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Morphology of anomalous polystyrene/polybutyl acrylate composite particles produced by seeded emulsion polymerization

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Abstract Recently, we found that “golf ball”-like polystyrene (PS)/polybutyl acrylate (PBA) composite particles could be produced by seeded emulsion polymerization of butyl acrylate (BA) with PS seed particles. In this article, the effects of the polymerization temperature, BA monomer concentration, and the presence of 1-octanol, which is a good

solvent for PBA and a poor solvent for PS in the polymerization, on the morphology was studied.

Key words Composite polymer particle – seeded emulsion polymerization – morphology – phase separation – viscosity

Introduction

Submicron-sized polymer particles produced by emulsion polymerization are normally spherical because this minimizes the surface tension energy. However, in a series of investigations on the production of composite polymer particles produced by seeded emulsion polymerization technique, we have found various anomalous particles [1–6]. Such anomalous shapes were based on heterogeneous structures formed in the early stage of the seeded emulsion polymerizations.

Recently, we found that anomalous polystyrene (PS)/polybutyl acrylate (PBA) composite particles having many dents at the surfaces could be produced by seeded emulsion polymerization of butyl acrylate (BA) with spherical PS seed particles [7]. We named them “golf ball”-like particles and investigated their formation mechanism [8].

Since the golf ball-like morphology has large interfacial area between both polymer phases, it should be thermodynamically unstable. In this article, effects of some factors in the seeded emulsion polymerization on the peculiar morphology will be discussed.

Experimental

Materials

Styrene (S) and BA were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Analytical grade potassium persulfate (KPS), 2,2'-azobisisobutyronitrile (AIBN), 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40) and 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) (Wako Pure Chemical Industries Ltd., Japan) were purified by recrystallization. Analytical grade sodium hydrogen carbonate and 1-octanol were used without further purification. Deionized water was distilled.

Seeded emulsion polymerization

According to the recipe listed in Table 1, PS seed particles were produced by emulsifier-free emulsion polymerization of S with KPS initiator in a four-necked, round-bottom flask under a nitrogen atmosphere at 70 °C for 24 h with stirring at 60 rpm. Three series of seeded emulsion

Table 1 Preparation of PS seed particles produced by emulsifier-free emulsion polymerization^{a)} in ethanol/water medium

Ingredient	
Styrene [g]	68.2
KPS [mg]	341
Ethanol [g]	444.0
Water [g]	187.5

^{a)} 70 °C; 24 h; N₂; stirring rate, 60 rpm.

Table 2 Preparations of PS/PBA (9/1, 7/3 and 5/5, w/w) composite particles produced by seeded emulsion polymerizations^{a)}

Ingredient	No. 1	No. 2	No. 3
PS seed [mg]	600	600	600
BA [mg]	67	257	600
KPS [mg]	20	20	20
Ethanol [g]	4.03	4.03	4.03
Water [g]	16.12	16.12	16.12
NaHCO ₃ [mg]	30	30	30

^{a)} 70 °C; 24 h; N₂.

Table 3 Preparations of PS/PBA (7/3, w/w) composite particles produced by seeded emulsion polymerizations^{a)} at different temperatures

Ingredient	No. 1	No. 2	No. 3
PS seed [mg]	600	600	600
BA [mg]	257	257	257
V-70 [mg]	23	—	—
AIBN [mg]	—	12	—
V-40 [mg]	—	—	18
Ethanol [g]	4.03	4.03	4.03
Water [g]	16.12	16.12	16.12
NaHCO ₃ [mg]	30	30	30
Polymn. Temp. [°C]	30	70	90

^{a)} 24 h; N₂.

polymerizations of BA with the PS seed particles were carried out in sealed glass tubes under a nitrogen atmosphere for 24 h with horizontal shaking at 120 cycles/min as follows: (i) PS/PBA composite particles having different compositions were produced with KPS at 70 °C under the conditions listed in Table 2; (ii) PS/PBA (7/3, w/w) composite particles were produced with different azoinitiators at different temperatures under the conditions listed in Table 3; (iii) after the medium of the seed emulsion was replaced from the ethanol/water to water by centrifugation, PS/PBA (9/1, w/w) composite particles were produced in an aqueous medium in the presence of 1-octanol under the conditions listed in Table 4.

