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ORIGINAL CONTRIBUTION

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Preparation of micron-sized, monodispersed, monomer-adsorbed polymer particles utilizing the dynamic swelling method with loosely cross-linked seed particles

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Abstract Influence of the water-addition rate (R_w) (ml/h) on the monodispersity of monomer-adsorbed polymer particles prepared by utilizing the dynamic swelling method (DSM) with 1.9-μm-sized, monodispersed, loosely cross-linked polystyrene/styrene-divinylbenzene copolymer [1/(47.5–2.5), w/w] composite particles was examined theoretically and experimentally. The thermodynamic simulation under a kinetic control state indicates that, at the R_w values below 4, the cross-linked composite particles adsorb all styrenes separated from ethanol/water media. The experimental result at the R_w value of 2.66 supported it. At the R_w values above 5.32 and below 1.33, polydispersed styrene-adsorbed particles were prepared. The former depended on the formation of some pure styrene droplets not containing the composite particle. The latter depended on coalescence among the adsorbed particles by DSM.

Key words Dynamic swelling method · Micron-size · Particle · Monodisperse · Adsorption

Introduction

For the production of monodispersed particles more than 5 μm in diameter, we have proposed a novel swelling method to make polymer seed particles absorb a large amount of monomer prior to the seeded polymerization, that was named the "dynamic swelling method (DSM)" [1–4]. The high swelling was carried out by slow, continuous, dropwise water addition with a microfeeder into an ethanol/water medium dissolving styrene, benzoyl peroxide (BPO) initiator, and poly(vinyl alcohol) (PVA) stabilizer, in which about 2-μm-sized, monodispersed, polystyrene (PS) seed particles were dispersed. The PS seed particles absorbed about 100 times weight of styrene and BPO which were gradually separated from the medium by dropwise water-addition, resulting in 8.5-μm-sized, monodispersed, styrene-swollen PS particles [1]. A similar high swelling was obtained by continuously cooling the dispersion, in which monomers were gradually separated from the medium on the basis of the decrease in solubility of the monomer [2].

In previous articles [5–7], the thermodynamic background of high swelling of polymer particles with monomer by DSM in both equilibrium and kinetic control states were discussed, and it was clarified that the high swelling by DSM is based on the size difference between micron-sized polymer seed particles and submicron-sized monomer droplets, and on highly saturated monomer concentration in an ethanol/water medium.

In the previous article [1], monodispersed styrene-swollen PS particles were not obtained by DSM at a high water-addition rate. It seems that since the separation rate of styrenes from the medium must be faster than the absorption rate by PS seed particles, some pure monomer droplets having no PS seed particle are formed and coalesced each other. However, it was not judged whether PS seed particles dissolved or not in styrene droplets.

In this study, in order to clarify – theoretically and experimentally – the influence of the water-addition rate in DSM on the preparation of monodispersity of highly monomer-swollen polymer particles, loosely cross-linked, PS/styrene-divinylbenzene copolymer

[P(S-DVB)] composite seed particles, which swell but not dissolve in styrene, will be used.

Experimental

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. Divinylbenzene (DVB, supplied by Nippon Steel Chemical, Co. Ltd., Tokyo, Japan) was washed with 1 N NaOH and deionized water to remove polymerization inhibitor before use. The purity of the DVB, which included a small amount of ethylvinylbenzene and diethylbenzene, was 96%. Deionized water was distilled with a Pyrex distillator. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Osaka, Japan) of reagent grade were purified by recrystallization. PVA as a colloidal stabilizer was supplied by Nippon Synthetic Chemical, Osaka, Japan (Gohsenol GH-17; degree of polymerization, 1700: degree of saponification, 88%). Reagent grade cupric chloride ($CuCl_2 \cdot 2H_2O$) and ethanol were used as received.

Production of PS seed particles

Submicron-sized, monodispersed PS seed particles were produced by emulsifier-free emulsion polymerization according to the previous article [6] 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 0.64 μm and 2.3%, respectively.

Production of loosely cross-linked PS/P(S-DVB) composite particles

Swelling of the PS particles with styrene and DVB was carried out utilizing DSM under the conditions listed in Table 1 (column A) as follows. PS seed particles were dispersed to the homogeneous ethanol/water (6/4, w/w) solution (10 g) dissolving styrene, DVB, V-70, and PVA. Then water (21.2 g), in which $CuCl_2$ as a water-soluble inhibitor was dissolved, was added to the dispersion with a microfeeder at a rate of 10.6 ml/h under stirring with a magnetic stirrer for 2 h at 20 °C. Seeded copolymerization for the dispersion was carried out in a sealed glass tube, which was horizontally shaken at 120 cycles/min (2-cm strokes) at 30 °C for 24 h. The particles were washed repeatedly by serum replacement with an ethanol/water (6/4, w/w) medium to remove any traces of by-produced P(S-DVB) particles and PVA. The prepared PS/P(S-DVB) composite particles were observed with TEM.

