

Influence of the Kind of Alkali on the Preparation of Multihollow Polymer Particles by the Alkali/Cooling Method

M. OKUBO, M. NAKAMURA, A. ITO

Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Rokko, Nada, Kobe 657, Japan

Received 3 October 1996; accepted 22 October 1996

ABSTRACT: The influence of the kind of alkali (KOH, NH₄OH, ethanolamine) in alkali treatment on the formation of multihollow structure within submicron-sized styrene-methacrylic acid copolymer particles by the alkali/cooling method proposed by the authors was examined. The original particles were produced by emulsion copolymerization. The obtained results indicate that there was no great difference in the preparation of the multihollow particles by the method using the three kinds of alkali and support the formation mechanism of multihollow structure proposed previously. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1947–1951, 1997

Key words: multihollow 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 a related series of articles, the effects of some factors in the alkali^{2,3} and acid⁴ treatment processes on the formation of multihollow structure were examined in detail. Moreover, in order to produce multihollow polymer particles having high glass transition temperature (T_g), styrene-methacrylic acid copolymer [P(S-MAA)] particles were treated by the stepwise alkali/acid method.⁵ In the experiment, it was also found that P(S-MAA) particles having a certain methacrylic acid (MAA) content were changed to

those having multihollow structure by alkali treatment and subsequent cooling, which was named the alkali/cooling method,⁶ and the effects of some factors in original particles, such as molecular weights and particle diameter. In the series of investigations on the preparation of multihollow particles, KOH has been used in the alkali treatment as the first step in both methods described above.

In this article, the influence of the kind of alkali on the formation of multihollow structure will be examined using volatile NH₄OH and ethanolamine, which may have an advantage in industrial applications, compared with KOH.

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 recrystalliza-

Correspondence to: M. Okubo. Address e-mail to okubo@appchem.chme.kobe-u.ac.jp.

This article is part CLXIV of the series "Studies on Suspension and Emulsion."

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Table I Recipe of Emulsion Polymerization for the Preparation of P(S-MAA) (MAA Content, 10 Mol %) Emulsion^a

Ingredient ^b		
S	(g)	55.0
MAA	(g)	5.0
KPS	(g)	0.24
Emulgen 911	(g)	4.0
Water	(g)	540

^a N₂; 70°C; 24 h; stirring rate, 120 rpm.

^b Abbreviations: S, styrene; MAA, methacrylic acid; KPS, potassium persulfate; Emulgen 911, polyoxyethylene nonyl phenylether nonionic emulsifier.

tion. Analytical grade KOH, NH₄OH, and ethanolamine 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 were prepared by emulsion copolymerizations at 70°C under the conditions listed in Table I. In this emulsion, the conversion was over 95% by gravimetric measurement. The molecular weight was measured by gel permeation chromatography (GPC) using tetrahydrofuran as the eluent. Calibration was performed with polystyrene standards.

Electron Microscopy

A JEOL JEM-200CX electron microscope was used for transmission electron microscopic (TEM) observation. Each emulsion was diluted down to about 50 ppm, and a drop was placed onto a Formvar film-coated grid and allowed to dry at room temperature in a desiccator. The inside structure of the particles was estimated from the observation of the ultrathin cross sections. The cross sections of the P(S-MAA) particles before and after the alkali/cooling treatment were prepared as follows. The emulsions were dropped on polyethylene terephthalate films (50 μm of thickness). After drying, the particles on the film were exposed to RuO₄ vapor at room temperature for 30 min in the presence of 1.0% RuO₄ solution and then dipped in epoxy matrix, cured at room temperature for 24 h, and microtomed.

