

A New Kind of Void Soap-free P(MMA-EA-MAA) Latex Particles

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Abstract: Soap-free P(MMA-EA-MAA) particles with narrow size distribution were synthesized by seeded emulsion polymerization of methyl methacrylate (MMA), ethyl acrylate (EA) and methacrylic acid (MAA), and large voids inside the particles were generated by alkali posttreatment in the presence of 2-butanone. Results indicated that the size of void and the particle volume were related with the amount of 2-butanone. The generation mechanism of voids was proposed.

Keywords: Particle morphology, soap-free latex particles, seeded emulsion polymerization, alkali posttreatment

Functional polymer microspheres have been widely studied and used in biomaterials and information industry¹⁻³. Interests have been focused on porous polymer latex particles both in theory and application in the past two decades. Vanderhoff *et al*⁴ prepared hollow particles simply by drying hydrophilic/hydrophobic composite latex particles with soft alkali-swelling core and hard shell. Okubo and his coworkers studied submicron-sized multihollow polymer particles using the stepwise alkali/acid method^{5,6}. In our previous work, functional latex particles with small multihollow morphology have been synthesized *via* seeded emulsion polymerization of styrene(St), methyl methacrylate (MMA) and acrylic acid(AA)/or methacrylate acid(MAA), and the influences of unsaturated acid, pH value, swelling agent and crosslinking agent on pore formation and pore morphology were investigated⁷⁻⁹.

Until now, all of porous polymer latexes were prepared by traditional emulsion polymerization, in which the emulsifier could potentially confer disadvantages to their applications. Moreover, most of the investigations were primarily focused on the polymerization system of St. Compared to St, methyl methacrylate (MMA) is more hydrophilic, and it is expected that PMMA particles with large voids and with surface carboxyl groups may have some promising applications in biomedical and biochemical fields. In this study, soap-free P(MMA-EA-MAA) particles with narrow size distribution and with surface carboxyl groups were prepared by seeded emulsion polymerization in the absence of surfactant materials, and large voids inside the particles

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were obtained by alkali posttreatment.

Experimental

Methyl methacrylate (MMA), ethyl acrylate (EA) and methacrylic acid (MAA) were purified by distillation under reduced pressure and kept in the refrigerator. Ammonium persulphate(APS) was purified by recrystallization twice in water before use. NH_4HCO_3 , NaOH, HCl and 2-butanone (all A. P. grade) were used as received. Deionized water was used in recipes.

Seed latex was first prepared using 120 g of H_2O , 19 g of MMA, 1 g of EA, 0.24 g of APS and 0.2 g of NH_4HCO_3 at 80°C for 6 h. Seeded emulsion copolymerization was conducted by continuous additions of mixed monomers (17.68 g of MMA, 0.93 g of EA and 1.39 g of MAA) into the diluted seed latex (20 mL of seed latex with 89 g of H_2O) from a funnel in nitrogen atmosphere at 80°C . APS dissolved in 24 g H_2O was introduced into the system in two steps at different polymerization time, 16 mL at the beginning and 8 mL at 4 h. After 8 h of monomer addition, the polymerization was continued for an additional 3 h.

For the alkali treatment, 10 mL of the original latex was diluted with 90 g of water, and 2-butanone was then added to the diluted latex. After stirring at ambient temperature for 15 min, the pH value of latex was adjusted to 11.0 with 5 % NaOH aqueous solution, then the reactor was dipped in a water bath at 80°C with stirring at 450 rpm for 90 min. After alkali treatment, the latex was cooled down to the ambient temperature and neutralized to pH 7 with 5 % HCl aqueous solution.

