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ORIGINAL CONTRIBUTION

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Micron-sized monodispersed polymer particles produced by seeded polymerization for the dispersion of high swelling of polymer particles with a large amount of monomer

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Abstract Micron-sized monodispersed polystyrene (PS)/poly(*n*-butyl methacrylate) composite particles were produced as follows. First, 1.77 μm-sized monodispersed PS seed particles produced by dispersion polymerization were dispersed in ethanol/water (1/2, w/w) medium dissolving poly(vinyl alcohol) as a stabilizer. *n*-Butyl methacrylate (BMA) monomer dissolving benzoyl peroxide initiator was emulsified in ethanol/water (1/2, w/w) solution of sodium dodecyl sulfate as emulsifier with ultrasonic homogenizer, and the BMA monomer emulsion was mixed with the PS seed emulsion. The PS seed particles absorbed with a large amount of BMA (about 150 times weight of the seed particles) for 2 h to about 10 μm in diameter while keeping good monodispersity and BMA droplets disappeared finally. The seeded polymerization was carried out at 70 °C after a certain amount of water was added to depress the redissolving of BMA from the swollen particles into the medium by raising from room temperature to the polymerzation temperature.

Key words Micron-size – monodisperse – swelling – monomer droplet – seeded polymerization – monomer concentration

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 [1–4]. Corner [5] and Almog et al. [6] suggested that dispersion polymerization is a useful technique for the production of micron-sized monodispersed polymer particles. We have been producing micron-sized monodispersed polymer particles having functional groups such as chloromethyl [7] and vinyl groups [8, 9] by seeded dispersion copolymerization with corresponding functional monomers in the presence of about 2 μm-sized monodispersed polystyrene (PS) particles as seed.

Moreover, in order to produce monodispersed particles having the diameter above 5 μm, we suggested a new type of swelling method of seed polymer particles with a large amount of monomer which was named "dynamic swelling method (DSM)" [10, 11]. In fact, about 7 μm-sized monodispersed PS particles were produced by seeded polymerization utilizing DSM. The swelling is based on that a large amount of monomer and oil-soluble initiator which are separated continuously from ethanol/water medium by slow dropwise water addition [10] or cooling [11] are absorbed by polymer seed particles.

In a previous article [12], we discussed the thermodynamic background of high swelling of polymer particles with monomer by DSM in both equilibrium and kinetic control states, and clarified that the high swelling by DSM is based on the size balance between submicron-sized monomer droplets and micron-sized polymer seed particles and on high saturated monomer concentration in medium.

Jansson et al. examined the swelling method utilizing the size balance between large seed particle and small monomer droplets [13]. They prepared about 1 μm-sized monomer-swollen polymer particles by mixing 0.49 μm-sized PS seed particles and small-sized styrene droplets prepared with homogenizer. Moreover, Kasai et. al. reported that above 3 μm-sized monomer-swollen polymer particles were prepared using similar swelling method, but they did not show the experimental conditions [14].

In this article, in order to produce monodispersed composite polymer particles having about 9 μm in diameter on the basis of the idea obtained by thermodynamic treatment on high swelling of seed particles with monomer by DSM in the previous article [12] described above, seeded polymerization for the dispersion of highly butyl methacrylate (BMA)-swollen PS particles prepared by mixing 1.77 μm-sized PS seed emulsion and submicron-sized BMA monomer emulsion was carried out.

Experimental

Materials

Styrene and BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) of reagent grade were purified by recrystallization. Deionized water was distilled once separately with a Pyrex distillator. Poly(vinyl alcohol) (PVA) as a stabilizer was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Reagent grade of sodium dodecyl sulfate (SDS) and ethanol were used as received. Poly(acrylic acid) (PAA) used as a stabilizer was produced by solution polymerization of acrylic acid in 1,4-dioxane, according to the previous article [7].

Production of PS seed particles

Table 1 Production of micron-sized monodispersed PS seed particles by dispersion polymerization[a]

Ingredients		
Styrene	(g)	40.0
AIBN	(g)	0.67
PAA	(g)	4.80
Ethanol	(g)	274.0
Water	(g)	80.0

[a] 70 °C; 24 h; N_2; stirring rate, 60 rpm.
Abbreviations: PS, polystyrene; AIBN, 2,2′-azobisisobutyronitrile; PAA, poly(acrylic acid).

