Synthesis of Greater Than 10-μm-Sized, Monodispersed Polymer Particles by One-step Seeded Polymerization for Highly Monomer-Swollen Polymer Particles Prepared Utilizing the Dynamic Swelling Method

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ABSTRACT: The thermodynamic simulation under the kinetic control state indicates that 1.77-μm-sized monodispersed polystyrene (PS) particles can absorb 500 times the amount of the styrene monomer with keeping the monodispersity by the "dynamic swelling method" (DSM) which the authors proposed in 1991. Actually, about 14.1-μm-sized monodispersed styrene-swollen PS particles in which PS seed particles absorbed 500 times the amount of styrene monomer were successfully prepared utilizing DSM. By one-step seeded polymerization for the dispersion of the swollen particles at 30°C for 48 h with the 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) initiator, 13.1-μm-sized monodispersed PS particles were produced. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 278–285, 1999

Key words: dynamic swelling method; particle; monodisperse; micron-size, seeded polymerization

INTRODUCTION

We have been trying to produce micron-sized monodispersed functional composite polymer particles by seeded dispersion polymerization.[1–6] Moreover, for the production of particles with diameters 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.[7–10] It was named the "dynamic swelling method (DSM)." The high swelling was carried out by slow, continuous, dropwise addition of water with a microfeeder into an ethanol/water medium dissolving styrene, the benzoyl peroxide (BPO) initiator, and the poly(vinyl alcohol) stabilizer, in which about 2-μm-sized monodispersed polystyrene (PS) seed particles were dispersed. The PS seed particles absorbed about 100 times the weight of styrene and BPO, which were gradually separated from the medium by the dropwise water addition, resulting in 8.5-μm-sized monodispersed styrene-swollen PS particles.[7] 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 the solubility of the monomer which derives from the lowering of the temperature.[9]

In previous articles,[11,12] we discussed the thermodynamic background of the high swelling of polymer particles with the monomer by the DSM in both equilibrium and kinetic control states and clarified that the high swelling by the DSM is

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Table I Recipes for Preparation of Micron-sized Monodispersed Styrene-swollen PS Particles Utilizing the Dynamic Swelling Method at Different Concentrations of PS Seed Particles

	$V_{m\ \mathrm{total}}/V_p$		
Ingredients	500	750	1000
PS seed particles[a] (mg)	0.8	0.53	0.4
Styrene (mg)	400	400	400
PVA (mg)	15	15	15
SDS (mg)	10	10	10
Ethanol (g)	6.0	6.0	6.0
Water (g)	4.0 + 11[b]	4.0 + 11[b]	4.0 + 11[b]

[a] D_n, 1.77 μm; C_v, 3.9%.

[b] Water, 11 g, was postadded using the microfeeder at the rate of 0.88 mL/h for 12.5 h at room temperature.

based on the size difference between the monomer droplets formed by monomers separated from the medium by water addition and the polymer seed particles and on the high saturated monomer concentration in an ethanol/water medium.

In this article, first, a maximum amount of absorption of styrene into 1.8-μm-sized monodispersed PS seed particles by the DSM, keeping the monodispersity, was simulated thermodynamically. Second, such a maximum absorption was conducted experimentally. Finally, seeded polymerization for the highly styrene-swollen PS particles was carried out for the production of greater than 10-μm-sized monodispersed PS particles.

EXPERIMENTAL

Materials

Styrene was purified by distillation under reduced pressure in a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Osaka, Japan) of reagent grade were purified by recrystallization. Deionized water with a specific conductivity of 5 × 10^6 Ω cm was distilled with a Pyrex distillator. Poly(vinyl alcohol) (PVA) was supplied by Nippon Synthetic Chemical, Osaka, Japan (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). Reagent-grade sodium dodecyl sulfate (SDS), ethanol, and cupric chloride ($CuCl_2 \cdot 2H_2O$) 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.[1]

Swelling of PS Seed Particles with Styrene Utilizing DSM and Seeded Polymerization

