

A kinetic model is presented for the post-gelation period of free-radical crosslinking copolymerization. The model takes into account the trapped radical centers in the gel forming system. It was shown that the weight fraction of sol,  $W_s$ , relates to the number of crosslinked units per weight-average primary molecule,  $\varepsilon$ , through the equation  $W_s = \frac{(n-\varepsilon)^{n-1}}{\varepsilon(n+\varepsilon)^{n-2}}$  where  $n = 2$  for Flory's most probable molecular weight distribution, and  $n = 3$  for primary molecules formed by radical combination. Calculation

results demonstrate that the existence of trapped radicals significantly affects the growth rate of the gel molecule. It increases the total radical concentration and accelerates the gel growth. The difference in the predictions with and without considering the trapped radicals becomes significant as the crosslinker concentration decreases or, as the vinyl group reactivity on the crosslinker or on the polymer decreases.

## Gel growth in free radical crosslinking copolymerization: Effect of inactive gel radicals

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(Received: April 12, 1999; revised: May 26, 1999)

### Introduction

The prediction of the gel growth in free-radical crosslinking copolymerization (FCC) is one of the major problems in the production of crosslinked materials. This is mainly due to the lack of understanding of diffusion controlled reactions<sup>1</sup>. However, neglecting these nonidealities, the growth of a gel molecule in a crosslinking system can easily be treated within the context of the statistical theories. The partition of polymer units between sol and gel in an ideal gelling system was given about half a century ago by Flory as<sup>2</sup>:

$$W_s = \sum_{r=1}^{\infty} w_r [1 - \rho(1 - W_s)]^r \quad (1)$$

where  $W_s$  is the weight fraction of sol,  $w_r$  is the weight fraction of primary molecules composed of  $r$  units, and  $\rho$  is the crosslink density. Eq. (1) suggests that in a random crosslinking process, the gel fraction  $W_g (= 1 - W_s)$  depends on the overall crosslink density of the reaction system and on the molecular weight distribution of primary molecules. (Primary molecules are the molecules which would result if all crosslinks in the reaction system were cut.) For a certain molecular weight distribution, Eq. (1) simplifies to<sup>3</sup>:

$$\sum_{i=1}^n W_s^{i/n} = \frac{n}{\varepsilon} \quad (2)$$

$(n = 2 \text{ and } 3)$

where  $\varepsilon$  is the number of crosslinked units per weight-average primary molecule,  $n = 2$  for Flory's most probable molecular weight distribution, i.e., if the primary molecules in FCC form exclusively by chain transfer to small molecules or by termination via disproportionation reactions, and  $n = 3$  for primary molecules formed by radical combination. Eq. (2) also known as Charlesby-Pinner equation is still widely used in the characterization of gel forming systems.

One of the unrealistic assumptions used in the derivation of Eq. (2) is the random formation of crosslinks between the polymer molecules. In order to remove this assumption, Tobita and Hamielec developed a crosslink density distribution (CDD) model, which predicts the crosslink densities of primary molecules depending on their birth conversions<sup>4</sup>. The CDD model shows that the crosslink densities of primary molecules largely deviate from the overall crosslink density of the system due to the different reactivities of monomeric and polymeric (pendant) vinyl groups as well as due to the cyclization and multiple crosslinking reactions<sup>4-6</sup>. These authors and, later on, Zhu and Hamielec combined the CDD model with gelation models to incorporate the effect of CDD on the growth rate of the gel molecules<sup>7,8</sup>. Calculation results show, however, only a slight difference in the predictions with and without consideration of the CDD of polymers.

Another unrealistic assumption involved in the derivation of Eq. (2) is the random termination of radicals throughout the gel formation process. In other words, the

radical centers locating on sol molecules and on the gel are assumed to have the same reactivities for termination. However, in free-radical polymerization, termination rates of radicals are known to be diffusion controlled during the course of the reaction. In crosslinking polymerization, termination reactions are even more hindered after radicals become attached onto the gel molecule<sup>9</sup>. Indeed, radicals with lifetimes of several months have been detected in FCC<sup>10,11</sup>) and the lifetimes were found to depend on the crosslink density of the gel<sup>12</sup>). In such systems, it is easy to imagine that the macroradicals on the gel are immobile (trapped) in the time scale of the kinetic events. Under these conditions, termination can occur only by diffusion of the radical chain ends toward each other as a result of their propagational growth (“propagation diffusion” or “reaction diffusion” mechanism<sup>13–15</sup>). Recent experimental works demonstrate the importance of the propagation diffusion mechanism in the termination of gel radicals in highly crosslinked systems<sup>16,17</sup>).

The effect of the diffusion controlled termination reactions on the growth rate of the gel in FCC systems has not been examined. However, for polymer modifications with crosslinking, Zhu recently developed a model, which takes into account the diffusion controlled termination reactions<sup>18</sup>). His calculation results indicate significant acceleration of the growth rate of the gel compared to the results predicted by the random termination models<sup>18</sup>). However, this model cannot be applied to the FCC system because the derived moment equations are not closed (i.e., the moment of the polymer distribution depends on the next higher moment), so that the resulting equations cannot be solved.

