Macromolecules 1991, *24*, 1833–1845

Models for the First Shell Substitution Effect in Stepwise Polymerization

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Received August 2, 1990; Revised Manuscript Received September 19, 1990

ABSTRACT: We present a branching process model of stepwise homopolymerization with the first shell substitution effect (FSSE). Some authors have stated that branching process statistical models are not appropriate for certain nonideal (nonrandom) kinetically controlled polymerizations; a stepwise homopolymerization with FSSE is an example of such a polymerization. Alternate approaches to modeling these systems include Monte Carlo analysis and purely kinetic modeling. Our model is exact given the assumptions of multiplicative kinetic rates and no cyclization; its implementation has a small numerical error due to discretization. We compare its predictions with those of an exact kinetic model found in the literature. The results of the comparison confirm the validity of correctly defined statistical models for nonideal irreversible polymerizations. In order to be exact, statistical models for nonideal polymerizations must contain a sufficient level of structural detail. Aggregation of structural detail may lead to inexact models. We illustrate the consequences of aggregation and refinement of modeling detail with our FSSE homopolymerization model.

Introduction

In a polymerization with a general substitution effect, the reactivity of any given unreacted site depends on the number of sites on the same molecule that have already reacted. In the most general case imaginable, each time a site reacts the reactivities of all unreacted sites on the same molecule change by different amounts. Unreacted sites close to the one that reacted suffer a much greater change than those that are farther away.[1] For sufficiently distant sites the change is negligible. If we assume that the presence of a reacted site only affects the reactivity of sites on the same monomeric unit, we have a "first shell" substitution effect. If the presence of a reacted site also affects the reactivity of sites on the next monomeric unit we have a "second shell" substitution effect, and so on. This paper is limited to the first shell substitution effect (FSSE).

Galina and Szustalewicz[2] claim that "the statistical methods, including the cascade theory, are *not appropriate* to deal with kinetically controlled polymerization processes, except for the rather rare systems with equal and conversion-independent reactivities of functional groups". Mikeš and Dušek[3] have made a similar claim in the past, adding, however, that the so-called "probability models" give good approximations for all systems of practical interest. These conclusions were drawn from comparisons of an exact kinetic model[2] and a Monte Carlo simulation[3] with a simple approximate probability model for the irreversible homopolymerization of f-functional molecules with a first shell substitution effect (a probability model that has also been presented by Durand and Bruneau[4]). While it is true that the simple probability model is an approximate one and that in cases of extreme substitution effect its answers have considerable error, that does not imply that all probability models of this system behave similarly. The generalization is not justified. We want to show that it is possible to construct an exact probability model for the same kinetically controlled polymerization process considered by Galina and Szustalewicz[2] and Mikeš and Dušek.[3] Not everyone will find it to be the method of choice for his or her particular system, but it is certainly "appropriate".

The original statistical polymer modeling of Flory[5,6] and Stockmayer[7] is based on three simplifying assumptions: namely, (1) all functional groups of the same type are equally reactive, (2) all groups react independently of one another, and (3) no intramolecular reactions occur in finite species. (Substitution effects violate the second assumption.) Flory and Stockmayer use subtle combinatorial reasoning in their models; with their approach it is very difficult to relax the three simplifying assumptions. This changed when Gordon[8] introduced the cascade theory (the theory of stochastic branching processes) to polymer modeling. Using cascade theory, Gordon and others have modeled many polymer systems that have nonideal behavior; some of these models are exact and some are approximate. These models are generally referred to as "statistical models" or "probability models" to distinguish them from "kinetic models". Two points must be emphasized: First, for a given nonideal polymerization, there may be multiple statistical models based on different levels of structural detail and giving different levels of accuracy. Second, both kinetic and statistical concepts can be used in a model of a nonideal polymerization; in fact, it may be the most efficient way to model.

The simplest case where FSSE may be studied is the copolymerization of an f-functional A monomer with a g-functional B monomer, $A_f + B_g$, where only one of the monomers, say A_f, exhibits a substitution effect. (We assume no intramolecular reactions in the finite species.) This situation can be modeled exactly by using a straightforward statistical model:[1,9] The number of reacted sites on each A monomer is determined by solving simple kinetic equations; for any time or conversion, this gives the proportion of A monomer units with exactly i reacted sites, $0 \leq i \leq f$. These reacted monomer units are randomly combined into polymer molecules or a polymer network; all pairs consisting of one reacted A site and one reacted B site are equally likely to combine (random combination). The structures for this model are illustrated in Figure 1. Using this scheme, polymer parameters (e.g., gel point) can be calculated from probability generating functions[1] or direct recursive analysis.[9] Note that the same analysis can be used if the A monomer reacts ideally and the B monomer reacts with FSSE. However, if both A monomer and B monomer experience FSSE, this analysis becomes inexact: even though we only have a first shell substitution effect the stochastic dependence propagates beyond one shell and the reacted monomers do not combine completely at random in the second stage in Figure 1. The same

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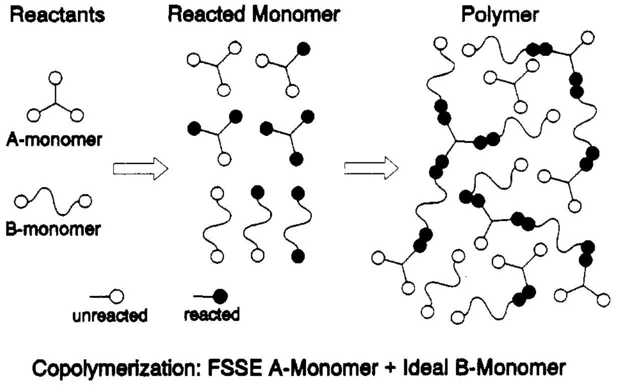

Figure 1. Conceptualization of the copolymerization of a three-functional A monomer with a two-functional B monomer. Bonds form between A groups and B groups. The A groups have a first shell substitution effect (FSSE). The B groups react independently, without any substitution effect. The first conceptual step is the kinetically controlled reaction of functional groups. The second conceptual step is the random combination of reacted groups to form the polymer. Black circles represent reacted groups; white circles represent unreacted groups.

modeling difficulty exists in homopolymerizations with FSSE: a statistical model (we call it the "minimal" model is this paper) based on such logic is inexact.

In kinetic models, a kinetic differential equation is established for the concentration of each possible molecule in the reacting system. An infinite system of equations results. Truncation, transform, or moment methods must be employed to solve these equations. Kuchenov and Povolotskaya[10] use a method of moments; they give a number of interesting examples. Galina and Szustalewicz[2] use a similar approach. Truncation has been used for kinetic equations of systems involving cyclization.[11,12]

It has been known that kinetic models and "ideal statistical models" give differing results for certain nonideal polymerizations. Kuchenov[13,14] reported disagreements for linear polymerizations with substitution effects. For polyfunctional systems, the divergence was predicted by Dušek[15] and then calculated in the case of substitution effect by Mikeš and Dušek[3] and by Kuchenov and Povolotskaya.[10]

It is possible to combine kinetic and statistical concepts in modeling nonideal polymerizations.[16] The idea is to generalize the scheme for FSSE copolymerization shown in Figure 1. The result is a two-stage modeling approach. The first stage captures the nonrandom kinetic aspects of the system. During this step, kinetic differential equations that take the nonideal behavior into account are solved. The result of the first stage is information about the "local" structure of the polymerization. We refer to these local structures as "superspecies". These superspecies are conceptual building blocks devised to give the true final product when they are combined at random. Random combination may involve juxtapositioning or overlapping. The superspecies are analogous to nonrandom subsequences ("blocks") in linear polymer chains.[17] Kuchenov and Dušek call them "fragments".

If the superspecies adequately capture the nonrandomness caused by nonideal kinetics, they can be randomly combined to give an exact model of the polymer product. This random combination will usually be dependent on nearest-neighbor pairs; i.e., the probability of two superspecies joining is a function of their types but not dependent on any additional superspecies with which they may have combined. Hence, we refer to this random combination in the second modeling stage as "Markovian". Models[5-8,17-19] in which the first kinetic step is ideal or trivial may be referred to as pure Markovian models; in Markovian models "elementary" structures are combined at random to give molecules. When each stage is nontrivial, we refer to the two-stage model as a "kinetic–Markovian" model. The statistical analysis of the Markovian structure is based on its "recursive" nature, so we may also refer to these as "kinetic–recursive" models. In most polymerizations the two stages occur simultaneously; separating the analysis into two stages is a modeling convenience. The general scheme is shown in Figure 2.

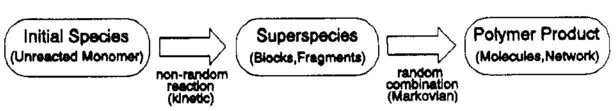

Figure 2. Abstract conceptual scheme for the kinetic–Markovian statistical model of polymerization.

