Macromolecules **1993,** *26,* 1369–1375

Intermolecular Reaction Kinetics for the PGE/NMA/BDMA Anhydride-Cured Epoxy

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Received May 27, 1992; Revised Manuscript Received November 17, 1992

ABSTRACT: Intermolecular reactions for a thermoplastic, epoxy resin cured with an anhydride hardener and catalyzed by a tertiary amine were studied extensively at the molecular level. The reaction mechanism described by Antoon and Koenig was condensed to two reactions: (i) a propagation reaction involving the epoxy monomer and a hydrogen-bonded carboxyl/tertiary amine and (ii) an equilibrium reaction between the hydrogen-bonded carboxyl/tertiary amine and a carboxyl/tertiary ammonium. For isothermal, batch reactions the model predicts an exponential decay for the two monomers with respect to increasing reaction time and a population density distribution of polymeric molecules described by a Poisson molar distribution. Both functions were experimentally observed. Data interpretation yielded numerical values for the propagation rate constant and for the equilibrium constant as Arrhenius functions in temperature. The concentration of initiator in the resin was also determined. Experimental measurements used the analytical capabilities of gel permeation chromatography.

Introduction

Anhydride-cured epoxies are one of a group of thermosetting resins that are used as the matrix in high-performance, fiber-reinforced composites. The polymerization is regulated by an invariant number of propagating sites. An anhydride reacts with a hydroxyl, forming a carboxylic acid, which in turn reacts with an oxirane, re-forming the hydroxyl moiety. Antoon and Koenig[1] polymerized the diglycidyl ether of Bisphenol A (DGEBA) and nadic methyl anhydride (NMA) in the presence of benzyldimethylamine (BDMA) and identified reaction intermediates with Fourier transform infrared spectroscopy (FTIR). Based on spectral observations, previously proposed reaction mechanisms, including those of Tanaka and co-workers,[2] Luston et al.,[3] and Fischer,[4] were updated. Reaction mechanisms had assumed that the initiation step produces an unsaturated alcohol. There was no spectral evidence to support this specific reaction when both monomers are present; however, the mechanism does describe the polyether polymerization when NMA is not present.[1]

Linear polymeric chains develop in the presence of monofunctional epoxides, anhydrides, and initiators. Except for the propagation site, these polymeric molecules are void of reactive moieties. A Poisson molar distribution describes the population density distribution. The Poisson distribution is distinct from the most probable distribution,[5,6] which describes a random, intermolecular polymerization. For the former, a maximum occurs in the population density distribution at a degree of polymerization nearly equal to the number-average degree of polymerization. The number-average and weight-average molecular weights are approximately equal. A small excess of one of the reactants will have a minor effect on the final molecular weight of the resin near 100% conversion. The ultimate molecular weight is dependent on the initial ratio of the concentrations of the limiting monomer and the initiator. The excess monomer will not react but will simply become a diluent or plasticizer within the resin. Multifunctional initiators yield starlike molecules, also distributed by Poisson molar distributions.[7] Sequential batch polymerizations with aliphatic and aromatic monomers, for example, yield block copolymers. On the other hand, the most probable distribution has a maximum in the population density distribution at a degree of polymerization of one. The weight-average molecular weight is twice the number-average molecular weight. For random polymerizations a small excess in one of the chemical moieties drastically limits the ultimate molecular weight. Finally, a sequentual batch polymerization will yield random copolymers.[5]

The current research provides a comprehensive, kinetic analysis of an anhydride-cured epoxy resin constrained to intermolecular reactions. The formulations used phenyl glycidyl ether (PGE), NMA, and BDMA. The initiator was 2-ethylhexanol (I). The kinetic reaction analysis incorporates the reaction mechanism described by Antoon and Koenig[1] and yields theoretical descriptions for the rate of monomer decay and the distribution of polymeric molecules at the time observation. Results show excellent agreement between theory and observation. The population density distribution is described by a Poisson molar distribution, indicating that the reaction models developed by Flory[8] and Fukui and Yamabe[9] are applicable to this resin system. Monomeric epoxides may be multifunctional. Experimental analysis incorporated molecular characterizations of monomeric, oligomeric, and polymeric fractions obtained by gel permeation chromatography (GPC).[10,11]

Reaction Mechanism. Antoon and Koenig[1] reported that the dominant, linear molecule in the reaction media has the basic structure $A_k\overset{-}{A}\overset{+}{C}$. The specific formula for this compound and formulas for the several molecules identified in the FTIR spectra appear in Table I. Inspection of Table I reveals that the left chain end of polymeric molecules is assumed to have formed from the initiator (R″OH). The repeating links in a chain are contained in braces and are comprised of coupled anhydride and epoxide units. The formed bond is an ester. Degree of polymerization is k. This fraction of a molecule is simply referenced as A_k in the acronym. Since a dissociated alcohol's structure has been totally defined, an alcohol of size k is simply represented by A_k. A hydrogen-bonded alcohol/catalyst is represented by A_kC. Inspection of formulas for other polymeric molecules and