Here, we present a gel growth model for FCC which takes into account the nonrandom termination of radicals in crosslinking systems. The model assumes that the termination reaction of radical centers bound to the growing gel molecule with each other occurs by propagation diffusion mechanism. A gel growth equation was derived using the method of moments. The calculation results were compared with the prediction of the classical theory (Eq. (2)) as well as with the experimental data taken from the literature.

## Theory

The reaction system in FCC beyond the gel point is occupied totally by a gel molecule (we assume no phase separation in the system) containing the monomers and the sol polymers (Fig. 1). In our notation, symbols with a prime and with a double prime denote the species locating on the sol molecules and on the gel, respectively, whereas those without any prime refer to overall species. Three types of vinyl groups exist in FCC of vinyl/divinyl monomers, namely those on monovinyl monomer ( $M_1$ ), on divinyl monomer ( $M_2$ ), and on polymer chains (i.e., pendant vinyls

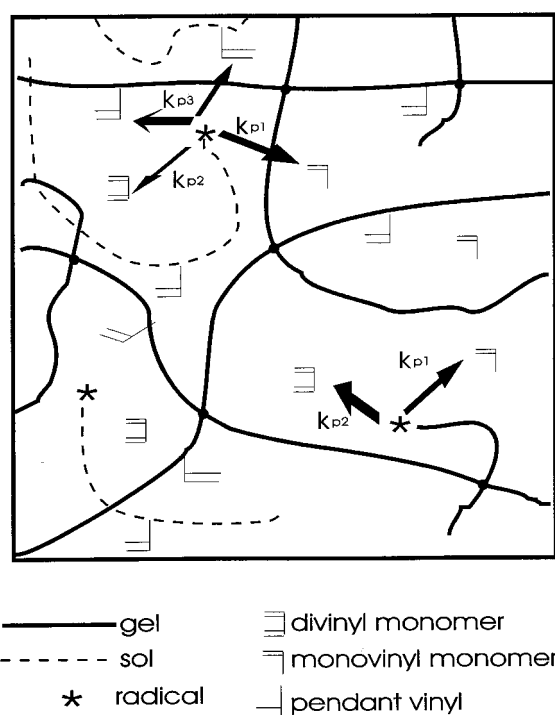


Fig. 1. Scheme of propagation and crosslinking reactions in FCC of vinyl/divinyl monomers beyond the gel point.  $k_{pi}$  ( $i = 1, 2,$  and  $3$ ) is the instantaneous propagation rate constant defined in ref.<sup>3,20</sup>

$M_3$ ). The radical centers are categorized as being either on sol molecules or on the gel molecule. Since the molecular weight distribution of sol molecules is infinite at the gel point and is very wide beyond the gel point, radical centers in the sol locate on molecules of various sizes. Those on small molecules are comparatively mobile whereas those on big molecules, as the gel radicals, are immobile so that they can only move by propagation diffusion.

Radical centers are generated in the sol phase by the initiation reaction with a rate  $r_i$ . Radical centers thus formed on the sol molecules ( $R'$ ) can attack the vinyl groups with the instantaneous rate constant<sup>3</sup>  $k_{pi}$  where  $i$  denotes the type of the vinyl group ( $i = 1, 2,$  and  $3$ ). If the sol radicals react with the pendant vinyl groups on the gel ( $M_3''$ ), they are transferred to the gel and become gel radicals. Radical centers formed on gel ( $R''$ ) can also attack the vinyl groups  $M_1$  and  $M_2$ , but they cannot attack the pendant vinyl groups  $M_3$  due to steric reasons (Fig. 1). Thus, the rate equations for the concentrations of the vinyl groups  $M_i$  are:

$$\frac{d[M_1]}{dt} = -k_{p1}[M_1][R] \quad (3a)$$

$$\frac{d[M_2]}{dt} = -2k_{p2}[M_2][R] \quad (3b)$$

$$\frac{d[M_3]}{dt} = k_{p2}[M_2][R] - k_{p3}[M_3][R'] \quad (3c)$$

where  $t$  is the reaction time. The rate equation for the fractional monomer conversion  $x$  follows from Eqs. (3) as:

$$\frac{dx}{dt} = [M]_0^{-1}(k_{p1}[M_1] + k_{p2}[M_2])[R] \quad (4)$$

where  $[M]_0$  is the initial monomer concentration. Eqs. (3) can be used to calculate the vinyl group conversions as a function of the reaction time  $t$  in FCC. However, it is preferable to use the monomer conversion  $x$  as an independent variable instead of time  $t$ . Dividing Eqs. (3) by Eq. (4) one obtains the rate equations for the vinyl groups with  $x$  as the independent variable, which are independent of the radical concentration. Note that, as defined in ref.<sup>3</sup>, the instantaneous propagation rate constant  $k_{pi}$  is not a constant but is changing with time or monomer conversion, depending on the type of the radical end. Here, for the sake of simplicity, the instantaneous propagation rate constants are assumed to be independent of conversion.

