

Influence of Solvent on Size of Poly(*p*-oxybenzoyl) Whiskers Prepared from *p*-Acetoxybenzoic Acid

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ABSTRACT: Poly(*p*-oxybenzoyl) (POB) crystals are prepared by the polymerization of *p*-acetoxybenzoic acid (*p*-ABA) at 320°C in various solvents to clarify the influence of miscibility between oligomer and solvent on the morphology as well as the size of the crystal. Concerning the morphology, whiskers are formed in less miscible solvents such as liquid paraffin and Barrel process oil B27. On the other hand, bundle-like aggregates of fibrillar crystals tend to be formed in the solvents having higher miscibility such as Therm S 900 and 800, which are aromatic heat exchange media. Further, the solvents having higher temperature at which *p*-ABA is completely dissolved during polymerization (T_s) yield a larger number of the whiskers with smaller width. The higher supersaturation of oligomers in less mis-

cible solvents causes the formation of a larger number of nuclei with smaller size. Bundle-like aggregates are formed in the solvents whose T_s is lower than 140°C by the fibrillation of pillar-like crystals during polymerization owing to the reorganization. This shows a clear relationship between the width and T_s , and between the number of the crystals and T_s . Hence, the size of the whisker such as the length and the width can be predicted by the calculation with T_s , which is very valuable for the preparation of POB whiskers for use as industrial materials. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1129–1136, 2003

Key words: poly(*p*-oxybenzoyl); whisker; miscibility; nucleation; crystallization; oligomers

INTRODUCTION

Poly(*p*-oxybenzoyl) (POB) is a wholly aromatic polyester characterized by its unique combination of thermal and mechanical properties, and by a remarkable chemical resistance. However, POB is a quite intractable material and it exhibits neither meltability nor solubility. This intractability brings about severe problems in industrial usage. Therefore, many attempts have been conducted with the aim of improving the poor processability from the point of both chemical modifications (for instance, Refs. 1–3)^{4–9} and processing techniques.¹⁰ Chemical modification, which had created many thermotropic polyesters, sacrifices the eventual properties predicted from the structure of POB. We have succeeded in obtaining the POB whisker by reaction-induced crystallization of oligomers during solution polymerization.^{11–15} This whisker exhibits an extended-chain single crystal in nature, and polymer chains are oriented along the long axis of the whisker. This morphological feature and the polymer chain alignment are ideal for withdrawing the essential properties of POB. POB whiskers are prepared from *p*-acetoxybenzoic acid (*p*-ABA) in poor solvent such as liquid paraffin (LPP) with the elimination of

acetic acid at high temperature solution polymerization. From morphological observation, it has been proposed that the formation mechanism of these whiskers bears the following steps: (1) The resulting oligomers are crystallized in the form of lamellae from solution polymerization as well as lamellae stacked up to the long axis of the whisker with spiral growth caused by screw dislocation. (2) The eventual whiskers are accomplished with the increase of degree of polymerization by postpolymerization in the interlamellar regions, and reorganization of crystals occurs. This preparation technique is stipulated as a very useful method for morphology control of intractable aromatic polyesters, and many other aromatic whiskers have been reported.^{16–27}

In our previous studies, the morphology of the POB crystal is changed drastically by miscibility between oligomer and solvent, and the miscibility is of great importance for the control of the morphology.^{12,17} However, the influence of solvent on the morphology and the size of POB crystals still remains unclear. The aim of this study is to clarify the influence of solvent on the morphology as well as the size of the POB whisker.

EXPERIMENTAL

Materials

p-ABA was purchased from Tokyo Kasei Co. Ltd. and purified by recrystallization from ethyl acetate. LPP

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was purchased from Nakalai Tesque Co. Ltd. and purified by vacuum distillation (220°C ~ 240°C/0.2 mm Hg). Therm S 800 (TS8) and Therm S 900 (TS9) were purchased from Nippon Steel Chemical Co. Ltd. TS8 was purified by vacuum distillation (140°C ~ 160°C/0.5 mm Hg) and TS9 was also done (150°C ~ 170°C 0.7 mm Hg). Barrel process oil B27 (B27) was purchased from Matsumura Oil Co. Ltd. and used as received.

