Macromolecules **1993,** *26,* 3131-3136

Modeling of Free-Radical Polymerization with Cross-Linking: Monoradical Assumption and Stationary-State Hypothesis

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Received January 11, 1993; Revised Manuscript Received March 8, 1993

ABSTRACT: The validity of the monoradical assumption and the stationary-state hypothesis in modeling of free-radical polymerization with branching and/or cross-linking was evaluated using the method of moments. The polymerization system involved the reactions of chain transfer to polymer and radical recombination. Therefore, the system was capable of gelation. The gelation behavior was controlled by the three groups of parameters: $K_{fp}M_0/K_tR$, K_{tc}/K_t, and K_p/K_t. It can be shown that polyradical chains accumulate only in the vicinity of the gel point and beyond. The presence of polyradical chains gives higher chain growth rates and thus promotes gelation. The monoradical assumption delays the gel point while the stationary-state hypothesis causes it to occur earlier. However, significant errors due to these assumptions were found only when the value of K_p/K_t was larger than 10^{-3}. Therefore, these assumptions should be considered valid for systems with $K_p/K_t < 10^{-3}$. The same conclusions are also applicable for free-radical copolymerizations involving divinyl monomers.

Introduction

Long-chain branching is often an important feature in free-radical polymerization even in the absence of divinyl monomers. It usually occurs via chain transfer to polymer and/or propagation with terminal double bonds. Its effect on certain polymer properties such as rheological properties is known to be quite significant even with a small number of branching points present (less than one per polymer molecule).[1] With certain monomer systems under appropriate conditions, the level of branching can be remarkably high and gelation is experienced, particularly when high monomer conversions are targeted. The best known examples are methyl acrylate and vinyl acetate. For methyl acrylate, cross-linked insoluble polymer networks were observed at very low monomer conversions.[2,3] For vinyl acetate, polymers with very high molecular weight form at high conversions.[4-7] Reactions of chain transfer to polymer combined with radical recombination have been long recognized to cause gelation.[8] In commercial practice, network polymers may not be desired for some applications, and chain-transfer agents are used to reduce molecular weights and delay or prevent gelation. However, network polymers are desired in other applications, and then most often free-radical copolymerization involving divinyl monomers is used. Those network polymers have found a wide range of applications as superabsorbents, size-exclusion chromatography column packing, dental materials, and controlled release systems. Numerous and extensive investigations have been carried out for various comonomer systems in the past half century.[9-15]

No matter whether branched and/or cross-linked polymers are desirable or not, in either case, it is essential to understand the polymerization process in order to have good control over polymer molecular properties. To this end, many models have been developed following the pioneering work of Flory[16] and Stockmayer.[17] Those by Gordon,[18] Macosko and Miller,[19,20] Pearson and Graessley,[21] and Durand and Bruneau,[22] to name just a few, are good examples. These models are statistical in nature and were often derived with stepwise polymerization in mind. They require the random formation of branching points on accumulated polymer and thus inherently treat gelation as a process in thermodynamic equilibrium. However, the processes involved in free-radical polymerization, as well as stepwise polymerization, are kinetically controlled. The development of polymer properties depends strongly on reaction path.[23-26] To overcome these shortcomings, the so-called kinetic approach provides an alternative. In this approach, one can write population balances on the polymer and radical species present and obtain expressions for instantaneous chain properties as functions of time or monomer conversion. The expressions are often differential equations. Accumulated properties are then found by integration. This approach has been widely used in calculating the effects of branching on molecular weight distributions using fundamental kinetic rate constants,[27-39] and more recently for divinyl copolymer systems.[40-43]

It is well-known that, in deriving these kinetic models, the following two assumptions are often employed: (1) monoradical assumption and (2) stationary-state hypothesis. The former means that no polymer chains have more than one radical center during the course of polymerization. The polymer chains contain either one radical center ("live" polymer) or no radical center at all ("dead" polymer). The latter means that, for individual polymer radical species, the rate of generation is approximately equal to that of consumption. The use of these two assumptions substantially simplifies the algebra in modeling. For linear polymer reaction systems (except for those initiated by multifunctional initiators), the monoradical assumption is exact since no polymer chain can possibly have more than one radical center. The stationary-state hypothesis was also justified for the linear systems without significant autoacceleration caused by diffusion-controlled radical termination.[44] However, the extension of these assumptions to systems with branching and/or cross-linking has received some criticism. Kuchanov and Pis'men[45] claimed that the monoradical assumption is "principally incorrect" and the stationary-state hypothesis is "generally inapplicable". Their argument was based on the fact that, in the vicinity of the gel point, the number of the polyradical chains (those containing more than one radical center) steadily increases although they do not exist at the start. Since a gel molecule has infinitely large molecular weight, intuitively it is likely to have many radical centers associated with it. Kuchanov and Pis'men[45] also developed

