Morphology Control of Poly(*p*-mercaptobenzoyl) by Modification of Oligomer End-group

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ABSTRACT: Influence of acyl end-group of oligomers on morphology of poly(*p*-mercaptobenzoyl)(PMB) was examined by the polymerization of *S*-acyl-4-mercaptobenzoic acids having the different acyl groups and their dimers in liquid paraffin at 260–300 °C. The polymerization of *S*-acetyl-4-mercaptobenzoic acid afforded PMB whiskers, whereas the polymerization of *S*-propionyl-4-mercaptobenzoic acid, *S*-butyryl-4-mercaptobenzoic acid and *S*-valeryl-4-mercaptobenzoic acid yielded PMB microspheres. The microspheres were formed by the liquid–liquid phase separation of oligomers induced by the longer acyl end-groups than acetyl group of the oligomers due to the reduction of freezing point of oligomers. In contrast to this, the polymerizations of their dimers afforded needle-like and slab-like crystals instead of microspheres. In these polymerizations, the crystallization was induced due to the increase of the molecular weight of the phase-separated oligomers, leading to the increase of the freezing point of oligomers. The morphology of PMB could be controlled by the chemical modification of oligomer end-groups.

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Phase Separation / End-group /

Performance and functionality of polymeric materials are usually governed by not only polymer structure but also morphology including polymer chain alignment, and therefore morphology control is of great importance to withdraw the potentiality expected from the polymer structure. Wholly aromatic polymers have been receiving considerable attention as hopeful candidates for high performance and functional polymeric materials due to their excellent properties such as thermal stability, mechanical properties, solvent resistance, optical properties and so on. However, many of them exhibit neither solubility nor fusibility due to their rigid structures. The relationship between the property and the processability is trade-off and many efforts have been made to overcome this antagonistic problem from the aspect of not only chemical modification of polymer structures¹ but also processing techniques.²

We have been studying morphology control of rigid aromatic polymers during solution polymerization and succeeded in preparing the whiskers of poly(*p*-mercaptobenzoyl) (PMB)^{3,4} and other aromatic polyesters.^{5–12} The PMB whiskers are prepared by the polymerization of *S*-acetyl-4-mercaptobenzoic acid (AMBA) in liquid paraffin (LPF) at 300 °C. The polymer chains are aligned along the long axis of the whiskers and the whiskers show single crystal nature.

The formation mechanism of the whisker contains following steps. Oligomers are precipitated from the solution to form lamellae, when molecular weight of oligomers exceeds a critical value. The lamellae pile up in the form of needle-like crystals with spiral growth. Solid-state polymerization occurs in the needle-like oligomer crystals and the whiskers consisted of high molecular weight extended polymer chains are eventually formed.^{3,4}

Reaction-induced phase-separation of oligomers which is a key process to control the morphology involves two modes, one is crystallization and another is liquid–liquid phase separation. Miscibility between oligomer and solvent is a determinant factor for phase-separation mode, and it is significantly affected by the structure of solvent and oligomer besides polymerization temperature. It seems likely that chemical structure of oligomer end-groups affects the miscibility leading to the morphology control. In this paper, influence of oligomer end-group on the morphology of PMB is elucidated by polymerization of *S*-acyl-4-mercaptobenzoic acids having different acyl groups. Furthermore, influence of molecular weight of phase-separated oligomers on the morphology is also examined by polymerization of *S*-(*S*-acyl-4-mercaptobenzoyl)-4-mercaptobenzoic acids as shown in Scheme 1.

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Scheme 1. Synthesis of poly(*p*-mercaptobenzoyl).

EXPERIMENTAL

Materials

4-Mercaptobenzoic acid and AMBA were prepared according to the previous procedure.^{13–16} Propionyl chloride, butyryl chloride, valeryl chloride, hexanoyl chloride, thionyl chloride and *N,N*-dimethylformamide were purchased from Aldrich Co. Ltd. and used as received. LPF was purchased from Nacalai Tesque Co. Ltd. and purified by vacuum distillation (220–240 °C/0.3 mmHg).