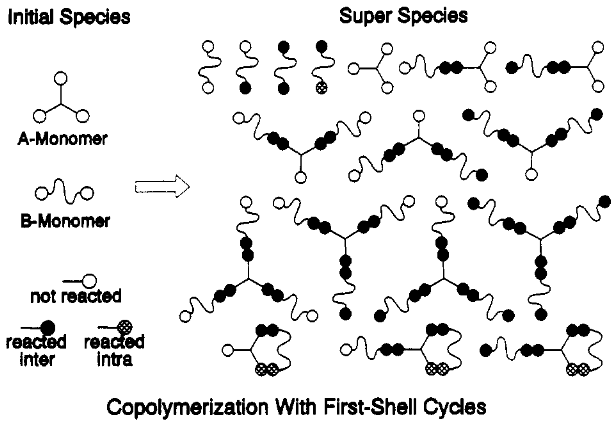

Figure 3. Superspecies for a copolymerization of three-functional A monomers and two-functional B monomers. The copolymerization is ideal except that cycles consisting of one A monomer and one B monomer are allowed to form (first shell cycles). The random combination of superspecies into polymer product is achieved by proper random overlapping of superspecies (instead of random juxtapositioning). White circles represent unreacted groups. Black circles represent groups that have reacted intermolecularly. Shaded circles represent groups that have reacted intramolecularly. See Sarmoria et al.[20]

At least four different general types of superspecies may be appropriate. First, the superspecies may consist of multishell structures around randomly chosen roots. Second, the superspecies may be defined by additional labeling (in addition to "reacted" and "unreacted" labels) of monomer units or local groups of monomer units. Third, there may be a physically meaningful breakdown determined by different chemistries in the two stages. Finally, the polymerization may actually occur in two (or more) separate stages. Sarmoria et al.[20] give an example of the first type for a copolymerization in which only the smallest cycles are allowed to form; the superspecies are all the local structures possible within one shell of an f-functional A monomer; see Figure 3. Dušek[21] expounds on the idea of superspecies on the basis of additional labeling of bonds and reacted sites; this is the main idea for our models of FSSE homopolymerizations presented here. Bokare and Gandhi[22] analyze a polymerization with a side reaction: the side reaction is a chain addition type of reaction and is treated in a kinetic step; the primary reaction is a step polymerization type of reaction and is treated in a random combination (recursive) step. Miller and Macosko[23] and Miller[24] treat some two-stage reactions: the first stage is chain growth by chain addition; the second stage is random cross-linking of chains. Tiemersma et al.[25] analyze multistage step reactions. Sarmoria et al.[20,26] used a kinetic-recursive approach to model linear polymers with cyclization. Dušek and co-workers have used the concept of superspecies (fragments) and their random combination in several papers; they analyze epoxy resins[27-29] and polyurethanes.[30]

In copolymerizations where both comonomers are subject to FSSE or in homopolymerizations with FSSE, a kinetic–Markovian model is needed. We present an exact kinetic–recursive model for stepwise irreversible homopolymerization with FSSE and no cyclization. We show that it gives the same results as kinetic models and Monte Carlo simulations, thus supporting the validity of statistical models, if they are correctly defined. We present several FSSE homopolymerization models based on different levels of structural detail. These models illustrate some effects of modeling detail on model accuracy. The modeling concepts presented here can be used to construct probability models of copolymerization systems with FSSE on both comonomers; the extension is straightforward.

Models for FSSE Homopolymerization

We will illustrate the statistical modeling of FSSE with the homopolymerization of a three-functional monomer, A_3. Similar models can be constructed for monomers with other values of functionality f. Since the rate at which a bond forms is a function of the reactivities of the two reacting sites, the A_3 homopolymerization involves a matrix of kinetic rates:

$$\mathbf{K} = \begin{bmatrix} k_{00} & k_{01} & k_{02} \\ k_{10} & k_{11} & k_{12} \\ k_{20} & k_{21} & k_{22} \end{bmatrix}$$

where k_{ij} is the rate at which a monomeric unit with i reacted sites forms a bond with a monomeric unit with j reacted sites; k_{ij} is equal to k_{ji}. Since the matrix is symmetric, it may be constructed from only six values. In this general problem, these six different kinetic constants do not satisfy any special relationships; they may take any nonnegative values.

The process may be modeled exactly by a combined kinetic–Markovian analysis. Superspecies are defined by labeling each reacted site on a monomeric unit with a pair of integers and a real number $(m,n;\alpha)$. A site labeled (m,n) is the mth one to react on the monomer unit, and its reaction partner is the nth one to react on the monomer to which it belongs; $m = 1, 2, 3$, and $n = 1, 2, 3$. We will say that the reacting sites have "ranks" m and n. The label α refers to the conversion at which the site reacted.

We call this model the "maximal" model, since it contains the maximum relevant detail. The set of superspecies at complete reaction may be indicated as

$$\mathcal{S}_{\max} = \{[(1,i;\beta),(2,j;\gamma),(3,k;\delta)] | i,j,k = 1,2,3; 0 \le \beta \le \gamma \le \delta \le 1\}$$

A $[(1,i;\beta),(2,j;\gamma),(3,k;\delta)]$ structure is an A unit where the first site reacted at conversion β with a site of rank i, the second site reacted at conversion γ with a site of rank j, and the third site reacted at conversion δ with a site of rank k. If the reaction has proceeded to an incomplete conversion equal to α, some of the superspecies at this conversion will have unreacted functional sites, which we label as #.

The superspecies are quite complicated. Because they contain all the information relevant to the bonding process, they may be combined at random. A bond forming at conversion α is the combination of an $(m,n;\alpha)$ site with an $(n,m;\alpha)$ site; all pairs of sites with these labels are equally likely to combine in the random combination step. The resulting structure does not have long-range interactions; it is a Markovian branching structure. One possible structure is shown in Figure 4.

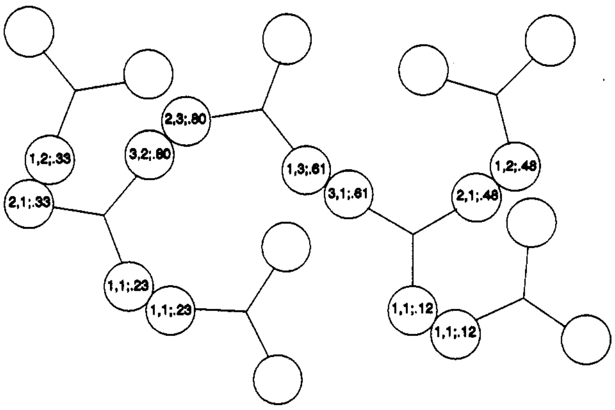

Figure 4. Possible structure generated from the superspecies of the maximal kinetic–Markovian model, $\mathcal{S}_{\max}$. Sites are labeled $(m,n;\alpha)$: m, the rank of the site; n, the rank of the site with which it reacts; α, the conversion value at which the bond formed.

The reason so many labels are needed on each site may not be obvious. Would it not be possible to use only conversion or only the ranks? We can answer that question by giving some examples. Suppose we construct superspecies by labeling sites only with the conversion at which they reacted. We refer to this as the "conversion" model. The set of superspecies at complete reaction for the conversion model of FSSE homopolymerization is

$$\mathcal{S}_{\alpha} = \{(\beta,\gamma,\delta) | 0 \le \beta \le \gamma \le \delta \le 1\}$$

For example, a (β,γ,δ) superspecies is an A_3 monomer whose sites reacted at conversions β, γ, and δ; and a $(\beta,\#,\#)$ superspecies is an A_3 monomer with exactly one reacted site, which reacted at conversion β. If the conversion model is a valid model, it should give correct answers for systems described by any admissible kinetic rate matrix. For example, consider the matrix

$$\mathbf{K} = \begin{bmatrix} 2 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 0 \end{bmatrix}$$

This means that two doubly reacted units may not react among themselves, although they may react with singly reacted units and with monomer (this is a system that may not achieve complete reaction). In the rank terminology, (3,3) bonds are not possible. This restriction will be respected in the kinetic step, when sites on superspecies are labeled, but it will be violated in the second step, when superspecies are combined at random by like labels. A structure such as the one in Figure 5 could be generated, where one of the bonds is a (3,3) bond. Since it generates impossible structures, this simpler conversion model is not exact.

We note that the maximal model and the conversion model both have an infinite number of possible superspecies because they are labeled with conversion, which is a continuous variable. In practice, any system consists of a huge, but finite, number of reacting monomers; thus, we will see only a finite number of superspecies, one for each monomer. If conversion is measured to infinite precision (and the reacting sites are so labeled), there will be a finite number of conversion values at which bonds form and exactly one bond forming at each such conversion value (and exactly two sites labeled with that conversion value). Thus, the conversion model is an exact model for the FSSE homopolymerization of a *finite* number of monomers. The implementation in this case would differ

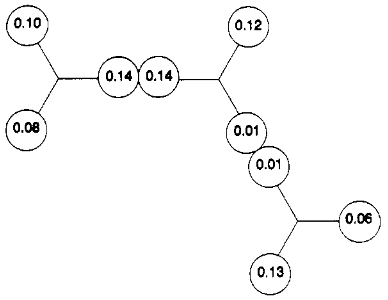

Figure 5. Physically impossible structure generated with superspecies from the conversion model ($\mathcal{S}_\alpha$) for a FSSE homopolymerization system with k_{22} equal to zero. Two doubly reacted monomers cannot react with each other, but they can react with monomers with zero or one reacted site. The sites are labeled with the conversion at which they reacted. Note that the bond forming at conversion 0.14 cannot be present in the real system, because the reacting sites are the third ones to react on each monomer. This example shows the conversion model to be inexact for *general* FSSE homopolymerizations.

from our kinetic–Markovian approach; the random nature of the polymerization must be captured in the kinetic step. This could be done with a Monte Carlo simulation based on a large but finite number of monomers; one realization of the Monte Carlo kinetic step will give all the superspecies formed, each reacted site labeled with conversion. The step of combining superspecies into molecules is then completely deterministic. This implementation based on a finite number of monomers is mathematically equivalent to a Monte Carlo model and will have the usual Monte Carlo sampling errors.

The usual kinetic–Markovian approach assumes an *infinite* number of monomers. Furthermore, it implicitly assumes that an infinite number of reactions occur at each instant of time. Thus, in the random combination step of the analysis there are infinite numbers of sites with compatible labelings. In this case the accuracy of the random combination step is crucial. The above counterexample reveals that the conversion model for FSSE homopolymerizations of an *infinite* number of monomers is not exact.

Solving the maximal and conversion models for FSSE homopolymerization of infinite systems of momomers requires resorting to numerical methods. The conversion labels must be discretized into a finite set of values of order to use numerical methods. This discretization is an example of aggregation of structural detail, which can destroy the precision of models. (See Appendix 5 for an illustration of this.) If the discretization is fine enough, only small numerical errors will be introduced.

If we only use rank labels, we have a "rank" model. The set of superspecies at complete conversion is

$$\mathcal{S}_{\text{rank}} = \{[(1,i),(2,j),(3,k)] | i,j,k = 1,2,3\}$$

This rank model is also incorrect. It is not even exact for ideal homopolymerizations; see Appendix 4 for details. Miller and Macosko[16] erroneously proposed this rank model as exact.

