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ORIGINAL CONTRIBUTION

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Control of hollow size of micron-sized monodispersed polymer particles having a hollow structure

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Abstract Micron-sized monodispersed cross-linked polymer particles having one hollow in the inside were produced by seeded polymerization for the dispersion of (toluene/divinylbenzene)-swollen PS particles prepared utilizing the dynamic swelling method which the authors proposed. In order to control the hollow size, the weight ratio of toluene/PS was changed in the range of 5 ~ 20. The hollow size increased with an increase in the weight ratio. Even if benzene and xylene were used in place of toluene, similar hollow particles were produced, though the hollow size was affected by their solubility in water.

Key words Dynamic swelling method – hollow – micron-size – monodisperse – cross-linking – seeded polymerization

Introduction

Recently, micron-sized monodispersed polymer particles have been applied in the biomedical field, microelectronics, etc. Many researchers studying polymer colloids concentrate their attention on the production of micron-sized monodispersed polymer particles [1–4]. Corner [5] and Almog et al. [6] suggested a useful dispersion polymerization technique. We have been producing micron-sized monodispersed polystyrene (PS) particles having functional groups such as chloromethyl [7] and vinyl groups [8, 9] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 μm-sized monodispersed PS particles as seed. Micron-sized monodispersed polymer particles having multihollow structures were also produced by extraction of PS with toluene under reflux from micron-sized monodispersed PS/poly(styrene-divinylbenzene) composite particles produced by seeded dispersion copolymerization [10].

Moreover, in order to produce monodispersed particles having a diameter above 5 μm, we suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named "the dynamic swelling method (DSM)" [11, 12]. In fact, about 7 μm-sized monodispersed PS particles were produced by seeded polymerization utilizing DSM. In a previous paper [13], we developed this technique to produce micron-sized monodispersed polymer particles having one hollow in the inside, as follows. About 2 μm-sized monodispersed PS seed particles produced by dispersion polymerization were dispersed in ethanol/water (7/3, w/w) solution in which divinylbenzene (DVB), benzoyl peroxide (BPO), poly(vinyl alcohol), and toluene were dissolved. Throughout the dynamic swelling process, water was slowly added continuously, the PS seed particles absorbed DVB, toluene and BPO. And then, the seeded polymerization of the monodispersed (toluene/DVB)-swollen PS particles was carried out.

In this article, the control of the hollow size of such particles will be tried by changing the kind and amount of solvent.

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Experimental

Materials

Divinylbenzene (DVB) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. The supplied DVB included ethylvinylbenzene and diethylbenzene, and the purity was 55%. Benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) of reagent grade were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Polyvinyl alcohol (PVA) was supplied by Nippon Synthetic Chemical Ind. Co. Ltd. (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification; 88%). Poly(acrylic acid) (PAA) used as a stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane [7]. Reagent grade of ethanol, toluene, xylene and benzene were used as received.

Preparation of seed particles

Micron-sized monodispersed PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous article [7]. The dispersion polymerization of styrene was carried out at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask under the conditions listed in Table 1. The reaction mixture in the flask was stirred with an anchor-type stirrer at 60 rpm. The PS seed particles were observed with a JEOL JEM-200CX transmission electron microscope (TEM).

Swelling of seed particles with DVB and toluene utilizing DSM

Swelling of the PS particles with DVB and toluene was carried out using DSM as follows. Ethanol (7 g), water (3 g), DVB (0.3 g), toluene (0 ~ 0.60 g), BPO (0.006 g), and PVA (0.015 g) were charged into a glass cylindrical reactor. To this homogeneous solution, the PS particles (0.03 g) were dispersed. Finally, water (40 g) was added to the mixture with a micro feeder under stirring with a magnetic stirrer at a rate of 2.88 ml/h or 1.44 ml/h. Instead of toluene, benzene or xylene was used according to the same procedure.

