

Molecular Weight and Branching Development in Vinyl Acetate Emulsion Polymerization

INTRODUCTION

The emulsion polymerization of vinyl acetate has been the subject of numerous experimental investigations.¹⁻¹³ While the major objective of these investigations has been to derive a model which can account for the kinetic behaviour of vinyl acetate emulsion polymerization, there have been no attempts to derive a model which can account for the molecular weight and branching development in this particular process.

Recently, Goosney et al.¹⁴ have performed an experimental study of the molecular weight development in vinyl acetate emulsion polymerization, and it is the purpose of the present paper to present a model which can account for their experimental findings and to then calculate the number of branch points as function of conversion. The model is derived by expressing the leading moments of distribution as function of conversion and is thus based on the same equations used by Graessley¹⁵ and Stein¹⁶ to predict molecular weight development in bulk polymerization of vinyl acetate.

PRESENTATION OF THE MODEL

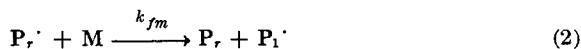
General Considerations

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

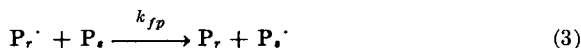
Propagation



Monomer transfer



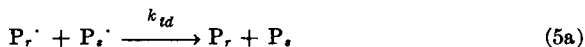
Polymer transfer



Terminal double-bond polymerization



Termination by disproportionation



Termination by combination



In emulsion polymerization of vinyl acetate, the rate of termination is relatively slow compared to the rates of transfer to monomer and polymer. Therefore, the contribution of termination reactions to molecular weight development may be considered negligible, even at ordinary initiation rates. This statement can easily be verified by comparing the rate of termination to the sum of rates of transfer to monomer and polymer. The rate of transfer to monomer is given by

$$R_{fm} = k_{fm} \bar{n} N M_p / N_A$$

where N is the total number of polymer particles per liter emulsion, \bar{n} is the average number of radicals per particle, M_p is the monomer concentration within the polymer particles, and N_A is Avogadro's number. In a typical vinyl acetate emulsion polymerization, N equals 8×10^{17} and \bar{n} is of the order 0.01.^{3,4,5} By using the value¹⁷ 0.75 l./mole-sec for k_{fm} at 50°C and 9 mole/l. for M_p , R_{fm} can be calculated to equal 9×10^{-8} mole/l.-sec. Since the product $\bar{n}NM_p$ remains constant in the interval 15–85% conversion,^{3,4} R_{fm} will remain equal to 9×10^{-8} mole/l.-sec throughout most of the conversion range, and since the rate of transfer to polymer during most of the conversion range is of the same order of magnitude as the rate of transfer to monomer, the sum of transfer rates is of the order 2×10^{-7} mole/l.-sec.

In a steady-state emulsion polymerization, the rate of termination equals the sum of initiation:

$$R_t = R_i = 2k_i f [I]$$

where k_i , f , and $[I]$ denote initiator decomposition rate constant, initiator efficiency factor, and initiator concentration, respectively. In a typical emulsion polymerization at 50°C and with $K_2S_2O_8$ as initiator, $[I]$ is of the order of 2×10^{-3} mole/l. and the value of $2k_i f$ is approximately equal to 10^{-6} /sec.¹⁸ Hence, the rate of termination is of the order 2×10^{-9} mole/l.-sec, a figure which is two orders of magnitude less than the sum of rates of transfer to monomer and polymer.

Further evidence that termination reactions are unimportant in comparison with transfer reactions is the fact that experimental investigations have shown that the limiting viscosity number of poly(vinyl acetate) produced by emulsion polymerization is independent of initiator concentration in the range of 5×10^{-4} to 4×10^{-2} mole $K_2S_2O_8$ /l.^{3,6} To simplify the model, termination reactions will therefore be neglected.

To derive a model for molecular weight development in emulsion polymerization, it is necessary to distinguish between two stages of the process. In stage 1, the reaction mixture composes three phases, namely, the water phase, the separate monomer phase, and the polymer phase, which consists of the monomer-swollen polymer particles. During stage 1, the composition of the particles remains constant. Stage 2 commences as the separate monomer phase disappears, and thus in stage 2 the reaction mixture consists of two phases only, namely, the water phase and the monomer-swollen polymer particles. During this stage, the composition of the particles varies with the overall monomer conversion.

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 moments of distribution in the statistical particle is the value of the moments in all particles when mixed together.

