

ORIGINAL ARTICLE

Preparation of hemispherical polystyrene particles utilizing the solvent evaporation method in aqueous dispersed systems

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Various nonspherical polystyrene (PS) particles were prepared by slow evaporation of toluene (used common good solvent) from homogeneous PS/hexadecane (HD)/toluene droplets dispersed in surfactant aqueous solutions at room temperature, followed by the rapid removal of HD from PS/HD particles with various phase-separated morphologies. The morphology of PS/HD particles was controlled by tuning the interfacial tension with various types of surfactants. Hemispherical PS particles with flat surfaces were obtained from phase-separated PS/HD/toluene droplets having a Janus structure, when polyoxyethylene nonylphenyl ether with an average ethylene oxide chain length of 30.8 was used as the surfactant.

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INTRODUCTION

Nonspherical polymer particles have attracted great attention because of their potential as materials with unique crystal structures,^{1–3} light scattering properties⁴ and external field-responsive properties (e.g., shear field⁵ and electric field⁶). In general, polymer particles synthesized by heterogeneous polymerizations under thermodynamic control have a spherical shape because of interfacial free energy minimization. However, nonspherical polymer particles have been synthesized under kinetic control utilizing various seeded polymerization methods,^{7–24} microfluidic techniques,^{25–28} deformation of spherical polymer particles by external force,^{29–31} the stepwise heterocoagulation method^{32,33} and the self-organized precipitation method.³⁴

In a previous work, we proposed a novel approach for the preparation of micrometer-sized, monodisperse, nonspherical (i.e., dimpled and hemispherical) polystyrene (PS) particles by successive heating and cooling of spherical PS particles dispersed in a methanol/water medium in the presence of droplets of decane.³⁵ Decane was absorbed by the particles during heating, and the particles subsequently phase-separated into PS and decane phases during cooling. Eventually, nonspherical particles reflecting the morphology of phase-separated PS/decane particles were formed by rapid removal of the decane phase. The final particle shape could be controlled simply with the amount of absorbed decane.

We have also recently demonstrated morphology control of PS/poly(methyl methacrylate) composite particles prepared by the slow release of toluene as a common good solvent from homogeneous PS/poly(methyl methacrylate)/toluene droplets dispersed in a surfactant aqueous solution at room temperature (the solvent evaporation method).^{36–38} It was revealed that the particle morphology could be

controlled by tuning the interfacial tensions by varying the types of surfactant.

In this article, we attempt to prepare various nonspherical (especially hemispherical) PS particles based on the above two experimental results. This will be achieved by morphology control of PS/hexadecane (HD) particles obtained by the solvent evaporation method (using toluene as the common good solvent) using various types of surfactants, followed by a rapid removal of the HD phase. HD is employed rather than decane because it will not evaporate during the toluene evaporation process.

EXPERIMENTAL PROCEDURE

Materials

Styrene was distilled under reduced pressure in a nitrogen atmosphere. Reagent-grade 1-pyrenylmethyl methacrylate (PM; Funakoshi, Tokyo, Japan) was used as a PS fluorescent moiety without further purification. Reagent-grade 2,2'-azobisisobutyronitrile (AIBN; Wako Pure Chemical Industries, Ltd., Osaka, Japan) was purified by recrystallization from methanol. Toluene and SDS were used as received from Nacalai Tesque, Inc (Kyoto, Japan). Poly(vinyl alcohol) (PVA; Gohsenol GH-17; degree of polymerization, 1700; degree of hydrolysis, 88%) was supplied by Nippon Synthetic Chemical (Osaka, Japan). Commercial-grade polyoxyethylene nonylphenyl ether non-ionic surfactants with average ethylene oxide chain lengths of 15.4, 30.8 and 50.6 units (Emulgen 930, Emulgen 931 and Emulgen 950, respectively) were supplied by Kao Co., Tokyo, Japan. Water was purified using an Elix UV system (Nihon Millipore K.K., Tokyo, Japan).

