Kinetics of gelation in free radical crosslinking copolymerization

Oğuz Okay
TÜBITAK Marmara Research Center, Department of Chemistry, PO Box 21, Gebze, Kocaeli, Turkey

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A general equation is derived for the critical conversion at the gel point in free radical crosslinking polymerizations by omitting the equal reactivity assumption from the Stockmayer criterion of gelation. Calculations show that the monomer depletion, the volume contraction during polymerization and the initiator depletion have to be taken into account when the pre-gelation period is sufficiently large. The nucleation and growth of the gel molecule are described using kinetic differential rate equations. If the assumptions of equal vinyl group reactivity and random crosslinking are introduced, the resulting equations are equal to those of the statistical theories.

(Keywords: gelation; crosslinking polymerization; critical conversion)

INTRODUCTION

Gelation in free radical polymerizations has generally been treated within the context of the statistical theories[1–8], Although these theories provide a full description of the system, they are based upon random reaction of functional groups (vinyl groups). However, the network formation in free radical polymerizations is a kinetically controlled process and application of statistical methods is only an approximation to the real situation[9].

During recent years much attention has been devoted to the kinetic network formation theories[10–17]. Compared to the statistical models, kinetic models take into account all the kinetic features of polymerization and so may offer a more realistic approach to the microscopic phenomena during the reactions. A kinetic model consists of an infinite system of kinetic differential equations for the concentration of each possible molecule in the reaction system. Using the method of moments, these equations can easily be solved up to the gel point. However, since at the gel point second or higher moments of the distribution diverge, the passage beyond the gel point is one of the main problems of the kinetic theories. One way to overcome this difficulty is to combine the kinetic and statistical concepts in modelling the post-gelation period[18–21].

Recently, a new kinetic model was proposed for the post-gelation period of free radical monovinyl–divinyl monomer (MVM–DVM) copolymerization[22]. The key assumption of this model is the steady-state approximation for the radical concentration in the sol phase. Using this assumption and neglecting the attack of the gel radicals on the pendent vinyls, the model predicts important features of the post-gelation period such as the weight fraction of gel and the chain length averages of both the primary and branched molecules in the sol. However, the moment equations of the model were solved in the original work using Flory's expression for the crosslinking density of the gel[23]. Therefore, the equations thus developed should be considered semistatistical. One of the purposes of the present study is to remove this restriction and to derive kinetic equations for the nucleation and growth of the gel molecule in free radical MVM–DVM copolymerization. Additionally, general expressions for the critical conversion at the gel point and the weight fraction of sol are derived, and compared with those of the statistical theories. The assumption of no cyclization in finite species will be retained as it is beyond the scope of this work.

KINETIC MODEL

In this section, a summary of the kinetic model is given so as to enable the understanding of its applications presented in the current study. Here, the polymer species present in the reaction system are considered as the 'primary molecules'[23], i.e. as the molecules that would result if all crosslinks in the system were cut. Moreover, symbols with a prime (′) or double prime (″) are used to denote the species in the sol or in the gel, respectively, whereas those without any primes refer to species in the whole polymerization system.

Copolymerization of a MVM with a DVM having symmetric vinyls involves three types of vinyl groups: those on MVM (M_1), those on DVM (M_2), and those on polymer chains, i.e pendent vinyls (M_3). Accordingly, MVM–DVM copolymerization can be considered as a special case of terpolymerization in which one of the vinyls (M_3) is created during the course of the reaction when the M_2 vinyl reacts. A schematic of the post-gelation period in free radical MVM–DVM copolymerization is shown in *Figure 1*. Neglecting cyclization and chain transfer reactions, the rate equations for the concen-

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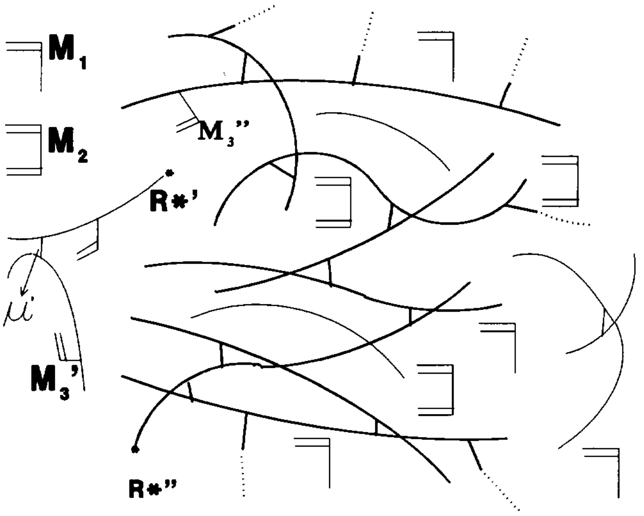

