Design of Polymer Particles Maintaining Dispersion Stability for the Synthesis of Hollow Silica Particles through Sol-Gel Reaction on Polymer Surfaces

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Abstract

To synthesize polystyrene-silica core-shell particles and silica hollow particles, soap-free emulsion polymerization was carried out using styrene and *N*-vinylacetamide (NVA), and the Stöber method using tetraethyl orthosilicate (TEOS) was performed on the polymer particle surfaces. Here, NVA acts as a stabilizer for the polymer colloids, maintaining dispersion stability by synthesizing hydration layers even when the electrostatic adsorption of TEOS had occurred, and as a catalyst for the sol-gel reaction. NVA was polymerized by the cationic initiator located on the surface of the polystyrene particles to maintain dispersion stability by a steric effect. Therefore, the sol-gel reactions proceeded more efficiently on the surface of polymer particles, facilitated by the much larger surface area. Finally, the polymer core was removed by heating to prepare highly monodisperse silica hollow particles.

1. Introduction

Polymer particles are utilized and studied in various fields [1-3]. In particular, soap-free emulsion polymerization is carried out as an environmental-friendly method to prepare polymer colloids because a surfactant is not required [4-6]. Recently, synthesis methods for composite particles have been developed to acquire novel functionalities from hybrid materials using inorganic and organic components [7, 8]. Polymer particles have been used as templates to synthesize core-shell particles [9-11]. For the shell, silica was often used to cover polymer core particles [12, 13]. In a second step, the polymer core can be removed through heating or chemical dissolution to synthesize silica hollow particles [14, 15]. Such polymer-silica core-shell particles are used as thermal insulators [16] and for drug delivery [17].

Many studies on the design of composite materials have focused on the interaction between polymers and negatively charged silica [18]. In such studies, cationic surfactants were used to carry out the surface modification of the polymer core particles. In addition, composite particles synthesized through only electrostatic interactions between the silica and polymer would be unstable with respect to coagulation on the basis of Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [19].

In the present study, the synthesis method of polystyrene-silica core-shell and silica hollow particles was developed without surfactants. *N*-vinylacetamide (NVA) monomers helped to produce hydration layers around the polystyrene particles, maintaining good dispersion stability without coagulation, on the basis of electrostatic theory [20]. Additionally, NVA has NH functional groups that

act as catalysts for the reaction of tetraethyl orthosilicate (TEOS). Moreover, the modification with NVA enabled in situ electrostatic adsorption of TEOS and the generation of silica on polymer particles. Thus, styrene and NVA monomers were polymerized to make core particles by soap-free emulsion polymerization using a cationic initiator.

2. Experimental

2.1. Materials

The water used in this study was purified by an Auto Still WG250 system (Yamato Scientific Co.), and then, nitrogen gas was bubbled into the water for removal of any dissolved oxygen. After the styrene monomer (FUJIFILM Wako Pure Chemical Co.) was washed using 10 wt.% sodium hydroxide (Nacalai Tesque, Inc.) to remove inhibitors for polymerization, it was purified through distillation under reduced pressure. NVA monomer (Showa Denko K. K.) was used during the polymerization step to fabricate polyNVA (PNVA) layers around the polystyrene particles without further purification. Thus, polymer core particles were prepared without removing the PNVA layers to make the silica shell for Stöber method. PNVA adsorbed on the polystyrene particles worked as a catalyst for the synthesis of silica and as a stabilizer for maintaining the dispersion stability of the polymer colloid. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, FUJIFILM Wako Pure Chemical Co.) was used as received as a cationic initiator to make the zeta potential positive, thus promoting the adsorption of TEOS on the polymer surface. TEOS (Nacalai Tesque, Inc.)

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was used as the precursor for the silica shell. 1-Propanol (Nacalai Tesque, Inc.) was used as the solvent medium for TEOS.

