

Making Hollows using Nitrogen Gas Emitted by the Decomposition of VAm-110 in Polystyrene Particles

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Abstract

Due to the useful features of hollow particles, such as the presence of nanovoids and their large specific surface areas, they have potential for use as drug carriers. Unfortunately, conventional methods for the synthesis of hollow particles involve complicated processes. In this study, we developed a template-free method for the production of hollow polymer particles. Polystyrene core particles containing 2,2'-azobis(*N*-butyl-2-methylpropionamide) (VAm-110) were initially formed via soap-free emulsion polymerization, after which shells were constructed using divinylbenzene. Nitrogen gas was then generated inside the particles by the decomposition of VAm-110 at 100 °C, which led to the formation of hollows. Consequently, this method involves three easy steps and is environmentally friendly, as it does not require the use of a surfactant or organic solvent. Furthermore, the morphology and size of the particle hollows can be controlled by varying the concentration of VAm-110.

Keyword: Hollow particles, Polystyrene, Decomposition reaction

1. Introduction

Hollow particles exhibit a range of attractive features, including the presence of nanovoids, their large specific surface areas, their insulating capabilities, and their ability to rapidly diffuse material within their shells. These appealing characteristics have captivated the minds of researchers globally, and a significant number of studies have been undertaken into the use of hollow particles in catalyst carriers and supercapacitor applications, among others [1-3].

Hollow polymer particles are most commonly synthesized by hard templating; however, this method has some serious drawbacks. For example, hard templating involves the synthesis of a hard template using silica or another hard material, which is followed by subsequent removal of the template [4, 5] using highly corrosive chemicals, such as hydrofluoric acid, which is problematic from the viewpoints of safety, processing costs, and environmental protection [6]. To solve these problems, micelles, block-copolymers, microbubbles, and organic-framework methods, which do not require template removal, have been reported [6-9]. However, these methods are not recognized as practical solutions due to their resulting large particle size distributions—which are consequences of the sensitivities of the representative templates to external factors [6]—in addition to

their complicated fabrication processes, and limited applications due to the use of special materials.

However, extensive research into polystyrene [10, 11] has found it to be the most basic polymer that can be used in polymer colloid chemistry due to its ease of polymerization [10-14] and potential for copolymerization with various conjugated monomers [13-15]. Furthermore, the size distribution of the polystyrene particles is easily controlled via soap-free emulsion polymerization [16]. Indeed, currently, various non-spherical particles [17], such as hollow, porous, Janus, and golf-ball-shaped particles, can be produced in a template-free manner [7, 17-22].

Thus, we herein report the development of a method for the preparation of hollows in polystyrene particles imbedded with an oil-soluble initiator which exhibits a high 10 h half-life temperature. This is achieved through the use of soap-free emulsion polymerization and heating. This method is based on the use of styrene and divinylbenzene particles, the most versatile monomers and crosslinkers in polymer colloid chemistry. Overall, we aim to develop a simple and flexible method for the synthesis of hollow polystyrene particles in an environmentally friendly manner through avoidance of the use of surfactants and organic solvents.

2. Experimental

2.1 Materials

Styrene (St) and divinylbenzene (as monomers), potassium persulfate (KPS) (as the initiator) [10], and 2,2'-azobis(*N*-butyl-2-methylpropionamide) (VAm-110) (as the foaming agent) were purchased from the FUJIFILM Wako Pure Chemical Corporation. In this study, VAm-110, which is an oil-soluble initiator and dissolves in the styrene monomer phase, was used as the foaming agent due to its high 10 h half-life temperature of 110 °C. Therefore, this temperature was used to trigger the emission of nitrogen gas and the formation of hollows within the particles, as shown in **Fig. 1**. NaOH was obtained from Nacalai Tesque, Inc. Styrene was rinsed with 10 wt% aqueous NaOH and purified by vacuum distillation. Distilled water was produced using a distillation system (Auto Still WG250, Yamato).