Figure 1 Schematic representation of the post-gelation period in free radical MVM–DVM copolymerization. M_1 and M_2 represent the vinyl groups on MVM and DVM, respectively, whereas M_3 represents the pendent vinyls. The symbol μ is used to denote crosslinks, i.e. two crosslinked units. The bold curves represent the primary chains of the gel molecule, whereas the thin curves represent those in the sol

Table 1 The reaction equations for the formation and consumption of primary molecules in the sol composed of r structural units. Here $A*$ is the primary radical, k_{ai} is the initiation rate constant for vinyl M'_i, and R'_r* and D'_r represent the active and the dead polymer of chain length r, respectively

Formation	$A* + M'_i \xrightarrow{k_{ai}} R'_1*$
	$\underset{(r>1)}{R'_{r-1}}* + M'_i \xrightarrow{k_{pi}} R'_r*$
	$R'_s* + \underset{(r>s)}{R'_{r-s}}* \xrightarrow{k_{tc}} D'_r$
	$R'_r* + R_s* \xrightarrow{k_{td}} D'_r + D_s$
Consumption	$R'_r* + M_i \xrightarrow{k_{pi}} R_{r+1}*$
	$R'_r* + R_s* \xrightarrow{k_t} D_{r+s}$ and/or $D'_r + D_s$
	$(r, s = 1, 2, 3, \ldots;\ i = 1, 2$ and $3)$

trations of the initiator I, vinyl groups M_i and crosslinks μ are[22]

$$r_I = -k_d[I] \tag{1}$$

$$r_{M_1} = -k_{p1}[R*][M_1] \tag{2}$$

$$r_{M_2} = -2k_{p2}[R*][M_2] \tag{3}$$

$$r_{M_3} = k_{p2}[R*][M_2] - k_{p3}[R*][M_3] \tag{4}$$

$$r_\mu = k_{p3}[R*][M_3] \tag{5}$$

where $[R*]$ is the total radical concentration and is given by the usual equation

$$[R*] = (2fk_d[I]/k_t)^{1/2} \tag{6}$$

where f is the initiator efficiency, k_d is the decomposition rate constant of the initiator, k_{pi} is the instantaneous propagation rate constant of the radical with vinyl of type i, and k_t is the sum of the instantaneous termination rate constants by coupling (k_{tc}) and by disproportionation (k_{td}), i.e. $k_t = k_{tc} + k_{td}$. Note that equation (6) is of the same form as that for homopolymerization except that k_t is not constant but is changing with time. Here, for the sake of simplicity, the instantaneous rate constants defined previously[22] are assumed to be independent of conversion.

The calculation of the molecular weight distribution of the sol species requires the concentration of each possible molecule in the reaction system. To deduce the evolution equations for the concentrations of active and total primary chains of degree of polymerization r, represented by $[R'_r*]$ and $[P'_r]$, respectively, the model considers the kinetic events given in *Table 1*. The equations can then be written as follows[22]

$$\begin{aligned} r_{R'_r*} = {} & \alpha_r \sum_{i=1}^{3} k_{ai}[A*][M'_i] + \sum_{i=1}^{3} k_{pi}[M'_i] \\ & \times \{(1-\alpha_r)[R'_{r-1}*] - [R'_r*]\} \\ & - (k_{p3}[M''_3] + k_t[R*])[R'_r*] \end{aligned} \tag{7a}$$

$$r_{P'_r} = k_{td}[R*][R'_r*] + 0.5k_{tc} \sum_{s=1}^{r-1} (1-\alpha_r)[R'_s*][R'_{r-s}*] \tag{7b}$$

