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ORIGINAL CONTRIBUTION

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Evaporation behavior of water from aqueous dispersions of multihollow particles prepared by the stepwise alkali/acid method

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Abstract In order to clarify the formation mechanism of multihollow structures inside styrene–methacrylic acid copolymer particles prepared by the stepwise alkali/acid method, which we proposed in 1990, the evaporation behavior of water from aqueous dispersions of the original carboxylated particles and those after the alkali treatment and the stepwise alkali/acid treatments was examined. It is concluded that the particle after the alkali treatment had a number of small water pools inside.

Keywords Evaporation behavior · Multihollow · Emulsion polymerization · Stepwise alkali/acid method · Styrene–methacrylic acid copolymer

Introduction

It was found that styrene (S)–butyl acrylate–methacrylic acid (MAA) terpolymer particles produced by emulsion copolymerization were changed to those having many hollows inside 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 a multihollow structure were examined in detail. Moreover, in order to produce multihollow polymer particles having high glass-transition temperatures, S–MAA copolymer [P(S-MAA)] particles were treated by the stepwise alkali/acid method [5].

On the other hand, we reported [6] the release behavior of water from a hollow in micron-sized, monodisperse cross-linked polystyrene (PS)/poly(divinylbenzene) composite particle produced by seeded polymerization for high (S–divinylbenzene)-swollen PS particles prepared by the dynamic swelling method [7, 8]. The release rate was influenced by the density of cross-linking and the shell thickness.

In this article, in order to clarify the multihollow structure in more detail, the evaporation behavior of water from the original P(S-MAA) particles and those after the alkali treatment and the stepwise alkali/acid treatments is reported.

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, HCl, and *n*-octyl mercaptan, and extra pure reagent grade poly(oxyethylene) sorbitan monooleate (Tween 80) were used as received from Nacalai Tesque Co. Commercial grade poly(oxyethylene) 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.

Preparation of P(S-MAA) particles

The original P(S-MAA) particles were prepared by emulsion copolymerization at 70 °C under the conditions listed in Table 1. The conversion was above 95% as determined by gravimetric measurement. The MAA content of the original particles was 5.0 mol% as determined by ^{1}H NMR measurement. The weight-average molecular weight of the original particles was measured by

Table 1 A recipe for the preparation of styrene-methacrylic acid (*MAA*) copolymer particles by emulsion copolymerization at 70 °C for 24 h under N_2 at a stirring rate of 120 rpm

Ingredients	Amount
Styrene (g)	56.0
MAA (g)	4.0
Potassium persulfate (g)	0.24[a]
Emulgen 911 (g)	3.3
Water (g)	540
n-Octyl mercaptan (g)	0.15
MAA content (mol%)[b]	5.0
M_w[c]	5.9×10^5

[a] First, 0.04 g potassium persulfate was added and 3 h later the remains (0.20 g) were added as an aqueous solution

[b] Measured by ^1H NMR

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

gel permeation chromatography. Calibration was performed with PS standards using tetrahydrofuran as the eluant.

The stepwise alkali/acid treatment

The original P(S-MAA) particles were treated stepwise with alkali and acid as follows. The original emulsion was diluted to 0.5 g/l and adjusted to pH 12.0 with 1 N KOH aqueous solution. This emulsion was placed in a stainless steel pressure-resistant vessel having a poly(tetrafluoroethylene) (PTFE) 50-ml-capacity inner container, and the vessel was dipped in an oil bath at 150 °C for 3 h. After the alkali treatment, this emulsion was cooled in air to room temperature. The treated emulsion was centrifuged twice to remove excessive KOH, diluted to 0.05 g/l, and adjusted to various pH values with 1 N HCl or KOH aqueous solution. The emulsion was placed in an oil bath at 130 °C for various times after Tween 80 (10 wt% of solid polymer) had been added to the emulsion to prevent coagulation. After the acid treatment, each emulsion was cooled in air to room temperature. Hereafter, these treatments are called the stepwise alkali/acid method.

The amount of polymer dissolved in aqueous KOH solution in the process of the alkali treatment was measured, according to the following procedure. First, the supernatant of the alkali-treated P(S-MAA) emulsion obtained by centrifugation at 16,000 rpm for 10 min with KOH aqueous solution, of pH 12.0, was collected three times. After that, in order to precipitate the polymer dissolved in the KOH aqueous solution, the pH of the supernatant collected was adjusted to 2.0 with 1 N HCl aqueous solution, and the supernatant was placed in a 50-ml-capacity stainless steel pressure-resistant vessel having a PTFE inner container, and the vessel was dipped in an oil bath at 150 °C for 3 h and subsequently cooled in air to room temperature. The weight percentage of the precipitated polymer to the total treated particles was measured by gravimetric analysis after they had been washed with thoroughly distilled water.

