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(36) The force profile for PS-PEO(184K) is given in ref 14.
(37) We observe no evidence of PS-X micellizing in the toluene or xylene; more direct evidence for absence of any micellization in a very similar system, polyisoprene-X in toluene, is presented in ref 17. Moreover, there is no evidence for PS-PEO in micellizing in toluene, a good solvent for both blocks (also: Gast, A. P., private communication).
(38) At the monomer concentrations, in the gap between the surfaces, associated with the high compressions $E(D')$, which are around $\phi \cong 0.1$, the approximation $\Pi(\phi) \propto \phi^2$ is good to about 1% (within the Flory-Huggins model). Use of the scaling expression $\Pi \propto \phi^{9/4}$ would not make a great difference in view of the spread in D' due to the scatter in the magnitude of the forces.
(39) We ignore the (weak) elastic contribution to $f(D)$ appearing in eq 3 and also neglect $\Gamma^2/(2L_0)$ relative to Γ^2/D', both of which are good approximations at $D' \ll 2L_0$.
(40) R_0 for PS in toluene is evaluated from[41] $R_0 = 0.69M_w^{0.5}$ (Å) while R_F for PS in toluene is evaluated from[42] $R_F = 0.32M_w^{0.585}$ (Å) where M is the PS molecular weight, from ref 41 and 42.
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Registry No. PS, 9003-53-6; (EO)(S) (block copolymer), 107311-90-0; toluene, 108-88-3; xylene, 1330-20-7.

Validity of Some Approximations Used To Model Intramolecular Reaction in Irreversible Polymerization

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ABSTRACT: We identify the main approximations underlying several methods that have been used to model stepwise, irreversible copolymerizations with intramolecular reaction allowed, and we study their ranges of validity. In order to do this, all approximations are applied to the linear $A_2 + B_2$ system, for which comparison against an exact solution is possible. We also combine approximations found in different models to give "hybrid" models. We have found that for this linear system some approximations never give good results, others may be used when ring formation is low, and the better ones may be applied with low to moderate levels of intramolecular reaction. None of them is satisfactory when ring formation is very high.

Introduction

Modeling of intramolecular reaction in stepwise, irreversible polymerization is an old problem that has not been completely solved for most systems. When the monomers have only two reactive sites (linear system), the problem can in principle be solved to any desired degree of accuracy using either a purely kinetic[1,2] or a kinetic recursive[3] model. Network-forming systems are much more complicated, and no exact solution is available for them. Modeling of such systems has been attempted using approximate treatments such as spanning tree,[4,5] rate theory,[6-8] or kinetic recursive[3] methods. Each of these methods is based on one or more approximations with varying degrees of accuracy; the models will be as reliable as the approximations on which they are based.

In this paper we study the range of validity of some of these approximations as applied to the linear system, where comparison against an exact solution can be made. In this way we expect to gain insights that will help us in the treatment of network-forming systems. In a future paper[9] we will show results obtained from several approximate treatments applied to a network-forming system and discuss the possibility of choosing a "best" method in light of the findings for the linear system.

Reference Model for Linear Polymerization

We want to model the copolymerization reaction of the difunctional monomers A–A and B—B. In this paper we choose for simplicity that A–A is small and B—B is long and flexible enough to have a Gaussian end-to-end distance distribution. Reaction is stepwise and irreversible; only A–B bonds may form. We assume equal reactivity of all groups and absence of substitution effects. Intermolecular reaction leads to the appearance of linear molecules or chains. In this system intramolecular reaction is also allowed: reaction occurs between reactive sites that belong to the same molecule. The closed structure that results from intramolecular reaction is called a ring or loop.

An unreacted B-site on an A···B chain may either react with the A-site on the other end of that same chain or with an A-site on a different molecule. These are competing reactions that result in either rings or chains, so in the literature it is common to speak of a chain–ring competition. An unreacted site will favor one of these reactions with a probability given by the relative concentration of unreacted sites belonging to other molecules against the concentration of the other end of the chain about the site in question. The latter concentration is calculated using a Gaussian density. All models studied in this paper refer to the system just described, although they may be modified to allow for other than Gaussian chain-end densities and for unequal reactivity or substitution effects.

The most rigorous possible description of the above polymerization process would require setting up a kinetic differential equation for each of the molecular species involved. This would result in an infinite set of simultaneous differential equations. The true, exact solution of this problem is not available.

If this infinite system is truncated, it may be solved, giving an approximation to the exact solution. This is the purely kinetic approach.[1] In order to keep the truncation error reasonably small, huge numbers of equations are needed. Systems of about 400 equations are reported in the literature for the process at hand.[2] The solution of this large system is an approximation to the exact solution, and it may be improved as much as desired, just by increasing the number of equations. This can be done but is computationally very expensive.

An approximation to the exact solution may be found in a different way. We recently developed a combined kinetic–recursive method[3] for calculating molecular and network parameters in polymerization systems—both linear and network forming—which have intramolecular reactions. The general approach used combines kinetic and Markovian analysis; Miller and Macosko discuss it generally in a recent paper.[9] The idea of combining two different techniques may also be found in some nonkinetic models.[8]

Intramolecular reactions lead to the appearance of closed structures or rings of several sizes. To identify them, we define a k-order ring as one having k A-monomer units in it. In our model, rings of up to a certain finite fixed value of k are allowed; all others are forbidden (that is, they are considered to have zero rate of formation).

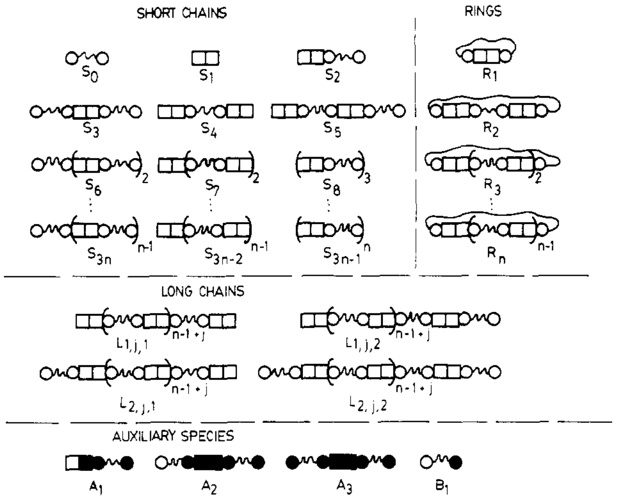

Figure 1. Species needed to describe the linear copolymerization of A–A + B—B using the kinetic–recursive method. In species A_1, A_2, A_3, and B_1 dark areas represent reacted sites and light areas represent unreacted sites.

