A Linkage Moment Approach to Modeling Condensation Polymerization with Multiple Monomers. II. Extension to Nonlinear Polymers

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ABSTRACT: In a previous article, a general model for the condensation copolymerization of mono and bifunctional monomers was developed in which the sequence length distribution was calculated statistically from the concentrations of linkages (e.g., —CONH—) labeled by the identities of the participating monomer units. A set of balance equations for the effect of each major reaction upon these concentrations, those of the end groups, and the moments of the chain-length distribution completed the general model framework for linear polymers. In this article, this technique is extended to the case of nonlinear polymerizations with multifunctional monomers capable of branch or gel formation. This modification is required because in nonlinear polymerization, the moments of the chain-length distribution diverge at the gel point, and the traditional description of the sequence length distribution is only well defined for macromolecules consisting of a single backbone chain. Although the balance equations for the end group and linkage concentrations presented in the previous article are completely transferable, the statistical techniques must be modified to accommodate branch and network chain architectures. By coupling the general kinetic model with the recursive approach of Macosko and Miller for the calculation of sol/gel properties, one can describe the microstructures of a wide variety of systems such as those in which the copolymer has a blocky microstructure caused by interchange reactions between multiple components. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 266–274, 2001

Key words: linkage moment approach; condensation polymerization; nonlinear polymers

INTRODUCTION

In recent years there has been increased interest in using condensation polymerization to produce copolymers with controlled microstructures. In a previous article, a general model was developed to describe these systems for an arbitrary number of mono- and bifunctional monomers. The characteristics of the sequence length distribution were calculated statistically from a set of transition probabilities, $P(U_j|U_i)$, that in marching down a chain in a consistent direction, a monomer unit of type i is followed by one of type j. These transition probabilities were, in turn, calculated from the concentrations of the end groups and linkages (e.g., —CONH—), labeled by the identities of the two joined monomers. Balance equations were presented for the effect of each reaction upon the concentration state variables, allowing a full dynamic description of batch and continuous copo-

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lymerization processes. As a process of moving down a chain in a consistent direction is only well defined for polymers comprised of a single backbone, a new approach is required for systems with long-chain branching or gelation. The moment approach to calculate the number and weight average chain lengths is also not applicable to nonlinear polymerization, as these properties diverge at the gel point.

In this article, an alternative method is presented to calculate the copolymer microstructure of nonlinear polymers based upon the end group and linkage concentrations. The recursive approach of Macosko and Miller[1–3] is used to predict the gelation properties for a system of arbitrary complexity, and a general criterion for gel formation is presented. In this method, the weight-average chain length is obtained by calculating the expected size of the molecule attached to a randomly chosen monomer unit through linkages of its functional groups. At the gel point, this expected weight diverges to infinity, beyond which point the sol fraction is calculated from the probability that a randomly chosen monomer unit is attached to a molecule of finite size.

Although this statistical model is strictly valid only for batch polymerizations because it neglects the past history when reconstructing sample chains from transition probabilities, in the previous article it was shown that such an approach is often applicable to continuous processes as well. Because each chain need suffer only one fracture event (from reverse condensation or interchange) on average during the mean residence time to relax the chain-length distribution, it is often the case that chain recombination yields uniform microstructures across all molecular weights, and that the product of a continuous process is similar to that of a batch polymerization at the same end-group conversion.

As the set of linkage concentrations encodes more information about the monomer connectivity than the set of monomer concentrations and end-group conversions, the statistical model presented here is equally valid for systems with blocky microstructures, such as would be expected with unequal reactivities between monomer pairs or from randomization of a physical blend of component polymers. The contribution of this work to the Macosko-Miller model is the ability to describe such nonrandom microstructures and the effect of monomer connectivity in such cases upon the gelation phenomena. Expressing the gelation model in terms of linkage probabilities also allows the use of the general polycondensation kinetics model presented in the first article for nonlinear polymerizations of any number of monomers with arbitrary functionalities.

The use of this general gelation model is introduced for the case in which a monomer undergoes interchange reaction with a preformed gel, altering the network connectivity as it modifies the copolymer microstructure. Such a process is similar to chemical healing, in which chain randomization fuses together two polymer samples. Expressing the gelation parameters in terms of the linkage moments allows the description of the gel microstructure at any time during the randomization process.

