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Formation of multihollow structures in crosslinked composite polymer particles*)

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Abstract: Micron-size monodisperse polymer particles having multihollow structures were prepared as follows. First, micron-size monodisperse polystyrene/poly(styrene-divinylbenzene) (PS/P(S-DVB)) composite particles were produced by seeded copolymerization of S and DVB with 2,2′-azobisisobutyronitrile as an initiator in the ethanol/water (76/24, weight ratio) medium in the presence of 2.37 μm-size monodisperse PS seed particles produced by dispersion polymerization. The molar ratio of S/DVB was changed in the range of 1/1 ~ 10/1. The uncrosslinked polymer within the composite particles was extracted with toluene under reflux. For the highest DVB content (S/DVB = 1/1, molar ratio), one large hollow was observed in a part of the composite particles after the extraction. For the middle DVB content (S/DVB = 4/1, molar ratio), multihollow structure was observed in all the particles. For the lowest DVB content (S/DVB = 10/1, molar ratio), fine multihollow structure was observed in all the particles.

Key words: Micron-size – monodispersity – microsphere – seeded polymerization – multihollow structure

Introduction

A micron-size monodisperse polymer particle is applied in the biomedical field, information industry, microelectronics, etc. Since the micron-size is between the diameter range (about 0.1 ~ 0.7 μm) of the particles produced by emulsion polymerization and that (about 100 ~ 1000 μm) of the beads produced by suspension polymerization, it has been difficult to produce the micron-size monodisperse particle, although recently several studies on the production of micron-size monodisperse polymer particles have been reported [1–5].

We also tried to produce micron-size monodisperse polystyrene (PS) particles by dispersion polymerization in ethanol/water media [6]. Moreover, micron-size monodisperse crosslinked particles having vinyl groups at surfaces were produced by seeded copolymerization of styrene (S) and divinylbenzene (DVB) in the presence of the PS particles as seed [7, 8]. In a previous paper [9], we found that a part of crosslinked PS/poly (styrene-divinyl benzene) (PS/P(S-DVB)) composite particles had hollow structures after extraction with toluene under reflux.

In this article, in order to produce such micron-size monodisperse particles having multihollow structures in high yield, PS/P(S-DVB) composite particles having various DVB contents were prepared and PS were extracted therefrom with toluene under reflux.

Experimental

Materials

S, DVB, and acrylic acid (AA) were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) of

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reagent grade was purified by recrystallization. Ethanol and deionized water with a specific conductivity of 5×10^6 $\Omega \cdot$cm were separately distilled once with a Pyrex distillator. The other materials were used as received.

Poly(acrylic acid) (PAA) used as a stabilizer was produced by solution polymerization of AA in 1,4-dioxane, according to the previous article [6].

Preparation of seed particles

Monodisperse PS particles used as seed were produced under the optimum dispersion polymerization conditions listed in Table 1, as determined in the previous article [6]. The PS particles were observed with a JEOL JEM-200CX transmission electron microscope, Tokyo, Japan.

Seeded copolymerization of S and DVB

Seeded copolymerization of S and DVB was carried out in the presence of the PS seed particles at 70 °C under the conditions listed in Table 2. Unless otherwise noted, the mixture was kept at 0 °C for 24 h under shaking horizontally at 120 cycles/min (2-cm strokes) prior to the polymerization, in order that the PS seed particles absorb S, DVB, and AIBN as much as possible.

Table 1. Conditions of dispersion polymerization[a]

Ingredient		
Ethanol	(g)	220
Water	(g)	64.3
S	(g)	32.2
AIBN	(g)	0.54
PAA	(g)	3.86

[a] N_2; 70 °C; 24 h; stirring rate, 120 rpm

The conversions of S and DVB were measured by gas chromatography (Yanigimoto Manufacturing, Kyoto, Japan, G-2800) with nitrogen as a carrier gas. Chromosorb W AW-DMCS (stationary phase, 25% polyethyleneglycol) was used as the column packing. Each temperature of the gas chromatographic measurement was: injector, 200 °C; column, 120 °C; detector, 200 °C. The conversions for the particles used in this experiment were above 97%.

