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SHORT COMMUNICATION

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Reconstruction of morphology of micron-sized, monodisperse composite polymer particles by the solvent-absorbing/releasing method

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Abstract Micron-sized, monodisperse polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) (2/1 w/w) composite particles having different morphologies were prepared by the solvent-absorbing/releasing method (SARM). There was an obvious influence of the releasing rate of toluene from the toluene-swollen composite particles on the reconstructed morphology by the SARM. In the case of fast release, the reconstructed morphology was a bicontinuous structure that is similar to that formed by spinodal decomposition. On the other hand, in the case of slow release, a hemispherical structure was formed that consisted of PS and PBMA phases.

Keywords Morphology · Composite particle · Phase separation · Micron-sized · Solvent-absorbing/releasing method · Releasing rate

Introduction

Micron-sized, monodisperse polymer particles have been used in biomedical, microelectronics, and other fields. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized, monodisperse polymer particles. Corner et al. [1] and Almog et al. [2] suggested that the dispersion polymerization technique is useful for the production of monodisperse polymer particles having a diameter below 5 μm. Later, Ober et al. [3], Tseng et al. [4], and ourselves [5] demonstrated the usefulness of this technique.

Nevertheless, this technique seemed to be restricted for a variety of monomers for producing particles having the functional groups required for the above-mentioned applications. Therefore, we have produced about 2-μm-sized, monodisperse composite polymer particles having chloromethyl groups [6, 7] or vinyl groups [8] at the surfaces. Production was achieved by the seeded dispersion copolymerizations of styrene and chloromethylstyrene, or of styrene and divinylbenzene, in ethanol/water media, in the presence of 1.8-μm-sized, monodisperse polystyrene (PS) seed particles. In the composite particles produced, the functional groups preferentially distributed at the surface layers. These results show the suitability of the seeded dispersion polymerization technique for the production of core/shell composite polymer particles [9, 10, 11].

A previous article [12] describes the production of poly(methyl methacrylate) (PMMA)/PS composite particles, consisting of a PMMA-core and PS-shell, by seeded dispersion polymerization. In order to examine the thermodynamic stability of the composite particles, ten times their weight of toluene was absorbed into the composite particles, and released slowly by evaporation under stirring. The morphology of the composite particles was changed to an inverted core/shell structure consisting of PS-core and PMMA-shell. This suggests the possibility of controlling the morphology of composite particles by post-treatment, in which a good solvent for both polymers is absorbed into composite particles and released out. We named it the "solvent-absorbing/releasing method" (SARM) [13, 14].

In this article, the influence of the release rate of solvent from swollen particles on the reconstructed morphology of PS/poly(*n*-butyl methacrylate) (PBMA) composite particles by the SARM will be clarified.

Experimental

Materials

Styrene and *n*-butyl methacrylate (BMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Poly(acrylic acid) (PAA), as a colloidal stabilizer for dispersion polymerization, was produced by solution polymerization of acrylic acid in 1,4-dioxane. Reagent grade toluene, sodium dodecyl sulfate (SDS) and ethanol were used as received.

Production of PS seed particles

Micron-sized, monodisperse PS particles as seeds were produced by dispersion polymerization in a 2000-mL four-necked, round-bottom flask under the conditions listed in Table 1. The PS seed particles were observed with a Hitachi H7100-TE transmission electron microscope (TEM).

Production of PS/PBMA composite particles

Seeded dispersion polymerization of BMA with PS seed particles was carried out in a 200-mL four-necked, round-bottom flask under the conditions listed in Table 2. The PS/PBMA composite particles were observed with TEM.

Swelling of PS/PBMA composite particles with toluene

Swelling of PS/PBMA composite particles with toluene was carried out under the conditions listed in Table 3 as follows. The PS/PBMA composite particles (0.1 g) were dispersed into ethanol/water (1/2 w/w) medium. Toluene emulsion consisting of toluene (1.0 g), SDS (0.01 g), ethanol (3.3 g), and water (6.6 g) was prepared with an ultrasonic homogenizer (US-300T, Nihonseiki Kaisha, Tokyo, Japan) at 0 °C for 10 min in a 30-mL cylindrical reactor (inside diameter 26 mm), and then mixed with the dispersion of the composite particles with a magnetic stirrer at 200 rpm for 2 h at room temperature.

