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Synthesis of snowman-shaped microparticles by monomer swelling and polymerization of crosslinked seed particles

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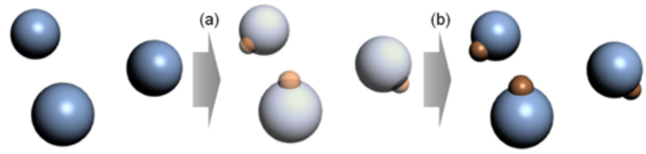
Abstract−Nonspherical snowman-shaped micro-sized particles were synthesized via monomer swelling and the polymerization of crosslinked seed particles. Monodispersed crosslinked polystyrene microspheres and methylmethacrylate were used as seed particles and the swelling monomer, respectively. Methylmethacrylate (MMA) induced crosslinked polystyrene microparticle swelling; however, compared to polystyrene, MMA is relatively hydrophilic. As a result, phase separation was observed, resulting in monomer-swollen, cross-linked particles protruding from the surface of the seed particles. By changing the monomer-to-particle weight ratio from 4 to 8, the ratio of the size of the head to the body of the snowman-shaped particles was varied from 0.3 to 0.7. The morphologies of the snowman-shaped particles were predicted using *Surface Evolver* software, and the simulation was applied to show the unique self-organization morphologies of snowman-shaped particles.



We synthesized snowman-shaped microparticles by swelling and polymerizing cross-linked PS seed particles with methylmethacrylate. The monomer-swollen, cross-linked particles exhibited protrusions from the surface of the microparticles due to the phase separation of seeds from the particles. The size of the protrusion or head of the snowman-shaped particles was controlled by changing the monomer-to-particle weight ratio during the swelling process. Simulations were applied to estimate the aspect ratio of snowman-shaped particles and their self-assembled morphologies.

Key words: Swelling, Seeded Polymerization, Nonspherical Particles

INTRODUCTION

The synthesis of polymeric particles has attracted a considerable amount of attention in industrial and scientific applications such as painting, adhesives, suspension rheology, drug delivery systems, colloidal masks, colloidal self-assembly, and photonic bandgap materials [1-5]. Thus far, a number of methods utilizing mini-emulsions or emulsions in the presence or absence of emulsifiers have been developed for the production of aqueous submicron-sized latex particles [6,7]. In particular, dispersion polymerization has been successfully adopted to synthesize micron-sized particles dispersed in organic media [8]. However, emulsion or dispersion polymerization is limited to the fabrication of polymeric particles with spherical morphologies; thus, to conduct research on complex fluid systems, other synthetic routes must be evaluated to obtain nonspherical particles.

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Several researchers have developed fabrication methods for the synthesis of nonspherical particles from spherical particles using physical or chemical techniques. For instance, spherical latex particles embedded in polymeric films have been stretched to obtain ellipsoidal particles [9] or dry etched to generate oblate spheroids [10]. However, the yields of these methods are relatively low because the aforementioned approaches cannot be used in the absence of film-type systems. Recently, a significant amount of research has been devoted to the generation of colloidal aggregates with exotic shapes other than spherical morphologies via the self-organization of polymeric microspheres inside shrinking droplets [12-14]. However, with this approach, additional processes are required to fractionate nonspherical colloidal aggregates according to their shape and the number of constituting particles. Alternatively, chemical synthetic routes for the synthesis of nonspherical particles have been developed. Namely, monomer swelling and seeded polymerization have been used to construct snowman-shaped particles [16-19]. These chemical synthetic routes present several advantages over physical methods. For instance, the fractionation of particles according to shape is not required, and nonspherical particles can be synthesized in relatively large quantities.

Seeded polymerization has been widely adopted for the synthesis of asymmetric snowman-shaped particles with controllable morphologies and compositions. For instance, crosslinked polystyrene seed particles have been used to obtain ice cream cone-shaped nonspherical particles through successive seeded polymerization [18], and polymerizable inorganic monomers have been utilized for the synthesis of organic-inorganic hybrid doublet particles [21]. Snowman-shaped particles synthesized by seeded polymerization have been successfully used as colloidal surfactants or building blocks for colloidal crystal films [19,20]. Despite these advances, the fabrication of snowman-shaped particles with various aspect ratios and polymeric compositions for use in colloid and emulsion technologies has not yet been studied. Nor has the experimental and theoretical structure of snowman-shaped particles as a function of the amount of monomer used during swelling yet been clarified.

