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ScienceDirect
Polymer 49 (2008) 1783−1791
polymer
www.elsevier.com/locate/polymer

Morphology control of poly(2,2′-phenylene-5,5′-bibenzimidazole) by reaction-induced crystallization during polymerization

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Received 24 December 2007; received in revised form 1 February 2008; accepted 12 February 2008
Available online 14 February 2008

Abstract

Morphology control of polybenzimidazoles was examined by reaction-induced phase separation during polymerization. Polymerizations of 3,3′-diaminobenzidine with terephthalic acid or diphenyl terephthalate were carried out in poor solvents. The morphology of the precipitated poly[2,2′-(1,4-phenylene)-5,5′-bibenzimidazole] (PpBBI) was significantly influenced by the polymerization conditions, and the aggregates of nano-scale PpBBI fibers were obtained by the polymerization at a concentration of 3−5% and 320−350 °C in dibenzyltoluene. The average diameter of the fibers was ca. 50 nm and inherent viscosities of the precipitates were 0.35−0.58 dL g^{-1}. They possessed high crystallinity and thermal stability. The oligomers were precipitated first by the reaction-induced crystallization to form the highly crystalline lath-like crystals at an initial stage of polymerization. Then the lath-like crystals were split into disentangled aggregates of fine fibers with maintaining the high crystallinity. The polymerization mainly proceeded when the oligomers were registered into the crystals. The obtained aggregates of nano-scale fibers could be recognized as nonwoven fabrics. Morphology control of poly[2,2′-(1,3-phenylene)-5,5′-bibenzimidazole] was also examined and particles were mainly formed.

Keywords: Morphology; Polybenzimidazole; Nanofiber

1. Introduction

Heterocyclic aromatic polymers have been developed as hopeful candidates for high performance plastics [1,2]. Polybenzimidazoles (PBIs) are one of the most successful classes among them, because they possess high chemical resistance, flame retardant, radiative stability, excellent mechanical strength and its retention over a wide range temperature, and so on [3−12]. Due to these excellent properties, PBI exhibits very high durability under thermally serious circumstances such as aerospace. Many efforts on fabricating PBI have been devoted for the practical usages and some of them are commercially available nowadays [13,14].

Nano- and micro-scale high performance fibers have been paid attention as new materials for supporting nanotechnology, and nano-scale poly[2,2′-(1,3-phenylene)-5,5′-bibenzimidazole] (PmBBI) fibers were fabricated by electro-spinning process [15]. However, few studies on the preparation of nano-scale poly[2,2′-(1,4-phenylene)-5,5′-bibenzimidazole] (PpBBI) fibers have been reported because of the poor processability. Morphology control of rigid-rod aromatic polymers had been studied by using reaction-induced phase separation of oligomers during solution polymerization [16,17]. These studies show that the reaction-induced phase separation has been proposing as the useful built-up type morphology control method for intractable and poor processable polymers. This paper aims to control the morphology of PpBBI and PmBBI by using reaction-induced phase separation during solution polymerization, focusing on the preparation of nano-scale PBI fibers.

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doi:10.1016/j.polymer.2008.02.016

2. Experimental section

2.1. Materials

3,3′-Diaminobenzidine (DAB), diphenyl isophthalate (DPIP) and diphenyl sulfone (DPS) were purchased from Aldrich Co., Ltd. DAB was recrystallized from methanol with activated charcoal. DPS was recrystallized from a mixture of methanol and water. Terephthalic acid (TPA) and isophthalic acid (IPA) were purchased from TCI Co. Ltd. TPA was used as received. IPA was recrystallized from methanol. Diphenyl terephthalate (DPTP) was purchased from Wako Pure Chemical Co. Ltd. DPIP and DPTP were recrystallized from ethyl acetate. Liquid paraffin (LPF) was purchased from Nacalai Tesque Co. Ltd. and purified by vacuum distillation (220–240 °C/0.3 mmHg). Number average molecular weight of LPF was 930 and tertiary carbon content was 15% evaluated by ^{13}C NMR spectroscopy according to the previous reports [18–20]. Dibenzyltoluene (DBT) which was a mixture of dibenzyltoluene isomers was purchased from Matsumura Oil Co. Ltd. (trade name: Barrel Therm 400) and purified by vacuum distillation (180–200 °C/0.3 mmHg).

2.2. Measurements

Morphologies of the polymer precipitates were observed on a Hitachi S-3500N scanning electron microscope (SEM). Samples for SEM observation were dried, sputtered with gold and observed at 20 kV. Average diameters of fibers were estimated with 150 observation values. Infrared (IR) spectra were measured on a JASCO FT/IR-410 spectrometer. The inherent viscosities (η_{inh}) of the polymers were measured in 97% sulfuric acid at a concentration of 0.2 g dL^{-1} in an Ubbelohde viscometer at 30 °C. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA-7A with a heating rate of 10 °C min^{-1} in N_2. Wide angle X-ray scattering (WAXS) patterns of the crystals were conducted on a Rigaku Miniflex with nickel-filtered Cu Kα radiation with a scanning rate of 1 degree min^{-1}. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Bruker Daltonics AutoFLEX MALDI-TOF MS system operating with a 337 nm N_2 laser. Spectra were obtained in the linear positive mode with accelerating potential of 20 kV. Mass was calibrated with angiotensin I (MW 1296.69) and insulin B (MW 3496.96) of a Sequazyme peptide mass standard kit. Samples were prepared by the evaporation–grinding method, and then measured in dithranol as a matrix doped with potassium trifluoroacetate salt according to the procedure [21]. Chemical structures of solvents were characterized on a Bruker AVANCE500 NMR spectrometer operating at 125 MHz (^{13}C) in $CDCl_3$.

