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The dissolution of ionized water-insoluble carboxylated polymer particles in the nonionic emulsifier solution*)

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Abstract: It was found that 276 nm-sized styrene-butyl acrylate-methacrylic acid terpolymer (P(S-BA-MAA)) (50.4/40.9/8.7, molar ratio) particles produced by emulsifier-free emulsion polymerization dissolved in a polyoxyethylene nonylphenylether nonionic emulsifier aqueous solution at pH values above 11 and above 25 °C resulted in polymer microemulsion. The weight-average diameter of P(S-BA-MAA) microparticles in the solution was 31 nm, which was measured by dynamic light scattering spectroscopy. Such a dissolution of the particles was not observed in the absence of the emulsifier.

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

Introduction

Submicron-sized carboxylated polymer emulsion produced by emulsion copolymerization with an unsaturated acid monomer is widely used commercially and there are many papers dealing with it. We have also carried out a series of investigations about it, especially, from the viewpoint of distribution of carboxyl groups within particles [1–6].

In recent articles, we produced multi-hollow particles from styrene-butyl acrylate-methacrylic acid terpolymer (P(S-BA-MAA)) particles by the "stepwise alkali/acid method" [7], and clarified the effects of alkali and acid treatment conditions on the formation of such a multihollow structure [8]. In the process of the experiment, it was found that the submicronsized ionized P(S-BA-MAA) particles dissolved in the nonionic emulsifier aqueous solution resulted in a transparent polymer micro-emulsion. This article will report the phenomenon.

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. Commercial grade polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 910, Kao Corp., Tokyo, Japan), analytical grade hydrochloric acid, and potassium hydroxide were used without further purification. Deionized water was distilled.

Preparation of polymer emulsions

Original P(S-BA-MAA) emulsion was produced by semi-continuous two-stage emulsifier-free emulsion terpolymerization at 70 °C under the conditions listed in Table 1. Five wt% of all the monomers were preliminarily terpolymerized for

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Table 1. Conditions of stage-type emulsion polymerization for the preparation of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) particles[a])

Ingredient		First stage [b])	Second stage [c])
S	(g)	1.73	32.9
BA	(g)	1.73	32.9
MAA	(g)	0.24	4.55
KPS [d])	(mg)	375	–
Water	(g)	223	–

[a]) Conducted at 70 °C for 26 h under nitrogen atmosphere

[b]) For 1.2 h; [c]) For 14.5 h; [d]) Potassium persulfate

1.2 h in a glass reaction flask and then the residual monomers were dropwise added with a micro feeder for 14.5 h. After the terpolymerization, no monomer was detected by gas chromatography (Yanagimoto Manufacturing G-2800, Kyoto, Japan). Therefore, the molar ratio of S/BA/MAA in the original terpolymer particles was calculated to be 50.4/40.9/8.7 from the polymerization recipe.

The glass transition temperature of the dried P(S-BA-MAA) separated from the original emulsion was measured to be 34.4 °C using a differential scanning calorimeter (Perkin Elmer Japan, DSC 7) at a heating rate of 10 °C/min.

Alkali treatment in the presence of nonionic emulsifier

After the original P(S-BA-MAA) emulsion and Emulgen 910 aqueous solution were mixed in a small glass vessel and diluted, the pH value was adjusted with 1.0 N KOH or 6.0 N HCl. The final polymer solid content was 2.2 g/l. The diluted emulsion was kept at various temperatures for a certain time. After the treatments, 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 about 0 °C and at a wavelength of 850 nm using a spectrophotometer (Hitachi Model 100-50, Tokyo, Japan) with a glass cell of 1 cm in thickness.

Dynamic light-scattering measurement

The particle diameter was meaured by a dynamic light scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan). The data at the light-scattering angle of 90° were analyzed with the DLS-700 system program mode Auto-2. The weight-average diameter and its standard deviation of the original P(S-BA-MAA) particles were, respectively, 276 nm and 12 nm.