Molecular Weight Development During Stage 1

During stage 1, there is an equilibrium between the monomer-swollen polymer particles and the separate monomer phase. Monomer is consumed within the particles to produce polymer. However, the monomer/polymer ratio within the particles remains constant, because the particles are supplied with monomer from the separate monomer phase. Hence, the volume of the particles increases with time, and the system can be regarded as a variable-volume reactor with constant composition.

On the basis of the equations derived by Graessley¹⁵ for a constant-volume system with varying composition, it is easily shown that for a variable-volume system with constant composition, the following equations apply:

$$\frac{Q_0}{V_p} \frac{dV_p}{dt} = (k_{fm}M_p - k_p^*Q_0)Y_0 \quad (6)$$

$$\frac{Q_1}{V_p} \frac{dV_p}{dt} = (k_pM_p + k_{fm}M_p)Y_0 \quad (7)$$

$$\frac{Q_2}{V_p} \frac{dV_p}{dt} = 2Y_0(k_p M_p + k_p^* Q_1) \left(\frac{k_p M_p + k_{fm} M_p + k_{fp} Q_2 + k_p^* Q_1}{k_{fm} M_p + k_{fp} Q_1} \right) + k_p M_p Y_0 \quad (8)$$

$$\frac{Q_0 B_n}{V_p} \frac{dV_p}{dt} = (k_{fp} Q_1 + k_p^* Q_0) Y_0 \quad (9)$$

where

$$Q_0 = \sum_{r=1}^{\infty} (P_r)$$

$$Q_1 = \sum_{r=1}^{\infty} r(P_r)$$

$$Q_2 = \sum_{r=1}^{\infty} r^2(P_r)$$

and

$$Y_0 = \sum_{r=1}^{\infty} (P_r')$$

where (P_r) and (P_r') denote the concentration of polymer and radicals, respectively, with r repeating units; V_p is the total volume of the monomer-swollen polymer particles; t is reaction time; and B_n is the average number of branch points per molecule.

From eqs. (6), (7), (8), and (9), the number-average and the weight-average molecular weights and the average number of branch points per molecule are obtained as

$$M_n = m_0 \frac{Q_1}{Q_0} = m_0 \frac{(k_p M_p + k_{fm} M_p + k_p^* Q_1)}{k_{fm} M_p} \quad (10)$$

$$M_w = m_0 \frac{Q_2}{Q_1} = m_0 \left(\frac{2(k_p M_p + k_p^* Q_1)^2 + k_p M_p (k_{fm} M_p + k_{fp} Q_1)}{k_p M_p (k_{fm} M_p + k_{fp} Q_1) - 2k_{fp} Q_1 (k_p M_p + k_p^* Q_1)} \right) \quad (11)$$

$$B_n = \frac{k_{fp} Q_1^2 / Q_0 + k_p^* Q_1}{M_p (k_p + k_{fm})} \quad (12)$$

Molecular Weight Development During Stage 2

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, since we consider a system in which all reactions are bimolecular, the volume contraction will not affect the molecular weight development, and hence we need only consider the change in concentration owing to chemical reactions.

Since a single polymer particle can be regarded as a locus of bulk polymerization with very slow initiation and termination reactions, the molecular weight development during stage 2 can be accounted for by direct application of the equations derived by Graessley¹⁵ and Stein¹⁶ for bulk polymerization of vinyl acetate:

$$\frac{dQ_0}{dx} = C_m M_0 - \frac{K Q_0 M_0}{M_p} \quad (13)$$

$$\frac{dQ_1}{dx} = M_0 \quad (14)$$

$$\frac{dQ_2}{dx} = M_0 + 2 \left(M_0 + \frac{K Q_1 M_0}{M_p} \right) \left(\frac{M_p + C_p Q_2 + K Q_1}{C_m M_p + C_p Q_1} \right) \quad (15)$$

$$\frac{d(Q_0 B_n)}{dx} = \frac{(C_p Q_1 + K Q_0) M_0}{M_p} \quad (16)$$

where x is degree of conversion, M_0 is the initial monomer concentration, and $C_m = k_{fm}/k_p$, $C_p = k_{fp}/k_p$, $K = k_p^*/k_p$, and $M_p = M_0(1 - x)$.

