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Polymer Whiskers Composed of *p*-Oxybenzoyl and *p*-Mercaptobenzoyl Having Graded Compositions

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ABSTRACT: Preparation of polymer whiskers composed of *p*-oxybenzoyl (O) units and *p*-mercaptobenzoyl (S) units having graded composition was examined by the polymerization of *S*-acetyl-4-mercaptobenzoic acid (AMBA) and 4-(4-acetoxybenzoyloxy)benzoic acid (OO) or 4-[4-(4-acetoxybenzoyloxy)benzoyloxy]-benzoic acid (OOO). Polymerizations were carried out in liquid paraffin at 300 °C for 6 h. The polymerization concentration was 1.0% and the molar ratio of O units in feed was 50%. Polymerization of AMBA and OO yielded copolymer whiskers by means of the crystallization of oligomers, which were 15 μm in average length and 0.4 μm in average width. The length and the width increased with polymer yield but the length increased preferentially rather than the width. The number of whiskers was constant during polymerization. The content of O units in the whiskers (χ_O) prepared for 8 min was 62 mol % and then decreased to 49 mol % after 6 h. This fact revealed that the center part of the whisker was rich in O units, and the outer and tip parts were rich in S units. This whisker possessed a graded composition from O units to S units along the directions of the length and width. The oligomers rich in O unit sequences were preferentially precipitated in the early stage of polymerization, and afterward the oligomers poor in O units were precipitated to form the whiskers leading to a graded composition. Polymerization of AMBA and OOO yielded copolymer whiskers with a larger gradient composition than that of whiskers prepared from AMBA and OO.

Introduction

Wholly aromatic polymers have excellent properties due to their rigid structures, such as thermal stability, mechanical properties, chemical resistance, and so on, and hence, they have been receiving much attention as promising candidates for high performance polymeric materials. However, they usually show neither solubility nor fusibility, and this intractability makes them inaccessible for processing by conventional techniques. Many attempts have been made to overcome this difficult problem from the aspect of not only chemical modification of polymer structures[1] but also processing techniques.[2]

We have been studying the morphological control of rigid polymers during solution polymerization and have successfully prepared whiskers of poly(*p*-oxybenzoyl) (POB), poly(*p*-mercaptobenzoyl) (PMB), and other aromatic polyesters by polymerizations in poor solvents such as liquid paraffin (LPF) at around 300 °C.[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 involves the following three steps. (1) When the degree of polymerization of 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) Post-polymerization occurs efficiently in the needlelike crystals, and whiskers consisting of high molecular weight extended polymer chains are eventually formed. [4] Many other aromatic polymer whiskers have been obtained by this method,[9−12] and this method can be regarded as the simultaneous control of morphology and chain orientation by means of reaction-induced crystallization of oligomers. It can be recognized as morphology-controlling polymerization without any templates, and this is a very valuable method for intractable aromatic polymers.

The preparation of copolymer whisker is very interesting and desirable to tailor the new functional polymeric materials. Recently, we have been studying the morphology of poly(*p*-oxybenzoyl-*co*-*p*-mercaptobenzoyl). The random copolymerization of 4-acetoxybenzoic acid (ABA) and *S*-acetyl-4-mercaptobenzoic acid (AMBA) did not afford copolymer crystals due to the lack of crystallizability of oligomers and its tendency to be phase-separated through liquid−liquid-phase separation.[13,14] The poly(*p*-oxybenzoyl-*alt*-*p*-mercaptobenzoyl) whiskers were successfully prepared by the control of short distance sequence regularity.[14] The morphology of copolymers is very sensitive to the short distance sequence regularity. In nature, complex functions of materials are usually caused by multicomplex structures such as graded composition structures, which give graded function to the materials. Recently, functionally gradient polymer composites have been expected as a new type of materials which possess continuous variation in composition and microstructure in the multiple directions of the materials. Since this concept has been applied for the first time to develop super heat resistant materials such as SiC and C by controlling gradiently the composition to improve effective thermal stress relaxation property of the materials,[15,16] much attention has been paid to other material systems such as polymer composites.[17−19] With respect to polymer materials, only polymer blend films are reported as the gradient materials having graded composition to my knowledge.[20] The polymer whiskers having graded composition will afford the new structural materials such as reinforce-

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ments for polymer blends and novel functional materials such as electronic devices.

This article describes our new finding on the preparation of polymer whiskers composed of *p*-oxybenzoyl (O) unit and *p*-mercaptobenzoyl (S) unit having graded composition.

Experimental Section

Materials. ABA and 4-hydroxybenzoic acid were purchased from TCI Co. Ltd. and recrystallized from ethyl acetate. AMBA was synthesized according to previous work.[21−24] LPF was purchased from Nacalai Tesque Co., Ltd., and purified by vacuum distillation (220−240 °C/0.3 mmHg).

