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SHORT COMMUNICATION

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Influence of particle diameter on the morphology of micron-sized, monodispersed composite polymer particles produced by seeded polymerization for the dispersion of highly monomer-swollen polymer particles

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Abstract Micron-sized, monodispersed polystyrene (PS)/poly (*n*-butyl methacrylate) (PBMA) composite particles, in which the PS domain(s) were dispersed in a PBMA continuous phase, were produced by seeded polymerization for dispersions of *n*-butyl methacrylate (BMA) swollen PS particles in a wide range of PS/BMA ratios in the presence of $NaNO_2$ as a water-soluble inhibitor. Moreover, in order to change the diameter of the composite particles at same PS/BMA ratio, PS/PBMA (1/150 w/w) composite particles were produced using five kinds of PS particles in a range of diameters from 0.64 to 3.27 μm as seeds. The percentages of the PS/PBMA composite particles having double and triple and over PS domains, which were thermodynamically unstable morphologies, increased with the increase in the diameter of BMA swollen PS particles. There was a clear influence of the size of the swollen particles on the morphology of the PS/PBMA composite particles produced.

Key words Dynamic swelling method · Morphology · Micron size · Seeded polymerization · Composite polymer particle

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

For the production of monodispersed polymer particles above 5 μm in diameter, we have proposed seeded polymerization with a new type of swelling method of seed polymer particles using a large amount of monomer, which was named the "dynamic swelling method" (DSM) [6–9]. The high swelling by the DSM is based on the size difference between micron-sized polymer seed particles and sub-micron-sized monomer droplets and on the highly saturated monomer concentration in the medium [10]. Moreover, about 10-μm-sized, monodispersed *n*-butyl methacrylate (BMA) swollen polystyrene (PS) particles were prepared by mixing 0.7-μm-sized BMA droplets and a 1.77-μm-sized PS emulsion [11] on the basis of the idea obtained from thermodynamic treatment of the DSM [10, 12].

In a previous article [13], we reported the production of about 10-μm-sized, monodispersed PS/poly(BMA) (PBMA) (1/150 w/w) composite particles in which single PS domains were dispersed in a PBMA continuous phase. The morphology was quite different from that produced by seeded dispersion polymerization [14–19]. This is because the viscosity within highly monomer-swollen polymer particles is extremely low in comparison with that of polymerizing particles in the latter system; that is, the seeded polymerization for the dispersion of highly monomer-swollen polymer particles gives composite polymer particles having a comparatively thermodynamically stable morphology. However,

Table 1 Recipes for the production of polystyrene (*PS*) seed particles having different diameters by emulsifier-free emulsion polymerization and dispersion polymerizations

Ingredients	No. 1[a]	No. 2[b]	No. 3[b]	No. 4[c]	No.5[c]
Styrene (g)	15	2.0	2.0	40.0	7.0
2,2-azobis (isobutyronitrile) (g)	–	0.04	0.04	0.67	0.15
Potassium persulfate (g)	0.35	–	–	–	–
Poly(acrylic acid) (g)	–	0.3	0.3	4.8	1.4
Methanol (g)	–	10.0	9.0	–	–
Ethanol (g)	–	4.0	4.0	274.0	70.0
Water (g)	200	6.0	7.0	80.0	–
$D_{\mathrm{n}}^{\mathrm{d}}$ (μm)	0.64	1.34	1.47	1.77	3.27

[a] In a flask: 70 °C; 24 h; N_2; stirring rate, 100 rpm

[b] In a sealed tube: 60 °C; 24 h; N_2; shaking rate, 50 cycles/min (3-cm strokes)

[c] In a flask: 70 °C; 24 h; N_2; stirring rate, 60 rpm

[d] The number-average diameter

some composite particles having double and triple and over PS domains were observed at the same time. This seemed to be based not on the coagulation of the composite particles during the seeded polymerization but on the incomplete aggregation of PS domains in polymerizing particles, because of the "long distance" among PS domains in the polymerizing particle.

In this study, in order to clarify this point, the influence of the size of highly BMA swollen PS particles on the morphology of the composite particles produced by the seeded polymerizations for the dispersions is examined.

