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ORIGINAL CONTRIBUTION

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Preparation of micron-sized monodispersed highly monomer-"adsorbed" polymer particles having snow-man shape by utilizing the dynamic swelling method with tightly cross-linked seed particles

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Abstract Micron-sized, monodispersed highly styrene-"adsorbed" particles having snow-man shape were prepared by the dynamic swelling method (DSM) with tightly cross-linked polymer seed particles as follows. First, 3.8 μm-sized monodispersed polystyrene (PS)/poly(divinylbenzene) (PDVB) (PS/PDVB = 1/10 wt. ratio) composite particles produced by seeded polymerization utilizing DSM were dispersed in an ethanol/water (6/4, w/w) solution dissolving styrene monomer, and poly(vinyl alcohol) as a stabilizer. Second, water was subsequently added to the dispersion with a micro-feeder at a rate of 2.88 ml/h at room temperature. The cross-linked seed particles adsorbed a large amount of styrene onto the surfaces and resulted in monodispersed highly styrene-"adsorbed" snow-man shape particles having about 10 μm in diameter.

Key words Dynamic swelling method – cross-linked polymer particles – monomer adsorption – micron-size – monodisperse – snow-man shape

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, for the production of monodispersed particles having the diameter above 5 μm, we suggested a novel swelling method to make polymer seed particles absorb a large amount of monomer prior to the seeded polymerization [10–14]. We named this the "dynamic swelling method (DSM)". In a previous article [15], 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.

Incidentally, it was observed by an optical microscope that PS seed particle rotated in the swollen particle with a large amount of ethyl methacrylate by DSM though it was limited in an early stage of DSM [13]. This suggests that in the early stage of DSM almost all monomers are not "absorbed", but "adsorbed" by the seed particles. Therefore, in a previous article [16], we discussed the thermodynamic background of DSM theoretically in the case of swollen particles in which seed polymer is not soluble in monomer.

In this article, on the basis of the idea obtained by the thermodynamic treatment [16], highly monomer-"adsorbed" polymer particles will be experimentally prepared by DSM with tightly cross-linked seed particles.

Experimental

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB) was washed with 1N NaOH and deionized water to remove polymerization inhibitor before use. The supplied DVB included ethyl vinylbenzene and diethylbenzene, and the purity was 55%. Deionized water was distilled with a pyrex distillator. Benzoyl peroxide (BPO) of reagent grade was purified by recrystallization. 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), toluene, 1,4-dioxane and ethanol were used as received.

PS seed particles

Monodispersed PS seed particles were produced by dispersion polymerization under the conditions listed in Table 1A and 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%.

Table 1 Productions of micron-sized monodispersed PS seed particles by dispersion polymerization[a)] and PS/PDVB composite seed particles by seeded polymerization[b)]

Ingredients [g]	A	B
PS particles[c)]	—	0.03
Styrene	40.0	
DVB	—	0.3
AIBN	0.67	
BPO	—	0.006
PAA	4.80	
PVA	—	0.015
Ethanol	274.0	7.0
Water	80.0	3.0 + 40[d)]

[a)] 70 °C; 24 h; N_2; in flask with stirring rate, 60 rpm.
[b)] 70 °C; 24 h; N_2; in sealed tube with shaking rate, 120 cycles/min (2-cm strokes).
[c)] D_n, 1.77 μm; C_v, 3.9%.
[d)] Water (40 g) was added using a micro-feeder at the rate of 2.88 ml/h.
Abbreviations: PS, polystyrene; DVB, divinylbenzene; AIBN, 2,2′-azobisisobutyronitrile; BPO, benzoyl peroxide; PAA, poly(acrylic acid); PVA, poly(vinyl alcohol).

Cross-linked PS/PDVB composite seed particles

Swelling of the PS particles with DVB was carried out using DSM under the conditions listed in Table 1B. Ethanol, water, DVB, BPO, and PVA were charged into a 100 ml glass cylindrical reactor (inside diameter: 35 mm). To this homogeneous solution, the PS particles produced by the dispersion polymerization under the conditions listed in Table 1A were dispersed. Finally, 40 g of water was added to the mixture with a micro feeder at a rate of 2.88 ml/h under stirring with a magnetic stirrer. Seeded polymerization for the dispersion was carried out in sealed glass tube which was horizontally shaken at 120 cycles/min (2 cm strokes) at 70 °C for 24 h. The particles were washed repeatedly by serum replacement with ethanol/water (6/4, w/w) mixture media to remove any traces of the by-product poly(divinylbenzene) (PDVB) particles and PVA. The solid content of redispersed particles was adjusted in the range of 10 g/l.

