Morphology of Micron-Sized, Monodisperse, Nonspherical Polystyrene/Poly(*n*-butyl methacrylate) Composite Particles Produced by Seeded Dispersion Polymerization

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ABSTRACT: Nonspherical polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) composite particles with uneven surfaces were produced by seeded dispersion polymerization of BMA with 1.65-μm, monodisperse, spherical PS seed particles. The composite particles consisted of a PS core and an incomplete PBMA shell. The formation mechanism of such nonspherical particles was discussed. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2013–2021, 2002

Key words: dispersion polymerization; *n*-butyl methacrylate; composite particle; nonspherical shape; morphology; micron size; monodisperse

INTRODUCTION

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

Nevertheless, the technique seemed to be restricted for a variety of monomers to producing particles having surface functional groups, which would be required for use in the above applications. Therefore, we proposed to utilize a seeded dispersion polymerization for producing such a particle. For example, about 2-μm, monodisperse polymer particles having chloromethyl groups[4,5]

and vinyl groups[6,7] at the surfaces were produced by seeded dispersion copolymerizations of styrene and chloromethylstyrene and those of styrene and divinylbenzene in ethanol/water media in the presence of 1.8-μm, monodisperse polystyrene (PS) seed particles produced by dispersion polymerization. In those produced composite particles the functional groups were preferentially distributed at the surface layers.

In a previous article[8] three types of seeded polymerization of *n*-butyl methacrylate (BMA) as one of a general methacrylic monomer were carried out with 1.76-μm, monodisperse PS seed particles. In them the PS/poly(BMA) (PBMA) composite particles produced by seeded dispersion polymerization had a nonspherical shape.

This article discusses the formation mechanism of such nonspherical PS/PBMA composite particles.

EXPERIMENTAL

Materials

Styrene and BMA were purified by distillation under reduced pressure in a nitrogen atmosphere.

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Reagent grade 2,2′-azobisisobutyronitrile (AIBN), 2,2′-azobis(2,4-dimethylvaleronitrile) (V-65), and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Japan) were purified by recrystallization. Deionized water with a specific resistivity of $5 \times 10^6 \ \Omega$ cm was distilled once with a Pyrex distillator. Poly-(vinylpyrrolidone) (Sigma Chemical Company) and reagent-grade ethanol, methanol, octanethiol, and toluene were used as received.

Production of PS and PBMA Particles

Micron-sized, monodisperse PS and PBMA seed particles were produced under the optimum dispersion polymerization conditions determined in previous articles.[4,9] Those particles were observed with a Jeol JEM-200CX transmission electron microscope (TEM). They were spherical and had high monodispersity. The number-average diameter (D_n) and coefficient of variation (C_v) measured from TEM photographs with image analysis software for the Macintosh (Mac Scope, Mitani Corporation) were 1.65 μm and 3.09% for the PS particles and 1.85 μm and 2.37% for the PBMA particles, respectively.

Production of PS/PBMA Composite Particles

Seeded dispersion polymerizations of BMA were carried out in the presence of the PS seed particles in 300-mL four-necked round-bottom flasks under the conditions listed in Table I. The reaction mixture was stirred with an anchor-type stirrer at 60 rpm for 24 h under a nitrogen atmosphere. The conversion was measured by gas chromatography (GC).

Shape of Particles

The shape of the particles was evaluated as D values on the TEM photographs with the Mac Scope software, and was defined as follows:

$$D = 4\pi A/C^2$$

where A is the area of the cross section of the particle and C is the circumference of the cross section of the particle.

Observation of Ultrathin Cross Sections of Particles

The PS/PBMA composite emulsions were dried under reduced pressure at about 0°C. 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 an epoxy matrix, cured at room temperature for 24 h, and microtomed. The ultrathin cross sections were observed with the TEM.

Table I   Recipes for Production of PS/PBMA (2/1, w/w) Composite Particles by Seeded Dispersion Polymerizations

	Sample No.									
	1[a]	2[a]	3[a]	4[a]	5[a]	6[a]	7[a]	8[a]	9[b]	10
PS particles[a] (g)					13.1					
BMA (g)					6.55					
V-70 (g)	—	—	—	—	—	—	—	—	0.14	—
V-65 (g)	—	—	—	—	—	—	—	—	—	0.11
AIBN (g)	0.075	0.375	0.75	1.5	0.075	0.075	0.075	0.075	—	—
Ethanol (g)	96.6	96.6	96.6	96.6	64.4	72.5	80.5	88.5	96.6	96.6
Water (g)	64.4	64.4	64.4	64.4	96.6	88.5	80.5	72.5	64.4	64.4
AIBN[b] (%, w/w)	0.046	0.23	0.46	0.93	0.046	0.046	0.046	0.046	0.046	0.046
Ethanol/water (w/w)	60/40	60/40	60/40	60/40	40/60	45/55	50/50	55/45	60/40	60/40
Temp. (°C)	70	70	70	70	70	70	70	70	36	58

The polymerizations were carried out for 24 h under N_2 in glass tubes at 60 cycles/min with 2-cm strokes. PS, polystyrene; PBMA, poly(n-butyl methacrylate); BMA, n-butyl methacrylate; V-70, 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile); V-65, 2,2′-azobis(2,4-dimethyl valeronitrile); AIBN, 2,2′-azobisisobutyronitrile.

