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Reaction Kinetics Analyses of Amine-Cured Epoxies: First Shell Substitution Effects

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ABSTRACT: Kinetic reaction theory was used to model first shell substitution effects for several amine-cured epoxy resins, subject to the constraint of intermolecular reactions. Moment analysis will allow numerical simulations to be extended beyond the gel point. Functionalities for several chemical moieties were correlated as a function of conversion. Simulations also incorporated population density distribution dynamics. Analyses of several oligomers clearly demonstrated the dependency of oligomeric weight fractions on first shell substitution effects and conversion. The ratio of rate constants for reactions of secondary amino hydrogens relative to reactions of primary amino hydrogens ranged from 0.5 to 1.2 for the resins analyzed.

Introduction

Flory[1] and Stockmayer[2] laid the foundation for statistical and kinetic analyses of polymerizations with multifunctional monomers. Relationships were developed for the population density distribution, mass fraction distribution, molecular weight averages, gel points, and sol fractions for random, intermolecular reactions for which bond formation consumes both chemical moieties. Fukui and Yamabe[3] used the kinetic approach to model Poisson-type polymerizations, including cures producing polyether networks. This class of polymerizations creates a Poisson distribution with monomers of functionality 2.[4,5] During bond formation the propagation site reforms so that its molar concentration is invariant.

Substitution Effects. First shell substitution effects (FSSE) have also been theoretically addressed. Gordon and co-workers[6] used an adaptation of Good's[7] theory of cascade processes. FSSE[8] and chain cyclization[9–11] were considered. Kuchonov and Povolotskaya[12] demonstrated that solutions in the presence of FSSE are distinct for an RA_f monomer. Subject to $f = 3$ Mikeš and Dušek[13] used Monte Carlo simulations and again showed that the gel point was dependent on FSSE. Relative large changes in rate constants are required to produce appreciable changes in gel points. Miller and Macosko[14,15] formulated random polymerization events in terms of expectation theory. They addressed FSSE associated with chemical moieties of inherently different reactivities, including primary and secondary alcohols and ortho- and para-isocyanates.

Galina and Szustalewicz[16] used the spanning tree theory and chemical reaction kinetics to simulate polymerizations of RA_3/RB_2 monomers. The reaction sequence of the chemical moieties A_1, A_2, A_3 and B_1, B_2 was used to assign distinct rate constants for the several competing, intermolecular reactions. Relatively large changes in the numerical values for the rate constants produced distinct gel points. Spanning tree theory consistently predicted higher critical conversions than did kinetic reaction theory. Bokare and Gandhi,[17] Gupta and Macosko,[18] and Dušek *et al.*[19] addressed distinct rate constants associated with primary and secondary amines in the presence of competing etherification reactions. Pregel and postgel properties were predicted. The methodology combines kinetic and statistical analysis. Kinetic rate expressions for molecular species and specific auxiliary chain structures that lead to branch nodes are required.

Chain Cyclization. Jacobson and Stockmayer[20] and Semlyen[21] addressed competing intermolecular and intramolecular chain cyclization reactions. Sarmoria *et al.*[22] studied the effects that model approximations have on simulations of bifunctional monomers. Spanning tree methodology yielded weight-average molecular weights that were low. Kinetic rate theory, limited to the formation of rings up to a maximum degree of polymerization of 3, yielded accurate simulations to high conversions in bulk polymerizations and polymerizations in the presence of a solvent. Dilution enhances chain cyclization. Noureddini and Timm[23] explicitly incorporated competing intermolecular and intramolecular reactions for polymerizations of an f-functional monomer using a truncated ring formation model. Liu *et al.*[24] observed that the method simulated the exact solutions presented by Temple[25] and accurately simulated the experimental data of Stanford and Stepto.[26] Cures were limited to the pregel stage.

Amine-Cured Epoxies. The reaction between an oxirane and a primary amine forms a secondary amine which reacts with a second epoxide, resulting in a tertiary amine. Each reaction results in the formation of a hydroxyl group. Reactions can be complex. Several experimental studies[27–31] have indicated different chemical reactivities for amino hydrogen atoms. Studies[32–34] have also indicated similar rate constants. In general, reported data for reaction rate constants for primary and secondary amino groups are very inconsistent. Discrepancies are due to differences in experimental conditions and methods of calculations. Rozenberg[35] concluded that some degree of substitution effect has been observed and that in some cases this effect can be substantial. In the extreme[34] aromatic amines may experience steric hinderance to the extent that primary and secondary amines react sequentially. In such cases a most probable linear chain structure initially forms with bifunctional primary amine and oxirane reactants. Subsequent reactions at secondary amines will cause cross-linking. Dušek[36] has modeled this cure using statistical methodology coupled with moment analysis. Luňák and Dušek[31] observed less server FSSE for the diglycidyl ether of Bisphenol A (DGEBA)/4,4′-diaminodiphenylmethane (DDM) resin. The FSSE has been attributed to steric and induction effects.

With aromatic reactants, the resultant tertiary amines are ineffective in catalyzing polyetherification reactions. Rozenberg[35] attributed this to steric factors. For aromatic

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systems, chain cyclization caused by intramolecular reactions can be neglected during the initial stages of the cure.[17,37] DGEBA is a stiff monomer, and during reactions with aromatic or even aliphatic diamines, it exhibits a very low tendency for cyclization. The ring free kinetic reaction theory can be applied with success. This conclusion is consistent with experimental observations that the critical conversion at the gel point was independent of dilution.[27,37,38] However, Charlesworth[32] reported contradictory evidence for cyclization reactions for the DGEBA/DDM resin in solutions. As the resin became more dilute, the relative amount of unreacted monomer increased. Assuming that amino hydrogens had reacted, the number of intramolecular reactions increased with increased dilution. However, cyclization reactions were negligible in bulk cures.

Eichler and Mleziva[39] considered electron densities for the atoms present in phenyl glycidyl ether (PGE). Because the electron density of the terminal epoxy carbon is the lowest, an amine-cured epoxy follows a nucleophilic addition. The higher the electron density of an amino group, the greater is its reactivity. The curing agent 4,4′-diaminodiphenyl sulfone (DDS) has a lower electron density Q_{NH_2} = 1.683 than 4,4′-diaminodiphenyl ether (DDE) Q_{NH_2} = 1.882. The DDE resin cures at lower temperatures. In addition the DDS system cures as a second-order reaction, whereas the DDE system cures according to a third-order, autocatalytic reaction with respect to hydroxyl moieties.[40,41] King and Bell[33] state that, if hydroxyls are tightly associated with amine or oxirane intermediates, second-order reactions prevail. Several investigations[27,32,35,37,38] have reported that the oxiranes on DGEBA experience equal reactivity.

In this paper reaction kinetic analysis and experimental determinations are presented for polymerizations of DGEBA with curing agents that may exhibit FSSE but that are relatively void of other complex events. A prevalent experimental method of analyses that is based on the moments of the population density distribution is used. Emphasis is placed on correlations that relate the concentrations of functional groups to time or conversion. A less commonly utilized experimental method that incorporates population density distribution dynamics is also developed. Results show that the latter technique is more sensitive to small changes in the rate constants associated with the reactivity of primary and secondary amino hydrogen sites. The technique can be used to assist in the development of rigorous reaction models that will be descriptive of the cure in the pregel and postgel stages. Such models are required to correlate molecular chain topology to a thermoset's macroscopic performance.

