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## Formation mechanism of micron-sized monodispersed polymer particles having a hollow structure

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**Abstract** Recently, the authors reported that micron-sized monodispersed cross-linked polymer particles having a single hollow in the inside were produced by seeded polymerization for the dispersion of (toluene/divinylbenzene)-swollen polystyrene (PS) particles prepared utilizing the dynamic swelling method which the authors had proposed. In this article, the particles at various conversions of the seeded polymerization were observed with an optical microscope in detail. From the obtained results, the formation mechanism of the hollow structure is suggested as follows. As seeded polymerization proceeds, poly-

divinylbenzene (PDVB) molecules precipitated in the swollen particle are trapped near the interface and gradually pile at the inner surface, which results in a cross-linked PDVB shell. PS which dissolves in the swollen particles is repelled gradually to the inside. After the completion of the polymerization, toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly.

**Key words** Dynamic swelling method – hollow – micron-size – monodisperse – cross-linking – formation mechanism

### Introduction

Micron-sized monodispersed polymer particles have been applied in the biomedical field, micro-electronics, etc. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed polymer particles [1–5]. We have been producing micron-sized monodispersed polystyrene (PS) particles having functional groups such as chloromethyl [6] and vinyl groups [7, 8] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2  $\mu\text{m}$ -sized monodispersed PS particles as seed. Micron-sized monodispersed polymer particles having multihollow structures were also

produced by extraction of PS with toluene under reflux from micron-sized monodispersed PS/poly(styrene-divinylbenzene) composite particles produced by seeded dispersion copolymerization [9].

Moreover, in order to produce monodispersed particles having the diameter above 5  $\mu\text{m}$ , we suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named "the dynamic swelling method (DSM)" [10, 11]. In a previous paper [12], we developed this technique to produce micron-sized monodispersed polymer particles having one hollow in the inside. We also succeeded in controlling the hollow size [13].

In this article, the formation mechanism of hollow structure in the micron-sized monodispersed polymer particles will be discussed.

## Experimental

### Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) was washed with 1 N NaOH and deionized water to remove polymerization inhibitors before use. The supplied DVB included ethylvinylbenzene and diethylbenzene, and the purity was 55%. Benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) of reagent grade were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Polyvinyl alcohol (PVA) was supplied by Nippon Synthetic Chemical Ind. Co. Ltd. (Gohsenol GH-17; degree of polymerization, 1700; degree of saponification; 88%). Poly(acrylic acid) (PAA) used as a stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane [6]. Reagent-grade ethanol and toluene were used as received.

### Preparation of polystyrene (PS) seed particles

Micron-sized monodispersed PS seed particles were produced by dispersion polymerization of styrene in ethanol/water (7/3, w/w) medium with AIBN initiator at 70°C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask. The optimum conditions have been reported in the previous article [6]. The PS seed particles were spherical and monodispersed: the number-average diameter ( $D_n$ ) and coefficient of variation ( $C_v$ ) were 1.71  $\mu\text{m}$  and 2.2%, respectively.

### Swelling of seed particles with DVB and toluene utilizing DSM

Swelling of the PS seed particles with DVB (or styrene) and toluene was carried out under the recipes listed in Table 1 using DSM as follows: Ethanol, water, DVB (or styrene), toluene, BPO and PVA were charged into a four-necked round-bottom flask or into a glass cylindrical reactor. To this homogeneous solution, the PS seed particles were dispersed. Finally, water was added to the mixture with a micro feeder at a rate of 18 ml/h or 2.88 ml/h under stirring.