for $r = 1, 2, 3, \ldots$, where $\alpha_r = 0$ for $r > 1$ and $\alpha_1 = 1$. Because all chain lengths are in principle possible, these equations form an infinite set of coupled differential equations. However, using the method of moments these equations can easily be solved. The moments for active or total primary chain distributions are defined as follows

$$Y_n^{\cdot\prime} \equiv \sum_{r=1}^{\infty} r^n [R'_r*] \tag{8a}$$

$$Q_n^{\cdot\prime} \equiv \sum_{r=1}^{\infty} r^n [P'_r] \tag{8b}$$

Using equations (7a) and (7b), one obtains the following moment equations

$$\begin{aligned} r_{Y_n^{\cdot\prime}} = {} & k_t[R*]^2 + (1-\alpha_n) \sum_{i=1}^{3} k_{pi}[M'_i] \sum_{v=0}^{n-1} \binom{n}{v} Y_v^{\cdot\prime} \\ & - (k_{p3}[M''_3] + k_t[R*]) Y_n^{\cdot\prime} \end{aligned} \tag{9a}$$

$$r_{Q_n^{\cdot\prime}} = k_{td}[R*] Y_n^{\cdot\prime} + 0.5k_{tc} \sum_{v=0}^{n} \binom{n}{v} Y_v^{\cdot\prime} Y_{n-v}^{\cdot\prime} \tag{9b}$$

for $n = 0, 1, 2, \ldots$, where $\alpha_n = 0$ for $n > 0$ and $\alpha_0 = 1$. Invoking the steady-state approximation, and since $Y_n^{\cdot\prime} \gg Y_{n-1}^{\cdot\prime}$ and $\sum_{i=1}^{3} k_{pi}[M'_i] \approx \sum_{i=1}^{3} k_{pi}[M_i]$ in free radical polymerization, equations (9a) and (9b) become

$$Y_n^{\cdot\prime} = n! \left(\frac{\sum_{i=1}^{3} k_{pi}[M_i]}{k_t[R*]} \right)^n [R*] \phi_s^{n+1} \tag{10}$$

$$r_{Q_n^{\cdot\prime}} = \left(\frac{k_{td}}{\phi_s} + \frac{n+1}{2} k_{tc} \right) Y_0^{\cdot\prime} Y_n^{\cdot\prime} \tag{11}$$

for $n = 0, 1, 2, \ldots$, where ϕ_s is the fraction of radicals belonging to the sol component and is given by

$$\phi_s = \frac{[R'*]}{[R*]} = \left(1 + \frac{k_{p3}[M''_3]}{k_t[R*]} \right)^{-1} \tag{12}$$

Owing to the differences in the densities of the MVM (d_1), DVM (d_2) and the polymer (d_p), the reaction volume V_r will change during a batch isothermal MVM–DVM copolymerization. If S represents the concentrations of species I, M_i and μ and the moments of the polymer distributions $Q_n^{\cdot\prime}$, a mass balance requires

$$r_S = \frac{d(V_r S)}{V_r dt} = \frac{dS}{dt} + \frac{S}{V_r} \frac{dV_r}{dt} \tag{13}$$

where $\mathrm{d}V_r/\mathrm{d}t$ is the rate of volume change, which, assuming ideal solutions, is given by

$$\frac{\mathrm{d}V_r}{\mathrm{d}t} = -\{k_{p1}[\mathrm{M}_1](d_1^{-1} - d_p^{-1})MW_1 + k_{p2}[\mathrm{M}_2](d_2^{-1} - d_p^{-1})MW_2\}[\mathrm{R}*]V_r \qquad (14)$$

where MW_1 and MW_2 are the molecular weights of MVM and DVM, respectively.

The mass balance equations of the kinetic model represented by equation (13) can be solved numerically to predict the conversions, number of active crosslinks and the moments of the polymers. The moments of the distribution allow the calculation of the instantaneous and accumulated nth average chain lengths of the primary molecules in the sol, which are defined by

$$X_n^{\cdot\prime} \equiv \mathrm{d}Q_n^{\cdot\prime}/\mathrm{d}Q_{n-1}^{\cdot\prime} \qquad (15a)$$

$$\bar{X}_n^{\cdot\prime} \equiv Q_n^{\cdot\prime}/Q_{n-1}^{\cdot\prime} \qquad (15b)$$

