Introduction

We have been carrying out a series of investigations on the control of the distribution of carboxyl groups in carboxylated polymer particles [1, 2, 3, 4, 5, 6]. In these studies, it was found that multihollow particles were prepared by two-step post-treatments of styrene-butyl acrylate-methacrylic acid terpolymer particles with alkali and acid, which was named the “stepwise alkali/acid method” [7, 8, 9]. Moreover, multihollow styrene-methacrylic acid terpolymer [P(S-MAA)] particles with higher glass transition temperature (Tg) were produced by the stepwise alkali/acid method [10, 11]. In the process of clarifying the formation mechanism of the multihollow structure with 1H NMR, it was assumed that nonionic emulsifier (used in the emulsion polymerization) was eluted from the inside of the particles to an aqueous medium in the alkali treatment process. The results indicate that the nonionic emulsifier was included inside the polymer particles during the emulsion polymerization process.

In a general emulsion polymerization, emulsifiers play significant roles in that they form micelles as the polymerization loci for the nucleation of particles, as well as stabilizing the formed particles. Some specific cases of emulsion polymerization with nonionic emulsifier have been reported. Pirrma et al. observed two constant-rate regions and obtained bimodal particle size distribution in the emulsion polymerization of styrene using (tridecyloxy)poly(ethyleneoxy)ethanol (Emulphogene BC-840) [12]. They suggested that liberation of the nonionic emulsifier from the monomer phase at the end of the interval II was the main reason for the phenomena. Chern et al. reported that emulsion polymerization of styrene using sodium dodecyl sulfate (SDS)/nonylphenol tetracountylethoxylate (NP-40) led to significant deviation from the Smith-Ewart theory [13] at relatively high levels of NP-40 [14, 15].

To our knowledge, there is no detailed information on the inclusion of nonionic emulsifier inside particles produced by emulsion polymerization. Such an inclusion has disadvantages for stabilizing produced particles. On the other hand, if an arbitrary amount of nonionic emulsifier is included inside P(S-MAA) particles, this may positively extend the treatment conditions for the...
preparation of the multihollow particles because they must accelerate the swelling of the particles with water. In these ways, it seems to be important to clarify the phenomenon of the inclusion, not only in the understanding of the emulsion polymerization with nonionic emulsifier but also in the preparation of the multihollow particles.

In this article, the inclusion behavior of nonionic emulsifier inside polymer particles will be clarified in the process of emulsion polymerization of styrene (S) and methacrylic acid (MAA).

**Experimental**

**Materials**

S and MAA were purified by distillation under reduced pressure in a nitrogen atmosphere. Analytical grade potassium persulfate (KPS) (Nacalai Tesque, Kyoto, Japan) was purified by recrystallization. Analytical grade potassium hydroxide, 3-(trimethylsilyl)propionic-2,2,3,3-d4 acid, sodium salt (TSP) (Nacalai Tesque, Kyoto, Japan) and deuterium oxide (D2O) (Nacalai Tesque, Kyoto, Japan) were used without further purification. Commercial grade nonionic polyoxyethylene nonyl phenyl ether nonionic emulsifier with an average of 10.9 ethylene oxides per molecule (Emulgen 911) (Kao, Tokyo, Japan) was used without further purification. Deionized water was distilled.

**Preparation of P(S-MAA) particles**

Original P(S-MAA) (MAA, 10 mol%) particles were produced by emulsion copolymerization and emulsifier-free emulsion copolymerization in a 1-L four-necked round-bottom flask under the conditions listed in Table 1. The conversions were over 95% by gravimetric measurements.

**Electron microscopy**

A JEOL JEM-2010 electron microscope was used for transmission electron microscopic (TEM) observation. Emulsion was diluted to about 50 ppm, and a drop was placed onto a carbon-coated copper grid and allowed to dry at room temperature in a desiccator for a day and under reduced pressure for a day.

