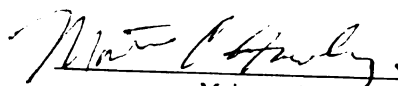




This is to certify that the
dissertation entitled
**Bulk-phase Kinetics and Physical Properties of
Apoxy-amine Systems**

presented by
Mark Christopher Finzel

has been accepted towards fulfillment
of the requirements for
Ph.D. degree in Chem. Engineering


Major professor

Date May 16, 1991.



PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
JUL 06 1995 JUL 06 1995	_____	_____
JUL 29 1999	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

MSU Is An Affirmative Action/Equal Opportunity Institution

c:\circ\datedue.pm3-p.1

BULK-PHASE KINETICS AND PHYSICAL PROPERTIES OF EPOXY/AMINE SYSTEMS

By

Mark Christopher Finzel

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1991

ABSTRACT

BULK-PHASE KINETICS AND PHYSICAL PROPERTIES OF EPOXY/AMINE SYSTEMS

By

Mark Christopher Finzel

The bulk-phase kinetics of an epoxy (DGEBA)/amine (DDS) thermoset have been studied using DSC, FTIR, and C-13 NMR. In the absence of catalyst, the reaction was found to involve a main exothermic reaction between epoxide and amine hydrogen and a side reaction between tertiary amine formed by the main reaction and epoxide. The side reaction had no discernable exotherm. Etherification did not appear to be significant. DSC was used for studying the main reaction kinetics. FTIR provided corroborating evidence. An IR band previously unused followed the amine hydrogen concentration. NMR confirmed the above mechanism by indentifying the formation of quaternary ammonium ion. Crosslinks formed in the main reaction are linkages between amine nitrogen and the terminal CH_2 group in the epoxy chain. These are the only crosslinks which influence the glass transition temperature. The side reaction results in the formation of a quaternary ammonium/alkoxide ion pair and does not result in the production of a true crosslink. The rate constant for the main reaction was found to depend upon reaction temperature, glass transition temperature, hydroxide concentration, and initial amine concentration. It involved an uncatalyzed part (second order) and an autocatayzed part including hydroxide concentration (third order). The side

reaction was second order. Dielectric properties change during cure due to changes in the relaxation mechanism and broadening of the distribution of relaxation times as the extent of cure increases. Glass transition temperature increases during cure due primarily to the reduction in mobility of chain-ending groups as crosslinks form.

This dissertation is fondly dedicated to my mother and father.

I FINALLY MADE IT!

ACKNOWLEDGEMENTS

The author would like to thank Kermit Johnson of the Max Rogers NMR Facility (MSU Chemistry Department) for running the NMR spectra.

Two undergraduates named Tom Kern (T_g measurements) and Mary Beth Pierce (FTIR scans) helped with the experimental work. Jinder Jow did all of the hard work involving dielectric properties while the author just did the modeling. John DeLong also helped do the FTIR work. Dr. Martin C. Hawley provided financial support, and gave me a free hand (for the most part) to do this project the way I wanted to do it. Others who helped in their own way were Jim Vivian, Mark Reath, Tony Oertling, Tony Ozzello, Stephany Angelacos (zowie!), the Whole Gang at Bilbo's, all the guys at 1174 Snyder, Drs. Eric Grulke and Kathy Hunt, anyone who was ever a Soma Cube, and all my other buddies (you know who you are). This work was funded by the Defense Advanced Research Projects Agency (DARPA) and the U. S. Navy.

TABLE OF CONTENTS

List of Tables	vii
List of Figures	viii
Introduction	1
Background and Previous Work	5
Mechanism of Crosslinking Reactions	5
Experimental Methods	12
Differential Scanning Calorimetry	13
Fourier-Transform Infrared Spectroscopy	13
C-13 Nuclear Magnetic Resonance Spectroscopy	24
Azochromophoric Labeling	28
Summary	29
Theoretical Methods	30
Rate Equations of Epoxy/Amine Reactions	31
Modeling of Dielectric Properties	37
Network Modeling	42
Modeling of Glass Transition (DiBenedetto Equation)	54
Modeling of Diffusion Limit (WLF Equation)	59
Summary	62
Methods and Results	63
Differential Scanning Calorimetry	63
Fourier-Transform Infrared Spectroscopy	80
C-13 Nuclear Magnetic Resonance Spectroscopy	102
Modeling of Cure Reactions	107
Modeling of Dielectric Properties	133
Discussion	141
Conclusion	164
Future Work	166
Appendix	167
Reference List	172

LIST OF TABLES

Table 1.	Structural Parameters Calculated Using Network Modeling.	p45
Table 2.	Epoxy/Amine Formulations.	p63
Table 3.	Scan Parameters and Results for Isothermal DSC Experiments.	p65
Table 4.	Results of T_g Measurements.	p79
Table 5.	Parameters for FTIR Scans.	p82
Table 6.	Comparision of FTIR and DSC Results.	p85
Table 7.	Theoretical Maximum Sample Exotherms	p86
Table 8.	Sample Preparation for NMR Experiments.	p103
Table 9.	Frequency Factors for Rate Constants.	p111
Table 10.	Values of Rate Constants - Theory vs. Experiment.	p112
Table 11.	Zero Extent Glass Transition Temperatures (Calculated).	p116
Table 12.	WLF Equation Parameters, .	p117
Table 13.	Additional WLF Equation Parameters.	p117
Table 14.	Values of Side Reaction Rate Constant k_s .	p119
Table 15.	Results of Numerical Integrations.	p120
Table 16.	Dielectric Relaxation Parameters.	p135
Table 17.	Additional Dielectric Relaxation Parameters.	p135
Table 18.	Additional Results of Network Calculation.	p160
Table 19.	Total Gel Time (min).	p160

LIST OF FIGURES

Figure 1.	Chemical structures of resin and curing agents.	p6
Figure 2.	Four reaction steps and exotherms.	p8
Figure 3.	Uncatalyzed and autocatalyzed reaction mechanisms.	p9
Figure 4.	Examples of DSC results.	p15
Figure 5.	Energy levels in Carbon-13 NMR.	p24
Figure 6.	C-13 NMR peak assignment of reactants and products of the reaction between o-cresol glycidyl ether and o-cresol (etherification).	p26
Figure 7.	Structure of p-aminoazobenzene (DAA).	p28
Figure 8.	Example of a DSC isothermal scan (2/2 mixture, 180 C).	p66
Figure 9.	Extent amine and DSC exotherm vs. time (1/2, 140 C).	p67
Figure 10.	Extent amine and DSC exotherm vs. time (1/2, 160 C).	p68
Figure 11.	Extent amine and DSC exotherm vs. time (1/2, 180 C).	p69
Figure 12.	Extent amine and DSC exotherm vs. time (1/2, 200 C).	p70
Figure 13.	Extent amine and DSC exotherm vs. time (2/2, 140 C).	p71
Figure 14.	Extent amine and DSC exotherm vs. time (2/2, 160 C).	p72
Figure 15.	Extent amine and DSC exotherm vs. time (2/2, 180 C).	p73
Figure 16.	Extent amine and DSC exotherm vs. time (2/2, 200 C).	p74

Figure 17.	Extent amine and DSC exotherm vs. time (3/2, 140 C).	p75
Figure 18.	Extent amine and DSC exotherm vs. time (3/2, 160 C).	p76
Figure 19.	Extent amine and DSC exotherm vs. time (3/2, 180 C).	p77
Figure 20.	Extent amine and DSC exotherm vs. time (3/2, 200 C).	p78
Figure 21.	Sample with hot cell used in FTIR experiment.	p83
Figure 22.	Peak area ratio for epoxy and amine (FTIR) vs. concentration.	p88
Figure 23.	Extent epoxide vs. time (1/2, 140 C).	p90
Figure 24.	Extent epoxide vs. time (1/2, 160 C).	p91
Figure 25.	Extent epoxide vs. time (1/2, 180 C).	p92
Figure 26.	Extent epoxide vs. time (1/2, 200 C).	p93
Figure 27.	Extent epoxide vs. time (2/2, 140 C).	p94
Figure 28.	Extent epoxide vs. time (2/2, 160 C).	p95
Figure 29.	Extent epoxide vs. time (2/2, 180 C).	p96
Figure 30.	Extent epoxide vs. time (2/2, 200 C).	p97
Figure 31.	Extent epoxide vs. time (3/2, 140 C).	p98
Figure 32.	Extent epoxide vs. time (3/2, 160 C).	p99
Figure 33.	Extent epoxide vs. time (3/2, 180 C).	p100
Figure 34.	Extent epoxide vs. time (3/2, 200 C).	p101
Figure 35.	C-13 NMR scan (1/2, 140 C, 4880 Hz).	p104
Figure 36.	C-13 NMR scan (1/2, 160 C, 4880 Hz).	p104
Figure 37.	C-13 NMR scan (1/2, 180 C, 4880 Hz).	p105
Figure 38.	C-13 NMR scan (1/2, 200 C, 1100 Hz).	p105
Figure 39.	C-13 NMR scan (3/2, 200 C, 4880 Hz).	p106
Figure 40.	C-13 NMR scan (1/2, unreacted liquid).	p106

Figure 41. Uncatalyzed rate constant vs. $1000/T$	p113
Figure 42. Autocatalyzed rate constant vs. $1000/T$	p114
Figure 43. Glass transition temperature vs. crosslink density.	p115
Figure 44. Isothermal DSC scan (1/2, 140 C).	p121
Figure 45. Isothermal DSC scan (1/2, 160 C).	p122
Figure 46. Isothermal DSC scan (1/2, 180 C).	p123
Figure 47. Isothermal DSC scan (1/2, 200 C).	p124
Figure 48. Isothermal DSC scan (2/2, 140 C).	p125
Figure 49. Isothermal DSC scan (2/2, 160 C).	p126
Figure 50. Isothermal DSC scan (2/2, 180 C).	p127
Figure 51. Isothermal DSC scan (2/2, 200 C).	p128
Figure 52. Isothermal DSC scan (3/2, 140 C).	p129
Figure 53. Isothermal DSC scan (3/2, 160 C).	p130
Figure 54. Isothermal DSC scan (3/2, 180 C).	p131
Figure 55. Isothermal DSC scan (3/2, 200 C).	p132
Figure 56. Logarithmic plot of loss factor vs. $1000/T$ for various extents (DER 332/DDS, 2.45 GHz).	p137
Figure 57. Logarithmic plot of mean relaxation time vs. $1000/T$ for various extents (DER 332/DDS, 2.45 GHz).	p138
Figure 58. Dielectric constant for a variety of extents (DER 332/DDS) as a function of temperature (experiment vs. theory, 2.45 GHz).	p139
Figure 59. Loss factor for a variety of extents (DER 332/DDS) as a function of temperature (experiment vs. theory, 2.45 GHz).	p140
Figure 60. 1/2, 180 C sample (FTIR, 4000 to 450 cm^{-1}), unreacted.	p142
Figure 61. 1/2, 180 C sample (FTIR, 4000 to 450 cm^{-1}), reacted (250 min).	p143

Figure 62.	Chemical shifts of Carbon-13 nuclei (DGEBA/ mPDA), aliphatic region (unreacted DGEBA/ secondary/tertiary/ether).	p146
Figure 63.	Potential energy surfaces.	p150
Figure 64.	Epoxide/amine hydrogen rate constants vs. extent amine (second order, 1/2 formulation).	p152
Figure 65.	Epoxide/amine hydrogen rate constants vs. extent amine (second order, 2/2 formulation).	p153
Figure 66.	Epoxide/amine hydrogen rate constants vs. extent amine (second order, 3/2 formulation).	p154

INTRODUCTION

In the past thirty years, thermosetting materials have attained rapidly increasing importance. These materials have a wide variety of applications in the automotive, plastics, electronics, and aerospace industries. The nature of these materials (liquids which upon heating form solids) makes them extremely useful for processing and molding. Liquid-like chain molecules crosslink when heated, forming a network of polymer chain molecules. The nature of monomers used determines the properties of the material and influences the chemical kinetics.

Epoxy resins are an example of such materials. There are many different types of epoxies which differ in the chain backbone; however, all of the different types of chains are terminated by the epoxide group. An accelerator or curing agent is necessary to promote the ring-opening polymerization of these molecules. The reaction may be carried out utilizing Lewis acids or bases. A more common curing agent involves the use of a crosslinker such as an aromatic amine. The reaction mechanism usually involves several different types of polymerization steps. There is always a diversity of opinion backed up with experimental evidence in the literature regarding the reaction mechanism for a particular formulation.

The purpose of the following research is to identify the important steps in a reaction between an epoxy (diglycidyl ether of bis-phenol A, hereafter referred to as DGEBA) and an aromatic amine curing agent (diamino diphenyl sulfone or DDS). The resin used is the minimum molecular weight DGEBA resin manufactured by

Dow Chemical Company and has the trade name DER 332. Since the DGEBA chain is terminated on both ends with an epoxy group, it is known as a difunctional resin. The amine curing agent has four hydrogen atoms in the amine groups available for reaction and is therefore called a tetrafunctional curing agent. Other resins and curing agents have different functionalities but this system is somewhat commonly used. No accelerators were used in these experiments.

Systems involving DGEBA and diamines have been studied previously. However, a comprehensive rate equation for the epoxy-amine hydrogen reaction valid over the entire extent of reaction has not yet been developed. Rate laws previously obtained break down at high extents of reaction due to the fact that the reaction becomes diffusion limited. There is also some uncertainty regarding other reactions which may occur in these systems and the circumstances under which they occur. The purpose of this work then will be to find a rate equation valid over the entire extent of reaction and to characterize the side reaction. Physical properties of these materials based upon extent of reaction (particularly for a stoichiometric formulation) are also characterized. These include glass transition temperature and complex dielectric constant. These properties are discussed in the light of network formation and network modeling, which entails the application of probability theory to the prediction of polymer characteristics.

The reaction conditions employed in these experiments involved curing three different formulations (deficient amine,

stoichiometric, and excess amine) at four different temperatures. The experimental methods involved employing Differential Scanning Calorimetry (DSC) and Fourier-Transform Infrared Spectroscopy (FTIR) to evaluate reaction exotherm and concentrations of reactive species. Utilizing the two methods simultaneously enabled separation of the reaction pathways into exothermic and non-exothermic parts. DSC therefore only measures the exothermic part of the epoxy cure. Additionally, a previously unutilized IR band at 695 cm^{-1} has been analyzed which characterizes amine hydrogen disappearance more accurately than those used by previous investigators. Carbon-13 Nuclear Magnetic Resonance (NMR) was carried out on certain selected samples and the nature of the non-exothermic side reaction has been precisely determined. This is not the etherification reaction involving hydroxide and epoxide commonly discussed in the literature but a reaction of tertiary amine formed during cure with epoxide to form a quaternary ammonium ion species. The fact that no etherification occurs is confirmed by FTIR experiments.

Rate laws for this reaction previously used do not sufficiently model epoxy cure over the entire extent of the cure process, nor is the side reaction treated with any detail in the literature. This work uses a WLF-type equation along with a rate law involving the uncatalyzed and autocatalyzed reactions of epoxy with amine hydrogen to fit data more successfully over the entire extent of cure. A rate law for the side reaction has also been developed. The prediction of dielectric properties and glass transition utilizing network modeling is also discussed.

Dielectric data at microwave frequencies collected by other investigators has been analyzed using a single-relaxation time model and the nature of the relaxation mechanism discussed. Additionally, the DiBenedetto Equation has been used to fit glass transition data. It has been found that the side reaction has no significant effect on glass transition temperature. This is because the side reaction does not form true crosslinks but a type of equilibrium-limited transition state.

The research discussed above will be presented in the following format. First, background material regarding previous experimental work and modeling efforts will be presented. Next, the experimental techniques and data analysis used in this investigation will be discussed in detail. Finally, the results of this research will be discussed and conclusions drawn from this research summarized. By the end of this dissertation the nature of the relationship between crosslinking and certain physical properties will be more clearly understood by the reader.

BACKGROUND AND PREVIOUS WORK

The following sections concern themselves with the pertinent background information necessary to carry out the following research. The first section discusses the reaction mechanistic steps which are believed to occur. While no catalysts are used in the experiments used in this research, their role in promoting epoxy crosslinking is nevertheless described. Next, descriptions of the three experimental techniques employed are presented along with short summaries of their use by other investigators. A recent technique known as azochromophoric labeling is discussed even though it was not used in this research. Rate laws used to model epoxy/amine cures are then discussed, followed by a summary of investigations of dielectric properties. Network modeling, the application of probability theory to the prediction of polymer properties, is discussed primarily with regard to the influence of the reaction mechanism upon network formation. Finally, the two equations used in the modeling of diffusion-limited reactions and glass transition temperature are described.

MECHANISM OF CROSSLINKING REACTIONS

The structures of the difunctional epoxy resin and tetrafunctional amine curing agent are given below. Each epoxy molecule contains two epoxide groups available for reaction, while each molecule of amine contains four hydrogen atoms

available as reaction sites (1).

