

## Gel properties in free radical crosslinking copolymerization: A kinetic approach

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### SUMMARY:

A kinetic model is presented for prediction of the gel properties in free-radical monovinyl-divinyl monomer copolymerization. It is an extension of the kinetic model proposed recently for the sol species. The model involves the moment equations of the primary chains in the gel, and predicts the gel growth and structure as a function of the reaction time. Formulae for the chain length averages of the primary chains in the sol and in the gel were derived. The equations for calculating the number- and weight-average primary chain lengths are identical to the equations derived by statistical methods.

### Introduction

Gelation in free-radical polymerizations has generally been treated within the context of the statistical theories<sup>1–6</sup>. Although these theories provide a full description of the reaction system, they all assume random reaction of functional groups (vinyl groups). However, the network formation in free-radical polymerization is a kinetically controlled process<sup>7</sup> and the statistical theories are thus not appropriate to deal with such polymerization systems.

Alternatively, kinetic gelation theories take into account all the kinetic features of polymerization and so may offer a more realistic approach to the microscopic phenomena during the reactions. Several kinetic models have been proposed to describe the process of gel formation in free-radical polymerizations<sup>8–14</sup>. 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<sup>15</sup>. Moreover, no kinetic theory is available until now that describes the interior structure of a gel, such as its average molecular properties.

Recently, a new kinetic model was proposed for the post-gelation period of free-radical monovinyl-divinyl monomer (MVM-DVM) copolymerization<sup>16</sup>. Using the steady-state approximation for the radical concentration in the sol phase, the model predicts important features of the post-gelation period such as the weight fraction of sol and the chain length averages of both the primary and branched molecules in the sol. (The primary molecules are defined as the molecules which would result if all crosslinks in the system were cut<sup>17</sup>.) However, the application of this model was restricted to the sol species of the polymerization system. In the present study, this

kinetic model is extended to the gel phase and used to predict the gel properties in free-radical MVM-DVM copolymerization. Attention will be paid to the chain length averages of the primary molecules in the gel, and the results will be compared with those of the statistical theories.

In the kinetic treatment that follows, the main assumptions made are (i) the steady-state concentration for the radicals located on the gel molecule, and (ii) no cyclization reactions occur in finite species. Moreover, in the interest of simplicity, (i) penultimate effects are neglected, (ii) the DVM is assumed to have symmetric vinyls, and (iii) chain transfer reactions are dismissed from the kinetic scheme.

### Basic kinetic theory

#### *Vinyl group conversions*

MVM-DVM copolymerization involves three types of vinyl groups with different reactivities, as schematically illustrated in Fig. 1, namely the vinyl groups

- i) on MVM ( $M_1$ ),
- ii) on DVM ( $M_2$ ), and
- iii) on polymer chains, i. e., pendant vinyls ( $M_3$ ).

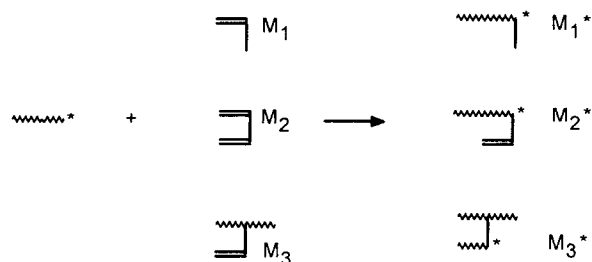


Fig. 1. Types of vinyl groups and radical centers in free-radical MVM-DVM copolymerization

Copolymerization of these three types of vinyl groups results in the formation of three types of active primary molecules (i. e., radical centers), those with

- i) MVM unit at the end ( $M_1^*$ ),
- ii) DVM unit with one unreacted vinyl (pendant vinyl) at the end ( $M_2^*$ ), and
- iii) DVM unit with both reacted vinyls at the end ( $M_3^*$ ).

