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Reaction Kinetics Analysis of Urethane Polymerization to Gelation

B. Liu,[†] H. Noureddini,[‡] J. S. Dorsey,[‡] and D. C. Timm*[,‡]

Caltex Services Corporation, Dallas, Texas 75261-9500, and Department of Chemical Engineering, University of Nebraska, Lincoln, Nebraska 68588-0126

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ABSTRACT: A chemical reaction analysis of a thermosetting, urethane resin formulated from a triol and a diisocyanate is reported. Population density distributions of oligomeric molecules, monomer concentration, the cumulative molar concentration of intramolecular bonds, the resin's average molecular weights, and extent of reaction were determined as a function of time. Rate expressions for intermolecular reactions were first order with respect to the concentration of each reactant and were proportional to the functionality of their respective chemical moieties. Rate expressions for intramolecular reactions were first order with respect to the concentration of the reactant and were proportional to the functionality of the limiting chemical moiety on the reactant. The initial ratio of the chemical equivalents and effects of dilution were incorporated into numerical simulations. Stanford and Stepto's experimental data were analyzed. Gel points and the concentration of intramolecular bonds were correlated as a function of conversion. Intramolecular reaction rate expressions derived with the aid of Gaussian chain statistics require the molar concentrations of all chemical isomers of a specified chemical composition. The present reaction rate expression allows chemical isomers to be lumped into a single population density distribution variable, substantially reducing the dimensions of the simulation. Numerical results demonstrate that the simplified rate expression is an excellent approximation.

Introduction

The current research explicitly addresses competing intermolecular and intramolecular polymerization reactions with multifunctional monomers. The approach is based on classic chemical reaction kinetics. A major objective was the development of a meaningful, simplified rate expression for intramolecular reactions which would not explicitly require populations of the numerous chemical isomers at specified chemical compositions. The selected rate expression is proportional to the limiting chemical moiety on the reacting molecule and to the molar concentration of similar molecules. Simulations are presented that indicate the approach is accurate for a random, step-growth reaction on molecules with flexible chains. For a thermosetting, polyurethane, the number of intramolecular bonds as a function of conversion correlate with experimental measurements. Gel points are accurately predicted. Simulations and experiments incorporated the effects of initial ratios of the chemical moieties and the effects of dilution.

Linear/Cyclic Chains. Theoretical polymerization models explicitly descriptive of intramolecular reactions have been developed for linear molecules.[1] Theoretical foundations were developed by Jacobson and Stockmayer[2] who assumed that molecules were distributed according to the most probable distribution[3,4] and that ring formation was dependent on Gaussian chain statistics. Semlyen[5] reviewed methods for calculating the concentration of cyclic chains, including the rotational, isomeric state model developed by Flory, Crescenzi, and Mark,[6–8] direct computation methods of Fluendy,[9] Carmichael and Kinsinger,[10] Semlyen,[11] and Winnik et al.[12] Flory et al.[13–15] and Mutter[16] continued the advancement by addressing the direction of terminal bonds in coiled chains. Equilibrium data for the resins poly(1,3-dioxolane), poly(decamethylene adipate), and poly(dimethylsiloxane) were discussed. For the larger rings, theoretical calculations correlate with experimental measurements.

For kinetically controlled ring closure, Gordon and Scantlebury[17] expressed the relative kinetic rate constant in terms of the mean bond length l

$$k_\sigma/(k_\alpha \nu^{3/2}) = \left(\frac{3(1+\cos\phi)}{2\pi\nu(1-\cos\phi)}\right)^{3/2} \frac{MC_0}{fNdl^3}$$

The molecular weight of the repeat unit is denoted by M, initial molar concentration of the monomer by C_0, chemical functionality by f, Avogradro's number by N, density by d, the valence angle by ϕ, and the number of atoms in the smallest ring by ν. Stepto and Waywell[18] observed the fraction of rings as a function of conversion for a polyurethane polymerized from bifunctional monomers. Gordon and Temple[19] analyzed these data using chemical reaction methodology. Intermolecular reactions were first order with respect to the molar concentration of each reactant (second order overall) and were proportional to the product of the chemical functionality on each reactant. Intramolecular reaction rate expressions for a ring of size $i\nu$ equaled $k_\sigma/(k_\alpha(\nu i)^{3/2})L_i$. Degree of polymerization of the cyclic chain is i. The molar concentration of the linear reactant is L_i.

Subject to an initial ratio of the isocyanate/hydroxyl moieties, the apparent rate constant was observed to be a function of dilution. The authors[19] evaluated the relative rate constant by achieving the best fit of all observations for each experiment. They noted that benzene is a relatively poor thermodynamic solvent. An increase in solvent concentration may cause a corresponding reduction in the dimension l which alters the rate constant's value. Stanford *et al.*[20] also analyzed Stepto and Waywell's data using the Frisch–Kilb modification[21] of the Jacobson–Stockmayer theory for the prediction of gel points. Emphasis of the regression was placed on initial conversion intervals during which time the smallest sized ring was most likely to form. The authors also noted that values for $\phi = 90°$, $l = b$ varied with dilution and suggested that dilution could effect the distribution of ring sizes that form. For linear polymers the variable b is known to

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[†] Caltex Services Corp.

[‡] University of Nebraska.

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increase with molecular weight. This factor would effect theoretical estimates of the number of the larger cyclic chain configurations. The linear polyurethane resins have also been analyzed with cascade theory by Gordon and Temple.[22] Stepto and Waywell[18] also provided an analysis.

Network Chains. In the area of multifunctional monomers, Flory[3] and Stockmayer[4] pioneered theories on gelation. Stockmayer stated that his stochastic solution for random, step-reaction polymerizations satisfied the Smoluchowski equation which can be derived from classic chemical reaction theory, subject to the constraint of intermolecular reactions. The resultant population density distribution yields moment equations that form conditionally convergent, infinite series with increasing conversion. Conditionally convergent series can be rearranged to converge to any limit.[23,24] The difference between two selected limits of convergence for specific rearrangements was interpreted implicitly as being descriptive of the mass of the insoluble gel fraction.[3] In related work, Shy and Eichinger[25] used Monte Carlo algorithms to simulate the polymerization reported by Stanford and Stepto.[26] Their model effectively calculated cyclization and gel points in bulk cures. The agreement was less than satisfactory with dilute reactions.

Competing intermolecular and intramolecular reactions have been explicitly addressed. Temple[27] incorporated Gaussian chain statistics into intramolecular rate expressions. The relative rate expression for a specific nonlinear molecule becomes a complex function of degree of polymerization, taking the form $k_\sigma/k_\alpha\Sigma_i No_i/(\nu i)^{3/2}P_j$. The number of ways that a ring of degree of polymerization i can form, given a specific chain configuration, is represented by No_i. The molar concentration of this chemical isomer is denoted by P_j. Since the variable No_i is a function of chain configuration for molecules of a specified chemical composition, the molar concentrations of all possible chemical isomers must be calculated. The summation accounts for competing ring closures of different dimensions.