Measurement of particle diameter and volume expansion

The hydrodynamic diameters (D_h) of the original P(S-MAA) particles and those after the treatments were measured at least twice by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Kyoto, Japan) at room temperature. The expansions of the particle volume by the alkali treatment and the stepwise alkali/acid treatments were calculated from the following equation in consideration of the amount (5 wt%) of polymer dissolved in aqueous KOH solution in the process of the alkali treatment:

$$\text{Volume expansion (\%)} = \left(\frac{D^3_{\text{h,after}}}{D^3_{\text{h,before}} \times (0.95)} - 1 \right) \times 100 \qquad (1)$$

where $D_{\text{h,before}}$ and $D_{\text{h,after}}$, respectively, mean D_h of the particles before and after the treatments.

Evaporation behavior of water from the P(S-MAA) emulsion

The evaporation behavior of water from the P(S-MAA) emulsion before and after the treatment was examined by measurement of the weight loss by thermogravimetry (TG/DTA 220 U, Seiko Instruments, Chiba, Japan). The measurement of the weight loss was carried out for 15 mg of each emulsion on an aluminum pan (5-mm diameter) at 50 °C under a nitrogen atmosphere after centrifugal washing with distilled water five times. The solid content of each emulsion was adjusted to about 20 wt% for the measurement. The instantaneous evaporation rate of water was determined by differentiation of the weight-loss curve.

Electron microscopy

A JEOL JEM-2010 electron microscope was used for transmission electron microscopy (TEM) observation. The emulsion was diluted to about 50 ppm, and a drop was placed onto a carbon-coated copper grid and allowed to dry at room temperature in a desiccator.

Detection of potassium atoms within the particles

Dried P(S-MAA) particles were dispersed in an epoxy matrix, cured at room temperature for 24 h, and at 40 °C for 1 h, and microtomed into about 100 nm. The existence of potassium atoms in the original particle and those after the alkali treatment and the stepwise alkali/acid treatments was estimated by an energy dispersive X-ray spectrometer (Voyager, Noran Instruments, Wis., USA) for the ultrathin cross-sections of those particles.

Results and discussion

TEM photographs of the original P(S-MAA) (MAA, 5.0 mol%) particles produced by emulsion copolymerization under the conditions listed in Table 1 and those after the alkali treatment and the stepwise alkali/acid treatments and of the ultrathin cross-sections of their particles are shown in Figs. 1 and 2, respectively. The alkali and acid treatments were performed at an initial pH of 12.0 at 150 °C for 3 h and at an initial pH of 3.0 at 130 °C for 3 h, respectively. The inside of the original particle was homogeneous, whereas the stepwise alkali/acid-treated particle had a multihollow structure. These results were also observed in their ultrathin cross-sections in Fig. 2. In the alkali-treated particle, although a multihollow structure was not observed in Fig. 1, some fine hollows were observed in the ultrathin cross-section in Fig. 2b. In the DLS measurement, the volume expansion before and after the alkali treatment was 49 ± 1 vol%, which was much larger than that calculated from the hollow size

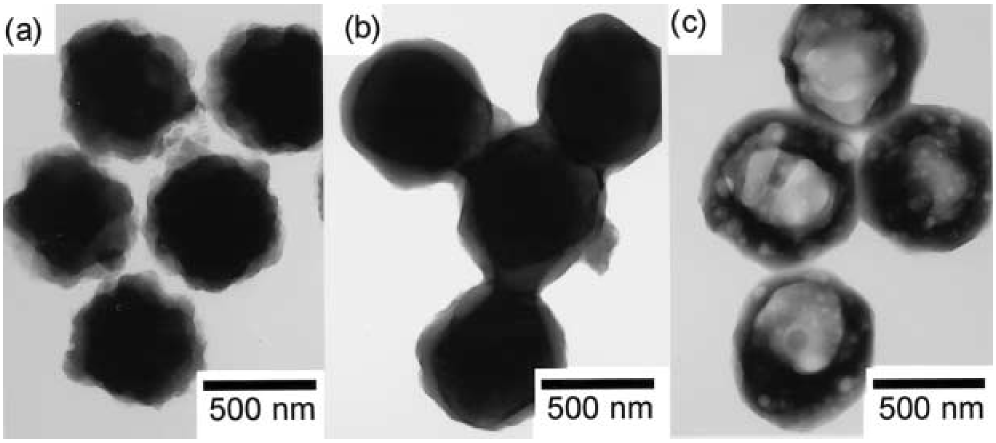

Fig. 1 Transmission electron microscope (*TEM*) photographs of original poly(stytene–methacrylic acid) [*P(S-MAA)*] (MAA, 5,0 mol%) particles **a** produced by emulsion copolymerization under the conditions listed in Table 1 and **b** those after the alkali treatment and **c** the stepwise alkali/acid treatments (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, 3 h)

