Kinetic Analysis of Competing Intramolecular and Intermolecular Polymerization Reactions

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ABSTRACT: Kinetic reaction theory was used to model a step-growth, thermoset polymerization of a monomer of even functionality f. Intermolecular additions were represented by second-order and intramolecular reactions were expressed by first-order rate expressions. All functional groups were assumed to react with equal reactivity. Independent variables are degree of polymerization i, extent of cross-linking j, and conversion ρ. The normalized rate constant for intramolecular reactions is c. The solution for the normalized population density distribution is

$$p_{i,j} = \frac{f(fi - i - j)![(f-2)i/2]!}{2[(f-2)i - j + 1]![(f-2)i/2 - j + 1]!i!j!} \frac{c^j \rho^{i+j-1}[(1-\rho+c)(1-\rho)]^{[(f-2)i-2j+2]/2}}{(1+c)^{fi/2}}$$

subject to $0 \leq j \leq (f-2)i/2 + 1$ and $c \geq 0$. Formulae for the number-, mass-, and cross-link-average molecular weights were derived.

Introduction

Literature describes polymerization kinetics for multifunctional monomers which utilize statistical methodology. Flory[1] and Stockmayer[2] laid the foundation for theories on gelation. Relationships were developed for population density distribution, mass fraction distribution, and molecular weight averages for the polymerization of the monomer RA_f. The independent variables were the extent of reaction and the degree of polymerization. Chemical reactions were restricted to irreversible, intermolecular additions. Functional groups had equal chemical reactivity. Molecular chain configurations were restricted to branched chains. Gordon,[3] using Good's[4] cascade theory, also evaluated the random polymerization of the f-functional monomer. First-shell substitution effects[5] and intramolecular reactions[6–8] were addressed. Macosko and Miller[9] presented a recursive method for calculating average molecular weights, extending stochastic methods to nonlinear polymerizations with unequal reactivity of functional groups. Dušek[10] applied Gordon's procedure to the curing of epoxy resins. Monte Carlo methods numerically simulate the polymerization process by randomly picking reactants from a population of molecules. Kuchanov and Povolotskaya[11] considered the three-dimensional placement of functional groups in space.

An alternate starting point for analysis is chemical reaction kinetics. Flory,[12] for example, modeled a polymerization comprised only of propagation kinetics, deriving a Poisson molar distribution for linear or starlike molecules. Stackmayer[2] stated that the stochastic solution for the polymerization of the f-functional monomer is also a solution of the Smoluchowski equation. The second-order, chemical reaction rate expression for intermolecular additions contains a kernel that is equal to the product of the chemical functionality of each reactant. Leyvraz[13] stated that if the kernel is a quadratic function of the degree of polymerization, analytical solutions exist. Ziff and Stell,[14] Leyvraz and Tschudi,[15] Stockmayer,[2] and Flory[1] observed that mass is apparently not conserved beyond the critical extent of reaction. The lost mass was described implicitly as the gel fraction. Multiple limits of convergence for each moment of the distribution are a consequence of conditionally convergent, infinite series.[16,17] Ziff[18] expressed conversion explicitly as a function of time.

Ziff and McGrady[19] addressed chemical degradation, subject to random bond scission. Blatz and Tobolsky[20] used chemical reaction methodology in addressing reversible reactions for an ARB polymerization constrained to intermolecular reactions. At large reaction times, a state of chemical equilibrium exists. The degradation mechanism was assumed to incorporate a molecular size dependency. Van Dongen and Ernst[21] incorporated reversible reactions in the analysis of RA_f and A_fRB_g polymerizations. Gelation may or may not occur implicitly, depending on the strength of the reversible kernel with respect to the degree of polymerization.

Solutions are also derived from generating functions. The set of equations describing population density distributions is transformed to an ordinary or partial differential equation. A solution yields the moments of the population density distribution.[22] Kuchanov and Povolotskaya[11] have applied this technique for solving multifunctional macromolecular systems. A solution was obtained for the random, f-functional monomer polymerization. The introduction of intramolecular reactions resulted in a complex partial differential equation which has not yielded an analytical solution.

