POLYMER PARTICLE FORMATION IN STYRENE POLYMERIZATION IN AQUEOUS MEDIA AT LOW SURFACTANT CONCENTRATIONS

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Emulsion polymerizations of styrene were carried out in the absence and presence of a surfactant and the number of polymer particles was measured mainly in a range of surfactant concentrations up to the critical micelle concentration with a change in initiator concentration. Experimental results for the number of polymer particles in the absence of the surfactant were compared with predictions from a homogeneous nucleation model which includes the assumption that the rate of radical entrance into the polymer particles is proportional to particle surface area uncovered by ionic end-groups of polymers contained in the polymer particles. The model also takes into account electrostatic effects on radical entrance into the polymer particles and coagulation between polymer particles. The experimental results in the absence of the surfactant compared well with the predictions. The model was extended to the reaction system in the presence of the surfactant, taking into consideration surfactant adsorption to the polymer particles and the adhesion of surfactant molecules to growing radicals. The model predicted well the tendency of the experimental results of the number of particles.

Introduction

Soapless emulsion polymerizations are utilized in the production of a wide variety of polymer latex particles. When appropriate reaction conditions are selected in these polymerizations, the particles produced have high purity and a high uniformity of particle size in comparison with those produced in conventional emulsion polymerizations, which are conducted in the presence of added surfactant above the critical micelle concentration (CMC).

Knowledge of the mechanism of polymer particle formation is important for the control of particle size. For soapless emulsion polymerization, Fitch *et al.*^{10,11)} proposed a mechanism which implies that primary particles are formed in the aqueous phase by precipitations of oligomeric radicals above a critical

chain length. The basic principle of this mechanism is that nucleation of the primary particles will take place up to a point where the rate of formation of radicals in the aqueous phase balances the rate of disappearance of the radicals by their entrance into already formed particles. Fitch's model of homogeneous particle nucleation was extended and modified by previous investigators. Hansen and Ugelstad¹⁴⁾ took the coagulation of the primary particles into account for particle formation. They applied the DLVO theory to particle coagulation and also to estimation of the capture rate of the radicals by the polymer particles. Arai *et al.*⁴⁾ added a term of polymer particle precipitation for termination reaction to the term for propagation reaction, and considered the effect of particle growth on the capture rate of radicals. To date, a number of other developed models^{9,12)} have also been proposed for soapless emulsion polymerizations, but a quantitative conclusion has not

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yet been reached because of the complexity of the phenomena.

Polymer particle nucleation of the conventional emulsion polymerizations has been intensively investigated. However, even in conventional emulsion polymerization the nucleation mechanism has sometimes been disputed. As is well-known, the classical theory of Smith-Ewart²⁵⁾ was proposed for conventional emulsion polymerizations. This model assumed the entry of radicals into micelles,¹⁵⁾ and succeeded in describing the dependence of the number of polymer particles on initiator and surfactant concentrations. However, Roe²³⁾ has shown that it is possible for the homogeneous nucleation mechanism to lead to the same expression for the number of particles as the mechanism derived by Smith-Ewart. Recently, Feeney *et al.*⁸⁾ reported experimental results suggesting that the Smith-Ewart theory cannot be applied to the explanation of the size distributions of polymer particles formed in the conventional emulsion polymerizations.

Most work by previous investigators was directed towards soapless emulsion polymerizations or conventional emulsion polymerizations, and very limited work^{16,23)} has been reported on emulsion polymerizations at subcritical concentrations of surfactants. However, experiments in this subrange may offer a key to the better understanding of particle formation in emulsion polymerizations.

Usually, polymer particles formed in soapless emulsion polymerizations are not so stably dispersed as those formed in conventional emulsion polymerizations. Therefore, surfactants may be added to soapless emulsion polymerization systems as long as the addition of surfactants does not compromise the required level of purity of product.

The present study is focused on the clarification of the nucleation mechanism of emulsion polymerizations in the range of subcritical surfactant concentrations. Polymerization experiments were carried out in the absence as well as in the presence of a surfactant at low surfactant concentrations. A homogeneous nucleation model is proposed to explain the experimental results of the numbers of polymer particles measured at various reaction conditions.

