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SHORT COMMUNICATION

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Effect of molecular weight on the production of multi-hollow polymer particles by the alkali/cooling method

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Abstract The effects of molecular weight, particle diameter and cooling condition on the formation of multi-hollow structure formed within submicron-sized styrene-methacrylic acid copolymer particles by the "alkali/cooling method" proposed by the authors were examined and the formation mechanism was proposed. The original particles were produced by emulsion copolymerization in the presence of *n*-octyl mercaptan as a chain transfer agent.

Key words Multi-hollow particle – emulsion polymerization – morphology – carboxyl group – alkali swelling

Introduction

Recently, we found that submicron-sized styrene-butyl acrylate-methacrylic acid terpolymer particles produced by emulsion copolymerization were changed to those having many hollows therein by stepwise treatments with alkali and acid [1]. We named it the stepwise alkali/acid method. In the following articles, the effects of some factors in the alkali [2, 3] and acid [4] treatment processes on the formation of multi-hollow structure were examined in detail. Moreover, in order to produce multi-hollow polymer particles having high glass transition temperature (*Tg*), styrene-methacrylic acid copolymer (P(S-MAA)) particles were treated by the stepwise alkali/acid method [5]. In this experiment, it was found that P(S-MAA) particles having a certain methacrylic acid (MAA) content were changed to those having multi-hollow structure by alkali treatment and subsequent cooling, which was named the alkali/cooling method [6].

In this article, the effects of molecular weight, particle diameter and the cooling condition on the formation of multi-hollow structure will be reported.

Experimental

Materials

Styrene (S) and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate was purified by recrystallization. Analytical grade potassium hydroxide and *n*-octyl mercaptan were used without further purification. Commercial grade nonionic polyoxyethylene nonylphenylether emulsifier (Emulgen 911, Kao Atlas Co.) was used without further purification. Deionized water was distilled.

Preparation of polymer emulsion particles

P(S-MAA)(MAA content, 10 mol%) particles having various molecular weights were prepared by emulsion copolymerizations at 70 °C under the conditions listed in Table 1. In all emulsions, the conversions were over 95% by gravimetric measurement. The molecular weight was controlled by the amount of *n*-octyl mercaptan as a chain transfer agent in the reaction systems (Nos. 1 ~ 4) and measured by gel permeation chromatography using tetrahydrofuran as the eluent. Calibration was performed with polystyrene standards. Particle size was controlled by changing initiator addition method.

Electron microscopy

A JEOL JEM-200CX electron microscope was used for transmission electron microscopic (TEM) observation. Each emulsion was diluted down about 50 ppm, and a drop was placed onto a Formvar film-coated grid and allowed to dry at room temperature in a desiccator.

Measurement of particle diameter

Weight-average diameter (*Dw*) of original P(S-MAA) particles and alkali/cooling-treated particles were measured by dynamic light-scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan). Each emulsion was diluted down to 10 ppm. The data at the light-scattering angle of 90° were analyzed with the DLS-700 system program.

Alkali/cooling treatment

The original P(S-MAA) emulsion was diluted to 0.5 g/l, and the pH value was adjusted to 12.0 with 1 N KOH aq. solution. This emulsion was placed in a 50 ml-capacity stainless steel pressure-resistant vessel having a polytetrafluoroethylene inner container and the vessel was dipped in oil bath at 150 °C for 24 h. After the treatment, each emulsion was cooled under the various conditions. Hereafter, these treatments will be called the alkali/cooling treatment.

Volume expansion

The expansion of particle volume by the alkali/cooling treatment was calculated from particle diameters measured by DLS before and after the treatment.

Result and discussion

Figure 1 shows a TEM photograph of P(S-MAA) particles, of which the weight-average molecular weight (*Mw*) was 5.9×10^5 prepared under the conditions of No. 1 in Table 1. The insides of the particles were observed to be homogeneous. Other P(S-MAA) particles having different *Mw* values also had the homogeneous structure (the photographs were omitted).

