

# Reaction Kinetics of Vinyl Acetate Emulsion Polymerization

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## Synopsis

Transport of free radicals out of latex particles into the aqueous phase plays an important role in the emulsion polymerization of vinyl acetate. This so-called "desorption" process involves chain transfer to monomer which generates a mobile and rather stable monomer-unit free radical followed by the diffusion of this free radical out of the latex particle. A kinetic model is developed based on the reaction mechanisms of such an emulsion system. The experimental data available in the literature are used to test the model under various polymerization conditions. Reasonable agreement between the model predictions and experimental data is observed.

## INTRODUCTION

Kinetic studies of the emulsion polymerization of vinyl acetate and vinyl acetate copolymers are of great interest due to the industrial importance of the latexes produced. Vinyl acetate emulsion polymerization does not follow Smith-Ewart case 2 kinetics<sup>1</sup> because of high monomer solubility in the water phase and a high rate of chain transfer to monomer. Several aspects of vinyl acetate emulsion polymerization such as reaction loci, nucleation mechanisms, and free radical transport phenomena are not fully understood.

Patsiga et al.<sup>2</sup> concluded that the predominate reaction locus was in the aqueous phase. Several other research groups,<sup>3-6</sup> however, have indicated that beyond interval I (the particle nucleation period), most of the polymerization takes place in the latex particles. This is presently the generally accepted reaction locus.

During interval I, polymer particles can be generated via various nucleation mechanisms such as micellar nucleation,<sup>7,8</sup> homogeneous nucleation,<sup>9-11</sup> coagulative nucleation,<sup>15</sup> and, in some cases, monomer droplet polymerization.<sup>16,17</sup> Poehlein,<sup>18</sup> based on these works, has proposed a comprehensive picture of particle nucleation mechanisms. The mechanism that prevails in a specific system depends on the solubility of monomer in water, surfactant concentration, and monomer droplet size. Interval I kinetics is not within the scope of this study.

Harriott,<sup>19</sup> based on the assumption of an equilibrium distribution of free radicals in the heterogeneous system, derived a very simple rate expression for the emulsion polymerization of vinyl acetate. His model predicts a first-order dependency of the polymerization rate on the monomer concentration in the

latex particle. Litt et al.<sup>20</sup> and Stannett et al.<sup>21</sup> postulated that soap-solubilized poly(vinyl acetate) free radicals exist in the aqueous phase. These water-soluble free radicals can be swept up by existing latex particles, which is an ionic-strength-dependent process. According to their analysis, the particle phase termination via the sweep-up of a polymeric free radical into an active particle is not important when compared with aqueous phase termination.

Harada et al.<sup>22</sup> and Nomura et al.<sup>23-25</sup> considered the transport of monomer-unit free radicals out of the latex particles into the aqueous phase and employed the Smith-Ewart recursion equation to calculate the average number of free radicals per particle for the emulsion polymerization of vinyl acetate. The desorption rate constant was correlated to several physical and kinetic parameters such as the diffusion coefficient of monomer-unit free radical in the latex particle and the particle size. The termination rate constant was expressed as a function of monomer conversion. Nomura et al.<sup>24</sup> also developed a kinetic model which is based on the assumptions that latex particles are generated from micelles and only particles containing 0, 1, and 2 free radicals need to be considered. Their model predicted the experimental data reasonably well.

Friis et al.<sup>26,27</sup> employed the rate expression for vinyl chloride derived by Ugelstad et al.<sup>28</sup> to investigate the emulsion polymerization of vinyl acetate. They indicated that the often observed linear conversion-vs.-time data is due to the decrease of the desorption rate constant and the termination rate constant with increasing monomer conversion. The treatments of the desorption rate constant and the termination rate constant were similar to those of Nomura et al.<sup>24</sup> Zollars<sup>29</sup> studied the reaction kinetics of vinyl acetate emulsion polymerization and developed an empirical model for the prediction of the number of polymer particles generated in interval I and polymerization rate under various reaction conditions.

Chang et al.<sup>30</sup> considered a sequence of elementary reactions involved in the emulsion polymerization of vinyl acetate and developed the most comprehensive kinetic model to date. The unique feature of their model is that the chain transfer to monomer reaction generates a rather stable monomer-unit free radical. This monomer-unit free radical can then diffuse easily out of the latex particle into the aqueous phase. These desorbed monomer-unit free radicals can diffuse through several particles until they either reinitiate or terminate. The termination reaction between two polymeric free radicals was proposed to be insignificant as compared with the major termination step via the reaction of a monomer-unit free radical with a polymeric free radical in a latex particle. They also postulated that the dependency of the desorption rate constant on the monomer concentration in the polymer particle at different polymerization temperatures is rather complicated in order to interpret the observed reaction rate data.

Although a number of publications have dealt with the kinetics of vinyl acetate emulsion polymerization, several fundamental reaction mechanisms involved in these processes have not been quantified. The purpose of this study is to reexamine these problems (e.g., the absorption of oligomeric free radicals into the particles, transport of monomer-unit free radicals out of the particles into the aqueous phase, reabsorption of these desorbed monomer-unit

free radicals into the particles, etc.) and develop a kinetic model to describe these emulsion polymerization reactions beyond interval I.

### EMULSION POLYMERIZATION KINETICS

Most emulsion polymerization reactions are initiated with water-soluble initiators. Persulfate, for example, is a commonly used water-soluble initiator. Persulfate thermally decomposes into two sulfate radicals ( $\text{SO}_4^- \cdot$ ) in the aqueous phase. These initiator free radicals are most likely to add monomer molecules before they enter the latex particles since the solubility of vinyl acetate in water is relatively high. Therefore, the absorbed oligomeric free radicals are considered incapable of diffusing out of the particles into the aqueous phase with the generally accepted assumption that only monomer-unit free radicals can desorb. The chance for the desorption of those initiator free radicals which enter the polymer particles without adding any monomer molecules is very small when taking into consideration the very high initiation rate constant for the initiator free radicals and high monomer concentration in the particles.

The oligomeric free radicals grow via propagation with monomer molecules in the particles until chain transfer to monomer occurs. This chain transfer process generates a small and rather mobile monomer-unit free radical which can diffuse out of the latex particle into the aqueous phase. This so-called "desorption" phenomenon plays an important role in the emulsion polymerization of vinyl acetate. Chang et al.<sup>30,31</sup> showed that the major chain transfer to monomer reaction takes place on the vinyl hydrogen (about 94%) instead of the acetyl hydrogen of vinyl acetate. The monomer-unit free radicals thus formed are rather stable and can escape very easily from the particles. Chang et al. postulated that the desorbed monomer-unit free radicals can be reabsorbed into the particles and repeat these processes until they either reinitiate or terminate in the particles. The process of transport of free radicals out of the latex particles into the aqueous phase will reduce the average number of free radicals per particle and consequently lower the polymerization rate. Chain transfer of a growing free radical to the acetyl hydrogen of vinyl acetate can also happen. Nevertheless, this chain transfer reaction is of no kinetic significance because the generated monomer-unit free radical is so reactive that it should reinitiate instantly before it can escape from the particle.

