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SHORT COMMUNICATION

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Behavior of nonionic emulsifier molecules on the preparation of nanoparticles from submicron-sized ionized styrene–methacrylic acid copolymer particles by the particle dissolution method

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Abstract Submicron-sized styrene–methacrylic acid copolymer (92/8 molar ratio) particles dissolved in the presence of polyoxyethylene nonylphenylether nonionic emulsifier under alkaline conditions at 90 °C, resulting in nanoparticles with diameters of about 30 nm. In order to clarify the role of the emulsifier molecules in the dissolution process, ^{1}H NMR measurements were carried out. As the particles swelled, the NMR integrals due to the emulsifier decreased markedly. This indicates that the emulsifier molecules permeated into the inside of the alkali-swelling particles and were adsorbed on the polymer molecules, which supports the formation mechanism of nanoparticles by the particle dissolution method proposed in a previous article.

Key words Carboxyl group · Emulsion polymerization · Nanoparticles · Microsphere · Emulsifier

Introduction

We found 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 at 40 °C, resulting in nanoparticles having a diameter of about 30 nm [1]. Hereafter, this method is called the "particle dissolution method".

Some effects on the dissolution of submicron-sized P(S-BA-MAA) particles were examined in detail and a dissolution mechanism was proposed [2]. In order to prepare nonhydrolyzable nanosized polymer particles having high glass-transition temperatures (T_g), which may be more useful in their applications than those having low Tg, submicron-sized P(S-MAA) particles having Tg above 100 °C were treated by the particle dissolution method [3]. As a result, P(S-MAA) nanoparticles were prepared in a similar way, and the effects of the MAA content and the molecular weight of P(S-MAA) on the dissolution behavior were clarified [4]. The preparation of the P(S-MAA) nanoparticles seems to proceed as shown in Fig. 1.

1. The submicron-sized carboxylated particles swell under alkali treatment conditions.
2. Nonionic emulsifier molecules permeate into the particles together with water and interact with the polymer molecules.
3. Several polymer molecules stabilized with the emulsifier molecules are gradually stripped from the surface layer, resulting in nanoparticles.

Processes 1 and 3 were clarified by diameter measurements. Process 2 must be a key factor for the dissolution process, however this point has not been made clear.

In this article, in order to clarify the behavior of the nonionic emulsifier molecules in the alkali-swelling process of P(S-MAA) particles, ^{1}H NMR measurements were carried out.

Experimental

Materials

S and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade potassium persulfate was purified by recrystallization from distilled water. Analytical grade potassium hydroxide, octyl mercaptan, 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) and D_2O were used without further purification. Commercial grade polyoxyethylene nonylphenylether nonionic emulsifier (Emulgen 900 series; Kao Corp., Tokyo, Japan) was used without further purification. Deionized water was distilled.

Preparation of polymer emulsions

PS and P(S-MAA) (92/8 molar ratio) emulsions were prepared by emulsion polymerization under the conditions listed in Table 1. The PS polymerization was carried in the absence of emulsifier to adjust the diameter of the PS particles to that of the P(S-MAA) particles. The conversions of both systems were measured by gravimetric methods to be over 95%; therefore, the molar ratio of S/MAA in the P(S-MAA) particles was calculated to be 92/8 from the polymerization recipe.

Characterization of particles

The particle diameter was measured at room temperature by dynamic light-scattering spectroscopy (Otsuka Electronics DLS-700, Kyoto, Japan) at 90° of the light-scattering angle. The molecular weight was measured by gel permeation chromatography (GPC). Calibration was performed with PS standards using tetrahydrofuran as the eluant.

Alkali treatment in the presence of nonionic emulsifier

The original P(S-MAA) or PS emulsion was mixed with a nonionic emulsifier aqueous solution in a small glass vessel. The concentrations of the particle, emulsifier and KOH were adjusted to 25.0 g/l, 10.0 g/l and 0.12 M, respectively. The mixture 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 90 °C for different times. After the treatment, the vessels were allowed to cool in air.

