

## Production of micron-sized monodispersed anomalous polymer particles having red blood corpuscle shape<sup>a)</sup>

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**SUMMARY:** Micron-sized monodispersed polymer particles having a "red blood corpuscle-shape" were produced effectively at the completion of the seeded polymerization for the dispersion of highly (divinylbenzene/toluene)-swollen polystyrene particles prepared in an ethanol/water medium by utilizing the dynamic swelling method under optimum ratios of xylene/divinylbenzene and vinyltoluene/divinylbenzene.

### Introduction

In general, emulsion polymerization produces spherical particles within the limits of resolution of electron microscope, of which shape is arisen from the surface tension force. However, in a series of investigations on the production of submicron-sized composite polymer particles by seeded emulsion polymerization technique, we have found the preparation of various anomalous polymer particles: "confetti-like" [1], "raspberry-like" [2, 3], "void-containing" [4], "snowman-like" [5], "octopus ocellatus-like" [6] and "golf ball-like" [7, 8].

On the other hand, recently, many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed polymer particles [9–13] which have been applied in the biomedical field, microelectronics, etc. We have been producing micron-sized monodispersed polymer particles having functional groups such as chloromethyl [14] and vinyl groups [15, 16] by seeded dispersion copolymerizations of styrene with chloromethyl styrene and divinylbenzene, respectively, in the presence of about 2  $\mu\text{m}$ -sized monodispersed PS particles as seed. Moreover, in order to produce monodispersed particles having the diameter above 5  $\mu\text{m}$ , we suggested seeded polymerization utilizing a novel swelling method of seed polymer particles with a large amount of monomer, which was named "the dynamic swelling method (DSM)" [17, 18]. In previous articles [19, 20], this technique was developed to produce micron-sized monodispersed polymer particles having one hollow in the inside, and the formation mechanism of hollow structure was proposed [21]. Moreover, in the production process of the hollow polymer particles, anomalous polymer particles having "rugby ball-like" and "red

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blood corpuscle-like" shapes were observed at low conversions of the seeded polymerization. Similar nonspherical polymer particles were prepared by Hoshino et al [22] and Rudin et al. [23], but their formation mechanisms should be quite different from that of our produced polymer particles.

In this article, it will be clarified the conditions under which such anomalous polymer particles are produced effectively at the completion of the seeded polymerization.

## Experimental

### *Materials*

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Purity 96 and 55% divinylbenzenes (96-DVB and 55-DVB, supplied by Nippon Steel Chemical. Co. Ltd) and vinyltoluene (VT) were washed with 1N NaOH and deionized water to remove polymerization inhibitors before use. Benzoyl peroxide (BPO) and 2, 2'-azobisisobutyronitrile (AIBN) of reagent grade were purified by recrystallization. Deionized water was distilled with a Pyrex distillator. Poly(vinyl 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 prepared by solution polymerization of acrylic acid in 1,4-dioxane [14]. Reagent grade ethanol and analytical grade xylene, toluene, tetrahydrofuran, 1,4-dioxane and N, N-dimethylformamide were used as received.

### *Preparation of PS seed particles*

Micron-sized monodispersed PS seed particles were produced by dispersion polymerization of styrene in an ethanol/water (7/3, w/w) medium in the presence of PAA as colloidal stabilizer with AIBN as initiator at 70°C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask according to the optimum conditions in the previous article [14]. 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 or xylene utilizing DSM*

Swelling of the PS seed particles with DVB (and VT) and toluene or xylene was carried out using DSM as follows. Ethanol, water, DVB (and VT), toluene or xylene, BPO, and PVA were charged into a four-necked round-bottom flask or into a glass cylindrical reactor. The homogeneous solution was mixed with the PS seed dispersion. 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 (monomer/solvent)-swollen PS particles were

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 conversion was measured by gas chromatography (Yanaco, G-2800, Japan) with nitrogen as a carrier gas. Dimethylformamide was used as solvent and *p*-xylene used as standard reagent. The dispersions were dropped onto slide glasses, and then each droplet was covered with a cover glass and observed with Nikon MICROPHOT-FXA optical microscope, a JEOL JEM-200CX transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM).