Ugelstad and Hansen<sup>32</sup> and Harada et al.<sup>22</sup> independently developed similar theoretical equations for the desorption rate constant. Both were based on the consideration of diffusion with chemical reaction in a spherical latex particle. Chang et al.<sup>30</sup> simply considered the molecular diffusion of a relatively stable monomer-unit free radical inside the particle and derived a somewhat different expression for the desorption rate constant. The desorption rate constant is proportional to the diffusion coefficient of the monomer-unit free radical and inversely proportional to the square of the particle size. During interval II the desorption rate constant decreases with increasing conversion since the particles continue to grow by polymerization of the monomer supplied by diffusion from the monomer droplets. After the disappearance of the monomer

reservoir, the desorption rate constant continues to decrease because of the decreasing diffusion coefficient of the monomer-unit free radical with increasing viscosity caused by the conversion of monomer into polymer.

Termination is of no kinetic significance for calculation of the average number of free radicals per particle since only a very small portion of the particles contain more than two free radicals. It could become an important factor for a reaction system with large particles or low termination rates. In these cases, the probability for two or more free radicals to coexist in a particle is greater.

## MODEL DEVELOPMENT

### Average Number of Free Radicals per Particle

Ugelstad and Mork<sup>33</sup> employed a population balance approach to calculate the average number of free radicals per particle for the emulsion polymerization of vinyl chloride. The absorbed oligomeric free radicals originating from the water-soluble initiator were assumed to be able to escape from the particles. As discussed above, such a transfer is improbable for the emulsion polymerization of relatively water-soluble monomers such as vinyl acetate and vinyl chloride. The present kinetic model is based on the assumption that only monomer-unit free radicals can desorb from particles.

For simplicity, it is first assumed that instantaneous termination occurs when one free radical enters an active particle. Thus, only those particles which contain at most one free radical need to be considered. Aqueous phase polymerization is assumed to be insignificant. With these assumptions, the following pseudo-steady state population balances can then be established:

$$\begin{aligned} dN_m/dt = & -\rho_i N_m/N + K_{fm}[M]_p N_p - K'_p[M]_p N_m \\ & - K_{dm} N_m + K_{dm} N_m (N_0/N - N_m/N) \\ = & 0 \end{aligned} \quad (1)$$

$$\begin{aligned} dN_p/dt = & \rho_i (N_0/N - N_p/N) - K_{fm}[M]_p N_p \\ & + K'_p[M]_p N_m - K_{dm} N_m N_p/N \\ = & 0 \end{aligned} \quad (2)$$

$$N = N_0 + N_m + N_p \quad (3)$$

where  $N$ ,  $N_0$ ,  $N_m$ , and  $N_p$  are the total number of particles, number of inactive particles, number of particles with one monomer-unit free radical, and number of particles with one polymeric free radical, respectively.  $\rho_i$  is the rate of transport of initiator free radicals into the particles.  $K_{fm}$ ,  $K'_p$ , and  $K_{dm}$  are the rate constants for the chain transfer to monomer, monomer-unit free radical reinitiation, and desorption, respectively.  $[M]_p$  is the monomer concentration in the latex particle and  $t$  is the reaction time.

If it is further assumed that  $N_0/N$  approximates unity (i.e.,  $N_0 \gg N_m, N_p$ ) and  $K_{dm}N_mN_p/N$  is negligible, then eqs. (1)–(3) can be solved simultaneously to calculate the average number of free radicals per particle,  $\bar{n}$ :

$$\begin{aligned}\bar{n} &\cong N_p/N \\ &= C_3 \left[ -C_2 + (C_2^2 + 4\rho_i C_1)^{1/2} \right] / 2C_1 \\ &\cong 0.5 \left\{ -\rho_i K'_p / NK_{dm} K_{fm} + \left[ (\rho_i K'_p / NK_{dm} K_{fm})^2 \right. \right. \\ &\quad \left. \left. + 4(\rho_i K'_p / NK_{dm} K_{fm}) \right]^{1/2} \right\} \quad (4)\end{aligned}$$

where

$$\begin{aligned}C_1 &= K_{dm} K'_p / NK_{fm} + \rho_i K_{dm} / N^2 K_{fm} [M]_p \\ &\cong K_{dm} K'_p / NK_{fm} \quad (5)\end{aligned}$$

$$\begin{aligned}C_2 &= \rho_i / N + \rho_i K'_p / NK_{fm} + \rho_i^2 / N^2 K_{fm} [M]_p \\ &\cong \rho_i K'_p / NK_{fm} \quad (6)\end{aligned}$$

$$\begin{aligned}C_3 &= K'_p / NK_{fm} + \rho_i / N^2 K_{fm} [M]_p \\ &\cong K'_p / NK_{fm} \quad (7)\end{aligned}$$

The validity of the approximate eqs. (4)–(7) can be tested by considering the emulsion polymerization of vinyl acetate at 50°C.  $K_{fm}$  is about 0.67 L/mol s and  $[M]_p$  is about 8.95 mol/L during interval II.<sup>23</sup>  $K'_p$ , the reinitiation rate constant for the monomer-unit free radical, is estimated to be about 30 L/mol s.<sup>30</sup>  $\rho_i/N$ , which is dependent on the experimental recipes, ranges from  $1 \times 10^{-3}$  to  $1 \times 10^{-3}$  1/s.<sup>23,26</sup> With these kinetic parameters and a wide range of  $\rho_i/N$ , the approximations are readily justified.

Nomura<sup>34</sup> derived a similar equation to calculate  $\bar{n}$  as shown below.

$$\bar{n} = 0.5 \left\{ -\rho_i / NK_f + \left[ (\rho_i / NK_f)^2 + 2\rho_i / NK_f \right]^{1/2} \right\} \quad (8)$$

where  $K_f$  is the desorption rate constant. Nomura also computed  $\bar{n}$  values from experimental data for emulsion polymerization of vinyl acetate and vinyl chloride as shown by the discrete points in Figure 1.  $K_f$  was calculated by the theoretical expression developed by Harada et al.<sup>22</sup> The dashed line in the same figure represents the calculated  $\bar{n}$  according to Nomura's theory [eq. (8)]. On condition that  $\rho_i K'_p / NK_{dm} K_{fm}$  in eq. (4) is set equal to  $\rho_i / NK_f$  in eq. (8), one can compare the predictions of  $\bar{n}$  by both models. The predicted  $\bar{n}$  by eq. (4) is shown as the solid line in Figure 1. The present model predicts a higher  $\bar{n}$  than that of Nomura and fits the experimental data better. Please note that eq. (4) is only valid for  $\bar{n} \ll 0.5$  due to the assumption of  $N_0/N \cong 1$ .