Extraction of PS from PS/PDVB composite particles

After removing a small amount of the by-product PDVB particles, the medium of the PS/PDVB composite dispersion was substituted from the ethanol/water to toluene via 1,4-dioxane by repeating centrifugation. The final toluene dispersion of the PS/PDVB composite particles was kept under reflux. The amount of PS extracted was measured by pyrolysis-gas chromatography according to the previous article [11]. The particles before and after the extraction were observed with TEM.

Monomer adsorption onto the cross-linked PS/PDVB composite seed particles utilizing DSM

Each swelling of cross-linked PS/PDVB composite seed particles with a large amount of styrene was carried out under the conditions listed in Table 2. Ethanol, water, styrene and SDS (or PVA) were charged into a 50 ml glass cylindrical reactor (inside diameter: 31 mm). To this homogeneous solution, 2 g of the PS/PDVB composite seed emulsion (solid content 10 g/l) was dispersed. Finally, water (5.8 g) was added to the mixture with a micro-feeder at a rate of 2.88 ml/h for 2 h at room temperature under stirring with a magnetic stirrer at 150 rpm.

Table 2 Preparations of styrene-adsorbed PS/PDVB composite particles utilizing the dynamic swelling method

Ingredients	
PS/PDVB particles[a)] (mg)	20
Styrene (mg)	400
SDS or PVA (mg)	0–75
Ethanol (g)	6.0
Water (g)	4.0 + 5.8[b)]

[a)] D_n, 3.81 μm; C_v, 2.6%.

[b)] Water (5.8 g) was added using a micro-feeder at the rate of 2.88 ml/h for 2 h at room temperature.

Abbreviations: PS, polystyrene; PDVB, poly(divinylbenzene); PVA, poly(vinyl alcohol); SDS, sodium dodecyl sulfate.

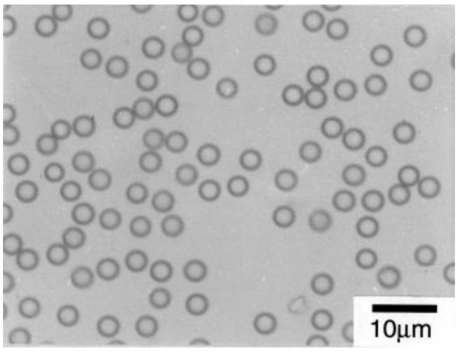

Fig. 1 An optical photograph of PS/PDVB (1/10, w/w) composite particles prepared by seeded polymerization under the conditions listed in Table 1B

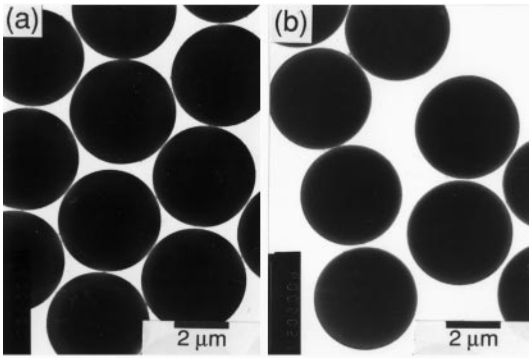

Fig. 2 TEM photographs of PS/PDVB (1/10, w/w) composite particles prepared by seeded polymerization under the conditions listed in Table 1B, before (a) and after (b) the extraction with toluene under reflux for 21 days

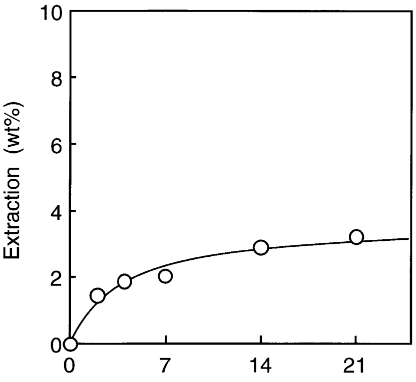

Fig. 3 A relationship between the extraction time with toluene under reflux and the percentage of extracted PS based on PS in PS/PDVB composite particles produced by seeded polymerization under the conditions listed in Table 1B

Optical microscopic observation of the seed particles and swollen particles

The dispersions of the seed particles and monomer-“adsorbed” particles were dropped onto slide glass, and observed with a Nikon MICROPHOTO FXA optical microscope. 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).

