

Surfactant Effects in the Emulsion Polymerization of Vinyl Acetate

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Synopsis

Continuous vinyl acetate emulsion polymerization was carried out by using a mixed surfactant system of "Aerosol" OT (AOT) and sodium dodecyl sulfate (SDS). It is well known that the AOT reduces surface tension considerably and has stronger monomer solubilization power than SDS. In this work, particular attention is given to observe the effects of the mixed surfactant on the molecular weights and polydispersities. In comparison with experiments using only SDS, the particle size appears similar, in the range of 190–280 nm. The conversion increased substantially to the 70% range from the 50% level observed with only SDS. All experiments were conducted at 60°C with a mean residence time of 30 min. The total surfactant concentration was maintained at 0.03 mol/L water for all experiments. It was found that once some AOT was included in the surfactant, the behavior was very similar to that observed with only AOT. The number average molecular weights were found to decrease substantially while the polydispersity increases dramatically to about 12. It is believed that AOT may act as a significant chain transfer agent in the polymerization.

INTRODUCTION

The emulsion polymerization of vinyl acetate is well known for its oscillatory behavior in continuous stirred tank reactors. Oscillations in conversion, particle size, and molecular weights have all been demonstrated.^{1–10} The generation of these oscillations is closely associated with surfactant availability and dependent upon particle numbers and their growth rates. Sensitivity analysis has shown that these variables are very sensitive to radical absorption and desorption rates into and out of the particles.¹¹ It is also known that particle sizes and polymer molecular weights are dependent upon surfactant solubilization effects and micelle size.

The effects of surfactant structures and properties on emulsion polymerization have been observed by a number of investigators.^{12–19} The effects of surfactants with different molecular weights on the rate of polymerization,¹² swelling and solubilization effects,¹³ effects of alkyl chain length of homologous series on the rate of polymerization, particle size and particle number,¹⁴ and mixed surfactant effects of anionic and nonionic mixtures^{15–18} have all been examined to some extent. In addition, structural and thermodynamic aspects in mixed micelle formation and practical applications using mixed surfactants have recently received attention.^{20–23}

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In this study, mixed surfactant effects on vinyl acetate emulsion polymerization were investigated through a continuous experimental reaction system. For surfactants, "Aerosol" OT (AOT) [sodium bis(2-ethylhexyl)sulfosuccinate] and sodium dodecyl sulfate were used. The total surfactant concentration was 0.03 mol/L water. The fraction of AOT in the surfactant mixture was gradually increased in separate experiments. It is commonly known that AOT reduces interfacial tension to a considerable degree even at very low concentrations. The basic differences between AOT and SDS are that the hydrophobic chain length of the AOT is about twice that of SDS and has an ester group in each of the two branched hydrophobic tails. Due to the long hydrophobic chain, AOT is more effective in stabilizing polymer particles than SDS. Furthermore, it may reduce the charge density around polymer particles due to its higher surface coverage per surfactant molecule. Rodakiewicz-Nowak has estimated that AOT's surface area per molecule, a_s , is about 0.61 nm² compared to 0.30 nm² for SDS.²⁴ This may lead to higher absorption rates of the initiator radicals into polymer particles.

The effects of the AOT concentration on conversion, average particle size, and molecular weight are examined here. In order to understand the mechanistic effects due to the surfactant, a simplified model analysis is used.

Total Particle Number and Average Number of Radicals

We recall Smith and Ewart's recursion formula²⁵:

$$\begin{aligned} \rho_A \left[\frac{N_{n-1}}{N_t} \right] + (n+1)k_d [N_{n+1}] + (n+1)(n+2) \frac{k_t}{v_p} [N_{n+2}] \\ = \rho_A \left[\frac{N_n}{N_t} \right] + nk_d [N_n] + n(n-1) \frac{k_t}{v_p} [N_n] \end{aligned}$$

where ρ_A = the total rate of water phase radical absorption in particles, k_d = desorption rate constant, k_t = termination rate constant, v_p = single particle volume, N_t = total particle number per unit volume, and N_n = total particle number per unit volume which has n radicals in a particle.

