

Green Synthesis of Hollow Structures through the Decomposition of Azo Compounds Incorporated inside Polystyrene Particles

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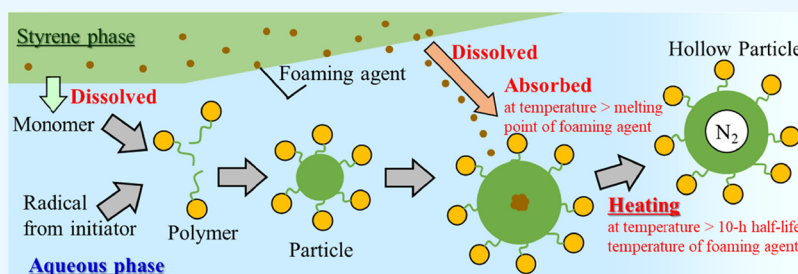
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ABSTRACT: Hollow polymer particles are applied in various fields owing to their high specific surface area and inner volume. The hollow regions in such particles are generally synthesized using a template. However, chemical agents must be used to remove the templates, which is associated with a high environmental load. To address this problem, we previously established a method for synthesizing hollow polymer particles without a template. However, the mechanism underlying this synthesis was unclear, which this study aimed to rectify. First, azo compounds were dissolved in a styrene monomer phase, and soap-free emulsion polymerization was performed to produce polystyrene particles. The azo compounds were incorporated into the polystyrene particles from the monomer phase at a polymerization temperature greater than the melting point of the azo compounds. Finally, the polystyrene particles were heated at a temperature greater than the 10 h half-life temperature of the azo compounds to emit nitrogen gas, and the azo compounds were decomposed to prepare the hollow regions in the polystyrene particles. However, the resulting particles were not hollow when the azo compound was not incorporated into the polystyrene particles. By comparing the melting behavior of different azo compounds, this study elucidates the mechanism underlying our template-free method for synthesizing hollow polystyrene particles.

1. INTRODUCTION

Polymer particles are widely used in not only the materials field^{1–3} but also the information⁴ and medical fields.⁵ Hollow polymer particles, which have a higher specific surface area and better insulative properties than their solid counterparts, are typically synthesized using a template.^{6,7} However, template removal necessitates using chemical agents, such as hydrofluoric acid,^{8–10} which entails a high environmental load. Therefore, we previously established a template-free method for synthesizing hollow polymer particles using azo compounds that emit nitrogen gas while undergoing decomposition by heating. The azo compounds were incorporated into the polymer particles and then decomposed to emit nitrogen gas inside the polymer particles to form hollow regions. For example, 2,2'-azobis(*N*-butyl-2-methylpropionamide) (VAm-110)¹¹ was incorporated into polymer particles synthesized through the soap-free emulsion polymerization of styrene (St) and divinyl benzene with potassium persulfate.^{12,13} The materials were heated to 100 °C to induce the decomposition of VAm-110—which has a 10 h half-life temperature (T_h) of 110 °C—to generate holes in the particles.¹⁴ Alternatively, 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydro chloride

(VA-044)¹⁵ was used as the radical initiator in the soap-free emulsion polymerization of St,^{16,17} and 2,2'-azobis(2-methylbutyronitrile) (V-59)¹⁸ with a T_h of 67 °C was used as the azo compound to be incorporated into the polystyrene particles. Polymerization and decomposition were implemented at 50 and 70 °C, respectively, to prepare hollow polystyrene particles.¹⁹

In this study, the abovementioned compounds and other azo compounds were used to prepare hollow polystyrene particles to clarify the mechanism of formation of hollow particles through the soap-free emulsion polymerization of St and subsequent heating process to decompose the azo compounds incorporated into the polystyrene particles. Especially, the

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temperatures of the reactions in this process were important for the synthesis of the hollow polystyrene particles.

