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# Structural Development during Nonlinear Free-Radical Polymerizations

**Neil A. Dotson, Rafael Galván,[†] and Christopher W. Macosko***

*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455.*

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ABSTRACT: Relationships have been derived which describe structural development in nonlinear free-radical polymerizations as a function of conversion. The recursive analysis is based on the assumptions of ideal network formation and those assumptions standard in the kinetic analysis of linear free-radical polymerizations. Significant is the fact that changes in average primary chain length (e.g., due to drift or Trommsdorff effect), which in linear systems give rise to large polydispersities, can be accounted for in these relationships. While it is shown that for many systems such rigor is unnecessary in the pregel regime, it is also shown that neglect of such effects in the postgel regime may lead to serious errors. For the case in which monomer depletion is the only source of a changing kinetic chain length, the gel point is observed to be delayed and the network observed to be looser in comparison with the case in which monomer depletion is neglected.

## Introduction

The paradigm for nonlinear polymerizations is the random step homopolymerization of *f*-functional monomers, in which cycles do not form in the sol. Such a system is amenable to study by a number of statistical approaches: (1) the combinatorial method,[1–4] (2) the use of probability generating functions,[5] (3) the recursive method,[6,7] and (4) other approaches.[8] These methods differ in their language and power but yield equivalent results because they are based upon the same model. In particular, the recursive method has found use mainly in obtaining those average quantities (e.g., number- and weight-average molecular weights) commonly measured. This fact, together with the simplicity of the mathematics involved and the avoidance of abstractions, makes it a useful tool both practically and pedagogically.

Complications arise when extending these theories beyond this paradigm to account for nonidealities such as unequal reactivity,[9–11] substitution effects,[9,12–14] cyclization,[15–22] and so forth. In this paper we concentrate on one particular kind of nonideality—that incurred by chainwise growth, wherein reaction is not random but conditional upon initiation. We will further restrict ourselves to free-radical polymerizations, for reasons to be given below. For such polymerizations one has to consider initiation, propagation, termination by disproportionation and combination, and transfer reactions. Even though treated in the first two papers on recursive method,[6,7] nonlinear free-radical polymerizations have complications not dealt with before.

One can conveniently visualize the polymerization symbolically as has been done for step polymerization;[1,6,7] Figure 1 shows such a representation. One should not take the figure too literally; whereas the A's in step polymerization refer to actual functional groups, here they refer to "halves" of a double bond and hence are always drawn in pairs. The directions "in" and "out" are also shown in the figure. Moreover, if we look at a terminated primary chain (i.e., consider the polymer with all cross-links and couplings cut) as shown in Figure 2, we see that there is an innate sense of direction on the chain: one end bears the initiator fragment, and the other is terminated, perhaps by combination. Hence, we define also the directions "up" and "down", referring to the directions toward the initiated end and toward the terminated end, respectively ("down" was the direction of propagation).

The complications that arise in the recursive analysis of chainwise polymerization (linear or nonlinear) are twofold. The first complication is that in general the two ends are not equivalent; that is, the directions up and down are fundamentally different. The previous analysis[6,7] overlooked this aspect of the chain structure, and so one purpose of this paper is to correct that work. More important, however, is the fact that the rates of the various reactions occurring will depend on conversion, and this is for a variety of reasons: monomer depletion ("drift"), initiator depletion (which may cause "dead-end" polymerization), and diffusional limitations of the termination step (which may lead to the Trommsdorff effect) and of the propagation step. All of these phenomena, which will hereafter be referred to as "conversion-dependent kinetics", affect ideal network growth by changing (as a function of conversion) the average primary chain length and the tendency for combination. In this paper we present a general method for the treatment of such effects (not treated in previous analyses[3–7,23–27]) and in particular work the case for which drift is the only source of conversion-dependent kinetics.

In the analyses that follow we will preserve the following ideal network assumptions: (1) all functional groups of the same type are equally reactive; (2) reactions are first-order Markovian; and (3) no intramolecular reactions occur in finite species. Implicit in the first assumption are a mean-field approach and batch polymerization. We will also apply the following assumptions common to the kinetic analysis of linear free-radical systems: (4) the quasi-steady-state assumption; (5) chains still propagating contribute negligibly to the total polymer (i.e., only dead chains are considered); and (6) chains formed prior to quasi steady state (and thus having a slightly longer kinetic chain length) also contribute negligibly to the total polymer. The earlier analyses[6,7] also employed these last assumptions, although not explicitly.

## Preliminary Considerations

Let us consider the simple case of equally reactive monomers combining by a chainwise mechanism to form polymer, restricting ourselves to the basic case given by

$$A_2 + A_f \rightarrow \text{polymer} \tag{1}$$

where *f* is twice the number of vinyl groups on the cross-linker. We can treat such a nonlinear chainwise polymerization by the recursive method on the monomer level if the primary chains (i.e., the polymer with all cross-links

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* To whom correspondence should be addressed.

[†] Present address: Dow Chemical, Midland, MI 48674.

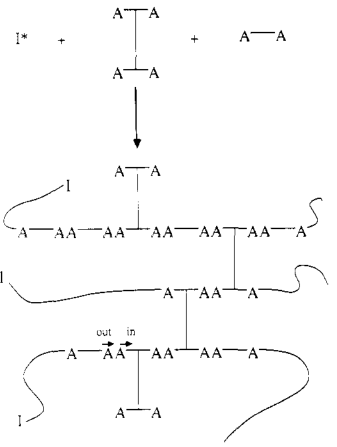

**Figure 1.** Schematic representation of nonlinear free-radical polymerization, for the case where the functionality of the cross-linker is four. I refers to an initiator fragment and A to half of a vinyl group.

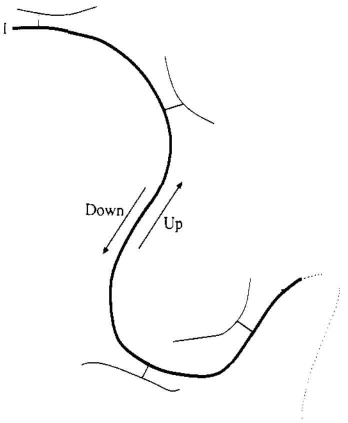

**Figure 2.** Directionality on the primary chain. The darkened chain is the primary chain under consideration. I refers to the initiator fragment, the lighter chains refer to chains cross-linked to the primary chain, and the dashed chain refers to a (possible) coupled chain.

and *couplings* cut) themselves have recursive structure, i.e., if when "walking" along a chain we can reach a point statistically equivalent to the starting point. The recursive structure of the network on this level exists if a given linear chain has a geometric (most probable) distribution in chain length. Thus, we do not consider anionic polymerizations[28,29] in this paper, as the primary chains there will ideally have a Poisson distribution. For free-radical kinetics, however, the quasi-steady-state approximation guarantees that the primary chains formed at any instant have a geometric distribution.[30] This geometric distribution is defined by the parameter $q$, the probability of propagation, given by

$$q = R_p/(R_p + R_{tr} + R_{td} + R_{tc}) \tag{2}$$

where $R_p$ is the rate of propagation, $R_{tr}$ is the rate of transfer, and $R_{td}$ and $R_{tc}$ are the rates of termination by disproportionation and by combination. The parameter $q$ (central to the recursive derivation to follow) changes as the individual rates change, as they will due to monomer depletion, diffusional limitations, and so forth. The recursive analysis only dictates that $q$ is constant along a chain, i.e., that the time scale for changes in $q$ is much greater than the lifetime of a chain. This requirement is equivalent to the quasi-steady-state assumption, a common and reasonable approximation. Thus, we can account for conversion-dependent kinetics from many sources by the recursive method. A general treatment (omitting transfer to polymer) follows.