Characterization

Morphology of the polymer crystal was observed with Hitachi S-3500N scanning electron microscope. Samples for SEM observation were dried, sputtered with gold and observed at 20 kV. FT-IR spectra were measured on JASCO FT/IR-410 spectrometer. Chemical structures of monomers, dimers and the oligomer model compounds were characterized by ¹H NMR Bruker AVANCE500 operating at 500 MHz. NMR spectra were measured in CDCl₃ or CDCl₃/CF₃COOH. WAXS pattern was measured by Rigaku diffractometer Gaiger Flex with nickel-filtered CuKα radiation (35 kV, 20 mA). Thermal stability was measured on a PerkinElmer TGA 7 at heating rate of 20 °C min^{−1} in nitrogen atmosphere. Melting temperature (*T*_m) was measured on a PerkinElmer DSC 7 at scanning rate of 10 °C min^{−1} in nitrogen atmosphere. Density of the microspheres was measured by floatation method using tetrachloromethane and *p*-xylene at 25 °C. Diameter of the microspheres was determined by the average of over 100 observation values.

Synthesis of S-Acyl-4-mercaptobenzoic Acids

Synthesis of S-propionyl-4-mercaptobenzoic acid (PMBA) was described as a typical procedure. Into a flask equipped with a dropping funnel, a thermometer and a gas inlet tube were placed 4-mercaptobenzoic acid (2.00 g, 13 mmol), triethylamine (3.95 g,

28.6 mmol) and 20 mL of dried tetrahydrofuran. Solution of propionyl chloride (1.20 g, 13.0 mmol) in 10 mL of dried tetrahydrofuran was added dropwise through the dropping funnel under slow stream of nitrogen at 5 °C. Reaction temperature was kept at 5 °C for 2 h and then 25 °C for 12 h. The reaction mixture was filtrated to separate triethylamine–HCl salts, and then acidified by diluted HCl solution. White precipitates were collected and washed with water. Recrystallization from toluene/*n*-hexane gave 1.91 g (70%) of PMBA crystals. Purity was over 99.5% checked by HPLC. Product characteristics: *T*_m: 162 °C. IR (KBr, cm^{−1}): 3300–2500 (OH), 3080 (1,4-phenylene C–H), 2981 (propionyl C–H), 1691 (ester, carboxylic acid C=O), 1593, 1564, 1492 (1,4-phenylene C=C). ¹H NMR (CDCl₃/CF₃COOH, ppm): δ = 8.13 (d, aromatic, 2H, *J* = 8.0 Hz), 7.56 (d, aromatic, 2H, *J* = 8.0 Hz), 2.78 (q, –CH₂CH₃, 2H, *J* = 7.4 Hz), 1.28 (t, –CH₂CH₃, 3H, *J* = 7.4 Hz).

S-Butyryl-4-mercaptobenzoic acid (BMBA) and S-valeryl-4-mercaptobenzoic acid (VMBA) were also synthesized by the similar procedure to PMBA. Characteristics of BMBA: *T*_m: 163 °C. IR (KBr, cm^{−1}): 3300–2500 (OH), 3079 (1,4-phenylene C–H), 2960 (butyryl C–H), 1702 (ester, carboxylic acid C=O), 1594, 1566, 1491 (1,4-phenylene C=C). ¹H NMR (CDCl₃/CF₃COOH, ppm): δ = 8.13 (d, aromatic, 2H, *J* = 8.6 Hz), 7.55 (d, aromatic, 2H, *J* = 8.6 Hz), 2.73 (t, –CH₂CH₂CH₃, 2H, *J* = 7.6 Hz), 1.78 (m, –CH₂CH₂CH₃, 2H), 1.02 (t, –CH₂CH₂CH₃, 3H, *J* = 7.3 Hz). Characteristics of VMBA: *T*_m: 166 °C. IR (KBr, cm^{−1}): 3300–2500 (OH), 3080 (1,4-phenylene C–H), 2956 (valeryl C–H), 1699 (ester, carboxylic acid C=O), 1595, 1566, 1493 (1,4-phenylene C=C). ¹H NMR (CDCl₃/CF₃COOH, ppm): δ = 8.12 (d, aromatic, 2H, *J* = 8.6 Hz), 7.55 (d, aromatic, 2H, *J* = 8.6 Hz), 2.73 (t, –CH₂CH₂CH₂CH₃, 2H, *J* = 7.8 Hz), 1.73 (m, –CH₂CH₂CH₂CH₃, 2H), 1.42 (m, –CH₂CH₂CH₂CH₃, 2H), 0.94 (t, –CH₂CH₂CH₂CH₃, 3H, *J* = 7.2 Hz).