CHARACTERIZATION OF MONOMER CONNECTIVITY

In the previous article, the statistical properties of the sequence length distribution were derived from a set of transition probabilities describing the likelihood that a monomer unit of a certain type follows another one along the chain backbone. In a system that is branched or forms a gel, one can no longer speak of travelling down a polymer chain in a consistent direction; therefore, different transition probabilities are required to describe the connectivity between monomers. First, the probability that an acid group from an i-type monomer chosen at random is bonded to a B_j group is calculated.

$$P(U_j - ba - U_i|a_i) = H(\alpha_i - 1)\,\frac{L_{ij}}{A_i + \Sigma_h L_{ih}} \quad (1)$$

Here, as in the first article, A_i is the concentration of acid end groups from monomer i, B_j is the concentration of base ends from monomer j, and L_{ij} is the concentration of the linkage formed from these two groups. The probability that a randomly chosen i-type acid group remains unreacted is

$$P(A_i|a_i) = H(\alpha_i - 1)\,\frac{A_i}{A_i + \Sigma_h L_{ih}} \quad (2)$$

The Heaviside function, $H(x)$, ensures that i-type monomer has at least one acid functional group. Equivalent probabilities are defined for the β_i base group sites on the type-i monomer.

$$P(U_j - ab - U_i|b_i) = H(\beta_i - 1)\,\frac{L_{ji}}{B_i + \Sigma_h L_{hi}} \quad (3)$$

$$P(B_i|b_i) = H(\beta_i - 1)\,\frac{B_i}{B_i + \Sigma_h L_{hi}} \quad (4)$$

For a branched or gelating system, the connectivity of the monomers is no longer simply expressed in terms of the distributions of the dyad and triad sequences. Because there are multiple acid and base groups on a single monomer unit, there are several possible arrangements of reacted and unreacted end groups and a more general expression than the triad concentrations is required. Of the α_i acid groups on an i-type monomer, if n_{A_i} is the number of groups that remain unreacted and $n_{a_{ij}}$ is the number that are bonded to B_j groups, the following partitionings of the acid end groups (and similarly for the base groups) are possible.

$$n_{A_i},\, n_{a_{ij}} \in [0,\, \alpha_i] \quad n_{A_i} + \sum_j n_{a_{ij}} = \alpha_i$$

$$n_{B_i},\, n_{b_{ji}} \in [0,\, \beta_i] \quad n_{B_i} + \sum_j n_{b_{ji}} = \beta_i \quad (5)$$

The probability that an i-type monomer unit chosen at random has one of these partitionings of the end group states is

$$\begin{aligned} P(n_{A_i},\, \{n_{a_{ij}}\},\, n_{B_i},\, \{n_{b_{ji}}\}|U_i) \\ = \left\{ \frac{\alpha_i!}{n_{A_i}!\,\prod_j n_{a_{ij}}!}\,[P(A_i|a_i)]^{n_{A_i}} \prod_j \right. \\ \left. \times\,[P(U_j - ba - U_i|a_i)]^{n_{a_{ij}}} \right\} \\ \times \left\{ \frac{\beta_i!}{n_{B_i}!\,\prod_j n_{b_{ji}}!}\,[P(B_i|b_i)]^{n_{B_i}} \prod_j \right. \\ \left. \times\,[P(U_j - ab - U_i|b_i)]^{n_{b_{ji}}} \right\} \quad (6) \end{aligned}$$

The first factor on the left in eq. (6) is the probability that of the α_i acid groups, n_{A_i} are unreacted and $n_{a_{ij}}$ are linked to a base group from j-type monomer; the ratio of factorials being the number of permutations with the same partitioning of the acid groups. The second factor is a similar expression for the base groups. When this formula is applied to a bifunctional monomer, one obtains probabilities for finding specific triad sequences. For example, if the i-type monomer has a single acid and a single base group ($\alpha_i = \beta_i = 1$), the probability $P(n_{A_i} = 0,\, n_{a_{ij}} = \delta_{jh},\, n_{B_i} = 0,\, n_{b_{ji}} = \delta_{jk})$ gives the likelihood that an i-type monomer unit chosen at random is the center of a $U_h - U_i - U_k$ triad sequence with the U_h bonded to the acid side and the U_k bonded to the base side.

CALCULATION OF GEL PROPERTIES

In addition to the copolymer composition, the effect of monomer conversion and connectivity upon the overall chain length distribution and the gelation properties (sol fraction, crosslink density, etc.) is also required. Although population balances for the sequence length distribution in gelating systems have been developed,[4–6] the evaluation of the breakage probabilities required for the reverse condensation reaction is complex, and a tractable moment equation approach is unavailable. The weight-average molecular weight and postgel properties can be calculated using the recursive statistical approach developed by Macosko and Miller.[1–3] This method is essentially an extension of the Flory most probable distribution to nonlinear gelating polymers, and therefore, does not include residence time effects; however, interchange and reverse condensation reactions often negate the effect of the residence time distribution so that the statistical approach is applicable also to many continuous systems. This model also assumes that all linkages are formed between different molecules, and therefore, ignores the presence of intramolecular cyclization. The effect of intramolecular reaction is to require higher end-group conversions for the formation of a gel than are predicted by the theory; however, one typically prefers such a conservative estimate of the gel-point conversion.

