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Novel Mini-Reactor of Silicone Oil Droplets for Synthesis of Morphology-Controlled Polymer Particles

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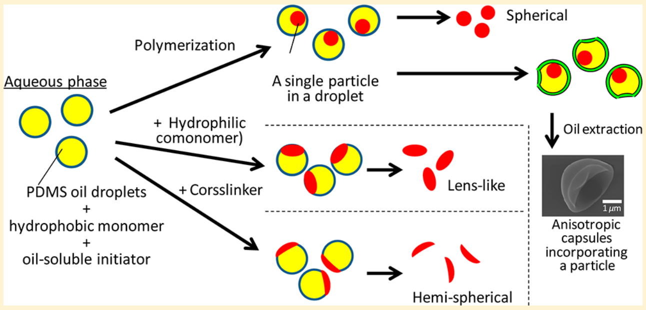
S Supporting Information



ABSTRACT: Inside spaces of emulsion droplets can be used as mini-reactors for material synthesis. The novel application of sol−gel derived silicone oil droplets as mini-reactors was examined for the case of polymerization of styrene (St) and comonomers with the oil-soluble initiator 2,2′-azobis(2,4-dimethylvaleronitrile). Polydimethylsiloxane (PDMS) droplets prepared from dimethylsiloxane were used as the mini-reactors, in which the polymerization of St without comonomers was first conducted. In the polymerization, the St/PDMS volume ratio was varied from 0.025 to 0.10. After the polymerization, each PDMS droplet contained a polystyrene (PSt) particle. The St/PDMS ratio of 0.05 enabled the synthesis of micrometer-sized, spherical PSt particles with low polydispsersity. Copolymerization of St with comonomers having hydrophilic groups deformed the spherical shape of particles to lens-like or disk-like morphologies that were obtained with acrylic acid or sodium 4-styrene sulfonate, respectively. In another copolymerization, with divinylbenzene used as a cross-linker, hemispherical polymer particles were formed. To diversify the particle morphologies further, the proposed mini-reactor synthesis was combined with the recently proposed silicone oil droplet templating method (Ohta et al., 2012). Around the PDMS droplets containing a polymer particle, polymeric shells with a depression were successfully formed with the proposed method. The remaining PDMS oil inside the polymeric shells was extracted with ethanol, which caused hemispherical polymeric bowl-shaped capsules having a protrusion on the inside.

INTRODUCTION

An emulsion confines a liquid to droplets dispersed in a liquid with which it is immiscible. The small spaces can be used as mini-reactors for the synthesis of morphology-controlled particles.[1−3] Inverse emulsion synthesis and mini-emulsion polymerization are typical examples that are widely applied to the production of functional materials. A problem of those synthetic methods is the size distribution of the produced particles, resulting from the coalescence and redispersion of dispersed phases in the former method and the mechanical dispersion, normally by ultrasonication, in the latter. This limitation can be resolved by droplet-based microfluidics, in which nanoparticles are synthesized by confining the reactions to the interior of droplets.[4,5]

Silicone emulsion prepared by the sol−gel process can also be prepared in the form of highly monodisperse silicone oil droplets dispersed in an aqueous phase.[6] The droplets are stably dispersed by electrostatic repulsion between the droplet surfaces. It has been reported that the size of the droplets can be controlled from a few hundred nanometers to several micrometers with additives such as surfactants and polymer stabilizers.[7,8] The silicone emulsion synthesis was further extended to the silica encapsulation of polydimethylsiloxane (PDMS) droplets.[9] An emulsion templating technique was developed for the synthesis of anisotropic, deformable hybrid silica/siloxane colloids.[8,10−12] Dopamine was also used as a coating material of silicone oil droplets.[13] Besides the syntheses of oil-containing particles, another technique was developed in which reactive silicone oil droplets are solidified and transformed to anisotropic shapes with polymerization-induced buckling.[14,15]

Recently, we proposed a novel method for preparing nonspherical oil-containing particles.[16] The method consisted of the preparation of PDMS oil droplets and a polymerization to form shells on the droplets. The monomer 3-methacryloxypropyltrimethoxysilane (MPTMS) or styrene (St) used in the polymerization was first absorbed into the droplets and then polymerized with a water-soluble, ionic initiator to form a polymeric shell on the droplet surface. The polymerization that continued after the shell formation reduced the droplet volume and led to the creation of anisotropic shapes.

