Self-Assembling Polycondensation for Preparation of Poly(*p*-oxybenzoyl-*alt*-*p*-mercaptobenzoyl) Whisker

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ABSTRACT: Self-assembling polycondensation was examined to prepare the whisker of poly(*p*-oxybenzoyl-*alt*-*p*-mercaptobenzoyl). Polymerizations were carried out in liquid paraffin (LPF) and aromatic solvents such as Therm S 800 and 1000 at 300 °C for 6 h. Polymerization concentration was 1.0 wt/vol %. The whisker was not obtained by the random copolymerization of *p*-acetoxybenzoic acid and *S*-acetyl-4-mercaptobenzoic acid at the molar ratio of 0.5 in feed. However, the whiskers were successfully prepared by the polymerization of *S*-(4-acetoxybenzoyl)-4-mercaptobenzoic acid (OS) and 4-(*S*-acetyl-4-mercaptobenzoyl)oxybenzoic acid (SO). The whisker prepared from OS (POS) in LPF was 18 μm in average length and 0.4 μm in average width, and that from SO (PSO) was slightly longer than POS. The whiskers prepared in aromatic solvents were much longer than those in LPF, for which the length was 36−49 μm. These whiskers consist of the alternating polymer chains, and the polymer chains align along the long axis of the whisker. The sequence regularity enhanced the crystallizability of the oligomers, and this led to the formation of whiskers. The oligomer formation rate was much higher than that of transesterfication reaction rate, and this large difference in these two rates made the oligomer precipitate with maintaining the alternating sequence. Further polymerization occurred in the crystals, and the whiskers having the alternating sequence were finally completed. The difference in the two rates increased with the decrease of the miscibility between the oligomer and the solvent, and therefore, OS and LPF were more advantageous to maintain the alternating sequence.

Introduction

Wholly aromatic polymers have been receiving much attention as candidates for high performance polymeric materials. They have excellent properties due to their rigid structures, such as thermal stability, mechanical properties, chemical resistance, and so on. However, they exhibit neither solubility or meltability, and the intractability makes them inaccessible for processing by conventional techniques. Several approaches have been attempted to improve the trade off relationship between their properties and intractability from the aspect of not only the chemical modification of polymer structures[1] but also the processing techniques.[2]

We have been studying on the morphology control of rigid polymers during solution polymerization, and succeeded in the synthesis of whiskers of poly(*p*-oxybenzoyl) (POB), poly(*p*-mercaptobenzoyl) (PMB), and other aromatic polyesters by polymerization in liquid paraffin (LPF).[3−8] These whiskers are formed by the reaction-induced crystallization of oligomers during solution polymerization. The polymer chains are aligned along the long axis of the whiskers, and they show single crystal nature. The formation mechanism of these whiskers contains the following three steps: (1) When the degree of polymerization of the oligomers exceeds a critical value, they are precipitated from the solution to form lamellae. (2) The lamellae pile up in the form of needlelike crystals with spiral growth. (3) Postpolymerization occurs topochemically in the needlelike crystals, and the whiskers consisting of high molecular weight extended polymer chains are eventually formed.[4] Aromatic polyester whiskers have been also prepared by other groups,[9−11] and other aromatic polymer whiskers besides polyesters such as poly(ester−imide)[12] and poly(azomethine)[13] have been synthesized so far. It has been recognized that the self-assembling polycondensation by means of the reaction-induced crystallization of oligomers is a valuable method for the morphology control of intractable polymers.

The preparation of the copolymer whisker is of great importance to tailor the novel functional polymeric materials. Recently, we have been studying the morphology of copolymers prepared by the polymerization of *p*-acetoxybenzoic acid (ABA) and *S*-acetyl-4-mercaptobenzoic acid (AMBA).[14] The crystal habit disappeared with copolymerization due to the lack of the crystallizability of oligomers. This article describes our new finding on the self-assembling polymerization to prepare poly(*p*-oxybenzoyl-*alt*-*p*-mercaptobenzoyl) (POB-*alt*-PMB) whiskers and the influence of the sequence regularity on the morphology as shown in Scheme 1.

Experimental Section

Materials. ABA was purchased from TCI Co. Ltd. and recrystallized from ethyl acetate. AMBA was prepared according to the previous papers.[14−18] LPF was purchased from Nacalai Tesque Co. Ltd. Therm S 800 (TS8), a mixture of isomers of triethylbiphenyl, and Therm S 1000 (TS10), a mixture of isomers of dibenzylbenzene, were obtained from Nippon Steel Chemical Co. Ltd. LPF, TS8, and TS10 were purified by vacuum distillation.

Monomer Synthesis. *S*-(4-Acetoxybenzoyl)-4-mercaptobenzoic Acid (OS). Into a three-necked flask equipped with a dropping funnel, a thermometer, and a gas inlet tube were

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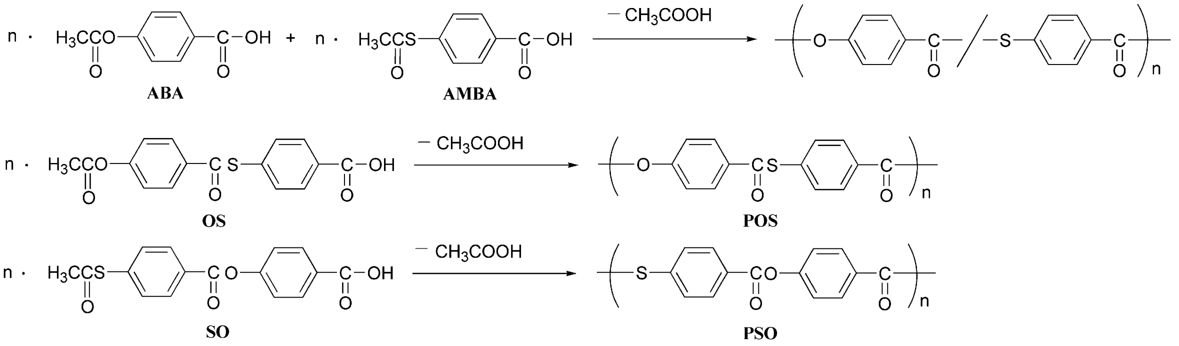
Scheme 1. Polymerization Systems



