Colloid Polym Sci 278:358–363 (2000)

ORIGINAL CONTRIBUTION

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Effect of nonionic emulsifier on the production of multihollow polymer particles by the stepwise acid/alkali method

Part CXCV of the series "Studies on suspension and emulsion"

Received: 22 June 1999
Accepted in revised form: 20 October 1999

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Abstract The effects of nonionic emulsifier on the formation of multihollow structures formed within sub-micron-sized polymer particles by the "acid/alkali method" proposed by the authors were examined. The original acid-swellable particles were produced by seeded emulsion terpolymerization of styrene, butyl acrylate, and dimethylaminoethyl methacrylate. The results indicate that the nonionic emulsifier had a great effect on the formation of multihollow particles.

Key words Hollow · Particle · Emulsion polymerization · Morphology · Swelling

Introduction

Sub-micron-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 structures [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 compositions.

We found that sub-micron-sized S–butyl acrylate (BA)–methacrylic acid terpolymer particles produced by emulsion terpolymerization were changed to those having many hollows by stepwise treatments with alkali and acid [2]; this was named the stepwise alkali/acid method. In addition, the effects of some factors in the alkali- [3, 4] and acid- [5] treatment processes on the formation of multihollow structure were examined in detail. On the basis of the results, the formation mechanism was proposed.

In a previous article, in order to extend the possibility of preparing such multihollow particles and to check the proposed formation mechanism, the particles were prepared by the reverse method in which acid-swellable particles produced by emulsion terpolymerization with dimethylaminoethyl methacrylate (DM) as an alkaline monomer were treated stepwise with acid and alkali; this was named the stepwise acid/alkali method [6]. Moreover, the effect of polymer composition on the formation of the multihollow structure was clarified [7]. The formation mechanism was proposed 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 "shell" 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 the series of investigations on the formation of multihollow particles, poly(oxyethylene nonylphenylether) nonionic emulsifier was added to the system to prevent the coagulation of particles prior to the treatments. In this article, the effect of the emulsifier on the formation of multihollow particles is discussed.

Experimental

Materials

S and BA were purified by distillation under reduced pressure in a nitrogen atmosphere and were 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. A series of commercial grade poly(oxyethylene nonylphenylether) nonionic emulsifiers (Emulgen 900 series; Kao Corp., Tokyo, Japan) were used without further purification. The hydrophile–lipophile balance (HLB) values, the numbers of ethylene oxide units and the cloud points of the Emulgen emulsifiers are shown in Table 1. Analytical grade potassium hydroxide and hydrochloric acid were used without further purification. Deionized water was distilled.

Preparation of polymer emulsion particles

Three stages of emulsion terpolymerizations of S, BA, and DM were carried out at 65 °C for the preparation of S–BA–DM terpolymer [P(S-BA-DM)] particles with a narrow size distribution and a relatively narrow polymer composition distribution according to the method described in a previous article [7] as follows. In the first stage, 1.50 g monomer mixture was polymerized for 2 h. In the second-stage polymerization, 16.87 g monomer mixture was added with a microfeeder over a period of 10 h, and the polymerization was allowed to proceed to completion. A part of the emulsion obtained (75 g) was used as the seed emulsion for the third-stage polymerization. The diameter of the seed particles 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 over a period of 10 h, and the polymerization was allowed to proceed to completion. The completion of the polymerization was checked by gas chromatography.

Since the emulsion obtained had water-soluble polymer and by-product particles, it was used as the original emulsion after their removal by centrifugal washing (44800*g*, 10 min, three times). The molar ratio of S/BA/DM in the original emulsion was determined to be 80.7/13.2/6.1 by elemental analysis. The particle diameter and the T_g calculated by applying Fox's equation were 350 nm and 57 °C, respectively.

Electron microscopy

A JEOL JEM-2010 electron microscope was used for transmission electron microscope (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.

