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Influence of Cross-Link Density Distribution on Network Formation in Free-Radical Copolymerization of Vinyl/Divinyl Monomers[†]

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ABSTRACT: The influence of the cross-link density distribution on polymer network formation in free-radical copolymerization of vinyl/divinyl monomers was investigated using the Tobita–Hamielec kinetic model coupled with the Macosko–Miller statistical gelation model. The properties investigated were molecular weight development of sol, the gelation point, the sol/gel fraction, and properties of primary polymer chains. Errors involved in neglecting the cross-link density distribution (or assuming a zero variance for the distribution) were correlated with an index of distribution variance in the gelation equations. These errors, though often minor, cannot be neglected for conditions where the reactivities of double bonds are very different and/or the cyclization is significant.

Introduction

Many theories have been developed to describe the molecular processes involved in gel formation during various polymerizations since Carothers[1] defined a gel as a three-dimensional molecule with an infinitely large molecular weight. The creative genius of Flory[2] and Stockmayer,[3] which led to the now called classical gelation theory, established the framework for further developments. Most statistical theories derived in the following decades are equivalent, but differ in mathematical language. Those by Gordon,[4] Macosko and Miller,[5,6] Pearson and Graessley,[7] and Durand and Bruneau[8] are some outstanding examples. However, it is also well known that the derivation of the classical gelation theory and its future developments employed three basic assumptions which are rather limiting. They are (1) all functional groups (equivalently, double bonds in free-radical copolymerization of vinyl/divinyl monomers) have equal reactivity, (2) there is no cyclization, and (3) all functional groups react independently of one another. Although much effort has been made to account for unequal reactivity,[9,10] the substitution effect,[9,10] and cyclization,[11-13] the mathematics involved are often complex. And above all, these statistical models require the random formation of cross-link points on accumulated polymer chains at all levels of monomer conversion during polymerization and thus inherently treat gelation as a process in thermodynamical equilibrium.

The reactions involved in free-radical polymerization are however kinetically controlled. The development of chain properties depends strongly on the reaction path. In this respect, the statistical models are not realistic.[14-17] Although some attempts have been made to modify statistical models to accommodate this point,[18-20] an alternative remedy is to derive kinetic models accounting for the dependence of polymer properties on the reaction path. This approach was tried by Dusek[21] and Mikos et al.[22] Very recently, Tobita and Hamielec[16,23,24] made a rather comprehensive contribution to this end. The core of the Tobita–Hamielec model is that it has demonstrated the inherent inhomogeneity of polymer networks formed in free-radical polymerization with cross-linking. Polymer chains born at different conversions (times) during the course of polymerization have different densities of cross-linked units. The successful kinetic calculation of the cross-link density distribution permits one to comprehend the dramatic differences in the cross-link density of primary polymer chains under real synthesis conditions of a network. Unfortunately, the kinetic approaches in modeling network formation meet some formidable obstacles, particularly in the postgel regime. The challenge lies in formulating the nucleation and growth of gel molecules.[29,30]

The objective of this paper is to investigate the influence of this cross-link density distribution on other aspects of polymer network formation, such as sol molecular weight development, the gelation point, and the gel/sol weight fraction. Since the problem of kinetic modeling in the postgel regime remains unsolved, the methods employed in this paper after Macosko–Miller[5,6] are statistical in nature. We place the Tobita–Hamielec cross-link density distribution in the framework of the Macosko–Miller model. The gelation equations thus developed should be considered semistatistical. The effect of unequal reactivities of double bonds and of cyclization have been taken into account in the cross-link density distribution.

Tobita–Hamielec Model and Cross-Link Density Distribution

The Tobita–Hamielec model,[16,23,24] developed for free-radical copolymerization of vinyl/divinyl monomers, is based on the pseudokinetic rate constant method[25,26] and has been evaluated using experimental data with some success. The key part of the model is the birth conversion dependence of the cross-link density. In the following is provided a brief review and clarification of the methods used to calculate the cross-link density distribution.

The cross-link density is defined as a ratio of the number of cross-linked units (two such units form one cross-linkage) to the total number of monomer units chemically bound in primary chains. The primary chains are rather imaginary linear polymer molecules which would exist if all cross-links connected to them were severed. At present conversion Φ, the cross-link density $\rho(\Theta,\Phi)$ of primary polymer chains born at birth conversion Θ ($\Theta \leq \Phi$) is the sum of the instantaneous cross-link density $\rho_i(\Theta)$ and the

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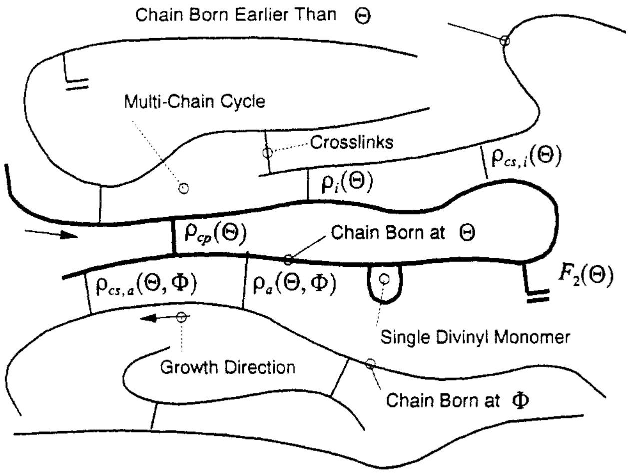

Figure 1. Schematic representation of the polymer network formation in free-radical copolymerization of vinyl/divinyl monomers. The instantaneous cross-links $\rho_i(\Theta)$ of a chain born at Θ are formed during the growth of the chain by propagating with pendant double bonds in those chains born earlier than Θ. The additional cross-links $\rho_a(\Theta,\Phi)$ are formed by consuming pendant double bonds in the chain by those born during the period from Θ to Φ. There are various types of cyclizations. The secondary cyclizations (intermolecular), instantaneous $\rho_{cs,i}(\Theta)$ and additional $\rho_{cs,a}(\Theta,\Phi)$, are formed among chains born at different conversions. The primary cyclizations (intramolecular) $\rho_{cp}(\Theta)$ occur within primary chains.

