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Spanning-tree models for A_f homopolymerizations with intramolecular reactions

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Abstract

The spanning-tree approximation model is one of the models used for polymerizations with intramolecular reaction regardless of the size of the ring formed. We present a modification of this model that uses more accurate internal estimates of the probabilities of intramolecular reaction. This requires limited Monte Carlo simulations of some molecular structures, resulting in a hybrid probability model (a combined analytic and Monte Carlo model). We then extend the spanning-tree model so that it may be used in the post-gel region. We show three possible extensions of varying degrees of complexity. The resulting models for stepwise A_f homopolymerizations have been coded into programs that run on desktop PCs in a few seconds. The models calculate the amount of intramolecular conversion, the weight-average molecular weight, the gel point, the weight fraction of soluble material, and the weight-average molecular weight of the sol fraction. We discuss the relative merits of the modified spanning-tree model and its three post-gel extensions and show sample calculations for arbitrary homopolymerization systems.

Keywords: Homopolymerization; Intramolecular; Mathematical model; Spanning tree

1. Introduction

The presence of intramolecular reactions in polymerizations introduces a number of defects in the resulting polymer. When two reactive sites that happen to belong to the same molecule react with each other, a cycle or loop forms. Conversion advances but the molecular weight remains unchanged. The reactive sites are in that sense "wasted". As a consequence of these intramolecular reactions, the molecular weight of the system at any given conversion is lower than what would be expected from the "ideal" classical formulae, such as those given by Flory [1] and Stockmayer [2,3]. The gel point is delayed, and after that the network that forms is imperfect, with more solubles and more dangling chains than would be expected in an ideal polymerization. It has been observed experimentally that some conditions tend to favor the presence of intramolecular reactions [4–6]: more diluted systems, more flexible chains, and stoichiometrically balanced systems.

Several efforts have been made in the past to be able to model intramolecular reactions in irreversible stepwise systems [5–10]. Modeling irreversible systems is a very challenging problem, since the resulting distribution of degrees of polymerization is not known beforehand, and the exact solution of the problem requires simultaneous knowledge of the relative positions of all unreacted sites that belong to the same molecules. Several approaches are possible, but they all involve adopting approximations [11].

One approach is the Spanning-Tree Approximation, due to Gordon and coworkers [6,7,12]. The spanning-tree approximation models a branched polymerization containing intramolecular reactions, which create cycles. The bonds formed by intramolecular reactions are cut and the intramolecularly reacting groups are labeled with "σ". This transforms a molecular structure with cycles into a tree-like (no cycles) structure: a spanning tree. The structure of a spanning tree can be modeled approximately using a stochastic branching process. The reactive groups are labeled: unreacted groups are labeled "ω", intermolecularly reacted groups are labeled "α" (tree forming), and intramolecularly reacted groups are labeled "σ" (cycle forming). An example is shown in Fig. 1. One advantage of this model is that it requires very few differential equations to account for all the intramolecularly reacted sites in a system. A disadvantage is that it does not keep track of the size of the loops formed, and that could lead to problems in the predictions. It has been noted [13] that it is not possible to

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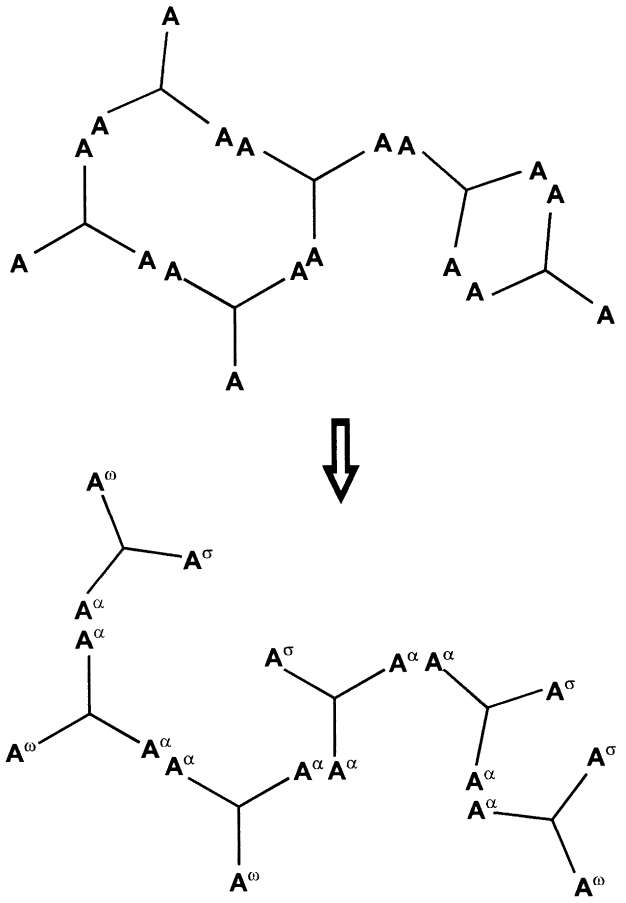

Fig. 1. An A_3 star-homopolymer molecule with cycles is transformed into a spanning-tree approximation of molecule by cutting the intramolecular bonds (and labeling them with σ).

fit gel point data and molecular weight data with the same adjustable parameter. If the parameter is adjusted so that molecular weight predictions are good over most of the pre-gel region, then the gel point delay is larger than the experimentally observed one [13]. A second problem with the model is that in its original form it may not be used beyond the gel point, because the equations that account for intramolecular reaction diverge. The post-gel region is very important for those working with thermosets or elastomers; therefore, it would be useful to extend the model to that region, especially in view of the low computational cost involved in a model with so few differential equations. As with any mean field theory, it should be applied with caution to systems with severe steric hindrances. It is however an attractive option for flexible systems where polymerization is not diffusion-controlled, provided its known shortcomings could be somehow alleviated.

In this work, we investigate the spanning-tree model and propose a modification and extensions that have two benefits: improvement of predictions in the pre-gel region, and validity of the model beyond the gel point. This modification results in a hybrid model that is in part analytic, and in part numerical Monte Carlo modeling.

There are different ways to implement a branching process model of the spanning tree. We can find the fraction of labeled reactive groups (ω, α, σ) by an approximate kinetic analysis, then randomly assign labels to the individual groups on monomers, and then, using the branching process model, randomly construct and analyze the molecular structure. Alternatively, it is possible to perform an approximate kinetic analysis of the simultaneous labeling of all groups on individual monomers, and then randomly combine these labeled monomers using a more complicated branching process model. This is the approach generally taken by Gordon and Scantlebury [6] who introduced the spanning-tree approximation model. It is also possible to perform a kinetic analysis on even larger structures, labeling reactive groups with ω, α, or σ, and then building up the molecular structure as a branching process; Sarmoria et al. [8] used larger fragments in modeling $A_f + B_2$ copolymerizations with unit cycles. All these approaches are approximations, but the second and third avoid such glaring impossibilities as a three-functional monomer labeled with two ωs and one σ. Here, we shall use the first approach which is simpler (and perhaps, no worse an approximation than the other approaches); we believe that it illustrates the general points that we wish to make concerning spanning tree-approximation models.

2. Model A: the spanning-tree model of A_f homopolymerization (stars)

In this paper, we will consider homopolymerizations of stars with f equal arms. Each arm contains exactly one reactive group at its end. The reactive site is denoted as "A", while the f-functional star monomer is denoted as A_f. Suppose that an A_f star-monomer homopolymerization in which cyclization is permitted has reacted to conversion β (counting both inter- and intramolecular reaction), where $0 \leq \beta \leq 1$. A-groups may be unreacted (ω), intramolecularly reacted (σ), or intermolecularly reacted (α); denote these groups as A^{ω}, A^{σ}, and A^{α}, respectively. At conversion β, let the fractions (or probabilities) of A-groups in different states be $\omega(\beta)$, $\sigma(\beta)$, and $\alpha(\beta)$, respectively, so $\beta = \alpha(\beta) + \sigma(\beta)$. At conversion β, we will use a branching process model to construct and analyze an approximation to the spanning-tree description of the polymer molecules. In the next increment of conversion, $[\beta, \beta + \Delta\beta]$, we would like to model the changes in $\omega(\beta)$, $\sigma(\beta)$, and $\alpha(\beta)$. We know that the change in $\omega(\beta)$ equals $-\Delta\beta$ and the change in $\alpha(\beta) + \sigma(\beta)$ equals $+\Delta\beta$, so it suffices to calculate the fractions (or probabilities) of reactions that are intramolecular or intermolecular.

