Modeling of First Shell Substitution Effects and Preferred Cyclization in Sol−Gel Polymerization

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ABSTRACT: We compare two approaches in modeling first shell substitution effects (FSSE) coupled with cyclization in acid-catalyzed sol−gel polymerization. First, an approximate, statistically based, kinetic-recursive model (KR) is developed that is computationally inexpensive for investigating trends in the polymerization. Second, an exact Monte-Carlo model (MC) that tracks a finite pool of growing polymer clusters is constructed for comparison to the KR model. The two models agree well prior to gelation when using rate constants typical of sol−gel polymerization. However, near the gel point, discrepancies between the two models arise because of the KR model's inability to account for correlations in the growing structure beyond the site distribution. We show that both FSSE and cyclization cause the polymer's structure distribution to be history dependent. We also show that the inclusion of both FSSE and cyclization in the model is capable of increasing gel conversions above the 0.50 limit of previous exclusive FSSE models. We show that FSSE aids cyclization by increasing the concentrations of oligomers that are candidates for intramolecular reaction and that a strong FSSE with cyclization causes a local maximum to occur in the polydispersity index as a function of conversion. Both models fall short of predicting experimentally observed gel conversions; indicating that, in addition to the small cycles allowed in the present work, cage formation may also be significant.

Introduction

The acid-catalyzed polymerization of tetraethoxysilane (TEOS) exhibits dramatic departure from the behavior predicted by the random branching assumptions of Flory[1] and Stockmayer.[2] A large body of experimental evidence now exists which details these deviations. ^{29}Si NMR studies have shown that the population of silicon sites with n condensed reactive groups cannot be described by a single condensation rate constant.[3−7] In addition, gel conversions (i.e. the fraction of condensed reactive sites at the sol−gel transition) of homogeneous gels produced under acidic conditions ($0.5 < pH < 2.5$) are consistently around 0.83;[8−11] much higher than the expected value of 0.33 for a four-functional monomer.

Two specific violations of random branching theory have been proposed to explain the deviations: a first-shell substitution effect (FSSE) and cyclization. By fitting site distributions at low conversion, Brinker and Assink,[3] Pouxveil and Boilot,[4] and Ling[5] have shown that a strong, negative FSSE exists for condensation. Moreover, cycles composed of three to four Si monomer units have been observed by a number of analytical techniques.[12−18] In this paper we construct and compare two models that take into account both nonidealities.

Much of the interest in modeling nonlinear polymerizations has involved developing approaches to handle nonidealities such as FSSE and cyclization. The main approaches to predicting structural features of a polymerization include statistical treatments, kinetic approaches, and Monte-Carlo simulation. All have been applied in various forms to FSSE and cyclization conditions. Homopolymerization with a FSSE has been investigated by Mikeš and Dušek[19] using both a statistical approach and a Monte-Carlo simulation. They show that A_f homopolymerization (i.e., polymerization of a monomer with f reactive A groups) cannot be quantitatively described by statistical techniques that only consider the site distribution of the system. More involved statistical techniques, however, can either solve or very closely approximate homopolymerization FSSE. Sarmoria and Miller[20] show that if sufficient detail is included in the statistical based recursive approach of Miller and Macosko[21] homopolymerization with an FSSE can be solved to any needed degree of accuracy. Furthermore, kinetic approaches, in which a system of differential equations for all molecular species in the system must be solved, have been considered by Galina and Szustalewicz[22] and Kuchanov and Povolotskaya.[23]

We have chosen in this work to use two approaches: an approximate statistical technique and a Monte-Carlo simulation. Similar approaches have been used previously for sol−gel polymerization but have been restricted to FSSE effects. An approximate recursive model has been applied to TEOS polymerization by Bailey *et al.*,[24] and Monte-Carlo simulations have been performed by Kallala *et al.*[25] and by Hendrickson *et al.*[26] One of the most important conclusions from these works is that a FSSE alone is insufficient to predict experimentally observed gelation conversions. As has been pointed out previously, the maximum gel conversion of a four-functional molecule under FSSE is 0.50.[8,24,26,27] This work builds on previous FSSE models but also includes cyclization in order to increase the value of the gel conversion that can be obtained in the model. The recursive model we use in this work is an improvement on the model of Bailey *et al.*,[24] and the Monte-Carlo simulation is similar in concept to Hendrickson *et al.*[26] with regard to FSSE.

Approaches to model cyclization during polymerization are more abundant than FSSE studies. Most studies of cyclization are of cases in which the rate of intramolecular reaction is a function of the local concentration of groups available for cyclization. A large

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difficulty exists in calculating this quantity. For the special case of linear copolymerization when Gaussian chain conformations are assumed, accurate approximate solutions can be obtained.[28] Nonlinear polymerizations prove to be even more difficult and further approximations have been incorporated into both statistical and kinetic approaches to determine cycle content.[29−32] Alternatively, Monte-Carlo or percolation modeling done in space, either on- or off-lattice, has been done to model the spatial constraints that can cause cyclization.[33−35] The typical approach is to place reactants in space and assign the probability of reaction as a function of distance between the two reactive species.

The cyclization reactions considered in this paper do not require the calculations used in either the modified kinetic and statistical approaches or the Monte-Carlo simulation. We consider only cyclization reactions of two small oligomers that are thought to occur preferentially to bimolecular reaction. This allows the rate of cyclization to be modeled using rate expressions that are only a function of the concentration of the corresponding linear oligomers. A similar case of small cycle formation has been considered by Matejka and Dušek[36] in an epoxy-amine system. They restrict their model, however, to predicting the number average degree of polymerization, which can be determined exactly from stoichiometry once the cycle content is known.

Prediction of gel conversion and the higher moments of the molecular weight distribution, which are more sensitive to nonidealities in the polymerization, must be performed with one of the approaches discussed above. We show that, even with the simplification that allows us to exactly determine cycle content, the statistical approach given here is only approximate in modeling the effect of cyclization on structure distribution. The Monte-Carlo (MC) model we present overcomes the deficiency in the statistical model and does not require the consideration of spatial constraints.

As mentioned earlier, FSSE alone can only move the gel conversion to 0.50 and, as has been pointed out by Ng *et al.*,[8] exclusive cyclization of trimers followed by random branching can only increase the gel conversion to 0.60. This paper presents models which begin to quantify the combined effects of FSSE and cyclization in sol−gel polymerization. The goal here is to begin to study the relative importance of FSSE and cyclization. The kinetic-recursive (KR) model we present is approximate but is computationally inexpensive and convenient for predicting trends in experimental data. The MC model allows us to evaluate the quality of the KR solution. The MC approach is more computationally intensive but also has the advantage of providing more detailed results than the KR model and has the potential flexibility of handling larger cycles and cages.

