

Decomposing Oil-Soluble Initiators in Particles: A Template-Free Method for the Preparation of Hollow Polymer and Silica Particles

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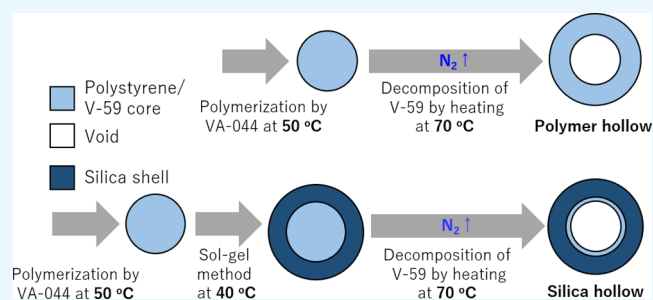


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ABSTRACT: Nanovoids contained in hollow particles render them potential drug carriers. However, conventional methods for the synthesis of these particles involve complex processes. In this study, we developed a template-free method for the synthesis of hollow polymer and silica particles by initially preparing polystyrene core particles containing 2,2'-azobis(2-methylbutyronitrile) (V-59) through soap-free emulsion polymerization. The subsequent generation of nitrogen gas inside these particles upon the decomposition of V-59 at 70 °C led to the formation of voids. In addition, silica shells were synthesized on the surfaces of the V-59-containing polystyrene core particles through a sol-gel reaction at 40 °C, following which voids were formed by the decomposition of V-59 at 70 °C. The developed method involves straightforward steps and is environmentally friendly, as it does not require the use of surfactants, organic solvents, or templates.



INTRODUCTION

Hollow particles^{1,2} have a range of attractive features, including the presence of nanovoids, insulating properties, and the ability to enable rapid diffusion of materials within their shells. These appealing characteristics have attracted significant attention from researchers in various fields, leading to a considerable number of studies^{3–5} on the use of these particles as catalyst carriers⁶ and in supercapacitor applications,^{7,8} among others.

Conventional methods for the synthesis of hollow particles involve complex processes. Recently, we developed a simple and environmentally friendly method for the preparation of hollow polystyrene particles⁹ that did not require the use of surfactants,¹⁰ organic solvents,¹¹ or templates¹² for the synthesis. This method consists of three steps, namely, the soap-free emulsion polymerization of styrene using potassium peroxydisulfate¹³ and 2,2'-azobis(*N*-butyl-2-methylpropionamide) (VAm-110),^{14,15} addition of divinylbenzene to the system at 70 °C,¹⁶ and heat treatment at 100 °C. The first step forms core particles at 70 °C, the second step constructs a cross-linked shell that prevents the gas generated inside the core particles from escaping, and the third step creates voids due to the nitrogen gas emitted from VAm-110. Although VAm-110, which has a high 10 h half-life temperature of 110 °C, is used as a foaming agent during the preparation of the polystyrene particles, it needs to be decomposed by heating at 100 °C to release the nitrogen gas¹⁷ that forms the voids within the particles. However, 100 °C is an extremely high reaction temperature when water is used as the reaction medium. Consequently, we improved the method by replacing VAm-110 with 2,2'-azobis(2-methylbutyronitrile) (V-59),¹⁸ a

foaming agent with a lower 10 h half-life temperature, to reduce the cost and eliminate the addition of divinylbenzene.

Herein, we report a method for the synthesis of V-59, oil-soluble initiator, and embedded hollow polystyrene or silica particles through soap-free emulsion polymerization, a sol-gel reaction, and heat treatment at 70 °C.

RESULTS AND DISCUSSION

Soap-Free Emulsion Polymerization of Styrene Using VA-044 and V-59: Particles without Silica Shells. Styrene monomer was subjected to soap-free emulsion polymerization using 2,2'-azobis[2-(2-imidazolin-2-yl)propane]-dihydrochloride (VA-044, an initiator for soap-free emulsion polymerization) and V-59 to afford polystyrene particles (Figure 1). The particles were synthesized at a low reaction temperature to suppress the decomposition of V-59 during the polystyrene particle formation. The average particle size and coefficient of variation (CV) were determined to be 173 nm and 25.9%, respectively. The particles exhibited a positive ζ -potential (36.7 mV) because a cationic water-soluble initiator, VA-044, was used during the soap-free emulsion polymerization of styrene to maintain the dispersion stability. The polystyrene yield was measured to be 65.7% by the gravimetric

