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ORIGINAL CONTRIBUTION

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Morphology of micron-sized monodispersed poly(butyl methacrylate)/polystyrene composite particles produced by seeded dispersion polymerization

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Abstract In order to develop the seeded dispersion polymerization technique for the production of micron-sized monodispersed core/shell composite polymer particles the effect of polymerization temperature on the core/shell morphology was examined. Micron-sized monodispersed composite particles were produced by seeded dispersion polymerizations of styrene with about 1.4-μm-sized monodispersed poly(*n*-butyl methacrylate) (P*n*-BMA) and poly(*i*-butyl methacrylate) (P*i*-BMA) particles in a methanol/water (4/1, w/w) medium in the temperature range from 20 to 90 °C. The composite particles, PBMA/polystyrene (PS) (2/1, w/w), consisting of a PBMA core and a PS shell were produced with 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) initiator at 30 °C for P*n*-BMA seed and with 2,2′-azobis(isobutyronitrile) initiator at 60 °C for P*i*-BMA seed. The polymerization temperatures were a little above the glass-transition temperatures (T_g) of both P*n*-BMA (20 °C) and P*i*-BMA (40 °C). On the other hand, when the seeded dispersion polymerizations were carried out at much higher temperatures than the T_g of the seed polymers, composite particles having a polymeric oil-in-oil structure were produced.

Key words Morphology · Core/shell · Micron size · Dispersion polymerization · Particle

Introduction

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

Nevertheless, the technique seemed to be restricted for a variety of monomers for producing particles having functional groups thereon, which would be required for use in the above applications. Therefore, we have produced about 2-μm-sized monodispersed polymer particles having chloromethyl groups [4, 5] and vinyl groups [6, 7] at the surfaces by the seeded dispersion copolymerizations of styrene and chloromethylstyrene and of styrene and divinylbenzene in ethanol/water media, in the presence of 1.8-μm-sized monodispersed polystyrene (PS) seed particles produced by dispersion polymerization. During the seeded dispersion copolymerizations, since almost all monomers exist in the medium, the viscosity of the seed particles is so high that polymer radicals should be unable to diffuse inside from the particle surface. As a consequence, each polymer containing the functional groups formed by the seeded dispersion copolymerizations described above seems to accumulate on the PS seed particle.

In previous research [8, 9] we applied seeded dispersion polymerization to the production of core/shell composite polymer particles. Indeed, poly(methyl methacrylate) (PMMA)/PS composite particles having a PMMA core and a PS shell, the morphology of which is unstable thermodynamically in a polar medium, were produced by seeded dispersion polymerization of styrene with 1.91-μm-sized monodispersed PMMA seed particles in a methanol/water (4/1, w/w) medium.

In all the above-mentioned seeded dispersion polymerizations, the polymerization temperatures were lower than glass-transition temperatures (T_g) of the seed polymers. Poly(*n*-butyl methacrylate) (P*n*-BMA) and poly(*i*-butyl methacrylate) (P*i*-BMA), whose T_g values are 20 and 40 °C, respectively, were used as seed polymers. In order to clarify the effect of the mobility of the polymers in composite particles during the seeded dispersion polymerization on the morphology in more detail, seeded dispersion polymerization with a temperature higher than the T_g of the seed polymer was carried out.

Experimental

Materials

Styrene, *n*-butyl methacrylate (*n*-BMA) and *i*-butyl methacrylate (*i*-BMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobis(4-methoxy-2,4-dimethyl valeronitrile), 2,2′-azobis(isobutyronitrile) (AIBN), 1,1′-azobis(cyclohexane 1-carbonitrile) and 2,2′-azobis(2,4-dimethyl valeronitrile) (V-65) of reagent grade (Wako Pure Chemical Industries, Japan) were purified by recrystallization. Deionized water with a specific conductivity of 5×10^6 Ω cm was distilled. Poly(vinyl pyrrolidone) (degree of polymerization, 3.6×10^5, Sigma Chemical Company) and reagent-grade methanol were used as received.