A model of FSSE homopolymerization with the minimal amount of structural detail has superspecies consisting of monomers labeled by the number of reacted sites. Let A_i denote a monomer with exactly i reacted sites, $i = 0, 1, 2, 3$. The minimal model has superspecies

$$\mathcal{S}_{\min} = \{A_0, A_1, A_2, A_3\}$$

Galina and Szustalewicz[2] and Mikeš and Dušek[3] use this minimal model as the probability model of FSSE homopolymerization; they compare calculations from this model to a kinetic model[2] and to a Monte Carlo simulation model,[3] respectively. Durand and Bruneau[4] also present this minimal model as the branching process probability model of FSSE homopolymerization.

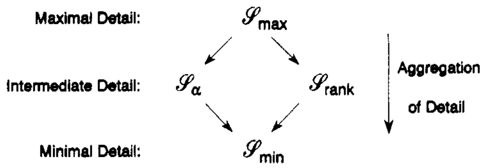

Figure 6. Relationship between the sets of superspecies for four models of homopolymerization with FSSE: maximal, conversion, rank, and minimal models.

So, there are several possible kinetic–recursive models for homopolymerization with a *general* FSSE and no cyclization. These models are based on different levels of aggregation of nonrandom structural detail. This aggregation can introduce approximations or errors into the analysis. The situation can be summarized by considering the relationships between the sets of superspecies of the different models; see Figure 6. In this family of models there is a trade-off between achieving enough structural detail for accuracy and having a small enough amount of detail to achieve mathematical tractability. The maximal model is the only exact model for *general* FSSE homopolymerization with no cyclization.

Model for the FSSE System with Multiplicative Kinetic Rates

One common assumption when treating FSSE is additivity of the activation energies.[1] In this special case, the kinetic constants take the form

$$k_{ij} = k_i k_j$$

This means that the kinetic matrix $\mathbf{K}$ is a function of only 3 values: k_0, k_1, and k_2. For this special case the conversion model is exact. There is no need to use the maximal model; the extract structural detail of the maximal model is not required for *multiplicative* FSSE. The proof that the conversion model is exact for *multiplicative* FSSE homopolymerization with no cyclization is given in Appendix 1.

The set of superspecies for the conversion model at complete conversion is

$$\mathcal{S}_\alpha = \{(\beta,\gamma,\delta) | 0 \le \beta \le \gamma \le \delta \le 1\}$$

(β,γ,δ) is an A unit where the first site reacted at conversion β, the second at conversion γ, and the third at conversion δ. There are infinite possible structures of the form (β,γ,δ).

In order to get a finite number of structures, we discretize conversion into N intervals. That is, given a maximum conversion of interest $\hat{\alpha}$ we divide the interval $[0,\hat{\alpha}]$ into N subintervals, such that the ith subinterval is $(\hat{\alpha}(i-1)/N, \hat{\alpha}i/N]$, or, using a different notation, the ith interval is $(\alpha_{i-1}, \alpha_i]$, $\alpha_i = \hat{\alpha}i/N$. Because of this discretization the model becomes approximate, but its precision may be increased as much as desired just by increasing the number of intervals. The set of superspecies at conversion $\hat{\alpha}$ is now

$$\mathcal{S}_N = \{(i,j,k) | 1 \le i \le j \le k \le N\}$$

where (i,j,k) is an A unit where the first site reacted during interval i, the second site reacted during interval j, and the third site reacted during interval k. Unreacted sites are represented by the symbol #. When reconstructing molecules we will assume that all sites marked as having reacted in interval i are equally likely to have reacted among themselves.

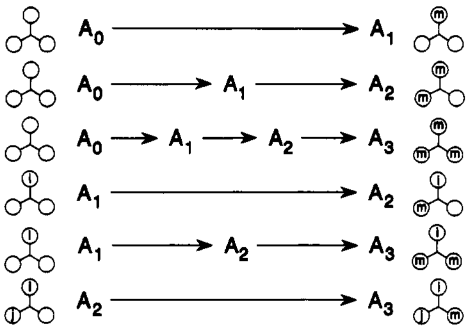

Figure 7. Possible transitions describing changes in superspecies for the minimal model during the mth interval of conversion, $\alpha_{m-1} < \alpha \leq \alpha_m$. Reacted sites are labeled with the interval number in which they reacted; $i, j < m$.

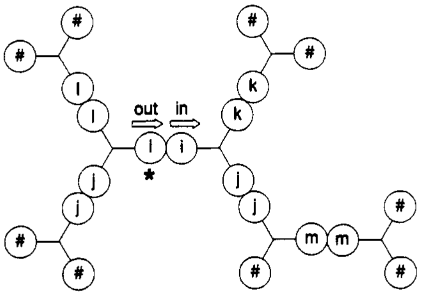

Figure 8. Example of a molecular structure of the discretized conversion model ($\mathcal{S}_N$) at conversion α_N (at the end of interval N). Reacted sites are labeled with the interval number in which they reacted; $i, j, k, l, m \leq N$. Unreacted sites are labeled with #. A randomly chosen site is indicated with *. The recursive computation of weight-average molecular weight is based on the expected weight seen looking out of a randomly chosen site and the expected weight seen looking into the site with which it reacts; these directions are shown by arrows.

In this paper we present the mathematical details of this model of *multiplicative* FSSE homopolymerization with no cyclization. The model is based on the $\mathcal{S}_N$ set of superspecies.

Let $s_N(i,j,k)$ equal the number fraction of (i,j,k) structures at conversion $\hat{\alpha}$. This will be a triangular $N \times N \times N$ array (with $(N^3 + 3N^2 + 2N)/6$ elements because $i \leq j \leq k$). These number fractions must be calculated in the first step of the kinetic–Markovian analysis for the *multiplicative* FSSE homopolymerization with no cyclization.

Evaluation of Superspecies at Conversion $\hat{\alpha}$. The evaluation of $s_N(i,j,k)$ is the kinetic step of the analysis. The first step in the calculation of these number fractions is to consider the number fractions of species in the minimal model: A_0, A_1, A_2, and A_3. Let $A_i(\alpha)$ denote an A unit with exactly i sites reacted at conversion α. Let $a_i(\alpha)$ equal the number fraction of A units that are A_i at conversion α. Calculation of $(a_0(\alpha),a_1(\alpha),a_2(\alpha),a_3(\alpha))$ for any given α is described in Appendix 2. During the mth interval $(\alpha_{m-1}, \alpha_m]$, one, two, or all three sites on an A unit may react. The possible transitions are indicated in Figure 7. Let $a_{ij}(\alpha_{m-1}, \alpha_m)$ equal the number fraction of A units that changed from A_i to A_j during the mth interval, i.e., structures that had i reacted sites at conversion α_{m-1} and have j reacted sites at conversion α_m. The calculation of the number fractions $a_{ij}(\alpha_{m-1}, \alpha_m)$, $0 \leq i \leq j \leq 3$, $m = 1, 2, ..., N$, is described in Appendix 3. From these number fractions we can calculate the number fractions of superspecies in the set $\mathcal{S}_N$.

We now compute the number fractions of the superspecies. Let $s_m(\cdot,\cdot,\cdot)$ denote the number fraction of particular superspecies existing at the end of the mth conversion interval. If we let # denote an unreacted site, the initial condition of the problem is

$$s_0(\#,\#,\#) = 1$$

For $m = 1, 2, ..., N$, once we reach the end of interval m at conversion α_m we label all sites reacted during this interval with the integer m.

$$s_m(m,\#,\#) = a_{01}(\alpha_{m-1}, \alpha_m)$$

$$s_m(m,m,\#) = a_{02}(\alpha_{m-1}, \alpha_m)$$

$$s_m(m,m,m) = a_{03}(\alpha_{m-1}, \alpha_m)$$

$$s_m(j,m,\#) = s_{m-1}(j,\#,\#)a_{12}(\alpha_{m-1}, \alpha_m)/a_1(\alpha_{m-1}) \qquad 1 \leq j \leq m-1$$

$$s_m(j,m,m) = s_{m-1}(j,\#,\#)a_{13}(\alpha_{m-1}, \alpha_m)/a_1(\alpha_{m-1}) \qquad 1 \leq j \leq m-1$$

$$s_m(j,k,m) = s_{m-1}(j,k,\#)a_{23}(\alpha_{m-1}, \alpha_m)/a_2(\alpha_{m-1}) \qquad 1 \leq j \leq k \leq m-1$$

Next, the arrays for structures that just reacted are updated

$$s_m(\#,\#,\#) = s_{m-1}(\#,\#,\#) - s_m(m,\#,\#) - s_m(m,m,\#) - s_m(m,m,m)$$

$$s_m(j,\#,\#) = s_{m-1}(j,\#,\#) - s_m(j,m,\#) - s_m(j,m,m) \qquad 1 \leq j \leq m-1$$

$$s_m(j,k,\#) = s_{m-1}(j,k,\#) - s_m(j,k,m) \qquad 1 \leq j \leq k \leq m-1$$

This procedure is iterated for all intervals, $m = 1, ..., N$.

This concludes the kinetic step of the model. In the recursive random combination step, the set $\mathcal{S}_N$ of $S_N(i,j,k)$ structures is used to build back molecules at conversion $\hat{\alpha} = \alpha_N$. For the purposes of this paper we only analyze the pregel stage, since Galina and Szustalewicz[2] and Mikeš and Dušek[3] only did as much for the comparison of models. (Mikeš and Dušek[3] also study the gel fraction with their Monte Carlo model.)

Evaluation of the Weight-Average Molecular Weight. In order to find the molecular weight at conversion $\hat{\alpha}$, we divide the interval $[0,\hat{\alpha}]$ into N subintervals and find the number fractions $s_N(i,j,k)$ as described in the previous section. The superspecies are joined at random by like labels. A sketch of such a labeled molecule is shown in Figure 8.