Table 2 Recipes for the production of micron-sized, PS poly(*n*-butyl methacrylate) (*PBMA*) composite particles by seeded polymerization in a flask: 70 °C; 24 h; N_2; stirring rate, 90 rpm for the dispersion of BMA swollen PS particles prepared by mixing the BMA-swollen PS emulsion by the dynamic swelling method (stage 1) and monomer emulsion (stage 2)

Ingredients	Stage 1	Stage 2[a]
PS seed particles[b] (mg)	20	–
BMA (g)	0.4	2.6
Benozyl peroxide (mg)	–	30
Poly(vinyl alcohol) (mg)	15	–
Sodium dodecyl sulfate (mg)	10	20
Ethanol (g)	5.0	3.47
Water (g)	5.0	6.93
Post-added water (g)	5.3[c]	60[d]
$NaNO_2$ (mg)	–	8.7

[a] The monomer emulsion was prepared with an ultrasonic homogenizer for 10 min at 0 °C

[b] Produced by emulsifier-free emulsion polymerization under the conditions listed in Table 1: D_{n}, 0.64 μm; C_{v}, 2.3%

[c] Water (5.3 g) was post-added using a microfeeder at a rate of 13.3 ml/h

[d] Water (60 g) dissolving $NaNO_2$ was post-added collectively after mixing

Experimental

Materials

Styrene and BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. Benzoyl peroxide (BPO) and 2,2′-azobis(isobutyronitrile) of reagent grade were purified by recrystallization. Poly(acrylic acid) as a stabilizer for dispersion polymerization was produced by solution polymerization of acrylic acid in 1,4-dioxane. Poly(vinyl alcohol) (PVA) as a stabilizer for seeded polymerization was supplied by Nippon Synthetic Chemical, Osaka, Japan (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Reagent grade sodium dodecyl sulfate (SDS), $NaNO_2$ and ethanol were used as received.

Production of PS seed particles having different diameters

Sub-micron-sized, monodispersed PS seed particles were produced by emulsifier-free emulsion polymerization under the condition 1 listed in Table 1. Four kinds of micron-sized, monodispersed PS seed particles having different diameters were produced by dispersion polymerizations under the conditions 2–5 listed in Table 1.

Table 3 Recipes for the production of micron-sized, monodispersed PS/PBMA composite particles by seeded polymerizations in a flask: 70 °C; 24 h; N_2; stirring rate 90 rpm for dispersions of BMA swollen PS particles prepared by mixing PS seed emulsions and BMA monomer emulsions

PS/BMA (w/w)	1/5	1/10	1/25	1/50	1/75	1/100	1/150	1/200
Monomer emulsion[a]								
BMA (g)	2.0	4.0	0.5	1.0	1.5	2.0	3.0	4.0
Benozyl peroxide (mg)	20	40	5	10	15	20	30	40
Sodium dodecyl sulfate (mg)	20	40	5	10	15	20	30	40
Ethanol (g)	4.0	4.0	0.66	1.33	2.0	3.33	4.0	5.33
Water (g)	8.0	8.0	1.34	2.67	4.0	6.67	8.0	10.67
Seed emulsion								
PS seed particles[b] (mg)	400	400	20	20	20	20	20	20
Poly(vinyl alcohol) (mg)	37	67	9	17	25	37	50	67
Ethanol (g)	2.60	2.60	1.65	1.65	1.65	1.65	1.65	1.65
Water (g)	5.20	5.20	3.35	3.35	3.35	3.35	3.35	3.35
Post-added water[c] (g)	70.1	70.1	24.5	31.6	38.7	52.9	60.0	74.1
$NaNO_2$ (mg)	9.2	9.2	3.2	4.1	5.1	6.9	8.7	10.5

[a] Monomer emulsions were prepared with an ultrasonic homogenizer for 10 min at 0 °C

[b] D_{n}, 1.77 μm; C_{v} 3.9%

[c] Water dissolving $NaNO_2$ was post-added using a microfeeder at a rate of 10.6 ml/h after swelling