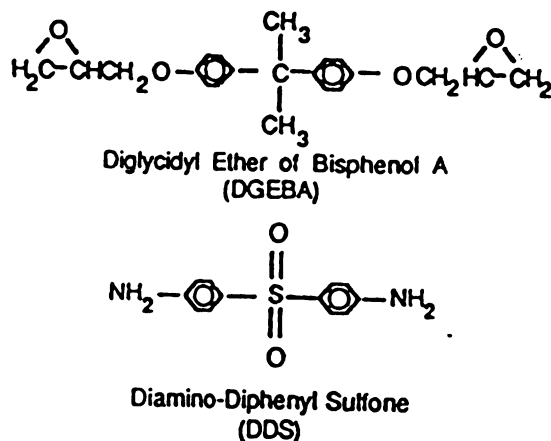


Figure 1. Chemical structures of resin and curing agent. (Ref. (1))

These materials react with one another or with species formed during the reaction in a number of ways. The basic reaction and the one which is most favorable is the reaction between epoxide and amine hydrogen. An epoxy group reacts with either a primary or secondary amine to form a secondary or tertiary amine, respectively. Hydroxide groups are formed in the reaction. These hydroxide groups act as catalysts for the reaction between epoxy and amine so the reaction is autocatalytic in nature. Another reaction in the literature is etherification. This involves the reaction of an epoxide group with a hydroxyl group to form an ether crosslink and another hydroxyl group in a manner such that no net production of hydroxyl occurs. Finally, the epoxide groups can react with tertiary amine formed in the reaction forming an ion pair containing a quaternary ammonium ion and an oxide ion. Lee

and Neville (2) have summarized fifty-five different reactions of epoxy groups with other species with the four mentioned above being included. Some others may be important such as rearrangement and self-polymerization. Using a table of bond energies (3) and the value of 22.5 kcal/mol for the ring-opening polymerization determined by McGrath (4), exotherms for the reactions described above may be estimated. The reactions and their exotherms are presented in Figure 2 on the next page.

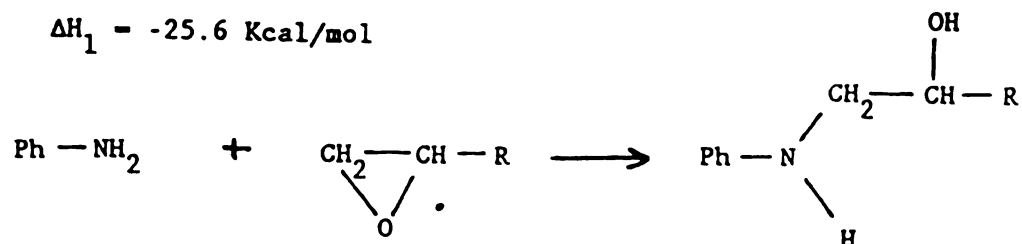
The amine/epoxy reaction proceeds as follows. The electron pair of the amine group bonds to the chain terminating carbon in the epoxide group, causing a bond breakage of the carbon-oxygen bond. The hydrogen atom detaches itself from the amine group and reattaches to the oxygen atom to form a hydroxide. The hydroxide catalyzes further epoxy/amine addition by providing a hydrogen bond to the epoxide group. The electron pair on the amine again bonds to the chain terminating carbon atom, causing the carbon-oxygen bond to break. The hydrogen atom from the catalyzing hydroxide group bonds to the epoxide oxygen, while the hydrogen atom originally attached to amine dissociates and replaces the hydrogen atom in the catalyzing hydroxide. This is referred to as a "push-pull" mechanism in the literature and was originally postulated by Swain in 1948 (5-7). This implies the reaction obeys both second- and third-order rate equations. The schemes for these reactions are shown in Figure 3.

Narracot (8) studied the addition of tertiary amine to epoxide. The reaction mechanism proceeds in a manner similar to that described above except for the fact that hydrogen atoms are

(1) Primary Amine/Epoxide

Secondary Amine/Hydroxide

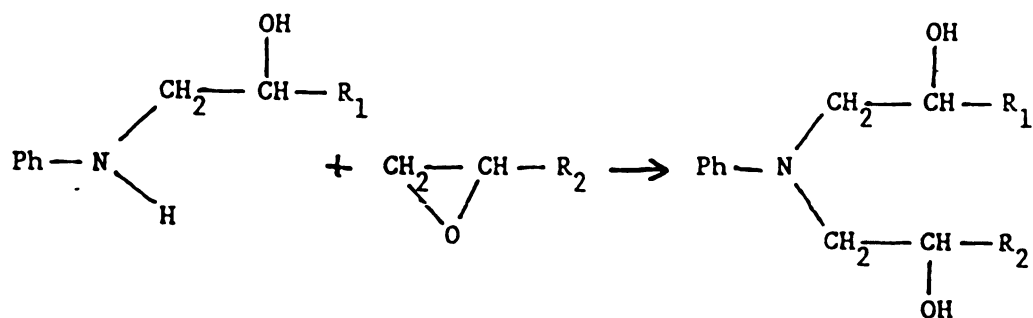
$$\Delta H_1 = -25.6 \text{ Kcal/mol}$$



(2) Secondary Amine/Epoxide

Tertiary Amine/Hydroxide

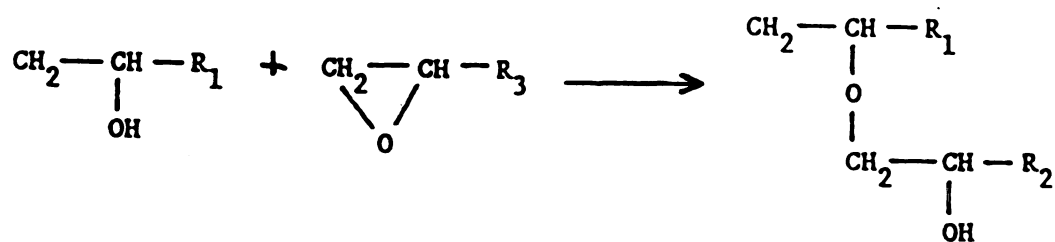
$$\Delta H_2 = -25.6 \text{ Kcal/mol}$$



(3) Hydroxide/Epoxide

Ether/Hydroxide

$$\Delta H_3 = -22.5 \text{ Kcal/mol}$$



(4) Tertiary Amine/Epoxide

Quaternary Ammonium/Oxide

$$\Delta H_4 = -1.2 \text{ Kcal/mol}$$

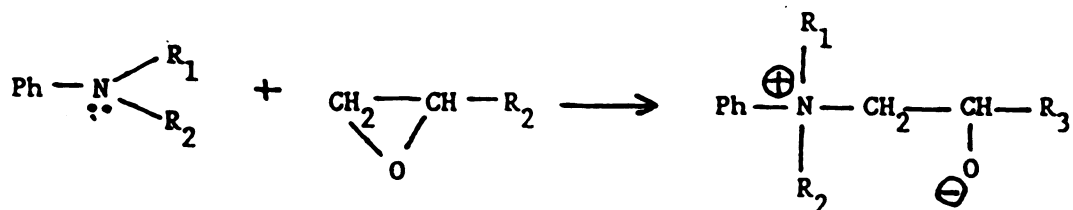


Figure 2. Four reaction steps and exotherms.

Uncatalyzed



Autocatalyzed

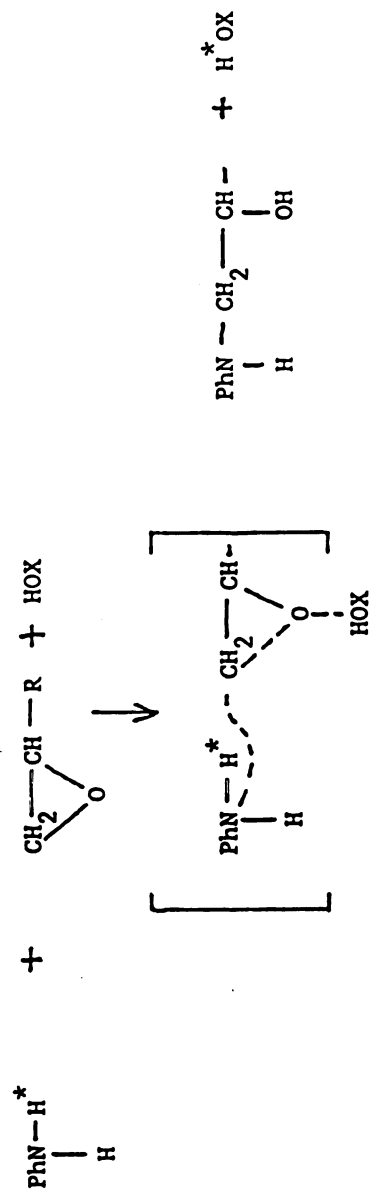


Figure 3. Uncatalyzed and autocatalyzed reaction mechanisms.

not involved. A quaternary ammonium ion is formed along with an oxide bonded to what was originally the inboard epoxy carbon. This reaction proceeds with virtually no exotherm. Tertiary amine is used as a Lewis base for the purpose of accelerating epoxy cures, but is also formed during epoxy/amine reactions and can therefore be thought of as an autocatalytic species (2).

Lewis bases catalyze crosslinking by breaking the epoxide carbon-oxygen bond and producing a negatively-charged oxide group (2). This reacts further with epoxide groups to form ether crosslinks. This is the standard mechanism of base-catalyzed epoxy curing. Hale (9) has studied this reaction in detail in some recent work involving carbon-13 NMR spectroscopy. This study used an amide species in order to crosslink epoxies. Inorganic bases have also been used (2). In the event that the Lewis base is a hydroxide-containing species, the reaction involves a "push-pull"-type mechanism with no net consumption of hydroxide. The reaction in Figure 2 involving production of an ether crosslink is an example of such a reaction. Lewis bases (electron pair donors) attack at the chain-ending carbon in the epoxide group, breaking the bond between this carbon and the oxygen atom in the ring. Lewis acids (electron pair acceptors) on the other hand attack at the oxygen atom. In either case, the reaction proceeds after the ring is opened via an anionic polymerization mechanism with alkoxide ions being consumed and formed in the same reaction. The reaction therefore propagates itself once initiated.

Acid curing accelerators can only be used if hydroxyl groups are present. Boron trifluoride is an example of a Lewis acid

commonly used. Other acidic curing agents are carboxylic acid anhydrides, organic acids, and phenols. Curing reactions involving these types of curing agents and accelerators also produce ether crosslinks. Again, Lee and Neville's monograph is a most useful source for this information (2).

Ether crosslink formation is commonly referred to in the literature and can occur with both difunctional and tetrafunctional resins. This reaction is sometimes referred to as polyetherification. One reference examined claimed that it occurred with no catalyst present (10), but this author is of the belief that these authors are in error. This author's interpretation is that ether crosslinks form only in the presence of a catalyst (2,6,7,9,11-14). It is highly unlikely that ether crosslinks will form in the reaction between DGEBA resin and DDS studied herein since no catalyst has been added. Evidence of this conclusion will be presented in more detail in the development of this thesis. The conclusion that etherification requires a catalyst results from examination of the literature.

Therefore, the main reactions involved in this study are the catalyzed and uncatalyzed epoxy/amine addition reactions as well as the reaction between epoxy and tertiary amine formed in the epoxy/amine addition. Most studies do not consider the epoxy/tertiary amine side reaction as important, instead assuming etherification to be present, while other studies only consider epoxy/amine addition (14-23).

EXPERIMENTAL METHODS

Three experimental techniques were employed in the course of this investigation. Differential Scanning Calorimetry was used to monitor the heat flux and total exotherm given off by samples as a function of time and (implicitly) amine extent. It has already been stated that the epoxy/amine hydrogen reaction provides the exothermic pathway, while the epoxy/tertiary amine reaction has no exotherm. Therefore, DSC measures the consumption of amine hydrogens. Fourier Transform Infrared Spectroscopy (FTIR) monitors the consumption of reactive groups which have IR absorption bands, in this case epoxide and amine hydrogen. Finally, Carbon-13 NMR was carried out on selected samples, particularly in order to determine if quaternary ammonium ions were formed.

It is therefore necessary to describe the basic theory behind each of these experimental techniques as well as to review some previous applications of these methods. In addition, a recently developed technique for the analysis of epoxy/amine kinetics known as azochromophoric labeling will be discussed (even though it is not directly used in this analysis) as a point of reference. Regarding the discussions of the experimental methods employed in this author's work, it should be mentioned that the experiments described below are not nearly all of the work done in this area. Rather, the intention is only to highlight the main points of a few particularly important studies.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

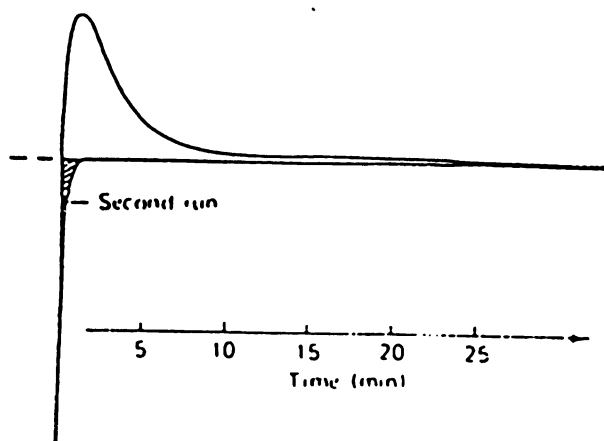
An excellent review of how DSC is used in the study of thermosets has been written by Prime (24). DSC is useful for the study of reaction kinetics (although often in a simplistic manner) as well as for the determination of specific heat, glass transition, and gel point. As a point of interest it should be mentioned that R. B. Prime is a pioneer in the use of DSC in the characterization of thermosets, having worked in this area since the late 1960's.

DSC scans are run using both a sample and a reference. The sample and reference are placed in a DSC cell (about 10 mg of sample is required). Various types of pans are used to contain the samples. Heating elements beneath both the sample and the reference are employed in conjunction with thermocouples to maintain the sample and the reference at the same temperature. Either the heating characteristics of the sample and reference are different, or the sample generates heat as the result of an exothermic chemical reaction. The difference in heat flux required to maintain both sample and reference at the same temperature is the primary quantity measured with this technique. Time and temperature are also of course important experimental quantities.

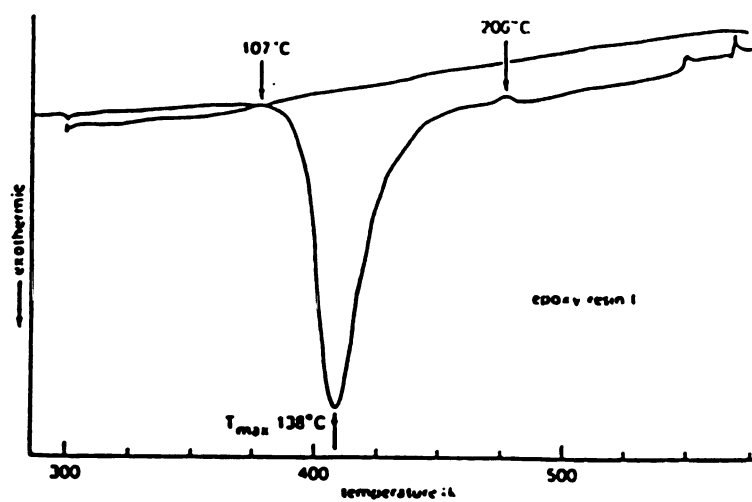
The scans are usually isothermal or dynamic. Isothermal scans of course involve a constant temperature and are useful for determining reaction kinetics and total evolved exotherm. Dynamic scans are run using selected temperature ramps (degrees/min) and are useful for investigation of quantities which vary with

temperature, such as reaction kinetics and specific heat. Dynamic scans give results for total exotherm measurement which depend on both ramping rate and final temperature, while isothermal scans give results which depend on the isothermal temperature only. Glass transition temperature is also measured using dynamic scans since the sample specific heat changes at the phase transition. Examples of both isothermal and dynamic scans are shown in Figure 4. The usual method is to determine exotherm using isothermal scans and then determine residual exotherms using dynamic scans up to temperatures at which the reaction is sure to be complete. Extents are then found by dividing sample exotherm by the quantity sample exotherm plus the residual exotherm.

Dynamic scans give results for exotherms which depend on the ramping rate. For low ramping rates, some of the initial and final exotherm is lost due to lack of instrument sensitivity and the result obtained therefore tends to be below the true value. For high ramping rates, the sample decomposes before complete cure is accomplished, again causing the value to be artificially lowered. Both dynamic and isothermal scans also depend on the maximum temperature. If the temperature is low the cure is incomplete. However, if the temperature is high, there may be sample decomposition as well as heat loss to the environment due to the large difference between the sample cell temperature and the ambient temperature. In both cases the results obtained are below what the true result ought to be. Isothermal scans have a horizontal baseline while dynamic scans have a diagonal baseline. An ideal dynamic scan would have a ramping rate of 2-4 deg C/min



(a) Isothermal



(b) Dynamic

Figure 4. Examples of DSC results. (Ref. (24))

and an ultimate temperature below the decomposition temperature but well above the glass transition temperature (24).

An early study of epoxy/amine kinetics was done by Acitelli et. al. (16) Isothermal studies were conducted at temperatures between 115 and 157 C. The epoxy/amine mixture studied was a stoichiometric formulation of DER 332 and metaphenylene diamine. Data were analyzed up to an extent of 70 % evolved exotherm and was fit to a equation using n-th order reaction kinetics. Dynamic scans were also used for samples reacted at temperatures below 100 C. The samples were cured for specific times and temperatures outside the DSC apparatus and then analyzed using a cycle of 10 C/min in order to determine the residual exotherms. According to the authors, the reason that data were not analyzed above an extent of 70 % was that the measured heat fluxes were so small that the experimental error made the measurement unreliable.

