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First Shell Substitution Effects: Diglycidyl Ether of Bisphenol A cured with 4,4'-Diaminodiphenylmethane

Hossein Nouredini

Department of Chemical Engineering, University of Nebraska-Lincoln, hnoured@unlnotes.unl.edu

Delmar C. Timm

University of Nebraska-Lincoln, dtimm1@unl.edu

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Nouredini, Hossein and Timm, Delmar C., "First Shell Substitution Effects: Diglycidyl Ether of Bisphenol A cured with 4,4'-Diaminodiphenylmethane" (1994). *Papers in Molecular Chemistry*. 6.

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ABSTRACT

First shell substitution effects were incorporated into a kinetic reaction model descriptive of the polymerization of an epoxy resin formulated from diglycidyl ether of bisphenol A and 4,4'-diaminodiphenylmethane. Analysis of population density distribution dynamics for the hardener and several oligomers in the sol fraction showed that the reactivity of secondary amino hydrogens is less than the reactivity of primary amino hydrogens.

INTRODUCTION

A chemical reaction analysis of a resin formulated with diglycidyl ether of bisphenol A (DGEBA) and 4,4'-diaminodiphenylmethane (DDM) is reported. The chemical structures of the epoxy and amine monomer are illustrated in Fig. 1. Population density distribution dynamics and the number average molecular weight as a function of conversion were originally reported by Charlesworth¹ and were correlated in this work. The kinetic reaction model incorporated intermolecular reactions subject to first shell substitution effects (FSSE) for amino hydrogen sites.^{2d}

First shell substitution effects

When FSSE are operative, the reactivity of a chemical moiety depends on the number of reacted groups on the same monomer unit but not on reaction states of other bonding sites in the molecule. FSSE have been attributed to steric and induction effects. Several studies^{1,2} have indicated different chemical reactivities for amino hydrogen atoms in primary and secondary amines. Other studies^{3,4} have indicated no departure from randomness.

