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SHORT COMMUNICATIONS

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Micron-sized, monodisperse, snowman/confetti-shaped polymer particles by seeded dispersion polymerization

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Abstract Snowman/confetti-shaped, micron-sized, monodisperse composite particles were prepared by seeded dispersion polymerizations of *n*-butyl methacrylate (*n*BMA) with 1.28 and 2.67 μm-sized polystyrene (PS) seed particles, respectively, in an ethanol/water (80/20, w/w) medium. These nonspherical composite particles consisted of one or several poly(*n*BMA) protuberances on the surfaces of the spherical PS particles.

Keywords Micron-size · Monodisperse · Dispersion polymerization · Nonspherical shape · Particle surface area

Introduction

Polymer particles prepared by emulsion, dispersion, and suspension polymerizations are normally spherical because they minimize the interfacial free energy between the particle and medium. However, in the course of our investigations on the preparations of submicron-sized composite particles by seeded emulsion polymerization, various nonspherical particles have been prepared; "confetti-like" [1], "raspberry-like" [2, 3], "void-containing" [4], and "octopus ocellatus-like" [5]. Their shapes are governed by corresponding heterogeneous structures formed by the phase separation of polymers within the particles during the seeded emulsion polymerizations under nonequilibrium conditions.

Recently, micron-sized, monodisperse, nonspherical polymer particles were also prepared by seeded polymerization [6–12] and seeded dispersion polymerization [13, 14]. El-Aasser and coworkers reported that nonspherical particles having "snowman-like" shape were prepared by seeded polymerization of styrene with cross-linked polystyrene (PS) seed particles [6–8]. We also reported that similar snowman-like particles were prepared by seeded polymerization of styrene that are adsorbed as "head" on the cross-linked PS particle ("body"), which were prepared by the dynamic swelling method [9–12]. Moreover, in a previous article [13], "egg-like" PS/poly(*n*-butyl methacrylate) (P *n*BMA) composite particle could be prepared by seeded dispersion polymerization of *n*BMA in ethanol/water (60/40, w/w) medium with 1.65 μm-sized PS seed particles, which were stabilized with poly(acrylic acid) (PAA). In a series of investigations, seeded dispersion polymerization has resulted in spherical core–shell particles [15–18]. However, in the case of PS/P *n*BMA, particle shape changed from spherical to egg-like with an increase in the ratio of ethanol/water media in the range of 40/60 to 60/40 and with a decrease in the initiator concentration. Formation mechanism of the egg-like particles was proposed as follows. Under the conditions of the slow adsorption rate (mol s^{-1} m^{-2}) of the polymer radical on the PS seed particle, which are derived from high ethanol content and low initiator concentration, the polymer radicals can gather to form a few P *n*BMA domains at the surface in an early stage of the polymerization. The P *n*BMA domains predominantly absorb *n*BMA from the ethanol/water medium, because P *n*BMA has higher affinity than PS to *n*BMA, and T_g values of PS and P *n*BMA are higher and lower than polymerization temperature, respectively. Therefore, the polymerization of *n*BMA proceeds much faster in the domains than in the PS bare surface and preferentially enlarges the P *n*BMA domains, resulting in nonspherical PS/P *n*BMA core/shell particles with nonuniform P *n*BMA thickness. However, particle coagulation occurred heavily in ethanol/water media above 70/30 (w/w). Thus, more nonspherical shapes than egg-like ones were not successfully formed. El-Aasser and coworkers reported that snowman-like PS/poly(*n*-butyl acrylate) composite particles were prepared by seeded dispersion polymerization of *n*-butyl acrylate with poly(vinyl pyrrolidone) (PVP) stabilized PS seed particles in methanol/water (90/10, w/w) [14]. The experimental results impressed us, but the formation mechanism was not explained. There seems to be a similar formation mechanism between the egg- and the snowman-like particles.

In this article, in order to reconfirm the formation mechanism of the egg-like particles described above, snowman-like PS/P *n*BMA composite particles will be prepared by the seeded dispersion polymerization of *n*BMA with PS seed particles, which were stabilized by PVP in ethanol/water.

Experimental

Materials

Styrene and *n*BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization with methanol. Deionized water with a specific resistance of 5×10^6 Ωcm was distilled. PVP (weight average molecular weight, 3.6×10^5 g/mol) and ethanol were used as received.