Monomer Synthesis. Synthesis of 4-(4-Acetoxybenzoyloxy)benzoic Acid (OO). Into a three-necked flask equipped with a dropping funnel, a thermometer, and a gas inlet tube were placed 4-hydroxybenzoic acid (3.02 g, 2.19×10^{-2} mol), 4-acetoxybenzoyl chloride (4.34 g, 2.19×10^{-2} mol), which was synthesized from ABA and thionyl chloride, and 60 mL of dried tetrahydrofuran. The solution of triethylamine (2.66 g, 2.63×10^{-2} mol) and 15 mL of dried tetrahydrofuran was added dropwise through the dropping funnel under a slow stream of nitrogen at 5 °C. The reaction mixture was stirred at 5 °C for 2 h and 25 °C for 12 h, and then filtered to separate triethylamine−HCl salts. The filtrate was acidified by diluted HCl solution. White precipitates were collected and washed with water. Recrystallization from ethyl acetate gave white OO crystals (1.64 g, yield 25.0%). Purity was more than 99% checked by HPLC. Product characteristics were as follows. T_m: 216 °C. FT-IR (KBr) (cm^{-1}): 3300−2500 (OH), 3074 (aromatic C−H), 1759 (ester C═O), 1737 (ester C═O), 1686 (carboxylic acid C═O), 1266 (carboxylic acid C−O), 1201 (ester C−O), 1185 (acetoxy C−O), 756 (aromatic C−H). ^{1}H NMR (ppm): 2.4 (3H: acetyl), 7.3 (2H: aromatic), 7.4 (2H: aromatic), 8.2 (2H: aromatic), 8.3 (2H: aromatic).

Synthesis of 4-[4-(4-Acetoxybenzoyloxy)benzoyloxy]benzoic Acid (OOO). OOO was synthesized by a similar procedure to that of OO. Purity was more than 99% checked by HPLC. Product characteristics were as follows. T_m: 236 °C. FT-IR (KBr) (cm^{-1}): 3300−2500 (OH), 3074 (aromatic C−H), 1742 (ester C═O), 1686 (carboxylic acid C═O), 1261 (carboxylic acid C−O), 1199 (ester C−O), 764 (aromatic C−H). ^{1}H NMR (ppm): 2.4 (3H: acetyl), 7.3−7.5 (6H: aromatic), 8.2−8.4 (6H: aromatic).

Polymer Synthesis. Polymerization of AMBA and OO is described in a typical procedure. Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed OO (0.12 g, 3.90×10^{-4} mol), AMBA (0.15 g, 7.80×10^{-4} mol), and 20 mL of LPF. The molar ratio of O units in the feed was 50%. The polymerization concentration was 1.0% w/v based on polymer weight and solvent volume. The reaction mixture was heated under a slow stream of nitrogen 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 polymer crystals 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 recovered by filtration. Characteristics of the polymer products were as follows. FT-IR (KBr) (cm^{-1}): 3072, 2925, 1735, 1673, 1594, 1506, 1413, 1398, 1260, 1203, 1156, 1012, 897, 755.

Characteristics of polymer crystals prepared from AMBA and OOO were as follows. FT-IR (KBr) (cm^{-1}): 3072, 2924, 1735, 1673, 1593, 1505, 1413, 1398, 1261, 1203, 1155, 1051, 1013, 896, 755.

Characterization. The morphology of the products was observed with a scanning electron microscope (Hitachi S-3500N). Samples were dried, sputtered with gold, and observed at 20 kV. Wide-angle X-ray scattering (WAXS) was conducted on a Rigaku 4012K2 with nickel-filtered Cu Kα radiation (30 kV, 20 mA). The crystallite size (*D*) was estimated according to Scherrer's equation. The half-width of the diffraction peaks was corrected with hexamethylenetetramine. The chemical structure of monomers and oligomers was characterized by a ^{1}H NMR instrument (JNM-AL-300) operating at 300 MHz. NMR spectra were measured in a mixed solvent of CF_3COOH/CD_2Cl_2. The composition of copolymers was determined by HPLC (Waters 600E) with Nova Pack HR C18 column after hydrolysis of copolymers. The eluent was a mixture of water containing 2.0 wt % acetic acid and acetonitrile, and the mixing volume ratio of these two solvents was changed linearly from 90/10 to 0/100 over 40 min. FT-IR spectrum was measured on a microscopic FT-IR spectrometer (FT-IR-410, Itron IRT30, JASCO Co. Ltd). Aperture size was 30 μm. Thermal properties were evaluated by DSC (Perkin-Elmer DSC-7) at a scanning rate of 10 °C·min^{-1} in a nitrogen atmosphere. The nematic transition temperatures were measured on an optical microscope (Yanaco MP-500D) equipped with hot stage under crossed polarization. The density of the whiskers was measured by the flotation method using bromoform and toluene at 25 °C. The shape parameters of the whiskers including the length and the width were determined from an average of over 100 observations.

