

## Preparation of Aromatic Polyamide Hollow Particles

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### Introduction

The preparation of hollow spheres has attracted great attention, because these materials have protected porous cores which 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 delivery carriers. Hollow spheres need mechanical strength and chemical stability for many applications, especially for high performance materials used under harsh conditions. Hollow spheres of aromatic polyimides have been recently developed. However, many of other aromatic polymers are infusible and insoluble owing to their rigidity and it is too difficult to control the morphology precisely. In this study, preparation of hollow sphere of aromatic polyamide is examined by using the phase separation during isothermal polymerization.

### Results and Discussion

Polymerizations of 5-hydroxyisophthalic acid (HIPA) and 1,4-phenylenediamine were carried out in dibenzyltoluene mixture (DBT) without stirring. With respect to poly(1,4-phenylene-5-hydroxyisophthalate) (PPHIA), spheres were obtained by the polymerization at 5% at 350°C (PPHIA-1) and 320°C (PPHIA-2) [Figure 1]. The spherical morphology suggests that these spheres were formed *via* liquid-liquid phase separation, but they were not hollow spheres. When the polymerizations were carried out at 320°C at a concentration of 1% (PPHIA-3) and 2% (PPHIA-4), the spheres having dimples were formed [Figure 1], with the yield of 32 and 64%, respectively. The average diameter of the PPHIA-3 and -4 were 4.4  $\mu\text{m}$  and 3.6  $\mu\text{m}$ , respectively. A peak was presented at ca. 1720  $\text{cm}^{-1}$  as a shoulder of the amide C=O which was attributed to the ester C=O, whereas a broad peak corresponding to phenolic OH and amide N-H was strongly observed at 3200-3350  $\text{cm}^{-1}$  in the IR spectrum of PPHIA. The obtained PPHIA was not dissolved even in the conc. sulfuric acid. This result suggests that the PPHIA possessed cross-linked structure *via* the formation of the ester linkage. The ester linkage is possibly formed by the exchange reaction between a phenolic OH group and an amide linkage, nevertheless the basicity of an amide group is higher than that of OH group. The content of the ester linkage (*Es*), defined as the peak intensity ratio of the ester C=O to the total of the amide C=O and the ester C=O, ranged from 5 to 13%. The polymerization at 280°C (PPHIA-5) gave the plate-like crystals with the yield of 29% [Figure 1]. The crystallization of oligomers was induced rather than the liquid-liquid phase separation at 280°C because of the lower temperature. The polymerizations of HIPA and 1,3-phenylenediamine were carried out under the similar conditions to form poly(1,3-phenylene-5-hydroxyisophthalamide) (PMHIA). The spheres were obtained at 320°C, but they were not hollow spheres. [Figure 1] The crystals having clear habit such as lozenges and plates were formed at 280°C. As shown in WAXS intensity profiles of the PPHIA-4 hollow spheres and the PMHIA-1 spheres [Figure 2], the PPHIA hollow spheres possessed high crystallinity. In contrast to this, only the broad halo was observed and PMHIA spheres were completely amorphous.

In order to clarify the formation mechanism of the PPHIA hollow spheres, the yield, the *Es* value and the average diameter were examined during the polymerization at a concentration of 2% at 320°C. The yield was 35% after 3 min and then increased with time. After 24 h, it became 64% [Figure 3]. 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 ca. 3.6  $\mu\text{m}$  despite the increase in the yield. Regarding the morphological development [Figure 4], hemispheres were observed after 3 min and the formation of the shell wall was observed, of which the thickness was ca. 0.5  $\mu\text{m}$ . During 5 to 60 min, spherical shape was completed and the dimple hole became smaller with time. 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. From TEM observation, the core part of this sphere was brighter than the skin part, suggesting the formation of the hollow structure. The inner structure of the PPHIA-4 spheres was directly observed by fracturing the spheres in liquid nitrogen. 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°C in 1.0 wt% potassium hydroxide methanol solution to investigate the formation mechanism of the shell wall. The PPHIA hollow spheres were hydrolyzed by potassium hydroxide and only 15 wt% were left after 30 min. It is noteworthy that the *Es* 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, but the spherical morphology reminded. The diameter of the hollow spheres was almost constant during etching, implying the thickness of the shell wall decreased with etching. The fact suggested that the skin layer was comprised of the highly cross-linked structure. It is reasonably thought that the hollow spheres of PPHIA are formed according to the following mechanism; the liquid-liquid phase separation was induced *via* the super-saturated state and the droplets of dense phase were formed in the dilute phase.

