Thermodynamics of High Swelling of Polymer Particles with a Large Amount of Monomer Utilizing the Dynamic Swelling Method

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SYNOPSIS

Recently, we suggested a novel swelling method to make polymer seed particles absorb a large amount of monomer prior to the seeded polymerization for preparing monodispersed polymer particles having diameter above 5 μm, which we named the "dynamic swelling method." This article discusses the thermodynamic background of this method, both theoretically and experimentally. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

We have been trying to produce micron-sized monodispersed functional polymer particles by seeded dispersion polymerization.[1-3] 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.[4,5] Here, the high swelling was carried out by slow, continuous, dropwise addition of water with a microfeeder into ethanol/water solution dissolving styrene (S) monomer, benzoyl peroxide (BPO) initiator, and 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 S monomer and BPO, which were gradually separated from the medium by the dropwise water addition, resulting in 8.5-μm-sized monodispersed monomer–swollen polymer particles. A similar high swelling was obtained by continuously cooling the dispersion,[6] in which monomers were gradually separated from the medium on the basis of the decreased solubility of

monomer that accompanied lowering of the temperature. We named this the "dynamic swelling method" (DSM).

In this article, a thermodynamic background of this method will be discussed.

EXPERIMENTAL

The diameters of droplets formed by monomers separated from homogeneous mixtures of ethanol/water/S utilizing DSM were determined by dynamic light scattering with an Otsuka Electronics DLS-700 particle analyzer at the angle of 90 degrees.

RESULTS AND DISCUSSION

Thermodynamic Treatment Under Equilibrium State

For the equilibrium distribution of monomer in a general emulsion polymerization system in which micron-sized monomer droplets and submicron-sized monomer-swollen polymer particles are dispersed in water, Morton and colleagues[7] gave the following basic equation by using the Flory–Huggins equation for the free energy of mixing and the Gibbs–Thomas equation for the interfacial free energy.
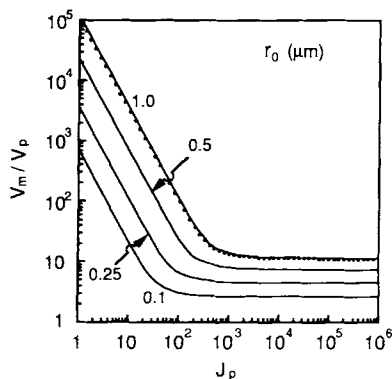

Figure 1 Simulation of the swelling ratio (V_m/V_p) as a function of the degree of polymerization (J_p) using eq. (1) with the following values: X_{mp}, 0.5; $\bar{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m. Dotted line: r_0, 0.92 μm.

$$\frac{\overline{\Delta G}}{RT} = \ln(1 - \phi_p) + \left(1 - \frac{1}{J_p}\right)\phi_p$$

$$+ X_{mp}\phi_p^2 + \frac{2\bar{V}_m\gamma}{RT}\frac{1}{r_s} = 0 \quad (1)$$

where subscripts m, p, and s denote monomer, seed polymer, and swollen particle, respectively. The $\overline{\Delta G}$ is the partial molar free energy of monomer, ϕ_p is the volume fraction of the seed polymer, J_p is the degree of polymerization of the seed polymer, X_{mp} is the Flory–Huggins interaction parameter between the monomer and the seed polymer, $\bar{V}_m$ is the molar volume of the monomer, R is the gas constant, T is the absolute temperature, and γ is the interfacial tension between the swollen polymer particle and the medium. The radius of the swollen polymer particle, r_s, is given by

$$r_s = \phi_p^{-1/3}r_0 \quad (2)$$

where r_0 is the radius of the seed particle. Gardon[8] calculated the swelling volume ratios (V_m/V_p) of various kinds of polymer particles with their own monomers as a function of r_0/γ for various values of X_{mp}, where V_p and V_m are, respectively, the volumes of seed polymer and absorbed monomer. The calculated V_m/V_p values are not large, e.g., at most 2–7. They are almost in accord with experimental data obtained in equilibrium absorption states. In order to produce micron-sized polymer particles whose volume corresponds to about 100 times that of submicron-sized seed particles, seeded emulsion polymerization must be repeated several times.