The swelling of PS seed particles with a large amount of styrene by DSM was carried out under the conditions listed in Tables I and II. PS seed particles were dispersed into the homogeneous ethanol/water solutions by dissolving styrene,

Table II Recipes for Seeded Polymerizations for Dispersion of Micron-sized Monodispersed Styrene-swollen PS Particles Prepared Utilizing the DSM

Ingredients	No. 1	No. 2
PS seed particles[a] (mg)	0.8	0.8
Styrene (mg)	400	400
V-70 (mg)	20	4
PVA (mg)	15	15
SDS (mg)	10	10
Ethanol (g)	6.0	8.0
Water (g)	4.0 + 11[b]	2.0 + 2.8[c] + 11[d] + 42.9[d]
$CuCl_2$ (mg)	—	Variable[d]

N_2; 30°C; 24 or 48 h.

[a] D_n, 1.77 μm; C_v, 3.9%.

[b] Water 11 g, was postadded using the microfeeder at the rate of 0.88 mL/h for 12.5 h at 20 or 10°C.

[c] Water, 2.8 g, was added at first, close to the saturated concentration of styrene in the medium.

[d] $CuCl_2$ aqueous solution was added collectively at 10°C.

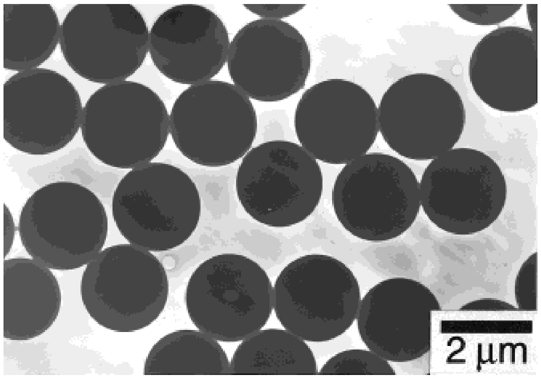

Figure 1 TEM photograph of PS seed particles produced by dispersion polymerization according to previous article.[1]

V-70 or nothing, PVA, and SDS. Then, 11 g water was added to the dispersions with a microfeeder at a rate of 0.88×10^{-6} m^3/h under stirring with a magnetic stirrer at the respective temperatures shown in Tables I and II.

Seeded polymerizations for the dispersion of styrene-swollen PS particles were carried out under the conditions of No. 2 listed in Table II. On the basis of our previous results,[7,10] $CuCl_2$ as a water-soluble inhibitor was added in order to depress the by-production of new submicron-sized PS particles. The conversion was measured by gas chromatography (Shimadzu GC-18APFsc). A capillary column (HR-20M, 30 m × 0.32 mm i.d., 1.0-μm film thickness; Shinwa Chemical Industries, Ltd.) was used with helium as a carrier gas. Each temperature of the gas chromatographic measurement was as follows: injector, 200°C; column, 120°C; detector, 200°C.

The dispersions of swollen particles were dropped onto a slide glass and observed with a Nikon Microphoto FXA optical microscope. The produced PS particles were observed with a Hitachi S-2500 scanning electron microscope (SEM).

Diameter Measurements

The number-average diameter (D_n), weight-average diameter (D_w), and coefficient of variation (C_v) were determined by measuring 150–200 droplets and particles on optical micrographs and a JEOL JEM-200CX transmission electron microscopic (TEM) photographs with the Personal Image Analysis System (PIAS Co., Ltd., LA-525).

RESULTS AND DISCUSSION

Figure 1 shows a TEM photograph of PS seed particles produced by dispersion polymerization according to the previous article.[1] The size distribution of the PS particles was D_n 1.77 μm, D_w/D_n 1.004, and C_v, 3.9%.