Consider a randomly chosen unreacted A-group, A^{ω}_{*}, which we shall denote as the "root" unreacted A-group. Suppose that the background concentration of A^{ω} groups on other molecules is $C_{\text{inter}}(\beta)$. This is the concentration of

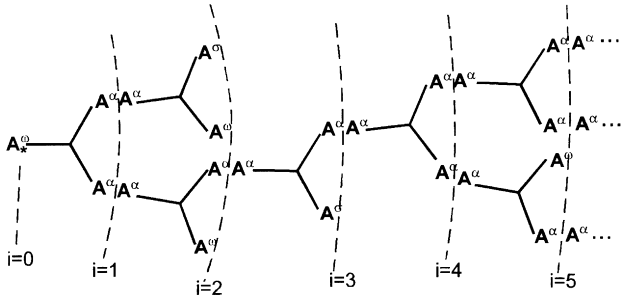

Fig. 2. The shell and generation structure around a random unreacted monomer, A_*^{ω}.

intermolecular-bonding candidates. So,

$$C_{\text{inter}}(\beta) = (1-\beta)f[A]_0, \tag{1}$$

where $[A]_0$ is the initial concentration of A_f-monomers. Furthermore, suppose that the mean (over different conformations of the molecule) concentration of additional A^{ω} groups on the same molecule in the neighborhood of the unreacted root A-group is $C_{\text{intra}}(\beta)$. This is the concentration of intramolecular-bonding candidates. We shall calculate an approximation to $E(C_{\text{intra}}(\beta))$, the average concentration of intramolecular-bonding candidates about a randomly chosen unreacted A-group. Then, we will use as probabilities of intramolecular and intermolecular bonding:

$$P(\text{intra}|\beta) = \frac{E(C_{\text{intra}}(\beta))}{E(C_{\text{intra}}(\beta)) + C_{\text{inter}}(\beta)} \tag{2}$$

$$P(\text{inter}|\beta) = \frac{C_{\text{inter}}(\beta)}{E(C_{\text{intra}}(\beta)) + C_{\text{inter}}(\beta)} \tag{3}$$

Note that this assumes second-order reactions. For small $\Delta\beta$, we get the difference scheme:

$$\omega(\beta+\Delta\beta) = \omega(\beta) - \Delta\beta \tag{4}$$

$$\sigma(\beta+\Delta\beta) = \sigma(\beta) + P(\text{intra}|\beta)\Delta\beta \tag{5}$$

$$\alpha(\beta+\Delta\beta) = \alpha(\beta) + P(\text{inter}|\beta)\Delta\beta \tag{6}$$

or, for infinitesimal $d\beta$, we get the system of differential equations:

$$\frac{d\omega(\beta)}{d\beta} = -1 \tag{7}$$

$$\frac{d\sigma(\beta)}{d\beta} = P(\text{intra}|\beta) \tag{8}$$

$$\frac{d\alpha(\beta)}{d\beta} = P(\text{inter}|\beta) \tag{9}$$

The initial values for both systems of equations are: $\omega(0) = 1$, $\sigma(0) = 0$, $\alpha(0) = 0$. The above difference scheme can be implemented using Euler's method for $0 \le \beta \le 1$. The differential equations can be solved using a numerical differential equation solver. Both approaches require that we calculate a value of $E(C_{\text{intra}}(\beta))$ from the current values of β, $\sigma(\beta)$, and $\alpha(\beta)$.

To derive a formula for $E(C_{\text{intra}}(\beta))$, we use a branching process model of molecular structure about a randomly chosen root unreacted A-group, A_*^{ω}. We use the shell and generation structure around A_*^{ω}, as illustrated in Fig. 2. (Burchard [14] gives a description of this modeling paradigm.) The molecule is organized as a family tree, with the chosen A_*^{ω}, in the 0th generation or shell. That position is indicated with $i = 0$ in Fig. 2. The remaining A-groups on the root monomer are placed on the first generation or first shell, $i = 1$ in Fig. 2. If these sites reacted, as is the case in the example in Fig. 2, they have "descendants" that are placed on the second shell, $i = 2$, and so on.

We require the following notation: Let $M(i)$ be the number of A-monomers in the ith shell about the root A_*^{ω}, $i = 0, 1, 2, \ldots$ Using this definition, $M(0)$ always equals unity, since it is the monomer with A_*^{ω}. In the example in Fig. 2, $M(1) = 2$ and $M(2) = 1$. Let $N_{\omega}(i)$, $N_{\sigma}(i)$, and $N_{\alpha}(i)$ equal the number of A^{ω}-groups, A^{σ}-groups, and A^{α}-groups, respectively, exactly i generations from the root A_*^{ω}, $i = 1, 2, 3, \ldots$ This notation is somewhat redundant, but hopefully it will make the presentation clearer. The redundant relationships are:

$$M(i) = N_{\alpha}(i) \tag{10}$$

$$(f-1)M(i) = N_{\omega}(i+1) + N_{\sigma}(i+1) + N_{\alpha}(i+1) \tag{11}$$

which equals the number of A-groups in the $i+1$st generation from A_*^{ω}.

Consider the random displacement of a particular A_i^{ω}-group in the ith generation about the root group A_*^{ω}. If we put A_*^{ω} at (0,0,0) and denote the position of A_i^{ω} as (X, Y, Z), then for long chains the random variables X, Y, and Z will be independent Gaussian random variables with zero means and variances $\text{Var}(X) = \text{Var}(Y) = \text{Var}(Z) = \sigma^2 n\ell^2 i/3$. Here n is the number of segments between A-groups on the A_f-star monomer (so the number of segments on an arm of the A_f-star monomer is $n/2$), ℓ is the length of each segment on the arms of the A_f-star monomer, and σ^2 is the flexibility coefficient for the arms of A_f-monomers ($\sigma^2 = 1$ corresponds to freely-jointed chain). Note that $E(X) = E(Y) = E(Z) = 0$; it then follows that $E(X^2) = E(Y^2) = E(Z^2) = \sigma^2 n\ell^2 i/3$. By independence of X, Y, and Z, the mean squared end-to-end distance is $E(R^2) = E(X^2) + E(Y^2) + E(Z^2) = \sigma^2 n\ell^2 i$, which is the well-known result. So, the joint density of (X, Y, Z) for a single A_i^{ω}, an unreacted A-group exactly i generations from the root unreacted group, is the three-dimensional (3D) Gaussian density

$$f_{X,Y,Z}(x,y,z) = \left(\frac{1}{\sqrt{2\pi\sigma^2 n\ell^2 i/3}}\right)^3 \exp\left(-\frac{x^2+y^2+z^2}{2\sigma^2 n\ell^2 i/3}\right),$$

$$-\infty \le x, y, z \le \infty \tag{12}$$

The density at (0,0,0) equals the mean concentration of a single A^{ω}-group in the ith generation about A_*^{ω}:

$$C_i = f_{X,Y,Z}(0,0,0) = (2\pi\sigma^2 n\ell^2 i/3)^{-3/2} \tag{13}$$

This concentration is given in units per volume. This value should be divided by Avogadro's number to obtain concentration in moles per volume. The number of A^{ω}-groups in the ith generation is $N_{\omega}(i)$, therefore the mean concentration (over all conformations) of the totality of these A^{ω}-groups in the neighborhood of the root A_*^{ω} is

$$C_{\text{intra}}(\beta) = \sum_{i=1}^{\infty} (2\pi\sigma^2 n\ell^2 i/3)^{-3/2} N_{\omega}(i) \tag{14}$$

and the expected mean concentration over all choices of random unreacted A-group roots is

$$E(C_{\text{intra}}(\beta)) = (2\pi\sigma^2 n\ell^2/3)^{-3/2} \sum_{i=1}^{\infty} i^{-3/2} E(N_{\omega}(i)) \tag{15}$$

We shall now use a branching process model, the shell method, to derive a formula for $E(N_{\omega}(i))$ to be used in the above formula for $E(C_{\text{intra}}(\beta))$. We need the following notation: Let $T_{i,j}$ equal the number of additional A^{α}-groups on the jth monomer in the ith shell (excluding the A^{α} connecting this monomer to the root A_*^{ω}), $i = 0, 1, 2, \ldots$ The random variables T have a Binomial(f–1, $\alpha(\beta)$) distribution; so, $E(T) = (f\text{–}1)\alpha(\beta)$. Let $U_{i,j}$ equal the number of additional A^{ω}-groups on the jth monomer in the ith shell (excluding the root A_*^{ω} in the 0th shell), $i = 0, 1, 2, \ldots$ The random variables U have a Binomial(f–1, $\omega(\beta)$) distribution; so, $E(U) = (f\text{–}1)\omega(\beta)$. Note that, for fixed i and j, $T_{i,j}$ and $U_{i,j}$ are not independent, but have a multinomial distribution. (Recall that Ts represent tree-forming bonds and Us represent unreacted groups.) The shell relationships for the molecular structure are:

$$M(0) = 1 \tag{16}$$

$$M(i+1) = N_{\alpha}(i+1) = \sum_{j=1}^{M(i)} T_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{17}$$

$$N_{\omega}(i+1) = \sum_{j=1}^{M(i)} U_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{18}$$

Taking expected values of the structural relationships in Eqs. (16)–(18) gives:

$$E(M(0)) = 1 \tag{19}$$

$$E(M(i+1)) = E\left(\sum_{j=1}^{M(i)} T_{i,j}\right) = E(M(i))E(T) = (f-1)\alpha(\beta)E(M(i)) \tag{20}$$

$$E(N_{\omega}(i+1)) = E\left(\sum_{j=1}^{M(i)} U_{i,j}\right) = E(M(i))E(U) = (f-1)\omega(\beta)E(M(i)) \tag{21}$$

Solving Eqs. (19) and (20) gives

$$E(M(i)) = (E(T))^i = ((f-1)\alpha(\beta))^i, \qquad i = 0, 1, 2, \ldots \tag{22}$$

and further substitution into Eq. (21) gives

$$E(N_{\omega}(i)) = E(M(i-1)E(U) = (f-1)^i \omega(\beta)\alpha(\beta)^{i-1}, \quad i = 0, 1, 2, \ldots \tag{23}$$

Finally, substitution into Eq. (13) gives

$$E(C_{\text{intra}}(\beta)) = (2\pi\sigma^2 n\ell^2/3)^{-3/2} \sum_{i=1}^{\infty} i^{-3/2} (f-1)^i \omega(\beta)\alpha(\beta)^{i-1}, \quad 0 \le \beta \le 1 \tag{24}$$

Using Eqs. (24)–(9) with Eq. (2) allows numerical calculation of $(\omega(\beta), \sigma(\beta), \alpha(\beta))$, $0 \le \beta \le 1$.