Ugelstad and coworkers,[9–12] using eq. (1), showed that seed particles consisting of low J_p polymers can

absorb a large amount of monomer, and proposed the "two-step swelling method" in which a low-molecular-weight, highly water-insoluble compound as a swelling agent is absorbed in the first step instead of using a low J_p seed polymer prior to monomer absorption in the second step.

Figures 1, 2, and 3 show, respectively, the simulations of V_m/V_p values as a function of the J_p at the various r_0 values and as a function of r_0 at the various J_p values, and of r_s value as a function of r_0 at the various J_p values, using eq. (1) with $X_{mp} = 0.5$, $\bar{V}_m = 1 \times 10^{-4}$ m³/mol, $\gamma = 5$ mN/m, $R = 8.314$ m² kg s⁻² K⁻¹ mol⁻¹ and $T = 300$ K, where the V_m/V_p is given by

$$V_m/V_p = \phi_p^{-1} - 1 \quad (3)$$

In Figure 1, the V_m/V_p values at the various r_0 values drastically increase with a decrease in the J_p value to less than 1000, because of increased chemical potential contribution due to free energy of mixing. In Figures 2 and 3, the V_m/V_p and r_s values at the various J_p values, respectively, increase with an increase in r_0 value because of decreased chemical potential contribution due to interfacial free energy. The dotted lines in Figures 1–5 show the simulation curves calculated using $r_0 = 0.92$ μm and $J_p = 1400$, which were, respectively, the radius and the degree of polymerization for the PS seed particles used in the DSM systems conducted experimentally in the previous articles.[4,6] As shown in the dotted lines in Figures 1 and 2, the V_m/V_p values calculated for the 1.8-μm-sized $(r_0 = 0.92 \mu$m) PS $(J_p = 1400)$ seed particles used in the previous DSM experiment[6] were about 10, and as shown by the dotted line in Figure 3, the seed particles only swell to 4 μm (r_s
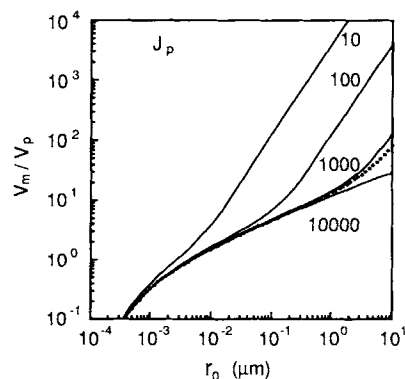

Figure 2 Simulation of the V_m/V_p as a function of the radius of the seed particles (r_0) using eq. (1) with the following values: X_{mp}, 0.5; $\bar{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m. Dotted line: J_p, 1400.
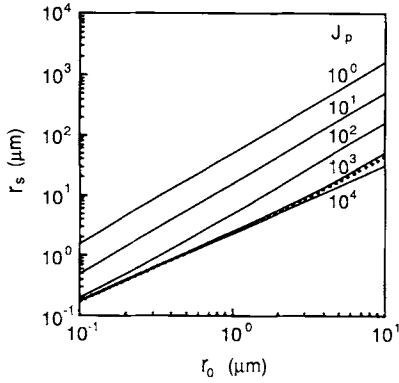
Figure 3 Simulation of the radius of the swollen particles (r_s) as a function of the radius of the seed particles (r_0) using eq. (1) with the following values: χ_{mp}, 0.5; $\bar{V}_m$, 1 $\times$ 10^{-4} m^3/mol; γ, 5 mN/m. Dotted line: J_p, 1400.

