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# Kinetic Reaction Analysis of Gelation: First-Shell Substitution Effects in Step-Growth $A_2{-}A_2{+}B_2$ Thermosets

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ABSTRACT: Purely deterministic derivations are reported regarding the internal, network chain structure that contributes to rubber elasticity in polymerizations of $A_2{-}A_2{+}B_2$ monomers. The $A_2{-}A_2$ monomer originally contained two primary sites. Upon reaction, secondary sites and ultimately tertiary moieties form. Therefore, the $A_2{-}A_2$ chain link becomes a fourth-order branch node. Reaction rate constants for primary and secondary sites were assumed to be distinct. The $B_2$ monomer was assumed to be independent of similar first-shell substitution effects. Kinetic reaction analysis based on Smoluchowski type equations yielded analytical descriptions of the molar concentration of molecules in the sol fraction as described by their chemical composition, including the number of primary sites reacted, the number of secondary sites reacted and unreacted, and the number of unreacted *B* moieties. Chemical reactions within the sol and between the sol and gel are explicitly described in deterministic methodology; reactions within the gel are implicitly described. Conditionally convergent properties of the moments of the population density distribution were used to predict the gel point and to describe the gel fraction. In this phase of the kinetic reaction analysis, branch node distribution dynamics are used to predict physical properties dependent on cross-link distribution dynamics, including the concentrations of elastically active junctions and strands. Because of long-range chain connectivity dependencies within the gel, several authors had stated that this intricate network topology must be based solely on stochastic reasoning. Solutions derived from expectation theory are shown to equal our deterministic solutions. The research clearly illustrates that solutions based on chemical reaction engineering can be evaluated at all levels of conversion. Furthermore, specifics of competing chemical reactions are readily incorporated into models at early stages of development.

## Introduction

Using stochastic reasoning, polymerization models for step-growth, multifunctional monomers were pioneered by Flory[20−25] and Stockmayer.[63−65] Gelation[2,46] has been simulated by mean-field[31,33] and percolation theories.[62] Network features associated with chain connectivity germane to the theory of rubber elasticity were modeled using expectation theory for step-growth[7,42,43−47,49,58] and for chain-growth polymerizations.[67−69,71−73] Thermosets formed from a single chemical reaction may be simulated by purely stochastic methods. With competing reactions, hybrid models have evolved. Kinetic models describe parts of molecules called superspecies.[3,7,13,35] Expectation theory simulates effective network junctions and elastically active chain segments or strands. Purely stochastic models are also capable of handling competing reactions.[58]

For multifunctional monomers Stockmayer,[63−65] Ziff,[74] and Fukui and Yamabe[28] illustrated derivations of population density distributions (PDDs) using chemical reaction or deterministic reasoning. Smoluchowski[60] relationships descriptive of molar concentrations of the resin's molecules as functions of degree of polymerization and conversion have been solved for several chemical reaction mechanisms and/or functionality.[20−23,50,63] Flory[25] stated that at conversions greater than the critical conversion for gelation, PDDs describe the concentrations of molecules in the sol fraction; the gel fraction is excluded. Ziff and Stell[75] explicitly modeled sol/gel reactions and showed that Flory's interpretation of gelation[25,63] implicitly contains intramolecular cross-linking reactions in the gel. The derivations of this manuscript are also subject to explicit intermolecular and implicit intramolecular reactions.

Chain cyclization in the sol phase has been addressed by Jacobson and Stockmayer[37] and Semlyen.[59] Equilibrium statistics of ring closure of Gaussian chains predict a first-order reaction with a coefficient dependency that includes $n^{-3/2}$, where $n$ is the number of atoms or units in the resultant ring. The dominant rings are relatively small, containing 6−8 repeating units. Highly branched sol molecules with flexible chains can experience appreciable chain cyclization.[61] The coefficient of the rate expression also contains a factor that equals the number of ways a ring can form on a specific molecule. Thus, a rigorous examination must include all isomers of a molecule of specified chemical structure.[66] Liu, et al.[40] and Noureddini and Timm[50] have demonstrated approximate solutions that do not require the calculation of chemical isomers. The method is constrained to the dominant ring. The cited literature was restricted to the pregel region. With relatively stiff molecular chains such as those that contain aromatics, Bokare and Gandhi[3] and Dušek[15] indicate that chain cyclization can be neglected during the initial stages of the cure. This conclusion is consistent with the critical conversion being independent of dilution.[15,41,57] Although Charlesworth[4] reported evidence attributed to cyclization in dilute solutions, cyclization was negligible in bulk cures. In this paper, chain cyclization in the sol is neglected.

Since kinetic models were believed incapable of predicting network topology because of long-range connectivity dependencies, authors[7,12,70] had stated that one

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must use probabilistic arguments. However, Robbins et al.[56] used purely deterministic models to simulate the resin's chemical infrastructure that relates to rubber elasticity. A step-growth $A_4+B_2$ polymerization, a paradigm of the pregel and postgel regimes, and a chain-initiated, Poisson-type $A_4+B_2$ resin were simulated. For these cures, PDDs had previously been derived by Stockmayer[63] and by Flory[19,25] and Fukui and Yamabe,[28] respectively. These thermosets are composed of a tetrafunctional branch node and a bifunctional connecting link. The reaction state of one chemical group did not influence the reactivity of another. Unequal chemical reactivity caused by reaction states of a functional group is called first-shell substitution effects (FSSEs).[32]

In this paper pregel and postgel deterministic models are derived for an $A_2-A_2+B_2$ resin in the presence of FSSEs on the $A_2-A_2$ tetrafunctional branch node only. An example of an $A_2-A_2$ monomer is a bifunctional, primary amine cured with a bifunctional epoxy $B_2$. Primary and secondary amines can experience distinct rate constants.[57] If the oxiranes are separated sufficiently, the comonomer is void of FSSEs.[4,15,25,41,57] In our notation each amino hydrogen as expressed by $A_2-$ is capable of forming a bond. Bokare and Gandhi[3] further note that resin systems based on epoxy/carboxylic acids, epoxy/alcohols, isocyanates/alcohols, and isocyanates/amines experience FSSEs.

## First-Shell Substitution Effects

Galina and Szustalewicz,[30] Kuchenov and Povolotskaya,[39] Mikes and Dušek,[46] and Sarmoria and Miller[58] modeled the homopolymerization of a three-functional monomer $A_3$. Chemical reaction rate constants $K_{i,j} = K_{j,i}$, $j$, $k = 0-2$ were dependent on the reaction state of each reactant. A chain link with $i$ reacted sites formed a bond with a branch node having $j$ reacted sites. When an index equals zero, monomer is the reactant. In these references, kinetic models,[30,39] Monte Carlo simulations,[46] and hybrid models[58] are discussed. The reaction states for this type of resin increase the number of reaction rate expressions necessary for simulations when compared to the resin currently being discussed. The additional chemical groups will result in a net increase in the number of independent variables. The cited literature provides alternate methods for formulating solutions to our problem.

Several papers previously addressed resin systems that are the subject of the present manuscript. Dušek et al.[10] used probability-generating functions to account for unequal reactivities of primary and secondary amines. Amine-cured epoxies also form hydroxyl groups that can provide initiation sites for polyetherization. Using hybrid models, Miller and Macosko,[47] Bokare and Gandhi,[3] Dušek,[11,13] Dušek et al.,[16] Riccardi and Williams,[54,55,70] and Gupta and Macosko[35] simulated these competing amidization and etherization reactions. Simulations also incorporated FSSEs in the absence of chain-initiated reactions. In this paper, their results provide a basis for comparisons. The cited literature also constrained the reactivity of functional groups on the comonomer to be invariant of reaction states. Chain cyclization in the sol was also neglected.

## Theory of Rubber Elasticity

The theory of rubbery elasticity provides a structure/property relationship.[7,45] Idealized networks are described by affine[25] and phantom models.[38] In the former, chain branch nodes are assumed to move linearly with respect to macroscopic deformation. No contribution results from the parts of a chain between junction points, but only from the number of strands connecting elastically active junctions. In the phantom model, junction positions move affinely but fluctuate about their mean positions. Chain connectivity restricts motion and, therefore, becomes a factor. In a constrained junction model,[26,27] the degree of interpenetration of a chain with neighboring junctions and strands is emphasized. This model predicts that the elastic free energy of deformation is intermediate between the values for the phantom and affine network.[18,45] Edwards and co-workers[1] and Kremer and associates[8] considered physical strand interactions in the form of entanglements. These interactions increase the elastic energy of deformation beyond that of the phantom or the affine models. Although initially entanglements were expressed by a "slip-link model", authors, including Miller and Macosko,[43,44] Graessley and co-workers[6,34,53] and Durand and Bruneau,[9] envision physical entanglements as two intertwined strands.

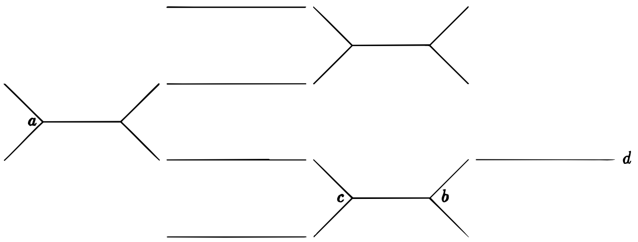

**Figure 1.** Cluster of $A_2-A_2$ and $B_2$ chain segments: an oligomer $P_{3,5,2}$ with primary, secondary and tertiary moieties at *a*, *b*, and *c*, respectively, and a B group at d.

Dotson et al.[7] summarized molecular contributions to the equilibrium tensile modulus $E$ with the expression

$$E = (\nu_c - h\mu_c)RT + T_e E° \qquad (1)$$

The concentration of elastically active strands in the network is $\nu_c$ and the number of elastically active junctions is $\mu_c$. A strand is a chain segment between two active junctions. An active junction has a minimum of three chain segments extending to the gel. The junction fluctuation parameter was represented as $h$. If $h = 0$, the model is affine, or if $h = 1$, the model is phantom, subject to $T_e = 0$. The entanglement trapping parameter is $T_e$ and the plateau modulus of an un-cross-linked material formed from the network strands is $E°$. The ideal gas constant is $R$; absolute temperature is $T$.

An objective of our research was the calculation of the several variables appearing in eq 1 as functions of conversion, subject to chemical reaction constraints. Specific emphasis addresses chemical contributions to the number of strands and to the concentration of active junctions. Entanglement contributions use published stochastic theory.

## Reaction Model and Constraints

The population density distribution (PDD) variable $P_{i,j,k}$ represents the molar concentration of molecules formed from $i$ tetrafunctional branch nodes and $j$ bifunctional chain links that contain $k$ unreacted primary moieties. Figure 1 is a sketch of an oligomer $P_{3,5,2}$. The analysis assumes that a primary moiety such as site a reacts with a rate constant $K_P$, forming a secondary group such as point b. When a secondary site subsequently reacts with a rate constant $K_S$, a tertiary moiety forms; see point c. A molecule may also contain unreacted B groups as indicated by d. Rate constants are distinct. Stockmayer[63] derived analytical PDDs subject to rate constants being equal. Although stochastic reasoning was employed, Stockmayer emphasized that a kinetic reaction analysis yields his solution. Ziff and Stell[75] derived Stockmayer's solution from an appropriate Smoluchowski relationship. The constraint $K_P = K_S$ allows the number of independent variables to be reduced, yielding $P_{i,j}$. The simplified model expresses primary and secondary sites in terms of amino hydrogen atoms. Time or conversion is an implicit independent variable in the notation. Constraints incorporate a well-mixed, isothermal, batch reaction.

**Limits for Independent Variables.** Bonding constraints require that

$$i - 1 \le j \le 3i + 1 \tag{2}$$

A minimum of $i - 1$ $B_2$ connecting links is required to form a molecule with $i$ branch nodes. The upper bound results when all chemical moieties on the $A_2{-}A_2$ units have reacted. Stoichiometric considerations yield $4i - 2(i - 1) - (j - i + 1) = 3i - j + 1 = 0$. The number of possible bonds is $4i$. Each of the $i - 1$ connecting links consumed two sites and the $j - i + 1$ pendent links each reacted once.

