Kinetics of the Emulsion Polymerization of Vinyl Acetate

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Synopsis

Recent investigations of the emulsion polymerization of vinyl acetate report a variable behavior. The reaction has been reported to exhibit a half-order rate dependence and no particle number dependence on the initiator level, or a first-order dependence for both the reaction rate and particle number on the initiator concentration, or some behavior between these two extremes. While two recent models have attempted to account for the changes in the reaction rate dependence by postulating either an aqueous phase or a polymer phase termination, no adequate explanation of the particle number behavior has been given, nor has a single model been suggested that agrees with all of the experimental data. This investigation confirms the results of previous investigators and develops an empirical model for the particle number, taking into account the effects of the initiator level, emulsifier level and alkyl chain length, temperature, and ionic strength on the particle number. This particle number model, used with a polymer phase termination reaction model, yields a polymerization rate expression which agrees with all previous data.

INTRODUCTION

The kinetics of the emulsion polymerization of vinyl acetate have been studied thoroughly because of the unique nature of the monomer and its polymerization. In general, it can be stated that vinyl acetate does not follow the classical Smith–Ewart-type emulsion polymerization kinetics and exhibits constant rate behavior far beyond the disappearance of the separate monomer phase. These phenomena are thought to occur because of the high transfer to monomer constant and the relatively high water solubility of vinyl acetate.

However, much of the data which have appeared in the literature concerning the emulsion polymerization of vinyl acetate seem to be contradictory and, to date, no one reaction mechanism has been proposed that accounts for all of the available experimental data. Recently, two well-developed reaction models have been proposed, one postulating an aqueous phase termination[1] and the other postulating a polymer phase termination.[2] Between the two models and their supporting data, all of the effects noted by the many investigators are included. However, each model, individually, fails to account for all of the phenomena observed during a vinyl acetate emulsion polymerization.

This study repeats some of the experimental work done by previous investigators to ensure that the variable nature of the polymerization data was not due to variations in the experimental equipment or materials. After an examination of all available experimental data, a reaction model is proposed to yield a single model applicable to all data.

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EXPERIMENTAL

Materials

Vinyl acetate monomer, freed from all inhibitors, was obtained from the South Charleston, West Virginia, plant of the Union Carbide Corporation and used without further purification. Deionized water supplied in the laboratory was used without further treatment. Potassium persulfate, to be used as the initiator, and potassium sulfate, to be used to adjust ionic strengths, were reagent-grade chemicals obtained from Merck and were used without further purification. The sodium lauryl sulfate, used as an emulsifier, was obtained as a 99% pure powder from Alcolac, Inc. (Sipex WD Crystals).

A similarly pure grade of sodium cetyl sulfate could not be obtained. Therefore, a modification of the method proposed by Weiss et al.[3] for the analysis of sodium alkyl sulfates was used to obtain the purified sodium cetyl sulfate from Sipex EC-111 (a 25% sodium cetyl sulfate emulsifier obtained from Alcolac, Inc.). To obtain 100 g purified product, 600 g EC-111 was added to 900 ml of a 50/50 volume mixture of isopropanol and water. After stirring the solution for 1 hr at 40°C anhydrous sodium carbonate was added until its saturation point was reached. The mixing was stopped and the liquid was transferred to a separatory funnel. Warm water (about 40°C) was run over the outside of the funnel while the alcohol and water phases were allowed to separate. After complete separation, the aqueous phase was discarded and the alcohol phase cooled to room temperature. At room temperature a crude sodium cetyl sulfate product precipitated from the alcohol phase. This precipitate was filtered from the alcohol, slurried with 600 ml ethanol, and heated at 50°C for 1 hr with constant agitation. The ethanol slurry then was cooled in an ice bath and the solids filtered out. The ethanol extraction was repeated twice more until a pure-white product was obtained. This final product was dried in a vacuum oven for 4 hr at 60°C to remove all traces of ethanol.

Procedure

The procedure for all experimental trials was the same. A 3000-ml glass-jacketed resin flask was charged with 1817 g water and the desired levels of emulsifier and neutral salts. After stirring to dissolve the emulsifier and salt, 614 g vinyl acetate was added and the system was thoroughly purged with nitrogen while the reaction mixture was heated to the desired reaction temperature. During this time the desired amount of initiator was dissolved in 25 g water and heated to the reaction temperature. After the reactor temperature had stabilized at the desired level (usually ½ hr), an initial sample was taken and the initiator solution was added. A 5- to 30-min induction time was noted at the start of most polymerizations, the length depending upon the temperature and intensity of the nitrogen purge. The length of the induction period did not noticeably affect the subsequent reaction rates. Ten milliliter samples of the reaction mixture were removed at prescribed intervals throughout the reaction (usually about 12 samples during the course of the polymerization) and shortstopped with hydroquinone. The temperature in the reactor was maintained at the desired level by an automatic temperature controller and did not vary from the desired temperature by more than ±1°C during any trial.

The samples that were withdrawn from the reactor were analyzed for residual monomer by dissolving the latex in methanol and injecting the solution into an F and M Model 720 gas chromatograph. The average particle diameter was determined using a dissymmetry light scattering technique. This method of particle size determination yields an average particle diameter which is approximately equal to the weight-average particle diameter. Thus, the particle number calculated using this value of the particle diameter will be a weight-average particle number, while the kinetic expressions require a number-average particle number. Other investigators[2,4] have determined that the number-average particle number should be 2.6 times greater than the weight-average particle number for vinyl acetate emulsion polymerizations. This 2.6 factor must be used whenever the particle number data are to be used in any kinetic calculation.

RESULTS

The results from a number of previous investigations of the emulsion polymerization kinetics of vinyl acetate using potassium persulfate as initiator and sodium lauryl sulfate as emulsifier are listed in Table I. While all of these investigators reported similar general behavior, the one major point of disagreement, as indicated in Table I, is the dependence of the polymerization rate R_p and particle number N_p on the initiator concentration [I]. The data shown in Table I indicate that in those studies in which a first-order dependence was observed between the polymerization rate and the initiator concentration, a first-order dependence between the particle number and the initiator existed. On the other hand, in those studies where a half-order dependence between the rate and the initiator was observed, the particle number was observed to be independent of the initiator concentration. Those investigators reporting reaction rate orders between 0.5 and 1.0 also reported a particle number dependence between 0.0 and 1.0.