In this section, the Macosko-Miller model is expressed in terms of the linkage concentrations, allowing one to describe blocky microstructures and to couple the gelation model to the general framework for polycondensation kinetics presented in the first article. The general idea behind the approach is to calculate the expected weights of sections of the molecule that are observed by looking outwards or inwards across bonds originating from a given monomer unit (Fig. 1). If we choose a monomer unit at random, the expected molecular weight of the chain to which the unit is attached is equal to the sum of the weight asso-

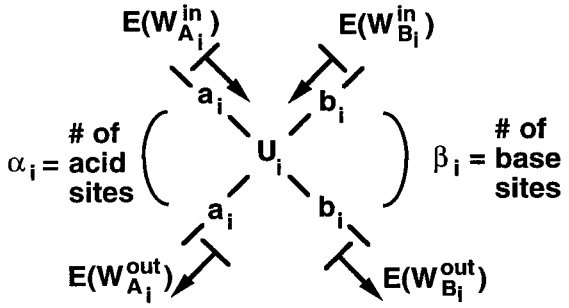

Figure 1 Definition of expected weights in the Macosko-Miller method for the simulation of gelation phenomena.

ciated directly with the monomer unit, $W_{U_i} + \alpha_i W_{a_i} + \beta_i W_{b_i}$, and the expected molecular weights of the sections of chain attached to each bond site. The definitions of the weights are explained in Figure 2.

The expected weight looking outwards from a given bond site on an i-type monomer unit is expanded in terms of the expected values if the functional site has not reacted, or if the site is linked with another monomer of a specified type. The set of equations obtained from this procedure is recursive in the sense that after a round of the expansion process, the possible outcomes from further expansion are statistically equivalent to states previously encountered. This closes the set of equations and allows the expected weight values to be calculated from simple matrix expressions. The sum of the expected weights averaged over the different monomer unit types yields the weight-average molecular weight. The weight-average degree of polymerization is obtained if all weight parameters are given the value of zero except for the weight of the monomer unit itself, W_{U_i}, which is given a value of 1.

The first step in the recursive calculation procedure is to expand the expected weight looking outwards from one of the acid sites on an i-type monomer unit in terms of the possible states of the acid site (unreacted or bonded to a B_j group).

$$E(W_{A_i}^{\text{out}}) = \sum_j E(W_{A_i}^{\text{out}}|U_j - ba - U_i) \times P(U_j - ba - U_i|a_i) + E(W_{A_i}^{\text{out}}|A_i)P(A_i|a_i) \quad (7)$$

The expected weight when the acid site is unreacted is simply the weight of the condensate fragment originating from the acid group (Fig. 2).

$$E(W_{A_i}^{\text{out}}|A_i) = W_{CA_i} \quad (8)$$

The expected weight when the acid site is bonded to a B_j group is equal to the expected weight looking in from a base site on a j-type monomer unit.

$$E(W_{A_i}^{\text{out}}|U_j - ba - U_i) = E(W_{B_j}^{\text{in}}) \quad (9)$$

The expected weight looking in across the B_j unit is equal to the sum of the weight associated directly with the j-type monomer unit and the expected weights looking out from each of the other sites on this unit.

$$E(W_{B_j}^{\text{in}}) = W_{U_j} + W_{b_j} + \alpha_j[W_{a_j} + E(W_{A_j}^{\text{out}})] + (\beta_j - 1)[W_{b_j} + E(W_{B_j}^{\text{out}})] \quad (10)$$

This expression is used to eliminate the expected "in" weights in eqs. (7) and (9) to yield

$$E(W_{A_i}^{\text{out}}) = \left\{ \sum_j [(W_{U_j} + \alpha_j W_{a_j} + \beta_j W_{b_j}) + \alpha_j E(W_{A_j}^{\text{out}}) + (\beta_j - 1)E(W_{B_j}^{\text{out}})]P(U_j - ba - U_i|a_i) \right\} + W_{CA_i}P(A_i|a_i) \quad (11)$$

The expected weight looking out from a B_i site is obtained from a similar calculation.

$$E(W_{B_i}^{\text{out}}) = \left\{ \sum_j [(W_{U_j} + \alpha_j W_{a_j} + \beta_j W_{b_j}) + (\alpha_j - 1)E(W_{A_j}^{\text{out}}) + \beta_j E(W_{B_j}^{\text{out}})]P(U_j - ab - U_i|b_i) \right\} + W_{CB_i}P(B_i|b_i) \quad (12)$$