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Table I. Elementary Reactions and Their Rate Constants in Free-Radical Polymerization with Chain Transfer to Polymer

initiator decomposition	$\mathrm{I} \xrightarrow{K_d} 2\mathrm{R}_0$
initiation	$\mathrm{R}_0 + \mathrm{M} \xrightarrow{f, K_i} \mathrm{P}_{1,1}$
propagation	$\mathrm{P}_{r,m} + \mathrm{M} \xrightarrow{mK_p} \mathrm{P}_{r+1,m}$
termination by disproportionation	$\mathrm{P}_{r,m} + \mathrm{P}_{s,n} \xrightarrow{mnK_{td}} \mathrm{P}_{r,m-1} + \mathrm{P}_{s,n-1}$
termination by recombination	$\mathrm{P}_{r,m} + \mathrm{P}_{s,n} \xrightarrow{mnK_{tc}} \mathrm{P}_{r+s,m+n-2}$
chain transfer to polymer	$\mathrm{P}_{r,m} + \mathrm{P}_{s,n} \xrightarrow{msK_{fp}} \mathrm{P}_{r,m-1} + \mathrm{P}_{s,n+1}$

a kinetic model by removing these two assumptions, but made no calculations. It is clearly important to compare the models by examining the magnitude of the error introduced with assumptions. This paper has the objective to clarify whether it is justified to use the models derived using these assumptions.[27-43]

Model Development

We first consider a polymerization system consisting of initiation, propagation, chain transfer to polymer, and radical termination either by disproportionation or recombination. Chain transfer to polymer reactivates "dead" polymer chains to produce branched points and thus increases molecular weight. However, a gel molecule would not form unless a certain number of polymeric radicals were terminated by recombination.[8,32,33,39,41-43,45] The elementary reactions and their rate constants are listed in Table I, where $\mathrm{P}_{r,m}$ represents the molar concentration of polymer chains with r monomeric units ($r \geq 1$) and m radical centers ($m \geq 0$); M, I, and R_0 are the concentration of monomer, initiator, and primary radical, respectively. The population balance equation for $\mathrm{P}_{r,m}$ is

$$\frac{\mathrm{d}P_{r,m}}{\mathrm{d}t} = \underbrace{K_p M m P_{r-1,m}}_{[1]} - \underbrace{K_p M m P_{r,m}}_{[2]} + \underbrace{K_{td}(m+1)P_{r,m+1}\sum_{s=1}^{\infty}\sum_{n=1}^{\infty} nP_{s,n}}_{[3]} - \underbrace{K_{td} m P_{r,m}\sum_{s=1}^{\infty}\sum_{n=1}^{\infty} nP_{s,n}}_{[4]} + \underbrace{{}^1/_2 K_{tc}\sum_{s=1}^{r-1}\sum_{n=0}^{m}(\mathrm{n}+1)(\mathrm{m}+1-\mathrm{n})P_{s,n+1}P_{r-s,m+1-n}}_{[5]} - \underbrace{K_{tc} m P_{r,m}\sum_{s=1}^{\infty}\sum_{n=1}^{\infty} nP_{s,n}}_{[6]} + \underbrace{K_{fp}(m+1)P_{r,m+1}\sum_{s=1}^{\infty}\sum_{n=0}^{\infty} sP_{s,n}}_{[7]} - \underbrace{K_{fp} m P_{r,m}\sum_{s=1}^{\infty}\sum_{n=0}^{\infty} sP_{s,n}}_{[8]} + \underbrace{K_{fp} r P_{r,m-1}\sum_{s=1}^{\infty}\sum_{n=1}^{\infty} nP_{s,n}}_{[9]} - \underbrace{K_{fp} r P_{r,m}\sum_{s=1}^{\infty}\sum_{n=1}^{\infty} nP_{s,n}}_{[10]} \qquad (1)$$

where t is the polymerization time.