[a] $D_n = 1.65 \ \mu$m; $C_v = 3.09\%$.
[b] Based on the medium.

Table II   Recipe for Solution Polymerization of BMA

Ingredients	Amounts
BMA (g)	8
Toluene (g)	22
AIBN (g)	0.45
Octanethiol (g)	0.11

The polymerization was carried out under N_2 at 70°C and 80 cycles/min.

Extraction of PBMA from PS/PBMA Composite Particles

The media of the PS/PBMA composite emulsions were changed from ethanol/water to acetic acid (99.7%) by repeated centrifugation and dispersion. Acetic acid dissolves PBMA but not PS. Acetic acid dispersions of PS/PBMA composite particles were maintained under stirring at 40°C for 72 h.

Molecular Weight of PBMA Dissolved in Ethanol/Water (60/40, w/w) Medium

Low molecular weight PBMA was prepared by solution polymerization in sealed glass tubes under the conditions listed in Table II. The tubes were horizontally shaken at 80 cycles/min with 2-cm strokes. The PBMA was purified by reprecipitation, washed with methanol, and dried under reduced pressure. The BMA pellets were dis-
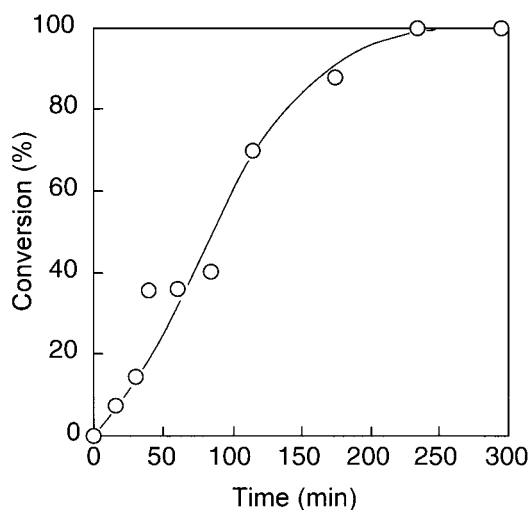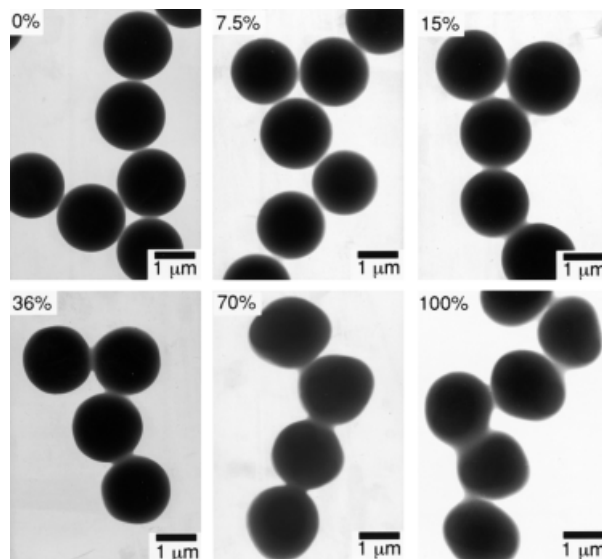

Figure 2   TEM photographs of PS/PBMA composite particles at different conversions in the seeded dispersion polymerization according to recipe 1 in Table I.

persed in the ethanol/water medium (60/40, w/w) at 36 or 70°C for 24 h. Then the supernatant was pipetted out and dried under reduced pressure. The weight-average molecular weight (M_w) was measured by gel permeation chromatography with tetrahydrofuran as the eluent and calibration using PS standards.
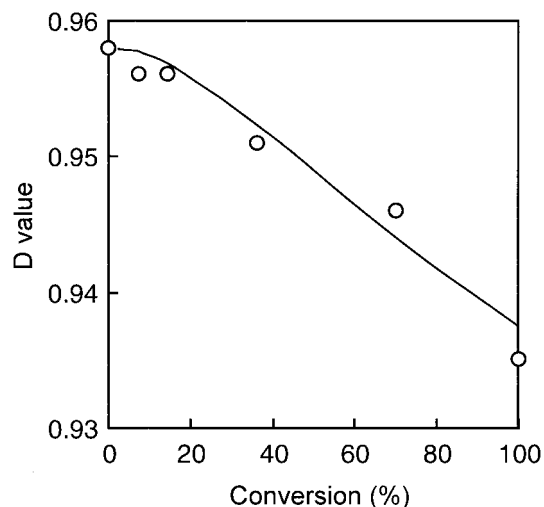

Figure 1   A time–conversion curve for seeded dispersion polymerization of BMA with 1.65-μm PS seed particles at 70°C using recipe 1 in Table I.