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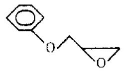
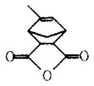
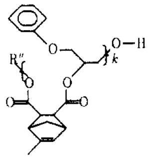
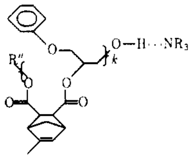
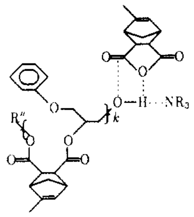
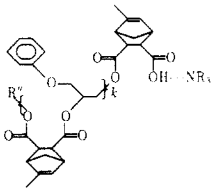
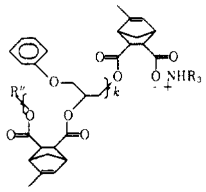
Table I
Abbreviated Notation and Chemical Formulas

Phenyl glycidyl ether	E	
Nadic methyl anhydride	A	
Dissociated alcohol	A_k	
Hydrogen-bonded hydroxyl complex	A_kC	
Tertiary amine/ epoxide/anhydride, transition state	A_kCA	
Hydrogen-bonded carboxyl/ tertiary amine	A_kAC	
Carboxyl/ tertiary ammonium	$A_k\overset{-}{A}\overset{+}{C}$	

intermediates in Table I reveals that the right chain end is explicitly represented by the remaining fraction of the chemical acronym. Specifically, the dominant molecule $A_k\overset{-}{A}\overset{+}{C}$ contains a terminal carboxyl/tertiary ammonium, which was referred to as a carboxylate/quaternary amine by Antoon and Koenig.[1] The anhydride unit is represented by A and the catalyst by C. Electrical charges are explicitly represented. The notation can be readily manipulated mathematically in the derivation of the kinetic reaction model describing the cure.

The polymerization is described by the following sequence of reactions. The tertiary amine catalyst C and initiator R″OH or A_0 (i.e., Table I, A_k, $k = 0$) initially form a hydrogen-bonded hydroxyl intermediate A_0C:

$$A_0C \overset{K_1}{\rightleftharpoons} A_0 + C$$

The anhydride monomer A rapidly reacts with the hydrogen-bonded hydroxyl A_0C, forming a transition state intermediate A_0CA, a tertiary amine/epoxide/anhydride complex described in Table I. The transition intermediate experiences rapid rearrangement, forming a hydrogen-bonded carboxylic acid/tertiary amine A_0AC. The latter is in a state of equilibrium with a carboxyl/tertiary ammonium $A_0\overset{-}{A}\overset{+}{C}$. This sequence is described by a series of reactions:

$$A + A_0C \xrightarrow[\text{fast}]{k_2} A_0CA \xrightarrow[\text{fast}]{k_3} A_0AC \overset{K_5}{\rightleftharpoons} A_0\overset{-}{A}\overset{+}{C}$$

The rate-limiting step involves the insertion of the epoxide monomer E into the propagating, hydrogen-bonded acid oligomer A_0AC. The product is a hydrogen-bonded alcohol of degree of polymerization one, A_1C. The dissociated alcohol A_1 is in a state of chemical equilibrium with A_1C:

$$A_0AC + E \xrightarrow[\text{slow}]{k_4} A_1C \overset{K_1}{\rightleftharpoons} A_1 + C$$

Similar reactions involving higher molecular weight intermediates are represented by the sequence

$$A + A_kC \xrightarrow[\text{fast}]{k_2} A_kCA \xrightarrow[\text{fast}]{k_3} A_kAC \overset{K_5}{\rightleftharpoons} A_k\overset{-}{A}\overset{+}{C}$$

$$A_kAC + E \xrightarrow[\text{slow}]{k_4} A_{k+1}C \overset{K_1}{\rightleftharpoons} A_{k+1} + C$$

$$A + A_{k+1}C \xrightarrow[\text{fast}]{k_2} A_{k+1}CA \xrightarrow[\text{fast}]{k_3} A_{k+1}AC \overset{K_5}{\rightleftharpoons} A_{k+1}\overset{-}{A}\overset{+}{C}$$

Kinetic Reaction Model

The analysis was constrained to isothermal, isometric, batch polymerizations. Antoon and Koenig[1] assumed a stationary state for all intermediates. The current work is fundamentally interested in the distribution of molecules comprising the resin. The reaction mechanism constraints were modified by assigning the rate-limiting step, the propagation reaction involving the epoxy monomer. This constraint is consistent with FTIR spectra. The alcohol is rapidly consumed during the early stage of the cure. Reversible reactions are assumed to be at a state of equilibrium. The carboxyl/tertiary ammoniums and the alcohols are terminated, nonreactive products. The tertiary amine catalyst is very selective when both the anhydride and epoxide are present. Esterification and etherification reactions are absent.[1,2,4] The low concentration of alcoholic ends eliminates cyclization reactions by transesterification. Flory[12] further noted that although the carboxyl group is capable of promoting transesterification reactions, the rate of reaction is several times less than the rate associated with alcoholysis. Random chain scission by hydrolysis was eliminated by maintaining a dry environment.

