

A Molecular Weight Model in Vinyl Chloride–Divinyl Monomer Suspension Copolymerization Before the Gel Point*

LUO YINGWU, PAN ZUREN,[†] WENG ZHIXUE, and HUANG ZHIMING

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

SYNOPSIS

In this paper, a molecular weight model in the vinyl chloride (VC)–divinyl monomer suspension copolymerization was derived from the mechanism of VC two-phase polymerization, with pseudokinetic constant method and the theory of the moments of chain length distribution. Furthermore, the behavior of average polymerization degree was simulated with the model at varied experimental parameters. The simulation phenomena were discussed in detail. It is concluded that our model can be useful to predict the behavior of \overline{DP}_w and to look inside the crosslinking mechanism in the VC–divinyl monomer copolymerization.

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INTRODUCTION

In the monovinyl and divinyl monomer copolymerization, a copolymerization reaction leads to a linear polymer chain with a pendent double bond, which is likely to react subsequently with a radical to produce a branched polymer or even an infinite network. Thus, the system can be very complicated.

On the assumptions of equal reactivity of functional groups and no intramolecular reactions, Flory¹ and Stockmayer² derived the expressions for the size distribution of the finite molecules as a function of reaction extent in the nonlinear polymerization with the probability theory, and then determined the average molecular weights of polymer, respectively. Gordon³ introduced the cascade theory to nonlinear polymerization and directly obtained a result equivalent to that of Stockmayer. Macosko and Miller⁴ also developed expressions for the average molecular weights with the recursive nature of the branching process and an elementary law of conditional expectation. All of the above theories are called the "statistics theory." They will not apply to many actual systems, which may involve diffusion control

of reactants, heterogeneous precipitation polymerization, etc., which often occur in free radical polymerization. Mikos, Tadooudis, and Peppas⁵ listed all possible steps of the monovinyl and divinyl monomer copolymerization and developed kinetically a model for the number average molecular weight before gel point. Hamielec et al.^{6,7} reduced the balance equations for copolymerization to the same forms as those for homopolymerization with the pseudokinetic rate constant method; they also derived the models of the average molecular weights before gel point with the moments of polymer distribution. In Hamielec's model, a parameter r , the reactivity of the pendant double bonds, was introduced. However, the fraction of the pendant double bond was substituted for the average composition, which would introduce some errors.

So far, all of the models were used to deal with homogeneous systems, whereas the heterogeneous polymerization of VC suspension polymerization is of commercial importance. The patents⁸ for the synthesis of ultrahigh molecular weight PVC in the presence of a small amount of divinyl comonomer have been reported since the late 1970s, whereas theoretical research on the molecular weight behavior of such systems has not been reported so far. In this paper, a model of the average molecular weights before the gel point for VC suspension polymerization in the presence of a small amount of divinyl monomer is developed from the VC two-phase polymerization.

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[†] To whom correspondence should be addressed.

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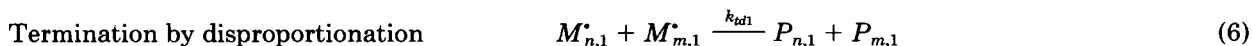
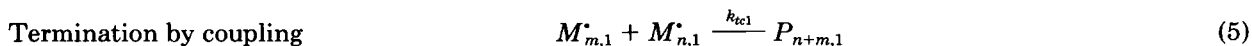
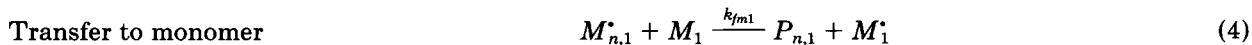
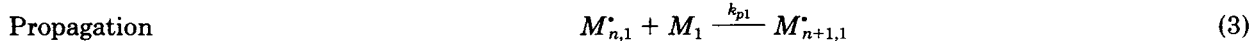
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POLYMERIZATION MECHANISM

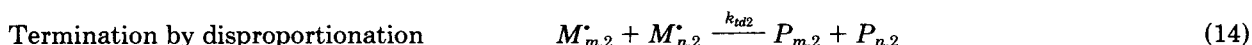
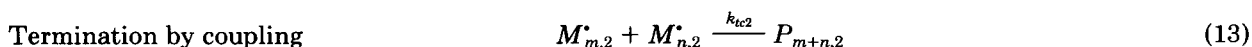
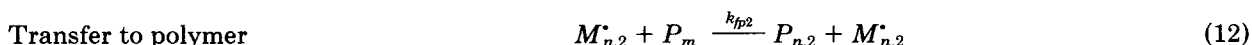
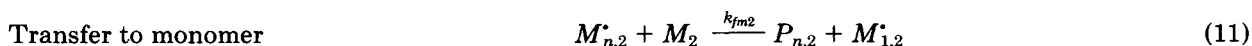
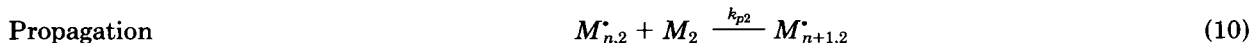
Polymerization occurs at the same time in both the polymer-rich and the monomer-rich phases in the range of 0.1–70% conversion. In both phases, there

are initiation, propagation, and termination reactions. Furthermore, there is radical exchange between two phases.^{9–11} The elementary reactions in the VC suspension polymerization are listed as follows:

Monomer-rich phase:

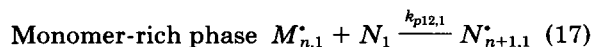


Polymer-rich phase:

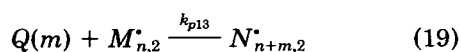


If a small amount of divinyl monomer (usually <1 mol %) is added, the elementary reactions that affect the system are listed as follows:

Radicals react with divinyl monomer, with the pendant double bond producing:



Crosslinking reaction in the polymer-rich phase



MODEL DEVELOPMENT

According to the features of the VC polymerization, we postulate:

- 1) Polymerization occurs in two phases, one composed mostly of monomers and the other composed of the polymer swollen with monomers. The ratios of polymer/monomer are constant in both phases.⁹
- 2) The polymer produced in the monomer-rich phase is precipitated immediately to the polymer-rich phase.
- 3) The effects of the precipitation of the radicals in the monomer-rich phase and the escape

of the radicals in the polymer-rich phase can be neglected.¹¹

- 4) The rate constants of both phases are equal, with the exception of those of terminations.⁹
- 5) A small amount of divinyl monomer has no effect on the partition of radicals between two phases.
- 6) The crosslinking reaction occurs only in the polymer-rich phase.
- 7) Cyclization and intramolecular crosslinking can be neglected.¹

CONCENTRATION OF PENDANT DOUBLE BONDS

According to the fourth assumption, the concentration of the pendant double bonds can be calculated the same as in the homogeneous system; thus, the equations for the concentrations of the various polymerizing species from the proposed mechanism may be written as follow:

$$-\frac{d[M]}{dt} = k_{p11}[M^*][M] \quad (20)$$

$$-\frac{d[N]}{dt} = 2k_{p12}[M^*][N] \quad (21)$$

$$-\frac{d[Q]}{dt} = k_{p13}[M^*]_2[Q] - k_{p12}[M^*][N] \quad (22)$$

The coefficient 2 in eq. (21) is due to the two double bonds in a divinyl monomer.

It has been shown^{10,11} that:

$$[M^*]_2 \gg [M^*]_1 \quad (23)$$

Therefore,

$$[M^*]_2 \approx [M^*] \quad (24)$$

Invoking the stationary-state hypothesis for radicals, from eqs. (20), (21), and (22) we obtain:

$$LN \frac{[N]_0}{[N]} = \frac{2}{r_1} LN \frac{[M]_0}{[M]} = \frac{2}{r_1} LN \frac{1}{(1-x_1)} \quad (25)$$

$$[Q] = \frac{1}{1-k} [N] \left[\left(\frac{[N]}{[N]_0} \right)^{k-1} - 1 \right] \quad (26)$$

where

$$r_1 = k_{11}/k_{12} \quad (27)$$

$$k = k_{p13}/2k_{p12} \quad (28)$$

MODEL OF THE AVERAGE MOLECULAR WEIGHTS

The *i*th moments of the distribution of the chain length of dead polymers and radicals are defined, respectively, as follows:

$$Q_i = \sum_{r=1}^{\infty} r^i [P_r] \quad (\text{dead polymers, } i = 0, 1, 2, \dots) \quad (29)$$

$$Y_i = \sum_{r=1}^{\infty} r^i [M_r^*] \quad (\text{free-radicals, } i = 0, 1, 2, \dots) \quad (30)$$

Define pseudo-kinetic rate constants as follows:
Propagation rate constant:

$$k_p = \sum_{i,j=1}^2 k_{p1j} \Phi_i^* f_j \quad (31)$$

Termination rate constant by disproportionation:

$$k_{td} = \sum_{i,j=1}^2 k_{tdij} \Phi_i^* \Phi_j^* \quad (32)$$

Termination rate constant by coupling:

$$k_{tc} = \sum_{i,j=1}^2 k_{tcij} \Phi_i^* \Phi_j^* \quad (33)$$

Transfer constant to monomer:

$$k_{fm} = \sum_{i,j=1}^2 k_{fmij} \Phi_i^* f_j \quad (34)$$

With the pseudo-kinetic rate constants, the balance equations for copolymerization reduce to the same forms as the equations for homopolymerization.

Invoking the stationary-state hypothesis for radicals, one can readily derive the following moment equations using the radical and polymer population balances, and then apply these equations to homopolymerization (the development in detail refers to the Appendix). The same equations can be used for

binary copolymerization using the pseudo-kinetic rate constants defined above.

$$\frac{d(V_1Q_{0,1})}{V_1dt} = (k_{td1} + k_{tc1}/2)[M^*]_1^2 + k_{fm1}[M]_1[M^*]_1 \quad (35)$$

$$\frac{d(V_1Q_{1,1})}{V_1dt} = k_{p1}[M]_1[M^*]_1 \quad (36)$$

$$\frac{d(V_1Q_{2,1})}{V_1dt} = \left\{ \frac{(2\tau_1 + 3\beta_1)}{(\tau_1 + \beta_1)^2} \right\} R_{p1} \quad (37)$$

$$\frac{d(V_2Q_{0,2})}{V_2dt} = \left(\tau_2 + \beta_2/2 - \frac{k_{p13}f_3Q_{1,2}}{k_p[M]_2} \right) R_{p2} + \frac{d(V_1Q_{0,1})}{V_1dt} V_1/V_2 \quad (38)$$