additional cross-link density $\rho_a(\Theta,\Phi)$:

$$\rho(\Theta,\Phi) = \rho_i(\Theta) + \rho_a(\Theta,\Phi) \tag{1}$$

As illustrated in Figure 1, the instantaneous cross-links of an identified chain born at Θ are formed during the growth of the chain by propagating with pendant double bonds in those chains born earlier than Θ. The additional cross-links are formed by consuming pendant double bonds in the identified chain by those born during the period from Θ to Φ. The fundamental equation for $\rho_a(\Theta,\Phi)$ is

$$\frac{\partial\rho_a(\Theta,\Phi)}{\partial\Phi} = \frac{K_p^*(\Phi)}{K_p(\Phi)}\,\frac{F_2(\Theta) - \rho_{cp}(\Theta) - \rho_{cs,a}(\Theta,\Phi) - \rho_a(\Theta,\Phi)}{1-\Phi} \tag{2}$$

which is derived on the basis of a mass balance of pendant double bonds. Please note that a correction to this equation in the original work[16,23,24] has been made to account for the fact that the instantaneous secondary cyclization does not consume pendant double bonds on primary chains born at Θ, and hence $\rho_{cs,i}(\Theta)$ should not appear in eq 2. It is also worth mentioning here that the Tobita–Hamielec cross-link density distribution is with respect to the birth conversion of primary polymer chains. $\rho(\Theta,\Phi)$ is an average value for all the chains born at Θ. Actually, there is also a cross-link density distribution among the chains born at the same time; e.g., the instantaneous cross-link points are clearly formed in a manner analogous to the Stockmayer bivariate distribution.[27]

$K_p^*(\Phi)$ and $K_p(\Phi)$ are the pseudokinetic rate constants for propagation with pendant double bonds and comonomers (refer to the Appendix). $F_2(\Theta)$ is the mole fraction of divinyl monomer bound in the primary chains, and $\rho_{cp}(\Theta)$ is the primary cyclization density. The primary cyclization is an intramolecular reaction. The intramolecular cyclization occurs within a primary polymer chain. It should be pointed out that there are two types of intramolecular cyclization formed via different mechanisms. Those formed by a radical center on a divinyl monomer unit on the chain end adding to its own double bond (let us call them divinyl loops, see Figure 1) have not been taken into account in the Tobita–Hamielec work.[16,23,24] Divinyl monomers, like ethylene glycol dimethacrylate and *N,N′*-methylenebis(acrylamide) but not divinylbenzene, with more than five units between the two vinyl groups are likely to form this type of cycle, if not chemically prohibited. The other intramolecular cycles (the primary cycles of interest in this work) are formed by propagation of radicals with the double bonds in their own chains, but not within single divinyl monomers. Intuitively, the primary cyclization is a strong function of the configuration of primary chains as a whole while the formation of the divinyl loops has little to do with the chain configuration, but the structure of divinyl molecules. However, both types of cycles do not make contributions to either gel formation or elastic properties of the polymer network. According to the "random flight model" [11]

$$\rho_{cp}(\Theta) = K_{cp}F_2(\Theta) \tag{3}$$

$\rho_{cs,a}(\Theta,\Phi)$ is an additional intermolecular cyclization. The intermolecular (secondary) cyclization occurs between two primary polymer chains (note that in the Tobita–Hamielec work[16,23,24] multichain cyclization is excluded). Although this type of cycle does not contribute to gel formation either, it may be elastically effective:

$$\frac{\partial\rho_{cs,a}(\Theta,\Phi)}{\partial\rho_a(\Theta,\Phi)} = \eta(\Theta,\Phi) \tag{4}$$

where $\eta(\Theta,\Phi)$ is the average number of intermolecular cycles per cross-link. It is equal to a constant K_{cs} using the "zeroth approximation".[16,23,24]

Since each additional cross-link needs one instantaneous partner, $\rho_i(\Theta)$ is therefore given by

$$\rho_i(\Theta) = \int_0^{\Theta} \frac{\partial\rho_a(\theta,\Theta)}{\partial\Theta}\,d\theta \tag{5}$$

The various types of cross-links and cyclizations mentioned above are clearly illustrated in Figure 1. In general, the total cross-link density $\rho(\Theta,\Phi)$ can be solved for numerically using eqs 1–5 together with eqs A1–A7 in the Appendix. The average cross-link density $\bar{\rho}(\Phi)$ is

$$\bar{\rho}(\Phi) = \frac{1}{\Phi}\int_0^{\Phi}\rho(\Theta,\Phi)\,d\Theta \tag{6}$$

In a simple case where $K_p^*(\Phi)/K_p(\Phi)$ and $F_2(\Theta)$ are independent of monomer conversion (strictly speaking, this can only be satisfied under azeotropic conditions and at low levels of divinyl monomer), we have

$$\rho(\Theta,\Phi) = \kappa F_2\left\{\frac{\xi}{1-\xi}[(1-\Theta)^{\xi-1} - 1] + \left[1 - \left(\frac{1-\Phi}{1-\Theta}\right)^{\xi}\right]\right\} \tag{7}$$

and

$$\bar{\rho}(\Phi) = 2\kappa F_2\left\{1 - \frac{1}{1-\xi}\,\frac{1-\Phi}{\Phi}[(1-\Phi)^{\xi-1} - 1]\right\} \tag{8}$$

where $\xi = (K_p^*/K_p)(1 + \mathrm{K}_{cs})$ and $\kappa = (1 - \mathrm{K}_{cp})/(1 + K_{cs})$.

As can be seen from Figure 2, the cross-link densities for the primary chains born at different conversions can be very different. Such information may be important in the design of the structure of network polymer products. However, the influence of the variance of the Tobita–Hamielec distribution on other aspects of network formation has not been fully examined to date, except for the recent work by Dotson[20] who developed a rigorous statistical model taking the polymerization path into account but with a rather narrow scope, i.e., the weight-average molecular weight in the pregel. In the following,

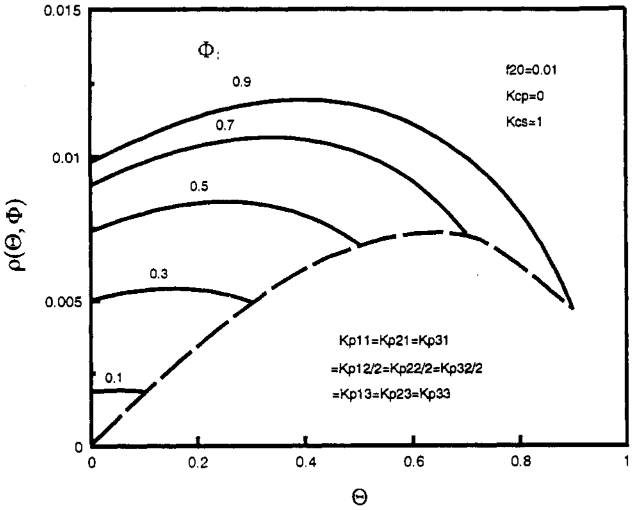

Figure 2. Cross-link density distribution of primary polymer chains $\rho(\Theta,\Phi)$ with respect to the birth conversion Θ at the present conversion Φ: 0.1, 0.3, 0.5, 0.7, and 0.9, predicted by the Tobita–Hamielec model.

this influence is investigated using statistical arguments. The properties investigated are sol and primary chain molecular weight development, the gelation point, and the sol/gel fraction.

