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SHORT COMMUNICATION

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Preparation of nanoparticles by "dissolution" of submicron-sized ionized styrene-methacrylic acid copolymer particles in nonionic emulsifier solution

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Abstract Styrene-methacrylic acid copolymer (P(S-MAA)) nanoparticles having high *Tg* were produced by a dissolution of submicron-sized P(S-MAA) particles as follows. Submicron-sized P(S-MAA) particles having various MAA contents were produced by emulsion copolymerization. Secondly, they were treated in a polyoxyethylene nonylphenylether nonionic emulsifier aqueous solution at pH 13.0 and above 90 °C. The nanoparticles having about 30 nm in diameter were only produced from the particles having MAA contents around 7 mol%, and above the contents, they were not produced. It seems to be based on that emulsifier molecules are not adsorbed onto the polymer molecules enough to dissolve them. The effect of MAA content on such a dissolution behavior was examined using seven kinds of different nonionic emulsifiers having hydrophile-lipophile-balance values between 12.2 and 18.2 at various temperatures and initial pH.

Key words Carboxyl group – emulsion polymerization – nanoparticles – microsphere – emulsifier

Introduction

In general, nano-sized polymer emulsion having below 50 nm in diameter has good penetration and wettability compared with a submicron-sized one, and a film cast from the former is more even and lustrous than that from the latter. Utilizing such properties, the nano-sized polymer emulsion has been used as undercoat of paper, wood and cloth. In addition, polymer nanoparticles have seen recent applications in drug delivery systems [1], photochemical reactions [2] and polymeric catalysis [3]. There are many papers dealing with the direct production of polymer nanoparticles by polymerization in microemulsion [1–7].

On the other hand, in a recent article [8], we reported that submicron-sized 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 the presence of polyoxyethylene nonylphenylether nonionic emulsifier at pH 13, 40 °C, resulting in nanoparticles having diameter of about 30 nm. Hereafter this will be named "Particle dissolution method". In a previous article [9], the dissolution mechanism of P(S-BA-MAA) particles was proposed. P(S-BA-MAA) used in these experiments contains hydrolyzable BA component and its glass transition temperature (*Tg*) was 34 °C. Polymer nanoparticles having high *Tg* may be more useful in their applications than those having low *Tg*.

In this article, the preparation of styrene-methacrylic acid copolymer P(S-MAA) nanoparticles which contain no hydrolyzable BA component and have *Tg* above 100 °C by the particle dissolution method will be tried.

Experimental

Materials

Styrene (S) 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 potassium hydroxide was used without further purification. Deionized water was distilled.

A series of commercial grade polyoxyethylene nonylphenylether nonionic emulsifiers (Emulgen 900 series; Kao Corp., Tokyo, Japan) were used without further purification. The hydrophile-lipophile balance (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 [10],

$$\mathrm{HLB} = E/5 \tag{1}$$

where E is the weight percentage of ethylene oxide unit.

Table 1 Properties of Emulgen emulsifiers

Emulsifier	HLB[a]	n[b]	Cloud point[a]
Emulgen 910	12.2	7.8	23.8
Emulgen 911	13.7	10.9	73.6
Emulgen 913	14.5	13.2	90.0
Emulgen 930	15.1	15.4	> 100
Emulgen 931	17.2	30.7	> 100
Emulgen 935	17.5	35.0	> 100
Emulgen 950	18.2	50.6	> 100

[a] By catalog.
[b] Number of ethylene oxide units calculated according to Griffin's equation.

Preparation of polymer emulsion

S-MAA copolymer (P(S-MAA)) emulsions having various MAA contents were prepared by emulsion copolymerization of S and MAA at 70 °C for 24 h under the conditions listed in Table 2. In all systems, the residual monomers were not detected by gas chromatography (Yanagimoto Manufacturing G-2800, Kyoto, Japan). Therefore, the molar ratios of P(S-MAA) in these emulsions were determined from the polymerization recipes.

Measurement of particle diameter

Weight-average diameter (*Dw*) and number-average diameter (*Dn*) of P(S-MAA) particles were measured at room temperature by dynamic light-scattering spectroscopy (Otsuka Electronics DLS-700, Kyoto, Japan). The data at 90° of the light scattering angle were analyzed with the DLS-700 system.

