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Fourier-Transform Infrared Analysis of a Linear, Anhydride-Cured Epoxy

R. Tadros and D. C. Timm*

Department of Chemical Engineering, University of Nebraska, Lincoln, Nebraska 68588-0126

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ABSTRACT: A linear-chained epoxy resin was formulated from phenyl glycidyl ether and nadic methyl anhydride catalyzed by benzyldimethylamine. Intermolecular polymerizations were modeled as a parallel set of propagation reactions. Fourier-transform infrared spectroscopy was used to determine the concentrations of the oxirane, anhydride, and ester moieties within the resin as a function of time for two isothermal cures. Data analyses yielded the propagation rate constant as a function of temperature and the initiator's concentration, including contributions from impurities within the resin. Results compared favorably with measurements on fractionated resins, using gel permeation chromatography. Population density distributions are described by Poisson molar distributions for this resin.

Introduction

Anhydride-cured epoxies are used as the matrix in high-performance, fiber-reinforced composites. Antoon and Koenig[1] used Fourier-transform infrared spectroscopy (FTIR) to identify reaction intermediates for the polymerization of the diglycidyl ether of Bisphenol A (DGEBA) and nadic methyl anhydride (NMA), catalyzed by benzyldimethylamine (BDMA), and updated prior reaction mechanisms.[2−4] Nielsen et al.[5] polymerized phenyl glycidyl ether (PGE), NMA, and BDMA, a linear-chained resin analog. In their analyses the reaction mechanism was condensed to (i) the rate-limiting propagation reaction that involves an oxirane and a hydrogen-bonded carboxyl/tertiary amine and (ii) an equilibrium reaction between the hydrogen-bonded carboxyl/tertiary amine and a carboxyl/tertiary ammonium. Subject to isothermal cures in a batch reactor, the monomer PGE decayed exponentially in time and polymeric molecules were described by a Poisson molar distribution, as predicted by chemical reaction theory. Fractionations were performed by gel permeation chromatography (GPC). Monomeric and polymeric fractions were interpreted by the analytical method described by Adesanya et al.[6]

Flory[7] initially derived the Poisson population density distribution function for resins composed of linear-chained molecules. Fukui and Yamabe[8] derived Poisson-type distribution functions for nonlinear, branched polymeric chains derived from multifunctional monomers. Derivations were based on principles of chemical reaction kinetics. Fukui and Yamabe specifically addressed polyethers, but the results of Nielsen et al.[5] demonstrated that their derivations are also applicable to the DGEBA/NMA/BDMA epoxy resin.

The current research continues the comprehensive, kinetic analyses of the anhydride-cured resin PGE/NMA/BDMA. The study coupled analytical capabilities of GPC and FTIR. Objectives of the research were to measure concentrations of several chemical moieties analytically and to integrate observations into a chemical reaction analysis using moment techniques. Consistency checks between data sets obtained by the FTIR and the GPC were made. The results of the research imply that fractionated, nonlinear, oligomeric and polymeric molecules contained within the sol fraction of a thermoset could be characterized by their chemical entities. This information could result in the comprehensive, molecular characterizations of intractable thermosets. Narrow fractions of the soluble molecules could be described in terms of their average degree of polymerization, extent of chain branching, and the number of cyclic chain configurations. When coupled with kinetic reaction models, this knowledge could be used to define kinetic rate expressions and model parameters for competing intermolecular and intramolecular condensations. The polymerization model could then be used to predict molecular chain features within the intractable gel fraction that determine mechanical performance.[9−11]

Authors have illustrated the potential for molecular analysis of thermosets. Stockmayer[12] described the molar concentrations of molecules formed from blends of monomers with distinct chemical functionalities. Mathematical descriptions of the population density distributions, chemical compositions, average molecular weights, and the gel points were given, subject to the constraints of intermolecular reactions and equal chemical reactivities. Nouredini et al.[13] explicitly addressed first shell substitution effects. Experimental population density distribution dynamics reported by Charlesworth[14] for the resin DGEBA and 4,4′-diaminodiphenylmethane were analyzed. Analyses of several oligomeric fractions revealed that the reactivity of the primary amines was distinct from the reactivity of the secondary amines. In a second study Stanford and Stepto[15] polymerized hexamethylene diisocyanate and a triol propylene oxide adduct of ethylene glycol. Intramolecular reactions were present at the earliest conversions observed. The ring fraction within the curing resin was determined. Since the molecular weight of the triol was large, the hydroxyls experienced equal chemical reactivities. Liu et al.[16] analyzed these data, determining the rate constant for intramolecular reactions relative to the rate constant for intermolecular reactions. A simplified first-order rate expression that incorporated the chemical functionality of the limiting chemical moiety was used.

