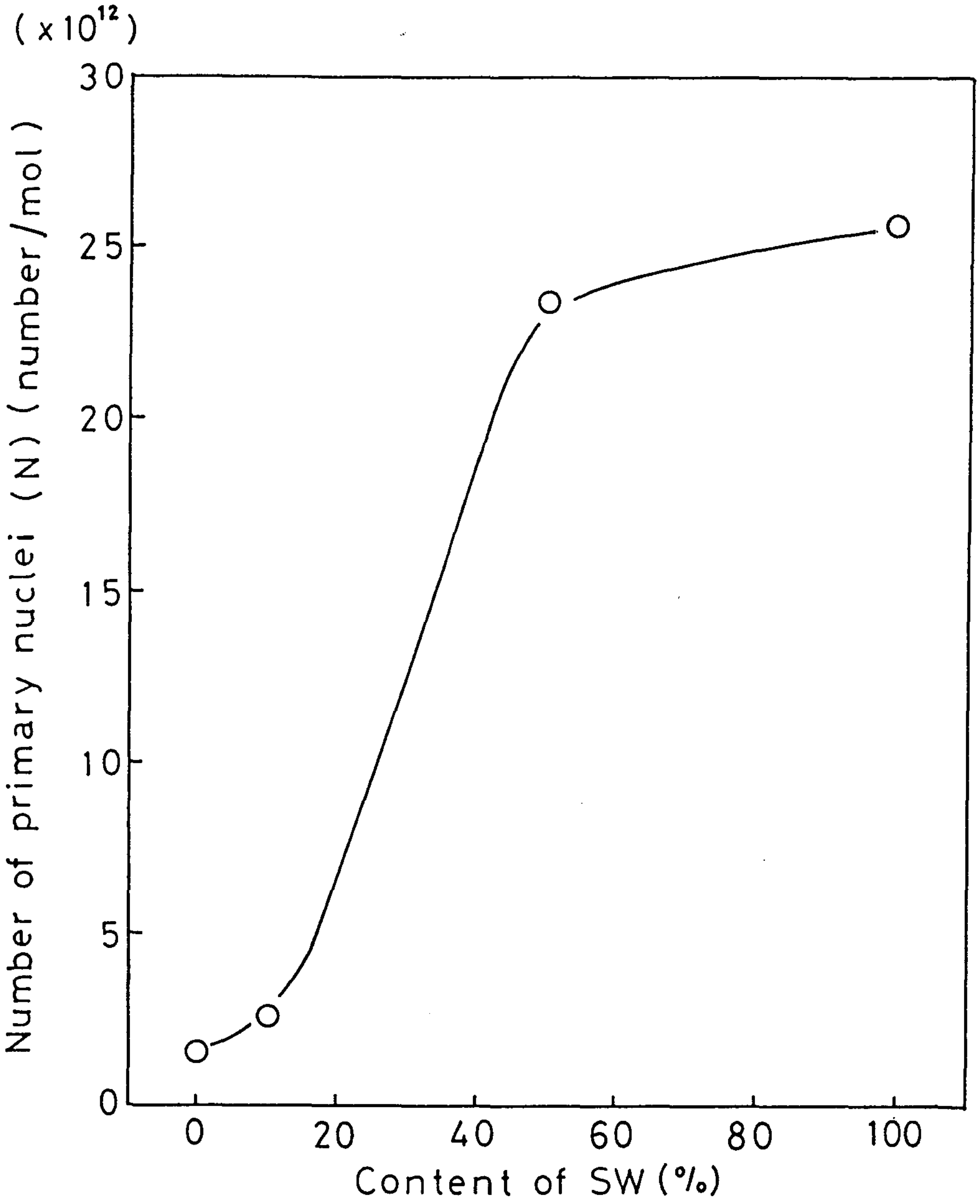


Figure 2-5. **Number** of primary nuclei for whisker growth (N) plotted as a function of content of SW in solvent.

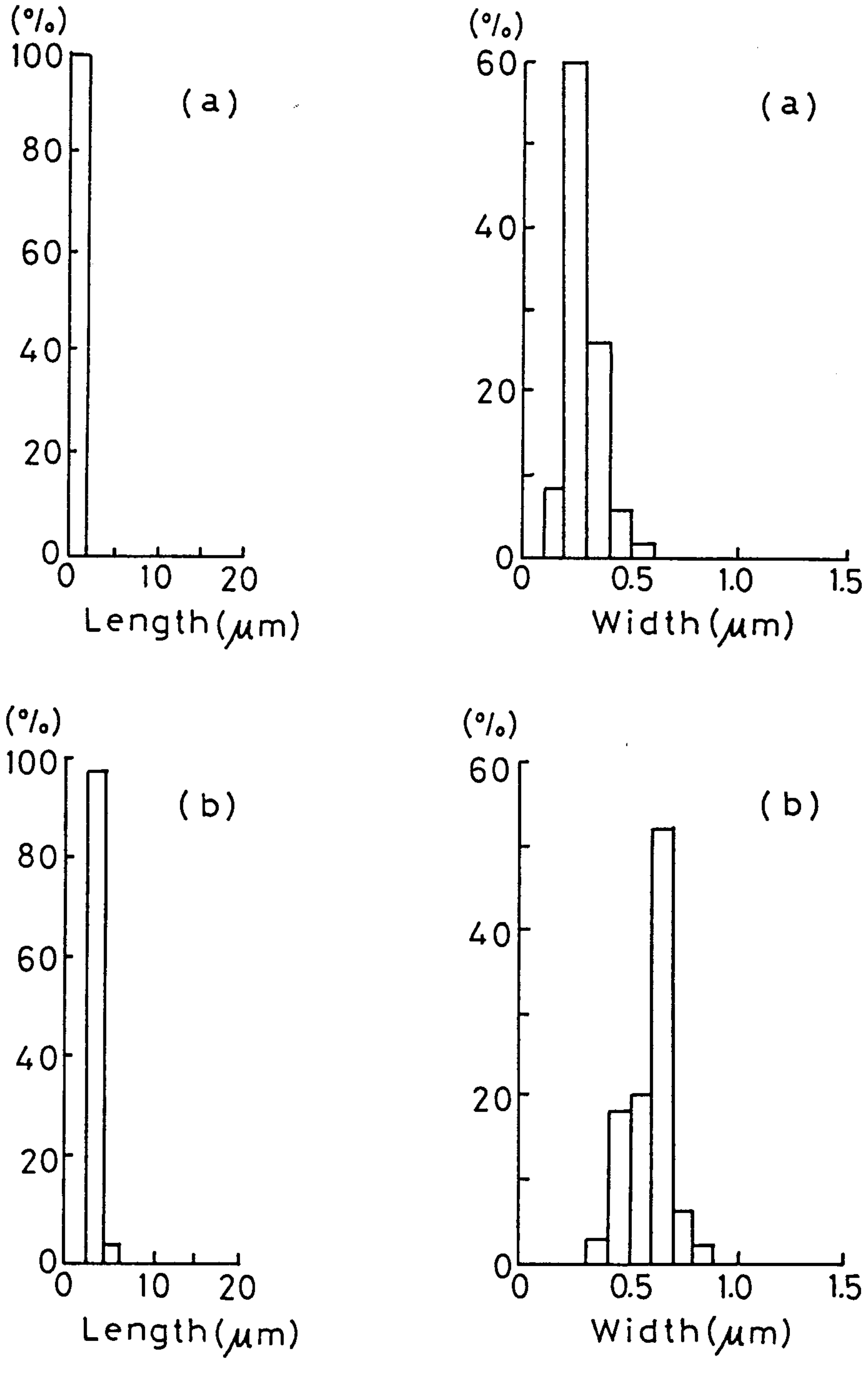


Figure 2-6. Distributions of length and width of whiskers prepared for 3min at 330℃ in (a) SW and (b) LP.

Table 2-3. Shape of incipient crystals and calculated number of primary nucleus for whisker growth

Polymer	Solvent	Yield (%)	Average size of crystals (μm) Length (L)	Trunk length (l)	Width (W)	Tip angle θ (°)	Number of primary nucleus (10^{12} N/mol)
POB-5	LP	1.5	3.00	2.29	0.60	80	1.2
POB-6	SW	2.8	1.32	0.99	0.28	80	24.7

lapse in the formation of primary nuclei for whisker growth.

These results are explicable on the basis of the following mechanism of formation for the POB whiskers: (1) POB oligomers precipitate out from the homogeneous solution and crystallize in the form of lamellae; (2) screw dislocations generate in the lamella (primary nuclei for whisker growth) and needle-like crystals are formed with a spiral growth; and (3) the molecular weight increases by transesterification in the interlamellar region and reorganization of crystals occurs. The formation of lamellar crystals, which correspond to primary nuclei for whisker growth, determines the crystal shape of the eventual whiskers. As described earlier, owing to the lower solubility of POB oligomers into SW, many more primary nuclei for whisker growth are formed in the early stage of polymerization in the SW solution, that is, the lamellar crystals are precipitated from a sufficiently highly supersaturated solution to give a large number of crystals with small diameter. The sublimation of p-ABA proceeds concurrently with the polymerization, and therefore the concentration of p-ABA decreases. Hence, the large number of primary nuclei and the decrease of p-ABA concentration by sublimation cause the whiskers to be small in SW. Both the solubility of POB oligomers and the decrease in p-ABA concentration by sublimation are strongly related to the content of SW in the solvent and it is clear that the size of the whisker obtained decreases as the content of SW increases.

The change of tip angle depending upon the content of SW in solvent is not clear. The tendency towards radial growth with increased SW content is ascribed to rapid nucleation from a highly supersaturated solution. Further study is required to elucidate the nature of the radial growth and the change in tip angle.

2-3 Thermal Properties of Poly(p-oxybenzoyl) Whisker

2-3-1 Experimental

Materials

The POB whiskers prepared in the previous section were used for thermal analysis.

Measurements

Thermal properties were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Perkin-Elmer DSC 7 at a heating rate of 100℃/min in nitrogen. TGA was performed on a Shimadzu TGA-30 at a heating rate of 10℃/min on a 5mg sample in nitrogen or air.

2-3-2 Results and Discussion

The Thermal properties of the POB whiskers are estimated by DSC and TGA.

DSC analysis confirms the presence of two reversible transitions at around 370℃ and around 450℃ on a heating scan, as shown in Figure 2-7. In order to avoid the influence of thermal decomposition, DSC was performed at an extremely high heating rate of 100℃/min. The transition temperatures, enthalpies and entropies for the first-heating scan are

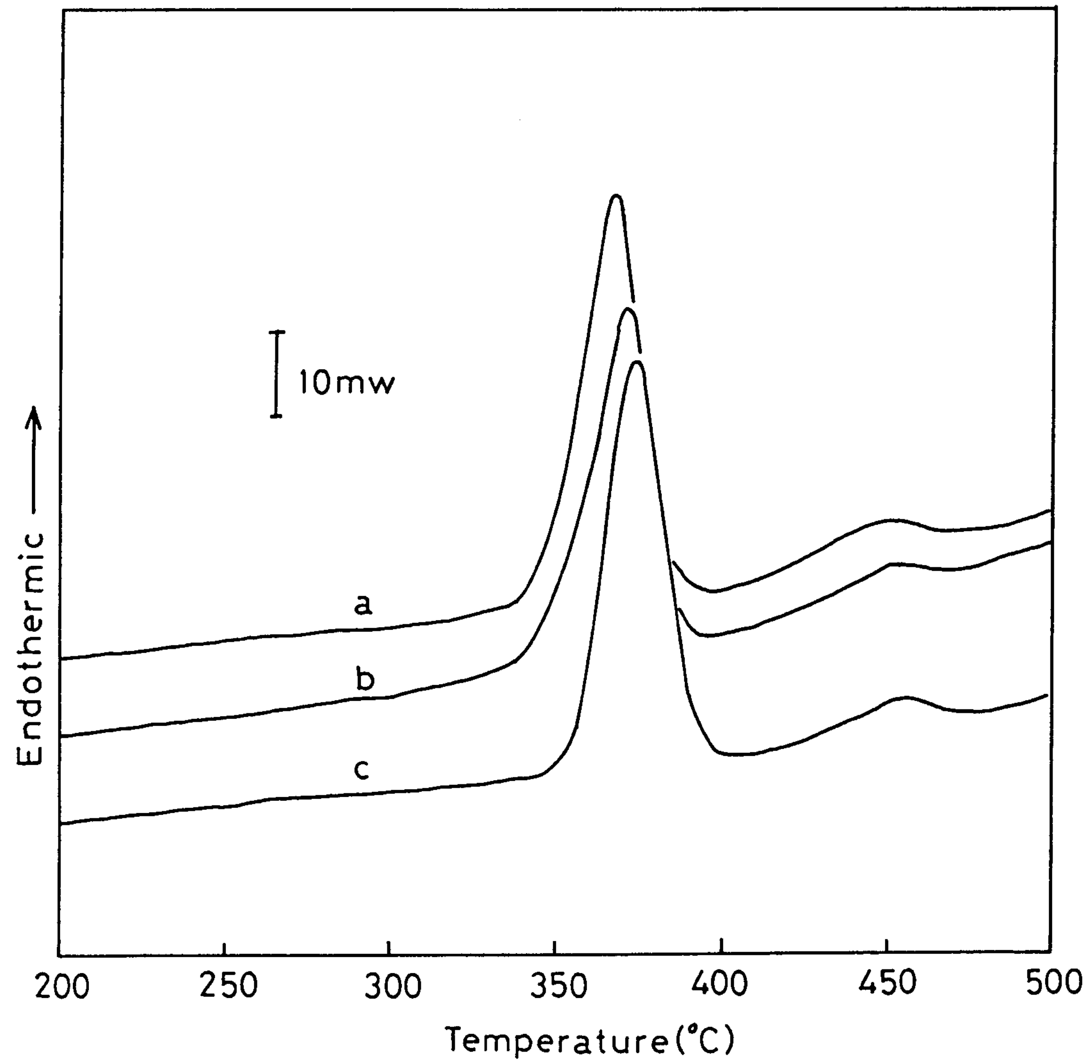


Figure 2-7. DSC profiles of (a) POB-1; (b) POB-3; (c) POB-4 on a heating scan at a heating rate of 100℃/min.

Table 2-4. Thermal transitions of POB whiskers$^{1)}$

	Lower-temperature transition			Higher-temperature transition		
Polymer	T_t (℃)	ΔH_t (kJ/mol)	ΔS_t (J/K·mol)	T_n (℃)	ΔH_n (kJ/mol)	ΔS_n (J/K·mol)
POB-1	374.4	6.82	10.53	454.4	0.63	0.87
POB-2	378.0	6.97	10.71	457.2	0.37	0.51
POB-3	371.7	6.28	10.53	451.7	0.53	0.72
POB-4	369.6	6.79	10.57	450.4	0.67	0.92

1) Transition temperatures on heating scan at a rate of 100℃/min.

tabulated in Table 2-4. Both transition temperatures of POB-4 were the lowest and the 100% SW content in the solvent is thought to be the cause of this. It is known that the POB crystal has two reversible thermal transitions. These transitions at 370℃ and 450℃ are regarded as a plastic crystal or a highly ordered smectic phase transition and a phase transition to a nematic mesophase, respectively.$^{5-8}$ It is clear as described in chapter 1 that these transition temperatures are strongly related to the densities of the POB whiskers, *i.e.* the packing densities of the polymer chains. On the basis of the previous studies, the low transition temperatures of POB-4 are due to the loose packing of the polymer chains in the crystals. It is thought that the packing of polymer chains in the crystals becomes looser as the content of SW in solvent becomes higher. This explanation rests on the poor efficiency of the transesterification in the interlamellar region.

Table 2-5. Thermal stabilities of POB whiskers[1)]

	Temperature of 5wt% loss (℃)	
Polymer	Nitrogen	Air
POB-1	510	501
POB-2	508	495
POB-3	498	483
POB-4	493	465

1) measured by TGA on a 5mg sample at a heating rate of 10℃/min.

Thermal stabilities, as analyzed by TGA are summarized in Table 2-5. These whiskers exhibit excellent thermal stabilities. The temperature of 5wt% loss decreased monotonously in both nitrogen and air as the content of SW increased. This relationship between thermal stability and SW content is substantially identical with the relationship between transition temperature and SW content described above. This identity indicates that the crystals in which the polymer chains pack more densely show the higher thermal stability.

2-4 Conclusion

The size of the POB whisker is controlled by the mixing ratio of LP and SW in the solvent. The conspicuous changes in crystal shape with increasing SW content in the solvent are: (1) both the length and the width of the whisker decrease from 78μm to 8μm and from 1.1μm to 0.4μm, respectively; (2) the tip angle of the whisker increases; and (3) the radial growth of whisker increases. These characteristic changes in size can be attributed to the solubility of POB oligomers in the solvent. Because of low solubility of POB oligomers in SW, many more primary nuclei for whisker growth are formed in the early stage of polymerization in SW than in LP, that is, the nucleation from a sufficiently highly supersaturated state produces a large number of nuclei with small diameter. The sublimation of p-ABA proceeds concurrently with the polymerization, and therefore the concentration of p-ABA decreases over time. Hence, the large number of primary nuclei and the decrease in p-ABA concentration by sublimation cause the whiskers to be small in SW. The results of observing the incipient whiskers obtained in 3min at 330℃ in SW and LP bore out this conclusion. The change in the tip angle and the increasing tendency towards radial growth with increasing SW content in the solvent seem to be attributable to the high degree of supersaturation, though further study is required.

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Chapter 3

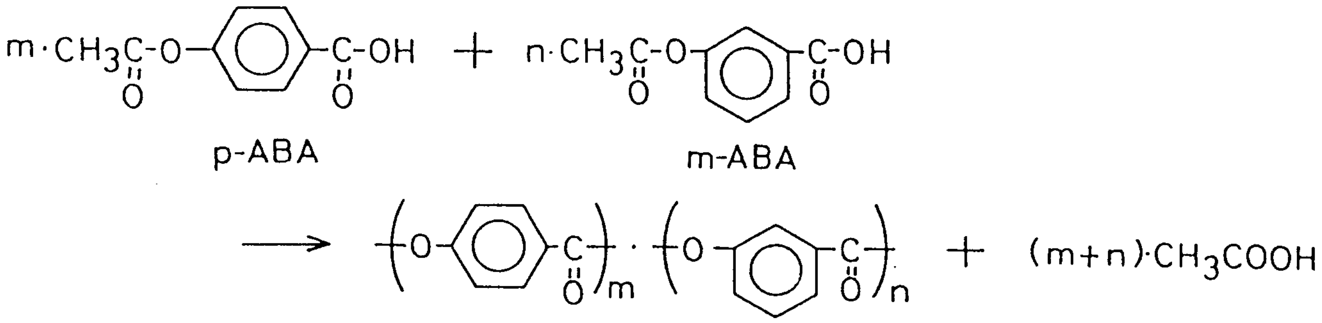
Crystallization of Copolymer of p-Hydroxybenzoic acid with m-Hydroxybenzoic acid during Solution Polymerization

3-1 Introduction

It have been reported in the previous chapter that the poly(p-oxybenzoyl) (POB) whiskers are obtained by crystallization during high-temperature solution polymerization. These whiskers have an almost uniform width of 1-2μm and a length of 30-70μm and they in which the polymer chains align along the long axis of the whisker are expectable to be useful as high-performance materials such as an organic reinforcement because of their outstanding properties including thermal stability and mechanical properties.

The factors which influence the morphology of the POB whisker including polarity of solvent, concentration of monomer, stirring, polymerization temperature, heating rate and chemical structure of monomers have been studied and it has been concluded that less-polar solvent such as liquid paraffin (LP) or Therm S 800, low concentration of monomer, no-stirring, heating rate of 15℃/min and p-acetoxybenzoic acid (p-ABA) are desirable for making the POB whiskers.

Generally, copolymerization of second monomer lowers the crystallizability of polymer chains and hence it may prevent the formation of polymer crystals. There have been a few studies on copolymerization effect on the crystal morphology about POB[1,2] and polyester-imides.[3] To the best of my knowledge systematic study of copolymerization effect on the morphology of the POB crystals, however, has never been reported so far. Thus, it is the purpose of the present work to clarify an influence of the copolymerization on the morphology of the POB whiskers in the copolymerization system of p-ABA and m-acetoxybenzoic acid (m-ABA) as described below.



Scheme 3-1. Copolymerization of p-ABA and m-ABA

3-2 Influence of Copolymerization on Morphology of Poly(p-oxybenzoyl) Whisker

3-2-1 Experimental

Materials

p-ABA and m-ABA were prepared as described in a literature.[4] LP was used as a polymerization solvent after the purification as described in chapter 1.

Preparation of Copolymers

Typical preparation procedures for copolymers are described in the following.

A. Solution polymerization. In a 200ml-cylindrical reactor equipped with a thermometer, a mechanical stirrer, and gas inlet and outlet tubes were placed 0.63g of p-ABA, 0.27g of m-ABA and 60g of LP. This reaction mixture was heated with stirring under a slow stream of nitrogen. When the monomers dissolved completely, stirring was stopped and heating was continued up to 330℃ at a heating rate of 15℃/min. Then the temperature was maintained at 330℃ for 6h. The reaction solution became turbid for 10min at 330℃ and then crystals were formed. The crystals formed were collected by filtration at 330℃. The collected crystals were washed in *n*-hexane several times and dried at 100℃ under reduced pressure to constant weight. The oligomers were precipitated from the filtrate while the filtrate was being allowed to cool to room temperature. The oligomers precipitated were also collected by filtration, washed in *n*-hexane several times and then dried at 50℃ under reduced pressure to constant weight.

B. Melt polymerization. The procedure of the melt polymerization was followed as described in a literature.[5]

Measurements

Morphological characterization was performed on a Hitachi 530-S scanning electron microscopy. Electron diffraction examinations were carried out on a Hitachi HU-11B transmission electron microscope.

Thermal properties were evaluated by using differential scanning calorimetry (DSC). DSC was performed on a Perkin-Elmer DSC 7 at a heating rate of 10℃/min in nitrogen.

Chemical structures and the degrees of polymerization (DP) of copolymers were analyzed by ^{1}H-NMR with a Varian Gemini-200 spectrometer after the hydrolysis of copolymers in an NMR tube as described in a literature.[6]

3-2-2 Results and Discussion

3-2-2-1 Copolymerization of p-Acetoxybenzoic acid and m-Acetoxybenzoic acid in Liquid Paraffin

Copolymerizations of p-ABA and m-ABA are carried out at a concentration of 1.0wt% in LP at 330℃ for 6h. The results are summarized in Table 3-1.

