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SHORT COMMUNICATION

Influence of hydrophilic–lipophilic balance of nonionic emulsifiers on emulsion copolymerization of styrene and methacrylic acid

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Abstract Emulsion copolymerizations of styrene and methacrylic acid (MAA) with various nonionic emulsifiers having a hydrophilic–lipophilic balance (HLB) range of 13.7–17.2 were performed to clarify the influence of emulsification state on polymerization. The emulsification state with a lower-HLB value emulsifier was worse than that with a higher one. In the lowest HLB value, MAA was predominantly polymerized over styrene in the early stage of the copolymerization, resulting in predominant (heterogeneous) distribution of MAA units in the inside of the final polymer particles. In the higher-HLB emulsifiers, styrene and MAA were simultaneously copolymerized, resulting in a homogeneous MAA distribution. The percentage of incorporation of the nonionic emulsifier inside the particles was the highest (49% based on the total amount of the emulsifier) in the lowest HLB, whereas it was 1% in the highest HLB.

Keywords Particle · Nonionic emulsifier · HLB · Emulsion polymerization · Carboxyl group

Introduction

Carboxylated polymer emulsion have been widely used in various industrial fields [1]. In recent years, such particles are applied as a carrier for bioactive protein to create bioreactors and biosensors [2–5]. In both cases, only functional groups at the particle surfaces are effective. Therefore, many fundamental studies have been conducted on the evaluation and control of the predominant distribution of carboxyl groups at the particle surfaces [6–12]. We have also carried out a series of investigations to distribute carboxyl groups predominantly at the particle surface [13–16]. Throughout these studies, it was found that styrene (S)–methacrylic acid (MAA) copolymer [P(S-MAA)] particles prepared by emulsion copolymerization with polyoxyethylene nonyl phenyl ether nonionic emulsifier were changed to those having one or more hollows in their insides by the alkali treatment at a higher temperature than their glass transition temperature followed by the acid treatment and by the alkali treatment followed by cooling to room temperature, which were named the alkali/acid method [17] and alkali/cooling method [18], respectively. Effects of various characters of the particles (MAA content, molecular weight, and particle diameter) and treatment conditions (temperature, pH, time, degree of neutralization) on the formation of multihollow structure were clarified [19].

Moreover, surprisingly, it was found that nonionic emulsifier was incorporated inside particles [20, 21] prepared by the emulsion copolymerization. At the low stirring rate, MAA was more predominantly polymerized than that of S in the early stage of the copolymerization, resulting in particles having a MAA-rich copolymer in their insides, which greatly influenced the preparation of multihollow particles [22].

In this article, the influence of emulsification state, changed by using various nonionic emulsifiers having different hydrophilic–lipophilic balance (HLB) values, on the polymerization prepared by emulsion copolymerization will be studied.

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Table 1 Recipe for the preparation of styrene (S)-methacrylic acid (MAA) copolymer [P(S-MAA)] particles by emulsion copolymerizations[a] using various nonionic emulsifiers

Ingredients	
S (g)	55.0
MAA (g)	5.0
Potssium persulfate (mg)	24.0
Nonionic emulsifier (g)[b]	4.0
Water (g)	540.0

[a] N_2, 70 °C; stirred with a half-moon type stirrer set below the monomer phase at 120 rpm

[b] C_9H_{19}–C_6H_4–O $(CH_2CH_2O)_nH$: n (HLB)=10.9 (13.7); 13.2 (14.5); 17.2 (15.5); 30.7 (17.2)

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 (KPS; Nacalai Tesque, Kyoto, Japan) was purified by recrystallization. Commercial grade polyoxyethylene nonylphenylether nonionic emulsifiers (Kao, Tokyo, Japan) with formula C_9H_{19}–C_6H_4–$O(CH_2CH_2O)_nOH$: Emulgen 911 (E911), Emulgen 913 (E913), Emulgen 920 (E920), Emulgen 931 (E931) (n=10.9, 13.2, 17.2, 30.7, HLB value=13.7, 14.5, 15.5, 17.2, respectively), were used without further purification. Analytical grade potassium hydroxide (KOH; Nacalai Tesque) and guaranteed reagent-grade methanol(Nacalai Tesque) were used as received. Deionized water with a specific resistance of 5×10^6 Ω cm was distilled before used.