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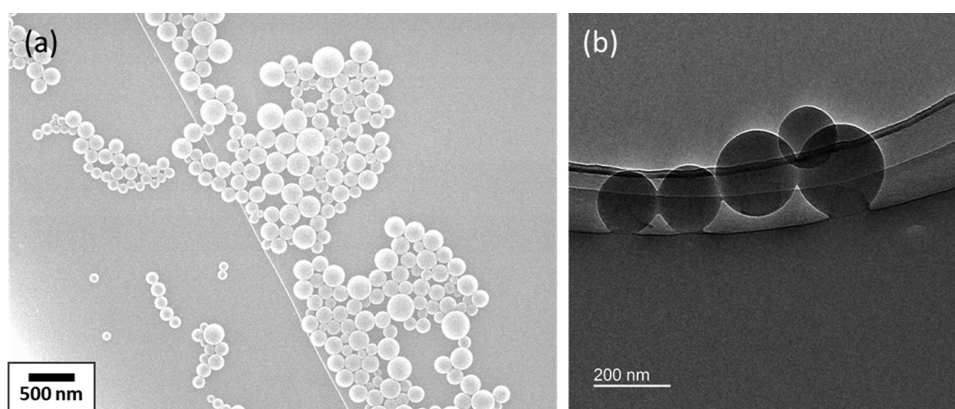


Figure 1. (a) Scanning electron microscopy (SEM) and (b) transmission electron microscopy (TEM) images of polystyrene particles before heating.

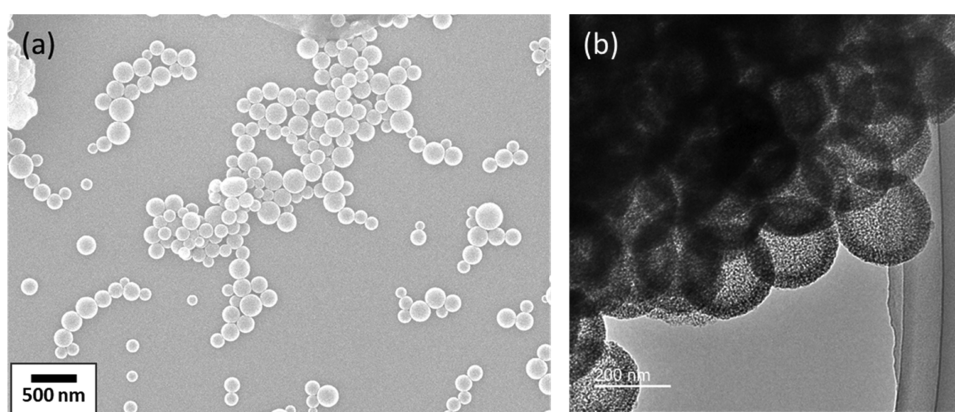


Figure 2. (a) SEM and (b) TEM images of polystyrene particles after heating.

method using a centrifugal separator. In this soap-free emulsion polymerization,^{19,20} particles swelled due to the absorption of the V-59-containing monomer phase, consequently, the cores contained V-59.

Figure 2 shows the SEM and TEM images of the polystyrene particles after heating at 70 °C. The analysis of the images revealed that the average particle size and CV were 180 nm and 22.8%, respectively. Because the melting point of V-59 was lower than the temperature of the void generation process (70 °C), some of the polystyrene particles were dissolved in the V-59 solution and the particles were swollen to greater sizes. The TEM image clearly shows that hollow particles were formed. The volume of the void was less than the calculated volume of the nitrogen gas emitted from V-59 inside the particles based on the ideal gas equation of state. Therefore, it is concluded that the voids were generated by the nitrogen gas through the decomposition of V-59 during the heating process at 70 °C (Figure 3). Thus, the developed template-free method for the synthesis of hollow polystyrene particles consists of two straightforward steps: the first requiring a temperature of 50 °C and the second requiring a temperature of 70 °C.

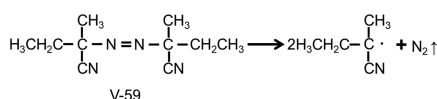


Figure 3. Decomposition of V-59 inside a polystyrene particle.

Preparing the Silica Shell Using Sol–Gel Chemistry.