Of the two most recently developed reaction models (an aqueous phase termination model proposed by Litt et al.[1] and a polymer phase termination model proposed by Friis and Nyhagen,[2] one supports data indicating that the reaction is first order for both the reaction rate and particle number, while the other

TABLE I
Results of Previous Investigations of Vinyl Acetate Emulsion Polymerizations

Investigator	Emulsi-fier	$K_2S_2O_8$ Range, $M \times 10^3$	Temp., °C	Reaction rate order on initiator	Particle number order on initiator
Dunn and Taylor[9]	SLS	0.185–1.48	60	0.64	0.35
Patsiga et al.[11]	SLS	0.8	60	0.8–1.0[a]	—
Priest[5]	SLS	0.12–0.16	50	—	0.0
Dunn and Chong[12]	SLS	0.1–0.8	60	0.6–0.9	0.6–0.9
Nomura[13]	SLS	4.62	50	0.5	0.0
Litt et al.[1]	SLS	0.25–2.0	60	1.0	1.2
Gershberg[15]	SLS	1.0–30.0	50	0.6	—
Friis[2]	SLS	0.5–4.0	50	0.5	0.0

[a] Seeded polymerizations.

supports data indicating a half-order dependence for the reaction rate. Rather than compare the results from all of the previous investigations, the results from these two studies will be used to represent the two extremes for the behavior of a vinyl acetate emulsion polymerization.

In order to rule out the possibility that these results could have been obtained because of differences in either the experimental equipment, materials, or procedure, a number of polymerizations were carried out under conditions simulating those used by Litt or by Friis. As in the studies mentioned in Table I, the general characteristics of a vinyl acetate emulsion polymerization were also observed in the experiments carried out during this investigation. These characteristics are as follows: (1) The separate monomer phase disappears at about 20% conversion. (2) A constant rate period is observed between about 20% and 80% conversion. (3) The emulsifier level was observed to have no significant effect on the polymerization rate under the conditions used during this study.

Polymerization Rate Results

Neither the study by Litt nor that by Friis presents extensive data at more than one temperature. Therefore, a series of experiments, at both 50 and 60°C, were run under conditions similar to those used by each investigator. The results of a series of experiments run at 50°C (reproducing the experimental conditions used by Friis) are shown in Figure 1. Over the range of initiator concentrations
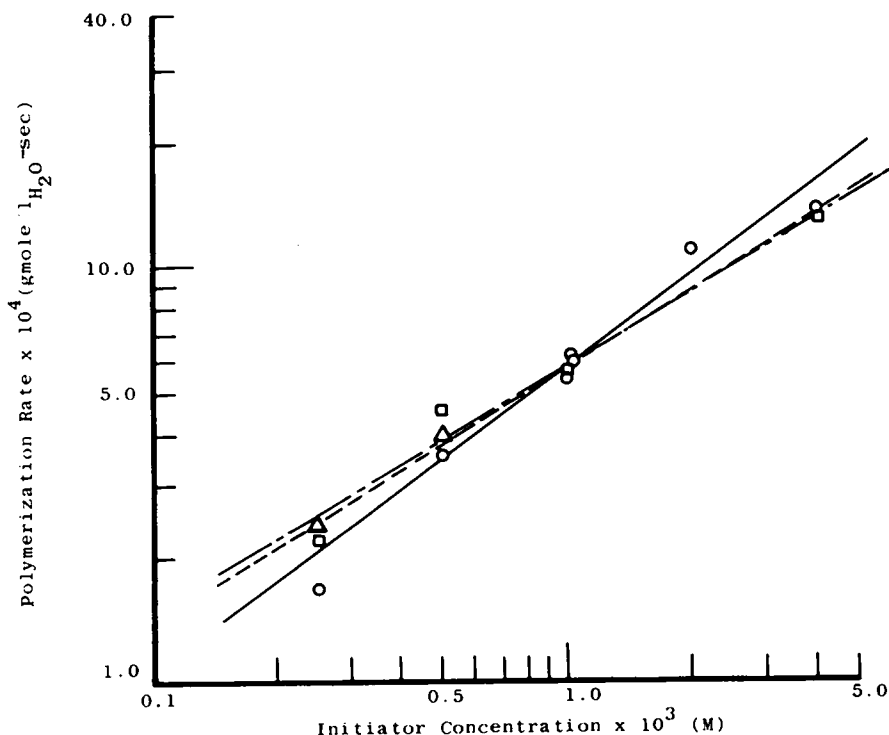

Fig. 1. Polymerization rate dependence on initiator concentration. Temperature = 50°C; (——O——) std. system (ionic strength $\propto$ I); (---$\triangle$---) constant ionic strength = 1.2 × $10^{-2}M$; (— - -□- - —) constant ionic strength = 3.0 × $10^{-2}M$.

from 0.25×10^{-3} to $4.0 \times 10^{-3} M$, the rate of polymerization was proportional to the 0.72 ± 0.07 power of the initiator concentration. However, in the range of initiator concentrations studied by Friis, from 1.0×10^{-3} to $4.0 \times 10^{-3} M$, the rate of polymerization is proportional to the initiator concentration to the 0.65 ± 0.07 power, while Friis reports the dependence to be to the 0.56 ± 0.03 power. The results of polymerizations run at 60°C (reproducing the experimental conditions used by Litt), Figure 2, indicate that the polymerization rate is dependent on the initiator concentration to the 0.88 ± 0.14 power, while Litt reports a value of 0.93 ± 0.12. Thus, the results of both investigators are reproducible in the same piece of equipment using the same source of reactants.

In this investigation the emulsifier level had no observable effect on the reaction rate at either 50° or 60°C. (The data in Figs. 1 and 2 arose from experiments using either 2.7 g/l. H_2O or 10.9 g/l. H_2O of the surfactant. No distinction is made on these figures between the reaction rates at the two different surfactant levels.) This is in agreement with the results of Litt. Friis reports a very weak dependence ($R_p \propto [E]^{0.12 \pm 0.02}$) which may not have been observable in this investigation because of the scatter in the data. As reported by Friis, the level of agitation, within reasonable bounds, had no observable effect on the polymerization rate at either temperature.

