



Incorporation of nonionic emulsifiers inside styrene–methacrylic acid copolymer particles during emulsion copolymerization[☆]

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ABSTRACT

Emulsion copolymerizations of styrene and methacrylic acid with polyoxyethylene nonylphenyl ether nonionic emulsifiers having various hydrophilic–lipophilic balance (HLB) values (13.7, Emulgen 911; 15.5, Emulgen 920; 17.2, Emulgen 931) were performed. The incorporation behavior of the nonionic emulsifiers, comprising polydisperse poly(ethylene oxide) (PEO) chain lengths, inside the particles was investigated. At the completion of the polymerization, the incorporated percentage of the lowest HLB emulsifier was 61%, much higher than that of the highest HLB one (10%). In both polymerizations, the amounts of the incorporated emulsifiers increased with conversion, and shorter PEO chain (i.e., lower molecular weight) components were predominantly incorporated over longer PEO chain components.

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1. Introduction

In a general emulsion polymerization with nonionic emulsifier, most of the emulsifier partitioned to the monomer phase before the start of the polymerization [1–9]. Two separate nucleation periods were observed, resulting in a bimodal particle size distribution, where the primary and secondary nucleations are based on homogeneous and micellar nucleation mechanisms, respectively. The latter was caused by release of emulsifier from the monomer droplets (layer) to the aqueous phase [2–5]. Moreover, nonionic emulsifier released from monomer droplets enters into the polymerizing particles swollen with monomer via the aqueous phase and some fractions remain there until the end of polymerization [8–13]. For example, 75% of poly(oxyethylene) nonylphenyl ether nonionic emulsifier (E911) (hydrophilic–lipophilic balance (HLB) value = 13.7) [10] was incorporated inside styrene (S)–methacrylic acid (MAA) copolymer, P(S-MAA), particles during emulsion polymerization.

In additional studies, incorporation of two kinds of poly(oxyethylene) lauryl ether nonionic emulsifiers with different HLB values, E109P (HLB 13.6) and E150 (HLB 18.3), was observed in the emulsion polymerization of styrene [8]. Moreover, incorporation of two emulsifiers (E911 and E109P), having similar HLB values but different structures, in emulsion polymerizations of methacrylic monomers (methyl methacrylate, ethyl methacrylate, or *iso*-butyl methacrylate) was investigated [9]. The incorporation of emulsifier

lowers the stability of the polymer colloids due to a decrease in the amount of emulsifiers used for stabilizing the particles. Moreover, incorporation causes several problems such as less control of the particle size distribution and a reduction in water resistance in film applications. On the other hand, we also found that E911 incorporated inside P(S-MAA) and PS particles promotes the formation of (multi-)hollow structures by the alkali/cooling method [11] and seeded emulsion polymerization [12]. Due to both advantages and disadvantages of the incorporation of nonionic emulsifiers inside polymer particles as described above, it is important to understand the mechanism of incorporation.

In this article, the influence of the HLB value and the molecular weight distribution of nonionic emulsifiers on the amount of incorporated emulsifier inside P(S-MAA) particles prepared by emulsion copolymerization is clarified.

2. Experimental

2.1. 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 nonylphenyl ether nonionic emulsifiers ($C_9H_{19}-C_6H_4-O(CH_2CH_2O)_nOH$; Kao, Tokyo, Japan) Emulgen 911 (E911), Emulgen 920 (E920) and Emulgen 931 (E931) ($n = 10.9, 17.2$ and 30.7 ; HLB value = 13.7, 15.5 and 17.2, respectively) were used without further purification. Analytical grade potassium hydroxide (KOH; Nacalai Tesque) and guaranteed reagent-grade methanol (Nacalai Tesque) were used

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as-received. Deionized water with a specific resistance of $5 \times 10^6 \Omega \text{ cm}$ was distilled before use.