In linear resins, chain cyclization is a function of the degree of polymerization of the reactant.[17,18] In branched systems, this rate expression requires simulations to incorporate all chemical isomers of a specified chemical

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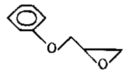
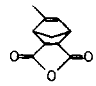
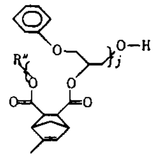
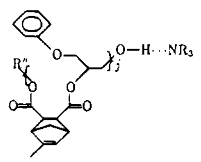
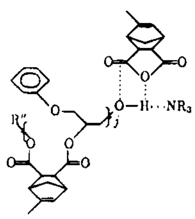
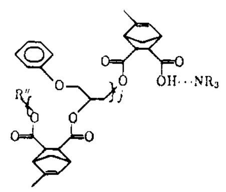
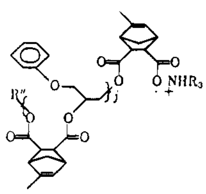
[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

Table 1. Abbreviated Notation and Chemical Formulas

Phenyl glycidyl ether	E	
Nadic methyl anhydride	A	
Dissociated alcohol	A_j	
Hydrogen-bonded hydroxyl complex	A_jC	
Tertiary amine/epoxide/anhydride transition state	A_jCA	
Hydrogen-bonded carboxyl/tertiary amine	A_jAC	
Carboxyl/tertiary ammonium	$A_j\bar{A}\overset{+}{C}$	

composition. Temple[19] developed numerical simulations for cyclization reactions which addressed the chain configuration for a monomer of functionality 3. The rate expression explicitly incorporated the degree of polymerization of the cyclic configuration and the number of independent reactions that could form this cyclic configuration. Liu et al.[16] also fit these simulations using the simplified kinetic rate expression. Essentially the same rate constants as used by Temple were determined. In thermosets, chemical moieties that form nearest neighbors, dominate intramolecular, cyclization reactions. Functional groups are not isolated at chain end positions as in the linear systems. Results are consistent with theory. The rate of formation of small cyclic configurations is the dominant reaction.

The resin DGEBA/NMA/BDMA may experience intramolecular reactions. Molecules contain chain pendent oxiranes and chain terminal carboxylic acids. However, chain cyclization reactions are absent for the PGE/NMA/BDMA resin since pendent oxiranes are absent and one chain end is chemically inert. A molecule has the basic structure $I(-AE_j) - AH$. The initiator contributes I segments, and the terminal carboxylic acid is represented by $-AH$. Chains are composed of coupled anhydride/epoxy links $-AE$.

Kinetic Reaction Model

Reaction Mechanism. Antoon and Koenig[1] described a probable reaction sequence for the initial part of the cure. Chemical structures and acronyms are defined in Table 1. The repeating link is contained in braces. Alcohols R″OH or A_0 (i.e., Table 1, A_j, $j = 0$) were assumed to initiate the polymerization. Hydrogen-bonded hydroxyl complexes A_jC are in a state of chemical equilibrium with dissociated alcohol moieties A_j and the tertiary amine catalyst C:

$$A_jC \rightleftharpoons A_j + C$$

Hydrogen-bonded hydroxyl intermediates rapidly combine with an anhydride A, forming tertiary amine/epoxy/anhydride transition states A_jCA, which rearrange, forming hydrogen-bonded carboxyl/tertiary amines A_jAC:

$$A + A_jC \xrightarrow{\text{fast}} A_jCA \xrightarrow{\text{fast}} A_jAC \overset{K}{\rightleftharpoons} A_jA^-C^+$$