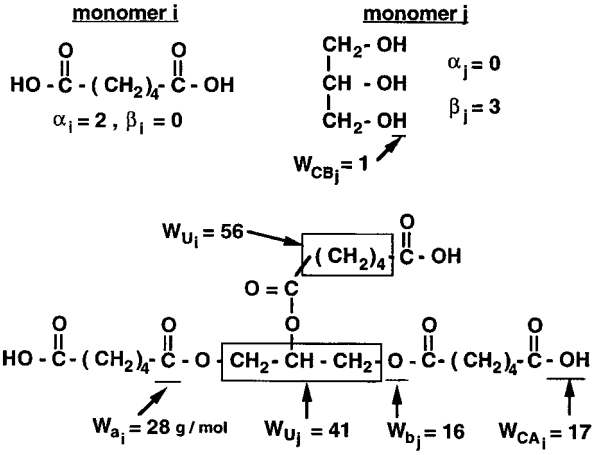

Figure 2 Definitions of molecular weights in gel equations.

When matrices and column vectors are defined with the following elements,

$$[\underline{\underline{P}}_{AB}]_{ij} = P(U_j - ba - U_i|a_i)$$
$$[\underline{\underline{P}}_{BA}]_{ij} = P(U_j - ab - U_i|b_i)$$
$$[\underline{\underline{\alpha}}]_{ij} = \alpha_j\delta_{ij} \qquad [\underline{\underline{\beta}}]_{ij} = \beta_j\delta_{ij}$$
$$[\underline{E}(W_A^{\text{out}})]_i = E(W_{A_i}^{\text{out}})$$
$$[\underline{E}(W_B^{\text{out}})]_i = E(W_{B_i}^{\text{out}})$$
$$[\underline{W}_{PCA}]_i = W_{CA_i}P(A_i|a_i)$$
$$[\underline{W}_{PCB}]_i = W_{CB_i}P(B_i|b_i)$$
$$[\underline{W}_U]_i = W_{U_i} + \alpha_i W_{a_i} + \beta_i W_{b_i} \quad (13)$$

the expressions for $E(W_{A_i}^{\text{out}})$ and $E(W_{B_i}^{\text{out}})$ can be rewritten in the following matrix forms.

$$\underline{E}(W_A^{\text{out}}) = \underline{\underline{P}}_{AB}\underline{W}_U + \underline{\underline{P}}_{AB}\underline{\underline{\alpha}}\,\underline{E}(W_A^{\text{out}}) + \underline{\underline{P}}_{AB}(\underline{\underline{\beta}} - \underline{\underline{I}})\underline{E}(W_B^{\text{out}}) + \underline{W}_{PCA} \quad (14)$$

$$\underline{E}(W_B^{\text{out}}) = \underline{\underline{P}}_{BA}\underline{W}_U + \underline{\underline{P}}_{BA}(\underline{\underline{\alpha}} - \underline{\underline{I}})\underline{E}(W_A^{\text{out}}) + \underline{\underline{P}}_{BA}\underline{\underline{\beta}}\,\underline{E}(W_B^{\text{out}}) + \underline{W}_{PCB} \quad (15)$$

$\underline{\underline{I}}$ is the identity matrix. Solving equation (15) for $\underline{E}(W_B^{\text{out}})$ yields

$$\underline{E}(W_B^{\text{out}}) = [\underline{\underline{I}} - \underline{\underline{P}}_{BA}\underline{\underline{\beta}}]^{-1}[\underline{\underline{P}}_{BA}\underline{W}_U + \underline{\underline{P}}_{BA}(\underline{\underline{\alpha}} - \underline{\underline{I}})\underline{E}(W_A^{\text{out}}) + \underline{W}_{PCB}] \quad (16)$$

When this is inserted into eq. (14), a decoupled expression is obtained.

$$\underline{E}(W_A^{\text{out}}) = [\underline{\underline{I}} - \underline{\underline{P}}_{AB}\underline{\underline{\alpha}} - \underline{\underline{P}}_{AB}(\underline{\underline{\beta}} - \underline{\underline{I}}) \times (\underline{\underline{I}} - \underline{\underline{P}}_{BA}\underline{\underline{\beta}})^{-1}\underline{\underline{P}}_{BA}(\underline{\underline{\alpha}} - \underline{\underline{I}})]^{-1}[\underline{\underline{P}}_{AB}\underline{W}_U + \underline{W}_{PCA} + \underline{\underline{P}}_{AB}(\underline{\underline{\beta}} - \underline{\underline{I}})(\underline{\underline{I}} - \underline{\underline{P}}_{BA}\underline{\underline{\beta}})^{-1}(\underline{\underline{P}}_{BA}\underline{W}_U + \underline{W}_{PCA})] \quad (17)$$