= 2 μm) at most. In this way, using eq. (1) we cannot reasonably explain the thermodynamic background for the result that the 1.8-μm-sized PS seed particles swelled with S monomer to a size of 8.5 μm utilizing the DSM in the previous article.[4]

In the conventional swelling method, since the size of monomer droplets is much larger than that of seed particles, the thermodynamic background can be discussed using eq. (1).[11,12] However, in the DSM, since the size of monomer droplets formed by monomers separated continuously from the medium is much smaller than that of seed particles, as shown later, we should discuss it using eq. (4).

$$\frac{\overline{\Delta G}}{RT} = \ln(1 - \phi_p) + \left(1 - \frac{1}{J_p}\right)\phi_p$$

$$+ \chi_{mp}\phi_p^2 + \frac{2\bar{V}_m}{RT}\left(\frac{\gamma}{r_s} - \frac{\gamma_m}{r_m}\right) = 0 \quad (4)$$

where r_m is the monomer droplet radius and γ_m is the interfacial tension between monomer droplet and medium. That is, the chemical potential contribution due to the interfacial free energy of monomer droplets cannot be neglected. Actually, Jannson and colleagues[13] confirmed experimentally that the particles absorbed above 10 times the volume of monomer when small-sized monomer droplets prepared by a hand-pump homogenizer were added to 0.49-μm-sized PS seed emulsion.

Figures 4 and 5 show, respectively, the simulations of V_m/V_p values as a function of r_m at the various J_p and r_0 values using eq. (4), where, for convenience, 5 mN/m was applied for γ_m as well as γ. It is no problem for our conclusion. In Figure 4, the V_m/V_p values increase infinitely with a decrease in
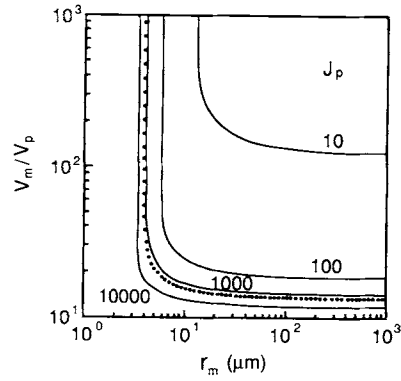

Figure 4 Simulation of the V_m/V_p as a function of the radius of the monomer droplets (r_m) using eq. (4) with the following values: r_0, 1.0 μm; χ_{mp}, 0.5; $\bar{V}_m$, 1 $\times$ 10^{-4} m^3/mol; γ, 5 mN/m. Dotted line: r_0, 0.92 μm; J_p, 1400.

the r_m value below about 3 μm. That is, a large amount of monomer is absorbed into seed polymer particles by preparing smaller monomer droplets than swollen particles, because of increased chemical potential contribution from the interfacial energy of monomer droplets. In Figure 5, at r_0 values less than 0.25 μm, which are in the size range of particles produced by a conventional emulsion polymerization, the simulation in the thermodynamic equilibrium state indicates that it is difficult to produce micron-sized monomer-swollen particles even when r_m is 1 μm. On the other hand, at r_0 values greater than 0.5 μm, which are in the size range of particles produced by a conventional dispersion polymerization, the simulation indicates that highly monomer-swollen polymer particles can be produced by using monomer droplets having r_m values below about 3 μm.

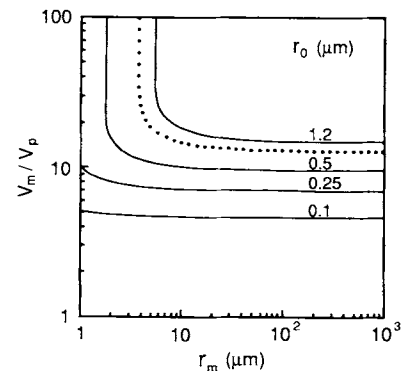We examined experimentally the diameter of monomer droplets formed using DSM, as follows.