Equilibrium constraints result in algebraic relationships for molecules containing a hydrogen-bonded hydroxyl/tertiary amine and a carboxyl/tertiary ammonium, respectively:

$$(A_kC) = K_1(C)(A_k)$$

$$(A_k\overset{-}{A}\overset{+}{C}) = K_5(A_kAC) \tag{1}$$

Elementary reaction kinetics result in relationships descriptive of the dynamics of hydrogen-bonded hydroxyl complexes and of tertiary amine/epoxide anhydride/transition states:

$$d(A_{k+1}C)/dt = k_4E(A_kAC) - k_2A(A_{k+1}C)$$

$$d(A_{k+1}CA)/dt = k_2A(A_{k+1}C) - k_3(A_{k+1}CA)$$

Stationary-state approximations, $d(A_{k+1}C)/dt = 0$ and $d(A_{k+1}CA)/dt = 0$, plus algebraic simplification yields

$$k_4E(A_kAC) = k_2A(A_{k+1}C) = k_3(A_{k+1}CA)$$

Population Density Distributions. The rate-limiting step yields a set of first-order, ordinary differential equations:

$$d(A_kAC)/dt = k_3(A_kCA) - k_4(A_kAC)E = k_4(A_{k-1}AC)E - k_4(A_kAC)E \tag{2}$$

The initial conditions, $A_0AC(0) \neq 0$ and $A_kAC(0) = 0$ for $k = 1, 2, 3, \ldots$, are consistent with constraints of the reaction mechanism. At $k = 0$, the intermediate $(A_{-1}AC)$ does not exist. Dimensionless time τ results in a set of equations with constant coefficients:

$$d\tau = k_4E\,dt \tag{3}$$

$$\mathrm{d}(\mathrm{A}_k\mathrm{AC})/\mathrm{d}\tau = (\mathrm{A}_{k-1}\mathrm{AC}) - (\mathrm{A}_k\mathrm{AC})$$

Integrations used the integrating factor $\exp(\tau)$ and yield a Poisson molar distribution:[8,9]

$$(\mathrm{A}_k\mathrm{AC}) = (\mathrm{A}_0\mathrm{AC}(0))\frac{\tau^k \exp(-\tau)}{k!}$$

Equation 1 also reveals that the carboxyl/tertiary ammoniums are also distributed according to a Poisson distribution.

The measured polymer concentration P_k equals the sum of the concentrations of the hydrogen-bonded carboxyl intermediates and the carboxyl/tertiary ammoniums at a specific degree of polymerization. Therefore,

$$P_k = (\mathrm{A}_k\mathrm{AC}) + (\mathrm{A}_k\overset{-}{\mathrm{A}}\overset{+}{\mathrm{C}}) = (1 + K_5)(\mathrm{A}_k\mathrm{AC})$$

and

$$P_k = P_0(0)\frac{\tau^k \exp(-\tau)}{k!} \tag{4}$$

The concentration of 2-ethylhexanol and impurities that initiate the reaction are described by $P_0(0)$. Initiators were assumed to be monofunctional since a single Poisson molar distribution was observed. For multifunctional initiators, the definition of dimensionless time can be modified to incorporate the initiator's functionality.[7] Star-shaped polymers form. Molar concentrations will be described by Poisson distributions.

Moments. The Poisson molar distribution forms absolutely convergent moments; therefore, limits of convergence are unique. The cumulative molar concentration of polymeric molecules is invariant:

$$\sum_{k=0}^{\infty} P_k = P_0(0)$$

This expression satisfies eq 2. It also can be derived with the aid of eq 4. Recall that the series $\sum \tau^k/k!$ equals $\exp(\tau)$. Higher order moments are a function of dimensionless time. They may be conveniently derived by initially weighting eq 2, forming the series $\sum k^n\, \mathrm{d}P_k/\mathrm{d}t \equiv \mathrm{d}(\sum k^n P_k)/\mathrm{d}t$, for $n = 1, 2$. Algebraic rearrangement and integration yield

$$\sum_{k=0}^{\infty} kP_k = P_0(0)\tau$$

$$\sum_{k=0}^{\infty} k^2P_k = P_0(0)(\tau^2 + \tau)$$

Monomer Concentration. The concentration of PGE is represented by E moles/gram of resin. The set of parallel, propagation reactions results in an expression for monomer concentration that predicts an exponential decay:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -k_4E\sum(\mathrm{A}_k\mathrm{AC}) = \frac{-k_4EP_0(0)}{1 + K_5}$$

$$E = E(t^*)\exp\left(-\frac{k_4P_0(0)}{1 + K_5}(t - t^*)\right) \tag{5}$$

The time to initially achieve an isothermal state during the cure is t^* and the monomer concentration at that time is $E(t^*)$. The moles of NMA reacted equal the moles of PGE reacted plus the moles of initiator consumed when the initiator contains a hydroxyl site.