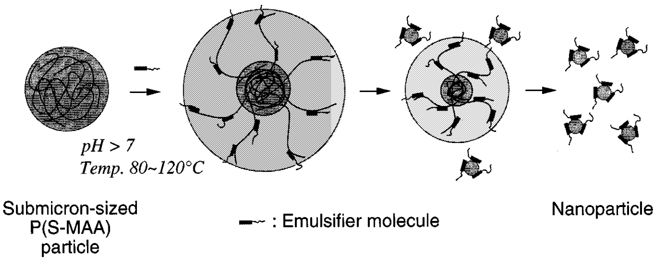

Fig. 1 Formation mechanism of nanoparticles from the submicron-sized styrene–methacrylic acid copolymer [*P*(*S-MAA*)] (92/8 molar ratio) particles in the presence of nonionic emulsifier under alkaline conditions

Table 1 Recipes of emulsion polymerizations for preparations of polystyrene (*PS*) and styrene–methacrylic acid copolymer [*P*(*S-MAA*)] (92/8 molar ratio) particles[a]

Ingredients		PS	P(S-MAA)
S	(g)	60.0	56.0
MAA	(g)		4.0
Potassium persulfate	(g)	0.99	0.24[b]
Emulgen 911	(g)		3.3
Water	(g)	1000	540
n-Octyl mercaptan	(g)		0.6

[a] N_2; 70 °C; 48 h for PS or 24 h for P(S-MAA); stirring rate, 120 rpm

[b] First, potassium persulfate (0.04 g) was added and 3 h later the remains (0.20 g) was added as an aqueous solution

NMR measurements

The mixtures of the P(S-MAA) emulsions or Emulgen 930 aqueous solution with the same volume of D_2O including 0.1 wt% DSS as a standard were poured into 5-mm NMR tubes.

^{1}H NMR spectra were obtained with a Bruker DPX250 NMR spectrometer operating at 250 MHz with 200 scans at 26 °C. Chemical shifts were obtained relative to the methyl groups of DSS. The normalized NMR integrals were determined by normalizing the integral intensity of each peak due to the emulsifier to the signal intensity from the methyl groups of DSS at 0 ppm.

Results and discussion

Molecular-weight distributions of PS and P(S-MAA) measured by GPC are shown in Fig. 2. M_w and M_w/M_n were 3.7×10^5 and 13.2 for PS, and 3.3×10^5 and 30.5 for P(S-MAA), respectively. PS and P(S-MAA) had similar molecular weights.

A ^{1}H NMR spectrum of Emulgen 930 measured at 26 °C is shown in Fig. 3. The resonances appeared around 1, 3.7 and 7 ppm, which corresponded to the protons of the alkyl group, the polyoxyethylene chain and the aryl group respectively. The relationships between the concentration of Emulgen 930 and the three kinds of normalized NMR integrals are shown in Fig. 4. Good linear relationships were established in all cases.

Figure 5 shows the particle size distributions of P(S-MAA) and PS particles treated at 90 °C for 1 h in the presence of Emulgen 930 at a KOH concentration of 0.12 M at which the pH value of the mixture is kept at 13 even if all carboxyl groups in the P(S-MAA) particles are neutralized. By this treatment, the diameter of the P(S-MAA) particles clearly increased by about 100 nm

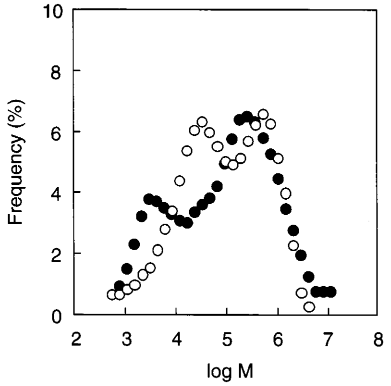

Fig. 2 Molecular-weight distributions of polystyrene (*PS*) (○) and P(S-MAA) (●) prepared under the conditions listed in Table 1

