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ORIGINAL CONTRIBUTION

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Preparation of micron-sized, monodisperse poly(methyl methacrylate)/polystyrene composite particles having a large number of dents on their surfaces by seeded dispersion polymerization in the presence of decalin

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Abstract Seeded dispersion polymerization of styrene with 1.77-μm-sized, monodisperse poly(methyl methacrylate) seed particles was carried out in a methanol/water medium (8/2, w/w) in the presence of decalin droplets. The monodisperse poly(methyl methacrylate)/polystyrene composite particles produced had a large number of dents on their surfaces. The effects of the amount of decalin in the polymerization system on the number, the diameter, and the depth of the dents on the surface of the composite particles were clarified.

Keywords Composite particle · Core/shell · Seeded dispersion polymerization · Morphology · Monodisperse

Introduction

Submicron-sized polymer particles produced by emulsion polymerization are normally spherical because this minimizes the interfacial free energy between the particle and the aqueous medium. However, in a series of investigations on composite polymer particles produced by seeded emulsion polymerization, various nonspherical particles have been prepared [1, 2, 3, 4, 5, 6]. In addition, others nonspherical shapes were reported by Cho and Lee [7]. Such nonspherical shapes were based on heterogeneous growth of particles owing to their heterogeneous morphologies formed in the early stage of the seeded emulsion polymerizations. A thermodynamic approach to these morphologies has been also discussed by Sundberg and Durant [8].

Recently, we found that nonspherical polystyrene (PS)/poly(butyl acrylate) (PBA) composite particles having many dents on their surfaces were produced by seeded emulsion polymerization of butyl acrylate (BA) with spherical PS seed particles [9], which were named "golf-ball"-like particles. We proposed a formation mechanism [10] and examined the effects of some factors on the formation [11]. The formation mechanism is as follows. Initiator radicals enter the PS seed particles swollen with BA and initiate the polymerization. Because PBA is more hydrophilic than PS, the PBA molecules produced tend to remain at the particle surface and form domains. Since BA monomer prefers to exist in PBA rather than PS it predominantly distributes in the PBA domains at the particle surface, resulting in a decrease in the mobility of PS molecules, which serves to fix the PS continuous phase. As the conversion of BA increases, the volume of PBA/BA domains contracts and results in dents on the particle surface.

On the other hand, micron-sized, monodisperse polymer particles have been applied in some advanced industrial fields, such as the biomedical field, microelectronics, and other areas, in recent years. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodisperse polymer particles. We have produced micron-sized, monodisperse particles having functional groups at the surface layer by the seeded dispersion polymerization (SDP) technique [12, 13, 14, 15].

The SDP in which almost all monomers and initiators exist in the medium has the advantage to produce core/shell polymer particles in which polymer layers accumulate in their order of their production regardless of the hydrophobicity of the polymers, because of the high viscosity within the polymerizing particles. On the basis of this idea, we have successfully produced core/shell and multilayered poly(methyl methacrylate) (PMMA)/PS composite particles by (multistage) SDP in a methanol/water medium, though the morphologies were unstable thermodynamically in polar media [16, 17].

According to the formation mechanism of the submicron-sized, golf-ball-like composite particle described earlier, the SDP technique seems to be effective for the production of micron-sized, monodisperse, golf-ball-like composite particles because in this polymerization the second polymers tend to form the domains at the surface of the seed particle in an early stage of the polymerization regardless of the polarity of the polymers. If there is something which promotes the growth of domains of the second polymer, a golf-ball-like composite particle may be produced.

In this work, in order to produce micron-sized, monodisperse, golf-ball-like composite particles, SDP of styrene with about 2-μm-sized, monodisperse PMMA seed particles was carried out in the presence of decalin droplets as a promoter for the formation of dents.

Experimental

Materials

Methyl methacrylate and styrene were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobisisobutyronitrile 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. Poly(vinylpyrrolidone) (weight-average molecular weight 3.6×10^5, Sigma Chemical Company), tricaprylyl methylammonium chloride (Aliquat 336, Aldrich Chemical Company.), and reagent-grade methanol and decalin were used as received.