Sourour and Kamal (17) studied the same system using DSC a few years later. Their work provided a much greater amount of detail than that provided by Acitelli's study. The method of integrating the DSC peaks and determining the proper baseline is presented more thoroughly. Only isothermal scans were conducted. In this case the reaction rate data was fit using a combined second- and third-order expression.

Hagnauer et. al. (15) studied a reaction between a tetrafunctional resin and DDS by scanning isothermally at 177 C and varying the DDS concentration. The rate law used to analyze data was first order in resin and second order in DDS. The samples were subjected to dynamic scans using a ramping rate of 2 C/min in

order to determine the residual exotherm. The rate constants thus determined increase with increasing DDS concentration.

Morgan (11) has also studied a reaction between a tetrafunctional resin and DDS accelerated with a boron trifluoride catalyst. The data is presented in a slightly different manner, however; plotting total evolved exotherm versus temperature for dynamic scans yields inflection points in the DSC curves which are interpreted as being associated with different reactions during cure, separating the reaction into uncatalyzed and catalyzed parts. Interestingly enough, no information about the temperature ramping rates used is given, leading this author to comment that the peak separations may have something to do with the ramping rate and not different reactions as Morgan postulates.

Moroni et. al. (18) have used both isothermal and dynamic DSC scans to analyze the kinetics of an epoxy/amine system containing a mixture of several difunctional epoxies and amines. Again, isothermal methods were used to determine heat flux and exotherm and dynamic methods were used to determine the residual exotherm. Extent was defined as evolved sample exotherm divided by ultimate sample exotherm plus residual exotherm. The rate law used to fit data is a combination of m-th and n-th order terms and is based upon a model involving uncatalyzed and autocatalyzed kinetics. As per Acitelli's work, the "diffusion limited" part of the reaction (high extents) was not analyzed due to the fact that the equation used to fit data breaks down under these conditions. This is a common occurrence when epoxy/amine data is fit to a reaction model. Carrozino et. al. (23) have recently studied a DGEBA/EDA system

using exactly the same experimental method and rate law.

Lee, Loos, and Springer (25) studied Hercules 3501-6 prepreg using the DSC methods described above and fit the data using the same kinetic model as Sourour and Kamal. At a higher extent the kinetic model used changes at an arbitrary point into a first-order model in order to take the diffusion-limited nature of the reaction into account. The authors forget that the system being analyzed is a partially-cured prepreg and therefore erroneously conclude that the catalyzed rate constant is negative in value. The study is most useful, however, since there is an effort to take the diffusion-limited rate constant into account.

Summarizing, DSC methods employing a combination of isothermal and dynamic methods are often used to analyze the thermal evolution of the exothermic epoxy/amine cure reaction. Rate laws used to fit data are generally combinations of second- and third-order expressions. Most often the rate law breaks down at higher extents due to changes in the reaction kinetics when the reaction becomes diffusion-limited due to proximity to the glass transition temperature.

FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared Spectroscopy relies on the physical principle that molecules vibrate about their chemical bonds at certain characteristic frequencies. When electromagnetic radiation of this characteristic frequency is used to determine the existence of a particular chemical bond, the bond absorbs the radiation at

the resonant frequency. When a particular chemical compound is exposed to a spectrum of infrared radiation, the chemical compound will absorb radiation of a variety of frequencies, therefore determining the different types of chemical bonds which are present. Chemical bonds oscillate about their equilibrium bond lengths at frequencies associated with the infrared region of the electromagnetic spectrum which is the reason infrared radiation is used for this type of analysis. There are two types of infrared spectroscopy currently in use. Classical dispersive infrared spectroscopy uses a grating or prism to geometrically disperse the infrared radiation. This dispersed radiation is passed over the sample being analyzed and a detector is used to isolate a narrow frequency range and measure how much energy passes through the sample as a function of frequency. Using this technique, only 10 % of original infrared beam is used due to the dispersive nature of the technique. The technique used in these experiments is called Fourier-Transform Infrared Spectroscopy and uses a Michelson interferometer to produce a beam of infrared radiation. The interferometer splits the source beam into two equal beams. The two arms of the interferometer contain a stationary mirror and a movable mirror. As the movable mirror changes position, the path lengths of the two beams change and the different frequencies in the beams will interfere constructively or destructively producing an interferogram at the detector which is a function of the rate at which the movable mirror changes position. The spectrum is taken in the time domain and Fourier-transformed into the frequency domain. The infrared beam produced in this manner

is of greater strength than that used in the dispersive method (26).

Absorption is of course dependent upon the Beer-Lambert Law. The absorption of electromagnetic radiation is dependent on analyte concentration and path length in the following manner (26).

$$1 - A/A_{\max} = \exp(-adc) \quad (1)$$

In this equation, A is the absorbance, $A_{\max}$ is the maximum absorbance, a is the absorptivity, d the path length, and c the concentration of analyte. When the argument of the exponential is low, the above reduces to the following equation.

$$A/A_{\max} = adc \quad (2)$$

Therefore, at low concentrations, absorbance can be used to measure concentration of analyte. The experiments used by this author are analyzed for concentrations of reactive species using this technique since the path lengths and concentrations are both low.

Studies of both di- and tetra-functional epoxies cured with amines with or without accelerators have been investigated using FTIR by a number of researchers. Groups analyzed include unreacted epoxy, aromatic and aliphatic ethers, hydroxyls, and primary and secondary amines. The rest of this section concerns

itself with some previous studies done in this area and provides information regarding the characteristic frequencies of the absorption bands for the above groups.

Neville (2) and Mertz el and Koenig (26) are useful as general references. Neville's reference material provides several IR spectra for epoxies cured and uncured with a variety of agents and accelerators. Isolated epoxy bands, that is to say bands which are not superimposed upon other bands, are found at around 865 cm^{-1} and 910 cm^{-1} . Aliphatic and aromatic ether bands are found at around 1250 cm^{-1} and 1120 cm^{-1} respectively. The hydroxide group is found to absorb at 3500 cm^{-1} . The C-H stretch in the aromatic ring is useful as a standard since it participates in no cure reactions. This group absorbs quite strongly at 1510 cm^{-1} . The method generally employed for preparing samples for IR analysis is to cure the samples outside the IR instrument for specified times and then scan for the presence of groups. Mertz el and Koenig list the absorption bands for more than 100 species as well as providing the discussion of FTIR fundamentals from which the first two paragraphs of this section were taken. Morgan (11) has studied tetrafunctional resin cures and has found the above bands to be in the same locations.

Smith et. al. (12) use the same bands as those listed above, with the C-H stretch located at 1517 cm^{-1} and the ether band located at 1072 cm^{-1} . This study also analyzes tetrafunctional resins. The bands are similar for both difunctional and tetrafunctional epoxy systems. Both Morgan and Smith have aliphatic ether bands in their spectra because they use

accelerators in their cures so that etherification can occur. Smith cured samples for selected times at 120 C and 160 C outside the FTIR and carried out static FTIR tests. A band at 3409 cm^{-1} has also been indentified and assigned to secondary amine. Primary amine absorbs at 1615 cm^{-1} . Both the secondary and primary amine bands in this case are superimposed upon other bands (the hydroxyl and aromatic C-H stretches respectively).

Moacanin et. al. (27) studied a reaction between a tetrafunctional resin and DDS. They analyze the hydroxide band at 3400 cm^{-1} and neglect the fact that there is a secondary amine band at the same location. The epoxy band at 915 cm^{-1} is also analyzed. Schiering et. al. (28) analyze hydroxyl and epoxy bands and reference them to a band at 1034 cm^{-1} which is assigned to a C-H out-of-plane vibration. The system analyzed is a DGEBA/metaphenylenediamine system. Moroni et. al. (18) studied a mixture of epoxies and amines using both DSC (cf. above discussion) and FTIR. The epoxy band at 915 cm^{-1} was referenced to a band at 1184 cm^{-1} associated with the phenyl group.

The fact that the absorption at 1510 cm^{-1} is a C-H stretch has already been mentioned. Other characteristic modes of vibration are the N-H bending mode at around 1600 cm^{-1} , the O-H stretch at 3500 cm^{-1} , and the C-O stretches between 1200 and 900 cm^{-1} . Additionally, an N-H rocking vibration absorbs around 700 cm^{-1} (29). Spectra obtained by this researcher indicate that this band is important in these systems and is isolated from (not superimposed upon) other bands. Careful examination of the literature indicate that this is the first time that this band has

been used for analysis of amine concentration. Most commonly, the band at 1600 cm^{-1} is used.

Perusal of the above discussion indicates that there is some uncertainty as to just which groups absorb at what frequencies. The only groups for which there appear to be universal agreement are the C-H stretch in the phenyl groups used as a reference absorption and the epoxide band at 915 cm^{-1} . These are two bands which will therefore be used in the analysis of the experimental results obtained in this author's experimental work. Additionally, the method of sample preparation used by the above investigators reduces the number of data points possible because sample preparation becomes too tedious. Meaningful kinetic analysis is not possible with the data points spread out over such a large amount of time. An automated means of data acquisition and a more reliable band for the determination of amine content will be used in these experiments. This will entail the use of the amine hydrogen band at 695 cm^{-1} in conjunction with appropriate FTIR instrument software and a hotcell so that the sample may be heated inside the instrument. The band at 695 cm^{-1} proved to be a more reliable band for the determination of amine hydrogen concentration in these experiments than any of the other bands described above. It should be emphasized, however, that analysis carried out using this band does not differentiate between primary or secondary amine concentrations.

CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear Magnetic Resonance Spectroscopy is based on the phenomena that certain atomic nuclei have spins. These spins result in the nucleus having a magnetic moment which can interact with a magnetic field. Generally, only nuclei with an odd number of protons and/or neutrons exhibit this phenomena. Magnetic resonance spectroscopy is carried out on a number of nuclei, most notably hydrogen-1, but also including phosphorus-31 and silicon-29. This study uses carbon-13 nuclei. When the nuclei are exposed to a magnetic field, the nuclei spin in a manner either parallel or antiparallel to the field lines. This causes the nuclei to populate different energy levels as in the diagram below. The number of levels created by this splitting is equal to $(2I + 1)$ where I is the nuclear spin. For carbon-13 this number is equal to $1/2$ which implies that two energy levels are created (Figure 5).

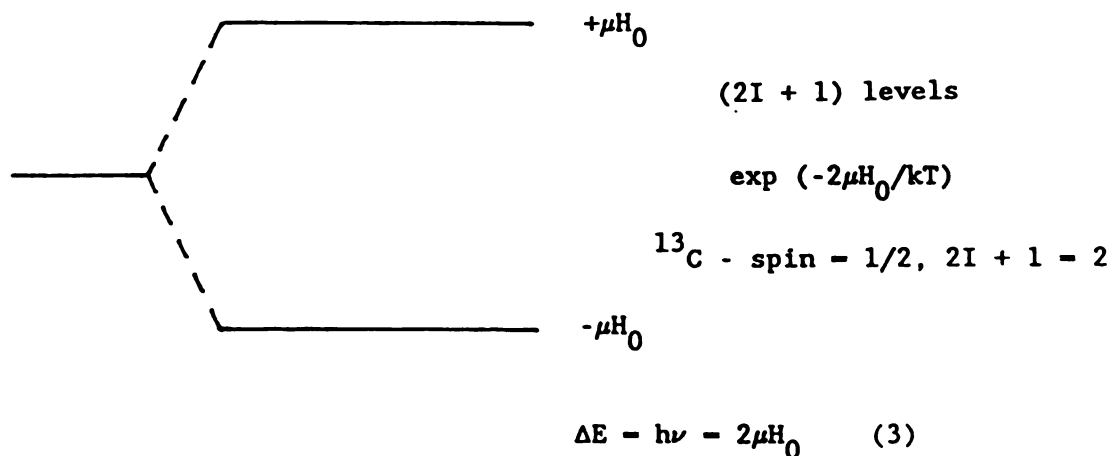
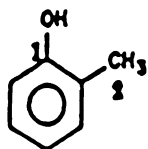


Figure 5. Energy levels in Carbon-13 NMR.

Both the upper and lower levels are occupied according to the Boltzmann distribution, so therefore both absorption and emission occur. More absorption than emission occurs due to the fact that the lower level is more populated. Note that there is a frequency term in the equation above. A source of electromagnetic radiation is required for this splitting to occur (usually around 10^7 Hz). Carbon-13 scans are run at around 100 MHz, while hydrogen-1 is usually run around 1 MHz. This has to do with the differing magnetic moments μ of the nuclei. Depending upon the electronic environment in which the nucleus exists, the splitting in energy levels will be different. It is easier to vary the field strength H_0 than the frequency so that is usually what is done. Therefore nuclei existing in different chemical environments have characteristic absorptions at different magnetic fields. This phenomena gives much useful information about chemical structure and is the essence of nuclear magnetic resonance. The amount that this magnetic field differs from a reference standard is expressed in ppm (parts per million) of the reference field and is called the chemical shift (30). Carbon-13 NMR chemical shifts are larger than hydrogen-1 chemical shifts. Aromatic carbons have shifts around 100-175 ppm, aliphatic carbons around 30-80 ppm, and hydrogen around 1-10 ppm.

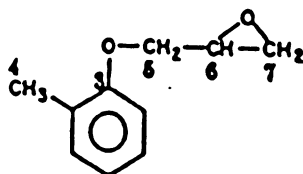
Examples of carbon-13 NMR studies on both the etherification reaction and the epoxy/amine hydrogen reaction are both in the literature. Hale (9) has studied the etherification reaction in the presence of an amide catalyst. Figure 6 gives his results and spectral assignments for the absorption bands for different

(a) o-cresol

Carbon δ (ppm)

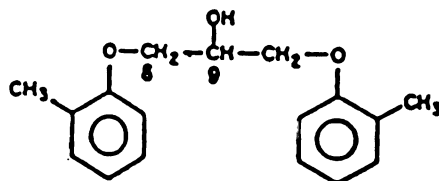
1	156.2
2	16.2

(b) o-cresyl glycidyl ether



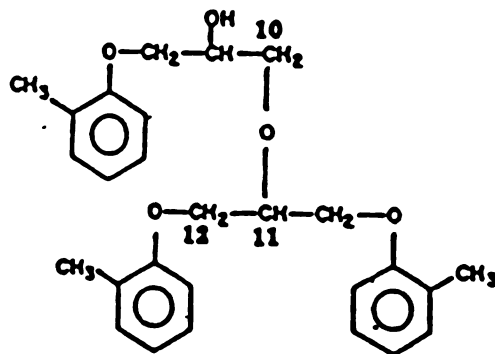
3	157.6
4	16.3
5	69.8
6	50.7
7	44.3

(c) a+b



8	70.0
9	69.3

(d) b+c



10	72.9
11	78.4
12	68.5

Figure 6. C-13 NMR peak assignment of reactants and products of the reaction between o-cresol glycidyl ether and o-cresol (etherification). (Ref. (9))

carbons resulting from the formation of ether crosslinks. Grenier-Loustalt and Grenier (14) carried out a reaction between metaphenylene diamine and DGEBA. The hydroxyl carbons have the same chemical shift as those in Hale's study (68-70 ppm). The chemical shift of the carbons attached to secondary or tertiary amine nitrogen have shifts of 47.5 and 53 ppm, respectively. The same carbon in unreacted epoxy has a shift of 44.1 which is similar to Hale's result (44.9). No chemical shift for the carbon attached to quaternary ammonium ion or the oxide ion attached to the inboard carbon has been located in the literature. This author believes that this is the first time anyone has thought to look. Additionally, Breitmayer (30) and Bates (31) give values of the effect of substituent groups on carbon atoms in aromatic and aliphatic environments. Grenier-Loustalt and Grenier's work is most comprehensive although the article is written in French (14). Their results are included in Figure 62 (in the Discussion section).

The reason that this experimental program uses carbon-13 NMR is to determine if these chemical shifts exist and what the values of them are. The above references give chemical shifts for carbon environments formed in etherification reactions as well, so if these species are formed carbon-13 NMR experiments should prove their existence. The above discussion focuses on aliphatic and not aromatic carbons since these are the ones which participate in the chemical reactions in these systems. Other details regarding NMR spectroscopy will be given in the experimental section.

AZOCHROMOPHORIC LABELING

A recently developed technique used to monitor the DGEBA/DDS reaction is azochromophoric labeling (20-22). The molecule DAA (p-diaminoazobenzene) is shown below (Figure 7). It can easily be seen

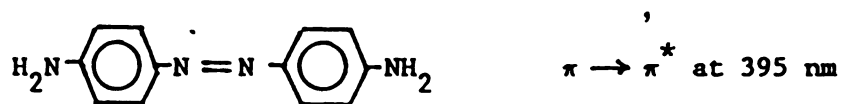


Figure 7. Structure of p-aminoazobenzene (DAA).

that this molecule closely resembles DDS in structure. DAA absorbs in the uv-vis range (395 nm). This dye can react with epoxide in the same manner as DDS. As the end amine groups accumulate substituents, the absorption peak shifts to a higher wavelength. This effect is known as a bathochromic shift. The intensity of the absorption increases with an increasing number of substituents. A very small amount of DAA (0.1 %) is mixed into a stoichiometric formulation of DGEBA/DDS at the spectra taken at various times for a specific cure temperature. Deconvolution of the spectra involves the assumption of Gaussian lineshapes for the amine species involved in the reaction for the fitting of the data. This technique can therefore distinguish between primary, secondary, and tertiary amine groups and can further distinguish branching at the ends of the DAA molecule. This technique would

possibly also be useful for the detection of quaternary ammonium ion. These authors do not detect this species since the formulation and reaction conditions do not favor its formation. The fact that the intensity increases with increasing number of substituents makes the technique more sensitive at advanced stages of cure.