### Radical concentration

The gel radicals can terminate with each other by propagation diffusion with rate constant  $k_{tgg}$ . The sol radicals can terminate with each other or with gel radicals. Let us consider the termination reaction of a sol radical on a “small” molecule with sol radicals on “large” molecules or with gel radicals. Small molecules are defined as those below a critical crosslink density and a critical molecular weight; we assume that all of these small molecules have the same self diffusion coefficient. Since the radical centers on large sol and infinite large gel molecules are immobile on the time scale of the motion of the small sol radical, the termination rate constant only depends on the diffusion coefficient of the small sol radical. This means that the small sol/gel termination rate constant is equal to the termination rate constant between small and large sol radicals. On the other hand, the termination rate constant between two small sol radicals depends on the mutual diffusion coefficient of both molecules so that it is utmost twice that of small sol/gel and small sol/large sol molecules. However, since the number fraction of small sol radicals is small, it is reasonable to consider a single termination rate constant for the reactions between sol/sol and sol/gel radicals. Here, we define  $k_t$  as the termination rate constant between sol/sol and sol/gel radicals, which is the sum of the termination rate constants by coupling and by disproportionation,  $k_{tc}$  and  $k_{td}$ , respectively ( $k_t = k_{tc} + k_{td}$ ). This termination model thus assumes that the termination rate in the sol is dominated by small/large sol termination events and is similar to the short/long termination model of polymer radicals in linear free-radical polymerization<sup>19</sup>. In ref.<sup>19</sup>, the macroradicals in linear polymerization are categorized as being either short or long radicals, whereas the short radicals are oligomeric in

length. Here, we extend this image to the sol and gel radicals of free-radical crosslinking copolymerization. Moreover, in ref.<sup>19</sup>, the termination rate constant is dependent on the chain length of short radicals; here, we assign a single rate constant for termination between sol-sol and sol-gel radicals.

Let  $\phi_s$  be the fraction of radical centers in the sol between the time interval  $t$  and  $t + dt$ , and  $\beta$  be the fraction of radicals that terminate in the sol and become sol polymer. Using the rate theory,  $\beta$  can be given as:

$$\begin{aligned} \beta &= \frac{k_t \phi_s^2}{k_t \phi_s^2 + 2k_t \phi_s (1 - \phi_s) + k_{tgg} (1 - \phi_s)^2} \\ &= \frac{\phi_s^2}{1 - (1 - \phi_s)^2 (1 - k_{tgg}/k_t)} \end{aligned} \quad (5)$$

The factor 2 in Eq. (5) takes into account symmetrical sol-gel and gel-sol terminations. Eq. (5) and the following equations will be solved for two limiting cases:

1)  $k_{tgg} = k_t$ , i.e., the radicals in FCC terminate in a random manner. In this case, Eq. (5) becomes

$$\beta = \phi_s^2 \quad (5a)$$

2) The radicals on the gel molecule are trapped, i.e., the termination rate constant by propagation diffusion is much smaller than  $k_t$  ( $k_{tgg} \ll k_t$ ). In this case Eq. (5) reduces to:

$$\beta = \phi_s / (2 - \phi_s) \quad (5b)$$

The radicals in the reaction system are generated by the initiation reaction and they are consumed by termination reactions between sol/sol, sol/gel, and gel/gel radicals so that the rate equation for the radicals (sol + gel) can be written as:

$$\frac{d[R]}{dt} = r_i - k_t [R]^2 \phi_s^2 / \beta \quad (6)$$

Introducing the steady-state approximation into Eq. (6) yields:

$$[R] = [R]_0 \left( \frac{\beta}{\phi_s^2} \right)^{1/2} \quad (7)$$

where  $[R]_0 = (r_i/k_t)^{1/2}$ . Eq. (7) together with Eq. (5) give the total radical concentration as:

$$[R] = \frac{[R]_0}{[1 - (1 - \phi_s)^2 (1 - k_{tgg}/k_t)]^{1/2}} \quad (8)$$

indicating that the radical concentration in the reaction system increases with decreasing  $\phi_s$  due to the simultaneous increase of the number of radicals trapped in the gel  $(1 - \phi_s)$ .

For case 1 (random termination,  $\beta = \phi_s^2$ ), Eq. (7) reduces to

$$[R] = [R]_0 \quad (8a)$$

i.e., for a constant initiation rate  $r_i$ , the radical concentration in the reaction system remains constant.