Our method is based on an exact calculation of concentration of small species and of certain auxiliary structures. For example, we see in Figure 1 all the necessary configurations needed to describe the linear copolymerization. Here molecular species are partitioned into four classes: short chains (S_0, S_1, ..., S_{3n}), rings (R_1, R_2, ..., R_n), long chains (L's), and auxiliary structures. All these molecular species react with one another to give other molecular species. For example S_1 reacts with S_2 to give S_4, and S_2 reacts intramolecularly to give R_1.

Both short and long chains are composed of overlapping auxiliary structures, A_1, A_2, and A_3. For example, S_4 contains two A_1 structures, and S_8 contains one A_1, one A_2, and one A_3 structure.

A system of simultaneous kinetic differential equations is set up to describe the rates of interconversion of short chains, rings, and auxiliary species as functions of time. The size of the system depends on the order N of the largest ring allowed. Since, as shown in Figure 1, description of the linear copolymerization requires $3N$ short chains, N rings, and 3 auxiliary species, a system of $4N + 3$ simultaneous differential equations results. After numerically solving this system, we use the auxiliary structures and the approximately recursive nature of the larger molecules to "build back" the long chains.

In the notation used in Figure 1, any chain with N or less A-monomer units is considered short. So we know that a long chain has at least $N + 1$ A-monomer units. If we randomly select a long chain by taking a chain end, the chosen end will be an A_1 or A_2 structure; at least $N - 1$ A_3 structures will follow, and the other end will be an A_1 or A_2 structure. We can then divide a long chain in two parts: a "root" of known length and composition and an "extension". The situation is pictured in Figure 2.

The auxiliary species, A_1, A_2, and A_3, are part of both short and long chains. Simple arithmetic manipulations allow us to calculate how many of those auxiliary structures make up long chains and furthermore how many of them are on the extension part. Then, assuming that the auxiliaries in the extension follow the most probable (Geometric) distribution, the concentration of each of the long chains may be calculated. The error involved in the assumption of Geometric distribution in the extension is negligible, as we have shown already.[3] So we have the

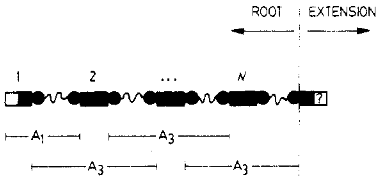

Figure 2. Root and extension of a long chain. In this example the randomly chosen end is an A_1 structure.

Table I

case	% polymer	% inert solv
C100	100	0
C50	50	50
C25	25	75
C10	10	90
C05	5	95

$MA_2{}^a = 134$
$MB_2{}^b = 3000$
$r^c = [A_2]_0/[B_2]_0 = 1$
$n_B{}^d = 100$
$l_B{}^e = 2.5$ Å

[a] MA_2 = molecular weight of the A–A monomer. [b] MB_2 = molecular weight of the B–B monomer. [c] r = stoichiometric imbalance. $[A_2]_0$ = initial concentration of the A–A monomer. $[B_2]_0$ = initial concentration of the B–B monomer. [d] n_B = number of links in the B–B monomer. [e] l_B = effective link length in the B–B monomer.

concentration of short chains and rings given directly by the solution of the differential equations and that of long chains calculated from auxiliary species using a slight approximation. This information may be organized to give the number distribution of all species. Then, all molecular parameters such as M_n, M_w, weight fraction of rings, etc., may be computed by standard methods.

The main approximation of the method lies in the assumption that rings of order greater than N are not important. By taking a large enough N, we can get a good approximation to the true answer. We calculated the weight distribution of species for all the arbitrary chemical systems in this paper using increasing values of N until no further change could be achieved. Depending on the system and the degree of dilution of the reaction, the required value of N to obtain constant answers ranged from 10 to 40.

Therefore, we take as a reference model the combined kinetic recursive model with rings up to order 40. This means solving a system of 163 simultaneous differential equations. The system is solved numerically using a library subroutine based on Gear's method.[11] It is a backward differentiation method suited for solving stiff problems. Run times depend on the extent of reaction P_A wanted. Calculations up to $P_A = 0.99$ with the reference model take about 7 min on a VAX 11/780.

Different states of dilution of an arbitrary chemical system are used for comparison purposes. They are summarized in Table I.

Spanning Tree Model

Gordon and co-workers developed a method for calculating molecular parameters (such as weight average molecular weight, weight fraction of soluble material, etc.) in chemical systems which undergo irreversible, stepwise copolymerization using the theory of stochastic branching processes.[12] The technique is strictly applicable to systems where rings are forbidden. In such systems molecules may be pictured as family trees. A monomer unit picked at random is the root, the units connected to the root are the first generation, and so on. Since roots are picked at random, the tree is really statistical in nature. The theory of stochastic branching processes—sometimes called "cascade theory"—provides a way of generating these statistical trees, thus modeling the ring-free reacting system.

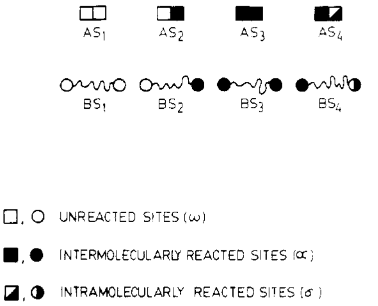

Figure 3. Species for A–A and B—B copolymerization using the spanning tree method.

In order to take ring formation into account, the above authors modified their previous model.[2,4,5] Given any molecule, intermolecularly reacted sites are labeled with α's and unreacted sites with ω's. Sites that reacted intramolecularly are labeled with σ's. The σ-sites are then considered dead ends in a ring-free molecule, as if the intramolecular bond has been broken retaining its σ label. Trees are generated in the same way as in the rings forbidden model using a fictitious extent of reaction based on the number of α-sites and taking both ω- and σ-sites as dead ends. In other words, σ-sites are randomly distributed in a tree structure. Such trees are called "spanning trees".

Gordon and co-workers formulated this model in terms of probability generating functions (PGF). That is not strictly necessary. The PGF is really a transform technique with no physical meaning. Furthermore, it is not part of the model itself; it is just a mathematical tool used to solve it. The same model may be formulated in a different way.[13] We have verified that the following treatment is totally equivalent to that of Gordon:

We keep track of the state of the monomeric building blocks of a particular system at each time step in the reaction. In order to describe an $A_2 + B_2$ copolymerization, for instance, the method calculates the concentrations of the eight species shown in Figure 3 as functions of time. AS_1, AS_2, AS_3, and AS_4 are the four possible states in which an A_2-unit may be found, namely, unreacted, reacted on one end, reacted on both ends (intermolecularly), and reacted on both ends, one intermolecularly and the other intramolecularly. BS_1, BS_2, BS_3, and BS_4 are the analogous four possible states of a B_2-unit. These species react with one another giving other species. Intermolecular reaction is straightforward. For example, reaction of AS_1 with any unreacted B-site gives AS_2, and reaction of BS_2 with any unreacted A-site gives BS_3. Unreacted A- and B-sites are easily accounted for, as they are on AS_1, AS_2, BS_1, and BS_2 species.