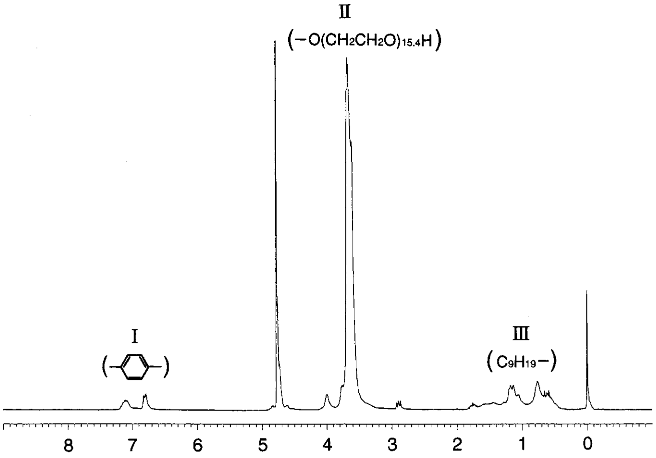

Fig. 3 ^{1}H NMR spectrum of Emulgen 930 (10.0 g/l) in D_2O measured at 26 °C

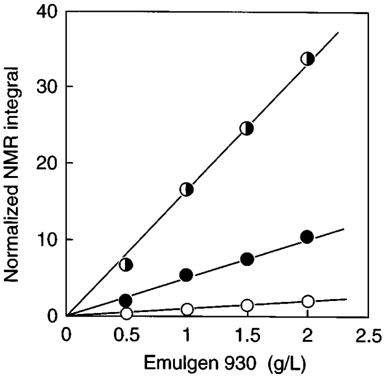

Fig. 4 Relationships between the concentration and the normalized NMR integrals due to the aryl group (○), the polyoxyethylene chain (◑), and the alkyl group (●) of Emulgen 930 in 0.12 M KOH aqueous solution measured at 26 °C

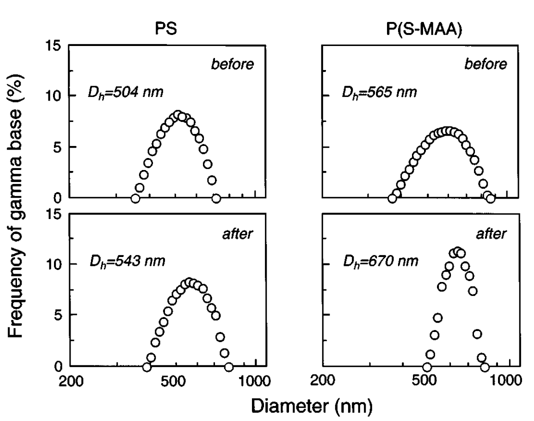

Fig. 5 Particle size distributions measured by dynamic light-scattering spectroscopy of PS and P(S-MAA) (92/8 molar ratio) emulsions (25.0 g/l) containing Emulgen 930 (10.0 g/l) and KOH (0.12 M) before and after the treatment at 90 °C for 1 h; D_h, hydrodynamic diameter

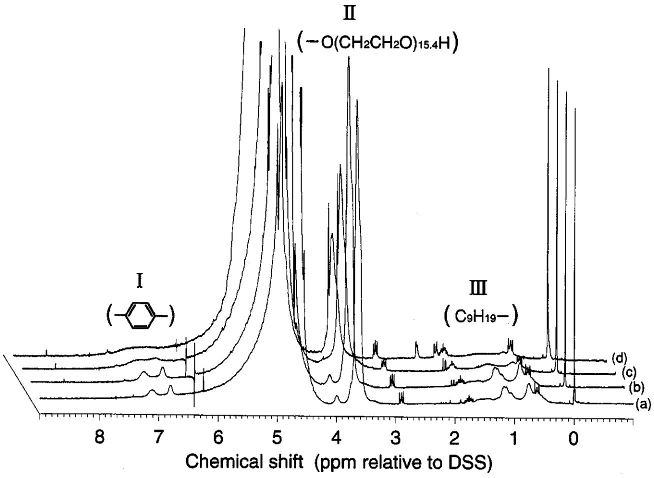

Fig. 6 ^{1}H NMR spectra of P(S-MAA) (92/8 molar ratio) emulsions (25.0 g/l) containing Emulgen 930 (10.0 g/l) measured at 26 °C: KOH: *a*, Emulgen free; *b*, *c* and *d*, Emulgen 930 present (0.12 M). Treatment time at 90 °C: *a*, *b*, 0; *c*, 15 min; *d*, 1 week