Noureddini and Timm[28] continued the development of reaction models that explicitly incorporate intramolecular reactions and sought analytical solutions for the polymerization of the multifunctional monomer $RA_{f/2}B_{f/2}$. To achieve this goal the rate expression for intramoelcular reactions had to be simplified. In Semlyen's publication,[5] data for linear/cyclic molecules are presented which show that the smallest ring formed dominates the molar concentration of cyclic molecules. Similar observations have been reported by Billmeyer[29] for hydroxyl acid and amino acid polymers. A five-member ring forms lactones or lactans exclusively, but monomers with chains containing less than five but more that seven atoms tend to form linear chains. Reactants containing six atoms in their chain form a mixture of cyclic and linear chains. Odian,[30] in discussing the formation of branches in low-density polyethylene, also stated similar conclusions. Intramolecular chain-transfer reactions produce the low molecular weight branches. The predominant n-butyl branch as well as the 2-ethylhexyl and 1,3-diethyl branches form from six-member transition states. If a proton is extracted from the sixth or seventh methylene group, n-amyl and n-hexyl branches form. A representative low-density polyethylene molecule contains five n-butyl branches and one or two each of the other branches per 500 monomer units. Subject to these observations, Noureddini and Timm[28] assumed that a specific functional group on a network molecule with relatively flexible chains will most likely react with a neighboring moiety in forming a cyclic ring configuration. The frequency of collisions between reaction sites on molecules of a specific composition may be proportional to the limiting chemical functionality. The molar concentration of the reactant accounts for parallel reactions. This assumption is a first approximation of the Jacobson–Stockmayer theory and has been mentioned by Stepto.[21] The assumption greatly reduces the dimensions of the mathematical description by allowing chemical isomers to be lumped into the dependent variable. Analytical solutions were derived for population density distributions and moments of the distribution. When data only descriptive of the moments are to be analyzed, the moment equations can be solved independently of the population density distribution dynamics which further reduces the dimensions of the problem.

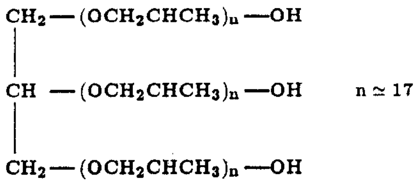

Figure 1. Niax triol a propylene oxide adduct of glycerol.

The present work tests the validity of this simplified rate expression for intramolecular reactions by examining experimental data. Stanford and Stepto[26] reported data for a polyurethane resin comprised of flexible chains. Intramolecular reactions competed with intermolecular reactions at the earliest stages of cure. The current work shows that numerical simulations accurately predict the experimentally observed extent of cyclization as a function of conversion and gel points. Experimental variants include the initial ratio of chemical equivalents and the mass fraction of resin in solution. The analysis further relates the measured relative rate constants to fundamental parameters of the Jacobson–Stockmayer theory as modified by Temple.[27]

The validity of the approximate rate expression was further tested by comparing numerically generated polymerization dynamics. Temple's work[27] incorporated Gaussian chain statistics explicitly in network forming polymerizations. The current model satisfactorily replicates his simulations, showing that the simplified rate expression is adequate. Constrained to intermolecular reactions, numerically calculated population density distributions also replicate Stockmayer's analytical solutions.[31]

Experimental Section

Stanford and Stepto[26] polymerized hexamethylene diisocyanate and a propylene oxide adduct of ethylene glycol, Niax Triol (LG56) manufactured by Union Carbide Corporation. The triol, see Figure 1, had a molecular weight of approximately 3000. The average degree of polymerization of a branch was approximately 17. The three hydroxyls experienced equal reactivity since the size of a branch is sufficiently large to negate first-shell substitution effects.[22] The present notation considers all molecules that contain at least one triol unit to be polymeric. The diisocyanate is the monomer. Polymers were prepared with an initial ratio of isocyanate equivalence to hydroxyl equivalence in the range of $^{1}/_{1.5}$ to $^{1.5}/_{1}$. Formulations were prepared in the bulk and in the presence of a solvent, benzene. Dilution encourages cyclization by reducing the rate for intermolecular reactions relative to the rate for intramolecular reactions. The fraction of resin ranged from 100% to 30%. No catalyst was present. Cures were at 70 °C. Experimentally, the number average molecular weight and the concentration of isocyanates were determined. From these data the number of intramolecular bonds within the resin was determined as a function of conversion. The gel point was determined as that conversion when the resin began to climb the shaft of the mixer. Specific details descriptive of the experiments and measurements can be found in the cited literature[26] and its references.

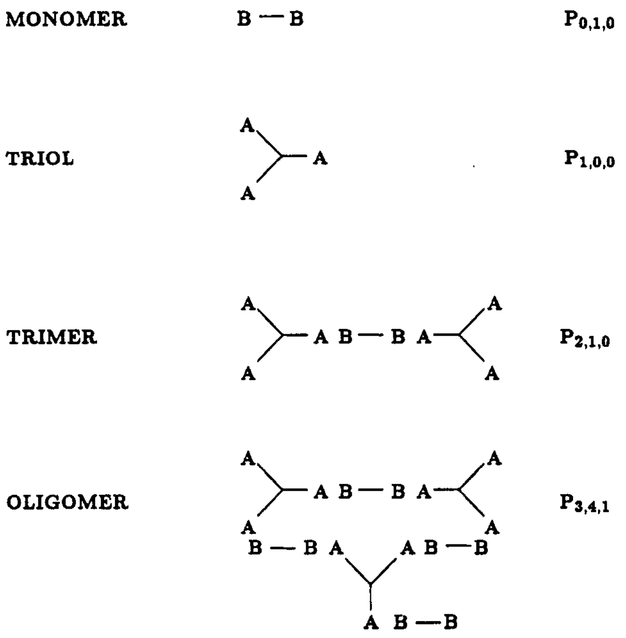

Figure 2. Examples of monomer and oligomeric molecules.

Notation

Stockmayer[31] considered random intermolecular polymerizations of mixtures of monomers A_1, A_2, ..., A_i, ..., having functionalities f_1, f_2, ..., f_i, ..., with monomers B_1, B_2, ..., B_i, ..., having functionalities g_1, g_2, ..., g_i, ..., respectively. The dependent variable $N\{m_i, n_i\}$ represented the molar concentration of molecules consisting of m_1, m_2, ..., m_i, ... residuals of monomers of type A and n_1, n_2, ..., n_i, ... units of monomers of type B. Fukui and Yamabe[32] addressed intermolecular homopolymerization of epoxides of functionality f. The population density distribution was described by $M_{p,\nu}$. The number of epoxy monomer links in the polyether was represented by p and the number of branches on the macromolecule was described by ν. Gordon and Temple[19] considered an RA_2 and an RB_2 resin and described molecules according to the functionality of terminal ends. Molecules containing two A moieties were labeled A_i; molecules containing two B moieties were indicated by B_i. Degree of polymerization i indicated the number of A type links and B type links in these chains, respectively. Linear-chain molecules that contained both chemical moieties were labeled L_i. Inert ringed-chains were labeled R_i. Degree of polymerization represented the number of A or B links in both of these configurations. Temple,[27] in addressing network forming polymerizations, simply numbered each molecule and provided a key for identification.