Further examination of the results for the standard system (ionic strength contributed by $K_2S_2O_8$ only) presented in Figure 1 reveals that there appears
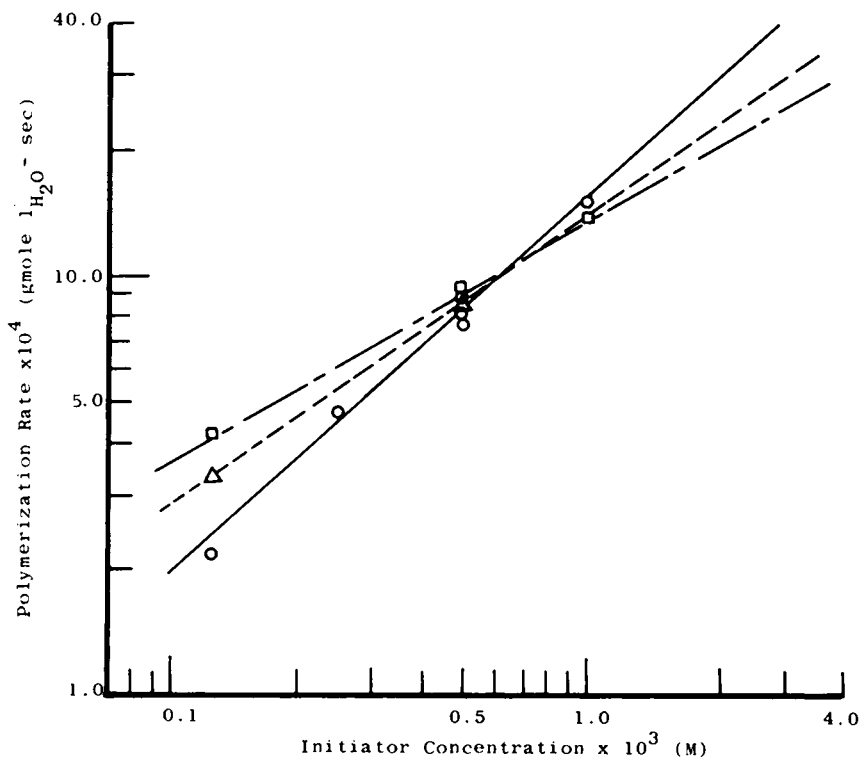

Fig. 2. Polymerization rate dependence on initiator concentration. Temperature = 60°C; (—O—) standard system (Ionic strength $\propto$ I); (- - - -Δ- - - -) constant ionic strength = $3.0 \times 10^{-3} M$; (— -□—) constant ionic strength = $3.0 \times 10^{-2} M$.

to be a slight curvature in the data which is especially noticeable for initiator concentrations below $1.0 \times 10^{-3}M$., In his investigation, Friis reported this trend also. When he included his data taken at $0.5 \times 10^{-3}M$, he found that the order of the reaction with respect to the initiator had risen to 0.65. Friis explained this phenomenon as being due to traces of oxygen present in the nitrogen used to blanket the reaction. It is in this region of initiator concentrations (less than $1.0 \times 10^{-3}M$) that Litt did his experimentation, however, and these results at 50°C are tending more toward a first-order dependence (as observed by Litt).

The results of a series of experiments run at 50°C using K_2SO_4 to maintain the ionic strength at $1.2 \times 10^{-2}M$, a level equivalent to the ionic strength present when $4.0 \times 10^{-3}M$ initiator is present, are shown in Figure 1. When the ionic strength is maintained at this level, the overall reaction order with respect to the initiator concentration becomes 0.64 ± 0.09 over the entire range of initiator concentrations studied. Note that maintaining a constant ionic strength had no observable effect above $1.0 \times 10^{-3}M$ initiator (as reported by Friis) but had a significant effect below $0.5 \times 10^{-3}M$ initiator. A further increase in the ionic strength to $3.0 \times 10^{-2}M$, a level equivalent to $0.01M$ initiator, had no additional effect on the reaction order. The results of a similar series of experiments performed at 60°C are shown in Figure 2. At a constant ionic strength, equivalent to $1.0 \times 10^{-3}M$ initiator, the reaction order with respect to the initiator concentration becomes 0.68, while at a level equivalent to $0.01M$ initiator the order becomes 0.58. Effects of this magnitude were reported by Litt.

Particle Number Results

Figure 3 shows the number of particles observed as a function of conversion for a number of polymerizations run under standard conditions at 50°C. All of the observations in this figure would indicate that the number of particles increases with increasing conversion at all levels of initiator. Friis reported that the number of particles remained constant beyond 20% conversion. This constant particle number above 20% conversion was also reported by Priest.[5] Priest, however, used electron micrographs to determine the particle number, and since this method is very insensitive to small particles, any new generation of particles may have gone unnoticed. Light scattering methods, which are more sensitive to small particles, were used in this study and the study by Friis. The reasons for the discrepancy between the experimental results obtained during this investigation and those obtained by Friis are not apparent at this time.

In the range of initiator concentrations for which Friis reports particle number data, the data shown in Figure 3 agree with Friis' observations, i.e., the final particle number remains almost constant in the initiator concentration range from 0.5×10^{-3} to $2.0 \times 10^{-3}M$. A further increase in the initiator concentration, to $4.0 \times 10^{-3}M$, appears to result in an increase in the final particle number.

The results of a series of experiments run under the conditions used by Litt are shown in Figure 4. Again there is an increase in the particle number with increasing conversion. The data at the lower initiator concentrations (between 0.125×10^{-3} and $0.5 \times 10^{-3}M$) would indicate that the final particle number does increase with increasing initiator concentration, as observed by Litt. There does appear to be a leveling off of the final particle number as the initiator concentration approaches $1.0 \times 10^{-3}M$, however.
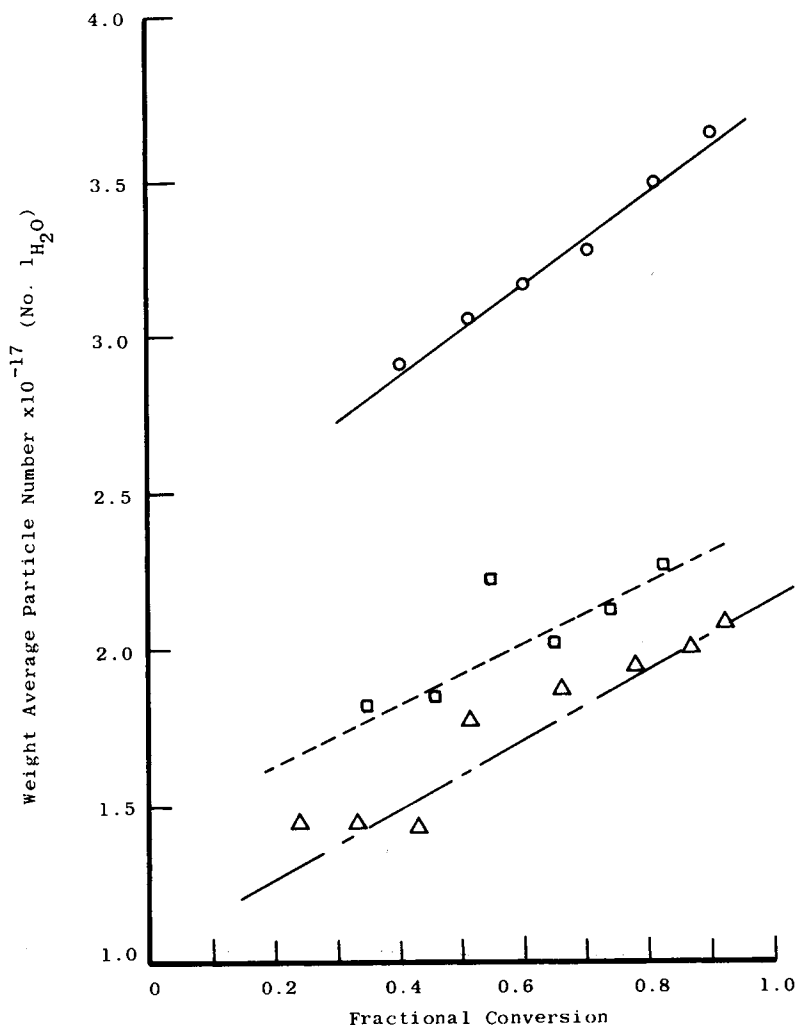
Fig. 3. Dependence of particle number on conversion and initiator concentration. Temperature = 50°C; (—○—) [I] = 4.0 × 10⁻³M; (---□---) [I] = 1.0 × 10⁻³M; (— -△—) [I] = 0.5 × 10⁻³M; [SLS] = 10.9 g/l. water.