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The silicone emulsion methods applied to the preparation of anisotropic particles in the literature[8−18] including our previous work[10−12,16] were based on the shell formation on the silicone oil droplets. The purpose of the present work is to develop a different method in which the silicone in the droplets is utilized as a solvent for material synthesis. The interior of the droplets can be used as highly monodisperse reactors for synthesizing materials consisting of monodisperse particles ranging from nano- to micrometers. To demonstrate the idea, we carried out polymerizations within the silicone oil droplets using an oil-soluble initiator. To be able to observe the products in water with an optical microscope, micrometer-sized silicone oil droplets are prepared in the sol−gel process. The polymerization inside the silicone oil is combined with our previous method for shell formation to diversify shape control of the resultant particles.

EXPERIMENTAL SECTION

Materials. Dimethyldiethoxysilane (DMDES, 97%) was obtained from Gelest, Inc. (Geneva, Swizerland). Aqueous ammonia solution (25% NH_3), styrene (St, 99%), acrylic acid (AA), divinylbenzene (DVB), sodium 4-styrene sulfonate (NaSS), sodium dodecyl sulfate (SDS), 2,2′-azobis(2,4-dimethylvaleronitrile (ADVN, V-65, 95%), potassium persulfate (KPS, 95%), and tetraethyl orthosilicate (TEOS, 95%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). 3-Methacryloxypropyltrimethoxysilane (MPTMS, 95%) was obtained from Shinetsu Chemical (Tokyo, Japan). Milli-Q deionized water (electrical resistivity = 18.2 MΩ·cm) bubbled with nitrogen was used to prepare all aqueous solutions.

Preparation of PDMS Droplets Containing a Polymer Particle. PDMS oil-in-water emulsions were prepared according to the method by Zoldesi et al.[11] The aqueous ammonia solution (2 mL) was mixed with deionized water (46 mL) and stirred for 10 min at room temperature. To the aqueous mixture 2 mL of DMDES dissolving 0.025 g ADVN was added. The DMDES solution was vigorously stirred for 4 min, and kept at 25 °C without stirring for 24 h to prepare the PDMS emulsion.

A quantity of St with and without a comonomer was added to the PDMS emulsion, which was then stirred for 30 min. Then, the glass vessel containing the reactants was transferred into a constant temperature bath at 70 °C. A point 20 min after the transfer, when a constant temperature was attained, was taken as the initiation time of the polymerization. The monomer was absorbed by the PDMS droplets and polymerized after initiation by ADVN preabsorbed in the droplets. In certain experiments, SDS was added to the aqueous phase 1 h after the initiation of polymerization. When NaSS was used as comonomer, its addition time was 1 h after the initiation.

Shell Formation on PDMS Droplets Containing a Polystyrene Particle. MPTMS and TEOS were examined as coating materials of PDMS droplets. The PDMS emulsion (50 mL) that had been used in the polymerization of St without comonomer and SDS was cooled to 25 °C under stirring in a constant temperature bath. TEOS was then added to the PDMS solution that was kept at the same temperature under stirring. In experiments with MPTMS, this was added to the PDMS emulsion, which was stirred for 30 min and then heated to 70 °C in a constant temperature bath. Polymerization of MPTMS was initiated by addition of a solution of 2 g water/0.135 g KPS. Extraction of PDMS component from the particles with a shell was performed by direct redispersion of the particles into ethanol. The particles with a shell were dried and calcined at temperatures above 500 °C for 1 h to examine the internal morphology of particles.

Characterization. The PDMS droplets containing a polymer particle in the aqueous phase were directly observed with an optical microscope (OM, Olympus BX51). A field emission scanning electron microscope (FE-SEM, Hitachi S4800) was used to observe polymer particle morphologies after drying a sample of the PDMS emulsion at ambient temperature without any pressure control. Energy dispersive X-ray spectroscopy (EDX) was performed for elementary analysis of the shell-coated PDMS particles on a 200 mesh copper grid with a scanning transmission electron microscope (FE-STEM, Hitachi HD-2700) equipped with an EMAX Energy (Horiba).

RESULTS AND DISCUSSION

Figure 1A shows an OM image of the PDMS droplets prepared after the St polymerization at a St/DMDES volume ratio of 0.05. Each PDMS droplet with a diameter of ca. 3 μm contains a polystyrene (PSt) particle that appears to be located near the droplet periphery. A SEM image of Figure 1B taken after the drying treatment indicates that the PSt particles are monodisperse spheres with a size of 1.2 μm. Although the St polymerization was also conducted at St/DMDES volume ratios of 0.025 and 0.10, the PSt particles formed were not monodisperse. PDMS is a typical hydrophobic substance and St is a little bit less hydrophobic. Since droplets prepared with a single component of DMDES has a relatively broad size distribution, as shown in the previous report,[16] an appropriate amount of such less hydrophobic component added probably enabled the size distribution of DMDES to be sharper than the one without the addition. The difference in hydrophobicity between PDMS and PSt might locate the PSt particle near the periphery of the PDMS droplet. Therefore, if hydrophilic groups were introduced onto the PSt particle, the particle may contact the PDMS droplet surface during the polymerization and change its final shape.