The model assumes that these building blocks combine randomly to give linear chains. That is the first approximation. Any of the physically impossible structures shown in Figure 4 can be generated under this assumption. They are "impossible" because they contain an intramolecularly reacted site on one end and either an intramolecularly reacted site of the same kind or a nonreacted site on the other end. A true ring should contain exactly two σ-sites: the A- and B-sites that reacted together to close it.

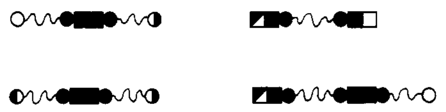

Figure 4. Some physically impossible structures that can be generated using the spanning tree approach.

There is a second approximation, this one concerning the rate of ring formation. When a ring forms, an AS_4 and a BS_4 species appear. The rate of that appearance is given by

$$d(AS_4)/dt = k\sum_{j=1}^{\infty}(\text{A–AB—B})_j C_j$$

$$d(BS_4)/dt = d(AS_4)/dt$$

where C_j = concentration of one chain end around the other for a chain containing j B-monomer units and j A-monomer units, k = kinetic rate constant, and $(\text{A–AB—B})_j$ = concentration of a chain with j A-monomer units and j B-monomer units (calculated from the species in Figure 3 assuming random combination). This is equivalent to the use of only one ring-closing concentration, C^*, averaged over all possible ring sizes. That is, if we define

$$C^* = \frac{\sum_{j=1}^{\infty}(\text{A–AB—B})_j C_j}{\sum_{j=1}^{\infty}(\text{A–AB—B})_j}$$

the rate of appearance of AS_4 could be written as

$$\frac{d(AS_4)}{dt} = kC^*(t)\sum_{j=1}^{\infty}(\text{A–AB—B})_j$$

C^* is a function of time because the concentrations of $(\text{A–AB—B})_j$ chains are functions of time.

The model just described combines kinetic and statistical analysis. The kinetic part is used to keep track of the concentration of the eight monomeric building blocks in Figure 3. This is done through a system of simultaneous differential equations. The statistical part is used to calculate average quantities that are needed in the differential equations, as C^*, or to give information about the physical properties of the system, as the gel point or the weight averages. In Gordon and co-workers' formulation[2] probability generating functions are used for the statistical part. These PGF are written as polynomials with time-dependent coefficients. In the linear system there are eight such coefficients, each one related to one of the eight monomeric building blocks already defined. The kinetic part describes the rate of change of those coefficients with time. We choose a more obvious formulation: for the kinetic part we set up a differential equation that describes the rate of change of the concentration of each monomeric building block with time, and for the statistical part we combine blocks randomly as the need arises and use a recursive method to evaluate any necessary quantities.

The effect of each of the two approximations described above may be studied separately by constructing models that involve only one of those approximations at a time. In this way we found that the use of an average ring-closing concentration results in a distortion in the size distribution of species. Both the very short and very long species are underestimated, while intermediate length ones are overestimated. Details are given in part A of the supplementary material.

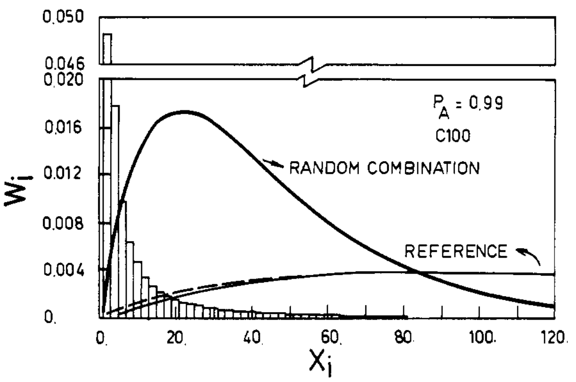

Figure 5. Weight distribution of species calculated from spanning tree and the reference models for the undiluted case C100. Dashed lines correspond to odd chains, full lines to even chains, and bars to rings.

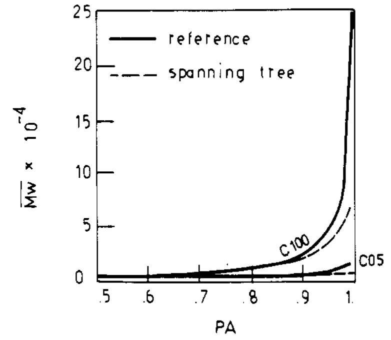

Figure 6. Predictions of weight average molecular weight.

In order to study the other approximation—random combination of monomeric building blocks—we use the reference model to simulate an arbitrary chemical reaction and decompose all the resulting molecular species into their monomeric building blocks. Then we combine these blocks at random. In this way we construct number or weight distributions of species that may be compared with the true ones. This is done in Figure 5 for case C100 at P_A = 0.99.

In Figure 5 even chains, odd chains, and rings are plotted separately for the reference model. In this context, even or odd refers to the number of monomeric building blocks that make up the chain. There is only one curve for the random combination approximation because all predicted species fall on the same curve. We see that the approximate distribution is very far from the true one. Even though the concentrations of the monomeric building blocks used are exact, those of longer molecular species cannot be reproduced at all. Random combination of the monomeric building blocks is then a bad approximation.

We conclude that both approximations in spanning tree result in deviations from the true answer that follow the same trend. Both the very short and the very long species are underestimated, while intermediate-length ones are strongly overestimated. This influences all calculations involving knowledge of the distribution of species, such as average molecular weights. Indeed, weight average molecular weight as calculated from spanning tree is always too low. Two examples are shown in Figure 6. There we plot weight average molecular weight against the extent of reaction using spanning tree and the reference model. Curves are shown for cases C100 and C05 from Table I. We see that spanning tree always underestimates M_w. Deviations from the true answer are specially dramatic near complete reaction. M_w as calcu-

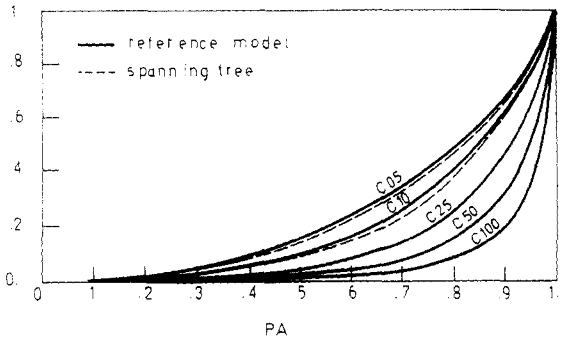

Figure 7. Total number fraction of rings from spanning tree and the reference model.

lated from spanning tree does not diverge at $P_A = 1$, as it should. This fact is only suggested by Figure 6, but it can be confirmed by close examination of the formulas for M_w. Details are given in part B of the supplementary material. In a future paper[9] we will show that this is related with the spanning tree method's ability of predicting the gel point in network-forming systems.