It can be seen in eq 1 that the polymer species $\mathrm{P}_{r,m}$ are formed and consumed by all the reactions listed in Table I, except for initiation. The formation rates are [1] by propagation (note: $\mathrm{P}_{1,1}$ formed by initiation), [3] by disproportionation termination, [5] by recombination termination, and [7] and [9] by chain transfer to polymer. The consumption rates are [2] by propagation, [4] by disproportionation termination, [6] by recombination termination, and [8] and [10] by chain transfer to polymer. To comprehend eq 1, the following points should be kept in mind: (1) The concentration of radicals associated with $\mathrm{P}_{r,m}$ is $mP_{r,m}$. (2) The factor $^1/_2$ in the term of formation by recombination termination accounts for the fact that the summation term twice counts the termination events due to the symmetry of $(n+1)(m+1-n)P_{s,n+1}P_{r-s,m+1-n}$. (3) There are two ways for $\mathrm{P}_{r,m}$ to be consumed by chain transfer: the m radicals can abstract atoms from other chains, and the atoms on r monomeric units can be abstracted from its chains. The reaction rate is proportional to $mP_{r,m}$ for the former and to $rP_{r,m}$ for the latter, provided the abstraction is a random process. It should be noted that each monomeric unit is assumed to have one site for chain transfer to polymer and that only a small fraction of the monomeric units undergo the transfer reaction.

In principle, eq 1 can be solved numerically for $P_{r,m}$. However, in practice, this is formidable if not impossible because of the huge value of r. One can therefore resort to the use of the method of moments[28,29] for average chain properties. Let us define the moments $Y_{i,j}$ as

$$Y_{i,j} = \sum_{m=0}^{\infty}\sum_{r=1}^{\infty} r^i m^j P_{r,m} \qquad (2)$$

Accordingly, the number- and weight-average chain lengths are

$$\bar{r}_N = Y_{1,0}/Y_{0,0} \qquad (3)$$

$$\bar{r}_W = Y_{2,0}/Y_{1,0} \qquad (4)$$

The total polymeric radical concentration is $R = Y_{0,1}$, and the total concentration of monomeric units in polymer chains is $M_0x = Y_{1,0}$, where M_0 and x are the initial monomer concentration and the monomer conversion (it assumes no change in reaction mixture volume). After a lengthy but straightforward algebra, the following moment equations can be obtained:

$$\frac{\mathrm{d}M_0x}{\mathrm{d}t} = K_p MR \qquad (5)$$

$$\frac{\mathrm{d}R}{\mathrm{d}t} = R_I - K_t R^2 \qquad (6)$$

$$\frac{\mathrm{d}Y_{0,0}}{\mathrm{d}t} = R_I - {}^1/_2 K_{tc} R^2 \qquad (7)$$

$$\frac{\mathrm{d}Y_{2,0}}{\mathrm{d}t} = (2K_p M + K_{tc} Y_{1,1}) Y_{1,1} \qquad (8)$$

$$\frac{\mathrm{d}Y_{1,1}}{\mathrm{d}t} = (K_p M + K_{tc} Y_{1,1}) Y_{0,2} + K_{fp} R Y_{2,0} - [(K_t + K_{tc})R + K_{fp} M_0 x] Y_{1,1} \qquad (9)$$

$$\frac{\mathrm{d}Y_{0,2}}{\mathrm{d}t} = R_I + (K_t + K_{tc})R^2 + K_{tc} Y_{0,2}{}^2 + 2K_{fp} R (Y_{1,1} + M_0 x) - 2[(K_t + K_{tc})R + K_{fp} M_0 x] Y_{0,2} \qquad (10)$$

where R_I ($=2fK_dI$) is the initiation rate. The reaction of chain transfer to polymer does not appear in eq 5–7. Therefore, it has no effect on the number-average chain length, $\bar{r}_N$, as expected on the basis of the fact that the reaction of chain transfer to polymer does not change the total number of polymer chains.

Eqs 5–10 are basically equivalent to those by Kuchanov and Pis'men,[45] except for the fact that their model is derived for the special case where the monomer concentration remains constant. For convenience in discussion, let us express these equations using conversion, x, as an independent variable with the help of eq 5.

$$\frac{d\nu}{dx} = \zeta - (\tau + \beta) \qquad (6a)$$

$$\frac{dy_{0,0}}{dx} = \zeta - {}^{1}/_{2}\beta \qquad (7a)$$

$$\frac{dy_{2,0}}{dx} = (2 + \beta y_{1,1})y_{1,1} \qquad (8a)$$

$$\frac{d\nu y_{1,1}}{dx} = (1 + \beta y_{1,1})y_{0,2} + C_{fp}y_{2,0} - (\tau + 2\beta + C_{fp}x)y_{1,1} \qquad (9a)$$

$$\frac{d\nu y_{0,2}}{dx} = \zeta + \tau + 2\beta + \beta y_{0,2}^{\;2} + 2C_{fp}(\nu y_{1,1} + x) - 2(\tau + 2\beta + C_{fp}x)y_{0,2} \qquad (10a)$$

where $\nu = R/M_0$, $y_{0,0} = Y_{0,0}/M_0$, $y_{2,0} = Y_{2,0}/M_0$, $y_{1,1} = Y_{1,1}/R$, $y_{0,2} = Y_{0,2}/R$, $\zeta = R_I/K_pRM$, $\tau = K_{td}R/K_pM$, $\beta = K_{tc}R/K_pM$, and $C_{fp} = K_{fp}M_0/K_pM$.

