Production of Hollow Polymer Particles by Suspension Polymerizations for Divinylbenzene/Toluene Droplets Dissolving Styrene-Methyl Methacrylate Copolymers [a)]

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SUMMARY: Suspension polymerizations for divinylbenzene/toluene droplets dissolving styrene (S)-methyl methacrylate copolymers having different compositions were carried out. Hollow particles were produced not with the copolymers having low S contents but with those having high S contents.

Introduction

Recently, micron-sized, monodispersed polymer particles have been applied in some advanced industrial fields. Many research groups studying polymer colloids concentrate their attention on the production of micron-sized, monodispersed polystyrene (PS) particles by dispersion polymerizations [1-5]. Using such PS particles as seed, about 2-μm-sized PS particles having chloromethyl [5] and vinyl groups [6, 7] at the surfaces were produced by seeded dispersion polymerizations of styrene (S) and chloromethylstyrene and of S and divinylbenzene (DVB) in ethanol/water media in which almost all of the monomers and 2,2′-azobis(isobutyronitrile) (AIBN) initiators dissolved. However, it has been difficult to produce monodispersed particles greater than 5 μm in size even by the dispersion polymerization and the seeded dispersion polymerization.

Therefore, in order to produce such particles, we have suggested a novel swelling method of seed polymer particles with a large amount of monomer, which was named "dynamic swelling method (DSM)" [8-10]. Actually, seeded polymerization for highly monomer-swollen particles prepared by the DSM with about 2-μm-sized, monodispersed PS seed particles gave about 5-μm-sized, monodispersed PS/polydivinylbenzene (PDVB) (1/10, w/w) composite particles having a tightly cross-linked structure and a high concentration of vinyl groups at the surfaces [11]. Such successes are based on a strong point of the technique that since almost all of the monomers and benzoyl peroxide (BPO) initiators exist in the swollen particles, the seeded polymerizations proceed smoothly therein. Moreover, we have developed this

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technique to produce micron-sized, monodispersed, cross-linked polymer particles having one hollow in the inside, by the seeded polymerization for about 5-μm-sized, monodispersed, highly (DVB/toluene) swollen PS particles prepared by the DSM [12-14]. In previous works [15, 16], hollow polymer particles were produced by suspension polymerization for DVB/toluene droplets dissolving PS. The kind of homopolymers such as PS, polymethacrylate and polyacrylate dissolving in the droplets greatly affected the formation of the hollow particles [16].

In this article, in order to clarify the effect of polarity of polymer dissolving in DVB/toluene droplets on the formation of the hollow structure more in detail, suspension polymerizations for DVB/toluene droplets dissolving S-methyl methacrylate (MMA) copolymers [P(S-MMA)] having different compositions were carried out.

Experimental

Materials

S and MMA were purified by distillation under reduced pressure in a nitrogen atmosphere. DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. Poly(vinyl alcohol) (PVA) (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%) was supplied by Nippon Synthetic Chemical, Osaka, Japan. Reagent grade AIBN and BPO were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Reagent grade toluene was used as received.

P(S-MMA) having different compositions were prepared by solution copolymerizations with AIBN initiator in sealed glass tubes under the conditions listed in Table 1. The copolymerizations were stopped at conversions less than about 10%. Each

Table 1 Preparations of P(S-MMA) having different compositions by solution polymerizations

S content (mol%)	0	10	30	50	70	90	100
S (g)	0	0.9	3.9	8.7	13.7	16.9	18
MMA (g)	13	17.1	14.1	9.3	4.3	1.1	0
AIBN (mg)	40	108	54	54	54	54	54
Toluene (g)	19	12	12	12	12	12	12
Polymn. time (h)	24	1.5	3.0	3.0	3.0	3.5	24
Polymn. temp. (°C)	70	60	60	60	60	60	60
Conversion[a] (%)	-	11.8	11.8	9.0	7.7	7.6	-
Mw[b] ($\times 10^5$)	1.4	1.5	1.5	1.5	1.2	1.8	1.6
Mw/Mn[c]	2.1	1.7	1.8	1.7	1.8	1.7	2.1
S content[d] (mol%)	0	10	28	49	72	92	100

