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ORIGINAL CONTRIBUTION

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Production of micron-sized monodispersed core/shell composite polymer particles by seeded dispersion polymerization

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Abstract The effect of the weight ratio of seed polymer/monomer on the morphology of the poly(methyl methacrylate) (PMMA)/polystyrene (PS) monodispersed composite particles produced by batch seeded dispersion polymerization of styrene with 1.64-μm-sized monodispersed PMMA seed particles in a methanol/water medium (4/1 w/w) was examined. In the PMMA/PS weight ratios of 3/1 and 2/1, the composite particles had a clear morphology consisting of a PMMA core and a PS shell. In the ratio of 1/1, a lot of small PS domains were observed in the PMMA core though the PS shell was still formed. By stepwise addition of styrene monomer, the formation of the small PS domain was depressed and complete core/shell morphology was formed. Absorption/release treatments of toluene into/from the PMMA/PS (1/1 w/w) composite particles resulted in a drastic morphological change from the core/shell structure to a multilayered one.

Key words Composite polymer particles · Core/shell · Seeded dispersion polymerization · Morphology · Monodisperse

Introduction

Recently, micron-sized monodispersed polymer particles have been applied in the biomedical field, microelectronics, and other areas. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed polymer particles; Almog et al. [1] have suggested that the dispersion polymerization technique is useful for their production. Ober et al. [2], Tseng et al. [3], and Okubo et al. [4] also recognized the usefulness of this technique.

Nevertheless, the technique seemed to be restricted for a variety of monomers for producing particles having functional groups which would be required for use in the above-mentioned applications. Therefore, we have produced about 2-μm-sized monodispersed composite polymer particles having chloromethyl groups [4, 5] and vinyl groups [6, 7] at the surfaces by the seeded dispersion copolymerizations 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 the composite particles produced, the functional groups preferentially distributed at the surface layers. These results show the suitability of seeded dispersion polymerization (SDP) for the production of core/shell composite polymer particles.

In order to clarify the idea, three types of seeded polymerizations of *n*-butyl methacrylate (*n*-BMA) as an example of a general methacrylic monomer were carried out with 1.76-μm-sized monodispersed PS seed particles [8]. PS/poly(*n*-BMA) (P*n*-BMA) composite particles produced by SDP consisted of a PS core and a P*n*-BMA shell. Since, in a general SDP, almost all monomers exist in the medium, the viscosity of the seed particles is so high that the polymer radicals are unable to diffuse into the inside from the particle surface. As a consequence, the polymers formed by the SDPs seem to

accumulate on the PS seed particles, i.e., the morphology of the composite particles seems to be controlled kinetically.

Moreover, on the basis of this idea, we have successfully produced poly(methyl methacrylate) (PMMA)/PS composite particles having a PMMA core and a PS shell by SDP of S with 1.91-μm-sized monodispersed PMMA seed particles in a methanol/water (4/1 w/w) medium, though the morphology is thermodynamically unstable in the polar medium [9].

In this paper, in order to clarify the SDP system in more detail, the effect of the weight ratio of PMMA/S on the morphology of the PMMA/PS composite particles is examined. In addition, the restructuring of the morphology of the PMMA/PS composite particles by the posttreatments with toluene is discussed.

Experimental

Materials

MMA and S were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) and [2,2′-azobis-(2,4-dimethyl valeronitrile)] (V-65, Wako Pure Chemical Industries, Japan) of reagent grade were purified by recrystallization. Deionized water with a specific conductivity of 5×10^6 Ω cm was distilled. Poly(vinylpyrrolidone) (PVP, degree of polymerization 3.6×10^5, Sigma Chemical Company), tricapryl methylammonium chloride (Aliquat 336, Aldrich Chemical Company) and reagent grade methanol and toluene were used as received.