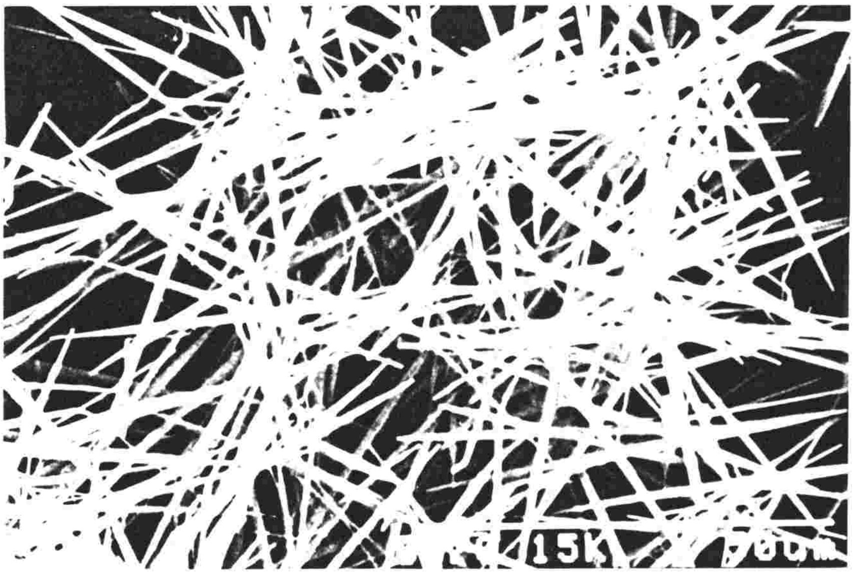
Whiskers are obtained when the content of m-ABA in the feed (χ_f) is in the range of 0-30 mol%. The needle-like crystals at χ_f of 0 mol%, 5 mol% (coPOB-1) and 30 mol%

Table 3-1. Results of copolymerization of p-ABA with m-ABA

Polymer	Content of m-ABA in feed (χ_f) (mol%)	Polymerization[1)] method	Yield (%)	Content of m-unit[2)] in the precipitated materials (mol%)	Crystal morphology
coPOB-1	5	SP	35.0	1.3	Needle-like
coPOB-2	10	SP	32.1	2.2	Needle-like
coPOB-3	20	SP	39.3	5.3	Needle-like
coPOB-4	30	SP	44.5	12.3	Needle-like
coPOB-5	40	MP	——	29.1	————
coPOB-6[3)]	40	SP	——	——	————

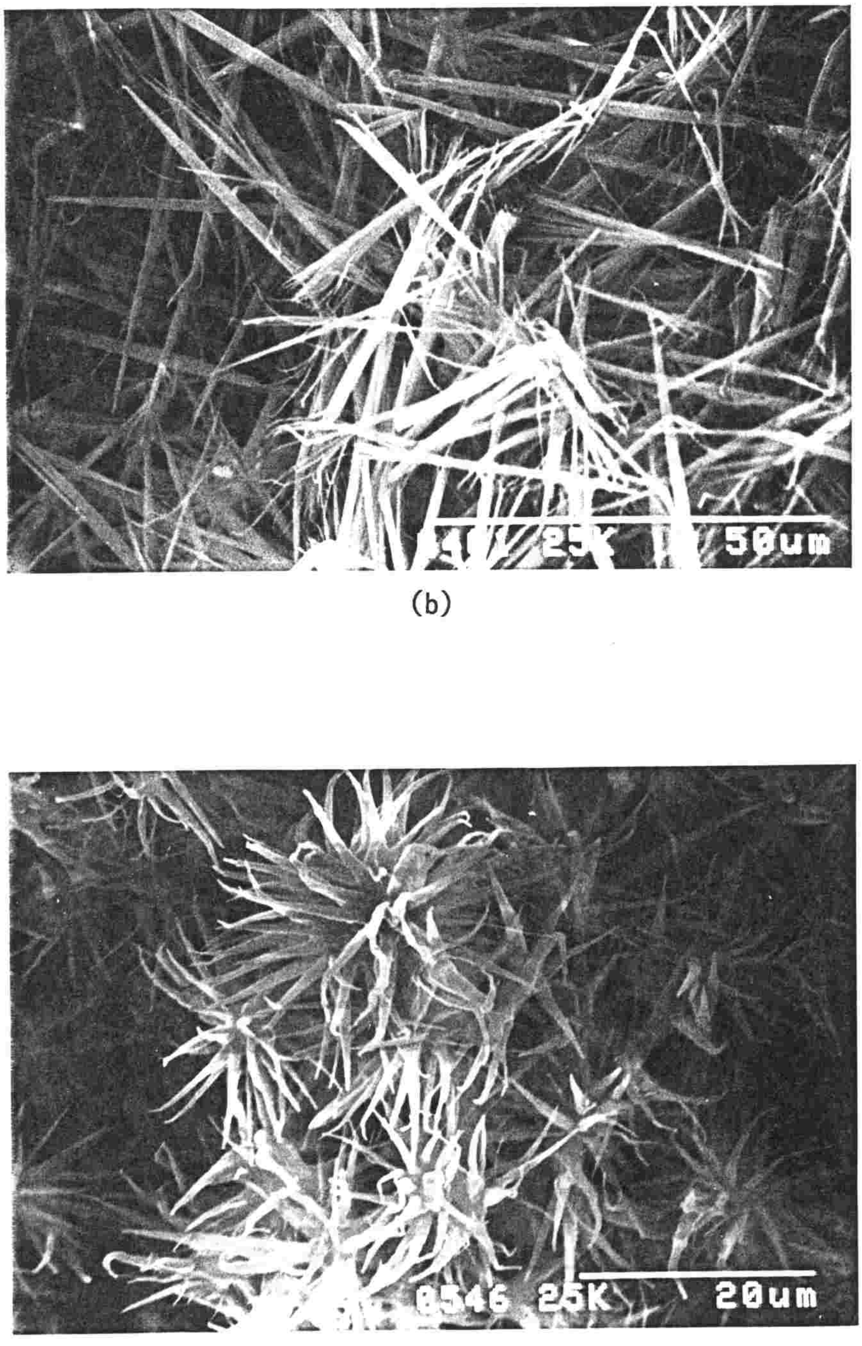
1) SP; Solution polymerization, MP; Melt polymerization
2) evaluated by ^{1}H-NMR measurements after hydrolysis of samples in conc. sulfuric acid
3) Crystals were not obtained.

(coPOB-4) are shown in Figure 3-1(a), (b) and (c), respectively. As can be seen in the micrographs of Figure 3-1, the crystals are inclined to show the fibrillation in their both ends and the radial growth from the central part as χ_f increases. When χ_f is higher than 40 mol%, crystals do not precipitated during polymerization. The precipitated materials during polymerization were isolate by vacuum filtration at 330℃ to avoid possibly the precipitation of the dissolving oligomers while cooling. The oligomers, which were dissolved in LP at 330℃, were precipitated from the filtrate by cooling to room temperature and they were also collected by filtration. In coPOB-4, the yield of the precipitated materials during polymerization and the



(a)

Figure 3-1. Scanning electron micrograph of whiskers at χ_f of (a) 0 mol%.



(b)

(c)

Figure 3-1. Scanning electron micrograph of whiskers at χ_f of (b) 5 mol% and (c) 30 mol%.

dissolving oligomers are examined as a function of the polymerization time as shown in Figure 3-2. The content of m-oxybenzoyl units in them which is determined by ^{1}H-NMR is shown in Figure 3-3. The total yield and the total content of m-oxybenzoyl units are not changed after 1h at ca. 50% and 20 mol%, respectively. This constancy shows that both monomers are sublimated in the early stage of polymerization (within 1h), but the sublimation no longer occurs after the polymerization proceeds. The sublimation of m-ABA is larger than p-ABA. The yield of the precipitated materials increases with the polymerization time and that of the dissolved oligomers, of course, decreases with an increase of the precipitated materials. It is, here, of interest that the content of m-oxybenzoyl units in the precipitated materials increases gradually with the polymerization time and that in the dissolving oligomers decreases. That is, oligomers with more m-oxybenzoyl units become to be precipitated from the solution with a progress of the polymerization.

The DP of the precipitated materials and that of the dissolving oligomers in coPOB-4 are determined by the acetyl end-group analysis by ^{1}H-NMR. The results are shown in Figure 3-4 as a function of the polymerization time. The DP of the dissolving oligomers is constant at *ca.* 3 until 4h and then increases to 7.5 at 6h. The DP of the precipitated materials increases with the polymerization time and this fact suggests the post-polymerization in solid state.

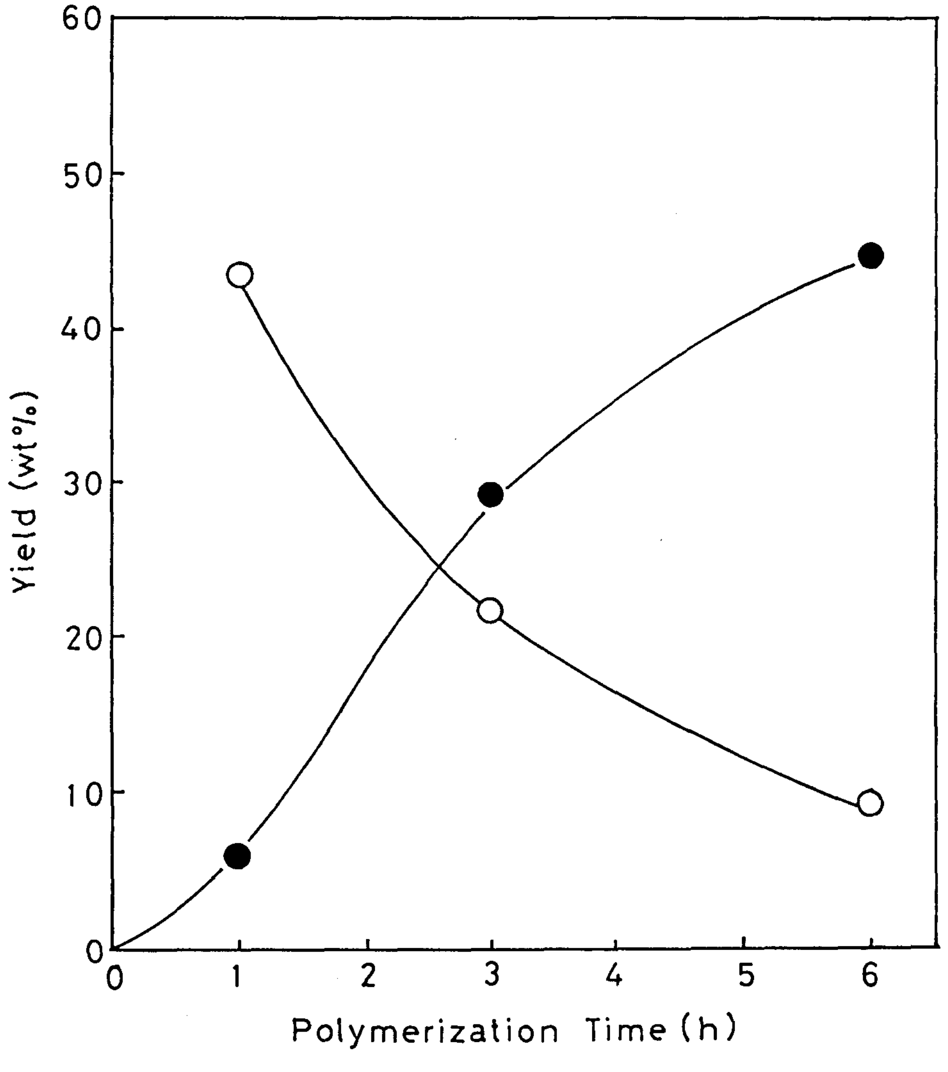


Figure 3-2. Variation of yield of precipitated materials (●) and dissolving oligomers (○) with polymerization time.
χ_f is 30 mol% (coPOB-4).

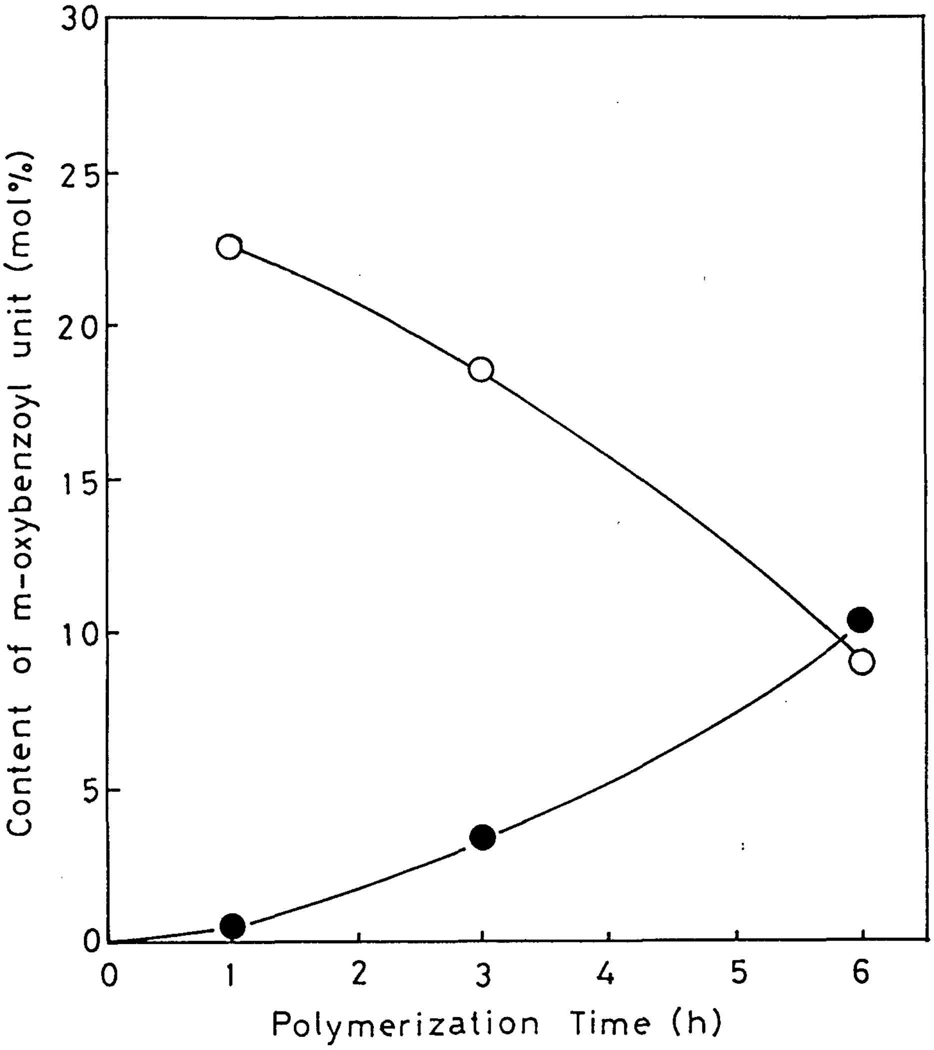


Figure 3-3. Variation of content of m-oxybenzoyl units in precipitated materials (●) and dissolving oligomers (○) with polymerization time. χ_f is 30 mol% (coPOB-4).

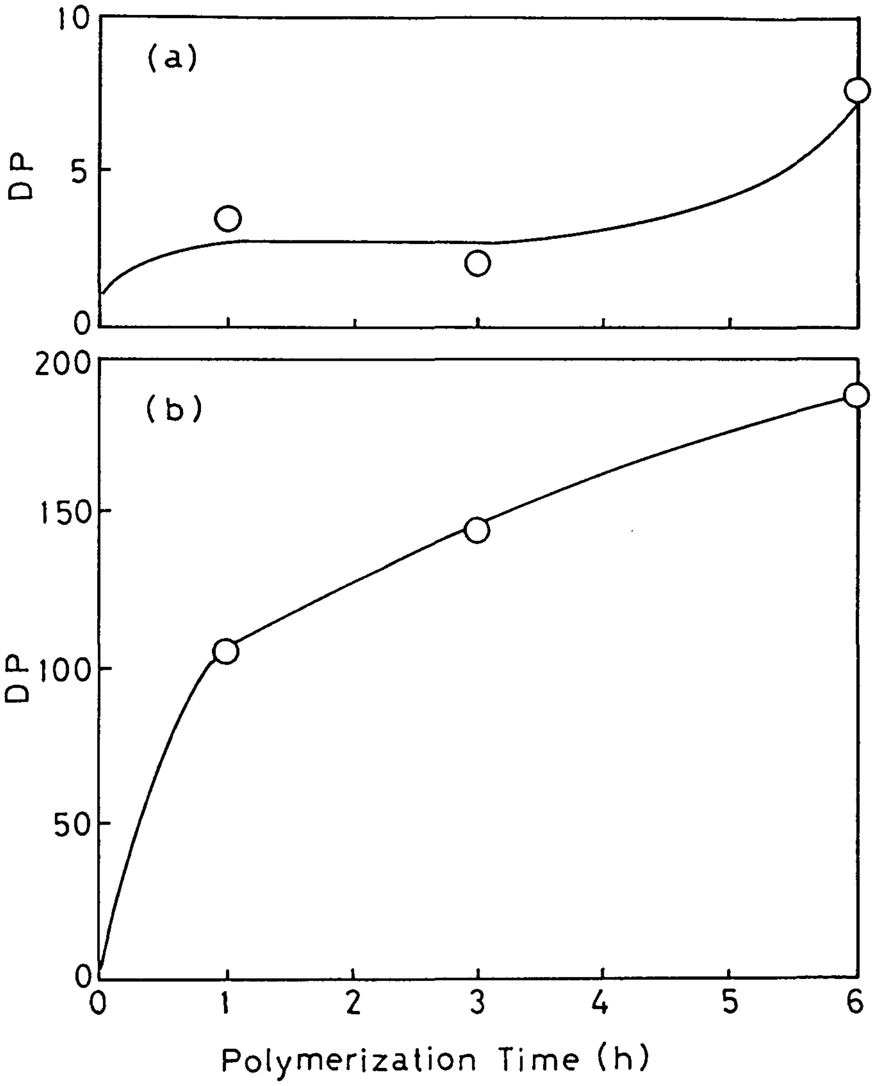


Figure 3-4. Variation of degree of polymerization of (a) dissolving oligomers and (b) precipitated materials with polymerization time. χ_f is 30 mol% (coPOB-4).

3-2-2-2 Features of Whiskers obtained by Copolymerization of p-Acetoxybenzoic acid and m-Acetoxybenzoic acid in Liquid Paraffin

The detailed observation of obtained whiskers seems to show that polymeric materials adhere on their surface. Therefore, the separation of the deposited materials from the whiskers is carried out by extraction with perfluorophenol in a soxhelt extractor. The results of this extraction experiments is shown in Table 3-2. In coPOB-4, 41wt% of the precipitated materials are removed by extraction with perfluorophenol. The extracted polymeric materials contain 25 mol% in the m-oxybenzoyl units. The actual content of m-oxybenzoyl units in the obtained whiskers (χ_w) is much lower than χ_f as shown in Table 3-2. On the other hand, the

Table 3-2. Results of extraction experiments of coPOB crystals by perfluorophenol$^{1)}$

Polymer	coPOB-1	coPOB-2	coPOB-3	coPOB-4
Content of m-ABA in feed (χ_f) (mol%)	5	10	20	30
Residual crystals				
Yield (%)	33.6	30.1	35.5	26.3
Content of m-units (χ_w) (mol%)	1.0	1.4	2.4	3.8
Extracted polymeric materials				
Yield (%)	1.4	2.0	3.8	18.2
Content of m-units (mol%)	8.5	14.2	32.4	24.6

1) Contents of m-units were determined by ^{1}H-NMR measurements after hydrolysis of samples in conc. sulfuric acid.

content of m-oxybenzoyl units in copolymers prepared with melt polymerization (coPOB-5) is nearly equal to the corresponding χ_f. These facts indicate that only co-oligomers containing a few m-oxybenzoyl units form the whiskers and co-oligomers containing much m-oxybenzoyl units may be excluded by the fractional crystallization during solution polymerization.

Thermal transition behaviors of these crystals are measured by DSC. It is well-known that the POB crystals have a reversible first order transition at around 350℃. This transition is solid-solid transition differing from the melting process and it is regarded as a transition to a pseudohexagonal packing of chains by rotation of the 1,4-phenylene rings.[7,8] This transition temperature (T_t) and its enthalpy (ΔH_t) are strongly related to the density of the crystal and the crystal having higher density exhibits higher T_t and larger ΔH_t. That is, the higher T_t and larger ΔH_t show the more densely packing manner of the chains in the crystal as reported in chapter 1. The results of DSC are tabulated in Table 3-3. T_t and ΔH_t of the crystals prepared by the solution polymerization (coPOB-2, 3 and -4) are much lower and smaller than those of the POB whisker, and they decrease with the increase in χ_f. Although the crystals obtained by the solution polymerization show the needle-like morphologies, their crystallinity is lowered by the copolymerization of m-oxybenzoyl units.

The electron diffraction experiments for there whiskers are carried out. The obtained diffraction patterns are under examination. It is clear that the features of these patterns

Table 3-3. Thermal transition behaviors of the whiskers obtained by solution copolymerization[1)]

Polymer	Content of m-units in crystal (mol%)	DSC[2)] T_t (℃)	ΔH_t (kJ/mol)	ΔS_t (J/K·mol)
coPOB-1	1.3 / 1.0	346.0 / 348.5	3.87 / 3.96	6.25 / 6.37
coPOB-2	2.2 / 1.4	335.0 / 337.8	4.19 / 4.16	6.89 / 6.81
coPOB-3	5.3 / 2.4	338.0 / 339.8	4.21 / 4.13	6.90 / 6.74
coPOB-4	12.3 / 3.8	312.3 / 312.1	1.68 / 2.88	2.88 / 4.92
POB	0.0	374.4	6.82	10.53

1) Results are described as before / after extraction.

2) Solid-solid transition temperatures were measured on the heating scan at a heating rate of 10℃/min in nitrogen.

are similar to that of the POB whisker but each spot becomes more diffuse with the increase of χ_f. This is also supported that co-oligomers are participated in the formation of whiskers. The detailed structural information will be discussed elsewhere.

3-3 Growth Mechanism of Whiskers in Copolymerization System

3-3-1 Discussion

From the experimental results as described in the previous section, the formation mechanism of the whiskers in the copolymerization system can be speculated as follows. Co-oligomers of low DP are formed in the homogeneous polymerization in solution and when the DP exceeds a critical value, oligomers containing only p-oxybenzoyl units or a very few m-oxybenzoyl units crystallize in the form of lamellae from the solution. In this process, co-oligomers containing more m-oxybenzoyl units are delayed to be precipitated because the critical value of DP for the precipitation is larger due to their higher solubility in LP. Therefore, only co-oligomers containing a few m-oxybenzoyl units crystallize in the form of lamellae in the early stage of the polymerization. And co-oligomers containing m-oxybenzoyl units are gradually precipitated from the solution as the polymerization proceeds. They, however, are excluded from the crystals by segregation effect and adhere on the surface of the crystals. It can be concluded that the whiskers are formed by the co-oligomers almost consisted of p-oxybenzoyl units via the similar mechanism as the POB whiskers. Polymerization also occurs in the solid state and then the DP increases like the POB whiskers. The consequent reorganization of crystals occurs as already suggested in chapter 1. On the other hand, the formation rate of stacking lamellae become more slow with the increase of χ_f. Hence, it can be deduced that the fibrillation of whiskers and the radial growth from the central part are due to the reorganization of stacking lamellae and the following growth of small needle crystals. That is, the apparent difference in crystal morphologies may be due to slow formation rate of crystallizable oligomers formed in solution copolymerization.

3-4 Conclusion

Whiskers are obtained at χ_fs of 0 - 30 mol% by high-temperature solution polymerization in LP. The whiskers are inclined to show the fibrillation in their both ends and the radial growth from the central part as χ_f increases. At higher χ_f than 40 mol%, crystals are not precipitated during polymerization. From the polymerization time dependencies of the yield, and the composition of the precipitated materials and the dissolving oligomers at 330℃, it becomes clear that the content of m-oxybenzoyl units in the precipitated materials increase gradually and that in the dissolving oligomers decrease. The actual content of m-oxybenzoyl units in the obtained whiskers (χ_w) is much lower than χ_f. The whiskers seem to be formed by co-oligomers almost consisted of p-oxybenzoyl units via the similar mechanism as the POB whiskers. The apparent difference in crystal morphologies may be due to slow formation rate of crystallizable oligomers and the reorganization of stacked lamellae. This study strongly support the proposal for the formation mechanism of the whiskers as described in chapter 1. It consists of two steps: the spiral growth of oligomer lamellae with a critical length from solution and the post-polymerization of oligomers between lamellae.

Furthermore, this fractional crystallization behavior during solution copolymerization suggests a new method of polymerization with molecular recognition.

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Chapter 4

Crystallization of Other Aromatic Condensation Polymers during Solution Polymerization

4-1 Introduction

Crystallization of poly(p-oxybenzoyl) (POB) during high-temperature solution polymerization has been reported in the previous chapter. It has been found that the crystal morphologies of POB can be controlled by the conditions of high-temperature solution polycondensation, and the POB whiskers are obtained in poor solvents such as liquid paraffin (LP) or Therm S 800 (TS 800) at very low concentration of monomers under no stirring conditions. The length of the POB whisker is 50-70μm and the width is 1-2μm. They are single crystals in which the polymer chains are oriented along the long axis of the whiskers. They are therefore expected to be brought into practical use such as organic reinforcements and so forth with their unique morphologies, outstanding thermal stabilities and good mechanical properties.

It has been revealed that the POB whisker is formed with a spiral growth of lamellae and post-polymerization occurs in the interlamellae region with reorganizing polymer chains.

From the viewpoint of the polymer processing, crystallization during solution polymerization is an extremely valuable in processing infusible polymers. That is, infusible polymers can be processed by building monomers into some crystal shape one by one while polymerizing.

It is of very interest in the studies on the crystallization of other aromatic polymers than POB during solution polymerization not only to control the crystal morphology but also to know whether the needle-like crystal formation occurs in other polymer systems.

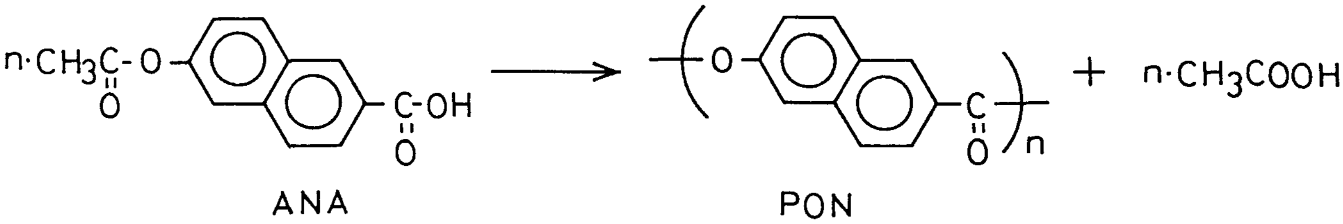
In this chapter, the crystallization of aromatic condensation polymers including poly(2-oxy-6-naphthoyl) (PON), poly(4'-oxy-4-biphenylcarbonyl) (POBP), poly(p-phenylene terephthalate) (PPTE) and poly(4-mercaptobenzoyl) (PMB) during high-temperature solution polymerization are studied from the standpoint of the control of crystal morphology, focusing on the synthesis of polymer whiskers.

4-2 Crystallization of Poly(2-oxy-6-naphthoyl)

PON which is a homologue of POB has very straight and rigid-rod molecular structure. While PON is expected from the molecular structure to possess desirable properties such as thermal properties, solvent resistance and mechanical properties, it has not been applied as industrial materials because PON is not amenable to conventional processing technique owing to its infusibility, *i.e.* it shows no melting temperature under decomposition and it is insoluble in common solvents.

Economy *et al.* had reported the high-temperature solution polycondensation of PON from 2-acetoxy-6-naphthoic acid (ANA) previously.[1] The obtained crystals were uniform well-oriented slab-like, but not needle-like. Needle-like crystals of PON, that is whiskers, have never obtained thus far.