An "in–out" recursion[9,18] may be established to find the weight-average molecular weight, $\bar{M}_w$. We pick a site at random, denoted as * in Figure 8. This site happened to have reacted in the ith interval and is therefore labeled with an i. We ask what is the weight attached to this site looking out from the monomer unit to which it belongs (direction out in Figure 8)? We call this variable W_i^{out}. W_i^{out} is a random variable, since the site was picked at random. We find that

$$W_i^{\text{out}} = W_i^{\text{in}} \tag{1}$$

where W_i^{in}, the weight looking into a bond that formed during interval i (direction in in Figure 8), is

$$\begin{aligned} W_i^{\text{in}} &= M_{A_3} && \text{with probability } P_N(\#,\#|i) \\ &= M_{A_3} + W_j^{\text{out}} && \text{with probability } P_N(j,\#|i) \\ &= M_{A_3} + W_j^{\text{out}} + W_k^{\text{out}} && \text{with probability } P_N(j,k|i) \end{aligned} \tag{2}$$

$i, j, k, = 1, 2, ..., N$, where $P_N(j,k|i)$ is the probability that, conditional on a randomly chosen site reacting during interval i, the site is on an A unit whose other sites reacted during intervals j and k; the two additional sites are observed in random order; the first one observed is j, the second k. So, $P_N(j,k|i)$ is equal to $P_N(k,j|i)$, since no order is assumed in looking at the remaining arms once i is picked. Similarly, $P_N(j,\#|i)$ and $P_N(\#,j|i)$ are the probabilities that a randomly chosen site that reacted during interval i is on an A unit with one unreacted site and a site reacted during interval j, and $P_N(\#,\#|i)$ is the probability that a randomly chosen site that reacted during interval i is on an A unit whose other two sites are unreacted. $P_N(j,k|i)$, $P_N(j,\#|i)$, $P_N(\#,k|i)$, and $P_N(\#,\#|i)$ are functions of the number fraction s_N of the $\mathcal{S}_N$ superspecies. If the randomly chosen site is unreacted the equations are

$$W_\#^{\text{out}} = 0 \tag{3}$$

$$\begin{aligned} W_\#^{\text{in}} &= M_{\text{A}_3} \quad \text{with probability } P_N(\#,\#|\#) \\ &= M_{\text{A}_3} + W_j^{\text{out}} \quad \text{with probability } P_N(j,\#|\#) \\ &= M_{\text{A}_3} + W_j^{\text{out}} + W_k^{\text{out}} \quad \text{with probability } P_N(j,k|\#) \end{aligned} \tag{4}$$

Taking the expectations of eqs 1–4, we get, for $1 \le i \le N$

$$EW_i^{\text{out}} = EW_i^{\text{in}} \tag{5}$$

$$EW_i^{\text{in}} = M_{\text{A}_3} + \sum_{j=1}^{N}(EW_j^{\text{out}})P_N(j,\#|i) + \sum_{k=1}^{N}(EW_k^{\text{out}}) \times P_N(\#,k|i) + \sum_{j=1}^{N}\sum_{k=1}^{N}(EW_j^{\text{out}} + EW_k^{\text{out}})P_N(j,k|i) \tag{6}$$

$$EW_\#^{\text{out}} = 0 \tag{7}$$

$$EW_\#^{\text{in}} = M_{\text{A}_3} + \sum_{j=1}^{N}(EW_j^{\text{out}})P_N(j,\#|\#) + \sum_{k=1}^{N}(EW_k^{\text{out}}) \times P_N(\#,k|\#) + \sum_{j=1}^{N}\sum_{k=1}^{N}(EW_j^{\text{out}} + EW_k^{\text{out}})P_N(j,k|\#) \tag{8}$$

Working with eq 6 we find

$$\begin{aligned} EW_i^{\text{in}} = M_{\text{A}_3} &+ \sum_{j=1}^{N}EW_j^{\text{out}}P_N(j,\#|i) + \sum_{k=1}^{N}(EW_k^{\text{out}}) \times P_N(\#,k|i) + \sum_{j=1}^{N}EW_j^{\text{out}}\sum_{k=1}^{N}P_N(j,k|i) + \sum_{k=1}^{N}EW_k^{\text{out}} \times \sum_{j=1}^{N}P_N(j,k|i) \\ = M_{\text{A}_3} &+ \sum_{j=1}^{N}EW_j^{\text{out}}\{P_N(j,\#|i) + P_N(\#,j|i)\} + \sum_{j=1}^{N}EW_j^{\text{out}}\{\sum_{k=1}^{N}P_N(j,k|i) + \sum_{k=1}^{N}P_N(k,j|i)\} \end{aligned}$$

If we replace the label # with the label $N + 1$, we get

$$EW_i^{\text{in}} = M_{\text{A}_3} + \sum_{j=1}^{N}EW_j^{\text{out}}\{\sum_{k=1}^{N+1}P_N(j,k|i) + \sum_{k=1}^{N+1}P_N(k,j|i)\} \tag{9}$$

for $1 \le i \le N + 1$. Letting

$$P_N(j|i) = \frac{1}{2}\{\sum_{m=1}^{N+1}P_N(j,m|i) + \sum_{m=1}^{N+1}P_N(m,j|i)\} = \sum_{m=1}^{N+1}P_N(j,m|i) \tag{10}$$

we get

$$EW_i^{\text{in}} = M_{\text{A}_3} + 2\sum_{j=1}^{N}EW_j^{\text{out}}P_N(j|i) \qquad 1 \le i \le N + 1 \tag{11}$$

where $P_N(j|i)$ is the probability, given we pick an A unit by selecting an i site at random, and then we randomly pick one of the remaining sites on the A unit and look at its label (in this context, # is also a label) and we see a j site. $P_N(j|i)$ is calculated from the number fractions $s_N(i,j,k)$. Let $Q_1(i)$ equal the expected number of i sites on a randomly chosen A unit; $i = 1, 2, 3, ..., N, N + 1$. Let $Q_2(i,j)$ equal the expected number of ordered (i,j) pairs of sites on a randomly chosen A unit; $i = 1, 2, 3, ..., N, N + 1$; $j = 1, 2, 3, ..., N, N + 1$. An (i,j,k) unit has three sites: one i site, one j site, and one k site. Recall that the definition of the superspecies $S_N(i,j,k)$ assumes that $i \le j \le k \le N + 1$, where the label $N + 1$ corresponds to an unreacted site; let the number fractions $s_N(i,j,k)$ equal 0 if the relationship $i \le j \le k \le N + 1$ is violated. Then

$$Q_1(i) = \sum_{m=1}^{N+1}\sum_{n=1}^{N+1}[s_N(i,m,n) + s_N(m,i,n) + s_N(m,n,i)] \tag{12}$$

$$Q_2(i,j) = \sum_{m=1}^{N+1}[s_N(i,j,m) + s_N(j,i,m) + s_N(i,m,j) + s_N(j,m,i) + s_N(m,i,j) + s_N(m,j,i)] \tag{13}$$

There are three equally likely ways to choose a site randomly from one of these superspecies, and there are six equally likely ways to choose a first site and then a second site from one of these superspecies. Therefore

$$P(\text{first random site is } i) = Q_1(i)/3 \tag{14}$$

$$P(\text{first random site is } i\text{, second random site is } j) = Q_2(i,j)/6 \tag{15}$$

By definition of conditional probability we have

$$P(j|i) = \frac{P(\text{first random site is } i\text{, second random site is } j)}{P(\text{first random site is } i)} = \frac{1}{2}\frac{Q_2(i,j)}{Q_1(i)} \tag{16}$$

Combining eqs 5, 7, and 11 we find

$$\begin{bmatrix} EW_1^{\text{out}} \\ EW_2^{\text{out}} \\ \vdots \\ EW_N^{\text{out}} \end{bmatrix} = \begin{bmatrix} M_{\text{A}_3} \\ M_{\text{A}_3} \\ \vdots \\ M_{\text{A}_3} \end{bmatrix} + \begin{bmatrix} 2\sum_{j=1}^{N}EW_j^{\text{out}}P_N(j|1) \\ 2\sum_{j=1}^{N}EW_j^{\text{out}}P_N(j|2) \\ \vdots \\ 2\sum_{j=1}^{N}EW_j^{\text{out}}P_N(j|N) \end{bmatrix} \tag{17}$$

After solving the algebraic system (17), we use the values of EW_i^{out} to find the weight-average molecular weight. An A monomer unit is chosen randomly from the polymerization and the expected weight of the molecule to which it belongs is computed. This expected weight is the sum of the molecular mass of the monomer plus the expected molecular weight attached to each of the three A sites on the monomer.

$$\bar{M}_{\text{w}} = M_{\text{A}_3} + \sum_{i=1}^{N}\sum_{j=i}^{N}\sum_{k=j}^{N}(EW_i^{\text{out}} + EW_j^{\text{out}} + EW_k^{\text{out}})s_N(i,j,k) \tag{18}$$

This is the weight-average molecular weight at the target conversion $\hat{\alpha}$ (i.e., at the end of interval N).

Evaluation of the Gel Point. When $\bar{M}_w$ diverges, we are at the gel point. One way of finding the gel point, then, is to repeat the procedure outlined in the previous section for different values of $\hat{\alpha}$. That is, for each selected value of $\hat{\alpha}$ we divide the interval $[0, \hat{\alpha}]$ into N subintervals, find the values of the EW_i^{out}, $i = 1, 2, ..., N$, from eq 17, and evaluate $\bar{M}_w$ from eq 18. While the target values of $\hat{\alpha}$ are smaller than the gel point, the values of $\bar{M}_w$ are finite and positive. If during this process one of the chosen values of $\hat{\alpha}$ is exactly the gel point ($\hat{\alpha} = \alpha_c$), the EW_i^{out} diverge and therefore $\bar{M}_w$ diverges. If the target conversion $\hat{\alpha}$ is beyond the gel point we get meaningless results, namely, negative values for both EW_i^{out} and $\bar{M}_w$. Knowing the functional behavior of $\bar{M}_w$ for values of $\hat{\alpha}$ before, at, and beyond the gel point, it is possible to set up a search algorithm (such as bisection) that will give the gel point to any desired precision.

The procedure just described is computationally expensive, since for each new value of $\hat{\alpha}$ the process of subdividing the interval $[0, \hat{\alpha}]$ and evaluating EW_i^{out} has to be done again, even for small changes in $\hat{\alpha}$. A more efficient procedure involves choosing a conversion $\tilde{\alpha}$ known to be beyond the gel point. The interval $[0, \hat{\alpha}]$ is subdivided into M subintervals, such that the ith one is defined as $(\tilde{\alpha}(i-1)/M, \tilde{\alpha}i/M]$. The molecular weight is evaluated at the end points of all subintervals, that is, at conversions $\tilde{\alpha}j/M$ ($j = 1, 2, ..., M$). At one particular interval, say interval m, the molecular weight will go from a large positive value at the beginning to a negative value at the end, indicating the gel point is within the mth interval so that

$$\tilde{\alpha}(m-1)/M < \alpha_c < \tilde{\alpha}m/M$$

The gel point α_c may be found to any desired precision by picking a large enough value of M. We used this more efficient method for our numerical computations.