Models

The first step in either model is to write a set of site-based kinetic equations. With two primary reactions (hydrolysis and condensation) and a substitution effect, the reaction network can become too large to handle easily. Fortunately, following Sanchez *et al.*,[37] an experimentally justified simplifying assumption can be made that hydrolysis is at equilibrium:

$$\mathrm{SiOEt} + \mathrm{H_2O} \overset{K_u}{\rightleftharpoons} \mathrm{SiOH} + \mathrm{EtOH}$$

A survey of existing literature has shown that the equilibrium coefficient for this reaction (K_u) is insensitive to the degree of hydrolysis or condensation of the silicon site.[38] Under acidic conditions, Sanchez *et al.*[37] observe equilibration within a very short period of the total reaction time. This equilibrium condition allows one to calculate the average fraction of uncondensed hydrolyzed groups (ξ).[43] The definition of the equilibrium coefficient for this reaction ($K_u = [\mathrm{SiOH}][\mathrm{EtOH}]/[\mathrm{SiOEt}][\mathrm{H_2O}]$) gives a quadratic expression for ξ ($0 = a\xi^2 + b\xi + c$) when the appropriate stoichiometric relationships are included. The coefficients for the equation are given as

$$a = ([\mathrm{SiOEt}]_0 - [\mathrm{SiOSi}])(1 - K_u) \tag{1a}$$

$$b = [\mathrm{EtOH}]_0 + [\mathrm{SiOSi}] + K_u([\mathrm{SiOEt}]_0 - 1.5[\mathrm{SiOSi}] + [\mathrm{H_2O}]_0) \tag{1b}$$

$$c = K_u(0.5[\mathrm{SiOSi}] - [\mathrm{H_2O}]_0) \tag{1c}$$

where [SiOSi] is the total concentration of condensed reactive groups. Because of the equilibrium condition, only condensation is important for structural information as a function of conversion. The value of K_u has no influence on, for example, the weight average degree of polymerization (P_w) as a function of conversion. Nevertheless, it is needed to accurately model data as a function of time.

Both inter- and intramolecular H_2O-producing condensation reactions are considered. The rate expression for the irreversible intermolecular reaction between a Q_i and a Q_j is given by

$$r_{ij} = k_{ij}^{h} Q_i Q_j \tag{2}$$

where Q_i is the concentration of silicon sites with i condensed reactive groups. The rate constant k_{ij}^{h} is a function of the average number of hydrolyzed groups on a site as follows:

$$k_{ij}^{h} = k_{ij}(4 - i)(4 - j)\xi^2 \tag{3}$$

where k_{ij} is the bimolecular rate constant for the reaction of a Q_i site with a Q_j site.

In the case of intramolecular reactions, we have chosen to limit ourselves to two simple reactions: cyclization of trimers (L_3) and linear tetramers (L_4). The cyclization rates are given by the following expressions:

$$r_{c3} = k_{c3}^{h} L_3 \tag{4a}$$

$$r_{c4} = k_{c4}^{h} L_4 \tag{4b}$$

The unimolecular rate coefficients are also modified by the extent of hydrolysis so that only oligomers hydrolyzed at both ends participate in cyclization ($k_{cx}^{h} = (3\xi)^2 k_{cx}$). Once cycles are formed, the sites can participate in further bimolecular reactions subject to eq 2.

Kinetic-Recursive Model. The simplest way to approximate P_w using the recursive method is to use sites as the smallest units or building blocks of the recursive relations. This requires the solution of kinetic equations for the concentrations of these units. The

Table 1. Kinetic Equations Used in the Kinetic-Recursive Model

linear sites

$$\dot{Q}_0 = -Q_0\Sigma_0$$
$$\dot{Q}_1 = Q_0\Sigma_0 - Q_1\Sigma_1 - 2k^h_{c3}L_3 - 2k^h_{c4}L_4$$
$$\dot{Q}_2 = Q_1\Sigma_1 - Q_2\Sigma_2 - k^h_{c3}L_3 - 2k^h_{c4}L_4$$
$$\dot{Q}_3 = Q_2\Sigma_2 - Q_3\Sigma_3$$
$$\dot{Q}_4 = Q_3\Sigma_3$$

cyclic sites

$$\dot{Q}_{2(c3)} = 3k^h_{c3}L_3 - Q_{2(c3)}\Sigma_2$$
$$\dot{Q}_{3(c3)} = Q_{2(c3)}\Sigma_2 - Q_{3(c3)}\Sigma_3$$
$$\dot{Q}_{4(c3)} = Q_{3(c3)}\Sigma_3$$
$$\dot{Q}_{2(c4)} = 4k^h_{c4}L_4 - Q_{2(c4)}\Sigma_2$$
$$\dot{Q}_{3(c4)} = Q_{2(c4)}\Sigma_2 - Q_{3(c4)}\Sigma_3$$
$$\dot{Q}_{4(c4)} = Q_{3(c4)}\Sigma_3$$

linear oligomers

$$\dot{L}_2 = 0.5k^h_{00}Q_0^2 - 2L_2\Sigma_1$$
$$\dot{L}_3 = 2k^h_{01}L_2Q_0 - 2L_3\Sigma_1 - L_3\Sigma_2 - k^h_{c3}L_3$$
$$\dot{L}_4 = 2k^h_{01}L_3Q_0 - 2k^h_{11}L_2^2 - 2L_4\Sigma_1 - 2L_4\Sigma_2 - k^h_{c4}L_4$$

where $\Sigma_m = \sum_{i=0}^{3} k_{im}Q_i^T$ and Q_i^T = noncyclic + cyclic Q_i sites

complete set of equations includes expressions for the rate of change in concentration of sites in noncyclic polymer fragments (Q_0, Q_1, Q_2, Q_3, Q_4), sites in rings ($Q_{i(cj)}$, $i = 2-4$ and $j = 3$ or 4), and the first three linear oligomers (L_2, L_3, L_4). The concentrations of L_i are needed in the equations for the cyclic sites. The complete set of kinetic equations is given in Table 1. Note that loss terms in the equations for L_i are written in terms of site concentrations. The equations for L_i do not require any knowledge about the rest of the molecular weight distribution.