Preparation of PMMA seed particles

Monodisperse PMMA seed particles were produced by dispersion polymerization under the conditions listed in Table 1. The polymerization was carried out in a 300-ml four-necked round-bottomed flask equipped with a Teflon paddle stirrer operating at 120 rpm. The number-average diameter, D_n, and the coefficient of variation, C_v, of the seed particles were measured with a Hitachi H7500 transmission electron microscope (TEM) using image analysis software for Macintosh (MacScope, Mitani Corporation).

Table 1. Preparation of micron-sized, monodispersepoly(methyl methacrylate) (*PMMA*) seed particles by dispersion polymerization. N_2, 60 °C, 24 h. 2,2′-Azobis(2,4-dimethyl valeronitrile) (*V-65*), poly(vinyl pyrrolidone) (*PVP*), tricaprylylmethylammonium chloride (Aliquat 336)

Ingredients	Weight (g)
MMA	24
V-65	0.36
PVP	5.6
Aliquat 336	1.6
Methanol	179.2
Water	44.8

Table 2. Recipes for the production of PMMA/polystyrene (*PS*) composite particles by seeded dispersion polymerization (N_2, 60 °C, 24 h) in the presence of decalin droplets. 2,2′-Azobis(isobutyronitrile) (*AIBN*)

Ingredients	PMMA/decalin (w/w)			
	2/1	2/2	2/3	2/4
PMMA seed particles (g)[a]	0.6	0.6	0.6	0.6
Styrene (g)	0.3	0.3	0.3	0.3
Decalin (g)	0.3	0.6	0.9	1.2
AIBN (mg)	4.7	4.7	4.7	4.7
PVP (g)	0.03	0.03	0.03	0.03
Methanol (g)	9.6	9.6	9.6	9.6
Water (g)	2.4	2.4	2.4	2.4

[a] $D_n = 1.77$ μm, $C_v = 2.5\%$

SDP of styrene

SDPs of styrene with PMMA seed particles were carried out in the presence of various amounts of decalin in sealed glass tubes under a nitrogen atmosphere at 60 °C for 24 h under the conditions listed in Table 2. The tubes were shaken horizontally at 120 cycles/min (2-cm strokes). The PMMA/PS composite particles obtained were repeatedly washed with methanol using a centrifugal separator.

Observation of PMMA/PS composite particles

The PMMA/PS composite particles were observed by using a TEM and a Hitachi S-2500 scanning electron microscope (SEM). The estimation of the dents at the particle surface was carried out using MacScope on SEM photographs and TEM photographs of ultrathin cross sections.

Ultrathin cross sections

Dried PMMA/PS 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 at 40 °C for 1 h, and microtomed. The ultrathin cross sections were observed with a TEM.

Determination of the polymer compositions of the PMMA/PS composite particles

The weight ratio of PMMA/PS in the composite particles was determined with ^1H NMR. The ^1H NMR measurement was carried out with a Bruker DPX250 MHz spectrometer at room temperature in $CDCl_3$. The chemical shifts were referred to tetramethylsilane. PS and PMMA, respectively, have exclusive resonance peaks at 6.2–7.5 ppm due to phenyl protons of the PS unit and the peak at 3.5–4.4 ppm due to methoxy protons of the PMMA unit.

Brunauer–Emmett–Teller measurement

Specific surface areas of the PMMA/PS composite particles were measured by the Brunauer–Emmett–Teller (BET) method using nitrogen gas with a Shimadzu Gemini-Micromeritics 2360.

Results and discussion

A TEM photograph of 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 1.77 μm and 2.5%, respectively.