### Seeded polymerization

Seeded polymerizations for the dispersions of (toluene/DVB) and (toluene/styrene)-swollen PS particles were

**Table 1** Recipe for the productions of PS/PDVB (1/5.5, w/w) composite particles and PS particles by seeded polymerizations<sup>a)</sup> for the dispersions of (toluene/DVB)- and (toluene/styrene)-swollen PS particles prepared utilizing dynamic swelling method at room temperature

Ingredient [g]	No. 1 <sup>b)</sup>	No. 2 <sup>c)</sup>
PS particles <sup>d)</sup>	0.3	0.03
DVB <sup>e)</sup>	3.0	0
Styrene	0	0.3
Toluene	1.5	0.15
BPO	0.06	0.015
PVA	0.15	0.015
Ethanol	70	6
Water	30 + 400 <sup>f)</sup>	4 + 40 <sup>g)</sup>

<sup>a)</sup> N<sub>2</sub>, 70°C, 24 h.

<sup>b)</sup> Polymerization was carried out in a four-necked round-bottom flask.

<sup>c)</sup> Polymerization was carried out in sealed glass tubes.

<sup>d)</sup> 1.7  $\mu\text{m}$ ;  $C_v$ , 2.2%.

<sup>e)</sup> Purity, 55% (by catalog).

<sup>f)</sup> 400 g of water was post-added at the rate of 18 ml/h.

<sup>g)</sup> 40 g of water was post-added at the rate of 2.88 ml/h.

Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoyl peroxide; PVA, polyvinyl alcohol.

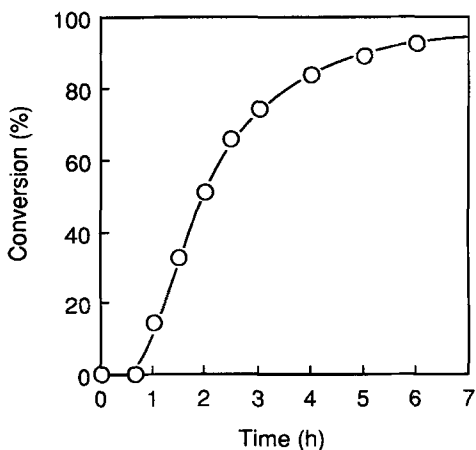
carried out in a four-necked round-bottom flask or in sealed glass tubes under a nitrogen atmosphere at 70°C for 24 h. The flask was stirred at 80 rpm and the tubes were horizontally shaken at 120 cycles/min (2 cm strokes). The emulsions pipetted out successively at chosen time intervals were dropped onto slide glasses, and then each droplet was covered with a cover glass and observed with Nikon MICROPHOT-FXA optical microscope. The conversion was measured by gas chromatography.

### Observations of the ultrathin cross sections of particles

PS/PDVB composite particles were exposed to O<sub>5</sub>O<sub>4</sub> vapor at 50°C for 2 h in the presence of 1% O<sub>5</sub>O<sub>4</sub> solution, and then dipped in epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross sections were put on copper grids and observed with TEM. To extract PS from the ultrathin cross sections of PS/PDVB composite particles, toluene was dropped onto the grid with the sections. When the grids dried up, toluene was dropped onto the grid again. After several repetitions of this procedure, the ultrathin cross sections were observed with TEM.

## Results and discussion

Figure 1 shows the time-conversion curve of DVB in seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in