2.3. Polymerization

2.3.1. Polymerization of DAB and TPA

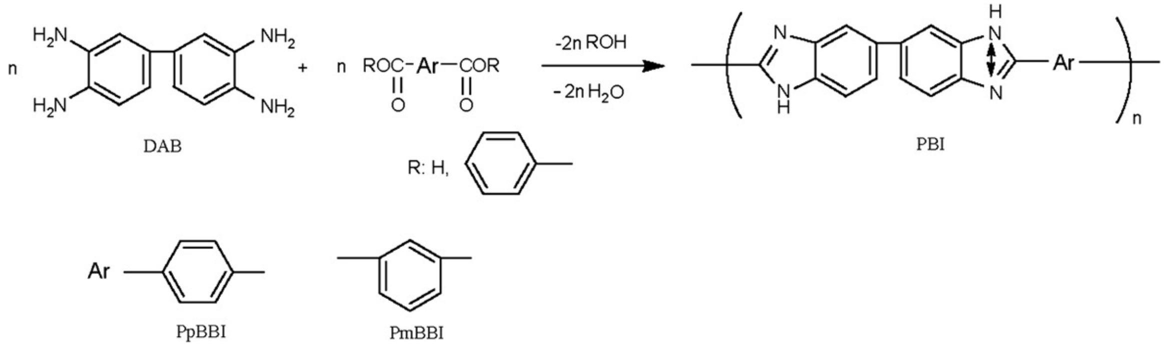
Into a cylindrical flask equipped with gas inlet and outlet tubes were placed TPA (0.54 g, 3.24 mmol) and 20 mL of DBT. The reaction mixture was heated under slow stream of nitrogen up to 350 °C with stirring. TPA was entirely dissolved during heating. After temperature reached 350 °C, DAB (0.69 g, 3.24 mmol) was added into the solution and stirring was stopped when the monomers were dissolved. The temperature was maintained at 350 °C for 6 h. The precipitates were collected by vacuum filtration at 350 °C, and washed with *n*-hexane and hot acetone.

2.3.2. Polymerization of DAB and DPTP

Into a cylindrical flask equipped with gas inlet and outlet tubes were placed DAB (0.69 g, 3.24 mmol) and 20 mL of DBT. The reaction mixture was heated under slow stream of nitrogen up to 350 °C with stirring and DAB was entirely dissolved during heating. After temperature reached 350 °C, DPTP (1.03 g, 3.24 mmol) was added into the solution. Polymerizations were carried out according to the same procedure as described above. The filtrate after the separation of precipitates was poured into *n*-hexane. The precipitated oligomers, which were dissolved in DBT at 350 °C, were recovered by filtration and washed with *n*-hexane.

3. Results and discussion

PBIs are generally prepared from aromatic tetraamines and activated aromatic acid derivatives such as diphenyl ester, acid chloride and so on [1,10]. It had been recently reported that aromatic polyamide could be prepared by the direct polycondensation of aromatic diamines and aromatic dicarboxylic acids at high temperature without any condensation reagents [22]. Therefore, TPA and IPA were also used in this study as monomers besides their diphenyl esters as depicted in Scheme 1. Solvents which were good to monomers and poor to PBI



Scheme 1. Synthesis of PBI.

Table 1
Synthesis of PpBBI under various conditions

Run no.	Polymerization conditions				Yield (%)	η_{inh}[a] (dL g^{-1})	Morphology of crystals	D_f[b] (nm)	$T_{5\%}$[c] (°C)
	Solvent	Conc. (%)	Temp. (°C)	Time (h)					
Monomers: DAB + TPA									
1	DBT	1	350	6	46	0.48	Plate	–	371
2		3		6	70	0.58		–	614
3		5		6	75	0.49		–	581
Monomers: DAB + DPTP									
4	LPF	1	320	6	38	0.25	Lath, plate	–	538
5		3		6	86	0.27		–	475
6		5		6	69	0.21		–	457
7	DBT	1	320	24	58	0.45	Plate, NF[d]	49	458
8		3		6	84	0.35	NF	52	499
9		5		6	98	0.45		52	537
10		1	350	6	36	0.42	Plate	–	320
11		3		6	91	0.52	NF	51	573
12		5		6	98	0.58		50	569
13	DPS	1[e]	350	6	80	0.61	Porous mass	–	583
14		3[e]		6	93	0.75		–	612
15		5[e]		6	99	0.75		–	594

[a] Inherent viscosity was measured in 97% sulfuric acid at 0.2 g dL^{-1} and 30 °C.
[b] D_f: average diameter of fibers.
[c] Temperature of 5 wt% loss measured on a TGA at a heating rate of 10 °C min^{-1} in N_2.
[d] NF stands for the aggregates of nano-scale fibers.
[e] Concentration (wt%) = (weight of PpBBI)/(weight of DPS) × 100.

were required to induce the phase separation of oligomers during polymerization. LPF and DBT were used as solvents in the present study.