in comparison with that of the PS particles. This indicates that the P(S-MAA) particles swelled under the experimental conditions. As already described in detail, the P(S-MAA) particles used in this experiment dissolved at high Emulgen 930 concentrations, resulting in nanoparticles. Because the objective of this research is to clarify the permeation of the emulsifier molecules into the particles, the experiment was carried out at an emulsifier concentration which was too low for the preparation of nanoparticles.

Figure 6 shows ^{1}H NMR spectra, measured at 26 °C, of P(S-MAA) emulsions before and after the treatment at 90 °C in the presence of Emulgen 930 (10.0 g/l) and KOH (0.12 M). As the treatment time increased, all the ^{1}H NMR signals due to the emulsifier molecules became extremely broad and weak. The normalized NMR integrals calculated from the ^{1}H NMR spectra in Fig. 6 are shown in Fig. 7. The integrals of these peaks decreased clearly with the alkali treatment time.

Table 2 shows the decreases in the normalized NMR integrals due to Emulgen 930 in PS or P(S-MAA) emulsions with alkali treatment time at 90 °C. In the case of the PS emulsion, in which the PS particles did not swell under alkaline conditions, the NMR integrals were not changed by the treatment, whereas in the case of the P(S-MAA) emulsion, in which the P(S-MAA) particles swelled under the alkaline conditions, the integrals decreased with alkali treatment time, and were about half the original values after 1 week.

Figure 8 shows the variations of the normalized NMR integrals of the emulsifier in P(S-MAA) emulsions

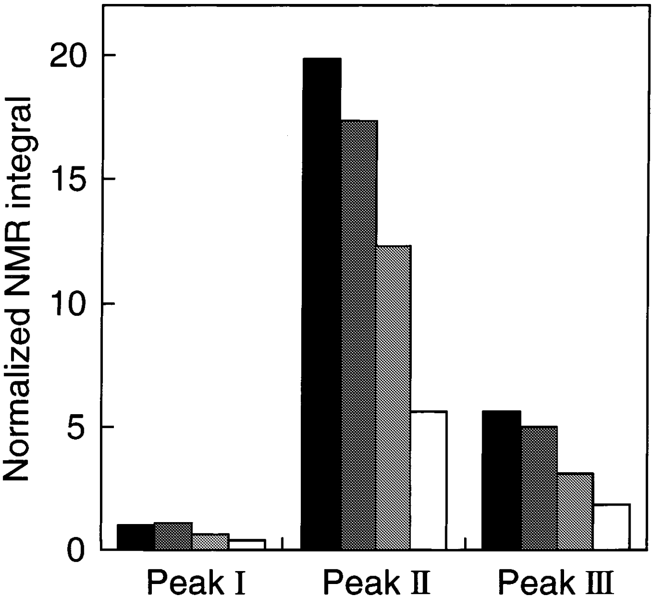

Fig. 7 Variations of the normalized NMR integrals (peak I, aryl group; peak II, polyoxyethylene chain; peak III, alkyl group) of Emulgen 930 (10.0 g/l) measured at 26 °C in the P(S-MAA) (92/8 molar ratio) emulsions (25.0 g/l): KOH: ■, Emulgen 930 free;▨ ░ □, Emulgen 930 present (0.12 M). Treatment time at 90 °C: ■ ▨, 0; ░, 15 min; □, 1 week

Table 2 Percentages of survival of normalized NMR integrals due to Emulgen 930 (10.0 g/l) in PS and P(S-MMA) (92/8 molar ratio) emulsions (25.0 g/l) containing KOH (0.12 M) as a function of treatment time at 90 °C

