

INFLUENCES OF ACID POST-TREATMENT ON THE MORPHOLOGY OF SOAP-FREE P(MMA-EA-MAA) PARTICLES PREPARED BY SEEDED EMULSION POLYMERIZATION*

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Abstract Soap-free poly(methyl methacrylate-ethyl acrylate-methacrylic acid) latex particles with narrow size distribution were synthesized by seeded emulsion polymerization, and the porous particles were created by a stepwise alkali/acid treatment method. Effects of acid treatment conditions on the particle morphology were investigated. Results show that one to three pores were formed inside most of particles after post-treatment. At pH 7.0, when the treatment temperature was lower than 70°C, the size of particles and the volume of pores remained almost unchanged, and these two values increased significantly when the temperature was higher than 70°C. Both the particle size and the pore volume decreased with the increase of initial pH value and treatment time in the acid treatment. As the pH was below 4.0 and the treatment time was longer than 180 min, the particles shrunk in size.

Keywords: Soap-free emulsion polymerization; Particle morphology; Porous structure; Acid treatment; Methyl methacrylate based copolymer.

INTRODUCTION

Functional polymer microspheres have been widely studied and used in biomedical and biochemical fields, material science, and information technology *etc.*^[1–3]. Most of the investigations were primarily focused on the particle morphology and the latex properties, which indicate that the morphology of latex particle was determined by both the thermodynamics and the kinetics factors^[4–6].

Porous latex particles are a new kind of functional materials studied intensively by some researchers in recent years. Vanderhoff *et al.*^[7] prepared hollow particles simply by drying hydrophilic/hydrophobic composite latex particles with a soft alkali-swelling core and a hard shell. Landry-Coltrain *et al.*^[8] produced porous polyester particles with a diameter of less than 500nm to be used as ink recording elements. Benson^[9] and Kitagawa^[10] prepared porous crosslinked hydrophilic polymer microbeads with cavities joined by interconnecting pores, which can be used as absorbent material and solid support in the biotechnology field. Okubo *et al.*^[11, 12] synthesized a series of multihollow latex particles of styrene (St)-butyl acrylate (BA)-methacrylic acid (MAA) and St-MAA using a stepwise alkali/acid treatment method, and found that alkali swelling of carboxylated polymer particles in the step of alkali treatment is the trigger in the formation of multihollow structure. Cheng *et al.*^[13] produced monodispersed porous St-divinylbenzene (DVB) polymer particles via seeded emulsion polymerization followed by diluent extraction.

In our previous work^[14–16], a series of monodispersed core/shell latex particles containing carboxyl groups have been prepared via seeded emulsion copolymerization, and the influences of ingredients and alkali/acid post-treatment on hollow formation were investigated.

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Until now, nearly all of porous polymer latices were prepared by traditional emulsion polymerization, in which the existence of emulsifier is adverse to many applications. Moreover, most of the investigations were mainly focused on the polymerization system of St. Compared to St, methyl methacrylate (MMA) is more hydrophilic and it is expected that carboxyl-containing porous PMMA particles may have some promising applications in biomedical and biochemical fields. Recently, we have prepared P(MMA-EA-MAA) latex particles with narrow size distribution and with surface carboxyl groups by seeded emulsion polymerization in the absence of surfactant, and the porous particles were obtained after alkali treatment^[17]. In this study, the effects of acid treatment conditions such as initial pH, temperature and time on the morphology of latex particles were investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), ethyl acrylate (EA) and methacrylic acid (MAA) (all were AR grade, First Chemical Reagent Factory, Tianjin, China) were purified by distillation under reduced pressure and kept in the refrigerator. Ammonium persulphate (APS) (AR grade, Aijian Modern Reagent Factory, Shanghai, China) was purified by recrystallization twice in water before use. NH_4HCO_3 , NaOH, HCl and 2-butanone (all were AR grade, Beihua Fine Chemical Products Co., Ltd., Beijing, China) were used as received. Deionized and distilled water was employed.

Synthesis of P(MMA-EA-MAA) Latex

Emulsion polymerization was carried out by soap-free seeded emulsion polymerization. The ingredients and conditions used are listed in Table 1. The P(MMA-EA) seed latex was first synthesized by batch emulsion polymerization, and then the mixture of monomers in the second step of polymerization was added drop-wise to the diluted seed latex in 8 h followed by an aging for additional 3 h.