The current work[23,33] incorporates the notations of Stockmayer, Fukui, and Yamabe and Temple. The population density distribution variable is represented by $P_{i_A,i_B,j}$. The number of chain links from the RA_3 triol is i_A and the number of RB_2 diisocyanate units is i_B. The number of intramolecular links in the molecule is described by the third independent variable j. A fourth independent variable, time, is implicit in the notation. Representative oligomers are presented by Figure 2. Numerical programs[23,33] incorporate the compact vector notation suggested by Temple. Program listings will be supplied on request.

Polyurethane Chemistry

Chemical Functionality. The number of hydroxyl moieties $A_{i_A,i_B,j}$ on a molecule $P_{i_A,i_B,j}$ is a linear combination of the independent variables. Initially the i_A monomers contained three i_A groups. A minimum of $(i_A - 1)$ diisocyanate links are required to join the i_A triols into a molecule. Each link consumed two hydroxyls. The remaining isocyanates $i_B - (i_A - 1)$ are pendent to the chains, being connected to the molecule's infrastructure via a single bond unless they formed one of the j intramolecular links. Algebra yields the hydroxyl functionality:

$$A_{i_A,i_B,j} = 2i_A - i_B - j + 1 \tag{1}$$

Analogous logic yields the isocyanate functionality:

$$B_{i_A,i_B,j} = i_B - i_A - j + 1 \tag{2}$$

Bonding Constraints. Stoichiometry considerations place bounds on the degree of polymerization variables. A minimum number of diisocyanate links, $i_A - 1$, are required to connect i_A triols. The maximum number of diisocyanate residues occurs when all of the hydroxyls on a molecule in the set $P_{i_A,i_B,j}$ have reacted by intermolecular additions, $A_{i_A,i_B,0} = 0$. Therefore

$$i_A - 1 \le i_B \le 2i_A + 1$$

A molecule can have a minimum of zero intramolecular links. The maximum number of intramolecular bonds occurs when all moieties of the limiting functional group have reacted. This upper limit, given specific permissible values for i_A and i_B, is the minimum of eqs 1 and 2, subject to $j = 0$

$$0 \le j \le \min\{A_{i_A,i_B,0};B_{i_A,i_B,0}\}$$

Monomer $P_{0,1,0}$ does not satisfy bonding constraints and, therefore, it is explicitly identified.

Reaction Kinetics

Intermolecular rate expressions assume that the first reactant supplied an isocyanate and that the second reactant provided a hydroxyl in forming the urethane bond. Traditionally, monomer–polymer reactions are called propagation reactions and polymer–polymer reactions are called polyaddition reactions: Intermolecular Reactions

Propagation: $P_{0,1,0} + P_{i_A,i_B-1,j} \rightarrow P_{i_A,i_B,j}$

Polyaddition: $P_{l_A,l_B,m} + P_{i_A-l_A,i_B-l_B,j-m} \rightarrow P_{i_A,i_B,j}$

Each reactant and product must satisfy bonding constraints. A second-order rate expression is consistent with collision theory and experimental analyses.[18,19] The rate expression is

$$\text{rate}_{\text{inter}} = k_1 B_{l_A,l_B,m} P_{l_A,l_B,m} A_{i_A-l_A,i_B-l_B,j-m} P_{i_A-l_A,i_B-l_B,j-m}$$

The notation $\sum_{l_A}\sum_{l_B}\sum_m$ will be used to describe molecules capable of forming $P_{i_A,i_B,j}$. Mathematically it is convenient to exclude monomers from such sums.

Intramolecular reactions are a consequence of collisions of functional groups on a specific molecule: Intramolecular Reactions

$$P_{i_A,i_B,j-1} \rightarrow P_{i_A,i_B,j}$$

The rate of reaction was defined as

$$\text{rate}_{\text{intra}} = k_2 \min\{A_{i_A,i_B,j-1};B_{i_A,i_B,j-1}\}P_{i_A,i_B,j-1} = k_2 C_{i_A,i_B,j-1} P_{i_A,i_B,j-1}$$

The minimum number of functional sites on the reactant is represented by the variable $C_{i_A,i_B,j-1}$. Experimental observations show that the smallest ring that can form dominates chain cyclization reactions. The frequency of fruitful collisions of one functional group with neighbors consisting of the second functional group is expected to be proportional to the number of limiting functional groups. The molar concentration factor accounts for parallel reactions occurring on similar molecules.

Polymerization Dynamics

Monomer Concentration. The diisocyanate's molar concentration is expected to decay according to second-order, intermolecular reaction kinetics:

$$\mathrm{d}P_{0,1,0}/\mathrm{d}t = -k_1 2P_{0,1,0}\sum_{i_A}\sum_{i_B}\sum_{j}A_{i_A,i_B,j}\,P_{i_A,i_B,j} \qquad (3)$$

$$P_{0,1,0}(0) > 0$$

The rate constant is k_1. The factor 2 represents the two isocyanate moieties on the monomer. Each has an equal chance to react with any hydroxyl group in the resin. The summation represents the resin's hydroxyl equivalents, including that of the triol. The initial condition is $P_{0,1,0}(0)$. The dimensions of eq 3 are (moles/liter)/time.

Population Density Distributions. The molar concentration of the oligomeric triol is represented by the relationship

$$\mathrm{d}P_{1,0,0}/\mathrm{d}t = -k_1\Big(\sum_{i_A}\sum_{i_B}\sum_{j}B_{i_A,i_B,j}P_{i_A,i_B,j} + 2P_{0,1,0}\Big)3P_{1,0,0} \qquad (4)$$

$$P_{1,0,0}(0) > 0$$

All isocyanate groups on polymeric and monomeric molecules are equally likely to react with the three hydroxyls on the coreactant, $P_{1,0,0}$. The initial condition is $P_{1,0,0}(0)$.

