Theory of Nonrandom Cross-Linking: Free-Radical Polymer Grafting

S. Zhu,*,†,‡ M. Ma,† and W. Zhou‡

Institute for Polymer Production Technology, Departments of Chemical Engineering and Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

Received November 16, 1995; Revised Manuscript Received April 22, 1996⊗

ABSTRACT: Free-radical polymer−polymer grafting may lead to gel formation. Due to the different possible combination and termination reactivities of each polymer backbone radical, polymer chains are cross-linked in a nonrandom manner. A general model has been developed using the method of moments to predict the development of molecular weights in the pregel period and the gel point. It is found that the gelation behavior is governed by the product of the radical termination reactivity ratios (r_1r_2) irrespective of their individual values. Analytical solutions of the differential equations of the moments have been derived for the limiting cases of $r_1r_2 = 0$, 1, and ∞. The model reduces to the Flory−Stockmayer classical gelation theory under the condition of random cross-linking. It deviates from the classical theory when the cross-linking process becomes nonrandom. The magnitude of the discrepancies depends on the kinetic parameters and reaction conditions.

Introduction

Polymer grafting allows the conversion of commodity polymers to value-added specialty polymers.[1] For examples, maleic anhydride oligomers are grafted onto polyolefins to improve the adhesion of the base polymers to metals and glass fibers. Grafting highly charged ionic polymers onto high molecular weight polyacrylamide can give better flocculation effects. Elastomers are grafted onto polypropylene to enhance impact strength for applications in the automobile industry.

Such polymer−polymer graftings are often implemented via free-radical mechanisms in solution or in melt phase. Chemical initiators such as peroxides and azo compounds and γ or electron beam radiation provide radical sources. The initiator molecules are decomposed into primary radicals at an elevated temperature. These primary radicals and γ-rays or electron beams have sufficient energy to abstract or eject atoms from polymer backbones, thus generating backbone radicals. For a binary polymer system, two types of backbone radicals are formed: R^I and R^{II} with the radical centers located on the base polymer (I) and on the graft polymer (II), respectively. The radicals are terminated by combination to form cross-linkages. There exist three types of possible cross-linkages (I−I, II−II, I−II). In the case of a I−II type of cross-linkage, a graft polymer chain is said to be grafted onto a base polymer.

Backbone radicals are continuously generated and terminated during the course of free-radical grafting. Successive cross-linking would eventually lead to gel formation. A gel molecule is a three-dimensional polymer network that has an infinitely large molecular weight, as defined by Carothers.[2] Gel formation is an important feature in free-radical polymer−polymer grafting. In almost all commercial applications, the level of cross-linking must be carefully controlled and optimized. Excessive amounts of cross-linking may cause inferior product properties and/or damage to equipment. It is therefore essential to understand the molecular processes involved in gel formation during the course of free radical grafting.

Following the pioneering work of Flory and Stockmayer,[3,4] many gelation models have been developed for these purposes (see refs 5−15 for examples). However, all models to date assume random cross-linking processes in which backbone radicals combine indiscriminately with each other. In other words, radicals of different types are assumed to have the same reactivities of termination by combination. In the present grafting system, reactivities of the two types of backbone radicals (R^I and R^{II}) can be very different; one type of radical might favor termination with either the same type or the other type. If the radicals are exclusively terminated with their own types, interpenetrating polymer networks are formed. For grafting purposes, the ideal condition occurs when the radicals prefer to be cross-terminated between different types.

Gel formation in such a grafting process proceeds in a non-random manner. The extent of nonrandomness depends on the relative magnitudes of the rate constants of termination by combination of the radicals R^I and R^{II}: $K_{tc,I/I}$, $K_{tc,II/II}$, and $K_{tc,I/II}$ (note $K_{tc,II/I} = K_{tc,I/II}$). Analogous to the terminal model of monomer propagations during chain-growth copolymerization (refer to basic polymer chemistry textbooks, e.g., Hiemenz[23]), let us define the reactivity ratios as $r_1 = K_{tc,I/I}/K_{tc,I/II}$ and $r_2 = K_{tc,II/II}/K_{tc,II/I}$. The magnitudes of r_1 and r_2 reflect the extent of nonrandomness of the gelation process.

Modeling of gel formation via non-random cross-linking provides a great theoretical challenge. The classical gelation models[3,4] based on random cross-linking need to be generalized to take into account the effect of variable termination reactivity ratios. This work presents a gelation model of non-random cross-linking for free-radical polymer grafting using the method of moments.

Theory

The polymer grafting system considered in this work is described by the following elementary reactions:

---

* Author to whom correspondence should be addressed.

† Department of Chemical Engineering.

‡ Department of Materials Science and Engineering.

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.

S0024-9297(95)01717-7 CCC: $12.00

backbone radical generation via atom abstraction

$$R_0 + P_{r,m} \xrightarrow{rK^{\mathrm{I}}_{\mathrm{ab}}} R^{\mathrm{I}}_{r,m} \tag{1}$$

$$R_0 + P_{r,m} \xrightarrow{\mathrm{mK}^{\mathrm{II}}_{\mathrm{ab}}} R^{\mathrm{II}}_{r,m} \tag{2}$$

backbone radical termination by combination

$$R^{\mathrm{I}}_{r,m} + R^{\mathrm{I}}_{s,n} \xrightarrow{K_{\mathrm{tc,I/I}}} P_{r+s,m+n} \tag{3}$$

$$R^{\mathrm{I}}_{r,m} + R^{\mathrm{II}}_{s,n} \xrightarrow{K_{\mathrm{tc,I/II}}} P_{r+s,m+n} \tag{4}$$

$$R^{\mathrm{II}}_{r,m} + R^{\mathrm{II}}_{s,n} \xrightarrow{K_{\mathrm{tc,II/II}}} P_{r+s,m+n} \tag{5}$$

