

Polymer whiskers based on *p*-mercaptobenzoyl and *p*-oxybenzoyl blocks

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Abstract

Preparation of polymer whisker based on *p*-mercaptobenzoyl (S) and *p*-oxybenzoyl (O) blocks was examined by the polymerization of S-acetyl-4-mercaptobenzoic acid (AMBA) and the following addition of 4-acetoxybenzoic acid (ABA). Polymerization of AMBA was carried out in liquid paraffin at 300 °C for 3 h yielding poly(*p*-mercaptobenzoyl) (PMB) whisker, and then ABA was added stepwise at 3-hour intervals into the solution. Initial polymerization concentration was 1.98%. The length of the whisker increased with the addition and it became 26.7 μm from 20.1 μm after third ABA addition. The width increased very slightly. Both length and width increased with polymer yield but the length increased preferentially rather than the width. The number of whiskers was constant even after the addition of ABA and poly(*p*-oxybenzoyl) (POB) whisker was not newly formed by the addition. Microscopic FT-IR and selected area electron diffraction measurements revealed that polymer molecules were aligned along the long axis of the whiskers, and the center and tip parts were comprised of PMB crystal and POB crystal, respectively. The polymer whisker based on S and O blocks was successfully prepared as grafting POB crystal on PMB whisker with stepwise addition of ABA. Thermal property of the resulting whiskers was also discussed.

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1. Introduction

Wholly aromatic polyesters and polythioesters such as poly(*p*-oxybenzoyl) (POB) and poly(*p*-mercaptobenzoyl) (PMB) are promising candidates for high performance materials due to excellent properties derived from rigid structures including thermal stability, mechanical property, chemical resistance and so on [1]. Some of them exhibit thermotropicity and afford the strong fibers, films and composites [2]. However, they are usually intractable and this makes them inaccessible for processing by conventional techniques.

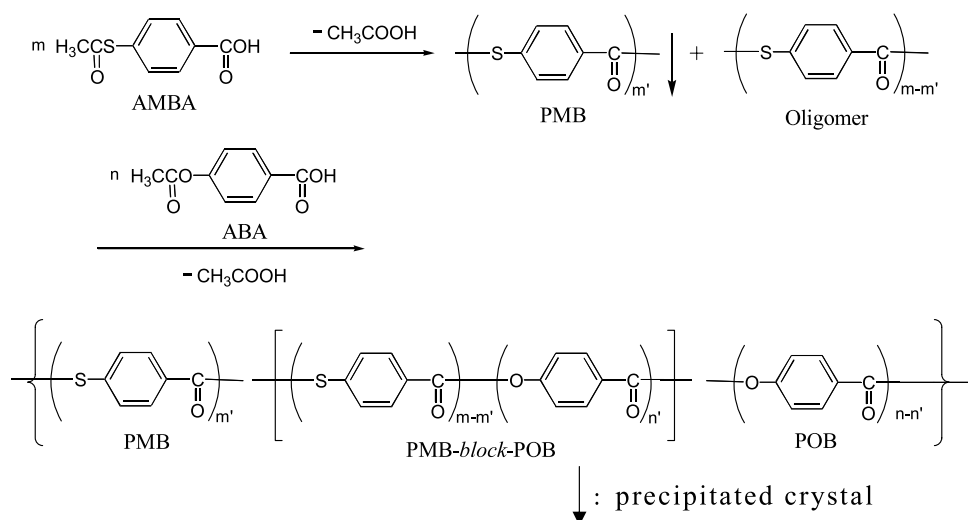
We have been studying morphology control of rigid polymers during solution polymerization to overcome the trade-off between property and processability derived from the rigid structure. POB and PMB whisker had been successfully prepared by the polymerizations of 4-acetoxybenzoic acid (ABA) [3,4] and S-acetyl-4-mercaptobenzoic

acid (AMBA) [5] in liquid paraffin (LPF) at around 300 °C. 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. The needle-like morphology with the polymer chain alignment is ideal to endow the essential properties. Formation mechanism of these whiskers involves the following three steps. When the degree of polymerization of oligomers exceeds a critical value, they are precipitated from the solution to form lamellae. The lamellae pile up in the form of needle-like crystals with spiral growth. Post-polymerization occurs efficiently in the needle-like crystals and the whiskers consisting of high molecular weight extended polymer chains are eventually formed.

