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SHORT COMMUNICATION

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Production of submicron-sized multihollow polymer particles by alkali/cooling method

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Abstract Submicron-sized styrene–methacrylic acid copolymer particles, which were produced by emulsion copolymerization, were changed to those having multihollow structure by treating stepwise the emulsion as follows. First alkali treatment was carried out at higher temperature than the glass transition temperature and subsequently the emulsion was cooled by keeping it at room temperature. This was named "alkali/cooling method". The effects of methacrylic acid content, pH, time and temperature in the alkali treatment on the formation of multihollow structure were clarified.

Key words Multihollow particles – emulsion polymerization – morphology – carboxyl group – alkali swelling

Introduction

Recently, we found that submicron-sized styrene-butyl acrylate-methacrylic acid terpolymer particles produced by emulsion copolymerization 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, the effects of various factors in the alkali [2, 3] and acid [4] treatment processes on the formation of multihollow structure were examined in detail. Moreover, multihollow styrene-methacrylic acid copolymer (P(S-MAA)) particles having high glass transition temperature (*Tg*), were produced by the stepwise alkali/acid method [5].

In this article, it will be reported that multihollow polymer particles were produced by the alkali treatment at a high temperature and subsequent cooling treatment.

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 potassium hydroxide was used without further purification. Commercial grade nonionic polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 911, Kao Atlas Co.) was used without further purification. Deionized water was distilled.

Preparation of P(S-MAA) particles

P(S-MAA) particles having various MAA contents were prepared by emulsion copolymerizations at 70 °C under conditions listed in Table 1. In all emulsions, the residual monomers were not detected by gas chromatography and there were no coagulated particles. Therefore, the molar ratio of P(S-MAA) was calculated from the polymerization recipe.

Electron microscopy

A JEOL JEM-200CX electron microscope was used for transmission electron microscopic (TEM) observation.

Table 1 Recipes of emulsion polymerization[a)]

Acid content	(mol%)	6	8	10	12	14
Styrene	(g)	57.0	56.0	55.0	53.9	52.9
Methacrylic acid	(g)	3.0	4.0	5.0	6.1	7.1
Potassium persulfate	(g)	0.24	0.24	0.24	0.24	0.24
Emulgen 911	(g)	2.5	3.3	4.0	4.8	5.5
Water	(g)	540	540	540	540	540
D_w[b)]	(nm)	512	422	438	398	494
Tg[c)]	(°C)	105	106	108	110	112

[a)] N_2; 70 °C; 24 h; stirring rate, 120 rpm.
[b)] Weight averaged diameter were measured by dynamic light scattering spectroscopy.
[c)] Calculated from the monomer compositions to apply Fox's equation.

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-sections prepared with ultramicrotome after the particles exposed to ruthenium tetroxide vapor for 30 min.

Alkali treatment

The original P(S-MAA) emulsion was treated with alkali as follows. The original emulsion was diluted in 0.5 g/l, and adjusted to various pH values with 1 N KOH aqueous solution. This emulsion was placed in a 50 ml-capacity stainless steel pressure-resistant vessel having a polytetrafluoroethylene inner container and the vessel was dipped in oil bath at various temperatures for different times. After the treatment, each emulsion was cooled by keeping it at room temperature. Hereafter, these treatments will be called "alkali/cooling treatment".

Result and discussion

Figure 1 shows TEM photographs of the original P(S-MAA) (86/14, molar ratio) particles. The insides of the particles were homogeneous. Other P(S-MAA) particles having different MAA contents also had homogeneous structures (the photographs were omitted).

Figure 2 shows TEM photographs of P(S-MAA) particles having the various MAA contents after the alkali/cooling treatment. The alkali treatment was carried out at 150 °C for 24 h at the initial pH value of 12.0. The insides of the treated particles having MAA contents of 6 and 8 mol% were observed to be homogeneous. Whereas, in those above 10 mol%, low contrast regions were observed. The low contrast seems to be based on the hollows inside the particles.