## Results and discussion

Figures 1 and 2 show, respectively, TEM and SEM photographs of PS/PDVB composite particles at various conversions produced by seeded polymerization for the dispersion of (55-

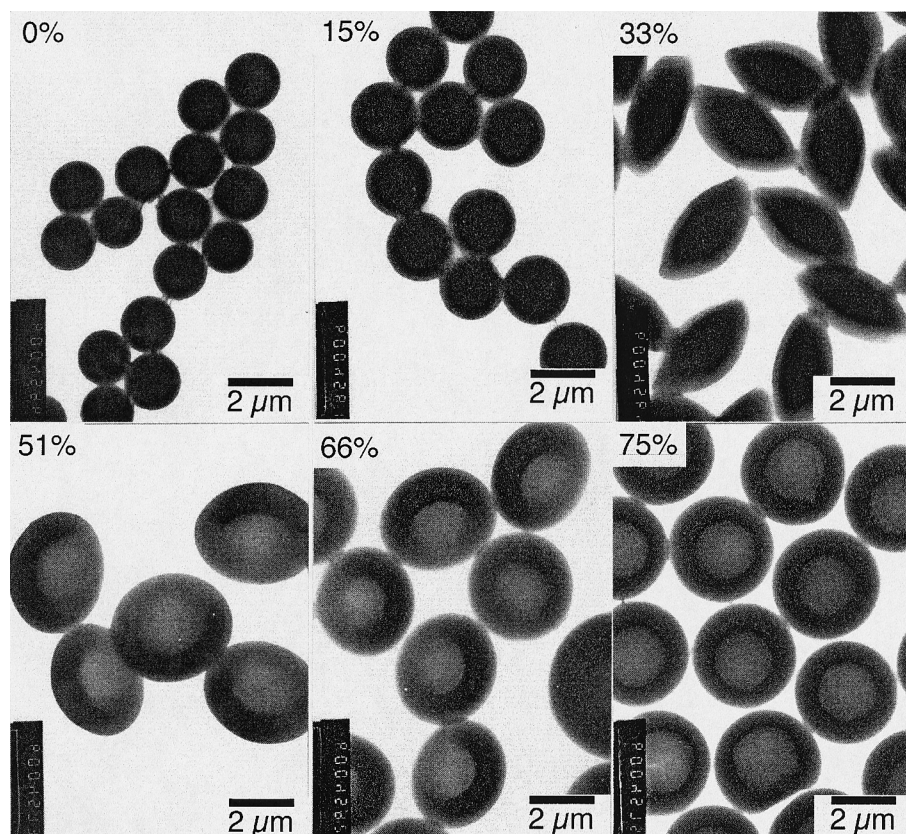


Fig. 1 TEM photographs of PS/PDVB composite particles at various conversions of the seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions listed in Table 1



