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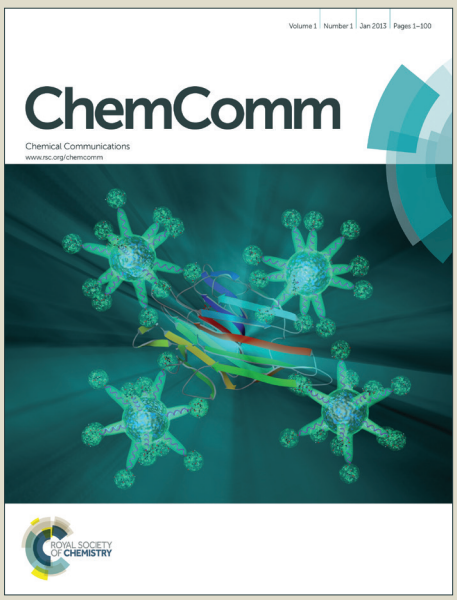

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One-step Synthesis of "Rattle-like" Polymer Particles via Suspension Polymerization

Cite this: DOI: 10.1039/x0xx00000x

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Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

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Multiple polymer particles encapsulated in a polymer shell are applied in electrophoretic ink. We demonstrated a simple one-step polymerization of polymer capsules containing small particles (Rattle-like particles). In the obtained capsules, encapsulated particles independently dispersed and moved in response to the electric field.

Microcapsules have been applied in many industrial fields; many researchers have investigated and proposed encapsulation techniques such as *in-situ* polymerization[1-3] microfluidic conjunction, interfacial polycondensation[4, 5], usage of template materials[6-9] including the layer-by-layer method[10], and solvent-evaporation[11]. Recently, the encapsulation of one or more small particles[12, 13], micelles[14, 15], or capsules[16-19] within larger shells has attracted increasing attention as electrophoretic ink for displays[20], catalysts, and sensor materials. Moreover, these multiple particles in a shell have the potential to be used as vibro-isolating and sound absorption materials[21] because the energy of the incoming sound is converted into that of the motion of the smaller encapsulated particles. The capsules containing small particles are typically prepared using a template-assisted method. The core particles are doubly coated with different materials using the layer-by-layer method[17], grafting-from polymerization[12], seeded emulsion polymerization[22], sol-gel process[23, 24] or crystal growth[25], and then the inner shell is selectively removed using a solvent or by calcination. The number of shells is determined by the number of coating layers[26]. Encapsulation has also been achieved using droplets prepared via the mechanical mixing of a dispersion of small particles[27,28]. In addition, double polymersomes containing several inner polymersomes were prepared using a microfluidic conjunction approach in which the inner material was not solid particles but vesicles[29,30]. Pinkhassik et al. have reported synthesis of nanorattle particles by simultaneous formation (one-step) of nano polymer capsules and entrapped metal nanoparticles with irradiation of UV of vesicle-template[31,32]. However, the almost all of avobe preparation methods for capsule with multiple particles involve multistep processes.