Literature data incorporated in the current analysis are for the pregel conversion interval. Analysis determined relative rate constants for primary and secondary amines. Simulations are shown to correlate the concentrations of functional groups as a function of cure state. Population density analysis shows that FSSE are operative for the resin DGEBA/DDM. Charlesworth[32] measured a variety of network parameters, including molecular weights, composition, and sol fraction for the DGEBA/DDM system in the postgel state. His analysis was based on Macosko and Miller's[14] method of conditional probabilities. Charlesworth concluded that substitution effects are insufficient to alter the random course of the polymerization for these resins. However, we will show that a small FSSE is likely present.

Reaction Model and Constraints

Model constraints incorporate the following: (1) each oxirane state can react with equal probability, (2) second-order, noncatalytic or third-order, autocatalytic reaction kinetics can be operative, (3) no intermolecular reactions occur, and (4) no etherification reactions are present.

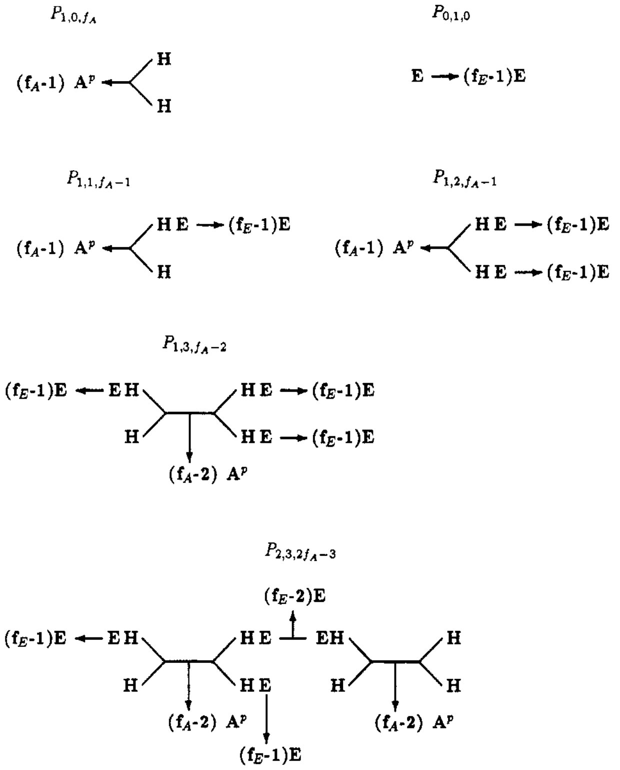

Figure 1. Examples of typical monomeric and oligomeric molecules resulting from the reaction of polyepoxides with polyamines.

The dependent variable $P_{i_A,i_E,k}$ represents the molar concentration of polymeric molecules which contain i_A hardener links, i_E monomeric units, and k primary amines. The fourth independent variable, time, is implicit in the notation. Examples of several monomeric and oligomeric molecules are presented in Figure 1. The hardener's functionality is represented by f_A which denotes the original number of primary amines. The functionality of the epoxy is denoted by f_E which describes the number of oxiranes. A sketch of a molecule emphasizes the number of primary amines A^p and the oxirane moieties E. Their respective numbers are denoted by an algebraic expression at the point of an arrow.

For each degree of polymerization i_A = 1,2,3,..., bonding constraints restrict the permissible number of epoxide links. A molecule with i_A hardener segments requires a minimum of $i_A - 1$ epoxy links. The maximum number of epoxy links occurs when all amino hydrogens have reacted. This limit may be evaluated from stoichiometric considerations. Initially, the i_A amine units contained $2f_A$ sites. The $i_A - 1$ connecting links each consumed two amino hydrogens during bond formation. The remaining $i_E - i_A + 1$ epoxy links are pendent to the chains of the molecule. Algebra yields the upper limit:

$$i_A - 1 \le i_E \le (2f_A - 1)i_A + 1 \tag{1}$$

Parallel arguments yield the range for permissible primary amines that can occur on molecules that contain i_A and i_E links:

$$\max\{0;(f_A-1)i_A-i_E+1\} \le k \le \\ \min\{\text{integ}[(2f_A-1)i_A-i_E+1]/2; \quad i_A(f_A-1+\delta_{1,i_E+1})\} \tag{2}$$

Initially consider the choice in the lower limits. If a sufficient number of epoxy links are present, no primary amines remain on a molecule. However, if fewer epoxy links are present, preferential bonding at primary amine sites will yield the arithmetic expression in the lower limit. Each connecting epoxy link will consume two primary amines and each pendent epoxy link will consume one site. The larger of the two limits indicated is the correct lower limit for the index k. The maximum permissible number of primary amines occurs when each hardener contributes one primary amine to the molecule. This yields the first algebraic expression of the upper limit. Integer division requires remainders to be truncated. The algebraic expression is also equated to the number of amino hydrogens on the molecule. The second limit expression allows the hardener to be included in the collection of polymeric molecules explicitly. The Kronecker delta function equals unity when $i_{\mathrm{E}} = 0$; otherwise, it equals zero.

Chemical Functionality. In general, a polymeric molecule $P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ can supply an epoxy site ($E_{i_{\mathrm{A}},i_{\mathrm{E}},k}$), a primary hydrogen site ($H'_{i_{\mathrm{A}},i_{\mathrm{E}},k}$), or a secondary hydrogen site ($H''_{i_{\mathrm{A}},i_{\mathrm{E}},k}$) during bond formation. The number of these functional sites on a molecule can be calculated from the three independent variables:

$$E_{i_{\mathrm{A}},i_{\mathrm{E}},k} = (f_{\mathrm{E}} - 1)i_{\mathrm{E}} - i_{\mathrm{A}} + 1$$

$$H'_{i_{\mathrm{A}},i_{\mathrm{E}},k} = 2k$$

$$H''_{i_{\mathrm{A}},i_{\mathrm{E}},k} = (2f_{\mathrm{A}} - 1)i_{\mathrm{A}} - i_{\mathrm{E}} - 2k + 1$$

Also, the number of tertiary amines equals

$$A^{t}_{i_{\mathrm{A}},i_{\mathrm{E}},k} = (1 - f_{\mathrm{A}})i_{\mathrm{A}} + i_{\mathrm{E}} + k - 1$$

The chemical functionality of hydroxyl groups formed is

$$OH_{i_{\mathrm{A}},i_{\mathrm{E}},k} = i_{\mathrm{A}} + i_{\mathrm{E}} - 1$$

The cumulative concentrations of primary hydrogen sites, secondary hydrogen sites, epoxide sites, and hydroxyl groups in the resin are functions of the zero- and first-order moments of the population density distribution:

$$H' = \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} H'_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} \tag{3}$$

$$H'' = \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} H''_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} \tag{4}$$

$$E = \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} E_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} + f_{\mathrm{E}} P_{0,1,0} \tag{5}$$

$$OH = \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} OH_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} \tag{6}$$