The hydrogen-bonded carboxyl/tertiary amines are the propagation sites. They are also in a state of chemical equilibrium with carboxyl/tertiary ammoniums $A_jA^-C^+$, the dominant nonreactive compounds present. The rate-limiting reaction combines the oxirane with the hydrogen-bonded carboxylic acid/catalyst, re-forming alcohols of degree of polymerization $j + 1$:

$$A_jAC + E \xrightarrow{k'} A_{j+1}C \rightleftharpoons A_{j+1} + C$$

Antoon and Koenig[1] and Nielsen et al.[5] assumed that the hydrogen-bonded hydroxyl catalyst complex and the carboxyl/tertiary ammonium were at equilibrium, respectively. The material balances for the hydrogen-bonded hydroxyl complexes and the tertiary amine/alcohol/anhydride/transition states were subjected to stationary-state approximations. Subject to these constraints, the set of reactions can be represented by propagation and equilibrium kinetics:

$$d[A_jAC]/dt = k'[A_{j-1}AC]E - k'[A_jAC]E$$

$$[A_jA^-C^+] = K[A_jAC]$$

Poisson Molar Distributions. In dilute solutions, the experimental, dependent variable P_j equals the sum of the molar concentrations of the carboxyl/tertiary ammoniums and the hydrogen-bonded carboxyl intermediates at a specific degree of polymerization j.

$$P_j = [A_jAC] + [A_jA^-C^+]$$

Therefore, the set of parallel propagation reactions can be effectively expressed by[5]

$$P_{j-1} + E \xrightarrow{k} P_j \qquad \text{where } j = 1, 2, 3, \ldots$$

The rate constant k equals $k'/(1 + K)$. Kinetic rate expressions are

$$\frac{dP_j}{dt} = kE(P_{j-1} - P_j)$$

and

$$\frac{dE}{dt} = -kE\sum_{j=0}^{\infty} P_j$$

The population density distribution is described by a Poisson molar distribution:

$$P_j = P_0(0)\frac{\tau^j \exp(-\tau)}{j!} \qquad (1)$$

The concentration of the initiator plus impurities that supply propagation sites initially is represented by $P_0(0)$. Poisson molar distributions are also produced by anionic polymerizations.[20-23] Dimensionless time τ is defined by

$$d\tau = kE\,dt \qquad (2)$$

The rate constant for the second-order, rate-limiting reaction is k; epoxy monomer concentration is E, and time is represented by the variable t.

Moments. Moments of the population density distribution are absolutely convergent; therefore, limits of convergence are unique. The cumulative molar concentration of polymeric molecules in the reactor is invariant:

$$\sum_{j=0}^{\infty} P_j = P_0(0) \qquad (3)$$

The cumulative molar concentration of chain links within the polymeric fraction of the resin is a linear function of dimensionless time:

$$\sum_{j=0}^{\infty} jP_j = P_0(0)\tau \qquad (4)$$

The second-order moment of the distribution is

$$\sum_{j=0}^{\infty} j^2P_j = P_0(0)(\tau^2 + \tau) \qquad (5)$$

The breadth of the distribution approaches unity with increasing τ:

$$\frac{\mathrm{MW_w}}{\mathrm{MW_n}} = \frac{\sum_{j=0}^{\infty} j^2P_j}{\sum_{j=0}^{\infty} jP_j}\,\frac{\sum_{j=0}^{\infty} P_j}{\sum_{j=0}^{\infty} jP_j} = 1 + 1/\tau$$

Monomer Dynamics. Monomer concentration decays exponentially in time

$$E = E(0)\exp(-kP_0(0)t) \qquad (6)$$

and is linear in dimensionless time:

$$E = E(0) - kP_0(0)\tau$$

Experimental Section

Resin Formulation and Cure. Formulations of PGE/NMA/BDMA/I were of a molar ratio of 10/10/0.1/0.1, respectively. Aldrich Chemical Co. supplied the raw materials, 1,2-epoxy-3-phenoxypropane, methyl-5-norbornene-2,3-dicarboxylic anhydride, dimethylbenzylamine, and 2-ethyl-1-hexanol, respectively. Materials were stored at 0 °C in the presence of a desiccant. A formulation was subdivided into glass vials of about 5 mL and sealed with screw-top lids. They were cured in an electrically heated oven with forced air circulation. Temperature control was within ±0.5 deg of the set temperature. Samples were withdrawn and thermally quenched.

FTIR Analyses. A Nicolet 510P FTIR spectrometer, a Spectra-Tech 620 beam condenser, and a Spectra-Tech ZnSe zero dead volume flow cell plus software were used to characterize samples collected from an isothermal, batch reactor. The solvent was carbon tetrachloride. Solutions contained 0.075 g of resin/50 mL of solvent. The resin was composed of monomeric and polymeric molecules.

