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SHORT COMMUNICATION

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Production of hollow polymer particles by suspension polymerizations for divinylbenzene/toluene droplets dissolving various polymers

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Abstract Suspension polymerizations for divinylbenzene/toluene droplets dissolving different kinds of methacrylate and acrylate homopolymers were carried out. Hollow polymer particles were produced not with high polarity polymers but with low polarity polymers. The results indicate that the preferential adsorption of the homopolymers having high polarity at the interface of the droplets depresses the formation of the hollow structure. A minimum polymer concentration was necessary to produce hollow particles.

Key words Suspension polymerization · Hollow · Porous · Particle · Interfacial tension

Introduction

Recently, micron-sized monodispersed polymer particles have been applied in the biomedical field, microelectronics, etc. Many research groups studying polymer colloids have concentrated 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 polymerizations of styrene and chloromethylstyrene and of styrene and divinylbenzene (DVB) in ethanol/water media in which almost all of the corresponding monomers and initiators dissolve. However, it was difficult to produce monodispersed particles of more than 5-μm-size even by dispersion polymerization and seeded dispersion polymerization.

Therefore, in order to produce such particles, we 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 the surface [11]. Such successes are based on the strong point of the technique that since almost all the monomers and initiators exist in the swollen particles, the seeded polymerizations proceed smoothly therein. Moreover, we developed this technique to produce micron-sized monodispersed cross-linked polymer particles having one hollow in the inside, where the seeded polymerization was carried out for about 5-μm-sized monodispersed highly (DVB/toluene) swollen PS particles prepared by the DSM [12, 13], and we discussed the formation mechanism of such hollow particles [14]. The cross-linking density and thickness of the PDVB shell had an important influence on the shape of the particles [15]. In previous work [16], hollow polymer particles were produced by suspension polymerization for DVB/toluene droplets dissolving PS. Throughout this experiment, it seems that PS in the droplets is one of the key factors for the formation of the hollow structure by

seeded polymerization with the DSM reported in the previous articles [12–15].

In this study, in order to clarify the function of the polymer dissolved in DVB/toluene droplets for the formation of the hollow structure in more detail, suspension polymerizations for DVB/toluene droplets dissolving various methacrylate and acrylate homopolymers were carried out.

Experimental

Materials

The monomers, except for DVB, were purified by distillation under reduced pressure in a nitrogen atmosphere. DVB was supplied by Nippon Steel Chemical. Co., Tokyo, Japan and the purity was 96%. DVB 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 Ind. Co., Osaka Japan. Benzoyl peroxide (BPO) and 2,2′-azobis(isobutyronitrile) (AIBN) of reagent grade were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Reagent grade toluene was used as received.

Various homopolymers were prepared by solution polymerizations with AIBN initiator in sealed glass tubes under the conditions listed in Table 1. The tubes were shaken horizontally at 80 cycles/min (3-cm strokes). Each homopolymer was purified by reprecipitation into methanol or petroleum ether and dried under reduced pressure. The molecular weight was measured by gel permeation chromatography with the calibration being obtained using PS standards with tetrahydrofuran as the elunt.

Soluble PDVB was prepared by solution polymerization with AIBN initiator in a sealed glass tube under the conditions listed in Table 1. The tube was shaken horizontally at 80 cycles/min (3-cm strokes). Inhibitor was added into the mixture just after polymerization, and toluene was evaporated under cooling. After that, PDVB was purified by reprecipitation into methanol and dried.

Suspension polymerizations

Solutions of DVB (250 mg) and toluene (250 mg) dissolving BPO (5 mg) and homopolymer (5 – 125 mg) were mixed with aqueous solutions (15 g) of 0.33 wt% PVA and stirred vigorously by a Nissei ABM-2 homogenizer 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 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).

