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ORIGINAL CONTRIBUTION

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Formation mechanism of a multihollow structure within submicron-sized styrene/methacrylic acid copolymer particles by the stepwise acid/alkali method

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Abstract The formation mechanism of a multihollow structure within submicron-sized styrene/methacrylic acid copolymer particles by the stepwise alkali/acid method, which we proposed in 1990, was discussed thermodynamically from the viewpoint of interfacial free energy.

Keywords Interfacial free energy · Multihollow · Emulsion polymerization · Stepwise alkali/acid method · Swelling

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 the particles by stepwise treatments with alkali and acid [1]; this was named the stepwise alkali/acid method. In following articles, the effects of some factors in the alkali-treatment [2, 3] and acid-treatment [4] processes on the formation of the multihollow structure were examined in detail. Moreover, multihollow S/MAA copolymer [P(S-MAA)] particles having a high glass-transition temperature were also prepared by the stepwise alkali/acid method [5].

In a previous article [6], in order to clarify the formation mechanism of a multihollow structure, the evaporation behavior of water from aqueous dispersions of original P(S-MAA) particles and the behavior after the alkali-treatment and the stepwise alkali/acid treatments were examined. It was concluded that the alkali-treated particle had a lot of water pools inside, the size of which was too small to observe with transmission electron microscopy (TEM).

In this article, the formation mechanism of the multihollow structure by coagulation of the water pools inside the P(S-MAA) particles in the acid-treatment process of the stepwise alkali/acid method is discussed thermodynamically from the viewpoint of interfacial free energy.

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, 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. Commercial grade poly(oxyethylene nonyl phenyl ether) nonionic emulsifier (Emulgen 911, Kao, 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

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 original particles were washed centrifugally three times with distilled water. The MAA content of the purified original

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

S (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 remaining amount (0.20 g) was added as an aqueous solution

[b] Measured by ^{1}H NMR

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

particles was 5.0 mol% as determined by ^{1}H NMR measurement. The weight-average molecular weight of P(S-MAA) was measured by gel permeation chromatography. Calibration was performed with polystyrene (PS) standards using tetrahydrofuran as the eluant. P(S-MAA) film was obtained by pressing dried original particles at 150 °C for 20 min at 4 MPa with aluminum plates and subsequently cooling in ice–water.

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 a pH of 12.0 with 1 N KOH aqueous solution. The molar ratio of KOH to carboxyl groups in the particles in the alkali-treatment process was 41/1, neglecting the carboxyl groups at the surfaces of the particles. This emulsion was placed in a stainless steel pressure-resistant vessel having a poly(tetrafluoroethylene) 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 molar ratio of HCl to carboxyl groups in the particles in the acid-treatment process at pH 3.0 was 41/1, neglecting the carboxyl groups at the particle surfaces. The emulsion was placed in an oil bath under various conditions (temperature, time), 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.

Measurement of particle diameter

The hydrodynamic diameters (D_h) of the original P(S-MAA) particles and those after the stepwise alkali/acid treatments were measured by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Kyoto, Japan) at room temperature.

Interfacial tension between P(S-MAA) and water

The interfacial tensions between P(S-MAA) and water ($\gamma_{p/w}$) at various pH values were obtained with Young's equation (Eqs. 1, 2) [7] and Owens' equation (Eqs. 3, 4) [8] from the measurement of the contact angles of air and CH_2I_2 on P(S-MAA) film in aqueous media at various pH values at room temperature according to the procedure in a previous article [9]

– Young's equation

$$\mathrm{Air}: \gamma_{P/A} = \gamma_{P/W} + \gamma_{W/A}\cos\theta \ , \tag{1}$$

$$\mathrm{CH_2I_2}: \gamma_{P/W} = \gamma_{P/L} + \gamma_{W/L}\cos\theta \ . \tag{2}$$

