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SHORT COMMUNICATION

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Influence of the kind of end groups of polysterene on the production of hollow particles by suspension polymerization for divinylbenzene/toluene droplets dissolving them

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Abstract Suspension polymerizations for divinylbenzene (DVB)/toluene droplets dissolving polystyrene (PS) having different end groups were carried out. Hollow polymer particles were not obtained with PS having polar sulfate end groups, which were prepared by emulsifier-free emulsion polymerization with potassium persulfate initiator. On the other hand, they were obtained with PS having low polarity isobutyronitrile end groups, which were prepared by solution polymerization with 2,2′-azobis(isobutyronitrile) initiator. The interfacial tensions between the water and xylene/toluene (1/1, w/w) mixture solution of PS having polar groups was smaller than that having low polarity groups. From these results, it is concluded that the preferential adsorption of PDVB molecules formed by the suspension polymerization at the interface of the droplets over PS molecules, which depended on the kind of the end groups, is one of the key factors for the formation of the hollow structure.

Key words Suspension polymerization · Hollow · End group · Particle · Interfacial tension

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 seeds, about 2-μm-sized PS particles having chloromethyl [5] and vinyl groups [6, 7] at the surfaces were produced by seeded dispersion copolymerizations of styrene (S) and chloromethylstyrene and of S and divinylbenzene (DVB) in ethanol/water media in which almost all of the monomers and the 2,2′-azobis(isobutyronitrile) (AIBN) initiator dissolved. However, it was difficult to produce monodispersed particles greater than 5 μm in size even by dispersion polymerization and 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 the dynamic swelling method (DSM) [8–10]. Actually, seeded polymerization for highly monomer-swollen particles prepared by the DSM using about 2-μm-sized, monodispersed PS seed particles gave about 5-μm-sized, monodispersed PS/poly(divinylbenzene) (PDVB) (1/10, w/w) composite particles having a tightly cross-linked structure and a high concentration of vinyl groups at their surfaces [11]. Such successes are based on a strong point of the technique that since almost all of the monomers and the benzoyl peroxide (BPO) initiator exist in the swollen particles, the seeded polymerizations proceed smoothly therein. Moreover, we have developed this technique to produce micron-sized, monodispersed, cross-linked polymer particles having one hollow in the inside by seeded polymerization for about 5-μm-sized, monodispersed, highly (DVB/toluene) swollen PS particles prepared by the DSM [12–14]. In a previous work [15], suspension polymerization for DVB/toluene droplets dissolving PS gave similar hollow polymer particles, though they were polydisperse. Moreover, the kind of homopolymers, which had different polarities, dissolving in DVB/toluene droplets greatly affected the formation of the hollow structure [16].

In this work, in order to clarify the effect of polarity of the polymer dissolved in DVB/toluene droplets on the formation of the hollow structure in more detail, suspension polymerizations for DVB/toluene droplets dissolving PS having different kinds of end groups were carried out.

Experimental

Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N 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, BPO, and potassium persulfate (KPS) were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Reagent grade toluene was used as received.

PS molecules having isobutyronitrile and sulfate end groups were prepared by solution polymerization with AIBN initiator and by emulsifier-free emulsion polymerizations with KPS initiator, respectively, under the conditions listed in Table 1. PS prepared by solution polymerization was purified by reprecipitation into methanol. PS particles prepared by the emulsifier-free emulsion polymerizations were washed by centrifugation with water more than three times. They were dried under reduced pressure before use. The molecular weight was measured by gel permeation chromatography with calibration obtained using PS standards with tetrahydrofuran as the eluant. PS particles prepared under the condition 3 listed in Table 1 were treated at 90 °C for 1 week at an initial pH of 1.0 adjusted with HCl to hydrolyze sulfate end groups to hydroxyl groups. Although the efficiency of the hydrolysis was not estimated, the dispersibility in an aqueous medium was changed, so almost all the sulfate end groups at the particle surfaces should be hydrolyzed.

