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Synthesis of micron-sized, monodisperse polymer particles of disc-like and polyhedral shapes by seeded dispersion polymerization

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Abstract Micron-sized, monodisperse polymer particles having unique "disc-like" and "polyhedral" shapes were produced by seeded dispersion polymerization of various methacrylates with 1.57 μm-sized polystyrene seed particles in the presence of saturated hydrocarbon droplets in methanol/water. Such nonspherical shapes were controllable by the polymerization conditions.

Keywords Nonspherical shape · Monodisperse · Dispersion polymerization · Particle

Introduction

Polymer particles produced by emulsion, dispersion, and suspension polymerizations are normally spherical because this minimizes the interfacial free energy between the particle and the medium. However, in the course of our investigations on the synthesis of submicron-sized composite particles by seeded emulsion polymerization, various nonspherical particles have been prepared—"confetti-like" [1], "raspberry-like" [2, 3], "void-containing" [4], and "octopus ocellatus-like" [5]. Their shapes are governed by corresponding heterogeneous structures formed by the phase separation of polymers within the particles during the seeded emulsion polymerizations under nonequilibrium conditions.

Recently, micron-sized, monodisperse polymer particles have been applied in some advanced industrial fields, such as biomedical materials and microelectronics. Many researchers studying polymer colloids are concentrating on the production of micron-sized monodisperse polymer particles. One of the useful methods to produce such particles is dispersion polymerization [6–9]. Nevertheless, dispersion polymerization seems to be restricted for a variety of monomers to produce particles having surface functional groups, which would be required for use in the above applications. Therefore, we have proposed a seeded dispersion polymerization with micron-sized, monodisperse homopolymer seed particles. For example, ca. 2.00 μm-sized, monodisperse spherical polymer particles having

chloromethyl groups [9, 10] and vinyl groups [11, 12] at the surfaces were produced by seeded dispersion copolymerization of styrene/chloromethylstyrene and styrene/divinylbenzene, respectively, with 1.80 μm-sized, monodisperse polystyrene (PS) seed particles in ethanol/water. The functional groups were located in the surface layers of the resulting composite particles.

Moreover, it was found that seeded dispersion polymerization of *n*-butyl methacrylate (*n*BMA) with 1.65 μm-sized, monodisperse PS particles gave ca. 1.80 μm-sized, monodisperse PS/poly(*n*BMA) (P*n*BMA) composite particles of "egg-like" shape [13]. Nonspherical shape is one of the functional properties for the application of micron-sized, monodisperse polymer particles. Thus, control of particle shape is an attractive object not only for academic interest but also for the application point of view. As another example, monodisperse "golf ball-like" particles larger than 2 μm in diameter were produced by seeded dispersion polymerization of styrene with 1.77 μm-sized, monodisperse poly(methyl methacrylate) particles in the presence of decalin droplets [14].

In this article, it will be reported that nonspherical polymer particles of "disc-like" and "polyhedral" shapes can be produced by seeded dispersion polymerization of various metacrylate monomers with 1.57 μm-sized PS seed particles in the presence of various hydrocarbon droplets in methanol/water.

Experimental

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobisisobutyronitrile (AIBN) was purified by recrystallization with methanol. Deionized water with a specific resistance of 5×10^6 Ω cm was distilled. Poly(acrylic acid) used as a colloidal stabilizer for dispersion polymerization was produced by solution polymerization of acrylic acid in 1,4-dioxane using AIBN as an initiator [9]. Hexyl methacrylate (HMA), 2-ethylhexyl methacrylate (EHMA), lauryl methacrylate (LMA), poly(vinyl pyrrolidone) (weight-average molecular weight, 3.6×10^5 g/mol), methanol, octanol, hexane, octane, decane, dodecane, tetradecane and hexadecane were used as received.

Seed particles

Monodisperse PS seed particles were produced under the optimum dispersion polymerization condition determined in the previous article [9]. The number-average diameter (D_n) and coefficient of variation (C_v) of the seed particles were measured with a transmission electron microscope (TEM) (H-7500, Hitachi Science Systems Ltd., Ibaraki, Japan) using image analysis software for Macintosh computer (MacSCOPE, Mitani Co. Ltd., Fukui, Japan). PS seed particles were used after centrifugal washing three times with methanol.

Seeded dispersion polymerization

Seeded dispersion polymerizations in the presence of various hydrocarbons were carried out in sealed glass tubes under the conditions listed in Table 1. The composite particles were observed with a scanning electron microscope (SEM) (S-2500, Hitachi Science Systems Ltd., Ibaraki, Japan).

