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SHORT COMMUNICATION

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Thermodynamic aspects of the heterogeneous structure of "golf-ball-like" polymer particles

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Abstract Recently, we found that "golf-ball-like" polystyrene (PS)/poly(butyl acrytlate) composite particles could be produced by seeded emulsion polymerization of butyl acrylate with PS seed particles. In this article, the theoretical and experimental thermodynamic instabilities of the golf-ball-like structure are discussed and are compared with core-shell and hemispherical morphologies.

Key words Composite polymer particle · Seeded emulsion polymerization · Golf-ball-like structure · Morphology · Thermodynamic stability

Introduction

Submicron-sized polymer particles produced by emulsion polymerization are normally spherical because this minimizes the interfacial free energy between the particle and the aqueous medium. However, in a series of our investigations on the composite polymer particles produced by seeded emulsion polymerization, various anomalously shaped particles have been prepared [1–6]. Such anomalous shapes were based on the heterogeneous growth of particles due to their heterogeneous morphologies formed in the early stage of the seeded emulsion polymerizations.

Recently, we found that anomalous polystyrene (PS)/poly(butyl acrylate) (PBA) composite particles having many dents on their surfaces could be produced by seeded emulsion polymerization of butyl acrylate (BA) with spherical PS seed particles [7], which were named "golf-ball-like" particles. We proposed the formation mechanism in a previous article [8] and examined the effects of some factors on the formation [9]. In brief the formation mechanism is as follows. Initiator radicals enter the PS seed particles swollen with BA and initiate the polymerization. Because PBA is more hydrophilic than PS, the PBA molecules remain at the particles surface and form domains. Almost all the BA monomers should be absorbed by the seed particles until the middle of the polymerization. Since BA monomers prefer to exist in the PBA phase rather than in the PS phase, the absorbed BA monomers predominantly distribute in PBA domains at the particle surface. As the conversion of BA increases, the volume of the PBA/BA domains contracts and results in dents at the particle surface.

The morphology seems to be thermodynamically unstable because of the large interfacial areas among the polymers and the medium. In this work, the theoretical and experimental thermodynamic stabilities of the golf-ball-like structure are discussed and are compared with core-shell and hemispherical morphologies.

Thermodynamic considerations

In general, phase separation of two kinds of polymer molecules takes place in composite polymer particles produced by seeded emulsion polymerization. It is important to understand the thermodynamic stability of the morphology of composite polymer particles. The thermodynamic stability can be estimated by the interfacial free energy (ΔG) which regards the initial seed particle as a reference, and can be expressed as

$$\Delta G = \sum_i \gamma_i A_i - \gamma_{\mathrm{P1/W}} A_0 \ , \qquad (1)$$

where γ_i is the interfacial tension of the ith interface, A_i is the corresponding interfacial area, $\gamma_{\mathrm{P1/W}}$ is the interfacial tension of seed polymer "1" particles suspended in water, and A_0 is the interfacial area between a seed particle and water.

In previous articles, it was reported that golf-ball-like composite particles were produced by seeded emulsion polymerization of BA with PS seed particles [7] and they had no PBA domains inside the particles [8]. The interfacial free energy of the golf-ball-like structure is given by Eq. 2 similarly to those of core-shell (Eq. 3) and hemispherical (Eq. 4) morphologies shown in Fig. 1. Equations (3) and (4) are described by Sundberg et al. [10].

$$\begin{aligned}\Delta G_{\text{golf ball}} &= \gamma_{\mathrm{PS/PBA}}(2\pi nkl) \\ &\quad + \gamma_{\mathrm{PS/W}}\left[4\pi R_{\mathrm{P}}^2 - 2\pi n R_{\mathrm{P}}\left(R_{\mathrm{P}} - \sqrt{R_{\mathrm{P}}^2 - l^2}\right)\right] \\ &\quad + \gamma_{\mathrm{PBA/W}}\left[\pi n(l^2 + h^2)\right] - \gamma_{\mathrm{PS/W}}(4\pi R_{\mathrm{S}}^2) \qquad (2)\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{core-shell}} &= \gamma_{\mathrm{PS/PBA}}(4\pi R_{\mathrm{S}}^2) + \gamma_{\mathrm{PBA/W}}(4\pi R_{\mathrm{P}}^2) \\ &\quad - \gamma_{\mathrm{PS/W}}(4\pi R_{\mathrm{S}}^2) \qquad (3)\end{aligned}$$