Smith and Ewart²⁵ solved the above recursion formula for only three limiting cases. A general solution of the above equation was developed later by Stockmayer and O'Toole^{26,27}:

$$\begin{aligned} \bar{n} &= \frac{bI_m(b)}{4I_{m-1}(b)}, & \alpha &= \frac{\rho_A v_p}{N_t k_t} \\ m &= \frac{k_d v_p}{k_t}, & b &= \sqrt{8\alpha} \end{aligned} \quad (1)$$

Ugelstad and Hansen²⁸ provides an alternative method for the solution by taking into account the radical reabsorption and water phase termination mechanisms. That is, the total rate of radical absorption into particles, ρ_A ,

was expressed in terms of the radical initiation rate:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2$$

$$\alpha = \frac{\rho_A v_p}{k_t N_t}, \quad \alpha' = \frac{\rho_i v_p}{k_t N_t}, \quad m = \frac{k_d v_p}{k_t}, \quad \rho_i = 2fk_d[I_F]$$

$$Y = \frac{2k_{tw}k_t}{k_a^2 N_t v_p} \quad (2)$$

where k_{tw} is the radical termination rate constant in water phase and k_a is the rate coefficient for the absorption of free radicals into particles.

Ugelstad and Hansen²⁸ calculated the \bar{n} as a function of m and Y by using eqs. (1) and (2). In this paper, in order to calculate the average number of radicals per particle using the experimental results of conversion and average particle size, the Bessel function in eq. (1) was expressed as a continued fraction.²⁸ In addition, an asymptotic expression for the Bessel function was used to complement this continued fraction.⁸

METHOD OF SOLUTION

In order to elucidate kinetic mechanisms involved in this polymerization system, several assumptions and hypothetical rate expressions are employed. First, although some polymerization occurs in the water phase, it is assumed that the rate of polymerization is determined only by the monomer concentration and radical concentration within particles. Second, the radical partition coefficient and the ratio of monomeric radical diffusion coefficients in the water phase and within particles are constant at steady state for both pure and mixed surfactant systems. Third, the radical absorption rate is dependent on Fick's first law. Finally, the average particle size determined by laser light scattering provides an acceptable estimate of the monomer-swollen polymer particle size.

For the radical desorption rate expression k_d , the following formula by Ugelstad and Hansen²⁸ was used:

$$k_d = \left\{ \frac{k_{mf}}{k_p} \right\} \left[\frac{12(\pi/6)^{2/3} D_w}{a + (D_w/D_p)} \right] / (v_p)^{(2/3)} \quad (3)$$

The term a is the radical partition coefficient, and D_w/D_p is the ratio of monomeric radical diffusion coefficients in the water phase and in particles. The values of a and D_w/D_p used here are 28.0 and 10, respectively, as suggested by Nomura and Harada.²⁹ The D_w value was assumed to be 1.0×10^{-5} cm²/s. Other parameter values are listed in Table I. The radical absorption rate is given by

$$k_a = 4\pi D_w [3v_p/4\pi]^{1/3} \quad (4)$$

TABLE I
 Major Kinetic Parameters at 60°C

Parameter	Value	Reference
k_{tw}	3.0×10^7 L/mol s	8
f/k_d	1.58×10^{-6} s ⁻¹	30
k_{mf}	1.20 L/mol s	31
k_t	3.55×10^8 L/mol s	32
k_p	9500 L/mol s	32

The rate of polymerization can be expressed as

$$R_p = k_p [M_p] \bar{n} [N_t] / N_a \quad (5)$$

where $[M_p]$ is the monomer concentration in particles and N_a is Avogadro's number.

By recognizing the expression for the R_p , found from a steady-state monomer material balance for the continuous reactor, the above equation may be expressed as

