Preparation of Copolymer Whiskers

Kunio Kimura, Kazufumi Kobashi and Yuhiko Yamashita
Faculty of Environmental Science and Technology, Okayama University,
3-1-1 Tsushima-naka, Okayama 700-8530, Japan
TEL & FAX: +81-86-521-8902, e-mail: polykim@cc.okayama-u.ac.jp

Introduction

We have been studying on the morphology control of rigid polymers during solution polymerization and successfully prepared the whiskers of poly(*p*-oxybenzoyl) (POB) and poly(*p*-mercaptobenzoyl) (PMB) by polymerizations in liquid paraffin (LPF) at around 300°C. [1] 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 preparation of copolymer whisker is very interesting and desirable to tailor the new functional polymeric materials. Recently, the morphology control of poly(*p*-oxybenzoyl-*co*-*p*-mercaptobenzoyl) has been studied and poly(*p*-oxybenzoyl-*alt*-*p*-mercaptobenzoyl) whiskers were prepared by the control of short distance sequence regularity. [2]

This paper describes new findings on the preparation of polymer whiskers comprised of *p*-oxybenzoyl (O) unit and *p*-mercaptobenzoyl (S) unit having graded composition, and polymer whiskers based on O and S blocks by means of self-assembling polymerization.

Experimental

Polymer whiskers comprised of O and S unit having graded composition: Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed and 4-(4-acetoxybenzoyloxy)benzoic acid (OO) (0.12g, 3.90×10^{-4} mol), of S-acetyl-4-mercaptobenzoic acid (AMBA) (0.15g, 7.80×10^{-4} mol) and 20 mL of LPF. Polymerization concentration was 1.0 wt/vol% based on polymer weight and solvent volume. 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 hours. The polymer

crystals were collected by vacuum filtration at 300°C, and washed with *n*-hexane and acetone. Polymerization of AMBA and 4-[4-(4-acetoxybenzoyloxy)benzoyloxy]-benzoic acid (OOO) was carried out under the same conditions.

Polymer whiskers based on O and S blocks: Polymerization of AMBA was carried out in 20 mL of LPF at the concentration of 1.98 wt/vol% and 300°C for 3 hours according to the procedure described above, and then 4-acetoxybenzoic acid (ABA) was added stepwise at 3 hours intervals into the solution. Polymerization was continued for another 3 hours after the last addition.

Characterization: Morphology was observed on SEM. Composition of copolymers was determined by HPLC after hydrolysis of copolymers.

Results and discussion

Polymer whiskers comprised of O and S unit having graded composition: Reaction-induced phase separation of oligomers in poor solvent is describable on the analogous concentration-temperature phase diagram to that of partially miscible polymer-solvent system. [3, 4] Phase separation curve in the repulsive system can be written as the combination of the freezing point curve of the oligomers and the upper critical solution temperature type consolute curve. When the DPn of the oligomers exceeds a critical value in solution, they are in super-saturation state and then phase-separated. If the super-saturated oligomers are across the freezing point curve, they are precipitated by the crystallization to form the crystals, and the polymer crystals are finally formed by the post-polymerization in the crystals. In order to make the composition graded, the composition of phase-separated oligomer should be altered from one component to the other and accumulated onto the needle-like crystals. The copolymerization between monomer of one component and oligomer of the other component is one of the desirable methods to phase-separate the oligomer with altering gradually the composition during polymerization. On the basis of this principle, we examine the self-assembling polycondensation of AMBA and OO or OOO in poor solvent.

Polymerizations were carried out in LPF at 300°C for 6 hours. Polymerization concentration was 1.0%. Molar ratio of O unit in feed was 50% in both polymerization systems. The solution became turbid at the early stage of polymerization due to the precipitation of oligomers, and then the polymer crystals

were obtained. Both the polymerization of AMBA and OO, and that of AMBA and OOO afforded the whiskers with the yield of 51% and 43%. The whiskers prepared from AMBA and OO (PODS) are 15 μm in average length and 0.4 μm in average width as shown **Figure 1**. Those prepared from AMBA and OOO (POTS) are 13 μm in average length and 0.4 μm in average width. The content of O unit (χ_o) in PODS whiskers and POTS whiskers are 49.0 and 48.0 mol%, and they are in good agreement with the content of in feed. XRD patterns of these whiskers reveal that these whiskers possess extremely high crystallinity.

