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SHORT COMMUNICATION

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Influence of the swelling state of seed polymer particles with monomer on the morphology of micron-sized monodispersed composite polymer particles produced by seeded polymerization utilizing the dynamic swelling method

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Abstract Micron-sized monodispersed polystyrene (PS)/poly(*n*-butyl methacrylate) (PBMA) composite particles (PS/PBMA = 2/1 by weight) having a heterogeneous structure in which many fine PBMA domains dispersed in a PS matrix near the particle surface were produced by seeded polymerization of *n*-butyl methacrylate (BMA) of which almost all had been absorbed by 1.8 μm-sized monodispersed PS seed particles utilizing the dynamic swelling method. The morphology was varied by changing the PS/BMA ratio and polymerization temperature. It was concluded that the swelling state of 2 μm-sized BMA-swollen PS particles in the seeded polymerization process is one of the important factors to control the morphology of the composite particles.

Key words Morphology – composite particles – micron-size – seeded polymerization – dynamic swelling method

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. Almog et al. [1] suggested that dispersion polymerization technique is useful for production. Later, Ober et al. [2], Tseng et al. [3], and we [4] have recognized the usefullness of this technique.

Nevertheless, the technique seemed to be restricted for a variety of monomers for producing such particle with functional groups thereon, which would be required for use in the above applications. Therefore, we have been producing about 2 μm-sized monodispersed polymer particles having chloromethyl groups [4, 5] and vinyl groups [6, 7] at the surfaces by seeded dispersion copolymerizations of styrene (S) and chloromethylstyrene, and of S and divinylbenzene (DVB) in ethanol/water media in the presence of 1.8 μm-sized monodispersed polystyrene (PS) seed particles produced by dispersion polymerization. The latter particles had a cross-linking structure.

Moreover, in order to produce monodispersed polymer particles having more than 5 μm in diameter, we suggested seeded polymerization utilizing a new type of swelling method which was named "the dynamic swelling method (DSM)" [8–11]. DSM enables the PS particles to swell with a large amount of monomer. By seeded polymerization of DVB utilizing DSM, about 5 μm-sized monodispersed highly cross-linked polymer particles were produced [10].

In PS/S-DVB copolymer composite particles produced by the seeded copolymerization utilizing DSM [10], the cross-linking structure and the distribution of vinyl groups due to DVB unit were different from those by the seeded dispersion copolymerizations [6, 7]. This difference was based on the difference in partition states of S and DVB monomers between the PS seed particle and media in both

seeded copolymerization systems [12]. In the former system, almost all monomers exist in the seed particles, whereas in the latter system exist in the medium. This suggests the possibility to control morphology in micron-sized monodispersed composite polymer particles though they are a special system because DVB is a cross-linking monomer.

Accordingly, the influences of the locations of monomer and initiator on the morphology of about 2 μm-sized monodispersed PS/poly(*n*-butyl methacrylate) (PBMA) composite particles (PS/PBMA = 2/1, w/w) produced by seeded polymerizations of *n*-butyl methacrylate (BMA) in the presence of 1.76 μm-sized monodispersed PS seed particles was examined [13]. The PS/PBMA composite particles produced by seeded polymerization utilizing DSM had a peculiar POO (Polymeric oil-in-oil) structure in which many fine PBMA domains are dispersed in a PS matrix near the particle surface. This seems to be based on the heterogeneity of BMA concentration within PS seed particles.

In this article, this point will be discussed to clarify a significant factor for controlling morphology in micron-sized monodispersed composite polymer particles.

Experimental

Materials

S and BMA were purified by distillation under reduced pressure in a nitrogen atmosphere. AIBN, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70), and 1,1′-azobis(1-cyclohexane carbonitrile) (V-40) (Wako Pure Chemical Industries, Ltd., Japan) of reagent grade were purified by recrystallization. Deionized water with a specific conductivity of 5×10^6 Ωcm was distilled. Poly(vinyl alcohol) (PVA) as a stabilizer was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification 88%). The other materials were used as received.