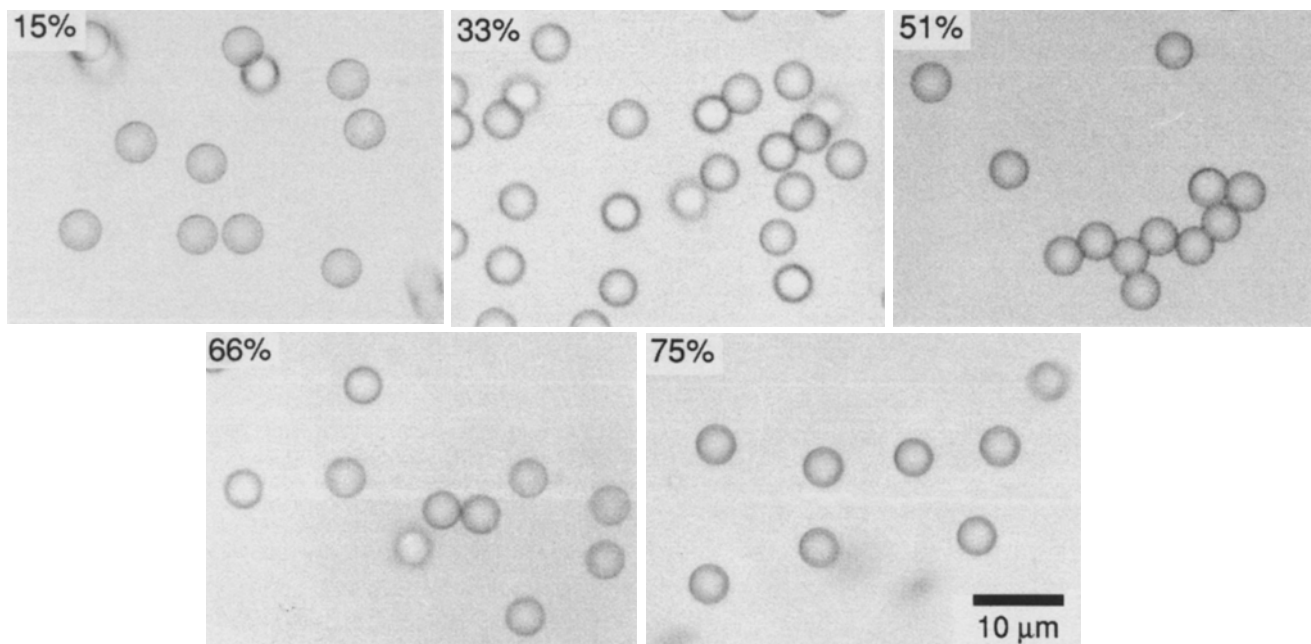


**Fig. 1** Time-conversion curve of DVB in seeded polymerization at 70°C for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1

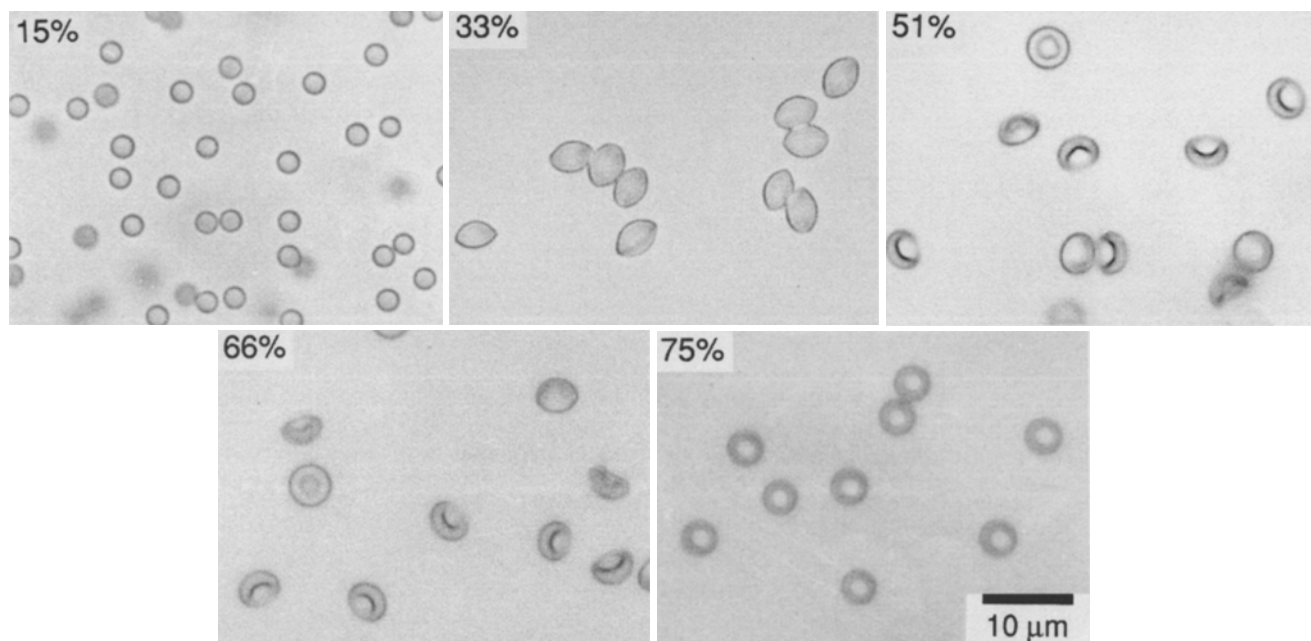
Table 1. The polymerization proceeded smoothly and the conversion rose to more than 90% after 6 h.