Accordingly, MVM-DVM copolymerization involves, as in terpolymerizations, 4 initiation, 9 propagation and 12 termination reactions. In order to simplify the kinetic treatment of MVM-DVM copolymerization, a series of instantaneous rate constants for propagation and termination reactions is defined:

$$k_{pi} = \sum_{j=1}^3 k_{pji} x_j \quad (1a)$$

$$k_{tc} = \sum_{i=1}^3 \sum_{j=1}^i k_{tcij} x_i x_j \quad (1b)$$

$$k_{td} = \sum_{i=1}^3 \sum_{j=1}^i k_{tdij} x_i x_j \quad (1c)$$

$$k_t = k_{tc} + k_{td} \quad (1d)$$

Here,  $k_{pji}$  is the propagation rate constant between radicals and vinyls  $M_j^*$  and  $M_i$ , respectively,  $k_{tcij}$  and  $k_{tdij}$  are the termination rate constants between radicals of types  $M_i^*$  and  $M_j^*$  by coupling (c) and by disproportionation (d), respectively,  $x_j$  is the instantaneous mole fraction of the radical  $M_j^*$ , i. e.,  $x_j = [M_j^*]/[R^*]$ , where  $[R^*]$  is the total radical concentration defined by  $[R^*] = \sum_{j=1}^3 [M_j^*]$ . Applying Eqs. (1 a)–(1 d), one may derive the rate equations for the concentration of the initiator I, vinyl groups  $M_i$  and crosslinks  $\mu$  as follows<sup>16)</sup>

$$r_I = -k_d[I] \quad (2)$$

$$r_{M_1} = -k_{p1}[R^*][M_1] \quad (3)$$

$$r_{M_2} = -2k_{p2}[R^*][M_2] \quad (4)$$

$$r_{M_3} = k_{p2}[R^*][M_2] - k_{p3}[R^*][M_3] \quad (5)$$

$$r_{\mu} = k_{p3}[R^*][M_3] \quad (6)$$

where

$$[R^*] = (2fk_d[I]/k_t)^{0.5} \quad (7)$$

$f$  is the initiator efficiency, and  $k_d$  is the decomposition rate constant of the initiator.

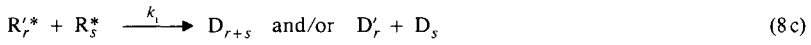
### *Molecular weight distribution of the primary chains in the sol*

Henceforth, the symbols with superscripts (') and (") are used to denote the species in the sol and in the gel, respectively, whereas those without superscript refer to the species in the whole reaction system. Neglecting the attack of the gel radicals to the pendant vinyl groups, the reaction equations for the formation and consumption of primary molecules in the sol composed of  $r$  structural units can be written as follows:

Formation:



Consumption:



( $t, s = 1, 2, 3, \dots; i = 1, 2$  and 3)

where  $A^*$  is the primary radical,  $k_{ai}$  is the initiation rate constant with vinyl  $M_i$ ,  $R_r^*$  and  $D_r'$  represent the active polymer and the dead polymer of chain length  $r$ , respectively. The method of moments can be applied to the kinetic model of the reactions represented by Eqs. (8a)–(8e) to calculate the  $n$ th moment of the active polymer and the polymer distributions in the sol defined as

$$Y_n^{*'} \equiv \sum_{r=1}^{\infty} r^n [R_r'^*] \quad (9a)$$

$$Q_n^{*'} \equiv \sum_{r=1}^{\infty} r^n [P_r'] \quad (9b)$$

respectively. Here,  $P_r'$  denotes the (active + dead) sol polymers of chain length  $r$ . From the moments of the distribution, the  $n$ th average chain length of the active polymer and that of the total polymer in the sol defined by

$$\bar{X}_n^{*'} \equiv Y_n^{*'} / Y_{n-1}^{*'} \quad (10a)$$

$$\bar{X}_n^{*'} \equiv Q_n^{*'} / Q_{n-1}^{*'} \quad (10b)$$

respectively can be calculated. From the balance equations given in ref. <sup>16)</sup>, the moments of the sol primary chains can be expressed as follows

$$Y_n^{*'} = n! \left( \frac{\sum_{i=1}^3 k_{pi} [M_i]}{k_t [R^*]} \right)^n [R^*] \phi_s^{n+1} \quad (11)$$

( $n = 0, 1, 2, \dots$ )

$$r_{Q_n^{*'}} = \left( k_{td} / \phi_s + \frac{n+1}{2} k_{tc} \right) Y_0^{*'} Y_n^{*'} \quad (12)$$

