

# Hollow Spheres of Aromatic Polyamide Prepared by Reaction-Induced Phase Separation

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**ABSTRACT:** Hollow spheres of aromatic polyamide are obtained by the reaction-induced phase separation during polymerization of 5-hydroxyisophthalic acid and 1,4-phenylene diamine in an aromatic solvent at a concentration of 1–2% at 320 °C without stirring. The hollow sphere has a dimple hole and the diameters of the hollow spheres are 3–4  $\mu\text{m}$ . The droplets are initially generated via liquid–liquid phase separation and then rigid cross-linked network structure formed the rigid skin layer on the

surface of the droplets. The solidification of the droplets occurred owing to the further polymerization in them with maintaining the morphology to form the hollow spheres. The hollow spheres exhibit outstanding thermal stability. © 2012 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, 51, 780–785

**KEYWORDS:** high-performance polymers; hollow spheres; morphology; phase separation; polyamides

**INTRODUCTION** The preparation of hollow spheres has attracted great attention in recent decades, because these materials have protected porous cores that are suitable for encapsulating a large variety of substances and thus they have great potential for applications such as catalysts, low-dielectric fillers, adsorbents, and drug storage and delivery carriers.<sup>1–6</sup> Hollow spheres need mechanical strength and chemical stability for many applications, especially for high-performance materials used under harsh conditions. Rigid-rod aromatic polymers are hopeful candidates for high-performance hollow spheres. Hollow spheres of aromatic polyimides have been recently developed by means of the usage of core templates,<sup>7,8</sup> reprecipitation,<sup>9–13</sup> and self-assembling.<sup>14</sup> Although the rigid polyimides exhibit poor tractability, hollow spheres can be prepared using the soluble precursor poly(amic acid)s. However, many of other aromatic polymers show neither fusibility nor solubility owing to their rigidity and it is too difficult to control the morphology precisely.

Morphology control of aromatic polymers has been studied by means of the phase separation during isothermal polymerization.<sup>15,16</sup> When the polymerization is performed in the solvent which is good to monomers and poor to polymers, phase separation is induced by the increase in the molecular

weight of oligomers formed in the solution. When the crystallization occurs, the oligomers are precipitated to form the crystals and the following polymerization proceeds in the precipitated crystals with maintaining the morphology. Conversely, when the liquid–liquid phase separation is induced, droplets of dense phase are formed in dilute phase and further polymerization occurs in the droplets owing to the higher concentration of oligomers, leading to solidification with maintaining spherical morphology. Ultimately, the spheres are obtained. The morphology is built by means of the phase separation during polymerization, and therefore this method is no longer limited by the intractability of polymers. With respect to the spherical morphology, microspheres<sup>15</sup> and those having needle-like crystals<sup>16</sup> have also been prepared by the reaction-induced liquid–liquid phase separation. Many of the high-performance polymers are usually synthesized by the polycondensation reaction that proceeds with eliminating small molecules. If the by-produced small molecules are phase-separated in the droplets formed via the liquid–liquid phase separation, hollow spheres can be possibly prepared. Based on this concept, the preparation of the hollow spheres of aromatic polyamides was examined by means of the reaction-induced phase separation during polymerization in this study.

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**TABLE 1** Results of Polymerization<sup>a</sup>