The preparation of copolymer whisker is very interesting and desirable to tailor new functional and structural polymeric materials. Recently, the morphology control of poly(*p*-oxybenzoyl-*co*-*p*-mercaptobenzoyl) (POB-*co*-PMB) has been studied and poly(*p*-oxybenzoyl-*alt*-*p*-mercaptobenzoyl) whiskers were prepared by the control of short distance sequence regularity [6]. Functionally gradient

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Scheme 1. Preparation of polymer whiskers based on S and O blocks.

polymer composites are expected as a new type of materials which exhibit continuous variation in composition and microstructure in the multiple directions of the materials. Much attention has been paid to polymer composites [7–9]. Only polymer blend films are reported as the gradient materials to my knowledge [10]. Block copolymers have received recently much attention as new materials for nanoscale technology due to their regular phase-separated structures and they will be used as new optical and microelectronic devices [11]. Many of them are amorphous and semicrystalline polymers. Although polymer crystals having block sequences are expected to afford the new functional and high performance materials such as electronic devices like a semiconductor, reinforcements of interface between two polymer phases and so on, they have never been synthesized so far.

This article describes our new finding on the preparation of polymer whiskers based on *p*-mercaptobenzoyl (S) and *p*-oxybenzoyl (O) blocks by means of the polymerization of AMBA and the following addition of ABA as illustrated in Scheme 1.

2. Experimental section

2.1. Materials

ABA was purchased from TCI Co. Ltd, and recrystallized from ethyl acetate. AMBA were prepared according to the previous work [12–15]. LPF was purchased from Nacalai Tesque Co. Ltd, and purified by vacuum distillation (220–240 °C/0.3 mm Hg).

2.2. Polymer synthesis

The whisker prepared by the polymerization with stepwise addition is abbreviated as PMB-OX in which X

stands for the number of additions. For example, PMB-O2 means the whisker prepared by the polymerization of AMBA with twice addition of ABA. Preparation procedure of PMB-O1 is described in a typical example. Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed AMBA (0.57 g, 2.91×10^{-3} mol) and 20 ml of LPF. Beginning concentration was 1.98% 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 dissolved completely. The temperature was maintained at 300 °C for 3 h and PMB whiskers were formed. Then ABA (0.19 g, 1.04×10^{-3} mol) was added into the solution as a tablet and the polymerization was continued at 300 °C for another 3 h. The formed whiskers 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. FT-IR of the whisker (KBr) (cm^{-1}): 3051, 2925, 1736, 1670, 1585, 1560, 1508, 1487, 1396, 1309, 1255, 1203, 1182, 1155, 1109, 1084, 1049, 1014, 885, 852, 825, 731.

2.3. Measurements

Morphology of the products was observed on a scanning electron microscopy (SEM, Hitachi S-3500N) and a transmission electron microscopy (TEM, JEOL 2000EXII). Samples for SEM observation were dried, sputtered with gold and observed at 20 kV. The shape parameters of the whiskers including the length (*l*), the width (*w*) and the thickness (*th*) were determined by the average of over 80 observations. Coefficients of variation (cv) of the length defined as the percentage of standard deviation to the average value were also determined by over 80 observations. The density (ρ) of the whiskers was measured by the floatation method using bromoform and