for $n = 1, 2, 3, \ldots$, respectively. On the basis of the distribution moments, some useful properties of network-forming systems may now be defined. The instantaneous crosslinking density of the sol polymer ρ', which is the fraction of branched structural units in the instantaneously formed sol polymer, is given by

$$\rho' = \frac{\mathrm{d}[\mu']}{\mathrm{d}Q_1^{\cdot\prime}} \qquad (16)$$

and the instantaneous number of branched units per weight-average primary molecule in the sol ε' is given by

$$\varepsilon' = \rho' X_2^{\cdot\prime} \qquad (17)$$

The average crosslinking densities can be obtained from equations (16) and (17) as

$$\bar{\rho}' = \frac{2}{Q_1^{\cdot\prime}} \int_0^{Q_1^{\prime}} \rho' \, \mathrm{d}Q_1^{\cdot\prime} = 2\frac{[\mu']}{Q_1^{\cdot\prime}} \qquad (18)$$

$$\bar{\varepsilon}' = \frac{2}{Q_1^{\cdot\prime}} \int_0^{Q_1^{\prime}} \varepsilon' \, \mathrm{d}Q_1^{\cdot\prime} = \bar{\rho}' \bar{X}_2^{\cdot\prime} \qquad (19)$$

GEL POINT

Up to the gel point all molecules present in the MVM–DVM copolymerization are finite. Thus, by setting $\phi_s = 1$ the equations given above can easily be solved numerically to predict the properties of the primary molecules prior to gelation. Both kinetic and statistical theories predict that the crosslinking density of the primary molecules $\bar{\varepsilon}$ reaches unity at the gel point at which the second moment of the branched polymer distribution diverges[22,23]

$$\bar{\varepsilon} = 1 \qquad (20)$$

It must be pointed out that equation (20) assumes a random formation of crosslinks between the primary chains. In fact, gelation occurs earlier if there is a crosslink density distribution among the primary chains[10]. However, as shown by the Tobita–Hamielec model[24], the extent of inhomogeneous crosslinking is negligible prior to gelation so that equation (20) is a good approximation for the position of the gel point.

To predict the gel point, equations (1) to (6) and (10) to (14) can be solved numerically until the condition of equation (20) is achieved. However, analytical solutions can also be obtained under specified conditions. When $\bar{X}_2^{\cdot}$, $[\mathrm{R}*]$ and the reaction volume V_r are assumed to be constant until the gel point, the time required for the onset of gelation t_g and the critical vinyl group conversion at the gel point x_c can be calculated from the above equations as

$$t_g = \frac{ak_t}{k_{p2}k_{p3}[\mathrm{M}_2]_0} \qquad (21)$$

$$x_c = \frac{1}{r\rho_0 \bar{X}_2^{\cdot}} \qquad (22)$$

where $a = (2 + k_{tc}/k_t)^{-1}$, ρ_0 is the initial mole fraction of the vinyl groups in the monomer mixture contributed by the DVM and r is a factor representing the unequal reactivity of the vinyl groups, and is given by the equation

$$r = \frac{r_{32}}{[r_{12} + \rho_0(1 - r_{12})]^2} \qquad (23)$$

where r_{ij} is the reactivity ratio, i.e. $r_{ij} = k_{pi}/\mathrm{k}_{pj}$. Note that the vinyl group conversion x is related to the vinyl group concentration through the equation $x = 1 - \sum_{i=1}^{3}[\mathrm{M}_i]/\sum_{i=1}^{2}[\mathrm{M}_i]_0$, where the subscript 0 refers the quantities to their initial values at the beginning of the reaction.

For equal vinyl group reactivity ($r = 1$), equation (22) reduces to the Stockmayer criterion for gelation[5]. In order to check the applicability of equation (22) to actual systems, the predicted gel points using equation (22) were compared with the predictions of the numerical results. Illustrative calculations of the critical vinyl group conversion for $\rho_0 = 0.01$ are show in *Figure 2* as a function of the reactivity ratio r_{ij}. The initial $\bar{X}_2^{\cdot}$ is 5×10^2 in *Figure 2a* and 5×10^3 in *Figure 2b*. The solid curves were calculated using equation (22). ($\bar{X}_2^{\cdot}$, $[\mathrm{R}*]$ and the reaction volume V_r are independent of conversion.) The dashed and dotted curves were obtained by numerical solution of equations (1) to (6) and (10) to (14) for the initial vinyl group concentrations $[\mathrm{M}]_0 = 4.7$ and 8.5 M, respectively. The calculation conditions are indicated in the legend to *Figure 2*.