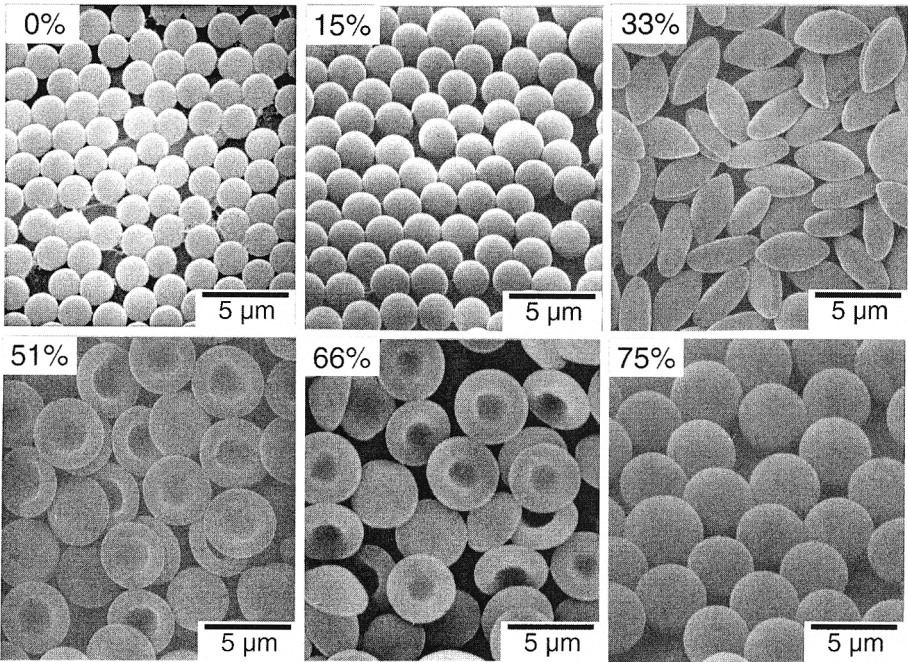


Fig. 2 SEM photographs of PS/PDVB composite particles at various conversions of the seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions listed in Table 1

DVB/toluene)-swollen PS particles prepared utilizing DSM, under the conditions listed in Table 1. The composite polymer particles at 15% conversion were bigger than the PS seed particles and spherical. They had a "rugby ball-like" shape at 33% conversion and "red blood corpuscle" shapes at 51 and 66% conversions. At 75% conversion, they were spherical ones having a hollow structure.

Table 1 A recipe for the production of PS/PDVB (1/5.5, w/w) composite particles by the seeded polymerization for the dispersion of (DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method at room temperature

Ingredients		
PS particles <sup>a)</sup>	(g)	0.3
55-DVB <sup>b)</sup>	(g)	3.0
Toluene	(g)	1.5
BPO	(g)	0.06
PVA	(g)	0.15
Ethanol	(g)	70
Water	(g)	30 + 400 <sup>c)</sup>

<sup>a)</sup> N<sub>2</sub>, 70°C, 24 h.  
<sup>b)</sup> D<sub>n</sub>, 1.7 μm; C<sub>v</sub>, 2.2%  
<sup>c)</sup> Purity, 55 % (by catalog).  
<sup>d)</sup> 400 g of water was post-added at the rate of 18 ml/h.  
Abbreviations: PS, polystyrene; DVB, divinylbenzene; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol).

Figure 3 shows optical micrographs of the PS/PDVB composite particles at 66% conversion of 55-DVB, whose dispersion was left at room temperature in a capless small vessel for 0 h (a), 12 h (b) and 24 h (c) after it was pipetted off. The particles transformed from spherical shape to anomalous one with the time. Such a transformation was not observed when the sample dispersion was kept in a sealed small vessel to prevent the



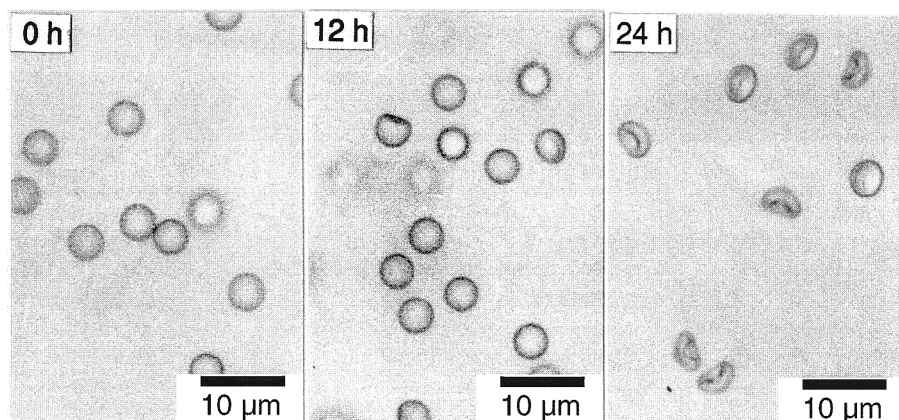


Fig. 3 Optical micrographs of PS/PDVB composite particles at 66% conversion of the seeded polymerization for the dispersion of (55-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions listed in Table 1, after the polymer dispersion was kept in a capless vessel for different times (h): (a) 0, (b) 12, (c) 24.