( $n = 0, 1, 2, \dots$ )

where  $\phi_s$  is the fraction of radicals belonging to the sol fraction, i. e.,

$$\phi_s = \left( 1 + \frac{k_{p3} [M_3'']}{k_t [R^*]} \right)^{-1} \quad (13)$$

Note that by setting  $\phi_s = 1$ , the equations given above predict the properties of the primary molecules prior to gelation or their average properties in the whole reaction system (sol + gel) beyond gelation. Moreover, the relation between the radical fraction in the sol phase  $\phi_s$  and the weight fraction of sol  $W_s$ , which is defined by  $W_s \equiv Q_1^{*'} / Q_1^*$ , can be obtained from Eq. (12) as

$$W_s = \phi_s^2 \left[ 1 - \frac{k_{tc}}{k_t} (1 - \phi_s) \right] \quad (14)$$

This equation will be used in the calculation of sol and gel parameters in terms of the weight fraction of sol.

From Eqs. (11) and (12), the  $n$ th average chain lengths of polymer radicals and total polymers in the sol can be calculated as

$$\bar{X}_n^{*'} = \phi_s \bar{X}_n^{**} \quad (15)$$

$$\bar{X}_n^{*'} = \phi_s \bar{X}_n^* \quad (16)$$

$$(n = 1, 2, 3, \dots)$$

where  $\bar{X}_n^{**}$  and  $\bar{X}_n^*$  are the corresponding quantities for the whole reaction system (sol + gel), and given by the following equations:

$$\bar{X}_n^{**} = n \frac{\sum_{i=1}^3 k_{pi} [M_i]}{k_t [R^*]} \quad (17)$$

$$\bar{X}_n^* = \left[ \frac{k_{td} + \frac{n+1}{2} k_{tc}}{k_{td} + \frac{n}{2} k_{tc}} \right] \bar{X}_n^{**} \quad (18)$$

$$(n = 1, 2, 3, \dots)$$

From Eqs. (15) and (16), it is clear that the chain length distribution of the polymers in the sol is equal to that of the polymers in the whole reaction system, i. e.,

$$\frac{\bar{X}_n^{*'}}{\bar{X}_{n-1}^{*'}} = \frac{\bar{X}_n^{**}}{\bar{X}_{n-1}^{**}} = \frac{n}{n-1} \quad (19)$$

$$\frac{\bar{X}_n^{*'}}{\bar{X}_{n-1}^{*'}} = \frac{\bar{X}_n^*}{\bar{X}_{n-1}^*} = \frac{n}{n-1} \quad (k_{tc} = 0) \quad (20)$$

$$= \frac{n+1}{n} \quad (k_{td} = 0)$$

### Kinetic treatment of the gel molecule

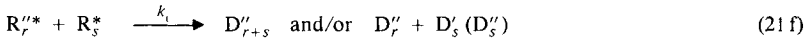
The reaction equations for the appearance and disappearance of the primary chains in the gel composed of  $r$  structural units can be written as follows:

Formation:





Consumption:



( $r, s = 1, 2, 3, \dots$ ;  $i = 1, 2$  and  $3$ )

Here, for the sake of simplicity, no distinction was made between the reactivity of the functional groups (radical centers, pendant vinyls) in the sol and in the gel. Thus, it is assumed that the sol can react with the gel and also that gel can react intramolecularly, obeying the same rules as the sol polymers. After invoking the steady-state approximation for the radicals located on the gel, the moments of the active and the total primary chains in the gel can be derived from the preceding kinetic scheme as follows:

Gel radical balances:

$$r_{R''_r} = k_{a3} [A^*][M''_3] - \left( \sum_{i=1}^3 k_{pi} [M_i] + k_t [R^*] \right) [R''_r] \cong 0 \quad (22 \text{ a})$$

$$r_{R''_r} = \sum_{i=1}^3 k_{pi} [M_i] ([R''_{r-1}] - [R''_r]) + k_{p3} [R''_{r-1}][M''_3] - k_t [R^*][R''_r] \cong 0 \quad (22 \text{ b})$$