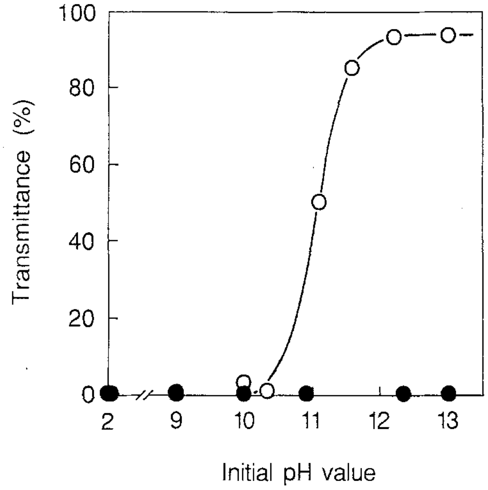

Fig. 1. Relationships between the initial pH value and the transmittances of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion (2.2 g/l) at 40 °C for 1 h in the presence (○)/absence (●) of Emulgen 910 (8.8 g/l). Incident wavelength, 850 nm

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) emulsion in the presence and absence of Emulgen 910 at 40 °C for 1 h. In the presence of Emulgen 910, whose amount was four times the weight of the polymer solid, the transmittance increased remarkably with an increase in the pH value above 11 and reached about 95% at pH 12. On the other hand, in the absence of Emulgen 910, the transmittance did not increase even at pH 13. This indicates that the above dissolution phenomenon is not a well known alkali dissolution [9] of carboxylated polymer particles.

Figure 2 shows the relationships between the standing time at pH 13 and at various temperatures from 25° to 40°C and the transmittances of P(S-BA-MAA) emulsion containing the Emulgen 910. The transmittances at the various temperatures increased clearly with an increase in the

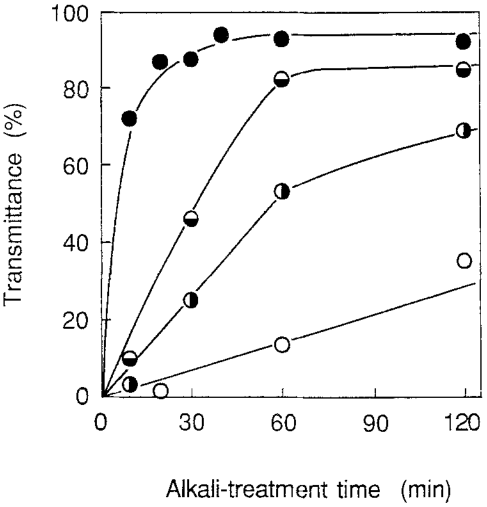

Fig. 2. Relationships between the treatment time and the transmittance of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion (2.2 g/l) at initial pH 13.0 and at various temperatures (○, 20 °; ◑, 25 °; ◒, 30 °; ●, 40 °C) in the presence of Emulgen 910 (8.8 g/l). Incident wavelength, 850 nm

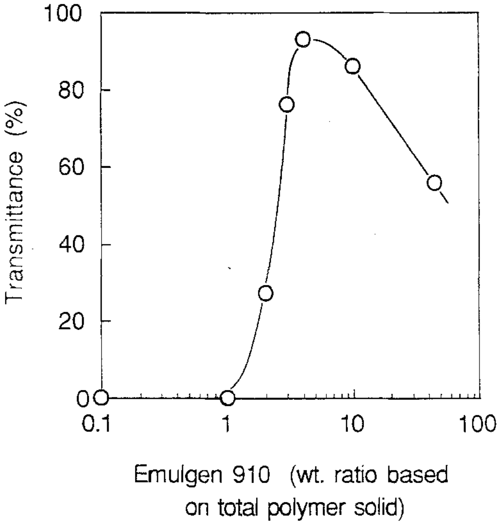

Fig. 4. Relationships between the amount of Emulgen 910 and the transmittance of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion (2.2 g/l) at initial pH 13.0 for 1 h at 40 °C in the presence of Emulgen 910 (8.8 g/l). Incident wavelength, 850 nm