Emulsion copolymerization

P(S-MAA) particles were prepared by emulsion copolymerizations under the conditions shown in Table 1. The polymerizations were carried out at 70 °C in a 1-L reactor equipped with an inlet of N_2, a reflux condenser, a half-moon type stirrer at stirring rate of 120 rpm, and the quantitative data of the reactor as shown in Fig. 1. Emulsifier aqueous solution (520 g) was charged into the reactor and then purged with N_2 for 30 min. After the addition of all monomers to the reactor, the mixture was stirred for 30 min, and then the copolymerization was initiated by the addition of KPS aqueous solution (1.2 wt%, 20 g).

Characterizations

The monomer concentration and the weight of copolymer particles in the emulsion were, respectively, measured by gas chromatography (GC-18A, Shimazu, Kyoto, Japan) and gravimetry. MAA content in the P(S-MAA) particles was determined by ^1H nuclear magnetic resonance (NMR) analysis with a Bruker DPX250 NMR spectrometer after methylation of carboxyl groups with diazomethane [19]. Weight- and number-average particle diameters (D_w and D_n, respectively) were detected by dynamic light scattering (FPAR-1000 RK, Fiber-optics particle analyzer, Photal Otsuka electronics, Kyoto, Japan). P(S-MAA) particles and their ultrathin cross-sections were observed with a transmission electron microscope (TEM, JEOL JEM-1230

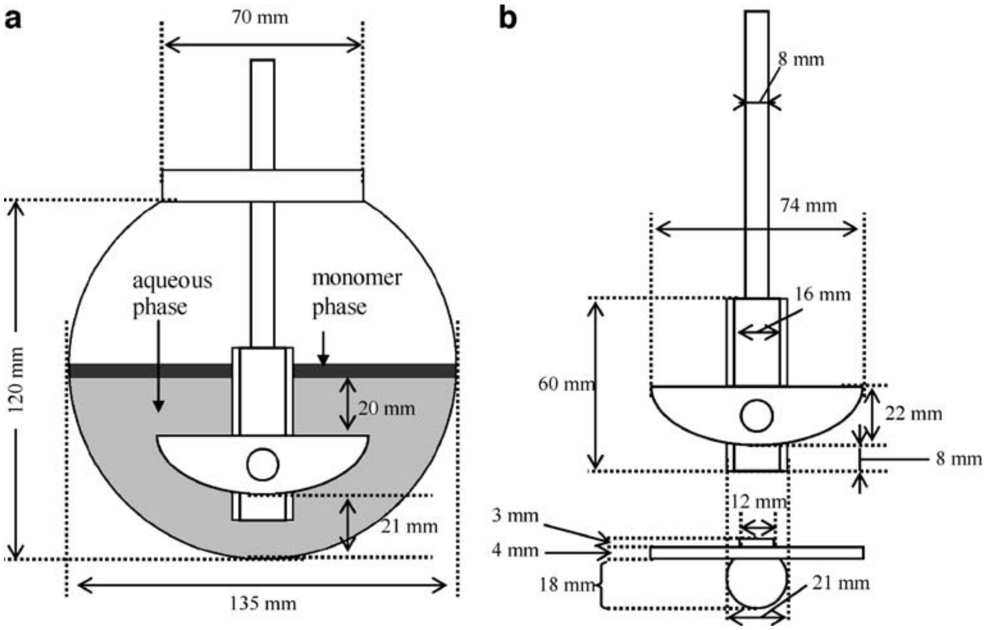


Fig. 1 Schematic diagram of the reactor (**a**) with a stirrer (**b**) used in the emulsion copolymerization under the conditions listed in Table 1