Table 1 Hydrophile–lipophile balance (*HLB*) values, numbers of ethylene oxide units calculated according to Giffin's equation (*n*), and cloud points of emulgen emulsifiers

Emulsifier	HLB[a]	*n*	Cloud point (°C)[a]
Emulgen 909	12.4	8.2	40.0
Emulgen 930	15.1	15.4	> 100
Emulgen 931	17.2	30.7	> 100
Emulgen 950	18.2	50.6	> 100
Emulgen 985	18.9	85.9	> 100

[a] By catalog

Measurement of particle diameter

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

Stepwise acid/alkali treatment

The P(S–BA–DM) emulsions were treated stepwise with acid and alkali as follows. For the acid treatment the original P(S–BA–DM) emulsion was diluted to 0.6 g/l. Various amounts of emulsifier were added to the emulsion, and the emulsions were adjusted to pH 2.0 with 5 N HCl 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. For the alkali treatment the acid-treated emulsions were adjusted to pH 12.0 with 5 N KOH aqueous solution and kept for 5 h at 70 °C. After both treatments, each emulsion was cooled by keeping the vessel at room temperature.

^{1}H NMR measurement

The medium of the original emulsion was replaced by D_2O, the pH of which was adjusted to 1.0 with HCl, and the solid content was adjusted to 50 g/l. Each Emulgen emulsifier (42 wt% based on polymer weight) was dissolved in the mixture. Each emulsion sample was placed in a 5-mm NMR tube. ^{1}H NMR analysis was performed with a Bruker DPX 250 NMR spectrometer operating at 250 MHz for protons at various temperatures. The measurement was started after 20 min since the temperature was changed, and 128 scans with a repetition delay of 2 s were accumulated; the measurement took 10 min. The integrated signal intensity of the ethylene oxide group of the emulsifier was normalized to the signal intensity due to the methyl group of dimethyl sulfoxide at 2.5 ppm.

Results and discussion

A TEM photograph of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) original particles produced under the conditions in Table 2 is shown in Fig. 1. The contrast

Table 2 Recipe of stage-type emulsion polymerization (N_2; 65 °C; stirring rate, 120 rpm) for the preparation of poly(styrene–butyl acrylate–dimethylaminoethyl methacrylate) [*P*(*S*–*BA*–*DM*)] emulsion

Ingredients	First stage[a]	Second stage[b]	Third stage[c]
Seed emulsion[d] (g)	–	–	75
S (g)	0.77	8.67	10.2
BA (g)	0.33	3.75	4.42
DM (g)	0.40	4.45	5.24
V-50 (g)	0.2	–	0.2
Emulgen 930 (g)	0.05	–	–
Water (g)	270	–	195

[a] For 2 h

[b] Monomer mixture was added over 10 h and further polymerization was carried out for 12 h

[c] Monomer mixture was added over 10 h and further polymerization was carried out for 14 h

[d] Synthesized in the second stage

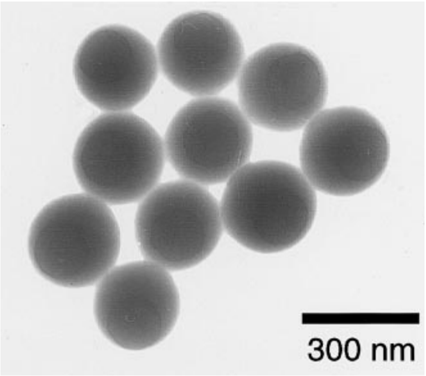


Fig. 1 A transmission electron microscope (*TEM*) photograph of the original poly(styrene–butyl acrylate–dimethylaminoethyl methacrylate) [*P*(*S–BA–DM*)] (80.7/13.2/6.1, molar ratio) particles produced by a stage type emulsion terpolymerization

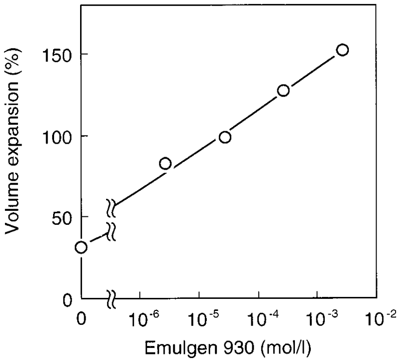


Fig. 2 Relationship between the concentration of Emulgen 930 and the volume expansion of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) particles by acid-treatment (initial pH, 2.0; 70 °C; 5 h). The volume expansion was calculated from the diameters measured by dynamic light scattering (*DLS*) at 40 °C

of the particle insides was observed to be homogeneous. This indicates that the original particles had no hollow structure.