Numerical solutions have also been formulated. Falk and Thomas[23] used a Monte Carlo algorithm. Reactive groups selected for bond formation were picked according to concentration. Prior to gelation the likelihood of selecting two sites on a single reactant was observed to be very remote. However, after the critical conversion cross-link formation occurred. The algorithm was constrained to intramolecular additions that were independent of chain configurations. A linear or a branched chain had the same probability of forming a cyclic configuration. Gordon and Temple[24] argued that the chain configuration will have a pronounced effect on intramolecular reactions. Equilibrium statistics of ring closure of Gaussian chains predict a dependency of $n^{-3/2}$ where n is the number of atoms or units in the resultant ring. Each of the resulting rate expressions contain a finite series that accounts for the number of rings of size n that can form, subject to a specific chain configuration. Temple,[25] in modeling an alternating copolymer formed from the comonomers RA_2 and RB_3, specifically addressed this effect. For a degree of polym-

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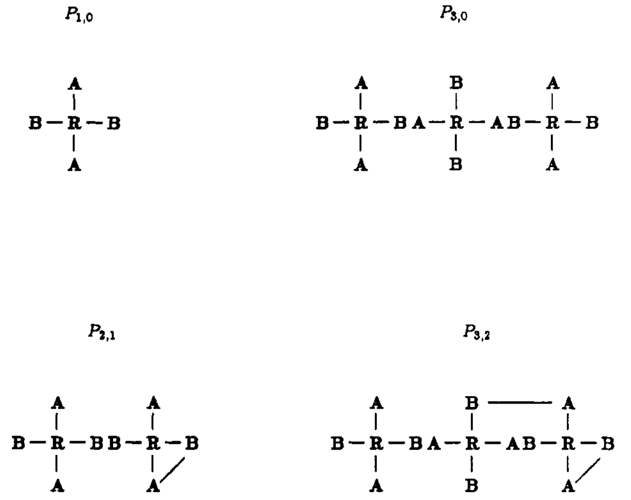

Figure 1. Examples of monomeric and oligomeric molecules, $f = 4$.

erization of 5 for the B-monomer, approximately 150 specific isomers had to be considered. Distinct rate constants were assigned to intermolecular and intramolecular reaction rates.

Fukui and Yamabe[26] addressed a step-growth, polyether polymerization subject to intermolecular reactions. The analysis is quite realistic for the initial stages of polymerization of relatively stiff chains. Two chemical moieties of distinct functionality are present on a molecule. A Poisson-type molar distribution was derived, using classic chemical reaction methodology. The current study utilized an analogous, mathematical formulation to model competing intramolecular and intermolecular reactions explicitly. Solutions for the population density distribution and moments of the distribution were obtained for the f-functional monomer.

Reaction Model and Constraints

The dependent variable $P_{i,j}$ represents the molar concentration of polymer molecules which contain i monomeric units and j cross-links as a function of time or conversion. Examples of multifunctional oligomeric molecules formed from a tetrafunctional monomer, $f = 4$, are presented in Figure 1. To achieve a balanced stoichiometry between functional groups A and B, molecules with $f = 2, 4, 6, \ldots$ are considered.

Intermolecular Reactions. Intermolecular reactions result in chain extension and are represented by the notation

$$P_{k,l} + P_{i-k,j-l} \xrightarrow{K} P_{i,j}$$

Bonding constraints and chemical functionality of the reactants require that

$$i = 2, 3, 4, \ldots$$

$$j = 0, 1, 2, \ldots, (f-2)i/2 + 1$$

$$k = 1, 2, 3, \ldots, i-1$$

$$\max\{0; j - (j-2)(i-k)/2 - 1\} \le l \le \min\{j; (f-2)k/2 + 1\}$$

The notation $\sum_k \sum_l$ implicitly assumes these limits for degree of polymerization k and extent of cross-linking l for formation reactions of molecules $P_{i,j}$. The elementary, second-order reaction rate is

$$\text{rate}_{i,j,\text{inter}} = K f_{k,l} P_{k,l} f_{i-k,j-l} P_{i-k,j-l}$$

The chemical functionality of a molecule $P_{i,j}$ is

$$f_{i,j} = (f-2)i - 2j + 2$$

The rate constant is K; the coefficients define the chemical functionality for each reactant. For the f-functional monomer the concentrations for each moiety are equal on a given molecule; therefore, the rate expression may be written in terms of the total functionality of the reactants. The second-order reaction is a consequence of collision theory. Catalytic effects are incorporated into the rate constant.