1. Experiments

An isothermal batch reactor with an inner volume of $0.5 \times 10^{-4} \text{ m}^3$ was used for the emulsion polymerizations of styrene. The reactor was a round-bottomed four-necked glass flask equipped with a T-shaped glass stirrer of 0.02 m in diameter. All the polymerizations were conducted in a nitrogen atmosphere using the following materials: styrene (Wako Co. Ltd., First grade) which was freed of inhibitor, dried and purified by rectification under

nitrogen at reduced pressure; an initiator, potassium persulfate (Wako Co. Ltd., Special grade), which was recrystallized twice from distilled water; a surfactant, sodium dodecylsulfate (Wako Co. Ltd., Special grade), which was doubly recrystallized from methanol and dried; and water which was distilled and deionized.

The desired amounts of the water, monomer and surfactant were added to the reactor, in which nitrogen was bubbled through the water to remove oxygen from the system. Then, agitation was started at a given speed and the aqueous solution of the initiator was put into the reactor. Each polymerization was performed at 70°C ($\pm 0.5^\circ\text{C}$) and an initial monomer concentration of 300 mol/m^3 with an initial volume of total reaction mixture of $4 \times 10^{-4} \text{ m}^3$. At appropriate intervals during the polymerization, a small amount of the reaction mixture (less than $2 \times 10^{-5} \text{ m}^3$) was taken from the reactor as a sample, to which hydroquinone was added to stop the polymerization.

After evacuation treatment for the removal of residual monomer the sample was subjected to measurements of monomer-to-polymer conversion and polymer particle diameters. The conversion was determined by weighing the polymer formed. More than 30 polymer particle diameters were measured by electron micrography to determine the volume-averaged diameter, d_v , defined as follows:

$$d_v = (\sum n_i d_i^3 / \sum n_i)^{1/3} \quad (1)$$

From the average diameter, the number of polymer particles, N_p , was calculated by the following equation:

$$N_p = M_0 M_w X / (\pi/6) d_v^3 \rho_p \quad (2)$$

2. Results

In previous works^{2,18,19)} the authors showed that emulsion polymerizations can be affected by agitation in the case of low speeds of stirring. However, the present work was restricted to the condition of sufficient stirring. Experimentally it was confirmed that both conversion and number of polymer particles were not affected by stirring speed in the region above 500 rpm. Some examples of those results are presented in **Figs. 1 and 2**, in which the surfactant concentration, S , ranges from 0 to 3.0 mol/m^3 at different stirring speeds. The figures show no significant dependence of the experimental results on stirring speed. It should also be noted that the number of polymer particles remains almost constant over the whole range of conversions measured. This suggests that polymer particle nucleation was completed at a very early stage of polymerization and that thereafter a stable dispersion of particles was maintained. This inference may also be supported by experimental evidence that

Fig. 1. Conversion versus reaction time at different stirring speeds ($I=2 \text{ mol/m}^3$)

Fig. 2. Number of polymer particles versus conversion at different stirring speeds ($I=2 \text{ mol/m}^3$)

polymer particles formed were highly uniform in size, as shown in Fig. 3.

Figure 4 shows the plot of the number of particles against the surfactant concentration measured at an initiator concentration of 2.0 mol/m^3 . The CMC of the surfactant in water is about 10 mol/m^3 , which is indicated by the arrow in the figure. Above the CMC the number of particles increases with the surfactant concentration, S , in accordance with the power law $N_p \propto S^{0.6}$ which is predicted by the Smith-Ewart theory for conventional polymerizations.