Table 1. Ingredients and conditions used in emulsion polymerization

		First stage	Second stage
Ingredients	Seed latex (g)	0	20
	MMA (g)	19	17.68
	EA (g)	1	0.93
	MAA (g)	0	1.39
	APS (g)	0.24	0.20
	NH_4HCO_3 (g)	0.20	0
	H_2O (g)	120	113
	Temperature ($^{\circ}\text{C}$)	80	80
Conditions	Stirring rate (r/min)	300	300
	Reaction time (h)	6	11

Alkali/acid Post-treatment

10 mL of the original latex was diluted with 90 mL of water, and 5 mL of 2-butanone was then added to the diluted latex. After stirring at an ambient temperature for 15 min, the pH value of the latex was adjusted to 11.0 with 5% NaOH aqueous solution, then the reactor was immersed in a water bath at 80°C with stirring at 450 r/min. After 90 min of alkali treatment, the pH was adjusted to 7–8 with 5% HCl aqueous solution.

In the acid treatment process, the pH value of the alkali-treated latex was adjusted with 5% HCl aqueous solution, and kept in a water bath for some time at a selected temperature. After acid treatment, the latex was cooled down to ambient temperature.

Characterization

The size and morphology of latex particles were observed on Hitachi H-800 transmission electron microscope (TEM; Hitachi, Japan) using aqueous phosphotungstic acid as a staining agent. Monomer conversion (*Conv.*), particle diameter (D_p) and particles number (N_p) were characterized as described elsewhere^[18].

The volume change (ΔV) of the particles was calculated as follows:

$$\Delta V = (D_e^3 - D_p^3)/D_p^3 \times 100\%$$

where D_p and D_e denote the mean diameter of the particles before and after alkali/acid treatment, respectively.

RESULTS AND DISCUSSION

Emulsion Polymerization and Alkali Treatment

Two-stage soap-free seeded emulsion polymerization was employed to synthesize P(MMA-EA-MAA) latex particles. Seed particles with a diameter of 335 nm were spheres and monodispersed (Fig. 1a). When the monomer-dripping time was controlled to 8 h, most of the monomers can be polymerized onto the seed particles with a monomer conversion of 94.5% in the second step of polymerization, and the diameter of resultant particles was 671 nm (Fig. 1b), 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 photomicrographs of the latex particles before and after alkali post-treatment are given in Figs. 1(b) and 1(c). It can be seen that the original P(MMA-EA-MAA) latex particles are spherical in form with a narrow size distribution. The porous structure was formed inside the particles after alkali treatment, and the particle size increased to 826 nm, *i.e.* the volume expansion of the particles reached 86.5%.

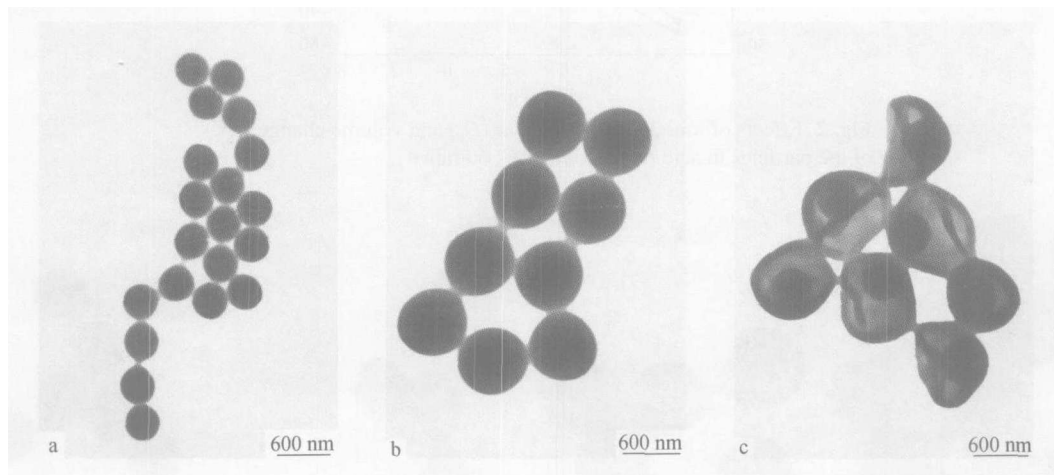


Fig. 1 TEM photomicrographs of P(MMA-EA) seed latex particles (a), and P(MMA-EA-MAA) seeded latex particles before (b) and after (c) alkali treatment