Styrene and *N*-vinylacetamide (NVA) were subjected to soap-free emulsion polymerization using VA-044 and V-59 to afford solid polystyrene particles (Figure 4). The average particle size and CV were determined to be 198 nm and 24.0%, respectively. Because NVA was used to construct hydration layers around the particles during the soap-free emulsion polymerization of styrene, the ζ -potential was lower (3.80 mV) than that of the abovementioned polystyrene particles; however, the dispersion stability was maintained due to the steric effects of the poly NVA (PNVA) hydration layers.²¹ Clearly, the PNVA shells, which maintained the colloidal stability, were synthesized using sol–gel chemistry at a low reaction temperature to suppress V-59 decomposition inside the polystyrene particles. The silica yield was measured to be 40.2% by the gravimetric method using a centrifugal separator.

Figure 5 shows the SEM and TEM images of the polystyrene silica particles formed by sol–gel chemistry at 40 °C; in this stage, coagulation is expected to occur under normal conditions because the electrostatic repulsive force between the particles is reduced by the reaction.^{22,23} However, the steric effects associated with the PNVA hydration layers on the polystyrene particle surfaces help to maintain good dispersion stability. The average particle size and CV are 204 nm and 23.1%, respectively. The TEM image clearly shows that the silica shells were synthesized by sol–gel chemistry. In addition, the silica shells on these particles exhibited a negative ζ -potential (−43.1 mV)²⁴ that was beneficial for maintaining dispersion stability. The silica shell was estimated to be 6 nm

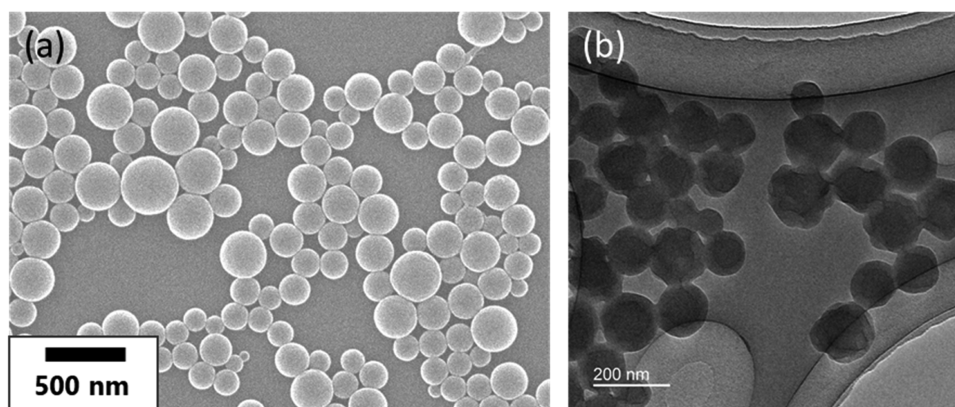


Figure 4. (a) SEM and (b) TEM images of polystyrene core particles before the sol-gel reaction.

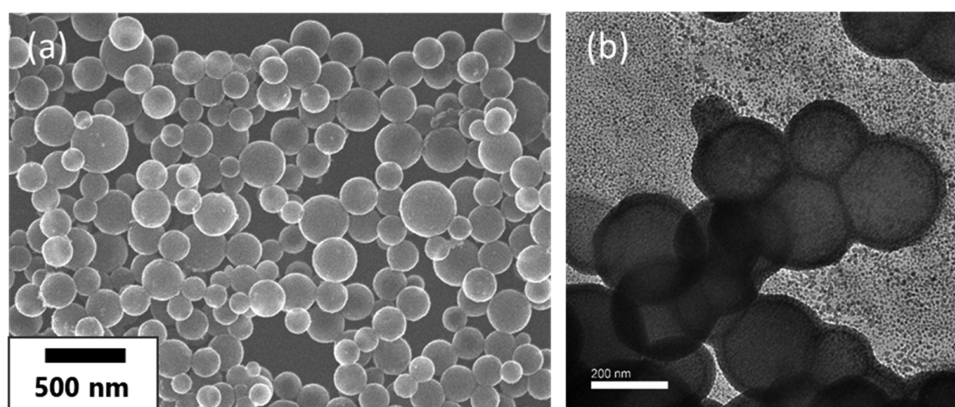


Figure 5. (a) SEM and (b) TEM images of polystyrene silica particles after the sol-gel reaction.