Figure 5 shows the dependence of the number of particles on the initiator concentration measured at three surfactant concentrations. At surfactant concentrations of 3 and 5.5 mol/m^3 the particle number increases sharply with increase in the initiator concentration in the range above 4 mol/m^3 . In discussing this point, we should take notice of the effect of the initiator concentration on the CMC. Since

Fig. 3. Electron micrographs of polymer particles: a) $S=0 \text{ mol/m}^3$, $I=2.0 \text{ mol/m}^3$, $X=0.92$, $N_p=1.2 \times 10^{18} \text{ m}^{-3}$; b) $S=5.5 \text{ mol/m}^3$, $I=2.0 \text{ mol/m}^3$, $N_p=1.5 \times 10^{19} \text{ m}^{-3}$

Fig. 4. Number of polymer particles versus surfactant concentration ($I=2.0 \text{ mol/m}^3$)

Fig. 5. Number of polymer particles versus initiator concentration in the absence and presence of K_2SO_4 at $S=5.5 \text{ mol/m}^3$: (□) data in the absence at initiator concentrations (1) 0.4, (2) 3.0 and (3) 5.5 mol/m^3 ; (○) data at a constant ionic strength adjusted by the addition of K_2SO_4

the initiator dissociates into ions in water, addition of the initiator lowers the CMC.⁵⁾ If the reduction in the CMC is responsible for the sharp increase in the number of particles, the addition of an electrolyte will have a significant effect on particle formation in the range where the sharp increase in the number of particles was observed. From this expectation, the present work included additional polymerization experiments, whose results are presented as the open circles in Fig. 5. In the additional experiments, an electrolyte, K_2SO_4 , was added to the system in order to adjust ionic strength to that of the experiment conducted at an initiator concentration of 8 mol/m^3 and a surfactant concentration of 5.5 mol/m^3 in the absence of the electrolyte. Interestingly, when the ionic strength was kept constant the experimental data revealed a relation similar to $N_p \propto I^{0.4}$ for conventional emulsion polymerizations. It can also be seen that the addition of the electrolyte greatly increased the number of polymer particle. This suggests that the sharp increase in the high initiator concentration range in the absence of K_2SO_4 resulted from the reduction in the CMC.

3. Estimation of the Number of Particles

In this section we will derive a nucleation model for the range below the CMC. First we will discuss problems encountered in the absence of the surfactant.

3.1 Soapless emulsion polymerization

Previously, some of the present authors⁴⁾ proposed a homogeneous nucleation model. The model did not take the coagulation of nucleated particles into account, and it may be more accurate to introduce this effect. In that case we should consider the reduction effect on the coagulation owing to electrostatic repulsion between the nucleated particles. The evolution equation for the number of polymer particles is expressed as follows:

$$\frac{dN_p}{dt} = k_p M_L R_J + (k_t/2) \cdot \sum_{i=1}^J R_i \sum_{j=1}^i R_{J+1-j} - (4k_b T/3\eta) N_p^2 / W_{pp} \quad (3)$$

Fuch's stability ratio concerning the coagulation among the polymer particles, W_{pp} , in the above equation is given by

$$W_{pp} = 2r_p \int_0^\infty \exp\{V_t(h)/k_b T\} dh / (2r_p + h)^2 \quad (4)$$

$V_t(h)$ in Eq. (4) is the total potential energy of interaction, expressed by the DLVO theory for homocoagulation:

$$V_t(h) = -(Ar_p/12h) + \epsilon r_p^2 \phi_p^2 / (2r_p + h) \exp(-kh) \quad (5)$$

On the other hand, the population balance of the growing radicals in the aqueous phase can be given

by

$$\frac{dR_1}{dt} = 2k_d f I - k_p M_L R_1 - k_t R_1 \sum_{i=1}^J R_i - 4\pi(D_p + D_i)(r_p + r_i)N_p R_1 / W_{p1} \quad (6)$$

$$\frac{dR_i}{dt} = k_p M_L R_{i-1} - k_p M_L R_i - k_t R_i \sum_{i=1}^J R_i - 4\pi(D_p + D_i)(r_p + r_i)N_p R_i / W_{pi} \quad (\text{for } i=2 \text{ to } J) \quad (7)$$