$$\frac{k_p [M_p] \bar{n} [N_t]}{N_a} = \frac{[M_F] X}{\theta} \quad (6)$$

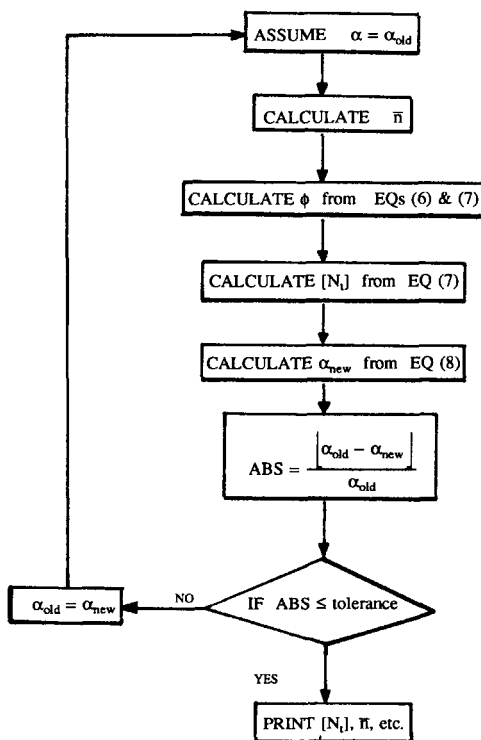


Fig. 1. Numerical procedure to calculate particle number and average number of radicals per particle.

The term $[M_F]$ is the monomer concentration in the feed and X is conversion. Furthermore, if the average particle size is determined, the total particle number concentration and α can be calculated as follows:

$$[N_t] = \frac{[M_F]XM_w}{(1-\phi)v_p\rho_p} \quad (7)$$

The terms of ϕ and ρ_p are the monomer volume fraction in particles and the polymer density, respectively. M_w is the molecular weight of vinyl acetate. Equation (2) can now be expressed in terms of α' , m , and \bar{n} :

$$\alpha = \frac{-1 + \sqrt{1 + 4Y(\alpha' + m\bar{n})}}{2Y} \quad (8)$$

Based on the two known quantities of conversion and average particle size, determined by experiments at steady state, the average number of radicals per particle and total particle number can be calculated by the numerical algorithm in Figure 1.

EXPERIMENTAL

Reagent grade vinyl acetate (VAc) was supplied by Fisher Scientific Co. and further purified by distillation in a rotary evaporator at a reduced pressure of 30 mm Hg to remove inhibitor. Sodium dodecyl sulfate (SDS) of 99% purity was obtained from Sigma Chemical Co. and used without further purification. Initiator, potassium persulfate (PPS), was obtained from J. T. Baker Chemical Co. and used directly as obtained. Water was purified by reverse osmosis, then deionized, and passed over a carbon filter before use. Nitrogen, bubbled through a strongly alkaline pyrogallol solution to remove trace oxygen, was used to purge the reactor, as oxygen acts as a radical scavenger.

For continuous operation, two separate feed streams were prepared. One is the solution of vinyl acetate, SDS and/or AOT (to total 0.03 mol surfactant/L water) and distilled water. The other feed is the initiator solution (0.01 mol PPS/L water). (These concentrations are for total water fed to the reactor.) To start up the reactor, the feed streams were introduced to a 1-L glass kettle reactor which was initially filled with 294 mL of distilled water. The two feed streams were continuously supplied to the stirred tank reactor at constant flow rates with a duplex-head Masterflex pump (Cole-Palmer Co.) through silicone tubing. Flow rates were 7 mL/min for monomer solution and 2.8 mL/min for initiator solution. Thus a ratio of vinyl acetate to water of 4 : 10 was maintained for all experiments with a residence time of 30 minutes. The reactor temperature was maintained at $60 \pm 2^\circ\text{C}$. The basic design follows that of Kiparissides et al.⁶ The conversion of the effluent emulsion was measured continuously by a Mettler Paar DMA 35 density meter. Samples of the effluent emulsion were quenched by concentrated hydroquinone solution, and were stored in 10-mL sampling bottles. Samples were taken every 10 min for analysis of molecular weights.

Molecular weights were determined by gel permeation chromatography (GPC) using a Waters Associates Model GPC I with a differential refractome-

ter and three 7.8 mm \times 30 cm columns packed with ultra-styragel having nominal pore sizes of 1×10^3 , 1×10^5 , and 1×10^6 Å. Tetrahydrofuran was used for the solvent. Samples were coagulated and dried before measurement.

Latex particle sizes were determined using a Coulter Model N4-SD laser light scattering system. These measurements were made on the samples as soon as they were taken and cooled to 25°C.