Molecular Weight Development in the Pregel Regime

The Macosko–Miller gelation theory[5,6] is based on the recursive nature of the branching process and the elementary laws of total probability and total probability for expectation. This theory, although virtually the same as the other statistical gelation theories, enjoys a great simplicity in the mathematical language and, at the same time, can provide most of the important property averages. It is therefore adopted in the following derivation.

Let us denote M as a primary polymer chain and B as a branch unit (two branch units form one cross-linkage). Pick a B at random. The probability that this B's partner belongs to a primary chain having length l, branch points b, and birth conversion Θ is proportional to the number of branching points on such chains. The cross-link density distribution for primary chains born at the same conversion is assumed to be binomial:

$$P(B_{l,b,\Theta}) = \frac{bw_p(l,\Theta)}{l\Phi\bar{\rho}(\Phi)}\binom{l}{b}\rho^b(\Theta,\Phi)[1-\rho(\Theta,\Phi)]^{l-b} \qquad (9)$$

where $w_P(l,\Theta)$ is the instantaneous weight-fraction chain length distribution for primary polymer chains born at conversion Θ, which is

$$w_p(l,\Theta) = [\tau(\Theta) + \beta(\Theta)] \times \left\{\tau(\Theta) + \frac{\beta(\Theta)}{2}[\tau(\Theta)+\beta(\Theta)]l\right\} le^{-[\tau(\Theta)+\beta(\Theta)]l} \qquad (10)$$

$\tau(\Theta)$ represents chains formed by disproportionation termination and chain transfer to small molecules; $\beta(\Theta)$ represents chains formed by radical recombination.[28]

Now let us find the molecular weight $W_{\mathrm{B}^{\mathrm{out}}}$, attached to B looking out through its partner. Using the law of total probability for expectation and assuming random formation of cross-linkage, we have (note, Θ and l are treated as continuous variables and b as discrete)

$$E(W_{\mathrm{Bout}}) = \int_0^{\Phi}\int_0^{\infty}\sum_{b=0}^{l} P(B_{l,b,\Theta})\, E(W_{\mathrm{Bin}_{l,b,\Theta}})\, \mathrm{d}l\, \mathrm{d}\Theta \qquad (11)$$

where $E(W_{\mathrm{B}^{\mathrm{out}}})$ is an expectation (average value) of $W_{\mathrm{B}^{\mathrm{out}}}$, and $W_{\mathrm{B}^{\mathrm{in}}{}_{l,b,\Theta}}$ is the molecular weight looking from B's partner into its chain. The expectation for $W_{\mathrm{B}^{\mathrm{in}}{}_{l,b,\Theta}}$ is

$$E(W_{\mathrm{Bin}_{l,b,\Theta}}) = l + (b-1)E(W_{\mathrm{B}^{\mathrm{out}}}) \qquad (12)$$

Substitution of eqs 9 and 12 into eq 11 gives (note $l \gg 1$)

$$E(W_{\mathrm{Bout}}) = \frac{(1/\Phi\bar{\rho}(\Phi))\int_0^{\Phi}\int_0^{\infty} lw_{\mathrm{P}}(l,\Theta)\,\rho(\Theta,\Phi)\,\mathrm{d}l\,\mathrm{d}\Theta}{1-(1/\Phi\bar{\rho}(\Phi))\int_0^{\Phi}\int_0^{\infty} lw_{\mathrm{P}}(l,\Theta)\,\rho^2(\Theta,\Phi)\,\mathrm{d}l\,\mathrm{d}\Theta} \qquad (13)$$

Now, If $M_{l,b,\Theta}$ is a primary chain having length l, branch points b, and birth conversion Θ, being randomly picked from the polymer population, belonging to a molecule of weight $W_{M_{l,b,\Theta}}$, the expectation for $W_{M_{l,b,\Theta}}$ is

$$E(W_{M_{l,b,\Theta}}) = l + bE(W_{\mathrm{Bout}}) \qquad (14)$$

The weight-average molecular weight (molecular size) is therefore

$$\bar{L}_{\mathrm{w}} = \int_0^{\Phi}\int_0^{\infty}\sum_{b=0}^{l}\frac{w_{\mathrm{p}}(l,\Theta)}{\Phi}\binom{l}{b}\rho^b(\Theta,\Phi) \times [1-\rho(\Theta,\Phi)]^{l-b}E(W_{M_{l,b,\Theta}})\,\mathrm{d}l\,\mathrm{d}\Theta \qquad (15)$$

Substitution of eqs 13 and 14 into eq 15 gives

$$\bar{L}_{\mathrm{w}} = \bar{L}_{\mathrm{pw}} + \frac{(1/\Phi^2\bar{\rho}(\Phi))[\int_0^{\Phi}\int_0^{\infty} lw_{\mathrm{P}}(l_{,\Theta})\,\rho(\Theta,\Phi)\,\mathrm{d}l\,\mathrm{d}\Theta]^2}{1-(1/\Phi\bar{\rho}(\Phi))\int_0^{\Phi}\int_0^{\infty} lw_{\mathrm{P}}(l,\Theta)\,\rho^2(\Theta,\Phi)\,\mathrm{d}l\,\mathrm{d}\Theta} \qquad (16)$$

where $\bar{L}_{\mathrm{pw}}$ is the weight-average length of primary chains:

$$\bar{L}_{\mathrm{pw}} = \frac{1}{\Phi}\int_0^{\Phi}\int_0^{\infty} lw_{\mathrm{p}}(l,\Theta)\,\mathrm{d}l\,\mathrm{d}\Theta \qquad (17)$$

The influence of the cross-link density distribution $\rho(\Theta,\Phi)$ on gelation is coupled with that of the chain length distribution $w_{\mathrm{P}}(l,\Theta)$. The drift of $w_{\mathrm{P}}(l,\Theta)$ during the course of polymerization can be quite dramatic due to monomer depletion[18] and, more importantly, to diffusion-controlled radical termination reactions.[29,30] However, in this paper, we concentrate on the discussion of cross-link density distribution. We therefore assume $w_{\mathrm{P}}(l,\Theta)$ independent of Θ. Equation 16 becomes

$$\frac{\bar{L}_{\mathrm{w}}}{\bar{L}_{\mathrm{pw}}} = 1 + \frac{\bar{\rho}(\Phi)\bar{L}_{\mathrm{pw}}}{1-\gamma\bar{\rho}(\Phi)\bar{L}_{\mathrm{pw}}} \qquad (18)$$

where γ is a distribution index defined as follows:

$$\gamma = \frac{\overline{\rho^2}(\Phi)}{\bar{\rho}^2(\Phi)} = \frac{(1/\Phi)\int_0^{\Phi}\rho^2(\Theta,\Phi)\,\mathrm{d}\Theta}{[(1/\Phi)\int_0^{\Phi}\rho(\Theta,\Phi)\,\mathrm{d}\Theta]^2} \qquad (19)$$