The recursive relations are written in terms of the three basic types of sites: linear (Q_L), three-member cyclic sites (Q_{c3}), and four-membered cyclic sites (Q_{c4}). The starting point for the derivation is to randomly choose a functional group and ask what is the expected weight looking out from that group. For each of the three types of groups this quantity is given by

$$E(W^{out}_{QL}) = p_{QL}(p'_{QL}E(W^{in}_{QL,r}) + p'_{Qc3}E(W^{in}_{Qc3,r}) + p'_{Qc4}E(W^{in}_{Qc4,r})) \quad (5a)$$

$$E(W^{out}_{Qc3}) = p_{Qc3}(p'_{QL}E(W^{in}_{QL,r}) + p'_{Qc3}E(W^{in}_{Qc3,r}) + p'_{Qc4}E(W^{in}_{Qc4,r})) \quad (5b)$$

$$E(W^{out}_{Qc4}) = p_{Qc4}(p'_{QL}E(W^{in}_{QL,r}) + p'_{Qc3}E(W^{in}_{Qc3,r}) + p'_{Qc4}E(W^{in}_{Qc4,r})) \quad (5c)$$

where p_{Qs} is the probability that a randomly chosen group on a site of type s (s = L, C3, or C4) has reacted and p'_{Qs} is the probability that a randomly chosen reacted group is on a type s site. $E(W^{in}_{Qs,r})$ is the expected weight looking in from a group given that it has reacted. Following an exact derivation from Miller and Macosko[39] for the special case of polymerization of an $A_4 + B_2$ system with a substitution effect, $E(W^{in}_{QL,r})$ can be written as

$$E(W^{in}_{QL,r}) = M_Q + \frac{(\mu - 1)E(W^{out}_{QL})}{p_{QL}} \quad (6)$$

where M_Q is the molecular weight of a Si unit and

$$\mu = \frac{\sum_{i=1}^{4} i^2 Q_i}{\sum_{i=1}^{4} iQ_i} \quad (7)$$

The equivalent equations for the cyclic species can be written as

$$E(W^{in}_{Qc3,r}) = 3M_Q + \frac{E(W^{out}_{Qc3})}{p_{Qc3}}\frac{2Q_{4(c3)}}{(Q_{3(c3)} + 2Q_{4(c3)})} + \frac{2E(W^{out}_{Qc3})}{p_{Qc3}}\frac{(Q_{3(c3)} + 2Q_{4(c3)})}{(Q_{2(c3)} + Q_{3(c3)} + Q_{4(c3)})} \quad (8a)$$

$$E(W^{in}_{Qc4,r}) = 4M_Q + \frac{E(W^{out}_{Qc4})}{p_{Qc4}}\frac{2Q_{4(c4)}}{(Q_{3(c4)} + 2Q_{4(c4)})} + \frac{3E(W^{out}_{Qc4})}{p_{Qc4}}\frac{(Q_{3(c4)} + 2Q_{4(c4)})}{(Q_{2(c4)} + Q_{3(c4)} + Q_{4(c4)})} \quad (8b)$$

The second term of eqs 8a and 8b is the expected weight looking out from the second reactive group of the site that is being looked into. The last term in each equation represents looking out from the other groups on the other sites that make up the cycle.

Equations 5−8 are the set of recursive equations that are used to calculate weight average molecular weight. M_w is given by

$$M_w = w_L E(W_{QL}) + w_{c3}E(W_{c3}) + w_{c4}E(W_{c4}) \quad (9)$$

where

$$E(W_L) = M_Q + 4E(W^{out}_{QL}) \quad (10a)$$

$$E(W_{c3}) = 3M_Q + \frac{3E(W^{out}_{Qc3})}{p_{Qc3}}\frac{(Q_{3(c3)} + 2Q_{4(c3)})}{(Q_{2(c3)} + Q_{3(c3)} + Q_{4(c3)})} \quad (10b)$$

$$E(W_{c4}) = 4M_Q + \frac{4E(W^{out}_{Qc4})}{p_{Qc4}}\frac{(Q_{3(c4)} + 2Q_{4(c4)})}{(Q_{2(c4)} + Q_{3(c4)} + Q_{4(c4)})} \quad (10c)$$

The KR model is evaluated by first solving the kinetic equations as a function of time using a fourth-order Runge−Kutta algorithm. Then at each time step eqs 5−8 are solved followed by eqs 10 and 9. It should be noted that the only information required by eqs 5−10 is the site distribution of the system.

Monte-Carlo Model. The Monte-Carlo model we present here is an equivalent statement of the rules that are used in the KR model. The most important difference between the two methods is that the complete reaction history is captured for a finite set of monomers with the Monte-Carlo method, while the sites are assumed to be randomly linked with the kinetic-recursive model. The principles of the Monte-Carlo method have been well described by Somvársky and Dušek.[40]

In the MC model, reaction rates are recast as reaction probabilities, so for example, the probability of reaction of a Q_i with a Q_j unit is

$$p_{ij} = \frac{r_{ij}}{r_{c3} + r_{c4} + \sum_{i=0}^{3}\sum_{j=i}^{3} r_{ij}} \quad (11)$$

where r_{ij}, r_{c3}, and r_{c4} are defined in eqs 2, 4a, and 4b. A flow chart of the code is given in Figure 1. The code is initiated with 10^5 Si units, which are tagged by their

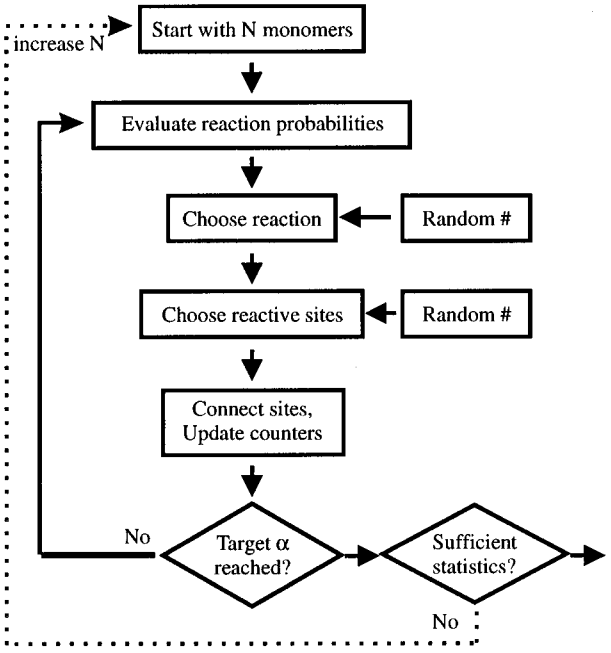

Figure 1. Flow chart of the algorithm used for the Monte-Carlo simulation.

monomer number and the label of the chain to which they belong. At each conversion step, the reaction probabilities are evaluated according to the current population of reactive species. A random number is used to choose which reaction will occur. Two additional random numbers are used to select available Si units (or an oligomer in the case of cyclization) for participation in the reaction. The Si units are connected by changing the chain label of the fragment to which one of the species belongs. The reaction probabilities are then reevaluated and the process is continued until a target conversion is reached.

Output from the MC model includes the site distribution and moments of the molecular weight distribution as a function of conversion as well as the full molecular weight distribution at the target conversion of the run. Because the product of the MC model is a collection of chains, other features of the final system can be extracted as desired. The gel conversion for the MC model is defined using the maximum of the reduced weight average degree of polymerization (rP_w) as defined by Shy *et al.*[41] The rP_w criteria was found to be indistinguishable from the maximum in $d(\log(P_w))/d\alpha$.