Table 1 Recipes for the preparations of micron-sized, monodispersed PS/PDVB composite particles be seeded copolymerization[a] (A) and styrene-adsorbed PS/P(S-DVB) composite particles utilizing the dynamic swelling method at various water-addition rates (B)

Ingredients	Units of weight	A	B
PS particles[b]	(mg)	8	–
PS/P(S-DVB) particles[c]	(mg)	–	4
Styrene	(mg)	380	400
DVB[d]	(mg)	20	–
V-70	(mg)	20	–
PVA	(mg)	15	15
Ethanol	(g)	6.0	6.0
Water	(g)	4.0 + 21.2[e]	4.0 + 40[f]
$CuCl_2$	(mg)	49	–

[a] In sealed tube: 70 °C; 24 h: N_2; shaking rate, 120 cycles/min (2-cm strokes)

[b] D_n, 0.64 μm; C_v, 2.3%

[c] D_n, 1.90 μm; C_v, 3.8%

[d] Purity, 96% (by catalog)

[e] Water (21.2 g) was post-added using a microfeeder at a rate of 10.6 ml/h for 2 h at 20 °C

[f] Water (40 g) was post-added using a microfeeder at various rates

Abbreviations: PS, polystyrene; PDVB, polydivinylbenzene; P(S-DVB), styrene-divinylbenzene copolymer; DVB, divinylbenzene; V-70, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile); PVA, poly (vinyl alcohol)

Saturation swelling of the PS/P(S-DVB) composite particles with styrene

Saturation swelling of the PS/P(S-DVB) composite particles with styrene was carried out with stirring at room temperature for 24 h in the dispersion system: the composite particles, 0.49 g; styrene, 3.0 g; SDS, 4.9 mg; water, 4.9 g. The saturation-swelling ratio $[(V_m/V_P)_s]$ was calculated using the equation

$$\left(\frac{V_m}{V_P}\right)_s = \left[\frac{(D_s)}{(D_o)}\right]^3 - 1 \qquad (1)$$

where D_s and D_0 are the number-average diameter of styrene-absorbed PS/P(S-DVB) composite particles and PS/P(S-DVB) composite particles, respectively.

Swelling of the PS/P(S-DVB) composite particles with styrene utilizing DSM

Swelling of the PS/P(S-DVB) composite particles with a large amount of styrene was carried out utilizing DSM under the conditions listed in Table 1 (column B) as follows. The composite particles were dispersed to the homogeneous ethanol/water (6/4, w/w) solution (10 g) dissolving styrene and PVA. Then water (40 g) was added to the dispersion with a microfeeder at various rates (R_w) (ml/h) under stirring with a magnetic stirrer at room temperature. Here, when the stirring speed is extremely slow, since the heterogeneousness of the composition of the medium where water is added does not disappear immediately, the formation of styrene droplets may proceed heterogeneously in the system. On the other hand, when the stirring speed is too fast, there is a fear that the collision of the styrene-swollen particles occurs. Accordingly, the stirring speed was set up at 220 rpm, which was an optimum value to avoid such problems.

Measurements of particle diameter and the number of domains in swollen particles

The dispersions of the swollen particles were dropped onto a 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 more than 100 droplets and particles on optical micrographs taken at room temperature with the image analysis software for Macintosh computers (MacSCOPE, Mitani Co. Ltd., Fukui, Japan). The number of PS/P(S-DVB) domains in the swollen particles was obtained as an average value for over 400 particles on the optical micrographs.