## Pregel Properties

**General Derivation. $M_w$.** To derive the weight-average molecular weight, we randomly choose a unit of mass and find the expected weight attached to it. Since experimentally we are only concerned with the molecular weight of the polymer, in the recursive analysis we only choose units of mass in the polymer, which will be denoted by an asterisk. When choosing a unit of mass, the permissible choices are a bifunctional unit ($A_2$*) or an $f$-functional unit with $m$ double bonds reacted ($A_{f|m}$*), $1 \leq m \leq (f/2)$, these according to their weight fractions.[31] Thus,

$$M_w = w_{A2}{}^*E(W_{A2}{}^*) + \sum_{m=1}^{f/2} w_{Af|m}{}^*E(W_{Af|m}{}^*) \tag{3}$$

where the weight fractions are defined as

$$w_{A2}{}^* = \frac{pM_{A2}A_2}{pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f} \tag{4}$$

$$wA_{f|m}{}^* = \frac{\binom{f/2}{m}p^m(1 - p)^{(f/2)-m}M_{Af}A_f}{pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f} \tag{5}$$

and $M_{A2}$ and $M_{Af}$ are the molecular weights of the two monomers, $A_2$ and $A_f$ are their molar concentrations in the initial monomer mixture, and $p$ is the overall double-bond conversion. The expected weights $E(W_{A2}{}^*)$ and $E(W_{Af}|_m{}^*)$ are

$$E(W_{A2}{}^*) = M_{A2} + 2E(W_A{}^{*out}) \tag{6}$$

$$E(W_{Af|m}{}^*) = M_{Af} + 2mE(W_A{}^{*out}) \tag{7}$$

where

$$E(W_A{}^{*out}) = (1/2)E(W_A{}^{*out}|\text{up}) + (1/2)E(W_A{}^{*out}|\text{down}) \tag{8}$$

and $E(W_A{}^{*out}|\text{up})$ and $E(W_A{}^{*out}|\text{down})$ are the expected weights looking out from an A* in the two directions (see Figure 2). These relations follow from the fact that A groups always react in pairs. Applying eq 4 and 5 allows us to rewrite eq 3 in the following way:

$$M_w = w_{A2}{}^*M_{A2} + (1 - w_{A2}{}^*)M_{Af} + \frac{pM_{A2}A_2 + (f/2)pM_{Af}A_f}{pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f}2E(W_A{}^{*out}) \tag{9}$$

When randomly choosing an A* unit, we realize that it is crucial to condition upon the conversion at which that unit was polymerized, for that will determine the value of $q$ for the chain to which it was added. Furthermore, it is equally likely that the functional unit reacted at any conversion up to $p$. Thus, the probability density of having chosen a unit reacted at any conversion $\bar{p}$ less than $p$ is $1/p$, and at that conversion $\bar{q} = q(\bar{p})$. So, we can write

$$E(W_A{}^{*out}|\text{up}) = \frac{1}{p}\int_0^p E(W_A{}^{*out}|\text{up}, \bar{p})\, d\bar{p} \tag{10}$$

$$E(W_A{}^{*out}|\text{down}) = \frac{1}{p}\int_0^p E(W_A{}^{*out}|\text{down}, \bar{p})\, d\bar{p} \tag{11}$$

Working first in the up direction, we write

$$E(W_A{}^{*out}|\text{up}, \bar{p}) = \bar{q}E(W_A{}^{*in}|\text{up}, \bar{p}) + (1 - \bar{q})(0) \tag{12}$$

where the weight of the initiator fragment (or transfer agent), encountered with probability $(1 - \bar{q})$, has been neglected. That the parameter $\bar{q}$ is applicable even when looking in the direction opposite to that in which propagation occurred is a result of the symmetry of the geometric distribution. Realizing that $a_f$, the mole fraction of double bonds belonging to the $f$-functional monomer (not to be confused with $A_f$), is the probability of encountering such a unit when looking out, we can write the following relations:

$$E(W_A{}^{*\text{in}}|\text{up}, \bar{p}) = (1 - a_f)E(W_{A2}{}^{*\text{in}}|\text{up}, \bar{p}) + a_f E(W_{Af}{}^{*\text{in}}|\text{up}, \bar{p}) \quad (13)$$

$$E(W_{A2}{}^{*\text{in}}|\text{up}, \bar{p}) = M_{A2} + E(W_A{}^{*\text{out}}|\text{up}, \bar{p}) \quad (14)$$

$$E(W_{Af}{}^{*\text{in}}|\text{up}, \bar{p}) = M_{Af} + E(W_A{}^{*\text{out}}|\text{up}, \bar{p}) + (f - 2)pE(W_A{}^{*\text{out}}) \quad (15)$$

It is significant that the final term in eq 15 is not conditional on $\bar{p}$ because of the random cross-linking: the double bonds on the cross-linker react independently and hence are equally likely to have reacted at any conversion $\bar{p}$ less than $p$. Solving this equations for $E(W_A{}^{*\text{out}}|\text{up}, \bar{p})$ gives

$$E(W_A{}^{*\text{out}}|\text{up}, \bar{p}) = \{(1 - a_f)M_{A2} + a_f M_{Af} + a_f(f - 2)pE(W_A{}^{*\text{out}})\}\left\{\frac{\bar{q}}{1 - \bar{q}}\right\} \quad (16)$$

Thus,

$$E(W_A{}^{*\text{out}}|\text{up}) = \{(1 - a_f)M_{A2} + a_f M_{Af} + a_f(f - 2)pE(W_A{}^{*\text{out}})\}\frac{1}{p}\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}}\right\} \mathrm{d}\bar{p} \quad (17)$$