Release of toluene from toluene-swollen PS/PBMA composite particles

Toluene was released from the toluene-swollen PS/PBMA composite particles at different rates according to two methods:

1. Fast release: the toluene-swollen PS/PBMA emulsion was dropped into methanol (500 g) using a 30-mL volumetric pipette (one drop 3.1×10^{-2} mL) under stirring at 250 rpm, and left at room temperature for 1 day
2. Slow release: the emulsion was stirred at 250 rpm at room temperature in a 100-mL cylindrical reactor (inside diameter 36 mm) for 3 days

Measurements of particle diameter

The number-average diameter (D_n)and the coefficient of variation (C_v) of PS seed particles and toluene-swollen PS/PBMA composite particles were determined by measuring the diameters of more than 100 droplets and particles on TEM and optical micrographs with the image analysis software for Macintosh computers (MacSCOPE, Mitani, Fukui, Japan).

Observation of ultrathin cross sections of PS/PBMA composite particles

Dried PS/PBMA composite particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross sections were observed with TEM.

Measurement of the solubility of toluene in methanol/water media

Toluene (1.0 g) was added to methanol/water (10/0–3/7 w/w) media (10 g) in 20-mL glass cylindrical reactors and these reactors were left at 30 °C for 3 h. The amounts of toluene dissolving in the methanol/water media were measured by gas chromatography (GC-18APFsc, Shimadzu, Kyoto, Japan). A capillary column (G-2800, Yanaco, Kyoto, Japan) was used with helium as a carrier gas. The temperatures for the gas chromatographic measurement were: injector 200 °C, column 120 °C, detector 200 °C. *N,N'*-Dimethylformamide was used as solvent and *p*-xylene was used as standard reagent.

Results and discussion

Figure 1a shows a TEM photograph of PS seed particles produced by dispersion polymerization under the conditions listed in Table 1. The PS seed particles were spherical and had high monodispersity: D_n and C_v were 1.59 μm and 3.1%, respectively. Figures 1b and c show, respectively, TEM photographs of original PS/PBMA composite particles produced by seeded dispersion polymerization under the conditions listed in Table 2 and their ultrathin cross sections after the exposure to RuO_4 vapor for 30 min. It is known that RuO_4 predominantly stains PS [10]. Both photographs indicate that the composite particles having anomalous shape had a spherical PS-core and a heterogeneous thickness of PBMA-shell. The result of ^{1}H NMR measurement indicates that PS/PBMA ratio in the composite particles was 2/1 w/w, which agreed well with the polymerization recipe.

Figure 2 shows optical micrographs of the PS/PBMA composite particles (a) and toluene-swollen PS/PBMA composite particles (b) prepared under the conditions listed in Table 3. The polymers/toluene ratio in the toluene-swollen composite particle, which was calculated from D_n of the swollen particle, was 1/6 w/w. The rest dissolved in an ethanol/water media. Because the swollen particles were observed to be homogeneous, and

