

Effect of Molecular Weight on Preparation of Nanoparticles by Particle Dissolution Method from Submicron-Sized Ionized Styrene–Methacrylic Acid Copolymer Particles in Nonionic Emulsifier Solution

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ABSTRACT: Styrene–methacrylic acid copolymer [P(S-MAA)] (92/8, molar ratio) nanoparticles were prepared by a dissolution of submicron-sized P(S-MAA) particles with various molecular weights in a polyoxyethylene nonylphenylether nonionic emulsifier aqueous solution at pH 13.0 and above 90°C. The latter particles were produced by emulsion copolymerization in the presence of various concentrations of *n*-octyl mercaptan. The effect of molecular weight on the dissolution behavior was examined at various conditions and using various kinds of the nonionic emulsifier. It was clarified that a decrease in the molecular weight led to the production of the nanoparticles at mild treatment conditions. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1461–1464, 1997

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 and 40°C. The result was nanoparticles having a diameter of about 30 nm.¹ Hereafter, this method is called the particle dissolution method.

There are similar reports^{2,3} that water-insoluble poly(vinyl 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 that show no effect and cationic ones that show only a

very small effect. The PVAc particles dissolved in the presence of the anionic emulsifier solutions of concentrations corresponding to about 3 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 that 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.

Some effects on the dissolution of submicron-sized P(S-BA-MAA) particles were examined in detail and a dissolution mechanism was proposed.⁴ The particles used in these experiments contain a hydrolyzable BA component, which was not the reason why the particles dissolved under the above conditions; its glass transition temperature (T_g) is 34°C. Polymer nanoparticles having high T_g may be more useful in their applications than that having low T_g . To prepare nonhydrolyz-

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Table I Recipes of Emulsion Polymerization for Preparation of P(S-MAA) (92/8, Molar Ratio) Particles Having Various Molecular Weights

S (g)	56.0	56.0	56.0	56.0
MAA (g)	4.0	4.0	4.0	4.0
KPS (g)	0.24	0.24 ^a	0.24 ^a	0.24 ^a
Emulgen 911 (g)	3.3	3.3	3.3	3.3
Water (g)	540	540 ^a	540 ^a	540 ^a
<i>n</i> -Octyl mercaptan (g)	0	0.15	0.6	1.2
M_w^b ($\times 10^5$)	6.4	5.9	3.3	2.2
D_w^c (nm)	422	637	569	308
D_w/D_n^c	1.07	1.48	1.01	1.33

Reaction was carried out in N_2 at 70°C for 24 h; stirring rate, 120 rpm. S, styrene; MAA, methacrylic acid; KPS, potassium persulfate; Emulgen 911, polyoxyethylene nonylphenylether nonionic emulsifier.

^a First 0.04 g of initiator was added, and 3 h after 20.2 g of initiator aqueous solution dissolving 0.20 g of the initiator was added.

^b Measured by gel permeation chromatography.

^c Measured by dynamic light-scattering spectroscopy.

able nano-sized polymer particles having high T_g in previous research,⁵ submicron-sized styrene–methacrylic acid copolymer [P(S-MAA)] particles with a T_g above 100°C and were treated by the particle dissolution method. The effect of the MAA content on the dissolution behavior was clarified.

This article will discuss the effect of the molecular weight of P(S-MAA) on the dissolution behavior.

EXPERIMENTAL

Materials

Styrene (S) and 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 and octyl mercaptan were used without further purification.

A 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

P(S-MAA) (92/8, molar ratio) emulsions having various molecular weights were prepared by emulsion copolymerization of S and MAA at 70°C for 24 h under the conditions listed in Table I. Because the conversions in all systems were over 95%, which were measured by gravimetric measurement, the molar ratios of P(S-MAA) were calculated from the polymerization recipes. The mo-

lecular weight was controlled by the amount of *n*-octyl mercaptan as a chain transfer agent in the reaction system and was measured by gel permeation chromatography. Calibration was performed using polystyrene standards and tetrahydrofuran as the eluent.