The above method is capable of some very detailed measurements and is not used in this experimental work but is included as a point of interest. As already mentioned, it would be interesting to use this method to analyze an epoxy/amine cure under conditions favorable for the formation of quaternary ammonium ion in order to determine its existence and the kinetics of its formation. While it is only speculation that this method would be useful under these circumstances, the addition of still another substituent at the end of the DAA molecule would be expected to alter the absorption characteristics of the conjugated diene system.

SUMMARY

Four experimental techniques have been described of which three have been used in these experiments. Their use in the characterization of the kinetics of epoxy/amine cure has been discussed. The uncertainties regarding their use that have been found by perusal of the literature have also been noted. The experimental program utilized in this research will highlight some new ways in which experiments of these types are used.

THEORETICAL METHODS

Since a large part of this project has to do with the modeling of results obtained via the application of the above experiments, some mention of the types of equations used to fit data is appropriate. A large number of reaction rate laws have been used to characterize the epoxy/amine reaction. Most of them are used to treat DSC data in the literature so they generally describe the reaction using extent as a variable rather than concentrations of reactive species. Network modeling, the application of probability theory to the understanding of polymer characteristics, is discussed with regard to the effect of the reaction rate law on the formation of the network. The work involving epoxy dielectric properties carried out in this research does not concern itself with the measurement of dielectric properties. However, results obtained by other investigators have been modeled so efforts in the area of modeling of dielectric properties are discussed. Finally, two equations used to model diffusion-limited kinetics and glass transition temperature are briefly described; the Williams-Landel-Ferry (or WLF) Equation regarding mobility as a function of free volume and the DiBenedetto Equation relating glass transition temperature as a function of crosslinking density.

RATE EQUATIONS OF EPOXY/AMINE REACTIONS

A number of rate laws have been used to fit epoxy/amine reaction data. Most of the rate laws used below have been used to characterize DSC data in the literature. Usually the reaction is analyzed in terms of extent of DSC exotherm evolved. The rate constants obtained from the application of these rate laws are universally analyzed in terms of Arrhenius behavior if the temperature dependence of the rate constant is a focus of the experiment. The addition of epoxy to amine is usually the focus of these investigations, but there is some interest in quantifying the etherification reaction. The reaction of epoxy with tertiary amine has not yet been treated quantitatively.

The most basic of these equations is an n-th order model. In the equation below (and in all of the others) α denotes the extent of DSC exotherm evolved. This quantity is determined experimentally by first conducting an isothermal scan to find Q_{iso} and then a dynamic scan to find Q_{res} . The methods for carrying out these scans are described in the background section.

$$\alpha = \frac{Q_{iso}}{Q_{iso} + Q_{res}} \quad (4)$$

This data for extent is then fit using the following equation.

$$d\alpha/dt = k(1 - \alpha)^n \quad (5)$$

When this equation is used, the reaction order changes through the course of the reaction. Acitelli analyzed his data for DER 332 and metaphenylenediamine and found that the reaction order changed from 2.3 at zero extent to 1.7 at 70 % extent. The activation energy was 12.7 Kcal/mol (16). Moroni obtained an exponent of 1.1-1.3 and an activation energy of 13.5 Kcal by studying a mixture of epoxies and amines (18). Moacanin (27) fit FTIR data by assuming first-order behavior and broke up the tetrafunctional epoxy/amine reaction into two Arrhenius-type regimes. No activation energies were reported.

Since the reaction mechanism has been identified as containing both an uncatalyzed and an autocatalyzed mechanism, a rate equation using parts to describe the parameters for both reactions has been used throughout the literature. Activation energies vary for different systems from 15-20 Kcal for the uncatalyzed reaction and 10-15 Kcal for the autocatalyzed reaction. Several equations of this general type have been used. The following equation has been used by a number of investigators (17,19,25). Note that there is a term where the autocatalyzed rate constant (k_2) is multiplied by the extent. This represents the hydroxide concentration in an abstract manner.

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)(B - \alpha) \quad (6)$$

In this equation, the B refers to the ratio of amine equivalents to epoxy equivalents. When these two quantities are equivalent, the equation becomes the following (32)

$$d\alpha/dt = (k_1 + k_2\alpha)(1 - \alpha)^2 \quad (7)$$

In all cases the equations above do not apply over the entire extent of the reaction. The reaction becomes diffusion-limited at higher extents causing a change in the kinetics. Lee, Loos, and Springer (25) include an expression to describe this behavior, modeling the diffusion controlled reaction as being first-order above a given extent of reaction.

$$d\alpha/dt = k_3(1 - \alpha), \alpha \geq \alpha_1 \quad (8)$$

The weakness in this approach is that it just does not make sense that the reaction kinetics magically transform at a given extent. The same rate law should work over the entire extent of reaction. In this author's opinion this anomaly in the literature regarding epoxy/amine reactions is the single greatest reason for carrying out this study.

Some more recent investigations have included terms varying the reaction order of the uncatalyzed and autocatalyzed reactions (18,23). This produces equations similar to those described above but with additional exponential terms.

$$d\alpha/dt = (k_1 + k_2\alpha^p)(1 - \alpha)^q \quad (9)$$

In these equations, the quantity denoted by p is representative of the autocatalyzed part and the part denoted by q is representative of the uncatalyzed part. The quantity p was found to be equal to 1 with q being equal to 2. This is consistent with the equations described above.

Hagnauer (15) has fit initial rate data for a reaction of DDS with tetrafunctional resin and obtained a rate law first order in resin and second order in DDS.

$$-d[\text{TGMDA}]/dt = k[\text{TGMDA}][\text{DDS}]^2 \quad (10)$$

Here, TGMDA denotes the tetrafunctional resin. Consideration of this data indicates that the initial rate constant depends upon amine concentration if second order behavior is assumed. This model breaks down at higher extents of reaction.

Dusek (14) writes the rate law for difunctional epoxy reacting with tetrafunctional amine as a series of second-order expressions. Rate constants for reaction with primary amine (k_1) and secondary amine (k_2) are considered as separate quantities.

$$dA_1/dt = -k_1A_1E \quad (11)$$

$$dA_2/dt = k_1A_1E - k_2A_2E \quad (12)$$

$$dA_3/dt = k_2A_2E \quad (13)$$

Here, A_1 represents primary amine, A_2 secondary amine, and A_3 tertiary amine. The rate constants are of the form

$$k = k_u + k_c OH \quad (14)$$

where k_u is the uncatalyzed rate constant and k_c the autocatalyzed rate constant. Dusek also formulates dimensionless versions of these equations for use in a network model (14). Discussion of these equations is reserved for later in this section (cf. Network Modeling).

Sung (22) breaks these equations down even further. Recall that the DDS molecule has amine groups at both ends. Sung's azochromophoric labeling technique can distinguish whether DDS has either one, two, three, four or no substituents at all. Therefore, amine concentrations are expressed in these terms. For instance, A_{11} denotes a species with primary amine at both ends of the DDS molecule, A_{33} represents tertiary amine at both ends, etc. The rate equations are then written as follows

$$-dA_{11}/dt = 4k_1 A_{11} E \quad (15)$$

$$-dA_{12}/dt = 2k_1 A_{12} E + k_2 A_{12} E - 4k_1 A_{11} E \quad (16)$$

$$-dA_{22}/dt = 2k_2 A_{22} E - 2k_1 A_{12} E \quad (17)$$

$$-dA_{13}/dt = 2k_1 A_{13} E - k_2 A_{12} E \quad (18)$$

$$-dA_{23}/dt = k_2 A_{23} E - 2k_2 A_{22} E - 2k_1 A_{13} E \quad (19)$$

$$-dA_{33}/dt = -k_2 A_{23} E \quad (20)$$

The ratio of the rate constants for reaction of primary amine to that of secondary amine has been confirmed to be 2.0 by Dusek, Charlesworth, and Sung (14,19,22). Since the ratio of reactive hydrogens of primary amine to those of secondary amine is also 2.0, this implies that the reactivity of amine hydrogens does not exhibit a substitution effect.

This cannot be said for reactions involving tetrafunctional amines. The ratio in these cases appears to be closer to 5.0 (10,11). Both Tsou and Peppas (10) as well as Morgan (11) also make efforts to quantify the etherification reaction. The reaction is treated as a second-order reaction between hydroxide and epoxide with a rate constant of 0.1-0.2 that of primary amine with epoxide. No research has been located in the literature quantifying the reaction of tertiary amine with epoxy.

All of the rate laws in the literature which have been found can be grouped into the above categories. The reaction is generally modeled as an uncatalyzed bimolecular step and an autocatalyzed termolecular step which is consistent with the reaction mechanism. Rate constants exhibit Arrhenius behavior. Information regarding rate equations for etherification and for the reaction of tertiary amine with epoxide is relatively sparse. The rate law for etherification is generally assumed to be second order with the rate constant taken to be proportional to the rate

constant of the epoxide/amine hydrogen reaction (10,11). No rate law for the reaction including tertiary amine has been identified or developed in a quantitative fashion.

MODELING OF DIELECTRIC PROPERTIES

Dielectric properties of thermosetting resins recently have been coming increasingly under study (33-38). These studies are carried out over a wide frequency range. Information regarding dielectric properties at microwave frequencies is important for control of electromagnetic absorption (and consequently temperature control) during microwave heating. Microwave heating is considered to be an alternative method of initiating curing reactions to the thermal methods more generally employed since the energy used to heat the resin is input directly into the resin rather than through the material boundaries. Rapid heating of the resin can therefore be accomplished (36).

This research does not provide information regarding measurement of dielectric properties at microwave frequencies. Rather, it seeks to construct a theoretical model for data already existing in the literature. For further information regarding how this data is obtained experimentally, the reader is referred to the original papers (36-38). Jow et. al. have measured dielectric constant and loss factor for the DER 332/DDS stoichiometric mixture as a function of DSC extent (see above). Figures 58 and 59 present data obtained by Jow et. al. (37) for dielectric constant and loss factor. The loss factor is the parameter which

influences electromagnetic absorption most strongly.

Consideration of Figure 59 reveals that the loss factor increases with temperature and decreases with extent of cure under these experimental conditions. Figures 58 and 59 can be found in the Methods and Results section since the results of the calculation are plotted along with the experimental results.

The first significant attempt to relate absorption of radiation to frequency and temperature for systems containing polar molecules was carried out by Debye (39). Absorption occurs when dipoles relax to a random orientation ordered with respect to an electric field imposed on an absorbing material. The energy required to hold the dipoles in an ordered orientation is released as thermal energy when the dipoles relax. This orientational polarization and subsequent relaxation is important near microwave frequencies for small molecules. The dipoles relax from the ordered to random configuration with a time constant τ . This represents the exponential decay of the dipole correlation function (40). Taking the Fourier transform of the time derivative of the dipole correlation function leads to an expression for susceptibility from which follows an expression for complex dielectric constant. The dielectric constant is the real part of this expression while the loss factor is the imaginary part. McQuarrie (40) presents the above in more detail. The resulting expressions for real and imaginary dielectric constant are

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_0 - \epsilon_{\infty})}{(1 + (\omega\tau)^2)} \quad (21)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty}) \omega\tau}{(1 + (\omega\tau)^2)} \quad (22)$$

where ω is the frequency of the electric field in rad/sec, τ the relaxation time, ϵ_0 the zero-frequency dielectric constant, and ϵ_{∞} the infinite-frequency dielectric constant. Debye (39) gives the relaxation time for a spherical polar molecule as

$$\tau = \frac{3V\eta}{kT} \quad (23)$$

where V is the molecular volume, η the viscosity, k is Boltzmann's constant and T is the temperature. Kauzmann and Eyring (40,41) express the relaxation process as a first-order reaction with an activation energy.

$$\tau = A \exp (E_a/RT) \quad (24)$$

Large molecules in highly viscous (or solid or networked) media can be expected to have large relaxation times, and the relaxation time would decrease with increasing temperature. While Debye's expression does not work for complicated systems it is useful for

considering phenomena important in dielectric relaxation. Debye's model works best for systems containing small molecules in gas media or media with low viscosity.

When one considers relaxation in polymeric systems one must deal with a multitude of relaxation processes, large chain molecules, and viscous liquid or solid phases. Usually there will be a distribution of relaxation times about a mean relaxation time with the distribution not always symmetric about the mean. The equations given below can be used much more effectively in such a situation and will therefore be used to model the dielectric results (43). These equations are an amalgamation of expressions used to construct Cole-Cole and Davidson-Cole plots (44,45). Moving from the expression for the complex dielectric constant

$$\epsilon^* = \epsilon_{\infty} + \frac{(\epsilon_0 - \epsilon_{\infty})}{(1 + (i\omega\tau)^{\beta})^{\alpha}} \quad (25)$$

one obtains

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_0 - \epsilon_{\infty}) \sin \alpha\phi}{(1 + 2(\omega\tau)^{\beta} \cos (\beta\pi/2) + (\omega\tau)^{2\beta})^{\alpha/2}} \quad (26)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty}) \cos \alpha\phi}{(1 + 2(\omega\tau)^{\beta} \cos (\beta\pi/2) + (\omega\tau)^{2\beta})^{\alpha/2}} \quad (27)$$

$$\tan \phi = \frac{(\omega\tau)^{\beta} \sin (\beta\pi/2)}{1 + (\omega\tau)^{\beta} \cos (\beta\pi/2)} \quad (28)$$

with α and β being numbers ranging from zero to one which describe the asymmetry and width of the relaxation time distribution respectively. These equations are equivalent to the Debye equations when α and β are set equal to one.

At high frequencies for systems far from the resonant maximum absorption ($\omega\tau = 1$) the above equation reduces to the following.

$$\ln \epsilon'' \propto - \ln (\omega\tau)^\beta \quad (29)$$

This is termed the "universal" dielectric response by Jonscher and Ngai and indeed this is characteristic of dielectric properties of condensed phases at high frequencies (46,47). Since this analysis involves microwave frequencies this property is expected to be useful here. This author's own M. S. thesis also contains some work in this area, particularly regarding the dependence of absorption on temperature for water, nylon 66, and ethylene glycol (48).

The above summarizes the physical nature of absorption of electromagnetic radiation by polymeric materials containing polar groups. These considerations will be used to model the dielectric properties of DER 332/DDS as a function of reaction extent. The exact methods of measuring these properties are outside the scope of this work and are therefore not included in the above discussion.

NETWORK MODELING

A rather obvious common feature of all polymerization reactions is the formation of large chain molecules from smaller ones. The purpose of network modeling is to treat the formation of large chain molecules statistically using probability theory. The information thus obtained is used to characterize polymer physical properties. The thermosetting process is an example of the above. The substituent monomeric units form a network as they react with one another.

Introduction of some of the terminology of network modeling would be helpful at this point of the discussion. The monomers are referred to as branch units. When one branch unit reacts with another branch unit, it is said to have issued a path to the next generation. Polymerization can then be conceptualized as the formation of a hierarchy of branch formation from one generation to the next. The initial branch unit in the hierarchy is referred to as the root (14).

Properties commonly predicted with this type of model are gelation and molecular weight distributions. Flory was the first to characterize gelation using network modeling nearly fifty years ago (49). He defines the gel point in a polymerization as the point where one bond on the average issues from generation to generation. An infinite molecular network is theoretically possible at this point. A branch unit in such a network issues one bond back to the previous generation and one bond forward to the next one. If the branch unit is tetrafunctional, a reaction

extent of 1/3 implies gelation since only 1/3 of the three possible branches to the next generation need be reacted. For a monomer of functionality f the following equation predicts the gel point.

$$\alpha_{gel} = 1/(f - 1) \quad (30)$$

Flory also calculates molecular size distributions as a function of extent for difunctional, trifunctional, and tetrafunctional branching units (49-51). The appropriate expression for difunctional units is

$$w_x = x(1 - \alpha)^2 \alpha^{x-1} \quad (31)$$

where w_x is the weight fraction of the species composed of x units and α is the fraction of functional groups which have undergone polymerization. There are two types of molecular weight averages important in the characterization of polymers. One is the number average molecular weight which is merely the total weight of material divided by the total moles of material and is important in the consideration of polymer colligative properties. For interpretation of the viscous behavior of polymers and their solutions the weight average molecular weight is used. For difunctional units in Flory's model this is given by

of
of
is

Note
water
articl
though
by othe
network
calcula
determi

$$M_{\text{wav}} = M \sum w_x x \quad (32)$$

where M is the molecular weight of an unreacted monomer. Since the molecular weight of a molecule is infinite at the gel point, this quantity does not mean a great deal after gelation. The molecular weight of the material is defined by the size of the vessel in which it is contained. Flory also calculates the sol-gel ratio. The sol fraction of a material is the total fraction of finite molecular species in the network which makes this quantity somewhat useful after the gel point. The sol fraction W_s is given by

$$W_s = 1 \quad \alpha \leq \alpha_{\text{gel}} \quad (33)$$

$$W_s = (1 - \alpha)^2 / \alpha^2 \quad \alpha > \alpha_{\text{gel}} \quad (34)$$

Note that this quantity is unity before gelation and zero when the material is completely reacted.

