Colloid Polym Sci (2002) 280: 822–827
DOI 10.1007/s00396-002-0686-z

ORIGINAL CONTRIBUTION

Masayoshi Okubo
Masahiro Okada
Kenjin Shiba

Heterogeneity among multihollow polymer particles prepared by the alkali/cooling method under partial neutralization conditions

Received: 17 October 2001
Accepted: 18 February 2002
Published online: 8 May 2002
© Springer-Verlag 2002

M. Okubo (✉) · M. Okada · K. Shiba
Graduate School of Science
and Technology, Kobe University,
Kobe 657–8501, Japan
E-mail: okubo@cx.kobe-u.ac.jp

Abstract Heterogeneity in the formation of multihollow structure among styrene-methacrylic acid copolymer particles, which were produced by emulsion copolymerization, by the alkali/cooling method under partial neutralization conditions with potassium hydroxide was investigated. There was a threshold acid content to form the multihollow structure. The heterogeneity among the multihollow particles was based on the heterogeneity of acid contents among the original particles.

Keywords Multihollow · Particle · Alkali/cooling method · Degree of neutralization · Emulsion polymerization

Introduction

Submicron-sized polymer emulsions prepared by emulsion polymerization have been used as films in many industrial fields, for example, in painting, printing, and manufacturing. Moreover, recently, attention has been focused on applying the particles directly. For example, thermoplastic styrene (S)/acrylic polymer particles containing one hollow at the center, which were produced by alkali-swelling of carboxylated polymer particles having core-shell structure [1], have received much attention. The hollow is filled with water in the polymer emulsion, but with air in the dry state. 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 [2], which was named the stepwise alkali/acid method. In following articles, the effects of some factors in the alkali [3, 4] and acid [5] treatment processes on the formation of the multihollow structure were examined in detail. Moreover, multihollow styrene-methacrylic acid copolymer [P(S-MAA)] particles having high glass transition temperature (Tg) were also prepared by the stepwise alkali/acid method [6], and the formation mechanism of multihollow structure was proposed [7, 8]. Furthermore, it was found that the P(S-MAA) particles having a certain methacrylic acid (MAA) content were changed to those having hollow structure by the alkali treatment at higher temperature than Tg, following by being cooled to room temperature, which was named alkali/cooling method [9], and effects of various factors on the formation of multihollow structure were clarified [10, 11]. Throughout these studies, a mixture of hollow and non-hollow P(S-MAA) particles in the alkali/cooling-treated emulsion under partial neutralization conditions with potassium hydroxide was prepared.

In this article, some factors giving the heterogeneity in the formation of 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. Analytical grade KOH and HCl, and guaranteed reagent grade tetrahydrofuran (THF), diethylether and acetic acid, and specially prepared reagent grade

N-methyl-*N′*-nitro-*N*-nitrosoguanidine were used as received from Nacalai Tesque Co. 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.

Production of original 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 original particles were centrifugally washed five times at 12,000 rpm [relative centrifugal force (RCF), 11,000 *g*] with distilled water. In following experiments the centrifugal particles were used. Weight-average hydrodynamic diameter (D_w) of the particles was measured at 10 ppm concentration by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Kyoto, Japan) with the data at the light-scattering angle of 90° at room temperature. Weight-average molecular weight (M_w) of the original particles was measured by a gel permeation chromatography (GPC). Calibration was performed with polystyrene standards using THF as the eluent.

Alkali/cooling treatment. Degree of neutralization was adjusted by changing the amount of the original particles added to the KOH aqueous solution of which pH value was 12.5. The degree of neutralization was defined by the following equation:

$$\text{Degree of neutralization } (\%) = M_{KOH}/M_{COOH} \times 100 \qquad (1)$$

where M_{KOH} is the total molar quantity of KOH in the aqueous medium, M_{COOH} is the total molar quantity of the carboxyl groups in the original particles added to the KOH aqueous solution. The emulsions, of which total volume were about 10 ml, were placed in 12-ml capacity glass sealed tubes, and the tubes were dipped in 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 alkali/cooling treatment.