The relationship between the concentration of the Emulgen 930 emulsifier and the volume expansion after the acid treatment (initial pH, 2.0; 70 °C; 5 h) based on the untreated original particles is shown in Fig. 2. The volume expansion was calculated from the particle diameters measured by DLS before and after the treatment. The volume expansion due to acid-swelling increased with an increase in the concentration of Emulgen 930. This indicates that the nonionic emulsifier supports the particle swelling in the acid-treatment process.

TEM photographs of the P(S–BA–DM) 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) at various concentrations of Emulgen 930 are shown in Fig. 3. Multihollow structures of the particles were not observed below 2.8×10^{-5} mol/l. Above 2.8×10^{-4} mol/l, multihollow structures were observed, and the number of hollows in the particles decreased with an increase in the concentration of Emulgen 930. These results show that the presence of nonionic emulsifier supports the formation of multihollow particles. The particle size of the hollow particles decreased with the increase in the concentration of Emulgen 930. A similar result was observed in the previous studies [8, 9] in which 276-nm-sized S–BA-methacrylic acid terpolymer particles were dissolved in a poly(oxyethylene nonylphenylether) emulsifier aqueous solution under alkaline conditions, resulting in nanoparticles. In these studies, it was concluded that the original carboxylated particles swell in alkaline conditions, and the nonionic emulsifier molecules permeate into the swollen particles and interact with polymer molecules. The polymer molecules stabilized with the emulsifier are gradually stripped from the surface layer and nanoparticles result. For the reasons mentioned earlier, the result in Fig. 3 can be explained as follows. In the acid-treatment process, polymer dissolution proceeded partially together with particle swelling. Subsequently, in the alkali-treatment process, the swollen particles shrink and form hollow particles of smaller size than the original particles, which corresponding with the amount of residual polymer.

The relationship between the concentration of Emulgen 930 and the volume expansion of the particle after the acid/alkali treatment is shown in Fig. 4. The volume expansion decreased with the increase in the concentration of the emulsifier, and above 2.8×10^{-4} mol/l, the particle volume was smaller than that of the original particle. This result also indicates that some of the polymer molecules from the particle dissolved in the treatment process.

The relationship between the HLB value of the emulsifiers and the volume expansion after the acid treatment (initial pH, 2.0; 70 °C; 5 h) is shown in Fig. 5). The volume expansion increased with a decrease in the HLB value. At the HLB value of 12.4 (Emulgen 909), the volume expansion was about 500%. In the HLB range 15.1–18.2, the volume expansions were about 100%. At the value of 18.9 (Emulgen 985), the particle showed almost no expansion. These results indicate that the increase in the hydrophobicity of the emulsifier in the HLB range increases the swelling ability of the particles under acidic conditions. One possible explanation for the larger expansion of the particles treated at the HLB value of 12.4 is that the cloud point of the emulsifier is lower than the treatment temperature.

In order to obtain more detailed information on the emulsifier behavior in the acid-treatment process, ^{1}H NMR measurements of the acidic (P(S–BA–DM) emulsion, to which Emulgen 931 or 985 emulsifier (42 wt% based on polymer weight) was added were carried out at different temperatures. To get higher sensitivity ^{1}H