Figure 3 shows TEM photographs of the ultrathin cross-sections of three kinds of particles. In the original P(S-MAA) (86/14, molar ratio) particles and the treated P(S-MAA) (94/6, molar ratio) particles, the insides were homogeneous. Whereas in the treated P(S-MAA) (86/14, molar ratio) particles, hollow structure was clearly observed. This indicates that hollow structure particles were obtained by alkali/cooling treatment. In this article, a large number of treated particles had a single hollow structure, because the treatment conditions were harder than those in the previous articles [2]. In fact, it is confirmed that the multihollow particles were prepared under mild conditions, which will be reported in a following article.

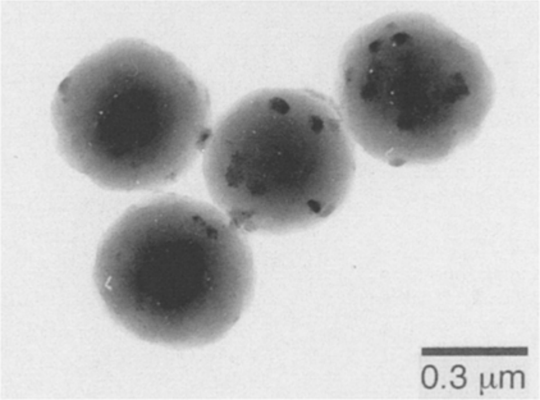

Fig. 1 TEM photograph of the original P(S-MAA) (MAA content: 14 mol%) particles

Figure 4 shows the relationship between the MAA content and the expansion of particle volume by the alkali/cooling treatment in which the alkali treatment was carried out at 150 °C for 24 h at the initial pH value of 12.0. The expansions of particle volume were determined with the comparison between the volume of original particles and treated particles which were measured by dynamic light scattering spectroscopy at room temperature. An increase in the expansion value indicates an increase in the total volume of hollows inside the particle. At the MAA