Amount of dissolved P(S-MAA). Supernatants obtained by centrifugation of the alkali/cooling-treated P(S-MAA) emulsion ten times at 16,000 rpm (RCF, 20,000 *g*) for 10 min with KOH aqueous solution, of which pH value was 12.0, were collected. After that, in order to precipitate the copolymer dissolved in the collected supernatant, the pH value was adjusted to 2.0 with 1 N HCl aqueous solution. Weight percentage of the dissolved copolymer to total treated particles was calculated by measuring gravimetrically the weight of the precipitated copolymer after washed thoroughly with distilled water.

Table 1 A recipe for the production of styrene-methacrylic acid copolymer [P(S-MAA)] particles by emulsion copolymerization[a]

Ingredients		
Styrene (S)	(g)	55.0
Methacrylic acid (MAA)	(g)	5.0
Potassium persulfate	(g)	0.24
Emulgen 911	(g)	4.0
Water	(g)	540
MAA content[b]	(mol%)	8.0
M_w[c]	($\times10^6$ g/mol)	1.3
M_w/M_n[d]		5.0
D_w[e]	(nm)	430
D_w/D_n[f]		1.01

[a] In flask: N_2; 70°C; 24 h; stirring rate, 120 rpm

[b] Measured by ^{1}H NMR after methylation with diazomethane

[c] Weight-average molecular weight measured by gel permeation chromatography (GPC)

[d] Number-average molecular weight measured by GPC

[e] Weight-average hydrodynamic diameter measured by dynamic light scattering (DLS)

[f] Number-average hydrodynamic diameter measured by DLS

Abbreviations: Emulgen 911, polyoxyethylene nonylphenylether nonionic emulsifier

Methylation of carboxyl groups in P(S-MAA). The original P(S-MAA) particles, those having hollow and non-hollow structures, and the copolymer dissolved in the alkali/cooling process were dried at room temperature, and dissolved in THF at 1 wt%. Subsequently, the carboxyl group in each P(S-MAA) was methylated with diazomethane as follows. For generation of diazomethane, 1 g of *N*-methyl-*N′*-nitro-*N*-nitrosoguanidine was added into a mixture of diethylether (10 ml) and 40% KOH aqueous solution (4 ml) in a test tube at 0 °C. The yellow diazomethane solution with diethylether was added to the polymer THF solution until the polymer solution became pale yellow. In order to consume the excessive diazomethane in the polymer solution, acetic acid was added until the solution became transparent again. Each methylated P(S-MAA) was precipitated in a large amount of methanol, washed thoroughly with methanol and water in sequence, and dried at room temperature.

MAA content in P(S-MAA). Each methylated P(S-MAA), that is, styrene-methyl methacrylate (MMA) copolymer was dissolved in pyridine-d_5 at 5 wt%, and the solution was poured into a 5-mm NMR tube. ^{1}H NMR spectrum was obtained with a Bruker DPX250 NMR spectrometer operating at 250 MHz with 64 scans at room temperature. Chemical shift was obtained relative to 2- and 6-protons of pyridine at 8.7 ppm. The MAA content in each P(S-MAA) before the methylation was calculated from the following equations:

$$A_{\text{styrene}} = (A_2 - 3/2A_1)/5 \qquad (2)$$

$$A_{MAA} = (A_3 - 3A_{\text{styrene}})/8 \qquad (3)$$

$$\text{MAA content (mol\%)} = A_{MAA}/(A_{MAA} + A_{\text{styrene}}) \times 100 \qquad (4)$$

