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Modeling of Network Formation in Free Radical Polymerization[†]

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ABSTRACT: Kinetic models for network formation in free radical polymerization based on the pseudokinetic rate constant method are proposed for both pre- and postgelation periods. Network formation in free radical polymerization is a nonequilibrium process; namely, it is kinetically controlled and therefore it is necessary to consider the history of the generated network structure. The present kinetic models consider all of the important reactions in free radical polymerization and are therefore quite general and realistic and capable of accounting for reaction types such as primary and secondary cyclization. These kinetic approaches provide greater insight into the phenomena of network formation in free radical polymerization.

Introduction

Though various models have been proposed for polymeric gelation since the pioneering work of Flory[1] and Stockmayer,[2] it is possible to classify these models mainly into two categories. One is called the classical theory, which is based on the Flory/Stockmayer treelike model and includes the cascade theory developed by Gordon[3] and the Macosko–Miller model[4] using conditional probabilities. These models are fully equivalent and enjoy the simplicity of a mean-field theory. Another type is called the percolation theory,[5-9] which is considered to be equivalent to a non-mean-field theory. Though the percolation theory may possess potential universality, it is still too immature to describe the course of network formation and its predictions are just qualitatively acceptable. At present, it is still considered controversial and unclear which theory is more suitable for polymeric gelation.

Generally these statistical theories give rather satisfactory predictions for an *f*-functional polycondensation system, but their predictions are quite often unsatisfactory for a free radical polymerization system. Free radical polymerization is kinetically controlled and involves various elementary reactions. A realistic model for network formation in free radical polymerization must account for the specific reaction mechanism of cross-linking; namely, a cross-linkage is formed only through a radical center whose concentration is very low and whose lifetime is very short. Recently, a new model for gelation in free radical polymerization based on the pseudokinetic rate constant method was proposed.[10] This model considers all of the important reactions in free radical polymerization. In principle, it belongs to the classical theory, but it is more general than the former classical models for free radical polymerization systems. Especially, the concept of pseudokinetic rate constants in which the treatment of a multicomponent polymerization reduces to that of a homopolymerization is useful.

In this paper the pseudokinetic rate constant method is extensively applied and models for both pre- and postgelation period are illustrated.

Pseudokinetic Rate Constant Method

The pseudokinetic rate constant method for multicomponent polymerization has been applied in some copolymerization studies,[11-13] and its derivation and specific approximations have been made clear.[10] In this section let us review the outline of this method.

Linear Copolymer. We now assume that the terminal model for copolymerization is applicable, and let us consider the copolymerization of M_1 and M_2 whose elementary reactions are shown below.

Initiation

$$\mathrm{I} \rightarrow 2\mathrm{R}^{\bullet}_{\mathrm{in}} \qquad (k_{\mathrm{d}}) \tag{1a}$$

$$\mathrm{R}^{\bullet}_{\mathrm{in}} + \mathrm{M}_1 \rightarrow \mathrm{R}^{\bullet}_{1,0,1} \qquad (k_1) \tag{1b}$$

$$\mathrm{R}^{\bullet}_{\mathrm{in}} + \mathrm{M}_2 \rightarrow \mathrm{R}^{\bullet}_{0,1,2} \qquad (k_2) \tag{1c}$$

Propagation

$$\mathrm{R}^{\bullet}_{m,n,1} + \mathrm{M}_1 \rightarrow \mathrm{R}^{\bullet}_{m+1,n,1} \qquad (k_{11}) \tag{2a}$$

$$\mathrm{R}^{\bullet}_{m,n,1} + \mathrm{M}_2 \rightarrow \mathrm{R}^{\bullet}_{m,n+1,2} \qquad (k_{12}) \tag{2b}$$

$$\mathrm{R}^{\bullet}_{m,n,2} + \mathrm{M}_1 \rightarrow \mathrm{R}^{\bullet}_{m+1,n,1} \qquad (k_{21}) \tag{2c}$$

$$\mathrm{R}^{\bullet}_{m,n,2} + \mathrm{M}_2 \rightarrow \mathrm{R}^{\bullet}_{m,n+1,2} \qquad (k_{22}) \tag{2d}$$

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Transfer to Monomer

$$R^{\bullet}_{m,n,1} + M_1 \rightarrow P_{m,n} + R^{\bullet}_{1,0,1} \qquad (k_{f11}) \qquad (3a)$$

$$R^{\bullet}_{m,n,1} + M_2 \rightarrow P_{m,n} + R^{\bullet}_{0,1,2} \qquad (k_{f12}) \qquad (3b)$$

$$R^{\bullet}_{m,n,2} + M_1 \rightarrow P_{m,n} + R^{\bullet}_{1,0,1} \qquad (k_{f21}) \qquad (3c)$$

$$R^{\bullet}_{m,n,2} + M_2 \rightarrow P_{m,n} + R^{\bullet}_{0,1,2} \qquad (k_{f22}) \qquad (3d)$$

Transfer to Small Molecule (T)

$$R^{\bullet}_{m,n,1} + T \rightarrow P_{m,n} + T^{\bullet} \qquad (k_{fT1}) \qquad (4a)$$

$$R^{\bullet}_{m,n,2} + T \rightarrow P_{m,n} + T^{\bullet} \qquad (k_{fT2}) \qquad (4b)$$

Termination

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,1} \rightarrow P_{m,n} + P_{r,s} \text{ or } P_{m+r,n+s} \qquad (k_{td11} \text{ or } k_{tc11}) \qquad (5a)$$

$$R^{\bullet}_{m,n,1} + R^{\bullet}_{r,s,2} \rightarrow P_{m,n} + P_{r,s} \text{ or } P_{m+r,n+s} \qquad (k_{td12} \text{ or } k_{tc12}) \qquad (5b)$$

$$R^{\bullet}_{m,n,2} + R^{\bullet}_{r,s,2} \rightarrow P_{m,n} + P_{r,s} \text{ or } P_{m+r,n+s} \qquad (k_{td22} \text{ or } k_{tc22}) \qquad (5c)$$

where $R^{\bullet}_{m,n,i}$ is a polymer radical with m units of monomer 1 (M_1) and n units of monomer 2 (M_2) bound in the chain and with active center located on monomer unit i. $P_{m,n}$ is a polymer molecule with m units of monomer 1 and n units of monomer 2. As it is shown above, a free radical copolymerization system involves various elementary reactions, and as the number of components increases, kinetic expressions become fairly complicated.[14] In order to avoid such complication we use the pseudokinetic rate constants defined below.