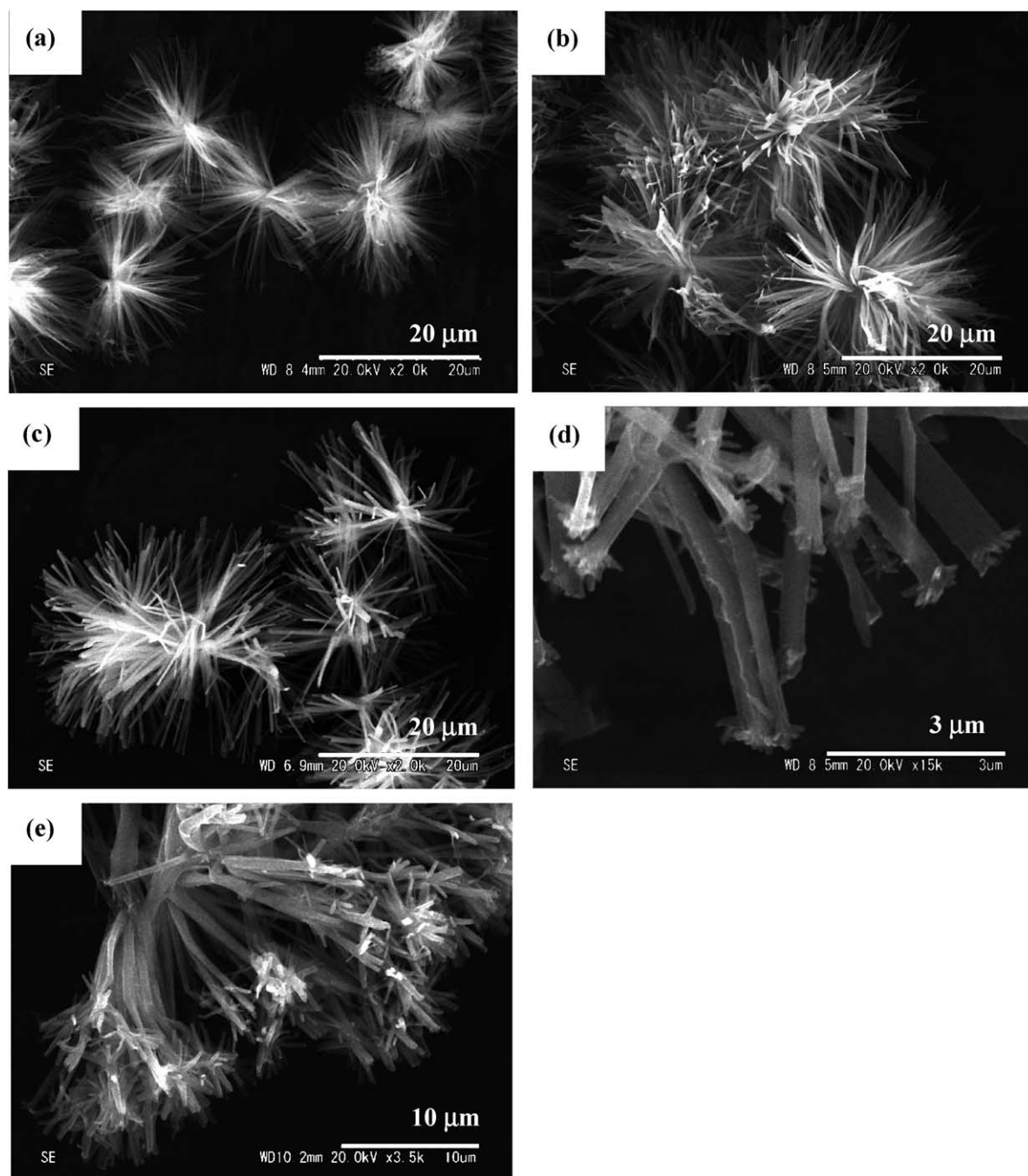


Fig. 1. Scanning electron micrographs of (a) PMB prepared for 3 h, (b) PMB-O1, (c) PMB-O3, (d) PMB-O5 and (e) PMB-O10.

toluene at 25 °C. The number of whiskers (N) in the solution was estimated with l , w , th , the yield and ρ according to the following equation. The th was constant at 0.10 μm.

$$N = \frac{\text{Yield}}{(lwth\rho)}$$

WAXS was conducted on a Rigaku RINT 2100 with nickel-filtered Cu K α radiation (40 kV, 30 mA). Chemical structure of polymers was measured on a microscopic FT-IR spectrometer (FT-IR-410, Itron IRT30, JASCO Co. Ltd.).

Aperture size was 20–40 μm. Intensity ratio of ester C=O and thioester C=O ($I_{1736\text{ cm}^{-1}}/I_{1672\text{ cm}^{-1}}$). Composition of copolymers was determined by HPLC (Waters 600E) with Nova Pack HR C18 column after hydrolysis of copolymers. 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. Thermal properties were evaluated by DSC (Perkin–Elmer DSC-7) at a scanning rate of 10 °C min $^{-1}$ in a nitrogen atmosphere.

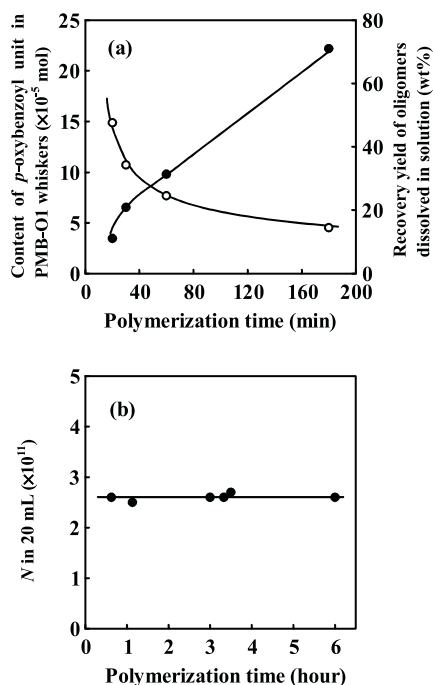


Fig. 3. Plots of (a) content of *p*-oxybenzoyl unit in PMB-O1 whiskers (●) and recovery yield of oligomers dissolved in solution (○), and (b) the number of whiskers (*N*) as a function of polymerization time.

of super-saturation of oligomers. Different amount of ABA was added into the solution after 3-hour polymerization of AMBA. Polymerizations with the addition of 0.52×10^{-3} , 1.04×10^{-3} and 1.55×10^{-3} mol ABA yielded the whiskers. These whiskers are 21.1, 22.4 and 23.0 μm in length, and 0.32, 0.33 and 0.35 μm in width, respectively. The length increases with the amount of ABA, and it is 1.0, 2.3 and 2.9 μm longer than PMB whiskers prepared for 3 h. The addition of 0.52×10^{-3} mol ABA makes the length slightly longer and the molar ratio of O units in the whiskers was quite low. Due to the sublimation, only a small amount of ABA was consumed for making whiskers. With respect to the width, the addition of 0.52×10^{-3} mol ABA keeps the width constant but that of 1.55×10^{-3} mol makes the width slightly wider due to the higher degree of super-saturation of oligomers. On the basis of these results, 1.04×10^{-3} mol is