Table 1 Preparation of four kinds of polysterene (*PS*) having different end groups and molecular weights by solution polymerization with 2,2′-azobis(isobutyronitrile) (*AIBN*) initiator and by emulsifier-free emulsion polymerizations with potassium persulfate (*KPS*) initiator, under N_2 atmosphere

Ingredients	No. 1	No. 2	No. 3	No. 4
Styrene (g)	18	17	60	15
AIBN (mg)	54	–	–	–
Toluene (g)	12	–	–	–
KPS (mg)	–	94	990	345
Water (g)	–	170	1000	200
Polymerization temperture (°C)	60	70	70	70
Polymerization time (h)	24	24	48	72
M_w ($\times 10^5$)[a]	1.6	2.2	4.1	8.2
M_w/M_n[b]	2.1	8.7	11.2	12.5

[a] Weight-average molecular weight, measured by gel permeation chromatography
[b] Number-average molecular weight, measured by gel permeation chromatography

Suspension polymerizations

Homogeneous solutions of DVB (250 mg), toluene (250 mg), BPO (5 mg), and PS (5–125 mg) were mixed with 0.33 wt% PVA aqueous solution (15 g) and were stirred vigorously using a NISSEI ABM-2 homogenizer at 1000 rpm for 2 min in glass cylindrical reactors. Suspension polymerizations for the dispersions 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 shaken horizontally at 80 cycles/min (3-cm strokes). The particles were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

Observation of the 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 were then dispersed in an epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross sections were observed with a Hitachi H-7100 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% PS were measured by the du Noüy ring method at room temperature with a Shimadzu DN surface tensiometer. Each PS solution (40 g) was gently poured into water (50 g), and after 3 h the measurement was carried out with a platinum ring (diameter, 19 mm).

Results and discussion

Optical micrographs of PS/PDVB composite particles produced by the suspension polymerizations for DVB/toluene droplets dissolving different amounts of PS [weight-average molecular weight (M_w), 1.6×10^5] under the conditions listed in Table 2 are shown in Fig. 1. The PS molecules were prepared by solution polymerization with AIBN initiator under the condition 1 listed in

Table 2 Suspension polymerizations for divinylbenzene (*DVB*)/toluene droplets dissolving PS having different end groups at 70 °C for 24 h under N_2 atmosphere

Ingredients	No. 1	No. 2	No. 3
PS (mg)[a]	0	5	50
DVB (mg)[b]	250	250	250
Toluene (mg)	250	250	250
Benzoyl peroxide (mg)	5	5	5
Poly(vinyl alcohol) (mg)	50	50	50
Water (g)	15.0	15.0	15.0

[a] Prepared by solution polymerization with AIBN and by emulsifier-free emulsion polymerizations with KPS under the conditions listed in Table 1
[b] Purity, 96% (by catalog)

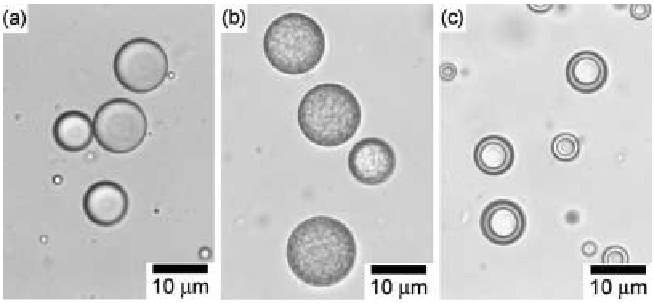

Fig. 1a–c Optical micrographs of polystyrene (*PS*)/poly(divinylbenzene) (*PDVB*) composite particles produced by suspension polymerizations for divinylbenzene (*DVB*)/toluene (1/1, w/w) droplets dissolving different amounts of PS having isobutyronitrile end groups under the conditions listed in Table 2. Benzoyl peroxide (*BPO*), 2 wt% based on DVB. PS/PDVB (w/w): **a** 0/50 (no. 1); **b** 1/50 (no. 2); **c** 1/5 (no. 3). The PS was prepared by solution polymerization with 2,2′-azobis(isobutyronitrile) under the condition 1 listed in Table 1

Table 1. It is known that in radical polymerization of S the termination of propagating radicals occurs exclusively by coupling; therefore, PS molecules prepared by solution polymerization should have two isobutyronitrile end groups as initiator fragments. In the optical micrograph of PDVB particles shown in Fig. 1a, the inside of the particles was observed to be homogeneous. In Fig. 1b, PS/PDVB (1/50, w/w) composite particles did not have a hollow structure, but a heterogeneous structure. In Fig. 1c, the particles (1/5, w/w) had a hollow structure, which was satisfied with the minimum content and M_w of PS in the droplets to prepare the hollow polymer particles by suspension polymerization using PS having isobutyronitrile end groups. The conditions were determined in previous work [15].