Table 1 Preparation of micron-sized monodispersed poly(methyl methacrylate) (*PMMA*) seed particles by dispersion polymerization (N_2; 46 °C; 24 h; stirring rate, 120 rpm)

Ingredients		
MMA	(g)	24
2,2′-Azobis-(2,4-dimethyl valeronitrile)	(g)	0.36
poly(vinyl pyrrolidone)	(g)	5.6
Aliquat 336	(g)	1.6
Methanol	(g)	179.2
Water	(g)	44.8

Preparation of PMMA seed particles

Monodispersed PMMA seed particles were produced by dispersion polymerization under the conditions listed in Table 1. The polymerization was carried out in a 300-ml three-neck round-bottom flask equipped with a Teflon paddle stirrer operating at 120 rpm. The diameter and distribution of each particle were observed with a Jeol JEM-2010 transmission electron microscope (TEM). The number-average diameter (D_n) and the coefficient of variation (C_v) were measured with a Personal Image Analysis System (PIAS Co., LA-525, Japan).

SDP of S

SDPs of S were carried out in the presence of the PMMA seed particles in a sealed glass tube under a nitrogen atmosphere at 60 °C for 24 h under the conditions listed in Table 2. The tube was shaken horizontally at 120 cycles/min (2-cm strokes).

Determination of the polymer compositions of PMMA/PS composite particles

The weight ratios of PMMA/PS in the composite particles were determined by ^{1}H NMR. The ^{1}H NMR measurement was carried out with a Bruker DPX 250 MHz spectrometer at room temperature in $CDCl_3$. The chemical shifts were referred to tetramethylsilane. PS and PMMA, respectively, have exclusive resonance peaks at $\delta = 6.2$–7.5 to phenyl protons of PS units and at $\delta = 3.5$–4.4 to methoxy protons of PMMA units.

Observation of ultrathin cross sections of particles

Dried PMMA seed particles and PMMA/PS composite particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of a 1% RuO_4 solution, and were then dispersed in an epoxy matrix, cured at room temperature for 24 h and at 40 °C for 1 h, and microtomed. The ultrathin cross sections were observed with the TEM.

Table 2 Recipes for the production of PMMA/polystyrene (*PS*) composite particles by one-step (nos. 1–3) and two-step (no. 4) seeded dispersion polymerizations (N_2; 60 °C; 24 h)

Ingredients		1	2	3	4
		PMMA/S (w/w)			
		3/1	2/1	1/1	1/1
PMMA particles[a]	(g)	0.6	0.6	0.6	–
No. 2 particles	(g)	–	–	–	0.6
Styrene	(g)	0.2	0.3	0.6	0.2
2,2′-Azobisisobutyronitrile	(mg)	3.14	4.71	9.46	3.14
Poly(vinyl pyrrolidone)	(g)	0.02	0.03	0.12	0.02
Methanol	(g)	9.6	9.6	9.6	9.6
Water	(g)	2.4	2.4	2.4	2.4
D_n	(μm)	1.76	1.86	1.99	2.04
C_v	(%)	3.5	2.9	2.4	3.0
PMMA/PS[b]	(w/w)	3/0.99	2/0.98	1/0.92	1/1.00

[a] $D_n = 1.64$ μm; $C_v = 3.3\%$
[b] Measured by ^{1}H NMR

Determination of the amounts of S monomer in the media

A part of the homogeneous methanol/water/S (16/4/1, w/w/w) media was separated prior to the SDPs by centrifugation at room temperature, and then the amounts of S dissolved in the media were determined by gas chromatography (Shimazu GC-18APFsc). A capillary column (HR-20 M, 30 m × 0.32 mm internal diameter, 1.0-μm film thickness, Shinwa Chemical Industries) was used with helium as a carrier gas.

Toluene treatment of the PMMA/PS composite particles

Under the conditions listed in Table 3, toluene was emulsified in a methanol/water medium dissolving sodium dodecyl sulfate using an ultrasonic homogenizer, and mixed with the PMMA/PS dispersion. The mixture, in which about 10 times the weight of toluene was absorbed into the particles, was stirred at room temperature for 24 h in a 50-ml glass cylindrical reactor with a magnetic stirrer at 140 rpm, and then the toluene was gradually released by evaporation at room temperature.