placed 1.79 g of 4-mercaptobenzoic acid (12.5 mmol), 2.49 g of *p*-acetoxybenzoyl chloride (12.5 mmol) synthesized from ABA and thionyl chloride, and 40 mL of dried tetrahydrofuran. The solution of 1.42 g of triethylamine (15.0 mmol) was added dropwise through the dropping funnel under the slow stream of nitrogen at 5 °C. The reaction temperature was kept at 5 °C for 2 h and then 25 °C for 12 h. The reaction mixture was filtrated to separate the triethylamine−HCl salts, and acidified by diluted HCl solution. The white precipitates were collected and washed with water. Recrystallization from ethyl acetate gave 1.80 g (45%) of white OS crystals. Purity was checked by HPLC. Product characteristics were as follows. T_m: 236 °C, FT-IR (KBr) (cm^{-1}): 3300−2500 (OH), 3078 (aromatic C−H), 1749 (ester C═O), 1678 (thioester C═O), 1701 (carboxylic acid C═O). ^{1}H NMR (ppm); 2.4 (3H, s, acetyl), 7.3 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.1 (2H, d, aromatic), 8.2 (2H, d, aromatic).

4-(*S*-Acetyl-4-mercaptobenzoyl)oxybenzoic Acid (SO). SO was synthesized by a procedure similar to that of OS. Purity was checked by HPLC. Product characteristics were as follows. T_m: 219 °C, FT-IR (KBr) (cm^{-1}): 3300−2500 (OH), 3068 (aromatic C−H), 1745 (ester C═O), 1687 (thioester C═O), 1703 (carboxylic acid C═O). ^{1}H NMR (ppm); 2.5 (3H, s, acetyl), 7.4 (2H, d, aromatic), 7.6 (2H, d, aromatic), 8.2 (2H, d, aromatic), 8.3 (2H, d, aromatic).

Polymer Synthesis. Solution polymerizations were carried out in several solvents at 300 °C for 6 h. Polymerization concentration was 1.0 wt/vol % based on polymer weight and solvent volume. Polymerization of OS in LPF was described as a typical procedure. Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed 0.25 g of OS (0.78 mmol) and 20 mL of LPF. The reaction mixture was heated under a slow stream of nitrogen up to 300 °C with stirring. The stirring was stopped after the monomers were completely dissolved. The temperature was maintained at 300 °C for 6 h. The products were collected by vacuum filtration at 300 °C and washed with *n*-hexane and acetone. The filtrate was poured into *n*-hexane, and the precipitated oligomers which were dissolved in LPF at 300 °C were collected by filtration. Characteristics of the polymer products were as follows. FT-IR (KBr) (cm^{-1}): 3067, 2922, 1735, 1673, 1587, 1500, 1399, 1261, 1203, 1156, 1054, 1011, 892, 742.

Polymerization of SO and random copolymerization of ABA and AMBA at molar ratio of 0.5 in feed were carried out by procedures similar to the polymerization of OS. Characteristics of the polymer products were as follows. FT-IR (KBr) (cm^{-1}): for polymer prepared from SO, 3068, 2924, 1736, 1672, 1591, 1502, 1398, 1261, 1203, 1157, 1055, 897, and 754; for copolymer prepared from ABA and AMBA, 3058, 2924, 1732, 1670, 1586, 1498, 1396, 1259, 1160, 1057, 1012, 890, and 736.

Melt polymerization of OS was carried out as follows. Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube was placed 1.0 g of OS. The flask was heated under a slow stream of nitrogen up to 250 °C, and the temperature was maintained for 30 min. Then the mixture was polymerized at 280 °C for 30 min and 300 °C for 2 h. The polymer melt was solidified with time. The reduced pressure was applied, and the polymerization was continued at 300 °C and 1.0 mmHg for 1 h.

Characterization. The morphology of the products was observed on SEM (Hitachi S-3500N). The length and the width of the whiskers was determined by the average of over 80 observation values. The density of the crystals was measured by the flotation method using bromoform and toluene at 25 °C.

$$N = 8Y/\{W^2 \times \rho\,(3L - 2W/\tan(\theta/2)\} \qquad (1)$$

where N = number of whiskers, Y = yield of whisker, W = average width of whisker, L = average length of whisker, ρ = density of whisker, and θ = tip angle of whisker. The number of whiskers (N) was calculated according to eq 1 assuming that the cross section of the whiskers was hexagonal like the POB whisker.[3]

The IR spectra were measured on FT-IR spectrometer (FT/IR-410, JASCO Co. Ltd). The electron diffraction was performed on TEM (JEOL 2000EXII). WAXS was conducted on a Rigaku 4012K2 with nickel-filtered Cu Kα radiation (35 kV, 20 mA). The chemical structure of oligomers was characterized by ^{1}H NMR (Varian Unity-500) operating at 500 MHz. The NMR spectra were measured in the mixed solvents of $CF_3COOH/CDCl_3$ or CF_3COOH/CD_2Cl_2. The composition of polymers was determined by HPLC (Waters 600E) after hydrolysis of polymers. Thermal properties were evaluated by DSC (Perkin-Elmer DSC-7) with a scanning rate of 10 °C · min^{-1} in nitrogen atmosphere. The nematic transition temperature was measured on an optical microscope (Yanaco MP-500D) equipped with a hot stage under crossed polarization.