This solution for $\underline{E}(W_A^{\text{out}})$ is then used to calculate $\underline{E}(W_B^{\text{out}})$ from eq. (16). The weight-average molecular weight is obtained by averaging over each monomer type the expected weight, $E(W_i)$, of the molecule to which a randomly chosen i-type monomer unit is attached. The mass fraction of each monomer type, ω_i, is used as the weight function in the averaging procedure.

$$\bar{M}_w = \sum_i E(W_i)\omega_i \quad (18)$$

$$E(W_i) = W_{U_i} + \alpha_i W_{a_i} + \beta_i W_{b_i} + \alpha_i E(W_{A_i}^{\text{out}}) + \beta_i E(W_{B_i}^{\text{out}}) \quad (19)$$

$$\omega_i = \frac{(W_{U_i} + \alpha_i W_{a_i} + \beta_i W_{b_i})U_i}{\Sigma_h(W_{U_h} + \alpha_h W_{a_h} + \beta_h W_{b_h})U_h} \quad (20)$$

In eq. (17), as the reaction proceeds towards higher conversions, the matrix inside the bracket that is inverted nears singularity, causing the weight average molecular weight to diverge. The singularity of this matrix, therefore, offers a general criterion for the onset of gelation that is valid for systems with a blocky microstructure as well as those following Bernoullian statistics.

$$D_{\text{gel}} = \det[\underline{\underline{I}} - \underline{\underline{P}}_{AB}\underline{\underline{\alpha}} - \underline{\underline{P}}_{AB}(\underline{\underline{\beta}} - \underline{\underline{I}}) \times (\underline{\underline{I}} - \underline{\underline{P}}_{BA}\underline{\underline{\beta}})^{-1}\underline{\underline{P}}_{BA}(\underline{\underline{\alpha}} - \underline{\underline{I}})] = 0 \quad (21)$$

These expressions allow the prediction of the critical gel point; however, the method can also model postgelation properties such as the sol fraction of each species and the concentration of each monomer species serving as a crosslink. The approach to calculate sol fractions involves calculating the probability that the section of chain looking out from a given functional site is of finite molecular weight. If all sites on an i-type monomer unit are attached to finite chain segments, the unit is in the sol phase; otherwise, it is part of the gel. The total sol fraction is equal to the average of the monomer sol fractions using the mass fraction of each monomer type as a weight function in the averaging procedure.

The probability $P(F_{A_i}^{\text{out}})$ that a randomly chosen A_i site is not joined to part of the infinite network is expanded in terms of the possible states (unreacted or linked to a B_j group) of this site.

$$P(F_{A_i}^{\text{out}}) = \sum_j P(F_{A_i}^{\text{out}}|U_j - ba - U_i) \times P(U_j - ba - U_i|a_i) + P(F_{A_i}^{\text{out}}|A_i)P(A_i|a_i) \quad (22)$$

If the end group has not reacted, the probability of finding a finite segment is obviously equal to 1.

$$P(F_{A_i}^{\text{out}}|A_i) = 1 \quad (23)$$

The probability of finding a finite chain at a reacted site is conditional upon the attached j-type monomer unit having finite chain segments at all of its other functional groups.

$$P(F_{A_i}^{\text{out}}|U_j - ba - U_i) = P(F_{B_j}^{\text{in}}) = [P(F_{A_j}^{\text{out}})]^{\alpha_j}[P(F_{B_j}^{\text{out}})]^{\beta_j - 1} \quad (24)$$

The equations for $P(F_{A_i}^{\text{out}})$, and similar ones for $P(F_{B_i}^{\text{out}})$, obtained using the recursion procedure are

$$P(F_{A_i}^{\text{out}}) = \sum_j [P(F_{A_j}^{\text{out}})]^{\alpha_j}[P(F_{B_j}^{\text{out}})]^{\beta_j - 1} \times P(U_j - ba - U_i|a_i) + P(A_i|a_i) \quad (25)$$

$$P(F_{B_i}^{\text{out}}) = \sum_j [P(F_{A_j}^{\text{out}})]^{\alpha_j - 1}[P(F_{B_j}^{\text{out}})]^{\beta_j} \times P(U_j - ab - U_i|b_i) + P(B_i|b_i) \quad (26)$$