where R_0 represents the molar concentration of primary radicals generated by thermal decomposition of initiator molecules (mostly peroxides). R_0 can also represent γ-ray or electron beam intensities depending on the exact radical source; $P_{r,m}$ is the concentration of polymer chains having r monomeric units of type I and m monomeric units of type II; $R^{\mathrm{I}}_{r,m}$ and $R^{\mathrm{II}}_{r,m}$ are the concentrations of radical chains having r monomeric units of type I and m monomeric units of type II, with the superscripts I and II indicating the type of radical center. It should be noted that the number of hydrogen (or any other abstractable) atoms associated with a polymer chain $P_{r,m}$ is proportional to its number of monomeric units r and m and, therefore, the rate constants for a primary radical abstracting an atom from polymer $P_{r,m}$ are $rK^{\mathrm{I}}_{\mathrm{ab}}$ in reaction 1 and $mK^{\mathrm{II}}_{\mathrm{ab}}$ in reaction 2. $K_{\mathrm{tc,I/I}}$, $K_{\mathrm{tc,I/II}}$, and $K_{\mathrm{tc,II/II}}$ are the rate constants of bimolecular termination by combination between the radicals $R^{\mathrm{I}}/R^{\mathrm{I}}$, $R^{\mathrm{I}}/R^{\mathrm{II}}$, and $R^{\mathrm{II}}/R^{\mathrm{II}}$, respectively.

We now define the following kinetic parameters:

$$\kappa = K^{\mathrm{II}}_{\mathrm{ab}}/K^{\mathrm{I}}_{\mathrm{ab}} \tag{6}$$

$$r_1 = K_{\mathrm{tc,I/I}}/K_{\mathrm{tc,I/II}} \tag{7}$$

$$r_2 = K_{\mathrm{tc,II/II}}/K_{\mathrm{tc,I/II}} \tag{8}$$

Analogous to the terminal model of monomer propagations in chain-growth copolymerization, r_1 and r_2 are termed the reactivity ratios of radical termination by combination. κ is the ratio of rate constants for backbone radical generation. The magnitudes of κ, r_1, and r_2 reflect the extent of nonrandomness of the gelation process.

We also define the relative moments of the polymer chains,

$$u_{i,j} = \frac{\displaystyle\sum_{r=1}^{\infty}\sum_{m=1}^{\infty} r^i m^j P_{r,m}}{\bar{r}_{\mathrm{wp}} \displaystyle\sum_{r=1}^{\infty}\sum_{m=1}^{\infty} (r+m) P_{r,m}} \tag{9}$$

and the cross-link density (i.e., the number of cross-link points per primary chain on a weight-average basis),

$$z = y\bar{r}_{\mathrm{wp}} \tag{10}$$

where y is the number of cross-link points per monomeric unit. (It should be noted that two cross-link points form one cross-linkage and that the cross-link points discussed in the present paper are those formed by intermolecular reactions.) $\bar{r}_{\mathrm{wp}}$ is the weight-average chain length of the blend of base and graft primary polymers

$$\bar{r}_{\mathrm{wp}} = w_1\bar{r}_{\mathrm{wp},1} + w_2\bar{r}_{\mathrm{wp},2} \tag{11}$$

w_1 and w_2 are the weight fractions of the two polymers. $\bar{r}_{\mathrm{wp},1}$ and $\bar{r}_{\mathrm{wp},2}$ are their weight-average chain lengths.

After some lengthy but straightforward algebra based on the population balances of polymer species and the method of moments,[16,17] the following equations for the second-order moments can be derived (as shown in Appendix A):

$$\frac{\mathrm{d}u_{2,0}}{\mathrm{d}z} = \frac{r_1r_2u_{2,0}^2 + 2\lambda u_{2,0}u_{1,1} + \lambda^2 u_{1,1}^2}{r_1r_2w_1^2 + 2\lambda w_1w_2 + \lambda^2 w_2^2} \tag{12}$$

$$\frac{\mathrm{d}u_{1,1}}{\mathrm{d}z} = \frac{r_1r_2u_{2,0}u_{1,1} + \lambda u_{1,1}^2 + \lambda u_{2,0}u_{0,2} + \lambda^2 u_{1,1}u_{0,2}}{r_1r_2w_1^2 + 2\lambda w_1w_2 + \lambda^2 w_2^2} \tag{13}$$

$$\frac{\mathrm{d}u_{0,2}}{\mathrm{d}z} = \frac{r_1r_2u_{1,1}^2 + 2\lambda u_{1,1}u_{0,2} + \lambda^2 u_{0,2}^2}{r_1r_2w_1^2 + 2\lambda w_1w_2 + \lambda^2 w_2^2} \tag{14}$$

where

$$\lambda = \frac{(\kappa w_2 - w_1) + \sqrt{(\kappa w_2 - w_1)^2 + 4\kappa r_1r_2w_1w_2}}{2w_2} \tag{15}$$

In this paper, we are only interested in the moments of second order since it is known that the weight-average chain length approaches infinity when the system reaches the gel point. The weight-average chain length can be calculated from the second-order moments as follows,

$$\bar{r}_{\mathrm{w}} = \sum_{r=1}^{\infty}\sum_{m=1}^{\infty}(r+m)^2P_{r,m}\Big/\sum_{r=1}^{\infty}\sum_{m=1}^{\infty}(r+m)P_{r,m} = (u_{2,0} + 2u_{1,1} + u_{0,2})\bar{r}_{\mathrm{wp}} \tag{16}$$

In general, eqs 12–14 can be solved numerically using the following initial conditions:

$$u_{2,0} = w_1/(w_1 + w_2\gamma) \tag{17}$$

$$u_{1,1} = 0 \tag{18}$$

$$u_{0,2} = w_2\gamma/(w_1 + w_2\gamma) \tag{19}$$

where

$$\gamma = \bar{r}_{\mathrm{wp},2}/\bar{r}_{\mathrm{wp},1} \tag{20}$$

A careful examination of eqs 12–14 reveals an interesting point: the molecular weight development and gelation behavior of such polymer grafting systems are governed not by the individual termination reactivity ratios r_1 and r_2, but by their product r_1r_2. As can be seen in these equations, the two reactivity ratios always appear together. Therefore, the present model has a total of four parameters. They are the following: (1) the ratio of the rate constants of atom abstraction from monomeric unit type II over type I, κ; (2) the product of the termination reactivity ratios, r_1r_2; (3) the weight fraction of graft primary polymer, w_2 (note: $w_1 = 1 - w_2$); and (4) the ratio of the weight-average chain lengths of primary polymers of type II over type I, γ. The first two parameters are rate constants while the last two are experimental conditions.