Production of seed particles

Monodispersed PS seed particles were produced under the optimum dispersion polymerization conditions determined in the previous work [4]. 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) measured with the Personal Image Analysis System (PIAS Co., Ltd., LA-525, Japan) were, respectively, 1.76 μm and 2.2%.

Seeded polymerizations of BMA utilizing DSMs

Two types of DSMs were carried out under the conditions listed in Tables 1 and 2. PS seed particles were dispersed in a homogeneous solution of ethanol, water, BMA, PVA (or without PVA) as a stabilizer, and initiator. In the first type of DSM, AIBN or V-40 as initiator was dissolved in the medium, and then water was added dropwise to the mixture at a rate of 8.64 or 5.32 ml/h for 9.4 or 9 h

Table 1 Recipes for the productions of PS/PBMA composite particles having different compositions by seeded polymerizations[a] for the dispersions of BMA-swollen PS particles prepared utilizing the dynamic swelling method

PS/BMA	(w/w)	3/1	2/1	1/1
PS particles[b]	[g]	3.6	2.4	1.2
BMA	[g]	1.2	1.2	1.2
AIBN	[mg]	13.9	13.9	13.9
Ethanol	[g]	18	18	18
Water	[g]	9 +81[c]	9 +81[c]	9 +81[c]

[a] 70 °C, 24 h, N_2.
[b] D_n, 1.76 μm; C_v, 2.2%.
[c] 81 g of water was post-added at the rate of 8.64 ml/h for 9.4 h at room temperature.
Abbreviations: PS, polystyrene; BMA, *n*-butyl methacrylate; AIBN, 2,2′-azobisisobutyronitrile.

Table 2 Recipes for the productions of PS/PBMA (3/1, w/w) composite particles by seeded polymerizations[a] with V-70 at 30 °C, with AIBN at 70 °C, and with V-40 at 90 °C for the dispersions of BMA-swollen PS particles prepared utilizing the dynamic swelling methods

Ingredients				
PS particles[b]	[g]	2.4	2.4	2.4
BMA	[g]	0.8	0.8	0.8
V-70[c]	[mg]	17.4	—	—
AIBN[c]	[mg]	—	9.2	—
V-40[c]	[mg]	—	—	13.7
PVA	[g]	0.08	0.08	0.08
Ethanol	[g]	12	12	12
Water	[g]	12 +48[d]	12 +48[e]	12 +48[e]
Polymn. Temp.		30 °C	70 °C	90 °C

[a] 24 h, N_2.
[b] D_n, 1.76 μm; C_v, 2.2%.
[c] Initiator/monomer (mol/mol), 0.01.
[d] 48 g of water was post-added at the rate of 2.66 ml/h for 18 h at 0 °C.
[e] 48 g of water was post-added at the rate of 5.32 ml/h for 9 h at room temperature.
Abbreviations: PS, polystyrene; BMA, *n*-butyl methacrylate; V-70, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile); AIBN, 2,2′-azobisisobutyronitrile; V-40, 1,1′-azobiscyclohexane-1-carbonitrile; PVA, poly(vinyl alcohol).

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with a micro feeder under stirring at room temperature. In the second type of DSM, V-70 was dissolved in the medium, and then water was added dropwise to the mixture at the rate of 2.66 ml/h for 18 h at 0 °C. After the swellings utilizing DSMs, the seeded polymerizations for the dispersions of the monodispersed BMA-swollen PS particles were carried out at 30 °C (V-70), 70 °C (AIBN) or 90 °C (V-40) for 24 h under nitrogen atmosphere. The 10 h half-life decomposition temperatures of V-70, AIBN, and V-40 were 30, 65, and 88 °C, respectively.

In each polymerization system listed in Table 1 or 2, conversion measured by gas chromatography (Yanagimoto MFG. Co., Ltd., G-2800, Japan) was higher than 90%. After centrifugal washing of the emulsions to remove small amounts of by-produced PBMA particles, the PS/PBMA composite particles produced were observed with TEM.

Extraction of PBMA from PS/PBMA composite particles

The medium of each PS/PBMA dispersion was changed from ethanol/water to acetic acid by repeated centrifugations. Acetic acid dissolves PBMA but not PS. Acetic acid dispersion of each PS/PBMA composite particles was maintained under stirring at 40 °C for 72 h.