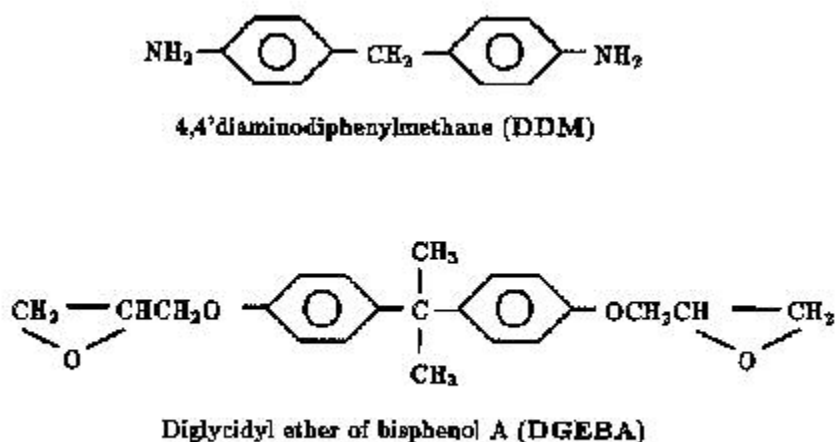


Figure 1: Chemical Structure of the DGEBA epoxy monomer and the DDM amine

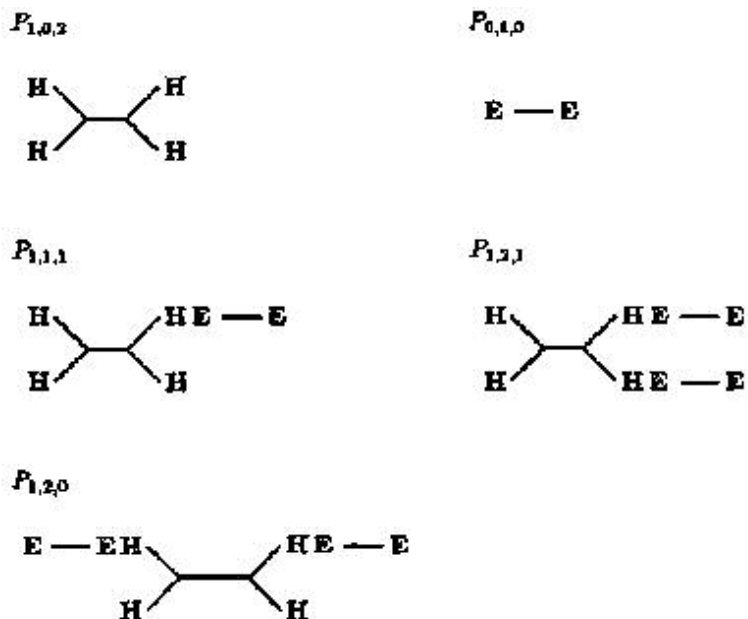


Figure 2 : Examples of monomeric and oligomeric molecules.

Discrepancies in reported rate constants are due to differences in experimental conditions and methods of calculations. Rozenberg⁹ concluded that some degree of substitution effect has been observed and that in some cases this effect can be substantial. Luiibk and DuSek¹ reported FSSE for the DGEBAIDDM resin. Bokare and Gandhi⁹ extended Macosko and Miller's⁴ method to account for different reactivities of primary and secondary amines and possible competing etherification reactions. The etherification reaction was reported to be very slow compared to the reaction of amino hydrogens with an epoxy group. Experimental investigations by DuSek et al.¹ showed that the etherification reaction does not have a significant effect when formulations contained a stoichiometric equivalent ratio for functional groups or when an excess of amines existed. Charlesworth's¹ data are also consistent with this conclusion. Charlesworth's data also imply that etherification reactions occur with excess oxiranes at high conversions. Several authors^{1,2,3} stated that epoxy sites on the monomeric DGEBA have equal reactivities. This observation was also incorporated in the current work. The difference in reactivity of hydrogen atoms of amino groups can significantly influence chain topology.¹ Aromatic amines may experience steric hindrance to the extent that primary and secondary amines react sequentially. A most probable linear chain structure initially forms with bifunctional amine and epoxy reactants. Subsequent reactions at amide sites cause crosslinking. In other resins, ladder structures form as in polyimides.

Intermolecular/intramolecular reactions

Bokare and Gandhi⁹ and DuSek¹ believe that relatively stiff-chained, aromatic based monomers do not experience appreciable intramolecular cyclization reactions during the initial phases of cure. Experimental observations indicated that the critical conversion is independent of dilution.^{1,2} However, Charlesworth¹ believed that analysis of the number average molecular weight as a function of conversion suggested that

some cyclization occurred with formulations having a balanced stoichiometric ratio of chemical moieties. One in 16 bonds was estimated to have formed by cyclization reactions at gelation. Data collected in the presence of a solvent also indicated cyclization. The current model was able to fit experimental population density distributions using intermolecular kinetic reaction rates with FSSE. FSSE have negligible effects on the correlation of the number average molecular weight as a function of conversion. Data by Charlesworth with excess oxiranes and excess amines did not indicate cyclization. Additional work may be required to resolve differences.

Autocatalytic reactions

Amine-cured epoxies can experience an autocatalytic reaction. King and Bell¹ stated that if hydroxyl moieties are tightly associated with amine or oxirane intermediates, second-order reactions dominate, otherwise third-order reactions prevail. With aromatic reactants, the resultant tertiary amines are ineffective in catalyzing polyetherification reactions. Rozenberg² attributed this to steric factors. The current work used a second-order model.