Constraints for the unreacted $k$ primary sites are

$$\left\{\begin{matrix} 0 & \text{when } j \ge i+1 \\ i - j + 1 & \text{when } j \le i \end{matrix}\right\} \le k \le \left\{\begin{matrix} \text{int}\{(3i - j + 1)/2\} & \text{when } j > i + 1 \\ i & \text{when } j \le i + 1 \end{matrix}\right\} \tag{3}$$

When considering the lower limits, primary sites may be assumed to be highly reactive, $K_P \gg K_S$. Figure 1 may be referenced. When sufficient $B_2$ links exist in the molecule, reactions at primary sites consume them and $k = 0$. If $j = i$ or $i - 1$, sufficient $B_2$ chain links are not available and one or two primary sites remain. To maximize the number of primary sites on a molecule, reactions are visualized to alternate between primary and secondary sites, i.e., $K_P \ll K_S$. Integer division in which remainders are truncated assigns two reactions per primary site. Since one unaccounted secondary site also reacts, an exception occurs when $j \le i + 1$.

**Chemical Functionalities.** Stoichiometric considerations yield linear arithmetic expressions for chemical moieties on a molecule $P_{i,j,k}$. The tetrafunctional monomer contains two primary A sites. By definition, the number of unreacted primary moieties $A_{i,j,k}$ is $k$:

$$A_{i,j,k} = k \tag{4}$$

The number of secondary sites equals the difference between the number of potential bonds $4i$, the number consumed by connecting $B_2$'s $2(i - 1)$ and pendent $B_2$'s $j - i + 1$, and those in unreacted primary groups $2k$:

$$S_{i,j,k} = 3i - j - 2k + 1 \tag{5}$$

The number of B moieties equals the number of pendent $B_2$ units:

$$B_{i,j,k} = j - i + 1 \tag{6}$$

**Intermolecular Reactions.** Intermolecular reactions at primary and secondary moieties are described by second-order rate expressions:

$$\begin{aligned} &P_{l,m,n} + P_{i-l,j-m,k-n+1} \xrightarrow{K_P} P_{i,j,k} \qquad \text{rate}_{\text{inter,p}} = \\ &\qquad K_P A_{l,m,n} P_{l,m,n} B_{i-l,j-m,k-n+1} P_{i-l,j-m,k-n+1} \\ &P_{l,m,n} + P_{i-l,j-m,k-n} \xrightarrow{K_S} P_{i,j,k} \qquad \text{rate}_{\text{inter,s}} = \\ &\qquad K_S S_{l,m,n} P_{l,m,n} B_{i-l,j-m,k-n} P_{i-l,j-m,k-n} \end{aligned} \tag{7}$$

Two reactants and one product cause a net loss of one molecule per intermolecular reaction. Subscripts conserve degrees of polymerization and primary sites.

**Intramolecular Reactions.** Cross-link formation is assumed to occur only within a megamolecule in the gel. As the megamolecule's branches meander between the walls of the reactor, locations exist where chemical moieties are in proximity and experience high collusion frequencies. Flory[25] noted that large molecules diffuse slowly but stated that collision rates between functional groups remain sufficient for step-growth reactions to be chemically controlled for extensive conversions. Functional groups traverse a considerable region about their mean position through rearrangements in local chain conformations. He concluded that collisions with neighbors occur at frequencies comparable to that happening in simple liquids. Therefore, competing intramolecular cross-linking reactions are expected to be controlled by a second-order reaction. At high conversions, rates of polymerization diminish.[17,36] The intermolecular rate constant becomes viscosity dependent.[5] We imposed these constraints on intramolecular cross-linking reactions in the gel and on intermolecular reactions within the sol and between the sol and gel. The transformation from time to dimensionless time $\tau$ to conversion $\rho$ readily incorporates these types of rate constants.

Ziff and Stell[75] unequivocally addressed reactions within the sol, between the sol and gel, and within the gel, subject to $K_P = K_S = K$. Reactions cause changes in the concentrations of chemical moieties $A_{i,j}$ on molecules $P_{i,j}$. Conservation principles applied to the concentration of $A$ sites on molecules $P_{i,j,\text{sol}}$ in the sol yield

$$\begin{aligned} \mathrm{d}(A_{i,j}P_{i,j,\text{sol}})/\mathrm{d}t = {}& -1KA_{i,j}P_{i,j,\text{sol}}B_{\text{sol}} - \\ & A_{i,j}KA_{i,j}P_{i,j,\text{sol}}B_{\text{gel}} - A_{i,j}KB_{i,j}P_{i,j,\text{sol}}A_{\text{gel}} \end{aligned}$$

In the first rate expression, the stoichiometric coefficient 1 reflects the fact that each sol/sol reaction consumes one A group. The rate of reaction is proportional to the product of the number of $A_{i,j}$ sites on molecules $P_{i,j}$ and the cumulative concentration of $B_{\text{sol}}$ sites in the sol. In the second and third rate expressions, the reaction between the molecule and the gel transports the reactant's chemical moieties to the gel. Thus, the stoichiometric coefficients are $A_{i,j}$; however, in the perspective of the gel, a net of $A_{i,j} - 1$ moieties is gained. Addition yields an expression descriptive of the total concentration of moieties in the sol $A_{\text{sol}}$ and in the gel $A_{\text{gel}}$. For the soluble sol and insoluble gel fractions

$$\mathrm{d}A_{\mathrm{sol}}/\mathrm{d}t = -KA_{\mathrm{sol}}B_{\mathrm{sol}} - K\sum_i\sum_j\{A_{i,j}^2P_{i,j,\mathrm{sol}}\}B_{\mathrm{gel}} - K\sum_i\sum_j\{A_{i,j}B_{i,j}P_{i,j,\mathrm{sol}}\}A_{\mathrm{gel}}$$

$$\mathrm{d}A_{\mathrm{gel}}/\mathrm{d}t = -KA_{\mathrm{gel}}B_{\mathrm{gel}} + K\sum_i\sum_j\{(A_{i,j}-1)A_{i,j}P_{i,j,\mathrm{sol}}\}B_{\mathrm{gel}} + K\sum_i\sum_j\{(A_{i,j}-1)B_{i,j}P_{i,j,\mathrm{sol}}\}A_{\mathrm{gel}}$$

Subject to the notation $A_{\mathrm{sol}} + A_{\mathrm{gel}} = A$, the concentration of A moieties in the resin, addition yields

$$\mathrm{d}A/\mathrm{d}t = -KAB \tag{8}$$

Since this relationship also results when the Smoluchowski expression is weighted by $A_{i,j}$ and summed, Ziff and Stell[75] concluded that Flory's[25,63] interpretation of gelation addressed reactions within the sol, between the sol and gel, and within the gel. The rate expression $KA_{\mathrm{gel}}B_{\mathrm{gel}}$ represents cross-link formation that consumes an A moiety but does not change the number of molecules within the resin.

**Extent of Reaction.** The concentration of primary moieties is represented by $A$ and the concentration of B groups as $B$ in eq 8. Initially, $A(0) = 2P_{1,0,2}(0)$ and $B(0) = 2P_{0,1,0}(0)$. A dimensionless transformation $\mathrm{d}\tau = K_PB\ \mathrm{d}t$ yields $A = A(0)\exp(-\tau)$. Conversion of primary sites $\rho = (A(0) - \mathrm{A})/A(0) = 1 - \exp(-\tau)$. The time/primary site conversion transformation is obtained by differentiation and substitution:

$$K_PB\ \mathrm{d}t = \mathrm{d}\tau = \mathrm{d}\rho/(1-\rho) \tag{9}$$

The concentration of secondary sites is described by $\mathrm{d}S/\mathrm{d}t = K_PAB - K_SSB$. In dimensionless time $\mathrm{d}S/\mathrm{d}\tau + CS = A(0)\exp(-\tau)$, where the ratio of rate constants $C = K_S/K_P \neq 1$. The solution $S = (A(0)/(1-C))\{\exp(-C\tau) - \exp(-\tau)\}$ incorporates the integrating factor[29] $\exp(C\tau)$ and

$$S = \frac{A(0)}{1-C}\{(1-\rho)^C - (1-\rho)\} \tag{10}$$

The total number of secondary sites formed at conversion $\rho$ equals the number of primary sites reacted $A(0)\rho$. Therefore, the fraction of unreacted secondary sites is

$$1 - \rho_S = \frac{(1-\rho)^C - (1-\rho)}{(1-C)\rho} \tag{11}$$

and the conversion of secondary sites equals

$$\rho_S = \frac{1 - C\rho - (1-\rho)^C}{(1-C)\rho} \tag{12}$$

The extent of reaction for the B group is $\rho_B = (B(0) - B)/B(0)$ and the formulation ratio is $\alpha = A(0)/B(0)$. The concentration of B sites satisfies $\mathrm{d}B/\mathrm{d}\tau = -A - CS = -A(0)\exp(-\tau) - (A(0)C/(1-C))(\exp(-C\tau) - \exp(-\tau))$. Integration yields $B = B(0) - A(0)(1 - \exp(-\tau)) - (A(0)/(1-C))\ \{1 - \exp(-C\tau) - C(1 - \exp(-\tau))\}$. Algebra yields

$$\rho_B = (\alpha/(1-C))\{1 + \rho - 2C\rho - (1-\rho)^C\} \tag{13}$$

**Population Density Distribution Dynamics.** In an appendix the analytical expressions describing the molar concentration of molecules in the resin are derived:

$$p_{i,j,k} = \frac{P_{i,j,k}}{P_{1,0,2}(0)} = C_{i,j,k}\alpha^{i-1}\rho^{2i-k}(1-\rho)^k\rho_S^{j-i+k-1}(1-\rho_S)^{3i-j-2k+1}(1-\rho_B)^{j-i+1} \tag{14}$$

$$C_{i,j,k} = \frac{2(j-1)!}{k!(j-i+1)!(i-k)!}\sum_{l=0}^{l_{\max}}\binom{i}{l}\binom{2i-k-1}{j-i+k-1-l} \quad \text{where} \quad l_{\max} = \min\begin{cases} i \\ j-i+1 \end{cases} \tag{15}$$

The several conversions represent the fraction of primary sites reacted and unreacted, the fraction of formed secondary sites reacted and unreacted, and the fraction of B moieties unreacted. The powers represent the number of the several moieties in the molecule reacted or unreacted. The initial molar ratio of monomers $P_{1,0,2}(0)/P_{0,1,0}(0) = \alpha$. The coefficient $C_{i,j,k}$ contains factorials and binomial coefficients.

## Gelation

The prediction of chemical infrastructure that contributes to the equilibrium rubbery modulus[45] is of primary interest. In this section the evaluation of the gel point is discussed in terms of the convergent properties of second moments and conditional convergent properties of leading moments. The notation $\sum_{i,j,k} \equiv \sum_i\sum_j\sum_k$ assumes lower and upper limits defined in eqs 2 and 3 for $i = 1, 2, 3, ....$

**Moments.** Moments with multifunctional monomers become conditionally convergent[29] at the critical conversion;[25,28,56,63] therefore, multiple solutions exist in the interval $\rho_C \leq \rho \leq 1$ when the stoichiometry is balanced ($\alpha = 0.5$) or when the primary site is the limiting reactant. Flory,[25] when discussing the homopolymerization of an $A_f$ monomer, used analytical PDDs to derive limits in the postgel state.

In this paper, weight fractions for a chain link type include unreacted monomer. Chain links become distributed between the sol and gel. The weight fraction $\omega_{A_2-A_2}$ for branch nodes equals $\sum_{i,j,k}iP_{i,j,k}/P_{1,0,2}(0)$ and in a batch reactor is expected to equal unity as expressed by the first two conditions in

$$\begin{cases} \omega_{A_2-A_2} = 1 & 0 \leq \rho \leq 1 \\ \mathrm{d}\sum_{i,j,k} ip_{i,j,k}/\mathrm{d}\rho = 0 & 0 \leq \rho \leq 1 \\ \sum_{i,j,k} ip_{i,j,k,\mathrm{sol}} < 1 & \rho_C \leq \rho \leq 1 \end{cases} \tag{16}$$

Normalization is with respect to the monomer's initial concentration $p_{i,j,k} = P_{i,j,k}/P_{1,0,2}(0)$. In derivations (see the appendix, **Moments**), Smoluchowski equations are initially multiplied by the degree of polymerization $i$, summed, and integrated. The initial two solutions are valid for all achievable conversions. The third limit of eq 16 is of primary interest. In this paper the third sum in eq 16[25,51,52,56] was generated using the weighted, analytical solutions, eqs 14 and 15. Truncation occurred at $i_{\max}$, subject to constraints of eqs 2 and 3. Ratios of factorials were factored to prevent numerical overflow errors. Results associated with truncation errors will be discussed.