3.1. Morphology of poly[2,2′-(1,4-phenylene)-5,5′-bibenzimidazole]

TPA was insoluble in LPF even at 350 °C and LPF could not be used as a solvent for the polymerization of TPA. DBT was a better solvent to TPA than LPF, and therefore polymerizations of DAB and TPA were carried out in DBT at a concentration of 1–5% and 350 °C for 6 h. The results were presented in Table 1. The reaction mixture of TPA and DBT was heated up to 350 °C with stirring and TPA was entirely dissolved while heating. Then DAB was added into the solution at 350 °C. When DAB was added to the solution, the polymerization started immediately with eliminating water and the solution became turbid. Orange plate-like crystals were finally obtained as precipitates with the yield of 46–75%. Chemical structure of the precipitates was analyzed by IR spectroscopy. The spectrum is shown in Fig. 1. The characteristic peaks of PpBBI were clearly observed at 3400–3000 cm^{-1} (N–H and aromatic C–H), 1622 cm^{-1} (–C=N–), and 806 cm^{-1} (imidazole ring). This spectrum is identical with that of the previously prepared PpBBI [9]. The inherent viscosities of the precipitates were in the range of 0.48–0.58 dL g^{-1}. WAXS profiles of the precipitates were shown in Fig. 2. These profiles indicate that the obtained products possess quite high crystallinity, implying that they are formed by the reaction-induced crystallization of oligomers. With respect to the morphology, they are aggregates of small plates as shown in Fig. 3(a). The morphology of the polymers prepared by the phase separation is strongly influenced by the chemical structure of oligomer end groups [23]. In this

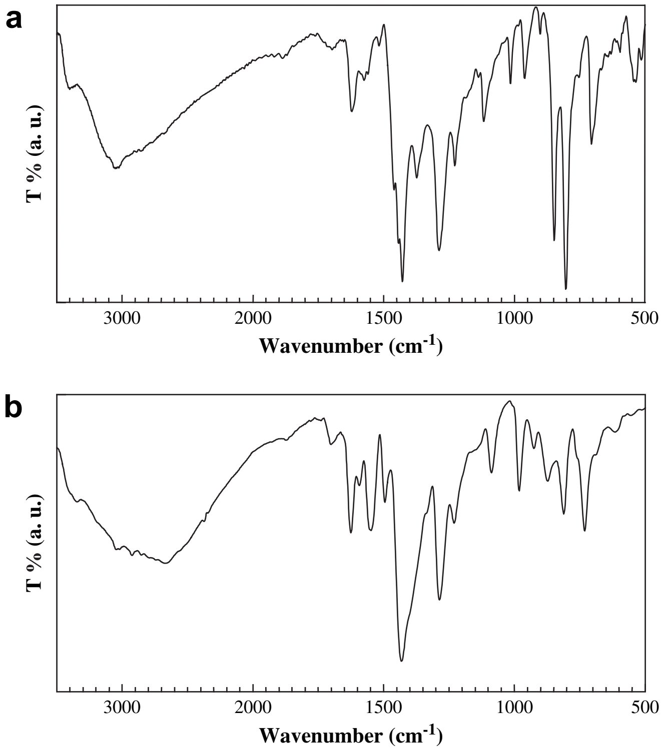


Fig. 1. IR spectra of (a) PpBBI precipitates prepared in DBT at 350 °C and a concentration of 3% from DAB and TPA (run no. 2) and (b) PmBBI precipitates prepared from DAB and DPIP (run no. 26).

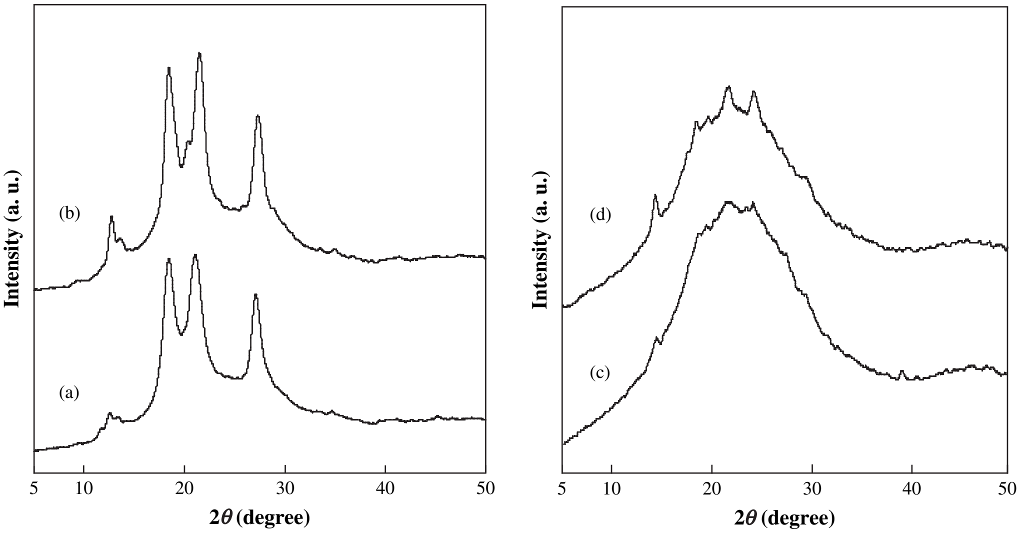


Fig. 2. WAXS intensity profiles of PpBBI precipitates prepared from (a) DAB and TPA in DBT at 350 °C and a concentration of 3% (run no. 2) and (b) DAB and DPTP in DBT at 320 °C and a concentration of 3% (run no. 8); and PmBBI precipitates prepared from (c) DAB and DPIP in DBT at 350 °C and a concentration of 3% (run no. 26) and (d) DAB and DPIP in DBT at 350 °C and a concentration of 10% (run no. 29).