Preparation of nonspherical particles

PS and S-PM copolymer (P(S-PM)) were synthesized by solution polymerization using 2,2'-azobisisobutyronitrile as an initiator. PS: M_w , 8.8×10^4 ; M_w/M_n , 2.1. P(S-PM) (PM, 0.5 mol%): M_w , 7.1×10^4 ; M_w/M_n , 1.7. PS/HD

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and P(S-PM)/HD particles were prepared as follows: a homogeneous toluene solution of PS (or P(S-PM)) (0.643 g) and HD (PS (or P(S-PM))/HD/toluene = 1/1/29, v/v/v) was mixed with a 0.33 wt% (relative to water) surfactant aqueous solution (15 g). The mixture was stirred vigorously using a homogenizer (NIHONSEIKI KAISHA Ltd., ABM-2 Tokyo, Japan) at 4000 r.p.m. for 2 min in a glass vial and toluene was then slowly released by evaporation during gentle stirring at room temperature for 24 h in an uncovered glass vial (surface area between dispersion and air was 8 cm²). The resulting particles were washed by centrifugation using methanol to remove HD and excess surfactant and then dried under vacuum at room temperature.

Measurements

The amount of toluene in the dispersion was determined by gas chromatography (Shimadzu Corporation, Kyoto, Japan, GC-2014) with helium as the carrier gas, *N,N*-dimethylformamide as a solvent and *p*-xylene as an internal standard. Molecular weight distribution was measured by gel permeation chromatography, with two styrene/divinylbenzene gel columns (TOSOH Corporation, Yamaguchi, Japan, TSK gel GMH_{HR}-H, 7.8 mm i.d. × 30 cm) using tetrahydrofuran as the eluent at 40 °C at a flow rate of 1.0 ml min⁻¹, employing refractive index (TOSOH Corporation) and ultraviolet detectors (TOSOH Corporation, UV-811). The columns were calibrated with six standard PS samples (1.05 × 10³–5.48 × 10⁶, $M_w/M_n = 1.01$ –1.15).

Interfacial tension measured by the pendant drop method

The densities of toluene solutions of PS and HD were measured with a pycnometer (volumetric flask type). Interfacial tensions ($\gamma_{PS-T/Surf-w}$ or $\gamma_{HD-T/Surf-w}$) between the PS (or HD)-toluene droplets and various surfactant aqueous solutions as functions of PS (or HD) weight fraction (w_{PS} or w_{HD}) were measured by the pendant drop method with a Drop Master 500 (Kyowa Interface Science Co., Ltd., Saitama, Japan). All of the measurements were performed at room temperature (ca. 20 °C). The accuracy of the interfacial tensions reported was ± 0.1 mN m⁻¹.

Microscope observation

The dispersions of PS/HD and P(S-PM)/HD particles were observed with a Nikon (Tokyo, Japan) Eclipse 80i optical microscope and an Olympus (Tokyo, Japan) FV1000-KDM confocal laser scanning microscope, respectively. Dried PS particles were observed with a Hitachi (Tokyo, Japan) S-2460 scanning electron microscope at an acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

The morphology of a PS/HD particle reflects the thermodynamic equilibrium morphology of the phase-separated PS/HD/toluene droplet determined by interfacial free energy minimization. Thus, the measurement of each interfacial tension enables prediction of the most stable droplet morphology. However, measurement of $\gamma_{PS-T/Surf-w}$ at high w_{PS} by the pendant drop method was difficult because of high viscosity. $\gamma_{PS-T/Surf-w}$ was thus calculated from the following equations:³⁹

$$\ln[(\phi_{PS}^S/\phi_{PS})^{1/r}/(\phi_T^S/\phi_T)] = [(\gamma_{T/Surf-w} - \gamma_{PS-T/Surf-w})a/kT] \quad (1)$$

$$+ \chi(l+m)(\phi_T - \phi_{PS}) - \chi l(\phi_T^S - \phi_{PS}^S)$$

$$(\gamma_{PS-T/Surf-w} - \gamma_{T/Surf-w})a/kT = \ln(\phi_T^S/\phi_T) + [(r-1)/r](\phi_{PS}^S - \phi_{PS}) \quad (2)$$