Intramolecular Reactions. Intramolecular reactions are a consequence of collisions between functional groups on the same molecule. Bond formation is represented by the reaction

$$P_{i,j-1} \xrightarrow{K'} P_{i,j}$$

The rate constant is K' and

$$i = 1, 2, 3, \ldots$$

$$j = 1, 2, 3, \ldots, (f-2)i/2 + 1$$

The notation $\sum_i \sum_j$ implicitly assumes these limits for moments. Gordon and Temple[24] and Temple[25] selected a first-order rate expression for intramolecular reactions. The current work also assumed a first-order rate expression for the formation of $P_{i,j}$:

$$\text{rate}_{i,j,\text{intra}} = K' f_{i,j-1} P_{i,j-1}$$

Intramolecular reaction rates have not been explicitly studied in the literature. Theoretical arguments indicate that entropy is strongly dependent on chain configurations. Munk[27] stated that the mean end-to-end distance between two functional groups on linear, Gaussian chains contributes $n^{-3/2}$ and ring closure contributes an additional n^{-1}. The rate constant for a specific ring may be dependent on $n^{-5/2}$, where n is the number of atoms in the ring.

Odian[28] discusses the formation of branches in a typical, low-density polyethylene. Intramolecular chain-transfer reactions produce low molecular weight branches. A six-member transition state (consisting of five carbons and one hydrogen) produces the predominant n-butyl branch. The addition of a monomer unit at the n-butyl branch site, coupled with a second intramolecular, backbiting reaction, produces 2-ethylhexyl and 1,3-diethyl branches. If the propagating free radical extracts a hydrogen from the sixth or seventh methylene group, n-amyl and n-hexyl branches form, respectively. A typical polyethylene may contain five n-butyl branches and one or two each of the other branches per 500 monomer units. Six-member intermediates dominate this particular resin's intramolecular reaction mechanism. Large branches also are present but are a consequence of intermolecular reactions. Similar observations are reported for hydroxy acid and amino acid monomers. If the ring contains less than five or greater than seven atoms, a linear polymer forms. A five-member ring forms lactones or lactans exclusively.[29] An example expected to be void of factors directly attributed to isomeric chain configurations is a polyimide.[30] The five-member ring forms from polyamic acids. These examples demonstrate that intramolecular reactions in essentially linear chains are restricted to neighboring sites along the chain.

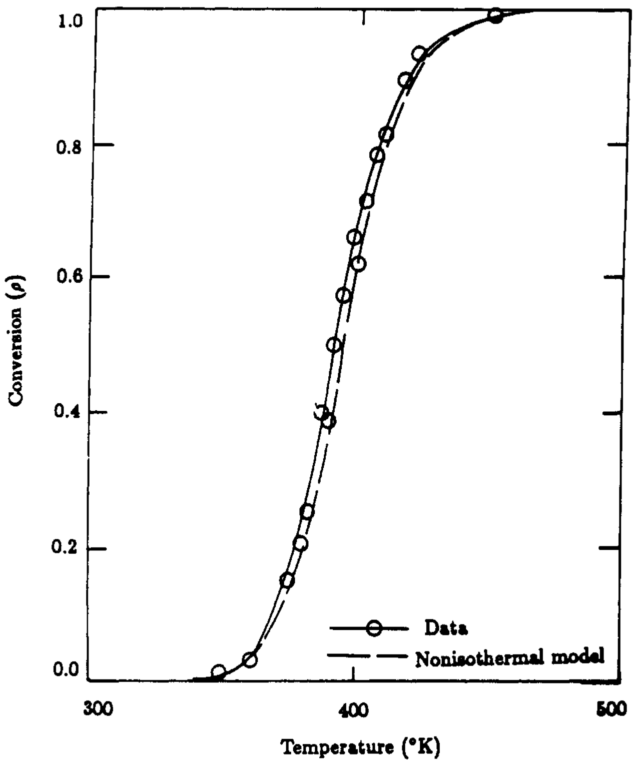

Figure 2. Calculated vs actual degree of cure for a 2 K/min scan by DSC analysis.

