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SHORT COMMUNICATION

Preparation of hollow poly(divinyl benzene) particles with multiple holes in the shell by microsuspension polymerization with the SaPSeP method

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Abstract Hollow polymer particles with multiple holes in the shell were prepared by aqueous microsuspension polymerization of micrometer-sized, monodisperse divinylbenzene/*n*-hexadecane droplets in the presence of sodium dodecyl sulfate (SDS) at concentrations above 4 mM utilizing the *S*elf-*a*ssembling *P*hase-*Se*parated *P*olymer (SaPSeP) method developed by the authors. The total surface area of the holes per particle increased with an increase in the SDS concentration. At [SDS] = 10 mM, “flower-like” non-spherical particles were formed.

Keywords Microsuspension polymerization · Diffusion · Adsorption · Multiple holes

Introduction

Polymer particles with hollow structures have a range of industrial applications such as microcapsules, hiding or opacifying agents in coating and molding compositions [1–9]. We have successfully produced 5-μm-sized, monodisperse, cross-linked polymer particles with one hollow at the center by seeded polymerization of highly divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles [10, 11] prepared by the *d*ynamic *s*welling *m*ethod (DSM) [12–14]. On the basis of the proposed formation mechanism, hollow polymer particles were also prepared by microsuspension polymerization using DVB/toluene droplets containing dissolved PS and benzoyl peroxide (BPO), although they were polydisperse [15]. This synthetic route to hollow particles was named the *S*elf-*a*ssembling of *P*hase-*Se*parated *P*olymer (SaPSeP) method [16]. As the polymerization proceeds, PDVB microgels appear in the droplets because of cross-linking. They are adsorbed near the interface based on surface coagulation and gradually piled at the inner surface, which results in a cross-linked PDVB shell. PS that dissolves in toluene and DVB are repelled gradually to the inside. After the completion of polymerization, the PDVB shell entraps toluene and dissolving PS, then toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly [11]. PS was required to accelerate the phase separation of polydivinylbenzene (PDVB) formed during polymerization [17]. Phase separation at the early stage is required for the formation of the hollow structure because at low conversion, the PDVB can diffuse and adsorb to the interface of the droplets due to the low viscosity. Moreover, the kind of polymers [15] and end groups [18], which had different polarities, dissolved in DVB/toluene droplets greatly affected the formation of the hollow structure. An additional requirement is preferential adsorption of PDVB at the interface—if PS also adsorbs at the interface, shell formation does not occur. Moreover, microsuspension polymerizations of DVB droplets containing toluene and non-solvent *n*-hexadecane (HD; instead of PS) at various ratios were also carried out to prepare the hollow particles [19].

It has recently been reported that seeded polymerization with monodisperse DVB/PS/*p*-xylene (Xy) droplets in the presence of sodium dodecyl sulfate (SDS) at concentrations above 43.3 mM in addition to poly(vinyl alcohol; PVA) as colloidal stabilizer, resulting in hollow particles having a single hole in the shell [20]. Preparation of hollow polymer particles with a hole in the shell have been reported by

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Table 1 Typical recipe for preparations of DVB/HD/BPO droplets utilizing SPG membrane emulsification[a], and PDVB/HD particles by the SaPSeP method by microsuspension polymerization[b]

Ingredients		Emulsion	Polymerization[c]
DVB/HD/BPO dispersion[d]	(g)	–	11.0
DVB[e]	(g)	1.50	–
HD	(g)	1.50	–
BPO	(mg)	30.0	–
PVA	(g)	0.50	–
SDS[f]	(g)	–	0.48
Water	(g)	50.0	10.0

SPG Shiras porous glass, *DVB* divinylbenzene, *HD* *n*-hexadecane, *BPO* benzoyl peroxide, *PVA* poly(vinyl alcohol), *SDS* sodium dodecyl sulfate

[a] Pore size of SPG membrane: 1.1 μm, pressure, 72 kPa

[b] 70°C; 24 h, N_2, 60 cycles/min

[c] Total content of DVB, HD, BPO was 3.66 wt.% relative to total weight of dispersion.