Results and discussion

Figure 1 shows an optical photograph of PS/PDVB (1/10, w/w) composite particles produced by seeded polymerization under the conditions listed in Table 1B. The produced spherical PS/PDVB composite particles had high monodispersity; D_n, 3.81 μm; D_w/D_n, 1.004; C_v, 2.6%.

Figure 2 shows TEM photographs of the PS/PDVB composite particles before (a) and after (b) the extraction with toluene under reflux for 21 days. The spherical shape and the size of the composite particles were not changed before and after the extraction treatment.

Figure 3 shows a relationship between the extraction time and the percentage of PS extracted from the PS/PDVB composite particles. Little PS was extracted from the composite particles even after the extraction for 21 days. This indicates that the PS/PDVB composite particles had tightly cross-linked structure.

Figure 4 shows optical micrographs of styrene-“adsorbed” PS/PDVB (1/10, w/w) cross-linked particles prepared under the conditions listed in Table 2 in the absence (a) and presences (b–e) of SDS (g/l-final solution): (b) 0.063; (c) 0.86; (d) 4.3; (e) 8.1. In Fig. 4a and b, all seed particles were adsorbed onto the polydispersed monomer droplets which seem to be formed from separated monomers by water addition regardless of the seed particles. On the other

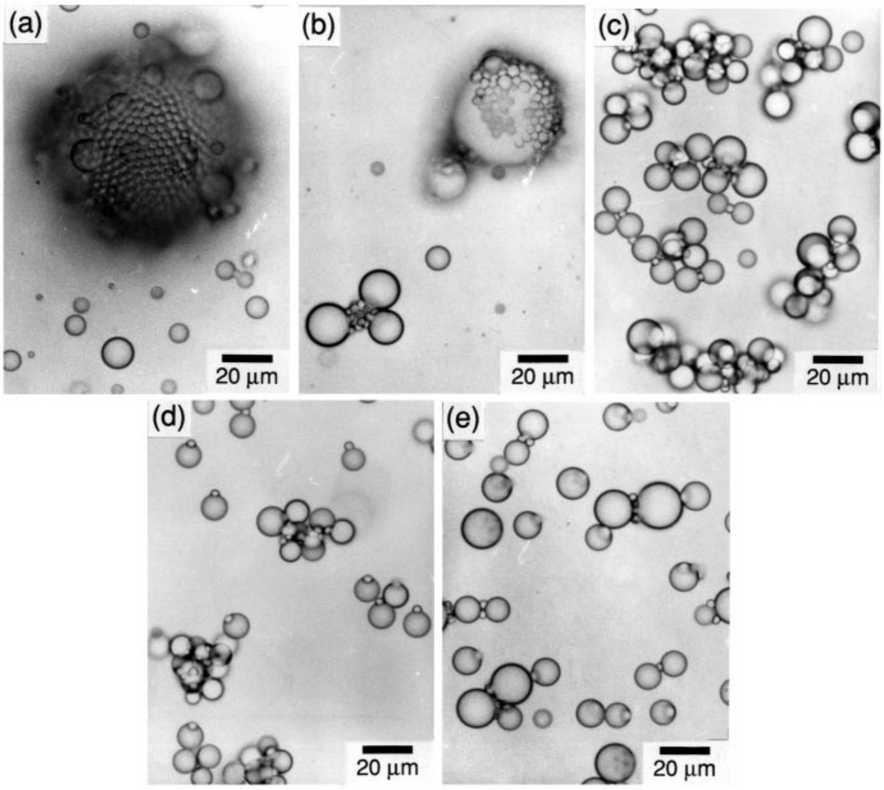

Fig. 4 Optical micrographs of styrene-"adsorbed" PS/PDVB cross-linked particles prepared by dynamic swelling method after the water addition for 2 h in the absence (a) and presence (b–e) of SDS (g/l-final solution): (b) 0.063; (c) 0.86; (d) 4.3; (e) 8.1

hand, in Fig. 4c–e, styrene-"adsorbed" particles were prepared by DSM. Colloidal stability of the particles increased with the amount of SDS, but it was not enough to depress the aggregation even in the case of the maximum concentration of SDS, which is sufficiently above the saturation concentration (1.6×10^{-2} g/l) of SDS needed to cover completely at the surface of styrene-"adsorbed" particles in the system. The value was calculated using the values of molecular occupied area of SDS (43×10^{-20} m^2), the number of seed particles, and the amount of styrene in the system. This indicates that it is difficult to prepare stable highly styrene-"adsorbed" particles using SDS as stabilizer.