2. EXPERIMENTAL SECTION

2.1. Materials. St (Fujifilm Wako Pure Chemicals Co., Ltd.) was used as the monomer, and VA-044 (Fujifilm Wako Pure Chemicals Co., Ltd.), with a low T_h of 44 °C, or 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Fujifilm Wako Pure Chemicals Co., Ltd.),^{20,21} with a lower T_h of 30 °C, was used as the radical initiator in soap-free emulsion polymerization. Distilled water was used as the reaction solvent. In general, 2,2'-azobis(isobutyronitrile) (AIBN, Fujifilm Wako Pure Chemicals Co., Ltd.), V-59 (Fujifilm Wako Pure Chemicals Co., Ltd.), or dimethyl 2,2'-azobis(2-methylpropionate) (V-601, Fujifilm Wako Pure Chemicals Co., Ltd.) is used as an oil-soluble initiator in polymerization. However, in this study, these azo compounds were incorporated into the polystyrene particles to function as foaming agents to emit nitrogen gas to produce hollow regions. The chemical structures of these materials are shown in Figure 1.

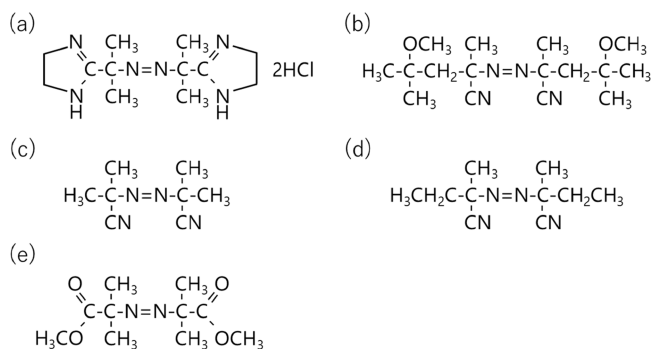


Figure 1. Chemical structures of azo compounds: (a) VA-044; (b) V-70; (c) AIBN; (d) V-59; and (e) V-601.

Distilled water was prepared using a pure water generator (Auto Still WG250, Yamato Kagaku Co., Ltd.) and degassed with nitrogen for a sufficient period before use to prevent dissolved oxygen from radicalizing and interfering with polymerization. NaOH was purchased from Nacalai Tesque Inc. St was rinsed with 10 wt % NaOH (aq) and purified by vacuum distillation.

2.2. Soap-Free Emulsion Polymerization. Polystyrene particles were prepared via soap-free emulsion polymerization. St (86.4 mM), VA-044, or V-70 (5.03 mM), a foaming agent (AIBN, V-59, or V-601), and distilled water (15.0 mL) were added to a 30 mL batch reactor (EYELA, RCH-20L). The mixture was allowed to polymerize by stirring at 130 rpm for 8 h at 50 °C in the case of VA-044 or at 130 rpm for 20 h at 30 °C in the case of V-70. The foaming agents with T_h greater than 65 °C dissolved in the St monomer phase and decomposed slightly because of the low temperature in the soap-free emulsion polymerization. Subsequently, the synthesized polystyrene colloids were heated to 70 °C, and the reaction was allowed to proceed at this temperature for 24 h. Specifically, the chemical reaction shown in Figure 2 occurred to form holes inside the polystyrene particles owing to the release of nitrogen gas by the foaming agent.²²

2.3. Characterization. The particle morphologies were observed through field-emission scanning electron microscopy

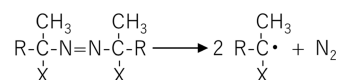


Figure 2. Decomposition of an azo compound inside a polystyrene particle (R and X indicate the functional groups of the azo compounds shown in Figure 1).

(JSM-7500F, JEOL). SEM samples were prepared by dropping a colloidal solution onto a piece of mica, whose surface layer was removed using cellophane tape. The sample was vacuum-dried, and an osmium layer with a thickness of 10 nm was deposited using an osmium coater (OPC60A, Filgen Co., Ltd.). The SEM images were analyzed using particle analysis software (AZo Kun, Asahi Kasei Engineering) to calculate the average particle diameter

$$d_p.$$

The hollow structures within the particles were examined through transmission electron microscopy (TEM, JEM-2100 plus, JEOL). The zeta potentials of the particles in the suspension at 25 °C were measured through laser Doppler velocimetry (Zetasizer Nano-ZS, Malvern PANalytical, Ltd.) after diluting the sample slurry with deionized water.