Propagation Rate Constant

$$k_p = \sum_{\substack{i=1\\j=1}}^{N} k_{ij}\Phi^{\bullet}_i f_j \qquad (6)$$

Transfer to Monomer

$$k_{fm} = \sum_{\substack{i=1\\j=1}}^{N} k_{fij}\Phi^{\bullet}_i f_j \qquad (7)$$

Transfer to Small Molecule

$$k_{fT} = \sum_{i=1}^{N} k_{fTi}\Phi^{\bullet}_i \qquad (8)$$

Termination by Disproportionation

$$k_{td} = \sum_{\substack{i=1\\j=1}}^{N} k_{tdij}\Phi^{\bullet}_i\Phi^{\bullet}_j \qquad (9)$$

Termination by Combination

$$k_{tc} = \sum_{\substack{i=1\\j=1}}^{N} k_{tcij}\Phi^{\bullet}_i\Phi^{\bullet}_j \qquad (10)$$

where $\Phi^{\bullet}_i$ is the mole fraction of polymer radical of type i, f_j is the mole fraction of monomer of type j in the reaction system, and N is the number of monomer types.

Applying the pseudokinetic rate constants defined above, the kinetic treatment (reaction rate, molecular weight, etc.) of a multicomponent polymerization reduces to that of a homopolymerization. Though these pseudokinetic rate constants are not constant but are changing with time, this concept facilitates the kinetic treatment greatly.

But one has to bear in mind that there is a condition that must be satisfied in order to use these pseudokinetic rate constants with negligible error, that is

$$\Phi^{\bullet}_{1,1} = \Phi^{\bullet}_{2,1} = ... = \Phi^{\bullet}_{r,1} = ... = \Phi^{\bullet}_1 \qquad (11a)$$

$$\Phi^{\bullet}_{1,2} = \Phi^{\bullet}_{2,2} = ... = \Phi^{\bullet}_{r,2} = ... = \Phi^{\bullet}_2 \qquad (11b)$$

$$\vdots$$

$$\Phi^{\bullet}_{1,i} = \Phi^{\bullet}_{2,i} = ... = \Phi^{\bullet}_{r,i} = ... = \Phi^{\bullet}_i$$

$$\vdots$$

where

$$\Phi^{\bullet}_{r,i} = \frac{[R^{\bullet}_{r,i}]}{\sum_{i=1}^{N}[R^{\bullet}_{r,i}]} = \frac{[R^{\bullet}_{r,i}]}{[R^{\bullet}_r]} \qquad \Phi^{\bullet}_i = \frac{\sum_{r=1}^{\infty}[R^{\bullet}_{r,i}]}{\sum_{r=1}^{\infty}[R^{\bullet}_r]} = \frac{[R^{\bullet}_i]}{[R^{\bullet}]}$$

i is the radical type, and r is the chain length. Namely, the mole fraction of radical type does not change with chain length. This condition is equivalent to stating that there is no compositional distribution for instantaneously formed polymers. For long chains this assumption is supported by the Stockmayer bivariate distribution,[10,15] which shows the bivariate distribution of chain length and composition is the product of both distributions and the compositional distribution is given by a normal distribution whose variance is inversely proportional to chain length r. Practically, if the chain length is less than 300, the effect of statistical distribution of composition might be significant, but for high polymers it is reasonable to neglect the compositional distribution.

Copolymer with Long-Chain Branching. The most common mechanisms to produce long-chain branching that result in network formation in free radical polymerization systems are chain transfer to polymer and reaction with internal double bonds, which includes reaction with pendant double bonds.

Chain Transfer to Polymer

$$R^{\bullet}_r + P_s \rightarrow P_r + R^{\bullet}_s \qquad (k_{fp}) \qquad (12)$$

Reaction with Internal Double Bond

$$R^{\bullet}_r + P_s \rightarrow R^{\bullet}_{r+s} \qquad (k^*_p) \qquad (13)$$

In this case the situation is more complicated than that for linear polymers. For linear polymers, once the polymer molecule is formed, it is inert and does not react further, but for polymers with long-chain branching, the dead polymer molecule is reborn as a polymer radical and it grows again. In this case the simplest definition of the pseudokinetic rate constant for each branching reaction type would be

$$k_{fp} = \sum_{\substack{i=1\\j=1}}^{N} k_{fpij}\Phi^{\bullet}_i(\bar{F}_j - \bar{\rho}_{H_j}) \qquad (14)$$

$$k^*_p = \sum_{\substack{i=1\\j=1}}^{N} k^*_{pij}\Phi^{\bullet}_i(\bar{F}_j - \bar{\rho}_j) \qquad (15)$$

where i is the polymer radical type, j is the monomer unit type bound in the chain which is involved in the reaction with the polymer radical, $\bar{F}_j$ is the mole fraction of monomer j in the accumulated copolymer, and $\bar{\rho}_j$ and $\bar{\rho}_{H_j}$ are the mole fractions of monomer j which has already been consumed in the accumulated copolymer. By application of the above pseudokinetic rate constants, the reaction rate for each reaction is given by

$$R_{\mathrm{fp}} = k_{\mathrm{fp}}[\mathrm{R}^\bullet]N_0X/V \qquad (16)$$

$$R^*_{\mathrm{p}} = k^*_{\mathrm{p}}[\mathrm{R}^\bullet]N_0X/V \qquad (17)$$

where N_0 is the initial total number of moles of monomer, X is the total monomer conversion, and V is the reaction volume. These kinetic expressions are quite simple and they imply that it is possible to apply the method of moments.[16,17]

One should realize that these pseudokinetic rate constants defined above are not exact but approximate for the calculation of moments. Strictly speaking, each term involved in eq 14 and 15 is a function of chain length as well as conversion. Since average values are used in eq 14 and 15, one cannot know the behavior of individual chains using the pseudokinetic rate constants defined in eq 14 and 15. However, if the copolymerization system includes reaction with internal double bonds (or pendant double bonds), gelation quite often occurs at fairly low conversions. In such cases, at least until the gel point, it is reasonable to apply the pseudokinetic rate constants defined in eq 14 and 15, as errors are expected to be negligible.[19]