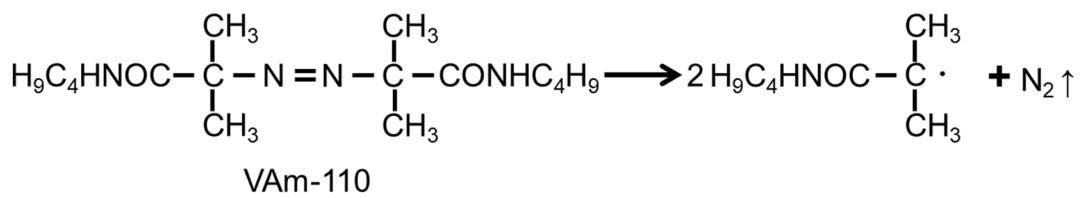
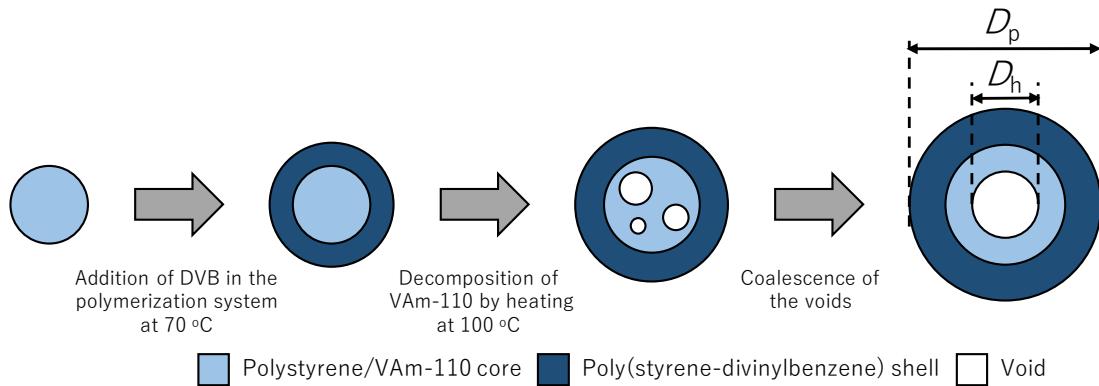


Fig. 1 Decomposition reaction of VAm-110.

2.2 Soap-free emulsion polymerization

Polystyrene/VAm-110 cores were prepared by soap-free emulsion polymerization. St (0.135 g), KPS (20.4 mg), VAm-110 (w g), and distilled water (15.0 mL) were added to a 30 mL batch reactor, and polymerization was carried out at 130 rpm for 2 h at 70 °C (EYELA, RCH-20L). Herein, VAm-110 was dissolved in the styrene monomer phase and did not decompose because of its high 10 h half-life temperature. According to the mechanism of soap-free emulsion polymerization [12, 23], particles are swollen by the absorption of the monomer phase containing VAm-110, and the cores contain VAm-110 as a consequence. Divinylbenzene (m g) was then added to prepare shells around the polystyrene cores and to initiate surface polymerization [24]. After 3 h, the reaction temperature was increased to 100 °C and maintained for 20 h, during which time the chemical reaction shown in **Fig. 1** proceeded to form holes within the polystyrene particles by the release of nitrogen gas. The boiling phenomenon was not observed due to the boiling point being raised by the presence of KPS. The polystyrene was then washed with water through centrifugation to obtain the polymer particles. The above processes are illustrated in **Scheme 1**.



Scheme 1 Illustrating the synthesis of a hollow polystyrene particle.

2.3 Analysis

The particle morphologies and sizes were determined by scanning electron microscopy (SEM, JSM-7500FA, JEOL). The hollow structures within the particles and their sizes were determined by transmission electron microscopy (TEM, JEM-2100 plus, JEOL). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS, AXINA-CFR+, SHIMADZU) was used to determine the molecular weights of the synthesized polymers, and to detect the VAm-110-derived moieties within the polymers. Polymer samples were prepared using dithranol (Sigma-Aldrich) and subsequently freeze-dried (EYELA, FDU-1200). Details regarding this method have been reported previously [25, 26].

