Preparation of Multihollow Polymer Particles by the Alkali/Cooling Method under Partial Neutralization Conditions[a]

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Summary: Heterogeneity in the formation of multihollow structure among submicron-sized styrene-methacrylic acid copolymer particles, which were produced by batch emulsion copolymerization, by the alkali/cooling method under partial neutralization of carboxyl groups was investigated. There was a threshold of the acid content to form the multihollow structure. The heterogeneity among the particles was based on the heterogeneity of the acid content among the original particles.

Keywords: emulsion polymerization; thermoplastics

Introduction

Submicron-sized polymer particles produced by emulsion polymerization have been used as films in many industrial fields, for example, in painting, printing, and manufacturing. Recently, attention has been focused on applying it as a particle state directly. For example, thermoplastic polymer particles containing one hollow at the center, which were prepared by alkali-swelling of carboxylated polymer particles having core-shell structure [1], have received much attention. Such particles are commercially supplied as a hiding or opacifying agent in coating and molding composition.

It was found that styrene-butyl acrylate-methacrylic acid terpolymer particles produced by emulsion copolymerization were changed to those having many hollows inside the particles by stepwise treatments with alkali and acid [1], which was named the stepwise alkali/acid method. In following articles, the effects of some factors in the alkali [2, 3] and acid [4] treatment processes on the formation of the multihollow structure were examined, and the formation mechanism of the multihollow structure was proposed [5, 6]. Furthermore, styrene (S)-methacrylic acid (MAA) copolymer [P(S-MAA)] particles, in which the MAA content exceeded 8 mol%, were changed to hollow particles by alkali treatment at higher temperature than glass transition temperature, following by being cooled to room temperature, which was named the

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alkali/cooling method [7]. Effects of various factors on the formation of the multihollow structure were clarified [8-10]. Throughout these studies, a mixture of hollow and non-hollow particles in the alkali/cooling-treated emulsion under partial neutralization of carboxyl groups was observed.

In this article, some factors giving the heterogeneity in the formation of the hollow structure among the particles and the reason will be clarified.

Experimental

Materials

S and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate (Nacalai Tesque Co., Kyoto, Japan) was purified by recrystallization. Commercial grade polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 911, Kao Co., Tokyo, Japan) was used without further purification. Deionized water with a specific resistance of 5×10^6 Ω.cm was distilled. The other materials were used as received from Nacalai Tesque Co.

P(S-MAA) particles

Original P(S-MAA) particles were produced by emulsion copolymerization under the conditions listed in Table 1. The conversion was above 95% by gravimetric measurement. The particles were centrifugally washed five times at 12000 rpm {relative centrifugal force (RCF), 11000 *g*} with distilled water.

Table 1. A recipe for the production of styrene-methacrylic acid copolymer [P(S-MAA)] particles by emulsion copolymerization (N_2; 70°C; 24 h).

Ingredients		
Styrene	(g)	55.0
Methacrylic acid	(g)	5.0
Potassium persulfate	(g)	0.24
Emulgen 911	(g)	4.0
Water	(g)	540

Abbreviation: Emulgen 911, polyoxyethylene nonylphenylether nonionic emulsifier

Alkali/cooling treatment

Degree of neutralization of the carboxyl groups was adjusted by changing the amount of the original particles added to KOH aqueous solution of which pH value was 12.5. The degree of neutralization was defined by molar ratio of the carboxyl groups in the original particles to KOH in the aqueous medium. The emulsions, of which total volumes were about 10 mL, were placed in 12-mL capacity glass sealed tubes, and the tubes were dipped in an oil bath at various temperatures for 1 h. After the treatment, each emulsion was cooled in air to room temperature. Hereafter, these treatments will be called the alkali/cooling treatment.

MAA content in P(S-MAA)

MAA content in each P(S-MAA) was calculated from ^{1}H NMR spectrum in pyridine-d_5, after methylation of carboxyl groups with diazomethane. The ^{1}H NMR spectrum was obtained with a Bruker DPX250 NMR spectrometer operating at 250 MHz with 128 scans at room temperature.

Electron microscopy

A JEOL JEM-2010 electron microscope was used for transmission electron microscope (TEM) observation. Percentage of the hollow particles in the alkali/cooling-treated particles was determined by counting at least 300 particles.