Analogous mathematical rearrangements yield expressions for the cumulative number of molecules and the weight fraction of the $B_2$ monomer within the sol and gel:

$$\begin{cases} \sum_{i,j,k} p_{i,j,k} = (1 + \alpha - 2\rho_B)/\alpha & 0 \le \rho \le 1 \\ \mathrm{d}\sum_{i,j,k} p_{i,j,k}/\mathrm{d}\tau = -A - CS & 0 \le \rho \le 1 \\ \sum_{i,j,k} p_{i,j,k,\mathrm{sol}} > \sum_{i,j,k} p_{i,j,k} & \rho_C \le \rho \le 1 \end{cases} \tag{17}$$

$$\begin{cases} \omega_{B_2} = 1 & 0 \le \rho \le 1 \\ \mathrm{d}\sum_{i,j,k} jp_{i,j,k}/\mathrm{d}\rho = 0 & 0 \le \rho \le 1 \\ \sum_{i,j,k} jp_{i,j,k,\mathrm{sol}} < 1 & \rho_C \le \rho \le 1 \end{cases} \tag{18}$$

Lumping intermolecular and intramolecular reactions in a single rate expression in the Smoluchowski equation affects the cumulative molar concentration variables expressed in eq 17. The right hand side of equation $\sum_{i,j,k} p_{i,j,k}$ satisfies stoichiometric arguments if both intermolecular and intramolecular reactions involving B sites reduced the population of the molecules. Even though this constraint is in error, the solution contains valuable information.

Recall that in our model being discussed, intramolecular reactions are constrained to the gel. In addition, eq 14 predicts that the gel (at very large $i$) is composed of a few molecules at most, and perhaps, only one.[25] Therefore, negligible intermolecular reactions occur within the gel. Intermolecular reactions are confined to the sol and to reactions between the sol and gel. Since each intermolecular reaction reduces the number of molecules in the sol by one, the two moments $\sum_{i,j,k} p_{i,j,k,\mathrm{sol}}$ and $\sum_{i,j,k} p_{i,j,k}$ can be used to determine the fraction of a chemical moiety consumed by intramolecular reactions at conversion $\rho$. To illustrate, the solution labeled $\rho'_B = (1 + \alpha + \alpha\sum_{i,j,k} p_{i,j,k,\mathrm{sol}}(\rho))/2$ is initially evaluated. A corresponding quantity $\rho'$ for primary sites is obtained with the aid of eq 13. The difference $\rho - \rho'$ is the fraction of primary sites consumed by intramolecular reactions. This is consistent with constraints. If both intermolecular and intramolecular reactions did consume two reactants and form a product, the population of molecules actually present at $\rho$ would have occurred earlier at $\rho'$. However, this is false. The reaction requires conversion $\rho$ to achieve this molar concentration. The difference $\rho_B - \rho'_B$ is the fraction of B moieties consumed by intramolecular reactions. Prior to gelation, these differences equal zero. Moments are absolutely convergent and, therefore, a single limit exists.

**Critical Conversion.** The weight average molecular weight was used to calculate the critical conversion $\rho_C$ at the gel point. Second moments diverge at the critical conversion. The derivation of the moment $\mathrm{d}\sum_{i,j,k} k^2 p_{i,j,k}/\mathrm{d}t$ from the weighted Smoluchowski equation is discussed in the appendix, **Moments**. Equations for the remaining second moments are presented. When coupled with the previous moments, there exists a closed set of first-order, differential equations, which were solved using MAPLE V (Mathcad), a symbolic, numerical, mathematical package. The gel point was specified as that conversion when the second moments approached infinity asymptotically. Integrations were with respect to $\rho$.

**Table 1. $A_2$–$A_2$ Cross-Link Nodes $X_{n,o}$: $n$ Reacted Sites, Primary + Secondary, $o$ Chain Segments Extending to Gel**

| reaction state, $n$ | extent of cross-linking, $o$: 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 0 | $X_{0,0}$ | | | | |
| 1 | $X_{1,0}$ | $X_{1,1}$ | | | |
| 2 | $X_{2,0}$ | $X_{2,1}$ | $X_{2,2}$ | | |
| 3 | $X_{3,0}$ | $X_{3,1}$ | $X_{3,2}$ | $X_{3,3}$ | |
| 4 | $X_{4,0}$ | $X_{4,1}$ | $X_{4,2}$ | $X_{4,3}$ | $X_{4,4}$ |
| | $\sum_{n=0}^{4} X_{n,0}$ | $\sum_{n=1}^{4} X_{n,1}$ | $\sum_{n=2}^{4} X_{n,2}$ | $\sum_{n=3}^{4} X_{n,3}$ | $X_{4,4}$ |

An alternate derivation can use the convergent properties of any moment, such as the cumulative numbers. Prior to gelation, moments are absolutely convergent, and therefore, all solutions presented by eq 17 are equal. At the gel point, the infinite series becomes conditionally convergent,[29] and the two solutions become distinct. Results of the two procedures were consistent. The advantage of this calculation is that second moments need not be calculated unless their values are of interest, as in predicting viscosity or pot life before gelation.

**Branch Node Dynamics.** Our objective now is to calculate chemical structures within the resin that contribute to properties. The deterministic derivations explicitly incorporate chemical reaction kinetics. Since rubber elasticity is a function of the number of elastically active junctions and strands, molecular infrastructure is now described in terms of the concentration of branch node dynamics (including monomer). A branch node for the $A_2$–$A_2$+$B_2$ resin is represented by the notation $n_{l,m}$, where the subscripts represent the number of primary sites and the number of secondary sites reacted. The monomer $p_{1,0,2}$ is equivalent to $n_{0,0}$. Their chemical reactions form a series of first-order reactions in conversion space:

$$\begin{array}{lll} (1-\rho)\,\mathrm{d}n_{0,0}/\mathrm{d}\rho = 2n_{0,0} & n_{0,0}(0) \neq 0 & n_{0,0} = (1-\rho)^2 \\ (1-\rho)\,\mathrm{d}n_{1,0}/\mathrm{d}\rho = -n_{1,0} - Cn_{1,0} + 2n_{0,0} & n_{1,0}(0) = 0 & n_{0,0} = 2\rho(1-\rho)(1-\rho_S) \\ (1-\rho)\,\mathrm{d}n_{1,1}/\mathrm{d}\rho = -n_{1,1} + Cn_{1,0} & n_{1,1}(0) = 0 & n_{1,1} = 2\rho(1-\rho)(\rho_S) \\ (1-\rho)\,\mathrm{d}n_{2,0}/\mathrm{d}\rho = -2Cn_{2,0} + n_{1,0} & n_{2,0}(0) = 0 & n_{2,0} = \rho^2(1-\rho_S)^2 \\ (1-\rho)\,\mathrm{d}n_{2,1}/\mathrm{d}\rho = -Cn_{2,1} + n_{1,1} + 2Cn_{2,0} & n_{2,1}(0) = 0 & n_{2,1} = 2\rho^2\rho_S(1-\rho_S) \\ (1-\rho)\,\mathrm{d}n_{2,2}/\mathrm{d}\rho = +\,Cn_{2,1} & n_{2,2}(0) = 0 & n_{2,2} = \rho^2{\rho_S}^2 \end{array} \tag{19}$$

Initial conditions appear in the center; solutions appear on the right. The relative rate constant for secondary and primary reactions remains $C$. The rate expressions for primary and secondary sites are proportional to the number of sites on a node. For example, the node $n_{1,0}$ contains one primary and one secondary site. The constant $C \neq 1$ identifies normalized secondary rate expressions. Solutions use integrating factors. Nodes are conserved. Concentrations are normalized relative to $P_{1,0,2}(0)$ and are expressed in terms of reacted and unreacted functional groups. Specifically, the node $n_{2,1}$ contains two reacted primary sites, one reacted secondary site, and one unreacted secondary site.

**Cross-Link Concentrations.** The chemical features within the resin that contribute to the modulus are the concentration of cross-links $X_{n,o}$'s appearing in Table 1. A cross-link is a node formed from the $A_2$–$A_2$ monomer that has $n$ primary plus secondary moieties reacted and $o$ chain extensions to the gel, $0 \le o \le n \le 4$. The monomer is $X_{0,0}$. The discussion of the resin's chemical infrastructure uses the sketch of Figure 1. Previously, primary and secondary moieties plus pendent B groups were assumed to be unreacted. When cross-linking is discussed, the primary site labeled a is arbitrarily assumed to have reacted with the gel. Since all nodes in this fragment now have one path to the gel, they are in the set $X_{n,1}$. In Table 1, these cross-links are represented by the column labeled $o = 1$. Intermolecular sol/gel reactions transport nodes on a given molecule from the sol to the gel according to a first-order transformation $X_{n,0} \rightarrow X_{n,1}$, $1 \leq n \leq 4$. The sol/gel reaction at the primary moiety is not unique to this event. Every reactive moiety on the molecule participates in these reactions. As it is not necessary for a site on a branch node to react with the gel, chain connectivity is a major consideration.

To further developments, the interpretation of the molecular cluster appearing in Figure 1 is again modified by assuming that the secondary site labeled b has also reacted with the gel. One intermolecular and one intramolecular reaction has now occurred relative to this chain fragment and the gel. The fraction of the nodes pendent to the chain segment a−b remains in the set $X_{n,1}$, but nodes connected by the segment a−b are now in the set $X_{n,2}$. These nodes have experienced at least two reactions, but only two bonds on nodes in the a−b chain segment extend to the gel. These events are described by the first-order transformation $X_{n,1} \rightarrow X_{n,2}$, $2 \leq n \leq 4$. Furthermore, the second reaction with the gel is not confined to the secondary site discussed but could have occurred at any chemically reactive group. If additional chemical moieties appearing in Figure 1 had reacted with the gel, events in which some cross-links experience further first-order transformations, $X_{n,2} \rightarrow X_{n,3}$, $3 \leq n \leq 4$ and $X_{4,3} \rightarrow X_{4,4}$, can be visualized.

**Extent of Cross-Linking.** In the extent of cross-linking space, conversion is invariant.[56] A bond has formed by either intermolecular or intramolecular reactions. These events are analogous to a chemical moiety being reacted or unreacted, as expressed by eqs 9 and 19. The extent of cross-linking $\rho_X$ is defined as the fraction of bonds formed at conversion $\rho > \rho_C$ that extend to the gel. The fraction of finite chain segments is $1 - \rho_X$. In our work, mathematical properties of conditionally convergent moments[29] are used to uncouple intramolecular and intermolecular reactions.

**Cross-Link Dynamics.** Cross-linking is described by a set of first-order, partial differential equations. Initially, consider the monomer $n_{0,0} = X_{0,0}$. Since monomer is exclusively in the sol, its partial derivative with respect to the extent of cross-linking is zero:

$$(1 - \rho_X)\, \partial X_{0,0}/\partial \rho_X = 0 \qquad X_{0,0}(0) = n_{0,0} \text{ and } X_{0,0} = n_{0,0} \tag{20}$$

Integration recovers the solution. Analogies exist with eq 19, but in this equation reactions affect the concentration of all nodes. The partial derivative indicates that conversion $\rho$ is invariant. Integration is from 0 to $\rho_X$ at $\rho = \text{constant} \geq \rho_C$.

Nodes with one reacted site $n_{1,0}$ are distributed between $X_{1,0}$, which has one exiting finite chain segment, and $X_{1,1}$, whose chain extends to the gel. Since $X_{1,0} \rightarrow X_{1,1}$

$$(1 - \rho_X)\, \partial X_{1,0}/\partial \rho_X = -1X_{1,0} \qquad X_{1,0}(0) = n_{1,0} \quad \text{and} \quad X_{1,0} = n_{1,0}(1 - \rho_X)$$

$$(1 - \rho_X)\, \partial X_{1,1}/\rho_X = +1X_{1,0} \qquad X_{1,1}(0) = 0 \quad \text{and} \quad X_{1,1} = n_{1,0}\, \rho_X \tag{21}$$

Solutions are the fractions of nodes $n_{1,0}$ that are in the sol $X_{1,0}$ and gel $X_{1,1}$, respectively. Constants appearing in the normalized rate expressions equal the number of finite chain extensions from the node.