Observation of ultrathin cross sections of PS/PBMA composite particles

Dried particles before and after the extraction of PBMA from PS/PBMA composite particles with acetic acid were exposed to 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 48 h, and microtomed. The ultrathin cross sections were observed with TEM.

Extraction of PBMA from the ultrathin cross sections of PS/PBMA composite particles

In order to extract PBMA from the ultrathin cross sections of original PS/PBMA composite particles, acetic acid was dropped onto the grid with the cross sections and the grid dried up at room temperature. After several repetitions of this procedure, the ultrathin cross sections were observed with TEM.

Results and discussion

Figure 1 shows TEM photographs of PS/PBMA (3/1, 2/1, and 1/1, w/w) composite particles produced by seeded

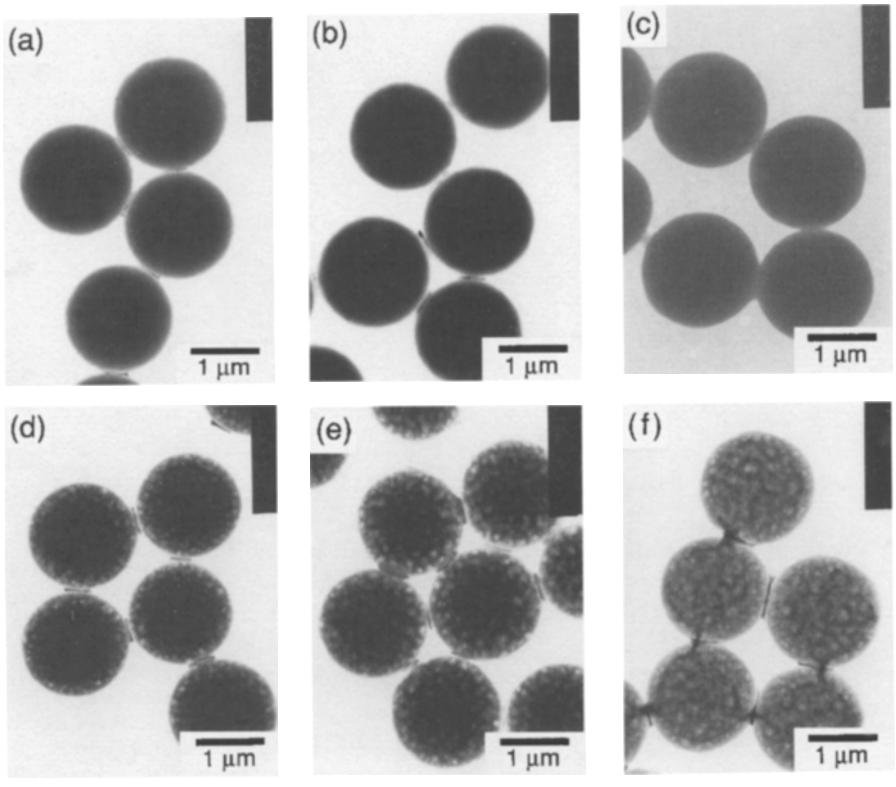

Fig. 1 TEM photographs of PS/PBMA composite particles produced by seeded polymerizations utilizing the dynamic swelling method under the conditions listed in Table 1, before (a–c) and after (d–f) the extraction of PBMA with acetic acid under stirring at 40 °C for 72 h: PS/PBMA (w/w): (a, d), 3/1; (b, e), 2/1; (c, f), 1/1

polymerizations for the dispersions of BMA-swollen PS particles prepared utilizing DSM under the conditions listed in Table 1, before (a–c) and after (d–f) extraction with acetic acid which is a good solvent for PBMA but a non-solvent for PS. In Figs. 1a–c, monodispersed spherical particles were observed, and the contrasts of the insides were homogeneous. In Figs. 1d–f, all acetic acid-treated particles had many small regions of low electron density which was due to the removal of PBMA domains by extraction with acetic acid, as shown as follows. The increase of PBMA content in the composite particles led to the increase of the low contrast regions.