It is also clear that when $\rho(\theta,\Phi)$ is independent of birth conversion Θ (no matter whether $w_{\mathrm{P}}(l,\Theta)$ is independent of Θ), eq 16 can be easily reduced to

$$\frac{\bar{L}_{\mathrm{w}}}{\bar{L}_{\mathrm{pw}}} = \frac{1}{1-\bar{\rho}(\Phi)\bar{L}_{\mathrm{pw}}} \qquad (20)$$

which fully agrees with the classical gelation theory.[2,3]

Gelation Point

At the gelation point, infinitely large molecules start to appear, and therefore, the weight-average molecular weight diverges; i.e.

$$\frac{1}{\Phi\bar{\rho}(\Phi)}\int_0^{\Phi}\int_0^{\infty} lw_{\mathrm{P}}(l,\Theta)\,\rho^2(\Theta,\Phi)\,\mathrm{d}l\,\mathrm{d}\Theta = 1 \qquad (21)$$

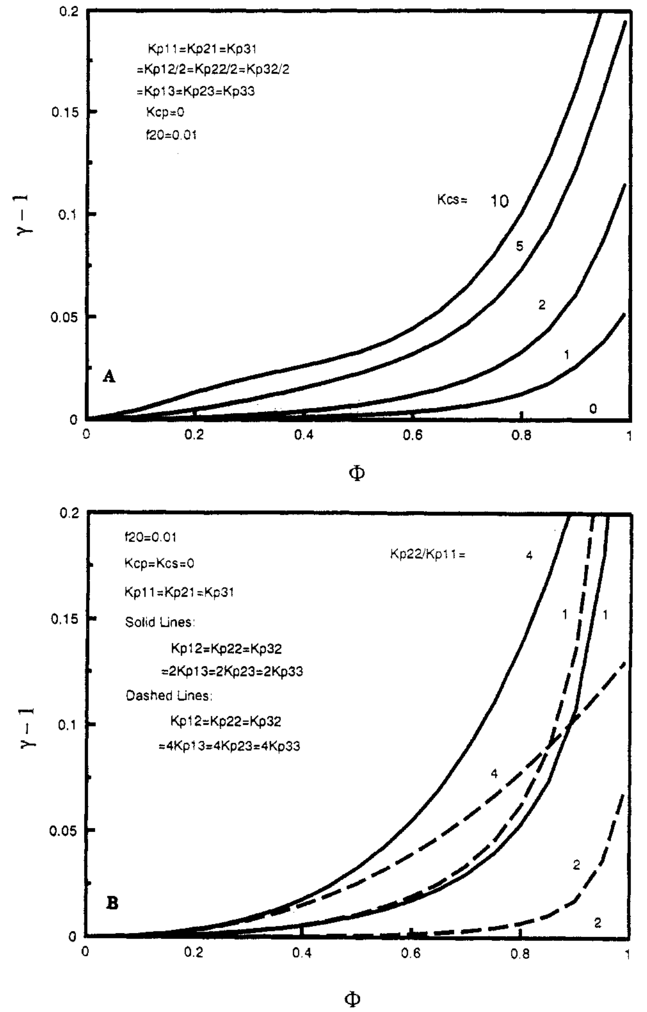

Figure 3. $\gamma - 1$ versus Φ: (A) the effect of cyclization; (B) the effect of unequal reactivities of double bonds.

from eq 16, in general, or

$$\gamma\bar{\rho}(\Phi)\bar{L}_{\mathrm{pw}} = 1 \tag{22}$$

from eq 18, with the assumption that $w_{\mathrm{p}}(l,\Theta)$ is independent of Θ.

It can be clearly seen, in eqs 18 and 22, that the influence of the cross-link density distribution on the pregel molecular weight development and the gelation point is reflected in the factor γ. In the classical gelation theory,[2,3] γ is unity.

Mathematically, the value of γ is always larger than or equal to unity. It can therefore be concluded that the inhomogeneity in cross-link density with respect to the birth conversion promotes gelation (gelation occurs at a smaller monomer conversion). A similar conclusion was drawn in the recent paper of Dotson.[20] The gelation point comes earlier when the variance of the cross-link density distribution is larger. According to our calculations, the deviation of γ from unity is often minor. However, under certain conditions where cyclization is significant and/or the reactivities of double bonds are highly unequal, the deviations may be large. The effect of the former is shown in Figure 3A, and the latter in Figure 3B. At higher conversions, the deviations are often larger.

Figure 4 shows a typical example of the molecular weight development in the pregel regime. In cross-linking polymerization, there exists a critical level of divinyl monomer below which gelation does not occur. The difference in model predictions with and without accounting for the distribution variance is significant near the critical cross-linker level. Equation 18 predicts a gel point, while eq 20 predicts no gelation. Figure 5 shows the effect of the distribution index, γ, on the gelation point. In the classical theories, at the gel point, each primary chain possesses one cross-link point on a weight-average basis. When the distribution variance is considered, this average number can be much lower.

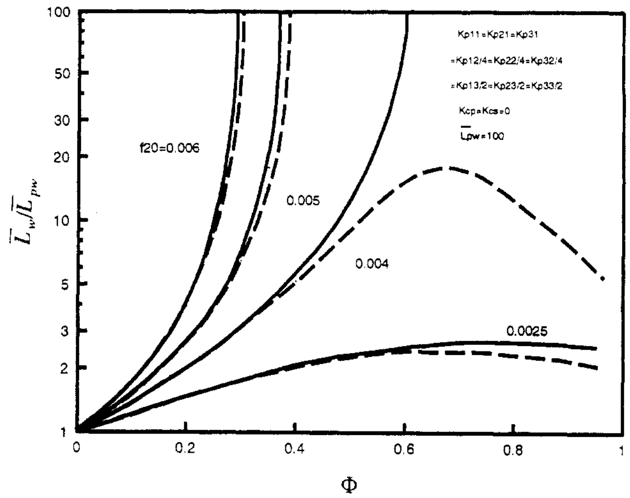

Figure 4. Development of the weight-average molecular weight in the pregel regime: (solid lines) predicted by eq 18; (dashed lines) predicted by eq 20.