TESTING THE MODEL

Evaluation of Rate Constants

The theoretical values of M_n , M_w , and B_n during stage 1 were obtained from eqs. (10), (11), and (12). The values of Q_1 and the monomer concentration M_p were obtained from

$$Q_1 = M_0 x_c$$

$$M_p = M_0(1 - x_c)$$

where x_c denotes the degree of conversion at which the separate monomer phase disappears. In the calculations we used the value 0.2 for x_c ,^{3,4} and the following values for the rate constants:

$$k_p = 1.89 \times 10^7 \exp(-5650/RT) \text{ l./mole-sec}$$

$$k_{fp} = 1.43 \times 10^6 \exp(-9020/RT) \text{ l./mole-sec}$$

$$k_{fm} = 3.55 \times 10^6 \exp(-9950/RT) \text{ l./mole-sec}$$

$$k_p^* = 1.07 \times 10^7 \exp(-5650/RT) \text{ l./mole-sec.}$$

The values of the rate constants and the energies of activation involved are in good agreement with data reported in the literature.^{15,17}

The theoretical values of M_n , M_w , and B_n during stage 2 were obtained by solving eqs. (13), (14), (15), and (16) by means of a second-order Runge-Kutta procedure. The initial values for Q_0 , Q_1 , Q_2 , and B_n were obtained from eqs. (10), (11), and (12). The rate constants k_p , k_{fp} , and k_{fm} were assumed to be independent of conversion, i.e., we used the above values for these constants. This assumption is reasonable, since neither of the corresponding reactions are diffusion controlled. However, the rate constant k_p^* may decrease during the polymerization, since the terminal double-bond polymerization involves a reaction between the ends of a polymer molecule and a macroradical; i.e., since both species have a low translational diffusion coefficient, they have to diffuse a relatively long time before an adequate encounter for chemical reaction occurs. In order to follow the decrease in k_p^* , we therefore fitted the measured number-average molecular weight-versus-conversion curve with the following expression:

$$k_p^* = A_0 + A_1 x + A_2 x^2 + A_3 x^3 \quad (17)$$

where $A_0 = 1.07 \times 10^7 \exp(-5650/RT)$, $A_1 = -169.59$, $A_2 = -479.92$, and $A_3 = -1014.3$.

Figure 1 shows a plot of k_p^* versus conversion x . It appears that in the interval 0–95% conversion, k_p^* must decrease by a factor 20 for the model to fit the experimental values of M_n . For the sake of comparison, it should be mentioned that in the same interval the termination rate constant k_t decreases by three orders of magnitude.³ Both reactions occur between macromolecules; but since k_t is much larger than k_p^* , k_t should be more dependent on diffusion rates and therefore should decrease much more rapidly with conversion. In their study of molecular weight development in bulk polymerization of vinyl acetate, Graessley¹⁵ and Stein¹⁶ did not consider the decrease in k_p^* with conversion. However, since these investigators measured M_n only until 70% conversion, and since the decrease in k_p^* has only a small effect on M_n below 60–70% conversion (see Fig. 2), they did not need to consider the possibility of a decreasing k_p^* .

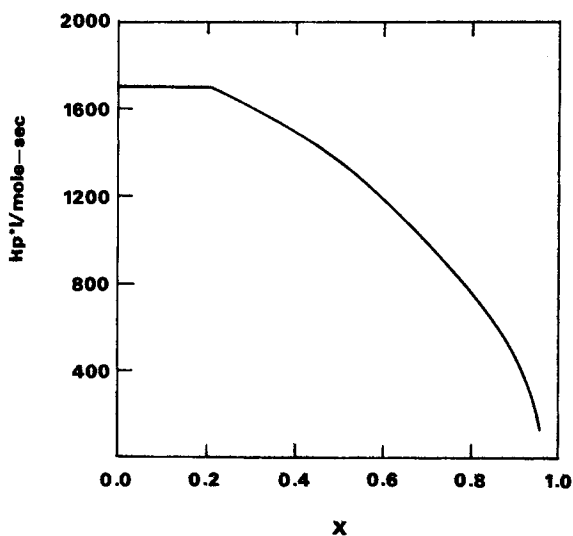


Fig. 1. Plot of k_p^* vs. conversion. Calculated from eq. (17) at 50°C.