It can be noted that there are one to three pores (white region) and a core (black region) inside the anomalous particles, and the size of the core is slightly larger than that of a seed particle. This special morphology with large pore dimension of several hundred nanometers was obviously different from the morphology of traditional multihollow latex particles reported by Okubo^[11, 12] and Kan^[14–16], in which many fine pores from several to tens of nanometers inside the particles were observed.

Acid Treatment

Okubo and his co-workers^[19] have disclosed the mechanism of pore generation of P(St-MAA) latex particles, and found that no obvious change of the particle morphology was observed if the particles just underwent alkali treatment, and the multihollow particles could be formed only by stepwise alkali/acid treatment method. However, our research^[20] on the soap-free batch P(MMA-EA-AA) latex disclosed that the anomalous multihollow structure of the particles formed during alkali treatment disappeared when the particles continuously underwent acid treatment. Here, the alkali-treated soap-free seeded latex particles were further treated at various acid conditions to clarify their effects on the porous structure.

Initial pH value

During acid treatment process, the deionizing degree of carboxylates in the latex particles increases with the decrease in pH. Since the hydrophilicity of polymer chains with $-\text{COOH}$ are lower than that of those with $-\text{COO}^-$, this deionization of polymer chains will certainly affect the morphology of the particles. The influences of initial pH on particle properties are showed in Figs. 2 and 3. One can see that, after acid treatment, the pores inside most of the particles combine with one another to form a large one, and the pore volume, the particle size (D_e) and the volume change of the particles (ΔV) decreases significantly with the lowering of the pH. Even when the pH was lower than 4.0, the particle shrunk to less than its original although the porous structure was also observed.

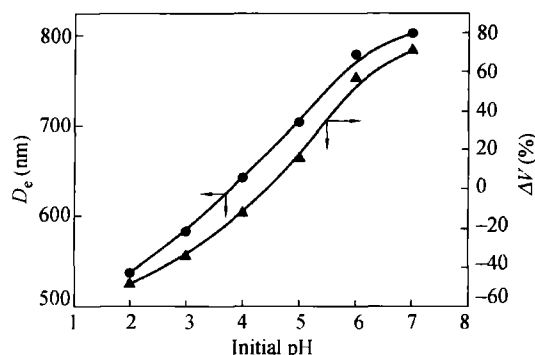


Fig. 2 Effects of initial pH on diameter (D_e) and volume change (ΔV) of the particles in acid treatment (80°C; 60 min)