Numerical Results. We have used the model described above to calculate molecular weights and gel points. We used the kinetic constants k_0, k_1, and k_2 that Galina and Szustalewicz[2] used in their Table III. We show our results in Table I. For comparison we have included the values reported by Galina and Szustalewicz.[2] The probability model that was used in their comparison is the simple minimal model, whose set of superspecies is

$$\mathcal{S}_{\min} = \{A_0, A_1, A_2, A_3\}$$

where the superspecies A_i is an A unit with exactly i reacted sites. We discussed details of this approximate model earlier in this paper. The minimal model consistently overestimates the gel point. We have used this gel point prediction as the conservative conversion $\tilde{\alpha}$ described in the previous section. In all cases we divided $[0,\tilde{\alpha}]$ into 200 subintervals. Results are reported with three significant digits in Table I.

We see that our gel point prediction agrees with the reported kinetic one within the accuracy of the numerical solution. This shows that an appropriately built probability model can take nonidealities into account, and so kinetic models or simulations are not the only choice for nonideal polymerizations.

Table I
Comparison of Gel Point Predictions[a]

kinetic rates			gel points for different models		
k_1	k_2	k_3	$\mathcal{S}_N$	kinetic	$\mathcal{S}_{\min}$
1.00	100.00	100.00	0.0145–0.0146	0.01458	0.01546
1.00	100.00	10.00	0.0352–0.0354	0.03627	0.04088
1.00	100.00	1.00	0.0780–0.0785	0.07809	0.1069
1.00	100.00	0.10	0.157–0.158	0.1571	0.2534
1.00	100.00	0.01	0.286–0.288	0.2866	0.4593
1.00	10.00	100.00	0.0611–0.0614	0.06074	0.06226
1.00	10.00	10.00	0.127–0.127	0.1272	0.1324
1.00	10.00	1.00	0.262–0.263	0.2628	0.2836
1.00	10.00	0.10	0.434–0.437	0.4351	0.4771
1.00	10.00	0.01	0.574–0.577	0.5748	0.6089
1.00	1.00	100.00	0.280–0.281	0.2802	0.2836
1.00	1.00	10.00	0.346–0.347	0.3451	0.3467
1.00	1.00	1.00	0.498–0.501	0.5000	0.5000
1.00	1.00	0.10	0.617–0.620	0.6171	0.6171
1.00	1.00	0.01	0.657–0.660	0.6569	0.6569
1.00	0.10	1.00	0.441–0.444	0.4433	0.4979
1.00	0.10	10.00	0.453–0.455	0.4538	0.5006
1.00	0.10	1.00	0.489–0.491	0.4902	0.5217
1.00	0.10	0.10	0.560–0.563	0.5619	0.5772
1.00	0.10	0.01	0.630–0.634	0.6302	0.6331
1.00	0.50	0.25	0.582–0.585	0.5835	0.5866
1.00	2.00	0.50	0.498–0.501	0.5002	0.5038

[a] Gel point predictions for several FSSE homopolymerizations of three-functional monomers; these systems have multiplicative kinetic rates. Three different models are used to make predictions: the discretized conversion statistical model, $\mathcal{S}_N$, of this paper; the kinetic model of Galina and Szustalewicz;[2] and the minimal statistical model, $\mathcal{S}_{\min}$. The minimal model is considered by Galina and Szustalewicz,[2] Mikès and Dušek,[3] and Durand and Bruneau[4] to be *the* statistical model of FSSE homopolymerizations. The conversions for the kinetic model and the minimal model are those given by Galina and Szustalewicz.[2] For our discrete conversion model, $\mathcal{S}_N$, the intervals in which gelation occurred are reported.

Conclusions

In this work we have shown that in principle it is possible to construct an exact probability model for a nonideal irreversible polymerization with no cyclization. This may always be achieved by sufficiently detailed labeling of superspecies. We have also shown that aggregating the detailed superspecies will cause the model to become approximate, except in special cases. A family of models is given based on different sets of superspecies: $\mathcal{S}_{\max}$, $\mathcal{S}_{\alpha}$, $\mathcal{S}_N$, $\mathcal{S}_{\text{rank}}$, and $\mathcal{S}_{\min}$. There are various aggregation relationships among the superspecies of these probability models considered. Aggregation of the superspecies in the maximal model gives either the rank or conversion models, and further aggregation of these gives the minimal model; aggregation of the conversion model via discretization gives a model based on discrete time intervals. We have shown that the maximal model is exact for any general FSSE, the rank model is never exact, the conversion model is exact when the kinetic constants factor, the discretized model is an approximation to the conversion model that requires a large number of intervals to achieve good precision, and the minimum model is exact only for the ideal case ($k_0 = k_1 = k_2 = 1$). It is not possible to know a priori for which cases, if any, an aggregated model will be exact. Therefore, aggregated models should be considered approximate until proven otherwise.

The exact probability model is not necessarily the best choice for every system. For example we see from Table I that, although the minimal probability model is only approximate, from the practical point of view the approximation seems to be good in most cases. Gel points may be measured with an accuracy of 5% or so, and the error of the approximate model is less than that in 17 of the 22 cases in Table I. The cases where the error is significant are those where the kinetic constants differ widely and are not in increasing or decreasing order; the rate of formation of doubly reacted units (k_1) is high while the rate of formation of branching points (k_2) is low or vice versa. If the substitution effect is due only to chemical reasons, such constants are unlikely in polymerization systems. So for many practical applications the approximate minimal model might be all that is needed.

For complex situations where the minimal model is not an acceptable approximation, there is no clear-but "best" model; some of the possible exact treatments may be intractible or impractical. The point in this paper has been to show that probability models, if correctly formulated, are one of the options to be considered.

Appendix 1: Proof of Exactness for Multiplicative Rates

For the special case of homopolymerization of the f functional monomer A_f with a first shell substitution effect and multiplicative kinetic rate constants

$$k_{ij} = k_i k_j \tag{A1}$$

we want to show that it is not necessary to use the general ("maximal") model with both rank and conversion labels on the superspecies. For this particular case the model with just conversion labels is exact, the so-called conversion model based on the set $\mathcal{S}_\alpha$ of superspecies. In other words, we want to prove that when the kinetic rate constants factor any site with a given conversion label, say α, is equally likely to have reacted with any other site labeled α. Mathematically this proposition may be expressed as

$$P((i,j)|\alpha) = P(i|\alpha)P(j|\alpha) \tag{A2}$$

where $P((i,j)|\alpha)$ is the probability that a randomly chosen bond that formed at conversion α is an (i,j) bond and $P(i|\alpha)$ is the probability that a randomly chosen site on a randomly chosen bond formed at conversion α has rank "i". An (i,j) bond is a bond where one site has rank i and the other has rank "j". Let

$r(i,j;\alpha)$ = rate of (i,j) bond formation at conversion α =

$$(f-i+1)(f-j+1)k_{i-1,j-1}a_{i-1}(\alpha)a_{j-1}(\alpha) \tag{A3}$$

$r_1(i;\alpha)$ = rate of $(i,*)$ bond formation at conversion α =

$$\sum_{j=1}^{f} r(i,j;\alpha) \tag{A4}$$

$r_2(j;\alpha)$ = rate of $(*,j)$ bond formation at conversion α =

$$\sum_{i=1}^{f} r(i,j;\alpha) \tag{A5}$$

$r(\alpha)$ = rate of bond formation at conversion α =

$$\sum_{i=1}^{f}\sum_{j=1}^{f} r(i,j;\alpha) \tag{A6}$$

$i = 1, 2, ..., f$, $j = 1, 2, ..., f$, where $a_i(\alpha)$ equals the number fraction of A_i superstructures at conversion α (A_i is an A unit with exactly i reacted sites). From eqs A4 and A5 it follows that

$$r_1(i;\alpha) = r_2(i;\alpha) = r(i;\alpha) \tag{A7}$$

The conditional probabilities of (i,j) bonds forming and i sites and j sites occurring at conversion α are

$$P(i,j|\alpha) = r(i,j;\alpha)/r(\alpha) \tag{A8}$$

$$P(i|\alpha) = r(i;\alpha)/r(\alpha) \tag{A9}$$

$$P(j|\alpha) = r(j;\alpha)/r(\alpha) \tag{A10}$$

If the rates factor, as in eq A1, then

$$r(i,j;\alpha) = (f-i+1)k_{i-1}a_{i-1}(\alpha)(f-j+1)k_{j-1}a_{j-1}(\alpha) \tag{A11}$$

Substituting (A11) in (A5) and (A6) we find

$$r(i;\alpha) = (f-i+1)k_{i-1}a_{i-1}(\alpha)\sum_{j=1}^{f}(f-j+1)k_{j-1}a_{j-1}(\alpha) \tag{A12}$$

$$r(j;\alpha) = (f-j+1)k_{j-1}a_{j-1}(\alpha)\sum_{i=1}^{f}(f-i+1)k_{i-1}a_{i-1}(\alpha) \tag{A13}$$

$$r(\alpha) = \sum_{i=1}^{f}(f-i+1)k_{i-1}a_{i-1}(\alpha)\sum_{j=1}^{f}(f-j+1)k_{j-1}a_{j-1}(\alpha) \tag{A14}$$

Therefore

$$P(i,j|\alpha) = \frac{(f-i+1)k_{i-1}a_{i-1}(\alpha)(f-j+1)k_{j-1}a_{j-1}(\alpha)}{\sum_{i=1}^{f}(f-i+1)k_{i-1}a_{i-1}(\alpha)\sum_{j=1}^{f}(f-j+1)k_{j-1}a_{j-1}(\alpha)} \tag{A15}$$

$$P(i|\alpha) = \frac{(f-i+1)k_{i-1}a_{i-1}(\alpha)}{\sum_{i=1}^{f}(f-i+1)k_{i-1}a_{i-1}(\alpha)} \tag{A16}$$

$$P(j|\alpha) = \frac{(f-j+1)k_{j-1}a_{j-1}(\alpha)}{\sum_{j=1}^{f}(f-j+1)k_{j-1}a_{j-1}(\alpha)} \tag{A17}$$

Equation A2 is now verified from eqs A15, A16, and A17. This completes the proof. Thus, in the special case of A_f homopolymerization with FSSE and multiplicative kinetic rate constants, the model with conversion labels only is exact.