Spanning tree has been used by Gordon and Temple to predict the total number fraction of rings (NR).[2] It turns out that this prediction is good. In Figure 7 plots of the total number fraction of loops as predicted by spanning tree and reference models are compared. We see that spanning tree underestimates the total number fraction of rings and becomes more precise when ring formation is not extreme, just as reported by Gordon and Temple.[2]

Rate Theory

All models based on kinetic differential equations find the concentration of the various configurations defined for each of those models as functions of time. It is possible to change all time-dependent concentrations into extent of reaction-dependent concentrations by computing the extent of reaction at each time step and relating the concentrations to it.

In Stanford and Stepto's rate theory[14,15] quantities that are a function of the extent of reaction are found directly, avoiding the intermediate time-dependent functions. The method gives a description of the polymerization process limited to molecular species of up to a certain fixed size. No assumption is made about larger molecules. In principle, continuing species (see below) could be combined under specific laws so as to give the concentrations of longer molecules. This possibility has been considered by Stepto and co-workers when applying rate theory to network-forming systems.[6-8] At this point we will restrict the analysis to the main rate theory approximation, without including any assumptions for the long chains. The authors formulated the model in a way they found convenient. As with Gordon's method in the previous section, the particular formulation chosen is not inherent to the model itself; other formulations are possible. We chose to use an alternative derivation of Stanford and Stepto's method. Our notation is slightly different; we start from whole molecules rather than half-states,[14] and we find the rates of interconversion of states in a more systematic way. We have verified that the two formulations are totally equivalent.

We see in Figure 8 all the species needed to describe an A_2 + B_2 copolymerization where the largest molecules considered have N A-monomers or N B-monomers. Here TA's are chains with two unreacted A-sites, and TB's are chains with two unreacted B-sites. TE's are chains with an even number of monomer units; they have an A-site on one end and a B-site on the other. TR's are rings. TA's, TB's, TE's, and TR's are the "whole species" in Stepto's definition. All molecules with more than $2N$ monomer units make up the "continuing species" (L's). Unlike whole species, they do not have a known length. The continuing species are not used to reconstruct molecules longer than $2N$ monomer units because no assumption is made about such molecules. The model gives a description limited to the whole species. This is consistent with the originally intended application of the method, namely, the prediction of the number fraction of rings. Notice that the value of N that defines the size of the set of whole species may be as large as desired.

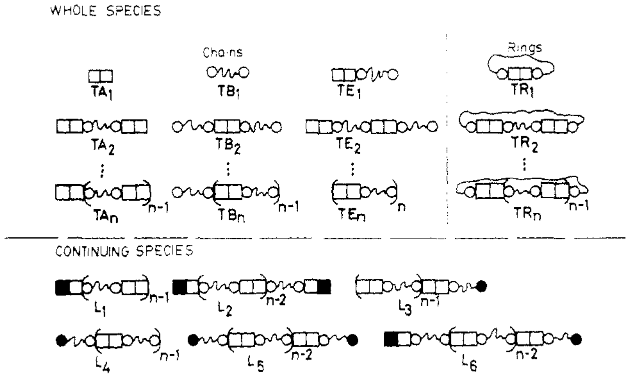

Figure 8. Species needed to describe the A–A and B—B copolymerization using rate theory.

A system of differential equations is set up which describes the rates of change of the weight fraction of the molecular species with respect to the extent of reaction. The approximations involve two stages. In the first stage, a Geometric (most probable) number distribution is assumed for the chains at each conversion for the linear reaction with no loops. The second stage concerns perturbation of this solution to take ring formation into account.

When no loops form, the possible reactions are

$$\mathrm{TA}_j + \mathrm{TB}_k \rightarrow \mathrm{TE}_{j+k-1}$$

$$\mathrm{TA}_j + \mathrm{TE}_k \rightarrow \mathrm{TA}_{j+k}$$

$$\mathrm{TB}_j + \mathrm{TE}_k \rightarrow \mathrm{TB}_{j+k}$$

$$\mathrm{TE}_j + \mathrm{TE}_k \rightarrow \mathrm{TE}_{j+k}$$

A system of differential equations is written, having the form

$$\mathrm{d}w_{\mathrm{TA}_j}/\mathrm{d}P_A = A(\mathrm{TA}_j) - D(\mathrm{TA}_j)$$

$$\mathrm{d}w_{\mathrm{TB}_j}/\mathrm{d}P_A = A(\mathrm{TB}_j) - D(\mathrm{TB}_j)$$

$$\mathrm{d}w_{\mathrm{TE}_j}/\mathrm{d}P_A = A(\mathrm{TE}_j) - D(\mathrm{TE}_j)$$

where w_{TA_j} = weight fraction of species TA_j, $A(\mathrm{TA}_j)$ = rate of appearance of species TA_j, and $D(\mathrm{TA}_j)$ = rate of consumption or disappearance of species TA_j. Similar definitions hold for w_{TB_j}, w_{TE_j}, $A(\mathrm{TB}_j)$, $A(\mathrm{TE}_j)$, $D(\mathrm{TB}_j)$, and $D(\mathrm{TE}_j)$.

All rates in the differential equations have a known expression in terms of the extent of reaction, P_A, the stoichiometric imbalance, r, and the weight fraction of each monomer, w_A and w_B. Deduction of these expressions is possible through the already mentioned assumption of Geometric number distribution in the chains. Detailed expressions for the rates of appearance and disappearance of the different species are given in part C of the supplementary material. The differential equations are

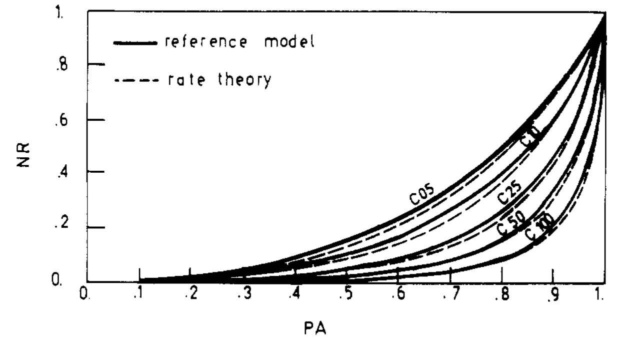

Figure 9. Total number fraction of rings as predicted by rate theory and the reference models.

independent and may be solved one at a time, an attractive feature.