Results and discussion

A TEM photograph of PS seed particles produced by dispersion polymerizations is shown in Fig. 1. The D_n and C_v of the PS particles were 1.57 μm and 2.61% respectively.

Figure 2 shows the SEM photographs of PS/poly(LMA) (PLMA) composite particles produced by seeded dispersion polymerizations at various weight ratios of methanol/water in the presence of dodecane droplets, which is good solvent for PLMA, under the conditions listed in Table 1. The particle shape dramatically changed with slight change of ratio of methanol/water. At methanol/water ratio of 80/20 (see Fig. 2a), the composite polymer particles having a large number of dents on their surfaces, golf ball-like particles, were observed similar to the ones previously reported [14]. At 84/16 (see

Table 1 Recipes for the production of PS/PHMA, PS/PEHMA, and PS/PLMA composite particle by seeded dispersion polymerizations

Ingredients	
PS seed particle[a] (g)	0.5
Secone monomer[b] (g)	0.25
AIBN (mg)	2.9
PVP (g)	0.05
Solvent[c] (g)	1.0
Methanol/water[d] (g)	10

In sealed glass tubes: N_2, 60°C, 24 h, shaking rate: 60 cycles/min (3-cm strokes)

PS polystyrene, *PHMA* poly(hexyl methacrylate), *PEHMA* poly(2-ethylhexyl methacrylate), *PLMA* poly(lauryl methacrylate), *AIBN* 2,2′-azobisisobutyronitrile, *PVP* poly(vinyl pyrrolidone)

[a]Number-average diameter 1.57 μm; coefficient of variation 2.61%

[b]Hexyl methacrylate, 2-ethylhexyl methacrylate, and lauryl methacrylate were used

[c]Hexane, octane, decane, dodecane, tetradecane, and hexadecane were used

[d]Weight ratios of methanol/water varied from 80/20 to 90/10

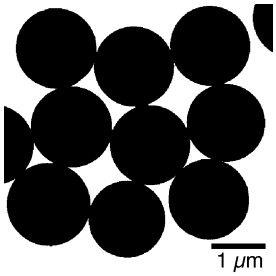

Fig. 1 Transmission electron microscope photograph of PS seed particles produced by dispersion polymerization

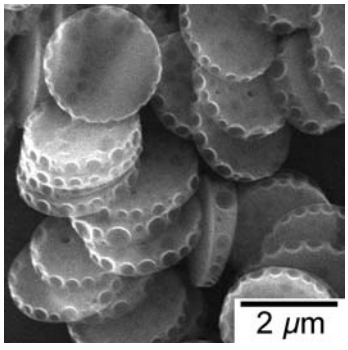

Fig. 3 Scanning electron microscope photograph of the PS/PLMA composite particles produced by seeded dispersion polymerization in methanol/water (90/10, w/w) medium in the presence of dodecane after extraction of PLMA

Fig. 2c), lower number of large dents were formed, resulting in a "wormy apple-like" appearance of the particles. At 90/10 (see Fig. 2f), disc-like particles of 2.80 μm diameter and 0.50 μm thickness were observed. Slight coagulation of the composite particles was observed in particular in the case of 90/10. However, the PS particles remaining after selective extraction of PLMA using octanol were dispersed in the octanol without any noticeable coagulation, and retained the disc-like shape and size (see Fig. 3). These findings indicate that almost all of the PLMA was located at the surface of the disc-like PS particles.

The optical micrograph shown in Fig. 4a indicates that the particles dispersed in the medium just after the seeded dispersion polymerization at the methanol/water ratio of 90/10 had a "hamburger-like" shape, in which a disc-like PS was sandwiched in between two pieces of dodecane/PLMA "breads". The hamburger-like shape changed to disc-like after release of dodecane from the dodecane/PLMA phases (see Fig. 4b). These observations indicate that in the seeded dispersion polymerization in the presence of dodecane droplets, the viscosity within the polymerizing particles was sufficiently low for changing the shape of the PS particles from spherical to disc-like. This is in spite of the polymerization temperature being below the glass transition temperature of PS presumably due to the absorption of dodecane and LMA.