Alkali treatment in the presence of nonionic emulsifier

The original P(S-MAA) emulsion and each nonionic emulsifier aqueous solution were mixed in a small glass vessel. The pH value was adjusted with 1 N KOH and the final polymer solid content was adjusted to 2.2 g/l. This emulsion was placed in a 50 ml-capacity Teflon-tube which was put in a stainless steel pressure-resistant vessel, and the vessel was dipped in an oil bath at various temperatures for different times. After the treatment, the vessel was immediately cooled to about 0 °C by dipping into ice-cold water. The degree of dissolution of the particles was estimated by measuring the transmittance of treated emulsion at a wavelength of 850 nm using a spectrophotometer (Hitachi Model 100-50, Tokyo, Japan) with a glass cell of 1 cm in thickness.

Table 2 Conditions of emulsion copolymerizations[a] for the production of P(S-MAA) particles having various MAA contents

Acid content	(mol%)	0	4	5	6	8	10	12	14
S	(g)	60.0	58.0	57.5	57.0	56.0	55.0	53.9	52.9
MAA	(g)	0	2.0	2.5	3.0	4.0	5.0	6.1	7.1
KPS	(g)	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Emulgen 911	(g)	0	1.8	2.5	2.5	3.3	4.0	4.8	5.5
Water	(g)	540	540	540	540	540	540	540	540
Dw[b]	(nm)	589	472	560	492	422	438	375	487
Dw/*Dn*[b]		1.18	1.01	1.43	1.04	1.07	1.05	1.06	1.01

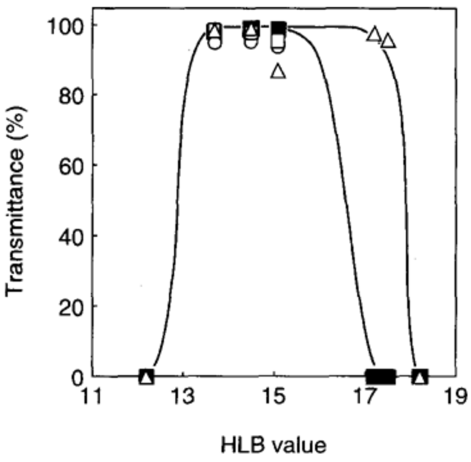
[a] 70 °C, 24 h, N_2; stirring rate, 120 rpm.
[b] Measured by dynamic light scattering spectroscopy.
Abbreviations: S, styrene; MAA, methacrylic acid; KPS, potassium persulfate.

Results and discussion

Figure 1 shows the relationships between the HLB value of the emulsifiers and the transmittances of the P(S-MAA) (92/8, molar ratio) emulsion treated at pH 13.0 for 1 h at 90 ~120 °C in the presence of each nonionic emulsifier. There was a HLB region at which the transmittance was above 95%, which was similar to the case of P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) emulsion [9]. This indicates that the P(S-MAA) particles dissolved in the HLB region. *Dw* and *Dw*/*Dn* of P(S-MAA) emulsion treated at pH 13.0 for 1 h at 120 °C were 26 nm and 1.14, respectively, which were measured by dynamic light-scattering spectroscopy.

Figure 2 shows the relationships between the MAA content and the transmittances of the P(S-MAA) emulsions after the treatments at initial pH 13.0 for 1 h at 80 ~120 °C in the presence of Emulgen 930 of which HLB value is 15.1. At each temperature, there was a region of the MAA content around 7 mol% at which the particles dissolved. The region was expanded somewhat by increasing the temperature from 80° to 120 °C. In the previous article [9], it was clarified that alkali swelling of the original particles was the trigger for production of nano-sized particles from submicron-sized P(S-BA-MAA) (50.4/40.9/8.7, molar ratio) by the particle dissolution method. According to this, it is easy to understand the result that in the MAA content below 5 mol% the nano-sized particles were not produced, because their alkali-swelling abilities were low. However it is difficult to understand the result that the nano-sized particles were not produced above 10 mol%, because P(S-MAA) (90/10, molar ratio) particles smoothly swelled as follows.