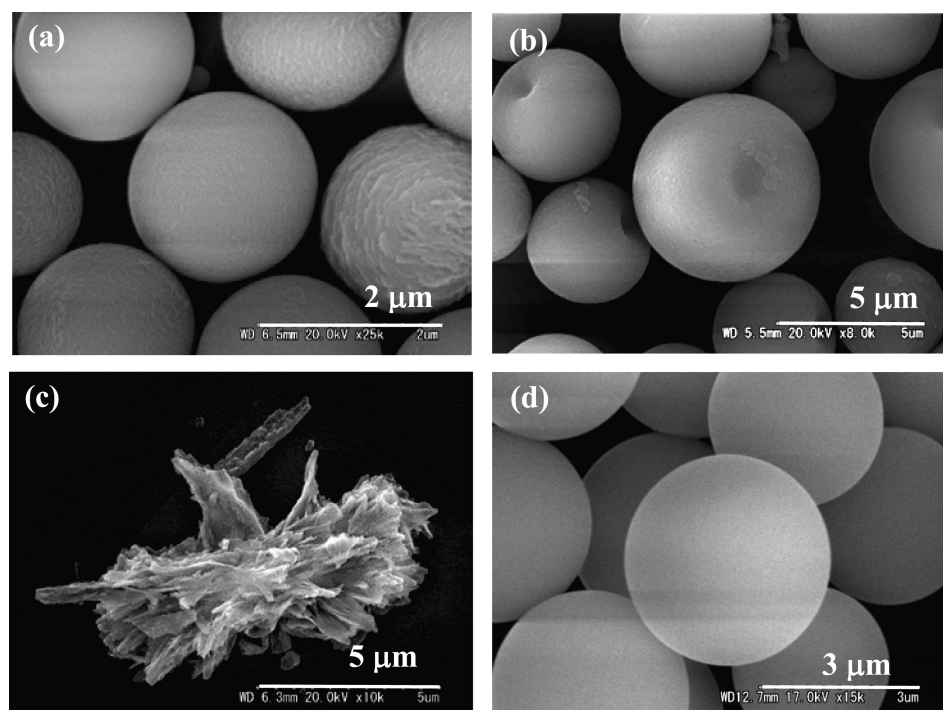
Polymer Code	Temp. (°C)	Conc. (%)	Yield (%)	Es <sup>b</sup> (%)	Morphology
PPHIA-1	350	5	70	6	Sphere
PPHIA-2	320	5	68	6	Sphere
PPHIA-3	320	1	32	13	Hollow sphere
PPHIA-4	320	2	64	5	Hollow sphere
PPHIA-5	280	1	28	9	Sphere, plate
PMHIA-1	320	2	60	21	Sphere
PMHIA-2	280	1	42	16	Sphere, lozenge, plate

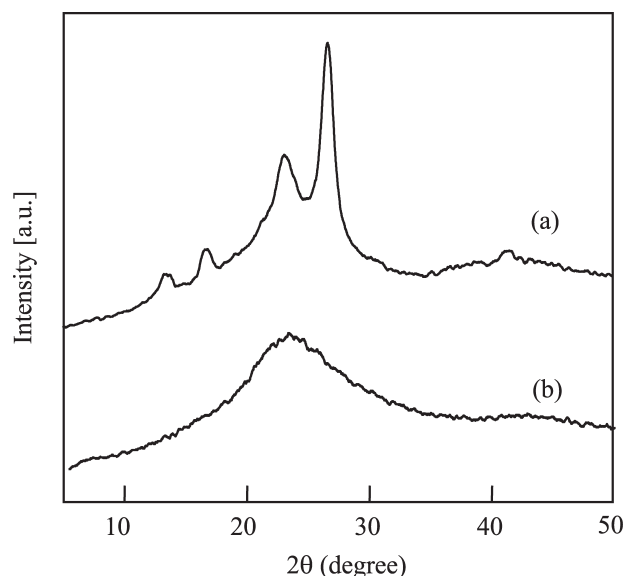
<sup>a</sup> Polymerizations were performed in DBT for 24 h.<sup>b</sup> The content of ester linkage described the peak intensity ratio of the ester C=O to the amide C=O.

## RESULTS AND DISCUSSION

Polymerizations of 5-hydroxyisophthalic acid (HIPA) and phenylene diamines were performed in dibenzyltoluene (DBT) at a concentration of 1–5% at 280–350 °C without stirring. These monomers were insoluble into DBT at 25 °C, but they became dissolved during heating to the polymerization temperature. Then, the solution became turbid owing to the phase separation and the polyamides were formed as precipitates after 24 h. Polymerization results are presented in Table 1. With respect to poly(1,4-phenylene-5-hydroxyisophthalamide) (PPHIA) prepared from HIPA and 1,4-phenylene diamine (PPDA), spheres were obtained by the polymerization at 5% at 350 °C (PPHIA-1) and 320 °C (PPHIA-2) with the yield of 70 and 68% as shown in Figure 1(a). The average diameter and its coefficient of variation (cv) of the