A general relationship for a molecule $P_{i_A,i_B,j}$ is of the form

$$\begin{aligned}\mathrm{d}P_{i_A,i_B,j}/\mathrm{d}t = {}& -k_1\Big(\sum_{i_A}\sum_{i_B}\sum_{j}B_{i_A,i_B,j}P_{i_A,i_B,j} + \\ & 2P_{0,1,0}\Big)A_{i_A,i_B,j}P_{i_A,i_B,j} - \\ & k_1B_{i_A,i_B,j}P_{i_A,i_B,j}\sum_{i_A}\sum_{i_B}\sum_{j}A_{i_A,i_B,j}P_{i_A,i_B,j} + \\ & k_1 2P_{0,1,0}A_{i_A,i_B-1,j}P_{i_A,i_B-1,j} + \\ & k_1\sum_{l_A}\sum_{l_B}\sum_{m}B_{l_A,l_B,m}P_{l_A,l_B,m}A_{i_A-l_A,i_B-l_B,j-m}P_{i_A-l_A,i_B-l_B,j-m} - \\ & k_2C_{i_A,i_B,j}P_{i_A,i_B,j} + k_2C_{i_A,i_B,j-1}P_{i_A,i_B,j-1} \end{aligned} \qquad (5)$$

$$P_{i_A,i_B,j}(0) = 0$$

The initial two intermolecular rate expressions account for reactions when the reactant $P_{i_A,i_B,j}$ contributes a hydroxyl or an isocyanate, respectively, to the formation of urethane bonds. The third and fourth rate expressions describe all possible intermolecular formation reactions involving two smaller reactants. In the third expression monomer reacts to form $P_{i_A,i_B,j}$ by supplying an isocyanate site and in the fourth all possible polyaddition reactions form $P_{i_A,i_B,j}$. The final two rate expressions describe intramolecular reactions. Reactants must satisfy bonding constraints. Initial conditions for polymeric molecules are zero except for the triol; see eq 4.

Moments of the Population Density Distribution

Equations descriptive of polymerization dynamics require that the zero- and first-order moments be evaluated as a function of time. For example, the isocyanate equivalents equals

$$\begin{aligned}\sum_{i_A}\sum_{i_B}\sum_{j}B_{i_A,i_B,j}P_{i_A,i_B,j} = {}& \sum_{i_A}\sum_{i_B}\sum_{j}i_B P_{i_A,i_B,j} - \\ & \sum_{i_A}\sum_{i_B}\sum_{j}i_A\,P_{i_A,i_B,j} - \sum_{i_A}\sum_{i_B}\sum_{j}jP_{i_A,i_B,j} + \sum_{i_A}\sum_{i_B}\sum_{j}P_{i_A,i_B,j}\end{aligned}$$

Expressions for moments were derived from the weighed differential equations which describe population density distribution dynamics, eqs 4 and 5. The zero-order moment represents the cumulative number concentration of polymeric molecules and changes with time due to intermolecular reactions:

$$\begin{aligned}\mathrm{d}\sum_{i_A}\sum_{i_B}\sum_{j}P_{i_A,i_B,j}/\mathrm{d}t = {}& - \\ & k_1\sum_{i_A}\sum_{i_B}\sum_{j}B_{i_A,i_B,j}P_{i_A,i_B,j}\sum_{i_A}\sum_{i_B}\sum_{j}A_{i_A,i_B,j}P_{i_A,i_B,j}\end{aligned} \qquad (6)$$

$$\sum_{i_A}\sum_{i_B}\sum_{j}P_{i_A,i_B,j}(0) = P_{1,0,0}(0)$$

Inspection of this equation shows that each polymeric isocyanate has an equal probability of reacting with every alcohol in the resin. Initially, the moment equals the concentration of the triol, $P_{1,0,0}(0)$.

The number of triol links in the resin is invariant since the notation assigns the Niax to be a polymeric molecule:

$$\mathrm{d}\sum_{i_A}\sum_{i_B}\sum_{j}i_A P_{i_A,i_B,j}/\mathrm{d}t = 0 \qquad (7)$$

$$\sum_{i_A}\sum_{i_B}\sum_{j}i_A P_{i_A,i_B,j}(0) = P_{1,0,0}(0)$$

On the other hand, the number of diisocyanate residues in the polymer fraction increases due to propagation kinetics:

$$\mathrm{d}\sum_{i_A}\sum_{i_B}\sum_{j}i_B P_{i_A,i_B,j}/\mathrm{d}t = k_1 2P_{0,1,0}\sum_{i_A}\sum_{i_B}\sum_{j}A_{i_A,i_B,j}P_{i_A,i_B,j} \qquad (8)$$

$$\sum_{i_A}\sum_{i_B}\sum_{j}i_B P_{i_A,i_B,j}(0) = 0$$

Equations 6–8 are consistent with basic principles associated with stoichiometry in a closed system.

Integration of several of the moment expressions yields simple solutions. For example, the number of triol links in the resin is readily obtained from eq 7:

$$\sum_{i_A}\sum_{i_B}\sum_{j}i_A P_{i_A,i_B,j} = P_{1,0,0}(0) \qquad (9)$$

Equation 3 was used in deriving eq 10 from eq 8. The number of isocyanate links in the resin is equivalent to the monomer reacted:

$$\sum_{i_A}\sum_{i_B}\sum_{j}i_B P_{i_A,i_B,j} = P_{0,1,0}(0) - P_{0,1,0} \qquad (10)$$

Moments associated with intramolecular bonds are complex due to the form of the intramolecular rate expression. The number of cycles in the resin is dependent on the nonlinear rate expression for intramolecular reactions:

$$\frac{\mathrm{d}\sum_{i_A}\sum_{i_B}\sum_{j} jP_{i_A,i_B,j}}{\mathrm{d}t} = k_2\sum_{i_A}\sum_{i_B}\sum_{j} C_{i_A,i_B,j}P_{i_A,i_B,j} \tag{11}$$

$$\sum_{i_A}\sum_{i_B}\sum_{j} jP_{i_A,i_B,j}(0) = 0$$

Numerically, the right-hand side of eq 11 was evaluated by addition of the weighted population density distributions. The Runge–Kutta algorithm was then used to perform the numerical integration.

Conversion. Conversion or extent of reaction is a function of the lower order moments. The extent of reaction for the hydroxyl is represented by ρ_A and the extent of reaction for the isocyanate is ρ_B. The difference between the number of functional sites initially present and those currently present represents the number of each moiety reacted. Extents of reaction equal

$$\rho_A = \frac{3P_{1,0,0}(0) - \sum_{i_A}\sum_{i_B}\sum_{j} A_{i_A,i_B,j}P_{i_A,i_B,j}}{3P_{1,0,0}(0)}$$

$$\rho_B = \frac{2P_{0,1,0}(0) - \sum_{i_A}\sum_{i_B}\sum_{j} B_{i_A,i_B,j}P_{i_A,i_B,j} - 2P_{0,1,0}}{2P_{0,1,0}(0)}$$

The ratio of the initial chemical equivalents formulated is represented by r:

$$\frac{\rho_A}{\rho_B} = \frac{2P_{0,1,0}(0)}{3P_{1,0,0}(0)} = r$$

Number Average Molecular Weight. The number average molecular weight was selected by Stanford and Stepto[26] to measure intermolecular reactions:

$$\mathrm{MW}_n = \frac{\sum_{i_A}\sum_{i_B}\sum_{j} \mathrm{mass}_{i_A,i_B,j}}{\sum_{i_A}\sum_{i_B}\sum_{j} \mathrm{moles}_{i_A,i_B,j}} = \frac{\mathrm{MW}_A P_{1,0,0}(0) + \mathrm{MW}_B P_{0,1,0}(0)}{\sum_{i_A}\sum_{i_B}\sum_{j} P_{i_A,i_B,j} + P_{0,1,0}} \tag{12}$$