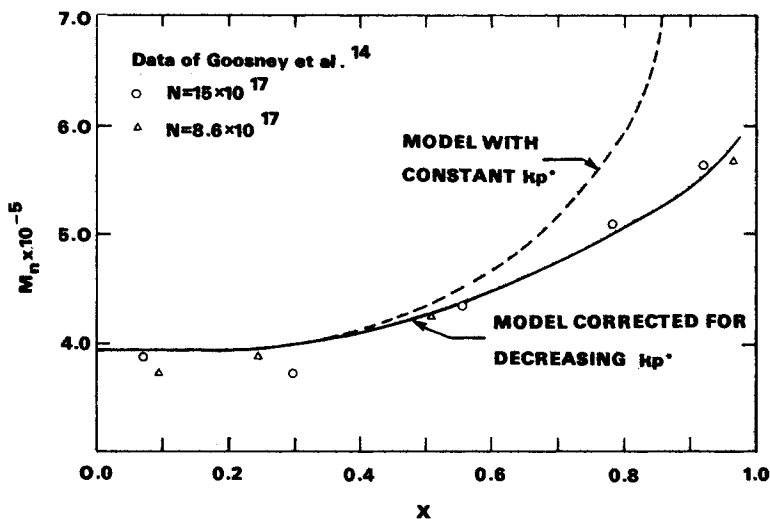


Fig. 2. Comparison between theoretical and experimental plots of M_n vs. conversion. $[I] = 10^{-3}$ mole $K_2S_2O_8/l.$ H_2O ; 50°C.

Figure 2 shows a comparison theoretical and experimental plots of M_n versus conversion x . The solid curve was obtained by taking into account the decrease in k_p^* , while the dashed curve corresponds to a constant value of k_p^* equal to 1700 l./mole-sec. It appears that when k_p^* is kept constant, the model overestimates the molecular weight appreciably at conversions beyond 60–70%.

Effect of Variables

In Figure 3 is shown a comparison between theoretical and experimental plots of M_w versus conversion, and it appears that there is a very good agreement between theory and

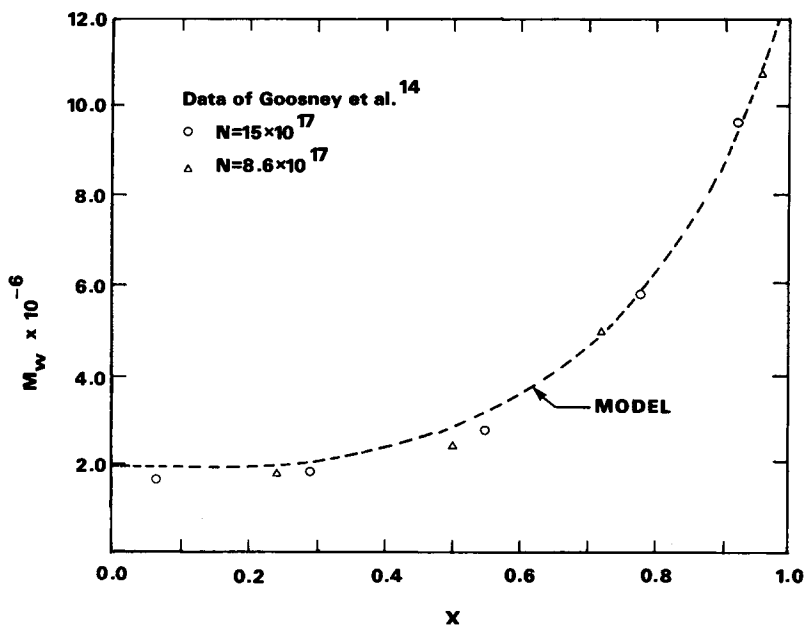


Fig. 3. Comparison between theoretical and experimental plots of M_w vs. conversion. $[I] = 10^{-3}$ mole $K_2S_2O_8/l.$ H_2O ; $50^\circ C$.

experiment. Since the derivation of the model is based on the hypothesis that any molecular weight-controlling reaction is unaffected by the number of particles, the model predicts that the molecular weights are independent of number of particles. The data in Figures 2 and 3 indicate that this is virtually the case. The validity of this conclusion is further supported by the data shown in Figure 4, where the limiting viscosity number $[\eta]$ is plotted against conversion at two different particle numbers. It appears that also $[\eta]$ is independent of number of polymer particles.

Figure 5 shows a plot of polydispersity P versus conversion. During the initial stage of the polymerization, P equals approximately 4.5. In bulk polymerization of vinyl acetate, P is very close to 2 in the beginning of the polymerization. This difference in polydispersity is due to the fact that in emulsion polymerization the concentration of polymer in the particles builds up immediately to a value of 20% and remains constant at this value until 20% conversion, while in bulk polymerization the concentration of polymer in the reaction mixture increases linearly from 0% to 20% in the interval 0–20% conversion. Hence, in emulsion polymerization, transfer to polymer takes place more frequently at low conversions, and this leads to a higher value of P . From Figure 5, it furthermore appears that P increases rapidly with conversion, indicating a broadening of molecular weight distribution with increasing conversion.