When rings form, reactions like $TE_j \rightarrow TR_j$ are allowed. The second stage of the method appears now in order to compute the rate of this new reaction. It is assumed that the rate of disappearance of all linear species when rings form is the same as in the ideal (no rings) case. In particular, the rate of disappearance of TE_j must remain unaltered, but a fraction of what disappears must result in ring formation. That fraction is postulated to be

$$f(E_j, R) = \frac{\rho j^{-3/2}}{C_A + C_B + \rho j^{-3/2}}$$

where $f(E_j, R)$ = fraction of the disappearance of TE_j that goes to ring formation, $\rho j^{-3/2}$ = concentration of one end of TE_j about the other assuming a Gaussian distribution, C_A = concentration of unreacted A-sites in the bulk, and C_B = concentration of unreacted B-sites in the bulk.

Notice that since part of TE_j goes to rings, less of it can produce linear species TA_k, TB_k, or TE_k. Therefore, the rates of appearance of all linear species are reduced while their rates of disappearance remain unaltered. This may result in negative concentration of some species as already noted by Stepto and co-workers.[13,15] According to these authors the problem of negative concentrations is due to the use of global extents of reaction P_A in the differential equations. They propose that the extent of reaction in the chains should be used instead, where

$$P_{A\,\text{chains}} = \frac{\text{no. of reacted sites in chains}}{\text{total no. of sites in chains}}$$

This requires correcting the extent of reaction at each step in the solution of the differential equations. It also destroys the independence of these equations, since $P_{A\,\text{chains}}$ depends on the concentrations of all species.

A system of $4N + 6$ simultaneous differential equations must be solved when using rate theory, N being the size of the largest species needed. When distribution of species is calculated up to degrees of polymerization of 200, $N = 100$.

We study now the effect of the approximation of the rate theory method: that rates of disappearance are the same whether rings form or not. Figures 9 and 10 show predictions of the total number or weight fraction of rings using rate theory and the reference model. Rate theory always underestimates rings, but prediction seems to be quite good at high polymer concentration. At low concentrations prediction is poorer; differences for weight fraction may be as large as 30% even at low extents of reaction. In general, predictions of the number fraction of rings look much better than those of the weight fraction.

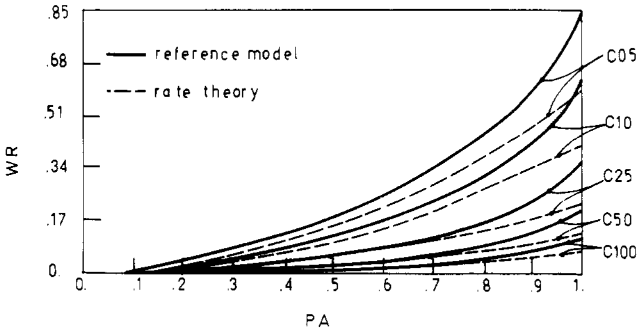

Figure 10. Total weight fraction of rings as predicted by rate theory and the reference models.

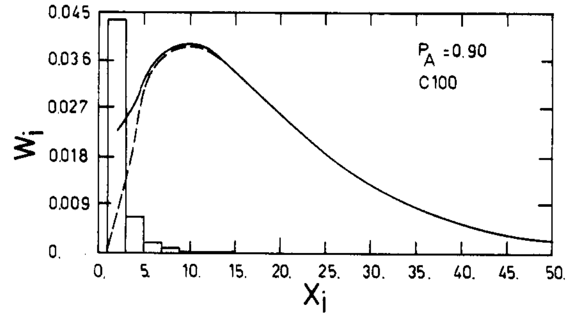

Figure 11. Even chains (full line), odd chains (dashed line), and rings (bars) calculated from rate theory.

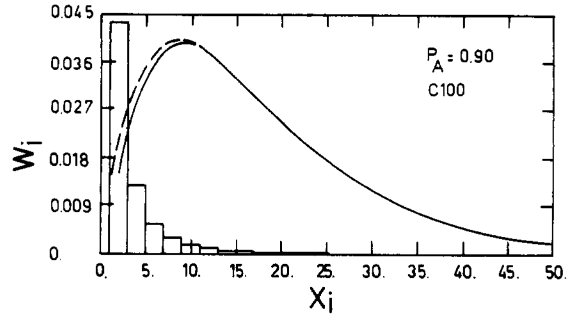

Figure 12. Even chains (full line), odd chains (dashed line), and rings (bars) calculated from the reference model.

We consider now the problem of predicting the distribution of species, something that affects the evaluation of most molecular parameters. The full distribution is not obtained, since only molecules of up to a certain fixed size are allowed for (a hybrid model that also made assumptions about continuing species[8] could be used to get the full distribution approximately). However, we may construct a partial distribution of the smaller molecules and study the predicted behavior. In all cases tried rate theory predicts that there are more even than odd chains, an incorrect result. The reference model predicts that even chains are fewer than odd chains. This result is reasonable, since even chains are depleted by both inter- and intramolecular reactions while odd chains may only react intermolecularly. For example, even chains, odd chains, and rings calculated from rate theory are shown in Figure 11 for case C100 at $P_A = 0.90$. The same parameters calculated from the reference model are plotted in Figure 12. We see that rate theory predictions for chains are worse at low degrees of polymerization, where rings are more important. When ring concentration drops, the distribution looks closer to the true one. Prediction of the weight fraction of the individual rings looks quite good also.

At high extents of reaction rate theory may predict negative concentrations of some chains, even though we

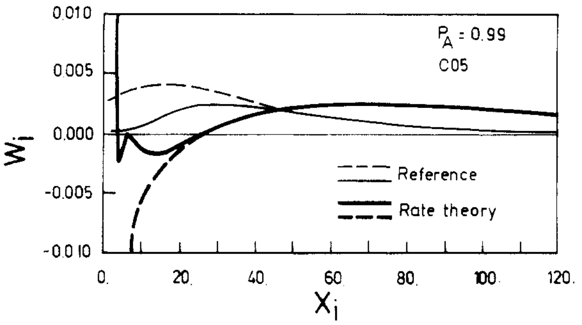

Figure 13. Even and odd chains from rate theory and the reference model for case C05 at $P_A = 0.99$. The figure is a partial enlargement of the complete plot; even chains from rate theory start at (2, 0.067), and odd chains from rate theory start at (1, -0.140).

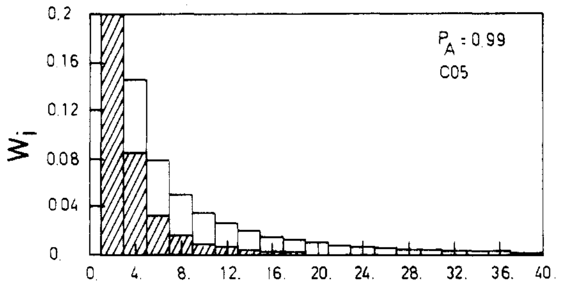

Figure 14. Weight fraction of rings from rate theory (gray bars) and the reference model (light bars) for case C05. Bars are superimposed. W_{R_1} (reference model), 0.4107; W_{R_1} (rate theory), 0.4197.

