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ORIGINAL CONTRIBUTION

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Adsorption of styrene on micron-sized, monodisperse, cross-linked polymer particles in a snowman-shaped state by utilizing the dynamic swelling method

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Abstract Polystyrene/styrene–divinylbenzene copolymer composite particles with different cross-linking densities were produced by seeded copolymerization for (styrene/divinylbenzene)-swollen polystyrene particles prepared by utilizing the dynamic swelling method (DSM) which was proposed by the authors in 1991. Using the cross-linked, composite particles as seeds, styrene-adsorbed (swollen) composite particles having snowman shapes were prepared by the DSM. With a decrease in the cross-linking density in the composite particles, the volume of the composite particle which was embedded in a spherical styrene phase in the snowman-shaped, styrene-adsorbed particle increased and the contact angle of the styrene phase on the composite particle decreased. In the DSM process, the absorption stage of styrene in the composite particles and the adsorption stage thereon were clearly observed. This suggests that the cross-linking density of the composite particles greatly affects the morphology of the snowman-shaped particles.

Key words Dynamic swelling method · Snowman shape · Particle · Morphology · Contact angle

Introduction

Recently, micron-sized, monodisperse polymer particles have been applied in the biomedical field, microelectronics, etc. Many researchers studying polymer colloids are concentrating their attention on the production of such particles by dispersion polymerization [1–5] and seeded dispersion polymerization [5–8]. For the production of monodisperse particles having large diameter, Ugelstad and coworkers [9–11] suggested a two-step swelling process with a swelling agent followed by a seeded polymerization.

On the other hand, we suggested a novel swelling method to make seed polymer particles absorb a large amount of monomer without any swelling agent in only one step [12–16], which was named the dynamic swelling method (DSM). In previous articles, the thermodynamic background of the DSM in the cases that the polymer particle dissolves in monomer [17] and it does not dissolve but swells [18] was discussed theoretically. In the latter case, snowman-shaped, styrene (S)-adsorbed polymer particles, in which a part of the cross-linked polystyrene (PS)/poly(divinylbenzene) (PDVB) composite particle was embedded into a spherical S phase and the remains protruded as a peak on its surface, were formed [19]. The morphology of such snowman-shaped particles would be affected thermodynamically by the total free energy related to each interfacial tension in the DSM system. In a previous article [20], the effects of the kind of monomers and poly(vinyl alcohol) (PVA) colloidal stabilizer dissolving in the medium on the morphology of such monomer-adsorbed particles were reported, where PS/PDVB (1/10, w/w) composite particles with high cross-linking density were used as seed particles.

In this article, the effect of cross-linking density in the composite particles on the morphology of S-adsorbed (swollen) polymer particles having a snowman shape prepared by the DSM is clarified from the viewpoint of control of the particle shape.

Experimental

Materials

S was purified by distillation under reduced pressure in a nitrogen atmosphere. DVB with a purity of 96% containing ethyl vinylbenzene and diethylbenzene was washed with 1 N NaOH and deionized water to remove polymerization inhibitor before use. Deionized water was distilled with a pyrex distillation apparatus. Benzoyl peroxide and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Japan) of reagent grade were purified by recrystallization. PVA was supplied by Nippon Synthetic Chemical (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Reagent grade ethanol was used as received.

Preparation of monodisperse, cross-linked PS/P(S–DVB) composite particles having different cross-linking densities

PS particles were swollen with S and DVB at different S/DVB ratios by utilizing the DSM under the conditions listed in Table 1 as follows. Ethanol, S, DVB, V-70, water and PVA were charged into a 400-ml glass cylindrical reactor and were shaken to form a homogeneous state. Monodisperse PS particles, which were produced by dispersion polymerization under the conditions described in a previous article [18] and which had a number-average diameter (D_n) of 2.08 μm and a coefficient of variation (C_v) of 6.0%, were dispersed into it. Water (64 g) was added to the dispersion with a microfeeder at a rate of 7.92 ml/h for 4 h (31.7 g) and then the residual water (32.3 g) dissolving $CuCl_2$ inhibitor (0.188 g) was added under stirring with a magnetic stirrer at 20 °C. Seeded polymerization for the dispersion was carried out in sealed glass tubes which were shaken horizontally at 80 cycles/min (2-cm strokes) for 24 h at 30 °C. The PS/P(S–DVB) composite particles produced were washed repeatedly by serum replacement with ethanol/water (1/4, w/w) to remove any traces of by-product P(S–DVB) particles and free PVA, and were then redispersed with ethanol/water (3/2, w/w) at a solid content of about 2 wt%.

