

Preparation of Brush-like Crystals of Poly [2,6-(1,4-phenylene)-benzobisimidazole]

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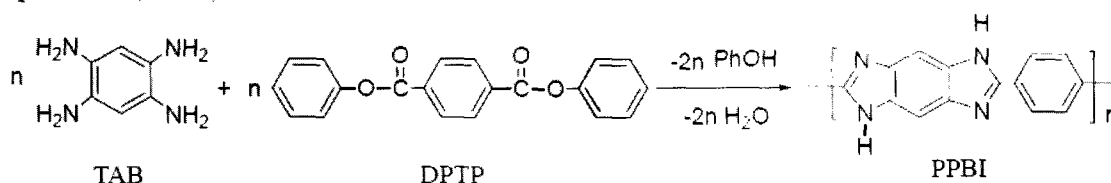
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1. Introduction

Polybenzimidazoles are aromatic heterocyclic polymers being notable as high-performance polymers^{1,2} and some of them are commercially used as heat-resistant materials. Their fully aromatic nature and stiffness of molecular chains endue them with superior properties such as thermal stability, mechanical strength, chemical resistance and so on. However, their molecular structures also bring about intractability.³ Poly[2,6-(1,4-phenylene)-benzobisimidazole] (PPBI) which is a representative of polybenzimidazole has a straight and planar molecular structure, and it is supposed to be one of the most ideal high-performance materials. PPBI does not melt under decomposition and it is soluble only in strong acids such as concentrated sulfuric acid and methanesulfonic acid. Therefore, it possesses the same perplexing problem of high performance versus tractability.

We have been studying morphology control of intractable aromatic polymers by using reaction-induced phase separation of oligomers during solution polymerization.^{4,5} These studies demonstrated that the reaction-induced phase separation of oligomers was a useful method to overcome the trade-off problem between high performance and poor processability. In this paper, morphology control of PPBI was examined by using the reaction-induced phase separation of oligomers during solution polymerization of 1,2,4,5-tetraaminobenzene (TAB) and diphenyl terephthalate (DPTP) as shown in Scheme 1.



Scheme 1. Synthesis of PPBI from TAB and DPTP

2. Polymerization

Polymerization in DBT was described as a typical example. DPTP (0.27g, 0.86mmol) and 20g of DBT were placed into a cylindrical flask equipped with gas inlet and outlet tubes. The reaction mixture was heated up to 350°C under slow stream of nitrogen with stirring. When DPTP was entirely dissolved in DBT during heating, TAB (0.12g, 0.86mmol) was added at 350°C into this solution. Polymerization was carried out for 6 h at 350°C without stirring. Precipitated polymers were isolated by hot filtration and washed with acetone. PPBI was obtained as precipitates with the yield of 81%. A

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filtrate was poured into *n*-hexane and the precipitated oligomers were collected, which were dissolved in DBT at 350°C. Polymerizations in other solvents were also carried out in the similar manner.

3. Results and Discussion

3.1 Influence of Solvent on Morphology

Polymerizations were carried out in LPF, DBT, DBT/DPS-50 (content of DPS was 50 wt%) and DPS at a monomer concentration of 1% at 350°C. Polymerization results were presented in **Table 1**. Morphology of the precipitates was drastically changed with the solvent. Brush-like crystals were obtained in LPF with the yield of 32%. Many protuberances were formed on the surfaces of the crystals as shown in **Figure 1 (a)**. In DBT, the precipitated crystals exhibited also brush-like morphology as shown in **Figure 1 (b)**. SEM images of the brush-like crystals taken from three different directions were shown in **Figure 2**. They were comprised of ribbon-like crystals and needle-like crystals. The brush-like crystal prepared in DBT possessed longer needle-like crystals than those prepared in LPF. In contrast to this, ribbon-like crystals having smooth surface were also formed in DBT/DPS-50 with the yield of 87%, and entangled fibrils were obtained in DPS with the yield of 97%, as shown in **Figure 1 (c) and (d)**. Inherent viscosities (η_{inh}) of the precipitated crystals prepared

