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Correlations in Nonlinear Free-Radical Polymerizations: Substitution Effect

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ABSTRACT: Polymer networks are often formed under conditions for which the history of reaction is important, but nonetheless such nonequilibrium polymerizations may be properly described by statistical methods. This is illustrated for a free-radical polymerization of a diunsaturated monomer subject to first-shell substitution effect. The distinction between first and second double bond reacted leads to long-range correlations which result in coupled integral equations as recursions rather than algebraic relations. The proper consideration of the history of the reaction gives an exact statistical treatment of the evolution of DP_w in the pregel regime, a treatment which is compared with various approximations which avoid the complicated mathematics at the cost of not properly maintaining the structural integrity of the polymer.

Introduction

Statistical methods, in particular the recursive formalism, have proven to be quite useful in the description of the structure of nonlinear polymers. Nonetheless, the classical statistical approach has been criticized in the past 10–15 years on two grounds. One criticism which has generated much literature is that the classical description must fail in the critical regime, as it is a mean-field theory;[1] this complaint (which is equally applicable to the solution of the *standard* kinetic rate equations) is both valid and quite important but does not concern us here. Of concern, rather, is the criticism that the statistical approach fails even by its own standards, as it does not correctly describe the mean-field growth of a polymer network. Thus, in comparing the statistical and kinetic approaches, Mikeš and Dušek[2] claim that the two are "nonequivalent because in the kinetic approach the integrity of existing structures, and so information on the formation history, is preserved, while it is not so in the statistical TBP [Theory of Branching Processes]." The difference between the two appears when the formation history is relevant, i.e. when the polymerization is kinetically controlled.

That this fault had gone unnoticed so long is due to the fact that for the paradigmatic cases, such as A_f homopolymerization without substitution effects, there is no difference between an equilibrium polymerization equilibrated at conversion p and a kinetically controlled polymerization reacted to conversion p. (For A_f step homopolymerization, this fact was recognized in 1943 by Stockmayer.[3]) Thus, while Galina and Szustalewicz[4] claim that "the statistical methods ... are *not appropriate* to deal with kinetically controlled polymerization processes," they do make exception for "the rather rare systems with equal and conversion-independent reactivities ..." These situations, even though kinetically controlled, turn out to be equilibrium-like such that the statistical and kinetic descriptions are identical. Any of a number of nonidealities can wreck this equivalence, though, first-shell substitution effect being the most studied example, and chain growth without the quasi-steady-state approximation providing a second example. These nonidealities, although originating locally, introduce *long-range correlations* such that the state of a monomer (e.g. whether it has reacted) is correlated with the states of monomers at any contour distance away within the same molecule. Such effects arising from the history of reaction supposedly cannot be captured within the statistical description, because "the molecules are generated from monomer units at any extent of reaction anew."[2]

All of these criticisms are valid for the typical statistical approaches which do ignore the history of reaction, but to claim that the statistical approach itself is at fault is wrong. The condemnation of the statistical approach is based on statistical models which in hindsight are obviously approximate. The question, then, is can we formulate an exact statistical model? The answer to this question in a number of cases has been shown to be "yes". The most common way of doing this is by a 'superspecies' approach which combines kinetic and statistical modeling.[5] In this method, all of the nonrandom elements are built up kinetically and then combined statistically. The resulting model is correct if one has carefully included all of the nonrandom aspects in the kinetic part of the analysis. We take substitution effects in stepwise polymers as our first example. In many of these cases the long-range effects are erased by copolymerization with a monomer which does not exhibit a substitution effect.[6] This simplification does not occur for homopolymerization exhibiting substitution effect, for which the numerous statistical approaches[7-9] were found by Mikeš and Dušek[2] to be exact only in the absence of the substitution effect. Similar conclusions had been reached in earlier research[10-13] and has since been elaborated by Galina and Szustalewicz.[4,14-16] A different statistical model, based upon different superspecies, was suggested by Miller and Macosko[5b] but is also inexact because nonrandomness was not accounted for correctly. In a recent paper, however, Sarmoria and Miller[17] correct this last and show that the appropriate model accounts for the long-range correlations correctly. Nonterminating chain growth serves as a second example. Dušek and Šomvársky[18] have pointed out that chains made by anionic polymerization cannot be modeled on the monomer level by simple statistical arguments (since a geometric distribution is not a Poisson distribution); Macosko and Miller[19] have recently elaborated on this case, substantiating the claim that such chains grown kinetically can be randomly combined into a network correctly. Similar arguments have been made with regards to the chainwise etherification reaction in epoxy systems;[18b,20] recently Gupta and Macosko[21] have shown that the model of Bokare and Gandhi[22] which treats the etherification chains kinetically avoids the pitfalls of the simpler statistical approaches.[23,24]

A second approach avoids the superspecies language to some extent and is formulated in a much more purely statistical way. The previous work on nonlinear free-radical polymerization is the first example of this, in the maintenance of the instantaneous distributions of chain lengths through a conditioning upon conversion, which prohibits equilibration between chains formed at different conversions.[25,26] For the degenerate case of linear polymerization, the cumulative dead chain DP_w and DP_n were found to be equivalent to the kinetic results regardless of the particularities of the conversion-dependent kinetics (or drifts) which produce the nonequilibrium distribution, including conversion-dependent reactivity, since the rate constants are allowed to change as a function of conversion. This, while being an example of maintenance of structural integrity, does not involve a long-range effect. Long-range correlations are, however, introduced by a residence time distribution resulting from reactor configuration other than batch. Thus, in the recursive derivation of DP_w for an A_f homopolymerization in a homogeneous continuous stirred tank reactor (HCSTR),[27] a conditioning on residence time distribution is necessary, and the long-range effect manifests itself in the fact that the residence time distributions for successive generations away from the root are not the same. Thus, a statistically equivalent point cannot be reached and an integral equation recursion, rather than an algebraic recursion, is obtained (in this case, one gets a double-integral equation). The analytic solution to this problem agrees completely with the kinetic solution at steady state, a nonequilibrium situation. To see whether long-range correlations introduced by chemistry can be described by this more purely statistical approach, we look at substitution effects in a nonlinear free-radical reaction. (This is more strictly what Galina and Szustalewicz[4] mean when referring to conversion-dependent reactivity.)

This paper will deal with a substitution effect occurring in a nonlinear free-radical polymerization of diunsaturated monomers. For this one simple system a statistical (recursive) analysis will be derived which is proposed to be as rigorous as solution of kinetic equations. Only one structural property, the weight-average degree of polymerization, will be examined, and that only in the pregel regime. The number-average degree of polymerization is of lesser interest, as it does not indicate gelation and (more importantly), since it is merely a ratio of the mass of polymer to the number of polymer molecules, it only depends on the number of connections and not on the fine details of connectivity. Thus, for the number-average degree of polymerization the long-range effects are invisible. Despite the seemingly narrow view, a good deal of insight can be gained.

The model will be formulated in a manner similar to that of A_f homopolymerization in an HCSTR.[27] The relationship between this model and that of Sarmoria and Miller[17] for substitution effects in stepwise polymerizations is that in the integral equation formulation one essentially has an infinite number of superspecies, which is moreover an *uncountable* infinity (since conversion is a continuous variable). This is a more difficult situation than that of nonterminating chain growth[21] where the number of superspecies is a countable infinity (since chain length is discrete). However, unless analytic solution of the integral equations is possible, one has to discretize to solve numerically. This can be viewed either as an approximate numerical technique to solve the exact model or as a redefinition of a finite number of aggregated superspecies (as in ref 17); this difference is only a semantic one. The only real advantage to formulating the problem exactly to begin with is that if analytic solutions are available, they can be obtained. Here, we will find that this is the case in absence of substitution effect.

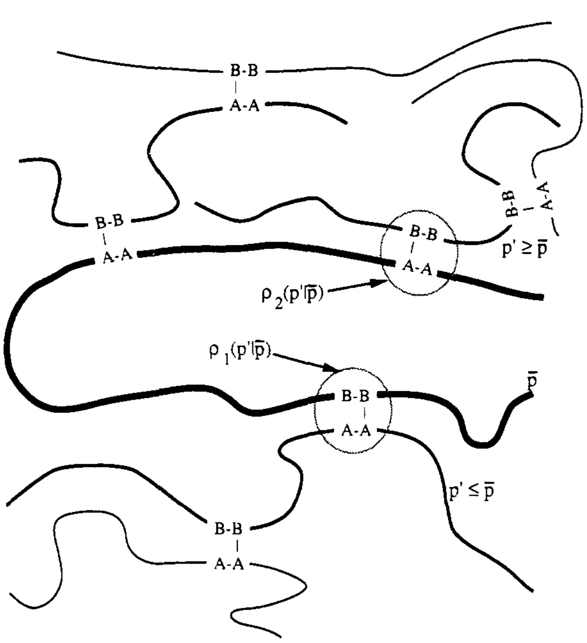

Figure 1. Schematic of free-radical polymerization of A_4 monomer with substitution effect. Zeroth-generation chain is in the middle with thickest line, first-generation chains are shown with thinner lines, and second-generation chains with the thinnest lines. Chains are arranged so that conversion at chain birth increases as the eye travels up the drawing.

The goal of this paper is not to supply general formulae in an attempt to construct a broad framework nor is it to provide a realistic model for nonlinear free-radical polymerization, which would require a treatment of cyclization[28] as well as size-dependent reactivity.[29] The purpose of this paper is rather to explore the sources of long-range correlations and the course which statistical modeling must take to follow these correlations faithfully.

Exact Statistical Solution for Ideal Copolymerization

We consider A_4 (diunsaturated) polymerization with a substitution effect. A_2 throughout will refer to an unsaturation, and B_2 to one with reactivity differing from that of A_2. By substitution effect we mean that upon reaction of one of the A_2 groups on the diunsaturated monomer, the remaining A_2 changes into a B_2. In both of these cases, it is important to realize that, if we only consider the linear constituent chains, the substitution effect results in a binary copolymerization with the second component being produced in situ. Thus, with respect to these primary chains, the only effect is that the comonomer composition (and thus the instantaneous copolymer composition) as a function of conversion is quite different than in normal copolymerizations. Nonetheless, once the fraction of A_2 groups in the comonomer, f_A, is known as a function of conversion (see Appendix 1), the cumulative primary chain statistics can be calculated by any of a number of methods.

The long-range correlations appear not in the primary chains themselves, but rather in how those chains are connected. Figure 1, a schematic of the reaction, illustrates this. Each A_2 unit on a root chain formed at conversion $\bar{p}$ bears a partner B_2 unit. If this partner unit has reacted (which is not required except at an overall conversion $p = 1$), it must have reacted at a conversion p' later than $\bar{p}$, for the B_2 did not exist before $\bar{p}$. Thus as we walk from A_2's to B_2's we move to chains formed at successively *later* conversions. Similarly, if we return to our root chain and now examine every B_2 unit, we note that each one bears an A_2 partner. This partner must have reacted, and that at a conversion p' earlier than $\bar{p}$, for our original B_2 could not have reacted before it came into existence. Thus as we travel from B_2's to A_2's we move to chains formed at successively *earlier* conversions. In both cases, such a walk will not lead to a statistically equivalent point, so that we cannot expect an algebraically closed recursion, and we have a long-range correlation.

