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ORIGINAL CONTRIBUTION

M. Okubo
H. Mori

Production of multi-hollow polymer particles by the stepwise acid/alkali method

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Prof. Dr. M. Okubo (✉) · H. Mori
Department of Chemical Science and Engineering
Faculty of Engineering
Kobe University
Rokko, Nada, Kobe 657, Japan
E-mail: okubo@cx.kobe-u.ac.jp

Abstract Recently, we reported that multi-hollow polymer particles can be prepared from carboxylated polymer particles by the stepwise alkali/acid method. In this article, an attempt was made to prepare similar particles from acid-swellable polymer particles by the stepwise treatment with acid and alkali, which was named the stepwise acid/alkali method. The acid-swellable particles were produced by emulsion terpolymerization of styrene, butyl acrylate, and dimethyl 2-amino ethyl methacrylate. The effects of initial pH value, temperature, and time in the acid and alkali treatment processes on the multi-hollow structure were examined.

Key words Multi-hollow particles – emulsion polymerization – morphology – acid swelling

Introduction

Recently, we found that submicron-sized styrene-butyl acrylate-methacrylic acid terpolymer particles produced by emulsion terpolymerization were changed to those having many hollows therein by stepwise treatments with alkali and acid [1], which was named the stepwise alkali/acid method. In the following articles, the effect of some factors in the alkali [2, 3] and acid [4] treatment processes on the formation of multi-hollow structure were examined in detail. On the basis of the results, the formation mechanism was proposed, in which alkali swelling of carboxylated polymer particles in the alkali treatment step is the trigger for formation of the multi-hollow structure.

In this article, in order to extend the possibility of preparation of such multi-hollow particles and to check the proposed formation mechanism, an attempt has been made to produce them by the reverse method in which the acid-swellable polymer particles will be treated stepwise with acid and alkali.

Experimental

Materials

Styrene (S) and butyl acrylate (BA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Dimethyl 2-amino ethyl methacrylate (DM) was used without further purification. Commercial grade 2,2′-azobis (2-amidinopropane) hydrochloride (V-50, Wako Pure Chemical Industries, Ltd.) and commercial grade nonionic polyoxyethylene nonylphenylether emulsifier (Emulgen 930, Kao Atlas Co.) were used without further purification. Deionized water was distilled.

Preparation of polymer emulsion particles

S–BA–DM terpolymer (P(S–BA–DM)) (69.1/23.9/7.0, molar ratio) particles were produced by emulsion terpolymerizations at 65 °C under the conditions listed in Table 1.

The glass transition temperature (T_g) calculated by applying Fox's equation was 50 °C.

Electron microscopy

JEOL JEM-200CX and JEOL JEM-2010 electron microscopes were used for transmission electron microscopic (TEM) observation. Each emulsion was diluted to 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. Each cross section was prepared as follows: Each diluted emulsion was dropped on polyethylene terephthalate film (50 μm of thickness). After drying, the particles on the film were exposed to RuO_4 vapor at room temperature for 30 min in the presence of 1.0% RuO_4 solution, and then dipped in epoxy matrix, cured at room temperature for 24 h and microtomed.

Measurement of particle diameter

The hydrodynamic diameters of the original P(S–BA–DM) particles and stepwise acid/alkali-treated particles were measured by dynamic light scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan) at room temperature, while that of acid-treated particles was measured at 40 °C. Each emulsion was diluted to 10 ppm. The data at the light-scattering angle of 90° were analyzed with the DLS-700 system program.

Stepwise acid/alkali treatment

The P(S–BA–DM) emulsion was treated stepwise with acid and alkali as follows:

Acid treatment: the original P(S–BA–DM) emulsion was diluted down to 1.7 g/l, and adjusted to various pH values with 5 N HCl solution. This emulsion was placed in a 50 ml glass vessel and the vessel was dipped in a water bath at various temperatures for different time.

Alkali treatment: the acid-treated emulsions were adjusted to various pH values with 5 N KOH aq. solution. This vessel was dipped in a water bath at various temperatures for different time. After the treatments, each emulsion was cooled by keeping the vessel at room temperature.

