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SHORT COMMUNICATION

Preparation of micrometer-sized, monodisperse, hollow polystyrene/poly(ethylene glycol dimethacrylate) particles with a single hole in the shell

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Abstract Micrometer-sized, monodisperse, hollow polystyrene (PS)/poly(ethylene glycol dimethacrylate) (PEGDM) composite particles with a single hole in the shell were prepared by seeded polymerization using (ethylene glycol dimethacrylate/xylene)-swollen PS particles in the presence of sodium dodecyl sulfate (SDS). Single holes were observed at SDS concentrations above 3 mM, much lower than in the PS/polydivinylbenzene (PDVB) system previously reported (above 45 mM). Phase separation inside droplets occurred at lower conversion in the PEGDM system than the PDVB system. Phase separation in the droplet at the early stage of the polymerization is an important factor for the formation of the single hole in the shell.

Keywords Micrometer size · Monodisperse · Hollow polymer particle · Single hole · Phase separation

Introduction

Submicrometer-sized polymer particles prepared by emulsion polymerization have been used as films in many industrial fields, for instance, in painting, printing, and manufacturing. Moreover, in recent years, attention has been focused on direct application as particles. For example, hollow polymer particles have received much attention as hiding or opacifying agents in coating and molding compositions [1–8].

Micrometer-sized, monodisperse polymer particles have also been the focus of much attention in advanced fields, such as microelectronics and biomedical fields, as well as other areas. A number of papers have reported preparation of such particles by dispersion polymerization [9–16], but in general, it is difficult to prepare monodisperse polymer particles having more than 5 μm in diameter using dispersion polymerization. To overcome this problem, we suggested a novel swelling method of seed polymer particles with a large amount of monomer, "dynamic swelling method (DSM)" [17, 18].

Moreover, we developed this technique to prepare micrometer-sized, monodisperse, cross-linked polystyrene/polydivinylbenzene (PS/PDVB) particles having a single hollow at the center obtained by seeded polymerization of [divinylbenzene (DVB)/organic solvent (such as toluene or xylene)]-swollen PS particles containing initiator prepared by the DSM [19]. Such hollow particles were also prepared by suspension polymerization, though they were polydisperse [20]. There are two requirements for the formation of the hollow structure [21, 22]: the formation mechanism of the hollow structure and clarified two required point: (1) phase separation in the droplets in the early stage of polymerization, (2) phase-separated PDVB preferentially adsorbs to the internal surface of the droplets. The formation of the hollow structure is based on the *s*elf-*a*ssembling of *p*hase-*se*parated *p*olymer at the internal surface of the droplet, named the SaPSeP method [23].

Application of the SaPSeP in the presence of sodium dodecyl sulfate (SDS) in addition to polyvinyl alcohol as colloidal stabilizer results in the formation of a single hole in the shell of the hollow PS/PDVB composite particles [24]. It had been reported that the yield of the hollow particles with a single hole increased with the SDS concentration, resulting in 100% at 45 mM. The preparation

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Table 1 Recipes for preparations of a dispersion of (BPO/EGDM/xylene)-swollen PS particles utilizing DSM at room temperature and PS/PEGDM particles by subsequent seeded polymerization

Ingredients	DSM	Seeded polymerization
(EGDM/xylene/BPO)-swollen PS particles (mg)		636
PS[a] (mg)	30	–
EGDM[b] (mg)	300	–
Xylene (mg)	300	–
BPO (mg)	6	–
PVA (mg)	15	–
Ethanol (g)	7	–
Water (g)	3+40[c]	50
SDS (mM)	–	0–40

Subsequent seeded polymerization: N_2, 70 °C, 3 h, 60 cycles/min shaking

PS poly(styrene), *EGDM* ethylene glycol dimethacrylate, *BPO* benzoyl peroxide, *PVA* poly(vinyl alcohol), *SDS* sodium dodecyl sulfate

[a] Prepared by dispersion polymerization: 1.75 μm; C_v, 3.31%

[b] Purity, 95% (by catalog)

[c] Post-addition of 40.0 g water at the rate of 2.66 ml/h

of hollow polymer particles having a hole in the shell was reported by others [25–30], but the hollow was ex-centered. The formation mechanism of such particles is expected to be different from that of the hollow composite particles with the single hole in the shell prepared using SaPSeP.

