Interface-initiated Emulsion Polymerization: Synthesis of Hollow Sphere with a Hole in the Shell

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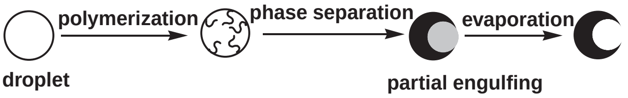
The polystyrene (PSt) hollow spheres with a hole in the shell can be successfully prepared by interface-initiated emulsion polymerization in the presence of isooctane. The results indicated that the St/isooctane ratio had a great influence on the final morphology and divinylbenzene (DVB) disadvantaged the form of the hollow structure.

Colloid particles with hollow interiors have attracted intense research attention because of its widespread applications, such as controlled release of drugs, cosmetics, inks, pigments or chemical reagent and protection shield of biological active species. Templating method is one of the most common methods for preparing hollow spheres. The simple and straightforward method works for a variety of materials that include polymers,[1–7] composite and metal.[8–10] For polymers, methods such as emulsion polymerization,[11–17] polyeletrolyte or block copolymer assembly[18,19] are also used to generate hollow structure.

Recently, the hollow spheres with a hole in their shell have stimulated great interest, because their structure can improve the rate of the loading and diffusion of the encapsulated materials. And some researchers[20,21] have obtained the polymer materials with such structures by the complicated process. Emulsion polymerization is an important method for preparing polymer. In the present paper, the PSt hollow spheres with a hole in the surface was synthesized via one step method of interfacial-initiated emulsion polymerization.

The overall synthetic procedure of hollow spheres with a hole in the shell is represented in Scheme 1. In a typical synthesis procedure, 2.00 g of styrene (St) is mixed with 2.00 g of isooctane and 0.12 g of cumyl hydroperoxide (CHPO). The solution is added into the 40.00 g of deionized water containing 0.40 g of sodium dodecyl sulfate (SDS) in a three-necked round-bottom flask equipped with a stirrer, a thermometer and a condenser. The mixture is emulsified for 30 min under nitrogen atmosphere. The emulsion is heated to 45 °C. The aqueous solution, containing 0.15 g of $FeSO_4{\cdot}7H_2O$, 0.07 g of sodium formaldehyde-sulfoxylate (SFS), in 5.0-mL distilled water, is dropped into the emulsion. The polymerization proceeds for 24 h.

According to the theory of the equilibrium morphology investigated by Torza and Mason,[22] two immiscible liquids droplets (Phase 1 and 3), suspended in a mutually immiscible liquid (Phase 2) and the resulting morphology is rationalized by the analysis of the interfacial tension between the phases (σ_{12}, σ_{23}, σ_{31}) and spreading coefficients for each phase as $S_1 = \sigma_{23} - (\sigma_{12} + \sigma_{13})$. In terms of the convention $S_1 < 0$ ($\sigma_{12} > \sigma_{23}$), Phase 1 is partially encapsulated by Phase 3 when $S_2 < 0$, $S_3 < 0$. When Phase 2 is evaporated, the hollow spheres with one-hole in the shell form. Besides the thermodynamic factor mentioned above, the kinetic factor including the locus of polymerization and viscosity during the polymer diffusion process has also influence on the morphology of the polymer particles.



Scheme 1. Schematic diagram of the formation of hollow spheres with a hole in the shell.

The redox initiator, CHPO with Fe^{2+} is chosen. CHPO is oil-soluble. However, CHPO only dissociates with an appreciable rate in conjuction with the transition-metal complex (Fe^{2+}), which is water-soluble. Therefore, the primary radicals producing reaction can only take place at the oil/water interface. That is, the locus of the polymerization of styrene (St) is the interface between the oil and the water. So the droplet nucleation is dominating in this emulsion system. Because isooctane is a nonsolvent for PSt, the phase separation occurs when the polymer is produced. Isooctane can be partially encapsulated by PSt. The transmission electron microscope (TEM) image of the hollow particles with a hole in the surface is shown in Figure 1. The hollow structure of the spheres is revealed by Figure 1a. The high-magnification of the TEM images (Figures 1b and 1c) show that the color of the center of the spheres is much paler. The shell thickness of the hollow spheres from Figure 1c is about 200 nm. From the scanning electron microscopy (SEM) image (Figure 2), we can see that there is a hole in the surface of the most of the spheres that confirms the hollow interior of the polymer particles. The sizes of the polymer sphere range from 0.5 to 2.3 µm. In this case, the oil/water interface becomes the locus of the polymerization of St and the monomers are supplied from the droplets inside. Therefore, the resulting polymer does not need to migrate to the interior of the particles, which favors the phase separation. Therefore, the good structure of the hollow with a hole in the shell is obtained.