Chemical reaction analyses

Flory³ and Stockmayer⁴ laid the foundations for analyses of polymerizations with multifunctional monomers. Exact solutions were derived for population density distributions, mass fraction distributions, molecular weight averages, gel points and sol fractions for random polymerization systems. Stockmayer stated that the stochastic solution is a solution of the Smoluchowski equation which can be derived from classical chemical reaction kinetics. Using chemical reaction theory, Flory⁵ and Fukui and Yamabe⁶ also derived Poisson-type solutions for a class of polymerizations with an invariant number of propagation sites. Reaction rates were constrained to intermolecular additions, subject to equal chemical reactivities. Competing intermolecular and intramolecular reactions have also been addressed in linear⁷ and nonlinear resins. Temple⁸ and Nouredini⁹ and explicitly incorporated competing intermolecular and intramolecular reactions for polymerizations of multifunctional monomers. For linear and nonlinear polyurethanes, Gordon and Temple¹⁰ and Liu *et al.*,¹¹ respectively, have shown that intramolecular reactions can be analyzed analytically using chemical reaction theory. Data reported by Stepto and Wavwelp¹² and Stanford and Stepto,¹³ respectively, were analyzed. Semlyen¹⁴ reported the progress of simulations for several linear/cyclic resins using rate expressions based on theory developed initially by Jacobson and Stockmayer.¹⁵

REACTION MODEL

Reaction analyses are presented for polymerizations which exhibit FSSE. Model constraints incorporated the following: (1) oxirane sites react with equal probability; (2) primary and secondary amines exhibit FSSE; (3) second-order, nonautocatalytic reaction kinetics exist; (4) no intramolecular reactions occur and (5) etherification reactions are negligible. The approach coupled population density distribution dynamics with moment equations. Analyses determined relative rate constants. The dependent variable represents the molar concentration of polymeric molecules which contain iA primary amine hardener links, iE epoxy monomer 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 Fig. 2. The hardener's functionality is represented by two primary amines. A bifunctional epoxy is denoted. A sketch of a molecule emphasizes the number of primary, secondary and tertiary amines and the epoxide moieties E . Bonds are represented by --HE-- and represent, for example, --NHCH₂CHOH-- for a secondary amine.

Bonding constraints

For each degree of polymerization $i, = 1, 2, 3, \dots$, bonding constraints result the permissible number of epoxide links. A molecule with i_A hardener segments requires a minimum of $i_A - 1$ connecting epoxy links. The maximum number occurs when all amino hydrogens have reacted. This limit may be evaluated from stoichiometric considerations. Initially the i_A amine units contained for i_A sites. Each $i_A - 1$ connecting link 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:

$$i_A - 1 \leq i_E \leq 3i_A + 1 \quad (1)$$

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

$$\max \{0; i_A - i_E + 1\} \leq k \leq \min \{ \text{int}[3i_A - i_E + 1] / 2; i_A(1 + \delta_{i_E + 1}) \} \quad (2)$$

Initially, consider the choice in the lower limit. If a sufficient number of monomeric 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. 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 truncation of remainders. The second choice in the upper limit expression allows the hardener to be explicitly included in the collection of polymeric molecules. The Kronecker delta function equals unity when $i, = 0$, otherwise it equals zero. The correct upper limit is the minimum of the two numbers.

Chemical Functionality:

A polymeric molecule $P_{i_A i_E k}$ is comprised of epoxy sites $E_{i_A, i_E k}$ primary amino hydrogen sites and/or secondary amino hydrogen sites $H'_{i_A i_E k}$. Their numerical values are functions of the independent variables:

$$E_{i_A, i_E k} = i_E - i_A + 1$$

$$H'_{i_A i_E k} = 2k$$

$$H''_{i_A i_E k} = 3i_A - i_E - 2k + 1$$

Cumulative molar concentrations are functions of the respective chemical equivalences:

$$H' = \sum_{i_A, i_E, k} H'_{i_A, i_E, k} P_{i_A, i_E, k} \quad (3)$$

$$H'' = \sum_{i_A, i_E, k} H''_{i_A, i_E, k} P_{i_A, i_E, k} \quad (4)$$

$$E = \sum_{i_A, i_E, k} E_{i_A, i_E, k} P_{i_A, i_E, k} + 2P_{0,1,0} \quad (5)$$