Discussion

The recursive relations used in the KR model are only an approximate solution. This can best be seen by considering a thought experiment analogous to the recursive relations. As written, the equations are equivalent to taking the growing polymer fragments at each conversion step, breaking all of the bonds, and then reassembling the collection of sites at random. As a result, correlations present in the polymer fragments larger than the site distribution are lost. For example, if reaction conditions dictate that Q_i-Q_i bonds have a strong tendency to form, the KR model will miss this and assume that the population of that particular type of bond is in proportion to the population of Q_i sites.

Such a condition exists in the case of a FSSE. It is well-known that the statistical approach represented by the recursive relations given here, termed a "minimal" model by Sarmoria and Miller,[20] is not completely

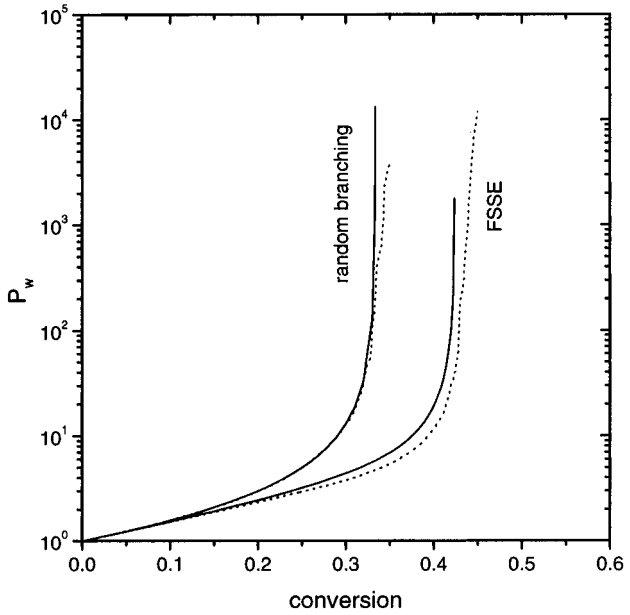

Figure 2. Comparison of the KR (—) and MC (···) models under conditions of random branching and the FSSE condition given by the rate constants in Table 2.

Table 2. Rate Constant Matrix with Values Used To Demonstrate FSSE and Cyclization[a]

					units
k_{ij} =	1.0	0.9	0.81	0.73	(conc·time)$^{-1}$
		0.1	0.09	0.081	
			0.01	0.009	
				0.001	
k_{c3}	1.0				time^{-1}
k_{c4}	10.0				time^{-1}

[a] Values are expected to be representative of experimental values.[37,42] Concentrations used unless otherwise noted: $[Si]_0 = 2.0$ M, $[H_2O]_0 = 6.0$ M, and $[EtOH]_0 = 8.0$ M.

accurate for homopolymerizations with FSSE.[19,20,22] However, as shown by Sarmoria and Miller, the approximation of the model can be quite good under certain conditions. Figure 2 compares P_w from both the KR and MC models for both the case of random branching and an example set of rate constants (Table 2) that are expected to be typical for sol−gel polymerization.[37,42] In the case of random branching, the models are equivalent and only disagree when the finite pool size of the MC model begins to be seen. For the example case of a FSSE in which the rate constants drop by an order of magnitude down the diagonal and decrease by 10% across each row (see the k_{ij} matrix in Table 2), the two models are in quantitative disagreement but are qualitatively equivalent. Because the KR model allows bonds between more highly substituted Si sites than is allowed by the FSSE condition (though this is not the only reason; see Appendix), the KR model tends to overpredict P_w by approximately 20% over most of the conversion range. In terms of gel conversion, however, the deviation between the two models is only 2%. The discrepancy between the two models is expected to be modest as long as the rate constants monotonically decrease (or increase) moving left to right and top to bottom of the rate constant matrix (k_{ij}).[20]

A similar discrepancy arises between the KR and MC models for the case of cyclization. Figure 3 plots P_w for the two models for $k_{c3} = k_{c4} = 1.0$, 10.0, and 100.0 with $k_{ij} = 1.0$. In this case, the KR model underpredicts P_w, worsening as the cyclization rate constants increase. The reason for the discrepancy is similar to the deviation seen for a FSSE. The KR model treats cyclic

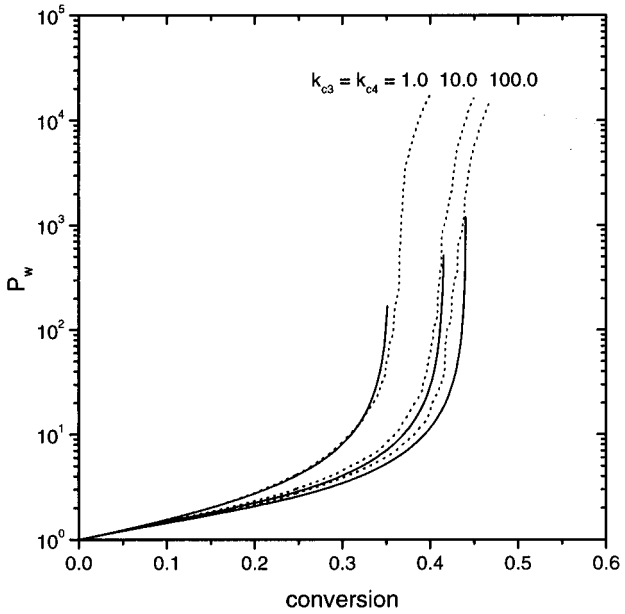

Figure 3. Comparison of the KR (—) and MC (···) models with cyclization.

species as separate types of units that, at a given conversion, are assumed to have existed in their present proportions since the beginning of the reaction. In fact, because cycles must be formed from their corresponding linear oligomers, the majority form over a narrow conversion range. As a result, a site which is a member of a cycle does not experience the entire history of the reaction bath as the KR model assumes. The situation is analogous to the existence of a residence time distribution for the cyclic species. The discrepancy is not a result of an approximation used to calculate the probability of cycle formation; the site distributions (Q_i, $Q_{i(c3)}$, and $Q_{i(c4)}$) found by the two methods match exactly. That quantity is completely defined by the kinetic equations. The discrepancy is due to the loss of information inherent in the statistical approach used here.

Despite the fact that the KR model as formulated in this work is not quantitative for cyclization, the approximation is again very reasonable. As shown in Figure 3, the discrepancy in P_w between the two models is less than 15% except very close to the gel point. The discrepancy in gel conversions is at most 5%. Given that typical values for k_{c3} and k_{c4} are on the order of 10 or less ($k_{00} = 1$ for the same units) the KR model may be a reasonable approximation to the current reaction scheme.