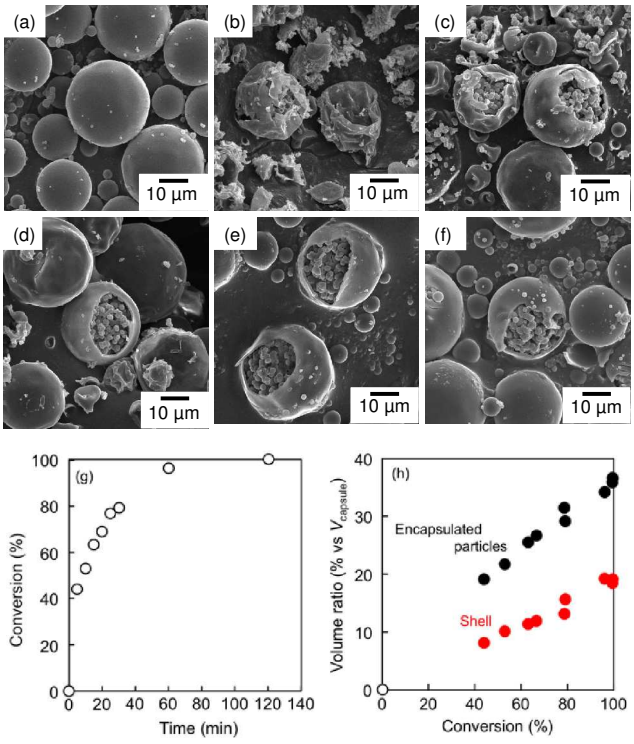

Fig. 1 ***a–f*** Scanning microscopy (SEM) photographs of PEGDM/PS particles (approximately 25 μm) at various conversions during suspension polymerization of EGDM/LC/PS (1/1/0.1, w/w/w) droplets prepared using a homogenizer. ***b–f***: The shells were fractured to observe the particles inside. Conversion (%): (a) 100, (b) 44, (c) 63, (d) 69, (e) 79, and (f) 100. ***g***: conversion vs time curve for the suspension polymerization, ***h***: volume fraction of PEGDM in the shell (red circles) and encapsulated particles (black circles) of capsules as a function of the conversion.

We have proposed an original preparation method of hollow polymer particles as suspension polymerization by using the self-assembling of phase separated polymer (SaPSeP) method[33,34] and developed it into a useful encapsulation technique[35,36]. In the study for the encapsulation of a liquid crystal (LC), we serendipitously discovered the formation of capsules containing small, closely packed particles during a suspension polymerization using the SaPSeP method. Herein, we propose the preparation of capsules containing small particles (Rattle-like particles) using a "one-step" suspension polymerization process and clarify the mechanism of capsule formation.

First, as shown in Fig. 1a–f, we investigated the detailed polymerization behavior of suspension polymerization: monomer droplets were prepared by dispersing EGDM (2.0 g), LC (2.0 g), polystyrene (PS, 0.2 g), and BPO (0.08 g) in an aqueous solution of 0.8 wt% poly(vinyl alcohol) using a homogenizer. The polymerizations were performed at 70 °C for 3 h under a nitrogen atmosphere in sealed glass tubes, which were shaken horizontally at 80 cycles/min (3-cm strokes). The LC used was E-7, which is a mixture of 4′-*n*-pentyl-4-cyanobiphenyl (51 wt%), 4′-*n*-heptyl-4-cyanobiphenyl (25 wt%), 4′-*n*-octoxy-4-cyanobiphenyl (16 wt%), and 4′-*n*-pentyl-4-cyanoterphenyl (8 wt%). PS was used as an accelerator for the phase separation of the poly(EGDM) (PEGDM) chains (microgels) that were dissolved in the droplets, which was crucial to form the PEGDM capsule shell. The polymerization smoothly proceeded with nearly 100% conversion, which was achieved within 120 min as shown in Fig. 1g.

Fig. 1a shows that the PEGDM particles at 100% conversion (approximately 25 μm in size) had smooth but slightly distorted surfaces. To observe the inner structure of the obtained particles by scanning electron microscopy (SEM), portions of the capsule shells were fractured by rubbing with a spatula after drying on an aluminum plate (Fig. 1f). The obtained capsules had a thin shell and were fully packed with many small particles. These encapsulated particles were partially coagulated and were nonspherical with a diameter of approximately 2 μm.

To clarify the mechanism of the formation of the encapsulated particles, capsules obtained at various levels of conversion were fractured, and the enclosed particles were evaluated using SEM. By observing the SEM images (Fig. 1b–f), it was found that the encapsulated particles formed at an early stage of the suspension polymerization process, and that both shell thickness and the diameter of the encapsulated particles appeared to increase with the conversion. To quantify this trend, the volume fraction of the encapsulated particles was calculated from the diameter and shell thickness of the encapsulated particles at various conversion levels, as shown in Fig. 1b–f, in which only particles with diameters of approximately 25 μm were measured. The volume fractions of both shell and encapsulated particles gently increased with the conversion as shown in Fig. 1h, i.e., the formation of the PEGDM shell and the encapsulated particles occurred competitively.