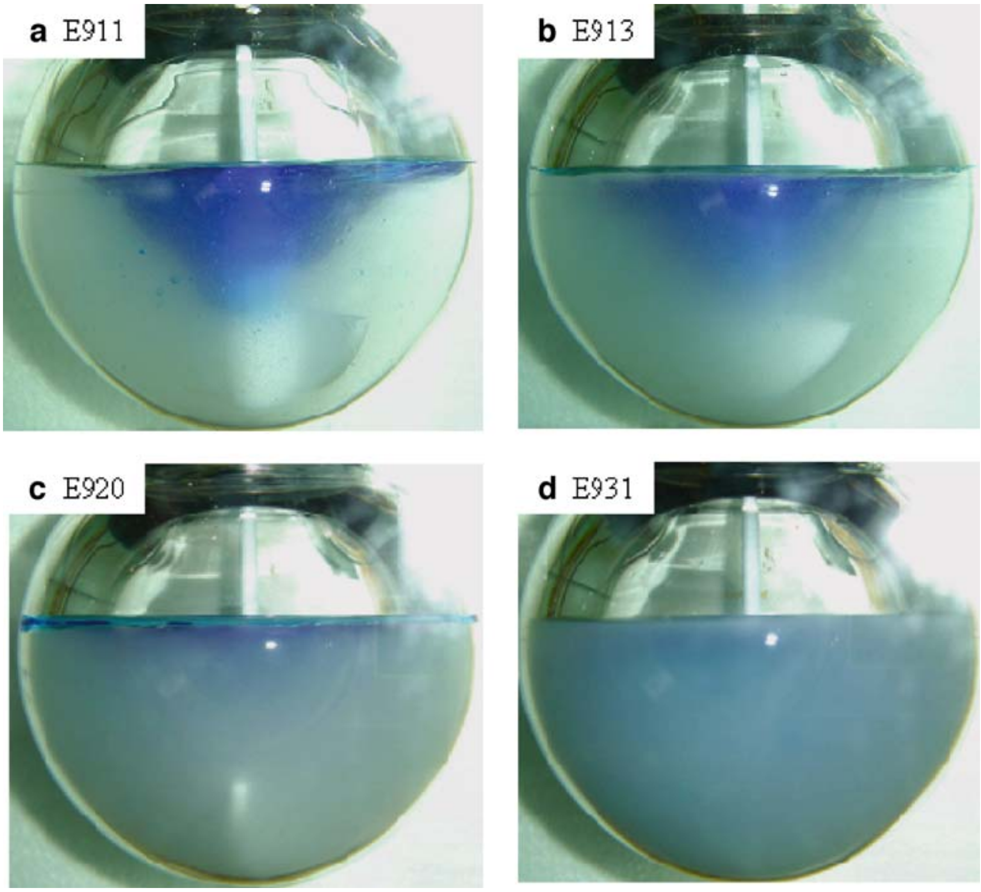


Fig. 2 Photographs indicating emulsification states just before starting emulsion copolymerizations under the conditions listed in Table 1 with nonionic emulsifiers having different HLB values: **a** 13.7, **b** 14.5, **c** 15.5, and **d** 17.2. Monomer phase was dyed with Oil Blue