In this work, the above equations were solved numerically using an initial-value ordinary differential equation solver LSODE based on the Gear method for stiff equations and the Adams method for nonstiff ones. The initial conditions are $Y_{i,j} = 0$ at $x = 0$.

Results and Discussion

Radical Distribution. Let us first define a distribution index in the following manner:

$$\sum_{m=0}^{\infty}\sum_{r=1}^{\infty} m^2 P_{r,m} \Big/ \sum_{m=0}^{\infty}\sum_{r=1}^{\infty} m P_{r,m} = y_{0,2} \qquad (11)$$

This index reflects the radical distribution. It equals unity when all polymeric radicals are monoradicals.

It is clear in eqs 6a–10a that, to have a full simulation, we need to specify six kinetic and reaction parameters. They are K_p, K_{fp}, K_{td}, K_{tc}, M_0, and R_I. However, a more careful examination reveals that the solution of these ordinary differential equations mainly depends on three parameter groups, particularly when gelation is being considered. They are $K_{fp}M_0/K_tR$, K_{tc}/K_t, and K_p/K_t. In our calculations, these parameter groups are assumed to be constant during the course of polymerization.

Figure 1A shows the calculated weight-average chain length, $\bar{r}_W/\bar{r}_{W,0}$, as a function of monomer conversion. It is well-known that weight-average chain length as well as other average chain lengths of higher order (z, $z + 1$, etc.) diverges when the reaction system approaches the gel point. Figure 1B shows the corresponding profiles of radical distribution index, $y_{0,2}$. It can be seen that the development of radical distribution coincides with that of weight-average chain length. The index is approximately unity for most monomer conversions. Deviation occurs near the gel point, indicating the growth in polyradical chain concentration. The polyradical chains have huge molecular weights and accumulate very rapidly. It is fair to say that gel formation is specifically linked to the presence of polyradical chains, and the gel molecule most have a large number of radical centers on it. We have found in our calculations that as long as the value of K_p/K_t is reasonably low (≤ 0.01), for the same set of $K_{fp}M_0/K_tR$ and K_{tc}/K_t the profiles of radical distribution index are virtually the same, i.e., the polyradical chains develop just before the gel point and the increase in the index is always very sharp. Slightly before the gel point, the polymer radicals are believed to be mostly monoradical. Significant numbers of polyradical chains at low conversions were found only for very large values of K_p/K_t (≥ 1). These values are unrealistic because, in typical free-radical polymerization,[46] K_p/K_t is in the range of 10^{-8}–10^{-3}.

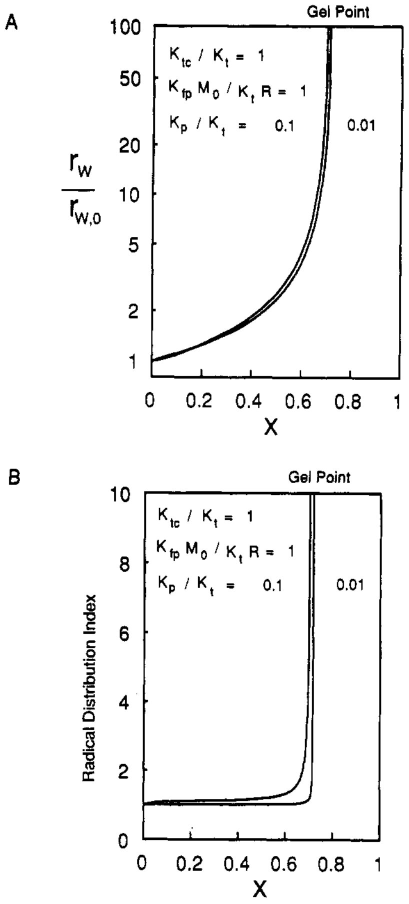

Figure 1. (A) Weight-average chain length, $\bar{r}_W/\bar{r}_{W,0}$, versus monomer conversion, x. The weight-average chain length approaches infinity at the gel point. (B) Radical distribution index, η, versus monomer conversion, x. The polyradical chains are rapidly accumulated in the vicinity of the gel point. The parameters are $K_{fp}M_0/K_tR = 1/K_{tc}/K_t = 1$, and $K_p/K_t = 0.1, 0.01$.

