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SHORT COMMUNICATION

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Effect of polymer composition on the production of cationic multihollow polymer particles by the stepwise acid/alkali method

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Abstract The effect of the polymer composition on the formation of multihollow structures formed within submicron-sized styrene–butyl acrylate–dimethylaminoethyl methacrylate terpolymer particles by the "acid/alkali method" proposed by the authors was examined. The cationic particles were produced by seeded emulsion terpolymerization with 2,2′-azobis(2-amidinopropane) hydrochloride initiator. The dimethylaminoethyl methacrylate content and the glass-transition temperature of the terpolymer greatly affected the formation of the multihollow structure.

Key words Hollow – Particle – Emulsion polymerization – Morphology – 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 by stepwise treatment with alkali and acid [1]; this was named the stepwise alkali/acid method. The effects of some factors in the alkali [2, 3] and acid [4] treatment processes on the formation of multihollow structures were examined in detail. On the basis of the results, a formation mechanism was proposed.

In a previous article [5], in order to extend the possibility of preparation of such multihollow particles and to check the proposed formation mechanism, we produced multihollow particles by the reverse method in which acid-swellable particles produced by emulsion terpolymerization using dimethylaminoethyl methacrylate (DM) as alkaline monomer were treated stepwise with acid and alkali; this was named the stepwise acid/alkali method. The formation mechanism was proposed to be as follows. First, the dimethylamino group-containing particles swell with water in acidic conditions at temperatures higher than the glass-transition temperature (T_g). Subsequently, in the early stage of the alkali-treatment process, the polymer wall is formed quickly at the surface of acid-swollen particles, because polymer molecules containing "soluble" segments having ionized dimethylamino groups are precipitated by their deionization. The shell prevents the particles 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 multihollow polymer particles.

In this article, the effect of the polymer composition on the formation of multihollow particles by the stepwise acid/alkali method will be clarified.

Experimental

Materials

Styrene (S) and butyl acrylate (BA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. DM was used without further purification. Commercial grade 2,2′-azobis(2-amidinopropane) hydrochloride (V–50, Wako Pure Chemical Industries) was purified by recrystallization. Commercial grade polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 930, Kao Atlas) was used as received.

Analytical grade potassium hydroxide and hydrochloric acid were used without further purification. Deionized water was distilled.

Preparation of polymer particles

Two series of S-BA-DM terpolymer [P(S-BA-DM)] particles having different polymer composition were prepared by three stages of emulsion terpolymerizations at 65 °C. The first series of particles had different DM contents at the same S/BA molar ratio of 74/26, and the second one had different S/BA molar ratios at the same DM content of 15 mol%. The second and third stages of emulsion terpolymerization were performed in a monomer-starved state for the preparation of P(S-BA-DM) particles having the same size, narrow size distribution, and relatively narrow polymer composition distribution.

Table 1 shows a recipe for the preparation of the P(S-BA-DM) (62.9/22.1/15.0 molar ratio) emulsion as an example of these polymerizations. In the first stage, 1.50 g of the monomer mixture was polymerized for 2 h. In the second stage, 18.04 g of the monomer mixture was added with a microfeeder for 10 h, and the polymerization was continued for a further 12 h. A part of the emulsion obtained (75 g) was used as the seed emulsion for the third stage polymerization. The diameter of the seed particle was measured by dynamic light scattering (DLS). In the third stage, the amount of the monomer mixture which was needed to increase the particle diameter to 300 nm was added with the microfeeder for 10 h, and the polymerization was further continued for 14 h. The residual monomer was not detected by gas chromatography. The other emulsions were prepared using a similar procedure. The recipes of the third stage for the preparations of various terpolymer emulsions having different DM contents and S/BA ratios are shown in Tables 2 and 3, respectively. Additionally, final particle diameters and the glass-transition temperatures calculated by applying Fox's equation are shown in Tables 2 and 3.

