Controlling the Morphology of “Rattle”-like Particles Prepared by One-step Suspension Polymerization

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Recently, the encapsulation of one or more small particles1, micelles2, or capsules3,4 within larger shells (“rattle”-like particles) has attracted increasing attention for applications such as electrophoretic ink for displays, catalysts, and vibro-isolating and sound-absorption materials. Such capsules are typically prepared using a template-assisted technique including the layer-by-layer method5, seeded emulsion polymerization, or a sol-gel process. Encapsulation has also been achieved using droplets prepared via the mechanical mixing of a dispersion of small particles and using a microfluidic conjunction approach, wherein the inner material was not solid particles but vesicles. However, these methods have the following disadvantages: multistep processes require delicate conditions and/or specific devices.

We have succeeded in synthesizing rattle-like particles (hollow polymer particles with encapsulated small particles) via a one-step process of suspension polymerization using the self-assembling phase separated polymer method. This was the preparation method proposed by Okubo et al.6 to synthesize hollow polymer particles, wherein ethylene glycol dimethacrylate (EGDM), toluene, and n-hexadecane (HD) droplets dissolve the azobisisobutyronitrile and oil-soluble stabilizer6. The obtained capsules had a thin shell and were fully packed with many small particles. During the polymerization, suspension polymerization led to the formation of a capsule shell, while competitive dispersion (precipitation) polymerization resulted in the formation of encapsulated particles. The Brownian motion of the encapsulated particles inside the capsule was observed using optical microscopy. The dispersibility of encapsulated particles inside the capsule is important in applications such as electrophoretic ink.

In this communication, to control the size and number of the encapsulated rattle-like particles, the influence of stabilizer type and content were investigated. Some types of nonionic surfactants such as polyoxyethylene lauryl ether (Emulgen 105) and poly(dimethylsiloxane) (PDM) (Silaplane FM-3321) were examined. Hollow polymer particles with encapsulated small particles were obtained. However, the dispersibility of the small particles in a shell was not improved. Moreover, the shells of the obtained capsules were imperfect because the surfactants prevented full encapsulation.

PDM macroazoinitiator VPS-0501 (Scheme 1, PDM chain length: 68) can be used as an initiator/surfactant and is covalently adsorbed onto the poly(EGDM) microgels. It was added as shown in Fig. 1. To analyze the morphology of the encapsulated particles using SEM, portions of the capsule shells were fractured after drying on an aluminum plate. The SEM micrographs show that the encapsulated particles were almost spherical and existed independently in the capsule. Those Brownian motion was clearly observed at dispersion state.

The number-averaged diameter \((d_n)\) of the encapsulated particles decreased from 4.04 \(\mu\)m to 3.13 \(\mu\)m, and the numbers of the encapsulated particles...
increased with increasing VPS-0501 content, although the particles were mono-dispersed in all systems. Comparing particles of similar size, the shell thicknesses of the capsules decreased with increasing VPS-0501 content, in other words, the total volume of encapsulated particles increased with increasing VPS-0501 content. These results indicate that the number of PEGDM nuclei at initial nucleation increased with increasing VPS-0501 content. This tendency is similar to general dispersion polymerization. These results show that the encapsulated particles should be prepared in the capsules by dispersion polymerization rather than by precipitation polymerization. Moreover, in the case of the rattle particles of Fig. 1c, the encapsulated particles were attracted to positive charge because those had -9.1 mV of zeta-potential and moved reversibly in response to the positive/negative inversion of an electrode.

To clarify the effect of the PDM chain lengths on the encapsulated particle size, suspension polymerization with VPS-1001 (whose PDMS length is almost two times that of VPS-0501) was carried out. Fig. 2 shows SEM images of the results. With increasing PDMS chain length, the $d_n$ of encapsulated particles became smaller, from about 3 μm to 1 μm, although the number of PDMS chain radicals was almost halved. Because PDMS chains from VPS-1001 provided stronger stability for initial nuclei than those from VPS-0501, the number of PEGDM nuclei at initial nucleation was increased. This result also has the same tendency as general dispersion polymerization. The $d_n$ of encapsulated particles decreased from about 2.6 μm to 1.3 μm with increasing VPS-1001 content from 2 wt% to 5 wt% based on EGDM similarly to VPS-0501 system. However, in the case of VPS-1001 (Fig. 2b), the mobility of the encapsulated particles was lower than that of VPS-0501 because the encapsulated particles were closely packed in the capsule.

It can be concluded that the size and number of encapsulated particles of rattle particles can be controlled with the addition of the PDM macroazoinitiator.

References