Figure 3   The variation of the D values of the PS/PBMA composite particles from TEM as a function of the conversion in the seeded dispersion polymerization according to recipe 1 in Table I with 0.075 g of AIBN and 60/40 (w/w) ethanol/water at 70°C.
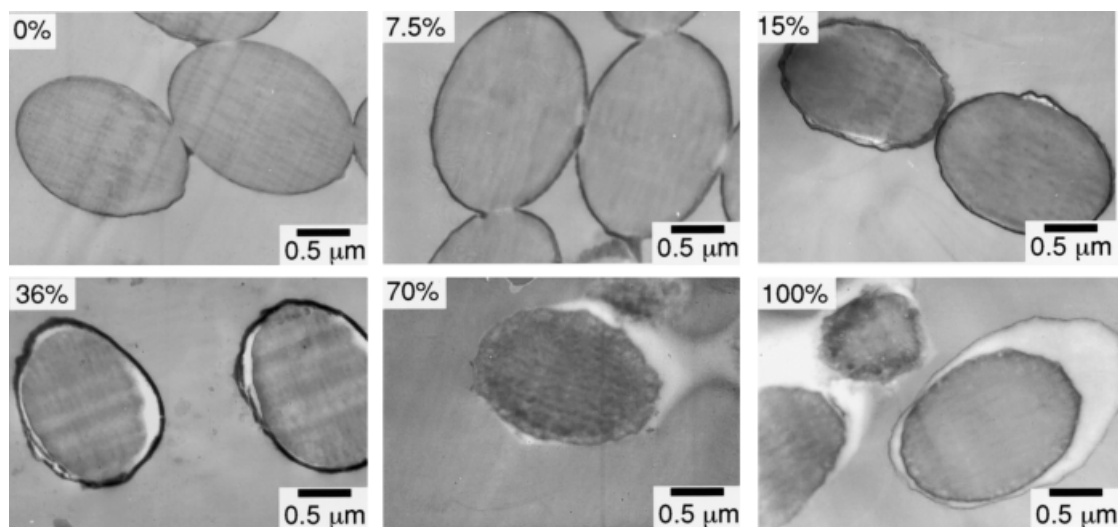
Figure 4 TEM photographs of ultrathin cross sections of the PS/PBMA composite particles at the different conversions in the seeded dispersion polymerization according to recipe 1 in Table I after exposure to RuO$_4$ vapor for 30 min.

Amount of BMA Absorbed in Particles

The BMA monomer (1.84 g) was dissolved in an ethanol (31.56 g)/water (13.52 g) mixture in which PS or PBMA particles (3.68 g) were dispersed at 36°C, and small amounts of emulsions were pipetted out successively at any time. The amount of BMA in the medium from which particles had been separated with a filter was measured by GC. The amount of BMA absorbed in the particles was calculated from the GC results.

RESULTS AND DISCUSSION

Figure 1 shows a time–conversion curve for seeded dispersion polymerization of BMA at 70°C under the sample 1 conditions listed in Table I. The polymerization proceeded smoothly and was complete in 4 h. The TEM photographs of PS/PBMA composite particles at different conversions are shown in Figure 2. At the conversions below 15% they had a spherical shape, but above 36% the shape was gradually changed to a nonspherical shape. In order to estimate the degree to which they were nonspherical, the D values of the PS/PBMA composite particles on the photographs were measured as a function of the conversion as shown in Figure 3. Its value for the "spherical" PS seed particles was 0.958, and it decreased monotonically with the conversion.

Figure 4 shows TEM photographs of ultrathin cross sections of the PS/PBMA composite particles at different conversions after exposure to RuO$_4$ vapor. All the particles look ellipsoidal because of compressive stress deformation by the microtome. It is known that RuO$_4$ stains PS but not PBMA.[10] The PBMA phase, which was formed locally on the PS seed particle, became larger with the conversion. When the PBMA phases were extracted from the composite parti-
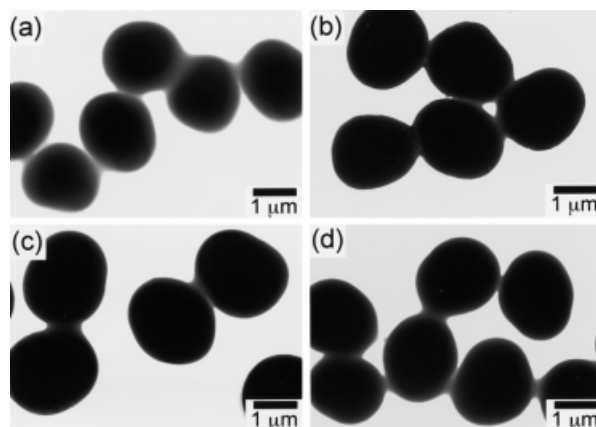

