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LETTER

Hollow particles prepared by polymerizing the spontaneous vesicles of anionic maleic surfmer and cationic monomer

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Preparation of hollow spheres has attracted great interest in recent years, because of their unique properties, such as low density, large surface area and great light scattering ability. Hollow spheres have been demonstrated to be useful in many fields, e.g. opacifying agents and white pigments for ink fillers and paper coatings, additives for coatings, plastics and rubbers, drug delivery or controlled release systems and catalyst carriers, etc. [1–6]. Several strategies have been developed to prepare polymeric and inorganic hollow particles, such as osmotic swelling, water-in-oil-in-water emulsion polymerization, emulsion/phase separation procedures, self-assembly processes, spray-drying and template-synthesis methods associated with core sacrifice techniques [1–13].

Recently, it was found that hollow particles could be readily fabricated from spontaneous vesicles and liposomes formed by amphiphilic bilayers, such as mixtures of anionic and cationic surfactants (catanionics) [14, 15]. Vesicles are formed rapidly and spontaneously after cationic and anionic surfactants are mixed in aqueous solutions [16]. The structure and size of the vesicles are readily changed upon changes in solution conditions or on being mixed with organic solvents, but polymerization/crosslinking in or of the vesicles can covalently fix the vesicular structure to provide stabilized hollow colloidal particles [17–19]. However, for conventional non-polymerizable surfactants, polymerization of monomers and/or crosslinkers in the swelled vesicles induces phase separation and significant deformation of the vesicles [16]. Moreover, to isolate the polymerized hollow spheres, surfactants need to be removed by time-consuming dialysis. Furthermore, the hollow spheres can only be redispersed in water with the aid of surfactant or after chemical modification. In order to resolve these problems, vesicles prepared from polymerizable surfactants or surfmers have been developed, which shows that polymerization of the surfmers can effectively stabilize the vesicular structure [17–19].

In this study, we prepared hollow spheres from the catanionic vesicles composed of the mixture of a simple anionic surfmer, sodium dodecyl maleate hemiester (HEC12-Na), a cationic monomer methacrylatoethyl trimethyl ammonium chloride (MAETAC), a hydrophobic monomer methyl methacrylate (MMA) and a crosslinker ethylene glycol dimethacrylate (EGDMA). The chemical structures of HEC12-Na and MAETAC are presented in Fig. 1. In previous studies, the surfmers employed to prepare catanionic vesicles were the derivatives of acrylate, methacrylate or styrene and the synthesis was relatively complicated [18, 19]. In this study, the cationic monomer MAETAC is commercially available and the anionic surfmer HEC12-Na can be easily synthesized and is inexpensive. In controlled experiment, a common non-polymerizable surfactant SDS was used to prepare vesicles. The result indicates that HEC-12Na is more effective than SDS for the preparation of well-separated hollow spheres.

HEC-12Na was synthesized according to the literature [20]. After a mixture of 1 mol of maleic anhydride and 1 mol of dodecanol was heated to 80 °C for 2 h, 300 mL *n*-heptane was added and stirred for another 2 h. The product was purified by recrystallization in *n*-heptane and then neutralized by sodium hydroxide in ethanol and dried (total yield is about 73%). In order to prepare hollow particles, 3×10^{-4} mol of HEC-12Na or SDS and 7×10^{-4} mol of MAETAC was added to 10 mL of deionized water and sonicated for 30 s. Then 1.5×10^{-4} mol of

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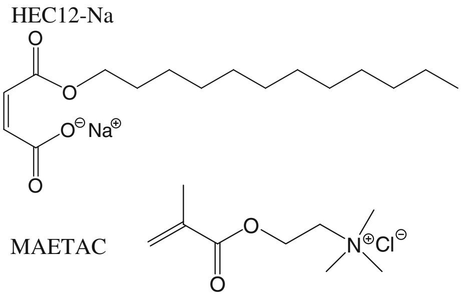

Fig. 1 Chemical structure of HEC-12Na and MAETAC

MMA, 1.5 × 10^{-4} mol of EGDMA and 0.2 × 10^{-4} mol of initiator AIBN were mixed and sonicated at room temperature for 5 min until AIBN resolved and subsequently was added to the aqueous solution of surfactant and MAETAC. The mixture was diluted to 100 mL, sonicated for 5 min, purged by nitrogen for 0.5 h and then heated to 70 °C. The polymerization was allowed to proceed for 6 h. The total yield of polymerization was 87.6%.