2.2. Reactions

Polymerization was conducted in a batch reactor. A magnetic stirrer equipped with a heater (RCH-20L, EYELA) controlled the reaction temperature and the rotation speed of the impeller in the reactor. The experimental conditions for the polymerization are shown in **Table 1**. Because our recent researches showed that polymerization was completed within 6 h [21], the reaction time was set to this time.

Table 1. Experimental recipes of the polymerizations

Water [g]	15
Styrene monomer [mM]	320
NVA monomer [mM]	< 783
VA-044 [mM]	2.03
Reaction temperature [°C]	70
Rotation speed of impeller [rpm]	130

The experiments for the polymerization were performed as follows. After the amounts of water and VA-044 as listed in **Table 1** were poured into a reactor, the monomers were added and they were

heated to 70 °C using a heater. The reaction mixture was agitated at 130 rpm with an impeller by a magnetic stirrer to facilitate the synthesis of the monodisperse particles [22].

Stöber process[23] was carried out to generate silica shells on the surfaces of the polymer particles as follows [24, 25]. TEOS (500 μL) was added to 10 mL of 1-propanol and heated to 40 °C with stirring. Then, 10 mL of the polymer colloid was added to the aboveprepared 1-propanol solution at 1 mL/min using a burette, covering the cationic polymer particles with TEOS electrostatically. At that time, the coagulations would be expected under normal conditions, however, the hydration layers made by PNVA on the polystyrene particle surfaces contributed to the maintenance of good dispersion stability by steric effects [26]. Finally, the mixture was stirred at 40 °C for 48 h to synthesize the polymer particles with silica shells. The unreactive TEOS and 1-propanol were removed by centrifugation (3700, KUBOTA), to be replaced by pure water.

2.3. Characterization

The morphologies of the particles synthesized in this study were observed with a field emission scanning electron microscope (FE-SEM; JSM-7500FA, JEOL). The FE-SEM samples were prepared as follows. A small amount of solution was sampled from the solution, and a drop of this solution was placed on a cleaved mica surface, and then dried at the room temperature. The specimen was covered with osmium tetroxide using an osmium plasma coater (OPC60A, Filgen).

The average size of the synthesized particle was determined by number-averaging the data of

ca. 300 particles in the SEM images using the image analysis software (A-zokun, Asahi Kasei Engineering Corporation).

After the particle concentration was diluted with deionized water, where the particle concentration was adjusted such that the intensity of scattered light was sufficiently detectable by our apparatus, the zeta potential of the particles in the suspension was determined by a Zetasizer Nano-ZS (Malvern Panalytical). The sample slurry was at a pH of ca. 7.0.

3. Results and discussion

3.1 Influence of NVA concentration on particle properties

Fig.1 shows the influence of NVA concentration on the size of polymer particles. The particle size decreased with increasing NVA concentration. The synthesized particles were washed by the centrifugation to remove the PNVA from the polymer particles. After washing, the particle size was decreased. The changes in the morphologies of the particles produced with the NVA concentration of 392 mM, before and after washing, were observed by FE-SEM, as shown in **Fig.2**. In the case of particles before washing, a clear SEM image was not obtained because of the PNVA coating, as shown in **Fig.2a**; on the other hand, a clear SEM image indicated that smooth surfaces were obtained after washing to remove PNVA, as shown in **Fig.2b**. From these two images, we can conclude that PNVA was located on the surfaces of the polystyrene particles.

**Fig.3** shows the effect of NVA concentration on zeta potential. These results indicate that the

zeta potential became smaller with the concentration of NVA in the synthesis, probably because the surfaces of the synthesized cationic polystyrene were covered with PNVA. After washing by the centrifugal method, the zeta potential increased because of the removal of a part of the PNVA coating.