A further advantage of the KR model, as shown in Figure 4, is that it is more quickly evaluated. Neither model as currently written is computationally expensive and can be run on a high-end PC. At $\alpha < 0.30$, both models can be evaluated in under 1 min. As shown in Figure 4, however, the MC model slows down considerably as conversion and cyclization content increase.

Application to TEOS Polymerization. One of the first questions to be asked is how effective is the limited form of cyclization used in this work in delaying gelation. Figure 5 plots gel conversion as a function of the dimensionless ratio $k_c/(k_{00}[Si])$ ($k_c = k_{c3} = k_{c4}$) for $k_{ij} = 1.0$ using the MC model. The ratio is a measure of the system's tendency to cyclize, which can be increased by either increasing k_c relative to k_{00} or by dilution (i.e., [Si] decreases). The gel conversion increases from 0.33 as the ratio increases but plateaus at a relatively low value of approximately 0.44, falling well

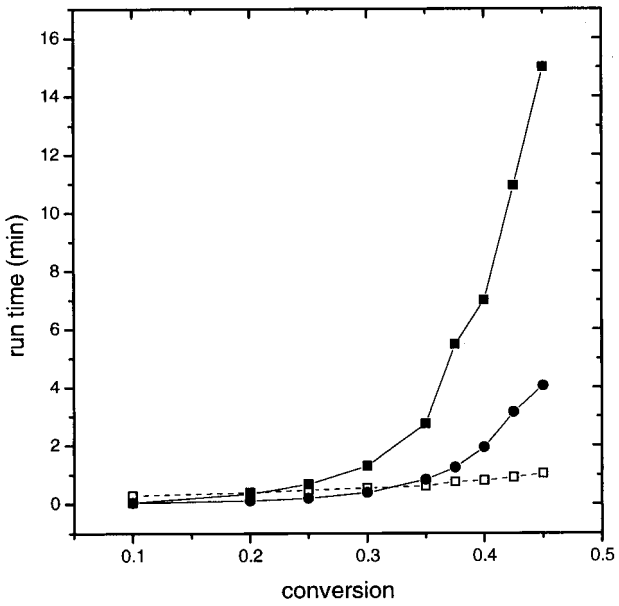

Figure 4. Comparison of run times for the KR and MC models using a Pentium 100 MHz PC: (●) MC model under cyclization conditions of Table 2; (■) MC model under both FSSE and cyclization conditions; (□) KR model under both FSSE and cyclization conditions.

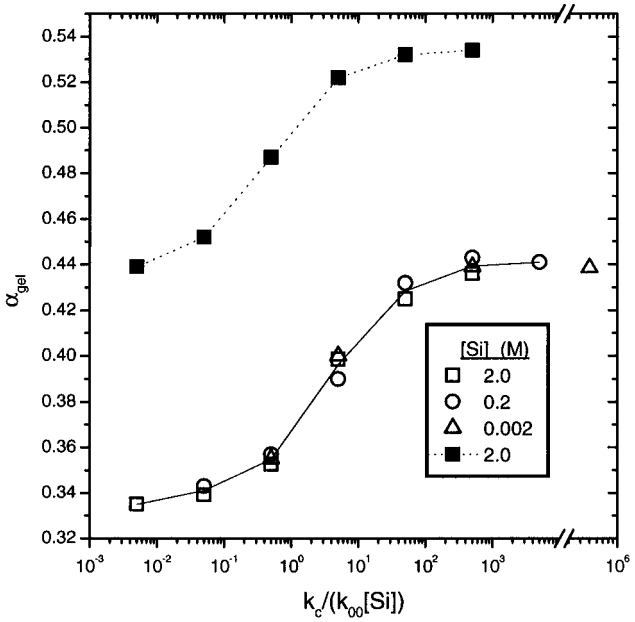

Figure 5. Gelation conversion as a function of cyclization under the conditions of $k_{ij} = 1.0$ (open symbols) and FSSE constants (closed symbols) of Table 2. Results were generated using the MC model.

short of the $\alpha_{gel} = 0.60$ limit described by Ng *et al.*[8] Irrespective of how dilute the solution is or how high the cyclization constant is set, significant fractions of Si units can polymerize without ever becoming a member of an L_3 or L_4 oligomer and then cyclizing. As the reaction proceeds, monomers and dimers avoid becoming trimers or tetramers by reacting with either cycles that have already formed or other larger polymer fragments. Note that the present model cannot describe the infinite dilution limit (i.e., all cycles) because only three- and four-membered cycles are allowed; larger cycles favored under dilution conditions are missed.

Gel conversion can be increased further by incorporating in the first shell substitution effect. Figure 5 also plots α_{gel} as a function of $k_c/(k_{00}[Si])$ for the case where k_{ij} follows the FSSE values given in Table 2. When both

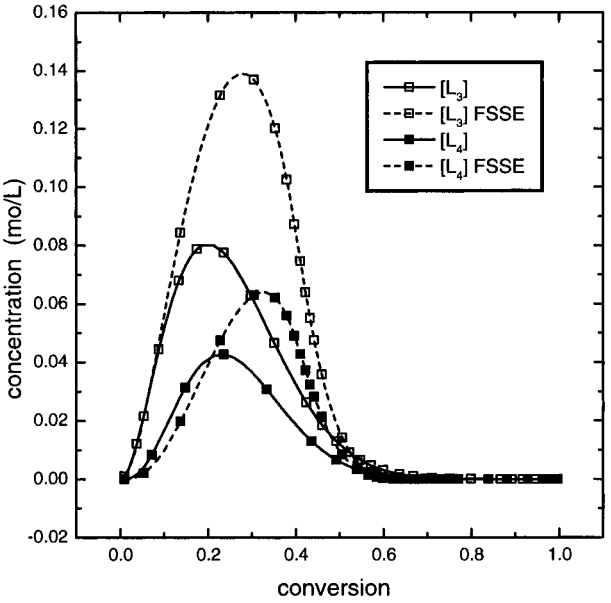

Figure 6. Concentrations of linear trimers and linear tetramers with and without FSSE. The results were generated by solving the kinetic equations given in Table 1.

cyclization and FSSE are considered, gel conversions can exceed the 0.50 conversion limit of FSSE alone. Although not obvious from Figure 5, FSSE has two effects in delaying gelation. Although FSSE does delay gelation by discouraging branching, it also promotes cyclization. As shown in Figure 6, by solving the set of kinetic equations for the populations of three- and four-membered oligomers under no cyclization, it is seen that FSSE increases their concentration at any given conversion. By discouraging the reaction of more highly substituted Si sites, FSSE forces a greater fraction of Si sites through a reaction pathway in which they are available for cyclization. In terms of gel conversion, this effect can be seen using the following set of rate constants: $k_{00} = k_{01} = 1$, $k_{22} = k_{23} = k_{33} = 0.01$, $k_{02} = k_{03} = k_{11} = k_{12} = k_{13} = 0$, and $k_{c3} = 1000$. The resulting gel conversion of 0.58 approaches the 0.60 theoretical limit of exclusive cyclization followed by random branching. In addition, as shown in Figure 7, two distinct regions can be seen in the buildup of P_w because of the increased cyclization due to FSSE. The first region, to approximately $\alpha = 0.45$, corresponds to the building of linear trimers and their subsequent cyclization. Over that region, P_w seems to approach a limiting value of 3−4 and $d(\log(P_w))/d\alpha$ initially decreases. For an ideal random polymerization, $d(\log(P_w))/d\alpha$ is an increasing function of the gel point. In the second region, bimolecular reactions of more highly substituted Si sites, which occur over a much longer time scale, finally cause gelation. Also shown in Figure 7, the effect of a large separation in the time scales of cyclization and branching is even more easily seen in the polydispersity index, which goes through a local maximum. This type of behavior cannot be predicted by FSSE alone.

