

One-pot Preparation of Aromatic Poly(azomethine ester) Fibrillar Crystals Using Reaction-induced Crystallization

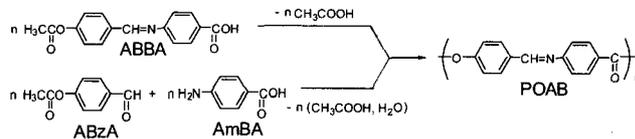
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INTRODUCTION

Poly[4-(4-oxybenzylideneamino)benzoyl] (POAB) which is an aromatic poly(azomethine ester) was predicted to possess unique combination of properties such as photochromic property, liquid crystallinity and thermal property derived from ester and azomethine moieties, and many poly(azomethine ester)s had been synthesized.¹⁾ However, it exhibits neither fusibility nor solubility, and thereby it is hardly used in spite of their predicted high-performance.

This paper describes the new finding on the preparation of fibrillar POAB crystals using the reaction-induced crystallization during polymerization of self-condensable 4-(4-acetoxybenzylideneamino)benzoic acid (ABBA). Further, the one-pot preparation of the fibrillar POAB crystals is also examined by the polymerization of 4-acetoxybenzaldehyde (ABzA) and 4-aminobenzoic acid (AmBA).



EXPERIMENTAL

A mixture of dibenzyltoluene (DBT, Matsumura Oil Co. Ltd) and liquid paraffin (LPF) (DBT-LPF, weight percent of DBT was 90%) was placed into a cylindrical flask equipped with gas inlet and outlet tubes, and heated up to 350°C under a slow stream of nitrogen. When the temperature reached to 350°C, ABBA²⁾ was added and then polymerization was carried out for 6 h at 350°C without stirring. Pale yellow crystals were obtained with the yield of 56%.

RESULTS AND DISCUSSION

Polymerization of ABBA

Self-condensable monomer ABBA was synthesized.²⁾

Three kinds of solvent such as LPF, DBT and their mixture (DBT-LPF) were used to induce crystallization of oligomers during polymerization. Content of DBT in DBT-LPF was 90 wt%. ABBA was not dissolved into these solvents at 25°C, but dissolved at around

TABLE I Polymerization results of POAB

Run no.	Polymerization condition			t_c^b (min)	Yield (%)	Morphology	T_{10}^c (°C)	η_{inh}^d (dL·g ⁻¹)
	Monomer	Solvent ^a	Conc. (%)					
1	ABBA	LPF	1.0	300	12	33	Plate	0.14
2	ABBA	DBT	1.0	300	22	9	Needle	0.15
3	ABBA	LPF	1.0	350	2	39	Slab	0.17
4	ABBA	DBT	1.0	350	7	15	Fiber	0.25
5	ABBA	DBTLPF	1.0	350	5	30	Fiber	0.19
6	ABBA	DBTLPF	5.0	350	1	56	Fiber	0.23
7	ABzA and AmBA	DBTLPF	5.0	350	5	34	Ribbon	0.27
8	ABzA and AmBA	DBTLPF	5.0	180, 350 ^e	2	44	Fiber, Ribbon	0.22
9	ABzA and AmBA	DBTLPF	5.0	140, 350 ^f	0	160	Ribbon	0.10

^aDBTLPF: Mixed solvent of DBT and LPF (weight ratio=9:1). ^b t_c stands for time when the solution became turbid after the solution temperature was reached at the polymerization temperature. ^c10% weight loss temperature measured on TGA with a heating rate of 20°C·min⁻¹ in nitrogen. ^dInherent viscosity (η_{inh}) was measured in 97% sulfuric acid at a concentration of 0.2 g·dL⁻¹ at 30°C. ^ePolymerization was carried out at 180°C for 2 h and then at 350°C for 6 h. ^fPolymerization was carried out at 140°C for 2 h and then at 350°C for 6 h.