Production of P*n*-BMA and P*i*-BMA seed particles

Monodispersed P*n*-BMA and P*i*-BMA seed particles were produced by dispersion polymerizations under the conditions listed in Table 1. These polymerizations were carried out in a three-neck round-bottom flask equipped with a Teflon paddle stirrer operating at 60 rpm. In the polymerization of P*i*-BMA (24 h), the conversion of *i*-BMA was above 98%, whereas in the polymerization of P*n*-BMA (14 h), the conversion of *n*-BMA was 87%. Almost all the residual monomer existed in the medium. When the polymerization time was extended to increase the conversion, the system became unstable and resulted in a cream gel. Because the colloid stability of the P*n*-BMA seed particles was not enough to remove the residual monomer in the system, the P*n*-BMA particles were just used as seeds in the seeded dispersion polymerization, as well as the P*i*-BMA particles.

Table 1 Preparations of poly(*n*-butyl methocrylate) (*Pn-BMA*) and poly(*i*-butyl methocrylate) (*Pi-BMA*) seed particles by dispersion polymerizations with *n*-butyl methocrylate (*n-BMA*), *i*-butyl methocrylate (*i-BMA*) 2,2′-azabis(4-methoxy-2,4-dimethylvaleronitrile (*V-70*), polyvinyl pyrrolidone (*PVP*), methanol and water

Ingredients	P*n*-BMA[a]	P*i*-BMA[b]
n-BMA (g)	4.8	–
i-BMA (g)	–	4.8
V-70 (g)	0.10	0.10
PVP (g)	0.48	0.96
Methanol (g)	43.2	43.2
Water (g)	4.8	4.8

[a] N_2; 30 °C; 14 h
[b] N_2; 30 °C; 24 h

The T_g values of P*n*-BMA and P*i*-BMA were determined with a differential scanning calorimeter (DSC 220CU, Seiko Instrument).

Production of P*n*-BMA/PS and P*i*-BMA/PS composite particles

Seeded dispersion polymerizations of styrene with the P*n*-BMA and P*i*-BMA seed particles were carried out with AIBN at 60 °C in a sealed glass tube and with V-40 at 90 °C in a stainless steel pressure-resistant vessel having a polytetrafluoroethyrene inner container, respectively, for 24 h under the conditions listed in Table 2. The tubes and vessels were shaken horizontally at 60 cycles/min (3-cm strokes). Moreover, the seeded dispersion polymerizations with the P*n*-BMA seed particles were also carried out at various temperatures under the conditions listed in Table 3.

Determination of the polymer compositions of P*n*-BMA/PS and P*i*-BMA/PS composite particles

The weight ratios of P*n*-BMA/PS in both composite particles were confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR measurement

Table 2 Production of P*n*-BMA/polystyrene (*PS*) (2/1, w/w) and Pi-BMA/PS (2/1, w/w) composite particles by seeded dispersion polymerizations at 60 and 90 °C for 24 h under N_2 atmosphere

Ingredients	Temperature (°C)			
	60	90	60	90
P*n*-BMA seed particles[a] (g)	0.5	0.5	–	–
P*i*-BMA seed particles[b] (g)	–	–	0.5	0.5
Styrene (g)	0.25	0.25	0.25	0.25
2,2′-Azobis(isobutyronitrile) (g)	0.004	–	0.004	–
1,1′-Azobis(cyclohexane 1-carbonitrile) (g)	–	0.012	–	0.012
PVP (g)	0.025	0.025	0.025	0.025
Methanol (g)	8.0	8.0	8.0	8.0
Water (g)	2.0	2.0	2.0	2.0

[a] $D_n = 1.40\ \mu$m; $C_v = 5.6\%$
[b] $D_n = 1.32\ \mu$m; $C_v = 5.7\%$

Table 3 Production of Pn-BMA/PS (2/1, w/w) composite particles by seeded dispersion polymerizations at various temperatures[a]

Ingredients	Polymerization temperature (°C)				
	20	30	40	50	60
P*n*-BMA seed particles (g)	0.5	0.5	0.5	0.5	0.5
Styrene (g)	0.25	0.25	0.25	0.25	0.25
V-70 (g)	0.015	0.008	0.004	–	–
2,2′-azobis(2,4-dimethyl valeronitrile) (g)	–	–	–	0.006	–
2,2′-azobis(isobutyronitrile) (g)	–	–	–	–	0.004
PVP (g)	0.025	0.025	0.025	0.025	0.025
Methanol (g)	8.0	8.0	8.0	8.0	8.0
Water (g)	2.0	2.0	2.0	2.0	2.0

[a] N_2; 24 h; stiring rate, 60 rpm

was carried out with a Bruker DPX 250MHz spectrometer at room temperature in $CDCl_3$. The chemical shifts, which were referred to tetramethylsilane, PS and PBMA, respectively, have exclusive resonance peaks at $\delta = 6.2$–7.5 to phenyl protons of PS units and a peak at $\delta = 3.5$–4.4 to methoxy protons of PBMA units.

