Molecular Weight Distribution in Free-Radical Polymer Modification with Cross-Linking: Effect of Chain-Length-Dependent Termination

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ABSTRACT: A general equation of molecular weight distribution has been derived for free-radical polymer modification with cross-linking. The equation takes into account chain-length-dependent diffusion-controlled radical termination. It reduces to Saito's equation when the termination becomes chain-length independent. A simple three-parameter chain-length-dependence function is employed. Calculations of molecular weight development, gel point, and gel/sol fraction for both polymer and radical populations have been made numerically with a uniform initial distribution. It has been shown that the chain-length-dependent termination has a strong effect on the molecular weight development and gelation behavior. It causes significant deviation from the well-studied random process of cross-linking. It delays gel point but accelerates gel growth.

Introduction

Polymer modification allows the conversion of commodity polymers to value-added specialty polymers. Such chemical modifications include grafting, chain scission, branching, and cross-linking and are often implemented via free-radical mechanisms during reactive processing.[1,2] A typical example, which has recently attracted considerable attention, is the system of polyolefin/peroxide. Peroxide as a radical initiator is mixed with the polymer. At an elevated temperature, the peroxide molecules are decomposed into primary radicals. These primary radicals have sufficient energy to abstract hydrogen atoms from polymer backbones and thus generate backbone radicals. The backbone radicals may undergo β-scission, which breaks the polymer chain into two segments. Two polymer radicals may also recombine with each other, which results in branching. Continuous branching eventually leads to cross-linking: the formation of a gel molecule. A gel molecule is a three-dimensional polymer network that has an infinitely large molecular weight, as defined by Carothers.[3] It is not soluble no matter how good the solvent is but may be swellable. In the presence of coagents, the backbone radicals may react with the coagent molecules to cause grafting.

The formation of polymer network is an important feature in the free-radical polymer modifications, particularly for polyethylenes. In almost all of the commercial exercises, the level of cross-linking must be carefully controlled. An excessive amount of cross-linking may cause inferior product properties and/or damage to equipment during processing. There are also many other cases in which cross-linking is absolutely unwanted and should be prevented by chemical means. No matter whether cross-linking is desirable or not, it is essential to understand the molecular processes involved in polymer network formation in order to have good control over the polymer properties. To this end, many gelation models have been developed following the pioneering work of Flory[4] and Stockmayer.[5,6] Among many others, the elegant formulation of Saito[7,8] is most useful for predicting molecular weight distribution for a polymer undergoing random cross-linking. Saito's equation was originally derived for polymer modifications by high-energy radiation. The change in molecular weight distribution is a function of the degree of cross-linking, which can be further related to radiation dosage. Saito's equation is also applicable to peroxide-initiated polymer modifications. In such cases, the degree of cross-linking should be related to the peroxide concentration and chemical reactivity.

An important assumption involved in the derivation of Saito's equation, as well as in all others, is that the rate of radical termination is chain-length independent. The event of cross-linking requires combination termination of two backbone radicals. The molecular processes involved in this reaction are very complex, generally consisting of three definable steps.[9] First, two radical molecules migrate together via translational diffusion and then the radical centers reorient by segmental diffusion. Finally, they overcome the chemical activation barrier and react. Activation energies for radical−radical reactions are usually very small. The termination reaction is therefore always diffusion-controlled, particularly for the modifications carried out in polymer melts where polymer chains are severely entangled with one another. The rate-determining step is either translational diffusion or segmental diffusion of the polymer chains. It is well-known that the diffusivity of a polymer chain strongly depends on its chain length. The rate of radical termination is therefore inherently chain-length dependent.

The chain-length-dependent termination has been a matter of study for over three decades.[10] Many functions have been proposed to relate the termination rate constant to reacting polymer chain lengths.[11−16] However, those investigations exclusively focused on free-radical polymerization systems with linear chains. Their objective was to provide a mechanistic explanation for the Trommsdoff[17] or "gel" effect—an autoacceleration in polymerization rate at intermediate monomer conversions caused by diffusion-controlled radical termination.

The effect of chain-length-dependent termination on free-radical polymer modification with cross-linking has

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not been examined. Does the dependence affect the molecular weight development and gelation behavior of the cross-linking system? If so, how significant is the effect? Answers to these questions are of fundamental importance and serve as the objective of this paper.