2.2. Emulsion copolymerization

P(S-MAA) particles were prepared by emulsion copolymerizations with reaction calorimetric technique (RC1e; Mettler Toledo, Switzerland) under the conditions shown in Table 1. The polymerizations were carried out at 70 °C and the stirring rate of 200 rpm. Emulsifier aqueous solution (520 g) was charged into the reactor and then purged with N₂ for 30 min. After the addition of all the monomers to the reactor, the temperature of the mixture was raised to and kept at 70 °C for approximately 2.5 h to calibrate the RC1e system and then the copolymerization was initiated by the addition (20 g) of KPS aqueous solution (1.2 wt%).

2.3. Characterizations

The monomer concentration in the emulsion was measured using a gas chromatograph (GC-18A; Shimadzu, Kyoto, Japan) equipped with polyethylene glycol capillary column (ULBON HR-20 M, 0.32 mm i.d. \times 30 m long, 1.0 μm thickness, Shinwa Chemical Industries). Emulsion sample (0.2 g) dissolved in 5.0 g of *N,N*-dimethylformamide containing *p*-xylene was used as internal standard. Thus, 1 μl of sample solutions was injected into the GC at 200 °C under a flow of helium carrier gas (221.5 ml/min) which reduced to 4.29 ml/min at the capillary column by splitter where the column temperature was maintained at 120 °C. The samples were detected with flame ionization detector at 200 °C. Number- and weight-average molecular weights (M_n and M_w , respectively) and molecular weight distributions were determined using a gel permeation chromatograph (GPC; Tosoh, Japan) with two S/divinylbenzene gel columns (TSK gel GMHHR-H, 7.8 mm i.d. \times 30 cm, TOSOH) connected in series and using THF as eluent. The flow rate was maintained at 1.0 ml/min with column temperature of 40 °C and elution monitored with 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). Number- and weight-average particle diameters (D_n and D_w , respectively) were measured using a dynamic light scattering (DLS, FPAR-1000 RK, Fiber-optics particle analyzer; Photal Otsuka Electronics, Osaka, Japan) at the light scattering angle 160° at room temperature using the Marquadt analysis routine. One to two droplets of emulsion samples withdrawn from the reactor were diluted with approximately 8 ml of distilled water before measurement in the dilution mode. P(S-MAA) particles were observed with transmission electron microscope (TEM, JEOL JEM-1230 electron microscope). Each emulsion was diluted to approximately 50 ppm, and then a drop was placed on a carbon-coated copper grid before drying at room temperature in a desiccator.

2.4. Analysis of incorporated nonionic emulsifiers

P(S-MAA) particles prepared by emulsion copolymerization with nonionic emulsifiers were withdrawn at different conversions

Table 1
Recipe for the preparation of P(S-MAA) particles by emulsion copolymerizations^a with various nonionic emulsifiers under stirring of 200 rpm

Ingredients	
S (g)	55.0
MAA (g)	5.0
Potassium persulfate (mg)	240.0
Nonionic emulsifier ^b (g)	4.0
Water (g)	540.0

^a In RC1e: N₂; 70 °C.

^b C₉H₁₉–C₆H₄–O (CH₂CH₂O)_{*n*}H: *n* (HLB) = 10.9 (13.7), 17.2 (15.5), 30.7 (17.2).

from the RC1 reactor and the polymerization was stopped by adding a hydroquinone solution. To prevent the escape of emulsifiers from the inside of the particles, the samples were quickly dried using a spray dryer (Spray dryer SD-1000, Eyela). The dried particles were washed with 2-propanol three times by centrifugation at 20,000 rpm to remove the emulsifier adsorbed on the particle surfaces. The washed particles were dried in a vacuum oven at room temperature overnight. The powder particles (50 mg) were dissolved in tetrahydrofuran (THF; 4.95 g). The sample solutions were filtered with a polytetrafluoroethylene (PTFE) membrane (pore size 0.45 μm) before GPC measurement. Calibration curves were constructed using original nonionic emulsifiers dissolved in THF at concentrations over the range in the actual polymerizations. The amount of nonionic emulsifier incorporated inside particles was obtained from the peak area using the calibration curves.