These apparent changes in the behavior of the particle number are more easily seen from a log–log plot of final particle number versus rate of initiator decomposition, $2fk_i[I]$, as shown in Figure 5. At both 50 and 60°C there appears to be an area of reduced dependence of the particle number on initiator concentration for initiator levels between 0.5×10^{-3} and $1.0 \times 10^{-3}M$. Above this range at 50°C and below this range at 60°C, the particle number exhibits a stronger dependence on the initiator level.

Effect of Alkyl Chain Length of Emulsifier

All of the investigations mentioned above used the same emulsifier, sodium lauryl sulfate. Napper and Alexander[6] have performed similar polymerizations using a variety of anionic, cationic, and nonionic emulsifiers. In investigations
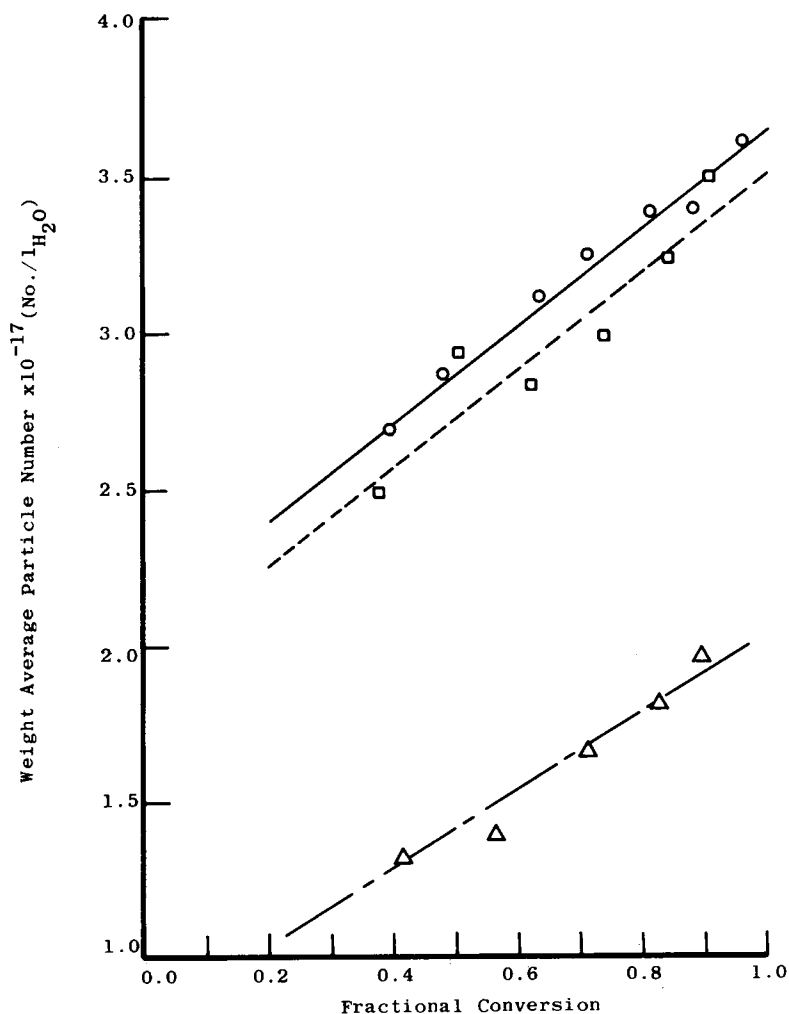
Fig. 4. Dependence of particle number on conversion and initiator concentration. Temperature = 60°C; (——○——) $[I] = 1.0 \times 10^{-3}M$; (- - -□- - -) $[I] = 0.5 \times 10^{-3}M$; (— -△——) $[I] = 0.125 \times 10^{-3}M$; $[SLS] = 10.9$ g/l. water.

concerning the effect of alkyl chain length for a sodium alkyl sulfate-stabilized vinyl acetate emulsion polymerization, they reported that the rate of polymerization and the number of particles both increase with increasing alkyl chain length. However, all of their results were obtained at very low monomer concentrations (less than the solubility of vinyl acetate in water) and emulsifier concentrations less than the *CMC*.

Repeating many of the experiments described in earlier sections, using sodium cetyl sulfate as the emulsifier (after purifying as described earlier), had no significant effect on any of the results reported above. Thus, the results observed by Napper and Alexander were not observed for systems using sodium alkyl sulfate emulsifiers in excess of the *CMC* or at monomer levels above the solubility of the monomer in water.
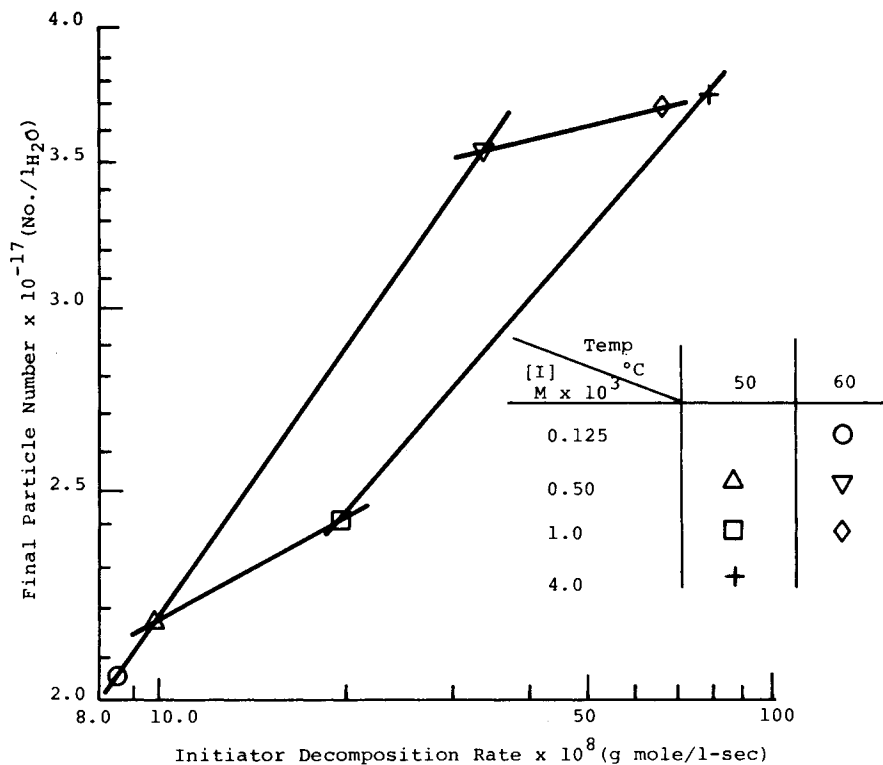
Fig. 5. Dependence of final particle number on rate of initiator decomposition.