Here, we report a method for the preparation of snowman-shaped nonspherical microparticles composed of a crosslinked polystyrene (CPS) body and a polymerized methylmethacrylate (MMA) head. We also investigated the swelling morphologies of CPS seed particles in the presence of MMA and their polymerized structures. In particular, the amount of polymerized MMA protruding from the seed particle surface was controlled by changing the concentration of the swelling monomer. The generation of snowman-shaped particles was also simulated via *Surface Evolver* software. These snowman-shaped particles were applied as building blocks for self-assembly. With the simulation tool, we also estimated a unique self-assembly of snowman-shaped particles during evaporation.

EXPERIMENTAL

1. Materials

CPS particles were purchased from Magsphere Inc. (1.88 μm in diameter, 5% divinyl benzene, lot number: PS/DVB2559A). Methylmethacrylate (MMA, 99%), sodium dodecyl sulfate (99%), 2,2′-azobis (2-methylpropionitrile) (AIBN, 98%), and sodium nitrate ($NaNO_3$, 99%) were purchased from Aldrich and were used as received without further purification. Pluronic F108 [$(PEG)_{129}$-$(PPG)_{43}$-$(PEG)_{129}$] was obtained from BASF.

2. Swelling of CPS Seed Particles with MMA

The concentration of CPS seed particles was adjusted to 1 wt% by adding DI water, and either 0.8 wt% sodium dodecyl sulfate (SDS) or 1.8 wt% Pluronic F108 [$(PEG)_{129}$-$(PPG)_{43}$-$(PEG)_{129}$, BASF] was added to stabilize the particles. The swelling of CPS particles was achieved by adding suitable amounts of MMA and vigorously stirring the resulting solution for at least one day.

3. Polymerization of MMA-swollen CPS Particles

Monomer-swollen CPS particles were combined with 0.2 mL of a sodium nitrate solution (1.25 wt%) under vigorous stirring and were heated at 80 °C. Sodium nitrate was used to suppress solution phase polymerization, which results in the generation of unnecessary secondary nuclei. Subsequently, 0.025 mL of AIBN, an oil-soluble initiator, was dissolved in the monomer (2 wt%) and was added to the reactor to polymerize MMA present in the swollen particles. Typically, the polymerization was conducted for one day. The final snowman-shaped particles were washed by centrifugation at 3,000 *g* for 10 minutes and were redispersed in fresh water.

4. Surface Evolver Simulations

The morphologies of snowman-shaped particles were simulated via *Surface Evolver*, which models interfaces shaped by surface tension and other energies by minimizing the total energy of the surfaces under various constraints [22-24]. The solid seed particles were modeled as liquid droplets with high surface tensions to fix their spherical shapes, and monomer droplets protruding from the seed particles were modeled as liquid droplets bound to solid particles at a fixed contact angle of 95°. The volume of monomer in the snowman-shaped particles was varied to compare the morphologies of snowman-shaped microparticles.

To simulate the self-organization of snowman-shaped particles inside the droplets, two differently sized solid particles with attached morphologies were bound to the surface of the main liquid droplet in the initial modeling step. Because the size of the main droplet decreased after each calculation, energetically stable equilibrium configurations of the doublet particle aggregates were obtained by iterative calculations until the main liquid droplet was depleted.

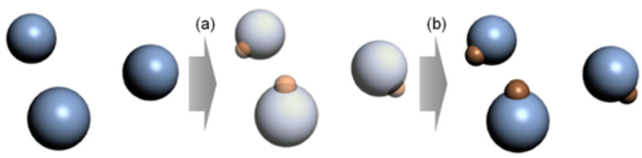
5. Characterization

MMA-swollen CPS particles and their polymerized structures were observed with an optical (Nikon TE2000-U) and scanning electron microscope (Hitachi 3500N), respectively.

RESULTS AND DISCUSSION

Scheme 1 describes the seeded emulsion polymerization of crosslinked seed particles swollen by monomer for the synthesis of nonspherical snowman-shaped microparticles. CPS particles were used as seed particles, and swelling was induced by MMA. The monomer and seed particles were incompatible during the monomer swelling process, resulting in phase separation and the hemispherical protrusion of monomer-swollen, cross-linked particles from the surface of seed particles. This protrusion was solidified by seeded polymerization, and snowman-shaped particles were produced. An oil-soluble initiator was required to achieve seeded polymerization. For comparison, a water soluble initiator was used to obtain the core-shell morphology of the seed and polymerized swollen monomers [25].