These equations must be solved numerically; however, the solution with all finite chain probabilities equal to 1 exists at all times. When the conversion is below the gel point, this is the solution of interest; however, for the postgelation regime, this solution is unwanted. Following Miller and Macosko,[2] this solution is factored out by putting eq. (25) in the following form.

$$0 = [P(F_{A_i}^{\text{out}}) - 1][P(U_i - ba - U_i|a_i)P(F_{B_i}^{\text{out}})^{\beta_i - 1} \times \sum_{h=0}^{\alpha_i - 1} P(F_{A_i}^{\text{out}})^h - c_{A_i}] \quad (27)$$

The term c_{A_i} is determined by comparing (27) with the original eq. (25). The desired solution is then calculated by setting the term in the second set of brackets on the left in (27) to zero to obtain eq. (28).

$$P(U_i - ba - U_i|a_i)P(F_{B_i}^{\text{out}})^{\beta_i - 1} \sum_{h=0}^{\alpha_i - 1} P(F_{A_i}^{\text{out}})^h = [1 - P(F_{A_i}^{\text{out}})]^{-1}\{P(U_i - ba - U_i|a_i)P(F_{B_i}^{\text{out}})^{\beta_i - 1} - P(F_{A_i}^{\text{out}}) + P(A_i|a_i) + \sum_{j \neq i} P(F_{A_j}^{\text{out}})^{\alpha_j}P(F_{B_j}^{\text{out}})^{\beta_j - 1} \times P(U_j - ba - U_i|a_i) \quad (28)$$

The unwanted root at $P(F_{B_m}^{\text{out}}) = 1$ is removed by an identical procedure to yield

$$P(U_i - ab - U_i|b_i)P(F_{A_i}^{\text{out}})^{\alpha_i - 1} \sum_{h=0}^{\beta_i - 1} P(F_{B_i}^{\text{out}})^h = [1 - P(F_{B_i}^{\text{out}})]^{-1}\{P(U_i - ab - U_i|b_i)P(F_{A_i}^{\text{out}})^{\alpha_i - 1} - P(F_{B_i}^{\text{out}}) + P(B_i|b_i) + \sum_{j \neq i} P(F_{A_j}^{\text{out}})^{\alpha_j - 1}P(F_{B_j}^{\text{out}})^{\beta_j}P(U_j - ab - U_i|b_i) \quad (29)$$

Once eq. (28) and (29) have been solved numerically, the probability that a randomly chosen U_i is part of the sol fraction is calculated directly.

$$P(F_i^{\text{out}}) = P(F_{A_i}^{\text{out}})^{\alpha_i}P(F_{B_i}^{\text{out}})^{\beta_i} \quad (30)$$

These sol fractions for each monomer are then averaged using the monomer mass fractions as a weight function to obtain the overall fraction of polymer in the sol phase.

$$\omega_{\text{sol}} = \sum_i \omega_i P(F_i^{\text{out}}) \quad (31)$$

From these probabilities that a given functional site is connected to a finite section of chain, the probability, $P(X_i, n_a, n_b)$, that a randomly chosen i-type monomer unit is a connected to the infinite network through n_a acid sites and n_b base sites is easily calculated.

$$P(X_i, n_a, n_b) = \binom{\alpha_i}{n_a} P(F_{A_i}^{\text{out}})^{\alpha_i - n_a}[1 - P(F_{A_i}^{\text{out}})]^{n_a} \binom{\beta_i}{n_b} \times P(F_{B_i}^{\text{out}})^{\beta_i - n_b}[1 - P(F_{B_i}^{\text{out}})]^{n_b} \quad (32)$$

The concentration of i-type crosslink units is equal to the product of the concentration of i-type monomer units with the probability that a randomly chosen unit is connected to the infinite network by at least three linkages.

$$X_i = U_i \sum_{n_a=1}^{\alpha_i} \sum_{n_b=1}^{\beta_i} H(n_a + n_b - 3)P(X_i, n_a, n_b) \quad (33)$$

The total crosslink density is simply the sum of the crosslink concentrations of each monomer type.