One escape from this quandary is to claim that the chain statistics may be independent of conversion. Unfortunately, the very nonideality which enforces nonrandom links also necessarily introduces conversion-dependent chain statistics. The zero-conversion polymer is certainly a linear homopolymer, but as conversion increases, the instantaneous chains unavoidably have more and more B_2's incorporated, since the concentration of polymer is increasing. Thus we must accept the long-range correlations and deal with them. We proceed then to derive the weight-average degree of polymerization.

If we randomly choose a monomer in the polymer, it must be an A_2–B_2, of which the A_2 must have reacted (indicated by an asterisk) and the B_2 may have reacted to form a cross-link. The weight-average degree of polymerization, $\mathrm{DP_w}$, is thus:

$$\mathrm{DP_w} = 1 + E(N_{A2*}{}^{\mathrm{out}}) + E(N_{B2}{}^{\mathrm{out}}) \tag{1}$$

which comprises the monomer chosen, the expected number of monomers attached to (or looking out of) the A_2 group, $E(N_{A2*}{}^{\mathrm{out}})$, and the expected number of attached to the B_2 group, $E(N_{B2}{}^{\mathrm{out}})$. As explained elsewhere,[25] we must condition on the conversion at which the monomers reacted. For this case we do this in the following way:

$$E(N_{A2*}{}^{\mathrm{out}}) = \frac{\int_0^p E(N_{A2*}{}^{\mathrm{out}}|\bar{p}) F_A \, \mathrm{d}\bar{p}}{\int_0^p F_A \, \mathrm{d}\bar{p}} \tag{2}$$

$$E(N_{B2}{}^{\mathrm{out}}) = \frac{\int_0^p E(N_{B2}{}^{\mathrm{out}}|_r\bar{p}) F_A \, \mathrm{d}\bar{p}}{\int_0^p F_A \, \mathrm{d}\bar{p}} \tag{3}$$

F_A describes the instantaneous copolymer composition, and is the fraction of A_2 monomers incorporated into the primary chains produced at conversion $\bar{p}$. The conditional expectations are conditioned in two different ways. $E(N_{A2*}{}^{\mathrm{out}}|\bar{p})$ is the expected number of monomers looking out of an A_2 group reacted at conversion $\bar{p}$. $E(N_{B2}{}^{\mathrm{out}}|_r\bar{p})$, on the other hand, is the expected number of monomers looking out of a B_2 group, the partner A_2 group of which reacted at $\bar{p}$. In the latter case we are thus conditioning upon the conversion at which that B_2 was created; the subscript "r" will throughout this derivation indicate conditioning upon the conversion at which the partner group, A_2 or B_2, reacted.

In this paper we will solely be concerned with the case of ideal copolymerization, which occurs when only the identity of the monomer (A_2 or B_2), but not that of the radical ($A^\bullet$ or $B^\bullet$), figures into the relative preference for one monomer over the other. Here monomers are truly randomly distributed on the chain, even though the chain composition F_A does not equal the comonomer composition f_A. (In the calculations, we will further assume that the identity of the radical is irrelevant to the absolute rates as well.) Given this, we can write:

$$E(N_{A2*}{}^{\mathrm{out}}|\bar{p}) = (\mathrm{DP_w}{}^0(\bar{p}) - 1)[1 + (1 - F_A)E(N_{A2*}{}^{\mathrm{out}}|_r\bar{p}) + F_A E(N_{B2}{}^{\mathrm{out}}|_r\bar{p})] \tag{4}$$

where $\mathrm{DP_w}{}^0(\bar{p})$ is the instantaneous weight-average degree of polymerization of the primary chains produced at $\bar{p}$, and $E(N_{A2*}{}^{\mathrm{out}}|_r\bar{p})$ the expected number of monomers looking out of an A_2 group the partner B_2 group of which reacted at $\bar{p}$. We can then rewrite eq 1 in the following way:

$$\mathrm{DP_w} = 1 + \frac{\int_0^p [\mathrm{DP_w}{}^0(\bar{p}) - 1] F_A \, \mathrm{d}\bar{p}}{\int_0^p F_A \, \mathrm{d}\bar{p}} + \int_0^p \{(\mathrm{DP_w}{}^0(\bar{p}) - 1)[(1 - F_A)E(N_{A2*}{}^{\mathrm{out}}|_r\bar{p}) + F_A E(N_{B2}{}^{\mathrm{out}}|_r\bar{p})] + E(N_{B2}{}^{\mathrm{out}}|_r\bar{p})\} F_A \, \mathrm{d}\bar{p} \Big/ \int_0^p F_A \, \mathrm{d}\bar{p} \tag{5}$$

where the first two terms comprise the degree of polymerization of the primary chains and the third that added by cross-linking. Note that the only difficult terms are $E(N_{A2*}{}^{\mathrm{out}}|_r\bar{p})$ and $E(N_{B2}{}^{\mathrm{out}}|_r\bar{p})$. (The more general equations applicable for nonideal copolymerization can be found in ref 26.)

To make any further progress, we must introduce two probability densities which describe the connections between A_2's and B_2's. The first, $\rho_1(p'|\bar{p})$, is the probability density that an A_2 reacted at p' given that the created B_2 reacted at $\bar{p}$ (see Figure 1). Thus, $\rho_1(p'|\bar{p})$ is zero for $p' > \bar{p}$ and is normalized over the interval $[0,\bar{p}]$. The second, $\rho_2(p'|\bar{p})$, is the probability density that a B_2 reacted at p' given that it was created at $\bar{p}$. It is thus zero for $p' < \bar{p}$ and is normalized over the interval $[\bar{p},1]$. Without determining yet what these densities are, we can write the following:

$$E(N_{A2*}{}^{\mathrm{out}}|_r\bar{p}) = \int_0^p E(N_{A2*}{}^{\mathrm{out}}|p')\rho_1(p'|\bar{p}) \, \mathrm{d}p' \tag{6}$$

$$E(N_{B2}{}^{\mathrm{out}}|_r\bar{p}) = \int_{\bar{p}}^p E(N_{B2*}{}^{\mathrm{out}}|p')\rho_2(p'|\bar{p}) \, \mathrm{d}p' \tag{7}$$

We are now in a position to write our recursive relations for the case of ideal copolymerization:

$$E(N_{A2*}{}^{\mathrm{out}}|_r\bar{p}) = \int_0^{\bar{p}} [\mathrm{DP_w}{}^0(p') - 1]\rho_1(p'|\bar{p}) \, \mathrm{d}p' + \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\{F_A E(N_{B2}{}^{\mathrm{out}}|_r p') + (1 - F_A)E(N_{A2*}{}^{\mathrm{out}}|_r p')\}\rho_1(p'|\bar{p}) \, \mathrm{d}p' \tag{8}$$

$$E(N_{B2}{}^{\mathrm{out}}|_r\bar{p}) = \int_{\bar{p}}^p [\mathrm{DP_w}{}^0(p') - 1]\rho_2(p'|\bar{p}) \, \mathrm{d}p' + \int_{\bar{p}}^p [\mathrm{DP_w}{}^0(p') - 1]\{F_A E(N_{B2}{}^{\mathrm{out}}|_r p') + (1 - F_A)E(N_{A2*}{}^{\mathrm{out}}|_r p')\}\rho_2(p'|\bar{p}) \, \mathrm{d}p' \tag{9}$$

The first integral of each is the linear chain contribution, the following integral being the cross-linking term. Thus, our recursion does not close algebraically but rather gives two coupled integral equations to solve. As expected, the situation is thus comparable to step polymerization in an HCSTR, where reactor configuration and the resulting residence time distribution, rather than chemistry, lead to the long-range correlations.[27] (Again, the more general relations for nonideal copolymerization can be found in ref 26.)

The probability densities $\rho_1(p'|\bar{p})$ and $\rho_2(p'|\bar{p})$ are given below

$$\rho_1(p'|\bar{p})\,\mathrm{d}p' = \frac{\exp\left\{-\int_{p'}^{p}\frac{F_B\,\mathrm{d}p''}{f_B(1-p'')}\right\}F_A\,\mathrm{d}p'}{\int_0^{p}\exp\left\{-\int_{p'}^{p}\frac{F_B\,\mathrm{d}p''}{f_B(1-p'')}\right\}F_A\,\mathrm{d}p'} \quad (10)$$

$$\rho_2(p'|\bar{p})\,\mathrm{d}p' = \exp\left\{-\int_{p}^{p'}\frac{F_B\,\mathrm{d}p''}{f_B(1-p'')}\right\}\frac{F_B\,\mathrm{d}p'}{f_B(1-p')} \quad (11)$$

where $F_B = 1 - F_A$ and $f_B = 1 - f_A$. (For a derivation, see Appendix 2.) It should also be noted that for the case of ideal copolymerization with constant reactivity ratio r, the linking probabilities $\rho_1(p'|\bar{p})$ and $\rho_2(p'|\bar{p})$ can be found analytically and are given in Appendix 2, eqs A2.9 through A2.18.

Equations 8 and 9 can be solved numerically for $E(N_{A2*}^{\mathrm{out}}|_r\bar{p})$ and $E(N_{B2}^{\mathrm{out}}|_r\bar{p})$. These can then be integrated according to eq 5 to yield $\mathrm{DP_w}$. Analytic solution is possible for the equal reactivity case and yields the same answer as obtained previously[25] (see Appendix 3).

Approximate Statistical Solutions

The solution presented in the previous section, which is claimed to be exact, is obviously not simple, since solution of two coupled integral equations is necessary. This difficulty motivates one to find approximations which involve only algebraic recursions. In this section we present three such approximations of increasing complexity, two of which have been suggested (more or less explicitly) before.

1. Naive Approximation. In the simplest approximation, one merely redefines the branching probability α as rp, and writes the following (cf. eq A3.10):

$$\mathrm{DP_w} = 1 + \frac{\mathrm{DP_w}^0 - 1}{1 - rp(\mathrm{DP_w}^0 - 1)} \quad (12)$$

where $\mathrm{DP_w}^0$ is the cumulative weight-average degree of polymerization of the primary chains produced up to conversion p. This is essentially the approach suggested in the previous work of Landin.[28] Note that it gives the correct answer for $r = 1$.

For $r \neq 1$, however, this model has several faults. The first of these is that the pendant conversion is not equal to rp, for several reasons. First, this can certainly not be the case as $p \rightarrow 1$, since the pendant conversion p_B (the conversion of the B_2 groups existing at overall conversion p) must approach unity in this case. Second, the pendant conversion depends on the "birth" conversion of the B_2 group. Third, even at low conversion the pendant conversion is not rp but, paradoxically, $p/2$ (independent of r!). This occurs because

$$p_B = 1 - \frac{2(1 - f_A)(1 - p)}{1 - f_A(1 - p)} \quad (13)$$

and $f_A = 1 - p$ as $p \rightarrow 0$, independent of r, a fact which can be checked from the solutions for p as a function of f_A given in Appendix 1.[31] Moreover, not all partner groups are pendants—some are A_2 groups rather than B_2 groups. The final complaint is that the number of cross-links is incorrect. Under this approximation the fraction of cross-links is $(rp)^2$, whereas (at sufficiently low p) it is actually p^2, for the same reason as the pendant conversion is $p/2$. Thus the naive model underestimates the number of cross-links when $r < 1$ and overestimates them when $r > 1$. This is also easily seen from the predictions at complete conversion; for $r < 1$ one obtains not all monomers doubly reacted when in fact they are; for $r > 1$ one obtains the nonsensical result that monomers are double reacted with a probability greater than unity! Note that since the number of cross-links is incorrect, we know that this model would incorrectly predict $\mathrm{DP_n}$.