Measurement of Particle Diameter

Particle diameter was measured at room temperature by dynamic light-scattering spectroscopy

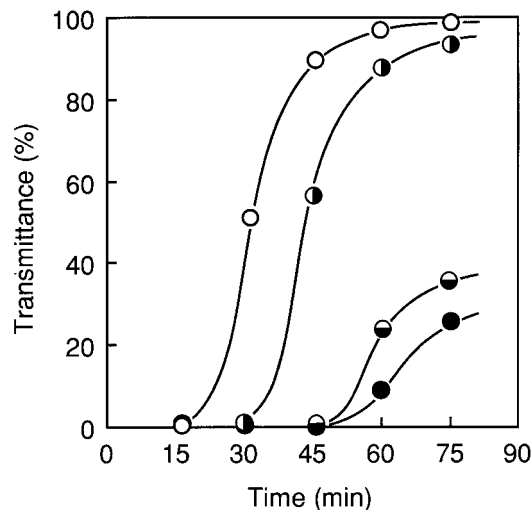


Figure 1 Increases of transmittances (incident wavelength, 850 nm) of P(S-MAA) (92/8, molar ratio) emulsions (2.2 g/L) with various M_w with the treatment time at 90°C at an initial pH of 13.0 in the presence of Emulgen 930 (8.8 g/L). M_w : (○) 2.2×10^5 ; (●) 3.3×10^5 ; (◐) 5.9×10^5 ; (●) 6.4×10^5 .

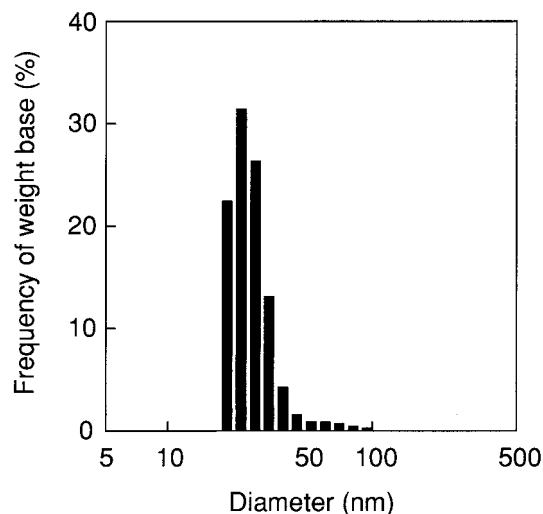


Figure 2 Particle size distribution measured by dynamic light-scattering spectroscopy of P(S-MAA) (92/8, molar ratio) emulsion (M_w , 6.4×10^5) (2.2 g/L) treated in the presence of Emulgen 930 (8.8 g/L) at an initial pH of 13.0 for 1 h at 120°C.

(Otsuka Electronics DLS-700, Kyoto, Japan) at 90° of the light-scattering angle.

Alkali Treatment in Presence of Nonionic Emulsifier

Each original P(S-MAA) emulsion and each nonionic emulsifier aqueous solution was mixed in a small glass vessel. The pH value was adjusted

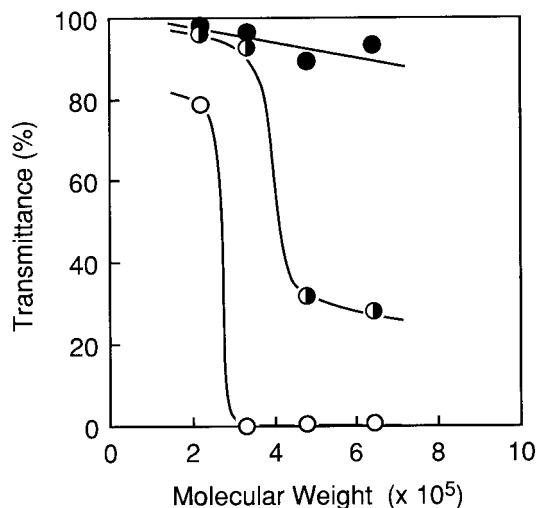


Figure 3 Relationships between the molecular weights and transmittances (incident wavelength, 850 nm) of P(S-MAA) (92/8, molar ratio) emulsions (2.2 g/L) treated in the presence of Emulgen 930 (8.8 g/L) at an initial pH of 13.0 for 1 h at various temperatures: (○) 80°C; (◐) 90°C; (●) 100°C.

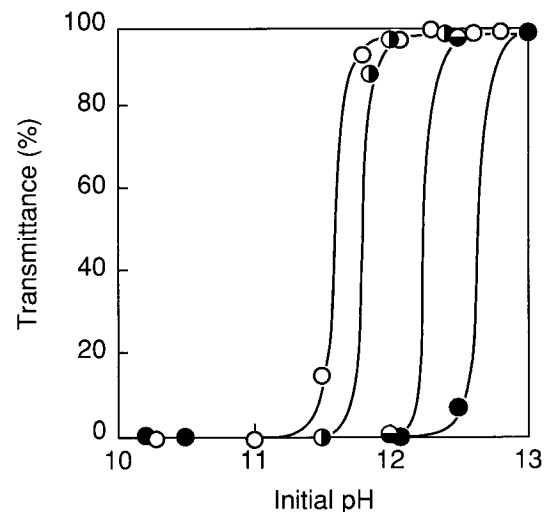


Figure 4 Relationships between the initial pH and transmittances (incident wavelength, 850 nm) of P(S-MAA) (92/8, molar ratio) emulsions (2.2 g/L) with various M_w and treated in the presence of Emulgen 930 (8.8 g/L) for 1 h at 120°C. M_w : (○) 2.2×10^5 ; (◐) 3.3×10^5 ; (◑) 5.9×10^5 ; (●) 6.4×10^5 .

