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SHORT COMMUNICATION

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Preparation of micron-sized, monodispersed, "onion-like" multilayered poly(methyl methacrylate)/polysterene composite particles by reconstruction of morphology with the solvent-absorbing/releasing method

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Abstract Micron-sized, monodispersed, "onion-like" multilayered poly(methyl methacrylate) (PMMA)/polystyrene (PS) (1/1, w/w) composite particles were prepared by the solvent-absorbing/releasing method (SARM). The viscosity within toluene-swollen composite particles, the release rate of toluene therefrom, the PMMA/PS ratio, and the kind of solvent had great influences on the reconstruction of the morphology of the PMMA/PS composite particles by the SARM. From these results, the conditions for the preparation of the multilayered composite particles by the SARM are clarified.

Key words Solvent absorbing/releasing method · Multilayer · Morphology · Micron-size · Monodisperse

Introduction

Recently, micron-sized, monodispersed 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, monodispersed polymer particles. Corner et al. [1] and Almog et al. [2] suggested that the dispersion polymerization technique is useful for the production of monodispersed polymer particles having diameters below 5 μm. Later, Ober et al. [3], Tseng et al. [4], and we [5] demonstrated the usefulness of this technique.

Nevertheless, the technique seemed to be inapplicable for a variety of monomers for producing particles having functional groups thereon, which would be required for use in the previously mentioned applications. Therefore, we have been producing about 2-μm-sized, monodispersed composite polymer particles having chloromethyl groups [5, 6] and vinyl groups [7, 8] by seeded dispersion copolymerization of styrene (S) and chloromethylstyrene and of S and divinylbenzene in ethanol/water media, in the presence of 1.8-μm-sized, monodispersed polystyrene (PS) seed particles produced by dispersion polymerization. In those composite particles produced, the functional groups preferentially distributed at the surface layers. These results suggest the applicability of seeded dispersion polymerization for the production of core/shell composite polymer particles.

In previous work, poly(methyl methacrylate) (PMMA)/PS composite particles consisting of a PMMA core and a PS shell were produced by seeded dispersion polymerization of S [9]. When toluene was absorbed into the composite particles and then released by evaporation, the morphology was drastically changed. Especially, in the case of PMMA/PS (1/1, w/w) composite particles, "onion-like" multilayered morphology was reconstructed [10]. We named this posttreatment the "solvent-absorbing/releasing method" (SARM).

The control of morphology related to the physical and mechanical properties is of great importance for industrial performance. To our knowledge, there have been no reports on the preparation of such multilayered composite particles. In this work, in order to clarify the conditions for the preparation of the "onion-like" multilayered composite particles, the effects of the amount of toluene absorbed, the release rate of toluene, the PMMA/PS ratio, and the kind of solvents on the morphology reconstructed by SARM are examined.

Experimental

Materials

Methyl methacrylate and S were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) and 2,2′-azobis-(2,4-dimethyl valeronitrile) (Wako Pure Chemical Industries, Japan) were purified by recrystallization. Deionized water with a specific resistance of 5×10^6 Ωcm was distilled. All other materials were used without further purification, including poly(vinylpyrrolidone) (weight-average molecular weight 3.6×10^5, Sigma Chemical Company), tricaprylyl methylammonium chloride (Aliquat 336, Aldrich Chemical Company), guaranteed reagent methanol, toluene, *p*-xylene, benzene, and sodium dodecyl sulfate (SDS).

Preparation of PMMA seed particles

Monodispersed PMMA seed particles were produced by dispersion polymerization in a 300-ml four-neck round-bottomed flask equipped with a Teflon paddle stirrer operating at 120 rpm under the conditions reported in Ref. [9]. The number-average diameter (D_n) and the coefficient of variation (C_v) of the seed particles were measured with a Jeol JEM-2010 transmission electron microscope (TEM) using image analysis software for a Macintosh computer (Mac Scope, Mitani Corporation).

Production of PMMA/PS composite particles

Seeded dispersion polymerizations of S was carried out with the PMMA seed particles in a 200-ml four-neck round-bottomed flask equipped with a Teflon paddle stirrer under the conditions listed in Table 1.