We can also calculate the weight-average molecular weight M_w at any conversion β. To do this, randomly pick an A-monomer and designate it as the root (*) of a random molecule selected by weight. The resulting structure could be, for example, the one indicated in Fig. 2. Let R equal the number of A-groups on the root monomer that have reacted intermolecularly; then R has a Binomial($f, \alpha(\beta)$) distribution and $E(R) = f\alpha(\beta)$. Let $M(i)$ equal the number of monomers in the ith shell around the root monomer, $i = 0, 1, 2, \ldots$ The number of monomers in successive generations satisfy the relationships

$$M(0) = 1 \tag{25}$$

$$M(1) = R \tag{26}$$

$$M(i+1) \sum_{j=1}^{M(i)} T_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{27}$$

Taking expectations of the structural relationships in Eqs. (25)–(27) gives

$$E(M(0)) = 1 \tag{28}$$

$$E(M(1)) = E(R) \tag{29}$$

$$E(M(i+1)) = E\left(\sum_{j=1}^{M(i)} T_{i,j}\right) = E(M(i))E(T), \quad i = 0, 1, 2, \ldots \tag{30}$$

Solving Eqs. (28)–(30) gives

$$E(M(i)) = E(R)E(T)^{i-1}, \qquad i = 0, 1, 2, \ldots \tag{31}$$

The molecular weight W of this random molecule satisfies:

$$W = M_A \sum_{i=0}^{\infty} M(i) \tag{32}$$

Taking the expected value gives the weight-average molecular weight:

$$M_w = E(W) = M_A E\left(\sum_{i=0}^{\infty} M(i)\right) = M_A \sum_{i=0}^{\infty} E(M(i)) \tag{33}$$

which by substitution using Eq. (31) becomes

$$M_w = M_A\left(1 + E(R)\sum_{i=0}^{\infty} E(T)^i\right) = M_A\left(1 + \frac{E(R)}{1 - E(T)}\right)$$

$$= M_A\left(\frac{1 + \alpha(\beta)}{1 - (f-1)\alpha(\beta)}\right) \tag{34}$$

Note that gelation occurs when $\alpha(\beta)$ equals $1/(f-1)$. Note also, that for this critical value of $\alpha(\beta)$, $E(C_{intra}(\beta)) < \infty$. But, for $\alpha(\beta) > 1/(f-1)$, $E(C_{intra}(\beta)) = \infty$ and $P(\text{intra}|\beta) = 1$. Thus, beyond the gel point, this model does not allow intermolecular reaction to occur. For this reason, the usual spanning-tree approximation is not appropriate for post-gel analysis.

3. Model B: an alternative formulation

Beyond the gel point, the probability of intramolecular reaction should still be less than one. The model for $P(\text{intra}|\beta)$ given in Eq. (2) yields a value of 1 for conversions beyond the gel point, creating a problem. A more accurate model for $P(\text{intra}|\beta)$ is the following. Consider that $C_{intra}(\beta)$ is a random variable; it equals the mean concentration of intramolecular-bonding candidate A-groups about a randomly chosen unreacted A-group, A_*^ω. The probability of an intramolecular bond around this particular random A-group is then

$$P(\text{intra for } A_*^\omega|\beta) = \frac{C_{intra}(\beta)}{C_{intra}(\beta) + C_{inter}(\beta)} \tag{35}$$

and the average, overall probability is obtained by taking the expected value of these random probabilities for random choices of A_*^ω :

$$P(\text{intra}|\beta) = E\left(\frac{C_{intra}(\beta)}{C_{intra}(\beta) + C_{inter}(\beta)}\right) \tag{36}$$

Note that

$$E\left(\frac{C_{intra}(\beta)}{C_{intra}(\beta) + C_{inter}(\beta)}\right) \neq \frac{E(C_{intra}(\beta))}{E(C_{intra}(\beta)) + C_{inter}(\beta)} \tag{37}$$

and that the values can differ significantly.

We propose using Eq. (36) to estimate the probability of intramolecular reactions. Making the appropriate modification to the previous model, the substitution into Eq. (36) gives

$$P(\text{intra}|\beta) = E\left(\frac{(2\pi\sigma^2 n\ell^2/3)^{-3/2}\sum_{i=1}^{\infty} i^{-3/2}N_\omega(i)}{(2\pi\sigma^2 n\ell^2/3)^{-3/2}\sum_{i=1}^{\infty} i^{-3/2}N_\omega(i) + C_{inter}(\beta)}\right) \tag{38}$$

where $C_{inter}(\beta)$ is in units per volume. Unfortunately, this expression for the intramolecular probability appears analytically intractable. Therefore, to solve Eqs. (4)–(6), we will estimate $P(\text{intra}|\beta)$ in Eq. (38) using Monte Carlo simulation for given values of $(\omega(\beta), \sigma(\beta), \alpha(\beta))$, $0 \leq \beta \leq 1$.

4. Monte Carlo simulation of $P(\text{intra}|\beta)$

Pick a random A^ω and designate it as the root unreacted A-group, A_*^ω. We want to simulate the mean concentration of intramolecular-bonding candidate A-groups around this particular A_*^ω. We shall simulate the random spanning-tree structure around this A_*^ω for the parameters $(\omega(\beta), \sigma(\beta), \alpha(\beta))$ and from this simulation estimate the mean concentration of possible intramolecular groups. From this concentration, we can estimate the probability that an intramolecular reaction occurs if the root group reacts. We replicate this Monte Carlo experiment n times, and average the n estimates of the intramolecular probability to obtain our estimate of $P(\text{intra}|\beta)$.

To simulate the random spanning-tree structure around A_*^ω, we simulate values of the random variables $T_{i,j}$ and $U_{i,j}$ until the molecule terminates or (in the gel) until we reach a truncation condition. For a given (i,j), the random variables $T_{i,j}$ and $U_{i,j}$ have a multinomial distribution with $(f-1)$ trials: the probability of "ω" is $\omega(\beta)$ and the probability of "α" is $\alpha(\beta)$. To simulate, sample $(f-1)$ random numbers; the number falling in the interval $[0, \omega(\beta)]$ equals $u_{i,j}$ and the number falling in the interval $[1-\alpha(\beta), 1]$ equals $t_{i,j}$. Then the spanning-tree structure is:

$$m(0) = 1 \tag{39}$$

$$m(i+1) = \sum_{j=1}^{m(i)} t_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{40}$$

$$n_\omega(i+1) = \sum_{j=1}^{m(i)} u_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{41}$$

The mean concentration of a single A^ω in the ith generation around the root A_*^ω is given by Eq. (13). Therefore the mean concentration of all A^ω-groups in the ith generation around the root A_*^ω is

$$c_{intra,i}(\beta) = n_\omega(i) f_i(0,0,0) = n_\omega(i)(2\pi\sigma^2 n\ell^2 i/3)^{-3/2} \tag{42}$$

The total mean concentration of all A^ω-groups near this

randomly chosen root A_*^ω is

$$c_{\text{intra}}(\beta) = \sum_{i=1}^{\infty} c_{\text{intra},i}(\beta) = \sum_{i=1}^{\infty} n_\omega(i)(2\pi\sigma^2 n\ell^2 i/3)^{-3/2} \quad (43)$$

So, for this particular A_*^ω we estimate the probability of intramolecular reaction to be

$$p(\text{intra}|\beta) = \frac{c_{\text{intra}}(\beta)}{c_{\text{intra}}(\beta) + C_{\text{inter}}(\beta)}, \quad (44)$$

the probability of intermolecular reaction to be

$$p(\text{inter}|\beta) = \frac{C_{\text{inter}}(\beta)}{c_{\text{intra}}(\beta) + C_{\text{inter}}(\beta)} \quad (45)$$

and the probability of a cycle of size i to be

$$p_i(\text{intra}|\beta) = \frac{c_{\text{intra},i}(\beta)}{c_{\text{intra}}(\beta) + C_{\text{inter}}(\beta)} \quad (46)$$

We replicate this Monte Carlo experiment n times for given values of $(\omega(\beta), \sigma(\beta), \alpha(\beta))$. In this way, we get n independent observations of each of the above values. Using k as an index for the replicates, we have values $(c_{\text{intra}}(\beta))_k$ and $(p(\text{intra}|\beta))_k$, $k = 1, 2, 3, \ldots, n$; and $(c_{\text{intra},i}(\beta))_k$ and $(p_i(\text{intra}|\beta))_k$, $i = 1, 2, 3, \ldots$; $k = 1, 2, 3, \ldots, n$. From these numbers, we estimate the probabilities of intramolecular reaction and also the probabilities of cycles of particular sizes

$$\hat{P}(\text{intra}|\beta) = \frac{1}{n}\sum_{k=1}^{n} (p(\text{intra}|\beta)_k)$$

$$= \frac{1}{n}\sum_{k=1}^{n} \frac{(c_{\text{intra}}(\beta))_k}{(c_{\text{intra}}(\beta))_k + C_{\text{inter}}(\beta)} \quad (47)$$

$$\hat{P}_i(\text{intra}|\beta) = \frac{1}{n}\sum_{k=1}^{n} (p_i(\text{intra}|\beta)_k)$$

$$= \frac{1}{n}\sum_{k=1}^{n} \frac{(c_{\text{intra},i}(\beta))_k}{(c_{\text{intra}}(\beta))_k + C_{\text{inter}}(\beta)} \quad (48)$$

$$\hat{P}(\text{inter}|\beta) = 1 - \hat{P}(\text{intra}|\beta) \quad (49)$$

These estimates of the probabilities are then used instead of the analytical values from Eq. (2) in the differential equations governing $(\omega(\beta), \sigma(\beta), \alpha(\beta))$. The rest of the analysis is the same as before.