Figure 2 shows optical micrographs of PS/PDVB composite particles at various conversions of DVB, just after each polymer emulsion was pipetted out from the polymerization system. The contrasts in the insides of the produced composite particles at all the conversions were observed to be homogeneous and the shapes were spherical.

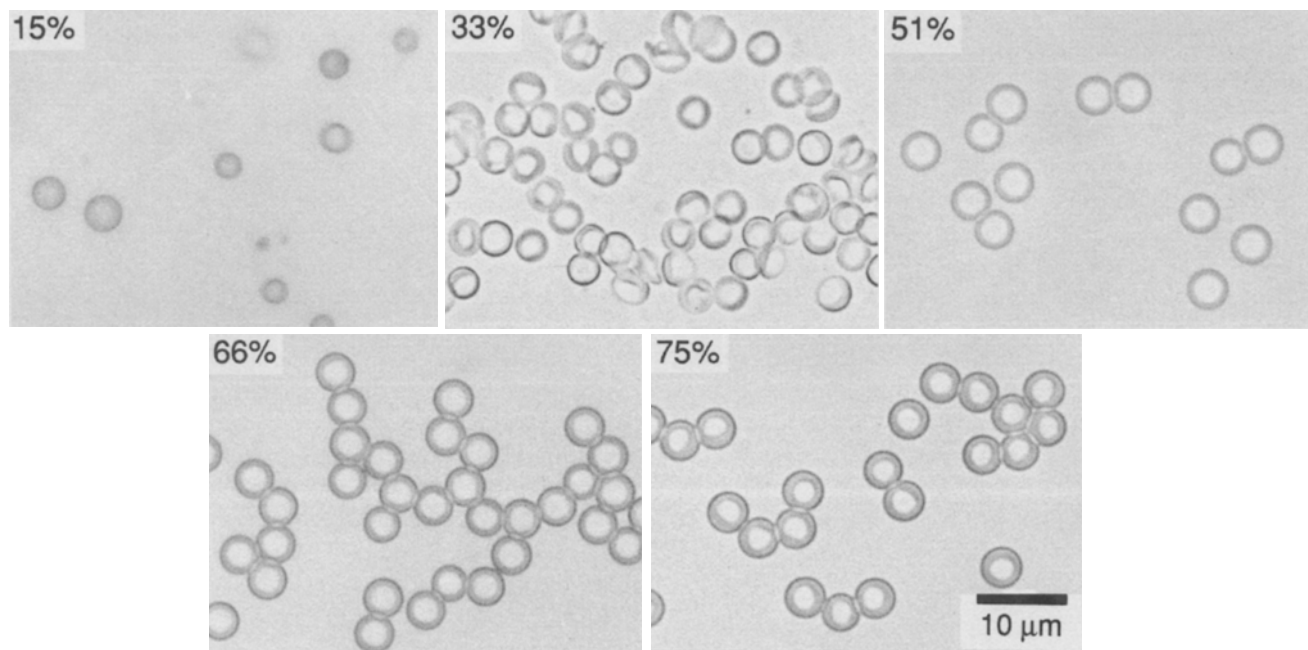
Figure 3 shows optical micrographs of the PS/PDVB composite particles at each conversion of DVB, whose emulsions were left at room temperature for 24 h in a capless small vessel after the polymerization was stopped. The composite particles at 15% conversion were spherical but clearly shrank compared to the composite particles observed just after pipetting out as observed in Fig. 2. Above 33%, such a shrinkage was not observed, but at 33–66% conversions flattened shapes of the particles were observed. Especially, the particles at 51% and 66% had such an anomalous shape as red blood corpuscle. This will be discussed in future. At 75% conversion a hollow structure was observed. These observations in Figs. 2 and 3 indicate that a cross-linked shell layer was formed, though at 15% conversion such a shell layer which depresses the shrinkage of particles with the evaporation of toluene and un-polymerized DVB therefrom was not formed yet. The reason why the shell layer was not observed at all the conversions in Fig. 2 seems to be based on the similar