Results and Discussion

Principle for Preparation of Whiskers Having Graded Composition. Polymer materials having graded composition have been prepared by polymer blend techniques to freeze the phase separation process leading to the continuous layer structure. All of them are amorphous materials. The principle of our approach to prepare the polymer crystal having graded composition is based on the reaction-induced crystallization of oligomers during solution polymerization. Reaction-induced phase separation of oligomers in poor solvent is describable on the analogous concentration−temperature phase diagram (*C*−*T* phase diagram) to that of partially miscible polymer−solvent system.[25,26] The phase separation curve in the repulsive system in which there is no attractive interaction between the oligomer and the solvent can be written as the combination of the freezing point curve of the oligomers and the upper critical solution temperature type consolute curve. The oligomers are formed by the reaction and the DP_n of the oligomers increases in the solution. When the DP_n of the oligomers exceeds a critical value, they are in a supersaturated state and then phase-separate. If the supersaturated oligomers phase-separate across the freezing point curve, they precipitate through crystallization to form the crystals, and the polymer crystals are finally formed by the post-polymerization in the crystals. To make the composition graded, the composition of phase-separated oligomer should vary from one component to the other with accumulation of the oligomers onto the tips of the needlelike crystals. The copolymerization between monomer of one component and oligomer of the other component is one of the desirable methods for phase separation of the resulting oligomers with altering gradually the composition during polymerization. On the basis of this principle, we examine the polymerization of AMBA and OO or OOO in poor solvent as shown in Scheme 1.

Morphology of Crystals. Polymerizations of AMBA and OO or OOO were carried out in LPF at 300 °C for 6 h. The beginning concentration was 1.0% w/v based on polymer weight and solvent volume. The solution became turbid in the early stages of polymerization due to the precipitation of oligomers. Polymer crystals were obtained after 6 h. The results of polymerization are summarized in Table 1. Both the polymerization of AMBA and OO and that of AMBA and OOO yield

Scheme 1. Polymerization of AMBA and OO or OOO

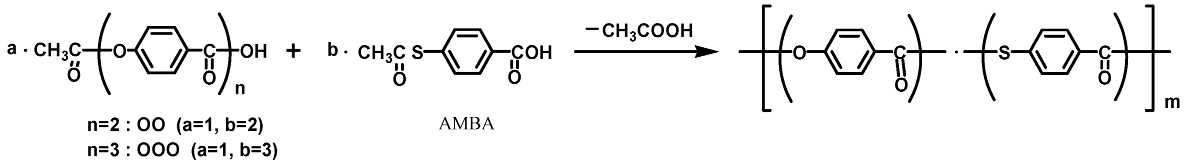

Table 1. Results of Polymerizations[a]

polymer code[b]	monomer	molar ratio of monomers	yield (%)	morphology	composition of *p*-oxybenzoyl unit in crystal (mol %)
PODS	OO + AMBA	1:2	51.4	needlelike	49
POTS	OOO + AMBA	1:3	42.7	needlelike	48

[a] Polymerizations were carried out in LPF at a concentration of 1.0% w/v and 300 °C. [b] Polymer codes are shown in Scheme 1.

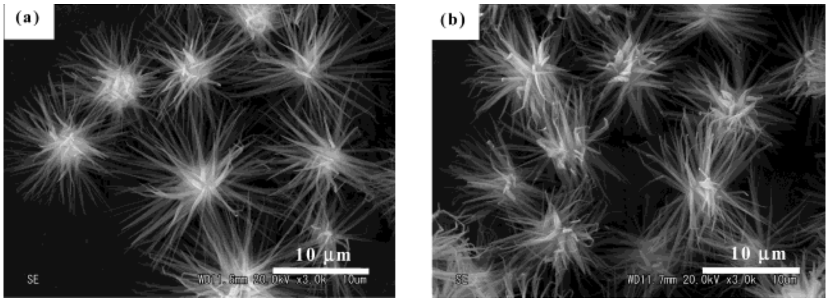

Figure 1. Scanning electron micrographs of (a) PODS and (b) POTS whiskers.

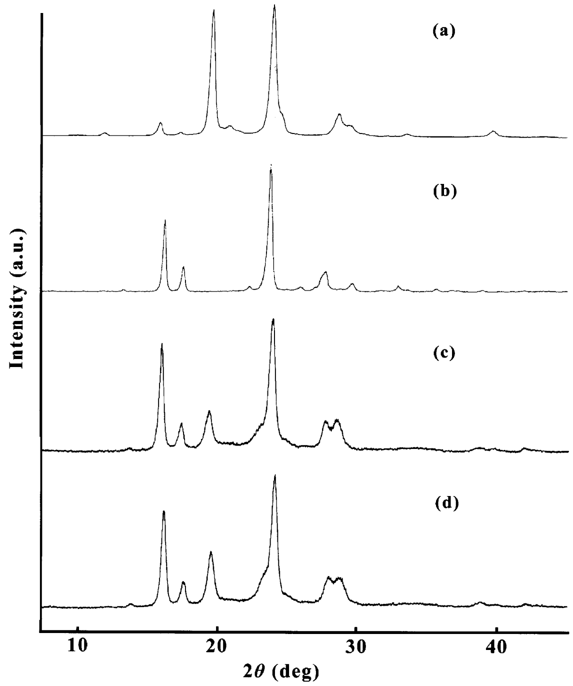

Figure 2. WAXS intensity profiles of (a) POB, (b) PMB, (c) PODS, and (d) POTS whiskers prepared in LPF for 6 h.