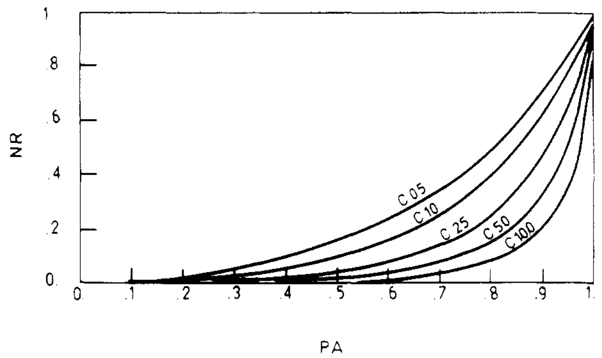

Figure 15. Number fraction of all rings using LNR ($N = 3$) and the reference models.

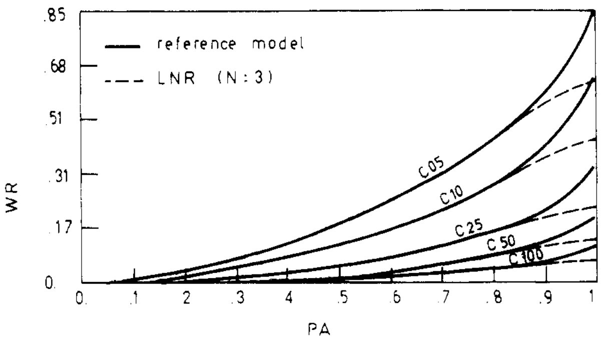

Figure 16. Weight fraction of all rings using LNR ($N = 3$) and the reference models.

are using differential equations in terms of $P_{A\,\mathrm{chains}}$ as recommended by the authors.[13,15] The effect is more important for diluted systems, such as the one shown in Figure 13. Here we see predictions for chains calculated from rate theory and the reference model for case C05 at $P_A = 0.99$. The appearance of negative concentrations is directly attributable to the main approximation of the model, namely, that rates of disappearance are the same whether rings form or not. As we explained when discussing this approximation, appearance rates are lower when rings form, so if disappearance rates are kept unchanged, negative concentrations may result.

Weight fractions of rings calculated from rate theory are always positive, even when some chains are negative. Rings are underestimated, as explained above, but they seem to be closer to reality than chains in all cases tried. Figure 14 is shown as an example. Here we plot weight fraction of rings against degree of polymerization for the same case used in Figure 13, where chains predicted by rate theory are greatly in error.

Limited Number of Rings Model

The reference method is a combined kinetic–recursive model[3] that considers rings of up to order N, N being a number large enough to ensure that the answer from this model is almost the true one. If N is small, we get an approximate model. We will call it the "limited number of rings" (LNR) model. There is one approximation here: rings of order greater than N are considered not important and are ignored. Keep in mind that we are testing in linear models some approximations that are also used to model network-forming systems with rings. In such systems the formulation of the combined kinetic–recursive model is not practical for N greater than 3 or 4. That is why we are interested in testing the approximation in the LNR model. We will do so for $N = 3$. In the past nonkinetic models for network-forming systems have also been forced to consider very few rings.[8] The results of this section do not apply to them because other approximations are also present in those models.

LNR with $N = 3$ requires solving 15 simultaneous differential equations. Run times to get to $P_A = 0.99$ are about 30 s on a VAX 11/780.

Figures 15 and 16 show predictions of the total number or weight fraction of rings using LNR and the reference model. The LNR prediction of the number fraction of rings is very good at all dilutions. This implies that, in fact, most rings are small.

The weight fraction of all rings from the LNR method is good up to $P_A = 0.90$–0.95. At higher extents of reaction large rings—too few to influence the number fraction of rings—contain a nonnegligible part of the mass, and so the LNR method underestimates the true answer. Deviations are not too large in undiluted systems; they increase with increasing dilution.

When we use the LNR method to calculate weight average molecular weights, we get almost exact results up to $P_A = 0.95$ for all dilutions. At higher extents of reaction LNR overestimates M_w. Deviations are negligible for undiluted systems and tend to increase with increasing dilution. This is shown in Figure 17.

From this evidence it seems that the approximation of neglecting all rings of order greater than 3 is good for number averages at all extents of reaction. For weight averages this approximation is good as long as larger rings are truly unimportant; this happens in concentrated systems at all extents of reaction, and for diluted systems at $P_A < 0.90$–0.95. This may be seen more clearly from the distribution of species.

In Figure 18 we see the weight distribution of even and odd chains for case C100 at $P_A = 0.99$ calculated from LNR with $N = 3$ and from the reference model. The curve for the ideal (no rings) distribution is included

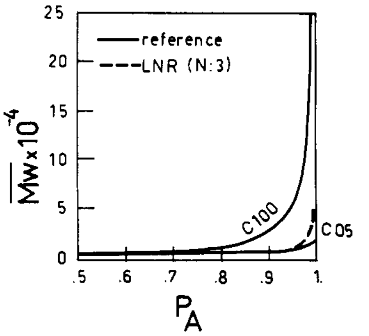

Figure 17. Weight average molecular weight from LNR and the reference methods.

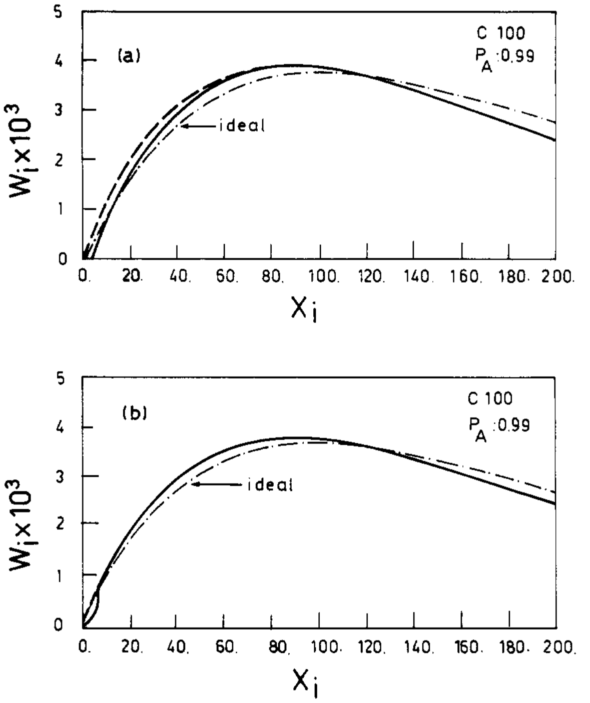

Figure 18. Weight distribution of even and odd chains in the undiluted case C100 (a) from the reference model and (b) from LNR with $N = 3$. Dashed lines correspond to odd chains and full lines to even chains.