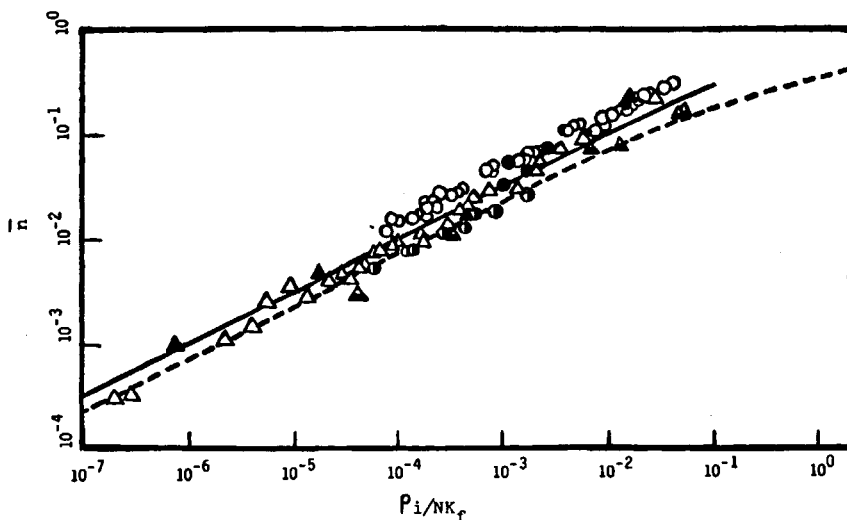


Fig. 1. Average number of free radicals per particle vs.  $\rho_i/NK_f$  profiles of vinyl acetate [(●) Friis; (○) Nomura<sup>34</sup>; (●) Zollars] and vinyl chloride [(△) Ugelstad; (▲) Giskehang; (△) Peggion] emulsion polymerizations<sup>34</sup>: (—) this work; (---) Nomura.<sup>34</sup>

The population balance equations can be extended to include particles which contain two free radicals as shown below.

$$\begin{aligned} dN_m/dt &= -\rho_i N_m/N + K_{fm}[M]_p N_p - K'_p[M]_p N_m \\ &\quad - K_{dm} N_m + (K_{dm} N_m + K_{dm} N_{pm}) N_0/N \\ &= 0 \end{aligned} \quad (9)$$

$$\begin{aligned} dN_p/dt &= \rho_i (N_0/N - N_p/N) - K_{fm}[M]_p N_p + K'_p[M]_p N_m \\ &\quad + K_{dm} N_{pm} - (K_{dm} N_m + K_{dm} N_{pm}) N_p/N \\ &= 0 \end{aligned} \quad (10)$$

$$\begin{aligned} dN_{pm}/dt &= \rho_i N_m/N + 2K_{fm}[M]_p N_{pp} - K'_p[M]_p N_{pm} \\ &\quad - K_{dm} N_{pm} + (K_{dm} N_m + K_{dm} N_{pm}) N_p/N \\ &\quad - (K'_t/v) N_{pm} \\ &= 0 \end{aligned} \quad (11)$$

$$\begin{aligned} dN_{pp}/dt &= \rho_i N_p/N - 2K_{fm}[M]_p N_{pp} + K'_p[M]_p N_{pm} \\ &\quad - (2K_t/v) N_{pp} \\ &= 0 \end{aligned} \quad (12)$$

$$N = N_0 + N_m + N_p + N_{pm} + N_{pp} \quad (13)$$

where  $N_{pm}$  is the number of particles with one polymeric free radical and one monomer-unit free radical and  $N_{pp}$  the number of particles with two polymeric free radicals.  $K'_t$  is the termination rate constant between a monomer-unit free radical and a polymeric free radical and  $K_t$  between two polymeric free radicals.  $v$  is the particle volume.

Equations (9)–(13) represent a set of five simultaneous nonlinear algebraic equations. To simplify the solution,  $N_0$  is assumed to change very slowly with increasing conversion. Thus,  $N_0$  can be treated as a constant within a very small conversion interval in eqs. (9)–(12). After some mathematical manipulations,  $\bar{n}$  can be calculated by the following equations:

$$\bar{n} \cong (N_p + N_{pm} + 2N_{pp})/N \quad (14)$$

$$N_p = \left[ -E_2 + (E_2^2 - 4E_1E_3)^{1/2} \right] / 2E_1 \quad (15)$$

$$N_m = D_1N_p + D_2 \quad (16)$$

$$N_{pp} = B_1N_m + B_2N_p + B_3 \quad (17)$$

$$N_{pm} = A_1N_m + A_2N_p + A_3N_{pp} + A_4 \quad (18)$$

where the constants  $A_1$ – $A_4$ ,  $B_1$ – $B_3$ ,  $D_1$ – $D_2$ , and  $E_1$ – $E_3$  are defined as follows:

$$A_1 = (K'_p[M]_p + \rho_i/N) / (K'_p[M]_p + K'_t/v)$$

$$A_2 = -(K_{fm}[M]_p + \rho_i/N) / (K'_p[M]_p + K'_t/v)$$

$$A_3 = 2K_{fm}[M]_p / (K'_p[M]_p + K'_t/v)$$

$$A_4 = \rho_i(N_0/N) / (K'_p[M]_p + K'_t/v)$$

$$B_1 = K'_p[M]_p A_1 / (2K_{fm}[M]_p - K'_p[M]_p A_3 + 2K_t/v)$$

$$B_2 = \frac{\rho_i/N + K'_p[M]_p A_2}{2K_{fm}[M]_p - K'_p[M]_p A_3 + 2K_t/v}$$

$$B_3 = K'_p[M]_p A_4 / (2K_{fm}[M]_p - K'_p[M]_p A_3 + 2K_t/v)$$

$$D_1 = \frac{K_{fm}[M]_p + K_{dm}(N_0/N)(A_2 + A_3B_2)}{\rho_i/N + K'_p[M]_p + K_{dm}[1 - (N_0/N)(1 + A_1 + A_3B_1)]}$$

$$D_2 = \frac{K_{dm}(N_0/N)(A_4 + A_3B_3)}{\rho_i/N + K'_p[M]_p + K_{dm}[1 - (N_0/N)(1 + A_1 + A_3B_1)]}$$

$$E_1 = K_{dm}D_1/N + K_{dm}[A_1D_1 + A_2 + A_3(B_1D_1 + B_2)]/N$$

$$\begin{aligned}
 E_2 &= \rho_i/N + K_{fm}[M]_p - K'_p[M]_p D_1 \\
 &\quad - K_{dm}[A_1 D_1 + A_2 + A_3(B_1 D_1 + B_2)] + K_{dm} D_2/N \\
 &\quad + K_{dm}[A_1 D_2 + A_3(B_1 D_2 + B_3) + A_4]/N \\
 E_3 &= \rho_i N_0/N + K'_p[M]_p D_2 \\
 &\quad - K_{dm}[A_1 D_2 + A_3(B_1 D_2 + B_3) + A_4]
 \end{aligned}$$

With the knowledge of  $\bar{n}$ , the rate of emulsion polymerization can be obtained by the following expression:

$$dX/dt = (K_p[M]_p M_w/M_0 N_{av}) \bar{n} N \quad (19)$$

where  $X$  is the monomer conversion,  $K_p$  the propagation rate constant,  $M_w$  the monomer molecular weight,  $M_0$  the initial amount of monomer added into the reactor (g/l  $H_2O$ ), and  $N_{av}$  is Avogadro's number. Equation (19) can be numerically integrated with the initial condition:  $X = 0$  at  $t = 0$ .