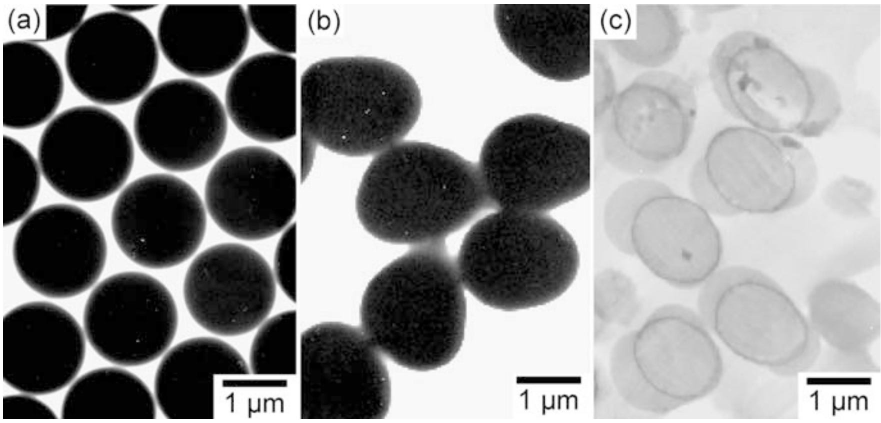

Fig. 1a–c TEM photographs of PS seed particles (**a**) produced by dispersion polymerization under the conditions listed in Table 1, PS/PBMA (2/1 w/w) composite particles (**b**) produced by seeded dispersion polymerization under the conditions listed in Table 2 and their ultrathin cross sections, (**c**) after the exposure to RuO_4 vapor for 30 min

Table 1 Recipe for the production of micron-sized, monodisperse polystyrene (PS) particles by dispersion polymerization at 70 °C for 24 h under N_2 at a stirring rate of 60 rpm

Ingredients	(g)
Styrene	100
2,2'-Azobis(isobutyronitrile)	1.68
Poly(acryl acid)	12
Ethanol	685
Water	200

Table 2 Recipe for the production of PS/poly (*n*-butyl methacrylate) (PBMA) (2/1 w/w) composite particles by seeded dispersion polymerization at 70 °C for 24 h under N_2 at a stirring rate of 60 rpm

Ingredients	(g)
PS particles[a]	13.0
n-Butyl methancrylate	6.5
2,2'-Azobis(isobutyronitrile)	75.5×10^{-3}
Ethanol	96.6
Water	64.4

[a] D_n 1.59 μm, C_v 3.1%

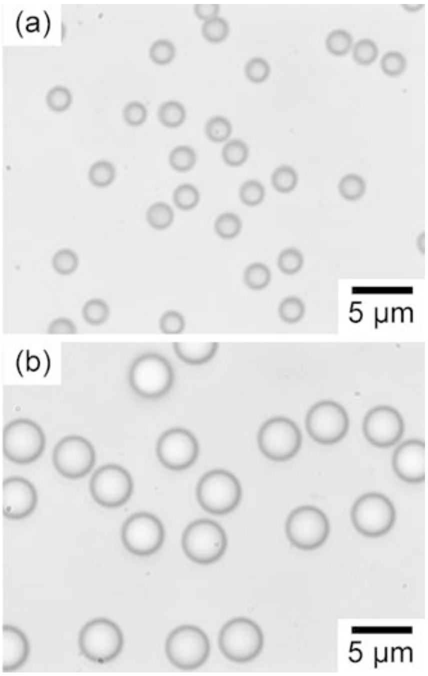

Fig. 2a,b Optical micrographs of PS/PBMA (2/1 w/w) composite particles produced by seeded dispersion polymerization (**a**) and toluene-swollen PS/PBMA composite particles (**b**) (polymers/toluene 1/6 w/w)

dried PS/PBMA composite particles dissolve easily in six times the amount of toluene, both polymers should dissolve completely in toluene droplets in 2 h.

Figure 3 shows TEM photographs of PS/PBMA composite particles treated with the SARM at the different release rates. In Fig. 3a, in which the toluene-swollen composite emulsion was dropped into methanol to release the toluene from the swollen particles quickly, the treated composite particles had anomalous shapes. In Fig. 3b, on the other hand, in which toluene was released slowly by evaporation, they were spherical.

Figure 4 shows TEM photographs of ultrathin cross sections of the treated PS/PBMA composite particles at fast (a) and slow (b) releases after the exposure to RuO_4 vapor for 30 min. In case of the fast release, the reconstructed morphology of the composite particles was a bicontinuous structure that is similar to that formed by spinodal decomposition. Because the treated composite particles had a large interfacial area between the two polymers, it should be thermodynamically unstable. In case of the slow release, the treated composite particles had a PS-core/PBMA-shell structure, which should be thermodynamically stable in a polar ethanol/water (1/2 w/w) medium. These results are considered as follows.