Experimental Section

Formulations of PGE/NMA/BDMA/I were of a molar ratio of 10/10/0.1/0.01, respectively. Industrial-grade reactants were supplied by Brunswick Defense. Materials were stored in the presence of a desiccant. After formulation the resin was divided into a number of samples of approximately 5 mL. The glass vials were sealed with screw-top lids. They were initially at room temperature. The sealed samples were placed on a wire rack in a preheated, electric oven with forced air circulation. Temperature was controlled to within ±0.5 °C of the set point and was uniform within the oven. Samples were withdrawn at predetermined times and were thermally quenched at −25 °C. Analyses of the original formulation and of each partially cured sample were performed by gel permeation chromatography (size exclusion chromatography).

A Waters Associates high-pressure liquid chromatograph was equipped with three μ-Styragel columns of size 100, 100 and 500 Å. Tetrahydrofuran was the solvent and was pumped at 0.01 mL/s. Samples of 0.075 of partially cured resin were dissolved in 50 mL of solvent. One-half milliliter of this solution was injected into the chromatograph. Output from a Waters differential refractometer was recorded by an interfaced Digital LSI-11 microcomputer. Refractive index is linear in mass concentration. Linear polymers made from PGE/NMA/BDMA/I were also used for calibration standards. Their respective number-average molecular weights were determined by vapor pressure osmometry after monomer had been removed.[10] Interpretation followed the procedure developed by Adesanya et al.[11] Overall calibration curves suggested that the molecules dissociated from the catalyst during the analysis and were likely of the form $\mathrm{A}_k\mathrm{A}$. This molecule is similar to the hydrogen-bonded carboxyl/tertiary amine in Table I, but it is void of the catalyst end ...NR_3.

Results

Monomer Dynamics. The GPC software[11] utilized stored data sets of normalized chromatograms for each monomer. A linear least squares algorithm compared the jth normalized chromatogram $W_{i,j}$ for a sample in the elution volume region i where monomer elutes with mass fraction α_k weighted standards $S_{i,k}$ for each of the k monomers, $\sum_i\sum_{k=1}^{2}(W_{i,j} - \alpha_kS_{i,k})^2$. A stepping algorithm readily converged, yielding best estimates for numerical values for the mass fractions. Material balances, subject to sample preparation and operating procedures, converted mass fractions to concentrations, expressed as moles of monomer per gram of resin. Data confirm the expected exponential decay, eq 5. The product $k_4P_0(0)/(1 + K_5)$ was determined at four reaction temperatures. Figure 1, a semilogarithmic correlation of monomer concentration as a function of time, illustrates. Results appear in Table II. The anhydride monomer NMA also exponentially decayed. The intercepts of Figure 1 reflect the experimental procedure. A cold sample was placed in the oven. A period of time was required to achieve cure temperature. For the higher set point temperatures, a greater level of conversion occurred during the nonisothermal segment. However, even at 120 °C a relatively small amount of monomer reacted during this period. Temperature dependence has been removed from the population density distribution analysis by using dimensionless time τ.

At high conversions, deviations between experimental concentrations and theoretical predictions became apparent but are not reported. Antoon and Koenig[1] noted that a changing dielectric constant during cure could have a pronounced effect on equilibrium. Reversible chemical reactions should also be addressed. Population density distribution analysis for reversible esterification reactions incorporating hydrolysis or transesterification have been addressed by Blatz and Tobolsky[14] and Flory,[12] respectively. Random chain scission ultimately results in the most probable population density distribution. Monomer

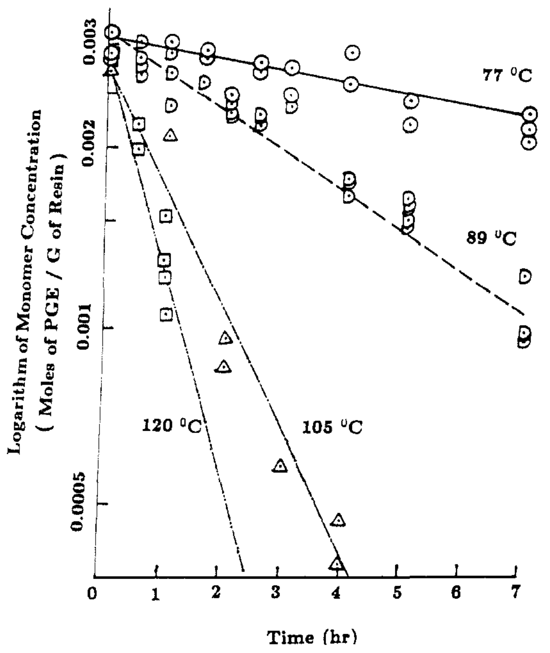


Figure 1. Monomer concentration decay.