PPHIA-1 and -2 were 1.9  $\mu\text{m}$ , 50% and 3.4  $\mu\text{m}$ , 31%, respectively. Although they exhibited spherical morphology suggesting that these spheres were formed via liquid–liquid phase separation as aforesaid, they were not hollow spheres. When the polymerizations were performed at 320 °C at a concentration of 1% (PPHIA-3) and 2% (PPHIA-4), the spheres having dimples were formed, as shown in Figure 1(b), with the yield of 32 and 64%, respectively. The average diameter and its cv value of the PPHIA-3 and -4 were 4.4  $\mu\text{m}$ , 30% and 3.6  $\mu\text{m}$ , 29%, respectively. From TEM observation shown in Figure 4(e), the core part of this sphere was brighter than the skin part, suggesting the formation of the hollow structure. The details will be discussed later. The structure of PPHIA was analyzed by infrared (IR). The characteristic peak of amide C=O was clearly visualized at 1629  $\text{cm}^{-1}$ . The peaks of carboxylic acid in HIPA were not observed and

**FIGURE 1** SEM images of (a) spheres of PPHIA-1, (b) hollow spheres of PPHIA-4, (c) plate-like crystals of PPHIA-5, and (d) spheres of PMHIA-1.

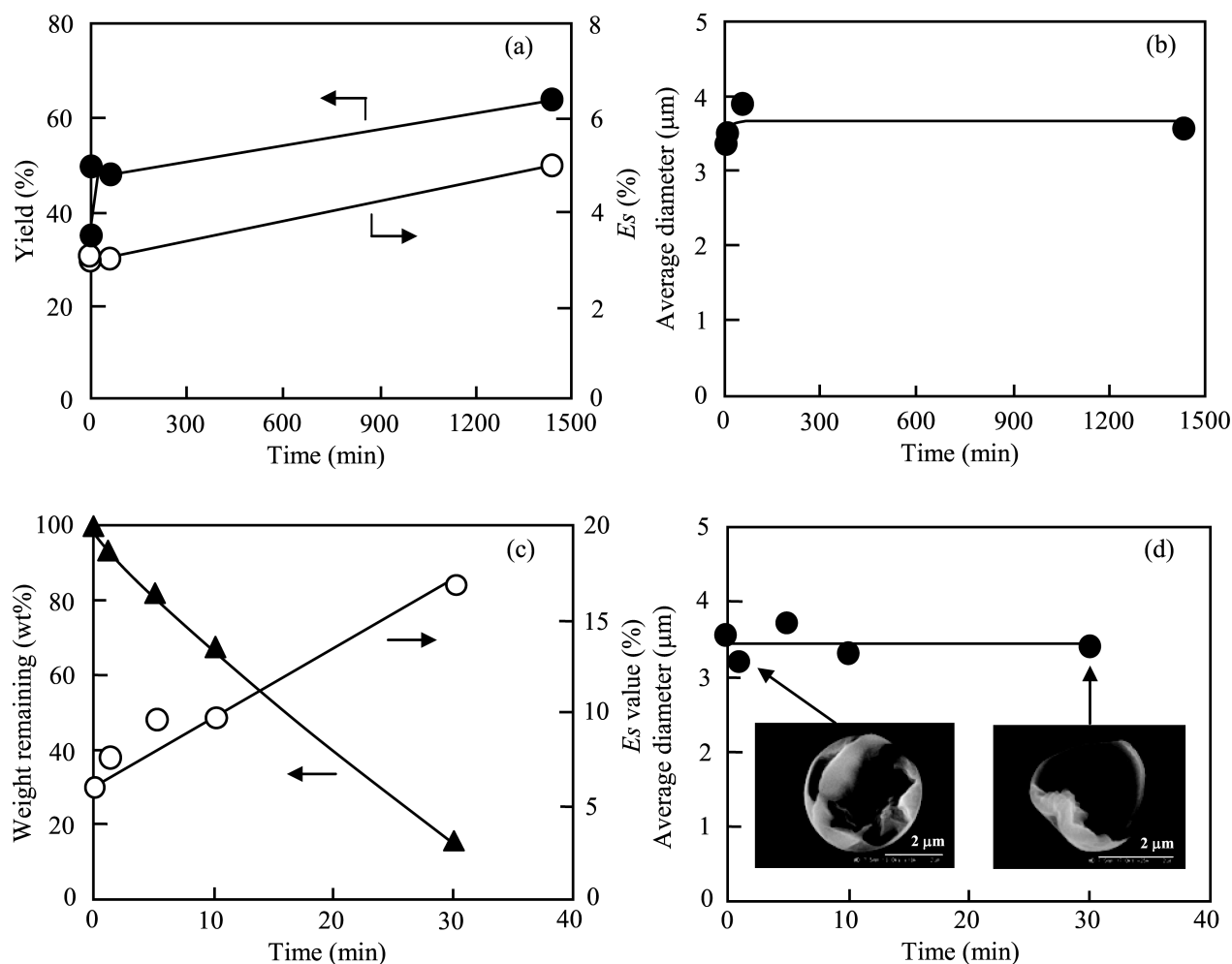


**FIGURE 2** WAXS intensity profiles of (a) PPHIA-4 hollow spheres and (b) PMHIA-1 spheres.

these results imply the formation of polyamide. A peak was presented at about  $1720\text{ cm}^{-1}$  as a shoulder of the amide  $\text{C}=\text{O}$  which was attributed to the ester  $\text{C}=\text{O}$ , whereas a broad peak corresponding to phenolic  $\text{OH}$  and amide  $\text{N}-\text{H}$  was strongly observed at  $3200\text{--}3350\text{ cm}^{-1}$ . The obtained PPHIA was not dissolved even in the conc. sulfuric acid which is a good solvent to aromatic polyamides like poly(1,4-phenylene terephthalamide). This result suggests that the PPHIA possessed cross-linking structure via the formation of the ester linkage. Even though an aromatic amide group reacts with a carboxylic acid to form an amide linkage as previously reported,<sup>17–21</sup> a phenolic  $\text{OH}$  group is not so reactive to form an ester linkage directly by the condensation reaction with a carboxyl group. The ester linkage is possibly formed by the exchange reaction between a phenolic  $\text{OH}$  group and an amide linkage, nevertheless the basicity of an amide group is higher than that of  $\text{OH}$  group. The content of the ester linkage (Es), defined as the peak intensity ratio of the ester  $\text{C}=\text{O}$  to