In this article, seeded polymerizations using [(ethylene glycol dimethacrylate (EGDM)/xylene)]-swollen PS particle in the presence of SDS were investigated in order to clarify the formation mechanism of the single hole in the shell using SaPSeP and develop it with other monomers.

Experimental

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. DVB was supplied by Nippon Steel Chemical Co. Ltd. (Tokyo, Japan). The purity of DVB, which included ethylvinylbenzene, was 96%. DVB and EGDM of reagent grade (Nacalai Tesque, Kyoto, Japan) were washed with 1 N NaOH and distilled water to remove polymerization inhibitors before use. The water used in all experiments was obtained from Elix® UV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ·cm^{-1}. PS (M_w, 1.6×10^5 g/mol; Wako Chemical, Kanagawa, Japan) were used as received. Benzoyl peroxide (BPO) and 2,2′-azobis-(isobutyronitrile; AIBN) of reagent grade (Nacalai Tesque) were purified by recrystallization. Poly(vinyl alcohol) (PVA) as a stabilizer was supplied by Nippon Synthetic Chemical Ind. Co. Ltd. (Osaka, Japan; Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Poly(acrylic acid) (PAA) used as a stabilizer was prepared by solution polymerization of acrylic acid in 1,4-dioxane according to a previous article.[11] SDS of extra pure reagent grade and ethanol, xylene, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and tetrahydrofuran of reagent grade (Nacalai Tesque) were used as received.

Preparation of PS seed particles

Micrometer-sized, monodisperse PS seed particles were prepared under optimum dispersion polymerization conditions [11] at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask. Styrene (46.7 g), ethanol (320 g), water (93.9 g), and PAA (5.6 g) were added to the reaction flask, and the mixture was stirred with an anchor-type stirrer at 100 rpm under a nitrogen atmosphere. After the solution was heated to 70°C, AIBN (0.8 g) solution was poured into the reaction flask. The particles were observed with transmission electron microscope (TEM, JEM-1230, JEOL Ltd., Tokyo, Japan). The number average diameter and the coefficient of variation were 1.75 μm and 3.3%, respectively.

Swelling of PS seed particles with EGDM and xylene utilizing the DSM and seeded polymerization

EGDM (0.3 g), xylene (0.3 g), BPO (6 mg), ethanol (7 g), water (3 g), and PVA (1.5 mg) were charged into a glass cylindrical reactor. The PS seed particles (0.03 g) were

Table 2 Recipes for preparations of PS/BPO/EGDM/xylene droplets utilizing SPG membrane emulsification and PS/PEGDM particles by subsequent micro-suspension polymerization

Ingredients	SPG emulsification	Micro-suspension polymerization
PS/BPO/EGDM/xylene droplets[a] (g)		30
PS[b] (mg)	37.5–150	–
EGDM[c] (g)	1.5	–
Xylene (g)	1.5	–
BPO (mg)	30	–
PVA (mg)	600	–
Water (g)	60	90
SDS (mg)	–	173

SPG membrane emulsification: pore size of membrane, 1.1 μm; subsequent micro-suspension polymerization: N_2, 70 °C, 3 h, 60 cycles/min shaking

SPG Shirasu porous glass

[a] Prepared by SPG membrane emulsification and washed with water times using centrifugation at 4,000 rpm for 10 min

[b] Prepared by solution polymerization: M_w, 1.6×10^5 g/mol

[c] Purity, 95% (by catalog)