The observations made so far regarding the relative effects of cyclization and FSSE can be derived from either the KR or MC model. The MC model, however, provides additional information that may be useful in assessing the two effects. Although FSSE and cyclization affect α_{gel} and P_w in a way that is difficult to distinguish, their effects on the full molecular weight distribution are quite different. Figure 8 compares the molecular weight distribution at $\alpha = 0.35$ under the conditions of a FSSE and cyclization independently. The cyclization constants were increased to 1000 so that the

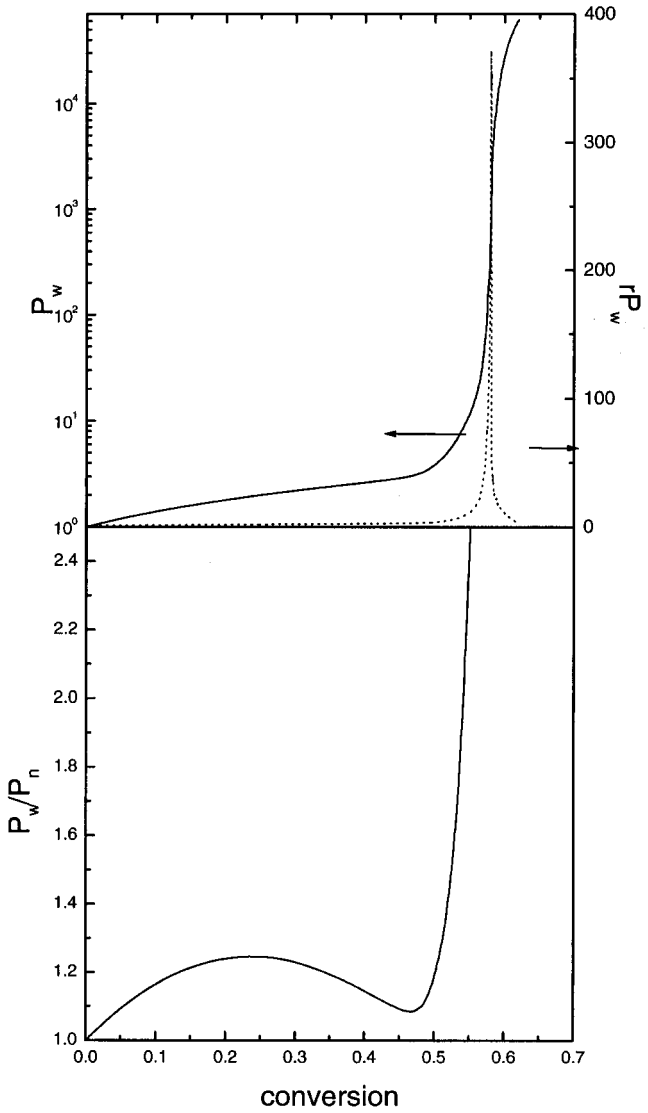

Figure 7. Growth in P_w and polydispersity index under conditions of an extreme FSSE and cyclization of linear trimers. The result was generated using the MC model.

gel conversion under both sets of conditions is approximately 0.44. As shown in Figure 8, FSSE tends to tighten the molecular weight distribution relative to cyclization. Although the values of P_w between the two cases shown may be experimentally difficult to identify, there are large differences in the weight fractions of monomer, dimer, and trimers between the two cases.

Although the combined effects of cyclization and FSSE can have a significant impact on the gel conversion, the most relevant question is whether the current model is sufficient to describe the sol−gel process. From the outset, the current model cannot predict the experimentally observed 0.83 gel conversion. The absolute limit of the models presented here is 0.75, which corresponds to first producing cyclic trimers and then allowing only $Q_{2(c3)}-Q_{2(c3)}$ reactions. The models are instructive, however, in their failure. Using rate constants given in Table 2 that are characteristic of TEOS polymerization,[37,42] a gel conversion of 0.51 is predicted. The limited cyclization allowed in the present work is completely insufficient to explain the experimentally observed gel point. Incorporation of larger isolated cyclic structures (i.e., five- and six-membered rings) is unlikely to improve the situation. This result lends further support to the suggestion of Ng *et al.*[8] that extensive cage formation occurs in TEOS polymerization.

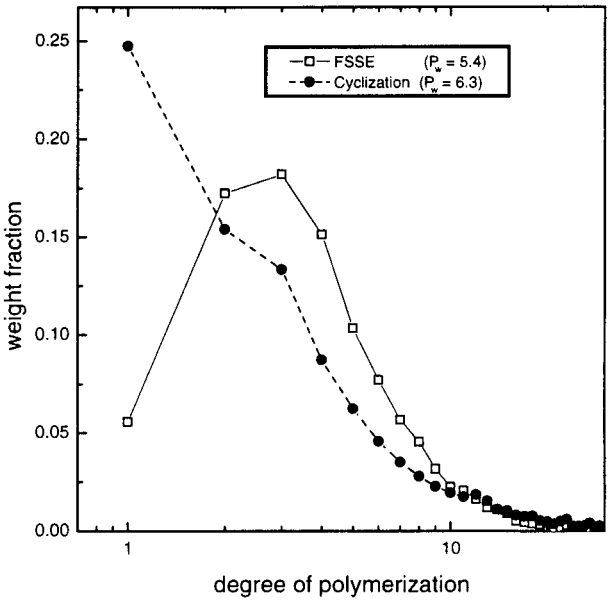

Figure 8. Molecular weight distributions at $\alpha = 0.35$ from the MC model under FSSE conditions and cyclization conditions. Rate constants k_{c3} and k_{c4} were set to 1000 in order to give approximately the same gel conversion as the FSSE case ($\alpha_{gel} = 0.44$).