### Physical and Kinetic Parameters

During interval II, in the presence of monomer droplets, the monomer concentration in the particle is constant and the particle size  $d$  can be calculated as

$$d = [3M_0/4\pi d_p(1 - \psi)]^{1/3} (X/N)^{1/3} \quad (20)$$

where  $d_p$  is the density of the monomer-swollen polymer particle and can be approximated as unity.  $\psi$  is the monomer weight fraction in the latex particles.

Beyond interval II the monomer concentration in the particle starts to decrease and the particle size remains relatively constant:

$$[M]_p = (1 - X)[M]_{pc}/(1 - X_c) \quad (21)$$

$$d = [3M_0/4\pi d_p(1 - \psi_c)]^{1/3} (X_c/N)^{1/3} \quad (22)$$

where  $[M]_{pc}$ ,  $X_c$ , and  $\psi_c$  are the monomer concentration, monomer conversion, and monomer weight fraction in the particle at the end of interval II, respectively.

The desorption rate constant ( $K_{dm}$ ) is proportional to the diffusion coefficient of the monomer-unit free radical ( $D_m$ ) and inversely proportional to the square of the particle size ( $d$ ),

$$K_{dm} = K(D_m/d^2) \quad (23)$$

where  $K$  is a proportional constant and dependent on the kinds of monomers and polymerization temperature.



In this study, the concept of free volume is used to relate changes in  $D_m$  with conversion. The relationship between the diffusion coefficient and free volume has been discussed in detail by Bueche.<sup>36</sup> This relationship is expressed as

$$D_m/D_{m0} = \exp\left[-V_m^*(1/V_f - 1/V_{f0})\right] \quad (24)$$

where  $D_{m0}$  is the diffusivity of the monomer-unit free radical at an arbitrarily chosen reference state,  $V_m^*$  an adjustable constant,  $V_f$  the fractional free volume of the reaction medium (monomer + polymer) and  $V_{f0}$  the fractional free volume of the reaction medium at an arbitrarily chosen reference state. The monomer-swollen polymer particle during interval II has been taken as the reference state in this kinetic model.

The fractional free volume of the monomer-swollen polymer particle is given by<sup>35</sup>

$$V_f = V_{fm}\phi_m + V_{fp}(1 - \phi_m) \quad (25)$$

where  $V_{fm}$  and  $V_{fp}$  are the fractional free volumes of monomer and polymer, respectively.  $\phi_m$  is the volume fraction of monomer which can be calculated from the information of the monomer conversion and densities of monomer and polymer. Furthermore, according to Soh and Sundberg,<sup>36</sup> the fractional free volume of  $V_{fm}$  and  $V_{fp}$  can be expressed as follows:

$$V_{fp} = 2.18 \times 10^{-2} + 5.0 \times 10^{-4}(T - 26.5) \quad (26)$$

$$V_{fm} = 1.54 \times 10^{-1} + 5.1 \times 10^{-4}T \quad (27)$$

where  $T$  is the reaction temperature.

At the latter stage of reaction, the viscosity of the reacting fluid is so high that the movement of the growing chain into a position where it may terminate with another free radical is hindered. This will lead to a decrease in the termination rate constant with increasing conversion, which is known as the gel effect. As suggested by Soh and Sundberg,<sup>36</sup> the termination rate constant between two polymeric free radicals in the latex particle takes the following form:

$$K_t/K_{t0} = \exp\left[-V_p^*(1/V_f - 1/V_{f0})\right] \quad (28)$$

where the subscript 0 refers to the selected reference condition.  $V_p^*$  is an adjustable parameter which is taken as unity in this study.<sup>36</sup>

The termination reaction between a monomer-unit free radical and a polymeric free radical is predominately controlled by the motion of the small and rather mobile monomer-unit free radical. Hence, the change of termination rate constant  $K_t'$  with conversion can be expressed as

$$K_t'/K_{t0} = \exp\left[-V_m^*(1/V_f - 1/V_{f0})\right] \quad (29)$$

TABLE I  
Recipes for the Experiments of Nomura et al.<sup>23 a</sup>

Run	$S_0$ (g/L H <sub>2</sub> O)	$I_0$ (g/L H <sub>2</sub> O)	$N$ (#/L H <sub>2</sub> O)
1	25	1.25	1.9E18
2	12.5	1.25	1.4E18
3	6.25	1.25	8.0E17
4	1.88	1.25	3.2E17
5	0.625	2.50	1.5E17
6	6.25	2.50	1.0E18
7	6.25	0.625	5.0E17
8	6.25	0.313	5.0E17
9	6.25	0.156	5.0E17

<sup>a</sup> $T = 50^\circ\text{C}$ ,  $M_0 = 500$  g/L H<sub>2</sub>O. S = sodium lauryl sulfate and I = potassium persulfate.

### Comparison of Model with Experiments

Nomura et al.<sup>23</sup> investigated unseeded, batch emulsion polymerization of vinyl acetate at  $50^\circ\text{C}$ . Their experimental data were used to assess the proposed kinetic model. The model is, in general, valid only for systems with narrow particle size distributions (PSD). Unfortunately, PSD data were not reported, but batch reactions with simple anionic emulsifiers normally yield rather narrow PSD latexes. In the following computer simulations, unless indicated otherwise, only those latex particles which contain at most two free radicals are considered. The recipes for these experiments are listed in Table I. Other parameters necessary in the calculations were obtained from the literature or estimated from the experimental conditions as shown in Table II.