Flory's work described above comes from a series of three articles published in 1941 (49-51). They can themselves be thought of as the root for a series of "branch" articles published by other investigators as virtually all other approaches to network modeling concern themselves with predicting the gel point, calculating molecular weight averages and distributions, and determining the sol-gel ratio. Another property commonly

Table 1. Structural Parameters Calculated Using Network Modeling.

Structural parameter	Experimental method	Utilization
	<i>Pregel stage</i>	
Molecular weight (MW) distribution	Gel permeation chromatography (GPC)	Ageing of resin-curing agent premixes Processing Chemorheology
Molecular weight averages	VPO, Light scattering and other suitable methods	
Molecular weight vs. compositional distribution	GPC + Liquid chromatography	
Radius of gyration	Light scattering (LS)	
Scattering functions	Static and dynamic light scattering	
	<i>Gel point</i>	
Critical conversion	Solubility Viscosity	
	<i>Postgel stage</i>	
Sol fraction	Extraction	Processing Mechanical, optical and ultimate properties Chemical and thermal stability Chemical and physical ageing
Characteristics of the sol	as above	
Concentration of elastically active network chains (EANC)	Equilibrium elasticity and visco-elasticity	
Length and distribution of EANC and dangling chains	Dynamic LS	
Entanglement trapping factor	Scattering methods	
Size distribution of clusters of chemically dissimilar units	Viscoelasticity	

d

th

in

for

this

can

metho

is no

or die

T

to net

be hig

(52-55

proces

assump

another

equally

Their w

predicted by network models is the concentration of elastically active network chains (14,53). An elastically active branch unit is a branch point which issues three paths with infinite continuation. Infinite continuation is defined by the extinction probability. This quantity denotes the probability that a functional group on a branch unit does not issue a path with infinite continuation. This quantity is equal to unity before the gel point and zero when the polymerization is complete, although it should not be taken to be equivalent to the sol fraction described above. The two are related, however, as will be seen in the subsequent discussion of Dusek's work (14). Dusek's article, in fact, serves as a good reference work regarding network formation in thermosets. The following table, duplicated from this article, provides a selection of structural parameters which can be calculated using network modeling as well as experimental methods and connections with material properties. Note that there is no mention of any connection with glass transition temperature or dielectric properties.

There have been a number of different mathematical approaches to network modeling as mentioned above. Two of these methods will be highlighted here. One is the approach of Macosko and Miller (52-55). Their method uses the recursive nature of the branching process and retains three of Flory's original simplifying assumptions. First, all groups react independently of one another. Second, all functional groups of the same type are equally reactive. Finally, no intramolecular reactions occur. Their work happens to use a tetrafunctional monomer reacting

h

re

ex

moi

mo

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

exci

This st
is comp
before
and bis

with a difunctional monomer as an example. The results of this work are summarized as follows. The weight average molecular weight of a tetrafunctional-difunctional monomer system is

$$M_{\text{wav}} = \frac{(r/2)(1 + r\alpha^2)M_4^2 + (1 + 3r\alpha^2)M_2^2 + 4r\alpha M_4 M_2}{(rM_4/2 + M_2)(1 - 3r\alpha^2)} \quad (35)$$

where r is the ratio of reactive groups on tetrafunctional monomers to reactive groups on difunctional monomers, α is the extent of reaction of tetrafunctional reactive groups, M_2 is the molecular weight of the difunctional monomer, and M_4 is the molecular weight of the tetrafunctional monomer.

The probability of a finite chain (sometimes called the extinction probability) is given for a tetrafunctional monomer as

$$P = (1/r\alpha^2 - 3/4)^{1/2} - 1/2 \quad (36)$$

This should equal one before gelation and zero when the reaction is completely finished. This means that all branches are finite before the gel point. The gel point condition for tetrafunctional and bifunctional monomer is

$$r\alpha_{\text{gel}} = 1/3 \quad (37)$$

Act

com

wri

Tea

form

func

incr

work

gel p

expres

A

function

This is equivalent to Flory's gel point condition applied to a combination of tetrafunctional and bifunctional monomers.

$$\alpha_{\text{Agel}} \alpha_{\text{Egel}} = 1 / ((f_A - 1)(f_E - 1)) \quad (38)$$

The sol fraction is therefore the probability that all of the branches from a root monomer lead to finite chains. This is also equal to one before the gel point but reaches zero much more rapidly as a function of extent after gelation.

$$w_s = p^4 \quad (39)$$

Actually, Macosko and Miller's equations are developed for combination bifunctional and f-functional monomers, but they are written as above since they are applicable to this research. The reader is referred to the original articles for the more general forms (52,53). They also work out the above for systems with functional groups of unequal reactivity and for systems including intramolecular reactions and substitution effects (54,55). This work is useful for calculating the extinction probabilities, the gel point, and the weight average molecular weight since the expressions derived are simple and easy to use.

A more general approach involving probability generating functions was developed by Gordon (56,57) and has been used

recently by Dusek (14). The root monomer is referred to as the zeroth generation ($g = 0$). The probability generating function (abbreviated as PGF) for a root monomer of functionality f is given as

$$F_0(z) = \sum_{i=0}^f p_i z^i \quad (40)$$

where z is a dummy variable through which operations on the PGF are performed and p_i is the probability of a root monomer which issues i branches to the next generation. The PGF equals one when z is set equal to one. The average number of bonds issuing from a monomer is determined by taking the derivative with respect to z .

$$dF_0(z)/dz_{z=1} = F_0'(1) = \sum_i^f i p_i z^{i-1} \quad (41)$$

The PGF for subsequent generations is

$$F(z) = \frac{dF_0(z)/dz}{dF_0(z)/dz_{z=1}} = \frac{\sum_i^f i p_i z^{i-1}}{\sum_i^f i p_i} \quad (42)$$

Note that the fraction p_0 cannot appear as an element of this PGF. The different p_i 's are determined in a rather interesting manner which is worth considering apart from its role in network modeling. Recall the forms of the reaction rate equations for a tetrafunctional amine-bifunctional epoxy system as given by Dusek mentioned in the previous section.

$$dA_1/dt = -k_1 A_1 E \quad (43)$$

$$dA_2/dt = k_1 A_1 E - k_2 A_2 E \quad (44)$$

$$dA_3/dt = k_2 A_2 E \quad (45)$$

Dividing this system of equations by the first equation makes them dimensionless. Note that the epoxy/amine hydrogen reaction is the only reaction considered in this system. The effect of side reactions will be considered in the Discussion section of this thesis. These equations can be numerically integrated to find the mole fractions of primary, secondary and tertiary amines if only the ratios of the rate constants are known. Equal reactivity implies k_2/k_1 equals 1/2.

$$dA_1/dA_1 = 1 \quad (46)$$

$$dA_2/dA_1 = (k_2/k_1)(A_2/A_1) - 1 \quad (47)$$

$$dA_3/dA_1 = -(k_2/k_1)(A_2/A_1) \quad (48)$$

If the epoxy/amine reaction is the only reaction, the PGF's for epoxy and amine molecules can be written for the zeroth and subsequent generations as

$$F_{A0}(z_A) = a_0 + a_1 z_A + a_2 z_A^2 + a_3 z_A^3 + a_4 z_A^4 \quad (49)$$

$$F_A(z_A) = (a_1 + 2a_2 z_A + 3a_3 z_A^2 + 4a_4 z_A^3) / (a_1 + 2a_2 + 3a_3 + 4a_4) \quad (50)$$

$$F_{E0}(z_E) = e_0 + e_1 z_E + e_2 z_E^2 \quad (51)$$

$$F_E(z_E) = (e_1 + 2e_2 z_E) / (e_1 + 2e_2) \quad (52)$$

The subscripts denote how many bonds issue from each monomer. The different a_i 's and e_i 's are given by the following. Epoxide reaction extent is denoted by α_E and amine extent by α_A .

$$a_0 = A_1 A_1 \quad (53)$$

$$a_1 = 2A_1 A_2 \quad (54)$$

$$a_2 = A_2 A_2 + 2A_3 A_1 \quad (55)$$

$$a_3 = 2A_2 A_3 \quad (56)$$

$$a_4 = A_3 A_3 \quad (57)$$

$$e_0 = (1 - \alpha_E)^2 \quad (58)$$

$$e_1 = 2\alpha_E (1 - \alpha_E) \quad (59)$$

$$e_2 = \alpha_E^2 \quad (60)$$

Note that there are two different a_2 's, one where two groups on one end are reacted and one where one group on each end are reacted. This is important in considering the effects of network formation on glass transition temperature, a point which will be considered at numerous junctures throughout the course of this work.

The gel point condition is defined again as the point where one bond on the average issues from generation to generation. Since generations alternate between epoxy and amine monomers the two must be considered simultaneously. The general form of this relationship is

$$F_A'(1)F_E'(1) - 1 \quad (61)$$

More specifically for this system

$$\frac{(2a_2 + 6a_3 + 12a_4)(2e_2)}{(a_1 + 2a_2 + 3a_3 + 4a_4)(e_1 + 2e_2)} - 1 \quad (62)$$

The extinction probability v is the root of the equation below on the interval zero to one.

$$v = F(v) \quad (63)$$

The sol fraction uses the extinction probability as the value of the dummy variable in the PGF for the zeroth generation, implying none of the branches issuing from the root monomer extend to infinity.

$$W_s = v^4 \quad (64)$$

Both quantities equal one before gelation and zero at a state of complete reaction. Dusek also derives an expression for weight average molecular weight but it is more complicated than Macosko and Miller's. The reader is referred to the article by Dusek for further information.

The above approaches to network modeling are referred to as statistical methods (14). Another approach is referred to as a kinetic method and involves writing a rate equation for each possible aggregation of monomers. This obviously involves a set of rate equations which grows in size along with the network. The kinetic method is absolutely intractable without a computer. It is not used nearly as often as are statistical methods (58). It would, of course, be most desirable for accurate calculations of molecular weight distributions and would be more effective for such a purpose than a statistical approach, which is useful for calculating averages.

The above is a brief summary of network modeling.

particularly as it has been applied to the reaction of epoxy and amine. Dusek's work is most useful for the discussion of the material properties investigated in this thesis and will therefore be the focus of subsequent discussion of these properties. Gelation also has a significant effect on the reaction rate constant. The above considerations will figure prominently in the next section regarding the modeling of glass transition and in the Discussion.

MODELING OF GLASS TRANSITION (DiBENEDETTO EQUATION)

The glass transition temperature of a polymeric material can be characterized in terms of group contributions to the total T_g (59,60). Different polymeric repeating units have different lattice energies which describe how they are held in place and different characteristic mobilities which describe how they are able to move. The T_g increases with large lattice energy contributions and decreases with large mobility contributions. Most correlations of glass transition temperature are based upon ratios of these two physical parameters for the repeating units for a particular polymer molecule.

These considerations apply to thermosetting materials as follows. As a material crosslinks, the available lattice energy changes since the polymer chains are more constrained regarding their ability to form contacts with one another. Naturally, this also results in an extensive reduction in the mobility of the chain units, particularly regarding the mobility of the end groups.

Since the mobility of the end groups and the chains to which they are attached reduces with increasing crosslinking at a rate much greater than any corresponding change in the material lattice energy, the glass transition temperature of a thermoset increases strongly with increasing crosslinking.

The DiBenedetto equation (61) is used by a variety of investigators to characterize changes in T_g in a material as it thermosets. It is based on the Principle of Corresponding States, relying on the assumption that all materials with the same general functional form of lattice energy will be in a corresponding state at a reduced glass transition temperature $(T_R)_g$ as described by the below equation.

$$(T_g)_R = T_g/T^* \quad (65)$$

The value of T^* for a particular functional group is dependent on the following parameters

$$T^* = s\epsilon^*/2kv_*c \quad (66)$$

where v^* is the characteristic group volume, c the degree of freedom, s the number of contact points per group, and ϵ^* the interaction energy per contact. This expression therefore has the lattice energy in the numerator and the mobility term in the

denominator. Large lattice energies and low chain mobilities would result in a high T^* and consequently a high T_g since the ratio of these must be constant if the model assumptions are correct (i. e., the Principle of Corresponding States is valid).

This sets up the derivation of the DiBenedetto Equation. The reduced glass transition temperature of a thermosetting material does not change with crosslinking by definition. If there are no changes in the characteristic group volumes or contacts per segment with crosslinking, the following relationship can be expected to hold

$$T_{gx}/T_{g0} = \frac{\epsilon_x/c_x}{\epsilon_0/c_0} \quad (67)$$

where the subscript x denotes the crosslinked materials. This can be rewritten as

$$T_{gx}/T_{g0} = \frac{\epsilon_x/\epsilon_0}{c_x/c_0} \quad (68)$$

The degree of crosslinking for a particular thermoset formulation is written as (dimensionless)

$$\rho = x/x_{\max} \quad (69)$$

where x is the crosslinking density and $x_{\max}$ the maximum crosslinking density possible for a particular set of monomers. The lattice energy and mobility are assumed to be linear functions of the degree of crosslinking.

$$\epsilon_x = \epsilon_0 + (\epsilon_x - \epsilon_0)\rho \quad (70)$$

$$c_x = c_0 + (c_x - c_0)\rho \quad (71)$$

Putting these values into the right hand side of the ratio of glass transition temperatures of crosslinked to uncrosslinked material given above one obtains

$$T_{gx}/T_{g0} = \frac{1 + (\epsilon_x/\epsilon_0 - 1)\rho}{1 + (c_x/c_0 - 1)\rho} \quad (72)$$

which is rearranged into

$$\frac{T_{gx} - T_{g0}}{T_{g0}} = \frac{(\epsilon_x/\epsilon_0 - c_x/c_0)\rho}{1 - (1 - c_x/c_0)\rho} \quad (73)$$

This is what is called the "DiBenedetto Equation" (61). It should be mentioned here that DiBenedetto never actually published this equation under his own name. It was derived in an informal

seminar and copied down by a fellow named Nielsen, who attributed it to DiBenedetto in a publication of his own (62). The recommended values of the lattice energy ratio and the chain mobility ratio are 1.1-1.2 and zero, respectively. It has been applied to DGEBA/amine thermosets by a number of investigators (1,23,38). One must be careful to use absolute temperature units in the data fitting or the results will be incorrect (see Ref. 38 for an example).

DiBenedetto himself revised this equation and applied it to a variety of situations including the effect of diluents on T_g , effect of chain length and molecular weight, and the effect of crosslinking of epoxy with amine (63). In his more recent derivation the effect of changes in lattice energy with crosslinking is neglected in favor of a more detailed examination of the effect of changes in the mobility of the chain end groups. The equation for prediction of the effect of the degree of crosslinking on glass transition contains terms for amine linkages with only one end group reacted and with both ends reacted, introducing a quadratic term into the expression.

$$T_{g0}/T_{gx} = 1 + \alpha_1 \rho + \alpha_2 \rho^2 \quad (74)$$

Unfortunately the new derivation neglects the fact that there are two sites at the end of each amine linkage available for reaction instead of just one. This author's efforts to fit both of these equations to data resulted in the conclusion that the older form

was superior. The newer form of the equation contains errors regarding the reaction mechanism of an epoxy/amine system.

Consideration of DiBenedetto's more recent work can still lead to some useful conclusions, however. The reaction of one hydrogen atom on the end of an amine linkage will result in much greater increases in T_g with crosslinking than will the reaction of the second hydrogen. This is mentioned in the light of some of Dusek's work in the previous section. The mole fraction of a_2 with both ends reacted will have a greater effect on T_g than the mole fraction a_2 with both hydrogens at one end reacted. Furthermore, the different a_i 's and e_i 's will each have an effect on T_g weighted according to their mole fraction in the thermosetting system.

MODELING OF DIFFUSION LIMIT (WLF EQUATION)

The Williams-Landel-Ferry Equation (1955) is an example of Free Volume Theory. Free Volume Theory characterizes physical properties of materials as a function of the free volume (free space) available for molecular motion to occur. Some examples of free volume-related processes include viscosity, mechanical and dielectric relaxation, and diffusion limited processes (64). The first application of this theory to polymer physical properties was carried out by Doolittle in 1952 (65) in order to correlate viscosity with free volume. The Doolittle Equation is

$$\ln \eta = \ln A + K(v_0/v_f) \quad (75)$$

where v_f and v_o are the free and occupied volumes, respectively. As would be expected, when free volume decreases the viscosity increases.

The WLF Equation relates free volume to system and glass transition temperature by considering thermal expansion and making a few simplifying assumptions (66). By assuming that v_f is small compared to v_o , the ratio v_f/v_o can be replaced by the fractional free volume

$$v_f/v_o = v_f/(v_o + v_f) = f \quad (76)$$

The viscosity term in the Doolittle Equation is then considered to be symbolic of a more general example of a mobility-related material property. The ratio of a mobility-related property at a temperature T to the same property at T_g is then

$$\ln a_T = \ln a/a_g = K(1/f - 1/f_g) \quad (77)$$

where f_g is the fractional free volume at T_g . By using the thermal expansion coefficient α_T and using T_g as the reference temperature the fractional free volume f can be expressed as

$$f = f_g + \alpha_T(T - T_g) \quad (78)$$

Plugging this into the expression for $\ln a_T$ above yields

$$\ln a_T = K \left[\frac{1}{f_g + \alpha_T(T - T_g)} - \frac{1}{f_g} \right] \quad (79)$$

or, more generally

$$\ln a_T = \frac{B(T - T_g)}{C + (T - T_g)} \quad (80)$$

$$B = K/f_g \quad (81)$$

$$C = f_g/\alpha_T \quad (82)$$

This is the final form of the WLF Equation.