Thermosetting resins may experience ring-closure reactions that are independent of chain configurations. Kinetics for the polymerization of diglycidyl ether of Bisphenol F cured with diaminodiphenylmethane using differential scanning calorimetry were evaluated.[31] A least-squares objective function was used to evaluate the parameters of the rate expression

$$\frac{d\rho}{dt} = 5.45 \times 10^5 \exp\left(-\frac{4.9 \times 10^4}{RT}\right)\rho^{0.540}(1-\rho)^{1.363}$$

The reaction is autocatalytic. Time was in minutes, and the activation energy was expressed as joules per mole. An excellent fit was obtained by this expression at all levels of conversion for both isothermal and nonisothermal cures. Data presented by Figure 2 illustrate this. Dušek[10] reported that such stiff-chain monomers initially experience chain extension reactions, as evidence by a glass transition temperature that is independent of dilution. At high conversions intramolecular reactions become prevalent. Since conversion is a function of both intermolecular and intramolecular reactions, one can conclude that the rate for intramolecular bond formation was not a strong function of chain configuration. The coefficient is void of an explicit expression defining chain configuration dependency. A power function seems to be adequate. The nonelementary reaction may be a result of competing reactions. The rate constants for primary and secondary amines may also be distinct.

Conversion. Conversion is proportional to the number of reacted functional groups:

$$\rho = \frac{fP_{1,0}(0) - \sum_i \sum_j f_{i,j} P_{i,j}}{fP_{1,0}(0)} \tag{1}$$

The summation expresses the number of sites not reacted.

Population Density Distribution Dynamics. The reactor was constrained to a batch, isothermal, isometric, well-mixed vessel. Transport processes were limited to chemical reaction rates. Conservation laws generate differential equations describing the molar concentration of each type of molecule. Analysis of the monomer yields

$$\frac{dP_{1,0}}{dt} = -2KfP_{1,0}\sum_i \sum_j f_{i,j}P_{i,j} - K'fP_{1,0}$$

The differential equation characterizing the population density distribution is

$$\begin{aligned}\frac{dP_{i,j}}{dt} = {} & -2Kf_{i,j}P_{i,j}\sum_i \sum_j f_{i,j}P_{i,j} + \\ & K(1-\delta_{1,i})\sum_k \sum_l [f_{k,l}P_{k,l}f_{i-k,j-l}P_{i-k,j-l}] - K'f_{i,j}P_{i,j} + \\ & K'(1-\delta_{0,j})f_{i,j-1}P_{i,j-1}\end{aligned} \tag{2}$$

$$\text{for} \quad i = 1, 2, 3, ... \quad \text{and} \quad 0 \le j \le (f-2)i/2 + 1$$

The first rate expression describes intermolecular reactions of a reactant $P_{i,j}$ with all molecules. The constant 2 is a consequence of the fact that a reactant can supply an A or a B site during bond formation. The second expression represents the cumulative rates of formation of $P_{i,j}$ from intermolecular reactions of two smaller reactants, $P_{k,l}$ and $P_{i-k,j-l}$ for $i > 1$. The third rate expression describes cross-linking or cyclization reactions involving $P_{i,j}$. The last term is the rate of formation of $P_{i,j}$ from the intramolecular reactions of molecules $P_{i,j-1}$. Initial conditions are zero, except for the monomer $P_{1,0}(0)$.

Zero- and First-Order Moments. Moments can be evaluated if the population density distribution equations are weighted by $i^m j^n$ where $m,n = 0, 1, 2, ...$ and then summed. The zero moment $\Sigma_i\Sigma_j P_{i,j}$ equals the cumulative molar concentration of molecules in the system. Intermolecular formation reactions were arranged as $f_{i,j}P_{i,j}\Sigma_i\Sigma_j f_{i,j}P_{i,j}$. Algebra readily yields

$$\frac{d}{dt}\left(\sum_i \sum_j P_{i,j}\right) = -K\left(\sum_i \sum_j f_{i,j}P_{i,j}\right)^2 \tag{3}$$