Nodes with two reacted sites $n_{1,1} + n_{2,0}$ are distributed between $X_{2,0}$, which has two finite chain extensions, $X_{2,1}$, which has one extension to the gel, and $X_{2,2}$. Since $X_{2,0} \rightarrow X_{2,1} \rightarrow X_{2,2}$

$$(1 - \rho_X)\, \partial X_{2,0}/\partial \rho_X = -2X_{2,0} \qquad X_{2,0}(0) = n_{1,1} + n_{2,0} \quad \text{and} \quad X_{2,0} = (n_{1,1} + n_{2,0})(1 - \rho_X)^2$$

$$(1 - \rho_X)\, \partial X_{2,1}/\partial \rho_X = -X_{2,1} + 2X_{2,0} \qquad X_{2,1}(0) = 0 \quad \text{and} \quad X_{2,1} = 2(n_{1,1} + n_{2,0})\rho_X(1 - \rho_X)$$

$$(1 - \rho_X)\, \partial X_{2,2}/\partial \rho_X = +X_{2,1} \qquad X_{2,1}(0) = 0 \quad \text{and} \quad X_{2,2} = (n_{1,1} + n_{2,0})\, {\rho_X}^2 \tag{22}$$

In general, the molar distribution of cross-link nodes $X_{n,\mathrm{o}}$ with $n$ reacted sites and $0 \leq o \leq n$ paths to the gel is described by a series of first-order transformations $X_{n,0} \rightarrow X_{n,1} \rightarrow \ldots \rightarrow X_{n,n}$ for which

$$X_{3,o} = \binom{3}{o} n_{2,1} \rho_X^o (1 - \rho_X)^{3-o} \quad \text{and} \quad X_{4,o} = \binom{4}{o} n_{2,2} \rho_X^o (1 - \rho_X)^{4-o} \tag{23}$$

The variable $\rho_X$, a function of conversion $\rho$ and chemistry, contains contributions from all sol/gel and gel/gel reactions. Information for the calculation of $\rho_X$ resides within moments of the population density distribution's multiple solutions.

**Evaluation of $\rho_X$.** In Table 1 the resin's mass is expressed in terms of cross-links $X_{n,\mathrm{o}}$. Specifically, an $A_2{-}A_2$ monomer has participated in the formation of $n$ bonds, of which $o$ extend to the gel. The sol fraction $\omega_{A_2-A_2} = \sum_{n=0}^{4} X_{n,0}$. Subject to eqs 19−23, algebra yields

$$\omega_{A_2-A_2} = \{(1 - \rho) + \rho(1 - \rho_S)(1 - \rho_X) + \rho\rho_S(1 - \rho_X)^2\}^2 \tag{24}$$

After the square root of both sides is taken, the quadratic equation may be readily solved for $\rho_X$. The third condition of eq 16, subject to eqs 14 and 15, was used to evaluate $\omega_{A_2-A_2}$. The algorithm added contributions from molecules that contained up to $i_{\max}$ branch nodes.

## Deterministic/Stochastic Model Comparisons

Using expectation theory, Dušek's group,[10,11,46] Bokare and Gandhi,[3] and Gupta and Macosko[35] addressed FSSE for an $A_2{-}A_2{+}B_2$ resin, but in the presence of a competing polyetherification reaction. The following discussion derives a solution based on their models for comparison. Probability functions express the expectation that a chain segment is of finite dimension. Expectation theory couples laws of total and conditional probability applicable to the reaction states of the several chemical moieties on branch nodes and chain links. In Figure 2 the reaction sequence at a branch

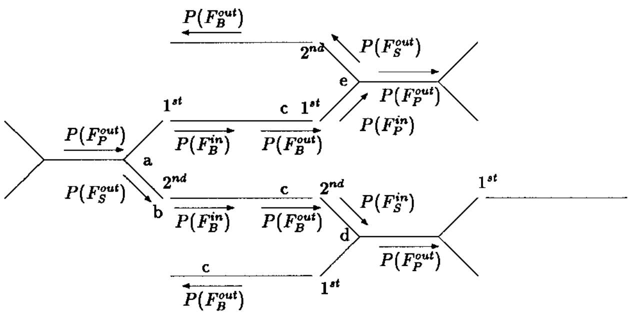

**Figure 2.** Cluster of $A_2$−$A_2$ and $B_2$ chain segments: stochastic gel-structural parameters related to rubber elasticity for arbitrary primary 1st and secondary 2nd reactions.

point is indicated by 1st and 2nd. A randomly selected primary site is reacted or unreacted. The fraction of finite, unreacted sites is $(1 - \rho)$. The fraction of primary sites reacted is $\rho$. Although a reacted primary site at point a is known to have bonded with a $B_2$ chain link, the reaction state of the secondary chemical moiety is uncertain. The conditional probabilities that finite chain segments extend from the primary and secondary sites are represented by $P(F_B^{in})$ and $P(F_S^{out})$. When looking toward the randomly chosen primary branch point along the atoms of the branch node $P(F_P^{out})$, the expectation that this path leads to finite chains through the branch equals

$$P(F_P^{out}) = (1 - \rho) + \rho P(F_B^{in})\,P(F_S^{out})$$

The expectation that the secondary site at b is connected to finite structures is

$$P(F_S^{out}) = (1 - \rho_S) + \rho_S P(F_B^{in})$$

where the fraction of secondary sites formed that are unreacted is $1 - \rho_S$ and the fraction reacted is $\rho_S$. The likelihood that a reacted site is part of finite chain segments equals the probability $P(F_B^{in})$ looking into the attached bifunctional chain link, which, in turn, equals $P(F_B^{out})$:

$$P(F_B^{in}) = P(F_B^{out})$$

Upon exiting a $B_2$ chain link, reaction states are described by three independent events, see points c for illustration. (1) The sight may be unreacted. The fraction of unreacted B's is $(1 - \rho_B)$. (2) The B moiety may have reacted with a primary group. In eq 25 the quantity $\alpha\rho$ expresses reacted primary sites per initial B's. Therefore, the term $\alpha\rho/\rho_B$ is the number of primary groups reacted per B sites reacted. The product $\rho_B(\alpha\rho/\rho_B)$ is the fraction of reacted B moieties that reacted with primary groups. (3) Alternately, the B site reacted with a secondary moiety. Since $\alpha\rho$ also equals the number of secondary sites formed per initial B moieties, the fraction of reacted secondary sites relative to reacted B sites is $\alpha\rho\rho_S/\rho_B$ , the conditional probability that the reaction at B occurred at a secondary site. The two functions $P(F_P^{in})$ and $P(F_S^{in})$ appearing in eq 25 are the probabilities that the respective paths leading into a branch node from a primary or secondary bond terminate with finite chain segments. Locations d and e may be referenced in Figure 2. The quantity in the braces in eq 25 is the conditional probability that a reacted B leads to finite chains $P(F_B^{out}|B)$:

$$P(F_B^{out}) = (1 - \rho_B) + \rho_B\left\{\frac{\alpha\rho}{\rho_B}P(F_P^{in}) + \frac{\alpha\rho\rho_S}{\rho_B}P(F_S^{in})\right\} \quad (25)$$

When a node from a reacted secondary site as at point d is entered, a branch point creates two independent events. The probability function $P(F_P^{out})$ is directed out of the site along the atoms of the branch node and the second, labeled $P(F_B^{out})$, is relative to the chain link that is known to be attached to the reacted primary site:

$$P(F_S^{in}) = P(F_P^{out})\,P(F_B^{out})$$

When a branch point is entered from a reacted primary moiety, as at e, the reaction state of the secondary site is unknown, as reflected by the probability function $P(F_S^{out})$:

$$P(F_P^{in}) = P(F_P^{out})\,P(F_S^{out})$$

A closed set of algebraic relationships exists. Solution yields the cubic expression

$$\begin{aligned}2\alpha\rho^2(\rho_S)^2P(F_B^{out})^3 + 3\alpha\rho^2\rho_S(1 - \rho_S)P(F_B^{out})^2 +\\ \{2\alpha\rho(1 - \rho)\rho_S + \alpha\rho^2(1 - \rho_S)^2 - 1\}P(F_B^{out}) +\\ \{\alpha\rho(1 - \rho)(1 - \rho_S) + (1 - \rho_B)\} = 0\end{aligned}$$

The root $P(F_B^{out}) - 1 = 0$ when $0 \le \rho \le \rho_C$ was factored, reducing the equation to a quadratic

$$\begin{aligned}2\alpha\rho^2{\rho_S}^2P(F_B^{out})^2 + \alpha\rho^2(3 - \rho_S)\rho_S P(F_B^{out}) +\\ \alpha\rho^2(1 - \rho_S)^2 + 2\alpha\rho\rho_S - 1 = 0\end{aligned}$$

Therefore, when $\rho_C \le \rho \le 1$

$$P(F_B^{out}) = [-\alpha\rho^2\rho_S(3 - \rho_S) + \sqrt{\{\alpha\rho^2\rho_S(3 - \rho_S)\}^2 - 4\{2\alpha\rho^2{\rho_S}^2\}\{\alpha\rho^2(1 - \rho_S)^2 + 2\alpha\rho\rho_S - 1\}}]/2\{2\alpha\rho^2{\rho_S}^2\} \quad (26)$$

and

$$P(F_P^{out}) = 1 - \rho + \rho P(F_B^{out})(1 - \rho_S + \rho_S P(F_B^{out})) \quad (27)$$

The several terms relate to the law of total probability of expectation and represent the fraction of primary moieties unreacted, $1 - \rho$, which are known to be finite, and the fraction reacted, $\rho$. The fraction of chain segments attached to the reacted primary sites that are finite is $P(F_B^{out})$. The path associated with the secondary site is governed by expectation theory. If the secondary site is not reacted $(1 - \rho_S)$, the chain segment terminates. If it is reacted $(\rho_S)$, the likelihood of being attached to finite chain segments is $P(F_B^{out})$.

For a branch node to be in the sol fraction $\omega_{A_2-A_2}$, each of its original two primary sites must be part of finite chain segments:

$$\omega_{A_2-A_2} = [P(F_P^{out})]^2 \quad (28)$$

Relationships 24 and 26−28 provide independent consistency checks. Specifically, the function $P(F_B^{out})$

equals $(1 - \rho_X)$, the fraction of reacted sites that lead to finite clusters. Solutions are identical. The fraction of $B_2$'s in the sol equals

$$\omega_{B_2} = [P(F_B^{out})]^2 \tag{29}$$

$$P(F_B^{out}) = 1 - \rho_x \tag{30}$$

## Contributions from Junctions, Strands, and Entanglements

Discussion returns to an original objective, the calculation of the modulus of elasticity from the theory of rubber elasticity. An elastically active junction $\mu_c$ contains three or more paths chemically bonded to the gel. Therefore,

$$\mu_c = \sum_{n=3}^{4} X_{n,3} + X_{4,4} = \rho^2 \rho_S {\rho_X}^3 (2 + 2\rho_S - 3\rho_S\rho_X) \tag{31}$$

Strands connect two elastically active junctions. The number of chemically formed strands $\nu_c$ equals

$$\nu_c = (3\sum_{n=3}^{4} X_{n,3} + 4X_{4,4})/2 = \rho^2 \rho_S {\rho_X}^3 (3 + 3\rho_X - 4\rho_S\rho_X) \tag{32}$$

For entanglements to contribute to the modulus, each of the four chain segments exiting the entanglement must enter branch nodes that are attached to the gel.[7,43] In one visualization, the entanglement occurs on the interior of two bifunctional links. Let $P(F_B^{out}|B)$ be the conditional probability that a reacted B leads to finite chain segments. The function $1 - P(F_B^{out}|B)$ is the expectation that the path out of the entanglement leads to the gel. Therefore, the four chain extensions from the entanglement yield

$$T_e@2B_2'\text{s} = (1 - P(F_B^{out}|B))^4 = \left[1 - \frac{\alpha\rho}{\rho_B}P(F_P^{in}) - \frac{\alpha\rho\rho_S}{\rho_B}P(F_S^{in})\right]^4 \tag{33}$$

The conditional probability function $P(F_B^{out}|B)$ appears in the braces of eq 25. Alternately, entanglements could occur on the interiors of two branch nodes. Each of the four paths exiting the entanglement depend on the product $P(F_S^{out})\ P(F_P^{out})$:

$$T_e@2A_2{-}A_2'\text{s} = (1 - P(F_S^{out})\ P(F_P^{out}))^4 \tag{34}$$

Although other physical entanglements could exist as well as mixtures, for illustration, simulations were limited to these two.