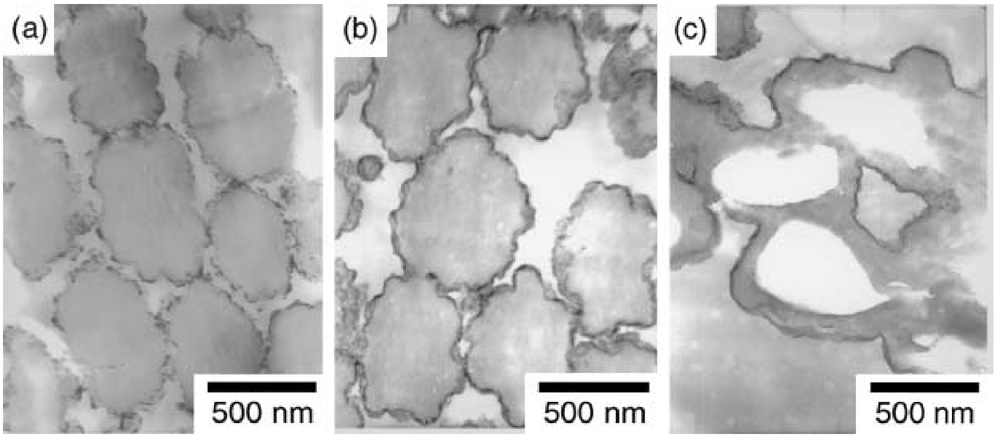

Fig. 2 TEM photographs of ultrathin cross-sections of **a** original P(S-MAA) (MAA, 5.0 mol%) particles and **b** those after the alkali treatment and **c** the stepwise alkali/acid treatments (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, 3 h)

and number in Fig. 2b. These data suggest that the alkali-treated particle had a number of water pools, the size of which was too small to observe clearly with TEM, in the inside.

Energy dispersive X-ray spectra of the ultrathin cross-sections of the three kinds of the particles shown in Fig. 2 are shown in Fig. 3. Before the measurements, the three kinds of emulsions were adjusted to pH 12.0 and stirred for 3 h at room temperature. Subsequently, they were washed centrifugally with distilled water five times to remove KOH in the medium and at their particle surfaces and dried at room temperature at reduced pressure. In the spectra of the original and the stepwise alkali/acid-treated particles, the peak at 3.2 keV due to potassium atoms was not observed. These results indicate that the potassium atoms physically adsorbed at the surfaces of the particles were completely removed by the washing. On the other hand, in the spectrum of the alkali-treated particles, a characteristic peak at about 3.2 keV was observed. This result indicates that the alkali-treated particle had potassium atoms, which were derived from the KOH used in the alkali treatment, in the inside. That is, they seem to exist as $-COO^{-}K^{+}$, which should be hydrated with some H_2O molecules, in the inside. This also supports the previous assumption that the alkali-treated particle had a number of water pools inside.

The weight-loss curves based on the evaporation of water at 50 °C from the aqueous dispersions of the three kinds of washed particles are shown in Fig. 4. In the TEM observations, it was confirmed that there were no changes in the internal structures of the particles before and after the thermogravimetry/differential thermal analysis measurements. In their final drying stages, the rates of the weight loss from the aqueous dispersions of the alkali-treated and the stepwise alkali/acid-treated particles were slower than that of the original particles. This seems to be based on the slow evaporation rate of water from the insides of the alkali-treated and the stepwise alkali/acid-treated particles.

The weight-loss curves based on the evaporation of water from the aqueous dispersions of the original and the stepwise alkali/acid-treated particles and the evaporation rate curves obtained by differentiation of the weight-loss curves are shown in Figs. 5 and 6, respectively. Both evaporation rates were constant in period I