The summation $\sum_{i_A, i_E, k}$ excludes the monomer. The limits for the summation are

$$\sum_{i_A, i_E, k} \equiv \sum_{i_A=1}^{\infty} \sum_{i_E=i_A-1}^{3i_A+1} \sum_{k=\max\{0; i_A - i_E + 1\}}^{\min\{\text{int}[3i_A - i_E + 1]; /2; i_A(1 + \delta_{i_E+1})\}}$$

Extents of reaction for amino hydrogen sites and for oxirane sites, subject to a balanced stoichiometric ratio of functionalities. equal

$$f = \frac{4P_{1,0,2}(0) - H' - H''}{4P_{1,0,2}(0)} = \frac{2P_{0,1,0}(0) - E}{2P_{0,1,0}(0)} \quad (6)$$

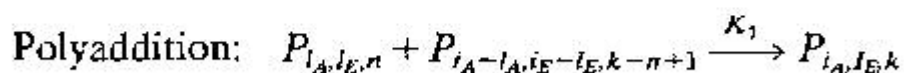
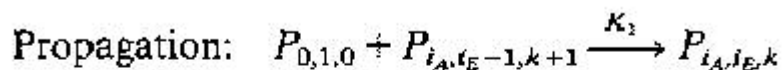
Conversion of primary amines is defined as

$$\rho_{A'} = \frac{2P_{1,0,2}(0) H'}{2P_{1,0,2}(0)} \quad (7)$$

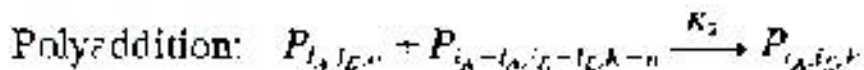
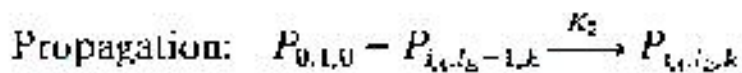
Intermolecular reactions

A molecule $P_{i,j,k}$, is formed by the union of monomeric and polymeric molecules or by the joining of two smaller polymeric molecules:

Reactions with Primary Amines



Reactions with secondary amines



Bonding constraints must be satisfied. The initial reactant is assumed to supply an oxirane and the second an amino hydrogen. The rate constants associated with the reaction of primary and secondary amines are K_1 and K_2 , respectively. Stoichiometric considerations result in subscripts.

POLYMERIZATION DYNAMICS

Monomer/hardener transients

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 are described by the relationship

$$\frac{dP_{0,1,0}}{dt} = -2P_{0,1,0}(K_1H' + K_2H'')$$

Each of the two oxiranes have the same probability of reacting with every amino hydrogen site. The hardener's dynamics were modeled by

$$\frac{dP_{1,0,2}}{dt} = -K_3E4P_{1,0,2}$$

Each epoxide in the resin, including those sites on monomeric molecules: can react with any of the four amino hydrogens. Initially, the monomer's concentration is $P_{0,1,0}(0)$ and the hardener's concentration is $P_{1,0,2}(0)$. If time is transformed to conversion space, integration yields

$$P_{0,1,0} = P_{0,1,0}(0)(1 - \rho)^2 = E^2/(2E(0)) \quad (8)$$

$$P_{1,0,2} = P_{1,0,2}(0)(1 - \rho_{AP})^2 = H'^2/(4H'(0)) \quad (9)$$

Stockmayer¹⁸ initially derived eqns (8) and (9)