[d] Prepared by SPG and washed with water three times using centrifugation at 3,000 rpm for 3 min, after the emulsification under the recipe listed in the column, the aqueous medium of the prepared dispersion was replaced three times with distilled water of which weight corresponded to 80~90% of the aqueous medium (50 g)

[e] Purity, 96% (by catalog)

[f] SDS concentration relative to water, 80 mM

others [21–26], but in all these cases, the hollow was excentered and the formation mechanisms differ from SaPSeP.

In this article, microsuspension polymerization of DVB droplets with HD (no PS) using the SaPSeP method was carried out in the presence of PVA and SDS as stabilizers in order to clarify the formation mechanism of the hole in the shell of the hollow particles.

Experimental

Materials

Divinylbenzene (DVB; DVB-960, Nippon Steel Chemical Co., Ltd., Japan) with a purity of 96% was washed with 1N sodium hydroxide and purified water to remove polymerization inhibitors before use. The water used in all experiments was obtained from an Elix® UV (Millipore Co., Ltd., Japan) purification system and had a resistivity of 18.2 MΩ cm^{-1}. PS (M_w: 1.6 × 10^5 g/mol, Wako Chemical Industries, Ltd., Japan) were used as received. PVA (Nippon Synthetic Chemical Ind. Co., Ltd., Japan; Gohsenol GH-17: degree of

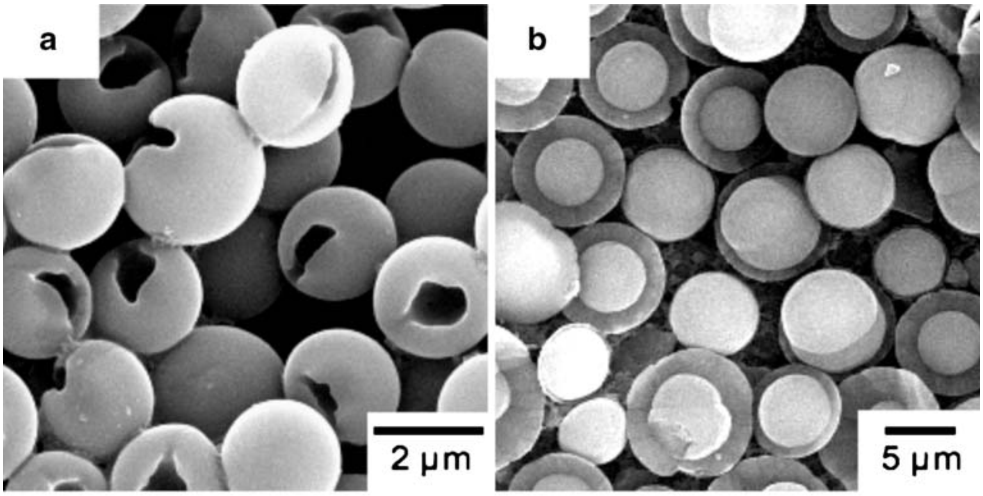
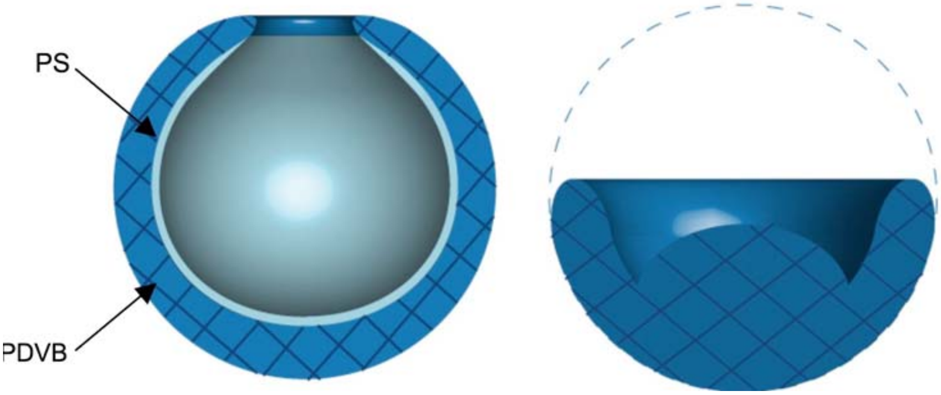


