Copolymerization of a Polydisperse Oligomer with a Monodisperse Chain Extender with Intramolecular Reaction Allowed

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ABSTRACT: We have modeled stepwise, irreversible copolymerizations with intramolecular reaction allowed where one of the reactants is a polydisperse oligomer. $A_2 + B_2$ systems are studied, where A_2 is the bifunctional chain extender and B_2 is the bifunctional oligomer. Two models are presented. They are both extensions of a previous one where B_2 was assumed to be monodisperse. In both cases B_2 is approximated as the sum of N monodisperse fractions. In one model, it is necessary to write a system of kinetic equations to describe the $A_2 + (B_2)_1 + (B_2)_2 + ... + (B_2)_N$ copolymerization where all the B-fractions are simultaneously available for reaction. In the second model, N different monodisperse systems are set up and made to react separate and simultaneously. The species from these N systems are then combined using probability theory. This results in an important reduction in the number of equations needed. The theoretical error involved in this second model is small. Our results indicate that disregard for both polydispersity and ring formation may result in sizable errors in the prediction of average molecular weights.

Introduction

Several models have been proposed to deal with stepwise, irreversible copolymerization with intramolecular reaction allowed. Possible approaches include the "spanning tree" method,[1,2] "rate theory",[3,4] the kinetic method,[5-7] the averaged kinetic method,[8] and the kinetic recursive[9] method. All these models are approximate, and their ranges of validity are different.[10] However, they share one basic assumption, namely, that all reactants are monodisperse. In practical situations it is more likely that at least one of the reactants will be polydisperse.

Here we present two new models that allow intramolecular reaction when one of the reactants is polydisperse. They are both extensions of the kinetic recursive model.[9] One of them is a direct extension of that model, without extra approximations. It is the more exact of the two models and may require a rather high number of differential equations. The other model contains an extra approximation that results in an important reduction in the number of differential equations needed while increasing the error of the results by a small amount. We believe this is the first time that both polydispersity of reactants and intramolecular reaction are allowed for in models for irreversible copolymerization.

Theory

We want to model the copolymerization reaction between A_f and B_2, where A_f is the small, monodisperse, f-functional chain extender. B_2 is a polydisperse oligomer. As such, it is a mixture of molecules of different sizes, all of which are assumed to be long and flexible enough to have a Gaussian end-to-end distance distribution. For our purposes the nature of the polydispersity in B_2 must be such that it may be represented as the sum of N $(B_2)_i$ monodisperse fractions of size i ($i = 1...N$). Reaction is stepwise and irreversible; only AB bonds may form. Other assumptions are equal reactivity of all groups and absence of substitution effects. Intramolecular reaction in such a system leads to the appearance of closed structures or rings of several sizes. In order to identify them we define an R-order ring as one having R A-monomers in it.

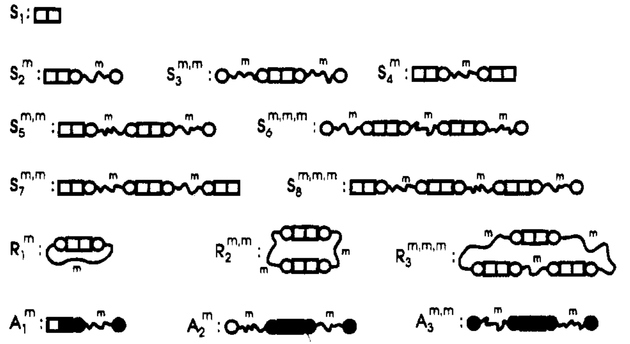

Figure 1. Part of the species needed to describe the copolymerization of a bifunctional A-monomer with a polydisperse B-oligomer made up of N monodisperse fractions using the simultaneous reaction model. Squares are A-sites, and circles are B-sites. In the auxiliary structures, clear areas are unreacted sites, and dark areas are reacted sites. The integers on top of the B-oligomers indicate the fraction to which they belong.

In this paper we will only consider the simplest copolymerization, where the functionality of the chain extender is $f = 2$. In this system the only products are either linear chains or rings; gelation is not possible. Gel-capable copolymerizations (those with $f \geq 3$) will be considered elsewhere. Let us now describe the two particular models we want to present.

(a) The "Simultaneous Reaction" Model. We model the system described above using an extension of the kinetic recursive model for monodisperse reactants,[9] where the main approximation is that only rings of up to a certain fixed order R are allowed. All other rings are neglected. For the particular case where rings up to order $R = 3$ are allowed, the species in Figures 1 and 2 would be required to describe the system. Figure 1 contains structures that are "homogeneous" in B-oligomer; that is, all the B-oligomers in any one struc-

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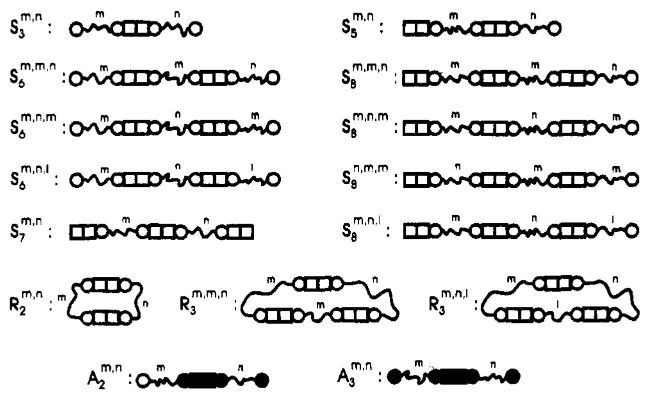

Figure 2. Remainder of the species needed to describe the copolymerization of a bifunctional A-monomer with a polydisperse B-oligomer made up of N monodisperse fractions using the simultaneous reaction model.

ture belong to the same fraction. Figure 2 contains structures that are "heterogeneous", since they contain B-oligomers from at least two different fractions. This is an $A_2 + (B_2)_1 + (B_2)_2 + ... + (B_2)_N$ copolymerization. Structures are divided into short chains (S's), rings (R's), and auxiliary structures (A's). Short chains are those that may give rise either to a ring or to another structure that will lead to a ring. Longer chains are constructed with the aid of the auxiliary structures. In Figure 1 S_1 is the unreacted A-monomer, S_2^1 is a dimer having an A-monomer and a B-oligomer that belongs to fraction 1, $S_3^{m,m}$ is a trimer containing an A-monomer and two B-oligomers from fraction m, and so on. In the "heterogeneous" linear structures of Figure 2, the order of the superscripts indicates the order of the $(B_2)_i$ units on the structure. If both ends of the linear structure are A-monomers (or both B-oligomers), then we may "read" the structure starting from any of the ends. If one end is an A-monomer and the other is a B-oligomer, then the order is from left to right. In other words, $S_8^{m,n,l}$ is different from $S_8^{l,n,m}$, but $S_6^{m,n,l}$ is not distinguished from $S_6^{l,n,m}$. In the same spirit, the order of the superscripts is meaningful for $A_2^{m,n}$ but not for $A_3^{m,n}$. For ring structures, the order of the superscripts has no significance.