Analyses were based on overlapping bands in which more than one functional group absorbs over the frequency range of interest. Nicolet's software was used, and therefore, the details of the algorithms are proprietary, but an algorithm based on a least squares objective function and a regression using the steepest descent method would be effective.[24] Standards were raw materials and epoxy polymers characterized in our laboratories in terms of their number average molecular weights.

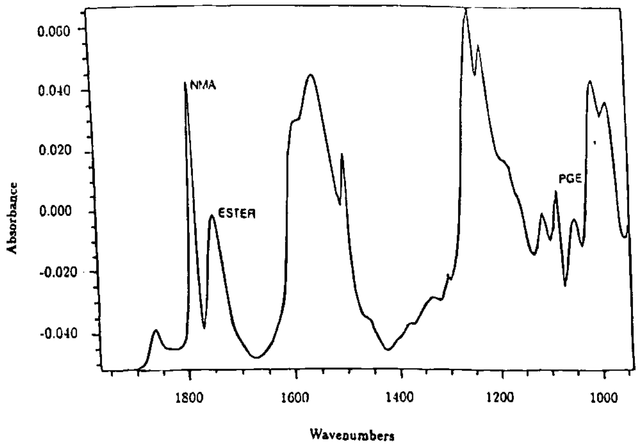


Figure 1. Characteristic groups for PGE/NMA/BDMA/I resin.

Chemical Moieties. A dissociated polymer of degree of polymerization j contains $2j + 1$ ester bonds, a terminal carboxylic acid, and an initiator fragment. Its molecular weight is $\mathrm{MW}_j = \mathrm{MW_{IH}} + (j + 1)\mathrm{MW_A} + j\mathrm{MW_E}$ where the molecular weights are those of the initiator, anhydride, and epoxy, respectively. The epoxy and anhydride bands correlate with the unreacted monomers. Antoon and Koenig[1] and Bellamy[25] recommend the bands 1089−1070, 1766−1706, and 1799−1766 cm^{-1} for the epoxy, ester, and anhydride, respectively. The number of ester moieties in the polymeric fraction is

$$\begin{aligned} \text{ester} &= \sum_{j=0}^{\infty}(2j + 1)P_j \\ &= (2\tau + 1)P_0(0) \\ &= 2(A(0) - A) - P_0(0) \qquad (7) \end{aligned}$$

The last equation is a consequence of stoichiometry. A chain terminal anhydride residue is linked to the chain by one ester bond. All of the other anhydride links are connected by two esters. The cumulative concentration of chain ends is $P_0(0)$. Equations 3 and 4 yield the relationship in dimensionless time.

GPC Fractionations. A Waters Associates high-performance liquid chromatograph was equipped with 2 × 100, 500, 1000, 10 000 Å μ-Styragel columns. Tetrahydrofuran (THF) was pumped at 0.01 mL/s. One-half milliliter samples of 0.075 g of resin/50 mL of THF were injected. A Waters differential refractometer was interfaced to a Gateway 2000, 486 personal computer. A Keithley MetraByte DAS-16 data acquisition board enabled chromatograms to be numerically recorded. The chromatograph was automated with respect to sample injection with the aide of a DDA-06 digital/analog board and in-house software and hardware. Data analyses[5,6] yielded the concentration of monomers and the mass of the polymer.

Results

FTIR Calibration. A spectrum for the resin after 8 h of cure at 80 °C is presented by Figure 1. Approximately 35% of the monomer had reacted. Bands for the anhydride, oxirane, and ester are indicated. Spectra in Figure 2 demonstrate that the anhydride band decreased and that the ester band increased as the time for reaction increased. Three spectra are superimposed. The reaction time increased from spectrum 1 to spectrum 3. A similar graph, Figure 3, presents data for the epoxy or oxirane moiety. Calibrations yielded correlations similar to Figure 4, a linear correlation of the area of the anhydride's absorption

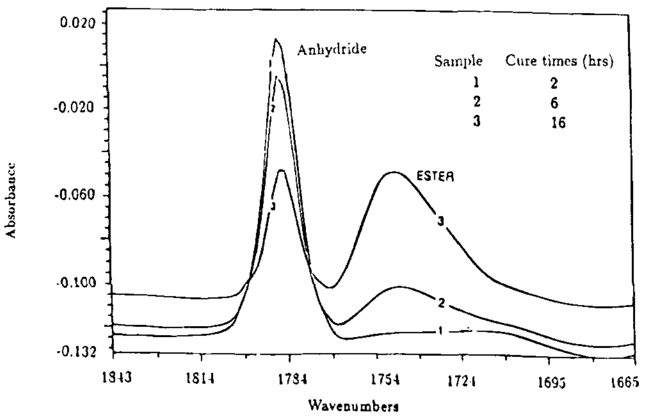


Figure 2. IR spectra showing ester bonds forming and anhydride bonds decaying with time at 80 °C.