Pregelation Period

We now assume that the pseudokinetic rate constants defined in eq 6–10, 14, and 15 are applicable. By application of the method of moments to the elementary reactions (1)–(5), (12), and (13), the ith moment of the polymer distribution is given by

$$Q_i = \sum_{r=1}^{\infty} r^i[\mathrm{P}_r]$$

and that for the polymer radicals by

$$Y_i = \sum_{r=1}^{\infty} r^i[\mathrm{R}^\bullet_r]$$

The moments can be calculated from the following equations with initial conditions $q_1 = q_2 = \ldots q_i = 0$ at $X = 0$. (See Appendix A for their derivation.)

$$y_0 = 1 \qquad (18)$$

$$y_i = \frac{iy_{i-1} + C_{\mathrm{p}(i+1)} + \sum_{j=1}^{i}\binom{i}{j}C^*_{\mathrm{p}(j+1)}y_{i-j}}{\tau + \beta + C_{\mathrm{p1}}} \qquad (i \ge 1) \qquad (19)$$

$$\mathrm{d}q_0/\mathrm{d}X = \tau + \beta - C^*_{\mathrm{p1}} \qquad (20)$$

$$\mathrm{d}q_1/\mathrm{d}X = 1 \qquad (21)$$

$$\mathrm{d}q_i/\mathrm{d}X = iy_{i-1} + \sum_{j=1}^{i-1}\binom{i}{j}\left\{\frac{\beta}{2}y_jy_{i-j} + C^*_{\mathrm{p}(j+1)}y_{i-j}\right\} \qquad (i \ge 2) \qquad (22)$$

where

$$y_i = \frac{Y_i}{Y_0} \qquad q_i = \frac{VQ_i}{V_0[\mathrm{M}]_0}$$

$$C_{\mathrm{p}i} = \frac{k_{\mathrm{fp}}Q_i}{k_{\mathrm{p}}[\mathrm{M}]} \qquad C^*_{\mathrm{p}i} = \frac{k^*_{\mathrm{p}}Q_i}{k_{\mathrm{p}}[\mathrm{M}]}$$

$$\tau = \frac{k_{\mathrm{fm}}[\mathrm{M}] + k_{\mathrm{fT}}[\mathrm{T}] + k_{\mathrm{td}}[\mathrm{R}^\bullet]}{k_{\mathrm{p}}[\mathrm{M}]} \qquad \beta = \frac{k_{\mathrm{tc}}[\mathrm{R}^\bullet]}{k_{\mathrm{p}}[\mathrm{M}]}$$

Though the explicit formulation appears to be complicated, for example, for the copolymerization of vinyl/divinyl monomer without chain transfer to polymer, the equations reduce to a simpler set as follows:

$$\mathrm{d}q_0/\mathrm{d}X = \tau + \beta/2 - C^*_{\mathrm{p1}} \qquad (23a)$$

$$\mathrm{d}q_1/\mathrm{d}X = 1 \qquad (23b)$$

$$\mathrm{d}q_2/\mathrm{d}X = P_{\mathrm{wp}}(1 + C^*_{\mathrm{p2}})^2 \qquad (23c)$$

$$\mathrm{d}q_3/\mathrm{d}X = P_{\mathrm{wp}}(1 + C^*_{\mathrm{p2}})\{3C^*_{\mathrm{p3}} + P_{\mathrm{zp}}(1 + C^*_{\mathrm{p2}})^2\} \qquad (23d)$$

$$\vdots$$

where P_{wp} is the instantaneous weight-average chain length of the primary polymer molecules and $P_{\mathrm{wp}} = (2\tau + 3\beta)/(\tau + \beta)^2$. P_{zp} is the instantaneous z-average chain length of the primary polymer molecules and $P_{\mathrm{zp}} = 6(\tau + 2\beta)/(\tau + \beta)(2\tau + 3\beta)$. Applying eq 18–22, it is easy to show that the instantaneous jth-order average chain length of the primary polymer molecules is given by

$$P_j = \left(\frac{j}{\tau + \beta}\right)\left(\frac{2\tau + (j+1)\beta}{2\tau + j\beta}\right) \qquad (24)$$

For example, P_1 represents the instantaneous number-average chain length for linear polymers (primary polymer molecules are linear).

When the second moment or higher goes to infinity, the onset of gelation occurs. In terms of the moments the number- and weight-average chain length of the accumulated polymer are given by

$$\bar{P}_{\mathrm{n}} = Q_1/Q_0 \qquad (25a)$$

$$\bar{P}_{\mathrm{w}} = Q_2/Q_1 \qquad (25b)$$

It is also possible to calculate the number- and weight-average chain length for polymer radicals as follows:

$$\bar{P}^\bullet_{\mathrm{n}} = Y_1/Y_0 \qquad (25c)$$

$$\bar{P}^\bullet_{\mathrm{w}} = Y_2/Y_1 \qquad (25d)$$

Sample calculations can be found in an earlier paper.[10] This method is unique in the fact that the difference in the size of polymer molecules with and without radical centers can be shown.

One of the interesting results of this analysis is that chain transfer to polymer plus termination by disproportionation can never cause gelation; however, if the bimolecular termination reaction includes combination, gelation is predicted to occur under certain conditions.[10]

Postgelation Period

The quantitative treatment of the postgelation period is, in general, much more difficult than that for the pregelation period. In this section, two kinds of models are proposed. The first model was also mentioned in our previous paper.[10] The second model is a new one in which Flory's model for the postgelation period[20] is generalized, applying pseudokinetic rate constants.