The possibility of the swelling of the produced PS seed particles with a large amount of styrene by DSM was examined using eq. (1), which was suggested by Ugelstad et al.[13–15]:

$$\frac{\overline{\Delta G}}{RT} = \ln\left(1 - \frac{V_p}{V_m + V_p}\right) + \left(1 - \frac{1}{J_p}\right)\frac{V_p}{V_m + V_p} + \chi_{mp}\left(\frac{V_p}{V_m + V_p}\right)^2 + \frac{2\overline{V_m}\gamma_s}{RT} \times \frac{2}{d_0} \times \left(\frac{V_p}{V_m + V_p}\right)^{1/3} - \frac{2\overline{V_m}\gamma_m}{RT}\frac{2}{d_m} \qquad (1)$$

where subscripts m, p, and s denote the monomer, seed polymer, and swollen particle, respectively. The $\overline{\Delta G}$ is the partial molar free energy of the monomer; $\overline{V_m}$, the molar volume of the monomer; R, the gas constant; T, the absolute temperature; γ_m and γ_s, respectively, the interfacial tensions of the monomer droplet and swollen particle with the medium; V_m and V_p, respectively, the volumes of absorbed monomer and seed polymer in swollen particle; J_p, the degree of polymerization of the seed polymer; χ_{mp}, the Flory–Huggins interaction parameter between the monomer and the seed polymer; and d_0

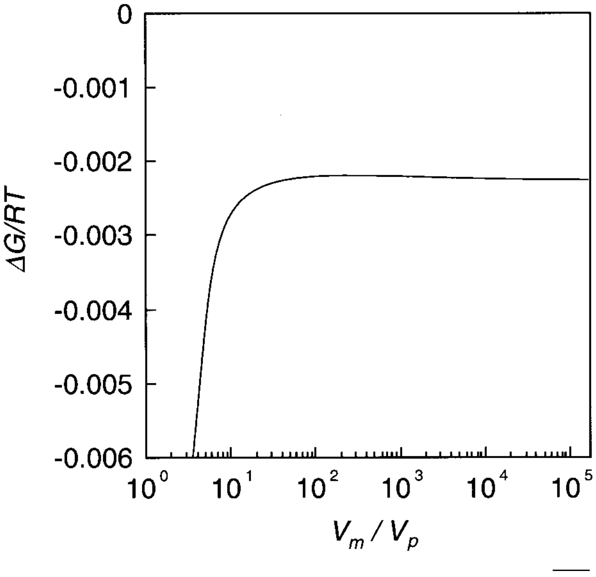

Figure 2 Simulation of the chemical potential ($\overline{\Delta G}$) of monomer in the system as a function of the V_m/V_p value using eq. (1) with the following values: χ_{mp}, 0.5; $\overline{V_m}$, 1×10^{-4} m^3/mol; $\gamma_m = \gamma_s$, 5 mN/m; J_p, 210; d_0, 1.8 μm; d_m, 0.35 μm.