	Treatment time	PS	P(S-MAA)
Peak I (aryl group)	0	~100	~100
	15 min		76
	1 week	~100	56[a]
Peak II (polyoryethylene chain)	0	~100	~100
	15 min		79
	1 week	~100	42[a]
Peak III (alkyl group)	0	~100	~100
	15 min		66
	1 week	~100	45[a]

[a] NMR measurements were carried out for the supernatant separated from the coagulated emulsion

before the heat treatment as a function of the P(S-MAA) solid content. There were no changes in the integrals in the range of the P(S-MAA) solid content. This indicates that the marked decrease in the integrals shown in Fig. 7 is based not on the total surface area of the P(S-MAA) particles increasing about 1.5 times by particle swelling but on the fact that the emulsifiers permeate into the inside of the swollen P(S-MAA) particles and are adsorbed on P(S-MAA) molecules.

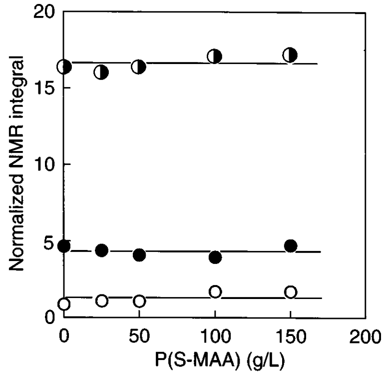

Fig. 8 Variations of the normalized NMR integrals due to the aryl group (○), the polyoxyethylene chain (◑) and the alkyl group (●) of Emulgen 930 (10.0 g/l) measured at 26 °C in the P(S-MAA) (92/8 molar ratio) emulsions containing KOH (0.12 M) as a function of the concentration of added P(S-MAA) particles

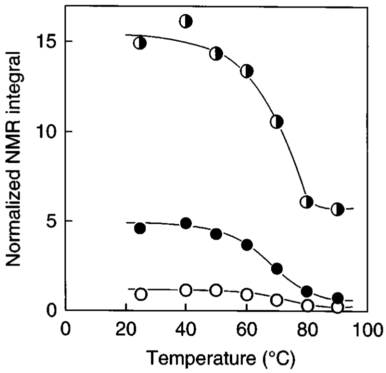

Fig. 9 Variations of the normalized NMR integrals (○, aryl group; ◑, polyoxyethylene chain; ●, alkyl group) of Emulgen 930 (10.0 g/l) measured at 26 °C in the P(S-MAA) (92/8 molar ratio) emulsion (25.0 g/l) containing KOH (0.12 M) as a function of treatment temperature for 1 h

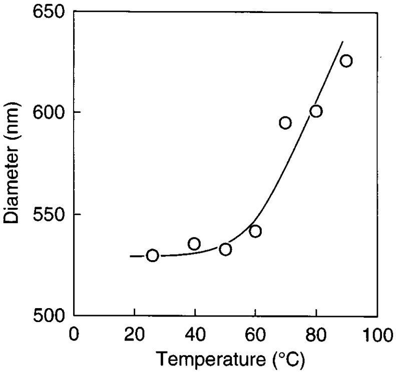

Fig. 10 Variation of the weight-average diameter measured by dynamic light-scattering spectroscopy of the P(S-MAA) (92/8 molar ratio) (25.0 g/l) emulsion containing Emulgen 930 (10.0 g/l) and KOH (0.12 M) as a function of treatment temperature for 1 h

The variations of the normalized NMR integrals of the emulsifier in the P(S-MAA) emulsion and the diameter of the particles as a function of alkali treatment temperature are shown in Figs. 9 and 10, respectively. In Fig. 9, the integrals markedly decrease above 60 °C. In Fig. 10, the diameter of the P(S-MAA) particles markedly increases above 60 °C.

From our results, it is clear that Emulgen 930 molecules permeate into the alkali-swollen P(S-MAA) particles and are adsorbed on P(S-MAA) molecules. This strongly supports the formation mechanism of nanoparticles by the "particle dissolution method" proposed in a previous article [4].

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