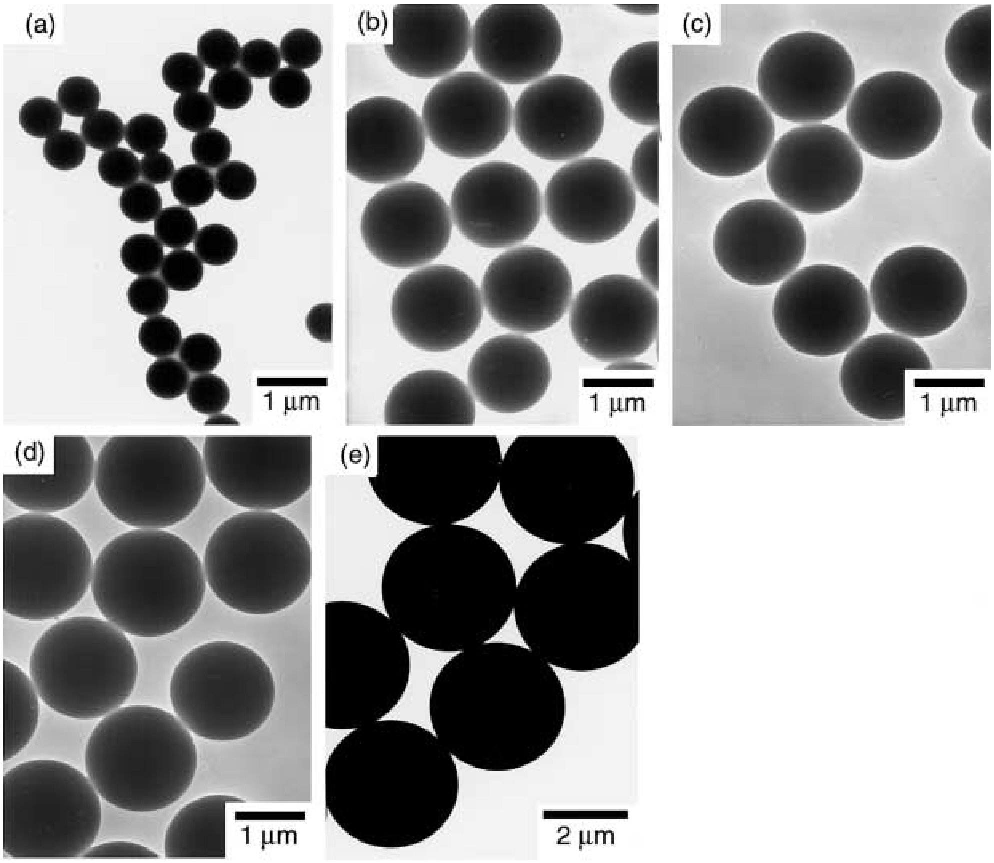


Fig. 1 Transmission electron microscope (*TEM*) photographs of polystyrene (*PS*) seed particles produced by **a** emulsifier-free emulsion polymerization and **b–e** dispersion polymerizations under the conditions listed in Table 1. The diameters of the PS seed particles were **a** 0.64 μm, **b** 1.34 μm, **c** 1.47 μm, **d** 1.77 μm and **e** 3.27 μm

Swelling of sub-micron-sized PS seed particles with BMA

Swelling of 0.64-μm-sized PS seed particles with BMA was carried out under the conditions listed in Table 2. BMA (0.4 g), SDS (0.01 g), PVA (0.015 g), ethanol (5 g) and water (5 g) were charged into a glass cylindrical reactor. The PS seed particles (0.02 g) were dispersed in this homogeneous solution. Next, water (5.3 g) was added to the dispersion with a microfeeder at a rate of 13.3 ml/h for 24 min at room temperature under stirring with a magnetic stirrer at 150 rpm. Separately, BMA monomer emulsion which consisted of BMA (2.6 g), BPO (0.03 g), SDS (0.02 g) ethanol (3.47 g) and water (6.93 g) was prepared with an ultrasonic homogenizer (Nihonseiki Kaisha, US-300 T, Tokyo, Japan) at 0 °C for 10 min and was mixed with the dispersion of BMA swollen PS particles. The mixture was stirred with a magnetic stirrer at 200 rpm for 2 h at room temperature.