Adsorption (absorption) of S by the cross-linked PS/P(S–DVB) composite particles

Adsorption (absorption) of S by cross-linked PS/P(S-D-VB) composite particles with different cross-linking densities was carried out with the DSM under the conditions listed in Table 2 as follows. Ethanol, S, water and PVA were charged into a 50-ml glass cylindrical reactor (inner diameter: 31 mm) and shaken. Then, about 1.0 g PS/P(S–DVB) composite emulsion (solid content: about 2 wt%) was mixed with the homogeneous solution using an ultrasonic wave for 20 min. Finally, water (5.3 g) was added to the mixture with a microfeeder at a rate of 0.887 ml/h for 6 h at room temperature under stirring with a magnetic stirrer at 130 rpm.

Optical microscope observation and image analysis

The dispersions of the PS/P(S–DVB) composite particles and their S-adsorbed (absorbed) particles were dropped onto a slide glass and observed with a Nikon MICROPHOTO FXA optical microscope. The number-average diameter of the composite particles saturated with monomer (D_p), the number-average diameter of the S phase (D_m) and the number-average diameter of the cross-sectional circle (l) between the composite particle and the S phase in the S-adsorbed polymer particles were determined on the basis of the data obtained by measuring 50–100 particles using image analysis software.

The schematic model of the monomer-adsorbed polymer particle having a snowman shape is illustrated in Fig. 1, which indicates geometric relationships among, D_p^s D_m, l, θ_p, θ_m and the contact angle (Θ_s) of the monomer phase on the composite particle in the snowman-shaped particle. θ_p and θ_m can be calculated according to Eqs. (1) and (2), and thereby Θ_s can be calculated according to Eq. (3).

Table 2 Preparation of S-adsorbed PS/P(S–DVB) composite particles in a snowman-shaped state utilizing the DSM

Ingredients	
PS/P(S-DVB) composites particles (mg)[a]	20
S (mg)	400
Poly(vinyl alcohol) (mg)	73
Ethanol (g)	6.0
Water (g)	4.0 + 5.3[b]

[a] Composite particles with different cross-linking densities prepared by seeded copolymerization with the DSM under the conditions listed in Table 1

[b] Water (5.3 g) was added using a microfeeder at a rate of 0.887 ml/h for 6 h at room temperature

Table 1 Preparation of polystyrene (*PS*)/poly(styrene–divinylbenzene) [*P*(*S-DVB*)] composite particles by seeded copolymerization utilizing the dynamic swelling method (*DSM*). 30 °C, 24 h, N_2, in a sealed tube with a shaking rate of 80 cycles/min (2-cm strokes)

Ingredients	S/DVB (w/w)						
	0/100	80/20	97/3	98/2	99/1	99.5/0.5	99.7/0.3
S (mg)	0	960	1,164	1,176	1,188	1,194	1,196.4
DVB (mg)[a]	1,200	240	36	24	12	6	3.6
PS particles (mg)[b]				120			
2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (mg)				30			
Poly(vinyl alcohol)				45			
$CuCl_2$ (mg)				118			
Ethanol (g)				18			
Water (g)				12 + 64[c]			

[a] Purity, 96%

[b] D_n, 2.08 μm, C_v, 6.0%

[c] Water (64 g) was added using a microfeeder at a rate of 7.92 ml/h for 4 h (31.7 g), then the residual water (32.3 g) dissolving $CuCl_2$ was added at 20 °C