A Kinetic Model for the Postgelation Period. One of the simplest methods is to consider the gel growth (or sol decrease), using the same pseudokinetic rate constants defined in eq 14 and 15. The equation which describes gel growth follows:

$$\frac{\mathrm{d}W_{\mathrm{g}}}{\mathrm{d}X} = \frac{\Phi^\bullet_{\mathrm{g}} - W_{\mathrm{g}}}{X} + \frac{k^*_{\mathrm{p}}/k_{\mathrm{p}}}{1 - X}\{\bar{P}_{\mathrm{n,s'}}\Phi^\bullet_{\mathrm{s}}W_{\mathrm{g}} + \bar{P}_{\mathrm{w,s}}\Phi^\bullet_{\mathrm{g}}W_{\mathrm{s}}\} + \frac{\beta_{\mathrm{sg}}}{X}\bar{P}_{\mathrm{n,s'}}\Phi^\bullet_{\mathrm{s}}\Phi^\bullet_{\mathrm{g}} \qquad (26)$$

where W_{g} and W_{s} are weight fraction of gel and sol and $\bar{P}_{\mathrm{n,s'}}$ and $\bar{P}_{\mathrm{w,s}}$ are number-average chain length of sol polymer radicals and weight-average chain length of sol polymer molecules, respectively. $\Phi^\bullet_{\mathrm{s}}$ and $\Phi^\bullet_{\mathrm{g}}$ are mole

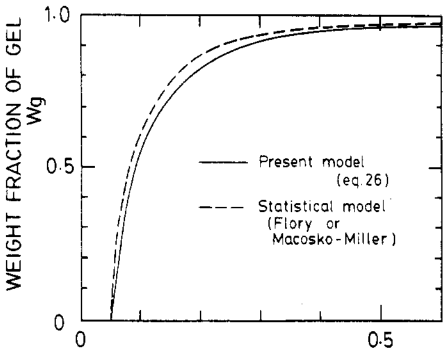

Figure 1. Comparison with the statistical model. (Gel growth equation, eq 26). Calculation conditions: $\tau = 2 \times 10^{-4}$, $\beta = 0$, $f_{20} = 1 \times 10^{-3}$, reactivities of all double bonds are equal. When $\beta = 0$, Flory's model[20] and the Macosko–Miller model[4] are fully equivalent.

fraction of radical centers located on sol and gel, and $\beta_{sg} = k_{tcsg}[R^\bullet]/k_p[M]$ where k_{tcsg} is the termination rate constant for comination of sol and gel radicals.

But there are several problems concerning the solution of the above equation. One of the problems is that one does not know the initial condition for eq 26; namely, at present there is no theory available to give the conditions right at the gel point. If the weight-average chain length for sol molecules $\bar{P}_{w,s}$ is known, it may be possible to obtain a solution by assuming the initial condition arbitrary because the calculation is not too sensitive to the initial condition. Nevertheless, there is no theoretical basis for that condition. One method of circumventing this is to combine the present analysis using the pseudokinetic rate constants with Flory's model.[20] Details are shown in part B of the Appendix. One of the calculation results is shown in Figure 1. The calculation results agree with the statistical models.[4,20] In the calculations, the effect of chain length drift, mainly due to the strong effect of diffusion controlled termination (and propagation at very high conversions) in the postgelation period, was neglected. Therefore, these calculations should be understood as valid when chain transfer to small molecules is significant and chain length drift is negligible.

Another problem with the use of eq 26 is that the pseudokinetic rate constants defined in eq 14 and 15 are clearly approximations for the high conversion region as it was shown earlier. Therefore, we developed another model in which the exact pseudokinetic rate constants for a cross-linking reaction can be defined.

Generalization of Flory's Theory for Vinyl/Divinyl Copolymerization Using Pseudokinetic Rate Constants

Since Flory's theory of network formation assumes an equilibrium system, modifications are necessary in order for it to apply to a kinetically controlled system, such as with free radical polymerization. Applying pseudokinetic rate constants, it is possible to generalize Flory's theory for the postgelation period[20] quite rigorously. In this method the concept of a primary polymer molecule[18] is extensively used. The primary polymer molecule is a rather imaginary molecule which would exist if all cross-links connected to it were severed; namely, the primary polymer molecule is a linear polymer. Flory's equation for the weight fraction of sol (W_s) is given by

$$W_s = \sum_{r=1}^{\infty} w_r (1 - \rho W_g)^r \quad (\rho \ll 1) \tag{27}$$

where w_r is the weight chain length distribution for primary molecules and ρ is the cross-linking density. Therefore, the quantity in parenthesis in eq 27 is the probability that a randomly selected monomer unit bound in the polymer chains belongs to sol, so that the meaning of eq 27 is clear.

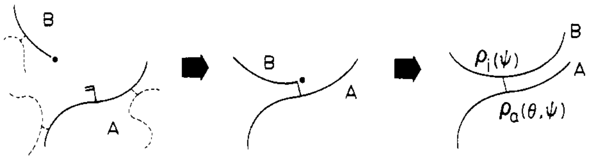

Figure 2. Schematic drawing of the process of cross-linking.

Applying the pseudokinetic rate constants, the instantaneous weight chain length distribution for primary molecules which are produced at $X = \theta$ is given by

$$w_r(\theta) = \{\tau(\theta) + \beta(\theta)\}\left[\tau(\theta) + \frac{\beta(\theta)}{2}\{\tau(\theta) + \beta(\theta)\}(r - 1)\right] r\Phi^{r+1}(\theta) \tag{28}$$

where

$$\Phi(\theta) = \frac{1}{1 + \tau(\theta) + \beta(\theta)}$$

At the present conversion $X = \Psi$ ($\Psi > \theta$), the weight fraction of sol for the primary molecules which were produced at $X = \theta$ is given by

$$\begin{aligned} W_s(\theta,\Psi) = \sum_{r=1}^{\infty} w_r(\theta)[1 - \rho(\theta,\Psi) W_g(\theta,\Psi)]^r = \\ A(\theta,\Psi)\{1 - \rho(\theta,\Psi) W_g(\theta,\Psi)\}[T(\theta,\Psi) + \\ A(\theta,\Psi)B(\theta,\Psi)\{1 - \rho(\theta,\Psi) W_g(\theta,\Psi)\}] \end{aligned} \tag{29}$$

where

$$T(\theta,\Psi) = \frac{\tau(\theta)}{\tau(\theta) + \beta(\theta) + \rho(\theta,\Psi) W_g(\theta,\Psi)}$$

$$B(\theta,\Psi) = \frac{\beta(\theta)}{\tau(\theta) + \beta(\theta) + \rho(\theta,\Psi) W_g(\theta,\Psi)}$$

$$A(\theta,\Psi) = T(\theta,\Psi) + B(\theta,\Psi)$$

$$W_g(\theta,\Psi) = 1 - W_s(\theta,\Psi)$$

The weight fraction of gel at $X = \Psi$ is given by

$$\bar{W}_g(\Psi) = \frac{1}{\Psi}\int_0^{\Psi} W_g(\theta,\Psi)\, d\theta \tag{30}$$

Using eq 29 and 30, one can easily calculate the weight fraction of gel as a function of conversion, if $\rho(\theta,\Psi)$, which is the effective cross-linking density at $X = \Psi$ for the primary molecules which were born at $X = \theta$, is known.