**Fig. 2** Optical micrographs of PS/PDVB composite particles at the various conversions of seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, just after each polymer emulsion was pipetted out from the polymerization system



**Fig. 3** Optical micrographs of PS/PDVB composite particles at the various conversions of the seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, after each polymer emulsion was kept for 24 h

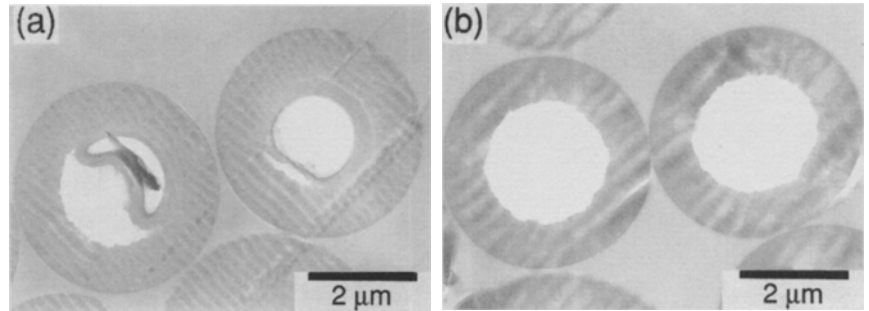


**Fig. 4** Optical micrographs of PS/PDVB composite particles at various conversions of seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, after a small amount of each polymer emulsion was mixed with a large amount of tetrahydrofuran

refractive indexes of PDVB and mixture of DVB and toluene. On the other hand, the reason why the shell layer was observed in Fig. 3 seems to be based on the evaporations of toluene and unpolymerized DVB from the particles.

In order to clarify these points, just after being pipetted out from the polymerization system at each conversion a small amount of emulsion was immediately dispersed in a large amount of tetrahydrofuran (THF) which is miscible

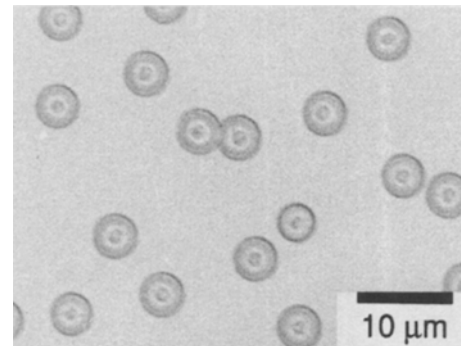
**Fig. 5** TEM photographs of ultrathin cross sections of PS/PDVB composite particles at 100% conversion exposed to  $O_3O_4$  vapor for 2 h, which had been produced by seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method, before (a) and after (b) the extraction of PS with toluene from the sections



with water, DVB and toluene, and a good solvent for PS. Its refractive index is relatively different from that of PDVB. As can be seen in Fig. 4, the particles at 33–75% conversions were observed to be spherical in shape having a shell layer, though the particles at 33% conversion slightly shrank. It is noted that the shell thickness increased with an increase in the conversion. At 15% conversion, some particles dissolved in THF, and the others maintained the spherical shape though they shrank. These also indicate that at 15% conversion the sufficient cross-linked shell layer was not formed and the cross-linking density was heterogeneous among the particles.