Theory

The polymer modification system to be considered in this work includes the following elementary reactions,

hydrogen abstraction

$$R_0 + \begin{pmatrix} P_\mathrm{r} \\ P^\mathrm{g} \end{pmatrix} \xrightarrow{rK_\mathrm{ha}} \begin{pmatrix} R_\mathrm{r} \\ R^\mathrm{g} \end{pmatrix} \tag{1}$$

radical termination by combination

$$\begin{aligned} R_r + \mathrm{R}_s &\xrightarrow{K_\mathrm{t}(r,s)} \mathrm{P}_{r+s} \\ R_r + \mathrm{R}^\mathrm{g} &\xrightarrow{K_\mathrm{t}(r,\infty)} \mathrm{P}^\mathrm{g} \\ R^\mathrm{g} + \mathrm{R}^\mathrm{g} &\xrightarrow{K_\mathrm{t}(\infty,\infty)} \mathrm{P}^\mathrm{g} \end{aligned} \tag{2}$$

where R_0 represents the molar concentration of primary radicals, which are generated by thermal decomposition of initiator molecules (mostly peroxides); P_r is the concentration of polymer chains having r monomeric units ($r \geq 1$); R_r and R_s are the concentrations of radical chains having r and s units; P^g and R^g represent the monomeric units and radical centers that belong to a gel molecule. It should be noted that the number of hydrogen (or any other abstractable atoms) associated with a polymer chain P_r is proportional to its chain length r, and therefore, the rate constant of a primary radical abstracting atoms from the polymer P_r is rK_ha in reaction 1. $K_\mathrm{t}(r,s)$ is the rate constant of termination by combination between two radical species having chain lengths r and s, respectively.

Reaction 2 offers a mechanism for joining two complex molecules together. According to Flory,[18] such a reaction is essential to yield circuitous connections within the chain structure. It is therefore responsible for polymer network formation. It is well-known that this system is capable of gelling if the termination rate constant, K_t, is chain-length independent, and numerous papers[19−22] have been published to report its gelation performance. In this work, we introduce a chain-length-dependence function to the scheme and investigate its effect on the molecular weight development and gelation behavior of the same system. Comparisons will be made to the well-established chain-length-independent results.

An effective starting point to develop a kinetic model is to constitute population balance equations for individual reactant species. The population balance equations for R_0 and P_r are

$$\frac{\mathrm{d}R_r}{\mathrm{d}t} = K_\mathrm{ha}R_0rP_r - [\sum_{s=1}^{\infty}K_\mathrm{t}(r,s)R_s + K_\mathrm{t}(r,\infty)Y_0^\mathrm{g}]R_r \tag{3}$$

$$\frac{\mathrm{d}P_r}{\mathrm{d}t} = \frac{1}{2}\sum_{s=1}^{r-1}K_\mathrm{t}(s,r-s)R_sR_{r-s} - K_\mathrm{ha}R_0rP_\mathrm{r} \tag{4}$$

where t is the reaction time; Y_0^g is the concentration of radicals associated with a gel molecule; $K_\mathrm{t}(r,\infty)$ is the termination rate constant between a sol radical R_r and a gel radical (note: a gel molecule has an infinitely large molecular weight). The factor $^1/_2$ in (4) accounts for double counting of the termination events due to the symmetry of $K_\mathrm{t}(s,r-s)R_sR_{r-s}$.

Let us define the following parameters: radical number fraction,

$$\phi_r = R_\mathrm{r}/Y_0 \tag{5}$$

polymer weight fraction,

$$w(r) = rP_r/Q_1 \tag{6}$$

where Y_0 and Q_1 are the total concentrations of radicals and monomeric units, and the latter remains constant during the course of polymer modification. It is obvious that the radical and polymer gel/sol fractions can be calculated using

$$y_0^\mathrm{s} = 1 - y_0^\mathrm{g} = \sum_{r=1}^{\infty}\phi_r \tag{7}$$

$$w_s = 1 - w_\mathrm{g} = \sum_{r=1}^{\infty}w(r) \tag{8}$$

Keep in mind that y_0^g and y_0^s are the number fractions of radicals associated with gel and sol molecules while w_g and w_s are the weight fractions of polymer chains that belong to gel and sol populations, respectively.

According to Smoluchowski,[23] the rate constant of a bimolecular reaction is proportional to the pairwise mutual diffusion coefficient. For the case of center-of-mass diffusion, the mutual diffusion coefficient equals the sum of the self-diffusion coefficients of the two individual reactants, i.e.,

$$K_t(r,s) \propto D_{r,s} = D_r + D_s \tag{9}$$

Although the Smoluchowski equation was originally proposed for reactions involving small molecules, the same relationship has long been assumed for macromolecules with some modification. In this work, we propose the following function for the chain-length-dependent termination rate constant,

$$K_t(r,s) = K_t\left[\frac{\epsilon(r) + \epsilon(s)}{2} + \epsilon_0\right] \tag{10}$$

The first term on the right-hand side represents the termination probability contributed by center-of-mass diffusions of the two radical species. The second term provides a residue termination caused by segmental reorientation of the radical chains. In the presence of a vinyl monomer, this term encompasses the residual termination contributed by propagation−diffusion[10,16].