Optical micrographs of PS/PDVB composite particles produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of PS having sulfate end groups and different M_w, under the conditions listed in Table 2, are shown in Fig. 2. The PS molecules were prepared by emulsifier-free emulsion polymerizations with KPS initiator under conditions 2–4 listed in Table 1. Hollow polymer particles were not obtained even for PS having high M_w.

SEM photographs of the composite particles (M_w of PS: 4.1×10^5) shown in Figs. 2 and TEM photographs of their ultrathin cross sections are shown in Fig. 3. The particles had rough surfaces and heterogeneous structures in the inside. That is, the results obtained using PS having polar sulfate end groups were inconsistent with those using PS having low polarity isobutyronitrile end groups shown in Fig. 1. The heterogeneous structures were similar to those obtained in previous work [16] using poly(methyl methacrylate) and poly(methyl acrylate) prepared by solution polymerization with AIBN initiator, which have relatively high polarities. These

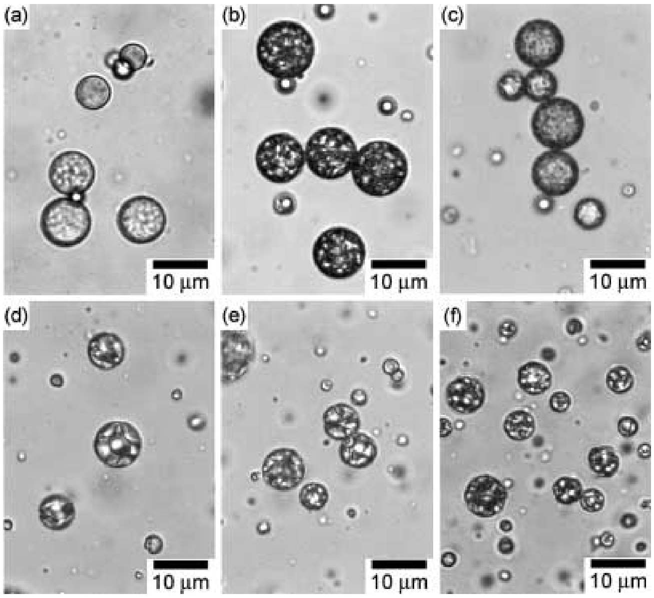

Fig. 2a–f Optical micrographs of PS/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving PS having different molecular weights under the conditions 2 and 3 listed in Table 2. M_w ($\times 10^5$): **a**, **d** 2.2; **b**, **e** 4.1; **c**, **f** 8.2. BPO, 2 wt% based on DVB. PS/PDVB (w/w): **a**, **b**, **c** 1/50 (no. 2); **d**, **e**, **f** 1/5 (no. 3). The PS was prepared by emulsifier-free emulsion polymerizations with potassium persulfate (*KPS*) under the conditions 2, 3, and 4 listed in Table 1