Population density distribution dynamics

The differential equations characterizing the population density distribution dynamics are

$$\begin{aligned} \frac{dP_{i_a, i_b, k}}{dt} = & -K_1 E H'_{i_a, i_b, k} P_{i_a, i_b, k} - K_2 E H''_{i_a, i_b, k} P_{i_a, i_b, k} \\ & - K_1 E_{i_a, i_b, k} P_{i_a, i_b, k} H' - K_2 E_{i_a, i_b, k} P_{i_a, i_b, k} H'' \\ & + K_1 2P_{0,1,0} H'_{i_a, i_b, k-1, k+1} P_{i_a, i_b, k-1, k+1} + K_2 2P_{0,1,0} H''_{i_a, i_b, k-1, k} P_{i_a, i_b, k-1, k} \\ & + K_1 \sum_{i_a, i_b, n} E_{i_a, i_b, n} P_{i_a, i_b, n} H'_{i_a, i_b, k} P_{i_a, i_b, n-1, k+1} \\ & + K_2 \sum_{i_a, i_b, n} E_{i_a, i_b, n} P_{i_a, i_b, n} H''_{i_a, i_b, k} P_{i_a, i_b, n-1, k+1} \end{aligned} \quad (10)$$

$$P_{i_a, i_b, k}(0) = 0$$

The first two rate expressions describe reactions of primary and secondary amino hydrogens on respectively; with the resin's oxiranes. The third and fourth rate expressions describe reactions with oxiranes on primary and secondary amino hydrogens in the resin. The fifth and sixth terms denote candidate formation reactions of $P_{i_a, i_b, k}^*$, when one reactant is the monomer. The last two rate expressions address polymer/polymeric formation reactions.

Time is represented by t . The dimensions are (moles/volume)/time. Initial conditions equal zero. Rate expressions are consistent with those observed for model compounds.¹³ A FORTRAN program initially considered candidate formation reactions⁹ and wrote eqn (10) for selected $P_{j,A}$ for inspection. For example: a molecule $P_{j,A}$ can be formed only from a primary amine when $P_{j-1,A} + P_{1,A}$ couple and from a secondary amine when $P_{j-2,A} + P_{2,A}$ combine. The molecule $P_{2,3}$ can be formed from a greater number of reactions, $P_{1,3} + P_{2,3}$, $P_{1,3} + P_{1,3}$, $P_{1,3} + P_{1,3}$, $P_{1,3} + P_{1,3}$, and $P_{1,3} + P_{1,3}$, respectively. The last two reactions are distinct; the initial reactant supplies an oxirane and the second an amino hydrogen. In general, functionalities are not equal. A second numerical program incorporated the logic of the first and performed numerical integrations using a Runge-Kutta algorithm.

Moments

The cumulative molar concentrations of the several chemical moieties are functions of the leading moments of the population density distribution. The zero-order moment $P_{j,A}$ equals the cumulative molar concentration. If rate expressions in eqn (10) are arranged in the form $C P_{j,A}$, where C equals H or H^2 , or addition coupled with algebra readily yields a first-order, ordinary differential equation describing the cumulative moles as a function of time

$$\frac{d}{dt} \left\{ \sum_{j,A} P_{j,A} \right\} = - (F - 2P_{0,1,0}) (K_1 H + K_2 H^2) \quad (11)$$

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

The number of molecules diminished due to polyaddition reactions. The first-order moment $i P_{i,A}$ presents the number of amine links in the resin. This moment may be generated by weighting eqn (10) by iA . Addition coupled with algebraic simplification yields

$$\frac{d}{dt} \left\{ \sum_{j,A} i P_{j,A} \right\} = 0$$

In a closed system the total number of hardener links in the numerous molecules is invariant. Integration, subject to the initial condition, yields

$$\sum_{i_A, i_E, k} i_A P_{i_A, i_E, k} - P_{1,0,2}(0)$$

The moment $\sum_{i_A, i_E, k} i_E P_{i_A, i_E, k}$ equals

$$\frac{d}{dt} \left\{ \sum_{i_A, i_E, k} i_E P_{i_A, i_E, k} \right\} = 2P_{0,1} (K_1 H + K_2 H^2)$$

$$\sum_{i_A, i_E, k} i_E P_{i_A, i_E, k}(0) = 0$$

(12)

The equation is consistent with fundamental principles. Propagation kinetics incorporate monomer links into molecular chains. The differential equation that describes the primary amine content of the resin is

$$\frac{d}{dt} \left\{ \sum_{i_A, i_E, k} k P_{i_A, i_E, k} \right\} = -K_1 E H$$

$$\sum_{i_A, i_E, k} k P_{i_A, i_E, k}(0) = 2P_{1,0,2}(0)$$

(13)

The equation confirms that primary amines are consumed by reactions with all oxiranes.