The values of  $N$  in Table I were obtained from a graph in Ref. 22. The data reported have considerable scatter and thus the  $N$  values listed are approximate ( $\pm 20$ –40%). Some of the literature values of parameters listed in Table II can also be questioned. Only one value of  $K_{fm}/K_p$  was found and this number was used for model simulations at 50 and  $60^\circ\text{C}$ . One would expect  $K_{fm}/K_p$  to increase modestly with temperature. The large difference in

TABLE II  
Parameters for Computer Modeling

Parameters	Values		Reference
$X_c$	0.23		23
$[M]_{pc}$	8.95 mol/L		23
$\psi_c$	0.77		23
	$T = 50^\circ\text{C}$	$T = 60^\circ\text{C}$	
$K_i f^a$	$1.7 \times 10^{-6}$	$8.3 \times 10^{-6}$ L/S	37, 38
$K_p$	3300	7000 L/mol s	23, 39
$K_{fm}/K_p$	$1.98 \times 10^{-4}$	$1.98 \times 15^4$	40
$K'_p$	30	41 L/mol s	30
$K_{t0}$	$1.17 \times 10^8$	$6 \times 10^8$ L/mol s	41, 42
$D_{m0}$	$1 \times 10^{-8}$	$1 \times 10^{-8}$ dm <sup>2</sup> /s	26

<sup>a</sup> $K_i f$  = the decomposition rate constant of initiator.

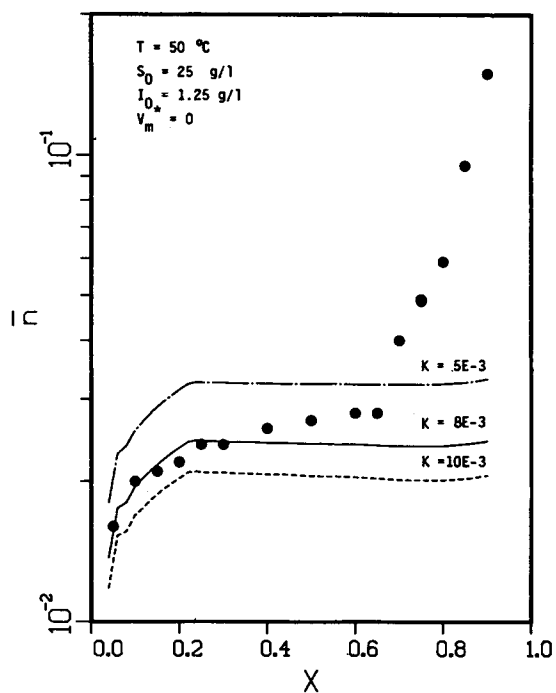


Fig. 2. Average number of free radicals per particle vs. conversion profiles of vinyl acetate emulsion polymerization.

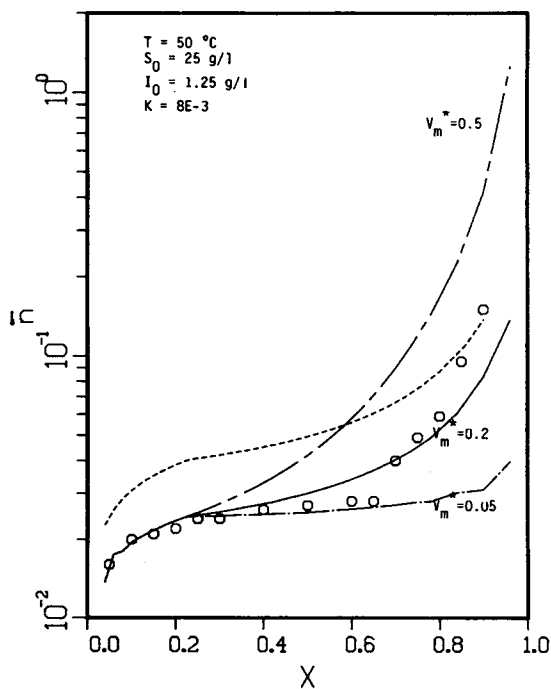


Fig. 3. Average number of free radicals per particle vs. conversion profiles of vinyl acetate emulsion polymerization: (---; —; - - -) "0-1-2" model; (----) "0-1" model.

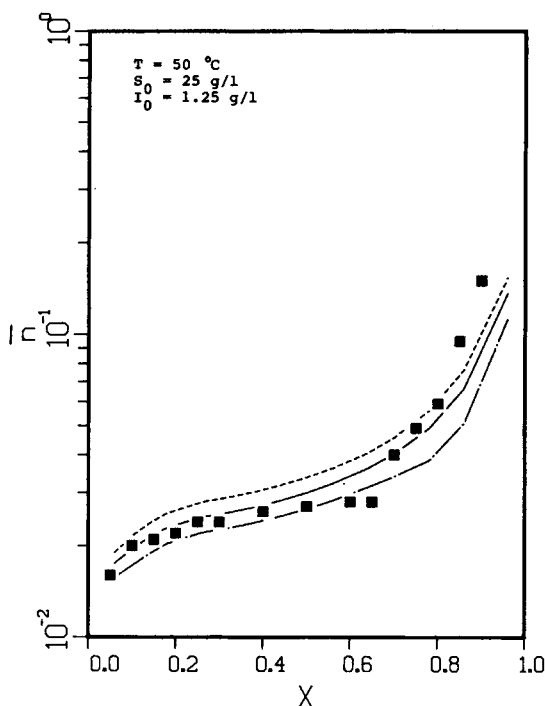


Fig. 4. Influence of different  $K_{t0}$  values (1/mol s) on the best-fit curve from Figure 3: (---)  $5.85 \times 10^7$  (—)  $1.17 \times 10^8$  (-·-)  $5.85 \times 10^8$ .

reported values of  $K_{t0}$  between 50 and 60°C is unexpected because termination reactions normally have small activation energies. The  $K_{t0}$  values listed in Table II are taken from separate references. The different experimental conditions and lack of accuracy in the determination of  $K_{t0}$  is probably responsible for the large change in values. Fortunately, modest errors in the values assigned to the parameters  $N$ ,  $K_{fm}/K_p$ , and  $K_{t0}$  do not alter the major results of this paper.

The only remaining parameters that need to be specified before computer simulations can be carried out are  $K$  and  $V_m^*$ .  $K$  determines the magnitude of  $K_{dm}$  and  $V_m^*$  only has an effect on  $K_{dm}$  beyond interval II. Therefore, the strategy used here is first to best fit the experimental data with  $K$  in interval II and then to shape the predicted curve in interval III with  $V_m^*$ .

The  $\bar{n}$ -vs.- $X$  data of run 1 (discrete points in Fig. 2) were employed to evaluate the parameters  $K$  and  $V_m^*$ . First,  $V_m^*$  is set equal to zero and  $K$  is varied to fit the experimental data as illustrated in Figure 2.  $K$  has a best fit value of  $8 \times 10^{-3}$  as shown by the solid line in Figure 2. As expected, the model prediction starts to deviate from the experimental data at about 30% conversion ( $X_c = 0.23$ ). Figure 3 shows that  $V_m^*$  has a best fit value of 0.2. Reasonable agreement between the model prediction and experimental data is observed. Figure 4 shows the influence of different  $K_{t0}$  values on the best-fit curve from Figure 3.