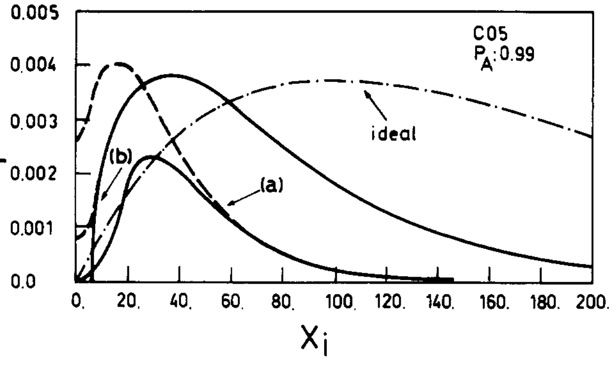

Figure 19. Weight distribution of chains for a diluted case, C05, from the reference model (a) and from LNR (b) with $N = 3$: dashed lines, odd chains; full lines, even chains.

for comparison. The same parameters are plotted for case C05 in Figure 19.

We see that for the undiluted system (C100) the approximate distribution is very close to the true one. As dilution increases (at the same extent of reaction), prediction worsens, and for a very dilute case such as the one in Figure 19 the approximate distribution is far from the true one. However, at a lower extent of reaction such as $P_A = 0.90$ the weight distribution for the same dilution using LNR is much closer to the true one. That is shown in Figure 20.

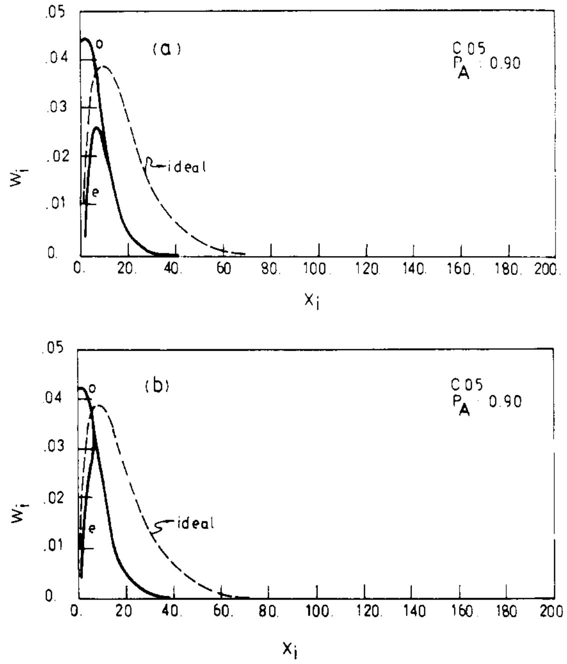

Figure 20. Weight distribution of even chains (full lines) and odd chains (dashed lines) for case C05 at $P_A = 0.90$ (a) from the reference model and (b) from LNR with $N = 3$.

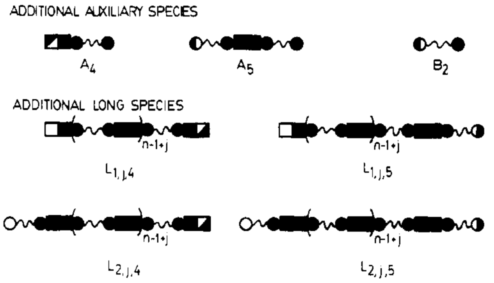

Figure 21. Extra species needed to describe an $A_2 + B_2$ copolymerization using the hybrid model. Only four of the additional long species are shown. The others are $L_{4,j,1}$, $L_{4,j,2}$, $L_{4,j,4}$, $L_{4,j,5}$, $L_{5,j,1}$, $L_{5,j,2}$, $L_{5,j,4}$, and $L_{5,j,5}$.

In all cases tried—including those of Figures 18–20—the weight fraction of each size of ring predicted by LNR agreed exactly with the one given by the reference model. The LNR model with $N = N_{max}$ always predicts the first N_{max} rings exactly.

Hybrid Model

We explained in the previous section that the formulation of the kinetic–recursive model in network-forming systems is not practical for N greater than 3 or 4. There are situations, however, where neglecting all rings of higher order may be unreasonable. One possible way out of this difficulty would be to compute the first few rings exactly and use an approximation to calculate the rest. We will call this a hybrid model.

For the linear $A_2 + B_2$ system we have developed a hybrid model that calculates the first N rings exactly and uses a modified spanning tree to compute the rest. For this model we need all the species from the reference model shown in Figure 3 and the extra ones shown in Figure 21. In the extra species the sites labeled with σ's are defined as sites that reacted intramolecularly to close a ring larger than R_N.

The model has a kinetic part and a statistical part, as others we have already discussed. In the kinetic part, a system of simultaneous differential equations must be solved to find the concentrations of short chains (S's), small rings (R's), and auxiliary structures (A's) as functions of time. The system has $4N + 5$ equations. B auxiliary structures are found from A and S species as

$$B_1 = A_2 + S_2 + 2S_3 \qquad B_2 = A_5$$

In the statistical part the concentration of the long chains is estimated using a modified spanning tree so that the complete distribution may be known and molecular parameters may be computed. Some statistical work must be done simultaneously with the integration of the kinetic differential equations, because the concentrations of some long chains are needed to calculate the rate of σ-site formation. For example

$$\frac{\mathrm{d}(A_4)}{\mathrm{d}t} = k\sum_{j=0}^{\infty} C_{n+1+j}L_{1j,2}$$

where k = kinetic rate constant, C_{n+1+j} = concentration of one chain end around the other for a chain containing $n + 1 + j$ B-monomer units, $L_{1j,2}$ = concentration of a chain with an A_1 on one end, an A_2 on the other end, and $n + j - 1$ A_3 units in the middle. See Figure 21. The differential equation above is equivalent to

$$\frac{\mathrm{d}(A_4)}{\mathrm{d}t} = kC^*\sum_{j=0}^{\infty} L_{1j,2}$$

where C^* is an average ring-closing concentration defined as

$$C^* = \frac{\sum_{j=0}^{\infty} C_{n+1+j}L_{1j,2}}{\sum_{j=0}^{\infty} L_{1j,2}}$$

This average ring-closing concentration differs from the one used in the pure spanning tree approach. Here we average over potential ring-closing chains longer than a certain fixed size (all chains containing more than N B-monomer units). In the pure spanning tree, averaging was done over all potential ring-closing chains. This is one reason we state that in the hybrid model we use a modified spanning tree.