3. Results and discussion

3.1 Optimizing the addition of divinylbenzene during soap-free emulsion polymerization

We initially used MALDI-TOF-MS to detect VAm-110 at $w = 0.018$ g inside polystyrene particles after washing. **Fig. 2a** reveals the presence of the compound through its two fragment radicals (shown in Fig. 1) in the polystyrene particles, since a peak at m/z 284.15 was observed following polymerization with VAm-110 and nitrogen gas emission upon heating. In contrast, no peak was observed at m/z 280–290 when polymerization was conducted in the absence of VAm-110, as shown in **Fig. 2b**. Hence, by comparing Fig. 2a with Fig. 2b, we concluded that the polystyrene cores contain VAm-110 within them.

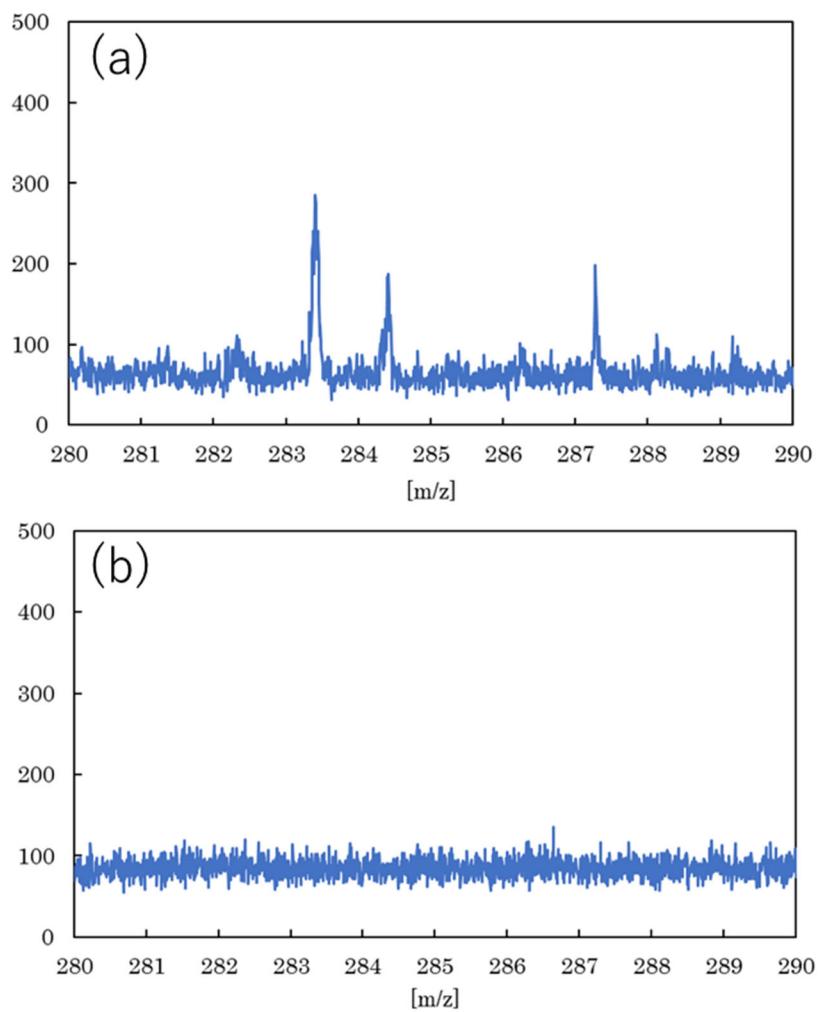


Fig. 2 MALDI-TOF-MS spectra of the polymers synthesized through: (a) polymerization with VAm-110, and (b) polymerization without VAm-110.