Looking in the down direction is similar but more complicated:

$$E(W_A{}^{*\text{out}}|\text{down}, \bar{p}) = \bar{q}E(W_A{}^{*\text{in}}|\text{down}, \bar{p}) + (1 - \bar{q})E(W_T|\bar{p}) \quad (18)$$

where the complication presents itself in $E(W_T|\bar{p})$, the expected weight added upon termination or chain transfer. Only in the case of combination is significant weight added, and in this case when we look out of the one chain, we look into the other in the up direction. Furthermore, since both chains must have been growing at the same time, they must share a common $\bar{p}$. Defining the probability of combination, $\bar{R}_{tc}' = \bar{R}_{tc}/(\bar{R}_p + \bar{R}_{tr} + \bar{R}_{td} + \bar{R}_{tc})$ (where the bars again denote evaluation at conversion $\bar{p}$), we have

$$(1 - \bar{q})E(W_T|\bar{p}) = \bar{R}_{tc}'E(W_A{}^{*\text{in}}|\text{up}, \bar{p}) \quad (19)$$

Substituting this relation and eq 12 into eq 18 yields

$$E(W_A{}^{*\text{out}}|\text{down}, \bar{p}) = \bar{q}E(W_A{}^{*\text{in}}|\text{down}, \bar{p}) + (\bar{R}_{tc}'/\bar{q})E(W_A{}^{*\text{out}}|\text{up}, \bar{p}) \quad (20)$$

The equations analogous to (13)–(15) for the down direction are

$$E(W_A{}^{*\text{in}}|\text{down}, \bar{p}) = (1 - a_f)E(W_{A2}{}^{*\text{in}}|\text{down}, \bar{p}) + a_f E(W_{Af}{}^{*\text{in}}|\text{down}, \bar{p}) \quad (21)$$

$$E(W_{A2}{}^{*\text{in}}|\text{down}, \bar{p}) = M_{A2} + E(W_A{}^{*\text{out}}|\text{down}, \bar{p}) \quad (22)$$

$$E(W_{Af}{}^{*\text{in}}|\text{down}, \bar{p}) = M_{Af} + E(W_A{}^{*\text{out}}|\text{down}, \bar{p}) + (f - 2)pE(W_A{}^{*\text{out}}) \quad (23)$$

Solving for $E(W_A{}^{*\text{out}}|\text{down})$ yields

$$E(W_A{}^{*\text{out}}|\text{down}, \bar{p}) = \{(1 - a_f)M_{A2} + a_f M_{Af} + a_f(f - 2)pE(W_A{}^{*\text{out}})\}\left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'}{(1 - \bar{q})^2}\right\} \quad (24)$$

Thus,

$$E(W_A{}^{*\text{out}}|\text{down}) = \{(1 - a_f)M_{A2} + a_f M_{Af} + a_f(f - 2)pE(W_A{}^{*\text{out}})\}\frac{1}{p}\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p} \quad (25)$$

Substituting eq 17 and 25 into eq 8 and solving for $E(W_A{}^{*\text{out}})$ gives

$$E(W_A{}^{*\text{out}}) = \left[\{(1 - a_f)M_{A2} + a_f M_{Af}\}\frac{1}{p}\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p}\right] \Bigg/ \left[1 - a_f(f - 2)\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p}\right] \quad (26)$$

So, we obtain the weight-average molecular weight by eq 9:

$$M_w = w_{A2}{}^*M_{A2} + (1 - w_{A2}{}^*)M_{Af} + \frac{pM_{A2}A_2 + p(f/2)M_{Af}A_f}{pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f}\left[\{(1 - a_f)M_{A2} + a_f M_{Af}\}\frac{2}{p}\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p}\right] \Bigg/ \left[1 - a_f(f - 2)\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p}\right] \quad (27)$$

**Gel Point.** The critical conversion for gelation, $p_c$, is the conversion at which the weight-average molecular weight diverges. This occurs when the denominator in eq 27 becomes zero; thus, the critical conversion satisfies the following equation:

$$1 = a_f(f - 2)\int_0^{p_c} \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p} \quad (28)$$

This equation is simply a restatement of the Stockmayer relation[3] for the critical branching probability, $\alpha_c$,

$$\alpha_c = 1/[\mathrm{DP}_w{}^0(p_c) - 1] \quad (29)$$

where for the present case the branching probability is given by

$$\alpha = a_f p((f - 2)/2) \quad (30)$$

and weight-average degree of polymerization of the primary molecules[30] (the polymer considered with all cross-links cut) is given by

$$\mathrm{DP}_w{}^0(p) = 1 + \frac{2}{p}\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\} \mathrm{d}\bar{p} \quad (31)$$

an equation which can be derived from kinetic equations[32-35] (see below).

It is important to notice here how strongly the integrand of eq 28 depends on $(1 - \bar{q})$. It appears that the appropriate question is not whether $q$ is fairly constant[6,7,24,25] but whether $(1 - q)$ is constant, and it is clear that small changes in $q$ (which is near unity) as conversion proceeds may induce large differences in $(1 - q)$. So we observe a possibility of the importance of conversion-dependent kinetics upon the gel point (and hence $M_w$). This will be discussed again below.

**$M_n$.** We can find the number-average molecular weight more easily by stoichiometry than by recursive techniques:

$$M_n = \text{mass of polymer/number of polymer molecules} \tag{32}$$

The mass of the polymer is the mass of reacted bifunctional monomer plus the mass of $f$-functional monomer with at least one reacted pair and is only a function of conversion. In a unit volume,

$$\text{mass of polymer} = pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f \tag{33}$$

where $A_2$ and $A_f$ are molar concentrations of the two monomers in the initial mixture, as before.

The number of molecules depends on the kinetics and hence is more problematic. First, we consider the number of molecules in a system where all of the cross-links are cut (but couplings left intact), and unreacted double bonds are ignored. The number of reacted A's is $[2pA_2 + fpA_f]$. The number of chain ends, which is twice the number of these primary molecules,[30] is the number of reacted A's multiplied by the probability that an A is an end, $P(\text{end})$. This probability depends on both direction and conversion $\bar{p}$:

$$P(\text{end}) = (1/2)\{P(\text{end}|\text{up}) + P(\text{end}|\text{down})\} \tag{34}$$

$$P(\text{end}|\text{up}) = \frac{1}{p}\int_0^p (1 - \bar{q})\,\mathrm{d}\bar{p} \tag{35}$$

$$P(\text{end}|\text{down}) = \frac{1}{p}\int_0^p (1 - \bar{q} - \bar{R}_{tc}')\,\mathrm{d}\bar{p} \tag{36}$$

$$P(\text{end}) = \frac{1}{p}\int_0^p (1 - \bar{q} - (\bar{R}_{tc}'/2))\,\mathrm{d}\bar{p} \tag{37}$$

In a unit volume, then, for the uncross-linked system,

$$\text{number of primary molecules} = (1/2)(2A_2 + fA_f)\int_0^p (1 - \bar{q} - (\bar{R}_{tc}'/2))\,\mathrm{d}\bar{p} \tag{38}$$

Now we reintroduce the cross-links; the number of these in a unit volume depends only on conversion and is

$$\begin{aligned}\text{number of cross-links} &= \sum_{m=2}^{f/2} (m - 1)\binom{f/2}{m} p^m (1 - p)^{(f/2)-m} A_f \\ &= [(f/2)p - (1 - (1 - p)^{f/2})]A_f \end{aligned} \tag{39}$$

Because each cross-link decreases the number of molecules by one (if cycles do not form), we have

$$M_n = [pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f]\Big/\Big[(1/2) \times (2A_2 + fA_f)\int_0^p (1 - \bar{q} - (\bar{R}_{tc}'/2))\,\mathrm{d}\bar{p} - [(f/2)p - (1 - (1 - p)^{f/2})]A_f\Big] \tag{40}$$

The number-average molecular weight is finite at the gel point, but nonetheless the above equation is not applicable thereafter because of intramolecular reaction in the gel,[4] which invalidates the stoichiometric argument.