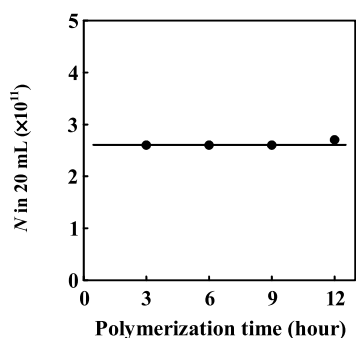


Fig. 4. Plot of *N* of PMB, PMB-O1, PMB-O2 and PMB-O3 as a function of polymerization time.

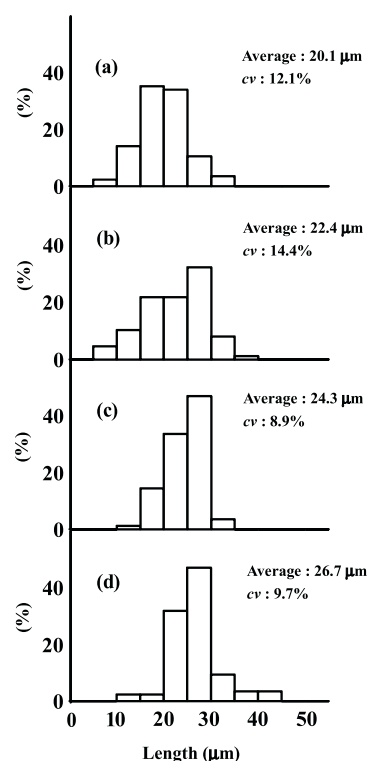


Fig. 5. Distribution diagrams of the length of (a) PMB, (b) PMB-O1, (c) PMB-O2 and (d) PMB-O3 whiskers.

determined as the suitable amount of ABA for the addition. The results of polymerization with stepwise addition of ABA are summarized in Table 1. Consumed O unit was defined as the amount of O unit consumed for the formation of the oligomers and polymers. Consumed O unit is much lower than added ABA as shown in Table 1 and this is caused by sublimation of ABA at 300 $^{\circ}\text{C}$. With respect to PMB-O1 were followed the change of content of O units in the whiskers, the yield of oligomers dissolved in the solution and the number of whiskers (*N*) in the course of polymerization. The results are plotted in Fig. 3. Content of O units in the whiskers increased gradually with polymerization time after the addition and the yield of oligomers decreased accordingly. The amount of oligomers dissolved in the solution was quite small after 3 h from the addition of ABA. *N* was constant at 2.6×10^{11} throughout the polymerization after the addition of ABA. This data reveals that new whisker is not generated by the addition of ABA. Stepwise addition of 1.04×10^{-3} mol ABA was conducted to extend the length of the whiskers. Interval for the addition was 3 h. Polymerization was continued for another 3 h after the last addition. The polymerizations with the stepwise addition of ABA also afforded the longer whiskers. PMB-O2 whisker is 24.3 μm in length and 0.35 μm in width, which are 1.9 μm longer and 0.2 μm wider than PMB-O1 whisker. PMB-O3 whisker is 26.7 μm in length and 0.35 μm in width, which is 2.4 μm longer than PMB-O2 whiskers but the width does not increase as shown