From the similarity of molecular structure of PON with POB, it is well-expected to obtain the PON whisker during high-temperature solution polymerization. Thus, it is the purpose of this work to control the crystal morphologies of PON by crystallization during solution polymerization of ANA focusing on the synthesis of the PON whisker as described below.



Scheme 4-1. Synthesis of PON from ANA

4-2-1 Experimental

Materials

ANA was prepared as described in a literature.[2] LP, TS 800), benzophenone (BP), 4-chlorobenzophenone (CBP), and diphenylsulfone (DPS) were used as solvents after purifications as described in chapter 1.

Preparation of Poly(2-oxy-6-naphthoyl) Crystals

A typical preparation procedure for PON whiskers is described in the following. Other crystals were also obtained in a similar manner.

In a 200ml-cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were placed 0.82g of ANA and 60g of LP. This reaction mixture was heated with stirring under a slow stream of nitrogen until the monomer dissolved completely. Then stirring was stopped and heating was continued up to 330℃ at a heating rate of 15℃/min and maintained at this temperature. In a couple of minutes, the reaction solution became turbid and the reaction was continued at 330℃ for 6h. The reaction mixture was allowed to cool to room temperature and chloroform was added. Polymer crystals were collected by filtration, washed several times with chloroform and acetone, and dried at 100℃ under reduced pressure to constant weight.

Measurements

Characterization of the crystals was performed by scanning electron microscopy, transmission electron microscopy, and wide-angle X-ray diffraction technique. The instruments used were a Hitachi 530-S, a Hitachi HU-11B, and a Rigaku 2028.

Thermal properties were evaluated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Rigaku R-DSC at a heating rate of 10℃/min in nitrogen. TGA was performed on a a Shimadzu TG-30 at a heating rate of 10℃/min on a 5-mg sample in air.

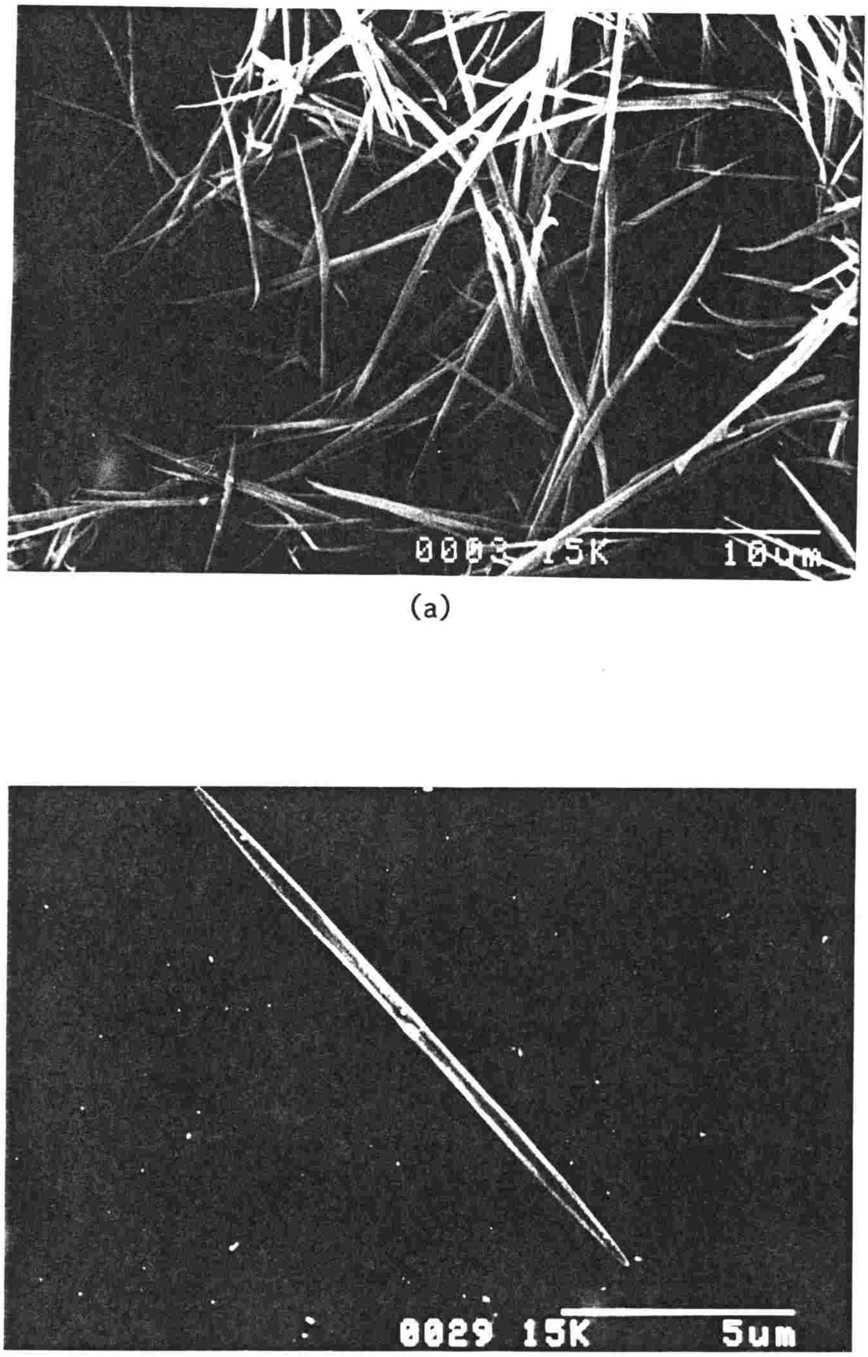
The densities of the crystals were measured by floating method using *n*-butyl bromide and carbon tetrachloride at 25℃.

4-2-2 Results and Discussion

4-2-2-1 Synthesis of Poly(2-oxy-6-naphthoyl) Whisker

The PON whiskers, shown in Figure 4-1(a), (b) and (c), are obtained by the high-temperature solution polycondensation of ANA. Economy *et al.* reported the high-temperature solution polycondensation of PON in an aromatic heat exchange medium under stirring condition previously.[1] The crystals which they obtained were uniform well-oriented slab-like, but not needle-like. A comparison of the morphologies of crystals prepared under various conditions is summarized in Table 4-1.

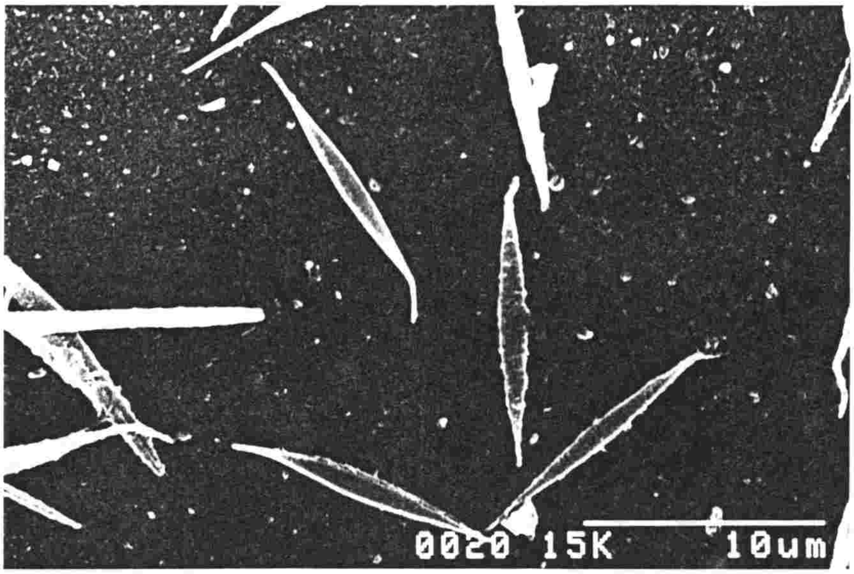
Concerning to the solvents, PON whiskers are obtained in LP or TS 800 which is an aromatic heat exchange medium. The size of PON whiskers is strongly related to the nature of solvents, summarized in Table 4-2.



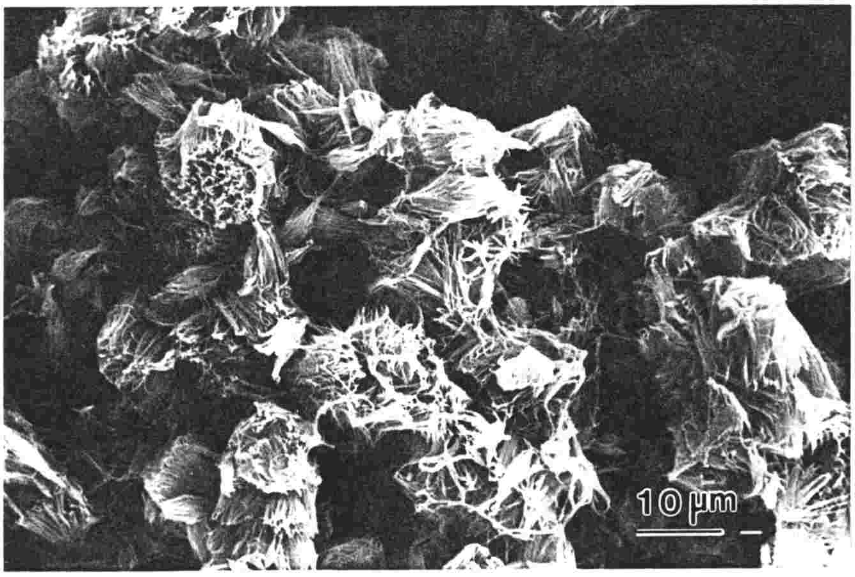
(a)

(b)

Figure 4-1. Scanning electron micrographs of PON crystals prepared in (a) and (b) LP.



(c)



(d)

Figure 4-1. Scanning electron micrographs of PON crystals prepared in (c) TS 800 and (d) BP.

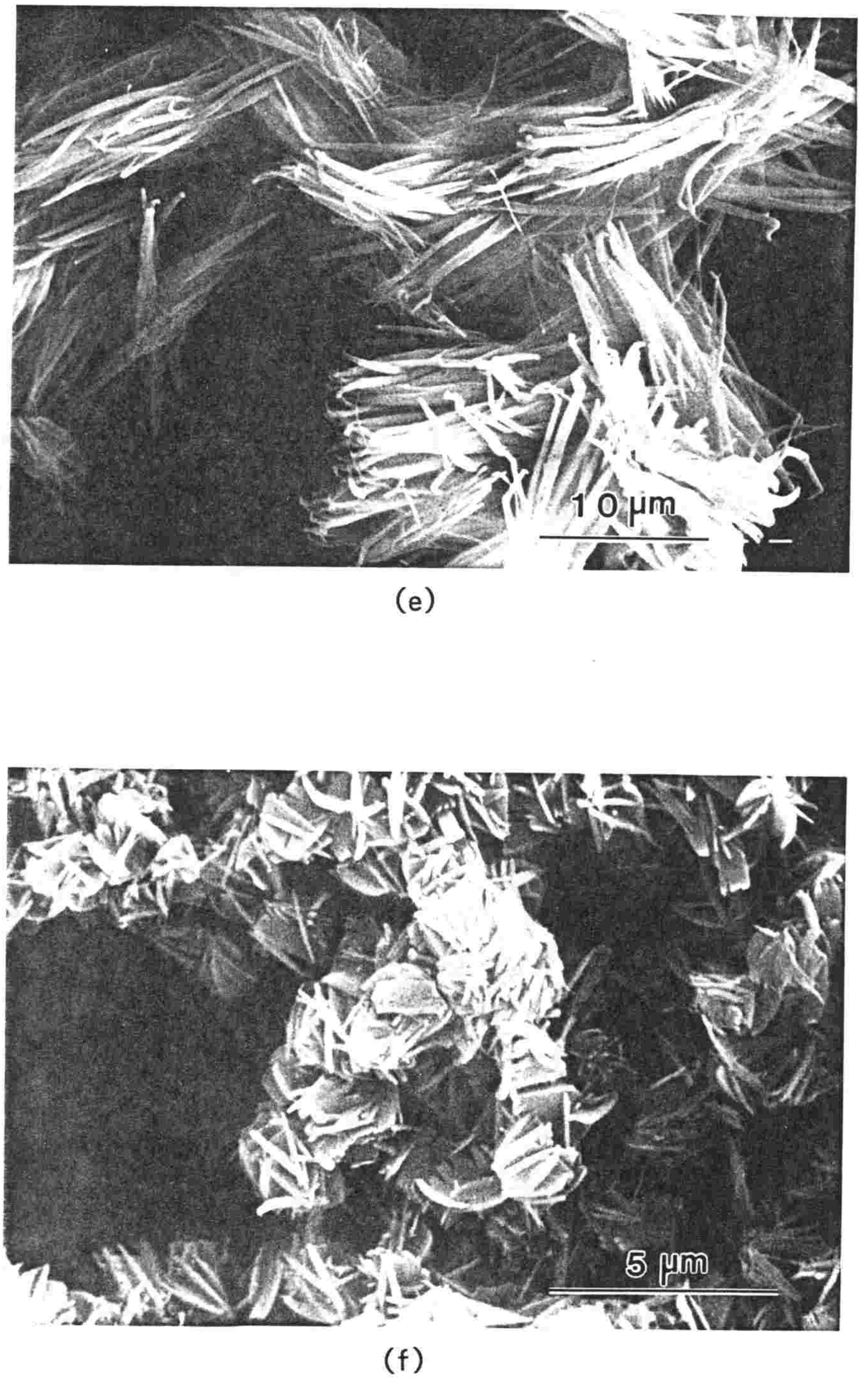


Figure 4-1. Scanning electron micrographs of PON crystals prepared in (e) DPS and (f) CBP.

Table 4-1. Comparison of PON crystal morphology from ANA

Polymer	Solvent[1)]	Conc.[2)] (%)	Polymerization Temperature (℃)	Time (h)	Stirring	Crystal morphology
PON-1	LP	1.0	330	6	No stirring	Needle-like
PON-2	TS 800	1.0	330	6	No stirring	Needle-like
PON-3	BP	1.0	320	6	No stirring	Fibrillar
PON-4	DPS	1.0	330	6	No stirring	Fibrillar
PON-5	CBP	1.0	330	6	No stirring	Slab-like
PON-6[3)]	Therminol-66	3.0	350	12	Stirring	Slab-like

1) Solvent; LP:liquid paraffin, BP:Benzophenone, DPS:Diphenylsulfone, CBP:4-Chlorobenzophenone, TS 800:Therm S 800 Aromatic heat exchange medium of Nippon Steel Chemical Co.Ltd. Therminol-66:Aromatic heat exchange medium of Monsanto Co.Ltd.

2) Conc.(%) = [Theoretical polymer yield (g) / Solvent weight (g)] x 100

3) Data from ref.1

Table 4-2. The size of PON and POB whiskers

Polymer	Size of whisker (μm) Length (L)	Size of whisker (μm) Width (W)	Axial ratio (L/W)
PON-1	10 - 17	0.5	20 - 34
PON-2	7 - 15	1.0	7 - 15
POB	30 - 70	1.0	30 - 70

The whiskers prepared in LP (PON-1) had 10-17μm length and 0.5μm width, and the whiskers prepared in TS 800 (PON-2) had 7-15μm length and 1.0μm width. TS 800 makes the length shorter, the width wider, and eventually decreases the axial ratio. In BP and DPS, fibrillar crystals which are uniform well-oriented are obtained, but each fibril does not separated as shown in Figure 4-1(d) and (e). In CBP, slab-like crystals are obtained as shown in Figure 4-1(f).

These results indicate that the polarity of the solvent seems to correlate qualitatively with the crystal morphology, *i.e.* less-polar solvent is preferable to obtaining PON whiskers having higher axial ratio. These facts could be explained as follows. ANA is found to react initially in a homogeneous state and then the reaction continues in the heterogeneous state once precipitation has occurred. This precipitation in the early stage of polymerization is due to the formation of the primary crystal nuclei by oligomers that dominate the final crystal habits. The precipitation, which is defined as when the reaction solution become turbid, occurs within 1min in LP after the temperature reached at 330℃, 6min in TS 800, 42min in BP, 58min in DPS, and 7min in CBP. The order of these precipitation times corresponds to the order of the polarity of solvents, but dose not correspond for the case of CBP:

Order of the precipitation time
early ◄————————————► *late*
LP < TS 800 ≪ BP, DPS
low ◄————————————► *high*
Order of polarity of solvent

It seems reasonable to assume that the polymerization rates are nearly equal in all solvents or the rates in polarer solvents are higher in the homogeneous state. Under these situations, the degrees of polymerization (DP) of oligomers precipitated are lower when the reaction is carried out in LP or TS 800 in comparison with others.

The difference in the DP of precipitated oligomers might have an influence on the crystal habits of the primary nuclei, and ultimately final crystal morphologies. The details about this will be discussed with the growth mechanism of whiskers in a latter section. What occurred in CBP might be different from others. This is not understood clearly and is under investigation.

Furthermore, concentration and stirring are also very important factors in controlling the crystal morphologies. At a high concentration (over 5%), whiskers are not obtained, but uniform, well oriented, slab-like crystals are formed. Stirring influences the crystal morphologies drastically as well. With vigorous stirring, inseparable fibrillar crystals are formed. In other words, lower concentration and no stirring are desirable for making whiskers.

From these results, it can be concluded that the most important factors in controlling the PON crystal morphologies from ANA are polarity of the solvent, concentration and stirring. PON whiskers can be obtained in less-polar solvents at a low concentration and under 'no stirring' condition. This conclusion is very similar to that for POB whiskers as described in chapter 1.

4-2-2-2 Characterization of Poly(2-oxy-6-naphthoyl) Whiskers

Examination of PON-1 whiskers using an electron microscope shows needle-like morphologies very similar to POB whiskers (see Figure 4-1(a)-(c) and 4-2). Both tips of this whisker are very sharp and the surface is very smooth. X-ray diffraction pattern in Figure 4-3 showed no amorphous peak and an extremely high degree of crystallinity. In order to determine the unit cell, the electron diffraction technique is used, and a diffraction pattern of PON-1 whisker is shown in Figure 4-4. This diffraction pattern does not show the true fiber pattern of cylindrical symmetry. This is due to the single-crystal nature of these whiskers. The meridian of this pattern corresponds to the long axis of the whisker. The fiber identity period is 16.81 Å, corresponding to two chemical residues. The unit-cell parameters are shown in Table 4-3. The observed densities of the PON whiskers summarized in Table 4-4 are in excellent agreement with the

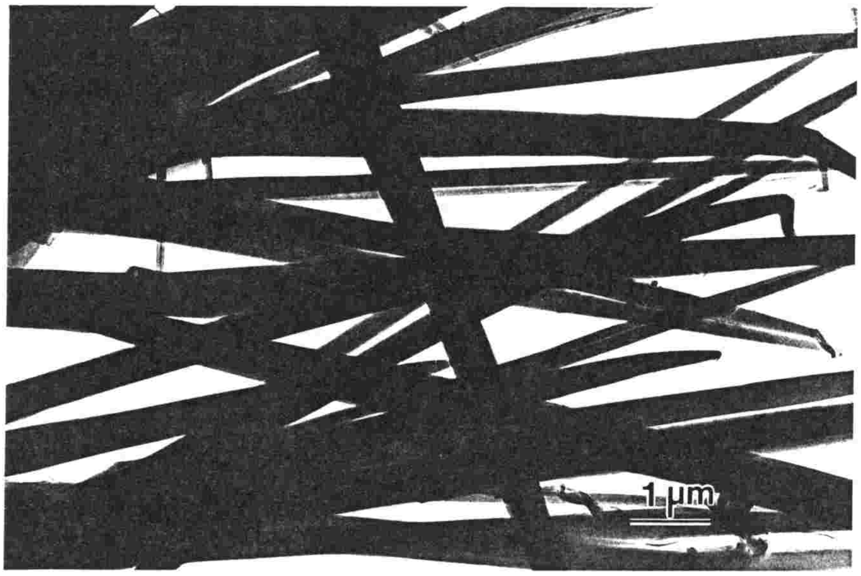


Figure 4-2. Transmission electron micrograph of PON whiskers prepared in LP.

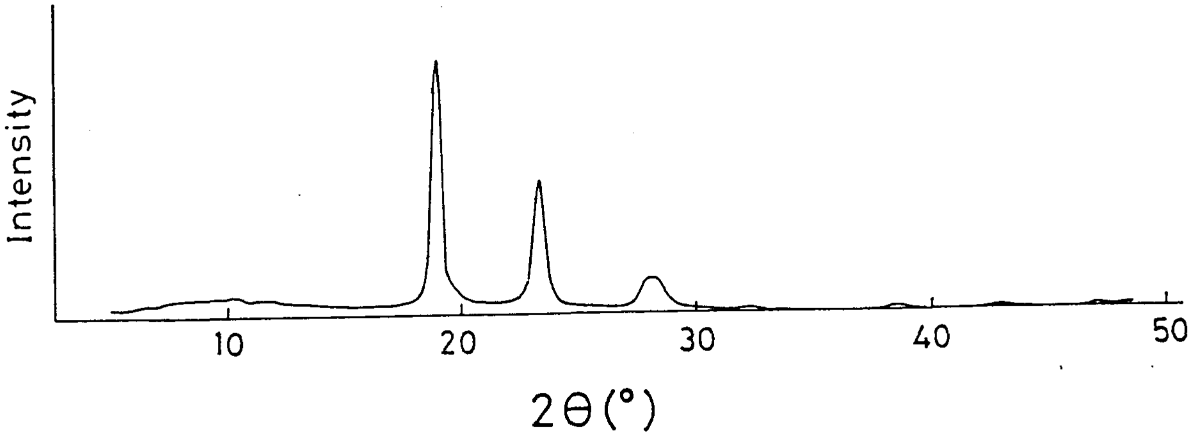


Figure 4-3. X-ray diffraction pattern of PON whiskers.

theoretical density. The densities of other crystals are lower except for PON-5. These results are sufficient to regard these whiskers as chain extended single crystals.

Table 4-3. Unit cell dimensions for PON whiskers

Crystal system :	Orthorohmbic
Lattice constants :	a = 7.96Å
	b = 5.82Å
	c (f.a.) = 16.81Å
Number of chains in a unit cell:	2 (4 repeating units)
Density Calcd. :	1.45 g/cm^3

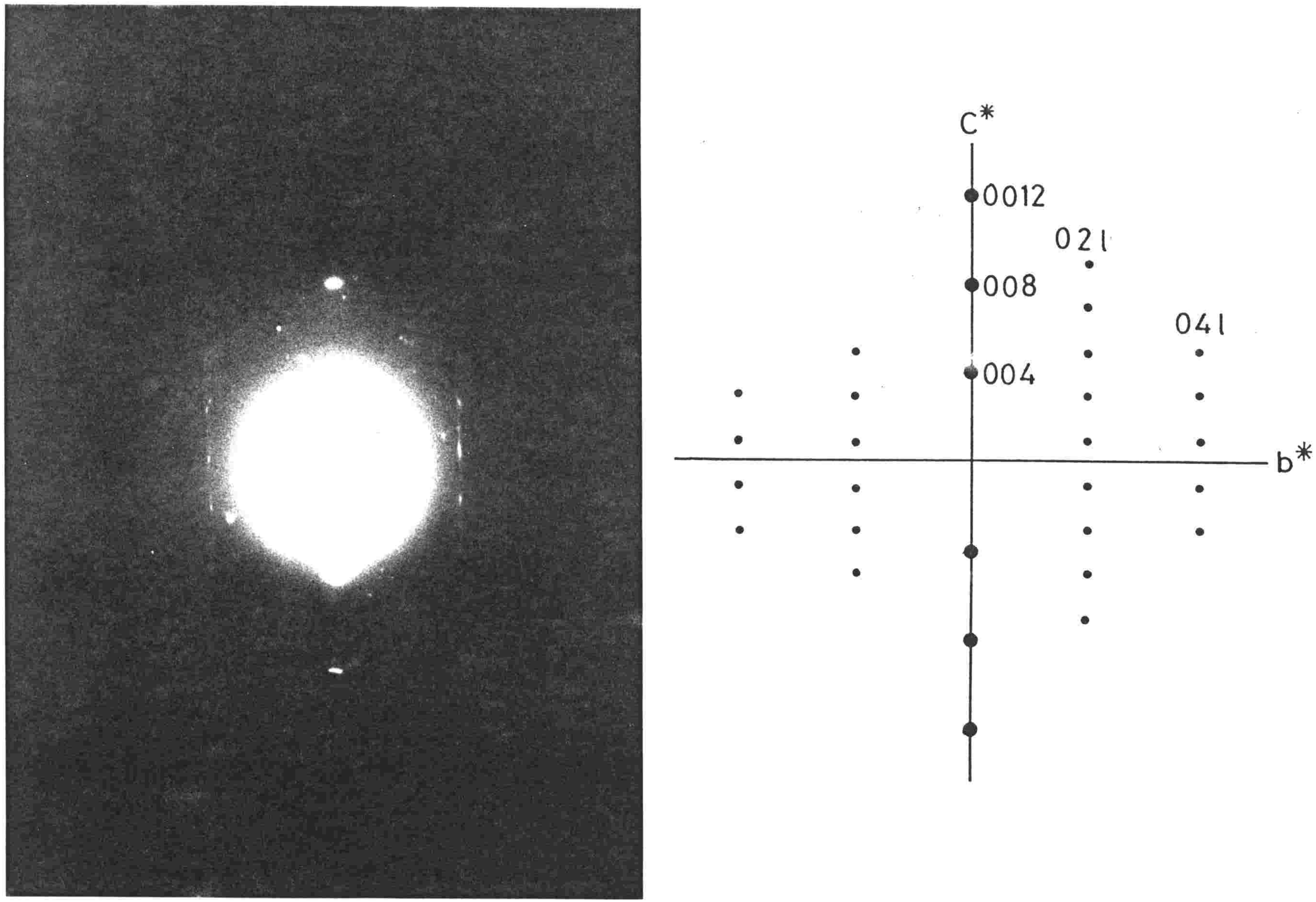


Figure 4-4. Electron diffraction pattern of PON whiskers.