In the beginning, only monomer is present in the reactor; therefore, the initial condition equals

$$\sum_i \sum_j P_{i,j}(0) = P_{1,0}(0)$$

The first-order moment $\Sigma_i\Sigma_j iP_{i,j}$ equals the total number of monomer units in the system. These appear as unreacted monomer and as repeat units in the molecular chains. If this moment is weighted by the molecular weight of the monomer, the moment equals the cumulative mass in the system. After eq 2 is weighted by the factor i, addition, coupled with algebraic rearrangement, yields

$$\frac{d}{dt}\left(\sum_i \sum_j iP_{i,j}\right) = 0 \tag{4}$$

The initical condition is

$$\sum_i \sum_j iP_{i,j}(0) = P_{1,0}(0)$$

Therefore, mass is invariant:

$$\sum_i \sum_j iP_{i,j} = P_{1,0}(0)$$

The first-order moment $\Sigma_i\Sigma_j jP_{i,j}$ represents the number of cross-links in the resin:

$$\frac{d}{dt}\left(\sum_i \sum_j jP_{i,j}\right) = K'\sum_i \sum_j f_{i,j}P_{i,j} \tag{5}$$

The initial condition equals zero:

$$\sum_i \sum_j j P_{i,j}(0) = 0$$

Time–Conversion Transformation. A change of variables transforms time to conversion space. Equation 1 was first differentiated with respect to time, generating an equation that contained the derivatives of the above three moments. The substitution of eqs 3–5 into this expression, coupled with eq 1, yields the equation

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 2K'(1-\rho) + 2KfP_{1,0}(0)(1-\rho)^2$$

At time zero, conversion equals zero. Separation of variables yields the transformation

$$\mathrm{d}\tau = 2KfP_{1,0}(0)\,\mathrm{d}t = \frac{\mathrm{d}\rho}{(1-\rho)(1-\rho+c)} \tag{6}$$

The denominator defines the cumulative rates for intermolecular and intramolecular reactions in dimensionless space. The dimensionless constant c is a relative rate constant and equals

$$c = K'/KfP_{1,0}(0)$$

Integration results in an implicit expression for conversion as a function of time:

$$\frac{1-\rho+c}{1-\rho} = (1+c)\exp[2cKfP_{1,0}(0)t]$$

Explicit Solutions

Moments. The normalized population density distribution variable is

$$p_{i,j} = P_{i,j}/P_{1,0}(0)$$

The three moment equations were integrated, subject to initial conditions, yielding the relationships

$$\sum_i \sum_j p_{i,j} = 1 - \frac{f}{2}\left[\rho - c\ln\left(\frac{1+c}{1-\rho+c}\right)\right] \tag{7}$$

$$\sum_i \sum_j i p_{i,j} = 1 \tag{8}$$

$$\sum_i \sum_j j p_{i,j} = \frac{cf}{2}\ln\left(\frac{1+c}{1-\rho+c}\right) \tag{9}$$

Number-Average Molecular Weight. The number-average molecular weight equals the mass of the resin divided by the cumulative moles:

$$\mathrm{MW}_\mathrm{n} = \frac{M_0}{1 - f\{\rho - c\ln[(1+c)/(1-\rho+c)]\}/2} \tag{10}$$

The molecular weight of the monomer, M_0, also equals the molecular weight of the repeat unit in the polymer chains. The cross-link-average molecular weight equals the mass of the resin divided by the number of cross-links:

$$\mathrm{MW}_\mathrm{c} = M_0/\left[\frac{cf}{2}\ln\left(\frac{1+c}{1-\rho+c}\right)\right] \tag{11}$$

Population Dynamics. An analytical solution for the population density distribution was derived by induction. Equation 2 was expressed in terms of conversion:

$$\frac{\mathrm{d}p_{i,j}}{\mathrm{d}\rho} + \frac{f_{i,j}}{2}\left(\frac{1}{1-\rho+c} + \frac{1}{1-\rho}\right)p_{i,j} = \frac{(1-\delta_{1,i})}{2f(1-\rho+c)(1-\rho)}\sum_k \sum_l [f_{k,l}p_{k,l}f_{i-k,j-l}p_{i-k,j-l}] + \frac{cf_{i,j-1}}{2(1-\rho+c)(1-\rho)}(1-\delta_{0,j})p_{i,j-1} \tag{12}$$

The equation was solved by an integrating factor, yielding the expression

$$p_{i,j} = C(i,j)\left(\frac{c^j p^{i+j-1}[(1-\rho+c)(1-\rho)]^{[(f-2)i-2j+2]/2}}{(1+c)^{fi/2}}\right)$$