Results and Discussion

Figure 1 shows TEM photographs of the original P(S-MAA) particles produced by emulsion copolymerization under the conditions listed in Table 1, and of the alkali/cooling-treated particles (60% neutralization; initial pH 12.5; 100°C; 1 h). In Fig. 1 (a), the inside of the original particles was homogeneous and weight-average diameter (Dw) and polydispersity (Dw/Dn)

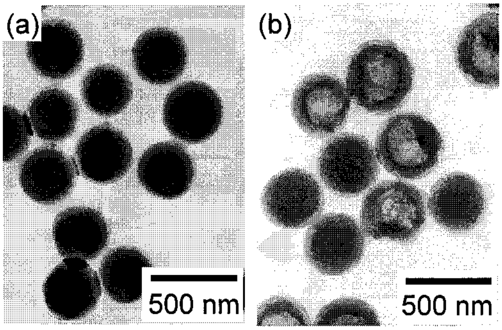

Figure 1. TEM photographs of the original styrene-methacrylic acid copolymer [P(S-MAA)] particles (a) produced by emulsion copolymerization under the conditions listed in Table 1, and of the alkali/cooling-treated ones (60% neutralization; initial pH 12.5; 100°C; 1 h).

were, respectively, 430 nm and 1.01 by dynamic light scattering measurement. The MAA content in the monomers before the emulsion copolymerization was 10.0 mol%, but that in the original particles after the centrifugal washing was 8.0 mol%. This difference seems to be based on dissolution of a part of P(S-MAA) having high MAA content into aqueous medium. In Fig. 1 (b), both the particles having hollow and non-hollow structures were observed in the alkali/cooling-treated emulsion. With an increase in the degree of neutralization, the percentage of hollow particles in the alkali/cooling-treated particles increased, but did not reach to 100% even above 100% neutralization.

Figure 2 shows the relationship between the alkali treatment temperature and the percentage of the hollow particles in the alkali/cooling-treated P(S-MAA) particles (100% neutralization; initial pH 12.5; 1 h). The percentage of the hollow particles increased with an increase in the treatment temperature above 40°C, and reached to 100% above 120°C. This result indicates the reason why a part of the original particles did not turn to hollow particles under low degree of neutralization and low temperature is based on insufficient mobility of the base polymer. That is, the above results suggest that there is heterogeneity in MAA content among the original P(S-MAA) particles which were produced by a general batch emulsion copolymerization. In order to clarify the chemical heterogeneity among the particles, the MAA contents in the hollow and non-hollow particles were measured after separation of them. For the separation, an aqueous dispersion of the alkali/cooling-treated P(S-MAA) particles after the centrifugal washing was further centrifuged with distilled water at 14000 rpm (RCF, 15000 *g*) for 10 min. The centrifuged emulsion consisted of three layers: top layer which was slightly clouded and contained

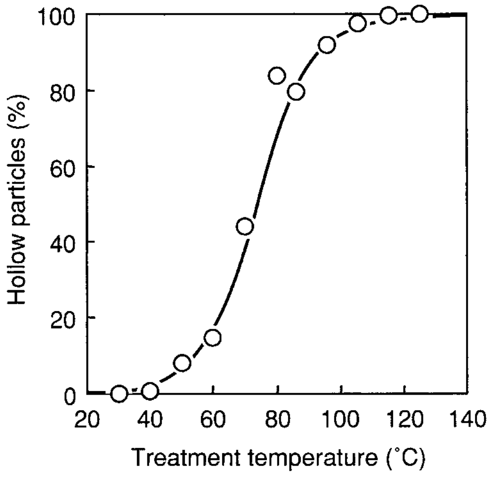

Figure 2. Relationship between the treatment temperature and the percentages of the hollow P(S-MAA) particles in the alkali/cooling-treated ones (initial pH 12.5; 100% neutralization; 1 h).