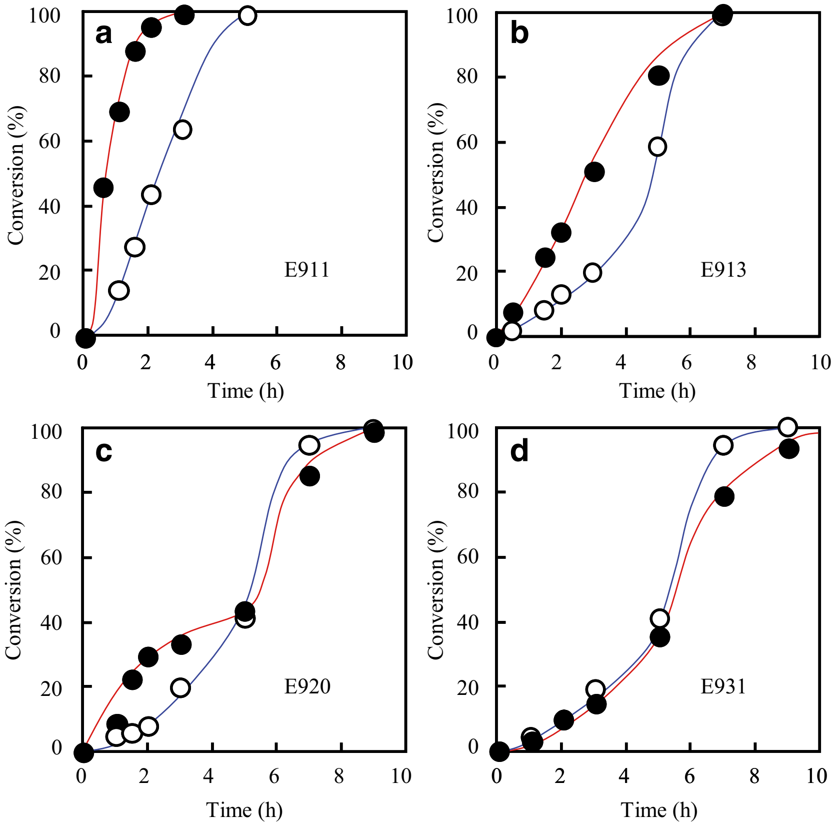


Fig. 3 Conversion–time curves for emulsion copolymerizations of S (*open circles*) and MAA (*filled circles*) with nonionic emulsifiers having different HLB values: **a** 13.7, **b** 14.5, **c** 15.5, and **d** 17.2

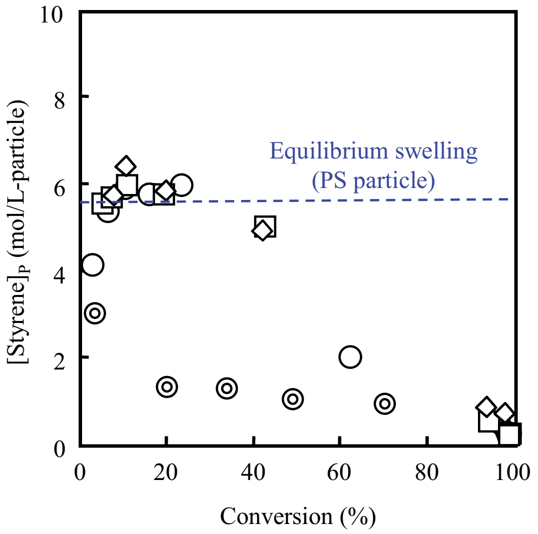


Fig. 4 S concentration in the P(S-MAA) (10 mol% MAA) particles as functions of conversion in emulsion copolymerizations with nonionic emulsifiers having different HLB values: ◎ 13.7, ○ 14.5; □ 15.5; ◇17.2. The *broken line* indicates S concentration in PS particles (unswollen diameter 94 nm) in the equilibrium swelling at 50 °C

electron microscope). The ultrathin cross-sections were made as follows. Dried P(S-MAA) particles were dispersed in an epoxy matrix (epoxy resin: Epok 812; curing agents: dodecenyl succinic anhyderide, methyl nadic anhyderide; Okensyoji, Tokyo, Japan), cured at 60 °C for 24 h, and then microtomed. The ultrathin cross-sections were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution.

MAA units at the particle surfaces

The amount of MAA units at the particle surfaces was estimated by measuring the heat of the neutralization reaction between carboxyl groups and KOH with an isothermal titration calorimeter (Model 4200 ITC, Calorimetry Sciences, Utah, USA) [23, 24]. The sample and reference cells filled with 1 mL 0.05 N KOH aqueous solution were set into the calorimeter maintained at 25 °C for several hours. Twenty-five microliters of centrifugally washed emulsions, which are the measurement of the heat of neutralization reaction including the heat of mixing and dilution, and 25 µL distilled water, which are the measurement of the heat of mixing and dilution, were separately injected into the stirred calorimeter vessel at the intervals of 20 min. The heat of neutralization was obtained by subtraction of the former with the later measurement. The amount of carboxyl groups was estimated from a calibration graph obtained by the same measurement for known concentration of MAA monomer aqueous solutions.

