Colloid & Polymer Science Colloid Polym Sci 272:933–937(1994)

# Production of multihollow polymer particles by the stepwise alkali/acid method IV. Acid treatment process*)

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*Abstract*: The effects of pH, temperature and time in the acid-treatment process on the multihollow structure formed within submicron-sized monodispersed polymer particles by the stepwise alkali/acid method proposed by the authors were examined in detail. The original particles were produced by emulsifier-free emulsion terpolymerization of styrene, butyl acrylate, and methacrylic acid. It was clarified that the number and the size of hollows per particle were drastically changed by the acid treatment conditions as well as those in the alkali treatment process.

*Key words*: Multihollow particle – emulsion polymerization – emulsion – latex – morphology – carboxyl group

## Introduction

We found that submicron-sized monodispersed styrene-butyl acrylate-methacrylic acid terpolymer particles produced by emulsifier-free emulsion terpolymerization were changed to those having many hollows therein by stepwise treatments with alkali and acid [1]. We named it the stepwise alkali/acid method.

In the following articles [2, 3], the effects of pH, temperature and time in the alkali treatment process as the first step on the multihollow structure were examined in detail, where the acid treatment as the second step was always conducted under the same conditions. As the result, it was clarified that the degree of alkali swelling of the particles, which depends on the pH value, the temperature and the time in the alkali treatment process, controls the multihollow structure.

In this article, the effects of pH, temperature and time in the acid treatment process as the second step on the multihollow structure will be examined in detail.

## Experimental

### *Materials*

Styrene (S), butyl acrylate (BA) and methacrylic acid (MAA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate was purified by recrystallization. Analytical grade hydrochloric acid and potassium hydroxide were used without further purification. Commercial grade nonionic polyoxyethylene-sorbitan monoleate emulsifier (Tween 80, Kao Corp., Japan) was used without further purification. Deionized water was distilled.

### *Preparation of polymer emulsion*

S-BA-MAA terpolymer (P(S-BA-MAA)) emulsion was prepared by emulsifier-free emulsion terpolymerization at 70 °C for 26 h under conditions listed in Table 1, where 5% of all monomers were preliminarily polymerized for 1.2 h and then the remainder was dropwise added to a glass reaction

*) Part CXLV of the series "Studies on Suspension and Emulsion"

Table 1. Preparation of Stage-type Emulsifier-free Emulsion Polymerization[a])

| Ingredient | | First stage[b]) | Second stage[c]) |
|---|---|---|---|
| S | (g) | 2.55 | 48.5 |
| BA | (g) | 0.72 | 13.7 |
| MAA | (g) | 0.24 | 4.55 |
| KPS[d]) | (g) | 0.375 | |
| Water | (g) | 223 | |

[a]) Conducted at 70 °C for 26 h under the nitrogen atmosphere;
[b]) All ingredients were collectively added and the polymerization was conducted for 1.2 h;
[c]) The monomers were dropwise added for 14.5 h;
[d]) Potassium persulfate.

flask from a micro-feeder for 14.5 h. Since the residual monomers were not detectable by gas chromatography, the molar composition of the resulting P(S-BA-MAA) was calculated to be 74.3/17.0/8.7 from the polymerization recipe.

*Electron microscopy*

A JASCO JEM-200CX electron microscope was used for transmission electron microscopy (TEM). Each emulsion was diluted down about 50 ppm, and a drop was placed onto a Formvar film-coated grid and allowed to dry at room temperature in desiccator. TEM photographs were taken with great care to minimize beam damage.

*Thermal analysis*

Glass transition temperature (*Tg*) of the dried P(S-BA-MAA) was measured using a differential scanning calorimeter (Seiko I & E SSC-560S) at a heating rate of 5 °C per min.

*Alkali/acid treatments*

The original P(S-BA-MAA) emulsion was diluted in 1.5 g/l in a small glass vessel, and treated stepwise with alkali and acid as follows.