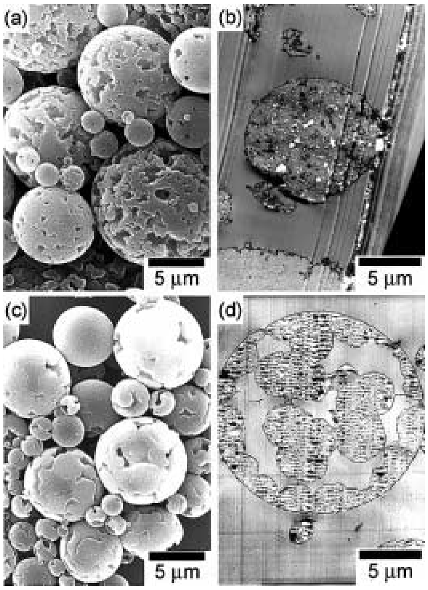

Fig. 3 Scanning electron microscope (SEM) photographs (**a**, **c**) of PS/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving PS having sulfate end groups under the conditions 2 and 3 listed in Table 2 and transmission electron microscope (*TEM*) photographs (**b**, **d**) of ultrathin cross sections of the composite particles exposed to RuO_4 vapor for 30 min. BPO, 2 wt% based on DVB. PS/PDVB (w/w): **a**, **b** 1/50 (no. 2); c, **d** 1/5 (no. 3). The PS was prepared by emulsifier-free emulsion polymerization with KPS under the condition 3 listed in Table 1

results indicate that the polarity of the end groups of PS, which were derived from initiator fragments, dissolved in the droplets affects the formation of the hollow structure.

Optical micrographs and SEM photographs of the composite particles produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of PS having hydroxyl end groups and TEM photographs of their ultrathin cross sections are shown in Fig. 4. The hydroxyl end groups of the PS (M_w: 4.1×10^5) were given by hydrolysis of the sulfate groups. The PS/PDVB (1/50, w/w) composite particles did not have a hollow structure (Fig. 4a, b, c). On the other hand, they (1/5, w/w) had an incomplete hollow structure (Fig. 4d, e, f), the inner surface of which was very rough. The structure was similar to those obtained by suspension polymerizations for DVB/toluene droplets dissolving poly(ethyl methacrylate) and poly(ethyl acrylate) having isobutyronitrile end groups [16].

The relationship between the interfacial tensions between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% PS and the structures of composite particles produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of PS having the different end groups is shown in Table 3. At a PS content of 1 wt% in the droplets, no hollow structure was observed in all the composite particles. At higher PS content in the droplets, the hollow particles were obtained by suspension polymerizations using PS having low polarity isobutyronitrile end groups. In the case of the PS having isobutyronitrile end groups, the interfacial tension was almost the same as that (34.8 mN/m) of the pure mixture solvent. In all cases of PS having sulfate end groups, which gave low interfacial tension values (22.9–27.1 mN/m), the hollow particles were not obtained. In the case of PS having hydroxyl end groups, which gave a medium interfacial tension (31.0 mN/m), incomplete hollow particles were obtained. The interfacial tension values suggest that the kind of the end groups affects the adsorption of PS at the interface of the droplets. As shown in Fig. 5, when PS molecules have polar end groups, they adsorb at the interface of the droplets owing to the strong interaction between the end groups and the medium, so they prevent the formation of the hollow structure at the interface. In the case of PS having low polarity end groups, PDVB molecules adsorb at the interface and

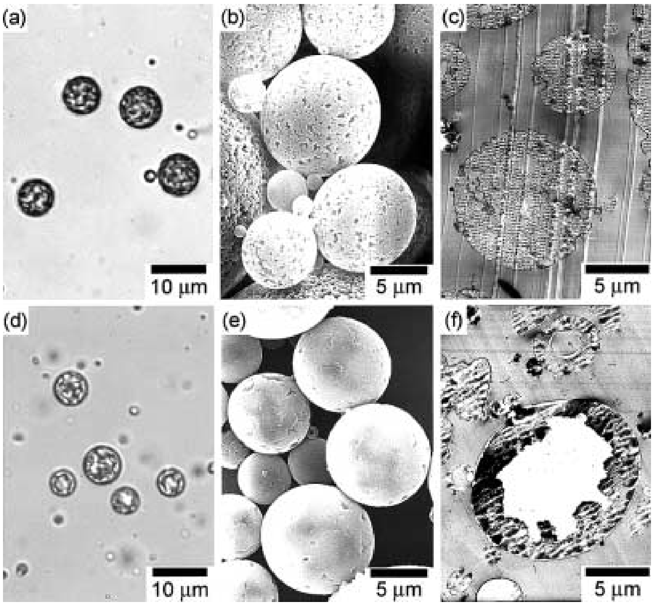

Fig. 4 Optical micrographs (**a**, **d**) and SEM photographs (**b**, **e**) of PS/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving PS having hydroxyl end groups under the conditions 2 and 3 listed in Table 2 and TEM photographs (**c**, **f**) of ultrathin cross sections of the composite particles exposed to RuO_4 vapor for 30 min. BPO, 2 wt% based on DVB. PS/PDVB (w/w): **a**, **b**, **c** 1/50 (no. 2); **d**, **e**, **f** 1/5 (no. 3). The end groups of PS prepared under the condition 3 listed in Table 1 were changed by hydrolysis from sulfate to hydroxyl groups