Seed particles

Two kinds of monodisperse PS seed particles were prepared by dispersion polymerizations under the conditions listed in Table 1. Number-average diameters (D_n) and its coefficient of variations (C_v) of both PS particles were measured with a transmission electron microscope (TEM) (H-7500, Hitachi Science Systems Ltd., Ibaraki, Japan) using image analysis software for Macintosh computer (MacSCOPE, Mitani Co. Ltd., Fukui, Japan). They were used after centrifugal washing with ethanol three times.

Table 1 Recipes for the preparations of micron-sized, monodisperse polystyrene (PS) particles by dispersion polymerizations

Ingredients (g)	No. 1	No. 2
Styrene	60	60
AIBN	0.48	0.48
PVP	2.88	3
Ethanol	302	336
Water	34	0

In flask: 70 °C; 24 h; N_2; shaking rate, 100 rpm
AIBN 2,2′-azobis(isobutyronitrile), *PVP* poly(vinyl pyrrolidone)

Seeded dispersion polymerization

Seeded dispersion polymerizations of *n*BMA were carried out in sealed glass tubes under the conditions listed in Table 2. The dried composite particles were observed with a scanning electron microscope (SEM) (S-2500, Hitachi Science Systems Ltd.).

Ultrathin cross sections

A small amount of PS/P *n*BMA composite emulsion was added to 20 wt% gelatin aqueous solution and frozen in a refrigerator for 24 h. Ultrathin cross sections with a thickness of 100 nm were obtained by sectioning the gelatin including particles at −100 °C with a microtome equipped with cryopump (Leica REIHERT FC S, Austria), transferred to TEM grid, stained with RuO_4 vapor for 30 min in the presence of 1% RuO_4 solution, and observed with TEM.

Results and discussion

Transmission electron microscope photographs of two kinds of PS seed particles prepared by the dispersion polymerizations under the conditions of Nos. 1 and 2 listed in Table 1 are shown in Fig. 1. The D_n and C_v of the PS particles were 1.28 μm and 3.24%, and 2.67 μm and 1.26%, respectively.

Figure 2 shows SEM photographs of PS/P *n*BMA (1/1, w/w) composite particles prepared by seeded dispersion polymerization with 1.28 μm-sized PS seed particles at various weight ratios of ethanol/water under the

Table 2 Recipes for the preparations of PS/P *n*-BMA composite particles by seeded dispersion polymerizations

Ingredients	Ethanol/water (w/w)		
	60/40[b]	70/30[b]	80/20[c]
PS particles[a] (g)	0.3	0.3	0.3
*n*BMA (g)	0.3	0.3	0.3
AIBN (mg)	3.0	3.0	1.0–9.0[d]
PVP (mg)	6.0	6.0	6.0
Ethanol (g)	4.8	5.6	6.4
Water (g)	3.2	2.4	1.6

In sealed glass tubes: 70 °C; 24 h; N_2; shaking rate, 60 cycles/min (3 cm strokes)
nBMA n-butyl methacrylate
[a] $D_n = 1.28$ μm, $C_v = 3.24\%$; $D_n = 2.67$ μm, $C_v = 1.26\%$
[b] Polymerization time: 24 h
[c] Polymerization time was changed to make the conversion ca. 90% at the different initiator concentrations
[d] 1.0, 2.0, 3.0, 6.0, 9.0 (mg)

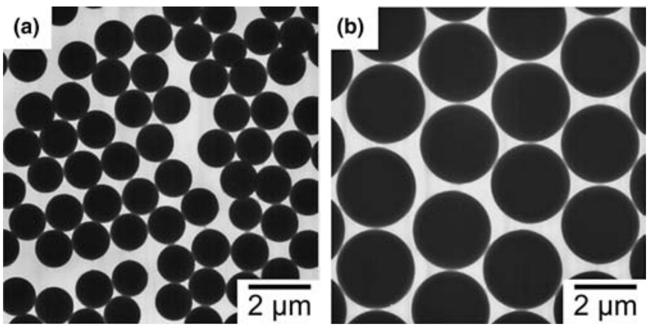


Fig. 1 TEM photographs of PS particles prepared by dispersion polymerizations under the conditions of Nos. 1 (**a**) and 2 (**b**) listed in Table 1

conditions listed in Table 2. At an ethanol/water ratio of 60/40, egg-like particles were prepared (see Fig. 2a) similar to that in the previous article [13]. At 70/30 and 80/20, snowman-like composite particles were prepared without noticeable coagulation (see Fig. 2b, c). When PAA was used as a stabilizer in place of PVP, particle coagulation occurred. This indicates that PVP is more effective than PAA as a stabilizer to prevent coagulation in this system.