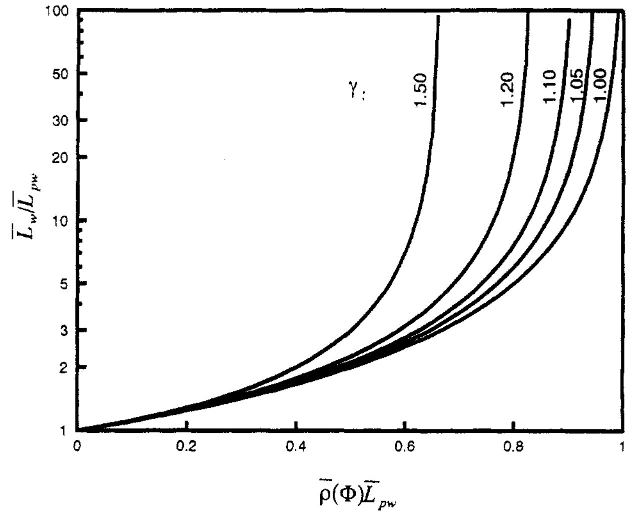

Figure 5. Effect of γ on gelation. γ is always larger than unity. The gelation point is therefore predicted to come earlier when the variance of the cross-link density distribution is considered.

Sol/Gel Fraction

In the statistical gelation theories, the nucleation and growth of gel molecules are ingeniously formulated using the recursive feature of the gelation process coupling techniques of probability and statistics. An outstanding example is the following equation for the gel/sol weight fraction:[31]

$$1 - W_{\mathrm{g}} = \int_0^\infty \left[\frac{1}{\Phi}\int_0^\Phi w_{\mathrm{p}}(l,\Theta)\,\mathrm{d}\Theta\right][1 - \bar{\rho}(\Phi)W_{\mathrm{g}}]^l\,\mathrm{d}l \tag{23}$$

where W_{g} is the gel weight fraction. Equation 23 requires that the cross-link points be randomly distributed over monomer units in the accumulated polymer chains. In free-radical polymerization with cross-linking, the cross-link density is inherently heterogeneous with respect to the primary chains having different birth conversions. In order to account for this effect, Tobita and Hamielec[16,23,24] have attempted to generalize eq 23 as follows:

$$1 - W_g(\Theta,\Phi) = \int_0^\infty w_p(l,\Theta)[1 - \rho(\Theta,\Phi)\, W_g(\Theta,\Phi)]^l \, dl \qquad (24)$$

where $W_g(\Theta,\Phi)$ is the gel weight fraction for those primary chains born at Θ. Integration of $W_g(\Theta,\Phi)$ over conversion gives the total gel fraction:

$$W_g = \frac{1}{\Phi}\int_0^\Phi W_g(\Theta,\Phi)\, d\Theta \qquad (25)$$

An examination of eqs 24 and 25 reveals that this generalization is not generally applicable because eq 24 requires that the primary polymer chains born at the same conversion cross-link exclusively among themselves. Actually in the derivation of the Tobita–Hamielec model,[16,23,24] the cross-link densities between primary chains born at the same conversion are assumed to be zero. This assumption is reasonable because, as illustrated in Figure 1, the cross-links are overwhelmingly formed among chains born at different conversions: for the polymer chains born at Θ, the instantaneous cross-links, $\rho_i(\Theta)$, are those formed with the chains born earlier than Θ, while the additional crosslinks, $\rho_a(\Theta,\Phi)$, are those formed with the chains born later (from Θ to Φ). The secondary cyclizations, both instantaneous $\rho_{cs,i}(\Theta)$ and additional $\rho_{cs,a}(\Theta,\Phi)$, are also formed among chains born at different conversions. The primary cyclizations $\rho_{cp}(\Theta)$ are the only ones requiring intramolecular cross-linkages (the branch units are of course born at the same conversion). However, the various cyclizations are not responsible for polymer network formation (the secondary cyclizations contribute to network elasticity while primary cyclization simply wastes pendant double bonds). It should be pointed out that eqs 24 and 25 may find some possible applications under special limiting conditions, e.g., gelation in precipitated chains.

In the following, using the Macosko–Miller method,[5,6] we derive a more general model for the gel/sol fraction taking the cross-link density distribution into account. First, let us pick a branch unit at random, and let $F_{B^{out}}$ be the event that B is the start of a finite molecule, looking out through its partner which is in a primary chain having length l, branch points b, and birth conversion Θ. According to the law of total probability, the probability of this event is given as follows:

$$P(F_{B_{out}}) = \int_0^\Phi \int_0^\infty \sum_{b=0}^{l} P(B_{l,b,\Theta})\, P(F_{B^{in}_{l,b,\Theta}})\, dl\, d\Theta \qquad (26)$$

where $P(F_{B^{in}_{l,b,\Theta}})$ is the probability of looking from B's partner into its primary chain leading to a finite molecule, which is

$$P(F_{B^{in}_{l,b,\Theta}}) = P^{b-1}(F_{B_{out}}) \qquad (27)$$

Substitution of eqs 9 and 27 into eq 26 gives (note $l \gg 1$)

$$P(F_{B_{out}}) = \frac{1}{\Phi\bar{\rho}(\Phi)}\int_0^\Phi \int_0^\infty w_P(l,\Theta)\, \rho(\Theta,\Phi) \times \{1 - \rho(\Theta,\Phi)[1 - P(F_{B_{out}})]\}^l \, dl\, d\Theta \qquad (28)$$

When $w_P(l,\Theta)$ and $\rho(\Theta,\Phi)$ are given, $P(F_{B^{out}})$ can be solved numerically using eq 28. The probability that a randomly chosen monomer unit in a primary chain M with length l, branch points b, and birth conversion Θ belongs to the sol population is

$$P(F_{M_{l,b,\Theta}}) = P^b(F_{B_{out}}) \qquad (29)$$

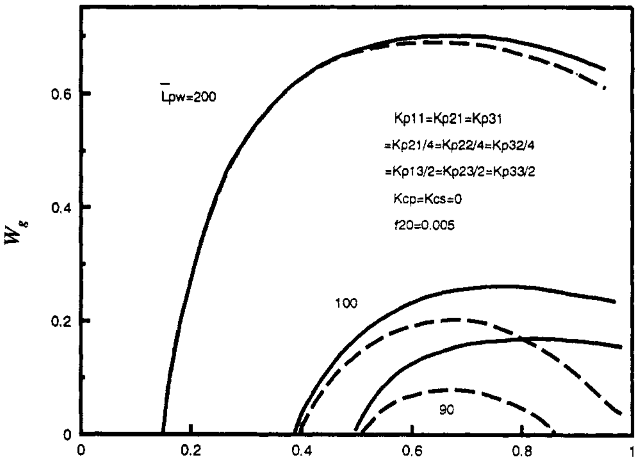

Figure 6. Development of the gel fraction: (solid lines) predicted by eqs 28 and 31; (dashed lines) predicted by eq 23.