Results

Analytical Solutions. Numerical results were initially compared with analytical solutions developed by Stockmayer,[31] subject to a bifunctional and a tetrafunctional reactant:

$$m_1 = i_A, \qquad n_1 = i_B, \qquad m_j = n_j = 0 \text{ for } j > 1$$

$$f_1 = \mathrm{A}_{1,0,0} = 4, \qquad g_1 = \mathrm{B}_{0,1,0} = 2$$

$$N(m_1,n_1) = P_{i_A,i_B,0}$$

$$N(i_A,i_B) = \frac{(3i_A)!\,i_B!}{(3i_A - i_B + 1)!\,(i_B - i_A + 1)!} \times \frac{4P_{1,0,0}(0)(1-\rho_A)^2}{\rho_A}\,\frac{(\rho_A(1-\rho_A))^{i_A}}{i_A!}\,\frac{\rho_A^{i_B}}{i_B!} \tag{13}$$

Initial conditions were

$$P_{1,0,0}(0) = P_{0,1,0}(0)/2$$

Stockmayer's equations are constrained to intermolecular reactions; therefore, the rate constant for intramolecular reactions k_2 was set to zero. Analytical and numerical population density distributions as a function of conversion are tabulated in Table I for selected molecules. The numerical solution converged to the analytical solution. Although the current paper presents the theory for a specific resin, Noureddini[23] generalized the equations for two reactants of any functionality. Liu[33] used his program for this comparison.

Table I. Comparison of Population Density Distributions

t	i_A	i_B	$P_{i_A,i_B,0}$[a]	$N(m_1,n_1)$[b]
0.1	2	2	9.33E–03	9.30E–03
	3	5	1.38E–04	1.40E–04
	4	6	2.05E–05	2.11E–05
	5	5	5.95E–06	6.07E–06
0.2	2	2	1.86E–02	1.86E–02
	3	5	1.77E–03	1.77E–03
	4	6	5.79E–04	5.79E–04
	5	5	1.22E–04	1.22E–04
0.3	2	2	1.89E–02	1.89E–02
	3	5	4.08E–03	4.08E–03
	4	6	1.76E–03	1.76E–03
	5	5	2.85E–04	2.85E–04
0.4	2	2	1.55E–02	1.55E–02
	3	5	5.22E–03	5.22E–03
	4	6	2.50E–03	2.50E–03
	5	5	3.19E–04	3.19E–04

[a] $P_{iA,iB,0}$, Liu,[29] $\mathrm{A}_{1,0,0} = 4$, $\mathrm{B}_{0,1,0} = 2$, $k_1 = 1$, $k_2 = 0$, $r = 1$. [b] $N(m_1,n_1)$, Stockmayer,[27] $f_1 = 4$, $g_1 = 2$, $r = 1$, $m_1 = i_A$, $n_1 = i_B$.

Noureddini[23] and Liu[33] developed FORTRAN codes to initially write the first-order differential equations for each permissible $P_{i_A,i_B,j}$, see eq 5, up to a maximum selected degree of polymerization $i_{A\,\max}$ and then to solve for the dynamics of the polymerization using a fourth-order Runge–Kutta algorithm.[34] Liu[33] used a compact vector notation suggested by Temple[27] to represent moment equations and population density distribution equations. Each moment and each population density variable were assigned to one element of the vector. A total of 619 simultaneous differential equations were solved when $i_{A\,\max} = 15$. Ten of these equations defined moments and one equation calculated monomer dynamics. Second-order moments appear in the Appendix. A prime consideration in selecting the value for $i_{A\,\max}$ was the convergence properties of the several truncated moments evaluated by addition at the critical conversion. The minimum sized molecule with 15 triol links has a molecular weight of nearly 50 000. For a point of reference, when the weight average molecular weight has reached its asymptotic limit with respect to gelation, the number average degree of polymerization was between 4000 and 10 000. Only two to three triols had contributed to the formation of an average molecule.

Cyclization. Stanford and Stepto[26] stated that the number of isocyanate groups consumed equals the number of molecules lost via intermolecular reactions plus the functionalities consumed by intramolecular reactions. Intermolecular reactions include polyaddition reactions and propagation reactions. Each polyaddition reaction results in the loss of one polymeric molecule. Each propagation reaction results in the loss of one monomeric molecule. Therefore, their statement is mathematically equivalent to

$$2P_{0,1,0}(0)\rho_B = \Big(P_{1,0,0}(0) - \sum_{i_A}\sum_{i_B}\sum_{j} P_{i_A,i_B,j} + P_{0,1,0}(0) - P_{0,1,0}\Big) + \sum_{i_A}\sum_{i_B}\sum_{j} jP_{i_A,i_B,j}$$

The authors also defined the number fraction of ring structures N_r:

$$N_r = \frac{\sum_{i_A}\sum_{i_B}\sum_{j} jP_{i_A,i_B,j}}{\sum_{i_A}\sum_{i_B}\sum_{j} P_{i_A,i_B,j} + P_{0,1,0}}$$

The variable N_r is equivalent to the average number of intramolecular bonds per molecule. Algebraic manipu-

Table II. Formulation Conditions and Results

initial $[-NCO]_0/[-OH]_0$ r	solvent %	$[-NCO]_0$ equiv per kg	relative rate constant k_2/k_1	conversion at gelation of limiting functionality		
				expt[25]	eq 15	eq 16
0.99	0	0.9173	0.175	0.765	0.707	0.771
1.00	50	0.4490	0.30	0.799	0.707	0.871
1.00	70	0.2738	1.00	0.831	0.707	0.940
1/1.50	0	0.9375	0.15	0.925	0.866	0.936
1/1.50	30	0.6352	0.175	0.946	0.866	0.971
1/1.50	60	0.3750	0.20		0.866	0.987
1.50/1	0	0.8797	0.18	0.945	0.866	0.936
1.50/1	50	0.4392	0.25		0.866	0.995
1.50/1	70	0.4065	1.00		0.866	>1.00

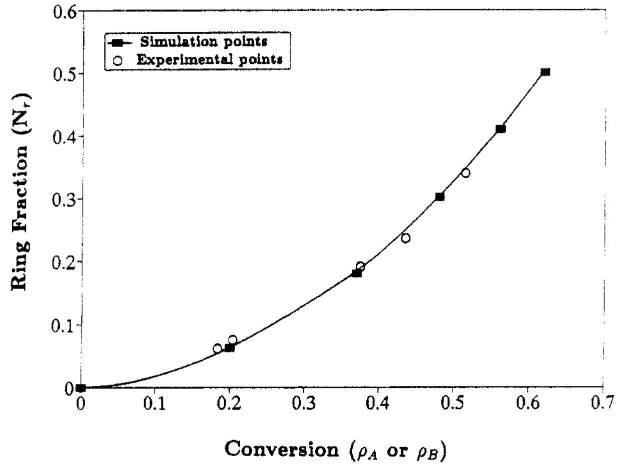

Figure 3. Number fraction of ring structures as a function of conversion (r = 1, k_2/k_1 = 1, 70% solvent).