Swelling of PMMA/PS composite particles with toluene

Swelling of PMMA/PS composite particles with various amounts of toluene was carried out under the conditions listed in Table 2.

Table 1 Recipes for the production of poly(methyl methacrylate) (*PMMA*)/polystyrene (*PS*) composite particles by seeded dispersion polymerization. N_2; 60 °C; 24 h

Ingredients	PMMA/PS (w/w)		
	2/1	1/1	2/3
PMMA seed particles (g)[a]	0.6	9.0	1.2
Styrene (g)	0.3	9.0	1.8
2,2′-Azobis(isobutyronitrile) (mg)	4.7	140.0	30.0
Poly(vinyl pyrrolidone) (g)	0.03	1.8	0.5
Methanol (g)	9.6	144.0	19.2
Water (g)	2.4	36.0	4.8

[a] D_n, 1.77 μm; C_v, 2.54%

Table 2 Preparation of PMMA/PS/toluene (1/1/20, weight ratio) particles by mixing PMMA/PS composite emulsions and toluene emulsions prepared with an ultrasonic homogenizer

Ingredients	
PMMA/PS emulsion	
PMMA/PS particles	0.1 g
Methanol	3.3 g
Water	6.6 g
Toluene emulsion	
Toluene	1.0 g
Sodium dodecyl sulfate	10 mg
Methanol	3.3 g
Water	6.7 g

Toluene was emulsified in a SDS methanol/water (1/2, w/w) solution with an ultrasonic homogenizer (Nihonseiki US-300T, Japan) at 0 °C for 10 min. The toluene emulsion prepared was mixed with the PMMA/PS composite emulsion and stirred with a magnetic stirrer at 140 rpm for 2 h at room temperature in a glass cylindrical vessel.

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

The toluene which evaporated naturally at room temperature from 24.5 ml of the emulsion was put in a large Petri dish, a small Petri dish, a 200-ml beaker, a 50-ml beaker, and an uncovered glass cylindrical vessel whose evaporation areas between the emulsion and air were 177, 64, 35, 17, and 10 cm^2, respectively.

Ultrathin cross sections

The morphology of the composite particles was estimated with TEM observation of their ultrathin cross sections. Each cross section was prepared as follows. The dried seed and composite particles were stained with RuO_4 vapor, which stains PS but not PMMA, 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.

Heat treatment of PMMA/PS composite particles

Aqueous dispersion of the PMMA/PS composite particles were shaken horizontally at 60 cycles/min (3-cm strokes) in the presence of twice the weight of toluene for PMMA/PS at 80 °C for 24 h, and then the toluene evaporated from the dispersion.

Results and discussion

TEM photographs of the PMMA/PS (1/1, w/w) composite particlesand their ultrathin cross sections before and after treatment by the SARM with toluene in an uncovered glass cylindrical vessel (evaporation area: 10 cm^2) are shown in Fig. 1. The weight ratio of solvent (toluene)/the particles, T_p, was 10. The composite particles before and after the treatment by the SARM had a similar size and a spherical shape. This indicates that coagulation did not occur during treatment by the

SARM. On the other hand, their morphologies were quite different. That is, the morphology was drastically changed by treatment by the SARM from a core/shell to an "onion-like" multilayered structure in which the thickness of each layer was about 100 nm.