Monodispersed PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous article [7]. The dispersion polymerization of styrene was carried out at 70 °C for 24 h under a nitrogen atmosphere in a four-necked flask under the conditions listed in Table 1. The reaction mixture in the flask was stirred with an anchor-type stirrer at 60 rpm. The PS seed particles were observed with a JEOL JEM-200CX transmission electron microscope (TEM). The number-average diameter (D_n) and the coefficient of variation (C_v) were, respectively, 1.77 μm and 3.9 %.

Swelling of the PS seed particles with BMA and the seeded polymerization

BMA (3 g) dissolving BPO (0.03 g) was emulsified in ethanol (4 g)/water (8 g) medium dissolving SDS (0.016 g) using an ultrasonic homogenizer. The prepared monomer emulsion was mixed with the PS seed emulsion which consisted of PS particles (0.02 g), PVA (0.05 g), ethanol (1.65 g) and water (3.35 g). The mixture was stirred at room temperature in a 50 ml glass cylindrical reactor (inside diameter: 31 mm) with a magnetic stirrer at 250 rpm for 2 h. The seeded polymerization for the dispersion of BMA-swollen PS particles was carried out at 70 °C for 24 h under nitrogen atmosphere.

Measurement of the solubility of BMA in ethanol/water medium

BMA (1.0 g) was added to ethanol/water (0/10-5/5, w/w) media (10 g) in 20 ml glass cylindrical reactors (inside diameter: 22 mm) and these reactors were left at 30 °C for 4 h. The amounts of BMA dissolving in ethanol/water media were measured by gas chromatography (Yanaco, G-2800, Japan) with nitrogen as a carrier gas. Dimethyl formamide was used as solvent and *p*-xylene was used as standard reagent.

Diameter measurements

D_n, the weight-average diameter (D_w), and C_v were determined by measuring the diameters of 50–150 droplets and particles on optical micrographs taken at room temperature with the Personal Image Analysis System (PIAS Co., Ltd., LA-525, Japan), and by dynamic light scattering with an Otsuka Electronics DLS-700 particle analyzer at the angle of 90°. The swelling ratio (V_m/V_p) was calculated from D_n values of PS seed particles and BMA-swollen PS particles.

Results and discussion

Figure 1 shows the optical micrographs of droplets of BMA (0.5 g) emulsified in water (5 g) dissolving SDS (0.01 g) with three kinds of mixing instruments (a, magnetic stirrer; b, generator-shaft typed homogenizer, c, ultrasonic homogenizer) for 10 min. Submicron-sized monomer droplets were prepared only with the ultrasonic homogenizer.

Figure 2 shows a histogram of size distribution of BMA droplets kept for about 10 min without stirring after the preparation with the ultrasonic homogenizer, which was measured by the dynamic light scattering. D_n of the monomer droplets was 0.70 μm. During the measurement, the size of the monomer droplets increased continuously and attained 1.39 μm after 1 h. This suggests that the size just after the preparation with the ultrasonic homogenizer should be less than 0.70 μm.

Monodispersed PS particles having 1.77 μm in diameter produced by dispersion polymerization were used as seed particles. In the previous article [12], we pointed out with thermodynamic simulation data that the size balance between large seed particles and small monomer droplets has a large effect on the amount of monomer absorbed by the seed particles. The simulation indicates that the size balance between the 1.77 μm-sized PS seed particles and the 0.70 μm-sized BMA droplets enable the PS seed particles to swell with a large amount of BMA in equilibrium state. However, it was difficult to prepare monodispersed highly BMA-swollen PS particles experimentally by mixing them in water, because monomer absorption rate from the monomer droplets to the seed particles via water was very slow, which resulted in large-sized monomer droplets by aggregation. In this way, the monomer absorption rate is important to prepare monodispersed highly monomer-swollen polymer particles, and it is greatly affected by saturated monomer concentration in medium.