Volume expansion

The expansion of particle volume by the stepwise acid/alkali treatment was calculated from particle diameters measured by DLS before and after the treatments.

Results and discussion

Figure 1 shows TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) original particles (a) produced under the conditions in Table 1 and of those (b) after the stepwise acid/alkali treatment (acid treatment: initial pH

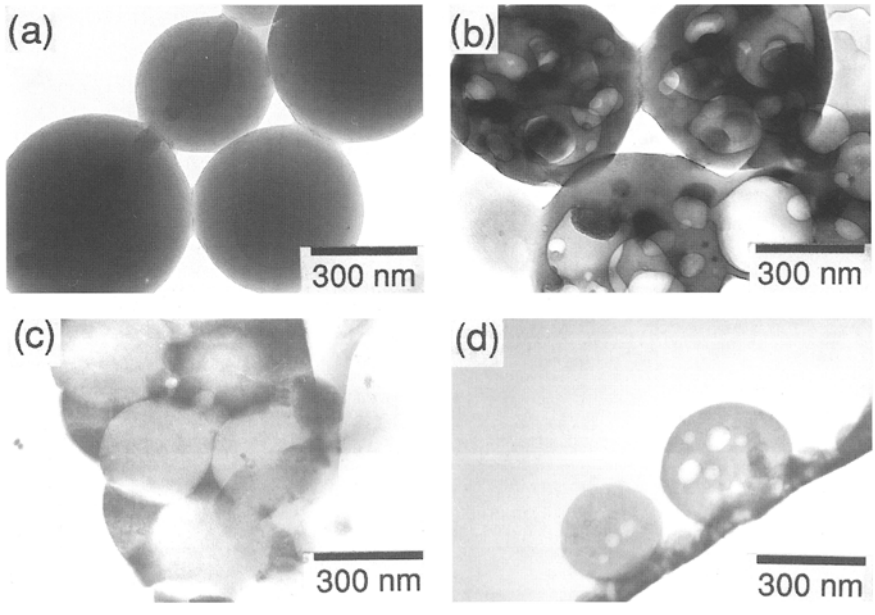

Fig. 1 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles (a, b), before (a, c) and after (b, d) treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, 70 °C, 1 h; alkali treatment: initial pH, 12.0, 70 °C, 1 h), and of their ultrathin cross sections (c, d)

Table 1 Recipe of emulsion polymerization for the preparation of P(S–BA–DM) (69.1/23.9/7.0, molar ratio; T_g[a)] = 50 °C) emulsion[b)]

Ingredient		
S	(g)	19.0
BA	(g)	8.1
DM	(g)	2.9
AIBA	(g)	0.15
Emulgen 930	(g)	1.5
Water	(g)	270

[a)] Calculated from the compositions by applying Fox's equation.
[b)] N_2; 65 °C; 24 h; stirring rate, 120 rpm.
Abbreviations: S, styrene; BA, butyl acrylate; DM, dimethyl 2-amino ethyl methacrylate; AIBA, 2,2′-azobis (2-amidinopropane) hydrochloride; Emulgen 930, polyoxyethylene nonyl phenylether nonionic emulsifier.

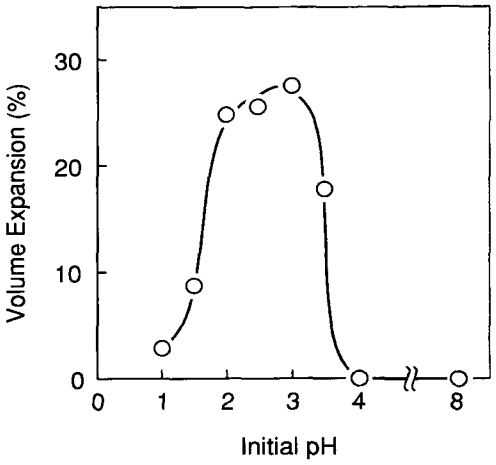

Fig. 2 Relationship between the initial pH value in the acid treatment at 70 °C for 1 h and the volume expansion of P(S–BA–DM) (69.1/23.9/7.0) particles. The volume expansion was calculated from the diameter measured by DLS at 40 °C and at each pH value

2.0, 70 °C, 1 h; alkali treatment: initial pH 12.0, 70 °C, 1 h) and of their ultrathin cross sections (c, d). In the photos (a, c), the inside of the original particles was observed to be homogeneous. Whereas in the photo (b), the inside of the stepwise acid/alkali-treated particles had many regions of low electron density which was based on the hollows as shown in photo (d).