The stability factor, W_{pi} , is introduced in the present model according to Hansen and Ugelstad,¹⁴⁾ and is expressed as

$$W_{pi} = 2 \int_2^\infty \exp(V_t'(h)/k_b T) dS / S^2 \quad (8)$$

where

$$S = 2(r_p + r_e + h) / (r_p + r_e) \quad (9)$$

In Eqs. (6) and (7) the first term expresses the radical formation rate by the initiator decomposition or propagation, and the second, third and fourth terms are the radical disappearance rates by propagation, termination and entry of the radicals into polymer particles, respectively. The diffusion coefficients can be estimated by the Stokes-Einstein equation and Wilke's equation:

$$D_p = k_b T / 6\pi\eta r_p \quad (10)$$

$$D_i = D / (i+1)^{0.6} \quad (11)$$

To facilitate analysis, a homogeneous distribution of the polymer particle sizes is assumed, and hence the value of r_p can be related to the total volume of the polymer particles, V_p :

$$r_p = \{(3/4\pi)(V_p/N_p)\}^{1/3} \quad (12)$$

As explained in our previous work,⁴⁾ the time variation of total volume can be formulated by considering three processes: the nucleation of polymer particles, the entrance of radicals into polymer particles and the propagation reaction in polymer particles. Accordingly,

$$\begin{aligned} \frac{dV_p}{dt} = & k_p M_L R_J (J+1) V_u + k_p M_p n (N_p / N_a) V_u \\ & + (k_t/2) V_u \sum_{i=1}^J \left\{ R_i \sum_{j=1}^i (J+1+i-j) R_{J+1-j} \right\} \\ & + 4\pi V_u N_p \sum_{i=1}^J \{ i(D_p + D_i)(r_p + r_i) R_i / W_{pi} \} \quad (13) \end{aligned}$$

The value of n can be approximated by 1/2 in the processes of particle formation.⁴⁾

The value of r_i in Eqs. (6) and (7) is estimated by Eq. (14):

$$r_i = k_b T / (6\pi\eta D_i) \quad (14)$$

In the diffusion of ionic molecules of low molecular weight, electrostatic force¹⁷⁾ dominates over the van der Waals attraction force. In other words, the integration in Eq. (8) is mainly determined by the electrostatic potential. Therefore,

$$V_t'(h) = \frac{\varepsilon r_p r_e (\varphi_p^2 + \varphi_e^2)}{4(r_p + r_e)} \left[\frac{2\varphi_p \varphi_e}{\varphi_p^2 + \varphi_e^2} \ln \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} + \ln \{1 - \exp(-2\kappa h)\} \right] \quad (15)$$

Following Hansen and Ugelstad,¹⁴⁾ φ_e is assumed to be approximated by

$$\varphi_e = Ze / \{\varepsilon r_e (1 + \kappa r_e)\} \quad (16)$$

Electrolyte valency, Z , equals 2 for the sulfate ion.

Similarly, the surface potential of the polymer particle is given by

$$\varphi_p = Ze E_p / (\varepsilon r_p (1 + \kappa r_p)) \quad (17)$$

where

$$E_p = E_r + E_s \quad (18)$$

The value of E_r is expressed as the summation of three terms arising from the entrance of the radicals into polymer particles and the precipitation by both the propagation and termination reactions of the radicals, as presented in Eq. (19):

$$N_p E_r = n_{rc} + n_{rp} + 2n_{rt} \quad (19)$$

The evolution of each of these quantities is given as follows:

$$dn_{rc}/dt = \sum_{i=1}^J \{4\pi(D_p + D_i)(r_p + r_i)N_p R_i / W_{pi}\} N_a \quad (20)$$

$$dn_{rp}/dt = k_p M_L R_J N_a \quad (21)$$

$$dn_{rt}/dt = (k_t/2) \sum_{i=1}^J R_i \left(\sum_{j=1}^i R_{J+1-j} \right) N_a \quad (22)$$

For the polymerization system in the absence of surfactants, we can calculate the nucleation process using the above equations. Calculations were performed on a digital computer with application of the Runge-Kutta-Maison method to the physical properties and the parameter values listed in **Table 1**.

Figure 6 shows the evolution of the number of polymer particles calculated at an initial initiator concentration of 2 mol/m³. Only in the early stage of the reaction does the number sharply increase with time; shortly it reaches a steady value, indicating that nucleation of the particles is completed within a very short period.