Table 2 Suspension polymerizations (N_2, 70 °C, 24 h) for divinylbenzene (*DVB*)/toluene droplets dissolving various kinds of homopolymers

Ingredient	Condition 1	Condition 2
Polymer[a] (mg)	12.5	25
DVB[b] (mg)	250	250
Toluene (mg)	250	250
Benzoyl peroxide (mg)	5.0	5.0
Poly(vinyl alcohol) (mg)	50	50
Water (g)	15.0	15.0

[a] Prepared by solution polymerizations
[b] Purity, 96% (by catalog)

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 they were 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 tension between water and xylene/toluene (1/1, w/w) solutions of various homopolymers (0.01 wt%) was measured by the du Noüy ring method at room temperature with a Shimadzu DN surface tensiometer. Each homopolymer solution of 20 g was poured into water of 50 g and the measurement was carried out with a platinum ring of 19-mm diameter after 3 h in a cylindrical vessel (inner diameter, 65 mm; height, 37 mm).

Results and discussion

Optical micrographs and SEM photographs of the poly(*n*-butyl methacrylate) (P*n*-BMA)/PDVB composite

Table 1 Preparations of different kinds of homopolymers [polystyrene, *PS*, poly(*n*-butyl methacrylate), *Pn-BMA*, poly(ethyl methacrylate), *PEMA*, poly(methyl methacrylate), *PMMA*, poly(*n*-butyl acrylate), *Pn-BA*, poly(ethyl acrylate), *PEA*, poly(methyl acrylate), *PMA* and polydivinylbenzene, *PDVB*] by solution polymerizations

Polymer	PS[a]	P*n*-BMA[b]	PEMA[b]	PMMA[b]	P*n*-BA[b]	PEA[b]	PMA[b]	PDVB[c]
Monomer (g)	18	20	15	13	13	13	13	3
Toluene (g)	12	13	15	19	17	17	17	27
2,2-azobis(isobutyronitrile) (mg)	54	60	30	40	130	130	130	120
M_W[d] ($\times 10^5$)	1.6	2.5	2.9	1.4	1.9	3.8	3.0	0.2
M_w/M_n[d]	2.1	2.4	2.0	2.1	32.2	26.5	11.3	1.9

[a] 60 °C, 24 h, N_2
[b] 70 °C, 24 h, N_2
[c] 60 °C, 30 min, N_2
[d] Measured by gel permeation chromatography