4-2-2-3 Growth Mechanism of Poly(2-oxy-6-naphthoyl) Whiskers

The size of the PON whiskers are different from that of the POB whiskers but the quite similar characteristics indicate a very close similarity in these two formation processes.

In order to know whether PON whiskers are formed via the same mechanism as the POB whiskers, the morphology of PON whiskers obtained in the early stage of polymerization is observed. The transmission electron micrograph of an incipient crystal is shown in Figure 4-5. In this micrograph, the lamellar structure piling up along the long axis of the needle-like crystal is observed clearly. Both tips of this crystal are sharp and the 'shish' as in 'shish-kebab' fibrous crystals dose not exist. On the other hand, the eventual whiskers do not have any lamellar structures but smooth surface (see Figure 4-2).

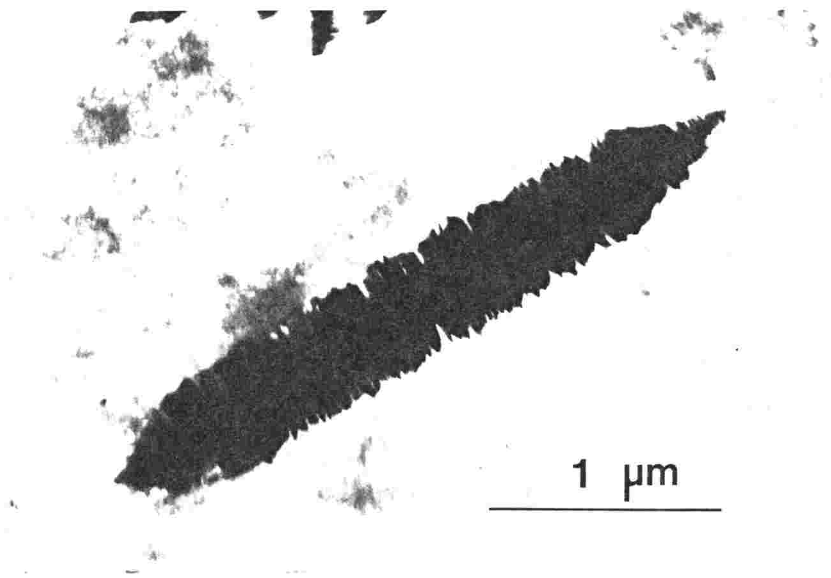


Figure 4-5. Transmission electron micrograph of incipient PON whiskers prepared in LP at 330℃ for 3min.

These facts are strong evidence that the formation mechanism of the PON whiskers is quite similar to that of the POB whiskers.

From this mechanism, the influence of the solvent properties on the crystal habits, which are fibrillar and slab-like crystals, can be speculated more clearly. The oligomers of higher DP that are produced in polar solvents form thicker primary nuclei. Because of this thickness, it is difficult for a screw dislocation to form in the thicker lamellae, and the lamellae grows preferentially in the lateral direction. Fibrillation is occurred even in the crystals that develop from the thicker and wider nuclei, because of the extended-chain packing along the same direction.

4-2-2-4 Thermal Properties of Poly(2-oxy-6-naphthoyl) Crystals

Thermal properties of PON crystals are tabulated in Table 4-4. The PON whiskers display much better thermal stability than the other crystals on the basis of TGA. The temperature of 5wt% loss of the PON whiskers prepared in LP is 506℃, which is the highest in PON crystals. But for PON-5, the temperature of 5wt% loss correlates very well with the density of crystal, *i.e.* the crystal in which the polymer chains pack more densely shows higher thermal stability.

DSC analysis confirmed the presence of a reversible solid-solid transition differing from the melting process (see Table 4-4). The transition temperatures of the PON whiskers are 343.5℃ on the heating scan and 327.0℃ on the cooling scan. The other crystals do not show these transitions distinctly. Economy *et. al* also reported the same kind of transition for slab-like PON crystals at 338℃

at a heating rate of 40℃/min.[1] These higher transition temperatures of the PON whiskers than for slab-like crystals are due to the closer packing of polymer chains in the crystals. The transition temperature of the PON whiskers is slightly lower than that of the POB whiskers (around 325-360℃) but basically both transitions may be described as a plastic crystal transition or a highly ordered smectic, which are identical with the interpretation for the POB crystals.[3-6]

4-2-3 Summary

The PON whiskers are obtained from ANA by the high-temperature solution polycondensation. The size of these

Table 4-4. The density and thermal properties of PON crystals

Polymer	Density (g/cm³)	DSC 1)			TGA 2) (℃)
		T_t (℃)	ΔH_t (kJ/mol)	ΔS_t (J/K·mol)	
PON-1	1.45	343.5 / 327.0	3.46	5.61	506
PON-2	1.44	343.5 / 327.0	3.38	5.48	498
PON-3 3)	1.42	――	――	――	482
PON-4 3)	1.43	――	――	――	489
PON-5	1.45	319.5 / ―― 4)	――	――	443

1) T_t;Solid-solid transition temperature, the temperature on heating / on cooling.
2) Temperature at which 5% weight loss was recorded in air in TGA curves
3) ― ; transition was not detected.
4) Transition peak was very weak and the peak on cooling scan was not detected.

whiskers are 7 - 17μm in length and 0.5 - 1.0μm in width. The most important factors in controlling the crystal morphology during polymerization the polarity of solvent, concentration, and stirring. In terms of these factors, less-polar solvents, such as LP or TS 800, lower concentration of ANA and no stirring are desirable for making whiskers. From the structural analysis, these whiskers can be regarded as chain extended single crystals. This PON whisker represents the second whisker for condensation polymer after the POB whisker.

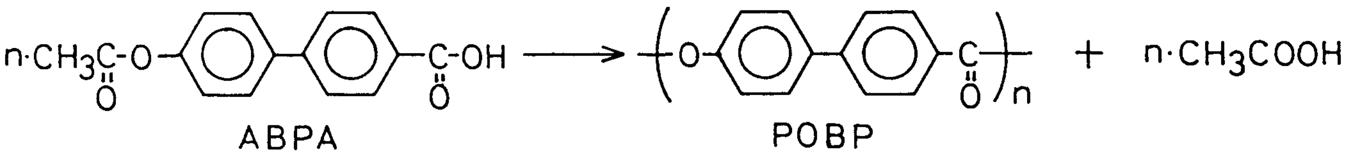
From the morphological observations, it is concluded that the PON whisker is formed with a spiral growth of lamellae and post-polymerization occurs in the interlamellar region, which is the same mechanism as for the POB whisker.

4-3 Crystallization of Poly(4'-oxy-4-biphenylcarbonyl) during Solution Polymerization

The result that the whiskers of POB and PON are obtained during solution polymerization as reported in the previous section suggests that the needle-like crystallization with a spiral growth of lamellae during solution polymerization may be not a specific phenomenon for aromatic condensation polymers.

POBP which is a homologue of POB has a straight and rigid-rod molecular structure and it is highly crystalline as reported.[7] POBP was previously synthesized by high-temperature solution polymerization in an aromatic solvent at high concentration of monomer. However, the morphological consideration of the POBP crystals has never conducted thus far.

Thus, it is the purpose of the present work to synthesize the POBP crystals from 4'-acetoxybiphenyl-4-carboxylic acid (ABPA) by high-temperature solution polymerization as shown below and to describe their crystal morphologies.



Scheme 4-2. Synthesis of POBP from ABPA

4-3-1 Experimental

Materials

ABPA was prepared as described in literatures.[8-12] Therm S 900 (TS 900) was a mixture of isomers of hydrogenated terphenyl purchased from Nippon Steel Chemical Co. Terphenyl was purchased from Nakarai Tesque Co. Ltd. LP and TS 800 were used after the purification as described in chapter 1. TS 900 was also used after vacuum distillation. Terphenyl was used as received.

Preparation of Poly(4'-oxy-4-biphenylcarbonyl) Crystals

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

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

Measurements

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

Thermal properties were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Perkin-Elmer DSC-7 at a heating rate of 10℃/min in nitrogen. TGA was performed on a Shimadzu TG-30 at a heating rate of 10℃/min on a 5mg sample in nitrogen or air.

The degree of polymerization (DP) of the crystal was determined by ^{1}H-NMR end-group analysis of the acetyl group after hydrolysis with conc. sulfuric acid in an NMR tube with a Varian Gemini-200 spectrometer, as described in a literatures.[13]

4-3-2 Results and Discussion

4-3-2-1 Morphology of Poly(4'-oxy-4-biphenylcarbonyl) Crystals

POBP crystals are prepared by solution polycondensation of ABPA at 330℃ in various solvents. Morphological features of the obtained crystals are summarized in Table 4-5. The yields of the crystals are around 55% in all solvents. The low yields seem to be mainly due to sublimation of ABPA at 330℃. When the polymerization is carried out in LP, dendritic

Table 4-5. Synthesis of POBP crystals from ABPA

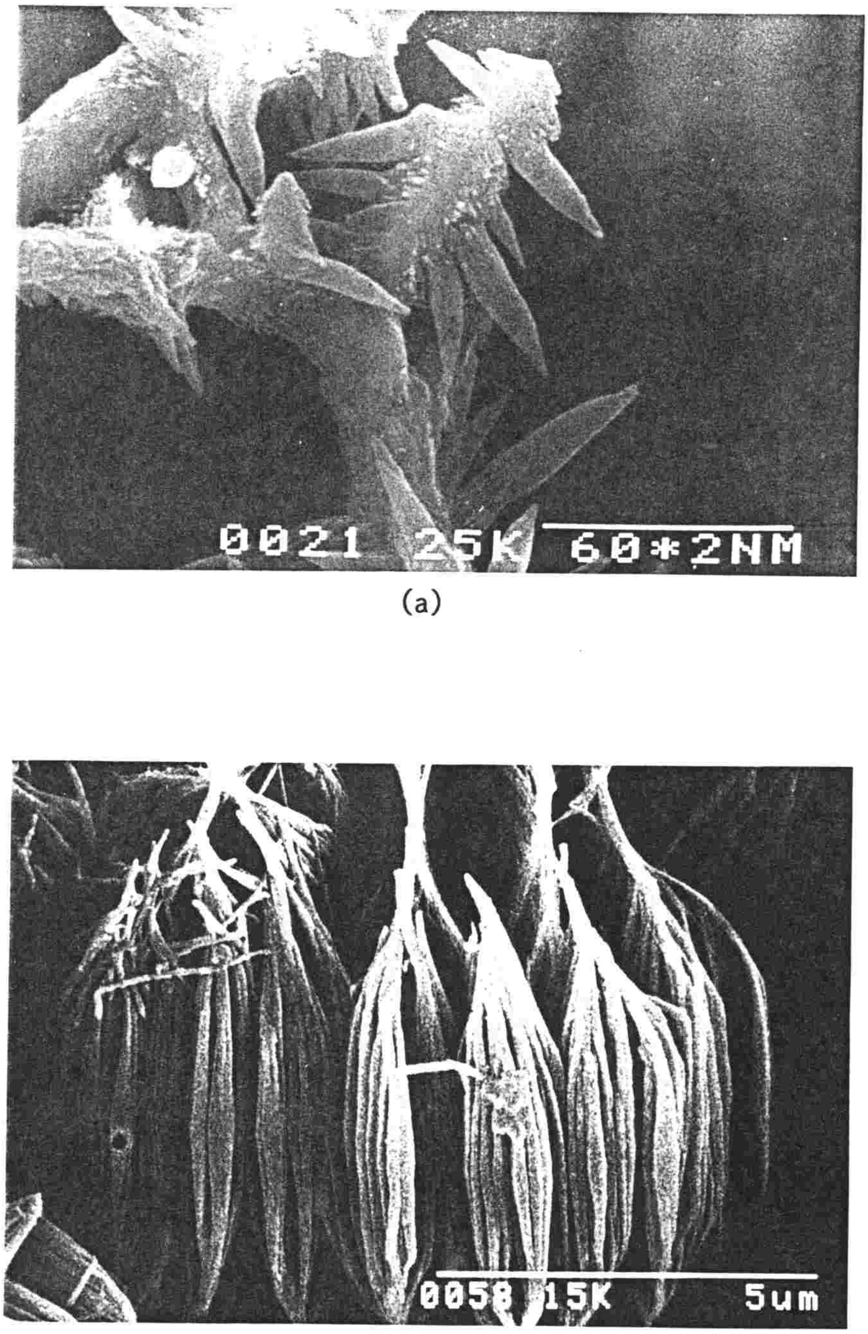
Polymer	Solvent[1]	Conc.[2] (%)	Polymerization Temperature (℃)	Time (h)	Yield (%)	Crystal morphology
POBP-1	LP	1.0	330	6	55.3	Dendritic
POBP-2	TS 800	1.0	330	20	55.0	Fibrillar
POBP-3	TS 900	1.0	330	20	55.6	Fibrillar
POBP-4	Terphenyl	1.0	330	20	54.0	Slab-like

1) Solvent; LP: liquid paraffin, TS 800: Therm S 800, TS 900: Therm S 900, TS 800 and TS 900 are aromatic heat exchange media of Nippon steel chemical Co. Ltd. Main components of TS 800 and TS 900 are triethylbiphenyl and hydrogenated terphenyl, respectively.

2) Conc.(%) = [Theoretical polymer yield (g) / Solvent weight (g)] x 100

crystals with irregular shape are formed as shown in Figure 4-6(a). In TS 800 or TS 900 are obtained the bundle-like aggregates of fibrillar crystals as shown in Figure 4-6(b) and (c), respectively. The length of each fibrillar crystals is 5-10μm and the width is 0.1-0.2μm. These fibrils are linked laterally to one another at the central part. In terphenyl are formed hexagonal slab-like crystals, of which the thickness is 2-3μm and the width is on the average 10μm, as shown in Figure 4-6(d). They are also fibrillated in the direction of the thickness. These results show that the crystal morphologies of POBP are quite different with the kind of solvents. Especially in LP, the resultant crystals have irregular shape and their formation mechanism seems to be different from that in the case of aromatic solvents. The formation mechanism will be described at length elsewhere.

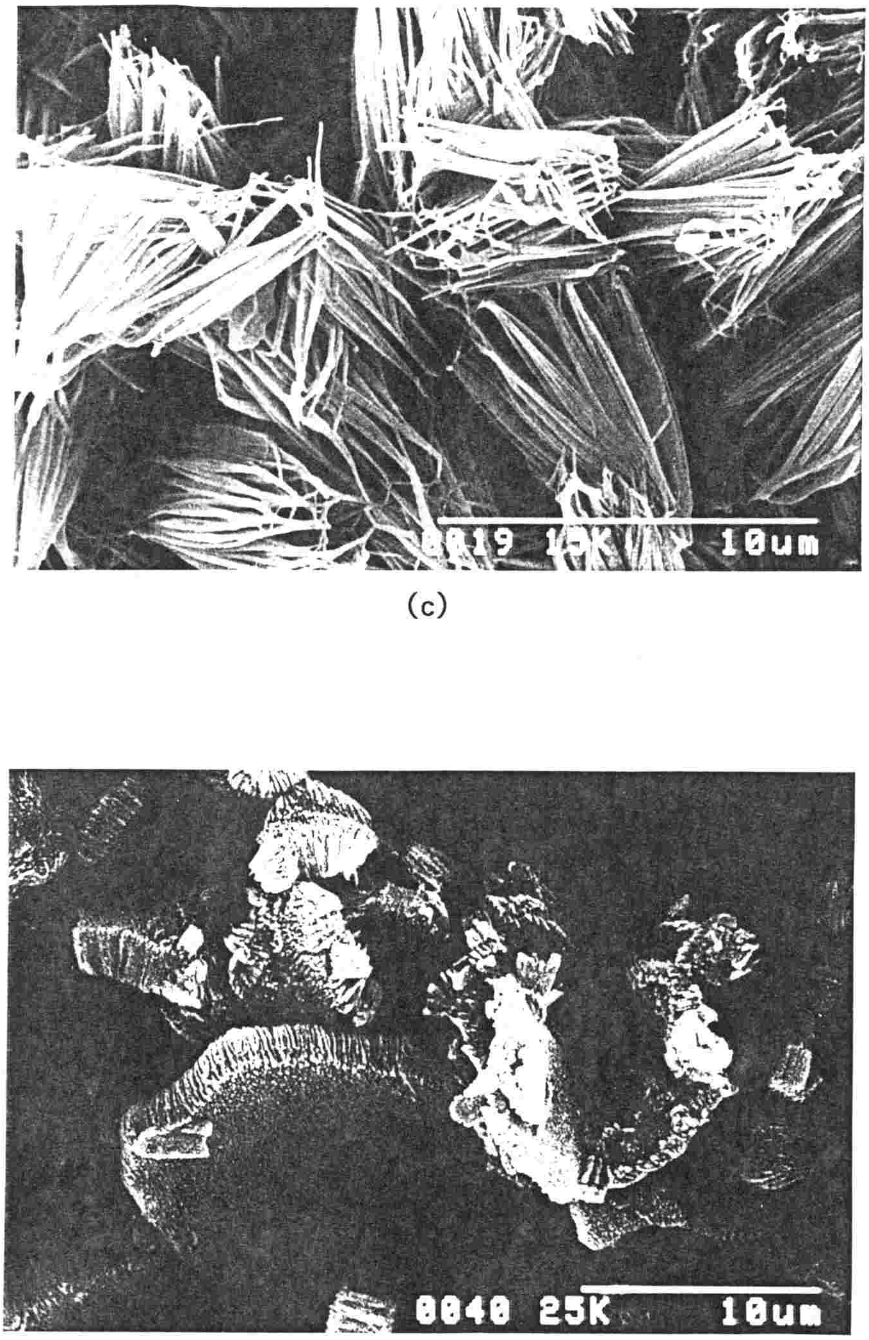
Here, the crystals obtained by polycondensation in



(a)

(b)

Figure 4-6. Scanning electron micrographs of POBP crystals prepared in (a) LP and (b) TS 800.



(c)

(d)

Figure 4-6. Scanning electron micrographs of POBP crystals prepared in (c) TS 900 and (d) terphenyl.

aromatic solvents will be mainly treated.

4-3-2-2 Crystal Features of Fibrillar Crystals of Poly(4'-oxy-4-biphenylcarbonyl)

An electron diffraction pattern of a fibril of fibrillar crystals is shown in Figure 4-7. This diffraction pattern does not show the true fiber pattern of cylindrical symmetry and it consists of sharp spots of lower to higher order reflections as observed clearly. This is due to the single-crystal nature of the fibrillar crystals. The meridian of this pattern corresponds to the long axis of the fibrillar crystal. The fiber identity period is 10.47Å, corresponding to one chemical residue. The unit cell parameters tentatively determined using the electron diffraction pattern of stacked lamellar are shown in Table 4-6. From the electron diffraction experiments, it is concluded that the fibrillar crystals are chain-extended single crystals and that the polymer chains align along the long axis of the fibrillar crystals.

Table 4-6. Unit cell dimensions for POBP fibrils

Crystal system :	Orthorohmbic
Lattice constants :	a = 7.32Å
	b = 5.35Å
	c (f.a.) = 10.47Å (= 1 repeating unit)

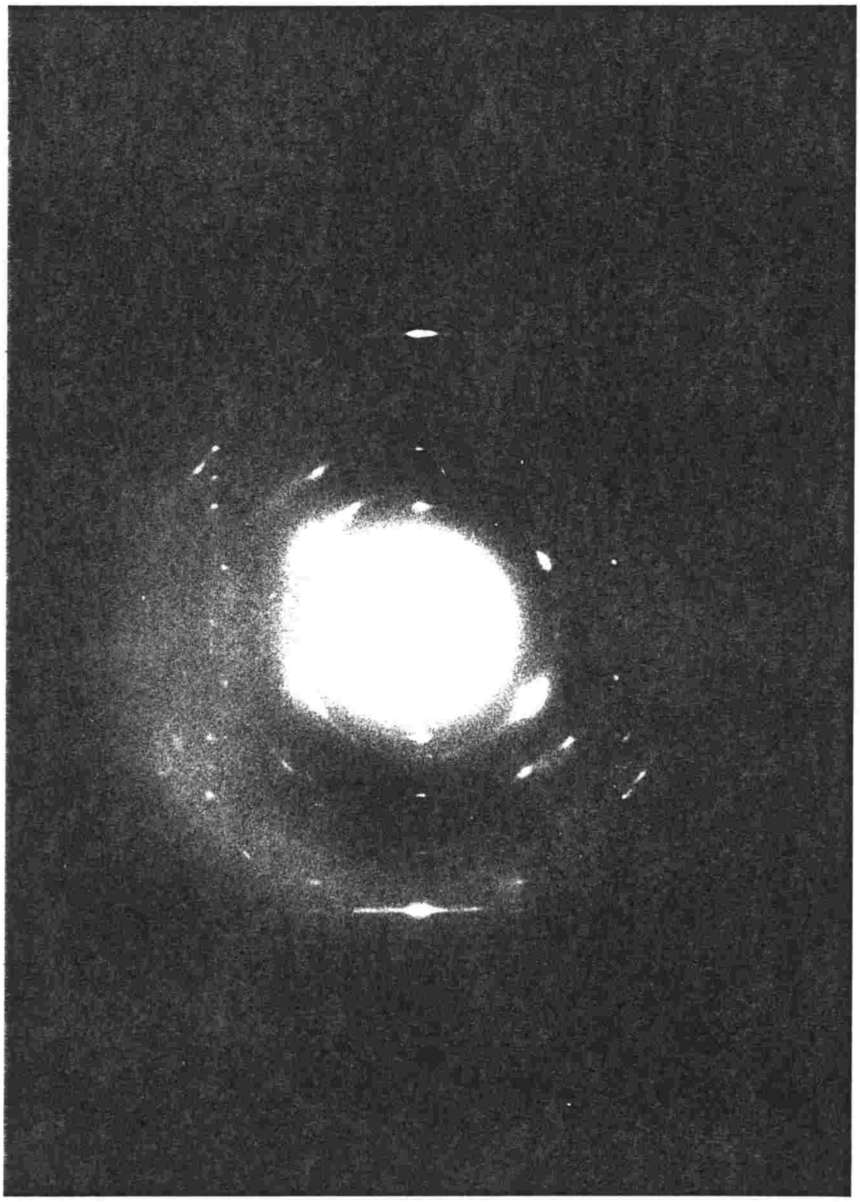


Figure 4-7. Electron diffraction pattern of POBP fibrillar crystals prepared in TS 800.

4-3-2-3 Thermal Properties of Poly(4'-oxy-4-biphenylcarbonyl) Crystals Obtained by Polymerization in Aromatic Solvents

Thermal properties of POBP fibrillar crystals obtained by polymerization in aromatic solvents are evaluated by DSC and TGA. The results are summarized in Table 4-7. The fibrillar crystals exhibit excellent thermal stabilities. 5wt% loss of POBP-2 and POBP-3 are found at around 496℃ in air and at around 527℃ in nitrogen. The temperatures of 5wt% loss of POBP-4 are lower.

Thermal transition behaviors of POBP crystals are measured by DSC analysis. It is well-known that POB and PON crystals show reversible solid-solid transitions differing from the melting process.[3-6] POBP crystals, however, do not show any detectable peaks under 500℃ and it is confirmed that POBP crystals do not exhibit any thermal transitions as described in the literature.[7]

Table 4-7. Thermal stabilities of POBP fibrillar crystals1)

	Temperature of 5wt% loss (℃)		Temperature of 10wt% loss (℃)	
Polymer	Air	Nitrogen	Air	Nitrogen
POBP-2	496	526	512	546
POBP-3	497	528	513	555
POBP-4	438	503	462	532

1) Thermal stabilities were measured by TGA at a heating rate of 10℃/min.

4-3-2-4 Growth Mechanism of Poly(4'-oxy-4-biphenylcarbonyl) Fibrillar Crystals

In order to clarify the growth mechanism of the bundle-like aggregates of the fibrillar crystals, morphological features of the crystals prepared in TS 800 are followed with the polymerization time. The crystals were collected by vacuum filtration at 330℃ to avoid an influence of the adhesion of oligomeric materials onto the surface of the crystals during cooling. The scanning electron microscopic observation of crystals obtained in the early stage of polymerization shows a convex lens-like shape, different from the final crystals as shown in Figure 4-8. The lens-like incipient crystals polymerized for 2h are 2-3μm in diameter and 0.1-0.2μm in thickness, which are apparently smaller than that of the final crystals polymerized for 20h.

Crystals polymerized for 1h are observed by transmission electron micrograph to know the formation mechanism of these lens-like crystals. A micrograph of the crystals is shown in Figure 4-9. As the remarkable result, the stacking of lamellae due to the spiral growth can be clearly observed at the thin edge of the crystal. (see an arrow in Figure 4-9) This fact supports that the formation of the incipient lens-like crystals is similar to that of the POB whiskers in growth mechanism.

