Kinetics of Vinyl Chloride and Vinyl Acetate Emulsion Polymerization

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Synopsis

The kinetics of vinyl chloride and vinyl acetate emulsion polymerization are reexamined. The validity of Ugelstad's model for systems with high desorption rate is confirmed by simulating conversion histories for both systems at different initiator concentrations and particle numbers. On the basis of the model, it is shown that at ordinary initiation rates, termination reactions are unimportant with respect to molecular weight development in both systems, and as a consequence, molecular weight development is independent of number and size distribution of polymer particles and of initiator and emulsifier level. Based on this conclusion, it is shown that in accordance with experimental facts, the molecular weight distribution obtained in vinyl chloride emulsion polymerization is the most probable distribution, and it is concluded that the number of long-chain branch points per repetition unit is less than 2×10^{-4} at high conversions. In vinyl acetate emulsion polymerization, an almost logarithmic normal distribution is obtained. The distribution is strongly broadened by branching reactions with the number of long-chain branch points increasing rapidly with monomer conversion. The increase of M_n with increasing conversion is due to terminal double-bond polymerization, while the increase in M_w is due mainly to transfer to polymer.

INTRODUCTION

The emulsion polymerization of vinyl chloride (VC) and vinyl acetate (VAc) has in recent years been the subject of numerous extensive investigations,[1-13] and today one can claim a relatively good understanding of the mechanism and kinetics of these processes although certain problems such as particle nucleation mechanism still remain equivocal.

For both processes it is generally concluded that polymerization takes place exclusively in the polymer particles and that the average population of free radicals per particle is much less than unity. On the basis of these conclusions, Ugelstad[1] derived a rate expression for VC emulsion polymerization which successfully could explain the effect of reaction parameters such as initiator concentration, particle number, and monomer:water ratio on polymerization rate and the shape of the conversion-versus-time curve. Recently, Nomura et al.[9] and Friis and Nyhagen[5,10] showed that the kinetic expression after Ugelstad also could explain the behavior of VAc emulsion polymerization, and it was concluded that the kinetics of the two systems in regard to monomer consumption rate are essentially identical.

However, owing to immense differences in physical properties of the two monomers and polymers, the two systems exhibit quite different polymerization curves. Thus, VC has a relatively low solubility in PVC, and consequently the separate monomer phase first disappears at 70–80% conversion. This means that the polymer particles grow during most of the reaction time; and in accordance with Ugelstad's expression, this leads to an accelerating rate of polymerization which is also observed experimentally. In the VAc system, on the other hand, the monomer dissolves with relatively high concentration in its polymer, and the separate monomer phase is therefore exhausted already at 20% conversion. Hence, in this system the polymer particles retain an almost constant volume after 20% conversion. Experimentally, the polymerization rate is found to be practically constant in the interval 20–85%, which in accordance with Ugelstad's expression can be explained as a result of a balance between a decreasing monomer concentration and an increasing average number of radicals per particle caused by a decrease in the desorption and termination rate constants.

With respect to molecular weight and branching development, the two systems behave very differently. PVC produced in emulsion polymerization has a polydispersity ratio close to 2 and only very few long branches.[14] Moreover, at ordinary initiation rates, the MWD of PVC produced in emulsion is not significantly different from the MWD obtained in bulk and suspension polymerization. PVAc produced in emulsion polymerization has a large polydispersity ratio, and at high conversions the polymer becomes highly branched. Furthermore, the polydispersity ratio is larger than that obtained in bulk polymerization.[15]

The present paper aims to give a short review of the kinetics of vinyl chloride and vinyl acetate emulsion polymerization and, on the basis of the kinetic equations, to conclude which factors are molecular weight controlling and finally, based on these conclusions, to derive equations which by solution predict molecular weight averages, branching densities, and MWD's in these systems. The theoretical results are compared with experimental data. For vinyl acetate, the MWD equations are very complex, and only solutions for the moments will be given. However, it will be shown that the experimental MWD's can adequately be described by a logarithmic normal distribution.

POLYMERIZATION KINETICS

Polymerization Rate

Numerous experimental studies on emulsion polymerization of vinyl acetate and vinyl chloride have revealed that the kinetics of these systems bear several similarities of which the most pertinent may be summarized as follows:

1. The rate of polymerization is half order with respect to initiator concentration.

2. The number of polymer particles is independent of initiator concentration.

3. The number of polymer particles becomes constant at 5–10% conversion.

4. The order of reaction with respect to particle number is small and lies between 0.05 and 0.2.

5. The average population of free radicals per particle is much less than unity and usually of the order of 0.01–0.001.

6. The molecular weight of the polymers produced is independent of particle number and size and initiator concentration.

These features strongly suggest that the kinetics of the two systems can be described with the same rate expression. For vinyl chloride, Ugelstad deduced the following rate expression[1,2]:

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

where k_p = propagation rate constant, $[M_p]$ = monomer concentration within polymer particles, N_A = Avogadro's number, f = initiator efficiency factor, k_i = initiator decomposition rate constant, $[I]$ = initiator concentration, V_p = total volume of monomer-swollen polymer particles, k_{tp} = termination rate constant, N = total number of particles, and k_d = desorption rate constant. The desorption rate constant k_d is a function of particle radius r. In their early work, Smith and Ewart[16] proposed that the rate of desorption was proportional to $1/r$. However, numerous experiments performed by Ugelstad have shown that the order of reaction lies between 0.3 and 0.5 with respect to V_p and between 0.05 and 0.15 with respect to N. These and other experimental facts suggest that k_d may be expressed as

$$k_d = k_d' (N/V_p)^{1/2} \tag{2}$$

where k_d' is a specific desorption rate constant which is only function of temperature and composition of the particles. In accordance with this expression, k_d is proportional to $1/r^2$. Substitution of eq. (2) into eq. (1) gives

$$R_p = k_p[M_p]/N_A(2fk_i[I])^{1/2} \left(\frac{V_p N_A^2}{2k_{tp}} + \frac{N^{1/2} V_p^{1/2}}{2k_d'} \right)^{1/2}. \tag{3}$$

