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ORIGINAL CONTRIBUTION

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# Production of submicron-sized multihollow polymer particles having high transition temperatures by the stepwise alkali/acid method

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**Abstract** Submicron-sized multihollow styrene-methacrylic acid (92.6/7.4, molar ratio) copolymer particles having high transition temperature above 100 °C were produced by using the stepwise alkali/acid method proposed by the authors. The original particles were prepared by emulsion copolymerization of styrene and methacrylic acid. The effects of pH, temperature and time in the alkali treatment process as the first step on the multihollow structure were clarified under the same acid treatment conditions.

**Key words** Multihollow particles – emulsion polymerization – morphology – carboxyl group – transition temperature

## Introduction

We have been studying a series of investigations on the production of carboxylated polymer particles in which carboxyl groups are predominantly localized at surfaces. As one way for the purpose, we proposed an alkali treatment method for carboxylated polymer particles in which most carboxyl groups were buried in the inside [1–3].

Throughout these experiments, we found that submicron-sized styrene-butyl acrylate-methacrylic acid terpolymer particles having many hollows in the inside were produced [4]. We named it multihollow particle. Such multihollow particles were produced by stepwise treatments with alkali and acid which was named stepwise alkali/acid method. Since then, the effects of conditions in the alkali [5, 6] and acid [7] treatments on the formation of multihollow structure were examined in detail and a formation mechanism was proposed as follows. First, the original carboxylated particles are swollen with water in the alkali-treatment process. Next, in the early stage of the acid-treatment process, the polymer shell is formed at the particle surface, because the "precipitation" of "soluble" polymer segments containing ionized carboxyl groups are caused by deionization of carboxyl groups. The rigid shell prevents to shrink to the original state. The precipitation and fixation of polymer molecules proceed gradually with the diffusion of acid into the inside of particles, and results in multihollow polymer particles.

In this article, in order to produce multihollow polymer particles having a high glass transition temperature ($Tg$) and to check the formation mechanism, styrene-methacrylic acid copolymer (P(S-MAA)) particles will be treated by the stepwise alkali/acid method. Such particles may be more useful in their applications than that having low $Tg$.

## Experimental

### Materials

Styrene (S) 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 nonylphenylethel nonionic emulsifier (Emulgen 911, Kao Atlas Co.) was used without further purification. Deionized water was distilled.

### Preparation of P(S-MAA) emulsion

P(S-MAA) emulsion was prepared by emulsion copolymerization of S and MAA at 70 °C for 24 h under conditions listed in Table 1. The residual monomers were not detected by gas chromatography. Since this emulsion contained coagulated polymer particles, it was used as original emulsion in the following experiments after its removal by centrifugation. The molar ratio of S/MAA in the original emulsion was determined to be 92.6/7.4, as follows. Methylethylketone (1.44 g) which is good solvent for the copolymer and 2 ml of 1 N KOH aq. solution were stepwise added to 10 g of emulsion (solid content: 14.4%) and stood at room temperature for 24 h. Conductometric back titration was carried out with 0.1 N HCl aq. solution at room temperature to determine the total amount of carboxyl groups.

### Electron microscopy

A JEOL JEM-200CX electron microscope was used for transmission electron microscopic (TEM) observation. 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 a desiccator. The inside structure of the particles was estimated from the observation of the ultrathin cross-section prepared with ultramicrotome after the particles were exposed to ruthenium tetroxide vapor for 30 min. Scanning electron microscopic (SEM) observation was taken with a Hitachi S-2500 scanning electron microscope. Each emulsion was dropped onto an aluminium plate.

**Table 1** Recipe of emulsion polymerization[a]

| Ingredient | | |
|---|---|---|
| Styrene | (g) | 109.9 |
| Methacrylic acid | (g) | 10.1 |
| Emulgen 911 | (g) | 5.5 |
| Potassium persulfate | (g) | 0.24 |
| Water | (g) | 480 |
| $Tg$[b] | (°C) | 104 |

[a] $N_2$; 70 °C; 24 h; stirring rate, 120 rpm.
[b] Measured by differential scanning calorimetry.