Appendix 2: Number Fractions of Structures for the Minimal Model

We consider the minimal model. This model has superspecies

$$\mathcal{S}_{\min} = \{A_0, A_1, A_2, A_3\}$$

where A_i is an A unit that has exactly i reacted sites. The number fraction of A_i superspecies at conversion α is denoted $a_i(\alpha)$ and at time t is denoted $a_i(t)$. The aggregated superspecies A_i react with one another; the kinetic equations that describe this are

$$\mathrm{d}a_0/\mathrm{d}t = -3k_0a_0[3k_0a_0 + 2k_1a_1 + k_2a_2] \tag{A18}$$

$$\mathrm{d}a_1/\mathrm{d}t = 3k_0a_0[3k_0a_0 + 2k_1a_1 + k_2a_2] - 2k_1a_1[3k_0a_0 + 2k_1a_1 + k_2a_2] \tag{A19}$$

$$\mathrm{d}a_2/\mathrm{d}t = 2k_1a_1[3k_0a_0 + 2k_1a_1 + k_2a_2] - k_2a_2[3k_0a_0 + 2k_1a_1 + k_2a_2] \tag{A20}$$

$$\mathrm{d}a_3/\mathrm{d}t = k_2a_2[3k_0a_0 + 2k_1a_1 + k_2a_2] \tag{A21}$$

These equations may be solved numerically as functions of time. We may also solve for a_1, a_2, and a_3 analytically in terms of a_0; see Mikeš and Dušek.[3] This analytic solution is

$$a_1 = \frac{1}{1-r_1}\{a_0^{r_1} - a_0\}; \quad r_1 \neq 1 \tag{A22}$$

$$a_1 = -a_0 \ln (a_0); \quad r_1 = 1 \tag{A23}$$

$$a_2 = \frac{r_1}{1-r_1}\left\{\frac{a_0 - a_0^{r_2}}{1-r_2} - \frac{a_0^{r_1} - a_0^{r_2}}{r_1 - r_2}\right\}; \quad r_1 \neq 1; r_2 \neq 1; r_1 \neq r_2 \tag{A24}$$

$$a_2 = \frac{a_0}{1-r_2} \ln (a_0) - \frac{a_0}{(1-r_2)^2}\{1 - a_0^{r_2-1}\}; \quad r_1 = 1; r_2 \neq 1 \tag{A25}$$

$$a_2 = -\frac{1}{1-r_1}\left\{\frac{a_0^{r_1}}{r_1 - 1} - a_0 \ln (a_0)\right\} + \frac{r_1 a_0}{(1-r_1)^2}; \quad r_1 \neq 1; r_2 = 1 \tag{A26}$$

$$a_2 = \frac{r}{1-r_1}\left\{\frac{a_0 - a_0^{r_1}}{1-r_1} - a_0^{r_1} \ln (a_0)\right\}; \quad r_1 \neq 1; r_2 \neq 1; r_1 = r_2 \tag{A27}$$

$$a_2 = \frac{a_0}{2} (\ln (a_0))^2; \quad r_1 = 1; r_2 = 1 \tag{A28}$$

$$a_3 = 1 - a_2 - a_1 - a_0 \tag{A29}$$

where

$$r_1 = 2k_1/3k_0; \quad r_2 = k_2/3k_0$$

The quantities a_0, a_1, a_2, and a_3 are molar fractions. The conversion α is calculated as

$$\alpha = (3a_3 + 2a_2 + a_1)/3 \tag{A30}$$

Using eqs A22–A30 it is possible to numerically evaluate the number fractions a_0, a_1, a_2, and a_3 as functions of α: $a_0(\alpha)$, $a_1(\alpha)$, $a_2(\alpha)$, $a_3(\alpha)$.

Appendix 3: Number Fraction Changes during Discrete Intervals

We consider the discretized conversion model. The superspecies of this model are

$$\mathcal{S}_N = \{(i,j,k) | 1 \le i \le j \le k \le N\}$$

In order to compute the number fractions of these species, we first consider the minimal model with superspecies

$$\mathcal{S}_{\min} = \{\mathrm{A}_0, \mathrm{A}_1, \mathrm{A}_2, \mathrm{A}_3\}$$

and compute the number fraction of A units that are A_i superspecies at conversion β and then have become A_j superspecies at conversion γ; this number fraction is denoted as $a_{ij}(\beta,\gamma)$.

During any given interval one, two, or all three sites on an A unit may react, as explained in the main text. Given an interval that starts at conversion β, ends at conversion γ, and contains intermediate conversions α, $\beta < \alpha < \gamma$, $a_{ij}(\beta,\alpha)$ equals the number fraction of structures that were A_i at conversion β and are A_j at conversion α. At the beginning of the interval (converison β) we have

$$a_{00}(\beta,\beta) = a_0(\beta) \tag{A31}$$

$$a_{11}(\beta,\beta) = a_1(\beta) \tag{A32}$$

$$a_{22}(\beta,\beta) = a_2(\beta) \tag{A33}$$

$$a_{33}(\beta,\beta) = a_3(\beta) \tag{A34}$$

$$a_{ij}(\beta,\beta) = 0 \qquad i \neq j \tag{A35}$$

During the time that conversion goes from β to γ the differential equations are

$$\mathrm{d}a_{00}/\mathrm{d}t = -3k_0 a_{00} R \tag{A36}$$

$$\mathrm{d}a_{01}/\mathrm{d}t = 3k_0 a_{00} R - 2k_1 a_{01} R \tag{A37}$$

$$\mathrm{d}a_{02}/\mathrm{d}t = 2k_1 a_{01} R - k_2 a_{02} R \tag{A38}$$

$$\mathrm{d}a_{03}/\mathrm{d}t = k_2 a_{02} R \tag{A39}$$

$$\mathrm{d}a_{11}/\mathrm{d}t = -2k_1 a_{11} R \tag{A40}$$

$$\mathrm{d}a_{12}/\mathrm{d}t = 2k_1 a_{11} R - k_2 a_{12} R \tag{A41}$$

$$\mathrm{d}a_{13}/\mathrm{d}t = k_2 a_{12} R \tag{A42}$$

$$\mathrm{d}a_{22}/\mathrm{d}t = -k_2 a_{22} R \tag{A43}$$

$$\mathrm{d}a_{23}/\mathrm{d}t = k_2 a_{22} R \tag{A44}$$

$$\mathrm{d}a_{33}/\mathrm{d}t = 0 \tag{A45}$$

where

$$R = 3k_0 a_0(\alpha) + 2k_1 a_1(\alpha) + k_2 a_2(\alpha)$$

and the following relationships hold

$$a_0(\alpha) = a_{00}(\beta,\alpha)$$

$$a_1(\alpha) = a_{01}(\beta,\alpha) + a_{11}(\beta,\alpha)$$

$$a_2(\alpha) = a_{02}(\beta,\alpha) + a_{12}(\beta,\alpha) + a_{22}(\beta,\alpha)$$

$$a_3(\alpha) = a_{03}(\beta,\alpha) + a_{13}(\beta,\alpha) = a_{23}(\beta,\alpha) + a_{33}(\beta,\alpha)$$

so

$$R = 3k_0 a_{00}(\beta,\alpha) + 2k_1(a_{01}(\beta,\alpha) + a_{11}(\beta,\alpha)) + k_2(a_{02}(\beta,\alpha) + a_1(\beta,\alpha) + a_{22}(\beta,\alpha))$$

Equations A31–A45 may be solved numerically as functions of time. They may also be solved analytically as functions of $a_0(\beta)$, $a_1(\beta)$, $a_2(\beta)$, $a_3(\beta)$, and $a_0(\gamma)$ (which are calculated in Appendix 2). The solutions are

$$a_{00}(\beta,\gamma) = a_0(\gamma) \tag{A46}$$

$$a_{01}(\beta,\gamma) = \frac{a_0(\beta)}{1-r_1}\{q(\gamma,\beta)^{r_1} - q(\gamma,\beta)\}; \quad r_1 \neq 1 \tag{A47}$$

$$a_{01}(\beta,\gamma) = -a_0(\gamma) \ln (q(\gamma,\beta)); \quad r_1 = 1 \tag{A48}$$

$$a_{02}(\beta,\gamma) = \frac{r_1 a_0(\beta)}{1-r_1}\left\{\frac{q(\gamma,\beta) - q(\gamma,\beta)^{r_2}}{1-r_2} - \frac{q(\gamma,\beta)^{r_1} - q(\gamma,\beta)^{r_2}}{r_1 - r_2}\right\}; \quad r_1 \neq r_2; r_1 \neq 1; r_2 \neq 1 \tag{A49}$$

$$a_{02}(\beta,\gamma) = \frac{a_0(\gamma) \ln (q(\gamma,\beta))}{1-r_2} - \frac{a_0(\gamma)\{1 - q(\gamma,\beta)^{r_2-1}\}}{(1-r_2)^2}; \quad r_1 = 1; r_2 \neq 1 \tag{A50}$$

$$a_{02}(\beta,\gamma) = -\frac{r_1 a_0(\beta)}{1-r_1}\left\{\frac{q(\gamma,\beta)^{r_1}}{r_1 - 1} - q(\gamma,\beta) \ln (q(\gamma,\beta))\right\}; \quad r_1 \neq 1; r_2 = 1 \tag{A51}$$

$$a_{02}(\beta,\gamma) = -\frac{r_1 a_0(\gamma)^{r_1} \ln (q(\gamma,\beta))}{1-r_1} + \frac{r_1 a_0(\gamma)\{1 - q(\gamma,\beta)^{r_1-1}\}}{(1-r_1)^2}; \quad r_1 = r_2; r_1 \neq 1 \tag{A52}$$