Figure 5 shows TEM photographs of ultrathin cross sections of PS/PDVB composite particles at 100% conversion exposed to  $O_3O_4$  vapor for 2 h, before (a) and after (b) the extraction of PS with toluene. In Fig. 5a, the phase separation of PS and PDVB was observed around the inner wall of the hollow in the PS/PDVB composite particles. By extraction of PS with toluene from the ultrathin cross section (Fig. 5b), a layer adhering to the inner wall of the hollow was removed. This indicates that the removed inner layer consisted of PS seed polymer. The PS/PDVB ratio calculated from the thickness of the layer agreed well with that calculated according to the polymerization recipe.

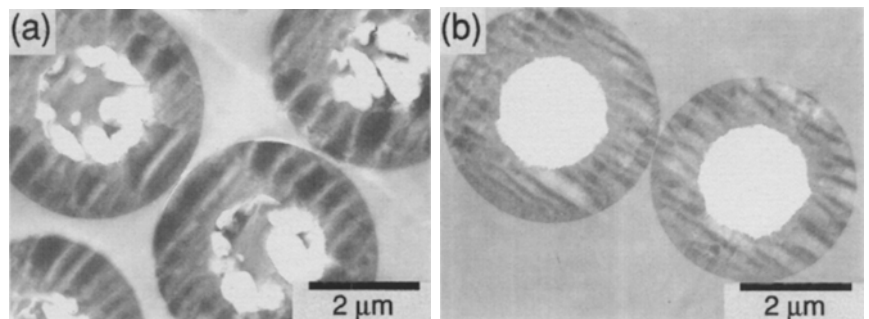
Figure 6 shows an optical micrograph of the PS/PDVB composite particles at 100% conversion of DVB, a small amount of which was dispersed in a large amount of ethanol immediately after polymerization. In all composite particles, high-contrast regions were observed at the center

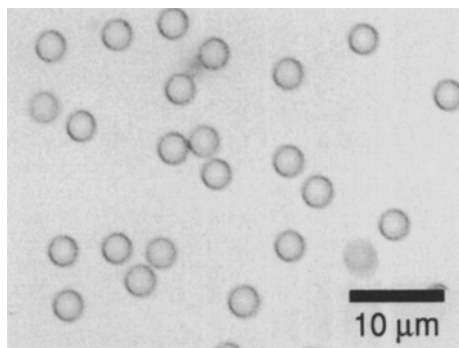


**Fig. 6** Optical micrograph of PS particles produced by seeded polymerization of DVB for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 1, a small amount of which was dispersed in a large amount of ethanol immediately after polymerization

as well as at the shell layer. The similar observation is more clearly shown in TEM photographs of ultrathin cross sections of the PS/PDVB composite particles exposed to  $O_3O_4$  vapor for 2 h (Fig. 7a). As can be seen, high-contrast regions which correspond to the high-contrast regions in Fig. 6 were observed in the inside of the hollow. The regions were removed by extraction of PS with toluene from the sections shown in Fig. 7b. This is because PS dissolved in the hollow was precipitated due to rapid exchange of the medium from toluene to ethanol. Ethanol

**Fig. 7** TEM photographs of ultrathin cross sections of the PS/PDVB composite particles, a small amount of which was dispersed in a large amount of ethanol immediately after polymerization, exposed to  $O_3O_4$  vapor for 2 h, before (a) and after (b) the extraction of PS with toluene from the sections