Substituting eq 10 into eq 3 yields

$$\frac{\mathrm{d}R_r}{\mathrm{d}t} = K_\mathrm{ha}R_0rP_r - \frac{1}{2}[\epsilon(r) + y_0^{s,\epsilon} + \epsilon(\infty)y_0^\mathrm{g} + 2\epsilon_0]K_tY_0R_r \tag{11}$$

where

$$y_0^{s,\epsilon} = \sum_{r=1}^{\infty}\epsilon(r)\phi_r \tag{12}$$

The mass balance of total radical concentration follows

$$\frac{\mathrm{d}Y_0}{\mathrm{d}t} = K_{\mathrm{ha}}R_0Q_1 - [\sum_{r=1}^{\infty}\sum_{s=1}^{\infty}K_t(r,s)R_rR_s + 2\sum_{r=1}^{\infty}K_t(r,\infty)R_rY_0^{\mathrm{g}} + K_t(\infty,\infty)Y_0^{\mathrm{g}}Y_0^{\mathrm{g}}] = K_{\mathrm{ha}}R_0Q_1 - [y_0^{s,\epsilon} + \epsilon(\infty)y_0^{\mathrm{g}} + \epsilon_0]K_tY_0Y_0 \quad (13)$$

Introducing the stationary-state hypothesis into eqs 11 and 13, i.e., $\mathrm{d}Y_0/\mathrm{d}t \approx 0$ and $\mathrm{d}R_r/\mathrm{d}t \approx 0$, and then dividing eq 11 by eq 13 yields

$$\phi_r = \frac{y_0^{s,\epsilon} + \epsilon(\infty)y_0^{\mathrm{g}} + \epsilon_0}{\frac{1}{2}[\epsilon(r) + y_0^{s,\epsilon} + \epsilon(\infty)y_0^{\mathrm{g}} + 2\epsilon_0]}\mathrm{w(r)} \quad (14)$$

For convenience of discussion, it is preferable to use the density of cross-linkages x as an independent variable instead of time t. The development of the density of cross-linkages can be followed during the course of polymer modification with cross-linking by

$$\frac{\mathrm{d}xQ_1}{\mathrm{d}t} = \frac{1}{2}K_{\mathrm{ha}}R_0Q_1 = \frac{1}{2}K_tY_0Y_0[y_0^{s,\epsilon} + \epsilon(\infty)y_0^{\mathrm{g}} + \epsilon_0] \quad (15)$$

Substituting eq 10 into eq 4 and dividing by eq 15 yields

$$\frac{1}{r}\frac{\mathrm{d}w(r)}{\mathrm{d}x} = -2w(r) + \frac{1}{2}\sum_{s=1}^{r-1}\frac{\epsilon(s) + \epsilon(r-s) + 2\epsilon_0}{y_0^{s,\epsilon} + \epsilon(\infty)y_0^{\mathrm{g}} + \epsilon_0}\phi_s\phi_{r-s} \quad (16)$$

In principle, eqs 16, 14, 12, 8, and 7 can be used solved simultaneously for changes of weight fraction distribution of sol polymers $w(r)$, number fraction distribution of sol radicals ϕ_r, weight fraction of gel polymers w_{g}, and number fraction of gel radicals y_0^{g}, with respect to the density of cross-linkages x, provided the chain-length-dependence function ϵ is given. Other chain properties of interest include the following chain length averages for both polymer and radical populations,

$$\bar{r}_{\mathrm{N}} = \sum_{r=1}^{\infty}w(r)/\sum_{r=1}^{\infty}\frac{w(r)}{r} \qquad \bar{r}_W = \sum_{r=1}^{\infty}rw(r)/\sum_{r=1}^{\infty}w(r)$$

$$\bar{r}_Z = \sum_{r=1}^{\infty}r^2w(r)/\sum_{r=1}^{\infty}rw(r)$$

$$\bar{r}_{\mathrm{N}}^{\bullet} = \sum_{\mathrm{r}=1}^{\infty}\mathrm{r}\phi_{\mathrm{r}}/\sum_{\mathrm{r}=1}^{\infty}\phi_{\mathrm{r}} \qquad \bar{r}_W^{\bullet} = \sum_{r=1}^{\infty}r^2\phi_r/\sum_{r=1}^{\infty}r\phi_r \quad (17)$$

It should be pointed out that many assumptions are employed in derivation of the present theory. Major assumptions include the following: (1) monoradical assumption, i.e., no polymer molecules are allowed to have more than one radical center with an individual chain bearing either one radical center or no radical at all; (2) the stationary-state hypothesis, which suggests that for individual polymer species the rate of generation is approximately equal to that of consumption; (3) random atom abstraction, i.e., atoms on monomeric units have equal probability to be abstracted regardless of their location in a polymer chain; and (4) no chain cyclization. Since a gel molecule has an infinitely large molecular weight, intuitively it is likely to have many radical centers attached onto its structure. Such polyradical chains may also be present prior to the gel point. Justification and/or clarification of the first two assumptions has recently been carried out for polymerization[24,25] and polymer modification systems.[26] It has been found that the errors introduced by the simultaneous use of the monoradical assumption and stationary-state hypothesis are minor for random polymer gelation calculation.