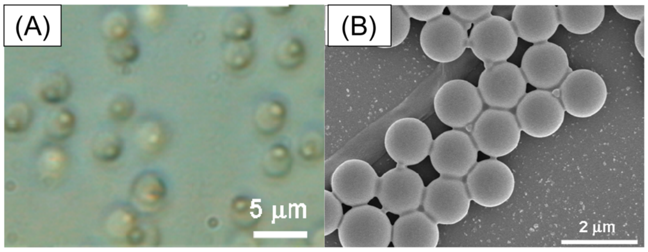

Figure 1. OM image of PDMS droplets containing a PSt particle (A) and SEM image (B) of PSt particles after drying the droplets of (A). The polymerization was conducted with the addition of 100 μL St (17.4 mM) at a St/DMDES volume ratio of 0.05.

To introduce hydrophilic groups, a polymerization was conducted with St and the comonomer AA at an AA/St volume ratio of 0.05. The ratio of total amount of monomer to PDMS was also 0.05, as before. In the polymerization, St dissolving AA was added to the system. Figure 2A shows an OM image of the

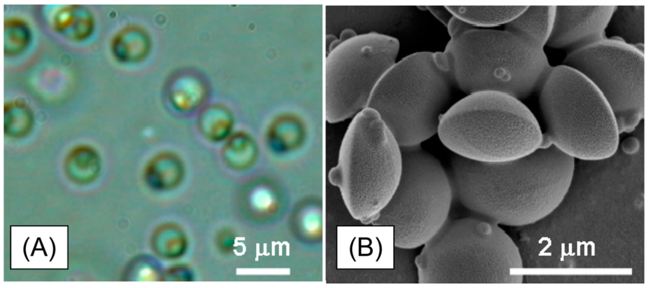

Figure 2. OM image (A) of PDMS droplets containing a polymer particle formed by AA-St copolymerization and SEM image (B) of the particles after drying the droplets of (A). The polymerization was conducted at AA/St volume ratio of 0.05. See Figure 1 for the total amounts of monomers and DMDES.

PDMS droplets with polymer particles. As expected, an anisotropic particle was formed between the continuous phase and the PDMS droplet, which might be caused by localization of hydrophilic polymer formed in the copolymerization. The shape of the anisotropic particle was lens-like, as seen in a SEM image of Figure 2B taken after drying. An additional polymerization experiment at an increased AA/St volume ratio of 0.10 produced thinner and larger polymer particles than those in Figure 2B, probably because of increased hydrophilicity of the resultant polymer particles.

A similar result was obtained in polymerization of St with ionic comonomer of NaSS. Figure 3 shows images of the emulsion and the dried polymer particles. The added amounts of St and NaSS in the polymerization were 100 μL (17.4 mM) and 0.0114 g (1.0 mM), respectively. A disc-shaped particle with a diameter of ca. 2.7 μm attached to each PDMS droplet (Figure 3A). The disc-shaped polymer particles were confirmed in SEM observation after the drying treatment (Figure 3B). Another SEM image is presented in Figure S1 of the Supporting Information to show thickness of the disc-shaped polymer particles. In the polymerization, most NaSS was dissolved in the water phase early in the reaction. Possibly, the NaSS copolymerizes with St in the polymer particles at their contact with the water phase. NaSS is a strong electrolyte and has high hydrophilicity in comparison with the comonomer, AA, in Figure 2. The higher hydrophilicity of NaSS might cause a thinner shape of the resulting particles than those of AA in Figure 2B.

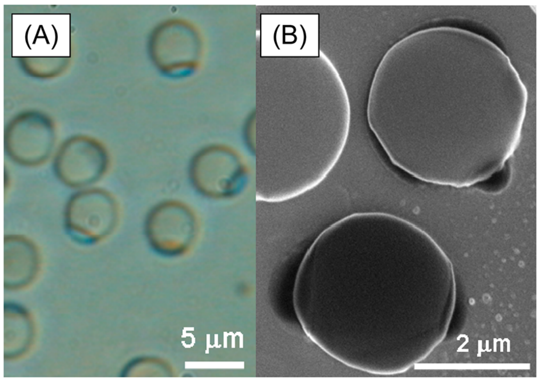

Figure 3. OM image (A) of PDMS droplets containing a polymer particle formed by NaSS-St copolymerization and SEM image (B) of the particles after drying the droplets of (A). The polymerization was conducted at 17.4 mM of St and 1.0 mM of NaSS. See Figure 1 for the total amounts of monomers and DMDES.