The summation $\Sigma_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ incorporates all polymeric molecules. Mathematically, the amine hardener ($P_{1,0,f_{\mathrm{A}}}$) is included but the epoxy monomer ($P_{0,1,0}$) is excluded. The precise limits for the triple summation are

$$\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} \equiv \sum_{i_{\mathrm{A}}=1}^{\infty} \sum_{i_{\mathrm{E}}=i_{\mathrm{A}}-1}^{(2f_{\mathrm{A}}-1)i_{\mathrm{A}}+1} \sum_{k=\max\{0;(f_{\mathrm{A}}-1)i_{\mathrm{A}}-i_{\mathrm{E}}+1\}}^{\min\{\mathrm{integ}[(2f_{\mathrm{A}}-1)i_{\mathrm{A}}-i_{\mathrm{E}}+1]/2;i_{\mathrm{A}}(f_{\mathrm{A}}-1+\delta_{1,i_{\mathrm{E}}+1})\}} \tag{7}$$

Intermolecular Reactions. A molecule $P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ is formed from bimolecular reactions that couple a monomeric and a polymeric molecule or two smaller polymeric molecules:

Reactions with Primary Amines:

Propagation

$$P_{0,1,0} + P_{i_{\mathrm{A}},i_{\mathrm{E}}-1,k+1} \xrightarrow{K_1} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$$

Polyaddition

$$P_{l_{\mathrm{A}},l_{\mathrm{E}},n} + P_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n+1} \xrightarrow{K_1} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$$

Reactions with Secondary Amines:

Propagation

$$P_{0,1,0} + P_{i_{\mathrm{A}},i_{\mathrm{E}}-1,k} \xrightarrow{K_2} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$$

Polyaddition

$$P_{l_{\mathrm{A}},l_{\mathrm{E}},n} + P_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n} \xrightarrow{K_2} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$$

All reactants must satisfy bonding constraints. The initial reactant is assumed to supply an oxirane and the second reactant an amino hydrogen. The rate constant associated with the reaction of primary amines is K_1, and the rate constant for secondary amines is K_2. Stoichiometric considerations result in the several subscripts.

Experiments with model compounds[35] indicate that competing reactions are described by rate expressions of the form

$$\mathrm{rate}'_{i_{\mathrm{A}},i_{\mathrm{E}},k} = K_1 E_{l_{\mathrm{A}},l_{\mathrm{E}},n} P_{l_{\mathrm{A}},l_{\mathrm{E}},n} H'_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n+1} P_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n+1} OH^{\omega}$$

$$\mathrm{rate}''_{i_{\mathrm{A}},i_{\mathrm{E}},k} = K_2 E_{l_{\mathrm{A}},l_{\mathrm{E}},n} P_{l_{\mathrm{A}},l_{\mathrm{E}},n} H''_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n} P_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n} OH^{\omega}$$

For third-order, autocatalytic reactions, the value for ω is 1. For second-order, noncatalytic reactions, ω is equal to zero. Rate expressions are consistent with collision theory.

Conversion. Extent of reaction is defined as the ratio of the number of reactive sites reacted divided by the initial number of sites. Several conversions may be defined. Two are presented, one for amino hydrogen sites and a second for oxirane sites:

$$\rho_{\mathrm{H}} = \frac{2f_{\mathrm{A}}P_{1,0,f_{\mathrm{A}}}(0) - H' - H''}{2f_{\mathrm{A}}P_{1,0,f_{\mathrm{A}}}(0)} \tag{8}$$

$$\rho_{\mathrm{E}} = \frac{f_{\mathrm{E}}P_{0,1,0}(0) - E}{f_{\mathrm{E}}P_{0,1,0}(0)} = \rho_{\mathrm{H}} \frac{2f_{\mathrm{A}}P_{1,0,f_{\mathrm{A}}}(0)}{f_{\mathrm{E}}P_{0,1,0}(0)} \tag{9}$$

Population Density Distribution Dynamics

The reactor is constrained to a batch, isothermal, isometric, well-mixed vessel. Transport processes are limited to chemical reaction rates. The epoxy monomer's concentration dynamics caused by chemical reactions are described by the relationship

$$\frac{1}{OH^{\omega}} \frac{\mathrm{d}P_{0,1,0}}{\mathrm{d}t} = -f_{\mathrm{E}}P_{0,1,0}(K_1H' + K_2H'') \tag{10}$$

Conservation laws applied to the hardener yield

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}P_{1,0,f_{\mathrm{A}}}}{\mathrm{d}t} = -K_1 E 2 f_{\mathrm{A}} P_{1,0,f_{\mathrm{A}}} \tag{11}$$

Initially, the monomer concentration is $P_{0,1,0}(0)$ and the hardener's concentration is $P_{1,0,f_{\mathrm{A}}}(0)$. The differential equation characterizing the population density distribution dynamics is

$$\begin{aligned}\frac{1}{OH^{\omega}}\frac{\mathrm{d}P_{i_{\mathrm{A}},i_{\mathrm{E}},k}}{\mathrm{d}t} = {} & -K_1 E H'_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} - K_2 E H''_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} - \\ & K_1 E_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} H' - K_2 E_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} H'' + \\ & K_1 f_{\mathrm{E}} P_{0,1,0} H'_{i_{\mathrm{A}},i_{\mathrm{E}}-1,k+1} P_{i_{\mathrm{A}},i_{\mathrm{E}}-1,k+1} + \\ & K_2 f_{\mathrm{E}} P_{0,1,0} H''_{i_{\mathrm{A}},i_{\mathrm{E}}-1,k} P_{i_{\mathrm{A}},i_{\mathrm{E}}-1,k} + \\ & K_1 \sum_{l_{\mathrm{A}},l_{\mathrm{E}},n} E_{l_{\mathrm{A}},l_{\mathrm{E}},n} P_{l_{\mathrm{A}},l_{\mathrm{E}},n} H'_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n+1} P_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n+1} + \\ & K_2 \sum_{l_{\mathrm{A}},l_{\mathrm{E}},n} E_{l_{\mathrm{A}},l_{\mathrm{E}},n} P_{l_{\mathrm{A}},l_{\mathrm{E}},n} H''_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n} P_{i_{\mathrm{A}}-l_{\mathrm{A}},i_{\mathrm{E}}-l_{\mathrm{E}},k-n}\end{aligned} \tag{12}$$

In eq 12 the first two rate expressions describe reactions of amino hydrogens on $P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ with all oxiranes in the system. The third and fourth rate expressions allow oxiranes on $P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ to react with any amino hydrogen in the resin. The fifth and sixth terms denote candidate formation reactions of $P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ from monomer. The last two rate expressions address possible polyaddition formation reactions. The autocatalytic effect of the hydroxyl moiety has been factored from all rate expressions. Time is represented by the variable t. The dimensions for these equations are $(\text{moles/volume})^{1-\omega}/\text{time}$. Except for the hardener and the monomer, initial conditions equal zero.