Polymerization method

The amount of 0.3 g of *p*-ABA and 20 mL of solvent were placed into a cylindrical polymerization reactor equipped with a thermometer and gas inlet tube. This reaction mixture was heated with stirring. When *p*-ABA was completely dissolved, the stirring was stopped. Then the mixture was heated up to 320°C and maintained at this temperature for 5 h under a slow stream of nitrogen. The whiskers were collected by filtration at 320°C, washed several times with *n*-hexane or toluene, and then dried in a vacuum oven at 50°C overnight.

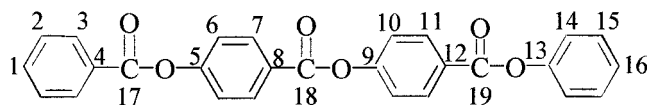
Synthesis of oligomer model compound

Phenyl[4-(4-benzoyloxy)benzoyloxy]benzoate

Ten grams of *p*-hydroxybenzoic acid (0.0724 mol), 16.12 g of triethylamine (0.159 mol), and 60 mL of distilled tetrahydrofuran were taken into a flask equipped with a thermometer, a dropping funnel, and gas inlet and outlet tubes under a slow stream of nitrogen. The amount of 10.17 g of benzoyl chloride (0.0724 mol) in 10 mL of distilled tetrahydrofuran was added dropwise through a dropping funnel in to the reaction mixture at 5°C for 30 min. The reaction was performed at 5°C for 2 h with continuous stirring and then 12 h at room temperature. Hydrochloride–triethylamine salt was filtrated and tetrahydrofuran was evaporated. The product was washed with dilute hydrochloric acid and water. The amount of 1.8 g of 4-benzoyloxybenzoic acid was obtained after recrystallization from the mixture of ethyl acetate and *n*-hexane. Then 4-benzoyloxybenzoyl chloride was synthesized from 4-(oxybenzoyl)benzoic acid with thionyl chloride and reacted with 4-hydroxybenzoic acid phenyl ester by a procedure similar to that described above. The amount of 1.24 g (yield 60.5%) of phenyl[4-(4-benzoyloxy)benzoyloxy]benzoate was obtained after recrystallization from ethyl acetate. Melting point was 173°C.

ELEMENTAL ANALYSIS: Calcd for C₂₇H₁₈O₆: C, 73.97%; H, 4.14%. Found: C, 73.93%; H, 4.12%, IR (KBr; cm⁻¹): 2960, 2925, 2850, 1743, 1598, 1509, 1274, 1207, 1162, 1061, 1018, 887, 802, 758, 700. ¹H-NMR (500 MHz, CDCl₃/CF₃COOH) δ

= 7.73 (H-1, tr, 1H), 7.58 (H-2, tr, 2H), 8.25 (H-3, d, 2H), 7.42 (H-6, d, 2H) or 7.44 (H-6, d, 2H), 8.35 (H-7, d, 2H) or 8.34 (H-7, d, 2H), 7.44 (H-10, d, 2H) or 7.42 (H-10, d, 2H), 8.34 (H-11, d, 2H) or 8.35 (H-11, d, 2H), 7.22 (H-14, d, 2H), 7.47 (H-15, tr, 2H), 7.34 ppm (H-16, tr, 1H). ¹³C-NMR (125 MHz, CDCl₃/CF₃COOH) δ = 134.8 (C-1), 129.0 (C-2), 130.5 (C-3), 128.2 (C-4), 155.5 or 155.3 (C-5), 122.4 or 122.3 (C-6), 132.4 (C-7), 126.9 or 126.4 (C-8), 155.3 or 155.5 (C-9), 122.3 or 122.4 (C-10), 132.4 (C-11), 126.4 or 126.9 (C-12), 150.4 (C-13), 121.5 (C-14), 129.8 (C-15), 126.7 (C-16), 165.4 (C-17), 166.8 or 166.6 (C-18), 166.6 or 166.8 ppm (C-19).



Measurements

Morphological observation was performed by scanning electron microscopy (SEM) using Hitachi S-2150. ¹H- and ¹³C-NMR spectra were measured on Bruker AVANCE 500.

Oligomers dissolved in solution were analyzed by high performance liquid chromatography (HPLC) using Waters 490E HPLC system with Nova Pack HR C18 column. The gradient elution method was used with the mixed solvent of acetic acid and acetonitrile, of which the mixing ratio of two solvents was changed from 90/10 to 0/100 by volume for 40 min.

The shape parameters including the length, width, and tip angle were determined by taking the average of over 60 observation values. The number of the crystal (*N*) was calculated according to the following equation:

$$N = \frac{Y}{(\sqrt{3}/8)W^2(L + 2l)\rho} \quad (1)$$

where *Y* is the yield, *W* the width of the crystal, *L* the average length, *l* the average trunk length,¹⁷ and *ρ* the density of the crystal (1.52 g cm⁻³).