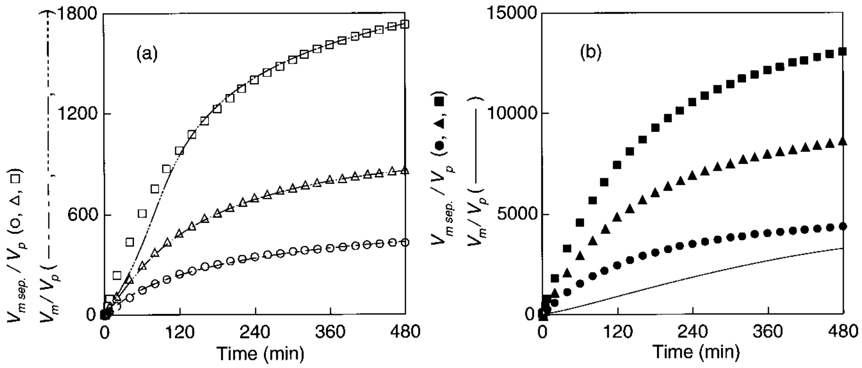

Figure 3 Variations of swelling ratios ($V_{m\ \mathrm{sep}}/V_p$) calculated using the solubility curve of the styrene monomer in the ethanol/water mixture assuming that all separated styrene monomers are absorbed by the PS seed particles and of those (V_m/V_p) simulated assuming that the size of monomer droplets is maintained at 0.35 μm all the time using eq. (2) with the following values (D, 10^{-10} m^2/s, C, variable; d_0, 1.8 μm; d_m, 0.35 μm; N_m, variable) as a function of water-addition time at various N_s values ($\times 10^{13}$/m^3): (— - — -) 2; (- - — — - —) 1; (- - - - -) 0.5; (——) 0.2–0.067. $V_{m\ \mathrm{total}}/V_p$: (— - — -, ○) 500; (- - — — - —, △) 1000; (- - - - - - - -, (□) 2000; (——, (●) 5000; (——, ▲) 10,000, (——, ■) 15,000.

and d_m, respectively, the diameters of the polymer seed particle and monomer droplet.

Figure 2 shows the simulation of the $\overline{\Delta G}$ value of styrene in the system as a function of the swelling volume ratio (V_m/V_p) using eq. (1) with $d_0 = 1.8$ μm, which corresponds to the D_n of the PS seed particles shown in Figure 1, and $d_m = 0.35$ μm, which corresponds to the measured average diameter of styrene droplets prepared by water addition of 3.3 g at a rate of 2.88 mL/h with a microfeeder to the homogeneous solution of 0.504 g (S, 4 mg; ethanol, 0.5 g) at 20°C. The other parameter values used were the same as those used in the previous articles.[11,12] The simulation result indicates that the free-energy change value ($\overline{\Delta G}$) is always negative at any V_m/V_p value, indicating that all separated styrenes from the medium can be absorbed into the 1.8-μm-sized PS seed particles by DSM.

The absorption rate of styrene into 1.8-μm-sized PS particles utilizing the DSM was discussed using eq. (2), which was suggested by Ugelstad et al.[13–16]:

$$\frac{dV_m}{dt} = 4\pi DC\left[\exp\left(\frac{\overline{\Delta G_m}}{RT}\right) - \exp\left(\frac{\overline{\Delta G_s}}{RT}\right)\right] \times \left(\frac{2}{d_m N_m} + \frac{2}{d_s N_s}\right)^{-1} \quad (2)$$

where D is the diffusion constant of monomer in the medium; C, the saturated monomer concentration in the medium; d_s, the diameter of the swollen particle; N_m and N_s, respectively, the numbers of monomer droplets and swollen particles; and $\overline{\Delta G_m}$ and $\overline{\Delta G_s}$, respectively, the partial molar free energies of the monomer in the monomer droplet and the swollen particle and expressed using eqs. (3) and (4):

$$\frac{\overline{\Delta G_m}}{RT} = \frac{2\bar{V}_m\gamma_m}{RT} \times \frac{2}{d_m} \quad (3)$$

$$\frac{\overline{\Delta G_s}}{RT} = \ln\left(1 - \frac{V_p}{V_m + V_p}\right) + \left(1 - \frac{1}{J_p}\right) \times \frac{V_p}{V_m + V_p} + \chi_{mp}\left(\frac{V_p}{V_m + V_p}\right)^2 + \frac{2\bar{V}_m\gamma_s}{RT} \times \frac{2}{d_0}\left(\frac{V_p}{V_m + V_p}\right)^{1/3} \quad (4)$$

Figures 3 and 4 show simulations for the increase of V_m/V_p as a function of the time by two types of algorithm methods using eq. (2) with parameters which are the same values as those used in the previous articles.[11,12] In Figure 3, the simulations (— - — -, - - — — - —, - - - - -, ——) were conducted assuming that the size of monomer droplets is maintained at 0.35 μm throughout the absorption process. On the other hand, in Figure 4, the simulations (— - — -, - - — — - —, - - - - - - - -, - - - - — - - - -, ——) were conducted