Table 1 Synthesis of PPBI in various solvents

run no.	solvent	yield (%)	η_{inh}^a (dL•g ⁻¹)	morphology	average size			$T_{5\%}^c$ (°C)	
					width (X10 ⁻¹ μm)	cv^b (%)	thickness (X10 ⁻¹ μm)		
1	LPF	35	0.61	brush	5.2	47	1.5	33	460
2	DBT	81	0.58	brush	7.5	25	1.1	30	531
3	DBT/DPS-50	87	0.76	ribbon	4.3	27	0.7	40	374
4	DPS	97	- ^d	fiber	1.0 ^e	32	-	-	332

a) η_{inh} was measured in 97% sulfuric acid at a monomer concentration of 0.2 g•dL⁻¹ at 30°C. b) Coefficients of variation. c) Temperature of 5% weight loss measured on a TGA at a heating rate of 20°C•min⁻¹ in N₂. d) Not measured because the precipitates were insoluble. e) Average diameter of fiber.

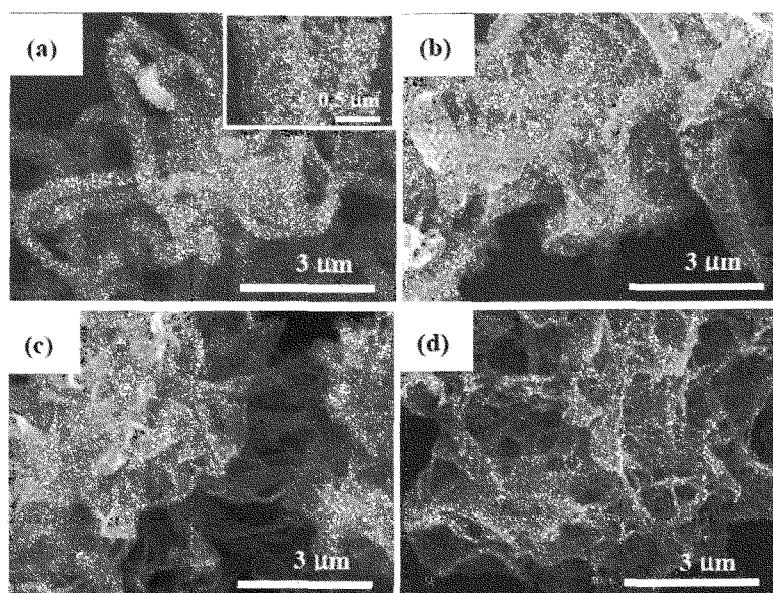


Figure 1. Morphologies of products prepared for 6 h in (a) LPF, (b) DBT, (c) DBT/DPS-50 and (d) DPS.