Transmission electron microscopic observations

The particles produced were observed with a JEOL JEM-2010 transmission electron microscope (TEM): accelerating voltage, 100 kV; current density, 30 pA/cm^2. TEM samples of P*n*-BMA and P*i*-BMA seed particles were covered with carbon by vacuum deposition. The number-average diameter (D_n) and the coefficient of variation (C_v) of the seed particles were measured with image analysis software for Macintosh Computers (Mac Scope, Mitani Corporation).

The inside structures of the seed and composite particles were estimated from the 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 at room temperature for 30 min in the presence of 1% RuO_4 solution, and were then dispersed in an epoxy matrix, cured at room temperature for 24 h, and microtomed.

Determination of the amount of styrene monomer in the media

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

Heat treatment of P*n*-BMA/PS and P*i*-BMA/PS composite particles

The P*n*-BMA/PS and P*i*-BMA/PS composite dispersions were shaken horizontally at 60 and 90 °C, respectively, using a stainless steel pressure-resistant vessel for 24 h. The dispersion of the P*n*-BMA/PS (2/1, w/w) composite particles produced by seeded dispersion polymerization at 20 °C in which decalin was absorbed was shaken at 60 °C for 24 hours.

Results and discussion

TEM photographs of P*n*-BMA and P*i*-BMA seed particles produced by dispersion polymerizations under the conditions listed in Table 1 are shown in Fig. 1. D_n, C_v and T_g values for P*n*-BMA particles were 1.40 μm, 5.6% and 20 °C, respectively, and those for P*i*-BMA particles were 1.32 μm, 5.7% and 40 °C, respectively. When first observed, the shapes of both seed particles were spherical, though the P*n*-BMA seed particles shown in Fig. 1a were anomalous. It was observed that the spherical shapes of the P*n*-BMA particles were instantly deformed by increasing the intensity of the electron beam. Accordingly, the anomalous shape is due to damage by the electron beam in the process of taking the photograph.

TEM photographs of P*n*-BMA/PS and P*i*-BMA/PS composite particles produced seeded dispersion polymerizations at 60 °C under the conditions listed in Table 2 are shown in Fig. 2. In both cases, no PS particle by-product was observed, and the diameters of the spherical particles produced were bigger than those of the seed particles. Moreover, the results of ^1H NMR measurements indicate that the PBMA/PS weight ratios in both composite particles were 2/1. These results indicate that both seeded dispersion polymerizations successfully proceeded in the seed particles.

TEM photographs of ultrathin cross sections of P*n*-BMA and P*i*-BMA seed particles and of P*n*-BMA/PS and P*i*-BMA/PS composite particles stained with RuO_4 vapor are shown in Fig. 3. It is known that RuO_4 predominantly stains PS [10]. In Fig. 3a and b, the insides of the P*n*-BMA and P*i*-BMA seed particles are seen to be homogeneous. In Fig. 3c, P*n*-BMA/PS composite particles had a polymeric oil-in-oil POO structure in which many fine PS domains dispersed in the continuous P*n*-BMA phase, though more of the PS domains distributed nearer the surface than the inside. In Fig. 3d, the surface layer, which was darker than the

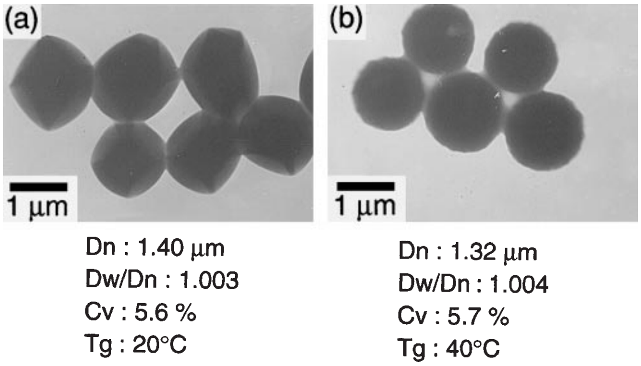


Fig. 1 Transmission electron microscopy (*TEM*) photographs of **a** poly(*n*-butyl methacrylate) (*Pn-BMA*) and **b** poly(*i*-butyl methacrylate) (*Pi-BMA*) seed particles produced by dispersion polymerizations under the conditions listed in Table 1