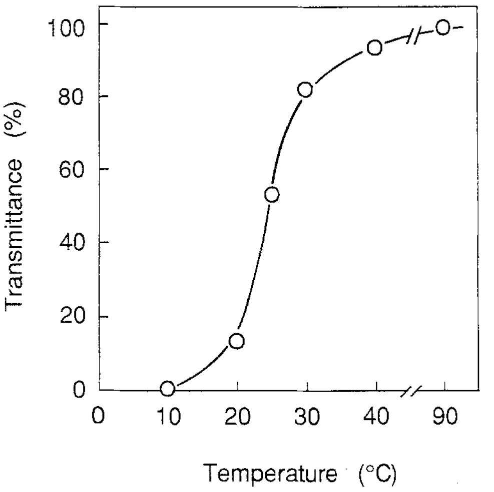

Fig. 3. Relationships between the treatment temperature and the transmittance of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion (2.2 g/l) at initial pH 13.0 for 1 h in the presence of Emulgen 910 (8.8 g/l). Incident wavelength, 850 nm

treatment time. For example, the emulsion became transparent within 40 min at 40 °C.

Figure 3 shows the relationship between the treatment temperature at pH 13 for 1 h and the transmittance of the P(S-BA-MAA) emulsion containing the Emulgen 910. The transmittance increased remarkably with an increase in the treatment temperature around about 25 °C.

Figure 4 shows the relationship between the amount of Emulgen 910 and the transmittance of the treated P(S-BA-MAA) emulsion at pH 13 for 1 h at 40 °C. The transmittance had a maximum value at four times the weight of Emulgen 910 based on the total polymer solid at which the emulsion was transparent.

Figure 5 shows the size distribution of the P(S-BA-MAA) particles treated at pH 13 for 1 h at 40 °C. The weight-average diameter was about 31 nm.

From these results, it was clarified that 276 nm-sized ionized P(S-BA-MAA) particles dissolved in the nonionic emulsifier solution, resulting in polymer microparticles.

There are similar reports [10, 11] that water-insoluble polyvinyl acetate (PVAc) particles produced by emulsion polymerization dissolved in emulsifier aqueous solutions. However, the dissolution of PVAc particles is limited to anionic emulsifiers such as sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfate, whereas nonionic emulsifiers showed no effect and cationic ones had only a very small effect. In the former cases, the PVAc particles dissolved in anionic emulsifier solutions had concentrations which

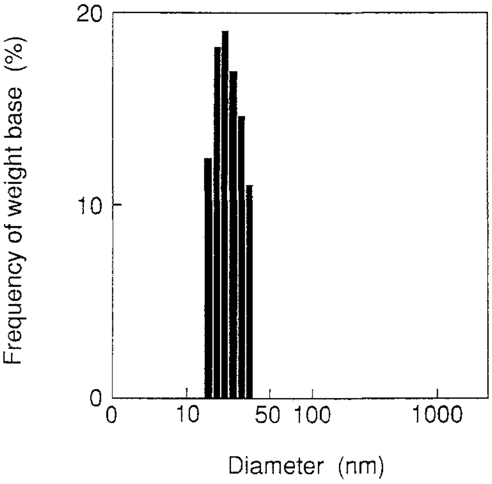

Fig. 5. Particle-size distribution of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion measured by dynamic light-scattering spectroscopy at initial pH 13.0 for 1 h at 40 °C in the presence of Emulgen 910 (400 wt% based on total polymer weight)

corresponded to about three times the weight of the polymer solid. On the other hand, the P(S-BA-MAA) particles did not dissolve in SDS solution at pH 13.0 for 1 h at 40 °C, even at a concentration which corresponded to 30 times the weight of the polymer solid.

In this way, PVAc particles dissolved in the only anionic emulsifier solution, whereas the P(S-BA-MAA) particles dissolved in the only nonionic emulsifier solution. This suggests that their dissolution mechanism is not the same. The mechanism of the dissolution reported in this article will be discussed in the near future.

Acknowledgements

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