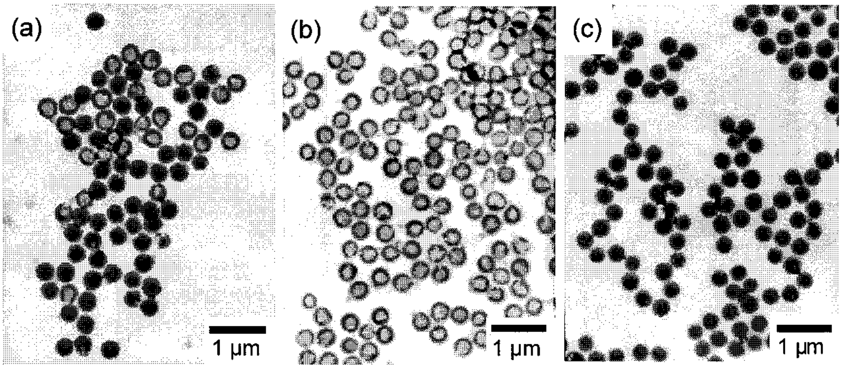

Figure 3. TEM photographs of the alkali/cooling-treated P(S-MAA) particles (a) (20% neutralization; initial pH 12.5; 100°C; 1 h) and of those in slightly clouded top layer (b) and in bottom layer (c) after the centrifugal separation.

only hollow particles; middle layer which was clouded and contained both hollow and non-hollow particles; bottom layer which mainly contained precipitated non-hollow particles. The top layers separated were collected, and centrifugally washed three times with distilled water at 17000 rpm (RCF, 23000 *g*) for 20 min. The precipitated particles in the bottom layer were collected, and centrifugally washed five times with distilled water at 12000 rpm (RCF, 11000 *g*) for 10 min to remove the hollow particles completely.

Figure 3 shows TEM photographs of the alkali/cooling-treated P(S-MAA) particles (20% neutralization; initial pH 12.5; 100°C; 1 h) and of those in the slightly clouded top

Table 2. MAA contents[a)] in the original P(S-MAA) particles[b)] and those having hollow and non-hollow structures, and copolymers dissolved in KOH aqueous solution after the alkali/cooling treatment.[c)]

	MAA content (mol%)	
Original particles	8.0	(8.0)[d)]
Hollow particles	6.9	(8.8)[d, e)]
Non-hollow particles	7.9	(7.9)[d)]
Dissolved polymers	29.5	

[a)] Determined by ^{1}H NMR after methylation with diazometane

[b)] Produced by emulsion copolymerization of S and MAA (MAA, 10 mol%) under the conditions listed in Table 1

[c)] 20% neutralization; initial pH 12.5; 100°C; 1 h

[d)] MAA content in each particle before the alkali/cooling treatment

[e)] Calculated by averaging the MAA contents in the hollow particles (A) and in the dissolved copolymers (B) (A/B: 91.8/8.2, w/w) layer and in the bottom layer after the centrifugal separation. Figures 3b and 3c indicate that the separations of the hollow and the non-hollow particles were successfully carried out by the controlled centrifugation. In the neutralization range from 10% to 100%, the only hollow particles were observed in the top layer. On the other hand, the only non-hollow particles were observed in the bottom layer up to 30% neutralization, and the percentage of the hollow particles, which may exist in the lower layer just before the centrifugal separation, increased with the increase in the degree of neutralization above 30%.

Table 2 shows the MAA contents in the original P(S-MAA) particles, those having hollow and non-hollow structures, and the copolymers dissolved in the KOH aqueous solution after the alkali/cooling treatment (20% neutralization; initial pH 12.5; 100°C, 1 h). Unexpectedly, the MAA content in the non-hollow particles was larger than that in the hollow particles, and both of them were smaller than that in the original particles. This result seems to be based on an elusion of P(S-MAA) molecules having high MAA content from the original particle into the KOH aqueous solution by the alkali/cooling treatment.

Figure 4 shows the relationship between the percentage of the hollow particle in the alkali/cooling-treated particles and the weight percentage of P(S-MAA) dissolved in the KOH aqueous solution in the alkali/cooling process under different conditions. The weight percentage of the dissolved polymer increased linearly with the increase in the percentage of the hollow particles, and the amount of the dissolved copolymer at 100% hollow particles was 8.2 wt%. This result indicates that the copolymer