Figures 6 and 7 show comparisons between theoretical and experimental values of M_n and M_w at two different initiator concentrations. The data shown in Figure 6 suggest that the molecular weight is independent of initiator concentration. However, the data in Figure 7 are too scattered to prove this hypothesis unequivocally, and it may be more convincing to consider Figure 8, where the limiting viscosity number $[\eta]$ is plotted against conversion. Figure 8 strongly indicates that $[\eta]$ is independent of initiator concentration, and since $[\eta]$ is more accurately measured than M_w , it is reasonable to conclude that the molecular weight is independent of initiator concentration, a conclusion which is in accordance with the model.

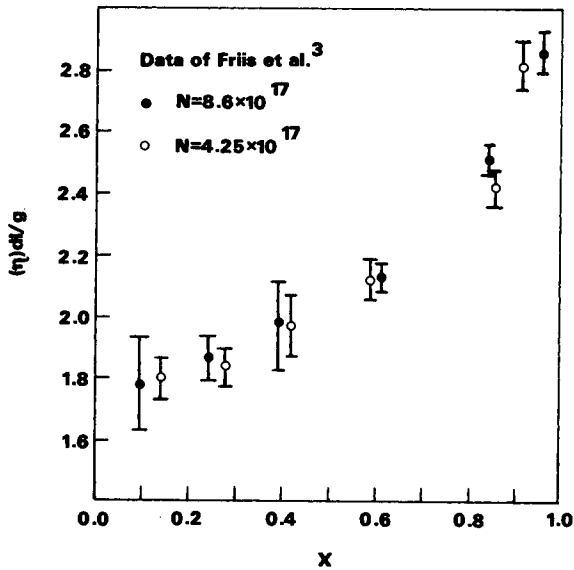


Fig. 4. Limiting viscosity number $[\eta]$ vs. conversion at different particle numbers. $[I] = 10^{-3}$ mole $K_2S_2O_8/l.$ H_2O ; $50^\circ C$.

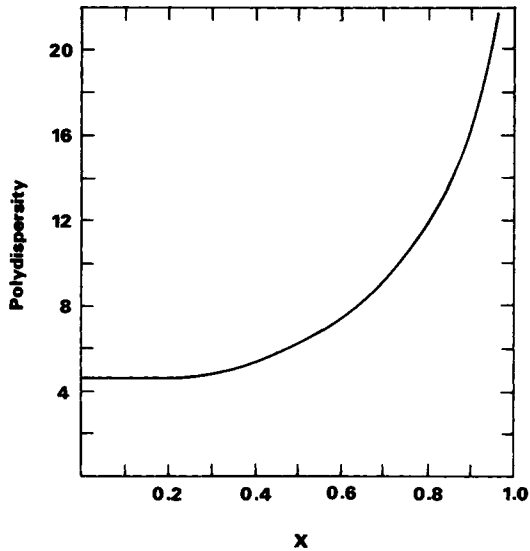


Fig. 5. Theoretical plot of polydispersity versus x at $60^\circ C$.

In Figure 9 is shown the effect of temperature on M_n . This plot is most interesting when considering the energies of activation of the various reactions involved. In order to fit the model to the data, we had to use an energy of activation of 5650 cal/mole for k_p . This value lies in the middle of the range reported in the literature.¹⁷ Furthermore, during stage 1, we used exactly the same energy of activation for k_p^* as for k_p . This is reasonable, since the two reactions are of the same nature, both involving addition of a radi-

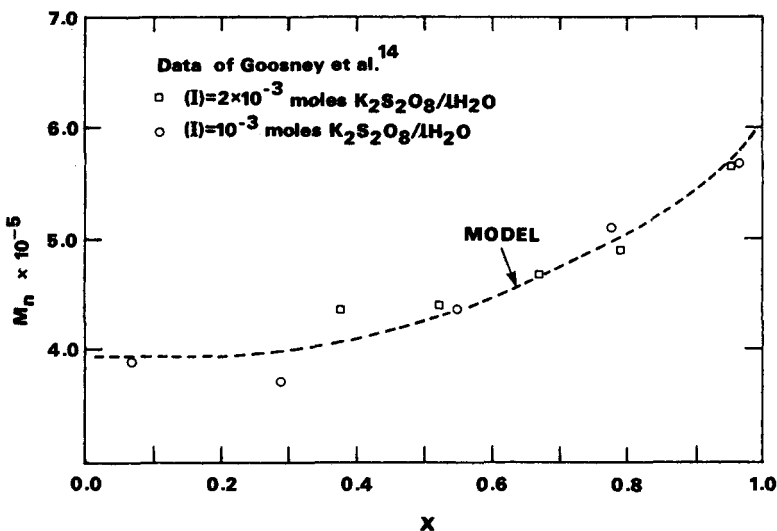


Fig. 6. Comparison between theoretical and experimental plots of M_n vs conversion at different initiator concentrations. $N = 15 \times 10^{17}$; 50°C .