Figure 5 shows the calculated  $K_{dm}$  vs.  $X$  curve with  $K = 8 \times 10^{-3}$  and  $V_m^* = 0.2$ .  $K_{dm}$  decreases from 240 1/s at  $X = 0.1$  to 10 1/s at  $X = 0.9$ . An

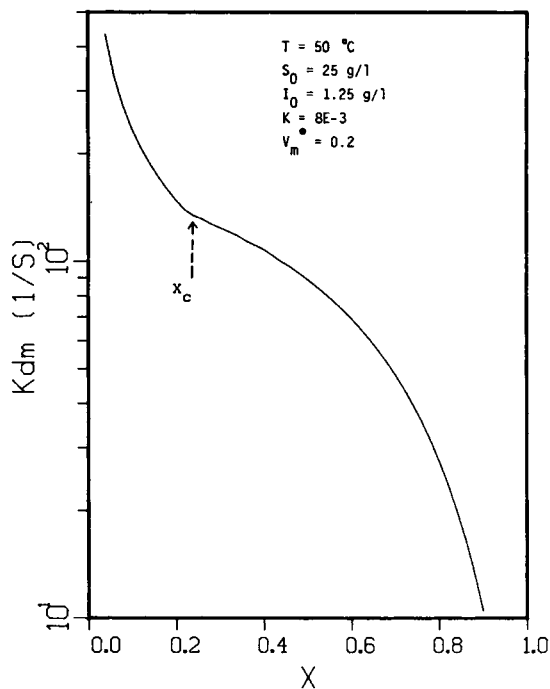


Fig. 5. Desorption rate constant vs. conversion curve of vinyl acetate emulsion polymerization.

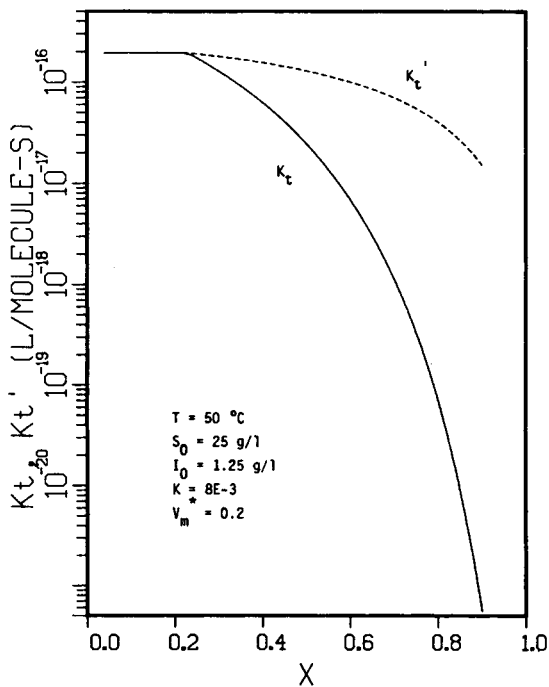


Fig. 6. Termination rate constant vs. conversion profiles of vinyl acetate emulsion polymerization.

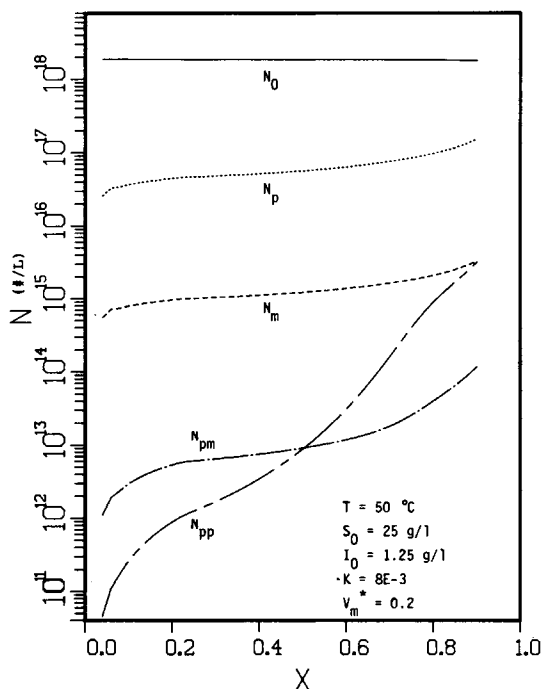


Fig. 7. Latex particle population vs. conversion profiles of vinyl acetate emulsion polymerization.

abrupt change in the slopes of the curve at  $X_c$  corresponds to the proposed mechanisms: (1) During interval II,  $K_{dm}$  decreases with increasing conversion due to the continuous growth of the particles by polymerization of the monomer supplied by diffusion from the monomer droplets. (2) After the disappearance of the monomer reservoir, the diffusion coefficient of the monomer-unit free radical decreases with increasing viscosity caused by the conversion of monomer into polymer. This will also lower the desorption rate constant, but at a different rate.

The calculated  $K_t$  and  $K'_t$  as a function of  $X$  are shown in Figure 6. Beyond interval II,  $K'_t$  is always greater than  $K_t$ . This is because the termination reaction between a monomer-unit free radical and a polymeric free radical is mainly controlled by the motion of the small and rather mobile monomer-unit free radical. Such a termination reaction is expected to be faster than that between two hindered polymeric free radicals if both concentrations of the monomer-unit free radical and polymeric free radical are equal. The calculated  $N$ 's as a function of  $X$  are presented in Figure 7. At low conversion, the termination reaction is not important in computing  $\bar{n}$  for this experiment because of the small populations of  $N_{pm}$  and  $N_{pp}$ . Below 50% conversion, the termination reaction between a monomer-unit free radical and a polymeric free radical is more important than that between two polymeric free radicals ( $K'_t > K_t$  and  $N_{pm} > N_{pp}$ ). After 50% conversion, these two termination reactions are comparable ( $K'_t > K_t$  and  $N_{pp} > N_{pm}$ ). This finding is not in agreement with that of Chang et al.<sup>30</sup>

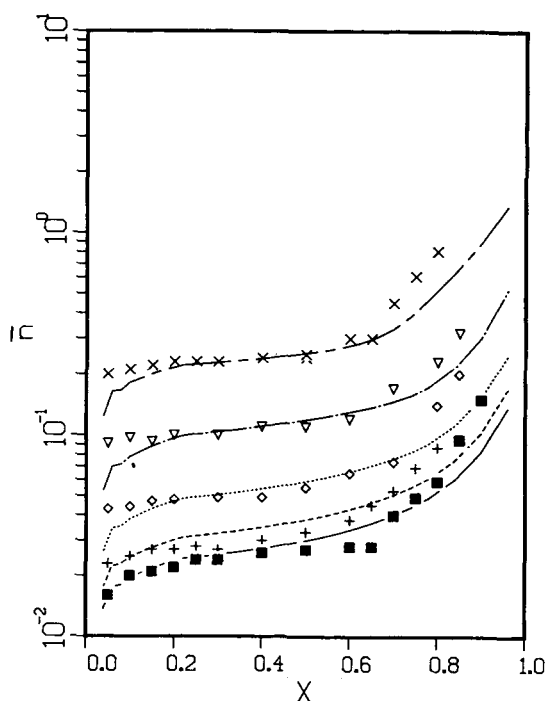


Fig. 8. Average number of free radicals per particle vs. conversion profiles of vinyl acetate emulsion polymerization [(■) used to evaluate  $K$  and  $V_m^*$ ].  $S_0$  (g/L),  $I_0$  (g/L): (■—) 25, 1.25; (+---) 12.5, 1.25; (◇····) 6.25, 1.25; (▽---) 1.88, 1.25; (×---) 0.625, 2.50.