To examine the effects of cross-linking on the particle morphology, St was polymerized in the presence of DVB in the PDMS droplets at molar DVB/St ratios of 0.01 and 0.05. However, coagulation of the PDMS droplets was observed in the polymerization. To prevent the droplets from coagulating, the surfactant SDS (1.0 mM) was added in the polymerization. At both DVB/St ratios, PDMS droplets containing a polymer particle were obtained. Figure 4 shows the PDMS droplets and the dried polymer particles at the DVB/St ratio of 0.05. The polymer particles had a hemispherical shape. Since the addition of DVB can produce the cross-linked polymer network to increase internal stress for particle contraction in the polymerization, the internal stress probably assisted the flattening of polymer particles to minimize surface free energy in the formation of particles as shown in Figure 4B. The less cross-linked polymer particles obtained at the DVB/St ratio of 0.01 had a rounder shape (see Figure S2). No significant influence of SDS addition on the polymer particle morphology was confirmed in polymerizations of St with and without SDS. Both cases produced a spherical polymer particle in each PDMS droplet (compare Figure.1 in the absence of SDS and Figure S3 in the presence of SDS). This is evidence that the transformation into hemispheres from the round shapes was not caused by the addition of SDS, but by the addition of DVB.

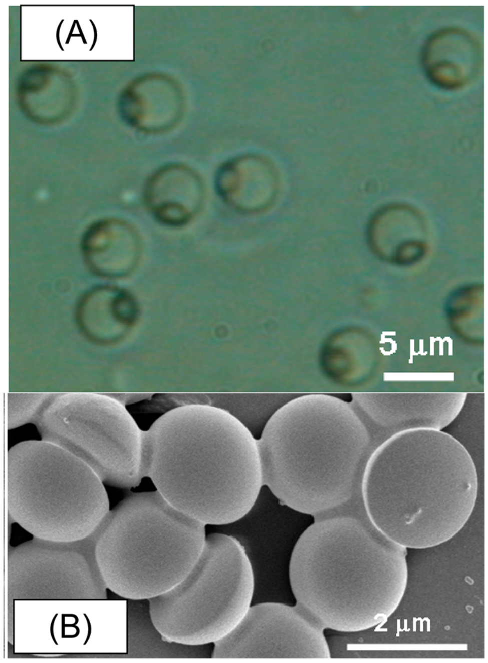

Figure 4. OM image (A) of PDMS droplets containing a polymer particle formed by DVB-St copolymerization and SEM image (B) of the particles after drying the droplets of (A). The polymerization was conducted at DVB/St volume ratio of 0.05. See Figure 1 for the total amounts of monomers and DMDES.

Thus, the present work has succeeded in preparation of spherical, lens-like, disc-like, and hemispherical polymer particles in the PDMS droplets. Wider varieties of polymer particle synthesis can be expected when the sizes and other properties of PDMS droplets are tuned by the addition of stabilizers or absorption of other solvents into the droplets.

The synthesis of particle-containing PDMS droplets can be combined with shell formation on PDMS droplets. The PSt/PDMS emulsion prepared in the experiment of Figure.1 was used for this demonstration. Although silica shell formation was examined with TEOS, the addition of TEOS to the PSt/PDMS emulsion caused the coagulation of the PDMS droplets. Another shell formation experiment was conducted with MPTMS that was first absorbed into PDMS droplets and then polymerized with the water-soluble initiator KPS.[16] An OM image of the resultant particles is presented in Figure 5A, where anisotropic particles with a deformed shell are observed. Figure 5B shows a STEM image of the anisotropic particle that has a depression in the shell. Elemental analysis confirmed the presence of a silica shell and an inner polymer core (see Figure S4 for STEM and elemental mapping). It was clearly observed from SEM images that each particle has a depression in the shell (see Figure S5). As explained in the previous work,[16] volume shrinkage caused by difference in densities of PDMS