Next, let us consider the functional form of $\rho(\theta,\Psi)$ for vinyl/divinyl copolymerization without chain transfer to polymer for simplicity. In this case it is convenient to consider the life of a polymer molecule and to distinguish two kinds of cross-linking. Now let us assume that the reaction shown in Figure 2 occurs at conversion Ψ and that the primary polymer molecule (A) was produced at conversion θ. At $X = \Psi$ the polymer radical (B) attacks the pendant double bond in the primary molecule (A), which results in a cross-linkage between two primary molecules. In this case, from the point of view of molecule B, this cross-linkage is formed immediately during its growth by polymerization ($\rho_i(\Psi)$). But, from the point of view of molecule A, this cross-linkage is formed after the primary polymer molecule (A) was formed, so that it can be considered as an additional amount of cross-linking ($\rho_a(\theta,\Psi)$). At $X = \Psi$ the cross-linking density of the primary molecules that were formed at $X = \theta$ is given by

$$\rho(\theta,\Psi) = \rho_i(\theta) + \rho_a(\theta,\Psi) \qquad (31)$$

The concept of the above equation was also originally proposed by Flory in 1947 for diene polymers.[21] However, this concept has not been generalized until now.

The average cross-linking density at $X = \Psi$ is given by

$$\bar{\rho}(\Psi) = \frac{1}{\Psi}\int_0^{\Psi} \rho(\theta,\Psi)\,\mathrm{d}\theta \qquad (32)$$

The pseudokinetic rate constants for each cross-linking type can be defined exactly as follows:

$$k^*_{pi}(\Psi) = k^*{}_p{}^0(\Psi)\{\bar{F}_2(\Psi) - \bar{\rho}_a(\Psi) - \bar{\rho}_c(\Psi)\} \qquad (33)$$

$$k^*_{pa}(\theta,\Psi) = k^*{}_p{}^0(\Psi)\{F_2(\theta) - \rho_a(\theta,\Psi) - \rho_c(\theta,\Psi)\} \qquad (34)$$

where ρ_c is the cyclization density, which is not effective in increasing the size of the molecule, and $\bar{F}_2$ and F_2 are mole fractions of divinyl monomer in the copolymer chain of accumulated and instantaneously produced polymer, and

$$k^*{}_p{}^0(\Psi) = k^*_{p13}\Phi^{\bullet}{}_1(\Psi) + k^*_{p23}\Phi^{\bullet}{}_2(\Psi) + k^*_{p33}\Phi^{\bullet}{}_3(\Psi)$$

Practically, $k^*_p(\Psi)$ can be considered constant when the mole fraction of divinyl monomer in the monomer mixture is small ($f_2 \ll 1$). In the above equation, the subscript 1 is used to designate vinyl monomer, 2 is used for divinyl monomer, and 3 is used for the pendant double bonds.

Applying these pseudokinetic rate constants, one can easily calculate each cross-linking density as follows. For $\rho_i(\Psi)$

$$\rho_i(\Psi) = \frac{k^*_{pi}(\Psi)\Psi}{k_p(1-\Psi)} = \frac{k^*{}_p{}^0\{\bar{F}_2(\Psi) - \bar{\rho}_a(\Psi) - \bar{\rho}_c(\Psi)\}\Psi}{k_p(1-\Psi)} \qquad (35)$$

where $\bar{\rho}_a(\Psi)$ and $\bar{\rho}_c(\Psi)$ are given by

$$\bar{\rho}_a(\Psi) = \frac{1}{\Psi}\int_0^{\Psi} \rho_a(\theta,\Psi)\,\mathrm{d}\theta = \frac{1}{\Psi}\int_0^{\Psi} \rho_i(\theta)\,\mathrm{d}\theta = \frac{\bar{\rho}(\Psi)}{2}$$

$$\bar{\rho}_c(\Psi) = \frac{1}{\Psi}\int_0^{\Psi} \rho_c(\theta,\Psi)\,\mathrm{d}\theta$$

For $\rho_a(\theta,\Psi)$

$$\frac{\partial \rho_a(\theta,\Psi)}{\partial \Psi} = \frac{k^*_{pa}(\theta,\Psi)}{k_p(1-\Psi)} \qquad (36a)$$

If the cyclization density ρ_c is only a function of the birth conversion, namely, $\rho_c(\theta,\Psi) = \rho_c(\theta)$

$$\rho_a(\theta,\Psi) = \{F_2(\theta) - \rho_c(\theta)\}\left\{1 - \left(\frac{1-\Psi}{1-\theta}\right)^K\right\} \qquad (36b)$$

where $K = k^*{}_p{}^0/k_p$.

In an idealized case in which the reactivities of all types of double bonds are equal (reactivity ratios $r_1 = 0.5$ and $r_2 = 2.0$, the reactivity of pendant double bonds $K = 1$), cyclization does not occur ($\rho_c = 0$), and $f_{20} \ll 1$, $\rho(\theta,\Psi)$ is given by

$$\rho(\theta,\Psi) = \rho_i(\theta) + \rho_a(\theta,\Psi) = 2f_{20}\Psi \qquad (37)$$

which corresponds to the case where cross-linkages occur at random.[1,2,18]

But if the conditions deviate from ideality, the cross-linking density has a distribution and varies with birth conversion, θ. Figure 3 shows the cross-linking density distribution for the condition in which the reactivity of pendant double bonds is smaller ($k^*{}_p{}^0/k_p = 0.5$) and there is no cyclization. Though the cross-linking density is rather uniform at low conversions (Ψ), it becomes a strong function of θ at high conversions. As the cross-linking density is a very important parameter for the understanding of gel properties, this kind of information is important for the design of gel structure.