Table II
Summary of Experimental Data

T (K)	monomer concn $E(0)$ [mol/(g of resin)]	monomer decay[a] (1/h)	conv[b]
350	0.00310	0.0453	0.0344
362	0.00305	0.160	0.0302
378	0.00284	0.482	0.0143
393	0.00307	0.872	0.0107

T (K)	propagation kinetics k_4 [(g of resin)/(mol h)]	equilib constant K_5
350	425	0.34
362	1740	0.55
378	11900	2.53
393	26500	3.35

[a] $=k_4P_0(0)/(1+K_5)$. [b] $=[k_4P_0(0)/(1+K_5)][1/k_4E(0)]$.

is considered to be polymeric and becomes the molecule with the greatest molar concentration. Chromatographic analysis has documented chain degradation in thermosets after extensive curve periods; dynamic mechanical spectroscopy showed corresponding changes in the complex modulus. At high conversions, most probable distributions were observed for cross-linked resins formulated with DGEBA/NMA/BDMA,[15] although Poisson-type distributions were observed initially.[16] Competing reactions and chemical and mass transport factors dependent on the changing environment during cure will ultimately have to be integrated into kinetic reaction models capable of describing the state of cure at high levels of conversion.

Poisson Molar Concentrations. The numerical algorithm that interpreted the polymeric fraction within the resin was based on the constraint of a Poisson molar distribution.[7,10] Adesanya et al.[11] correlated the logarithm of molecular weight $\mathrm{MW}_{i,j}$ as a function of solvent volume increment VE_i for the jth sample:

$$\log \mathrm{MW}_{i,j} = A_j - B_j\,\mathrm{VE}_i \tag{6}$$

The theoretical weight fraction $W_k(\tau)$ equals the product of molecular weight and population density distribution:

$$W_k(\tau) = (\mathrm{MW}_0\,k + \mathrm{MW}_1)P_k(\tau) \tag{7}$$

The molecular weight of the chain link MW_0 is the sum of the molecular weights for PGE and NMA. The initiator and an anhydride link contribute an additional MW_1.

The theoretical, number-average, and weight-average molecular weights were expressed in terms of dimensionless time. Experimentally, moments were observed as functions of elution volume VE_i:

$$\mathrm{MW}_\mathrm{n} = \frac{\sum_{k=0}^{\infty}\mathrm{MW}_k\,P_k(\tau)}{\sum_{k=0}^{\infty}P_k(\tau)} = \mathrm{MW}_0\,\tau + \mathrm{MW}_1$$

$$= \frac{1.0}{\sum_{i=i_\mathrm{min}}^{i_\mathrm{max}} W_{i,j}/\mathrm{MW}_{i,j}} \simeq \frac{\exp(\mathrm{A}_j)}{\sum_{i=i_\mathrm{min}}^{i_\mathrm{max}} W_{ij}\exp(B_j\,\mathrm{VE}_i)}$$

$$\mathrm{MW}_\mathrm{w} = \frac{\sum_{k=0}^{\infty}\mathrm{MW}_k^{\,2}\,P_k(\tau)}{\sum_{k=0}^{\infty}\mathrm{MW}_k\,P_k(\tau)} = \frac{\mathrm{MW}_0^{\,2}(\tau^2+\tau) + 2\,\mathrm{MW}_0\,\mathrm{MW}_1\,\tau + \mathrm{MW}_1^{\,2}}{\mathrm{MW}_0\,\tau + \mathrm{MW}_1}$$

$$= \frac{\sum_{i=i_\mathrm{min}}^{i_\mathrm{max}}\mathrm{MW}_{i,j}\,W_{i,j}}{1.0} \simeq \exp(A_j)\sum_{i=i_\mathrm{min}}^{i_\mathrm{max}} W_{i,j}\exp(-B_j\,\mathrm{VE}_i) \tag{8}$$

The polymer fraction elutes in the solvent volume interval $i_\mathrm{min} \le i \le i_\mathrm{max}$. Polydispersity is an implicit function of the calibration curve's slope B_j:

$$\frac{\mathrm{MW}_\mathrm{w}}{\mathrm{MW}_\mathrm{n}} = 1 + \frac{\mathrm{MW}_0^{\,2}\tau}{\mathrm{MW}_0^{\,2}\,\tau^2 + 2\,\mathrm{MW}_0\,\mathrm{MW}_1\,\tau + \mathrm{MW}_1^{\,2}}$$

$$\simeq \sum_{i=i_\mathrm{min}}^{i_\mathrm{max}} W_{i,j}\exp(-B_j\,\mathrm{VE}_i)\sum_{i=i_\mathrm{min}}^{i_\mathrm{max}} W_{i,j}\exp(B_j\,\mathrm{VE}_i) \tag{9}$$