DISCUSSION

The reaction models and data presented by Friis and Nyhagen and Litt et al. were selected not only because they represented the two extreme views for the emulsion polymerization of vinyl acetate but also because they represent the most recent and reasonable kinetic models.   Both models have many features in common: a high degree of transfer to monomer with the resulting escape of radicals from the latex particles, a relatively low concentration of particles containing radicals, and a constant rate period arising from a decrease in the escape of the radicals from the particles with increasing conversion.   However, whereas Litt proposes an aqueous phase termination mechanism, Friis proposes that the termination occurs within the polymer particles and is conversion dependent.

Previous Reaction Models

The model proposed by Litt has the following form:

$$R_p = C_1([I][M_p]N_p)^{1/2}\left(1 + C_2\frac{[M_p]}{r^2[M_{aq}]}\right)^{-1/2} \tag{1}$$

where R_p is the rate of polymerization, $[I]$ is the initiator concentration (moles/ liter H_2O), $[M_p]$ is the monomer concentration in the polymer phase (moles/liter), N_p is the number of particles present (number/l. H_2O), r is the radius of a polymer particle, $[M_{aq}]$ is the monomer concentration in the aqueous phase

(moles/liter), and C_1 and C_2 are groups of rate constants. In arriving at this model, Litt assumed that the main termination reaction occurs in the aqueous phase but allowed for a polymer phase termination. The extended constant rate period is said to occur because of the decrease in the rate of transfer to monomer caused by the reduction of monomer content in the particles with increasing conversion. Since monomeric radicals can rapidly escape from the particle, the reduced rate of transfer leads to a higher radical concentration in the polymer particles which offsets the effect of the lower monomer concentration on the polymerization rate.

Friis and Nyhagen propose that the emulsion polymerization of vinyl acetate follows the model proposed by Ugelstad[7] for the emulsion polymerization of vinyl chloride. This model has the form

$$R_p = \frac{k_p[M_p]}{N_A} (2fk_i[I])^{1/2} \left(\frac{V_p N_A^2}{2k_{t_p}} + \frac{N_p}{2k_d} \right)^{1/2} \tag{2}$$

where k_p is the polymerization rate constant, k_i is the rate constant for initiator decomposition, f is the initiator efficiency, V_p is the polymer volume, k_{t_p} is the termination rate constant, N_A is Avogadro's number, k_d is the rate constant for the desorption of radicals, and all other variables are as defined earlier. This model differs from that of Litt in that it postulates that the only significant termination reaction occurs within the particles. The existence of the extended constant rate period is explained not only by the decrease in the rate of transfer to monomer but also because of the reduction in the rate of termination with increasing conversion (gel effect).

Friis also suggested that as the monomer level within the particles decreases, the probability of desorption of a radical also decreases. Considering that only monomeric radicals are capable of escape, the rate constant for desorption is given by

$$k_d = \frac{2D_p k_{tr_m}[M_p]}{N_A(2D_p + k_p[M_p]r^2)} \tag{3}$$

where k_{tr_m} is the transfer-to-monomer rate constant and D_p is the molecular diffusivity for a radical within the particle. The dependence of the diffusivity on the monomer content of the particle was expressed as

$$D_p = D_p^0 \exp \left[\frac{-\beta x \rho_m (1 - \alpha)}{(1 - x)\rho_p + \alpha x \rho_m} \right] \tag{4}$$

where x is the fractional conversion; ρ_m and ρ_p are the densities of the monomer and polymer, respectively; D_p^0 is a zero-conversion diffusivity; and α and β are parameters related to the free volume fractions in the particles.

This form for the rate equation is similar to that proposed by Harriot[14]:

$$R_p = k_p[M_p](2k_i[I] V_w' V_p'/k_{t_p})^{1/2} \tag{5}$$

where V_w' and V_p' are the volume fractions of the aqueous and polymer phases, respectively. Equation (5) was derived by assuming a rapid exchange of radicals between the polymer particles and the aqueous phase. Neglecting any resistance to diffusion of the radicals, i.e., let $D_p \rightarrow \infty$, the model developed by Friis still does not reduce to that proposed by Harriot. By allowing $k_{tr_m} \rightarrow \infty$ or $N_p \rightarrow 0$, Friis' model reduces to

$$R_p = k_p[M_p](fk_i[I] V_p/k_{t_p})^{1/2} \tag{6}$$

which is similar in form to that proposed by Harriot. Note, however, that this form of Friis' model would predict that the reaction rate will increase with increasing polymer volume. Harriot's model, on the other hand, indicates a maximum rate when $V'_p = 0.5$ and $V'_w = 0.5$. Thus, Harriot's model predicts the reaction rate to first increase and then decrease with V'_p and is therefore not equivalent to any limiting form of eq. (2).

Recently, Stannett[8] has examined both models and suggested that the results obtained by Friis were a result of the higher ionic strengths used in his experiments (a result of the higher initiator concentrations used at the lower reaction temperature) and more energetic agitation. The agitation level was found to have no significant effect on the reaction rate in this study, however. Both of these factors, Stannett claims, may cause the termination to occur in the polymer phase, which then gives rise to half-order kinetics. In his paper, Stannett also suggests that the rate constant for the diffusion of radicals out of the polymer particles used in Litt's reaction model should also be conversion dependent, as is the constant used by Friis. However, to do this would destroy one of the arguments in support of the model proposed by Litt, namely, that his model agrees with the data using only one parameter and that this agreement was not obtained by a curve-fitting technique. In the model proposed by Friis, both of the parameters, α and β, were determined via a curve-fitting technique and arose from the modeling of the conversion-dependent diffusion rate constant.