– Owens' equation

$$\mathrm{Air}: \gamma_{P/W} = \gamma_{P/A} + \gamma_{W/A} - 2\left(\gamma^{d}_{P/A}\gamma^{d}_{W/A}\right)^{1/2} - 2\left(\gamma^{p}_{P/A}\gamma^{p}_{W/A}\right)^{1/2} \ , \tag{3}$$

$$\mathrm{CH_2I_2}: \gamma_{P/L} = \gamma_{P/A} + \gamma_{L/A} - 2\left(\gamma^{d}_{P/A}\gamma^{d}_{L/A}\right)^{1/2} - 2\left(\gamma^{p}_{P/A}\gamma^{p}_{L/A}\right)^{1/2} \ , \tag{4}$$

where the subscripts A, L and P, respectively, mean air, CH_2I_2 and P(S-MAA), and superscripts d and p, respectively, mean the dispersion and the polar component. γ^d, γ^p and γ are defined by the following relation:

$$\gamma = \gamma^d + \gamma^p \ . \tag{5}$$

The values reported in Ref. [8] were used for the interfacial free energies of air and CH_2I_2 and are shown in Table 2.

Electron microscopy

A JEOL JEM-2010 electron microscope was used for 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.

Evaluation of total interfacial area of P(S-MAA) particles

The total interfacial area (A_t) of the multihollow particle was calculated from the number and the size of the hollows inside the particle and the particle diameter on the TEM photograph with image analysis software (Mac Scope, Mitani, Fukui, Japan).

Results and discussion

TEM photographs of the stepwise alkali/acid-treated P(S-MAA) particles for different acid-treatment times (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C) are shown in Fig. 1. While the MAA content in the monomers before the emulsion copolymerization was 8.0 mol%, that in the original P(S-MAA) particles after the centrifugal washing was 5.0 mol% as determined by ^{1}H NMR measurement. This

Table 2 Components of the interfacial free energies (γ) for water and CH_2I_2 at 20 °C [8]. The superscripts d and p represent the dispersion and polar components, respectively. Water (*W*), air (*A*), CH_2I_2 (*L*)

	γ (mJ/m^2)	γ^d (mJ/m^2)	γ^p (mJ/m^2)
W/A	72.8	21.8	51.0
L/A	50.8	49.5	1.3
W/L	41.6		

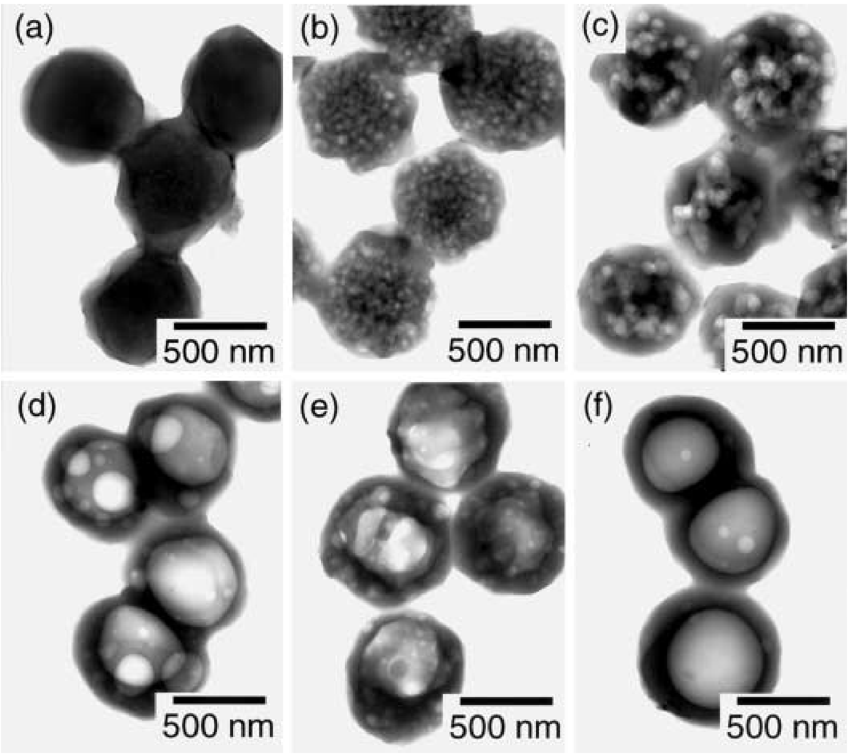


Fig. 1 Transmission electron microscopy (*TEM*) photographs of the stepwise alkali/acid-treated styrene/methacrylic acid copolymer [*P(S-MAA)*] (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 130 °C) for different acid-treatment times (h): **a** 0, **b** 0.25, **c** 0.5, **d** 1, **e** 3, **f** 12

should be based on dissolution of a part of P(S-MAA) having a high MAA content in the aqueous medium. The multihollow structure was not observed inside the alkali-treated particle as shown in Fig. 1a, though it should have a lot of small water pools inside as clarified in a previous article [6]. Small hollows were clearly observed after 15-min acid treatment, and the hollow size increased with the acid-treatment time. After 12-h acid treatment, only a large hollow was observed inside.