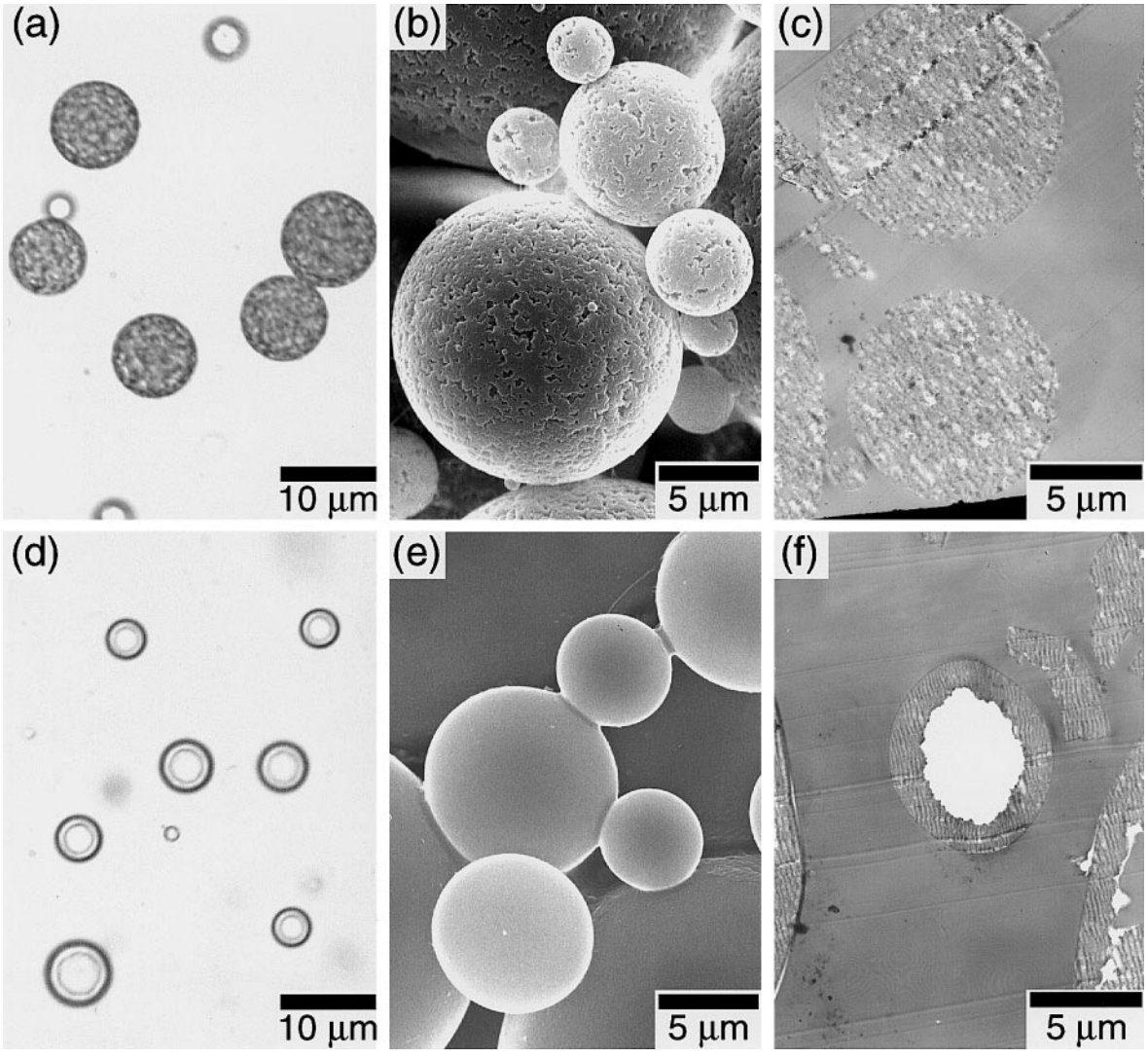


Fig. 1 Optical micrographs (**a**, **d**) and scanning electron microscope (*SEM*) photographs (**b**, **e**) of poly (*n*-butyl methacrylate) (*Pn-BMA*)/poly(divinylbenzene) (*PDVB*) composite particles produced by suspension polymerizations for divinylbenzene (*DVB*)/toluene (1/1, w/w) droplets dissolving benzyl peroxide (*BPO*) and P*n*-BMA under conditions 1 and 2 listed in Table 2 and transmission electron microscope (*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*n*-BMA in the droplets (wt%): (**a**, **b**, **c**) 2.4 (no.1); (**d**, **e**, **f**) 4.8 (no.2)

particles and TEM photographs of their ultrathin cross sections are shown in Fig. 1. The composite particles were produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of P*n*-BMA under the conditions listed in Table 2. P*n*-BMA/PDVB (1/20, w/w) composite particles did not have a hollow structure (Fig. 1a), but they had a porous structure (Fig. 1b, c). On the other hand, P*n*-BMA/PDVB (2/20, w/w) composite particles had a hollow structure (Fig. 1d, f) and had a smooth surface (Fig. 1e). These results indicating that the hollow polymer particles were produced at high contents of P*n*-BMA in DVB/toluene droplets were similar to those obtained with PS [15].

Optical micrographs and SEM photographs of the poly(ethyl methacrylate) (PEMA)/PDVB composite particles and TEM photographs of their ultrathin cross sections are shown in Fig. 2. The composite particles were produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of PEMA under the conditions listed in Table 2. It was observed that polymer particles had a porous structure at low contents of PEMA in the droplets (Fig. 2a–c) and a hollow structure at high contents of PEMA (Fig. 2d–f). These results are similar to those with PS or P*n*-BMA, although the inner surface of the PDVB shell was very rough.