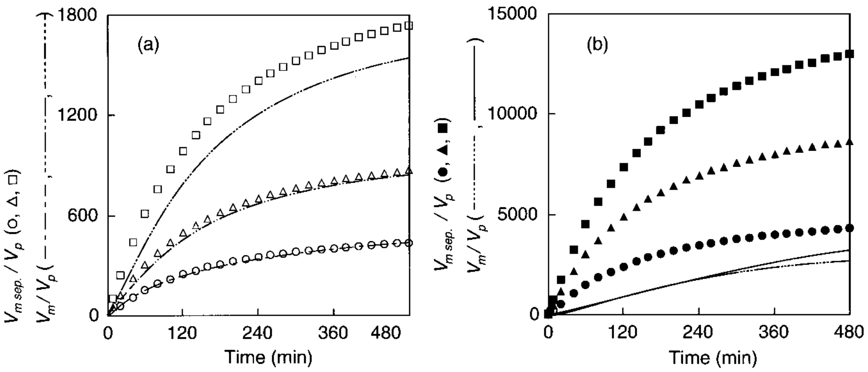

Figure 4 Variations of swelling ratios ($V_{m\ \mathrm{sep}}/V_p$) calculated using the solubility curve of the styrene monomer in the ethanol/water mixture assuming that all separated styrene monomers are absorbed by the PS seed particles and of those (V_m/V_p) simulated assuming that large pure monomer droplets are formed by coalescence which do not contribute to the absorption using eq. (2) with the following values (D, 10^{-10} m^2/s; C, variable; d_0, 1.8 μm; d_m, 0.35 μm; N_m, variable) as a function of water-addition time at various N_s values (×10^{13}/m^3): (— - — -) 2; (– - — – - —), 1; (– - - - – - - - -) 0.5; (– - - - — - - - - —) 0.2; (——) 0.1–0.067. $V_{m\ \mathrm{total}}/V_p$: (— - — -, ○) 500; (– - — – - —, △) 1000; (– - - - – - - - -, □) 2000; (– - - - — - - - - —, ●) 5000; (——, (▲) 10,000, (——, ■) 15,000.

assuming that large pure monomer droplets, which do not contribute the absorption, are formed by coalescence. In both figures, $V_{m\ \mathrm{total}}$ and $V_{m\ \mathrm{sep}}$, respectively, denote the volumes of all the monomers in the system and all separated monomers. The symbols (○, △, □, ●, ▲, ■) indicate the $V_{m\ \mathrm{sep}}/V_p$ values calculated from the solubility curve of styrene in the media assuming that all separated styrenes are instantly absorbed by the PS seed particles. In both systems, at the $V_{m\ \mathrm{total}}/V_p$ value of 500, the V_m/V_p values completely agreed with the $V_{m\ \mathrm{sep}}/V_p$ values at any time. This thermodynamic simulation under the kinetic control state indicates that all separated styrenes are absorbed into the 1.8-μm-sized PS seed particles by the DSM at the $V_{m\ \mathrm{total}}/V_p$ value of 500. In Figure 3, at the $V_{m\ \mathrm{total}}/V_p$ values of 1000–2000, the V_m/V_p values were nearly equal to the $V_{m\ \mathrm{sep}}/V_p$ values. At the $V_{m\ \mathrm{total}}/V_p$ values above 5000, the V_m/V_p values were clearly smaller than the $V_{m\ \mathrm{sep}}/V_p$ values. On the other hand, in Figure 4, at the $V_{m\ \mathrm{total}}/V_p$ values above 1000, the V_m/V_p values were smaller than were the $V_{m\ \mathrm{sep}}/V_p$ values. The difference in the simulated results at the $V_{m\ \mathrm{total}}/V_p$ values of 1000 and 2000 between Figures 3 and 4 is based on the difference in the variation of sizes of the monomer droplets between the two types of algorithm methods.

The absorption of styrene into the 1.8-μm-sized PS seed particles by the DSM was carried out at the $V_{m\ \mathrm{total}}/V_p$ values of 500, 750, and 1000 to confirm whether the simulation results can be applied to the experimental DSM system. Figure 5 shows optical micrographs of styrene-swollen PS particles prepared by the DSM at the $V_{m\ \mathrm{total}}/V_p$ values of (a) 500, (b) 750, and (c) 1000 under the conditions listed in Table I. All the obtained swollen particles and/or droplets were much larger than the 1.77-μm-sized PS seed particles. At 500, monodispersed particles were obtained: D_n, 14.1 μm; D_w/D_n, 1.019; and C_v, 6.7%. At 750 and 1000, the monodispersities were lower than that obtained at 500.