Results and discussion

The absorption rate of styrene by 1.8-μm-sized PS particle utilizing DSM was discussed using the following equation, which was suggested by Ugelstad et al. [8–12]:

$$\frac{\mathrm{d}V_{\mathrm{m}}}{\mathrm{d}t} = 4\pi DC\left[\exp\left(\frac{\overline{\Delta G_m}}{RT}\right) - \exp\left(\frac{\overline{\Delta G_s}}{RT}\right)\right] \times \left(\frac{2}{d_{\mathrm{m}}N_{\mathrm{m}}} + \frac{2}{d_{\mathrm{s}}N_{\mathrm{s}}}\right)^{-1} \tag{2}$$

where subscripts m and s denote monomer and swollen particle, respectively. V_{m} is the volume of absorbed monomer; D is the diffusion constant of monomer in the medium; C is the saturated monomer concentration in the medium; d_{m} and d_{s} are the diameters of monomer droplet and swollen particle, respectively; N_{m} and N_{s} are the numbers of monomer droplet and swollen particle, respectively; $\overline{\Delta G_m}$ and $\overline{\Delta G_s}$ are the partial molar free energies of monomer in the monomer droplets and the swollen particles, respectively, expressed using the following pair of equations:

$$\frac{\overline{\Delta G_m}}{RT} = \frac{2\overline{V_m}\gamma_{\mathrm{m}}}{RT}\cdot\frac{2}{d_{\mathrm{m}}} \tag{3}$$

$$\frac{\overline{\Delta G_s}}{RT} = \ln\left(1 - \frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right) + \left(1 - \frac{1}{J_{\mathrm{p}}}\right)\cdot\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}} + \chi_{\mathrm{mp}}\left(\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right)^2 + \frac{2\overline{V_m}\gamma_{\mathrm{s}}}{RT}\cdot\frac{2}{d_0}\left(\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right)^{1/3} \tag{4}$$

where $\overline{V_m}$ is the molar volume of the monomer; R is the gas constant; T is the absolute temperature; γ_{m} and γ_{s} are the interfacial tensions of the monomer droplet and the medium, and the swollen particle and the medium, respectively; V_{m} and V_{p} are the volumes of absorbed monomer and seed polymer in swollen particle, respectively; J_{p} is the degree of polymerization of the seed polymer; χ_{mp} is the Flory-Huggins interaction parameter between the monomer and seed polymer; d_0 is the diameter of the polymer seed particle.

Figure 1 shows the relationships between R_{w} values and the experimental values (solid lines) of size distribution of styrene-swollen PS particles measured in the previous article [1] and the simulation result (broken line) of the percentages of unabsorbed styrene to styrene separated from an ethanol/water medium obtained by using Eq. (2). In Fig. 1, V_m^{sep} denotes the volume of all the separated styrene in the system. In the simulation, at the R_{w} values below 7 ml/h, $(V_m^{sep}–V_{\mathrm{m}})/V_m^{sep}$ values were zero and C_{v} and $D_{\mathrm{w}}/\mathrm{D}_{\mathrm{n}}$ values were low. At the R_{w} values above 8 ml/h, $(V_m^{sep}–V_{\mathrm{m}})/V_m^{sep}$ values were not zero, and C_{v} and $D_{\mathrm{w}}/\mathrm{D}_{\mathrm{n}}$ values were large. These results indicate that when the separation rate of styrene from the medium is too fast, some pure monomer droplets not containing PS seed particle are formed, which agreed well with the results obtained in the previous article [7].

In the experimental results obtained by the optical microscopic observation, it was not ascertained whether the observed particles were swollen particles derived from the seed particle or pure styrene droplets not containing it. Therefore, it was difficult to clarify the reason why the monodispersity of the dispersed particles (droplets) was low at the higher R_{w} values in the DSM process. In order to overcome this problem, loosely cross-linked PS/P(S-DVB) composite particles, which swell but do not dissolve in styrene, are applied as a seed. The existence of the composite particle should be observed in styrene droplets with the optical microscope. In addition, it is expected to estimate the coalescence of swollen particles by counting the number of the seed particles therein.

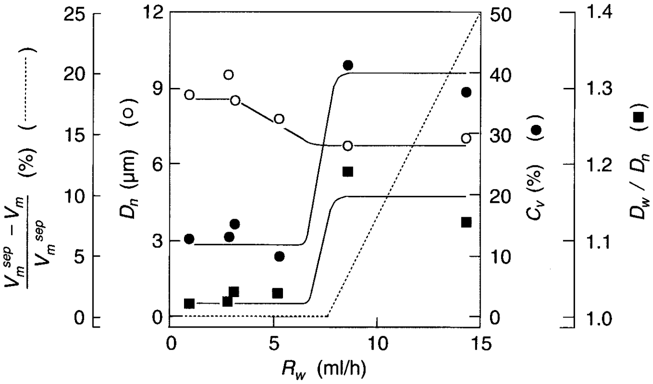


Fig. 1 Relationships between the water-addition rates (R_{w}) and the experimental values (*solid lines*) of size distribution (D_{n}, C_{v}, and $D_{\mathrm{w}}/D_{\mathrm{n}}$) of styrene droplets and simulation values (*broken line*) of the percentages $[(V_m^{sep}–V_{\mathrm{m}})/V_m^{sep}]$ of unabsorbed styrene to separated styrene from medium using Eqs. (2)–(4) with following values: D, 10^{-10} m^2/sec; C, variable; N_{m}, variable; N_{s}, 8.4×10^{13}/m^3; d_0, 1.80 μm; d_{m}, 0.35 μm; $\overline{V_m}$, 1×10^{-4} m^3/mol; $\gamma_{\mathrm{m}} = \gamma_{\mathrm{s}}$, 5 mN/m; J_{p}, 210; χ_{mp}, 0.5