It should be pointed out that there are some assumptions involved in deriving the above model. The major ones are as follows: (1) monoradical assumption, i.e., no polymer molecule is allowed to have more than one radical center; an individual chain bears either one radical center or none 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 of the same type have equal probability to be abstracted regardless of their location in a polymer chain; and (4) no chain cyclization. Justification and/or clarification of the first two assumptions has recently been carried out.[18,19]

Results and Discussion

Flory's Classical Gelation Theory.[3,4] According to the gelation theories based on random cross-linking, at the gel point,

$$\bar{r}_{\mathrm{w}} \to \infty,\ z_{\mathrm{c}} = 1 \tag{21}$$

i.e., the system becomes gelled when, in terms of the weight average, each primary polymer chain bears one cross-link point. This criterion is general for a random cross-linking process. For nonrandom cross-linking processes, the results deviate from eq 21 with the magnitude of the deviations depending on the four parameters: κ, r_1r_2, w_2, and γ.

In general, the differential equations 12−14, with the initial conditions eqs 17−19, can be solved numerically for an arbitrary set of the parameters. However, in this paper, we provide analytical solutions for the following useful limiting cases.

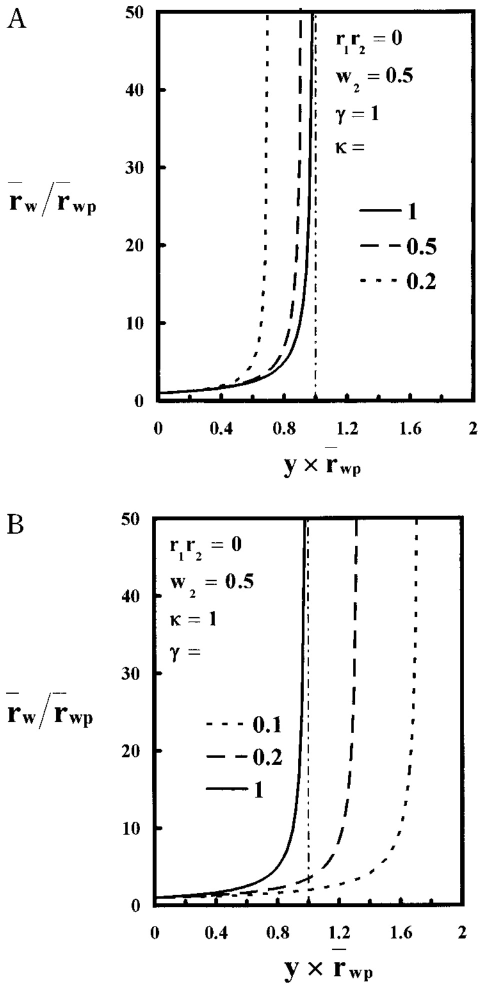

Figure 1. Weight-average chain length, $\bar{r}_{\mathrm{w}}/\bar{r}_{\mathrm{wp}}$, versus cross-link density, $z(= y \times \bar{r}_{\mathrm{wp}})$. The weight-average chain length diverges rapidly when the reaction system approaches the gel point. The classical gelation theory[3,4] based on random cross-linking predicts the gel point at $y\bar{r}_{\mathrm{wp}} = 1$. The present model takes into account the effect of the nonrandomness on gelation. The curves are calculated using eq 22, which is the analytical solution of eqs 12−14 under the condition of $r_1r_2 = 0$. Parameters: (A) $w_2 = 0.5$, $\gamma = 1$, and $\kappa = 1, 0.5, 0.2$; (B) $w_2 = 0.5$, $\kappa = 1$, and $\gamma = 1, 0.2, 0.1$.

Case I, $r_1r_2 \to 0$. At least one type of radical is disallowed to terminate with its own type (i.e., $K_{\mathrm{tc,I/I}} = 0$ and/or $K_{\mathrm{tc,II/II}} = 0$). This type of radical is exclusively cross-terminated with the other type ($K_{\mathrm{tc,I/II}} \neq 0$). This is an ideal situation for grafting. Under this condition, the following analytical solution of eqs 12−14, with the initial conditions eqs 17−19, can be obtained in two sequences.

$$\frac{\bar{r}_{\mathrm{w}}}{\bar{r}_{\mathrm{wp}}} = \frac{\dfrac{4\kappa^2 w_1 w_2 \gamma}{(w_1-\kappa w_2)^2+4\kappa^2 w_1 w_2 \gamma}\left\{1+\dfrac{[(2\kappa-1)w_1+\kappa w_2]w_2\gamma z}{w_1(w_1+\kappa w_2)(w_1+w_2\gamma)^2}\right\}}{1-\dfrac{1}{(w_1-\kappa w_2)^2+4\kappa^2 w_1 w_2\gamma}\left[(w_1-\kappa w_2)+\dfrac{2\kappa^2 w_2\gamma z}{(w_1+\kappa w_2)(w_1+w_2\gamma)}\right]^2} \tag{22a}$$

for $w_2 \leq 1/(1 + \kappa)$, and

$$\frac{\bar{r}_{\mathrm{w}}}{\bar{r}_{\mathrm{wp}}} = \frac{1+\dfrac{[(2-\kappa)w_2+w_1]w_1\gamma z}{w_2(w_1+\kappa w_2)(w_1+w_2\gamma)^2}}{1-\dfrac{\gamma z}{w_2(w_1+\kappa w_2)(w_1+w_2\gamma)}\left[(\kappa w_2-w_1)+\dfrac{w_1 z}{(w_1+\kappa w_2)(w_1+w_2\gamma)}\right]} \tag{22b}$$

for $w_2 > 1/(1 + \kappa)$.