The auxiliary structures have reacted ends, and they can be thought of as pieces of chains. These structures make up both the short and long chains in the system. By definition, they do not make up any rings. For example, $S_5^{m,n}$ is made up of an A_1^m on one end and an $A_2^{n,m}$ on the other. Note that the structures are partially overlapping. The information contained in the auxiliary structures is in part redundant, since the short structures are specifically enumerated and their concentrations will be calculated separately. But it is a simple matter to subtract from the concentration of all auxiliary structures the part that corresponds to the making up of short chains. After that operation, it is possible to construct long chains from what remains, subject to the condition that these chains must be longer than the longest short chain. Construction of long chains is necessary to calculate average properties such as molecular weights. We assume that all long chains may be constructed from pieces of chains such as these by random combination. It has previously been shown[9] that this is a reasonable approximation.

The total number of species required to describe the system is $14 + 13(N - 1) + (5/3)N(N^2 + 3N - 4)$. In the first $14 + 13(N - 1)$, all the B-oligomers in any one species belong to the same fraction. However, since all B-fractions are simultaneously available for reaction, some species with mixed B-fractions must exist. The ones needed to describe our system are the remaining $(5/3)N(N^2 + 3N - 4)$.

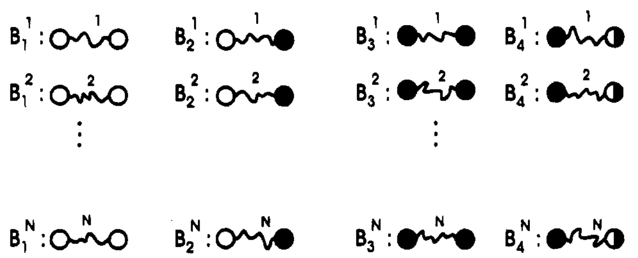

Figure 3. B-species used in the simultaneous reaction model. The half-shaded areas indicate intramolecularly reacted sites.

For convenience, the species in Figure 3 are also considered. B_1^1 is the unreacted B-oligomer that belongs to fraction 1, B_1^2 is the unreacted B-oligomer of fraction 2, B_4^2 is a B-oligomer of fraction 2 that is involved in a ring, and so on. The molar concentrations of the species in Figure 3 are defined through the molar concentrations of the species of Figures 1 and 2. If we denote the concentrations of the various species at time t as $A_1^1(t)$, $A_2^1(t)$, $S_1^1(t)$, $S_2^m(t)$, etc., we would have for example

$$B_4^m(t) = R_1^m + R_2^{m,m} + \sum_{j=1}^{N} R_2^{m,j} + 2R_3^{m,m,m} + \sum_{j=1}^{N}\sum_{k=1}^{N} R_3^{m,j,k}$$

The structures of Figures 1, 2, and 3 react with one another to give other species. For example, S_1 reacts with B_1^2 to give S_2^2; S_2^2 may react intramolecularly to give R_1^2, or it may react with any A-site to give A_1^2, or with B_1^1 to give $S_3^{1,2}$, and so on. Reactions occur at rates equal to the products of a kinetic rate constant, k, and the number (molar) concentrations of the reactants. The concentrations of all the species in Figures 1 and 2 are calculated exactly through the solution of a system of simultaneous kinetic differential equations. $14 + 13(N - 1) + (5/3)N(N^2 + 3N - 4)$ equations are required. The equations for the "homogeneous" structures are

$$S_1(t)' = -2kS_1(t)B_0(t)$$

$$S_2^m(t)' = 4kS_1(t)B_1^m(t) - kS_2^m(t)[A_0(t) + B_0(t) + C_m]$$

$$S_3^{m,m}(t)' = 2kS_2^m(t)B_1^m(t) - kS_3^{m,m}(t)[2A_0(t)]$$

$$S_4^m(t)' = 2kS_2^m(t)S_1(t) - kS_4^m(t)[2B_0(t)]$$

$$S_5^{m,m}(t)' = kS_2^m(t)S_2^m(t) + 4kS_3^{m,m}(t)S_1(t) + 4kS_4^m(t)B_1^m(t) - kS_5^{m,m}(t)[A_0(t) + B_0(t) + C_{m+m}]$$

$$S_6^{m,m,m}(t)' = 2kS_5^{m,m}(t)B_1^m(t) + 2kS_2^m(t)S_3^{m,m}(t) - kS_6^{m,m,m}(t)[2A_0(t)]$$

$$S_7^{m,m}(t)' = 2kS_5^{m,m}(t)S_1(t) + 2kS_2^m(t)S_4^m(t) - kS_7^{m,m}(t)[2B_0(t)]$$

$$S_8^{m,m,m}(t)' = 4kS_6^{m,m,m}(t)S_1(t) + 2kS_2^m(t)S_5^{m,m}(t) + 4kS_3^{m,m}(t)S_4^m(t) + 4kS_7^{m,m}(t)B_1^m(t) - kS_8^{m,m,m}(t)[A_0(t) + B_0(t) + C_{m+m+m}]$$

$$R_1^m(t)' = kS_2^m(t)C_m$$

$$R_2^{m,m}(t)' = kS_5^{m,m}(t)C_{m+m}$$

$$R_3^{m,m,m}(t)' = kS_8^{m,m,m}(t)C_{m+m+m}$$

$$A_1^m(t)' = 2kS_1(t)B_2^m(t) + kS_2^m(t)A_0(t) - kA_1^m(t)B_0(t) - k\sum_{i=1}^{N} S_5^{m,i}(t)C_{m+i} - k\sum_{i=1}^{N}\sum_{j=1}^{N} S_8^{m,i,j}(t)C_{m+i+j}$$

$$A_2^{m,m}(t)' = kS_2^m(t)B_2^m(t) + 2kA_1^m(t)B_1^m(t) + 2kS_3^{m,m}(t)A_0(t) - kA_2^{m,m}(t)A_0(t) - kS_5^{m,m}(t)C_{m+m} - k\sum_{i=1}^{N} S_8^{i,m,m}(t)C_{m+m+i}$$

$$A_3^{m,m}(t)' = kA_1^m(t)B_2^m(t) + kA_2^m(t)A_0(t) - k\sum_{i=1}^{N} S_8^{m,m,i}(t)C_{m+m+i}$$

There are similar equations for the "heterogeneous" structures. Interested readers are referred to the Appendix.

In the above equations the quantities $A_0(t)$ and $B_0(t)$ are the concentrations of unreacted A-sites and B-sites, respectively. They are defined as

$$A_0(t) = 2S_1(t) + \sum_{i=1}^{N}(S_2^i(t) + A_1^i(t))$$

$$B_0(t) = \sum_{i=1}^{N}(2B_1^i(t) + B_2^i(t))$$

The quantities C_i are the concentrations of one chain end around another for a Gaussian chain that belongs to fraction i. Assuming that the A-monomers contribute a negligible amount to the end-to-end distance, these concentrations are[11]

$$C_i = \left(\frac{1.5}{x_i \pi}\right)^{3/2} \frac{1}{l_B^3 \times 6.023 \times 10^{23}} \frac{\text{moles}}{\text{volume}}$$

where x_i equals the number of freely jointed segments in the B-oligomers from fraction i, $i = 1, 2, ..., N$, and l_B equals the length of those segments. C_{i+j} is calculated for a chain that is as long as one $(B_2)_i$ and one $(B_2)_j$ joined by one end.