the total of the amide  $\text{C}=\text{O}$  and the ester  $\text{C}=\text{O}$ , ranged from 5 to 13%. The polymerization at  $280\text{ }^{\circ}\text{C}$  (PPHIA-5) gave the plate-like crystals with the yield of 29% as shown in Figure 1(c). The formation of plate-like crystals reveals that the crystallization of oligomers was induced rather than the liquid–liquid phase separation at  $280\text{ }^{\circ}\text{C}$  because of the lower temperature. The polymerizations of HIPA and 1,3-phenylene diamine (MPDA) were performed under the similar conditions to form poly(1,3-phenylene-5-hydroxyisophthalamide) (PMHIA). The spheres were obtained at  $320\text{ }^{\circ}\text{C}$  at a concentration of 2% (PMHIA-1) with the yield of 60% as shown in Figure 1(d), but they were not hollow spheres. The crystals having clear habit such as lozenges and plates were formed at  $280\text{ }^{\circ}\text{C}$  at a concentration of 1% (PMHIA-2) with the yield of 42%. The lower polymerization temperature tends to induce the crystallization as well as PPHIA. The Es value of PMHIA-1 and -2 were 21 and

16%, respectively, which were higher than those of PPHIA. Wide angle X-ray scattering (WAXS) intensity profiles of the PPHIA-4 hollow spheres and the PMHIA-1 spheres are shown in Figure 2. Although a broad halo attributed to the amorphous region coexisted, four sharp reflection peaks were mainly observed at  $2\theta$  of  $13.32^{\circ}$  ( $d$  spacing =  $0.664\text{ nm}$ ),  $16.70^{\circ}$  ( $d$  spacing =  $0.530\text{ nm}$ ),  $23.18^{\circ}$  ( $d$  spacing =  $0.383\text{ nm}$ ), and  $26.85^{\circ}$  ( $d$  spacing =  $0.332\text{ nm}$ ) in the profile of the PPHIA-4. It has been reported that highly crystalline poly(1,4-phenylene isophthalate) were obtained as precipitated plate-like crystals by the reaction-induced crystallization during the polymerization of isophthalic acid and PPDA.<sup>22</sup> The PPHIA hollow spheres were formed via the liquid–liquid phase separation. The PPHIA hollow spheres possessed high crystallinity, nevertheless the liquid–liquid phase separation mode, bulky  $\text{OH}$  substituent and the irregular cross-linking structure ought to lower the crystallinity. In contrast to this, only the broad halo was observed and PMHIA spheres were completely amorphous. Although poly(1,3-phenylene isophthalate) was also a crystalline polymer,<sup>23,24</sup> the PMHIA spheres lost the crystallinity owing to all *meta*-structure and the higher Es values.