As can be seen in the enlarged micrograph of the crystal in Figure 4-8, many protrusion exist clearly on the surface of the lens crystal. These protrusions may be formed by the reorganization of crystals accompanying the increase of DP by post-polymerization.

A scanning electron micrograph of the crystals polymerized for 4h is shown in Figure 4-10. Many fibrillar crystals develop into bundle-like aggregates. These fibrillar crystals have sharp tips and the almost same length in the aggregate. The width of each fibrillar crystal is consistent with that of protrusion on the lens crystals. This fact suggests that the fibrillar crystals grow independently from the protrusions and become longer.

Polymerization time dependencies of the yield, the thickness and the width of the crystals are shown in Figure 4-11. Here, the thickness is defined as the central thickness of lens-like crystals in the early stage of polymerization and thereafter the length of fibrillar crystals. The width is defined as the diameter of the lens-like crystals and the bundle-like aggregates of fibrillar crystals. The yield of crystals increases slowly compared with that in the case of polymerization of p-acetoxybenzoic acid in LP as described in

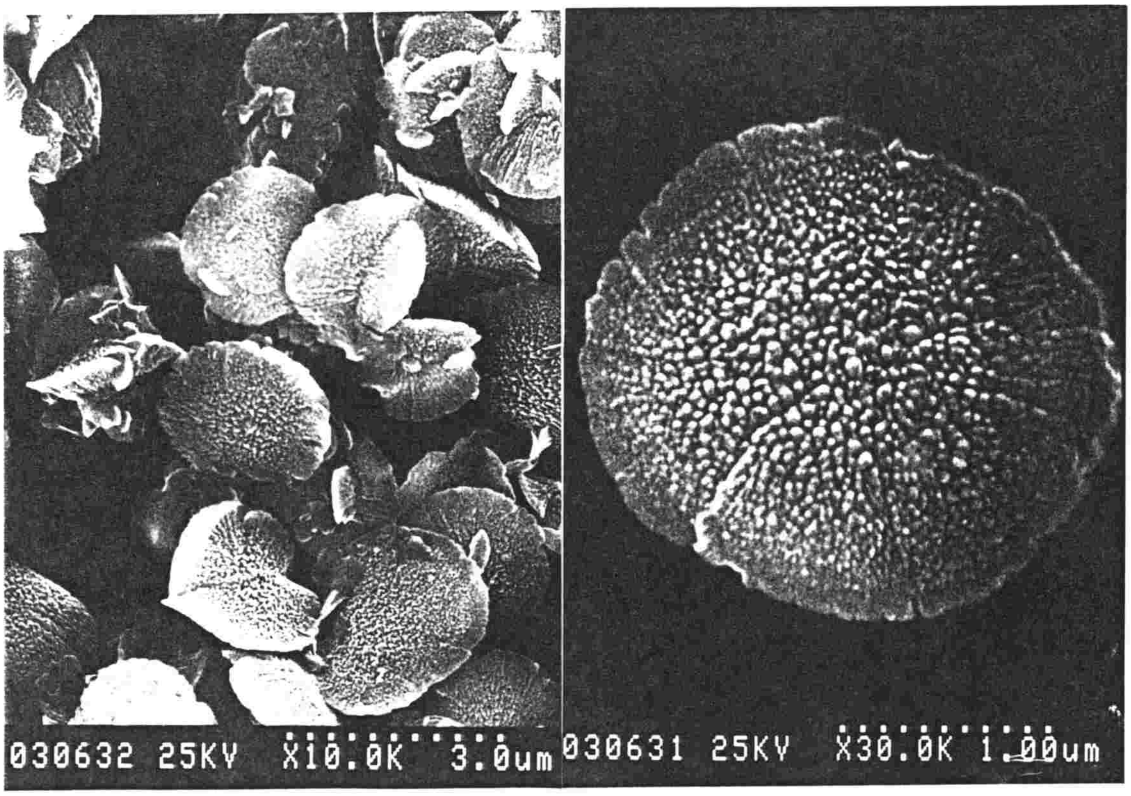


Figure 4-8. Scanning electron micrograph of POBP crystals prepared in TS 800 at 330℃ for 2h.

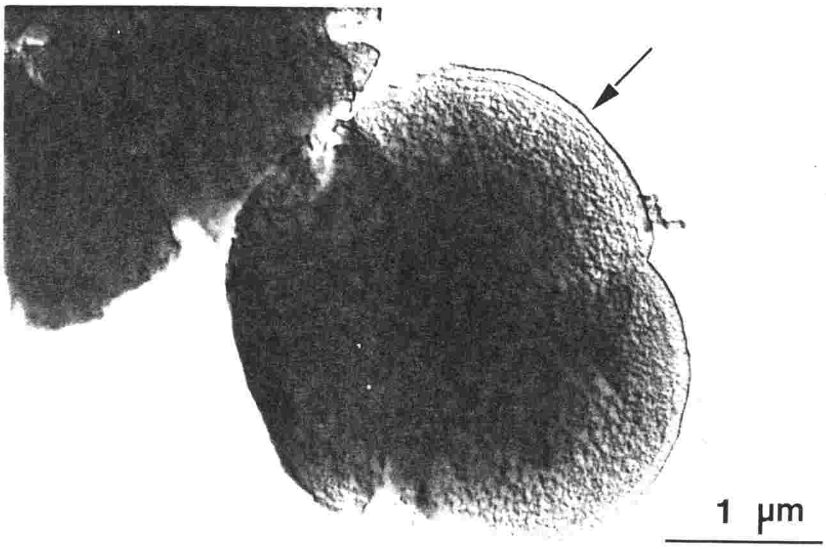


Figure 4-9. Transmission electron micrograph of incipient POBP crystals prepared in TS 800 at 330℃ for 1h.

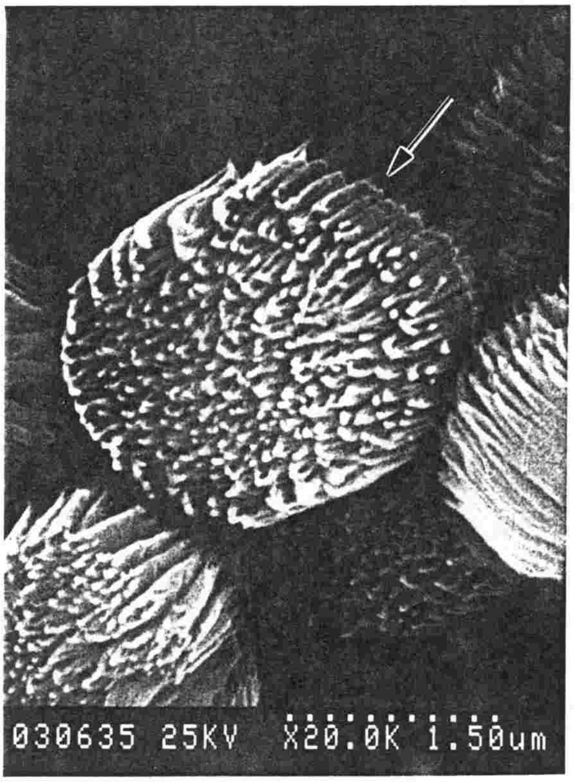


Figure 4-10. Scanning electron micrograph of POBP crystals prepared in TS 800 at 330℃ for 4h.

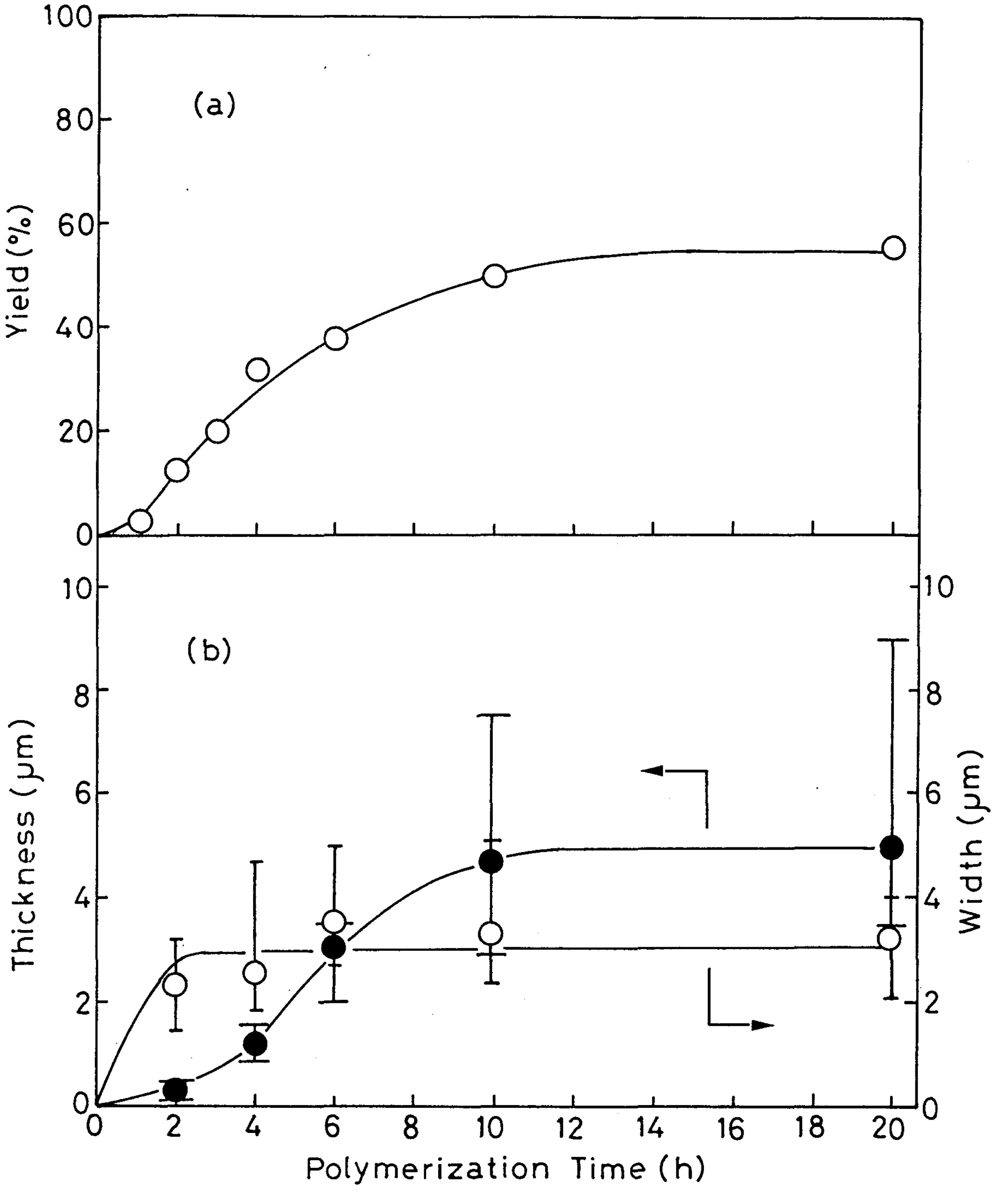


Figure 4-11. Polymerization time dependencies of (a) yield, (b) thickness (●) and width (○) of POBP crystals.

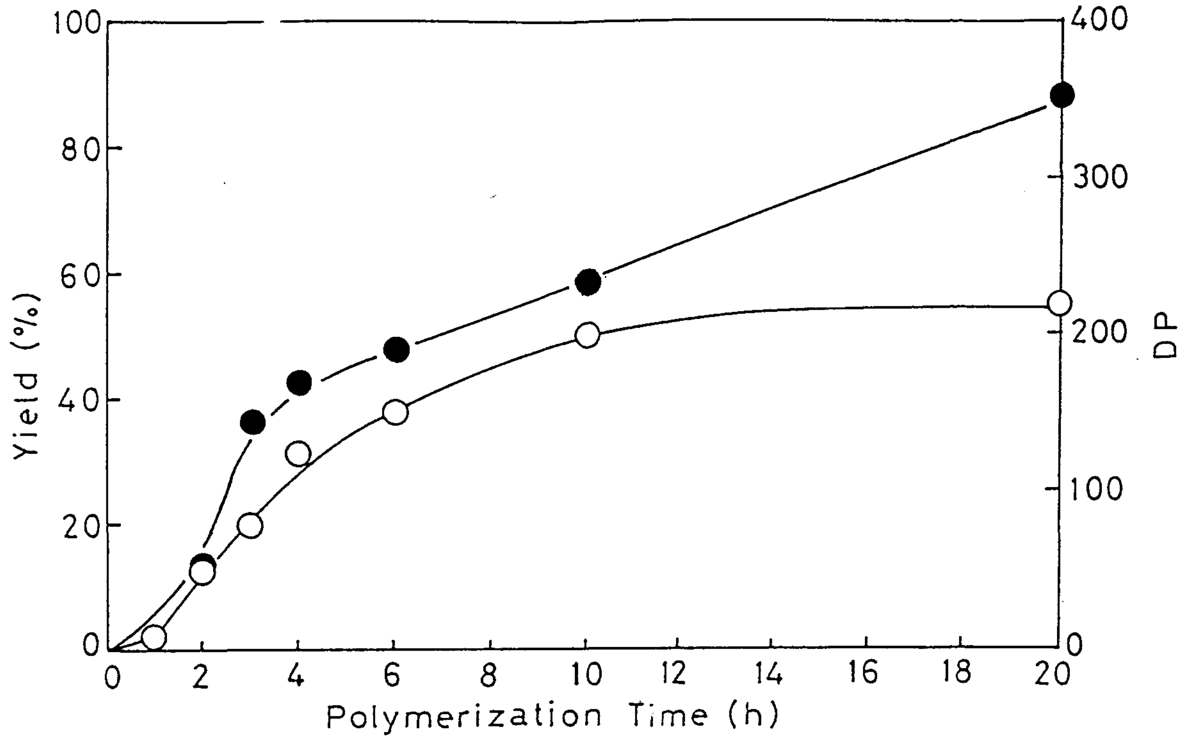


Figure 4-12. Variation of yield (○) and degree of polymerization (●) of POBP crystals with polymerization time.

chapter 1. This is the reason that the reorganization of crystals influences the followed crystal growth. The thickness of the crystals increases until 10h with the yield of the crystals but the width does not increase after 6h.

The variation of the DP with the polymerization time is shown in Figure 4-12. The DP increases with the yield of the crystals until 10h and continues to increase after the yield levels off. This fact shows that post-polymerization occurs in the crystal.

The results described above conclude the most suitable growth mechanism of the bundle-like aggregates of fibrillar crystals obtained in TS 800 or TS 900 as schematically described in Figure 4-13. The oligomers are formed in a homogeneous state and the oligomers are crystallized in the

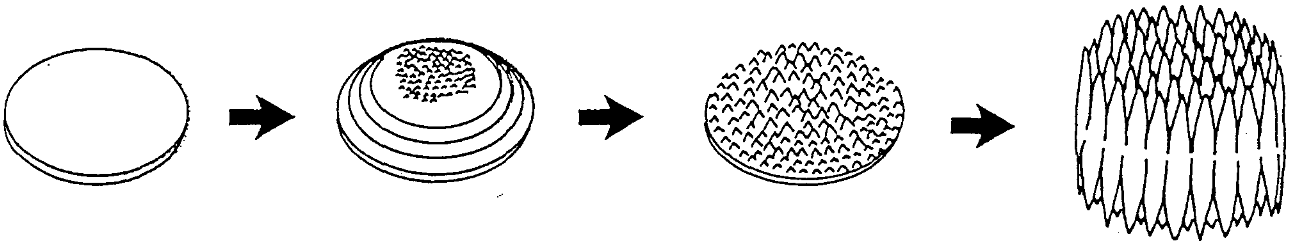


Figure 4-13. Schematic drawing of formation mechanism of bundle-like aggregate of fibrillar POBP crystals

form of lamellae from the solution as soon as the DP exceeds a critical value. The lamella grow to the lateral direction preferentially prior to the occurrence of a screw dislocation. Once the screw dislocation is formed in the precipitated lamellae, subsequent crystallization occurs at the slip plane rather than the usual growth plane because of the advantage of the secondary nucleation for crystal growth, and the convex lens-like crystals are formed by spiral growth. Reorganization of crystal occurs in the crystal accompanying the post-polymerization and many protrusions are formed on the surface of the lens crystals. Many fibrillar crystals develop from the incipient protrusions. The central part at which the fibrillar crystals are linked laterally is regarded as the primary lamella of crystal growth. The transesterification proceeds in the crystal and the DP increases even after the yield of the crystals levels off.

4-3-3 Summary

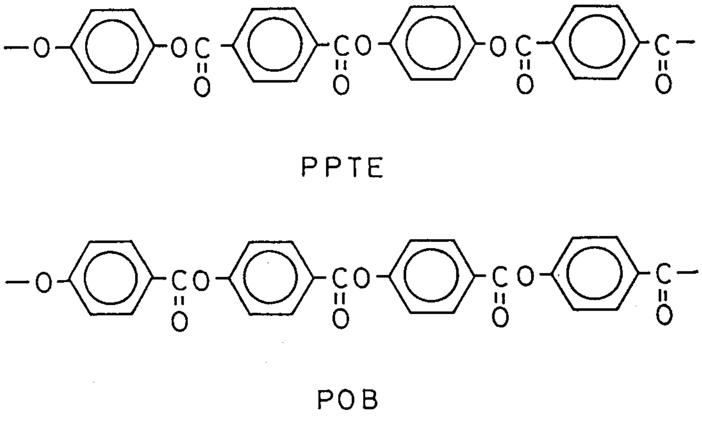
Crystallizations of POBP during high-temperature solution polymerization of ABPA are studied. When the polymerization is carried out in aromatic solvents such as TS 800 or TS 900 the bundle-like aggregates of fibrillar crystals are obtained. Their length and width are 5-10μm and 0.1-0.2μm. These fibrillar crystals are linked laterally to one another at the central part. The electron diffraction examinations reveal that these fibrillar crystals are chain extended single crystals and the polymer chains align along the long axis of the fibrillar crystals. In terphenyl are obtained hexagonal slab-like crystals, of which the thickness is 2-3μm and the width is on the average 10μm. These slab-like crystals are also fibrillated to the direction of the thickness.

The growth mechanism of the bundle-like aggregates of fibrillar crystals obtained in TS 800 is followed by the observations of crystal morphologies. It is revealed that the bundle-like aggregates of fibrillar crystals are formed via following steps. Convex lens-like crystals are formed by piling up lamellae with a spiral growth in the early stage of the polymerization, and then many protrusions with width of 0.1-0.2μm are formed in terms of reorganization of crystals accompanying post-polymerization. Fibrillar crystals are developed from the protrusions by the further crystallization. The formation mechanism of the lens crystals is fundamentally similar to that of the POB and PON whiskers, and reorganization of crystals during slow crystallization makes the morphology of the final crystal different.

These experimental facts indicate that the spiral growth of lamellae is not a specific mechanism in the crystallization of aromatic polyesters.

4-4 Crystallization of Poly(p-phenylene terephthalate) during Solution Polymerization

Poly(p-phenylene terephthalate) (PPTE) which is an aromatic condensation polyester of terephthalic acid with hydroquinone is well-known as a very straight and stiff polymer.[14,15] The molecular structure of PPTE is similar to that of POB, that is, both PPTE and POB comprise 1,4-phenylene groups and ester linkages. The structural difference is only the direction of ester linkage as shown below.



Scheme 4-3. Molecular structure of PPTE and POB

In other words, the molecular structure of POB is directional and that of PPTE is non-directional.

The synthesis of PPTE crystals by high-temperature solution polymerization is of interest to know whether PPTE crystal is formed as a needle-like crystals like POB whisker or not. Thus, it is the purpose of this work to compare the morphology of PPTE crystals with the POB whiskers under identical polymerization conditions.

4-4-1 Experimental

Materials

LP and TS 800 were used as polymerization solvents after purification as described in the previous section.

Synthesis of Monomers

The requisite monomers were either obtained commercially or synthesized according to the procedure described below.

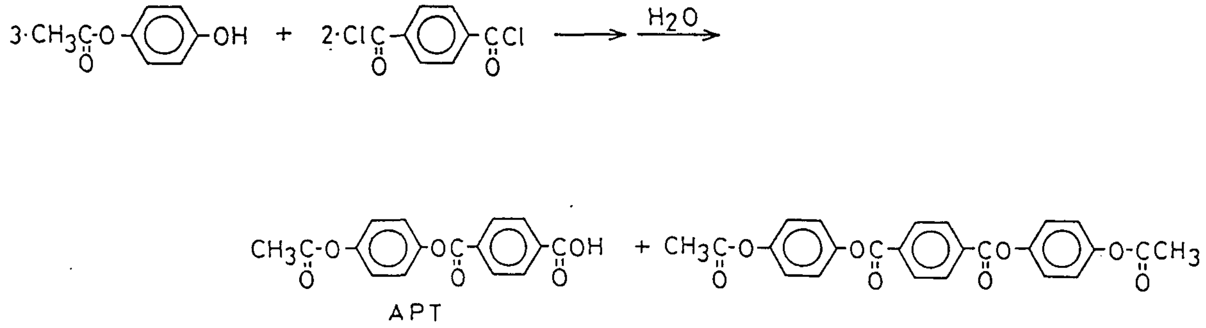
Terephthalic acid (TPA) was obtained from Mitsubishi Gas Chemical Co. Ltd. and used as received.

Hydroquinone (HQ) was obtained from Nakarai Tesque Co. Ltd. and used as received.

1,4-Diacetoxybenzene (DAB) was prepared as described in a literature.[16]

Diphenyl terephthalate (DPT) was synthesized from terephthaloyl chloride and phenol.

Mono(4'-acetoxyphenyl) terephthalate (APT) was synthesized according to the procedure as shown below, using the following procedure.



Scheme 4-4. Synthetic procedure of APT

In a 300ml-flask equipped with a cooler, a stirrer, a dropping funnel and a thermometer, were placed 13.3g of terephthaloyl chloride (6.6mmol), 15.0g of hydroquinone monoacetate (9.8mmol) and 200ml of dried tetrahydrofuran under a slow stream of nitrogen. After being cooled to 2℃, 9.9g of triethylamine (9.8mmol) was added through a dropping funnel while keeping the temperature below 10℃. The reaction was continued at 10℃ for 0.5h and at 25℃ for 0.5h. After filtering off trimethylamine hydrochloride salt and by-produced bis(4'-acetoxyphenyl) terephthalate, 3ml of water was added to the filtrate and the mixture was stirred over night. Tetrahydrofuran was evaporated and the crude product obtained was dried at 60℃ for 24h under reduced pressure. Recrystallization from p-xylene with charcoal once and ethylacetate twice gave white crystalline product; mp. 252-253℃. Purity was checked by silica gel TLC (elution solvent; chloroform / methanol = 90/10 by volume). The infrared and ^{1}H-NMR spectra were shown in Figure 4-13 and 4-14, respectively.

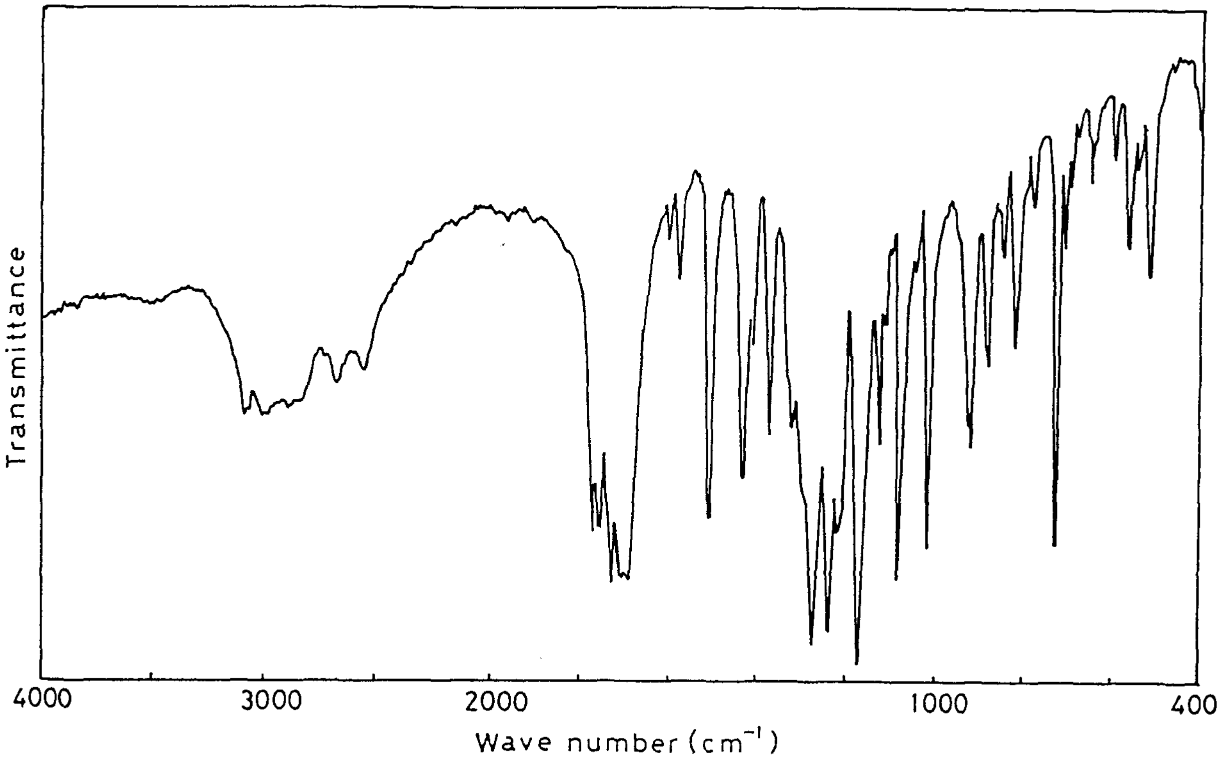


Figure 4-14. IR spectrum of APT.