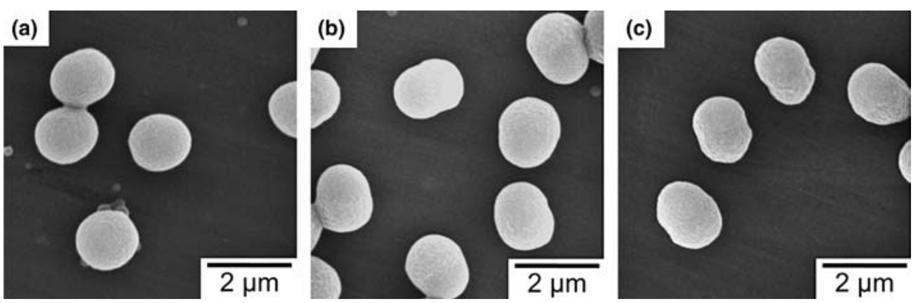
Figure 3 shows SEM photographs of PS/P *n*BMA composite particles prepared with 1.28 μm-sized PS seed particles in ethanol/water (80/20, w/w) at various initiator concentrations (0.90, 0.60, 0.30, 0.20 and 0.10 g/L). In their polymerizations, the conversion of *n*BMA was adjusted to be ca. 90% by changing the polymerization time. With a decrease in the initiator concentration, the nonspherical shape of the composite particles changed from egg-like to snowman-like.

Transmission electron microscope photographs of ultrathin cross sections of the RuO_4-stained PS/P *n*BMA composite particles prepared with the 1.28 μm-sized PS seed particles at the initiator concentrations of 0.90 and 0.10 g/L are shown in Fig. 4. It is known that RuO_4 predominantly stains PS [19]. The PS seed particles were covered with incomplete P *n*BMA shell at the highest AIBN concentration of 0.90 g/L. On the other hand, the snowman-like particle prepared at the lowest AIBN concentration of 0.10 g/L consisted of spherical PS seed particle and a P *n*BMA protuberance located on its surface. The high solubility and low generation rate of oligomer radicals, which are derived, respectively, from high ethanol content and low initiator concentration, led to the slow adsorption rate (mol $s^{-1}m^{-2}$) of the oligomer radicals adsorbed by the PS seed particle. Under the conditions, the P *n*BMA molecules were allowed to gather and the number of P *n*BMA domain on the PS seed particle decreased to one resulting in snowman-like particles. Accordingly, the formation mechanism of the snowman-like particles seems to be similar to that of egg-like particles [13].

Next, 2.67 μm-sized monodisperse PS particles were used as seed particles to investigate the effect of particle surface area on the particle shape.

Figure 5 shows SEM photographs of PS/P *n*BMA composite particles prepared by the seeded dispersion polymerization with the 2.67 μm-sized PS seed particles at various weight ratios of ethanol/water. At an ethanol/water ratio of 60/40 (see Fig. 5a), the shape of prepared particles were almost spherical, which was similar to that observed in Fig. 2a, although by-products of many small P *n*BMA particles were observed. With an increase in the ethanol/water ratio, the shape changed to confetti-like, and the by-products drastically decreased (see Fig. 5b, c).

Fig. 2 SEM photographs of PS/P *n*BMA composite particles prepared by seeded dispersion polymerizations with 1.28 μm-sized PS seed particles at various ethanol/water media (w/w): **a** 60/40; **b** 70/30; **c** 80/20