For case 2 ( $k_{tgg} \ll k_t$ ), Eq. (7) is given by:

$$[R] = \frac{[R]_0}{[\phi_s(2 - \phi_s)]^{1/2}} \quad (8b)$$

### Moment equations

The calculation of the distribution of polymer units between the sol and the gel requires the concentration of macroradicals and polymers in the reaction system. Considering the kinetic events shown in Fig. 1, one may write the following differential equations for the concentration of sol polymer radicals ( $[R'_r]$ ) and sol polymer molecules of degree of polymerization  $r$  ( $[P'_r]$ ):

$$\begin{aligned} \frac{d[R'_r]}{dt} = & a_r r_i + \sum_{i=1}^2 k_{pi}[M_i] \{ (1 - a_r)[R'_{r-1}] - [R'_r] \} \\ & + (1 - a_r)k_{p3} \sum_{j=1}^{r-2} [M'_{3,j}][R'_{r-j-1}] - k_{p3}[M'_3][R'_r] \\ & - (k_{p3}[M''_3] + k_t[R])[R'_r] \end{aligned} \quad (9a)$$

$$\begin{aligned} \frac{d[P'_r]}{dt} = & k_{td}[R'_r][R] \\ & + 0.5k_{tc} \sum_{s=1}^{r-1} (1 - a_r)[R'_s][R'_{r-s}] - k_{p3}[M'_{3,r}][R'_r] \end{aligned} \quad (9b)$$

( $r = 1, 2, 3, \dots$ ,  $a_r = 0$  for  $r > 1$  and  $a_1 = 1$ )

where  $M'_{3,r}$  denotes the pendant vinyl groups belonging to sol molecules composed of  $r$  units so that the total concentration of pendant vinyls in the sol is given by  $[M'_3] = \sum_{r=1}^{\infty} [M'_{3,r}]$ .

Defining the  $n$ th moment of the radical and the polymer distributions in the sol as  $Y'_n = \sum_{r=1}^{\infty} r^n [R'_r]$  and  $Q'_n = \sum_{r=1}^{\infty} r^n [P'_r]$ , respectively ( $n = 0, 1, 2, \dots$ ), Eqs. (9) yield the following moment equations:

$$\begin{aligned} \frac{dY'_n}{dt} = & r_i + (1 - a_n) \left\{ \sum_{i=1}^2 k_{pi}[M_i] \sum_{v=0}^{n-1} \binom{n}{v} Y'_v + k_{p3}[M'_3] \right. \\ & \left. \sum_{v=0}^{n-1} \binom{n}{v} Y'_v Q'_{(n-v)\gamma+1} / Q'_1 \right\} - (k_{p3}[M''_3] + k_t[R]) Y'_n \end{aligned} \quad (10a)$$

$$\begin{aligned} \frac{dQ'_n}{dt} = & k_{td} Y_0 Y'_n + 0.5k_{tc} \sum_{v=0}^n \binom{n}{v} Y'_v Y'_{n-v} \\ & - \gamma k_{p3}[M'_3] Y'_0 Q'_{n+1} / Q'_1 \end{aligned} \quad (10b)$$

where  $a_n = 0$  for  $n > 0$  and  $a_0 = 1$ . For  $\gamma = 1$ , Eqs. (10) and the following equations describe the moments of the branched molecules. For  $\gamma = 0$ , they reduce to the moment equations of the primary molecules due to the fact that the degree of polymerization of primary molecules increases only by one unit by crosslinking reactions in the sol. Introducing the steady-state approximation into Eq. (10a) ( $dY'_n/dt \cong 0$ ), since  $Y'_n \gg Y'_{n-1}$  in FCC, the following equations were obtained for the first and second moments of polymers:

$$\frac{dQ'_1}{dt} = a\beta \sum_{i=1}^2 k_{pi}[M_i][R] - k_{p3}[M'_3][R] \frac{Q'_{1+\gamma}}{Q'_1} (\gamma\phi_s - a\beta) \quad (11a)$$

$$\begin{aligned} \frac{dQ'_2}{dt} = & 2Y_1'^2 (k_{td}/\phi_s + 1.5k_{tc}) - \gamma k_{p3}[M'_3][R] \frac{Q'_2}{Q'_1} \\ & (1 - \beta a/\phi_s) \end{aligned} \quad (11b)$$

where

$$Y'_1 = \beta \left( \frac{\sum_{i=1}^2 k_{pi}[M_i]}{k_t} + \frac{k_{p3}[M'_3]}{k_t} \left( 1 + \gamma \frac{Q'_2}{Q'_1} \right) \right) \quad (12)$$

$$\phi_s = \beta \left( 1 + \frac{k_{p3}[M''_3]}{k_t[R]} \right) \quad (13)$$

$$a = 1 - \frac{k_{tc}}{k_t} (1 - \phi_s) \quad (14)$$

About the above equations we here note the following:

1) For the sake of clarity, the equations ignore volume contraction during the polymerization, cyclization, and multiple crosslinking reactions. Although these features of FCC can also be accounted for<sup>3,20,21</sup>, our purpose here is to highlight the effect of the diffusion controlled termination reactions on the gel growth process.

