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10-17-2003

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Choi, Sungjae; Liu, Xiangdong; and Timm, Delmar C., "Deterministic Solutions for a Step-growth Polymerization" (2003). *Papers in Molecular Chemistry*. 1.
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# Deterministic Solutions for a Step-growth Polymerization*

Sungjae Choi, Xiangdong Liu, Delmar C. Timm

**Abstract**:

Chain topology, including branch node, chain link and cross-link dynamics that contribute to the number of elastically active strands and junctions, are calculated using purely deterministic derivations. Solutions are not coupled to population density distributions. An eigenzeit transformation assists in the conversion of expressions derived by chemical reaction principles from time to conversion space, yielding transport phenomena type expressions where the rate of change in the molar concentrations of branch nodes with respect to conversion is expressed as functions of the fraction of reactive sites on precursors and reactants. Analogies are hypothesized to exist in cross-linking space that effectively distribute branch nodes with *i* reacted moieties between cross-links having *j* bonds extending to the gel. To obtain solutions, reacted sites on nodes or links with finite chain extensions are examined in terms of stoichiometry associated with covalent bonding. Solutions replicate published results based on Miller and Macosko's recursive procedure and results obtained from truncated weighted sums of population density distributions as suggested by Flory.

**Keywords**:

cross-linking, gelation, modelling, nonlinear polymers, step-growth polymerization

## Introduction:

This paper addresses the prediction of network chain structures within a thermosetting resin's insoluble gel fraction that contribute to the rubbery equilibrium modulus. Authors have stated that only stochastic-based models can achieve this task. However, the literature suggests approaches that may provide equivalent information based on chemical reaction reasoning coupled with transport phenomena. Analysis addresses branch node and chain-link distribution dynamics for ideal step-growth polymerizations. The level of mathematics used in deterministic derivations presented is comparable to that used in the statistical, recursive method developed by Macosko and Miller.[1,2] Original contributions appear in sections addressing the extent of cross-linking.

## Rubbery Elasticity:

Mark and Erman[3] discussed the theory of rubbery elasticity in terms of developing network structures. The resin's equilibrium modulus for idealized networks includes affine[4] and phantom[5] models. The paper's emphasis is on the calculation of strands $\upsilon_c$ that connect two active junctions and junctions $\mu_c$ that have three or more covalent bonds attached to chain segments leading to the gel.

**Chain Topology**:

Authors have used probabilistic reasoning[7–9] to estimate chain contributions to the equilibrium modulus. The recursive method by Miller, Macosko and co-workers is widely cited.[6,10–13] With competing polymerization reactions, hybrid models couple deterministic chemical reaction models with stochastic-based reasoning.[14–16] A purely kinetic-based approach is believed incapable of yielding descriptions of required network features within the gel. For example, Flory,[4] Dotson *et al*.,[6] Dusek and Somvársky,[17] Williams *et al*.,[18] and Galina and Lechowicz[19] have stated that one must use stochastic-based methodology. A purely kinetic-based approach is believed to be incapable of yielding descriptions of required chain connectivity in the insoluble gel fraction. And yet, the literature provides a basis for contemplating deterministically based derivations.

Flory[4] discussed two limits obtained by summing weighted population density distributions (PDDs) descriptive of the molar concentration of constituent molecules within network-forming resins. Moments become conditionally convergent as conversion advances, and, therefore, multiple sums or limits exist,[20] Although Flory[4] and Stockmayer[21] frequently used stochastic reasoning in deriving PDDs, exact or numerical solutions can be obtained from Smoluchowski[22] type derivations.[23–26] Flory concluded that PDDs are confined to the soluble sol portion of the resin. Ziff and Stell[27] explicitly addressed reactions within the sol, between the sol and gel and within the gel and concluded that derivations for PDDs included both intermolecular and intramolecular cross-linking reactions. In an ideal polymerization the latter is confined to the gel. Robbins *et al*.[28,29] described required chain structures for predicting the equilibrium modulus, *i.e.,* chain-link and branch node dynamics, based solely on deterministic models. A criticism lies in the area of illustrated mathematical complexity since conditionally, convergent properties of the leading moments were incorporated in solutions. In the research reported, the dependency on PDDs is eliminated.