Figure 2 shows the relationship between initial pH values in the acid treatment and the volume expansion based on the untreated original particles. An increase in the expansion means an increase in the swelling of the particles. The volume expansion was not changed at the initial pH values above 4.0, but in the range from 4.0 to 3.0 it increased remarkably with decreasing pH value, and then it decreased below 3.0. The decrease seems to be based on the suppression of acid-swelling due to an increase in the electrolyte concentration.

Figure 3 shows TEM photographs of P(S–BA–DM) particles treated by the stepwise acid/alkali method (acid treatment: *initial pH, variable*, 70 °C, 1 h; alkali treatment: initial pH 12.0, 70 °C, 1 h). At the initial pH value of 4.0 (a) in the acid treatment, the multi-hollow structure was not observed inside the particles, but observed at 3.0 (b), 2.0 (c), and 1.0 (d). The hollow size increased with decreasing the

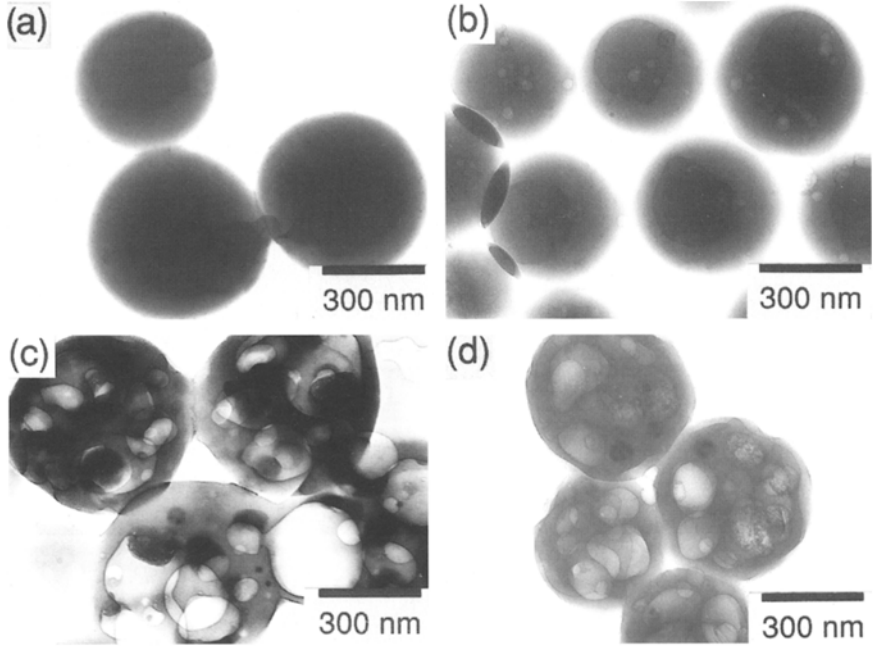

Fig. 3 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: *initial pH, variable*, 70 °C, 1 h; alkali treatment: initial pH, 12.0, 70 °C, 1 h). Initial pH values in the acid treatment: (a) 4.0, (b) 3.0, (c) 2.0, (d) 1.0

pH value in the acid treatment. The results in Figs. 2 and 3 indicate that acid swelling of the particles is the trigger for formation of multi-hollow structures.