In **Fig. 7**, steady-state number of particle calculated at various initiator concentrations are presented as a solid line, together with experimental ones denoted by closed circles. Before we compare the calculated results

Table 1. Physical properties and parameter values used in calculations

Parameter	Value	Reference
A	0.5×10^{-20} (J)	(21)
D	2.4×10^{-9} (m ² /s)	(21)
f	1 (—)	(6)
J	5 (—)	(14)
k_d	2.7×10^{-5} (1/s)	(6)
k_p	2.48×10^2 (m ³ /kmol·s)	(6)
k_t	7.99×10^7 (m ³ /kmol·s)	(6)
M_L	6.1×10^{-3} (kmol/m ³)	(7)
M_p	7.0 (kmol/m ³)	(14)
r_e	2.0×10^{-10} (m)	(*)
R_s	16×10^{-10} (m)	(*)
S_{cmc}	10×10^{-9} (kmol/m ³)	(21)
V_u	536 (m ³ /mol)	(**)
η	0.00041 (kg/m·s)	(21)
ρ_p	1.05×10^3 (kg/m ³)	(7)

(*) Calculated from molecular structure.

(**) Calculated from M_p and densities of polymer and monomer.

Fig. 6. Number of transient polymer particles calculated at $I = 2$ mol/m³ in the absence of surfactant

Fig. 7. Number of polymer particles versus initiator concentration in the absence of surfactant: (●) experimental; (—) calculated with W_{pi} in Eq. (8); (---) calculated with $W_{pi} = 1$; (···) calculated with W_{pi} in Eq. (24)

with the experimental ones, it is meaningful to examine how the electrostatic repulsion force affects the number of particles in the present model. The broken line in Fig. 7 shows numbers of particles calculated with $W_{pi}=1$, which assumes the nonexistence of electrostatic repulsion between a polymer particle and a radical. Clearly, the electrostatic repulsion has a strong effect on the number of particles, and calculations involving the electrostatic effect offer better results. At low initiator concentrations the calculated results involving the electrostatic effect are almost consistent with the experimental ones. However, with increasing initiator concentration the calculated value gradually differs from the experimental results, finally revealing a different dependence on concentration.

In the calculations (solid line in Fig. 7), which involved the electrostatic repulsion, the increase in the initiator concentration was found to increase the surface potential of the polymer particle. In such a case, we might imagine simply that the increase in surface potential of the polymer particle reduces the entrance rate of the radicals into it. But according to the heterocoagulation theory regarding the collision of two particles, when the surface potential of the large particle is significantly higher than that of the smaller particle an increase in the surface potential of the larger particle tends to decrease the stability factor of the coagulation of the particles. In the present calculations, this heterogeneous effect appeared as the promotion of radical entrance into the polymer particles, which brought about a decrease in the number of particles with increase in initiator concentration.

In the calculations it was also found that the surface coverage defined by Eq. (23) could exceed unity in the early stage of reaction.

$$\theta = \pi r_e^2 E_r / 4\pi r_p^2 \quad (23)$$

However, it seems improbable for the ionic end-groups of the radicals to form multiple layers on the surface of the particles.

There are probably a number of reasons for the insufficiency of the estimation. It might result from inaccuracy inherent in the Debye-Huckel approximation or the heterogeneous nucleation theory. In addition, in the calculations the irreversible absorption of the radicals into the polymer particles was assumed, but it is highly possible for small radicals to desorb from the polymer particle, as pointed out by many investigators^{1,14}). Since it is not easy to formulate this effect accurately, we assume the following simple equation to modify the rate of radical entrance into the polymer particle:

$$1/W'_{pi} = (1 - \theta)/W_{pi} \quad (24)$$

The correction factor $(1 - \theta)$ means that the radical entrance rate is proportional to the fraction of surface not covered with ionic end-groups. This assumption only allows the formation of a single layer of ionic end-groups on the particle surface.

W'_{pi} was used in place of W_{pi} in Eqs. (6), (7), (13) and (20) to calculate numbers of particles. Calculated results are shown by the dotted line in Fig. 7. The calculated results well express the tendency of the experimental results.

3.2 Emulsion polymerization in the presence of surfactant

In the reaction systems where surfactant exists, two major points should be considered. One is the adsorption of surfactant molecules to the polymer particles. Another is the association of surfactant molecules with a growing radical in the aqueous phase. Such association is caused by affinity between the alkyl chain of the surfactant molecule and the hydrophobic chain of the growing radical. The adsorption and the association may become significant, in particular, when the surfactant concentration closely approaches the critical micelle concentration. The present section is primarily concerned with whether or not these two factors could affect the nucleation processes of the polymer particles.