$$\frac{d(V_2Q_{1,2})}{V_2dt} = k_{p2}[M]_2[M^*]_2 + \frac{d(V_1Q_{1,1})}{V_1dt} V_1/V_2 \quad (39)$$

$$\frac{d(V_2Q_{2,2})}{V_2dt} = \frac{(2\tau_2 + 3\beta_2)(1 + k_{p13}f_3Q_{2,2}/k_p[M]_2)^2}{(\tau_2 + \beta_2)^2} R_{p2} + \frac{d(V_1Q_{2,1})}{V_1dt} V_1/V_2 \quad (40)$$

where

$$f_3 = \frac{[Q]}{[M]_0x} \quad (41)$$

$$\tau_i = \frac{k_{fm,i}[M]_i}{k_{p,i}[M]_i} + \frac{k_{td,i}[M^*]_i}{k_{p,i}[M]_i} \quad i = 1, 2 \quad (42)$$

$$\beta_i = \frac{k_{tc,i}[M^*]_i}{k_{p,i}[M]_i} \quad i = 1, 2 \quad (43)$$

$$R_{pi} = k_{pi}[M]_iY_{0,i} \quad i = 1, 2 \quad (44)$$

for the whole system

$$\frac{d(VQ_i)}{dt} = \frac{d(V_2Q_{i,2})}{dt} \quad (45)$$

$$Q_{2,2} = VQ_2/V_2 \quad (46)$$

The two-phase model of VC homopolymerization¹² gives:

$$[M]_1V_1 = M_T \frac{x_f - x}{x_f} \quad (47)$$

$$[M]_2V_2 = M_T \frac{x(1 - x_f)}{x_f} \quad (48)$$

$$[M^*]_2 = P[M^*]_1 \quad (49)$$

$$Q_{1,2} = \frac{VQ_1x_f}{M_Tx(1 - x_f)} [M]_2 \quad (50)$$

Substituting eqs. (45) through (50) into eqs. (35) through (40) and rearranging gives:

$$\frac{d(VQ_0)}{dt} = M_Tk_p[M^*]_1 \left\{ \frac{x_f - x}{x_f} (\tau_1 + \beta_1/2) + \frac{Px}{x_f} (1 - x_f) \left(\tau_2 + \beta_2/2 - \frac{x_fk_{p13}f_3VQ_1}{k_pM_Tx(1 - x_f)} \right) \right\} \quad (51)$$

$$\frac{d(VQ_1)}{dt} = M_Tk_p[M^*]_1(1 + qx) \quad (52)$$

$$\frac{d(VQ_2)}{dt} = M_Tk_p[M^*]_1 \left\{ \frac{(x_f - x)(2\tau_1 + 3\beta_1)}{x_f(\tau_1 + \beta_1)^2} - \frac{Px}{x_f} \times (1 - x_f) \frac{(2\tau_2 + 3\beta_2)}{(\tau_2 + \beta_2)^2} \left(1 + \frac{k_{p13}x_fk_{p13}VQ_2}{k_pM_Tx(1 - x_f)} \right)^2 \right\} \quad (53)$$

where

$$q = \frac{P(1 - x_f) - 1}{x_f} \quad (54)$$

The definition of the first moment of the chain length of polymer gives

$$M_T \frac{dx}{dt} = \frac{d(VQ_1)}{dt} = M_Tk_p[M^*]_1(1 + qx) \quad (55)$$

For convenience, time is placed by conversion as the independent variable throughout eqs. (42) to (44) and the moment equations take the form

$$\frac{d(VQ_0)}{M_Tdx} = \frac{1}{(1 + qx)} \left\{ \frac{x_f - x}{x_f} (\tau_1 + \beta_1/2) + \frac{Px}{x_f} (1 - x_f) \left(\tau_2 + \beta_2/2 - \frac{x_fk_{p13}f_3VQ_1}{k_pM_Tx(1 - x_f)} \right) \right\} \quad (56)$$

$$\frac{d(VQ_1)}{M_T dx} = 1 \quad (57)$$

$$\frac{d(VQ_2)}{M_T dx} = \frac{1}{(1+qx)} \left\{ \frac{(x_f - x)(2\tau_1 + 3\beta_1)}{x_f(\tau_1 + \beta_1)^2} - \frac{Px}{x_f} \right. \\ \left. \times (1 - x_f) \frac{(2\tau_2 + 3\beta_2)}{(\tau_2 + \beta_2)^2} \left(1 + \frac{k_{p13}x_f f_3 VQ_2}{k_p x(1 - x_f) M_T} \right)^2 \right\} \quad (58)$$

With the numerical integration, Q_0 , Q_1 , and Q_2 can be solved, and the average polymerization degrees can be obtained from the following equations at some conversion.