The coefficient function $C(i,j)$ can be evaluated if the preceding equation is substituted into eq 12. A recursive formula develops

$$C(i,j) = \frac{(1-\delta_{0,j})f_{i,j-1}}{2(i+j-1)}C(i,j-1) + \frac{(1-\delta_{1,i})}{2f(i+j-1)}\sum_k \sum_l [f_{k,l}C(k,l)f_{i-k,j-l}C(i-k,j-l)]$$

where $C(1,0) = 1.0$. The first expression to the right of the equality is a consequence of intramolecular reactions; the second expression is a consequence of intermolecular, formation reactions. This equation was simplified by initially substituting the expression for $C(i,j-1)$ and then expressions for $C(i,j-2)$, ..., $C(i,0)$ sequentially into the term for $C(i,j-1)$. This arithmetic expression yields an implicit expression for the coefficient function that is partially factored:

$$C(j,j) = \frac{(1-\delta_{1,i})}{2f[(f-2)i/2-j+1]!(i+j-1)!} \times \sum_{s=0}^{j}[[(f-2)i/2-j+s+1]!(i+j-s-2)! \times \sum_k \sum_l (f_{k,l}C(k,l)f_{i-k,j-s-l}C(i-k,j-s-l))]$$

In the preceding equation, the limits equal

$$k = 1, 2, 3, ..., i-1$$

$$\max\{0; j-s-(f-2)(i-k)/2-1\} \le l \le \min\{j-s; (f-2)k/2+1-s\}$$

A solution was obtained by induction:

$$C(i,j) = \frac{f(fi-i-j)![(f-2)i/2]!}{2[(f-2)i-j+1]![(f-2)i/2-j+1]!i!j!}$$

The general solution for the molar distribution of molecules within the thermoset resin is

$$p_{i,j} = \frac{f(fi-i-j)![(f-2)i/2]!}{2[(f-2)i-j+1]![(f-2)i/2-j+1]!i!j!} \times \frac{c^j\rho^{i+j-1}[(1-\rho+c)(1-\rho)]^{[(f-2)i-2j+2]/2}}{(1+c)^{fi/2}} \tag{13}$$

Subject to the constraint of intermolecular reactions, the constant $c = 0$ and the index $j = 0$. Equation 13 reduces to the equation reported by Flory[1] and Stockmayer:[2]

$$p_i = \frac{f(fi-i)!}{[(f-2)i+2]!i!}\rho^{i-1}(1-\rho)^{(f-2)i+2}$$

Second-Order Moments. The weight-average molecular weight requires second-order moments. Moment analysis increases in complexity with competing intermolecular and intramolecular reactions. The $\sum_i\sum_j i^2 p_{i,j}$ moment must be solved simultaneously with $\sum_i\sum_j ijp_{i,j}$ and $\sum_i\sum_j j^2 p_{i,j}$ moments. Initially, the differential equations descriptive of the population density distribution, eq 2, were weighted by the factor i^2. Resultant equations were added:

$$\frac{d}{d\tau}(\sum_i\sum_j i^2 p_{i,j}) = \frac{1}{f}(\sum_i\sum_j if_{i,j}p_{i,j})^2 \qquad (14)$$

The differential equations for the remaining second-order moments are

$$\frac{d}{d\tau}(\sum_i\sum_j ijp_{i,j}) = \frac{c}{2}\sum_i\sum_j if_{i,j}p_{i,j} + \frac{1}{f}(\sum_i\sum_j if_{i,j}p_{i,j})(\sum_i\sum_j jf_{i,j}p_{i,j}) \qquad (15)$$

and

$$\frac{d}{d\tau}(\sum_i\sum_j j^2 p_{i,j}) = \frac{c}{2}(\sum_i\sum_j (2j+1)f_{i,j}p_{i,j}) + \frac{1}{f}(\sum_i\sum_j jf_{i,j}p_{i,j})^2 \qquad (16)$$

To uncouple the moments, eq 13 was first rearranged:

$$p_{i,j} = c^j C(i,j)\left(\frac{\rho}{1+c}\right)^{i+j-1}\left(1-\frac{\rho}{1+c}\right)^{(f-2)i/2-j+1}(1-\rho)^{(f-2)i/2-j+1} \qquad (17)$$