polymerization, the oligomer end-groups are carboxylic acid and/or amino group, and these polar end-groups possess strong interaction, leading to the aggregation.

DPTP was used instead of TPA to reduce the aggregation force of oligomers caused by the carboxylic end-groups. DPTP was soluble in DBT and LPF at the polymerization temperature, and therefore the polymerizations were carried out in both solvents. In this polymerization, DAB was more insoluble in the solvents than DPTP. Therefore DAB was dissolved first at polymerization temperature, and then DPTP was added to the DAB solution. When DPTP was added to the solution, polymerization started with elimination of phenol and water. Orange crystals were precipitated in LPF with the yields of 38–86% after 6 h. Even though the inherent viscosities were low, the concentration of 3% afforded the highest inherent viscosity of 0.27 dL g^{-1}. The products obtained in LPF were the mixture of lath-like crystals and spherical aggregates of plate-like crystals as shown in Fig. 3(b). DBT was used as the solvent to increase the miscibility. Although nothing precipitated at 320 °C and a concentration of 1% for 6 h, orange precipitates were obtained at a concentration of 3 and 5% in good yields of 84 and 98%. The IR spectra of these precipitates were also identical with PpBBI. Interestingly, the precipitates were the aggregates of fine fibers having average diameter of ca. 50 nm as shown in Fig. 3(c) and (d). The inherent viscosities of them obtained at a concentration of 3 and 5% were 0.35 and 0.45 dL g^{-1}, respectively, which were higher than those prepared in LPF. At 350 °C, the aggregates of fine fibers were also formed at a concentration of 3 and 5%, of which the average diameter was also ca. 50 nm. The higher temperature gave the higher molecular weight fibers quantitatively, of which the inherent viscosity was 0.58 dL g^{-1}. WAXS patterns of the fibers prepared in DBT were also measured as shown in Fig. 2. The obtained patterns show quite sharp diffraction peaks and these precipitates possess high crystallinity as well as those prepared in LPF. The morphology of the network structure of nano-scale fibers can be regarded as nonwoven fabrics. DPS is a polar solvent and might have higher miscibility than DBT. Polymerizations were also carried out in DPS at a concentration of 1–5% and 350 °C for 6 h. In this case, the aggregates of fibers were not formed and the clear fibrillar morphology disappeared. The porous precipitates were obtained in the yield over 80% as shown in Fig. 3(f). The inherent viscosities were higher than others and the concentration of 3 and 5% gave the highest viscosity of 0.75 dL g^{-1}. It concludes that the polymerization of DAB and DPTP in DBT is desirable for the fabrication of the PpBBI nano-scale fibers. Thermal stability was measured on a TGA in N_2. Temperature of 5% weight loss of the precipitates crystals was related to the molecular weight and higher molecular weight higher temperature. The temperatures of 5% weight loss of the PpBBI nano-scale fibers prepared at 350 °C were in the range of 569–573 °C and they show good thermal stability.

In order to clarify the formation mechanism of the aggregates of the nano-scale fibers were examined the morphology, the crystallinity, the inherent viscosity and the yield of the precipitates in the course of the polymerization of DAB and DPTP in DBT at 350 °C. The inherent viscosity of the recovered oligomers was also examined. Polymerization concentration was 5%. The plots of the results, WAXS intensity profiles are shown in Fig. 4, and the morphologies were shown in Fig. 5. The yield of the precipitates increased with time and they were formed by the consecutive supply of oligomers from the solution into the crystals. The viscosity of the precipitates increased with the yield and it became constant at 0.58 dL g^{-1} after 6 h when the yield was leveled off. On the other hand, the viscosity of the oligomers recovered from the solution at 30 min was 0.06 dL g^{-1} and it was almost constant throughout the polymerization. The oligomers dissolved in the solution were collected from the solution after 30 min,