( $r = 2, 3, 4, \dots$ )

Gel radical moments:

$$r_{Y''_n} = \sum_{i=1}^3 k_{pi} [M_i] \sum_{v=0}^{n-1} \binom{n}{v} Y''_v + k_{p3} [M''_3] \sum_{v=0}^n \binom{n}{v} Y''_v - k_t [R^*] Y''_n \cong 0 \quad (23)$$

( $n = 0, 1, 2, \dots$ )

Gel polymer balances:

$$r_{P''_r} = k_{td} [R^*][R''_r] + \frac{1}{2} k_{tc} \sum_{s=1}^{r-1} [R''_s] ([R''_{r-s}] + 2[R''_{r-s}]) \quad (24)$$

( $r = 1, 2, 3, \dots$ )

Gel polymer moments:

$$r_{Q''_n} = k_{td} [R^*] Y''_n + \frac{1}{2} k_{tc} \sum_{v=0}^n \binom{n}{v} Y''_v (Y''_{n-v} + 2Y''_{n-v}) \quad (25)$$

( $n = 0, 1, 2, \dots$ )

Since  $Y_n^* \gg Y_{n-1}^*$  in free-radical polymerization, Eqs. (23) and (25) yield the following equations for the moments of the primary molecules in the gel:

$$r_{Q_n''} = \left\{ k_{td} + \left( \frac{n+1}{2} \right) \left( \frac{1 - \phi_s^{n+2}}{1 - \phi_s^{n+1}} \right) k_{tc} \right\} Y_0^* Y_n'' \tag{26}$$

$$(n = 0, 1, 2, \dots)$$

$$Y_n'' = Y_n^* - Y_n' \tag{27}$$

$$(n = 0, 1, 2, \dots)$$

*Molecular weight distribution of the primary chains in the gel*

The  $n$ th average chain length of the active primary chains in the gel can be calculated from Eqs. (11) and (27) as

$$\bar{X}_n''' = \left( \frac{1 - \phi_s^{n+1}}{1 - \phi_s^n} \right) \bar{X}_n^* \tag{28}$$

$$(n = 1, 2, 3, \dots)$$

This means that the first three (number-, weight- and z-) averages of the active primary chain lengths are

$$\bar{X}_1''' = (1 + \phi_s) \bar{X}_1^* \tag{29a}$$

$$\bar{X}_2''' = \left( \frac{1 + \phi_s + \phi_s^2}{1 + \phi_s} \right) \bar{X}_2^* \tag{29b}$$

$$\bar{X}_3''' = \left( \frac{(1 + \phi_s)(1 + \phi_s^2)}{1 + \phi_s + \phi_s^2} \right) \bar{X}_3^* \tag{29c}$$

and their limiting values at or just beyond the gel point ( $t_g$ ) are:

$$\lim_{t \rightarrow t_g} \bar{X}_1''' = 2 \bar{X}_1^* \tag{30a}$$

$$\lim_{t \rightarrow t_g} \bar{X}_2''' = \frac{3}{2} \bar{X}_2^* \tag{30b}$$

$$\lim_{t \rightarrow t_g} \bar{X}_3''' = \frac{4}{3} \bar{X}_3^* \tag{30c}$$

Thus, the chain length distribution of active primary chains in the gel becomes at the point of gelation

$$\bar{X}_3''' / \bar{X}_2''' / \bar{X}_1''' = 2/1,5/1 \tag{31}$$

compared to the ratio 3/2/1 for the primary chains in the sol (Eq. (19)). Thus, the model predicts that the number-average molecular weight of the active primary chains in the gel is twice as high as that in the sol at the point of gelation, and the other averages are also higher than those of the sol species. Moreover, compared to the sol species, there is a sharp chain length distribution within the gel molecules. These results indicate that, when gelation occurs, preferentially the largest species in the sol are connected to the gel, in accord with the experimental results of Hild et al.<sup>18)</sup>