Results and Discussion

Chain-Length-Independent Termination. When the termination becomes chain-length independent, i.e., $\epsilon(r) = \epsilon(\infty) = 1$ and $\epsilon_0 = 0$, the following relationships exist: $y_0^{s,\epsilon} = y_0^s$, $\phi_r = w(r)$, and as a result, $y_0^{\mathrm{g}} = w_{\mathrm{g}}$, $\bar{r}_{\mathrm{N}}^{\bullet} = \bar{r}_W$, and $\bar{r}_W^{\bullet} = \bar{r}_Z$. Equation 16 also reduces to Saito's equation[7,8]

$$\frac{1}{r}\frac{\mathrm{d}w(r)}{\mathrm{d}x} = -2w(r) + \int_0^r w(s)w(r-s)\,\mathrm{d}s \quad (18)$$

(note: the number of monomeric units r is treated as a continuous variable in eq 18). The condition of chain-length-independent termination indicates a random process of cross-linking. The process of random cross-linking has been studied for over a half-century since the pioneering work of Flory[4] and Stockmayer.[5,6] Equation 18 has been solved analytically for a uniform initial distribution[27]

$$w(r) = \frac{(2xr)^{r-1}\mathrm{e}^{-2xr}}{r!} \quad (19)$$

with the initial chain length chosen to be unity, and for a random initial distribution[28,29]

$$w(r) = \tau^2re^{-(\tau+2x)r}\sum_{n=0}^{\infty}\frac{(2x)^n\tau^{2n}\mathrm{r}^{3n}}{(n+1)!(2n+1)!} \quad (20)$$

where τ is the reciprocal of the number-average chain length of primary polymer chains. The chain-length-dependent termination inevitably causes departure of the gelation behavior from the random process. In this work, the results of Saito's equation provide a basis for comparisons.

Chain-Length-Dependence Function. Although polymer diffusion in melts and solutions has received a deal of great attention for a long time, our knowledge is still rather rudimentary due to the complication of chain overlap and entanglement. Depending on polymer concentration and molecular weight, there may exist many regimes.[30] The diffusion behavior of polymer chains in each regime can be very complex and different, particularly when chain-length dependence is considered.[31–35] To remain general, we use the following two-parameter chain-length-dependence function in this work,

$$\epsilon(r) = 1 \qquad r \le r_{\mathrm{c}}$$

$$\epsilon(r) = (r_{\mathrm{c}}/r)^{\alpha} \qquad \mathrm{r} > r_{\mathrm{c}} \quad (21)$$

where r_{c} is a critical chain length above which a polymer chain starts to experience difficulty in diffusion; α is a nonnegative exponential factor, and thus, $\epsilon(\infty) = 0$. The value of α depends on polymer concentration, e.g., 0.6 at an infinite dilution,[36] 1 when the "screening" effect due to chain interaction is taken into account,[37] 2 according to the famous de Gennes reptation theory,[38] and 2.5 as derived by Bueche, who focused on the entanglement effect.[39]

Substituting eq 21 into eqs 14 and 16 finally results in

$$\phi_r = \frac{y_0^{s,\epsilon} + \epsilon_0}{\epsilon(r) + y_0^{s,\epsilon} + 2\epsilon_0}2w(r) \quad (22)$$

and

$$\frac{1}{r}\frac{\mathrm{d}w(r)}{\mathrm{d}x} = -2w(r) + \frac{1}{2}\sum_{s=1}^{r-1}\frac{\epsilon(s)+\epsilon(r-s)+2\epsilon_0}{y_0^{s,\epsilon}+\epsilon_0}\phi_s\phi_{r-s} \quad (23)$$

Substituting eq 22 into 12 yields

$$f(y_0^{s,\epsilon}) = 2\sum_{r=1}^{\infty}\frac{\epsilon(r)w(r)}{\epsilon(r)+y_0^{s,\epsilon}+2\epsilon_0} - \frac{y_0^{s,\epsilon}}{y_0^{s,\epsilon}+\epsilon_0} = 0 \quad (24)$$

which can be solved for $y_0^{s,\epsilon}$ to assure a closed form of eqs 22 and 23.

Equations 22−24 can be solved numerically to obtain the polymer and radical distributions. However, with an arbitrary initial distribution, the assignment is very laborious because of the large number of r, particularly when the system approaches the gel point. An examination reveals that, for the case of a uniform initial distribution, these equations are still applicable if the physical meanings of the parameters are changed as follows: the chain lengths r and s become the numbers of primary chains associated with a polymer molecule, and x becomes the number of cross-linkages per primary chain instead of per monomeric unit. In so doing, the number of differential equations is significantly reduced. Let us use the initial chain length 10^3 to illustrate this point. The possible chain lengths of polymer are 1×10^3, 2×10^3, 3×10^3, 4×10^3, ...; the chain length of 10^3 becomes a "basic unit". It is therefore necessary to solve only 10^3 differential equations to follow polymer species with chain length up to 10^6. The assignment then becomes tractable. In contrast, it requires 10^6 equations to carry out the same task for an arbitrary initial distribution. It should also be pointed out that this argument does not alter the numerical results if the physical meanings of the parameters remain the same but the initial chain length is chosen to be unity.