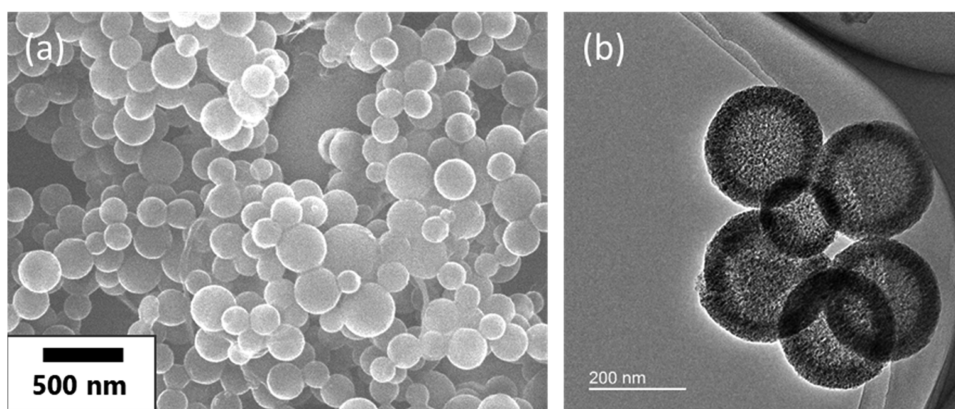


Figure 6. (a) SEM and (b) TEM images of polystyrene silica particles after heating.

thick based on the differences in the average sizes of the particles before and after the sol-gel reaction.

Preparation of Hollow Silica Particles by Heating at 70 °C. The results discussed in the previous section confirmed the successful synthesis of the polystyrene@silica particles. These particles were then heated at 70 °C, resulting in the formation of hollow silica particles due to the evolution of the nitrogen gas during V-59 decomposition (Figure 6). The average particle size and CV were determined to be 205 nm and 21.8%, respectively. Because the TEM image shown in Figure 6b is very similar to that of the polystyrene hollow particles shown in Figure 2b, it can be speculated that although the polystyrene cannot be observed clearly, it exists inside the

silica shell. To confirm this, the particles were examined by thermogravimetric analysis (TGA). As shown in Figure 7, weight loss was observed at temperatures greater than 370 °C for the silica hollow particles and the synthesized polystyrene solid and hollow particles.²⁵ Furthermore, the color of the samples after the TGA measurements changed to black (Supporting Information, shown in Figure S1) due to the carbonization of polystyrene inside the particles. These indicated that the silica hollow particles contained polystyrene inside their silica shells. The silica of these hollow particles did not degrade even at a temperature of 530 °C.

Clearly, the template-free method for the synthesis of hollow silica particles consisted of three steps, namely, soap-free

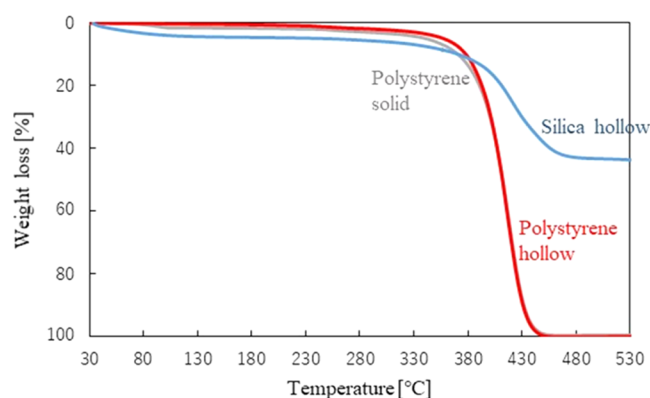


Figure 7. TGA curves of the synthesized particles.

emulsion polymerization, the sol–gel reaction, and heat treatment at 70 °C.

CONCLUSIONS

We successfully synthesized hollow polystyrene and silica particles through sequential soap-free emulsion polymerization, a sol–gel reaction, and heat treatment. This method does not require the use of a surfactant, organic solvent, or template. The nitrogen gas generated upon heating of V-59 (which has a 10 h half-life temperature of 67 °C) at 70 °C for 24 h resulted in the formation of a void within each particle. Our results show that the ideal temperature for triggering the formation of voids inside polystyrene or silica particles is 70 °C.