Fig. 1 SEM photographs of PS/PDVB composite particles **a** obtained by seeded polymerization of dispersions of monodisperse (DVB/Xy/BPO) droplets with dissolved PS prepared by DSM, and PDVB particles **b** obtained by microsuspension polymerization of DVB/HD/BPO (DVB/HD=1/1, *w*/*w*) droplets prepared by SPG membrane emulsification. SDS, 80 mM



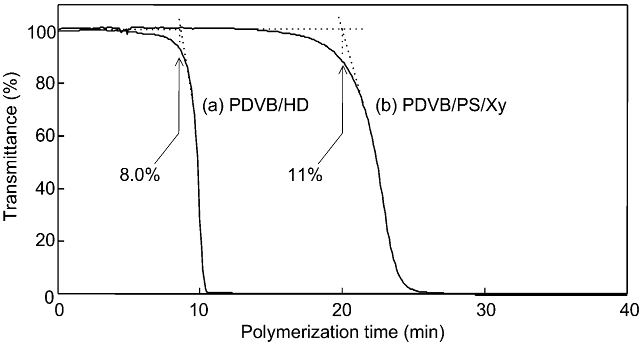


Fig. 2 Transmittances as functions of time for solution polymerization of DVB in HD **a** and in Xy containing dissolved PS (PS content, 10 wt.% based on DVB; M_w, 1.6×105) **b** initiated by BPO (BPO content, 2 wt.% based on DVB) at 70°C. Percentages in figure show the conversions of DVB

polymerization, 1700; degree of saponification, 88%), Sodium dodecyl sulfate (SDS) of extra pure reagent grade, *n*-hexadecane (HD), ethanol, xylene (Xy), and *N*, *N*-dimethylformamide (DMF; Nacalai Tesuque, Inc., Japan) were used as received. Reagent-grade benzoyl peroxide (BPO; Nacalai Tesuque, Inc., Japan) was purified by recrystallization.

SPG membrane emulsification and microsuspension polymerization

According to our previous study [15], a homogeneous solution of DVB, HD, and BPO was dispersed in a 1-wt.% PVA aqueous solution by use of the Shiras Porous Glass (SPG) membrane technique (Micro kit®, External pressure; SPG Technology Co., Ltd., Japan) under the conditions listed in Table 1. After three centrifugal washings of the dispersion to remove free PVA, various amounts of SDS were added. Microsuspension polymerizations were carried out at 70°C for 24 h under nitrogen atmosphere in sealed glass tubes at a shaking rate of 60 cycles/minute (10-cm stokes). It was confirmed that there was no difference in the droplets size distribution before and after the centrifugal washings. When the microsuspension was carried out without the centrifugal washing, a lot of coagulum was prepared because of byproduct of submicron-sized particles by emulsion polymerization.