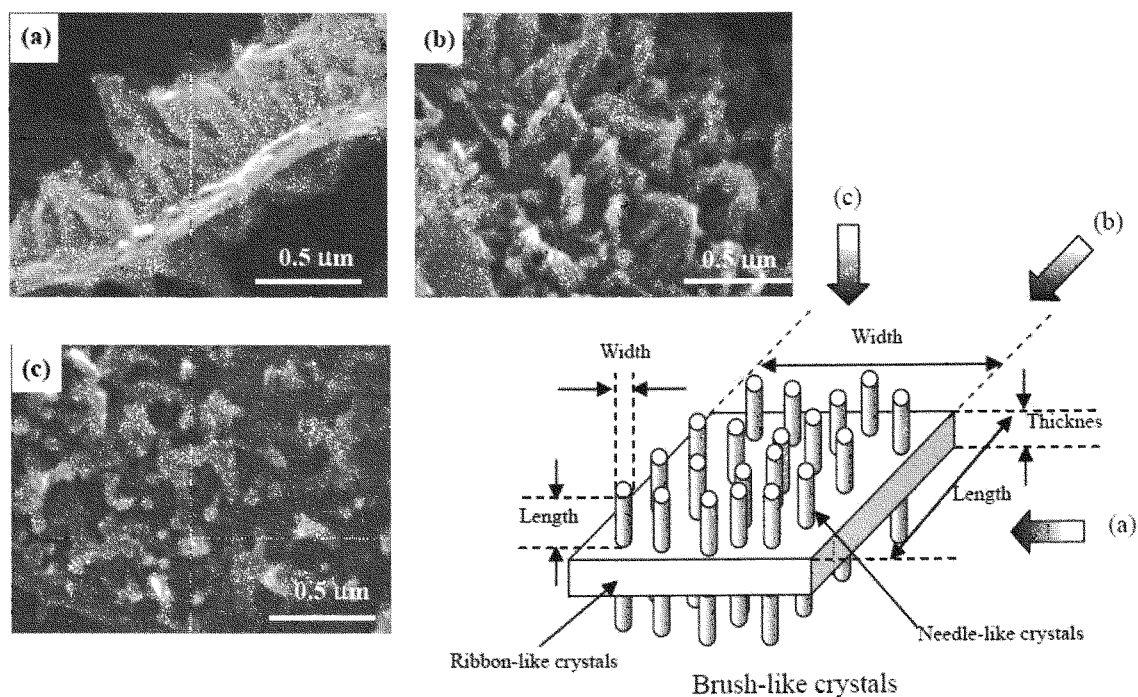


Figure 2. Micrographs of brush-like crystals taken from the three different directions. The crystals were prepared in DBT for 6 h.

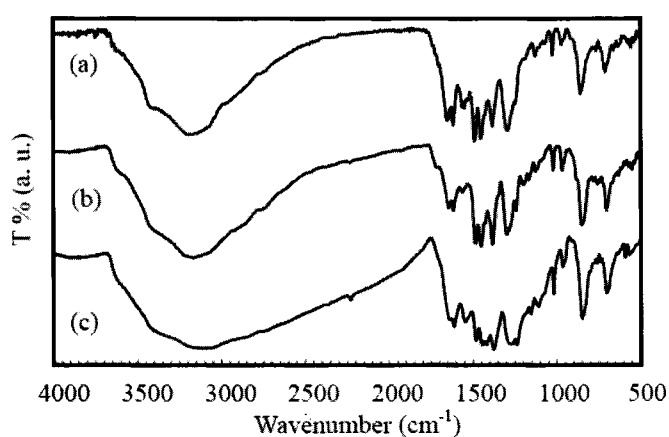


Figure 3. IR spectra of crystals prepared for 6 h in (a) LPF, (b) DBT and (c) DPS.

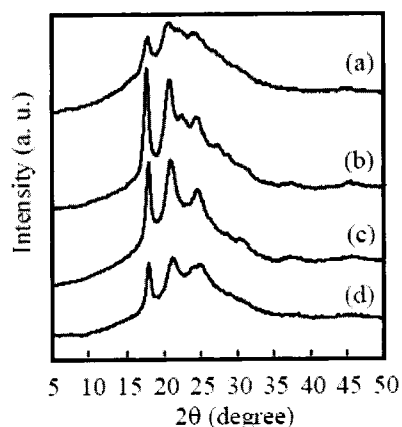


Figure 4. WAXS patterns of products prepared for 6 h in (a) LPF, (b) DBT, (c) DBT/DPS-50 and (d) DPS.

in LPF, DBT and DBT/DPS-50 were 0.61, 0.58 and 0.76 $\text{dL}\cdot\text{g}^{-1}$, being comparable to those previously prepared by solution polymerization.⁶ These precipitated crystals were high molecular weight polymers. IR spectra of crystals prepared in LPF, DBT and DPS were shown in **Figure 3**. In the spectra of the brush-like crystals prepared in LPF and DBT, the characteristic peaks of PPBI were clearly observed at 3500-3000 cm^{-1} (N-H and aromatic C-H stretching), 1640 cm^{-1} (C=N stretching of imidazole ring) and 1612 cm^{-1} (C=N stretching of imidazole ring), 1375 cm^{-1} (ring vibration of imidazole), and the formation of PPBI was confirmed. In contrast to this, unassignable peaks were

observed at 1415 and 1273 cm^{-1} in the spectrum of the precipitates in DPS besides the characteristic peaks of PPBL, which were not the uncyclized precursors. According to the wide-angle X-ray scattering (WAXS) (Figure 4) and thermogravimetric analysis (TGA) (in Table 1) results, the brush-like crystals prepared in DBT possessed the high crystallinity and thermal resistance.