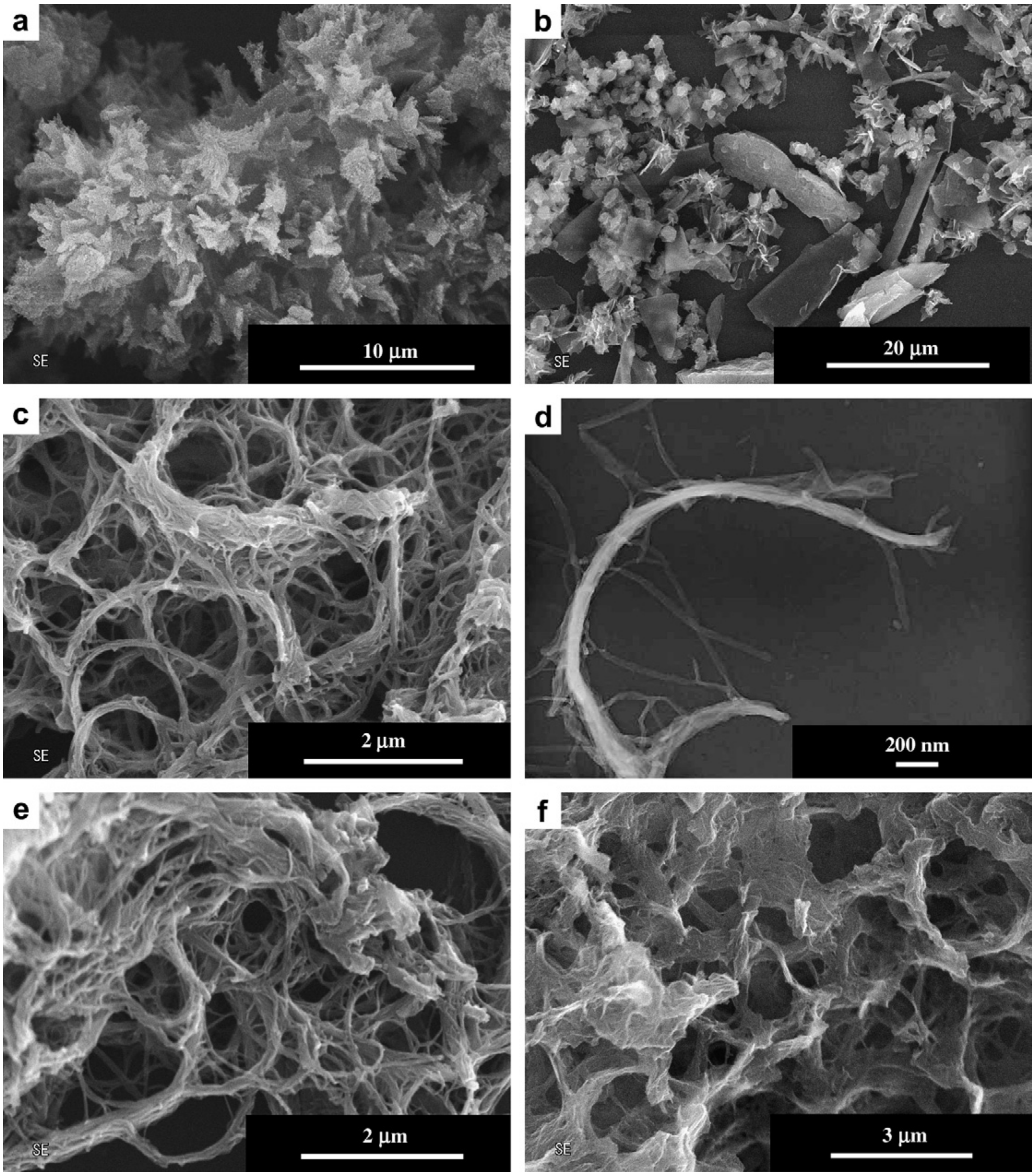


Fig. 3. PpBBI precipitates prepared from (a) DAB and TPA in DBT at 350 °C and a concentration of 3% (run no. 2), (b) DAB and DPTP in LPF at 320 °C and a concentration of 3% (run no. 5), (c) and (d) DAB and DPTP in DBT at 320 °C and a concentration of 3% (run no. 8), (e) DAB and DPTP in DBT at 350 °C and a concentration of 5% (run no. 12) and (f) DAB and DPTP in DPS at 350 °C and a concentration of 3% (run no. 14).

1 and 6 h, and they were analyzed by MALDI-TOF MS spectroscopy. The spectra are shown in Fig. 6. The dissolved oligomers were the mixtures of the one and two repeating unit oligomers and one to two adducts of monomers. Although the oligomers containing amino amide moiety were observed, many of them were fully cyclized imidazole oligomers. These facts reveal that the low molecular weight imidazole oligomers were constantly precipitated to form the crystals and they were mainly polymerized when crystallized. The further polymerization in the solid state didn't occur efficiently due to the rigidity of the polymer molecules. The spherical aggregates of lath-like crystals were initially formed at 30 min. Then they were exfoliated to the belt-like crystals, of which the width was ca. 0.8 μm, and changed to the disentangled aggregates with slipping to fine fibers. With respect to WAXS intensity profiles of the precipitates shown in Fig. 4, the diffraction pattern of the precipitates at 30 min already exhibited polymer crystal structure and the diffraction peaks were quite sharp. The diffraction pattern didn't change throughout the polymerization. The PpBBI precipitates are formed by the crystallization of oligomers as aforesaid and they maintain the high crystallinity during the morphology development.