TEM photographs of the stepwise alkali/acid-treated P(S-MAA) particles at different pH values in the acid-treatment process (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: 130 °C, 3 h) are shown in Fig. 2. Larger and fewer hollows were observed with a decrease in the pH. This result seems to be based on an increase in $\gamma_{\mathrm{p/w}}$ with a decrease in the degree of ionization of carboxyl groups in the P(S-MAA) particles. In order to clarify this point, $\gamma_{\mathrm{p/w}}$ was determined by the measurement of contact angles of air and CH_2I_2 on the P(S-MAA) (MAA, 5.0 mol%) film in water at various pH values.

The relationships between the pH in the acid-treatment process and $\gamma_{\mathrm{p/w}}$ and A_{t} of the stepwise alkali/acid-treated particle are shown in Fig. 3. The measured contact angles of air and CH_2I_2 on the P(S-MAA) films in water, calculated surface free energies of the films, and $\gamma_{\mathrm{p/w}}$ at various pH values are summarized in Table 3. $\gamma_{\mathrm{p/w}}$ decreased with an increase in the pH. $\gamma_{\mathrm{p/w}}$ at pH 5.6 was lower than that (16.8 mN/m) between distilled water (pH 6) and PS film prepared by melt-pressing the dried PS particles produced by emulsifier-free emulsion polymerization [9]. These results should be due to the carboxyl group in copolymerized MAA, and its ionization. A_{t}, which increases with a decrease in the size of the hollows at the same total hollow volume, increased with the increase in the pH. These results suggest that the multihollow structure formed by the stepwise alkali/acid treatments correlates with $\gamma_{\mathrm{p/w}}$.

In Fig. 4, lines show simulations for the variation of the interfacial free energies (G), which are defined by the product of A_{t} and $\gamma_{\mathrm{p/w}}$, as a function of A_{t} at various pH values at which the $\gamma_{\mathrm{p/w}}$ values were different. The open circle, the crossed circle, the triangle, the open square, and the crossed square indicate the experimental G values just after the stepwise alkali/acid treatments, and the filled square indicates the G value calculated from the diameter (0.75 nm) of the water pool inside the alkali-treated particle assuming that H_2O molecules, the total volume of which corresponds to 46 vol% of the alkali-treated particle determined by DLS measurement, uniformly surround each carboxyl group which exists separately from others within the particle. The G value just before the acid treatment was higher at lower pH values because $\gamma_{\mathrm{p/w}}$ was higher at lower pH values. Beside, the experimental G values just after the acid treatments (130 °C, 3 h) at the different pH values were almost the same. These results indicate that the rate of decrease in the G value, which is caused by the decrease in the A_{t} value, was larger at lower pH values.