If we use Euler's method for β: $0 \le \beta \le 1$, with $\Delta\beta = 0.01$, then we go through the Monte Carlo simulation step 100 times. At each value of β, we randomly grow statistically larger structures around a random unreacted root A-group, A_*^ω. One approach is to execute 100 independent simulation experiments, building n new structures each time. Another, more efficient approach, is to save the n structures created at conversion β and then add to them at time $\beta + \Delta\beta$ rather than starting all over with n new structures. In the interval $[\beta, \beta + \Delta\beta]$, fraction $\Delta\beta$ of all groups are reacted, which equals fraction $\Delta\beta/\omega(\beta)$ of all groups unreacted at conversion β. So, during the interval $[\beta, \beta + \Delta\beta]$, fraction $P(\text{intra}|\beta)\Delta\beta/\omega(\beta)$ of ω-groups become σ-groups and fraction $P(\text{inter}|\beta)\Delta\beta/\omega(\beta)$ of ω-groups become α-groups. At conversion$(\beta$, a spanning tree rooted at A_*^ω is described by $(n_\omega(1), n_\omega(2), n_\omega(3), \ldots)$, the number of unreacted groups in each generation from A_*^ω. We consider each ω-group in the rooted tree, except for the root. With probability $P(\text{intra}|\beta)\Delta\beta/\omega(\beta)$, we randomly change the ω-group to a σ-group. With probability $P(\text{inter}|\beta)\Delta\beta/\omega(\beta)$, we randomly change the ω-group to form an α-bond and then continue building using probabilities $\alpha(\beta + \Delta\beta)$ and $\sigma(\beta + \Delta\beta)$ to continue the tree out from that α-group, updating the n_ω-vector appropriately.

We have presented two spanning-tree approximation models: we refer to them as Models A and B. In Model A, we calculate $P(\text{intra}|\beta)$ as the ratio of expected concentrations from Eq. (2); this is the original method of Gordon and Scantlebury [6]. In Model B, using Monte Carlo simulation, we estimate $P(\text{intra}|\beta)$ in Eq. (36) as the average of probabilities for individual unreacted groups; this is a new method. Model B is a more accurate representation of the physical intramolecular reaction phenomenon than Model A; therefore Model B should be the a priori model of choice.

5. Some numerical results and conclusions for conversions up to the gel point

We have run several cases for monomers with functionality f ranging from 3 to 7. As a first step, we had to establish the parameters that would make the Monte Carlo simulation reliable. Two parameters were involved: the number of replications that would be used to obtain the averages, and the maximum number of generations in any one soluble molecule (molecules with more generations are considered to belong to the gel fraction). We performed the simulations with a $\Delta\beta$ step-size of 0.001, and increased the number of replications "n" and the number of generations in the sol "*nsol*" until the gel point calculated by Model B became stable, with a maximum variation of 0.002 in β. We performed this test for concentrated and diluted systems (in the latter, there is greater ring formation), and for different functionalities in the starting monomer. From these simulations, the values of 150 replications and 20 generations in the sol give good accuracy. These values were used for the remainder of the work reported in this paper.

We compared the results of Models A and B. The results given by the two models are not always different. If the amount of ring formation causes the gel point to be delayed by less than 20% compared with the ideal (no rings) case, then both models give practically identical results. If ring formation is more important, then Model A always predicts a greater delay than Model B does. As an example, we show in Fig. 3 the results obtained from both models for a system of A_3 homopolymerization, with the same molecular weight

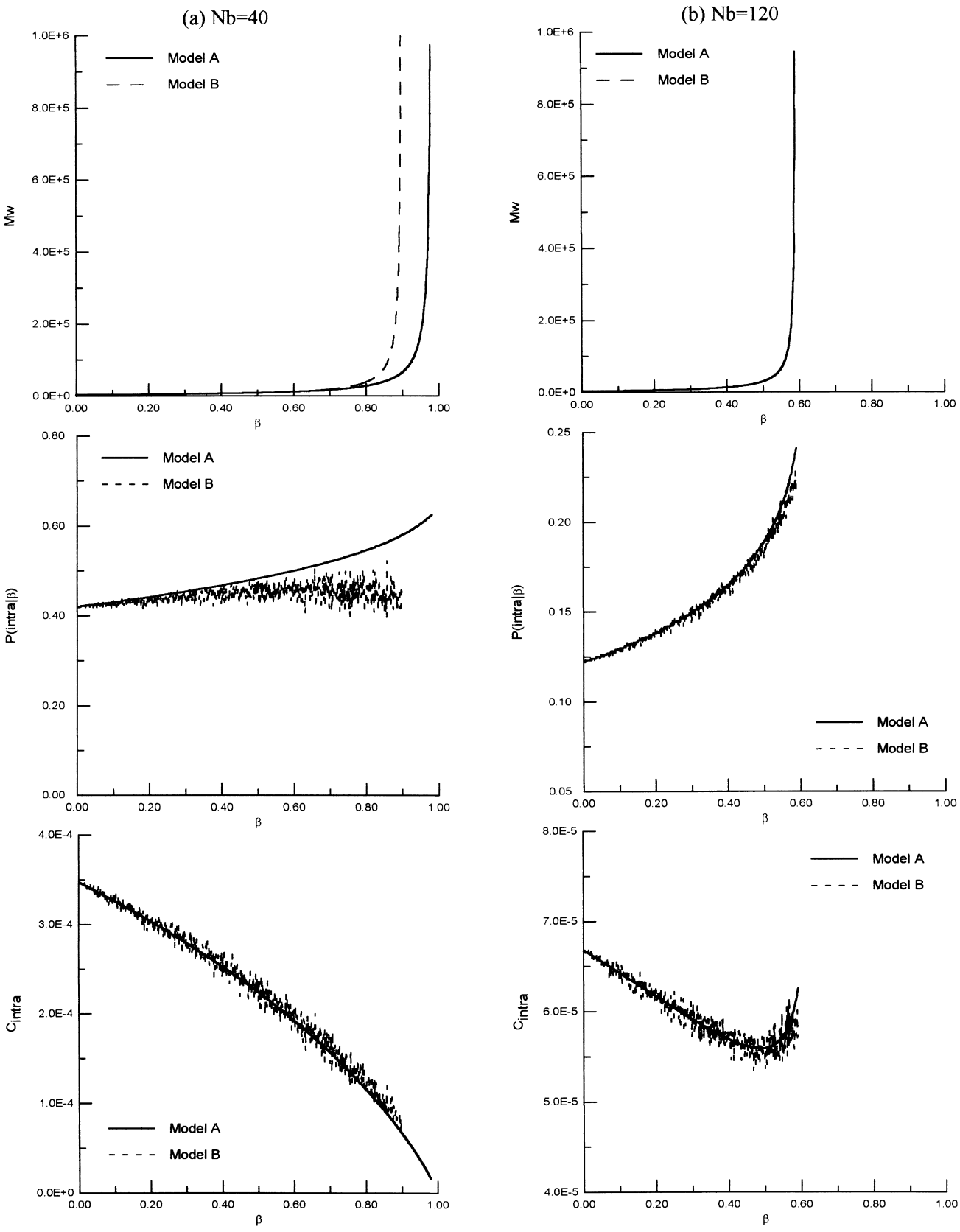

Fig. 3. Predictions from Models A and B for an A_3 homopolymerization: (a) with 40 bonds in each arm; and (b) with 120 bonds in each arm.

(3000), the same dilution (50%), the same end-to-end distance distribution (Gaussian) and different number of segments in their arms. For Fig. 3(a), there are 40 segments in each arm, while for Fig. 3(b) there are 120 segments in each arm. It is expected that the system with longer arms will generate fewer rings, since the concentrations $C_{\text{intra},i}$ will be lower in that case. We know that for the ideal case, the gel point should be at $\beta = 0.5$. When there are 40 segments in each of the three arms of the A_f monomer, the predicted gel points are 0.984 for Model A, and 0.900 for Model B. Weight average molecular weight predictions differ accordingly. The prediction of $P(\text{intra}|\beta)$ is different between the two models, even though the average value of C_{intra} is practically the same for both of them. This was to be expected, as discussed above. For the case where the number of bonds in each arm is 120, the predicted gel points are 0.593 for Model A and 0.592 for Model B. As can be seen in Fig. 3(b), all quantities are almost identical.