with 1N 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 that 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 vessels were immediately cooled to about 0°C by dipping into ice-cold water. When alkali treatments were carried out for a certain time they were cooled in air. The degree of dissolution of the particles was estimated by measuring the transmittance of the treated emulsion at a wavelength of 850 nm using a spectrophotometer (Hitachi Model 100-50, Tokyo, Japan) with a glass cell of 1-cm thickness.

RESULTS AND DISCUSSION

Figure 1 shows the increases of transmittances of P(S-MAA) emulsions having various molecular weights with the treatment time at 90°C and a pH of 13.0 in the presence of nonionic Emulgen 930 of which the hydrophile-liphophile balance (HLB) was 15.1. For 45 min the transmittances were about 0% for the two higher weight-average molecular weight (M_w : 6.4×10^5 , 5.9×10^5) particles, about 60% for the 3.3×10^5 , and about 90% for the lowest one (2.2×10^5). The last emulsion was transparent.

Figure 2 shows a size distribution of the P(S-

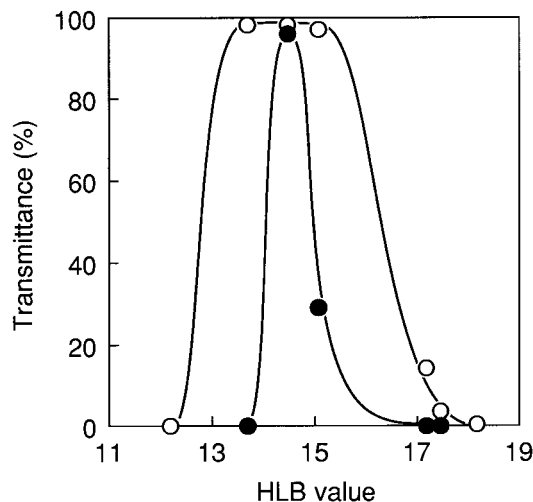


Figure 5 Relationships between the HLB value of Emulgen emulsifiers and the transmittances (incident wavelength, 850 nm) of P(S-MAA) (92/8, molar ratio) emulsion (2.2 g/L) treated at an initial pH of 13.0 for 1 h in the presence of Emulgen emulsifiers (8.8 g/L) at 90°C. M_w : (○) 2.2×10^5 ; (●) 6.4×10^5 .

MAA) particles (M_w , 6.4×10^5) treated at pH 13.0 for 1 h at 120°C. The transmittance of the treated emulsion was 98.3%. The weight-average diameter (D_w) was about 26 nm.

Figure 3 shows the relationships between the molecular weight and the transmittances of the P(S-MAA) (92/8, molar ratio) emulsions with various molecular weights after the treatments at 80–100°C for 1 h in the presence of Emulgen 930 emulsifier. At 80°C the transmittances were about 0% for the three higher molecular weight particles, but it was about 80% for the lowest molecular weight one. At 90°C the transmittances were less than 40% for the two higher molecular weight particles, but they were above 90% for the two lower ones. At 100°C they were above 90% for all the emulsions, and the treatment time at which they attained 90% decreased with a decrease in the molecular weight (figure omitted). These results indicate that the P(S-MAA) particles of lower molecular weight tend to dissolve

at lower treatment temperature and with shorter treatment time.

Figure 4 shows the relationships between the initial pH and the transmittances of the P(S-MAA) emulsions having various molecular weights after the treatments at 120°C for 1 h in the presence of Emulgen 930. The minimum pH value at which the transmittance reached more than 90% decreased from 13.0 to 11.8 with the decrease in the molecular weight.

Figure 5 shows the relationships between the HLB value of Emulgen 900 series emulsifiers and the transmittances of the P(S-MAA) emulsions treated at pH 13.0 for 1 h at 90°C. The HLB region at which the transmittance was above 90% was somewhat broader for the lowest molecular weight particles than for the highest ones.

From these results it is clear that nanoparticles can be prepared from submicron-sized particles of lower molecular weight P(S-MAA) by the particle dissolution method at more mild conditions. This seems to be based on the high alkali swelling of the low molecular weight particles because of high solubility and high mobility, which is a trigger for the preparation of nanoparticles. The obtained data support the mechanism of preparation of polymer nanoparticles by the method that we proposed.⁴

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