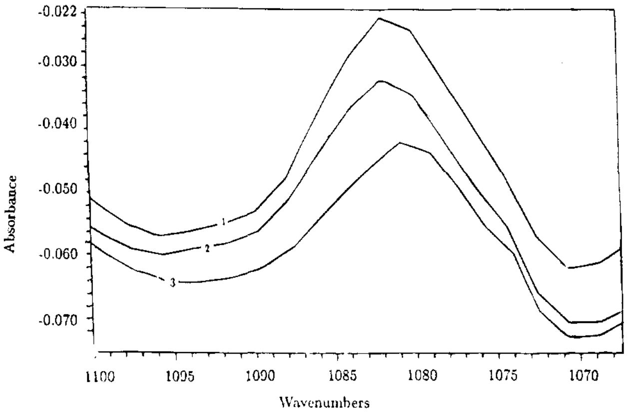


Figure 3. IR spectra showing PGE bonds decaying with time at 80 °C.

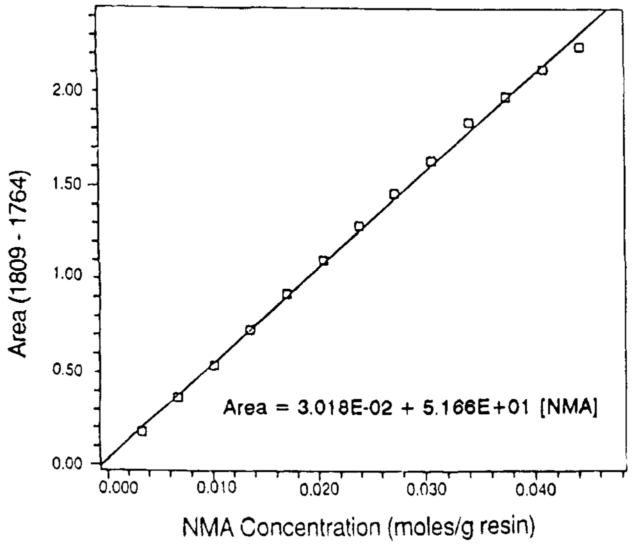


Figure 4. Calibration curve for NMA using area in CCl_4.

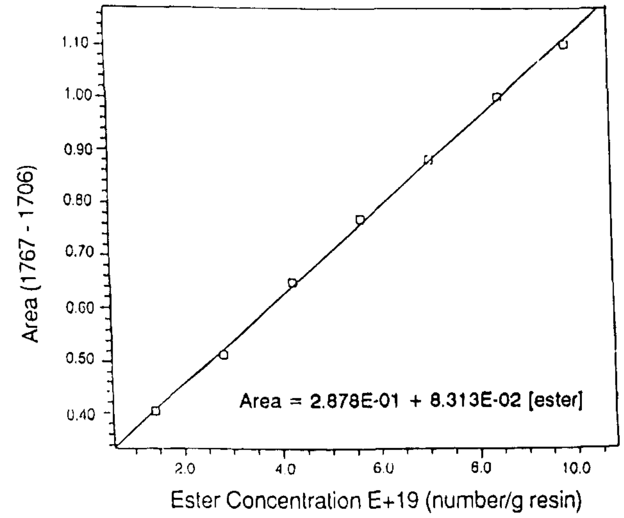


Figure 5. Calibration curve for ester using area in CCl_4.