Table 1 Preparation of micron-sized monodispersed PS seed particles by dispersion polymerization[a)]

Ingredient		
Styrene	(g)	140
AIBN	(g)	2.35
PAA	(g)	16.8
Ethanol	(g)	959
Water	(g)	280

[a)] N_2; 70 °C; 24 h; stirring rate, 60 rpm.

Seeded polymerization

Seeded polymerizations for the dispersions of (solvent/DVB)-swollen PS particles were carried out in sealed glass tubes under a nitrogen atmosphere at 70 °C for 24 h. The tubes were horizontally shaken at 120 cycles/min (2-cm strokes). After the polymerization, the emulsion was dropped onto slide glass, and then the droplet was covered with cover glass and observed with Nikon MICROPHOT-FAX optical microscope. Each particle was also observed with TEM. The conversion was measured by gas chromatography.

Observations of the ultrathin cross-sections of particles

PS/PDVB composite particles were exposed to O_sO_4 vapor at room temperature for 24 h in the presence of 1% O_sO_4 solution, and then dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross-sections were observed with TEM.

Diameter measurements

The number-average diameter (D_n) and coefficient of variation (C_v) were determined by measuring on TEM negative films with a Personal Image Analysis System (PIAS Co. Ltd, LA-525, Otsuka, Japan).

Results and discussion

Figure 1 shows a TEM photograph of PS particles produced by dispersion polymerization under the conditions listed in Table 1. PS particles were spherical and monodispersed: D_n and C_v were 1.71 μm and 2.2%, respectively.

Figure 2 shows optical micrographs of PS/polydivinylbenzene (PDVB) composite particles produced by seeded polymerization for the dispersions of swollen PS particles prepared utilizing DSM under the conditions of Nos. 1(a), 2(b), 3(c), and 4(d), respectively, listed in Table 2. Each conversion of DVB was more than 97%, and all composite particles produced were highly monodispersed. The particle size increased with the increase in the toluene content.

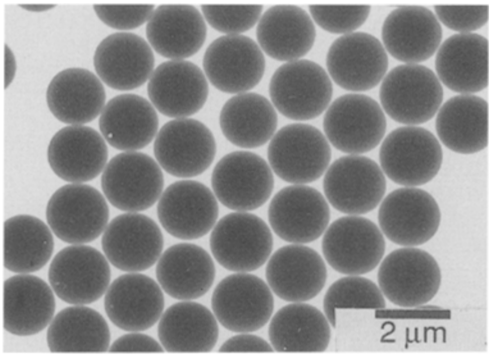


Fig. 1 TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1

The insides of the No. 1-particles were observed to be homogeneous, whereas the Nos. 2-, 3-, and 4-particles had a hollow at their center. The hollow size increased with the increase in the toluene content. In the observation of No. 4-particles just after the polymerization with the optical microscope, the hollow structure was not observed in almost all particles. However, the structure gradually appeared in the particles existing at the edge of the cover glass and the hollow size increased to give rise to the structure as shown in Fig. 2d. Finally, the hollow structure was observed in all particles. This seems to be based on the fact that toluene in the hollow is replaced by ethanol/water mixture medium because of evaporation of toluene. The refractive index of toluene is close to those of PS and PDVB, but that of the medium is different from them. When Nos. 2 ~ 4-particles were completely dried under reduced pressure at room temperature and redispersed in water, their hollow structures, which should be filled with air, were more distinct.

Figure 3 shows TEM photographs of Nos. 1-(a), 2-(b), 3-(c), and 4-particles (d). As will be seen, the contrast of the inside of No. 1-particles was homogeneous, whereas in the other Nos. 2 ~ 4-particles there was a less dark circular region due to the hollow structure. Both diameters of the composite particle and the less dark region increased with the increase in the toluene content. It was also observed that the hollow inside of No. 4-particles was rugged. This will be discussed in a future article.