This work combines the DiBenedetto Equation with the WLF Equation in order to characterize the effect of crosslinking on T_g and subsequently on the diffusion limit of the reaction rate. By including this type of expression in the rate constant for the epoxy/amine reaction a rate law valid over the entire extent of reaction can be constructed. Changes in T_g as the reaction progresses results in changes in free volume available and reduces the rate constant as extent of cure increases. Dusek (14) proposes that the diffusion-limited reaction is a mobility-related process and the WLF equation would be useful in fitting the high-extent portion of epoxy/amine reaction data.

SUMMARY

The above discussion concisely summarizes the important points developed by examination of the literature. There is still some uncertainty regarding the mechanism of the reaction. Breakdown of infrared spectroscopy data is clouded by uncertainty regarding which absorption bands to use in data analysis. The diffusion-limited reaction has not been characterized by a rate law. Dielectric properties have been extensively investigated both theoretically and experimentally, although just how the properties of a thermoset are affected by cure is not sufficiently understood. The effect of network formation on such physical properties of glass transition temperature has not been characterized nor has its effect on dielectric properties. The remainder of this work will focus on developing new information regarding these questions.

METHODS AND RESULTS

This section is concerned with the experimental and theoretical methods used in this research and also with the results of these methods. Experimental methods included DSC, FTIR, and Carbon-13 NMR. Models were constructed in order to analyze reaction rates, glass transition data, and dielectric properties.

DIFFERENTIAL SCANNING CALORIMETRY

Materials used in this study were the DGEBA epoxy resin DER 332 (Dow Chemical Company) and the amine curing agent DDS (Aldrich Chemical Company). The chemical structures of these materials have already been presented. The DGEBA resin has a functionality of two and an epoxide equivalent weight of 173. The curing agent is tetrafunctional and has an amine hydrogen equivalent weight of 62. Therefore, a stoichiometric mixture of these materials will contain 173 g of epoxy and 62 g of amine or fractional ratios thereof. The mixtures studied in this research were formulated using the following ratios of materials. The 2/2 mixture is the stoichiometric mixture. The other two mixtures were either deficient or in excess with respect to amine.

Table 2. Epoxy/Amine Formulations

Parts Epoxy	Parts Amine	g Amine/100 g Epoxy
2	1	18
2	2	36
2	3	54

The above mixtures were prepared for use in DSC studies in the following manner. The epoxy and curing agent were mixed in a beaker and placed on a hot plate and heated to the solution temperature of 125 C. Since this was above the temperature at which reaction initiates (110 C) the process was carried out as rapidly as possible. Fortunately, the reaction rate at this temperature is slow enough so that no appreciable reaction occurs in the samples. After mixing, the amber liquids resulting were cooled and stored in a dessicator. Fresh samples were prepared every 3-4 days.

Small amounts of the samples (5-10 mg) were placed in the bottom of aluminum pans designed for use with the DSC instrument (Dupont Model 910 Differential Scanning Calorimeter with Model 9900 Computer/Thermal Analyzer) using the head of a small nail. The pans were sealed using a press also manufactured by Dupont. The reference pans were also prepared using this press although of course no sample was used. The sample chamber of the DSC was purged with 50 cc/min of nitrogen.

DSC scans of two distinct types were carried out. First, isothermal scans were conducted in order to measure total evolved exotherm and heat flux as a function of evolved exotherm, temperature, and time. This involved using the Iso-Trak method of the Dupont Model 9900. The sample chamber was allowed to reach the scanning temperature. When this point was reached, the lid of the sample chamber was removed and the sample placed in the calorimeter. The lid was immediately replaced and the chamber sealed. Speed is of the essence in this particular part of the

experiment because the temperature drops when the lid is removed. After this is done, the experiment and data acquisition are automated so that no further attention is required. The scanning temperatures and times are given in Table 3.

Table 3. Scan Parameters and Results for DSC Experiments

Formulation	Temp., deg C	Time, min	Exotherm, J/g
1/2	140	1200	229.7
	160	720	269.9
	180	480	273.3
	200	360	254.9
2/2	140	600	319.3
	160	480	396.7
	180	360	437.7
	200	240	339.0
3/2	140	360	368.1
	160	300	391.5
	180	240	338.0
	200	210	390.8

Exotherms and fluxes are determined by breaking up the DSC curves into sections and using a trapezoidal method. A typical isothermal scan is shown in Figure 8. The fluxes determined using this method are shown in Figures 44-55. The evolved exotherm as a function of time is shown in Figures 9-20. The baseline for the isothermal experiment was a straight line at zero heat flux. The zero-time point was when the instrument again reached the scanning temperature after the lid was replaced as described above. In Figures 9-20, the data for evolved exotherm corresponds to the vertical axis on the right-hand side. The flux at the zero-time point is not zero as is often taken to be the case when DSC

Sample: DER 332/DDS, 1/1, 180 (300)

Size: 6.0000 mg

Method: FINZ

Comment: 50 cc/min N2, Cell Const=1.060, Onset=-13.12, Bline=4.99

DSC

File: A: MCF22180.01

Operator: FINZ

Run Date: 03/22/88 00:15

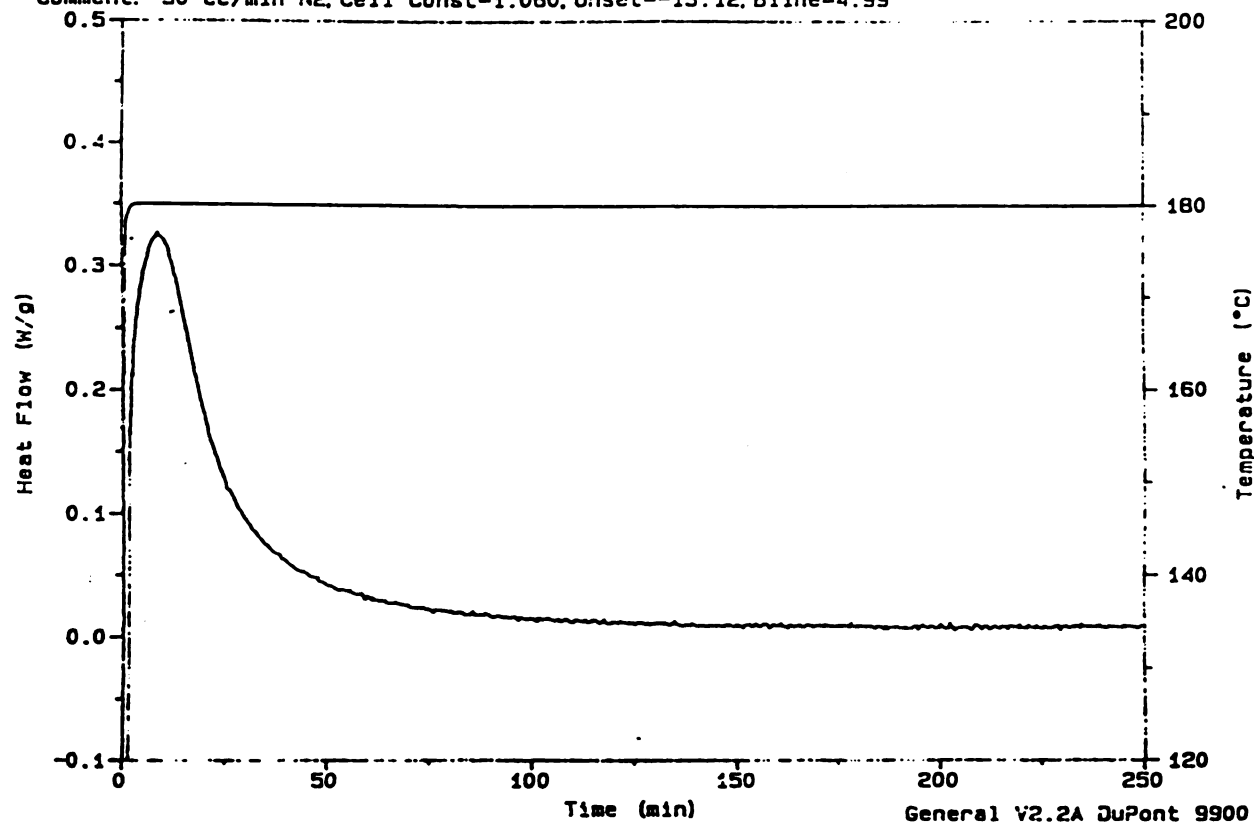


Figure 8. Example of a DSC isothermal scan (2/2 mixture, 180 C).

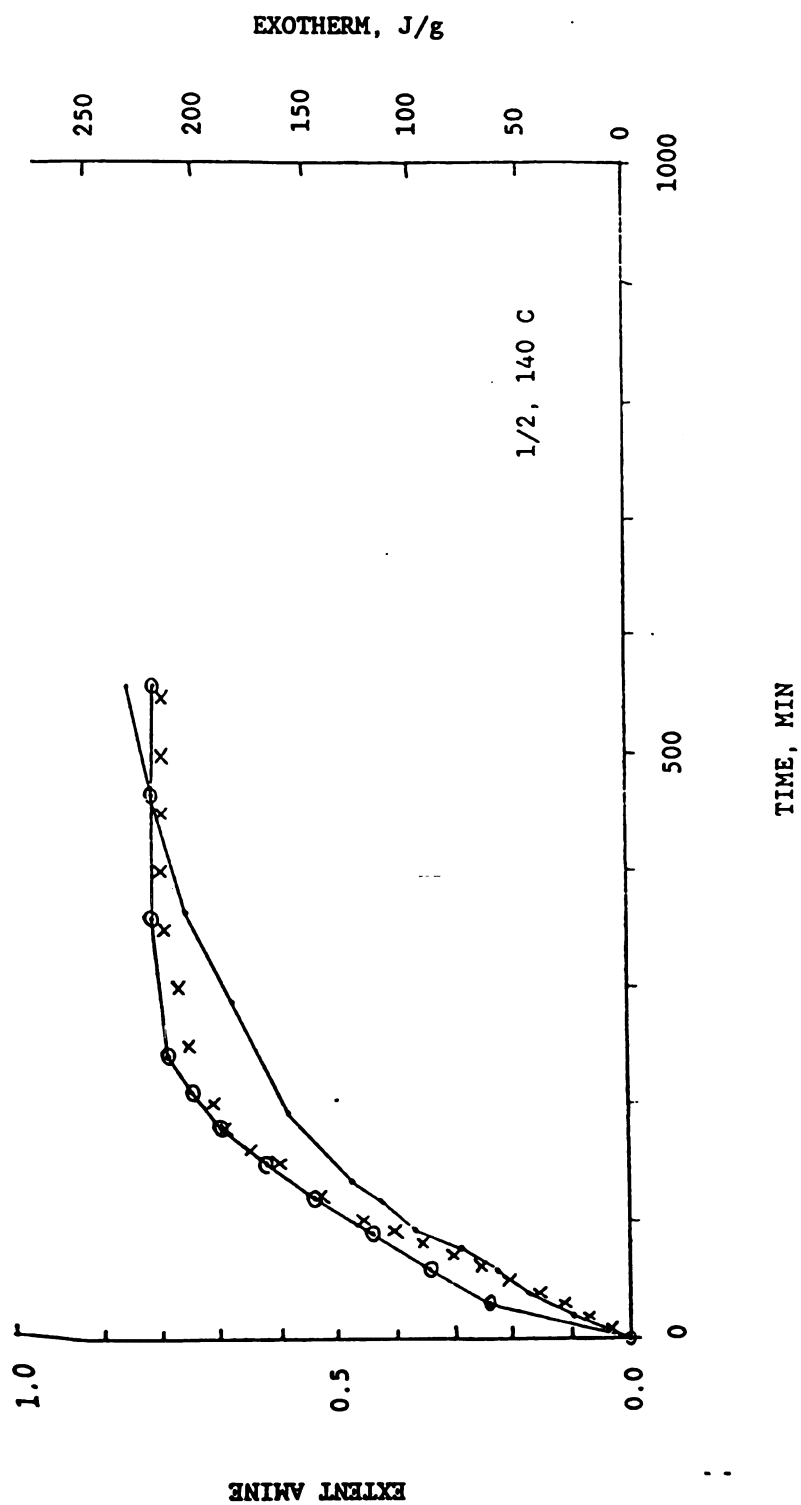


Figure 9. Extent amine and DSC exotherm vs. time (1/2, 140 C).
FTIR (—○—), DSC (—×—), theory (x).

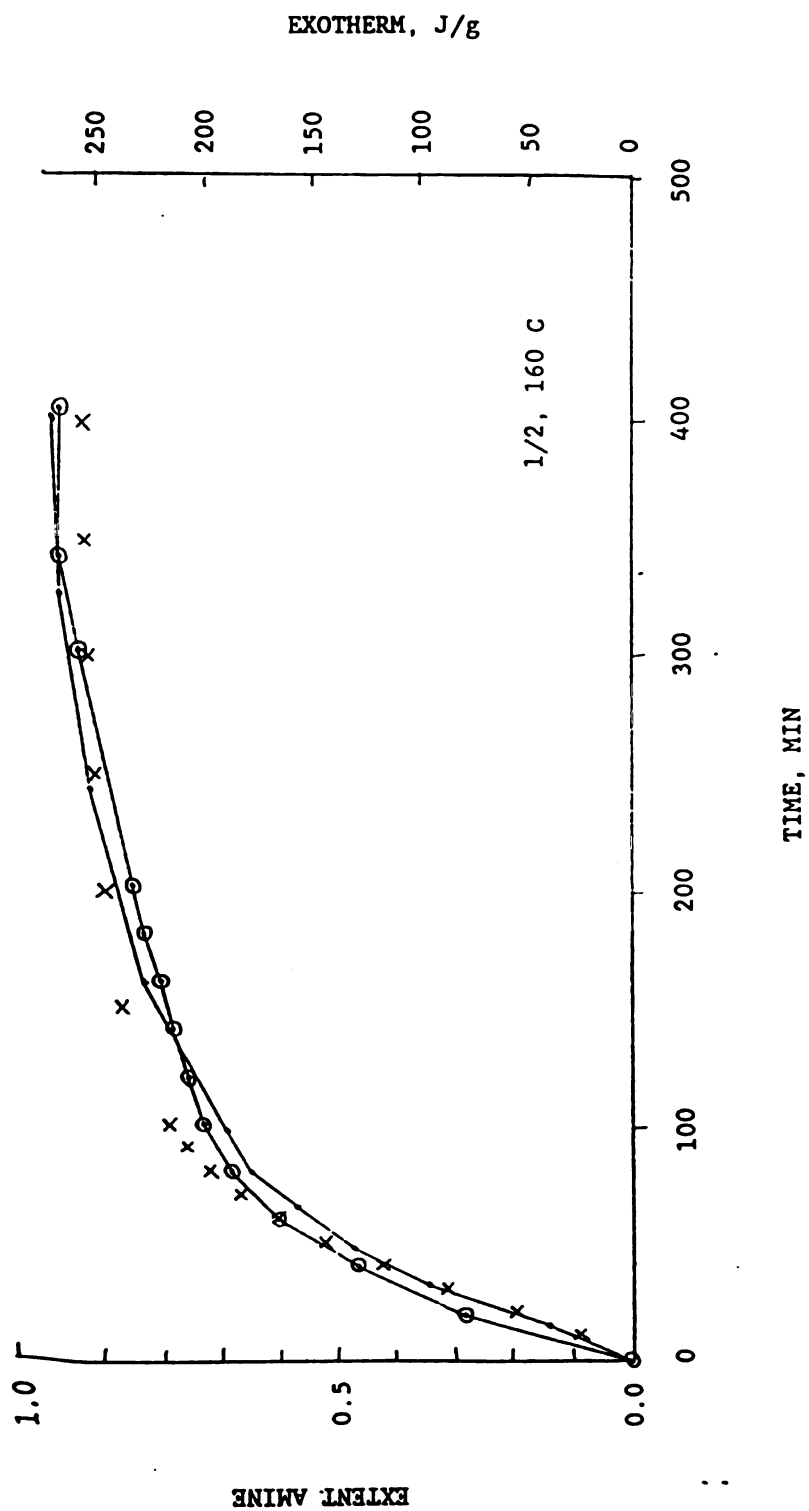


Figure 10. Extent amine and DSC exotherm vs. time (1/2, 160 C).
FTIR (—○—), DSC (—×—), theory (x).