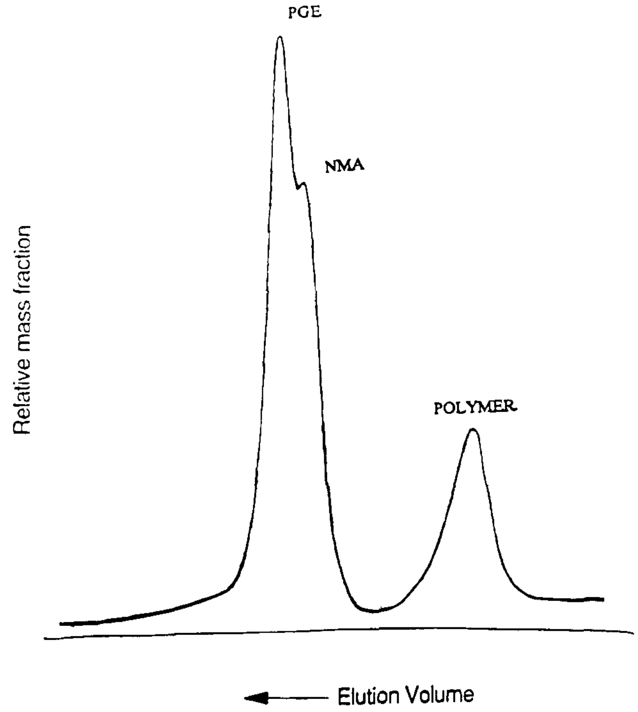


Figure 6. GPC chromatogram for cure resin at 80 °C for 6 h.

band in the wavelength interval 1809–1764 cm^{-1} as a function of the anhydride's concentration. Ester standards were prepared using different concentrations of the resin cured for 12 h at 120 °C. The intensity of absorption in the wavelength interval 1767–1706 cm^{-1} as a function of concentration can be observed in Figure 5. A linear calibration was also observed for the oxirane moiety. Analyses of the band 3573–3563 cm^{-1} indicated that the hydroxyl content of the resin rapidly disappeared. It had not reappeared after 7 h of cure at 90 °C. This had also been observed by Antoon and Koenig.[1] The carboxylic acid is the dominant end group on polymeric chains. The propagation reaction is limited by the insertion of the oxirane moiety.

GPC Calibration. Fractionations separate the resin into polymeric and monomeric regions. Figure 6 illustrates. The area of the chromatogram is proportional to mass concentration. The abscissa is related to the volume of carrier solvent eluting from the chromatograph. The anhydride and epoxy monomers overlap. The algorithm developed by Adesanya[6] decomposed the monomeric fraction into the molar concentration of each monomer. Results confirmed molar concentrations obtained by FTIR analysis.

Monomer Dynamics. Monomer concentrations were determined as a function of reaction time from the absorption bands assigned to the anhydride and the oxirane moieties. Data were graphed in accordance with eq 6 in Figure 7, a semilogarithmic correlation of concentration as a function of reaction time. After an initial delay associated with warming the sample from ambient temperature to the reaction temperature of 80 °C, an exponential decay was observed. A similar

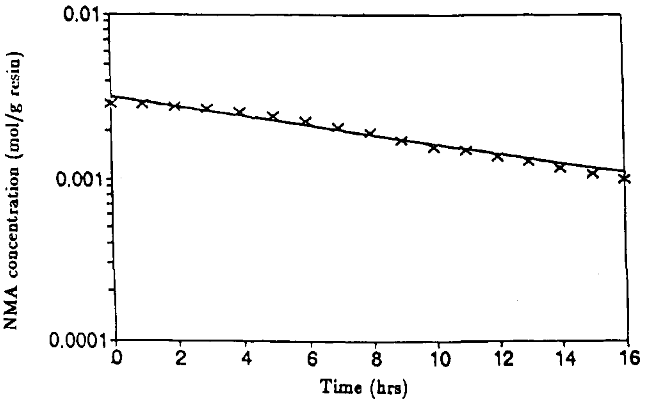


Figure 7. NMR decay between 1 and 16 h at 80 °C in CCl_4.

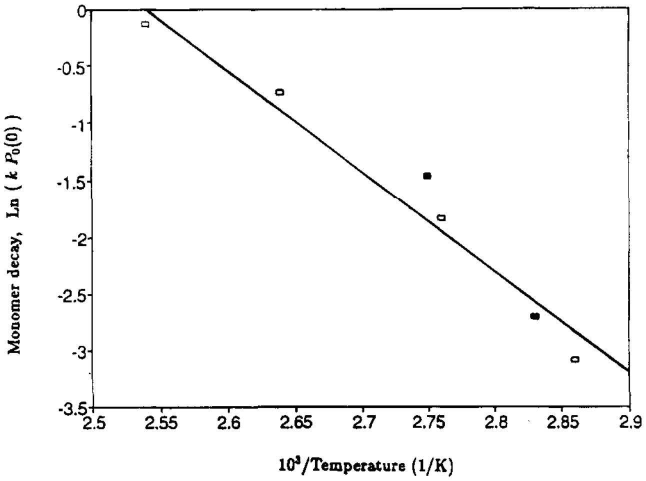


Figure 8. Arrhenius diagram for the rate-limiting reaction.