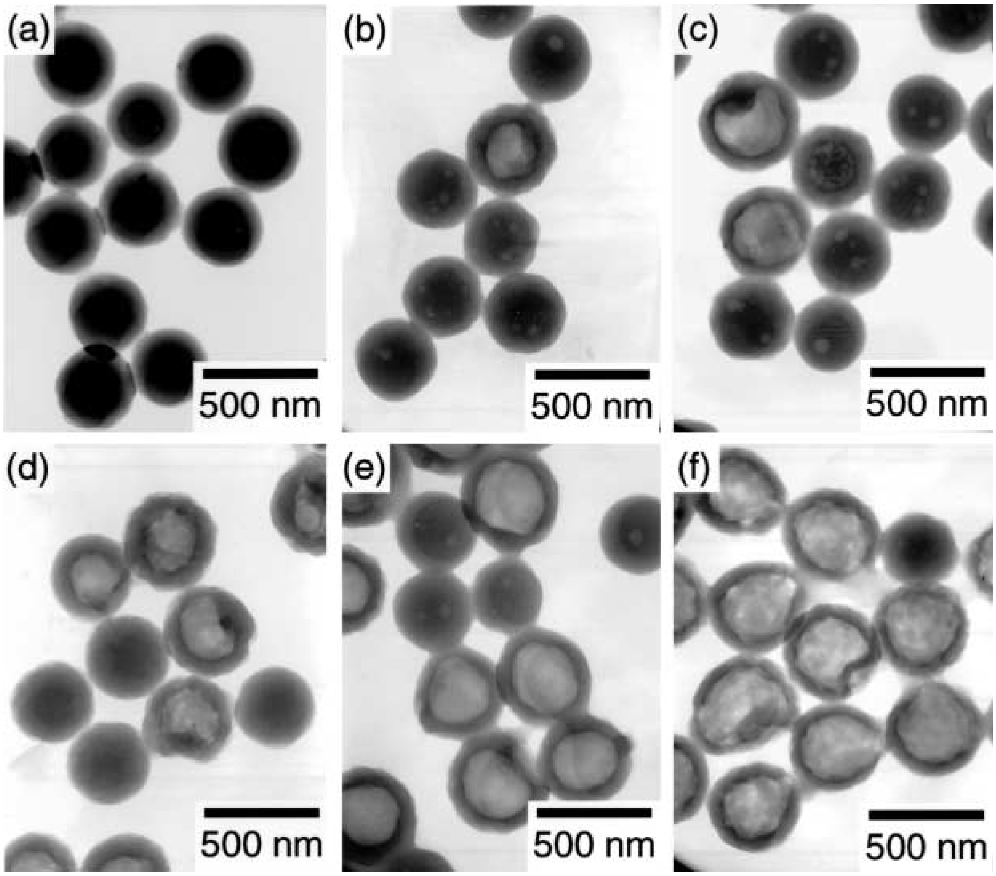
where A_{styrene} and A_{MAA} refer to the molar ratios of styrene and methacrylic acid units in the copolymer to pyridine, respectively, A_1, A_2, and A_3 refer to the integrals of peaks at 8.7 ppm (2- and 6-protons of pyridine), 7.7–6.3 ppm (3-, 4-, and 5-protons of pyridine, and phenyl protons of styrene units), and 3.9–0.3 ppm (methoxy, α-methyl, and methylene protons of MMA units, and methine and methylene protons of styrene units), respectively.

Electron microscopy. A JEOL JEM-2010 electron microscope was used for transmission electron microscope (TEM) observation. Each P(S-MAA) emulsion was diluted to about 50 ppm, and a drop was placed onto a carbon-coated grid and allowed to dry at room temperature in a desiccator. Percentage of hollow particles in the alkali/cooling-treated ones 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 ones (initial pH 12.5; 100 °C; 1 h) under different degrees of neutralization. The degree of neutralization, which was defined by Eq. (1), was adjusted by changing the amount of the original particles added

Fig. 1a–f TEM photographs of: **a** the original P(S-MAA) (MAA, 8.0 mol%) particles produced by emulsion copolymerization under the conditions listed in Table 1; **b–f** the alkali/cooling-treated ones (initial pH 12.5; 100 °C; 1 h) under different degrees of neutralization (%): (b) 10; (c) 30; (d) 60; (e) 80; (f) 100. pH after the treatments: (b) 7.9; (c) 8.4; (d) 10.7; (d) 10.9; (e) 11.3



to the KOH aqueous solution of which pH value was 12.5. In Fig. 1a, the inside of the original particles was homogeneous and D_w/D_n value was 1.01 by DLS 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% by ^{1}H NMR measurement for the methylated P(S-MAA). This difference seems to be based on dissolution of a part of P(S-MAA) having high MAA content in aqueous medium. In Fig. 1b–f, both the particles having hollow and non-hollow structures were observed in the alkali/cooling-treated emulsions.