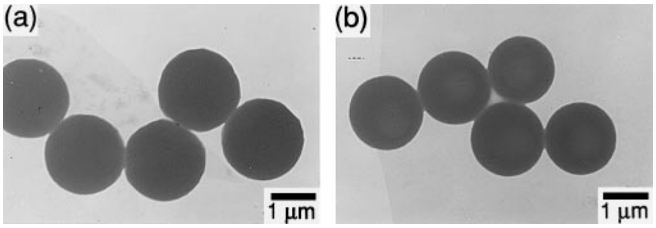


Fig. 2 TEM photographs of **a** P*n*-BMA/polystyrene (*PS*) and **b** P*i*-BMA/PS (2/1, w/w) composite particles produced by seeded dispersion polymerizations at 60 °C under the conditions listed in Table 2

inside, is observed in the P*i*-BMA/PS composite particles. The thickness of the surface layer was in accord with that of PS shell which was calculated from the polymerization recipe assuming that all polymerized PS accumulate on the P*i*-BMA seed particles. This indicates that the composite particles had a core/shell structure consisting of a P*i*-BMA core and a PS shell. The difference in the morphologies between both the composite particles seems to be due to the difference in the T_g values between the P*n*-BMA and P*i*-BMA seed particles.

TEM photographs of ultrathin cross sections of P*n*-BMA/PS and P*i*-BMA/PS composite particles produced at 90 °C under the conditions listed in Table 2 and stained with RuO_4 vapor are shown in Fig. 4. In both composite particles produced, POO structures were observed, but there was still a difference. In the P*n*-BMA/PS composite particles the PS domains homogeneously distributed within the particles, whereas in the P*i*-BMA/PS composite particles they distributed much nearer the surface than the inside.

TEM photographs of ultrathin cross sections of P*n*-BMA/PS (2/1, w/w) composite particles produced by seeded dispersion polymerizations at various temperatures under the conditions listed in Table 3 are shown in Fig. 5. At 20 and 30 °C, the composite particles had the core/shell structure. At 40 °C, many fine PS domain appeared inside the P*n*-BMA phase though the PS shell was still observed. At 50 °C, the PS shell was roughly subdivided and the size of the PS domains became bigger. At 60 °C, the PS shell completely disappeared, and the composite particles had a perfect POO structure. These results suggest that the morphology of the composite particles produced by seeded dispersion polymerization were affected by the polymerization temperature above the T_g of the seed polymer.