A numerical search for the best estimate of τ, A_j, and B_j, given a normalized chromatogram $W_{i,j}$ for a sample, was programmed. Initially, the overall calibration curve, the semilogarithmic correlation of the number-average molecular weight of each polymer standard as a function of its peak elution volume, was used to estimate the sample's average molecular weight. An initial estimate of dimensionless time τ was determined using eq 8. A Newton convergence technique was used with eq 9 to evaluate B_j. The number-average molecular weight was then solved for A_j. To obtain best estimates, the objective function $\sum_{i_\mathrm{min}}^{i_\mathrm{max}}(W_k(\tau)|_i - W_{i,j})^2$ was minimized as a function of τ. The GPC calibration allowed the theoretical weight fraction $W_k(\tau)$ to be evaluated as a function of elution volume $W_k(\tau)|_i$. The trial value for τ was used to evaluate the weight fraction $W_k(\tau)$ at each degree of polymerization k. The calibration curve, eq 6, converted the molecular weight at τ to elution volume space. The least squares objective function compared the theoretical and experimental weight fraction distributions in elution volume space. The initial estimate of τ has proven to be a good estimate. The slope of the overall calibration curve near the sample's peak volume provided an initial estimate for the slope B_j.

Illustrative results are presented by Figure 2. Two weight fraction distributions are presented as a function

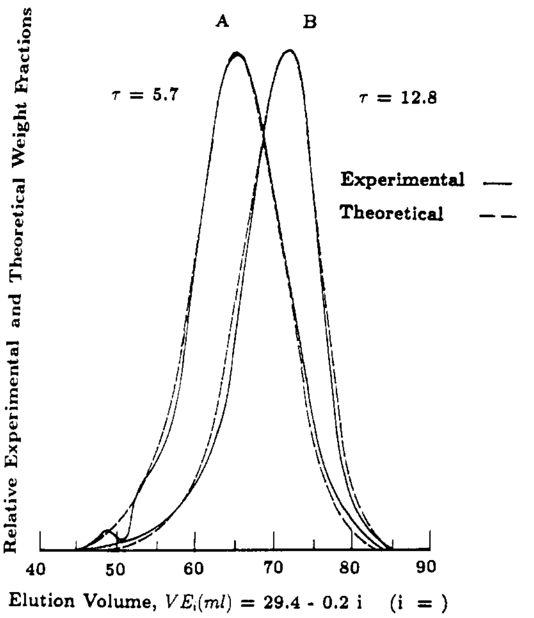


Figure 2. Experimental chromatograms: (A) 2-h cure at 89 °C; (B) 3-h cure at 120 °C.

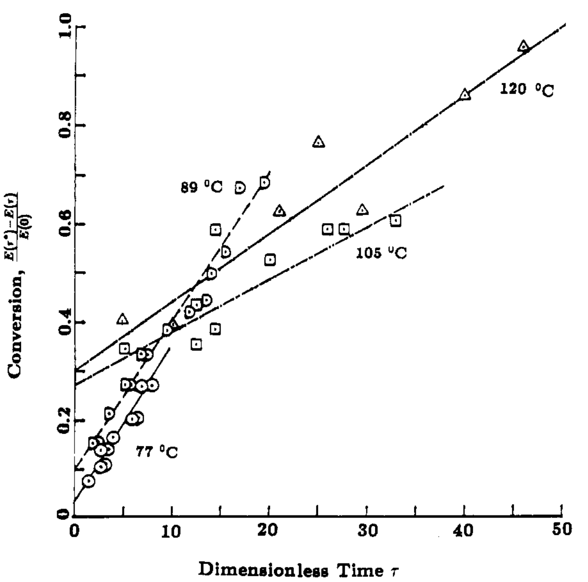


Figure 3. Conversion as a function of dimensionless time τ.

of elution volume. Higher molecular weight material is excluded from a greater fraction of the pores within the packing and, therefore, elutes at lower solvent volumes. Dimensionless times for the two chromatograms are 5.7 and 12.8, respectively. The latter corresponds to an average molecular weight of approximately 4000. The ordinate of the graph is relative for each sample. The relative scale enables one to emphasize the correlation between theory and experimental observation. Excellent fits were observed. The polymer molecules are distributed according to Poisson molar distributions.