To clarify the formation mechanism of the PPHIA hollow spheres, the yield, the Es value and the average diameter was examined during the polymerization at a concentration of 2% at  $320\text{ }^{\circ}\text{C}$ . They are plotted as a function of polymerization time in Figure 3(a,b). The morphological developments are shown in Figure 4. The yield was 35% after 3 min and then increased with time. After 24 h, it became 64%. The Es value slightly increased with time from 3 to 5%. In contrast to this, the average diameter slightly increased at an initial stage of the polymerization and then it became almost constant at about  $3.6\text{ }\mu\text{m}$  despite the increase in the yield. Regarding the morphological development, hemispheres were observed after 3 min and the formation of the shell wall was observed, of which the thickness was about  $0.5\text{ }\mu\text{m}$ . During 5–60 min, spherical shape was completed and the dimple hole became smaller with time. TEM images of a PPHIA hollow sphere prepared for 5 min and 24 h (PPHIA-4) are also shown in Figure 4(c,e). As aforesaid, the brighter core part was observed in the sphere, and the size of the spherical vacancy in the sphere prepared for 5 min seems to be larger than that prepared for 24 h (PPHIA-4). This fact suggests that the shell wall became thicker toward to the inside with time, being consistent with the polymerization time dependency of the yield and the average diameter. The inner structure of the PPHIA-4 spheres was directly observed by fracturing the spheres in liquid nitrogen. The fractured sphere was shown in Figure 4(f). The cavity was clearly observed at the center of spheres and this result directly proves the formation of hollow structure. Etching treatment with potassium hydroxide was performed at  $25\text{ }^{\circ}\text{C}$  in 1.0 wt % potassium hydroxide methanol solution to investigate the formation mechanism of the shell wall. Weight remaining, Es values and average diameters of PPHIA-3 hollow spheres were plotted as a function of etching time in Figure 3(c,d) with the morphologies. As shown in Figure 3(c), The PPHIA hollow spheres were hydrolyzed by potassium



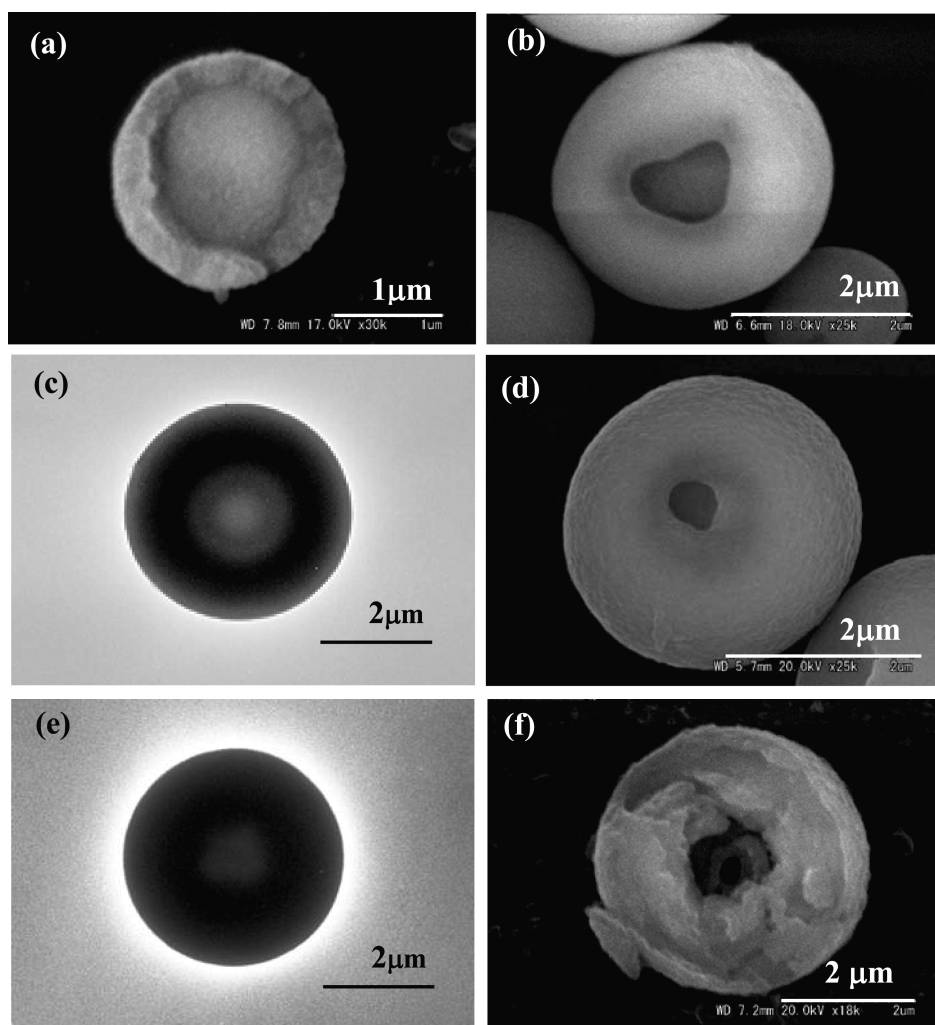
**FIGURE 3** Plots of (a) yield and  $E_s$  value and (b) average diameter of PPHIA hollow spheres prepared at a concentration of 2% at 320 °C as a function of polymerization time. Plots of (c) weight remaining,  $E_s$  value, and (d) average diameter of PPHIA-4 hollow spheres as a function of etching time. Etching was performed at 25 °C in 1.0 wt % KOH methanol solution.

