

Polymerization of 4-Acetoxybenzoic Acid and 4-(4-Acetoxyphenyl)benzoic Acid via Reaction-induced Crystallization of Oligomers

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Abstract: The one-pot preparation of polyester crystals having different morphology was examined in the copolymerization of 4-acetoxybenzoic acid (ABA) and 4-(4-acetoxyphenyl)benzoic acid (APBA). Copolymerizations were carried out in aromatic solvent at various ABA molar ratios in feed (χ_f). When the χ_f was 20 - 10 mol%, star-like aggregates of needle-like crystals and fibrillated slab-like crystals were separately formed, exhibiting the similar morphology to the poly(4-oxybenzoyl) (POB) and poly[4-(4-oxyphenyl)benzoyl] (POPB) crystals. 4-(Oxyphenyl)benzoyl (4-OPB) homo-oligomers and co-oligomers rich in 4-OPB were more rapidly precipitated due to the lower miscibility, and the slab-like crystals were formed. Afterward, the 4-oxybenzoyl (4-OB) homo-oligomers and the co-oligomers rich in 4-OB were precipitated to form the spindle-like crystals. The 4-OPB homo-oligomers and the co-oligomers rich in 4-OPB were continuously crystallized on both crystals due to the high degree of supersaturation, and therefore the spindle-like crystals grew to the needle-like crystals. This result provides a new methodology for the morphology formation of the crystals in copolymerization system.

INTRODUCTION

Aromatic polyesters such as POB and POPB are hopeful candidates of high-performance polymers. Morphology control by using phase separation of oligomers during solution polymerization had been studied, and the whiskers of POB¹ and POPB² were prepared by the polymerization of ABA and APBA in poor solvents. These whiskers were formed via the crystallization of oligomers and the subsequent solid-state polymerization in the precipitated needle-like oligomer crystals. The molecular chains are aligned along the long axes of the whiskers and this morphology with the molecular orientation is of great importance to obtain the essential properties. It had been well known that copolymerization usually lowered the crystallizability and the clear morphology of the homo-polymer crystals was drastically damaged.³⁻⁷ The morphology control of the crystals was difficult in copolymerization systems. If the miscibility and crystallizability of the oligomers vary

significantly with their compositions, the clear morphology of the crystals can be created even in the copolymerization system by using the crystallization of oligomers.

This paper describes, herein, the one-pot preparation of polyester crystals having different morphology by means of the crystallization of oligomers during copolymerization of ABA and APBA.

EXPERIMENTAL

Polymerization

Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed ABA (0.30g, 1.67 mmol), APBA (0.26g, 1.02 mmol) and 20 ml of Barrel Therm 400 (BT4), which was a mixture of isomers of dibenzyl toluene. The reaction mixture was heated under a slow stream of nitrogen up to 330°C with stirring. Stirring was stopped when the monomers were entirely dissolved. The temperature was maintained at 330°C for 6 hours. The precipitates were collected by

Table 1 Results of copolymerization of ABA and APBA^a

run no.	χ_f^b (mol%)	yield (%)	χ_p^c (mol%)	morphology
1	100	59	100	needle
2	99	53	>99	fibril
3	95	58	96	
4	90	47	92	sphere
5	25	49	23	
6	20	52	15	fibrillated slab,
7	10	62	6	needle
8	0	52	0	slab

a: Polymerizations were carried out at 330°C and a concentration of 1.0% in BT4.

b: molar ratio of ABA in feed

c: molar ratio of 4-oxybenzoyl moiety in precipitates

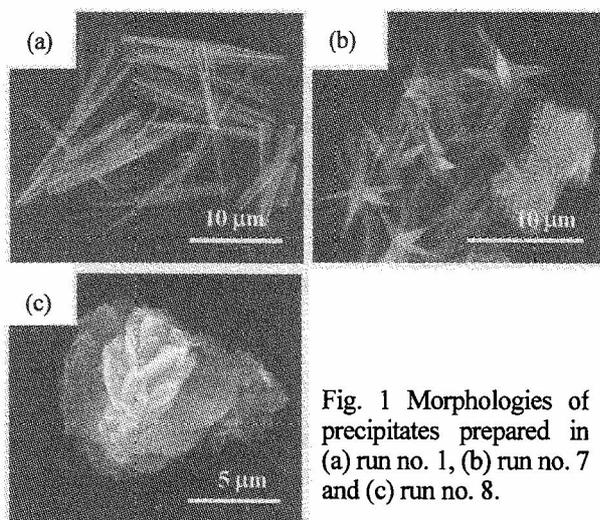


Fig. 1 Morphologies of precipitates prepared in (a) run no. 1, (b) run no. 7 and (c) run no. 8.

vacuum filtration at 330°C, and washed with *n*-hexane and then acetone. The filtrate was poured into *n*-hexane and the precipitated oligomers were recovered by filtration.