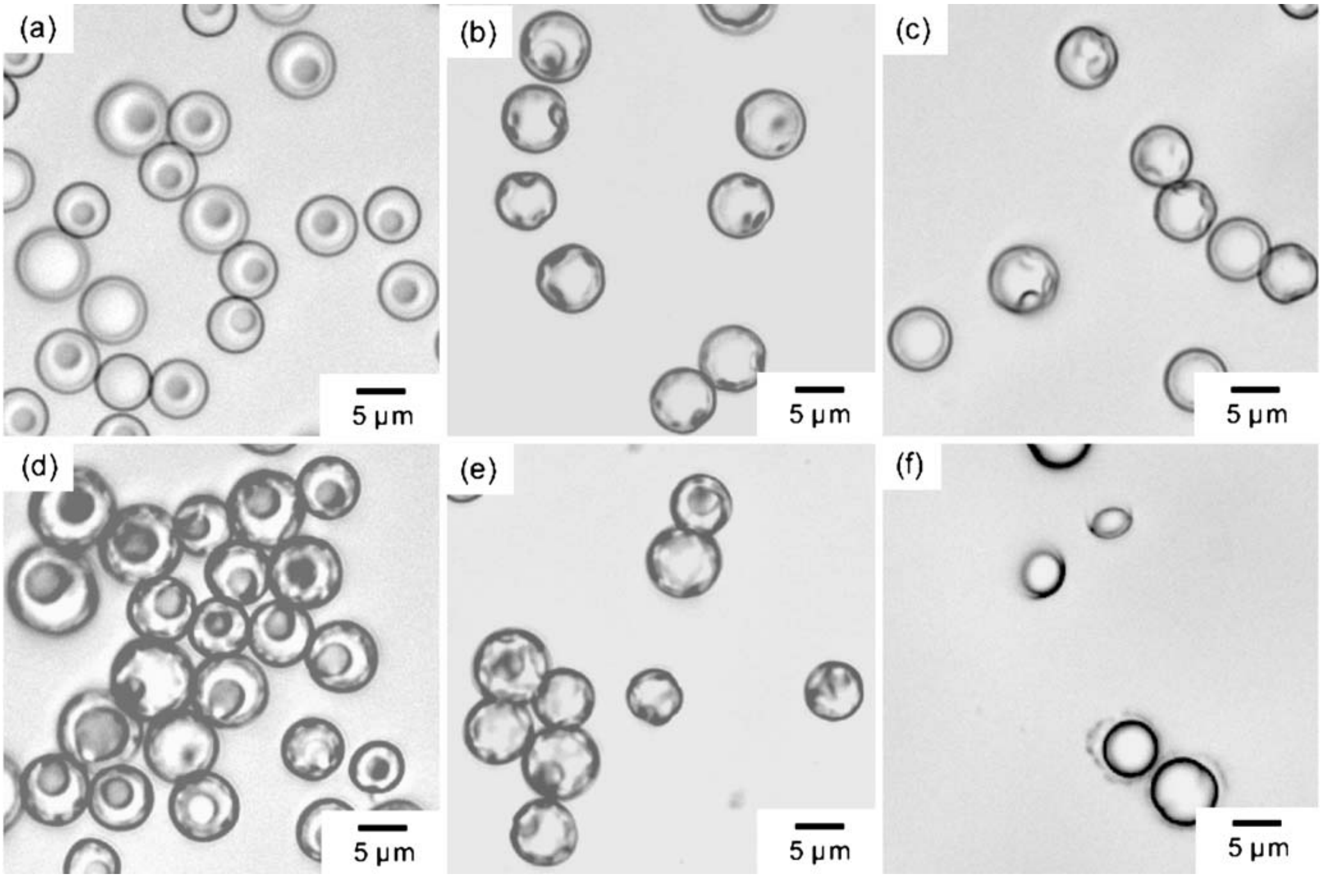


Fig. 3 Optical micrographs of PDVB particles prepared by microsuspension polymerizations using dispersions of DVB/HD/BPO (BPO content, 2 wt.% based on DVB). The droplets were prepared by SPG membrane emulsification. SDS (mM): **a** 0; **b** 3; **c** 3.75; **d** 4; **e** 5; (**f**) 10

Observation of particles

The hollow PDVB particles encapsulated HD (PDVB/HD particles) were observed with an optical microscope (Nikon ECLIPSE 80i, Nikon Co., Ltd., Japan). Five centrifugal washings were carried out to remove byproduct particles prior to scanning electron microscope (SEM; S-2460, Hitachi Science Systems, Ltd., Japan) observation. Particles sizes were measured using image analysis software (MacScope®, Mitani Co., Ltd., Japan) from optical microscope images based on >150 particles.