$$\overline{DP}_n = Q_1/Q_0 \quad (59)$$

$$\overline{DP}_w = Q_2/Q_1 \quad (60)$$

SIMPLIFICATION OF THE MODEL

The level of divinyl monomer is far lower than that of VC, so

$$k_p = k_{p11} \quad (61)$$

$$k_{td} = k_{td11} \quad (62)$$

$$k_{tc} = k_{tc11} \quad (63)$$

$$k_{fm} = k_{fm11} \quad (64)$$

As for the VC homopolymerization, it is evident that the rate constants of the two phases are equal to each other, with the exception of the termination rate constants⁹; that the predominant method of chain termination is to transfer to monomer; that the termination between two radicals is limited only to the disproportionation, with the couple being neglected¹²; and that the following inequality stands at the ordinary polymerization temperature:

$$k_{td11}[M^*] \ll k_{fm11}[M] \quad (65)$$

thus,

$$\tau_1 \approx \tau_2 \approx C_{M11} \quad (66)$$

Thus, the model is simplified as:

$$\frac{d(VQ_0)}{M_T dx} = C_{M11} - \frac{2kPx f_3}{(1+qx)r_1} \quad (67)$$

$$\frac{d(VQ_1)}{M_T dx} = 1 \quad (68)$$

$$\frac{d(VQ_2)}{M_T dx} = \frac{2}{C_{M11}(1+qx)} \left\{ \frac{(x_f - x)Px}{x_f} (1 - x_f) \right. \\ \left. \times \left(1 + \frac{2kx f_3 VQ_2}{r_1 x(1 - x_f) M_T} \right)^2 \right\} \quad (69)$$

At last, the average polymerization degrees can be calculated from eqs. (59) and (60), together with eqs. (67) through (69).

SIMULATION AND DISCUSSION

The results from VC homopolymerization give $C_{M11} = 79.316 \text{ EXP}(3639.68/T)$,¹¹ $P = 22.85$, $x_f = 0.785$.¹⁰ Substituting these results into the model gives Figures 1-4. (The simulation temperature is 45°C.)

Figure 1 simulates the development of the weight average degree of polymerization (\overline{DP}_w) for various

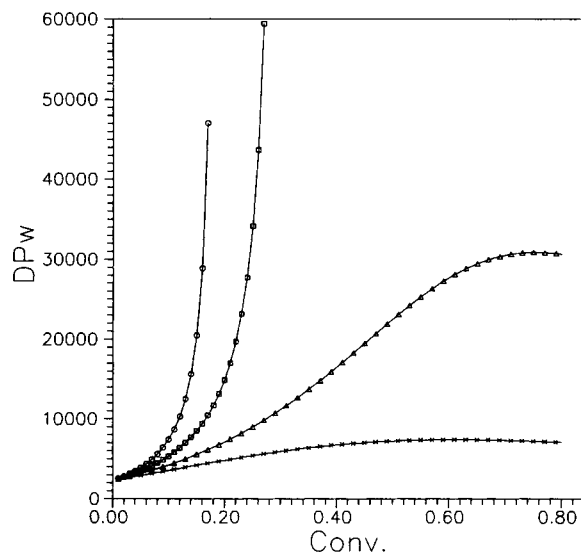


Figure 1 Variation of \overline{DP}_w with conversion at various levels of divinyl monomer, $r_1 = 1$ and $k = 0.5$.

- ××××× Divinyl monomer level: $4.0 \cdot 10^{-5}$ mol/mol VC
- △△△△△ Divinyl monomer level: $5.0 \cdot 10^{-5}$ mol/mol VC
- Divinyl monomer level: $6.0 \cdot 10^{-5}$ mol/mol VC
- Divinyl monomer level: $7.0 \cdot 10^{-5}$ mol/mol VC

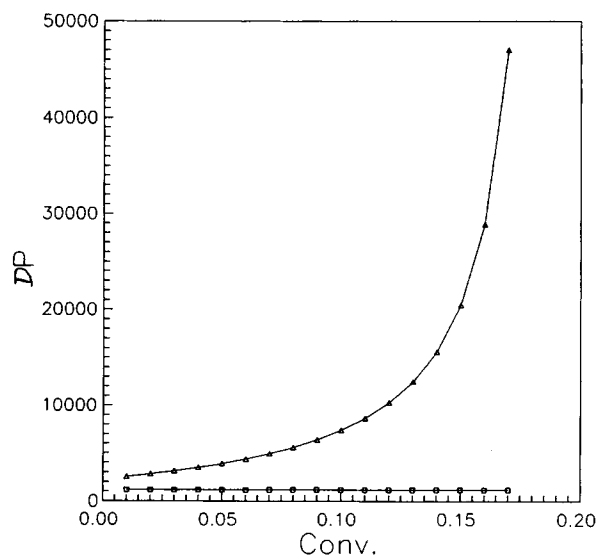


Figure 2 Variation of \overline{DP}_n with conversion at $r_1 = 1$, $k = 0.5$ and the level of divinyl monomer: 7.0×10^{-5} mol/mol VC.

$$\begin{array}{l} \square-\square-\square-\square-\square \overline{DP}_n \\ \triangle-\triangle-\triangle-\triangle-\triangle \overline{DP}_w \end{array}$$

amounts of divinyl monomer with the same reactivity of all doubles. It shows that the critical conversion (C_c) where \overline{DP}_w tends to be indefinite increases with the decrease of the amount of divinyl monomer. The behavior of the number average degree of polymerization (\overline{DP}_n) before gel point is simulated in Figure 2. It shows that the increase of the \overline{DP}_n with the conversion is much more gradual than that of \overline{DP}_w . It is concluded that there are only a few ultra-high molecular weight molecules.

Figure 3 simulates the effects of the monomer reactivity on the \overline{DP}_w , showing that C_c increases with the increase of r_1 .