Figure 5 TEM photographs of PS/PBMA (2/1, w/w) composite particles produced by seeded dispersion polymerizations of BMA according to recipes 1–4 listed in Table I with the 1.65-μm PS seed particles in an ethanol/water (60/40, w/w) medium. The amounts of AIBN in the medium (wt %) are (a) 0.046 (recipe 1), (b) 0.23 (recipe 2), (c) 0.46 (recipe 3), and (d) 0.93 (recipe 4).
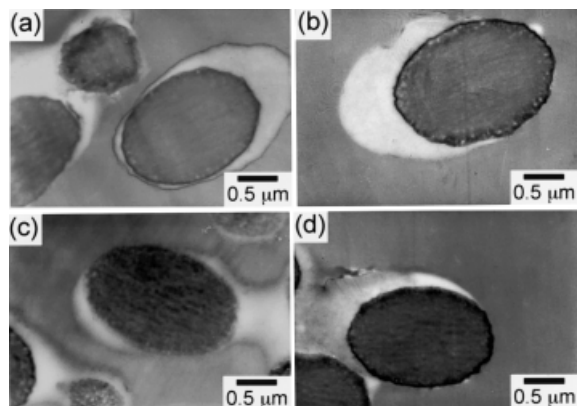
Figure 6 TEM photographs of ultrathin cross sections of the PS/PBMA (2/1, w/w) composite particles after exposure to RuO_4 vapor for 30 min as shown in Figure 5. The amounts of AIBN in the medium (wt %) are (a) 0.046 (recipe 1), (b) 0.23 (recipe 2), (c) 0.46 (recipe 3), and (d) 0.93 (recipe 4).

cles at the different conversions with acetic acid, which is a good solvent for PBMA but a nonsolvent for PS, all the particles became spherical again. These results obviously indicate that in the seeded dispersion polymerization the PBMA phase was formed and grew locally on the spherical PS seed particles, resulting in the nonspherical PS/PBMA composite particles.

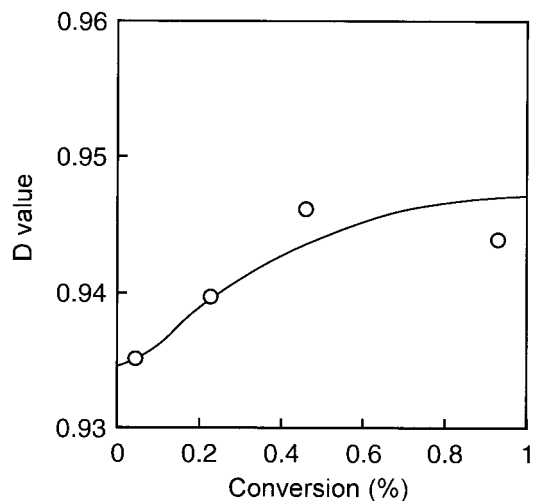Figure 5 shows TEM photographs of PS/PBMA composite particles produced at AIBN initiator

Figure 8 TEM photographs of PS/PBMA (2/1, w/w) composite particles produced by seeded dispersion polymerizations of BMA according to recipes 1 and 5–8 in Table I with 1.65-μm PS seed particles in ethanol/water (w/w) media ratios of (a) 40/60 (recipe 5), (b) 45/55 (recipe 6), (c) 50/50 (recipe 7), (d) 55/45 (recipe 8), and (e) 60/40 (recipe 1).

concentrations of 0.046–0.93 wt % based on recipes 1–4 listed in Table I. In all cases, the particles produced were not spherical. Above 0.93 wt % similar nonspherical particles were produced, and some aggregates and by-product particles were

