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Production of polymer microparticles by "dissolution" of submicron-sized water-insoluble ionized carboxylated polymer particles in the presence of various nonionic emulsifiers*)

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Abstract: Styrene-butyl acrylate-methacrylic acid terpolymer (50.4/40.9/8.7, molar ratio) particles, 276 nm in diameter, were produced by emulsifier-free emulsion terpolymerization. The emulsifier-free carboxylated terpolymer particles did not dissolve in water even under alkaline condition. However, they dissolved in the presence of nonionic emulsifier under alkaline condition, resulting in polymer microparticles having diameter less than 40 nm. Such a dissolution behavior was examined using five kinds of different polyoxyethylene nonylphenylether nonionic emulsifiers having hydrophilic–lipophilic balance values between 12.2 and 17.5 at various initial pH values, temperatures and times, and its mechanism was discussed.

Key words: Carboxyl group – emulsion polymerization – microemulsion – microsphere – emulsifier

Introduction

In a previous article [1], it was found that submicron-sized ionized styrene-butyl acrylate-methacrylic acid terpolymer (P(S-BA-MAA), 50.4/40.9/8.7, molar ratio) particles produced by emulsion terpolymerization dissolved in an aqueous solution of polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 910, Kao Corp., Tokyo, Japan) at pH 13, 40 °C, resulted in the microparticles having diameter of about 30 nm.

There are similar reports [2, 3] that water-insoluble polyvinyl acetate (PVAc) particles produced by emulsion polymerization dissolved in emulsifier aqueous solutions. However, the dissolution of PVAc particles was limited to anionic emulsifiers such as sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfate, nonionic emulsifiers showing no effect and cationic ones having only a very small effect. The PVAc particles dissolved in the presence of the anionic emulsifier solutions of which concentrations corresponded to about three times the weight of the polymer solid. On the other hand, the P(S-BA-MAA) particles used in this study did not dissolve in SDS solution even at the concentration which corresponded to 30 times the weight of the polymer solid. In this way, PVAc particles dissolved in the anionic emulsifier solution, whereas the P(S-BA-MAA) particles dissolved in the nonionic emulsifier solution. This suggests that their dissolution mechanisms are not the same.

In this article, the dissolution mechanism of P(S-BA-MAA) particles will be discussed using five kinds of polyoxyethylene nonylphenylether emulsifiers having different hydrophilic–lipophilic balance (HLB) values under the various conditions.

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Experimental

Materials

Styrene (S), butyl acrylate (BA) and methacrylic acid (MAA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent-grade potassium persulfate (KPS) was purified by recrystallization from distilled water. Analytical grade hydrochloric acid, and potassium hydroxide were used for pH adjustment. Deionized water was distilled.

A series of commercial grade polyoxyethylene nonylphenylether nonionic emulsifiers (Emulgen 906, 910, 930, 931, 935; Kao Corp., Tokyo, Japan) were used without further purification. The HLB value, the number of ethylene oxide unit, and cloud point of Emulgen emulsifiers used in this experiment are shown in Table 1. The number of ethylene oxide unit was calculated according to the following Griffin's equation [4],

$$\mathrm{HLB} = E/5 - (1)\,,$$

where E is the weight fraction of ethylene oxide unit.

Preparation of polymer emulsion

Original P(S-BA-MAA) emulsion (50.4/40.9/8.7, molar ratio) was produced by semi-continuous two-stage emulsifier-free emulsion terpolymerization with potassium persulfate initiator at 70 °C according to the previous article [1]. Five wt% of all the monomers were preliminarily terpolymerized for 1.2 h in a glass reaction flask and then the residual monomers were dropwise added with a micro feeder for 14.5 h.

Alkali treatment in the presence of nonionic emulsifier

The original P(S-BA-MAA) emulsion and each nonionic emulsifier aqueous solution were mixed in a small glass vessel. The pH value was adjusted with 1 N KOH or 6 N HCl. The final polymer solid content was adjusted to 2.2 g/l and the diluted emulsion was kept at the various temperatures for a certain time. After the treatment, the glass vessel was immediately cooled to about 0 °C by dipping into ice water. The degree of dissolution of the particles was estimated by measuring the transmittance of the emulsion at a wavelength of 850 nm using a spectrophotometer (Hitachi Model 100-50, Tokyo, Japan) at about 0 °C with a glass cell of 1 cm in thickness.