Table 3 Relationship between the interfacial tensions (measured by the du Noüy ring method at 23 ± 3 °C) between water and xylene/toluene (1/1, w/w) solutions of 0.01 wt% PS having various end groups and the structures (○, hollow; ●, nonhollow; ◐, hollow + nonhollow; ⊙, incomplete hollow) of composite particles produced by suspension polymerizations (N_2, 70 °C, 24 h) for DVB/toluene droplets dissolving the PS

End group	M_w ($\times 10^5$)	Interfacial tension (mN/m)[a]	PS content in the droplet (wt%)				
			1.0	2.4	4.8	9.1	20.0
$C(CH_3)_2CN$[b]	1.6	35.0	●	●	◐	○	○
SO_4^-[c]	2.2	22.9	●	●	●	●	●
	4.1	24.1	●	●	●	●	●
	8.2	27.1	●	●	●	●	●
OH[d]	4.1	31.0	●	⊙	⊙	⊙	⊙

[a] The values of PDVB and without polymer were 29.5 and 34.8 mN/m, respectively

[b] Prepared by solution polymerization with AIBN under the conditions listed in Table 1

[c] Prepared by emulsifier-free emulsion polymerizations with KPS under the conditions listed in Table 1

[d] Given by hydrolysis of the sulfate groups at the particle surfaces at 90 °C for 1 week at pH 1.0 adjusted with HCl

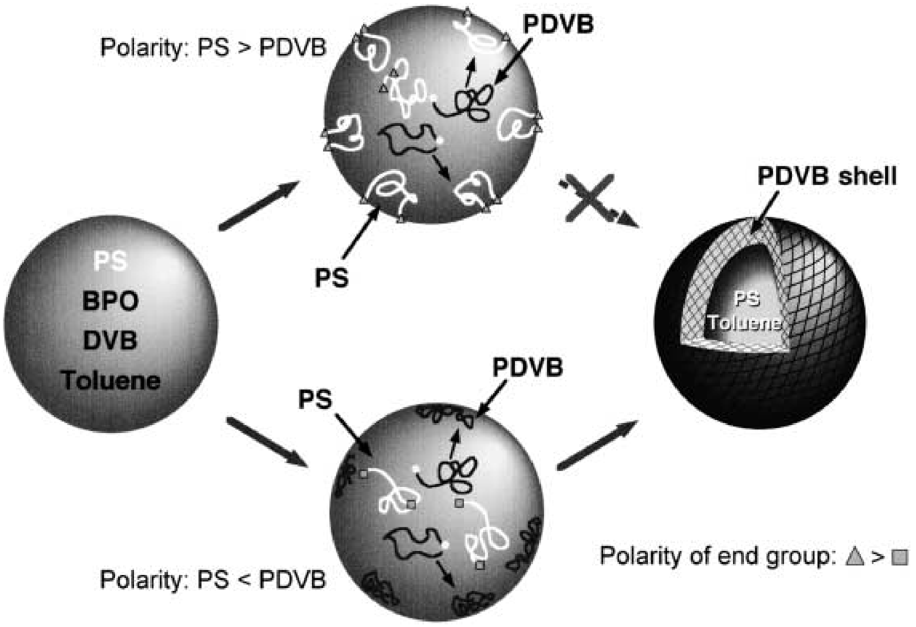

Fig. 5 Influence of end groups of PS dissolved in DVB/toluene droplets on the formation of the hollow structure

hollow particles are obtained. These results accord well with those obtained using various homopolymers that the adsorption of a homopolymer molecule at the interface of the droplet greatly affects the formation of the hollow structure [16].

From these results, it is concluded that the preferential adsorption of a PDVB molecule at the interface of the droplet over PS, which depends on the kind of the end groups, is one of the key factors for the formation of the hollow structure.

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