Swellings of micron-sized PS seed particles with BMA

Swellings of micron-sized PS seed particles having different diameters with various amounts of BMA were carried out under the conditions listed in Table 3. BMA dissolving BPO was emulsified in an ethanol/water (1/2 w/w) medium dissolving SDS using the ultrasonic homogenizer at 0 °C for 10 min. The monomer emulsion prepared was mixed with each PS seed emulsion and stirred with a magnetic stirrer at 200 rpm for 2 h at room temperature in a glass cylindrical reactor.

Seeded polymerizations of BMA-swollen PS particles

The seeded polymerization for each dispersion of BMA swollen PS particles was carried out at 70 °C for 24 h under a nitrogen atmosphere in a four-necked flask with a paddle-type stirrer at 90 rpm.

Measurements of particle diameter and the number of domains in the composite particles

PS seed particles were observed with a Hitachi H-7100 transmission electron microscope (TEM). PS/PBMA composite particles were observed with a Nikon MICROPHOTO FXA optical microscope and TEM. The number-average diameter (D_n), the weight-average diameter (D_w) and the coefficient of variation (C_v) were determined by measuring the diameters of more than 100 particles on optical or TEM photographs taken at room temperature with a personal image analysis system (PIAS Co., LA-525, Japan). D_n and C_v of the PS seed particles produced by dispersion polymerization under the condition 5 listed in Table 1 were measured after centrifugal washing.

The number of PS domains in the PS/PBMA composite particles was shown as an average value for over 400 particles on the optical micrographs.

Observations of ultrathin cross sections of PS/PBMA composite particles

A small amount of PS/PBMA composite emulsion was added to 20 wt% gelatin aqueous solution and frozen in a refrigerator for