Figure 7 The D values of the PS/PBMA (2/1, w/w) composite particles shown in Figure 5 and produced by seeded dispersion polymerizations at the different AIBN concentrations with 60/40 (w/w) ethanol/water at 70°C.
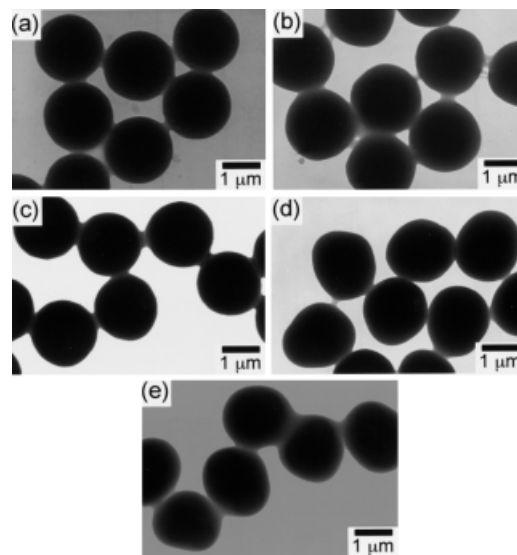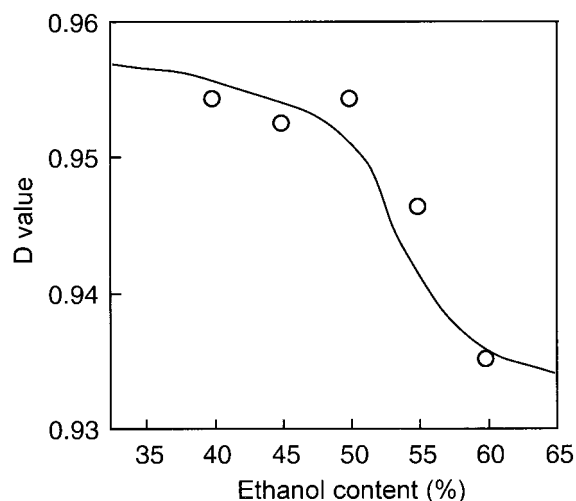

Figure 9 The D values of the PS/PBMA (2/1, w/w) composite particles shown in Figure 8 and produced by seeded dispersion polymerization in the various compositions of ethanol/water media with 0.075 g of AIBN at 70°C.
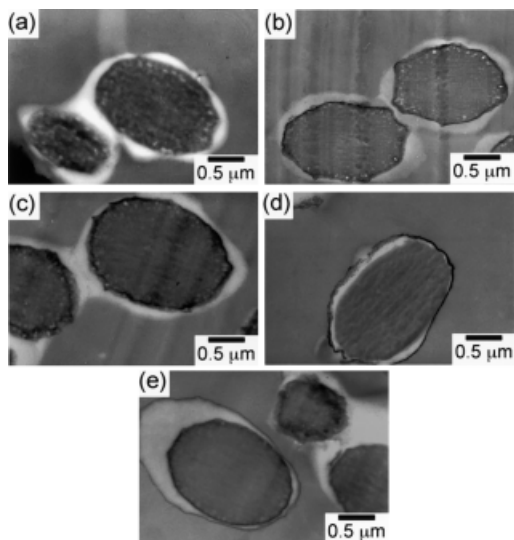
Figure 10   TEM photographs of ultrathin cross sections of the PS/PBMA (2/1, w/w) composite particles after exposure to RuO₄ vapor for 30 min, as shown in Figure 8 in ethanol/water (w/w) media ratios of (a) 40/60 (recipe 5), (b) 45/55 (recipe 6), (c) 50/50 (recipe 7), (d) 55/45 (recipe 8), and (e) 60/40 (recipe 1).

Figure 12   The D values of the PS/PBMA (2/1, w/w) composite particles produced by seeded dispersion polymerizations at the constant decomposition rate of the azoinitiators at the different temperatures shown in Figure 11 with 60/40 (w/w) ethanol/water.

observed. As seen in the TEM photographs of ultrathin cross sections in Figure 6, the thickness of the PBMA shells was not uniform. In Figure 7 the D values of the composite particles somewhat decreased with a decrease in the AIBN concentration. This may be based on the fact that because the number of oligomer radicals adsorbed by the PS seed particles per a certain time decreases with the decrease in the AIBN concentration; there is a time to gather PBMA molecules at the surface, resulting in the formation of a few PBMA
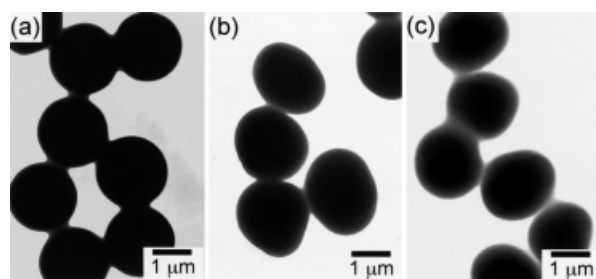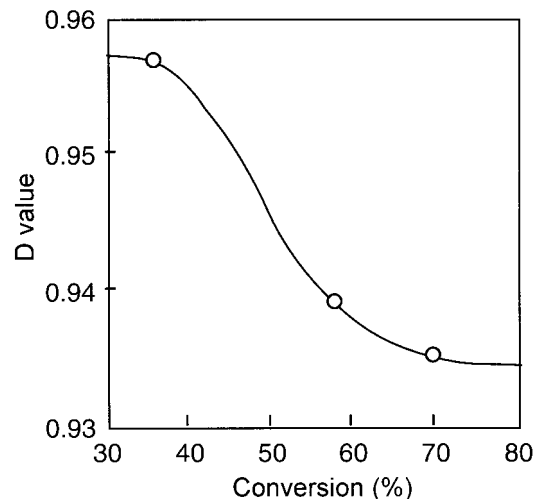
domains that predominantly absorb BMA monomer over the bare PS surface layer.