Next, to confirm the composition of the encapsulated particles, the fractured particles (polymer shells and encapsulated particles) were washed with tetrahydrofuran (THF) to remove any PS that precipitated from the droplets as the polymerization proceeded because of its insolubility in the LC. The morphologies of the encapsulated particles were not changed before (Fig. 2a) and after (Fig. 2b) the removal of PS, although the boundaries between the small particles became clearer, indicating that the encapsulated particles consisted of PEGDM. It is thought that as the polymerization proceeded, the precipitated PS inside the droplets adhered to the surface of the encapsulated particles, leading to their coagulation. It should also be noted that the washed encapsulated particles (Fig. 2b) were very similar size and shape to PEGDM particles prepared via the precipitation polymerization of EGDM in solution system under the similar conditions to Fig.1 (Fig. 2c). In precipitation polymerization, particle size should be depend on the critical chain length (the phase-separation behavior) of growing polymer chain from the continuous medium[37]. Because the compositions of inside the droplet and solution were same, obtained particles via precipitation polymerization would be similar size. In fact, when the EGDM content increased, the size of encapsulated particles increased (no image). These results indicate that the encapsulated particles were formed inside the EGDM/LC/PS droplets via the precipitation polymerization of EGDM simultaneously with the formation of the shell.

Considering the mechanism of the SaPSeP method, it is assumed that as the polymerization proceeds, the PEGDM chains (microgels) precipitate in the droplets because of cross-linking reactions. They then diffuse and adsorb onto the inner interface of the droplets to decrease the interfacial tension. As they gradually pile up at the inner interface, the formation of the cross-linked PEGDM shell occurs. At the same time, however, because the diffusion of the precipitated microgels inside the droplet to the inner interface is difficult due to the high viscosity of the LC, some of the PEGDM microgels form particles that are encapsulated in the shell.

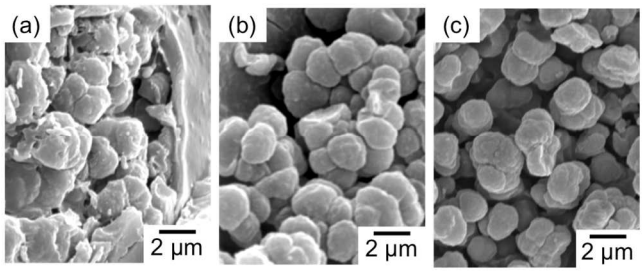

Fig. 2 Scanning electron microscopy (SEM) photographs of the fractured PEGDM/PS particles prepared via suspension polymerization of EGDM/LC/PS (1/1/0.1, w/w/w) droplets (a) before and (b) after the removal of PS with THF, and (c) PEGDM particles prepared via precipitation polymerization of an EGDM/PS/LC solution with a composition similar to that in the droplets

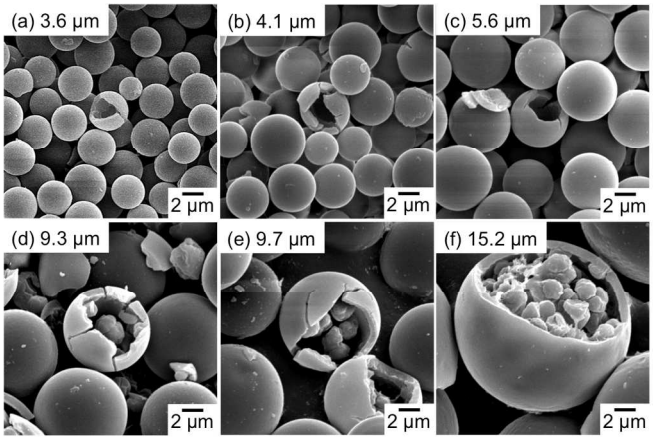

Fig. 3 Scanning electron microscopy (SEM) photographs of the fractured PEGDM/PS particles prepared via suspension polymerization of EGDM/LC/PS (1/1/0.1, w/w/w) droplets with various diameters (d_n) prepared using the Shirasu porous glass (SPG) membrane emulsification technique. d_n (μm): (a) 3.6, (b) 4.1, (c) 5.6, (d) 9.3, (e) 9.7, and (f) 15.2.

If the mechanism described above is correct, then the formation of the polymer shell and the encapsulated particles should be influenced by the distance of the microgels that must diffuse to reach the interface, which can be controlled by changing the diameter of the droplets. Therefore, to clarify the mechanism of the formation of the encapsulated particles, suspension polymerizations were conducted using monodispersed droplets with various diameters prepared using the Shirasu porous glass (SPG) method.