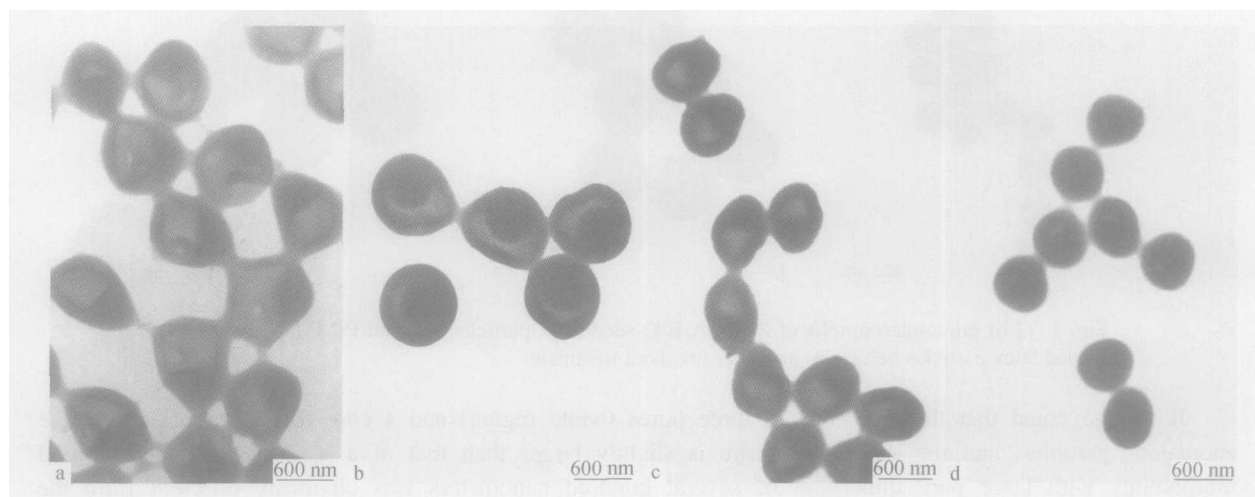


Fig. 3 TEM photomicrographs of P(MMA-EA-MAA) latex particles after acid treatment (80°C; 60 min) at different initial pH (a) 7.0, (b) 6.0, (c) 4.0 and (d) 2.0

TEM photomicrographs (Fig. 3) show that when pH was below 6.0, there was only one pore left inside all of the particles, and this pore structure in some of the particles disappeared completely at pH 2.0.

During alkali treatment, since particles can be swelled by 2-butanone, and also $-\text{COOH}$ on polymer chains are neutralized to COO^- , which can be hydrated with H_2O , the actual T_g of the polymer in such system is much lower than that of polymer in the dried state. Moreover, the mobility of carboxylate-containing polymer chains toward particle surface increases because of their higher hydrophilicity. In this case, rearrangement of the polymer segments and polymer chains will occur, which generates the pores and leads to the expansion of particle volume. Since the pores inside the particles are full of water in the system (these pores can also be called water pools)^[19], when the pH is rapidly adjusted to acidic in the following acid treatment, the interfacial free

energy between the water pools and polymer phase drastically increases because of the marked deionization of carboxylate-containing polymer chains, *i.e.*, the state of the particles with some water pools becomes remarkably thermodynamically unstable. For this reason, the acid treatment at a temperature higher than the T_g of polymers will cause the coagulation of water pools within the particles, and as a result, the relatively small pores inside the particles will combine with each other to form a larger one. The water inside the one pore is gradually released into the medium along with further decrease in pH to counteract the further increase of interfacial free energy. This leads the particles to a more thermodynamically stable state by decreasing the total interfacial area between the aqueous phase and the polymer phase. Along with the water releasing, some polymer chains with enriching carboxyl groups can also dissolve gradually into the aqueous phase due to their affinity to water, which results in the shrink of particles.

Treatment Temperature

The influence of treatment temperature on the particle morphology was investigated under the conditions of initial pH 7.0 and 60 min. Results are presented in Figs. 4 and 5, which show that the structure of particles remain unchanged and particle size increases slightly at a temperature below 70°C. Once the temperature is elevated to above 70°C, only one large pore inside the particles is observed, and ΔV and pore volume increase significantly with the increase in temperature.

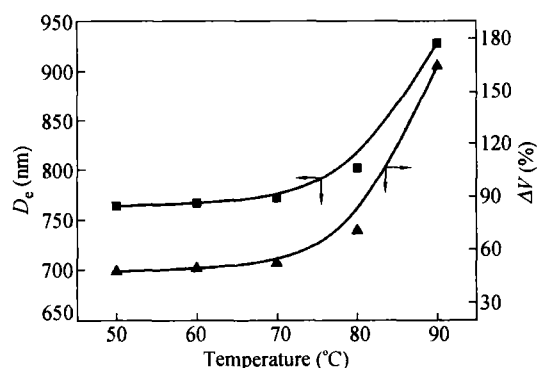


Fig. 4 Effects of temperature on diameter (D_e) and volume change (ΔV) of the particles in acid treatment (pH = 7.0; 60 min)