## Simulations

In simulations, a balanced stoichiometry was used, $\alpha = 0.5$. The several extents of reaction are expressed in eqs 9–13 as functions of conversion of primary sites $\rho$ and the relative rate constant for secondary and primary reactions $C$. The conversion of B moieties $\rho_B$ is correlated as a function of the conversion of primary sites $\rho$ in Figure 3. When the secondary site is relatively reactive $C = 9$, the two extents of reaction are nearly linear. The secondary site reacts rapidly after its formation. Thus two B's react for each primary group. However, when the primary site is relatively reactive $C = 0.09$, conversion $\rho_B$ lags the conversion of primary sites. Secondary sites accumulate. This may also be observed in Figure 4, a correlation of the conversion of secondary sites $\rho_S$ as a function of $\rho$. When $C = 9$, the conversion of the forming secondary sites remains relatively high, whereas when $C = 0.09$ the conversion of the secondary sites is low until high extents of reaction for primary sites.

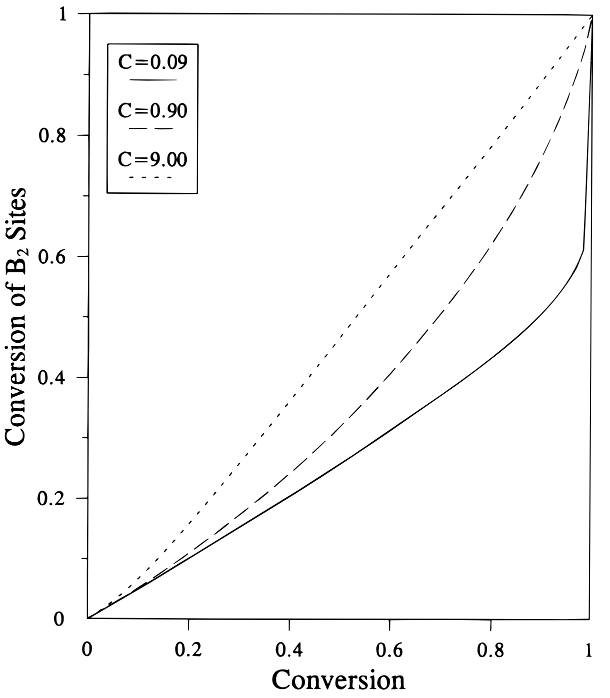

**Figure 3.** Conversion of B moieties $\rho_B$ as a function of the conversion of primary moieties $\rho$ and the relative rate constant $C$.

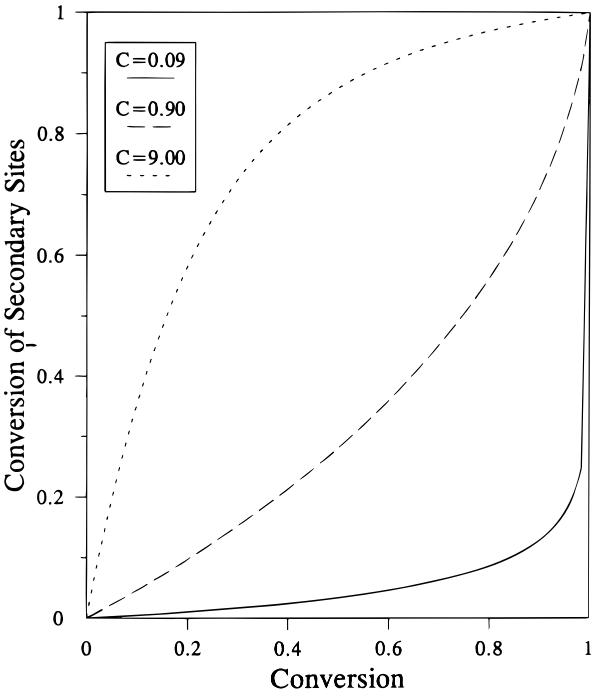

**Figure 4.** Conversion of secondary sites S as a function of the conversion of primary moieties $\rho$ and the relative rate constant $C$.

The sol fraction was calculated by two methods, (1) the analytical solution of eq 28 and (2) an approximate

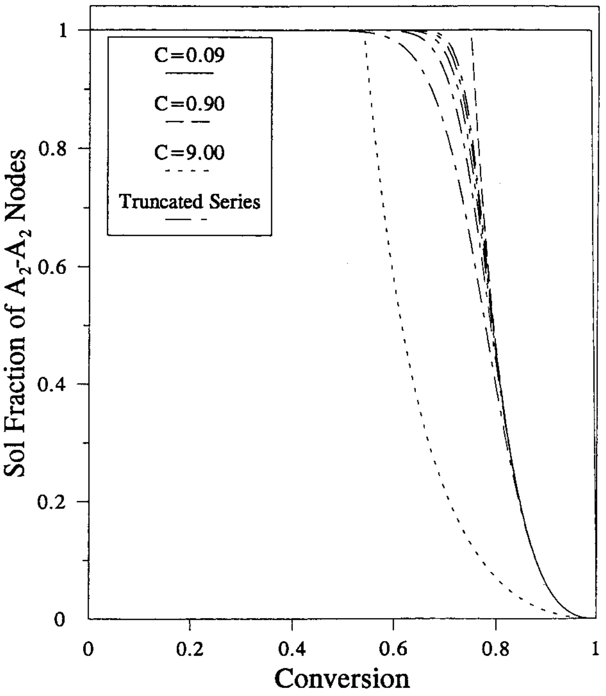

**Figure 5.** Sol fraction of branch nodes as a function of conversion, relative rate constants $C$, and truncation $i_{\max} = 10, 20, 30, 40, 50$.

solution based on a truncated series of eq 16. Results discussed are generally subject to $i_{\max} = 50$ and constraints expressed by eqs 2 and 3. In Figure 5 the fraction of the $A_2{-}A_2$ branch nodes in the sol $\sum_{n=0}^{4} X_{n,0}$ is correlated as a function of the conversion of primary amines and the relative rate constant $C$. Although numerical approximations experienced errors in the vicinity of their critical conversions, truncated solutions rapidly converged to the exact solution at intermediate conversions.

To illustrate errors associated with the truncation of infinite sums, a series of results is also shown in Figure 5, constrained to a relative rate constant $C = 0.9$. One will observe that at lower values for $i_{\max}$, the sums $\sum_{i,j,k} i p_{i,j,k}$ are sensitive to the value selected; however, little variation occurs between the values for $40 \le i_{\max} \le 50$. All truncated sums converged to the analytical solution at higher conversions. The limits used in the algorithm are expressed by eqs 2 and 3 for $i = 1, 2, 3, ..., i_{\max}$. The algorithm calculates a considerable population of molecules that do not substantially contribute to the moment. A more effective algorithm would increment on the number of bonds contained within the molecules and not all possible molecules that contain $i$ branch nodes, as was programmed. An objective was to demonstrate that numerical solutions are possible at conversions greater than the critical conversion. This has been demonstrated.

The critical conversion was also numerically calculated from the closed set of second moments, eqs 45–50. Assignment was based on their asymptotic limit. Interpolation based on data at intermediate conversions appearing in Figure 5 and $\rho_C$ would effectively reduce errors near the critical conversion when precise results are required, as in estimating pot lives for resin systems. Alternately, the critical conversion can be evaluated from the convergent properties of the leading moments, such as the number moment.

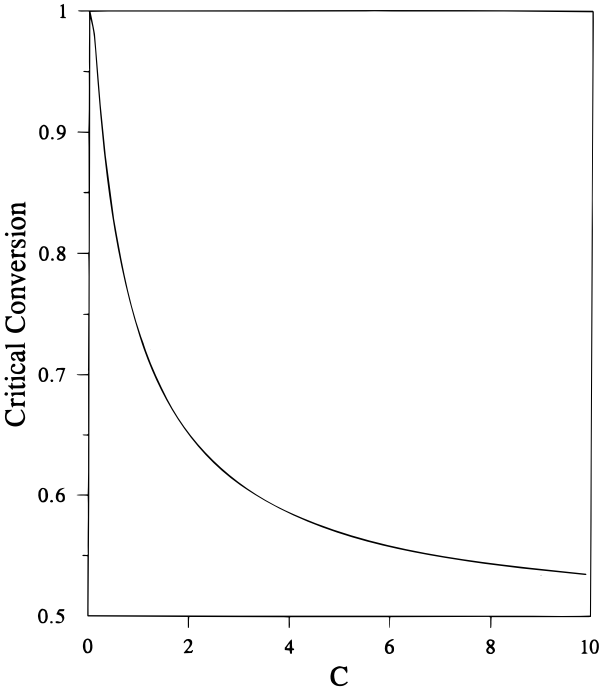

**Figure 6.** Gel point correlated as a function of the relative rate constants. When $C$ is large, $\rho_C = 0.50$.

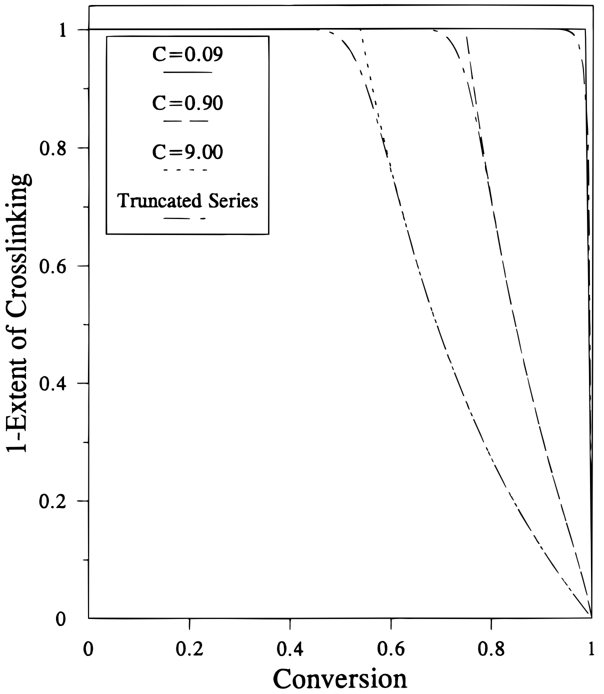

**Figure 7.** Fraction of finite chain extensions from a branch node as a function of conversion and relative rate constants.

In Figure 6 solutions for the critical conversion are graphed as a function of the relative rate constant $C = K_S/K_P$. As the constant $C$ becomes larger, chains in the sol are transformed from linear to branched configurations. The critical conversion dropped from unity to a value near 0.53. When $C = \infty$, $\rho_C = 0.50$. Stockmayer's solution at $C = 1$ may be obtained by interpolation.

Extents of cross-linking $\rho_X$ calculated from truncated sums of the analytical PDD are correlated in Figure 7 as $1 - \rho_X$ vs $\rho$. The probability function $P(F_B^{\mathrm{out}})$ is graphed for reference. Although errors exist near the critical conversion, at intermediate conversions the

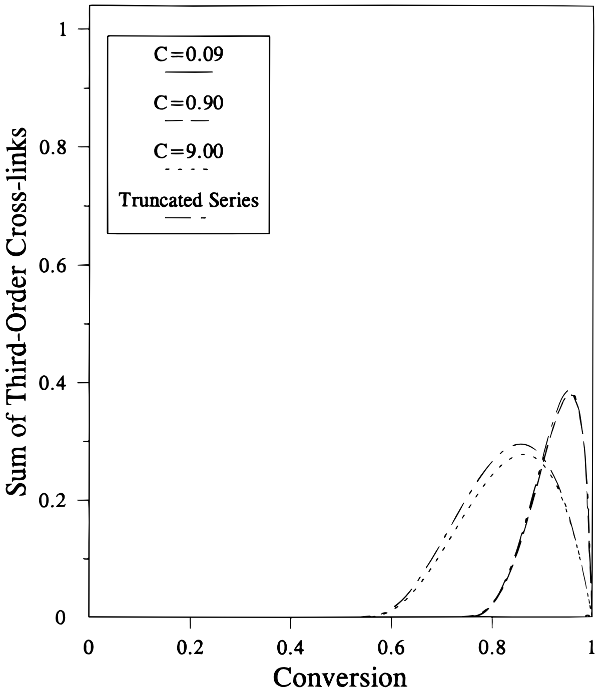

**Figure 8.** Third-order cross-link dynamics.

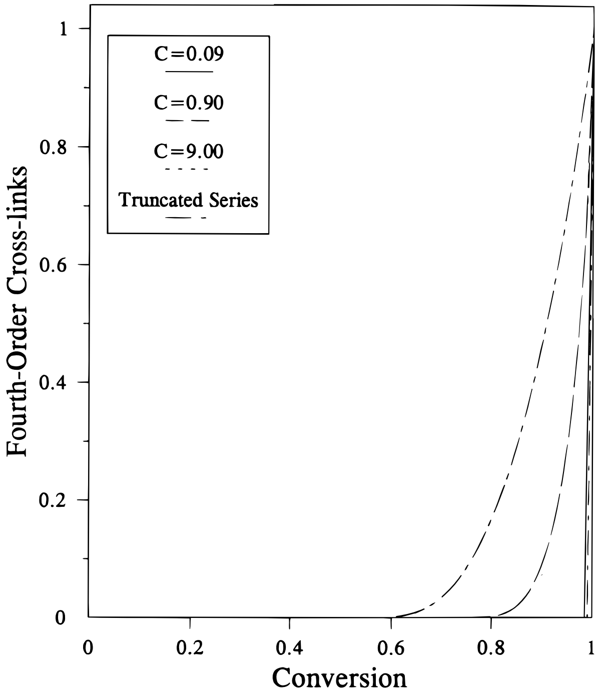

**Figure 9.** Fourth-order cross-link dynamics.

truncated estimate converges rapidly to the exact solution. The exact solution was obtained from eq 27. Simulations for three relative rate constants are shown. When secondary sites are not very reactive ($C = 0.09$) linear chain configurations delay cross-link formation until relatively high conversions of primary sites $\rho$. If secondary sites are reactive ($C = 9$), gelation begins near a conversion of 0.53.