We need make only one more observation about this approximation. In the language of the McMaster group,[32,33] it is a uniform cross-link density distribution model; the fraction of cross-links on a primary chain is independent of the conversion at which that chain was formed.

2. Random Combination Approximation. In improving upon the first approximation, we turn to a model which properly distinguishes A_2 groups from B_2 groups, and which predicts the correct number of cross-links. Nonetheless, it is approximate in that the details of connectivity which result in the integral equation recursions are overlooked. Instead, it is as if at the conversion p in the exact process all A_2–B_2 connections are severed and then randomly recombined. Note that this sort of equilibration allows for connections to be made which in the true kinetically controlled situation are forbidden; e.g. an A_2 on a chain formed at $\bar{p}$ connected to a B_2 on a chain formed at $p' < \bar{p}$.

Under this approximation, eqs 1 and 2 are written as before, but eq 3 is rewritten in the following way (this is not an approximation):

$$E(N_{B2}^{\mathrm{out}}) = p_B\frac{\int_0^p E(N_{B2*}^{\mathrm{out}}|\bar{p})F_B\,\mathrm{d}\bar{p}}{\int_0^p F_B\,\mathrm{d}\bar{p}} \quad (14)$$

where $E(N_{B2*}^{\mathrm{out}}|\bar{p})$ is the expected number of monomers looking out of a B_2 group reacted at $\bar{p}$. Next we write that

$$E(N_{A2*}^{\mathrm{out}}|\bar{p}) = E(N_{B2*}^{\mathrm{out}}|\bar{p}) = (\mathrm{DP_w}^0(\bar{p}) - 1) + (\mathrm{DP_w}^0(\bar{p}) - 1)(F_A E(N_{B2}^{\mathrm{out}}) + (1 - F_A)E(N_{A2*}^{\mathrm{out}})) \quad (15)$$

which is approximate since the dependence on the conversion at which the partner reacted is ignored. By substitution into eqs 2 and 3 we find that under this approximation the integral equation recursions (eqs 8 and 9) on the conditional values are replaced by algebraic recursions on the integral values. Moreover, if we note that

$$\int_0^p F_A\,\mathrm{d}\bar{p} = {}^1/_2(1 - f_A(1 - p)) \quad (16)$$

and recall eq 13, we find that

$$\frac{1}{\int_0^p F_A\,\mathrm{d}\bar{p}} = \frac{p_B}{\int_0^p F_B\,\mathrm{d}\bar{p}} = \frac{2}{1 - f_A(1 - p)} \quad (17)$$

This allows the algebraic recursions to be written in the following manner:

$$E(N_{A2*}^{\mathrm{out}}) = I_1 + I_2 E(N_{B2}^{\mathrm{out}}) + (I_1 - I_2)E(N_{A2*}^{\mathrm{out}}) \quad (18)$$

$$E(N_{B2}^{\mathrm{out}}) = (I_0 - I_1) + (I_1 - I_2)E(N_{B2}^{\mathrm{out}}) + (I_0 - 2I_1 + I_2)E(N_{A2*}^{\mathrm{out}}) \quad (19)$$

where:

$$I_0 = \frac{2}{1 - f_A(1-p)} \int_0^p (\mathrm{DP_w}^0(\bar{p}) - 1)\, \mathrm{d}\bar{p} \tag{20}$$

$$I_1 = \frac{2}{1 - f_A(1-p)} \int_0^p (\mathrm{DP_w}^0(\bar{p}) - 1) F_A\, \mathrm{d}\bar{p} \tag{21}$$

$$I_2 = \frac{2}{1 - f_A(1-p)} \int_0^p (\mathrm{DP_w}^0(\bar{p}) - 1) F_A^{\,2}\, \mathrm{d}\bar{p} \tag{22}$$

Solution of eqs 18 and 19 yields the following:

$$\mathrm{DP_w} = 1 + \frac{I_0 - I_1}{1 - I_1 + I_2} + \left(1 + \frac{I_0 - 2I_1 + I_2}{1 - I_1 + I_2}\right) \frac{I_0 I_2 + I_1 - I_1^{\,2}}{1 - 2I_1 + 2I_2 + I_1^{\,2} - I_0 I_2} \tag{23}$$

It is the last denominator which gives the divergent term, which is intuitive since it is the denominator arising from connections to later and earlier chains.

This approximation predicts the correct number of cross-links, but the connections are not as they should be. The reason for this is 2-fold. First, improper connections are allowed. Second, the cross-linking density distribution is incorrect, even though not uniform as in the naive model. To see why this is, consider the following. Tobita and Hamielec[32] and Zhu[33] disintguish between the instantaneous cross-link density ($\rho_i(\Theta)$) and the additional cross-link density ($\rho_a(\Theta,\Phi)$), where Φ corresponds to p and Θ corresponds to $\bar{p}$. The instantaneous cross-link density simply corresponds to B_2 groups which are incorporated into the chain in question, and hence is only a function of the conversion at which that chain was formed (Θ). Since it is in fact equal to F_B, and since the random combination approximation maintains the structural integrity of the primary chains, the instantaneous cross-link density is properly accounted for. The additional cross-link density, on the other hand, corresponds to the reaction of the B_2 groups pendant to our chain formed at Θ, and hence is a function both of Θ and the overall conversion Φ. This is improperly accounted for, since we have ignored the dependence on Θ. Thus it is in the additional cross-link density that the approximation has been made.

3. Cross-Link Density Distribution Approximation. In this last approximation, we answer the second complaint against the random combination model, namely, that the cross-link distribution was incorrect. As was argued above, only the additional cross-link density was incorrect, so that only the term $E(N_{B2}^{\mathrm{out}})$ in the recursion need be corrected. To do this, we recast eq 15 in the following way:

$$E(N_{A2*}^{\mathrm{out}}|\bar{p}) = E(N_{B2*}^{\mathrm{out}}|\bar{p}) = (\mathrm{DP_w}^0(\bar{p}) - 1) + (\mathrm{DP_w}^0(\bar{p}) - 1)(F_A p_B'(\bar{p}) E(N_{B2*}^{\mathrm{out}}) + (1 - F_A) E(N_{A2*}^{\mathrm{out}})) \tag{24}$$

where $p_B'(\bar{p})$ is the conversion of B_2 groups born at conversion $\bar{p}$, which is given by:

$$p_B'(\bar{p}) = \int_{\bar{p}}^{p} \rho_2(p'|\bar{p})\, \mathrm{d}p' \tag{25}$$

Making the following replacement:

$$E(N_{B2*}^{\mathrm{out}}) = \frac{1}{p_B} E(N_{B2}^{\mathrm{out}}) \tag{26}$$

we find the following algebraic recursions need solving:

$$E(N_{A2*}^{\mathrm{out}}) = I_1 + I_4 E(N_{B2}^{\mathrm{out}}) + (I_1 - I_2) E(N_{A2*}^{\mathrm{out}}) \tag{27}$$

$$E(N_{B2}^{\mathrm{out}}) = (I_0 - I_1) + (I_3 - I_4) E(N_{B2}^{\mathrm{out}}) + (I_0 - 2I_1 + I_2) E(N_{A2*}^{\mathrm{out}}) \tag{28}$$

where I_0, I_1, and I_2 are defined in eqs 20–22, and the additional integrals are

$$I_3 = \frac{2}{1 - f_A(1-p)} \frac{1}{p_B} \int_0^p (\mathrm{DP_w}^0(\bar{p}) - 1) F_A p_B'(\bar{p})\, \mathrm{d}\bar{p} \tag{29}$$

$$I_4 = \frac{2}{1 - f_A(1-p)} \frac{1}{p_B} \int_0^p (\mathrm{DP_w}^0(\bar{p}) - 1) F_A^{\,2} p_B'(\bar{p})\, \mathrm{d}\bar{p} \tag{30}$$

Solution yields the following equation for $\mathrm{DP_w}$:

$$\mathrm{DP_w} = 1 + \frac{I_0 - I_1}{1 - I_3 + I_4} + \left(1 + \frac{I_0 - 2I_1 + I_2}{1 - I_3 + I_4}\right) \times \frac{I_0 I_4 + I_1 - I_1 I_3}{1 - (I_1 + I_3) + (I_2 + I_4) + I_1 I_3 - I_0 I_4 + (I_1 I_4 - I_2 I_3)} \tag{31}$$

(If one replaces I_3 with I_1 and I_4 with I_2 in this equation, one obtains eq 23.) We note that although we have corrected the cross-link density distribution, it is still appropriate to call this model approximate since improper connections are still allowed. Thus it can be stated that the statistical analyses of the postgel regime of Tobita and Hamielec[32] (and those of the pregel regime by Zhu[33]), although intricate, are still only approximate. This is easily discerned since no integral equations arise in those derivations.

Comparison of Exact and Approximate Solutions

Now that three approximate models and the exact model have been outlined, we would like to evaluate the performance of the approximate models as a function of the two "variables" of the system: the relative pendant reactivity *r*, and the chain length $\mathrm{DP_w}^0$ and how it changes with conversion. The relative reactivity *r* will be varied from $(512)^{-1}$ to 512, so that 5 orders of magnitude in *r* will be examined. (This is probably much greater than physically realizable, but this is unimportant since the purpose of this paper is to illustrate a theoretical point, not to model a real system.) Three different kinetic situations will be examined, the large share of the results being for chains with an initial $\mathrm{DP_w}^0 = 2001$.

In order to compare the approximate statistical models with the exact statistical model, we need first to substantiate the validity of the exact model. The exact statistical model is proven to be exact for the case of equal reactivity (see Appendix 3), but the naive approximation is exact here as well, so that we wish to support the validity of the exact model for $r \neq 1$. This we will do with a particular kinetic situation for which an analytic solution of the kinetic rate equations is known. Since analytic solution of the exact statistical model is not available here, the most we will be able to do is numerically show that the exact statistical model is consistent with the kinetic results. We will then proceed to a second kinetic situation for which no analytic kinetic solution is available; here the exact statistical model will serve as the basis for comparison.