3. RESULTS AND DISCUSSION

3.1. Polymerization Using AIBN as the Foaming Agent. V-601 (7.00 mM) was used as the foaming agent in the polymerization of St by VA-044 at 50 °C. The results of the polymerization of particles with zeta potentials of 41.2 mV after heating at 70 °C are shown in Figure 3. Hollow particles

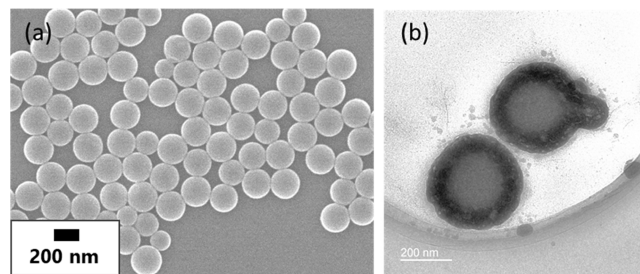


Figure 3. (a) SEM and (b) TEM images of particles generated by polymerization by VA-044, using V-601 as the foaming agent.

were synthesized because V-601 with a T_h of 66 °C decomposed when heated at 70 °C and emitted nitrogen gas inside the particles. These results were consistent with those of the polymerization of St by VA-044 at 50 °C using V-59 as the foaming agent observed in our previous work.¹⁹

AIBN (7.00 mM) was used as a foaming agent in the soap-free emulsion polymerization of St by VA-044, a water-soluble initiator, at 50 °C. The zeta potential of the synthesized particles was measured to be 40.7 mV, which shows their good dispersion stability,²³ corresponding to the decomposition of the functional groups from VA-044.²⁴ Particles were observed after the heating process at 70 °C, as shown in Figure 4. The TEM images did not indicate the presence of hollow structures.

These results indicate that the polymerization of St must be performed at a reaction temperature above the melting point of the foaming agent to synthesize hollow particles. Table 1 lists the melting points of different foaming agents.²⁵ Notably, above the melting point, the foaming agents were liquid and

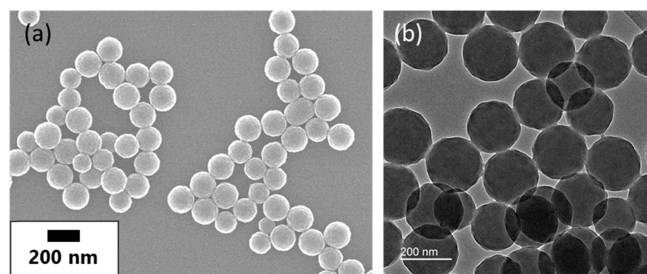


Figure 4. (a) SEM and (b) TEM images of particles generated by the polymerization of St by VA-044, using AIBN as the foaming agent.

Table 1. Melting Points of the Foaming Agents

foaming agent	melting point [°C]
V-601	22–28
V-59	48–52
AIBN	100–103

could be easily absorbed by the polystyrene particles²⁶ to coalesce and form a single droplet in the particle during polymerization, thereby forming hollow structures through decomposition induced by heating at 70 °C.

When AIBN with a melting point of over 100 °C was used, hollow particles were not synthesized because the foaming agents in the solid-state were not effectively incorporated by the polystyrene particles. In other words, the foaming agent dissolved in the St monomer phase did not reach the polystyrene particles. Instead, the foaming agent, that is, the azo compound, started to dissolve in the aqueous phase at the molecular scale as the St monomer was consumed in the polymerization, and it was absorbed by the polystyrene particles in the liquid state in the aqueous phase when the polymerization temperature was above the melting point of the foaming agent. Therefore, hollow structures were observed in the cases shown in Figure 3 because the polymerization temperature was above the melting point of the foaming agent, which was inside the polystyrene particles. These results and reaction mechanisms are summarized in Figure 5. This mechanism was applied to the other system, as supported by Figure S1.