Figure 2 shows TEM photographs of ultrathin cross sections of their particles before the extraction with acetic acid exposed to RuO_4 vapor which stains PS, but not PBMA [13]. POO structure in which many fine PBMA domains dispersed in the PS matrix was observed regardless of the difference in the PS/PBMA ratio. The size of PBMA domains increased with PBMA content. This suggests that the formation of the POO structure which is thermodynamically unstable is based on high viscosity in the swollen particles during the seeded polymerization. The polymer concentration in the particles was more than 50% even at initial states in all the systems. In the highest PBMA content (PS/PBMA = 1/1, w/w), PBMA domains comparatively dispersed homogeneously. On the other hand, in the lower PBMA contents (PS/PBMA = 3/1 and 2/1, w/w), most of fine PBMA domains dispersed near the particle surface.

The difference in the distribution states of PBMA domains in the composite particles seems to be based on the difference in the swelling states before the polymerization as shown in a schematic model in Fig. 3. In the highest PBMA content (PS/PBMA = 1/1, w/w), since the amount of BMA is enough to plasticize the whole of PS seed particles (homogeneous swelling) in the short time, the seeded polymerization proceeds homogeneously in the swollen particles and formed PBMA domains disperse homogeneously (upper scheme). Whereas, in the lowest PBMA content (PS/PBMA = 3/1, w/w) since the amount of BMA plasticizes only at surface layer of the seed particles (heterogeneous swelling) in short time, PBMA

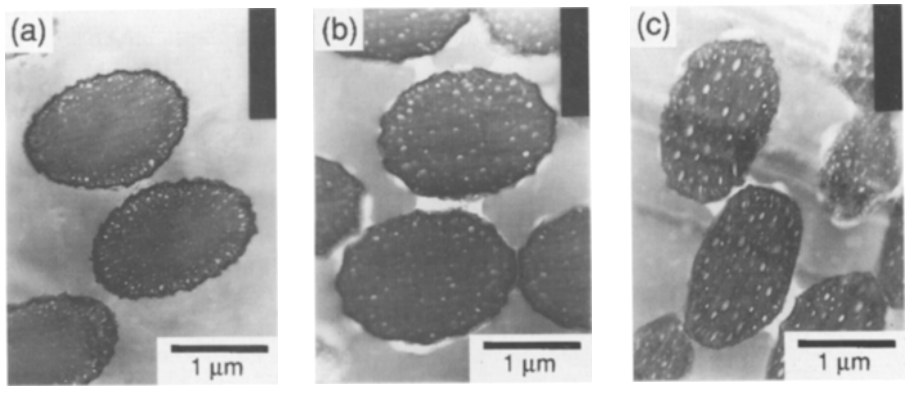

Fig. 2 TEM photographs of ultrathin cross sections of PS/PBMA composite particles produced by seeded polymerizations utilizing the dynamic swelling method under the conditions listed in Table 1, after exposure to RuO_4 vapor for 30 min: PS/PBMA (w/w): (a), 3/1; (b), 2/1; (c), 1/1

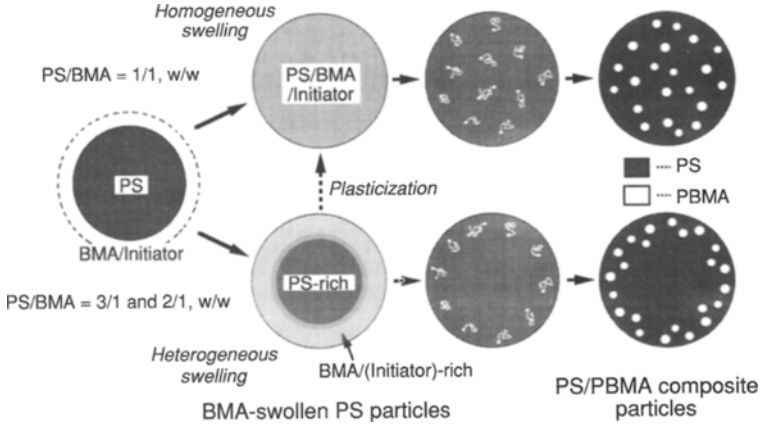

Fig. 3 A schematic model for the production of PS/PBMA composite particles by seeded polymerizations for the dispersions of BMA-swollen PS particles containing oil-soluble initiators utilizing dynamic swelling method