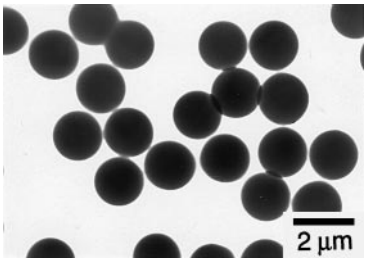


Fig. 1 Transmission electron microscope (*TEM*) photograph of Poly(methyl methacrylate) (*PMMA*) seed particles produced by dispersion polymerization under the conditions listed in Table 1

Fig. 2 TEM photographs of PMMA/Polystyrene (*PS*) composite particles produced by batch seeded dispersion polymerizations **a** before and **b** after centrifugal washing. The *ratios* on the photographs indicate the weight ratio of PMMA/PS

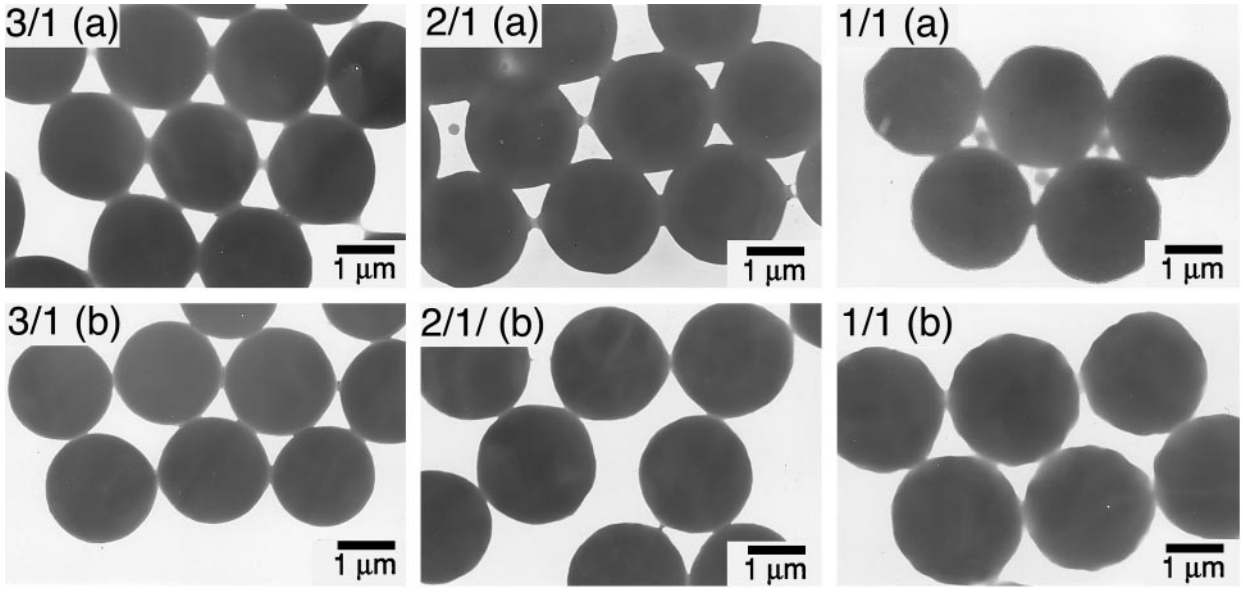
Results and discussion

A TEM photograph of the PMMA seed particles produced by dispersion polymerization under the conditions listed in Table 1 is shown in Fig. 1. D_n and C_v were 1.64 μm and 3.3% respectively.

Figures 2 and 3, respectively, show TEM and scanning electron microscope (SEM) photographs of PMMA/PS composite particles produced by batch SDPs at different PMMA/S ratios under the conditions listed under nos. 1–3 in Table 2, before and after centrifugal washing. Only at a PMMA/PS ratio of 1/1 w/w was a small amount of by-product PS particles observed, but these particles were easily removed by washing. The results of ^{1}H NMR measurements indicate that the weight ratios of PMMA/PS in the composite particles produced agreed well with those calculated from the polymerization recipe. As the S content increased, the diameter of the composite particles increased. PMMA/PS (1/1 w/w) composite particles had an uneven surface.