Figure 3 shows a solubility curve of BMA in ethanol/water media at 30 °C . The solubility of BMA increased with an increase in the ethanol content. Using this curve, the saturated BMA concentration in ethanol/water (1/2, w/w) medium at 30 °C in the swelling experiments shown in Table 2 was determined to be 0.51 g/100 g-solvent. This value is about ten times higher than that in water. Above the ethanol content of 40%, the amount of BMA monomer absorbed into seed particles becomes low because of high solubility of BMA in medium as shown in Fig. 3.

In order to examine the effect of the size of BMA droplets on the absorption rate and the swelling ratio (V_m/V_p) of the PS seed particles with BMA, the PS seed emulsion and the three kinds of BMA emulsions having the different droplet sizes shown in Fig. 1 were mixed under the conditions of No. 1 listed in Table 2, where the media consisted of ethanol/water of 1/2 by weight. In order to prevent creamings among the prepared micron-sized BMA-swollen PS particles and among BMA droplets throughout the swelling process, the mixture was gently stirred at room temperature in a glass cylindrical reactor with a magnetic stirrer at 250 rpm. This gentle stirring should not redisperse original BMA droplets finely.

Figure 4 shows the results (○, △, □). The results in the swelling systems of ethanol/water (◇) and water (◆) media in which BMA was in a state of layer which corresponds to the system dispersing BMA droplets having infinite diameter are also shown in Fig. 4. In the four swelling systems of the ethanol/water medium (○, △, □, ◇), the initial absorption rate and V_m/V_p value increased with a decrease in the size of BMA droplets. In the system of water (◆)

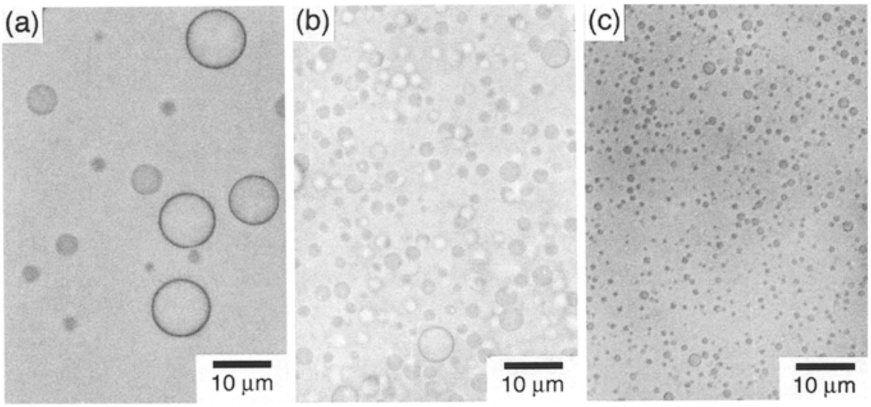

Fig. 1 Optical micrographs of BMA droplets prepared from the dispersions of BMA/SDS/water (0.5/0.01/5, wt ratio) by three kinds of mixing instruments with a) magnetic stirrer, b) generator-shaft typed homogenizer, and c) ultrasonic homogenizer

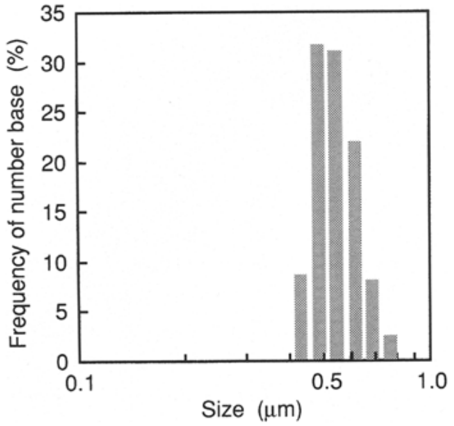

Fig. 2 A histogram of size distribution of BMA droplets prepared from the dispersion of BMA/SDS/water (0.5/0.01/5, wt ratio) by ultrasonic homogenizer for 10 min

Table 2 Preparations of micron-sized BMA-swollen PS particles by mixing PS seed emulsion and BMA monomer emulsions prepared with mixing instruments

Ingredients		No. 1[a]	No. 2[b]
Monomer emulsion			
BMA	(g)	1.0	3.0
BPO	(mg)		30.0
SDS	(mg)	10.0	16
Ethanol	(g)		4.0
Water	(g)	5.0	8.0
Seed emulsion			
PS seed particles[c]	(mg)	20.0	20.0
PVA	(mg)		50
Ethanol	(g)	5.0	1.65
Water	(g)	5.0	3.35

[a] Prepared with magnetic stirrer, generator-shaft-type homogenizer and ultrasonic homogenizer for 10 min
[b] Prepared with ultrasonic homogenizer for 10 min
[c] D_n, 1.77 μm, C_v, 3.9%.