Preparation of Concentration–temperature (*C-T*) phase diagram of oligomer model compounds

The oligomer model compound and solvent were put into glass tubes at different concentrations. They were placed into an oil bath and heated until the oligomer model compound was completely dissolved. Then temperature was lowered gradually at a rate of 5°C h⁻¹ and the cloud point temperature was determined. The phases and conjugate line between liquid and solid were confirmed by a microscope equipped with heating stage (MP-500D, Yanaco Co. Ltd.) under crossed polarization.

TABLE I
Results of Polymerization

Solvent ^a	T_s^b (°C)	t_t^c (min)	Yield (%)	Morphology of Crystal
LPF	177	8	27.5	Needle-like
B27	165	8	31.0	Needle-like
TS9	135	26	45.0	Bundle-like ^d
TS8	128	30	42.0	Bundle-like

^a LPF: liquid paraffin; B27: alkylbenzene; TS9: hydrogenated terphenyl; TS8: triethylbiphenyl.

^b Temperature at which *p*-ABA was completely dissolved.

^c Time when the solution became turbid.

^d Bundle-like aggregates of fibrillar crystals.

RESULTS AND DISCUSSION

Morphological characteristics of POB whiskers

In order to further clarify the influence of solvent on the morphology, polymerization was carried out at 320°C in several solvents. Polymerization concentration was 1.0% based on polymer weight.

B27, TS8, and TS9 are aromatic heat exchange media. B27 is a mixture of alkylbenzene. TS8 and TS9 are a mixture of triethylbiphenyl and hydrogenated terphenyl, respectively. The polymerization results are summarized in Table I and the morphology is shown in Figure 1. POB crystals are formed in all solvents. Whiskers are obtained in LPF and B27. The length and

the width of the whiskers prepared in LPF are 10 and 0.4 μm , respectively. Concerning the whisker prepared in B27, the length is 8.0 μm and the width is 0.81 μm . The whiskers having shorter length and wider width are formed in B27 compared with those in LPF. On the other hand, bundle-like aggregates of fibrillar crystals are formed in TS9 and TS8, in which the fibrillar crystal is ca. 0.3 μm in width. The width of the center part in the bundle-like aggregates is ca. 1.5 μm . The detail observation of these bundle-like crystals shows that the fibrillar crystals are tied up at the center part into the bundle. This morphological feature suggests that the bundle-like aggregates of fibrillar crystals seem to be formed by the fibrillation of pillar-like crystals during polymerization. Further, the tips of the whisker prepared in B27 are about to be fibrillated. Fibrillation of the crystal tends to occur in aromatic solvent rather than aliphatic solvent. The morphological feature described above is undoubtedly brought about by the solvent, in other words, miscibility between oligomer and solvent. The temperature at which *p*-ABA is completely dissolved (T_s) during polymerization and the time when the solution becomes turbid (t_t) are adaptable as criterion to estimate the miscibility between oligomer and solvent. Lower T_s and later t_t suggest higher miscibility. Concerning T_s , it becomes lower in order of LPF, B27, TS9, and TS8. The t_t also becomes longer in the same order