EXPERIMENTAL SECTION

Materials. Styrene (St monomer), VA-044 (initiator for soap-free emulsion polymerization),²⁶ and V-59 (foaming agent) were purchased from FUJIFILM Wako Pure Chemical Corporation. *N*-Vinylacetamide (NVA) monomer (Showa Denko K.K.)²⁷ was used without further purification in the polymerization step to allow the formation of PNVA layers around the polystyrene particles. Polymer core particles were synthesized without removing the PNVA layers during the preparation of the silica shell using the Stöber method.²⁸ PNVA adsorbed on the polystyrene particles acted as a catalyst for the synthesis of silica and as a stabilizer for maintaining the dispersion stability of the polymer colloid.^{24,29–31} Tetraethyl orthosilicate (TEOS, Nacalai Tesque, Inc.) was used as the precursor for the synthesis of the silica shell,³² and 1-propanol (Nacalai Tesque, Inc.) was used as the solvent for TEOS. In this study, VA-044, which is a water-soluble initiator and dissolves in the aqueous phase, was used due to its low 10 h half-life temperature (44 °C). V-59 decomposes slightly around this temperature due to its higher 10 h half-life temperature of 67 °C. Increasing the temperature to 70 °C led to the decomposition of V-59 and the evolution of nitrogen gas, leading to the formation of voids within the particles.

Styrene was rinsed with 10 wt % aqueous NaOH (Nacalai Tesque, Inc.) and purified by vacuum distillation. Distilled water was obtained from a distillation system (Auto Still WG250, Yamato).

Soap-Free Emulsion Polymerization and the Sol–Gel Reaction. Polystyrene/V-59 cores were prepared by soap-free emulsion polymerization. St (0.135 g), VA-044 (0.024 g), V-59 (0.020 g), and distilled water (15.0 mL) were added to a 30 mL batch reactor (EYELA, RCH-20L), and the mixture was allowed to polymerize by stirring at 130 rpm for 8 h at 50 °C.

It is noted that V-59 dissolved in the styrene monomer phase and decomposed slightly due to the low reaction temperature.

The reaction temperature was increased to 70 °C, and the reaction was allowed to progress at this temperature for 24 h, during which the chemical reaction shown in Figure 3 proceeded to form holes inside the polystyrene particles due to the release of the nitrogen gas by V-59.

To prepare silica shells, polystyrene/V-59 cores were initially prepared by soap-free emulsion polymerization. St (0.135 g), NVA (0.1 g), VA-044 (0.024 g), V-59 (0.020 g), and distilled water (15.0 mL) were added to a 30 mL batch reactor, and the mixture was allowed to polymerize by stirring at 130 rpm for 8 h at 50 °C. Silica shells were generated on the surfaces of the polymer particles using the Stöber process, as follows: TEOS (0.500 mL) was added to 10 mL of 1-propanol and heated to 40 °C with stirring, following which 10 mL of the polymer colloid was added to it at a flow rate of 1 mL/min using a burette to electrostatically cover the cationic polymer particles with TEOS. Finally, polymer particles with silica shells were prepared by stirring the mixture at 40 °C for 48 h. The unreacted TEOS and 1-propanol were removed by centrifugation (model 3700, KUBOTA) and replaced with pure water. The temperature was increased to 70 °C, and the reaction was allowed to proceed at this temperature for 24 h to form voids within the silica shell particles through the release of nitrogen gas by V-59.

Characterization. Particle sizes and morphologies were determined by field-emission scanning electron microscopy (FE-SEM, JSM-7500FA, JEOL),³³ and the hollow structures within the particles were examined by transmission electron microscopy (TEM, JEM-2100 plus, JEOL). The FE-SEM samples were prepared by placing a drop of the sample solution on a cleaved mica surface, followed by drying at room temperature. The specimen was covered with osmium tetroxide using an osmium plasma coater (OPC60A, Filgen). The average size of the synthesized particles was determined by number-averaging the data for ~300 particles in each SEM image using image analysis software (A-Zokun, Asahi Kasei Engineering Corporation). The coefficient of variation (CV) is calculated using eq 1

$$CV [\%] = \frac{\text{standard deviation}}{\text{average particle size}} \times 100 \quad (1)$$

The ζ -potentials of the particles in suspension were measured by laser Doppler velocimetry (Zetasizer Nano-ZS, Malvern PANalytical, Ltd.) after diluting the sample slurry with deionized water. The error bars were less than 2.0 mV.

The synthesized particles were examined by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min using an STA7200 instrument (Hitachi High-Tech Science Corporation).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04197>.

Samples before and after the TGA of the synthesized silica hollow particles are shown in Figure S1 (PDF)

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Notes

The authors declare no competing financial interest.

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