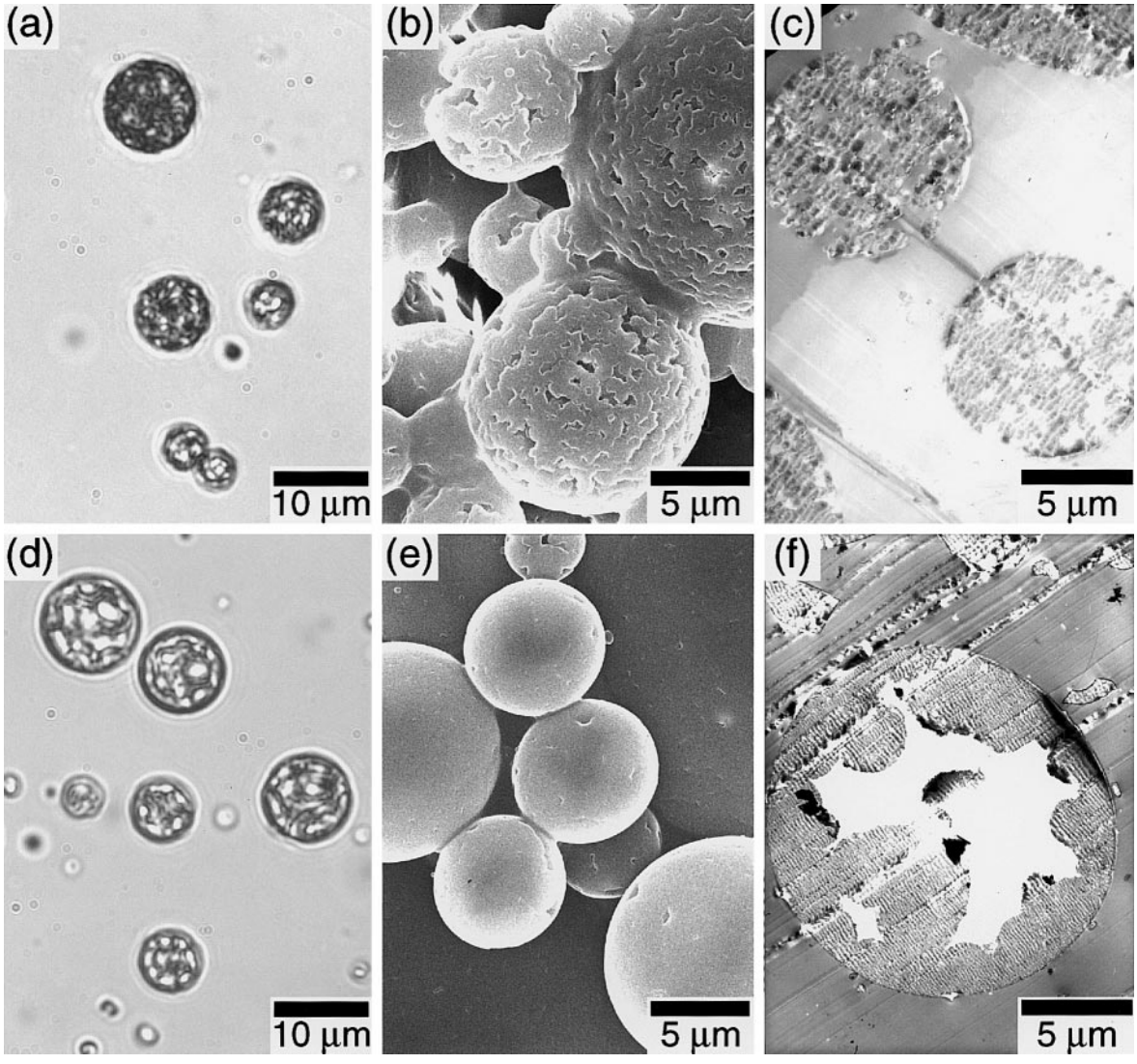
Optical micrographs and SEM photographs of the poly(methyl methacrylate) (PMMA)/PDVB composite

particles and TEM photographs of their ultrathin cross sections are shown in Fig. 3. They were produced by suspension polymerizations for DVB/toluene droplets dissolving different amounts of PMMA under the conditions listed in Table 2. In both cases, the PMMA/PDVB composite particles did not have hollow structures (Fig. 3a, c, d, f), but had rough surfaces (Fig. 3b, e).