whiskers which grow radially from a center point, as shown in Figure 1. The whiskers prepared from AMBA and OO, which is a dimer of ABA (PODS), are 15 μm in average length and 0.4 μm in average width. The whiskers prepared from AMBA and OOO, which is a trimer of ABA (POTS), are 13 μm in average length and 0.4 μm in average width. These morphological features reveal that these whiskers are formed through the crystallization of oligomers as well as the POB whisker. The composition of O and S units in these whiskers prepared for 6 h was determined from the molar ratio of *p*-hydroxybenzoic acid and *p*-mercaptobenzoic acid analyzed by HPLC after hydrolysis. The content of O units (χ_O) in PODS whiskers and POTS whiskers are 49.0 and 48.0 mol %, respectively. These values are in good agreement with the content of O units in the feed (50 mol %), and fractional polycondensation defined as the polymerization to form the crystal having the quite different composition from that in feed,[27] does not occur in these polymerizations. Figure 2 shows the WAXS patterns of these whiskers with those of POB and PMB whiskers. The diffraction peaks of PODS and POTS whiskers are very sharp and the diffuse halo attributed to amorphous parts is not apparent. These patterns reveal that these whiskers are extremely crystalline. There is good similarity between the profiles of PODS and POTS, and peak positions are almost the same. The peaks of 2θ at 19, 24, and 29° are characteristic peaks of the POB crystals, and those at 2θ of 16, 18, 24, and 27° are characteristic peaks of the PMB crystals. These patterns contain the characteristic peaks of both the POB and PMB crystals. The average size of the crystalline area (D) of the whisker was estimated by Scherrer's equation with the reflective width at 2θ of 16 and 19° derived from the PMB and POB crystals, respectively. The peak of 19° for the POB diffraction can be indexed as (110) according to the previously reported unit cell parameter.[28] With respect to the peak of 16° for the PMB diffraction, it cannot be indexed because the unit cell parameter of the PMB crystal has not been determined. Table 2 summarizes the calculations. The diffraction peaks at 2θ of 16° are slightly larger than that of the PMB whisker, but relatively narrow with half-width equal to 0.36° for PODS and POTS. Thus, Ds are on the order of 300 Å, and there is no significant difference between Ds of PODS and POTS whiskers obtained after 6 h. With respect to the diffraction peaks at 2θ of 19°, they are also slightly larger than that of the POB whisker but are relatively narrow with half-widths equal to 0.52° for PODS and 0.47° for POTS. Ds of PODS and POTS are estimated to be on the order of 180−200 Å. These data indicate that the regularity of

Table 2. Average Diameter of Crystalline Area (*D*) of PODS and POTS Whiskers

	peak at 2θ of 16°		peak at 2θ of 19°	
polymer code[a]	reflective half-width (deg)	D (Å)[b]	reflective half-width (deg)	D (Å)[b]
POB	*c*		0.39	268
PMB	0.26	697	*c*	
PODS	0.36	303	0.52	180
POTS	0.36	300	0.47	194

[a] Polymer codes are shown in Scheme 1. [b] *D* was estimated by using Scherrer's equation from the reflective width at 2θ around 16 and 19°. [c] Not detected.

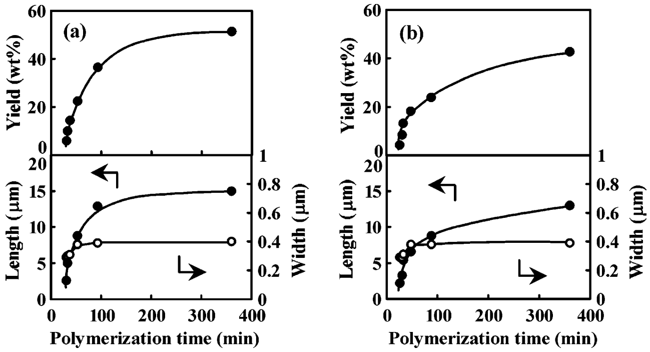

Figure 3. Polymerization time dependence of length, width, and yield of (a) PODS and (b) POTS whiskers.

the crystalline structure of these whiskers is slightly lower compared with data for homopolymer whiskers due to a paracrystalline structure or axially shifted polymer chain orientation.

