Morphology Control of Poly(*p*-phenylene pyromelliteimide) by Means of Self-Assembling Polymerization

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Introduction. Poly(*p*-phenylene pyromelliteimide) (PPPI) has been receiving much attention[1−3] because of the predicted outstanding properties, especially the highest modulus over 500 GPa.[4] However, PPPI exhibits neither solubility nor meltability, and the intractability derived from the rigid structure makes it inaccessible for processing by conventional techniques. PPPI has been usually prepared by a two-step procedure including the synthesis of a soluble poly(amic acid) precursor and the following imidization.[5,6] The difficulty of the orientation of poly(amic acid) precursor and the rapid crystallization during imidization prevent to control the morphology of PPPI.

We have been studying the morphology control of rigid polymers during solution polymerization and successfully prepared the whiskers and the microspheres of aromatic polyesters[7−13] and polythioester[14] by the polymerization in poor solvents. They are formed by the phase separation of oligomers including crystallization and liquid−liquid phase. These studies reveal that the self-assembling polymerization by means of the reaction-induced crystallization of oligomers is a valuable method for the morphology control of intractable polymers.

This Communication describes the results of our new finding on the morphology control of PPPI by means of the phase separation of oligomers during the solution polymerization of *p*-phenylenediamine (PPDA) and pyromellitic dianhydride (PMDA).

Results and Discussion. a. General Principle of Morphology Control. Several publications have been devoted to the preparation of polyimide particles.[15−18] Many of them are based on the precipitation from polymer solution by using the progressive decrease of solubility of rigid poly(aromatic amic acid) precursor in an aprotic polar solvent undergoing a thermal imidization. However, the preparation of the PPPI crystal and the morphology control are not achievable by these preparative procedures.

The principle of our approach to control the morphology of PPPI is based on the reaction-induced phase separation of oligomers during solution polymerization. Reaction-induced phase separation of oligomers in poor solvent is describable on the analogous concentration−temperature phase diagram ($C-T$ phase diagram) to that of the partially miscible polymer−solvent system.[19,20] The 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. The oligomers are formed by the polymerization reaction, and the molecular weight of oligomers increases in the solution. When the molecular weight of oligomers exceeds a critical value, the oligomers are in the supersaturation state and then phase-separated. If the supersaturated 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 postpolymerization in the crystals. On the other hand, if across the consolute curve, the oligomers are precipitated through liquid−liquid phase separation and the microdroplets of the dense phase are generated in the dilute phase. Finally, polymer microspheres are formed due to the solidification of the microdroplets caused by the further polymerization in the microdroplets.

b. Morphology of PPPI. Polymerizations were carried out at 330 °C.[21] After the addition of PPDA, the solution became turbid immediately, and the orange precipitates were obtained with a yield of over 80%. The morphology of the products is susceptible to not only the polymerization concentration but also the solvent, as shown in Table 1. Figure 1 shows the morphology of the products. With respect to the polymerization in liquid paraffin,[22] the polymerizations at the concentration of 1.00% and 0.50% yield the microspheres, of which the surface is slightly rough. The average diameter of the microspheres is dependent on the concentration, and those prepared at the concentration of 1.00 and 0.50% are 1.05 and 0.55 μm, respectively. The higher concentration gives the longer diameter. These microspheres exhibit a broader distribution of the diameter. In contrast to this, the morphology of the products is drastically changed when the polymerization is carried out at concentrations lower than 0.50%. The starlike aggregates of needle crystals and the lozenge-shaped crystals are formed. The large lozenge-shaped crystal is found in the product prepared at the concentration of 0.15%, of which the length of the longer diagonal line is 4.9 μm and that of the shorter line is 0.7 μm. It has been reported that the lower concentration has a tendency to induce the crystallization of oligomers because the molecular weight of the phase-separated oligomers becomes higher, and this brings about the increase of the freezing point of the oligomers.[23] In the case of this study, the influence of the polymerization concentration on the morphology is consistent with the previous results, and this fact suggests that the phase separation behavior of the oligomers governs the morphology of PPPI.

To elucidate the influence of the solvent on the morphology, polymerization was carried out in Therm S 1000 (TS10)[24] at a concentration of 0.50%. In contrast to the result in liquid paraffin, the starlike aggregates of needle crystals and the lozenge-shaped crystals are formed. The miscibility between the oligomers and TS10 is higher compared with liquid paraffin. It has been clarified that the higher miscibility between the oligomer and the solvent makes the two immiscible liquid phase narrow on the $C-T$ phase diagram and leads to the crystallization of oligomers.[25,26] The solvent effect in the polymerization of PPPI is in agreement with the previously reported tendency. The temperature at which PPDA is added also influences the morphology. When