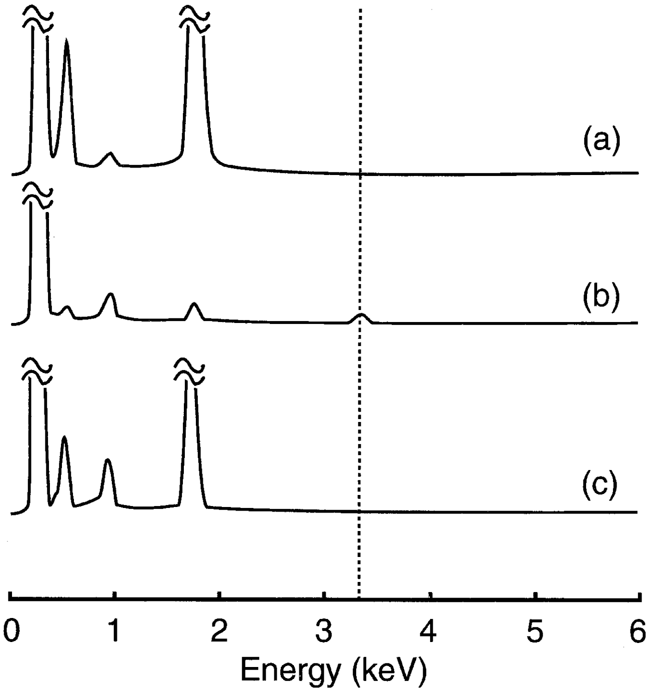

Fig. 3 Energy dispersive X-ray spectra of **a** original P(S-MAA) (MAA, 5.0 mol%) particles and **b** those after the alkali treatment and **c** the stepwise alkali/acid treatments (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, 3 h)

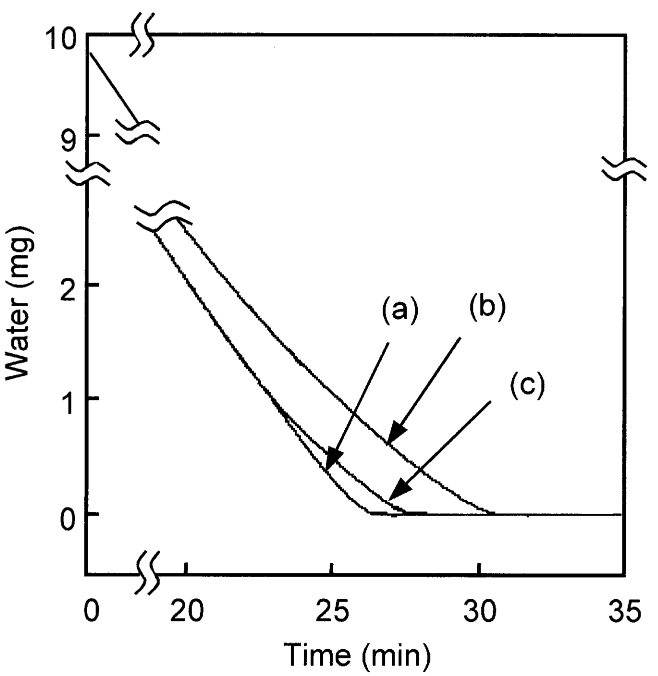

Fig. 4 Weight-loss curves based on the evaporation of water at 50 °C from aqueous dispersions of **a** original P(S-MAA) (MAA, 5.0 mol%) particles and **b** those after the alkali treatment and **c** the stepwise alkali/acid treatments (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, 3 h)

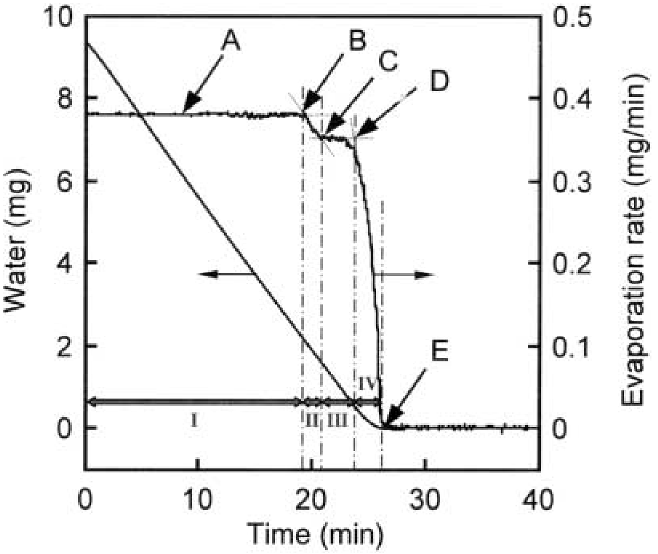

Fig. 5 Weight-loss curve based on the evaporation of water at 50 °C from an aqueous dispersion of original P(S-MAA) (MAA, 5.0 mol%) particles and an evaporation rate curve obtained by differentiation of the weight-loss curve