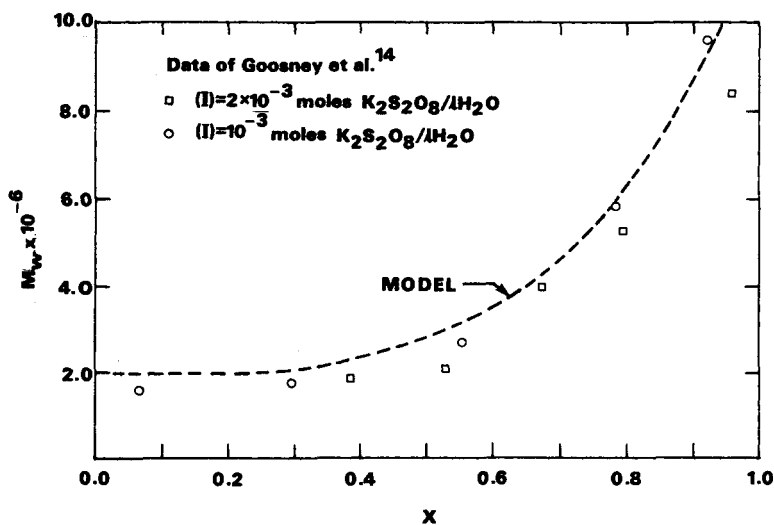
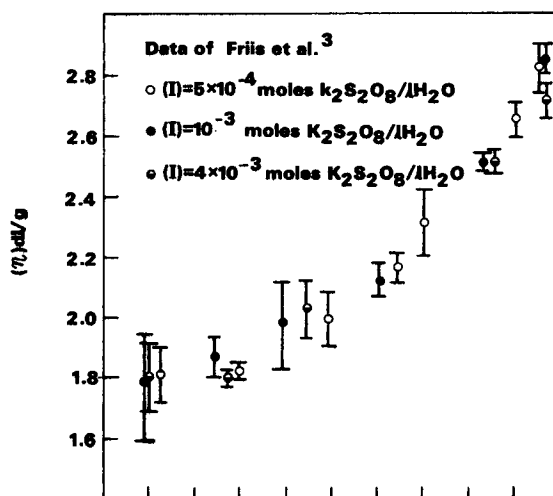


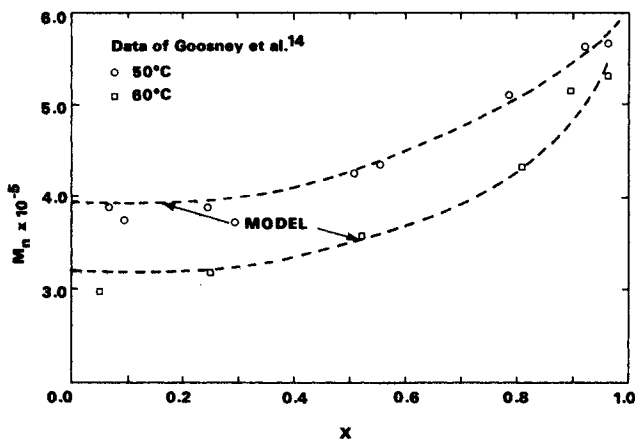
Fig. 7. Comparison between theoretical and experimental plots of M_w vs conversion at different initiator concentrations. $N = 15 \times 10^{17}$; 50°C .

cal to a vinyl double bond. For k_{fp} and k_{fm} , the energies of activation giving the best fit equalled 9020 and 9950 cal/mole, respectively. Because of the similar nature of these reactions, it is expected that they show almost the same dependence on temperature. Moreover, the energies of activation used for k_{fp} and k_{fm} are very close to previously reported values.¹⁷ Thus, the model correctly reflects the molecular weight development and leads to reasonable activation energies.



X

Fig. 8. Plot of limiting viscosity number $[\eta]$ vs. conversion x at different initiator concentrations. $N = 8.6 \times 10^{17}$; 50°C .



X

Fig. 9. Comparison between theoretical and experimental plots of M_n vs. conversion at 50°C and 60°C .