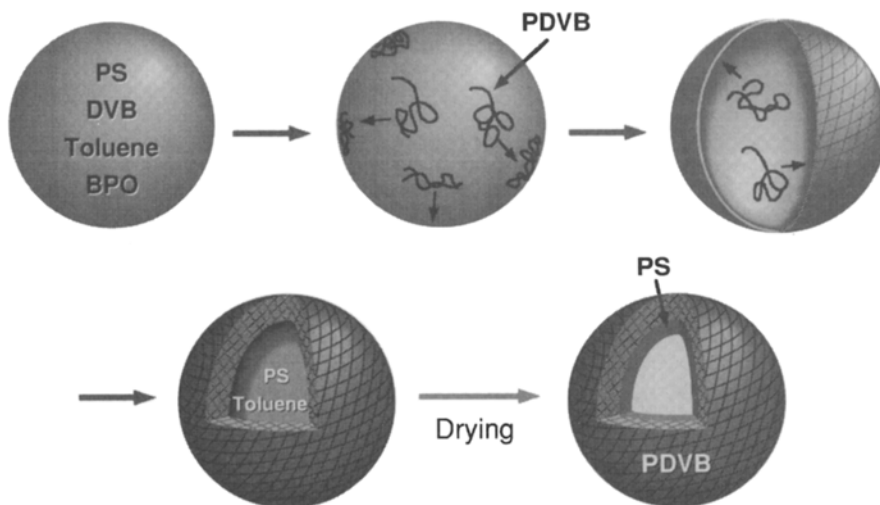


**Fig. 8** Optical micrograph of PS particles produced by seeded polymerization for the dispersion of (toluene/styrene)-swollen PS particles prepared utilizing the dynamic swelling method under the conditions of No. 2 listed in Table 1

is non-solvent for PS. In other words, these results suggest that PS seed polymer dissolved in toluene inside the PDVB shell before evaporation of toluene.

Figure 8 shows optical micrographs of PS particles produced by seeded polymerization for the dispersions of

**Fig. 9** The formation mechanism of micron-sized monodispersed hollow polymer particles by seeded polymerization for the dispersion of (toluene/DVB)-swollen PS particles prepared utilizing the dynamic swelling method



(toluene/styrene)-swollen PS particles prepared utilizing DSM under the conditions of No. 2 listed in Table 1. The produced PS dispersion was left at room temperature for 24 h in a capless small vessel before the observation. The obtained particles had no hollow structure. This suggests that cross-linking is needed to form hollow structure.

From these results, we propose the formation mechanism of hollow polymer particles as schematically shown in Fig. 9. Initially, PS particles absorb toluene and DVB by the dynamic swelling method, and PS dissolved therein homogeneously. As the seeded polymerization proceeds, PDVB molecules in the swollen particles precipitate in (toluene/DVB)-swollen PS particle because of cross-link. They are trapped near the interface based on surface coagulation [14] and gradually piled at the inner surface, which results in a cross-linked PDVB shell. PS which dissolves in toluene and DVB are repelled gradually to the inside. After the completion of the polymerization, toluene and dissolving PS are entrapped by the PDVB shell, then toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly.

## References

1. Coner T (1981) *Colloids and Surfaces* 3:119
2. Ugelstad J (1978) *Makromol Chem* 179:815
3. Ugelstad J, Kaggerud Kh, Hansen FK, Berge A (1979) *Adv Makromol Chem* 180:737
4. Ugelstad J, Mørk PC, Kaggerud Kh, Ellingsen T, Berge A (1980) *Adv Colloid Interface Sci* 13:101
5. Vanderhoff JW (1984) *J Dispersion Sci Tech* 5 (3&4):231
6. Okubo M, Ikegami K, Yamamoto Y (1989) *Colloid Polym Sci* 267:193
7. Okubo M, Katayama Y, Yamamoto Y (1991) *Colloid Polym Sci* 269:217
8. Yamamoto Y, Okubo M, Iwasaki Y (1991) *Colloid Polym Sci* 269:1126
9. Okubo M, Nakagawa T (1994) *Colloid Polym Sci* 272:530
10. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) *Colloid Polym Sci* 269:222
11. Okubo M, Shiozaki M (1993) *Polym Int* 30:469
12. Okubo M, Minami H, Yamashita T (1996) *Makromol Chem Macromol Symp* 101:509
13. Okubo M, Minami H (1996) *Colloid Polym Sci* 274 (5):433
14. Piirma I (1982) *Emulsion Polymerization*, Academic Press, New York, p 39