The total sol fraction is therefore

$$W_s = \int_0^\Phi \int_0^\infty \sum_{b=0}^{l} \frac{w_p(l,\Theta)}{\Phi}\binom{l}{b}\rho^b(\Theta,\Phi) \times [1 - \rho(\Theta,\Phi)]^{l-b} P(F_{M_{l,b,\Theta}})\, dl\, d\Theta \qquad (30)$$

Substitution of eq 29 into eq 30 gives

$$W_s = \frac{1}{\Phi}\int_0^\Phi \int_0^\infty w_P(l,\Theta)\{1 - \rho(\Theta,\Phi)[1 - P(F_{B_{out}})]\}^l \, dl\, d\Theta \qquad (31)$$

where $W_s = 1 - W_g$. It can be easily seen that, at the gelation point, eqs 28 and 31 fully agree with eq 21, and that when $\rho(\Theta,\Phi)$ is independent of the birth conversion Θ, eq 28 or 31 reduces to eq 23.

Figure 6 shows the development of gel molecules. Flory's most probable molecular weight distribution is used for the primary chains; i.e., $\beta = 0$ in eq 10. The differences in the predictions with and without consideration of the cross-link density distribution are larger when the cross-linker level is smaller and/or the primary chains are shorter. The gel fractions predicted by eq 28 are often higher than those by eq 23. The biggest differences are found at higher monomer conversions.

Properties of Primary Chains

It is also of interest to know the properties of primary polymer chains during polymerization. One of them is the content of linear chains (weight fraction on polymer base):

$$W_l = \frac{1}{\Phi}\int_0^\Phi \int_0^\infty w_P(l,\Theta)[1 - \rho(\Theta,\Phi)]^l \, dl\, d\Theta \qquad (32)$$

Comparing eq 32 with eq 31, it can be seen that W_l is always less than W_s. This agrees with the fact that the sol population consists of both linear and branched chains. During the course of polymerization, the weight fraction of linear chains over total polymer decreases monotonously. However, when the content is expressed as the weight fraction of the chains in the sol polymer, the fraction increases beyond the gelation point. The reason for this is that the branched sol chains have a higher probability of being "sponged" into gel molecules (see Figure 7).

Another interesting property is the content of dangling chains (a primary chain having only one of its branch points connected to the polymer network). Although these chains belong to the gel population, they do not contribute to network elasticity. The number of dangling chains per

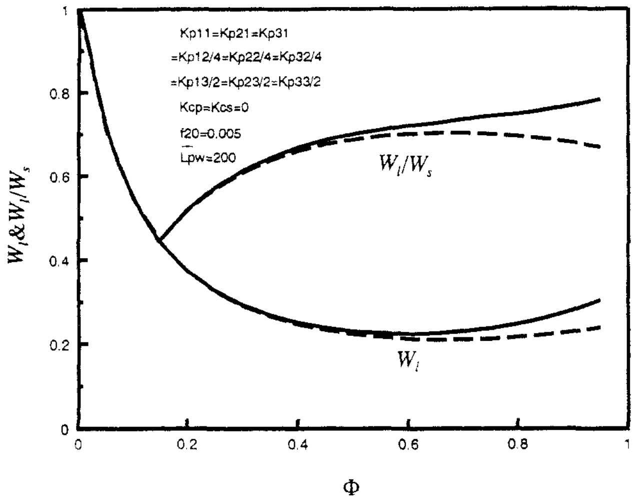

Figure 7. Content of linear polymer chains (the weight fraction over total polymer, W_l, and the weight fraction over sol polymer, W_l/W_s): (solid lines) predicted by taking the variance of the cross-link density distribution into account; (dashed lines) predicted without considering the distribution variance.

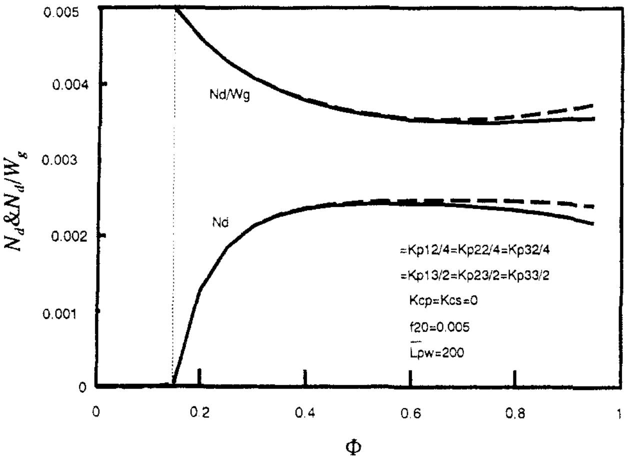

Figure 8. Content of dangling chains in the polymer network (the number of dangling chains per monomeric unit over total polymer, N_d, and the number of dangling chains per monomeric unit over gel polymer, N_d/W_g): (solid lines) predicted by taking the variance of the cross-link density distribution into account; (dashed lines) predicted without considering the distribution variance.

monomeric unit can be formulated (and further simplified with the help of eq 28) as follows:

$$N_d = \frac{1}{\Phi}\int_0^{\Phi}\int_0^{\infty}\frac{w_P(l,\Theta)}{l}\sum_{b=1}^{l}\left\{\binom{l}{b}\rho(\Theta,\Phi)^b \times [1-\rho(\Theta,\Phi)]^{l-b}\binom{b}{l}P^{b-l}(F_{Bout})[1-P(F_{Bout})]\right\} dl\, d\Theta = \bar{\rho}(\Phi)\, P(F_{Bout})[1-P(F_{Bout})] \quad (33)$$

Figure 8 shows the development of dangling chains after the gel point. The content of dangling chains increases as the gel molecules grow. However, the number of dangling chains per unit mass of gel decreases. This indicates the embellishment of gel structures in the postgel regime.