Table 3 Preparation of PMMA/PS/toluene (polymers/toluene = 1/10 w/w) particles by mixing a PMMA/PS composite emulsion and a toluene emulsion prepared with an ultrasonic homogenizer

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



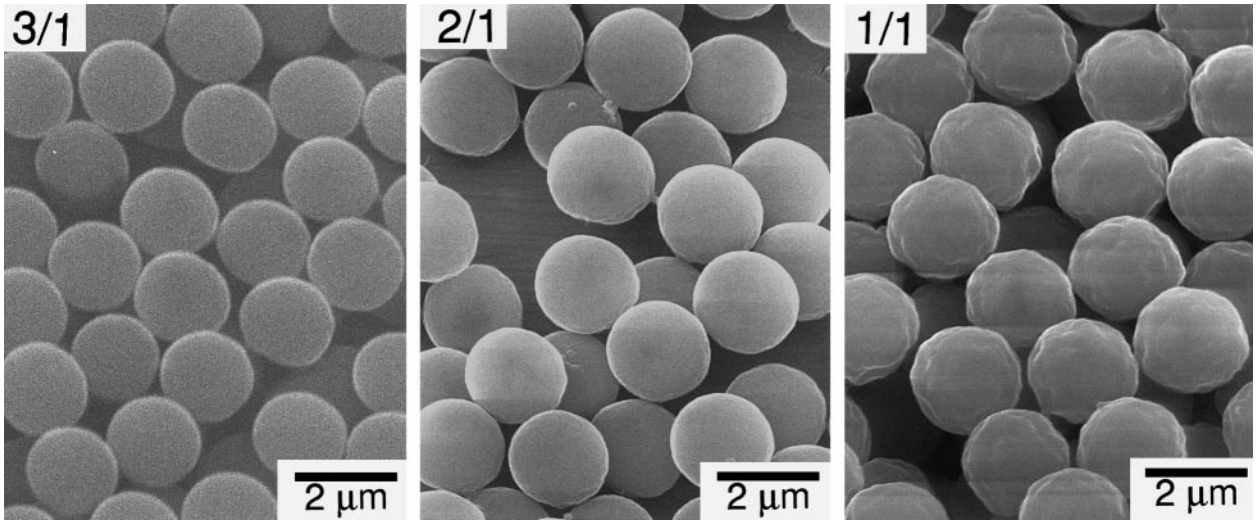


Fig. 3 Scanning electron microscope (*SEM*) photographs of PMMA/PS composite particles produced by batch seeded dispersion polymerizations under conditions 1, 2 and 3 listed in Table 2. The *ratios* on the photographs indicate the weight ratio of PMMA/PS

Table 4 Distributions of S in the PMMA particles and in the methanol/water (4/1 w/w) medium at room temperature (PMMA particle, 0.6 g; the medium, 12.0 g

PMMA/S (w/w)	In particles (%)	In medium (%)	S in PMMA particles (wt%)
3/1	5.0	95.0	1.6
2/1	6.3	93.7	3.1
1/1	7.1	92.9	6.7

TEM photographs of ultrathin cross sections of the PMMA/PS composite particles stained with RuO_4 vapor for 30 min are shown in Fig. 4. It is known that RuO_4 selectively stains PS [10]. The thickness of the shell, which was darker than the core, increased with the increase in the PS content. In the PMMA/PS (3/1 and 2/1 w/w) composite particles, both morphologies were a complete core/shell structure. On the other hand, in the PMMA/PS (1/1 w/w) composite particles, many fine PS domains were observed in the PMMA core. These findings suggest that there is a limit to the weight ratio of PMMA/PS needed to produce PMMA/PS composite particles having the complete core/shell structure by batch SDP. One of the reasons for the formation of the incomplete core/shell morphology by batch SDP at the PMMA/PS ratio of 1/1 seems to be the increase in the S concentration in the particles with an increase in the S concentration in the system as shown in Table 4.

In order to clarify this point, two-step SDP was carried out. In the first step, PMMA/PS (2/1 w/w) composite particles were produced by SDP of S with PMMA seed particles under the conditions listed under no. 2 in Table 2. In the second step, SDP of S with the PMMA/PS (2/1 w/w) seed particles was carried out under the conditions listed under no. 4 in Table 2.