Therefore, gelation occurs at

$$z_{\mathrm{c}} = [(w_1 + \kappa w_2)(w_1 + w_2\gamma)/2\kappa^2 w_2\gamma] \times [\sqrt{(w_1 - \kappa w_2)^2 + 4\kappa^2 w_1 w_2\gamma} - (w_1 - \kappa w_2)] \tag{23a}$$

when $w_2 \leq 1/(1 + \kappa)$, or at

$$z_{\mathrm{c}} = [(w_1 + \kappa w_2)(w_1 + w_2\gamma)/2w_1] \times [\sqrt{(\kappa w_2 - w_1)^2 + 4w_1 w_2/\gamma} - (\kappa w_2 - w_1)] \tag{23b}$$

when $w_2 > 1/(1 + \kappa)$.

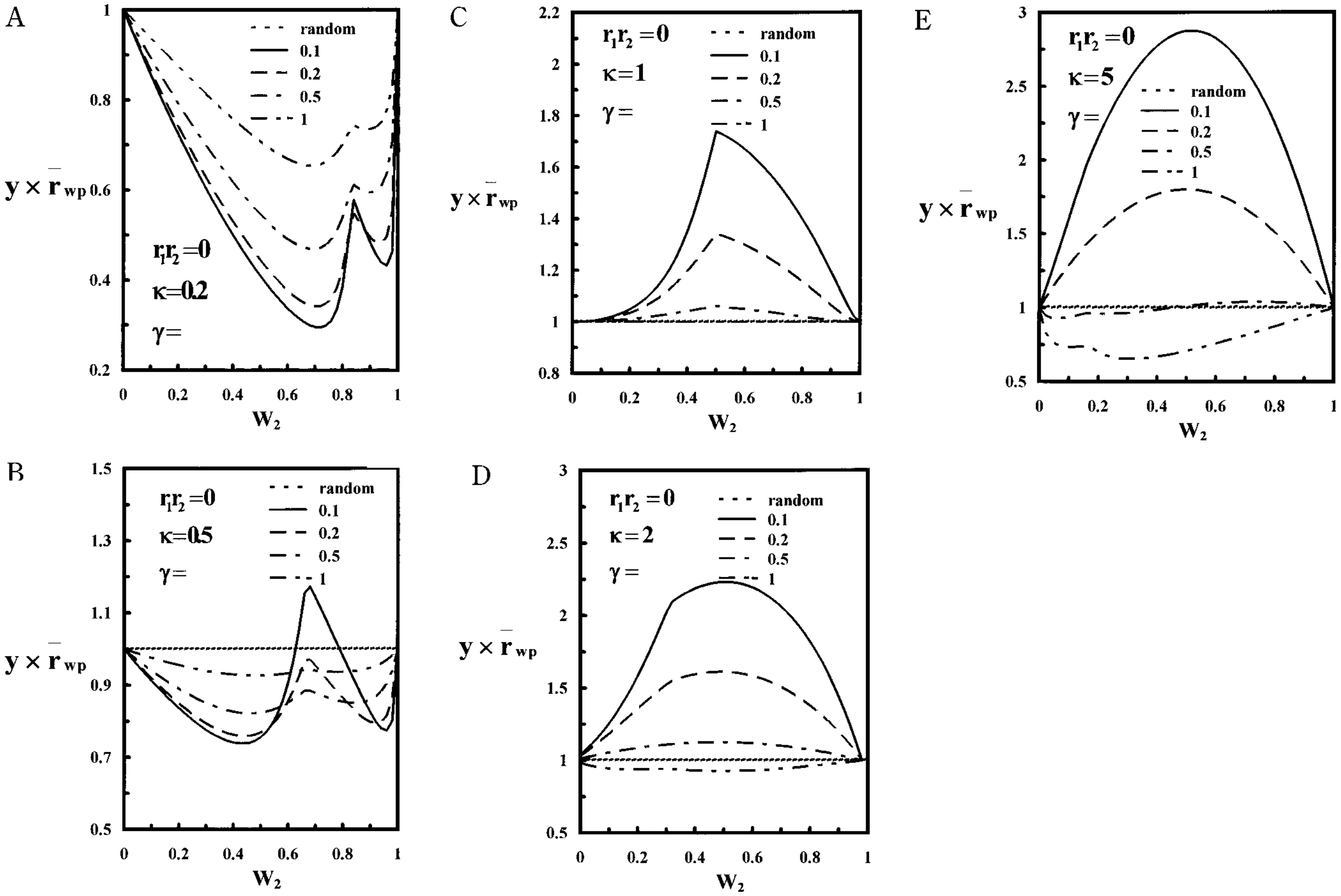

Figure 2. Prediction of the gel point, $y \times \bar{r}_{wp}$, as a function of the weight fraction of graft primary polymer, w_2, for the case of $r_1r_2 = 0$. The curves are the prediction of eq 23. Parameters: (A) $\kappa = 0.2$ and $\gamma = 1, 0.5, 0.2, 0.1$; (B) $\kappa = 0.5$ and $\gamma = 1, 0.5, 0.2, 0.1$; (C) $\kappa = 1$ and $\gamma = 1, 0.5, 0.2, 0.1$; (D) $\kappa = 2$ and $\gamma = 1, 0.5, 0.2, 0.1$; (E) $\kappa = 5$ and $\gamma = 1, 0.5, 0.2, 0.1$. The line of $y \times \bar{r}_{wp} = 1$ is the result of random cross-linking. The further removed from unity κ and γ are, the farther the z curve will be displaced from the line.

