Preparation of Polymeric Nanocapsules by Gamma-ray-initiated Miniemulsion Polymerization

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(Received October 10, 2006; CL-061182; E-mail: zczhang@ustc.edu.cn)

Hollow polystyrene (PS) nanocapsules were synthesized through gamma-ray-initiated miniemulsion polymerization by using an alkali-soluble polymeric surfactant (ASPS) as surfactant in the presence of hexadecane (HD). The results indicated that nanocapsules with different particle size and shell thickness could easily prepared by this method, and ASPS can promote the formation of completely hollow structures.

Nanocapsules are generally considered as spherical, hollow structures with an average diameter smaller than 1 μm and a polymeric wall with a thickness in the nanometer region.[1] Due to the attractive perspective in various fields such as drug carriers,[2] controlled release vesicles in pharmaceutical applications, protecting light-sensitive material devices, and optical applications,[3–5] nanocapsules have been attracted broad academic and industrial interest.

Nanocapsules can be prepared by a variety of approaches among which the osmotic swelling method developed in the research laboratories of the Rohm and Haas Co. was the earliest processes for making hollow latex particles.[6] Other methods soon followed such as interfacial polymerization,[7] modified emulsion polymerization,[8] dynamic swelling method,[9] cross-linking of micelles, and self-assembly,[10] double emulsion technique, and recently developed freeze–warm PS beads swollen by toluene.[11,12] In addition to these approaches, miniemulsion polymerization has been proved to be a suitable method for the preparation of these types of systems.[13]

In the present paper, we report a facile route to prepare polymeric nanocapsules by miniemulsion polymerization using alkali-soluble polymeric surfactant (ASPS) and gamma-ray irradiation, a combination of which to our knowledge has not been studied so far. A probable mechanism of the encapsulation process is shown in Figure 1.

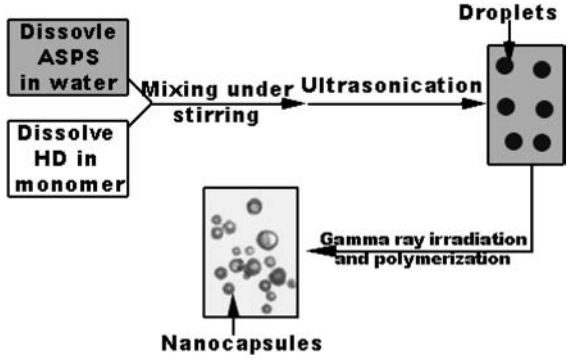

Figure 1. Schematic representation of the formation of nanocapsules.

By shearing the system containing styrene (St), water, ASPS, and hexadecane (HD), the oil phase, which consists of the St and HD, will form droplets which will serve as the main loci of monomer polymerization. The polymerization is started by placing the mixture in the field of Co-60 gamma-ray at room temperature and under ambient pressure. Phase separation can take place during the polymerization with consequent formation of latex particles with the demixing structure, leading to formation of nanocapsules and the morphology of final latexes investigated by TEM was shown in Figure 2.

The ASPS (38000 g/mol, $[COOH] = 2.98 \times 10^{-3}$ mol/g) used in this method is the random copolymer of butyl methacrylate and methacrylic acid, which was synthesized according to our previous work.[14] When sufficiently long, this type of polymeric surfactant exhibits a rather high surface area demand per molecule due to mutual static and steric repulsion, and hence a rather high interfacial energy being felt by the monomer molecules, which will promote the formation of completely hollow structures. The recipes are listed in Table 1.

PS_{ASPS1} is a standard miniemulsion recipe used as a reference where the hexadecane is only used as osmotic stabilizing agent in order to keep the droplets stable. The relatively small quantity of hexadecane is distributed homogeneously in the particles (see Figure 2a). The average particle diameter is 243 nm. Dramatically, in the case of a lower St to HD ratio 6.0:0.2, the combination of using ASPS and gamma-ray irradiation leads to relatively larger amounts of nanocapsules though coexisting with compact solid polystyrene latexes (see Figure 2b). Moreover, the distribution of HD in the particles plays a certain extent role in this phenomenon as well. As the St/HD ratio decreases, the yield of hollow particles increases (see Figure 2c). The different particle size distributions achieved in this series of experiments can be contributed to the evaporation of the HD and its distribution in the particles. The particle will be enlarged while the hollow structure was formed under evaporation of the