For this purpose we assume the following simple form for the adsorption:

$$\Gamma = \Gamma_s (S/S_{cmc}) \quad (25)$$

The value of Γ_s is given by $1/\pi r_e^2$, since the ionic end-group of the surfactant molecule is the same as that of the growing radicals. In the presence of the surfactant, the surface coverage in Eq. (23) is redefined by

$$\theta = \pi r_e^2 (E_r + 4\pi r_p^2 \Gamma N_a) / 4\pi r_p^2 \quad (26)$$

and the surface potential of the polymer particle is given by

$$\phi_p = Ze(E_r + 4\pi r_p^2 \Gamma N_a) / (\epsilon r_p (1 + \kappa r_p)) \quad (27)$$

Regarding the association between the surfactant molecules and the radical, precise discussion seems difficult. However, it may be considered that the number of surfactant molecules adhering to the growing radical dissolved in the aqueous phase, m_{as} , will increase with surfactant concentration. At the critical micelle concentration, m_{as} will have a value similar to the number of surfactant molecules constituting a micelle. To express this tendency, the following simplified relation is assumed:

$$m_{as} = m_s (S/S_{cmc}) \quad (28)$$

where the value of m_s for sodium dodecylsulfate is about 100.²¹⁾ As a consequence, the surface potential of an agglomerate formed by the adhesion of the

surfactant molecules to the growing radical is taken as

$$\varphi_{as} = Ze(1 + m_{as})/(\varepsilon R_s(1 + \kappa R_s)) \quad (29)$$

Although the present work considers the adhesion of the surfactant to the radicals, it is expected that adhesion does not occur when the chain length of the radicals is too short. It is then assumed that adhesion occurs for radicals with a chain length i larger than unity.

In radical polymerizations, the termination reaction of growing radicals is strongly dependent on the diffusion rate of the reactants.³⁾ The diffusion of the radicals is affected by the adhesion of the surfactant molecules to the growing radicals. According to Rubinowitch,²⁴⁾ the overall rate constant for the termination, $k_{t,a}$, is given by

$$1/k_{t,a} = 1/k_{t,D} + 1/k_{t,C} \quad (30)$$

where $k_{t,D}$ and $k_{t,C}$ are diffusion-controlled and reaction-controlled rate constants for the termination reaction. The value of $k_{t,C}$ is thought to equal k_t used in the previous section. On the other hand, $k_{t,D}$ is presented by the encounter frequency defined by the diffusion coefficient and Fuch's stability ratio of the radicals. In the derivation of $k_{t,D}$, three cases are considered. In the case of $i \geq 2$ and $j \geq 2$,

$$k_{t,D}(i, j) = (8k_b T/3\eta R_s) N_a / W_{rr} \quad (31)$$

where W_{rr} is the stability factor calculated from Eqs. (4) and (5) by substituting φ_{as} and R_s for φ_p and r_p . In the case of $i = 1$ and $j \geq 2$,

$$k_{t,D}(1, j) = 4\pi \{D_1 + (k_b T/6\eta R_s)\} (r_1 + R_s) N_a / W_{r1} \quad (32)$$

W_{r1} is calculated from Eqs. (8), (9), (15) and (16) by substituting φ_{as} and R_s for φ_p and r_p in Eqs. (9) and (15). For $i = 1$ and $j = 1$, the adhesion effect does not appear; hence the overall rate constant for this combination of chain lengths equals $k_{t,C}$. Thus, the overall rate constant, $k_{t,a}(i, j)$, is expressed as follows:

$$1/k_{t,a}(i, j) = \begin{cases} 1/\{(8k_b T/3\eta R_s) N_a / W_{rr}\} + 1/k_{t,C} & (\text{for } i, j \geq 2) \\ 1/[4\pi \{D_1 + (k_b T/6\eta R_s)\} (r_1 + R_s) N_a / W_{r1}] + 1/k_{t,C} & (\text{for } i = 1, j \geq 2) \\ 1/k_{t,C} & (\text{for } i, j = 1) \end{cases} \quad (33)$$

Equation (33) was applied to the calculation of N_p , where W'_{pi} in Eq. (24) was determined from Eqs. (8), (9), (15) and (26) by using φ_p of Eq. (27) and substituting φ_{as} and R_s for φ_e and r_e in Eqs. (9) and (15). From Eqs. (25) through (37), the number of polymer particles was calculated at various surfactant concentrations and are shown by the solid line in Fig.