Results and Discussion

Morphology of Polymer Crystals. Polymerization of ABA and AMBA in LPF at a molar ratio of 0.5 in feed gave a random copolymer having spherical morphology, and the whisker was not formed as previously reported.[14] This morphological feature was attributed to not only the lack of crystallizability of random co-oligomer but also propensity for liquid−liquid phase separation of co-oligomers due to lower freezing point of co-oligomers. OS and SO were synthesized as monomers to introduce the alternating sequence regularity into polymer chains. The solution became turbid at the early stage of polymerization due to the precipitation of oligomers, and then the polymer precipitates were obtained after 6 h. The results of polymerizations of these monomers are summarized in Table 1 in comparison with the result of random copolymerization. In contrast to the random copolymerization, both the polymerization of OS and SO in LPF yielded the whiskers which grew radially from center point as shown in Figure 1. The whiskers prepared from OS in LPF (POS_{LPF}) are 18 μm in average length and 0.4 μm in average width. The whiskers prepared from SO in LPF (PSO_{LPF}) are slightly longer and wider than POS_{LPF}, for which the average length is 23 μm and the average width is 0.6 μm. These morphological features reveal that these whiskers are formed by the crystallization

Table 1. Results of Polymerizations

polymer code	solvent	monomer	T_s[a] (°C)	t_t[b] (min)	yield (wt %)	morphology of products	composition of *p*-oxybenzoyl unit in products (mol %)
	LPF	ABA + AMBA	220	10	26.9	spherical	57
POS_{LPF}	LPF	OS	265	12	54.0	needlelike	49
PSO_{LPF}	LPF	SO	245	36	40.1	needlelike	50
POS_{TS10}	TS10	OS	215	18	61.0	needlelike	42
PSO_{TS10}	TS10	SO	205	45	33.9	needlelike	48
POS_{TS8}	TS8	OS	215	33	31.7	needlelike	45
PSO_{TS8}	TS8	SO	200	20	21.4	needlelike, not clear	46

[a] Temperature at which monomer is completely dissolved. [b] Time when the solution becomes turbid.

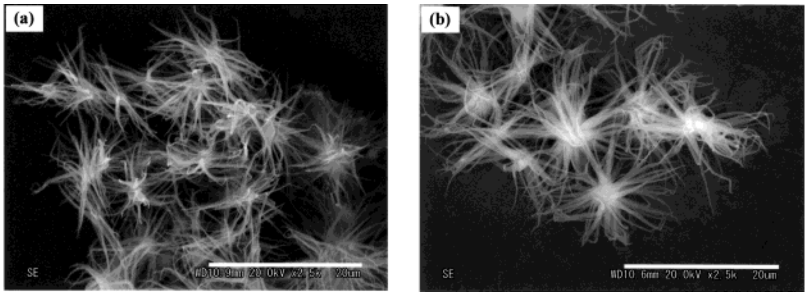


Figure 1. Scanning electron micrographs of (a) POS_{LPF} and (b) PSO_{LPF}.

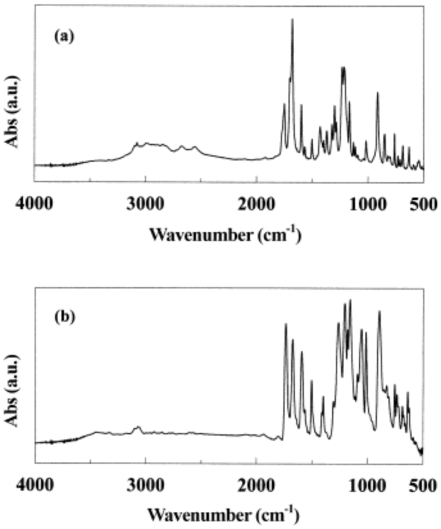


Figure 2. FT-IR spectra of (a) OS and POS_{LPF}.

of oligomers as well as the POB whisker. The compositions of the *p*-oxybenzoyl unit and the *p*-mercaptobenzoyl unit in POS_{LPF} and PSO_{LPF} were in good agreement with those of the monomers. These whiskers are totally insoluble into organic solvents, and thereby the chemical structure and the sequence regularity cannot be directly evaluated by NMR. Accordingly, the chemical structure of the obtained whiskers was analyzed by FT-IR. The spectra of the POS_{LPF} prepared for 6 h and OS are shown in Figure 2 as representatives. The peaks for C=O of ester group and thioester group appeared newly at 1735 and 1673 cm^{-1}, respectively. The peaks for C=O of acetyl group at 1749 cm^{-1} and carboxylic acid at 1701 cm^{-1} and that for OH of carboxylic acid at 3300−2500 cm^{-1} of OS disappeared significantly. This result confirms that the whiskers are composed of high molecular weight polymers. Selected area electron diffraction was performed to estimate the sequence regularity. The diffraction patterns of POS_{LPF} and PSO_{LPF} do not show the true fiber pattern with cylindrical symmetry, and they consist of the sharp spots of lower to higher order diffraction as clearly observed in Figure 3. These are due to the single-crystal nature of these whiskers.

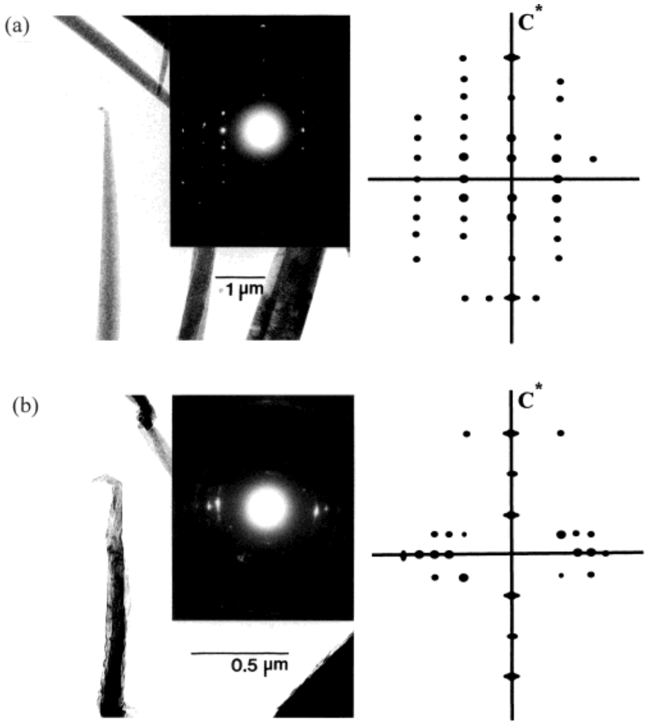


Figure 3. TEM and selected area electron diffraction pattern of (a) POS_{LPF} and (b) PSO_{LPF}.