The set of formation reactions, including propagation and polyaddition reactions for a given $P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$, were initially determined numerically using FORTRAN code.[42] Candidate limits for the summation $\sum_{l_{\mathrm{A}},l_{\mathrm{E}},n}$ were determined by satisfying bonding constraints, eqs 1 and 2, for each reactant. For example, a molecule $P_{2,2,2}$ can only be formed from a single reaction with a primary amine, $P_{1,2,1} + P_{1,0,2}$, and from two reactions with a secondary amine, $P_{0,1,0} + P_{2,1,2}$ and $P_{1,1,1} + P_{1,1,1}$. The molecule $P_{2,3,1}$ can be formed from a greater number of formation reactions, $P_{0,1,0} + P_{2,2,2}$, $P_{1,1,1} + P_{1,2,1}$, $P_{1,2,1} + P_{1,1,1}$, $P_{1,3,0} + P_{1,0,2}$ and $P_{0,1,0} + P_{2,2,1}$, $P_{1,1,1} + P_{1,2,0}$, $P_{1,2,0} + P_{1,1,1}$, respectively. Recall that the initial reactant supplies an oxirane and the second amino hydrogen. Therefore, the last two reactions are distinct. A numerical program was initially written to expand eq 12 in detail for verification. A second program incorporated the logic and performed numerical integrations.

Zero- and First-Order Moments. Conversion and the population density distributions are functions of zero- and first-order moments of the distribution. To generate expressions descriptive of the leading moments of the distribution, the differential eqs 10 and 12 may be initially multiplied by the weight factor $i_{\mathrm{A}}^{\alpha} i_{\mathrm{E}}^{\beta} k^{\gamma}$, where α, β, γ = 0, 1, 2, ..., and then summed. The zero moment $\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ equals the cumulative molar concentration of molecules in the system excluding monomer. If terms for the same rate expression in several differential equations are initially arranged in the form of $\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} C P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$, where C is equal to $H'_{i_{\mathrm{A}},i_{\mathrm{E}},k}$, $H''_{i_{\mathrm{A}},i_{\mathrm{E}},k}$, or $E_{i_{\mathrm{A}},i_{\mathrm{E}},k}$, addition and algebra readily yields the zero moment of the distribution:

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}}{\mathrm{d}t}\Big\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}\Big\} = -(E - f_{\mathrm{E}} P_{0,1,0})(K_1 H' + K_2 H'') \tag{13}$$

As expected, the population of molecules diminishes due to polyaddition reactions, only; see eq 5. Equation 13 expresses the cumulative rates for these intermolecular reactions in terms of the chemical equivalences of oxiranes and primary and secondary amines on polymeric species. The initial condition equals

$$\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}(0) = P_{1,0,f_{\mathrm{A}}}(0)$$

The first-order moment $\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ equals the total number of amine units in the system. This moment may be generated by weighting eqs 10 and 12 by i_{A}. Addition coupled with algebraic simplification yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}\Big\} = 0 \tag{14}$$

The initial condition is

$$\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}(0) = P_{1,0,f_{\mathrm{A}}}(0)$$

Integration yields a constant:

$$\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k} = P_{1,0,f_{\mathrm{A}}}(0)$$

Therefore, the number of hardener units in the system is conserved.

The moment $\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$ was generated in an analogous manner:

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}}{\mathrm{d}t}\Big\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}\Big\} = f_{\mathrm{E}} P_{0,1,0}(K_1 H' + K_2 H'') \tag{15}$$

The equation is consistent with fundamental principles. Propagation kinetics incorporates monomer into the molecular chains of the resin. The initial condition is

$$\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}} P_{i_{\mathrm{A}},i_{\mathrm{E}},k}(0) = 0$$

The differential equation that describes the primary amine content of the resin is the remaining first-order moment $\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k P_{i_{\mathrm{A}},i_{\mathrm{E}},k}$:

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}}{\mathrm{d}t}\Big\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k P_{i_{\mathrm{A}},i_{\mathrm{E}},k}\Big\} = -K_1 E H' \tag{16}$$

The equation confirms that primary amines are consumed by reactions with all oxiranes in the system. The initial condition is

$$\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k P_{i_{\mathrm{A}},i_{\mathrm{E}},k}(0) = f_{\mathrm{A}} P_{1,0,f_{\mathrm{A}}}(0)$$

This moment generating technique yields expressions that satisfy basic tenets of stoichiometry and the principle of conservation of mass for achievable levels of conversion. Multifunctional monomers generate population density distributions that form conditionally convergent, infinite series.[43] Therefore, rearrangements exist that converge a specific moment when expressed in terms of population density distributions to any limit. Flory[1] used a specific rearrangement of Stockmayer's[2] analytical population density distributions to derive a second set of limits for the leading moments of the population density distribution. The differences between the two limits for mass is the foundation for the theory of gelation. Intramolecular bonding is implicit in the theory. Mathematics does not provide uniqueness beyond the limit of absolute convergence which is less than the critical conversion.

Dynamics of the Functional Sites. Analytical solutions that describe the concentration of several functional groups were obtained. Initially eqs 3–6 were differentiated. Resultant equations were coupled with moment expressions, eqs 13–16. Algebraic rearrangement yielded

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}H'}{\mathrm{d}t} = -2K_1EH' \qquad (17)$$

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}H''}{\mathrm{d}t} = E(K_1H' - K_2H'') \qquad (18)$$

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}E}{\mathrm{d}t} = -E(K_1H' + K_2H'') \qquad (19)$$

$$\frac{1}{OH^{\omega}}\frac{\mathrm{d}OH}{\mathrm{d}t} = E(K_1H' + K_2H'') \qquad (20)$$

Initial conditions are $H'(0) = 2f_AP_{1,0,f_A}$, $H''(0) = 0$, $E(0) = f_EP_{0,1,0}(0)$, and $OH(0) = OH_{\mathrm{initial}}$, respectively. In order to achieve analytical solutions, the independent variable was transformed to the variable ϕ:

$$\mathrm{d}\phi = E(OH^{\omega})\,\mathrm{d}t \qquad (21)$$

Integration, subject to initial conditions and $2K_1 \neq K_2$, yields the following expressions for the concentration of primary hydrogen sites, secondary hydrogen sites, epoxide moieties, and hydroxyls, respectively:

$$H' = H'(0)\exp(-2K_1\phi)$$

$$H'' = \frac{K_1H'(0)}{K_2 - 2K_1}[\exp(-2K_1\phi) - \exp(-K_2\phi)]$$

$$E = E(0) + \frac{(3K_2 - 4K_1)H'(0)}{2(K_2 - 2K_1)}\exp(-2K_1\phi) - \frac{K_1H'(0)}{K_2 - 2K_1}\exp(-K_2\phi) - 3H'(0)$$

$$OH - OH(0) = E(0) - E \qquad (22)$$

Solutions for the time, ϕ transformation can be obtained by numerical integration. The above solutions show that, if the rate constant for the reaction with secondary amines is diminished relative to the rate constant for primary amines, the concentration of secondary amines tends to accumulate during the initial phase of the cure. Molecules form with fewer branch nodes, which delays gelation.