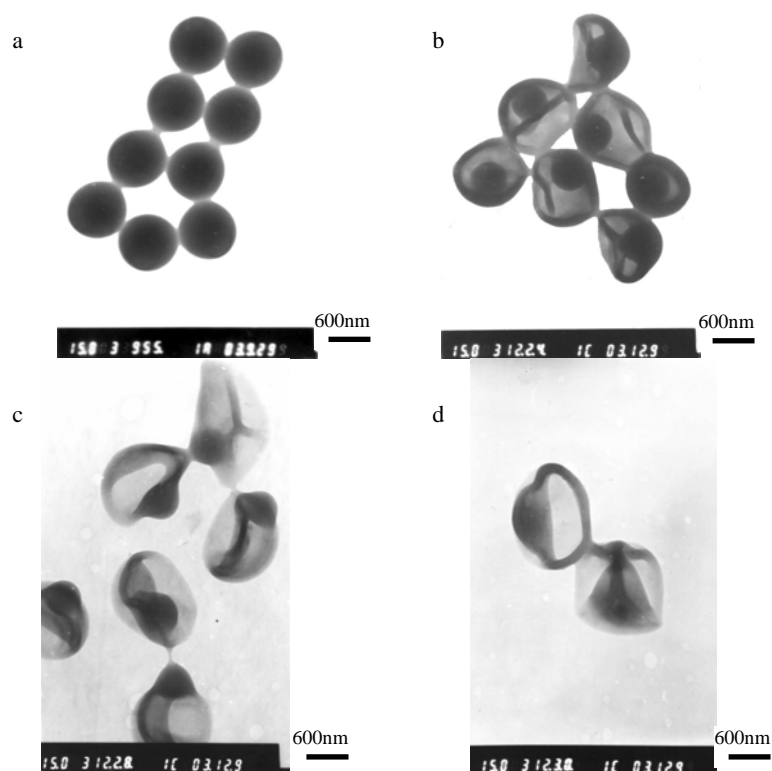
The size and morphology of latex particles were characterized on Hitachi H-800 transmission electron microscope(TEM; Hitachi, Japan) using 2% aqueous phosphotungstic acid as a staining agent.

Results and Discussion

In this study, two-stage soapless seeded emulsion polymerization was employed to synthesize P(MMA-EA-MAA) latex particles. Seed particles with diameter of 335 nm were spheric and monodisperse. When the monomer-dripping time was controlled at 8 h, most of monomers can polymerize onto the seed particles in the second step of polymerization with the monomer conversion of 94.48 %, and the diameter of the resultant particles was 671 nm, which is very close to its theoretical value of 672 nm assuming that all of monomers were polymerized onto the seed particles with 100 % monomer conversion.

TEM photographs of the latex particles before and after posttreatment using different amount of 2-butanone were given in **Figure 1**. It can be seen that the original P(MMA-EA-MAA) latex particles were spheric and of narrow distribution. The void structure was formed inside the particles after undergoing alkali treatment, and the particle volume expansion and void dimension increased significantly with the increase in 2-butanone.

Figure 1 TEM photographs of P(MMA-EA-MAA) latex particles before (a) and after alkali post treatment using different amount of 2-butanone: (b) 5.0 mL, (c) 9.0 mL, and (d) 10.0 mL



It can be seen that there are one to three voids (white region) and a core (black region) inside the anomalous particles, and the size of the core was slightly larger than that of seed particles used in the seeded emulsion polymerization. This specific morphology with large pore dimension of several hundred nanometers was obviously different from the morphology of traditional multihollow latex particles reported by Okubo^{5,6} and Kan⁷⁻⁹, in which many fine pores of from several to tens of nanometers inside the particles were observed.

During alkali treatment process, carboxyl groups on chains of shell polymer were neutralized gradually to carboxyl ion. Because the hydrophilicity of polymer chains with $-\text{COO}^-$ are better than that of those with $-\text{COOH}$, and because the existence of 2-butanone, the immigration of carboxyl ion-containing chains of shell polymer towards particle surface occurred at the temperature of alkali posttreatment, leaving voids inside the particles¹⁰. Since there are no carboxyl groups in core polymer, the seed particle remained immovable in this process. Thus, anomalous particles with void morphology were formed.

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