Experimental Procedures

Charlesworth recrystallized DGEBA from methyl ethyl ketone and methanol solutions. Analysis by gel permeation chromatography (GPC) showed that the material's purity exceeded 99.5%. DDM was recrystallized from a watercharcoal decolorizing solution. Polymerizations were conducted in a forced draft oven for various times in a cure cycle comprised of 24 h at 60°C followed by 3 h at 160°C and an additional 0.5 h at 200°C. Sol fractions were obtained using chloroform in a soxhlet apparatus. Filed and crushed samples were initially swollen for 15-20 h and then leached at boiling temperatures for 24 h. The soluble fraction or sol was then subject to evaporation to remove the solvent. Number average molecular weights were determined using vapor pressure osmometry. Details are presented in the cited work. The current work analyzed oligomeric fractions reported by Charlesworth as a function of the remaining weight of the monomer, which is a function of conversion (see eqn (8)).

Results

Numerical simulations were conducted for several values for the relative rate constant c_1 . Zero- and first-order moments, equations (11)-(13), were used to evaluate the coefficients in eqn (10). The formulation was expressed by ζ :

$$c_1 = \frac{K_2}{K_1} \quad (14)$$

$$\zeta = \frac{P_{0,1,0}(0)}{P_{1,0,1}(0)}$$

Charlesworth used a GPC to fractionate the monomer, hardener and several oligomers, including $P_{0,1,0}$ and $P_{1,0,1}$, as a function of extent of cure. Their peaks on a chromatogram were large and distinct. The oligomer $P_{2,1,2}$ was relatively dilute and positioned such that neighboring materials severely overlapped. Data graphed in figures 3 to 5 represent the molar concentrations of these materials relative to the molar concentration of the monomer as a function of the mass of the monomer. As conversion increases the mass of the monomer decreases. Charlesworth assumed that FSSE were inoperative and used Stockmayer's most probable distribution for analysis. These results are labeled $c_1 = 1.0$ in Figs 3-5 and were replicated in our numerical simulations. Nouredini then explored the effect of FSSE. Illustrative results of numerical simulations appear in Figs 3-5 and are labeled $c_1 = 0.8$ and 0.6 . Inspection of the correlation for molar ratios $P_{0,1,0}/P_{1,0,1}$ in Fig. 3 reveals that the model with FSSE improves the quality of the fit at intermediate conversions where $0.2 < P_{0,1,0}/P_{1,0,1} < 0.4$. Examination of Figs 4 and 5 reveals similar improvements between theoretical predictions and experimental observations in the ratios $P_{1,0,1}/P_{0,1,0}$ and $P_{2,1,2}/P_{0,1,0}$, respectively. Substantial improvement should be noted in the areas of the maximum of Figs 4 and 5. If the three figures are considered as a set, a good estimate for the relative rate constant is 0.8. For this resin FSSE reduced the reactivity of the secondary amine relative to the reactivity of amino hydrogens on primary amines.