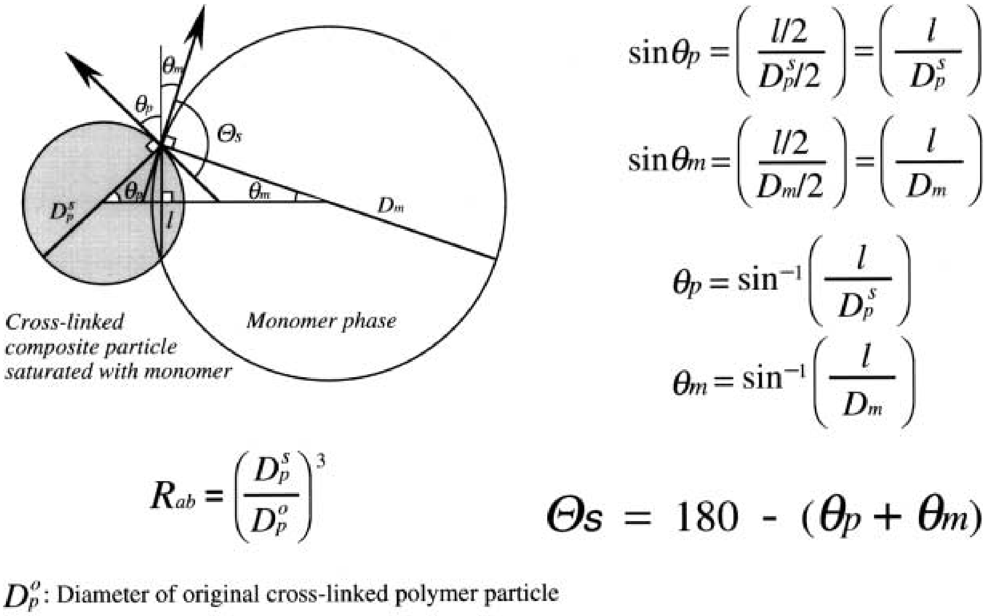

Fig. 1 Schematic model of a monomer-adsorbed polymer particle having a snowman shape indicating the geometrical relationships among D_p^s, D_m, l, θ_p, θ_m and Θ_s

$$\theta_p = \sin^{-1}(l/D_p^s) \ , \quad (1)$$

$$\theta_m = \sin^{-1}(l/D_m) \ , \quad (2)$$

$$\Theta_s = 180 - (\theta_p + \theta_m) \ . \quad (3)$$

Measurement of the contact angle

P(S–DVB) blocks, which had different cross-linking densities and a smooth surface, were prepared by bulk copolymerizations of S and DVB in different ratios at 30 °C in a 50-ml glass cylindrical reactor without stirring under the conditions listed in Table 3. The contact angles (Θ) of the S droplets on these blocks were measured in a medium of 0.05 g/l PVA aqueous solution at room temperature. The blocks were dipped in S for a sufficient time to absorb S at a maximum swelling state prior to the measurement.

Results and discussion

PS/P(S–DVB) composite particles with different cross-linking densities were produced by seeded polymerization for (S–DVB)-swollen PS particles at different S/DVB ratios prepared by the DSM under the conditions listed in Table 1. They had monodispersity and a number-average diameter of about 4 μm. A scanning electron microscope photograph of the PS/P(S–DVB) [1/(9.7–0.3), w/w] composite particles as one example is shown in Fig. 2. Using these PS/P(S–DVB) composite particles, the dynamic swelling with S was carried out at

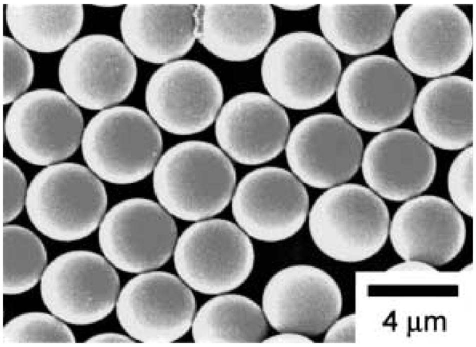

Fig. 2 A scanning electron microscope photograph of cross-linked polystyrene (*PS*)/poly(styrene–divinylbenzene) [*P(S–DVB)*] [1/(9.7–0.3), w/w] composite particles produced by seeded polymerization at 30 °C for (S-DVB)-swollen PS particles prepared by the dynamic swelling method (*DSM*) at 20 °C

Table 3 Preparation of P(S–DVB) blocks by bulk copolymerization (30 °C, 24 h, N_2)

Ingredients	S/DVB (w/w)						
	0/100	80/20	97/3	98/2	99/1	99.5/0.5	99.7/0.3
S (g)	0	1.600	1.940	1.960	1.980	1.990	1.994
DVB (g)	2.000	0.400	0.060	0.040	0.020	0.010	0.006
2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (g)	0.04	0.04	0.04	0.04	0.04	0.04	0.04

room temperature by adding water into the DSM system at a rate of 0.887 ml/h under the conditions listed in Table 2.