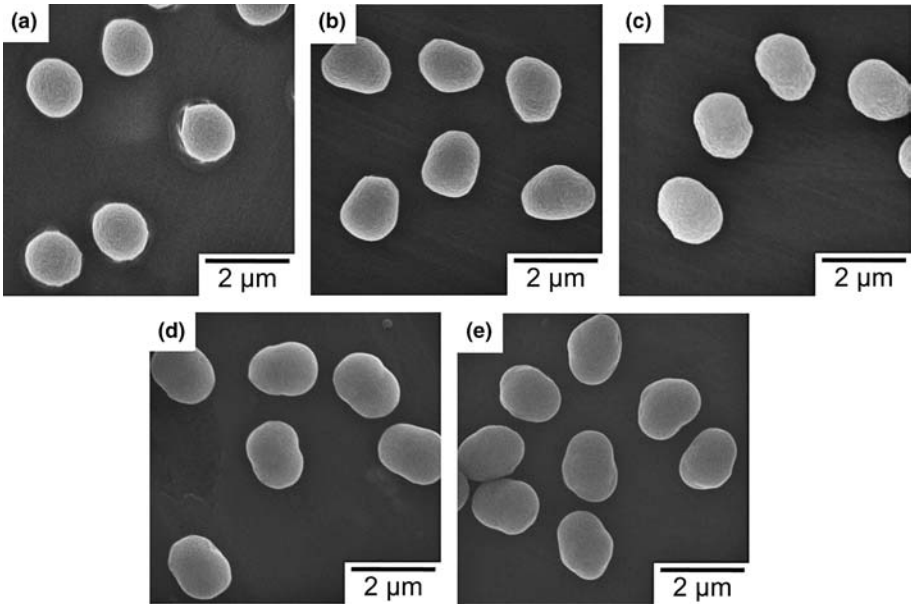


Fig. 3 SEM photographs of PS/P *n*BMA composite particles prepared by seeded dispersion polymerizations with 1.28 µm-sized PS seed particles in the ethanol/water (80/20, w/w) medium at various AIBN concentrations (g/L): **a** 0.90; **b** 0.60; **c** 0.30; **d** 0.20; **e** 0.10

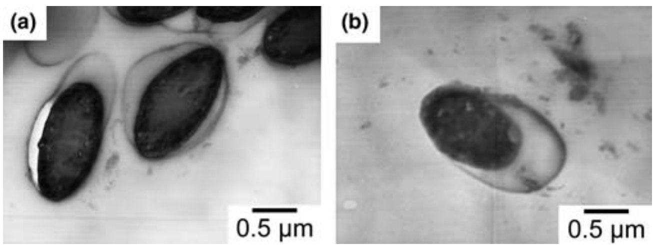


Fig. 4 TEM photographs of ultrathin cross sections of the PS/P *n*BMA composite particles prepared by seeded dispersion polymerizations with 1.28 µm-sized PS seed particles in the ethanol/water (80/20, w/w) medium at different AIBN concentrations (g/L): **a** 0.90; **b** 0.10

Figure 6 shows SEM photographs of PS/P *n*BMA composite particle prepared with 2.67 µm-sized PS seed particles at various AIBN concentrations. The confetti-like shape became more obvious with a decrease in the AIBN concentration. TEM photographs of ultrathin cross sections of the PS/P *n*BMA composite particles at the AIBN concentrations of 0.90 and 0.10 g/L are shown in Fig. 7. The PS seed particles were homogeneously covered with P *n*BMA shell at the highest AIBN concentration of 0.90 g/L. On the other hand, the confetti-like particle prepared at the lowest AIBN concentration of 0.10 g/L consisted of spherical PS seed particle and several P *n*BMA protuberances located on its surface. It is not easy to explain clearly the effect of the diameter of the PS seed particles on the particle shape with the limited data, because the particle shape should be influenced not only by the adsorption rate of P *n*BMA radicals, but also the distance among the adsorbed P *n*BMA radicals. As the particle diameter increases at a constant PS concentration, the total surface area of the PS seed particles decreases, but the surface area per particle increases. The decrease in the total surface area would increase the amount of adsorbed P *n*BMA radicals per unit area, resulting in a homogeneous P *n*BMA shell. On the other hand, the increase in the surface area per particle would lead to an increase in the distance among adsorbed P *n*BMA radicals, resulting in several P *n*BMA protuberances on the seed particle. The preparation of the confetti-like particles using the 2.67 µm-sized PS seed particles suggests that the diffusion distance of P *n*BMA radicals on the PS particle is important.