RESULT AND DISCUSSION

Polymerization results were presented in Table 1 and the morphologies of the precipitates are shown in Fig. 1. Needle-like POB crystals were formed by the polymerization of ABA (χ_f of 100 mol%), of which the average length and width were 17.0 μm and 6.5 μm , respectively. On the other hand, aggregates of POBP slab-like crystals were formed by the polymerization of APBA (χ_f of 0 mol%). The average thickness of the slab-like crystals was 0.1 μm . The morphology of the precipitates was drastically changed by the copolymerization. The fibrillar crystals having had spherical parts in the center were formed at

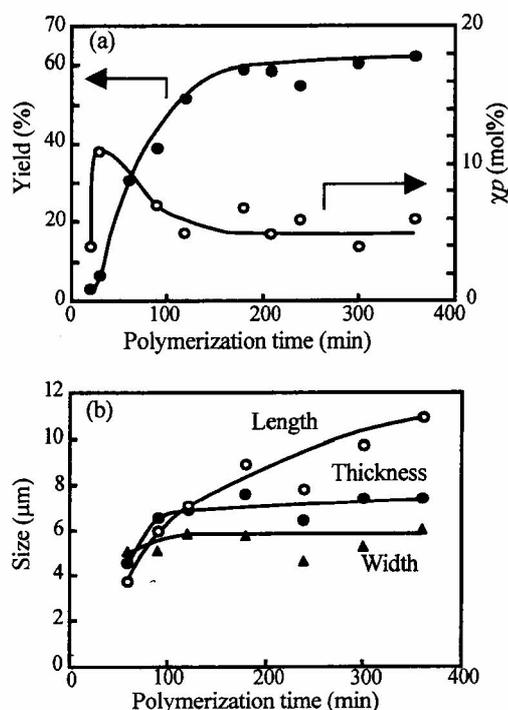


Fig. 2 Plots of (a) yield and χ_p , and (b) size parameters of the precipitated crystals as a function of time in copolymerization at χ_f of 10 mol% and 330°C.

χ_f of 95 mol%. The clear crystal habit was extinguished and the spherical precipitates were obtained at χ_f of 90-25 mol%. This drastic change in the morphology is attributed to that the copolymerization lowers the crystallizability of oligomers and the co-oligomers is liable to be precipitated by the liquid-liquid phase separation because of the reduction of the freezing point. When the χ_f was 20-10 mol%, two different crystals were formed separately, which were star-like aggregates of needle-like crystals and fibrillated slab-like crystals. These morphologies are similar to those of the POB⁷ and POBP⁴ crystals. The values of χ_p of the precipitates prepared at χ_f of 10 and 20 mol% were 6 and 15 mol%, respectively. Diffraction peaks became broader even at χ_f of 90 mol% and crystallinity was lowered. In the profile of the precipitates prepared at χ_f of 30 mol%, one strong peak was clearly observed at 2θ of 20.0 degree and crystal structure tends to change from orthorhombic to hexagonal structure. However, the profile of the precipitates prepared at χ_f of 10 mol% was quite different and six sharp peaks were clearly observed at 2θ of 19.3, 20.0, 23.5, 28.9, 29.8, 39.0 degree. Although χ_p only 6 mol%, five characteristic