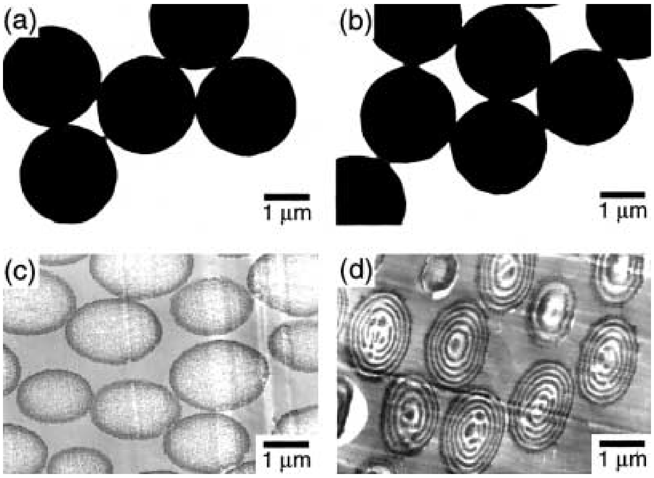


Fig. 1 Transmission electron microscope (*TEM*) photographs of poly(methyl methacrylate) (PMMA)/polystyrene (*PS*) composite particles (**a**, **b**) and ultrathin cross sections (**c**, **d**) before (**a**, **c**) and after (**b**, **d**) treatment by the solvent-absorbing/releasing method (*SARM*), of which the weight ratio of toluene/particles (T_p) was 10, in an uncovered glass cylindrical vessel (evaporation area: 10 cm^2)

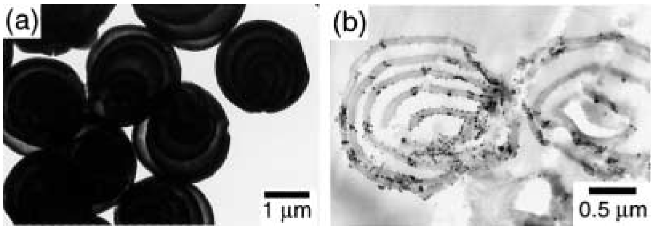


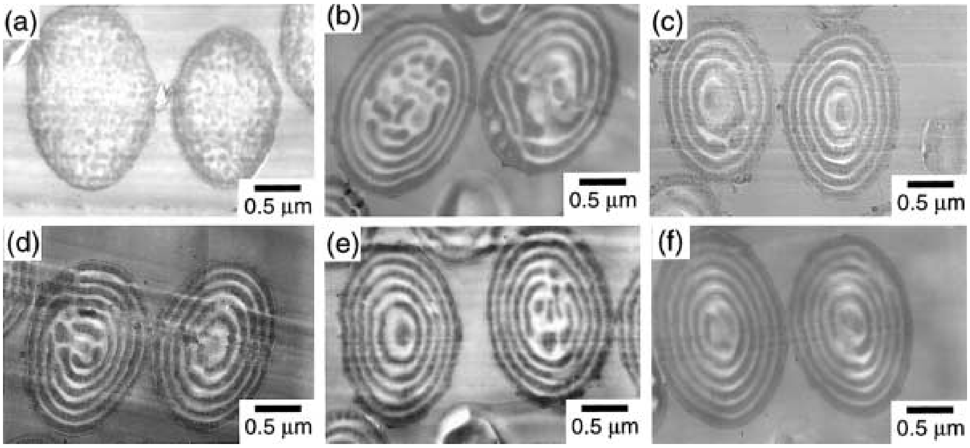
Fig. 2 TEM photographs of **a** composite particles and **b** their ultrathin cross sections after the extraction of PMMA with acetic acid at 40 °C for 48 h from the SARM-treated PMMA/PS composite particles shown in Fig. 1b ($T_p = 10$)

TEM photographs are shown in Fig. 2 of the composite particles and their ultrathin cross sections after the extraction of PMMA with acetic acid under stirring at 40 °C for 48 h from the SARM-treated PMMA/PS composite particles shown in Fig. 1b. Acetic acid dissolves PMMA but not PS. The lower contrast layers due to PMMA shown in Fig. 1d are clearly not present in Fig. 2b. These results indicate that the "onion-like" multilayered structure consisted of the alternate accumulation of PMMA and PS layers.