Observation of ultrathin cross sections of particles

The dried particles were microtomed (EMU-C6i, LEICA, Co., Ltd., Switzerland) after curing with epoxy resin. Ultrathin cross sections were observed with a transmission electron microscope (TEM) (JEM-1230, JEOL, Ltd., Japan).

Measurement of cloud conversion

The conversion of DVB was measured by gas chromatography (GC-18A, Shimazdu Co., Ltd., Japan) with helium as a carrier gas. In the DVB/HD system, DMF and Xy were used as internal standard and solvent, respectively. In the DVB/PS/Xy system, DMF and ethanol were used as internal standard and solvent. The phase separation behavior was estimated by transmittance of the polymerizing system. The solution polymerizations of DVB/PS/Xy/BPO and DVB/HD/BPO were carried out in a spectrophotometer cell at 70°C. The transmittance of the solution was measured with a SHIMAZDU UV-2500 at 550 nm. The cloud conversion, which indicates the conversion at the beginning of the phase separation, was measured by gas chromatography.

Evaporation behavior of HD from the particle

The evaporation behaviors of HD from PDVB/HD particles without/with multiple holes in the shell were examined by measurement of the weight loss of HD by thermogravimetry (TG/DTA 6200, Seiko Instrument, Japan). The measurement of the weight loss was carried out for 5-mg PDVB/HD particles without/with multiple holes in the shell, after burning each emulsion at 70°C for 30 min, on an aluminum pan (5-mm diameter) at a heating rate 10°C/min