Table 1 Recipe of stage-type emulsion polymerization[a] for the preparation of the terpolymer of styrene (*S*), butyl acrylate (*BA*), and dimethlyaminoethyl methacyrlate (*DM*) [P(S-BA-DM)] (62.9/22.1/15.0 molar ratio; glass-transition temperature T_g^b = 31 °C) emulsion

Ingredients	1st stage[c]	2nd stage[d]	3rd stage[e]
Seed emulsion[f]	–	–	75
S	0.84	10.1	4.11
BA	0.36	4.37	1.78
DM	0.30	3.66	1.49
V-50[g]	0.2	–	0.2
Emulgen 930[h]	0.05	–	–
Water	270	–	210

[a] N_2; 65 °C; stirring rate 120 rpm
[b] Calculated from the monomer composition using Fox's equation
[c] For 2 h
[d] Monomer mixture was added for 10 h and further polymerization was continued for 12 h
[e] Monomer mixture was added for 10 h and further polymerization was continued for 14 h
[f] Synthesized in the second stage (solid content 68.6 g/l)
[g] 2,2′-Azobis(2-amidinopropane) hydrochloride
[h] Polyoxyethylene nonylphenylether nonionic emulsifier

Electron microscopy

A JEOL JEM-2010 electron microscope was used for transmission electron microscopic (TEM) observation. Each emulsion was diluted down 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.

Measurement of particle diameters

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

Measurement of emulsion viscosity

The viscosity of each emulsion, which was concentrated to 27 wt%, was measured at 70 °C with an ARES 100FRTNI rheometer (Rheometrics) using Couette geometry at a shear rate of 1000 s^{-1}, which was large enough to produce a measurable torque.

Stepwise acid/alkali treatment

The P(S-BA-DM) emulsions were treated stepwise with acid and alkali as follows.

Acid treatment: Each original P(S-BA-DM) emulsion was diluted down to 0.6 g/l, and adjusted to pH 2.0 with 5 N HCl

Table 2 Recipes of seeded emulsion polymerizations[a] for the preparation of P(S-BA-DM) (S/BA molar ratio 74/26) emulsions having different DM contents

DM content (mol%)	10.0	12.5	15.0	17.5	20.0	22.5
Seed emulsion[b] (g)	0	75	75	75	75	75
S (g)	10.4	4.4	4.1	11.3	10.2	9.8
BA (g)	4.5	1.9	1.8	4.9	4.4	4.2
DM (g)	2.4	1.3	1.5	4.9	5.2	5.8
V-50 (g)	0.2	0.2	0.2	0.2	0.2	0.2
Emulgen 930 (g)	0.05	0	0	0	0	0
Water (g)	270	210	210	195	195	195
D_h^c (nm)	314	314	303	300	312	277
T_g^d (°C)	32.2	31.7	31.2	30.7	30.2	29.9

[a] N_2; 65 °C; 24 h stirring rate 120 rpm
[b] Each seed emulsion was prepared by a similar procedure as shown in the first and second stages of Table 1
[c] Hydrodynamic diameter measured by dynamic light scattering
[d] Calculated from the monomer composition using Fox's equation

Table 3 Recipes of seeded emulsion polymerizations[a] for the preparation of P(S-BA-DM) (DM 15 mol%) emulsions having different S/BA ratios

S/BA (molar ratio)	60/40	70/30	74/26	80/20	90/10	100/0
Seed emulsion[b] (g)	75	75	75	75	75	0
S (g)	2.5	3.1	4.1	4.2	4.3	15.1
BA (g)	2.1	1.6	1.8	1.3	0.6	0
DM (g)	1.1	1.2	1.5	1.4	1.3	4.1
V-50 (g)	0.2	0.2	0.2	0.2	0.2	0.2
Emulgen 930 (g)	0	0	0	0	0	0.1
Water (g)	210	210	210	210	210	270
D_h^c (nm)	286	302	303	300	292	318
T_g^d (°C)	11.1	26.2	31.2	40.7	57.9	78.9

[a] N_2; 65 °C; 24 h stirring rate 120 rpm
[b] Each seed emulsion was prepared by a similar procedure as shown in the first and second stages of Table 1
[c] Hydrodynamic diameter measured by dynamic light scattering
[d] Calculated from the monomer composition using Fox's equation

aqueous solution. These emulsions were placed in 50-ml glass vessels and the vessels were dipped in a water bath at 70 °C for 5 h.