The change in the yield, size, and number of the whiskers were followed during the course of polymerization. Figure 3 shows the plots of the yield, the length, and the width of the whiskers as a function of polymerization time. In both polymerizations, the length of the whiskers increased preferentially with the yield, while the width increased slightly at the initial stage of polymerization and then became constant. This increase of the width was observed in the growth of the POB whisker as previously reported.[29] This result is due to lateral growth accompanied by spiral growth, which is caused by the significantly high degree of supersaturation of oligomers. The whiskers grow with the crystallization of the oligomers supplied continuously from the solution by the condensation reaction. The number of whiskers (N) was calculated from the yield, the density, and the experimentally obtained shape parameters of the whiskers assuming that the cross section of these whiskers is hexagonal like POB whiskers.[3] Figure 4 shows N at different polymerization times. Ns of PODS and POTS are almost constant at 3.7×10^{12} and 3.5×10^{12} L^{-1} throughout the polymerization, respectively. Once the nuclei are formed at the initial stage of polymerization, the oligomers precipitated from the solution after nucleation are incorporated to grow the whiskers. Figure 5 is also a plot of the composition of the whiskers as a function of polymerization time. χ_O of PODS whiskers obtained at 8 min is 62 mol % and it is 12 mol % larger than the corresponding value in the feed. Then χ_O decreases with time to 49 mol % at 100 min. Of course, the molar ratio of S unit (χ_S) in the whiskers increased from 38 mol % to 51 mol % until 100 min, corresponding to the decrease of χ_O. With respect to POTS whiskers, χ_O obtained at 8 min is 77 mol % and it is 27 mol % larger compared with that in the feed. Then χ_O also decreases gradually with time to 48 mol %. χ_S increases from 23 to 52 mol % with time, as well as PODS whiskers. These facts obviously reveal that these whiskers possess a graded composition from O-unit-rich in center part to S-unit-rich in the tip. These results also suggest that the

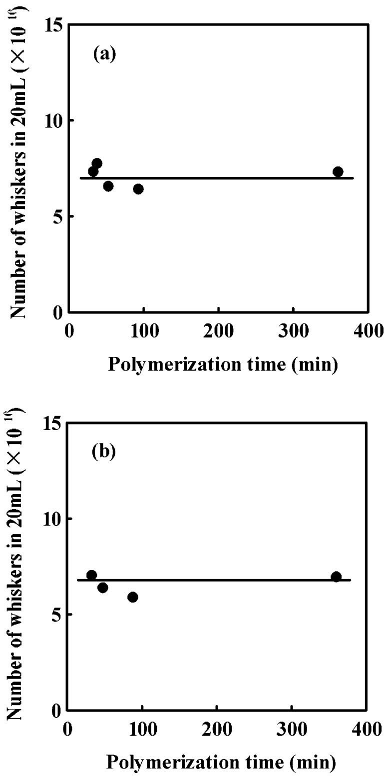

Figure 4. Plots of number of (a) PODS and (b) POTS whiskers as a function of polymerization time.

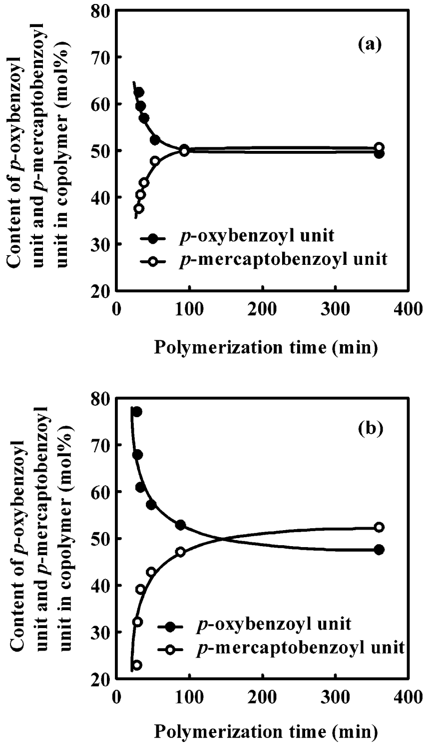

Figure 5. Plots of content of *p*-oxybenzoyl unit and *p*-mercaptobenzoyl unit in (a) PODS and (b) POTS whiskers as a function of polymerization time.

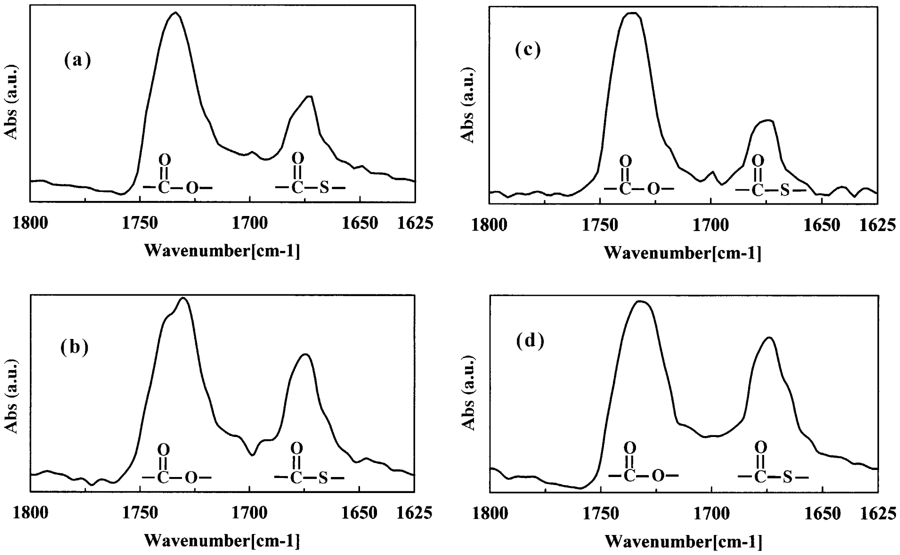

Figure 6. FT-IR spectra of PODS whiskers prepared for (a) 8 min and (b) 6 h, and POTS whiskers prepared for (c) 8 min and (d) 6 h.