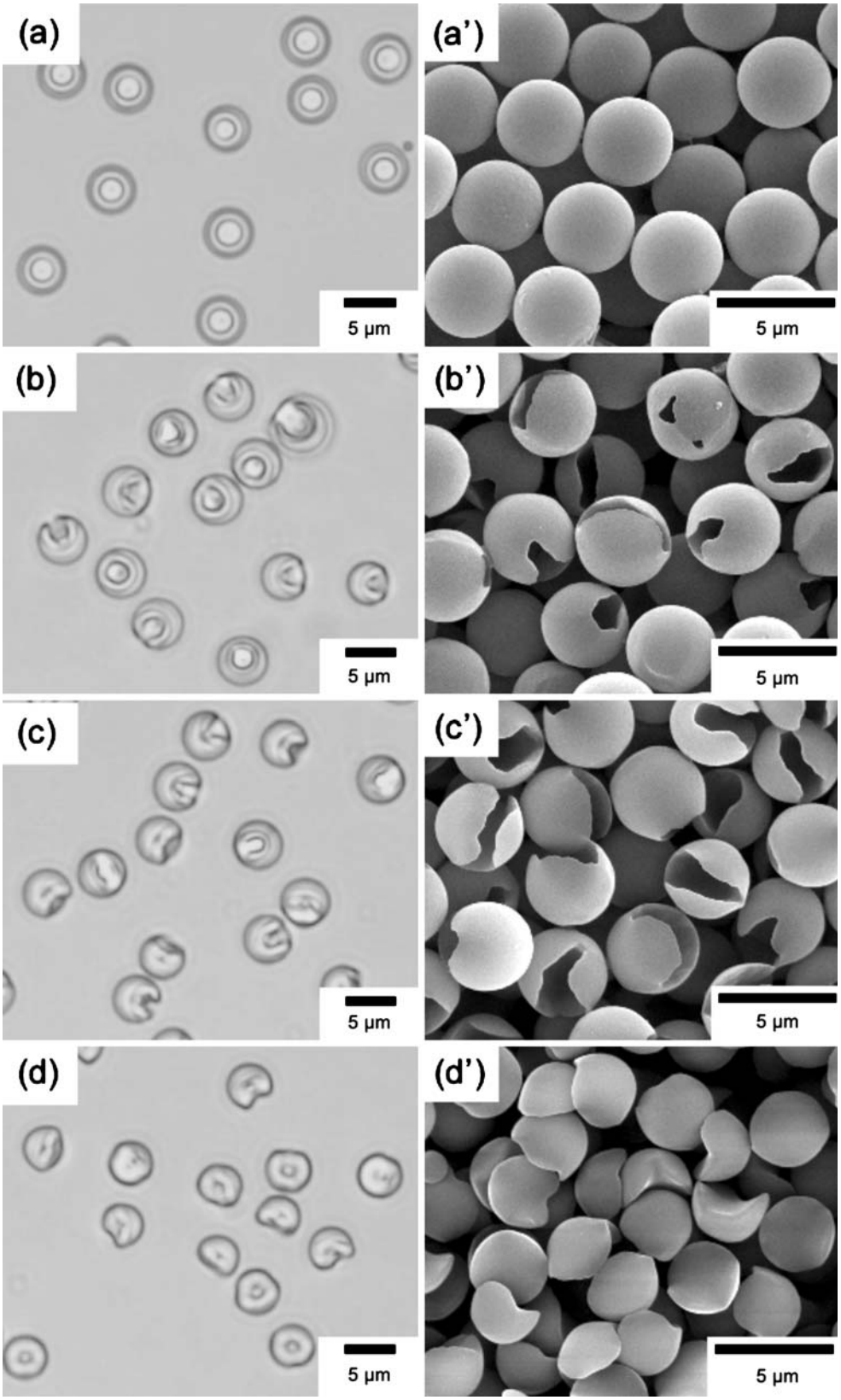

Fig. 1 Optical micrographs (**a**–**d**) and SEM photographs (**a′**–**d′**) of PS/PEGDM particles prepared by seeded polymerizations of dispersions of (EGDM/xylene/BPO)-swollen PS particles in the absence and presence of SDS (Table 1). SDS concentration (mM): **a**, **a′** 0; **b**, **b′** 3; **c**, **c′** 5; **d**, **d′** 40

dispersed in the above homogeneous solution. Finally, water (40 g) was added to the mixture at a rate of 2.66 ml/h with a micro-feeder under magnetic stirring at room temperature. Various amounts of SDS were added to the ethanol/water (7:43, *w*/*w*) medium of the dispersion of (EGDM/xylene)-swollen PS particles prepared utilizing the DSM. Seeded polymerizations were carried out in sealed glass tubes under a nitrogen atmosphere at 70 °C for 3 h (Table 1). The tubes were shaken horizontally at 60 cycles/min (3-cm strokes).

SPG membrane emulsification and micro-suspension polymerization

Homogeneous solutions of EGDM (1.5 g), xylene (1.5 g), BPO (7.5 mg), and various amounts of PS were forced continuously by nitrogen gas pressure through the Shirasu Porous Glass (SPG) membrane (pore size, 1.1 μm; SPG Technology, Japan) into 1 wt% PVA aqueous solution (60 g). The excess PVA in the aqueous phase was subsequently removed by centrifugation at 4.0×10^3 rpm for 10 min. SDS (173 mg) was added to the final aqueous medium. Micro-suspension polymerizations were carried out in sealed glass tubes under a nitrogen atmosphere at 70 °C for 3 h (Table 2). The tubes were shaken horizontally at 60 cycles/min (3-cm strokes).