lation allows this variable to be expressed explicitly as a function of the formulation parameter r, conversion ρ_B, and the number average molecular weight MW_n:

$$N_r = 1 - \frac{(1 + 2/(3r) - 2\rho_B)MW_n}{MW_B + 2MW_A/(3r)} \qquad (14)$$

Conversion was determined experimentally by titration of the isocyanate and the number average molecular weight was determined from cryoscopic measurements.[26]

Initial conditions appear in Table II. The relative rate constant k_2/k_1 was adjusted until the simulation visually fit the data. This ratio results in the independent variable k_1t in the numerical program. Illustrative results appear in Figures 3–5 and represent the average number of intramolecular bonds per molecule, N_r, as a function of conversion of the limiting functional site. Data in Figure 3 were constrained to a polymerization with equal chemical equivalents of hydroxyl and isocyanate moieties, r = 1. The formulation included 30% resin and 70% solvent. Agreement between theoretical and experimental data was realized when the relative rate constant was unity. Data of Figure 4 present similar results when excess hydroxyl moieties were present, r = 1/1.5. The solvent fraction was 30%. Figure 5 shows representative results with an excess of isocyanate moieties, r = 1.5/1. The solvent fraction was 70%.

Rate Constants. Calculated relative rate constants for several experiments are presented in Table II. The relative rate constant is a function of dilution and is tabulated for the three sets of data at r = 1, 1/1.5, and 1.5/1, respectively. The data reveal that the dependency in the relative rate constant when r = 1 and r = 1.5/1 is similar. With 70% solvent the rate constant has increased approximately 6-fold compared to bulk polymerization data. Gordon and Temple[22] and Stepto[21] reported similar trends for a linear polyurethane. The relative rate constant doubled as the solution became dilute. The network resin experienced a greater number of rings and a greater dependency on solvent concentration.

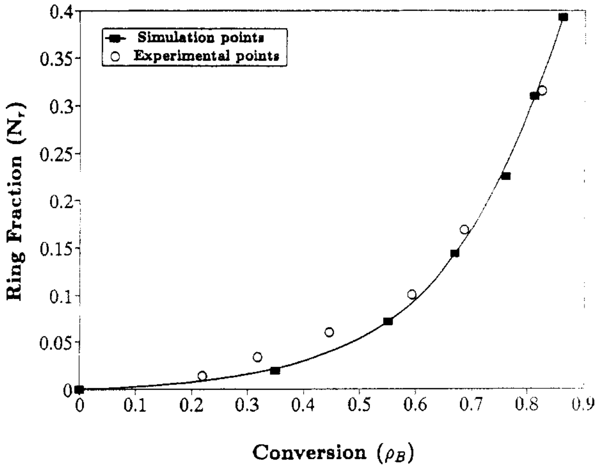

Figure 4. Number fraction of ring structures as a function of conversion of the limiting reactant (r = 1/1.5, k_2/k_1 = 0.15, 30% solvent).

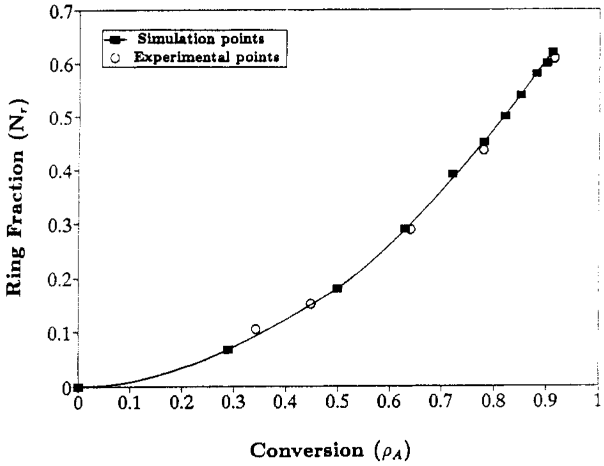

Figure 5. Number fraction of ring structures as a function of conversion of the limiting reactant (r = 1.5, k_2/k_1 = 1, 70% solvent).

The data tabulated in Table II indicate when hydroxyl groups are in excess, r = 1/1.5, the relative rate constant is considerably less sensitive to solvent concentration. Gordon and Temple[19] observed similar findings for the linear polyurethane and stated that in a hydroxyl-rich environment, the "shielding of the –OH groups by H-bonding might well affect differently the rate of their intramolecular and intermolecular reactions".

Mean Bond Lengths. The Jacobson–Stockmayer theory can be interpreted, yielding the mean bond length b. The form for the intramolecular rate expression is a first approximation of the rate expression representing Gaussian chain statistics described by Temple.[27] If $No_i \approx C_{i_A,i_B j}$ and if the series in Temple's work is truncated after the initial term, i = 1, then the relative rate constants are approximately equal, $k_2/k_1 \simeq (k_\sigma/k_\alpha)/(\nu)^{3/2}$. The relative rate constants tabulated in Table II yield a range in bond dimensions b of 0.13–0.07 nm. Stepto[21] reported a value of 0.16 nm. First approximations associated with theory likely contributed to errors, but results are approximate. Results may also indicate that current theory may have to be advanced to accurately predict the rate of cyclization in network resins.

Gelation. Stanford and Stepto[26] measured the critical conversion at the gel point for several of their experiments. These data are tabulated in Table II if the resin gelled. For the case $r = 1$, dilution shifted the critical conversion to larger values, 0.765–0.831. Increased levels in intramolecular bonding reduced functionalities on a reactant and consequently its rate of growth was retarded and the critical conversion increased. Data of Figure 3 show that approximately one out of three molecules contain a cyclic chain configuration at 50% conversion and more than one out of two at 70%. Data in Table II collected with an imbalance in stoichiometry show that the critical conversion is higher due to the substantial imbalance in the concentration of functional groups and due to environmental effects. The critical conversion 0.925 with excess hydroxyls is less than the conversion at gelation for experiments with excess isocyanates, 0.945. This fact is reflected by the values of the relative rate constants, 0.15 and 0.18, respectively.

Stockmayer[31] developed an implicit theory for predicting the gel point. Subject to the constraints of intermolecular reactions, $f_A = 3$ and $f_B = 2$, the critical conversion can be estimated:

$$(\rho_A \rho_B)_{\text{gel}} = 1/2$$

Therefore

$$\rho_{B\,\text{gel}} = (1/(2r))^{0.5} \tag{15}$$

Estimates of the gel point based on this expression appear in Table II under the column labeled "eq 15". The model does not account for functional groups consumed by intramolecular reactions and, therefore, consistently predicts gelation at lower levels of conversion.