Table 2 shows pH values of the P(S-MAA) emulsion and percentages of consumed KOH before and after the alkali/cooling treatment (60% neutralization; initial pH 12.5; 100 °C; 1 h). The percentage of consumed KOH was calculated from the pH values before and after the alkali/cooling treatment. The percentage of consumed KOH before the treatment was almost 0%, and that after the treatment at 100 °C was almost 100%. This result indicates that the neutralization of the carboxyl groups inside the particles scarcely occurred before the heat treatment, but did after that. The neutralization reaction of the carboxyl groups should occur without distinction between the non-hollow particles and the hollow ones, because the temperature was raised to 100 °C after the particles dispersed uniformly in the KOH aqueous solution.

Table 2 pH values of the P(S-MAA) emulsion and percentages of consumed KOH[a] before and after the alkali/cooling treatment[b]

	pH value	Consumed KOH (%)
Before the treatment	12.5	0
After the treatment	10.7	98.4

[a] Calculated from the pH values before and after the alkali/cooling treatment

[b] 60% neutralization; initial pH 12.5; 100 °C; 1 h

Figure 2 shows the relationship between the degree of neutralization and the percentage of hollow particles in the alkali/cooling-treated P(S-MAA) ones (initial pH 12.5; 100 °C; 1 h). The percentage of the hollow particles increased linearly with an increase in the degree of neutralization, and attained 90% under 100% neutralization.

Figure 3 shows the relationship between the alkali treatment temperature and the percentage of the hollow particles in the alkali/cooling-treated P(S-MAA) ones (60% neutralization; initial pH 12.5; 1 h). The percentage of the hollow particles increased with an increase in the alkali treatment temperature above 60 °C, and reached to 100% above 130 °C in spite of the fact that

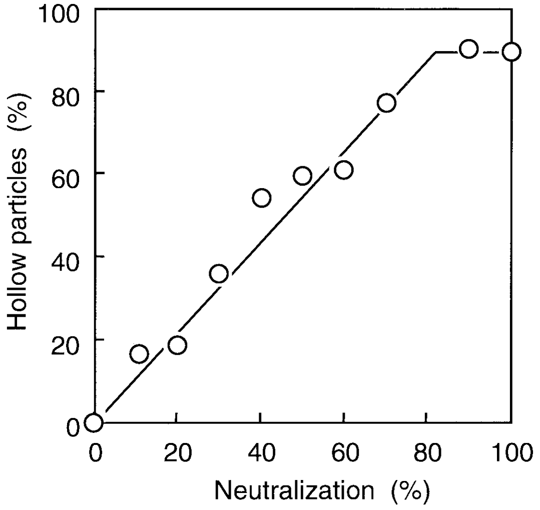


Fig. 2 Relationship between the degree of neutralization and the percentage of the hollow P(S-MAA) particles prepared by the alkali/cooling treatment (initial pH 12.5; 100 °C; 1 h)