6. After the gel point: Model I

The original spanning-tree approximation model (Model A) is a poor one after the gel point and no one has attempted to use it in its original form. The theoretical expected concentration $C_{\text{intra}}(\beta)$ is infinite after gelation. Thus, $P(\text{intra}|\beta)$ equals 1 and all reactions after the gel point will be intramolecular. This results in all molecular and network parameters being fixed at the values they had at the gel point.

Using our modification of the usual spanning-tree model (Model B) in which we compute $P(\text{intra}|\beta)$ as the expected value of the intramolecular reaction probabilities over randomly chosen molecules is a modest improvement after the gel point: If the root unreacted A-group, A_*^ω, belongs to the soluble fraction we will get $P(\text{intra}|\text{sol}, \beta)$ less than 1; if it belongs to the gel fraction, we get $P(\text{intra}|\text{gel}, \beta) = 1$. The overall $P(\text{intra}|\beta)$ will then be less than one, so we still get some intermolecular reaction and network build-up after the gel point.

So, for this first post-gel model (Model I), we concede complete intramolecular reaction in the gel fraction. We model the sol fraction, estimate $P(\text{intra}|\text{sol}, \beta)$, and then average it with 1 to get $P(\text{intra}|\beta)$. We can estimate $P(\text{intra}|\text{sol}, \beta)$ in two ways: (a) as the ratio of theoretical expected concentrations (in the spirit of the original spanning tree); or, (b) as the expected value of probabilities of intramolecular reaction for randomly chosen A_*^ω (using Monte Carlo simulation). In both cases, we model the molecular structure of the sol fraction.

The molecules in the sol fraction of an A_f homopolymerization (reacted to intermolecular conversion $\alpha(\beta)$) are statistically identical to those of a pre-gel A_f homopolymerization at conversion $\alpha_s(\beta)$, where the subscript "s" represents "soluble material" [1,15]. For an A_f homopolymerization, the relationship between α_s and α is: $\alpha_s = \alpha P(F_A^{\text{out}})^{f-2}$, where $P(F_A^{\text{out}})$ equals the probability of seeing a finite branch when looking "out" from a randomly chosen A-group [15]. $P(F_A^{\text{out}})$ satisfies the equation

$$P(F_A^{\text{out}}) = (1 - \alpha)1 + \alpha P(F_A^{\text{out}})^{f-1} \tag{50}$$

For $f = 3$,

$$P(F_A^{\text{out}}) = \frac{(1-\alpha)}{\alpha}, \qquad \alpha_s = 1 - \alpha, \quad \frac{1}{2} \le \alpha \le 1 \tag{51}$$

For $f = 4$,

$$P(F_A^{\text{out}}) = \frac{\sqrt{4\alpha - 3\alpha^2} - \alpha}{2\alpha},$$
$$\alpha_s = 1 - \frac{\alpha + \sqrt{4\alpha - 3\alpha^2}}{2}, \quad \frac{1}{3} \le \alpha \le 1 \tag{52}$$

For $f \ge 5$, $P(F_A^{\text{out}})$ must be calculated by numerically solving Eq. (50). The fraction $1 - \alpha_s(\beta)$ of remaining groups will be labeled "ω" and "σ" in the same proportion as in the overall polymerization:

$$\omega_s(\beta) = [1 - \alpha_s(\beta)]\frac{\omega(\beta)}{\omega(\beta) + \sigma(\beta)} \tag{53}$$

$$\sigma_s(\beta) = [1 - \alpha_s(\beta)]\frac{\sigma(\beta)}{\omega(\beta) + \sigma(\beta)} \tag{54}$$

Finally, note that

$$P(A_*^\omega \in \text{sol}|\beta) = P(F_A^{\text{out}})^{f-1} \tag{55}$$

Thus, we can calculate $P(\text{intra}|\text{sol}, \beta)$ either theoretically as the ratio of expected concentrations (call it Model I-A) or by Monte Carlo simulation as the average of probabilities (call it Model I-B). We use the same equations as above for $P(\text{intra}|\beta)$ but instead of using $(\omega(\beta), \sigma(\beta), \alpha(\beta))$, we use $(\omega_s(\beta), \sigma_s(\beta), \alpha_s(\beta))$ to get $P(\text{intra}|\text{sol}, \beta)$. At the beginning of the interval $[\beta, \beta + \Delta\beta]$ we have $(\omega(\beta), \sigma(\beta), \alpha(\beta))$; from these values we calculate $(\omega_s(\beta), \sigma_s(\beta), \alpha_s(\beta))$, from which we calculate $P(\text{intra}|\text{sol}, \beta)$. We then calculate

$$P(\text{intra}|\beta) = P(\text{intra}|\text{sol}, \beta)P(A_*^\omega \in \text{sol}|\beta) + 1(1 - P(A_*^\omega \in \text{sol}|\beta)) \tag{56}$$

and

$$P(\text{inter}|\beta) = 1 - P(\text{intra}|\beta) \tag{57}$$

Finally, for this interval, we calculate

$$\omega(\beta + \Delta\beta) = \omega(\beta) - \Delta\beta \tag{58}$$

$$\alpha(\beta + \Delta\beta) = \alpha(\beta) + P(\text{inter}|\beta)\Delta\beta \tag{59}$$

$$\sigma(\beta + \Delta\beta) = \sigma(\beta) + P(\text{intra}|\beta)\Delta\beta \tag{60}$$

and then repeat the process all over again for the next $\Delta\beta$-interval.

7. Weight fraction and weight-average molecular weight of soluble material

The first post-gel polymerization parameter we seek is the weight fraction of soluble material, *wfs*. For an A_f homopolymerization,

$$wfs = (P(F_A^{out}))^f \tag{61}$$

where $P(F_A^{out})$ is the probability of a finite branch seen looking "out" from a random A-group [15]; it satisfies the equation:

$$P(F_A^{out}) = (1 - \alpha(\beta))1 + \alpha(\beta)P(F_A^{out})^{f-1} \tag{62}$$

For $f = 3$,

$$wfs = \left(\frac{(1 - \alpha(\beta))}{\alpha(\beta)}\right)^3, \qquad \frac{1}{2} \le \alpha \le 1 \tag{63}$$

For $f = 4$,

$$wfs = \left(\frac{\sqrt{4\alpha(\beta) - 3(\alpha(\beta))^2} - \alpha(\beta)}{2\alpha(\beta)}\right)^4, \qquad 1/3 \le \alpha \le 1 \tag{64}$$

For $f \ge 5$, $(P(F_A^{out}))^f$ must be calculated by numerically solving Eq. (62).

We can also calculate the weight-average molecular weight of molecules in the sol fraction:

$$(\bar{M}_s)_w = M_A \frac{1 + \alpha_s(\beta)}{1 - (f-1)\alpha_s(\beta)} \tag{65}$$

as in Eq. (34).

8. After the gel point: Model II

Model I assumes that there is infinite concentration of intramolecular-bonding candidates around every unreacted group in the gel fraction of the post-gel polymer, implying unit probability of intramolecular reaction in the gel fraction; this is clearly an overestimation. Instead, we could assume that the probability of intramolecular bond formation is the same in the gel fraction of the polymer as it is in the sol fraction of the polymer. This may be an underestimate of cyclization in the gel, but if we are primarily concerned about the sol fraction, it may not be a bad approximation. Under this assumption

$$P(\text{intra}|\beta) = P(\text{intra}|\text{gel}, \beta) = P(\text{intra}|\text{sol}, \beta) \tag{66}$$

$$P(\text{inter}|\beta) = P(\text{inter}|\text{gel}, \beta) = P(\text{inter}|\text{sol}, \beta) \tag{67}$$

These values are calculated using the methods for the sol fraction in the above Model I. There are again two numerical approaches: use either the ratio of the theoretical expected concentrations (Model II-A) or the Monte Carlo simulation of the average probability (Model II-B).

9. After the gel point: Model III

There is another approach to intermolecular vs. intramolecular reactions within the gel fraction of the polymer. The point of view is that of "wasted bonds". A "wasted bond" is one that does not contribute to the molecular or network performance of the polymer. Cyclization in the sol fraction does not contribute to molecular weight build-up, so all σ-bonds in the sol fraction are wasted. In the gel fraction, any random root unreacted A-group, A_*^{ω}, is pendant; an intramolecular bond that connects this group to another group without changing the pendant status may not contribute to the elastic structure of the network and therefore is wasted in some sense that is difficult to quantify or model. We shall assume the following. If there is an elastically active junction point (a monomer with at least three paths to the infinite network) between the root A_*^{ω} and the group with which it reacts, then the bond contributes to the elastic structure and is not wasted; we consider it an α-bond rather than a σ-bond, even though it is intramolecular. In this way, we define the "wasted bonds" in the gel fraction as those involving intramolecular reaction between groups in the gel fraction with no intervening effective junction point. The remaining bonds in the gel fraction are modeled as intermolecular. This modeling idea is due to Dusek et al. [10]; they derived it from Scanlan's [16] theory of rubber elasticity.

Consider a randomly chosen unreacted A-group, which we designate as the root A_*^{ω}. We want the mean concentration of additional intramolecular A^{ω}-groups about this root, under the restriction that we ignore all A^{ω}-groups connected at or beyond effective junction points. Fig. 4 shows a realization of the situation. We have labeled all the A-groups and monomers.