Table 4 Preparation of PS/PBA (9/1, w/w) composite particles produced by seeded emulsion polymerization^{a)} with 1-octanol

Ingredient	
PS seed [mg]	600
BA [mg]	67
KPS [mg]	20
1-Octanol [mg]	196
Water [g]	20.15
NaHCO ₃ [mg]	30

^{a)} 70 °C; 24 h; N₂.

Heat treatment of the composite particles

Heat treatment of PS/PBA (7/3, w/w) composite emulsion was carried out as follows. To 4 g of the emulsion which was diluted with water to 1 g/l, 20 mg of toluene was added. After the emulsion was kept at 0 °C for 24 h to make toluene absorb into the composite particles with horizontal shaking at 120 cycles/min, it was kept at 80 °C for 24 h with the same shaking condition.

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 ethanol/water to 1-butanol by centrifugation and left at room temperature for a week with continuous stirring. During the extraction, the 1-butanol medium was replaced with a fresh one three times.

Electron microscopy

The particle shape was observed with a JEOL JEM-2010 transmission electron microscope (TEM). Each emulsion was diluted down to appropriate solid content, and its drop was placed onto a carbon-coated grid and allowed to dry at room temperature in a desiccator.

Results and discussion

Monodispersed spherical PS seed particles were produced by emulsifier-free emulsion polymerization under the conditions listed in Table 1. Number-average diameter and the coefficient of variation were, respectively, 462 nm and 2.35%. Golf ball-like PS/PBA (7/3, w/w) composite particles were produced by seeded emulsion polymerization of BA with the PS seed particles using KPS as an initiator under the conditions listed in Table 2, as shown in Fig. 1a.

Figure 1b shows a TEM photograph of the composite particles treated at 80 °C for 24 h after they had absorbed

Fig. 1 TEM photographs of original PS/PBA (7/3, w/w) composite particles (a) and those (b, c) treated with toluene at 80 °C for 24 h, before (b) and after (c) extraction of PBA with 1-butanol at room temperature for a week

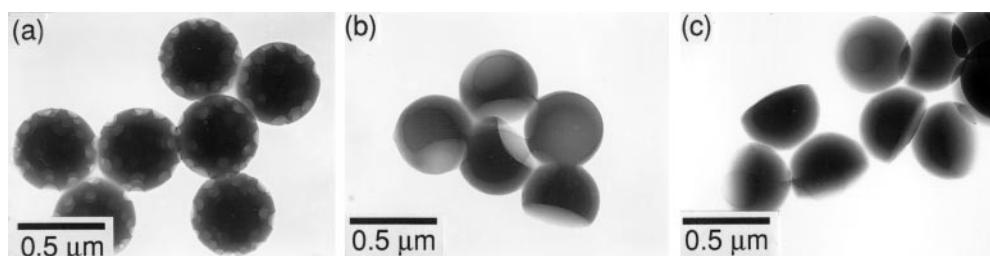
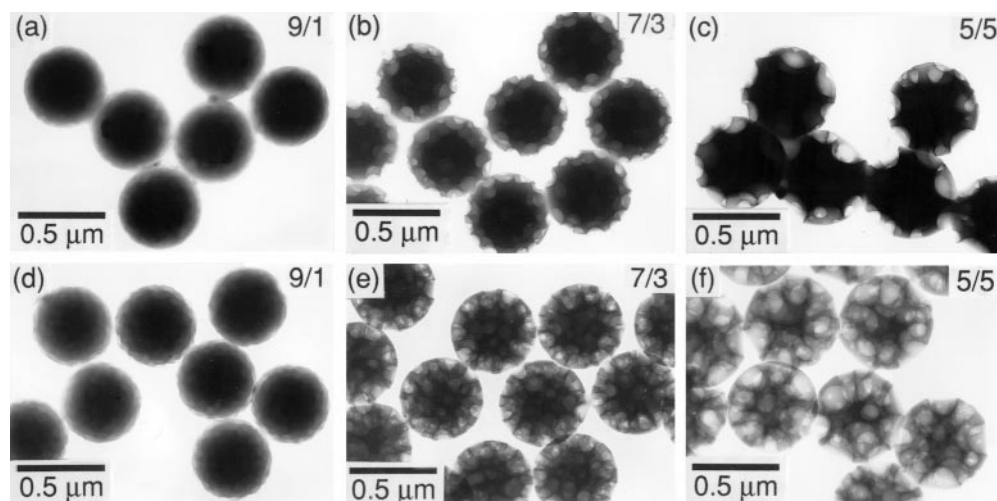