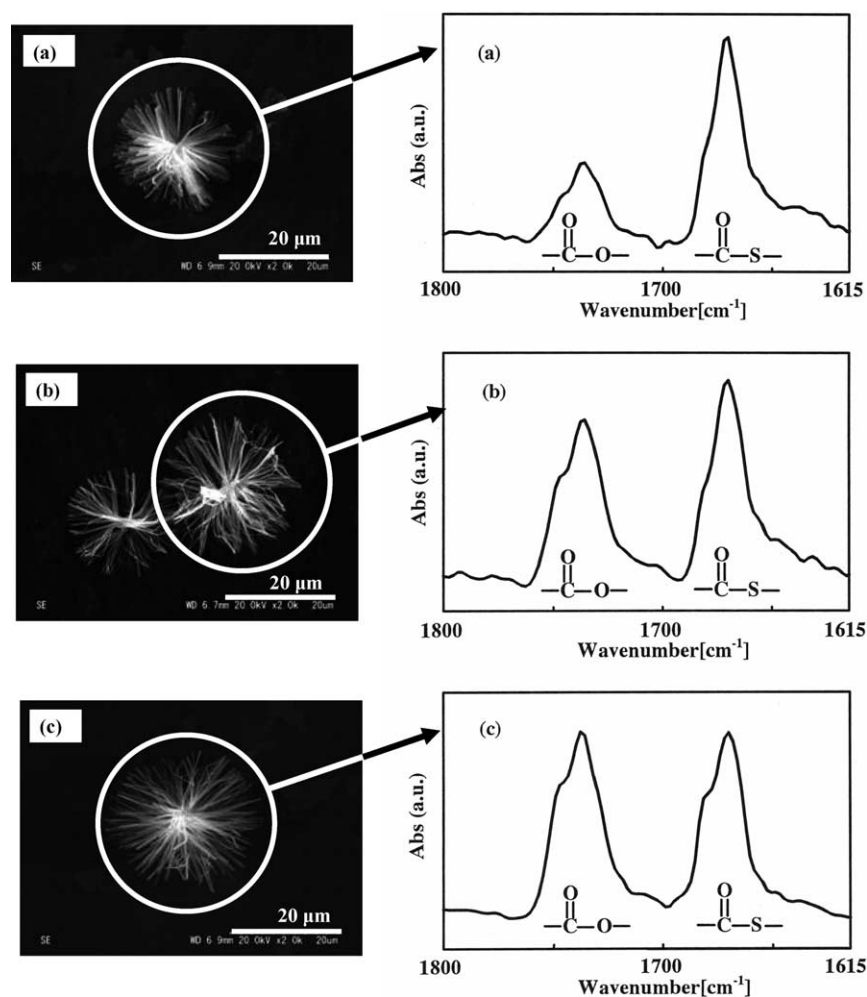


Fig. 6. Microscopic FT-IR spectra of (a) PMB-O1, (b) PMB-O2, and (c) PMB-O3 whiskers. Circle in SEM shows the measurement area of IR spectrum.

in Fig. 1. PMB-O5 and PMB-O10 whiskers are 28.2 and 32.1 μm in length, respectively, and 0.35 μm in width. The length increases ca. 2 μm with one addition up to PMB-O3, but the increment of the length becomes small after fifth addition. It is observed that tip parts of POB-O5 and PMB-O10 whiskers are branched as shown in Fig. 1. The average branch length of PMB-O5 and PMB-O10 are 0.7 and 1.7 μm , respectively. The branch length of PMB-O10 whisker is longer than that of PMB-O5. This fact indicates that the branches also grow gradually with the addition. The small increment of the length of PMB-O5 and PMB-O10 whiskers results from the branching of the tip parts. Figs. 4 and 5 show the plot of N and the distribution diagrams of the length of PMB, and PMB-O1, PMB-O2 and PMB-O3. N is constant at 2.6×10^{11} even after the addition of ABA. The distribution diagrams of the length are unimodal. The cv value of the length of PMB is 12.1%. Those of POM-O1, PMB-O2 and PMB-O3 are 14.4, 8.9, and 9.7%, respectively. The average length increases with maintaining the cv value. Distribution at the shorter length is not newly generated after the addition of ABA. These data prove that the nucleation is not induced by the addition leading to the

formation of POB whiskers and the oligomers are consumed only for growth of the whiskers once nucleation occurs in the beginning of polymerization.

The composition of O units in the whiskers increases with the number of additions. The weight of the oligomers left in the solution is constant at ca. 20 mg after every polymerization and the molar ratio of O units is also constant at ca. 0.9 after second addition. These results imply that certain amount of S units is constantly left in solution, and the homo-oligomers of O units and the oligomers rich in O units are precipitated due to the lower solubility. O-unit content is obviously enhanced at tip parts. The composition of each whisker was analyzed by microscopic FT-IR spectroscopy. Fig. 6 is the representative spectra of PMB-O1, PMB-O2, and PMB-O3 whiskers. The spectra of these whiskers do not show the bands characterized as monomers such as C=O of acetyl group and carboxyl group. The bands of C=O of ester linkage and thioester linkage are observed at 1736 and 1672 cm^{-1} , respectively. This result confirms the formation of polymer whiskers comprised of S and O units. Intensity ratio of ester C=O and thioester C=O ($I_{1736 \text{ cm}^{-1}}/I_{1672 \text{ cm}^{-1}}$) is 0.45 for PMB-O1 whisker. With