The change in the yield, size and number of the whiskers were followed in the course of polymerization. In both polymerizations, the length of the whiskers increases preferentially with the yield. In contrast to this, the width increases slightly at the initial stage of polymerization. The composition of the whiskers was analyzed as a function of polymerization time. χ_o of PODS whiskers obtained at 8 min is 62 mol% and then decreases with time to 49 mol% at 100 minutes. With respect to POTS whisker, χ_o obtained at 8 min is 77 mol% and then also decreases gradually with time to 48 mol%. These facts obviously reveal that these whiskers possess the graded composition from O unit rich in center part to S unit rich in the tip part. And these results suggest that the oligomers rich in O unit are preferentially precipitated at the early stage of polymerization and then the oligomers containing S unit are gradually precipitated to form the crystals. The gradient of the composition is amplified by the increase of O unit in raw materials.

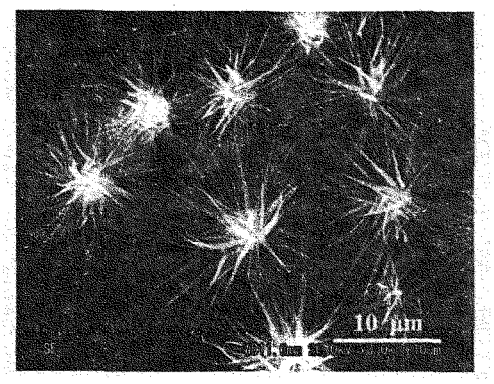

Figure 1. PODS whiskers.

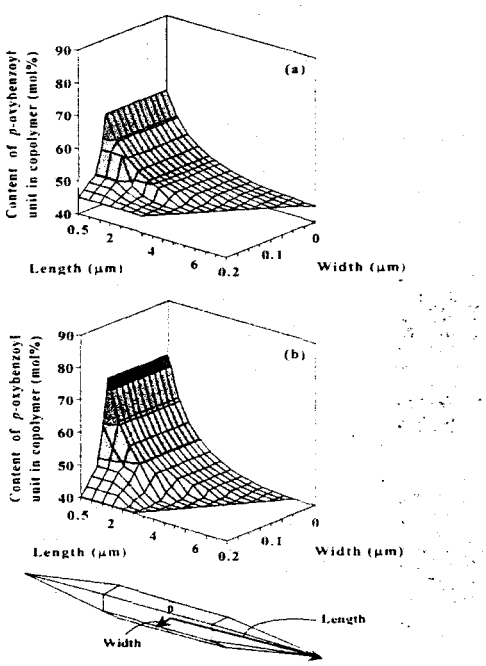

Figure 2. Plots of gradient composition in (a PODS and (b) POTS whiskers as a function of the length and the width from the center part.

On the basis of these results, the gradient composition in the whiskers is plotted in **Figure 2** as a function of the length and the width from the center of the whiskers. As shown in this figure, the whiskers possess the graded composition along the two directions of the length and width, and the composition is altered from O unit to S unit from the center part to the outer part. The slope of the gradient in POTS is slightly steeper than that in PODS.

Polymer whiskers based on O and S block: Firstly, formation behavior of PM B whisker was examined in detail. The obtained PMB whiskers grew radially from the center part, of which the average length, width and thickness were 20.6 μm, 0.32 μm and 0.10 μm. The yield of the whisker increases rapidly until 1 hour and then it becomes leveled off at 3 hours. Correspondingly, the oligomers dissolved in solution decreases with time. On the basis of these results, ABA was added to the polymerization of AMBA at 3 hours to make the whisker based on O and S blocks. Optimum ABA added amount for growth of the whiskers was examined and th e length became 22.4 μm by the addition of 1.04×10^{-3} mol ABA. The number of the whisker was unchanged through the addition. Stepwise addition of 1.04×10^{-3} mol ABA was conducted to extend the length of the whiskers. The polym erizations with the stepwise addition of ABA also afforded the longer whiskers. The length of the whisker increased with the addition and it became 26.3, 28.2 and 32. 1 μm from 20.6 μm after third, fifth and tenth addition, respectively as shown in **Figure 3**. The width increased very slightly to 0.35 μm. The thickness was constant at 0.10 μm throughout the polymerization. The composition of O unit in the whiskers increases with the number of the addition. XRD patterns of the whiskers show that they possess the extremely hi gh crystallinity. 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 part and the tip part were comprised of the PMB crystal