Fig. 2 TEM photographs of PS/PBA composite particles produced by seeded emulsion polymerizations with KPS at 70 °C for 24 h, (a–c) and after (d–f) extraction of PBA with 1-butanol at room temperature for a week: PS/PBA (w/w): (a, d), 9/1; (b, e), 7/3; (c, f), 5/5



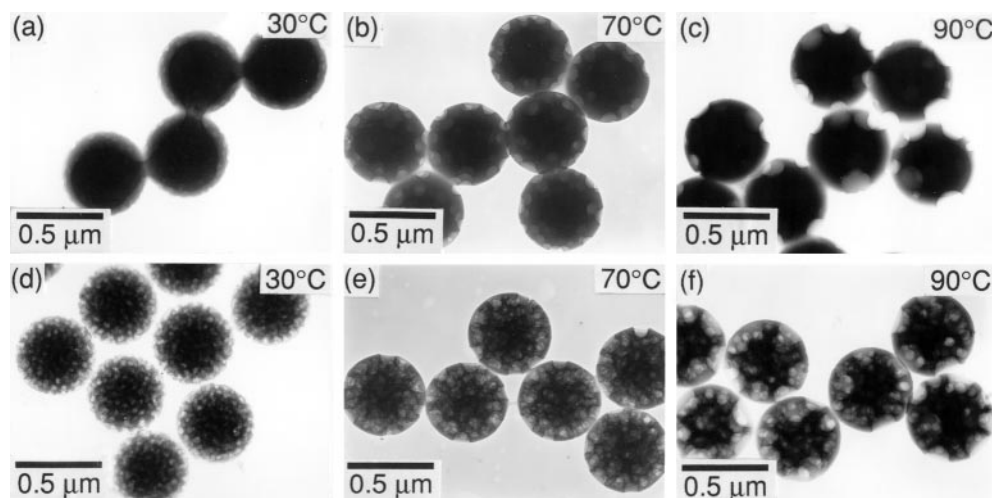
toluene at 0 °C. Since viscosity within the particles should be lowered by the absorption of toluene and by rising the temperature from 0 °C to 80 °C, PS and PBA molecules can move therein, which may result in thermodynamically stable morphology. In actual, the golf ball-like particle shape was changed to a hemispherical one by the treatment. As shown in Fig. 1c, the treated particle from which PBA was extracted with 1-butanol which is a good solvent for PBA and a non-solvent for PS had a similar shape. The hemispherical shape of the particles before the extraction of PBA is probably due to effluence of PBA component from the composite particles onto the grid for TEM observation because of its softness [5]. The result indicates that the particle has a half-moon-like structure which must be thermodynamically stable. In other words, the result clearly indicates that the golf ball-like morphology is thermodynamically unstable. These points will be discussed in detail in a following article.

Figure 2 shows TEM photographs of PS/PBA (9/1, 7/3, and 5/5, w/w) composite particles produced by seeded emulsion polymerization at 70 °C with KPS initiator under the conditions listed in Table 2, before (Figs. 2a–c) and after (Figs. 2d–f) extraction of PBA with 1-butanol. At the lowest BA monomer content (Figs. 2a and d), the particles were almost spherical. However, as the BA monomer content was increased, the PBA domains became larger, and

golf ball-like particles were produced. Since the increase of BA concentration in the polymerizing particle should reduce the viscosity therein, this result suggests that the mobility of polymer molecules within the polymerizing particle is related to the formation of golf ball-like particle.

Figure 3 shows TEM photographs of PS/PBA (7/3, w/w) composite particles produced by seeded emulsion polymerization at different temperatures under the conditions listed in Table 3, before (Figs. 3a–c) and after (Figs. 3d–f) extraction of PBA with 1-butanol. Three kinds of oil-soluble initiators, V-70, AIBN and V-40, of which 10 h half-life decomposition temperatures are 30 °C, 65 °C and 88 °C, respectively, were used to carry out each polymerization at a similar rate. As the polymerization temperature was increased, the dents at the composite particle surface became larger and the PBA domains became larger. Since the increase of the temperature should reduce the viscosity in the polymerizing particle, this result also suggests that the mobility of the polymer molecules within the polymerizing particle is related to the formation of golf ball-like particle. PS/PBA (7/3, w/w) composite particles produced with AIBN at 70 °C (Fig. 3b) had a similar shape as that produced with KPS at 70 °C (Fig. 2b). This indicates that an anchoring effect of sulfate group as KPS initiator fragment is not key factor on the formation of the golf ball-like morphology.