Effect of Polyradicals on Gelation. It has been shown that polyradical chains do exist, particularly when the reaction system approaches the gel point. Now, let us consider their effect on the development of polymer properties. Polyradicals are associated with large polymer molecules. Intuitively, they will enhance the growth of these molecules and therefore accelerate gelation. The question to be addressed is to what extent has the gelation process been accelerated. In this section, we use the monomer conversion at the gel point, X_{gel}, as an indicator. The comparisons are made for predicted results with/without the monoradical assumption.

Polyradical chains are formed via the reaction of chain transfer to polymer radicals, which is presented by $C_{fp}\nu y_{1,1}$ in eq 10a. When the monoradical assumption is introduced, this term is removed. Eqs 10a and 6a then become equivalent, i.e., $y_{0,2} = 1$. Substitution of $y_{0,2} = 1$ into eq 9a gives

$$\frac{d\nu y_{1,1}}{dx} = 1 + C_{fp}y_{2,0} - (\tau + \beta + C_{fp}x)y_{1,1} \qquad (9b)$$

Figure 2 shows the gel point, X_{gel}, as a function of K_p/K_t for various K_{tc}/K_t and $K_{fp}M_0/K_tR$. The solid lines are the polyradical results predicted by eqs 6a–10a, while the dashed lines are the corresponding monoradical results by eqs 6a–8a and 9b. The following conclusions can be drawn from these gelation diagrams: (1) Both polyradical and monoradical models predict gelation for the same set

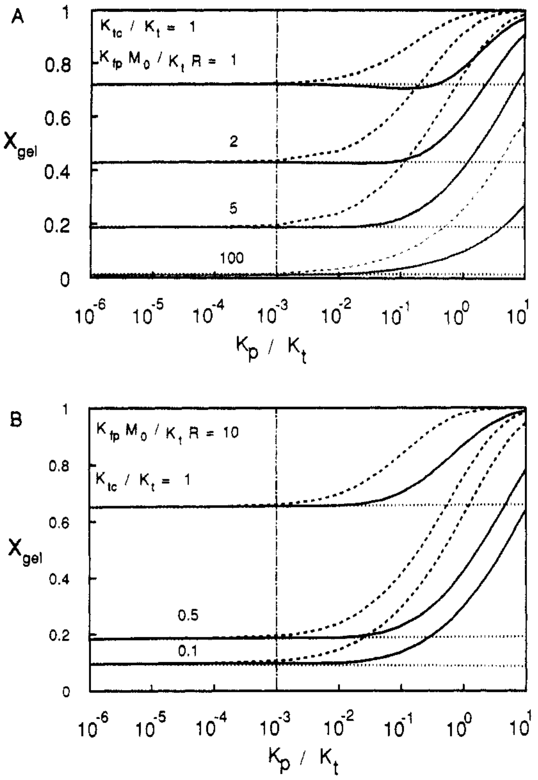

Figure 2. Prediction of the gel point, x_{gel}, as a function of the kinetic parameter groups. The solid lines are the prediction of the polyradical model, eqs 6a–10a. The dashed lines are the monoradical model, eqs 6a–8a and 9b. The dotted lines are the model employing the monoradical assumption and the stationary-state hypothesis, eq 12. Their differences are negligible when $K_p/K_t < 10^{-3}$. The parameters are as follows: (A) $K_{tc}/K_t = 1$ and $K_{fp}M_0/K_tR = 1, 2, 5, 100$; (B) $K_{fp}M_0/K_tR = 10$ and $K_{tc}/K_t = 1, 0.5, 0.1$.

of parameters. This indicates that gelation is not exclusively caused by polyradical chains. Even when polyradical chains are absent, the system is still capable of gelation. Later, we will learn that the reaction mainly responsible for gelation is radical termination by recombination. (2) The errors introduced by the monoradical assumption are negligible when $K_p/K_t < 10^{-3}$. The two lines are practically identical. Significant deviation can only be noticed when $K_p/K_t > 10^{-3}$. In this range, the monoradical assumption delays the prediction of gel point. We have used various values of K_{tc}/K_t (0–1) and $K_{fp}M_0/K_tR$ (10^{-3}–10^{3}) in our calculations and found no violation. Since the typical value of K_p/K_t in free-radical polymerization is in the range of 10^{-8}–10^{-3}, the use of the monoradical assumption is therefore justified.

Stationary-State Hypothesis. We now examine the validity of the stationary-state hypothesis. In order to separately evaluate the effect of the stationary-state hypothesis and that of polyradicals, the following comparisons are made to the monoradical cases.