3.2. Morphology of poly[2,2′-(1,3-phenylene)-5,5′-bibenzimidazole]

Polymerizations of DAB and IPA or DPIP were carried out in LPF and DBT at 320–350 °C and a concentration of

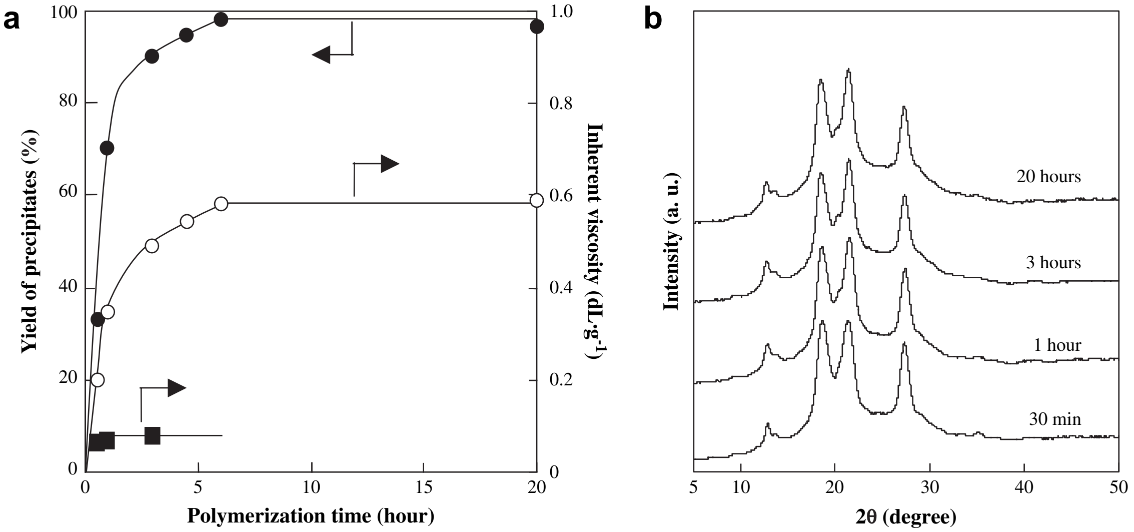


Fig. 4. (a) Plots of the viscosity of PpBBI precipitates (○), the viscosity of compounds recovered from solution (■) and yield of precipitates (●). (b) WAXS intensity profiles of PpBBI precipitates prepared from DAB and DPTP in DBT at a concentration of 5% and 350 °C during polymerization.

1–10%. The results were presented in Table 2 and the morphologies were shown in Fig. 7. In contrast to PpBBI, particles of PmBBI were mainly obtained under these conditions. The average diameters of these particles were in the range of 3.3–6.7 μm. The polymerizations of DAB and DPIP in DBT at 320 °C yielded a few lath-like crystals besides the particles as shown in Fig. 7(d). The polymerization at 350 °C afforded the particles, but the lath-like crystals besides the particles were formed at a concentration of 10% as shown in Fig. 7(e) and (f). The formation of PmBBI was confirmed by IR analysis as also shown in Fig. 1 and the inherent viscosities of the precipitates were in the range of 0.17–0.48 dL g^{-1}. Higher polymerization temperature gave higher molecular weight. WAXS intensity profiles of these particles are shown in Fig. 2. Weak diffraction peaks were detected in the profile of the precipitate prepared in run no. 29 which contained

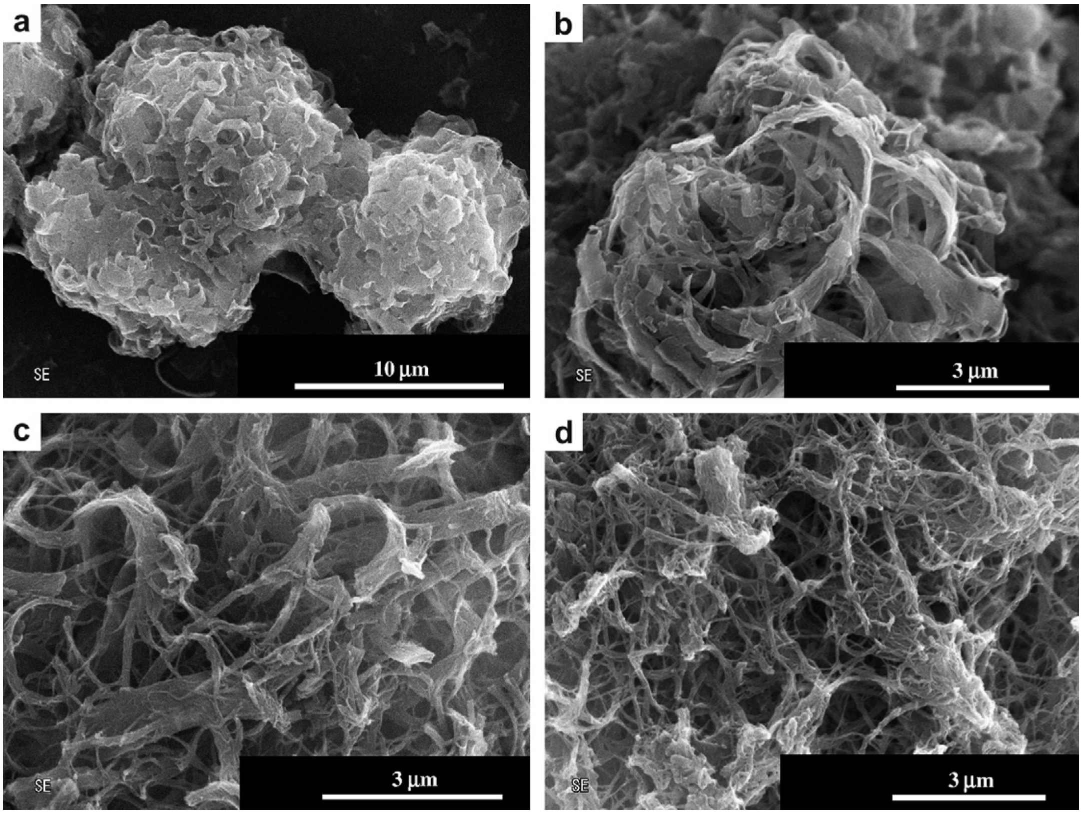


Fig. 5. PpBBI precipitates prepared from DAB and DPTP in DBT at 350 °C and a concentration of 5% for (a) 30 min, (b) 1 h, (c) 3 h and (d) 24 h.