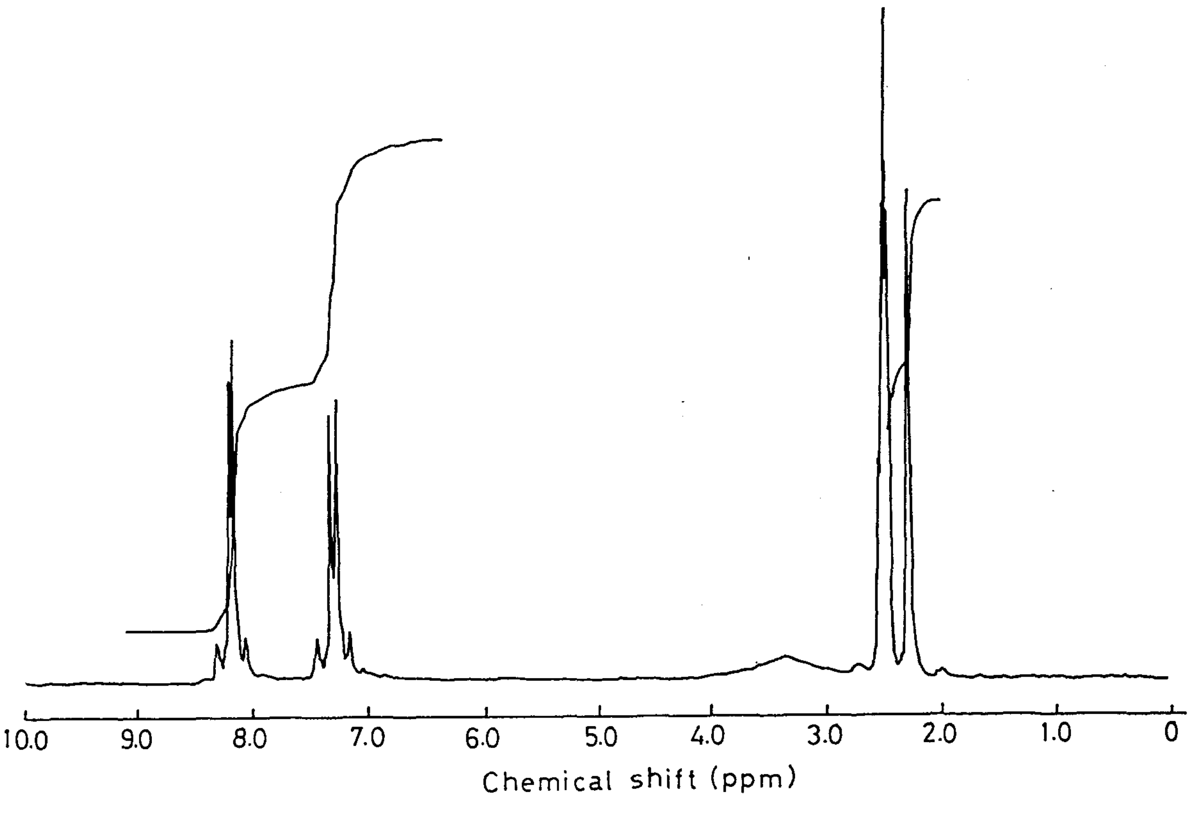


Figure 4-15. ^{1}H-NMR spectrum of APT.

Preparation of Poly(p-phenylene terephthalate) Crystals

A typical preparation procedure for PPTE crystals is described in the following. Other crystals were also obtained in a similar manner.

In a 200ml-cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were placed 0.42g of TPA (2.5mmol), 0.49g of DAB (2.5mmol) and 60g of LP. This reaction mixture was heated with stirring until the monomer dissolved completely, when stirring was stopped. Heating was continued up to 330℃ and maintained at this temperature. In a couple of minutes, the reaction solution became turbid and polymer crystals were then precipitated. The reaction was continued at 330℃ for 6h under a slow stream of nitrogen. The reaction mixture was allowed to cool at room temperature and chloroform was added. Polymer crystals were collected by filtration, washed several times with chloroform and acetone, and then dried at 100℃ under reduced pressure to constant weight.

Measurements

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

Thermal properties were evaluated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Rigaku R-DSC at a heating rate of 10℃/min in nitrogen. TGA was performed on a Shimadzu TG-30 at a heating rate of 10℃/min on a 5 mg sample in nitrogen or air.

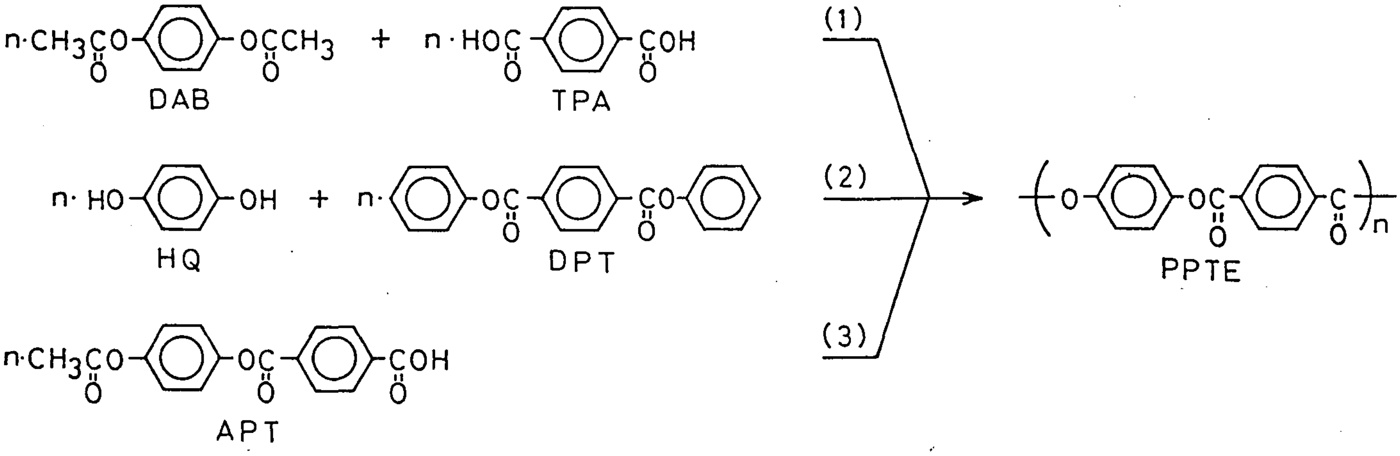
The chemical structure of the monomers was checked by infrared spectroscopy and ^{1}H-NMR spectroscopy. The instruments were a Hitachi 270-30 and a Varian Gemini-200.

The degree of polymerization (DP) was determined by ^{1}H-NMR end-group analysis of the acetyl group after hydrolysis of PPTE with conc. sulfuric acid in an NMR tube.[13]

4-4-2 Results and Discussion

4-4-2-1 Synthesis of Poly(p-phenylene terephthalate) Crystals

POB whisker were obtained by the condensation reaction of p-ABA with eliminating acetic acid or PHB with eliminating phenol as reported in chapter 1. On the basis of the results with the POB whiskers, three different types of reaction are selected for obtaining PPTE crystals, as shown below, that is, bimolecular condensation of (1) DAB and TPA, (2) HQ and DPT, and self-condensation of (3) APT.

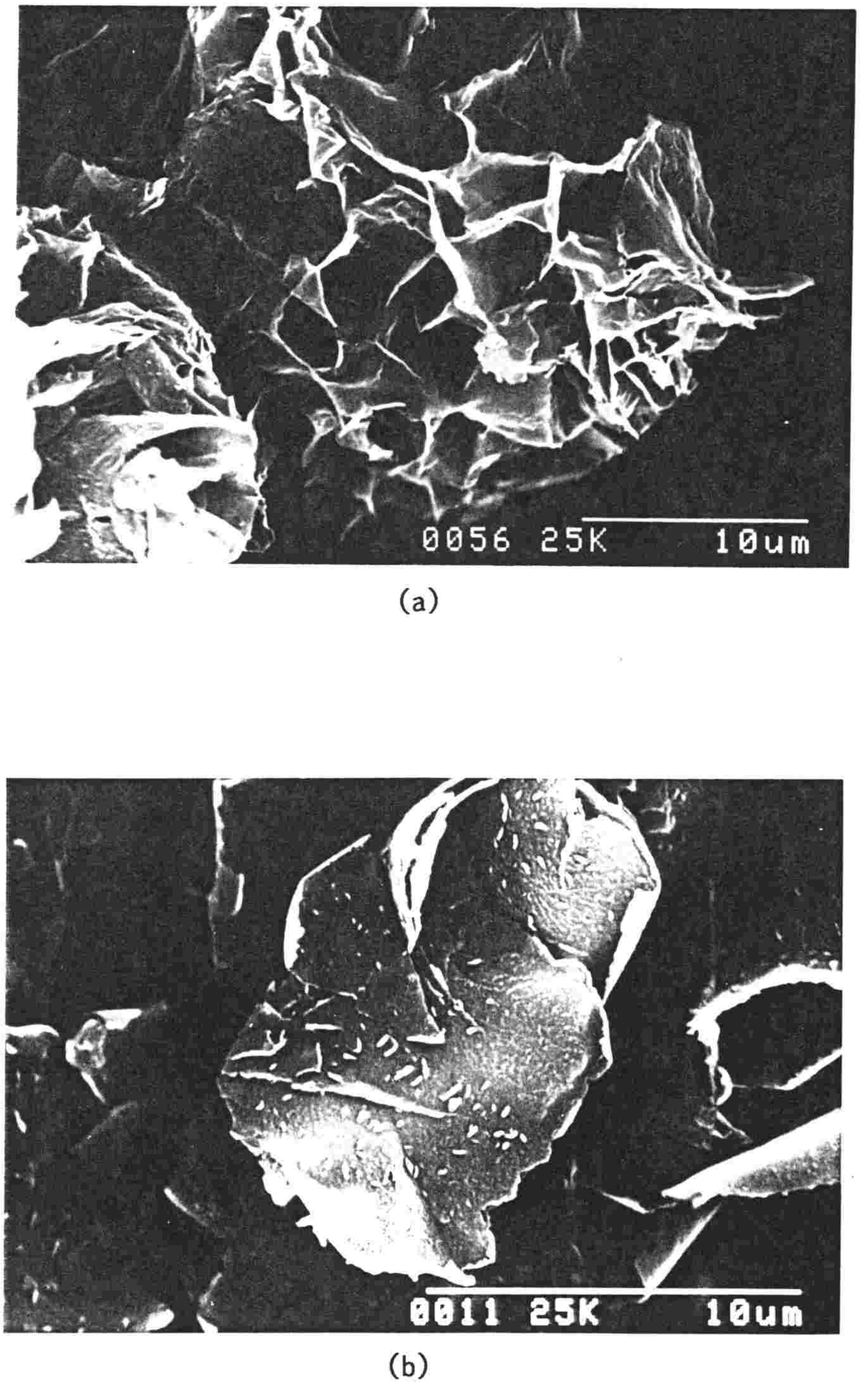


Scheme 4-5. Synthesis of PPTE

Polymerizations are carried out under conditions identical to those for the preparation of the POB whisker. All monomers dissolve until the reaction temperature goes up to 330℃ and polymerization proceeds in homogeneous solution. After several minutes at 330℃, the reaction solution becomes turbid and polymer crystals are then precipitated. The features of polymerization are similar to that of the POB whisker. The polymerization conditions and the results are presented in Table 4-8, including the results of the POB whiskers. In spite of the reaction types, needle-like crystals are not obtained. The PPTE crystals obtained are sheaf-like or plate-like. Typical scanning electron micrographs of sheaf-like crystals and plate-like crystals are shown in Figure 4-15(a) and (b), respectively. Crystals are not precipitated during the reaction between HQ and DPT at a concentration of 1.0%.

Bimolecular reaction is not conducive to the formation of polymer crystals during polymerization because any deviation from stoichiometric monomer ratio tends to stop the polymerization and the different end-groups of polymers are liable to prevent homogeneous crystallization. The self-condensation-type reaction prevents such problems and it seems to be preferable to bimolecular reaction for preparation of the polymer crystal. APT is used as a self-condensation-type monomer. However, PPTE crystals from APT are plate-like (see Figure 4-15(b)) and needle-like crystals are not obtained.

Needle-like PPTE crystals are not obtained under conditions identical with those for the preparation of the POB whiskers. The growth feature of the PPTE crystals will be discussed in a later section but further study is required to clarify the effect of the directionality of molecular structure on the crystal morphology.



(a)

(b)

Figure 4-16. Scanning electron micrographs of (a) sheaf-like PPTE crystals (PPTE-1); (b) plate-like PPTE crystals (PPTE-7).

Table 4-8. Synthesis of PPTE crystals under various conditions

Polymer	Momomer[1]	Solvent[2]	Conc.[3] (%)	Yield (%)	Crystal morphology
PPTE-1	DAB + TPA	LP	1.0	38.3	Sheaf-like
PPTE-2	DAB + TPA	TS 800	1.0	63.3	Sheaf-like
PPTE-3[4]	HQ + DPT	LP	1.0	—	———
PPTE-4	HQ + DPT	LP	5.0	56.0	Sheaf-like
PPTE-5[4]	HQ + DPT	TS 800	1.0	—	———
PPTE-6	HQ + DPT	TS 800	5.0	55.6	Sheaf-like
PPTE-7	APT	LP	1.0	57.9	Plate-like
PPTE-8	APT	TS 800	1.0	58.4	Plate-like
POB-1	p-ABA	LP	1.0	55.7	Needle-like
POB-2	p-ABA	TS 800	1.0	57.4	Needle-like
POB-3	PHB	LP	1.0	18.0	Needle-like

1) Monomer; DAB:1,4-diacetoxybenzene, TPA:terephthalic acid, HQ:hydroquinone, DPT:diphenyl terephthalate, APT:mono(4'-acetoxyphenyl) terephthalate, p-ABA:p-acetoxybenzoic acid, PHB:phenyl-4-hydroxybenzoic acid

2) Solvent; LP:liquid paraffin, TS 800:Therm S 800 An aromatic heat exchange medium of Nippon Steel Chemical Co. Ltd.

3) Conc.(%) = [Theoretical polymer yield (g) / Solvent weight (g)] x 100

4) Crystals were not obtained.

4-4-2-2 Crystal Features and Thermal Properties of Poly(p-phenylene terephthalate) Crystals

The determination of the polymer chain packing manner in the PPTE crystal is carried out by using the electron diffraction technique. A diffraction pattern of the plate-like crystal (PPTE-7) is shown in Figure 4-16, in which the direction of electron incidence is perpendicular to the plane of the crystal. From this diffraction, *a* spacing of 7.87 Å

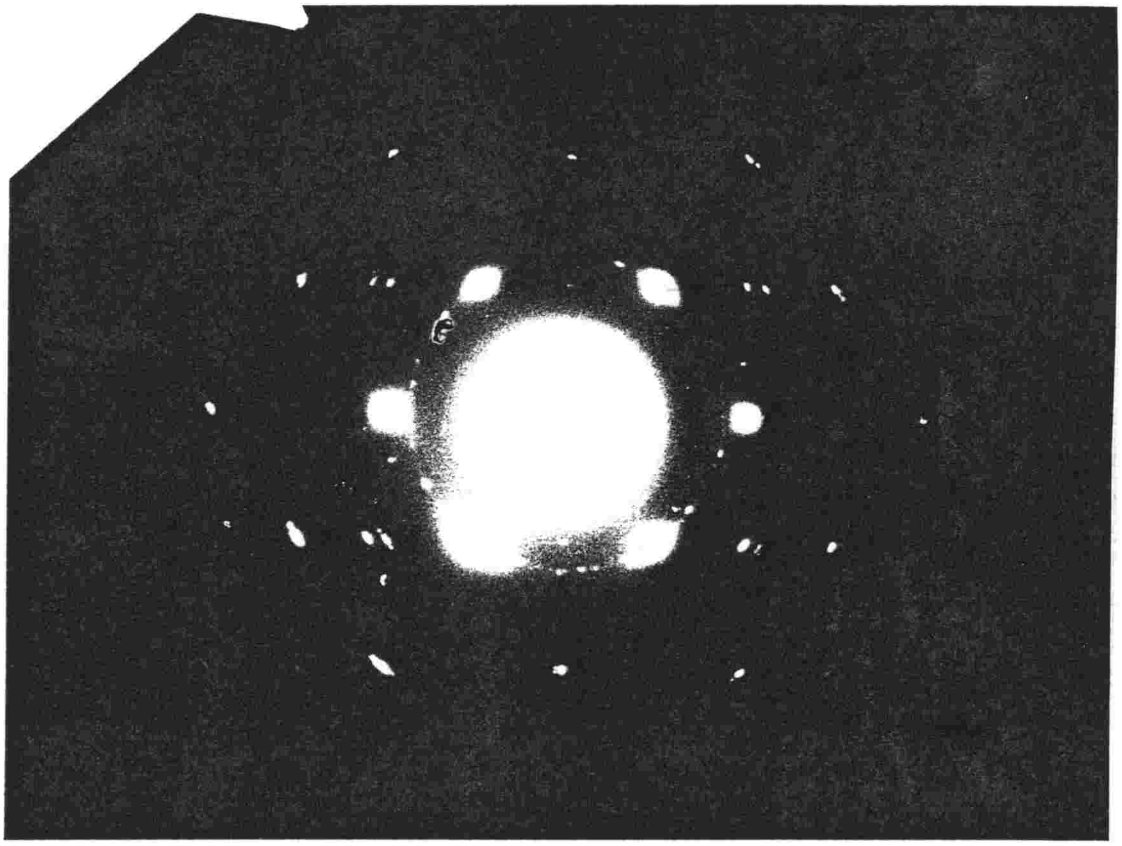


Figure 4-17. Electron diffraction pattern of plate-like PPTE crystal (PPTE-7).

and *b* spacing of 5.55Å are estimated; they do not correspond to one chemical repeat of PPTE (*trans*-conformation 14.2Å, *cis*-conformation 13.8Å). The polymer chain direction is therefore perpendicular to the plane of the crystal. In addition the pattern shows that each crystals a true single-crystal with no amorphous scattering.

Thermal transition behaviors of the PPTE crystals are estimated by DSC analysis. It is known that POB crystal has two reversible transition at 370℃ and 450℃.[3-6] These transitions are regarded as a plastic crystal or a highly ordered smectic phase transition and a phase transition to nematic mesophase, respectively. In contrast, PPTE does not show any detectable peaks below 500℃ and it does not have the thermal transition like the POB crystal.

Thermal stabilities of the PPTE crystals are measured by TGA performed at a heating rate of 10℃/min in air or nitrogen. They show good thermal stabilities. 5wt% loss of PPTE-7 is found at 409℃ and 10wt% at 456℃ in air. 5wt% loss of PPTE-7 is found at 422℃ and 10wt% at 492℃ in nitrogen.

4-4-2-3 Growth Feature of Poly(p-phenylene terephthalate) Crystals

The growth mechanism of the POB whisker has been studied in the chapter 1 and it has be concluded that the whisker is formed by piling up lamellae with a spiral growth and subsequent post-polymerization in the interlamellae region.

Though both PPTE and POB comprise 1,4-phenylene groups and ester linkages, the final shapes of these crystals are very different and the PPTE crystals seem to be formed via different mechanism from the POB whisker.

In order to understand the growth feature of the PPTE crystals, polymerization time dependencies of the yield, the thickness of the crystal and the DP, which are determined by ^{1}H-NMR end-group analysis, of PPTE-7 are investigated. The results are shown in Figure 4-17 and 4-18. The yield of the crystal appears to level off within 3h. The thickness of the crystal estimated by direct observation with scanning electron microscopy is almost constant at ~0.16μm through the polymerization. These results indicate that the crystals grow preferentially in the lateral direction which is perpendicular to the alignment of the polymer chains. The DP increases gradually with the polymerization time even after the yield levels off. The DP reaches 12.5 after 6h but it is not so high compared with that of the POB whiskers as described in chapter 1. These facts indicate that post-polymerization occurs gradually, but it does not proceed so effectively in the crystal region, probably because of random arrangements of the polymer chain ends.

From these results, it is supposed that plate-like PPTE crystals are formed as follows. (1) PPTE oligomers are formed in a homogeneous state and as soon as the DP exceeds a critical value, oligomers crystallize in the form of lamellae. The lateral crystal growth occurs by the crystallization of oligomers onto the lateral surfaces preferentially. (2) the molecular weight increases gradually by transesterification in the crystal region. The growth feature of the sheaf-like crystal may be similar. The main difference in the growth feature between the PPTE crystals and the POB whiskers is that a screw dislocation that serves the whisker growth does not

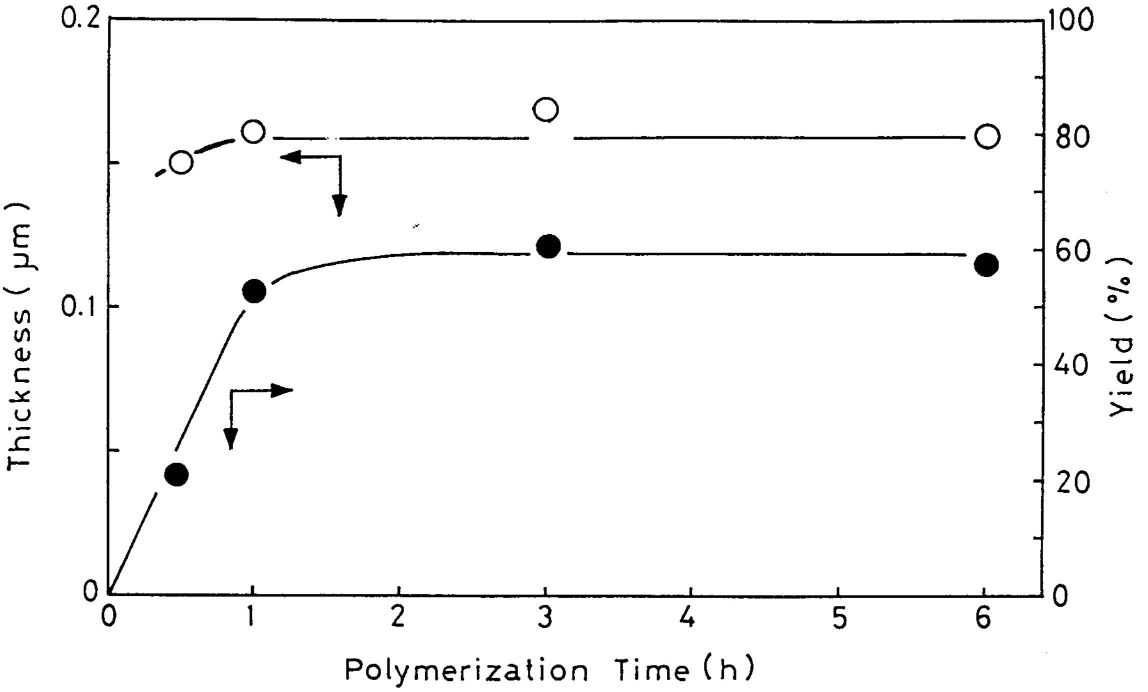


Figure 4-18. Polymerization time dependencies of yield (●) and thickness (○) of plate-like PPTE crystals (PPTE-7).

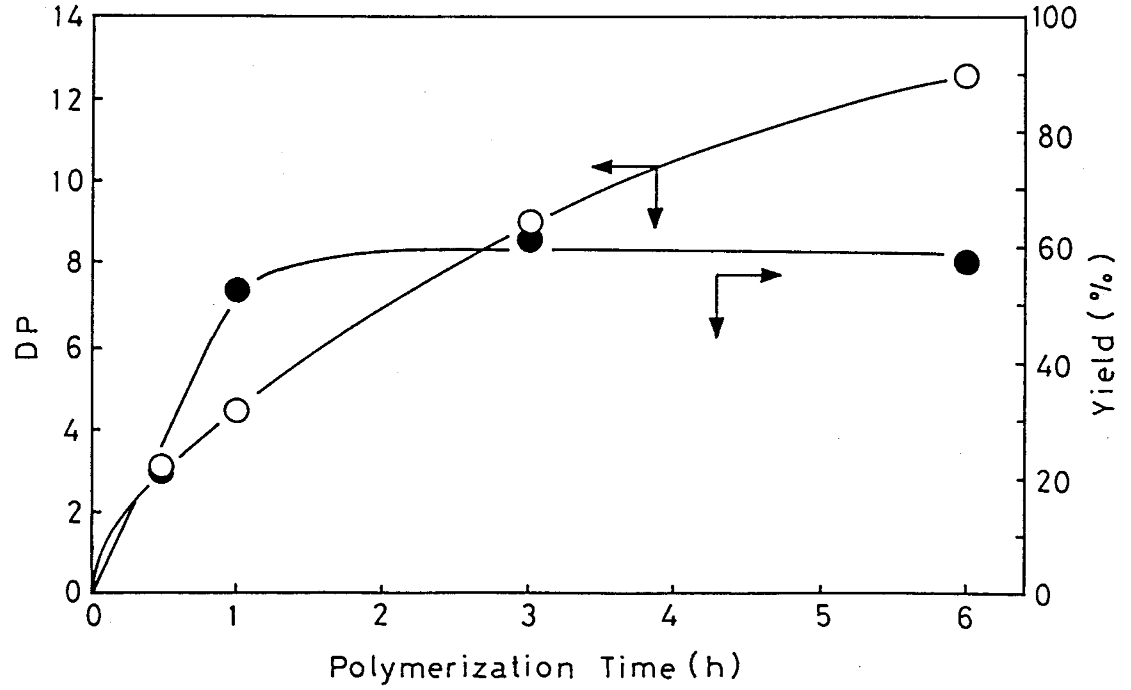


Figure 4-19. Polymerization time dependencies of yield (●) and degree of polymerization (○) of plate-like PPTE crystals (PPTE-7).

generate in the precipitated lamellar of PPTE. The difference in the growth feature may rest on the differences in the magnitude of fiber identity period, the polymer chain packing manner in terms of the directionality of molecule or the thickness of lamellae.