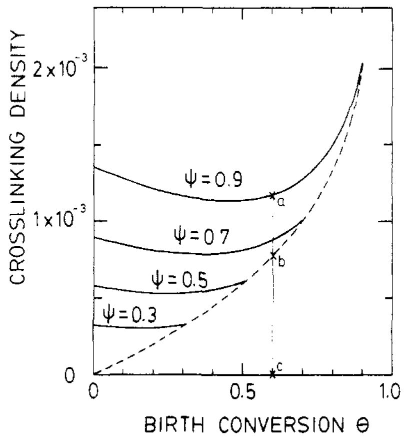

Figure 3. Cross-linking density distribution: $k^*{}_p{}^0/k_p = 0.5$; $r_1 = 0.5$; $r_2 = 2.0$; $f_{20} = 1 \times 10^{-3}$; $\rho_c = 0$; (—) $\rho(\theta,\Psi) = \rho_i(\theta) + \rho_a(\theta,\Psi)$; (- - -) $\rho_i(\theta)$. For example, with the present conversion $\Psi = 0.9$, the additional cross-linking density for the primary molecules born at conversion $\theta = 0.6$ is given by $\overline{ab}$, namely, $\overline{ab} = \rho_a(0.6, 0.9)$. $\overline{bc}$ gives instantaneous cross-linking density for primary molecules born at $\theta = 0.6$, namely, $\overline{bc} = \rho_i(0.6)$, $\overline{ac} = \rho(0.6, 0.9)$.

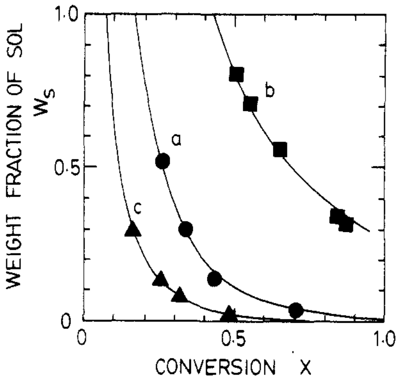

Figure 4. Weight fraction of sol; comparison with experimental data (MMA/EGDMA). Bulk polymerization at 70 °C with initiation of AIBN (0.3 wt %). (a) $f_{20} = 1.52 \times 10^{-3}$, without chain-transfer agent. (b) $f_{20} = 1.52 \times 10^{-3}$, with chain-transfer agent; CBr_4 0.027 mol/L. For (a) and (b) the same parameter $\bar{k}_p{}^{*0}/k_p = 0.6$ was used for the calculations. (c) $f_{20} = 5.05 \times 10^{-3}$, without chain-transfer agent. $\bar{k}^*{}_p{}^0/k_p = 0.4$.

Since we know the functional form of $\rho(\theta,\Psi)$, we can use eq 29 and 30. Some of the comparison with experimental data[22] are shown in Figure 4. For these cases with low mole fractions of divinyl monomer, the effect of cyclization should not be significant, and we therefore used the following pseudokinetic rate constants:

$$k^*_{pi}(\Psi) = \bar{k}^*{}_p{}^0\{\bar{F}_2(\Psi) - \bar{\rho}_a(\Psi)\} \qquad (33')$$

$$k^*_{pa}(\theta,\Psi) = \bar{k}^*{}_p{}^0\{F_2(\theta) - \rho_a(\theta,\Psi)\} \qquad (34')$$

with $\bar{k}^*{}_p{}^0$ assumed constant as a first approximation. Since the effect of diffusion-controlled termination in the network polymer is far more significant than that for linear polymers, the primary chain length drift should be fairly significant. At present, it is unclear how to estimate the decrease in the termination rate constant theoretically, and therefore, an empirical correlation shown in eq 38 was applied.

$$k_t = k_{t0} \quad \text{for} \quad X < Z_2$$

$$k_t = k_{t0}\exp\{-Z_1(X - Z_2)\} \quad \text{for} \quad X > Z_2 \qquad (38)$$

Two adjustable parameters, Z_1 and Z_2, were estimated

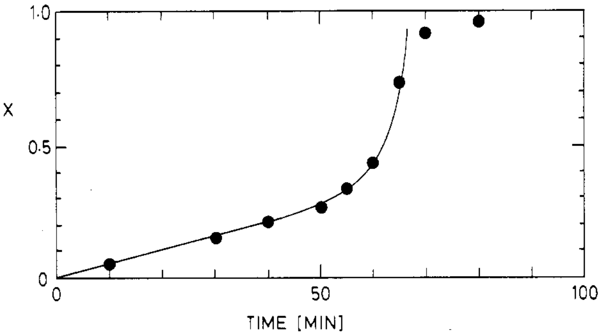

Figure 5. Time–conversion curve: $f_{20} = 1.52 \times 10^{-3}$, without chain-transfer agent. $Z_1 = 18.0$; $Z_2 = 0.193$.

from the time–conversion curve. One of the curve fittings to the time–conversion data is shown in Figure 5. The calculations agree with data over a useful range of conversion. This kind of correlation is necessary even when one uses the statistical methods of Flory and others to account for the primary chain length drift.

Even with these rough approximations the calculation results agree with experimental data fairly well. At present, since we do not consider the effect of cyclization, we cannot comment on the general tendencies of reactivity of pendant double bonds and cycle formation to change with conversion. It is worth noting that the reactivity of pendant double bonds seems not to depend on the primary chain length, since in Figure 4 the primary chain length for case b is about one-third that for case a with the same $\bar{k}^*{}_p{}^0/k_p$ applied for the calculations. This result is in agreement with the observations of Landin and Macosko[23] who measured the number of pendant double bonds on polymer molecules in the pregelation period by ^{1}H NMR.

At present, the kinetics of diffusion-controlled reactions in free radical polymerization are not fully understood at high conversions, but the agreement with gel formation data is satisfactory, and therefore, this model seems applicable for the prediction of the actual gelation phenomena. (Some of the equations for other properties of interest can be found in another paper.[19])

Discussion

In order to build a realistic model for network formation in free radical polymerization, it is necessary to consider the following effects, which were not considered in the original Flory/Stockmayer model: (1) differences in the reactivities of monomeric double bonds; (2) the reactivity of pendant double bonds; (3) the effect of cyclization. The effect of differences in the reactivities of monomeric double bonds can conveniently be included in the present models through the use of reactivity ratios. There are, however, rather large variations in the published values of reactivity ratios for copolymerization of vinyl/divinyl monomers. When the reactivity ratios are estimated in experiments with high mole fraction of divinyl monomer, one should not forget to account for the consumption of monomer by the radical centers located on pendant double bonds. Once valid reactivity ratios are determined, the present kinetic models can account for the effect of compositional drift during network formation quite rigorously.