2.5. Partition ratio

The partition ratio of nonionic emulsifier between monomer and aqueous phases with the same composition as in the polymerization recipe (without initiator) was measured as follows. The mixture, in which the emulsifier had been dissolved in the monomers, was stirred and kept at 70 °C for approximately 2.5 h, and then a 50 mg sample was withdrawn from the monomer phase. The amount of emulsifier in the monomer phase was determined by GPC.

2.6. Critical micelle concentration

The critical micelle concentration (CMC) values of the nonionic emulsifiers were obtained from surface tension measurements using the pendant drop method with a Drop Master 500 (Kyowa Interface Science, Japan). The emulsifier fractions dispersed in aqueous mediums of the partition ratio experiment were used to measure CMC. The present study revealed that the emulsifier was preferentially partitioned to monomer phase and incorporated into the polymer particles depending on the molecular weight of emulsifier. This approach ensures that the CMC value obtained corresponds to emulsifier with the same molecular weight distribution as that present in the aqueous medium at the initial stage of the polymerization. Emulsifier solutions of various concentrations were prepared as follows. The aqueous phases obtained from the emulsifier partition experiments were dried in an oven. The accurate weights of the dried emulsifiers were dissolved in monomer saturated aqueous solution (obtained from the partition ratio experiment without emulsifier and initiator) with different amounts.

3. Results and discussion

3.1. HLB values of nonionic emulsifiers

Table 2 shows percentages of nonionic emulsifiers with different HLB values partitioned into the monomer phase at 70 °C before starting the emulsion polymerization of S and MAA and of incorporated emulsifiers inside P(S-MAA) particles at over 93% conversion prepared by emulsion copolymerization under the conditions shown in Table 1. In all cases, more than 84% of emulsifier, initially dissolved in the aqueous phase, partitioned to the monomer phase, although the monomers only comprised 10 wt% of the total emulsion. That is, most of the nonionic emulsifiers partitioned to the monomer phase in agreement with previous work [3,8,9]. The percentage of nonionic emulsifier partitioned to the monomer phase increased slightly with a decrease in the HLB values in the order of E911 (HLB 13.7) > E920 (HLB 15.5) > E931 (HLB 17.3). This trend is consistent with the percentage of incorporated nonionic emulsifier inside the P(S-MAA) particles

Table 2

Percentages of nonionic emulsifiers with different HLB values partitioned to the monomer phase and incorporated emulsifier inside P(S-MAA) particles at over 93% conversion prepared by emulsion copolymerization

	Nonionic emulsifiers		
	E911	E920	E931
HLB value	13.7	15.5	17.2
$(W_m^a/W_t^b) \times 100$ (%)	91	88	84
$[E]_{aq}^c$ (mM)	1.0	0.91	0.74
Incorporation (%)	61	18	10

^a Amount of emulsifier in monomer phase.

^b Total amount of emulsifier.

^c Emulsifier concentration in aqueous phase.

increasing with decreasing HLB value. It was much greater for E911 (61%) than that for E920 (18%) and E931 (10%). All P(S-MAA) emulsions were obtained without coagulum, even though especially in the case of E911, 61% of total emulsifier was incorporated and thus did not contribute to the colloidal stability. The colloidal stability is a function of electrostatic and steric repulsions, which are based on ionic groups (sulfate group) from KPS and nonionic emulsifier, respectively. Because most carboxylic groups of MAA units copolymerized are not ionized under the polymerization conditions (low pH), MAA units located at the particle surfaces do not contribute to colloidal stability.

Fig. 1 shows TEM photographs of P(S-MAA) particles at over 93% conversion prepared using nonionic emulsifiers with different HLB values. In the case of E911, monodisperse nonspherical particles with uneven surface were obtained, while in the cases of E920 and E931, polydisperse particles were obtained comprising larger (nonspherical) and smaller (spherical) particles. When the emulsions were kept for approximately one month, in the case of E911, most of the particles precipitated resulting in iridescence. This supports the fact that they were monodisperse [14]. The supernatant was slightly turbid which shows the coexistence of few small particles, although this was not obvious from the DLS measurement and TEM observation (Fig. 1). On the other hand, in the cases of E920 and E931, the precipitated particle layer did not result in iridescence and the supernatant was still turbid. These observations were also in accord with the particles being polydisperse.