Alkali treatment: The acid-treated emulsions were adjusted to pH 12.0 with 5 N KOH aqueous solution. The vessel in which the emulsion for alkali treatment was placed was dipped in a water bath for 5 h at 60 or 70 °C.

After both treatments, each emulsion was cooled by keeping the vessel at room temperature.

Volume expansion

The expansion of the particle volume by the acid or the stepwise acid/alkali treatment was calculated from the hydrodynamic diameters (D_h) of the particles measured by DLS before and after treatment.

Results and discussion

A TEM photograph of P(S-BA-DM) (62.9/22.1/15.0 molar ratio) particles produced under the conditions listed in Table 1 is shown in Fig. 1. The contrast of the particle inside was homogeneous. This indicate that the original particles had no hollow structure. The other P(S-BA-DM) particles having different DM contents and S/BA ratios, which were produced under the conditions listed in Tables 2 and 3, also had homogeneous structures (the photographs were omitted). As shown in Tables 2 and 3, since the D_h values of the particles used in this experiment were about 300 nm, the influence of particle diameter on the data obtained in this paper should be neglected.

The relationship between the DM content in P(S-BA-DM) (S/BA molar ratio 74/26) particles and the volume expansion of the acid-treated particles based on the untreated original particles is shown in Fig. 2. The volume expansion had a maximum value at a DM content of 17.5 mol%. This seems to be based on the increase in the polymer hydrophilicity with an increase in the DM content; that is, the increase in the polymer hydrophilicity causes swelling of the particles and some of the polymers to dissolve in the aqueous medium.

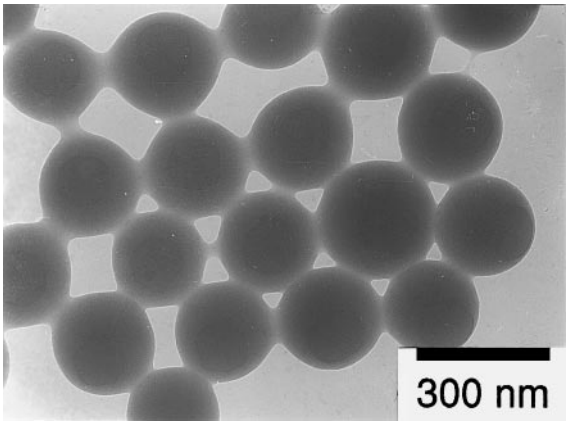

Fig. 1 A transmission electron microscope (*TEM*) photograph of the terpolymer of styrene (*S*), butyl acrylate (*BA*), and dimethylamino ethyl methacrylate (*DM*) [P(S-BA-DM)] (62.9/22.1/15.0 molar ratio) particles produced by emulsion terpolymerization

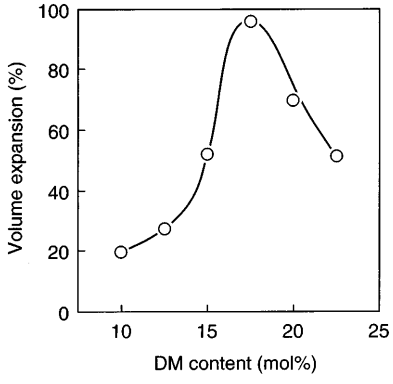

Fig. 2 Relationship between the DM content and the volume expansion of P(S-BA-DM) (S/BA molar ratio 74/26) particles by acid treatment (initial pH 2.0; 70 °C; 5 h). The volume expansion was calculated from the diameters measured by dynamic light scattering (*DLS*) at 40 °C

The relationships between the DM content and the viscosity of P(S-BA-DM) original emulsions and those after acid treatment (initial pH 1.0; 70 °C; 8 h) are shown in Fig. 3. Below 15.0 mol%, there was little difference in the viscosity between the emulsions before and after acid treatment. Above 17.5 mol%, the difference increased with the increase in the DM content. This supports the above idea that a some of the polymer molecules having high DM contents dissolve from the particle into the medium in the acid-treatment process.