Figure 6 shows the relationships between $V_{m\ \mathrm{total}}/V_p$ and the volume percentage of the unabsorbed styrene to the separated styrene from

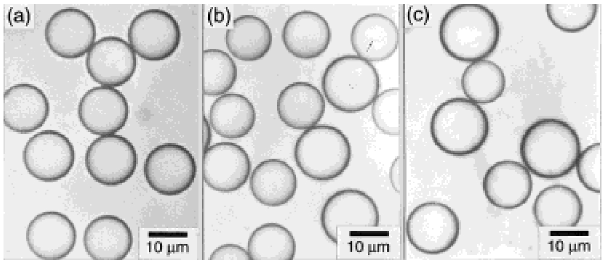

Figure 5 Optical micrographs of the styrene-swollen PS particles prepared utilizing the dynamic swelling method at the $V_{m\ \mathrm{total}}/V_p$ values of (a) 500, (b) 750, and (c) 1000, respectively, under the conditions listed in Table I.

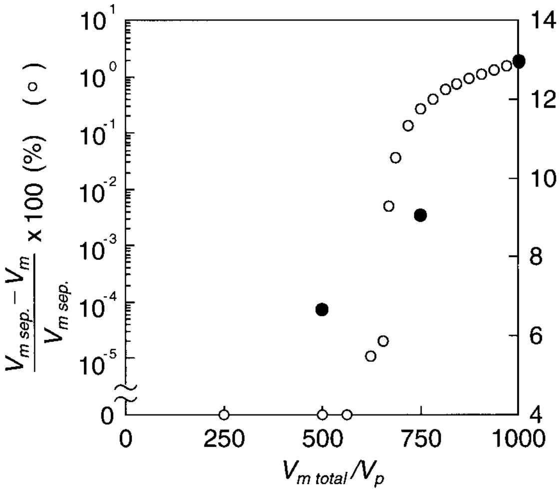

Figure 6 Relationships between $V_{m\ \mathrm{total}}/V_p$ value and percentage of unabsorbed styrene to separated styrene from medium, $\{(V_{m\ \mathrm{sep}} - V_m)/V_{m\ \mathrm{sep}} \times 100\}$, by the DSM calculated from the simulation results in Figure 4 and the C_v value obtained in Figure 5.

the medium, $\{(V_{m\ \mathrm{sep}} - V_m)/V_{m\ \mathrm{sep}} \times 100\}$, by the DSM calculated from the simulation results in Figure 4 and the C_v value obtained in Figure 5. At the $V_{m\ \mathrm{total}}/V_p$ values below 500, the $\{(V_{m\ \mathrm{sep}} - V_m)/V_{m\ \mathrm{sep}} \times 100\}$ value was zero and the C_v value was low. With increase in $V_{m\ \mathrm{total}}/V_p$ above 750, the $\{(V_{m\ \mathrm{sep}} - V_m)/V_{m\ \mathrm{sep}} \times 100\}$ values were not zero and increased and the C_v values became larger. These results suggest that some pure styrene droplets not containing the PS seed polymer are formed at the $V_{m\ \mathrm{total}}/V_p$ values of 750 and 1000.

Figure 7 shows optical micrographs of styrene-swollen PS particles produced at different amounts of water postadded at a rate of 0.88 mL/h. As shown in Figure 7(b–h), the D_n value of the swollen particles increased with the water addition, keeping the high monodispersity. The variations of the D_n and C_v values with the water-addition time are shown in Figure 8. The D_n values agreed well with those (solid line) obtained with the $V_{m\ \mathrm{sep}}/V_p$ values calculated from the solubilities of styrene in the media, assuming that all separated styrenes are instantly absorbed by the PS seed particles. This indicates that the swelling of the PS seed particles is based mainly on the rapid absorption of styrene separated from the medium by the water addition.