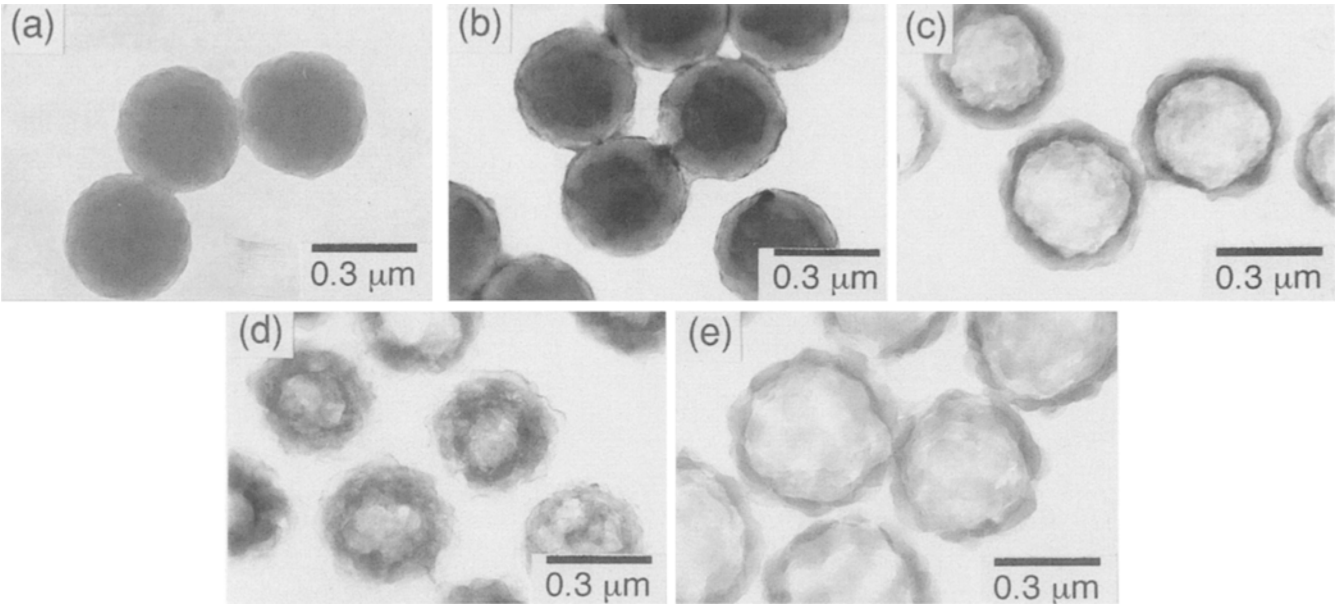

Fig. 2 TEM photographs of P(S-MAA) (MAA content (mol%): **A** 6, **B** 8, **C** 10, **D** 12, **E** 14) particles after the alkali/cooling treatment: the alkali treatment: 150 °C, 24 h, initial pH value 12.0

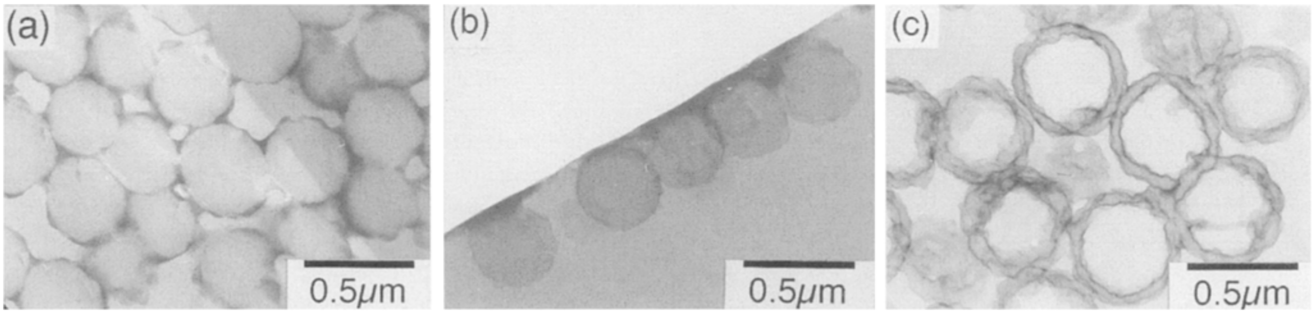

Fig. 3 TEM photographs of ultrathin cross-sections of the P(S-MAA) particles before **A** and after **B**, **C** the alkali/cooling treatment: MAA content (mol%): b) 6; a, c) 14: the alkali treatment: 150 °C, 24 h, initial pH value 12.0

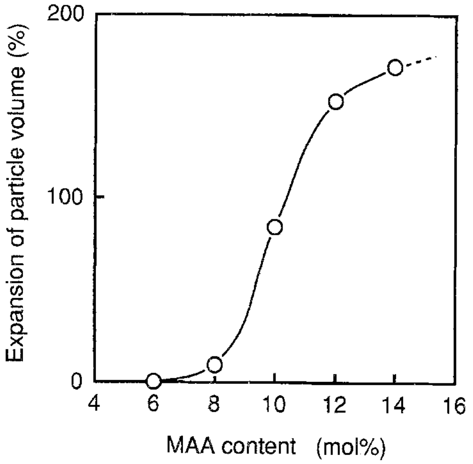

Fig. 4 Relationship between the MAA content and the expansion of P(S-MAA) particle volume by the alkali/cooling treatment: the alkali treatment: 150 °C, 24 h, initial pH value 12.0

contents below 8 mol%, there was almost no expansion. This is in accord with the result of Fig. 2. Above 10 mol%, the total hollow volume increased with increasing of the MAA content.

Figure 5 shows the relationship between the alkali treatment time at 100 °C at the initial pH value of 12.0 and the expansion of particle volume by the alkali/cooling treatment. The expansion increased with an increase in the treatment time, and leveled off after 12 h. The saturated value seems to be based on the limit of the particle swelling under the conditions.

Figure 6 shows the relationship between the initial pH value of alkali treatment for 24 h at 150 °C and the expansion of particle volume by the alkali/cooling treatment. At the pH values below 10.5, there was almost no expansion. Whereas, above 11, the particle volume drastically increased, and had a maximum value at the pH value of 11.5.