Figure 4 shows TEM photographs of P(S–BA–DM) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0, *temperature, variable*, 1 h; alkali

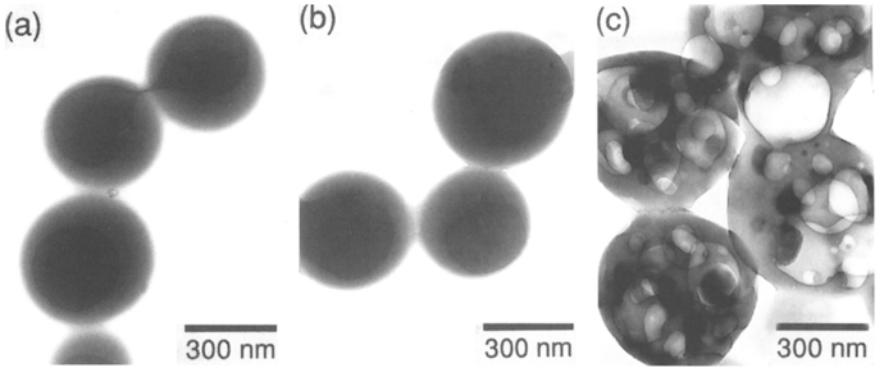

Fig. 4 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, *temperature, variable*, 1 h; alkali treatment: initial pH, 12.0, 70 °C, 1 h). Acid treatment temperatures (°C): (a) 30, (b) 50, (c) 70

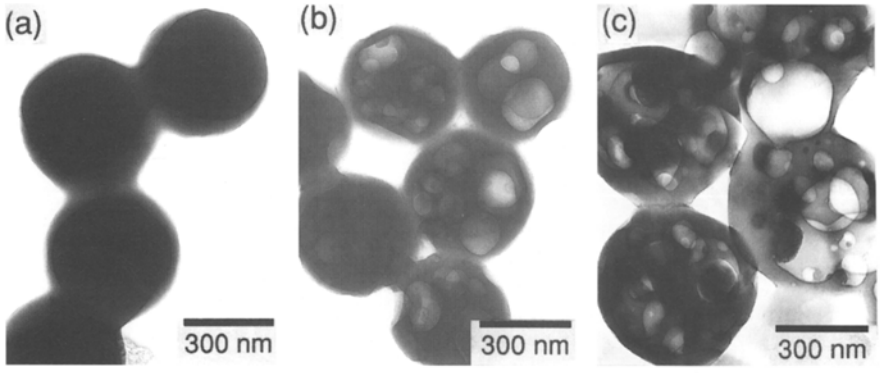

Fig. 5 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, 70 °C, *time, variable*; alkali treatment: initial pH, 12.0, 70 °C, 1 h). Acid treatment times (min): (a) 5, (b) 15, (c) 60

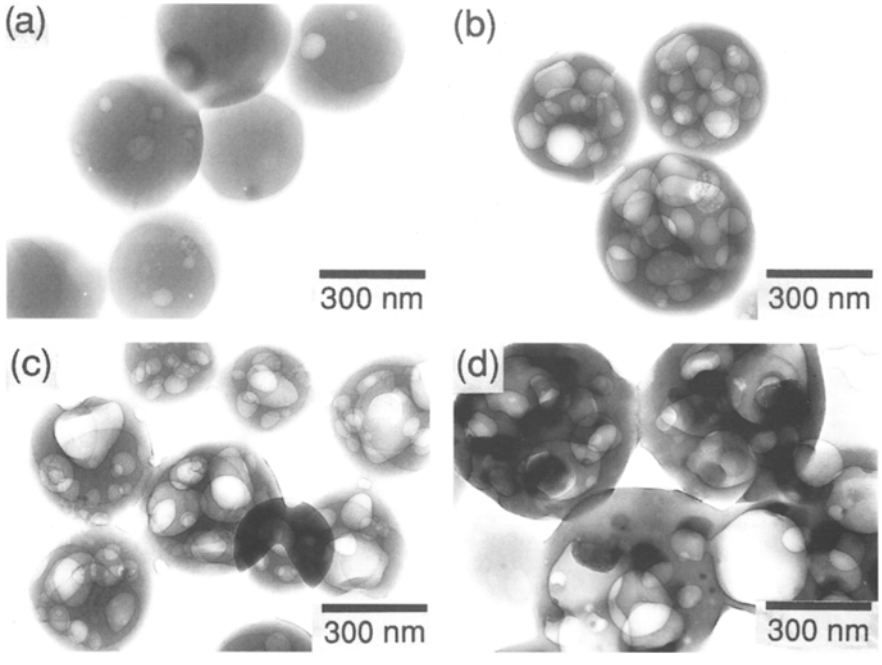

Fig. 6 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, 70 °C, 1 h; alkali treatment: *initial pH, variable*, 70 °C, 1 h). Initial pH values in the alkali treatment: (a) 8.0, (b) 9.0, (c) 10.0, (d) 12.0