The mechanism of snowman-shaped particles synthesis by seeded polymerization can be explained by thermodynamics. The contribution of the chemical potential of the monomer in the particle phase, $\Delta G_{m,P}$, is equal to the sum of the monomer-polymer particle mixing force (ΔG_m), the elastic retractile force of the crosslinked particle network (ΔG_{el}), and the interfacial tension between the particle and dispersion medium (ΔG_t). Thus, $\Delta G_{m,P}$ can be expressed as the summation of the aforementioned terms in the following equation [14]:



Scheme 1. Schematic depiction of the generation of snowman-shaped particles by (a) monomer swelling and (b) polymerization.

$$\Delta G_{m,P}=\Delta G_m+\Delta G_{el}+\Delta G_t$$

To obtain a phase-separated protrusion from the monomer-swollen particles and to expel monomers from the particle surface, $\Delta G_{m,P}$ must be positive. Typically, ΔG_{el} and ΔG_t make positive contributions to the chemical potential in the particle phase, whereas ΔG_m makes negative contributions. Thus, monomers that are incompatible with seed particles (for ΔG_m) display sufficient cross-linking density (for ΔG_{el}) with the dispersion medium and possess high surface tensions must be used (for ΔG_t). In the present study, the relative energy difference (RED) of MMA and PS during mixing was 0.9 [26]. Although this criterion implies miscibility, the RED is close to 1, so MMA and PS are not highly miscible. Water, which has a higher surface tension than organic solvents, was used as a dispersion medium. Thus, we can expect sufficient phase separation during swelling and polymerization, resulting in the synthesis of snowman-shaped particles.

Fig. 1(a) displays an optical microscope image of MMA-swollen CPS particles dispersed in water. During the synthesis of the particles shown in the figure, MMA was added to a dispersion of CPS at a weight ratio of MMA to CPS of 6.3, and the swelling time was set to 17.5 hours. Fig. 1(b) displays an SEM image of the resultant snowman-shaped particles after polymerization. The morphology and size of the protruded head before and after polymerization are similar. We also investigated the morphology of the particles as a function of the polymerization time (at 80 °C), as shown in the optical microscope images of Fig. 1(c), (d). After swelling with MMA at a weight ratio of MMA to CPS of 9.1 and polymerizing for 6 and 21 hours, the snowman-shaped particles displayed similar head-to-body aspect ratios (0.65 for 6 hours and 0.70 for 21 hours) and morphologies, suggesting that the growth of the PMMA head from the seed particles occurred predominantly in the swelling step rather than polymerization step.

Protrusion growth during the polymerization of CPS particles swollen by styrene is shown in **Fig. S1**. As shown in the figure, the polymerization of styrene induced greater phase separation from the seed particles than that of MMA due to the relatively high elastic force in the crosslinking networks of seed particles at high temperatures [20]. Namely, the elastic retractile force of cross-linked networks inside the seed particles promoted the generation of monomer protrusions from the particles. MMA is more hydrophilic than styrene; thus, MMA and CPS seed particles were less miscible than styrene and CPS. As a result, the phase separation of MMA from PS seed particles was insufficient, and less phase separation occurred during polymerization.

The amount of MMA used in the swelling step was varied to control the size of the protruded head. The weight ratio of MMA to CPS seed particles was set to 4.2, 6.3, and 8.2. Fig. 2(a) shows SEM images of polymerized MMA protrusions from CPS particles at various weight ratios. Fig. 2(c) shows the relationship between the amount of monomer and the size of the protrusions. Specifically, the size of the head of the snowman-shaped microparticles increased proportionally as the monomer concentration increased, and the ratio of the diameter of the head to the body of snowman-shaped parti-