Table 1. Properties of Emulgen Emulsifiers

Emulsifier	HLB[a]	n[b]	Cloud point[a]	Symbol
Emulgen 906	10.8	5.9	–	●
Emulgen 910	12.2	7.8	23	○
Emulgen 930	15.1	15.4	> 100	□
Emulgen 931	17.2	30.7	> 100	△
Emulgen 935	17.5	35	> 100	■

[a] by catalog

[b] number of ethylene oxide units calculated according to Griffin's equation

Dynamic light scattering measurement

The particle diameter was measured at room temperature by dynamic light scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan). The data at 90° of the light scattering angle were analyzed with the DLS-700 system program mode Auto-2.

Results and discussion

Figure 1 shows the relationships between the initial pH value and the transmittances (incident wavelength: 850 nm) of the P(S-BA-MAA) emulsions after the treatment at 90 °C for 1 h in the presence of the various nonionic emulsifiers of which the amount was four times that of the particles. In the case of Emulgen 906 which has the lowest HLB values of 10.8 in the emulsifiers used in this experiment, the transmittance did not change even at pH 13. That is, the P(S-BA-MAA) particles did not dissolve in the alkaline aqueous solution of Emulgen 906. This may be the reason why it is too hydrophobic to stabilize produced microparticles. In the cases of the other emulsifiers, the transmittance increased remarkably with an increase in the initial pH value above 10. The minimum pH value at which the original emulsion became transparent increased from 11 to 13 with an increase in the HLB value. This seems to be based on whether the particles can smoothly absorb the emulsifier molecules. The volume of

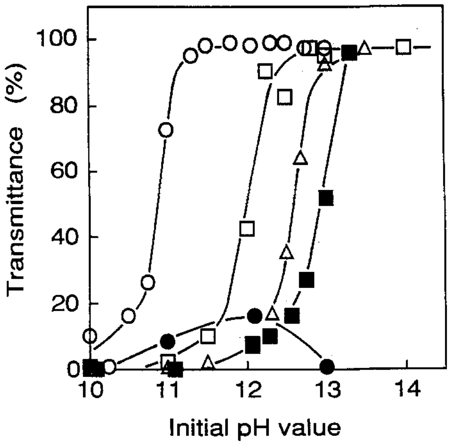

Fig. 1. Relationships between the initial pH value and the transmittances of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsions (2.2 g/l) at 90 °C for 1 h in the presence of various Emulgen emulsifiers (8.8 g/l). Incident wavelength, 850 nm. The symbols are shown in Table 1

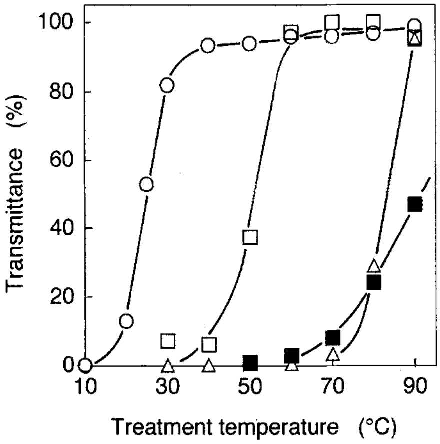

Fig. 3. Relationships between the treatment temperatures and the transmittance of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsions (2.2 g/l) at initial pH 13.0 for 1 h in the presence of various Emulgen emulsifiers (8.8 g/l). Incident wavelength, 850 nm. The symbols are shown in Table 1

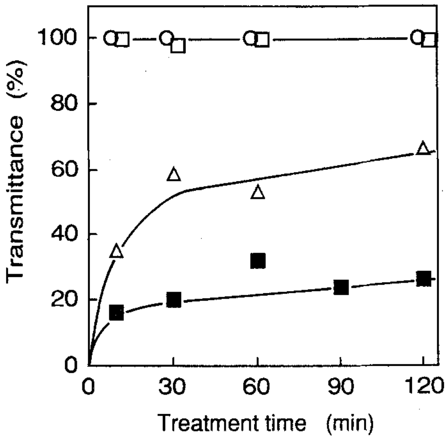

Fig. 2. Relationships between the treatment time and the transmittances of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsions (2.2 g/l) at initial pH 12.7 and at 90 °C in the presence of various Emulgen emulsifiers (8.8 g/l). Incident wavelength, 850 nm. The symbols are shown in Table 1

P(S-BA-MAA) particles increased with the increase in the pH value in alkaline side [5] because of ionization of carboxyl groups. The size of the nonionic emulsifier molecules in water should increase with the increase in the HLB value.