The reactivity of pendant double bonds can be accounted for in the present models through the parameter $k^*{}_p{}^0/k_p$. This reactivity ratio may be affected not only by chemical effects but also by physical effects. In the pregelation period, the physical effects may be explained by the schematic diagram shown in Figure 6. The reaction between huge molecules (A and B) may be hindered sterically since there are many inaccessible pendant double bonds and radical centers. The reduction in the reactivity between huge molecules has a significant effect on the formation of the gel molecule. Especially, when the mole fraction of divinyl monomer is high, the apparent reactivity of pendant double bonds is suppressed by the tighter structure. However, the reaction between a huge molecule (A) and a small molecule (C) may not be hindered physically due to the high mobility of the small molecule. Since the mole fractions of radical centers and pendant double bonds located on small molecules are far higher than those on huge molecules in the pregelation period, the overall consumption rate of pendant double bonds may not decrease. Deviation from basic models including the present kinetic model may arise from this chain length dependent reaction of cross-linking, especially when the mole fraction of divinyl monomer is high.

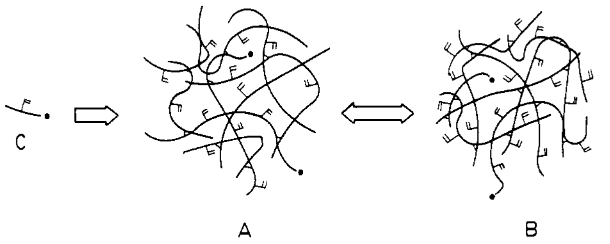

Figure 6. Physical effect on the reactivity of pendant double bonds (pregelation period). The reaction between huge molecules A and B may be slower than the overall reaction rate since there are inaccessible pendant double bonds and radical centers. However, the reaction between A and C may not be hindered sterically.

The apparent decrease in the pendant double bond reactivity may be enhanced by intramolecular reactions, i.e., cyclization. The fraction of internally cyclized pendant double bonds is as high as 40% in diallyl phthalate[24] and the polymer chains are extensively cyclized with the formation of a relatively large number of small rings at low conversions for styrene/*p*-divinylbenzene.[25] The fraction of intramolecular cyclization depends strongly on dilution, mole fraction of divinyl monomer, solvent used, and, to a lesser extent, the length of the cross-linker chain.[25–27] As for the theoretical treatment of cyclization, several studies have been done for solid polymers[28] and polycondensation.[29–36] For free radical polymerization, Dusek and Ilavsky[37] proposed a model in the context of the cascade theory. One of the important features of cyclization is that it is controlled not by the conventional rate law using average concentrations of functional groups but by conformational statistics of the sequence of bonds.

In our formalism, it is convenient to divide the intramolecular reactions into two groups, namely, primary and secondary.[23] The primary cyclization is the cycle formed within one primary molecule, while the secondary cyclization is formed between two or more primary molecules. The mathematical importance of the difference between primary and secondary cyclization is that primary cyclization is solely a function of the birth conversion ($\rho_{c,p}(\theta)$), while secondary cyclization is a function of both birth conversion and present conversion ($\rho_{c,p}(\theta,\Psi)$). Simple models for each type of cyclization will be shown in a future publication. When the effect of cyclization is significant, the apparent reactivity of pendant double bonds may be enhanced from the point of view of the consumption rate of pendant double bonds.

There are still many problems to be solved to build a more realistic model for network formation, and more experimental information will be necessary to clarify these complicated phenomena. We do, however, believe that the kinetic models proposed in this paper will provide greater insight into the phenomenon of network formation in free radical polymerization.

Conclusions

We have developed kinetic models for both pre- and postgelation periods by applying pseudokinetic rate constants. The concept of the pseudokinetic constant method has proven to be quite useful for treating a free radical polymerization system which consists of two or more components not only for linear polymers but also for branched polymers.

For the pregelation period we have developed a model that consists of general moment equations. This model, which considers all of the important reactions in free radical polymerization, can be used to make calculations of average properties during network formation.

Flory's theory of network formation has been generalized for free radical polymerization by applying the concept of pseudokinetic rate constants. This model has given satisfactory predictions for gel/sol ratios.

Though our kinetic models are, in principle, equivalent to the classical theories which enjoy the simplicity of a mean-field theory, our models are more general and realistic than the former classical models for free radical polymerization systems.

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Appendix

A. Formulations of the Moment Equations. For a batch reactor, balanced equations of a polymer radical with chain length r can be found as eq A9a and A9b in the Appendix of an earlier paper.[10] From those equations, one can readily formulate the following equation

$$\frac{1}{V}\frac{\mathrm{d}(VY_i)}{\mathrm{d}t} = \frac{1}{V}\sum_{r=1}^{\infty} r^i \frac{\mathrm{d}(V[\mathrm{R}^{\bullet}{}_r])}{\mathrm{d}t} = R_{\mathrm{I}} + (k_{\mathrm{fm}}[\mathrm{M}] + k_{\mathrm{fT}}[\mathrm{T}])Y_0 + k_{\mathrm{fP}}Q_{i+1}Y_0 + k^*{}_{\mathrm{p}}\sum_{j=1}^{i}\binom{i}{j}Q_{j+1}Y_{i-j} + k_{\mathrm{p}}[\mathrm{M}]\sum_{j=0}^{i-1}\binom{i}{j}Y_j - \{k_{\mathrm{fm}}[\mathrm{M}] + k_{\mathrm{fT}}[\mathrm{T}] + (k_{\mathrm{td}} + k_{\mathrm{tc}})Y_0 + k_{\mathrm{fP}}Q_1\}Y_i \quad (\mathrm{A1})$$

If the steady-state hypothesis is invoked

$$y_i = \left[\tau + \beta + C_{\mathrm{p}(i+1)} + \sum_{j=1}^{i}\binom{i}{j}C^*{}_{\mathrm{p}(j+1)}y_{i-j} + \sum_{i=0}^{i-1}\binom{i}{j}y_j\right] \bigg/ (\tau + \beta + C_{\mathrm{p1}}) \quad (\mathrm{A2})$$

In practice, τ and β are 10^{-2}–10^{-6} in free radical polymerizations, and therefore

$$\tau + \beta \ll 1 \leq y_i \quad (\mathrm{A3})$$

Furthermore, $y_i \gg y_{i-1}$, as was shown in Figure 5 in an earlier paper.[10]

$$\sum_{j=0}^{i-1}\binom{i}{j}y_i \simeq iy_{i-1} \quad (\mathrm{A4})$$

Therefore, eq A2 reduces to eq 19 in the text.