It can be seen that when the pre-gelation period is short (with respect to conversion), equation (22) agrees with the numerical solution satisfactorily, independent of r_{ij}. As x_c increases, deviations appear between the results of the two calculations, and they become more pronounced for short primary chains. Significant deviations only occur for late-gelling systems and equation (22) predicts no gelation for $x_c > 0.8$–0.9. Another interesting feature shown from *Figure 2a* is that equation (22) predicts lower or higher gel points depending on the initial vinyl group concentration.

To explain the observed deviations, it should be borne in mind that a decrease in the primary chain length with conversion because of monomer depletion (drift) delays the gel point, whereas volume contraction during polymerization promotes gelation. Furthermore, initiator depletion which may cause 'dead-end' polymerization will increase the primary chain length and also promotes gelation.

In *Figure 3* the drift in the primary chain length and the volume contraction at the point of gelation are plotted against the critical conversion for the same system as in *Figure 2*. It is clear that only in the limit $x_c \rightarrow 0$, the

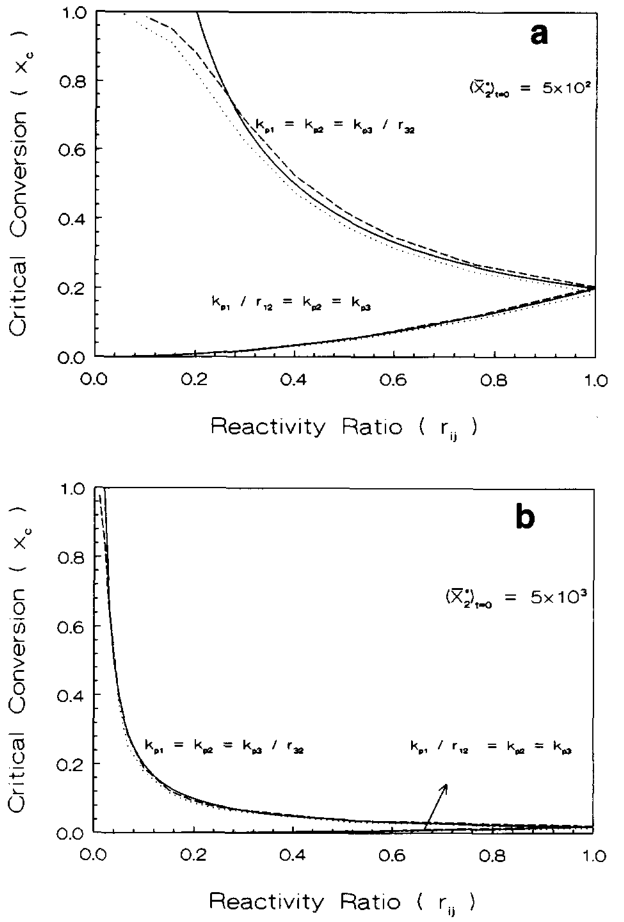

Figure 2 Variation in the critical conversion x_c with the reactivity ratio r_{ij} for $\rho_0=0.01$. The initial $\bar{X}_2^{\cdot}$ are 5×10^2 (a) and 5×10^3 (b). The solid curves were calculated using equation (22). The dashed and dotted curves were obtained by numerical solution of equations (1) to (6) and (10) to (14) for initial vinyl group concentrations of 4.7 and 8.5 M, respectively. Calculation conditions: $f=0.5$, $k_d=10^{-5}\,s^{-1}$, $k_{tc}=10^7\,l\,mol^{-1}\,s^{-1}$, $k_{td}=0$, $[I]_0=0.08$ M, $d_1=d_2=0.91\,g\,ml^{-1}$, $d_p=1.08\,g\,ml^{-1}$, $MW_1=104\,g\,mol^{-1}$, $MW_2=130\,g\,mol^{-1}$