Generally, the enhancement of surface potential enabled the particle size to be reduced [27, 28], however, the present results show that particle size was decreased despite a reduced zeta potential. On the basis of our previous work, dispersion stabilities were enhanced by covering the polystyrene surfaces with PNVA to produce hydration layers on the particle surfaces [20]. The hydration layers generated by PNVA reduced the surface potential, however, preventing coagulation-induced particle growth during polymerization by their steric effects, and thus decreasing the size of the polymerized particles.
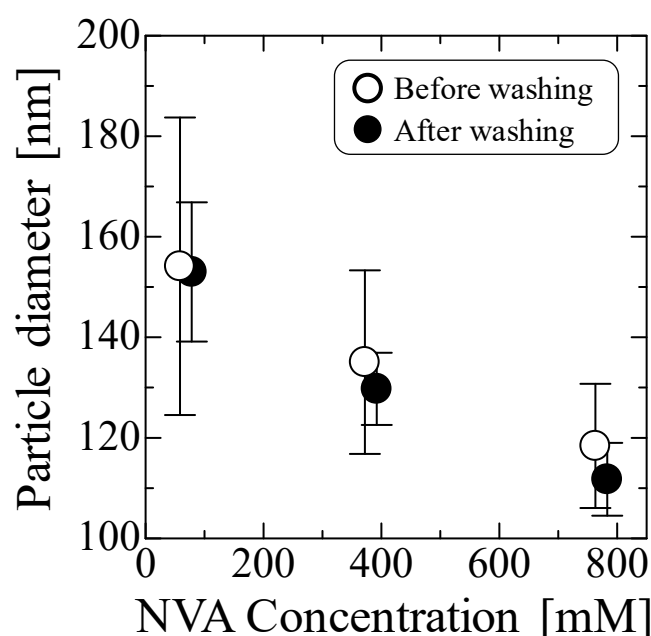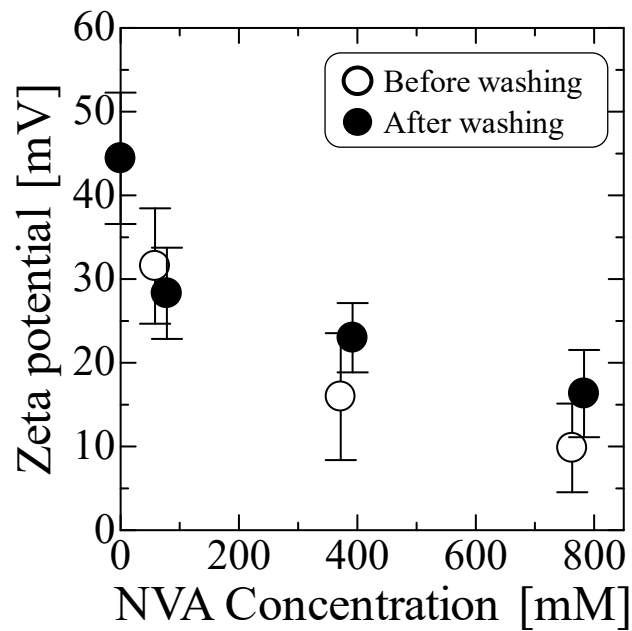

Fig.1 Influence of NVA concentration on size of polymer particles before and after washing.
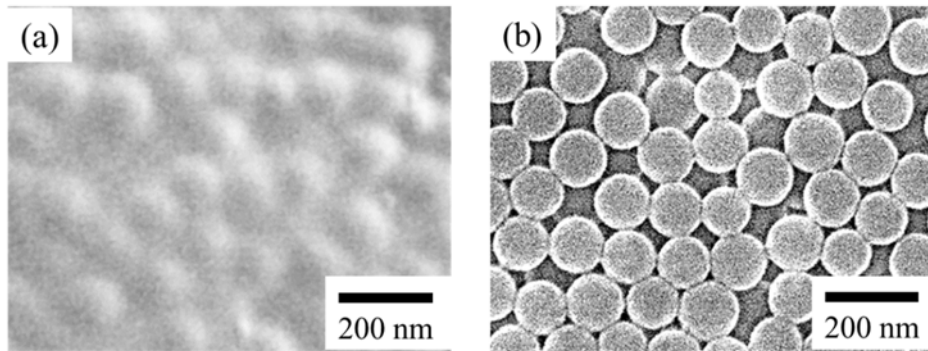
Fig.2 FE-SEM observations of polymer particles synthesized with an NVA concentration of 392 mM: (a) before washing; (b) after washing.