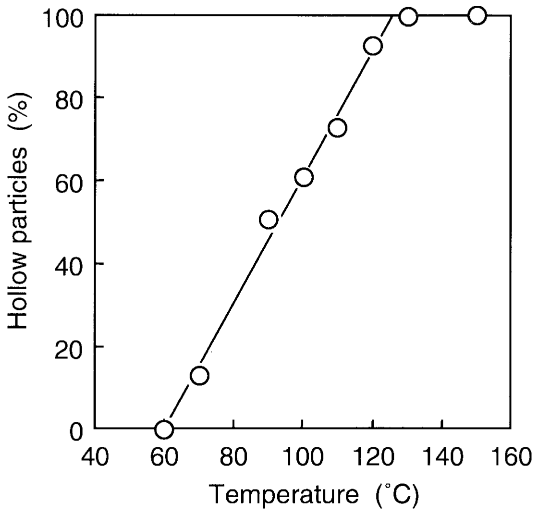


Fig. 3 Relationship between the alkali treatment temperature and the percentage of the hollow P(S-MAA) particles prepared by the alkali/cooling treatment (60% neutralization; initial pH 12.5; 1 h)

the percentage of neutralization was 60%. This result indicates the reason why about 10% of the original particles did not turn to hollow ones under 100% neutralization at 100 °C as shown in Fig. 2 is based on insufficient mobility of the base polymer at 100 °C. This seems to correspond to the result that the treatment temperature, above which the multihollow particles obtained by the stepwise acid/alkali method [12] for acid-swelling particles, increased by an increase in Tg of S-butyl acrylate (BA)-dimethylaminoethyl methacrylate copolymer particles having different S/BA ratios [13]. From these results, it seems that the only a particle treated at higher temperature than its Tg, which is lowered by plasticization due to water absorption, turns to a hollow one by the alkali/cooling method and that the degree of plasticization is based on the MAA content and the degree of neutralization of MAA.

The above results suggest that the MAA content may be different among the original P(S-MAA) particles which were produced by a general emulsion copolymerization. In a previous article [14], a similar result was reported: a mixture of hollow and non-hollow polymer particles were obtained by extraction of polystyrene (PS) from PS/styrene-divinylbenzene copolymer core/shell composite particles produced by seeded dispersion copolymerization of S and divinylbenzene with PS seed particles. This result also seemed to be based on the heterogeneity in the degree of cross-linking of the copolymer shell among the composite particles. To our knowledge there has been no clear report dealing in the heterogeneity of polymer particles produced by 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, in this article, in order to clarify the chemical heterogeneity among the particles, the MAA contents in the hollow and non-hollow particles were measured after their separation in the alkali/cooling-treated ones. The hollow particle had closer density to aqueous medium than the non-hollow one, because the hollow one had a lot of water in the inside. Accordingly, the separation of those particles seems to be achieved by centrifugation. For the separation, an aqueous dispersion of the centrifugally washed P(S-MAA) particles after the alkali/cooling treatment was centrifuged with distilled water at 14,000 rpm (RCF, 15,000 *g*) for 10 min. The centrifuged emulsion consisted of three layers: top layer which was slightly clouded and contained 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 layer was collected ten times, and centrifugally washed three times with distilled water at 17,000 rpm (RCF, 23,000 *g*) for 20 min. The precipitated particles in the bottom layer were centrifugally washed five times with distilled water at 12,000 rpm (RCF, 11,000 *g*) for 10 min to remove the hollow ones completely.

Figure 4 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 layer and in the bottom layer after the centrifugal separation. The separation of the hollow and the non-hollow particles in both layers were succeeded by the controlled centrifugation. In a range from 10% to 100% neutralization, the only hollow particles were observed in the top layer. On the other hand, the only non-hollow particles were observed in the bottom