To confirm the mechanism illustrated in Figure 5, St was polymerized by VA-044 using V-59 (7.00 mM) as the foaming agent. This reaction was carried out at 44 °C, which was below the melting point of V-59, and the results are shown in Figure 6. In our previous work, the hollow structures were observed through polymerization at 50 °C.¹² The resulting particles were not hollow because V-59 was not incorporated into the

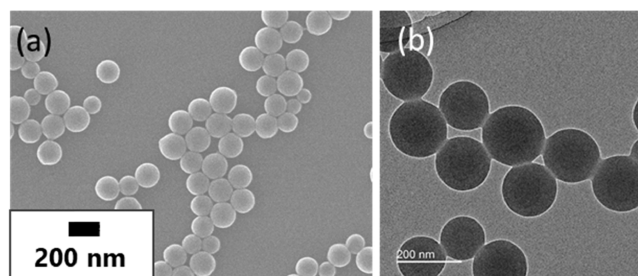


Figure 6. (a) SEM and (b) TEM images of particles obtained through polymerization by VA-044 at 44 °C, using V-59 as the foaming agent.

polystyrene particles, as polymerization occurred below the melting point of V-59. If a monomer droplet including V-59 was incorporated into the polystyrene particles during polymerization at a temperature below the melting point, 44 °C, then, under the subsequent decomposition by heating at 70 °C, the incorporated V-59 would melt, creating liquid droplets in the polystyrene particles and then generating hollows owing to decomposition. However, hollows were not observed in the case shown in Figure 6b, indicating that V-59 was not incorporated into the polystyrene particles through the monomer droplet below the melting point.

Next, V-70, which is an oil-soluble initiator, was used as the radical initiator in the soap-free emulsion polymerization of St.^{27,28} V-59 (7.00 mM) was used as the foaming agent in the polymerization of St using V-70 at 30 °C. The results of the polymerization of particles with a zeta potential of −56.6 mV after heating at 70 °C are shown in Figure 7. A high dispersion

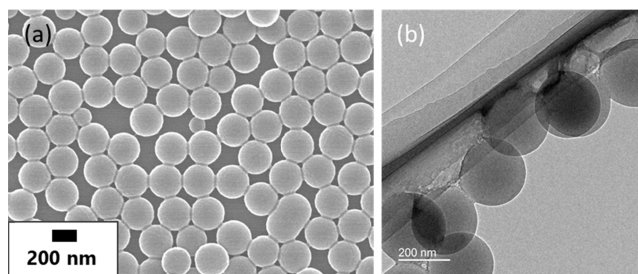


Figure 7. (a) SEM and (b) TEM images of particles obtained through polymerization by V-70 at 30 °C, using V-59 as the foaming agent.

stability could be maintained because of the phenyl rings in polystyrene.²⁹ Hollow particles were not synthesized, which indicated that V-59 was not incorporated into the polystyrene particles when the polymerization was performed at a temperature under the melting point of V-59.

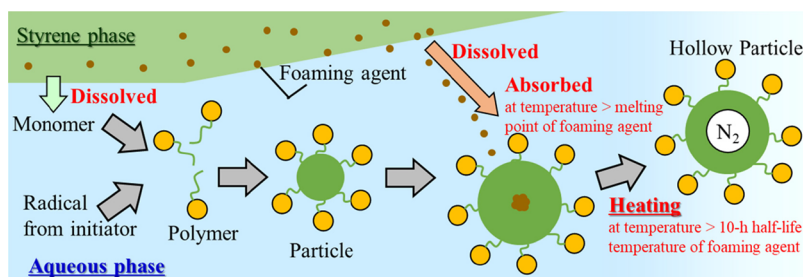


Figure 5. Mechanism of the generation of hollow polystyrene particles through soap-free emulsion polymerization of St using an oil-soluble initiator as the foaming agent, with decomposition induced by heating.

4. CONCLUSIONS

We determined the conditions for the decomposition of azo compounds inside polystyrene particles to form hollow structures. The melting point of the azo compound is a critical parameter to ensure the incorporation of the compound into polystyrene particles during the soap-free emulsion polymerization of St. The polymerization temperature must be higher than the melting point of the azo compound to allow the foaming agent to be absorbed by the polystyrene particles; however, it must be lower than the 10 h half-life temperature of the azo compound to prevent the decomposition from occurring outside the polystyrene particles. Under these conditions, hollow polystyrene particles can be synthesized through only soap-free emulsion polymerization and heating processes without using a template.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03351>.

Synthesis of the hollow polymer particles using other azo compounds or monomers (PDF)

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Notes

The authors declare no competing financial interest.

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