Measurement of Particle Diameter

Hydrodynamic diameter (D_h) 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 degrees 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 each alkali aqueous solution. This emulsion was placed in a 50 mL capacity stainless steel

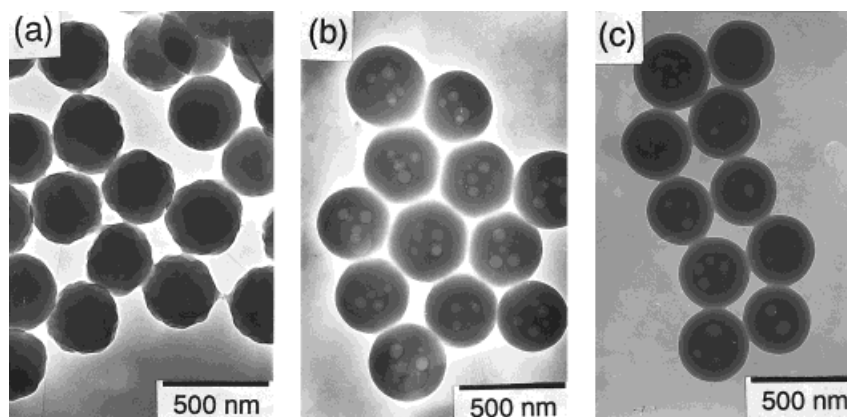


Figure 1 TEM photographs of P(S-MAA) (MAA content, 10 mol %) particles before (a) and after (b) and (c) treated at 150°C for 3 h at initial pH value of 10.5 adjusted with NH₄OH (b) and ethanolamine (c).

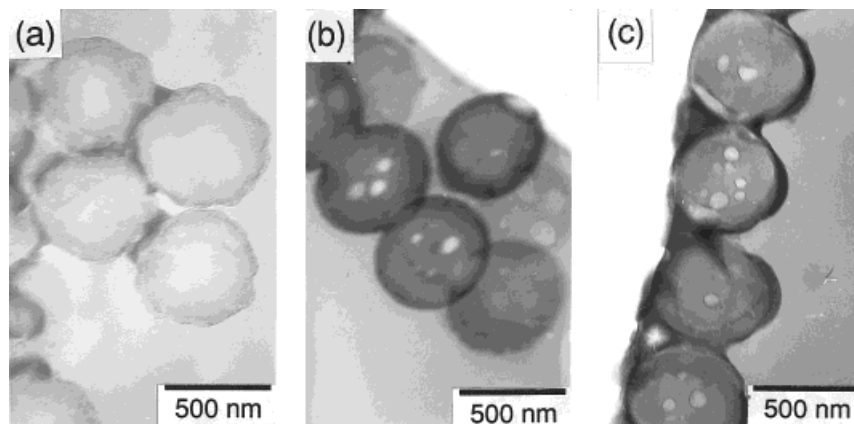


Figure 2 TEM photographs of ultrathin cross sections of P(S-MAA) (MAA content, 10 mol %) particles before (a) and after (b) and (c) treated at 150°C for 3 h at initial pH value of 10.5 adjusted with NH_4OH (b) and ethanolamine (c).

pressure-resistant vessel having a polytetrafluoroethylene inner container, and the vessel was dipped in oil bath at 150°C for 3 h. After the treatment, each emulsion was cooled under the room temperature. Hereafter, these treatments will be called the alkali/cooling treatment.

RESULTS AND DISCUSSION

Figure 1 shows TEM photographs of P(S-MAA) (MAA content, 10 mol %) particles before and

after the alkali/cooling treatment in which the emulsions were treated at 150°C for 3 h at an initial pH value of 10.5 adjusted with NH_4OH and ethanolamine and subsequently cooled in the room temperature. The insides of the original particles were observed to be homogeneous; but in both alkali/cooling-treated particles, some regions of low contrast were observed.