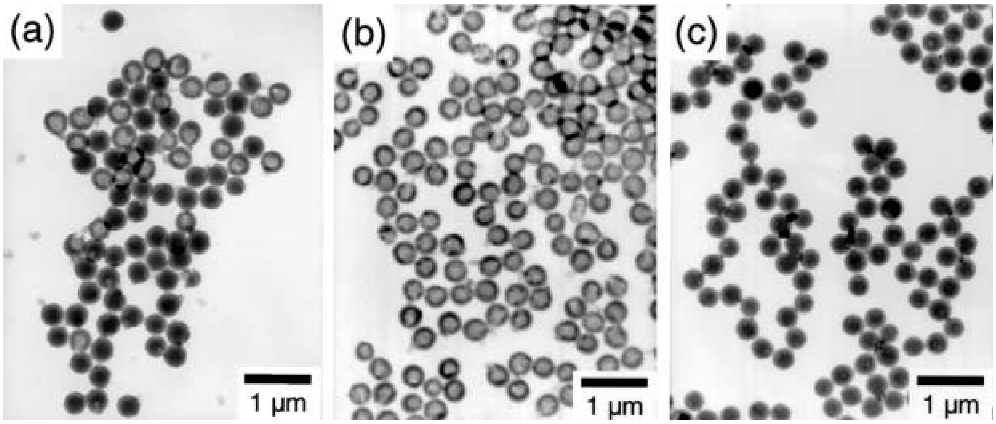


Fig. 4a–c TEM photographs of: **a** the alkali/cooling-treated P(S-MAA) particles (20% neutralization; initial pH 12.5; 100°C; 1 h); **b** those in the slightly clouded top layer; **c** those in the bottom layer after the centrifugal separation

layer up to 30% neutralization, and percentage of the hollow ones, which may exist in lower layer just before the centrifugal separation, increased with an increase in the degree of neutralization above 30%.

Table 3 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 ones, and both of them were smaller than that in the original ones. This result was based on elusion of copolymer having high MAA content from the original particle into the KOH aqueous solution in the alkali/cooling treatment process.

Figure 5 shows the relationship between the degree of neutralization and the weight percentage of the P(S-MAA) dissolved in the KOH aqueous solution by the alkali/cooling treatment (initial pH 12.5; 100 °C; 1 h) to the total treated particles. The M_w of each copolymer dissolved at each degree of neutralization was almost constant (about 10^5 g/mol measured by GPC). The weight percentage of the dissolved copolymer increased with the increase in the degree of neutralization. It is worth pointing out that the hollow structure should not be caused by the extraction of the copolymer having high MAA content from the particle, because the volume (8.2 vol.% to the original ones) of the dissolved copolymer was much smaller than the hollow volume (120 vol.% to the original ones) calculated from particle diameters, which were measured by DLS, before and after the alkali/cooling treatment under 100% neutralization at 100 °C.

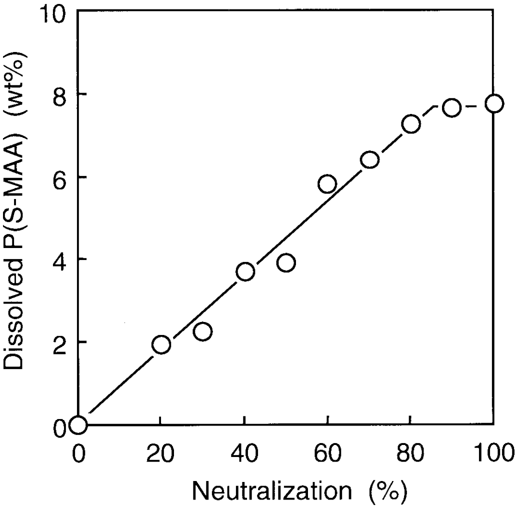


Fig. 5 Relationship between the degree of neutralization and the weight percentage of the P(S-MAA) dissolved in the KOH aqueous solution by the alkali/cooling treatment (initial pH 12.5; 100 °C; 1 h)

Table 3 MAA contents[a] in the original P(S-MAA) particles[b], those having hollow and non-hollow structures, and the copolymers dissolved in the 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[f]	29.5

[a] Determined by ^{1}H NMR after methylation with diazomethane
[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 and in the dissolved copolymers in consideration of their amounts
[f] M_w of the dissolved copolymer was 0.8×10^5 g/mol measured by GPC

Figure 6 shows the relationship between the percentage of the hollow particles and the weight percentage of the P(S-MAA) dissolved in the KOH aqueous solution by the alkali/cooling treatment (initial pH 12.5; 100 °C; 1 h) under different degrees of neutralization shown in Figs. 2 and 5. The weight percentage of the dissolved polymer increased linearly with the increase in