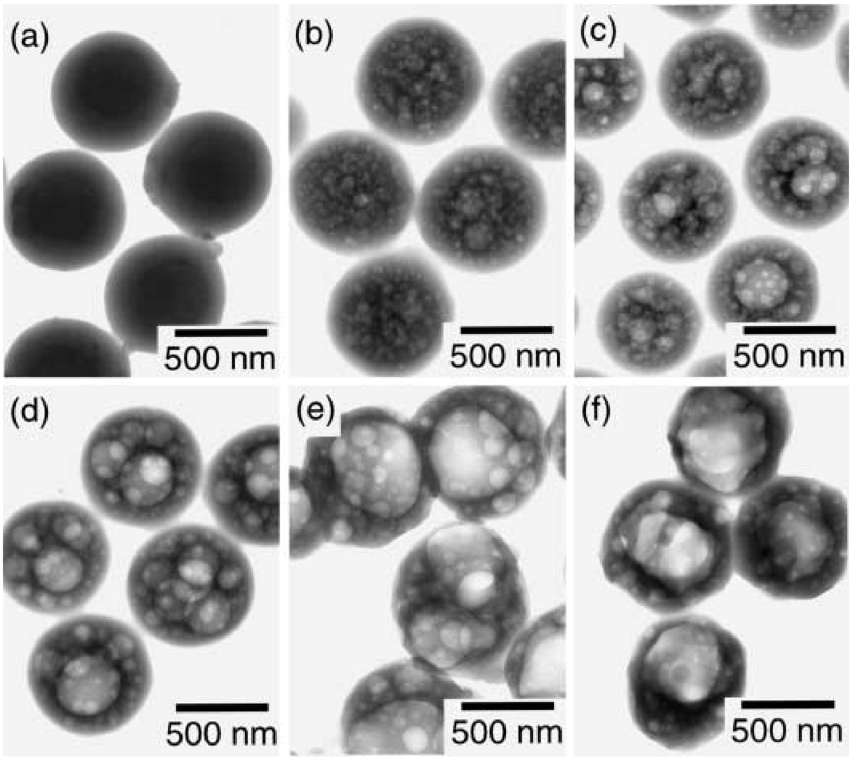


Fig. 2 TEM photographs of the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: 130 °C, 3 h) at different initial pH values in the acid-treatment process: **a** 12.0, **b** 10.0, **c** 9.0, **d** 7.0, **e** 5.0, **f** 3.0

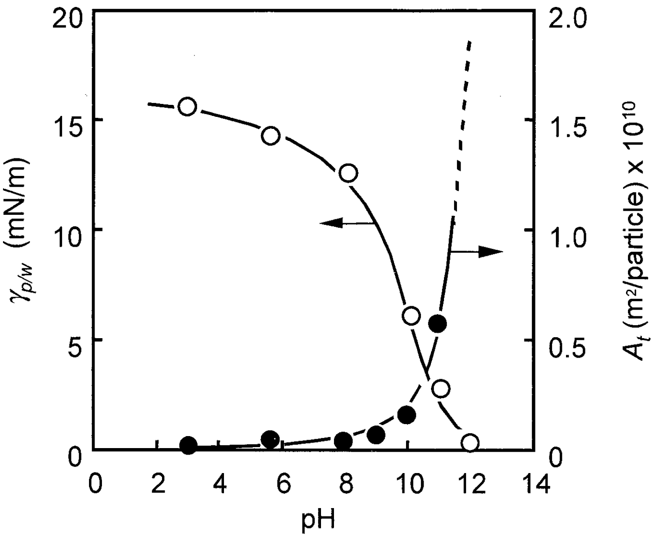


Fig. 3 Relationships between pH value and interfacial tension of P(S-MAA)/water, $\gamma_{p/w}$ (*open circles*), calculated from the contact angles of air and CH_2I_2 on P(S-MAA) (MAA, 5.0 mol%) films in water and between the initial pH value in the acid-treatment process and total interfacial area, A_t (*filled circles*), calculated from the number and the size of hollows in TEM views of each stepwise alkali/acid-treated P(S-MAA) particle (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: 130 °C, 3 h)

Table 3 Contact angles (measured at about 0.5 s after air or CH_2I_2 drop attached on the film) of air and CH_2I_2 on P(S-MAA) (MAA, 5.0 mol%) film (prepared by pressing at 150 °C for 20 min) in water at various pH values, surface free energies of the film and interfacial tensions between P(S-MAA) and water

pH	Contact angle (degrees)		Surface free energy (mJ/m^2)		Interfacial tension (mN/m)	
	θ_{air}	$\theta_{CH_2I_2}$	$\gamma^d{}_P$	$\gamma^p{}_P$	γ_P	$\gamma_{P/W}$
3	57	78	43.5	13.7	57.2	15.6
5.6	51	81	44.5	15.5	60.0	14.3
7	44	86	46.1	18.4	64.5	12.6
10	32	106	39.7	28.0	67.7	6.1
11	13	123	36.3	37.4	73.7	2.9
12	23	152	21.7	45.5	67.2	0.2

TEM photographs of the stepwise alkali/acid-treated P(S-MAA) particles at initial pH 3.0 and 10.0 for different times in the acid-treatment process (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: 130 °C) are shown in Fig. 5. At pH 3.0, only one hollow was observed inside the particle after 12-h acid treatment. At pH 10.0, though it was not real "acid" treatment, the multihollow structure was still observed inside the particle after long acid treatment for 48 h. This result indicates that the rate of decrease of A_t becomes larger with a decrease in the pH value in the acid-treatment process.