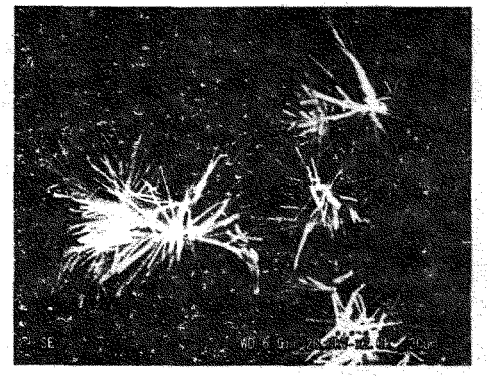

Figure 3. Whiskers formed after their addition

and POB crystal, respectively as shown in **Figure 4**. Selected area electron diffraction was performed. 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 the PMB whisker[5] and that of the tip part is consistent with that of the POB whisker.[1] 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 that of PMB and POB whiskers, respectively. It can be concluded that the center and the tip parts of the whiskers are comprised of PMB crystal and POB crystal. The composition of the whiskers was analyzed as a function of polymerization time as aforesaid. The composition in the whiskers is also analyzed and plotted in **Figure 5** as a function of the length and the width from the center of the whiskers. The center part of the whisker is comprised of S unit and then the composition of the middle part is drastically altered from S to O unit along with the length of ca. 11 μm from the center. The tip part is practically made up of O unit in which contains less than 1 mol% of S unit. The whisker is comprised of S and O blocks.

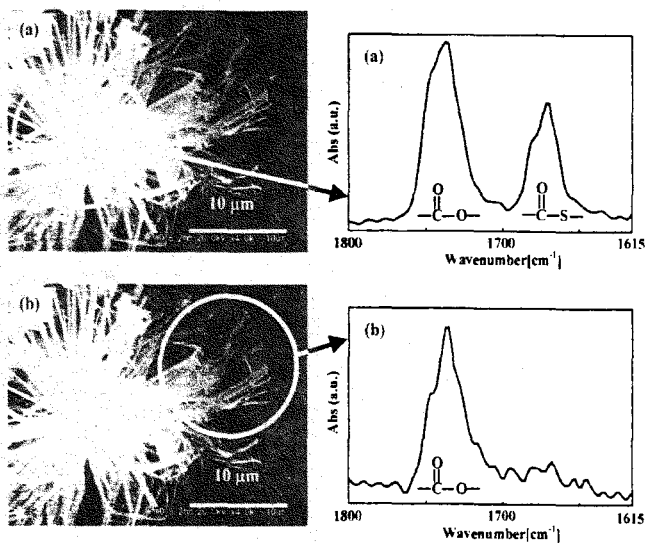

Figure 3. Microscopic FT-IR of (a) center and (b) tip part of whiskers

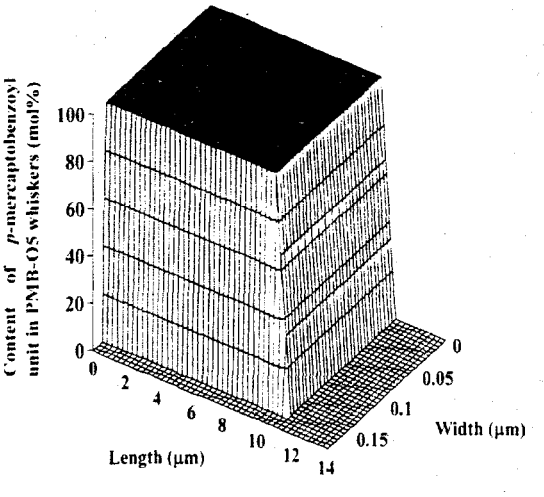

Figure 4. Plot of S unit composition in whiskers as a function of length and width from the center part.

Conclusions

The whiskers comprised of O unit and S unit having graded composition are successfully prepared by the 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 part. The increase of O unit in raw oligomers enhances the gradient composition of the whiskers. POTS whiskers possess the larger graded composition than that of PODS whiskers. Furthermore, the polymer whisker based on O and S blocks was successfully prepared as grafting POB crystal on PMB whisker with stepwise addition of ABA. These results provide the novel methodology for the preparation of copolymer whiskers having various sequence regularity.

References

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