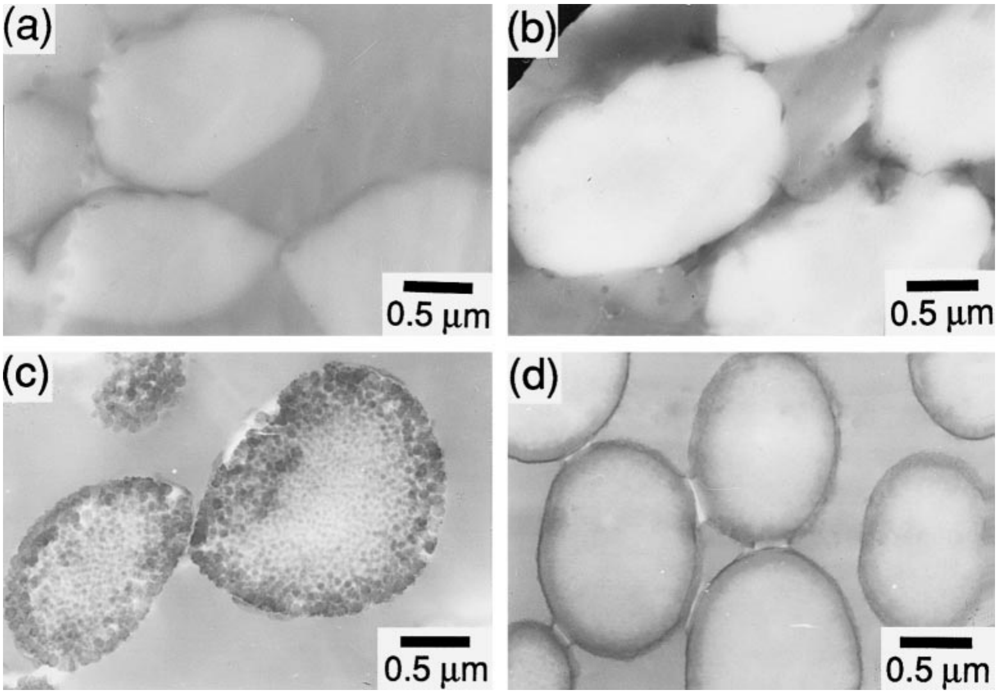


Fig. 3 TEM photographs of ultrathin cross sections of **a** P*n*-BMA and **b** P*i*-BMA seed particles, and of **c** P*n*-BMA/PS and **d** P*i*-BMA/PS (2/1, w/w) composite particles produced at 60 °C and stained with RuO_4 vapor for 30 min

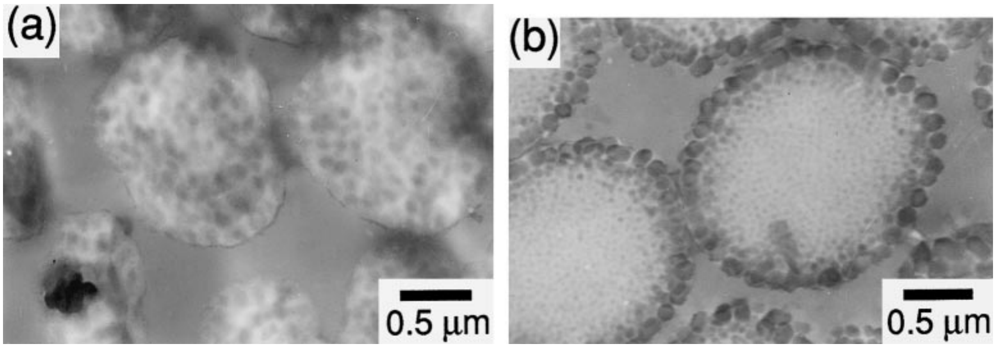


Fig. 4 TEM photographs of ultrathin cross sections of **a** P*n*-BMA/PS and **b** P*i*-BMA/PS (2/1, w/w) composite particles produced by seeded dispersion polymerizations at 90 °C under the conditions listed in Table 2, stained with RuO_4 vapor for 30 min