Figure 2a shows a TEM photograph of PS/P(S-DVB) [1/(47.5–2.5), w/w] composite particles produced by seeded copolymerization of styrene and DVB with PS seed particles utilizing DSM under the conditions listed in Table 1 (column A) according to the previous article [6]. D_{n} and C_{v} were 1.90 μm and 3.8%, respectively. Figure 2b shows an optical micrograph of the styrene-saturated PS/P(S-DVB) composite particles. The saturated particles had values of 2.80 μm for D_{n} and 3.9% for C_{v}. According to Eq. (1), $(V_{\mathrm{m}}/V_{\mathrm{p}})_{\mathrm{s}}$ was calculated to be 2.2.

The saturation swelling of the PS/P(S-DVB) composite particles with styrene by DSM was examined using Eq. (5) which was suggested by Gardon [13]:

$$\frac{\overline{\Delta G}}{RT} = \ln\left(1 - \frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right) + \left(1 - \frac{1}{J_{\mathrm{p}}}\right)\cdot\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}} + \chi_{\mathrm{mp}}\left(\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right)^2 + \frac{2\overline{V_m}\gamma_{\mathrm{s}}}{RT}\cdot\frac{2}{d_0}\cdot\left(\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right)^{1/3} + \frac{\overline{V_m}\rho_{\mathrm{p}}}{M_{\mathrm{c}}}\left[\left(\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right)^{1/3} - \frac{1}{2}\left(\frac{V_{\mathrm{p}}}{V_{\mathrm{m}} + V_{\mathrm{p}}}\right)\right] \tag{5}$$

where ρ_{p} is the density of polymer and M_{c} is the molar mass between cross-linking points.

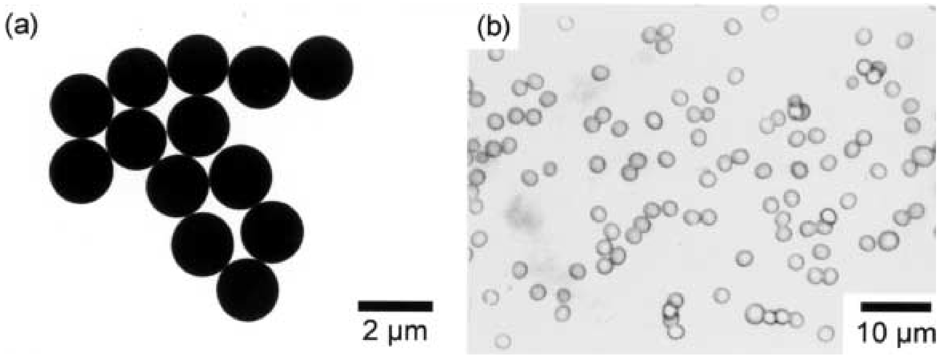


Fig. 2 **a** A TEM photograph of PS/P(S-DVB) [1/(47.5–2.5), w/w] composite particles produced by seeded copolymerization utilizing DSM under the conditions listed in Table 1 (column A). **b** An optical micrograph of the styrene-saturated composite particles prepared under the conditions listed in Table 1 (column B)

Figure 3 shows a simulation of the M_c values of the PS/P(S-DVB) composite particles as a function of the J_p values using Eq. (5) with $\overline{\Delta G}$ value of 0 and $V_\mathrm{m}/V_\mathrm{p}$ value of 2.2. The M_c value increased with an increase in the J_p value, and attained a saturated value. Because the composite particles had a cross-linking structure, the J_p value of these particles should be very large, i.e., $1/J_\mathrm{p}$ value was equal to zero. The M_c value was decided to be 4220.