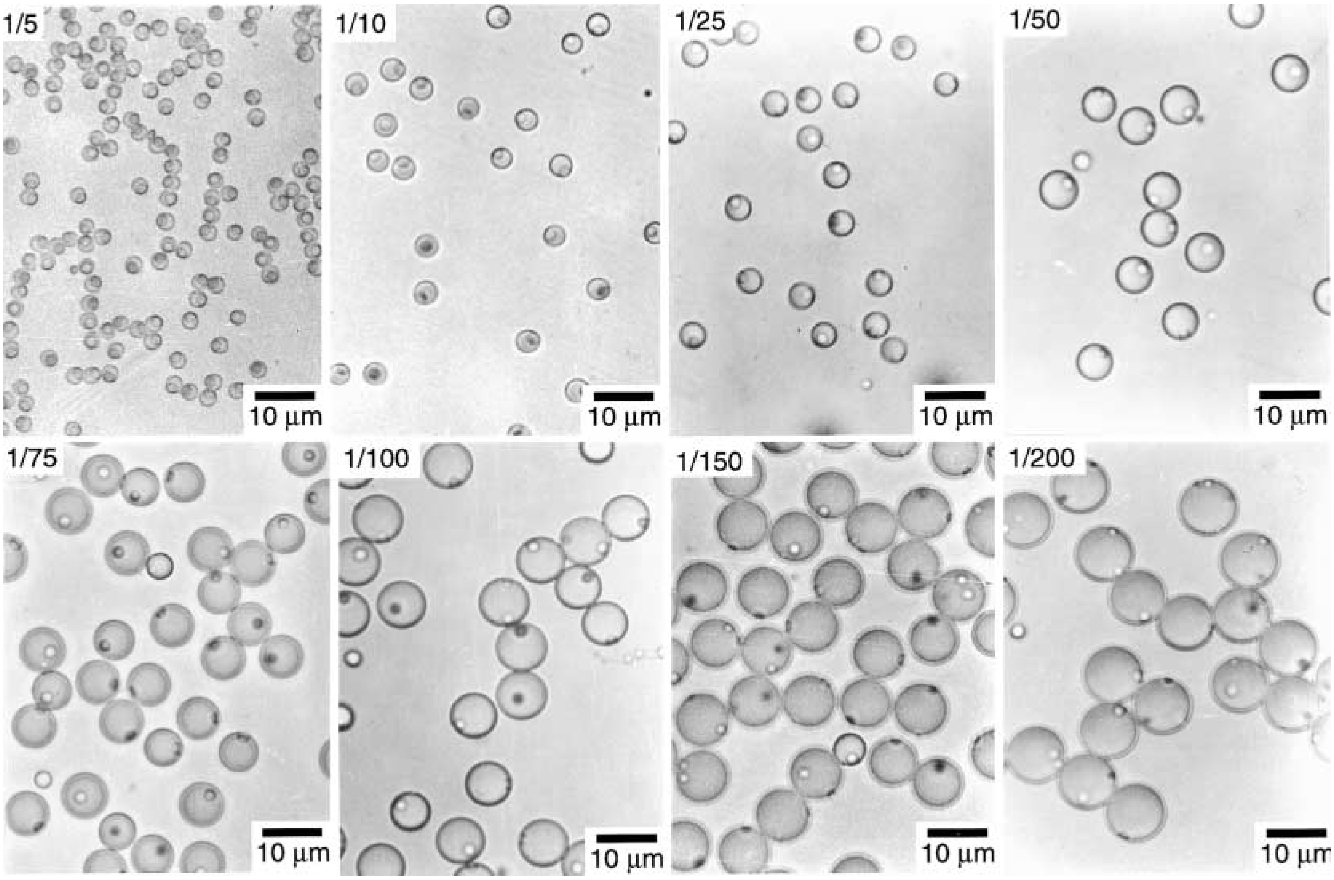


Fig. 2 Optical micrographs of PS poly(*n*-butyl methacrylate) (*PBMA*) composite particles produced by seeded polymerizations for the dispersions of BMA swollen PS particles prepared by mixing PS seed and BMA monomer emulsions. The *ratios* on the photographs indicate the weight ratio of PS/PBMA

24 h. Ultrathin cross sections with a thickness of about 80 nm were obtained by sectioning at −100 °C with a microtome equipped with a cryopump (Leica, REIHERT FC S, Austria), transferred to TEM grids and observed with the TEM.

Results and discussion

TEM photographs of the five kinds of PS particles used as seeds are shown in Fig. 1. The diameter distribution of the PS seed particles produced by emulsifier-free emulsion polymerization (Fig. 1a) was D_n 0.64 μm, C_v 2.3%; those produced by dispersion polymerizations were D_n 1.34 μm, C_v 3.6%; D_n 1.47 μm, C_v 3.7%; D_n 1.77 μm, C_v 3.9%; D_n 3.27 μm, C_v 2.0%, as shown in Fig. 1b–e, respectively.

When the temperature of the seeded polymerizations for the dispersions of the highly BMA swollen PS particles under the conditions shown in Tables 2 and 3 was raised to 70 °C, almost all the BMA in the swollen particles was redissolved in the media. In order to prevent this, an appropriate amount of water, in which $NaNO_2$ as a water-soluble inhibitor was dissolved, was

Table 4 Relationship between the weight ratio of PS/PBMA and the percentages of the composite particles having single, double, and triple and over PS domains

PS/PBMA (w/w)	1/5	1/10	1/25	1/50	1/75	1/100	1/150	1/200
D_n^a (μm)	3.1	4.0	4.8	6.2	7.2	8.3	9.6	10.4
D_w^b/D_n	1.004	1.003	1.012	1.012	1.011	1.008	1.006	1.004
C_v^c (%)	3.6	3.0	6.1	6.6	6.9	3.8	5.2	3.8
Single^d (%)	100	100	100	100	100	73.7	43.3	19.5
Double^d (%)	0	0	0	0	0	25.6	51.7	60.5
Triple and over^d (%)	0	0	0	0	0	0.7	5.0	20.0

[a] The number-average diameter
[b] The weight-average diameter
[c] The coefficient of variation
[d] Percentage of the composite particles having each type of PS domain