Figure 5 shows PS/PLMA composite particles produced in the presence of various hydrocarbon droplets. Observed shapes were similar to those observed in Fig. 2. With an increase in the length of the alkyl chain

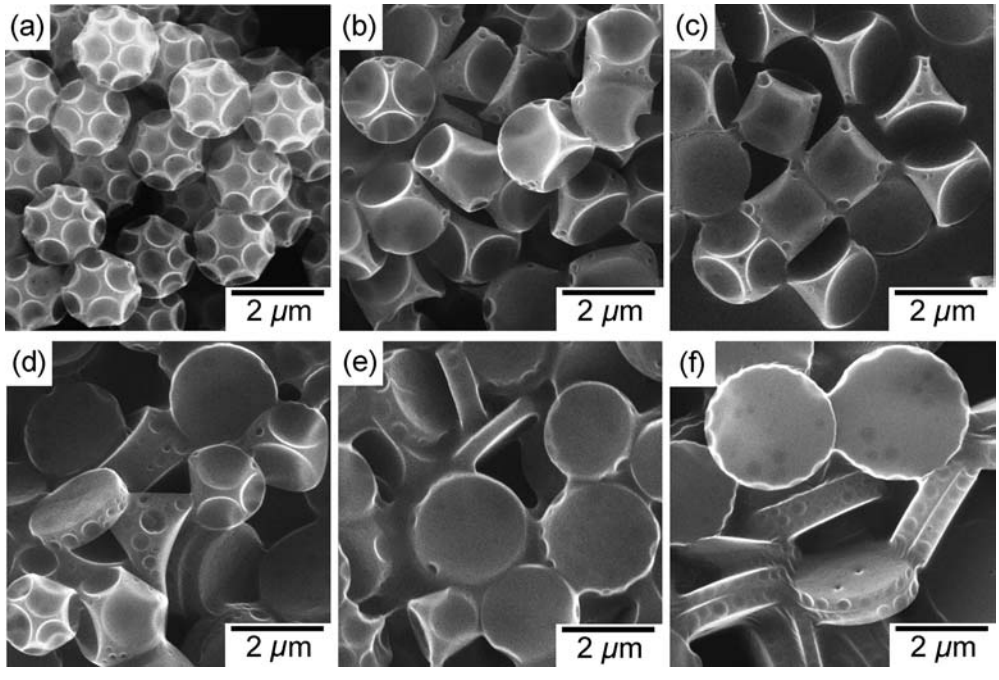

Fig. 2 Scanning electron microscope photographs of PS/poly(lauryl methacrylate) (PLMA) composite particles produced by seeded dispersion polymerization in the presence of dodecane at various weight ratios of methanol/water media: **a** 80/20; **b** 82/18; **c** 84/16; **d** 86/14; **e** 88/12; **f** 90/10

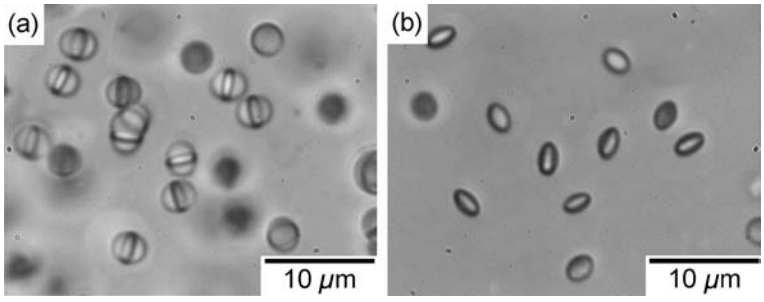

Fig. 4 Optical microscope photographs of PS/PLMA composite particles produced by seeded dispersion polymerization in methanol/water (90/10, w/w) medium in the presence of dodecane droplets **a** before and **b** after release of dodecane

of the hydrocarbons, particle shapes changed disc-like shape to golf ball-like shape. These results indicate that the particle shape was influenced not only by the medium composition but also the kind of hydrocarbon.

Figures 6 and 7 show, respectively, the PS/poly (EHMA) (PEHMA) and PS/poly(HMA) (PHMA) composite particles produced in the presence of various hydrocarbon droplets. In Fig. 6, nonspherical shapes were similar to those of PS/PLMA composite particles shown in Fig. 5 although the lengths of the alkyl chain of the hydrocarbons which operated to form the same shapes were different. Whereas, in Fig. 7, the PS/PHMA composite particles had polyhedral shapes as substitutes for the golf ball-like shapes observed in the cases of the PS/PLMA and PS/PEHMA composite particles. These results indicate that the ester-alkyl group of the methacrylate monomer had some influence on the particle shape.