Synthesis of S-(S-Acyl-4-mercaptobenzoyl)-4-mercaptobenzoic Acids

Synthesis of *S*-(*S*-propionyl-4-mercaptobenzoyl)-4-mercaptobenzoic acid (PMBA dimer) was described as a typical procedure. Into a flask equipped with a thermometer and a gas inlet tube were placed PMBA (2.00 g, 9.5 mmol) and 20 mL of thionyl chloride. Several drops of *N,N*-dimethylformamide were added into the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 24 h. *N,N*-Dimethylformamide–HCl salts were filtrated off and then excess of thionyl chloride was stripped off under vacuum. The pale yellow oil of *S*-propionyl-4-mercaptobenzoyl chloride was obtained with the yield of 2.30 g (96%). Into a flask equipped with a thermometer, a dropping funnel and a gas inlet tube were placed 4-mercaptobenzoic acid (1.60 g, 10.1 mmol), crude *S*-propionyl-4-mercaptobenzoyl chloride (2.30 g, 10.1 mmol) and 20 mL of dried tetrahydrofuran. Solution of triethylamine (1.30 g, 12.8 mmol) in 10 mL of dried tetrahydrofuran was added dropwise through the dropping funnel under slow stream of nitrogen at 5 °C. Reaction temperature was kept at 5 °C for 2 h and then 25 °C for 12 h. The reaction mixture was filtrated to separate triethylamine–HCl salts and then acidified by diluted HCl solution. White precipitates were collected and washed with water. Recrystallization from ethyl acetate/*n*-hexane gave 2.10 g (60%) of PMBA dimer crystals. Purity was 99.4% checked by HPLC. Product characteristics: T_m : 177 °C. IR (KBr, cm^{-1}): 3300–2500 (OH), 3080, 3060 (1,4-phenylene C–H), 2960 (propionyl C–H), 1699 (ester C=O), 1678 (carboxylic acid C=O), 1590, 1562, 1490 (1,4-phenylene C=C). ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$, ppm); δ = 8.19 (d, aromatic, 2H, J = 8.6 Hz), 8.06 (d, aromatic, 2H, J = 8.7 Hz), 7.67 (d, aromatic, 2H, J = 8.6 Hz), 7.59 (d, aromatic, 2H, J = 8.7 Hz), 2.80 (q, $-\text{CH}_2\text{CH}_3$, 2H, J = 7.5 Hz), 1.29 (t, $-\text{CH}_2\text{CH}_3$, 3H, J = 7.5 Hz).

S-(*S*-Butyryl-4-mercaptobenzoyl)-4-mercaptobenzoic acid (BMBA dimer), and *S*-(*S*-valeryl-4-mercaptobenzoyl)-4-mercaptobenzoic acid (VMBA dimer) were also synthesized by the similar procedure to the PMBA dimer. Characteristics of BMBA dimer: T_m : 162 °C. IR (KBr, cm^{-1}): 3300–2500 (OH), 3080, 3060 (1,4-phenylene C–H), 2960 (butyryl C–H), 1699 (ester C=O), 1678 (carboxylic acid C=O), 1591, 1562, 1491 (1,4-phenylene C=C). ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$, ppm); δ = 8.19 (d, aromatic, 2H, J = 8.5 Hz), 8.07 (d, aromatic, 2H, J = 8.5 Hz), 7.67 (d, aromatic, 2H, J = 8.5 Hz), 7.59 (d, aromatic, 2H, J = 8.5 Hz), 2.75 (t, $-\text{CH}_2\text{CH}_2\text{CH}_3$, 2H, J = 7.6 Hz), 1.80 (m, $-\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 1.03 (t, $-\text{CH}_2\text{CH}_2\text{CH}_3$, 3H, J = 7.4 Hz). Characteristics of VMBA dimer: T_m : 147 °C. IR (KBr, cm^{-1}): 3300–2500 (OH), 3080, 3060 (1,4-phenylene C–H), 2960 (valeryl C–H),