Discussion and Conclusions

The statistical gelation models[2-8] require that the monomeric units as well as the cross-link units in primary polymer chains be randomly distributed. This is equivalent to saying that gel molecules are in an equilibrium state. At every step during the polymerization, all the chemical bonds connecting monomeric units are severed and instantaneously reformed in a random manner. In free-radical polymerization with cross-linking, the buildup of network structures strongly depends on the polymerization path (or history). The transition from sol to gel is irreversible. Once gel molecules are formed, they are always in the system. However, in the statistical models, the network properties are expressed as functions of the average cross-link density only. When this density is lower than a critical value, no gel is predicted. In free-radical polymerization, when the divinyl monomers are highly reactive, the cross-links are formed at low monomer conversions. At high conversions, the polymer chains produced may be homopolymer chains. The increase in the sol content can reduce the average cross-link density below the critical value. The statistical models without considering the cross-linking density distribution therefore predict no gel; i.e., the gel molecules formed disappear later. This can be clearly seen in Figure 6 (the dotted lines). It should be pointed out that the present model is not fully kinetically-controlled, and therefore can also predict this type of gel disappearance in some cases. However, when the variance of the cross-link density distribution is accounted for, this unrealistic feature is largely removed.

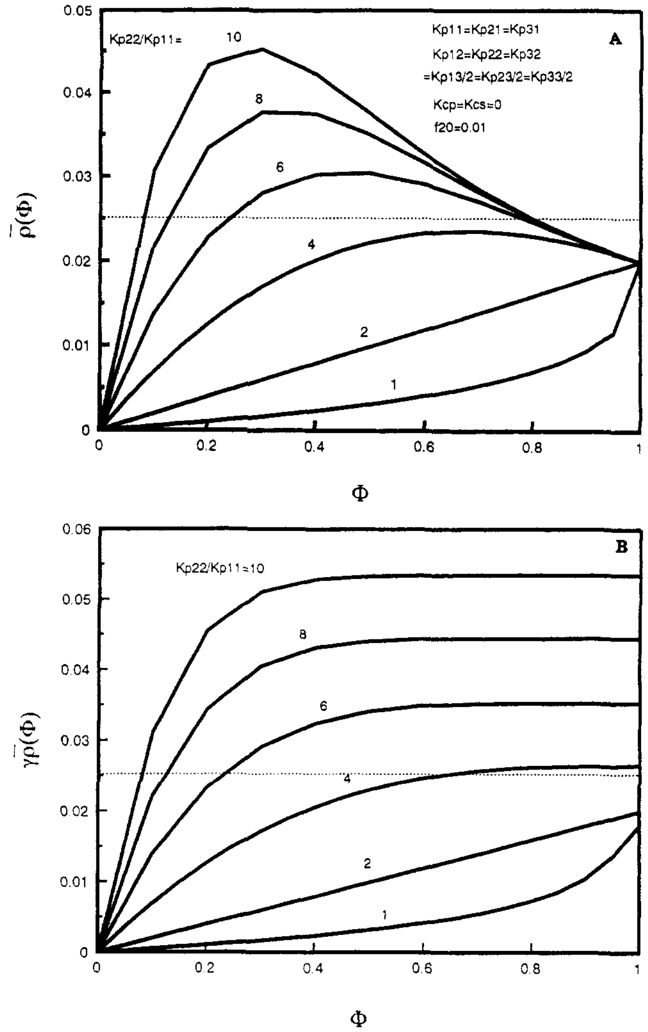

Figure 9. Development of the cross-link densities during free-radical polymerization with cross-linking and the effect of unequal reactivities of double bonds: (A) $\bar{\rho}(\phi)$; (B) $\gamma\bar{\rho}(\phi)$. The parameters are the same as in part A.

Figure 9A further illustrates this point. The average cross-link density is plotted versus monomer conversion for various reactivity ratios. When the reactivity ratio equals 2, i.e., the double bonds on vinyl and divinyl monomers are equally reactive, the average cross-link density increases linearly with the monomer conversion. When the reactivity ratio is higher than 2, the density increases first and then decreases. Let us assume that the weight-average length of primary polymer chains ($\bar{L}_{pw}$) is 40. The critical average cross-link density for gelation in the statistical models is then 0.025 (the dotted line in Figure 9A). In the cases when the reactivity ratios are 6, 8, and 10, the gel molecules are predicted to form first and then to disappear at high monomer conversion (about 0.80 in Figure 9A).

On the other hand, when the full cross-link density distribution is taken into account, the gel point is not only a function of the average cross-link density but also the distribution variance as expressed in $\gamma\bar{\rho}(\Phi)$. Figure 9B shows $\gamma\bar{\rho}(\Phi)$ versus the monomer conversion using the same kinetic parameters as in Figure 9A. As can be seen from the dotted line, the gel molecules once formed do not disappear as predicted by the classical gelation theories.

However, the model derived in this paper is still not a fully kinetically-controlled one. The only difference compared with the classical gelation models[2,3] is that the classical models assume the cross-link points randomly redistributed over the accumulated polymer mass at every moment during the course of polymerization while the model in this paper assumes the cross-link points randomly distributed over the primary polymer chains born at the same conversion. The cross-link densities of the primary polymer chains born at different conversions are calculated using the Tobita–Hamielec model.[16,23,24] This is reflected in the formulation of eq 9. In reality, the cross-link points are formed at different times (or monomer conversions). The instantaneous cross-link points ($\rho_i(\Theta)$ in eq 1) are formed by consuming pendant double bonds on other primary chains at the moment the present chain is born. The additional cross-link points ($\rho_a(\Theta,\Phi)$) are formed by consuming the pendant double bonds on the chains. Since the two types of cross-link points are formed in a different manner, the cross-link density of the primary chains having the same birth conversion may not obey a binomial distribution as used in eq 9. A possible remedy for this is to extend the Stockmayer's bivariate distribution[27] to terpolymerization, taking the pendant double bonds as a third component. The development of the distribution can then be closely followed.

Another assumption which persists in this model (eqs 9, 12, and 27) is the random formation of cross-linkages between primary chains born at different conversions. It requires that cross-linkages be severed and re-formed instantaneously at every stage of polymerization. In contrast, as has been mentioned before, in the classical model every monomeric unit is required to be severed and re-formed. To remove this assumption, the exact number of cross-linkages between primary chains born at any two specific conversions is needed. Even then, the numerical solutions can still be formidable. This point has been well illustrated and discussed in the recent paper by Dotson.[20]

In conclusion, we have derived the equations for the weight-average molecular weight of the sol polymer in the pregel region, for the gel point, for the sol/gel fraction, for the weight fraction of linear polymer, and for the number of dangling chains in the gel molecules. These properties are all expressed as functions of the cross-link density distribution $\rho(\Theta,\Phi)$ and the chain length distribution of primary polymers $w_p(l,\Theta)$, which in turn are functions of the monomer conversion Φ. These equations can be used to investigate the influences of both $\rho(\Theta,\Phi)$ and $w_p(l,\Theta)$ on the gel formation. The equations are in agreement with the classical gelation theories[2,3] under limiting conditions when $\rho(\Theta,\Phi)$ and $w_p(l,\Theta)$ are independent of birth conversion Θ. Since our objective in this paper is to investigate the influence of $\rho(\Theta,\Phi)$,$w_p(l,\Theta)$ was assumed to be independent of the polymerization path. Our simulation shows that the inhomogeneity in the cross-link density promotes gelation. The gel point occurs earlier, and often the gel content is predicted to be larger. The differences in the model predictions with and without accounting for the cross-link density distribution are often small. However, they can be significant under some limiting conditions, e.g., highly unequal reactivities of double bonds and/or substantial cyclization. These conditions give large cross-link density distribution variances.