The spots on the meridian of PSO_{LPF} are slightly diffuse, and this may be accounted for by the smaller crystalline area or the axial shifted structure found in aromatic polyazoles.[19] The meridians of these patterns correspond to the long axes of the crystals, and the polymer chains align along the long axes of the whiskers. The observed fiber identity periods of POS_{LPF} and PSO_{LPF} are 12.73 and 12.96 Å, respectively, which correspond to the calculated fiber identity period of POB-*alt*-PMB. It can be concluded that these polymers maintain the alternating sequence, and the sequence regularity leads to the formation of the whiskers.

As described, the length and width of the POS_{LPF} are slightly shorter than those of the PSO_{LPF} whiskers. To understand a difference in the size, the number of the

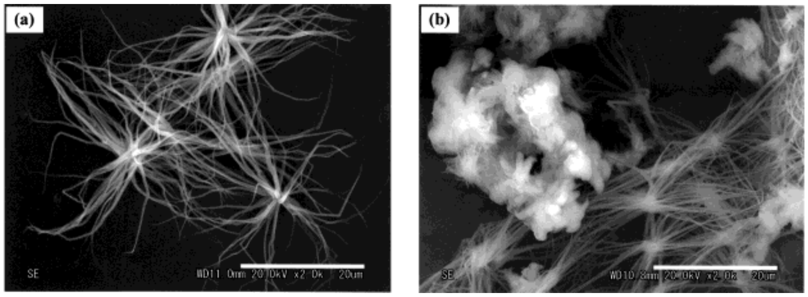


Figure 4. Scanning electron micrographs of (a) POS_{TS8} and (b) PSO_{TS8}.

Table 2. Size Parameters and Number of Whiskers

polymer code	size parameter: length (μm)	width (μm)	tip angle (deg)	no. of whiskers ($\times 10^{10}$)
POS_{LPF}	18.1	0.38	4.3	6.7
PSO_{LPF}	21.8	0.59	3.9	2.0
POS_{TS10}	48.6	0.41	2.0	2.2
PSO_{TS10}	37.6	0.58	3.1	0.9
POS_{TS8}	35.6	0.41	2.8	1.6

Table 3. Second-Order Rate Constants for Formation of Crystallized Oligomer and Trans-Esterification[a]

monomer	solvent	formation rate constant of crystallized oligomer k_{2f} (L·mol^{-1}·min^{-1})	trans-esterification rate constant k_{2t} (L·mol^{-1}·min^{-1})	k_{2f}/k_{2t}
OS	LPF	1.68	1.90×10^{-2}	88.6
	TS8	0.16	3.60×10^{-2}	4.4
SO	LPF	0.60	7.10×10^{-2}	8.3

[a] Polymerizations were carried out at 300 °C. Initial concentration was 3.90×10^{-2} mol·L^{-1}.

whiskers generated in polymerization solution (N) was calculated according to eq 1 with the shape parameters, the yields and the densities of the whiskers. The shape parameters and the calculated Ns are summarized in Table 2. POS_{LPF} and PSO_{LPF} have the same density of 1.51 g·cm^{-3}. N of POS_{LPF} is 6.7×10^{10}, which is 3.4 times larger than that of PSO_{LPF}. Many more nuclei used in the whisker formation are generated in the polymerization of OS compared with that of SO, and this results ultimately in forming the shorter whiskers. It is well-known that critical radius of nucleus (r^*) and nucleation rate (J) depend on the degree of supersaturation as follows.[20,21]

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

$$r^* = 2v\gamma/\Delta\mu$$

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

where μ = chemical potential, C = concentration of solute, C_e = equilibrium concentration, r^* = critical radius of nucleus, v = volume of molecule, γ = density of surface energy, J = nucleation rate, ν_+ = rate of crystallization of one molecule into critical nucleus, and q = density of free molecule.

When the degree of supersaturation (σ) increases, $\Delta\mu$, which is a driving force for nucleation, becomes larger. This large $\Delta\mu$ leads to small r^* and large J, indicating that many more nuclei having smaller radius are formed. There seems to exist several parameters to influence the degree of supersaturation such as miscibility between oligomer and solvent, formation rate of oligomer, concentration, temperature and so on. Polymerizations were carried out at the same concentration and temperature, and thereby the former two parameters are more dominant in this study. First, the miscibility between the oligomer and the solvent is discussed. The temperature at which the monomer is completely dissolved during heating (T_s) and the time when the solution becomes turbid (t_t) are adaptable as criteria to estimate the miscibility between the oligomer and the solvent, and the lower T_s and the later t_t imply the higher miscibility. The T_s of SO is 20 °C lower and the t_t of SO is 24 min later than those of OS. These differences in T_s and t_t indicate the higher miscibility of the SO oligomers than that of the OS oligomers. Secondary, the rate constants for the formation of crystallized oligomers (k_{2f}) in LPF are estimated as shown in Table 3. The k_{2f} of OS is 2.8 times larger than the k_{2f} of SO. The kinetics will be discussed in detail in the following section. It can be explained on the basis of these results that the higher degree of supersaturation of the OS oligomer than that of the SO oligomer results in the formation of a larger number of nuclei, and hence, the length of the POS_{LPF} become reasonably shorter.