Table 2. Data for an Arrhenius Diagram

T (K)	$kP_0(0)$ (1/h)	$10^3/T$	$\ln(kP_0(0))$
350[a]	0.0453	2.86	−3.094
353[b]	0.067	2.83	−2.703
362[a]	0.160	2.76	−1.832
363[b]	0.232	2.75	−1.461
378[a]	0.482	2.64	−0.730
393[a]	0.872	2.54	−0.137

[a] Nielsen et al.[5] [b] This work.

correlation was also observed with isothermal data collected at 90 °C.

The slope of the semilogarithmic correlation yields the product of the rate constant and the initiator concentration, including impurities. The data for two isothermal experiments are graphed in Figure 8 with data previously reported by Nielsen et al.[5] Data are tabulated in Table 2. Satisfactory agreement was observed.

Initiator Concentration. Equation 7 provides a means for determining the concentration of the initiator, including impurities. FTIR analyses provided the cumulative concentration of ester bonds in the resin as a function of time. A linear fit of the data of Figure 9 indicated that the effective initiator concentration was 2.6×10^{-4} mol/g of resin. Data are tabulated in Table 3. Contaminants are a major source of initiators.

Discussion and Conclusions

FTIR spectroscopy is an effective method for quantifying the state of cure in polymeric systems. A procedure based on the concentration of ester bonds and the extent of reaction for the anhydride was demonstrated to be effective in measuring the initiator's concentration. Contaminants in the formulation contributed significantly to the initiation step. Specifically, the actual initiator's concentration (2.6×10^{-4} mol/g of resin) can be compared to that formulated (3×10^{-6} mol/g of resin). The product of the rate constant and initiator concentration for the propagation reaction at two temperatures was determined. Results were consistent with data reported by Nielsen et al.[5] The effective propagation rate constant equals $k = 9.3 \times 10^{13} \exp(-18700/RT)$ (g of resin/mol)/h. The gas constant $R = 1.987$ (cal/g mol)/K. The research demonstrated that analytical results can be achieved for the oxirane, anhydride, and ester moieties in unfractionated, curing systems. The former two chemical groups correlate with the monomers' dynamics. Antoon and Koenig[1] previously demonstrated the FTIR's effectiveness in studies of reaction mechanisms by identifying chemical intermediates.

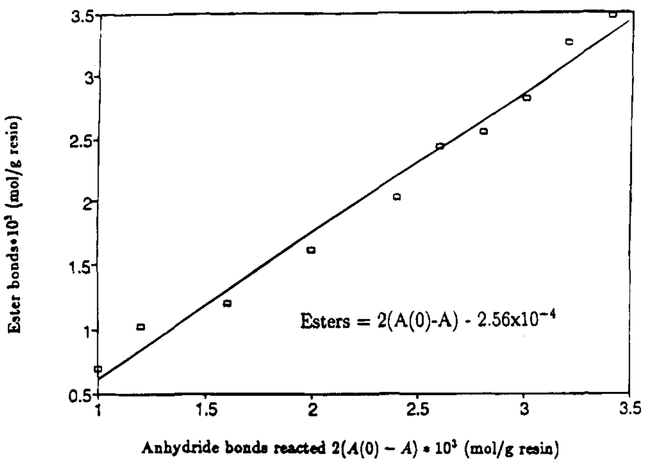


Figure 9. Determination of initiator concentration.

Table 3. Data for Evaluation of the Initiator's Concentration[a]

ester bonds × 10^3 (mol/g of resin)	$2(A(0) - A) \times 10^3$ (mol/g of resin)
0.69	1.00
1.02	1.20
1.20	1.58
1.61	2.00
2.03	2.39
2.34	2.55
2.56	2.79
2.82	3.00
3.19	3.24
+3.40	+3.67
20.86	23.42

[a] $P_0(0) \times 10^3 = (23.42 - 20.86)/10 = 0.256$.

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