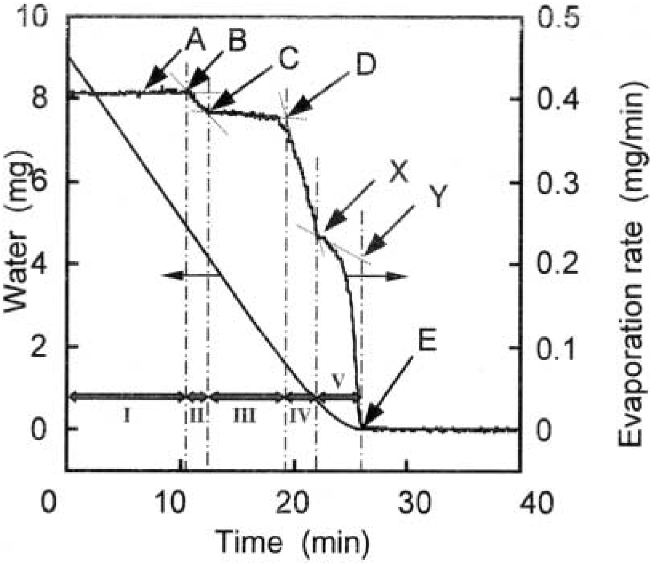

Fig. 6 Weight-loss curve based on the evaporation of water at 50 °C from an aqueous dispersion of the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, 3 h) and an evaporation rate curve

(A–B) and decreased gradually in period II (B–C). In the case of the original particles in Fig. 5, the rate was constant in period III (C–D) and rapidly decreased monotonously to zero in period IV (D–E). On the other hand, in the case of the stepwise alkali/acid-treated particles in Fig. 6, one more change for the rate was observed at the point X between D and E. The

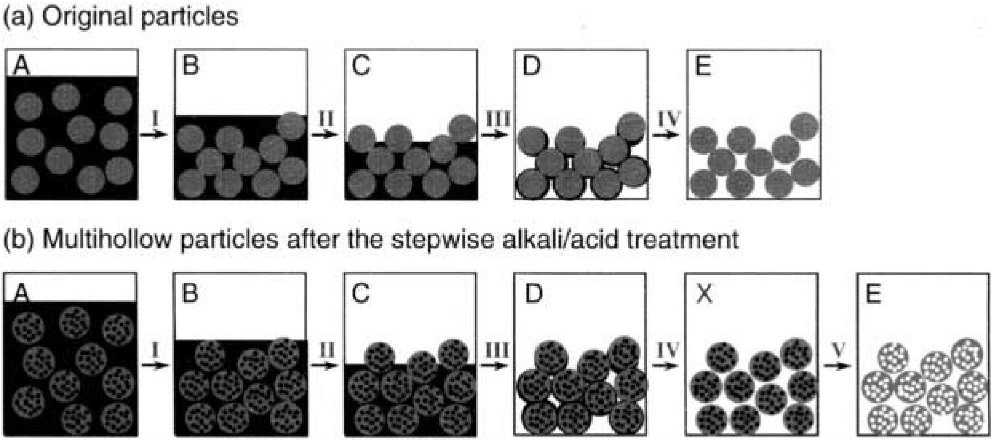

Fig. 7 Schematic models of the evaporation behavior of water from aqueous dispersions of **a** original and **b** the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, 3 h)

difference in the evaporation behavior of water from the aqueous dispersions of the original and the stepwise alkali/acid-treated particles seems to be explained reasonably according to the schematic model shown in Fig. 7.

First, the evaporation rate is constant in period I in which free water evaporates from the aqueous medium. As the free water evaporates, the particles are randomly packed and some of them near the water surface begin to be exposed to air at point B. Accordingly, the evaporation rate decreases in period II because the surface area of the free water becomes less than that in period I. While the free water evaporates among the particles, the rate is constant in period III. Finally, in the case of the original particle, a small amount of water adsorbed at the particle surface evaporates and the rate rapidly decreases to zero in period IV. On the other hand, the alkali/acid-treated particle, which has a multihollow structure inside, has much water inside the hollows. The evaporation rate of water from the hollows is much slower than that of free water because the water in the hollows must diffuse through the hydrophobic polymer phase. That is, the weight loss after point X seems to be based on the evaporation of the water in the hollows. The amount of water remaining at point X in the case of the stepwise alkali/acid-treated particles was 0.7 mg in 5.0 mg dried particles. Therefore, the volume of the water at point X was 14 vol% of the particle assuming that the density of the dried particle is 1.04 g/cm^3. This percentage was smaller than 26 ± 6 vol%, which was