evaporations of unpolymerized DVB and toluene. These results suggest that the shapes of the dried composite particles at the various conversions shown in Figs. 1 and 2 are formed as follows.

At the low conversion of 15%, since the shell is not formed yet, the composite particles shrink homogeneously to spherical ones by evaporations of unpolymerized DVB and toluene. At the middle conversions (33~66%), the composite particles have cross-linked shells. When unpolymerized DVB and toluene are evaporated from the composite particles having cross-linked shell, water (and ethanol) should penetrate into the hollow from the medium (ethanol/water:

14/86, w/w) because the hollow space is evacuated.

However, since the shell is hydrophobic, the

penetration rate of water into the hollow is much slower than the evaporation rates of DVB and toluene from the hollow [24]. As the result, a part of the shell caves in because the thicknesses are not enough to withstand the pressure. At the high conversion

Table 2 Recipes for the productions of PS/PDVB and PS/P(DVB-VT) composite particles by seeded polymerizations<sup>a)</sup> for the dispersions of (DVB/xylene)- and (DVB/VT/xylene)-swollen PS particles, respectively, prepared by utilizing the dynamic swelling method at room temperature

Ingredients	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
PS particles <sup>b)</sup> (mg)	30	30	30	30	30	30
96-DVB <sup>c)</sup> (mg)	300	120	60	60	30	15
VT (mg)	-	-	-	60	90	105
Xylene (mg)	150	330	390	330	330	330
PVA (mg)	15	15	15	15	15	15
BPO (mg)	6.0	2.4	1.2	2.4	2.4	2.4
Ethanol (g)	7	7	7	7	7	7
Water (g)	43 <sup>d)</sup>	43 <sup>d)</sup>	43 <sup>d)</sup>	43 <sup>d)</sup>	43 <sup>d)</sup>	43 <sup>d)</sup>

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

<sup>b)</sup>D<sub>n</sub>, 1.7 μm; C<sub>v</sub>, 2.2%

<sup>c)</sup>Purity, 96% (by catalog).

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

Abbreviations: PS, polystyrene; DVB, divinylbenzene; VT, vinyltoluene; PVA, poly(vinyl alcohol); BPO, benzoyl peroxide.