Equation (3) predicts that the order of reaction with respect to N should decrease with decreasing number of particles and the order with respect to V_p should decrease with increasing particle number. Furthermore, with constant N and $[I]$, the polymerization rate should increase in the interval $0 < x < x_c$, where x_c is the conversion at which the separate monomer phase disappears. All of these effects have been confirmed experimentally by Ugelstad.

In Figures 1 and 2 are shown comparisons between experimental and theoretical conversion versus time plots at different initiator concentrations
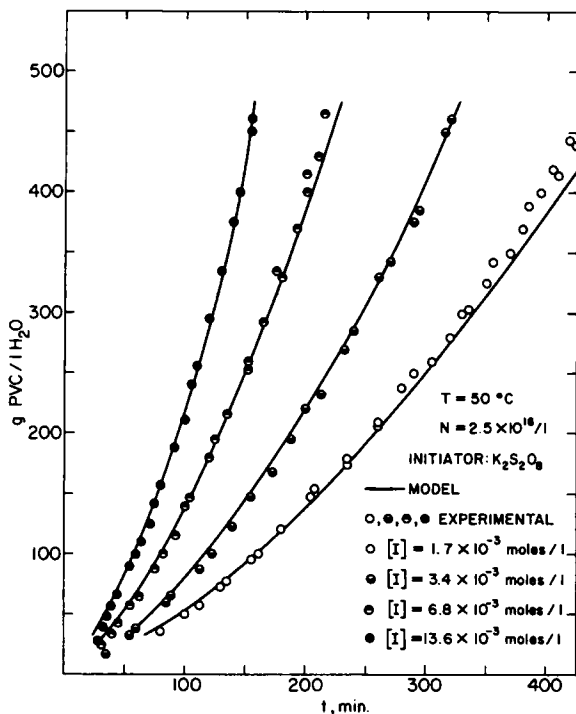
Fig. 1. Comparison between experimental and theoretical conversion histories for vinyl chloride emulsion polymerization. The experimental data are obtained from the literature.[1]

and particle numbers for VC emulsion .polymerization at 50°C. The theoretical plots were obtained by integration of eq. (3) using the following values for the rate constants: k_p = 10000 l./mole-sec, $2fk_i$ = 10^{-6}/sec, k_{tp} = 3 X 10^7 l./mole-sec, and k_d' = 2.86 X $10^{-11}/N_A$ l.-mole-dm/sec. The monomer concentration was calculated as

$$[\text{M}_p] = \frac{(1 - x_c)\, d_m}{(1 - x_c + x_c d_m/d_p)m_0} \tag{4}$$

where x_c = 0.7, d_m = density of monomer = 850 g/l., d_p = density of polymer = 1400 g/l., and m_0 = molecular weight of monomer = 62.5. It appears that the model correctly reflects the shape and slope of the polymerization curve over a wide range of particle number and initiator concentration.

Friis and Nyhagen[5,10] have recently demonstrated that the rate expression given in eq. (1) also applies to VAc emulsion polymerization. However, instead of the expression given in eq. (2), they used the following expression for k_d:

$$k_d = k_{fm}[\text{M}_p]/N_A \left(\frac{2D_p/r^2}{2D_p/r^2 + k_p[\text{M}_p]}\right) \tag{5}$$
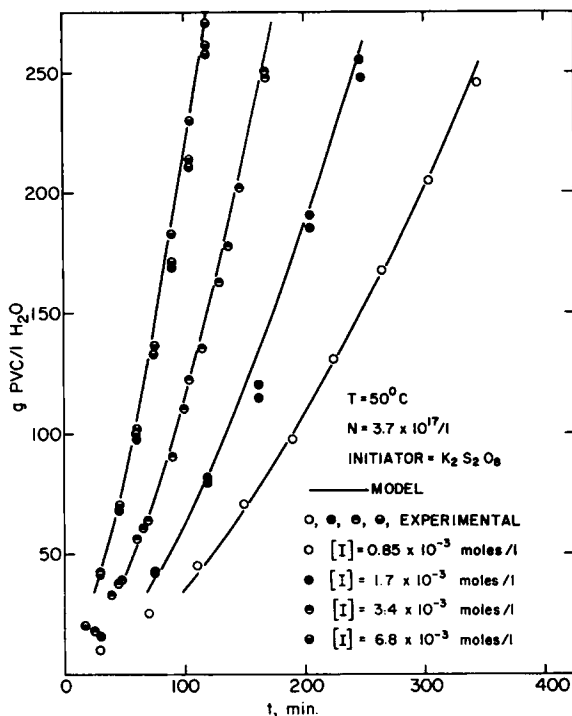
Fig. 2. Comparison between experimental and theoretical conversion histories for vinyl chloride emulsion polymerization. The experimental data are obtained from the literature.[1]

where k_{fm} is the rate constant for transfer to monomer and D_p is the effective diffusion coefficient of monomeric radicals in the polymer particles. Introduction of eq. (5) into eq. (1) leads to a rate expression which predicts the order with respect to N to lie between 0 and 0.5 depending on the number of polymer particles. The order 0.25 was found experimentally in the range of particle numbers investigated. However, further investigations and extensive electron microscopy studies conducted in this laboratory have shown a somewhat smaller order ranging from 0.1 to 0.15. This suggests that k_d may be expressed in the form given in eq. (2) and hence that eq. (3) is applicable also to VAc emulsion polymerization.