Measurements

The conversion of EGDM was measured by gas chromatography (Shimazdu Corporation, GC-18A) with helium as a carrier gas. DMSO and DMF were used as internal standard and solvent, respectively. In the measurement of the conversion of DVB, DMF and ethanol were used as internal standard and solvent, respectively.

Polymer particles were observed with a Nikon ECLIPSE 80i optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

The phase separation behavior was estimated by transmittance of the polymerizing system. The solution polymerizations of monomer in xylene (monomer/xylene, 1:1 *w*/*w*) containing dissolved PS and 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.

Results and discussion

Figure 1 shows optical micrographs (a–d) and SEM photographs (a′–d′) of PS/PEGDM particles prepared by seeded polymerizations of (EGDM/xylene/BPO)-swollen PS particles at various SDS concentrations. The swollen PS particles were prepared by DSM [17, 18]. In all systems, the polymerizations proceeded smoothly with the conversion, reaching almost 100% in 3 h regardless of the absence or presence of SDS. By-product particles were generated, which were not clear in optical micrographs. In order to prepare SEM samples, by-product particles were removed by serum replacement under centrifugation at 2.0×10^3 rpm for 10 min. In the absence of SDS, the particles were monodisperse and had low contrast region at the center as shown in the optical micrograph (a), which indicates the hollow structure. In the SEM photograph (a′) as well as the optical micrograph, no hole was formed in the shell of the hollow polymer particles. In the presence of SDS (above 3 mM), a single hole was formed in the shell, and the open surface area due to the hole increased with an increase in the SDS concentration. At an SDS concentration of 40 mM (d, d′), the occupied percentage of the open surface area was approximately 50%, resulting in non-spherical particles. The particle size was smaller than at low SDS concentrations because of generation of a lot of a significant number of by-product particles.

As reported previously [24], hollow PS/PDVB particles with a single hole in the shell were formed in the presence of SDS at concentrations above about 40 mM. The SDS concentration required for the formation of the single hole in PEGDM system was as low as one tenth of the SDS concentration in the PDVB system. In addition, the percentage of the hole occupied at the shell surface was higher in the PEGDM system (10% at 5 mM of SDS concentration). Such large holes were not formed in the PDVB system even at high SDS concentration (5% at 78 mM of SDS concentration) [24].

The formation mechanism of hollow polymer particles by SaPSeP has been proposed as follows [21, 22]. As the polymerization proceeds, polymer microgels are formed and phase separation occurs in the droplets. The microgels

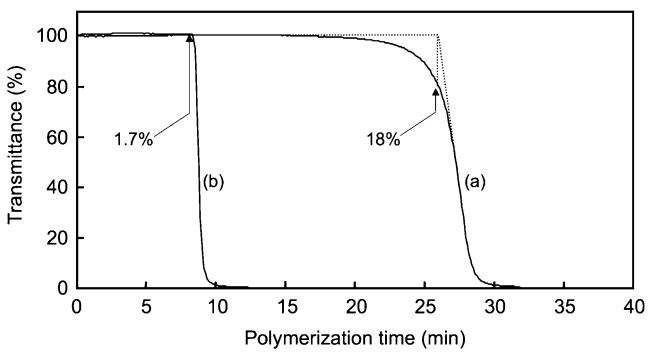

Fig. 2 Transmittance as a function of time at 70 °C for solution polymerizations of DVB (**a**) and EGDM (**b**) in xylene containing dissolved PS (10 wt% based on monomer) initiated by BPO. *Numbers* indicate the conversions at which the transmittance began to decrease drastically

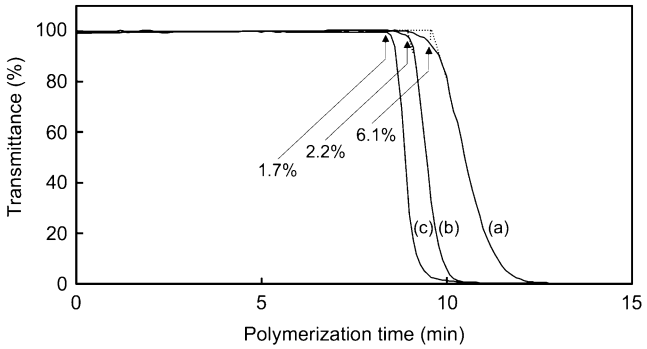

Fig. 3 Transmittance as a function of time at 70 °C for solution polymerizations of EGDM initiated by BPO (2 wt% based on EGDM) in xylene containing different amounts of dissolved PS: contents (wt% based on EGDM): **a** 2.5, **b** 5.0, **c** 10. *Numbers* indicate the conversions at which the transmittance began to decrease drastically