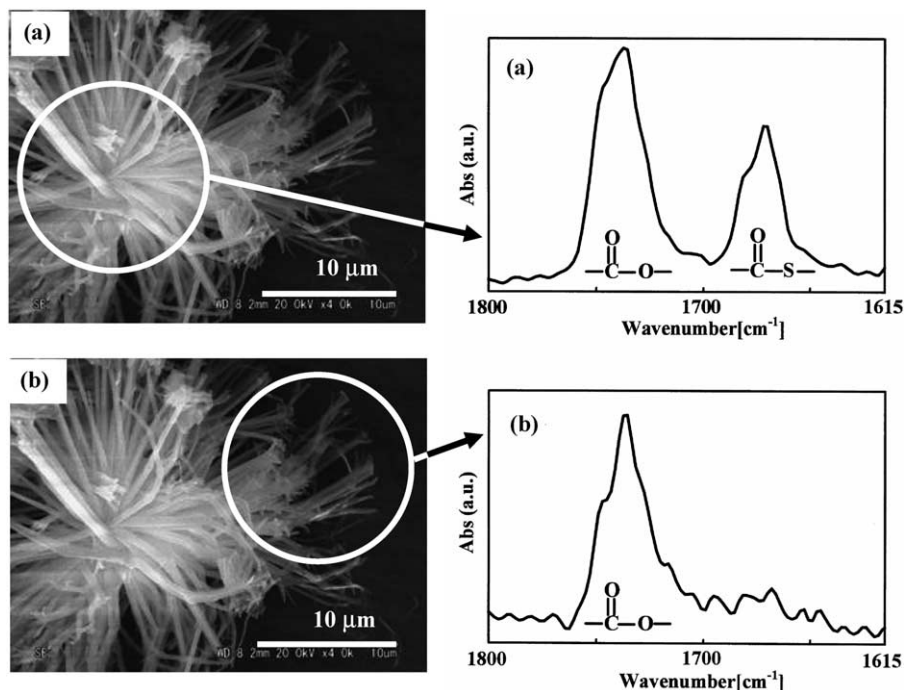


Fig. 7. Selected area FT-IR spectra of (a) center and (b) tip part of PMB-O10 whiskers. Circle in SEM shows the measurement area of IR spectrum.

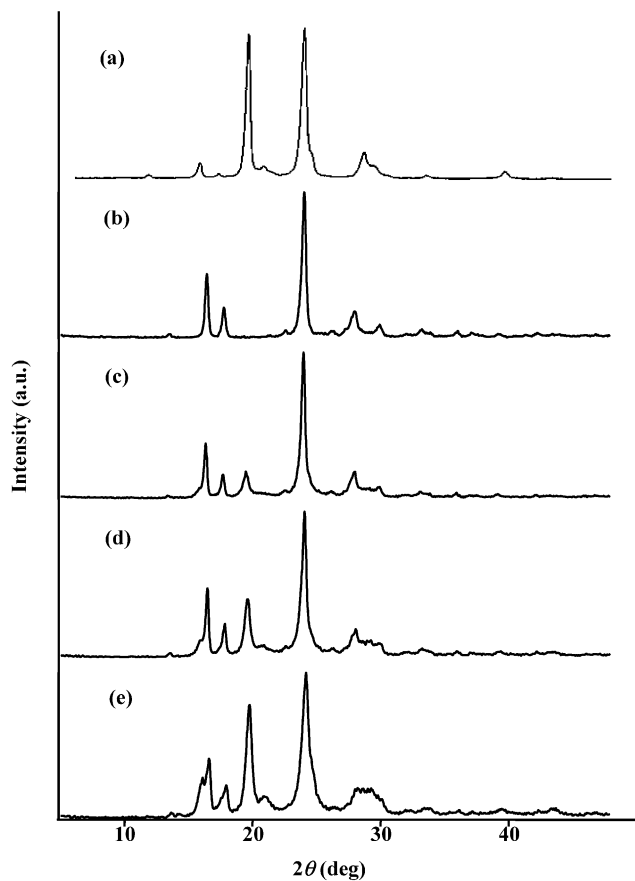


Fig. 8. WAXS intensity profiles of (a) POB, (b) PMB, (c) PMB-O3, (d) PMB-O5 and (e) PMB-O10 whiskers.

respect to PMB-O2 and PMB-O3, the intensity ratios are 0.87 and 1.04, respectively. The intensity ratio increases with the number of additions and this also reveals that the content of O units increases with the length. The selected area FT-IR spectra of the tip and center part of PMB-O10 whisker are shown in Fig. 7. The thioester C=O band appears with the ester C=O band in the spectrum of the center part. These whiskers grow radially and, therefore, the ester C=O band is observed in the spectrum of the center part. In contrast to this, the thioester C=O band is not detected and only the ester C=O band is observed in the spectrum of tip part. This result proves directly that these whiskers are comprised of S units at center parts and O units at tip parts.