4-4-3 Summary

PPTE crystals are prepared by high-temperature solution polycondensation via three different types of reaction as follows: bimolecular condensation of (1) DAB and TPA, (2) HQ and DPT, and self-condensation of (3) APT. In spite of the reaction types, the obtained PPTE crystals are sheaf-like or plate-like crystals and needle-like crystals are not formed. Though both PPTE and POB comprise 1,4-phenylene groups and ester linkages, the morphologies of crystals obtained under identical polymerization conditions are quite different.

From the electron diffraction examination, the obtained PPTE crystals in which the polymer chains align perpendicular to the plane of the plate-like crystal are single crystals.

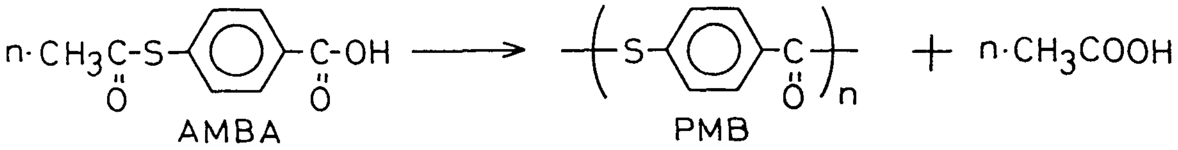
The thickness of the plate-like PPTE crystal is almost constant through the polymerization and the DP increases even after the yield of crystals levels off. It is revealed from these results that the crystal grows more laterally than longitudinally by the crystallization of the oligomers onto the lateral surface of the crystal and post-polymerization occurs gradually in the crystal. A screw dislocation which serves the whisker growth does not generate in the precipitated lamellar of PPTE. It should be clarified with further examination whether the generation of a screw dislocation in the precipitated lamellar is attributable to the magnitude of fiber identity period, the polymer chain packing manner in terms of the directionality of molecules or the thickness of lamellae.

4-5 Crystallization of Poly(4-mercaptobenzoyl) during Solution Polymerization

POB and PON which are self-condensation-type aromatic polyester crystallize in the form of whisker with a spiral growth of lamellae during high-temperature solution polymerization as reported previously. Moreover, as for the crystallization of POBP, the whisker is not formed but the bundle-like aggregates of fibrillar crystals are formed also with a spiral growth of lamellae. These results imply that crystallization of self-condensation-type polyester is inclined to proceed with a spiral growth of lamellae during solution polymerization under optimal conditions and there exists some probability of the preparation of the whisker for aromatic condensation polymers other than polyester.

Poly(4-mercaptobenzoyl) (PMB) which is a polythioester has a straight rigid-rod molecular chain and it is highly crystalline as reported.[17] The molecular structure of PMB is very similar to that of POB, *i.e.* ether oxygen of POB is replaced by sulfur, and hence it is expectable that the PMB whiskers are formed during solution polymerization. It was shown that PMB was obtained by high-temperature solution polymerization in an aromatic solvent at high concentration of monomers.[17] However, morphological considerations for the PMB crystals have not been conducted so far.

Thus, it is the purpose of the present work to synthesize the PMB whiskers from S-acetyl-4-mercaptobenzoic acid (AMBA) by solution polymerization as shown below and to describe their crystal morphologies.



Scheme 4-6. Synthesis of PMB from AMBA

4-5-1 Experimental

Materials

AMBA was prepared as described in literatures.[17-20] Purity was checked by GC-MS spectrometry. LP and TS 800 were used as polymerization solvents after the purification as described in chapter 1.

Preparation of Poly(4-mercaptobenzoyl) Crystals

A typical preparation procedure for the PMB whiskers is described in the following. Other crystals were prepared in a similar manner.

In a 200ml-cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were placed 0.87g of AMBA and 60g of LP. This reaction mixture was heated with stirring under a slow stream of nitrogen. When the monomer dissolved completely by the temperature elevation, stirring was stopped. Heating was continued up to 300℃. When the temperature reached 260℃, the reaction solution became turbid and then the crystals began to precipitate. The temperature was finally maintained at 300℃ for 6h. The reaction mixture was allowed to cool to room temperature and chloroform was added. The polymer crystals were collected by filtration, washed several times with chloroform and acetone, and then dried at 100℃ under reduced pressure to a constant weight.

Anal. Calcd for C_7H_4OS polymer: C,61.74; H,2.96; S,23.55
Found : C,61.81; H,3.01; S,23.10

Measurements

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

Thermal properties were evaluated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed on a Perkin-Elmer DSC-7 at a heating rate of 20℃/min or 100℃/min in nitrogen. TGA was performed on a Shimadzu TG-30 at a heating rate of 10℃/min on a 5mg sample in nitrogen or air.

The degree of polymerization (DP) was measured by ^{1}H-NMR end-group analysis of the acetyl group after hydrolysis of PMB with conc. sulfuric acid in an NMR tube with a Varian Gemini-200 spectrometer as described in a literatures.[13]

4-5-2 Results and Discussion

4-5-2-1 Synthesis of Poly(4-mercaptobenzoyl) Whiskers

The PMB whiskers are obtained by high-temperature solution polymerization of AMBA in LP. The morphological features of crystals prepared in various conditions are summarized in Table 4-9. The PMB whisker prepared in LP at 300℃ (PMB-2) has a length of 5-8μm and a width of 0.3-0.5μm as shown in Figure 4-19(a). The whiskers show the radial growth from the central part.

When the polymerization is carried out in TS 800, crystals are not precipitated even after 6h. Oligomers are precipitated after cooling the polymerization mixture to 25℃ and the average DP of them is 3.4. This fact shows that further polycondensation of AMBA does not proceed at a

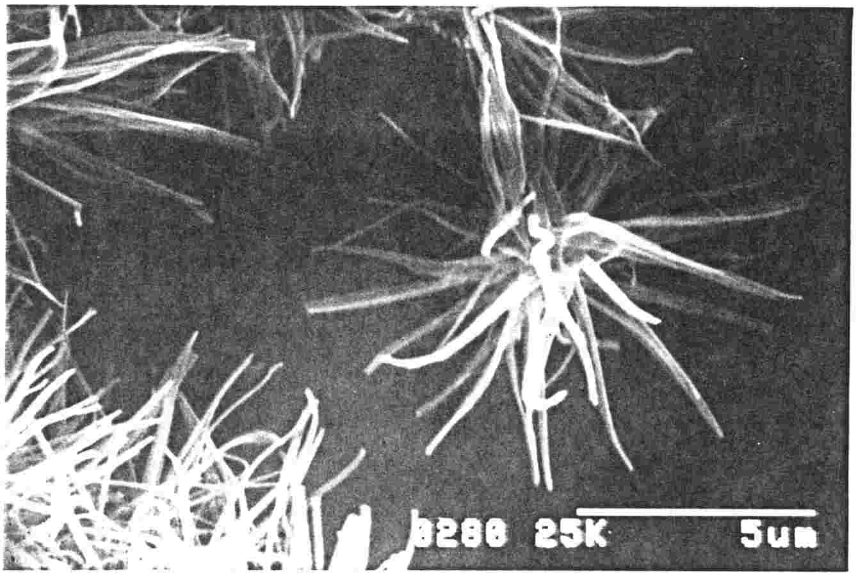
Table 4-9. Polymerization conditions and morphological features of the PMB crystals

Polymer	Solvent[1]	Conc.[2] (%)	Polymerization Temperature(℃)	Time(h)	Yield (%)	Crystal morphology
PMB-1	LP	1.0	330	6	50.0	Fibrillar
PMB-2	LP	1.0	300	6	61.6	Needle-like
PMB-3	LP	1.0	280	6	61.7	Needle-like
PMB-4	LP	1.0	260	6	50.0	Needle-like
PMB-5	LP	5.0	300	6	72.9	Fibrillar
PMB-6[3]	TS 800	1.0	300	6	——	——

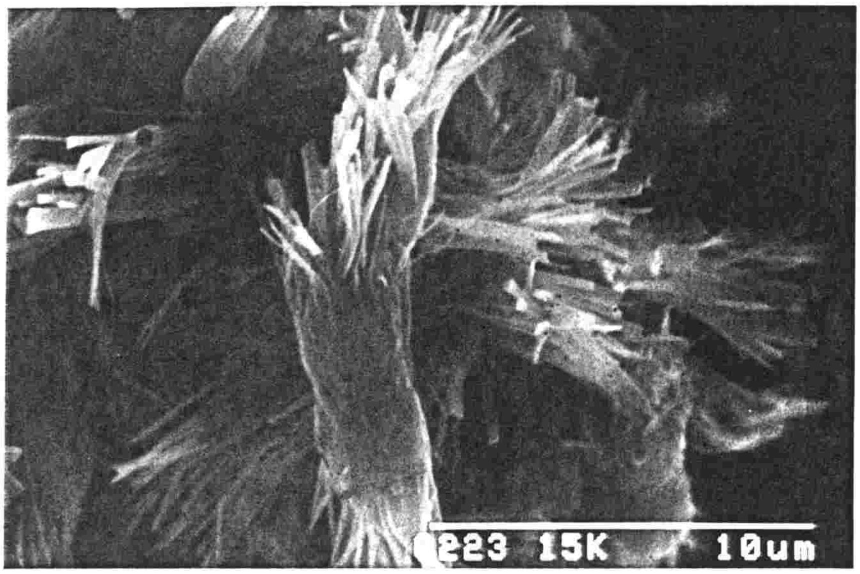
1) Solvent; LP:liquid paraffin, TS 800:Therm S 800

2) Conc.(%) = [Theoretical polymer yield (g) / Solvent weight (g)] x 100

3) Crystals were not obtained.



(a)



(b)

Figure 4-20. Scanning electron micrograph of (a) PMB whiskers prepared in LP at 300℃ (PMB-2); (b) PMB crystals prepared in LP at 330℃ (PMB-1).

concentration of 1.0wt% in TS 800 at 300℃. Under the condition of low concentration of monomers, the precipitation of oligomers seems to be an important process for further polycondensation. In the case of POB, crystals were not obtained at a concentration of 1.0wt% in diphenylsulfone as described in chapter 1. Also in the present case of PMB in TS 800, the similar consideration may be allowable. If the oligomers of low DP are not precipitated because of their good solubility, it is thought that the effective rate of polycondensation decreases with the decrease of the concentration of end-group and the polycondensation actually stops. The DP of oligomers does not exceed the critical value for the precipitation and therefore crystal is not formed.

Concerning the polymerization temperatures, the PMB whiskers are obtained at a range of 260-300℃ in LP. The crystals prepared in LP at 330℃ (PMB-1) are the bundle of fibrillar crystals as shown in Figure 4-19(b) and they are colored. PMB is relatively thermally unstable and thermal decomposition begins at around 330℃ even under nitrogen. The higher temperature than 300℃ is undesirable condition for preparing the PMB whiskers as thermal decomposition of PMB prevents ideal crystallization during polymerization.

4-5-2-3 Characterization of Poly(4-mercaptobenzoyl) Whiskers

Electron diffraction pattern of PMB whisker is shown in Figure 4-20. This diffraction pattern consists of sharp spots of lower to higher order reflections as observed clearly. This is due to the single-crystal nature of these whiskers. The meridian of this pattern corresponds to the long axis of the crystal, and therefore it is concluded that polymer chains

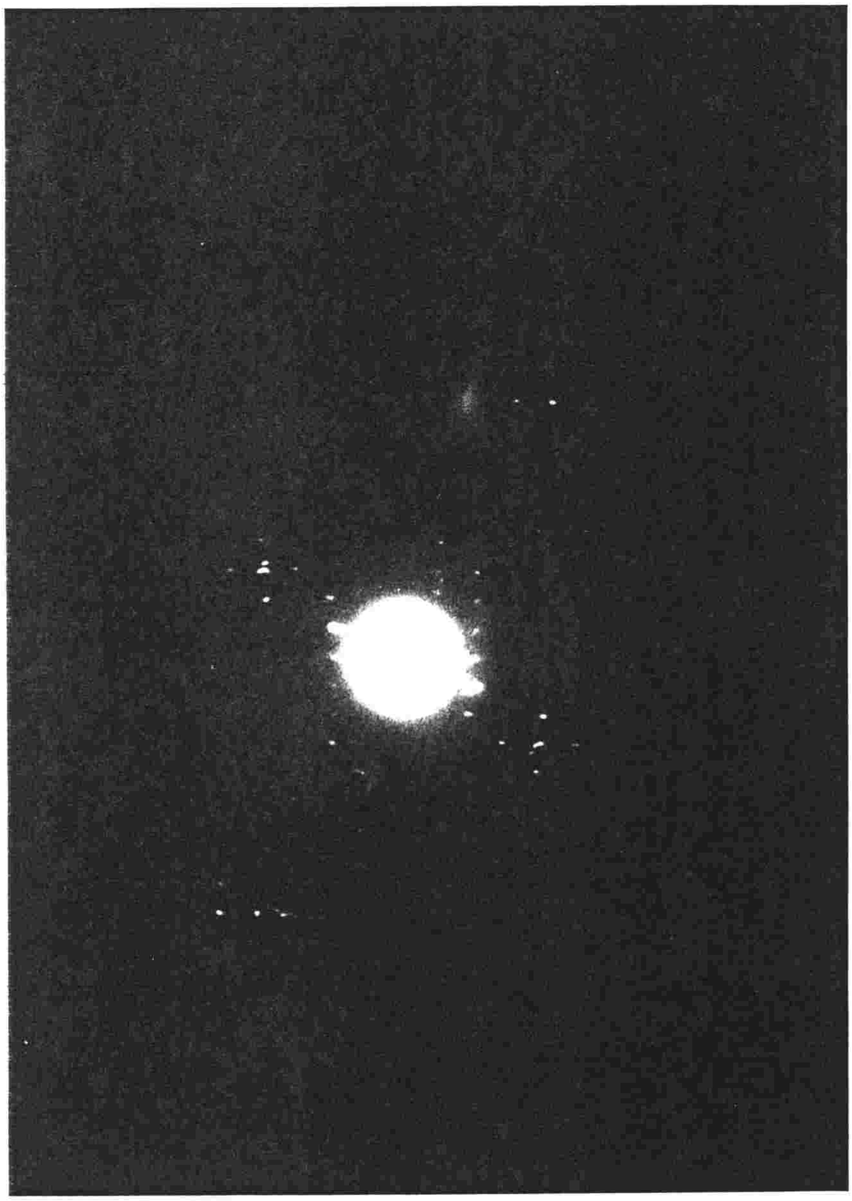


Figure 4-21. Electron diffraction pattern of PMB whiskers.

are aligned along the long axis of the whisker. The fiber identity period is 13.30Å, corresponding to two chemical residues. The detailed observation of this electron diffraction pattern shows diffuse streaks around 004 and 006 reflections. These streaks may be caused by the nematic-like disorder in chain direction.

4-5-2-4 Thermal Properties of Poly(4-mercaptobenzoyl) Crystals

It has been reported that PMB crystal has a reversible first-order transition with an endotherm at around 366℃ on a heating scan and an exotherm at around 328℃ on a cooling scan by the analysis of DSC.[17] This transition is solid-solid transition differing from the melting process and it is closely analogous to that of POB crystals. It is revealed by WAXS measurements with synchrotron radiation that this solid-solid transition is regarded as a transition to a pseudohexagonal packing of chains by rotation of the 1,4-phenylene rings.[17]

DSC analysis of the PMB crystals obtained here confirms the presence of the reversible solid-solid transition when the measurements are performed until 400℃ with a rate of 20℃/min. The solid-solid transition temperatures (T_t) and their enthalpies (ΔH_t) measured on the heating scans are listed in Table 4-10. T_t and ΔH_t of the PMB whiskers (PMB-2, 3, and 4) are higher and larger than others, and this suggests the closer packing of polymer chains in the whiskers than the crystals with other morphologies. The existence of a higher transition temperature where significant flow may occur should be predictable from the results of POB crystals[3,21] but it has not been reported previously. Here, a higher transition than T_t might be masked by the thermal decomposition of PMB during the heating process. DSC experiments are carried out at a faster heating rate of 100℃/min to avoid the thermal decomposition. Then, it is found that an endotherm is detected at around 420℃ as shown in Figure 4-21. Optical micrograph with crossed polarizers as shown in Figure 4-22 is obtained from the specimen which is molten at 450℃ in the absence of externally applied shear and then quenched rapidly to room temperature to avoid the change of texture by the thermal decomposition. This micrograph shows the presence of nematic-like domain structures and therefore this higher temperature modification may be called a liquid crystal phase. An exothermic peak corresponding to this higher transition can not be detected on the cooling scan due to probable decomposition of the sample. The higher transition temperatures (T_n) and their enthalpies (ΔH_n) are also listed in Table 4-10. T_n of the PMB whiskers is higher than PMB-5 but lower than PMB-1. ΔH_n of the PMB whiskers, however, is much larger than others. The larger value of ΔH_n of the PMB whiskers is also ascribed to the closer packing of polymer chains.

The thermal stabilities of the PMB crystals evaluated by TGA measurements are also summarized in Table 4-10. It is found that the thermal decomposition of the PMB crystals begins at around 310℃ in air and 330℃ in nitrogen. The PMB-2

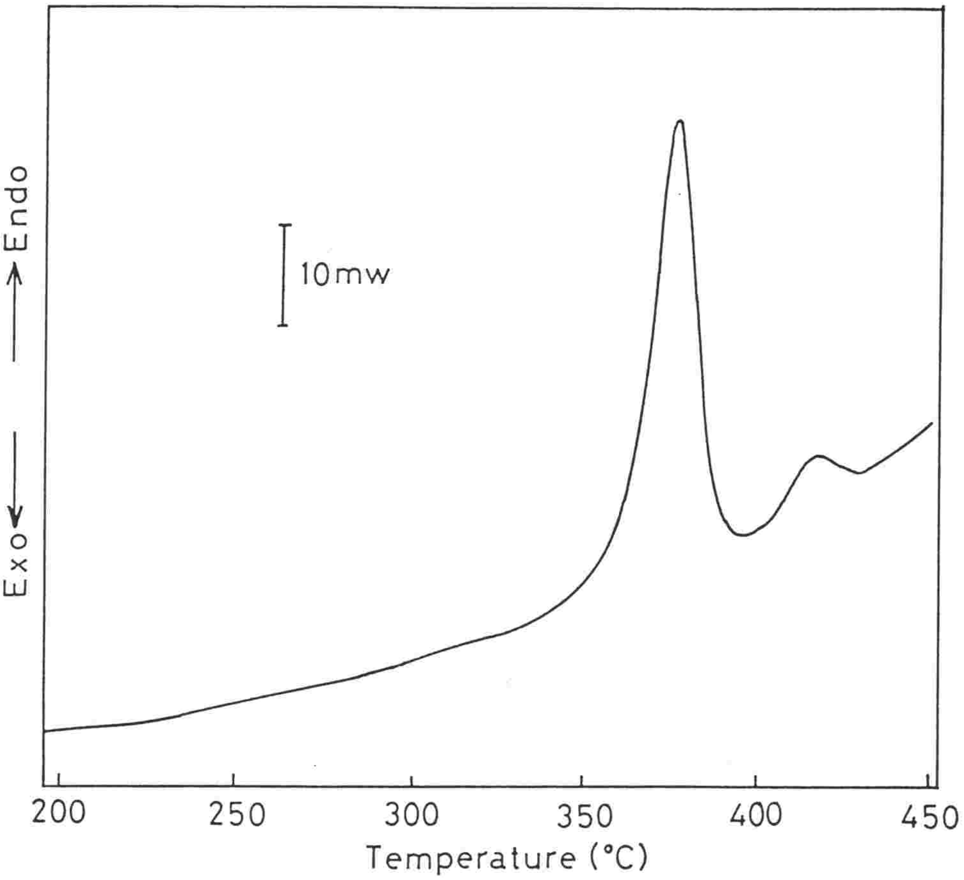


Figure 4-22. Tyipical DSC profile of PMB crystals measured at a scanning rate of 100℃/min under 450℃.

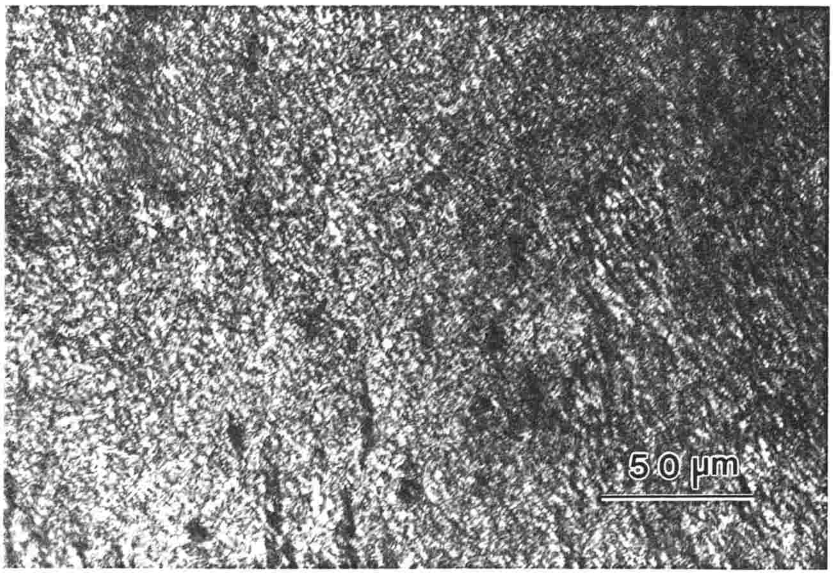


Figure 4-23. Optical micrograph with crossed polarizers of PMB specimen quenched to 25℃ from melt phase at 450℃.

whiskers display the most excellent thermal stability.

Table 4-10. Thermal properties of PMB crystals

	DSC1)						TGA2)	
Polymer	T_t (℃)	ΔH_t (kJ/mol)	ΔS_t (J/K·mol)	T_n (℃)	ΔH_n (kJ/mol)	ΔS_n (J/k·mol)	Air (℃)	Nitrogen (℃)
PMB-1	358.0	9.08	14.39	424.2	0.25	0.35	387	395
PMB-2	365.3	9.46	14.82	416.4	0.89	1.28	385	404
PMB-3	364.6	10.00	15.68	421.2	0.50	0.73	383	396
PMB-4	362.9	9.14	14.37	414.0	1.00	1.46	382	389
PMB-5	339.2, 355.2	3.32, 7.28	5.42, 11.59	398.9	0.25	0.37	373	374

1) T_t ; Solid-solid transition temperature measured on the heating scan at a heating rate of 20℃/min.
T_n ; Solid-liquid crystal transition temperature measured on the heating scan at a heating rate of 100℃/min.

2) Temperature at which 5% weight loss was recorded in TGA curves.

4-5-2-5 Growth Mechanism of Poly(4-mercaptobenzoyl) Whisker

In order to understand the growth mechanism of the PMB whiskers, the change of the crystal morphologies is observed with the polymerization times at 300℃ in LP. The crystals are collected by vacuum filtration at 300℃ to avoid an influence of the crystallization of oligomers onto the surface of the crystals during cooling. The transmission electron micrograph of incipient crystals prepared for 3min at 300℃ is shown in Figure 4-23. As can be seen in this micrograph, many fibrillar crystals of which the length is 1.0-1.5μm and the width is 0.1-0.3μm grow radially. These incipient crystals have smooth surfaces. The lamellar structure piling up along the long axis of needle-like crystals as observed in the incipient crystals of the POB whiskers is not observed.

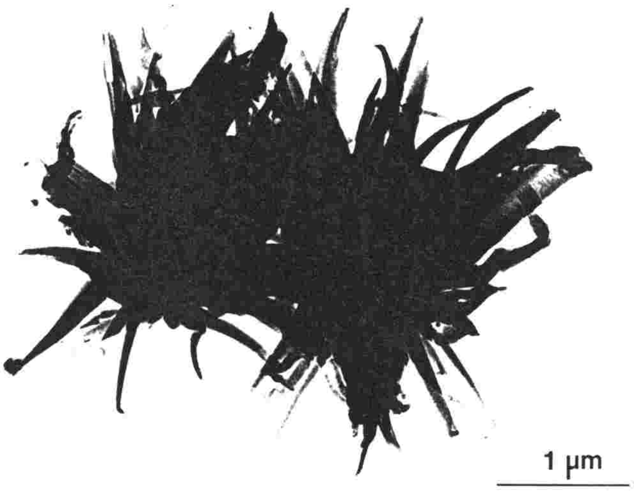


Figure 4-24. Transmission electron micrograph of incipient PMB whiskers prepared in LP at 300℃ for 3min.