1699 (ester C=O), 1678 (carboxylic acid C=O), 1591, 1562, 1491 (1,4-phenylene C=C). ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOH}$, ppm); δ = 8.19 (d, aromatic, 2H, J = 8.3 Hz), 8.07 (d, aromatic, 2H, J = 8.1 Hz), 7.67 (d, aromatic, 2H, J = 8.3 Hz), 7.59 (d, aromatic, 2H, J = 8.1 Hz), 2.77 (t, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H, J = 7.9 Hz), 1.75 (m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 1.43 (m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 0.96 (t, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 3H, J = 7.3 Hz).

Synthesis of Oligomer Model Compounds

Synthesis of phenyl *S*-(*S*-propionyl-4-mercaptobenzoyl)-4-mercaptobenzoate (PMBA oligomer model compound) was described as a typical procedure. Into a flask equipped with a thermometer and a gas inlet tube were placed PMBA dimer (3.64 g, 10.5 mmol) and 20 mL of thionyl chloride. Several drops of *N,N*-dimethylformamide were added into the reaction mixture at 25 °C. Reaction mixture was stirred at 25 °C for 24 h. *N,N*-Dimethylformamide–HCl salts were filtrated off and then excess of thionyl chloride was stripped off under vacuum. The crude solid of *S*-(*S*-propionyl-4-mercaptobenzoyl)-4-mercaptobenzoyl chloride was obtained with the yield of 3.50 g (96%). Into a flask equipped with a thermometer, a dropping funnel and a gas inlet tube were placed thiophenol (1.32 g, 12.0 mmol), crude *S*-(*S*-propionyl-4-mercaptobenzoyl)-4-mercaptobenzoyl chloride (2.93 g, 8.01 mmol) and 20 mL of dried tetrahydrofuran. Solution of triethylamine (0.97 g, 9.61 mmol) in 10 mL of dried tetrahydrofuran was added dropwise through the dropping funnel under the slow stream of nitrogen at 5 °C. Reaction temperature was kept at 5 °C for 2 h and then 25 °C for 12 h. The reaction mixture was filtrated to separate triethylamine–HCl salts and then acidified by diluted HCl solution. White precipitates were collected and washed with water. Recrystallization from ethyl acetate/*n*-hexane gave 2.11 g (60%) of PMBA oligomer model compound as crystals. Purity was 99.3% checked by HPLC. Product characteristics: T_m : 99 °C. IR (KBr, cm^{-1}): 3300–2500 (OH), 3080, 3060, 3051 (1,4-phenylene C–H), 2973 (propionyl C–H), 1699 (ester C=O), 1666 (thioester, C=O), 1585, 1558, 1477 (1,4-phenylene C=C). ^1H NMR (CDCl_3 , ppm); δ = 8.09 (d, aromatic, 2H, J = 8.5 Hz), 8.03 (d, aromatic, 2H, J = 8.5 Hz), 7.46–7.67 (m, aromatic, 9H), 2.73 (q, $-\text{CH}_2\text{CH}_3$, 2H, J = 7.5 Hz), 1.25 (t, $-\text{CH}_2\text{CH}_3$, 3H, J = 7.5 Hz).

Phenyl *S*-(*S*-acetyl-4-mercaptobenzoyl)-4-mercaptobenzoate (AMBA oligomer model compound) was also synthesized by the similar procedure to *S*-(*S*-propionyl-4-mercaptobenzoyl)-4-mercaptobenzoate. Characteristics of phenyl *S*-(*S*-acetyl-4-mercaptobenzoyl)-4-mercaptobenzoate: T_m : 107 °C. IR (KBr, cm^{-1}): 3300–2500 (OH), 3080, 3052 (1,4-phenylene

C–H), 1706 (ester C=O), 1670 (thioester, C=O), 1585, 1560, 1477 (1,4-phenylene C=C). ^1H NMR (CDCl_3 , ppm); δ = 8.09 (d, aromatic, 2H, J = 8.5 Hz), 8.04 (d, aromatic, 2H, J = 8.6 Hz), 7.46–7.66 (m, aromatic, 9H), 2.47 (s, acetyl, 3H).