Monomer, Hardener Concentration Dynamics. Equation 10 describes the rate of change of the monomer's concentration in terms of the concentrations of the oxiranes and amino hydrogens in the resin. When this expression is combined with eq 19, the resultant equation can be integrated, yielding

$$P_{0,1,0} = \frac{E^{f_E}}{f_EE(0)^{f_E-1}} = P_{0,1,0}(0)(1 - \rho_E)^{f_E} \qquad (23)$$

An analogous transformation occurs when eqs 11 and 17 are solved, yielding the change in the hardener's concentration as a function of conversion of primary amines, ρ_{A^p}:

$$P_{1,0,f_A} = \frac{H'^{f_A}}{2f_AH'(0)^{f_A-1}} = P_{1,0,f_A}(0)(1 - \rho_{A^p})^{f_A} \qquad (24)$$

Stockmayer[2] initially derived eqs 23 and 24. These solutions reveal a simple experimental method for estimating conversions. The concentration of secondary amino hydrogen sites may be evaluated from eqs 8 and 9, for example.

Average Molecular Weights. The molecular weight of a polymeric molecule $P_{i_A,i_E,k}$ is

$$MW_{i,j,k} = i_EMW_{0,1,0} + i_AMW_{1,0,f_A}$$

The number-average molecular weight for the resin fraction is

$$MW_n = \frac{\sum_{i_A,i_E,k}(i_EMW_{0,1,0} + i_AMW_{1,0,f_A})P_{i_A,i_E,k}}{\sum_{i_A,i_E,k}P_{i_A,i_E,k}} \qquad (25)$$

The simultaneous solution of the first-order moments, eqs 13–16, yields the number-average molecular weight. The weight-average molecular weight equals

$$MW_w = \frac{\sum_{i_A,i_E,k}(i_EMW_{0,1,0} + i_AMW_{1,0,f_A})^2P_{i_A,i_E,k}}{\sum_{i_A,i_E,k}(i_EMW_{0,1,0} + i_AMW_{1,0,f_A})P_{i_A,i_E,k}} \qquad (26)$$

Expressions for second-order moments are presented in the Appendix. At the gel point the weight-average molecular weight diverges.

Experimental Procedures

Four amine-cured epoxy resins were evaluated. Dušek and co-workers[27,30,37] cured DGEBA with dodecylamine (DDA) and 1,6′-hexamethylenediamine (HMD). King and Bell[33,34] reported results with 1,4-diaminobutane (DAB), and Charlesworth[32] used the curing agent DDM. For these resins experimental procedures have been published. For a fourth resin, Zhang[44] used the hardener DDE. DGEBA was supplied by Shell Chemical Co. (EPON 828, 185–192 epoxide equivalent weight). DDE was supplied by Aldrich Chemical Co. (purity > 98%). Raw materials were stored in the presence of a desiccator. About 50 g of DGEBA plus the hardener plus 100 mL of acetone was warmed and mixed to achieve a solution. Acetone was then degassed under vacuum. Samples of about 10 mL were placed in test tubes and sealed. Cures were at 100 ± 1 °C in a forced-air, electrically-heated oven. Samples, were withdrawn as a function of time and thermally quenched at 0 °C. Epoxide groups were analyzed by titration using the method described by Bell.[34] Tertiary amino groups were analyzed using the method developed by Wagner *et al.*[45] and Chapman *et al.*[46]

Results

Zero- and first-order moment equations, eqs 13–16, were used to evaluate several coefficients in eq 12. Equations were numberically integrated using a Runge Kutta algorithm.[42] Temple[25] generated moments by adding weighted population density distributions. A large number of equations had to be integrated to achieve convergence even at low conversions. The current procedure allows the population density distribution to be truncated at convenient degrees of polymerization. If only information that is dependent on moments is of interest, the population density distribution equations need not be solved. Furthermore, the current technique allows numberical simulations to advance beyond the gel point.

Results for the curing of diepoxides with diamines are discussed in terms of normalized population density distributions $p_{i_A,i_E,k}$, dimensionless time τ, relative rate constants c_1, and the initial formulation variable ζ:

$$p_{i_A,i_E,k} \equiv \frac{P_{i_A,i_E,k}}{P_{1,0,f_A}(0)}$$

$$\tau \equiv K_1 P_{1,0,f_A}^{\omega+1}(0)\, t$$

$$c_1 \equiv K_2/K_1 \qquad (27)$$

$$\zeta \equiv \frac{P_{0,10}(0)}{P_{1,0,f_A}(0)}$$

Simulations. Illustrative population density distributions appear in Figure 2. Simulations where subjected to the constraint of equal chemical reactivities, $c_1 = 1.0$. The overall order for the reaction was 2, $\omega = 0$. Initially, the chemical equivalences for oxiranes and for amino hydrogens were equal, $\zeta = 2.0$. The distributions shown are at an extent of reaction $\rho_E = \rho_H = 0.250$. The ordinate is the sum of the molar concentrtions of molecules $\sum_{i_E,k} p_{i_A,i_E,k}$, subject to specified degrees of polymerization for the hardener, $i_A = 1, 2, ..., 5$, respectively. The abscissa is the total number of epoxy and amine units, subject to the value for i_A specified. This degree of polymerization is also an indicator for the molecular weight of the sets of molecules graphed. The collections of molecules shown form envelopes which start at $i_E = i_A - 1$ and stop at the maximum permissible value for i_E. Each set is dominated by molecules that are close to a balanced stoichiometry with respect to the number of monomer and hardener chain links. One of the more concentrated molecules is the hardener, $i_A + i_E = 1$. The semilogarithmic correlation further shows that larger, more complex molecules are present at relatively low concentrations at this extent of cure.

DGEBA/DDA and DGEBA/HMD Resins. Dušek and co-workers[27,30,37] analyzed resins cured with DDA and HMD resin using differential eqs 17–20 to obtain solutions for the concentration of secondary and tertiary amines as functions of the concentration of primary amines and the relative rate constant c_1. A probability generating function was used to obtain expressions for the average molecular weights. Experimentally, the mole fraction of teritary amines was correlated as a function of the conversion of amino hydrogens ρ_H. Excellent theoretical/experimental agreement was achieved when $c_1 = 0.82$. Using the same rate constant, our simulations replicated this work. This examination provided additional tests of the numerical code. The form of the data prevents an analysis of the order of the reaction with respect to the concentration of the hydroxyl moiety. Expressions dA^s/dA^p and dA^t/dA^p are independent of hydroxyl concentration. In the current work, the constant c_1 is based on amino hydrogen sites. Dušek based the relative rate constant on primary amines. These definitions result in a factor of 2 difference between the relative rate constants.