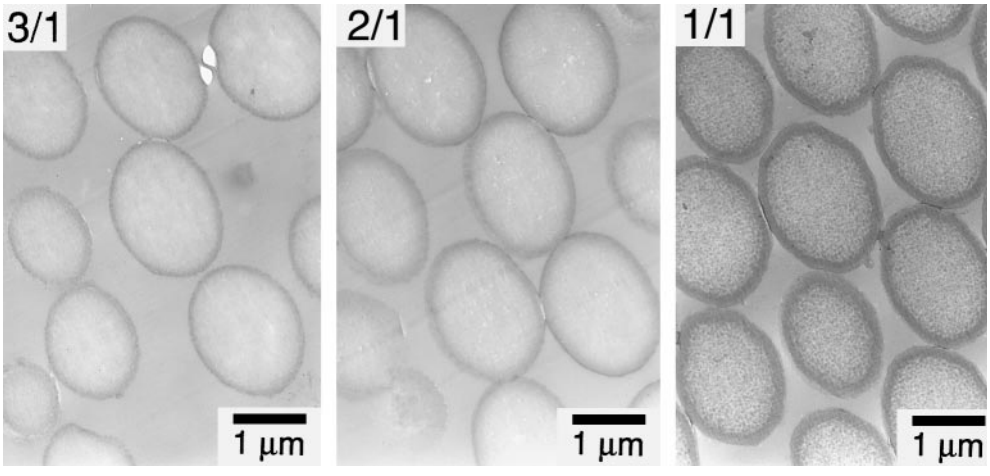


Fig. 4 TEM photographs of ultrathin cross sections of PMMA/PS composite particles produced by batch seeded dispersion polymerizations stained with RuO_4 vapor for 30 min. The *ratios* on the photographs indicate the weight ratio of PMMA/PS