2) The equations given above also ignore the chain transfer reactions. Chain transfer to small molecules in free-radical crosslinking copolymerization may generate oligomeric radicals from the immobile radical centers locating on the gel molecule or on the large sol molecules. Thus, these reactions will make the gel growth model complicated. It is known that the chain transfer to small molecules is, like propagation, not generally diffusion controlled until very high monomer conversions. As a result, at high monomer conversions at which the termination reactions slow down, the chain transfer may become an important kinetic event<sup>1</sup>. Thus, the existence of chain transfer reactions or increasing relative importance of chain transfer with respect to termination at high

monomer conversions may invalidate the predictions of the present model.

3) The moment equations assume the existence of one or zero radical center on each polymer molecule (monoradical assumption). Monoradical assumption neglects the reaction of a radical center with the pendant vinyl groups on other macroradicals. The monoradical models thus count the number of units on a polyradical with  $n$  radical centers  $n$  times. For example, the number of units on macroradicals  $Y'_1$ , which should be much smaller than  $Q'_1$ , goes to infinity at the gel point (Eq. (12)), which is clearly incorrect. However, it has been found that the errors introduced by the simultaneous use of the monoradical assumption and the steady-state assumption are minor in the modelling of the free-radical crosslinking copolymerization<sup>22</sup>.

4) The equations assume homogeneous distribution of pendant vinyl groups among the polymer chains. The validity of this assumption was confirmed previously in FCC systems<sup>5</sup>.

5) Introducing  $[M'_3] = 0$  and  $\beta = \phi_s = 1$  into the above equations, they predict the molecular weight distribution of polymers prior to gelation and they are identical to the moment equations derived by Tobita and Hamielec<sup>4</sup>. Furthermore, for  $\beta = \phi_s^2$ , i.e., for random termination of polymer radicals, these equations are identical to those derived previously by the author<sup>20</sup> as well as by Zhu and Hamielec<sup>9</sup>.

Dividing Eqs. (11) by Eq. (4), one obtains the moment equations with  $x$  as the independent variable, which are independent of the radical concentration. Since in the pregelation period gel fraction is zero ( $\alpha = \beta = \phi_s = 1$ ), these equations can easily be solved for the moments of the polymer distribution prior to gelation. At the gel point, the second moment of the polymer distribution  $Q'_2$  goes to infinity. Beyond the gel point both sol and gel coexist so that the second terms of Eqs. (11) are nonzero; thus, since every moment depends on the next higher moment, the equations are not closed for the postgelation period. This hinders solution of Eqs. (11) in the postgelation period of FCC. However, an examination reveals that Eqs. (11) are soluble for the primary molecules, i.e., for  $\gamma = 0$ . For instance, Eq. (11a) can be written for the primary molecules as follows:

$$\frac{dQ'_1}{dt} = \alpha\beta \left( \sum_{i=1}^2 k_{pi}[M_i][R] + k_{p3}[M'_3][R] \right) \quad (15)$$

Since  $Q'_1$  represents the number of units in the sol, its value should be the same both in the primary molecules and in the branched molecules. As already indicated, Eq. (15) assumes that the radical centers on the gel molecule cannot react with pendant vinyls on sol molecules. This assumption is critically important to reduce Eq. (11a) into Eq. (15), i.e., to make Eq. (11a) solvable.

## Fraction of radicals and polymers in the sol

The weight fraction of sol  $W_s$  which is the ratio of the number of units in the sol  $Q'_1$  to the overall number of units  $Q_1$  can be obtained from Eq. (15) as

$$W_s = \alpha\beta \quad (16)$$

For random termination ( $k_{igg} = k_t$ ), since  $\beta = \phi_s^2$ , the fraction of radicals in the sol can be calculated using Eq. (13) as:

$$\phi_s = \left( 1 + \frac{k_{p3}[M'_3]}{k_t[R]} \right)^{-1} \quad (17)$$

and substitution of Eqs. (5a), (14), and (17) into Eq. (16) leads to the gel fraction equation given by Flory's theory (Eq. (2)).

Another limit of interest is the case in which the termination rate constant by propagation diffusion  $k_{igg}$  is much smaller than  $k_t$ . Substitution of Eqs. (5b) into Eq. (13) yields the fraction of sol radicals as:

$$\phi_s = 1 - \frac{k_{p3}[M'_3]}{k_t[R]} \quad (18)$$

and Eqs. (5b), (16) and (18) give:

$$W_s = \frac{(n - \varepsilon)^{n-1}}{\varepsilon(n + \varepsilon)^{n-2}} \quad (19)$$

where  $n = 2$  and  $3$  for  $k_{ic} = 0$  and  $k_{id} = 0$ , respectively, and the crosslinking index  $\varepsilon$  is defined as:

$$\varepsilon = \left( 2 + \frac{k_{ic}}{k_t} \right) \frac{k_{p3}[M_3]}{k_t[R]} \quad (20)$$