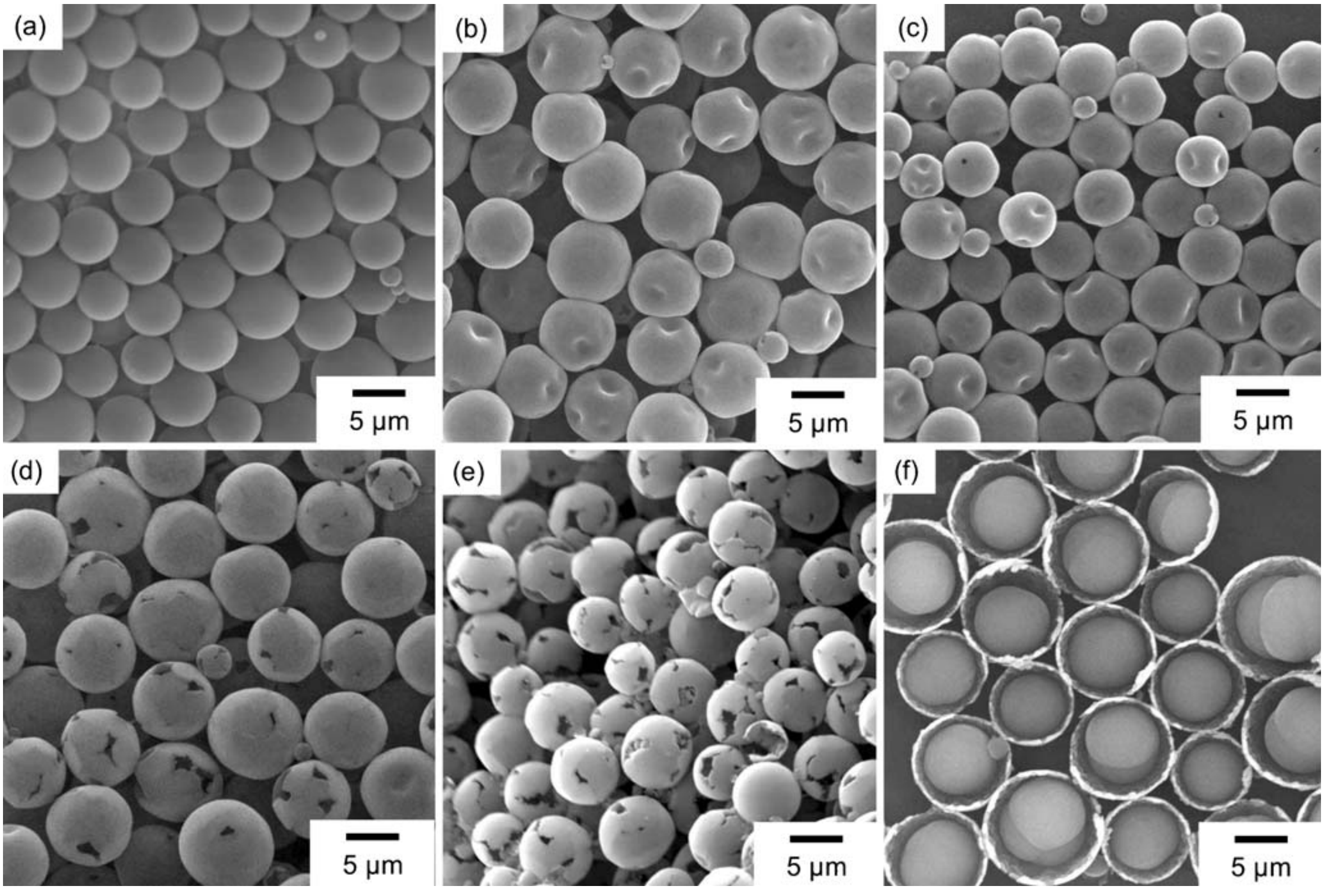


Fig. 4 SEM photographs of PDVB particles prepared by microsuspension polymerizations using dispersions of DVB/HD/BPO (BPO content, 2 wt.% based on DVB). The droplets were prepared by SPG membrane emulsification. SDS (mM): **a** 0; **b** 3; **c** 3.75; **d** 4; **e** 5; **f** 10

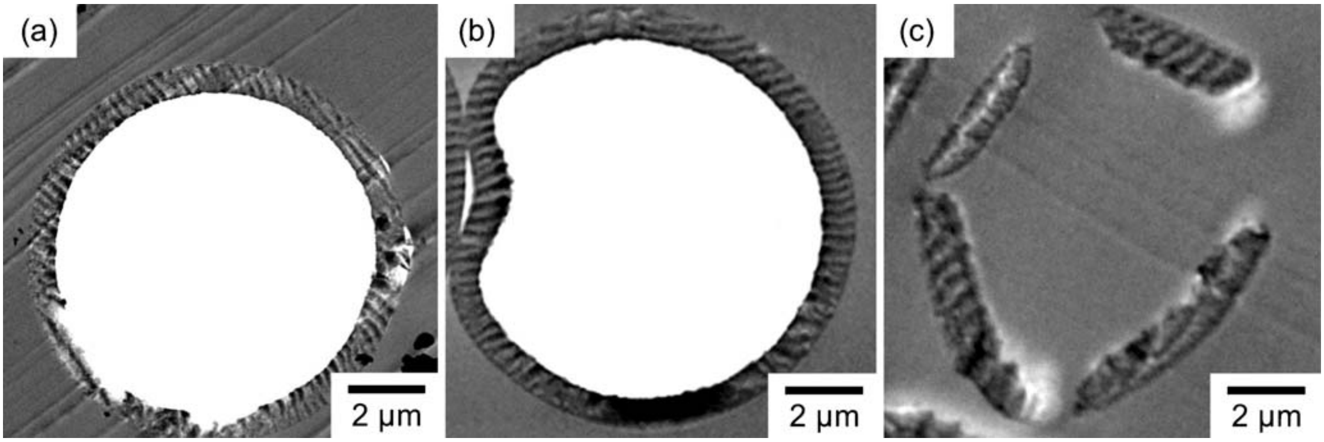


Fig. 5 TEM photographs of ultrathin cross sections of PDVB particles prepared by microsuspension polymerizations using dispersions of DVB/HD/BPO (BPO content, 2 wt.% based on DVB). The droplets were prepared by SPG membrane emulsification. SDS (mM): **a** 0; **b** 3.75; **c** 5

from 30°C to 150°C and hold for 30 min under a nitrogen atmosphere.