Figure 5 Simulation of the V_m/V_p as a function of the radius of the monomer droplets (r_m) using eq. (4) with the following values: χ_{mp}, 0.5; $\bar{V}_m$, 1 $\times$ 10^{-4} m^3/mol; γ, 5 mN/m; J_p, 1400. Dotted line: r_0, 0.92 μm.
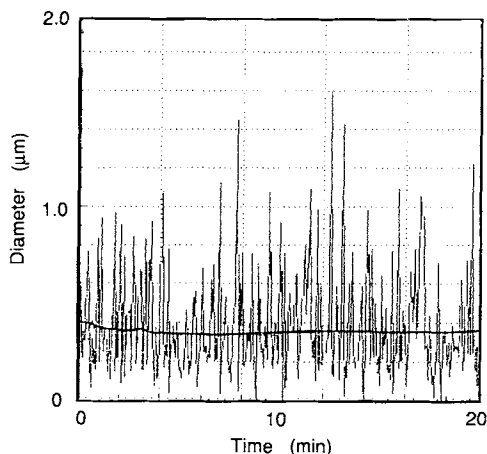
Figure 6 The variation of diameter of S droplets prepared by slow dropwise water addition to the homogeneous solution of S/ethanol/water at 20°C.
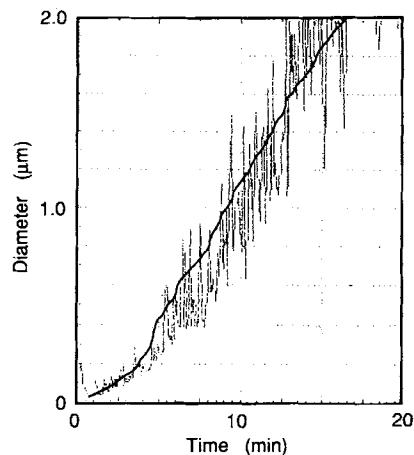

Figure 7 The variation of diameter of S droplets separated by cooling the homogeneous solution of S/ethanol/water from 60°C to 10°C.

Figure 6 shows the variation of diameter of droplets formed by monomers separated from the homogeneous solution of 0.504 g (S, 4 mg; ethanol, 0.5 g) by stepwise water addition of 3.3 g with standing time without stirring. Under the final state, our calculation shows that a small percentage of the total amount of monomer should be separated from the homogeneous solution, resulting in droplets. During the measured time, the diameter of monomer droplets was almost constant at 0.35 μm. This means that the monomer droplets did not coagulate, at least within that time, although there was no stabilizer.

Figure 7 shows the variation of diameter of droplets formed by monomers separated from the homogeneous solution of S (9 mg)/ethanol (1 g)/water (4.5 g) by cooling at a rate of 1°C/min from 60°C to 10°C. The diameter increased from about 0.02 μm with the time where the monomer separation proceeded continuously.

These experimentally measured diameters of monomer droplets prepared by DSM were small enough in comparison with the calculated diameter of monomer droplets needed to make the seed particles absorb a large amount of monomer—above 100 times, as shown in Figure 4.

Figure 8 shows the simulation of the chemical potential ($\overline{\Delta G}$) of monomer in this system as a function of the swelling ratio (V_m/V_p) using eq. (4) with $r_m = 0.175$ μm, which corresponds to the radius of monomer droplets formed in the experiment shown in Figure 6. Other parameter values were the same as those used for the simulations in Figures 1–5. As shown in Figure 8, because the $\overline{\Delta G}$ value is negative at any V_m/V_p, all monomers are absorbed in seed particles. In this way, high swelling of seed particles

with monomer by DSM can reasonably be explained from thermodynamic treatment under equilibrium state.

Thermodynamic Treatment Under Dynamic State

Though monomer droplets having r_m value of about 1 μm can easily be prepared in water by ordinary stirring, highly monomer-swollen polymer particles were not experimentally prepared by a conventional swelling method (CSM), in which the medium is water, even at r_0 values above 0.5 μm. This seems to be based on a low absorption rate of monomer into polymer particles, as described below.