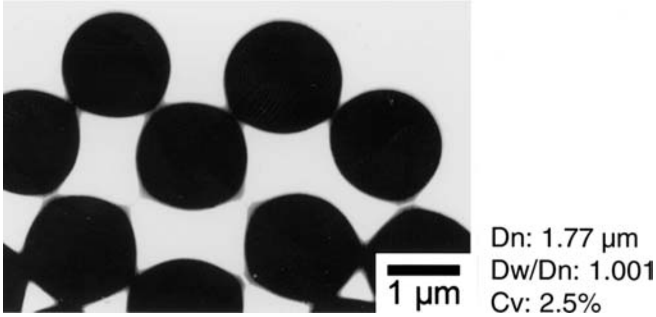


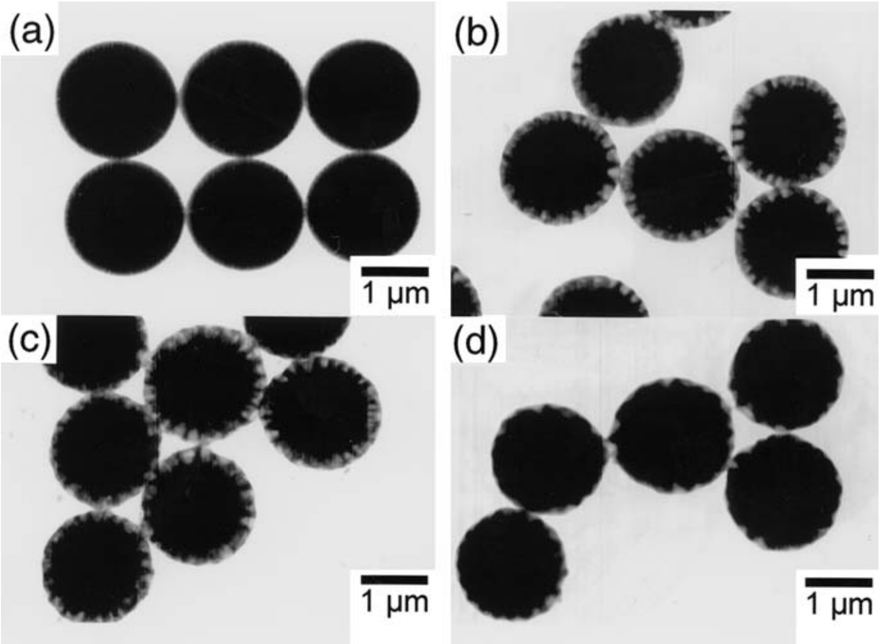
Fig. 1. A transmission electron microscope (*TEM*) photograph of poly(methyl methacrylate) (*PMMA*) seed particles produced by dispersion polymerization under the conditions listed in Table 1

TEM photographs of PMMA/PS (2/1, w/w) composite particles produced by SDPs in the presence of various amounts of decalin which were dispersed as droplets in a methanol/water medium are shown in Fig. 2. All the particles were monodisperse, and seem to have uneven surfaces because the composite particles had less contrast at their surfaces though this was unclear in case of a PMMA/decalin ratio of 2/1. This was confirmed in the SEM photographs of the PMMA/PS (2/1, w/w) composite particles shown in Fig. 3. All the particles had a large number of dents on their surfaces.

TEM photographs of ultrathin cross sections of the PMMA/PS (2/1, w/w) composite particles, stained with RuO_4 vapor for 30 min, are shown in Fig. 4. It is known that RuO_4 selectively stains PS [18]. There were two darker parts, which are due to PS, in the PMMA/PS composite particle. One was around the dents on the surface of the composite particle. These seem to be formed by evaporation of decalin from PS/decalin domains. The other was PS domains dispersed in PMMA matrix. The size of the PS domains increased with the increase in the amount of decalin in the SDP.

Table 3 shows that the number of dents decreased and the diameter of dents increased with the increase in the amount of decalin. The increase in the amount of decalin should soften the surface layer of the PMMA particles in each system because of plasticization, and therefore PS domains formed at the surface containing decalin tend to aggregate. On the other hand, the depth of the dents had a peak for the amount of decalin. In these ways, the amount of decalin has an influence on the number, the diameter, and the depth of the dents.