In Figures 3, 4, and 5 are shown comparisons between experimental and theoretical conversion plots at different particle numbers and initiator concentrations for VAc emulsion polymerization at 50°C. The theoretical plots were obtained by integration of eq. (3) using the following values for the constants: $k_p = 3000$ l./mole-sec, $2fk_i = 10^{-6}$/sec, $k_d' = 4.55 \times 10^{-13} \left[\left(\dfrac{1 - x}{1 - 0.19x} \right)^2 + 0.0017x \right] \Big/ N_A$ l.-mole-dm/sec, $d_m = 930$ g/l., $d_p = 1150$ g/l., $k_{tp} = 2 \exp(A + A_1x + A_2x^2 + A_3x^3)$ l./mole-sec, $A = 17.6620$, $A_1 = -0.4407$, $A_2 = -6.7530$, and $A_3 = -0.3495$. The expres-
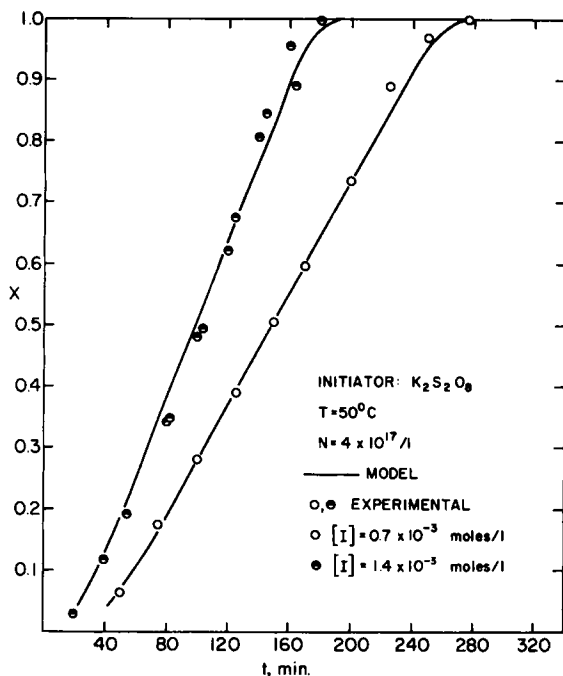
Fig. 3. Comparison between experimental and theoretical conversion histories for vinyl acetate emulsion polymerization.

sion for k_{tp} was obtained in a previous investigation from bulk polymerization of VAc at 50°C[10]; k'_d was obtained by fitting eq. (3) to experimental results. It is expected that k'_d must decrease fairly rapidly with conversion in the interval $x_c \leqslant x \leqslant 1$ because the particles become richer in polymer in this interval and therefore the mobility of radicals decreases rapidly, i.e., desorption of radicals becomes less probable with increasing conversion. In the interval $0 \leqslant x \leqslant x_c$ where the composition of the particles remains constant, the value $x_c = 0.2$ was substituted for x in the expressions for k_{tp}, $[M_p]$, and k'_d. The plots shown for vinyl chloride all correspond to $x < x_c$, and therefore the decrease in k'_d and k_{tp} is not taken into consideration with this monomer. From Figures 3, 4, and 5, it appears that the model, eq. (3), adequately describes the effect of initiator concentration and particle number in VAc emulsion polymerization.

It is interesting to compare the values of k'_d for the two systems at the same volume fraction of monomer in the particles. The value $2.86 \times 10^{-11}/N_A$ for VC corresponds to a volume fraction of monomer equal to 0.4. At the same volume fraction, k'_d for VAc is $2.2 \times 10^{-13}/N_A$, i.e., a value two orders of magnitude smaller than the value of k'_d for VC. At present, we cannot offer a complete explanation for this large difference in k'_d. The desorption process probably depends on several factors such as size and polarity of the desorbing molecule, polarity of the environment, electrical
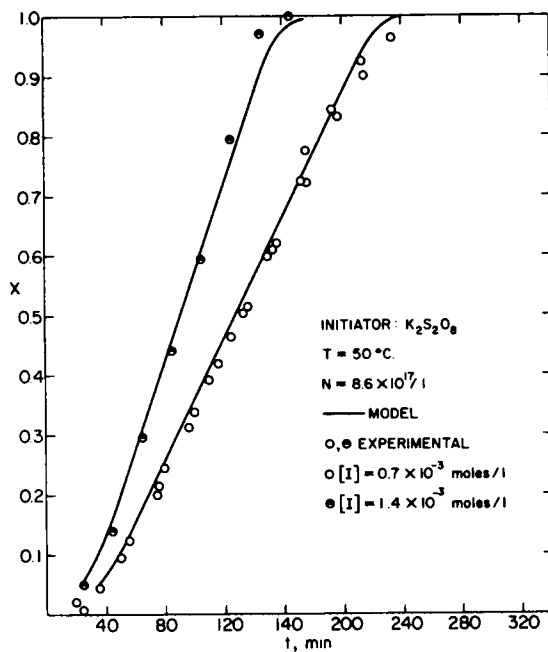
Fig. 4.   Comparison between experimental and theoretical conversion histories fo
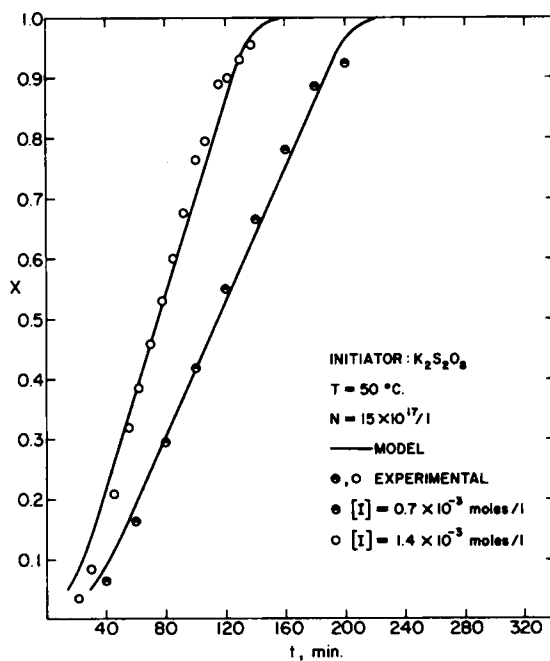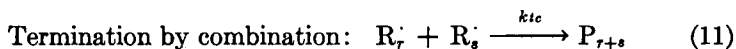vinyl acetate emulsion polymerization.