First Kinetic Situation: Transfer-Dominated, Constant $R^{\bullet}$. Here, a free-radical polymerization occurs in which a constant concentration of radicals ($R^{\bullet}$) propagate, either to A_2 groups with a rate constant k_p, or to B_2 groups with rate constant rk_p. The polymer chains are ended

Table I
Comparison of Gel Points from Approximate and Exact Solutions for First Kinetic Situation ($k_{tr}/k_p = 0.001$)

r	p_c(naive)	p_c(random comb.)	p_c(xlink density)	p_c(kinetic)	p_c(exact statistical)
$^1/_{512}$	2.560×10^{-1}	1.761×10^{-1}	1.864×10^{-1}	1.883×10^{-1}	1.888×10^{-1}
$^1/_{256}$	1.280×10^{-1}	1.014×10^{-1}	1.082×10^{-1}	1.090×10^{-1}	1.091×10^{-1}
$^1/_{128}$	6.399×10^{-2}	5.475×10^{-2}	5.869×10^{-2}	5.892×10^{-2}	5.904×10^{-2}
$^1/_{64}$	3.200×10^{-2}	2.850×10^{-2}	3.063×10^{-2}	3.069×10^{-2}	3.080×10^{-2}
$^1/_{32}$	1.600×10^{-2}	1.455×10^{-2}	1.565×10^{-2}	1.567×10^{-2}	1.572×10^{-2}
$^1/_{16}$	7.999×10^{-3}	7.352×10^{-3}	7.916×10^{-3}	7.919×10^{-3}	7.940×10^{-3}
$^1/_8$	3.999×10^{-3}	3.695×10^{-3}	3.980×10^{-3}	3.980×10^{-3}	3.990×10^{-3}
$^1/_4$	2.000×10^{-3}	1.853×10^{-3}	1.996×10^{-3}	1.995×10^{-3}	1.995×10^{-3}
$^1/_2$	9.998×10^{-4}	9.274×10^{-4}	9.990×10^{-4}	9.990×10^{-4}	1.003×10^{-3}
1	4.999×10^{-4}	4.639×10^{-4}	4.999×10^{-4}	4.997×10^{-4}	5.013×10^{-4}
2	2.500×10^{-4}	2.321×10^{-4}	2.501×10^{-4}	2.500×10^{-4}	2.506×10^{-4}
4	1.250×10^{-4}	1.161×10^{-4}	1.250×10^{-4}	1.250×10^{-4}	1.253×10^{-4}
8	6.249×10^{-5}	5.804×10^{-5}	6.251×10^{-5}	6.251×10^{-5}	6.265×10^{-5}
16	3.125×10^{-5}	2.902×10^{-5}	3.126×10^{-5}	3.126×10^{-5}	3.133×10^{-5}
32	1.563×10^{-5}	1.451×10^{-5}	1.563×10^{-5}	1.563×10^{-5}	1.566×10^{-5}
64	7.811×10^{-6}	7.255×10^{-6}	7.818×10^{-6}	7.815×10^{-6}	7.832×10^{-6}
128	3.906×10^{-6}	3.628×10^{-6}	3.909×10^{-6}	3.907×10^{-6}	3.916×10^{-6}
256	1.953×10^{-6}	1.814×10^{-6}	1.955×10^{-6}	1.954×10^{-6}	1.958×10^{-6}
512	9.764×10^{-7}	9.068×10^{-7}	9.772×10^{-7}	9.768×10^{-7}	9.790×10^{-7}

only by chain transfer to A_2 groups (i.e. to double bonds of free monomer) with a transfer constant k_{tr}. Here the instantaneous primary chain length of chains formed at a given conversion $\bar{p}$ is given as

$$\mathrm{DP_w}^0(\bar{p}) = 1 + 2\frac{k_p}{k_{tr}}\left(\frac{f_A + r(1 - f_A)}{f_A}\right) \tag{32}$$

In this case the primary chain length increases with conversion (with decreasing f_A) because while propagation to B_2 is possible, transfer to B_2 is prohibited. Hence as time goes on, the possibilities for transfer decrease more rapidly than those for propagation. As $\bar{p} \to 1$, $\mathrm{DP_w}^0(\bar{p})$ either diverges for $r \leq 2$, or, for the case $r > 2$, reaches a limiting value as follows:

$$(\mathrm{DP_w}^0(1) - 1) = \frac{2(r-1)}{r-2}(\mathrm{DP_w}^0(0) - 1) \tag{33}$$

This chain-length dependence is very slight, however, in the pregel regime, at least for chains of moderate length, so that for practical purposes this can be considered a constant chain length model. We have two parameters in this scheme: r and k_{tr}/k_p.

This somewhat artificial case is of interest because direct comparison with a kinetic solution is possible. Derivation of $\mathrm{DP_w}$ from kinetic equations is of course possible in general (most conveniently by the pseudo-kinetic rate constant method[32]), but in this special case an analytic solution is known.[34] In addition to assuming the kinetic scheme outlined above, this derivation makes the following assumptions: (1) the rate at which a radical reacts with a polymer to form a cross-link is proportional to the degree of polymerization of the polymer, i.e. depletion of polymeric double bonds (B_2) is neglected; and (2) primary chains are long, so that a variety of terms may be neglected in the derivation of the evolution equations for the moments. In fact, the first approximation as well is essentially a long-chain approximation. Therefore, when the primary chains are short, these equations are inapplicable.

Under these assumptions, $\mathrm{DP_w}$ is given as[35]

$$\mathrm{DP_w} = \frac{k_{tr}}{2k_p r^2}\,\frac{1-x}{x}\,\frac{\{(1-x)^{-M} - 1\}(M-1)^2}{1 - (1-x)^{-M}\left(\frac{M-1}{M+1}\right)^2} \tag{34}$$

where M is defined by

$$M = \left(1 + \frac{4k_p r}{k_{tr}}\right)^{1/2} \tag{35}$$

The gel point is thus given by[34]

$$x_c = 1 - \left(\frac{M-1}{M+1}\right)^{2/M} \tag{36}$$

The conversion used here, x, is not the conversion of double bonds but rather the mass conversion and can be shown to be related to the conversion p by the following:

$$x = 1 - f_A(1 - p) \tag{37}$$

These equations constitute the kinetic solution with which we want to compare, but the comparison must be done at primary chain lengths sufficiently large that the long-chain approximations made are good. To estimate when these approximations become severe, we look at the case $r = 1$ for which we have an exact statistical result which suffers from no long-chain approximations. In the case at hand, the exact gel point is (see eq 28 of ref 25)

$$p_c = 1 - e^{-k_{tr}/2k_p} \tag{38}$$

whereas the kinetic result reads

$$p_c = 1 - \left(\frac{(1 + 4(k_p/k_{tr}))^{1/2} - 1}{(1 + 4(k_p/k_{tr}))^{1/2} + 1}\right)^{1/(1+4(k_p/k_{tr}))^{1/2}} \tag{39}$$

It is clear that as $k_p/k_{tr} \to \infty$ (i.e. infinitely long chains) that the two are equivalent. For short chains, however, the kinetic solution predicts an earlier gelation than would actually occur. This is due to neglecting the depletion of B_2-type double bonds, which more than compensates for the slightly lower primary chain length (by one monomer unit) in the kinetic approach (both answers also converge at $p_c = 1$ for $k_p/k_{tr} = 0$). For $\mathrm{DP_w}^0 = 100$, the error between the two is less than 0.4%, and so we will take $k_{tr}/k_p = 0.02$ as a practical upper bound for applicability of the kinetic results, and will in fact always work well below this.

We first consider $k_{tr}/k_p = 0.001$, so that the chains have an initial $\mathrm{DP_w}^0$ of 2001. The results for the gel point are tabulated in Table I and shown in Figure 2. The approximate solutions were found by numerical integration with ~5000 increments. The exact statistical model was solved here as elsewhere by approximating the integral equations with Simpson's rule (plus trapezoidal if necessary) so as to obtain a large number of linear equations to solve, which was done with a full pivoting routine. In order to reduce error due to discretization, ~400 increments up to the gel point were used, so that one might expect ~0.25% error in the gel point. The gel point was

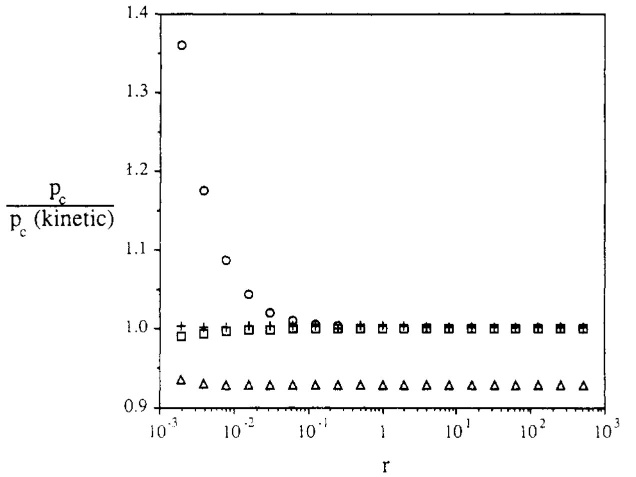

Figure 2. p_c/p_c(kinetic) versus r for first kinetic situation, $k_{tr}/k_p = 0.001$. (○) naive approximation; (△) random combination approximation; (□) cross-link density distribution approximation; and (+) exact statistical model.

determined as the midpoint between the latest conversion at which DP_w was large and positive, and the next at which it was large but negative. These calculations were performed on a Hewlett-Packard Apollo computer; the approximate models were solved either on an Apollo or on a MacIntosh.

Both Table I and Figure 2 reveal several interesting features. First and foremost is that the exact statistical solution is always within approximately 0.25% of the kinetic solution. Since that error can be attributed to the discretization, this supports the claim that the exact statistical solution is in fact exact and that the long-range correlations have been correctly accounted for.

As expected, the approximations meet with varying success. The random combination approximation is uniformly bad, giving an incorrect answer even at $r = 1$. Indeed, it can be shown that for systems gelling early that

$$\frac{p_c(\text{random combination})}{p_c(\text{exact})} = 2\sqrt{3}(2-\sqrt{3}) \approx 0.9282 \quad (40)$$

independent of r (this is because $f_A = (1-p)$ as $p \to 0$, independent of r). This more complicated approach is therefore not recommended. The naive approximation works amazingly well, but when it fails, as it does here at low r, it fails more dramatically than the others. By far the best approximation seems to be the cross-link density approximation, which exhibits only slight deviations at low r. The evolution of DP_w for these approximations at $r = {}^1/_{512}$, shown in Figure 3, illustrates these points quite clearly.

Another striking feature is that the discrepancy of the various approximations is not symmetric about $r = 1$, but rather appears only at small r (ignoring the random combination approximation for the moment). This is so because only for small r is the pregel regime sufficiently large to allow for significant drift in the statistics of the primary chains. This drift cannot be in chain length, for this is very nearly a constant primary chain length situation, as is easily seen by comparing the gel points predicted by the naive approximation in Table I with $(2000r)^{-1}$. Rather, the drift must be in the composition. If this is so, then, for longer chains which gel earlier we should not see deviations as large. This is indeed the case, as is shown in Figure 4, for chains approximately 10 times larger than those with which we have been dealing. This 10-fold increase in chain length causes approximately a 10-fold decrease in p_c, and so one sees less effect of composition drift, and thus the naive approximation is better over a larger range of r (note the much smaller scale in this graph).