### Thermal analysis

$Tg$ of the dried P(S-MAA) was measured to be 104 °C using a differential scanning calorimeter (Seiko I & E SCC-560S) at a heating rate of 10 °C per min.

### Stepwise alkali/acid treatment

The P(S-MAA) emulsion was treated stepwise with alkali and acid as follows.

Alkali treatment: The original emulsion was diluted in 50 mg/l, and adjusted to various pH values with 5 N KOH aq. solution. This emulsion was placed in a 50 ml-capacity Teflon-tube which was put in a stainless steel pressure-resistant vessel and the vessel was dipped in oil bath at various temperatures for different times. After the treatment, each emulsion was cooled by keeping the vessel at room temperature.

Acid treatment: The alkali-treated emulsion was diluted in 10 mg/l. The acid treatment was always carried out under the same conditions: initial pH value, 3.0 (with 1 N HCl); 24 h; 80 °C.

## Result and discussion

Figure 1 shows SEM photographs of the original P(S-MAA) particles (a), the ones after the alkali treatment (b) and the ones after the stepwise alkali/acid treatment (c). The alkali treatment was carried out at 150 °C for 24 h at the initial pH value of 13.5. The original particles had smooth surface, whereas the alkali-treated and stepwise alkali/acid-treated particles had uneven surfaces.

Figure 2 shows TEM photographs of the three kinds of particles. The insides of original and alkali-treated particles were observed to be homogeneous. Whereas, the inside of the stepwise alkali/acid-treated particles had many small regions of low electron density which seems to be based on the hollows.

Figure 3 shows TEM photographs of ultrathin cross-sections of the three kinds of particles. In the original and the alkali-treated particles, the insides were homogeneous. Whereas, it was clearly observed that the stepwise alkali/acid-treated particles had many hollows in the inside.

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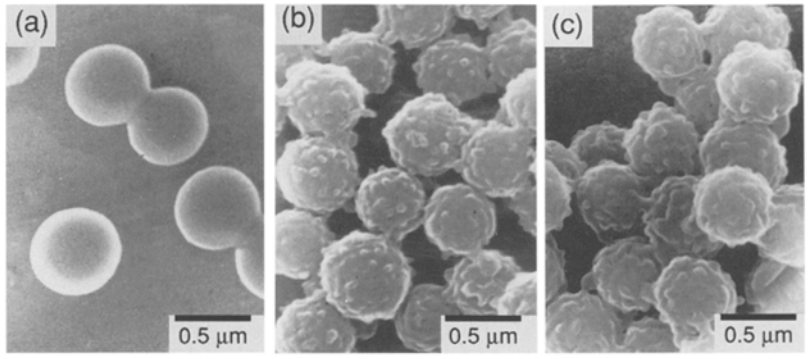


**Fig. 1** SEM photographs of the original P(S-MAA) (92.6/7.4, molar ratio) particles (a), the ones after the alkali treatment (b) and the ones after the stepwise alkali/acid treatment (c). The alkali treatment: 150 °C, 24 h, initial pH value of 13.5; acid treatment: 80 °C, 24 h, initial pH value of 3.0

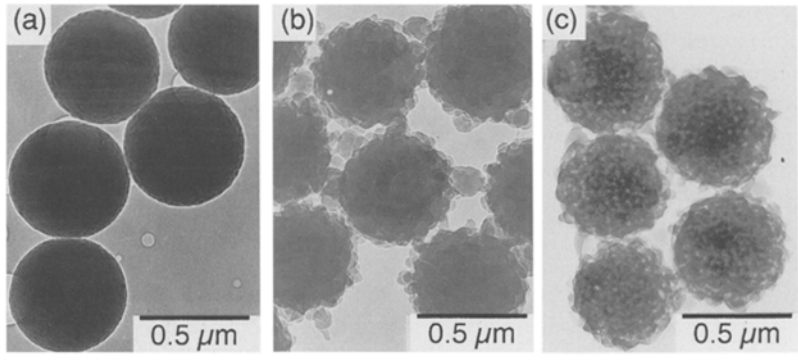


**Fig. 2** TEM photographs of the original P(S-MAA) (92.6/7.4, molar ratio) particles (a), the ones after the alkali treatment (b) and the ones after the stepwise alkali/acid treatment (c). The alkali treatment: 150 °C, 24 h, initial pH value of 13.5; acid treatment: 80 °C, 24 h, initial pH value of 3.0

