



Size control of aromatic polyamide hollow spheres prepared by reaction-induced phase separation



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ABSTRACT

Size control of the poly (1,4-phenylene-5-hydroxyisophthalamide) hollow spheres was examined by tuning the polymerization condition, focusing on concentration, temperature and solvent. Higher concentration lowered the diameter owing to the higher degree of super-saturation for nucleation. Temperature drop during the polymerization just before the nucleation was so effective to make the diameter smaller. Moreover, the diameter was susceptible to the solubility of oligomers in the solvent, and higher content of liquid paraffin in the aromatic solvent lowered the solubility, resulting in the decrease in the diameter. Based on these results, the combination of the temperature drop and the solvent effect was the most desirable to prepare the smallest hollow spheres, and the diameter of hollow spheres could be controlled from 4.4 to 0.7 μm .

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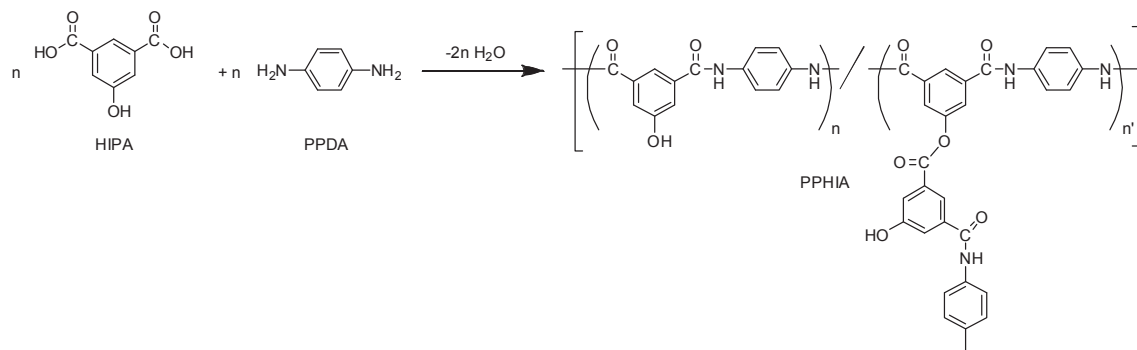
1. Introduction

Polymer hollow spheres have porous cores suitable for weight-saving, heat-insulating and encapsulating a huge variety of substances. Therefore, they have great potential for applications such as low-dielectric fillers, catalysts, adsorbents and drug storage and delivery carriers [1–6]. High-performance hollow spheres possessing higher mechanical strength, chemical stability, irradiation durability and thermal resistance are recently required to use under harsh conditions. Rigid aromatic polymers are desirable candidates for high-performance hollow spheres owing to their outstanding properties derived from the rigid structure [7–13]. However, they become antagonistically infusible and insoluble also derived from their rigid structures, and this intractability makes difficult to prepare the hollow spheres of rigid aromatic polymers. Although spheres of aromatic polyamide had been prepared by the precipitation polymerization method [14–16], hollow spheres of rigid aromatic polymers have not been obtained but for polyimides. Core-shell polystyrene-polyimide particles were prepared by dispersion polymerization of styrene using poly (amic acid) which was a

precursor of polyimide as a stabilizer [17]. However, clear polyimide hollow spheres were not formed by removing the polystyrene core with washing toluene because of the shrinkage of spheres. Hollow spheres were prepared by using self-assembly of the pair of a rigid carboxyl-ended polyimide and a coil poly (4-vinylpyridine) in solutions [18]. Porous polyimide nanoparticles were successfully fabricated by using the reprecipitation method of polyamic acid with a second polymer as a porogen and subsequent imidization [19–21]. Poly (acrylic acid) was used as a suitable porogen to form polyimide nanoparticles having superficial nanopores, of which the sizes were in the range 20–70 nm. The preparation of polyimide spheres by reprecipitation of poly (amic acid) precursor was investigated in detail [22]. Many intriguing shapes of polyimide spheres were prepared through fine-tuning the concentration of poly (amic acid), including deflated capsules, bowl-shaped and dimple-like hollow spheres. The addition of salt to the poly (amic acid) solution was desirable to form polyimide hollow spheres with complete shells. Besides polyimide hollow spheres, poly (1,4-phenylene-5-hydroxyisophthalamide) (PPHIA) hollow spheres which was an aromatic polyamide had been recently prepared by means of reaction-induced phase separation during direct polymerization of 5-hydroxyisophthalic acid (HIPA) and 1,4-phenylene diamine (PPDA) at 320 °C in aromatic solvent as depicted in Scheme 1 [23]. PPHIA was not soluble in solvent, and