Table 2 The amount of incorporated nonionic emulsifiers inside P(S-MAA) prepared by emulsion copolymerizations under the conditions listed in Table 1

	Nonionic emulsifier	
	E911	E931
Incorporation (%)	49	1

Incorporation of nonionic emulsifier

P(S-MAA) particles prepared by emulsion copolymerizations with nonionic emulsifiers having different HLB values were centrifugally washed three times with 2-propanol at 20,000 rpm. The washed particles were dried in a vacuum oven at room temperature overnight. The dried particles of 50 mg were dissolved in 4.95 g of tetrahydrofuran (THF). The sample solutions were filtered with

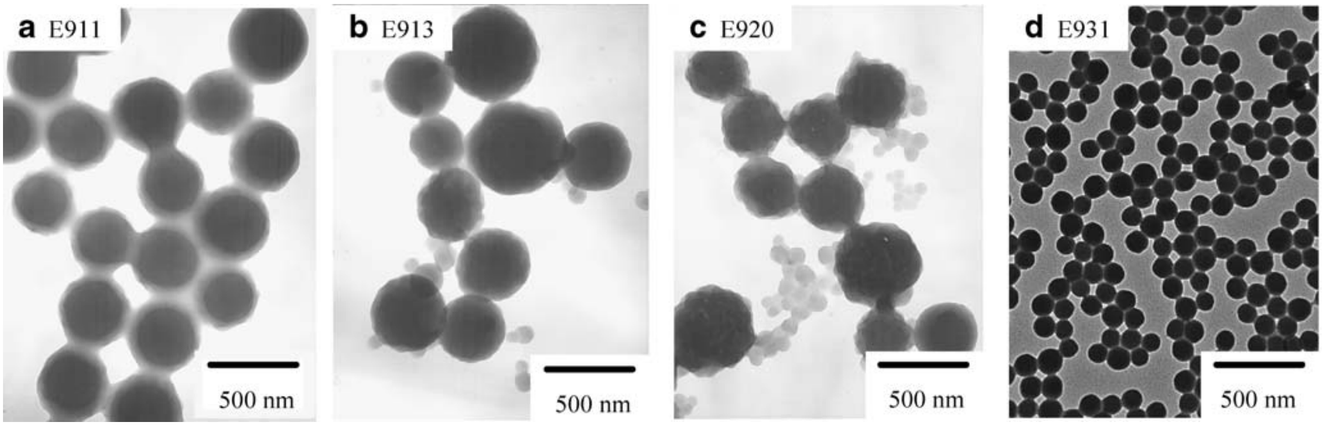


Fig. 5 TEM photographs of P(S-MAA) particles prepared by emulsion copolymerizations using nonionic emulsifiers having different HLB values: **a** 13.7, **b** 14.5, **c** 15.5, and **d** 17.2

0.45 μm of polytetrafluoro ethylene membrane before gel permeation chromatography measurement with two S/divinylbenzene gel columns (TOSOH, TSK gel GMHHR-H, 7.8 mm inner diameter×30 cm) using THF as eluent at 40 °C at a flow rate of 1.0 mL/min employing a refractive index detector (RI 8020). The columns were calibrated with six standard PS samples (1.05×10^3–5.48×10^6, M_w/M_n= 1.05–1.15). The amounts of the nonionic emulsifier incorporated inside the particles were obtained from peak areas because of the nonionic emulsifier using the calibration curves of corresponding emulsifier standards.

Results and discussion

Figure 2 shows emulsification states of emulsion copolymerization systems under the conditions listed in Table 1 before adding the initiator. When E911 was used, which has the lowest HLB value in this experiment, the monomer phase was mostly floated on the aqueous medium; while increasing the HLB value, the amount of monomer droplets dispersed in the aqueous medium was increased. These observations indicate that emulsification state was improved with an increase in the HLB value. In the previous article [22], the emulsification state, which was changed by changing the stirring rate, greatly affected the distribution state of carboxyl groups within P(S-MAA) particles as described in "Introduction." Accordingly, the HLB values of the nonionic emulsifiers may also affect the distribution state of carboxyl groups in the P(S-MAA) particles.