TEM photographs of ultrathin cross sections of PMMA/PS (1/1, w/w) composite particles treated by the SARM with toluene at various T_p values in the uncovered glass cylindrical vessel at room temperature, stained with RuO$_4$ vapor, are shown in Fig. 3. At a T_p of 2, the morphology was similar with that of the original particle (Fig. 1c), except that a lot of PS domains were clearly observed in the inside. At a T_p of 3, many PS domains dispersed in the PMMA matrix at the center of the particle, whereas a multilayered structure was formed at the outside part of the particle. In the Tp range 5–20 (Fig. 3c–f), the multilayered structure was observed in the whole of the particle. This indicates that the viscosity within the toluene-swollen particles is one of the key factors in the formation of the multilayered structure. An increase in the viscosity within the toluene-swollen particles decreases the mobility of the polymers therein; therefore, it should be difficult to reconstruct the multilayered morphology at high viscosity within the toluene-swollen particles by treatment with the SARM.

The zero-shear viscosities of various concentrations of PMMA/PS (1/1, w/w) toluene solutions measured using an ARES 100 FRTNI rheometer with cone and Couette configurations at room temperature in the range 0.1–1000 1/s are shown in Fig. 4. In the T_p range 3–7 the PMMA/PS solutions were turbid under stirring because

Fig. 3 TEM photographs of ultrathin cross sections of PMMA/PS (1/1, w/w) composite particles treated by the SARM with toluene at various T_p values in an uncovered glass cylindrical vessel (evaporation area: 10 cm^2) at room temperature, stained with RuO$_4$ vapor: T$_p$ (w/w): **a** 2; **b** 3; **c** 5; **d** 7; **e** 10; **f** 20



of phase separation though the dried PMMA/PS particles were completely dissolved in toluene for 24 h. The viscosity of the toluene solution increased with the polymer concentration. Assuming that the viscosities of the toluene solutions correspond to those within the toluene-swollen particles at the same T_p values, the results in Figs. 3 and 4 indicate that the "onion-like" multilayered structure was formed in the toluene-swollen particle in which the viscosity was less than about 10 Pas. Thus, the high mobilities of the polymer within the toluene-swollen particles, which are related to the low viscosity, would need to reconstruct the multilayered structure by treatment with the SARM.

A TEM photograph of ultrathin cross sections of the SARM-treated PMMA/PS (1/1, w/w) composite particles which were kept at 80 °C for 24 h at a T_p of 2 before the release of toluene in the uncovered glass cylindrical vessel at room temperature, stained with RuO_4 vapor, is shown in Fig. 5. At the center of the particle, a sea-islands structure in which PS domains were dispersed in the PMMA matrix was observed. On the other hand, a multilayered structure was observed at the outside part of the particle. In comparison with the morphology of the SARM-treated composite particles at room temperature at the same T_p and release rate shown in Fig. 3a, the result indicates that an increase in the mobility of the polymers within the toluene-swollen particle, because of the high temperature, stimulates the formation of the mulilayered structure. That is, the high mobility of the polymers within the toluene-swollen particles is one of the key factors in the formation of the multilayered structure.

TEM photographs of ultrathin cross sections of the SARM-treated PMMA/PS (1/1, w/w) composite particles at different release rates of toluene at a T_p of 10, stained with RuO_4 vapor, are shown in Fig. 6. The release rate was changed by using various vessels having different interfacial areas with air: a large Petri dish (177 cm^2); a small Petri dish (64 cm^2); a 200-ml beaker (35 cm^2); a 50-ml beaker (17 cm^2). As shown in Table 3, in these systems the release rates of toluene were fast compared with that of the system with the capless glass cylindrical vessel (10 cm^2) in Figs. 1, 3, and 5. At the higher release rates, the morphologies of the composite

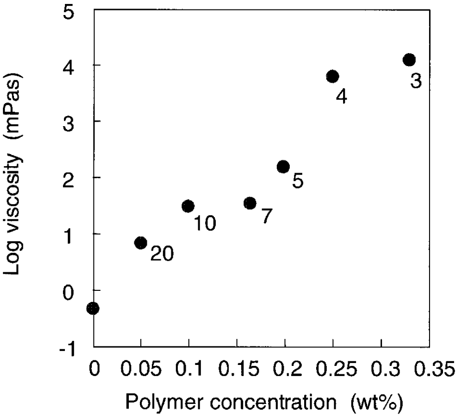


Fig. 4 Zero-shear viscosities of various concentrations of PMMA/PS (1/1, w/w) toluene solutions measured by using a rheometer at room temperature: The *numbers* in the figure indicate the weight ratio of toluene/polymers