Extraction of polymer from PS/P(S-DVB) composite particles

The medium of the PS/PDVB composite dispersion was substituted from the ethanol/water to toluene via 1,4-dioxane by repeating centrifugation at 8000 rpm for 10 min as follows. After each centrifugation, the particles were dispersed in 1,4-dioxane twice and then dispersed in toluene twice. The final toluene dispersion of the PS/P(S-DVB) composite particles was kept under reflux.

Transmission electron microscopic (TEM) observations of ultrathin cross-sections

The ultrathin cross-sections of the PS/P(S-DVB) composite particles before and after the extraction were observed as follows. The toluene dispersions of the PS/P(S-DVB) composite particles were dropped on polyethylene terephthalate

Table 2. Preparation of PS/P(S-DVB) composite particles by seeded copolymerization[a]

Sample No.		1	2	3	4	5
Ethanol	(g)	12.6	57.6	12.6	10.8	12.6
Water	(g)	4.0	18.3	4.0	3.4	4.0
S	(g)	0.34	2.44	0.53	0.49	0.702
DVB[b]	(g)	0.80	2.77	0.40	0.28	0.088
AIBN	(g)	0.011	0.050	0.011	0.011	0.012
PS seed particles	(g)	1.57[c]	7.93[d]	1.57[c]	1.20[c]	1.50[e]
S/DVB (molar ratio)		1/1	2/1	3/1	4/1	10/1

[a] N_2; 70 °C; 24 h; PS seed/(S + DVB) = 2/1 (wt. ratio)

[b] Purity, 55% (by catalog)

[c] 2.6 μm-size PS particles were used as a seed.

[d] 2.4 μm-size PS particles were used as a seed.

[e] 1.9 μm-size PS particles were used as a seed.

films (50 μm of thickness). After drying, the particles on the film were exposed to RuO_4 vapor at room temperature for 40 min in the presence of 0.5% RuO_4 solution, and then dipped in epoxy matrix, cured at 70 °C for 8 h and microtomed. Ultrathin cross-sections were observed with Hitachi H-800 transmission electron microscope, Tokyo, Japan.

Results and discussion

Figure 1 shows a TEM photograph of the PS seed particles produced by dispersion polymerization under the conditions listed in Table 1. The number-average diameter (*Dn*) and the coefficient of variation measured with Personal Image Analysis System (PIAS Co. Ltd, LA-525, Osaka, Japan) were, respectively, 2.37 μm and 2.67%.

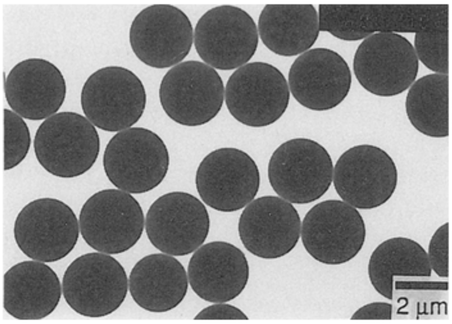


Fig. 1. TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1

Figures 2–6 show TEM photographs of PS/P(S-DVB) composite particles (PS seed/(S + DVB) = 2/1 (weight ratio); S/DVB molar ratio, variable), prepared by seeded copolymerizations of S and DVB with the PS seed particles under the conditions listed in Nos. 1–5 shown in Table 2, before (a) and after (b, c, d) the extraction with toluene under reflux for different times.

In Fig. 2 (S/DVB = 1/1, (molar ratio), No. 1 in Table 2), a part of the composite particles after the extraction for 1 day (Fig. 2b) had a similar single large hollow structure as already observed in previous paper [9]. Even if the extraction time was extended to 7 (Fig. 2c) and 14 days (Fig. 2d), the yield for the production of such hollow particles did not increase. This suggests that the degree of crosslinking had a wide distribution among the composite particles.

In Fig. 3 (S/DVB = 2/1, molar ratio; No. 2 in Table 2), the remarkable change was not observed in the composite particles before (Fig. 3a) and after (Fig. 3b) the extraction for 1 day. Whereas, those extracted for 3 (Fig. 3c) and 7 days (Fig. 3d) showed a multihollow structure.