Figure 2 shows TEM photographs of P(S-MAA) particles having the various *Mw* values after the alkali/cooling treatment in which the emulsions were treated at 150 °C for 24 h at the initial pH value of 12.0 and subsequently

Table 1 Recipes of emulsion polymerization for the preparation of P(S-MAA) (MAA content, 10 mol%) particles having various *Mw* values[a)]

Sample No.		1	2	3	4	5
S	(g)	55.0	55.0	55.0	55.0	55.0
MAA	(g)	5.0	5.0	5.0	5.0	5.0
KPS	(g)	0.24	0.24[b)]	0.24[b)]	0.24[b)]	0.24
Emulgen 911	(g)	4.0	4.0	4.0	4.0	4.0
Water	(g)	540	540[b)]	540[b)]	540[b)]	540
n-Octyl mercaptan	(g)	0	0.06	0.3	0.6	0.6
Mw[c)]	($\times 10^5$)	5.9	4.2	1.2	0.4	2.6
Dw[d)]	(nm)	438	615	593	481	186

[a)] N_2; 70 °C; 24 h; stirring rate, 120 rpm.
[b)] First, 0.04 g of initiator was added and 20.2 g of aq. solution dissolving 0.20 g of the initiator was added after 3 h.
[c)] Weight-average molecular weight measured by gel permeation chromatography.
[d)] Weight-average diameter measured by dynamic light-scattering spectroscopy.
Abbreviations: S, styrene; MAA, methacrylic acid; KPS, potassium persulfate; Emulgen 911, polyoxyethylene nonylphenylether nonionic emulsifier.

cooled in the room temperature. The particle morphology was drastically changed with the difference of *Mw*.

Figure 3 shows the relationship between the *Mw* values and the volume expansions by the alkali/cooling treatment. An increase in the expansion means an increase in the total volume of hollows inside the particle. The volume expansion had a maximum value in the *Mw* range. This seems to be based on the fact that as the *Mw* decreases, the alkali swelling of the particles increases, but the fixation ability of the polymer molecules decreases, as described as follows. The low molecular weight polymer should have a higher mobility than the high molecular weight one at the same conditions. The higher mobility leads the particles to the higher swelling state in the alkali treatment, but the alkali-swollen particles will shrink more in the cooling treatment. In the cooling process in which the temperature was gradually decreased from 150 °C to room temperature, the copolymer molecules containing "soluble" segments having ionized carboxyl groups in the swollen particles are fixed to the "solid" state at the glass transition temperature in the alkali swelling state.

Figure 4 shows the relationships between the cooling conditions and the volume expansions. In the case of the particles consisting of higher molecular weight polymers, the volume expansion was not affected by the cooling conditions, whereas in the case of the particles consisting of lower molecular weight polymers, it increased with

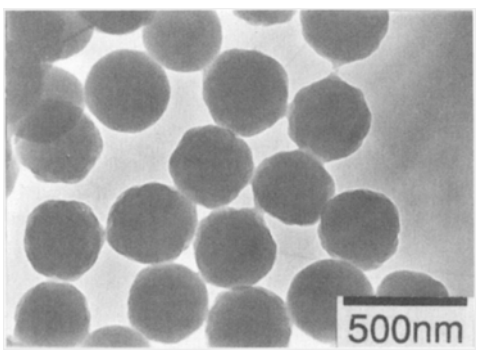

Fig. 1 TEM photograph of P(S-MAA) particles (No. 1 in Table 1). *Mw*: 5.9×10^5

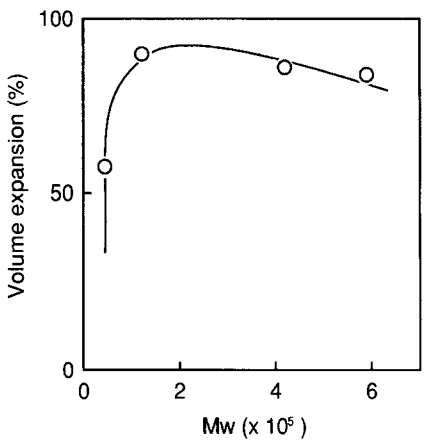

Fig. 3 Relationship between *Mw* and the volume expansion of P(S-MAA) particles before and after the treatment at initial pH value of 12.0 for 24 h at 150 °C, subsequently cooled in air