Fig. 2. TEM photographs of PMMA/polystyrene (*PS*) (2/1, w/w) composite particles produced by seeded dispersion polymerizations (*SDPs*) in the presence of decalin droplets at various decalin contents: PMMA/decalin (w/w) **a** 2/1; **b** 2/2; **c** 2/3; **d** 2/4



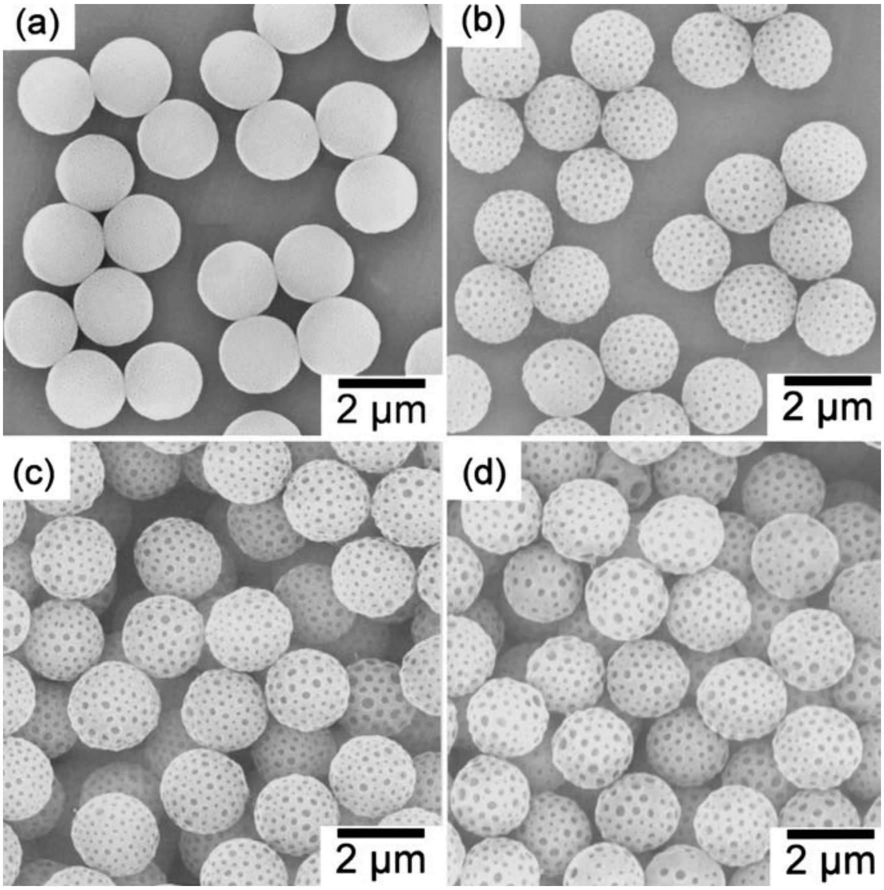


Fig. 3. Scanning electron microscope photographs of PMMA/PS (2/1, w/w) composite particles produced by SDPs in the presence of decalin droplets at various decalin contents: PMMA/decalin (w/w) **a** 2/1; **b** 2/2; **c** 2/3; **d** 2/4