Results and discussion

Figure 1 shows SEM photographs of PS/PDVB composite particles (a) produced by seeded polymerization of monodisperse (DVB/Xy/BPO) droplets with dissolved PS prepared by DSM from our previous work [20], and PDVB particles (b) produced by microsuspension polymerization of DVB/HD/BPO (DVB/HD = 1/1, *w*/*w*) droplets prepared by SPG membrane emulsification in the present work (Table 1). Both polymerizations were carried out at [SDS] ≈ 80 mM. In the former seeded polymerization, hollow PS/PDVB composite particles with a single hole in the shell were obtained without coagulum. On the other hand, in the microsuspension system (Fig. 1b), the obtained PDVB particles exhibited a "flower-like" non-spherical morphology. The influence of HD on the formation of the hole in the shell was different from that of Xy containing dissolved PS. In the polymerization, numerous byproduct particles (hydrodynamic diameter (D_h) ≈ 300 nm) were also produced. This may be because the polymerizations were carried out at a high SDS concentration (80 mM), which was above the critical micelle concentration. Next, in order to understand the difference in both polymerization systems, each cloud conversion that indicates the conversion at beginning of the phase separation was measured.

Figure 2 shows the variations in the transmittance at 550 nm during solution polymerizations of DVB (a) in HD (b) in Xy containing dissolved PS (M_w, 1.6×10^5 g/mol) at 70°C. In both cases, the transmittance drastically decreased after a certain time, which indicates that the solution became turbid during the solution polymerization because of phase separation. In the case of DVB/HD, phase separation occurred at 9 min. On the other hand, in the case of DVB/PS/Xy, phase separation occurred at 20 min. The cloud conversions were 8.0% and 11% for DVB, respectively. In the microsuspension system, the phase-separated polymer microgels would be able to diffuse and adsorb to the interface more smoothly because of the low viscosity within the particle at the lower conversion. It seems that the phase separation behavior affects hole formation in the shell of the hollow particles.

Figures 3 and 4, show optical micrographs and SEM photographs respectively of PDVB particles prepared by microsuspension polymerization at various SDS concentrations under the conditions listed in Table 1 with a

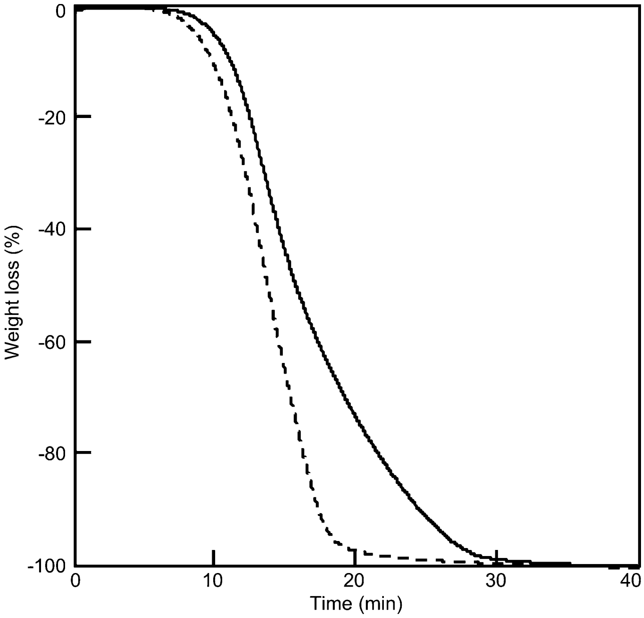


Fig. 6 TGA curves of HD in hollow particles without (*solid line*) and with (*dashed line*) multiple holes in the shell, measured with a heating rate of 10°C/min from 30°C to 150°C and hold for 30 min

1.1-μm-pore-sized SPG membrane. The PDVB particles size and these distributions were reflected of DVB/HD droplets. For example, in the case of [SDS] = 5 mM, the number average diameter and coefficient of variance of droplets and obtained PDVB particles were 6.3 μm, 23%, and 6.3 μm, 21%, respectively.