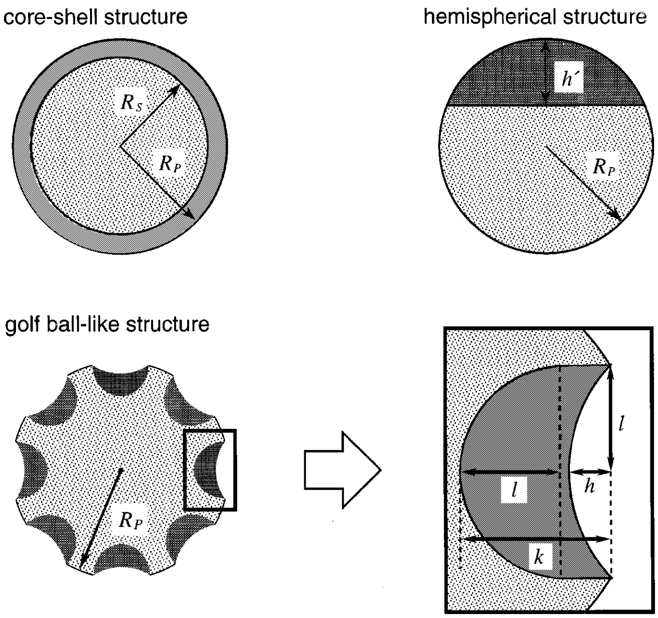


Fig. 1 Morphologies of polystyrene (*PS*) poly(butyl acrylate) (*PBA*) composite particles with core-shell, hemispherical, and golf-ball-like structure: PS (▨); PBA (■)

$$\begin{aligned}\Delta G_{\text{hemispherical}} &= \gamma_{\mathrm{PS/PBA}}(2\pi R_{\mathrm{P}} h' - \pi h'^2) \\ &\quad + \gamma_{\mathrm{PS/W}}(4\pi R_{\mathrm{P}}^2 - 2\pi R_{\mathrm{P}} h') \\ &\quad + \gamma_{\mathrm{PBA/W}}(2\pi R_{\mathrm{P}} h') - \gamma_{\mathrm{PS/W}}(4\pi R_{\mathrm{S}}^2) \ , \qquad (4)\end{aligned}$$

where R_{P} and R_{S} are the radii of PS/PBA composite and PS seed particles, respectively, and n is the number of PBA domains.

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. Analytical grade sodium hydrogen carbonate was used without further purification. Deionized water was distilled.

Film formation

PS and PBA emulsions were produced by emulsifier-free emulsion polymerization with KPS initiator under the conditions listed in Table 1. PS films were obtained by pressing dried PS particles, which were separated from the PS emulsion, at 150 °C for 20 min at 4 MPa. PBA films were prepared by casting the PBA emulsion on a glass plate and allowing it to dry at room temperature in a desiccator.

Measurement of interfacial intentions between polymers and water

The contact angles of air and CH_2I_2 in water as shown in Fig. 2 were measured. The interfacial tension between PS and water, $\gamma_{\mathrm{PS/W}}$, and that between PBA and water, $\gamma_{\mathrm{PBA/W}}$, were calculated by combining Young's equations (Eqs. 5, 6), Owens' equations (Eqs. 7, 8) and already known interfacial tensions listed in Table 2 [11].
Young's equation:

Air: $$\gamma_{\mathrm{P/A}} = \gamma_{\mathrm{P/W}} + \gamma_{\mathrm{W/A}} \cos\theta \qquad (5)$$

CH_2I_2: $$\gamma_{\mathrm{P/W}} = \gamma_{\mathrm{P/L}} + \gamma_{\mathrm{W/L}} \cos\theta \qquad (6)$$

Owens' equation:

Air: $$\begin{aligned}\gamma_{\mathrm{P/W}} &= \gamma_{\mathrm{P/A}} + \gamma_{\mathrm{W/A}} \\ &\quad - 2\left(\gamma_{\mathrm{P/A}}^{\mathrm{d}}\gamma_{\mathrm{W/A}}^{\mathrm{d}}\right)^{1/2} - 2\left(\gamma_{\mathrm{P/A}}^{\mathrm{p}}\gamma_{\mathrm{W/A}}^{\mathrm{p}}\right)^{1/2} \qquad (7)\end{aligned}$$

Table 1 Preparation of polytyrene (*PS*) and poly(butyl acrylate) (*PBA*) produced by emulsifier-free emulsion polymerization

Ingredient	PS[a]	PBA[b]
Styrene (g)	68.2	–
Butyl acrylate (g)	–	89
Potassium persulfate (mg)	341	446
Ethanol (g)	444	–
Water (g)	187.5	376

[a] 70 °C; 24 h; N_2; stirring rate, 60 rpm
[b] 75 °C; 34 h; N_2; stirring rate, 120 rpm

$$\mathrm{CH_2I_2}: \quad \gamma_{\mathrm{P/L}} = \gamma_{\mathrm{P/A}} + \gamma_{\mathrm{L/A}} - 2(\gamma^{\mathrm{d}}_{\mathrm{P/A}}\gamma^{\mathrm{d}}_{\mathrm{L/A}})^{1/2} - 2\left(\gamma^{\mathrm{p}}_{\mathrm{P/A}}\gamma^{\mathrm{p}}_{\mathrm{L/A}}\right)^{1/2} , \tag{8}$$

where the subscripts A and L mean air and $\mathrm{CH_2I_2}$, respectively, and superscripts d and p mean dispersion and polar component, respectively. $\gamma^{\mathrm{d}}, \gamma^{\mathrm{p}}$ and γ are defined by the following relation:

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} \ . \tag{9}$$

Heat treatment of the composite particles

Toluene (20 mg) was added to 4 g PS/PBA (7/3, w/w) composite emulsion whose polymer solid was 1 g/l, which was produced under the conditions determined in a previous article [9]. After the emulsion was kept at 0 °C for 24 h to make toluene absorb into the composite particles, it was kept at 80 °C for 24 h with horizontal shaking at 120 cycles/min.

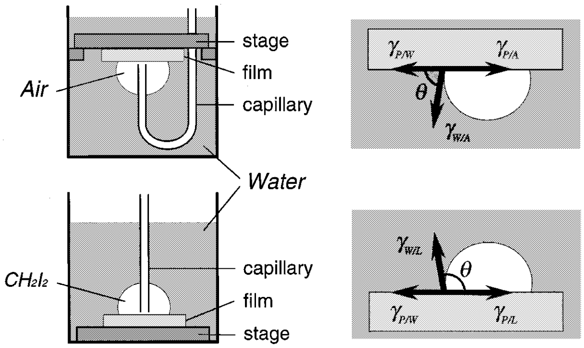


Fig. 2 Schematic diagram for the measurement of contact angles of air and $\mathrm{CH_2I_2}$ on polymer films in water

Table 2 Dispersion (γ^{d}) and polar (γ^{p}) components of interfacial free energies (γ) for water and $\mathrm{CH_2I_2}$ at 20 °C

	γ	γ^{d}	γ^{p}
	(mN/m)		
Water/air	72.8	21.8	51.0
$\mathrm{CH_2I_2}$/air	50.8	49.5	1.3
Water/$\mathrm{CH_2I_2}$	41.6		

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 is a nonsolvent for PS. The medium of the PS/PBA composite emulsion was changed from ethanol/water to 1-butanol by centrifugation and was left at room temperature for 1 week with continuous stirring. During the extraction, the 1-butanol medium was replaced with a fresh one 3 times.

Ultrathin cross sections of the composite particles

Sample particles were microtomed at −100 °C with a Reichert Ultracut S/FC S cryoultramicrotome. The microtomed specimens were stained with $\mathrm{RuO_4}$ vapor.

Electron microscopy

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

Results and discussion

Interfacial free energy

Figure 3 shows TEM photographs of golf-ball-like PS/PBA (7/3, w/w) composite particles produced by seeded emulsion polymerization of BA with PS seed particles ($R_{\mathrm{S}} = 219$ nm) using KPS as an initiator before and after extraction with 1-butanol.

Each value shown in Fig. 1 was measured on the TEM photographs (Fig. 3): $R_{\mathrm{P}} = 243$ nm; $k = 62$ nm; $l = 41$ nm; $h = 23$ nm. The number of PBA domains (n) at the particle surface was estimated to be 50 from the scanning electron microscope photographs shown in previous articles [7, 8]. As for the hemispherical structure, h' was calculated to be 167 nm. $\gamma_{\mathrm{PS/W}}$ and $\gamma_{\mathrm{PBA/W}}$ obtained by contact-angle measurement were 1.4 and 0.8 mN/m, respectively. These interfacial tension values were smaller than those reported by Sundberg et al. [10]. The reason for this difference seems to be related to the polymer end group. Since KPS initiator

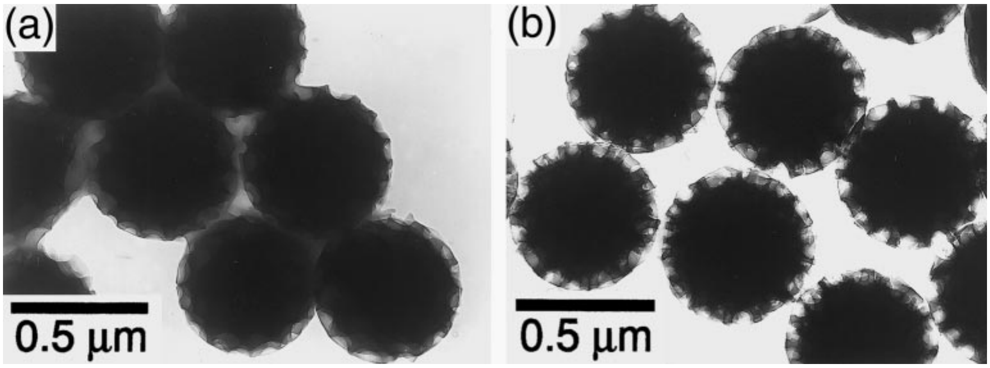


Fig. 3 Transmission electron microscope (*TEM*) photographs of PS/PBA (7/3, w/w) composite particles produced by seeded emulsion polymerization with KPS at 70 °C for 24 h, **a** before and **b** after extraction of PBA with 1-butanol at room temperature for 1 week