Optical micrographs of a series of S-adsorbed PS/P(S–DVB) composite particles having snowman shapes are shown in Fig. 3. With a decrease in the cross-linking density of the PS/P(S–DVB) composite particles owing to a decrease in the DVB content in P(S–DVB), the volume of the composite particle engulfed by the spherical S phase increased. Only a small part of the composite particle having the highest cross-linking density was embedded in the S phase (Fig. 3a). On the other hand, at the S/DVB weight ratio of 99.7/0.3 in P(S–DVB) only a small part of the composite particle having the lowest cross-linking density protruded at the surface of the S phase (Fig. 3f).

The variations of θ_p and Θ_s of the S-adsorbed PS/P(S–DVB) composite particles are shown in Fig. 4 as a function of the DVB content in P(S–DVB). θ_p and Θ_s were constant at DVB contents above 3 wt%, but θ_p increased and Θ_s decreased markedly with the decrease in the DVB content below 3 wt%. This also indicates that the volume of the composite particle embedded in the S phase increased with the decrease in the cross-linking density of the composite particles.

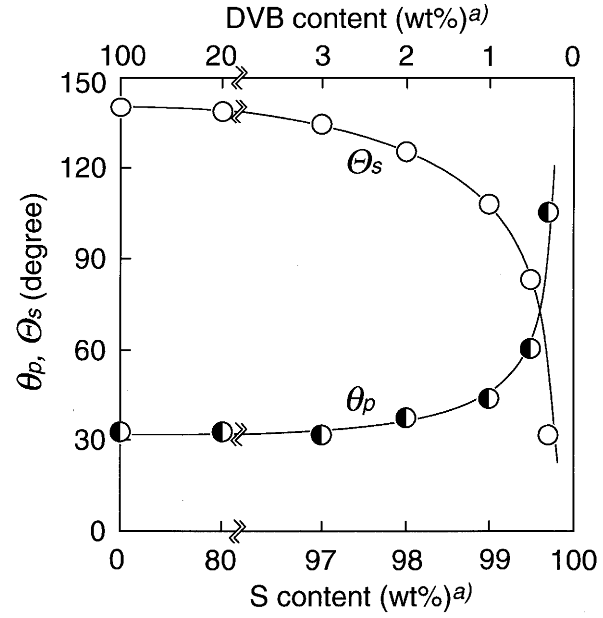

Fig. 4 Angles, θ_p (◐), and contact angles Θ_s (○) of S-adsorbed PS/P(S–DVB) (1/10, w/w) composite particles having different cross-linking densities prepared by the DSM
a) S or DVB content in the P(S-DVB)