Fig. 2 shows the number of P(S-MAA) particles (N_p) at various conversions in the emulsion copolymerizations using E911 and E931. In the case of E911, N_p decreased in the early stage (<10% conversion) of the polymerization and then increased slightly with conversion. In the early stage of polymerization, even though most of the emulsifier (91%) partitioned to the monomer phase, the emulsifier concentration in aqueous medium ($[E]_{aq}$) was still higher than CMC (0.72 mM) (Table 2). Thus, micellar nucleation would take place. Because most of the emulsifier partitioned to the

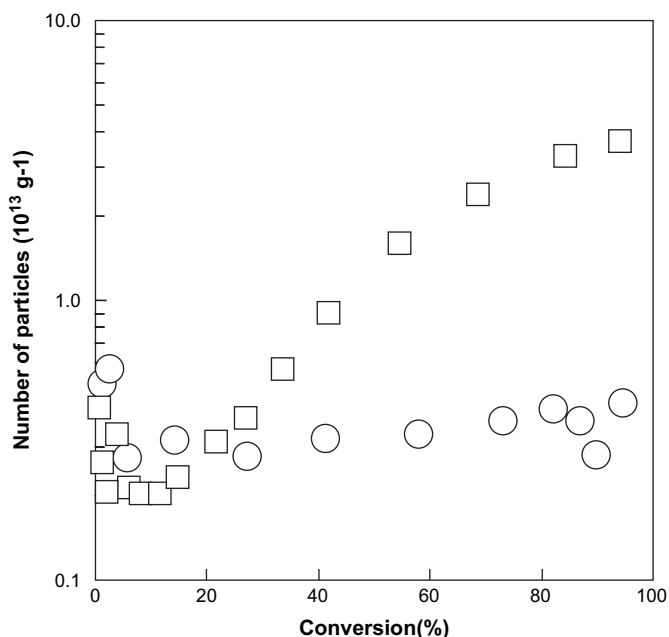


Fig. 2. N_p of P(S-MAA) particles at various conversions of emulsion copolymerization of S and MAA using E911 (open squares) and E931 (open circles) nonionic emulsifiers.

monomer phase and was incorporated inside polymerizing particles swollen with monomer, the surface of forming particles might lack emulsifier resulting in coagulation (<10% conversion). The total interfacial area of polymerizing particles was low and not sufficient to capture all oligomeric radicals formed in the aqueous medium; small particles might therefore form by homogeneous nucleation. The small particles were unstable and quickly adsorbed onto larger particles throughout the polymerization (after 10% conversion) resulting in nonspherical particles with uneven surface as observed in Fig. 1. This behavior will be discussed in more detail elsewhere [15].

In the case of E931, $[E]_{aq}$ in the early stage of the polymerization was lower than CMC (2.76 mM) resulting in homogeneous nucleation. Because of less incorporation, $[E]_{aq}$ would gradually increase due to escape of emulsifier from the monomer phase because of a decrease in the volume with conversion and from polymerizing particles (explained in the next section). Thus, $[E]_{aq}$ should be higher than CMC and new particles might form by the secondary nucleation (Fig. 2) giving rise to broad particle size distributions (small spherical particles in Fig. 1c). In this case (E931), the colloidal stability of the new particles might be higher than that for E911 after 15% conversion where micellar nucleation took place after the