Equation 17 was weighted by i, summed with respect to i and j, and then differentiated. Since the differential of the left-hand side of this equation equals zero, the result is

$$-\frac{1}{2(1+c-\rho)}\sum_i\sum_j if_{i,j}p_{i,j} + \frac{1}{\rho}\sum_i\sum_j (i^2+ij-i)p_{i,j} - \frac{1}{2(1-\rho)}\sum_i\sum_j if_{i,j}p_{i,j} = 0$$

Further arrangement in conjunction with eq 8 results in the expression

$$\sum_i\sum_j i^2 p_{i,j} = (1-\sum_i\sum_j ijp_{i,j}) \times \left[\frac{2(1+c-\rho)(1-\rho)+2\rho(1-\rho)+2\rho(1+c-\rho)}{2(1+c-\rho)(1-\rho)-\rho(f-2)(1-\rho)-\rho(f-2)(1+c-\rho)}\right] \qquad (18)$$

The ij moment was expressed in terms of the i^2 moment, and this equation was substituted into eq 14. Integration resulted in the solution for the second-order moment:

$$\sum_i\sum_j i^2 p_{i,j} = \frac{2(1+c)(1+c-\rho)}{[f(2+c)-2(1+c)]\rho^2-2f(1+c)\rho+2(1+c)^2} \qquad (19)$$

The weight-average molecular weight equals

$$\mathrm{MW_w} = \frac{2M_0(1+c)(1+c-\rho)}{[f(2+c)-2(1+c)]\rho^2-2f(1+c)\rho+2(1+c)^2} \qquad (20)$$

At the critical conversion the weight-average molecular weight is infinite. The critical conversion for a polymerization of a multifunctional monomer with competing intermolecular and intramolecular reactions is

$$\rho_c = \frac{(1+c)}{f(2+c)-2(1+c)}[f-[f^2-2f(2+c)+4(1+c)]^{1/2}]$$

If the polymerization is constrained to intermolecular reactions, the constant c equals zero and

$$\rho_c = \frac{1}{f-1}$$

The presence of intramolecular reactions shifts the critical conversion to higher values.

Discussion

Chemical reaction theory was demonstrated as a mathematical technique for the analysis of network-forming polymerization reactions. Solutions were obtained for an f-functional monomer with competing intramolecular and intermolecular reactions. Expressions for population density distributions, mass fraction distributions, and the number-, weight-, and cross-link-average molecular weights were derived. Conversion was expressed as a function of time.

Simulations[17] reveal the complexity of the dynamics of network-forming polymerizations as a function of cure. At high extents of reaction an oligomeric, soluble fraction will be present. Molecules that are cross-linked to the extent that they are chemically inert accumulate. At low conversions a population of molecules with cross-links is also present. Molecular analysis of these oligomeric molecules, if leached from a curing thermoset, could reveal the intricacies of the competing intermolecular and intramolecular reaction rates. Molecular characterizations of the sol fraction may ultimately allow rate expressions descriptive of cross-linking to be formulated with precision. The resultant models will describe the state of cure in thermoset resins, including average chain configurations.

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Nomenclature

$C_{i,j}$	dimensionless constants
c	normalized intramolecular rate constant
d	differential operator
f	chemical functionality of monomer
$f_{i,j}$	chemical functionality of molecules $P_{i,j}$
K	intermolecular reaction rate constant, volume/mole/time
K'	intramolecular reaction rate constant, 1/time
M_0	monomer's molecular weight, mass/mole
$\mathrm{MW_c}$	cross-link-average molecular weight, mass/mole
$\mathrm{MW_n}$	number-average molecular weight, mass/mole
$\mathrm{MW_w}$	weight-average molecular weight, mass/mole
n	units in a cyclic chain configuration
$P_{1,0}(0)$	monomer concentration initially, mole/volume

$P_{i,j}$	molar concentration of molecules of degree of polymerization i with j intramolecular cross-links, moles/volume
$p_{i,j}$	normalized molar concentration of molecules
t	time

Greek Letters

$\delta_{i,j}$	Kronecker delta, $\delta_{i,j} = \begin{cases} 1.0 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases}$
ρ	conversion of functional groups
τ	dimensionless time, $2fKP_1(0)t$

Subscripts

c	critical
i, k	degree of polymerization
j, l	number of intramolecular cross-links

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