In this system, for the purpose of producing the polymer particles, the V-70 initiator, of which the half-life period is 10 h at 30°C, was absorbed together with the styrene monomer into the PS seed particles according to the previous articles.[10,12] When the DSM was carried out at 20°C, a large amount of submicron-sized PS particles were produced during the process. When it was carried out at 10°C to prevent the decomposition of V-70, larger monomer droplets were formed in

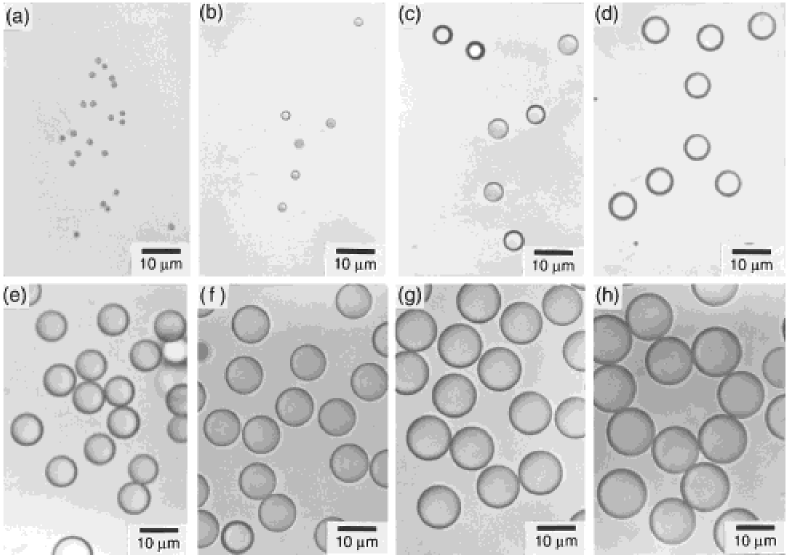

Figure 7 Optical micrographs of styrene-swollen PS particles prepared with water addition at a rate of 0.88 mL/h. Amount of water postadded (mL): (a) 0; (b) 1.3; (c) 2.0; (d) 2.4; (e) 2.6; (f) 3.7; (g) 5.3; (h) 10.6.

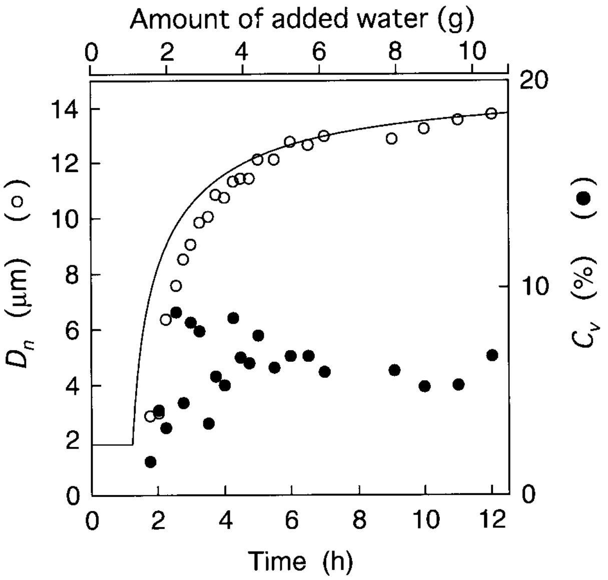

Figure 8 Variations of (○) D_n and (●) C_v with water addition at a rate of 0.88 mL/h. The solid line indicates D_n calculated using the solubility curve of the styrene monomer in an ethanol/water mixture assuming that all the styrene monomers separated in the ethanol/water mixture are absorbed by the PS seed particles.

addition to the styrene-swollen particles. Since the reason seems to be based on the lower solubility of styrene in the ethanol/water medium (6/4, w/w) at 10°C than at 20°C, the initial ratio of ethanol to water was changed to 8/2 (w/w) as shown in No. 2 in Table II. As the result, monodispersed 14.1-μm-sized styrene-swollen particles were obtained without monomer droplets (the photo was omitted). But only submicron-sized PS particles were produced by seeded polymerization for the 14.1-μm-sized styrene-swollen particles. These suggest that the polymerization hardly proceeded in the swollen particles and mainly proceeded in the medium. Therefore, $CuCl_2$ was added to the system as a water-soluble inhibitor to depress the polymerization there in accordance to the previous articles.