The use of the stationary-state hypothesis in eq 6 results in the total radical concentration being given by $R = (R_I/K_t)^{1/2}$. In a typical free-radical polymerization, this approximation does not introduce significant errors. The reason for this is that the time period required for the total radical concentration to reach its stationary-state value is negligible (in subseconds). This is true no matter whether branching and/or cross-linking are involved, because chain-transfer reactions neither generate nor consume radicals. Actually, little difference in our calculations has been found between using or not using this approximation. In this paper, we focus on radical moments of higher order or equivalently individual radical species.

Application of the stationary-state hypothesis in eq 9b and substitution of $y_{1,1}$ obtained from eq 9b into eq 8a gives

$$\frac{\mathrm{d}x\bar{r}_W}{\mathrm{d}x} = \left(2 + \beta\frac{1 + C_{fp}x\bar{r}_W}{\tau + \beta + C_{fp}x}\right)\frac{1 + C_{fp}x\bar{r}_W}{\tau + \beta + C_{fp}x} \qquad (12)$$

Equation 12 is clearly controlled by $K_{fp}M_0/K_tR$ and K_{tc}/K_t, but not K_p/K_t, as shown by the straight dotted lines in Figure 2. In contrast to the monoradical assumption, the stationary-state hypothesis expedites the prediction of gel point. The model using both monoradical assumption and stationary-state hypothesis is therefore more accurate than using monoradical assumption alone, due to their opposite effects. Now, the significant errors can be found only when $K_p/K_t > 10^{-2}$.

Criteria for Gelation. Gelation in this system is caused by corporation of chain transfer to polymer or radical recombination. The former constructs branched chains. The latter ties the branched chains together and thus substantially increases molecular weights. Chain transfer to polymer alone or *vice versa* would never gel the system. It is of interest to know precisely what combination of the two reactions is required. Under the limiting condition of $X_{gel} \ll 1$, the following analytical solution for the weight-average chain length can be obtained.

$$\bar{r}_W = \frac{2\tau + 3\beta + C_{fp}x}{(\tau + \beta)^2 - \beta C_{fp}x} \qquad (13)$$

At gel point,

$$\frac{\beta}{\tau + \beta}\left(\frac{C_{fp}x}{\tau + \beta}\right) = \frac{K_{tc}}{K_t}\left(\frac{K_{fp}RM_0x}{K_tRR}\right) = 1 \qquad (14)$$

It is clear that both chain transfer to polymer and radical recombination are essential. The interpretation of eq 14 is that in order to have gelation occur, the rate of chain transfer to polymer, $K_{fp}RM_0x$, should be at least K_t/K_{tc} times the radical termination rate, K_tRR. For the case where termination is exclusively by recombination ($K_t/K_{tc} = 1$), statistically, a polymeric radical should experience more than one chain transfer before it terminates. Participation of disproportionation termination will increase this statistical average and make gelation more difficult. For example, two chain transfers are required if 50% of the polymeric radicals are terminated by disproportionation, and ten chain transfers are required for 90%.

The condition $X_{gel} \ll 1$ is virtually the same as that of constant monomer concentration. The polymerization process is instantaneous. Equation 14 is identical to that by Kuchanov and Pis'men.[45] However, in reality, gelation often occurs at high conversions. The process is accumulative and depends on reaction path. One must therefore resort to numerical solution of Eqs 6a–10a for more realistic cases. Figure 3 presents a diagram of gel point, X_{gel}, as a function of the parameters $K_{fp}M_0/K_tR$ and K_{tc}/K_t. The solid lines are obtained with $K_p/K_t < 10^{-3}$. It can be seen that eq 14 gives adequate predictions (the dashed lines) only if gelation occurs at low conversion (say, less than 20% conversion). At high conversions, discrepancies are large.

This type of gelation diagram can be useful. It provides a guide for control of molecular weight and network development. The area below the curves is the pregel region, and that above the curves is the postgel region. For example, if a system polymerizes at a certain temperature and gives the following rate constants and reaction conditions: $K_p = 10^4$, $K_t = 10^7$ ($K_{tc}/K_t = 0.2$), $K_{fp} = 1$ (L/mol s), $M_0 = 10$, $R = 10^{-7}$ (mol/L), then the polym-

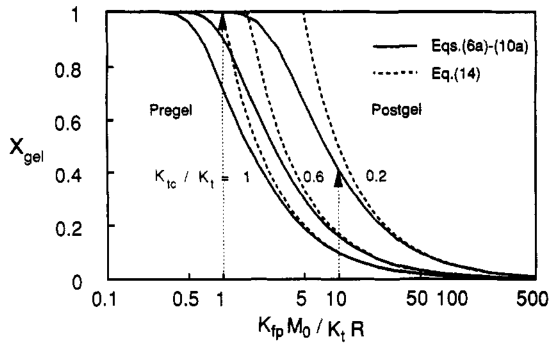

Figure 3. Gelation diagram for the polymerization system involving the reactions of chain transfer to polymer and radical recombination. The solid lines are predicted by the polyradical model, eqs 6a–10a, with $K_p/K_t < 10^{-3}$. The dashed lines are predicted by eq 14, which employs the stationary-state hypothesis, the monoradical assumption, and the constant monomer concentration.