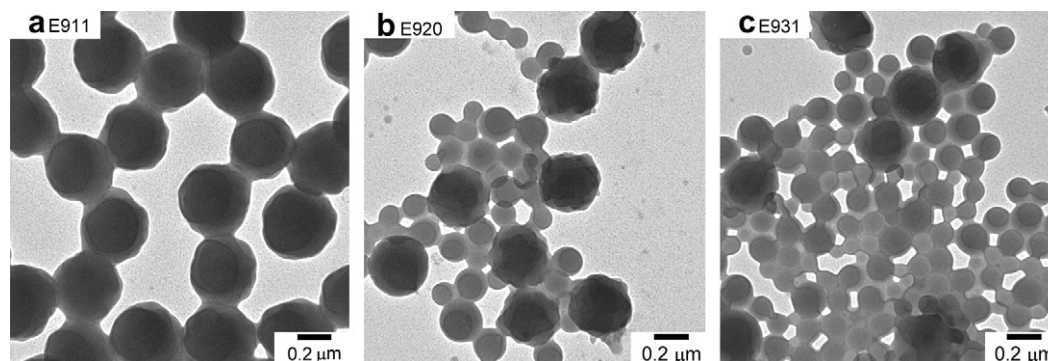


Fig. 1. TEM photographs of P(S-MAA) particles with over 93% conversion prepared by emulsion copolymerizations using nonionic emulsifiers having different HLB values: (a) 13.7, (b) 15.5, (c) 17.2.

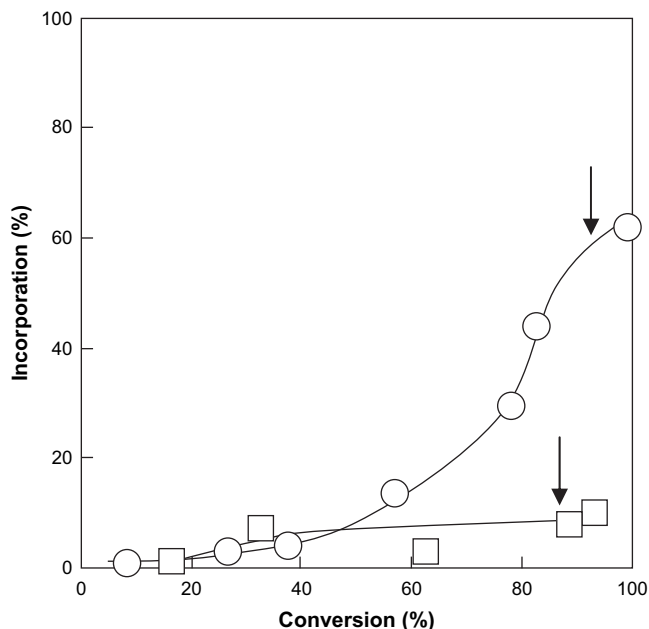


Fig. 3. Incorporation of E911 (open circles) or E931 (open squares) inside polymerizing particles at various conversions of emulsion copolymerization of S and MAA. The arrows represent the conversion at which the monomer phase disappeared.

homogeneous nucleation. Such a phenomenon was also observed when the nonionic surfactant Triton X-405 (octylphenoxy polyethoxy ethanol) was used in the homopolymerizations of S [3] and *n*-butyl acrylate (BA) [4], and copolymerization of S and BA [5]. This indicates that the difference in the amount of emulsifier incorporated inside the polymer particles in the emulsion polymerizations does affect secondary nucleation. Therefore, the incorporation behavior of nonionic emulsifiers is important to understand the mechanism of particle formation.

Fig. 3 shows percentages of E911 and E931 incorporated inside P(S-MAA) particles during the emulsion copolymerization. In the case of E911, the percentage increased remarkably above 50% conversion, while in the case of E931 it increased slightly

throughout the polymerization. These results indicate that the emulsifiers continuously enter into the particles via the aqueous medium from the monomer phase, in which most of the emulsifiers exist prior to polymerization (Table 2). In the latter half of the polymerizations, the amount of E911 incorporated was much higher than that of E931. In other words, $[E]_{aq}$ at intermediate/high conversion would be lower for E911 than that for E931, and thus secondary new (small) particles nucleated in the latter case would be more stable than in the former case, resulting in a broad particle size distribution as described above and shown in Figs. 1 and 2.