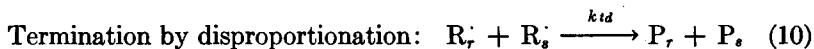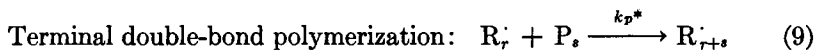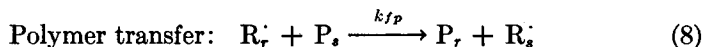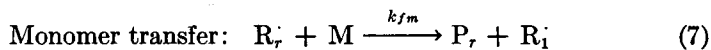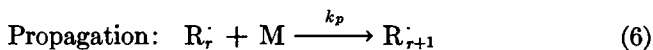Fig. 5.   Comparison between experimental and theoretical conversion histories for
vinyl acetate emulsion polymerization.

forces at the interphase, etc. These factors cannot be accounted for quantitatively at present. However, we believe that part of the explanation for the large difference in the k'_d values lies in the difference between the monomer transfer constants of the two systems. Since large radicals have an extremely low mobility and consequently a very small chance of escaping a particle, it is expected that by far most of the radicals escaping the particles are very small radicals and presumably mainly monomeric radicals formed by transfer to monomer. It is, therefore, reasonable to conclude that k'_d is proportional to the rate constant of transfer to monomer. For VAc, k_{fm} equals 0.75 l./mole-sec, while for VC it equals 11 l./mole-sec. Thus, in a PVC particle containing one radical, monomeric radicals are being generated at a frequency 15 times higher than in a PVAc particle, and this will lead to a higher desorption rate constant for VC.

Molecular Weight Development

In this section, we shall compare molecular weight development in VC and VAc emulsion polymerization. We shall first, however, derive the basic equations from which molecular weight averages and distributions can be computed.

In free-radical polymerization reactions, each growing radical $R_r^{\cdot}$ may enter any one of the following competitive reactions:

$$\text{Propagation:} \quad R_r^{\cdot} + M \xrightarrow{k_p} R_{r+1}^{\cdot} \tag{6}$$

$$\text{Monomer transfer:} \quad R_r^{\cdot} + M \xrightarrow{k_{fm}} P_r + R_1^{\cdot} \tag{7}$$

$$\text{Polymer transfer:} \quad R_r^{\cdot} + P_s \xrightarrow{k_{fp}} P_r + R_s^{\cdot} \tag{8}$$

$$\text{Terminal double-bond polymerization:} \quad R_r^{\cdot} + P_s \xrightarrow{k_p^*} R_{r+s}^{\cdot} \tag{9}$$

$$\text{Termination by disproportionation:} \quad R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{td}} P_r + P_s \tag{10}$$

$$\text{Termination by combination:} \quad R_r^{\cdot} + R_s^{\cdot} \xrightarrow{k_{tc}} P_{r+s} \tag{11}$$

The instantaneous molecular weight of the polymer formed depends on the relative rate of these reactions. If the ratio between transfer and termination rates is large compared with unity throughout the reaction course, then termination reactions can be neglected in molecular weight considerations. From eq. (3) the rate of transfer to monomer can be calculated by substituting k_{fm} for k_p. The rate of transfer to polymer is similarly obtained from eq. (3) by substituting $[M_p]x/(1 - x)$ and k_{fp}, the transfer constant to polymer, for $[M_p]$ and k_p, respectively. In the steady-state emulsion polymerization, the termination rate is with very good approximation equal to the initiation rate, and it is thus possible to evaluate the ratio between transfer and termination rates. In Figures 6 and 7 are

shown plots of this ratio versus conversion for VC and VAc emulsion polymerization at different initiator concentrations.   The plots were obtained by using $k_{fm} = 11$ l./mole-sec for VC and $k_{fm} = 0.75$ l./mole-sec and $k_{fp} = 1.25$ l./mole-sec for VAc.   It appears that at ordinary conditions
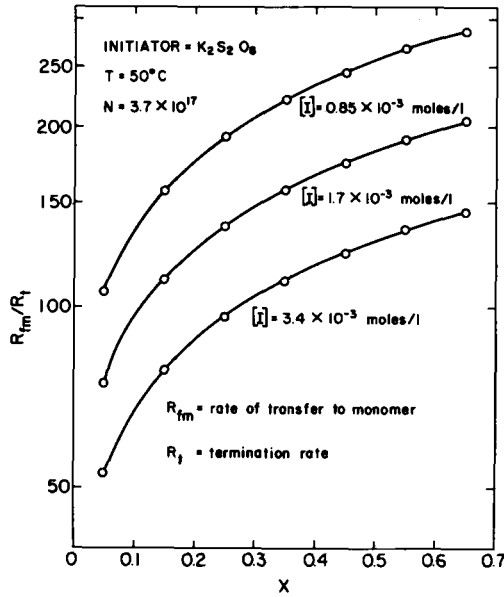