Further experimental details are available elsewhere.^{10,11}

RESULTS AND DISCUSSION

Conversion, Particle Size, and Number

Figure 2 shows the experimental results for conversion. A series of experiments was carried out with AOT and SDS at a fixed initiator concentration of 0.01 mol/L water. "S/OT" indicates the molar ratio between SDS and AOT per liter of water used as the polymerization medium. The reaction temperature was 60°C and the residence time was 30 min. For mixed surfactant systems as shown, 70% conversion was achieved. This substantial increase over experiments using only SDS may be due to the increased number of particles, as calculated. AOT might be expected to generate more micelles than pure SDS because the CMC (critical micelle concentration) of AOT is approximately 6.8×10^{-4} mol/L at 25°C, whereas the CMC of pure SDS is 8.2×10^{-3} mol/L. Aggregation number and micelle size data do not appear to be available for this surfactant system. The fact that homogeneous nucleation is significant for the vinyl acetate system suggests that micellar effects may not be of great importance, however. The much larger surface area per molecule, as mentioned earlier, may contribute to this behavior due to the concomitant decrease in surface charge density. This could allow increased radical absorption and desorption rates and this agrees with our estimate of an increased k_d with AOT present in the system.

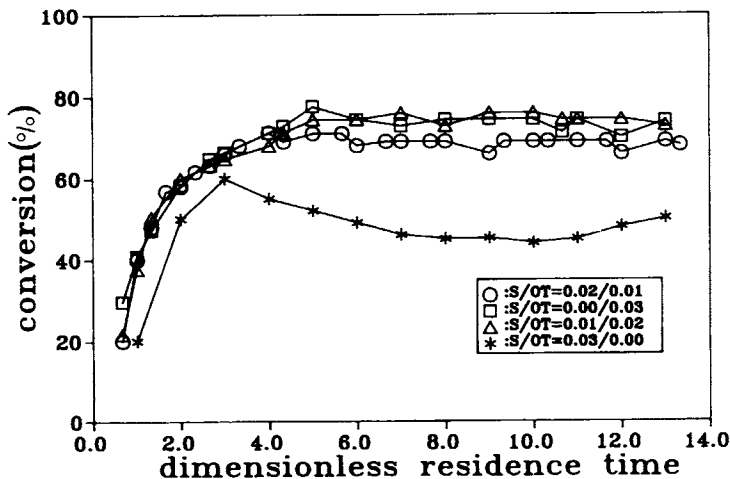


Fig. 2. Conversion vs. dimensionless residence time.

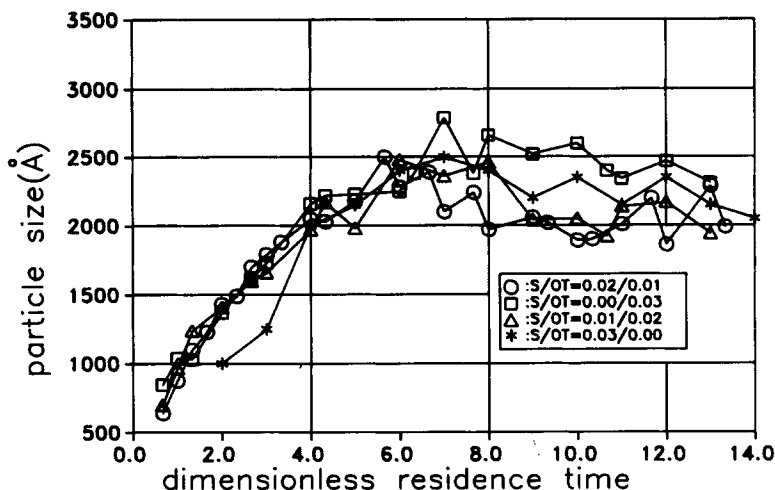


Fig. 3. Average particle vs. dimensionless residence time.

Figure 3 shows the variations of average particle size during the polymerization. At steady state, all of the average particle sizes are in the range of 190–280 nm. There were no identifiable variations observed in the average particle size due to the mixed surfactant system. The behavior of the particle size in the mixed surfactant system was very similar to that observed with pure SDS.

Figure 4 indicates that there are significant differences in the kinetic mechanism for the mixed and unmixed surfactant systems. The total number of particles calculated in the mixed systems is three times larger compared to the number for SDS only. For the mixed surfactant system, the average number of radicals in a particle is approximately 0.25, and the desorption rate constant is about 0.8 s^{-1} . These results were obtained by solving Smith and Ewart's recursion formula²⁵ as it was forced to satisfy the experimental data for conversion and particle size.