Polymerization time dependencies of the length and the yield of the PMB whiskers are shown in Figure 4-24. The yield increases rapidly in the early stage of polymerization accompanying an increase of the length of the PMB whiskers. This shows the high reactivity of mercapto group for transesterification reaction. And it is also clear that the needle-like crystals are not formed by fibrillation of a large crystal but formed by independent growth through polymerization.

The change of the DP of the PMB whiskers with the polymerization time is shown in Figure 4-25. The DP increases rapidly with the yield until 30min and then it increases gradually even after the yield levels off. This fact implies that polymerization proceeds with the crystal growth and post-

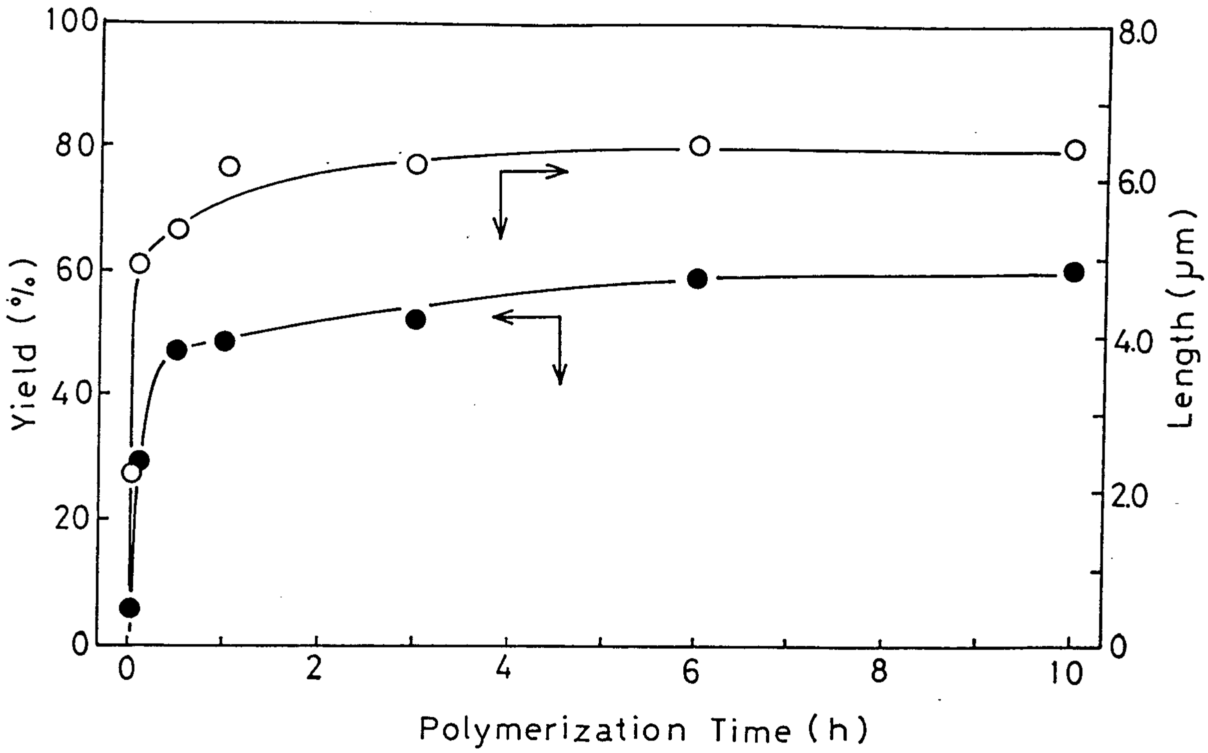


Figure 4-25. Polymerization time dependencies of length (○) and yield (●) of PMB whiskers.

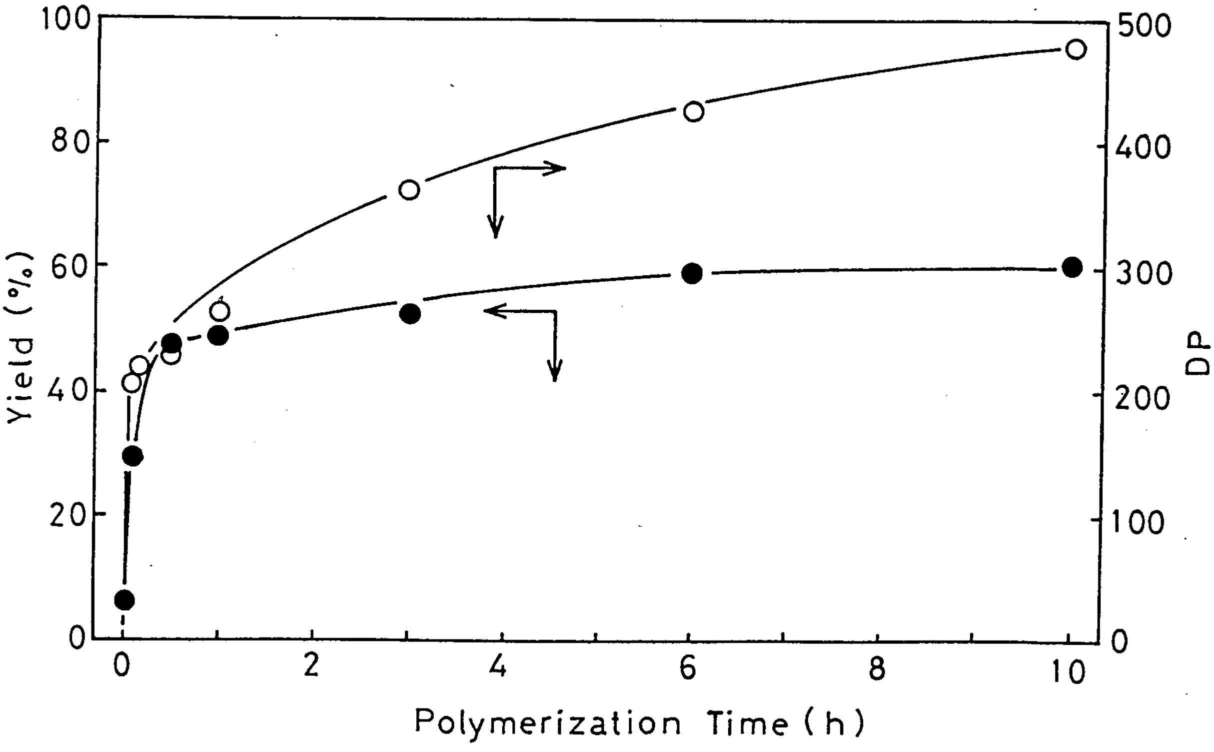


Figure 4-26. Polymerization time dependencies of degree of polymerization (○) and yield (●) of PMB whiskers.

polymerization also occurs in the crystal regions after the crystal growth ceases.

The solid-solid transition temperature (T_t) and the enthalpy (ΔH_t) of the PMB whiskers are plotted against the polymerization time in Figure 4-26. While both T_t and ΔH_t increase within 5min, they are almost constant after 5min through the polymerization. The change of an endothermic peak measured on the heating scan with the polymerization time is shown in Figure 4-27. An endothermic peak of the crystals polymerized for 3min is broader with a discernible shoulder at lower temperature side of the main peak. This shoulder peak disappears after further polymerization for 5min. The peak of

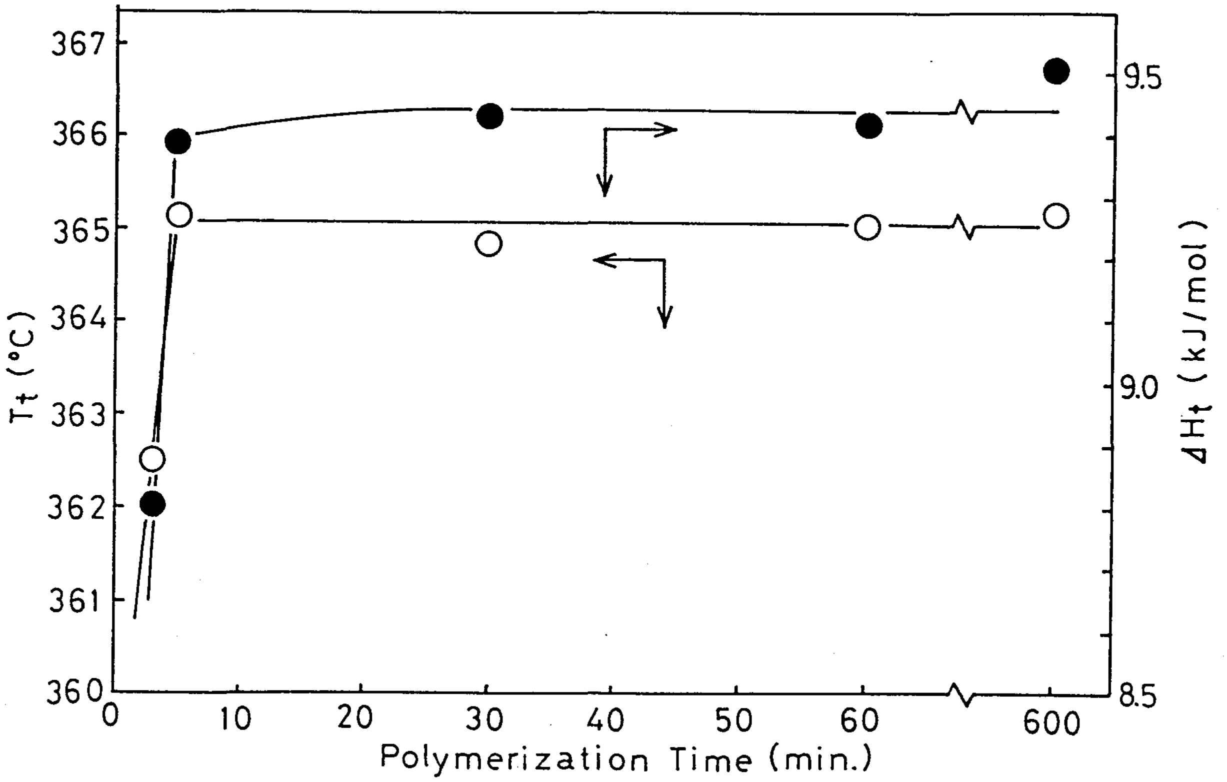


Figure 4-27. Polymerization time dependencies of transition temperature (T_t) (O) and enthalpy (ΔH_t) (●) of PMB whiskers.

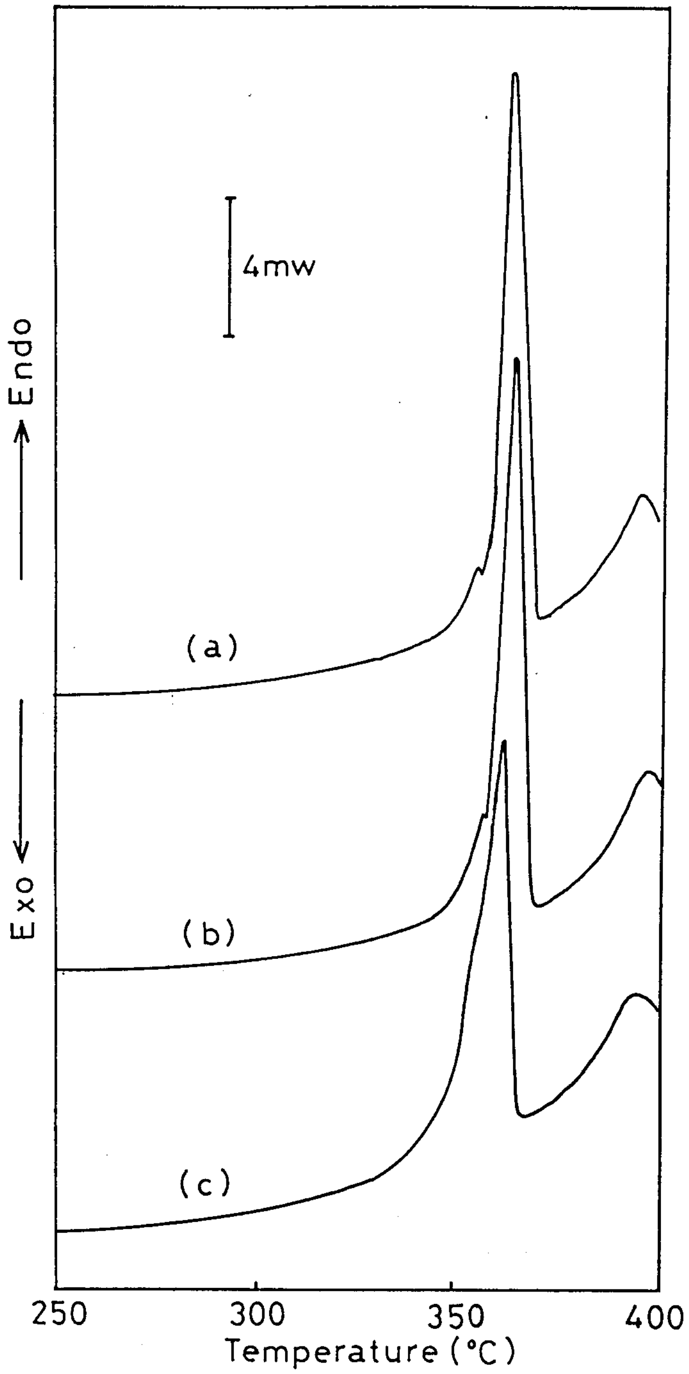


Figure 4-28. Variation of endothermic peak of PMB whiskers polymerized in LP at 300℃ for (a) 600min; (b) 5min; (c) 3min.

the crystals polymerized for 5min is as sharp as that of the crystals polymerized for 600min. The previous study about the POB whiskers reveals that the temperature and the enthalpy of the solid-solid transition are closely related to the densities of POB crystals and the crystal having higher density exhibited higher transition temperature and larger enthalpy. In other words, higher transition temperature and larger enthalpy show more densely packing manner of polymer chains in the crystal. From the similarity of the nature of the solid-solid transition between POB and PMB, the change of this transition behavior of the PMB whiskers suggests that the reorganization of the polymer chains occurs accompanying the polymerization as soon as the oligomers crystallize from the solution, and densely packed polymer crystals are formed immediately.

From these experimental results the growth of the PMB whiskers can be speculated. The oligomers of low DP are formed in a homogeneous solution, and the oligomers are crystallized in the form of needle-like crystals as soon as the DP exceeds a critical value. In detailed observation of the incipient crystals, the needle-like crystals are found to be an extended chain fibrillar crystals. At present, it can not be concluded whether the formation of such needle-like crystals are due to spiral growth like the POB whiskers.

4-5-3 Summary

The PMB whiskers are obtained from AMBA by high-temperature solution polymerization. The PMB whisker prepared in LP at 300℃ for 6h has a length of 5-8μm and a width of 0.3-0.5μm. These whiskers show radial growth from central part.

The important factors in obtaining the PMB whiskers during the polymerization are nature of solvent and polymerization temperature. LP is the only solvent to provide the PMB whiskers and the optimal polymerization temperatures are in the range of 260-300℃.

Electron diffraction experiment reveals that the PMB whiskers show a single crystal nature and the polymer chains align along the long axis of the whisker.

DSC analysis of the PMB whiskers shows the presence of the reversible solid-solid transition at around 360℃ as reported by Kricheldorf *et. al* and the solid-liquid crystal transition at around 420℃. The temperatures and the enthalpies of these transitions of the PMB whiskers are relatively higher and larger than the crystals with other morphologies and this fact suggests the closer packing of polymer chains in the whiskers.

The growth mechanism of the PMB whiskers can be speculated by the results of the polymerization time dependencies of the length, the DP and the yield. The oligomers of low DP are formed in a homogeneous solution, and the oligomers are crystallized in the form of needle-like crystals as soon as the DP exceeds a critical value. The change of the solid-solid transition behavior of the resulting whiskers with the polymerization time suggests that the polymerization of oligomers and the reorganization of polymer chains in crystals occur as soon as the oligomers crystallize from the solution, and densely packed polymer crystals are formed immediately. Further, the post-polymerization follows in the crystals and the DP increases after the crystal growth ceases.

4-6 Conclusion

Crystallization of other aromatic condensation polymers than POB during high-temperature solution polymerization are studied from the viewpoint of the control of the crystal morphology focusing on the synthesis of polymer whisker.

PON which is a homologue of POB crystallizes in the form of the whisker during the polymerization of ANA in less-polar solvents such as LP or TS 800 at a low concentration under no stirring condition. The PON whiskers in which the polymer chains align along the long axis of the whisker have a length of 7-17μm and a width of 0.5-1.0μm. The formation mechanism of the PON whisker is the same as that of the POB whisker.

POBP which is also a homologue of POB does not form the whisker but crystallize in the form of the bundle-like aggregates of fibrillar crystals during the polymerization of ABPA in TS 800 or TS 900 at a low concentration under no stirring condition. The bundle-like aggregates of fibrillar crystals are morphologically different from the whisker but they both are formed with a spiral growth of lamellae. In the case of POBP, the crystal formation occurs very slowly and hence the fibrillation of the crystal emerges by the reorganization of the polymer chains in the crystal during slow crystal formation process.

PPTE is a condensation polyester of terephthalic acid with hydroquinone. Though PPTE has a very similar molecular structure to POB, *i.e.* they comprise 1,4-phenylene groups and ester linkages, PPTE crystals obtained are sheaf-like or plate-like despite the types of condensation reaction including bimolecular-condensation reaction and self-condensation reaction. PPTE does not crystallize in the form of the whisker under identical polymerization conditions with that for the POB whisker.

PMB which is an aromatic polythioester forms the whisker by the polymerization of AMB in LP at a low concentration under no stirring condition. The PMB whiskers have a length of 5-8μm and a width of 0.3-0.5μm, and they show radial growth from central part. This PMB whisker in which the polymer chains align along the long axis of the whisker is also a chain extended single crystal.

The crystal morphologies of PON, POBP and PMB can be controlled by the conditions of crystallization during solution polymerization, and the polymer whiskers of PON and PMB are obtained. The crystallization feature of PPTE is different from others and PPTE does not form needle-like crystals but sheaf-like or plate-like crystals.

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Concluding Remarks

Wholly aromatic polymers comprising straight and rigid-rod molecular structure have been receiving much attention as potential candidates of high-performance materials because they are expected to possess good mechanical properties, thermal stability and chemical resistance as well as many other desirable properties.

Generally, these stiff polymers are not amenable to the conventional processing techniques because of their infusibility, *i.e.* they show no melting temperatures under thermal decomposition and they show very low solubilities in common solvents, and it has been therefore hard to use them as industrial materials as they are. In order to improve such infusibility, chemical modifications of their structures or special processing techniques are necessary. However, the modifications result in the loss of the excellent properties.

With these in view, the present study has been undertaken. This thesis is concerned with the crystallization of infusible aromatic condensation polymers during solution polymerization for the purpose of the control of crystal morphology and ultimately the synthesis of polymer whiskers. In other words, this thesis propose a new processing method of infusible polymers into some crystal form by crystallization during solution polymerization of monomers.

Chapter 1 deals with the morphology control of poly(p-oxybenzoyl) (POB) crystal by high-temperature solution polymerization of p-acetoxybenzoic acid (p-ABA) and the synthesis of the POB whisker. The relationship between the conditions of crystallization during solution polymerization and the crystal morphologies has been investigated. It is concluded that the important factors in controlling the crystal morphology of POB are polarity of solvents, concentration of monomer and stirring. Less-polar solvents such as liquid paraffin or Therm S 800, low concentration of monomer and no stirring are desirable for making whiskers. These conditions give the whiskers of which the length is 30-70μm and the width is 1-2μm. These whiskers are single crystals and the polymer chains align along the long axis of the whisker.

It is found that the POB whisker is formed with a spiral growth of lamellae and subsequent post-polymerization in the interlamellae region.

The POB whisker is the first polymer whisker obtained by condensation reaction and the synthetic method of the whisker provides a new concept for morphological processing of infusible polymers.

Chapter 2 is concerned with the control method of the size of the POB whisker. The size of the POB whisker is controlled by the chemical structure of paraffin of the polymerization solvent. Both the length and the width of the whisker decrease with increasing linear paraffin content in the solvent. The dependence of the size of the whisker on the chemical structure of paraffin is explained on the basis of the solubility of oligomers in the solvent. The degree of supersaturation of oligomers becomes higher with increasing the content of linear paraffin in the solvent due to the lower solubility of oligomers and then many more primary nuclei for whisker growth with smaller diameter are formed from sufficiently highly supersaturated state of oligomers.

It is therefore concluded that the size of the whisker such as the length and the width is determined by the number and the diameter of the primary nuclei for whisker growth which are controllable by the nature of the solvents.

In chapter 3, crystallization of copolymers of POB with m-hydroxybenzoic acid during solution polymerization is described. The whiskers are formed in the solution copolymerization system of p-ABA and m-acetoxybenzoic acid (m-ABA) in liquid paraffin when the content of m-ABA in the feed (χ_f) is in the range of 0-30mol%. Actual contents of m-oxybenzoyl units in the obtained crystals are much lower than χ_f.

It is therefore concluded that the co-oligomers containing only a few m-oxybenzoyl units form the whiskers and co-oligomers containing much m-oxybenzoyl units are excluded by the fractional crystallization.

This fractional crystallization behavior during solution polymerization suggests a new method of polymerization with molecular recognition.

Chapter 4 is concerned with the crystallization of other aromatic condensation polymers than POB including poly(2-oxy-6-naphthoyl) (PON), poly(4'-oxy-4-biphenylcarbonyl) (POBP), poly(p-phenylene terephthalate) (PPTE) and poly(4-mercaptebenzoyl) (PMB). PON and PMB form the whiskers during high-temperature solution polymerization. POBP forms the bundle-like aggregates of fibrillar crystals. Although the crystal morphology of POBP is different from the whisker, the formation mechanism of the bundle-like aggregates of fibrillar crystals is similar to that of the whisker. The crystallization feature of PPTE is quite different from others and PPTE does not crystallize in the form of the whisker but sheaf-like or plate-like crystals.

It is shown that the crystallization during solution polymerization is new methodology of processing for the infusible polymers and polymer whiskers are obtainable by using this method.

List of Publications

1. Preparation of Poly(p-oxybenzoyl) Whiskers
   Y.Kato, S.Endo, K.Kimura, Y.Yamashita, H.Tsugita and K.Monobe,
   Koubunshi Ronbunshu, 44(1), 35 (1987)

2. Formation Mechanism of Poly(p-oxybenzoyl) Whiskers
   Y.Yamashita, Y.Kato, S.Endo, K.Kimura, H.Tsugita and K.Monobe,
   Koubunshi Ronbunshu, 44(1), 41 (1987)

3. Preparation and Formation Mechanism of Poly(oxycarbonyl-1,4-phenylene) Whiskers from 4-Acetoxybenzoic acid
   Y.Yamashita, Y.Kato, S.Endo and K.Kimura,
   Makromol. Chem., Rapid Commun., 9, 687 (1988)

4. Shape Change of Poly(p-oxybenzoyl) Whiskers formed during the Solution Polymerization
   Y.Kato, Y.Yamashita, K.Kimura, S.Endo and K.Kajisaki,
   Koubunshi Ronbunshu, 45(12), 973 (1988)

5. Molecular Weight Change during Poly(p-oxybenzoyl) Whiskers Formation
   Y.Kato, Y.Yamashita, K.Kimura, S.Endo and T.Ohta,
   Koubunshi Ronbunshu, 47(7), 583 (1990)

6. Synthesis and Characterization of Poly(oxy-2,6-naphthalenediylcarbonyl) Whiskers from 2-Acetoxy-6-naphthoic acid
   K.Kimura, S.Endo, Y.Kato and Y.Yamashita,
   Polymer, 34(5), 1054 (1993)

7. Solvent Effect on the Morphology of Poly(oxy-1,4-benzenediylcarbonyl) Whiskers from p-Acetoxybenzoic acid
   K.Kimura, S.Endo, Y.Kato and Y.Yamashita,
   Polymer, 35(1), 123 (1994)

8. Synthesis and Characterization of Poly(p-phenylene terephthalate) Crystals obtained by Crystallization during Polymerization
   K.Kimura, S.Endo, Y.Kato and Y.Yamashita,
   High Performance Polymers, 6(1), 83 (1994)

9. Synthesis and Characterization of Poly(4-mercaptobenzoyl) Whiskers from S-Acetyl-4-mercaptobenzoic acid
   K.Kimura and Y.Yamashita,
   Polymer, 35(15), 3311 (1994)

10. Formation Mechanism of Poly(4'-oxy-4-biphenylcarbonyl) Crystals obtained by Solution Polymerization
    K.Kimura, S.Endo, Y.Kato, T.Inaba and Y.Yamashita,
    Macromolecules, in press

11. Copolymerization Effect of m-Acetoxybenzoic acid on
Morphology of Poly(oxy-1,4-benzenediylcarbonyl) Whiskers
K.Kimura and Y.Yamashita,
submitted to *J. Polym. Sci., Polym. Chem.*

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