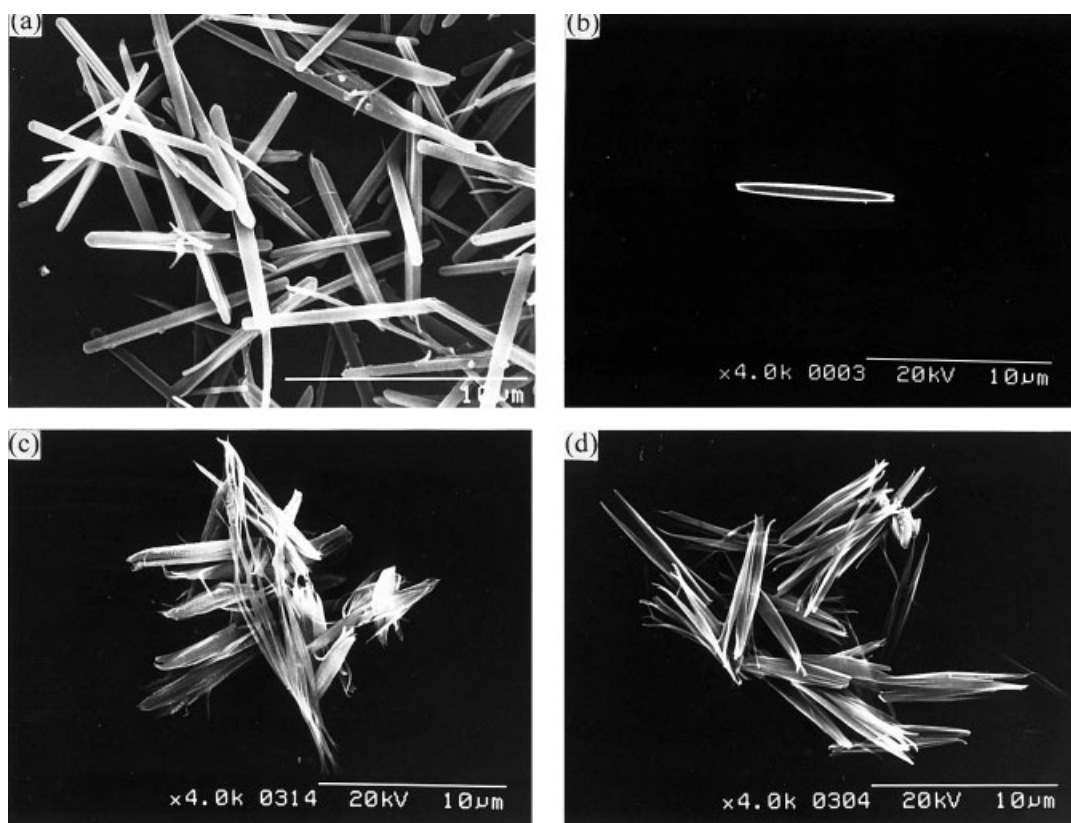


Figure 1 POB crystals prepared at 320°C for 5 h in (a) LPF, (b) B27, (c) TS9, and (d) TS8.

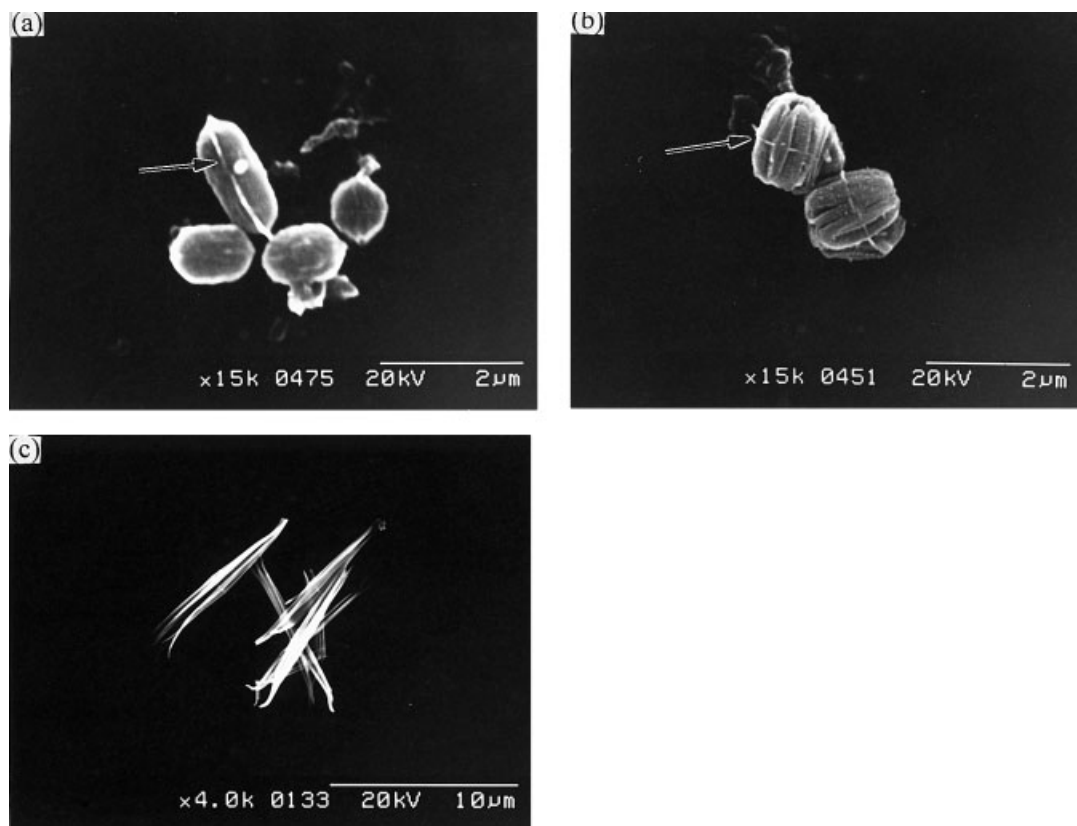


Figure 2 POB crystals prepared in TS8 for (a) 8 min, (b) 15 min, and (c) 180 min.