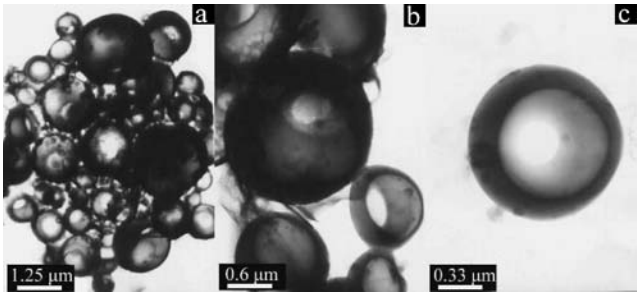


Figure 1. TEM images of PSt hollow spheres with a hole in the shell (a) a low-magnification (b), (c) high-magnification (St/isooctane = 1:1).

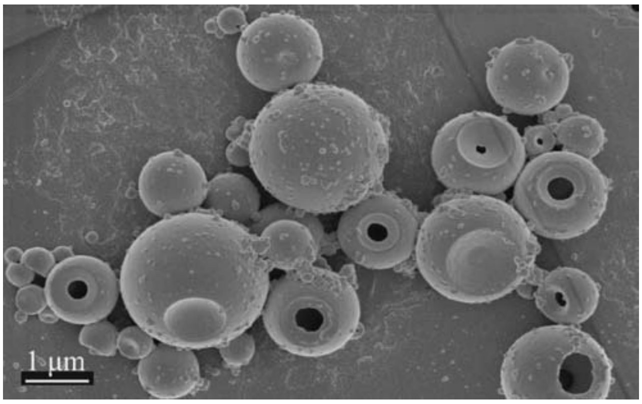


Figure 2. SEM image of PSt hollow spheres with a hole in the shell.

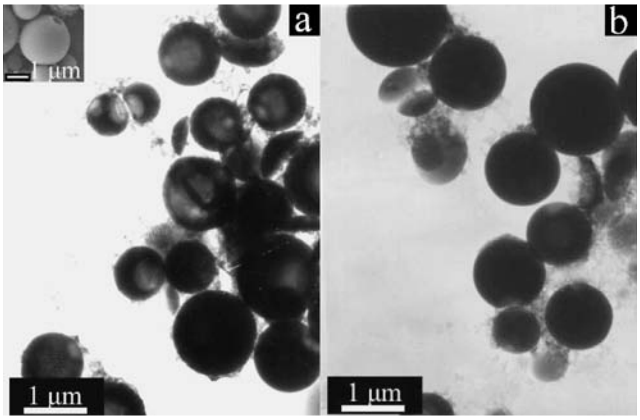


Figure 3. TEM of images of the polymer spheres with different St/isooctane: (a) 4:3, (b) 2:1.

Figure 3a is the TEM image of the polymer spheres with monomer/isooctane ratio of 4:3. Compared with the hollow polymer spheres with monomer/isooctane ratio of 1:1, the hollow volume of polymer spheres becomes small and the shell thickness is large. Furthermore, there exist solid spheres, which attributes to the micellar nucleation. When the ratio of St to isooctane is 2:1, there are almost solid particles (Figure 3b).

When 2.0% DVB was introduced in the system, particles seem to be solid and there is a hole in the shell (Figure 4a). From SEM image (Figure 4b), it is found that there are solid spheres and the spheres with multi-pinholes. In case of higher St/isooctane ratio, the addition of DVB will limit the mobility of the polymer, which results in a decrease in the rate of phase separation. The local phase separation results in the spheres with multi-pinholes.

In the FT-IR spectrum of synthesized particles, the strong peaks at 699 and 757 cm^{-1} and several characteristic absorbing peaks at 1029, 1452, 1493, 1601, 2851, and 3026 cm^{-1} are corresponding to PSt absorbed spectrum. It can be deduced that polystyrene was successfully formed.

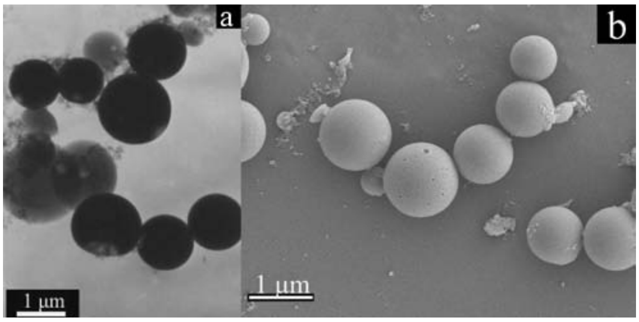


Figure 4. TEM and SEM images of polymer spheres with 2.0% (to the monomer) DVB (St/isooctane = 4:3).

In conclusion, the polystyrene hollow spheres with a hole in the shell can be successfully prepared by interfacial-initiated emulsion polymerization in the presence of isooctane. At the low St/isooctane ratio, the amount of isooctane has influence on the hollow volume of hollow polymer spheres. Higher St/isooctane ratio disadvantages the form of the hollow structure. Because the addition of DVB hinders the phase separation, the polymer spheres with multi-pinholes can be formed.

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