The relationship between the interfacial tension between water and xylene/toluene (1/1, w/w) solutions of various homopolymers (0.01 wt%) and the structures of the composite particles produced by the suspension polymerizations for the DVB/toluene droplets dissolving different amounts of homopolymers is shown in Table 3. The solubility parameter (SP) values of the polymers are also shown in Table 3. At a polymer content of 1 wt% in the droplets, no hollow structure was observed in all the composite particles. At higher polymer content in the droplets, hollow polymer particles were produced by suspension polymerizations with PS, P*n*-BMA and poly(*n*-butyl acrylate), the interfacial tensions of which

Fig. 2 Optical micrographs (**a**, **d**) and SEM photographs (**b**, **e**) of poly(ethyl methacrylate) (*PEMA*)/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving BPO and PEMA under conditions of 1 and 2 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. PEMA in the droplets (wt%): (**a**, **b**, **c**) 2.4 (no. 1); (**d**, **e**, **f**) 4.8 (no. 2)

Fig. 3 Optical micrographs (**a**, **d**) and SEM photographs (**b**, **e**) of poly(methyl methacrylate) (PMMA)/PDVB composite particles produced by suspension polymerizations for DVB/toluene (1/1, w/w) droplets dissolving BPO and PMMA under conditions 1 and 2 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. PMMA in the droplets (wt%): (**a**, **b**, **c**) 2.4 (no.1); (**d**, **e**, **f**) 4.8 (no. 2)