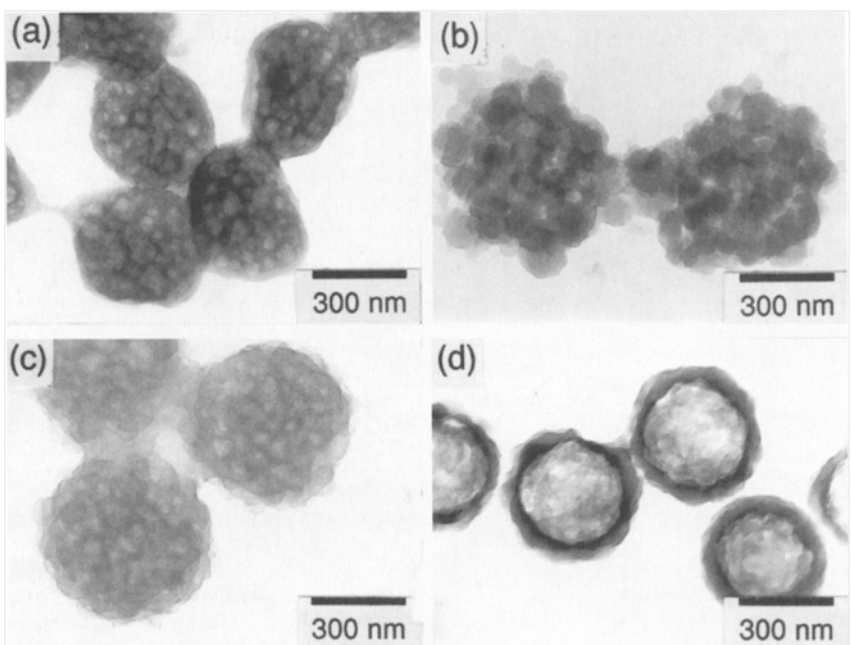

Fig. 2 TEM photographs of P(S-MAA) particles having various *Mw* treated at initial pH value of 12.0 for 24 h at 150 °C. *Mw* ($\times 10^5$): (a) 0.4; (b) 1.2; (c) 4.2; (d) 5.9

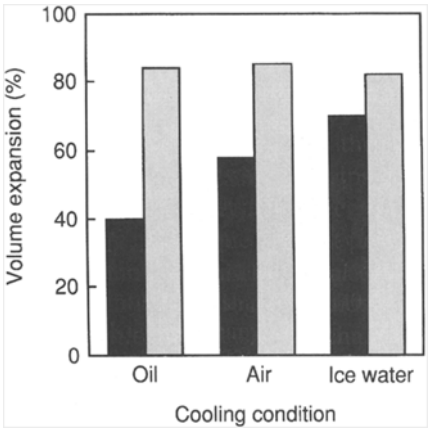

Fig. 4 Relationships between the cooling condition and the volume expansion of P(S-MAA) particles treated at initial pH value of 12.0 for 24 h at 150 °C, subsequently cooled. *Mw*: (■) 0.4×10^5; (□) 5.9×10^5

increasing of the cooling rate. These results support the above explanation.

Figure 5 shows a TEM photograph of P(S-MAA) particles (No. 4 in Table 1) (*Mw*, 2.6×10^5) after the same alkali/cooling treatment as shown in Fig. 2. *Dw* of the original particles before the treatment was 186 nm. The treated particles were observed to be homogeneous. On the other hand, already as shown in Fig. 2(b), particles (No. 3 in Table 1) which had similar *Mw* (1.2×10^5) and larger *Dw* (593 nm), became multi-hollow ones by the treatment. These suggest that in the case of smaller original particles, the alkali-swollen particles shrink more homogeneously, because the temperature in the cooling process transmits rapidly from the particle surface to the inside.

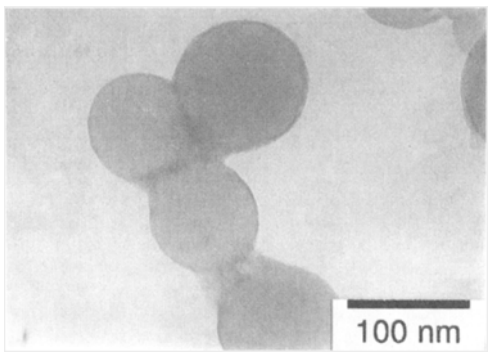

Fig. 5 TEM photograph of P(S-MAA) particles (No. 5 in Table 1) treated at initial pH value of 12.0 for 24 h at 150 °C, subsequently cooled in air. *Mw*, 2.6×10^5; Dw, 186 nm

From these results, we propose the formation mechanism of multi-hollow particles by alkali/cooling method as follows. First the carboxylic particles swell in alkali condition at the higher temperature than *Tg*. Subsequently, in the cooling process, polymer molecules containing "soluble" segments having ionized carboxyl groups are fixed in the alkali swelling state at the glass transition temperature. The fixation may take place in turn from the particle surface to the inside. This means that the cooling process corresponds to the acid treatment process in the stepwise alkali/acid method [1–5].

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