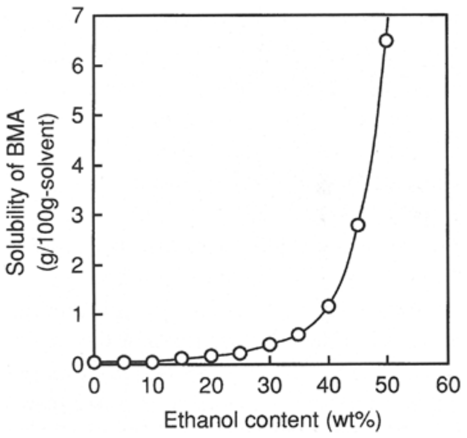

Fig. 3 Solubility curve of BMA in ethanol/water media at 30 °C

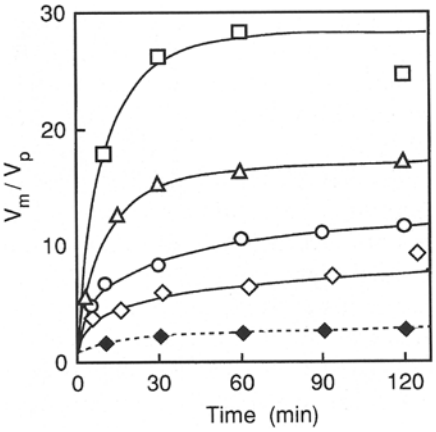

Fig. 4 Relationships between time and V_m/V_p value in BMA-swollen PS particles in the systems of ethanol/water (1/2, w/w) medium in which BMA exists as layer (◇) or droplets (○,△,□) prepared with magnetic stirrer (○), generator-shaft typed homogenizer (△), and ultrasonic homogenizer (□) under the conditions of No. 1 listed in Table 2. Dotted line indicates the system (◆) in which BMA exists as layer and the medium is water

medium in which BMA was in a state of layer, the initial absorption rate and V_m/V_p value were much slow and low, respectively. Thermodynamic stimulations of the four swelling system in both equilibrium and kinetic control states as well as the previous articles [12] indicate that in the only swelling system (□) in which 0.70 μm-sized BMA droplets prepared with the ultrasonic homogenizer were mixed, almost monomer in swelling system could be absorbed into seed particles. However, the saturated V_m/V_p value in the highest swelling system (□) was smaller than calculated value ($V_m/V_p = 56$) assuming that all monomers were absorbed evenly by the seed particles. In the swelling system just after the mixing, some large-sized droplets were observed by optical microscopy. Because this seems to be based on the difference in the ethanol contents in the media between PS seed emulsion and BMA emulsion, continuously the swelling experiment was carried out under the conditions of No. 2 listed in Table 2, in which the ethanol content in BMA emulsion was the same as that of PS seed emulsion.

Figure 5 shows optical micrographs of the prepared BMA-swollen PS particles (a) and PS/PBMA composite particles (b) produced by the seeded polymerization at 70 °C. After the swelling for 2 h, monodispersed swollen particles were prepared: D_n, 9.68 μm; D_w/D_n, 1.004; C_v, 3.46%. It is obvious that the swollen particles were derived from PS seed particles, based on the fact that unswollen PS seed particles and 0.70 μm-sized BMA droplets were not observed, and that D_n value of the swollen particles agreed