Applying Eqs. (26) and (14), the  $n$ th average chain length of the primary chains in the gel can be calculated as follows:

$$\begin{aligned} \bar{X}_n^{*''} &= \left( \frac{1 - \phi_s^{n+1}}{1 - \phi_s^n} \right) \bar{X}_n^* \\ &= \left( \frac{1 - W_s^{(n+1)/2}}{1 - W_s^{n/2}} \right) \bar{X}_n^* \end{aligned} \quad (k_{tc} = 0) \tag{32}$$

$(n = 1, 2, 3, \dots)$

$$\begin{aligned} \bar{X}_n^{*''} &= \left( \frac{1 - \phi_s^{n+2}}{1 - \phi_s^{n+1}} \right) \bar{X}_n^* \\ &= \left( \frac{1 - W_s^{(n+2)/3}}{1 - W_s^{(n+1)/3}} \right) \bar{X}_n^* \end{aligned} \quad (k_{td} = 0) \tag{33}$$

$(n = 1, 2, 3, \dots)$

Hence, for termination by disproportionation, i. e., for  $k_{tc} = 0$  (Flory distribution), the chain length averages and the polydispersity of the polymer chains are identical to those of the living chains (Eqs. (28)–(31)). For termination reactions occurring by coupling only, the first three chain length averages become

$$\bar{X}_1^{*''} = \left( \frac{1 + \phi_s + \phi_s^2}{1 + \phi_s} \right) \bar{X}_1^* \tag{34 a}$$

$$\bar{X}_2^{*''} = \left( \frac{(1 + \phi_s)(1 + \phi_s^2)}{1 + \phi_s + \phi_s^2} \right) \bar{X}_2^* \tag{34 b}$$

$$\bar{X}_3^{*''} = \left( \frac{\sum_{\nu=0}^4 \phi_s^\nu}{\sum_{\nu=0}^3 \phi_s^\nu} \right) \bar{X}_3^* \tag{34 c}$$

so that their limiting values at the gel point are:

$$\lim_{t \rightarrow t_g} \bar{X}_1^{*''} = \frac{3}{2} \bar{X}_1^* \tag{35 a}$$



$$\lim_{t \rightarrow t_g} \bar{X}_2^{*''} = \frac{4}{3} \bar{X}_2^* \quad (35 \text{ b})$$

$$\lim_{t \rightarrow t_g} \bar{X}_3^{*''} = \frac{5}{4} \bar{X}_3^* \quad (35 \text{ c})$$

Thus, the chain length distribution of the primary chains in the gel at or just beyond the gel point is

for  $k_{tc} = 0$ :

$$\bar{X}_3^{*''} / \bar{X}_2^{*''} / \bar{X}_1^{*''} = 2/1,5/1 \quad (36)$$

compared to 3/2/1 for the sol chains, and

for  $k_{td} = 0$ :

$$\bar{X}_3^{*''} / \bar{X}_2^{*''} / \bar{X}_1^{*''} = \frac{5}{3} / \frac{4}{3} / 1 \quad (37)$$

compared to 2/1,5/1 for the sol chains. The results demonstrate the fractionation of the polymer chains with the onset of gelation.

In Tab. 1 the main results of the present study concerning the chain length averages of the primary molecules in the sol and in the gel are summarized. The general equations for calculating the number- and weight average chain lengths of the primary chains are identical to the equations derived by statistical methods<sup>17, 19)</sup>.

Tab. 1. Chain length averages of the primary chains in free-radical MVM-DVM copolymerization