The balance equation for polymer molecule with chain length r can be found in eq A9c in an earlier paper.[10] Q_i can readily be formulated as follows:

$$\frac{1}{V}\frac{\mathrm{d}(VQ_i)}{\mathrm{d}t} = \{k_{\mathrm{fm}}[\mathrm{M}] + k_{\mathrm{fT}}[\mathrm{T}] + (k_{\mathrm{td}} + k_{\mathrm{tc}})Y_0 + k_{\mathrm{fp}}Q_1\}Y_i + \frac{1}{2}k_{\mathrm{tc}}\sum_{j=1}^{i-1}\binom{i}{j}Y_jY_{i-j} - (k^*{}_{\mathrm{p}} + k_{\mathrm{fp}})Q_{i+1}Y_0 \quad (\mathrm{A5})$$

The above equation can be transformed into the conversion domain X by using eq A6.

$$\left(\frac{[\mathrm{M}_0]V_0}{V}\right)\frac{\mathrm{d}X}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}^{\bullet}] \quad (\mathrm{A6})$$

$$\therefore \frac{\mathrm{d}q_i}{\mathrm{d}X} = (\tau + \beta + C_{\mathrm{p1}})y_i + \frac{\beta}{2}\sum_{j=1}^{i-1}\binom{i}{j}y_jy_{i-j} - C^*{}_{\mathrm{p}(i+1)} - C_{\mathrm{p}(i+1)} \quad (\mathrm{A7})$$

By substitution of eq A2 into eq A7, the following equation can be derived:

$$\frac{\mathrm{d}q_i}{\mathrm{d}X} = \tau + \beta + \sum_{j=0}^{i-1}\binom{i}{j}y_j + \frac{\beta}{2}\sum_{j=1}^{i-1}\binom{i}{j}y_jy_{i-j} + \sum_{j=1}^{i-1}\binom{i}{j}C^*{}_{\mathrm{p}(j+1)}y_{i-j} \quad (\mathrm{A8})$$

Applying the relationships (A3) and (A4), we obtain eq 22 in the text.

A kinetic model which involves the moment equations was also derived by Mikos et al.[38] But it is worth noting here that their equations give the moments of the primary molecules, so that their method can only calculate the properties of linear polymers that would be available if all cross-links were severed, while the present equations can be used to calculate the properties of molecules which include cross-links. Therefore, in the method by Mikos et al. the critical change cannot be derived. Furthermore, their definition of gel point is clearly incorrect (eq 24 in the ref 38). The number of effective cross-links per primary molecule υ_{e} is given by

$$\upsilon_{\mathrm{e}} = \bar{P}_{\mathrm{np}}\rho \quad (\mathrm{A9})$$

where $\bar{P}_{\mathrm{np}}$ is the accumulated number-average chain length of the primary molecules. From the statistical theory of Flory[1] and Stockmayer,[2] the condition at gel point is given by

$$\bar{P}_{\mathrm{wp}}\rho = 1 \qquad (\rho \ll 1) \quad (\mathrm{A10})$$

where $\bar{P}_{\mathrm{wp}}$ is the accumulated weight-average chain length of the primary molecules. Since $\bar{P}_{\mathrm{wp}} \geq \bar{P}_{\mathrm{np}}$, at the gel point

$$\upsilon_{\mathrm{e}} \leq 1 \quad (\mathrm{A11})$$

When $f_{20} \ll 1$, the correct gel point in the notation of Mikos et al.[38] will be given by eq A14.

$$\bar{P}_{\mathrm{wp}} \simeq \Psi_{2,0,0}/\Psi_{1,0,0} \quad (\mathrm{A12})$$

$$\rho \simeq \frac{\Psi_{0,0,1}}{\Psi_{1,0,0} + \Psi_{0,1,0} + \frac{1}{2}\Psi_{0,0,1}} \quad (\mathrm{A13})$$

$$\therefore \bar{P}_{\mathrm{wp}}\rho = \frac{\Psi_{2,0,0}\Psi_{0,0,1}}{\Psi_{1,0,0}(\Psi_{1,0,0} + \Psi_{0,1,0} + \frac{1}{2}\Psi_{0,0,1})} = 1 \qquad (f_{20} \ll 1) \quad (\mathrm{A14})$$

B. A Calculation Method of Equation 26. It is possible to solve eq 26 by combining it with an equation for the critical change of weight-average chain length of sol polymers. Two types of equation have been proposed:

Flory/Stockmayer Theory[1,2]

$$\bar{P}_{\mathrm{w,s}} = c(1 - X_c/X)^{-1} \tag{B1}$$

Percolation Theory[7]

$$\bar{P}_{\mathrm{w,s}} = c'(1 - X_c/X)^{-1.74} \tag{B2}$$

where X_c is the conversion at gel point. As we have already proven in the previous paper,[10] our model is equivalent to the Flory/Stockmayer model. Therefore, eq B1 is more appropriate to use in our model. On the basis of the Flory/Stockmayer theory

$$\bar{P}_{\mathrm{w,s}} = \bar{P}_{\mathrm{wp,s}} \frac{1 + \rho'}{1 - \rho'(\bar{P}_{\mathrm{wp,s}} - 1)} \simeq \frac{\bar{P}_{\mathrm{wp,s}}}{1 - \rho'\bar{P}_{\mathrm{wp,s}}} \tag{B3}$$

where ρ' is the cross-linking density of sol polymers and is given by

$$\rho' \simeq \rho(1 - W_{\mathrm{g}}) \tag{B4}$$

Applying eq B3 and B4 and assuming k_{t} is independent of the size of the molecules, one can calculate the initial slope of gel growth as follows:

$$\lim_{X \to X_c} \frac{\mathrm{d}W_{\mathrm{g}}}{\mathrm{d}X} = \frac{(k^*{}_{\mathrm{p}}/k_{\mathrm{p}})^2 X_c \bar{P}_{\mathrm{wp}}|_{X=X_c}}{(1 - X_c)^2} P_{\mathrm{wp}}|_{X=X_c} \tag{B5}$$

$$\simeq \frac{k^*{}_{\mathrm{p}}}{k_{\mathrm{p}}} P_{\mathrm{wp}}|_{X=X_c} \qquad (X_c \ll 1) \tag{B6}$$

Equation B5 or B6 and $W_{\mathrm{g}}|_{X=X_c} = 0$ give initial conditions for eq 26.

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