Fig. 1 Relationship between the HLB value of Emulgen emulsifiers and the transmittances (incident wavelength, 850 nm) of P(S-MAA) (92/8, molar ratio) emulsion (2.2 g/l) treated in the presence of Emulgen emulsifiers (8.8 g/l) at initial pH 13.0 for 1 h at various temperatures: ○, 90°; □, 100°; ■, 110°; △, 120 °C



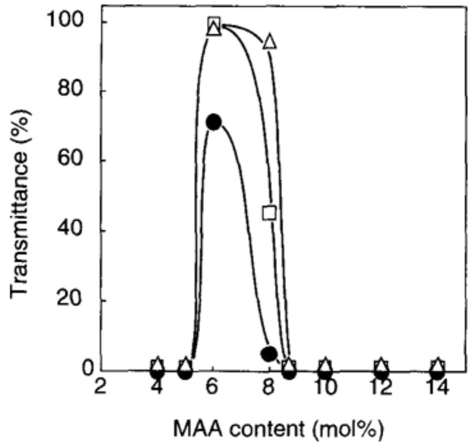


Fig. 2 Relationship between the MAA content and the transmittances (incident wavelength, 850 nm) of P(S-MAA) (92/8, molar ratio) emulsions (2.2 g/l) treated in the presence of Emulgen 930 (8.8 g/l) at initial pH 13.0 for 1 h at various temperatures: ●, 80°; □, 100°; △, 120 °C

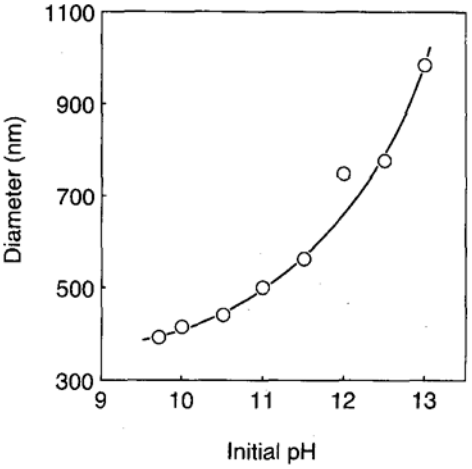


Fig. 3 Relationship between the initial pH and the weight-average diameter measured by dynamic light-scattering spectroscopy of P(S-MAA) (90/10, molar ratio) particles treated in the presence of Emulgen 930 (400 wt% based on total polymer weight) for 1 h at 90 °C

Figures 3 and 4 show the swelling behaviors of P(S-MAA) (90/10, molar ratio) particles treated in the presence of Emulgen 930 for 1 h, respectively, at various initial pH values at 90 °C and at various temperatures at initial pH 13. The diameter of the original particles increased markedly with an increase in the initial pH and the treatment temperature.

Figure 5 shows the states of P(S-MAA) (90/10, molar ratio) emulsions at room temperature after the treatment

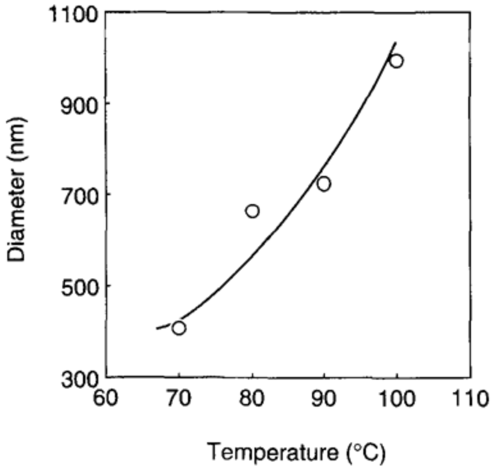


Fig. 4 Relationship between the treatment temperature and the diameter of P(S-MAA) (90/10, molar ratio) particles treated at initial pH 13.0 for 1 h at 90 °C in the presence of Emulgen 930 (400 wt% based on total polymer weight)