3.2. Molecular weight distributions of nonionic emulsifiers

Fig. 4 shows molecular weight distributions of original emulsifiers (E911 and E931) and emulsifier incorporated inside the P(S-MAA) particles at the completion of the polymerization (>93% conversion). The M_n values of the original E911 and E931 were 720 ($M_w/M_n = 1.12$) and 1313 ($M_w/M_n = 1.12$), respectively, while those of the incorporated emulsifiers were 693 ($M_w/M_n = 1.09$) and 871 ($M_w/M_n = 1.05$), respectively. Thus, in the case of E911 both M_n values and polydispersity index (PDI) of the original and incorporated emulsifiers were approximately the same, i.e., most (61%) of E911 component was uniformly incorporated inside the particles regardless of the molecular weight. On the other hand, in the case of E931 most of the incorporated fraction (10%) was of lower M_n (shorter PEO chains, less than approximately 900) and had a lower PDI. In other words, high M_n components (longer PEO chains) would mainly adsorb on the particle surfaces and exist in the aqueous medium during the polymerization.

Fig. 5 shows the S concentration in P(S-MAA) particles ($[S]_p$) and the percentage based on total S at various conversions of the emulsion copolymerization using E911 or E931. $[S]_p$ of both systems monotonously decreased with increasing conversion. In the case of E911, the percentage of S in the particles linearly increased from the beginning of the polymerization to approximately 80% conversion and then decreased until the end of polymerization. On the other hand, in the case of E931 it increased remarkably up to 30% conversion and then decreased with conversion. Most (>84%) of the emulsifier partitioned to the monomer phase (Table 2). Therefore, it seems that the increase in the percentage of S in the particles

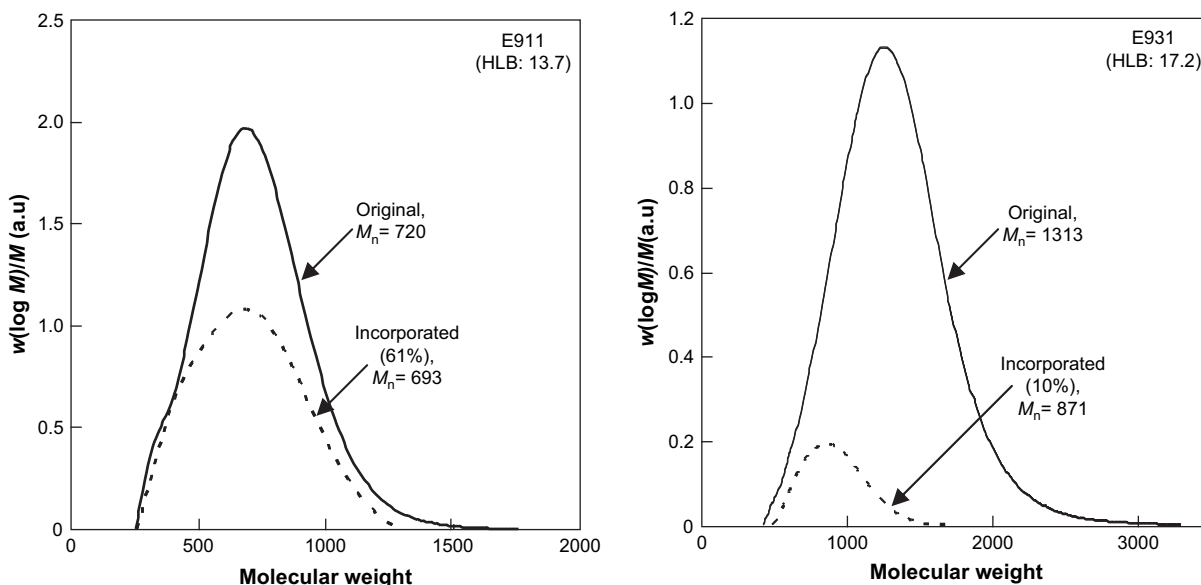


Fig. 4. Molecular weight distributions of original (solid lines) and incorporated (dotted lines) emulsifiers (E911, E931) inside the P(S-MAA) particles. Areas under curves have been normalized according to relative weights of original and incorporated emulsifiers.