The differential equations are solved numerically with initial conditions

$$S_1(0) = [\text{A-monomer}](0)$$

$$B_1^1(0) = [\text{B-oligomer}]_1(0)$$

$$B_1^2(0) = [\text{B-oligomer}]_2(0)$$

$$\vdots$$

$$B_1^N(0) = [\text{B-oligomer}]_N(0)$$

After the equations have been solved, we have the concentrations of the small species in the system and the auxiliary structures. Then, the longer molecules are "built back" using the auxiliary structures and the approximately recursive nature of those long molecules. The details have been explained elsewhere.[9] The information on short and long species is organized to give the number distribution of all species. Once that is known, all molecular parameters such as weight-average molecular weight, weight fraction of rings, and others may be calculated by standard methods.

One may wonder whether this model is complete enough to be used as a reference for comparison against a more approximate one. Rings of up to order 3 are allowed in all fractions, but $R_4^{1,1,1,1}$, which is neglected, may contain fewer links in the chain that forms the loop than R_1^N, which is not neglected. Does this introduce a serious error? In order to answer that, we have used the "simultaneous reaction" model on several arbitrary systems where the B-oligomers have five fractions. The systems are summarized in Tables 1−3. The systems

Table 1. Polydisperse B-Oligomers in the Systems That Approximate a Uniform Distribution Used in This Paper[a]

	individual fractions					distribution averages	
	x_1 (0.2)	x_2 (0.2)	x_3 (0.2)	x_4 (0.2)	x_5 (0.2)	x_w	x_w/x_n
P5EA	20	50	100	150	200	104	1.91
P5EB	50	100	150	200	250	150	1.37
P5EC	100	200	300	400	500	300	1.37
P5EF	200	400	600	800	1000	600	1.37
P5EG	20	120	220	320	420	220	3.01
P5EH	50	150	250	350	450	250	1.79
P5EI	20	220	420	620	820	420	5.02

[a] x_1 to x_5 are the number of monomer units in each of the five monodisperse fractions that make up the B-oligomer. The composition by mass of the polydisperse B-oligomer is indicated in parentheses. x_w and x_n are the weight-average and the number-average lengths of the B-oligomer, respectively. In all cases the density ϱ is 0.96, the weight of each segment is 74, the weight of the A-monomer is 194, the segment length is 1.64 Å, and the stoichiometric imbalance r is unity.

Table 2. Polydisperse B-Oligomers in the Systems with Approximately Bell-Shaped Distribution Used in This Paper[a]

	individual fractions					distribution averages	
	x_1 (0.1)	x_2 (0.2)	x_3 (0.4)	x_4 (0.2)	x_5 (0.1)	x_w	x_w/x_n
P5BA	20	26	100	184	200	104	1.90
P5BB	50	62	150	238	250	150	1.37
P5BC	100	124	300	476	500	300	1.37
P5BF	200	248	600	952	1000	600	1.37
P5BG	20	33	220	407	420	220	3.00
P5BH	50	70	250	430	450	250	1.79
P5BI	20	35	420	804	820	420	5.05

[a] Notation and assumptions are the same as for Table 1.

Table 3. Polydisperse B-Oligomers in the Systems with Low Molecular Weight Tail Used in This Paper[a]

	individual fractions					distribution averages	
	x_1 (0.15)	x_2 (0.12)	x_3 (0.33)	x_4 (0.3)	x_5 (0.1)	x_w	x_w/x_n
P5LA	20	24	100	150	200	104	1.90
P5LB	50	58	150	203	250	150	1.37
P5LC	100	117	300	407	500	300	1.37
P5LF	200	233	600	813	1000	600	1.37
P5LG	20	34	220	328	420	220	3.01
P5LH	50	68	250	356	450	250	1.79
P5LI	20	39	420	639	820	420	5.02

[a] Notation and assumptions are the same as for Table 1.

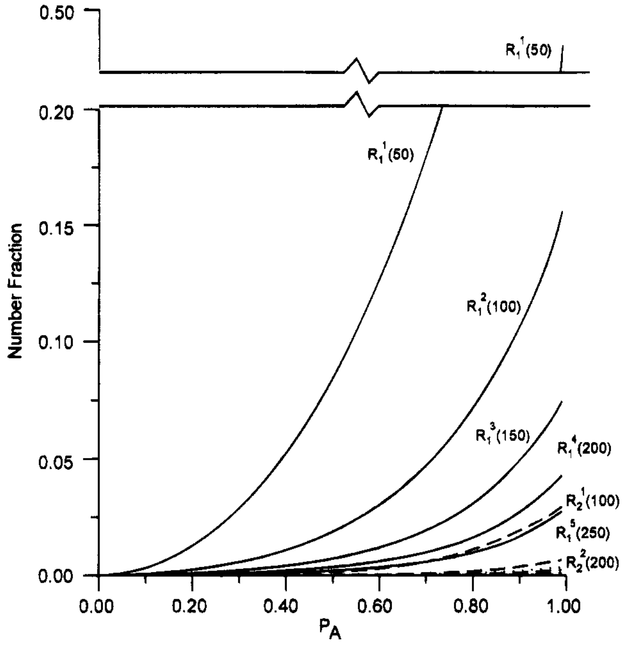

Figure 4. Number fraction of all homogeneous rings in case P5EB using the simultaneous reaction model. Full lines: rings of order 1; dashed lines: rings of order 2; dotted lines: rings of order 3. The numbers in parentheses indicate the number of links involved in each ring. Rings of order 3 and the largest rings of order 2 have negligible concentrations and can hardly be distinguished.

in each of the three tables have the same weight and number degree of polymerization, but they have different distributions. The polydisperse B-oligomers from Table 1 approximate a uniform distribution, those from Table 2 have an approximately bell-shaped distribution, and those from Table 3 approximate a bell-shaped distribution with a tail of low molecular weight.

We show in Figure 4 the number fraction of all homogeneous rings plotted against the extent of reaction for case P5EB. Full lines correspond to rings of order 1, dashed lines to rings of order 2, and dotted lines to rings of order 3. As expected, the most abundant ring is R_1^1. Within any given B-fraction, the number fractions of the smaller rings are greater than those of the larger rings, which is also an expected result. But when all number fractions are compared together, as in Figure 4, we see that the number fraction of R_2^1 is less than that of R_1^4 at all extents of reaction. This may look surprising at first, since R_2^1 contains 100 links while R_1^4 contains 200. The concentration of one chain end around the other is larger for the ring with fewer links. However, the rate of appearance of any given ring is given by a product where this concentration of chain ends is one of the factors. The other factor is the concentration of the linear chain that may react to give the particular ring in question. Therefore, if the ring precursor is abundant enough, it may more than compensate for a low value of the end-to-end distance concentration. If we study the weight fraction of homogeneous rings for the same case, as in Figure 5, we see the same trend just described. In both figures, rings of order 3 can hardly be seen. We obtained similar results for all the cases proposed in Tables 1−3.

These results suggest that it is very reasonable to set a limit on the *order* of the rings allowed in each fraction, as was done in the proposed model, rather than setting a global limit on the maximum *size* (in links) of allowed rings. Furthermore, for all the cases tried in this paper, rings of order 3 could safely be neglected, and it is even reasonable to think of neglecting rings of order 2 for an approximate model. In that case, where only rings of order $R = 1$ would be allowed, the required number of species would be $6N + 1 + 2N(N - 1)$.