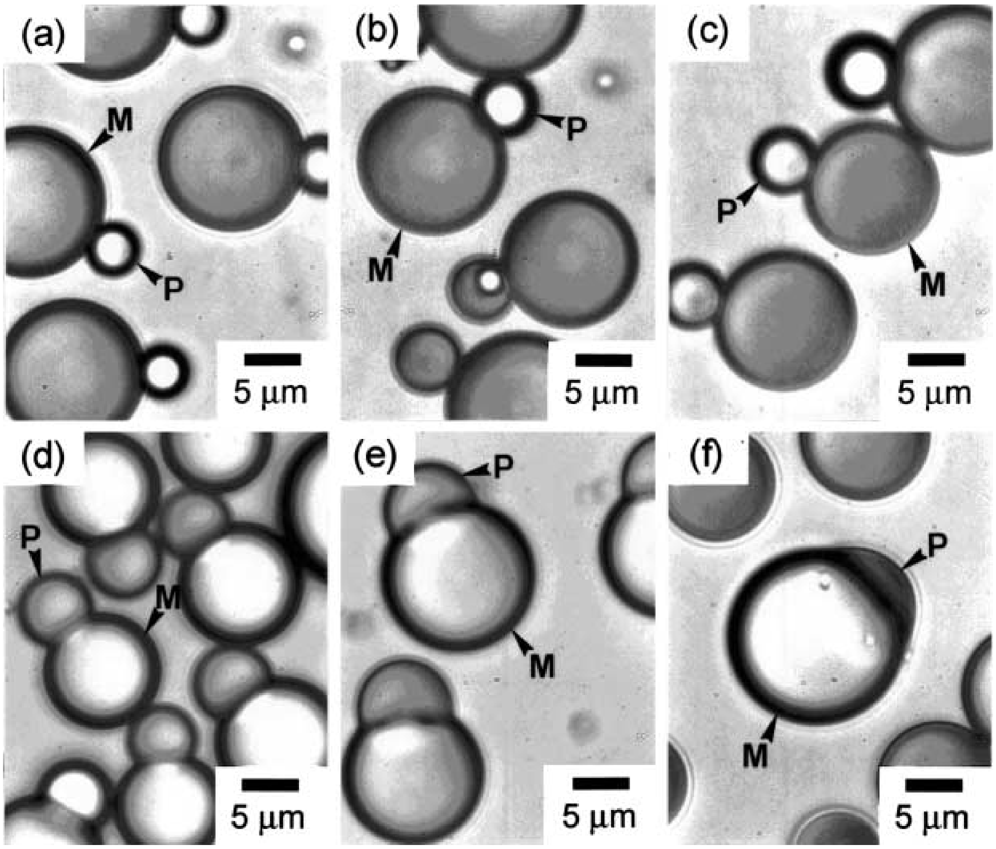

Fig. 3a–f Optical micrographs of S-adsorbed PS/P(S–DVB) (1/10, w/w) composite particles having different cross-linking densities prepared by the DSM: S/DVB (w/w) in P(S–DVB): **a** 0/100; **b** 97.0/3.0; **c** 98.0/2.0; **d** 99.0/1.0; **e** 99.5/0.5 and **f** 99.7/0.3. *P* and *M* indicate particle and monomer phases respectively

On the other hand, it was found that the composite particles in the snowman-shaped, monomer-adsorbed particles became larger in comparison with the corresponding original particles because of the absorption of S, and the diameter of the saturated particles with S increased with the decrease in the DVB content in P(S–DVB) (Fig. 3). The maximum absorption ratios [$R_{ab} = (D_p^s/D_p^0)^3$] of the PS/P(S–DVB) composite particles with S in the snowman-shaped particles are listed in Table 4. The R_{ab} depended on the cross-linking density of the composite particles.

Table 4 The maximum absorption ratios of PS/P(S–DVB) composite particles with different cross-linking densities in S-adsorbed composite particles having snowman shapes

S/DVB (w/w)[a]	D_p^0 (μm)[b]	D_p^s (μm)[b]	R_{ab} (v/v)[c]
0/100	4.10	4.56	1.38
80/20	4.07	4.70	1.54
97/3	3.91	5.61	2.95
98/2	4.09	6.05	3.24
99/1	3.81	6.88	5.89
99.5/0.5	4.00	7.95	7.85
99.7/0.3	3.99	8.81	10.77

[a] Initial weight ratio of S and DVB in ethanol/water (3/2, w/w) medium in the DSM for the preparation of the PS/P(S–DVB)(1/10, w/w) composite particles

[b] D_p^0 and D_p^s are diameters of each original composite particle and that at the end of the DSM, respectively

[c] Volume ratio of the composite particles with S at the end of the DSM to that of the original particles

Figure 5 shows optical micrographs of particles in the dynamic swelling process of composite particles with S, in which the PS/P(S–DVB) [1/(9.7–0.3), w/w] composite particles with smaller R_{ab} and larger Θ_s were used for easily and clearly observing the growth process of the adsorbed S phase at its small amount. The composite particles became large gradually but no snowman-shaped particles were observed until the water was added into the medium for 100 min. Then the S-swollen PS/P(S–DVB) particles began to adsorb S, resulting in snowman-shaped particles. The adsorbed S phase grew up with the continuous addition of water. The changes in D_p and D_m, which are shown in Fig. 1, were estimated from the image analysis on the optical micrographs obtained during the process.