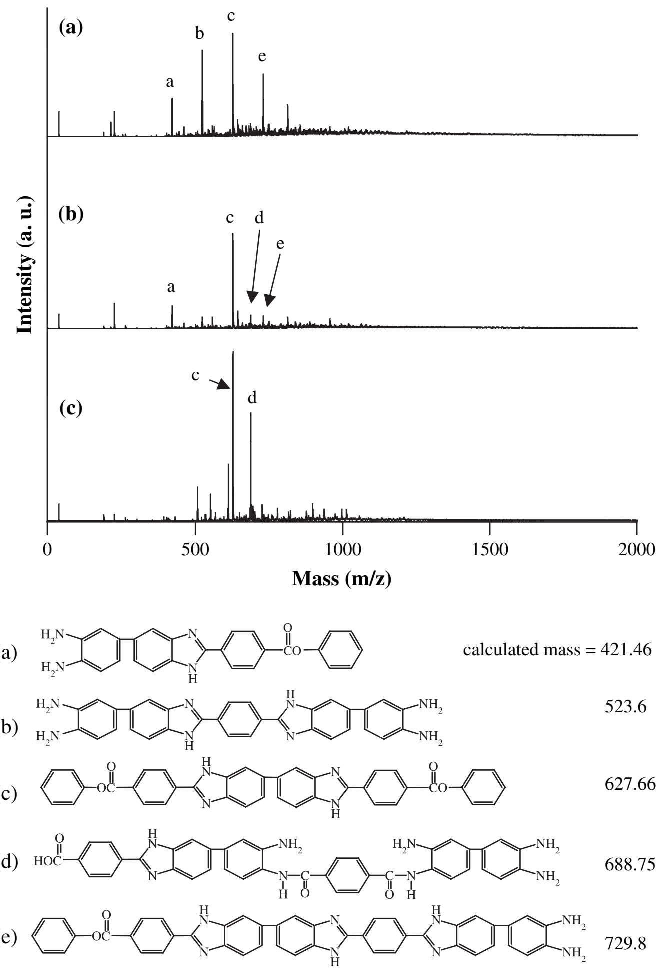


Fig. 6. MALDI-TOF MS spectra of PpBBI oligomer dissolved in solvent after (a) 30 min, (b) 1 h and (c) 6 h.

lath-like crystals, whereas the diffuse halo attributed to amorphous part was significantly observed. The obtained particles are amorphous. These results suggest that the particles are formed via the formation of microdroplets by the liquid–liquid phase separation during polymerization and the subsequent polymerization in them leading to solidification as previously reported [24]. Incorporation of 1,3-phenylene moiety in the polymer backbone lowers the freezing point of oligomers, and therefore the liquid–liquid phase separation might be induced under these polymerization conditions. The temperatures of 5% weight loss were 482–604 °C and they also exhibited good thermal stability.

4. Conclusions

The morphology of PBI was changed by the polymerization conditions. With respect to PpBBI, the polymerization of DAB and TPA afforded the plate-like crystals having high crystallinity. On the other hand, the polymerizations of DAB and DPTP in DBT at 320–350 °C afforded the aggregates of PpBBI fine fibers in good yields. The average diameter of the fibers was ca. 50 nm. Inherent viscosities were 0.35–0.58 dL g^{-1}, and the obtained nano-scale fibers also have high crystallinity and thermal stability. The oligomers were initially precipitated to form the highly crystalline lath-like crystals and the crystals were split into disentangled aggregates of fine fibers during polymerization, leading to the aggregates of fine fibers. The polymerization proceeded when the oligomers were registered into the crystals. In contrast to PpBBI, fine fibers were not formed by the polymerization of PmBBI, and particles were mainly obtained of which the average diameters were in the range of 3.3–6.7 μm. The particles were formed via the liquid–liquid phase separation.

Table 2
Synthesis of PmBBI under various conditions

Run no.	Polymerization conditions				Yield (%)	η_{inh}[a] (dL g^{-1})	Morphology of crystals	D_p[b] (μm)	$T_{5\%}$[c] (°C)
	Solvent	Conc. (%)	Temp. (°C)	Time (h)					
Monomers: DAB + IPA									
16	DBT	1	350	6	7	–	Sphere	–	–
17		3		6	61	0.48		4.3	604
18		5		6	64	0.39		–[d]	581
Monomers: DAB + DPIP									
19	LPF	1	320	6	43	0.17	Sphere	6.2	557
20		3		6	81	0.21		6.5	566
21		5		6	76	0.24		5.2	547
22	DBT	1		6	37	–	Sphere, lath	3.6	489
23		3		6	84	0.25		3.8	482
24		5		6	88	0.28		4.4	504
25		1	350	6	53	0.38	Sphere	5.0	602
26		3		6	85	0.39		5.3	563
27		5		6	98	0.37		6.7	544
28		7		6	94	0.37		3.3	547
29		10		6	96	0.33	Sphere, lath	6.4	523

[a] Inherent viscosity was measured in 97% sulfuric acid at 0.2 g dL^{-1} and 30 °C.