oligomers rich in O units are preferentially precipitated at the early stages of polymerization and then the oligomers containing S unit are gradually precipitated to form the crystals. The gradient in composition is amplified by the increase of O units in raw oligomers. The composition of each crystal was analyzed by microscopic FT-IR spectroscopy. FT-IR spectra of more than 60 samples were measured. Figure 6 illustrates the representative spectra of PODS whiskers prepared for 8 min and 6 h. The spectra of the crystals do not show the bands characterized as the raw materials such as C═O of acetyl group and carboxyl group. The bands of C═O of ester linkage and thioester linkage were observed at 1735 and 1673 cm^{-1}, respectively, and this result confirms the formation of copolymers. To estimate the intensity ratio of these two bands, these two bands were clearly resolved using the combined Lorentzian and Gaussian functions, as previously reported.[14] Intensity ratio of the ester C═O and thioester C═O ($I_{1735\text{cm}^{-1}}/I_{1673\text{cm}^{-1}}$) is 1.99 for PODS whiskers obtained for 8 min and 1.52 for those obtained after 6 h. Their coefficients of variation (c_v), defined as the percentage of standard deviation divided by the average value, are 8.6 and 6.9%, respectively. There is no significant difference among more than 60 spectra and the composition is almost the same in the whiskers. With respect to POTS, the intensity ratio is 2.16 for the whiskers obtained for 8 min and 1.43 for those after 6 h. Their c_v values are 8.6 and 6.2%, respectively. The composition of the whiskers is graded from O-unit-rich to S-unit-rich along the direction from the center to the tip, and POTS possesses the larger gradient composition compared to PODS.

On the basis of these results, the gradient composition in the whiskers is plotted in Figure 7 as a function of the length and the width from the center part of the whiskers. As shown in this figure, the whiskers possess a graded composition along the length and width, and the composition is altered from O-unit to S-unit from the center to the outer part. The slope of the gradient in POTS is slightly steeper than that in PODS.

The dissolved oligomers were analyzed by ^{1}H NMR as shown in Figures 8 and 9. With respect to the polymerization of AMBA and OO, the average molar ratio of 1,4-phenylene group and acetyl end group of the dissolved oligomers is ca. 2 and it is constant during polymerization. This fact suggests that many oligomers crystallized in the form of whiskers contain OO se-

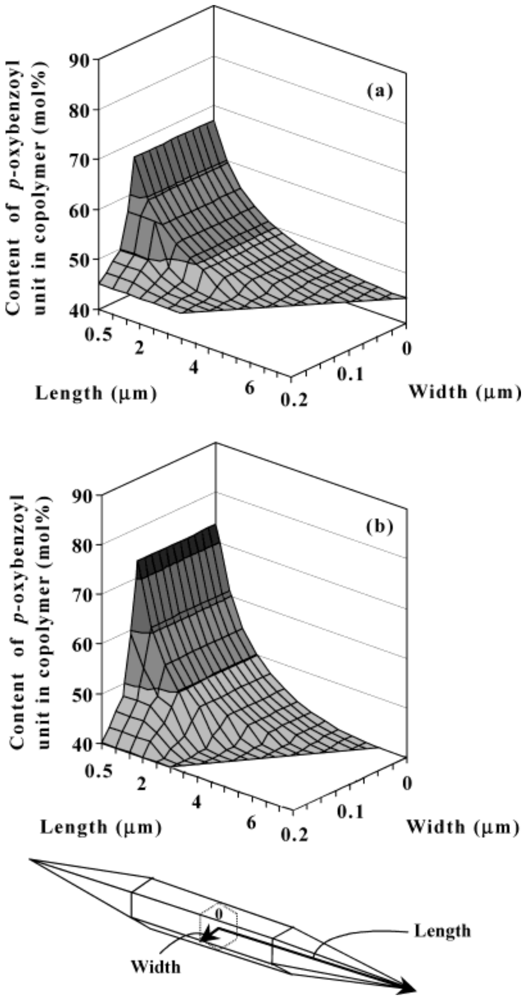

Figure 7. Plots of gradient composition in (a) PODS and (b) POTS whiskers as a function of the length and the width from the center part.