$$+ \chi[l(\phi_{PS}^S)^2 - (l+m)(\phi_{PS})^2]$$

where, T and Surf-w subscripts denote toluene and surfactant aqueous solutions, respectively, ϕ_i and ϕ_i^S are the volume fractions of the *i*th component in the particle and of the *i*th component at the surface, respectively. $\gamma_{i-T/Surf-w}$ is the interfacial tension between the *i*th component and the surfactant aqueous phase, *r* is the ratio of the component molar volumes ($r = 856$), *a* is the surface area occupied by

a toluene molecule (31.4 Å²), *k* is the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹), *T* is the temperature (300 K), χ is the interaction parameter between PS and toluene (0.40) and *l* and *m* are constants ($l = 0.5$ and $m = 0.25$).^{40–42} Equations 1 and 2 give the interfacial tension between the PS and surfactant aqueous phases ($\gamma_{PS-T/Surf-w}$) as a function of ϕ_{PS} . The χ parameter between PS and toluene depends on the polymer concentration. These effects were not considered in the calculation of interfacial tensions, and as assumed previously,³⁸ the χ parameter was treated as constant in the current study.

Figure 1 shows $\gamma_{PS-T/Surf-w}$ and $\gamma_{HD-T/Surf-w}$ with various types of surfactants as functions of w_{PS} and w_{HD} . The $\gamma_{PS-T/Surf-w}$ values calculated based on the above equations indicate constant values at low w_{PS} and were consistent in all cases with those measured by the pendant drop method at $w_{PS} = 0.17$. At high w_{PS} , $\gamma_{PS-T/Surf-w}$ drastically increased with increasing w_{PS} . On the other hand, $\gamma_{HD-T/Surf-w}$ gradually increased with increasing w_{HD} . The magnitude relations of $\gamma_{PS-T/Surf-w}$ and $\gamma_{HD-T/Surf-w}$ were reversed in the cases of PVA, Emulgen 931 and Emulgen 950.

Morphological development of phase-separated PS/HD/toluene droplets associated with intergradations of the interfacial tensions is retarded by increasing viscosity inside the droplet because of increasing polymer fraction (i.e., evaporation of toluene) because the glass transition temperature (*T*_g) of PS is well above the room temperature. The *T*_g of the PS-toluene phase in the phase-separated droplet was calculated with the Fox equation,⁴³ assuming that the melting temperature of toluene is its *T*_g (−93 °C). Because the *T*_g of the PS-toluene phase reached room temperature at $w_{PS} = 0.75$, the w_{PS} where the droplet morphology is fixed was defined as 0.75 in this experiment.

Table 1 shows $\gamma_{PS-T/Surf-w}$ and $\gamma_{HD-T/Surf-w}$ with various types of surfactants at w_{PS} and $w_{HD} = 0.75$; the difference between $\gamma_{PS-T/Surf-w}$ and $\gamma_{HD-T/Surf-w}$ ($\Delta\gamma$) decreased in the order Emulgen 930 > SDS > Emulgen 931 > Emulgen 950 > PVA. The thermodynamically stable morphology of phase-separated PS/HD/toluene droplets is expected to change from PS-core/HD-shell to HD-core/PS-shell when $\Delta\gamma$ decreases from positive to negative. The resulting particle morphology, which reflects the thermodynamically stable droplet morphology, should also exhibit the same tendency.