(The original analysis[6] included unreacted double bonds attached to polymer chains when counting chain ends but did not subtract these out when correcting for cross-links. The previous work thus overcalculated the number of primary molecules and undercalculated $M_n$.)

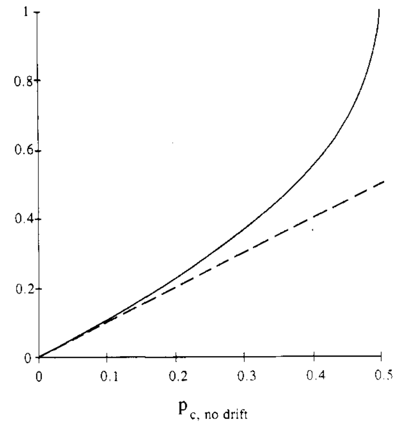

**Figure 3.** Gel point for a system with drift versus that for one without drift (see eq 47). This result is restricted to systems with no combination and no transfer. Dashed line gives the reference (45°) line for comparison.

**Specific Cases. Linear Chains.** Before proceeding to the specific calculations for network-forming systems, we show the results for the degenerate case of linear systems ($a_f = w_{Af}{}^* = A_f = 0$). For this case we obtain

$$\mathrm{DP_w} = 1 + \frac{2}{p}\int_0^p \left\{\frac{\bar{q}}{1 - \bar{q}} + \frac{\bar{R}_{tc}'/2}{(1 - \bar{q})^2}\right\}\mathrm{d}\bar{p} \tag{41}$$

$$\mathrm{DP_n} = \frac{p}{\int_0^p (1 - \bar{q} - (\bar{R}_{tc}'/2))\,\mathrm{d}\bar{p}} \tag{42}$$

These results are equivalent to those resulting from the kinetic equations[32-35] for cumulative dead chain distributions derived for batch polymerizations under the quasi-steady-state assumption, in the absence of the long-chain hypothesis, and if transfer is not excessive. Note that eq 41 and 31 are the same.

**Drift.** We restrict ourselves to the case for which monomer depletion is the only source of conversion-dependent kinetics. Comparison of these results with those valid for no drift (i.e., $q$ and $R_{tc}'$ independent of conversion) will be useful. For the case of no drift we can write

$$M_w = w_{A2}{}^*M_{A2} + (1 - w_{A2}{}^*)M_{Af} + \frac{pM_{A2}A_2 + p(f/2)M_{Af}A_f}{pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f} \times \frac{\{(1 - a_f)M_{A2} + a_fM_{Af}\}(2q(1 - q) + R_{tc}')}{(1 - q)^2 - pa_f(f - 2)[q(1 - q) + (R_{tc}'/2)]} \tag{43}$$

$$p_c = \frac{(1 - q)^2}{a_f(f - 2)[q(1 - q) + (R_{tc}'/2)]} \tag{44}$$

$$M_n = [pM_{A2}A_2 + (1 - (1 - p)^{f/2})M_{Af}A_f]/[(1/2)p(2A_2 + fA_f)(1 - q - (R_{tc}'/2)) - [(f/2)p - (1 - (1 - p)^{f/2})]A_f] \tag{45}$$

For such a system with no combination and no transfer,

$$q = \frac{k_pM_0(1 - p)}{k_pM_0(1 - p) + k_tP} \tag{46}$$

where $k_p$ is the propagation rate constant, $M_0$ the initial double bond concentration, $k_t$ the disproportionation rate constant, and $P$ the concentration of living polymer chains (constant in this case). For this system the integrals in eq 27, 28, and 40 are analytic. In particular, a direct relationship exists between the gel point for the system with

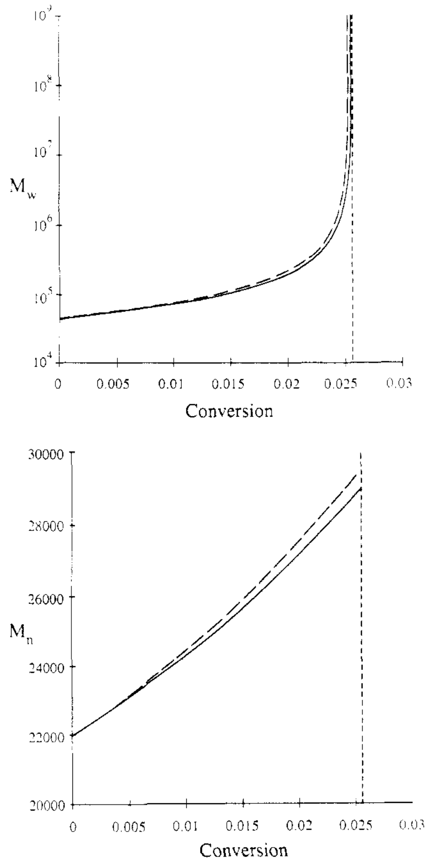

**Figure 4.** $M_w$ and $M_n$ for the following system: $q = 0.995$, $f = 4$, $a_4 = 0.10$, $M_{A2} = 100$, $M_{A4} = 200$, and $R_{tc}' = 0$. (a, top) $M_w$ with drift (—) and without drift (--) (note logarithmic scale). (b, bottom) $M_n$ with drift (—) and without drift (--) (note linear scale). Dashed vertical line in both plots indicates $p_{c,drift}$.

drift as a function of that without, when both share the same initial $q$:

$$p_{c,drift} = 1 - (1 - 2p_{c,no\ drift})^{1/2} \qquad (47)$$

where $p_{c,no\ drift}$ contains all of the dependences on the rate constants and concentrations. Figure 3 shows this function. Drift delays the gel point, because monomer depletion leads to shorter chains. For sufficiently small critical conversions, this delay is negligible, for the simple reason that little drift has occurred. Thus, we may also expect that the error incurred by neglecting drift in the calculations of $M_n$ and $M_w$ will increase as the critical conversion increases. This is borne out in Figures 4 and 5. Figure 4 shows the results for an early gelling system ($p_{c,no\ drift} \cong 0.025$); significant deviation only occurs for $M_w$ in a neighborhood very close to the gel point. Figure 5, however, shows the results for a late gelling system ($p_{c,no\ drift} \cong 0.25$); for this situation, deviations are significant over a great part of the pregel regime. Many systems of commercial interest gel quickly, so that the rigorous integrals become unnecessary. Thus, we can conclude that for pregel calculations drift (and conversion-dependent kinetics in general) will only be important for systems gelling late.