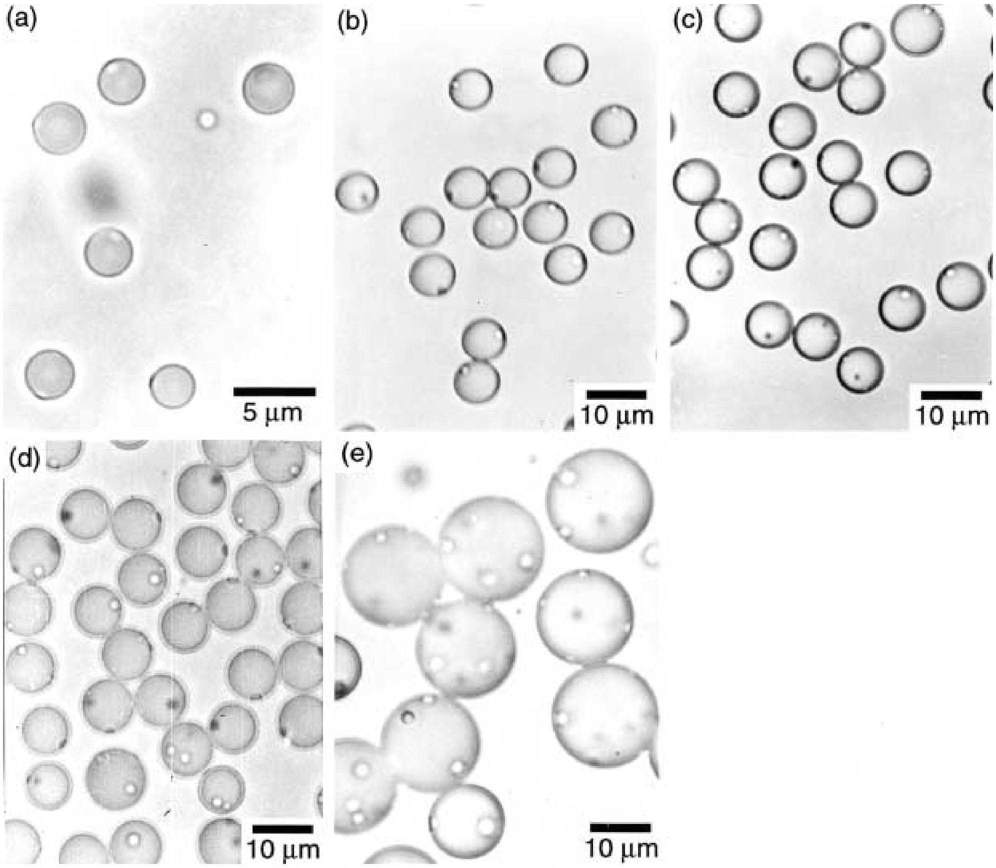


Fig. 3 Optical micrographs of PS/PBMA (1/150 w/w) composite particles produced by seeded polymerizations with PS seed particles having different diameters: **a** 0.64 μm, **b** 1.34 μm, **c** 1.47 μm, **d** 1.77 μm and **e** 3.27 μm

added to the dispersions with a microfeeder at a rate of 10.6 ml/h at room temperature under stirring with a magnetic stirrer. The stirring speed was raised gradually from 200 to 350 rpm. The final $NaNO_2$ concentration in the media was 0.1 g/l [7].

Optical micrographs of PS/PBMA composite particles produced by the seeded polymerizations for the dispersions of swollen particles having different PS/BMA ratios prepared with 1.77-μm-sized PS seed particles under the conditions listed in Table 3 are shown in Fig. 2. In all the photographs, the composite particles produced are spherical and have high monodispersity (Table 4). The D_n values of the composite particles agreed well with the diameters presumed on the basis of the polymerization recipes. All the composite particles had a few spherical domains in the insides. The domains consisted of a PS-rich component [13]. The percentage of the PS/PBMA composite particles having a single PS domain, which is the most thermodynamically stable morphology in the polar ethanol/water mixture media because PS is more hydrophobic than PBMA [13], decreased with an increase in the BMA content.