[a] Determined by gravimetry
[b] Weight-average molecular weight
[c] Number-average molecular weight
[b, c] Measured by gel permeation chromatography
[d] Measured by ^{1}H NMR

Abbreviations: S, styrene; MMA, methyl methacrylate; AIBN, 2,2'-azobis(isobutyronitrile) copolymer was purified by reprecipitation into methanol and dried under reduced pressure. Molecular weight was measured by gel permeation chromatography with calibration obtained using PS standards with tetrahydrofuran as the eluent. The S contents in the copolymers were measured by ^{1}H NMR using $CDCl_3$ as a solvent at room temperature.

Suspension polymerizations

Homogeneous solutions of DVB (250 mg), toluene (250 mg), BPO (5 mg), and P(S-MMA) (5~125 mg) were mixed with 0.33 wt% PVA aqueous solution (15 g), and stirred vigorously by Nissei ABM-2 homoge-nizer at 1000 rpm for 2 min in glass cylindrical reactors. The suspension polymerizations were carried out at 70°C for 24 h under a nitrogen atmosphere in sealed glass tubes under the conditions listed in Table 2. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). Particles were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

Table 2 Suspension polymerizations[a] for DVB/toluene droplets dissolving S-MMA copolymer having different compositions

Ingredients		No. 1	No. 2	No. 3	No. 4	No. 5
P(S-MMA)[b]	(mg)	5	12.5	25	50	125
DVB[c]	(mg)	250	250	250	250	250
Toluene	(mg)	250	250	250	250	250
BPO	(mg)	5.0	5.0	5.0	5.0	5.0
PVA	(mg)	50	50	50	50	50
Water	(g)	15.0	15.0	15.0	15.0	15.0

[a] N_2, 70°C, 24 h

[b] Prepared by solution copolymerizations under the conditions listed in Table 1

[c] Purity, 96% (by catalog)

Abbreviations: DVB, divinylbenzene; S, styrene; MMA, methyl methacrylate; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

Observation of ultrathin cross sections of particles

Composite particles were exposed to RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were observed with a Hitachi H-7100 TEM transmission electron microscope (TEM).

Measurement of interfacial tension

The interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% P(S-MMA) were measured by the du Noüy ring method at room temperature with a Shimadzu DN surface tensiometer. Each P(S-MMA) solution (40 g) was poured gently into water (50 g), and after 3 h the measurement was carried out with a platinum ring (diameter, 19 mm).

Results and discussion

Figure 1 shows the interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% P(S-MMA) having different compositions, which were polymerized under the conditions listed in Table 1. The interfacial tension decreased linearly with a decrease of S content in the copolymers.

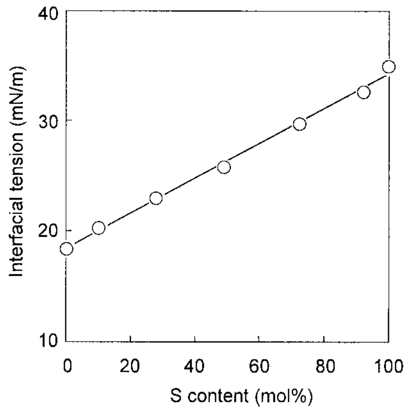

Figure 1. Interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% P(S-MMA) having different compositions at 23 ± 2°C

Figures 2-4 show optical micrographs (a, d) and SEM photographs (b, e) of P(S-MMA)/PDVB (1/20, 4/20; w/w) composite particles and TEM photographs (c, f) of their ultrathin cross sections. The composite particles were produced by the suspension polymerizations for DVB/toluene droplets dissolving the different amounts of P(S-MMA) under the conditions of Nos. 2 (a, b, c) and 4 (d, e, f) listed in Table 2 and the S contents of 49, 28 and 10 mol% in P(S-MMA), respectively, in Figs. 2, 3 and 4.