In this work, the differential equations, eq 23, were solved by Gear's method and eq 24 was solved by Newton's method.[40] Comparisons were made between the numerical solution of eq 18 and the corresponding analytical solution of eq 19. Errors were found to be negligible provided the number of differential equations was over 500.

Molecular Weight Development. Figure 1A shows the development of weight-fraction molecular weight distribution of sol polymers. The dotted lines are the results of Saito's equation of random cross-linking, eq 18 or 19, which does not consider chain-length-dependent termination. The weight fraction has a monotonous relationship with the chain length. The solid lines are calculated using eqs 21−24, which take into account the effect of chain-length-dependent termination. These curves exhibit a different distribution shape. The fractions of low chain lengths become smaller due to higher termination rates of these shorter chains. The differences between the solid and dotted curves become more severe with an increase in the density of cross-linkages. At the condition of $x = 0.5$, the dotted line intends to diverge indicating the gel point; however, the solid line still appears to have a finite upper limit.

Figure 1B shows the number-fraction molecular weight distribution of sol radicals under the same condition. Recall that the radical number fraction equals the polymer weight fraction if the termination is chain-length independent. The dotted lines in Figure 1B are therefore identical to those in Figure 1A. The features exhibited by the polymer weight-fraction distribution in Figure 1A become more profound for the radical number-fraction distribution when the chain-length-dependent termination is introduced. The fraction of the primary chains ($r = 1$) having radical centers is much lower than that without radicals. This reflects the nature of a free-radical polymer modification system: the radical population, though very small, is more dynamic and instantaneous than the large polymer population.

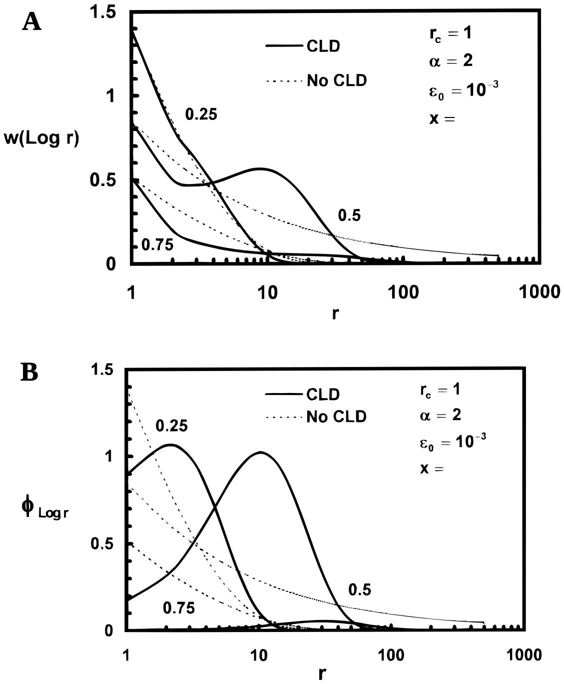

Figure 1. Change in molecular weight distribution during free-radical polymer modification with cross-linking: (A) weight fraction of polymer population, $w(r)$, and (B) number fraction of radical population, ϕ_r. Initial distribution is given by the uniform distribution with chain length r chosen to be unity. Distributions are normalized in a logarithm scale with the area under each curve equal to a sol fraction. The solid lines are the results of eqs 22−24, which takes into account chain-length-dependent termination. The parameters for the chain-length-dependence function, eq 21, are as follows: $r_c = 1$, $\alpha = 2$, $\epsilon_0 = 10^{-3}$. The densities of cross-linkage, x, are 0.25, 0.5, and 0.75. The dotted lines are the results of Saito's equation, eq 18 or 19, which does not consider chain-length-dependent termination. The chain-length-dependent termination shows a strong effect on the distribution shape and magnitude.

Figure 2A shows the development of the leading average chain lengths of sol polymers. It is well-known that the weight-average chain length as well as other average chain lengths of higher order (z, $z + 1$, etc.) diverge when the reaction system approaches the gel point, while the number-average chain length remains finite. With the chain-length-dependent termination, the average chain length profile shifts toward a higher density of cross-linkage. In the postgel regime, the decline of the chain lengths appears to be more drastic. In the radical population as shown in Figure 2B, the number-average chain length also diverges at the gel point. In a random cross-linking system, the number-average chain length of radical chains equals the weight-average of polymers; the weight-average of radicals equals the z-average of polymers; and so on. The radical population is always 1 order higher than that of polymers. The chain-length-dependent termination increases these differences, i.e., $\bar{r}^{\bullet}_{\mathrm{N}} > \bar{r}_W$, $\bar{r}^{\bullet}_W > \bar{r}_Z$, ...