Eq. (19) is the main theoretical result of the present work. Compared to the classical equation (Eq. (2)), it takes into account the trapped radical centers in the reaction system. Eq. (19) also takes into account the chain length drift of the primary molecules during polymerization. As the gel grows, the fraction of radicals in the sol  $\phi_s$  decreases (Eq. (18)). This results in an increase in the total radical concentration  $[R]$  due to the trapped radicals on the gel molecule (Eq. (8b)). As a consequence, the weight-average chain length of the primary molecules  $X_2$  given by<sup>3,20</sup>

$$X_2 = \left( 2 + \frac{k_{ic}}{k_t} \right) \frac{\sum_{i=1}^2 k_{pi}[M_i]}{k_t[R]} \quad (20a)$$

increases as the gel grows. Note that in Eq. (19) the variation of the primary chain length with conversion is included in the crosslinking index term  $\varepsilon$ , which is the product of the crosslink density  $\rho$  and the weight-average primary chain length  $X_2^{20}$ .

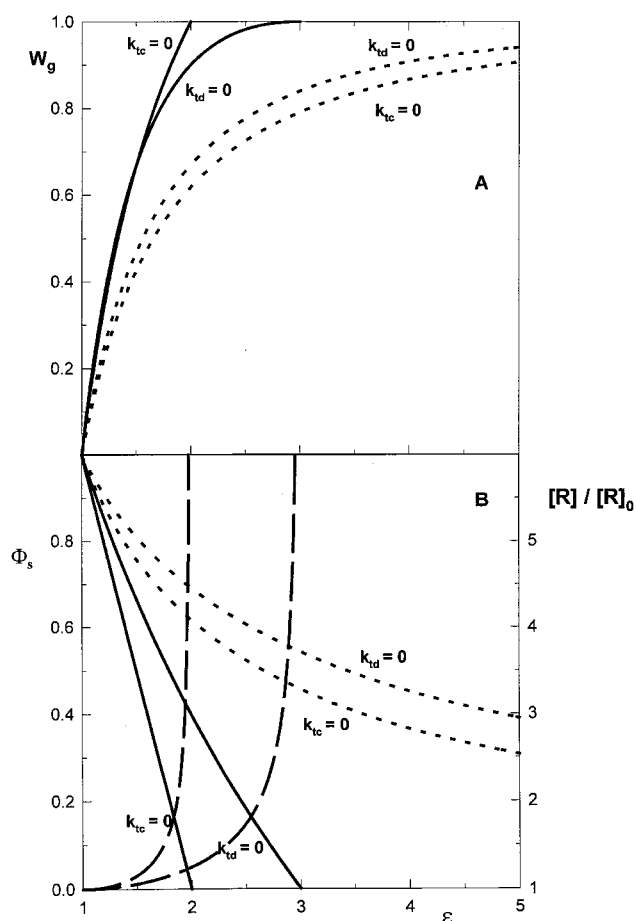


Fig. 2. (A) Weight fraction of gel  $W_g$  shown as a function of  $\varepsilon$  (the number of crosslinked units per weight-average primary molecule). The solid curves were calculated using Eq. (19), whereas the dotted curves are predicted by the statistical theory (Eq. (2)). (B) Variation of the fraction of radicals in the sol  $\phi_s$  and the radical concentration  $[R]/[R]_0$  with  $\varepsilon$ . The solid and dotted curves represent  $\phi_s$  versus  $\varepsilon$  dependencies predicted by the present model (Eq. (18)) and by the classical theory (Eq. (17)), respectively. The dashed curve represents the variation of the radical concentration with  $\varepsilon$ .

Fig. 2A compares the gel growth in FCC predicted using Flory's theory (Eq. (2), dotted curves) and using the present model (Eq. (19), solid curves) for two different modes of termination. Here,  $\varepsilon$  was taken as the independent variable. The weight fraction of gel  $W_g$  increases much more rapidly than that predicted by the classical theory. All the sol molecules attach to the gel, i.e., the gel fraction becomes unity at  $\varepsilon = 2$  ( $k_{tc} = 0$ ) or  $\varepsilon = 3$  ( $k_{td} = 0$ ). However, according to Flory's theory the gel fraction never becomes unity.

In Fig. 2B, the fraction of radicals in the sol  $\phi_s$  and the total radical concentration normalized with respect to the radical concentration at the gel point  $[R]/[R]_0$  are shown as a function of  $\varepsilon$ . The solid and dotted curves represent  $\phi_s$  versus  $\varepsilon$  dependencies predicted by the present model (Eq. (18)) and by the classical theory (Eq. (17)), respec-