200°C on heating. The solution became turbid within several minutes at polymerization temperature, and then the polymer precipitates were obtained. Table 1 presents the polymerization results. With respect to the polymerization at 300°C, spherical aggregates of plate-like crystals were obtained in LPF with the yield of 33%

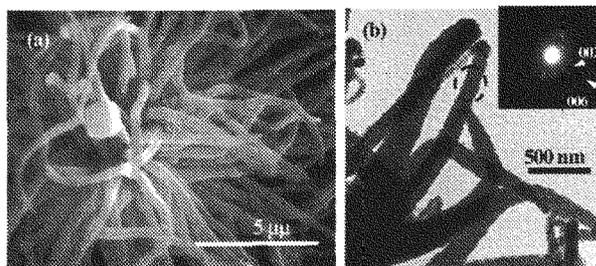


Figure 1 (a) SEM and (b) TEM of POAB fibrillar crystals

(run no. 1). Although the yield was 9% because of higher solubility, the needle-like crystals were formed in DBT (run no. 2), of which the average length and width were 30 μm and 2 μm , respectively. The surface of the needle-like crystals was rugged with many thin plate-like crystals. POAB was dissolved only in sulfuric acid, and therefore the inherent viscosity (η_{inh}) measured in 97% sulfuric acid was used to evaluate molecular weight. Their values of η_{inh} were 0.14 and 0.15 $\text{dL} \cdot \text{g}^{-1}$ respectively and the molecular weights of the precipitates are low. In order to increase the molecular weight of the precipitates, the polymerizations were carried out at 350°C. The polymerization in DBT at 350°C afforded fibrillar crystals with the yield of 15% (run no. 4) as shown in Figure 1. Their width ranged from 50 to 140 nm and the average was ca. 100 nm. Their average length was 25 μm . The value of η_{inh} of the fibrillar crystals was 0.25 $\text{dL} \cdot \text{g}^{-1}$ which was higher than that prepared at 300°C. The polymerization proceeds more effectively in the crystals at higher temperature. The low yield of the crystals prepared in DBT is due to the higher solubility of the oligomers as aforesaid. DBT is a mixture of dibenzyltoluene isomers and the structural similarity to POAB predicts readily higher solubility of oligomers in DBT than that in LPF. The time when the solution became turbid due to the precipitation (t_t) is adaptable as a criterion to evaluate the solubility of the oligomers, as shown in Table 1. The value of t_t at the same polymerization temperature was larger in DBT than in LPF, suggesting the higher solubility of the oligomers in DBT. DBT-LPF was used as the solvent to increase the yield of the crystals. The fibrillar crystals were formed in DBT-LPF at a concentration of 1% at 350°C with the yield of 30% (run no. 5). They also grew radially from the center points and they were 150 - 450 nm in width and 25 μm in average length. At higher concentration of 5% in DBT-LPF (run no. 6), the similar fibrillar crystals were also formed with the yield of 56%. Morphological difference from the fibrillar crystals prepared at a concentration of 1% was that the surface was covered with the nanometer-scaled rugged protrusions. The width of the fibrillar crystals ranged from 80 to 220 nm. As for the length, it is hardly possible to estimate because it is quite difficult to find the tail end of the fiber due to entangling and fusion. But the length is longer than 25 μm . The value of η_{inh} of these fibrillar crystals was 0.23 $\text{dL} \cdot \text{g}^{-1}$. The IR spectrum of the fibrillar crystals reveals the formation of POAB. In the WAXS profiles of the fibrillar crystals, the three sharp Bragg-type reflection peaks were observed at 2θ of 19.80, 23.09 and 28.43°, and the broad halo attributed to the amorphous region was hardly observed in the profile. The crystallinity of the fibrillar crystals is quite high. In order to evaluate the molecular orientation, the fibrillar crystals were observed in details on a TEM. Figure 1 shows the morphology and a SAED pattern taken from the circled area. Reflection spots were sharp and the fiber identity period is estimated to be 1.25 nm. If it is assumed that the POAB is all *trans* conformation, the fiber identity period is in good agreement to the length of one repeating unit of POAB. Even though the lattice constants of POAB crystals have not been determined so far, the reflection spots corresponding to those of 002 and 006 crystal planes are clearly observed perpendicular to the long direction of the fibrillar crystals. This assignment speculates that the molecular chains might vertically orient along the long axis of fibrillar crystals. Since the spot of 006 is diffused and streaked, the orientation of the molecular chains is slightly fluctuated.