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Table 1. Results of Polymerization[a]

run no.	polymerization condition				yield (%)	morphology	10 wt % loss temp[c] (°C)
	solvent	concn (%)	time (h)	addition temp[b] (°C)			
1	LPF	1.00	6	280	80.0	spherical (D = 1.05, cv = 34.2[d])	710
2	LPF	0.50	6	280	85.0	spherical (D = 0.55, cv = 41.8)	737
3	LPF	0.25	6	280	80.4	SA[e], lozenge-shaped	727
4	LPF	0.15	18	280	84.3	SA, lozenge-shaped	681
5	TS10	0.50	6	240	83.8	spherical (D = 0.83, cv = 39.2)	685
6	TS10	0.50	6	280	85.0	SA, lozenge-shaped	721
7	TS10	0.50	6	330	85.1	SA, lozenge-shaped	721

[a] Polymerizations were carried out at 330 °C. [b] Temperature at which PPDA was added after PMDA was completely dissolved. [c] Measured on TGA with a scanning rate of 20 °C min^{-1} in nitrogen. [d] D is the average diameter (μm) and cv is the coefficient of variation (%) of the microspheres. [e] SA stands for the starlike aggregates of needle crystals.

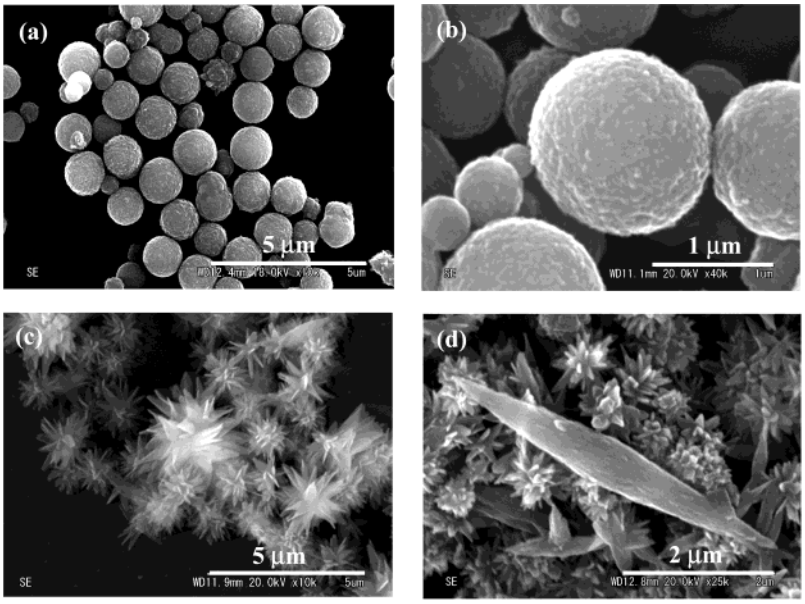

Figure 1. Morphology of PPPI. Micrographs of (a) and (b) are the microspheres of run no. 1. Those of (c) and (d) are the starlike aggregates of needle crystals and the lozenge-shaped crystals of run no. 7.

PPDA is added at 240 °C, the microspheres are formed, of which the average diameter is slightly longer than that prepared in liquid paraffin at the same concentration. The crystals are formed when PPDA is added over 280 °C.

All the obtained products were totally insoluble into organic solvents, and therefore the chemical structure of the products was analyzed by FT-IR. The spectra of the microspheres and the dissolved oligomers are shown in Figure 2 as representatives. The characteristic bands of imide group appear clearly at 1784 and 1722 cm^{-1} which are the C═O stretch.[27] The band of the C−N stretch appears at 1376 cm^{-1}. Furthermore, the band attributed to the deformation of the imide ring or to the imide carbonyl groups also appears at 722 cm^{-1}. The bands for end groups such as the amino group and anhydride group, which are observed at ca. 3400 and 1855 cm^{-1} in the spectrum of the dissolved oligomers, do not appear in the spectrum of the products. This spectrum is identical with that of PPPI. In the spectrum of the dissolved oligomers, the characteristic bands for imide appear from the beginning of the precipitation. Additionally, the band of N−H in the amino group and/or amic acid moiety and that of anhydride are observed. The broad band of OH in carboxylic acid and that of amide linkage slightly appear at 3150−2600 and 1605 cm^{-1}, respectively. These results indicate that the almost imidized oligomers containing a little amic acid moiety are formed in the solution via the formation of oligo(amic acid) and the subsequent thermal imidization due to the higher temperature. And then they are phase-separated through the supersaturation state to form the microspheres or the crystals. The postpolymerization occurs in the products due to the high polymerization temperature, as previously reported,[28] and the microspheres or the crystals of PPPI are finally obtained.