Figure 4 shows a TEM photograph of ultrathin cross-sections of No. 2-particles exposed to O_sO_4 vapor for 2 h and a schematic model of sections sliced from different positions of particles. As shown in the schematic model, the sections having similar diameter to that of the composite particles (y-part) were sliced from the center particles and those having smaller diameter (x-, z-part) were sliced from the edges of particles. The sections having a small diameter did not have a hollow structure, but those having similar diameters as the composite particles had the hollow whose size increased with an increase in the diameter of the section. These findings indicate that No. 2-particles have a single hollow at the center. The hollow size observed in the part sliced from the center of the particles was similar to the diameter of the less dark region in the particles shown in Fig. 3b. Therefore, it is concluded that the diameter of the less dark regions in the TEM photographs corresponds to the hollow size.

Figure 5 shows relationships between the volume ratio of toluene to PS seed particle and the volume of PS/PDVB composite particles or the volume of hollow, which were, respectively, calculated from the diameters of composite

Fig. 2 Optical micrographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1(a), No. 2(b), No. 3(c) and No. 4(d), respectively, listed in Table 2

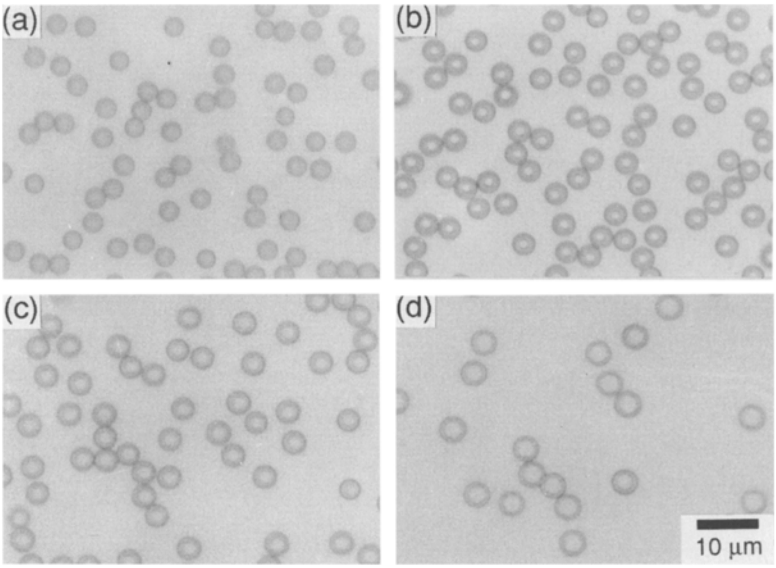


Table 2 Recipes for the productions of four kinds of PS/PDVB (1/5.5, w/w) composite particles by seeded polymerizations[a] for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method at room temperature

Ingredient		No. 1	No. 2	No. 3	No. 4
PS particles[b]	(g)	0.03	0.03	0.03	0.03
DVB[c]	(g)	0.3	0.3	0.3	0.3
Toluene	(g)	0	0.15	0.3	0.6
PVA	(g)	0.015	0.015	0.015	0.015
BPO	(g)	0.006	0.006	0.006	0.006
Ethanol	(g)	7.0	7.0	7.0	7.0
Water	(g)	3.0 + 40.0[d]	3.0 + 40.0[d]	3.0 + 40.0[d]	3.0 + 40.0[e]

[a] N_2, 70 °C, 24 h.

[b] 1.7 μm; C_v, 2.2%.

[c] Purity, 55% (by catalog).

[d] 40.0 g of water was post-added at the rate of 2.88 ml/h.

[e] 40.0 g of water was post-added at the rate of 1.44 ml/h.

Abbreviations: DVB, divinylbenzene; PS, polystyrene; PVA, polyvinyl alcohol; BPO, benzoyl peroxide.