Gel Point. It is well established that the density of cross-linkage at the gel point x_{gel}, equals 0.5 for a random cross-linking system.[4−8] In the case of a uniform initial distribution, each primary chain on

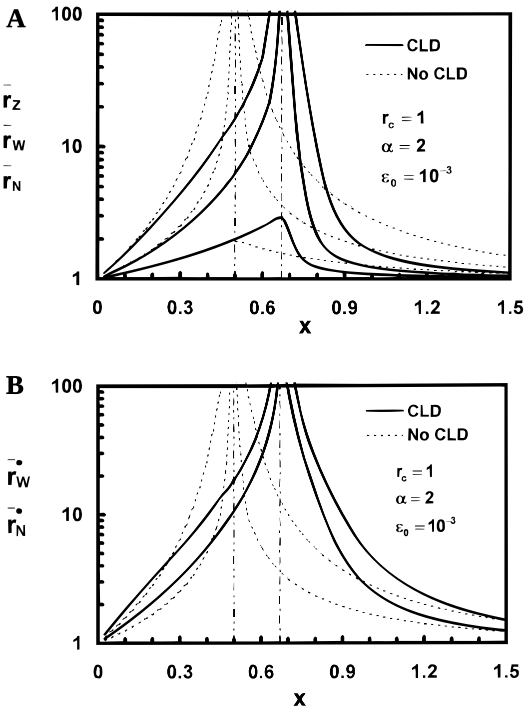

Figure 2. Molecular weight development during polymer modification with cross-linking. The solid lines take into account the effect of chain-length-dependent termination, eqs 22–24, while the dotted lines are the results of Saito's equation, eqs 18 and 19. The parameters for the chain-length dependence function, eq 21, are the same as Figure 1. (A) Number-, weight-, and z-average chain lengths, $\bar{r}_N$, $\bar{r}_W$, $\bar{r}_Z$ of polymers versus the density of cross-linkage. The average chain lengths of higher order, $\bar{r}_W$ and $\bar{r}_Z$, diverges when the reaction system approaches the gel point, while the number-average remains finite. (B) Number- and weight-average chain lengths, $\bar{r}^{\bullet}_N$, $\bar{r}^{\bullet}_W$, of radical chains. For the radical population, the number-average chain length also diverges at the gel point.

average should possess half a cross-linkage (i.e., one branching point) at the gel point. When the termination becomes chain-length dependent, the mechanism involved in radical termination becomes nonrandom. Radicals are no longer identical in terms of the termination reactivity. Those radicals associated with short chains are more active. The rates of termination events with respect to chain lengths are in the order of short–short > short–long > long–long. Since the favored short–short chain combination does not make a sufficient contribution to the molecular weight buildup, the chain-length-dependent termination always delays the gel point. The magnitude of discrepancies from the random process strongly depends on the three parameters of the chain-length dependence function, eqs 10 and 21. Figure 3 presents the values of x_{gel} versus α, r_c, and ϵ_0, respectively. The differences become minor with a decrease in α and/or an increase in r_c and ϵ_0.

Gel/Sol Fraction. Figure 4A shows the weight fraction of polymer chains that belong to a gel molecule w_g. In the case of random cross-linking, the gel fraction increases with the density of cross-linkage in a smooth manner. With chain-length-dependent termination, the development appears to be rather abrupt. Gel formation is delayed but the gel growth rate is significantly accelerated. The discrepancies are found to be greatest in the vicinity of the gel points. These fractions tend to merge at high cross-link densities. These features are more dramatic in the radical population as shown in Figure 4B. The number fraction of radicals attached onto the gel structure, y_0^g $(= 1 - y_0^s)$, increases almost instantaneously at the gel point. In the postgel regime, few radicals are associated with sol polymers.