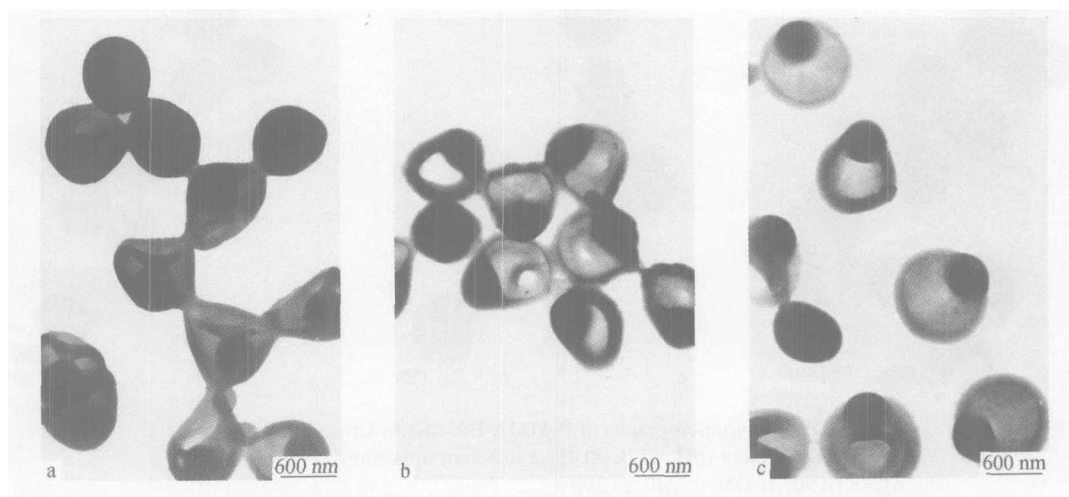


Fig. 5 TEM photomicrographs of P(MMA-EA-MAA) latex particles after acid treatment (pH = 7.0; 60 min) at different temperature (°C)

a) 60; b) 70; c) 90

The photomicrograph of particles treated at 80°C is showed in Fig. 3(a).

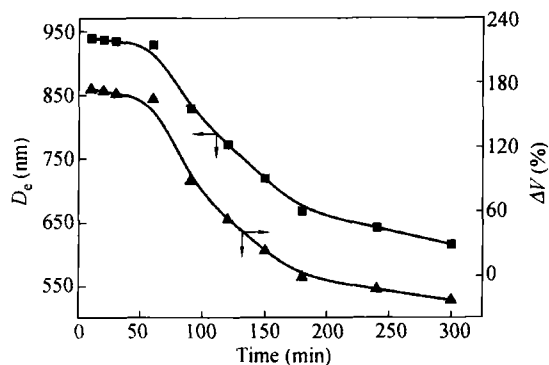


Fig. 6 Effects of time on diameter (D_e) and volume change (ΔV) of the particles in acid treatment (pH = 7.0; 90°C)