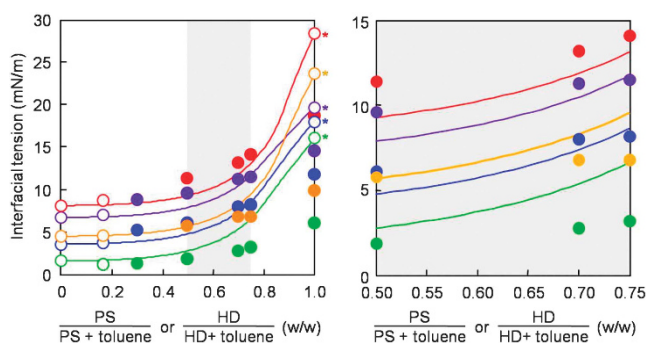


Figure 1 Interfacial tensions between 0.33 wt% surfactant aqueous solutions and toluene droplets containing dissolved PS (○, ○, ○, ○, ○) or HD (●, ●, ●, ●, ●) measured by the pendant drop method as functions of PS or HD weight fraction. Surfactants: (○, ●) PVA; (○, ●) SDS; (○, ●) Emulgen 930; (○, ●) Emulgen 931; (○, ●) Emulgen 950. Asterisks denote calculated values using the Young equation based on contact angles of surfactant aqueous solutions on a PS film. The lines are the interfacial tensions between 0.33 wt% surfactant aqueous solutions (corresponding to each color) and PS-containing toluene droplets calculated using Equations 1 and 2.

Table 1 Interfacial tension between 0.33 wt% surfactant aqueous solutions and toluene (T) droplets dissolving of PS or HD (PS or HD)/toluene = 3/1, w/w)

| | Interfacial tension (mN m^{-1}) | | | | |
|--|--|-------------|-------------|-------------|------|
| | SDS | Emulgen 930 | Emulgen 931 | Emulgen 950 | PVA |
| $\gamma_{\text{PS-T/Surf-w}}^{\text{a}}$ | 9.5 | <6.6 | 8.6 | 11.7 | 13.1 |
| $\gamma_{\text{HD-T/Surf-w}}^{\text{b}}$ | 6.8 | 3.2 | 8.2 | 11.5 | 14.1 |
| $\Delta\gamma^{\text{c}}$ | 2.7 | <3.4 | 0.4 | 0.2 | -1.0 |

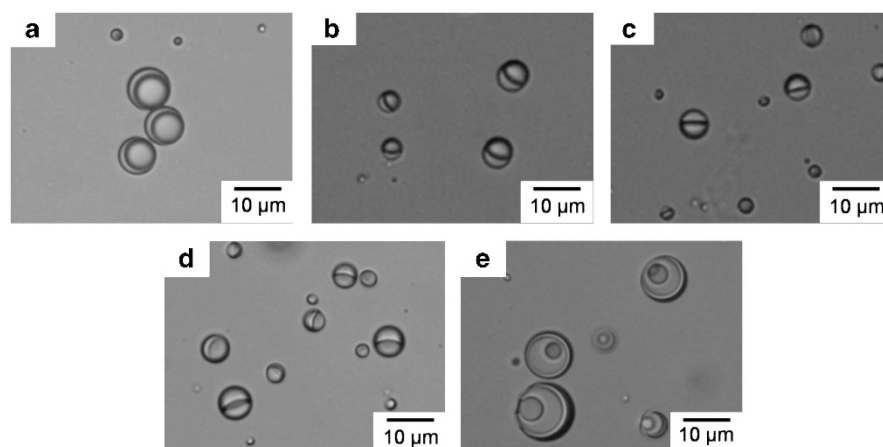
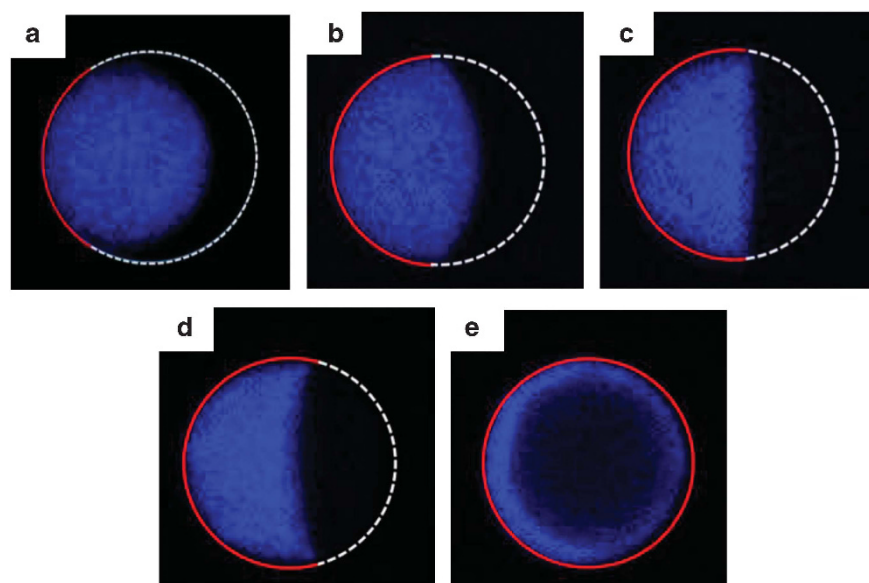
Abbreviations: HD, hexadecane; PS, polystyrene.