Figure 2 shows TEM photographs of the ultrathin cross sections of the particles shown in Figure 1. The insides of original particles were homo-

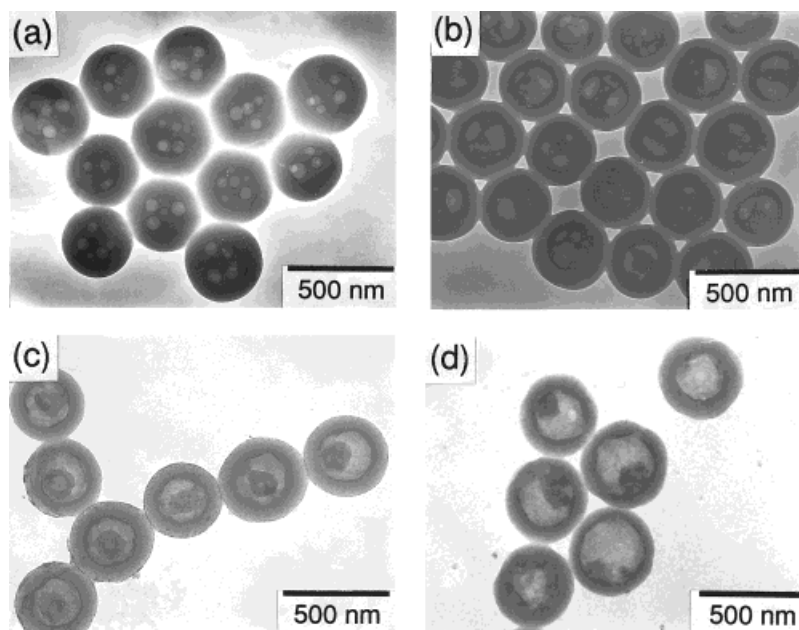


Figure 3 TEM photographs of P(S-MAA) (MAA content, 10 mol %) particles treated at 150°C for 3 h at various initial pH values with NH_4OH : (a) 10.5; (b) 11.0; (c) 11.5; (d) 12.0.

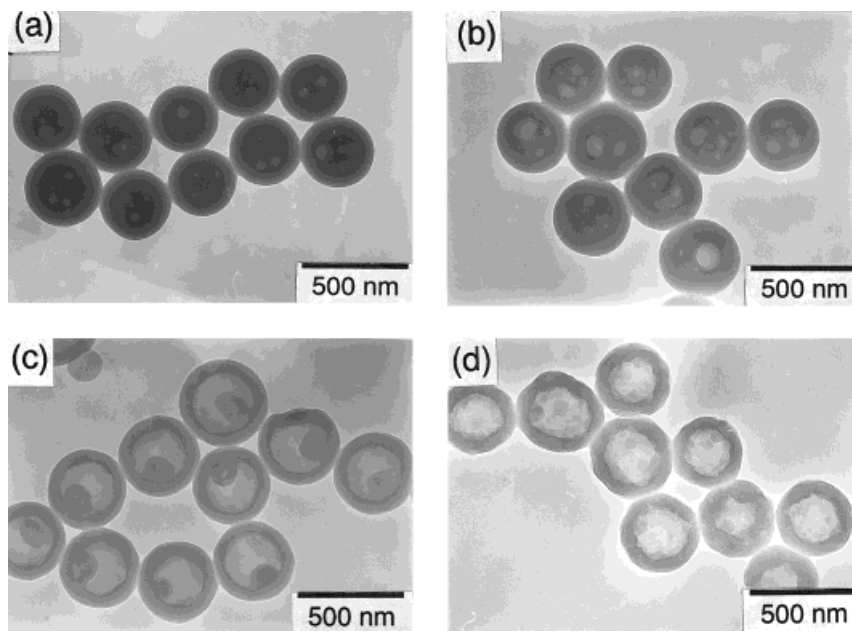


Figure 4 TEM photographs of P(S-MAA) (MAA content, 10 mol %) particles treated at 150°C for 3 h at various initial pH values with ethanolamine: (a) 10.5; (b) 11.0; (c) 11.5; (d) 12.0.

geneous, but it was clearly observed that both alkali/cooling-treated particles had multihollow structure.

From these results, it is clear that multihollow P(S-MAA) particles can be produced by the alkali/cooling method using volatile mild alkali aqueous solutions such as NH_4OH and ethanolamine.

Figures 3 and 4 show TEM photographs of P(S-MAA) particles after the alkali/cooling treatment in the initial pH range from 10.5 to 12.0 adjusted with NH_4OH and ethanolamine, respectively. In both cases, with an increase in the initial pH value, the hollow size and the total volume of hollows inside the particle increased, and the number of hollows per particle decreased.