Figure 1 shows some typical examples of the weight-average chain length development for sol polymers in the pregel period. It is well-known that the weight-average chain length, as well as other average chain lengths of higher order, diverges rapidly and simultaneously when the reaction system approaches the gel point. At the gel point, a three-dimensional polymer network with infinitely large molecular weight starts to appear. In the pregel period, branched polymers are formed by combination of the primary chains through termination of backbone radicals. The branching process substantially increases polymer molecular weights. Continuation of the branching process eventually leads to gelation. Once a gel molecule is nucleated, it grows rapidly (analogous to "sponging") by coupling with highly branched sol polymers.

Depending on the values of κ, γ, and w_2, the weight-average chain length diverges at different cross-link densities. Figure 2 shows the predicted gel point z ($= y \times \bar{r}_{wp}$) as a function of the weight fraction of graft primary polymer w_2 for different κ and γ. In the case of random cross-linking, the value of z at the gel point equals unity regardless of the weight fractions, which coincides with the condition of $\kappa = \gamma = 1$. Deviation of κ from unity tends to hasten the gel point, while deivation of γ from unity tends to delay the gel point. However, the function is rather complicated when both parameters depart from unity as shown in the figures. In general, the further removed from unity κ and γ are, the farther the z curve will be displaced from the $z = 1$ line.

It should be pointed out that in principle eqs 22 and 23 are also applicable to the coupling of two reactive polymers.[20-22] In such a system, each polymer chain bears many functional groups along its backbone. Grafting is implemented through in situ condensation of the coreactive functional groups associated with different polymers. However, functional groups of the same type do not react. It therefore satisfies the condition of $r_1r_2 \rightarrow 0$.

Case II, $r_1r_2 \rightarrow \infty$. In this case, the cross-termination of radicals of different types are disallowed (i.e., $K_{tc,I/II} = 0$). Radicals are therefore exclusively terminated with their own types (i.e., $K_{tc,I/I} \neq 0$ and $K_{tc,II/II} \neq 0$). Two interpenetrating polymer networks are thus formed. Substituting $r_1r_2 \rightarrow \infty$ into eqs 12–14 yields

$$\frac{\bar{r}_w}{\bar{r}_{wp}} = \frac{\dfrac{w_1}{w_1 + w_2\gamma}}{1 - \dfrac{z}{(w_1 + \kappa w_2)(w_1 + w_2\gamma)}} + \frac{\dfrac{w_2\gamma}{w_1 + w_2\gamma}}{1 - \dfrac{\kappa\gamma z}{(w_1 + \kappa w_2)(w_1 + w_2\gamma)}} \qquad (24)$$

A gel molecule based on type I polymer chains is formed when the first term on the right-hand side of eq 22 approaches infinity, i.e.

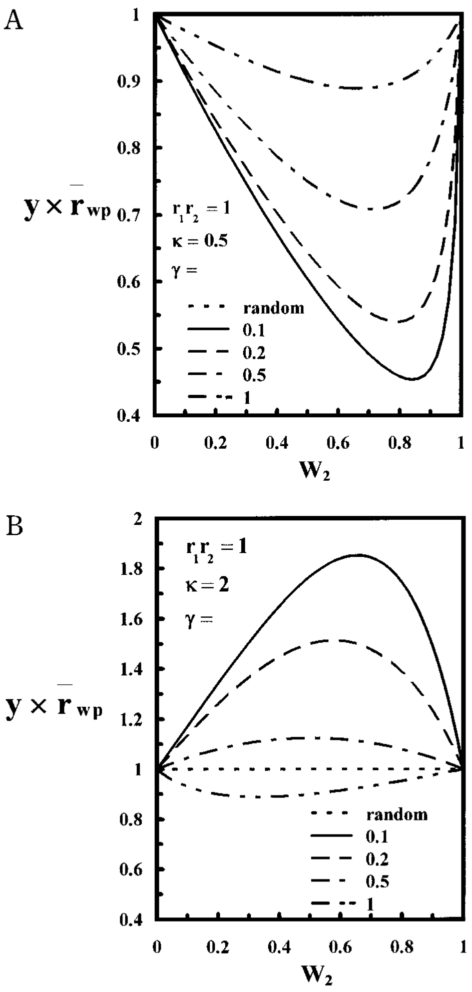

Figure 3. Prediction of the gel point, $y \times \bar{r}_{wp}$, as a function of the weight fraction of graft primary polymer, w_2, for the case of $r_1r_2 = 1$. The curves are the prediction of eq 27. Parameters: (A) $\kappa = 0.5$ and $\gamma = 1, 0.5, 0.2, 0.1$; (B) $\kappa = 2$ and $\gamma = 1, 0.5, 0.2, 0.1$. The condition of $r_1r_2 = \kappa = 1$ corresponds to the random cross-linking.

$$z_c = (w_1 + \kappa w_2)(w_1 + w_2\gamma) \tag{25a}$$

Another gel molecule based on type II polymers is formed when the second term on the right-hand side of eq 22 approaches infinity, i.e.

$$z_c = (w_1 + \kappa w_2)(w_1 + w_2\gamma)/\kappa\gamma \tag{25b}$$

Which gel molecule appears first in the system depends on the value of $\kappa\gamma$. If $\kappa\gamma < 1$, the gel molecule of type I appears first; otherwise, the gel molecule of type II emerges earlier. The system is gelled when the first gel molecule appears.