Effects of Parameter Variations

In the previous section, several important variables, such as the average number of radicals in a particle, desorption rate, and total particle numbers, were investigated in detail according to the increase of the AOT content in the mixed surfactant system. Calculations used the parameter values listed in Table I. The purpose of this section is to discuss the effects of parameter variations of the above variables with respect to the values of the parameters. This parametric sensitivity on the total particle number, average number of radicals, and desorption rate were carried out by "forcing the fit of the calculated conversion and particle sizes to the steady-state experimental data." The variations in the model output show the possible tolerances due to uncertainties of the parameter values in the data.

The sensitivity results for variations in the parameter values of up to -100 or $+140\%$ of their initial values show that the propagation rate constant is the most sensitive parameter for the total number of particles, and for the

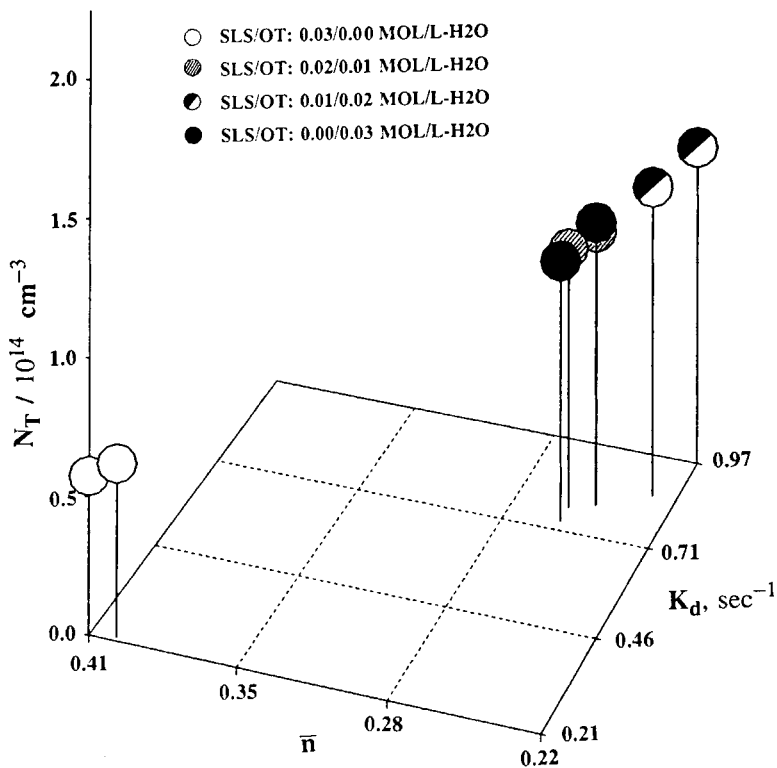


Fig. 4. Total particle number and average radical numbers at steady state.

average number of radicals per particle the propagation rate constant and decomposition rate constant are sensitive parameters. However, the ratio of the monomeric radical diffusion coefficient in the water phase to that in particles is a relatively insensitive parameter compared to the others. Although the radical partition coefficient shows a strong sensitivity for the average number of radicals in a particle and the desorption rate, it has little effect on the total number of particles per unit volume. Furthermore, this radical partition coefficient has larger sensitivities for the mixed surfactant system than those for pure SDS.

Molecular Weight

In Figures 5 and 6, the solid lines represent best-fits for the experimental molecular weight data. The general trend observed is that increases of the AOT fraction of the total surfactant concentration decreases both weight and number average molecular weights. In addition, the observed polydispersity for the mixed surfactant system was approximately 14, while it was 4.2 for the pure SDS system. These observations may indicate that the long hydrophobic tails of the AOT may provide a radical transfer site generating shorter polymer chains. The use of the AOT may also promote a termination mechanism which results in a reduced average molecular weight. This phenomenon may be caused by the decrease in the charge density around the polymer