Conclusion

We have presented two models that quantify the effects of FSSE and cyclization of linear trimers and tetramers in sol−gel polymerization. The KR model we present is computationally quick, which makes it convenient for comparison to experimental data. Although comparisons with the MC model confirm that the KR model is approximate, it is shown to be a good approximation in terms of gel conversion and P_w at low conversion when rate constants typical of sol−gel polymerization are used. Neither model, however, is capable of predicting experimentally observed gel conversions. Further refinement of the model is needed to allow cyclization of any possible three- or four-membered ring. By relaxing the cyclization conditions, greater fractions of cycles can form, sites can participate in multiple cycles, and cages are allowed to form. Such a restatement of the cyclization conditions further argues against a statistical approach like the KR model. The determination of the potential cycles, which is needed in the kinetic equations, is more suited to a Monte-Carlo approach like that given here. Inclusion of all possible three- and four-membered rings into the model, which is currently under development, makes the simulation extremely computationally expensive. The simulation then requires supercomputer resources instead of the high-end PC that was used in this work. Finally, the MC approach more easily gives details of the structure distribution than the KR model. A MC model can give populations of linear fragments, cycles, and even cages that may be useful for comparison to chromatography experiments.

Appendix. Modification of Recursive Relations To Include Bond Distribution in A_f Homopolymerization with a FSSE

The argument used for failure of site based statistical approaches to handle FSSEs in homopolymerizations is that bonds are allowed to form that are disfavored by the actual reaction conditions. Although a correct site distribution can be calculated by kinetic equations and fed into a statistical approach, such an approach incorrectly assumes that the bond distribution is directly proportional to the site distribution:

$$B_{ij} = \frac{\binom{2}{1}_{i=j}^{-1} ijA_iA_j}{\sum_{i=1}^{f}\sum_{j=i}^{f}\binom{2}{1}_{i=j}^{-1} ijA_iA_j} \tag{A1}$$

where B_{ij} is the fraction of bonds formed between A_i and A_j sites. Modifications to the statistical approach can be made, however, to include a correct bond distribution. Analogous to the calculation of the site distribution, the bond distribution for an example case of A_3 homopolymerization is given by

$$\dot{B}_{11} = (9/2)k_{00}A_0^2 - 4B_{11}(3k_{01}A_0 + 2k_{11}A_1 + k_{12}A_2) \tag{A2a}$$

$$\dot{B}_{12} = 6k_{01}A_0A_1 + 4B_{11}(3k_{01}A_0 + 2k_{11}A_1 + k_{12}A_2) - 2B_{12}(3k_{01}A_0 + 2k_{11}A_1 + k_{12}A_2) - B_{12}(3k_{02}A_0 + 2k_{12}A_1 + k_{22}A_2) \tag{A2b}$$

$$\dot{B}_{13} = 3k_{02}A_0A_2 + B_{12}(3k_{02}A_0 + 2k_{12}A_1 + k_{22}A_2) - 2B_{13}(3k_{01}A_0 + 2k_{11}A_1 + k_{12}A_2) \tag{A2c}$$

$$\dot{B}_{22} = (4/2)k_{11}A_1^2 + 2B_{12}(3k_{01}A_0 + 2k_{11}A_1 + k_{12}A_2) - 2B_{22}(3k_{02}A_0 + 2k_{12}A_1 + k_{22}A_2) \tag{A2d}$$

$$\dot{B}_{23} = 2k_{12}A_1A_2 + 2B_{13}(3k_{01}A_0 + 2k_{11}A_1 + k_{12}A_2) + 2B_{22}(3k_{02}A_0 + 2k_{12}A_1 + k_{22}A_2) - B_{23}(3k_{02}A_0 + 2k_{12}A_1 + k_{22}A_2) \tag{A2e}$$

$$\dot{B}_{33} = (1/2)k_{22}A_2^2 + B_{23}(3k_{02}A_0 + 2k_{12}A_1 + k_{22}A_2) \tag{A2f}$$

The difference between eqs A1 and A2 in shown in Figure 9 using an example case of an order of magnitude decrease down the diagonal of the k_{ij} matrix and a 10% decrease across each row. The difference between the two solutions is modest and suggests that the majority of the nonideality can be explained by alterations in the site distribution. In the case of the above rate constants, the bond distribution is a small additional perturbation while, as shown in Figure 10, changes in the site distribution are much more significant. This is the reason that the minimal statistical model is often a good approximation for FSSE.

The bond distribution can be included in a recursive form of the statistical approach by using the same starting point. Looking out from a randomly selected A group, the expected weight looking out is

$$E(W_A^{out}) = pE(W_{A,r}^{out}) \tag{A3}$$

where p is the probability the group has reacted and $E(W_{A,r}^{out})$ is the expected weight looking out from a randomly selected reacted group. $E(W_{A,r}^{out})$ can be written as

$$E(W_{A,r}^{out}) = \sum_{i=1}^{f} P(\text{A on } A_i)E(W_{A,r}^{out}|A_i) \tag{A4}$$

where $P(\text{A on } A_i)$ is the probability of choosing a reacted A on an A_i and $E(W_{A,r}^{out}|A_i)$ is the expected weight

Table 3. Comparison of Gel Conversions Predicted by Various Treatments of Homopolymerization with FSSE

k_0	k_1	k_2	statistical conv model[a]	kinetic[b]	"minimal" statistical[c]	statistical bond dist model[d]
1.0	1.0	1.0	0.498−0.501	0.5000	0.5000	0.500
1.0	1.0	10.0	0.346−0.347	0.3451	0.3467	0.346
1.0	10.0	10.0	0.127−0.127	0.1272	0.1324	0.128
1.0	10.0	100.0	0.0611−0.0614	0.06074	0.06226	0.0613
1.0	100.0	100.0	0.0145−0.0146	0.01458	0.01546	0.0147
1.0	1.0	0.1	0.617−0.620	0.6171	0.6171	0.617
1.0	0.1	0.1	0.560−0.563	0.5619	0.5772	0.553
1.0	0.1	0.01	0.630−0.634	0.6302	0.6331	0.628
1.0	100.0	10.0	0.0352−0.0354	0.03627	0.04088	0.0375
1.0	100.0	1.0	0.0780−0.0785	0.07809	0.1069	0.0963
1.0	100.0	0.1	0.157−0.158	0.1571	0.2534	0.231
1.0	100.0	0.01	0.286−0.288	0.2866	0.4593	0.435

[a] Statistical model of Sarmoria and Miller,[20] which considers site distribution and allows only bonds between sites that have formed during a given conversion interval. [b] Kinetic model of Galina and Szustalewicz.[22] [c] Statistical model that only considers site distribution; termed a "minimal" model by Sarmoria and Miller.[20] [d] Statistical model presented here, which considers both site distribution and bond distribution. [e] Rate constants below the line increase and then decrease in substitution effect as a function of substitution and can show both large positive and negative FSSE for different degrees of substitution. Such trends have not been observed experimentally.