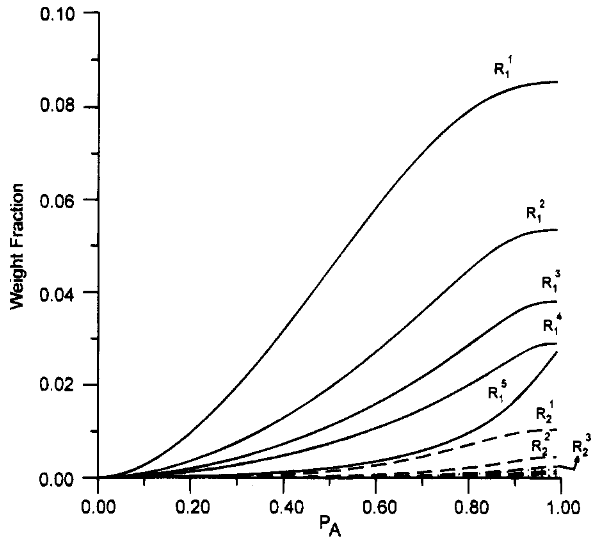

Figure 5. Weight fraction of all homogeneous rings in case P5EB using the simultaneous reaction model.

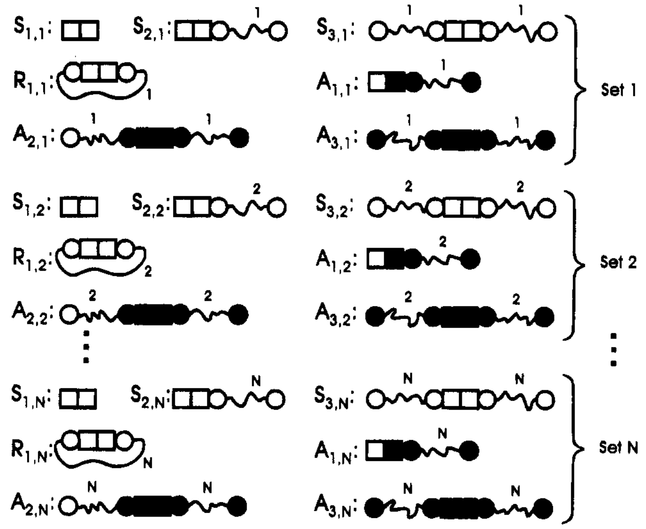

Figure 6. Species needed to describe the copolymerization of a bifunctional A-monomer with a polydisperse B-oligomer made up of N monodisperse fractions using the separate reaction model.

(b) The "Separate Reaction" Model. In this model we again take a polydisperse bifunctional B-oligomer as a mixture of N monodisperse fractions of size i, where N is any finite fixed integer. However, we do not allow these monodisperse $(B_2)_i$ fractions to be simultaneously available for reaction with any other molecule; they are set up as N isolated systems with the appropriate amount of A-monomer. The necessary species are shown in Figure 6. Notice that in this model the only rings allowed are of order $R = 1$. Notice also that within each set only one length of B-oligomer is present, and since the A-monomer is monodisperse, each set really contains a monodisperse system. We need one such set of species for each B-oligomer fraction. The total number of species is then $7N$, considerably fewer than the number that would be required for a comparable "separate reaction" model (one where only rings of order $R = 1$ were allowed).

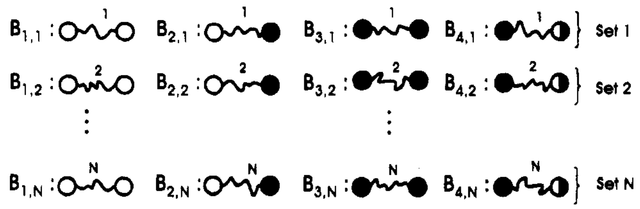

Figure 7. B-species used in the separate reaction model.

It is convenient to define the set of B-structures shown in Figure 7. Their concentrations are found through those of the A-structures as

$$B_{4,i}(t) = R_{1,i}(t)$$

$$B_{3,i}(t) = \frac{1}{2}(A_{1,i}(t) + A_{2,i}(t) + 2A_{3,i}(t))$$

$$B_{2,i}(t) = S_{2,i}(t) + 2S_{3,i}(t) + A_{2,i}(t)$$

$$B_{1,i}(t) = B_{1,i}(0) - B_{4,i}(t) - B_{3,i}(t) - B_{2,i}(t) \qquad i = 1...N$$

The N systems in Figure 6 are made to react separate and simultaneously. In the final step, the species from the N systems are combined using probability theory to give the final product.

In order to mathematically achieve the "separate and simultaneous reaction", we set up a system of kinetic differential equations for each set of structures. The equations from any one set are completely self-contained; they are independent of the other sets. The equations are

$$S'_{1,i}(t) = -2kS_{1,i}(t)B_{0,i}(t)$$

$$S'_{2,i}(t) = 4kS_{1,i}(t)B_{1,i}(t) - kS_{2,i}(t)(A_{0,i}(t) + B_{0,i}(t) + C_i)$$

$$S'_{3,i}(t) = 2kS_{2,i}(t)B_{1,i}(t) - 2kS_{3,i}(t)A_{0,i}(t)$$

$$R'_{1,i}(t) = kS_{2,i}(t)C_i$$

$$A'_{1,i}(t) = 2kS_{1,i}(t)B_{2,i}(t) + kS_{2,i}(t)A_{0,i}(t) - kA_{1,i}(t)B_{0,i}(t)$$

$$A'_{2,i}(t) = kS_{2,i}(t)B_{2,i}(t) + 2kA_{1,i}(t)B_{1,i}(t) + 2kS_{3,i}(t)A_{0,i}(t) - kA_{2,i}(t)A_{0,i}(t)$$

$$A'_{3,i}(t) = kA_{1,i}(t)B_{2,i}(t) + kA_{2,i}(t)A_{0,i}(t) \qquad i = 1...N$$

Here $A_{0,i}(t)$ and $B_{0,i}(t)$ are the concentrations of unreacted A-sites and B-sites, respectively, defined as

$$A_{0,i}(t) = 2S_{1,i}(t) + S_{2,i}(t) + A_{1,i}(t)$$

$$B_{0,i}(t) = 2B_{1,i}(t) + B_{2,i}(t)$$

The initial conditions are for $i = 1...N$

$$A_{1,i}(0) = [\text{A-monomer}](0)$$

$$B_{1,i}(0) = \sum_{m=1}^{N} [\text{B-oligomer}]_m(0)$$

This choice of initial conditions gives each of the N sets the same molar concentration of species and the same stoichiometric imbalance as those present in the original system. This is done to ensure that the ring–chain competition, which is driven by a relative concentration difference, will not be artificially biased in any one set.

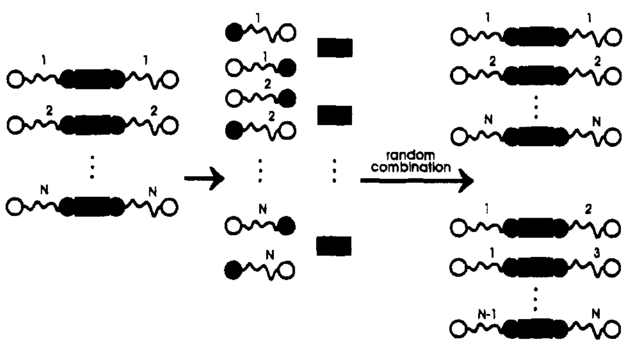

Figure 8. Reconstruction of all trimers from the ones obtained in the separate reaction model.