Figure 3 shows the WAXS intensity profiles of the microspheres and the mixture of the starlike aggregates of needle crystals and the lozenge-shaped crystals. The reflection peaks are clearly observed, and these products possess high crystallinity. These peaks can be described with the PPPI orthogonal unit cell.[4,29] The peaks from the mixture of the starlike aggregates of needle crystals and the lozenge-shaped crystals are shaper than those from the microspheres. In particular, the mixture of the starlike aggregates of needle crystals and the lozenge-shaped crystals prepared in TS10 by the addition at 330 °C exhibit quite sharp and well-resolved peaks, and the diffuse halo attributed to amorphous parts is scarcely observed. These products are comprised of well-organized crystal structure. Thermal properties of the products were evaluated.[30] Thermal decomposition temperatures of 10 wt % loss in nitrogen are quite high in the range 681−737 °C recorded on TGA. That of PPPI prepared by a conventional procedure was reported as 632 °C.[31] The PPPI products prepared in this study exhibit better thermal stability than that prepared by a conventional method due to the higher crystallinity.

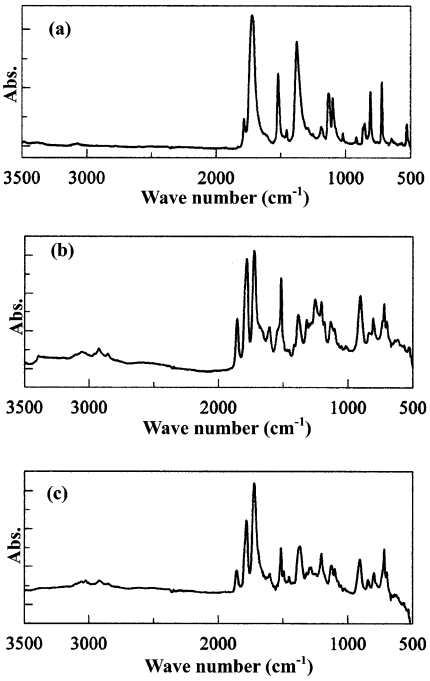

Figure 2. IR spectra of (a) the microspheres prepared in liquid paraffin at the concentration of 1.00% for 6 h and the oligomers collected from the solution after (b) 1 min and (c) 6 h at 330 °C.

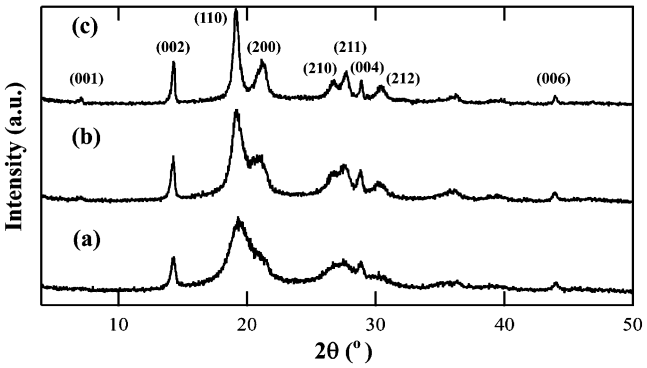

Figure 3. WAXS intensity profiles of microspheres of run no. 5 (a) and the mixture of starlike aggregates of needle crystals and lozenge-shaped crystals of run no. 6 (b) and no. 7 (c).

These products exhibit neither glass transition temperature nor melting temperature under the thermal decomposition temperature. These products are in the highest class of thermally stable polymers.

References and Notes

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(21) A typical run was described as follows (run no. 2 in Table 1). Into a cylindrical flask equipped with a mechanical stirrer and a gas inlet tube were placed PMDA (0.075 g, 0.34 mmol), which was purchased from Aldrich Co. Ltd. and recrystallized from acetic anhydride, and 20 mL of liquid paraffin. The reaction mixture was heated under a slow stream of nitrogen up to 330 °C with stirring. When PMDA was completely dissolved on heating, PPDA (0.037 g, 0.34 mmol), which was a gift of Taishin Kasei Kogyo Co. Ltd. and used as received, was added at 280 °C into the solution. PPDA was completely dissolved within 1 min under stirring, and then the stirring was stopped. The solution became turbid within 30 s due to the precipitation of oligomers. The temperature was maintained at 330 °C for 6 h. The precipitated products were collected by vacuum filtration at 330 °C and washed with *n*-hexane and acetone. The filtrate was poured into *n*-hexane, and the precipitated oligomers which were dissolved in liquid paraffin at 330 °C were collected by filtration. IR of the polymer products (KBr) (cm^{-1}): 1784, 1721, 1520, 1454, 1376, 1187, 1131, 1098, 1021, 918, 854, 809, 722, 646, 529. IR of the recovered oligomers (KBr) (cm^{-1}): 3391, 3150−2600, 3056, 2924, 2854, 1854, 1781, 1724, 1605, 1515, 1381, 1317, 1253, 1203, 181, 1132, 1017, 904, 805, 720, 699, 618, 529.
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