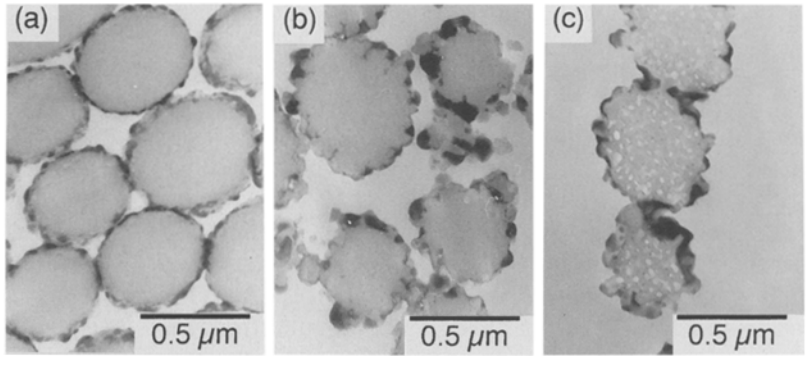


**Fig. 3** TEM photographs of ultrathin cross-sections of the original P(S-MAA) (92.6/7.4, molar ratio) particles (a), the ones after the alkali treatment (b) and the ones after the stepwise alkali/acid treatment (c). The alkali treatment: 150 °C, 24 h, initial pH value of 13.5; acid treatment: 80 °C, 24 h, initial pH value of 3.0. Each particles were exposed to $RuO_4$ vapor for 40 min before cutting

Figure 4 shows TEM photographs of the particles treated for 24 h at the initial pH value of 13.5 in the temperature range from 80° to 180 °C. At the temperatures below 130 °C, no hollow was observed inside the particles. At 140 °C, some particles had hollow structures. Above 140 °C, the multi-hollow structure was observed for all particles. The hollow tended to increase in size and to decrease in number with increasing of the alkali-treatment temperature.

Figure 5 shows TEM photographs of the particles treated for 18, 24 and 48 h at 150 °C in the initial pH value of 13.5. The multihollow structure was not observed in the particles treated for 18 h, but was observed in those for 24 and 48 h. This suggests that there is a minimum alkali treatment time to make the particles swell enough for the formation of multihollow structure.

Figure 6 shows TEM photographs of the particles treated at the initial pH values of 13.0 and 13.5 for 24 h at 150 °C. The multihollow structure was not observed at pH 13.0, but observed at pH 13.5. This seems to be based on a similar reason as just described above.