DGEBA/DAB Resin. King and Bell[33,34] cured DGEBA with DAB in the presence of an initial concentration of isopropyl alcohol. The concentrations of epoxy, primary amine, secondary amine, and tertiary amine were reported as a function of time. The method of initial rates was used in their analysis. The current research is based on an integral analysis. Figure 3 summarizes the results. A balanced stoichiometry was used, $\zeta = 2.0$. Simulations in time used a third-order overall reaction, $\omega = 1$. Results shown were performed for $c_1 = 1.0$ and 1.2. The concentrations of the functional groups are correlated as a function of conversion of the amino hydrogen sites ρ_H which equals the conversion for epoxies ρ_E. When $c_1 = 1.2$, simulations reveal that more primary and tertiary amines are present, but fewer secondary amines exist in the resin at a given conversion.

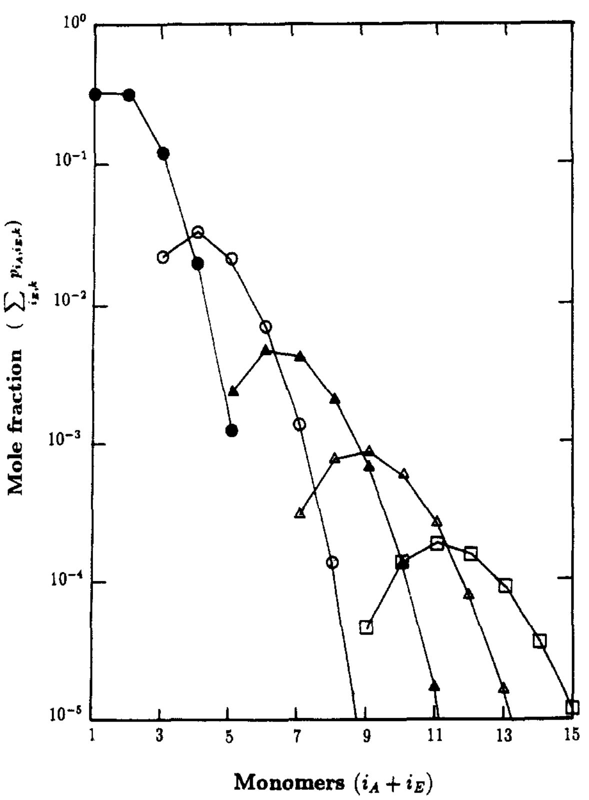

Figure 2. Mole fraction of various molecules as a function of the total number of epoxy and amine monomers at conversion equal to 0.250, subject to $c_1 = 1.0$, $\zeta = 2.0$, $f_A = f_E = 2$ and second-order kinetics. (●) $\sum_{i_E,k} p_{1,i_E,k}$; (○) $\sum_{i_E,k} p_{2,i_E,k}$; (▲) $\sum_{i_E,k} p_{3,i_E,k}$; (△) $\sum_{i_E,k} p_{4,i_E,k}$; (□) $\sum_{i_E,k} p_{5,i_E,k}$.

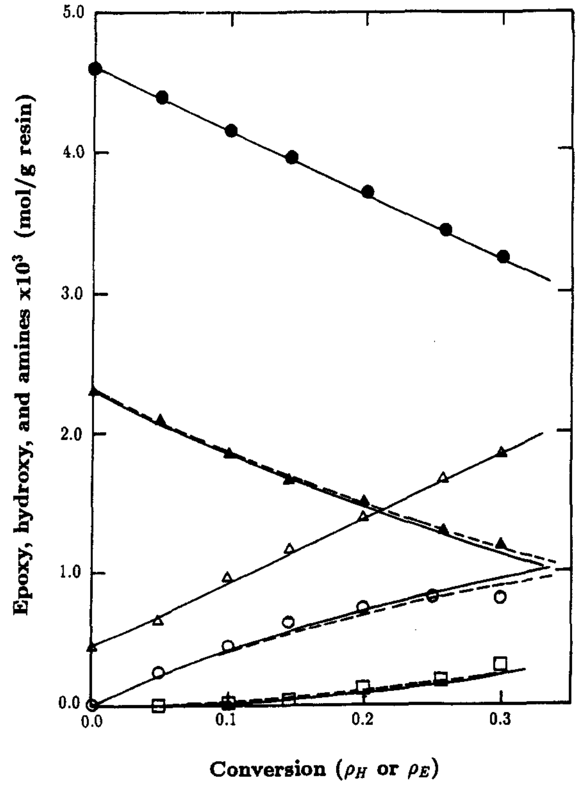

Figure 3. Numerical simulations and experimental results of functional groups as a function of conversion in the system DGEBA/DAB subjec to $\zeta = 2.0$ and third-order kinetics. (●) Epoxy groups; (▲) primary amines; (△) hydroxyl groups; (○) secondary amines; (□) tertiary amines; (—) $c_1 = 1.00$; (- - -) $c_1 = 1.20$.

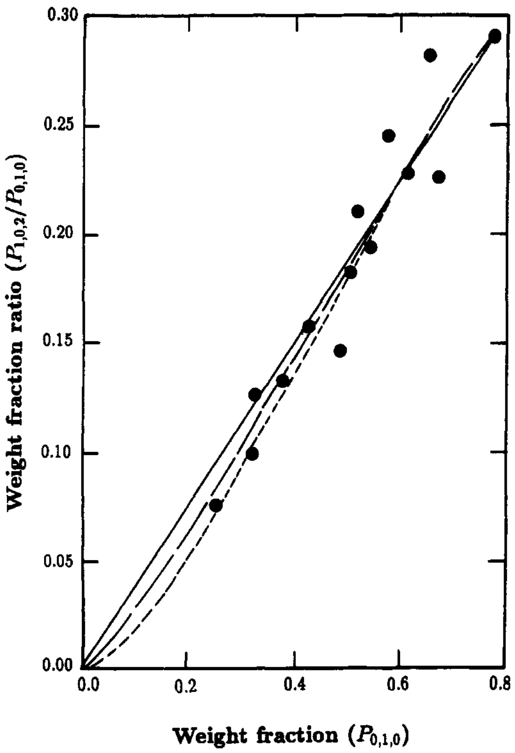

Figure 4. Theoretical and experimental relative moles of $P_{1,0,2}$ and $P_{0,1,0}$ compared to $P_{0,1,0}$ in the system DGEBA/DDM subject to $\zeta = 2.0$ and second-order kinetics. (●) Experimental data; (—) $c_1 = 1.00$; (- -) $c_1 = 0.80$; (- - -) $c_1 = 0.60$.

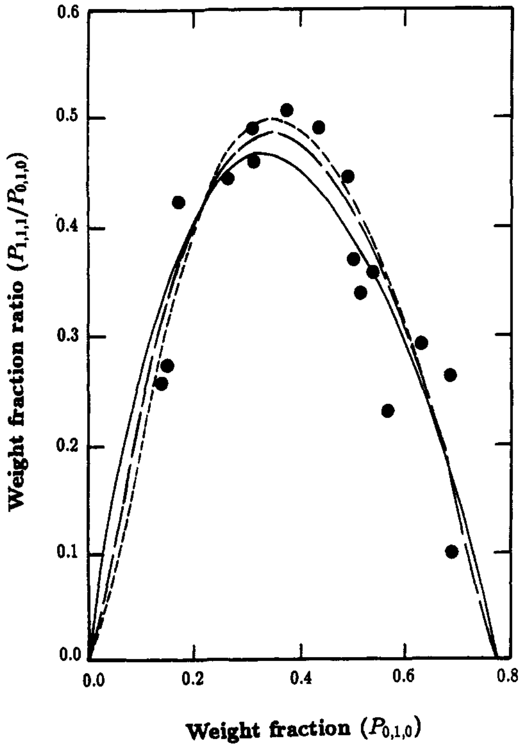

Figure 5. Theoretical and experimental relative moles of $P_{1,1,1}$ and $P_{0,1,0}$ compared to $P_{0,1,0}$ in the system DGEBA/DDM subject to $\zeta = 2.0$ and second-order kinetics. (●) Experimental data; (—) $c_1 = 1.00$; (- -) $c_1 = 0.80$; (- - -) $c_1 = 0.60$.