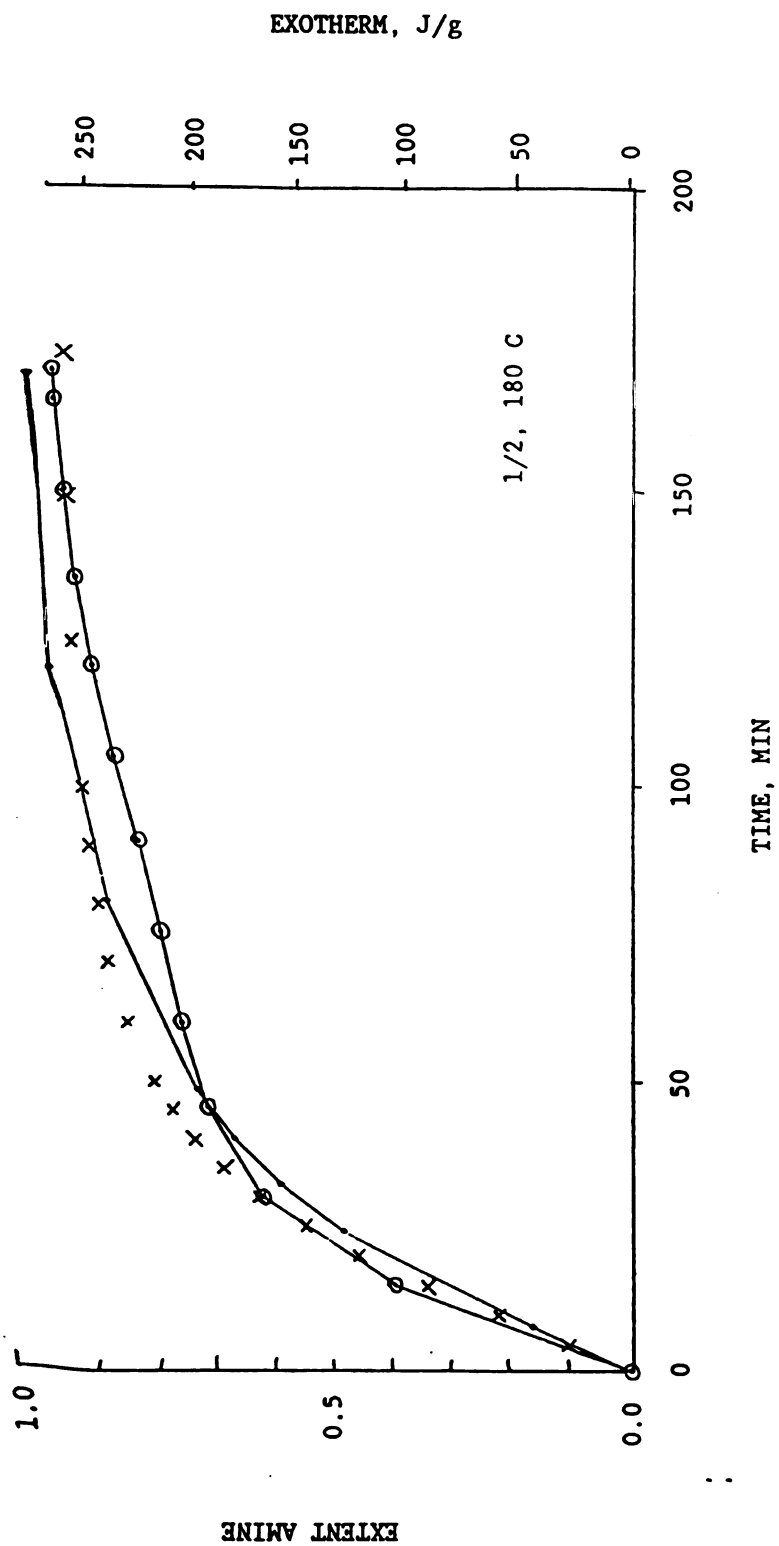


Figure 11. Extent amine and DSC exotherm vs. time (1/2, 180 C).
 FTIR (—○—), DSC (—x—), theory (x).

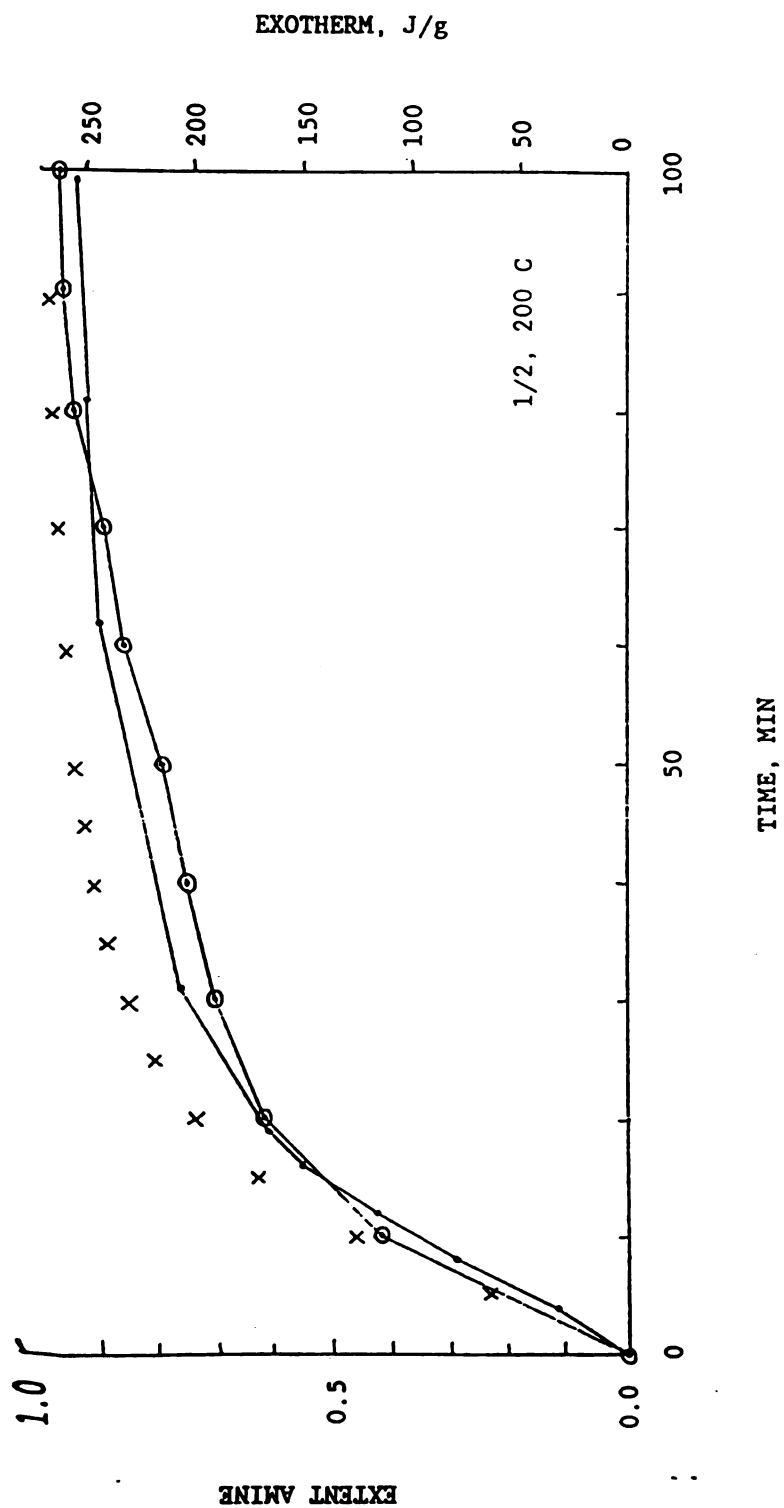


Figure 12. Extent amine and DSC exotherm vs. time (1/2, 200 C).
 FTIR (—○—), DSC (—×—), theory (x).

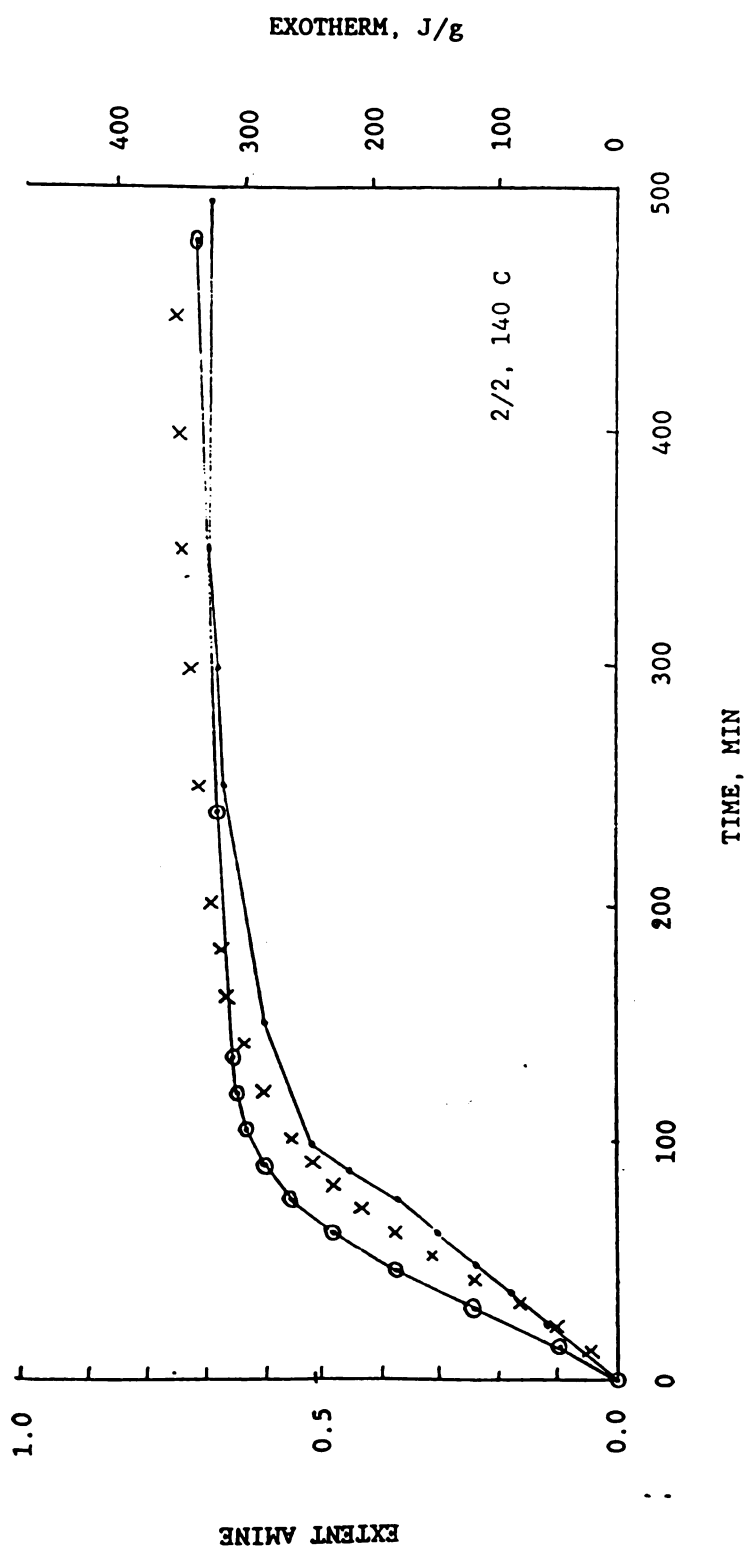


Figure 13. Extent amine and DSC exotherm vs. time (2/2, 140 C).
 FTIR (—○—), DSC (—×—), theory (x).

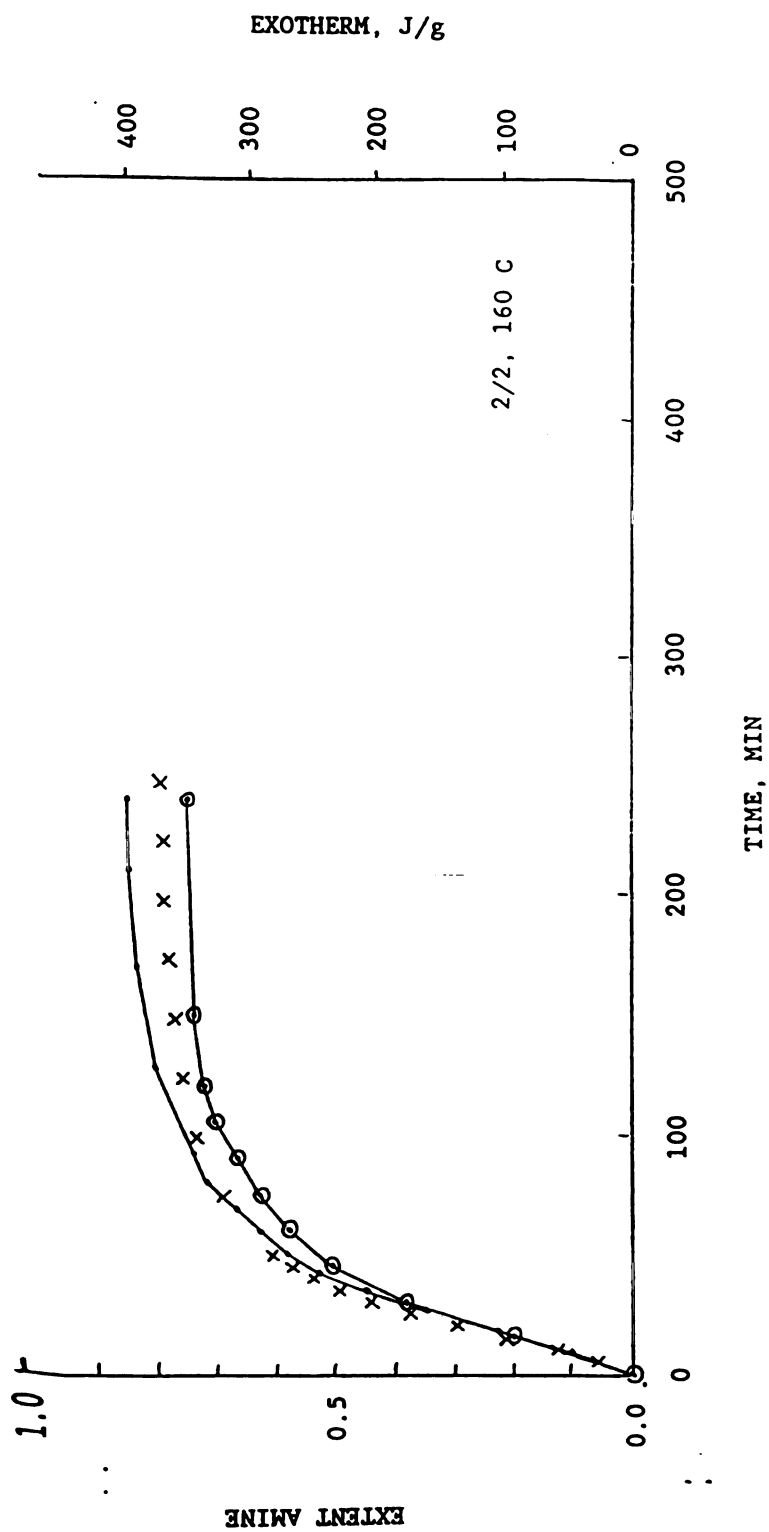


Figure 14. Extent amine and DSC exotherm vs. time (2/2, 160 C).
FTIR (—x), DSC (—o), theory (—).

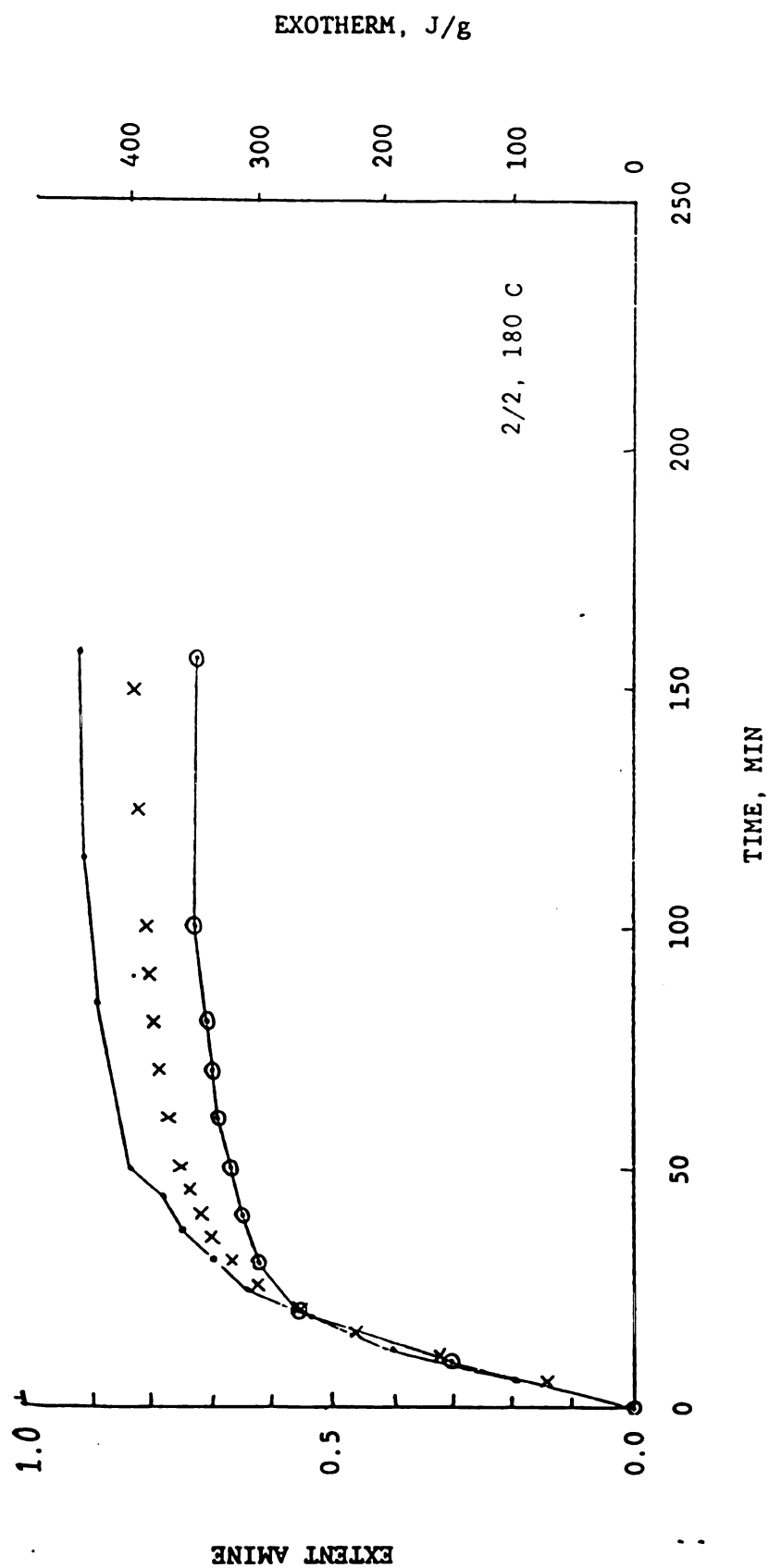


Figure 15. Extent amine and DSC exotherm vs. time (2/2, 180 C).
 FTIR (—○—), DSC (—×—), theory (×).