The A-groups (or the bonds to which they belong) have

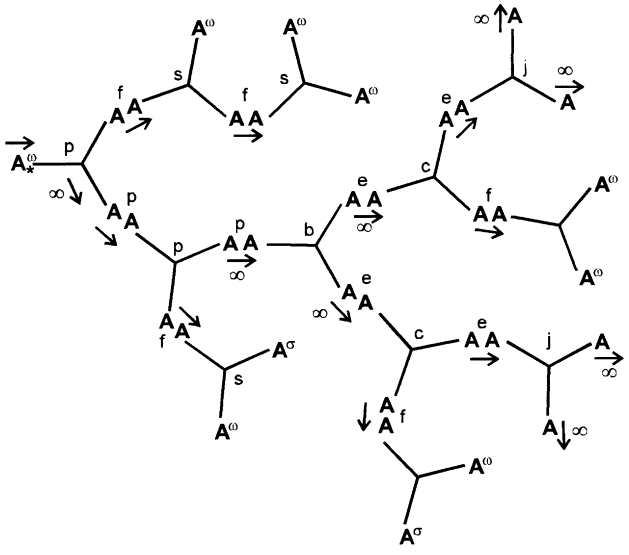

Fig. 4. Example of a path from an A^{ω} site to effective junction points when $f = 3$. Labels on A-sites and monomers correspond to Model III.

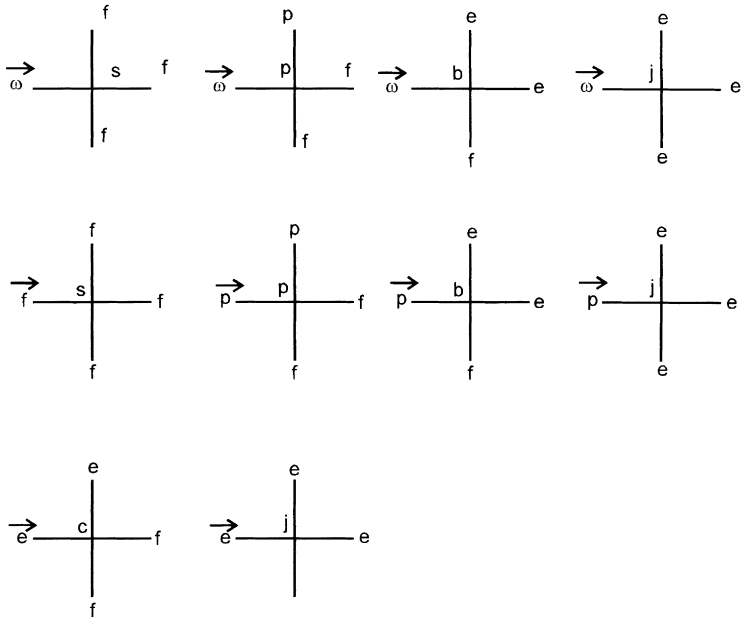

Fig. 5. Possible combinations of labeled groups and monomers in Model III when $f = 4$.

the following labels: ω is the unreacted A-group, p is a pendant bond, representing a single path from A_*^ω to the infinite network, f is a finite bond, representing a bond to a tree with a finite number of monomers, and e is an elastically effective bond, representing a bond in the elastically effective network. Note that α-bonds may be labeled p, f, or e.

The A-monomers have the following labels (relative to the direction we are looking from A_*^ω as indicated by the arrows in Fig. 4). p is pendant, representing a monomer that is on the single path from A_*^ω to the network. s is sol-like, representing monomers that are on finite branches. b is a branch point of a pendant link from A_*^ω with the elastically active part of the network. c is a chain monomer, representing a monomer whose connection to A_*^ω is part of an elastically active chain. j is a junction point, representing a monomer with at least three paths to the infinite network.

Notice that, in our "thought experiment" walk from A_*^ω into the effective network, there are 10 cases involving combinations of the number of labeled groups and the labeling of the monomer. The 10 cases are depicted in Fig. 5 along with the possible labeling of the groups via which we leave the monomer. Note that for $f = 3$ there are only eight cases. For $f = 4$ there are the 10 cases shown in Fig. 5.

We introduce the following random variable notation to describe the statistical structure of the molecule from A_*^ω into the elastically effective network: let $I_{g,m}$ be the indicator random functions that represent seeing a monomer labeled m when coming "in" from a group labeled g on the monomer, e.g. if $g = \omega$ and $m = p$ then $I_{\omega,p} = 1$, otherwise $I_{\omega,p} = 0$. Then

$$I_{\omega,p} = 1, \text{ w.p.}.(f-1)(1-P(F_A^{out}))(P(F_A^{out}))^{f-2} \tag{68}$$

$$I_{\omega,s} = 1, \text{ w.p.}.(P(F_A^{out}))^{f-1} \tag{69}$$

$$I_{\omega,b} = 1, \text{ w.p.}.((f-1)(f-2)/2)(1-P(F_A^{out}))^2(P(F_A^{out}))^{f-3} \tag{70}$$

$$I_{f,s} = 1, \text{ w.p.}1 \tag{71}$$

$$I_{p,p} = 1, \text{ w.p.}.(P(F_A^{out}))^{f-2} \tag{72}$$

$$I_{p,b} = 1, \text{ w.p.}.(f-2)(1-P(F_A^{out}))(P(F_A^{out}))^{f-3} \tag{73}$$

$$I_{e,c} = 1, \text{ w.p.}.(P(F_A^{out}))^{f-2} \tag{74}$$

where "w.p." means "with probability" and $P(F_A^{out})$ is the probability of seeing a finite branch when looking out from a random A-group. The remaining three of the 10 indicators take up the slack:

$$I_{\omega,j} = 1, \text{ w.p.}P(I_{\omega,p} = 0,\ I_{\omega,s} = 0,\ I_{\omega,b} = 0) \tag{75}$$

$$I_{p,j} = 1, \text{ w.p.}P(I_{p,p} = 0,\ I_{p,b} = 0) \tag{76}$$

$$I_{e,j} = 1, \text{ w.p.}P(I_{e,c} = 0) \tag{77}$$

Let $L_{m,g}$ equal the number of A-groups labeled g seen going "out" from a monomer labeled m. Then