Figure 5 shows optical micrographs of styrene-"adsorbed" PS/PDVB cross-linked particles prepared by DSM under the conditions listed in Table 2 in the presences of PVA (g/l-final solution): (a) 0.86; (b) 2.6; (c) 4.2. In Fig. 5a, a large number of about 10 μm-sized droplets and some 20–40 μm-sized droplets adsorbing a large number of the particles, and very few styrene-"adsorbed" particles were observed. This is based on that styrene droplets formed by water addition are unstable because of the lack of PVA. The colloidal stability of styrene-"adsorbed" particles increased with an increase in PVA concentration and stable highly styrene-"adsorbed" particles were prepared at 4.2 g/l of PVA as shown in Fig. 5c. In the styrene-"adsorbed" particles, half part of the cross-linked particle was imbedded in spherical styrene phase (body) and the remainder protruded as peak (head) on the particle surface. That is, they had "snow-man" shape, though the shape was sometimes apparently observed to be spherical as the "head" was located just under the "body" in optical microscopic observation.

Figure 6 shows optical micrographs of the styrene-"adsorbed" polymer particles prepared in the presence of PVA (4.2 g/l) as a function of the amounts of water subsequently added at the rate of 2.88 ml/h. In Fig. 6b, each seed particle adsorbed styrene monomers which were separated from the medium by the water addition and appeared like a small head of the snow-man. As shown in Fig. 6b–d, the volume of the head increased with the water addition and in Fig. 6e–h head and body of each snow-man particle were exchanged, that is, the "head" consists of the seed particle and the "body" consists of styrene monomer. Throughout the water addition, the monodispersity was maintained. The variations of the volume fraction of styrene monomer to seed particle (V_m/V_p) calculated from D_n values and of the C_v value with the

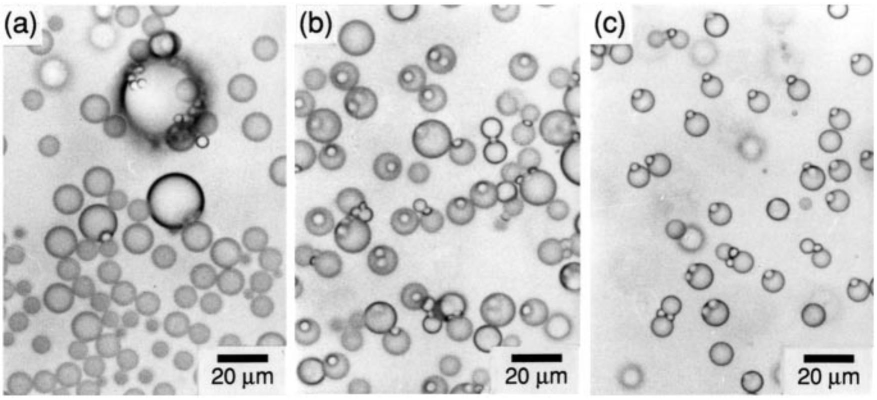

Fig. 5 Optical micrographs of styrene-“adsorbed” PS/PDVB cross-linked particles prepared by dynamic swelling method after the water addition for 2 h in the presence of PVA (g/l-final solution): (a) 0.86; (b) 2.6; (c) 4.2