Figure 4 shows simulations of the $\overline{\Delta G}$ values of styrene in the system as a function of the $V_\mathrm{m}/V_\mathrm{p}$ values. When the loosely cross-linked PS/P(S-DVB) composite particles are used as seed particles in DSM, they "absorb" styrene in an early stage of the water-addition. The saturation swelling state, $\overline{\Delta G}$ is expressed using Eq. (6):

$$\frac{\overline{\Delta G}}{RT}=\ln\left(1-\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)+\left(1-\frac{1}{J_\mathrm{p}}\right)\cdot\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}+\chi_\mathrm{mp}\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^2+\frac{\overline{V_m}\rho_\mathrm{p}}{M_\mathrm{c}}\left[\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^{1/3}-\frac{1}{2}\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)\right]+\frac{2\overline{V_m}\gamma_\mathrm{s}}{RT}\cdot\frac{2}{d_0}\cdot\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^{1/3}-\frac{2\overline{V_m}\gamma_\mathrm{m}}{RT}\cdot\frac{2}{d_\mathrm{m}} \tag{6}$$

On the other hand, after the saturation swelling state, at which $V_\mathrm{m}/V_\mathrm{p}$ value was 2.2, the styrene-swollen composite particles do not absorb styrene any more, but adsorb. Under the "adsorption" state, $\overline{\Delta G}$ is expressed as follows:

$$\frac{\Delta G}{RT}=\frac{2\overline{V_m}\gamma_\mathrm{s}}{RT}\cdot\frac{2}{d_0}\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^{1/3}-\frac{2\overline{V_m}\gamma_\mathrm{m}}{RT}\cdot\frac{2}{d_\mathrm{m}} \tag{6'}$$

The simulation result indicates that the free energy $\overline{\Delta G}$ value is always negative at any $V_\mathrm{m}/V_\mathrm{p}$ value. This means that all styrenes separated from the medium by DSM can be absorbed (adsorbed) to the composite particles.

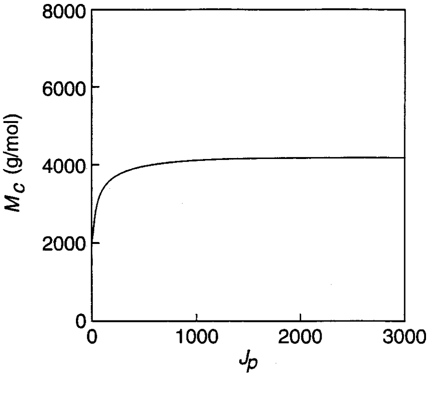


Fig. 3 A simulation of the M_c as a function of the J_p of polymer seed particles using Eq. (5) with following values: $\overline{\Delta G}$, 0; $V_\mathrm{m}/V_\mathrm{p}$, 2.2; χ_mp, 0.5; $\overline{V_m}$, 1×10^{-4} m^3/mol; γ_s, 5 mN/m; d_0, 1.90 μm; ρ_p, 1.06×10^3 kg/m^3

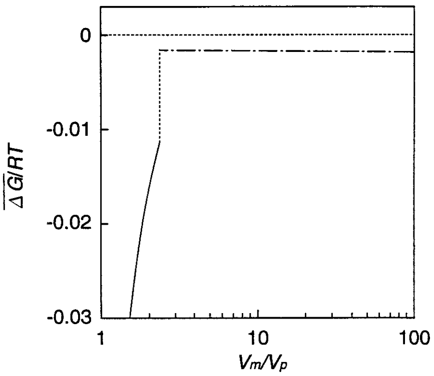


Fig. 4 Simulations for the variations of the chemical potential $\overline{\Delta G}$ of monomer in the system as functions of the absorbing and adsorbing ratios ($V_\mathrm{m}/V_\mathrm{p}$) using Eqs. (6) and (6′), respectively, with the following values: $1/J_\mathrm{p}$, 0; χ_mp, 0.5; $\overline{V_m}$, 1×10^{-4} m^3/mol; ρ_p, 1.06×10^3 kg/m^3; M_c, 4.2 kg/mol; $\gamma_\mathrm{m}=\gamma_\mathrm{s}$, 5 mN/m; d_0, 1.90 μm; d_m, 0.35 μm

Figure 5 shows simulations using Eq. (2) for the increases of V_m^{sep}/V_p values and $V_\mathrm{m}/V_\mathrm{p}$ values as a function of water-addition time at various R_w values. During composite particles "absorb" styrene until the saturation swelling state, $\overline{\Delta G_s}$ in Eq. (2) is expressed using Eq. (4′):

$$\frac{\overline{\Delta G_s}}{RT}=\ln\left(1-\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)+\left(1-\frac{1}{J_\mathrm{p}}\right)\cdot\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}+\chi_\mathrm{mp}\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^2+\frac{2\overline{V_m}\gamma_\mathrm{s}}{RT}\cdot\frac{2}{d_0}\cdot\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^{1/3}+\frac{\overline{V_m}\rho_\mathrm{p}}{M_\mathrm{c}}\left[\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)^{1/3}-\frac{1}{2}\left(\frac{V_\mathrm{p}}{V_\mathrm{m}+V_\mathrm{p}}\right)\right] \tag{4'}$$