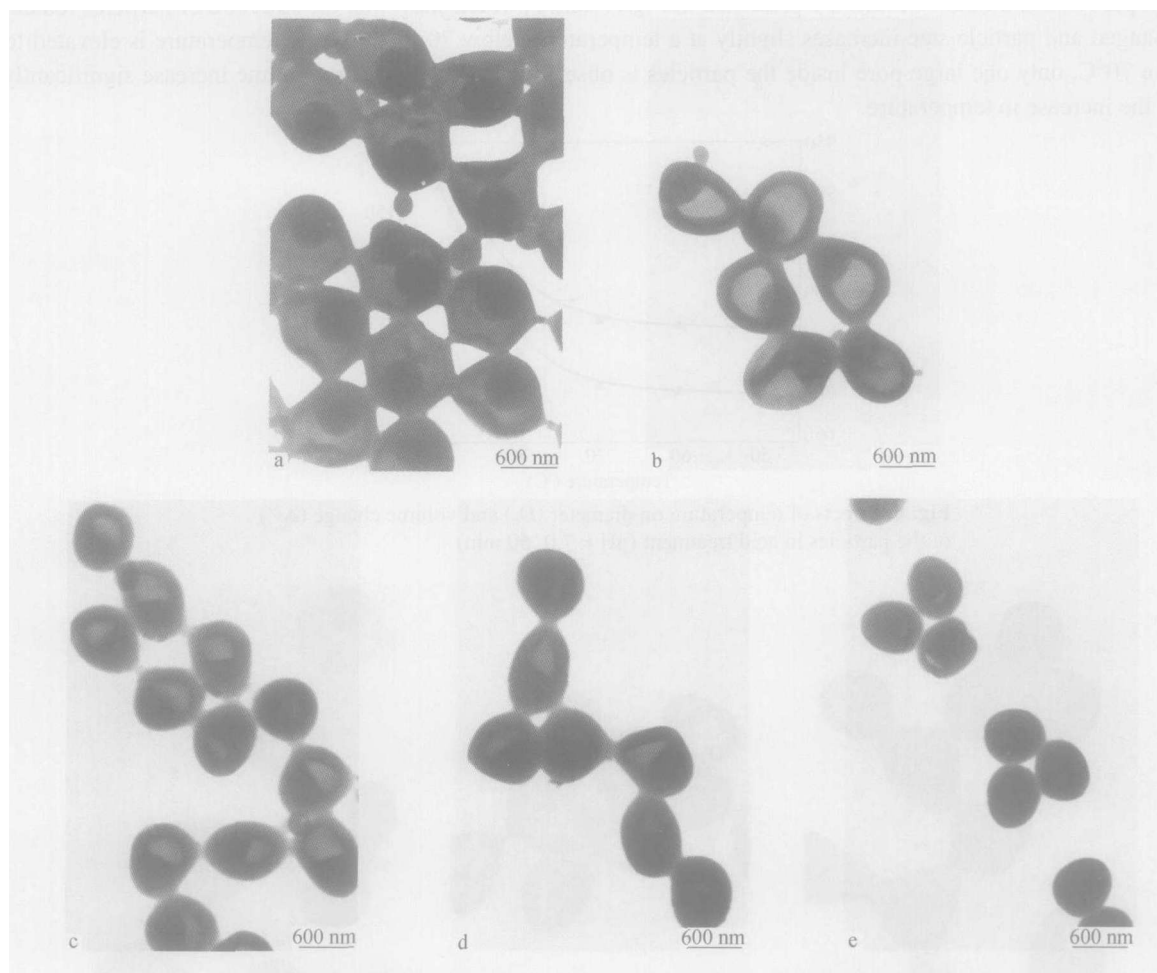


Fig. 7 TEM photomicrographs of P(MMA-EA-MAA) latex particles after acid treatment (pH = 7.0; 90°C) at different time (min)
a) 30; b) 90; c) 180; d) 240; e) 300

The photomicrograph of particles treated for 60 min is showed in Fig. 5(c).

The flexibility of polymer chains is essential in the formation of pores inside the particles. At a relatively low treatment temperature, the rearrangement of polymer chains is very difficult, so no obvious change of the

particle morphology can be observed. With the increase in temperature, the polymer chains become more and more flexible, and the pores inside most of particles can combine through the movement of polymer chains, and finally, leave only one large pore. Because the interfacial free energy between water pool and the polymer phase is not too high at pH 7.0 and the 60 min of treatment time is not too long, few hydrophilic polymer chains dissolve into the aqueous phase although they could migrate out from inside to the surface of the particles. Thus, the particle size and pore volume increase monotonously with the increase in temperature.

Treatment Time

Acid treatment time has also an important effect on the particle morphology. Results in Figs. 6 and 7 indicate that when acid treatment time is over 60 min, a single pore is formed inside all of the particles, and ΔV and the pore volume decrease quickly with the increase in time. When the treatment time was prolonged to more than 180 min, the particle size was even smaller than that of its original one. Once the treatment time was prolonged to 300 min, the pore inside most of the particles disappeared. Although the pH is relatively high, there are still some carboxyl-containing polymer chains which dissolve into the aqueous phase after undergoing a long treatment. Along with this, the water inside the particle pore is also released gradually into the aqueous phase, which causes the further decrease in particle size.

CONCLUSION

In this study, soap-free P(MMA-EA-MAA) latex particles with porous morphology were prepared *via* seeded emulsion polymerization followed by alkali/acid treatment. The water pools inside particles formed during alkali treatment coagulated into a large one, and the water inside this large pool was gradually released into the aqueous phase at drastic acid treatment conditions. The optimum acid treatment conditions to obtain particles with a single pore and with large volume expansion of 164.5% were 90°C, initial pH 7.0 for 60 min.

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