A deterministically based chemical reaction model is discussed for the $\mathbf{A_4 + B_2}$ resin system. The system is representative of numerous resins, including select amine-cured epoxies.[30–33] Depending on formulated monomers, primary and secondary amines may experience identical rates of reaction.[30] Selected bi-functional epoxy monomers may also be void of first-shell substitution effects.[34–36] Solutions initially presented are based on chemical reaction principles, but yield to transport phenomena type interpretation. The deterministic approach illustrated may have advantage when addressing complex reaction mechanisms, where authors couple deterministic and stochastic methodology.[10,37,38] In the reported work transformations from time to extent of reaction to extent of cross-linking are discussed.

## Analysis of an $\mathbf{A_4 + B_2}$ Resin

Several treatises have addressed step-growth polymerizations with tetra-functional $\mathbf{A_4}$ and bi-functional $\mathbf{B_2}$ monomers.[1,2,4,21,28,29,39] Random molecular motions coupled with large-scale translational displacements ultimately place reactive moieties in proximity, yielding second-order reactions. Analyses are constrained by equal reactivity of functional groups, intermolecular within the sol and between the sol and gel and intramolecular reactions within the gel. Transients associated with the dependent variables descriptive of the molar concentrations of branch nodes $n_i$ and chain links $l_j$ having $i$ reacted sites are developed. With increasing conversion, these entities become distributed between the sol and gel within the molecules that form the resin.

Conservation principles yield a set of ordinary differential equations:

$$\frac{dn_i}{KBdt} = (1-\rho)\frac{dn_i}{d\rho} = -(4-i)n_i + (5-i)n_{i-1}(1-\delta_{i,0}); \quad n_i(0) = \delta_{i,0}n_0(0); \quad 0 \le i \le 4 \tag{1}$$

Branch nodes react proportionately to the product of their molar concentrations $n_i$ and to the number of their chemically reactive *A* sites *(4 – i)*. The cumulative concentration of the second moiety in the resin is expressed by *B*. The rate constant is *K*. The dimensionless transform used in solutions is explicit. The Kronecker delta function appears in solutions and equals

$$\delta_{i,j} = \begin{cases} 0 & when \quad i \neq j \\ & or \\ 1 & when \quad i = j \end{cases} \tag{2}$$

The delta function permits eq 1 to represent monomer dynamics. Conservation of *A* moieties associated with the second-order reaction permits the transformation to conversion space $\rho$:

$$\rho = \frac{A(0)-A}{A(0)} = \frac{B(0)-B}{B(0)}\frac{B(0)}{A(0)} = \rho_B\frac{B(0)}{A(0)} = \frac{\rho_B}{r} \tag{3}$$

Equations 1 are linear first ordering differential equations in conversion space. Subject to initial conditions $n_i(0)$ , integration yields

$$n_i = \frac{4!}{i!(4-i)!}n_0(0)\rho^i(1-\rho)^{4-i}; \quad 0 \le i \le 4; \quad 0 \le \rho \le 1 \tag{4}$$

Integrating factors provide an effective method of solution.

Similarly, the molar concentration of chain links may be derived and equal

$$l_i = \frac{2!}{i!(2-i)!}l_0(0)\rho_B^i(1-\rho_B)^{2-i}; \quad 0 \le i \le 2; \quad 0 \le \rho \le 1 \tag{5}$$

Solutions expressed by eqs 4 and 5 yield stochastic interpretations. Conversion terms express the likelihood (a mole fraction) that a site is reacted or not. These independent events associated with the reaction states of moieties yield the power expressions. Coefficients address the number of permutations for placing *i* reacted sites on the selected branch node or chain link.

**Transport Phenomena:**

The form of eq 1 is noteworthy. Its derivation is based on chemical reaction theory. Mathematics transformed eq 1 to a linear, ordinary, differential equation but in the process moved the model to the realm of transport phenomena. Specifically, the derivative or gradient represents the rate of change of the molar concentration of nodes $n_i$ with respect to the fraction of **A** moieties reacted in the resin $\rho$. The coefficient $(1 - \rho)$ equals the fraction of **A** groups. After dividing by this coefficient, terms on the right hand side address the mole fractions of **A** sites on reactants and precursors, the driving forces for chemical change. Limits of integration specify an arbitrary but bounded conversion $0 \le \rho \le 1$. The model explicitly addresses the fact that a chemical group may be either unreacted or reacted. Solutions distribute the initial number of nodes $n_0(0)$ within the set $n_i$.