In Fig. 4 (S/DVB = 3/1, molar ratio; No. 3 in Table 2), the multihollow structure was observed in almost all the particles after the extractions for 3 (Fig. 4c) and 7 days (Fig. 4d). The residual particles had a similar singular hollow structure

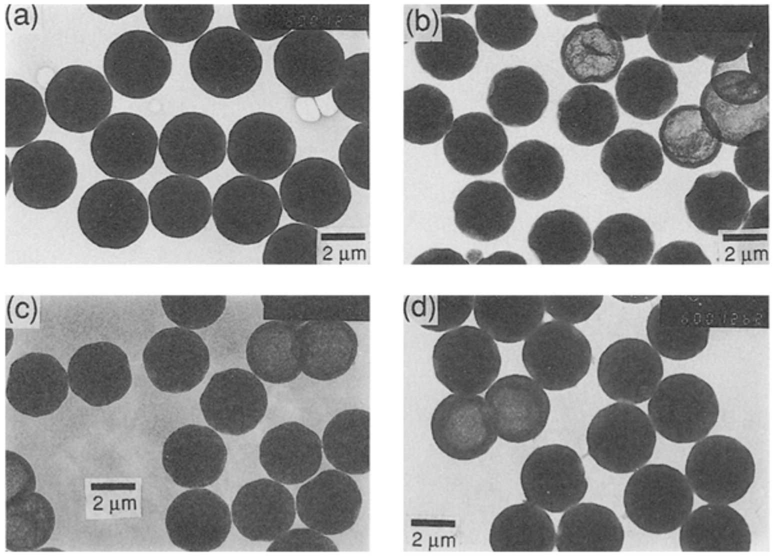
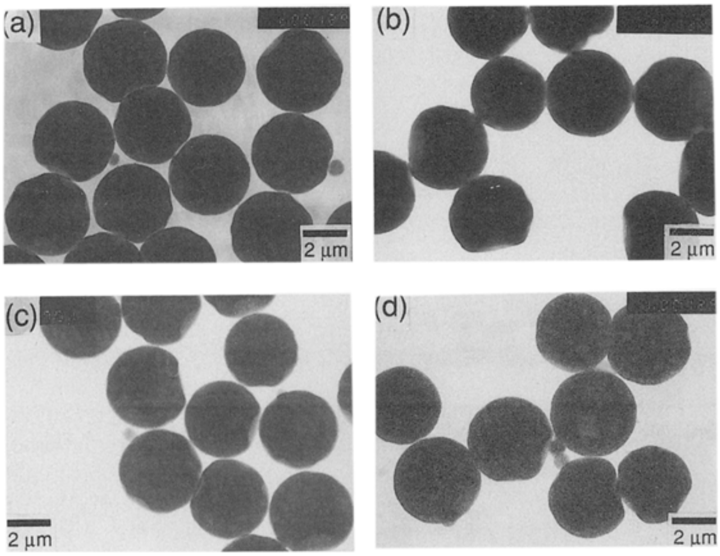


Fig. 2. TEM photographs of PS/P(S-DVB) composite particles produced under the conditions of No. 1 shown in Table 2 after the extraction with toluene under reflux: extraction time (days); (a), 0; (b), 1; (c), 7; (d), 14. PS seed/(S + DVB) = 2/1 (wt. ratio), S/DVB = 1/1 (molar ratio)



ig. 3. TEM photographs of PS/P(S-DVB) com- osite particles produced under the conditions of o. 2 shown in Table 2 after the extraction with oluene under reflux: extraction time (days); (a), 0; b), 1; (c), 3; (d), 7. PS seed/(S + DVB) = 2/1 (wt. atio), S/DVB = 2/1 (molar ratio)