To our knowledge, there has been no report showing direct production of micron-sized, monodisperse polymer particles of the nonspherical shapes described above. The particle shape was greatly influenced even by a small change in the methanol/water ratio of the medium. Additionally, the kind of hydrocarbon and the ester alkyl group of the methacrylate monomer also influenced the particle shape. As reported in a previous article [15], we obtained similar disc-like particles by extraction of P *n*BMA from 5.20 μm-sized, monodisperse spherical PS/P *n*BMA composite particles with acetic acid, which were produced by seeded polymerization of an aqueous dispersion of *n*BMA–swollen PS particles (PS/*n*BMA = 1/5, w/w), in which the PS molecules were completely dissolved. Considering that the disc-like PS phase was contained within the spherical PS/P *n*BMA composite particles prior to extraction, the formation mechanism of such an internal morphology

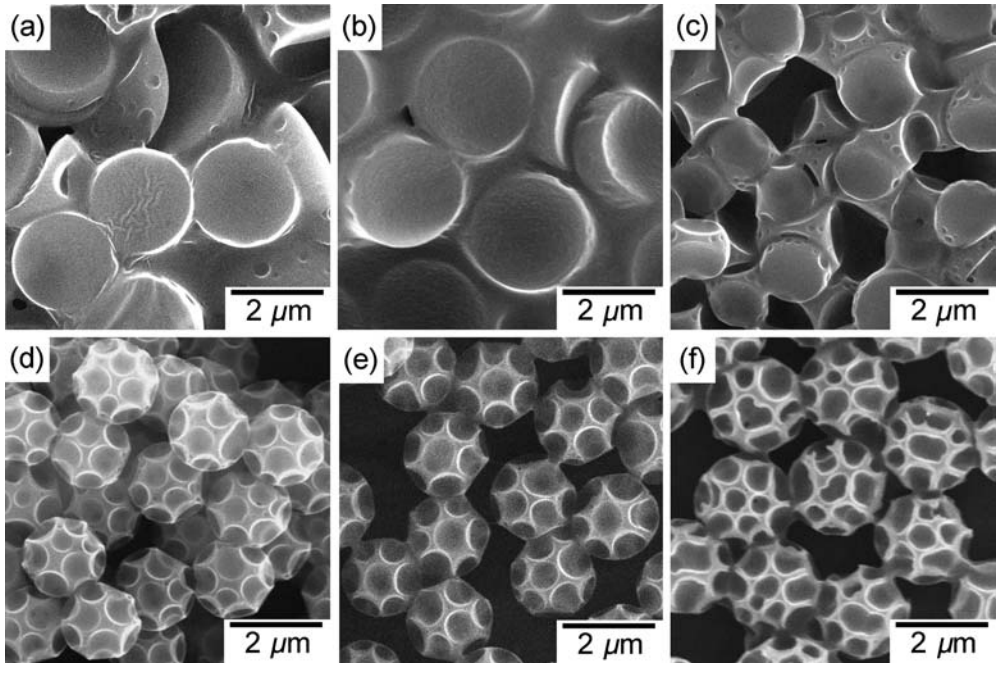

Fig. 5 Scanning electron microscope photographs of the PS/PLMA particles by seeded dispersion polymerization in methanol/water (80/20, w/w) medium in the presence of various hydrocarbons: **a** hexane; **b** octane; **c** decane; **d** dodecane; **e** tetradecane; **f** hexadecane