The current analysis explicitly addressed gelation. At the gel point the weight average molecular weight becomes infinite:

$$\mathrm{MW}_w = \frac{\sum_{i_A}\sum_{i_B}\sum_{j}\mathrm{MW}_{i_A,i_B,j}\,\mathrm{mass}_{i_A,i_B,j}}{\sum_{i_A}\sum_{i_B}\sum_{j}\mathrm{mass}_{i_A,i_B,j}} = \frac{\sum_{i_A}\sum_{i_B}\sum_{j}(\mathrm{MW}_A i_A + \mathrm{MW}_B i_B)^2 P_{i_A,i_B,j} + \mathrm{MW}_B{}^2\, P_{0,1,0}}{\mathrm{MW}_A P_{1,0,0}(0) + \mathrm{MW}_B P_{0,1,0}(0)} \tag{16}$$

The molecular weights of the two monomers are denoted by MW_A and MW_B. The set of differential equations that describe second-order moments appear in the Appendix. Illustrative, numerical results are presented in Figure 6, a graph of the number average and weight average molecular weight as a function of conversion of the limiting functional group. The asymptotic limit in the weight average molecular weight was used to approximate the critical conversion. Results tabulated in Table II in the column labeled "eq 16" were based on the tabulated rate constants and show that gel point predictions can be within 1 or 2% of the experimental points. When $r = 1.0$ and 50% and 70% solvent was present, the prediction experienced a greater error. These results were effected adversely by extrapolations. The data set used in determining the relative rate constant with 70% solvent stopped at 52% conversion, but gelation occurred at a conversion of 0.831; see Figure 3. The extrapolation to gelation resulted in a greater uncertainty, $\rho_A = 0.940$. But even with this difficulty, the maximum error is only 11%.

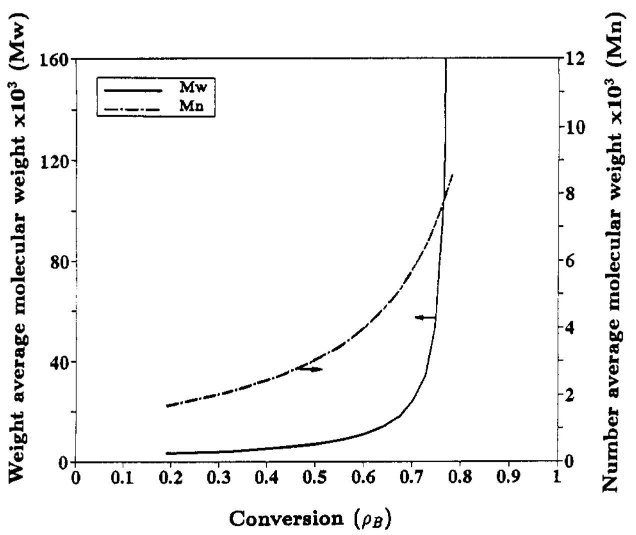

Figure 6. Prediction of gelation ($f_A = 2, f_B = 3, r = 0.989, P_{0,1,0}(0) = 0.454, P_{1,0,0}(0) = 0.306$, 0% solvent).

Three experiments summarized in Table II did not gel. Simulations indicated that two of the experiments would gel close to 100% in conversion, 0.987 and 0.995. For the third experiment, the critical gel point was predicted to exceed 100% and, therefore, one could say with a high level of confidence that gelation would not occur. In summary, the chemical reaction analysis accounted for intramolecular reactions on gelation accurately.

Numerical Simulations. The present research also addressed consequences of the simplified form for the intramolecular rate expression. Temple[27] used a theoretical approach when modeling thermosetting resins. Reaction rate expressions derived for cyclization reactions of linear chains were extended to multifunctional resins. To demonstrate, consider a potential intramolecular reaction on the molecule $P_{3,4,1}$ shown in Figure 2. For simplicity, the chain segments represented by lines and bonds –AB– are assumed to be identical with respect to their atomic structure. Each segment represented by a line is assumed to contain ν atoms. The pendent –B group has an equal chance to react with each of the two –A sites, making ringed chain configurations which contain six chain segments. These candidate intramolecular reactions result in the rate expression

$$-k_\sigma/k_\alpha\left(\frac{2}{(6\nu)^{3/2}}\right)P_{3,4,1}$$

The numerator acknowledges that there are two independent ways to form a ring with six chain segments. The denominator contains the product 6ν which represents the contour length of the ringed chain that could form. The integer is the degree of polymerization for this ring. A more complex molecule will yield a series of reaction rate expressions to represent distinct rings that can form. Each term in this series will be inversely dependent on the degree of polymerization of the specific ring to the three-half power and will be proportional to the number of ways the numerous chemical moieties can react to form it.

Temple[27] addressed the polymerization kinetics associated with a trifunctional and a bifunctional reactant. Numerical calculations included the fraction of all functionalities which reacted intramolecularly σ as a function of all functionalities which reacted intermolecularly α. A balanced stoichiometry was used. These two variables

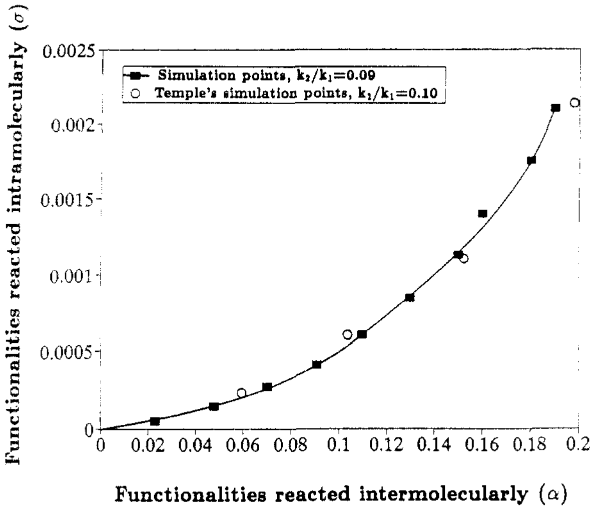

Figure 7. Fraction of functional groups reacted intramolecularly *vs* the fraction of functional groups reacted intermolecularly ($f_A = 2$, $f_B = 3$, $r = 1$).

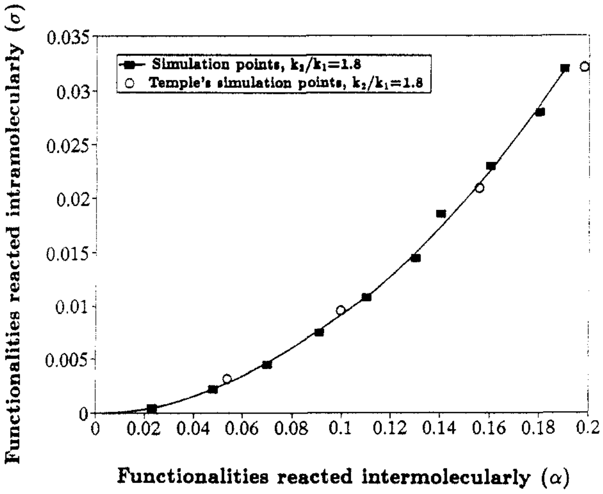

Figure 8. Fraction of functional groups reacted intramolecularly *vs* the fraction of functional groups reacted intermolecularly ($f_A = 2$, $f_B = 3$, $r = 1$).