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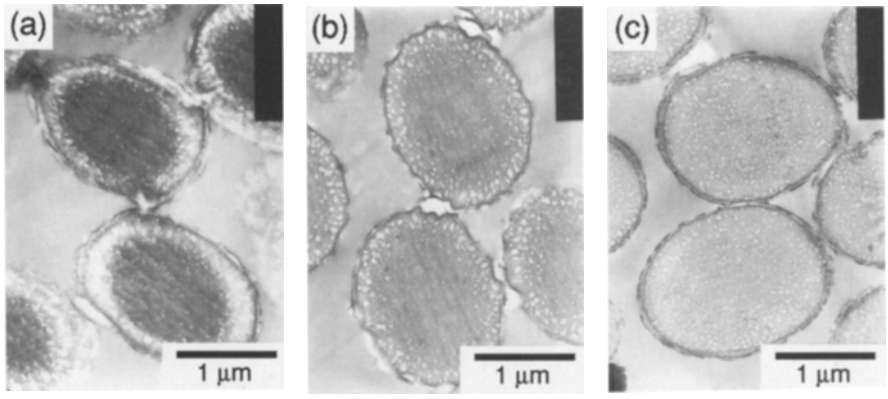

Fig. 4 TEM photographs of ultrathin cross sections of PS/PBMA (3/1, w/w) composite particles produced by seeded polymerizations with V-70 at 30 °C (a), with AIBN at 70 °C (b), and with V-40 at 90 °C (c) utilizing the dynamic swelling methods under the conditions listed in Table 2, after exposure to RuO_4 vapor for 30 min and the extraction of PBMA from untrathin cross sections with acetic acid

domains are formed near the particle surface predominantly (lower scheme). In order to examine this point, first, it was tried to keep the dispersion of BMA-swollen PS particles for 3 to 7 days at room temperature prior to each seeded polymerization. In the 3 days-aging system, the distribution states of PBMA domains in the produced composite particles were similar as shown in Fig. 2a (photograph was omitted). This indicates that at room temperature it needs a longer time to attain homogeneous swelling state because the inside of the particles is a glassy state. In the 7 days-aging system, coagulation among the swollen particles took place during the aging and the seeded polymerization was not completed. Subsequently, for the same purpose seeded polymerizations for the dispersions of BMA-swollen PS particles (PS/BMA =3/1, w/w) prepared under the conditions listed in Table 2 were carried out at 30 °C (V-70), 70 °C (AIBN) or 90 °C (V-40) for 24 h. In each system, the decomposition rates of the initiators are similar.

Figure 4 shows TEM photographs of ultrathin cross sections of PS/PBMA (3/1, w/w) composite particles exposed to RuO_4 vapor, from which PBMA is extracted with acetic acid on the grid. Many hollows formed by the removal of PBMA domains with acetic acid treatments were clearly observed in all photographs. At the highest polymerization temperature (90 °C), which was near the glass-transition temperature of PS, fine PBMA domains homogeneously dispersed in the composite particles. Whereas, at the lower temperatures (30 °C and 70 °C), most of PBMA domains dispersed near the particle surface and the tendency was more clear at 30 °C than 70 °C. These results indicate that at 90 °C the polymerization proceeds homogeneously in the swollen particles because of homogeneous swelling, whereas at 30 °C it does mainly at the surface layer because of heterogeneous swelling.

From these results, it is concluded that the formation of the peculiar POO structure in which many fine PBMA domains were dispersed near the surface of PS/PBMA composite particles which was observed in the previous article [13] is based on the heterogenous swelling state of BMA-swollen PS particles in the seeded polymerization process. In other words, the swelling state of micron-sized seed particles with the monomer in the seeded polymerization process is one of the important factors to control the morphology of the composite particles produced.

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