Fig. 8. Number of polymer particles versus surfactant concentration at $I = 2 \text{ mol/m}^3$: (I) experimental; (—) calculated with consideration of surfactant adhesion to growing radicals; (---) calculated without consideration of surfactant adhesion to growing radicals; (- - -) calculated with $C_0 = 0.5$.

8. These results are compared with the particle numbers (broken line) calculated without consideration of the adhesion of the surfactant to the growing radicals. The calculated results without consideration of adhesion show no change with surfactant concentration. In contrast, the calculated results considering the adhesion (solid line) shows a sharp increase in the number of particles with increase in surfactant concentration in its intermediate range. The increase in the calculated number of particles is caused by both a decrease in the rate of radical entrance into polymer particles and a reduction in the rate of termination reaction between the radicals. Thus the present model considering the adhesion effects expresses the tendency of the experimental results, though it is inadequate in a quantitative sense, especially in the intermediate range of surfactant concentration. However, it should be emphasized that no fitting parameters were used in the calculations.

Equation (28) was assumed to estimate roughly the order of magnitude of m_{as} . Therefore, this simplified assumption regarding m_{as} may be regarded as a reason for the discrepancy between calculated and experimental results. To examine the effect of m_{as} on the number of particles we introduce a correction factor C_0 into Eq. (28), assuming that $m_{as} = C_0 m_s(S/S_{cm})$. Numbers of polymer particles calculated with $C_0 = 0.5$ are presented in Fig. 8. In the ranges of high and low surfactant concentrations the number of surfactant molecules constituting a micelle, m_{as} , has no strong effect on the number of particles. In the intermediate surfactant concentration range, m_{as} has a stronger effect, and the introduction of C_0 gives results closer to the experimental ones. Though the present work is not concerned with the region above the CMC, it does

Fig. 9. Comparison of experimental and calculated results for number of polymer particles: surfactant concentrations = (1) 0.4, (2) 3.0 and (3) 5.5 mol/m³

not seem that the model expresses the relation of $N_p \propto S^{0.6}$.

Numbers of polymer particles calculated with $C_0 = 0.5$ at various initiator concentrations below the CMC are shown in Fig. 9, together with the experimental results. The calculated results coincide with the experimental ones fairly well.

Conclusions

Emulsion polymerizations of styrene in water at low surfactant concentrations were carried out. The number of polymer particles was measured at various surfactant concentrations and initiator concentrations.

A homogeneous nucleation model was derived for soapless emulsion polymerization. The model took into account particle growth and particle coagulation. The DLVO theory was applied to estimate electrostatic effects on the rates of particle coagulation and radical entrance into the particles. Numbers of particles calculated by the model were compared with experimental ones, together with numbers of particles calculated without consideration of electrostatic effects. Comparison showed that the calculation considering the electrostatic effects derives values much closer to the experimental ones than those without consideration of the electrostatic effects. The model successfully predicted the variation in number of particles with initiator concentration when a monolayer of ionic end-groups of polymers was assumed to form on the polymer particle.

The model was extended to polymerizations in the presence of a surfactant by considering the adsorption of surfactant molecules to the polymer particles and the adhesion of the surfactant to growing radicals. The model expressed the tendency of the experimental results.