$$L_{s,f} \sim \text{Binomial}((f-1),\ \alpha_s(\beta)) \tag{78}$$

$$L_{s,\omega} \sim \text{Binomial}((f-1),\ \omega_s(\beta)) \tag{79}$$

$$L_{p,p} = 1, \text{ w.p.}1 \tag{80}$$

$$L_{p,f} \sim \text{Binomial}((f-2),\ \alpha_s(\beta)) \tag{81}$$

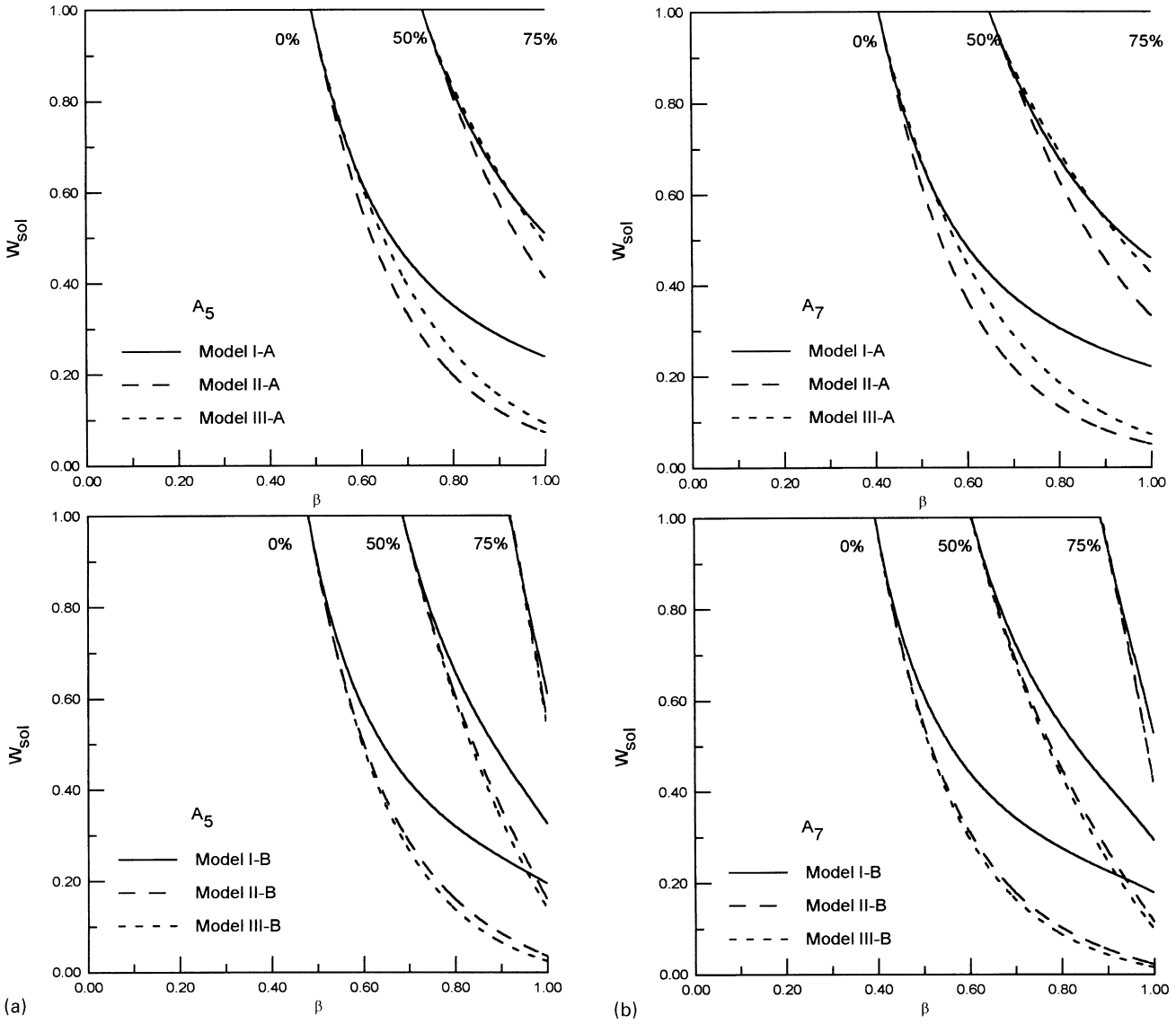

Fig. 6. Predictions of weight fraction of solubles at three different dilutions for: (a) $f = 5$ or (b) $f = 7$. At 75% dilution Model A predicts no sol, so the corresponding *wfs* is zero.

$$L_{p,\omega} \sim \text{Binomial}((f-2),\ \omega_s(\beta)) \tag{82}$$

$$L_{b,e} = 2,\ \text{w.p.1} \tag{83}$$

$$L_{b,f} \sim \text{Binomial}((f-3),\ \alpha_s(\beta)) \tag{84}$$

$$L_{b,\omega} \sim \text{Binomial}((f-3), \omega_s(\beta)) \tag{85}$$

$$L_{c,e} = 1,\ \text{w.p.1} \tag{86}$$

$$L_{c,f} \sim \text{Binomial}((f-2), \alpha_s(\beta)) \tag{87}$$

$$L_{c,\omega} \sim \text{Binomial}((f-2), \omega_s(\beta)). \tag{88}$$

Note that each of the above pairs of Binomial random variables are dependent. The joint distributions are multinomial distributions.

Let $M_m(i)$ equal the number of monomers labeled m in the ith shell from the root A-group, A^{ω}_{*}, $m = s, p, b, c$, and j. Let $N_g(i)$ equal the number of A-groups labeled g in the ith generation from the root A-group, A^{ω}_{*}, $g = f$, p, e, and ω. Then, the statistical structure of the branch connecting A^{ω}_{*} to the infinite network is given by the following relationships:

$$M_s(0) = I_{\omega,s} \tag{89}$$

$$M_p(0) = I_{\omega,p} \tag{90}$$

$$M_b(0) = I_{\omega,b} \tag{91}$$

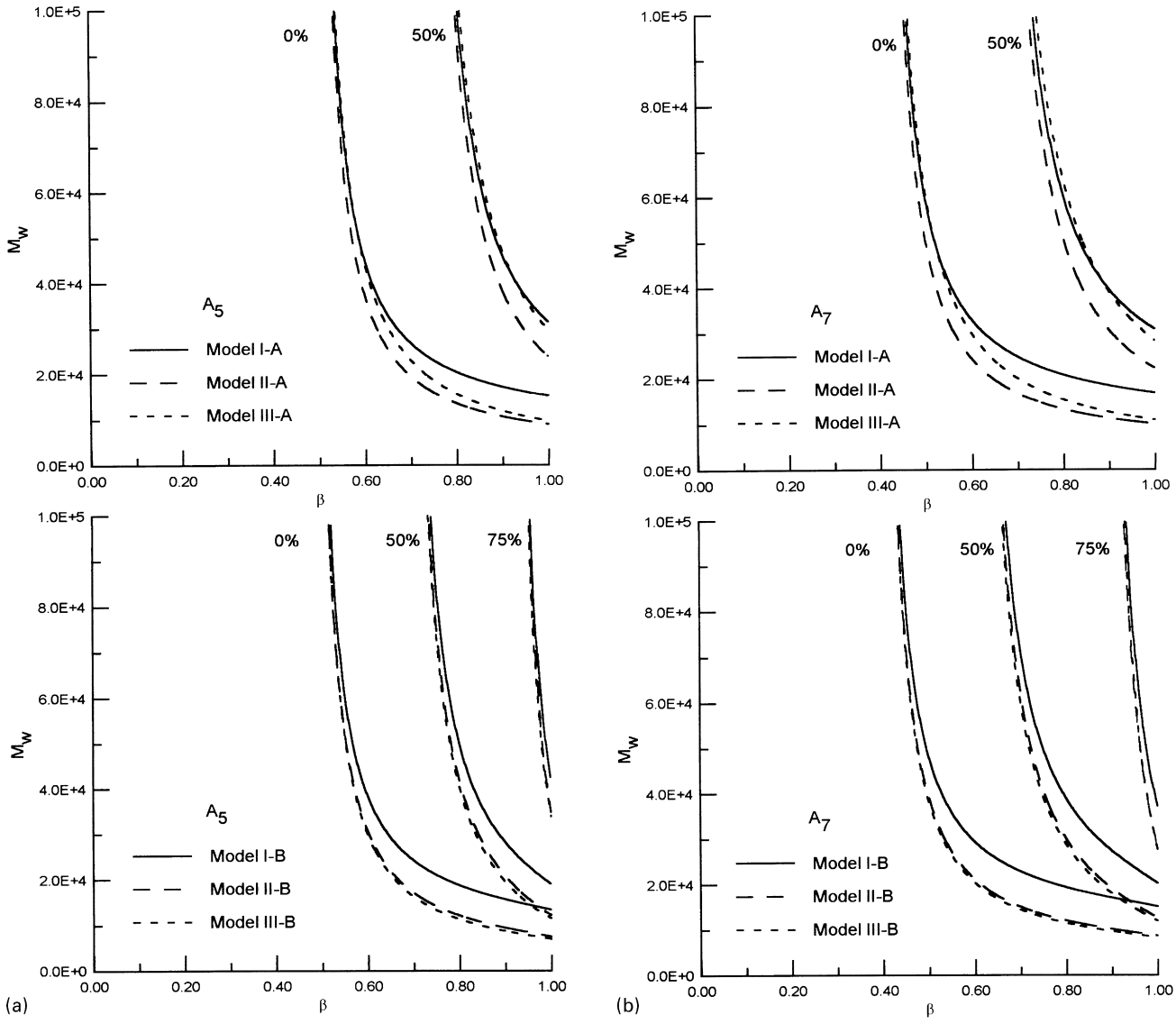

Fig. 7. Predictions of average molecular weights in the sol fraction at three different degrees of dilution for: (a) $f = 5$ or (b) $f = 7$. At 75% dilution Model A predicts no sol, so the corresponding molecular weight is zero.

$$M_c(0) = 0 \tag{92}$$

$$N_f(i+1) = \sum_{j=1}^{M_s(i)} (L_{s,f})_{i,j} + \sum_{j=1}^{M_p(i)} (L_{p,f})_{i,j} + \sum_{j=1}^{M_b(i)} (L_{b,f})_{i,j} + \sum_{j=1}^{M_c(i)} (L_{c,f})_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{93}$$

$$N_p(i+1) = M_p(i), \qquad i = 0, 1, 2, \ldots \tag{94}$$

$$N_e(i+1) = 2M_b(i) + M_c(i), \qquad i = 0, 1, 2, \ldots \tag{95}$$

$$N_\omega(i+1) = \sum_{j=1}^{M_s(i)} (L_{s,\omega})_{i,j} + \sum_{j=1}^{M_p(i)} (L_{p,\omega})_{i,j} + \sum_{j=1}^{M_b(i)} (L_{b,\omega})_{i,j} + \sum_{j=1}^{M_c(i)} (L_{c,\omega})_{i,j}, \qquad i = 0, 1, 2, \ldots \tag{96}$$

$$M_s(i) = \sum_{j=1}^{N_f(i)} (I_{f,s})_{i,j} = N_f(i), \qquad i = 1, 2, 3, \ldots \tag{97}$$

$$M_p(i) = \sum_{j=1}^{N_p(i)} (I_{p,p})_{i,j}, \qquad i = 1, 2, 3, \ldots \tag{98}$$

$$M_b(i) = \sum_{j=1}^{N_p(i)} (I_{p,b})_{i,j}, \qquad i = 1, 2, 3, \ldots \tag{99}$$

$$M_c(i) = \sum_{j=1}^{N_e(i)} (I_{e,c})_{i,j}, \qquad i = 1, 2, 3, \ldots \tag{100}$$

For Model III-A we take expected values of the above random variables and solve for $E(N_\omega(i))$, $i = 1, 2, 3, \ldots$ Details are in the Appendix A. Substitution into Eq. (15) gives $E(C_{\text{intra}}(\beta))$ which is then used in Eq. (2) to get values of $P(\text{intra}|\beta)$ for Model III-A.