Alkali treatment: First, as a stabilizer to prevent coagulation of particles, Tween 80 (10 wt% of polymer solid) was added to the diluted emulsion. The alkali treatment was always carried out under the same conditions: initial pH value of 12.2 (with 0.2 N KOH); 3 h; 75 °C. After the treatment, each emulsion was rapidly cooled to room temperature by dipping the vessel in running water. The hydrolysis of BA unit in the alkali treatment was less than several %.

Acid treatment: Tween 80 (10 wt% of polymer solid) was added to the alkali-treated emulsions to prevent the coagulation of particles. The sample was adjusted to various pH values using 0.2 N HCl aq. solution and then treated at various temperatures for different times. After the acid treatment, the sample was rapidly cooled as above.

## Results and discussion

In order to clarify the effects of the acid treatment conditions on the multihollow structure, the alkali-swollen particles prepared under the same conditions (initial pH 12.2; 3 h; 75 °C) were treated at various acid conditions.

Figure 1 shows TEM photographs of the particles treated at the various initial acidic pH values for 3 h at 75 °C. At pH 6.6, hollows were barely observed inside the particles. At the pH values below 6.0, the multihollow structures were clearly observed for all particles. The hollow increased in the size and decreased in the number with descending of the pH value. At pH 2.2, several large and small hollows were coexisted inside the particles.

Figure 2 shows the relationship between the initial pH value and the expansion of particle volume based on the untreated original particles. The particle volume increased with descending of the initial pH value. This suggests that at a lower pH range, the fixation of polymer segments takes place more quickly at the "surfaces" of alkali-swollen particles before shrinking homogeneously of the particles.

Figure 3 shows TEM photographs of the particles treated at the various temperatures for 3 h at pH 2.2 after the alkali treatment at pH 12.2 for 3 h at 75 °C. At the acid-treatment temperatures of 50 and 60 °C, the multihollow structure was not observed. Even if the acid-treatment time at 50 °C was extended to 9 days, the multihollow structure did not appear (the photograph was omitted). At the temperatures above 65 °C, the treated particles had multihollow structures. The hollow size was larger at 75 °C than at 65 °C, whereas the number of hollows per particle was fewer at 75 °C