3.2 Formation of brush-like crystals

In order to examine the formation mechanism of the brush-like crystals, morphology of the precipitates was observed in the course of polymerization in DBT. As shown in Figure 5, aggregates of plate-like crystals were formed after 0.5 h. The surface of these plate-like crystals was very smooth and protuberances were not observed. The protuberances appeared on the surface after 1 h and their length increased leading to the formation of the needle-like crystals on the surface. Then the brush-like crystals

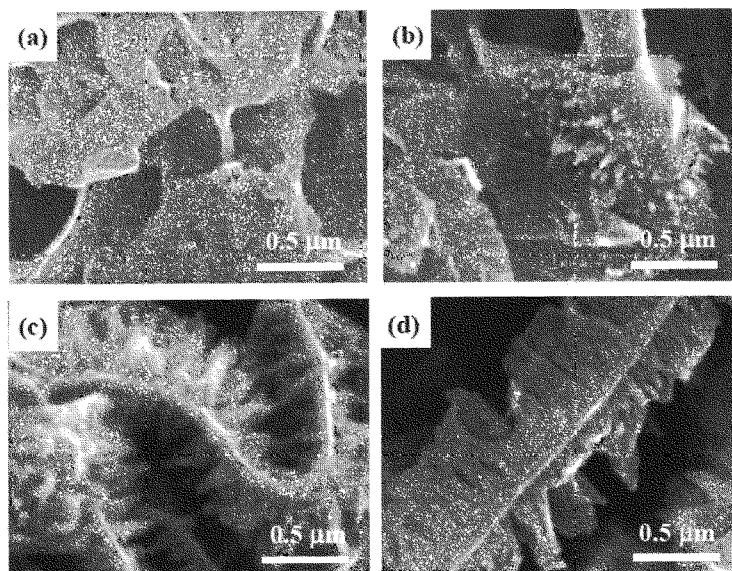


Figure 5. Micrographs of crystals prepared in DBT for (a) 0.5 h, (b) 1 h, (c) 3 h and (d) 21 h.

were formed after 3 h. The length of needle-like increased with polymerization time, that is, the yield of the crystals, while their width and the thickness were almost constant at 0.75 μm and 0.11 μm throughout the polymerization. Yield and η_{inh} of the crystals and the oligomers collected from solution were examined during polymerization. As shown in Figure 6, the yield increased with polymerization time and then it became constant after 6 h. This reveals that the crystals were grown by the consecutive supply of oligomers precipitated from solution as aforesaid. The η_{inh} of the crystals also increased with polymerization time until 6 h, and then leveled off. In contrast to this, the η_{inh} of the oligomers was almost constant throughout the polymerization. These results implied that when the molecular weight of oligomers exceeded a critical value, they were precipitated through the supersaturated state to form the crystals. The

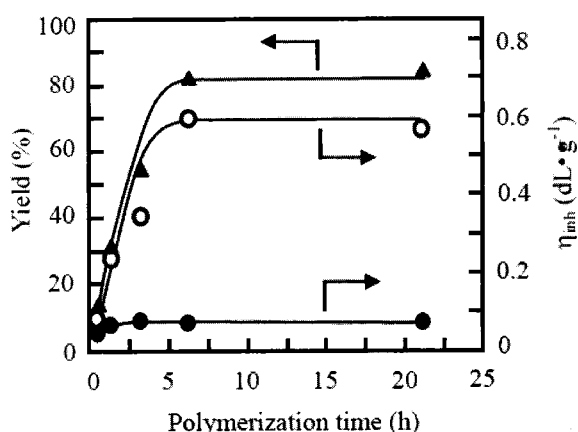


Figure 6. Plots of yield (\bullet), inherent viscosity of crystals (\circ) and oligomers recovered from solution ($\bullet \bullet$) as a function of polymerization time. Polymerizations were carried out in DBT.