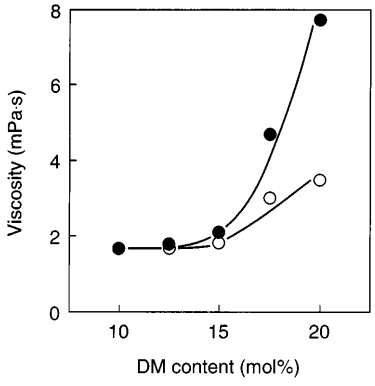

Fig. 3 Relationships between the DM content and the viscosity of P(S-BA-DM) (S/BA molar ratio 74/26) emulsions at 70 °C before (○) and after (●) acid treatment (initial pH 1.0; 70 °C; 8 h) at a shear rate of 1000 s^{-1}

TEM photographs of P(S-BA-DM) particles having various DM contents treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0; 70 °C; 5 h; alkali treatment: initial pH 12.0; 70 °C; 5 h) as shown in Fig. 4. The relationship between the DM content and the volume expansion is shown in Fig. 5. The number of hollows per particle was a maximum at a DM content of 12.5 mol%. Above 12.5 mol%, the number decreased with the increase in the DM content, and reached 1 above 20 mol%. Below 17.5 mol%, the volume expansion increased with the increase in the DM content, whereas above 20 mol% it became smaller. At 22.5 mol%, the particles had almost the same size as the original particle, though they had a hollow structure. This obviously indicates that swelling and dissolution occurred at the same time. The relationship shown in Fig. 5 was in agreement with that of the particle after acid treatment shown in Fig. 2. This indicates that the hollow volume depends on the degree of particle swelling in the acid-treatment process.

From these results, it is clear that there is an optimum DM content in P(S-BA-DM) particles to form a multihollow structure by acid/alkali treatment.

The relationship between the S/BA ratio in P(S-BA-DM) (DM content 15 mol%) particles and the volume expansion by acid treatment (acid treatment: initial pH 2.0; 70 °C; 5 h) is shown in Fig. 6. At S/BA ratios below 80/20, their volume expansions were constant at a high