Fig.3 Influence of NVA concentration on zeta potential of polymer particles before and after washing.

3.2 Synthesis of core-shell particles

Fig.4 shows the SEM images of particles synthesized with different NVA concentrations, after the addition of the silica shell using TEOS. The reaction with TEOS proceeded more efficiently only the surfaces of the polymer particles because the PNVA worked as catalyst of the reaction and kept dispersion stability to sustain much larger surface area. Because most of the PNVA on the polystyrene

particles was covered with the silica formed from the reaction, clear SEM images were obtained. We were able to synthesize highly monodisperse silica-polymer particles with coefficients of variation in the range 4-9%.
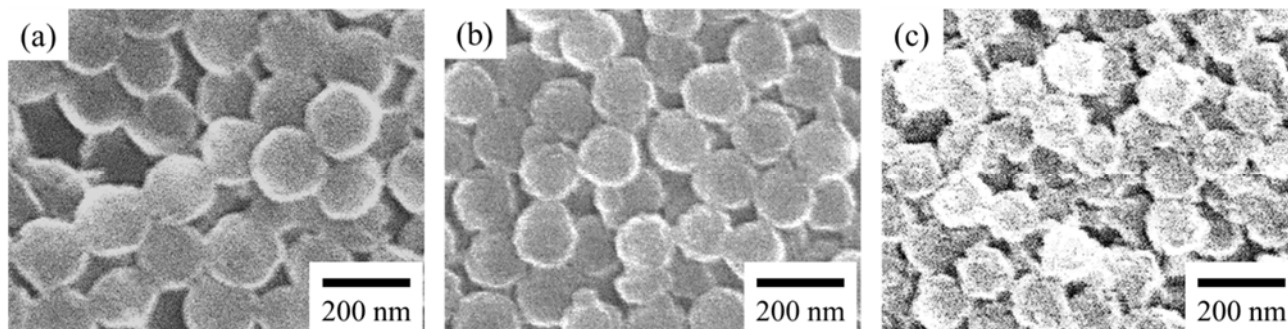

Fig.4 FE-SEM observations of core-shell particles at NVA various concentrations: (a) 78.3 mM; (b) 392 mM; (c) 783 mM.

Fig.5 shows the change in particle size with NVA concentration. Because the polymer particles were coated with silica, the size became larger after the sol-gel reactions. Because of the silica shell, the zeta potential became negative, as shown in **Fig.6**. We note that in the case of higher concentration of NVA, the difference in zeta potential between the particles with and without silica was very small. When 5 h had passed after the completion of all reactions, the dispersions were photographed as shown in **Fig.7**. Although the surface potential was higher for the sample made with a NVA concentration of 78.3 mM, almost all the particles sedimented. By contrast, an extremely good dispersion stability was exhibited even when the surface potential was smaller at NVA concentrations of 392 or 783 mM. These high dispersion stabilities were attributed to the hydration layers formed on
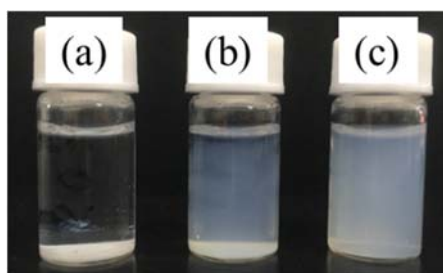
the silica shells where PNVA had penetrated. Therefore, the effect of silica on surface potential was