The equilibrium modulus is a function of third- and fourth-order cross-links $\sum_{n=3}^{4} X_{n,3}$ and $X_{4,4}$, respectively. Node dynamics are shown in Figures 8 and 9. As the relative rate constant diminishes from $C = 9$ to 0.09, properties dependent on branching and cross-linking are delayed to higher conversions of primary

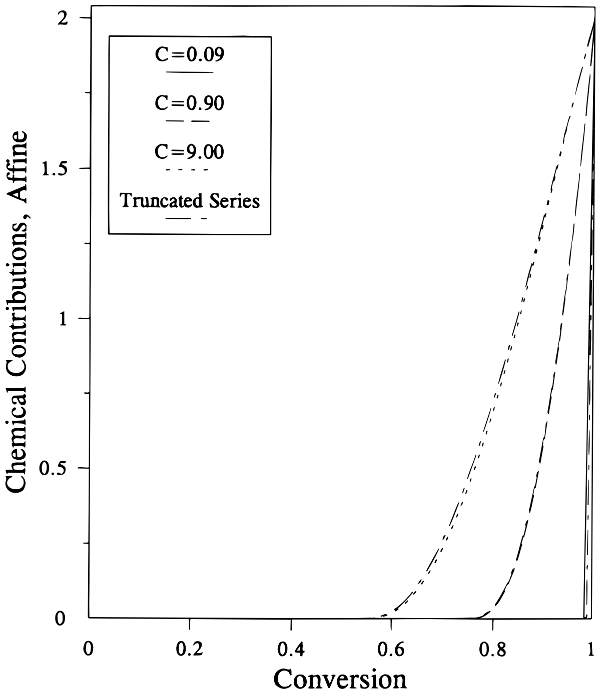

**Figure 10.** Chemical contribution to the equilibrium modulus for an affine resin.

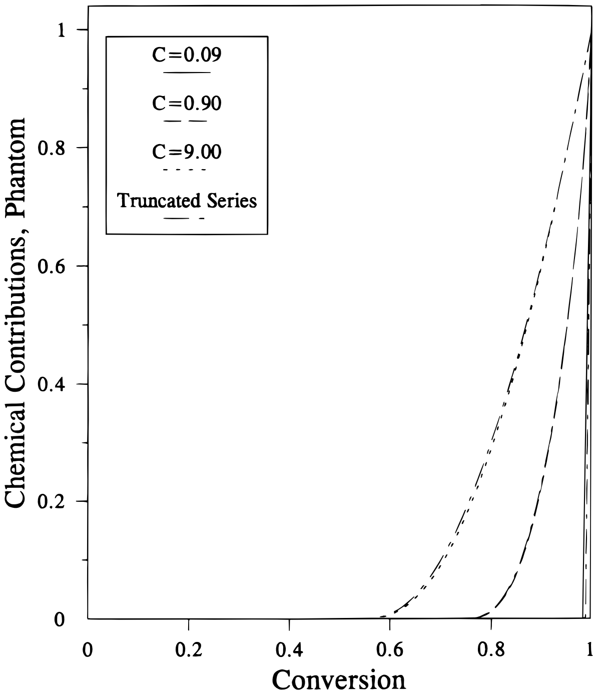

**Figure 11.** Chemical contribution to the equilibrium modulus for a phantom resin.

sites. As with step-growth polymerizations of bifunctional monomers, high conversions are required to optimize the modulus. When one line is present on these figures, errors between truncated approximate solutions and analytical solutions are minimal. In Figure 8 the third-order nodes formed and decayed as a spike near complete conversion when $C = 0.09$ and are not graphed. In reference to eq 32, the chemical contribution to the modulus for affine and phantom networks is presented in Figures 10 and 11. Although final values are dependent on the node fluctuation parameter $h$, transients are similar. Results are not

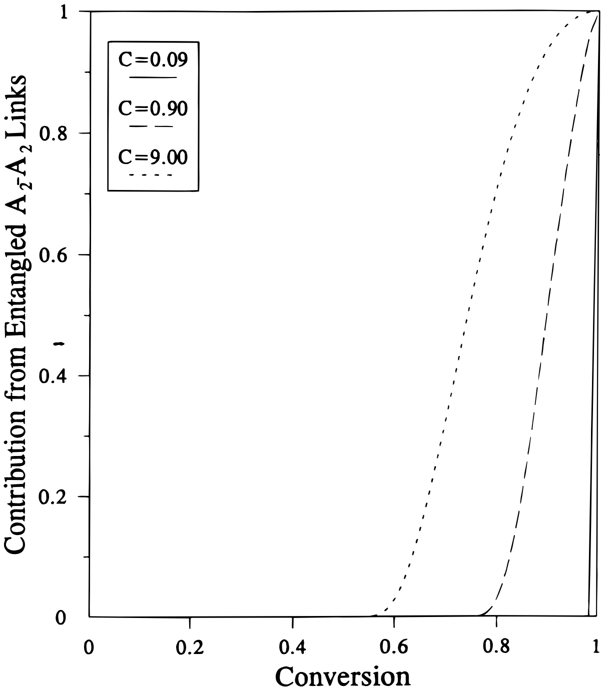

**Figure 12.** Physical contribution to the equilibrium modulus when branch nodes entangle.

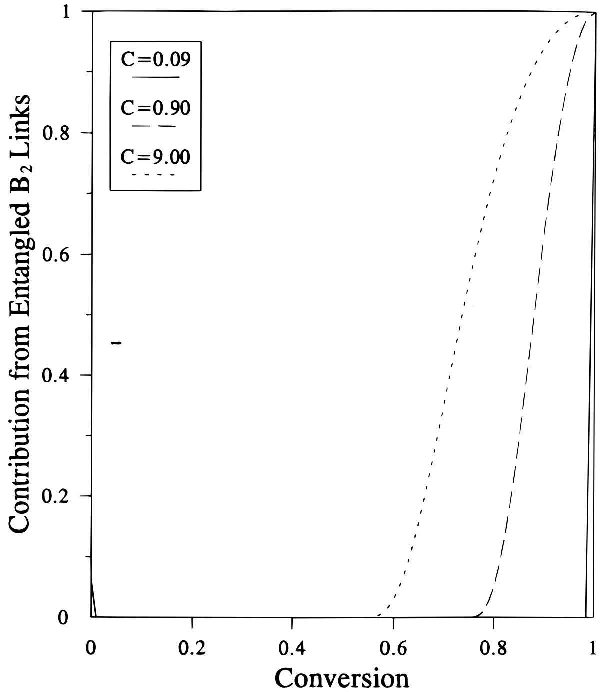

**Figure 13.** Physical contribution to the equilibrium modulus when chain links entangle.

affected by the error associated with the truncated series solutions. Estimates from physical entanglements are shown in Figures 12 and 13; see eqs 33 and 34. Although there are differences in these graphs, the general rates of development of contributions from entangled chains are similar. Recall that entanglements were assumed to occur on the interior of two $A_2-A_2$ or two $B_2$ chain segments.

## Discussion

The molecular structure of a curing, step-growth thermoset resin subject to first-shell substitution effects has been calculated from a purely deterministic analysis. The resin was composed of branch nodes of chemical functionality 4 and connecting links of functionality 2. The $A_2-A_2$ monomer initially contained two primary sites. The primary site reacts, forming a secondary site, which reacts to form a tertiary site. The two reactions were constrained to distinct rate constants. The resin was described in terms of molar concentrations of constituent molecules that contained $i$ $A_2-A_2$ nodes, $j$ $B_2$ bifunctional chain links, and $k$ unreacted primary sites. Exact solutions were derived for population density distribution dynamics. As with models discussed by Stockmayer[63] and Fukui and Yamabe,[28] the chemical structure was emphasized. Solutions incorporated the number of reacted and unreacted primary and secondary moieties plus pendent B sites. This information is fundamental to chemical reaction analysis and molecular characterization. Intramolecular cross-linking reactions were constrained to the gel. When activation energies are known, nonisothermal cures can be analyzed with slight program modifications. With autocatalytic cures, the analysis is valid since this factor may be lumped into dimensionless time $\tau$. However, an initial concentration of the catalytic moiety should be present to initiate reactions, otherwise competing reaction mechanisms must be simulated.

Moment analyses yielded sol and gel fractions. At the gel point, moments become conditionally convergent and, therefore, multiple limits exist. One set of limits was derived by initially weighting the Smoluchowski equation before addition and subsequent integration. Following Flory[25] and Stockmayer[63] analysis of second-order moments yielded the critical conversion for gelation. Using analytical population density distributions, truncated series approximations for several moments were evaluated, yielding values constrained to the sol fraction. Solutions are valid in the interval of $0 \leq \rho \leq 1$ and are not restricted to pregel conversions.[14,66]

The resin was also described in terms of branch node and cross-link dynamics. Smoluchowski-based formulations lump intermolecular and intramolecular reactions. Chemical structure dependent on these reactions was identified through a series of first-order events in the extent of cross-linking space. Solutions emphasized the chemical reaction states of the $A_2-A_2$ chain-link and the fraction of bonds that extend to infinite chains. Authors[7,12,70] have stated that deterministic solutions are not capable of calculating this molecular topology. This resin system complements deterministic derivations by Robbins et al.[56] Although exact PDDs were derived, numerical simulations of the Smoluchowski equation will also generate required data for more complex cures. The incorporation of moment equations allows the former to be truncated at manageable degrees of polymerization.

Expectation theory developed by Bokare and Gandhi[3] and Gupta and Macosko[35] was integrated into the analyses. Results show that the deterministic and stochastic formulations are identical. Numerical simulations of chemical infrastructure required for the prediction of the resin's equilibrium modulus were illustrated. Truncated infinite series in the neighborhood of the gel point resulted in acceptable errors. At intermediate conversions, truncated solutions converged to exact solutions. Results demonstrate that high conversions are required to maximize the equilibrium modulus and other properties dependent on extent of cross-linking. Gel points were precisely calculated using moments.