We subsequently investigated the influence of divinylbenzene during polymerization on the nature of the particle hollows. The polystyrene particles shown in **Fig. 3a** were synthesized upon polymerization in the absence of divinylbenzene, whereby hollow polystyrene particles were not formed since the nitrogen gas escaped due to the fluidity of the polystyrene during heating at 100 °C. Solid polymer particles were also synthesized when divinylbenzene was added at the start of the polymerization process, as shown in **Fig. 3b**, whereby rough particle surfaces were obtained due to cross-linking with divinylbenzene [27]. In addition, no hollows were detected within the particles due

to the rigidity of the divinylbenzene-crosslinked polystyrene, which was too hard for the gas to coalesce and form hollows sufficiently large to be distinguished by TEM. In contrast, the addition of divinylbenzene 2 h after beginning the polymerization process generated hollow particles, as shown in **Fig. 3c**. Nitrogen gas did not escape from the particles due to the crosslinked structure of the shells formed through the surface polymerization of styrene with added the divinylbenzene [28, 29]. Since the glass transition temperature of polystyrene is 90 °C, the voids generated by the decomposition of VAm-110 coalesced to form a single hollow inside each particle. **Fig. 4** shows a TEM image of the polystyrene particles presented in Fig. 3c, prior to heating. Since hollows are not observed in these particles, the hollows found in the particles shown in Fig. 3c clearly originated from the nitrogen gas evolved by the reaction of VAm-110 upon heating. The particles, with an average size of 373.1 nm, were larger after heating than before heating (308.0 nm) since the evolved nitrogen gas pushed against the inside walls of the particles. In addition, when the polymerization of St and divinylbenzene was conducted in the absence of VAm-110, the resulting particles were exposed to water at 100 °C for 20 h, then observed by TEM, as shown in **Fig. 5**. Since hollow-free solid particles were obtained, it was concluded that the hollows originated from the VAm-110.

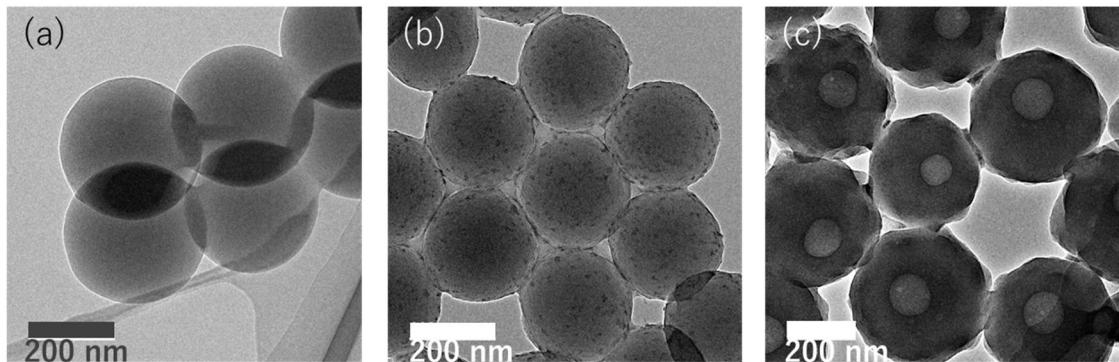


Fig. 3 TEM images of polystyrene particles: (a) without divinylbenzene, (b) with the addition of the divinylbenzene at $m = 0.135$ g at the commencement of polymerization, and (c) with the addition of the divinylbenzene at $m = 0.135$ g, 2 h after the commencement of polymerization.

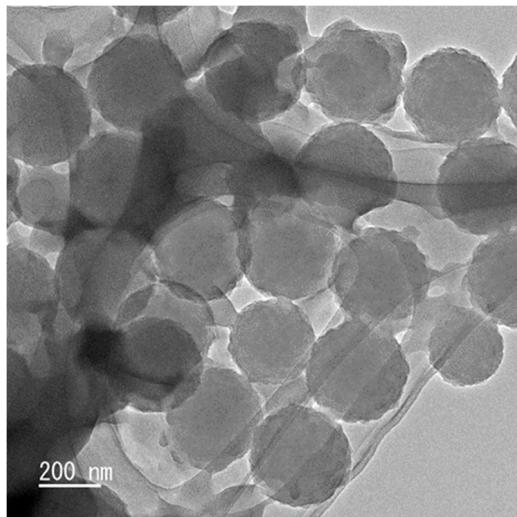


Fig. 4 TEM image of polystyrene particles formed when divinylbenzene was added 2 h after the commencement of polymerization but prior to heating.