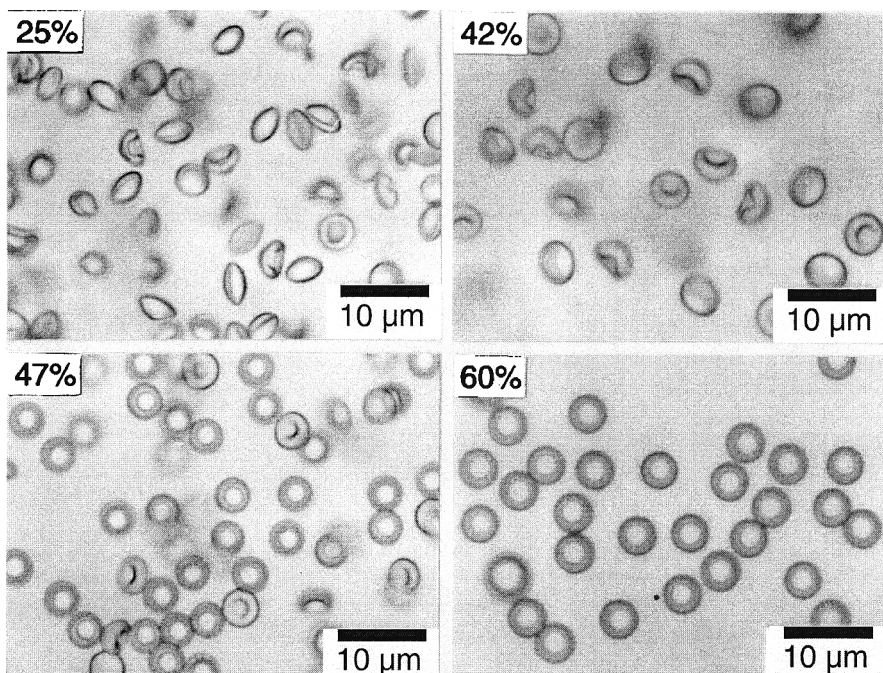


Fig. 4 Optical micrographs of PS/PDVB composite particles at the various conversions of the seeded polymerization for the dispersion of (96-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions of No. 1 listed in Table 2, after each polymer dispersion was kept in a capless vessel for 24 h.

(75%), the composite particles have an enough tough cross-linked shell to maintain spherical shape and the space from which unpolymerized DVB and toluene evaporate is occupied by the medium after some time lag.

Figure 4 shows optical micrographs of PS/ PDVB composite particles at various conversions of seeded polymerization for the dispersion of (96-DVB/toluene)-swollen PS particles prepared by utilizing DSM, under the conditions of No. 1 listed in Table 2. They were left in capless vessels for 24 h after pipetted off. In comparison with the result obtained using 55-DVB shown in Fig. 2, a similar result was obtained, but there was a clear difference around conversion of 60%. That is, the composite particles prepared with 96-DVB at 60% conversion had a spherical shape, but those with 55-DVB at 66% conversion had the red blood corpuscle-like shape. This difference seems to be based on the difference in cross-linking densities between their shells.

In order to change the penetration rate of the medium into the hollow of the composite particle, a small amount of dispersion at 25% conversion of 96-DVB, just after pipetted off from the polymerization system, was immediately dispersed in a large amount of various solvents which have different solubility parameters as shown in Table 3 and are miscible with water, DVB and toluene.