Equations 43, 44, and 45 correspond to the results presented in the earlier work[6,7] corrected in the various ways previously noted, the major correction accounted for being directionality. How important is the correct treatment of directionality? This question is significant because combination is the dominant mode of termination[36] (a notable exception being methyl methacrylate). Figure 6 addresses this question by comparing two systems, one of which only experiences disproportionation ($R_{tc}' = 0$) and the other only combination ($R_{tc}' = 1 - q$). Because combination produces longer dead chains, the gel point occurs much earlier, emphasizing the importance of correctly including combination in the analysis.

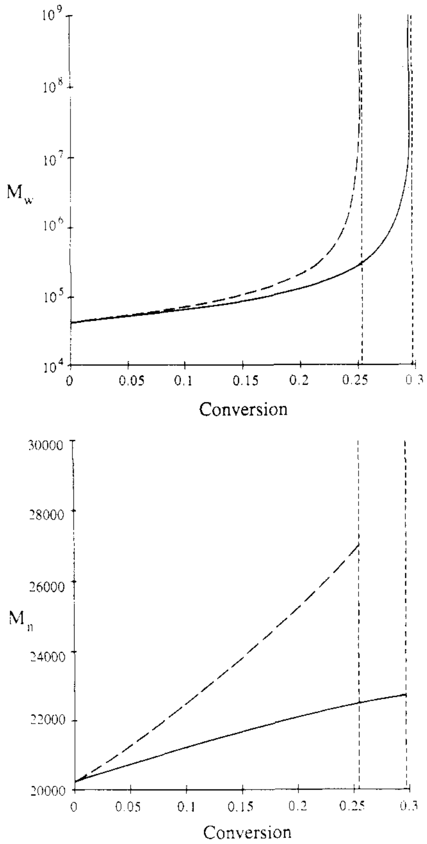

**Figure 5.** $M_w$ and $M_n$ for the same system as in Figure 4, except $a_4 = 0.01$. (a, top) $M_w$ with drift (—) and without drift (--) (note logarithmic scale). (b, bottom) $M_n$ with drift (—) and without drift (--) (note linear scale). Dashed vertical lines on both plots indicate gel points for the cases with and without drift.

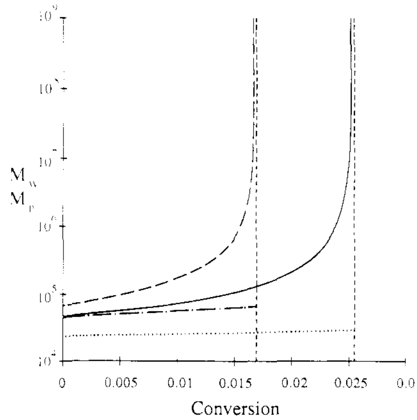

**Figure 6.** $M_n$ and $M_w$ for the two different termination mechanisms, for the following system: $q = 0.995$, $f = 4$, $a_4 = 0.10$, $M_{A2} = 100$, $M_{A4} = 200$. $M_w$ under disproportionation (—) and under combination (--). $M_n$ under disproportionation (···) and under combination (- - -). Calculations neglect drift.

## Postgel Properties

**General Derivation. $P(F_A{}^{*out})$.** The key to postgel properties is the probability that looking out from a randomly chosen A* (here restricted to a *reacted* A) we see only a finite structure, $P(F_A{}^{*out})$ (a quantity related to the extinction probability[37,38] used in other treatments of network formation). The probability of seeing a finite chain is dependent upon whether we are looking up or down the chain, but there will be in general no need to define the average, $P(F_A{}^{*\text{out}})$. We must again condition, however, upon the conversion $\bar{p}$ at which the monomer reacted:

$$P(F_A{}^{*\text{out}}|\text{up}) = \frac{1}{p}\int_0^p P(F_A{}^{*\text{out}}|\text{up}, \bar{p})\, d\bar{p} \tag{48}$$

$$P(F_A{}^{*\text{out}}|\text{down}) = \frac{1}{p}\int_0^p P(F_A{}^{*\text{out}}|\text{down}, \bar{p})\, d\bar{p} \tag{49}$$

Working first in the up direction gives

$$P(F_A{}^{*\text{out}}|\text{up}, \bar{p}) = (1 - \bar{q})(1) + \bar{q}P(F_A{}^{*\text{in}}|\text{up}, \bar{p}) \tag{50}$$

The probability looking in, however, depends on whether we look into a bifunctional unit or into an $f$-functional unit:

$$P(F_A{}^{*\text{in}}|\text{up}, \bar{p}) = (1 - a_f)P(F_A{}^{*\text{out}}|\text{up}, \bar{p}) + a_f P(F_A{}^{*\text{out}}|\text{up}, \bar{p})P(E) \tag{51}$$

where $E$ is the event that none of the remaining $(f - 2)$ functionalities on the incorporated cross-linker leads to an infinite structure. Because of independent reaction, this event is not conditioned on $\bar{p}$. Since A pairs react independently, this is the product of the probabilities that we see only a finite structure looking out of each pair. Thus,

$$P(E) = [pP(F_A{}^{*\text{out}}|\text{up})P(F_A{}^{*\text{out}}|\text{down}) + (1 - p)]^{(f-2)/2} \tag{52}$$

Solving for $P(F_A{}^{*\text{out}}|\text{up}, \bar{p})$ and applying eq 48 yields

$$P(F_A{}^{*\text{out}}|\text{up}) = \frac{1}{p}\int_0^p \frac{1 - \bar{q}}{1 - \bar{q}(1 - a_f(1 - P(E)))}\, d\bar{p} \tag{53}$$

Working in the down direction gives

$$P(F_A{}^{*\text{out}}|\text{down}, \bar{p}) = (1 - \bar{q} - \bar{R}_{tc}')(1) + \bar{R}_{tc}'P(F_A{}^{*\text{in}}|\text{up}, \bar{p}) + \bar{q}P(F_A{}^{*\text{in}}|\text{down}, \bar{p}) \tag{54}$$

The relation analogous to eq 51 is

$$P(F_A{}^{*\text{in}}|\text{down}, \bar{p}) = (1 - a_f)P(F_A{}^{*\text{out}}|\text{down}, \bar{p}) + a_f P(F_A{}^{*\text{out}}|\text{down}, \bar{p})P(E) \tag{55}$$