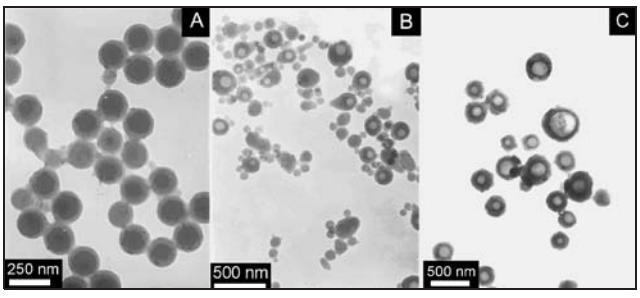

Figure 2. TEM images of PS latex prepared by gamma-ray initiated miniemulsion polymerization using ASPS as surfactant. Dose rate:64 Gy/min.

Table 1. The recipes for this work (dose rate:64 Gy/min)

Latex	St/g	HD/g	ASPS/g	Solid Content/%
PS_{ASPS1}	6.0	0.1	0.7	16.3
PS_{ASPS2}	6.0	0.2	0.7	16.4
PS_{ASPS3}	3.0	3.0	0.7	8.2

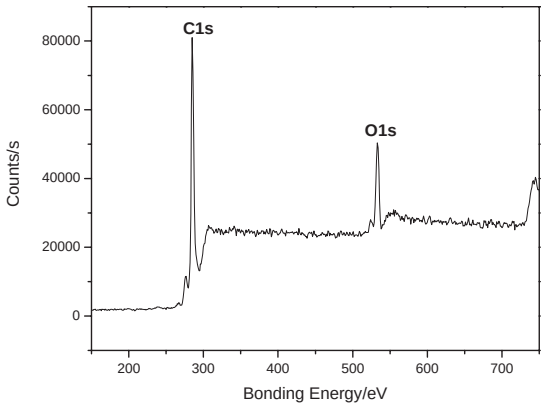

Figure 3. XPS spectrum of extracted PS latex obtained by this method.

HD. The extent of enlargement was determined by the concentration of HD in the particle. In the case of no HD located in the particle, compact solid particles with smaller particle size will be obtained.

According to the theoretical prediction of three-phase interactions of Torza and Mason[15] and previous work of Tiarks et al.,[1] it is more difficult to create nanocapsules with more hydrophobic monomer such as St. However, in our work, nanocapusles are really observed even in case of a lower St to HD ratio 6.0:0.2, in which HD is only used as osmotic stabilizing agent. This phenomenon could be contributed to the so-called "anchoring effect" due to the graft reaction between PS and ASPS, which will play an important role in the reduction of the interfacial tension and in increasing the surface polarity of the latex particles.[16] Due to their high energy, gamma-rays produce large numbers of ASPS, PS, and solvent radicals, which can react with each other. When ASPS radicals react with PS radicals or St, a grafting reaction takes place.[17–19]

In order to confirm the occurrence of grafting between ASPS and PS, PS prepared by this method was characterized by XPS and FT-IR.

The oxygen peak corresponding to oxygen atom of ASPS together with the carbon peak in XPS spectrum (see Figure 3) of the extracted final polymer particles is a strong evidence for the graft reaction between styrene and ASPS. In addition, from the FT-IR spectrum of the PS particles extracted for 48 h with methanol, the adsorption peak at 1730 cm^{-1} corresponding to C=O stretching mode of ASPS is clearly observed. The existence of PS could be confirmed by the frequencies associated with the aromatic rings, for example three sharp peaks near 3060 cm^{-1} from CH stretching, a series of bands related to substituents on the benzene ring in the 2000–1600 cm^{-1} region, skeletal in-plane ring vibrations near 1600 and 1490 cm^{-1}, and CH out-of-plane vibrations at 755 and 698 cm^{-1}.

In conclusion, polystyrene nanocapsules were successfully prepared by gamma-ray-initiated miniemulsion polymerization stabilized by ASPS. The formation of hollow particles could be attributed to relatively low reaction temperature, the combination of mutual static and steric repulsion of polymeric surfactant, and especially grafting reaction between polystyrene and surfactant in gamma-ray induced heterophase polymerization, which promotes the encapsulation process by affecting the kinetic factors.

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Published on the web (Advance View) December 2, 2006; doi:10.1246/cl.2007.120