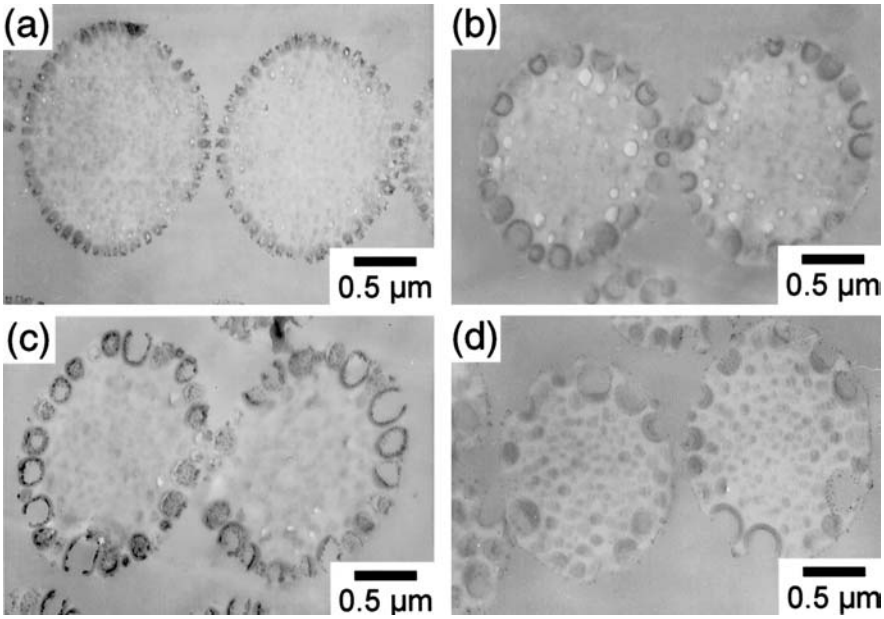


Fig. 4. TEM photographs of ultrathin cross sections of PMMA/PS (2/1, w/w) composite particles produced by SDPs in the presence of decalin droplets at various decalin contents, stained with RuO_4 vapor for 30 min: PMMA/decalin (w/w) **a** 2/1; **b** 2/2; **c** 2/3; **d** 2/4

The weight ratios of the PMMA/PS in the composite particles are shown in Table 4. The PS contents in all the particles measured by ^1H NMR were smaller than those calculated on the basis of the recipies because the polymerizations of styrene were not complete. No by-product of the PS particles was observed, as shown in

Table 3. Estimation of the dents on the surface of the PMMA/PS composite particles by image analysis on scanning electron microscope and transmission electron microscope photographs

Decalin (g)	Number[a]	Diameter (nm)[a]	Depth (nm)[b]	D_n of particles (µm)[a]
0.3	403	51	65	1.90
0.6	155	108	138	1.86
0.9	143	125	190	2.03
1.2	90	157	151	1.97

[a] From the scanning electron microscope photographs

[b] From the transmission electron microscope photographs of ultrathin cross sections

Table 4. The weight ratios of PMMA/PS in the composite particles produced by seeded dispersion polymerizations in the presence of decalin droplets

PMMA/decalin (w/w)	PMMA/PS (w/w)[a]
2/1	2/0.69
2/2	2/0.42
2/3	2/0.46
2/4	2/0.44

[a] Determined by ^{1}H NMR

Fig. 2. The PMMA/PS ratios determined by ^{1}H NMR were agreement with those calculated on the basis of the conversions of styrene determined by gas chromatography. The incompleteness of the SDP seems to be due to a decrease in the styrene concentration in the medium by increasing the amount of styrene distributed in the decalin droplets, which reduces the rate of the polymerization. The distribution was confirmed by gas chromatography.

The relationship between the amount of decalin and the specific surface area of the PMMA/PS composite particle measured by BET measurement is shown in Fig. 5. The specific surface area of the composite particles increased with the increase in the amount of decalin, and it had a peak at which the composite particle had about 4 times the specific surface area of those having no void at the surfaces. The peak was due to the competition between the increase in the size of the dents and the decrease in the number of the dents.

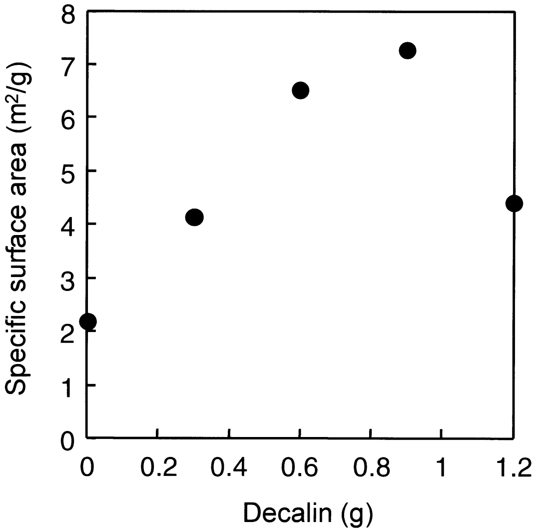


Fig. 5. Relationship between the amount of decalin and the specific surface area of PMMA/PS composite particles produced by SDPs in the presence of decalin droplets

From these results, it is concluded that the 1.77-µm-sized, monodisperse PMMA/PS composite particles having a large number of dents were produced by SDP of styrene in the presence of decalin droplets. The size, the depth and the number of dents, and the specific surface area of the composite particles would be controllable.

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