Figure 3 shows the conversion–time data for the emulsion copolymerization of S and MAA using the various nonionic emulsifiers. The copolymerization rate increased with decreasing the HLB value. In the case of the lowest-HLB emulsifier (Fig. 3a), most of MAA was polymerized for 3 h, while approximately 40% S still remained. This indicates that the MAA-rich copolymer was formed in the early stage of the polymerization, and then residual S was polymerized. The conversion–time curves of S and MAA converged with increasing the HLB value (Fig. 3b,c). At the highest-HLB emulsifier (Fig. 3d), both curves were in good agreement. Another interesting point is that after 40% conversion in those polymerizations containing the three higher-HLB emulsifiers (E913, E920, E931), the rates of polymerization increased, while it disappeared in the case of the lowest-HLB emulsifier (E911). This can be rationalized when one considers the gel effect; that is, at approximately 40% conversion, the monomer phase disappears in a general emulsion polymerization thus causing the viscosity to increase in the particles. From the above result, one can conclude that the polymerization in the presence of the lowest-HLB emulsifier did not proceed under equilibrium condition, and the gel effect seemed to be presented throughout the polymerization because of having a much higher rate in the early stage of polymerization than the other emulsifiers. This point was confirmed in the following experiment.

Figure 4 shows S concentrations in the particles during the emulsion polymerizations with the nonionic emulsifiers. The S concentrations in the early stage of the polymerizations conducted with the higher-HLB emulsifiers (E913, E920, E931) corresponded to that of the equilibrium state. On the other hand, in the case of the lowest-HLB emulsifier (E911), the S concentration in the particles throughout the polymerization was much lower than that (5.5-mol/L particles) [25] at the equilibrium swelling. These results support the notion that the emulsion polymerization with E911 (Fig. 3a) did not proceed under the monomer equilibrium condition, and one can clarify rationally why the polymerization rate of S was much high in the initial stage.

Figure 5 shows TEM photographs of P(S-MAA) particles prepared by emulsion copolymerizations with the nonionic

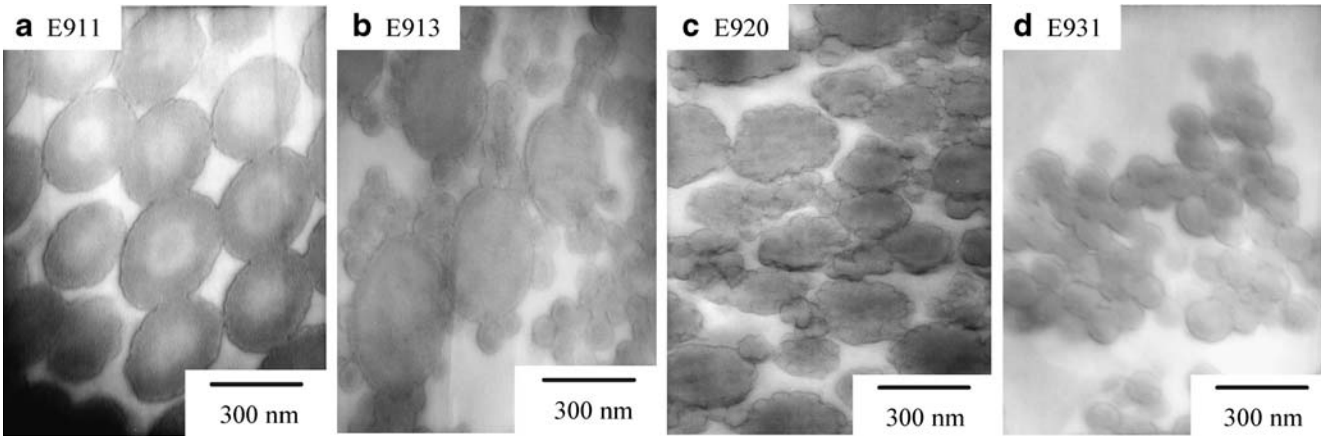


Fig. 6 TEM photographs of ultrathin cross sections of RuO_4-stained P(S-MAA) particles prepared by emulsion copolymerizations with nonionic emulsifiers having different HLB values: **a** 13.7, **b** 14.5, **c** 15.5, **d** 17.2