Fig. 8 shows WAXS patterns of PMB-O3, PMB-O5 and PMB-O10 whiskers with those of POB and PMB whiskers. The diffraction peaks of the resulting whiskers are very sharp and the diffuse halo attributed to amorphous is not apparent. These patterns reveal that these whiskers are extremely crystalline. The peaks of 2θ at 15, 19, 24 and 29° are characteristic peaks of POB crystals, and those at 2θ of 16, 18, 24 and 27° are characteristic peaks of PMB crystals. These patterns are superimposed with those of POB and PMB crystals. Relative peak intensity at 2θ of 19, 24 and 29° characterized as POB crystals to those as PMB crystals increases with the number of additions. The oligomers comprised of O units formed by the stepwise addition of ABA are crystallized on PMB whiskers as heterogeneous nucleation to form POB crystals. Selected area electron diffraction was performed to examine the structure of the center and tip part of the whisker. Fig. 9 shows electron

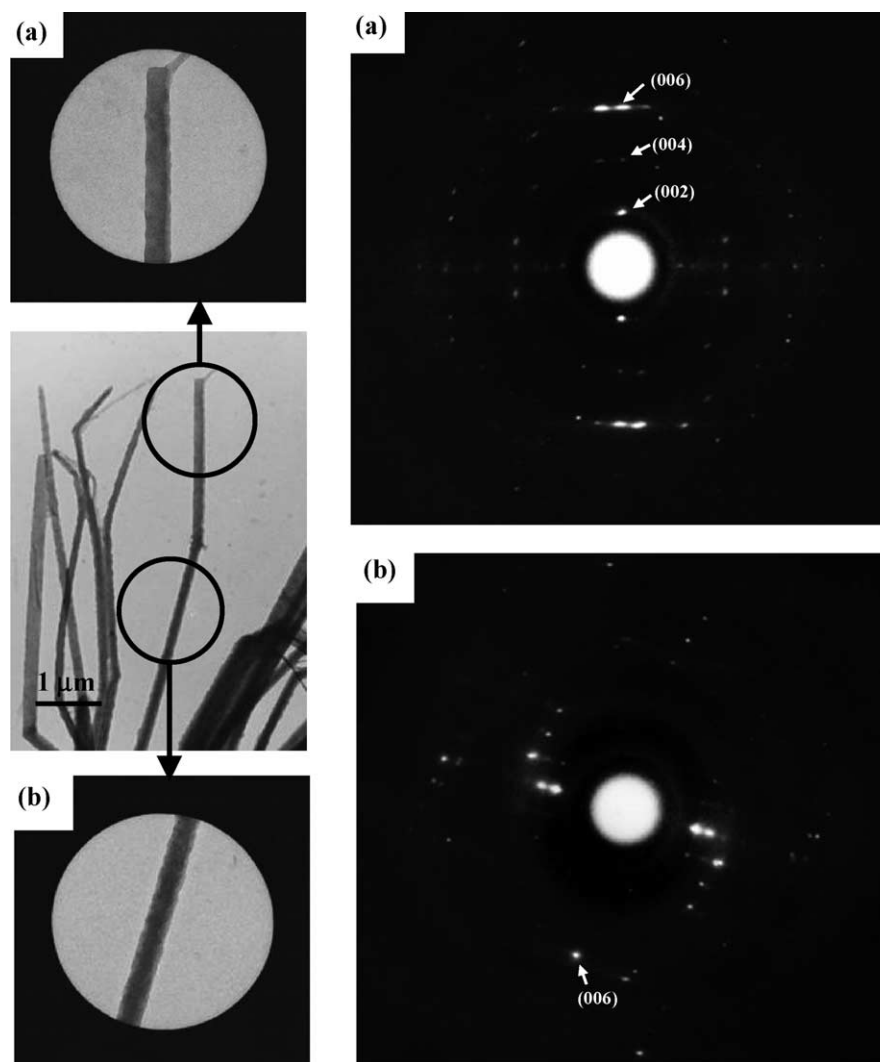


Fig. 9. Selected area electron diffraction patterns of (a) tip and (b) center part of PMB-O3 whisker.

diffraction patterns of PMB-O3 whisker. The diffraction patterns 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. These are due to the single-crystal nature of the whisker. The meridians of these patterns correspond to the long axes of the crystal, and the polymer chains align along the long axes of the whisker. The diffraction pattern of the center part is consistent with that of PMB whiskers [5] and that of the tip part is consistent with that of POB whiskers [3,4]. The fiber identity periods of the center and the tip part of the whisker are estimated as 13.09 and 12.67 Å, and they correspond to those of PMB and POB whiskers, respectively. It can be concluded that the center and the tip parts of the whiskers are PMB crystals and POB crystals. The compositions at different positions in the whisker were calculated from the results of the changes in the shape parameters and the corresponding composition of the whiskers estimated from the HPLC analysis. The composition map is plotted in Fig. 10 as a function of the length and the width from the center of PMB-O5 whisker.

The center part of the whisker is comprised of S units and then the composition of the middle part is drastically altered from S to O units at the length of ca. 11 μm from the center. The tip part is practically made up of O units in which contains less than 1 mol% of S units. The whisker is comprised of S and O blocks. Number-average degree of polymerization (DP_n) of this whisker cannot be estimated due to the intractability. It can be presumed from the result of POB whiskers prepared by the same condition that DP_n of this whisker is ca. 500 [3] and the length of extended molecular chain is calculated as ca. 0.3 μm. This length is smaller than the length of the whisker, and, therefore, this suggests that this whisker is comprised of PMB, poly(*p*-mercaptobenzoyl-*block-p*-oxybenzoyl) and POB.