For comparison, the calculated  $\bar{n}$ -vs.- $X$  curve ( $K = 8 \times 10^{-3}$  and  $V_m^* = 0.2$ ) with the assumption that each latex particle can contain at most one free radical is also shown as the dashed line in Figure 3. At each point in the conversion range, the "0-1" model (---) always predicts a higher value for  $\bar{n}$  than the "0-1-2" model (—). The deviation is caused by the neglect of  $N_{pm}$  and  $N_{pp}$ . Termination reactions in these latex particles can reduce the average number of free radicals per particle. It should be noted here that the  $\bar{n}$ -vs.- $X$  curve predicted by the "0-1" model can be shifted downwards by varying  $K$  and changed in shape during interval III by varying  $V_m^*$ . Thus, one can still predict the experimental data by the "0-1" model reasonably well.

With the best-fit values of  $K$  and  $V_m^*$ , the model predictions for runs 1-5 are shown by the continuous curves in Figure 8. The  $\bar{n}$ -vs.- $X$  data represented by the discrete points are also shown in Figure 8. The model predicts the  $\bar{n}$  behavior very well, although some discrepancies between the model and experimental data are observed. At constant  $M_0$  and  $I_0$  (except one experiment:  $I_0 = 2.50$  g/L), the higher the surfactant concentration, the greater the number of particles generated in interval I and consequently the smaller the portion of the particles which contain free radicals (i.e., the smaller the average number of free radicals per particle).

Runs 3 and 6-9 in Table I were used to evaluate the effect of the concentration of initiator. Figure 9 shows the calculated and experimental conversion vs. time curves. The discrete points represent the experimental

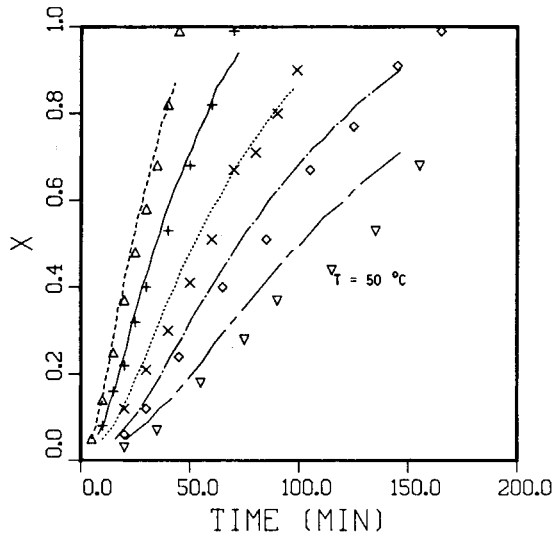


Fig. 9. Conversion vs. time profiles of vinyl acetate emulsion polymerization:  $S_0 = 6.25$  g/L;  $I_0$  (g/L): ( $\Delta$ ---) 2.5; (+—) 1.25; ( $\times$  ···) 0.625; ( $\diamond$ -·-·) 0.313; ( $\nabla$ ---) 0.156.

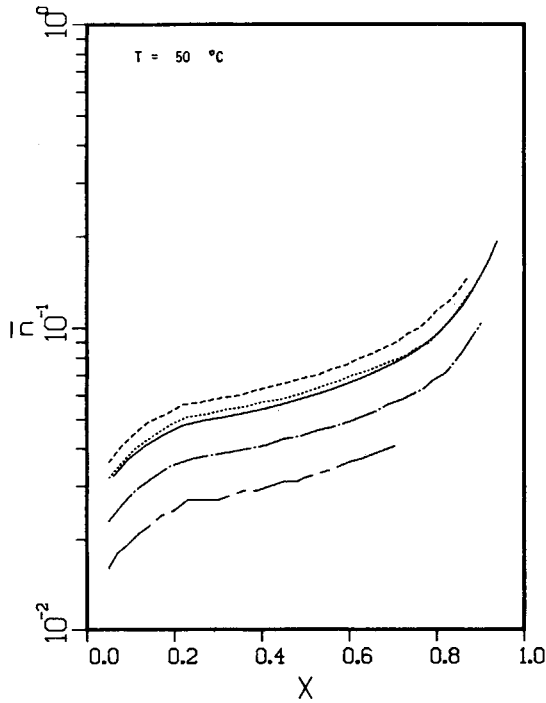


Fig. 10. Average number of free radicals per particle vs. conversion profiles of vinyl acetate emulsion polymerization:  $S_0 = 6.25$  g/L;  $I_0$  (g/L): (---) 2.5; (···) 1.25; (—) 0.625; (-·-) 0.313; (---) 0.156.



TABLE III  
Recipes for the Experiments of Chang et al.<sup>30 a</sup>

Run	$V_{\text{org}}/V_{\text{aq}}$	$N$ (#/L H <sub>2</sub> O)
a	0.33	$7.27 \times 10^{17}$
b	0.46	$3.31 \times 10^{17}$
c	0.33	$3.31 \times 10^{17}$
d	0.125	$3.31 \times 10^{17}$

<sup>a</sup> $T = 60^\circ\text{C}$ ,  $S_0 = 2.5 \times 10^{-3}$  g/L H<sub>2</sub>O,  $I_0 = 5 \times 10^{-4}$  mol/L H<sub>2</sub>O. Number average diameter of seed particle = 0.045  $\mu\text{m}$ . S = sodium lauryl ether sulfate, I = potassium persulfate, and  $V_{\text{org}}/V_{\text{aq}}$  = volume ratio of organic phase to aqueous phase.

data and the continuous curves the model predictions. The model predicts the  $X$ -vs- $t$  data reasonably well except for the experiment with the lowest initiator concentration. The calculated  $\bar{n}$ -vs- $X$  profiles with various initiator concentrations are shown in Figure 10. At any conversion,  $\bar{n}$  increases with increasing initiator concentration. Therefore, the rate of emulsion polymerization increases with increasing initiator concentration as shown in Figure 9.

With a polymerization temperature change from 50 to 60°C, runs a-d conducted by Chang et al.<sup>30</sup> were employed to test the proposed model. The recipes for these seeded, batch experiments are summarized in Table III. The physical and kinetic parameters necessary for computer simulations are also listed in Table II. Please note that  $D_{m0}$  is taken as a constant at different polymerization temperatures since it is very difficult to estimate the dependency of  $D_m$  on  $T$ . The error introduced by using an inaccurate value for  $D_{m0}$  in the computer simulation will be compensated by adjusting  $K$  in the best-fit procedure.