Fig. 3 TEM photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1(a), No. 2(b), No. 3(c) and No. 4(d), respectively, listed in Table 2

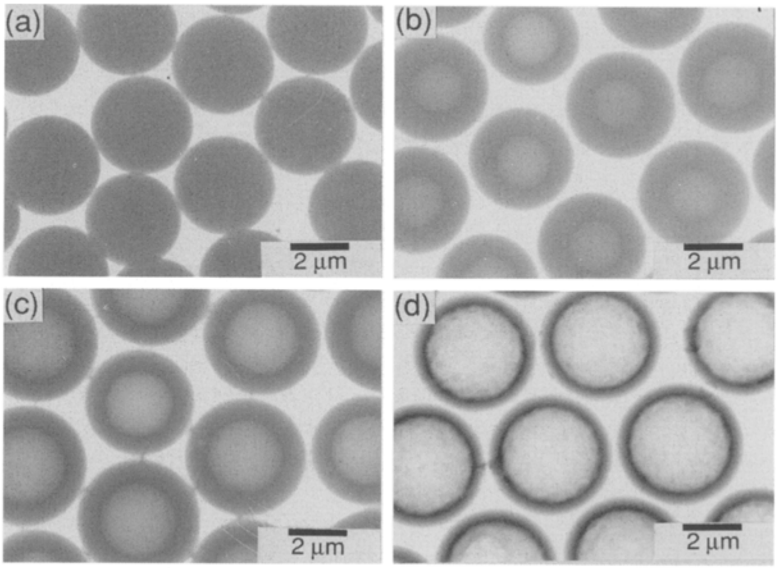
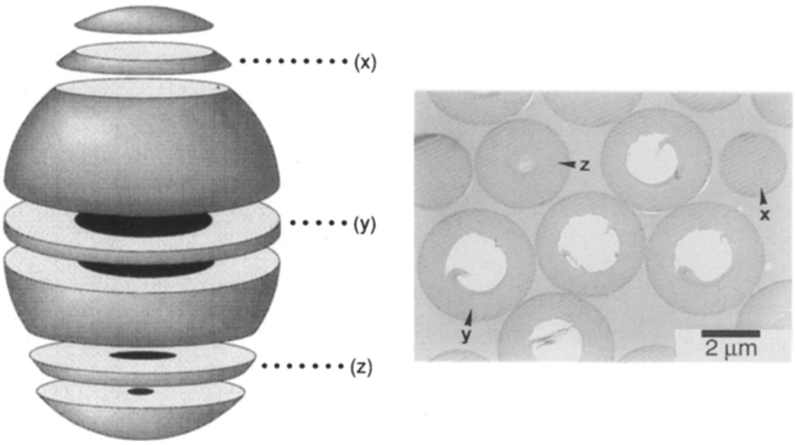


Fig. 4 TEM photograph of ultrathin cross-sections of PS/PDVB composite particles exposed to O_sO_4 vapor for 2 h which had been produced by seeded polymerizations for the dispersions of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 2 listed in Table 2



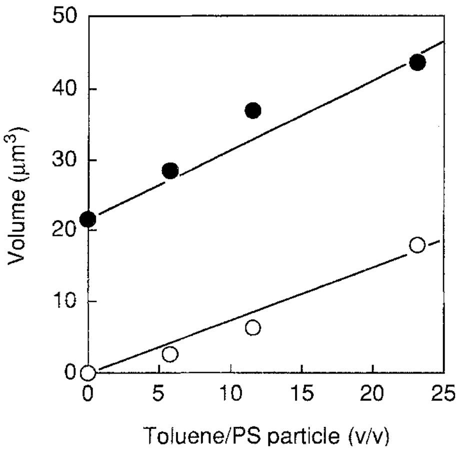


Fig. 5 Relationships between the volume ratio of toluene to PS seed particle and the volume of PS/PDVB composite particles (●) or the volume of hollow (○) produced by seeded polymerizations for the dispersions of DVB- and (toluene/DVB)-swollen PS particles utilizing the dynamic swelling method under the conditions listed in Table 2