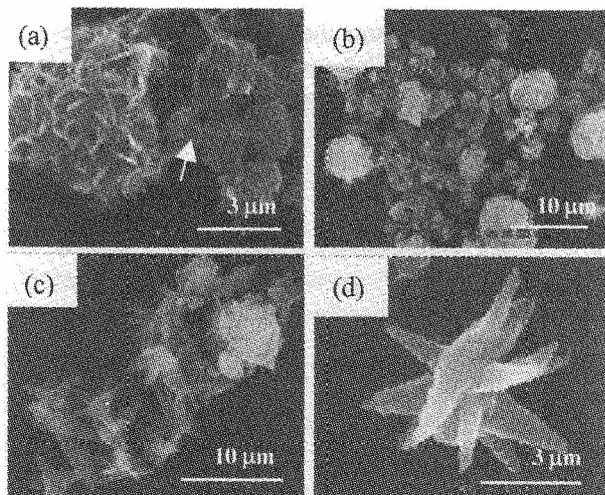


Fig. 3 Morphology of the precipitated crystals prepared at χ_f of 10 mol% and 330°C for (a) 30 min, (b) 60 min, (c) and (d) 90 min.

peaks of the POB crystals at 2θ of 19.3, 23.5, 28.9, 29.8, 39.0 degree were detected clearly besides the peak of the POBP crystals, and the POB crystals were contained in these precipitates suggested from the morphological feature.

In order to clarify the crystal formation mechanism, the yield and the values of χ_p of the precipitated crystals were examined in the course of polymerization at χ_f of 10 mol%. Further, the changes in the length of the needle-like crystals, and the width and the thickness of the fibrillated slab-like crystals were measured in the course of polymerization. The results were plotted in Fig. 2. The morphological changes were shown in Fig. 3. The yield increased rapidly from 30 min to 3 hours to 60% and thereafter it increased gradually. The average length of the needle-like crystals prepared for 1 hour was 3.5 μm and then it increased continuously to 10.9 μm after 6 hours. The average width and thickness of the fibrillated slab-like crystals were 5.0 and 4.5 μm after 1 hour. The width increased slightly at the initial stage of polymerization to ca. 6 μm . The thickness increased rapidly up to 2 hours to 6.8 μm and then it also increased very slowly to 7.4 μm after 6 hours. In contrast to this, the value of χ_p increased rapidly from 20 to 30 min from 4 to 11 mol%. Then it decreased until 2 hours and became constant at ca. 6 mol%. This maximum in χ_p suggests that the oligomers rich in 4-OB were precipitated at the initial stage in the polymerization with the oligomers rich in

4-OPB. It was clearly observed that the precipitated crystals prepared for 30 min contained aggregates of slab-like crystals and spindle-like crystals which had very sharp tips (arrow in Fig. 3 (a)). Then they grew independently with time. The spindle-like crystals grew to the needle-like crystals. Interestingly the initial needle-like crystals showed lamellae-stacking structures and the thickness of the lamellae was averagely 0.33 μm . The needle-like crystals prepared for 90 min were washed with KOH solution to observe the inner structure. The lamellae-stacking structure was not observed and the streaks along the long axis of the needle-like crystals were seen. After 3 hours, the trace of the lamellae-stacking structure was not observed and the surface of the needle-like crystals was very smooth. This structure resembles with the initial crystal structure of the POB whiskers,¹ and it implies that the needle-like crystals are formed by the spiral growth of oligomers caused by the screw dislocation and the subsequent solid-state polymerization in them. The chemical structures of the needle-like crystal and the fibrillated slab-like crystals prepared for 1 hour were analyzed on a microscopic FT-IR spectroscopy. The measured spectra were resolved in the range of 1450-1400 cm^{-1} by using the combined function of Lorentzian and Gaussian to detect the aromatic bands corresponding to 1,4-phenylene and 4,4'-biphenyl moiety at 1415 and 1425 cm^{-1} . The intensity ratio of these two bands ($I_{1415} \text{ cm}^{-1} / I_{1425} \text{ cm}^{-1}$) of the spindle-like crystals and the fibrillated slab-like crystals were 0.5 and 0.3 respectively, and that of spindle-like crystals was larger than that of the slab-like crystals. This result implies that the spindle-like crystals contained more 4-OB.