are preferentially adsorbed to the inner interface of the droplet to reduce the interfacial tension. The phase-separated polymer microgels gradually self-assemble at the inner interface, resulting in the formation of the cross-linked shell. Moreover, phase separation at an early stage of the polymerization was an important factor for the formation of the hollow structure because the viscosity in the droplet is low at the low conversion, and the phase-separated polymer is able to diffuse at the inner interface of the droplet [21]. On the basis of this mechanism, the phase separation behavior was investigated to understand the reason why single holes form at different SDS concentrations in the PEGDM and PDVB systems.

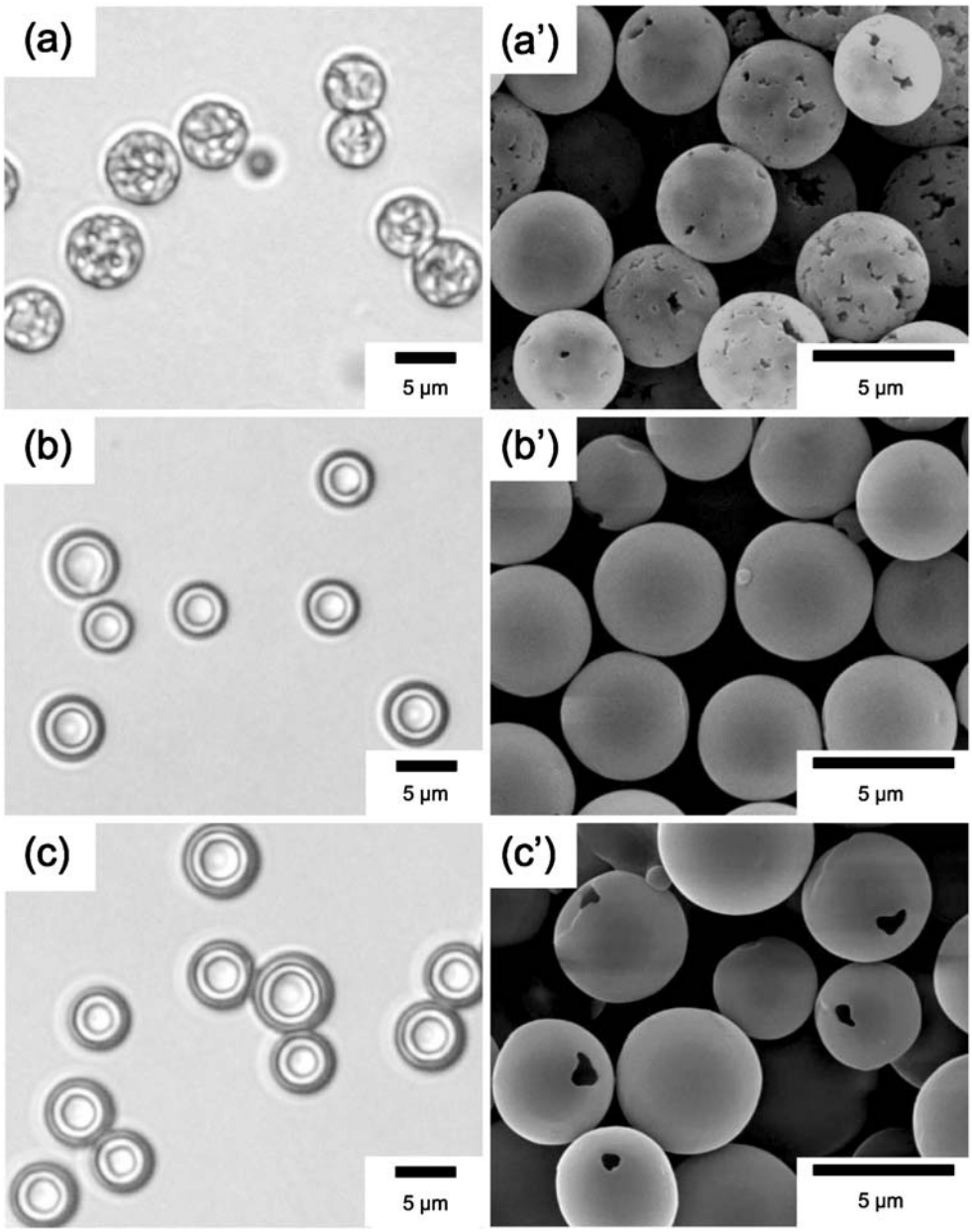

Fig. 4 Optical micrographs (**a**–**c**) and SEM photographs (**a′**–**c′**) of PS/PEGDM composite particles prepared by micro-suspension polymerizations using a dispersion of PS/EGDM/xylene/BPO droplets (BPO content, 2 wt% based on EGDM) in the presence of SDS (5 mM) under the conditions listed in Table 2: PS contents (wt% based on EGDM): **a**, **a′** 2.5; **b**, **b′** 5.0; **c**, **c′** 10. The droplets were prepared by SPG membrane emulsification

Figure 2 shows the variations in the transmittance at 550 nm during solution polymerizations of DVB (a) and EGDM (b) in xylene (monomer/xylene, 1:1 *w*/*w*) 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 absence of dissolved PS, phase separation did not occur in both cases. In the case of EGDM, phase separation occurred at 8.5 min, whereas for DVB, phase separation occurred at 26 min. The cloud conversions, which indicate the conversion at beginning of the phase separation, were 1.7% and 18% for EGDM and DVB, respectively. In the EGDM system, the phase-separated polymer microgels would be able to move 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 the single hole formation in the shell of the hollow particles.

It has previously been reported that phase separation occurs at shorter time with increasing PS content in the DVB system [21].

Figure 3 shows the variations in the transmittance at 550 nm during solution polymerization of EGDM in xylene (monomer/xylene, 1:1 *w*/*w*) containing different amounts of dissolved PS (M_w, 1.6×10^5 g/mol) at 70 °C. The time of phase separation decreased with an increase in the PS contents, which was the same as that in DVB system. The cloud conversions were 6.1%, 2.2%, and 1.7% for 2.5, 5.0 and 10 wt% PS, respectively.