The miscibility of the oligomer and the solvent governs N leading to the length control of the whiskers, and the higher miscibility which results in the lower degree of supersaturation of the oligomers makes the whiskers longer due to the smaller N. Therefore, the solvent effect on the size of the whisker was examined with two kinds of aromatic solvents which were TS10 and TS8. The polymerization results and the morphology of the crystals are shown in Table 1 and Figure 4. The polymerizations of OS and SO in these aromatic solvents yielded the whiskers with the lower yields than that in LPF. In the polymerization of SO in TS8, products having unclear morphology were also formed together with the whiskers. The sizes of the obtained whiskers are also summarized in Table 2. The whiskers prepared from OS in TS10 (POS_{TS10}) are 49 μm in average length and 0.4 μm in average width, and those in TS8 (POS_{TS8}) are 36 μm in average length and 0.4 μm in average width. Concerning SO, the whiskers prepared in TS10 (PSO_{TS10}) are 38 μm in average length and 0.6 μm in average width. The whiskers prepared in aromatic solvents are much longer than those in LPF. The observed densities of POS_{TS10}, POS_{TS8}, and PSO_{TS10} were 1.52, 1.52, and 1.51 g·cm^{-3}, respectively. The Ns in aromatic solvents tabulated in Table 2 are from one-fourth to one-third of those in LPF, and this is due to the higher miscibility anticipated from T_s and t_t. The longer whiskers can be prepared in aromatic solvents and the length is tunable by the miscibility between the oligomer and the solvent.

WAXS patterns of these whiskers show that the diffraction peaks are quite sharp, and the diffuse halo attributed to amorphous parts is not detected at all as

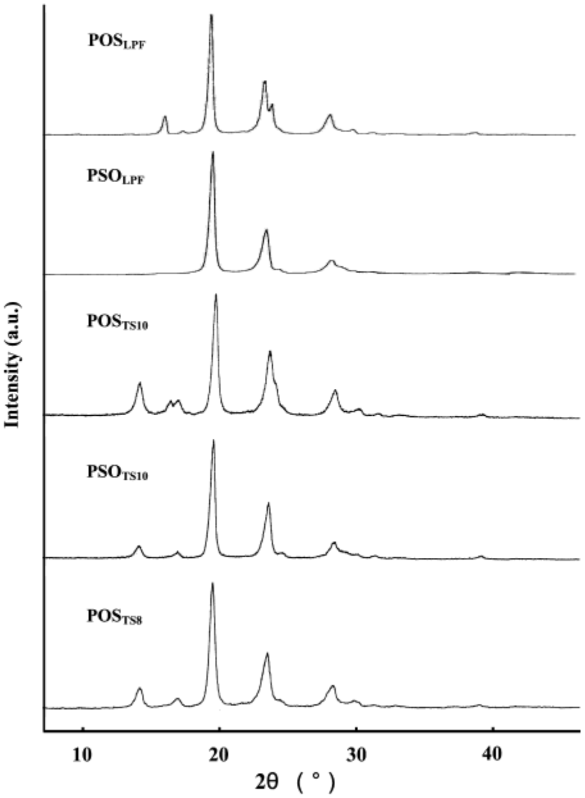


Figure 5. WAXS intensity profiles of various whiskers.

Table 4. Avarage Diameter of Crystalline Area (*D*) of Whiskers

polymer code	*D* (Å)[a]
POS$_{\mathrm{LPF}}$	346
PSO$_{\mathrm{LPF}}$	247
POS$_{\mathrm{TS10}}$	223
PSO$_{\mathrm{TS10}}$	266
POS$_{\mathrm{TS8}}$	214

[a] *D* was estimated by using Scherrer's equation from the reflective width at 2θ of 19.5°.

shown in Figure 5. They possess the extremely high crystallinity. There is some similarity between these WAXS profiles and the peak positions are almost the same. The average diameters of the crystalline area (*D*) of the whisker were estimated by Scherrer's equation with the sharpest peak around 19.5° as shown in Table 4. The *D*s of these whisker are on the order of 300 Å for POS$_{\mathrm{LPF}}$ and 200 Å for the other whiskers. POS$_{\mathrm{LPF}}$ possesses better packing regularity than other whiskers because of higher sequence regularity.

Growth Mechanism of Whisker. To understand the growth mechanism of POB-*alt*-PMB whisker, the yields and the sizes of the whiskers were followed during the polymerization of OS and SO in LPF. The length and the width of both POS$_{\mathrm{LPF}}$ and PSO$_{\mathrm{LPF}}$ increase with the yields as shown in Figure 6, and the length increases preferentially rather than the width. The large increments of the length and the width were observed at the early stage of the polymerization within 60 min in both cases. This is due to the higher degree of supersaturation of the oligomers in the initial stage of the polymerization. The increment of the width of PSO$_{\mathrm{LPF}}$ in the initial stage is much larger than that of POS$_{\mathrm{LPF}}$. If these whiskers are formed by the spiral growth as well as the POB whiskers, the increase of whisker length is caused by which oligomer lamellae pile up along the long axis of the needlelike crystals. The secondary nucleation on the spiral step leading to the increase of the length is easier than that on the lateral side surface because of the advantage of surface energy. However, when the degree of supersaturation of the oligomers is quite high, secondary nucleation occurs on not only the spiral step but also the lateral side surface leading to the increase of the width. To evaluate the degree of supersaturation of the oligomers during polymerization more precisely, the k_{2f}s were converted into the rate per one nucleus (k'_{2f}). The k_{2f} of OS is larger than that of SO as described above, but the k'_{2f} of SO is 3.0×10^{-11} L·mol^{-1}·min^{-1} which is 20% larger than that of OS of 2.5×10^{-11} L·mol^{-1}·min^{-1}. This slightly higher degree of supersaturation of the oligomers leads to much growth on the lateral side surface of PSO$_{\mathrm{LPF}}$ whiskers.