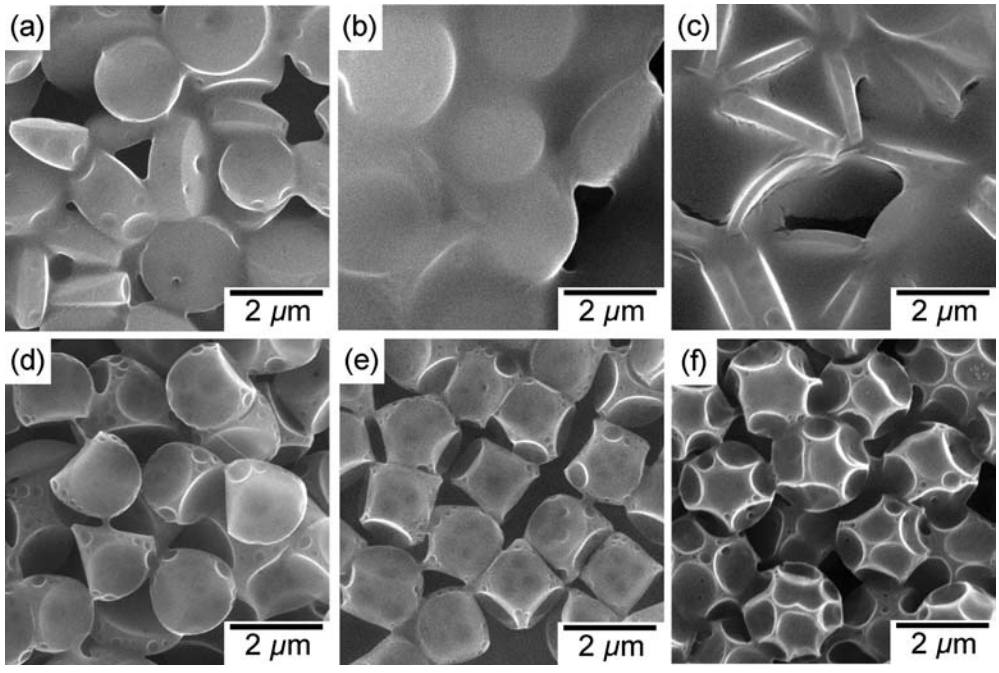

Fig. 6 Scanning electron microscope photographs of the PS/poly(2-ethylhexyl methacrylate) (PEHMA) particles by seeded dispersion polymerization in methanol/water (80/20, w/w) medium in the presence of various hydrocarbons: **a** hexane; **b** octane; **c** decane; **d** dodecane; **e** tetradecane; **f** hexadecane

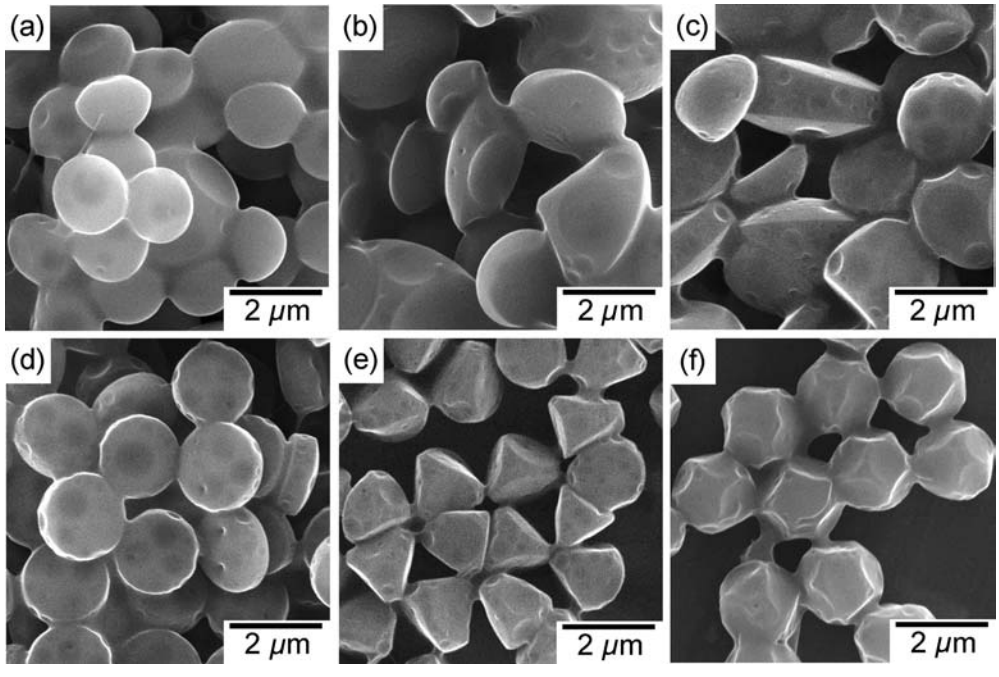

Fig. 7 Scanning electron microscope photographs of the PS/poly(hexyl methacrylate) (PHMA) particles by seeded dispersion polymerization in methanol/water (80/20, w/w) medium in the presence of various hydrocarbons: **a** hexane; **b** octane; **c** decane; **d** dodecane; **e** tetradecane; **f** hexadecane

may provide a variable information to elucidate the formation mechanism of the disc-like particles prepared by seeded dispersion polymerization in the presence of dodecane droplets. This will be discussed in a following article.

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