as T_g . From these results, the miscibility between oligomer and solvent is supposed to enhance in order of LPF, B27, TS9, and TS8, which is reasonably understood by the chemical structure of the solvent and POB. Hence, there is a tendency that the whisker is preferentially formed in less miscible solvents and the bundle-like aggregate of fibrillar crystals is formed in more miscible solvents.

The yields of the crystals are not quantitative and increase in order of miscibility. The oligomers did not remain after 5 h and the low yield is due to the sublimation of *p*-ABA during polymerization, especially in the initial stage of polymerization. *p*-ABA sublimates easier in poorer solvent and the yield in LPF is the lowest.

Formation mechanism of Bundle-like aggregate of fibrillar crystals

Bundle-like aggregates of the fibrillar crystals were obtained in TS9 and TS9. In order to know the formation mechanism of the bundle-like aggregates of fibrillar crystals, the change in the morphology was observed with various times. The crystals prepared in TS8 for various times are shown in Figure 2. The slab-like crystals are formed at 8 min after the crystallization begins, the width of which is $1.5\ \mu\text{m}$ and the thickness is $0.8\ \mu\text{m}$. The trace of the lamella nucleus is

clearly observed in the center of the slab-like crystal (arrow in Fig. 2) and the shape of the crystal is very symmetrical with regard to this trace. This morphological feature indicates that these crystals are formed via spiral growth caused by screw dislocation as well as the formation mechanism of POB whisker. This morphology of the incipient crystal is very similar to that of POB whiskers prepared in LPF as shown in Figure 3. The polymer chains are aligned perpendic-

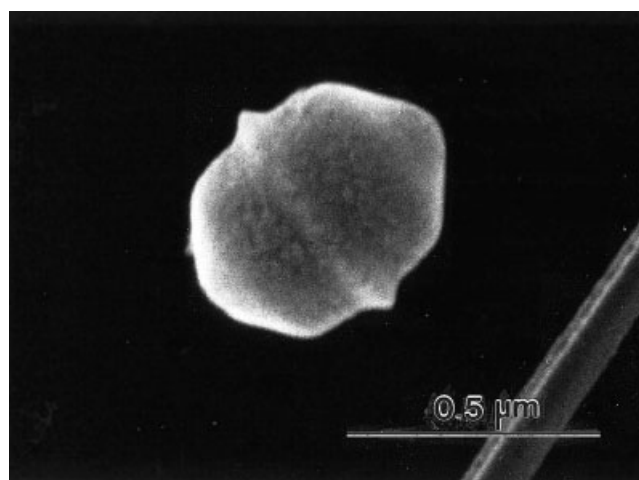


Figure 3 POB whisker prepared in LPF for 2 min.

TABLE II
Width and Number of Crystal Prepared
in Various Solvents

Solvent ^a	Width (μm)	Number of Crystals in 20 mL × 10 ⁻⁹
LPF	0.45	16.9
B27	0.81	13.4
TS9	1.51	3.0
TS8	1.66	1.4

^a Solvent codes are shown in Table I.

ular to the trace of nuclei. The crystals are growing with polymerization and the thickness increases to 1.5 μm after 15 min. The width is not changed so much. The crystals formed after 15 min also possess the trace of nuclei at the center part. It is of great interest that the many lines are observed along the direction of crystal growth, which is perpendicular to the trace of nuclei. This is surely the beginning of fibrillation. The width of the fibril is ca. 0.3 μm, which corresponds to that appearing in the crystal prepared for 5 h. After 3 h, bundle-like aggregates of fibrillar crystals are completed by the growth of each fibril with fibrillation. When the growth rate of the crystal is very low in aromatic solvent, fibrillation often occurs with reorganizing the crystals, as previously reported.¹⁹ It is concluded that bundle-like aggregates of fibrillar crystals are formed by the fibrillation of pillar-like crystals which grow according to a similar mechanism as the whiskers.