Table II. Elementary Reactions and Their Rate Constants in Free-Radical Copolymerization Involving Divinyl Monomers

initiator decomposition	$1 \xrightarrow{K_d} 2R_0$
initiation	$R_0 + M \xrightarrow{f, K_i} P_{1,1}$
propagation with comonomers	$P_{r,m} + M \xrightarrow{mK_p} P_{r+1,m}$
termination by disproportionation	$P_{r,m} + P_{s,n} \xrightarrow{mnK_{td}} P_{r,m-1} + P_{s,n-1}$
termination by recombination	$P_{r,m} + P_{s,n} \xrightarrow{mnK_{tc}} P_{r+s,m+n-2}$
propagation with pendant double bond	$P_{r,m} + P_{s,n} \xrightarrow{msK_p^*} P_{r+s,m+n}$

erization path follows the dotted line at $K_{fp}M_0/K_tR = 10$. The gel point is expected at $X = 0.4$. Let us suppose that gelation is undesirable in this system, and at the same time a high conversion is needed. We can either reduce polymer radical size by increasing initiator concentration or by using a more dilute monomer solution. If the value of $K_{fp}M_0/K_tR$ is reduced to unity, no gel would be expected to form at all. The principle is also applicable for the reverse situation.

Copolymerization of Vinyl/Divinyl Monomers. Now, consider free-radical polymerization involving divinyl comonomers. The kinetic scheme is listed in Table II. Using the same derivation procedure as before, one can obtain the following set of differential equations.

$$\frac{d\nu}{dx} = \zeta - (\tau + \beta) \tag{15}$$

$$\frac{dy_{0,0}}{dx} = \zeta - {}^1/_2\beta - C_p{}^*x \tag{16}$$

$$\frac{dy_{2,0}}{dx} = 2(1 + C_p{}^*y_{2,0})y_{1,1} + \beta y_{1,1}{}^2 \tag{17}$$

$$\frac{d\nu y_{1,1}}{dx} = (1 + \beta y_{1,1} + C_p{}^*y_{2,0})y_{0,2} + C_p{}^*\nu y_{1,1}{}^2 - (\tau + 2\beta)y_{1,1} \tag{18}$$

$$\frac{d\nu y_{0,2}}{dx} = \zeta + \tau + 2\beta + \beta y_{0,2}^2 + 2C_p{}^*\nu y_{0,2}y_{1,1} - 2(\tau + 2\beta)y_{0,2} \tag{19}$$

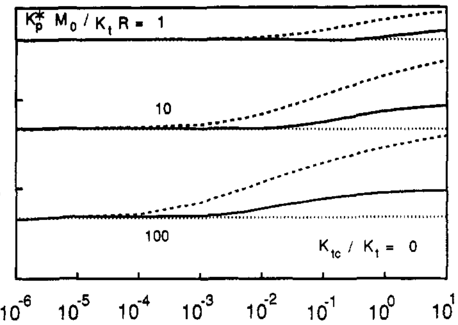

Figure 4. Prediction of the gel point, x_{gel}, as a function of the kinetic parameter groups for the copolymerization of vinyl/divinyl monomers. The solid lines are predicted by the polyradical model. The dashed lines employ the monoradical assumption. The dotted lines employ the monoradical assumption and the stationary-state hypothesis. The parameters are $K_{tc}/K_t = 0$ and $K_{fp}M_0/K_tR = 1, 10, 100$.