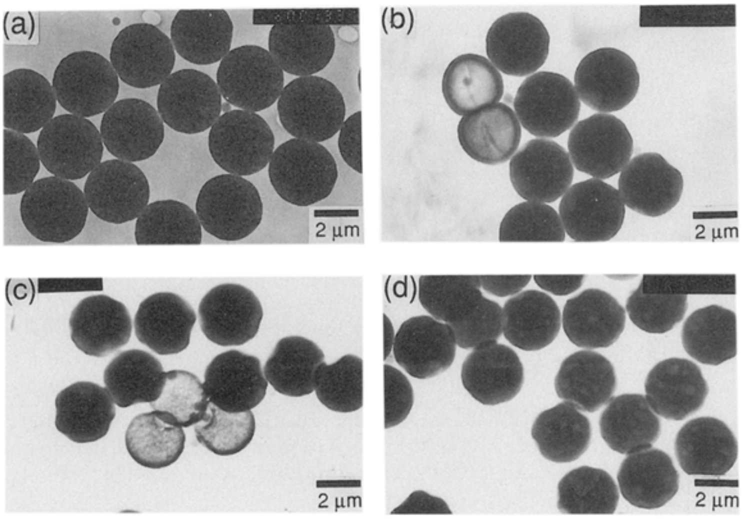


Fig. 4. TEM photographs of PS/P(S-DVB) composite particles produced under the conditions of No. 3 shown in Table 2 after the extraction with toluene under reflux: extraction time (days); (a), 0; (b), 1; (c), 3; (d), 7. PS seed/(S + DVB) = 2/1 (wt. ratio), S/DVB = 3/1 (molar ratio)

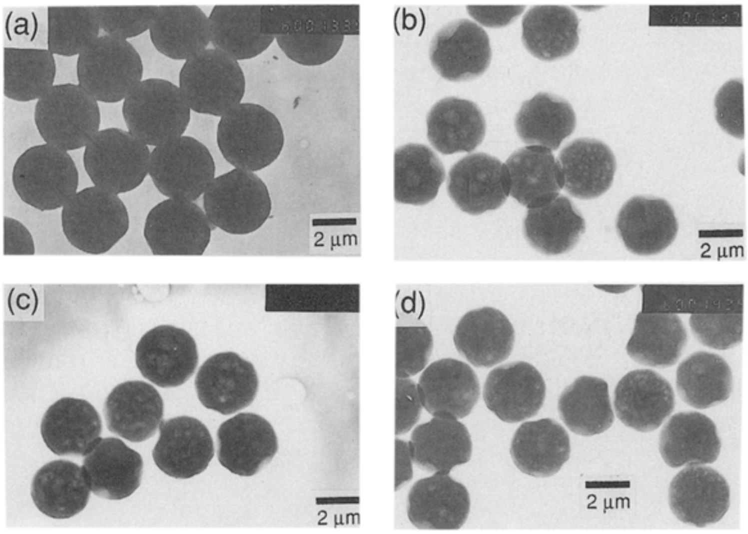


Fig. 5. TEM photographs of PS/P(S-DVB) composite particles produced under the conditions of No. 4 shown in Table 2 after the extraction with toluene under reflux: extraction time (days); (a), 0; (b), 1; (c), 3; (d), 7. PS seed/(S + DVB) = 2/1 (wt. ratio), S/DVB = 4/1 (molar ratio)

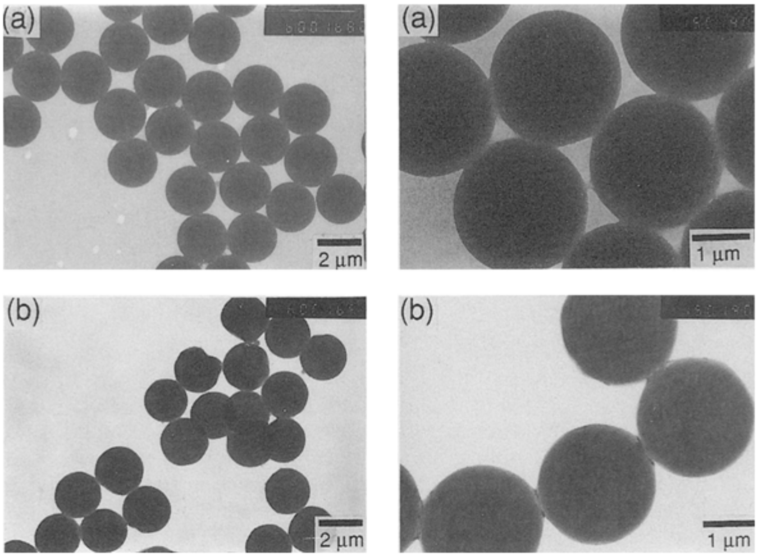


Fig. 6. TEM photographs of PS/P(S-DVB) composite particles produced under the conditions of No. 5 shown in Table 2 after the extraction with toluene under reflux: extraction time (days); (a), 0; (b), 14. PS seed/(S + DVB) = 2/1 (wt. ratio), S/DVB = 10/1 (molar ratio)