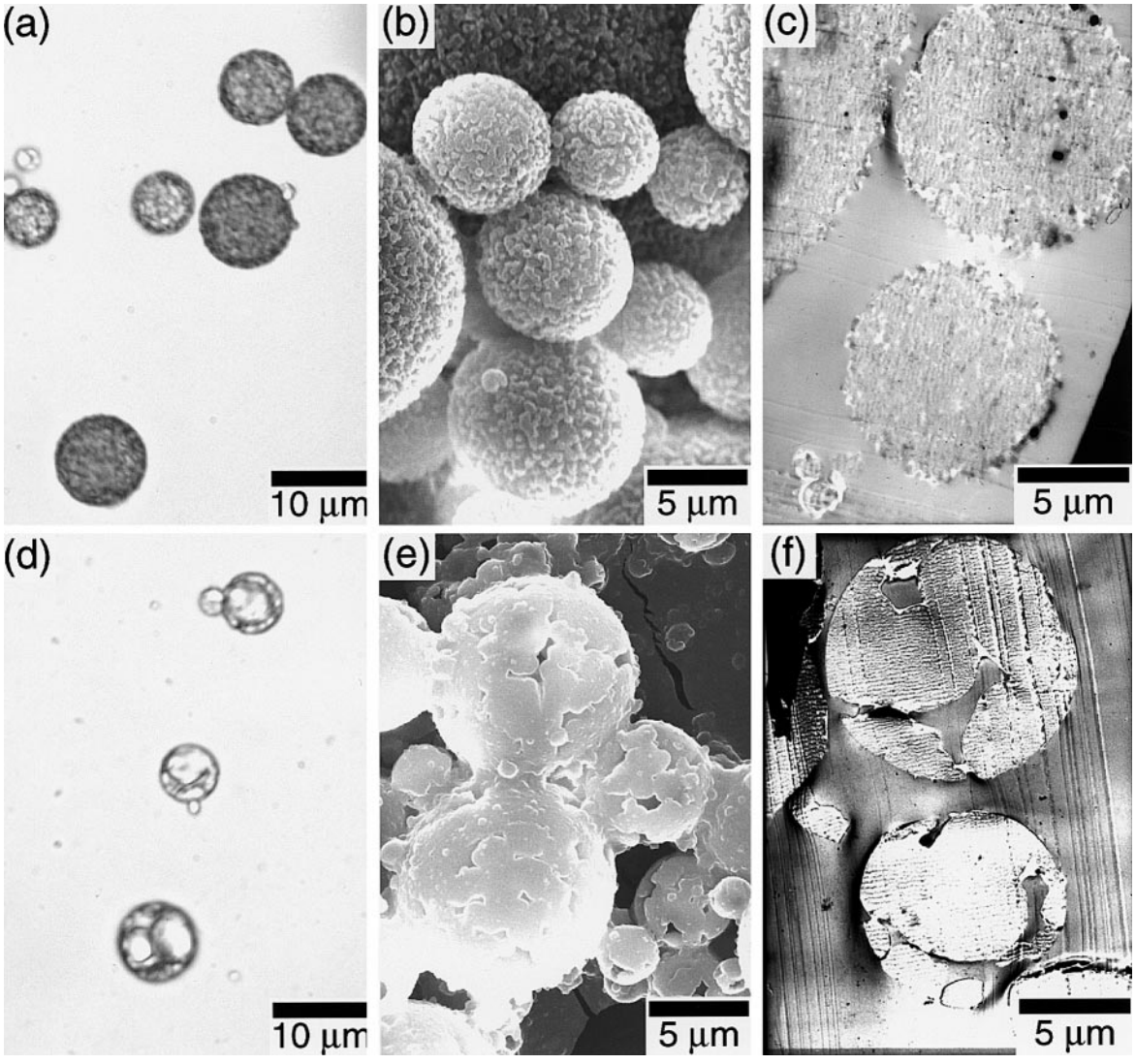


Table 3 Relationship between the interfacial tension (measured by the du Noüy ring method at 23 ± 3 °C) between water and xylene/toluene (1/1, w/w) solutions of various homopolymers (0.01 wt%) and the structures (○, hollow; ●, nonhollow; ◐, hollow + nonhollow; ⊙, incomplete hollow) of composite particles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

	Solubility parameter[a] $(MPa)^{1/2}$	Interfacial tension (mN/m)	Polymer content in the droplet (wt%)				
			1.0	2.4	4.8	9.1	20.0
PS	18.7	35.0	●	●	◐	○	○
P*n*-BMA	17.8	31.7	●	●	○	○	○
P*n*-BA	17.4	29.8	●	●	●	○	○
PEMA	18.2	25.5	●	●	⊙	⊙	⊙
PEA	19.8	22.4	●	⊙	⊙	⊙	⊙
PMMA	19.3	18.4	●	●	●	●	●
PMA	20.1	12.9	●	●	●	●	●

[a] Ref. [17]

were above about 30 mN/m. In the cases of PEMA and poly(ethyl acrylate), the interfacial tensions of which were in the range 20–30 mN/m, hollow polymer particles having a rough inner surface were observed and the structure of the shell was unclear. No hollow particles were produced in the cases of PMMA and poly(methyl acrylate), the interfacial tensions of which were below about 20 mN/m. The interfacial tensions between water and xylene/toluene (1/1, w/w) solution of 0.01 wt% PDVB and without polymer were 29.5 and 34.8 mN/m, respectively. These results suggest that the preferential adsorption of the homopolymers having high polarity (high SP value; low interfacial tension) at the interface over the PDVB depresses the formation of the hollow structure; on the other hand, those having low polarity promote it.

From these results, it is concluded that the polarity and the amount of homopolymer dissolving in DVB/toluene droplets greatly affect the formation of the hollow particles formed by suspension polymerization.

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