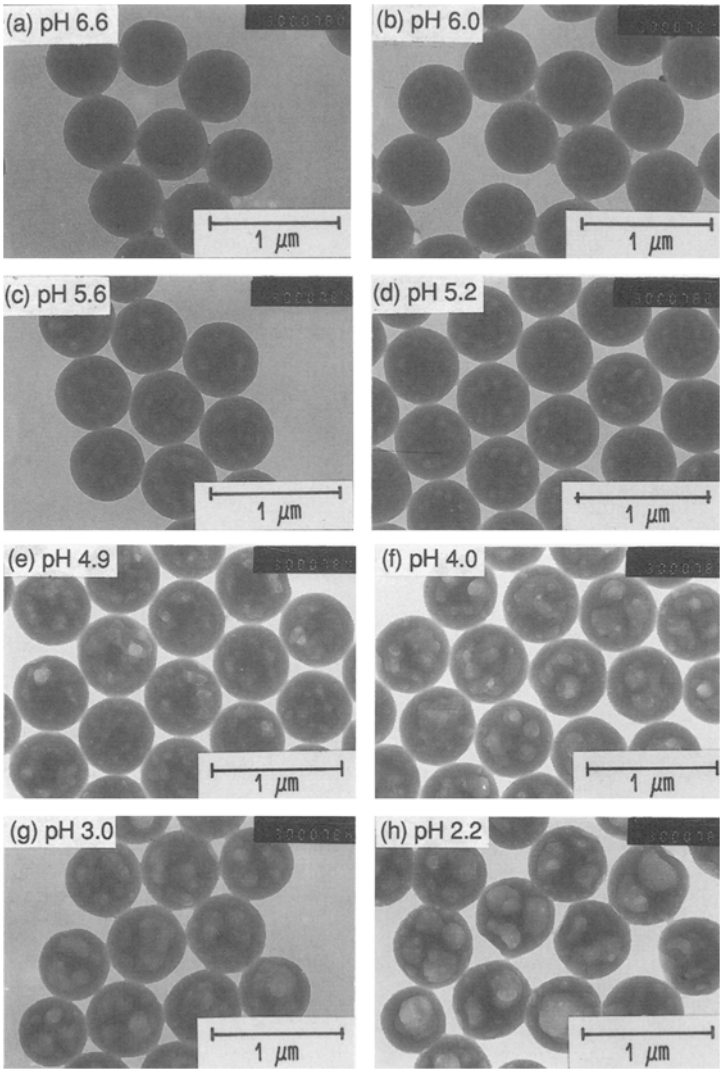


Fig. 1. TEM photographs of P(S-BA-MAA) (74.3/17.0/8.7, molar ratio) treated by the stepwise alkali/acid method (alkali treatment: initial pH 12.2; 75 °C; 3 h; acid treatment: initial pH, variable; 75 °C; 3 h)

than at 65 °C. The minimum acid-treatment temperature at which the multihollow structure was observed is consistent with the minimum alkali-treatment temperature at which the multihollow structure was observed. The latter temperature was measured as 65 °C in the previous article [3]. The minimum temperatures were lower than the glass transition temperature ($Tg$ = 78 °C) of the dried base terpolymer measured by differential scanning calorimetry. The $Tg$ of base polymer in carboxylated polymer particles seems to descend in comparison with that in the dried state because of plasticization due to water absorption [3, 4]. This may be the reason.

Figure 4 shows TEM photographs of the particles treated further at 75 °C for 3 h after the acid treatment at 50 °C for 3 h by which multihollow structure was not formed as already shown in Fig. 3(a). A similar multihollow structure as that (Fig. 3(d)) of the particles treated directly at 75 °C for 3 h at pH 12.2 was observed. The similar result was also obtained by treating the particle further at 75 °C for 3 h, which had been treated at 50 °C for 9 days at pH 2.2 (the photograph was omitted).

These results suggest that it is necessary to carry out the acid treatment at higher temperature than $Tg$ of polymer in particles for the production of multihollow particles.

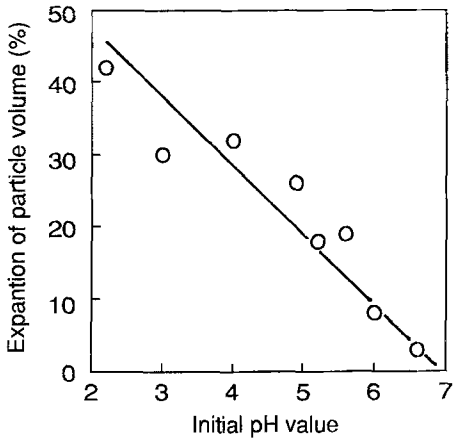


Fig. 2. Relationship between the initial pH value in the acid treatment at 75 °C for 3 h and the volume expansion of P(S-BA-MAA) (74.3/17.0/8.7, molar ratio) particles treated by the stepwise alkali/acid method (alkali treatment: pH 12.2; 75 °C; 3 h)

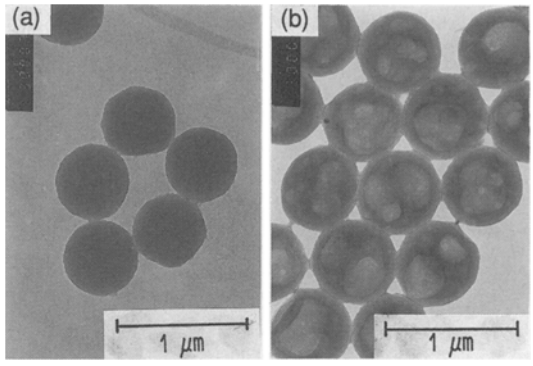


Fig. 4. TEM photographs of P(S-BA-MAA) (74.3/17.0/8.7, molar ratio) particles (a) treated by the stepwise alkali/acid method (alkali treatment: initial pH 12.2;75 °C; 3 h; acid treatment: initial pH, 2.2; temperature, 50 °C; 3 h) and of the particles (b) treated further additionally at 75 °C for 3 h

Figure 5 shows TEM photographs of the particles treated at the various treatment times at pH 2.2 and at 75 °C. The hollow increased in the size and decreased in the number with the acid-treatment time.