Case III, $r_1r_2 = 1$. Under this condition, the following analytical solution can be obtained for eqs 12−14 with the initial conditions eqs 17−19,

$$\frac{\bar{r}_w}{\bar{r}_{wp}} = \frac{1 - \dfrac{(1-\kappa)^2 w_1 w_2 \gamma z}{(w_1 + \kappa w_2)^2 (w_1 + w_2\gamma)^2}}{1 - \dfrac{(w_1 + \kappa^2 w_2 \gamma) z}{(w_1 + \kappa w_2)^2 (w_1 + w_2\gamma)}} \tag{26}$$

At the gel point,

$$z_c = \frac{(w_1 + \kappa w_2)^2 (w_1 + w_2\gamma)}{w_1 + \kappa^2 w_2 \gamma} \tag{27}$$

It becomes clear that eq 27 fully agrees with the classical gelation theory[3,4] (i.e., $z_c = 1$) provided $\kappa = 1$. Indeed, the condition of $r_1r_2 = \kappa = 1$ corresponds to the random cross-linking process: the backbone radicals are randomly generated and randomly terminated regardless of the polymer types. The gel point deviates from $z = 1$ when $\kappa \neq 1$. Figure 3 shows some results for $\kappa = 0.5$ and $\kappa = 2$.

A final point worth noting is that all the three limiting cases, i.e., eqs 23, 25, and 27, are reduced to

$$z_c = (w_1 + \kappa w_2)(w_1 + w_2\gamma) = 1 + [(\gamma - 1)^2/\gamma]w_2 - [(\gamma - 1)^2/\gamma]w_2^2 \tag{28}$$

under the condition of $\kappa\gamma = 1$. In this situation, deviation of γ from unity always delays the gel point with the maximum value of $z = (\gamma + 1)^2/(4\gamma)$ at $w_2 = 0.5$.

Conclusion

Gel formation is an important feature in free-radical polymer grafting. Due to the different possible generation and termination reactivities of polymer backbone radicals, the molecular processes involved in cross-linking proceed in a nonrandom manner. In other words, one type of radical might be preferentially terminated either with the same type or with the other type.

In this work, the classical theory of random cross-linking is extended to take into account the effect of the nonrandomness on gelation. A general model in the form of differential equations, eqs 12−14, is developed using the method of moments. It is found that the development of molecular weights in pregel period and the gel point are controlled by two kinetic constants, the ratio of the rate constants of atom abstraction κ and the product of the termination reactivity ratios r_1r_2, and two experimental parameters, the polymer weight fraction w_2 and the ratio of the weight-average chain lengths of two primary polymers γ.

Analytical solutions are also provided for three useful limiting cases: $r_1r_2 = 0$, 1, and ∞. The model fully agrees with the classical gelation theory[3,4] under the condition of random cross-linking (i.e., $r_1r_2 = \kappa = 1$). It deviates from the classical theory when the cross-linking process becomes nonrandom. Our calculations show that the further removed from unity κ and/or r_1r_2 is, the farther the cross-link density, z, at the gel point will be displaced from the random cross-linking line ($z = 1$).

Acknowledgment. The authors acknowledge the financial support from the Canadian Natural Sciences and Engineering Research Council (NSERC), the Ontario Center for Materials Research (OCMR), and the McMaster Science and Engineering Research Board (MSERB).

Appendix A

An effective starting point to develop a kinetic model is to constitute population balance equations for individual reactant species. Based on the elementary reactions, i.e., eqs 1−5, the population balance equations for $R^{\mathrm{I}}_{r,m}$, $R^{\mathrm{II}}_{r,m}$ and $P_{r,m}$ are

$$\frac{\mathrm{d}R^{\mathrm{I}}_{r,m}}{\mathrm{d}t} = K^{\mathrm{I}}_{\mathrm{ab}}R_0 rP_{r,m} - (K_{t,\mathrm{I/I}}Y^{\mathrm{I}}_{0,0} + K_{t,\mathrm{I/II}}Y^{\mathrm{II}}_{0,0})R^{\mathrm{I}}_{r,m} \approx 0 \tag{A1}$$

$$\frac{\mathrm{d}R^{\mathrm{II}}_{r,m}}{\mathrm{d}t} = K^{\mathrm{II}}_{\mathrm{ab}}R_0 mP_{r,m} - (K_{t,\mathrm{I/II}}Y^{\mathrm{I}}_{0,0} + K_{t,\mathrm{II/II}}Y^{\mathrm{II}}_{0,0})R^{\mathrm{II}}_{r,m} \approx 0 \tag{A2}$$

$$\begin{aligned}\frac{\mathrm{d}P_{r,m}}{\mathrm{d}t} = {}& \frac{1}{2}K_{t,\mathrm{I/I}}\sum_{s=1}^{r-1}\sum_{n=0}^{m} R^{\mathrm{I}}_{s,n}R^{\mathrm{I}}_{r-s,m-n} + \\ & K_{t,\mathrm{I/II}}\sum_{s=1}^{r}\sum_{n=0}^{m-1} R^{\mathrm{I}}_{s,n}R^{\mathrm{II}}_{r-s,m-n} + \frac{1}{2}K_{t,\mathrm{II/II}}\sum_{s=0}^{r}\sum_{n=1}^{m-1} R^{\mathrm{II}}_{s,n}R^{\mathrm{II}}_{r-s,m-n} - \\ & (rK^{\mathrm{I}}_{\mathrm{ab}} + mK^{\mathrm{II}}_{\mathrm{ab}})R_0P_{r,m}\end{aligned} \tag{A3}$$

where t is the reaction time.