$$a_{02}(\beta,\gamma) = a_0(\gamma)\left\{\frac{[\ln (a_0(\gamma))]^2 - [\ln (a_0(\beta))]^2}{2} - \ln (a_0(\gamma)) \ln (a_0(\beta))\right\}; \quad r_1 = 1; r_2 = 1 \tag{A53}$$

$$a_{03}(\beta,\gamma) = a_0(\beta) - a_{00}(\beta,\gamma) - a_{01}(\beta,\gamma) - a_{02}(\beta,\gamma) \quad \text{(A54)}$$

$$a_{11}(\beta,\gamma) = a_1(\beta)q(\gamma,\beta)^{r_1} \quad \text{(A55)}$$

$$a_{12}(\beta,\gamma) = -\frac{r_1 a_1(\beta)}{r_1 - r_2}\{q(\gamma,\beta)^{r_1} - q(\gamma,\beta)^{r_2}\}; \quad r_1 \neq r_2 \quad \text{(A56)}$$

$$a_{12}(\beta,\gamma) = r_1 a_1(\beta)q(\gamma,\beta)^{r_1} \ln (q(\gamma,\beta)); \quad r_1 = r_2 \quad \text{(A57)}$$

$$a_{13}(\beta,\gamma) = a_1(\beta) - a_{11}(\beta,\gamma) - a_{12}(\beta,\gamma) \quad \text{(A58)}$$

$$a_{22}(\beta,\gamma) = a_2(\beta)q(\gamma,\beta)^{r_2} \quad \text{(A59)}$$

$$a_{23}(\beta,\gamma) = a_2(\beta) - a_{22}(\beta,\gamma) \quad \text{(A60)}$$

$$a_{33}(\beta,\gamma) = a_3(\beta) \quad \text{(A61)}$$

where

$$r_1 = 2k_1/3k_0,\ r_2 = k_2/3k_0, \text{ and } q(\gamma,\beta) = a_0(\gamma)/a_0(\beta)$$

Appendix 4: Counterexample for Precision of Rank Model

If we label superspecies only with their ranks, we say that we have a rank model. The superspecies at complete conversion are

$$\mathcal{S}_{\text{rank}} = \{[(1,i),(2,j),(3,k)]|i,j,k = 1,2,3\}$$

We now show that the rank model is not exact even in the *ideal* case, i.e., where there is no substitution effect. It suffices to consider the *ideal* homopolymerization of the bifunctional monomer A_2. The seven superspecies for this model are

G_1: (0)—(0)
G_2: (1,1)—(0)
G_3: (2,1)—(0)
G_4: (1,1)—(2,1)
G_5: (1,1)—(2,2)
G_6: (2,1)—(2,1)
G_7: (2,1)—(2,2)

Here the inside number on the label is the rank of the site; the outside number is the rank of the site with which the labeled site reacts. We shall find the number fractions of these seven superspecies at a given conversion α. Then, using the rank model, we shall randomly combine these superspecies and calculate the number fractions of some polymer molecules. We shall compare these number fractions to the known number fractions for linear chains; they will not agree. This shows that the rank model is not exact.

By the end of the reaction, any A unit will have two reacted sites labeled with the conversions at which the reactions took place. Let those labels be β and γ, $\beta < \gamma$. At any given conversion α such that $\alpha < \beta < \gamma$ this A unit was an unreacted monomer, a G_1 superspecies. For all α such that $\beta < \alpha < \gamma$, the unit had one reacted site and one unreacted site, and for any α where $\beta < \gamma < \alpha$, the unit had two reacted sites. Therefore, if we want to find the number fraction of unreacted monomer at conversion α, we may find it from the number fraction of all structures with labels that satisfy the condition $\alpha < \beta < \gamma$.

The quantity we are interested in is $P(\alpha<\beta<\gamma)$, the probability that a randomly chosen A_2 unit reacts at conversions β and γ. β and γ are uniformly distributed over the unit square and conditionally independent given they are ordered. Their joint probability density function is given by

$$f(\beta,\gamma) = 2, \quad 0 \le \beta \le \gamma \le 1$$
$$= 0, \quad \text{otherwise} \quad \text{(A62)}$$

Therefore, the number fraction of unreacted monomer at conversion α is

$$g_1(\alpha) = P(\alpha<\beta<\gamma) = \int_{\beta=\alpha}^{1}\int_{\gamma=\beta}^{1} f(\beta,\gamma)\,\mathrm{d}\gamma\,\mathrm{d}\beta = (1-\alpha)(1-\alpha) \quad \text{(A63)}$$

Now we find the number fraction of the remaining structures. We will define the A structure we are focusing on as the "base structure", while the A structures that become attached to it by reaction will be "adjacent structures". On the adjacent structures, "near sites" are the ones that reacted with the base structure, "far sites" are the remaining ones. The next number fraction to be found is

$$g_2(\alpha) = P(\beta<\alpha<\gamma \text{ and } \bar{R}_\beta) \quad \text{(A64)}$$

where R_β is the event that the far site on the adjacent structure (with which the base structure reacted at conversion β) was already reacted at conversion β; $\bar{R}_\beta$ is the complementary event that the far site was unreacted at conversion β. Recall that this is an *ideal* homopolymerization; i.e., the far site reacts independently of the near site. It is true that

$$P(\beta<\alpha<\gamma, \bar{R}_\beta|\beta,\gamma) = 1-\beta \quad \text{if } \beta < \alpha < \gamma$$
$$= 0 \quad \text{otherwise} \quad \text{(A65)}$$

With that, we have

$$g_2(\alpha) = P(\beta<\alpha<\gamma, \bar{R}_\beta) = \int_0^\infty\int_0^\infty P(\beta<\alpha<\gamma, \bar{R}_\beta|\beta,\gamma)f(\beta,\gamma)\,\mathrm{d}\gamma\,\mathrm{d}\beta = \int_{\beta=0}^{\alpha}\int_{\gamma=\alpha}^{1}(1-\beta)2\,\mathrm{d}\gamma\,\mathrm{d}\beta = (1-\alpha)(2\alpha-\alpha^2) \quad \text{(A66)}$$

Similarly

$$g_3(\alpha) = P(\beta<\alpha<\gamma, R_\beta) = \int_0^\infty\int_0^\infty P(\beta<\alpha<\gamma, R_\beta|\beta,\gamma)f(\beta,\gamma)\,\mathrm{d}\gamma\,\mathrm{d}\beta = \int_{\beta=0}^{\alpha}\int_{\gamma=\alpha}^{1}\beta 2\,\mathrm{d}\gamma\,\mathrm{d}\beta = (1-\alpha)\alpha^2 \quad \text{(A67)}$$

$$g_4(\alpha) = P(\beta<\gamma<\alpha, \bar{R}_\beta, \bar{R}_\gamma) = \int_{\beta=0}^{\alpha}\int_{\gamma=\beta}^{\alpha}(1-\beta)(1-\gamma)2\,\mathrm{d}\gamma\,\mathrm{d}\beta = \alpha^2\left(1-\alpha+\frac{\alpha^2}{4}\right) \quad \text{(A68)}$$

$$g_5(\alpha) = P(\beta<\gamma<\alpha, \bar{R}_\beta, R_\gamma) = \int_{\beta=0}^{\alpha}\int_{\gamma=\beta}^{\alpha}(1-\beta)\gamma 2\,\mathrm{d}\gamma\,\mathrm{d}\beta = \frac{2\alpha^3}{3} - \frac{\alpha^4}{4} \quad \text{(A69)}$$

$$g_6(\alpha) = P(\beta<\gamma<\alpha, R_\beta, \bar{R}_\gamma) = \int_{\beta=0}^{\alpha}\int_{\gamma=\beta}^{\alpha}\beta(1-\gamma)2\,\mathrm{d}\gamma\,\mathrm{d}\beta = \frac{\alpha^3}{3} - \frac{\alpha^4}{4} \quad \text{(A70)}$$

$$g_7(\alpha) = P(\beta<\gamma<\alpha, R_\beta, R_\gamma) = \int_{\beta=0}^{\alpha}\int_{\gamma=\beta}^{\alpha}\beta\gamma 2\,\mathrm{d}\gamma\,\mathrm{d}\beta = \frac{\alpha^4}{4} \quad \text{(A71)}$$

Now that we have the number fraction of all superspecies at conversion α, let's see if we can find the correct number fraction of molecular species in the reacting system. We will start with the dimer. Since this is an *ideal* polymerization, we know the correct answer beforehand: The number fraction of dimer is

$$n(\text{A–AA–A}) = \alpha(1-\alpha) \quad \text{(A72)}$$

In terms of superspecies, the dimer has this form

$$(0)\text{—}(1,1)(1,1)\text{—}(0)$$

In order to find the number fraction of dimer from the superspecies of the rank model, we reason as follows: We pick an unreacted end. The probability that it is on a G_2 superstructure is

$$P(\mathrm{G}_2|(0)\ \text{site}) = \frac{g_2(\alpha)}{2g_1(\alpha) + g_2(\alpha) + g_3(\alpha)} \qquad \text{(A73)}$$

Given that we are on a G_2 superstructure, we now need to know what is attached to the (1,1) site. We will be on a dimer if a G_2 structure is attached to the (1,1) site. That will happen with probability

$$P(\mathrm{G}_2|(1,1)\ \text{site}) = \frac{g_2(\alpha)}{g_2(\alpha) + g_3(\alpha) + g_4(\alpha)} \qquad \text{(A74)}$$

The number fraction of dimer according to the rank model is then

$$\begin{aligned} n(\text{A–AA–A}) &= P(\mathrm{G}_2|(0)\ \text{site})P(\mathrm{G}_2|(1,1)\ \text{site}) \\ &= \frac{g_2(\alpha)}{2g_1(\alpha) + g_2(\alpha) + g_3(\alpha)}\,\frac{g_2(\alpha)}{g_2(\alpha) + g_3(\alpha) + g_4(\alpha)} \\ &= \left\{\alpha - \frac{\alpha^2}{2}\right\}\left\{\frac{3}{2}\,\frac{(1-\alpha)(2-\alpha)}{(3-3\alpha+\alpha^2)}\right\} \\ &= \alpha(1-\alpha)\frac{3}{4}\,\frac{(2-\alpha)^2}{3-3\alpha+\alpha^2} \\ &= \alpha(1-\alpha)\frac{12-12\alpha+3\alpha^2}{12-12\alpha+4\alpha^2} \qquad \text{(A75)} \end{aligned}$$

We know that the correct number fraction of dimer for this *ideal* case is

$$n(\text{A–AA–A}) = \alpha(1-\alpha) \qquad \text{(A76)}$$

The rank model gives an incorrect answer. Therefore, it is not an exact model; it is only approximate.