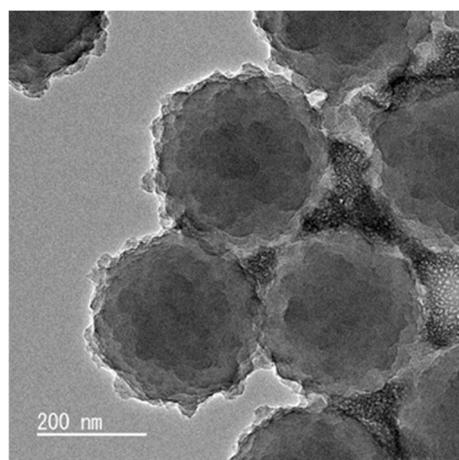


Fig. 5 TEM images of polystyrene particles without VAm-110 with the addition of the divinylbenzene at $m = 0.135$ g, 2 h after the commencement of polymerization.

Moreover, upon heating at 85 °C, which is below the glass transition temperature of polystyrene, some nanovoids were detected within the particles synthesized under the same conditions as those shown in Fig. 3c, as indicated by the white arrows in **Fig. 6**.

Since heating was carried out at a lower temperature ($85\text{ }^{\circ}\text{C}$), the treatment time was increased to 80 h. In comparison to heating at $100\text{ }^{\circ}\text{C}$, it was more difficult for the nitrogen gas to move around within these polystyrene particles, and so some of the smaller voids generated by the decomposition of VAm-110 remained, and did not coalesce within the polystyrene particles. Hence, the morphology of the void can be changed by adjusting the process temperature.

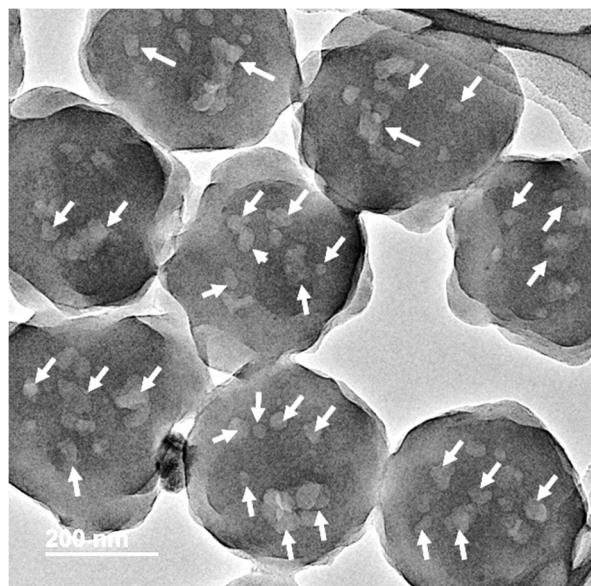


Fig. 6 TEM image of polystyrene particles with average size of 359.3 nm formed by heating at $85\text{ }^{\circ}\text{C}$ for 80 h. White arrows highlight particle hollows.

3.2 Influence of the VAm-100 and divinylbenzene concentrations on the hollows

Polymerization was then carried out under the synthetic conditions employed for formation of the hollow particles shown in Fig. 3c. Thus, **Fig. 7** shows the influence of the VAm-110 concentration in the styrene monomer phase on the ratio of the hollow size (D_h in Scheme 1) to the particle size (D_p in Scheme 1). It was found that D_h/D_p increased upon increasing the VAm-110 concentration due to the fact that the concentration of the nitrogen precursor in the particle gas increased. Thus, the size of the hollow can be

controlled in the present method by adjusting the VAm-110 concentration.

Fig. 8 shows the influence of the amount of divinylbenzene present during polymerization on D_h/D_p . More specifically, this ratio was found to decrease upon increasing the divinylbenzene concentration, likely due to the higher rigidity that originates from divinylbenzene crosslinking. As a consequence, the nitrogen gas was unable to increase the size of the hollow by pushing against the inside walls of the rigid particles.