Even this change does not eliminate the one factor that still remains unaccounted for in all of the models—the change in the nature of the dependence of the particle number on the initiator level. Both models, eqs. (1) and (2), contain only an explicit half-order dependence of the rate upon the initiator concentration. However, Litt reports that the number of particles, N_p, is also directly dependent upon the initiator concentration, making the overall reaction rate first order with respect to the initiator concentration. Friis, on the other hand, reports that the number of particles is independent of the initiator concentration and thus reports that the overall reaction is half order with respect to the initiator concentration. Note that either model, eq. (1) or (2), will predict a half-order rate dependence on the initiator level if the particle number is independent of the initiator level. For a vinyl acetate emulsion polymerization, the second term in the last set of parentheses in eq. (2) is approximately ten times greater than the first, so that both models will also predict a first-order rate dependence on the initiator level if the particle number exhibits a first-order dependence on the initiator level. If either model is a true description of the actual process, therefore, the dependence of the particle number on the initiator level may be inferred from the relationship between the reaction rate and the initiator level.

However, neither in Litt's original paper nor in the modifications proposed by Stannett is the changing nature of the particle number dependence accounted for. Instead, in these papers the onset of polymer phase termination causes the term involving the constant C_2 in eq. (1) to vanish. This results in the same equation as given at the top of page 149 in Stannett's paper, where a half-order dependence is claimed. This is true if, and only if, the particle number is independent of the initiator level. This disagrees with the experimental results presented in Litt's paper. Friis, meanwhile, makes no attempt to explain the changing nature of the particle number behavior with the changes in initiator level.

Particle Formation Mechanism

Because of the solubility of vinyl acetate in water and the relatively unimportant role played by the emulsifier, the particle formation in a vinyl acetate emulsion polymerization is assumed to occur via a precipitation of oligomers from the aqueous phase. These aqueous phase oligomers are initially generated at a rate proportional to the initiator concentration so that the particle number should also exhibit a linear dependence on initiator concentration.[16] As the particle number increases, the aqueous phase oligomers may be "swept up" by existing particles before they precipitate to form particles.

A second mechanism which controls particle number is coagulation. For electrostatically stabilized particles, such as the latex particles under consideration here, the rate of coagulation may be calculated using the Deryaguin–Landau–Verwey–Overbeek (DLVO) theory of colloidal stability.[12] The results from the DLVO theory are most easily expressed in terms of the Fuch's stability ratio, the ratio of the rate of coagulation hindered by an electrostatic energy barrier to the coagulation rate which would be observed if only the attractive forces between particles are considered. Particle stability increases with increasing surface potential or particle diameter but decreases exponentially with increasing ionic strength of the suspending medium. In the limit of high ionic strengths, Fuch's stability ratio will approach 1.

The apparent change in the behavior of the particle number with respect to the initiator concentration reported earlier could therefore be a result of the effect of changing ionic strength on particle stability. For the standard systems, in which the initiator is the only salt added, low initiator levels produce low ionic strengths and therefore high particle stability. For this situation, coagulation would not play an important role in determining the particle number. The rate of particle generation will be the main factor in determining particle number which would give rise to a first-order dependence between particle number and initiator level for low initiator concentrations.

As the initiator level increases, ionic strength increases and coagulation plays a more important role in the determination of the particle number. It then becomes possible for the tendency of the particle number to increase with increasing initiator to be offset by the increase in the rate of coagulation brought on by higher ionic strength. The further increase in particle number at high initiator levels observed in the data at 50°C could be the result of a "salting out" of the surfactant at high ionic strength or an increase in the surface potential of the particles due to a larger number of sulfate endgroups per particle arising from the coagulation. All experiments run at a constant ionic strength were performed at high ionic strengths where coagulation should be the dominant factor in determining the particle number. The constant coagulation rate in these experiments should give rise to a constant particle number, an outcome consistent with the results which were observed.

Development of Particle Number Model

To study the effects of variations in the initiator level, temperature, ionic strength, and emulsifier type and level on the particle number during a vinyl acetate emulsion polymerization, a designed set of experiments, as indicated above the dashed line in Table II, was performed. This set of experiments was

TABLE II
Designed Set of Experiments for Vinyl Acetate Emulsion Polymerization

Expt. No.	[I] $M \times 10^3$	[S], $M \times 10^2$	Ionic strength, $M \times 10^3$	T, °C	Reaction rate, (g-mole/liters H$_2$O-sec) $\times 10^4$	Particle number, (#/liters H$_2$O) $\times 10^{-17}$ Intercept	Slope
1	4.0	1.7	30.0	50	12.35	1.221	0.8216
2	0.25	6.9	30.0	50	2.13	0.7403	1.160
3	0.25	1.7	3.0	50	2.10	1.108	1.105
4	0.5	6.9	30.0	60	9.77	1.128	1.301
5	0.125	1.7	30.0	60	4.05	0.8520	0.8147
6	0.5	1.7	3.0	60	9.02	1.323	0.9463
7	0.125	6.9	3.0	60	3.53	0.5786	1.531
8	4.0	6.9	12.0	50	12.75	2.309	1.446
9	0.5	6.9	1.5	50	5.10	1.668	1.246
10	0.5	6.9	1.5	60	10.51	1.943	1.580
11	0.125	6.9	0.375	60	3.22	0.7096	1.343
12	1.0	6.9	3.0	60	14.92	2.106	1.559
13	1.0	6.9	3.0	50	6.16	1.558	0.8370

repeated using sodium cetyl sulfate as the emulsifier to give a 2^{5-1} fractional factorial set of experiments.

Since the particle generation during a vinyl acetate emulsion polymerization occurs via a precipitation of aqueous oligomeric radicals, the particle number will increase rapidly during the first few percent conversion. Subsequent particle generation, although present as indicated in Figures 3 and 4, proceeds more slowly. While a theoretical model could possibly be formulated to simulate this process, a model of the form

$$N_p = a + bx \qquad (7)$$

where a and b are functions of the initiator level, emulsifier level and type, temperature, and ionic strength and x is the fractional conversion, can be used to approximate the particle number behavior shown in Figures 3 and 4. A multiple linear regression analysis of the particle number data from the designed set of experiments described earlier could then be used for reaction simulations, although it would be limited to describing the particle number behavior only within the ranges of the variables studied. While such a model has no theoretical basis, it allows the effects of the reaction variables on the particle number to be included in any reaction model.