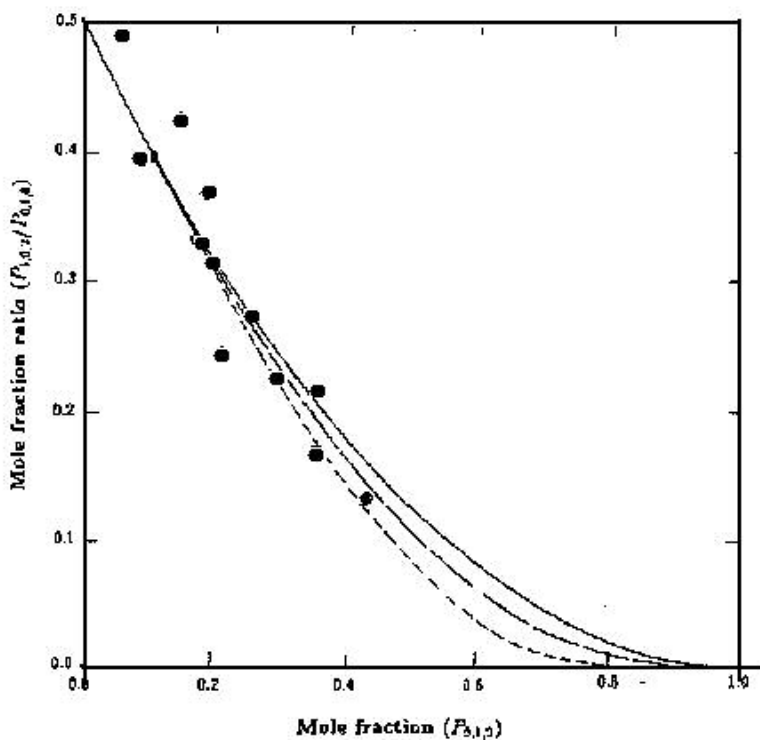


Figure 3 Hardener's molar concentration as a function of the monomer's molar concentration subject to $\zeta = 2.0$. (*), Experimental data; (—), $c_1 = 1.00$; (---), $c_1 = 0.80$; (- · - · -), $c_1 = 0.60$.

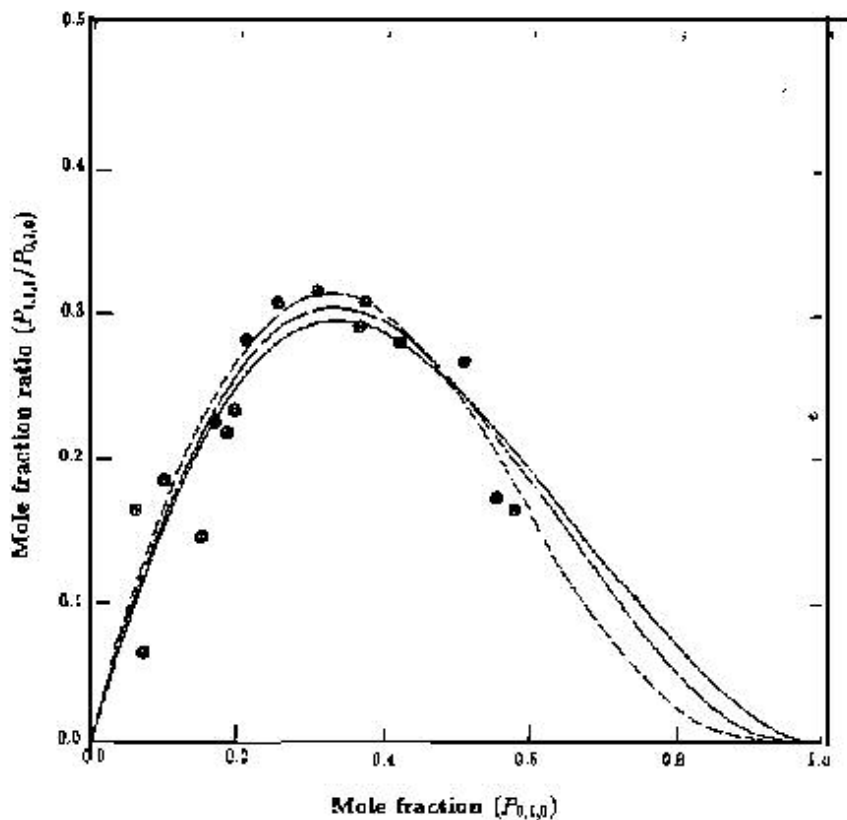


Figure 4. The dimer's molar concentration as a function of the monomer's molar concentration subject to $\zeta = 2.0$.
(•), Experimental data; (—), $c_2 = 1.00$; (---), $c_1 = 0.80$; (- - - -), $c_1 = 0.60$.