Figure 2 shows the relationships between the treatment time at pH 12.7, 90 °C and the transmittance of P(S-BA-MAA) emulsion containing each nonionic emulsifier. The transmittance increased with an increase in the treatment time. In the cases of Emulgen 910 and 930, the transmittance reached about 100% within a minute. The transmittance of the original emulsifier-free emulsion did not increase under the same conditions.

Figure 3 shows the relationships between the treatment temperature at pH 13 for 1 h and the transmittance of the P(S-BA-MAA) emulsion containing each nonionic emulsifier. The minimum temperature at which the original emulsion became transparent increased with the increase in the HLB value. This seems to be also based on whether the particles can smoothly absorb the emulsifier molecules. However, the cloud point of the emulsifiers, at which the size of nonionic emulsifier drastically decreases, did not directly control the minimum dissolution temperature. In the case of Emulgen 910 it was close to the cloud point of 23 °C, but in the cases of Emulgen 930, 931 and 935 (cloud point > 100 °C) they did not agree.

Figure 4 shows the relationships between the amount of emulsifiers and the transmittance of the P(S-BA-MAA) emulsion treated at pH 12.7 for 1 h at 90 °C. In the case of Emulgen 906, the transmittance did not change even at about 50 times the amount of emulsifier based on the total polymer solid. In the cases of Emulgen 910 and 930, the transmittance increased drastically, to 100%, i.e., around the same amount of emulsifiers as that of the total polymer solid, and in the cases of Emulgen 931 and 935, it increased gradually

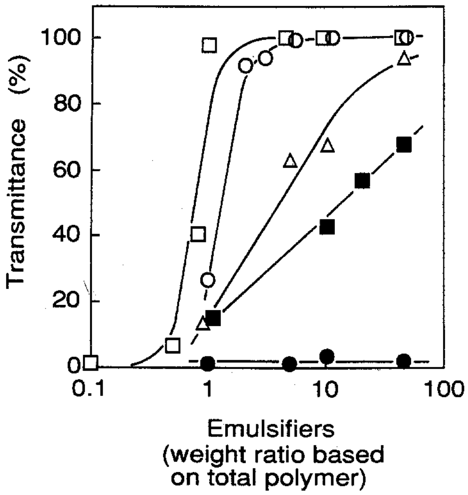

Fig. 4. Relationships between the amount of emulsifiers and the transmittance of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsions (2.2 g/l) at initial pH 12.7 for 1 h at 90 °C in the presence of various Emulgen emulsifiers. Incident wavelength, 850 nm. The symbols are shown in Table 1

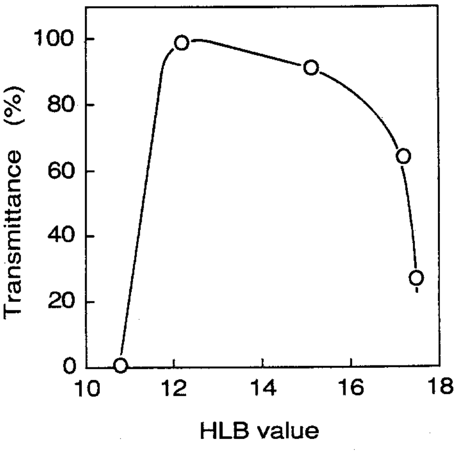

Fig. 5. Relationship between the HLB value of emulsifiers and the transmittance of the P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsions (2.2 g/l) at initial pH 12.7 for 1 h at 90 °C in the presence of various Emulgen emulsifiers (8.8 g/l). Incident wavelength, 850 nm

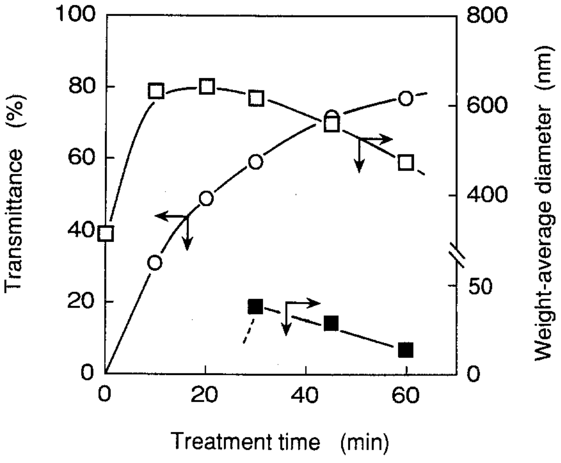

Fig. 6. Relationships between the treatment time and the transmittance (o) at 850 nm of the original P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion (2.2 g/l) and the weight-average diameters of particles coming from original P(S-BA-MAA) particles (□) and newly produced microparticles (■). Treatment conditions; initial pH 13.0; 55 °C; Emulgen 930, 8.8 g/l