In principle, eqs A1−A3 can be solved numerically to obtain the bivariate values of $P_{r,m}$. However, the assignment is very laborious if not impossible because of the huge numbers of r and m values, particularly when the system approaches the gel point. One can therefore resort to the use of the method of moments[16,17] to obtain average chain properties. Let us define the following moments:

$$Q_{i,j} = \sum_{r=1}^{\infty}\sum_{m=1}^{\infty} r^i m^j P_{r,m} \tag{A4}$$

$$Y^{\mathrm{I}}_{i,j} = \sum_{r=1}^{\infty}\sum_{m=1}^{\infty} r^i m^j R^{\mathrm{I}}_{r,m} \tag{A5}$$

$$Y^{\mathrm{II}}_{i,j} = \sum_{r=1}^{\infty}\sum_{m=1}^{\infty} r^i m^j R^{\mathrm{II}}_{r,m} \tag{A6}$$

After very lengthy but straightforward algebra, the following set of ordinary differential equations of moments can be obtained:

$$\frac{\mathrm{d}Y^{\mathrm{I}}_{i,j}}{\mathrm{d}t} = K^{\mathrm{I}}_{\mathrm{ab}}R_0Q_{i+1,j} - (K_{t,\mathrm{I/I}}Y^{\mathrm{I}}_{0,0} + K_{t,\mathrm{I/II}}Y^{\mathrm{II}}_{0,0})Y^{\mathrm{I}}_{i,j} \approx 0 \tag{A7}$$

$$\frac{\mathrm{d}Y^{\mathrm{II}}_{i,j}}{\mathrm{d}t} = K^{\mathrm{II}}_{\mathrm{ab}}R_0Q_{i,j+1} - (K_{t,\mathrm{I/II}}Y^{\mathrm{I}}_{0,0} + K_{t,\mathrm{II/II}}Y^{\mathrm{II}}_{0,0})Y^{\mathrm{II}}_{i,j} \approx 0 \tag{A8}$$

$$\begin{aligned}\frac{\mathrm{d}Q_{i,j}}{\mathrm{d}t} = {}& \frac{1}{2}K_{t,\mathrm{I/I}}\sum_{k=0}^{i}\sum_{l=0}^{j}\binom{i}{k}\binom{j}{l}Y^{\mathrm{I}}_{k,l}Y^{\mathrm{I}}_{i-k,j-l} + \\ & K_{t,\mathrm{I/II}}\sum_{k=0}^{i}\sum_{l=0}^{j}\binom{i}{k}\binom{j}{l}Y^{\mathrm{I}}_{k,l}Y^{\mathrm{II}}_{i-k,j-l} + \\ & \frac{1}{2}K_{t,\mathrm{II/II}}\sum_{k=0}^{i}\sum_{l=0}^{j}\binom{i}{k}\binom{j}{l}Y^{\mathrm{II}}_{k,l}Y^{\mathrm{II}}_{i-k,j-l} - \\ & (K^{\mathrm{I}}_{\mathrm{ab}}R_0Q_{i+1,j} + K^{\mathrm{II}}_{\mathrm{ab}}R_0Q_{i,j+1})\end{aligned} \tag{A9}$$

Introducing the steady-state hypothesis to eqs A7 and A8 yields

$$Y^{\mathrm{I}}_{i,j} = \alpha Q_{i+1,j} \tag{A10}$$

$$Y^{\mathrm{II}}_{i,j} = \beta Q_{i,j+1} \tag{A11}$$

$$\begin{aligned}\frac{\mathrm{d}Q_{i,j}}{\mathrm{d}t} = {}& \\ & K_{t,\mathrm{I/I}}\alpha^2\left[\frac{1}{2}\sum_{k=0}^{i}\sum_{l=0}^{j}\binom{i}{k}\binom{j}{l}Q_{k+1,l}Q_{i-k+1,j-l} + Q_{1,j}Q_{i+1,0}\right] + \\ & K_{t,\mathrm{I/II}}\alpha\beta\left[\sum_{k=0}^{i}\sum_{l=0}^{j}\binom{i}{k}\binom{j}{l}Q_{k+1,l}Q_{i-k,j-l+1} + Q_{1,j}Q_{i,1} + \right. \\ & \left. Q_{i+1,0}Q_{0,j+1}\right] + K_{t,\mathrm{II/II}}\beta^2 \times \\ & \left[\frac{1}{2}\sum_{k=0}^{i}\sum_{l=0}^{j}\binom{i}{k}\binom{j}{l}Q_{k,l+1}Q_{i-k,j-l+1} + Q_{i,1}Q_{0,j+1}\right]\end{aligned} \tag{A12}$$

where

$$\alpha = \frac{K^{\mathrm{I}}_{\mathrm{ab}}R_0}{K_{t,I/I}Y^{\mathrm{I}}_{0,0} + K_{t,\mathrm{I/II}}Y^{\mathrm{II}}_{0,0}} \tag{A13}$$

$$\beta = \frac{K^{\mathrm{II}}_{\mathrm{ab}}R_0}{K_{t,\mathrm{I/II}}Y^{\mathrm{I}}_{0,0} + K_{t,\mathrm{II/II}}Y^{\mathrm{II}}_{0,0}} \tag{A14}$$

For the first moments, eq (A12) gives

$$\begin{aligned}&\mathrm{d}Q_{1,0}/\mathrm{d}t = 0 \\ &\mathrm{d}Q_{0,1}/\mathrm{d}t = 0\end{aligned} \tag{A15}$$

i.e., the total numbers of monomeric units of both types remain unchanged during grafting.

For convenience in discussion, we use the cross-link density instead of time as the independent variable. The concentration of cross-link points B can be followed up by

$$\begin{aligned}\mathrm{d}B/\mathrm{d}t &= K_{t,\mathrm{I/I}}Y^{\mathrm{I}}_{0,0}Y^{\mathrm{I}}_{0,0} + 2K_{t,\mathrm{I/II}}Y^{\mathrm{I}}_{0,0}Y^{\mathrm{II}}_{0,0} + K_{t,\mathrm{II/II}}Y^{\mathrm{II}}_{0,0}Y^{\mathrm{II}}_{0,0} \\ &= K_{t,\mathrm{I/I}}\alpha^2Q_{1,0}Q_{1,0} + 2K_{t,\mathrm{I/II}}\alpha\beta Q_{1,0}Q_{0,1} + \\ &\qquad K_{t,\mathrm{II/II}}\beta^2Q_{0,1}Q_{0,1}\end{aligned} \tag{A16}$$