Simulations are in close agreement with experimental measurements. Data of Figure 3 show that, as the relative rate constant is increased, the fit for the primary, secondary, and tertiary amines improves in the interval $0.2 \leq \rho_H \leq 0.3$. The errors between the simulations and data at a conversion of 0.3 are the greatest. These deviations could be due to the presence of intramolecular reactions. These competing reactions are expected to reduce the effective functionality of the resin, resulting in an increased number of tertiary amines and a decreased number of secondary amines as experimentally observed. Charlesworth[32] stated that polymerizations of DGEBA/DDM in the presence of solvents experience intramolecular reactions prior to gelation. Interpretations were based on observations of the number-average molecular weight. Contradictions also exist in the literature. Dušek[27,37] reported that the critical conversion is nearly independent of dilution, suggesting that stiff, aromatic polymers do not experience appreciable cyclization in the early stages of the cure. Improvements in experimental measurements and theoretical calculations need to advance to resolve this issue.

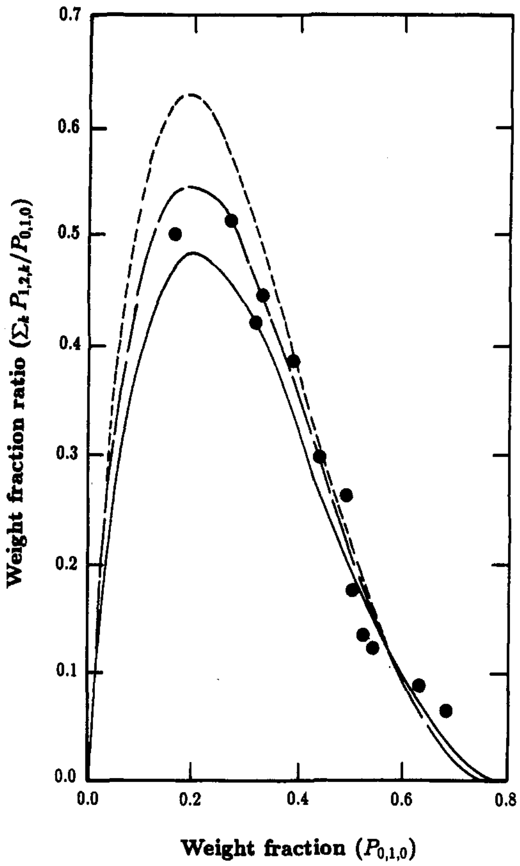

Figure 6. Theoretical and experimental relative moles of $\sum_k P_{1,2,k}$ and $P_{0,1,0}$ compared to $P_{0,1,0}$ in the system DGEBA/DDM subject to $\zeta = 2.0$ and second-order kinetics. (●) Experimental data; (—) $c_1 = 1.00$; (- -) $c_1 = 0.80$; (- - -) $c_1 = 0.60$.

DGEBA/DDM Resin. Charlesworth[32] used gel permeation chromatography to fractionate monomer, hardener and several oligomers of the resin DGEBA/DDM, including $P_{1,1,1}$, $P_{2,1,2}$, $\sum_k P_{1,2,k}$ plus higher molecular weight species, as a function of cure. The monomer, hardener, $P_{1,1,1}$ and $P_{1,2,1} + P_{1,2,0}$ peaks were large and distinct. The $P_{2,1,2}$ was relatively small and positioned such that neighboring materials severely overlapped. Data graphed in Figures 4–6 represent the relative mass concentrations of these molecules relative to the mass of the monomer. The monomer's mass diminishes with increasing conversion. Mass concentrations are defined in eqs 25 and 26. Charlesworth assumed that the FSSE was inoperative and used Stockmayer's[2] most probable distribution during analysis. These results are labeled $c_1 = 1.0$ in Figures 4–6 and were replicated in our simulations.

Noureddini[42] explored the effect of FSSE. Results of numerical simulations appear in Figures 4–6 and are labeled $c_1 = 0.6$ and 0.8. Inspection of the correlation for mass ratios for $P_{1,0,2}$ and $P_{0,1,0}$ in Figure 4 reveals that the model with FSSE improves the fit of data at higher conversions. Measurements scatter about the simulation.

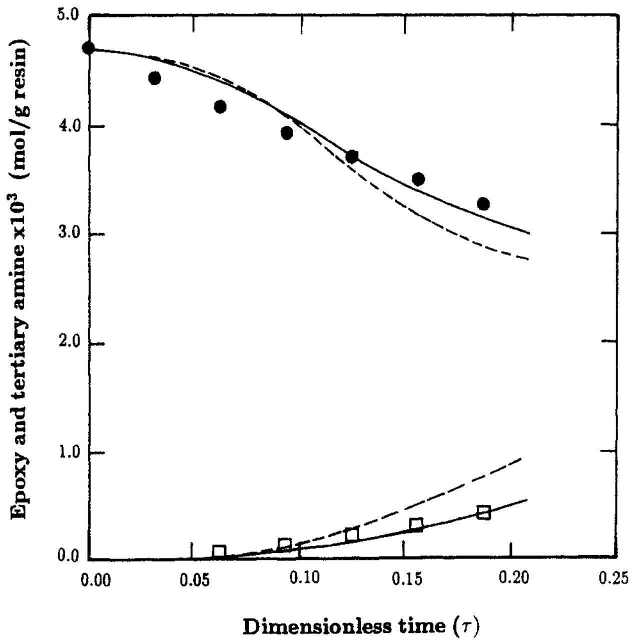

Figure 7. Numerical simulations and experimental results for epoxy groups and tertiary amines as a function of time in the system DGEBA/DDE subject to ζ - 4.0 and third-order kinetics. (●) Epoxy groups; (□) tertiary amines; (—) c_1 = 0.50; (- - -) c_1 = 1.00.

Examination of Figures 5 and 6 reveals similar improvements in the numerical data fits for oligomers. The data for the mass ratio for $P_{1,1,1}/P_{0,1,0}$ of Figure 5 are closer to the simulation with c_1 = 0.8 in the neighborhood of the maximum, as are the data of Figure 6. Simulation results are also shown for the case when c_1 = 0.6 for reference. For this resin FSSE reduced the reactivity of the secondary amine relative to the reactivity of amino hydrogens on primary amines.