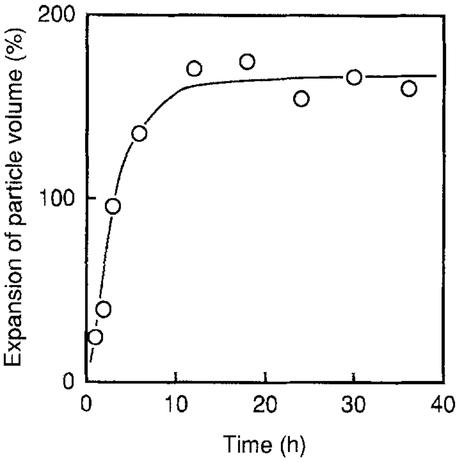

Fig. 5 Relationship between the alkali treatment time at 100 °C in the initial pH value of 12.0 and the expansion of P(S-MAA) (MAA content: 14 mol%) particle volume by the alkali/cooling treatment

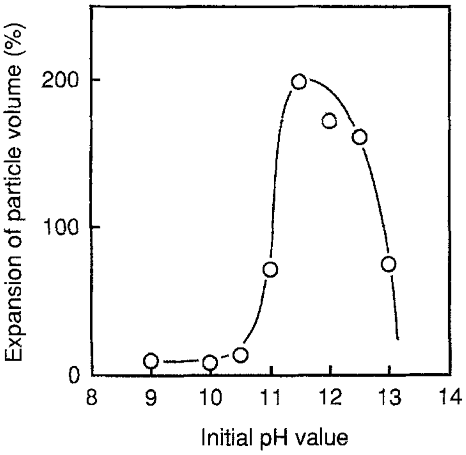

Fig. 6 Relationship between the initial pH value of alkali treatment at 150 °C for 24 h and the expansion of P(S-MAA) (MAA content: 14 mol%) particle volume by the alkali/cooling treatment

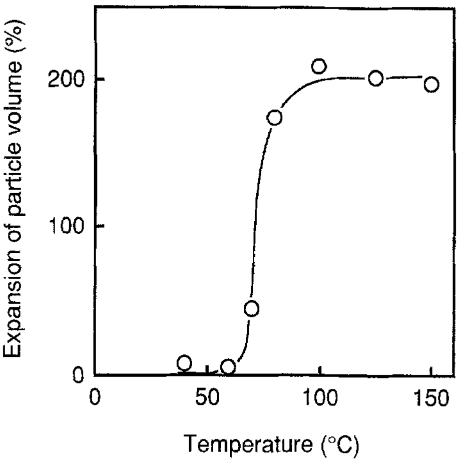

Fig. 7 Relationship between the alkali treatment temperature for 24 h in the initial pH value of 11.5 and the expansion of P(S-MAA) (MAA content: 14 mol%) particle volume by the alkali/cooling treatment

The pH values after the treatment were always lower than the initial pH value. The amount of KOH consumed before and after the treatment, which was calculated from the difference of initial and final pH values, always corresponded to the amount of carboxyl groups inside the particles. This suggests that the carboxyl groups inside the particle were not neutralized before the heat treatment. The amount of KOH required to attain the initial pH of 11.5 was in accord with the total amount of carboxyl groups in the emulsion. This is the reason why the volume expansion had maximum value at the initial pH value of 11.5.

Figure 7 shows the relationship between the alkali treatment temperature for 24 h at the initial pH value of 11.5 and the expansion of particle volume by the alkali/cooling treatment. The particle volume drastically increased with an increase in the treatment temperature around 70 °C and leveled off at 100 °C. This seems to be based on the fact that the *Tg* of the copolymer in the particles decreased from 112° to about 70 °C by the plasticization due to water adsorption [6].

From these results, it is clear that multihollow P(S-MAA) particles can be produced by the alkali/cooling treatment. Hereafter the treatment is named the alkali/cooling method. The cooling treatment seems to correspond to the acid treatment in the stepwise alkali/acid method [1–4], which operates the fixation of polymer molecules within the alkali swollen particles. This will be clarified in a future article.

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