much smaller at higher concentrations of NVA.
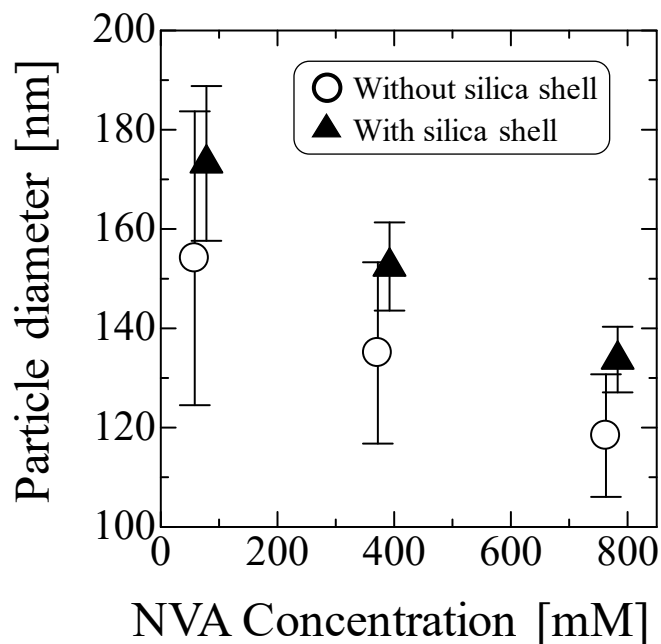
Fig.5 Influence of NVA concentration on size of silica-polymer particles with and without silica shells.
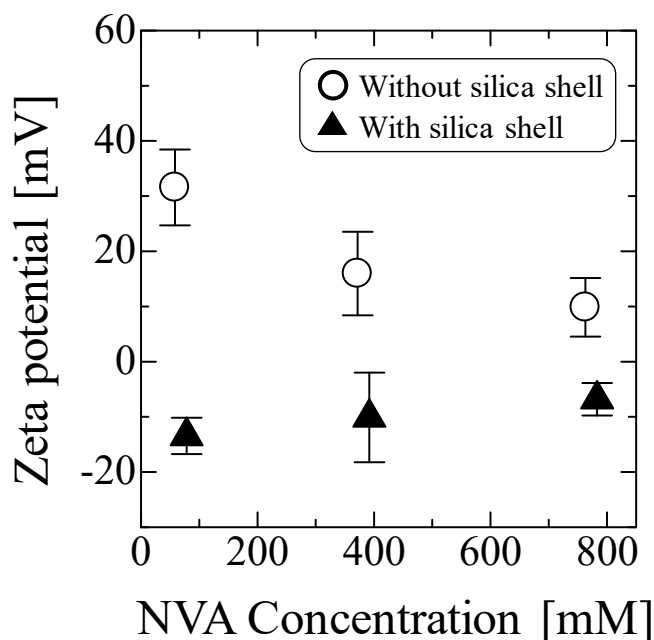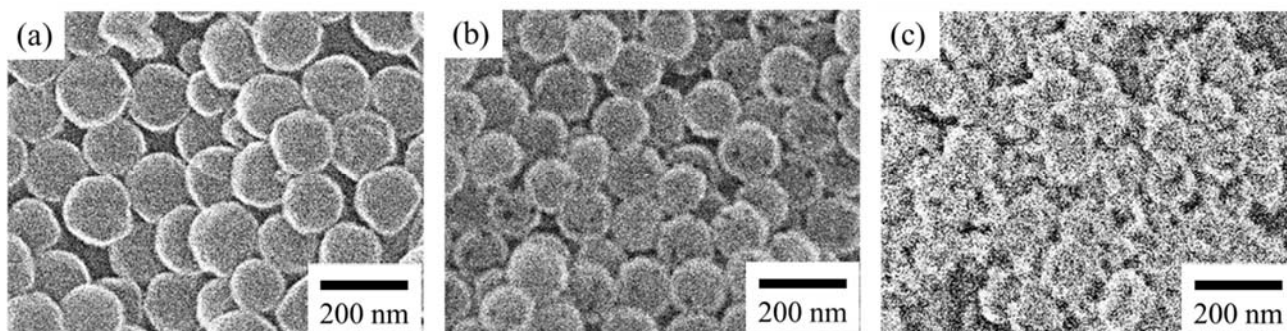
Fig.6 Influence of NVA concentration on zeta potential of polymer particles with and without silica shells.