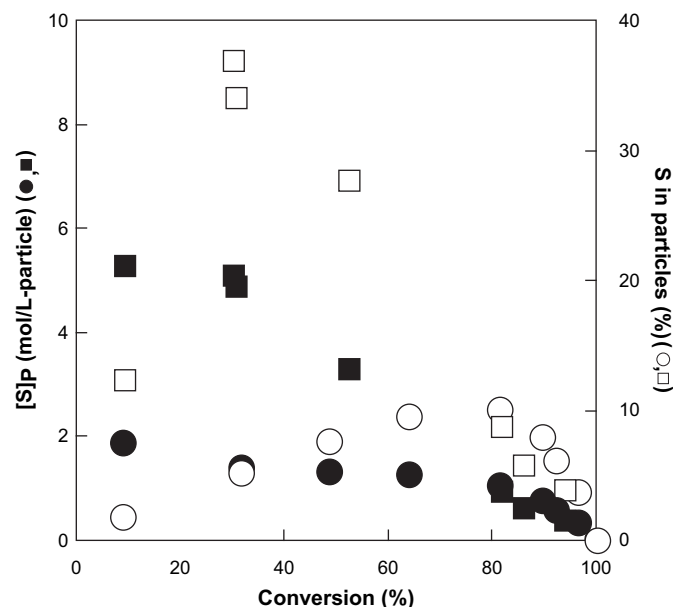


Fig. 5. Percentage of S based on total amount (open symbols) and S concentration (filled symbols) inside polymerizing particles at various conversions of emulsion copolymerization of S and MAA using E911 (circles) or E931 (squares) nonionic emulsifier.

caused the raise in the incorporation of emulsifiers inside particles (Fig. 3). However, the incorporation still increased even after 80% and 30% conversions for E911 and E931, respectively (Fig. 3), where the percentage of S inside particles decreased. The results shown in Figs. 3 and 5 indicate that there is another factor(s) influencing the amount of incorporated emulsifier in addition to the amount of absorbed S.

Fig. 6 shows M_n of incorporated emulsifiers inside P(S-MAA) particles against conversion in the emulsion copolymerization using E911 or E931. In both cases, M_n decreased monotonously with

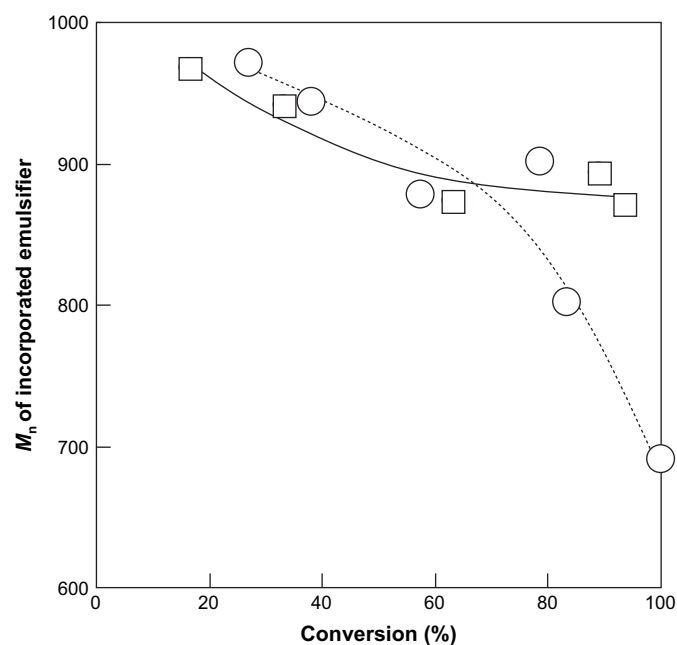


Fig. 6. Number-average molecular weight (M_n) of incorporated emulsifier inside polymerizing particles at various conversions of emulsion copolymerization of S and MAA using E911 (circles) or E931 (squares) nonionic emulsifiers.