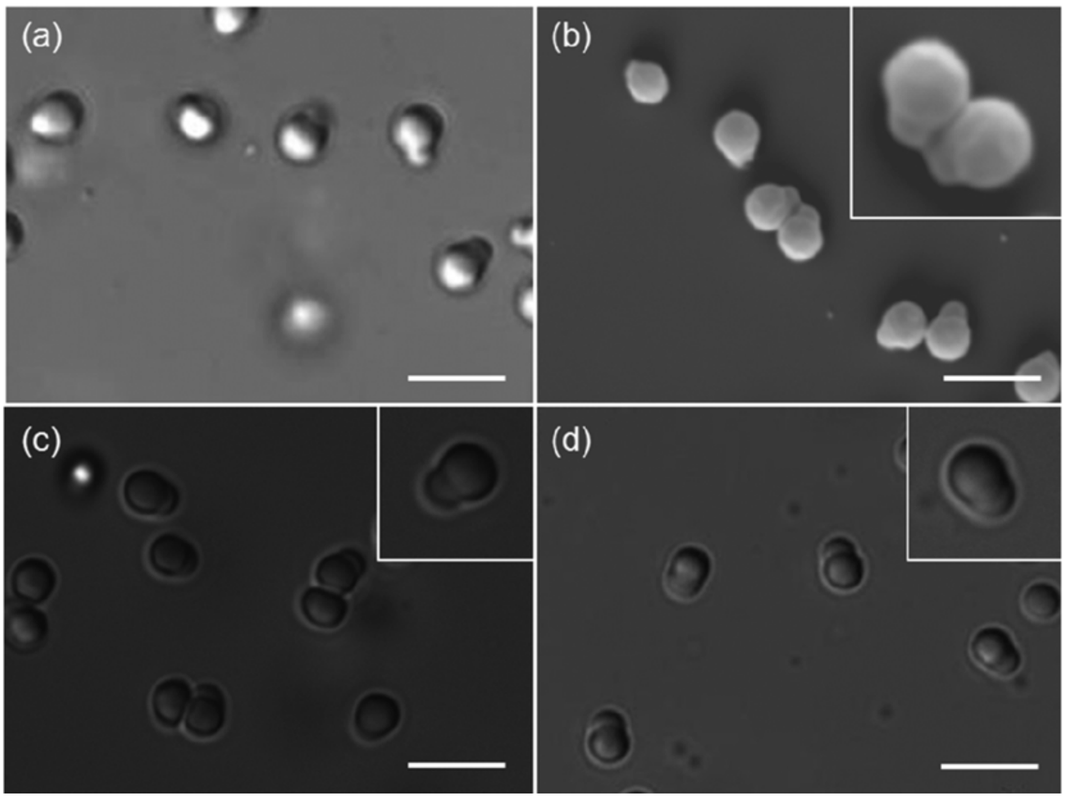


Fig. 1. (a) Optical microscope image of CPS particles swollen with MMA (scale bar: 2 μm), (b) SEM image of polymerized CPS particles after swelling with MMA (scale bar: 5 μm). Optical microscope images of polymerized monomer in swollen CPS particles after different polymerization times; (c) 6 hours and (d) 21 hours (scale bar for (c) and (d): 5 μm).