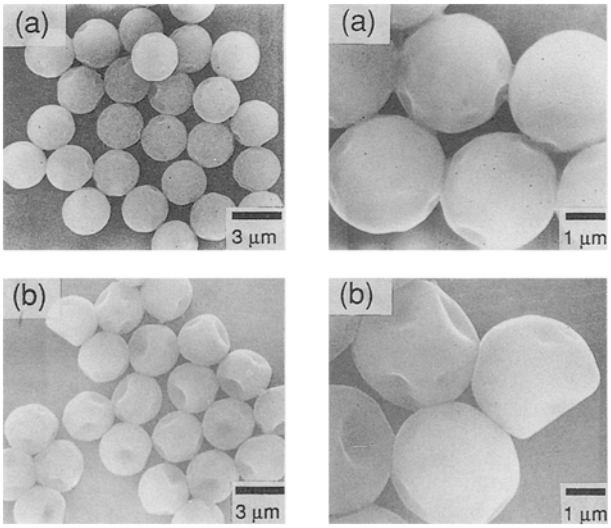


Fig. 7. SEM photographs of PS/P(S-DVB) composite particles before (a) and after (b) the extraction with toluene under reflux for a week: PS seed/(S + DVB) = 2/1 (wt. ratio), S/DVB = 4/1 (molar ratio)

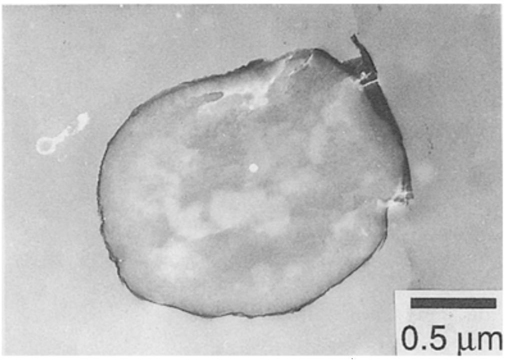


Fig. 8. TEM micrograph of ultrathin cross-section of PS/P(S-DVB) composite particles exposed to RuO_4 vapor for 40 min after the extraction with toluene under reflux

(Figs. 4b, c) as those shown in Figs. 2 (b), (c) and (d). This also suggests that degree of crosslinking had a wide distribution even among the composite particles produced in the same vessel.

In Fig. 5 (S/DVB = 4/1, molar ratio; No. 4 in Table 2), the multihollow structure was observed in all the composite particles after the extraction. The average diameters of the particles was not changed before and after the extraction.

In Fig. 6 (S/DVB = 10/1, molar ratio; No. 5 in Table 2), the multihollow structure in which the hollow size was small in comparison with those shown in Figs. 4 and 5 was obtained for all the composite particles after the extraction for 2 weeks. The average diameter of the particles was decreased by the extraction.

Figure 7 shows SEM photographs of PS/P(S-DVB) composite particles prepared by the seeded copolymerization of S and DVB (S/DVB = 4/1, molar ratio; No. 4 in Table 2, Fig. 5) before (Fig. 7a) and after (Fig. 7b) the extraction with toluene under reflux for 1 week. The original composite particle surfaces had unevenness and it became more remarkable after the extraction.

Figure 8 shows a TEM photograph of ultrathin cross-section of the PS/P(S-DVB) (S/DVB = 4/1, molar ratio; No. 4 in Table 2, Figs. 5, 7) composite particles exposed to RuO_4 vapor after the extraction with toluene under reflux. Many light portions were observed in the cross-section of the PS/P(S-DVB) composite particle after the extraction. Such a portion was not observed in the cross-section of original PS/P(S-DVB) composite particles before the extraction. These observations indicate that the extracted particle had the multihollow structure.

From the above results, it is concluded that micron-size monodisperse crosslinked polymer particles having multihollow structures can be produced in 100% of yield by extracting PS from PS/P(S-DVB) composite particles having appropriate DVB contents with toluene under reflux.

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