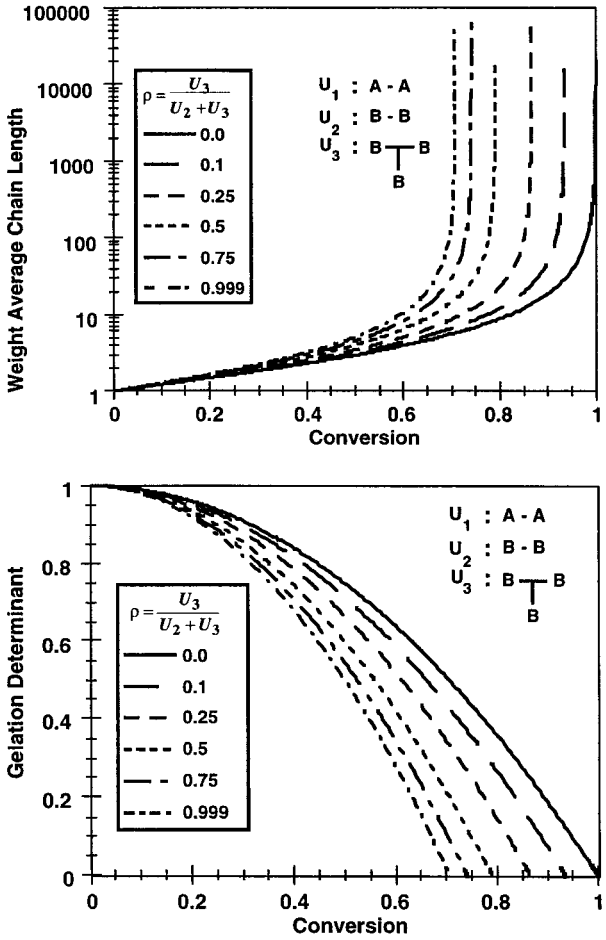

Figure 3 Gelation of a system of an *AA*, a *BB*, and a *BBB* monomer at different concentrations of the *BBB* monomer. (a) DP_w. (b) Gelation Determinant D_{gel}.

$$X_{\text{tot}} = \sum_i X_i \tag{34}$$

Figure 3 demonstrates the use of this model for the simulation of simple gelation phenomena. This figure shows the dependence of the gelation point upon the trifunctional base (*BBB*) monomer concentration in a system of *AA*, *BB*, and *BBB* monomers. The parameter ρ is the mol fraction of the base monomer that is trifunctional, and for each ρ the monomer concentrations are adjusted such that the end-group concentrations are balanced. The weight-average molecular weights diverge when the determinant D_{gel} approaches zero.

The capability of this model to handle blocky microstructures in gelating systems is illustrated in Figure 4. For an initial network of a bifunctional *AA* monomer, $U_{AA} = 0.6$, and a trifunctional *BBB* monomer, $U_{BBB} = 0.4$, at 85% conversion, unreacted bifunctional *BB* monomer, $U_{BB} = 0.15$, is added at time zero and the system undergoes interchange by alcoholysis. Initially, none of the *BB* monomer is linked to the infinite network and the fraction of *BB* in the sol phase is one. The incorporation of the *BB* monomer into the network through interchange eventually loosens the network and increases the overall sol fraction. Above a certain concentration of *BB* monomer, the network is completely dissolved.

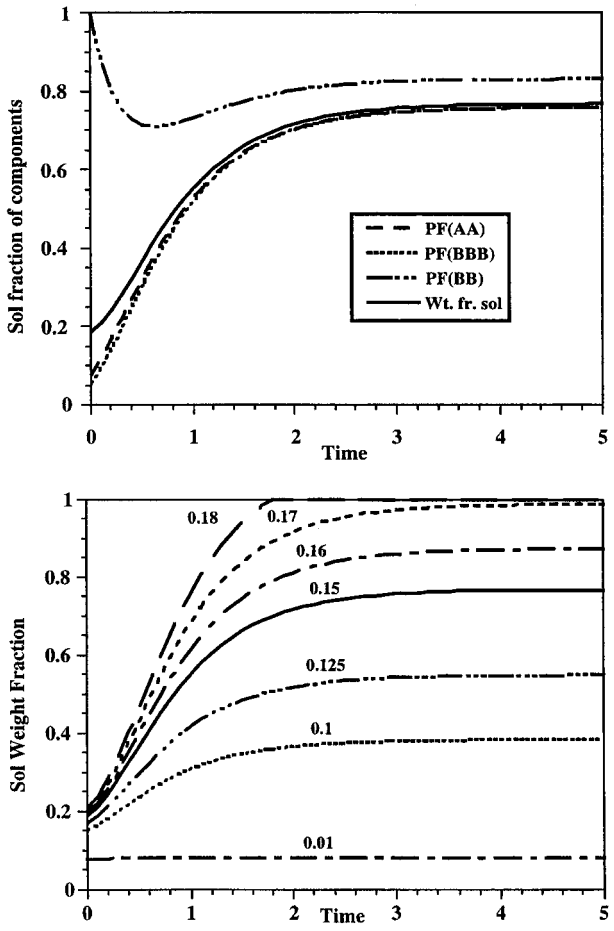

Figure 4 Modification of the structure of a network of *AA* and *BBB* monomers after incorporation of *BB* monomer into network through alcoholysis interchange. Initial *AA*/*BBB* conversion of 85% with $U_{AA} = 0.6$, $U_{BBB} = 0.4$. (a) Probability that a randomly chosen *AA*, *BBB*, or *BB* monomer will be in the sol phase (i.e., joined to chain of finite size). Overall weight fraction in the sol phase. Calculated for $U_{BB} = 0.15$. (b) Overall sol weight fraction at different U_{BB}.