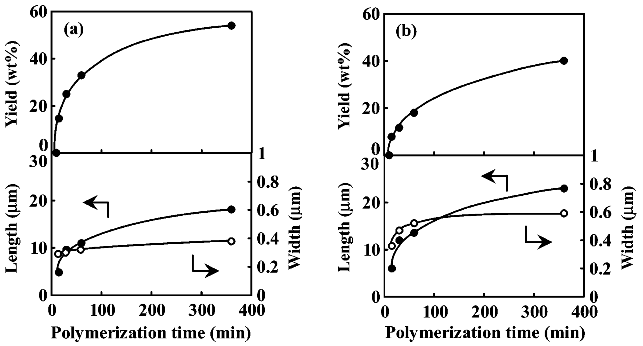


Figure 6. Polymerization time dependency of length, width and yield of (a) POS$_{\mathrm{LPF}}$ and (b) PSO$_{\mathrm{LPF}}$.

The oligomers dissolved in solution were analyzed by ^{1}H NMR, and the spectra are shown in Figure 7. In the polymerization of OS in LPF, the average molar ratio of 1,4-phenylene group and the acetyl end group of the dissolved OS oligomers is ca. 2, and it is constant during polymerization as shown in Figure 8. This fact suggests that OS is mainly left in the solution and dimers are precipitated in the form of the needlelike crystals. The peak of acetyl proton of *S*-acetyl-4-mercaptobenzoyl unit is newly found at 2.55 ppm which is not included in OS, and its peak intensity increases with time. The appearance of this peak means the occurrence of transesterification reaction in the solution via the mixed anhydride formation mechanism.[22−26] The molar ratio of *S*-acetyl end group in acetyl end groups of the oligomers increases with time as also shown in Figure 8. The transesterification reaction brings about the randomization of the regular sequences of the oligomers and ultimately the polymers. The oligomers are continuously precipitated with time in this polymerization system, and this results in the gradual decrease of the concentration of the oligomers in the solution. Thus, the transesterification reaction was followed within 10 min until the precipitation began. The formation of the dimers was monitored by the recovery of OS dissolved in the solution. It has been reported that both the polycondensation of ABA[27−30] and the transesterification of aromatic copolyesters[31−34] obeyed second-order kinetics. Figure 9 shows that both the transesterification reaction and the formation of oligomers obey second-order kinetics and the rate constants are determined from the slopes as shown in Table 3. The OS dimers are formed 88.6 times faster than the transesterification reaction in LPF. It can be said that the OS dimers are mainly precipitated to form the whiskers while keeping the regular sequences. On the other hand, the average molar ratio of 1,4-phenylene group and acetyl end group