If we could solve the equations analytically, then it would be possible to solve the equations from each set sequentially and then combine the species as needed to give the complete reaction product at any time t. However, we can only solve this system numerically, and so it is necessary for us to be able to combine species from all the sets at the same time step. One way to achieve this is to solve all the equations simultaneously, even though there are N sets of independent equations. This is the approach we have chosen.

In order to build back the "real" reacting system at any time t, where all B-fractions are present, we take a fraction of everything present in each of the N sets. These fractions are proportional to the number fraction of the particular B_i, $i = 1...N$, that is present in each set. That is

$$S_{i,j}(t)|_{\text{mix}} = S_{i,j}(t)|_{\text{set}j} \frac{[\text{B-oligomer}]_j(0)}{\sum_{m=1}^{N} [\text{B-oligomer}]_m(0)} \qquad i = 1...3, \quad j = 1...N$$

$$A_{i,j}(t)|_{\text{mix}} = A_{i,j}(t)|_{\text{set}j} \frac{[\text{B-oligomer}]_j(0)}{\sum_{m=1}^{N} [\text{B-oligomer}]_m(0)} \qquad i = 1...3, \quad j = 1...N$$

$$R_{1,j}(t)|_{\text{mix}} = R_{1,j}(t)|_{\text{set}j} \frac{[\text{B-oligomer}]_j(0)}{\sum_{m=1}^{N} [\text{B-oligomer}]_m(0)} \qquad j = 1...N$$

In the above equations the subscript "mix" corresponds to concentrations in the "real" mixture that the method intends to evaluate, and the subscript "set" corresponds to concentrations in one of the artificial separate sets that are used as intermediate steps in the calculation. This procedure gives as a result a system with the correct total concentration of species. The concentrations of monomers, rings, dimers, and reacted dimers should also be correct. However, there are no trimers with B-oligomers belonging to different fractions, and these should clearly be present in the real system. In order to solve that, we take all species $S_{3,i}|_{\text{mix}}$, $i = 1...N$, decompose them into their elements, and combine them again at random. The same procedure is applied to species $A_{2,i}|_{\text{mix}}$ and $A_{3,i}|_{\text{mix}}$, $i = 1...N$. Figure 8 summarizes the idea.

At this point the concentrations of long species may be estimated through the auxiliary structures in a manner analogous to the one used in the "simultaneous reaction" model and in the original kinetic recursive[9] model. With these concentrations and those of the short species, which were calculated from the differential equations, it is possible to construct the number distribution of species. From this distribution, all molecular parameters may be calculated using standard methods.

Results and Discussion

We have presented two models for the copolymerization of a monodisperse bifunctional A-monomer with a polydisperse bifunctional B-oligomer when rings of up to a certain fixed order R are allowed. The "simultaneous reaction" model is a direct extension of the original kinetic recursive model.[9] Therefore it should be subject to the same kind of errors. Errors will depend on the dilution of the system, because the competition between inter- and intramolecular reaction is driven by a relative concentration difference. If the local concentration of unreacted chain ends that belong to the same molecule is greater than the average concentration of chain ends, as would be the case in a dilute system, intramolecular reaction will be favored. As the system gets more and more dilute, the bias toward ring formation increases, and so larger and larger rings will form in nonnegligible amounts. And since the original kinetic recursive model neglects rings larger than a certain fixed order R, its errors will increase with increasing dilution. It has been shown[10] that the original model with only a few sizes of rings allowed gives good results for systems with low to moderate dilution and is less reliable at very high dilutions (<5% polymer) where rings of larger size cannot be neglected. The same should be true for this model. The "separate reaction" model, on the other hand, uses the extra approximation that each of the B-fractions may be treated separately from the rest and that the final reaction product may be calculated by combining the products of the artificial separate reactions according to probability theory. There is a significant saving in the number of differential equations required when this extra approximation is used. Our final aim is to treat systems where networks can form (that is, where the chain extender A_f has a functionality $f > 2$). In those systems the difference in the number of required differential equations is even higher, and so this second model is of interest.

We want to evaluate the validity of this extra approximation in the "separate reaction" model. One way to do this is to compare its predictions with those of an exact model under conditions where the only difference between them is this extra approximation. The simultaneous reaction model is a good candidate to be used as this kind of reference. When all our assumptions are true, including the one about rings of order $R > 3$ being negligible, it is exact. If we want the two models to operate under identical assumptions, except for the one we want to test, then we should neglect all rings of order $R > 1$, since the separate reaction model was formulated for this situation. In this way we get the reference model we need to evaluate the extra approximation in the separate reaction model.

Both models reduce to the correct solution in the ideal case, that is, when no rings are allowed. If the B-oligomer is monodisperse, both models agree completely. We have also compared the two models for the same arbitrary systems used for the evaluation of the simultaneous reaction model. The systems are summarized in Tables 1−3.

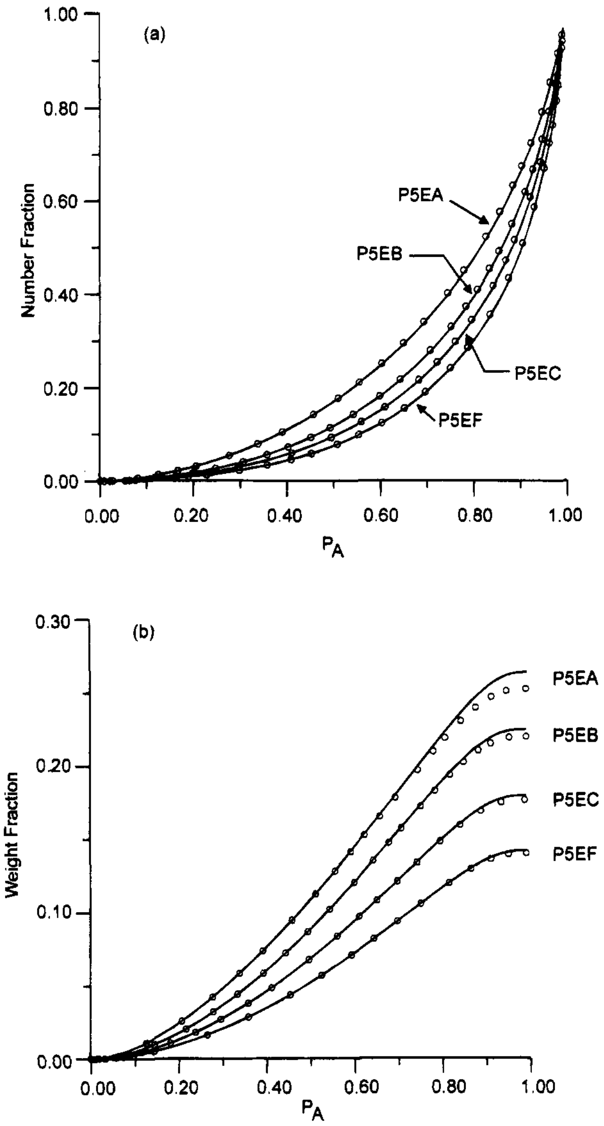

Figure 9. (a) Number fraction and (b) weight fraction of all rings vs the extent of reaction for some of the systems in Table 2. Full lines: simultaneous reaction model; circles: separate reaction model.