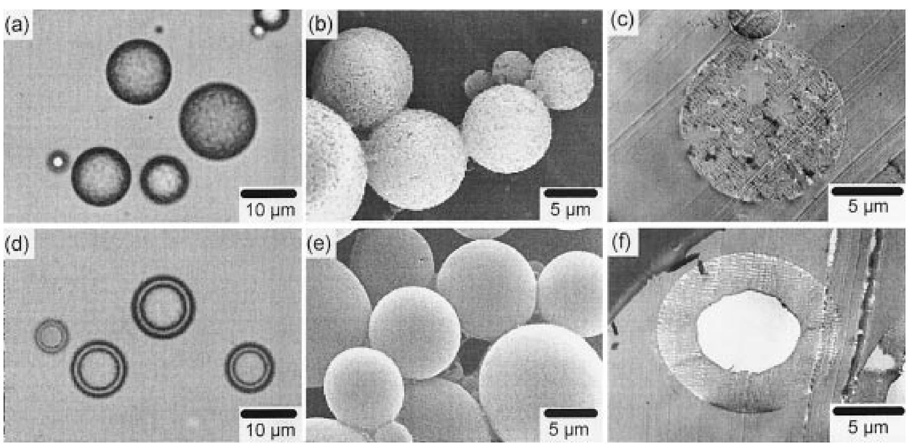

Figure 2. Optical micrographs (a, d) and SEM photographs (b, e) of P(S-MMA)/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving P(S-MMA) (S content, 49 mol%) under the conditions of Nos. 2 and 4 listed in Table 2, and TEM photographs (c, f) of ultrathin cross sections of the composite particles exposed to RuO_4 vapor for 30 min. BPO, 2 wt% based on DVB. P(S-MMA)/PDVB (w/w): (a, b, c) 1/20 (No. 2); (d, e, f) 4/20 (No. 4).

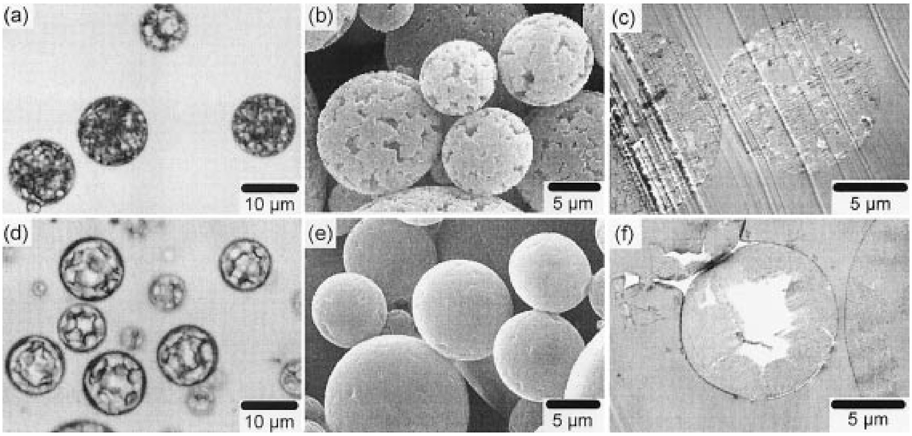

Figure 3. Optical micrographs (a, d) and SEM photographs (b, e) of P(S-MMA)/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving P(S-MMA) (S content, 28 mol%) under the conditions of Nos. 2 and 4 listed in Table 2, and TEM photographs (c, f) of ultrathin cross sections of the composite particles exposed to RuO_4 vapor for 30 min. BPO, 2 wt% based on DVB. P(S-MMA)/PDVB (w/w): (a, b, c) 1/20 (No. 2); (d, e, f) 4/20 (No. 4).