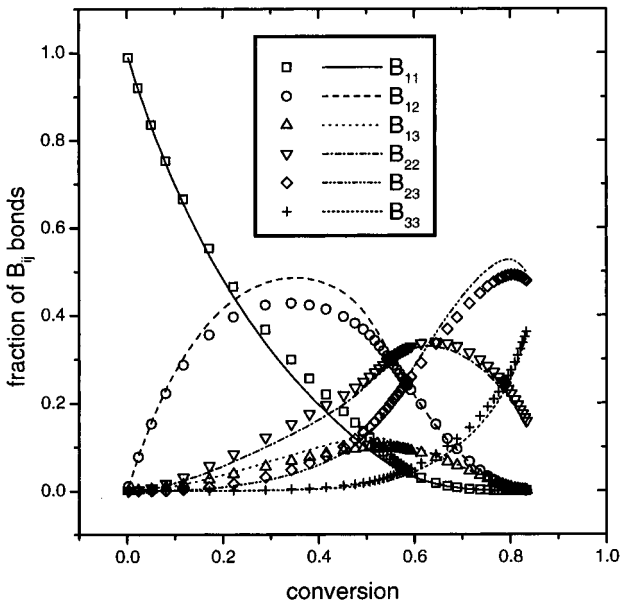

Figure 9. Bond distribution solved for by eq A1 (symbols), which is assumed by the KR model, and true bond distribution under FSSE solved for by eq A2 (lines).

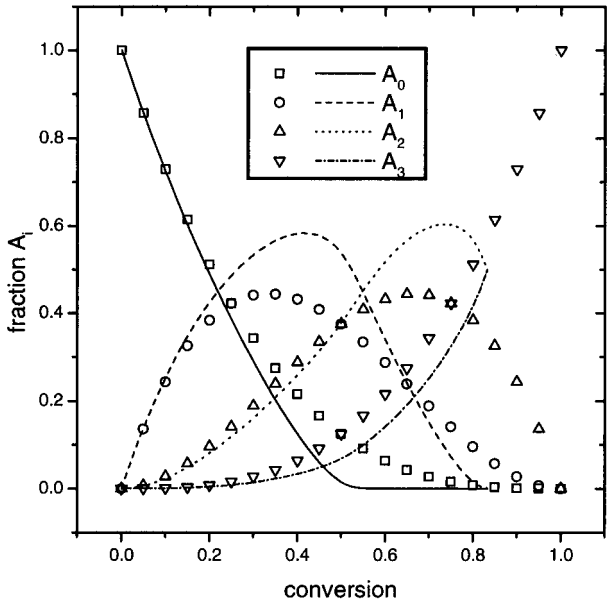

Figure 10. Site distribution in the cases of random branching (symbols) and FSSE (lines).

looking out from a randomly selected reacted A group given that it is on an A_i site. Note that the variable $E(W_{A,r}^{out}|A_i)$ is written to incorporate the bond distribution; it represents information on the condition of the site of the group that is being looked out from. $E(W_{A,r}^{out}|A_i)$ is written as

$$E(W_{A,r}^{out}|A_i) = \sum_{j=1}^{f} P(B_{ij}|i)E(W_{A,r}^{out}|B_{ij}) \qquad (A5)$$

where $P(B_{ij}|i)$ is the probability that a randomly chosen bond is a B_{ij} given that one end is an A_i. $E(W_{A,r}^{out}|B_{ij})$ is the expected weight looking out from an A given that it is a participant in a B_{ij} bond. $P(B_{ij}|i)$ is given by

$$P(B_{ij}|i) = \frac{\binom{2}{1}_{i=j}\binom{1}{1}_{i\neq j} B_{ij}}{\sum_{j=1}^{f}\binom{2}{1}_{i=j}\binom{1}{1}_{i\neq j} B_{ij}} \qquad (A6)$$

and $E(W_{A,r}^{out}|B_{ij})$ is given by

$$E(W_{A,r}^{out}|B_{ij}) = M + (j-1)E(W_{A,r}^{out}|A_j) \qquad (A7)$$

Equations A4 through A7 complete the recursive relations and M_w can then be calculated as

$$M_w = M + fE(W_A^{out}) \qquad (A8)$$

Although the above equations remove any errors associated with disfavored bonds being formed, they are still insufficient to quantitatively predict FSSE. This can be seen by comparing the predicted gel conversions using the modified recursive relations with those generated by other methods. Sarmoria and Miller[20] report results using a statistical model in which each reacted group carries an additional label that indicates the conversion of the system when it reacted. In the special case of multiplicative rate constants (i.e., $k_{ij} = k_i k_j$) the model is exact provided that the discretization needed to solve the model is made sufficiently small. They present gel conversion results from their model as well as from a minimal model and a kinetic model derived by Galina and Szustalewicz.[22] Selected comparisons between those models and the one given here are shown in Table 3.

Comparison of the models shows that the bond-distribution modified model agrees quite closely with the kinetic and Sarmoria−Miller models for most of the rate constant sets studied. In fact, with the exception of the last four entries, the bond distribution model is

probably within the margin of error of the other models. All of the models are likely to have some error in them associated with the numerical technique used to solve for the site (and bond) distribution. It is also clear by inspection of Table A1 that, in all cases, the bond-distribution model gives an improved result over the minimal model.

The last four entries of the table in which the bond distribution model fails worst are instructive. The bond distribution model fails most miserably, as expected, for cases where the rate constants vary widely in an erratic manner. In fact, in such cases the bond distribution model is only a marginal improvement over the minimal model. The lack of improvement seen in the model shows that the failure of the statistical models is more serious than an inability to discriminate between bonds that are either disfavored or disallowed by the reaction conditions. In the cases of worst disagreement, correlations exist in the structure well past the site and bond distribution. In the other cases, the correlations die out quickly and the site distribution alone is nearly sufficient.

The recursive model can be further modified by, for example, solving for the populations of $A_i((B_{ij})(B_{ik})(B_{il})...)$ fragments. It is worth noting, though, that to get satisfactory results the recursive approach used by Sarmoria and Miller must go to the lengths of tagging each bonded pair of A_i sites with the conversion interval during which they reacted. Furthermore, this approach is only valid when the rate constants are multiplicative. What Sarmoria and Miller call a "maximal" model is required to treat the general FSSE case quantitatively. In addition to the conversion tag, in the "maximal" model each site must also carry a rank tag; each reactive site is labeled as the *n*th group to react on that monomer with the *m*th group to react on its partner.

The above results also indicate, however, that by extending the recursive model to the next largest fragment or superspecies, the improvement in performance will be *negligible for the type of cases most often encountered* (i.e., FSSE in which reaction of a site becomes consistently harder or easier with progressive substitution). For that reason, we have chosen to modify the minimal model for cyclization and apply that to sol−gel polymerization.

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