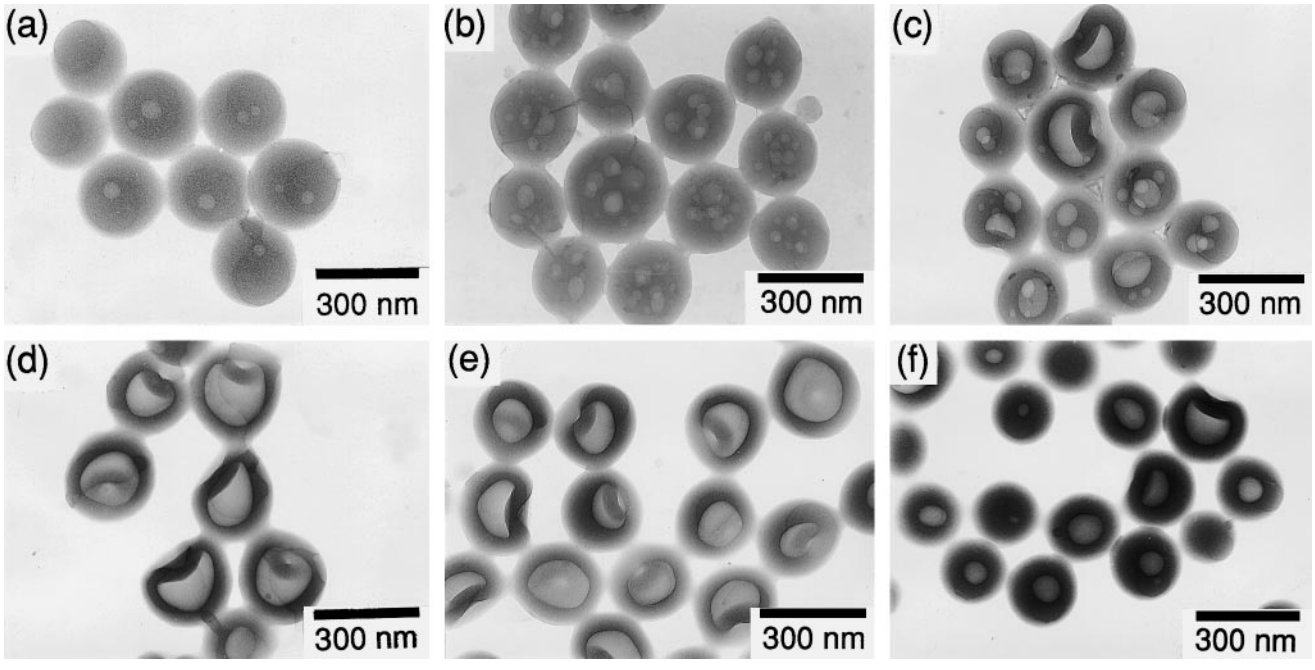

Fig. 4 TEM photographs of P(S-BA-DM) (S/BA molar ratio 74/26) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0; 70 °C; 5 h; alkali treatment: initial pH 12.0; 70 °C; 5 h). DM content (mol%): **a** 10.0, **b** 12.5, **c** 15.0, **d** 17.5, **e** 20.0, **f** 22.5

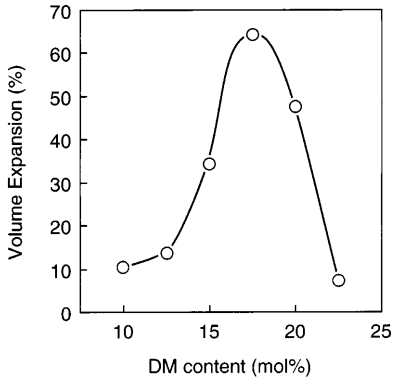

Fig. 5 Relationship between the DM content and the volume expansion of P(S-BA-DM) (S/BA molar ratio 74/26) particles by the acid/alkali method (acid treatment: initial pH 2.0; 70 °C; 5 h; alkali treatment: initial pH 12.0; 70 °C; 5 h)

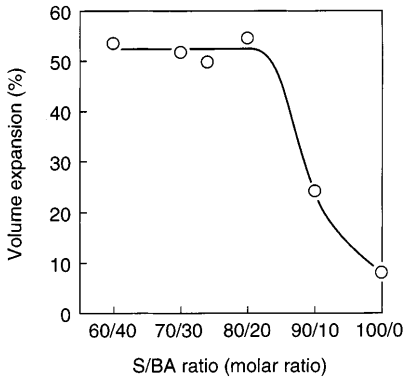

Fig. 6 Relationship between the S/BA ratio and the volume expansion of P(S-BA-DM) (DM 15 mol%) particles by acid treatment (initial pH 2.0; 70 °C; 5 h). The volume expansion was calculated from the diameters measured by DLS at 40 °C

level value. Above 90/10, the volume expansion decreased markedly with an increase in the ratio. As shown in Table 3, T_g of the terpolymers increased with the increase in the ratio. This indicates that the polymer particles having T_g values lower than the treatment temperature can swell in the acid treatment.

TEM photographs of P(S-BA-DM) particles having various S/BA ratios treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0; 70 °C; 5 h; alkali treatment: initial pH 12.0; 70 °C; 5 h) are shown in Fig. 7. At the S/BA ratios of 74/26 (Fig. 7c) and 80/20 (Fig. 7d), multihollow structures was clearly observed. At 90/10 (Fig. 7e) and 100/0 (Fig. 7f), the particles had no hollow structure. At ratios of 60/40 (Fig. 7a) and 70/30 (Fig. 7b), multihollow structures were hardly observed inside the particles, although both particles had a similar swelling state as those having S/BA ratios of 74/26 and 80/20 in the acid treatment as shown in Fig. 6.