In order to clarify the formation mechanism of the fibrillar crystals, the changes in morphology, yield and inherent viscosity of the precipitated crystals were investigated. The morphologies are shown in Figure 2 and the others are plotted in Figure 3. The oligomers dissolved in the solution were recovered from the filtrate and the recovery yield was also plotted in Figure 3. Oligomer precipitation started after 1 min. As shown in Figure 2 (a) and (b), plate-like crystals were formed after 10 min with the yield of 15% and they grew larger with time. Edges of the plate-like crystals became undulated after 30 min. As shown in Figure 2 (c), the large plate-like crystals drastically changed to the fine fibrillar crystals with the width of 120-380 nm after 1 h. The fibrillar crystals grew with the yield until 2 h, and then the yield became almost leveled off. The recovery yield of oligomers decreased corresponding to the increase in the yield of the POAB crystals and this reveals that the plate-like crystals were formed by the consecutive supply of oligomers from solution. It notes interestingly that many bundle-like structures were observed at the edge of the plate-like crystals formed after 1 h as marked in Figure 2 (d). Their width was approximately 150-200 nm corresponding to the width of the fibrillar crystals prepared for 6 h. These bundle-like structures were developing from the edge to the center of the plate-like crystals. Although the reason why the plate-like crystals drastically reorganized to the fine fibrillar crystals is not exactly clear so far, the observed bundle-like structure might be the initial structure of the final fibrils. As for the inherent viscosity of the precipitated crystals, it continuously increased even after 2 h when the yield of the crystals became almost constant. This fact reveals that the molecular weight increased by the efficient polymerization in the crystals.

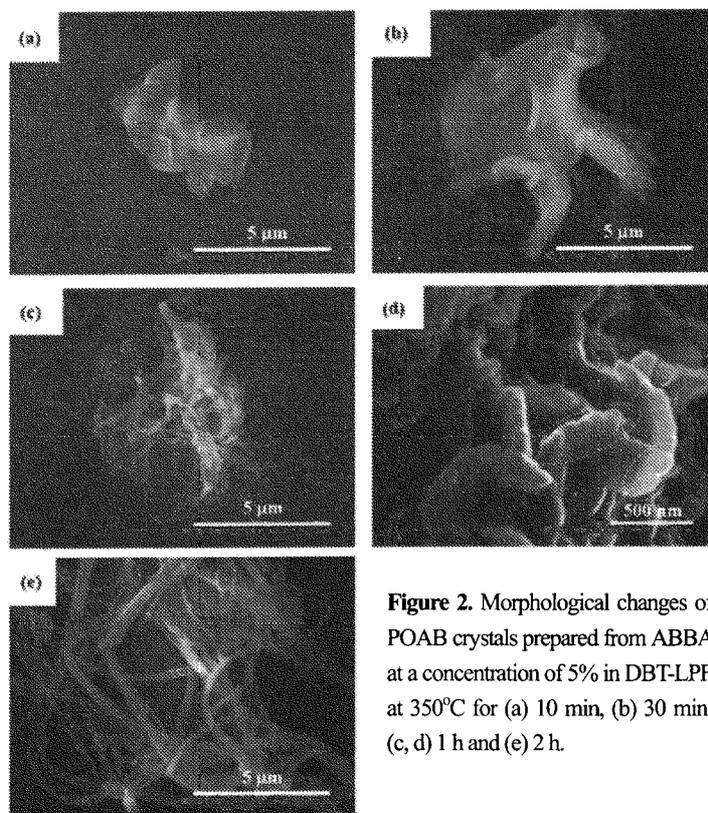


Figure 2. Morphological changes of POAB crystals prepared from ABBA at a concentration of 5% in DBT-LPF at 350°C for (a) 10 min, (b) 30 min, (c, d) 1 h and (e) 2 h.

Polymerization of ABzA and AmBA

Preparation of the fibrillar POAB crystals from ABzA and AmBA was examined by making both the azomethine linkage and the ester linkage in a one-pot procedure. The polymerizations were carried out in DBT-LPF at a concentration of 5% at 350°C which was the desirable condition for the preparation of the fibrillar crystals from ABBA. Table 1 also presents the polymerization results. The solvent was heated at 350°C, and then ABzA and AmBA were added to make the azomethine linkage and the ester