^aCalculated interfacial tension according to Siow *et al.*³⁹^bMeasured by the pendant drop method.^c $\Delta\gamma = \gamma_{\text{PS-T/Surf-w}} - \gamma_{\text{HD-T/Surf-w}}$

Figure 2 shows optical micrographs of PS/HD particles prepared by the solvent evaporation method. The morphologies of the resulting particles depended on the type of surfactant. To distinguish between the PS and HD phases, P(S-PM) incorporating a fluorescent unit was employed instead of PS. It was confirmed that a very small amount of copolymerized fluorescent PM did not affect the particle morphology⁴⁴ (i.e., PS/HD and P(S-PM)/HD particles had the same morphology).

Figure 3 shows confocal laser scanning micrographs of P(S-PM)/HD particles prepared under the same conditions as those in Figure 2. The interfacial area between the P(S-PM) phase and the aqueous media increased with decreasing $\Delta\gamma$, except in the cases of SDS and Emulgen 930 (see Table 1).

Previous work³⁷ has shown that a non-ionic surfactant (polyoxyethylene nonylphenylether with an average ethylene oxide

**Figure 2** Optical micrographs of PS/HD particles prepared by slow release of toluene from PS/HD/toluene (1/1/29, v/v/v) droplets dispersed in 0.33 wt% aqueous solutions of SDS (a), Emulgen 930 (b), Emulgen 931 (c), Emulgen 950 (d) and PVA (e).**Figure 3** Confocal laser scanning micrographs of P(S-PM)/HD particles prepared by slow release of toluene from P(S-PM)/HD/toluene (1/1/29, v/v/v) droplets dispersed in 0.33 wt% aqueous solutions of SDS (a), Emulgen 930 (b), Emulgen 931 (c), Emulgen 950 (d) and PVA (e). The red and white curve lines indicate interfaces of the P(S-PM) and HD phases, respectively, contacting with each surfactant aqueous medium.

chain length of 10.9) dissolved into both the oil and aqueous phases and significantly reduced the oil-aqueous medium interfacial tension.

Figure 4 shows the variation of Emulgen concentrations in aqueous media as a function of the toluene weight fraction relative to the total amount of toluene, water and Emulgen. Emulgen 930, with an average ethylene oxide unit length of 15.4, dissolved into the toluene phase whereas nearly all Emulgen 931 and 950 dissolved in the aqueous phases. The effect of partitioning was not considered in the equations calculating $\gamma_{\text{PS-T/Surf-w}}$; the actual $\gamma_{\text{PS-T/Surf-w}}$ would thus be

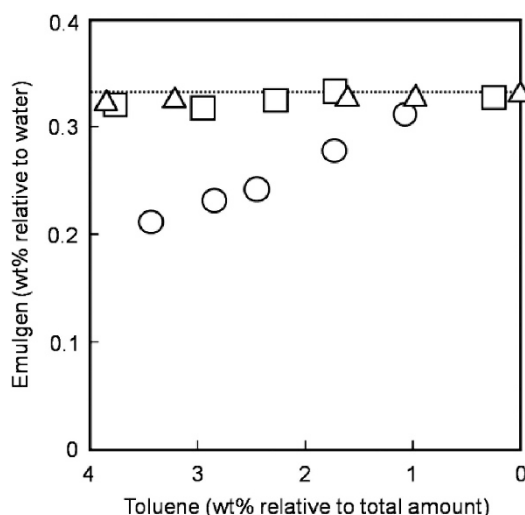


Figure 4 Emulgen loading content in the aqueous phases as a function of toluene content (relative to total amount of toluene, water and Emulgen) during evaporation of toluene from dispersions of toluene and 0.33 wt% Emulgen aqueous solution (toluene/water = 4/100, w/w). Emulgen: (○) 930; (□) 931; (△) 950. Dotted line shows the initial Emulgen concentration.

lower than the calculated one in the Emulgen 930 case, resulting in a lower $\Delta\gamma$ for Emulgen 930 than for SDS. This could explain the unexpected results (a) and (b) in Figure 3.