Since such a model would, in general, only be applicable within the ranges of the variables studied, the results from the designed set of experiments were supplemented by adding those experiments indicated below the dashed line in Table II. The data from all of the experiments in the designed set then were analyzed using a multiple linear regression analysis to give the following model for the particle number during a vinyl acetate emulsion polymerization stabilized with sodium alkyl sulfates:

$$N_p \times 10^{-17} = 18.64 + 4.972 \times 10^8 fk_i[I] - 1.081 \times 10^3 (\text{ionic strength})$$
$$- 5.405 \times 10^{-2}T - 1.1 \times 10^{10} fk_i[I](\text{ionic strength})$$
$$+ 3.276(\text{ionic strength})T + x(0.7847 + 14.63[S]) \quad (8)$$

where N_p has units of number/liter H_2O, T is temperature (K), and all other variables are as described earlier. The particle numbers obtained for all of the experiments listed in Table II as well as these calculated by eq. (8) were all obtained using the average particle diameter determined via a light scattering technique. Thus, the use of eq. (8) will yield a weight-average particle number. However, the particle number required for use in the reaction models, eqs. (1) and (2), are the number-average particle numbers. Both Friis and Vanso[4] have observed that for vinyl acetate emulsion polymerizations, the polydispersity (ratio $\overline{V}_n/\overline{V}_w$) is 2.6. Therefore, whenever eq. (8) is used in a reaction rate model, the particle number calculated will have to be multiplied by 2.6 to obtain the number-average particle number. The variables included in eq. (8) are only those which showed a 90% or higher significance level in the regression analysis. As noted earlier, the alkyl chain length of the emulsifier was not a significant variable at the 90% confidence level and is therefore not included in eq. (8). Thus, eq. (8) can be applied to both sodium lauryl sulfate- and sodium cetyl sulfate-stabilized systems.

Comparison of Reaction Models with Experimental Data

Equation (8) can now be used to predict the particle number behavior during a vinyl acetate emulsion polymerization. Substituting eq. (8) into the reaction models proposed by Friis and Litt, eqs. (2) and (1), respectively, the two models can be tested to determine if one or the other is now in agreement with the experimental data at both temperatures and over the range of initiator concentrations and ionic strengths studied. The reaction model proposed by Litt, eq. (1), contains one unknown parameter, the rate constant for the sweep-up of an aqueous oligomeric radical by a particle, which is contained in the constant C_2, while the model proposed by Friis, eq. (2), contains the two unknown parameters α and β, describing the effect of the changing particle composition on the diffusivity of the monomer.

Data from one run at 60°C was used to estimate the single parameter in Litt's model, while data from a run at 50°C was used to estimate the two parameters in Friis' model. The values of these parameters were 2.609×10^{-12} mole-sec-cm²/liter for the rate constant for radical sweep-up in Litt's model and 0.42 and 3.69 for the α and β parameters in Friis' model. In his original paper, Litt reported the value of the rate constant to be in the range of 4.25×10^{-12} to 1.30×10^{-12} mole-sec-cm²/liter while Friis used the values 0.3 and 3.2 for α and β in his paper. Thus, the values determined in this study are well within experimental error of the values reported originally. The values for all other rate constants, such as k_p, k_{t_p}, k_{tr_m}, and k_i, were obtained from the original papers. Using these values in the two rate expressions, under all conditions, and eq. (8) to model the particle number behavior, eqs. (1) and (2) can be integrated to yield conversion versus time predictions for the experimental results.

Figures 6 and 7 are typical plots of conversion versus time for polymerizations run during this investigation. In both figures the induction time for the reaction has been deleted so that the time axis is the time from the start of the reaction rather than the time from the addition of the initiator. Also shown on each figure are the results calculated using both the model proposed by Litt and the model proposed by Friis. While at 60°C the model proposed by Litt shows good
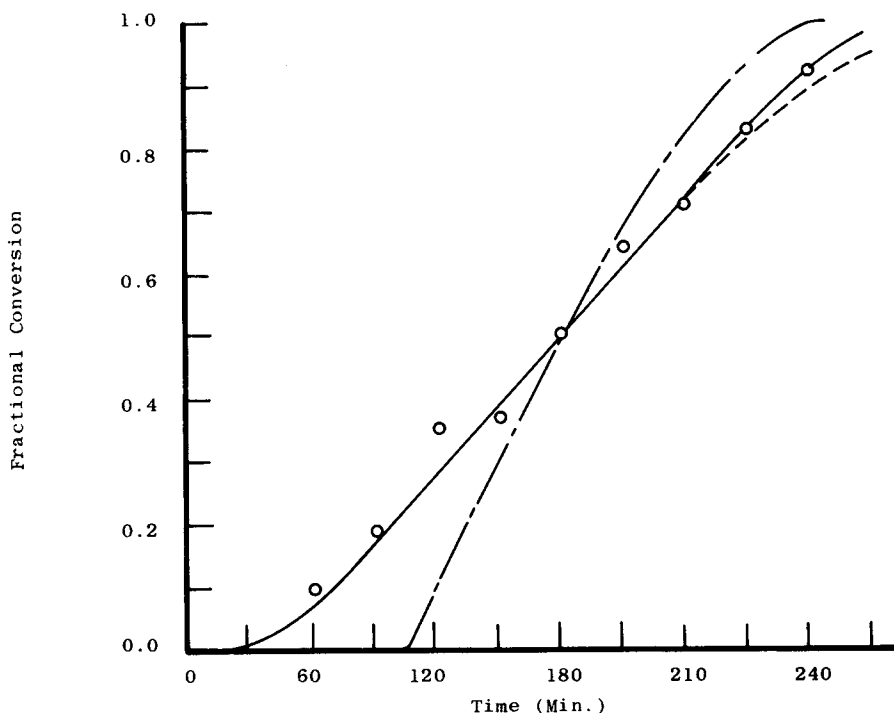
Fig. 6. Conversion-vs-time curve. Temperature = 50°C; $[K_2S_2O_8]$ = 0.25 × $10^{-3}M$; [SLS] = 2.7 g/l. water; (——) eq. (2) (Friis); (- - - - - - - -) eq. (2) (constant k_{t_p}); (— · —) eq. (1) (Litt); (O) experimental data.

agreement with the data, it gave a very poor agreement with the data at 50°C. The model proposed by Friis, however, shows good agreement at both temperatures.

Both models tend to overpredict the conversion for conversions above 95%. This is probably due to the manner in which the partitioning of the monomer between the aqueous and polymer phases was handled. In both models it was assumed that the aqueous phase monomer concentration was proportional to the square root of the polymer phase concentration, as had been observed by Dunn and Taylor.[9] This relationship begins to break down at higher conversions, as reported by Dunn, where the relationship becomes more linear. Thus, the model used here will underpredict the monomer concentration in the polymer at high conversions, which leads to calculated reaction rates that are lower and fractional conversions that are greater than those observed experimentally whenever the conversion exceeds 95%.