hydroxide and only 15 wt % were left after 30 min. It is noteworthy that the  $E_s$  value increased with the treatment time and it became 17% after 30 min. The cross-linking density increased gradually from inner part to the outer part. With respect to the morphology, the hollow spheres were hydrolyzed and the some parts of spheres were broken, but the spherical morphology reminded. The diameter of the hollow spheres was almost constant during etching, implying that the thickness of the shell wall decreased with etching. Based on these results, the hydrolysis proceeded from inside of the hollow spheres to the surface, and the skin layer existed which was hard to be hydrolyzed. The fact that the  $E_s$  value of the shell wall part was higher suggested that the skin layer was comprised of the highly cross-linked structure of the poly(amide-ester). Cross-linking reaction seems to be one of the important factors, and therefore the polymerization of isophthalic acid, trimesic acid, and PPDA was examined. In this polymerization, plate-like crystals were mainly formed via crystallization because the linear oligomers derived from isophthalic acid and PPDA were selectively precipitated at the initial stage of polymerization owing to the lower solubility

than that of co-oligomers containing trimesic acid residues. Spherical aggregates of plate-like crystals were also formed, but they were not hollow spheres. It is quite important that the linear oligomers derived from HIPA and PPDA are precipitated to form the microdroplets and then the skin layer is formed by the following cross-linking reaction between phenolic OH and amide linkage. Moreover, *N,N'*-(1,4-phenylene)-diacetamide was polymerized with HIPA instead of PPDA under the same condition as that for the hollow spheres. Although the water molecules were eliminated by the polymerization of HIPA and PPDA, the eliminated small molecules were acetic acids in this polymerization. Microspheres of PPHIA were formed, but they were not hollow spheres. This result indicates that insolubility of by-produced small molecules to DBT is important and water is effective to form hollow spheres.

It is reasonably thought that the hollow spheres of PPHIA are formed according to the following mechanism; the molecular weight of amide oligomers increased in the solution by direct polycondensation with elimination of the





**FIGURE 4** Morphology of PPHIA hollow spheres prepared at 320 °C at a concentration of 2% for (a) 3 min, (b) 5 min, (d) 60 min, (e) 24 h (PPHIA-4), and (f) a PPHIA-4 hollow sphere fractured in liquid nitrogen.