The relationships between the PS/PBMA weight ratios and the percentages of the PS/PBMA composite particles having single, double, and triple and over PS domains are shown in Table 4. At the PS/PBMA ratios above 1/75, all the composite particles had only single PS domain in the insides, but at the ratios below 1/100, the percentages of the composite particles having double, and triple and over PS domains increased with the increase in the BMA content. This suggests that the

Table 5 Relationship between the diameters of PS/PBMA (1/150 w/w) composite particles and the percentages of the composite particles having single, double, and triple and over PS domains

	No. 1	No. 2	No. 3	No. 4	No. 5
D_n^a (μm)	0.64	1.34	1.47	1.77	3.27
D_n^b (μm)	3.5	7.7	8.7	9.6	17.3
D_w^c/D_n	1.124	1.004	1.005	1.006	1.008
C_v^d (%)	23.8	3.6	4.0	5.2	5.2
Single[e] (%)	98.8	75.5	52.5	43.1	0
Double[e] (%)	1.2	24.3	42.5	50.7	0
Triple and over[e] (%)	0.0	0.2	5.0	6.2	100.0

[a] The number-average diameter of PS seed particles
[b] The number-average diameter of PS/PBMA composite particles produced
[c] The weight-average diameter of PS/PBMA composite particles produced
[d] The coefficient of variation of PS/PBMA composite particles produced
[e] Percentage of the composite particles having each type of PS domain

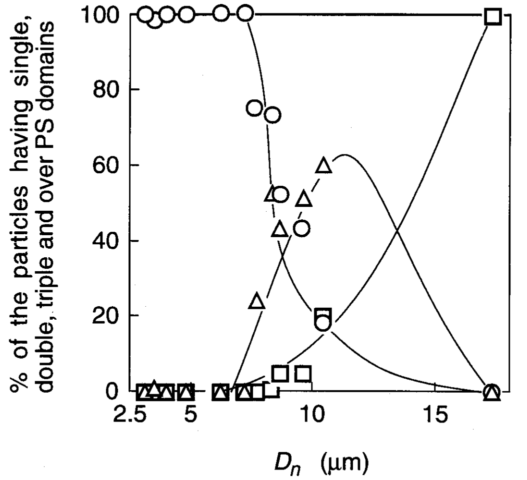


Fig. 4 Relationship between the diameters (D_n) of the composite particles and the percentages of PS/PBMA composite particles having single (○), double (△), and triple and over (□) PS domains

percentages of the composite particles having thermodynamically unstable morphologies increased with the decrease in viscosity in the polymerizing particles. However, this is inconsistent with the results obtained in previous work [13–15], which was described in the Introduction.

Optical micrographs of PS/PBMA composite particles produced by seeded polymerizations for dispersions of BMA swollen PS particles having different diameters at a constant PS/BMA (1/150 w/w) ratio at which the viscosity in the swollen particles should be similar are shown in Fig. 3. The size of the BMA swollen PS particles increases with an increase in the diameter of the PS seed particles prepared under the conditions listed in Tables 2 and 3. The results for the number of PS domains in their composite particles are shown in Table 5. The percentages of the composite particles having double, and triple and over PS domains increased with the increase in the diameter of the composite particles; that is, with the increase in the size of the swollen particles.