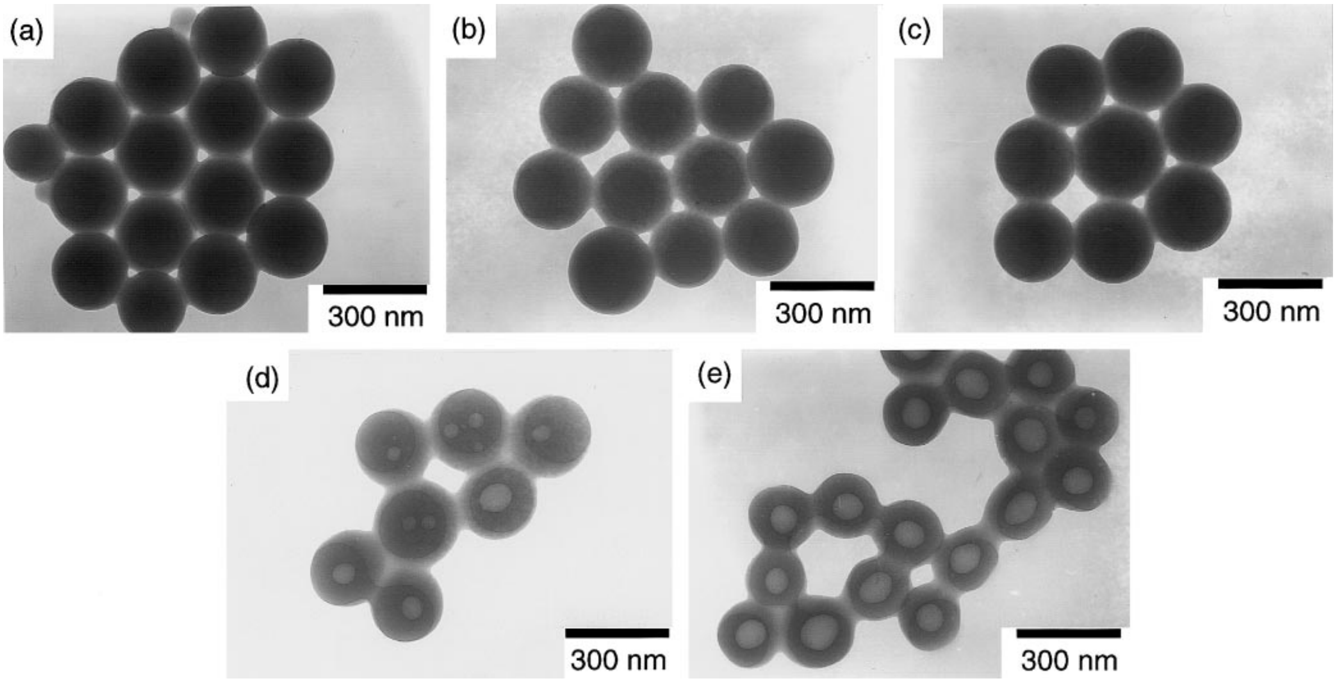


Fig. 3a–e TEM photographs of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) particles treated by the stepwise acid/alkali method (acid treatment: initial pH, 2.0; 70 °C; 5 h; alkali treatment: initial pH, 12.0; 70 °C; 5 h) in the presence of Emulgen 930. Emulgen 930 (mol/l): **a** 0; **b** 2.8×10^{-6}; **c** 2.8×10^{-5}; **d** 2.8×10^{-4}; **e** 2.8×10^{-3}

NMR measurements, the solid content of the emulsion was raised from the concentration of the standard treatment condition to 50 g/l and the pH value was adjusted to 1.0, where all DM groups are sufficiently neutralized.

The relationships between the measurement temperature and the integrated ^{1}H NMR signal intensity due to the ethylene oxide units of the emulsifiers are shown in Fig. 6. In the case of Emulgen 931, the integral intensity decreased as the temperature increased and reached about 85% after treatment at 70 °C for 2 h, whereas in Emulgen 985, it decreased slightly with increasing temperature. The decrease in the integral intensity is based on the decrease in the mobility of adsorbed emulsifier on the polymer [10]. The result indicates that the free emulsifier molecules, which dissolve in an aqueous medium, permeate into the inside of the acid-swollen particles together with water and are adsorbed on the polymer inside the particle. As seen in Fig. 5, the particles treated in the presence of Emulgen 931 swelled to twice the original volume, whereas the particles