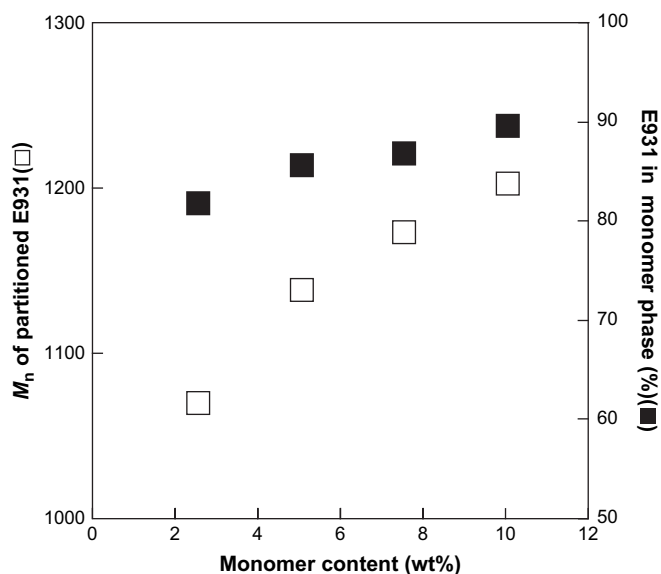


Fig. 7. M_n and percentage of E931 partitioned into monomer phase (S, MAA) at different monomer contents at 70 °C [E931 4 g; S + MAA (MAA content, 10 mol%) 15–60 g; total weight of aqueous solution, 600 g].

conversion above 10%. There seem to be two possible reasons for M_n decreasing with conversion: (1) continuous entry of the lower M_n (shorter PEO chains) into the particles; (2) selective desorption of the high M_n (long PEO chains) from the particles, in which $[S]_p$ decreased with conversion, to the aqueous medium.

Most of E911 are the shorter PEO ($M_n < 900$) chains (from original M_n in Fig. 4). Thus, it has much more shorter PEO components released from monomer droplets with conversion than those of E931. This is the reason that the amount of the incorporated E911 was much larger than that of E931. The monomer layer disappeared at approximately 91% and 85% conversions for E911 and E931, respectively (Fig. 3), much higher than that in a general emulsion polymerization. $[S]_p$ values of E911 (throughout polymerization) and E931 (after 30% conversion) as shown in Fig. 5 were much lower than those at the equilibrium state (5.5 mol/l particles) [16]. This may be because the large amount of nonionic emulsifier partitioned to the monomer droplets acts as hydrophobe to retard monomer transportation from droplets to particles [7]. In addition, the total interfacial areas between the monomer droplets and the aqueous medium were much lower than those in a general emulsion polymerization, because of inefficient stirring with a separate monomer layer above the aqueous phase [13].

Fig. 7 shows the M_n and percentage of E931 partitioned to the monomer phase under similar conditions as the recipe in the polymerization (Table 1) in the absence of initiator. Both values decreased with a decrease in the volume of the monomer phase. This agreed well with those (Figs. 3, 5 and 6) of the incorporated emulsifiers into the polymerizing particles during the emulsion copolymerization, where $[S]_p$ decreased with conversion (Fig. 5). Thus, M_n of the emulsifiers absorbed by the polymerizing particles swollen with monomer seems to be similar as that in the monomer droplets (layer) at each conversion. The decrease of $[S]_p$ with conversion would release predominantly longer PEO chain components to the aqueous medium and absorb mainly shorter PEO chain components from the aqueous medium. This seems to be the reason that M_n of the incorporated emulsifier decreased with the conversion.

4. Conclusions

P(S-MAA) copolymer particles were prepared by emulsion copolymerization using polyoxyethylene nonylphenyl ether nonionic

emulsifiers having different HLB values. Emulsifier comprising polydisperse PEO chain lengths affects the incorporation. Shorter PEO chain components of the nonionic emulsifiers were predominantly incorporated inside the polymerizing particles. The amount of incorporated emulsifier inside the particles increased with conversion, and was much larger for E911 than that for E931. Secondary nucleation would take place by homogeneous nucleation for the higher incorporation (E911), and unstable secondary particles were adsorbed onto the large particles resulting in monodisperse nonspherical particles. The lower incorporations (E920 and E931) gave more stable secondary particles and thus less adsorption onto the preformed particles, resulting in polydisperse particles (spherical small and nonspherical large particles).

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