assumptions used in the derivation of equation (22) true, thus the two calculation methods are equivalent. As the critical conversion increases both drift and volume change increase, leading to the observed deviations in *Figure 2*. However, these deviations are small over a large part of the pre-gelation period owing to the opposite effects of drift and volume contraction on the location of the gel point which compensate for one another. *Figure 3a* shows that an increase in the initial $\bar{X}_2^{\cdot}$ increases drift; but since long chains give early gelation, equation (22) provides a better agreement with the numerical solution for long primary chains. At low initial monomer concentrations, since the extent of volume contraction during polymerization is small (*Figure 3b*), the drift dominates the direction of the deviation so that equation (22) predicts an early gelation owing to the neglected drift. However, at high monomer concentrations equation (22) overestimates x_c as it neglects the volume contraction during polymerization, which more than compensates the effect of drift (*Figure 3b*). For late-gelling systems $\bar{X}_2^{\cdot}$ increases again, as shown in *Figure 3*, owing to initiator depletion, causing significant deviations between the calculated results. Thus, one may conclude that equation (22) is generally applicable to systems in which little drift has occurred.

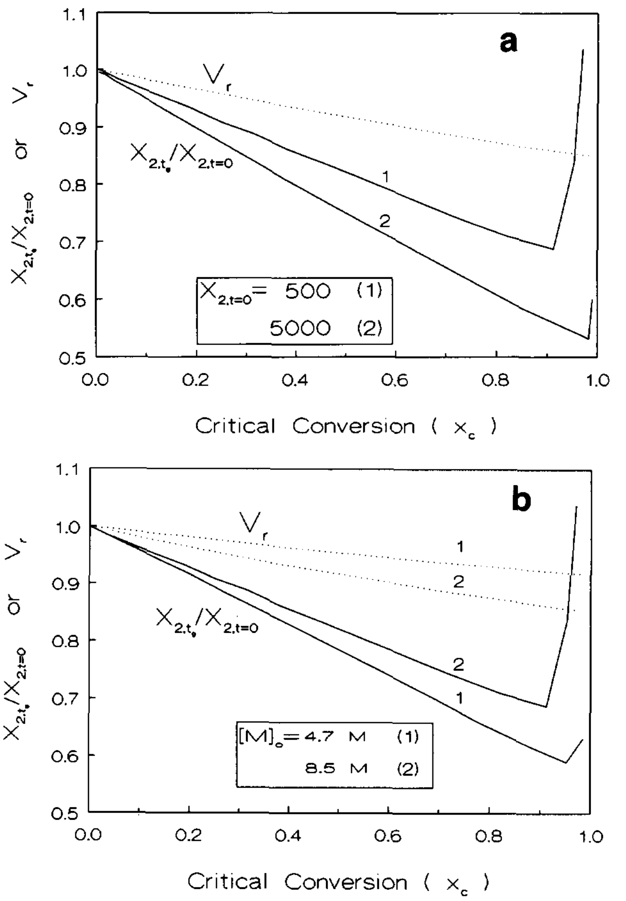

Figure 3 Variations in the relative weight-average primary chain length (solid curves) and the relative reaction volume (dotted curves) at the point of gelation with the critical conversion: (a) effect of the initial $\bar{X}_2^{\cdot}$ at $[M]_0=8.5$ M; (b) effect of the initial vinyl group concentration for an initial $\bar{X}_2^{\cdot}$ of 5×10^2. See legend to *Figure 2* for calculation conditions

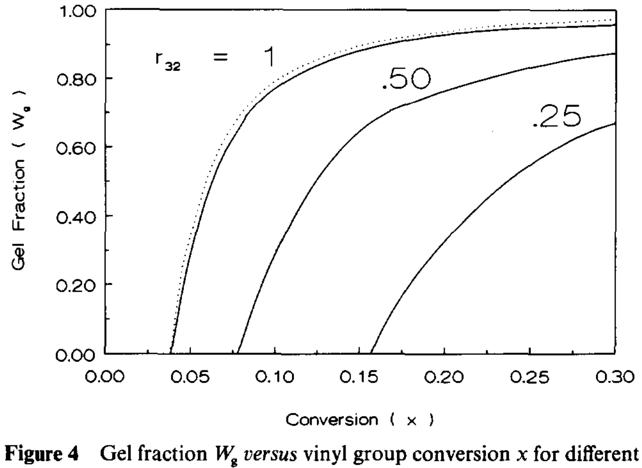

Figure 4 Gel fraction W_g *versus* vinyl group conversion x for different pendent vinyl group reactivities ($\rho_0=0.05$, $[M]_0=4.9$ M). The initial $\bar{X}_2^{\cdot}$ was 5×10^2. See legend to *Figure 2* for calculation conditions. The dotted curve was calculated using Flory's statistical theory