On the transfer process of monomer molecules from monomer droplets to swelling particles via medium, the diffusion of monomer molecules in the
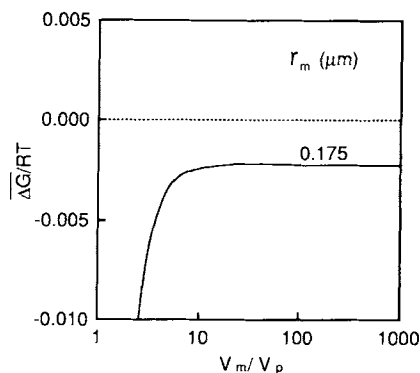

Figure 8 Simulation of the chemical potential of monomer in system as a function of the V_m/V_p value using eq. (4) with the following values: r_m, 0.175 μm; χ_{mp}, 0.5; $\overline{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m; r_0, 0.92 μm; J_p, 1400.

medium may be the rate-determining step, assuming monomer droplets disappear only according to the process of molecular diffusion. The absorption rate of monomers into the polymer particles was calculated by Ugelstad and coworkers[11,12] using eq. (5).

$$\frac{dV_m}{dt} = 4\pi DC \left\{ \exp\left(\frac{\overline{\Delta G_m}}{RT}\right) \right.$$
$$\left. - \exp\left(\frac{\overline{\Delta G_s}}{RT}\right) \right\} \left(\frac{1}{r_s N_s} + \frac{1}{r_m N_m}\right)^{-1} \quad (5)$$

where D is the diffusion coefficient of monomer in medium; N_m and N_s are, respectively, the numbers of monomer droplets and swelling particles; C is a saturated monomer concentration in the medium; and $\overline{\Delta G_m}$ and $\overline{\Delta G_s}$ are, respectively, free energies of the monomer droplet and the swelling particle, where $\overline{\Delta G_m}$ and $\overline{\Delta G_s}$ are expressed as follows using eqs. (1) and (3):

$$\frac{\overline{\Delta G_m}}{RT} = \frac{2\bar{V}_m\gamma}{RT}\frac{1}{r_m}, \quad \frac{\overline{\Delta G_s}}{RT} = \ln\left(\frac{V_m}{V_m + V_p}\right)$$
$$+ \left(1 - \frac{1}{J_p}\right)\frac{V_m}{V_m + V_p} + \chi_{mp}\left(\frac{V_m}{V_m + V_p}\right)^2 + \frac{2\bar{V}_m\gamma}{RT}\frac{1}{r_s}$$

Figure 9 shows the simulations of the V_m/V_p values calculated as a function of the time at various r_m values in a CSM using eq. (5) with C_W (C in water) = 6×10^{-4} m³/m³ and $D = 10^{-10}$ m²/s for styrene at 50°C in water, as quoted in the literature.[12] The number of monomer droplets per m³, N_m, was determined with the constant r_m value and the volume of the monomer. The number of initial seed particles per m³, N_s, used is 9.54×10^{15}, the concentration used in the DSM system in the previous article.[4] The simulation curves indicate that the absorption rate of monomer is extremely slow even at the r_m value of 1 μm. This seems to be one reason why highly monomer-swollen particles are not produced by the CSM as described above; that is, the CSM system has a disadvantage for the absorption rate of monomer into polymer particles.