Fig. 3 shows the SEM photographs of fractured PEGDM/PS particles prepared via suspension polymerization of EGDM/LC/PS (1/1/0.1, w/w/w) droplets with various average diameters (d_n) prepared using the SPG membrane emulsification technique. When droplets with d_n < 5.6 μm were used, hollow polymer particles without any encapsulated particles were observed, while hollow particles with encapsulated smaller particles were obtained when droplets with d_n > 9.3 μm were employed. In addition, the number of encapsulated particles increased with the diameter of the droplets, but the size (approximately 2 μm) and morphology of the encapsulated particles remained nearly the same for all the droplet sizes, which would be based on the same nucleation conditions of precipitation polymerization inside the droplet as described above[37].

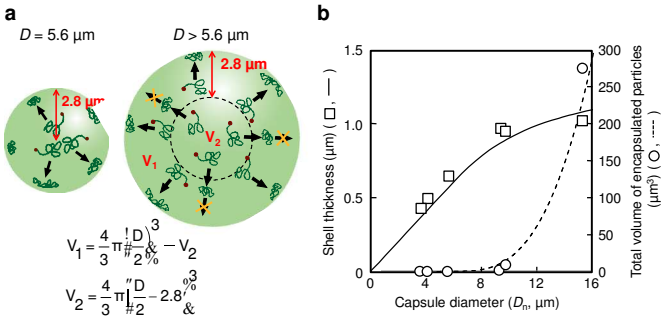

Fig. 4 ***a*** Proposed mechanism of the formation of capsules with encapsulated particles. ***b*** Calculated (solid line) and measured (squares) shell thicknesses, and the total volume of the encapsulated particles calculated using V_2 (dotted line) and using the measured shell thicknesses (circles) for various capsule particle sizes.

On the basis of these results, it can be concluded as indicated in following Fig. 4a that the EGDM microgels can diffuse at least for a distance of 2.8 μm, which corresponds to the radius of the 5.6-μm sized droplets, in which all the precipitated microgels diffused to the interface and formed the shell, resulting in the synthesis of hollow particles without any encapsulated particles as shown in Fig. 3. Conversely, for droplets greater than 5.6 μm in diameter, the microgels that precipitate at sites less than 2.8 μm from the interface (area V_1 in Fig. 4a) diffuse to the interface and form the shell, while the microgels that precipitate at the center of the droplets (area V_2 in Fig. 4a) cannot reach the interface and form encapsulated particles. To confirm this prediction, the calculated and experimental values of shell thickness and total volume of encapsulated particles were compared. The predicted shell thicknesses and volumes of the encapsulated particles were calculated on the basis of the amount of monomer expected to be present in the areas V_1 and V_2, respectively.

Fig. 4b shows the calculated (solid line) and measured (squares) shell thicknesses and the calculated total volume of the encapsulated particles using the area V_2 (dotted line) and the measured shell thicknesses (circles) at various diameters of capsule particles. Fortunately, the exprimental values of both shell thickness and total volume of the encapsulated particles were in very good agreement with the calculated values. Because of these results, the mechanism of the formation of the encapsulated particles is proposed as follows: the phase-separated microgels in the droplets, which propagate during diffusion toward the droplet interface, lose their mobility and precipitate, leading to precipitation polymerization inside the droplets. Thus, the formation of the polymer shells (suspension polymerization via the SaPSeP method) and precipitation polymerization proceed competitively (Fig. 1). Notably, with this mechanism it is possible to control the number, volume, and diameter of the encapsulated particles by changing the polymerization conditions.

As mentioned in the introduction, these "rattle-like" particles are receiving attention as electric ink or vibro-isolating materials because the encapsulated particles aremovable independently in the hollow particles. However, as shown in Fig. 3, the encapsulated particles prepared using the current system were coagulated by the PS and their motion was restricted. Therefore, on the basis of a previous study based on the SaPSeP method[22], to increase the motion of the particles, *n*-hexadecane (HD) and toluene were used instead of PS and LC, respectively. Consequently, in the EGDM/toluene/HD (2/1/1, w/w/w) system, simillar capsules were prepared, however, the threshold diameters of droplets which obtained the capsules with small particles, shifted to avobe 15 μm. Phase-separated PEGDM microgels could more easily diffuse in the EGDM/toluene/HD (2/1/1, w/w/w) droplets than in EGDM/LC/PS (1/1/0.1, w/w/w) droplets because of the lower viscosity of toluene and HD than that of LC and PS. The obtained capsules with encapsulated 4-6 μm particles having distorted shape, and the dispersity of the small particles in a shell was still not improved.