TEM photographs of the stepwise alkali/acid-treated P(S-MAA) particles prepared at different temperatures in the acid-treatment process (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 3 h) are shown in Fig. 6. At the same acid-treatment time,

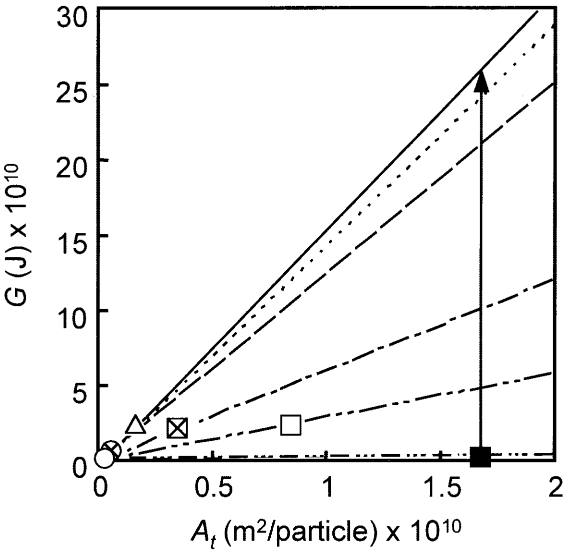
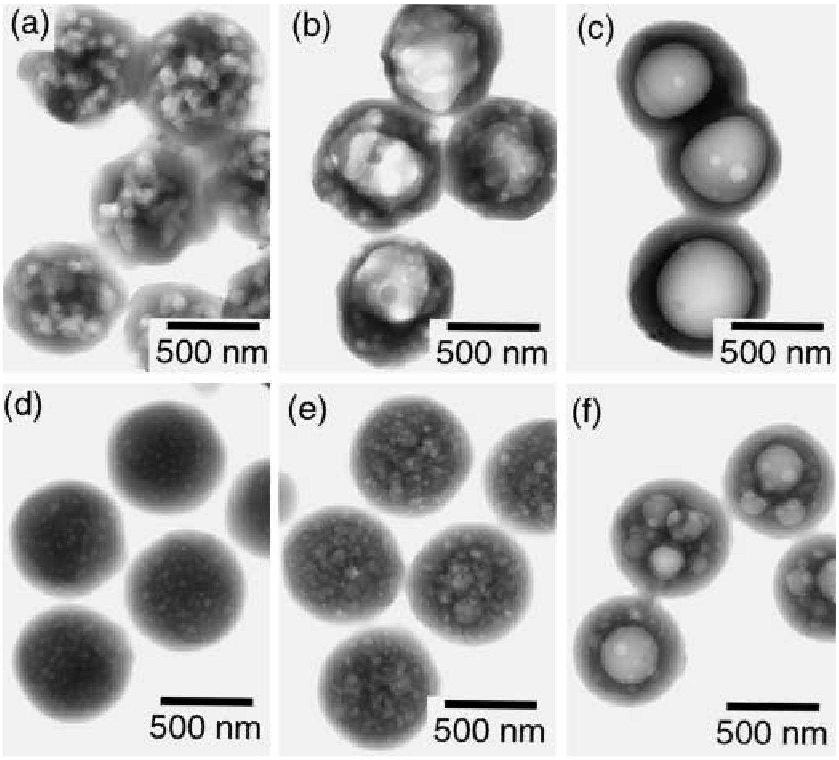


Fig. 4 Simulations for the variation of interfacial free energies (G) calculated using the experimental $\gamma_{p/w}$ values at various pH values (—— 3.0, ······ 5.6, - - - - 8.0, –·– 10.0, –··– 11.0, –···– 12.0) as a function of A_t of the P(S-MAA) (MAA, 5.0 mol%) particle. The *filled square* indicates the G value for the alkali-treated particle supposing that the size of the water pools inside the particle is 0.75 nm, and the other symbols indicate the G value obtained with the experimental A_t values for the stepwise alkali/acid-treated particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: 130 °C, 3 h) at different initial pH values in the acid-treatment process: 3.0 (*open circle*), 5.6 (*crossed circle*), 8.0 (*triangle*), 10.0 (*crossed square*), 11.0 (*open square*)

larger and fewer hollows were observed with an increase in the acid-treatment temperature. This indicates that the rate of decrease of A_t becomes larger at higher acid-treatment temperature.