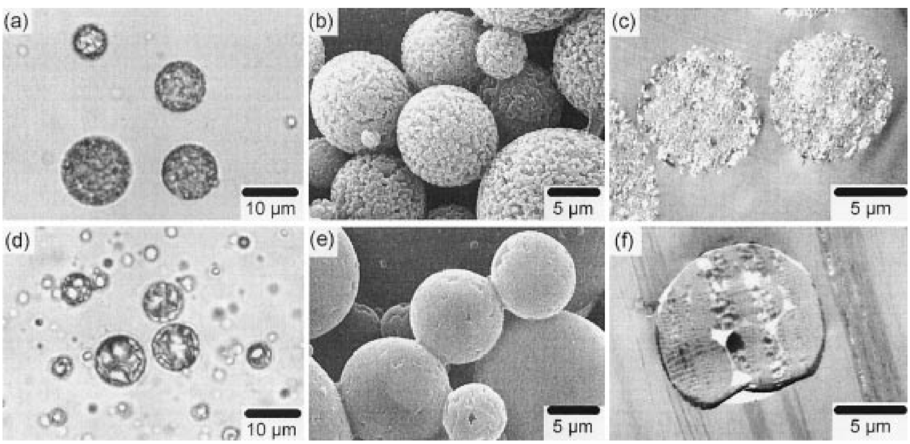

Figure 4. Optical micrographs (a, d) and SEM photographs (b, e) of P(S-MMA)/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving P(S-MMA) (S content, 10 mol%) under the conditions of Nos. 2 and 4 listed in Table 2, and TEM photographs (c, f) of ultrathin cross sections of the composite particles exposed to RuO_4 vapor for 30 min. BPO, 2 wt% based on DVB. P(S-MMA)/PDVB (w/w): (a, b, c) 1/20 (No. 2); (d, e, f) 4/20 (No. 4).

In the case of 49 mol% of S content in P(S-MMA) in Fig. 2, the P(S-MMA)/PDVB (1/20, w/w) composite particles had a porous structure (a, b, c), but it (4/20, w/w) had a hollow at the center (d, f) and smooth inner and outer surfaces (e). This hollow structure was similar to those obtained with PS and poly(*n*–butyl methacrylate) in the previous articles [15, 16].

In the case of 28 mol% of S content in P(S-MMA) in Fig. 3, the P(S-MMA)/PDVB (1/20, w/w) composite particles had a porous structure. On the other hand, it (4/20, w/w) had a hollow structure, though the inner surface was very rough.

In the case of 10 mol% of S content in P(S-MMA) in Fig. 4, hollow composite particles were not obtained at any concentrations of the copolymers.

Table 3 Relationship between the interfacial tensions[a)] between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% P(S-MMA)[b)] having different compositions and the structures (○, hollow; ●, nonhollow; ◐, hollow + nonhollow; ⊙, incomplete hollow) of composite particles produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of the copolymers

S content (mol%)	Interfacial tension [c)] (mN/m)	Polymer content in the droplet (wt%)				
		1.0	2.4	4.8	9.1	20.0
100	35.0	●	●	◐	○	○
92	32.6	●	●	●	○	○
72	29.8	●	●	●	○	○
49	25.8	●	●	○	○	○
28	22.9	●	●	⊙	⊙	⊙
10	20.2	●	●	●	●	●
0	18.4	●	●	●	●	●

a) Measured by the du Noüy ring method at 23 ± 2 °C.
b) Prepared by solution polymerizations under the conditions listed in Table 1
c) The values of PDVB and without polymer were, respectively, 29.5 and 34.8 mN/m.