Under the "adsorption" state after the saturation swelling state, $\overline{\Delta G_s}$ in Eq. (2) is expressed using the following equation:

$$\frac{\overline{\Delta G_s}}{RT} = \frac{2\overline{V_m}\gamma_s}{RT} \cdot \frac{2}{d_0} \left(\frac{V_p}{V_m + V_p} \right)^{1/3} \qquad (4'')$$

The symbols (●, ▲, ■) indicate the V_m^{sep}/V_p values calculated from the solubility curve of styrene in the medium assuming that all separated styrenes are instantly absorbed (adsorbed) by the PS/P(S-DVB) composite particles. In addition, the simulations were assuming that separated styrenes, which are not absorbed (adsorbed) by the composite particles within 1 s, are not absorbed (adsorbed) any longer because they coalesce each other, resulting in large pure styrene droplets. At the R_w value of 2.66 (●), the V_m/V_p values completely agreed with the V_m^{sep}/V_p values at any time. At the R_w values of 5.32 (▲) and 13.3 (■), their V_m/V_p values were always smaller than the V_m^{sep}/V_p values. These thermodynamic simulations under kinetic control state indicate that all separated styrene are absorbed (adsorbed) by the composite particles in DSM at the R_w value of 2.66, but only a part of all separated styrene is absorbed (adsorbed) at the R_w values of 5.32 and 13.3 because the separation rate of styrene

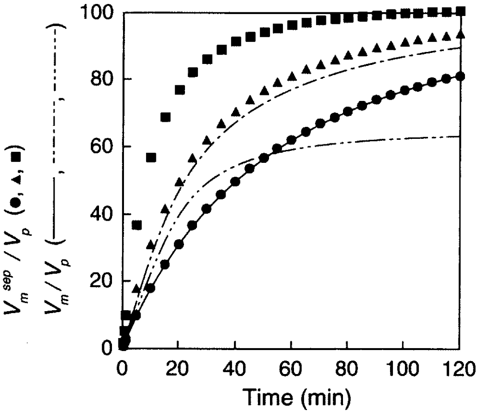


Fig. 5 Variations of absorbing (and adsorbing) ratios (V_m^{sep}/V_p) calculated using the solubility curve of styrene monomer in ethanol/water media assuming that all separated styrenes are absorbed (and adsorbed) by PS/P(S-DVB) composite particles, and of those (V_m/V_p) simulated assuming that large pure monomer droplets are formed and do not contribute the absorption or adsorption, using Eqs. (2) and (4′) or (4″) with following values (D, 10^{-10} m^2/sec; C, variable; N_m, variable; N_s, 8.4×10^{13}/m^3; $1/J_p$, 0; χ_{mp}, 0.5; $\overline{V_m}$, 1×10^{-4} m^3/mol; ρ_p, 1.06×10^3 kg/m^3; M_c, 4.2 kg/mol; $\gamma_m = \gamma_s$, 5 mN/m; d_0, 1.90 μm; d_m, 0.35 μm) as a function of water-addition time at various water-addition rates (ml/h): ●, ——: 2.66; ▲, –·–·–: 5.32; ■, –··–··–: 13.3