The morphology of the hollow spheres was observed by transmission electron microscopy (TEM, JEM-200CX, JEOL, Japan) and field emission scanning electron microscopy (FE-SEM, SIRION-100, FEI, The Netherlands). For TEM observation, a drop of the as-prepared aqueous suspension of the polymerized hollow spheres was dipped onto a copper grid covered with formvar film and observed at a voltage of 120 kV. For the FE-SEM observation, the dried powder of hollow spheres was adhered onto specimen stages by conductive tapes and sputter coated with gold. The particle size was analyzed by dynamic light scattering on a Brookhaven BI-90 plus Particle Size Analyzer (Brookhaven Instruments, USA).

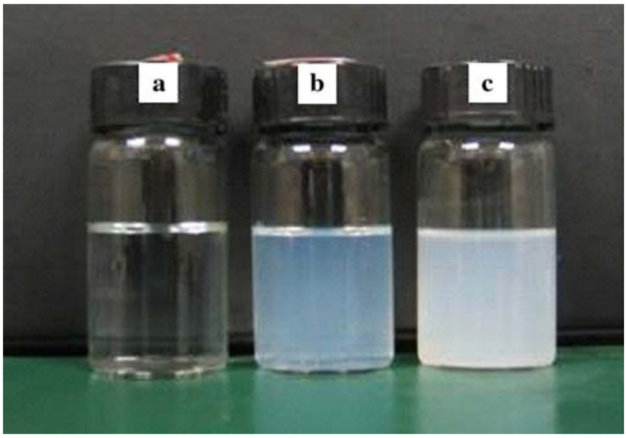

Fig. 2 Aqueous dispersion of the mixture of (**a**) 30 mM of HEC-12Na, 70 mM of MAETAC, and (**b**) 30 mM of HEC-12Na, 70 mM of MAETAC, 15 mM of EGDMA and 15 mM of MMA before and (**c**) after polymerization

The mixture of HEC-12Na and MAETAC in aqueous solution was almost clear as shown in Fig. 2a. After MMA and EGDMA were added and sonicated, the aqueous mixture became bluish (Fig. 2b), which demonstrated that the monomer and crosslinker dissolved in the catanionic vesicles of HEC-12Na and MAETAC. After being heated to 70 °C and throughout the whole polymerization process, the aqueous mixture remained stable and bluish, and precipitation or phase separation was not observed in the resultant aqueous dispersion for more than a month (Fig. 2c). After the product was isolated from the solution by filtration and drying, white powder was obtained. The white powder can be redispersed in water without the aid of external surfactant, indicating that HEC-12Na is fixed in the vesicles. The powder could not be dissolved in any organic solvents, such as acetone, tetrahydrofuran and chloroform, but dispersed readily in them, indicating that the vesicles were crosslinked.

Figure 3a and b presents the TEM and FE-SEM images of the hollow spheres obtained from the vesicles with HEC12-Na. The particles are single and well separated with voids in the center. The particle size is about 100–150 nm, the shell thickness is about 20–30 nm and the size of voids is about 30–50 nm. In controlled experiment, non-polymerizable SDS was used to prepare hollow spheres, as shown in Fig. 3c. Some of the particles are separated and their particle size, shell thickness and void size are similar to those of hollow particles prepared from the surfmer HEC12-Na. However many particles are heterocoagulated as indicated by the arrows, and the thicknesses of the walls between neighboring voids are similar or even smaller than that of the shells, indicating that the vesicles fuse during polymerization. Figure 3d also indicates that the particles are adhered to each other which is obviously different from the particles prepared from HEC12-Na in Fig. 3b.