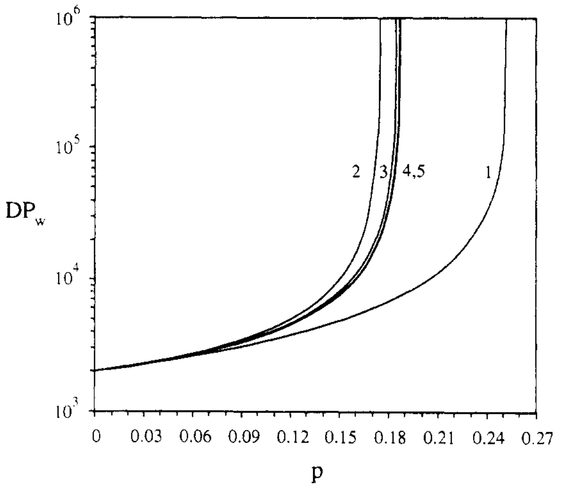

Figure 3. DP_w versus p for $r = {}^1/_{512}$, first kinetic situation, $k_{tr}/k_p = 0.001$. Curve 1, naive approximation; curve 2, random combination approximation; curve 3, cross-link density distribution approximation; curve 4, kinetic solution; and curve 5, exact statistical solution.

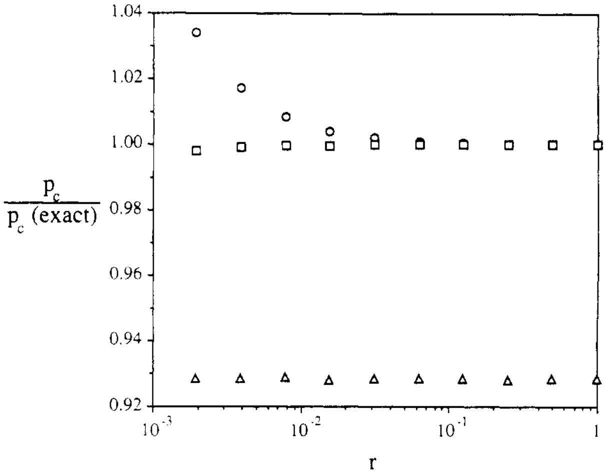

Figure 4. p_c/p_c(kinetic) versus r for first kinetic situation, $k_{tr}/k_p = 0.0001$. (○) naive approximation; (△) random combination approximation; and (□) cross-link density distribution approximation.

As a final point with respect to this situation, we ask what the critical behavior of DP_w is. The kinetic eq 34, despite its complicated appearance, can be shown to exhibit a critical exponent $\gamma = 1$. We thus expect our exact statistical result to do the same. Figure 5 shows that this is so, where ϵ was calculated using the statistical result $p_c = 0.1888$; after an initial lower apparent γ, DP_w does diverge with $\gamma = 1$. The apparent upturn around $\epsilon = 0.01$ is due to numerical error giving a gel point slightly later than in reality; the figure shows that the last three data points only are responsible for this upturn. We can thus conclude that the substitution effect does not alter the mean-field nature of the model, despite the long-range correlations that it invokes. This is as expected, since to alter the critical behavior we would require that the effect itself be long-ranged (e.g. size-dependent reactivity, cyclization, or fluctuation effects).

Second Kinetic Situation: Constant $R^\bullet$, Monomer Depletion. In this situation, propagation occurs as above, but polymer chain termination occurs only by dispropor-

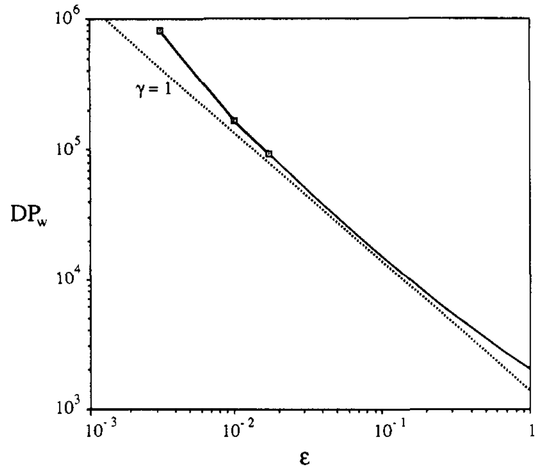

Figure 5. Critical behavior exhibited under first kinetic situation; $r = {}^1/_{512}$, $k_{tr}/k_p = 0.001$.

tionation, not by transfer or by coupling. In this case we get:

$$\mathrm{DP_w}^0(\bar{p}) = 1 + \frac{2(f_A + r(1 - f_A))}{\dfrac{k_t}{k_p}\dfrac{R^\bullet}{A_2(0)(1 - \bar{p})}} \tag{41}$$

where $A_2(0)$ is the initial concentration of double bonds. This situation involves, besides r, a kinetic parameter (k_t/k_p) and a concentration parameter ($R^\bullet/A_2(0)$), which can be combined into one parameter, $\mathrm{DP_w}^0(0)$, the initial primary chain length.

Here again we look at the case where the initial chains have $\mathrm{DP_w}^0(0) = 2001$. The results are listed in Table II and plotted in Figure 6. Comparing the exact results listed in Tables I and II shows that the gel point is delayed by monomer depletion, as expected from ref 25, and that this effect is felt more acutely as r decreases, for the simple reason that the pregel regime becomes increasingly broader as r decreases. What is more noteworthy is the behavior of the approximate solutions. The naive approximation fails much more catastrophically, apparently not predicting gelation at all for $r = {}^1/_{512}$ (numerical problems are encountered here because of the extremely small f_A past $p = 0.5$). In fact, as Figure 7 shows, $\mathrm{DP_w}$ under the naive approximation levels off and (though not shown in the figure) actually decreases beyond $p = 0.5$. The random combination approximation appears to be improving, but this is of course just errors compensating for one another. The cross-link density distribution again performs the best, but it deviates slightly more than in the previous case, and in the opposite direction. Thus, it is worth pointing out that not only do approximations either predict lower or higher gel points depending on the approximation used (see Figure 2), but the direction of deviation for each approximation may vary depending on the kinetic situation. Thus, rules of thumb such as assuming that approximate solutions always supply a lower bound on the gel point are incorrect.

Third Kinetic Situation: Constant $R^\bullet$, Monomer Depletion, and Rapid Transfer Agent Depletion. In this case we get

$$\mathrm{DP_w}^0(\bar{p}) = 1 + \frac{2(f_A + r(1 - f_A))}{\dfrac{k_t}{k_p}\dfrac{R^\bullet}{A_2(0)(1 - \bar{p})} + \dfrac{k_{trS}}{k_p}\dfrac{S}{A_2(0)(1 - \bar{p})}} \tag{42}$$

where, within the long-chain approximation, the concentration of transfer agent is given as

$$S = S(0)(f_A(1 - p))^{k_{trS}/2k_p} \tag{43}$$

In this case, then, the primary chain length depends on three kinetic parameters (r, k_t/k_p, and k_{trS}/k_p), and two concentration parameters ($R^\bullet/A_2(0)$, and $S(0)/A_2(0)$).

When no transfer reactions occur and chains are ended solely by termination, as in the previous kinetic situation, chain length decreases steadily with conversion because of monomer depletion. In the presence of a transfer agent the conversion-dependence of the primary chain length may be more complicated. For example, when a highly reactive and rapidly depleted transfer agent is present, an initial steep increase in the primary chain length may occur, followed by a steady decline due to monomer depletion. This is the situation we will examine in this section; there are, of course, other possibilities.

The particular case we examine is one for which $\mathrm{DP_w}^0(0)$ is 201, but would be 2010 if the transfer agent were absent. Here, $k_t/k_p = 10^4$, $k_{trS}/k_p = 100$, $R^\bullet/A_2(0) = 10^{-5}$, and $S(0)/A_2(0) = 9 \times 10^{-5}$. Under these conditions, the transfer agent is quickly depleted in the first few percents of conversion. The results are shown in Figure 8 and are tabulated in Table III.

This kinetic situation in enlightening for several reasons. First, it shows that the deviations of the naive and random combination approximations can certainly be worse than our previous situations suggest, and that the deviations are not necessarily monotonic with r. More importantly, though, is that the cross-link density approximation is not necessarily good at $r = 1$, as is the naive approximation. In this situation, the cross-link density approximation falls below the exact result by over 2%. The final point is that the naive approximation can show deviations for $r > 1$, which it does here because of the rapidly changing primary chain length.

In concluding this section, it should be stressed that all of the evaluations of the different approximations have been made only with respect to $\mathrm{DP_w}$, and that in the pregel. To assume that the success of an approximation with respect to this criterion would ensure its success with respect to other quantities, or over the entire reaction, is not justified. In fact, the naive approximation serves as a useful warning. We have seen that this simple approximation often works quite well with respect to $\mathrm{DP_w}$, especially for $r > 1$, and yet we know that $\mathrm{DP_n}$ will be very wrongly calculated under such an approximation, since the number of cross-links is wrong by a factor of r. Thus, there is no assurance from this work that the cross-link density approximation, which by far performs the best, will necessarily perform well with respect to other criteria in the pregel regime (e.g. $\mathrm{DP_z}$) or with respect to postgel properties since the conversion regime is much broader and thus more susceptible to the various sources of conversion-dependent kinetics.

Conclusions

In conclusion, it is worth pointing out the variety and ubiquity of effects which may lead to long-range correlations despite local sources. These include but are not limited to (a) substitution effects; (b) a "triggering" of reactions; and (c) a residence time distribution, as in an HCSTR,[27] a semibatch process in general,[36] or a multistage process.[37] For example, transfer to polymer and terminal double-bond polymerization, which are prevalent in polymerizations of vinyl acetate and vinyl chloride,[38] should introduce such correlations as has been pointed out by Galina,[39] so that the author's previous comment that

Table II
Comparison of Gel Points from Approximate and Exact Solutions for Second Kinetic Situation ($DP_w^0(0) = 2001$)

r	p_c(naive)	p_c(random comb.)	p_c(xlink density)	p_c(exact statistical)
$^1/_{512}$	$>6.000 \times 10^{-1}$	2.267×10^{-1}	2.348×10^{-1}	2.310×10^{-1}
0.001 995 9	5.157×10^{-1}	2.222×10^{-1}	2.303×10^{-1}	2.262×10^{-1}
0.002 040	4.279×10^{-1}	2.176×10^{-1}	2.259×10^{-1}	2.219×10^{-1}
0.002 130	3.757×10^{-1}	2.090×10^{-1}	2.173×10^{-1}	2.134×10^{-1}
0.002 323	3.132×10^{-1}	1.926×10^{-1}	2.008×10^{-1}	1.982×10^{-1}
0.002 762	2.372×10^{-1}	1.632×10^{-1}	1.712×10^{-1}	1.690×10^{-1}
$^1/_{256}$	1.507×10^{-1}	1.166×10^{-1}	1.233×10^{-1}	1.223×10^{-1}
$^1/_{128}$	6.870×10^{-2}	5.892×10^{-2}	6.289×10^{-2}	6.273×10^{-2}
$^1/_{64}$	3.309×10^{-2}	2.959×10^{-2}	3.174×10^{-2}	3.166×10^{-2}
$^1/_{32}$	1.626×10^{-2}	1.483×10^{-2}	1.594×10^{-2}	1.590×10^{-2}
$^1/_{16}$	8.063×10^{-3}	7.423×10^{-3}	7.986×10^{-3}	8.005×10^{-3}
$^1/_{8}$	4.015×10^{-3}	3.713×10^{-3}	3.998×10^{-3}	4.007×10^{-3}
$^1/_{4}$	2.004×10^{-3}	1.857×10^{-3}	2.000×10^{-3}	2.005×10^{-3}
$^1/_{2}$	1.001×10^{-3}	9.286×10^{-4}	1.000×10^{-3}	1.003×10^{-3}
1	5.001×10^{-4}	4.643×10^{-4}	5.001×10^{-4}	5.013×10^{-4}
512	9.764×10^{-7}	9.068×10^{-7}	9.772×10^{-7}	9.796×10^{-7}