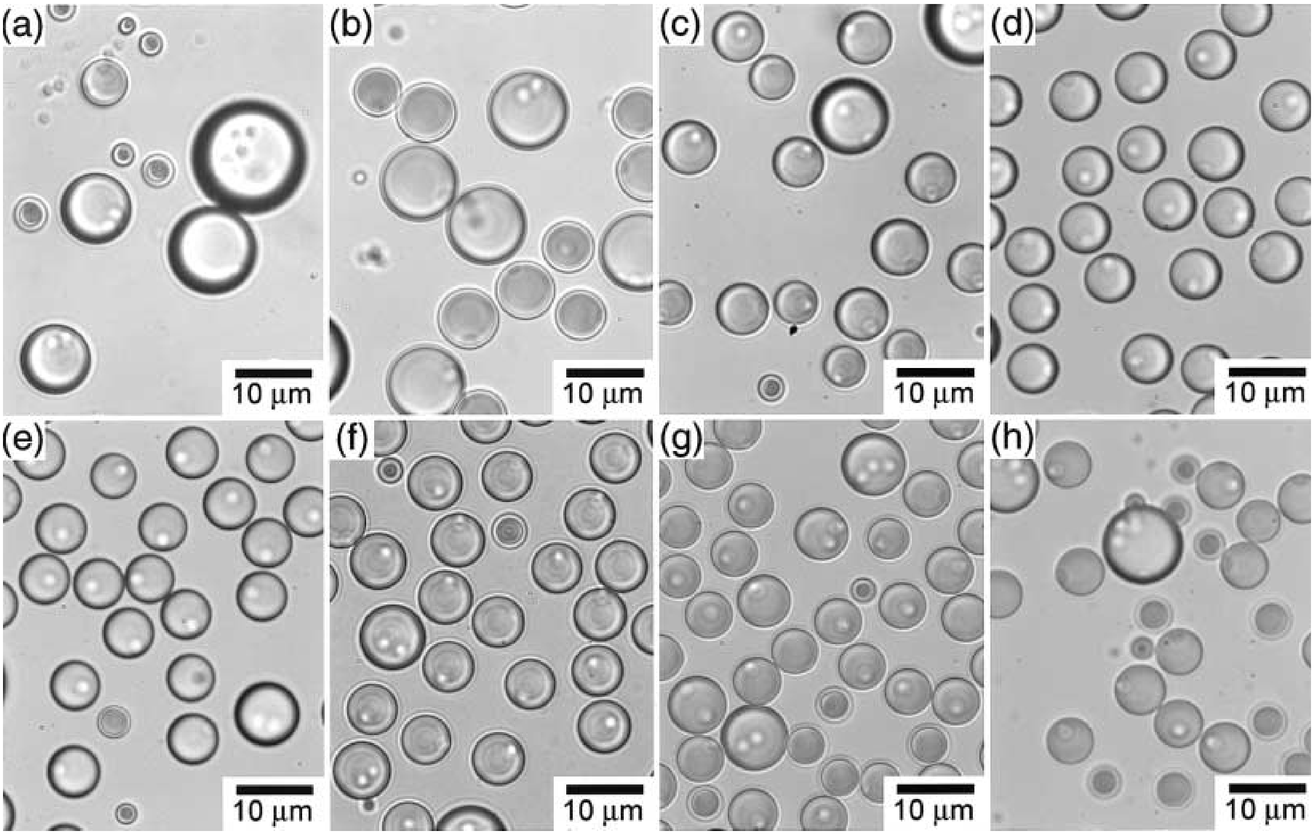


Fig. 6a–h Optical micrographs of styrene droplets prepared in the presence of PS/P(S-DVB) composite particles by utilizing DSM at various water-addition rates (ml/h): **a** 0.66; **b** 0.88; **c** 1.33; **d** 2.66; **e** 5.32; **f** 7.92; **g** 10.6; **h** 13.3

from the medium was much faster than the absorption (adsorption) rate of that by the composite particles.

Figure 6 shows optical micrographs of styrene droplets prepared in the presence of the PS/P(S-DVB) composite particles utilizing DSM at various R_w values (ml/h) of 0.66 (a), 0.88 (b), 1.33 (c), 2.66 (d), 5.32 (e), 7.92 (f), 10.6 (g), and 13.3 (h) under the conditions listed in Table 1 (column B). In cases of 2.66 (d) and 5.32 (e), monodispersed styrene droplets having single composite particle were prepared, but in other cases (a–c and f–h), polydispersed styrene droplets having zero or some composite particles were prepared.

Figure 7 shows relationships between R_w values and experimental values of size distribution (D_n, C_v and D_w/D_n) of the styrene droplets obtained in Fig. 6 and percentages $[(V_m^{sep}-V_m)/V_m^{sep}]$ of unadsorbed styrene (broken line) simulated after the water-addition was finished. At the R_w value of 2.66, monodispersed styrene droplets having single composite particle were obtained.