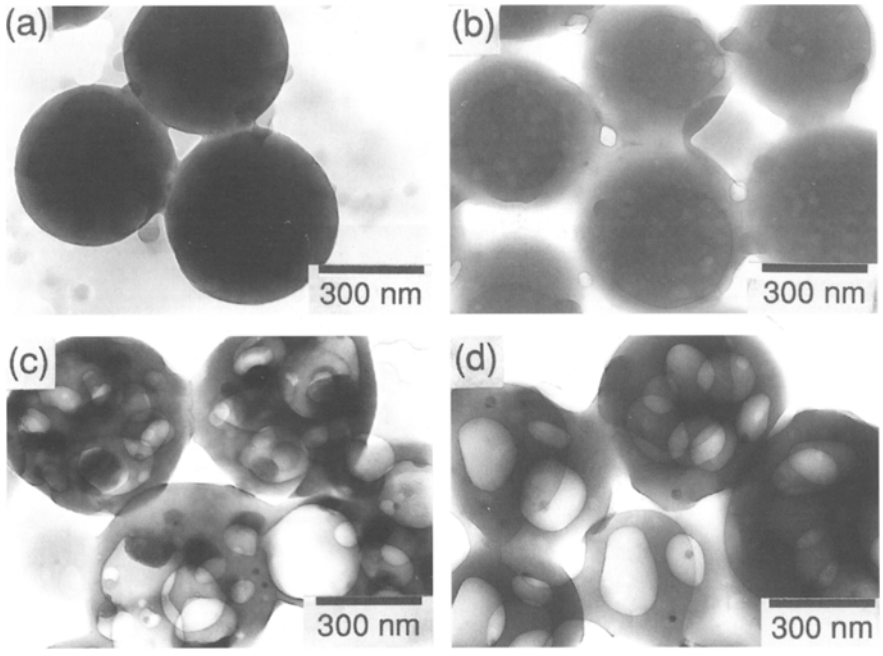

Fig. 7 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, 70 °C, 1 h; alkali treatment: initial pH, 12.0, *temperature, variable*, 1 h). Alkali treatment temperatures (°C): (a) 30, (b) 50, (c) 70, (d) 90

treatment: initial pH 12.0, 70 °C, 1 h). At 30 °C (a) and 50 °C (b) in the acid treatment, the multi-hollow structure was not observed inside the particles, but observed at 70 °C (c). This indicates that it is necessary to carry out the acid treatment at a temperature higher than T_g (= 50 °C) of the base polymer for the formation of multi-hollow structures.

Figure 5 shows TEM photographs of P(S–BA–DM) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0, 70 °C, *time, variable*; alkali treatment: initial pH 12.0, 70 °C, 1 h). The multi-hollow structure was not observed inside the particles treated for 5 min (a) at pH 2.0, but observed for 15 min (b) and 1 h (c). This suggests that there is a minimum acid treatment time to make the particles swell enough for the formation of multi-hollow structures.

Figure 6 shows TEM photographs of P(S–BA–DM) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0, 70 °C, 1 h; alkali treatment: *initial pH, variable*, 70 °C, 1 h). At the initial pH range of 8.0 to 12.0 in the alkali treatment, a few hollows were observed inside the particles. The hollow size increased with increasing the pH value in the alkali treatment.

Figure 7 shows TEM photographs of P(S–BA-DM) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0, 70 °C, 1 h; alkali treatment: initial pH 12.0, *temperature, variable*, 1 h). The multi-hollow structure was not observed inside the particles at 30 °C (a), but observed at 50 °C (b) and above (c, d). The hollow size increased with increasing the alkali treatment temperature.