Influence of miscibility on size of POB crystal

As discussed, the width of the crystal is quite different with each solvent in spite of the similar formation mechanism. The width increases in order of LPF, B27, TS9, and TS8, which is in good agreement with the order of miscibility. From the formation mechanism of whiskers, this fact can be understood with the spiral growth caused by screw dislocation occurring on the incipient lamellar crystals. The lamellar crystals formed in less miscible solvents become smaller size owing to the higher nucleation rate. If the screw dislocation occurs in the incipient lamellar crystals, the crystals preferentially grow to the long axis of whiskers and the width of the crystals ideally keeps constant because the surface energy for crystallization at the step of spiral growth is more advantageous than that at the lateral side.²⁸ The number of the crystals is calculated according to eq. (1). The results are summarized in Table II. The solvent having lower miscibility yields a larger number of the crystals with smaller width.

It is well known that critical radius of nucleus (r^*) and nucleation rate (J) depend on the degree of supersaturation as shown in the following equations^{29,30}:

$$\Delta\mu = kT \ln(1 + \sigma) \quad \sigma = (C - C_e)/C_e \quad (2)$$

$$r^* = 2\nu\gamma/\Delta\mu \quad (3)$$

$$J = \nu_+ q \exp(-\Delta G^*/kT) \\ = \nu_+ q \exp(-16\pi\gamma^3\nu^2/3\Delta\mu^2kT) \quad (4)$$

where μ is the chemical potential, C the concentration of solute, C_e the equilibrium concentration, r^* the critical radius of nucleus, ν the volume of molecule, γ the density of surface energy, J the nucleation rate, ν_+ the rate of crystallization of one molecule into critical nucleus, and q the density of free molecule. When the degree of supersaturation increases, $\Delta\mu$, which is a driving force for nucleation, becomes larger. This large $\Delta\mu$ leads to small r^* and large J , which means that many more nuclei having smaller radius are formed. There seems to exist several parameters to influence the degree of supersaturation in of this study such as miscibility between oligomer and solvent, formation rate of oligomer, concentration, and temperature. Polymerizations were carried out at the same concentration and temperature, and thereby former two parameters are more dominant.

Miscibility between oligomer and solvent was discussed on the basis of T_s and t_i . Comparison of C - T phase diagrams of oligomer and the solvents gives very useful information about the miscibility in order to confirm the above discussion. However, the phase-separated oligomers are insoluble in common organic solvents under the temperature at which the polymerization starts, and the phase-separated oligomers cannot be isolated. Therefore, the phase diagram of oligomer cannot be accurately determined. In this study, the miscibility between oligomer and solvents is discussed by a clue of the miscibility of oligomer model compound and solvent. Phenyl[4-(4-benzoyloxy)benzoyloxy]benzoate was synthesized as the oligomer model compound, which was end-capped by the phenyl group to avoid an influence of polymerization during preparation of phase diagrams. C - T phase diagrams prepared by cloud point measurements are shown in Figure 4. Reaction-induced phase separation of oligomers in poor solvent is describable in the analogous C - T phase diagram to that of the partially miscible polymer-solvent system.^{31,32} The phase separation curve in the repulsive system in which there is no attractive interaction between oligomer and solvent is written as the combination of the freezing point curve of oligomers and the UCST(upper critical solution temperature)-type consolute curve. In the diagram of the oligomer model compound and LPF, the phase separation curve appears as the combination of the freezing point curve of the model compound and the UCST-type consolute curve as described above. On the other hand, the consolute curve does not appear