With some variation in definitions, future sections utilize transport phenomena to distribute nodes and links between the sol and gel. Now a reacted site is either covalently bonded to a finite or infinite chain extension. Initial conditions identify the existing population of nodes or links $n_i$ or $l_i$; transformations distribute bonds within cross-link junctions $X_{i,j}$ and chain-link extensions $L_{i,j}$ that have $i$ reacted sites and $j$ attached chain segments extending to the gel. Fundamentals reside in the underlying chemical reactions, *i.e.* the constraint that intermolecular/intramolecular reactions are governed by random collisions controlled by large scale molecular translations and localized atomic vibrations. Flory[4] addressed expected relative reaction rates and concluded that sufficient collisions will exist in a curing thermosetting resin to sustain both second-order reactions for extended conversions. Such is universally accepted in models descriptive of polymerization reactions and is consistent with experimental measurement. Chain connectivity is simply related to this course of events.

**Sol/Gel Node Dynamics:**

Nodes $n_i$ are distributed as cross-link junctions $X_{i,j}$ where $0 \le j \le i \le 4$. When $j = 0$, molecules containing nodes $X_{i,0}$ are in the soluble sol. The monomer's molar concentration $n_0$ is equivalent to $X_{0,0}$. If $j = 1$ the molecular clusters that contain $X_{i,1}$ are pendent to the gel's network chain structure. When $j = 2$, nodes appear in elastically active strands and when $j = 3$ or 4, cross-links contribute to elastically active junctions. Analogous statements apply to chain-links $L_{i,j}$ but $0 \le j \le i \le 2$ .The molar concentrations for each type of cross-link and chain-link will now be calculated as a function of conversion.

In conversion space, competing reactions describe a series of events expressed through $n_0 \rightarrow n_1 \rightarrow n_2 \rightarrow n_3 \rightarrow n_4$, also see eq 1. The second-order reactions in time become first-order reactions in conversion space. Since the law of mass action describes both intermolecular and intramolecular reactions, we hypothesize that nodes may also be distributed mathematically between the sol and gel fractions according to an analogous sequence of events at conversion greater than the critical conversion for gelation $\rho_c$ :

$$X_{i,0} \rightarrow X_{i,1} \rightarrow \ldots \rightarrow X_{i,i}\,; \quad 0 \le i \le 4\,; \quad \rho_c \le \rho \le 1$$

Chain connectivity is simply a convergence of random bond formation. In cross-linking space a reacted moiety has either an attached finite or infinite chain. Since only reacted sites are addressed, conversion is invariant as is the number of reacted sites $i$ on the cross-links. The rate of transport, a consequence of this bonding, is proportional to the product ofthe number of reacted groups with finite attachments on the several nodes and their respective molar concentrations (analogous to eq 1 in conversion space). Equation 4 provides the required constants of integration. Likewise, competing reactions require that

$$L_{i,0} \rightarrow \ldots \rightarrow L_{i,j}\,; \quad 0 \le i \le 2\,; \quad \rho_c \le \rho \le 1$$

**Extent of Cross-linking:**

The extents of cross-linking $\rho_x$ and $\rho_y$ are defined as the fraction of reacted sites attached to infinite chain segments at a specified conversion $\rho$:

$$\rho_x = \frac{\sum_{i=0}^{4}\sum_{j=0}^{i} iX_{i,j}(\rho) - \sum_{i=0}^{4}\sum_{j=0}^{i}(i-j)X_{i,j}(\rho)}{\sum_{i=0}^{4}\sum_{j=0}^{i} iX_{i,j}(\rho)} \text{ and } \rho_y = \frac{\sum_{i=0}^{2}\sum_{j=0}^{i} iL_{i,j}(\rho) - \sum_{i=0}^{2}\sum_{j=0}^{i}(i-j)L_{i,j}(\rho)}{\sum_{i=0}^{2}\sum_{j=0}^{i} iL_{i,j}(\rho)} \quad (6)$$

Initial sums equal the number of reacted chemical groups within the resin. The second sums equal the number of reacted sites within the resin that have attached finite chain clusters. Differences equal the number of sites with attached chains extending to the gel. The notation further denotes that dependent variables are functions of conversion.

**Cross-link Dynamics:**

For a node to be in the gel, it has experienced a minimum of one reaction. Since monomer is transported from the sol only through chemical reactions with the gel, in cross-linking space where conversion is invariant, its rate of transport is zero:

$$(1-\rho_x)\frac{\partial X_{0,0}}{\partial \rho_x} = -(0)X_{0,0}; \qquad X_{0,0}(0) = n_0; \qquad X_{0,0} = n_0 \quad (7)$$

The partial derivative emphasizes an invariant conversion and expresses the rate of transport of the dependent variable in terms of the fraction of sites with chain segments extending to the gel. The coefficient of the derivative equals the fraction of reacted sites with finite attachments. On the right hand side of the expression, the coefficient equals the number of reacted sites of finite dimension at conversion $\rho$ on the monomer. The dependent variable equals the molar concentration of the monomer.