When the apparent reactivity (k value) of the pendant double bond reduces because of the different physical effects, the behavior of \overline{DP}_w is observed as shown in Figure 4. It is observed that \overline{DP}_w reduces dramatically with the reduced k value. It is concluded that it is practicable to obtain the k value, which is greatly affected by the physical nature of the system, through fitting the model with the experimental development of \overline{DP}_w .

On examining Figures 1–4, it is clear that the model predicts dramatic changes of \overline{DP}_w vs conversion with relatively small changes in the experimental parameters being investigated. These phenomena will be discussed from the points of view of crosslinking reactions and VC two-phase polymerization mechanism.

As shown in elementary reaction (19), crosslinking reactions occur when a macroradical attacks another macromolecule. The crosslinking reaction rate of a given size macromolecule can be expressed as follows:

$$R_c = k_{p13}[M^*]_2 f_3 r [P_r] \quad (70)$$

It is clear from eq. (70) that the crosslinking reaction rate is proportional to the size of macromolecules, i.e., the bigger a macromolecule is, the higher the probability is that the macromolecule will be crosslinked. On the other hand, once a macromolecule is crosslinked it becomes bigger. Consequently, the bigger crosslinked macromolecule has a higher probability of being further crosslinked. It is inferred that from the point of view of a huge single macromolecule, the crosslinking reaction rate is auto-accelerated, i.e., the bigger parent macromolecules increase their sizes much more rapidly than the smaller. Thus, for the whole system, a very small amount of crosslinking can cause a dramatic increase of \overline{DP}_w which is very sensitive to the presence of huge macromolecules; at the same time, however, \overline{DP}_n , which is determined by the number of mac-

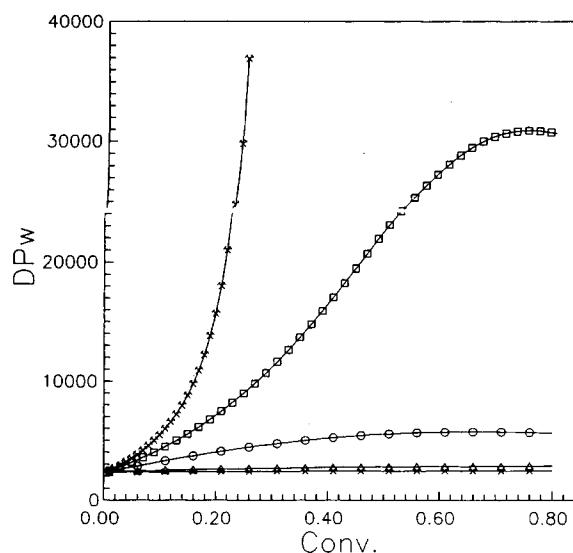


Figure 3 Variation of \overline{DP}_w with conversion at various monomer reactivity ratios, $k = 0.5$ and the level of divinyl monomer: 5.0×10^{-5} mol/mol VC.

$$\begin{array}{l} \times \times \times \times \times r_1 = 5.00 \\ \triangle \triangle \triangle \triangle \triangle r_1 = 2.50 \\ \circ \circ \circ \circ \circ r_1 = 1.25 \\ \square \square \square \square \square r_1 = 1.00 \\ * * * * * r_1 = 0.90 \end{array}$$

romolecules in the system, increases only a little. These phenomena are shown in Figure 2.

The following equations can easily be derived from eq. (70):

$$\frac{\partial R_c}{\partial f_3} = f_{p13}[M^*]_2 r [P_r] \quad (71)$$

$$\frac{\partial R_c}{\partial k_{p13}} = f_3[M^*]_2 r [P_r] \quad (72)$$

It is inferred that the sensitivity of R_c with respect to experimental parameters, such as f_0 , r_1 , and k , is proportional to the local polymer level.

VC polymerization occurs at the same time in two phases, one of which is composed mostly of monomers and the other composed of the polymer swollen with about 30 wt % monomer in the range of 0.1–70% conversion. It is clear that crosslinking reactions take place in the swollen-polymer phase. Consequently, in the early stage of polymerization, the local concentration of polymers is much higher than that in the homogeneous system. Thus, for VC-divinyl monomer copolymerization, R_c and \overline{DP}_w (just as shown in Figures 1–4) are much more sensitive to the simulation parameters as a result of the high macromolecule level and the auto-accelerated effect of crosslinking presented above.

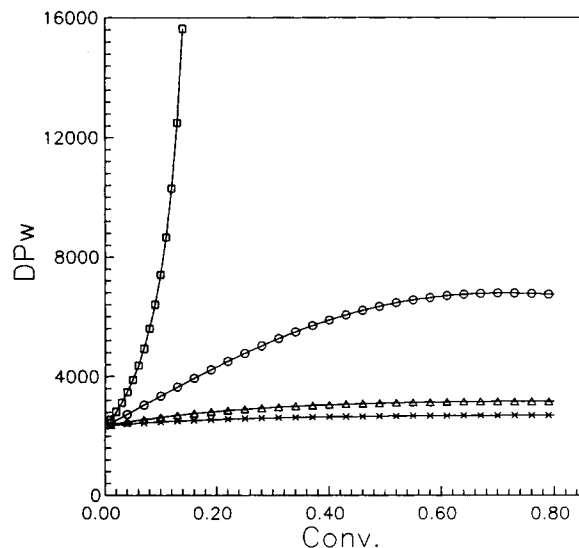


Figure 4 Variation of \overline{DP}_w with conversion at various apparent reactivities of pendant double bond, r_1 , and the level of divinyl monomer: 7.0×10^{-5} mol/mol VC.