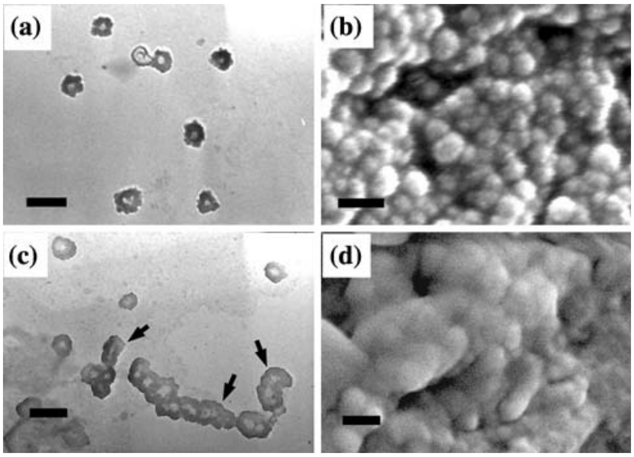

Fig. 3 (**a**) TEM and (**b**) FE-SEM images of the polymerized vesicles with HEC12-Na, (**c**) TEM and (**d**) FE-SEM images of the polymerized vesicles with SDS. Length of scale bar = 200 nm

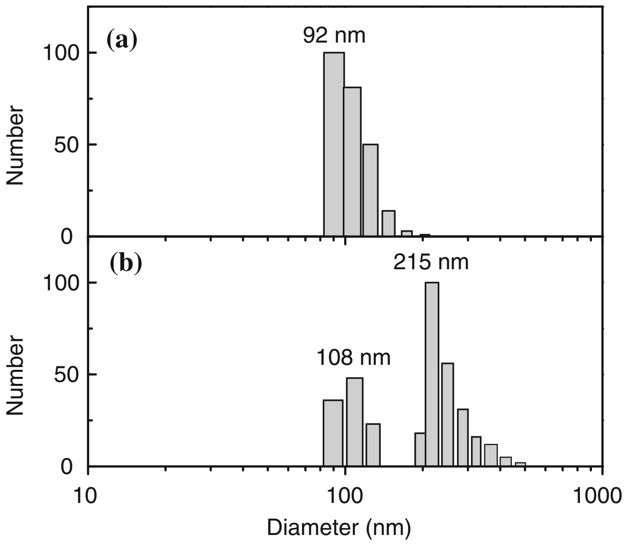

Fig. 4 Size distributions from dynamic light scattering for the polymerized vesicles with (**a**) HEC12-Na and (**b**) SDS

Therefore, as a non-polymerizable surfactant, SDS is less effective than HEC12-Na in preparing well-separated hollow particles.

The dynamic light-scattering histograms of vesicles prepared from HEC12-Na and SDS are shown in Fig. 4a and b, respectively. The average particle size of the vesicles prepared from HEC12-Na is about 100 nm, which is consistent with the result of TEM. However, for the vesicles made from SDS, the distribution of the particle size is much wider and a bimodal distribution of particle size centered at about 108 nm and 215 nm, respectively, is observed. This is consistent with the TEM observations, indicating that many of the vesicles prepared from SDS are non-spherical and heterocoagulated.

According to previous studies [21], maleic surfmer has high reactivity, and the hydrophilic groups of the surfmers can be covalently attached onto the surface of colloid particles due to the copolymerization between hydrophobic monomers and surfmers, so the emulsion polymerization process is stable even at high solid content. On the contrary, non-polymerizable surfactants are only physically adsorbed onto the colloid particles and tend to desorb from the colloids and agglomerate during emulsion polymerization, so the emulsion is not as stable as the emulsions prepared from surfmers. Therefore, it is reasonable to say that when SDS was used in the polymerization of vesicles, some vesicles fused due to the weak interaction between SDS and the polymerized vesicles; on the contrary, copolymerization between HEC12-Na and vesicles increased the stability of the reaction system and prevented the fusion of the vesicles.

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