Polymer Synthesis

Polymerization of PMBA was described as follows. Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed PMBA (0.31 g, 1.47 mmol) and 20 mL of LPF. Reaction mixture was heated under slow stream of nitrogen up to 300 °C with stirring. Stirring was stopped when PMBA was entirely dissolved. Temperature was maintained at 300 °C for 6 h. Precipitated polymer products were collected by vacuum filtration at 300 °C and washed with *n*-hexane and acetone. After being allowed to cool, filtrate was poured into *n*-hexane, and precipitated oligomers which were dissolved in LPF at 300 °C were recovered by filtration. IR of polymer (KBr, cm^{-1}): 3080, 3046, 1670, 1584, 1558, 1486, 1396, 1300, 1278, 1203, 1181, 1085, 1018, 913, 886, 852, 826, 731, 638, 584, 465.

Determination of Number Average Degree of Polymerization of Polymer and Oligomer

Sample (10 mg) and 1 mL of 7.0 wt % KOH methanol solution were placed in a test tube, and kept at 25 °C until the sample was completely hydrolyzed. The solution was neutralized with dilute hydrochloric acid and then analyzed by using Shimadzu GC-14B gas chromatography with a Thermo-3000 (60–80 mesh) packed column. Number average degree of polymerization (DP_n) was calculated by the molar ratio of 4-mercaptobenzoic acid and corresponding aliphatic acid.

Preparation of Phase Diagrams of Oligomer Model Compounds

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

RESULTS AND DISCUSSION

Polymerization of *S*-Acyl-4-mercaptobenzoic Acids

Four *S*-acyl-4-mercaptobenzoic acids having different acyl group were synthesized and polymerized in

Table I. Results of polymerization^a

Monomer and dimer code ^b	Polymerization temperature (°C)	Yield (%)	Morphology
AMBA	300	36.0	Needle-like
	280	47.5	Needle-like
	260	33.5	Needle-like
PMBA	300	44.5	Spherical
	280	28.5	Spherical
	260	5.5	Spherical
BMBA	300	30.6	Spherical
	280	22.5	Spherical
	260	8.8	Spherical
VMBA	300	21.8	Spherical
	280	20.2	Spherical
	260	19.0	Spherical
PMBA dimer	300	21.0	Needle-like
BMBA dimer	300	6.7	Slab-like
VMBA dimer	300	25.0	Needle-like

^aPolymerizations were carried out in LPF for 6 h. ^bMonomer and dimer codes are shown in Scheme 1.

LPF at 260–300 °C. Table I summarizes the polymerization results. All monomers were insoluble into LPF at room temperature, but they were dissolved around 230 °C during heating. As aforesaid, polymerizations of AMBA yielded the PMB whiskers at every temperature. In contrast to this, polymerizations of other monomers did not afford the whiskers and the products did not exhibit clear crystal habit as shown in Figure 1. Microspheres were obtained from PMBA, of which the diameter was *ca.* 3 μm . Aggregates of microspheres having 1–2 μm diameter were obtained from BMBA and VMBA. PMB is insoluble into organic solvents, and hence FT-IR spectra were measured to analyze the chemical structure. C=O stretching band of thioester linkage appears at around 1670 cm^{-1} , and three sharp bands of 1,4-phenylene C=C are observed at 1590–1480 cm^{-1} in the spectra of the obtained microspheres. O–H stretching band of carboxylic acid at 3300–2500 cm^{-1} and C–H stretching band of acyl group at 3000–2900 cm^{-1} of monomers disappear. These results confirm that the obtained microspheres are comprised of PMB. DP_n of the microspheres prepared from PMBA at 300 °C was estimated 53 by the end-group analysis after hydrolysis. WAXS pattern of the microspheres prepared from PMBA is shown in Figure 2. Sharp Debye-Scherrer rings are clearly observed and the diffuse ring from amorphous parts does not exist. These microspheres possess quite high crystallinity. The morphology of PMB is drastically changed from the needle-like crystals to the microspheres by the chemical modification of the acyl group in monomers.