Fig. 3 TEM photographs of PS/PBA (7/3, w/w) composite particles produced by seeded emulsion polymerizations with V-70 at 30 °C (a, d), with AIBN at 70 °C (b, e) and with V-40 at 90 °C (c, f) for 24 h, before (a–c) and after (d–f) extraction of PBA with 1-butanol at room temperature for a week



The formation mechanism of the golf ball-like particles, which was proposed in the previous article [8], is simply explained as follows. In the early stage of the polymerization, PBA domains are formed at the particle surface and absorbed BA monomers in the particles are predominantly localized there. As the result, PS-rich continuous phase is always fixed because the glass transition temperature of PS is about 100 °C which is higher than the polymerization temperatures. In the polymerization system, since almost all BA monomers have been absorbed at low conversion, as the conversion of BA increases, the PBA domains swollen with the BA monomer gradually contract and result in dents at the particle surface.

When 1-octanol which is a good solvent for PBA but a poor solvent for PS coexists within the polymerizing particles, it should also exist predominantly in PBA domains. Therefore, according to the above-mentioned formation mechanism, the dents should be more clearly formed at the particle surface by removing 1-octanol from PBA domains after the polymerization.

Figure 4 shows TEM photographs of PS/PBA (9/1, w/w) composite particles produced by seeded emulsion polymerization in an aqueous medium in the presence of 1-octanol under the conditions listed in Table 4, before (Fig. 4a) and after (Fig. 4b) extraction of PBA with 1-butanol. The golf ball-like particles having dents at the

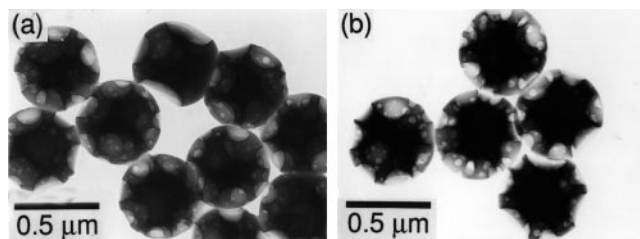


Fig. 4 TEM photographs of PS/PBA (9/1, w/w) composite particles produced by seeded emulsion polymerization with KPS at 70 °C for 24 h in the presence of 1-octanol, before (a) and after (b) extraction of PBA with 1-butanol at room temperature for a week

surfaces were produced. In the absence of 1-octanol, as already shown in Fig. 2a and Fig. 2d the PS/PBA (9/1, w/w) composite particles produced in the ethanol/water medium had almost spherical shape. This was the same as that produced in water (the photograph was omitted). These results indicate that the golf ball-like particles can be also produced by using an appropriate solvent for PBA in the process of the seeded emulsion polymerization and strongly supports the formation mechanism of the golf ball-like particles which we proposed.

From these results, the formation mechanism of the golf ball-like particles reported in the previous articles [8] was clarified more in detail, and the formation conditions was extended.

References

1. Matsumoto T, Okubo M, Shibao S (1976) *Kobunshi Ronbunshu* 33:575
2. Okubo M, Katsuta Y, Yamada A, Matsumoto T (1979) *Kobunshi Ronbunshu* 33:565
3. Okubo M, Katsuta Y, Matsumoto T (1981) *J Polym Sci Polym Chem Ed* 18:481
4. Okubo M, Ando M, Yamada A, Katsuta Y, Matsumoto T (1981) *J Polym Sci Polym Lett Ed* 19:143
5. Okubo M, Katsuta Y, Matsumoto T (1982) *J Polym Sci Polym Lett Ed* 20:45
6. Okubo M, Kanaida K, Matsumoto T (1987) *Colloid Polym Sci* 265:876
7. Okubo M, Murakami Y, Tsukuda Y (1993) *Chem Express* 4:253
8. Okubo M, Murakami Y, Fujiwara T (1996) *Colloid Polym Sci* 274:520