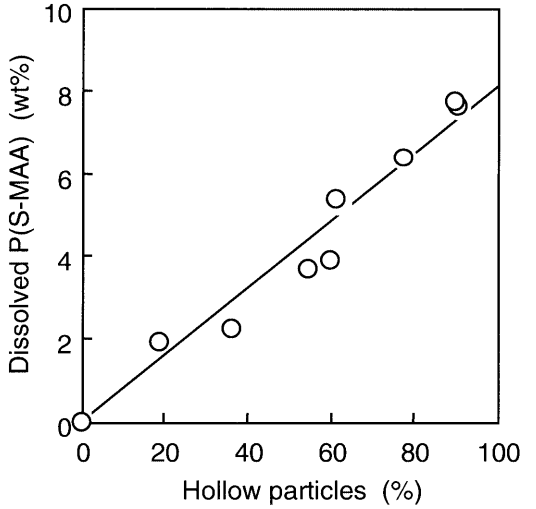


Fig. 6 Relationship between the percentage of the hollow particles and the weight percentage of the P(S-MAA) dissolved in the KOH aqueous solution by the alkali/cooling treatment (initial pH 12.5; 100 °C; 1 h) under different degrees of neutralization shown in Figs. 2 and 5

the percentage of the hollow particles, and the amount of the dissolved copolymer at 100% hollow ones was 8.2 wt%, which was calculated by extrapolation of the line in Fig. 6 to 100% hollow ones. This result indicates that the copolymer having high MAA content dissolved only from the hollow particle, and the amount of the copolymer dissolved from each hollow one was 8.2 wt% to that of the original one, assuming that the weight of all the original ones were uniform. Accordingly, the MAA content in the hollow particles before the alkali/cooling treatment should be calculated by averaging those in the dissolved copolymer and in the hollow ones after the treatment in consideration of their amounts, and that in non-hollow ones 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 3. This result suggests that the MAA content in the original particles, which turned to the hollow ones, was larger than that in the other original ones, which did not turn to hollow ones after the alkali/cooling treatment (20% neutralization; initial pH 12.5; 100 °C, 1 h).

From the above results, it is concluded that the only P(S-MAA) particle having high MAA content turned to a hollow one by the alkali/cooling treatment. In other words, it is clarified that the MAA contents in the P(S-MAA) particles produced by a general emulsion copolymerization were heterogeneous among the particles. In a following article, distribution of acid contents among the carboxylated polymer particles will be evaluated by utilizing the alkali/cooing method.

References

1. Kowalski A (1984) US Patent 4,427,836
2. Okubo M, Kanaida M, Fujimura M (1990) Chem Express 5:797
3. Okubo M, Ichikawa K, Fujimura M (1991) Colloid Polym Sci 269:1257
4. Okubo M, Ichikawa K, Fujimura M (1992) In: Daniels ES, Sudol ED, El-Aasser MS (eds) Polymer latexes: preparation, characterization, and application. ACS Symposium Series No 492, p 282
5. Okubo M, Ichikawa K (1994) Colloid Polym Sci 272:933
6. Okubo M, Ito A, Hashiba A (1996) Colloid Polym Sci 274:428
7. Okubo M, Sakauchi A, Okada M (2002) Colloid Polym Sci 280:38
8. Okubo M, Sakauchi A, Okada M (2002) Colloid Polym Sci 280:303
9. Okubo M, Ito A, Kanenobu T (1996) Colloid Polym Sci 274:801
10. Okubo M, Ito A, Nakamura M (1997) Colloid Polym Sci 275:82
11. Okubo M, Nakamura M, Ito A (1997) J Appl Polym Sci 64:1947
12. Okubo M, Mori H (1997) Colloid Polym Sci 275:634
13. Okubo M, Mori H, Ito A (1999) Colloid Polym Sci 277:589
14. Okubo M, Nakagawa T (1994) Colloid Polym Sci 272:530