Applying eq 50 and 49 yields

$$P(F_A{}^{*\text{out}}|\text{down}) = P(F_A{}^{*\text{out}}|\text{up}) - \frac{1}{p}\int_0^p \frac{\bar{R}_{tc}'a_f(1 - P(E))}{[1 - \bar{q}(1 - a_f(1 - P(E)))]^2}\, d\bar{p} \tag{56}$$

The probability of seeing a finite chain in the down direction is thus less than that in the up direction if there is combination, the reason being that the coupled chain gives added opportunities for paths to infinity. When there is no combination, the following relation clearly holds:

$$P(F_A{}^{*\text{out}}|\text{down}) = P(F_A{}^{*\text{out}}|\text{up}) = P(F_A{}^{*\text{out}}) \tag{57}$$

Neither eq 53 nor eq 56 is explicit, because of the presence of $P(E)$, given by eq 52, through which the two equations are also coupled. Solution will thus be difficult, especially considering that the integrals may not be analytic. To eliminate the coupling between the two equations, one can first obtain the solution for no combination (by iteration) and then use this solution as the initial guess for a case with finite $R_{tc}'$. By increasing $R_{tc}'$ by intervals to its appropriate value, one may obtain the correct solution. Once this labor is done and $P(F_A{}^{*\text{out}}|\text{up})$ and $P(F_A{}^{*\text{out}}|\text{down})$ have been determined, though, we can directly determine many postgel properties, using the relations outlined below.

**Weight Fraction Solubles.** We proceed as in the original article.[7] The weight fraction of solubles in the entire reaction mixture, $w_s$, is

$$w_s = w_{A2}\{pP(F_A{}^{*\text{out}}|\text{up})P(F_A{}^{*\text{out}}|\text{down}) + (1 - p)\} + (1 - w_{A2})\{pP(F_A{}^{*\text{out}}|\text{up})P(F_A{}^{*\text{out}}|\text{down}) + (1 - p)\}^{f/2} \tag{58}$$

where $w_{A2}$ is the weight fraction of bifunctional unit in the entire reaction mixture (independent of conversion, unlike $w_{A2}{}^*$). We may be interested, however, in only that portion of the *polymeric* species which is soluble, $w_s{}^*$. If $w_p$ is the weight fraction of polymer in the mixture, clearly $(w_s + w_p)$ will exceed unity, the excess being related to $w_s{}^*$. Thus,

$$w_s{}^* = (w_s + w_p - 1)/w_p \tag{59}$$

Since

$$w_p = pw_{A2} + (1 - (1 - p)^{f/2})(1 - w_{A2}) \tag{60}$$

then

$$w_s{}^* = \{w_{A2}pP(F_A{}^{*\text{out}}|\text{up})P(F_A{}^{*\text{out}}|\text{down}) + (1 - w_{A2})[\{pP(F_A{}^{*\text{out}}|\text{up})P(F_A{}^{*\text{out}}|\text{down}) + (1 - p)\}^{f/2} - (1 - p)^{f/2}]\}/\{pw_{A2} + (1 - (1 - p)^{f/2})(1 - w_{A2})\} \tag{61}$$

***P*(*X*$_{m,f}$).** The probability that a cross-linker of functionality $f$ will have $m$ paths to the infinite network, $P(X_{m,f})$, is useful in the calculation of cross-link density, the concentration of dangling chains, and so forth. The correspondences are as follows:

$$P(X_{1,f}) \leftrightarrow \text{dangling}$$

$$P(X_{2,f}) \leftrightarrow \text{connecting link}$$

$$P(X_{3,f}) + P(X_{4,f}) + \ldots + P(X_{f,f}) \leftrightarrow \text{effective junctions}$$

($P(X_{0,f})$ of course corresponds to cross-linkers in the soluble fraction, but this is not equivalent to the sol fraction, which is of more interest.) To calculate these probabilities, we could condition upon the $A_f$ being in the polymer as was done in the original reference.[7] Alternatively, we consider all $A_f$ units:

$$P(k\text{ pairs react}) = \binom{f/2}{k}p^k(1 - p)^{(f/2)-k} \tag{62}$$

Then, for $m \neq 0$,

$$P(X_{m,f}) = \sum_{k=g(m)}^{f/2} P(m\text{ paths lead to infinity}|k\text{ pairs react})P(k\text{ pairs react}) \tag{63}$$

where $g(m)$ is $[(m + 1)/2]$ truncated to the integer value (i.e., the sum runs over integer values from $m/2$ to $f/2$, inclusive, so that $2k \geq m$, as it must be). The probability that $m$ paths lead to infinity depends on how those $m$ paths are partitioned between the up and down directions. Hence, we must condition, for example, on how many paths leading to infinity are in the up direction. If we consider a molecule with $k$ reacted pairs and $m$ paths to infinity, the minimum number of A groups looking up that lead to infinity must be the greater of zero and $(m - k)$. Likewise, the maximum number must be the lesser of $k$ and $m$. Then we can write

$$P(m\text{ paths lead to infinity}|k\text{ pairs react}) = \sum_{i=\max(0,m-k)}^{\min(k,m)} \binom{k}{i}\binom{k}{m-i}(1 - P(F_A{}^{*\text{out}}|\text{up}))^i(1 - P(F_A{}^{*\text{out}}|\text{down}))^{m-i}(P(F_A{}^{*\text{out}}|\text{up}))^{k-i}(P(F_A{}^{*\text{out}}|\text{down}))^{k-m+i} \tag{64}$$

where the combinatoric terms account for the number of possible configurations in the up and down directions, respectively. Equations 62–64 then define $P(X_{m,f})$. To obtain quantities in terms of concentration is straightforward:

$$[X_{m,f}] = [A_f]P(X_{m,f}) \tag{65}$$

To obtain these probabilities conditional upon being in the

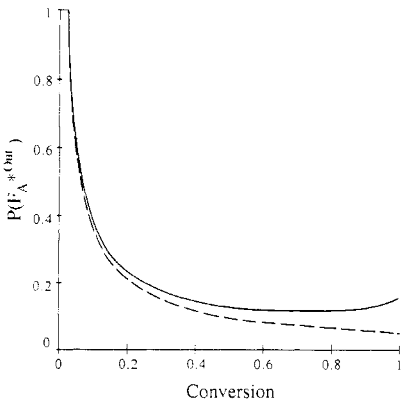

**Figure 7.** Calculations of the probability of a finite structure, $P(F_A{}^{*out})$, for the following system: $q = 0.995$, $f = 4$, $a_4 = 0.10$, and $R_{tc}' = 0$. With drift (—) and without drift (--).

polymer (as in the original paper[7] and as desirable), we have

$$P(X_{m,f}{}^*) = P(X_{m,f})/[1 - (1 - p)^{f/2}] \qquad (66)$$

which is equivalent to the formula given before (eq 46 in ref 7).