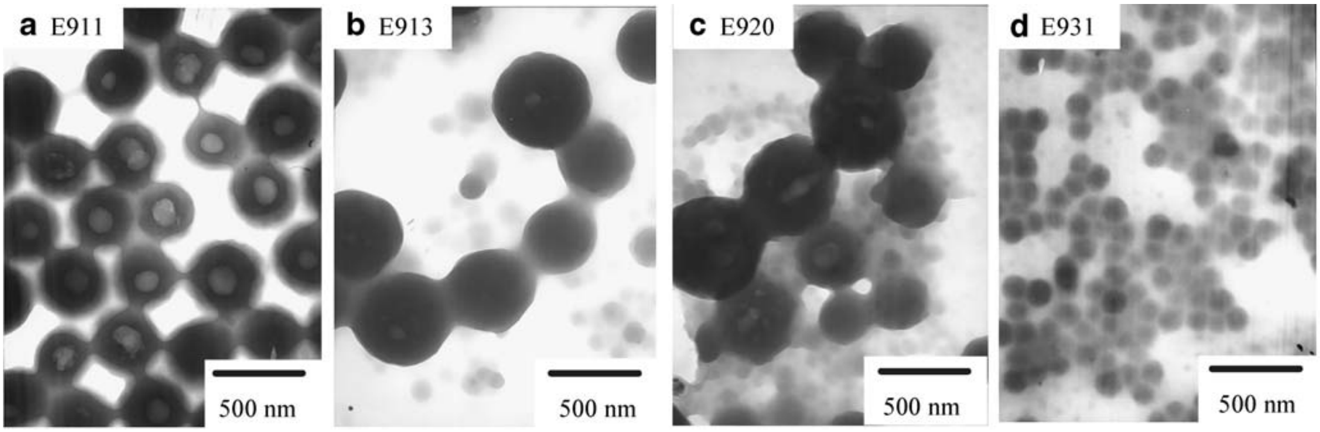


Fig. 7 TEM photographs of P(S-MAA) particles after extraction with methanol (50 °C; 24 h). The original particles were prepared by emulsion copolymerizations with nonionic emulsifiers having different HLB values: **a** 13.7, **b** 14.5, **c** 15.5, **d** 17.2

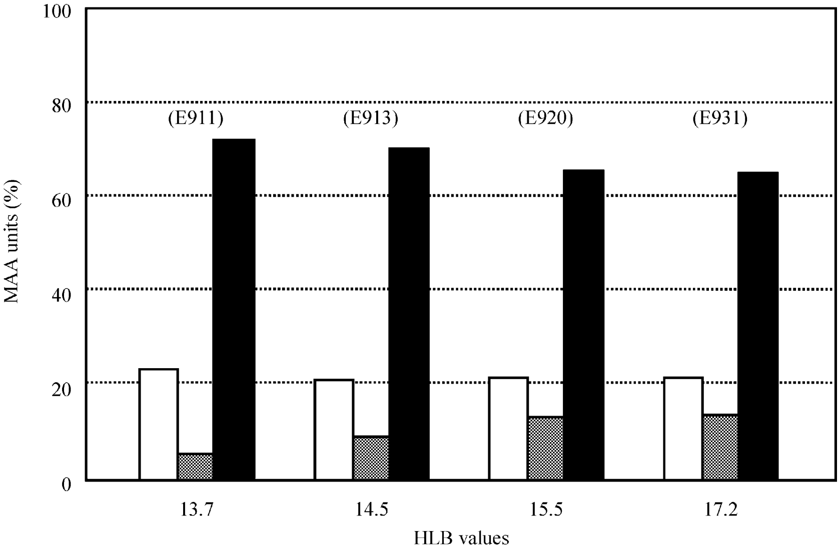
emulsifiers having different HLB values. In the lowest-HLB emulsifier (E911), the larger particle size and monodisperse particles were prepared, while the polydisperse particles were prepared in the higher-HLB emulsifiers (E913 and E920). In the highest-HLB emulsifier (E931), quite smaller monodisperse particles were prepared. The reason for the differences in the particle size and the monodispersity seems to be because during the emulsion copolymerizations the amounts of incorporated emulsifier are different, as described below.