Branching Development

Next, we consider the application of the model to predict the development of branching. The number of branches per molecule, B_n , is calculated from eqs. (12) and (16). Figure 10 shows theoretical plots of B_n versus conversion at 60°C . The solid curve was obtained by taking into account the decrease in k_p^* , while the dotted curve corresponds to a constant value of k_p^* equal to 2200 l./mole-sec. It is seen that the decrease in k_p^* has a tremendous effect on the branching density at high conversions.

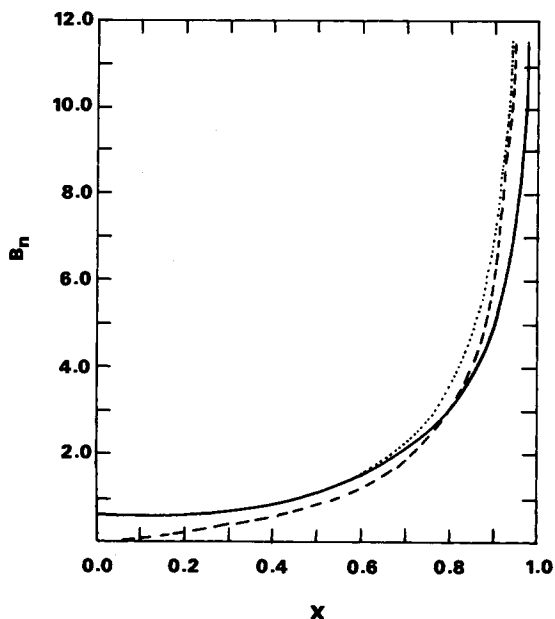


Fig. 10. Average number of branch points per molecule, B_n , as function of conversion x at 60°C. Solid curve: emulsion polymerization corrected for decreasing k_p^* ; dotted curve: emulsion polymerization with constant k_p^* ; dashed curve: bulk polymerization with constant k_p^* .¹⁶

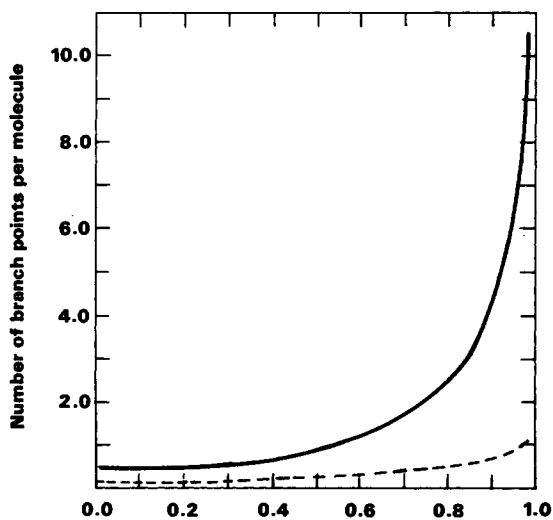


Fig. 11. Average number of branch points per molecule as function of conversion x at 60°C. Solid curve: branching due to transfer to polymer; dashed curve: branching due to terminal double-bond polymerization.

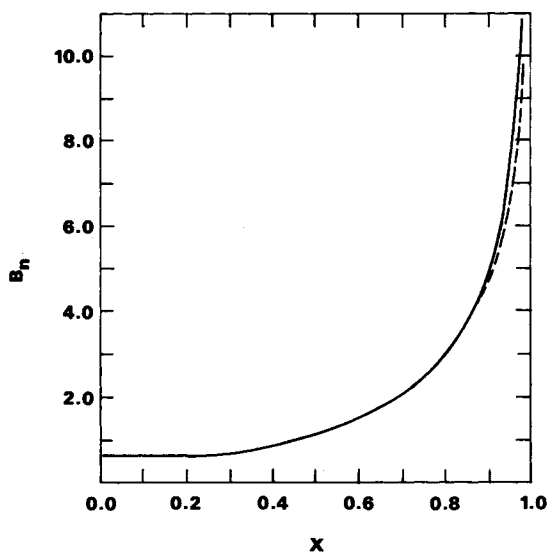


Fig. 12. Average number of branch points per molecule as function of conversion x at different temperatures. Solid curve: 60°C; dashed curve: 50°C.

For the sake of comparison a similar plot is shown calculated by Stein¹⁶ for bulk polymerization of vinyl acetate at 60°C. At low conversions, where k_p^* is constant, the curves from bulk and emulsion polymerization are comparable; and as one would expect, the number of branch points per molecule is higher when the polymer is produced by emulsion rather than by bulk polymerization. Again, this is due to the relative high concentration of polymer in the particles in the beginning of an emulsion polymerization. However, since Stein¹⁶ did not consider the possibility of a decreasing k_p^* , the curve for bulk polymerization rises more steeply at higher conversions than the emulsion curve corrected for a decreasing k_p^* .