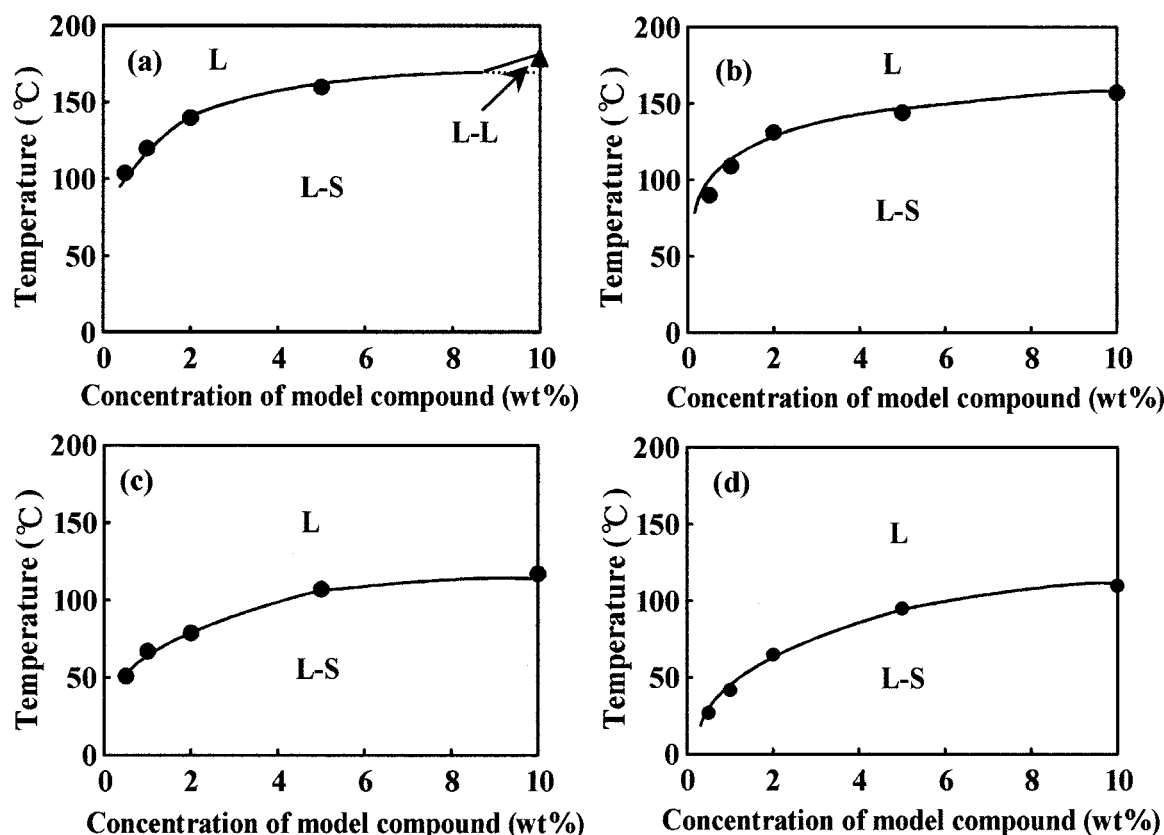


Figure 4 C-T phase diagrams of oligomer model compound and (a) LPF, (b) B27, (c) TS9, and (d) TS8 prepared by the cloud point measurements. L: miscible liquid phase; L-L: immiscible two liquids phase; L-S: liquid-solid phase.

under 10 wt % and the freezing point curves shift toward lower temperature in the diagrams of other solvents compared with that in LPF. The shift toward lower temperature becomes larger in order of B27, TS9, and TS8. The miscible liquid region is most largely expanded in TS8. Lower miscibility leads to the lower C_e in eq. (2), which results in the smaller r^* and higher J due to the higher $\Delta\mu$ in eqs. (3) and (4). This result confirms the above discussion.

The reaction rate of *p*-ABA was examined in various solvents next. Polymerization kinetics is followed by the titration of by-produced acetic acid with sodium hydroxide solution. The reaction obeys the secondary order kinetics in all solvents prior to the beginning of crystallization. The rate constants are presented in Table III. The polymerization rate constant k_2 is the biggest in LPF and it becomes smaller as the miscibility enhances. *p*-ABA polymerizes four times faster in LPF than TS8. The oligomers collected from the solution just when the crystallization began were analyzed by HPLC. The oligomers collected from LPF and B27 contain from *p*-ABA to heptamer, and thereby the oligomers more than octamer are crystallized in these solvents. On the other hand, those collected from TS9 and TS8 contain from *p*-ABA to octamer and the oligomers more than nonamer are crystallized in these

solvents. It can be thought on the basis of these results that the degree of supersaturation of oligomer in LPF is the highest among the solvents, and this results in the formation of the largest number of nucleus with the smallest size in LPF. The smaller number of nuclei having larger width are generated in the solvents having higher miscibility.

It is found that the width of the crystal is related to the miscibility of the solvent. When the whisker is used as an industrial material such as for reinforcement, control of the size and aspect ratio, which de-

TABLE III
Rate Constant and Critical Degree of Polymerization (CDPn) of Phase-Separated Oligomer in Various Solvents

Solvent ^a	Rate Constant k_2^b (L mol ⁻¹ min ⁻¹)	Critical DPn of Phase-Separated Oligomer ^c
LPF	0.63	8
B27	0.36	8
TS9	0.20	9
TS8	0.16	9

^a Solvent codes are shown in Table I.