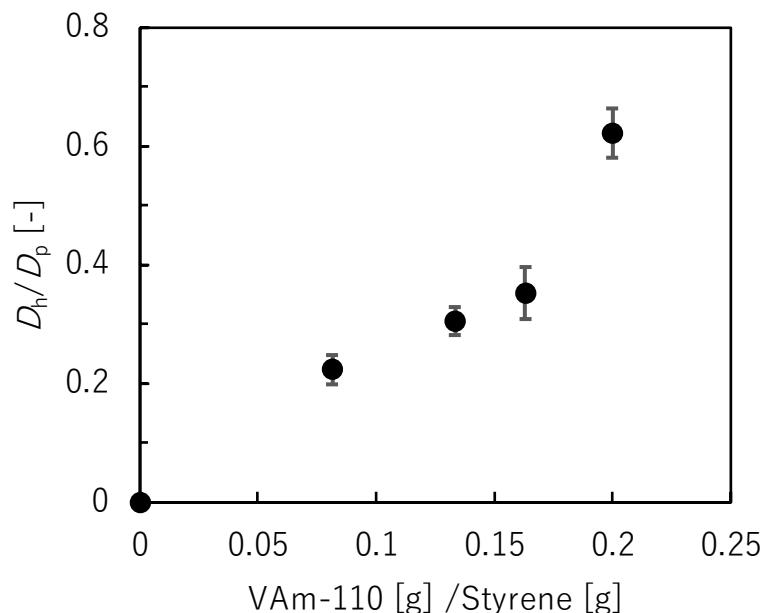


Fig. 7 Ratio of hollow-size (D_h) to particle-size (D_p) as a function of the weight ratio of added VAm-110 to the styrene monomer.

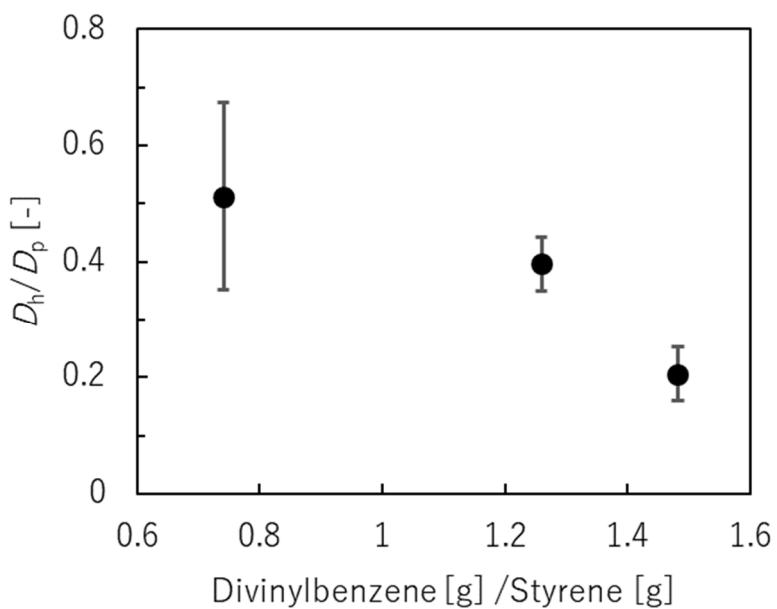


Fig. 8 Ratio of hollow-size (D_h) to particle-size (D_p) as a function of the weight ratio of divinylbenzene to the styrene monomer.

4. Conclusion

We successfully synthesized hollow polystyrene particles by soap-free emulsion polymerization without the use of a surfactant, organic solvent, or template. The addition of divinylbenzene created a particle shell with a crosslinked structure. The crosslinked shell retained the nitrogen gas generated by VAm-110 (which has a 10 h half-life temperature of 110 °C) when heated at 100 °C for 20 h, which resulted in the formation of a single hollow within each particle. Solid particles were formed under other conditions since the nitrogen gas escaped from the particles due to the lower rigidity of the polystyrene during heating at 100 °C. In addition, the particles were found to contain

many smaller voids when heated at 85 °C for 80 h. Our results therefore indicate that temperature is a trigger for the formation of hollows inside polystyrene particles.

Supporting Information

The SEM images of these synthesized particles in Fig. 3 were shown in **Fig. S1** in supporting information. The data in **Figs. 7 and 8** were summarized in **Tables S1 and S2**.

Acknowledgment

This study was financially supported in part by Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, (No. 18H01777).

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