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Scheme 1. Preparation of PPHIA hollow spheres.

hence the reprecipitation method described above could not be applied for the intractable polyamide. The reaction-induced phase separation during polymerization is not limited by the insolubility of polymers and it is useful to control the morphology of the intractable polymers. It is noteworthy that each PPHIA hollow sphere had one dimple on the surface. The PPHIA hollow spheres show neither solubility nor fusibility, and they exhibited the excellent thermal stability. Hence, they are expected to be useful as high performance polymer hollow spheres. The formation mechanism of the PPHIA hollow spheres had been proposed and they were formed *via* the reaction-induced liquid-liquid phase separation [23,24]. The microdroplets were first formed by the reaction-induced liquid-liquid phase separation. The water molecules eliminated by condensation reaction played an important role of the formation of gas-bubbles in the microdroplets. Further, the cross-linking reaction between phenolic hydroxyl groups in 5-hydroxy-1,3-phenylene moieties of the polymers caused the ester-amide exchange reaction to form ester linkages, leading to the formation of the cross-linked skin layer near the surface of the droplets. The efficient formation of the skin layer was important to encapsulate gas-bubbles in the droplets, resulting in the formation of hollow structure. The dimple of the hollow sphere mentioned above was formed during the escaping water molecules from the microdroplets.

The size control of the hollow spheres is of great importance to use them practically for industrial applications. In this study, the diameter control of the PPHIA hollow spheres toward smaller size was examined based on the formation mechanism by tuning the polymerization condition, focusing on concentration, temperature and solvent.

2. Experimental

2.1. Materials

HIPA was purchased from TCI Co. Ltd. and purified by the recrystallization from water. PPDA was purchased from Sigma-Aldrich and purified by sublimation. A mixture of isomers of dibenzyltoluene (DBT) was purchased from Matsumura Oil Co. Ltd. (Trade name: Barrel Therm 400) and purified by distillation under reduced pressure (160 °C/0.1 mmHg). Liquid paraffin (LPF) was purchased from Nacalai Tesque Inc. and purified by distillation under reduced pressure (180 °C/0.1 mmHg). 5-Hydroxyisophthalanilide (HIPAn) was synthesized according to the previously reported procedure [25,26].

2.2. Measurements

Morphology was observed on a HITACHI S-3500 N scanning

electron microscope (SEM). Samples were dried, sputtered with platinum-palladium and observed at an acceleration voltage of 20 kV. Average diameters of spheres (D) and the coefficient of variation (Cv) were determined by taking the average of over 100 observation values. Morphology was also observed on a JEOL 2000EX (Tokyo, Japan) transmission electron microscope (TEM) at an acceleration voltage of 200 kV. Density of spheres was measured by flotation method using mixtures of bromoform and toluene.

2.3. Preparation of PPHIA hollow spheres

HIPA (287 mg, 1.57 mmol) and DBT (20 g) were placed into a cylindrical flask equipped with gas inlet and outlet tubes and a thermometer. Concentration of the polymerization was 2.0% based on theoretically formed polymer weight and the solvent weight. The mixture was heated up to 340 °C under nitrogen with stirring. When HIPA was dissolved, PPDA (170 mg, 1.57 mmol) was added into the mixture at 340 °C. Stirring was stopped when PPDA was entirely dissolved. The polymerization was carried out at 340 °C for 24 h without stirring. The solution became turbid at the initial stage of polymerization, and then the PPHIA hollow spheres were formed as precipitates. The precipitates were collected by vacuum filtration at 340 °C to avoid the precipitation of oligomers left in the solution during cooling, and washed with *n*-hexane and acetone. The PPHIA hollow spheres were dried at 50 °C under reduced pressure for 12 h. Polymerizations under other conditions were performed in the similar manner.

2.4. Preparation of solubility curves of HIPAn

HIPAn and solvent were put into glass tubes at different concentrations. They were placed into oil bath and heated until HIPAn was completely dissolved. Then temperature was lowered gradually at a rate of 5 °C · h⁻¹, and the cloud point temperatures were determined.

3. Results and discussion

The growth feature of the hollow spheres is the nucleation and growth mechanism [24]. The microdroplets of intractable aromatic polyesters had been previously prepared by the reaction-induced liquid-liquid phase separation, which were not hollow spheres [27]. In the formation of the microspheres of aromatic polyesters, the nucleation occurred to form microdroplets at the beginning of the polymerization and the microdroplets became larger by not only consecutive supply of oligomers from solution but also coalescence of microdroplets. Additionally, there was another possibility of Ostwald ripening to increase the size. Solidification occurred by the further polymerization in the microdroplets,

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