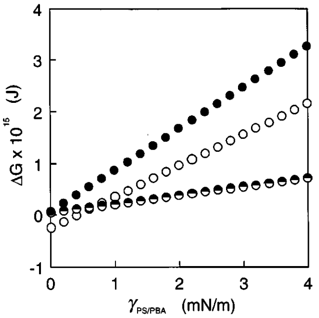


Fig. 4 Simulations of the interfacial free energy (ΔG) as a function of the interfacial tension between PS and PBA ($\gamma_{PS/PBA}$) on core-shell (○), hemispherical (◓), and golf-ball-like (●) structures using the following values: *n*, 50; *k*, 62 nm; *l*, 41 nm; *h*, 23 nm; *h'*, 167 nm; R_P, 243 nm; R_S, 219 nm; $\gamma_{PS/W}$, 1.4 mN/m; $\gamma_{PBA/W}$, 0.8 mN/m

was used for both the preparation of PS seed particles and PS/PBA composite particles, PS and PBA molecules should have -SO_4^- end groups. The relationship between the polymer end group and the morphology of composite particles will be discussed elsewhere.

Figure 4 shows simulations for core-shell, hemispherical, and golf-ball-like morphologies for the relationship between ΔG and $\gamma_{PS/PBA}$ obtained using the above values. ΔG for the golf-ball-like structure always has the largest interfacial free energy regardless of $\gamma_{PS/PBA}$. This indicates that the golf-ball-like structure is the most unstable structure thermodynamically. Because an adjustable $\gamma_{PS/PBA}$ value is unknown, it is difficult to judge which morphology of core-shell or hemispherical structures is more stable.

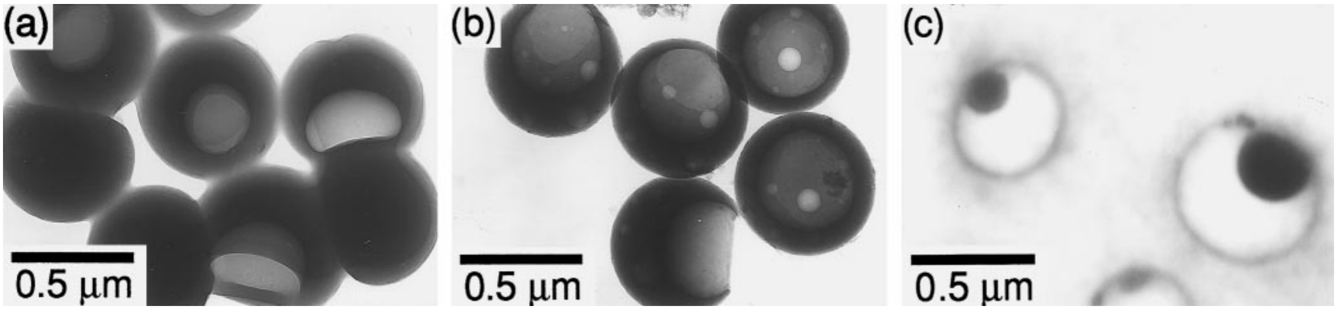
Morphology

The formation of the golf-ball-like structure seems to be kinetically controlled. In order to move both PS and PBA molecules within the composite particles, the golf-ball-like composite particles shown in Fig. 3a were treated at 80 °C for 24 h after toluene had been absorbed by the composite particles at 0 °C.

Figure 5 shows TEM photographs of PS/PBA (7/3, w/w) composite particles treated with toluene at 80 °C for 24 h, before and after extraction of PBA with 1-butanol at room temperature for 1 week, and the ultrathin cross sections of the treated particles stained with RuO_4 vapor. Many PBA domains localized at the surface of the composite particles shown in Fig. 3a. Some particles lacked a part of a full sphere (Fig. 5a). This was probably due to effluence of the PBA component from the composite particles during the preparation of the TEM specimen because of their softness [5]. These photographs show that the golf-ball-like shape changed into the hemispherical morphology having smaller interfacial areas.

From the theoretical and experimental results reported here, it is concluded that the golf-ball-like morphology is thermodynamically unstable and is based on kinetic control.

Fig. 5 TEM photographs of PS/PBA (7/3, w/w) composite particles treated with toluene at 80 °C for 24 h, **a** before and **b** after extraction PBA with 1-butanol at room temperature for 1 week, and **c** the ultrathin cross sections of the treated particles (**a**) stained with RuO_4 vapor



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