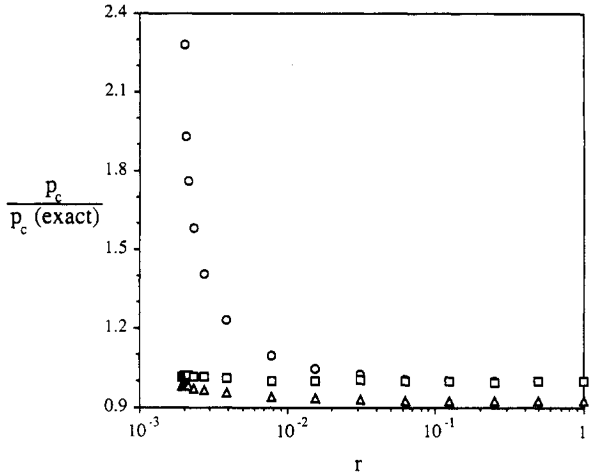

Figure 6. p_c/p_c(exact) versus r for second kinetic situation, $DP_w^0(0) = 2001$. (○) naive approximation; (△) random combination approximation; and (□) cross-link density distribution approximation.

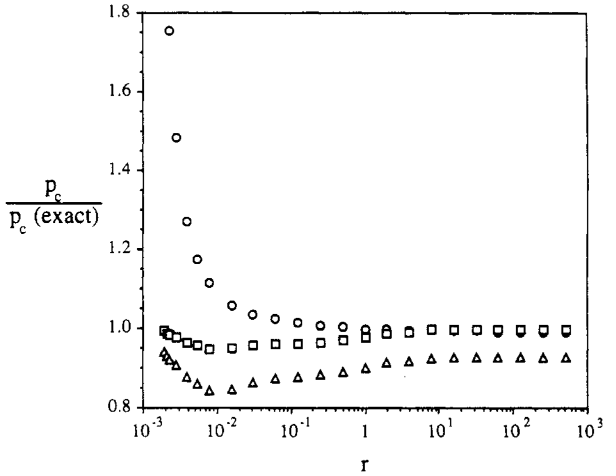

Figure 8. p_c/p_c(exact) versus r for third kinetic situation, $k_t/k_p = 10^4$, $kt_{rS}/k_p = 100$, $R^{\cdot}/A_2(0) = 10^{-5}$, and $S(0)/A_2(0) = 9 \times 10^{-5}$. (○) naive approximation; (△) random combination approximation; and (□) cross-link density distribution approximation.

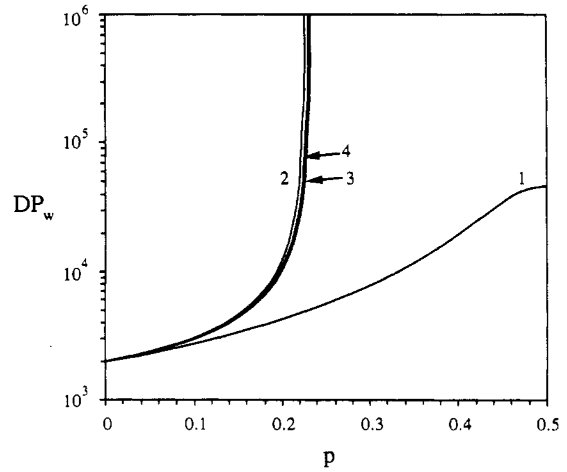

Figure 7. DP_w versus p for $r = {}^1/_{512}$, second kinetic situation, $DP_w^0(0) = 2001$. Curve 1, naive approximation; curve 2, random combination approximation; curve 3, cross-link density distribution approximation; curve 4, exact statistical solution.

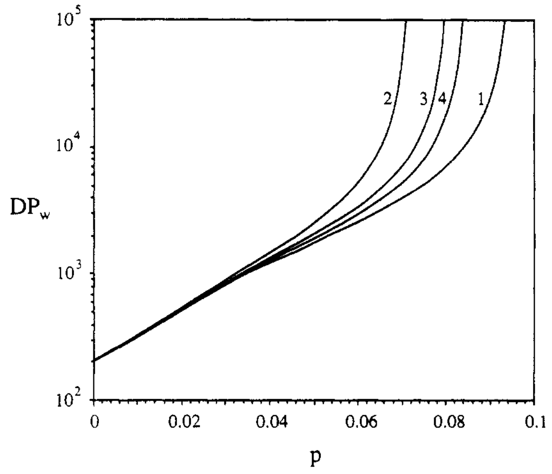

Figure 9. DP_w versus p for $r = {}^1/_{128}$, third kinetic situation, $k_t/k_p = 10^4$, $k_{trS}/k_p = 100$, $R^{\cdot}/A_2(0) = 10^{-5}$, and $S(0)/A_2(0) = 9 \times 10^{-5}$. Curve 1, naive approximation; curve 2, random combination approximation; curve 3, cross-link density distribution approximation; curve 4, exact statistical solution.

"accounting for transfer to polymer should be possible"[25] within the simple recursive framework of ref 25 is false.

Caution must be exercised in this and other cases, as has already been pointed out in the literature (e.g. with respect to multistage processes see the recent publication of Tiemersma-Thoone et al.[37]). Failure to recognize the correlations which thus arise leads to incorrect answers. However, in many cases, such as the substitution effect treated in this paper, *exact statistical models can be devised.* This does not mean that such a model would necessarily be the best choice; a kinetic model might be less computationally expensive, for example. If, however, the internal structure of the gel is to be determined, the statistical model remains the only choice (aside from simulations), and so it is worthwhile to accurately evaluate

Table III

Comparison of Gel Points from Approximate and Exact Solutions for Third Kinetic Situation ($k_t/k_p = 10^4$, $k_{trS}/k_p = 100$, $R^{\bullet}/A_2(0) = 10^{-5}$, and $S(0)/A_2(0) = 9 \times 10^{-5}$

r	p_c(naive)	p_c(random comb.)	p_c(xlink density)	p_c(exact statistical)
$^1/_{512}$	$>6.000 \times 10^{-1}$	2.356×10^{-1}	2.489×10^{-1}	2.507×10^{-1}
0.002 130	$>6.000 \times 10^{-1}$	2.180×10^{-1}	2.316×10^{-1}	2.344×10^{-1}
0.002 323	3.840×10^{-1}	2.016×10^{-1}	2.153×10^{-1}	2.190×10^{-1}
0.002 762	2.819×10^{-1}	1.724×10^{-1}	1.860×10^{-1}	1.902×10^{-1}
$^1/_{256}$	1.829×10^{-1}	1.265×10^{-1}	1.390×10^{-1}	1.441×10^{-1}
0.005 524	1.285×10^{-1}	9.396×10^{-2}	1.048×10^{-1}	1.094×10^{-1}
$^1/_{128}$	9.443×10^{-2}	7.150×10^{-2}	8.039×10^{-2}	8.483×10^{-2}
$^1/_{64}$	5.654×10^{-2}	4.532×10^{-2}	5.084×10^{-2}	5.351×10^{-2}
$^1/_{32}$	3.756×10^{-2}	3.135×10^{-2}	3.478×10^{-2}	3.635×10^{-2}
$^1/_{16}$	2.607×10^{-2}	2.224×10^{-2}	2.448×10^{-2}	2.549×10^{-2}
$^1/_8$	1.790×10^{-2}	1.548×10^{-2}	1.697×10^{-2}	1.767×10^{-2}
$^1/_4$	1.174×10^{-2}	1.028×10^{-2}	1.123×10^{-2}	1.165×10^{-2}
$^1/_2$	7.212×10^{-3}	6.416×10^{-3}	6.984×10^{-3}	7.196×10^{-3}
1	4.145×10^{-3}	3.746×10^{-3}	4.064×10^{-3}	4.155×10^{-3}
2	2.257×10^{-3}	2.066×10^{-3}	2.235×10^{-3}	2.262×10^{-3}
4	1.184×10^{-3}	1.093×10^{-3}	1.181×10^{-3}	1.193×10^{-3}
8	6.071×10^{-4}	5.637×10^{-4}	6.081×10^{-4}	6.096×10^{-4}
16	3.076×10^{-4}	2.865×10^{-4}	3.088×10^{-4}	3.095×10^{-4}
32	1.548×10^{-4}	1.444×10^{-4}	1.557×10^{-4}	1.560×10^{-4}
64	7.768×10^{-5}	7.249×10^{-5}	7.815×10^{-5}	7.834×10^{-5}
128	3.890×10^{-5}	3.632×10^{-5}	3.915×10^{-5}	3.925×10^{-5}
256	1.947×10^{-5}	1.819×10^{-5}	1.959×10^{-5}	1.964×10^{-5}
512	9.736×10^{-6}	9.096×10^{-6}	9.803×10^{-6}	9.827×10^{-6}

the boundaries of the statistical approach, rather than to dismiss the approach because past approximate treatments have been found wanting.

We do not imply, however, that the statistical method has no boundaries and that all effects which lead to long-range correlations can be properly captured within a statistical model. Indeed, when the source of the nonideality is itself long-ranged, it seems that statistical description is beyond grasp. This is because one would in the worst case need to know all the details of the molecule at the time of the reaction of the functional group in question in order to derive the properties of the molecule at the conversion of interest. Unfortunately, this is not an unusual situation; cyclization[28] is one example of this. Another is a pendant reactivity dependent on the size of the molecule bearing the pendant, for which there is experimental support in systems such as that described in this paper.[29] The physical rather than chemical source of reduced pendant reactivity in these systems forces the pendant reactivity itself to be a distributed quantity, dependent on size and location in the polymer, rendering the treatment in this paper inappropriate.

This proposed inability of statistical models to account for these sorts of correlations is a severe drawback, since it limits application to systems exhibiting mean-field critical exponents, which cannot in reality be the case.[1] This is not necessarily a limitation of the kinetic approach, if the coagulation kernel is formulated properly.[40] The only apparent exception to this rule is the statistical description of a nonlinear polymerization which exhibits a very different molecular weight distribution than predicted by classical (or, for that matter, percolation) theory. Typical nonlinear polymerizations yield a molecular weight distribution which has the form of a power law in size with an exponential cutoff. The exponential cutoff vanishes at the gel point, allowing the exponent of the power law (a constant) to determine the divergent moments. For A_f homopolymerization in an HCSTR, however, the distribution is always merely power law, with no exponential cutoff, and the exponent of the power law is a function of conversion.[41] This is qualitatively different behavior than in batch-wise polymerization, and yet the statistical method has been properly extended to predict average molecular weights in this case. Whether this implies (contrary to the doubts stated above) that nonclassical polymerizations within the percolation paradigm are accessible to the statistical approach is unknown.