The result is shown in Fig. 6. In the initial mixing period with an ultrasonic wave before the addition of water, the composite particles became large because

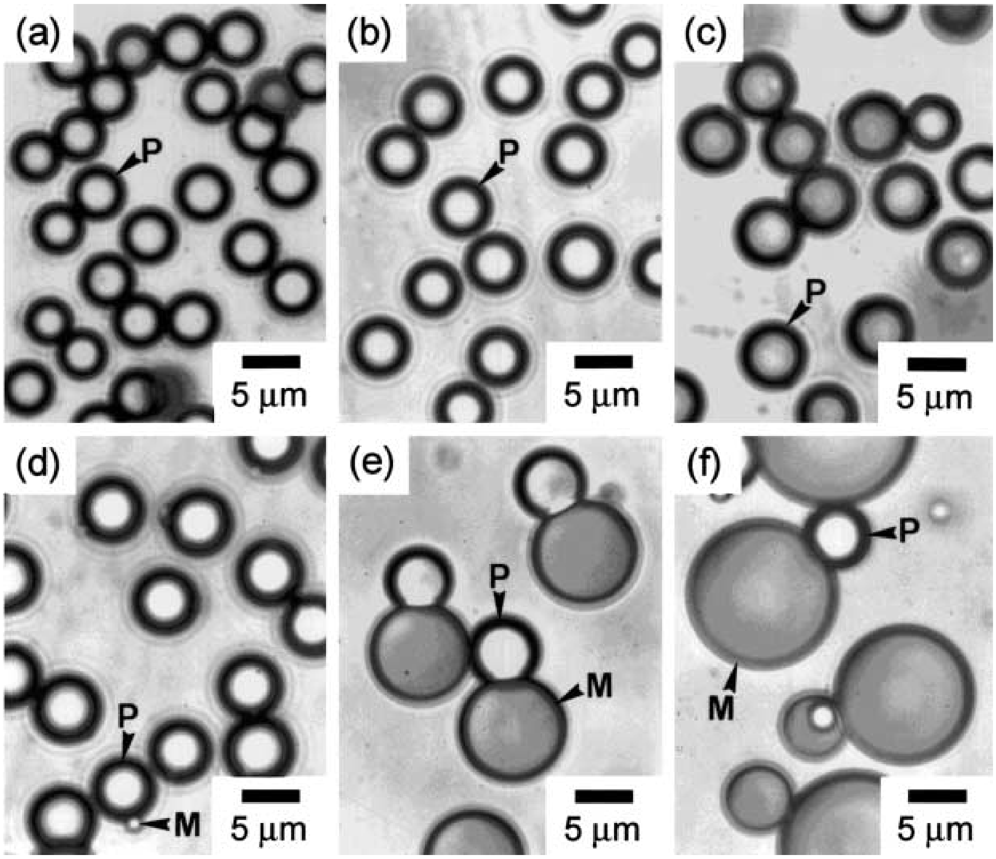

Fig. 5a–f Optical micrographs of PS/P(S–DVB) [1/(9.7–0.3), w/w] composite particles in the DSM process of S at a rate of water addition of 0.887 ml/h under the conditions shown in Table 2. Dropwise addition time (min): **a** 0; **b** 60; **c** 80; **d** 100; **e** 180; **f** 360. *P* and *M* indicate particle and monomer phases respectively

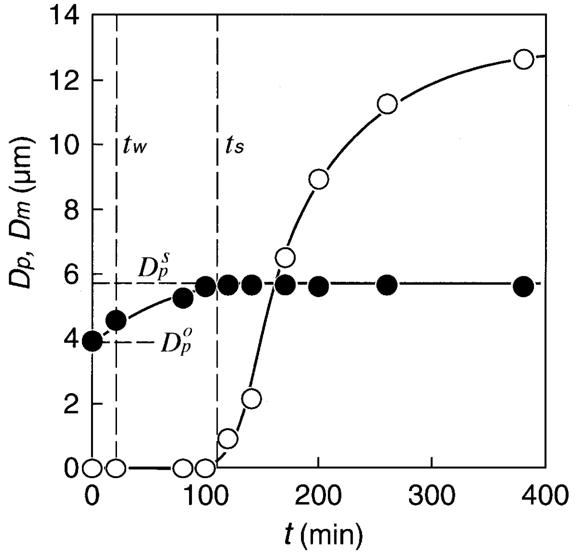

Fig. 6 Changes in D_p (●) of PS/P(S–DVB) [1/(9.7–0.3), w/w] composite particle and D_m (○) of the S phase in S-adsorbed (absorbed) PS/P(S–DVB) composite particles having a snowman shape during the DSM process. t_w is start time of adding water by a microfeeder at a rate of 0.887 ml/h and the t_s is time at which the S phase appeared on the composite particle