Nodes with a single reacted site appear in the sol and in the gel. Transport equations are

$$(1-\rho_x)\frac{\partial X_{1,0}}{\partial \rho_x} = -1X_{1,0}; \qquad X_{1,0}(0) = n_1; \quad X_{1,0} = n_1(1-\rho_x)$$

$$(1-\rho_x)\frac{\partial X_{1,1}}{\partial \rho_x} = 1X_{1,0}; \qquad X_{1,1}(0) = 0; \quad X_{1,1} = n_1\rho_x$$

In the initial expression, the rate expression to the right of the equal sign is proportional to the fraction of reacted sites with finite chain extensions appearing on the reactant. In the second expression, this cross-link becomes the precursor for cross-links with a single reacted site attached to the gel according to the hypothesized series of first-order events. For nodes with a higher extent of reaction, the rate of transport satisfies

$$(1-\rho_x)\frac{\partial X_{i,j}}{\partial \rho_x} = (i-j)X_{i,j} + (i-1-j)X_{i,j-1}(1-\delta_{j,0}); \; X_{i,j}(0) = n_i\delta_{j,0}; \; 0 \le j \le i \le 4 \quad (8)$$

Products of coefficients and dependent variables, after dividing by $(1 - \rho_x)$, equal the fraction of reacted sites at $\rho \geq \rho_c$ that are part of finite chain clusters on reactants and precursors. The partial

derivative expresses the rate of change for a specified node in terms of the number of bonds that have chains extending to the gel. Solutions equal

$$X_{i,j} = n_i \frac{i!}{j!(i-j)!}(1-\rho_x)^{i-j}\rho_x^j \quad \text{and} \quad L_{i,j} = l_i \frac{i!}{j!(i-j)!}(1-\rho_y)^{i-j}\rho_y^j \tag{9}$$

Solutions have statistical interpretations, except now a reacted site on a node $n_i$ or link $l_i$ is either attached to a finite or infinite chain segment.

**Evaluation of the Extent of Cross-linking:**

In addressing cross-linking functions $\rho_x$ and $\rho_y$, conservation principles associated with chemical bonding are implemented. Initially, reacted **A** groups are addressed. The total number of reacted groups on nodes that are bonded to finite structures may be calculated. Algebra associated with eq 4 and 9 yields

$$\text{Reacted A groups} \rightarrow \text{finite} = \sum_{i=1}^{4} \sum_{j=0}^{i-1} (i-j) X_{i,j} = 4n_o(0)\rho(1-\rho_x) \tag{10}$$

These reacted **A** groups are covalently bonded to chain-links that also must lead to finite structures. Chain-links $L_{1,0}$ and $L_{1,1}$ contribute. With the former, the bond leads through the link to a **B**, terminating the chain. With $L_{1,1}$ a second reacted **A** on the node exists that leads to the gel. Chain-links $L_{2,0}$ provide two locations for bonding, each of which leads to finite chain segments. Links $L_{2,1}$ have only one bonded site leading to finite clusters. The path to the gel again exists at the node. Links $L_{2,2}$ contribute only infinite chain segments. Therefore, chain-links associated with the chain clusters equal

$$\text{Links}_{\text{AB}} \rightarrow \text{finite} = \sum_{i=1}^{2} (iL_{i,0} + L_{i,1}) = 4n_o(0)\rho\ [(1-\rho_B) + \rho_B(1-\rho_y)\ ] \tag{11}$$

Since both reacted moieties addressed describe the same bond eq 10 equals eq 11:

$$1-\rho_x = 1-\rho_B + \rho_B(1-\rho_y) \tag{12}$$

Statistical interpretations exist. When referencing eq 10, the coefficient $4n_0(0)\rho$ equals the fraction of bonds at conversion $\rho$. The expression $(1 - \rho_x)$ represents the fraction of bonds that lead to chain clusters through links $l_i$. When addressing eq 12, reacted A groups on nodes were initially specified. The fraction of reacted A that leads to finite structures is $1 - \rho_x$. In the first expression on the right hand side, the second B on the link has not reacted; the attachment leads to a finite structure with 100% confidence. The term $\rho_B$ represents the case when the second B moiety on the link has reacted. The fraction belonging to finite clusters is $1 - \rho_y$. Thus, algebra associated with a finite bond relative to the node and the attached link yields a form of the law of total probability for expectations.