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Appendix 1: Comonomer Composition as a Function of Conversion

The differential equation governing the evolution of f_A with p, known as Skeist's equation,[38,42] can be easily derived in the following way:

$$\frac{\mathrm{d}f_A}{\mathrm{d}p} = \frac{\mathrm{d}}{\mathrm{d}p}\left(\frac{A_2}{A_2 + B_2}\right) = \frac{(A_2 + B_2)\dfrac{\mathrm{d}A_2}{\mathrm{d}p} - A_2\dfrac{\mathrm{d}(A_2 + B_2)}{\mathrm{d}p}}{(A_2 + B_2)^2} \tag{A1.1}$$

$$= \frac{1}{1-p}\,\frac{\mathrm{d}A_2}{\mathrm{d}(A_2 + B_2)} + f_A\frac{1}{1-p} \tag{A1.2}$$

where A_2 denotes the concentration of A_2-type double bonds, and B_2 the concentration of B_2-type double bonds. This can be rearranged to give

$$\frac{\mathrm{d}p}{1-p} = \frac{\mathrm{d}f_A}{\dfrac{\mathrm{d}A_2}{\mathrm{d}(A_2 + B_2)} - f_A} \tag{A1.3}$$

Now, in the usual case $[\mathrm{d}A_2/\mathrm{d}(A_2 + B_2)]$ is identified with F_A, the copolymer composition. In the present case, though, monomer A_2 is lost not only through incorporation into polymer, but also by transformation into B_2. As is clear, though, only half of all A_2 groups are incorporated into the polymer, so that this term is $2F_A$, and so we can write

$$\frac{\mathrm{d}p}{1-p} = \frac{\mathrm{d}f_A}{2F_A - f_A} \tag{A1.4}$$

a modified form of Skeist's equation, appropriate to the case at hand. The copolymer composition, F_A, is given by the standard Mayo–Lewis equation:[38,43]

$$F_A = \frac{r_A f_A^2 + f_A(1-f_A)}{r_A f_A^2 + 2f_A(1-f_A) + r_B(1-f_A)^2} \qquad \text{(A1.5)}$$

For ideal copolymerization, $r_A = 1/r$, and $r_B = r$, and this equation reduces to

$$F_A = \frac{f_A}{f_A + r(1-f_A)} \qquad \text{(A1.6)}$$

Inserting this relation into eq A1.4 yields

$$\frac{dp}{1-p} = \frac{(r-1)\,df_A}{(r-1)f_A - (r-2)} + \frac{r\,df_A}{f_A((r-1)f_A - (r-2))} \qquad \text{(A1.7)}$$

If the relative reactivity r is held constant, eq A1.7 can be integrated in the same manner as done for usual copolymerizations,[38,44] with the initial condition that $f_A(0) = 1$. We obtain three different cases, depending on the value of r. The general form of eq A1.7 valid for nonideal copolymerization, as well as the solutions thereof, is given in ref 26. It should also be noted that similar equations to those above have been set up by Dušek[45] for the more complex case for which a monounsaturated monomer is also present. Numerical solution was only suggested for those equations; here we present analytical results.

$\boldsymbol{r = 2}$. Here we see that

$$p = 1 - \frac{1}{f_A}\exp\left[-\frac{2(1-f_A)}{f_A}\right] \qquad \text{(A1.8)}$$

and $f_A(1) = 0$.

$\boldsymbol{r \neq 2, r \neq 1}$. Here we find

$$p = 1 - \frac{1}{f_A}\left[\frac{(r-1)f_A - (r-2)}{f_A}\right]^{-2/(2-r)} \qquad \text{(A1.9)}$$

Here, $f_A(1) = 0$ only if $r < 2$. If $r > 2$, there exists a limiting comonomer composition given by

$$f_A(1) = \frac{r-2}{r-1} \qquad \text{(A1.10)}$$

which is caused by consumption of B_2 groups sufficiently rapid so as not to allow $f_A \rightarrow 0$ as $p \rightarrow 1$.

$\boldsymbol{r = 1}$. For the case of equal reactivity we find that

$$p = 1 - f_A \qquad \text{(A1.11)}$$

which is also intuitively obvious.

Furthermore, we may relate the conversion of both A_2 and B_2 double bonds to the overall conversion p and comonomer composition f_A. For normal copolymerizations, the following relations hold:

$$p_A = 1 - \frac{f_A}{f_A(0)}(1-p) \qquad \text{(A1.12)}$$

$$p_B = 1 - \frac{1-f_A}{1-f_A(0)}(1-p) \qquad \text{(A1.13)}$$

In this case, because of the peculiarities of the polymerization, these equations are incorrect and are replaced by

$$p_A = 1 - \frac{2f_A(1-p)}{1+f_A(1-p)} \qquad \text{(A1.14)}$$

$$p_B = 1 - \frac{2(1-f_A)(1-p)}{1-f_A(1-p)} \qquad \text{(A1.15)}$$

Also, the total amounts of both reacted and unreacted A_2-type groups, $[A_2]_t$, and B_2-type groups, $[B_2]_t$, are given below:

$$[A_2]_t = \frac{A_2(0)}{1+p_A} \qquad \text{(A1.16)}$$

$$[B_2]_t = \frac{p_A A_2(0)}{1+p_A} \qquad \text{(A1.17)}$$

The mass yield, x, is given as

$$x = 1 - f_A(1-p) \qquad \text{(A1.18)}$$

The final relation which finds utility in the paper is the following:

$$\int_0^p F_A\,d\bar{p} = {}^1/_2(1 - f_A(1-p)) \qquad \text{(A1.19)}$$

i.e. half the mass yield, which is intuitively obvious.

Appendix 2: Derivation of Linking Probability Densities

$\boldsymbol{\rho_2(p'|\bar{p})\,dp'}$. We begin with the second linking probability density, $\rho_2(p'|\bar{p})dp'$, which describes the connections to chains produced at later conversions. This is a better place to start since it is easier to derive and since some quantities must be developed here for derivation of $\rho_1(p'|\bar{p})\,dp'$. We can write the following:

$$\begin{aligned}\rho_2(p'|\bar{p})\,dp' &= \\ &\rho(B_2 \text{ reacted at } p'|\text{partner } A_2 \text{ reacted at } \bar{p})\,dp' \\ &= \rho(B_2 \text{ reacted at } p'|B_2 \text{ created at } \bar{p})\,dp' \\ = P(B_2 \text{ survived until } p'|B_2 \text{ created at } \bar{p}) \times \\ &\rho(B_2 \text{ reacts at } p'|B_2 \text{ survived until } p')\,dp' \quad \text{(A2.1)}\end{aligned}$$

where ρ is used to indicate probability density rather than mass. The first term here can be expressed as the probability of no arrivals, $P(N(p') - N(\bar{p}) = 0)$, in the "time" interval from $\bar{p}$ to p' in a nonhomogeneous or nonstationary Poisson process.[46] To find this, we first realize that the second term is the arrival rate of that nonhomogeneous Poisson process at $\bar{p}$, and ask, what is this arrival rate? This is given by the increment of B_2's reacted divided by the total number of B_2 groups available at that conversion:

$$\rho(B_2 \text{ reacts at } p'|B_2 \text{ survived until } p')\,dp' = \frac{F_B(-dM)}{B_2} = \frac{F_B\,dp'}{f_B(1-p')} \qquad \text{(A2.2)}$$

where M is the total concentration of double bonds. Since this is the arrival, or failure, rate, we can immediately write:

$$P(\mathrm{B}_2 \text{ survived until } p'|\mathrm{B}_2 \text{ created at } \bar{p}) = \exp\left\{-\int_{\bar{p}}^{p'} \frac{F_\mathrm{B}\,\mathrm{d}p''}{f_\mathrm{B}(1-p'')}\right\} \quad \text{(A2.3)}$$

Thus, the second linking probability is given as in eq 11.

$\rho_1(p'|\bar{p})\mathrm{d}p'$. In this section, we derive eq 10 which gives the probability density, $\rho_1(p'|\bar{p})\ \mathrm{d}p'$, for connections to chains formed at earlier conversions. This probability density can be written in the following way:

$$\rho_1(p'|\bar{p})\ \mathrm{d}p' = \rho(\mathrm{A}_2 \text{ reacted at } p'|\text{partner } \mathrm{B}_2 \text{ reacted at } \bar{p})\ \mathrm{d}p'$$

$$= \rho(\mathrm{B}_2 \text{ created at } p'|\mathrm{B}_2 \text{ reacted at } \bar{p})\ \mathrm{d}p' \quad \text{(A2.4)}$$

This last can be expressed in another way by invoking Bayes' formula:[46]

$$\rho(\mathrm{B}_2 \text{ created at } p'|\mathrm{B}_2 \text{ reacted at } \bar{p})\ \mathrm{d}p' = \frac{\rho(\mathrm{B}_2 \text{ reacted at } \bar{p}|\mathrm{B}_2 \text{ created at } p')\rho(\mathrm{B}_2 \text{ created at } p')}{\rho(\mathrm{B}_2 \text{ reacted at } \bar{p})}\,\mathrm{d}p' \quad \text{(A2.5)}$$

Equations A2.1 and 11 show that the first term in the numerator is given simply by

$$\rho(\mathrm{B}_2 \text{ reacted at } \bar{p}|\mathrm{B}_2 \text{ created at } p')\ \mathrm{d}\bar{p} = \exp\left\{-\int_{p'}^{\bar{p}} \frac{F_\mathrm{B}\,\mathrm{d}p''}{f_\mathrm{B}(1-p'')}\right\}\frac{F_\mathrm{B}\,\mathrm{d}\bar{p}}{f_\mathrm{B}(1-\bar{p})} \quad \text{(A2.6)}$$

The second term in the numerator is given as follows:

$$\rho(\mathrm{B}_2 \text{ created at } p')\ \mathrm{d}p' = \frac{F_\mathrm{A}(p')\ \mathrm{d}p'}{\int_0^{\bar{p}} F_\mathrm{A}\ \mathrm{d}p'} \quad \text{(A2.7)}$$

since in any increment of conversion $\mathrm{d}p' F_\mathrm{A} A_2$ monomers are incorporated into polymer, and an equal number of B_2 monomers are created.

The denominator in eq A2.5 is different than the probability that a B_2 still surviving at $\bar{p}$ reacts at $\bar{p}$. This probability density is the probability that any B_2 (formed up to that conversion) reacts at $\bar{p}$. It is thus a normalizing factor and is given as

$$\rho(\mathrm{B}_2 \text{ reacted at } \bar{p}) = \int_0^{\bar{p}} \rho(\mathrm{B}_2 \text{ reacted at } \bar{p}|\mathrm{B}_2 \text{ created at } p')\rho(\mathrm{B}_2 \text{ created at } p') \quad \text{(A2.8)}$$

Thus the probability density $\rho_1(p'|\bar{p})$ is given as in eq 10.

Analytic Evaluation for Ideal Copolymerization. Despite the somewhat difficult appearance of these two linking probabilities, analytic evaluation is straightforward for the case of ideal copolymerization with constant r. We will look at each of the three cases presented in Appendix 1.