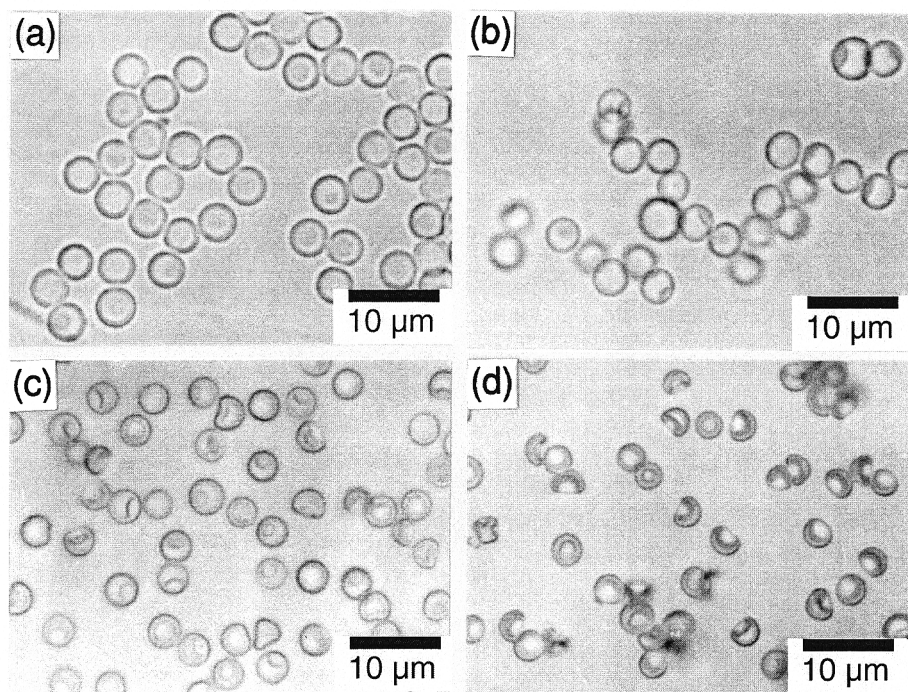


Fig. 5 Optical micrographs of PS/PDVB composite particles at 25% conversion of the seeded polymerization for the dispersion of (96-DVB/toluene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions listed in Table 2, of which a small amount of pipetted dispersion was mixed with a large amount of tetrahydrofuran (a), 1,4-dioxane (b), N, N-dimethylformamide (c) and ethanol (d)

Figure 5 shows optical micrographs of the dispersed particles. In the tetrahydrofuran system (a), they were spherical hollow particles. In 1,4-dioxane (b) and N,N-dimethylformamide (c) systems, the hollow structure was observed in the composite particles, and the shape of some particles was not spherical and the shell lightly caved in. In the ethanol system (d), all the particles completely caved in. As the solubility parameter of the solvents deviates from that of PS, the degree of dent of the composite particles became remarkable. This suggests that the transformation is based on the difference between the release rates of DVB and toluene and the penetration rates of the media.

Figure 6 shows optical micrographs of PS/PDVB composite particles at 100% conversion of the seeded polymerizations for the dispersions of (96-DVB/xylene)-swollen PS particles prepared by utilizing DSM, under the conditions of Nos. 2 (a) and 3 (b) listed in

Table 3 Solubility parameters  $\delta$  of polystyrene and solvents

	$\delta$ [(MPa) <sup>1/2</sup> ]
Polystyrene	17.5
Tetrahydrofuran	18.6
1, 4-Dioxane	20.5
N, N-Dimethylformamide	24.8
Ethanol	26.0

<sup>a)</sup> "POLYMER HANDBOOK" 3rd Ed., JOHN WILLY & SONS (1989).



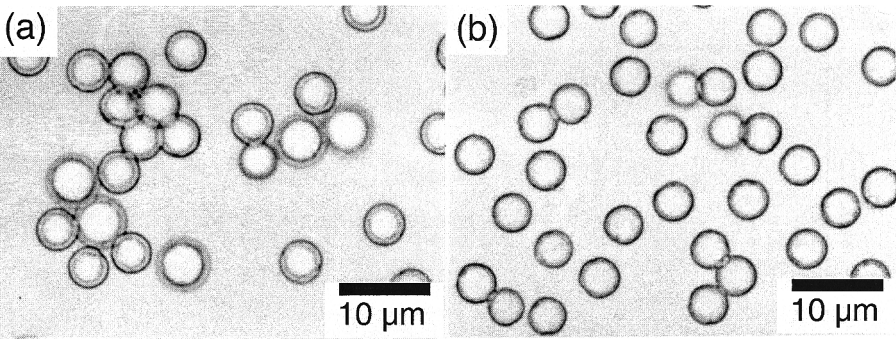


Fig. 6 Optical micrographs of PS/PDVB composite particles at 100% conversion of the seeded polymerizations for the dispersions of (96-DVB/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions of Nos. 2 (a) and 3 (b) listed in Table 2: PS/96-DVB/xylene (weight ratio): (a) 1/4/11; (b) 1/2/13

Table 2. These composite particles produced at the two xylene/96-DVB ratios should have the same diameter as No. 1-particle at 100% conversion and different shell thicknesses, if the produced composite particles have the hollow structure. All the composite particles had the hollow structure. Nos. 2 and 3-particles were spherical. No. 3-particles didn't cave in,

