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ORIGINAL CONTRIBUTION

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Formation mechanism of anomalous "golf ball-like" composite polymer particles by seeded emulsion polymerization

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Abstract Recently, the authors found that anomalous polystyrene/polybutyl acrylate composite particles, whose surfaces had many dents, were produced by emulsifier-free seeded emulsion polymerization of butyl acrylate with polystyrene seed particles. Such a particle was named a "golf ball-like" particle. In this article, the morphology and the formation mechanism of the golf ball-like composite polymer particles were studied.

Key words Composite polymer particle – emulsion polymerization – morphology– anomalous shape – phase separation

Introduction

Emulsion polymerization generally produces spherical particles within the limits of resolution of electron microscope, whose shape arises from the surface tension forces. However, in a series of investigations on the production of composite polymer particles by seeded emulsion polymerization technique, we have found the preparation of various anomalous particles: "confetti-like" [1], "raspberry-like" [2, 3], "void-containing" [4], "snowman-like" [5] and "octopus ocellatus-like" [6]. Their productions are based on the corresponding heterogeneous structures formed by the phase separation of polymers within the particles during the polymerizations.

Recently, polystyrene (PS)/polybutyl acrylate (PBA) composite particles having many dents at the surfaces were produced by seeded emulsion polymerization of butyl acrylate (BA) with spherical PS seed particles [7]. We named them "golf ball-like" particles.

In this article, the morphology and the formation mechanism of the "golf ball-like" particle will be discussed.

Experimental

Materials

Styrene and BA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate (KPS) was purified by recrystallization. Deionized water was distilled.

Seeded emulsion polymerization

PS seed particles were produced by emulsifier-free emulsion polymerization with KPS initiator in ethanol/water medium under the conditions listed in Table 1. PS/PBA composite particles having various compositions were produced by seeded emulsion polymerization of BA with the PS seed particles under the conditions listed in Table 2 using the two kinds of monomer addition methods. One is absorption method in which all the ingredients were kept at 0 °C for 24 h under gentle stirring to make BA

Table 1 Preparation of PS seed particles produced by emulsifier-free emulsion polymerization[a] in ethanol/water medium

Ingredient		
Styrene	(g)	136
KPS	(mg)	682
Ethanol	(g)	888
Water	(g)	375

[a] 70 °C; 24 h; N_2; stirring rate, 60 rpm.

Table 2 Conditions of seeded emulsion polymerization[a] of BA

Ingredient		PS/PBA 9/1	8/2	7/3	6/4
PS seed	(g)	6.00	6.00	6.00	6.00
BA	(g)	0.67	1.50	2.57[b]	4.00
KPS	(mg)	200	200	200	200
Ethanol	(g)	40	40	40	40
Water	(g)	160	160	160	160

[a] 70 °C; 24 h; N_2; stirring rate, 60 rpm; [b] BA was dripped into the reactor at 1.34 g/h or 0.42 g/h in the monomer dropwise method.

absorb into PS seed particles prior to the polymerization. The other is dropwise method in which BA was dropwise added to the reaction flask using a microfeeder at constant rates of 1.34 g/h and 0.42 g/h throughout the polymerization. A conversion of BA was measured with gas chromatography.

Extraction of PBA from the composite particles

PBA in the PS/PBA composite particles was extracted by 1-butanol, which is a good solvent for PBA and a non-solvent for PS. The medium of PS/PBA composite emulsion was replaced from the ethanol/water to 1-butanol by centrifugation and left at room temperature for 1 week with occasionally stirring. During the extraction, the 1-butanol medium was replaced with fresh medium three times.

Electron microscopy

The particle shape was observed with a JEOL JEM-200CX transmission electron microscope (TEM) and a Hitachi S-2500 scanning electron microscope (SEM). Each emulsion was diluted down to appropriate solid content, and its drop was placed onto a Formvar film (when the medium was water) or a carbon (when one was 1-butanol) coated grid and allowed to dry at room temperature in a desiccator. The inside structure of the particles was observed using the ultrathin cross-section method after the particles were exposed to RuO_4 vapor for 40 min.

Result and discussion

PS seed particles produced by emulsifier-free emulsion polymerization under the conditions listed in Table 1 were spherical and monodisperse: the number-average diameter, 632 nm; the coefficient of variation, 1.65%.