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Appendix

The pseudokinetic rate constants used in eq 2 are defined in the following:

$$K_p = \sum_{i=1}^{3}\sum_{j=1}^{2} K_{pij}\Phi_i^* f_j \tag{A1}$$

$$K_p^* = \sum_{i=1}^{3} K_{pi3}\Phi_i^* \tag{A2}$$

The copolymer composition, F_2, is calculated from

$$F_2 = \frac{\sum_{i=1}^{3} K_{pi2}\Phi_i^* f_2}{\sum_{i=1}^{3}\sum_{j=1}^{2} K_{pij}\Phi_i^* f_j} \tag{A3}$$

where K_{pij} is the propagation rate constant of radicals of type i with monomers of type j, K_{pi3}^* is the propagation rate constant of radicals of type i with pendant double bonds, Φ_i^* is the number fraction of radicals of type i, and f_i is the fraction of monomers of type i. The subscripts 1–3 denote monomers of type 1 and type 2 and pendant double bonds, respectively. Applying the steady-state hypothesis, we have the following equation for Φ_i^*:

$$\sum_{i=1}^{3} K_{pik}\Phi_i^* f_k = \sum_{j=1}^{3} K_{pkj}\Phi_k^* f_j \tag{A4}$$

where $k = 1–3$. The divinyl monomer composition, f_2, is calculated using

$$\frac{df_2}{d\Phi} = \frac{f_2 - F_2}{1 - \Phi} \tag{A5}$$

Note that Φ is the monomer conversion. Since the fractions are based on monomers, $f_1 = 1 - f_2$. f_3 is the concentration ratio of pendant double bonds over monomers:

$$f_3 = \left[(1 - K_{cp})\bar{F}_2 - \frac{1}{2}(1 + K_{cs})\bar{\rho}\right]\frac{\Phi}{1 - \Phi} \tag{A6}$$

where $\bar{F}_2$ is the accumulated fraction of divinyl monomer

$$\bar{F}_2 = \frac{f_{20} - (1 - \Phi)f_2}{\Phi} \tag{A7}$$

and $\bar{\rho}$ is the average cross-link density (see eq 6 in the text). Equations A1–A7 should be solved together with eqs 1–6.

The pseudokinetic rate constant method[25,26] is a powerful tool in kinetic modeling of multicomponent polymerization. In essence, it reduces the analysis of multicomponent polymerization into that of homopolymerization. The major assumption in the method is that the radical fractions, Φ_i*, are independent of chain length; i.e.

$$\Phi_{i,1}^* = \Phi_{i,2}^* = \dots = \Phi_{i,r}^* = \dots = \Phi_i^* \qquad (A8)$$

where the subscript r denotes the monomeric units in the polymer chain. The possible error introduced by this assumption was fully investigated by Tobita and Hamielec.[32] It was found that the error is negligible when the length of the polymer chains is over 10 monomeric units.

References and Notes

(1) Carothers, W. H. *Trans Faraday Soc.* **1936**, *32*, 39.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(3) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45; **1944**, *12*, 125.
(4) Gordon, M. *Proc. R. Soc. London, A* **1962**, *268*, 240.
(5) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(6) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.
(7) Pearson, D. S.; Graessley, W. W. *Macromolecules* **1978**, *11*, 528.
(8) Durand, D.; Bruneau, C.-M. *Makromol. Chem.* **1982**, *183*, 1007, 1021.
(9) Miller, D. R.; Macosko, C. W. *Macromolecules* 1978, *11*, 656; **1980**, *13*, 1063.
(10) Durand, D.; Bruneau, C.-M. *Polymer* **1983**, *24*, 587, 592.
(11) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600.
(12) Gordon, M., Scantlebury, G. R. *J. Polym. Sci., Part C* **1968**, *16*, 3933.
(13) Stepto, R. F. T. In *Development in Polymerization*; Haward, R. N., Ed.; Applied Science Publishers Ltd.: London, 1982; p 18.
(14) Mikes, J.; Dusek, K. *Macromolecules* **1982**, *15*, 93.
(15) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(16) Tobita, H.; Hamielec, A. E. *Makromol. Chem., Macromol. Symp.* **1988**, *20/21*, 501.
(17) Galina, H.; Szustalewicz, A. *Macromolecules* **1989**, *22*, 3124.
(18) Dotson, N. A.; Galvan, R.; Macosko, C. W. *Macromolecules* **1988**, *21*, 2560.
(19) Galina, H.; Szustalewicz, A. *Macromolecules* **1990**, *23*, 3833.
(20) Dotson, N. A. *Macromolecules* **1992**, *25*, 308.
(21) Dusek, K. *Makromol. Chem., Suppl.* **1979**, *2*, 35.
(22) Mikos, A. G.; Takoudis, C. G.; Peppas, N. A. *Macromolecules* **1986**, *19*, 2174.
(23) Tobita, H.; Hamielec, A. E. *Macromolecules* **1989**, *22*, 3098.
(24) Tobita, H. Ph.D. Thesis, McMaster University, 1990.
(25) Hamielec, A. E.; MacGregor, J. F. In *Polymer Reaction Engineering*; Reichert, K.-H., Gerseler, W., Eds.; Hanser Publishers: New York, 1983.
(26) Broadhead, T. O.; Hamielec, A. E.; MacGregor, J. F. *Makromol. Chem., Suppl.* **1985**, *10/11*, 105.
(27) Stockmayer, W. H. *J. Chem. Phys.* **1945**, *13*, 199.
(28) Zhu, S.; Hamielec, A. E. *Macromolecules* **1989**, *22*, 3039.
(29) Zhu, S.; Hamielec, A. E. *Makromol. Chem., Symp.*, in press.
(30) Zhu, S. Ph.D. Thesis, McMaster University, 1991.
(31) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(32) Tobita, H.; Hamielec, A. E. *Polymer* **1991**, *32*, 2641.