^b Determined by titration of by-produced acetic acid with NaOH.

^c Determined by HPLC.

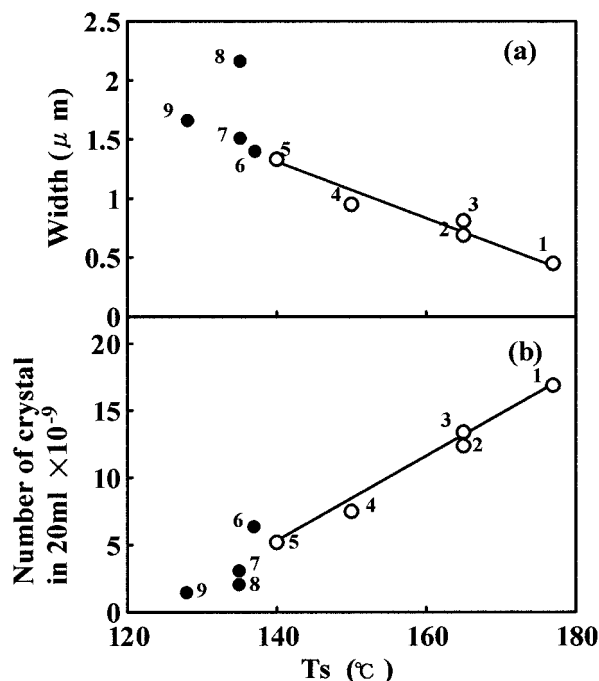


Figure 5 Relationship between T_s and (a) width and (b) number of crystal prepared in various solvents. 1: LPF; 2: B27/LPF; 3: B27; 4: TS9/LPF; 5: TS9/B27; 6: TS8/LPF; 7: TS9; 8: TS8; and 9: TS8/TS9. Mixing ratio of two solvents is 50/50 by volume. ○: Needle-like crystal; ●: bundle-like aggregate of fibrillar crystal.

termine the performance, is very important. The relationship between the width of the crystal and the miscibility can be taken advantage of in the control of the size. In order to quantitatively understand the relationship, POB crystals were prepared in the various solvents obtained by mixing two different solvents having different miscibilities with the ratio of 50/50 by volume. The width and the number of the crystals are mutually correlated with T_s , as shown in Figure 5. The whisker can be prepared in over a T_s of 140°C, and under that temperature a bundle-like aggregate is formed. Concerning the whisker, its width is linearly related to T_s , as shown in Figure 5, and it can be described as a function of T_s . The number of whiskers also has good linear relationship with T_s . From these results, the size of the POB whiskers prepared at 320°C and 1.0% concentration can be empirically calculated by T_s according to eqs. (5) and (6), and it is very valuable to produce them as industrial materials.

$$W = -2.20 \times 10^{-3}T_s + 9.82 \times 10^{-1} \quad (5)$$

Length of whisker ($L + 2l$)

$$= \frac{Y}{(\sqrt{3/8})W^2\rho(3.20 \times 10^{-1}T_s - 3.97 \times 10^3)} \quad (6)$$

CONCLUSION

POB crystals are prepared in various solvents to clarify the influence of miscibility between oligomer and solvent on the morphology as well as the size of the crystal. Concerning the morphology, whiskers are formed in less miscible solvents such as LPF and B27. Bundle-like aggregates of fibrillar crystals tend to be formed in more miscible solvents such as TS9 and TS8. Further, the size, especially the width, of these crystals is highly related to T_s , which is a criterion for evaluation of miscibility, that is, the solvents having higher T_s yield a larger number of whiskers with smaller width. Whiskers can be prepared in the solvents whose T_s is higher than 140°C. This tendency can be explained by the supersaturation of oligomers during the nucleation process. The supersaturation of oligomers becomes higher in a less miscible solvent due to both its lower miscibility and higher polymerization rate. This higher supersaturation of oligomers causes the formation of larger number of nuclei with smaller size. Bundle-like aggregates are formed by the fibrillation of pillar-like crystals during polymerization owing to the reorganization. This indicates a clear relation between the width and T_s and between the number of crystals and T_s . Hence, the size of the whisker such as the length and the width can be empirically predicted by the calculation with T_s , which is very valuable for the preparation of POB whiskers for use as industrial materials.

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