Figure 5 shows the relationships between the initial pH value and the D_h of P(S-MAA) particles after the alkali/cooling treatments using KOH (\circ), NH_4OH (\bullet), and ethanolamine (\bullet) measured by DLS at room temperature. The D_h of any alkali/cooling-treated particles drastically increased around pH 11 regardless of the kind of alkali. It is clear that the increase in the particle volumes corresponds to that of the total volumes of hollows inside the particle.

Figure 6 shows TEM photographs of P(S-MAA) particles after the alkali/cooling treatment at the same pH value of 12.0 adjusted with KOH (a),

NH_4OH (b), and ethanolamine (c). It was observed that the treated particles had a similar multihollow structure.

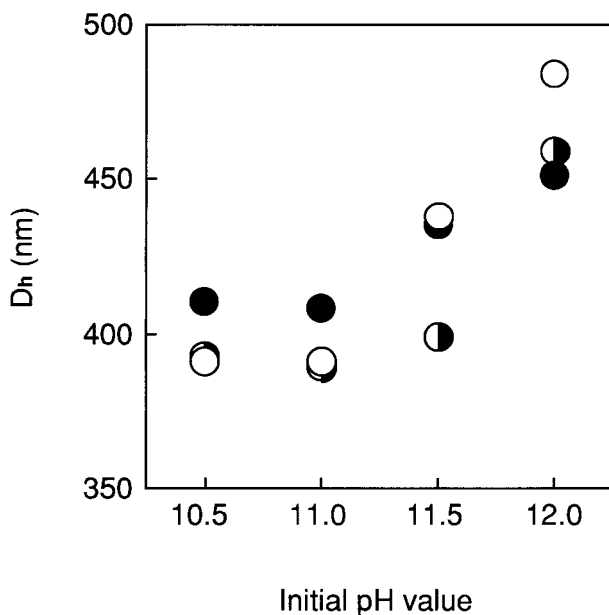


Figure 5 Relationships between the initial pH value and hydrodynamic diameter (D_h) of P(S-MAA) particles measured at room temperature after the alkali treatments with KOH (\circ), NH_4OH (\bullet), and ethanolamine (\bullet) at 150°C for 3 h.

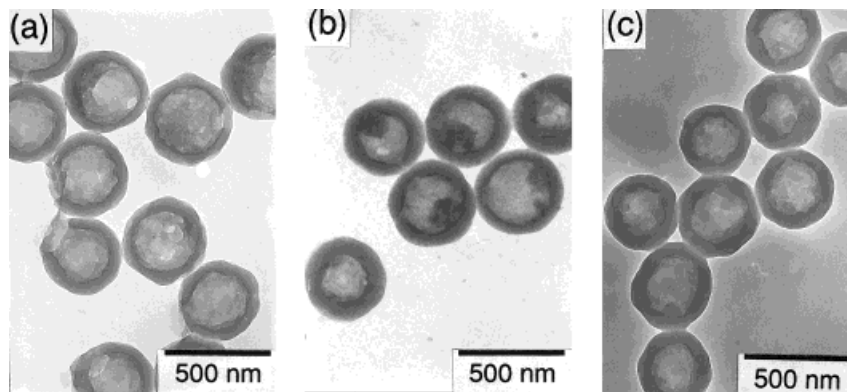


Figure 6 TEM photographs of P(S-MAA) (MAA content, 10 mol %) particles treated at 150°C for 3 h at initial pH value of 12.0 adjusted with KOH (a), NH₄OH (b), and ethanolamine (c).

The above results indicate that, regardless of the kind of alkali, the particles treated at the same pH value with each alkali swell with a similar tendency and then form a similar multihollow structure and support the formation mechanism of multihollow structure by the alkali/cooling method proposed by us.⁷

The authors thank the Hyogo Science and Technology Association for their partial support of this scientific research.

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