When the toluene is released out quickly from the toluene-swollen composite particle in which both

Table 3 Recipe for the preparation of toluene-swollen PS/PBMA composite particles by mixing PS/PBMA composite emulsion and toluene emulsion[a]

Ingredients	(g)
PS/PBMA emulsion	
PS/PBMA particles	0.1
Ethanol	6.6
Water	13.2
Toluene emulsion	
Toluene	1.0
Sodium dodecyl sulfate	0.01
Ethanol	3.3
Water	6.6

[a]Prepared using an ultrasonic homogenizer for 10 min at 0 °C

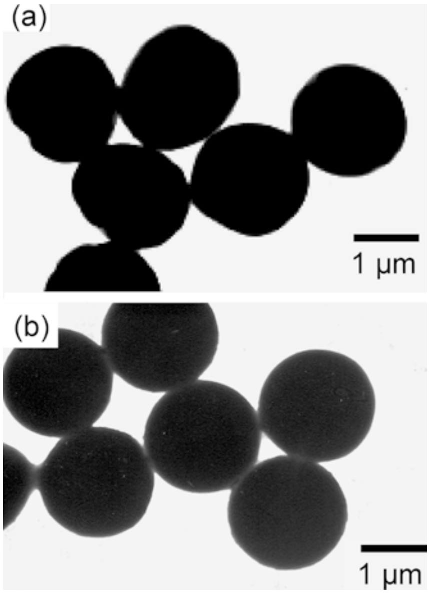

Fig. 3a,b TEM photographs of PS/PBMA (2/1 w/w) composite particles treated by the SARM at fast (**a**) and slow (**b**) releases of toluene from the toluene-swollen composite particles (polymers/toluene 1/6 w/w)

polymers completely dissolve, the viscosity of the swollen particle increases so suddenly that the phase separation in the swollen particle stops at an incomplete state, resulting in the composite particles having a thermodynamically unstable morphology. On the other hand, when toluene is released from the swollen particle gradually, the viscosity of the swollen particle increases so slowly that the phase separation proceeds smoothly, resulting in the composite particles having a thermodynamically stable morphology.

Figure 5 shows a solubility curve of toluene in methanol/water media (100 g) at 30 °C. The solubility of toluene decreased with a decrease in methanol content. This suggests that the releasing rate can be controlled by changing the composition of the methanol/water media, that is, it decreased with the decrease in methanol content [13].

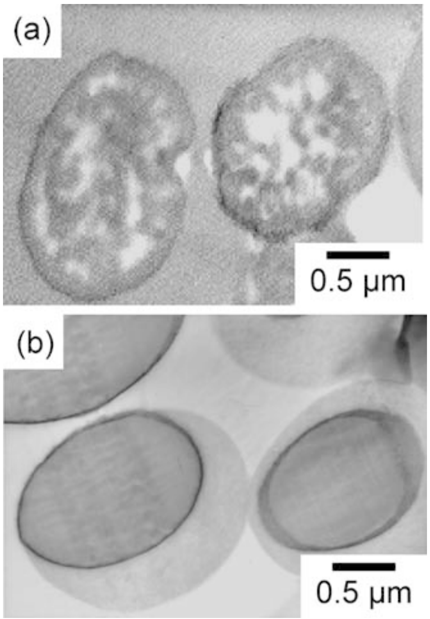

Fig. 4a,b TEM photographs of ultrathin cross sections of PS/PBMA (2/1 w/w) composite particles treated by the SARM at fast (**a**) and slow (**b**) releases of toluene from the toluene-swollen composite particles after the exposure to RuO_4 vapor for 30 min

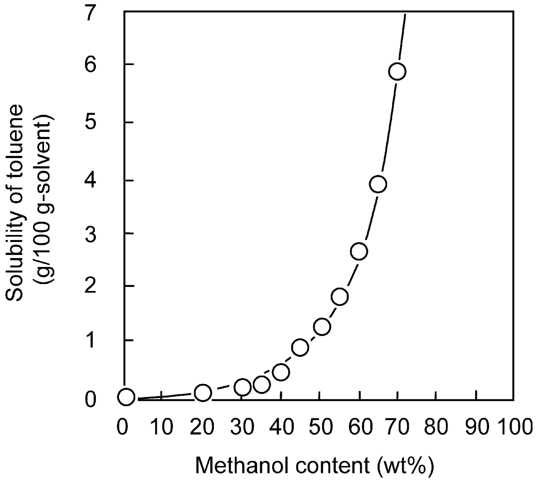

Fig. 5 Solubility curve of toluence in methanol/water media (100 g) at 30°C

Figures 6a–d show TEM photographs of PS/PBMA composite particles treated by the SARM at various compositions of the methanol/water media (100/0–30/70 w/w) to change the release rate of toluene. The release rate decreased with a decrease in the methanol content in the media. The treated composite particles at high methanol content were anomalous, whereas at low methanol content, they were spherical. The ultrathin cross sections of the composite particles are shown in