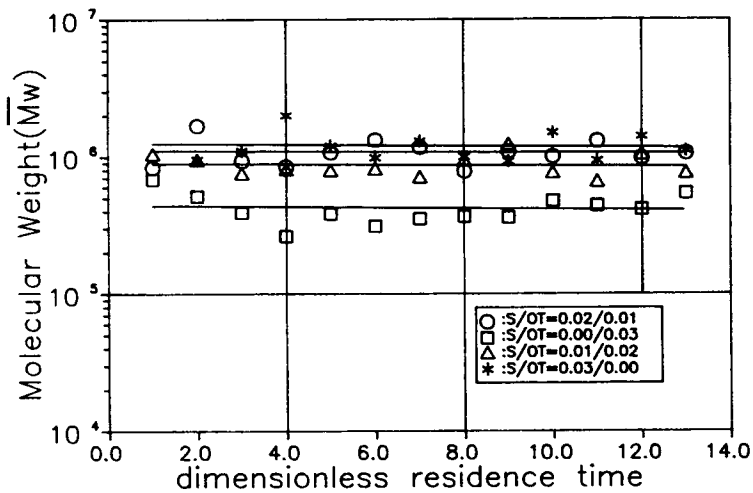


Fig. 5. Weight average molecular weight vs. dimensionless residence time.

particles. Figure 7 shows that the number degree of polymerization has a linear relationship with the AOT concentrations in the total surfactant concentration on a semi-logarithmic graph. This plot is based on the best-fit data in Figure 6.

Kinetic Model

Many complex phenomena are involved in the development of molecular weight. The kinetic mechanisms in this area have been studied by many investigators.^{2,7,31-34} In this section, in order to explain the broad molecular weight distribution often found in emulsion polymerization, a kinetic mecha-

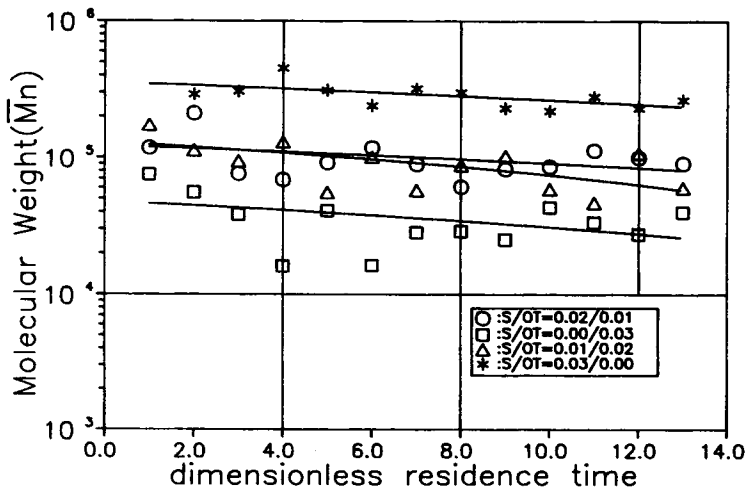


Fig. 6. Number average molecular weight vs. dimensionless residence time.

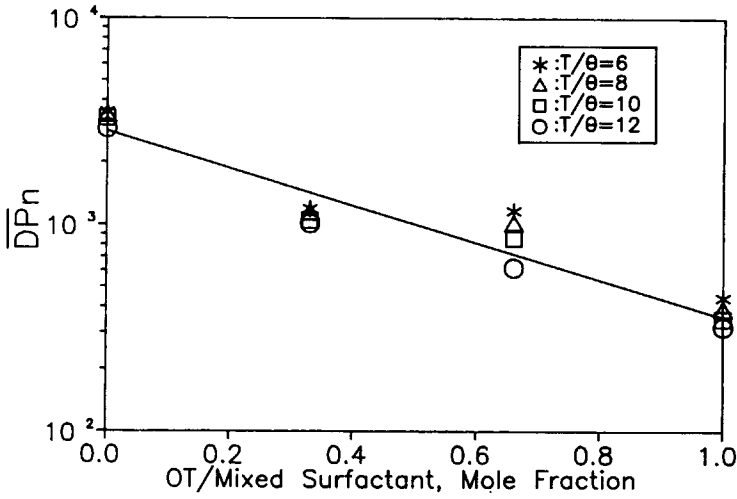
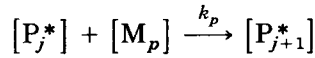


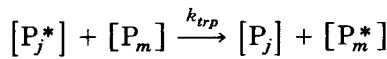
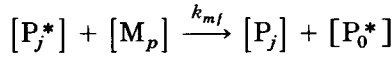
Fig. 7. Number degree of polymerization vs. mole fraction of aerosol OT.

nism for the free radical chain growth polymerization which has the usual steps is employed¹⁰:

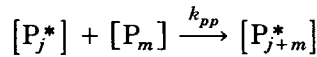
Propagation:



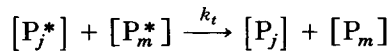
Chain transfer:



Terminal double bond reaction:



Termination:



Model Formulation

From the reaction steps, we can construct the set of differential equations for the living and dead polymer mass balances. The dead polymer mass

balance is

$$\begin{aligned} \frac{d[P_j]}{dt} = & k_t[P_j^*] \left[\sum_{m=1}^{\infty} P_m^* \right] + k_{mf}[M_p][P_j^*] + k_{trp}[P_j^*] \left[\sum_{m=1}^{\infty} P_m \right] \\ & - k_{trp}[P_j] \left[\sum_{m=1}^{\infty} P_m^* \right] - k_{pp}[P_j] \left[\sum_{m=1}^{\infty} P_m^* \right] - \frac{[P_j]}{\theta} \end{aligned} \quad (9)$$

The living polymer mass balance is

$$\begin{aligned} \frac{d[P_j^*]}{dt} = & k_p[M_p][P_{j-1}^*] - k_p[M_p][P_j^*] - k_t[P_j^*] \left[\sum_{m=1}^{\infty} P_m^* \right] \\ & - k_{mf}[M_p][P_j^*] + k_{trp}[P_j] \left[\sum_{m=1}^{\infty} P_m^* \right] - k_{trp}[P_j^*] \left[\sum_{m=1}^{\infty} P_m \right] \\ & + k_{pp} \left[\sum_{m=1}^{j-1} P_{j-m}^* P_m \right] - k_{pp}[P_j^*] \left[\sum_{m=1}^{\infty} P_m \right] - \frac{[P_j^*]}{\theta} \end{aligned} \quad (10)$$

By assuming that the reactor is at steady state, we obtain the following simplified equations for the dead and living polymer mass balances:

$$[P_j] = \left\{ \frac{k_t[\sum_{j=1}^{\infty} P_j^*] + k_{mf}[M_p] + k_{trp}[\sum_{j=1}^{\infty} P_j]}{k_{trp}[\sum_{j=1}^{\infty} P_j^*] + k_{pp}[\sum_{j=1}^{\infty} P_j] + 1/\theta} \right\} [P_j^*] \Omega [P_j^*] \quad (11)$$

$$\begin{aligned} [P_j^*] = & \left([P_0^*] + \frac{k_{trp}[\sum_{j=1}^{\infty} P_j^*]}{k_p[M_p]} \left\{ \sum_{m=1}^j P_m (1 + \beta)^{m-1} \right\} \right. \\ & \left. + \frac{k_{pp}}{k_p[M_p]} \left\{ \sum_{m=1}^{j-1} (1 + \beta)^m \sum_{k=1}^m P_{m+1-k}^* P_k \right\} \right) / (1 + \beta)^j \\ = & \frac{\Lambda_j}{(1 + \beta)^j} \end{aligned} \quad (12)$$

where

$$\beta = \left\{ \frac{k_t[\sum_{j=1}^{\infty} P_j^*] + k_{mf}[M_p] + k_{trp}[\sum_{j=1}^{\infty} P_j] + k_{pp}[\sum_{j=1}^{\infty} P_j] + 1/\theta}{k_p[M_p]} \right\} \quad (13)$$

The term β is usually much less than 1.0 at reasonable degrees of polymerization. Therefore, the term of $(1 + \beta)$ can be approximated as

$$1 + \beta \approx e^\beta \quad (14)$$

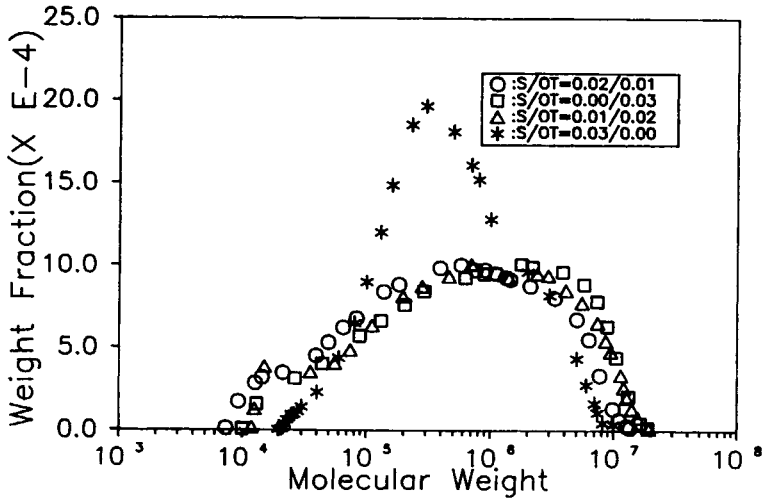


Fig. 8. Weight fractional distribution.