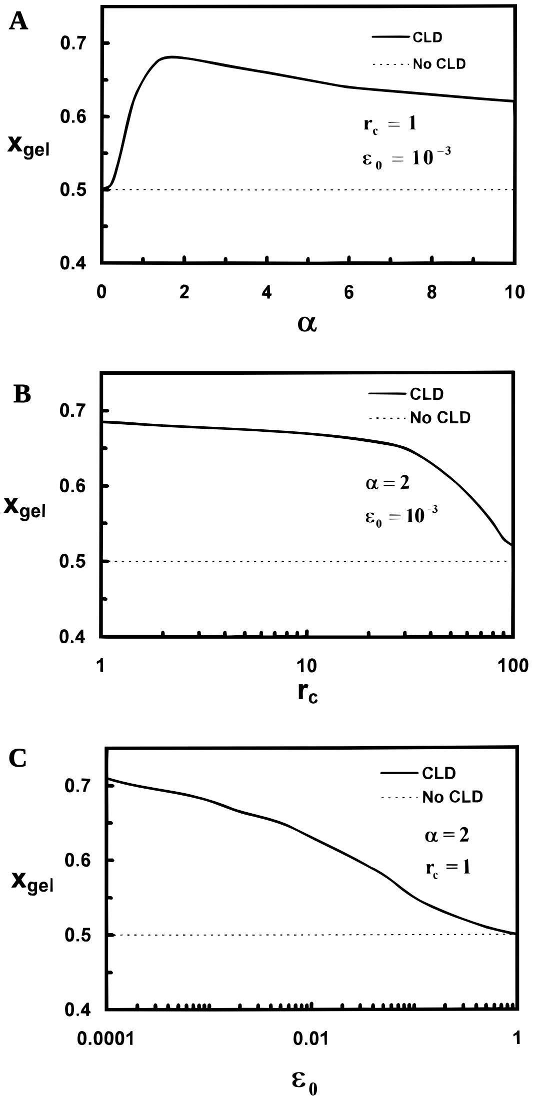

Figure 3. Prediction of the gel point. x_{gel} is the density of cross-linkage at the gel point, equivalently the number of cross-linkages per primary chain in the case of a uniform initial distribution. It is well established that the value of x_{gel} equal 0.5 for a random cross-linking system,[4-6] eq 21. The chain-length-dependent termination always delays the gel point. The magnitude of discrepancies depends on the three parameters of the function $(r_c/r)^{\alpha} + \epsilon_0$: (A) x_{gel} versus α with $r_c = 1$ and $\epsilon_0 = 10^{-3}$, (B) x_{gel} versus r_c with $\alpha = 2$ and $\epsilon_0 = 10^{-3}$, (C) x_{gel} versus ϵ_0 with $\alpha = 2$ and $r_c = 1$. The differences become minor with decrease of α and/or increase of r_c and ϵ_0.

Figure 5 shows the parameter $y_0^{s,\epsilon}$, defined by eq 12, versus the cross-link density x. For random cross-linking, $y_0^{s,\epsilon} = y_0^s$. The chain-length-dependent termination significantly reduces the value of $y_0^{s,\epsilon}$. The order of magnitude of $y_0^{s,\epsilon}$ drops dramatically in the vicinity of gel point. It appears that its postgel value is mainly determined by ϵ_0, while the pregel value depends on α.

Conclusion

Chain-length-dependent diffusion-controlled termination is an important feature in free-radical polymer modification with cross-linking. It is of fundamental importance to investigate the possible effect of this reaction on the molecular weight development and gelation behavior of the system. A general model of molecular weight distribution, eqs 22–24, has been proposed to accomplish this objective. The model gen-

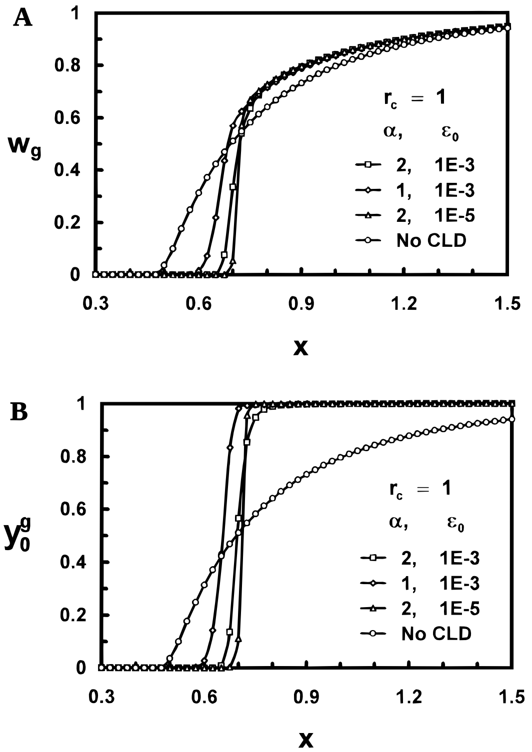

Figure 4. Sol/gel fractions. (A) Weight fraction of polymer chains that belong to a gel molecule, w_g, and (B) number fraction of radicals associated with the gel structure, y_0^g. The parameters for the chain-length dependence function are as follows: (square) $r_c = 1$, $\alpha = 2$, $\epsilon_0 = 10^{-3}$, (diamond) $r_c = 1$, $\alpha = 1$, $\epsilon_0 = 10^{-3}$, and (triangle) $r_c = 1$, $\alpha = 2$, $\epsilon_0 = 10^{-5}$. In contrast to the random cross-linking process (circle), the gel molecule appears at higher cross-link densities but develops more rapidly. Radical centers are more inclined to be associated with the gel molecule than polymer mass.