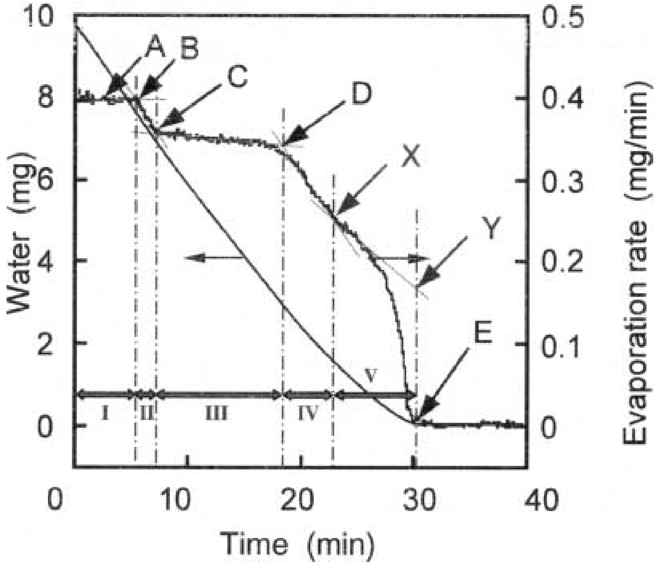

Fig. 8 Weight-loss curve based on the evaporation of water at 50 °C from an aqueous dispersion of the alkali-treated P(S-MAA) (MAA, 5.0 mol%) particles at initial pH 12.0 for 3 h at 150 °C and an evaporation rate curve

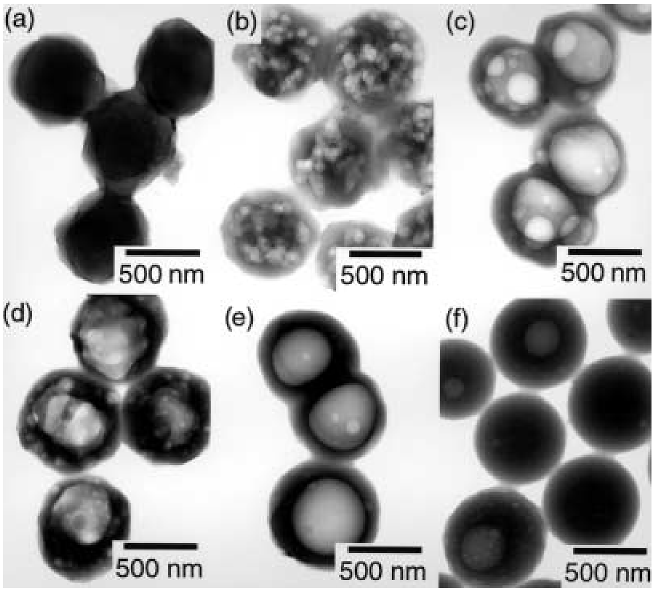

Fig. 9 TEM photographs of the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C) for different acid treatment times (hours): **a** 0, **b** 0.5, **c** 1, **d** 3, **e** 12, **f** 24

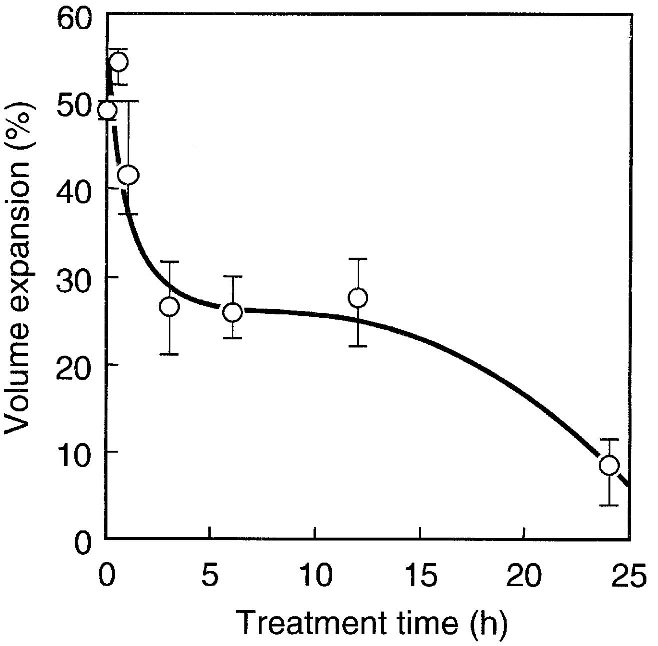

Fig. 10 Relationship between the acid treatment time and the volume expansion of the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C)

the volume expansion calculated from Eq. (1) using the D_h of the particles before and after the stepwise alkali/acid treatments. This seems to be based on the fact that the evaporation of water from the hollows in the particles exposed to air already proceeds in ranges III and IV before point X, though the rate might be smaller than that in period V because of the difference in the humidities surrounding the particles.

The weight-loss curve based on the evaporation of water from the aqueous dispersion of the alkali-treated particles and an evaporation rate curve is shown in Fig. 8. Point X was observed similarly as in case of the stepwise alkali/acid-treated particle. The amount of water remaining at point X was 1.6 mg in 3.5 mg dried particles. Thus, the volume of the water at point X was 46 vol% of the particles. This percentage was nearly equal to 49 ± 1 vol%, which was the volume expansion calculated from Eq. (1) using the D_h of the particles before and after the alkali treatment. These results suggest that the alkali-treated particle has a number of small water pools.