Figure 1 shows TEM photographs of PS/PBA composite particles having various PBA contents produced by the seeded emulsion polymerization of BA with the PS seed particles under the conditions listed in Table 2. The

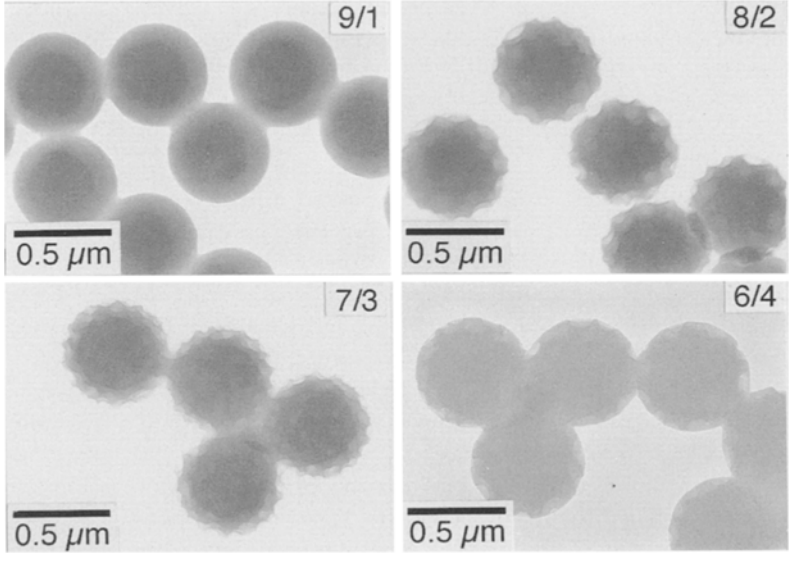

Fig. 1 TEM photographs of PS/PBA composite particles produced by the seeded emulsion polymerization of BA in ethanol/water (2/8, w/w) medium

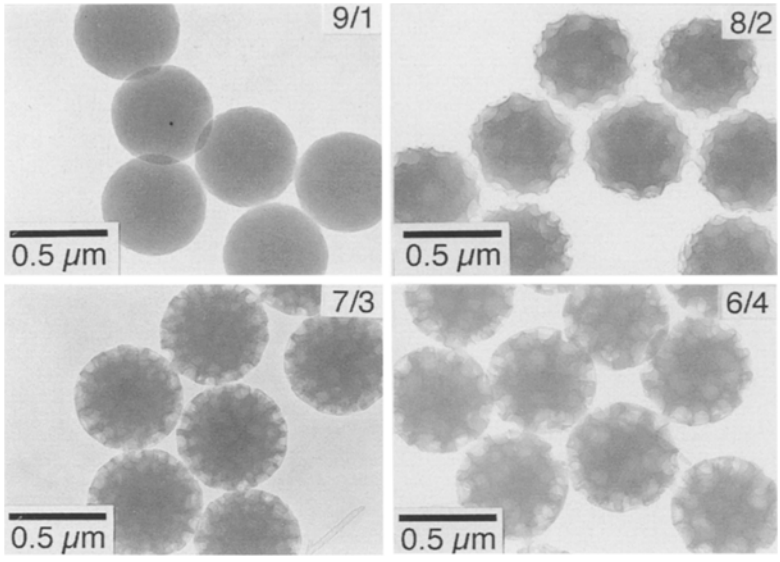

Fig. 2 TEM photographs of particles after extraction of PBA from PS/PBA composite particles with 1-butanol at room temperature for 1 week

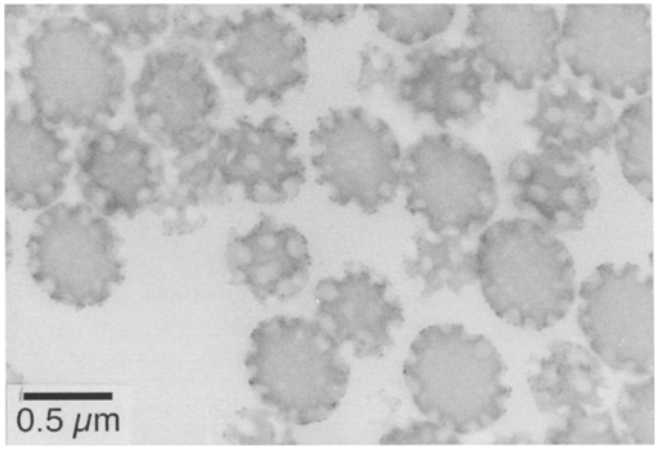

Fig. 3 TEM photograph of ultrathin cross-section of PS/PBA (7/3, w/w) composite particles exposed to RuO_4 vapor for 40 min

composite particles having PBA content of 10% had smooth surfaces, whereas those having PBA contents of 20 ~ 40% had many dents at the surfaces. As the PBA content increased, the surface unevenness became remarkable. In the TEM observation of the particles after the extraction treatment of PBA with 1-butanol, the tendency became clearer (see Fig. 2). This indicates that the PBA domain exists around the bottom of each dent of the "golf ball-like" particles.