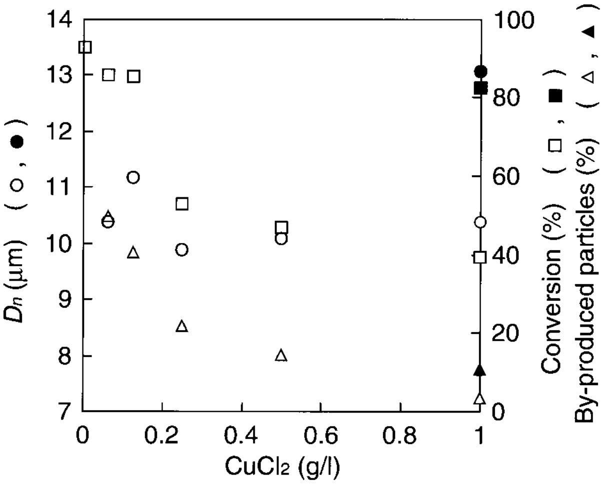

Figure 9 Effects of $CuCl_2$ concentration on (○, ●) the D_n values of PS particles produced by seeded polymerization under the conditions of No. 2 listed in Table II and the (□, ■) conversions of the styrene monomer and (△, ▲) the percentage of by-produced submicron-sized PS particles to the total PS. Polymerization times: (○, □, △) 24 h; (●, ■, ▲) 48 h.

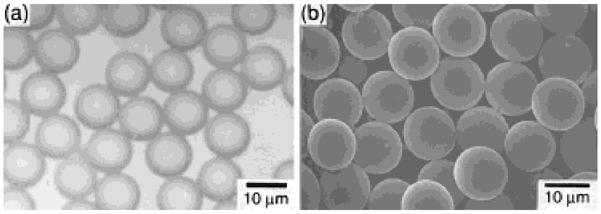

Figure 10 (a) Optical micrograph and (b) SEM photograph of PS particles produced by the seeded polymerization for 48 h (a) before and (b) after centrifugal washing under the conditions listed in Table II.

Figure 9 shows the effects of $CuCl_2$ concentration on the D_n values and the conversions of the styrene monomer and the percentage of by-produced submicron-sized PS particles to the total PS. After the polymerization for 24 h, as the $CuCl_2$ concentration increased, the conversion (□) and the percentage (△) of the by-produced submicron-sized PS particles decreased. As a result, at any $CuCl_2$ concentration, about 10-μm-sized PS particles were obtained. However, the D_n values were much smaller than was the presumed one (13.4 μm). At a $CuCl_2$ concentration of 1 g/L, after the polymerization of 48 h, the conversion (■) of styrene was 83% and the percentage (▲) of the by-produced submicron-sized PS particles was only 9.1%. The by-produced particles were easily removed by centrifugal separation.

Figure 10 shows an optical micrograph (a) and SEM photograph (b) of PS particles produced by the seeded polymerizations for 48 h after centrifugal washing. The produced PS particles had 13.1 μm in D_n and were monodispersed: D_w/D_n, 1.015; C_v, 7.6%.

From the above results, it was clarified theoretically and experimentally that there was a maximum swelling value for the preparation of monodispersed highly monomer-swollen particles by DSM. Actually, 13.1-μm-sized monodispersed PS particles were produced by one-step seeded polymerization for the dispersion in which 1.8-μm-sized PS seed particles absorbed 500 times the weight of the styrene monomer.

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