In the DSM system with water-addition process conducted in the previous article,[4] the ethanol content in ethanol/water mixture as medium decreases with the water-addition time. The S monomer concentration before the water addition was 40 kg/m³, which corresponds to a concentration just less than the saturated concentration in the medium. Since the saturated S monomer concentration in the medium decreases with a decrease in the ethanol con-
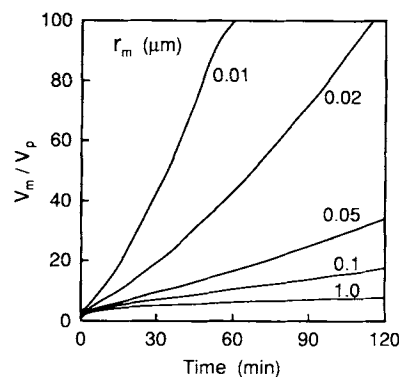

Figure 9 Simulation of the V_m/V_p as a function of time at various r_m values in CSM system using eq. (5) with following values: D, 10^{-10} m²/sec; C, 6×10^{-4} m³/m³; r_0, 0.92 μm; $\bar{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m; N_s, 9.54×10^9 per mL; $(V_m/V_p)_{max}$, 110.

tent, S monomer is continuously separated from the medium with the water-addition time. In the experiment, the ethanol content in the medium of 10.3×10^{-6} m³ before the water addition was 55 vol % and the rate of water addition was 2.88×10^{-6} m³/h. The C value is calculated using eq. (6):

$$C(\text{m}^3/\text{m}^3) = 3.03 \times 10^{-4} \exp\left(\frac{44.2}{8.97 + 8 \times 10^{-4} \cdot t}\right)$$
$$(6)$$

where t is the water-addition time (in seconds). The equation was obtained using the solubility value of S monomer in the various ethanol contents measured at 20°C in the previous articles.[4]

Figures 10 and 11 show the simulations of V_m/V_p values as a function of the time at the various r_m values using eq. (5) in the above water-addition system and in the cooling system, respectively. The dotted lines indicate the V_m/V_p value calculated assuming that all separated S monomers are instantly absorbed by PS seed particles. The C value was calculated in both the cooling and the water-addition systems, where D value of 10^{-10} m²/s is used for convenience, which is the same value as that used for the simulation shown in Figure 9. N_m values were calculated from the r_m values and the volume of the monomer separated from the ethanol/water medium. In Figure 10, the simulation curves obtained at r_m values less than 0.5 μm indicate that the absorption rate of monomer into PS seed particles is faster than its separation rate from ethanol/water medium with water addition. The r_m value of 0.175 μm measured by DLS in Figure 6 was small enough in comparison with that of 0.5 μm; that is, it is pos-
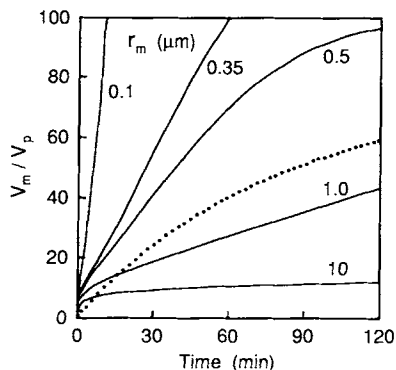
Figure 10 Simulation of the V_m/V_p as a function of water-addition time in DSM system at various r_m values using eq. (5) with the following values: D, 10^{-10} m²/sec; C, variable; r_0, 0.92 μm; $\bar{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m; N_s, 9.54 $\times$ 10⁹ per mL; $(V_m/V_p)_{max}$, 110. Dotted line indicates V_m/V_p calculated using the solubility curve of S monomer in ethanol/water mixture assuming that all S monomers separated are absorbed by PS seed particles.

Figure 11 Simulation of the V_m/V_p as a function of cooling time in DSM system at various r_m values using eq. (5) with the following values: D, 10^{-10} m²/sec; C, variable; r_0, 0.92 μm; $\bar{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m; N_s, 9.54 $\times$ 10⁹ per mL; $(V_m/V_p)_{max}$, 110. Dotted line indicates V_m/V_p calculated using the solubility curve of S monomer in ethanol/water mixture assuming that all S monomers separated are absorbed by PS seed particles.
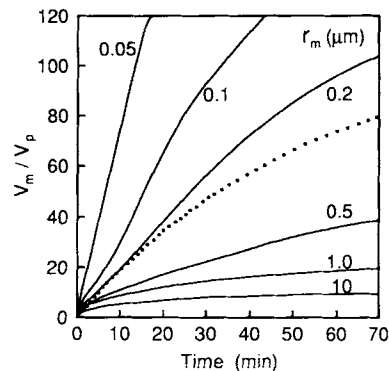
sible that under the conditions PS seed particles absorb all separated S monomers. The results in Figures 7 and 11 indicate that PS seed particles can absorb all separated S monomers in the cooling system as well as the water-addition system.