The number of cross-link points per monomeric unit is

$$y = B/(Q_{1,0} + Q_{0,1}) \tag{A17}$$

Defining the relative moments as

$$q_{i,j} = Q_{i,j}/(Q_{1,0} + Q_{0,1}) \tag{A18}$$

and replacing t by y in eq A12 yields

$$\frac{\mathrm{d}q_{i,j}}{\mathrm{d}y} = \frac{1}{r_1 r_2 w_1^2 + 2\lambda w_1 w_2 + \lambda^2 w_2^2} \times \left\{ r_1 r_2 \left[\frac{1}{2} \sum_{k=1}^{i-1} \sum_{l=1}^{j-1} \binom{i}{k} \binom{j}{l} q_{k+1,l} q_{i-k+1,j-l} + q_{1,j} q_{i+1,0} \right] + \lambda \left[\sum_{k=1}^{i-1} \sum_{l=1}^{j-1} \binom{i}{k} \binom{j}{l} q_{k+1,l} q_{i-k,j-l+1} + q_{1,j} q_{i,1} + q_{i+1,0} q_{0,j+1} \right] + \lambda^2 \left[\frac{1}{2} \sum_{k=1}^{i-1} \sum_{l=1}^{j-1} \binom{i}{k} \binom{j}{l} q_{k,l+1} q_{i-k,j-l+1} + q_{0,j+1} \mathrm{q}_{\mathrm{i},1} \right] \right\} \tag{A19}$$

where

$$\lambda = \frac{\beta r_2}{\alpha} = \frac{(\kappa w_2 - w_1) + \sqrt{(\kappa w_2 - w_1)^2 + 4\kappa r_1 r_2 w_1 w_2}}{2 w_2} \tag{A20}$$

Note that the first relative moments are the weight fractions of the two types of monomeric units, i.e.

$$w_1 = q_{1,0}$$

$$w_2 = q_{0,1} \tag{A21}$$

For a gelation study, only the following second-order moments need to be considered,

$$\frac{\mathrm{d}q_{2,0}}{\mathrm{d}y} = \frac{r_1 r_2 q_{2,0}^2 + 2\lambda q_{2,0} q_{1,1} + \lambda^2 q_{1,1}^2}{r_1 r_2 w_1^2 + 2\lambda w_1 w_2 + \lambda^2 w_2^2} \tag{A22}$$

$$\frac{\mathrm{d}q_{1,1}}{\mathrm{d}y} = \frac{r_1 r_2 q_{2,0} q_{1,1} + \lambda q_{1,1}^2 + \lambda q_{2,0} q_{0,2} + \lambda^2 q_{1,1} q_{0,2}}{r_1 r_2 w_1^2 + 2\lambda w_1 w_2 + \lambda^2 w_2^2} \tag{A23}$$

$$\frac{\mathrm{d}q_{0,2}}{\mathrm{d}y} = \frac{r_1 r_2 q_{1,1}^2 + 2\lambda q_{1,1} q_{0,2} + \lambda^2 q_{0,2}^2}{r_1 r_2 w_1^2 + 2\lambda w_1 w_2 + \lambda^2 w_2^2} \tag{A24}$$

The initial conditions are

$$q_{2,0} = w_1 \bar{r}_{\mathrm{wp},1} \tag{A25}$$

$$q_{1,1} = 0 \tag{A26}$$

$$q_{0,2} = w_2 \bar{r}_{\mathrm{wp},2} \tag{A27}$$

Equations 12−14 in the text are obtained by substituting

$$u_{i,j} = q_{i,j} / \bar{r}_{\mathrm{wp}} \tag{A28}$$

into eqs A22−A24.

References and Notes

(1) Lambla, M. *Makromol. Chem., Macromol. Symp.* **1994**, *83*, 37.
(2) Carothers, W. H. *Trans. Faraday Soc.* **1936**, *32*, 39.
(3) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(4) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45, 393; **1944**, *12*, 125.
(5) Gordon, M. *Proc. R. Soc. London, A* **1962**, *268*, 240.
(6) Macosko, C. M.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(7) Pearson, D. S.; Graessley, W. W. *Macromolecules* **1978**, *11*, 528.
(8) Dusek, K. *Makromol. Chem., Suppl.* **1979**, *2*, 35.
(9) Durand, D.; Bruneau, C.-M. *Makromol. Chem.* **1982**, *183*, 1007.
(10) Mikos, A. G.; Takoudis, C. G.; Peppas, N. A. *Macromolecules* **1986**, *19*, 2174.
(11) Tobita, H.; Hamielec, A. E. *Macromolecules* **1989**, *22*, 3098.
(12) Scranton, A. B.; Peppas, N. A. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 39.
(13) Dotson, N. A. *Macromolecules* **1992**, *25*, 308.
(14) Zhu, S.; Hamielec, A. E. *Macromolecules* **1992**, *25*, 5457.
(15) Okay, O. *Polymer* **1994**, *35*, 976.
(16) Bamford, C. H.; Tompa, H. *J. Polym. Sci.* **1953**, *10*, 345.
(17) Bamford, C. H.; Tompa, H. *Trans. Faraday Soc.* **1954**, *50*, 1097.
(18) Zhu, S.; Hamielec, A. E. *Macromolecules* **1993**, *26*, 3131.
(19) Zhu, S. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 505.
(20) Cimmino, S.; D'Orazio, L.; Greco, R.; Maglio, G.; Malinconico, M.; Mancarella, C. *Polym. Eng. Sci.* **1984**, *24*, 48.
(21) Angola, J. C.; Fujita, Y.; Sakai, T.; Inoue, T. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 807.
(22) Biermann, C. J.; Narayan, R. *Polymer* **1987**, *28*, 2176.
(23) Hiemenz, P. C. *Polymer Chemistry, The Basic Concepts*; Marcel Dekker Inc.: New York, 1984.

MA951717N