Litt considers the main termination step to occur in the aqueous phase and therefore uses a fixed value for the termination rate constant. Friis, on the other hand, proposes that the termination occurs within the particle and describes the termination rate constant as a decreasing function of conversion (gel effect). Holding the termination rate constant at 9.37 × 10^7 liter/mole-sec, its value at 0% conversion, the conversion-versus-time plot calculated from Friis' model showed only a slight difference from the plot calculated allowing the termination rate constant to vary (Figs. 6 and 7). This is in agreement with Friis, who observed only a very slight gel effect in this range of particle sizes. Allowing the
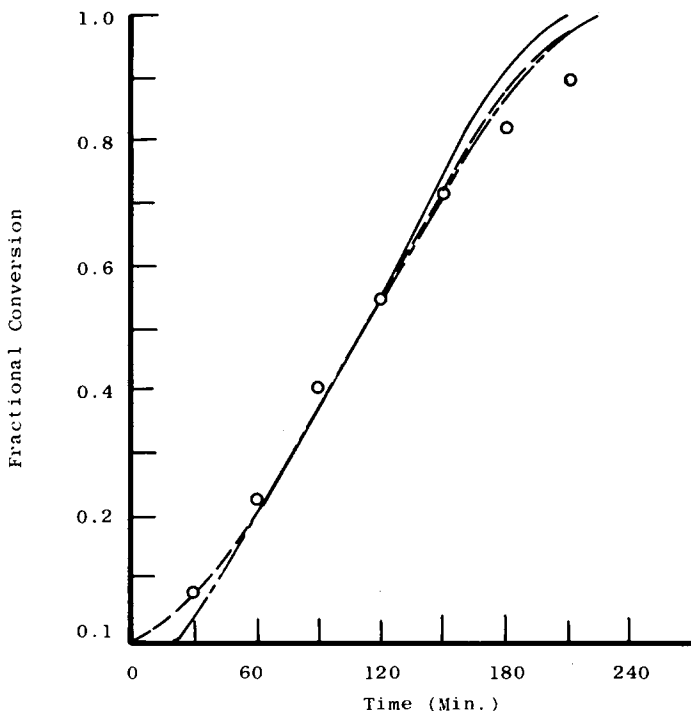
Fig. 7. Conversion-vs-time curve. Temperature = 60°C; $[K_2S_2O_8]$ = 0.125 × $10^{-3}M$; [SLS] = 10.9 g/l. H_2O; (——) eq. (2) (Friis); (- - - - - -) eq. (2) (constant k_{t_p}); (— · —) eq. (1) (Litt); (○) experimental data.

termination rate constant to vary with conversion affects the predicted conversion-versus-time plot only in the conversion range above 75%. In his original paper Litt admits that in this range of conversions the termination within particles may become significant, and thus a consideration of the gel effect should be included.

Litt also proposed that the increase in the reaction rate observed when a neutral salt was added to the reaction mixture arose because of a salting-out effect on the aqueous phase oligomeric radicals. Adding a neutral salt tends to decrease the particle stability, causing a decrease in the particle number which would, according to either eq. (1) or (2), tend to decrease the reaction rate. A recent paper by Klein, Kuist, and Stannett[10] reports that as the ionic strength of the aqueous phase is increased, the monomer partitions more strongly in favor of the polymer phase. Thus, as the ionic strength is increased, the monomer concentration in the polymer particles will increase and possibly the driving force for the diffusion of monomeric radicals out of the particles may be reduced. Both of these effects will tend to increase the reaction rate. Using the data presented by Klein et al. to correct for the effect of the ionic strength on the polymer phase monomer concentration only, the effect of an increasing ionic strength on the reaction rate, as calculated using Friis' model, was determined. For initiator levels greater than 0.5 × $10^{-3}M$, no significant effects were noted. At 0.25 × $10^{-3}M$ initiator, but with an ionic strength of 1.2 × $10^{-2}M$, an increase of 4% in the reaction rate was predicted. While this is smaller than the increase actually observed, it does indicate that the effect of the ionic strength on the partitioning

of the unreacted monomer is strong enough to overcome the rate reducing effect of the ionic strength on the particle number.

The two reaction models under consideration in this investigation differ mainly in that the model proposed by Friis considers a polymer phase, conversion-dependent termination in addition to a conversion-dependent diffusivity for monomeric radicals in the polymer particles. While the experimental data do not conclusively prove or disprove either theory, there is evidence to suggest that the model proposed by Friis, using a polymeric termination step, may be correct. This model yields consistently better predictions for the conversion-versus-time histories over a much wider range of reaction variables than does Litt's model. Further, the effects of such various reaction variables as initiator concentration, ionic strength, temperature, and emulsifier concentration on the reaction rate can be accounted for using Friis' reaction model, the particle number model derived in this investigation, and Klein's data on the effect of the ionic strength on the monomer partitioning. If all the modifications suggested by Litt and Stannett (allowing for a polymeric phase termination at high conversion and considering the diffusivity of monomeric radicals to be a function of the conversion) were made to their original model, it may do as well in predicting the results of a polymerization as does Friis' model.

CONCLUSIONS

The main shortcoming of all recent reaction models proposed for the emulsion polymerization of vinyl acetate has been their failure to account for the changes in the dependence of the particle number with changes in the initiator concentration and ionic strength. This changing dependence of the particle number on the initiator level may be the cause of the wide variations in the reaction rate order with respect to the initiator level reported by other investigators. Proposals that a change in the rate constant for the "sweep-up" of aqueous oligomers is responsible for the change in the reaction rate order have ignored the observed changes in the particle number. The results of this investigation reveal that for systems where the initiator is the only salt added to the reactor, the particle number increases with increasing initiator concentration at low initiator levels, becomes almost constant for initiator levels around $1.0 \times 10^{-3}M$, and increases again at higher initiator levels.

An empirical model describing the effects of initiator concentration, ionic strength, emulsifier level, and temperature on the particle number of a sodium alkyl sulfate-stabilized vinyl acetate emulsion polymerization has been developed. When this model is used in combination with the reaction model proposed by Friis, a model for vinyl acetate emulsion polymerization is formed which agrees with all of the available experimental data and is suitable for reactor simulation purposes. Since the alkyl chain length of the emulsifier had no significant effect on either the reaction rate or the particle number, the model described above is suitable for simulating either sodium lauryl sulfate- or sodium cetyl sulfate-stabilized systems. The reaction model proposed by Litt, when used with the particle number model described above, agreed with the data at 60°C but differed significantly from the data at 50°C.

While the particle number model described above does an adequate job of predicting the particle number within the ranges of the reaction variables used

in this study, its extension beyond these ranges is questionable.   Further studies should be conducted to obtain a more complete understanding of the effects of the initiator level, ionic strength, and particle diameter on the rate of flocculation and generation of latex particles.   These data are especially necessary for the description of continuous or semicontinuous processes.   In addition, the effects of increasing ionic strength, whether caused by increasing initiator levels or the addition of other salts, on both the partitioning of the monomer between the aqueous and polymeric phases and the escape of monomeric radicals from the latex particles need to be investigated to fully describe the effect of the ionic strength on the polymerization rate.

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