To achieve a solution finite reacted **B** sites on chain-links is addressed:

$$\text{Reacted B} \rightarrow \text{finite} = \sum_{i=1}^{2} \sum_{j=0}^{i-1} (i-j) L_{i,j} = 2l_o(0)\rho_B(1-\rho_y) \tag{13}$$

Attached nodes must also contribute finite structures:

$$\text{Nodes}_{\text{BA}} \rightarrow \text{finite} = \sum_{i=1}^{4} (iX_{i,0} + X_{i,1}) = 4n_o(0)\rho[(1-\rho) + \rho(1-\rho_x)]^3 \qquad (14)$$

With expressions $X_{i,1}$ the gel is assessable through the second reacted moiety on the original chain-link $L_{2,1}$. After equating eqs 13 and 14, one obtains

$$1 - \rho_y = [(1-\rho) + \rho(1-\rho_x)]^3 \qquad (15)$$

A stochastic interpretation of eq 15 addresses the likelihood $1 - \rho_y$ that a reacted **B** group is attached to a branch node contributing finite chain extensions. The attached branch node has three remaining sites, each of which must lead to finite structures. These independent events contribute the power of three. A selected **A** moiety in this group may not be reacted (with probability of $(1 - \rho)$) and, therefore, leads to finite entities. Alternately, if the **A** site is reacted (with a likelihood of $\rho$), the fraction of resultant bonds that lead to finite chains is $(1 - \rho_x)$. Equations 12 and 15 may now be solved simultaneously:

$$\rho_x = \begin{cases} 0 & \text{when} \quad 0 \le \rho \le \rho_c \\ & \text{or} \\ [3r\rho - (-3r^2\rho^2 + 4r)^{1/2}]/(2r\rho^2) & \text{when} \quad \rho_c \le \rho \le 1 \end{cases} \quad \text{where } r = A(0)/B(0) \qquad (16)$$

The extent of cross-linking $\rho_y$ was evaluated from eq 15:

$$\rho_y = \rho_x / (r\rho) \qquad (17)$$

The critical conversion $\rho_c$ at the inception of gelation is the intercept of equations in eq 16:

$$\sum_{j=3}^{4} \sum_{i=j}^{4} jX_{i,j} / 2 \qquad (18)$$

**Rubber Elasticity:**

The number of elastically active strands[40] equal $\sum_{j=3}^{4} \sum_{i=j}^{4} jX_{i,j} / 2$ or

$$\upsilon_c = 2n_0(0)\rho^3 \rho_x^3 (3 - 2\rho\rho_x) \qquad (19)$$

and the number of elastically active junctions[40] equal $\sum_{j=3}^{4} \sum_{i=j}^{4} X_{i,j}$ or

$$\mu_c = n_0(0)\rho^3\rho_x^3(4-3\rho\rho_x) \tag{20}$$

**Extent of Cross-linking Dynamics:**

Solutions to eqs 16 and 17 are graphed in Figure 1, showing effects of formulation A(0)/B(0) and conversion on the extent of cross-linking variables $\rho_x$ and $\rho_y$. Prior to gel formation, the extent of cross-linking variables equals zero; the ordinate of Figure 1 equals unity. At the gel point, eq 18 predicts the critical conversion. At higher conversions, eqs 16 and 17 apply. When **A** sites are 50% in excess (r = 2), the limiting reactant B is consumed at $\rho$ = 0.5 where the extents of cross-linking equal approximately 0.76. Also $\rho_x \approx \rho_y$. When a stoichiometric balanced resin is cured, gelation occurs at a critical conversion of approximately 0.58. At complete conversion, the model further predicts that extents of cross-linking will equal unity. Therefore, high conversions are necessary to maximize network develop. When **B** moieties are in excess, the critical conversion is delayed and the extents of cross-linking are less than unity at complete conversion for the limiting reactant due to chain defects associated with dangling **B** groups.