DSC profiles of the resulting whisker are shown in Fig. 11 with those of PMB and POB whiskers prepared at 300 °C for 6 h. It is known that 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 pseudo-hexagonal packing of polymer

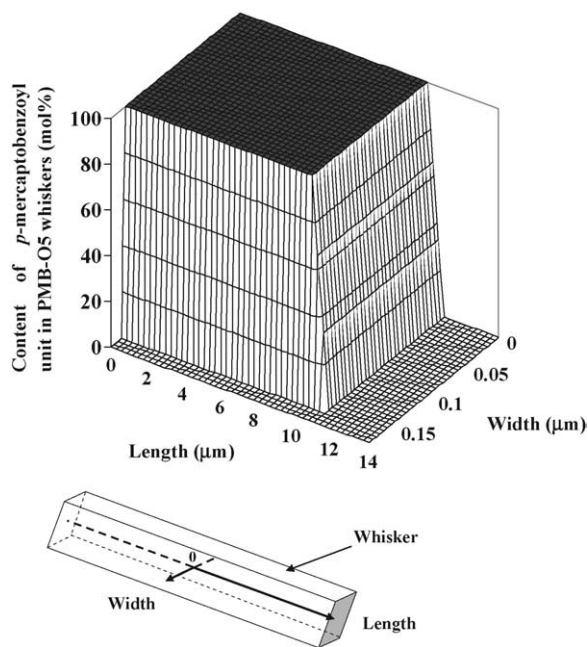


Fig. 10. Plots of *p*-mercaptobenzoyl unit composition in PMB-O5 whiskers as a function of length and width from the center part.

molecules by a rotation of 1,4-phenylene rings around σ -bonds in the *para* position [5,12,16–18]. Random POB-*co*-PMB prepared at the middle copolymerization ratio did not exhibit this solid–solid transition due to the lack of crystallinity [6]. POB-O3, POB-O5 and POB-O10 whiskers exhibit two endothermic peaks on heating scan at 280–325 and 340–375 °C. The higher transition peaks are corresponding to the transition of PMB crystal. The higher transition temperature shifts slightly toward higher tem-

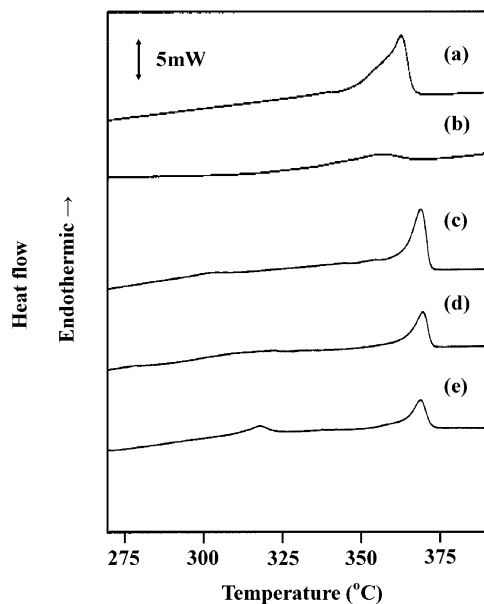


Fig. 11. DSC profiles of (a) PMB, (b) POB, (c) PMB-O3, (d) PMB-O5 and (e) PMB-O10 measured with a scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere.

perature with the number of additions. This is due to more closely packed polymer chains during longer polymerization time. The transition temperature of POB crystal is very sensitive to the copolymerization ratio. POB crystal exhibits the transition at 356 °C. But random POB-*co*-PMB prepared from ABA and AMBA at the molar ratio of AMBA of 0.1 exhibits the transition at 283 °C and it shifts toward the lower temperature with the ratio. This lower transition temperature moves from 302 to 318 °C with the number of additions and its enthalpy increases. As aforesaid, POB crystal part formed by stepwise addition of ABA contains less than 1 mol% S units and the content of S units decreases with the number of additions. Hence, the lower transition peaks are likely attributed to the transition of POB crystals and the existence of two transition peaks is consistent with other results as discussed above.

4. Conclusions

Polymer whisker based on different blocks was prepared by the polymerization of AMBA and the following addition of ABA. The length of the whisker increased with the number of the addition of ABA and it became 26.7 μm after third addition from 20.1 μm . The width increased very slightly and thickness was constant at 0.10 μm . The addition of ABA more than fifth resulted in the branching of the tips. The polymer molecules were aligned along the long axis of the whiskers. The microscopic FT-IR and the selected area electron diffraction results proved that the center and tip parts of the obtained whisker were based on S and O blocks, respectively. This result affords the new methodology for the preparation of polymer whisker based on different blocks.

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