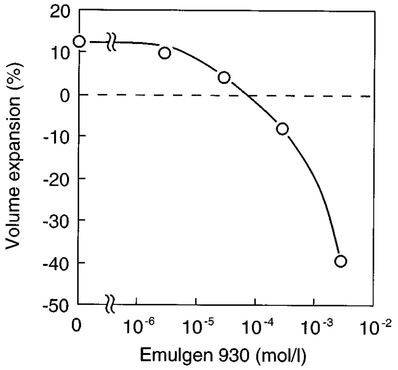


Fig. 4 Relationship between the concentration of Emulgen 930 and the volume expansion of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) particles by the stepwise acid/alkali method (acid treatment: initial pH, 2.0; 70 °C; 5 h; alkali-treatment: initial pH, 12.0; 70 °C; 5 h). The volume expansion was calculated from the diameters measured by DLS at room temperature

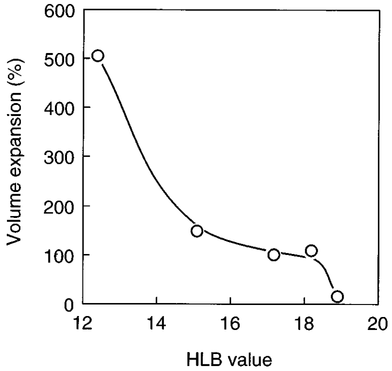


Fig. 5 Relationship between the hydrophile–lipophile balance (*HLB*) value of Emulgen emulsifiers and the volume expansion of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) particles by acid-treatment (initial pH, 2.0; 70 °C; 5 h) in the presence of various Emulgen emulsifiers (2.8×10^{-3} mol/l). The volume expansion was calculated from the diameters measured by DLS at 40 °C

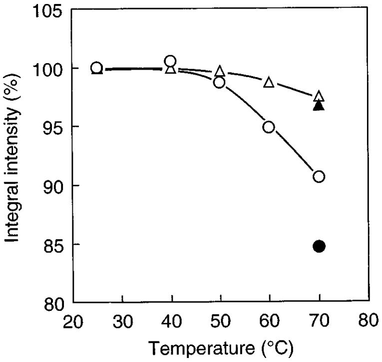


Fig. 6 Relationships between the measurement temperature and integrated ^{1}H NMR signal intensity due to ethylene oxide groups of Emulgen 931 (○) and 985 (△) dissolved (42 wt% based on polymer weight) in P(S–BA–DM) (80.7/13.2/6.1, molar ratio) emulsion (solid content, 50 g/l; pH, 1.0). Intensities were scaled to one at 25 °C as 100. The interval between measurements was 0.5 h. The *closed symbols* (●, ▲) show the data for the emulsion treated for an additional 1.5 h at 70 °C after the initial measurement at 70 °C