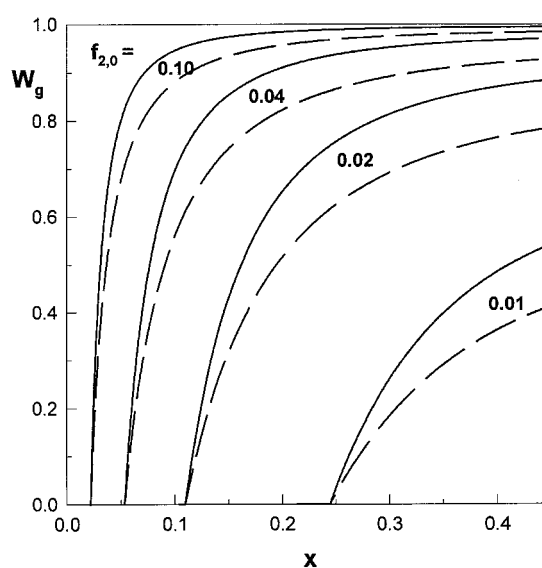


Fig. 3. Variation of the gel fraction  $W_g$  with the monomer conversion  $x$  in FCC of vinyl/divinyl monomers.  $r_{21} = 1$ ,  $r_{32} = 0.5$ . Calculations were for various concentrations of the divinyl monomer  $f_{2,0}$  indicated in the figure

tively. It is seen that our model predicts a much more rapid consumption of the radical centers in the sol. According to the classical theory, the radical concentration remains constant throughout the crosslinking process, i.e.,  $[R]/[R]_0 = 1$ . However, the present model predicts, as was repeatedly observed experimentally<sup>9)</sup>, an increase in the radical concentration during the reactions (dashed curves in Fig. 2B). This is due to the fact that the radicals captured by the gel become trapped and cannot terminate.

Solution of Eqs. (19) and (20) together with the rate equations (3)–(4) gives the variation of the gel fraction  $W_g$  with the monomer conversion  $x$  in FCC. The following kinetic parameters and concentrations were used for the calculations:

$$\begin{aligned} k_{p1} &= 10^2 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \\ k_{tc} &= 0 \\ k_{td} &= 10^7 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \\ k_{tgg} &= 0 \\ r_1 &= 10^{-6} \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \\ [M]_0 &= 8.0 \text{ mol/l} \end{aligned}$$

Parameters varied were: a) the mole fraction of the divinyl monomer in the initial monomer mixture  $f_{2,0}$ , b) the reactivity ratio of monomeric vinyl groups  $r_{21}$  ( $k_{p2}/k_{p1}$ ), and c) the reactivity ratio of pendant to monomeric vinyls  $r_{32}$  ( $k_{p3}/k_{p2}$ ). Calculation results for various values of  $f_{2,0}$ ,  $r_{21}$  and  $r_{32}$  are shown in Fig. 3–5, respectively, as solid curves. The classical results are illustrated by the dashed curves. It is seen that the difference in the model predictions with and without accounting for the trapped radicals becomes significant as the divinyl monomer concentration decreases (Fig. 3) or as the pendant or monomeric vinyl group reactivity decreases (Fig. 4 and Fig. 5).

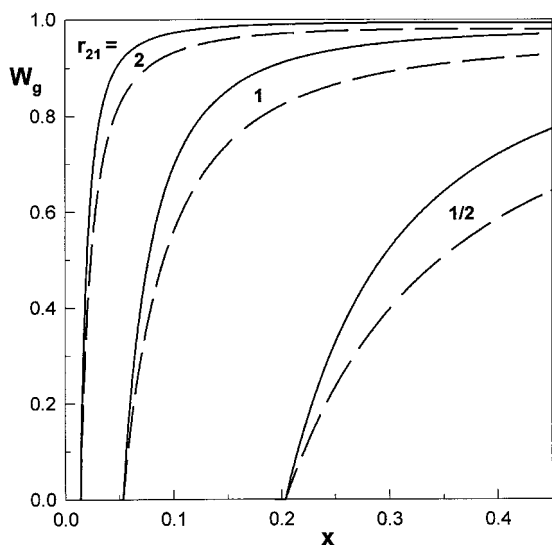


Fig. 4. Variation of the gel fraction  $W_g$  with the monomer conversion  $x$  in FCC of vinyl/divinyl monomers.  $r_{32} = 0.5$ ,  $f_{2,0} = 0.04$ . Calculations were for various values of  $r_{21}$  indicated in the figure

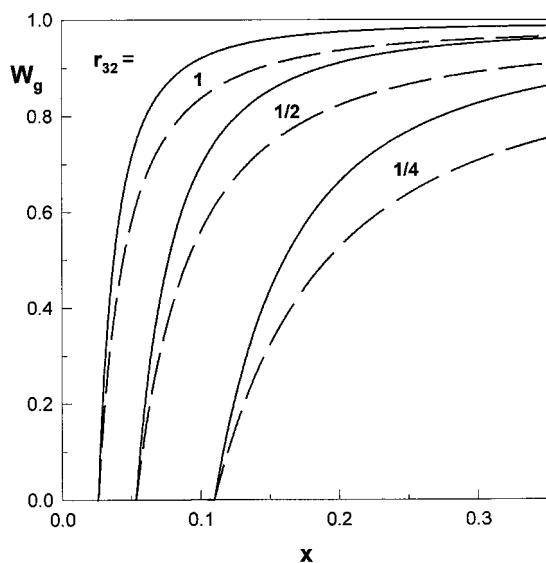


Fig. 5. Variation of the gel fraction  $W_g$  with the monomer conversion  $x$  in FCC of vinyl/divinyl monomers.  $r_{21} = 1$ ,  $f_{2,0} = 0.04$ . Calculations were for various values of  $r_{32}$  indicated in the figure