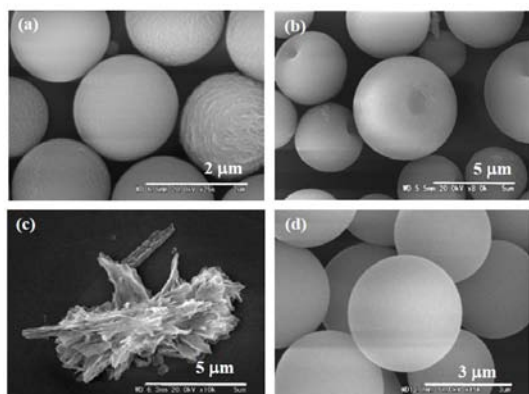
Further polymerization occurred in the droplets occurred with the elimination of water molecules. The polycondensation proceeded rapidly on the surface of the droplets because of the easy diffusion of the by-produced water molecules. After that, the ester linkages were formed by the exchange reaction, 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>1,2</sup> and further study is needed. The temperatures of the 10% weight loss in N<sub>2</sub> of PPHIA-3 and -4 hollow spheres were 535 and 537°C respectively, and they exhibit outstanding thermal stability

## Conclusions

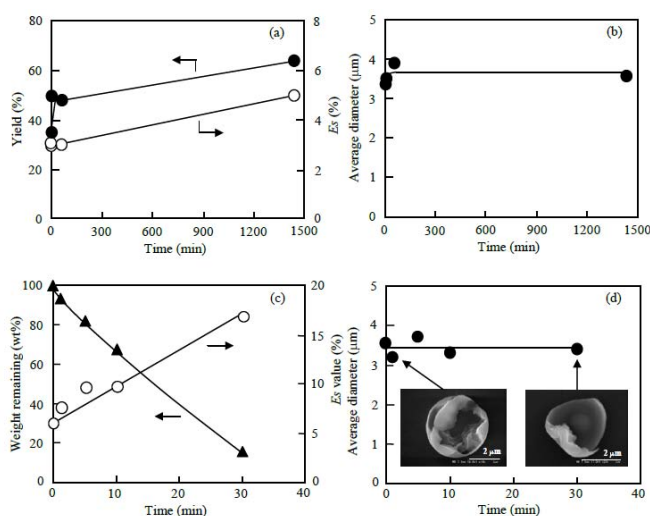
Hollow spheres of PPHIA were obtained by the reaction-induced phase separation during polymerization in DBT at a concentration of 1-2% at 320°C. The diameters of the hollow spheres are 3-4 μm and the hollow sphere has a dimple hole. Rigid networks cross-linked by the ester linkage form the rigid skin 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.

## Reference

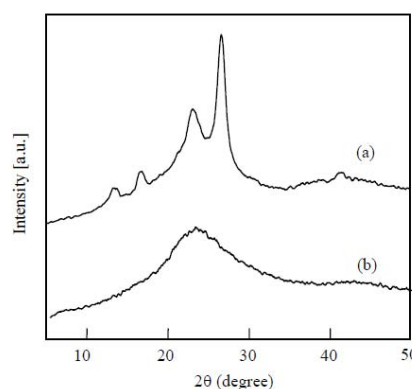
1. M. Mazur, *J. Phys. Chem. C*, **112**, 13528 (2008)
2. Y. Yan, L. Chen, X. Li, Z. Chen, X. Liu, *Polym. Bull.* DOI 10.1007/s00289-012-0754-6



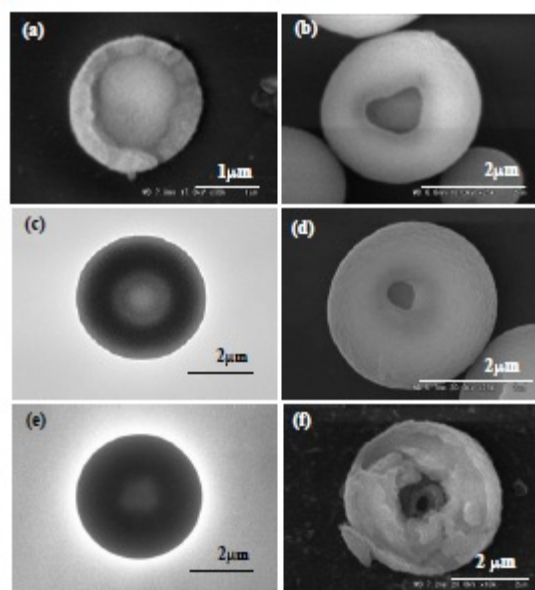
**Figure 1** SEM images of (a) PPHIA-1 spheres, (b) hollow spheres of PPHIA-4, (c) plate-like crystals of PPHIA-5 and (d) PMHAI spheres



**Figure 3** Plots of (a) yield and *Es* value, and (b) average diameter of PPHIA hollow spheres as a function of polymerization time. Plots of (c) weight remaining, *Es* value and (d) average diameter of PPHIA-4 hollow spheres as a function of etching time. Etching was carried out at 25°C in 1.0 wt% KOH/MeOH.



**Figure 2** WAXS intensity profiles of (a) PPHIA-4 hollow spheres and (b) PMHAI spheres



**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.