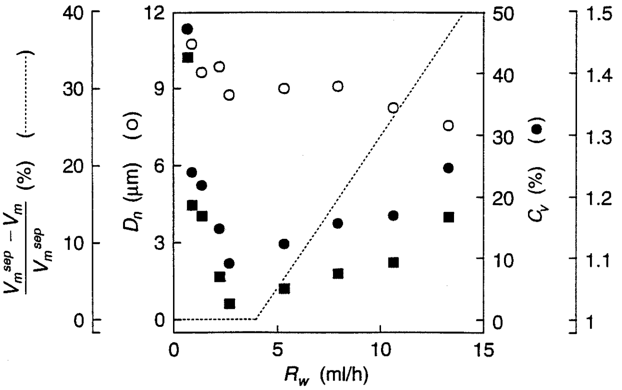
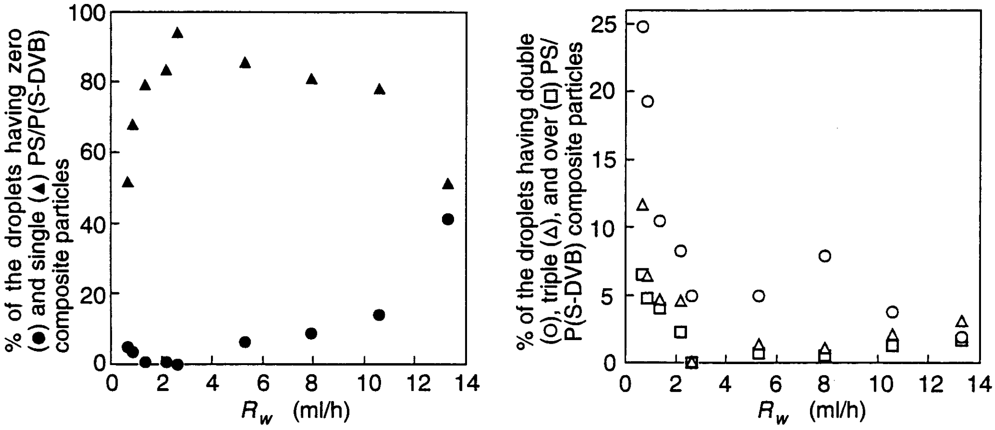


Fig. 7 Relationships between the water-addition rates (R_w) in DSM and the experimental values of size distribution (D_n, C_v, and D_w/D_n) of styrene droplets and calculated values (*broken line*) of the percentages $[(V_m^{sep}-V_m)/V_m^{sep}]$ of unabsorbed styrene to separated styrene

The polydispersity of the droplet size increased with an increase in the R_w values above 5.32. These experimental results agreed well with the simulation results that the $(V_m^{sep}-V_m)/V_m^{sep}$ value was zero at the R_w values below 4 and increased linearly with the increase in the R_w values. The range which the $(V_m^{sep}-V_m)/V_m^{sep}$ value was zero in Fig. 7 was smaller than that of Fig. 1 because of cross-linking structure of the seed particles. However, at the R_w values below 1.33, prepared particles were polydisperse though $(V_m^{sep}-V_m)/V_m^{sep}$ values were zero.

Figure 8 shows relationships between R_w values and the percentages of the styrene droplets having zero (●), single (▲), double (○), triple (△), and over (□) PS/P(S-DVB) composite particles. At the R_w value of 2.66, the percentage of styrene droplets having single composite particle was 95%, and that having no composite particle was below 0.5%. This indicates that monodispersed styrene droplets having single composite particles were prepared by DSM at a suitable R_w value. The styrene droplets having double, triple, and over composite particles, which were formed by the coalescence of styrene droplets having single composite particle, were very few. With the increase in the R_w values above 5.32, the percentage of the styrene droplets having no composite particle increased. These results indicate that the separated styrenes from the media, which was not absorbed (adsorbed) by the composite particles, coalesced each other and pure styrene droplets having no composite particle were formed at the R_w values above 5.32. The percentages of the styrene droplets having double, triple, and over composite particles were also higher than those at the R_w value of 2.66. This seems to be because a part of the PVA stabilizer is consumed to stabilize the pure styrene droplets having no composite particle, i.e., the colloidal stability of the styrene droplets having single composite particle is reduced. This was confirmed experimentally (the photograph was omitted). On the other hand, at the R_w values below 1.33, the

Fig. 8 Relationships between the water-addition rates (R_w) in DSM and the percentages of styrene droplets having zero (●), single (▲), double (○), triple (△), and over (□) PS/P(S-DVB) composite particle



percentage of pure styrene droplets having no composite particle was very few. This indicates that at the R_w values below 1.33, the composite particles absorbed (adsorbed) all the separated styrenes as well as at the R_w value of 2.66. However, the styrene droplets having double, triple, and over composite particles coexisted. This indicates that the coalescence among the styrene droplets having single composite particle took place during the DSM process, because water-addition time was too long at these R_w values.

From the above results, it is concluded that there is an appropriate R_w range in DSM for the preparation of micron-sized, monodispersed, monomer-absorbed (adsorbed) particles.

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