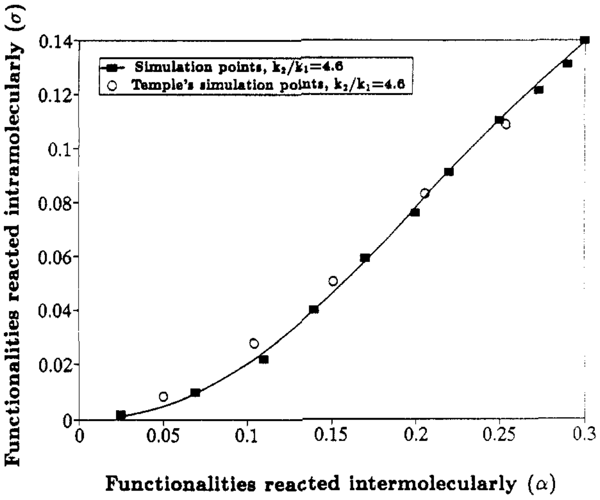

Figure 9. Fraction of functional groups reacted intramolecularly *vs* the fraction of functional groups reacted intermolecularly ($f_A = 2$, $f_B = 3$, $r = 1$).

can be expressed in terms of current notation:

$$\sigma = \frac{\sum_{i_A}\sum_{i_B}\sum_{j} jP_{i_A,i_B,j}}{3P_{1,0,0}(0)}$$

$$\alpha = \frac{2P_{0,1,0}(0) - \sum_{i_A}\sum_{i_B}\sum_{j}(i_B - i_A + 1)P_{i_A,i_B,j}}{2P_{0,1,0}(0)}$$

Simulations were for three values of the relative rate constant and demonstrated dynamic effects of intramolecular reactions.

Liu[33] used the simplified rate expression presented and fit Temple's simulations visually, adjusting the relative rate constant as required. Comparisons of the two numerical simulations appear in Figures 7–9 for the three values of the relative rate constant selected by Temple, $k_2/k_1 = (k_\sigma/k_\alpha)(\nu)^{3/2} = 0.10$, 1.8, and 4.6, respectively. The current model satisfactorily approximates Temple's simulations using the same or nearly the same relative rate constant, 0.09, 1.8, and 4.6, respectively. Therefore, if the prime variables of interest are functions of the leading moments of the distribution, the simplified intramolecular rate expression approach is a satisfactory approximation. A second consideration for selecting the simplified rate expression lies in the area of experimental measurement. The population density distribution variable $P_{i_A,i_B,j}$ can potentially be measured using modern fractionation techniques, but it is very questionable if the numerous isomers of molecules at a specific chemical composition can ever be characterized.

Conclusions

The chemical reaction analysis of the thermosetting resin was successful. The reaction rate expression selected for intramolecular reactions is sufficiently complex to approximate reality in a polyurethane resin up to gelation. The extent of cyclization as a function of conversion correlated data from the literature. The model is sufficiently sensitive to its environment to allow for the determination of the relative rate constant as a function of dilution, a phenomenon which is fundamentally consistent with cyclization theory.

Simulations revealed that the present approach reproduces results of simulations based on fundamental, intramolecular rate expressions developed by Temple.[27] A significant reduction in the dimensions of the numerical program is realized through the approximate rate expression. Temple was able to achieve conversions of only about 0.25 using 150 equations to describe the chemical isomers that contained up to 11 monomer units and three intramolecular bonds. The current model would require only 40 equations. Greater reductions in the dimension of the simulation are achieved as degree of polymerization increases. With an increase of the maximum number of trifunctional monomer units in a molecule to 15, the current work extented the range in conversion to the gel point. The analysis by Noureddini and Timm[28] reveals that for monomers that yield polymeric molecules with the same number of each chemical moiety, similar simulations could be limited to moment equations.

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Appendix

The equations describing the second-order moments are listed in the Appendix. The equations were derived from the weighted, population density distributions, eq 5. Initial conditions equal zero, except for the moment $\sum_{i_A}\sum_{i_B}\sum_j i_A^2 P_{i_A,i_B,j}(0) = P_{1,0,0}(0)$.

$$\mathrm{d}\sum_{i_A}\sum_{i_B}\sum_{j} i_A^2 P_{i_A,i_B,j}/\mathrm{d}t = 2k_1\Big(\sum_{i_A}\sum_{i_B}\sum_{j} i_A B_{i_A,i_B,j} P_{i_A,i_B,j}\Big)\Big(\sum_{i_A}\sum_{i_B}\sum_{j} i_A A_{i_A,i_B,j} P_{i_A,i_B,j}\Big) \tag{A-1}$$

$$\begin{aligned}
&\mathrm{d}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} {i_\mathrm{B}}^2 P_{i_\mathrm{A},i_\mathrm{B},j}/\mathrm{d}t = \\
&2k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) + \\
&\qquad k_1 2P_{0,1,0}\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} (2i_\mathrm{B} + 1) A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) \qquad \text{(A-2)}
\end{aligned}$$

$$\begin{aligned}
&\mathrm{d}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j^2 P_{i_\mathrm{A},i_\mathrm{B},j}/\mathrm{d}t = \\
&\qquad k_2\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} (2j + 1) C_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) + \\
&2k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) \qquad \text{(A-3)}
\end{aligned}$$

$$\begin{aligned}
&\mathrm{d}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} i_\mathrm{B} P_{i_\mathrm{A},i_\mathrm{B},j}/\mathrm{d}t = \\
&\qquad k_1 2P_{0,1,0}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j} + \\
&k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) + \\
&\quad k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) \\
&\qquad \text{(A-4)}
\end{aligned}$$

$$\begin{aligned}
&\mathrm{d}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} j P_{i_\mathrm{A},i_\mathrm{B},j}/\mathrm{d}t = k_2\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} C_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) + \\
&k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) + \\
&k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{A} B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) \qquad \text{(A-5)}
\end{aligned}$$

$$\begin{aligned}
&\mathrm{d}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} P_{i_\mathrm{A},i_\mathrm{B},j}/\mathrm{d}t = \\
&\qquad + k2P_{0,1,0}\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j} + \\
&\qquad k_2\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} C_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j} + \\
&k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) + \\
&k_1\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} i_\mathrm{B} B_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big)\Big(\sum_{i_\mathrm{A}}\sum_{i_\mathrm{B}}\sum_{j} j A_{i_\mathrm{A},i_\mathrm{B},j} P_{i_\mathrm{A},i_\mathrm{B},j}\Big) \qquad \text{(A-6)}
\end{aligned}$$

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