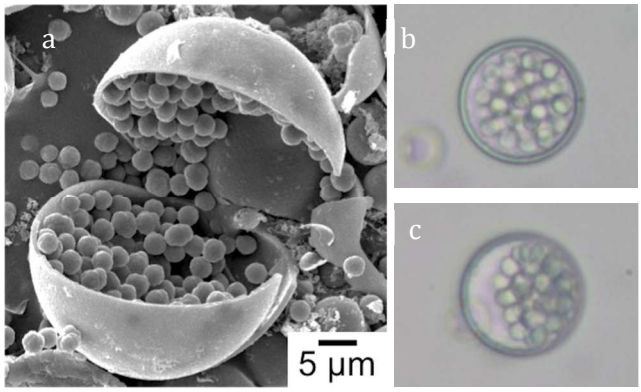

Fig. 5 Scanning electron microscopy (SEM) photographs of fractured PEGDM particles prepared via suspension polymerization of EGDM/toluene/HD (2/1/1, w/w/w) droplets containing dissolved AIBN (4 wt% based on EGDM) and VPS-0501 (5 wt% based on EGDM) prepared using a homogenizer. AIBN used instead of BPO because VPS-0501 was azo compound. The number ratio of azo group (AIBN:VPS-0501) was 1:0.04. (b, c) Optical micrographs of the rattle particles before (b) and after (c) voltage application (the right side was positive) of obtained particles on a slide-glass having electrodes fixed with a 3-mm interval by Conductive Epoxy using a direct power supply unit (50 mV was applied) .

We examined the effect of the addition of oil-soluble surfactant for the encapsulated particles in the EGDM/toluene/HD phase to increase their colloidal stability. We selected nonionic surfactants such as polyoxyethylene lauryl ether nonionic surfactant (Emulgen 105) and amino group-containing poly(dimethylsiloxane) (Silaplane FM-3321). However, the shell of obtained capsules were imperfection because surfactants prevented from forming capsule shells[38]. Next, poly(dimethylsiloxane) macroazoinitiator (VPS-0501), which can be used as initiator/oil-soluble stabilizer and would be adsorbed onto the PEGDM microgels covalently, was added as shown in Fig. 5a. The encapsulated particles were nearly spherical

and monodispersed, and had diameters of 3.3 μm. The Brownian Motion of each encapsulated particle inside the capsule was clearly observed by an optical microscope. The poly(dimethylsiloxane) groups from VPS-0501 combined to the encapsulated PEGDM particles and worked as colloidal stabilizer inside the capsule, in which the encapsulated particles should be prepeard by dispersion polymerization rather than precipitation polymerization.

Moreover, the encapsulated particles were attracted to positive charge because those had -9.1 mV of zeta potential as shown in Fig. 5b and c. The particles moved reversibly in response to the positive/negative inversion of an electrode. These "rattle-like" particles are expected to possess good properties.

Conclusions

PEGDM hollow particles containing numerous encapsulated, nonspherical PEGDM particles (approximately 2 μm in diameter) were prepared via suspension polymerization using the SaPSeP method. During polymerization, suspension polymerization using the SaPSeP method led to the formation of a polymer shell, while competitive precipitation (dispersion) polymerization resulted in the formation of encapsulated particles. The number of encapsulated particles increased with the diameter of the droplets, while the diameter and morphology of the encapsulated particles remained nearly the same for all droplet diameters. Furthermore, the encapsulated particles prepared using toluene and HD instead of LC and PS exhibited independent motion, and move in response to the electric field inside the hollow particles. Using this synthesis, the rattle-particles are prepared not only with homo-PEGDM system, but can also be prepared with the systems of copolymers and other closs-linking polymers.

Notes and references

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