We show in parts a and b of Figure 9 the prediction of the weight fraction and number fraction of the sum of all rings for cases P5EA, P5EB, P5EC, and P5EF, respectively. The remaining cases with uniform distribution are omitted for clarity. The results are almost identical for the polymers with the other two distributions. The prediction is very good in all cases. For the number fraction of all rings, the largest error is 3% or less. For the weight fraction of rings the largest error is for case P5EA at complete reaction, where the error is 4%. It is interesting to note that although the number fraction of rings approaches unity at high extents of reaction, the weight fraction of rings does not. This indicates that at high conversions there are few long linear chains compared to a large number of rings.

If we study the prediction of either the weight fraction or number fraction of the individual rings, the errors are somewhat higher than those observed for the sum of all rings. As an example we show in Figure 10 the number fraction of individual rings in case P5BA. Curves are identified using the number of segments in

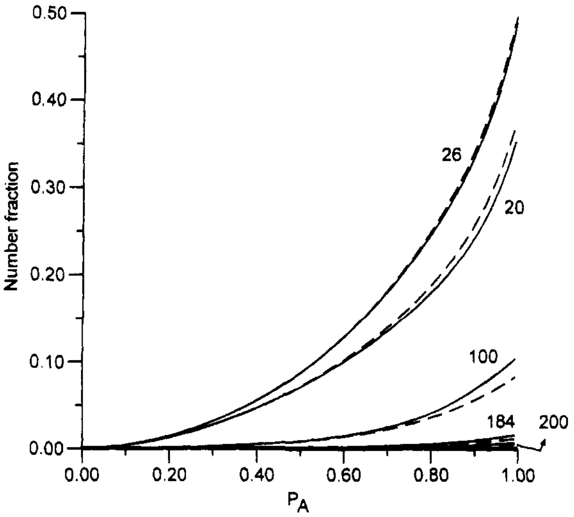

Figure 10. Number fraction of individual rings in case P5BA vs the extent of reaction. Full lines: simultaneous reaction model; dashed lines: separate reaction model. Curves are identified by the number of segments in the ring they represent.

the ring they represent. Note that the concentration of the ring with 26 links is higher than that of the ring with 20 links. This is due to the distribution of the oligomer in this sample. As indicated in Table 2, there is twice as much B-oligomer with 26 links as there is B-oligomer with 20 links. This concentration difference offsets the fact that the end-to-end distance is smaller for the shorter oligomer and results in the ring number fractions shown in the figure. The error of the separate reaction model is 6 and 10% for the rings that contain the smallest B-fractions and ranges from 20 to 29% for those that contain the remaining B-fractions. The latter, however, are ring species whose molar fraction in the total mixture is 5% or less at all times, so this error has small effect in the calculation of overall quantities, such as the weight-average molecular weight or the total number of rings. In all the cases studied we have found that the error in the prediction of individual rings with the separate reaction model is at most 10% for all those rings whose molar fraction in the mixture at the end of the reaction is more than 5%. The errors can be considerably higher for those rings with smaller molar fractions (up to 50% for the biggest ring in case P5BA, which has a molar fraction of 1% at the end of the reaction).

From a structural point of view, it is of interest to know the amount of dimers, trimers, reacted dimers, and other such species that are present in the system, without regard to their actual size. The total concentration of dimers, for example, could be found in the simultaneous reaction model as

$$\mathrm{DIM} = \sum_{i=1}^{N} S_2^i$$

and in the separate reaction model as

$$\mathrm{DIM} = \sum_{i=1}^{N} S_{2,i}$$

We show a typical prediction in Figure 11. Here DIM corresponds to the number fraction of dimers, DIMR to the number fraction of dimers reacted on one end, TRIM to the number fraction of trimers, and TRIMR to the number fraction of trimers reacted on one end. The agreement is very good in all cases studied. Errors range from 2 to 5% for all species except dimers. When the number fraction of dimers in the total mixture is less than 5%, the errors in its prediction can be of the order of 30%. In Figure 11 the largest error is for DIM at $P_A = 0.85$, where the simultaneous reaction model predicts a number fraction of 3.66%, and the separate reaction model predicts 2.85%. This gives an error of 28%.

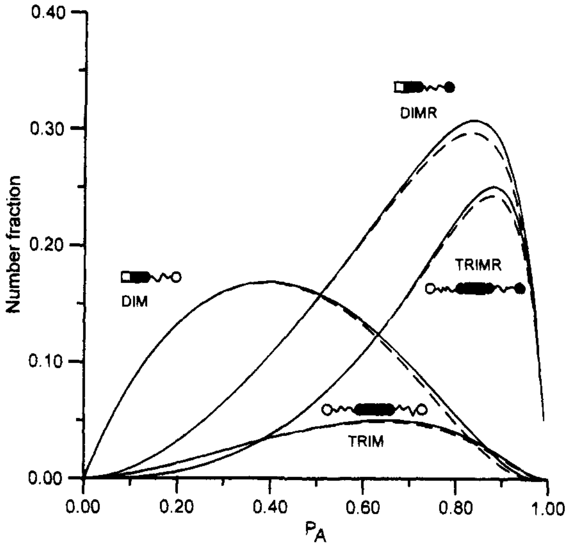

Figure 11. Number fraction of all dimers, reacted dimers, trimers, and singly reacted trimers in case P5LH. Full lines: simultaneous reaction model; dashed lines: separate reaction model.

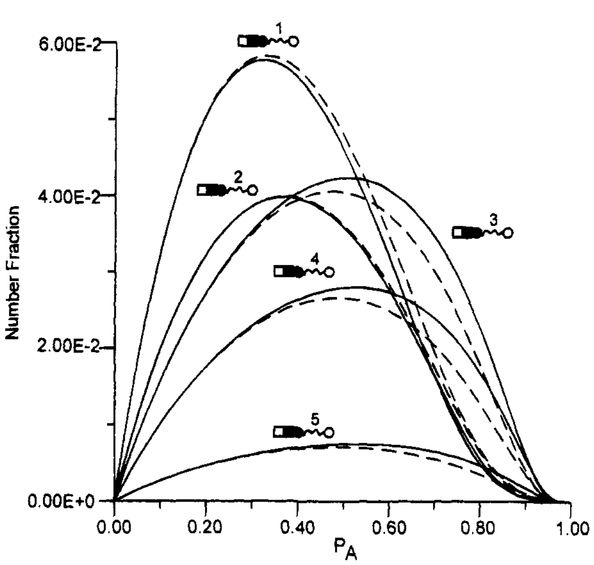

Figure 12. Number fraction of all species that make up DIM in Figure 11. Full lines: simultaneous reaction model; dashed lines: separate reaction model.

The structures shown in Figure 11 are global or aggregated structures, made up of the sum of several individual structures that involve B-oligomers of different sizes. The predictions of number fractions of the particular species that make up those aggregated structures have a somewhat higher error, as can be seen from the example in Figure 12. Similar results are found for all aggregated structures in all cases from Tables 1–3.