From the above results, it is clear that the multihollow structure can be greatly changed by the acid treatment conditions as well as by the alkali treatment conditions described in the previous articles [2, 3]. The formation of multihollow structure seems to proceed as follows. In the early stage of the acid treatment process, the polymer wall (i.e., shell) is formed quickly at the surface of alkali-swollen particle, because the "soluble" polymer segments containing ionized carboxyl groups are precipitated by their deionization. The shell prevents to shrink to the original state. The fixation of polymer molecules proceeds gradually in the inside with the diffusion of acid through the shell, resulting in the multihollow structure. This formation mechanism is similar to that of an asymmetrical polymer membrane consisting of skin and sponge layers formed by wet cast method [5].

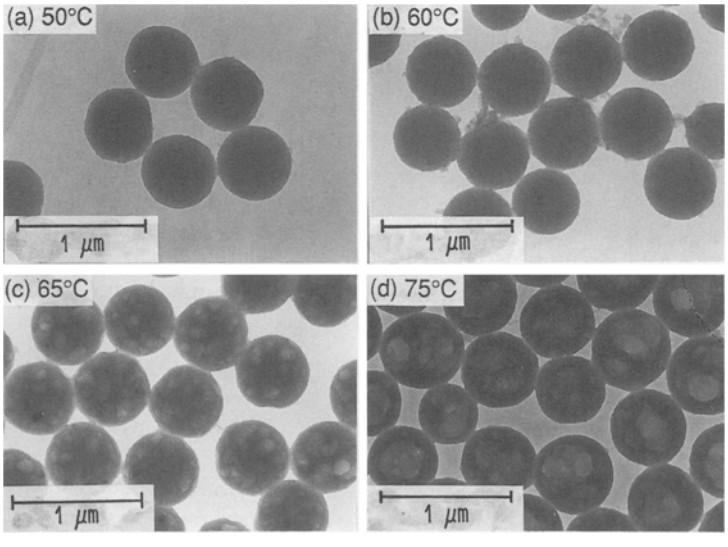


Fig. 3. TEM photographs of P(S-BA-MAA) (74.3/17.0/8.7, molar ratio) treated by the stepwise alkali/acid method (alkali treatment: initial pH 12.2;75 °C; 3 h; acid treatment: initial pH, 2.2; temperature, variable; 3 h)

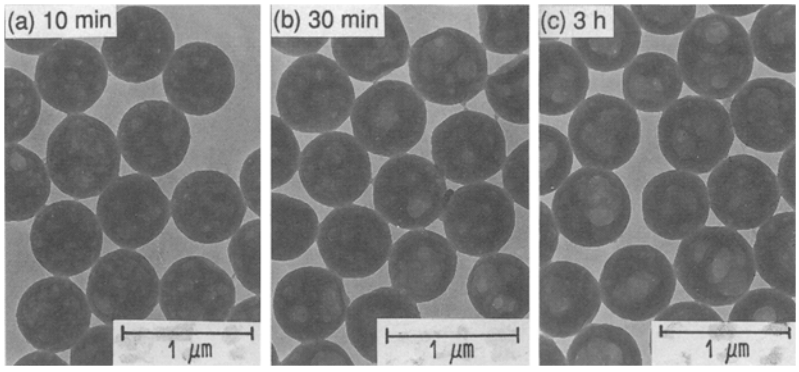


Fig. 5. TEM photographs of P(S-BA-MAA) (74.3/17.0/8.7, molar ratio) particles treated by the stepwise alkali/acid method (alkali treatment: initial pH 12.2; 75 °C; 3 h; acid treatment: initial pH, 2.2; 75 °C; time, variable)

*Acknowledgement*

This research was supported by Grand-in-Aid for Developmental Scientific Research from The Ministry of Education, Science and Culture, Japan.

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Received November 12; 1993;
Accepted January 18, 1994

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