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Facile fabrication of hollow polystyrene nanocapsules by microemulsion polymerization†

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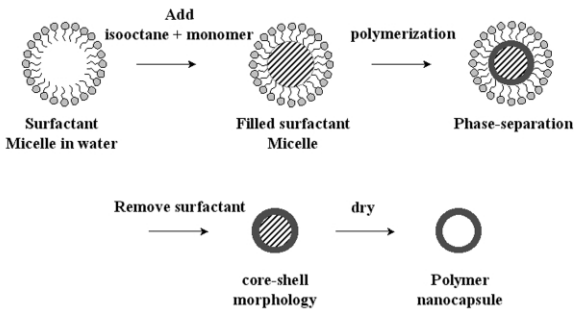
The fabrication of polymer nanocapsules with tailored dimensions has been accomplished by microemulsion polymerization using different surfactants.

Polymer nanocapsules have been used for potential applications such as nanoreactors, dye dispersants, controlled-release of drugs (DDS), cosmetics, fillers, catalysis, coatings, protection of light-sensitive components, *etc*.[1] These hollow polymer capsules have been prepared using various types of synthetic methods. The phase separation method of diblock copolymers was employed in preparing vesicular structure.[2] In addition, surface-crosslinked hollow polymeric structures were prepared by crosslinking the shell of a block copolymer micelle and subsequent degradation of the core.[3] Colloidal templating has been successfully applied to produce hollow silicate spheres.[4]

One of the facile methods for fabricating hollow polymer nanocapsules is the encapsulation of a nonsolvent using phase separation, because of the differences of interfacial tension.[5–7] This process involves polymer separation in a dispersed hydrocarbon-monomer mixture in order to make latex particles having voids with facile control of particle diameter, void fraction, and structure. Recently, microemulsion polymerization has been widely applied for the fabrication of polymer nanoparticles.[8] In the case of microemulsion polymerization, the sizes and morphologies of polymer latexes are primarily dependent upon the concentration and type of surfactants and thermodynamically stable micelles form due to the high surfactant : water ratio. However, previous work has mostly only achieved the preparation of hollow polymer nanocapsules of size greater than 100 nm. In this work, we report the fabrication of hollow polystyrene nanocapsules with dimensions of less than 20 nm using microemulsion polymerization. The size of nanocapsule polymers could be controlled by using different surfactants.

The overall synthetic procedure of hollow polymer nanocapsules is represented in Scheme 1. 2.5 g (10.3 wt%) of surfactants (cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), octyltrimethylammonium bromide (OTAB), sodium dodecyl sulfate (SDS)), 2.3 ml of methanol and 20 ml of water were mixed by high shear dispersion for 1 h in order to form micelles in the water. 4.2 ml of isooctane was added dropwise into the solution for 2 h and a mixture of 3 ml of styrene and 1 ml of divinylbenzene was added dropwise into the micelle formed solution for 2 h. Isooctane and monomer penetrated into the micelles in aqueous media and the system was heated up to 70 °C. 0.04 g of the initiator (potassium persulfate) was added into the mixed solution and the polymerization proceeded for 3 h. The separation of the polymer phase from the nonsolvent phase occurs as the polymerization proceeds. It is known that the polymerization occurs primarily at the interface between isooctane and water due to the low interfacial energy in this system.[5] In addition, the water-soluble initiator generates radicals in the aqueous phase, which are adsorbed and anchored to the dispersion.[5] Divinylbenzene (DVB) plays an important role in terms of improving stability of the polystyrene hollow nanocapsules. The residual surfactants were removed by excess methanol and the polystyrene nanocapsules filled with isooctane were dried at room temperature until the isooctane was completely removed from the polymer nanocapsules.



Scheme 1 Schematic diagram for hollow polymer nanocapsules fabrication.

The theoretical prediction of the equilibrium morphology, which is adopted by three-phase interactions, was investigated by Torza and Mason.[9] They proposed the equilibrium morphology of two immiscible liquids droplets (phase 1 and 3) suspended in a mutually immiscible liquid (phase 2). The resulting morphology is rationalized by the analysis of the interfacial tensions between the phases (γ_{12}, γ_{23}, and γ_{13}) and spreading coefficients for each phase as $S_1 = \gamma_{23} - (\gamma_{12} + \gamma_{13})$. In terms of the convention $S_1 < 0$ ($\gamma_{12} > \gamma_{23}$), phase 1 is encapsulated by phase 3 when $S_2 < 0$ and $S_3 > 0$. In our experiments, the polymer encapsulation might be limited due to the polarity difference between polystyrene and water. However, the high concentration of emulsifier and the resulting lower interfacial energy between polystyrene and water promotes the formation of core-shell morphology. Moreover, a short-chain alcohol is adsorbed mainly in the outer locus of the micelle and the penetration of alcohol brings about a screen effect that lowers interfacial tension.[8]

The formation of the polystyrene nanocapsules was investigated by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDAX). The FT-IR spectrum of the polystyrene nanocapsules is shown in Fig. 1. The band at 758 cm^{-1} results from the out-of-plane hydrogen deformation of a mono-substituted phenyl group. The peak at 698 cm^{-1} is due to the out-of-plane ring deformation for a mono-substituted phenyl group. The absorption at 3024 cm^{-1} was attributed to the aromatic C–H stretching. The peak at 1640 cm^{-1}, which is designated to the C=C stretching peak of a monomer, completely disappeared after polymerization. Judging by the spectrum, it can be deduced that the polystyrene was successfully formed.