Figure 8 shows TEM photographs of PS/PBMA composite particles produced in ethanol/water media compositions from 40/60 to 60/40 (w/w) according to recipes 1 and 5–8 in Table I. The BMA monomer was completely soluble in all the media, as confirmed with an optical microscope. The shape of the composite particles was changed from spherical to nonspherical with an increase in the ethanol content in the media. As shown in Figure 9, the D values decreased markedly with the increase in the ethanol content. In the TEM photographs of those ultrathin cross sections shown in Figure 10, the thickness of the PBMA shells at 40/60 and 45/55 were uniform, but those

Figure 11   TEM photographs of PS/PBMA (2/1, w/w) composite particles by seeded dispersion polymerizations of BMA according to recipes 1, 9, and 10 in Table I with 1.65-μm PS seed particles in an ethanol/water (60/40, w/w) medium at a constant decomposition rate of azoinitiators at different temperatures (°C) of (a) 36 (recipe 9), (b) 58 (recipe 10), and (c) 70 (recipe 1).

Figure 13   TEM photographs of ultrathin cross sections of the PS/PBMA (2/1, w/w) composite particles after exposure to RuO₄ vapor for 30 min, as shown in Figure 11 at temperatures (°C) of (a) 36 (recipe 9), (b) 58 (recipe 10), and (c) 70 (recipe 1).
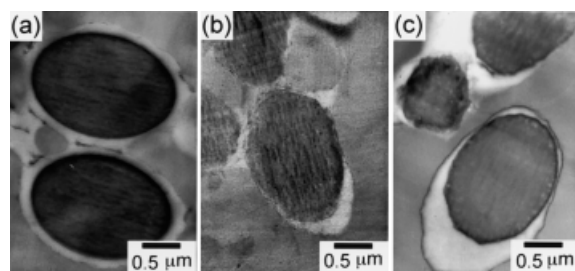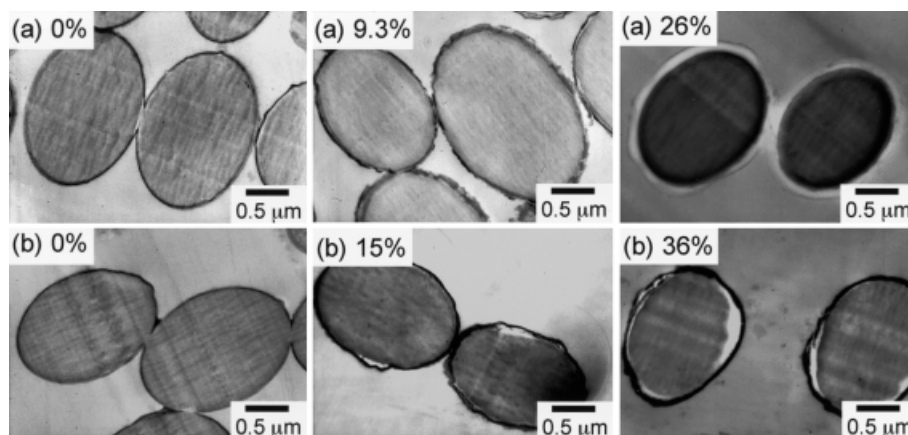
Figure 14 TEM photographs of ultrathin cross sections of the PS/PBMA (2/1, w/w) composite particles after exposure to RuO$_4$ vapor for 30 min at low conversions of seeded dispersion polymerizations of BMA at the constant decomposition rate of the azoinitiators at (a) 36°C and (b) 70°C according to recipes 9 and 1, respectively, as listed in Table I.

at 50/50, 55/45, and 60/40 were not uniform. These results also suggest that the formation of the nonspherical particles is based on the decrease of the adsorption rate of the oligomer radicals onto the PS seed particles because of their high solubility in the media. In addition, although the other systems were carried out (e.g., composite particles produced in the 70/30 system were nonspherical), these results were omitted because we thought the results from the 40/60 to 60/40 compositions were enough to show the tendency.