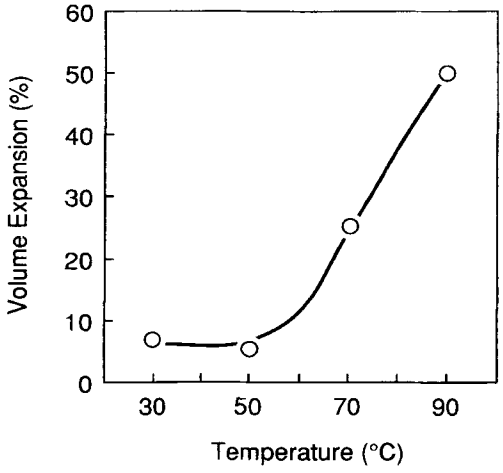

Fig. 8 Relationship between the temperature in the alkali treatment and the volume expansion of P(S–BA–DM) (69.1/23.9/7.0) particles by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, 70 °C, 1 h; alkali treatment: initial pH, 12.0, *temperature, variable*, 1 h). The volume expansion was calculated from the diameters measured by DLS at room temperature before and after the treatments

Figure 8 shows the relationship between the temperature in the alkali treatment and the volume expansion based on the untreated original particles by the acid/alkali treatment. An increase in the expansion means an increase in the total volume of hollows inside the particles. At the

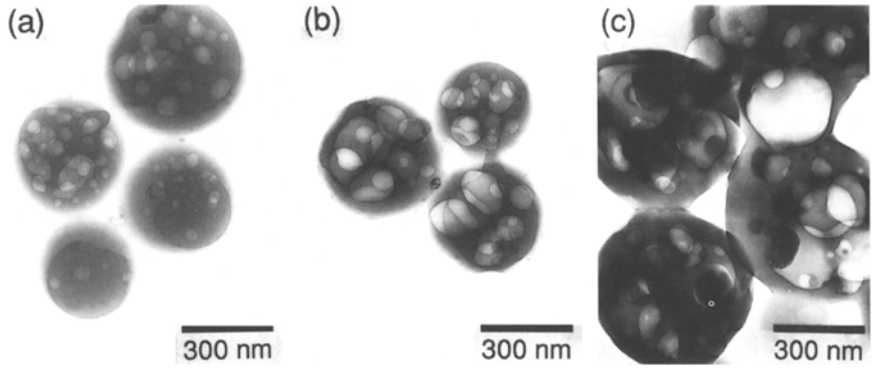

Fig. 9 TEM photographs of P(S–BA–DM) (69.1/23.9/7.0, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0, 70 °C, 1 h; alkali treatment: initial pH, 12.0, 70 °C, *time, variable*). Alkali treatment times (min): (a) 5, (b) 15, (c) 60

temperatures above 50 C, the volume expansion increased with increasing the temperature in the alkali treatment. The results in Figs. 7 and 8 indicate that it is necessary to carry out the alkali treatment at temperatures higher than T_g for the formation of multi-hollow structures.

Figure 9 shows TEM photographs of P(S–BA–DM) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0, 70 °C, 1 h; alkali treatment: initial pH 12.0, 70 °C, *time, variable*). The hollows increased in the size and decreased in number with the alkali treatment time.

The above data indicate the possibility of preparation of such multi-hollow particles was extended, and support the mechanism of formation of multi-hollow particles by the stepwise alkali/acid method [2]. According to it, the formation of the multi-hollow structure by the acid/alkali method can be explained as follows: First, dimethyl amino group-containing particles swell in acid condition at a temperature higher than T_g. Subsequently, in the early stage of the alkali treatment process, the polymer wall is formed quickly at the surfaces of acid-swollen particles, because polymer molecules containing "soluble" segments having ionized dimethyl amino groups are precipitated by their deionization. The shell prevents the particles from shrinking back to the original state. The fixation of polymer molecules proceeds gradually in the inside with the diffusion of alkali through the shell, resulting in the multi-hollow structures.

References

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