Nomenclature

A	= Hamaker constant	[J]
D	= diffusion coefficient of monomer	[m ² /s]
D_i	= diffusion coefficient of radical with polymerization degree i	[m ² /s]
D_p	= diffusion coefficient of polymer particle	[m ² /s]
d_i	= diameter of polymer particle	[m]
d_v	= volume-averaged diameter of polymer particles	[m]
E_p	= total number of ionic end-groups in polymer particle defined by Eq. (18)	[—]
E_r	= number of ionic end groups of radicals and polymers contained in polymer particle	[—]
E_s	= number of ionic groups of surfactant molecules adsorbed to polymer particle	[—]
e	= electronic charge	[C]
f	= initiator efficiency	[—]
h	= closest distance between surfaces of particles	[m]
I	= initial initiator concentration	[kmol/m ³]
J	= critical chain length of radicals for precipitation	[—]
k_b	= Boltzmann constant	[J/K]
k_d	= rate constant for initiator decomposition reaction	[1/s]
k_p	= rate constant for propagation reaction	[m ³ · kmol/s]
k_t	= rate constant for termination reaction	[m ³ · kmol/s]
$k_{t,a}$	= overall rate constant for termination reaction	[m ³ · kmol/s]
$k_{t,C}$	= reaction-controlled rate constant for termination reaction	[m ³ · kmol/s]
$k_{t,D}$	= diffusion-controlled rate constant for termination reaction	[m ³ · kmol/s]
M_0	= initial monomer concentration in aqueous phase	[kmol/m ³]
M_L	= monomer concentration in aqueous phase	[kmol/m ³]
M_w	= monomer molecular weight	[kg/kmol]
M_p	= monomer concentration in polymer particle	[kmol/m ³]
m_{as}	= number of surfactant molecules adhering to growing radical	[—]
m_s	= number of surfactant molecules constituting micelle	[—]
N_a	= Avogadro number	[1/mol]
N_p	= number of polymer particles in aqueous phase	[1/m ³]
n	= average number of radicals in polymer particle	[—]
n_i	= number of polymer particles with diameter d_i	[—]
n_r	= stirring speed	[s]
n_{rc}	= number of radicals entering into particle	[—]
n_{rp}	= number of polymers formed by propagation reaction	[—]
n_{rt}	= number of polymers formed by radical termination reaction	[—]
R_i	= concentration of radicals with polymerization degree of i in aqueous phase	[kmol/m ³]
R_s	= molecular length of surfactant	[—]
r_i	= effective radius of radical with polymerization degree i	[m]
r_p	= radius of polymer particle	[m]
r_e	= radius of sulfate ion	[m]
S	= surfactant concentration	[kmol/m ³]
S_{cmc}	= critical micelle concentration	[kmol/m ³]
T	= absolute temperature	[K]
V_p	= total volume of polymer particles per unit volume of aqueous phase	[m ³ /m ³]

$V_i(h)$	= total potential energy of particle interaction at distance h	[J]
V_u	= particle volume per mole of repeating polymer unit	[m ³ /kmol]
$V_i'(h)$	= potential energy between radical and polymer particle	[J]
W_{pi}	= Fuch's stability factor for heterocoagulation between polymer particle and radical with polymerization degree i	[—]
W_{pp}	= Fuch's stability ratio for homocoaguration between polymer particles	[—]
W_{r1}	= Fuch's stability factor concerning coagulation between radical with $i=1$ and radical with $j \geq 2$.	[—]
W_{rr}	= Fuch's stability factor concerning coagulation between radicals with $j \geq 2$	[—]
W'_{pi}	= modified stability factor defined by Eq. (24)	[—]
X	= conversion of monomer to polymer	[—]
Z	= electrolyte valency	[—]
Γ	= number density of surfactant molecules adsorbed to surface of polymer particle	[—]
Γ_s	= Γ at S_{cmc}	[—]
ε	= permittivity of aqueous phase	[C ² /mJ]
η	= viscosity of aqueous phase	[kg · m/s]
θ	= surface coverage of defined by Eq. (23)	[—]
κ	= reciprocal of Debye length	[1/m]
ρ_p	= density of polymer	[kg/m ³]
ϕ_e	= surface potential of sulfate ions defined by Eq. (16)	[J/C]
ϕ_p	= surface potential of polymer particle defined by Eq. (17)	[J/C]
ϕ_{as}	= surface potential of agglomerate formed by association of surfactant molecules and growing radical	[J/C]
<Subscript>		
i, j	= polymerization degree	

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