The separate reaction model introduced another approximation in order to account for the particular trimers present in the reacting mixture, some of which

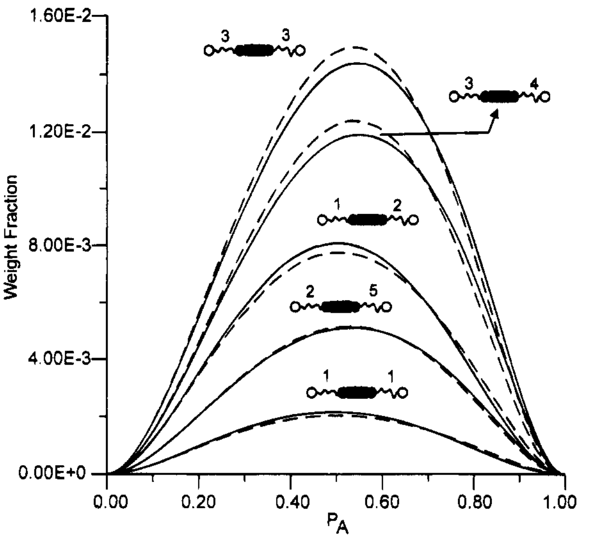

Figure 13. Weight fraction of particular trimers in case P5BC. Full lines: simultaneous reaction model; dashed lines: separate reaction model.

have B-oligomers of different lengths. As explained above, after mixing the structures from each of the *N* artificial separate systems, only structures with B-oligomers from the same fraction exist. In order to be able to account for the species that have B-oligomers of different sizes, the model takes all species $S_{3,i}|_{\mathrm{mix}}$, $i = 1...N$, decomposes them into their elements, and combines them again at random. The same procedure is applied to species $A_{2,i}|_{\mathrm{mix}}$ and $A_{3,i}|_{\mathrm{mix}}$, $i = 1...N$. Figure 8 summarizes the idea. This extra approximation may be tested by calculating the weight fraction of several trimers, some with B-oligomers of equal size and some with B-oligomers of different sizes, for a case where the prediction of the number fraction of all trimers (TRIM) has almost no error. The results for a few structures are shown in Figure 13 for case P5BC. The maximum error is 6%, indicating that this is indeed a good approximation.

If we calculate the weight-average molecular weight of the reacting mixture with either model, we find a very small difference. The question might arise of whether going to the trouble of calculating ring formation in a polydisperse system is really worthwhile. In order to evaluate that, we have calculated several quantities using the two models proposed in this paper together with other simpler models. These other models are (a) copolymerization of a polydisperse system with no ring formation allowed, (b) copolymerization of a monodisperse system with B-oligomers whose weight equals the M_n of the real system with no rings allowed, (c) copolymerization of a monodisperse system with B-oligomers whose weight equals the M_w of the real system and no rings are allowed, (d) copolymerization of a monodisperse system with B-oligomers whose weight equals the M_n of the real system and with rings of order 1 allowed, and (e) copolymerization of a monodisperse system with B-oligomers whose weight equals the M_w of the real system and with rings of order 1 allowed. We show in Figure 14 the weight-average molecular weight calculated using the simultaneous reaction model, the separate reaction model, and models a, b, and c. In Figure 15 we calculate the weight-average molecular weight using the simultaneous reaction model, the separate reaction model, and models d and e. We see that the simpler models give errors that can be sizable. In order to quantify that, we show in Table 4 the predicted weight-average molecular weight for case P5EA at several degrees of polymerization using all the models. The table shows that neglecting rings altogether gives the worst results, with predicted molecular weights that can be well over 3 times higher than the true ones. If rings of order 1 are allowed but the B-oligomer is considered monodisperse, model e predicts weights with an error of approximately 100%. Model d gives more acceptable errors at high extents of reaction but severely underestimates the weight-average molecular weight at low extents of reaction.

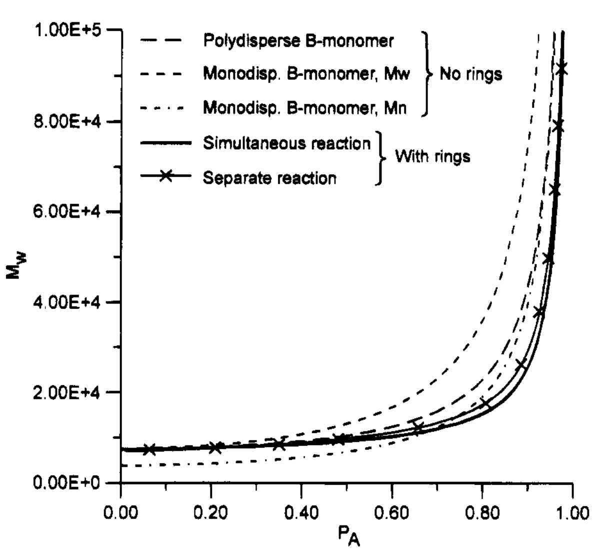

Figure 14. Weight-average molecular weight of case P5EA using the simultaneous reaction model, the separate reaction model, and three more naive approximate models that do not allow ring formation.

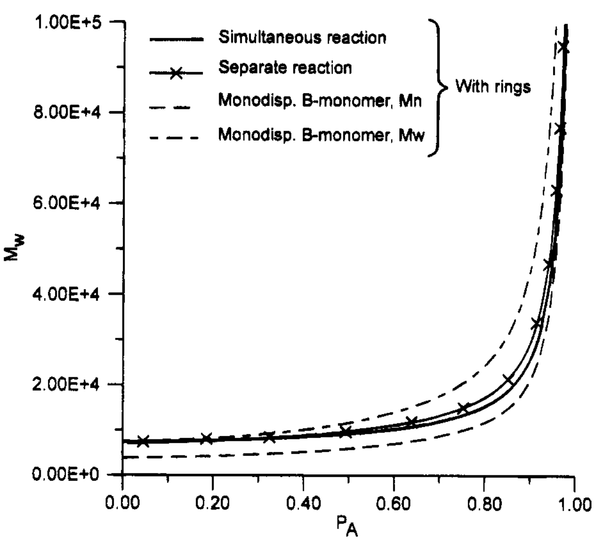

Figure 15. Weight-average molecular weight of case P5EA using the simultaneous reaction model, the separate reaction model, and two more naive approximate models that allow rings.

Conclusions

In this paper we have presented two models that deal with the problem of copolymerization with intramolecular reaction when one of the reactants is polydisperse. One of them, the simultaneous reaction model, was formulated for cases where rings of up to order $R = 3$ are allowed. We found that in the cases we studied most of the rings of order 1 are in greater concentration than

Table 4. Predictions for the Weight-Average Molecular Weight for Case P5EA at Five Different Extents of Reaction Using Different Models

	models with rings				models without rings		
P_A	simult reaction	separate reaction	(d)	(e)	(a)	(b)	(c)
0.3	8 075	8 149	4 642	8 933	8 361	4 821	9 248
0.5	9 225	9 787	5 951	11 669	10 420	6 860	13 074
0.90	25 570	29 205	21 036	45 511	43 908	39 900	76 300
0.95	48 045	54 907	41 964	89 233	86 524	82 957	154 531
0.99	230 489	261 840	209 566	461 380	425 021	418 160	797 268

most of the rings of order 2, regardless of their size in links. Rings of higher orders are practically negligible. This behavior suggests that the order R of the ring is more important than its size when establishing a truncation strategy for the types of allowed rings. The other model, separate reaction, was formulated for the case where only rings of order $R = 1$ may form.