EDAX spectra of polymer nanocapsules before and after washing (see ESI†) confirmed the removal of surfactant. The peaks at 1.0 keV and 2.3 keV were associated with Na and S, respectively and those peaks disappeared after washing.

Table 1 shows the number average diameters (D_n) of PS nanocapsules for using surfactants with different hydrocarbon

† Electronic supplementary information (ESI) available: materials and EDAX spectra. See http://www.rsc.org/suppdata/cc/b2/b201977a/

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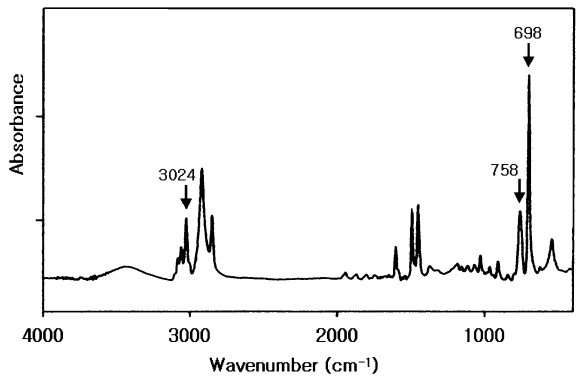

Fig. 1 FT-IR spectrum of polystyrene nanocapsules with using CTAB.

Table 1 The number average diameters (D_n) of PS nanocapsules and micelle aggregation numbers of *n*-alkyltrimethylammonium bromides

Surfactant	D_n/nm	Micelle aggregation number, n
OTAB	18.5	15[12]
DTAB	24.3	40[13]
CTAB	47.8	90[13]

chain lengths in a microemulsion polymerization. The particle diameters of PS nanocapsules were measured directly from each TEM image.‡ In a common procedure, the sizes of 100 particles were measured and the values averaged. The number average diameter (D_n) was calculated from following equation.[10]

$$D_n = \Sigma N_i D_i / \Sigma N_i$$

When the amount of water, monomer, surfactant and initiator were fixed, the number average diameter of PS nanocapsules increased with increasing the spacer group of surfactant. This result can be explained by micellar characteristics of surfactants. The micelle aggregation number (n) is the amount of surfactant needed to form a micelle and becomes smaller with shorter hydrocarbon chain lengths. It is independent of the surfactant concentration in the range expanding from critical micelle concentration to fairly high surfactant concentration. Considering the view point of micelle aggregation number, it can be assumed that surfactants with a small n form small micelles[11] and lead to latexes with smaller sizes. In addition, for the same amount of surfactant, the number of micelles increases with decreasing micelle aggregation number. The size of latexes becomes smaller due to the increase of micelles. Therefore, the size of PS nanocapsules formed in this system decreases as the surfactant with shorter hydrocarbon spacer group is used.

TEM images confirmed the hollow morphology of the polymer nanocapsules and Fig. 2 shows the PS nanocapsules using cationic surfactant (OTAB) in a microemulsion polymerization. The diameters of PS nanocapsules was *ca*. 20 nm and the shell thickness was *ca*. 3 nm.

In this work, polystyrene nanocapsules were fabricated by microemulsion polymerization and the diameters of hollow polystyrene nanocapsules were *ca*. 20 nm–50 nm. The size of polystyrene nanocapsules could be controlled using different surfactant spacers due to micellar characteristics of surfactants.

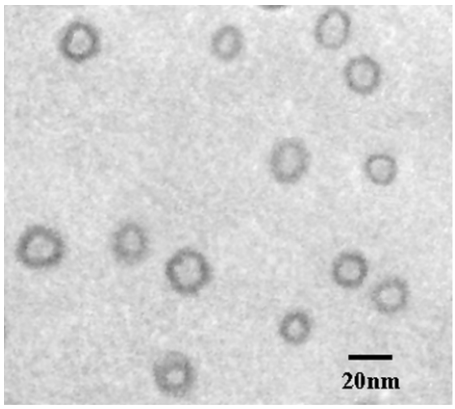

Fig. 2 Transmission electron micrograph (TEM) of polystyrene nanocapsules when using OTAB (10.3 wt%).

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Notes and references

‡ Instrumentation: IR spectra were obtained by a Bomem MB 100 FT-IR spectrometer using a transmission technique with 32 scans and a spectral resolution of 4 cm^{-1}. The images of PS nanocapsules were observed with transmission electron microscopes (JEOL JEM-200CX and JEOL JEM-2000EXII). In the sample preparation for TEM, the PS nanocapsules diluted in ethanol were cast onto a copper grid. The acceleration voltage of TEM was 200 kV. In the preparation of EDAX, a drop of a dispersed solution of PS nanocapsules in ethanol was placed onto a carbon tape. After evaporation of solvent, the dried sample was gold-coated to reduce charging effect. The acceleration voltage of EDAX was 5 kV. The energy dispersive X-ray spectrometer (JEOL JSM 5410LV) confirmed the removal of surfactant.

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