Propagation Rate Constant. Experimental measurement of dimensionless time and extent of reaction allowed for the calculation of the rate constant k_4 as an Arrhenius function of temperature. Integration of eq 3 with the aid of eq 5 yields

$$\frac{E(\tau^*) - E(\tau)}{E(0)} = \frac{1}{E(0)} \frac{k_4 P_0(0)}{1 + K_5} \frac{1}{k_4}(\tau - \tau^*) \qquad (10)$$

Data are correlated in Figure 3. The constant $E(\tau^*)$ is the monomer concentration after the reaction temperature had equilibrated. Initially, the resin was formulated with a monomer concentration $E(0)$. The slope of the correlation is of fundamental interest. Results are given in Table II in columns labeled "conversion" and "propagation kinetics", respectively. Data were fit using a least-squares algorithm. The intercepts again reflect the initial, nonisothermal segment of the cure. The resultant Arrhenius diagram for the rate constant is presented in Figure 4. The frequency factor equals 1.87 × 10^{19} (g of resin/mol)/h and the activation energy equals 26 600 cal/mol.

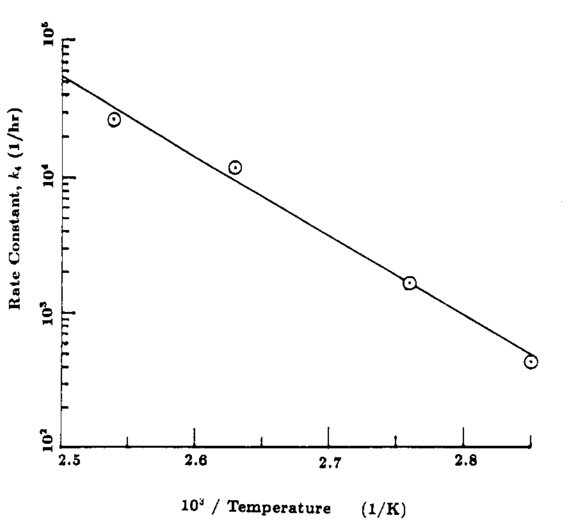


Figure 4. Arrhenius diagram for the rate-limiting reaction.

$$k_4 = 1.87 \times 10^{19} \exp(-26600/RT)$$

Initiator Concentration. The concentration of the initiator was determined from the ratio of the mass of polymer formed and the monomer's concentration.

$$\frac{\sum \mathrm{MW}_k P_k}{\mathrm{MW}_A A + \mathrm{MW}_E E} \simeq \frac{(\mathrm{MW}_0 \tau + \mathrm{MW}_1) P_0(0)}{\mathrm{MW}_0 E(0) \exp(-k_4 P_0(0) t/(1 + K_5))}$$

In excess of 60 samples were averaged, yielding an average initiator concentration:

$$P_0(0) = (1.43 \pm 0.49) \times 10^{-4} \text{ mol/g of resin}$$

The formulations incorporated 3 × 10^{-6} mol/g of resin of the initiator 2-ethylhexanol. Therefore, a major source for initiation was contaminants present in the raw materials. Industrial-grade reactants were stored in the presence of desiccants to minimize moisture concentration. Polymerizations were also conducted[7] using reagent-grade chemicals supplied by Aldrich, including 1,2-epoxy-3-phenoxypropane, methyl-5-norbornene-2,3-dicarboxylic anhydride, *N*,*N*-dimethylbenzylamine, and 2-ethyl-1-hexanol. Additional initiators supplied by Fisher Scientific included ethylene glycol, glycerol, and pentaerythritol. Similar results were obtained, confirming that the major initiator was an unknown contaminant. The multifunctional initiators were selected to make star-type polymers with two to four branches, but the level of contaminant initiators negated results.

Equilibrium Constant. Experimental measurements were sufficient to calculate the equilibrium constant K_5. Data are given in Table II for four isothermal experiments and are summarized by Figure 5, an Arrhenius diagram. Analysis resulted in the following expression:

$$K_5 = 1.15 \times 10^{10} \exp(-17000/RT)$$

The activation energy is 17 000 cal/mol. The equation is dimensionless.

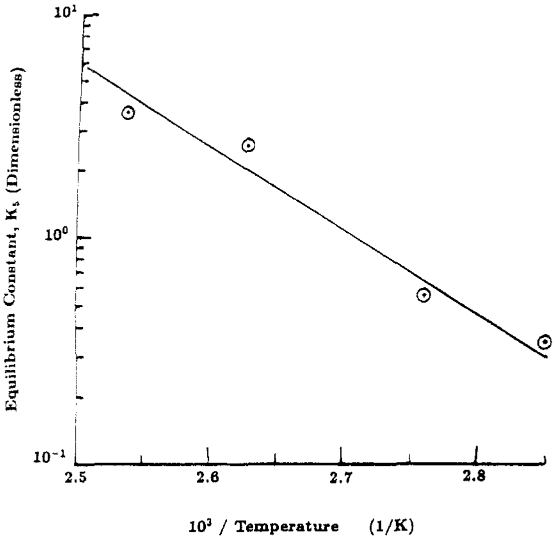


Figure 5. Arrhenius diagram for the equilibrium reaction.