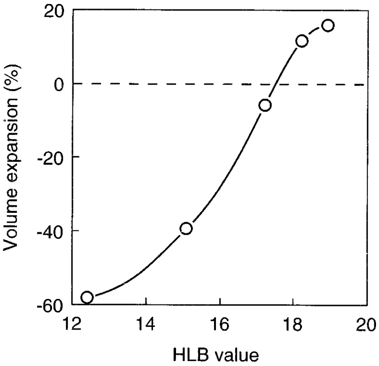


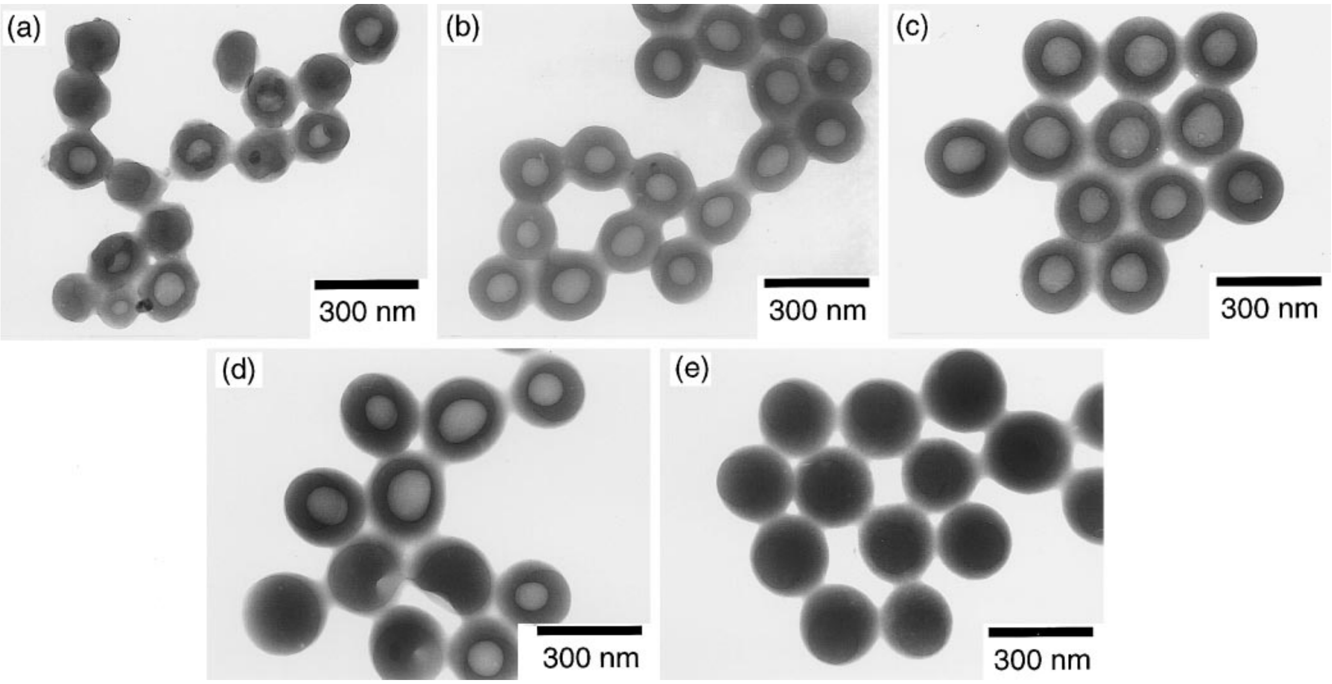
Fig. 8 Relationship between the HLB value of Emulgen emulsifiers and the volume expansion of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) particles by the stepwise acid/alkali method (acid treatment: initial pH, 2.0; 70 °C; 5 h; alkali treatment: initial pH, 12.0; 70 °C; 5 h) in the presence of various Emulgen emulsifiers (2.8 × 10^{-3} mol/l). The volume expansion was calculated from the diameters measured by DLS at room temperatur

treated in the presence of Emulgen 985 did not swell. The results in Figs. 5 and 6 support the idea that the emulsifier adsorption on the polymer increases the swelling ability of the particles.

TEM photographs of P(S–BA–DM) 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) in the presence of Emulgen emulsifier having various HLB values are shown in Fig. 7. The hollow structure was observed inside the particles except for the case with a HLB value of 18.9 (Fig. 7e). Each particle had a single hollow, and the diameters of the particles decreased with a decrease in the HLB value. This shows that there is an optimum HLB value of emulsifier for the formation of hollow particles having large hollow volumes.

The relationship between the HLB value and the volume expansion after the acid/alkali treatment (acid-treatment: initial pH, 2.0; 70 °C; 5 h; alkali-treatment:

Fig. 7a–e TEM photographs of P(S–BA–DM) (80.7/13.2/6.1, molar ratio) 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) in the presence of various Emulgen emulsifiers (2.8 × 10^{-3} mol/l). HLB value: **a** 12.4; **b** 15.1; **c** 17.2; **d** 18.2; **e** 18.9



initial pH, 12.0; 70 °C; 5 h) is shown Fig. 8. The volume expansion decreased with the decrease in the HLB value. The results in Figs. 7 and 8 indicate that the decrease in the hydrophilicity of the emulsifier in the HLB range has more effect on the formation of the hollow structure.

From the results presented here, it has been obvious that the poly(oxyethylene nonylphenylether) emulsifier on the formation of the multihollow particles by the acid/alkali method is due to the increase in the swelling ability of particles in the acid-treatment process resulting from the adsorption of emulsifier on the polymer inside the particles. These results support the formation mechanisms discussed in previous articles [2–7].

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