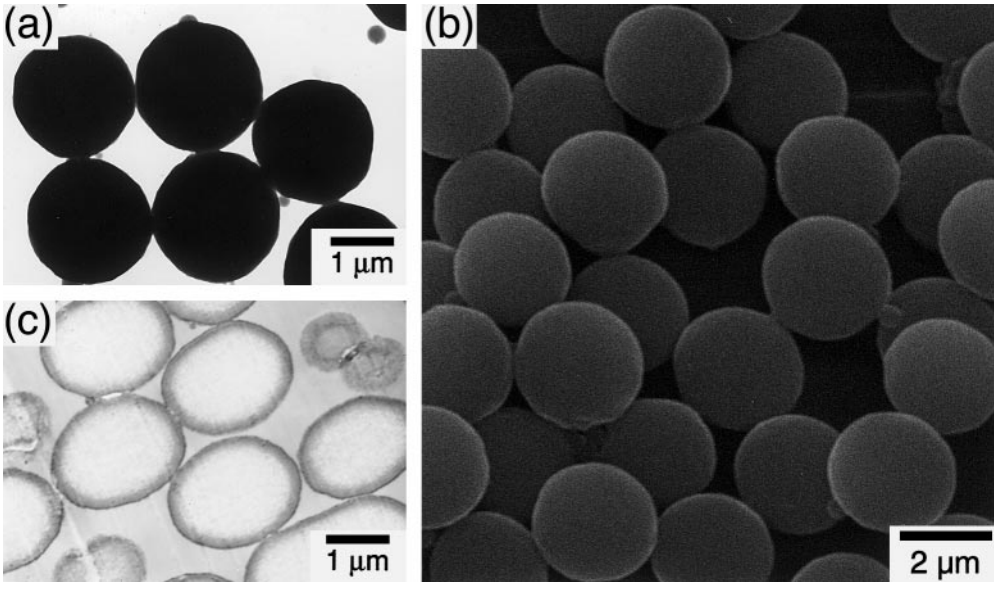
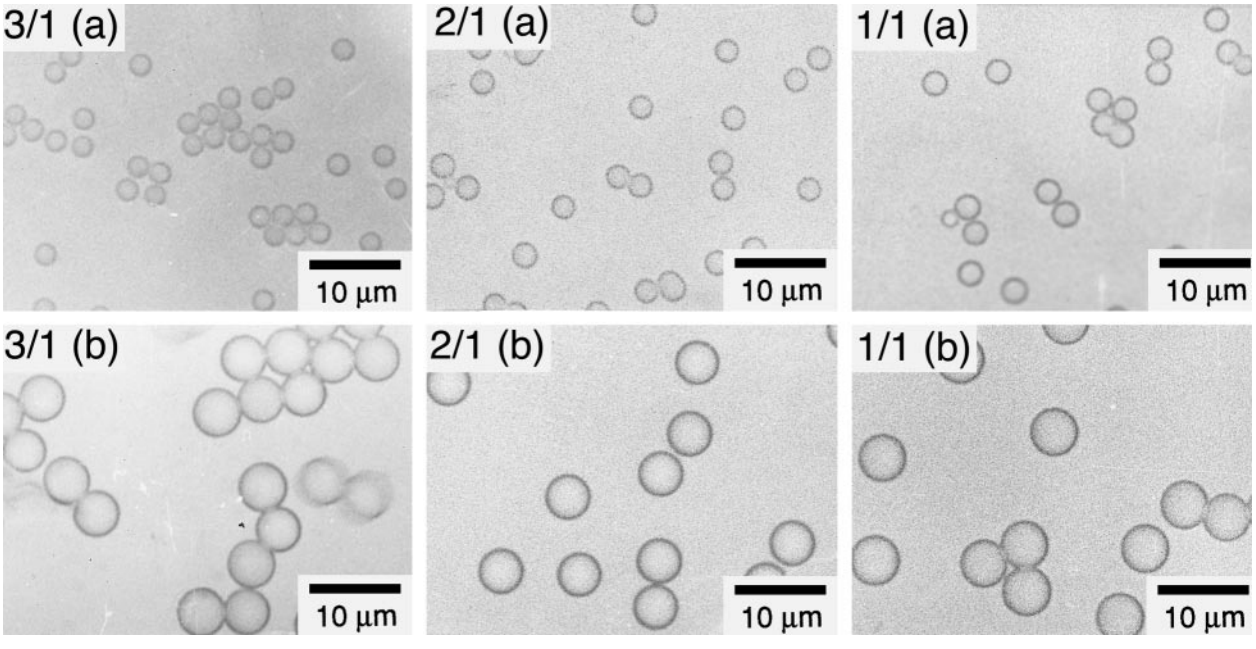


Fig. 5 **a** TEM and **b** SEM photographs of PMMA/PS (1/1 w/w) composite particles produced by the two-step seeded dispersion polymerization after centrifugal washing and **c** a TEM photograph of the ultrathin cross section stained with RuO_4 vapor

Figure 5 shows TEM and SEM photographs of PMMA/PS (1/1 w/w) composite particles produced by two-step SDP after centrifugal washing and a TEM photograph of the ultrathin cross section stained with RuO_4 vapor. A very small amount of by-product PS particles was observed before washing, but the particles were easily removed by washing. In Fig. 5a and b, the composite particles were spherical and had a smooth surface. In Fig. 5c, a complete core/shell morphology was observed, i.e., many fine PS domains observed in the PMMA core of the PMMA/PS (1/1 w/w) composite particles produced by the batch SDP shown in Fig. 4c could not be found in the PMMA core of that produced by the two-step SDP. This indicates that complete core/shell composite particles can be produced by SDP in which the monomer concentration in the polymerizing particles is reduced by stepwise monomer addition.

These results suggest that multi layered composite particles can be obtained by using different types of monomers in the stepwise SDP. Indeed, such a multi

Fig. 6 Optical micrographs of **a** PMMA/PS composite particles and **b** toluene-swollen particles (particles/toluene = 1/10 w/w). The *ratios* on the photographs indicate the weight ratio of PMMA/PS