The use of the original Macosko-Miller method with Bernoullian statistics (i.e., linkage concentrations proportional to monomer concentrations and the functional group conversions of each) only describes the final properties of the system as $t \rightarrow \infty$. The modified expressions with transition probabilities defined in terms of linkage moments allow the calculation of the sol/gel properties at each point during the randomization process.

CONCLUSIONS

A general model for the description of monomer connectivity and network properties of condensation copolymers has been presented in which the method of Macosko and Miller is expressed in terms of the concentrations of monomer-specific linkage groups. The extension of the method to include these linkage concentrations encodes sufficient information to model the effect of nonrandom microstructures upon gelation phenomena. The effect of the condensation and interchange reactions upon the properties of nonlinear polymers is calculated from the rates of change of the end group and linkage concentrations using the balance equations presented in the first article of this two-part series. The use of the model is demonstrated for a system in which two components have been brought into contact and allowed to undergo interchange reaction, thereby modifying the network properties as the microstructure is randomized.

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NOTATIONS

A_i	Concentration of active acid groups from i-type monomer
B^*_m	mth element of Bernoulli series
B_j	Concentration of active base groups from j-type monomer
D_{gel}	determinant in general gel point criterion
$E(W^{\text{out}}_{A_i})$	Expected weight outward from A_i site
$E(W^{\text{out}}_{B_i})$	Expected weight outward from B_i site
$E(W_i)$	Total expected weight attached to a random U_i
$H(x)$	Heaviside step function (1 if $x \geq 0$ else 0)
L_{ij}	Concentration of linkages between A_i and B_j
M_w	Weight average molecular weight
p_{A_i}	Conversion of A_i
p_{B_j}	Conversion of B_j
$P(A_i\|a_i)$	Probability that acid site on i-type monomer (a_i) is unreacted
$P(U_j - ba - U_i\|a_i)$	Probability that a_i is linked to a b_j
$P(B_i\|b_i)$	Probability that base site on i-type monomer (b_i) is unreacted
$P(U_j - ab - U_i\|b_i)$	Probability that b_i is linked to an a_j
$P(n_{A_i}, \{n_{a_{ij}}\}, n_{B_i}, \{n_{b_{ji}}\}\|U_i)$	Probability of finding specific connectivity on U_i
$[\underline{\underline{P}}_{AB}]_{ij}$	Matrix of $P(U_j - ba - U_i\|a_i)$
$[\underline{\underline{P}}_{BA}]_{ij}$	Matrix of $P(U_j - ab - U_i\|b_i)$
$P(F^{\text{out}}_{A_i})$	Probability of finite chain at A_i site
$P(F^{\text{out}}_{B_i})$	Probability of finite chain at B_i site
$P(F^{\text{out}}_i)$	Probability that randomly chosen U_i is in sol phase
$P(X_i, n_a, n_b)$	Probability that randomly chosen U_i is a crosslink
U_i	Concentration of type i repeat unit
W_{CA_i}	Weight of condensate residue from A_i
W_{a_i}	Weight of linkage residue from A_i
W_{CB_i}	Weight of condensate residue from B_i
W_{b_i}	Weight of linkage residue from B_i
W_{U_i}	Weight of i-type monomer without functional groups
$[\underline{W}_{\text{PCA}}]_i$	Vector of $W_{CA_i}P(A_i\|a_i)$
$[\underline{W}_{\text{PCB}}]_i$	Vector of $W_{CB_i}P(B_i\|b_i)$

$[\underline{W}_U]_i$ Vector of $W_{U_i} + \alpha_i W_{a_i} + \beta_i W_{b_i}$
X_i Concentration of i-type monomer units serving as a crosslink
X_{tot} Total concentration of crosslinks

Greek Letters

α_i Number of acid groups on i-type monomer
$[\underline{\underline{\alpha}}]_{ij}$ Matrix of $\alpha_i \delta_{ij}$
β_i Number of base groups on i-type monomer
$[\underline{\underline{\beta}}]_{ij}$ Matrix of $\beta_i \delta_{ij}$
δ_{ij} Kronecker delta (1 if $i = j$ else 0)
ω_i Weight fraction of i-type monomer units
ω_{sol} Weight fraction of the sol phase

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