Fig. 6.   Calculated ratio between rate of transfer to monomer and termination rate in vinyl chloride emulsion polymerization as function of conversion.
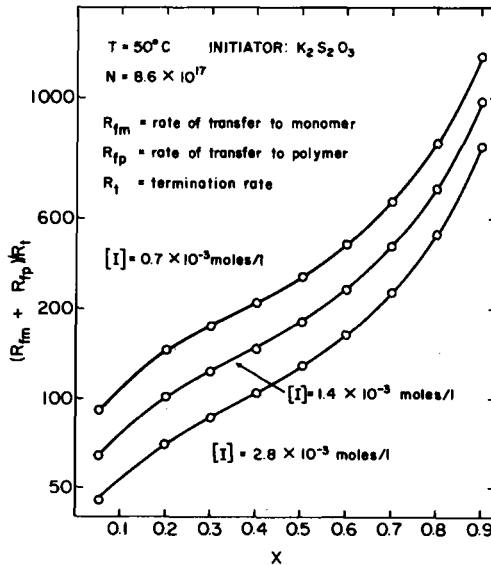

Fig. 7.   Calculated ratio between transfer rates and termination rate in vinyl acetate emulsion polymerization as function of conversion.

of emulsion polymerization of VC and VAc, the rate of termination is much less than the rates of transfer, and termination reactions can therefore be neglected in molecular weight considerations.

To simplify the analysis, we will make the hypothesis that the treatment can be limited to the consideration of a single statistical particle which is representative of the whole population of particles. The MWD of the statistical particle is the MWD obtained when all particles are mixed together.

On the basis of the kinetic scheme given in eqs. (6), (7), (8), and (9), we can now derive the basic equations which serve to define the molecular weight development. In the analysis, we shall distinguish between two stages of the polymerization, namely, stage 1 in which $x \leqslant x_c$ and stage 2 in which $x \geqslant x_c$. In stage 1, the volume of the particles increases with time but the composition remains constant. The system can therefore be regarded as a variable-volume reactor with constant composition; and from a material balance on radicals and polymer molecules, the following equations are obtained:

$x \leqslant x_c$:

$$\frac{1}{V_p} \frac{d(V_p R_r^{\cdot})}{dt} = k_p[M_p]R_{r-1}^{\cdot} - (k_p[M_p] + k_{fm}[M_p] + k_{fp}Q_1 + k_p^*Q_0)R_r^{\cdot}$$

$$+ k_{fp}rP_rY_0 + k_p^* \sum_{s=1}^{r-2} P_{r-s}R_s^{\cdot} = 0 \quad (12)$$

$$\frac{P_r}{V_p} \frac{dV_p}{dt} = (k_{fm}[M_p] + k_{fp}Q_1)R_r^{\cdot} - (k_{fp}rP_r + k_p^*P_r)Y_0 \quad (13)$$

where

$$Y_0 = \sum_{r=1}^{\infty} R_r^{\cdot}$$

$$Q_0 = \sum_{r=2}^{\infty} P_r$$

$$Q_1 = \sum_{r=2}^{\infty} rP_r$$

During stage 2, the concentration of any species in the particles varies. The variation is due partly to polymerization reactions and partly to the volume contraction accompanying the conversion of monomer to polymer. However, the change in concentration due to contraction is small compared to the change due to reaction and can therefore be neglected. Since we consider a system in which all reactions are bimolecular and first order with respect to radical concentration, the volume contraction will affect all moments to the same degree and will therefore not have any influence on the ratio between moments. Therefore, when considering molecular weight averages only, it is completely correct to neglect the change in

concentration due to contraction. For stage 2, we thus obtain the following equations:

$x \geqslant x_c$:

$$\frac{dR_r^{\cdot}}{dt} = k_p[M_p]R_{r-1}^{\cdot} - (k_p[M_p] + k_{fm}[M_p] + k_{fp}Q_1 + k_p^*Q_0)R_r^{\cdot}$$

$$+ k_{fp}rP_rY_0 + k_p^* \sum_{s=1}^{r-2} P_{r-s}R_s^{\cdot} \quad (14)$$

$$\frac{dP_r}{dt} = (k_{fm}[M_p] + k_{fp}Q_1)R_r^{\cdot} - (k_{fp}rP_r + k_p^*P_r)Y_0. \quad (15)$$

Equations (12) and (13) can be solved analytically for the moments; and after Friis et al.,[15] the following expressions are obtained for stage 1:

$$M_n = m_0\frac{Q_1}{Q_0} = m_0(1 + Kx_c/(1 - x_c))/C_m \quad (16)$$

$$M_w = m_0\frac{Q_2}{Q_1} =$$

$$m_0\frac{2[1 + Kx_c/(1 - x_c)]^2}{[C_m + C_px_c/(1 - x_c)] - (2C_px_c/(1 - x_c))(1 + Kx_c/(1 - x_c))} \quad (17)$$

$$B_n = C_pM_nx_c/(1 - x_c)m_0 + Kx_c/(1 - x_c) \quad (18)$$

where B_n is the average number of branch points per molecule, Q_2 is the second moment of the distribution, $C_m = k_{fm}/k_p$, $C_p = k_{fp}/k_p$, and $K = k_p^*/k_p$.