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## Appendix 1: Population Density Distribution Dynamics

In this appendix, derivations of the population density distribution function are presented. Conservation laws generate differential equations describing the molar concentration of molecules $P_{i,j,k}$. Analysis of the $B_2$ monomer yields

$$K_PB\,\mathrm{d}P_{0,1,0}/(K_PB\,\mathrm{d}t) = K_PB(1-\rho)\,\mathrm{d}P_{0,1,0}/\mathrm{d}\rho = -K_PA2P_{0,1,0} - K_SS2P_{0,1,0}$$

The monomer contains two B moieties, each of which reacts independently with all primary and secondary sites in the resin. Equations 9–13 permit the transformation to conversion:

$$[(1-C) - \alpha\{1+\rho-2C\rho-(1-\rho)^C\}]\,\mathrm{d}P_{0,1,0}/\mathrm{d}\rho + 2\alpha\{1-2C+C(1-\rho)^{C-1}\}P_{0,1,0} = 0$$

This equation may be solved by an integrating factor, the numerator in

$$P_{0,1,0} = P_{0,1,0}(0)\left[\frac{1-C-\alpha\{1+\rho-2C\rho-(1-\rho)^C\}}{1-C}\right]^2 = P_{0,1,0}(0)(1-\rho_B)^2 \quad (35)$$

For the $A_2$–$A_2$ monomer, reactions at the two primary sites are restricted to the resin's B moieties:

$$K_PB(1-\rho)\,\mathrm{d}P_{1,0,2}/\mathrm{d}\rho = -K_P2P_{1,0,2}B$$

Separation of variables plus integration yields

$$P_{1,0,2} = P_{1,0,2}(0)(1-\rho)^2 \quad (36)$$

The dimer $P_{1,1,1}$ satisfies the equation

$$K_PB(1-\rho)\,\mathrm{d}P_{1,1,1}/\mathrm{d}\rho = -K_PA1P_{1,1,1} - K_SS1P_{1,1,1} - K_P1P_{1,1,1}B - K_S1P_{1,1,1}B + K_P2P_{1,0,2}2P_{0,1,0}$$

The several rate expressions describe reactions involving chemical moieties on the reactant, including its B group with primary A and secondary S moieties in the resin and its primary and secondary sites with the resin's B groups. The formation expression involves reactions between primary sites and B groups on the monomers. The solution may be obtained by using an integrating factor. Recall that $-A - CS = (1-\rho)\,\mathrm{d}B/\mathrm{d}\rho = 2P_{0,1,0}(0)(1-\rho)\mathrm{d}(1-\rho_B)/\mathrm{d}\rho$. Substitution and rearrangement yields

$$\mathrm{d}P_{1,1,1}/\mathrm{d}\rho + \left[\frac{-1}{1-\rho_B}\frac{\mathrm{d}(1-\rho_B)}{\mathrm{d}\rho} + \frac{1+C}{1-\rho}\right]P_{1,1,1} = 2\alpha P_{0,1,0}(0)(1-\rho)(1-\rho_B)$$

The exact differential is

$$\frac{\mathrm{d}}{\mathrm{d}\rho}\left[\frac{P_{1,1,1}}{(1-\rho_B)(1-\rho)^{1+C}}\right] = \frac{2\alpha P_{0,1,0}(0)}{(1-\rho)^C}$$

Integration, subject to a null initial condition, yields

$$\frac{P_{1,1,1}}{(1-\rho_B)(1-\rho)^{1+C}} = 2P_{1,0,2}(0)\frac{1-(1-\rho)^{1-C}}{1-C}$$

and

$$P_{1,1,1} = 2P_{1,0,2}(0)\rho(1-\rho)(1-\rho_S)(1-\rho_B) \quad (37)$$

In summary, the population density distribution function reflects the reaction states of the several chemical moieties. The molecule $P_{0,1,0}$ contains two B groups. The $P_{1,0,2}$ monomer contains two primary sites. The dimer contains one reacted and one unreacted primary site, one unreacted secondary site, and one unreacted B moiety. Solutions, eqs 35–37, suggest that the form of the PDD solution is

$$p_{i,j,k} = \frac{P_{i,j,k}}{P_{1,0,2}(0)} = C_{i,j,k}\alpha^{i-1}\rho^{2i-k}(1-\rho)^k\rho_S^{j-i+k-1}(1-\rho_S)^{3i-j-2k+1}(1-\rho_B)^{j-i+1} = C_{i,j,k}f_{i,j,k} \quad (38)$$

Normalization is with respect to the $A_2$–$A_2$ monomer. The coefficient $C_{i,j,k}$ is a function of the degrees of polymerization and the primary site's functionality. The several powers represent the number of primary sites reacted $2i - k$, the remaining primary sites' chemical functionality $k$, the number of reacted secondary sites $j - i + k - 1$, the number of secondary moieties $3i - j - 2k + 1$ and the unreacted B groups $j - i + 1$. Conversion dependencies are lumped into the factor $f_{i,j,k}$.

Coefficients $C_{i,j,k}$ were evaluated with the aide of the Smoluchowski[60] equation:

$$\mathrm{d}P_{i,j,k}/\mathrm{d}t = K_PB(1-\rho)\,\mathrm{d}P_{i,j,k}/\mathrm{d}\rho = -(K_PA + K_SS)B_{i,j,k}P_{i,j,k} - K_PA_{i,j,k}P_{i,j,k}B - K_SS_{i,j,k}P_{i,j,k} + \sum_{l,m,n}\{K_PA_{l,m,n}P_{l,m,n}B_{i-l,j-m,k-n+1}P_{i-l,j-m,k-n+1} + K_SS_{l,m,n}P_{l,m,n}B_{i-l,j-m,k-n}P_{i-l,j-m,k-n}\} \quad (39)$$

The several rate expressions describe bond formation at the reactant's $B$, primary, and secondary groups, respectively. Formation reactions involve the union of smaller molecules and yield the sum. The notation is based on eq 7. Differentiation of eq 14 yields

$$\mathrm{d}p_{i,j,k}/\mathrm{d}\rho = C_{i,j,k}f_{i,j,k}\left\{\frac{2i-k}{\rho} - \frac{k}{1-\rho} + \frac{j-i+k-1}{\rho_S}\frac{\mathrm{d}\rho_S}{\mathrm{d}\rho} - \frac{3i-j-2k+1}{1-\rho_S}\frac{\mathrm{d}\rho_S}{\mathrm{d}\rho} - \frac{j-i+1}{1-\rho_B}\frac{\mathrm{d}\rho_B}{\mathrm{d}\rho}\right\} = C_{i,j,k}f_{i,j,k}g_{i,j,k}$$

Substitution and rearrangement of eq 39 produces a recursive equation:

$$C_{i,j,k} = \frac{f_{i,j,k+1}}{f_{i,j,k}} \left[ \frac{\sum_{l,m,n} \{A_{l,m,n} C_{l,m,n} B_{i-l,j-m,k-n+1} C_{i-l,j-m,k-n+1}\}}{B(1-\rho) g_{i,j,k} + A_{i,j,k} B + CS_{i,j,k} B + (A + CS) B_{i,j,k}} + \frac{\sum_{l,m,n} \{CS_{l,m,n} C_{l,m,n} B_{i-l,j-m,k-n} C_{i-l,j-m,k-n}\}}{B(1-\rho) g_{i,j,k} + A_{i,j,k} B + CS_{i,j,k} B + (A + CS) B_{i,j,k}} \right]$$

Coefficients are independent of conversion, formulation, and rate constants. Coefficients calculated by a FORTRAN algorithm satisfy

$$C_{i,j,k} = \frac{2(j-1)!}{k!(j-i+1)!(i-k)!} \sum_{l=0}^{l_{\max}} \binom{i}{l} \binom{2i-k-l}{j-i+k-1-l} \quad \text{where} \quad l_{\max} = \min \begin{cases} i \\ j-i+1 \end{cases} \tag{40}$$

Binomial coefficients $\binom{i}{j}$ equal $i!/j!(i-j)!$. One objective is now completed. PDDs are described by eqs 14 and 15. Flory[25] and Stockmayer[63] used a stochastic approach in solutions for $P_{i,j}$, subject to $C = 1$.

## Appendix 2: Moments

Moment equations forming weighted Smoluchowski relationships (39) are derived by using algebraic manipulations. The initial derivation addresses the conservation of branch nodes within the resin, including monomer. Chemical equivalents equal $\Phi^{\mathrm{A}}_{i,j,k} = A_{i,j,k} p_{i,j,k}$, $\Phi^{\mathrm{S}}_{i,j,k} = S_{i,j,k} p_{i,j,k}$, and $\Phi^{\mathrm{B}}_{i,j,k} = B_{i,j,k} p_{i,j,k}$. Initially, eq 39 is weighted by the degree of polymerization, yielding

$$\begin{aligned} \mathrm{d}\sum_{i,j,k} i p_{i,j,k}/\mathrm{d}t = {} & -(K_{\mathrm{P}} A + K_{\mathrm{S}} S) \sum_{i,j,k} i \Phi^{\mathrm{B}}_{i,j,k} - \{K_{\mathrm{P}} \sum_{i,j,k} i \Phi^{\mathrm{A}}_{i,j,k} + K_{\mathrm{S}} \sum_{i,j,k} i \Phi^{\mathrm{S}}_{i,j,k}\} B + \\ & K_{\mathrm{P}} \sum_{l,m,n} \{\Phi^{\mathrm{A}}_{l,m,n} \sum_{i-l,j-m,k-n+1} (i-l+l) \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} + \\ & K_{\mathrm{S}} \sum_{l,m,n} \{\Phi^{\mathrm{S}}_{l,m,n} \sum_{i-l,j-m,k-n} (i-l+l) \Phi^{\mathrm{B}}_{i-l,j-m,k-n}\} \end{aligned} \tag{41}$$

The initial four rate expressions are a consequence of $P_{i,j,k}$ being a reactant. In these reactions $P_{i,j,k}$ molecules contribute B, primary and secondary groups, respectively. The last two expressions correlate formation reactions of molecules $P_{i,j,k}$; see eq 7. Since the infinite $\sum_{i,j,k}$ includes all molecules in the resin, molecules in a specific set $P_{l,m,n}$ also react with all molecules. The original weight $i$ equals $i - l + l$ in this mathematical arrangement. Since subscripts in these infinite sums are dummy variables, the above equation is equivalent to

$$\begin{aligned} \mathrm{d}\sum_{i,j,k} i p_{i,j,k}/\mathrm{d}t = {} & -(K_{\mathrm{P}} A + K_{\mathrm{S}} S) \sum_{i,j,k} i \Phi^{\mathrm{B}}_{i,j,k} - \{K_{\mathrm{P}} \sum_{i,j,k} i \Phi^{\mathrm{A}}_{i,j,k} + K_{\mathrm{S}} \sum_{i,j,k} i \Phi^{\mathrm{S}}_{i,j,k}\} B + \\ & K_{\mathrm{P}} \sum_{l,m,n} \{\Phi^{\mathrm{A}}_{l,m,n} \sum_{i-l,j-m,k-n+1} (i-l) \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} + \\ & K_{\mathrm{P}} \sum_{l,m,n} \{l \Phi^{\mathrm{A}}_{l,m,n} \sum_{i-l,j-m,k-n+1} \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} + \\ & K_{\mathrm{S}} \sum_{l,m,n} \{\Phi^{\mathrm{S}}_{l,m,n} \sum_{i-l,j-m,k-n} (i-l) \Phi^{\mathrm{B}}_{i-l,j-m,k-n}\} + \\ & K_{\mathrm{S}} \sum_{l,m,n} \{l \Phi^{\mathrm{S}}_{l,m,n} \sum_{i-l,j-m,k-n} \Phi^{\mathrm{B}}_{i-l,j-m,k-n}\} = 0 \end{aligned} \tag{42}$$

The first term to the right of the equality equals the sum of the third and fifth expressions; the second term equals the sum of the fourth and sixth groups. The null solution is the second condition of eq 16. Integration subject to initial conditions $\sum_{i,j,k} p_{i,j,k}(0) = p_{1,0,2}(0) = 1$ yields the first condition of eq 16. The number of branch nodes in the batch reactor is conserved. They become distributed between the monomer and polymeric chains in the sol and molecules in the gel with increasing conversion. Reactions in the Smoluchowski formulation include intermolecular additions within the sol and between the gel and sol and intramolecular cross-link formations within the gel. This is consistent with Ziff and Stell's[75] observations as expressed by eq 8. It differs from Flory's[25] interpretation in so far that conversions greater than the critical conversion are permitted.

Traditional derivations of the gel point are based on second moments. This set of moments is now discussed. The moment $\sum_{i,j,k} k^2 p_{i,j,k}$ is used for illustration. Equation 14 may be referenced. Weighted formation reactions involving primary sites on molecules $P_{l,m,n}$ are manipulated, illustrating algebra as expressed by the subscripts of the formation reactions. The original weight $k^2$ is expressed in terms of the independent subscripts $k^2 = (k+1)^2 - 2k - 1 = \{(k-n+1) + n\}^2 - 2\{(k-n+1) + n\} + 1$. After the quadratic is expanded, the products of the infinite sums are equivalent to

$$\begin{aligned} & \{\sum_{l,m,n} \Phi^{\mathrm{A}}_{l,m,n}\}\{\sum_{i-l,j-m,k-n+1} (k-n+1)^2 \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} + \\ & 2\{\sum_{l,m,n} n \Phi^{\mathrm{A}}_{l,m,n}\}\{\sum_{i-l,j-m,k-n+1} (k-n+1) \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} + \\ & \{\sum_{l,m,n} n^2 \Phi^{\mathrm{A}}_{l,m,n}\}\{\sum_{i-l,j-m,k-n+1} \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} - \\ & 2\{\sum_{l,m,n} \Phi^{\mathrm{A}}_{l,m,n}\}\{\sum_{i-l,j-m,k-n+1} (k-n+1) \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} - \\ & 2\{\sum_{l,m,n} n \Phi^{\mathrm{A}}_{l,m,n}\}\{\sum_{i-l,j-m,k-n+1} \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} + \\ & \{\sum_{l,m,n} \Phi^{\mathrm{A}}_{l,m,n}\}\{\sum_{i-l,j-m,k-n+1} \Phi^{\mathrm{B}}_{i-l,j-m,k-n+1}\} \end{aligned} \tag{43}$$

The first and third expressions are equivalent to the weighted reactions when the reactant $p_{i,j,k}$ in the Smoluchowski relationship contributes a primary site.