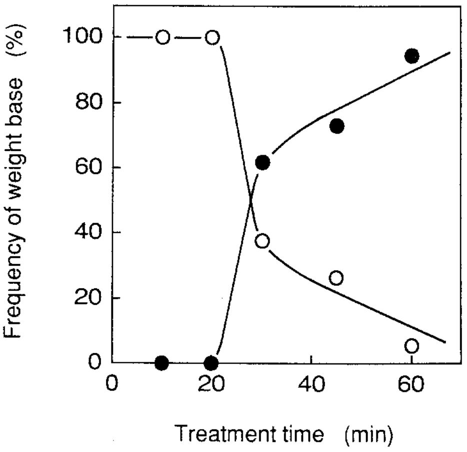

Fig. 7. Variations of the frequencies of weight base of original P(S-BA-MMA) (50.4/40.9/8.7, molar ratio) particles (O) and the microparticles (●) with the alkali treatment time at initial pH 13.0 and at 55 °C in the presence of Emulgen 930 (8.8 g/l, 400 wt% based on total polymer solid)

with an increase in the amount of emulsifier above that.

Figure 5 shows the relationship between the HLB value of the emulsifiers and the transmittance of the P(S-BA-MAA) emulsion treated at pH 12.7 for 1 h at 90 °C in the presence of each nonionic emulsifier. The result indicates that there is an appropriate HLB region of the nonionic emulsifiers that makes the particles dissolve in the alkaline solution.

Figure 6 shows the variations of transmittance of the P(S-BA-MAA) emulsion (2.2 g/l) and the weight-average diameters of original particles and produced microparticles with the treatment time at initial pH 13.0 and at 55 °C in the presence of Emulgen 930 (8.8 g/l). The particle diameter in-

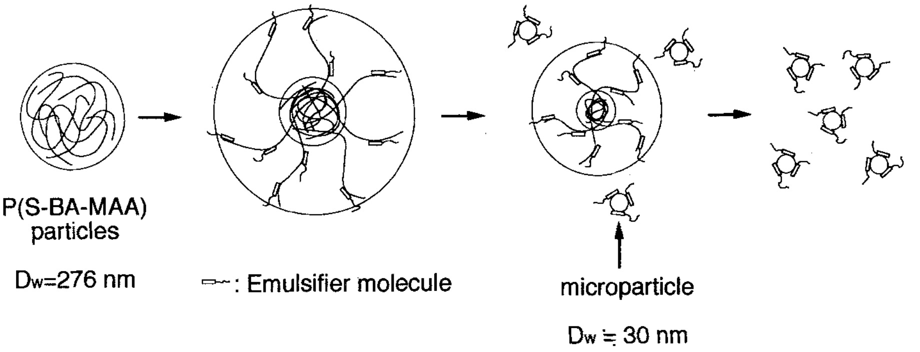

Fig. 8. Schematic model for preparation of the microemulsion by dissolution of submicron-sized ionized P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) particles in the presence of the nonionic emulsifier

creased with the treatment time and then decreased. At 20 min, it had a maximum value at which the particles volume corresponds to 8 times that of original particles. The microparticles were not observed until 20 min, but after 30 min at which the diameter of the expanded particles began to decrease, the microparticles having diameter of about 30 nm was newly observed.

Figure 7 shows the variations of the frequencies of weight base of the P(S-BA-MAA) particles and the newly produced microparticles with the treatment time at 55 °C in the system shown in Fig. 6. After 20 min the percentage of the original particles remarkably decreased and finally reached zero, whereas as a matter of course that of the microparticles indicates an opposite variation.

From the above results that some factors greatly affect the dissolution of the submicron-sized P(S-BA-MAA) particles, it is concluded that the production of the microparticles proceeds as shown in Fig. 8. At first, the submicron-sized original carboxylated particles swell under an alkaline condition. At this time, the nonionic emulsifier molecules permeate into the particles together with water and interact with the polymer molecules. Several polymer molecules stabilized with the emulsifiers are gradually stripped from the surface layer and result in microparticles.

Acknowledgements

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References

1. Okubo M, Fujimura M, Kusano T Colloid Polym Sci (in press)
2. Isemura T, Imanishi A (1958) J Polym Sci 33:337
3. Isaacs PK, Edelhauser HA (1966) J Appl Polym Sci 10:171
4. Griffin WC (1954) J Soc Cosmet Chemists 5:249
5. Okubo M, Ichikawa K, Fujikura M (1991) Colloid Polym Sci 269:1257

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