For stage 2, the following differential equations are obtained from eqs. (14) and (15):

$$\frac{dQ_0}{dx} = C_mM_0 - \frac{KQ_0M_0}{[M_p]} \quad (19)$$

$$\frac{dQ_1}{dx} = M_0 \quad (20)$$

$$\frac{dQ_2}{dx} = M_0 + 2\left(M_0 + \frac{KQ_1M_0}{[M_p]}\right)\left(\frac{[M_p] + C_pQ_2 + KQ_1}{C_m[M_p] + C_pQ_1}\right) \quad (21)$$

$$\frac{d(Q_0B_n)}{dx} = \frac{(C_pQ_1 + KQ_0)M_0}{[M_p]} \quad (22)$$

where $[M_p]$ now is defined as $[M_p] = M_0(1 - x)$ and M_0 is the molar concentration of pure monomer, $M_0 = d_m/m_0$; M_n, M_w, and B_n can be obtained from eqs. (19), (20), (21), and (22) by numerical integration.

It is generally believed that in VC polymerization, transfer to polymer and terminal double-bond polymerization are of minor importance for molecular weight development in comparison with transfer to monomer.

If, therefore, these reactions are neglected we obtain from eqs. (12), (13), (14), and (15), the following expression for the molecular weight distribution:

$0 < x \leqslant 1$:

$$W(M) = \frac{MC_m{}^2}{m_0{}^2} \exp\left(-\frac{M}{m_0} C_m\right) = \frac{M}{M^2{}_n} \exp\left(-\frac{M}{M_n}\right) \qquad (23)$$

which is the most probable distribution. In Figure 8 is shown a plot of $W = W(M)M_n$ versus M/M_n. Together with the theoretical MWD are shown experimental MWD's for two PVC samples obtained at 5% and 92% conversion at a polymerization temperature of 55°C. It appears that, within experimental error, eq. (23) is a very good description of the experimental data.

Equation (23) was derived on the assumption that k_{fp} and k_p^* are both zero. This implies that long-chain branching is absent in the polymer produced. It has, however, been reported that there are few long branches in PVC. A value of 2×10^{-4} or less long branches per repetition unit has been reported by Jorgenson.[14] It is interesting to investigate the effect on the theoretical MWD for the case that the polymer obtained at 100% conversion has this number of branches. This can easily be accomplished by searching for a value of C_p which by solution of eqs. (20), (21), and (22) leads to a value of 2×10^{-4} for $m_0 B_n/M_n$, which is the number of branch points per repetition unit. With the assumption that terminal double-bond polymerization is negligble, we have in this way found the value of 5×10^{-5} for C_p. The solution of eqs. (12) and (13) for the case that $C_p \neq 0$ and $K = 0$ is found to be

$x < x_c$:

$$W(M) = MK_1\beta^{-K_2} \qquad (24)$$

or

$$W(M)M_n = MM_nK_1\beta^{-K_2} \qquad (25)$$

where

$$K_1 = \frac{[C_m + C_p x_c/(1 - x_c)]C_m}{m_0{}^2} \qquad (26)$$

$$\beta = \frac{1}{1 + MC_p x_c/(1 - x_c)m_0} \qquad (27)$$

$$K_2 = 2 + \frac{C_m(1 - x_c)}{C_p x_c} \qquad (28)$$

Equation (25) is represented by the dashed curve in Figure 8. Although the two theoretical curves are not greatly different, it appears, however, that at the peak, where the experimental measurements are most accurate, the most probable distribution is the better representation of the experimental data. In other words, it seems likely that the number of branch points is less than 2×10^{-4} per repetition unit.
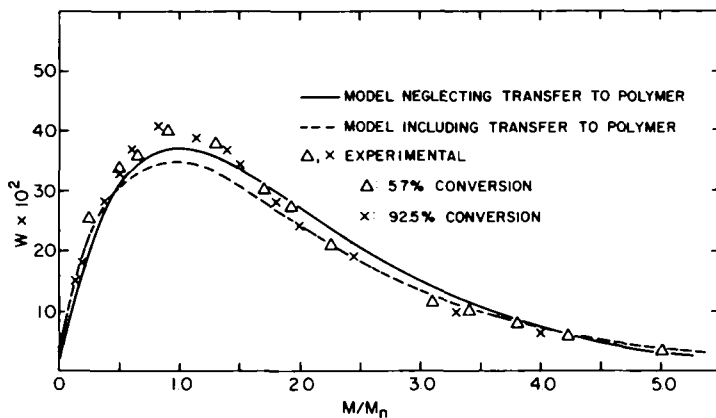
Fig. 8. Comparison between theoretical and experimental molecular weight distributions in vinyl chloride emulsion polymerization. The experimental data are obtained from the literature.[14]
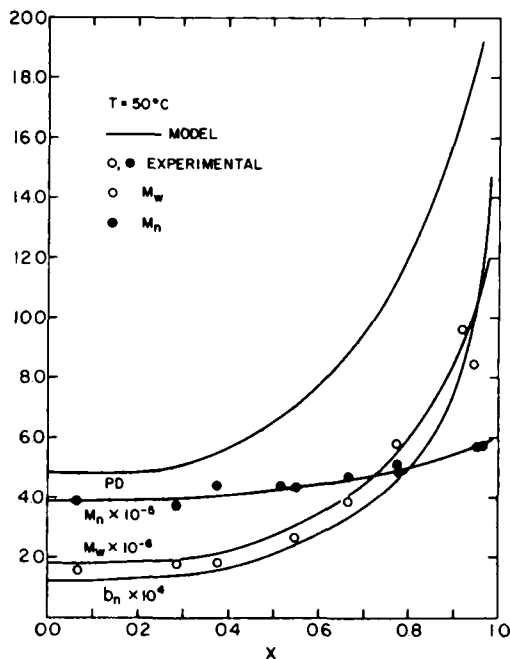