Discussion and Conclusions

Gel permeation chromatography is an effective analytical tool for the molecular characterization of a curing, thermoplastic epoxy resin. Fractionations allow for the determination of the concentration of each monomer and the population density distribution of polymeric molecules. Results and theory are in agreement. Monomers decay exponentially and population density distributions are Poisson distributions. The constants associated with the kinetic reaction model were evaluated, providing numerical values for the frequency factors and the activation energies for the rate-limiting propagation step and the equilibrium constant. The concentrations of initiators within the resin were also determined. The predominant initiator was an impurity present in the raw materials. The chromatographic equipment was not configured to measure intermediates, and, therefore, other models capable of yielding Poisson molar distributions[10] were not discriminated.

The derived kinetic reaction model condensed the intermolecular reaction mechanism of Antoon and Koenig[1] into an equilibrium reaction and a propagation reaction. The equilibrium reaction is analogous to a reversible, termination reaction. Inspection of eqs 3 and 4 reveals a mathematically equivalent reaction mechanism:

$$\mathrm{d}(P_k)/\mathrm{d}t = k_4 E(\mathrm{P}_{k-1} - \mathrm{P}_k)$$

and

$$\mathrm{P}_k + \mathrm{E} \rightarrow \mathrm{P}_{k+1}$$

This reaction satisfies the kinetic reaction analysis described by Flory.[8] Fukui and Yamabe[9] addressed ring-opening, intermolecular reactions with multifunctional oxiranes using an analogous reaction. The current research demonstrates that their kinetic reaction analysis of a branching polyether is applicable to the polymerization of multifunctional epoxides with monofunctional anhydrides, subject to the constraint of intermolecular reactions.[13] The model increases in complexity since the number of propagation sites and the number of chain-dependent epoxies on a reactant must be described. A three-dimensional variable $P_{i,j}$ may be selected. A molecule contains i epoxy monomer units and j reacted oxiranes. The notation is implicit in time. The dimensionless time variable originally defined[9] must be modified to $\tau = k_4 P_{0,0}(0)t/(1 + K_5)$. The variable $P_{0,0}(0)$ represents the initial initiator concentration. Fukui and Yamabe[9] provided analytical solutions for monomer concentration, population density distributions, conversion, and the critical conversion for gelation. However, one should note that intramolecular reactions were not explicitly incorporated into the model.

Acknowledgment. Financial support for the research was contributed by the University of Nebraska's Center of Materials and Measurement and the Engineering Research Center.

Nomenclature

A	anhydride, mol/g of resin
A_j	GPC calibration constant, dimensionless
A_k	$(\mathrm{AE})_k$ links in the polymeric chain or a polymeric alcohol
$(\mathrm{A}_k\mathrm{AC})$	hydrogen-bonded carboxylic acid/tertiary amine, mol/g of resin
$\left(\mathrm{A}_k\overset{-}{\mathrm{A}}\overset{+}{\mathrm{C}}\right)$	carboxyl/tertiary ammonium, mol/g of resin
$\mathrm{A}_k\mathrm{C}$	a chain terminated by a hydrogen-bonded hydroxyl
$\mathrm{A}_k\mathrm{CA}$	a chain terminated by a transition state intermediate
B_j	GPC calibration constant, 1/mL
C	BDMA catalyst, mol/g of resin
d	differential operator
E	epoxy monomer, mol/g of resin
I	initiator, mol/g of resin
k	degree of polymerization
K_5	equilibrium constant, dimensionless
k_4	rate-limiting kinetic constant, (g of resin/mol)/h
MW_k	molecular weight of P_k
MW_n	number-average molecular weight
MW_w	weight-average molecular weight
MW_0	molecular weight of the epoxy plus anhydride
MW_1	molecular weight of the initiator plus anhydride
$\mathrm{MW}_{i,j}$	experimental molecular weight, g of resin/mol
P_k	polymer molecules $(\mathrm{A}_k\overset{-}{\mathrm{A}}\overset{+}{\mathrm{C}})$ + $(\mathrm{A}_k\mathrm{AC})$, mol/g of resin
R	gas constant, 1.987 cal/(mol K)
$S_{i,j}$	GPC calibration standards, mass fractions
T	absolute temperature, K
t	time, h
t^*	time required to achieve reaction temperature, h
VE_i	GPC elution volume, mL
$W_k(\tau)$	theoretical Poisson weight fraction distribution
$W_{i,k}$	GPC weight fraction distribution, kth standard
Greek Letters	
α_k	weight fraction, kth GPC standard
τ	dimensionless time
Subscripts	
i	GPC elution volume
j	GPC sample number
k	degree of polymerization
k	GPC standard number

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