Fig.7 Dispersion in water of the silica-polymer particles, synthesized at various NVA concentrations: (a) 78.3 mM; (b) 392 mM; (c) 783 mM.

3.3 Synthesis of hollow silica particles

Finally, polymer templates were removed from the core-shell particles by heating using an electric furnace (FT-101FM, FULL-TECH FURNACE CO., Ltd), at 500 °C for 6 h. The obtained hollow particles with coefficients of variation in the range 7-10% were observed by FE-SEM, as shown in **Fig.8**; spherical particles can be observed, which indicates the formation of the silica shell around the polymer template by the present method. As the concentration of NVA increased, a porous appearance of the surface of the hollow particles is observed. As PNVA penetrated the silica shell before heating, the particles were pyrolyzed to the porous form after heating [29]. Large amounts of PNVA penetrating into the silica shell led to the synthesis of hollow particles with a rough surface, as shown in **Fig.8c**. **Fig.9** shows the difference of the particle sizes among the procedures in the present study. After pyrolysis, the size was reduced probably because the removal of polymer led to shrinkage of the shell by sintering. At the highest concentration of NVA, the size reduction was larger because a larger amount of PNVA was included in the silica shell.

Fig.8 FE-SEM observations of hollow particles from synthesis at the following NVA concentrations: (a) 78.3 mM; (b) 392 mM; (c) 783 mM.
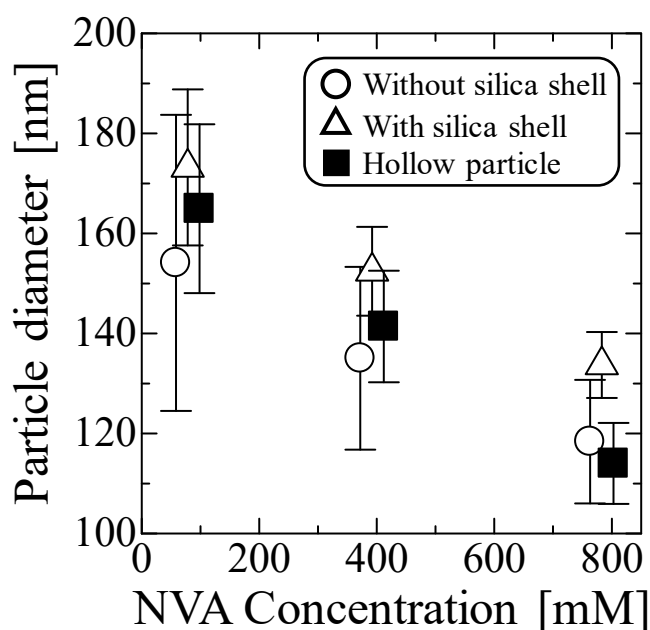
Fig.9 Influence of NVA concentration on particle size, for the particles synthesized with and without silica shell and the hollow particles.

4. Conclusions

The method of synthesis of core-shell and hollow particles was developed through soap-free emulsion polymerization and the Stöber method. First, polymerization was carried out using styrene and NVA to synthesize core polymer particles. Second, the Stöber method using TEOS in 1-propanol was conducted to fabricate silica shells around the core polymer particles. In this reaction, PNVA made

a significant contribution, maintaining good dispersion stability during the sol-gel reactions. The PNVA on the polystyrene particles penetrated the silica shell, forming a hydration layer that enabled good dispersion stability, thus preventing coagulation during shell formation on the polymer core. Finally, the polymer core templates were removed by heating to obtain highly monodisperse hollow particles.

Acknowledgement

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