Figure 1. Morphology of PMB products prepared from (a) AMBA, (b) PMBA, (c) BMBA and (d) VMBA at 300 °C.

Figure 2. WAXS patterns of (a) microspheres prepared from PMBA and (b) whiskers prepared from PMBA dimmer at 300 °C for 6 h.

Reaction-induced phase separation of oligomers in poor solvent is describable on an analogous concentration-temperature phase diagram (C - T phase diagram) to that of partially miscible polymer-solvent system as previously reported.^{17,18} Phase separation curve in repulsive system in which there is no attractive interaction between oligomer and solvent is written as the combination of a freezing point curve of oligomers and an upper critical solution temperature type consolution curve. Figure 3 is a schematic illustration of the phase diagram. DPn of the oligomers in homogeneous solution increases with the progress of condensation reaction. When DPn of oligomers exceeds a critical value, oligomers are phase-separated

via super-saturated state. If the oligomers are precipitated across the freezing point curve, they are precipitated by the crystallization to form the crystals. On the other hand, if precipitated across the consolution curve, microdroplets are formed *via* liquid-liquid phase separation and microspheres are finally obtained as previously reported.^{19,20} The polymerization of AMBA yields the PMB whiskers formed *via* the crystallization of oligomers as aforesaid. Other monomers afford only the microspheres and the spherical morphology indicates that these microspheres are obtained *via* the formation of microdroplets by liquid-liquid phase separation of oligomers and further polymerization in them. Longer acyl end-groups than

Figure 3. Schematic illustration of C - T phase diagrams for the system of LPF and oligomers prepared from (a) AMBA and (b) PMAB. L: miscible liquid phase, L-L: two liquids phase, L-S: liquid and solid phase.

acetyl end-group induce liquid-liquid phase separation of oligomers. In order to clarify the formation mechanism, location of the phase separation curve in the polymerization system of PMBA is compared with that of AMBA by being divided into the freezing point curve and the consolution curve. The oligomers are insoluble into organic solvents under the temperature at which the polymerization starts. Therefore, the phase-separated oligomers cannot be isolated. Absolute location of the consolution curve and the freezing point curve of the phase-separated oligomer cannot be accurately determined. Oligomers dissolved into LPF were collected just before the solution became turbid, and DPn of the oligomers dissolved in solution at which the phase separation started were estimated by end-group analysis after hydrolysis. DPns of the oligomers prepared from AMBA and PMBA are 1.81 and 1.85, respectively. This fact suggests that DPn of the phase-separated oligomers prepared from PMBA is slightly higher than that from AMBA. The structural difference in acyl end-groups of the oligomers, that is one methylene moiety, does not influence markedly the miscibility of oligomers. It can be inferred that the consolution curve of the oligomer prepared from PMBA is located at nearly the same position as that from AMBA or slightly shifted toward lower temperature on the C - T phase diagram. With respect to the freezing point curve, it is governed by both the freezing point of oligomers and its depression in LPF. Relative location of the freezing point curve is inferred from thermal data of monomers. Table II

Table II. Thermal properties of S -acyl-4-mercaptobenzoic acids^a

Monomer code ^b	T_m (°C)	ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)
AMBA	206	24.9	52.0
PMBA	162	18.3	42.1

^ameasured on DSC with a scanning rate of 10 °C min⁻¹ in nitrogen atmosphere. ^bMonomer codes are shown in Scheme 1.