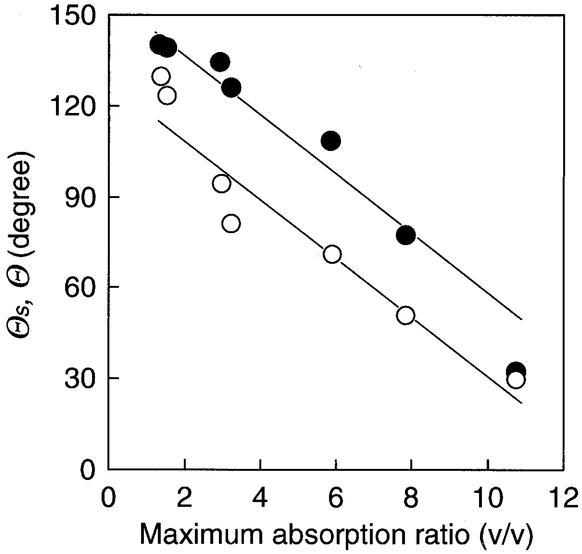

Fig. 7 Relationships between the maximum absorption ratio of the composite particles with S and Θ_s (●) of the S phase on PS/P(S–DVB) composite particles saturated with S and Θ (○) of the S droplet on P(S–DVB) blocks saturated with S

they absorbed a certain amount of S dissolved in the medium. After t_w, they continued to absorb S separated from the medium and D_p increased further. The saturated particles with S started to adsorb S at t_s, resulting in snowman-shaped particles. D_m increased with the continuous addition of water, whereas D_p remained constant after t_s. The results were obtained by the image analysis of the composite particles in the snowman-shaped, monomer-adsorbed particles after the S of 70% had been separated from the medium, while water was added into the medium for 6 h. Assuming that all S separated from the medium is absorbed and adsorbed by the composite particles, the time for the S-adsorbed particles having snowman shape to appear was calculated to be 140 min on the basis of the solubility curve of S in the water/ethanol mixture. The time was almost in agreement with the t_s of 120 min shown in Fig. 6. This suggests that the PS/P(S–DVB) composite particles reached their saturated absorption state at t_s. In this way, the DSM process can be clearly divided into the absorption and adsorption stages at t_s.

Because the amount of S in each PS/P(S–DVB) particle at the saturated absorption state depends on the cross-linking density, the interfacial tension between the composite particle saturated with S and the S phase thereon should depend on it. The relationship between the maximum absorption ratio (R_{ab}) and the contact angles (Θ_s) of the S phase on the composite particles is shown in Fig. 7. Θ_s decreased with the increase in the amount of S in the composite particle and there was a liner relationship between Θ_s and R_{ab}. The contact angle (Θ) of the S droplet on P(S–DVB) blocks with different cross-linking densities, which were prepared directly by bulk copolymerization of S and DVB, saturated with S was measured according to the procedure described in a previous article [21]. The result is also shown in Fig. 7. There was also a linear relationship between Θ and R_{ab}, and the slope was similar to that of the straight line of Θ_s versus R_{ab}, though a gap existed between them, which may be due to the different amounts of PVA added into the two systems. This suggests that S absorbed in the cross-linked composite particles played a role in decreasing the interfacial tension between the composite particle and the S phase and, thereby, led to a change in the morphology of the snowman-shaped, S-adsorbed PS/P(S–DVB) particles.

From the results presented here, it is clarified that snowman-shaped morphology of S-adsorbed PS/P(S–DVB) composite particles prepared by the DSM can be controlled by changing the cross-linking density of the composite particles. A detail discussion about the thermodynamics of the DSM process and the seeded polymerization to produce the snowman-shaped composite particles will be presented elsewhere.

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