The numerator in eq. (12) is associated with molecular chain branching; the results of the terminal double bond reaction and transfer to polymer chains. When the produced polymer is quenched by an inhibitor, such as hydroquinone, existing radicals are instantly terminated. Hence, from eqs. (11) and (12), the number fractional distribution of polymer with j repeating units will be

$$N_j = \frac{[P_j] + [P_j^*]}{M_{0,t}} = \frac{(1 + \Omega)[P_j^*]}{M_{0,t}} = C_j \cdot \exp(-\beta \cdot j) \quad (15)$$

where

$$C_j = \frac{(1 + \Omega) \cdot \Lambda_j}{M_{0,t}}, \quad M_{0,t} = \left[\sum_{j=1}^{\infty} P_j \right] + \left[\sum_{j=1}^{\infty} P_j^* \right]$$

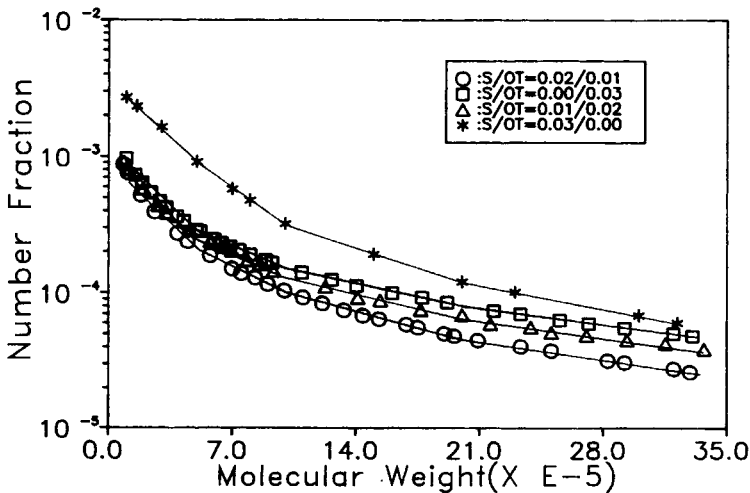


Fig. 9. Number fractional distribution.

From eq. (15), if the coefficients of C_j are constant with respect to j , the number fractional distribution assumes the form of a most probable distribution. Figure 8 presents weight fractional distributions obtained from GPC analysis. As shown, the mixed surfactant gives a broader molecular distribution and larger polydispersity compared to that for the pure SDS.

If the C_j in eq. (15) are constant, the number fractional distribution will be exponential with respect to j . However, the experimental data, shown in semilog form in Figure 9, clearly show deviations from linearity on the plot. This indicates that the radical transfer to polymer reaction and terminal double bond reaction cause deviations from the most probable distribution. In other words, these two kinetic mechanisms give rise to the large polydispersity ratios observed, which are a typical characteristic of emulsion polymerization.

CONCLUSIONS

For the investigation of surfactant effects on continuous vinyl acetate emulsion polymerization, mixtures of AOT having branched hydrophobic chains and SDS were used. In order to show the differences involved in kinetic mechanisms of the mixed and pure surfactant systems, a simple model and efficient numerical algorithm was used. This method calculated both particle number and average number of radicals per particle. The results clearly showed that there were large differences in particle number concentration, average number of radicals per particle, and desorption rate constant. In addition, parametric sensitivities for several key parameters were calculated.

The experimental data of molecular weights showed that the branched long chain surfactant, AOT, probably acted as a chain transfer site during the polymerization. The strong evidence for this was observed from the decrease in the number average degree of polymerization when AOT was part of the surfactant system. Furthermore, the terminal double bond reaction and radical transfer to polymer chains were shown to cause especially large polydispersity ratios.

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