Abbreviations: P(S-MMA), styrene-methyl methacrylate copolymer; DVB, divinylbenzene

Table 3 shows the relationship between the structure of their composite particles and the interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% P(S-MMA) copolymers having the different compositions. Xylene was used instead of DVB. The hollow particles were produced at relative high concentration of the P(S-MMA) giving the interfacial tensions above about 25 mN/m. The interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0 and 0.01 wt% PDVB were, respectively, 34.8 and 29.5 mN/m. These results indicate that the copolymers having high polarity adsorb preferentially at the interface of the droplets over PDVB, which was discussed in the previous article [16].

Table 4 Suspension polymerizations[a)] for DVB/toluene droplets dissolving PS and PMMA

Ingridients		No. 1	No. 2	No. 3	No. 4	No. 5
PS[b)] + PMMA[b)]	(mg)	5	12.5	25	50	125
DVB[c)]	(mg)	250	250	250	250	250
Toluene	(mg)	250	250	250	250	250
BPO	(mg)	5.0	5.0	5.0	5.0	5.0
PVA	(mg)	50	50	50	50	50
Water	(g)	15.0	15.0	15.0	15.0	15.0

a) N_2, 70 °C, 24 h
b) Produced by solution polymerizations under the conditions listed in Table 1
c) Purity, 96% (by catalog)

Abbreviations: DVB, divinylbenzene; PS, polystyrene; PMMA, poly(methyl methacrylate); BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

Figure 5 shows optical micrographs of the PS/ poly(MMA) (PMMA)/

PDVB composite particles having different compositions under the conditions of Nos. 2 (a, b, c) and 4 (d, e, f) listed in Table 4. The composite particles were produced by the suspension polymerizations for DVB/toluene droplets dissolving both PS and PMMA at various ratios and contents. Nonhollow particles were observed at any ratios and contents. The interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% PS and PMMA at various ratios were about 19 mN/m which was almost the same as that of 0.01 wt% PMMA. These results indicate that the preferential adsorption of a small amount of PMMA at the interface of the droplet disturbs the formation of PDVB shell even if enough concentration of PS to form the hollow particles is dissolved.

From these results, it is concluded that the polarity of polymer dissolving in DVB/toluene droplets greatly affects the formation of the hollow particles.

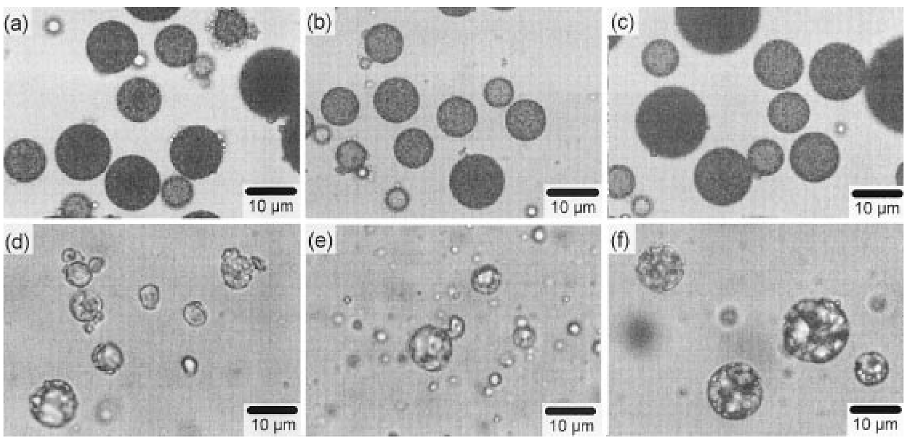

Figure 5. Optical micrographs of PS/PMMA/PDVB composite particles produced by suspension polymerizations for DVB/toluene droplets dissolving both PS and PMMA at various ratios under the conditions of Nos. 2 and 4 listed in Table 4. S/MMA (molar ratio): (a, d) 10/90; (b, e) 50/50; (c, f) 90/10. BPO, 2 wt% based on DVB. (PS + PMMA)/PDVB (w/w): (a, b, c) 1/20 (No. 2); (d, e, f) 4/20 (No. 4).

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