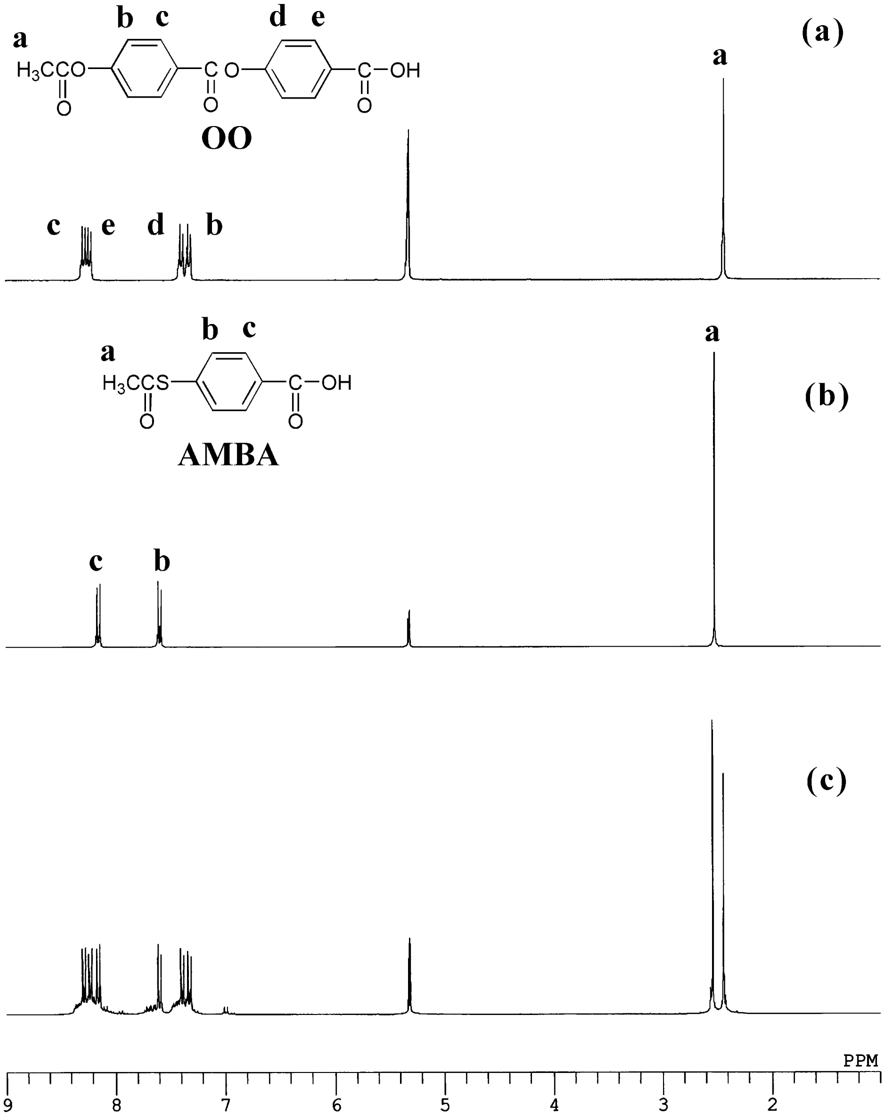

Figure 8. ^{1}H NMR spectra of (a) OO, (b) AMBA, and (c) dissolved oligomers prepared from OO and AMBA for 28 min.

quences in the early stage of polymerization. The transesterification reaction occurs during the copolymerization. The transesterification reaction may cause reshuffling of OO sequences in oligomers and, ultimately, the sequence randomization of the copolymers. As previously reported,[13,14] if the formation rate of phase-separated oligomers is much higher than that of the transesterification reaction, the oligomers are precipitated to form crystals that maintain the sequence. In the polymerization of monomers with an alternating sequence consisting of O unit and S unit, the rate constant of the transesterification reaction has been reported and is tabulated for comparison in Table 3. The formation of the crystallized oligomers was monitored by the recovery of the oligomers dissolved in the solution at different polymerization time. It has been reported that the polycondensation of ABA obeyed second-order kinetics[30−33] and the transesterification of aromatic copolyesters also obeyed second-order kinetics.[34−37] Figure 10 shows that the formation of oligomers obeys second-order kinetics and rate constants are determined as summarized in Table 3. The crystallized oligomers are formed 13.3 times faster than the transesterification reaction. It can be said that the oligomers containing OO sequence are preferentially precipitated to form the whiskers at the early stage of polymerization. On the other hand, the average molar ratio of 1,4-phenylene group and acetyl end group of the dissolved oligomers formed from OOO and AMBA is ca. 2.0. This result indicates that the average degree of polymerization of the precipitated oligomers is almost the same in both polymerizations. Figure 10 also shows that the formation of oligomers obeys second-order kinetics as does the polymerization of OO and AMBA. The crystallized oligomers are formed 8.6 times faster than the transesterification reaction. The oligomers rich in O units containing OOO sequences are preferentially precipitated to form the whiskers at the early stage of polymerization. In both polymerizations, the oligomers rich in O unit sequences are precipitated at the early stage and then the oligomers poor in O units are precipitated to form the whiskers.