TEM photographs and volume expansions of the stepwise alkali/acid-treated particles prepared for different times in the acid treatment process (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C) are shown in Figs. 9 and 10,

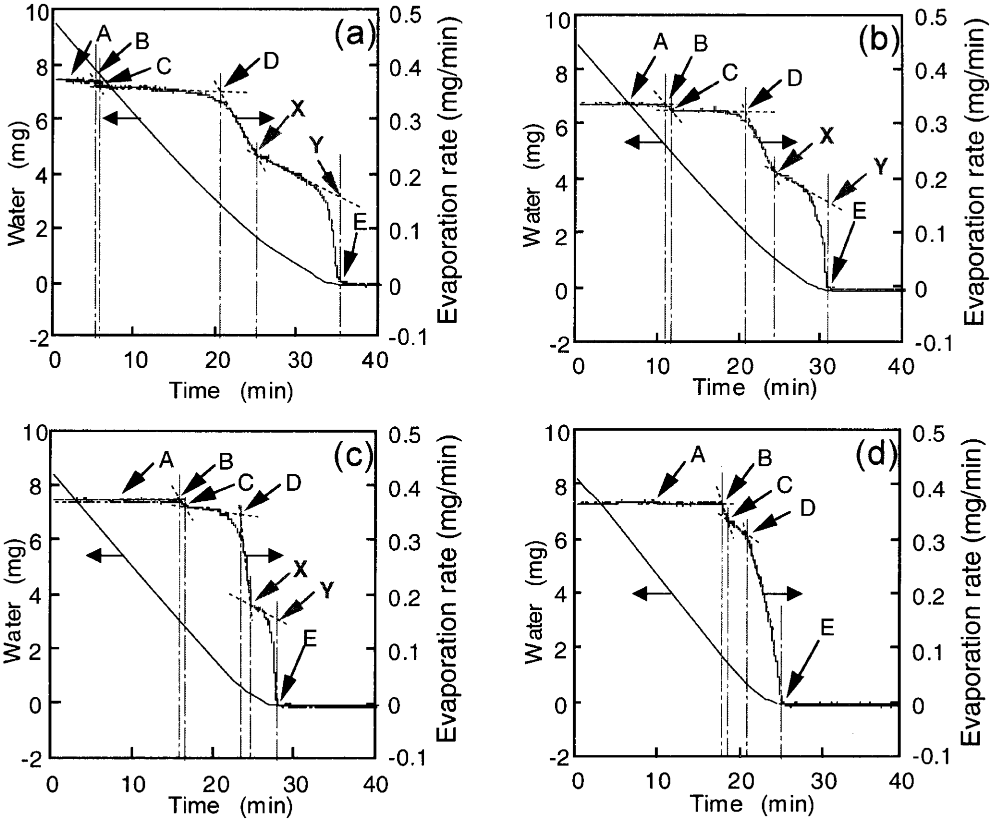

Fig. 11 Weight-loss curves based on the evaporation of water at 50 °C from aqueous dispersions of the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles for different acid treatment times (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C, time (hours): **a** 0.5, **b** 1, **c** 12, **d** 24) and evaporation rate curves

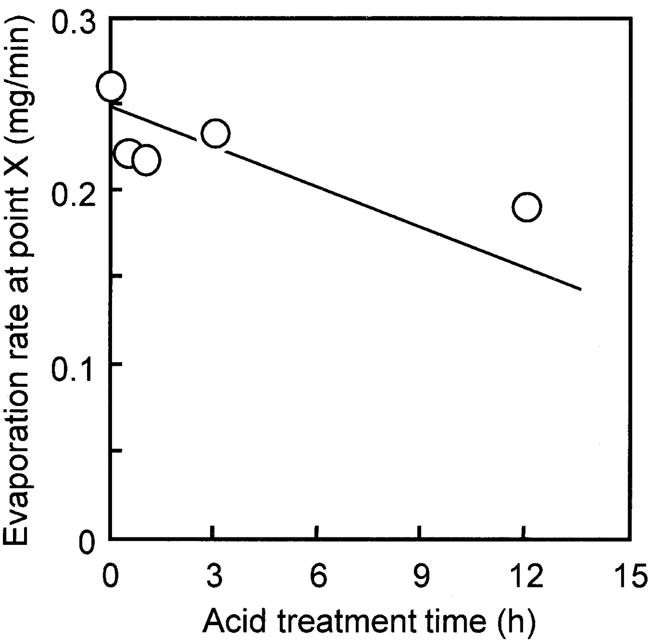

Fig. 12 Relationships between the acid treatment times in the stepwise alkali/acid treatments and the evaporation rates of water at point X on the evaporation rate curves shown in Figs. 6, 8, and 11

respectively. In Fig. 9, as the acid treatment time increased, the number and the size of the hollows decreased and increased, respectively, and the hollows tend to locate more in an inner part. The volume expansion became smaller with the increase in the acid treatment time as shown in Fig. 10. These results suggest that the hollows existing near the particle surface were gradually discharged into the medium with the acid treatment time.