WEIGHT FRACTION OF SOL

The weight fraction of sol W_s, defined by $W_s \equiv Q_1^{\cdot\prime}/Q_1^{\cdot}$, can be calculated from equation (11) as

$$W_s=\phi_s^2\left[1-\frac{k_{tc}}{k_t}(1-\phi_s)\right] \qquad (24)$$

In order to evaluate W_s, one needs to know, according to equations (12) and (24), the concentration of pendent vinyl groups on the gel $[M_3'']$. According to the kinetic model, $1-\phi_s$ is the fraction of radicals captured by the gel molecules in an infinitesimal period of time, whereas ϕ_s is the fraction of radicals remaining in the sol phase to give sol polymers. These sol polymers exhibit, depending on their 'birth times', different compositions and chain lengths, and are exposed to attack by radicals over a long period of time. Thus, they will pass to the gel phase subsequent to their formation and this delay depends on the birth time of the sol polymers as well as on their microenvironment between the birth time and the present.

Let t_{cr} be the critical time for the sol–gel transition of the primary chains born at t_i, and $\rho'_{cr(t_i)}$ be their crosslinking density at t_{cr}, then the residual concentration of pendent vinyl groups bound to these chains $[M_3']_{(t_i,t_{cr})}$ is given by

$$r_{M'_{3(t_i,t_{cr})}}=(k_{p2}[R*][M_2]\phi_s)_{t_i}-(\rho'_{cr(t_i)}-\rho'_{(t_i)})\left(\frac{dQ_1^{\cdot\prime}}{dt}\right)_{t_i} \quad (25a)$$

Since the second term is negligible in crosslinking polymerizations compared to the first term, equation (25a) can be simplified to

$$r_{M'_{3(t_i,t_{cr})}}\approx(k_{p2}[R*][M_2]\phi_s)_{t_i} \quad (25b)$$

These pendent vinyl groups are transferred to the gel phase; thus, they become gel pendent vinyls at time t_{cr}. Moreover, the pendent vinyl groups on the gel also appear by the reaction of the gel radicals with M_2 vinyls and they disappear owing to the attack of the radicals passing to the gel phase. If $[M''_{3,i}]$ represents the pendent vinyl groups on the gel formed instantaneously, its rate equation can be expressed as

$$r_{M''_{3,i}}=(1-\phi_s)(k_{p2}[M_2]-k_{p3}[M_3''])[R*] \quad (26)$$

Thus, the rate equation for the formation of gel pendent vinyls can be obtained from equations (25b) and (26) as

$$r_{M_3''}=r_{M'_{3(t_i,t_{cr})|t_{cr}=t}}+r_{M''_{3,i}} \quad (27)$$

An exact solution of equation (27) is obviously not simple since it requires the relation between t_i and t_{cr}, which is presently unknown. In fact, for a given t_{cr}, t_i may not be constant and depends on the spatial distribution of the primary chains in the reaction system. However, if one assumes a short pre-gelation period, equation (27) becomes

$$\begin{aligned}r_{M_3''}=&(k_{p2}[R*][M_2])_{t_i=0}+(1-\phi_s)(k_{p2}[M_2]\\&-k_{p3}[M_3''])[R*]\end{aligned} \quad (28a)$$

with the initial condition $[M_3''](t_g)=0$. Equation (28a) holds until time t^* at which all primary chains which were born prior to gelation have attached onto the gel ($t^*=2t_g$). Thereafter, since t_{cr} is close to t_i for chains born beyond gelation, equation (28a) modifies to

$$r_{M_3''}=\{k_{p2}[M_2]-(1-\phi_s)k_{p3}[M_3'']\}[R*] \quad (28b)$$

By application of equations (1) to (6), (10) to (14) and (28a) and (28b), it is possible to calculate the weight fraction of sol as a function of time or conversion. Illustrative calculations relating the gel fraction W_g to conversion x for different pendent vinyl group reactivities are shown in *Figure 4* as solid curves. The dotted curve was calculated using the statistical theory of Flory[23]. The reaction conditions are indicated in the legend to *Figure 4*.