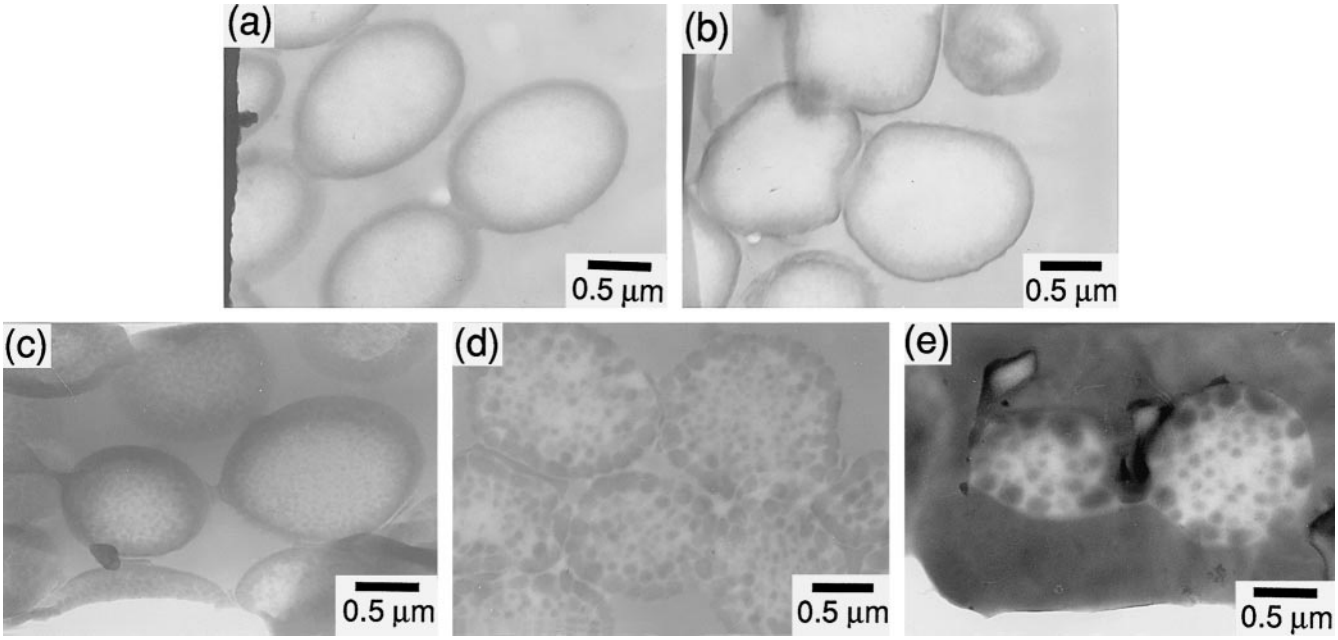


Fig. 5 TEM photographs of ultrathin cross sections of P*n*-BMA/PS (2/1, w/w) composite particles, stained with RuO_4 vapor for 30 min, which were produced by seeded dispersion polymerizations under the conditions listed in Table 3 at various temperatures (°C): **a** 20; **b** 30; **c** 40; **d** 50; **e** 60

The percentages of styrene monomer absorbed in the P*n*-BMA seed particles before the seeded dispersion polymerizations at the various temperatures are shown in Fig. 6. In the range of temperatures from 0 to 60 °C, the percentages were about 20% which corresponded to 10 vol% based on the seed particle, and increased only a little with temperature. This suggests that the absorption of styrene monomer in the P*n*-BMA seed particles is not the main reason why the morphologies in the temperature range were different. In order to clarify the effect of the mobilities of polymer and polymer radical on the morphology of the composite particles, heat treatment of the core/shell composite particles obtained was carried out.

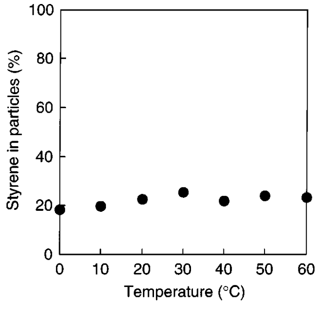


Fig. 6 The percentages of styrene monomer absorbed in the P*n*-BMA particles dispersed at various temperatures for 3 h without initiator in the seeded dispersion polymerization system shown in Table 3

Figure 7 shows TEM photographs of ultrathin cross sections of P*n*-BMA/PS (2/1, w/w) and P*i*-BMA/PS (2/1, w/w) composite particles, which were produced at 20 and 60 °C, respectively, before (Fig. 7a, b) and after heat treatment for 24 h at 60 (Fig. 7c) and 90 °C (Fig. 7d) and stained with RuO_4 vapor for 30 min. The results indicate that in both cases the heat treatments only had a minor influence on the morphology of the composite particles. This seems to be based on the thermodynamic instability of the morphology and the low mobilities of the polymers even at 60 and 90 °C. As shown in Fig. 6, for the seeded dispersion polymerizations since styrene monomers, which are good solvents for both PS and PBMA, were absorbed in the polymerizing particles, though the amount was very low in comparison with that in a general seeded emulsion polymerization, the influence of the absorbed styrene must be reconsidered. Therefore, heat treatment of P*n*-BMA/PS composite particles absorbing decalin in place of styrene by which the mobility of the polymers must be increased was carried out at 60 °C for 24 h.

TEM photographs of ultrathin cross sections of P*n*-BMA/PS (2/1, w/w) composite particles produced at 20 °C before and after heat treatment in the presence of decalin and stained with RuO_4 vapor for 30 min are shown in Fig. 8. As the weight percentage of decalin based on the composite particle was increased, the morphology changed from the core/shell structure to the POO structure. This suggests that the mobilities of the polymer and the polymer radical, which depend on the polymerization temperature and the amount of

Fig. 7 TEM photographs of ultrathin cross sections of **a**, **c** P*n*-BMA/PS (2/1, w/w) and **b**, **d** P*i*-BMA/PS (2/1, w/w) composite particles which were produced at 20 and 60 °C, respectively, **a**, **b** before and after heat treatment for 24 h at **c** 60 and **d** 90 °C, stained with RuO_4 vapor for 30 min