Table 3 Recipes for the productions of two kinds of PS/PDVB (1/5.5, w/w) composite particles by seeded polymerizations[a] for the dispersions of (solvent/DVB)-swollen PS particles prepared utilizing the dynamic swelling method at room temperature

Ingredient		
PS particles[b]	(g)	0.03
DVB[c]	(g)	0.3
Benzene or xylene	(g)	0.3
PVA	(g)	0.015
BPO	(g)	0.006
Ethanol	(g)	7.0
Water	(g)	3.0 + 40.0[d]

[a] N_2, 70 °C, 24 h.
[b] 1.7 μm; C_v, 2.2%.
[c] Purity, 55% (by catalog).
[d] 40.0 g of water was post-added at the rate of 2.88 ml/h.
Abbreviations: DVB, divinylbenzene; PS, polystyrene; PVA, polyvinyl alcohol; BPO, benzoyl peroxide.

Table 4 Solubilities of solvents in water (25 °C) and densities of solvents (25 °C)

Solvent	Solubility (%)	Density (g/ml)
DVB	0.005[a]	0.9126[a]
Toluene	0.052[b]	0.8623[b]
Benzene	0.178[b]	0.8737[b]
p-Xylene	0.019[b]	0.8567[b]

[a] "Tanryotai I" 1st Ed., Kyoritsu Syuppan Co. Ltd (1976).
[b] "Organic Solvents" 3rd Ed., The Chemical Society of Japan (1993).

particles or the less dark region. The particle and hollow volumes increased proportionately with the amount of toluene. This indicates that the increase in the particle volume is due to the increase in the hollow volume. In this way, the hollow size is controllable by the amount of toluene. However the hollow volume was much smaller than the hollow volume as calculated from the recipe. This is because a part of toluene added existed also in the medium and gas phase in the sealed glass tube used in the polymerization.

Figure 6 shows TEM photographs of PS/PDVB composite particles produced by seeded polymerization for the dispersions of (benzene/DVB) –(a) and (xylene/DVB) –swollen PS particles (b) prepared utilizing DSM under the conditions listed in Table 3. Both composite particles had the hollow structure. Because the recipes of these systems were the same as that of No. 3 listed in Table 2 and the densities of the solvents are nearly equal as shown in Table 4, the volume ratios of solvents to PS seed particle can be considered to be the same. However, as can be seen, the hollow size increased in order of the benzene- < the toluene- < the xylene-containing system. This seems to be affected by the nature of solvents: solubility in medium, vaporization rate and vapor pressure. From the viewpoint of solubility, that order is in accord with the decreasing order of solubilities of the solvents in water as shown in Table 4. This suggests that a solvent having low solubility in the medium should be chosen to produce the hollow particles efficiently.

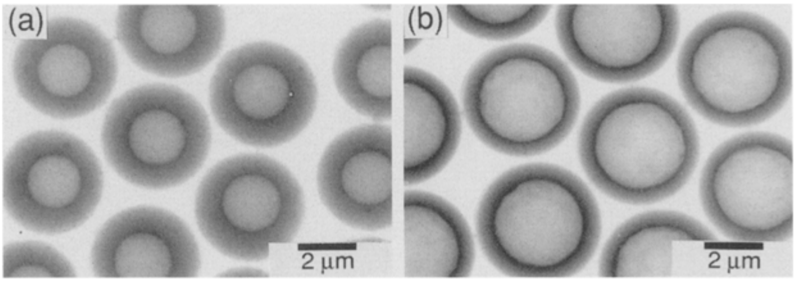


Fig. 6 TEM photographs of PS/PDVB composite particles produced by seeded polymerizations for the dispersions of (solvent/DVB)-swollen PS particles prepared utilizing the dynamic swelling method using benzene (a) and xylene (b) respectively, under the conditions listed in Table 3

From these results, it is concluded that the hollow size of micron-sized monodispersed cross-linked polymer parparticles produced by seeded polymerization utilizing the dynamic swelling method can be controlled by changing the amount and the nature of solvent.

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