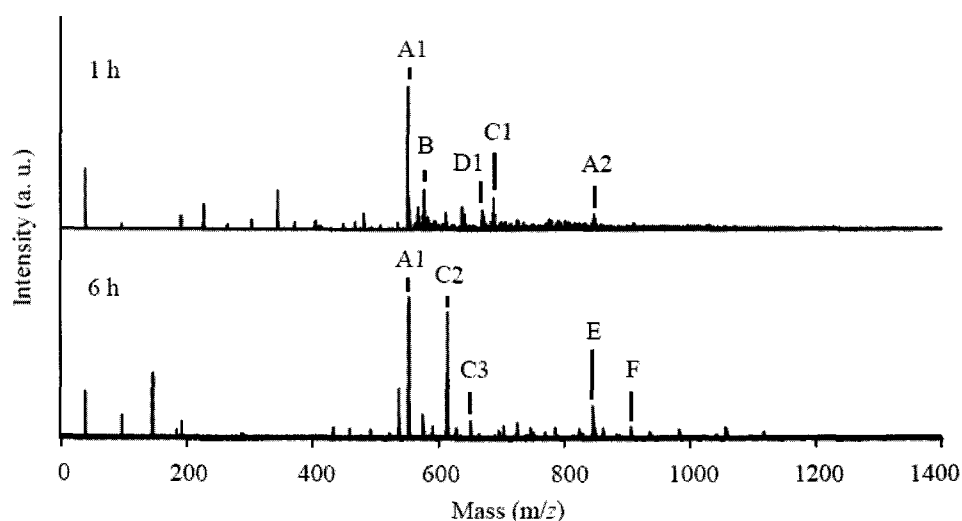
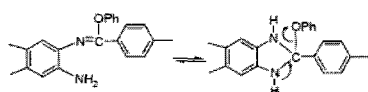


Figure 7. MALDI TOF mass spectra of PPBI oligomers collected from solution. Polymerization was carried out in DBT for different time.

Table 2 Assignments of peaks in the MALDI-TOF mass spectra of Figure 7

peak code	mass (m/z)			structure	n	cation
	measured		calculated			
	1 h	6 h				
A1	551.40	552.01	551.58		1	H ⁺
A2	848.18	-	846.96		2	K ⁺
B	577.56	-	577.63		1	H ⁺
C1	687.83	-	688.85		1	K ⁺ K ⁺
C2	-	612.28	613.66		1	H ⁺
C3	-	650.38	650.75		1	K ⁺
D1	669.74	-	670.84		1	K ⁺ K ⁺
E*	-	845.00	845.91		2	H ⁺
F*	-	905.14	905.19		1	K ⁺ K ⁺ K ⁺

*



condensation reaction occurred effectively on the crystals when the oligomers were crystallized. The fact that the molecular weight of polymers became constant after the yield was leveled off exhibits that the solid-state polymerization hardly occurred in the crystals because of the low mobility of molecular chains in the crystals. WAXS profiles of these crystals were also determined. The crystallinity of crystals prepared for 1 h was as high as that of crystals prepared for 21 h. This result strongly supports the above discussion that the PPBI brush-like crystals were formed by the crystallization of the oligomers. In order to make the structure of the precipitated oligomers clear, the oligomers dissolved in the solution were collected after 1 h and 6 h, and analyzed by the MALDI-TOF mass spectrometry. The spectra are shown in **Figure 7** and the peaks were identified listing in **Table 2**. The recovered compounds contained one or two repeating unit, indicating that the precipitated oligomers might be mainly more than trimers. The cyclized imidazole oligomers were detected both after 1 h and 6 h. Because of the straight, rigid and planar structure of the cyclized imidazole oligomers, they can crystallize to form the clear morphology. On the contrary, the uncyclized oligomers would prevent to form the crystal because of the structure irregularity and the structural defects. It is also noticed that the content of the cyclized imidazole oligomers became lower with the polymerization time, and the cyclized oligomers were preferably precipitated due to the lower solubility in DBT than the uncyclized oligomers.

The brush-like crystals were also obtained in LPF, but they did not exhibit the high crystallinity as shown in **Figure 4**. In order to clarify the difference, yield and η_{inh} of the crystals and the oligomers collected from solution, morphological changes, WAXS, and the MALDI-TOF mass spectrometry were also determined. In contrast to the results in DBT, it was concluded that the precipitation of uncyclized polar oligomers in LPF caused the lower crystallinity of the brush-like crystals prepared in LPF.

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