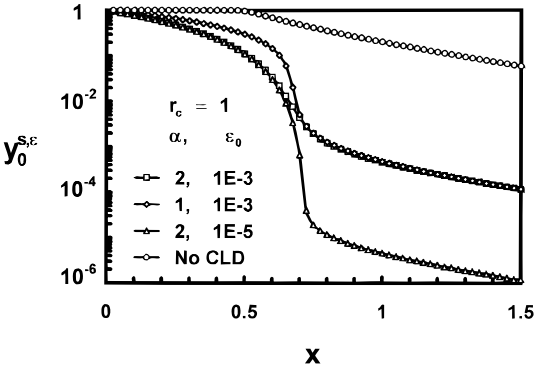

Figure 5. $y_0^{s,\epsilon}$ versus x. The parameter $y_0^{s,\epsilon}$ is defined by eq 12. For the random cross-linking, it equals the number fraction of sol radicals, y_0^s. The chain-length-dependent termination significantly reduces the value of $y_0^{s,\epsilon}$. The order of magnitude of $y_0^{s,\epsilon}$ drops dramatically at the vicinity of gel point. Its postgel value is mainly determined by ϵ_0, while the pregel value depends on α. The parameters for the chain-length dependence function are the same as in Figure 4.

eralizes Saito's equation of random cross-linking; it reduces to Saito's equation when the termination becomes chain-length independent. A simple chain-length-dependence function, eq 21, is introduced into the scheme. The numerical simulation with a uniform initial distribution shows that the chain-length-dependent termination delays the gel point but accelerates gel growth. The level of deviation from Saito's random cross-linking depends on the three parameters of the dependence function. It becomes more severe with an increase in the exponential factor α and/or a decrease in the critical chain length r_c and the residue termination term ϵ_0. The differences of chain properties between polymer and radical populations are also more significant with fewer radical centers attached onto sol polymer chains in the postgel regime.

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References and Notes

(1) Hamielec, A. E.; Gloor, P. E.; Zhu, S. *Can. J. Chem. Eng.* **1991**, *69*, 611.
(2) Lambla, M. *Makromol. Chem., Macromol. Symp.* **1994**, *83*, 37.
(3) Carothers, W. H. *Trans. Faraday Soc.* **1936**, *32*, 39.
(4) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(5) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45, 393.
(6) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(7) Saito, O. *J. Phys. Soc. Jpn.* **1958**, *13*, 198, 1451, 1465.
(8) Saito, O. In *The Radiation Chemistry of Macromolecules*; Dole, M., Ed.; Academic Press: New York, 1972; p 223.
(9) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935.
(10) Schulz, G. V. *Z. Phys. Chem.* **1956**, *8*, 284.
(11) Cardenas, J. N.; O'Driscoll, K. F. *J. Polym. Sci. Polym., Chem. Ed.* **1976**, *14*, 883.
(12) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1759.
(13) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(14) Boots, H. M. J. *J. Polym. Sci.: Polym. Phys. Ed.* **1982**, *20*, 1695.
(15) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1299, 1315, 1331, 1345.
(16) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2141.
(17) Trommsdorff, E.; Kohle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1*, 169.
(18) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(19) Graessley, W. W.; Mittelhauser, H.; Maramba, R. *Makrom. Chem.* **1965**, *86*, 129.
(20) Saidel, G. M.; Katz, S. *J. Polym. Sci.: A-2* **1968**, *6*, 1149.
(21) Tobita, H.; Hamielec, A. E. *Makromol. Chem., Macromol. Symp.* **1988**, *20/21*, 501.
(22) Zhu, S.; Hamielec, A. E. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 929.
(23) Smoluchowski, M. Z. *Phys. Chem.* **1917**, *92*, 129.
(24) Kuchanov, S. I.; Pis'men, L. M. *Polym. Sci. USSR* **1971**, *13*, 2288.
(25) Zhu, S.; Hamielec, A. E. *Macromolecules* **1993**, *26*, 3131.
(26) Zhu, S. Effect of Polyradicals on Gel Formation in Free-Radical Polymer Modification. *J. Polym. Sci., Part B: Polym. Phys.*, in press.
(27) Amemiya, A. *J. Phys. Soc. Jpn.* **1967**, *23*, 1394.
(28) Kimura, T. *J. Phys. Soc. Jpn.* **1962**, *17*, 1884.
(29) Kimura, T. *J. Phys. Soc. Jpn.* **1964**, *19*, 777.
(30) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(31) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Macromolecules* **1987**, *20*, 839.
(32) Bamford, C. H. *Eur. Polym. J.* **1989**, *25*, 683.
(33) Mahabadi, H. K. *Macromolecules* **1985**, *18*, 1319.
(34) Mahabadi, H. K. *Macromolecules* **1991**, *24*, 606.
(35) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1993**, *26*, 3538.
(36) Kirkwood, J.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(37) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(38) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(39) Bueche, F. *Physical Properties of Polymers*; Interscience: New York, 1962.
(40) Gerald, C. F.; Wheatley, P. O. *Applied Numerical Analysis*, 4th ed.; Addison-Wesley Publishing Co., Inc.: New York, 1989.

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