It should be pointed out that, in a divinyl copolymer system, there are at least three types of double bonds (vinyl, divinyl, and pendant) and three types of corresponding radicals. Once various reactions of cyclization are involved, this number inevitably goes higher.[41–43,47] The kinetic parameters listed in Table II, K_p, K_{td}, K_{tc}, and $K_p{}^*$, are actually pseudo-kinetic rate constants,[48–50] which are functions of radical fractions, $\phi_i{}^*$, and compositions of monomers, f_j, and polymers, $\bar{F}_2$ (subscripts "2" and "3" denoting divinyl monomer and pendant double bond, respectively).

$$\begin{aligned} K_p &= \sum_i \sum_j K_{pij}\phi_i{}^*f_j \\ \mathrm{K}_t &= \sum_i \sum_j K_{tij}\phi_i{}^*\phi_j{}^* \\ K_p{}^* &= \sum_i K_{pi3}\phi_i{}^*(\bar{\mathrm{F}}_2 - \bar{\rho}) \end{aligned} \tag{20}$$

where $\bar{\rho}$ is the total density of cross-linking and various cyclizations which consume pendant double bonds. However, in our calculation, K_p, K_{td}, K_{tc}, and $K_p{}^*$ are assumed to be constant to avoid complication.

An examination of eqs 15–19 reveals that the role played by K_{fp} in the gelation via chain transfer to polymer is now played by $K_p{}^*$. The gelation behavior is controlled by $K_p{}^*M_0/K_tR$, K_{tc}/K_t, and K_p/K_t. Figure 4 shows the gel point, X_{gel}, as a function of K_p/K_t for $K_p{}^*M_0/K_tR = 1, 10$, and 100, by solving the above equations. Compared with Figure 2, gel points appear earlier for same set of parameters. This is because the copolymerization produces tetrafunctional branched points while the chain transfer produces trifunctional points. In addition, the absolute value of $K_p{}^*$ is likely to be higher than that of K_{fp}.

Equations 15–19 are a polyradical model. When the monoradical assumption in introduced, the propagations with pendant double bonds on radical polymers are not allowed. $C_p{}^*\nu y_{1,1}{}^2$ in eq 18 and $2C_p{}^*\nu y_{0,2}y_{1,1}$ in eq 19 should be absent. Equations 19 and 15 then become equivalent, i.e., $y_{0,2} = 1$. The solutions of the monoradical model are presented in Figure 4 by dashed lines. The significant deviations from those polyradical results are found when $K_p/K_t > 10^{-4}$. The monoradical model predicts later gelation. However, if the stationary-state hypothesis is superimposed on eq 18, the range of K_p/K_t expands to 10^{-3}, as shown by the dotted lines.

Cyclization. A final point worth mentioning is that the recognition of the presence of polyradicals will accommodate modeling of intramolecular cyclization, particularly in the system with chain transfer to polymer. When a polymer chain contains more than one radical center, these radical centers stay very close and are likely to be terminated with each other. If the termination is by recombination, chain cycles will be formed. Cyclization as well as other intramolecular reactions are an important feature in free-radical polymerization. They are crucial in chain microstructure development. However, its formulation remains unsolved. On the basis of a mean-field picture where the radicals are assumed to be distributed randomly over reaction mass, the number of these cycles is negligible. The correct formulation relies on non-mean-field approaches. It should be pointed out that, in a monoradical model, this type of cyclization is excluded.

Conclusion

The following conclusions are made on the basis of the above model investigations using the method of moments:

(1) The polymerization systems involving the reactions of chain transfer to polymer and radical recombination are capable of gelation. The gelation behavior is controlled by the following three parameter groups: $K_{fp}M_0/K_tR$, K_{tc}/K_t, and K_p/K_t.

(2) The presence of the polyradical chains is an important feature in free-radical polymerization with branching. These chains are mostly accumulated at the vicinity of the gel point. They promote gelation.

(3) The use of the monoradical assumption delays the prediction of the gel point. However, the significant differences between using or not using this assumption are found only when K_p/K_t is larger than 10^{-3}. Therefore, the monoradical assumption should be considered valid for the systems of $K_p/K_t < 10^{-3}$.

(4) The stationary-state hypothesis expedites the prediction of gel point. When it is simultaneously employed with the monoradical assumption, the gel point is a function of $K_{fp}M_0/K_tR$ and K_{tc}/K_t only. The differences between using or not using these assumptions are negligible when K_p/K_t is smaller than 10^{-2}. For the systems of $K_p/K_t > 10^{-2}$, the model predicts earlier gel points.

(5) The same criteria are applicable for the validity of the stationary-state hypothesis and the monoradical assumption in the modeling of the free-radical copolymerization of vinyl/divinyl monomers. These assumptions are justified for $K_p/K_t < 10^{-3}$.

Acknowledgment. This work was supported by the Mechanical and Chemi-mechanical Wood-pulps Network of the Canadian Federal Network of Centres of Excellence Program, the Canadian Natural Sciences and Engineering Research Council, and the Ontario Centre for Materials Research. S.Z. cordially thanks Professor R. H. Pelton, McMaster University, for helpful discussions and encouragement.

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