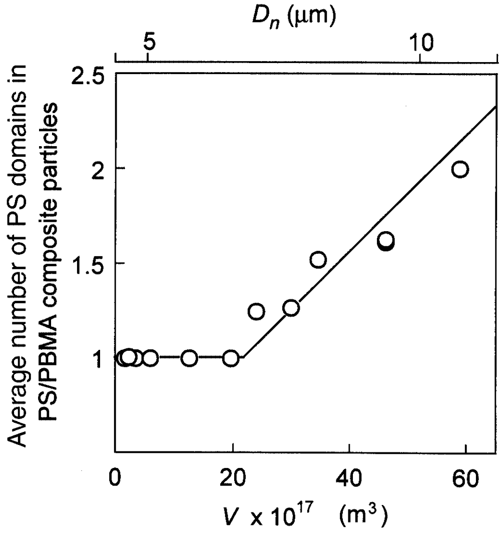
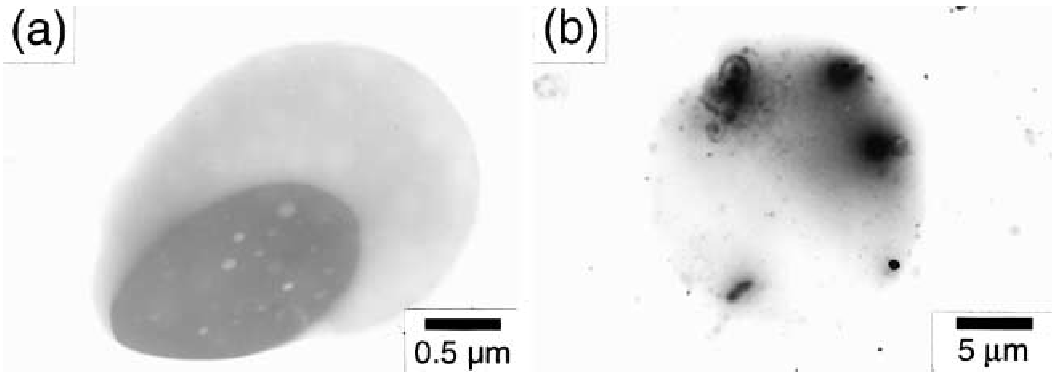


Fig. 5 Relationships between the volume (V) of PS/PBMA composite particles with diameter (D_n) and with the average number of inner PS domains

The relationship between the diameters of the PS/PBMA composite particles produced by seeded polymerization for the dispersions of the swollen particles having different PS/BMA ratios prepared with the PS seed particles having different diameters and the number of PS domains in their composite particles which was obtained from Tables 4 and 5 is shown in Fig. 4. The relationships indicate that the percentages of the composite particles having thermodynamically unstable morphologies increased with the increase in the diameter of the composite particles, regardless of the PS/BMA ratios.

The relationships between the volume of the PS/PBMA composite particles with diameter and with the average number of inner PS domains, which was obtained in Fig. 4, is shown in Fig. 5. Until the volume

Fig. 6 TEM photographs of the ultrathin cross sections of PS/PBMA composite particles having different diameters: **a** 3.1 µm, **b** 17.3 µm. The PS/BMA ratios were **a** 1/5 w/w and **b** 1/150 w/w. The diameters of the PS seed particles were **a** 1.77 w/w and **b** 3.27 w/w



was 20×10^{-17} m^3, the PS/PBMA composite particles had only a single PS domain in the inside. Above 20×10^{-17} m^3, the average number of PS domains increased directly with the increase in the volume of the composite particles.

From the results shown in Figs. 4 and 5, it is concluded that PS domains deposited homogeneously in polymerizing particles during the seeded polymerization move and aggregate because the viscosity within the swollen particles is extremely low. However, the particle size of a swollen particle is larger and the distance through the PS domains is so long that PS domains cannot aggregate before the viscosity within the polymerizing particle is high in the seeded polymerization process.

Since it is difficult to observe sub-micron-sized PS domains by optical microscopy, the ultrathin cross sections of the smallest or the largest composite particles were observed with the TEM.

TEM photographs of ultrathin cross sections of PS/PBMA composite particles having the smallest (3.1 μm) and the largest (17.3 μm) diameters are shown in Fig. 6a and b, respectively. The PS/BMA ratios (w/w) were 1/5 (Fig. 6a) and 1/150 (Fig. 6b). The diameters of the PS used seed particles were 1.77 μm (Fig. 6a) and 3.27 μm (Fig. 6b). The smallest composite particles had only a single PS domain and the largest one had many PS domains. In no sub-micron-sized PS domains did both composite particles exist, which agreed well with the data shown in Fig. 4. These results indicate that the increase in the size of the swollen particles retards the aggregation of micron-sized PS domains and results in the composite particles having thermodynamically unstable morphologies.

From these results, it is concluded that the size of the swollen particles is also one of the key factors which has a great influence on the morphology of micron-sized, monodispersed composite particles produced by seeded polymerization for highly BMA swollen PS particles.

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