Fig. 9. Plots of polydispersity ratio (PD), number of long-chain branch points per repetition unit, M_n, and M_w vs. conversion in vinyl acetate emulsion polymerization at 50°C.

In an earlier investigation,[15] we have shown that in VAc emulsion polymerization transfer to polymer and terminal double-bond polymerization are both of significant importance for molecular weight development. Both of these reactions lead to a branched polymer structure and the number of branches increases with conversion, particularly at high conversions
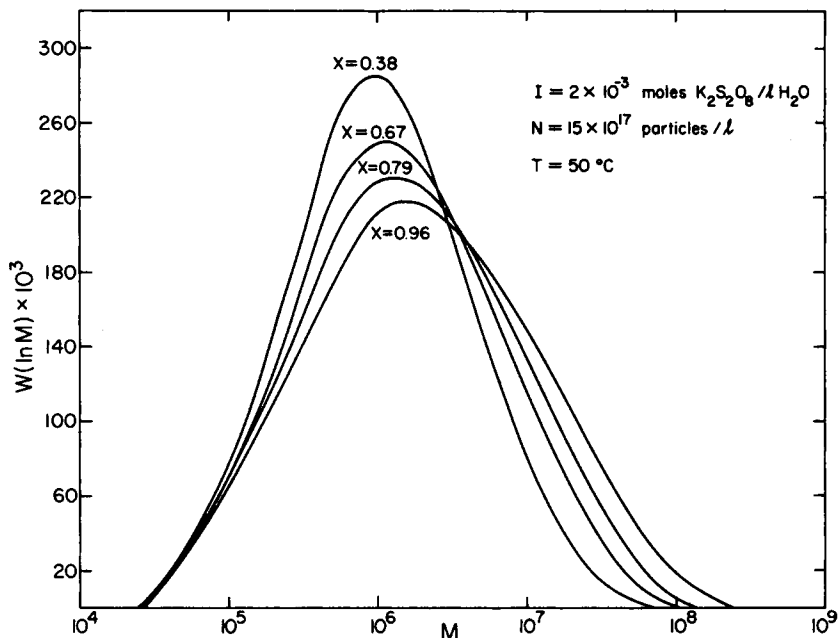
Fig. 10. Experimental molecular weight distributions obtained in vinyl acetate emulsion polymerization at different conversions at 50°C.

where the particles are highly concentrated in polymer. In Figure 9 are shown comparisons between theoretical and measured M_n and M_w as function of conversion for VAC emulsion polymerization at 50°C. Also shown is the polydispersity ratio (PD) and the calculated number of branch points per repetition unit, b_n, as function of conversion.

The theoretical curves were obtained by solution of eqs. (16)–(22) using the rate constants reported in a previous publication.[15] The increase in M_n with increasing conversion is due to terminal double-bond polymerization, while the increase in M_w is due mainly to transfer to polymer. In contrast to VC polymerization, where PD remains close to 2 throughout the reaction course, there is in the VAc system a rapid increase in PD with conversion. Also notice the high initial value of 4.9 for PD. In bulk polymerization, the initial value of PD is 2. The reason for this difference is attributed to the fact that in emulsion polymerization the reaction locus (monomer-swollen polymer particles) contains 20% polymer from the very beginning of the reaction, while in bulk polymerization the concentration of polymer increases gradually from 0 to 20% in the interval 0 to 20% conversion. Hence, in emulsion polymerization, transfer to polymer and terminal double-bond polymerization are more important during the initial stages of reaction than in bulk polymerization, and this leads to a larger polydispersity ratio.

Finally, in VAc emulsion polymerization, the number of branch points per repetition unit reaches a value close to 1.5×10^{-3} at 98% conversion compared to a value less than 2×10^{-4} in VC polymerization.
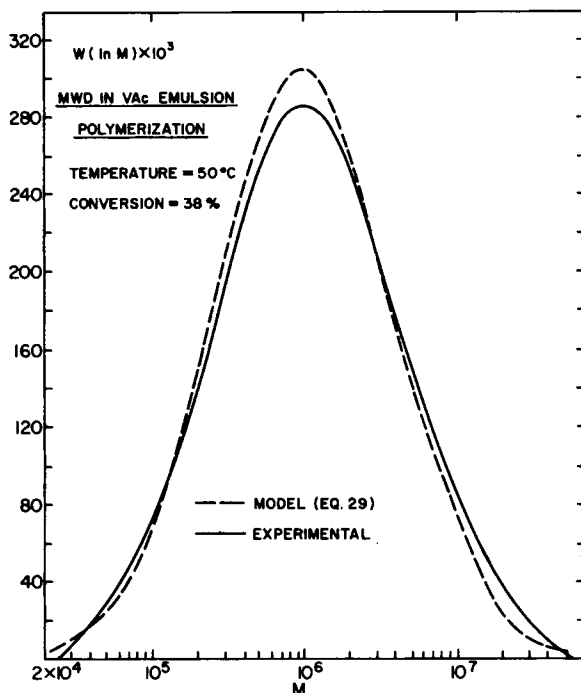
Fig. 11. Comparison between logarithmic normal MWD and experimental MWD in VAC emulsion polymerization.