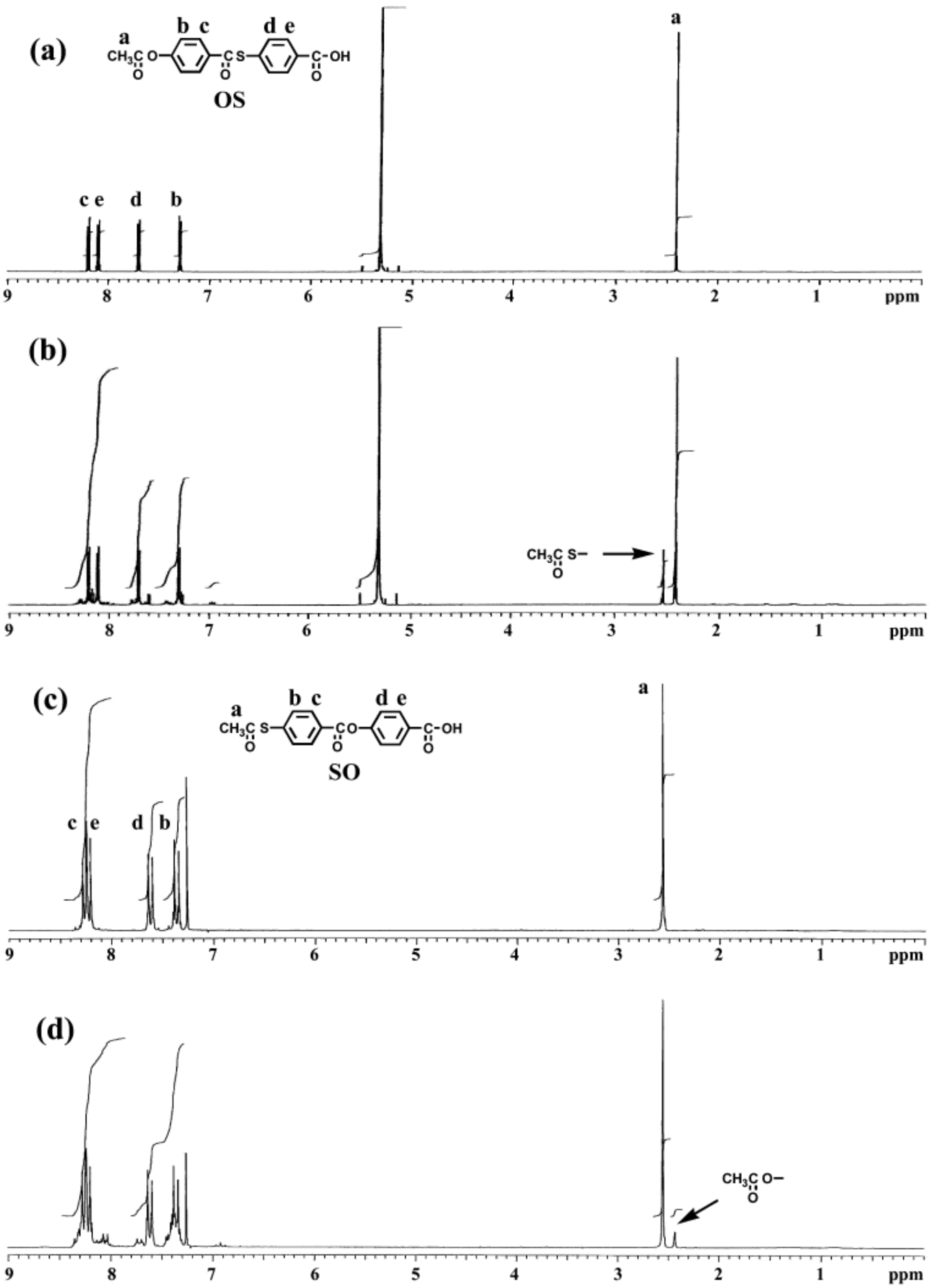


Figure 7. ^{1}H NMR spectra of (a) OS, (b) dissolved oligomers prepared from OS for 72 min in LPF, (c) SO, and (d) dissolved oligomers prepared from SO for 96 min in LPF.

of the SO oligomers dissolved in LPF is ca. 2.5, and the molecular weight of the precipitated SO oligomers are larger than that of OS oligomers, which is attributed to the higher miscibility as described before. The transesterification and the formation rate of the SO oligomers are also evaluated as shown in Table 3. The transesterification reaction of SO occurs more rapidly than OS, and the SO oligomers are precipitated 8.3 times faster than the transesterification reaction. The SO oligomers are also precipitated to form the whiskers while keeping the regular sequences. Though the oligomers are precipitated more rapidly than transesterification reaction in both polymerizations, the difference in the two rate constants of OS is much larger than that of SO. Hence, OS is of greater advantage for the formation of POB-*alt*-PMB whiskers.

Concerning the polymerization of OS in TS8, the average molar ratio of 1,4-phenylene group and acetyl end group of the dissolved oligomers is ca. 3.0. This indicates that the oligomers having higher molecular weight are precipitated in TS8 than those in LPF due to the higher miscibility. The reactions of OS in TS8 also obey the second-order kinetics and their rate constants are estimated as shown in Table 3. The k_{2f} of OS in TS8 is 0.16 $L{\cdot}mol^{-1}{\cdot}min^{-1}$, which is 10.5 times smaller than that in LPF. The transesterification reaction for which the k_2t is 3.6×10^{-2} $L{\cdot}mol^{-1}{\cdot}min^{-1}$ occurs 1.9 times faster than that in LPF. The precipitated oligomers are formed 4.4 times faster than the transesterification reaction in TS8, but the difference in the two rate constants of OS in TS8 is much smaller than that in LPF. As shown in Table 1, there are some

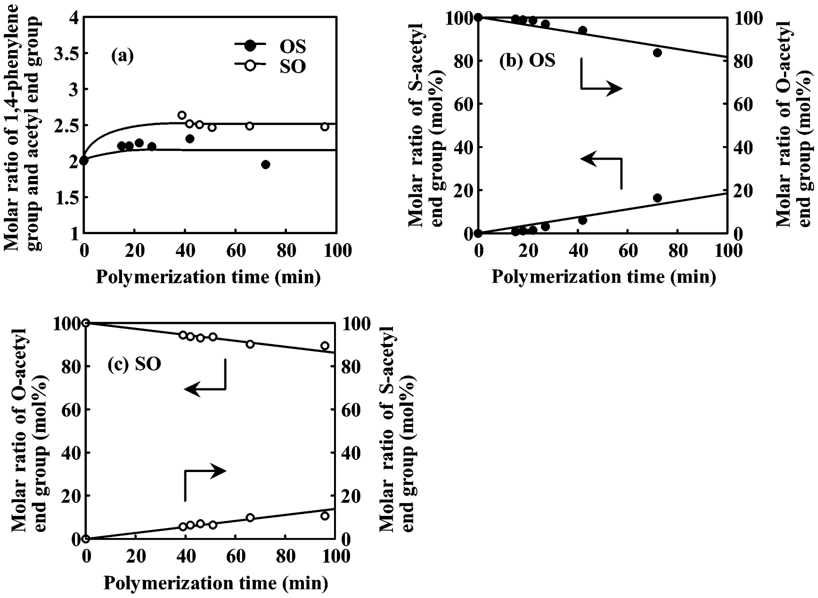


Figure 8. Polymerization time dependency of (a) molar ratio of 1,4-phenylene group and end group of dissolved oligomers prepared from OS and SO, and content of end groups of dissolved oligomers prepared from (b) OS and (c) SO in LPF.

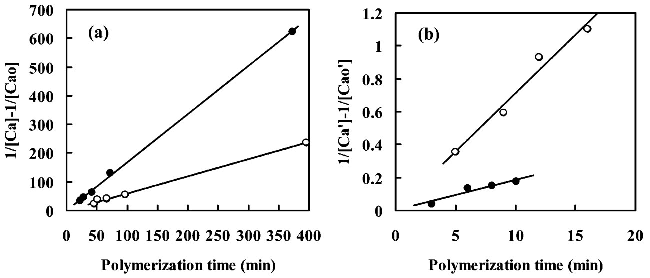


Figure 9. Kinetics of second-order reaction for (a) formation of crystallized oligomers and (b) transesterification reaction in the polymerization of OS (●) and SO (○) in LPF. [Ca]: Concentration of crystallized oligomer. [Ca′]: Concentration of *S*-acetyl or *O*-acetyl group. [Cao] = [Cao′] = 3.90 × 10^{-2} mol·L^{-1}.

deviations between the composition of polymer crystals prepared in aromatic solvents and monomers. The whiskers are rich in the *p*-mercaptobenzoyl unit. This indicates that the oligomers having randomized sequence are precipitated to form whiskers. It can be supposed that the polymerization of OS and SO in aromatic solvents is advantageous to prepare the longer whiskers but disadvantageous to maintain the alternating sequence compared with that in LPF.