Table 2 shows the percentages of E911 and E931 inside the particles at the completion of the polymerization. The incorporation of the highest-HLB emulsifier (E931) was only 1 wt%, while it was 49 wt% in the lowest HLB emulsifier (E911). Therefore, during the polymerization, E931 should exist much more in the aqueous medium than that of E911 and should play effectively as an emulsifier, resulting in smaller particles. In other words, in the E911, much larger particle sizes were prepared because of less emulsifier existing in the aqueous medium. These phenomena will be discussed more in the next article.

Figure 6 shows TEM photographs of ultrathin cross-sections of the four kinds of P(S-MAA) particles, which were stained with RuO_4. Because RuO_4 predominantly stains PS, it is possible to identify S-rich and MAA-rich regions [7, 26, 27]. In the case of E911, the MAA-rich region observed at the inside of the particles was significantly brighter than the surface layer. On the other hand, in the cases of E913, E920, and E931, the contrasts in the particles were observed to be homogeneous.

Figure 7 shows TEM photographs of the P(S-MAA) particles after extraction of MAA-rich copolymer with methanol, which is a good solvent for PMAA. Dried P(S-MAA) particles were dispersed in methanol at 50 °C for 24 h and then were centrifugally washed for a few times with methanol at room temperature. In the case of E911, a low-contrast region appeared in the inside, while in the

Fig. 8 Distribution of MAA units in P(S-MAA) (10 mol% MAA) emulsions prepared by emulsion copolymerizations using nonionic emulsifiers having different HLB values: *unshaded bars*, in aqueous medium; *light gray bars*, at the surface; *dark gray bars*, in inside



cases of E913, E920, and E931, such a change was not observed in most of the particles. These results (Figs. 6 and 7) indicate that the core and the shell in the particle prepared using E911, respectively, consisted of MAA-rich and MAA-poor copolymers, whereas MAA units (i.e., carboxyl group) comparatively distributed homogeneously in the particles prepared using the other emulsifiers. In the case of E911, as the interfacial area between the monomer droplets and the aqueous medium was low (Fig. 2), the diffusion rate of MAA to particles should be much higher than that of S because of a large difference in their water solubilities. Therefore, a MAA-rich copolymer was prepared in the early stage and because the viscosity within polymerizing particles was so high because of low S concentration (Fig. 4) that the MAA-rich copolymer hardly diffused from the inside toward the particle surface during the polymerization.

Figure 8 shows the percentages of MAA units in the aqueous medium, at the surfaces and in the inside of the P(S-MAA) particles. The amount at the particle surfaces was directly measured by isothermal titration calorimetry [23, 24] after the particles were centrifugally washed with deionized water, while that in the inside was indirectly obtained by the subtraction of the amount at the surfaces from the total amount of MAA units in the washed P(S-MAA) particles measured by ^{1}H-NMR. In the centrifugal washing, most of the small particles, which were byproducts in the cases of E913 and E920 (Fig. 5b,c), were removed. In the cases of E911, E913, and E920, in which the washed polymer particles used for the isothermal titration calorimetry had nearly the same size, the percentage of MAA units distributed at the particle surfaces was increased with an increase in the HLB value. In other words, the percentage in the inside was decreased with the increase in the HLB value. This result is in accord with the TEM observation results (Figs. 6 and 7). The tendency seems to be also established in the highest HLB emulsifier (E931), but it may be difficult to compare the percentages between E931 and the others (E911, E913, E920) because the size of particles prepared with E931 was much smaller than those with the others (Fig. 5).

Conclusions

P(S-MAA) particles were prepared by emulsion polymerization using the four kinds of nonionic emulsifiers having different HLB values (13.7–17.2). The emulsification state was improved with an increase in the HLB value. MAA-rich copolymer was formed in the early stage of the polymerization using the lowest HLB emulsifier (E911) where the total interfacial area between the monomer and aqueous phases was the minimum, resulting in core–shell particles in which the MAA-rich copolymer distributed in the core. On the other hand, the copolymerizations using higher-HLB emulsifiers (E913, E920, and E931) gave copolymer particles having uniform structures. The amount of MAA unit at the particle surfaces increased with the increase in the HLB value. It is concluded that the difference in S concentration in polymerizing particles is the reason why the emulsification state greatly affected the emulsion copolymerization and morphology of the prepared carboxylated particles.

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