- □ □ □ □ $k = 0.50$
- ○ ○ ○ ○ $k = 0.25$
- △ △ △ △ △ $k = 0.10$
- × × × × × $k = 0.05$

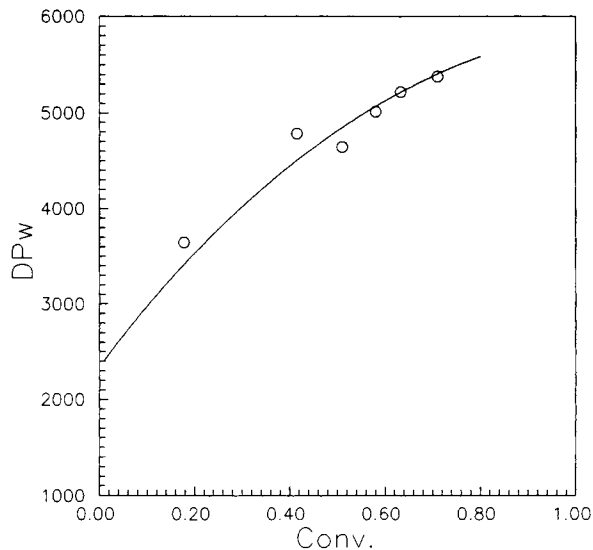


Figure 5 History of \overline{DP}_w by experiment and the model.

- ○ ○ ○ ○ Exp. values
- Model values

To verify the model, the reactivity ratio of VC-diallyl phthalate was measured at 45°C in the routine. The data were processed by the Kelen-Tudos method¹⁴ with intramolecular reaction neglected, which has been justified by some researchers.¹⁵ We obtained $r_1 = 0.71$, which is close to the 0.84 value at 60°C obtained by Matsumoto, Matsuo, and Oiwa.¹⁶ Furthermore, the \overline{DP}_w history polymerized at 45°C and $f_0 = 4.25 \times 10^{-4}$ was recorded experimentally. Figure 5 shows that the experimental \overline{DP}_w history fits well with our model at $k = 0.0572$, which means that the apparent reactivity of the pendant double bonds reduces by about one order. It is indicated that the crosslinking reactions are diffusion-controlled because they take place in the swollen-polymer phase. As a matter of fact, it has been proved that the termination reactions between macroradicals, which also occur in the swollen-polymer phase, are diffusion-controlled,¹¹ which conforms with our conclusion about crosslinking reactions.

CONCLUSION

A molecular weight model of copolymer in the VC-divinyl monomer suspension polymerization is derived from the feature of VC two-phase polymerization, with pseudokinetic constant method and the theory of the moments of chain length distribution.

The level of the pendant double bond which was substituted for the average composition by Hamielec is derived to avoid the errors in Hamielec's model.^{6,7}

The model is used to simulate the behaviors of \overline{DP}_w at varied experimental parameters. The simulation phenomena were discussed in detail from the points of view of the auto-accelerated effect of crosslinking and VC two-phase polymerization.

Experiments were carried out to verify our model. It is concluded that our model can be useful in predicting the behavior of \overline{DP}_w and looking inside the crosslinking mechanism in the VC-divinyl monomer copolymerization.

APPENDIX

Transfer reaction to polymer can be neglected in the monomer-rich phase because the level of polymer is very low. The rate equations for the various length polymers may be written as follows:

$$\begin{aligned} \frac{d(V_1[P_r]_1)}{V_1 dt} &= k_{td1}[M^*]_1[M^*]_1 \\ &+ k_{tc1}/2 \sum_{s=1}^{r-1} [M^*]_1[M^*]_{r-s} + k_{fm1}[M]_1[M^*]_1 \end{aligned} \quad (r \geq 2) \quad (A1)$$

$$\frac{d(V_1[P_1]_1)}{V_1 dt} = k_{td1}[M^*]_1[M^*]_1 \quad (r = 1) \quad (A2)$$

Eqs. (A1) and (A2) must be considered as the producing rate of the polymers instead of the change of the concentrations of the various length polymers, because polymers producing in the monomer-rich phase precipitate immediately to the polymer-rich phase.

The following equations can be derived from the definition of the moments:

$$\begin{aligned} \frac{d(V_1Q_{0,1})}{V_1 dt} &= (k_{td1} + k_{tc1}/2)[M^*]_1^2 \\ &+ k_{fm1}[M]_1[M^*]_1 \end{aligned} \quad (A3)$$

$$\frac{d(V_1Q_{1,1})}{V_1 dt} = k_{p1}[M]_1[M^*]_1 \quad (A4)$$

$$\begin{aligned} \frac{d(V_1Q_{2,1})}{V_1 dt} &= \{(k_{td1} + k_{tc1})[M^*]_1 \\ &+ k_{fm1}[M]_1\} Y_{2,1} + k_{tc1} Y_{1,1}^2 \end{aligned} \quad (A5)$$