**Measurement of particle diameter**

The hydrodynamic diameter of the P(S-MAA) particles was measured by dynamic light scattering (DLS) (Otsuka Electronics DLS-700, Kyoto, Japan) at the light-scattering angle of 90° at room temperature. Emulsion was diluted to 10 ppm.

**1H NMR measurement**

The original P(S-MAA) particles were centrifuged and subsequently dispersed in water five times to eliminate the emulsifiers from the particle surfaces and the medium. The particles were then dried at room temperature in a desiccator and under reduced pressure for a week. The dried particles were redispersed using ultrasonic waves in D2O (pH 13 adjusted with KOH) including 0.1 wt% TSP as an internal standard. The solid content was adjusted to 4.8 wt%. 1H NMR spectra were obtained with a Bruker DPX 250 NMR spectrometer operating at 250 MHz with 128 scans with a repetition decay of 2 s at different temperatures. The measurement was started after 30 min since the temperature was changed. Chemical shifts were obtained relative to the methyl groups of TSP at 0 ppm. The normalized NMR integrals were determined by normalizing the integral intensity of each peak due to the emulsifier to that due to the methyl groups of TSP. The relative intensities of the ethylene oxide protons due to the emulsifier (concentration, 4.0 g/L) were constant regardless of the presence/absence of the KOH and the measurement temperature range of 25 °C to 100 °C. The variations of the relative intensities in both the cases were similar to each other.

**Quantitative analysis of Emulgen 911 in each locus**

**In the media**

Original P(S-MAA) emulsion was centrifuged and the 10 mL supernatant liquid was dried at room temperature in a desiccator until the water disappeared and then under reduced pressure for a week. The dried remains from the supernatant were redispersed in 1 mL D2O including 0.1 wt% TSP as an internal standard. Emulgen 911 concentration was calculated from 1H NMR relative intensity due to ethylene oxide protons of Emulgen 911.

**At the P(S-MAA) particle surface**

First, the occupied area of Emulgen 911 at the particle surface was determined by soap titration for P(S-MAA) (MAA, 10 mol%) emulsion prepared by the emulsifier-free emulsion copolymerization. Surface tension was measured by the du Noüy ring method at 25 ± 2 °C. Next, soap titration was carried out for the original P(S-MAA) emulsions. The amount of Emulgen 911 at the particle surface was calculated from the end point of the titration using the occupied area of Emulgen 911 on P(S-MAA) particle surface and the hydrodynamic diameter of the P(S-MAA) particle measured using DLS.

**Inside the particle**

The amount of Emulgen 911 inside P(S-MAA) (MAA, 10 mol%) particle was calculated by the subtraction of the amount of Emulgen 911 in the medium and on the particle surface from the total amount of Emulgen 911.

**Table 1 Recipes for the preparation of P(S-MAA) (MAA, 10 mol%) emulsion by emulsifier-presenta and emulsifier-freeb emulsion polymerizations**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>No. 1</th>
<th>No. 2</th>
<th>First stagec</th>
<th>Second staged</th>
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</thead>
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<tr>
<td></td>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
<td>(g)</td>
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<tr>
<td>S</td>
<td>55.0</td>
<td>0.92</td>
<td>12.8</td>
<td></td>
</tr>
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<td>MAA</td>
<td>5.0</td>
<td>0.08</td>
<td>1.2</td>
<td></td>
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<tr>
<td>KPS</td>
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<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulgen 911</td>
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<td></td>
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<tr>
<td>Water</td>
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<td>133</td>
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</tr>
</tbody>
</table>

a N2; 70 °C; 24 h; stirring rate 120 rpm
b N2; 70 °C; 16 h; stirring rate 120 rpm
c For 1.2 h
d For 5.3 h

Abbreviations: S: styrene MA: methacrylic acid P (S-MAA): styrene-methacrylic copolymer KPS: potassium persulfate Emulgen 911: polyoxyethylene nonyl phenylether nonionic emulsifier