Figure 11 shows TEM photographs of PS/PBMA composite particles produced at temperatures of 36–70°C in an ethanol/water (60/40, w/w) medium at an initiator concentration of 1 mol % based on the BMA monomer according to recipes 1 and 8–10 in Table I. In order to keep a constant decomposition rate of the initiator at each temperature, three kinds of azoinitiators were used. The BMA monomer was completely soluble in the ethanol/water medium at each temperature. All the systems were colloidally stable during the polymerizations and no by-product PBMA particles were observed. The shape of the composite particles produced at 36°C was spherical, but those at 58 and 70°C were nonspherical. As shown in Figure 12, the D values decreased markedly with an increase in the polymerization temperature. In the TEM photographs of those ultrathin cross sections shown in Figure 13 the thickness of the PBMA shell was uniform at 36°C but not at 58 and 70°C.

Figure 14 shows TEM photographs of ultrathin cross sections of PS/PBMA composite particles at low conversion of the seeded dispersion polymerizations at 36 and 70°C after exposure to RuO$_4$ vapor. At 36°C, at which spherical composite particles were produced at the completion of the polymerization, many PBMA domains (white region) homogeneously distributed at the surface of PS seed particles at 9.3% of the conversion, and a uniform thickness of the PBMA shell was formed at 26% and kept until the completion of the polymerization. On the other hand, at 70°C, at which nonspherical composite particles were produced at the completion of the polymerization, a few PBMA domains on the PS seed particles were locally formed at 15%, and a heterogeneous thickness of the PBMA shell was observed at 36% and kept until the completion of the polymerization. In this way, the numbers of PBMA domains formed on the PS seed particles were different in the early stages of the seeded dispersion polymerizations at 36 and 70°C.

Table III   Weight-Average Molecular Weight (M_w) of PBMA Prepared by Solution Polymerization and Dissolved in Ethanol/Water (6/4, w/w) Medium

	36°C	70°C	36–70°C
M_w	1834	1886	2070

The conditions are listed in Table II. The M_w was measured by gel permeation chromatography.
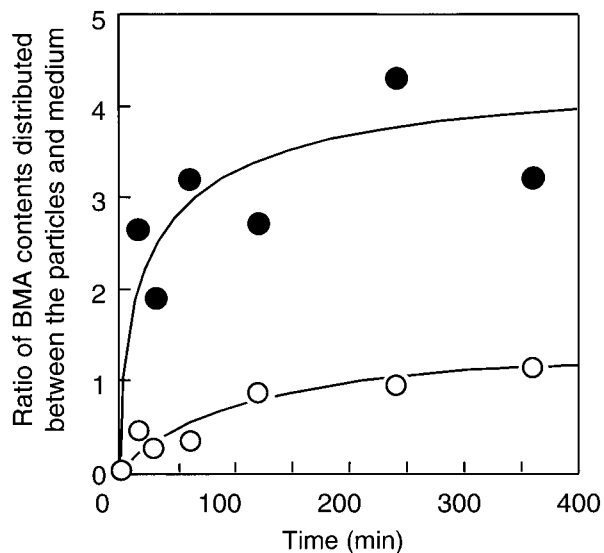
Figure 15 The variations of the partition ratios of BMA between particles and ethanol/water (70/30, w/w) medium at 36°C: (○) 1.65-μm PS particles, (●) 1.85-μm PBMA particles; 3.68 g particles, 1.84 g BMA, 31.56 g ethanol, and 13.52 g water.

Table III shows the M_w values of PBMA dissolved in the ethanol/water (60/40, w/w) medium at 36 and 70°C. The M_w value was larger at 70°C than at 36°C. The last column indicates that the M_w of the PBMA, which dissolved at 70°C after removal of that solubilized at 36°C, was the highest value. These results indicate that the nonspherical particles are formed when the BMA oligomer radical has high solubility in the medium.

Figure 15 shows variations of the partition ratios of BMA between the 1.65-μm PS particles or the 1.85-μm PBMA particles and ethanol/water (70/30, w/w) medium at 36°C. Both particles had monodispersity and similar number-average diameters, and no coagulation in their emulsions was observed throughout the measurements. The PS particle absorbed BMA slowly and the BMA concentration in the PS particles was almost the same as that in the medium at an equilibrium state. On the other hand, the PBMA particle absorbed BMA about 30 times faster than the PS particle, and the BMA concentration in the PBMA particle was 3 times that in the medium. These results suggest that, in the production process of PS/PBMA composite particles, the preferential absorption of BMA at PBMA domains over the bare PS surface accelerates the polymerization, resulting in rapid enlargement of the PBMA domains.
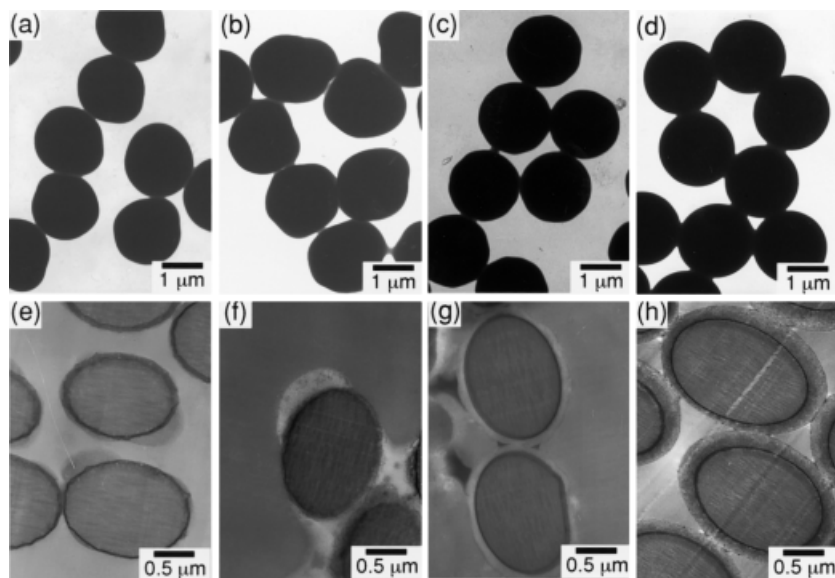
Figure 16(a,b,e,f) shows TEM photographs of