From these results, the formation mechanism of the multihollow structure can be explained as follows. In the alkali-treatment process, because carboxyl groups ionize, the P(S-MAA) particle absorbs a certain amount of water and results in a lot of small water pools inside. This gives large A_t value but the G value is still small because of small $\gamma_{p/w}$. However, when the pH is rapidly changed to acidic in the acid-treatment process, the G value drastically increases because of a marked increase in $\gamma_{p/w}$, i.e., the state of the particle having a lot of small water pools becomes remarkably thermodynamically unstable. Accordingly, the acid treatment at higher temperature than the glass-transition temperature causes coagulation of water pools within the particle, and results in hollows. This leads the particle to a more thermodynamically stable state by decreasing A_t. In other words, the variation of the multihollow structures in the stepwise alkali/acid-treated particles at the various pH values in the acid-treatment process causes the decrease in the large G value. Therefore, the slope of each line ($\gamma_{p/w}$) in Fig. 4 indicates the degree of driving force for the coagulation of the water pools within the particle in the acid-treatment process, and the increase in the

Fig. 5 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: 130 °C, initial pH: **a**, **b**, **c** 3.0; **d**, **e**, **f** 10.0; times (h): **a**, **d** 0.5, **b**, **e** 3, **c** 12, **f** 48



acid-treatment temperature accelerates the rate of the coagulation.

TEM photographs of the alkali-treated P(S-MAA) particles at initial pH 12.0 at 150 °C for long times are shown in Fig. 7. The multihollow structure was observed after long alkali-treatment times of 3 and 5 days for which the *G* value is low because of low $\gamma_{p/w}$. This supports the previously discussed formation mechanism.

TEM photographs of the stepwise alkali/acid-treated P(S-MAA) particles for different acid-treatment times (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 5.0, 130 °C) are shown in Fig. 8.

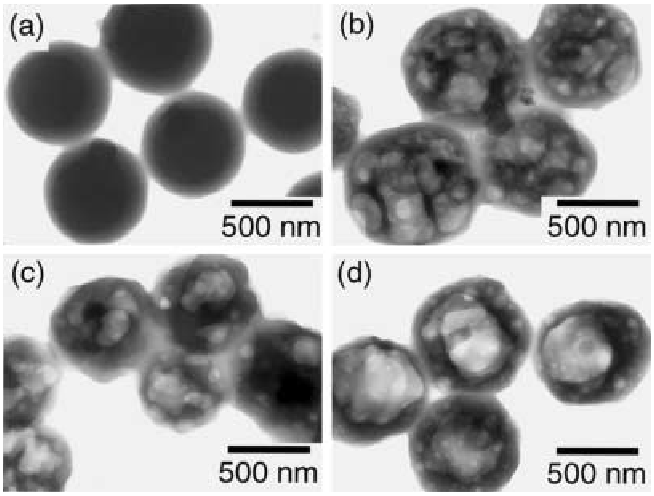


Fig. 6 TEM photographs of the stepwise alkali/acid-treated P(S-MAA) (MAA, 5.0 mol%) particles (alkali treatment: initial pH 12.0, 150 °C, 3 h; acid treatment: initial pH 3.0, 3 h) at different acid-treatment temperatures (°C): **a** 50, **b** 80, **c** 100, **d** 130