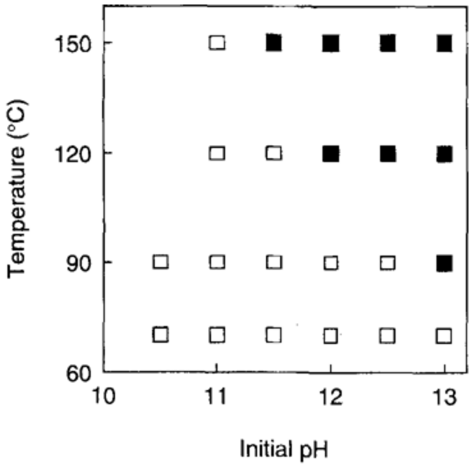


Fig. 6 The state of Emulgen 930 aqueous solution (8.8 g/l) at various pH values and temperatures for 1 h: □, transparent; ■, turbid

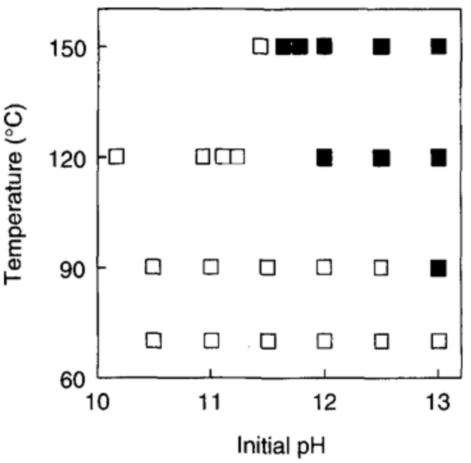


Fig. 5 The state of P(S-MAA) (90/10, molar ratio) emulsion (2.2 g/l) treated at various pH values and temperatures for 1 h in the presence of Emulgen 930 (8.8 g/l): □, emulsion (turbid); ■, coagulation

Table 3 Comparison between emulsifier state and PS emulsion state after alkali treatment[a]

Emulsifier	Emulsifier state	Emulsion state
Emulgen 910	turbid	coagulation
Emulgen 930	turbid	coagulation
Emulgen 935	turbid	coagulation
Emulgen 950	clear	stable
Emulgen 985	clear	stable

[a] PS emulsion (2.2 g/l) at initial pH 13.0 for 1 h at 120 °C in the presence of emulsifier (8.8 g/l).

in the presence of Emulgen 930 at various pH and temperatures. Open squares indicate that the emulsion state did not change before and after the treatment. Closed squares indicate that after the treatment it drastically changed, to the state consisting of a transparent supernatant and irreversibly coagulated particles.

Figure 6 shows the states of Emulgen 930 emulsifier aqueous solutions at various pH and temperatures. Open squares indicate that the solution was transparent, whereas closed squares indicate that the solutions became turbid and a part of emulsifier separated out. The latter became again a transparent homogeneous solution with decreasing the temperature. In comparison with Figs. 5 and 6, it seems that the coagulation of P(S-MAA) (90/10, molar ratio) particles in Fig. 5 is based on that the Emulgen 930 emulsifier molecules in the medium attains cloud point which is a typical character of a nonionic emulsifier aqueous solution. In other words, this suggests that almost Emulgen 930 molecules are not absorbed into the alkali-swollen P(S-MAA) (90/10, molar ratio) particles, but remain in the medium because of the high hydrophilicity of the ionized P(S-MAA) (90/10, molar ratio) molecules. In order to confirm this, similar experiment was carried out using PS emulsion in which most of the emulsifier molecules should exist in the medium.

Table 3 shows the states of the PS emulsions at room temperature after the treatment at initial pH 13.0 for 1 h at 120 °C in the presence of Emulgen 930 and of Emulgen 930 aqueous solutions at initial pH 13.0 and at 120 °C. The PS particles coagulated under the condition that Emulgen 930 aqueous solutions attained the cloud point. In these ways, the reason why nanoparticles were not produced from particles having MAA contents above 10 mol% seems to be based on that Emulgen 930 emulsifier molecules are not adsorbed onto the polymer molecules enough to "dissolve" them, though the particles swell enough to absorb them.

From the above results it is concluded that P(S-MAA) nanoparticles having high *Tg* can be prepared by the particle dissolution method from submicron-sized P(S-MAA) particles having the optimum MAA contents. The obtained data supported the mechanism of production of polymer nanoparticles by the method which we proposed [9].

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