Figure 5 shows scanning electron microscope photographs of PS particles after rapid removal of HD with methanol from the PS/HD particles shown in Figure 2. PS particles with various shapes corresponding to the phase-separated morphology were formed. PS particles prepared using PVA had a single deep dimple at the surface; this was attributed to the volume reduction of the HD phase after hardening of the PS phase during toluene evaporation from the droplets.³⁶ In particular, hemispherical PS particles were obtained when Emulgen 931 was employed. Such particles can be oriented on planar surfaces, with their curved surfaces pointing upward and can act as microlens.^{45,46} This simple preparation method should be applicable to other polymer and poor solvent systems, and can thus be a very useful tool for the preparation of hemispherical particles for industrial applications.

CONCLUSIONS

Various nonspherical PS particles were prepared by a rapid removal of HD from phase-separated PS/HD particles obtained by the slow release of toluene from PS/HD/toluene droplets dispersed in various surfactant aqueous solutions at room temperature. The phase-separated morphology of the PS/HD particles and the final PS particle shape could be controlled by tuning $\gamma_{\text{PS-T/Surf-w}}$ and $\gamma_{\text{HD-T/Surf-w}}$. As a result, hemispherical PS particles were obtained from the phase-separated PS/HD/toluene droplets having a Janus structure when Emulgen 931 was used as the surfactant.

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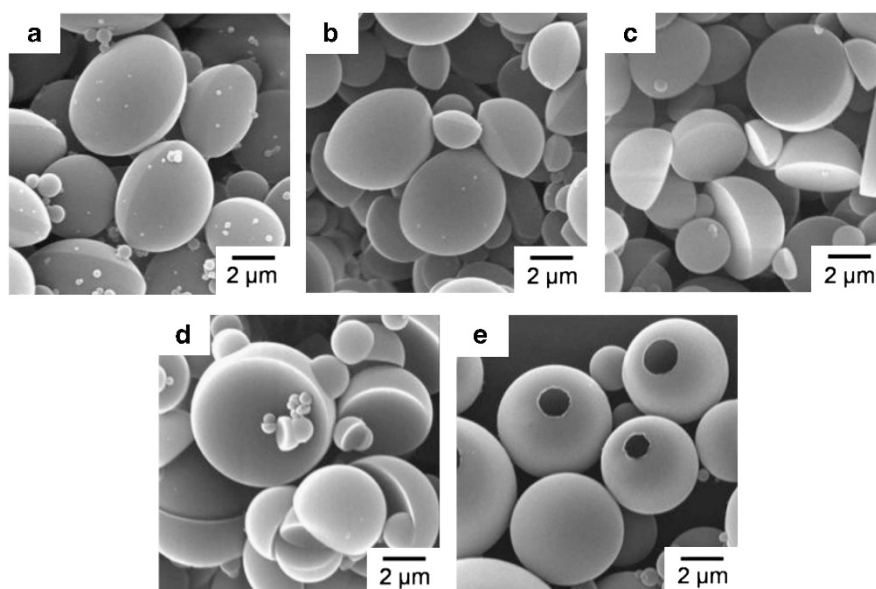


Figure 5 Scanning electron microscope micrographs of PS particles after the rapid removal of HD with methanol from PS/HD particles prepared by the slow release of toluene from PS/HD/toluene (1/1/29, v/v/v) droplets dispersed in 0.33 wt% aqueous solutions of SDS (a), Emulgen 930 (b), Emulgen 931 (c), Emulgen 950 (d) and PVA (e).

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