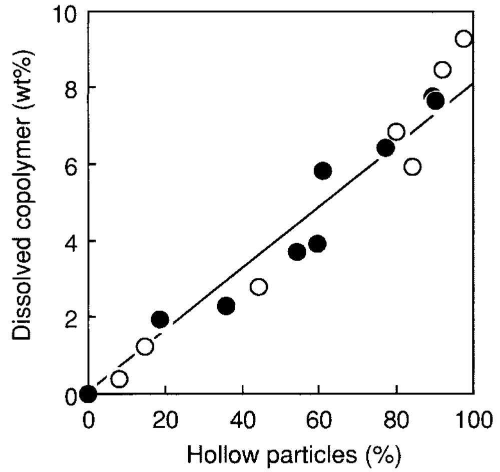

Figure 4. Relationship between the percentage of the hollow P(S-MAA) particle in the alkali/cooling-treated particles and the weight percentage of P(S-MAA) dissolved in the KOH aqueous solution in the alkali/cooling process at initial pH 12.5 for 1 h under different degrees of neutralization at 100°C ○, and at different treatment temperatures under 100% neutralization ●

having high MAA content dissolved only from the hollow particle. Accordingly, the MAA content in the hollow particles before the alkali/cooling treatment should be calculated to be 8.8 mol% by averaging those in the dissolved copolymer (29.5 mol%) and in the hollow particles (6.9 mol%) after the treatment, and the MAA content in non-hollow particles before the treatment should be the same as that after the treatment. The calculated MAA contents before the alkali/cooling treatment were listed in parentheses in Table 2. This result suggests that the MAA content in the original particles, which turned to the hollow particles, was larger than that in the other original particles, which did not turn to hollow particles after the alkali/cooling treatment (20% neutralization; initial pH 12.5; 100°C, 1 h). In other words, it is clarified that the MAA contents in the P(S-MAA) particles produced by the general batch emulsion copolymerization were heterogeneous among the particles.

The degree of heterogeneity should be quantitatively evaluated by repeating the measurement of the MAA content in the particles after the fractionations utilizing the alkali/cooling method and the centrifugal separation, because the only particles having more than certain MAA content turns to hollow particles by the alkali/cooling treatment. For the practical evaluation of the heterogeneity in the MAA content among the P(S-MAA) particles, summative fractionation, which is similar to Spencer method [11] used for analytical evaluation of distribution of molecular weight, was carried out as follows. First, the alkali treatments were carried out at different temperatures, and after cooling, the percentages and the average MAA contents in the hollow particles were measured. Based on the changes in the percentage and the MAA content by rising the treatment temperature, the fractionation was analytically achieved.

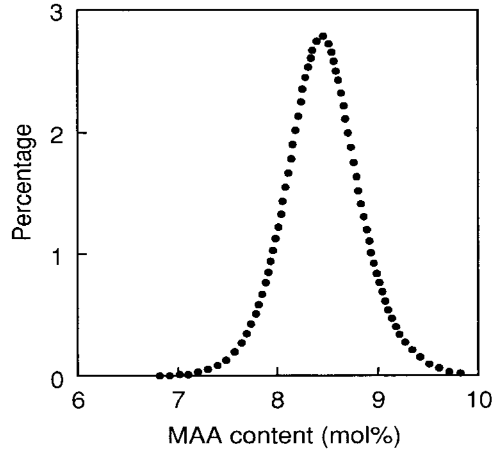

Figure 5. Distribution of the MAA content among P(S-MAA) particles produced by emulsion co-polymerization under the conditions listed in Table 1.

Figure 5 shows the result. The number-average MAA content (8.4 mol%) in the P(S-MAA) particles obtained from Fig. 5 was almost equal to that (8.0 mol%) obtained by the ^{1}H NMR measurement for the purified original particles before the alkali/cooling treatment.

From the above results, it is concluded that the only P(S-MAA) particle having more than a certain MAA content, which depends on the degree of neutralization and alkali treatment temperature, turned to hollow particle by the alkali/cooling treatment. In addition, it is clarified that the MAA content in the P(S-MAA) particles produced by the general batch emulsion copolymerization was heterogeneous among the particles. To our knowledge, there has been no report dealing in such heterogeneity among carboxylated polymer particles produced by bathch emulsion copolymerization. This topic must be important to develop not only production technology of functional polymer particles, but also more detailed description of the kinetics of emulsion copolymerization. Therefore, this will be discussed more in detail in a future.

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