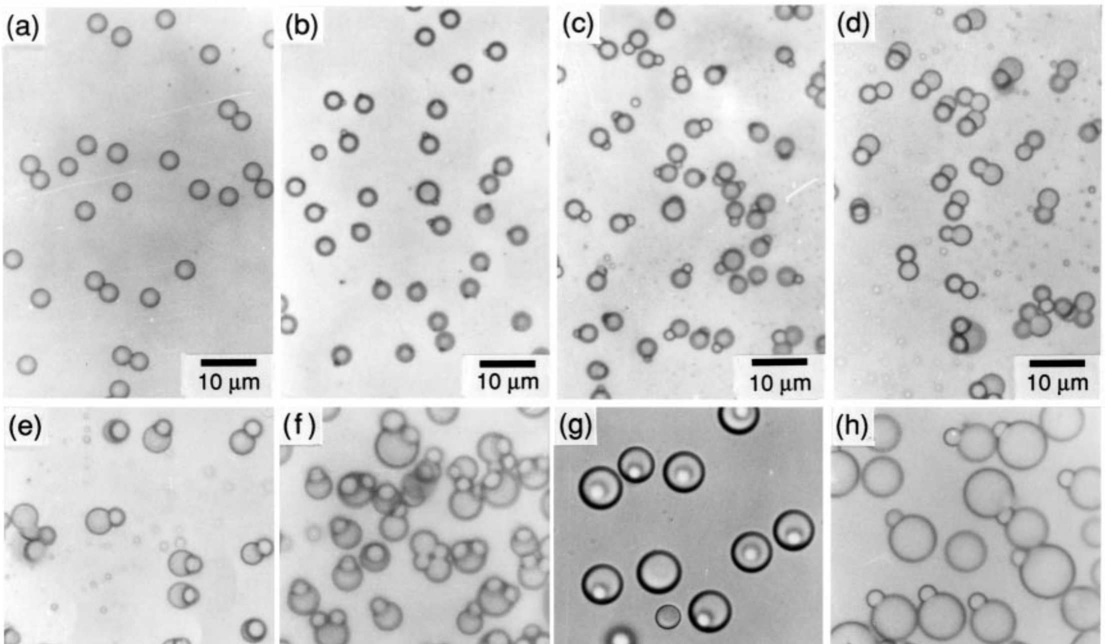

Fig. 6 Optical micrographs of styrene-“adsorbed” PS/PDVB cross-linked particles prepared in the presence of PVA (4.2 g/l) as a function of the amounts of water post-added at the rate of 2.88 ml/h: amount of water post-added (ml) : (a) 0; (b) 1.7; (c) 1.9; (d) 2.2; (e) 2.4; (f) 2.9; (g) 4.3; (h) 5.88

water-addition time is shown in Fig. 7. The experimental V_m/V_p value (○) increased markedly to about 2–5 ml of the amount of water added. The behavior agreed with that (dotted line) of the V_m/V_p values calculated from a solubility curve of styrene monomer in ethanol/water mixtures assuming that all styrene monomers separated from the medium are adsorbed [10]. This indicates that the adsorption of styrene monomers onto the surfaces of the PS seed particles is mainly based on the separation of styrene monomers from the medium by the water addition.

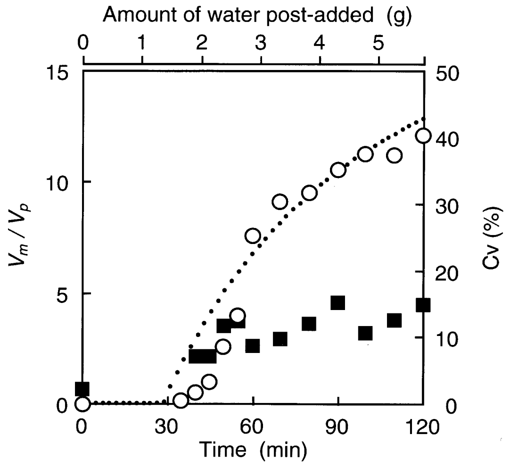

Fig. 7 Variations of the volume fraction of spherical styrene monomer phase to seed polymer (V_m/V_p) (○) and of the C_v value (■) of the monomer-"adsorbed" particles with water addition at a rate of 2.88 ml/h. Dotted line indicates V_m/V_p calculated using the solubility curve of styrene monomer in ethanol/water mixture assuming that all styrene monomers separated from the medium are adsorbed by PS seed particles

From the above-experimental results, it was concluded that the DSM can make a large amount of monomer "adsorb" onto the surfaces of the seed particles which do not dissolve in the "adsorbed" monomer.

In the previous article [16], thermodynamic background of DSM for the preparation of "spherical" monomer-"adsorbed" polymer particles in which seed particle was completely included by monomer shell was discussed under both equilibrium and kinetic control states. Thermodynamic background of DSM for the preparation of the "snow-man" shape styrene-"adsorbed" polymer particles and the seeded polymerization will be examined in a future article.

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