In order to examine the effect of the concentration of PS dissolved in EGDM/xylene/BPO droplets on the formation of the hole, micro-suspension polymerizations were carried out with comparatively monodisperse droplets of similar size to those prepared by DSM (prepared by SPG emulsification). The optical micrographs (a–c) and SEM photographs (a′–c′) of PS/PEGDM particles prepared are shown in Fig. 4. At the PS content of 2.5 wt%, obtained particles were not hollow but porous (a) and had several holes at the surface (a′). The cloud conversion was higher (6.1%) than in the other systems (2.2%, 1.7%; PS contents, 5, 10 wt%). The viscosity at the beginning of phase separation was higher for 2.5 wt% PS than 5.0 and 10 wt % PS, although the initial viscosity of the 2.5 wt% PS system was lower than for 5 and 10 wt% PS. This phenomenon was also observed for the DVB system [21]. Although the cloud conversion (6.1%) in the EGDM system at the PS content of 2.5 wt% (Fig. 3) was lower than (18%) in the DVB system, the viscosity in the EGDM system was higher than for the DVB system. The state of EGDM system at phase separation was rigid and with no fluidity, whereas the DVB system retained fluidity at phase separation. Consequently, the adsorption of PEGDM microgels at the interface of the droplet (inner wall of shell) was suppressed, resulting in porous particles. At 5 wt% PS, all particles had a hollow structure, and some particles had a single hole in the shell. At 10 wt%, a single hole in the shell was obtained in almost all particles, though the hole of several particles were not visible due to the angle of SEM observation. The fraction of hollow particles with a single hole seemed to increase with the PS content. It seems likely that the formation of the hole was related to the viscosity in the droplet, which affects the mobility of phase-separated PEGDM microgels.

Conclusions

Micrometer-sized, monodisperse, hollow PS/PEGDM composite particles with a single hole in the shell were successfully prepared by seeded polymerization of (EGDM/xylene)-swollen PS particles in the presence of SDS. In comparison with the corresponding DVB system, there was a clear difference in the amount of SDS required to obtain hollow particles with a single hole and the area of the hole. The phase separation in the droplets in the early stage of the polymerization was one of key factors for the formation of the single hole. The formation mechanism of the hole remains to be clarified, and work is currently in progress to elucidate the mechanistic details of this process.

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