It can be seen that both the position of the gel point and the growth rate of the gel are very sensitive to the reactivity of the pendent vinyls. For equal vinyl group reactivity, the prediction of the kinetic model is close to that of the statistical theory. Indeed, by introducing a random crosslinking assumption, Flory's sol fraction equation for an arbitrary primary chain length distribution can be obtained from the present model. Defining p as the probability that a radical propagates rather than terminates, i.e. $p=1/[1+(a\bar{X}_2^{\cdot})^{-1}]$, the sol weight fraction equation of the kinetic model (equation (24)) can be written as

$$\begin{aligned}W_s=&(k_{td}/k_t)(1-p)^2[1-p(1-\rho W_g)]^{-2}\\&+(k_{tc}/k_t)(1-p)^3[1-p(1-\rho W_g)]^{-3}\end{aligned} \quad (29)$$

Since $\int_1^\infty rx^{r-1}\,dr=(1-x)^{-2}$ and $\int_1^\infty r(r-1)x^{r-1}\,dr=2x(1-x)^{-3}$, equation (29) becomes in terms of the chain length r of the primary chains

$$\begin{aligned}W_s=\int_1^\infty&[(k_{td}/k_t)rp^{r-1}(1-p)^2(1-\rho W_g)^{-1}\\&+0.5(k_{tc}/k_t)r(r-1)p^{r-2}(1-p)^3(1-\rho W_g)^{-2}]\\&\times(1-\rho W_g)^r\,dr\end{aligned} \quad (30)$$

The term in square brackets is equal to the weight fraction of $r$mers in the reaction system w_r. Thus, equation (30) can also be expressed as

$$W_s=\int_1^\infty w_r(1-\rho W_g)^r\,dr \quad (31)$$

which is Flory's well-known sol fraction equation[23].

Equations for a specific primary chain length distribution can also be derived starting from the kinetic model as follows. Assuming a homogeneous distribution of pendent vinyls in the system, i.e. $[M_3'']=[M_3]W_g$, one obtains from equations (12) and (24)

$$W_s=\frac{1+\varepsilon W_g(3a-1)}{(1+a\varepsilon W_g)^3} \quad (32)$$

The above equation can be solved for Flory ($k_{tc}=0$) and Schulz–Flory ($k_{td}=0$) distributions to yield

$$W_s^{1/2}+W_s=\frac{2}{\varepsilon} \quad (33a)$$

$$W_s^{1/3}+W_s^{2/3}+W_s=\frac{3}{\varepsilon} \quad (33b)$$

which were derived previously using statistical methods.

It must be noted that the calculations presented in *Figure 4* are merely an illustration of the applicability of the kinetic model. In fact, termination reactions become strongly diffusion controlled beyond gelation owing to the steric hindrance of the network chains. As a result, k_t will decrease continuously as polymerization proceeds, which would lead to a much more abrupt increase in the gel fraction with conversion than that illustrated in *Figure 4*. In order to account for this effect, one may evaluate the functional dependence of k_t on conversion by fitting the experimental conversion data and then using this dependence in the model calculations.

CONCLUSIONS

The equal reactivity assumption present in the Stockmayer criterion of gelation was omitted and a general equation was derived for the position of the gel point in free radical crosslinking copolymerization. It was shown that for systems gelling early, this equation agrees with the numerical solution satisfactorily, independent of the reactivity ratio of the vinyl groups. However, when the pre-gelation period is sufficiently large, numerical methods have to be used in order to account for the monomer and initiator depletions as well as the volume contraction during the polymerization. Moreover, kinetic differential rate equations were derived for the nucleation and growth of the gel molecule. If the assumptions of equal vinyl group reactivity and random crosslinking are introduced, the equations thus developed reduce to those of the statistical theories.

It must be pointed out that, when applied to actual systems, these concepts have to be integrated into models accounting for the presence of other non-idealities like cyclization[16], diffusion-controlled termination and crosslinking reactions.

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