The change in the molecular weight of POS_{LPF} was qualitatively investigated during polymerization by FT-IR. The spectrum between 1800 and 1615 cm^{-1} are made up by the superposition of four C=O peaks, which are those of acetyl at 1749 cm^{-1}, thioester at 1673 cm^{-1}, ester at 1735 cm^{-1}, and carboxylic acid at 1701 cm^{-1}, and they are resolved by the combined Lorentzian and Gaussian function as illustrated in Figure 10. The absorbance ratio of C=O of thioester group and that of ester group is constant during polymerization. The others become smaller with time. The change in the absorbance ratio of C=O of ester group and that of carboxylic acid is monitored to clarify the change in molecular weight. This absorbance ratio increases linearly with time. This indicates that the solid-state polymerization occurs very effectively in the crystals as well as the POB whiskers,[3] and the molecular weight increases with maintaining the alternating sequences.

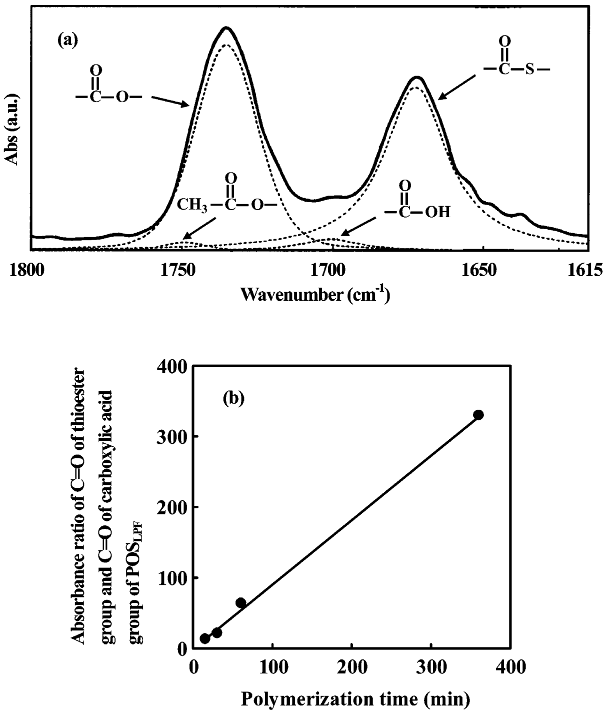


Figure 10. (a) FT-IR spectrum of POS_{LPF} prepared for 15 min and (b) polymerization time dependency of absorbance ratio of C=O of thioester group and C=O of carboxylic acid group of POS_{LPF}.

Thermal Properties of Whiskers. Thermal properties of the resulting whiskers are summarized in Table 5 compared with those of the random copolymer prepared from ABA and AMBA at a molar ratio of 0.5 in feed. It is known that the POB and PMB crystals show a reversible first-order solid–solid transition at around 350 °C differing from the melting process and it is regarded as a transition to pseudohexagonal packing of polymer molecule by a rotation of 1,4-phenylene ring around σ-bond in the para position.[35−39] The transition temperature (T_t) and its enthalpy (ΔH) are susceptible to both crystallinity and packing of polymer chains. The crystals having higher crystallinity and closer packing

Table 5. Thermal Properties of Copolymers

monomer	polymerization method[a]	polymer code	DSC[b] T_t (°C)	DSC[b] ΔH (J/g)	T_n[c] (°C)
ABA + AMBA	SP		d		377
OS	SP	POS_{LPF}	277.3	6.25	418
	MP				369
SO	SP	PSO_{LPF}	281.6	3.65	408

[a] SP: solution polymerization in LPF. MP: melt polymerization. [b] Solid−solid transition temperature (T_t) was measured on DSC with a heating rate of 10 °C/min in nitrogen. [c] T_n: Nematic transition temperature was measured on an optical microscope with heating stage under crossed polarization. [d] Transition was not detected.

show higher T_t and larger ΔH.[7,40] Concerning random copolymer, the transition was not detected. POS_{LPF} and PSO_{LPF} show similar transitions at around 280 °C. This indicates that the regular sequences enhance the crystallinity and the closer chain packing.

All these polymers exhibit liquid crystal transition from crystalline to nematic phase. Transition temperature (T_n) of POS_{LPF} and PSO_{LPF} are 417 and 408 °C, respectively, which are 30−40 °C higher than that of the random copolymers of 377 °C. It has been reported that T_n of copolymers depends on the sequence regularity and the regular sequence increases T_n due to stronger interaction.[41] The polymer prepared by the melt polymerization of OS shows T_n of 369 °C which comes close to T_n of the random copolymer. The polymer prepared by the melt polymerization of OS does not maintain the alternating sequence, and the randomization of sequence occurs by the transesterification reaction in the melt polymerization process.

Conclusions

The whiskers of POB-*alt*-PMB are successfully prepared by the polymerization of OS and SO. They possess extremely high crystallinity. They consist of the alternating polymer chains and the polymer chains aligned along the long axis of the whisker. The chemical structure of the monomer and the miscibility between the oligomer and the solvent are very important parameters used to control the length and the regular sequence. Concerning the chemical structure of the monomer, SO gives an advantage in making the longer whiskers rather than OS due to the higher miscibility, which brings about the formation of a smaller number of nuclei. However, OS gives an advantage in maintaining the alternating sequence because the difference in the rate constant between the oligomer formation and the transesterification reaction is much larger than that of SO. Concerning the solvent, aromatic solvents yield the longer whiskers than LPF, but they give a disadvantage in maintaining the alternating sequence due to the higher miscibility. The formation mechanism of the whiskers can be proposed as follows; When the molecular weight of the oligomers exceeds the critical value, they are precipitated prior to the randomization by transesterification reaction and form the needlelike crystals. Further polymerization occurs in the crystals and the whiskers of POB-*alt*-PMB are finally completed. These whiskers exhibit better thermal properties compared with the random copolymers.

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