shows T_m and thermodynamic parameter of monomers determined on DSC. T_m s of S -acetyl-4-mercaptobenzoic acids having longer acyl group than acetyl group such as PMBA, BMBA and VMBA are *ca.* 40 °C lower than that of AMBA and it is predominantly ascribed to the decrease of ΔH rather than ΔS . The longer acyl group weakens significantly cohesive force between 4-mercaptobenzoyl unit in monomers, and it results in the enormous decrease in the T_m . The freezing point curves of oligomers can be discussed from the analogy with these results of monomers as follows. The oligomers prepared from PMBA, BMBA and VMBA possess lower freezing points compared with that from AMBA, and thereby the freezing point curves of these oligomers shift toward lower temperature than that of the oligomers from AMBA. The depression of the freezing point is highly related to the miscibility between the oligomers and the solvent, and the degree of the depression becomes larger in the more miscible system. In the case of PMB, the miscibility between LPF and the oligomers having longer acyl end-groups than acetyl end-group is slightly higher compared with that between the oligomers prepared from AMBA and LPF. Thereby, the degree of the depression is slightly larger in the polymerization system of PMBA, BMBA and VMBA. After all, the consolution curve is located at nearly the same position and the freezing point curve of the phase-separated oligomers having longer acyl end-groups than acetyl end-group shifts toward lower temperature compared with that having acetyl end-group. As a result, the shift of the curves brings about a broad expansion of immiscible two liquids phase toward lower temperature, and the liquid-liquid phase separation is induced during the polymerization of monomers except AMBA as schematically shown in Figure 3. In order to confirm this interpretation, phenyl S -(S -acetyl-4-mercaptobenzoyl)-4-mercaptobenzoate (AMBA oligomer model compound) and phenyl S -(S -propionyl-4-mercaptobenzoyl)-4-mercaptobenzoate (PMBA oligomer model compound) were synthesized as the model compounds for the oligomer prepared from AMBA and PMBA, respectively. The C - T phase diagrams of these oligomer model compounds in LPF were obtained by the cloud point meas-

Figure 4. *C-T* phase diagrams for the system of LPF and (a) AMBA oligomer model compound and (b) PMBA oligomer model compound. L: liquid phase, L-L: two liquids phase, L-S: liquid and solid phase.

Figure 5. Plots of (a) (○) yield and (●) diameter, and (b) number of microspheres prepared from PMBA at 280 °C as a function of polymerization time.

urement as shown in Figure 4. The consolution curve of PMBA oligomer model compound shifts slightly toward lower temperature and its freezing point curve shifts largely toward lower temperature compared with that of AMBA oligomer model compound. Hence, the boundary line between two liquids phase and liquid-solid phase is located at lower temperature, and two liquids phase is widely expanded toward lower temperature in PMBA oligomer model compound-LPF system. This result strongly substantiates the above discussion.

Change in yield, diameter and number of the microspheres were examined in the course of the polymerization of PMBA to understand growth process of the microspheres as plotted in Figure 5. The diameter increases with the yield and this shows that the microspheres grow by consecutive supply of the oligomers from liquid phase. The number of the microspheres decreases at an initial stage in polymerization. This initial decrease can be ascribed to both the coalescence

of microdroplets and Ostwald ripening which is the dissolving process of small microdroplets due to the difference in the surface tension. The concentration of oligomer end-groups in the microdroplets becomes quite high and the further polymerization occurs rapidly in them. The increase of molecular weight reduces the solubility of oligomers, and thereby Ostwald ripening process cannot be a major process. The number of the microspheres becomes constant after 3 h. The increase of the molecular weight caused by the further polymerization results in the solidification of microdroplets and then the surface of the microspheres becomes stable. This stabilization of the surface ceases the coalescence of the microdroplets.

Inner structure of the microspheres was observed after etching the surface of the microsphere with *aq.* KOH solution as shown in Figure 6. The microspheres prepared for 6 h consist of small particles, of which the size is 0.1–0.5 μm. Plate-like morphology is observed in the microspheres obtained for 2 h and it is

Figure 6. Inner structures of PMB microspheres prepared from PMBA at 280 °C for (a) 2 h and (b) 6 h. Samples were etched in *aq.* KOH solution.