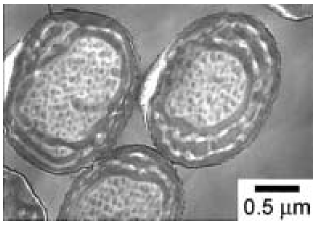


Fig. 5 A TEM photograph of ultrathin cross sections of the SARM-treated PMMA/PS (1/1, w/w) composite particles which were kept at 80 °C for 24 h at a T_p of 2 before the release of toluene in an uncovered glass cylindrical vessel at room temperature, stained with RuO_4 vapor

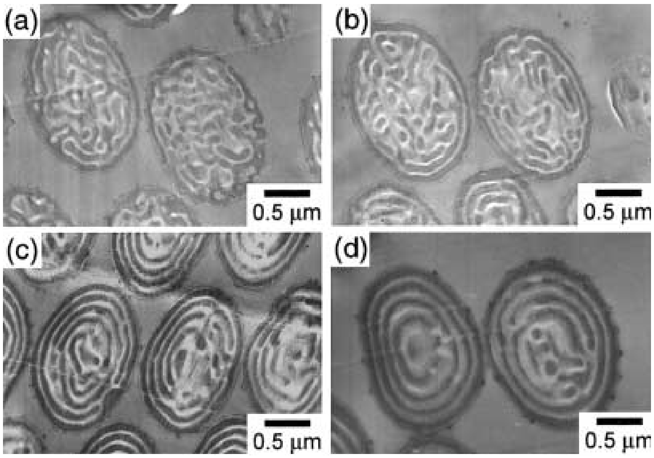


Fig. 6 TEM photographs of ultrathin cross sections of the SARM-treated PMMA/PS (1/1, w/w) composite particles at a T_p of 10 in various vessels having different interfacial areas with air (cm^2): **a** a large Petri dish (177); **b** a small Petri dish (64); **c** a 200-ml beaker (35); **d** a 50-ml beaker (17)

Table 3 Evaporation times of toluene (1 g) in various vessels at room temperature

Type of vessel	Interfacial area (cm^2)^a	Evaporation time
Large Petri dish	177	12 min
Small Petri dish	64	23 min
200-ml beaker	35	158 min
50-ml beaker	17	285 min
50-ml glass cylindrical vessel	10	20 h

^{a} Between toluene and air

particles had bicontinuous structures. At the intermediate release rate, the multilayered structure was clearly observed at the outside part of the particles, whereas it was incomplete at the center of the particles. At the slowest release rate, an almost complete multilayered structure was observed. This indicates that the reconstructed morphology of the composite particles was close to the multilayered structure with a decrease in the release rate and the construction of the multilayered structure proceeding from the particle surface to the center. That is, the slow release of toluene from toluene-swollen particle is one of key factors in the formation of the multilayered structure.

TEM photographs of ultrathin cross sections of PMMA/PS composite particles at different PMMA/PS ratios before and after treatment by the SARM at a T_p of 10, stained with RuO4 vapor for 30 min, are shown in Fig. 7. Before treatment by the SARM (Fig. 7a–c), with an increase in the PS content, the thickness of PS shell in the core/shell composite particles increased and the size of PS domains dispersed in each core increased. These phenomena were already discussed in Ref. [10]. After the treatment by the SARM (Fig. 7d–f), the reconstructed morphologies were quite different. At the PMMA/PS ratio of 2/1 (Fig. 7d), the morphology of the composite particles had a sea-islands structure consisting of a PMMA matrix and PS domains. At 2/3 (Fig. 7f), it had an inverse sea-islands structure consisting of a PS matrix and PMMA domains. At 1/1 (Fig. 7e), the multilayered structure was observed. These results indicate that the polymer composition in the PMMA/PS composite particles is one of the key factors in the formation of the multilayered structure.