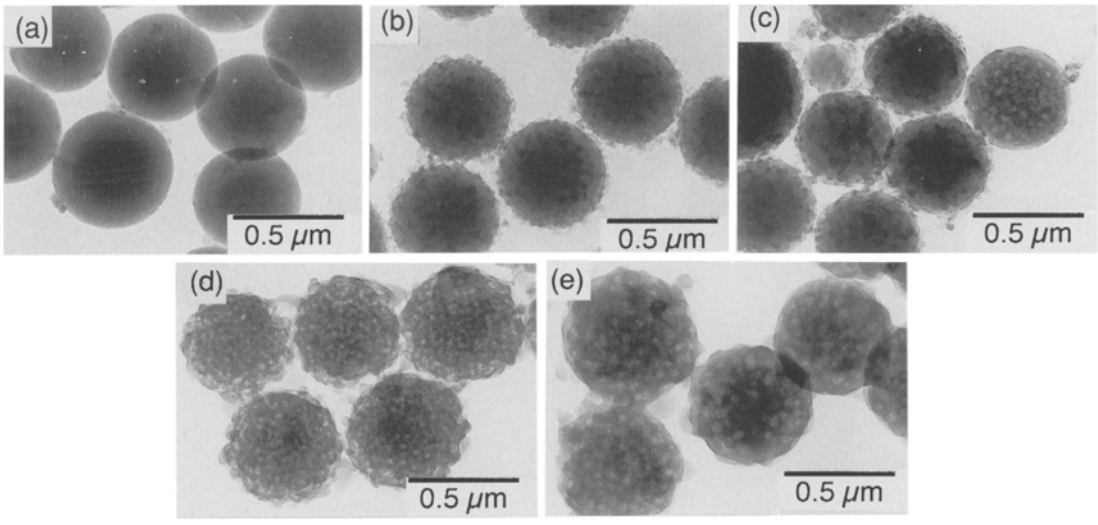


**Fig. 4** TEM photographs of the P(S-MAA) (92.6/7.4, molar ratio) particles after the stepwise alkali/acid treatment. The alkali treatment: 24 h, initial pH value of 13.5, temperatures (°C):(a) 80, (b) 130, (c) 140, (d) 150, (e) 180; acid treatment: 80 °C, 24 h, initial pH value of 3.0

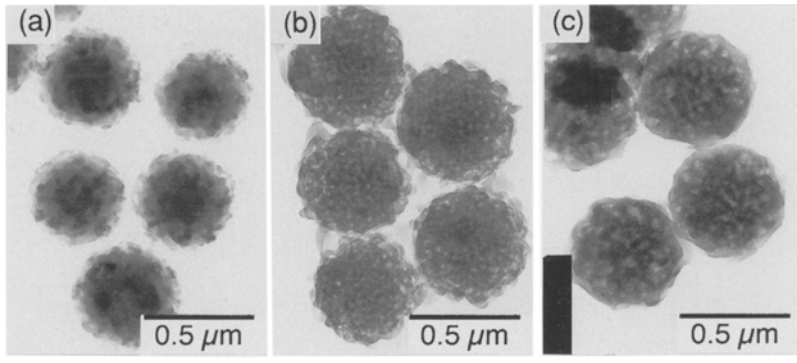


**Fig. 5** TEM photographs of the P(S-MAA) (92.6/7.4, molar ratio) particles after the stepwise alkali/acid treatment. The alkali treatment: 150 °C, initial pH value of 13.5, times (h): (a) 18, (b) 24, (c) 48; acid treatment: 80 °C, 24 h, initial pH value of 3.0

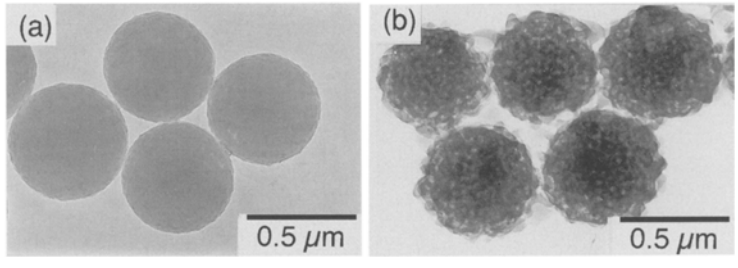


**Fig. 6** TEM photographs of the P(S-MAA) (92.6/7.4, molar ratio) particles after the stepwise alkali/acid treatment. The alkali treatment: 150 °C, 24 h, initial pH values: (a) 13.0, (b) 13.5; acid treatment: 80 °C, 24 h, the initial pH value of 3.0

From these results, it is clear that the initial pH value, temperature and time in the alkali treatment process have a great influence on the formation of the multihollow structure. These behaviors were in accord with those observed in the styrene-butyl acrylate-methacrylic acid terpolymer particles [4–7].

In this way, multihollow P(S-MAA) (92.6/7.4, molar ratio) particles having high $Tg$ above 100 °C were produced by the stepwise alkali/acid method. The obtained data support the mechanism of forming multihollow particles by the stepwise alkali/acid method which we proposed [5].

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