Weighted secondary formation reactions yield a slight modification in the algebra $k^2 = \{(k - n) + n\}^2 = (k - n)^2 + 2n(k - n) + n^2$ and contribute

$$\begin{aligned}\{\sum_{l,m,n}\Phi^{S}_{l,m,n}\}\{\sum_{i-l,j-m,k-n}(k-n)^2\Phi^{B}_{i-l,j-m,k-n}\} +\\ 2\{\sum_{l,m,n}n\Phi^{S}_{l,m,n}\}\{\sum_{i-l,j-m,k-n}(k-n)\Phi^{B}_{i-l,j-m,k-n}\} +\\ \{\sum_{l,m,n}n^2\Phi^{S}_{l,m,n}\}\{\sum_{i-l,j-m,k-n}\Phi^{B}_{i-l,j-m,k-n}\}\end{aligned} \quad (44)$$

The first and third expressions are equivalent to the weighted reactions when the reactant $p_{i,j,k}$ in the Smoluchowski equation contributes a secondary site. After canceling terms and substituting

$$\begin{aligned}\mathrm{d}\sum_{i,j,k}k^2p_{i,j,k}/\mathrm{d}t =\\ 2K_{\mathrm{P}}\{\sum_{i,j,k}k^2p_{i,j,k}\}\{\sum_{i,j,k}(jk - ik + k)p_{i,j,k}\} -\\ 2K_{\mathrm{P}}\{\sum_{i,j,k}kp_{i,j,k}\}\{\sum_{i,j,k}(jk - ik + k)p_{i,j,k}\} -\\ 2K_{\mathrm{P}}\{\sum_{i,j,k}k^2p_{i,j,k}\}\{\sum_{i,j,k}(j - i + 1)p_{i,j,k}\} +\\ K_{\mathrm{P}}\{\sum_{i,j,k}kp_{i,j,k}\}\{\sum_{i,j,k}(j - i + 1)p_{i,j,k}\} +\\ 2K_{\mathrm{S}}\{\sum_{i,j,k}(3ik - jk - 2k^2 + k)p_{i,j,k}\}\\ \{\sum_{i,j,k}(jk - ik + k)p_{i,j,k}\}\end{aligned} \quad (45)$$

Differential equations for the remaining moments were evaluated using analogous algebra. The primary formation reactions in eq 39, subject to the notation of eq 7, contribute the weight $jk = j(k + 1) - j = \{(j - m) + m\}\{(k - n + 1) + n\} - \{(j - m) + m\}$ and secondary formation reactions yield $jk = \{(j - m) + m\}\{(k - n) + n\}$. Therefore,

$$\begin{aligned}\mathrm{d}\sum_{i,j,k}jkp_{i,j,k}/\mathrm{d}t =\\ K_{\mathrm{P}}\{\sum_{i,j,k}jkp_{i,j,k}\}\{\sum_{i,j,k}(jk - ik + k)p_{i,j,k}\} +\\ K_{\mathrm{P}}\{\sum_{i,j,k}k^2p_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij + j)p_{i,j,k}\} -\\ K_{\mathrm{P}}\{\sum_{i,j,k}kp_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij + j)p_{i,j,k}\} -\\ K_{\mathrm{P}}\{\sum_{i,j,k}jkp_{i,j,k}\}\{\sum_{i,j,k}(j - i + 1)p_{i,j,k}\} +\\ K_{\mathrm{S}}\{\sum_{i,j,k}\{(3ij - j^2 - jk + j)p_{i,j,k}\}\{\sum_{i,j,k}(jk - ik + k)p_{i,j,k}\} +\\ K_{\mathrm{S}}\{\sum_{i,j,k}\{(3ik - jk - 2k^2 + k)p_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij + j)p_{i,j,k}\}\end{aligned} \quad (46)$$

By factoring the weight $ik = \{(i - l) + l\}\{(k - n + 1) + n\} - \{(i - l) + l\}$ and $\{(i - l) + l\}\{(k - n) + n\}$ for reactions in eq 39, the weighted Smoluchowski equation becomes

$$\begin{aligned}\mathrm{d}\sum_{i,j,k}ikp_{i,j,k}/\mathrm{d}t = K_{\mathrm{P}}\{\sum_{i,j,k}ikp_{i,j,k}\}\{\sum_{i,j,k}(jk - ik + k)p_{i,j,k}\} +\\ K_{\mathrm{P}}\{\sum_{i,j,k}k^2p_{i,j,k}\}\{\sum_{i,j,k}(ij - i^2 + i)p_{i,j,k}\} -\\ K_{\mathrm{P}}\{\sum_{i,j,k}kp_{i,j,k}\}\{\sum_{i,j,k}(ij - i^2 + i)p_{i,j,k}\} -\\ K_{\mathrm{P}}\{\sum_{i,j,k}ip_{i,j,k}\}\{\sum_{i,j,k}(j - i + 1)p_{i,j,k}\} +\\ K_{\mathrm{S}}\{\sum_{i,j,k}\{(3i^2 - ij - 2ik + j)p_{i,j,k}\}\{\sum_{i,j,k}(jk - ik +\\ k)p_{i,j,k}\} + K_{\mathrm{S}}\{\sum_{i,j,k}\{(3ik - jk - 2k^2 + k)p_{i,j,k}\}\\ \{\sum_{i,j,k}(ij - i^2 + i)p_{i,j,k}\}\end{aligned} \quad (47)$$

The weight $j^2 = \{(j - m) + m\}\{(j - m) + m\}$, therefore,

$$\begin{aligned}\mathrm{d}\sum_{i,j,k}j^2p_{i,j,k}/\mathrm{d}t = 2K_{\mathrm{P}}\{\sum_{i,j,k}jkp_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij + j)p_{i,j,k}\} +\\ 2K_{\mathrm{S}}\{\sum_{i,j,k}\{(3ij - j^2 - 2jk + j)p_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij + j)p_{i,j,k}\}\end{aligned} \quad (48)$$

Likewise

$$\begin{aligned}\mathrm{d}\sum_{i,j,k}i^2p_{i,j,k}/\mathrm{d}t =\\ +2K_{\mathrm{P}}\{\sum_{i,j,k}ikp_{i,j,k}\}\{\sum_{i,j,k}(ij - i^2 + i)p_{i,j,k}\} +\\ 2K_{\mathrm{S}}\{\sum_{i,j,k}\{(3i^2 - ij - 2ik + i)p_{i,j,k}\}\{\sum_{i,j,k}(ij - i^2 + i)p_{i,j,k}\}\end{aligned} \quad (49)$$

and

$$\begin{aligned}\mathrm{d}\sum_{i,j,k}ijp_{i,j,k}/\mathrm{d}t =\\ +K_{\mathrm{P}}\{\sum_{i,j,k}ikp_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij + j)p_{i,j,k}\} +\\ K_{\mathrm{P}}\{\sum_{i,j,k}jkp_{i,j,k}\}\{\sum_{i,j,k}(ij - i^2 - i)p_{i,j,k}\}+\\ K_{\mathrm{S}}\ \{\sum_{i,j,k}\{(3i^2 - ij - 2ik + i)p_{i,j,k}\}\{\sum_{i,j,k}(j^2 - ij +\\ j)p_{i,j,k}\} + K_{\mathrm{S}}\{\sum_{i,j,k}\{(3ij - j^2 - 2jk + j)p_{i,j,k}\}\\ \{\sum_{i,j,k}(ij - i^2 + i)p_{i,j,k}\}\end{aligned} \quad (50)$$

The closed set of moment equations may be solved numerically. We used MAPLE V, a symbolic numerical mathematical package. At the gel point, second moments approach infinity asymptotically. Integrations were in conversion $\rho$.

## Nomenclature

$A$ = concentration of primary moieties in the resin, M
$A_{\mathrm{gel}}$ = concentration of A moieties in the gel, M
$A_{\mathrm{sol}}$ = concentration of A moieties in the sol, M
$A_{i,j}$ = functionality of primary sites on molecules $P_{i,j}$, $K_{\mathrm{S}} = K_{\mathrm{P}}$
$A_{i,j,k}$ = functionality of primary sites on molecules $P_{i,j,k}$, $K_{\mathrm{S}} \neq K_{\mathrm{P}}$
$B$ = concentration of B moieties in the resin, M
$\mathrm{B}_{\mathrm{gel}}$ = concentration of B moieties in the gel, M
$B_{\mathrm{sol}}$ = concentration of B moieties in the sol, M

$B_{i,j}$ = chemical functionality for B groups on $P_{i,j}$, $K_S = K_P$
$B_{i,j,k}$ = functionality for B sites on $P_{i,j,k}$, $K_S \neq K_P$
$C$ = ratio of rate constants $K_S/K_P \neq 1$
$C_{i,j,k}$ = constants in PDD
$E$ = equilibrium tensile modulus, Pa
$E°$ = plateau modulus for un-cross-linked material, Pa
$f_{i,j,k}$ = function of conversion in $P_{i,j,k}$
$g_{i,j,k}$ = function of conversion in $\mathrm{d}P_{i,j,k}/\mathrm{d}\rho$
gel = insoluble resin fraction
$h$ = junction fluctuation parameter
$K$ = second-order rate constant, $\mathrm{M}^{-1}\ \mathrm{h}^{-1}$
$K_P$ = second-order rate constant, primary moieties, $\mathrm{M}^{-1}\ \mathrm{h}^{-1}$
$K_S$ = second-order rate constant, secondary moieties, $\mathrm{M}^{-1}\ \mathrm{h}^{-1}$
$n_{l,m}$ = concentration of nodes, $l$ reacted primary groups, $m$ reacted secondary sites, M
$P_{i,j}$ = concentration of molecules with $i$ $A_4$'s, $j$ $B_2$'s, $K_P = K_S$, M
$P_{i,j,k}$ = concentration of molecules with $i$ $A_2{-}A_2$'s, $j$ $B_2$'s, $k$ primary sites, $K_P \neq K_S$, M
$p_{i,j,k}$ = normalized concentration of polymer molecules $P_{i,j,k}/P_{1,0,2}(0)$
$p_{i,j,\mathrm{sol}}$ = normalized polymer concentration of molecules in the sol, $K_P = K_S$
$P(F_X^{\mathrm{in/out}})$ = probability that paths in or out of reactive sites X are finite
$P(F_B^{\mathrm{out}}|B)$ = probability that paths out of a reacted B site are finite
$R$ = ideal gas constant, Pa L $\mathrm{K}^{-1}\ \mathrm{mol}^{-1}$
$S_{i,j}$ = functionality of secondary moieties, $K_S = K_P$
$S_{i,j,k}$ = functionality of secondary moieties, $K_S \neq K_P$
sol = soluble resin fraction
$t$ = time, h
$T$ = absolute temperature, K
$T_e$ = entanglement trapping parameter, Pa
$X_{n,o}$ = concentration of nodes with $n$ reacted moieties and $o$ strands

*Greek Symbols*

$\alpha$ = initial ratio of A/B moieties
$\nu_c$ = concentration of elastically active strands, M
$\rho$ = conversion of primary sites
$\rho_B$ = conversion of B sites
$\rho_C$ = critical conversion at the gel point
$\rho_S$ = conversion of secondary sites
$\rho_X$ = extent of cross-linking, fraction of reacted sites leading to infinite chains
$\mu_c$ = concentration of elastically active junctions, M
$\tau$ = dimensionless time
$\tau_c$ = critical dimensionless time at $\rho_c$
$\Phi_{i,j,k}^{X}$ = chemical equivalence, X = A, B, or S
$\omega_X$ = soluble weight fraction of species X = $A_2{-}A_2$ or $B_2$

## References and Notes

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