Making the balance of radical population gives:

$$\begin{aligned} \frac{d(V_1[M^*]_1)}{V_1 dt} &= k_{p1}[M]_1[M^*]_{r-1} \\ &- k_{p1}[M]_1[M^*]_1 - (k_{td1} + k_{tc1})[M^*]_1[M^*]_1 \\ &- k_{fm1}[M]_1[M^*]_1 + k_{de}[M^*]_2 V_2/V_1 - k_{ab}[M^*]_1 \end{aligned} \quad (r \geq 2) \quad (A6)$$

$$\begin{aligned} \frac{d(V_1[M^*]_1)}{V_1 dt} &= M_{r1} - k_{p1}[M]_1[M^*]_1 \\ &- (k_{td1} + k_{tc1})[M^*]_1[M^*]_1 + k_{fm1}[M]_1[M^*]_1 \\ &+ k_{de}[M^*]_2 V_2/V_1 - k_{ab}[M^*]_1 \end{aligned} \quad (r = 1) \quad (A7)$$

It has been evident that the effects of the radical precipitation in the monomer phase and the radical escape in the polymer-rich phase can be neglected,¹³ and the following equations are obtained from the definition of the moments of the chain length distribution of radicals and the stationary-state hypothesis.

$$Y_{1,1} = \frac{k_{p1}[M]_1[M^*]_1 + k_{fm1}[M]_1[M^*]_1 + R_{I1}}{(k_{td1} + k_{tc1})[M^*]_1 + k_{fm1}[M]_1} \quad (A8)$$

$$Y_{2,1} = \frac{k_{p1}[M]_1([M^*]_1 + 2Y_{1,1}) + k_{fm1}[M]_1[M^*]_1 + R_{I1}}{(k_{td1} + k_{tc1})[M^*]_1 - k_{fm1}[M]_1} \quad (A9)$$

Substituting equations (80) and (81) into eq. (77) gives:

$$\begin{aligned} \frac{d(V_1Q_{2,1})}{V_1 dt} &= \left\{ \frac{(2 + \tau_1 + \beta_1)R_{CM}}{(\tau_1 + \beta_1)} \right. \\ &\left. + \beta_1 \left(\frac{R_{CM}}{(\tau_1 + \beta_1)} \right)^2 \right\} R_{p1} \end{aligned} \quad (A10)$$

where

$$R_{p1} = k_{p1}[M]_1[M^*]_1 \quad (A11)$$

$$R_{CM} = 1 + C_{M1} + R_{I1}/R_{p1} \quad (A12)$$

$$C_{M1} = k_{fm1}/k_{p1} \quad (A13)$$

at the usual commercial polymerization temperature. The orders of both C_{M1} and R_{I1}/R_{p1} are 10^{-3} , so $R_{CM} = 1$. Then,

$$\frac{d(V_1Q_{2,1})}{V_1 dt} = \left\{ \frac{2\tau_1 + 3\beta_1}{(\tau_1 + \beta_1)^2} \right\} R_{p1} \quad (A14)$$

Although the transfer to the polymers is obvious because of the high polymer level in the polymer-rich phase, it is evident that this has little effect on the average degree of polymerization.¹³

Thus, making the population balance of the dead polymers gives:

$$\begin{aligned} \frac{d(V_2[P_r]_2)}{V_2 dt} &= k_{td2}[M^*]_2[M^*]_2 \\ &+ k_{tc2}/2 \sum_{s=1}^{r-1} [M^*]_2[M^*]_{r-s} + k_{fm2}[M]_2[M^*]_2 \\ &- k_{p13}r f_3 [P_r]_2 [M^*]_2 + \frac{d(V_1[P_r]_1)}{V_1 dt} V_1/V_2 \end{aligned} \quad (r \geq 2) \quad (\text{A15})$$

$$\frac{d(V_2[P_1]_2)}{V_1 dt} = k_{td2}[M^*]_2[M^*]_2 \quad (r = 1) \quad (\text{A16})$$

The following equations can be obtained from the definition of the moments:

$$\begin{aligned} \frac{d(V_2 Q_{0,2})}{V_2 dt} &= (k_{td2} + k_{tc2}/2)[M^*]_2^2 + k_{fm2}[M]_2[M^*]_2 \\ &- k_{p13} f_3 Q_{1,2} [M^*]_2 + \frac{d(V_1 Q_{0,1})}{V_1 dt} V_1/V_2 \end{aligned} \quad (\text{A17})$$

$$\frac{d(V_2 Q_{1,2})}{V_2 dt} = k_{p2}[M]_2[M^*]_2 + \frac{d(V_1 Q_{1,1})}{V_2 dt} V_1/V_2 \quad (\text{A18})$$

$$\begin{aligned} \frac{d(V_2 Q_{2,2})}{V_2 dt} &= \{(k_{td2} + k_{tc2})[M^*]_2 + k_{fm2}[M]_2\} Y_{2,2} \\ &+ k_{tc2} Y_{1,2}^2 - k_{p13} f_3 Q_{3,2} [M^*]_2 \\ &+ \frac{d(V_1 Q_{2,1})}{V_1 dt} V_1/V_2 \end{aligned} \quad (\text{A19})$$