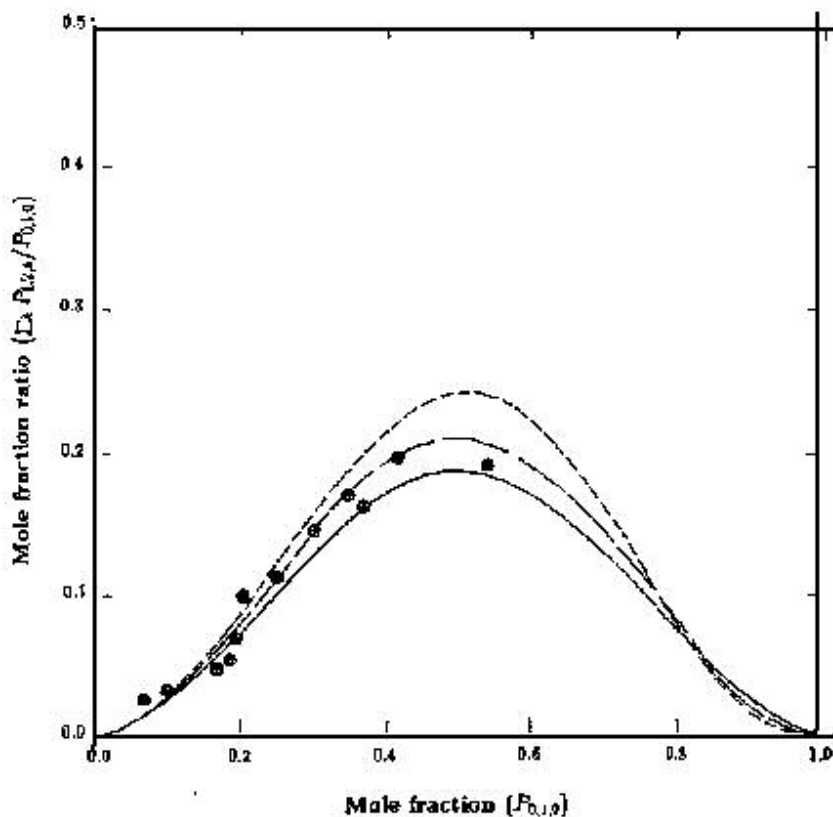


Figure 5 The cumulative molar concentration of trimers that contain one hardener link as a function of the monomer's molar concentration subject to $\zeta = 2.0$. (*), Experimental data; (—), $c_1 = 1.00$; (---), $c_1 = 0.80$; (-·-·-), $c_1 = 0.60$.

DISCUSSION AND CONCLUSIONS

Theoretical relationships were derived describing the molar concentration of constituent resin molecules as a function of chemical composition, extent of reaction or degree of cure. FSSE were explicitly considered. Equations descriptive of population density distribution dynamics and moment transients were derived specifically for the DGEBA/IDDM epoxy resin. Numerical solutions with FSSE improved the correlation of experimental population density distributions for the hardener and several oligomers. The relative rate constant based on amino hydrogens is 0.8. Secondary amines are less reactive than primary amines. Luitisk and DuSek5 used moment techniques to express the chemical concentrations of primary, secondary and tertiary amines as a function of conversion and reported a relative rate constant for FSSEs of 0.82 when expressed in terms of amino hydrogen moieties. This value is in excellent agreement with present observations. This work was supported by the Engineering Research Center and the Center for Materials Research and Analysis, University of Nebraska.

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