Figure 7. Whiskers prepared from (a) PMBA dimer, (b) BMBA dimer and (c) VMBA dimer.

quite different from that obtained for 6 h. The inner structure is developed by crystallization induced by the further polymerization in the microdroplets. From these results, the growth mechanism of the microspheres is proposed as follows. The microdroplets grow by not only the consecutive supply of oligomers from liquid phase but also the coalescence. Then the microdroplets are changed to microspheres by the solidification caused by further polymerization.

Polymerization of S-(S-Acyl-4-mercaptobenzoyl)-4-mercaptobenzoic Acids

It is indicated that the phase-separation curve comprised of a consolution curve and a freezing point curve is highly influenced by molecular weight of phase-separated oligomers and the phase-separation curve shifts toward higher temperature with the increase of molecular weight. It is expected that if the

phase-separation mode can be changed by the increase of DP_n of the phase-separated oligomers under the same polymerization condition, the morphology will be naturally varied. *S*-(*S*-Acyl-4-mercaptobenzoyl)-4-mercaptobenzoic acids having different acyl groups, which are the dimers of *S*-acyl-4-mercaptobenzoic acids, were synthesized and polymerized in LPF at 300 °C. Table I also summarizes the polymerization results. Figure 7 shows the obtained crystals from the PMBA dimer, BMBA dimer and VMBA dimer. The polymerizations of PMBA, BMBA and VMBA yield the microspheres as described before. In contrast to this, the polymerizations of these dimers afford polymer crystals, of which the morphology is needle-like or slab-like. Microspheres are not formed at all. The whiskers are formed from PMBA dimer and VMBA dimer and they grow radially from center points, of which the length is *ca.* 10 μm and the width

is *ca.* 0.5 μm . WAXS pattern of the whiskers prepared from PMBA dimers at 300 °C was also shown in Figure 2. Sharp Debye-Scherrer rings are clearly observed and these whiskers possess extremely high crystallinity.

This drastic change in the morphology of PMB can be accounted for the difference in the phase separation behavior of the oligomers. Relative location of the phase separation curve in the polymerization system of PMBA dimer is compared with that of PMBA. The oligomers were collected just before the polymerization solution becomes turbid. The DP_ns of the oligomers prepared from PMBA and PMBA dimer are 1.85 and 2.50, respectively. The phase-separated oligomers prepared from PMBA dimer have obviously higher DP_n compared with that from PMBA. On the *C*–*T* phase diagram, the difference in the DP_n of the phase-separated oligomers leads to the shift of the freezing point curve of the oligomers prepared from PMBA dimer toward higher temperature than that of PMBA. The miscibility of oligomer prepared from PMBA dimer into LPF is lower than that from PMBA due to the higher DP_n of the phase-separated oligomers and this leads to the shift of the consolution curve of the oligomers prepared from PMBA dimer toward higher temperature. Eventually the phase separation curve of the oligomers prepared from PMBA dimer is relatively located at higher temperature on the *C*–*T* phase diagram and the crystallization of oligomer is induced. The polymerizations of the dimers of *S*-acyl-4-mercaptobenzoic acids afford the PMB crystals *via* the crystallization of oligomers induced by the increase of the DP_n of the phase-separated oligomers.

CONCLUSIONS

The polymerization of AMBA yields the PMB whiskers, whereas the polymerizations of *S*-acyl-4-mercaptobenzoic acids having the longer acyl groups than acetyl group afford the PMB microspheres. The longer acyl end-groups induce the liquid–liquid phase separation due to the reduction of the freezing point of oligomers and the oligomers are phase-separated by liquid–liquid phase separation mode to form the microdroplets. The microdroplets grow by not only the consecutive supply of oligomers from liquid phase but also the coalescence, and they turn out to be microspheres by the solidification caused by further polymerization. On the other hand, the polymeriza-

tions of the dimers of *S*-acyl-4-mercaptobenzoic acid yield the PMB crystal of which the morphology is needle-like or slab-like. In these polymerizations, the crystallization of oligomers is induced due to the increase of molecular weight of the phase-separated oligomers and the crystals are obtained. The various morphology of PMB can be tuned by the chemical modification of the acyl end-group and the molecular weight of the phase-separated oligomers.

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