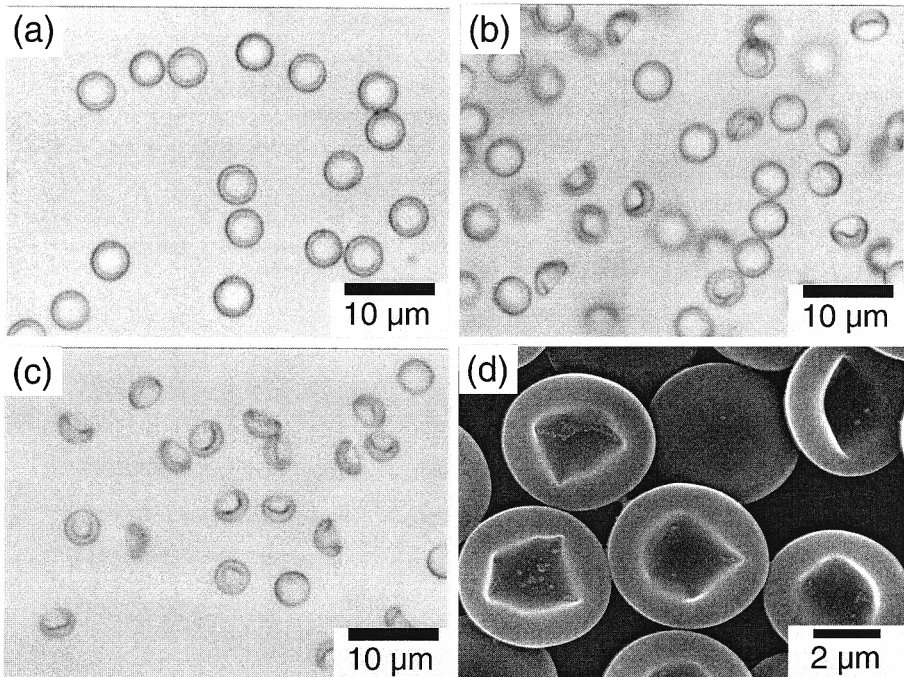


Fig. 7 Optical (a, b, c) and SEM (d) micrographs of PS/P(DVB-VT) composite particles at 100% conversion of the seeded copolymerizations for the dispersions of (96-DVB/VT/xylene)-swollen PS particles prepared by utilizing the dynamic swelling method under the conditions of Nos. 4 (a), 5 (b) and 6 (c, d) listed in Table 2: PS/96-DVB/VT/xylene (weight ratio): (a) 1/2/2/11; (b) 1/1/3/11; (c, d) 1/0.5/3.5/11

although their shell thickness was thinner than that (Fig. 4) of the dented No. 1-particles at 25% conversion. This seems to be based on that the cross-linking density in the shell of No.3-particles is higher than that of No. 1-particles at 25% conversion, because the possibility of reaction of the dangling vinyl groups, which gives cross-linking, must be higher in the former than in the latter.

Figure 7 shows optical micrographs of PS/P(DVB-VT) composite particles at 100% conversion of the seeded polymerizations for the dispersions of (96-DVB/VT/xylene)-swollen PS particles prepared utilizing DSM, under the conditions of Nos. 4 (a), 5 (b) and 6 (c) listed in Table 2: 96-DVB/VT (w/w): (a) 1/1; (b) 1/3; (c) 1/7. The three kinds of composite particles should have different cross-linking densities and the same shell thickness as No. 1-particles at 40% conversion at which the dented composite particles were observed. The percentage of dented composite particles increased with a decrease in the cross-linking density, and all No. 6-particles had the red blood corpuscle-shape. This was more clearly shown in SEM observation (d).

From the above results, it is concluded that micron-sized monodispersed anomalous polymer particles having the red blood corpuscle shape can be prepared by evaporation of xylene from the hollow in the composite particles having an optimum cross-linking density and shell thickness, produced by the seeded polymerization for (DVB and/or VT/xylene)-swollen PS particles prepared by utilizing DSM.

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