Figure 8 shows TEM photographs of P(S-BA-DM) particles treated at 60 °C alkali treatment temperature under the same conditions as those in Fig. 7. At the S/

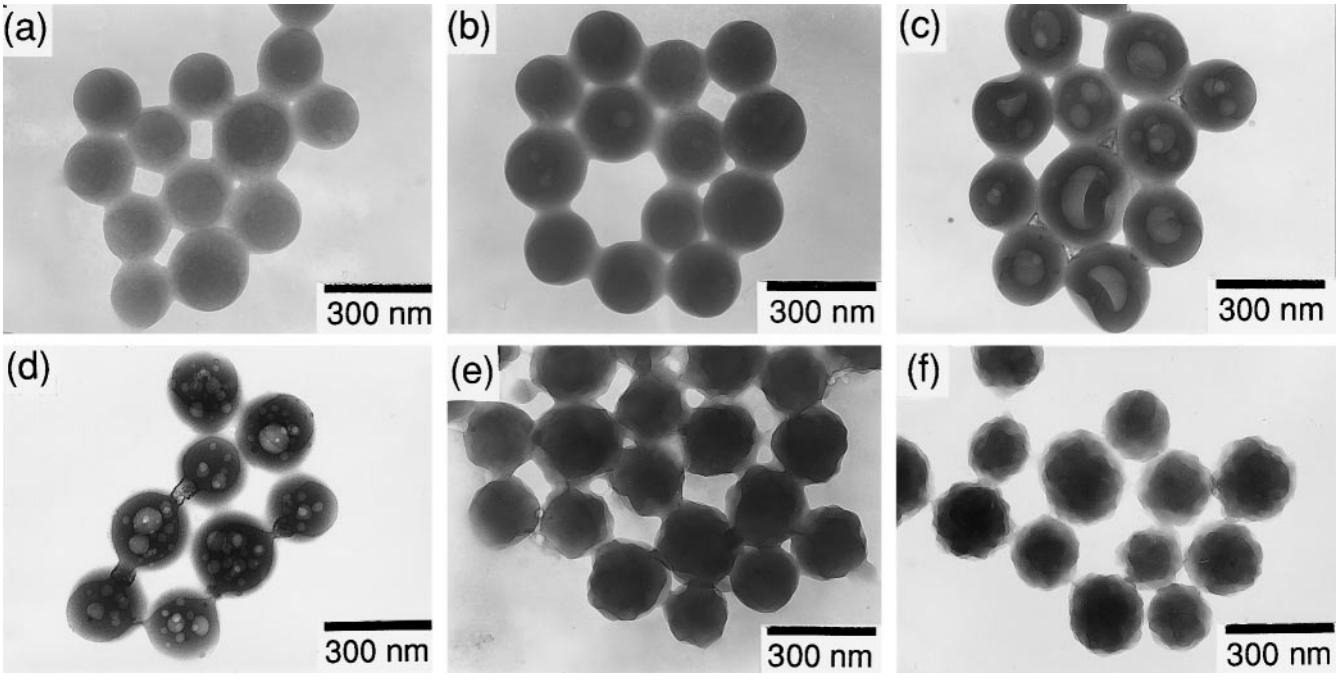

Fig. 7 TEM photographs of P(S-BA-DM) (DM 15 mol%) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0; 70 °C; 5 h; alkali treatment: initial pH 12.0; 70 °C; 5 h). S/BA (molar ratio): **a** 60/40, **b** 70/30, **c** 74/26, **d** 80/20, **e** 90/10, **f** 100/0