Thermal Properties. Thermal properties of the resulting whisker are summarized in Table 4. 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 molecules by a rotation of *p*-phenylene rings around σ-bonds in the para position.[38−42] Both crystallinity and

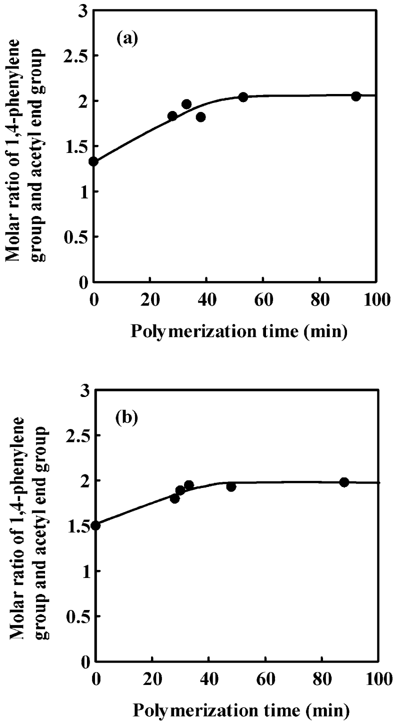

Figure 9. Polymerization time dependence of the molar ratio of 1,4-phenylene groups and end groups of dissolved oligomers prepared from (a) OO + AMBA and (b) OOO + AMBA.

Table 3. Second-Order Rate Constants at 300 °C in LPF

monomer	formation rate constant of crystallized oligomer k_2f (L·mol^{-1}·min^{-1})	trans-esterification rate constant[a] k_2t (L·mol^{-1}·min^{-1})	k_2f/k_2t
OO + AMBA	0.93	0.07	13.3
OOO + AMBA	0.60		8.6

[a] Cited from ref 14.

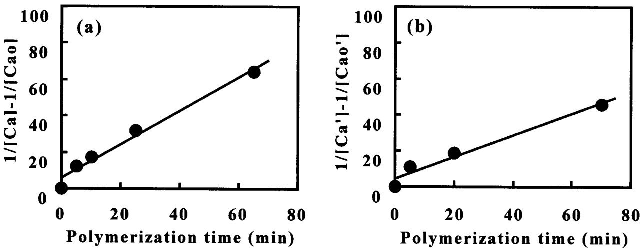

Figure 10. Kinetics of second-order reaction for formation of crystallized oligomers in the polymerization of OO + AMBA and (b) OOO + AMBA. [Ca], [Ca′]: concentrations of crystallized oligomers, [Cao] = 5.85 × 10^{-2} mol·L^{-1}, [Cao′] = 5.20 × 10^{-2} mol·L^{-1}.

Table 4. Thermal Properties of Whiskers[a]

polymer code[b]	monomer	DSC		
		T_t[c] (°C)	ΔH (J·g^{-1})	T_n[d] (°C)
PO/S-0.5	ABA + AMBA	*e*		377
PODS	OO + AMBA	217.0	10.5	392
POTS	OOO + AMBA	226.0	9.5	388

[a] Polymers were prepared at 300 °C for 6 h. [b] PO/S-0.5 stands for a random copolymer prepared from ABA and AMBA. PODS and POTS are shown in Scheme 1. [c] T_t: Solid−solid transition temperature was measured on the heating scan at a heating rate of 10 °C·min^{-1} in nitrogen. [d] T_n: Nematic transition temperature was measured on an optical microscope with heating stage under crossed polarization. [e] Not detected.

packing of polymer chains have a great influence on the transition temperature (T_t) and its enthalpy (ΔH). The crystals having higher crystallinity and closer packing show higher T_t and larger ΔH.[7,43] Concerning the random copolymer of ABA and AMBA at a molar ratio of 0.5 (PO/S-0.5), the transition is not detected due to the absence of well-organized chain packing.[13,14] In contrast to this result, PODS and POTS show the transition at 217 and 226 °C with ΔH values of 10.5 and 9.5 J·g^{-1}, respectively. This finding indicates that the regular sequence enhances crystallinity and better chain packing.

These copolymers exhibit liquid crystal transition from crystalline to nematic phase. It has been reported that transition temperature (T_n) of copolymers depends on the sequence regularity and that a regular sequence increases T_n due to stronger interaction between polymer molecules.[44] T_n values of PODS and POTS are 392 and 388 °C, respectively. They are 10−15 °C higher than that of PO/S-0.5, which is 377 °C, as previously reported.[13,14]

Conclusions

Whiskers composed of O units and S units having graded composition are successfully prepared by reaction-induced crystallization of oligomers. They possess extremely high crystallinity. The compositions of the whiskers are graded from O-unit-rich to S-unit-rich in the direction from the center part to the tip. The increase of O unit in raw oligomers enhances the gradient composition of the whiskers. POTS whiskers possess a larger gradient composition than that of PODS whiskers. The crystallized oligomer formation rate was much higher than the transesterification reaction rate and this leads to precipitation of oligomers with maintaining O unit sequence in raw oligomers. In both polymerizations, the oligomers rich in O unit sequences precipitated in the early stage of polymerization, and then the oligomers poor in O units were precipitated to form the whiskers.

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