Fig. 6 TEM photographs of PS/PBMA (2/1, w/w) composite particles (a–d) treated by the SARM at the releases of toluene from the toluene-swollen composite particles by dropping them into various compositions of methanol/water media and their ultrathin cross sections (e–h) after the exposure to RuO_4 vapor for 30 min. Methanol/water ratios (w/w): (a, d) 100/0; (b, e) 80/20; (c, f) 50/50; (d, h) 30/70

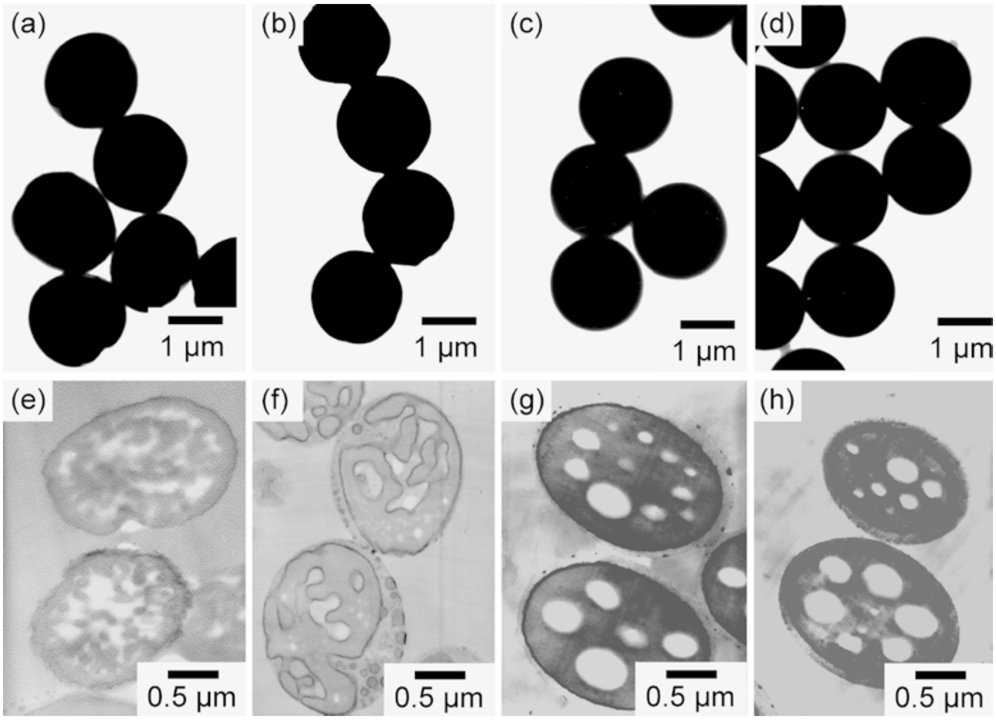

Fig 6e–h. The reconstructed morphology was changed to more thermodynamically stable structures with the decrease in the methanol content in the media, which made the release rate slower. Since the amount of toluene (1.0 g) in swollen particles was below 1.2 g, which is the solubility of toluene in methanol/water (30/70 w/w) media (500 g) calculated from the results of Fig. 5, all of the toluene in the swollen particles should be released to methanol/water media in 1 day. Thus, the morphology was reconstructed in the SARM process, not in the drying process before exposure to RuO_4 vapor. These results were in accord with the result in Fig. 4.

From these results, it is concluded that the reconstruction of morphology of about 2-μm-sized, monodisperse PS/PBMA composite particles by the SARM can be controlled by the release rate of solvent.

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