Appendix 5: Destruction of Independence by Aggregation

The models in this paper that label superspecies using conversion are mathematically intractable because conversion is a continuous variable. In order to perform calculations this continuous variable must be discretized into a finite number of intervals. Labels with different values of conversion that fall into the same interval are grouped into a single labeling. This is tantamount to aggregating many different distinct superspecies into just one. Structural detail of the model is reduced. The resulting less detailed model may become inexact even if the original detailed model was an exact model. The conversion model is an exact model for multiplicative FSSE homopolymerization with no cycles; but this model is mathematically intractible. The discretized version of the conversion model becomes mathematically tractible, but it is not exact. The discretization has aggregated structural detail that is necessary for exact analysis.

Another instance of discretization introducing errors occurs in polymerization systems that change over time. At any instant of time we might have an exact model of the polymer formed at that instant of time. But, in effect, we have a slightly different model (parameters may change) for each point in time. This is almost always mathematically intractible; so the models are combined for time intervals by averaging parameter values or in some other way.

In this appendix we give a numerical example to illustrate this phenomenon: Independence plays a crucial role in branching process modeling. The whole idea of this kinetic–Markovian approach is to define superspecies that combine randomly. The rank model fails. At any instant of time, sites with different rank labels will combine randomly and independently subject to proper matching of labels. But at different times the probabilities may change even though independence still holds. When time is ignored and only ranks are used, we are in effect aggregating the structural detail and introducing errors. The following simplified numerical example illustrates this.

Suppose we polymerize a bifunctional monomer and label reacted sties with ranks as in Appendix 4. Consider two points in time: t_1 and t_2. At time t_1, 2/3 of the reacting sites have rank 1 and 1/3 have rank 2. Sites combine independently of rank. Thus at time t_1 we have four different types of bond forming with probabilities $P(1,1) = (2/3)(2/3) = 4/9$, $P(1,2) = 2/9$, $P(2,1) = 2/9$, and $P(2,2) = 1/9$. At time t_2, 1/3 of the reacting sites have rank 1 and 2/3 have rank 2. Sites still combine independently of rank. So at time t_2 we have the following probabilities of different bonds forming: $P(1,1) = 1/9$; $P(1,2) = 2/9$; $P(2,1) = 2/9$; $P(2,2) = 4/9$. Suppose that an equal number of bonds form at times t_1 and t_2. The total (aggregated) material formed at the two times has the following distribution of bonds (obtained by averaging the above two distributions): $P(1,1) = 5/18$; $P(1,2) = 4/18$; $P(2,1) = 4/18$; $P(2,2) = 5/18$. We see that for the combined material 1/2 of the reacted sites have a rank 1 and 1/2 have rank 2. In this total material, if reacted sites combined independently of rank, then all four types of bonds should be equally likely (each with probability 1/4). So, as far as the aggregated material is concerned, sites do not combine independently of rank. We have destroyed the independence by aggregating over different time values.

If the behavior of the system does not change much over each time interval (or interval of conversion), it should be possible to aggregate over each of those intervals without introducing an unacceptable numerical error.

Notation

A_f	monomer with f functional groups (A groups)
A_i	superspecies for minimal model: a monomer unit with exactly i reacted sites, $i = 0, 1, 2, 3$
a_0, a_1, a_2, a_3	number fractions of A_i superspecies
$A_i(\alpha)$	an A monomer unit which is an A_i superspecies at conversion α
$a_i(\alpha)$	number fraction of A_i superspecies at conversion α
$a_i(t)$	number fraction of A_i superspecies at time t
$a_{ij}(\beta,\gamma)$	number fraction of A units that are A_i superspecies at conversion β and then have become A_j superspecies at conversion γ
α	conversion
α_c	critical conversion; the gel point
$\hat{\alpha}$	a fixed value of conversion, at which the weight-average molecular weight is to be computed
$(\alpha_{i-1}, \alpha_i]$	the ith subinterval of conversion in $[0,\hat{\alpha}]$; $\alpha_i = \hat{\alpha}i/N$
$\tilde{\alpha}$	a fixed value of conversion, which is assumed to be beyond the gel point
β, γ, δ	values of conversion, may be random
(β,γ,δ)	representation of a superspecies in the conversion model, in which the sites reacted at conversions β, γ, and δ

$(\beta,\#,\#)$	representation of a superspecies in the conversion model, in which exactly one site is reacted, the reaction occurring at conversion β
B_g	monomer with g functional groups (B groups)
EW_i^{out}	expected weight seen on branch looking out from a reacted site which reacted during the ith conversion interval
EW_i^{in}	expected weight seen looking into a reacted site, which reacted during the ith interval
$f(\beta,\gamma)$	joint probability density function of the random conversion times β and γ
G_i	superspecies in rank model of homopolymerization bifunctional monomers (Appendix 4)
$g_i(\alpha)$	number fraction of G_i at conversion α (Appendix 4)
(i,j,k)	representation of superspecies in the discretized conversion model whose sites reacted during conversion intervals i, j, and k
$\mathbf{K}$	matrix of kinetic rates
k_i	kinetic rate of the next site on an A_i superspecies reacting
k_{ij}	kinetic rate of an A_i and an A_j reacting
$(m,n;\alpha)$	label for a site in the maximal model; the site is the mth to react; the site with which it reacts is the nth to react on its monomer; the reaction occurs at conversion α
(m,n)	label for a site in the rank model; the site is the mth to react; the site with which it reacts is the nth to react on its monomer; the conversion is ignored
M	number of conversion intervals
M_{A_3}	molecular weight of a trifunctional monomer with A groups
$\bar{M}_w$	weight-average molecular weight
N	number of conversion intervals
$n(\text{A–AA–A})$	number fraction of dimer in a homopolymerization of bifunctional monomer
$P_N(j,k\|i)$	probability (for discretized conversion model) of having the second and third sites observed to react in intervals j and k, given the unit was chosen by first randomly choosing a site that reacted in interval i
$P_N(j\|i)$	probability (for discretized conversion model) that a second randomly chosen site reacted in interval j, given the unit was chosen by first randomly choosing a site that reacted in interval i
$P((i,j)\|\alpha)$	conditional probability of a bond forming between sites with ranks i and j given the reaction occurred at conversion α (Appendix 1)
$P(i\|\alpha)$	probability that a site reacting at conversion α has rank i (Appendix 1)
$P(i,j\|\alpha)$	joint probability that two randomly chosen sites reacting at conversion α have ranks i and j
$P(\alpha<\beta<\gamma)$	probability that a random bifunctional monomer reacts at conversions β and γ, satisfying $\alpha < \beta < \gamma$ (Appendix 4)
$P(\beta<\alpha<\gamma, \bar{R}_\beta)$	probability that a random bifunctional monomer reacts at conversions β and γ satisfying $\beta < \alpha < \gamma$ and furthermore that the event $\bar{R}_\beta$ occurs
$P(\beta<\alpha<\gamma, \bar{R}_\beta\|\beta,\gamma)$	the above probability conditional on specific fixed values of β and γ
$P(G_2\|(0)\text{ site})$	conditional probability that a randomly chosen (0) site belongs to the G_2 superspecies (Appendix 4)
$q(\gamma,\beta)$	notation to simplify formulas, equals $a_0(\gamma)/a_0(\beta)$
$Q_1(i)$	expected number of i sites on a randomly chosen A unit
$Q_2(i,j)$	expected number of ordered (i,j) pairs of sites on a randomly chosen A unit
r_1	$2k_1/3k_0$, ratio of kinetic rates
r_2	$k_2/3k_0$, ratio of kinetic rates
$r(i,j;\alpha)$	rate of (i,j) bond formation at conversion α (Appendix 4)
$r_1(i;\alpha)$	rate of $(i,*)$ bond formation at conversion α, where * represents a site with an arbitrary rank label
$r_2(j;\alpha)$	rate of $(*,j)$ bond formation at conversion α
$r(\alpha)$	rate of bond formation at conversion α
R_β	event that the far site on the adjacent structure was already reacted at conversion β
$\bar{R}_\beta$	complementary event that the far site was unreacted at conversion β
$\mathcal{S}$	used to denote a set of superspecies
$\mathcal{S}_\alpha$	set of superspecies for the conversion model
$\mathcal{S}_{\max}$	set of superspecies for the maximal model
$\mathcal{S}_{\min}$	set of superspecies for the minimal model
$\mathcal{S}_N$	set of superspecies for the discretized conversion model
$\mathcal{S}_{\text{rank}}$	set of superspecies for the rank model
$S_m(i,j,k)$	superspecies for the discretized conversion model; by the mth interval of conversion the three sites had already reacted in intervals i, j, and k
$s_m(\cdot,\cdot,\cdot)$	number fraction of superspecies in discretized conversion model after the mth interval
$s_N(i,j,k)$	number fraction of superspecies $S_N(i,j,k)$ in the discretized conversion model
s_N	a number fraction in the discretized conversion model
S_N	a superspecies in the discretized conversion model
W_i^{out}	weight seen on branch looking out from a randomly chosen reacted site that reacted during the ith conversion interval, a random variable
W_i^{in}	weight seen looking into a randomly chosen reacted site that reacted during the ith interval, a random variable
$[0, \hat{\alpha}]$	a conversion interval of interest
$[(1,i;\beta), (2,j;\gamma), (3,k;\delta)]$	representation of superspecies in the maximal model
$[(1,i),(2,j), (3,k)]$	representation of superspecies in the rank model
#	label for unreacted site

Acknowledgment. We thank the Office of Naval Research for supporting this work under ONR Contract N00014-88-K-0366. We thank Karel Dušek for giving us some valuable comments and literature references related to this research.

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