Figure 3 shows a TEM photograph of the ultrathin cross-sections of the PS/PBA (7/3, w/w) composite particles stained with RuO_4. PS is predominantly stained with RuO_4 in PS/PBA composite system. In the sections having a size similar to the particle size, which were sliced from the center of the particles, low contrast parts were slightly observed at the center, but obviously around the dents at the fringe. In the sections having a smaller size than the particle size, which were sliced from the edge of the particles, the low contrast parts were observed not only around the dents at the fringe but also at the center. These suggest that almost PBA domains exist at the particle surfaces.

On the basis of these results, the morphology of the golf ball-like particle is expressed as a schematic model shown in Fig. 4.

Figure 5 shows TEM photographs of PS/PBA composite particles produced with batch monomer addition method (a) and monomer dropwise method (b, c). The former method corresponds to the latter one with infinitely great dropwise rate of BA. As the dropwise rate decreased, the particle shape was changed to spherical. This suggests that the absorption of BA monomer to PS particle is needed to produce the golf ball-like particles. The monomer absorption decreases the viscosity within the particles, which is one of the factors greatly affecting the morphology of composite polymer particles [8].

Figure 6 shows TEM photographs of golf ball-like particles produced with monomer absorption method at various conversions of BA. Surface dent structure was observed even at 20% of conversion at which the ratio of PS/PBA is 9/0.77. On the other hand, PS/PBA (9/1, w/w) composite particles at 100% of conversion shown in Fig. 1 were almost spherical. In the former case, the composite particles were swollen with BA monomer, so that the viscosity within the particles was comparatively low. These

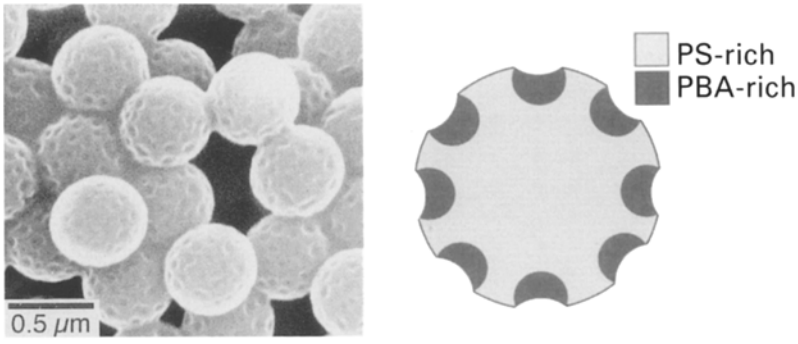

Fig. 4 SEM photograph of PS/PBA (7/3, w/w) composite particles and schematic view for the morphology of "golf ball-like" particles

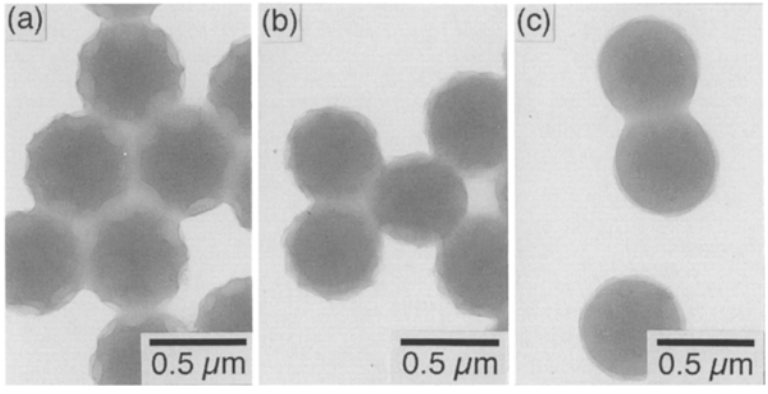

Fig. 5 TEM photographs of PS/PBA (7/3, w/w) composite particles: (a), batch monomer addition method; (b) and (c), monomer dropwise method: (b), 1.34 g/h; (c) 0.42 g/h