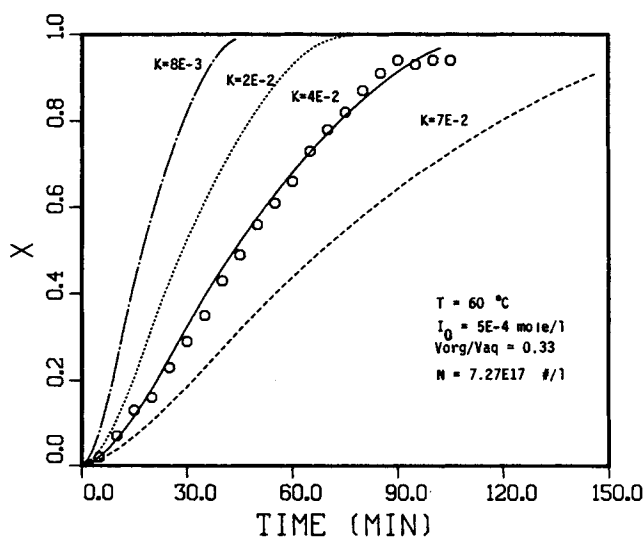


Fig. 11. Conversion vs. time profiles of vinyl acetate emulsion polymerization.

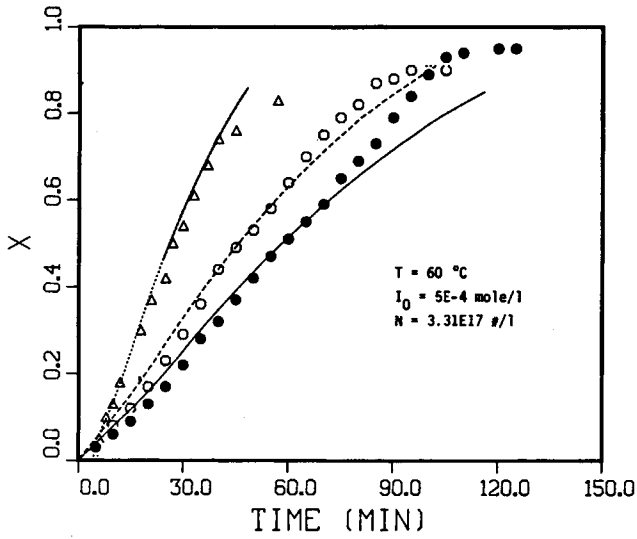


Fig. 12. Conversion vs. time profiles of vinyl acetate emulsion polymerization [(O) used to evaluate  $K$  and  $V_m^*$ .  $V_{org}/V_{aq}$ : ( $\Delta \cdots$ ) 0.125; ( $\circ \cdots$ ) 0.33; ( $\bullet \text{---}$ ) 0.46.

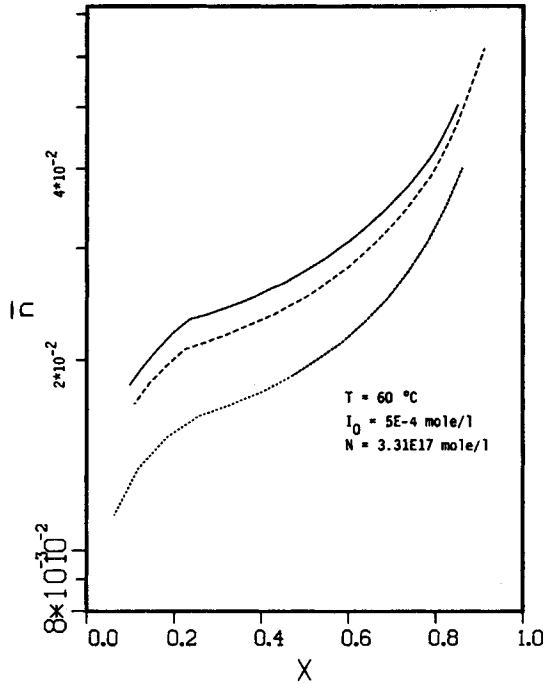


Fig. 13. Average number of free radicals per particle vs. conversion profiles of vinyl acetate emulsion polymerization:  $V_{org}/V_{aq}$ : ( $\cdots$ ) 0.125; ( $\text{---}$ ) 0.33; ( $\text{---}$ ) 0.46.

The  $X$ -vs.- $t$  data of run a (discrete points in Fig. 11) were used to evaluate the value of  $K$  at 60°C.  $V_m^*$  is only dependent on the kinds of monomer and it is kept constant (0.2) at this temperature. A similar fitting procedure was carried out as illustrated in Figure 10. In this case,  $K$  has a best fit value of  $4 \times 10^{-2}$  as shown by the solid line.

The model predictions for runs b-d with various initial monomer charges are shown by the continuous curves in Figure 12. The discrete points in the same graph represent the experimental data. Again, the agreement between the model and experimental data reinforces the proposed reaction mechanisms. Please note that the conversion-time curves shown must be adjusted for the initial monomer charge to obtain polymerization rate data, that is,  $R_p = M_0(dX/dt)$ . Figure 13 shows the calculated  $\bar{n}$ -vs.- $X$  curves. The average number of free radicals per particle increases with increased initial monomer charge within the range of Chang's experiments. This result seems to disagree with the conversion-time behavior shown in Figure 12. This is simply because less time is required for the system with a smaller monomer charge to complete the reaction.

## CONCLUSIONS

Initiator free radicals, in the emulsion polymerization of vinyl acetate, will add monomer molecules before they enter the latex particles. Thus the absorbed oligomeric free radicals will be unable to escape from the latex particles. These free radicals will grow via propagation with monomer molecules in the particles until chain transfer to monomer takes place. This chain transfer process generates a mobile and rather stable monomer-unit free radical which can easily transport out of the latex particle into the aqueous phase. The desorbed monomer-unit free radicals can be reabsorbed into the particles and repeat the desorption process until they either reinitiate or terminate. The process of transport of free radicals out of the latex particles into the aqueous phase will lower the polymerization rate. Termination is not important for calculation of the average number of free radicals per particle since only a very small portion of the particles contain two free radicals. Thus the estimates of  $K_i$  and  $K_t'$  shown in Figure 6 can only be considered to be approximate.

A kinetic model based on these reaction mechanisms has been developed to calculate the average number of free radicals per particle. The desorption rate constant is proportional to the diffusion coefficient of the monomer-unit free radical and inversely proportional to the square of the particle size. The concept of free volume was used to relate changes in the diffusion coefficient with conversion. The experimental data available in the literature were used to assess the proposed model under various polymerization conditions. The model predicts the experimental data reasonably well.

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