**Specific Case: Drift.** As before, we treat the case for which only drift occurs. Comparison against those predictions obtained by neglecting drift will again be instructive. For constant $q$ and $R_{tc}'$ we have

$$P(F_A{}^{*out}|\text{up}) = \frac{1 - q}{1 - q(1 - a_f(1 - P(E)))} \qquad (67)$$

where

$$P(F_A{}^{*out}|\text{down}) = P(F_A{}^{*out}|\text{up})\{1 - [R_{tc}'/(q(1 - q))][1 - P(F_A{}^{*out}|\text{up})]\} \qquad (68)$$

which is the corrected result for the original work.[7] Since by eq 52 and 68 $P(E)$ depends on the $[(3/2)(f - 2)]$ power of $P(F_A{}^{*out}|\text{up})$, eq 67 gives a $((3f/2) - 2)$ order equation in $P(F_A{}^{*out}|\text{up})$. In theory we can reduce the order by one since $P(F_A{}^{*out}|\text{up}) = 1$ is a known solution (in the simplest case, $f = 4$, the order is reduced from 4 to 3). One should realize, however, that $P(F_A{}^{*out}|\text{up}) = 1$ is the pregel solution, thus valid up to the gel point, which is analytically known by eq 44. Note that if $R_{tc}' = 0$, the order of the equation reduces from $((3f/2 - 2)$ to $(f - 1)$. A special case arises for $f = 4$, $R_{tc}' = 0$. Here the results from the original work are correct (since combination does not occur) and the following can be written:

$$P(F_A{}^{*out}) = [((1 - q)/qa_4p) + 1/4]^{1/2} - 1/2 \qquad (69)$$

For systems with neither transfer nor combination and with $f = 4$, eq 46 defines $q$, and the integral of eq 53 is analytic, so that we can use a zero finder to determine $P(F_A{}^{*out})$. Figure 7 shows this function and that obtained by eq 69. Because monomer depletion encourages shorter chains, there is a greater tendency for branches to be finite. Indeed, in this case one sees a minimum in $P(F_A{}^{*out})$ because of the addition of very short chains as the conversion approaches unity.

Figure 8 shows the predictions for the sol fractions $w_s$ and $w_s{}^*$. Note that in both the case with drift and that without, the polymeric sol fraction $w_s{}^*$ drops very rapidly after the gel point, so that over a wide conversion range the total sol fraction $w_s$ can be attributed to the unreacted monomer only. A consequence of the chainwise mechanism is that the total sol fraction does not drop as rapidly as in the stepwise case (cf. ref 7). Drift causes appreciable error only at high conversions for which the sol fractions are so small that the discrepancies would not be experimentally accessible.

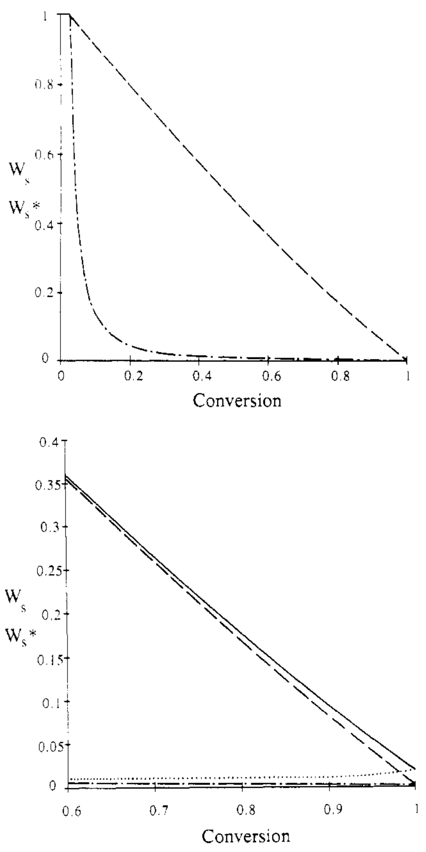

**Figure 8.** Total and polymeric sol fractions for the same system as in Figure 7 with $M_{A2} = 100$ and $M_{A4} = 200$. (a, top) For the case of no drift, $w_s$ (--) and $w_s{}^*$ (---). (b, bottom) Comparison of the calculations with drift with those without drift over the last 40% conversion. For the case of drift, $w_s$ (—) and $w_s{}^*$ (···). For the case of no drift, $w_s$ (--) and $w_s{}^*$ (---).

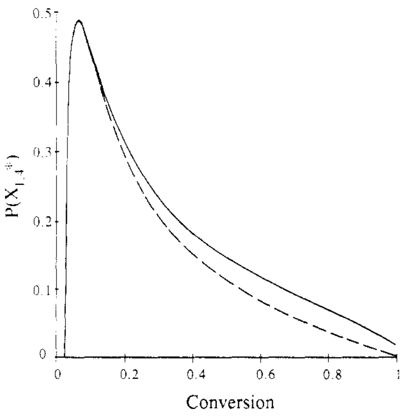

**Figure 9.** Dangling chains. $P(X_{1,4}{}^*)$, the probability that a cross-linker in the polymeric fraction is involved in a dangling chain, for the same system as in Figure 7. With drift (—) and without drift (--).

The predictions for $P(X_{m,f}{}^*)$ are more dramatic. Figures 9–12 show the results for $P(X_{1,4}{}^*)$, $P(X_{2,4}{}^*)$, $P(X_{3,4}{}^*)$, and $P(X_{4,4}{}^*)$. Noteworthy is that, while the probabilities of dangling and connecting units do peak, they do not fall to zero at complete conversion because both ends of the chain must dangle due to initiation and termination (since no combination is occurring). Significant discrepancies occur when we do not account for drift. The shorter chains provided by drift encourage dangling ends, connecting chains (at high conversion), and effective junctions with three arms to the network but discourage junctions with

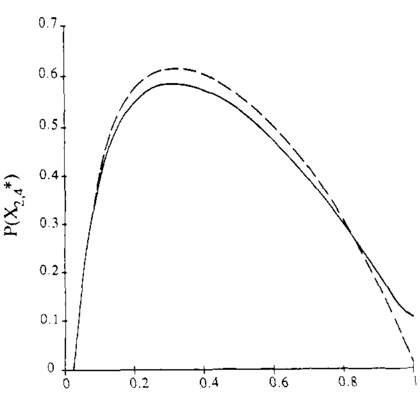

**Figure 10.** Connecting links. $P(X_{2,4}^*)$, the probability that a cross-linker in the polymeric fraction acts as a connecting link with two arms to the network, for the same system as in Figure 7. With drift (—) and without drift (– –).