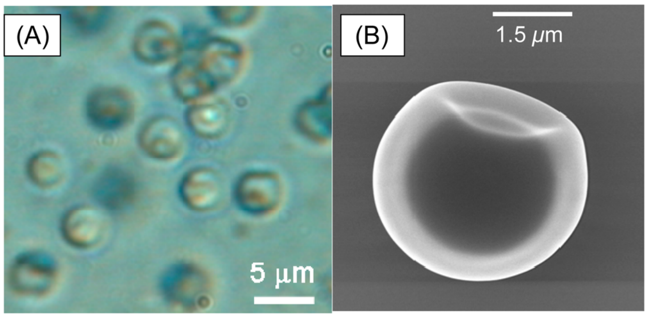

Figure 5. OM image (A) of PDMS droplets formed by MPTMS polymerization and SEM image (B) of the particles after drying the droplets of (A). The polymerization was conducted to form polymer shell at the MPTMS concentration of 16.8 mM. See Figure 1 for the amount of DMDES.

and its polymerized product might generate the depression on the shell during the shell formation process.

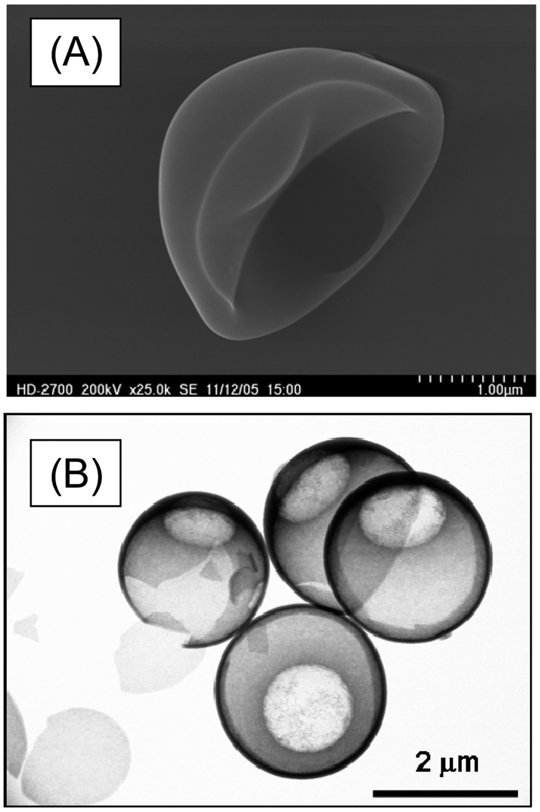

Figure 6. SEM image (A) of a particle obtained by extraction of silicone oil from the PDMS droplets shown in Figure 5A and TEM image of the shells taken after calcining the particles of Figure 5A.

Since the shell is elastic, the silicone oil in the PDMS droplets can be extracted without breaking the shell. Figure 6A shows a particle image taken with STEM after extraction with ethanol. The shell shape was transformed into a hemispherical bowl with a protrusion that elemental analysis identified to be the polymer core. This transformation indicates permeability of the shell.

Figure 6B shows an STEM image of the shells taken after calcination of the emulsion of Figure 5A. Each shell had a hole-like structure that probably formed from the thin layer resulting from the attachment of the polymer core during the shell formation. The PSt/PDMS particles (Figures 5B and S5) had smoothly deformed surfaces without any holes. In addition to this, the deformation of the shells in water and in air (Figures 5A and 6A) suggests that the whole surface of the PDMS droplets was completely surrounded with an organo-silica shell.

■ CONCLUSIONS

Polymerization inside monodisperse PDMS oil droplets was used successfully to control the morphologies of polymer particles formed within these droplets. The monomers were first absorbed by the droplets and then polymerized using an oil-soluble initiator. Polymerization of St led to the formation of spherical PSt particles with low polydispersity. On the other hand, copolymerization of styrene with AA or NaSS deformed the spherical particles to lens-like or disk-like, respectively, due to their being attached to the PDMS/water interface. Introduction of cross-linking by copolymerization with divinylbenzene formed hemispherical polymer particles. A second polymerization, using 3-methacryloxypropyltrimethoxysilane with a water-soluble initiator, was able to form polymer shells onto the PDMS droplets containing a PSt particle. When the oil component of PDMS inside the polymeric shell was extracted with ethanol, hemispherical polymeric capsules having a protrusion inside were obtained. The diverse shapes of polymeric particles indicate that the silicone oil droplets are useful mini-reactors for controlling the morphology of polymer particles, as well as forming polymeric shells surrounding them.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The effects of DVD and SDS concentrations on particle morphology are shown in the Supporting Information. Elemental mapping and SEM image of particles in Figure 5A are also presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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