$r = 2$. In order to analytically integrate the integral in the exponential term, a change of variable from p'' to $f_\mathrm{A}(p'')$ is necessary. As a result, the answer is expressed in terms of $f_\mathrm{A}(p')$ and $f_\mathrm{A}(\bar{p})$ rather than in terms of the conversion itself. This is expected and presents no difficulties in application, since the implicit relation $f_\mathrm{A}(p)$ must be solved anyhow. The results from such a treatment are

$$\rho_1(p'|\bar{p})\ \mathrm{d}p' = \frac{f_\mathrm{A}(\bar{p})}{1-f_\mathrm{A}(\bar{p})}\frac{1}{2-f_\mathrm{A}(p')}\frac{\mathrm{d}p'}{1-p'} \quad \text{(A2.9)}$$

$$= \frac{f_\mathrm{A}(\bar{p})}{1-f_\mathrm{A}(\bar{p})}\frac{1}{f_\mathrm{A}^{\,2}(p')}(-\mathrm{d}f_\mathrm{A}(p')) \quad \text{(A2.10)}$$

$$\rho_2(p'|\bar{p})\ \mathrm{d}p' = e^{-2}e^{2/f_\mathrm{A}(\bar{p})}\frac{2f_\mathrm{A}(p')}{2-f_\mathrm{A}(p')}\,\mathrm{d}p' \quad \text{(A2.11)}$$

$$= e^{2/f_\mathrm{A}(\bar{p})}e^{-2/f_\mathrm{A}(p')}\frac{2}{f_\mathrm{A}^{\,2}(p')}(-\mathrm{d}f_\mathrm{A}(p')) \quad \text{(A2.12)}$$

Using this second form of each of these, it is easy to check that ρ_1 is normalized over the interval $[0,\bar{p}]$ and that ρ_2 is normalized over the interval $[\bar{p},1]$ (since $f_\mathrm{A}(1) = 0$), as must be.

$r \neq 2$, $r \neq 1$. Here:

$$\rho_1(p'|\bar{p})\ \mathrm{d}p' = \left(\frac{(r-1)f_\mathrm{A}(\bar{p})-(r-2)}{1-f_\mathrm{A}(\bar{p})}\right)\times \frac{1}{(r-1)f_\mathrm{A}(p')-(r-2)}\frac{f_\mathrm{A}(p')}{r+(1-r)f_\mathrm{A}(p')}\frac{\mathrm{d}p'}{1-p'} \quad \text{(A2.13)}$$

$$= \left(\frac{(r-1)f_\mathrm{A}(\bar{p})-(r-2)}{1-f_\mathrm{A}(\bar{p})}\right)\frac{(-\mathrm{d}f_\mathrm{A}(p'))}{[(r-1)f_\mathrm{A}(p')-(r-2)]^2} \quad \text{(A2.14)}$$

$$\rho_2(p'|\bar{p})\ \mathrm{d}p' = \left(\frac{f_\mathrm{A}(\bar{p})}{(r-1)f_\mathrm{A}(\bar{p})-(r-2)}\right)^{-r/(2-r)}\times ((r-1)f_\mathrm{A}(p')-(r-2))\frac{r}{r+(1-r)f_\mathrm{A}(p')}\,\mathrm{d}p' \quad \text{(A2.15)}$$

$$= \left(\frac{f_\mathrm{A}(\bar{p})}{(r-1)f_\mathrm{A}(\bar{p})-(r-2)}\right)^{-r/(2-r)}\times \left(\frac{f_\mathrm{A}(p')}{(r-1)f_\mathrm{A}(p')-(r-2)}\right)^{r/(2-r)}\frac{r(-\mathrm{d}f_\mathrm{A}(p'))}{f_\mathrm{A}(p')[(r-1)f_\mathrm{A}(p')-(r-2)]} \quad \text{(A2.16)}$$

Using the second forms of these equations, it is easy to show that these densities are normalized (although one must keep in mind that for $r > 2$, f_A has a nonzero limiting value given by eq A1.10).

$r = 1$. For the case of equal reactivity, we recall that the relation between f_A and p is simple, so that all answers can be expressed in terms of conversion. We find that both of the linking probabilities are analytic and are given as

$$\rho_1(p'|\bar{p})\ \mathrm{d}p' = \frac{\mathrm{d}p'}{\bar{p}} \quad \text{(A2.17)}$$

$$\rho_2(p'|\bar{p})\ \mathrm{d}p' = \frac{\mathrm{d}p'}{1-\bar{p}} \quad \text{(A2.18)}$$

The remarkable fact about these linking probabilities is that they are independent of p', i.e. both are uniform distributions over the intervals of interest. This is the expected result, since equal reactivity (absence of substitution effect) results in random cross-linking. The fact that this is the answer obtained is testimony to the fact that the linking probabilities are formulated correctly.

$p_B'(\bar{p})$. A quantity closely related to the probability density of linking to later chains, $\rho_2(p'|\bar{p})$, is the conversion of B_2 groups born at overall conversion $\bar{p}$, denoted as $p_B'(\bar{p})$. This conditional conversion is necessary for the cross-link density approximation, and its use ensures that the additional cross-link density of chains born at conversion $\bar{p}$ is correct. The following equation is used to find $p_B'(\bar{p})$:

$$p_B'(\bar{p}) = \int_{\bar{p}}^{p} \rho_2(p'|\bar{p})\,\mathrm{d}p' \qquad \text{(A2.19)}$$

It is worth noting in passing that the overall conversion of B_2 groups at conversion p is given by the following:

$$p_B = \frac{\int_0^p F_A(\bar{p}) p_B'(\bar{p})\,\mathrm{d}\bar{p}}{\int_0^p F_A(\bar{p})\,\mathrm{d}\bar{p}} \qquad \text{(A2.20)}$$

where the term F_A properly gives each conversion increment a weight proportional to the moles of B_2 groups produced in that increment. The conditional conversion of eq A2.19 can be found analytically for ideal copolymerization with constant r. The results are summarized below.

$r = 2$. For this case we have

$$p_B(\bar{p}) = 1 - e^{2/f_A(\bar{p})} e^{-2/f_A(p)} \qquad \text{(A2.21)}$$

where, since $f_A(1) = 0$, $p_B(\bar{p}) = 1$ at complete conversion, as must be.

$r \neq 2$, $r \neq 1$. Here we have

$$p_B(\bar{p}) = 1 - \left(\frac{f_A(\bar{p})}{(r-1)f_A(\bar{p}) - (r-2)}\right)^{-r/(2-r)} \times \left(\frac{f_A(p)}{(r-1)f_A(p) - (r-2)}\right)^{r/(2-r)} \qquad \text{(A2.22)}$$

where $p_B(\bar{p}) = 1$ at complete conversion, either because $f_A(1) = 0$ ($r < 2$) or because $f_A(1) = (r-2)/(r-1)$ ($r > 2$).

$r = 1$. For the case of equal reactivity we obtain the following intuitive answer:

$$p_B(\bar{p}) = 1 - \frac{1-p}{1-\bar{p}} \qquad \text{(A2.23)}$$

where $p_B(\bar{p}) = 1$ at complete conversion.

Appendix 3: Solution of DP_w for the Case of Equal Reactivity

For equal reactivity, the composition depends on the conversion in a simple way (see eq A1.11) and the linking probability densities are given by eqs A2.17 and A2.18. The recursive equations, eqs 8 and 9, can then be written as follows:

$$E(N_{A2*}{}^{\mathrm{out}}|_{\mathrm{r}}\bar{p}) = \frac{1}{\bar{p}}\int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p' + \frac{1}{\bar{p}}\int_0^p [\mathrm{DP_w}{}^0(p') - 1]\{(1-p')E(N_{B2}{}^{\mathrm{out}}|_{\mathrm{r}}p') + p'E(N_{A2*}{}^{\mathrm{out}}|_{\mathrm{r}}p')\}\,\mathrm{d}p' \qquad \text{(A3.1)}$$

$$E(N_{B2}{}^{\mathrm{out}}|_{\mathrm{r}}\bar{p}) = \frac{1}{1-\bar{p}}\int_{\bar{p}}^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p' + \frac{1}{1-\bar{p}}\int_{\bar{p}}^p [\mathrm{DP_w}{}^0(p') - 1]\{(1-p')E(N_{B2}{}^{\mathrm{out}}|_{\mathrm{r}}p') + p'E(N_{A2*}{}^{\mathrm{out}}|_{\mathrm{r}}p')\}\,\mathrm{d}p' \qquad \text{(A3.2)}$$

Defining

$$E(p') = (1-p')E(N_{B2}{}^{\mathrm{out}}|_{\mathrm{r}}p') + p'E(N_{A2*}{}^{\mathrm{out}}|_{\mathrm{r}}p') \qquad \text{(A3.3)}$$

we find that

$$E(\bar{p}) = \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p' + \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,E(p')\,\mathrm{d}p' \qquad \text{(A3.4)}$$

Since the right side of the equation does not depend on $\bar{p}$, $E(\bar{p})$ is independent of $\bar{p}$ and is merely a function of the conversion p. Thus eq A3.6 has a simple algebraic solution:

$$E(\bar{p}) = E = \frac{\int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'}{1 - \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'} \qquad \text{(A3.5)}$$

From eqs A3.1 and A3.2 we obtain $E(N_{A2*}{}^{\mathrm{out}}|_{\mathrm{r}}\bar{p})$ and $E(N_{B2*}{}^{\mathrm{out}}|_{\mathrm{r}}\bar{p})$ (which *are* functions of $\bar{p}$):

$$E(N_{A2*}{}^{\mathrm{out}}|_{\mathrm{r}}\bar{p}) = \frac{\frac{1}{\bar{p}}\int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'}{1 - \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'} \qquad \text{(A3.6)}$$

$$E(N_{B2*}{}^{\mathrm{out}}|_{\mathrm{r}}\bar{p}) = \frac{\frac{1}{1-\bar{p}}\int_{\bar{p}}^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'}{1 - \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'} \qquad \text{(A3.7)}$$

Integrating these according to eq 5 yields the following equation for $\mathrm{DP_w}$:

$$\mathrm{DP_w} = 1 + \frac{2}{2-p}\,\frac{\frac{1}{p}\int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'}{1 - \int_0^p [\mathrm{DP_w}{}^0(p') - 1]\,\mathrm{d}p'} \qquad \text{(A3.8)}$$

which is in agreement with the answer obtained by simpler recursive techniques; see eq 27 of ref 25, letting $f = 4$, $w_{A2}{}^* = A_2(0) = 0$, $a_4 = 1$, $M_{A4} = 1$, and finding the instantaneous $\mathrm{DP_w}{}^0(p')$ from the derivative of eq 41.

It is worth noting that in the equal reactivity case, the long-range correlations do not disappear (i.e. random combination of A_2 and B_2 groups yields the wrong answer). This is counter-intuitive, but is due to the fact that by merely making the distinction between A_2 (the double bond which reacted first) and B_2 (that which reacted second) one forces long-range correlations. Only when one does not make this distinction (see refs 25 and 26) is random combination acceptable. Of course, when substitution effects are present, one is forced to make this distinction.

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