For Model III-B, we perform Monte Carlo simulations of the random structure described by Eqs. (68)–(100) to get observations of $N_\omega(i)$, $i = 1, 2, 3, \ldots$ From this simulation data, we estimate $P(\text{intra}|\beta)$ for Model III-B.

10. Numerical results and comparison of models beyond the gel point

We have run some cases for models I-A, I-B, II-A, II-B, III-A, and III-B. We varied the functionality of the monomers and the degree of dilution. As examples, Figs. 6 and 7 show some results for monomers with functionalities $f = 5$ and $f = 7$ at dilutions ranging from 0 to 75% solvent. We show predictions for sol fractions in Fig. 6 and weight average molecular weight of the soluble fraction in Fig. 7. It may be observed that the general trends are the same for all models: as the importance of intramolecular reactions grows larger (at higher dilutions), gel point delays are greater and network defects more noticeable, in the form of nonzero sol fractions at complete reaction. Both in models A and B, variations II and III give very similar results. This is especially true for Model B, where Monte Carlo simulations are performed. Variation I, on the other hand, is always far removed from the other predictions. Similar results are obtained for other post-gel parameters such as weight fraction of pendant material and weight fraction of elastically effective material. We tentatively conclude that Models II-B and III-B are superior among the six choices.

We could argue that variation III is the most complete one of all the models. It is also the most complex one to calculate. Variation II, then, becomes attractive because it is very simple to program and calculate, and it gives results that are very close to those of variation III.

11. Conclusions

We have presented an alternative to the traditional spanning-tree approximation model calculations, using a hybrid model that uses both numerical Monte Carlo simulations and analytic formulas. This hybrid model allows the evaluation of the probability of intramolecular reaction for an unreacted site in a way that is mathematically more sound, taking averages of the probabilities instead of using averages of concentrations. This allows extension of the spanning-tree approach to the post-gel region, something impossible with the original model. In this work, we have proposed three different ways of achieving this extension. Since Monte Carlo simulations were not used to solve the entire problem, just parts of it, the model did not become computationally intensive.

Out of the three proposed ways of extending the spanning-tree approach beyond the gel point, two are rather simple, and the third one is a reformulation of a modeling idea due to Scanlan [16]. We have found that Model II gives results that are very similar to those of Model III, a more complete and complex model. This makes Model II-B a good choice for a working model.

Appendix A. Expected values for Model III-A

Taking expected values of Eqs. (68)–(100) gives:

$$E(I_{\omega,p}) = (f-1)(1 - P(F_A^{\text{out}}))(P(F_A^{\text{out}}))^{f-2} \tag{A1}$$

$$E(I_{\omega,s}) = (P(F_A^{\text{out}}))^{f-1} \tag{A2}$$

$$E(I_{\omega,b}) = ((f-1)(f-2)/2)(1 - P(F_A^{\text{out}}))^2\,(P(F_A^{\text{out}}))^{f-3} \tag{A3}$$

$$E(I_{f,s}) = 1 \tag{A4}$$

$$E(I_{p,p}) = (P(F_A^{\text{out}}))^{f-2} \tag{A5}$$

$$E(I_{p,b}) = (f-2)(1 - P(F_A^{\text{out}}))(P(F_A^{\text{out}}))^{f-3} \tag{A6}$$

$$E(I_{e,c}) = (P(F_A^{\text{out}}))^{f-2} \tag{A7}$$

$$E(L_{s,f}) = (f-1)a_s(\beta) \tag{A8}$$

$$E(L_{s,w}) = (f-1)\omega_s(\beta) \tag{A9}$$

$$E(L_{p,p}) = 1 \tag{A10}$$

$$E(L_{p,f}) = (f-2)\alpha_s(\beta) \tag{A11}$$

$$E(L_{p,\omega}) = (f-2)\omega_s(\beta) \tag{A12}$$

$$E(L_{b,e}) = 2 \tag{A13}$$

$$E(L_{b,f}) = (f-3)\alpha_s(\beta) \tag{A14}$$

$$E(L_{b,\omega}) = (f-3)\omega_s(\beta) \tag{A15}$$

$$E(L_{c,e}) = 1 \tag{A16}$$

$$E(L_{c,f}) = (f-2)\alpha_s(\beta) \tag{A17}$$

$$E(L_{c,\omega}) = (f-2)\omega_s(\beta) \tag{A18}$$

$$E(M_s(0)) = E(I_{\omega,s}) \tag{A19}$$

$$E(M_p(0)) = E(I_{\omega,p}) \tag{A20}$$

$$E(M_b(0)) = E(I_{\omega,b}) \tag{A21}$$

$$E(M_c(0)) = 0 \tag{A22}$$

$$E(N_f(i+1)) = E(M_s(i))E(L_{s,f}) + E(M_p(i))E(L_{p,f}) + E(M_b(i))E(L_{b,f}) + E(M_c(i))E(L_{c,f}), \qquad i = 0,1,2,\ldots \tag{A23}$$

$$E(N_p(i+1)) = E(M_p(i)), \qquad i = 0,1,2,\ldots \tag{A24}$$

$$E(N_e(i+1)) = 2E(M_b(i)) + E(M_c(i)), \qquad i = 0,1,2,\ldots \tag{A25}$$

$$E(N_\omega(i+1)) = E(M_s(i))E(L_{s,\omega}) + E(M_p(i))E(L_{p,\omega}) + E(M_b(i))E(L_{b,\omega}) + E(M_c(i))E(L_{c,\omega}), \quad i = 0,\ 1,\ 2,\ \ldots \tag{A26}$$

$$E(M_s(i)) = E(N_f(i)), \qquad i = 1,2,3,\ldots \tag{A27}$$

$$E(M_p(i)) = E(N_p(i))E(I_{p,p}), \qquad i = 1,2,3,\ldots \tag{A28}$$

$$E(M_b(i)) = E(N_p(i))E(I_{p,b}), \qquad i = 1,2,3,\ldots \tag{A29}$$

$$E(M_c(i)) = E(N_e(i))E(I_{e,c}), \qquad i = 1,2,3,\ldots \tag{A30}$$

In vector/matrix form, Eqs. (A23)–(A26) become

$$E(\tilde{N}(i+1)) = \mathbf{A}\cdot E(\tilde{M}(i)), \qquad i = 0,1,2,\ldots \tag{A31}$$

and Eqs. (A27)–(A30) become

$$E(\tilde{M}(i)) = \mathbf{B}\cdot E(\tilde{N}(i)), \qquad i = 1,2,3,\ldots \tag{A32}$$

where

$$E(\tilde{M}(i)) = \begin{bmatrix} E(M_s(i)) \\ E(M_p(i)) \\ E(M_b(i)) \\ E(M_c(i)) \end{bmatrix}, \qquad i = 0,1,2,\ldots \tag{A33}$$

$$E(\tilde{N}(i)) = \begin{bmatrix} E(N_f(i)) \\ E(N_p(i)) \\ E(N_e(i)) \\ E(N_\omega(i)) \end{bmatrix}, \qquad i = 1,2,3,\ldots \tag{A34}$$

$$\mathbf{A} = \begin{bmatrix} E(L_{s,f}) & E(L_{p,f}) & E(L_{b,f}) & E(L_{c,f}) \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1 \\ E(L_{s,\omega}) & E(L_{p,\omega}) & E(L_{b,\omega}) & E(L_{c,\omega}) \end{bmatrix} \tag{A35}$$

$$\mathbf{B} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & E(I_{p,p}) & 0 & 0 \\ 0 & E(I_{p,b}) & 0 & 0 \\ 0 & 0 & E(I_{e,c}) & 0 \end{bmatrix} \tag{A36}$$

Combining Eqs. (A31) and (A32) gives

$$E(\tilde{M}(i+1)) = \mathbf{C}\cdot E(\tilde{M}(i)), \qquad i = 0,1,2,\ldots \tag{A37}$$

where

$$\mathbf{C} = \mathbf{B}\cdot\mathbf{A} = \begin{bmatrix} E(L_{s,f}) & E(L_{p,f}) & E(L_{b,f}) & E(L_{c,f}) \\ 0 & E(I_{p,p}) & 0 & 0 \\ 0 & E(I_{p,b}) & 0 & 0 \\ 0 & 0 & 2E(I_{e,c}) & E(I_{e,c}) \end{bmatrix} \tag{A38}$$

Solving Eq. (A37) gives

$$E(\tilde{M}(i)) = \mathbf{C}^i\cdot E(\tilde{M}(0)), \qquad i = 0,1,2,\ldots \tag{A39}$$

Eq. (A26) becomes

$$E(N_\omega(i+1)) = \tilde{L}\cdot\tilde{M}(i) = \tilde{L}\cdot\mathbf{C}^i\cdot\tilde{M}(0), \qquad i = 0,1,2,\ldots \tag{A40}$$

where

$$\tilde{L} = \begin{bmatrix} E(L_{s,\omega}) & E(L_{p,\omega}) & E(L_{b,\omega}) & E(L_{c,\omega}) \end{bmatrix} \tag{A41}$$

$$\tilde{M}(0) = \begin{bmatrix} E(I_{\omega,s}) \\ E(I_{\omega,p}) \\ E(I_{\omega,b}) \\ 0 \end{bmatrix} \tag{A42}$$

Substituting the values from Eq. (A40) into (15) and then further substitution into Eq. (2) gives values of $P(\text{intra}|\beta)$ for Model III-A.

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