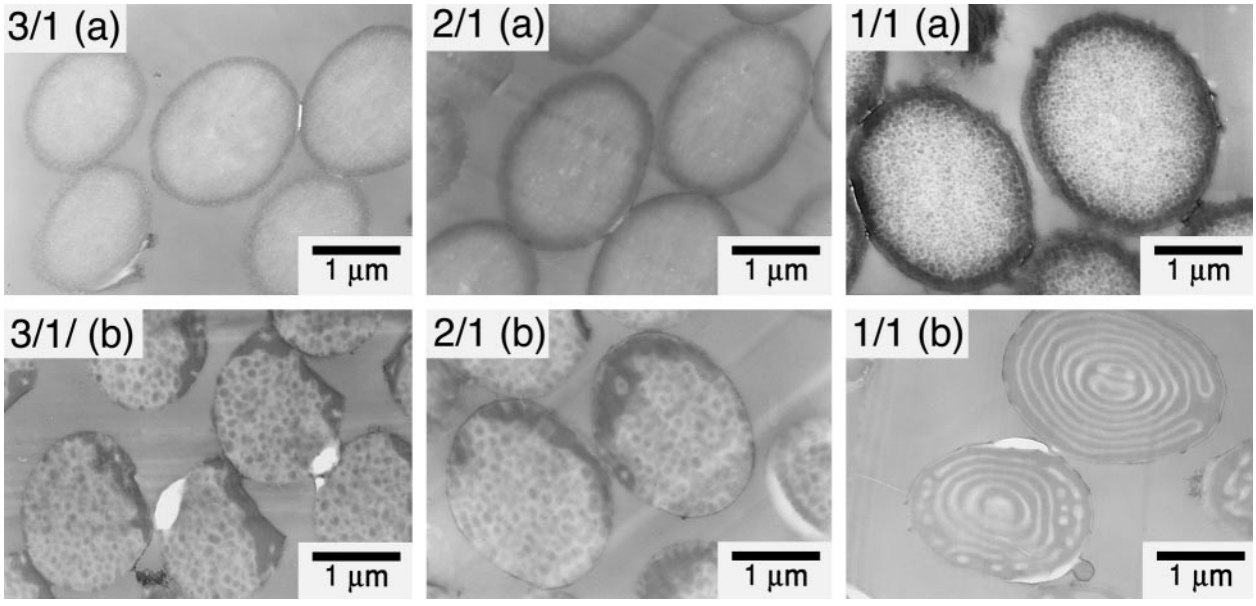


Fig. 7 TEM photographs of ultrathin cross sections of PMMA/PS composite particles stained with RuO_4 vapor for 30 min **a** before and **b** after absorption/release treatment with toluene (particles/toluene = 1/10 w/w). The *ratios* on the photographs indicate the weight ratio of PMMA/PS

layered composite particle could be successfully produced by stepwise SDP. The details will be reported in the near future.

Next, the restructuring of the morphology of the PMMA/PS composite particles by absorption/release treatments of toluene was examined. Optical micrographs of the three kinds of PMMA/PS composite particles and their toluene-swollen particles (particles/toluene = 1/10 w/w) are shown in Fig. 6. In all cases, monodispersed toluene-swollen particles were obtained.

Figure 7 shows TEM photographs of ultrathin cross sections of the PMMA/PS composite particles before and after the absorption/release treatment with toluene, subjected to staining with RuO_4 vapor for 30 min. All morphologies of the composite particle were changed by the treatment. At the PMMA/PS ratios of 3/1 and 2/1, the morphologies after the treatment were similar. Both morphologies consisted mainly of a polymeric oil-in-oil structure in which many small PS domains were dispersed in the PMMA continuous phase. At the PMMA/PS ratio of 1/1, the particles after the treatment had a multilayered structure like an "onion skin". A similar onion-skin morphology was observed in PMMA/PS (1/1 w/w) composite particles produced by the two-step SDP after the same treatment. Since this morphology is very interesting, the formation mechanism will be discussed in the near future. Our results indicate that the core/shell structure obtained by SDP is unstable thermodynamically in the polar medium. In other words, the results suggest that the morphology can be restructured by the absorption/release treatments of toluene.

From the above-mentioned results, it is concluded that using the SDP technique complete core/shell particles can be formed at an appropriate ratio of seed polymer/monomer at which the monomer in the seed particles is maintained at a low concentration. The absorption/release treatments of toluene into/from the composite particles suggest the possibility of morphological control.

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