In the absence of SDS, PDVB particles with one hollow at the center were observed as the reported in previous study [10]. The shell and a water domain were observed clearly in the optical micrograph [27]. The amount of byproduct particles ($D_h \approx 300$ nm) was approximately 10wt.% relative to DVB monomer. At [SDS] = 3 and 3.75 mM, hollow PDVB particles with some dents were obtained. In previous studies, only PDVB hollow particles having a dent [27] or a red-blood-cell shape [28] were obtained because the shell strength was not sufficient to withstand the external pressure due to the evaporation of organic solvent or remaining monomer, causing part of the shell to buckle during the drying process. From these results, it seems that the phase-separated PDVB microgels might not adsorb uniformly to the droplet/water interface because of absorbed SDS, resulting in non-uniform shell thickness. The shell strength of the thinner part would not be sufficient to withstand the external pressure, resulting in multiple dents in the shell. At [SDS] = 4 and 5 mM, the hollow PDVB particles did not have a dent but multiple holes in the shell, which are characteristic in the case of HD. High dense SDS “domains” may be formed at the interface, to which PDVB microgels did not adsorb, resulting in multiple holes in the shell. The total surface area of the multiple holes per particle increased with an increase in SDS concentration, and some small particles having a big hole in the shell were observed. The amount of byproduct particles ($D_h \approx 300$ nm) was approximately 22wt.% relative to DVB monomer, which is much more than that in the absence of SDS. With an increase in SDS concentration, the byproduct particles would be nucleated by emulsion polymerization in the aqueous phase. At [SDS] = 10 mM, flower-like non-spherical particles similar to those in Fig. 1b were obtained. Thus, these flower-like non-spherical particles might be hollow particles with a single very large hole due to “big” SDS domain.

Figure 5 shows TEM photographs of ultrathin cross sections of hollow PDVB particles prepared at various SDS concentrations. At [SDS] = 0 and 3.75 mM, the hollow structure was complete, the thickness of the shell was uniform, and the epoxy resin used as embedding material did not permeate into the hollow. On the other hand, at [SDS] = 5 mM, some holes were observed in the shell and the hollow was occupied by epoxy resin having penetrated through the holes. The thickness of the shell was not uniform. These results indicate that PDVB microgels did not adsorb in a uniform manner to the interface.

Based on the above results, a mechanism for the formation of holes in the shell can be proposed: At the early stage of the microsuspension polymerization in the presence of SDS, phase-separated PDVB microgels adsorb at the oil–water interface in accordance with the SaPSeP mechanism. When the microgel concentration at the interface increases beyond a certain point, phase separation between the microgels and SDS occurs at the interface, resulting in domains of high SDS concentration. The driving force for adsorption of microgels at the interface at these areas of high SDS density is substantially reduced as a result of the reduction in the interfacial tension caused by the high SDS concentration, eventually, resulting in holes in the shell.

Figure 6 shows TGA curves of HD in hollow particles without/with multiple holes in the shell, measured with a heating rate of 10°C/min from 30°C to 150°C and held for 30 min. In both cases, the weight loss drastically decreased after a certain time, which indicates that HD evaporated. In the case of hollow particles with multiple holes (dot line), evaporation of HD is faster than that in the case of hollow particles without multiple holes (solid line). These results indicate that the evaporation rate of encapsulating materials can be controlled voluntarily using hollow PDVB particles without/with multiple holes. These specific properties of hollow particles will be reported in detail in the future.

Conclusions

Hollow PDVB particles with multiple holes in the shell were prepared by microsuspension polymerization at SDS concentration above 4 mM using the SaPSeP method. The total surface area of the holes per particle increased with increasing SDS concentration. At [SDS] = 10 mM, “flower-like” non-spherical particles were formed. Holes are formed as a result of reduced microgel adsorption at the oil–water interface domains of high SDS content.

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