Parameter	$k_{tc} = 0$	$k_{td} = 0$
<i>Sol phase:</i>		
$\bar{X}_1^* / \bar{X}_1^*$	$W_s^{1/2}$	$W_s^{1/3}$
$\bar{X}_2^* / \bar{X}_2^*$	$W_s^{1/2}$	$W_s^{1/3}$
$\bar{X}_3^* / \bar{X}_3^*$	$W_s^{1/2}$	$W_s^{1/3}$
⋮		
$\bar{X}_n^* / \bar{X}_n^*$	$W_s^{1/2}$	$W_s^{1/3}$
$\bar{X}_3^* / \bar{X}_2^* / \bar{X}_1^*$	3/2/1	2/1,5/1
<i>Gel phase:</i>		
$\bar{X}_1^{*''} / \bar{X}_1^*$	$1 + W_s^{1/2}$	$\frac{1 - W_s}{1 - W_s^{2/3}}$
$\bar{X}_2^{*''} / \bar{X}_2^*$	$\frac{1 - W_s^{3/2}}{1 - W_s}$	$\frac{1 - W_s^{4/3}}{1 - W_s}$
$\bar{X}_3^{*''} / \bar{X}_3^*$	$\frac{1 - W_s^2}{1 - W_s^{3/2}}$	$\frac{1 - W_s^{5/3}}{1 - W_s^{4/3}}$
⋮		
$\bar{X}_n^{*''} / \bar{X}_n^*$	$\frac{1 - W_s^{(n+1)/2}}{1 - W_s^{n/2}}$	$\frac{1 - W_s^{(n+2)/3}}{1 - W_s^{(n+1)/3}}$
$\bar{X}_3^{*''} / \bar{X}_2^{*''} / \bar{X}_1^{*''}$ (at $t_g$ )	2/1,5/1	$\frac{5}{4} / \frac{4}{3} / 1$

## Conclusions

A kinetic model was developed to predict the gel properties in free-radical MVM-DVM copolymerization. Equations were derived which describe gel growth and structure during the polymerization and crosslinking reactions.

In order to apply this model to a real system, one has to consider the effect of cyclization reactions occurring in finite species as well as the concentration dependence of the elementary rate constants such as those of termination and crosslinking reactions. Moreover, in the development of the model, it is assumed that the sol radicals can crosslink and terminate with the gel molecule, and also the gel can react intramolecularly. This means that the bonds can form within the gel molecule with the same kinetic rules as in the sol. However, one may expect a greatly reduced accessibility of the radicals and the pendant vinyls located on the gel due to steric reasons. In order to account for this effect, one has to distinguish sol-sol, sol-gel and gel-gel termination and crosslinking reactions with different apparent rate constants such as  $k_{tss}$ ,  $k_{tsg}$ ,  $k_{tgg}$ ,  $k_{p3ss}$ ,  $k_{p3sg}$  and  $k_{p3gg}$ , and evaluate their values by fitting the experimental data. The idealized kinetic model presented here is thought to form the basis for treating these deviations.

- 1) P. J. Flory, *J. Am. Chem. Soc.* **63**, 3083, 3091, 3096 (1941)
- 2) W. H. Stockmayer, *J. Chem. Phys.* **11**, 45 (1943)
- 3) W. H. Stockmayer, *J. Chem. Phys.* **12**, 125 (1944)
- 4) M. Gordon, *Proc. R. Soc. London, A*: **268**, 240 (1962)
- 5) C. W. Macosko, D. R. Miller, *Macromolecules* **9**, 199 (1976)
- 6) D. R. Miller, C. W. Macosko, *Macromolecules* **9**, 206 (1976)
- 7) K. Dusek, in "Development in Polymerization-3"; R. N. Haward, Ed., Applied Science, London 1982, p. 143
- 8) R. M. Ziff, *J. Chem. Phys.* **73**, 3492 (1980)
- 9) H. Galina, A. Szustalewicz, *Macromolecules* **22**, 3124 (1989)
- 10) A. G. Mikos, C. G. Takoudis, N. A. Peppas, *Macromolecules* **19**, 2174 (1986)
- 11) H. Tobita, A. E. Hamielec, *Makromol. Chem., Macromol. Symp.* **20/21**, 501 (1988)
- 12) H. Tobita, A. E. Hamielec, *Makromol. Chem., Macromol. Symp.* **35/36**, 193 (1990)
- 13) D. T. Landin, C. W. Macosko, *Macromolecules* **21**, 849 (1988)
- 14) G. L. Batch, C. W. Macosko, *J. Appl. Polym. Sci.* **44**, 1711 (1992)
- 15) K. Dusek, *J. Macromol. Sci.-Chem.* **A28**, 843 (1991)
- 16) O. Okay, *Polymer*, in press
- 17) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY 1953, chapter 9
- 18) G. Hild, R. Okasha, P. Rempp, *Makromol. Chem.* **186**, 407 (1985)
- 19) K. te Nijenhuis, *Makromol. Chem.* **192**, 603 (1991)