Weight-loss curves based on the evaporation of water from the aqueous dispersions of the stepwise alkali/acid-treated particles having the different multihollow structures shown in Fig. 9 and evaporation rate curves are shown in Fig. 11. The evaporation behavior of water seems to depend on the multihollow structure, particularly in periods IV and V, in which the water evaporates from the inside of the particle. Point X was not observed in case of the alkali/acid-treated particles for 24 h. This indicates that the alkali/acid-treated particles for 24 h did not have much water inside as shown in Figs. 9f and 10.

The relationship between the acid treatment time and the evaporation rates of water at point X shown in Figs. 6, 8, and 11 is shown in Fig. 12. The evaporation rate at point X, which indicates the initial evaporation rate of water from the insides of the particles, became smaller with an increase in the acid treatment time. The evaporation rate from the particle should depend on the diffusion rate through the polymer phase. Here, supposing that the polymer phase is homogeneous, the diffusion rate per unit area depends on the distance between the hollow and the particle surface. From this viewpoint, it is likely that a number of small water pools located near the particle surface give a large initial evaporation rate from the particle because of the large diffusion area and the short diffusion distance. Accordingly, the decrease in the initial evaporation rate from the particles with the acid treatment time seems to be based on the fact that the number of small water pools, which existed near the surface of the alkali-treated particle, decreased because the water pools coagulated and became larger pool, and because they were discharged into the medium with the acid treatment time as shown in Fig. 9. The coagulation and discharge should decrease the interfacial free energy of the particle because of the decrease in the total interfacial area.

The relationships between the acid treatment time and the values of the slopes between points X and D and between points X and Y shown in Figs. 6, 8, and 11 are shown in Fig. 13. The value of the slope between points X and D became larger with an increase in the acid treatment time. This seems to be based on an increase in the difference between the evaporation rate of water inside the hollows at point X

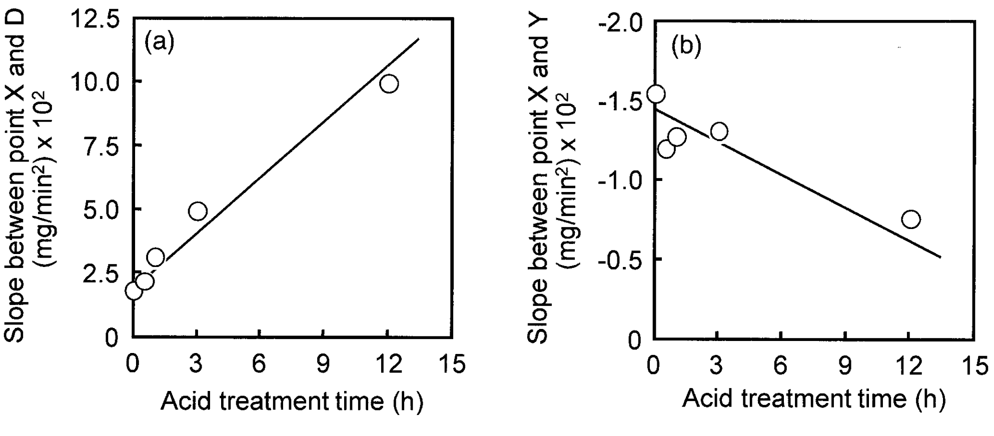

Fig. 13 Relationships between the acid treatment time in the stepwise alkali/acid treatments and the values of the slopes **a** between points X and D and **b** between points X and Y on the evaporation rate curves shown in Figs. 6, 8, and 11

and that of the free water among the particles in period III. The value of the slope between points X and Y became smaller with the acid treatment time. This seems to be based on a decrease in the amount of the water in the hollows, which corresponds to a decrease in the volume expansion of the stepwise alkali/acid-treated particles with the acid treatment time as shown in Fig. 10.

From these results, it is concluded that the P(S-MAA) (MAA, 5.0 mol%) particle after the alkali treatment had a number of small water pools inside. The formation mechanism of the multihollow structure by the stepwise alkali/acid method will be discussed in a thermodynamical treatment with this result elsewhere.

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