Branching in poly(vinyl acetate) is due partly to transfer to polymer and partly to terminal double-bond polymerization. From eqs. (12) and (16), it is possible to determine the contribution to branching of each of these reactions. Figure 11 shows the result of this calculation. In the beginning of the reaction, approximately 25% of the branches are due to terminal double-bond polymerization. However, because the molecular weight increases during the process, the fraction of monomer molecules incorporated as terminal units decreases with increasing conversion, and therefore the fraction of branch points owing to terminal double-bond polymerization decreases steadily with increasing conversion; at 100% conversion, only 10% of the branches are due to this reaction.

Figure 12 shows a plot of B_n versus conversion at 50° and 60°C. It appears that the number of branch points per molecule is almost identical at the two temperatures. However, the number of branch points per mer is higher at 60°C since the molecular weights are lower.

Analysis of Viscosity Data

Figure 13 shows a plot of $\log [\eta]$ versus $\log M_w$ at 50°C. It appears that within the limits of error, this plot can be fitted with a straight line throughout the range of molecular weights investigated. This is probably fortuitous and may be attributed to the relatively narrow range of molecular weights, since usually the relationship between $\log [\eta]$ and $\log M_w$ is nonlinear when the polymers are highly branched, as in this case.

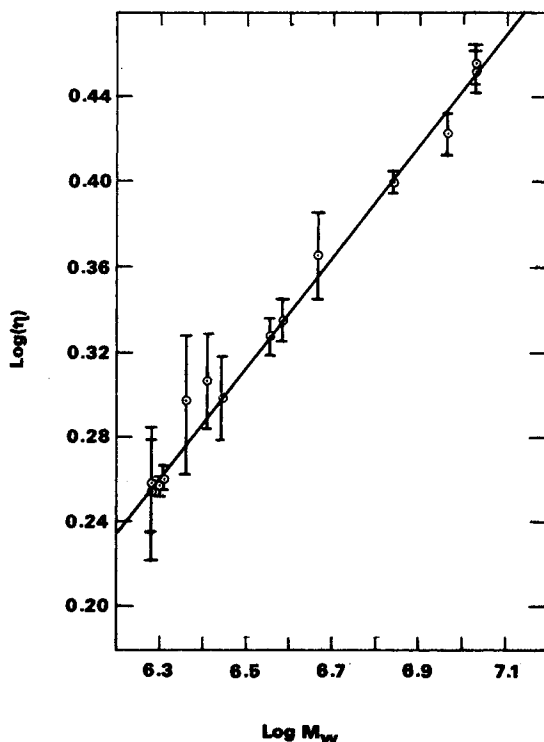


Fig. 13. Plot of $\log [\eta]$ vs. $\log M_w$ at 50°C .

From the slope and the intercept of the straight line, we derived the following empirical relationship:

$$[\eta] = 4.85 \times 10^{-2} M_w^{0.26} \text{ dl/g} \quad 2 \times 10^4 < M_w < 10^7.$$

This expression is valid when $[\eta]$ is measured at 30°C with acetone as solvent. The low value of the exponent clearly indicates a rapid increase in number of branches with increasing M_w . This Mark-Houwink relation may find some useful application with branched poly(vinyl acetate) produced with emulsion polymerization.

CONCLUSIONS

In conclusion, we may say that in vinyl acetate emulsion polymerization, molecular weight and branching development are largely controlled by transfer to polymer and monomer, and the average molecular weights are functions only of temperature and conversion. The particle number and the initiator concentration do not affect the molecular weights. Furthermore, the average number of branch points per molecule is larger in emulsion than in bulk polymerization when the polymerizations are conducted at the same temperature.

In view of the molecular weight and branching development in the emulsion polymerization of vinyl acetate, it is of interest to speculate on the applicability of core-shell morphology after Grancio and Williams¹⁹ to this system. The dramatic increase in weight-average molecular weight and in branching frequency with conversion found in this study is related to the increase in polymer concentration in monomer. It is also of interest in this regard to point out that polymer particle size in emulsion poly(vinyl ace-

tate) is generally much smaller than observed in emulsion polystyrene. With core-shell morphology, polymerization would occur in a pure monomer shell leading to linear poly(vinyl acetate). With this brief argument in mind, it appears unlikely that the core-shell morphology would play a role in the emulsion polymerization of vinyl acetate.

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