In Figure 10 are shown experimental MWD's obtained at different conversions in VAc emulsion polymerization at 50°C. It is clear that the distribution is broadened and that the peak moves to higher molecular weights with increasing conversion. It is interesting to compare these plots with the theoretical plots obtained by Saito et al.[17] for bulk polymerization of VAc. These investigators predict that the peak should move to lower molecular weights with increasing conversion. Although bulk and emulsion polymerization are kinetically different, it is, however, only the difference during the first 20% conversion which will give rise to a difference in MWD, and it is unlikely that this should cause an entirely opposite effect on MWD development during the later stages of the two processes. At present, we cannot offer any reasonable explanation for this discrepancy.

An interesting feature of the distributions shown in Figure 10 is that they are all symmetrical in a logarithmic plot, i.e., they are apparently logarithmic normal distributions. To test whether this is the case, we have in Figures 11, 12, and 13 shown comparisons between experimental distributions and the logarithmic normal distribution:

$$W(\ln M) = \frac{\exp\left(-(\ln M - \ln \bar{M})^2/2\sigma^2\right)}{\sigma\sqrt{2\pi}} \tag{29}$$

where $\sigma^2 = \ln (PD)$ and $\bar{M} = M_n \exp(\sigma^2/2)$. PD and M_n are calculated from the model, eqs. (16)–(27), and it appears that eq. (29) is a reasonably good representation of experimental data.
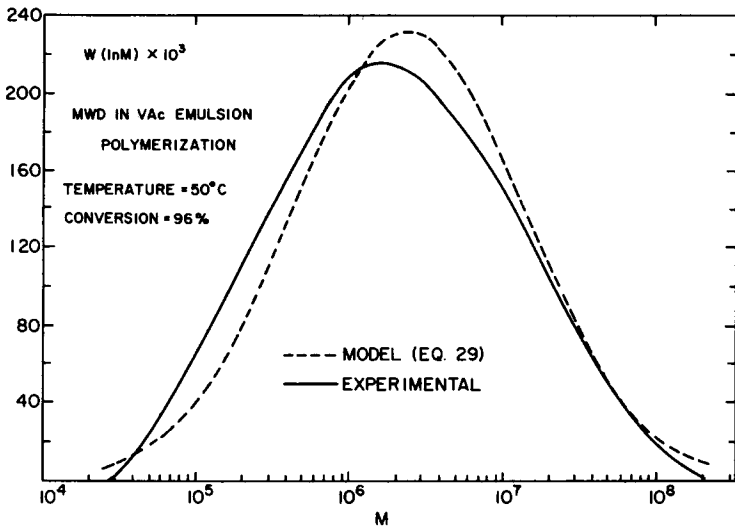
Fig. 12.   Comparison between logarithmic normal MWD and experimental MWD in
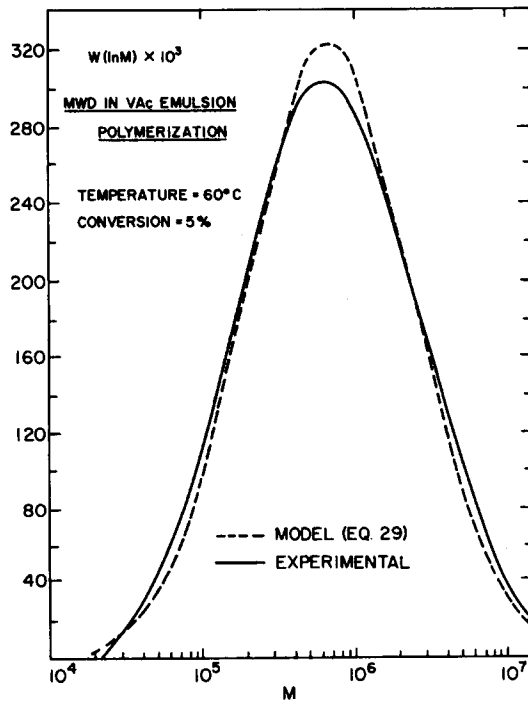VAc emulsion polymerization.

Fig. 13.   Comparison between logarithmic normal MWD and experimental MWD in
VAc emulsion polymerization.

CONCLUSIONS

In conclusion, we may say that VC and VAc emulsion polymerization both conform to the rate expression deduced by Ugelstad. In both processes, desorption of radicals from the polymer particles is an essential feature of the reaction kinetics, and as a consequence, the average population of radicals per particle is very small.

In VC emulsion polymerization, transfer to monomer is the molecular weight-controlling reaction, and this leads to a most probable molecular weight distribution. In VAc emulsion polymerization, transfer to monomer, transfer to polymer, and terminal double-bond polymerization are all molecular weight controlling. The molecular weight distribution, which is almost a logarithmic normal distribution, broadens strongly with increasing conversion. The increase in M_n with conversion is due to terminal double-bond polymerization, while the increase in M_w is mainly due to transfer to polymer. The number of long-chain branches increases rapidly with conversion.

At ordinary initiation rates, termination reactions are unimportant for molecular weight development in both systems; and as a consequence, molecular weight development is independent of number and size distribution of polymer particles and of initiator and emulsifier level.

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