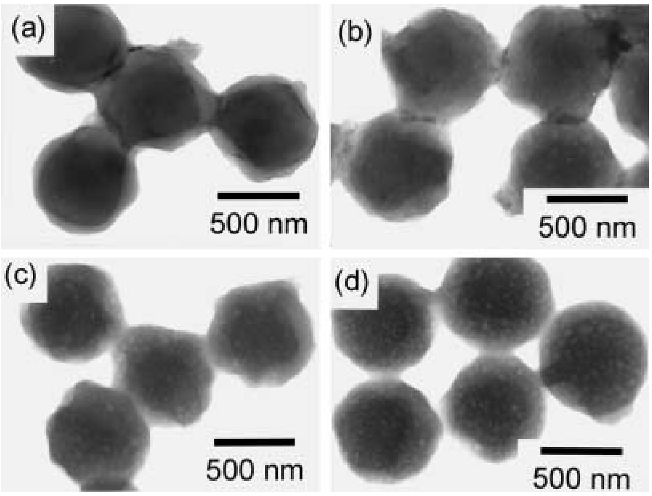
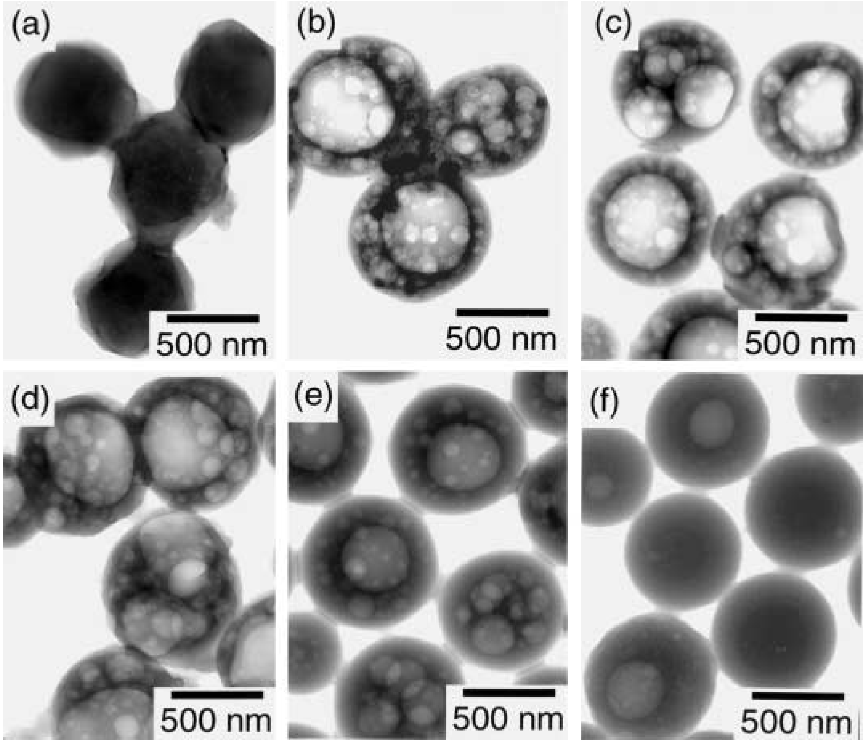


Fig. 7 TEM photographs of the alkali-treated P(S-MAA) (MAA, 5.0 mol%) particles at initial pH 12.0 at 150 °C for different times (h): **a** 3, **b** 24, **c** 72, **d** 120

Fig. 8 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 5.0, 130 °C) at different acid-treatment times (h): **a** 0, **b** 0.5, **c** 1, **d** 3, **e** 12, **f** 24



Finally, the hollows within the particle disappeared after the acid treatment for 24 h, which indicates that the particle attained a thermodynamically stable state again. This result agrees with the assumption made in a previous article [6] that the number of hollows inside the stepwise alkali/acid-treated particles decreases with the acid-treatment time by being discharged into the medium as well as by coagulation into large ones in order to decrease the G value based on a decrease in the A_t value.

From these results, the formation of the multihollow structure by the stepwise alkali/acid method is reasonably explained thermodynamically from the viewpoint of the interfacial free energy as follows. In the alkali-treatment process, the ionized P(S-MAA) particle absorbed a certain amount of water as a lot of water pools. The size of the water pools is too small to be observed clearly with TEM. Therefore, the A_t value between the water pools and the ionized P(S-MAA) is very large. However, since the $\gamma_{p/w}$ value between the water pool and ionized P(S-MAA) is small, the G value is not so large in the alkali-treatment process. In the acid-treatment process, ionized carboxyl groups are deionized. Since the $\gamma_{p/w}$ value between the water pool and deionized P(S-MAA) is large, the G value is instantly increased drastically. The water pools start to coagulate at a high rate to decrease the A_t value, which decreases the G value, and results in hollows.

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