Finally, in order to examine the influence of the affinities between the polymers and solvent on the preparation of multilayered composite particles, the SARM process treated with *p*-xylene, toluene, and benzene was carried out. TEM photographs of ultrathin cross sections of the PMMA/PS composite particles (1/1, w/w) treated with *p*-xylene, toluene, and benzene, stained with RuO_4 vapor for 30 min, are shown in Fig. 8. The composite particles treated with *p*-xylene had the sea-islands structure consisting of a PS matrix and PMMA domains. In case of benzene, they had an inverse sea-islands structure consisting of a PMMA matrix and PS domains. That is, the multilayered structure was reconstructed by treatment by the the SARM only with toluene. These results suggest that the kind of absorbed solvent is also one of key factors in the formation of the multilayered structure.

From these results, it is clarified that micron-sized, monodispersed, "onion-like" multilayered PMMA/PS (1/1, w/w) composite particles were prepared by treatment by the SARM under optimum conditions of the viscosity within the toluene-swollen particle, the release rate of the toluene, the PMMA/PS ratio, and the kind of the solvent. The formation mechanism will be discussed in a following article.

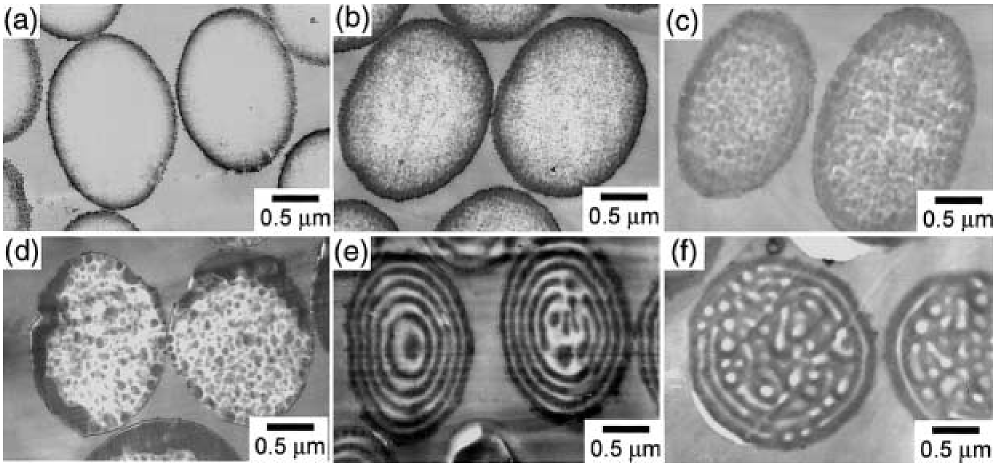


Fig. 7 TEM photographs of ultrathin cross sections of PMMA/PS composite particles [PMMA/PS (w/w): **a**, **d** 2/1; **b**, **e** 1/1; **c**, **f** 2/3] before (**a**, **b**, **c**) and after (**d**, **e**, **f**) treatment by the SARM at a T_p of 10, stained with RuO_4 vapor for 30 min

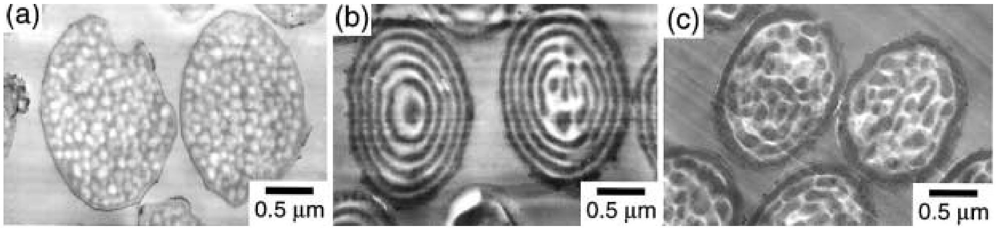


Fig. 8 TEM photographs of ultrathin cross sections of the PMMA/PS composite particles (1/1, w/w) after treatment by the SARM with **a** p-xylene, **b** toluene, and **c** benzene, stained with RuO_4 vapor for 30 min: $T_p = 1$

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