In order to evaluate the concentrations of long species we make use of the concept of root and extension already explained for the reference model. In this model long chains are composed of overlapping A_1, A_2, A_3, A_4, and A_5 structures. A long chain chosen at random by picking a chain end will have as its chosen end an A_1, A_2, A_4, or A_5 structure. At least $N - 1$ A_3 structures will follow, and the other end will be an A_1, A_2, A_4, or A_5 structure. The chosen end and the first $N - 1$ A_3 structures make up the root of the chain and the rest is the "extension", as shown in Figure 2. We assume that the auxiliary structures in the extension follow a Geometric distribution. Then, after some operations similar to the ones performed in the reference model, the concentrations of the long chains are recovered. Not all of these long chains are physically possible, since σ-sites are distributed at random in them. Random distribution of σ-sites is one of the ideas of the spanning tree model. However, this way of recovering chains is not the one used in the pure spanning tree model, where chains were constructed by random combination of monomeric building blocks. This is the second reason for stating that in the hybrid model a modified spanning tree is used.

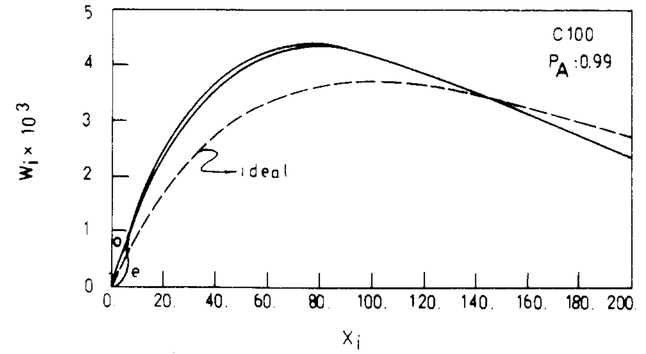

Figure 22. Weight distribution of even and odd chains in case C100 calculated from the hybrid model with $N = 3$. The ideal (no rings) distribution is shown for comparison.

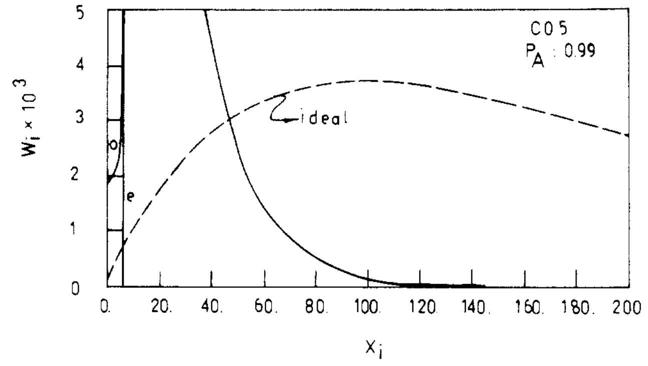

Figure 23. Weight distribution of even and odd chains in case C05 calculated from the hybrid model with $N = 3$. The plot does not fit in the figure because we kept the same scale used in Figure 19. The abscissa should go up to 0.012 for the whole plot to fit in the figure.

Once the concentrations of both short and long species are known, molecular parameters such as average molecular weights are computed by standard methods.

Weight distributions of species were calculated using the hybrid model with $N = 3$ for cases C100 and C05 in Table I. Rings of order 1, 2, and 3 were predicted exactly. Predictions for even and odd chains are shown in Figures 22 and 23. Comparison with Figures 18 and 19 shows that neglecting higher order rings gives better results than accounting for them with a spanning-tree-like approximation. Ring estimation must be done with a better method. Since rate theory does not lend itself to combination with kinetically based models, we cannot test other hybrid approaches any further. Better methods of approximation are needed.

Conclusions

We have studied some of the approximations used in the literature to account for intramolecular reaction in irreversible copolymerization. Those approximations are found in several already existing models and may be combined in different ways to give hybrid models.

All approximations studied work better at low dilution, where ring formation is also low, and worsen progressively with increasing dilution. Some are better than others.

The spanning tree model is based on two approximations: random combination of monomeric building blocks and use of average ring-closing concentrations. By studying each of these approximations separately we find that both give poor results. The use of average ring-closing concentrations like C^* seriously distorts the size distribution of rings even when ring formation is kept low.

The other approximation, random combination of monomeric building blocks, is always far from the truth. Monomers do not retain enough information about the molecules they belong to; all the nonidealities in the distribution involve longer range interactions that cannot possibly be accounted for in this approximation. When used together in the spanning tree model the approximations yield distorted size distribution of species; both the very short and very long species are underestimated, while intermediate length ones are overestimated. As a consequence the predicted weight average molecular weight is always too low, and it does not diverge at $P_A = 1$.

It is impossible to calculate concentrations of individual rings using this model. However, the number fraction of the sum of all rings may be calculated, giving good predictions.

Rate theory is essentially a perturbation treatment on the ideal (no rings) model. Its main approximation is that the rate of disappearance of linear species is the same whether rings form or not. At low degrees of dilution and not very high extents of reaction the distributions obtained under this approximation are acceptable, although they contain more even than odd chains. As we have shown, that is an incorrect result. At high extents of reaction ($P_A > 0.95$ for case C100, $P_A > 0.80$ for case C05) negative concentrations of linear species appear.

The method allows calculation of concentrations of each size of ring separately. Rings are usually underestimated, but predictions are quite reasonable even in the cases where some chains are assigned negative concentrations. In general, predictions of the number fraction of rings are much better than those of the weight fraction.

In the limited number of rings model the main approximation is to neglect all rings larger than a certain fixed size. We find that neglecting rings larger than order 3 results in good number averages at all dilutions and good weight averages at low to moderate dilutions. The method allows calculation of the full distribution of species. Therefore, average molecular weights can be computed. Weight average molecular weights as calculated from this model are almost exact up to $P_A = 0.95$ at all dilutions. At higher extents of reaction LNR overestimates M_w. Deviations are negligible for undiluted systems and tend to increase with increasing dilution. The concentration of each one of the three allowed rings is always predicted exactly. The LNR prediction of the number fraction of the sum of all rings is very good at all dilutions. The prediction of the weight fraction of the sum of all rings is also good at all dilutions up to $P_A = 0.90$–0.95. At higher extents of reaction this quantity is underestimated.

The limited number of rings model is by far the best of the methods studied for linear systems. Its predictions are very good in a broader range of dilutions, while its computational cost is about the same (LNR solves in 30 s the same problem spanning tree solves in 20 s).

At extremely large dilutions none of the approximations studied is really satisfactory. For such cases better approximations are needed.

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Supplementary Material Available: Approximations in spanning tree (part A), divergence of M_w (part B), and deduction of differential equations in rate theory (part C) including Figures S.1 (weight distribution of species) and S.2 (the four states that make up the tetramer TE_2 in Stepto and co-workers' original formulation of the rate theory model) (19 pages). Ordering information is given on any current masthead page.

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