The results at the same r_m value (0.1 μm) shown in Figures 9, 10, and 11 indicate that the absorption rate of monomer in the DSM system is much higher than that in the CSM. This is based on C values in the DSM systems being much higher than those in the CSM system.

In the DSM system before the water addition, the initial concentration of monomer in medium (C_0) is adjusted to be just below the saturated concentration. In the system containing no monomer droplets, the chemical potential of monomer in medium is presented as $\overline{\Delta G_w} = RT \ln a$, where a is the activity of monomer in the medium. Since the $\overline{\Delta G_m}$ is changed to $\overline{\Delta G_w}$ and r_m and N_m terms disappear, eq. (5) is simplified to

$$\frac{dV_m}{dt} = 4\pi DC_0 r_s N_s \left\{ 1 - \exp\left(\frac{\overline{\Delta G_s}}{RT}\right) \right\} \qquad (7)$$

Using eq. (7) with $D = 10^{-10}$ m²/s and $C_0 = 3.76 \times 10^{-2}$ m³/m³, V_m/V_p values in the system were simulated as a function of the time.

Figure 12 shows the result. The dotted line is the same one as that in the DSM system shown in Figure 10. The simulation curve (line) indicates that the V_m/V_p value at the initial stage increases much faster than that calculated (dotted line) assuming that all monomers separated from the medium in

the DSM system are absorbed by PS seed particles; but attains the saturated value within a short time, which corresponds to only about 2 times the amount of the seed polymer. In the system containing no monomer droplets and a high C value in ethanol/water medium, large amounts of monomer as well as DSM system cannot be absorbed into seed particles, as shown in Figure 12. This clearly indicates that the presence of small monomer droplets as well as a high C value is important in generating a high enough absorption rate of monomer into seed particles. That is, the size of monomer droplets is an
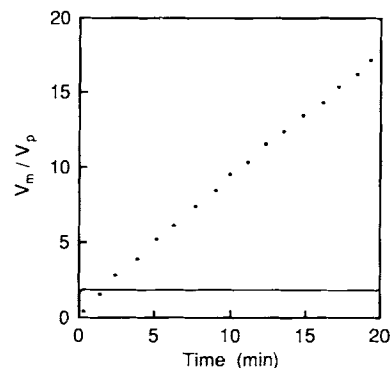
Figure 12 Simulation of the V_m/V_p as a function of time using eq. (7) with the following values: D, 10^{-10} m²/sec; C_0, 3.76 $\times$ 10^{-2} m³/m³; r_0, 0.92 μm; $\bar{V}_m$, 1×10^{-4} m³/mol; γ, 5 mN/m; N_s, 9.54 $\times$ 10⁹ per mL; $(V_m/V_p)_{max}$, 110. Dotted line indicates V_m/V_p calculated using the solubility curve of S monomer in ethanol/water mixture assuming that all S monomers separated are absorbed by PS seed particles.

important factor in the thermodynamic treatment of the dynamic state as well as the equilibrium state.

These results indicate that the absorption rate of monomer into polymer particles in the DSM system is much higher than those in the CSM system and in the system containing no monomer droplets and a high C value in ethanol/water medium, because of both parameters of C and r_m.

From the above results, we concluded that the theoretical background of DSM was clarified from the thermodynamic treatment under equilibrium and dynamic states.

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