The difference in the morphology of the crystals and the fluctuation of the composition between two the crystals might be attributed to the difference in the formation rate of the oligomers and the phase separation behaviors of the oligomers on their compositions. The formation rates of oligomers were estimated by the self-condensation reaction of ABA and APBA in BT4 at 330°C. The self-condensation reactions of these monomers obeyed second

order kinetics and the rate constants (k_2) were estimated from the plots of number average degree of polymerization (DP_n) calculated from the evolved acetic acid as a function of polymerization time. The rate constants (k_2) of ABA and APBA were calculated as 9.7×10^{-2} and $12.3 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, respectively. APBA reacts only ca. 1.3 times faster than ABA and there was no big difference in them. The miscibility of the homo-oligomers of 4-OB and 4-OPB into BT4 was estimated by the temperature at which the monomers were entirely dissolved during heating (T_s) and the time when the solution became turbid at 330°C due to the precipitation of oligomers (t_t). The values of T_s of ABA and APBA were 170 and 260°C respectively, and APBA is less miscible than ABA. The values of t_t of ABA and APBA were 11 and 6 min, and the 4-OPB oligomers were more rapidly precipitated than the 4-OB oligomers. These results indicate that the oligomers rich in 4-OPB were more rapidly formed and precipitated at the initial stage in polymerization than those rich in 4-OB.

Selected area electron diffraction of the tip part of the needle-like crystals prepared at χ_f of 10 mol% for 6 hours and that of the center part of the spindle-like crystals prepared at χ_f of 10 mol% for 6 hours were taken to know the details of the structure. The diffraction pattern was not the fiber pattern of the cylindrical symmetry and sharp spots were clearly observed. The diffractions observed at the tip parts of the needle-like crystals were assignable as the crystal unit of POBP and therefore at least the tip parts of the needle-like crystals were comprised of POBP crystals. The diffraction (00 l) of POBP was clearly detected on the meridian corresponding to the long axis of the needle-like crystals and the polymer molecules were aligned along the long axis of the needle-like crystals. From these results, the formation mechanism of the two different crystals is as follows; Homo-oligomers of 4-OB and 4-OPB and co-oligomers are formed in the solution. When the molecular weight of oligomers exceeds the critical value, they are phase-separated through the supersaturated state. Among the oligomers, the 4-OPB homo-oligomers and the co-oligomers rich in 4-OPB are more rapidly precipitated due to the

lower miscibility, and they form the slab-like crystals. Then 4-OB homo-oligomers and the co-oligomers rich in 4-OB are precipitated and segregated from the slab-like crystals. Then they form the spindle-like crystals. The 4-OPB homo-oligomers and the co-oligomers rich in 4-OPB are continuously precipitated and the slab-like crystals grow. The spindle-like crystals grow to needle-like crystals by the crystallization of the 4-OPB homo-oligomers and the co-oligomers rich in 4-OPB and the polymerization in the crystals because the degree of supersaturation of oligomers is quite high at the initial stage of polymerization. Finally the slab-like crystals and needle-like crystals are simultaneously and separately formed during polymerization.

CONCLUSIONS

At χ_f of 20-10 mol%, star-like aggregates of needle-like crystals and fibrillated slab-like crystals were separately formed, exhibiting the similar morphology to the POB and POBP crystals. The homo-oligomers of 4-OPB and the co-oligomers rich in 4-OPB were more rapidly precipitated due to the lower miscibility, and the slab-like crystals were formed. The 4-OB homo-oligomers and the co-oligomers rich in 4-OB were next precipitated to form the spindle-like crystals. The homo-oligomers of 4-OPB and the co-oligomers rich in 4-OPB were continuously precipitated, and the slab-like crystals and the spindle-like crystals grew by the crystallization of them. Solid-state polymerization occurred between the oligomers in the precipitated crystals.

REFERENCES AND NOTES

- [1] Yamashita, Y; Kimura, K. *Polymeric Materials Encyclopedia*, CRC Press, Boca Raton, 8707, 1996.
- [2] Liu, J.; Rybnikar, F.; East, A. J.; Geil, P. H. *J. Polym. Sci., Part B: Polym. Phys.*, **31**, 1923, 1993.
- [3] Kimura, K.; Nakajima, D.; Kobashi, K.; Yamashita, Y.; Yokoyama, F.; Uchida, T.; Sakaguchi, Y. *Polym. for Adv. Tech.*, **11**, 747, 2000.
- [4] Schwarz, G.; Zemann, U.; Kricheldorf, H. R. *High Perform. Polym.*, **9**, 61, 1997.
- [5] Kricheldorf, Hans R.; Adebahr, Thorsten. *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 159, 1994.
- [6] Kricheldorf, H. R.; Loehden, G.; Wilson, D. J. *Macromolecules*, **27**, 1669, 1994.
- [7] Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1611, 1983.