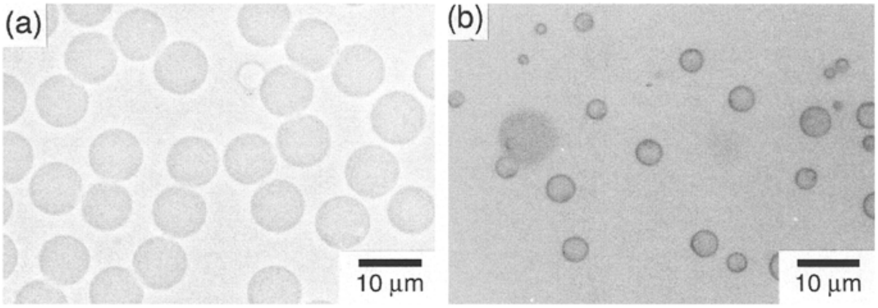

Fig. 5 Optical micrographs of BMA-swollen PS particles (a) prepared under the conditions of No. 2 listed in Table 2 and of PS/PBMA composite particles (b) produced by the seeded polymerization for the dispersion

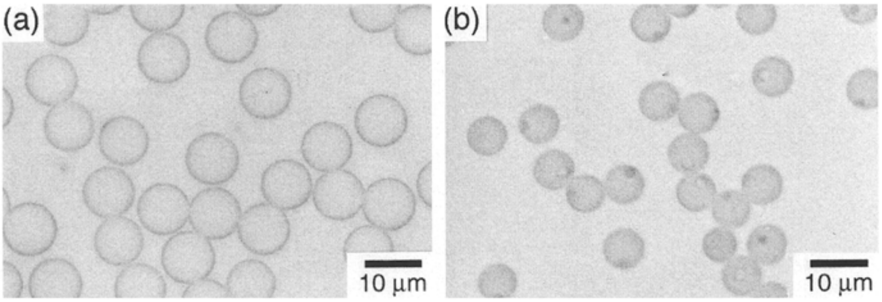

Fig. 6 Optical micrographs of BMA-swollen PS particles (a) after 60 g of water was added at the rate of 14.4 ml/h to the dispersion of the BMA-swollen PS particles prepared under the conditions of No. 2 listed in Table 2 and of PS/PBMA composite particles (b) produced by the seeded polymerization

well with calculated size, D_c (= 9.86 μm), assuming that all monomers were absorbed evenly by seed particles. As shown in Fig. 5(b), polydispersed PS/PBMA composite particles were produced by seeded polymerization for the dispersion of the monodispersed BMA-swollen PS particles: D_n, 5.62 μm; D_w/D_n, 1.265; C_v, 31.9%. All produced micron-sized particles was determined to be PS/PBMA composite particles by optical microscopic observation because of the morphology of the particles. The size of PS/PBMA composite particles was much smaller than that of the BMA-swollen PS particles before the polymerization. This was based on that a large amount of submicron-sized PBMA particles were by-produced and the coagulation took place during the seeded polymerization. The reason seems to be due to the redissolving of BMA from the swollen particles into the medium by raising from room temperature to the polymerization temperature of 70 °C.

In order to depress it, after the absorption of BMA into PS seed particles, 60 g of water was added to the monodispersed BMA dispersion at a rate of 14.4 ml/h utilizing a microfeeder at room temperature. The swollen particles absorbed BMA which was separated continuously from the medium by the slow dropwise water addition. After the water addition, the ethanol content in the medium was 7.3%, which resulted in a decrease of the saturated concentration of BMA in the swelling system at 70 °C from 2.56 to 0.18 g/100 g-solvent.

Figure 6 shows optical micrographs of the BMA-swollen PS particles a) after the water addition and of PS/PBMA composite particles b) produced by the seeded polymerization at 70 °C. The swollen particles a) were monodisperse as well as those before the water addition and the produced PS/PBMA composite particles b) also had good monodispersity as follows: a) D_n, 9.77 μm; D_w/D_n, 1.004; C_v, 3.34%: b) D_n, 8.76 μm; D_w/D_n, 1.008; C_v, 5.8%. In comparision with the result shown in Fig. 5(b), it is clear that by the addition of water, the D_n value of the produced composite particles was increased, though it was a little smaller than the calculated size, D_c (= 9.31 μm), assuming that all monomers in the swollen particles are polymerized. A small amount of submicron-sized by-produced PBMA particles were observed by TEM, but they were easily removed by centrifugal washing.

From the above results, it is clarified that micron-sized monodispersed PS/PBMA composite particles can be produced by seeded polymerization for the dispersion of monodispersed highly BMA-swollen PS particles, which are prepared by mixing micron-sized monodispersed PS particles and submicron-sized BMA droplets in ethanol/water medium.

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