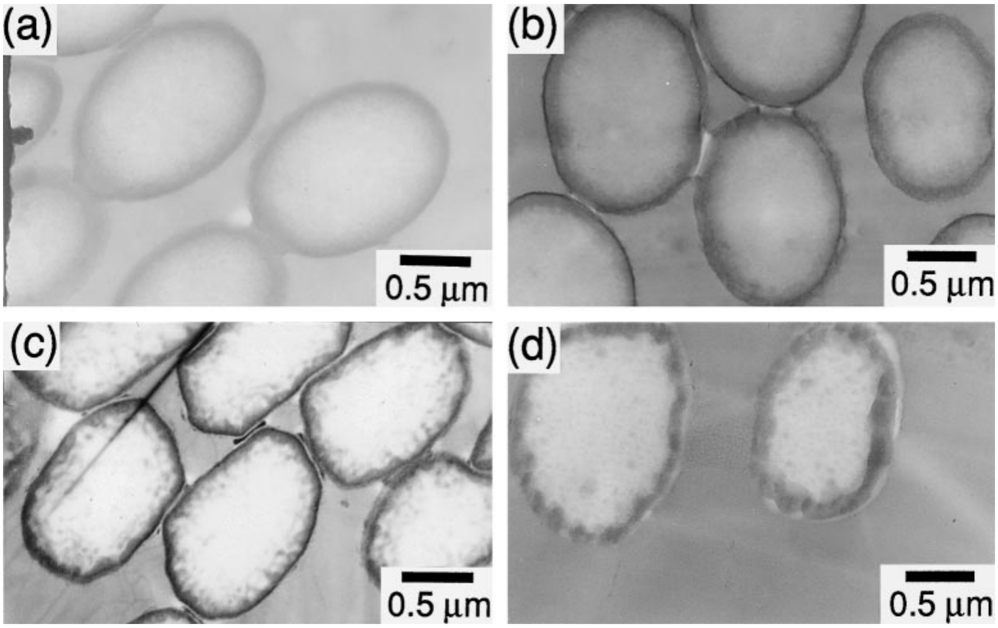
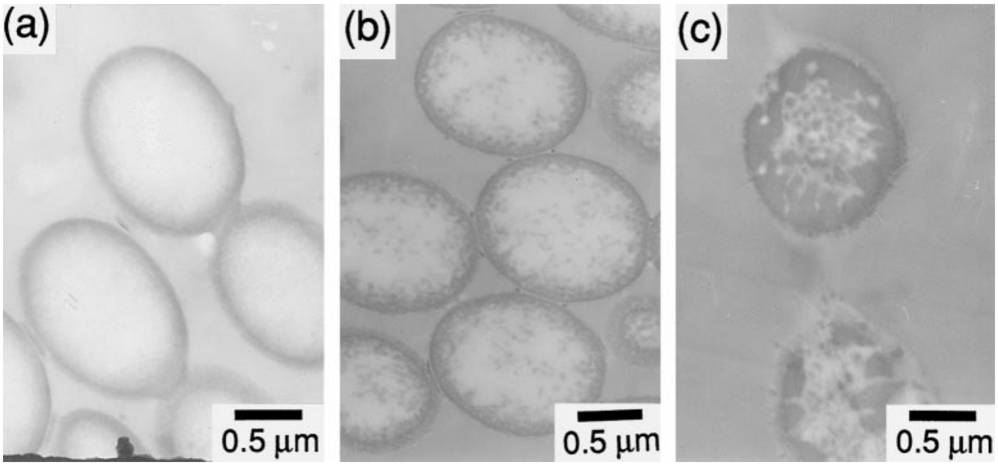


Fig. 8 TEM photographs of ultrathin cross sections of P*n*-BMA/PS (2/1, w/w) composite particles produced at 20 °C **a** before and **b**, **c** after heat treatment at 60 °C for 24 h in the presence of decalin (weight percent based on the particle: **b** 8; **c** 32), stained with RuO_4 vapor for 30 min



monomer absorbed, have an influence on the morphology of the composite particles.

From the above results, it is clear that when the seeded dispersion polymerizations were carried out at much higher temperatures than the T_g of the seed polymers, composite particles having the POO structure were produced. In other words, it has been clarified that seeded dispersion polymerization has the advantage that polymer layers accumulate in their order of production, resulting in core/shell morphology, regardless of the hydrophobicity of the polymer pairs even if the core/shell morphology is unstable thermodynamically, if it is carried out at temperatures below the T_g of the seed particles.

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