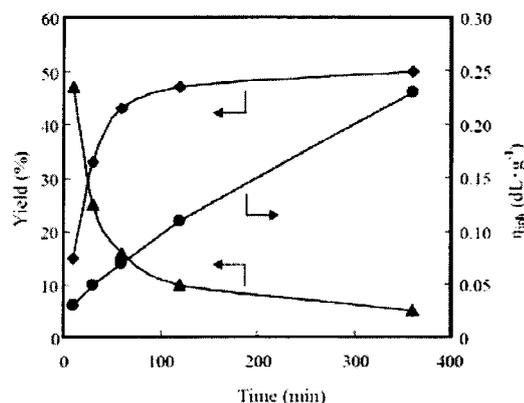


Figure 3. Plots of yield (◆) and inherent viscosity (●) of POAB crystals and yield of oligomers recovered from filtrate (▲) as a function of polymerization time. Polymerizations were carried out from ABBA at a concentration of 5% in DBT-LPF at 350°C.

linkage simultaneously. The mixture was stirred for 5 sec to dissolve ABzA and AmBA entirely, and then heated at 350°C without stirring for 6 h. Although the crystals were obtained with the yield of 34% and the value of η_{inh} of 0.27 dL·g⁻¹, the obtained crystals was morphologically different from the fibrillar crystals prepared from ABBA. Ribbon-like crystals with a very broad width from 50 to 800 nm were formed. In the IR spectrum of the obtained ribbon-like crystals, bands observed from 1600 to 1800 cm⁻¹ were resolved by the Gaussian-Lorentzian function. The characteristic peaks of POAB (C=O of ester, 1718 cm⁻¹, CH=N of azomethine, 1630 cm⁻¹) were detected, but a new peak appeared additionally at 1656 cm⁻¹ corresponding to the amide C=O. Further, the relative intensity of the ester C=O to the azomethine CH=N was quite low and that of the amide C=O is very high. An overtone or combination band of 1,4-phenylene ring was observed at 1667 cm⁻¹, whereas the peak of amide C=O was not detected at all in the resolved IR spectrum of the fibrillar crystals prepared from ABBA. This IR result implies that the self-polymerization of AmBA occurred to form *p*-benzamide sequence at the elevated temperature besides the formation of azomethine and ester linkages, and this plate-like crystal presumably contains *p*-benzamide sequences. It was previously reported that the polymerization of AmBA using reaction-induced crystallization yielded plate-like crystals of poly(*p*-benzamide) due to the strong interaction between polymer molecules through hydrogen bonding of the amide linkage.²⁸ The ribbon-like morphology seems to be attributed to the formation of *p*-benzamide sequences.

It has been already known that an aromatic amine react with an aromatic aldehyde to form the azomethine linkage without any catalysts below 200°C,^{3a, 26, 29-31} and this reaction was used for the synthesis of ABBA. The formation of the ester linkage from an aromatic carboxylic acid and a phenyl acetate needs higher temperature than 250°C.³²⁻³⁵ In order to depress the unfavorable side-reaction to form the *p*-benzamide sequence, the reaction of ABzA and AmBA was designed to carry out at 180°C for 2 h under stirring to form azomethine linkage, and then at 350°C without stirring to make ester linkage (run no. 8). These monomers became dissolved on heating up to 180°C and then the solution became turbid probably due to the precipitation of ABBA *in-situ* formed with the elimination of water. The turbid reaction mixture became homogeneous at 220°C on heating up to 350°C. The solution became turbid again after 2 min due to the precipitation and then the precipitates were obtained with the yield of 44% and the value of η_{inh} of 0.22 dL·g⁻¹ after 6 h. The yield became higher, but the value of η_{inh} became slightly lower than those prepared at 350°C. Fibrillar crystals were predominantly formed besides ribbon-like crystals. The fibrillar crystals were morphologically different from the ribbon-like crystals. The length of the fibrillar crystals was 0.5-3 μm quite shorter than that from ABBA and the width was 100-350 nm. On the other hand, the width of the ribbon-like crystals was ca. 150 nm. The IR spectrum of the products suggested that the side-reaction to generate *p*-benzamide sequences was not completely depressed.

CONCLUSION

The fibrillar POAB crystals were prepared by the crystallization of oligomers during the polymerization of ABBA at 350°C in DBT and DBT-LPF at low concentrations. The fibrillar crystals possessed high crystallinity and the molecule chains might orient vertically to the long axis of fibrillar crystals. The polymerization of AmBA and ABzA at 180°C for 2 h and then at 350°C for 6 h afforded the fibrillar crystals with a small amount of the ribbon-like crystals.

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