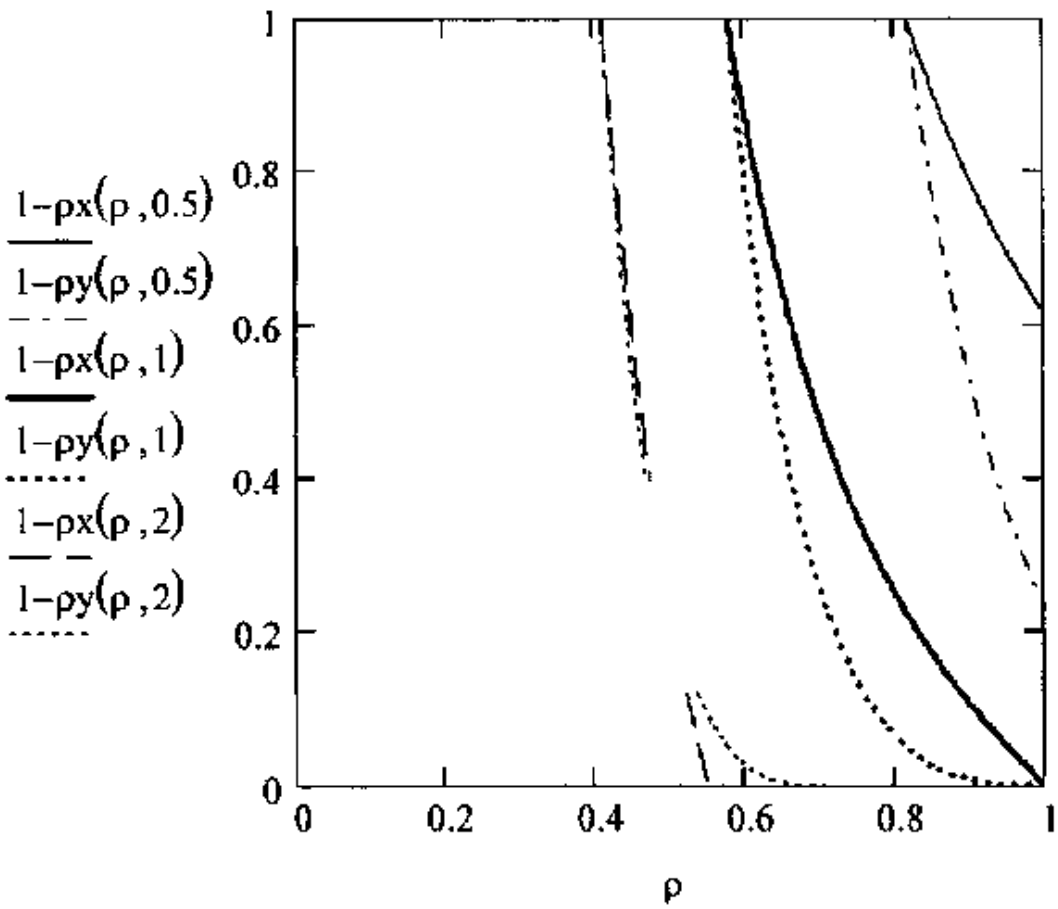


Fig. 1. Extent of cross-linking as a function of conversion $\rho$ and the ratio A(0)/B(0) in step-growth $\mathbf{A_4}$ + $\mathbf{B_2}$ system.

**Discussion:**

Flory[4] addressed multiple solutions for the leading moments of population density distribution functions associated with multi-functional monomers. Phenomena addressed included the gel point and the fraction of the gel relative to the sol. He concluded that the molecules described by the PDDs reside within the sol. Stochastic based models have since been developed to describe chain infrastructure within the gel. Macosko and Miller[1,2] developed recursive, statistical solutions based on chain connectivity associated with competing reactions. Solutions replicated Gordon' s contributions to network development.[41,42] For the resin systems currently addressed, Robbins, *et al.*,[28,29] utilizing Flory's arguments, illustrated a purely deterministic solution for gelation; however, the evaluation of truncated, infinite summations associated with moments is mathematically complex and labour intensive. The current research has combined salient concepts from this prior research to develop deterministic solutions that parallel the recursive, statistical approach. The basic hypothesis is that chain connectivity correlates with random events associated with chemical reaction. Results of derivations equal results from both Robbins and Miller and Macosko type formulations. Advantages of a purely deterministic approach may be realized 1) with formulations based on chemistry fundamentals when polymerizations involve complex, competing reactions and 2) with analytical or numerical solutions using mathematics associated with differential equations when compared to computational time demanding Monte Carlo techniques.

**Acknowledgements:**

The authors acknowledge financial contributions from Nebraska Research Initiative and the Center for Material Testing and Analysis.

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