Figure 16 TEM photographs of (a–d) PS/PBMA composite particles (2/1, w/w) produced by two types of two-step seeded dispersion polymerizations of BMA according to (a,b,e,f) recipe 1 and (c,d,g,h) recipe 2 as listed in Table IV, and TEM photographs of (e–h) their ultrathin cross sections after exposure to RuO_4 vapor for 30 min at polymerization temperatures for the first step of (a,e) 70°C and (c,g) 36°C and for the second step of (b,f) 36°C and (d,h) 70°C.

Table IV   Recipes for Production of PS/PBMA (2/1, w/w) Composite Particles by Two-Step Seeded Dispersion Polymerizations

Ingredients	Sample 1		Sample 2	
	First Step[a] at 70°C	Second Step[b] at 36°C	First Step[b] at 36°C	Second Step[a] at 70°C
PS particles[c] (g)	0.72	—	0.72	—
BMA (g)	0.18	0.18	0.18	0.18
AIBN (mg)	2.08	—	—	2.08
V-70 (mg)	—	3.95	3.95	—
Ethanol (g)	5.83	—	5.83	—
Water (g)	2.67	—	2.67	—

[a] The polymerization was carried out under N_2 at 70°C for 24 h at 60 cycles/min with 2-cm strokes.
[b] The polymerization was carried out under N_2 at 36°C for 24 h at 60 cycles/min with 2-cm strokes.
[c] $D_n = 1.65$ μm; $C_v = 5.2\%$.

PS/PBMA composite particles [Fig. 16(a,b)] and of their ultrathin cross sections [Fig. 16(e,f)] after exposure to RuO_4 vapor for 30 min, which are produced by first-step and second-step seeded dispersion polymerizations of BMA carried out at 70 and 36°C, respectively, under the sample 1 conditions listed in Table IV. The emulsions were colloidally stable throughout the polymerizations and no by-product particles were produced. In the photos in Figure 16(a,e) the PS/PBMA (4/1, w/w) composite particles produced by the first-step polymerization at 70°C had a nonspherical shape consisting of a few PBMA domains on the PS particles. In the photos in Figure 16(b,f) the PS/PBMA (2/1, w/w) composite particles produced by the second-step polymerization kept the nonspherical shape, and the thickness of the PBMA shell on the PS seed particles was heterogeneous. These results suggest that the PBMA domains were predominantly enlarged through the second-step one. On the other hand, Figure 16(c,d,g,h) shows TEM ones in first-step [Fig. 16(c,g)] and second-step [Fig. 16(d,h)] seeded dispersion polymerizations at 36 and 70°C, respectively, under the sample 2 conditions listed in Table IV, which were opposite in the polymerization temperatures to those (sample 1) shown in the photos [Fig. 16(a,b,e,f)]. In Figure 16(c,g) the PS/PBMA (4/1, w/w) composite particles produced by the first-step polymerization at 36°C had a spherical shape and homogeneously thick PBMA shell. In Figure 16(d,h) PS/PBMA (2/1, w/w) composite particles produced by the second-step polymerization at 70°C kept the spherical shape and homogeneously enlarged the thickness of the PBMA shell.

From these results it is concluded that the nonspherical PS/PBMA composite particles were produced as follows. In the early stage of the seeded dispersion polymerization the BMA oligomers that are adsorbed by the PS particles gather and form PBMA domains at the surface. The PBMA domains preferentially absorb BMA quickly from an ethanol/water medium over the bare PS surface, and the polymerization of BMA proceeds much faster in the domains than in the PS bare surface and preferentially enlarges the PBMA domains, resulting in nonspherical PS/PBMA composite particles with nonuniform PBMA thickness.

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