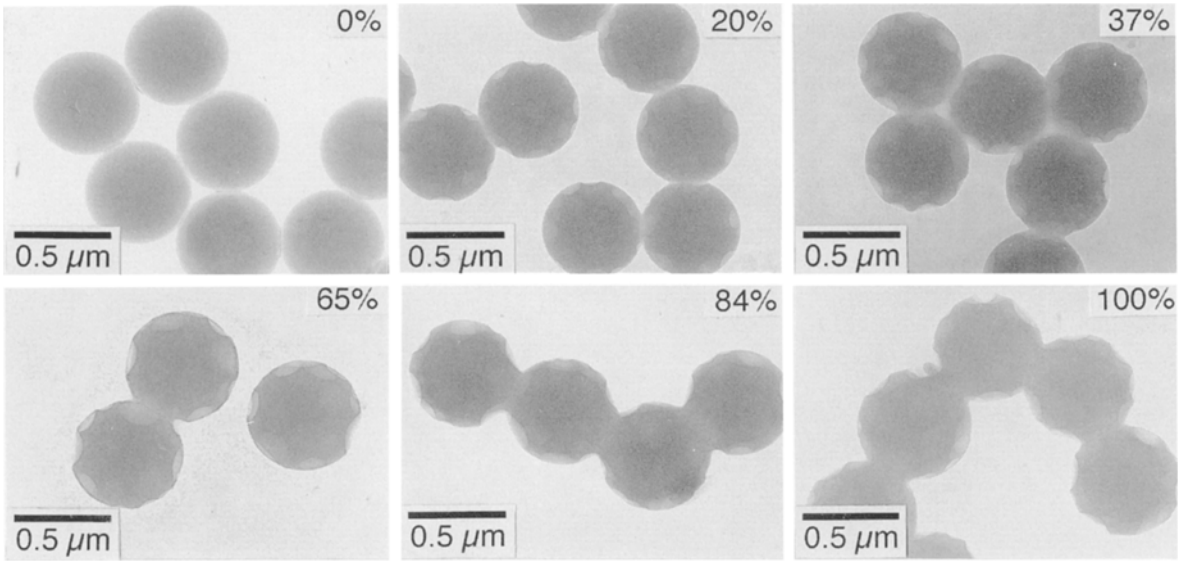

Fig. 6 TEM photographs of PS/PBA composite particles produced at various conversions of BA in the seeded emulsion polymerization in ethanol/water (2/8, w/w) medium: PS/PBA (w/w) at 100% conversion, 7/3

results also indicate that the viscosity within the particle greatly affects the particle morphologies. The surface dent structure did not significantly change throughout the polymerization after 37%.

From these results, we propose the formation mechanism of the "golf ball-like" particle as a schematic model shown in Fig. 7. KPS initiator radicals ($\bullet SO_4^-$) enter PS seed particle from medium and initiate the polymerization.

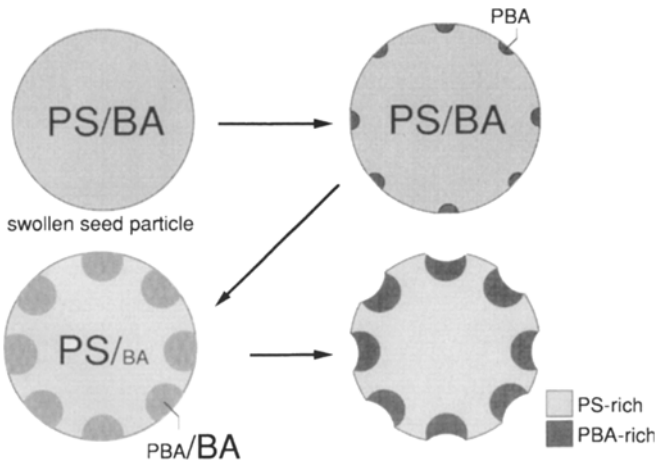

Fig. 7 A schematic view of the formation mechanism of "golf ball-like" PS/PBA composite particles

Because the viscosity in the inside is high and $-SO_4^-$ group of growing PBA radical is hydrated and PBA is more hydrophilic than PS, produced PBA molecules remain at the particle surface and form domains. Since BA monomer prefers to exist in PBA rather than PS, it predominantly distributes in PBA domains at the particle surface, and the viscosity in PS-rich phase increases, which serves to fix the PS phase. As the conversion of BA increases, the volume of PBA/BA domains contracts and results in dents at the particle surface.

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