[b] D_p: average diameter of particles.

[c] Temperature of 5 wt% loss measured on a TGA at a heating rate of 10 °C min^{-1} in N_2.

[d] Diameter could not be measured because of coalescence.

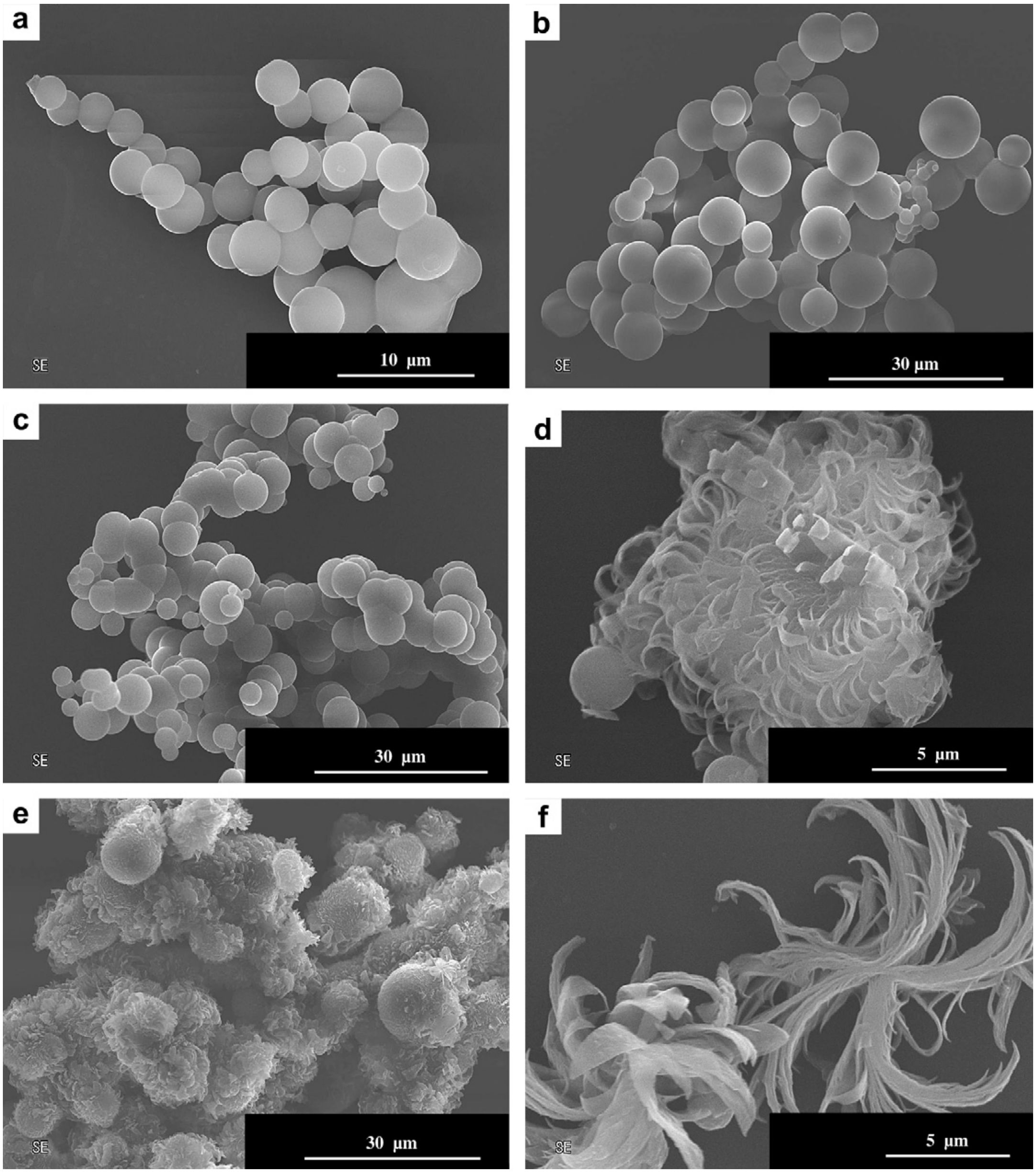


Fig. 7. PmBBI precipitates prepared from (a) DAB and IPA in DBT at 350 °C and a concentration of 3% (run no. 17), (b) DAB and IPA in LPF at 320 °C and a concentration of 3% (run no. 20), (c) and (d) DAB and IPA in DBT at 320 °C and a concentration of 3% (run no. 23), (e) and (f) DAB and IPA in DBT at 350 °C and a concentration of 10% (run no. 29).

Acknowledgement

This study was financially supported by Strategic Solid Waste Management for Sustainable Society, Centre of Excellence Program for the 21st Century, Ministry of Education, Culture, Sports, Science and Technology, Japan.

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