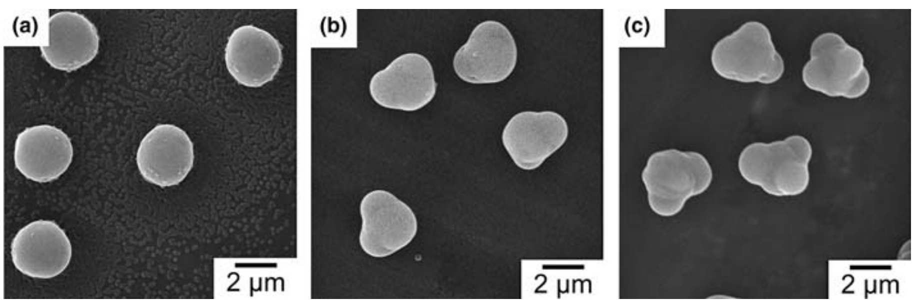


Fig. 5 SEM photographs of PS/P *n*BMA composite particles prepared by seeded dispersion polymerizations with 2.67 µm-sized PS seed particles at various ethanol/water media (w/w): **a** 60/40; **b** 70/30; **c** 80/20

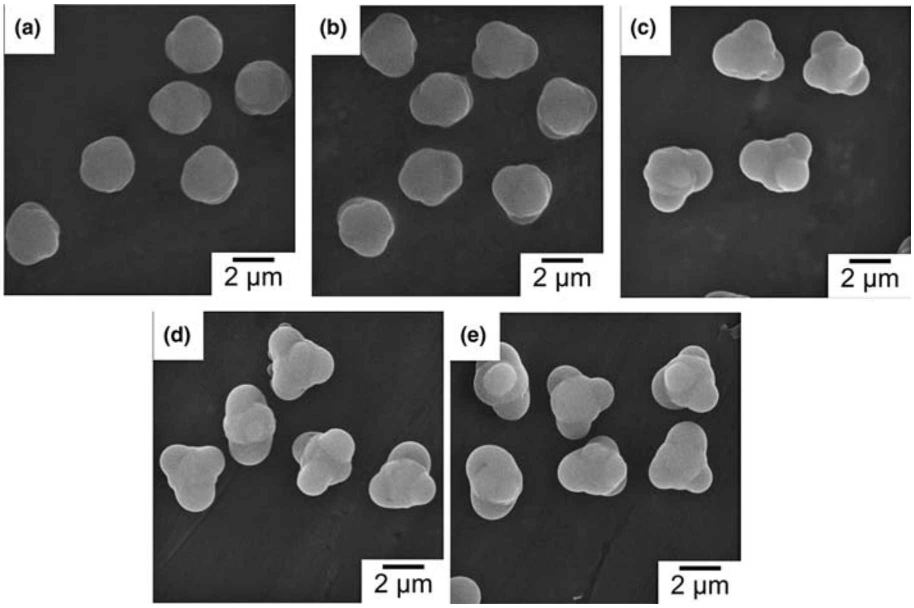


Fig. 6 SEM photographs of PS/P *n*BMA composite particles prepared by seeded dispersion polymerizations with 2.67 μm-sized PS seed particles in the ethanol/water (80/20, w/w) medium at various AIBN concentrations (g/L): **a** 0.90; **b** 0.60; **c** 0.30; **d** 0.20; **e** 0.10

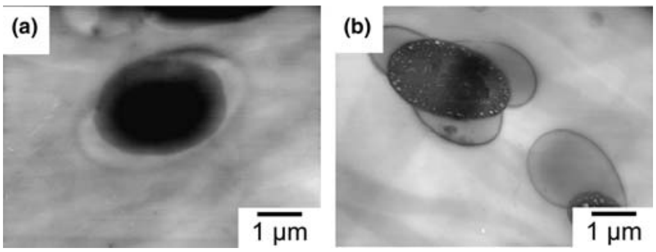


Fig. 7 TEM photographs of ultrathin cross sections of the PS/P *n*BMA composite particles prepared by seeded dispersion polymerizations with 2.67 μm-sized PS seed particles in the ethanol/water (80/20, w/w) medium at different AIBN concentrations (g/L): **a** 0.90; **b** 0.10

From the above results, it is clarified that snowman-like and confetti-like PS/P *n*BMA composite particles were prepared by seeded dispersion polymerization of *n*BMA with 1.28 and 2.67 μm-sized PS seed particles in an ethanol/water medium of 80/20. The formation of such particles seems to be based on a similar formation mechanism as that of egg-like particles, which was discussed in the previous paper [13]. That is, they were prepared under the condition that the adsorption rate of P *n*BMA radicals on the PS particles was slow, which were controllable by changing the AIBN concentration and the size of seed particles.

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