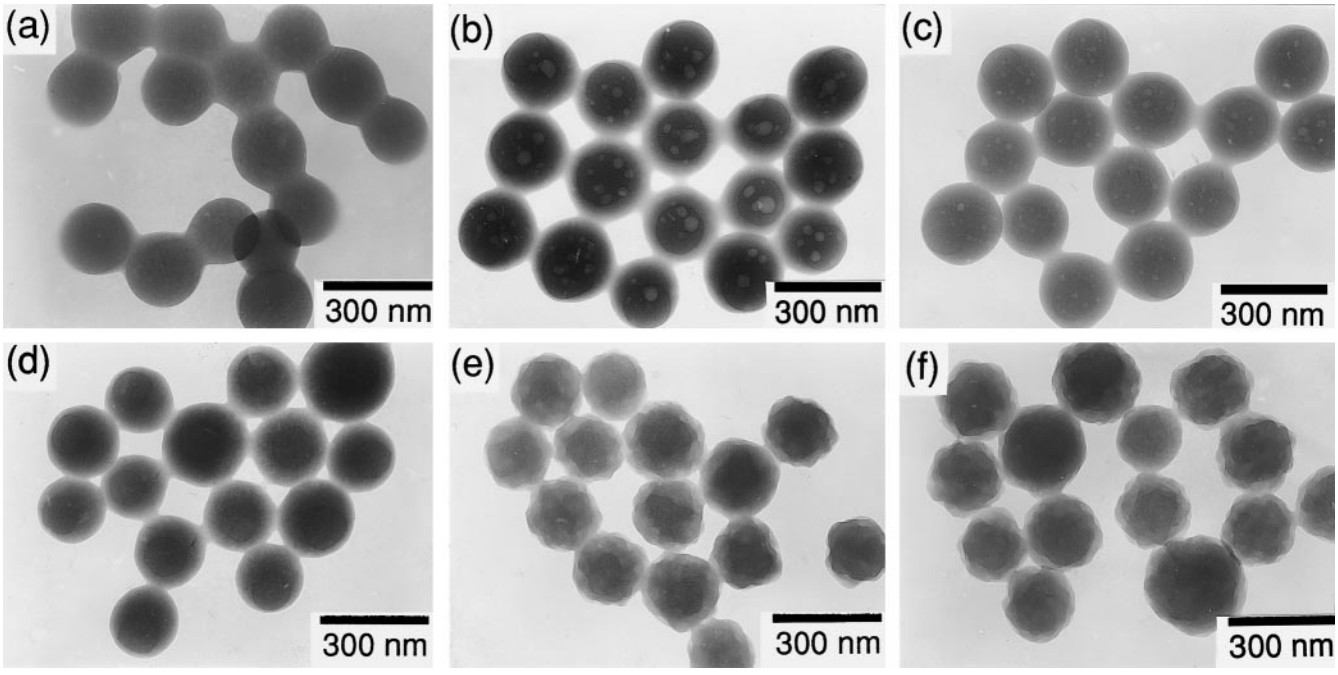

Fig. 8 TEM photographs of P(S-BA-DM) (DM 15 mol%) particles treated by the stepwise acid/alkali method (acid treatment: initial pH 2.0; 70 °C; 5 h; alkali treatment: initial pH 12.0; 60 °C; 5 h). S/BA (molar ratio): **a** 60/40, **b** 70/30, **c** 74/26, **d** 80/20, **e** 90/10, **f** 100/0

BA ratio of 70/30 (Fig. 8b), the hollow structure was observed clearly, though it was hardly observed in the particles treated at 70 °C in the alkali treatment (Fig. 7b). At 74/26 (Fig. 8c), very fine hollows were observed with difficulty, and at 80/20 (Fig. 8d) the particles had no hollow structure, though those treated at 70 °C (Fig. 7c, d) had clear multihollow structures. At other S/BA ratios, multihollow structures were not observed.

From these results, it is obvious that the composition of P(S-BA-DM) had a great influence on the formation of multihollow structures by the stepwise acid/alkali method, which supports the formation mechanisms of multihollow particles discussed in previous articles [1–5].

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