The relationship between the different sizes and orders of rings may seem surprising at first because the end-to-end distance is greater the shorter the chain is. However, the rate of appearance of any given ring is given by a product where this concentration of chain ends is one of the factors. The other factor is the concentration of the linear chain that may react to give the particular ring in question. Therefore, if the ring precursor is abundant enough, it may more than compensate for a low value of the end-to-end distance concentration. This explains the behavior we found in the simultaneous reaction model.

We have compared both models for the case where only rings of order $R = 1$ may form. Under that condition the simultaneous reaction model is exact. For that same case the other model is an approximation. The approximate model requires $7N$ equations, while the exact one requires $6N + 1 + 2N(N - 1)$. This savings in the number of equations comes at a price: the weight or number fraction of some species in the reacting mixture may have an error of up to 30% in the cases we tried. The weight-average molecular weight, on the other hand, suffers a very small error. While the separate reaction model is an approximation and has some errors in its predictions, these predictions are much better than those obtained using simpler probability models that neglect either the polydispersity of the B-oligomer, the possibility of ring formation, or both.

To our knowledge, this is the first time that probability models have been presented to deal with this problem. The simultaneous reaction model can always be used whenever the errors involved in the separate reaction model are inadmissible. However, we feel that the latter is promising for treating systems where the functionality of the chain extender is greater than 2, that is, for network-capable systems. In such systems the saving in the number of equations would be even greater than in the systems studied in this paper, and in some instances it would be the only way to keep the problem tractable. We are currently studying one such system.

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Appendix

Differential equations for the nonhomogeneous structures of the simultaneous reaction model with rings of up to order 3 are as follows:

$$\begin{aligned} S_3^{m,n}(t)' = {} & 2kS_2^m(t)B_1^n(t) + 2kS_2^n(t)B_1^m(t) - \\ & 2kS_3^{m,n}(t)A_0(t) \end{aligned}$$

$$\begin{aligned} S_5^{m,n}(t)' = {} & 2kS_3^{m,n}(t)S_1(t) + kS_2^m(t)S_2^n(t) + \\ & 4kS_4^m(t)B_1^n(t) - kS_5^{m,n}(t)[A_0(t) + B_0(t) + C_{m+n}] \end{aligned}$$

$$\begin{aligned} S_7^{m,n}(t)' = {} & 2kS_5^{m,n}(t)S_1(t) + 2kS_5^{n,m}(t)S_1(t) + \\ & 2kS_2^m(t)S_4^n(t) + 2kS_2^n(t)S_4^m(t) - kS_7^{m,n}(t)[2B_0(t)] \end{aligned}$$

$$\begin{aligned} S_6^{m,m,n}(t)' = {} & 2kS_5^{m,n}(t)B_1^m(t) + kS_2^m(t)S_3^{m,n}(t) + \\ & 2kS_3^{m,m}(t)S_2^n(t) + 2kS_5^{m,m}(t)B_1^n(t) - kS_6^{m,m,n}(t)[2A_0(t)] \end{aligned}$$

$$\begin{aligned} S_6^{m,n,m}(t)' = {} & 2kS_5^{n,m}(t)B_1^m(t) + kS_2^m(t)S_3^{m,n}(t) - \\ & kS_6^{m,n,m}(t)[2A_0(t)] \end{aligned}$$

$$\begin{aligned} S_8^{m,m,n}(t)' = {} & 2kS_6^{m,m,n}(t)S_1(t) + kS_2^m(t)S_5^{m,n}(t) + \\ & 2kS_4^m(t)S_3^{m,n}(t) + kS_5^{m,m}(t)S_2^n(t) + 4kS_7^{m,m}(t)B_1^n(t) - \\ & kS_8^{m,m,n}(t)[A_0(t) + B_0(t) + C_{m+m+n}] \end{aligned}$$

$$\begin{aligned} S_8^{m,n,m}(t)' = {} & 4kS_6^{m,n,m}(t)S_1(t) + kS_2^m(t)S_5^{n,m}(t) + \\ & 2kS_4^m(t)S_3^{m,n}(t) + kS_5^{m,n}(t)S_2^m(t) + 2kS_7^{m,n}(t)B_1^m(t) - \\ & kS_8^{m,n,m}(t)[A_0(t) + B_0(t) + C_{m+n+m}] \end{aligned}$$

$$\begin{aligned} S_8^{n,m,m}(t)' = {} & 2kS_6^{m,m,n}(t)S_1(t) + kS_2^n(t)S_5^{m,m}(t) + \\ & 4kS_4^n(t)S_3^{m,m}(t) + kS_5^{n,m}(t)S_2^m(t) + 2kS_7^{m,n}(t)B_1^m(t) - \\ & kS_8^{n,m,m}(t)[A_0(t) + B_0(t) + C_{n+m+m}] \end{aligned}$$

$$R_2^{m,n}(t)' = kC_{m+n}(S_5^{m,n}(t) + S_5^{n,m}(t))$$

$$R_3^{m,m,n}(t)' = kC_{m+m+n}(S_8^{m,m,n}(t) + S_8^{m,n,m}(t) + S_8^{n,m,m}(t))$$

$$\begin{aligned} A_2^{m,n}(t)' = {} & 2kA_1^n(t)B_1^m(t) + kS_3^{m,n}(t)A_0(t) + \\ & kS_2^m(t)B_2^n(t) - kA_2^{m,n}(t)A_0(t) - kS_5^{n,m}(t)C_{n+m} - \\ & k\sum_{i=1}^{N} S_8^{i,n,m}(t)C_{n+m+i} \end{aligned}$$

$$\begin{aligned} A_3^{m,n}(t)' = {} & kA_2^{m,n}(t)A_0(t) + kA_2^{n,m}(t)A_0(t) + \\ & kA_1^m(t)B_2^n(t) + kA_1^n(t)B_2^m(t) - k\sum_{i=1}^{N} (S_8^{m,n,i}(t) + \\ & S_8^{n,m,i}(t))C_{n+m+i} \end{aligned}$$

$$\begin{aligned} S_6^{m,n,l}(t)' = {} & 2kS_5^{n,l}(t)B_1^m(t) + kS_2^m(t)S_3^{n,l}(t) + \\ & kS_3^{m,n}(t)S_2^l(t) + 2kS_5^{n,m}(t)B_1^l(t) - kS_6^{m,n,l}(t)[2A_0(t)] \end{aligned}$$

$$S_8^{m,n,l}(t)' = 2kS_6^{m,n,l}(t)S_1(t) + kS_2^{m}(t)S_5^{n,l}(t) + 2kS_4^{m}(t)S_3^{n,l}(t) + kS_5^{m,n}(t)S_2^{l}(t) + 2kS_7^{m,n}(t)B_1^{l}(t) - kS_8^{m,n,l}(t)[A_0(t) + B_0(t) + C_{m+n+l}]$$

$$R_3^{m,n,l}(t)' = kC_{m+n+l}(S_8^{m,n,l}(t) + S_8^{n,m,l}(t) + S_8^{m,l,n}(t) + S_8^{n,l,m}(t) + S_8^{l,m,n}(t) + S_8^{l,n,m}(t))$$

In all these equations $m \neq n \neq l$, $m = 1...N$, $n = 1...N$, and $l = 1...N$.

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