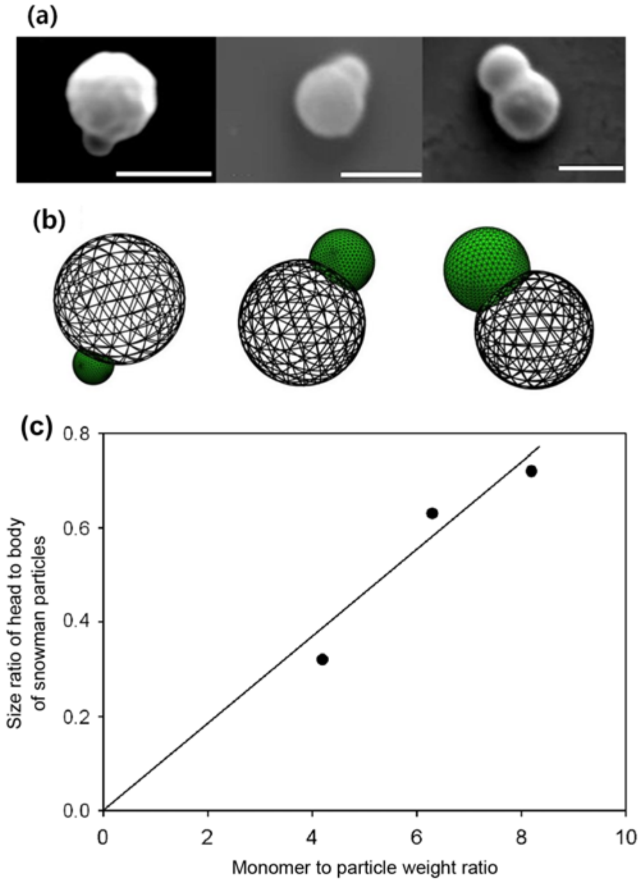


Fig. 2. (a) SEM images of polymerized CPS particles after swelling with MMA at different monomer concentrations. The weight ratio of monomer to particle was 4.2 (left), 6.3 (center), and 8.2 (right), respectively (scale bar: 2 μm). (b) Surface Evolver simulation of snowman-shaped particles as a function of volumetric amount of monomer. The contact angle of monomer on the surface of seed particle was fixed at 95°. (c) The size ratio of the head to body of snowman-shaped particles as a function of the monomer-to-particle weight ratio.

cles could be controlled at 0.3 to 0.7. As shown in Fig. 2(b), we simulated the morphologies of snowman-shaped particles with *Surface Evolver*. During the simulation, the contact angle between the liquid monomer droplets and the solid seed particles was fixed at 95°, and the volume of the droplets was varied as a function of the seed particle volume. The energetically favorable equilibrium configurations of the snowman-shaped particles were almost identical to those of the snowman-shaped particles shown in Fig. 2(a).

Fig. 3 displays an SEM image of aggregated snowman-shaped particles obtained by centrifuging a suspension of nonspherical particles. Unlike the self-assembled spherical colloids, the particles were packed in a somewhat random fashion [3] due to the shape anisotropy of snowman-shaped particles. This result implies that the regular packing of particles can only be achieved through sophisticated means such as guided assembly inside confined geometries such as emulsions or aerosols.

As shown in Fig. 4, we simulated the self-assembled morphologies of a finite number of snowman-shaped particles. Nonspherical

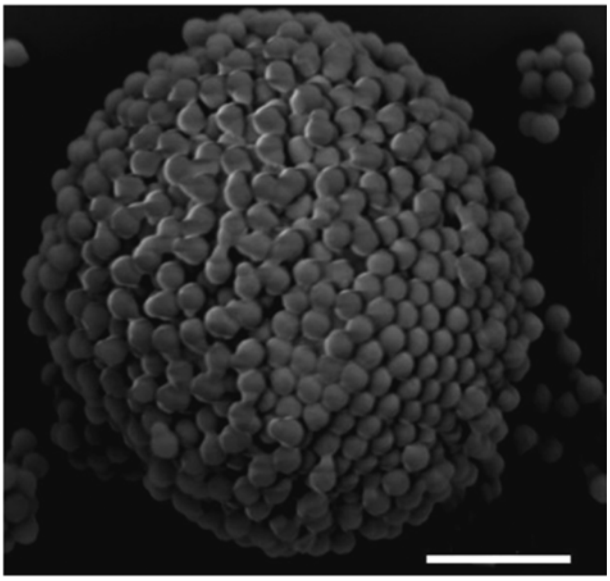


Fig. 3. SEM image of self-assembled snowman-shaped particles (scale bar: 10 μm).

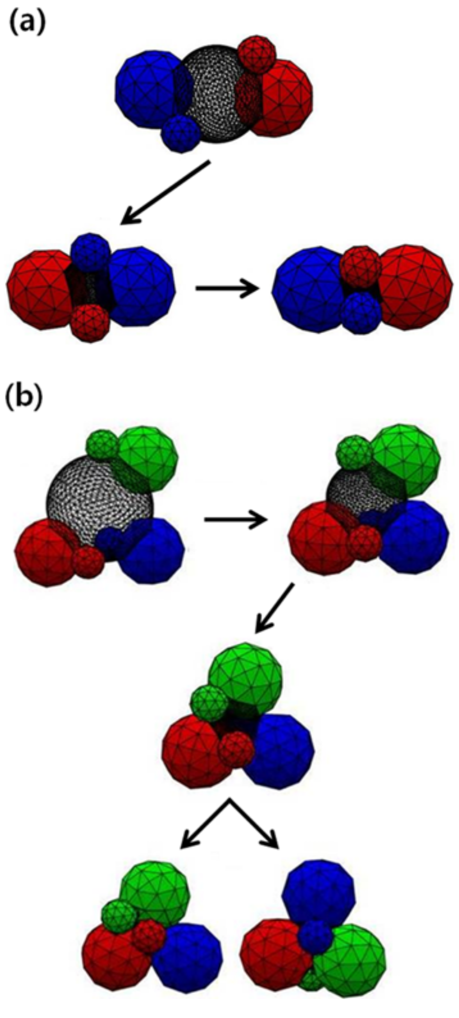


Fig. 4. Surface Evolver simulations of self-organized snowman-shaped particles inside a droplet: (a) two snowman-shaped particles and (b) three snowman-shaped particles.