The effects of the radical precipitation in the monomer-rich phase and the radical escape in the polymer-rich phase can be neglected.¹³ Making the balance of radical population gives:

$$\begin{aligned} \frac{d(V_1 Y_{1,2})}{V_2 dt} &= R_{11} + k_{p13} \sum_{j=1}^i C_j^i Q_{j+1,2} Y_{i-j,2} \\ &+ k_{p2}[M]_2 \sum_{j=0}^{i-1} C_j^i Y_{j,2} - (k_{td1} + k_{tc1}) Y_{0,2} Y_{i,2} \\ &- k_{fm2}[M]_2 Y_{i,2} + k_{fm}[M]_2 Y_{0,2} \end{aligned} \quad (i = 1, 2) \quad (\text{A20})$$

Invoking the stationary-state hypothesis for the radicals in the polymer-rich phase gives:

$$\begin{aligned} Y_{i,2} &= Y_{0,2} \left(\tau_2 + \beta_2 + k_{p13}/k_p \sum_{j=1}^i C_j^i Q_{j+1,2} / \right. \\ &\left. [M]_2 Y_{i-j,2} / Y_{0,2} + \sum_{j=0}^{i-1} C_j^i Y_{j,2} / Y_{0,2} \right) / (\tau_2 + \beta_2) \end{aligned} \quad (\text{A21})$$

Substituting eq. (A21) into eqs. (A19) and (20) and rearranging gives:

$$\begin{aligned} \frac{d(V_2 Q_{0,2})}{V_2 dt} &= \left(\tau_2 + \beta_2/2 - \frac{k_{p13} f_3 Q_{1,2}}{k_p [M]_2} \right) R_{p2} \\ &+ \frac{d(V_1 Q_{0,1})}{V_1 dt} V_1/V_2 \end{aligned} \quad (\text{A22})$$

$$\begin{aligned} \frac{d(V_2 Q_{2,2})}{V_2 dt} &= \frac{(2\tau_2 + 3\beta_2)(1 + k_{p13} f_3 Q_{2,2}/k_p [M]_2)^2}{(\tau_2 + \beta_2)^2} R_{p2} \\ &+ \frac{d(V_1 Q_{2,1})}{V_1 dt} V_1/V_2 \end{aligned} \quad (\text{A23})$$

Eqs. (A3), (A4), (A14), (A22), (A16), and (A23) are eqs. (35) to (40) in the text, respectively.

NOMENCLATURE

$\frac{C_M}{DP_n}$	transfer constant to monomers number average degree of polymerization
\overline{DP}_w	weight average degree of polymerization
f_j	molar fraction of monomer j
f_0	molar fraction of divinyl monomer in the feed
$I_i, i = 1, 2$	initiator (subscript $i = 1$ refers to monomer-rich phase, $i = 2$ refers to polymer-rich phase, the same as below)
k_{pi}	propagation rate constant in the i th phase
k_{di}	initiator degradation rate constant for initiator in the i th phase
k_{fmi}	transfer rate constant to monomers in the i th phase
k_{tdi}	termination rate constant by disproportionation in the i th phase
k_{tci}	termination rate constant by coupling in the i th phase
k_{ab}	rate constant for polymer-rich phase to catch the radicals in the monomer-rich phase

k_{de}	rate constant for radicals to escape from the polymer-rich phase	$Q_{j,i}$	the j th moment of the distribution of the chain length for "dead polymers" in the i th phase
k_p	pseudo-kinetic propagation rate constant	r_1	monomer reactivity
k_{fm}	pseudo-kinetic transfer rate constant to monomers	$R_{I,i}$	initiation rate
k_{td}	pseudo-kinetic disproportionation termination rate constant	R_i	initiator degradation radicals
k_{tc}	pseudo-kinetic couple termination rate constant	t	polymerization time
k_{pij}	propagation rate constant for the reaction between the radicals which end with i and j monomers	$Y_{j,i}$	the j th moment of the distribution of the chain length for the radicals in the i th phase
k_{fmij}	transfer rate constant to monomers for the transfer reaction between radicals which end with i and j monomers	V_i	reaction volume of the i th phase
k_{tdij}	termination by disproportionation rate constant for the termination reaction between radicals which end with i and j monomers	V_T	total reaction volume
k_{tcij}	termination by coupling rate constant for the termination reaction between radicals which end with i and j monomers	x	conversion
$k_{p12,i}$	propagation rate constant for the reaction between radicals which end with vinyl chloride and divinyl monomer in the i th phase	x_f	conversion where the monomer-rich phase is consumed
k_{p13}	crosslinking rate constant	Φ_j	molar fraction of the radicals which end with the monomer j
k_{fp}	transfer rate constant to polymers		
$[M^*]_i$	concentration of radicals in the i th phase		
$[M^*]$	total concentration of radicals		
$M^*_{n,i}$	chain radicals with chain length n		
$[M]_i$	monomer concentration in the i th phase		
$[M]_0$	initial total monomer concentration		
$[N]_0$	initial divinyl monomer concentration		
M_T	total molar number of monomers		
N_i	divinyl monomer		
P	ratio of the concentration of radicals between two phases		
$P_{n,i}$	polymer with chain length n producing in the i th phase		
Q	pendent double bond		
$Q(m)$	macromolecules with degree of polymerization m		
$[Q]$	concentration of pendent double bond		
Q_j	the j th moment of the distribution of the degree of polymerization for dead polymer ($j = 0, 1, 2, \dots$)		

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