water and then the liquid–liquid phase separation was induced via the super-saturated state. The droplets of dense phase were formed in the dilute phase. Further polymerization occurred in the droplets occurred with the elimination of water molecules. The polycondensation proceeded rapidly on the surface of the droplets because of the easy diffusion of the by-produced water molecules. After that, the ester linkages were formed by the exchange reaction, leading to the cross-linked rigid skin layer. Water molecules generated by the condensation reaction formed a bubble in a sphere having rigid skin layer, owing to the insolubility of water molecules into DBT. The oligomers flew into the droplet from the dilute phase to replace the bubble and deposited on the skin layer from the inside, bringing about the decrease in the size of the core vacancy and the dimple hole. The droplets were solidified by the increase in the molecular weight with maintaining hollow spherical morphology. Another possibility was the formation of the DBT droplet in the sphere by the solidification process instead of the water bubble. There still reminds other possibility for

the formation mechanism such as a bubble template mechanism<sup>25–28</sup> and further study is needed.

PPHIA shows neither glass transition temperature ( $T_g$ ) nor melting temperature ( $T_m$ ) on a differential scanning calorimetry (DSC) scan due to the rigid aromatic polyamide and the cross-linking structure. Thermal stability was evaluated by thermogravimetric analysis (TGA) in nitrogen. The temperatures of the 10% weight loss ( $T_{10}$ ) of PPHIA-3 and -4 hollow spheres were 535 and 537 °C, respectively.  $T_{10}$ s of PPHIA-1 and -2 spheres, which were not hollow spheres, were 542 and 545 °C, respectively. Although  $T_{10}$  of the hollow spheres were slightly lower than that of solid spheres, they exhibit outstanding thermal stability.

## CONCLUSIONS

Hollow spheres of PPHIA were obtained by the reaction-induced phase separation during polymerization in DBT at a concentration of 1–2% at 320 °C. The diameters of the hollow spheres are 3–4 μm and the hollow sphere has a dimple hole.

Rigid networks cross-linked by the ester linkage form the rigid skin layer of the droplets initially, and then the solidification of the droplets occurred owing to the further polymerization in them with maintaining the hollow spherical morphology, resulting in the formation of the hollow spheres.

## EXPERIMENTAL

### Materials

HIPAA was purchased from TCI and purified by the recrystallization from water. PPDA was purchased from Sigma-Aldrich and used as received. MPDA was purchased from Sigma-Aldrich and purified by sublimation. A mixture of isomers of DBT was purchased from Matsumura Oil (Trade name: Barrel Therm 400, MW: 380, b.p.: 382 °C) and purified by distillation under reduced pressure (160 °C/0.5 mmHg).

### Measurements

Morphology of precipitates was observed on a HITACHI S-3500N scanning electron microscope (20 kV) and a JEM 2000EX transmission electron microscope (200 kV). Average diameters of the spheres were determined by taking the average of over 100 observation values. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. WAXS was performed on a Rigaku Gager Flex with nickel-filtered CuK $\alpha$  radiation (35 kV, 20 mA). TGA was performed on a Perkin-Elmer TGA-7 with a scanning rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere. DSC was performed on a Perkin-Elmer DSC-8000 with a scanning rate of 10 °C min<sup>-1</sup> in nitrogen atmosphere. The content of Es was described the peak intensity ratio of the ester C=O to the total intensity of the amide and the ester C=O in an IR spectrum after the peak resolution using Lorentz-Boltzmann function (see Supporting information).

### Polymerizations

HIPAA (142 mg, 0.78 mmol) and DBT (10 mL) were placed into a cylindrical flask equipped with gas inlet and outlet tubes and a thermometer, and then heated up to 320 °C under nitrogen. PPDA (84 mg, 0.78 mmol) was then added into the mixture at 320 °C, and the mixture was stirred for 5 s to dissolve completely. The polymerization was performed at 320 °C for 24 h without stirring. Concentration of the polymerization, defined as (calculated polymer weight/solvent volume)  $\times$  100, was 2.0%. The solution became turbid and PPHIA was formed as precipitates after 6 h. The precipitates were collected by vacuum filtration at 330 °C, washed with *n*-hexane and acetone, and then dried at 50 °C for 12 h. IR (KBr, cm<sup>-1</sup>): 3200–3350, 1720, 1629, 1581, 1555, 1530, 1442, 1400, 1343, 1318, 1231, 1203, 1112, 1002, 980, 887, 860, 833, 742, 700, 675, 610. The polymerizations under other conditions were performed in the similar manner.

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