DGEBA/DDE Resin. In a fourth study, Zhang[44] determined the concentration of functional groups as a function of time for the resin formulated with DGEBA/DDE. Excess oxiranes were used, ζ = 4.0. Data of Figure 7 show the fraction of oxiranes and the concentration of tertiary amines as functions of dimensionless time τ. Simulations based on third-order kinetic rate expressions suggest that the relative rate constant c_1 = 0.5.

Discussion and Conclusions

Theoretical relationships were derived describing the molar concentration of constituent resin molecules as a function of chemical composition and cure time. FSSE were explicitly considered. Equations descriptive of population density distribution dynamics and moment transients were dervied, numerically solved, and compared with experimental data. Population density distributions were shown to correlate with experimental data observed by gel permeation chromatography. Analyses showed that a first shell substitution effect was operative for the resin DGEBA/DDM. The relative rate constant based on amino hydrogens equalled 0.8. Dušek and co-worker[27,37] have reported a value of 0.4. This work was based on moment analysis for comparison. The value for the relative rate constant is similar to that for the resins DGEBA/DDA and DGEBA/HMD. For the resin DGEBA/DAB, analysis indicated that FSSE likely increased the reactivity of the amino hydrogen on the secondary amine relative to sites on primary amines, c_1 = 1.2. For the resin DGEBA/DDE analysis of epoxy groups and tertiary amines as a function of time showed that a significant FSSE was operative, c_1 = 0.5. A third-order, autocatalytic reaction was also appropriate for this resin.

Analyses were based on chemical reaction kinetics. The associated mathematics are very effective for developing molecular descriptions of complex phenomena associated with multifunctional monomers. For those cases where moment equations can be derived, analysis can be extended beyond the gel point. The potential exists for correlating mechanical performance to molecular chain topology estimated by theoretical calculations, subject to molecular feedback provided by analyses of molecules in the sol fraction.[47] Charlesworth's data demonstrated that population dynamics are very sensitive to kinetic parameters. Timm *et al.*[48] have further shown that the number-average molecular weight of the sol fraction at high extents of cure correlates with the resin's cross-link average molecular weight observed by dynamical mechanical spectroscopy. This observation is consistent with expectation theory. In the latter statistics are used to generate chain features from the kinetically calculated distribution of junction nodes. Both data sets are fundamental to the moments of the population density distribution. Chain topology plays a significant role on a material's properties at elevated temperatures. The present research illustrates that information contained in population density distributions can be interpreted analytically. Relationships 8, 9, 23, and 24, subject to model constraints, couple population density distributions to moments expressed as primary, secondary, and tertiary amines. In the present work the treelike molecules' chain topology is a function of the concentrations of secondary and tertiary amines. A secondary amine is a node for chain extension, and a tertiary amine is a branch point.

Results are consistent with model constraints and errors associated with experiments analyzed. Intramolecular and polyetherification reactions are not prevalent in the cures studied. Population density distribution dynamics and cumulative concentrations of functional sites within the resin are explicitly dependent on competing reactions. Intramolecular reactions have been explicitly addressed by Noureddini and Timm,[23] Liu *et al.*,[24] Temple,[25] and Stanford and Stepto,[26] for example. Bokare and Gandhi,[17] Gupta and Mascoko,[18] and Dušek *et al.*[19] are representative of authors that explicitly addressed competing polyetherification reactions. The quality of the data fit in Figures 3–6 shows that side reactions are minor at the stages of the cure reported. Polymerization dynamics studied reflect the number of functional sites on oligomers as well as the cumulative concentrations of sites within the resin. Likewise, the branching process has also been fundamentally addressed at the molecular level. Moments of the population density distribution, monomer, hardener, and oligomer concentrations are fundamentally dependent on network development. Gel points, for example, were observed to correlate with Charlesworth's[31] measurements. The value for c_1 = 0.8 is not sufficiently different from unity to create a measurable shift in the critical conversion,[12,13,15,16] and yet the relative distribution between primary, secondary, and tertiary amines within the resin and particularly within oligomeric molecules can be readily observed.

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Appendix

Second-Order Moments. Second-order moments are required to calculate the weight-average molecular weight. The differential equation descriptive of the $i_A{}^2$ moment was obtained by initially weighting eq 12 by the factor i_{A}^2 and adding the resultant equations. Algebraic rearrangement yields

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{Oh}^{\omega-2}\,\mathrm{d}\tau}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}^{2}p_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} = {}&\\ 2\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}&\end{aligned}\tag{28}$$

An analogous procedure may be applied to all other second-order moments. The results are summarized in eqs 29–33.

$$\begin{aligned}\frac{\mathrm{d}}{Oh^{\omega-2}\,\mathrm{d}\tau}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}i_{\mathrm{E}}p_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} = \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} +{}&\\ c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} + \{f_{\mathrm{E}}p_{0,1,0} + \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} +{}&\\ c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}&\end{aligned}\tag{29}$$

$$\begin{aligned}\frac{\mathrm{d}}{Oh^{\omega-2}\,\mathrm{d}\tau}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}kp_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} = {}&\\ -\{f_{\mathrm{E}}p_{0,1,0} + \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} \mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} +{}&\\ \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} +{}&\\ \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{A}}\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} (k-1)h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} kh''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}&\end{aligned}\tag{30}$$

$$\begin{aligned}\frac{\mathrm{d}}{Oh^{\omega-2}\,\mathrm{d}\tau}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}kp_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} = {}&\\ -\{f_{\mathrm{E}}p_{0,1,0} + \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} \mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + \{f_{\mathrm{E}}p_{0,1,0} +{}&\\ \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} (k-1)h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},K} kh''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} +{}&\\ \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}&\end{aligned}\tag{31}$$

$$\begin{aligned}\frac{\mathrm{d}}{Oh^{\omega-2}\,\mathrm{d}\tau}\{\sum_{i_{\mathrm{a}},i_{\mathrm{E}},k} i_{\mathrm{E}}^{2}p_{i_{\mathrm{A}},i_{\mathrm{E}}}k\} = {}&\\ f_{\mathrm{E}}p_{0,1,0}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} + 2\{f_{\mathrm{E}}p_{0,1,0} +{}&\\ \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} + c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} i_{\mathrm{E}}h''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}&\end{aligned}\tag{32}$$

$$\begin{aligned}\frac{\mathrm{d}}{Oh^{\omega-2}\,\mathrm{d}\tau}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k^{2}p_{i_{\mathrm{A}},i_{\mathrm{E}},k}\} = {}&\\ -\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} - 2c_1\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} kh''_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\{f_{\mathrm{E}}p_{0,10} +{}&\\ \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} \mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k} - \sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} k\mathrm{e}_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}\{\sum_{i_{\mathrm{A}},i_{\mathrm{E}},K} h'_{i_{\mathrm{A}},i_{\mathrm{E}},k} - 2\sum_{i_{\mathrm{A}},i_{\mathrm{E}},k} kh'_{i_{\mathrm{A}},i_{\mathrm{E}},k}\}&\end{aligned}\tag{33}$$

The lower case letters for functional moieties indicate that they have been normalized with respect to the initial concentration of the hardener.

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