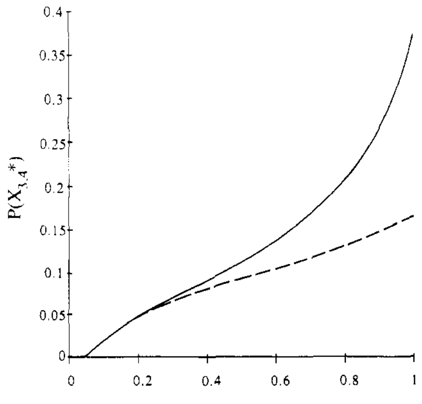

**Figure 11.** Effective junctions. $P(X_{3,4}^*)$, the probability that a cross-linker in the polymeric fraction acts as a junction with three arms to the network, for the same system as in Figure 7. With drift (—) and without drift (– –).

four arms to the network. Thus, we see severe discrepancies in the postgel properties which indicate that conversion-dependent kinetics in general should be significant in the postgel regime.

## Conclusions

We have presented a general method for obtaining average molecular weights and network parameters for nonlinear free-radical systems which can account for the conversion-dependent kinetics generally found for these systems. The rigorous treatment of conversion dependence may be unnecessary in the pregel regime (if gelation occurs very early), but such neglect in the postgel calculations would lead to significant errors. The general method can account for any conversion dependence within the six assumptions listed in the Introduction. (A good example of an exception is a termination rate constant dependent upon the molecular weight of the particular chains,[39] used to model the diffusion limitation of the termination step which may lead to the Trommsdorff effect. Such a dependence violates the assumption of first-order Markovian reaction and thus would destroy the recursive structure at the monomer level.) This theory has the advantage over the probability generating function approach in that it is much simpler mathematically. Moreover, this theory is simpler than direct solution of the kinetic equations[40] because of a much smaller number of equations to solve.

We have shown calculations only for the case of drift, but we can reason the influence of other effects. If we neglect combination for a moment, we can just think in terms of the primary chain length. Monomer depletion, as we have seen, leads to progressively shorter chains as conversion proceeds, delaying the gel point and leading to a looser network. Initiator depletion increases the primary chain length (through the quasi-steady-state assumption) and thus would lead to a tighter network, as would diffusional limitations on the termination step. These effects, especially the latter, may be sufficiently severe so as to reverse the trends for drift alone. Diffusion-limited propagation, on the other hand, would lead to shorter chains. We can also account for nonisothermal conditions by this method, as long as the temperature is assumed to be uniform throughout the reaction mixture at any given time (in accordance with the first assumption of the introduction). All other things remaining the same, the temperature rise provided by the exothermic reaction will lead not only to shorter primary chains but to a greater tendency toward disproportionation,[36] both of which will intensify the trends predicted on the basis of drift alone. The different effects have opposing results, and so the end result will depend upon their relative magnitudes.

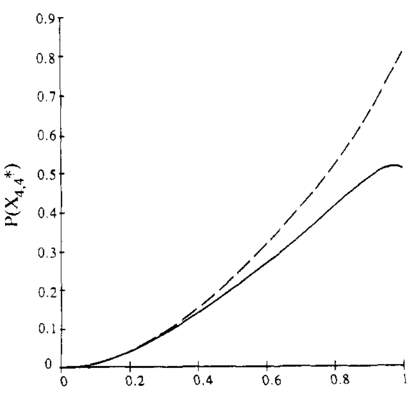

**Figure 12.** Effective junctions. $P(X_{4,4}^*)$, the probability that a cross-linker in the polymeric fraction acts as a junction with four arms to the network, for the same system as in Figure 7. With drift (—) and without drift (– –).

It must be admitted that few, if any, systems obey the restrictions of this model.[41] Many common systems, such as the styrene/divinylbenzene, exhibit unequal reactivity or substitution effect. Solving the problem of unequal reactivity requires extending the present method, which would entail treatment of the drift in monomer composition with conversion as well as the reactivity ratios which together would determine the probabilities of looking from one type of monomer into another. Accounting for transfer to polymer should be possible since each reacted section will maintain its geometric distribution. In addition to substitution effect, a reduction in pendant reactivity (from physical sources) termed shielding often occurs,[42] which is apparently sensitive to molecular weight.[23] Finally, there are the problems of cyclization[22,23,43-45] and inhomogeneity.[46,47] It is reasonable to ask, in light of this, what the value of this highly idealized theory is. First, theoretical understanding of the complex situations occurring in reality can only follow understanding of simpler, albeit less realistic, processes. The simple theory can then form the basis for systematically treating deviations from ideality. One can use an idealized theory such as this, then, to estimated the magnitudes of these deviations present. Finally, it provides an alternative derivation for the cumulative molecular weight averages for linear systems.

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(30) In our terminology, primary *chains* are obtained by ignoring all cross-links and couplings, but primary *molecules* are obtained by ignoring only cross-links. Primary *chains* are thus not affected by the termination mechanism and hence will have a geometric distribution. Primary *molecules*, however, are affected by the termination mechanism and will only have a geometric distribution if there is no combination. If combination is dominant, the primary molecules will have a self-convoluted geometric distribution (or a negative binomial distribution with $r = 2$; see: Feller, W. *An Introduction to Probability Theory and Its Applications*, 3rd ed.; Wiley: New York, 1968; Vol. 1).
(31) The original derivation[7] did not distinguish between the different cross-linker species and then said that $E(W_{Af}^{*}) = M_{Af} + (1 + ((f-2)/2)p)2E(W_{A}^{*\mathrm{out}})$. This is incorrect because it grabs cross-linker molecules not at random but by reacted bonds, and thus preferentially grabs more highly reacted cross-linkers. The authors acknowledge W. Merrill of the University of Minnesota for help in correcting this error.
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# Statistics of Free-Radical Polymerizations Revisited Using a Fragment Approach. 1. Bifunctional Monomers

**Roberto J. J. Williams**

*Institute of Materials Science and Technology (INTEMA), University of Mar del Plata, and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina.*

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ABSTRACT: A fragment approach is used to obtain statistical parameters for free-radical polymerizations of bifunctional monomers, allowing every possibility for chain termination, i.e., combination, disproportionation, and/or chain transfer. The method is based on (i) fragmentation of the system into all distinguishable units, comprising monomers and polymer fragments; (ii) determination of the concentration of every species and fragment in terms of kinetic parameters; and (iii) generation of average statistical parameters by joining the different fragments using a recursive algorithm. Number- and weight-average molecular weights result in a very simple way.

## Introduction

Average statistical parameters of polymers produced by free-radical mechanisms, i.e., chainwise polymerizations, have been reported and discussed both for systems starting from bi- and polyfunctional monomers. In the former case, the resulting number- and weight-average degrees of polymerization of the polymer fraction, $\bar{x}_n$ and $\bar{x}_w$, can be derived from the molecular weight distribution obtained by assuming a random polymerization. For the case of termination by transfer and/or disproportionation, the following expressions are obtained (the derivation is reported in many standard polymer textbooks):

$$\bar{x}_n = 1/(1-q) \tag{1}$$

$$\bar{x}_w = (1+q)/(1-q) \tag{2}$$

where

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