In Fig. 6, the predictions of Eqs. (2) and (19) are compared with the experimental data taken from the literature<sup>23</sup>. The experimental data points were for the crosslinking copolymerization of acrylamide (AAm) and 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS) with  $N,N'$ -methylenebis(acrylamide) (BAAm) as the crosslinker<sup>23</sup>. Both the crosslinker ratio (mole ratio of crosslinker to monomer) and the initial monomer concentration were fixed by the experiments at 1/82 and 0.700 mol/l, respectively, while the AMPS content in the monomer mixture was varied from 0 to 100 mol-%. Since the

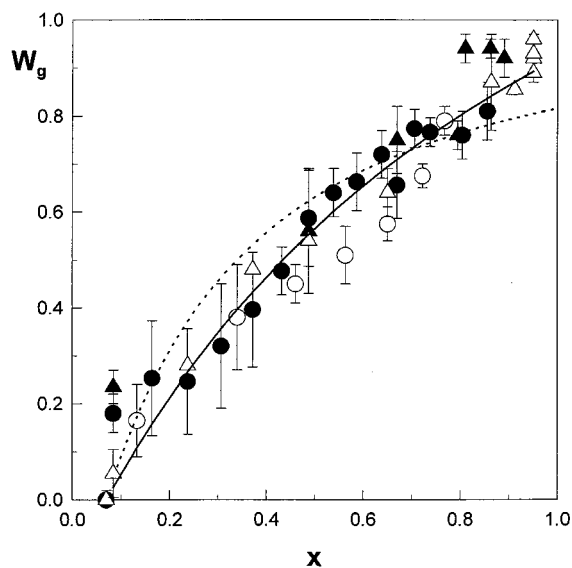


Fig. 6. Variation of the gel fraction  $W_g$  with the monomer conversion  $x$  in FCC of acrylamide (AAm) and 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS) with  $N,N'$ -methylenebis(acrylamide) (BAAm) as the crosslinker<sup>23</sup>. Both the crosslinker ratio (mole ratio of crosslinker to monomer) and the initial monomer concentration were fixed by the experiments at 1/82 and 0.700 mol/l, respectively, while the AMPS content in the monomer mixture varied from 0 to 100 mol-%. Experimental data are shown as symbols. AMPS = 0 (●), 40 (○), 60 (▲), and 100 mol-% (△). The solid and dotted curves are predicted by the present model and by the classical theory, respectively

kinetic parameters for this reaction system are unknown, we used another strategy to solve the gel fraction equations. One of the assumptions used in the derivations is the random formation of crosslinks between the polymer molecules. This assumption is equivalent to state that  $\varepsilon$  is a linear function of  $x$ , i.e.,

$$\varepsilon = 1 + a(x - x_c) \quad (21)$$

where  $x_c$  is the monomer conversion at the gel point and  $a$  is a constant. The critical conversion  $x_c$  was reported to be 0.07 in ref.<sup>23</sup> The best fitting curve of Eqs. (2) and (21) for  $n = 2$  to the experimental  $W_g$  versus  $x$  data data gives the dotted curve in Fig. 6 with  $a = 2.438$ . It is seen that the classical theory predicts a much steeper rise in the amount of gel than the observed results for  $x < 0.40$ . Then, in the region of higher monomer conversions, the gel fraction curve given by the statistical theory gradually bends downward apart from the observed tendency. Calculation results for  $n = 3$  also gave a similar curve.

Fitting Eqs. (19) and (21) for  $n = 2$  to the experimental data gives the solid curve in Fig. 6 with  $a = 0.916$ . Eq. (19) which neglects the termination reactions between gel radicals provides a much better agreement with the experimental data than the statistical theory.

## Conclusions

The existence of trapped radicals is an important feature of gel forming systems. Here, we derived a gel fraction equation (Eq. (19)) that takes into account the trapped radical centers in the reaction system. Calculation results demonstrate that the existence of trapped radicals significantly affects the growth rate of the gel molecule. It accelerates the gel growth and increases the total radical concentration. The difference in the predictions with and without considering trapped radicals becomes significant as the crosslinker concentration decreases or, as the reactivity of the vinyl groups on crosslinker or on polymer decreases.

*Acknowledgement:* Work was supported by the *Scientific and Technical Research Council of Turkey (TUBITAK)*, TBAG-1561 and by the *Istanbul Technical University Research Fund*, ITU-1054.

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