particles were modeled as snowman-shaped doublets with two different-sized solid particles, and the doublet particles were considered to be bound to the surface of the main evaporating droplet. Rather than the random packing shown in Fig. 3, regular bimodal clusters were observed (Fig. 4). The size of the main droplet decreased during the iterative calculations, and the final equilibrium configuration of aggregates with two and three doublets are shown in Fig. 4(a) and Fig. 4(b), respectively. The final and energetically stable morphology of the aggregate containing two doublets possessed a unique structure, as shown in Fig. 4(a). Alternatively, two different isomeric structures were obtained for aggregates with three doublets (Fig. 4(b)). The experimental realization of the self-organization of nonspherical particles will be the topic of future research.

SUMMARY AND CONCLUSIONS

The synthesis of snowman-shaped nonspherical microparticles was studied using crosslinked PS seed particles swollen by MMA during seeded polymerization. The phase separation of MMA from swollen seed particles generated small protrusions from the particle surface, and subsequent polymerization resulted in the solidification of protruded monomers. Compared to styrene, which showed protrusion growth during polymerization, MMA protrusions presented similar sizes before and after polymerization due to the incompatibility of MMA and CPS seed particles during swelling. Moreover, the head-to-body aspect ratio of snowman-shaped particles was controlled by changing the monomer used during swelling and the ratio was increased from 0.3 to 0.7 as increasing the amount of monomer. The morphologies of snowman-shaped particles with different amount of monomers were predicted using *Surface Evolver*. The protruded distance and aspect ratio of calculated structures were similar to those of the synthesized snowman-shaped particles. Finally, the snowman-shaped particles were applied as building blocks for self-assembly, resulting in a rather random packing with less orderedness. However, the self-assembly of small number of snowman-shaped particles obtained unique packing symmetries.

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SUPPORTING INFORMATION

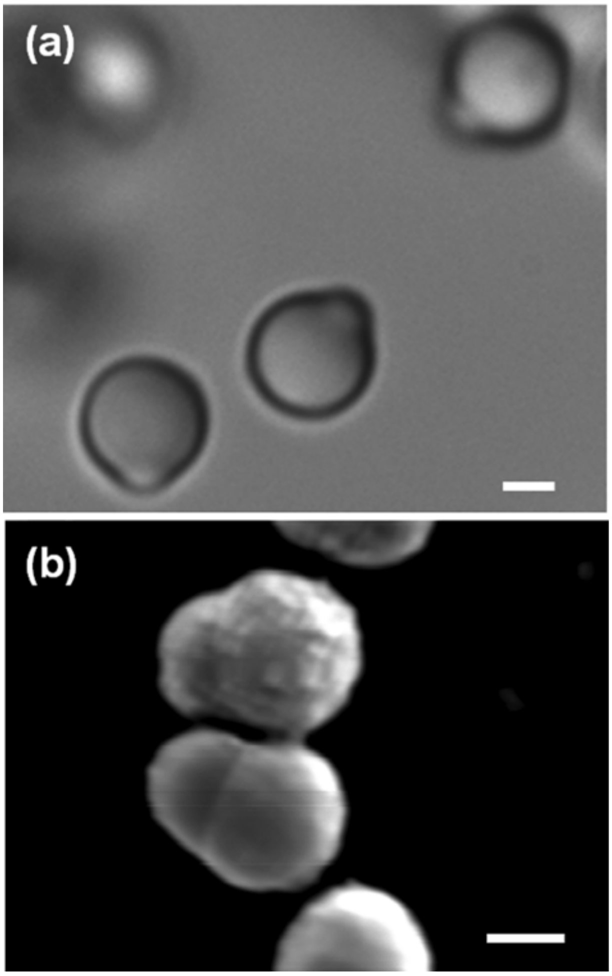

Fig. S1. Optical microscope image of CPS particles swollen by styrene monomer (the weight ratio of monomer to particle was equal to 8.4) (b) SEM image of polymerized swollen CPS particles (Scale bar: 1 μm).