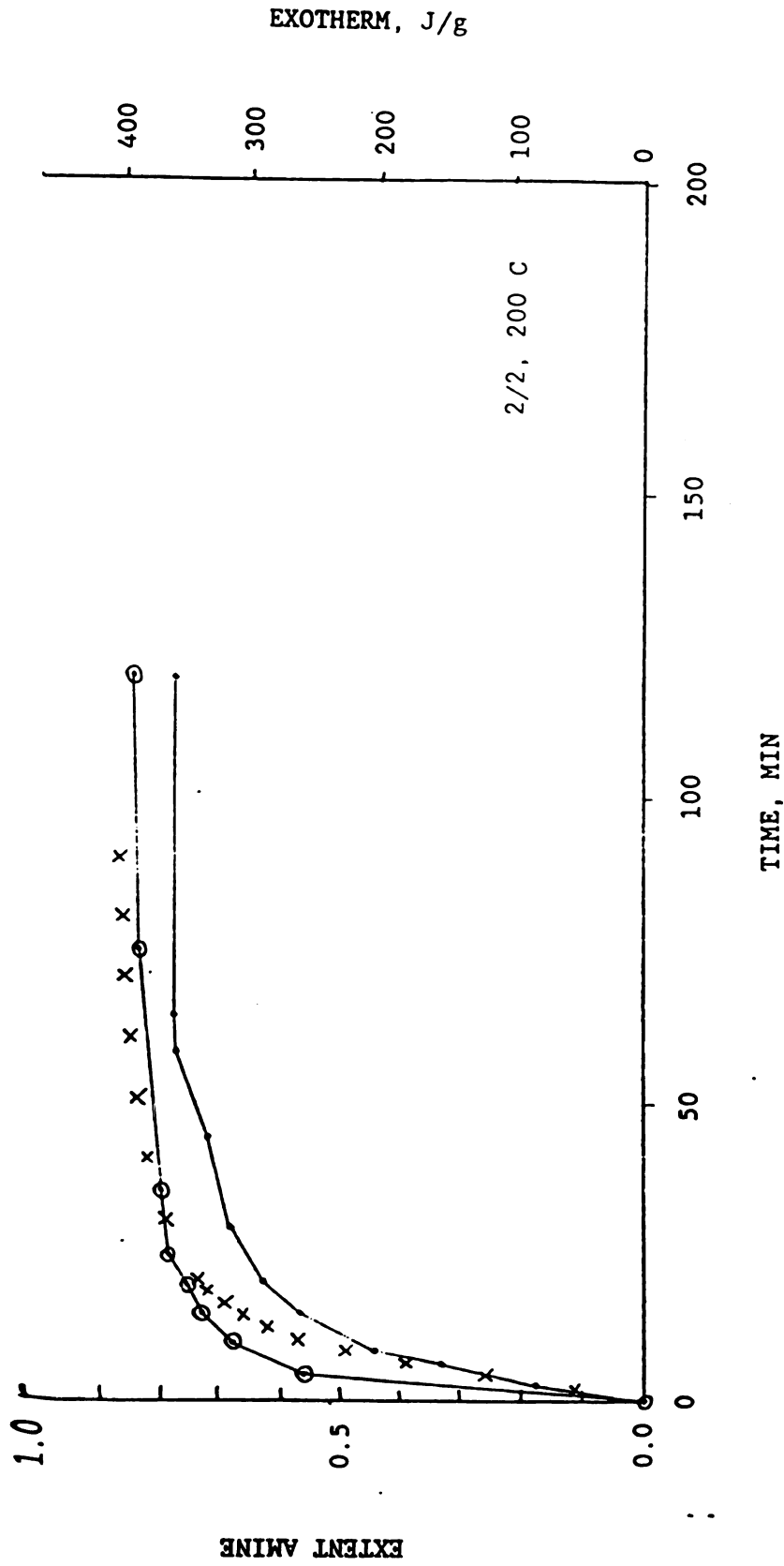


Figure 16. Extent amine and DSC exotherm vs. time (2/2, 200 C).
FTIR (—○—), DSC (—x—), theory (x).

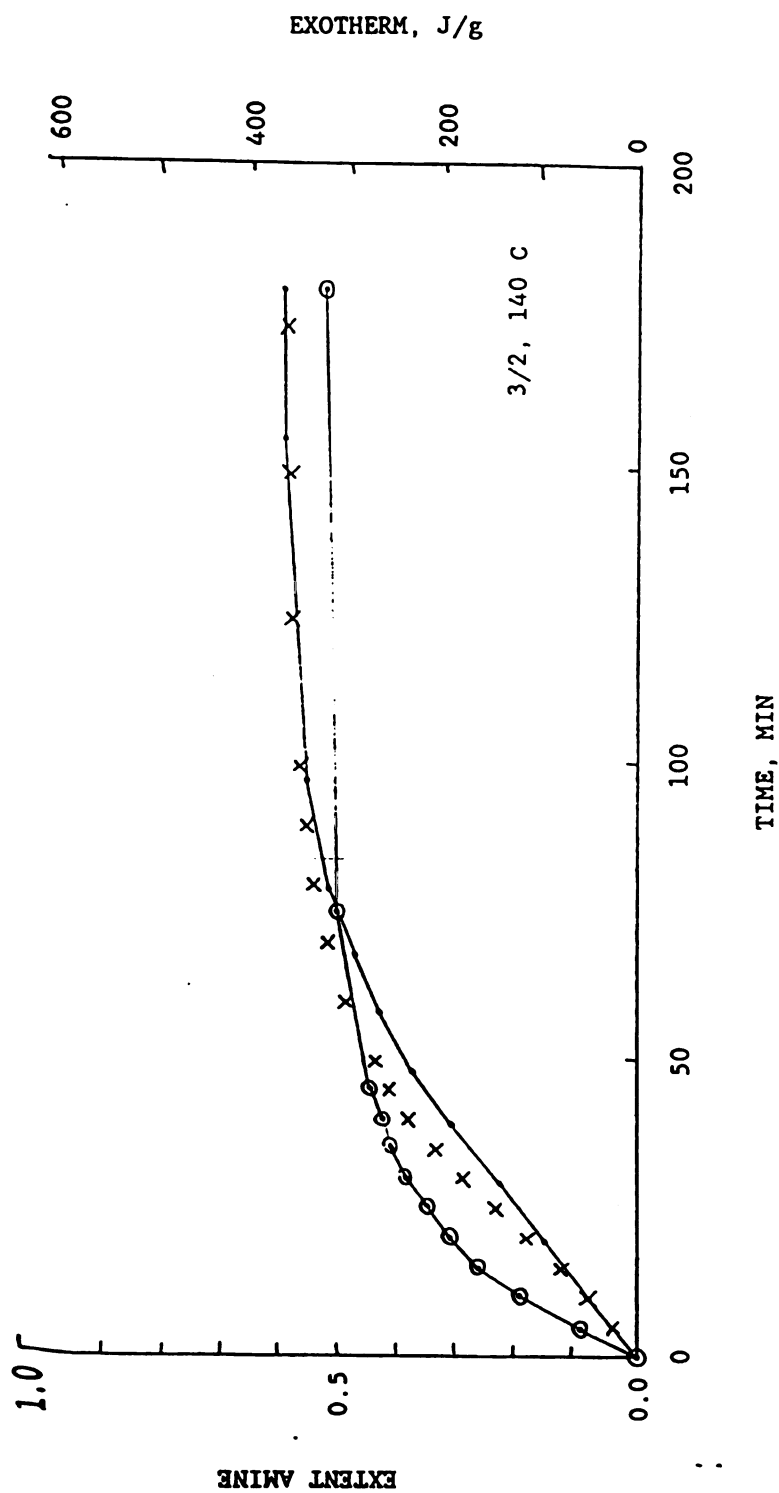


Figure 17. Extent amine and DSC exotherm vs. time (3/2, 140 C).
FTIR (—○—), DSC (—×—), theory (x).

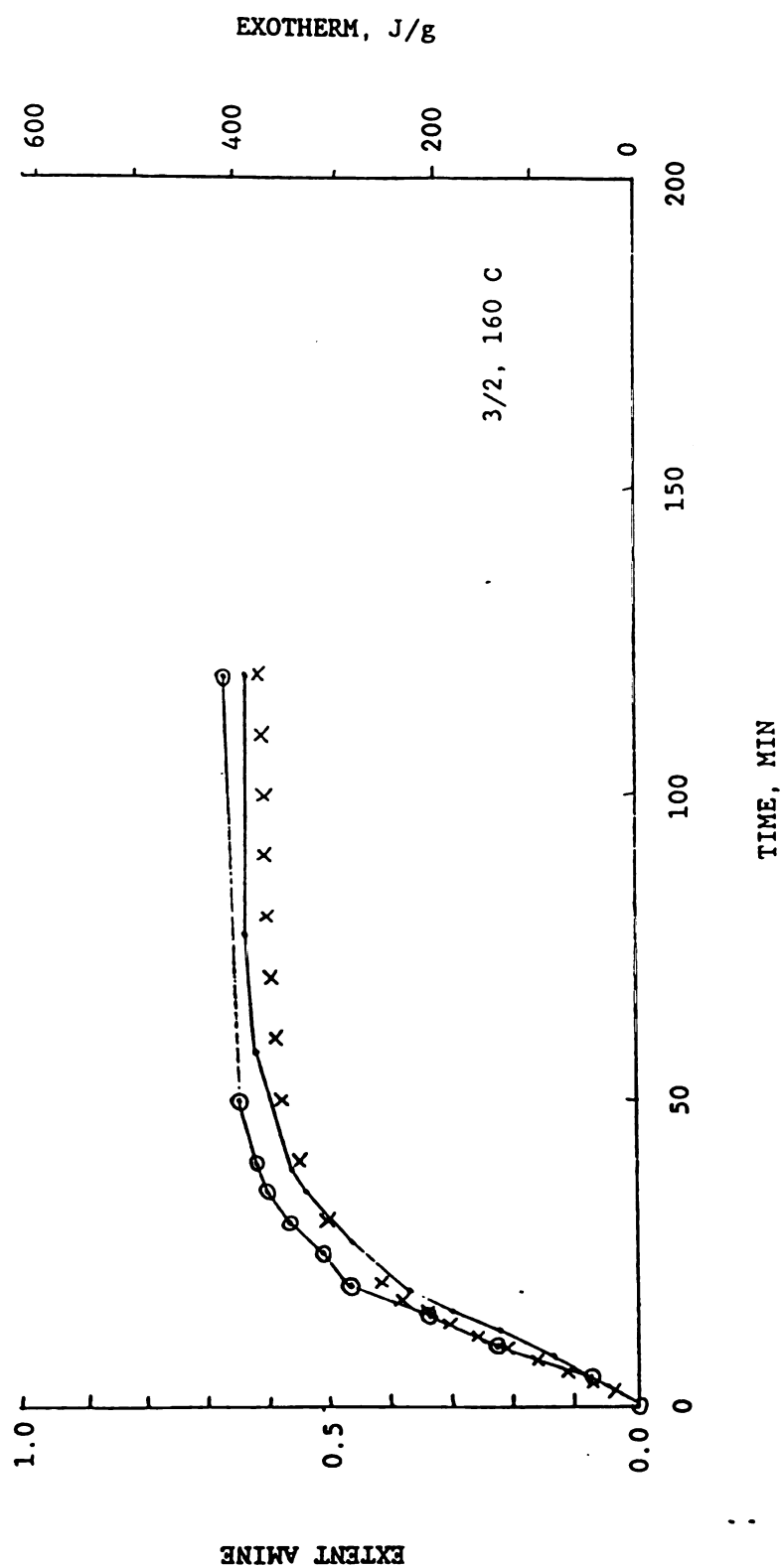


Figure 18. Extent amine and DSC exotherm vs. time (3/2, 160 C).
FTIR (—○), DSC (—×), theory (×).

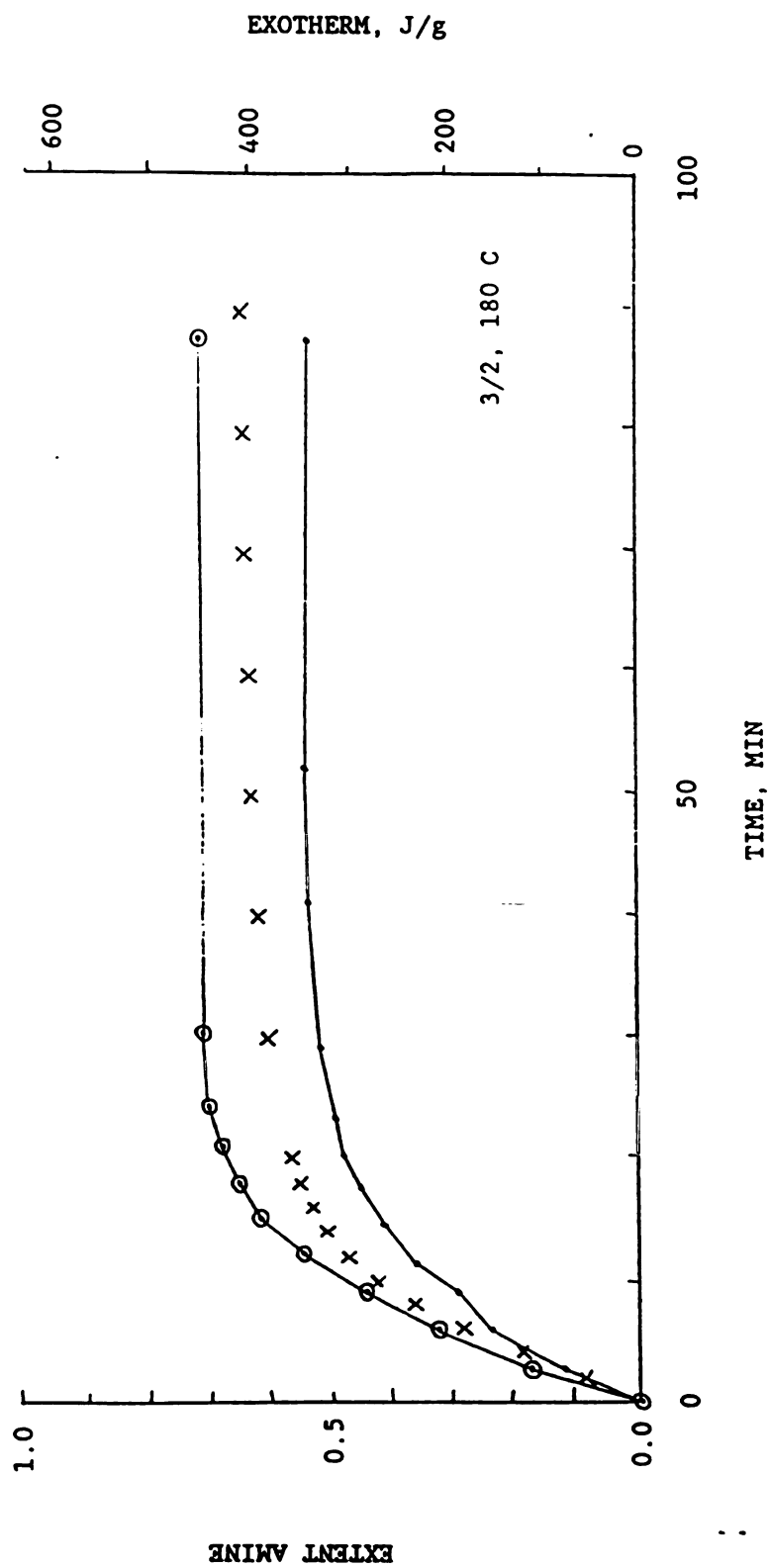


Figure 19. Extent amine and DSC exotherm vs. time (3/2, 180 C).
 FTIR (—○—), DSC (—x—), theory (x).

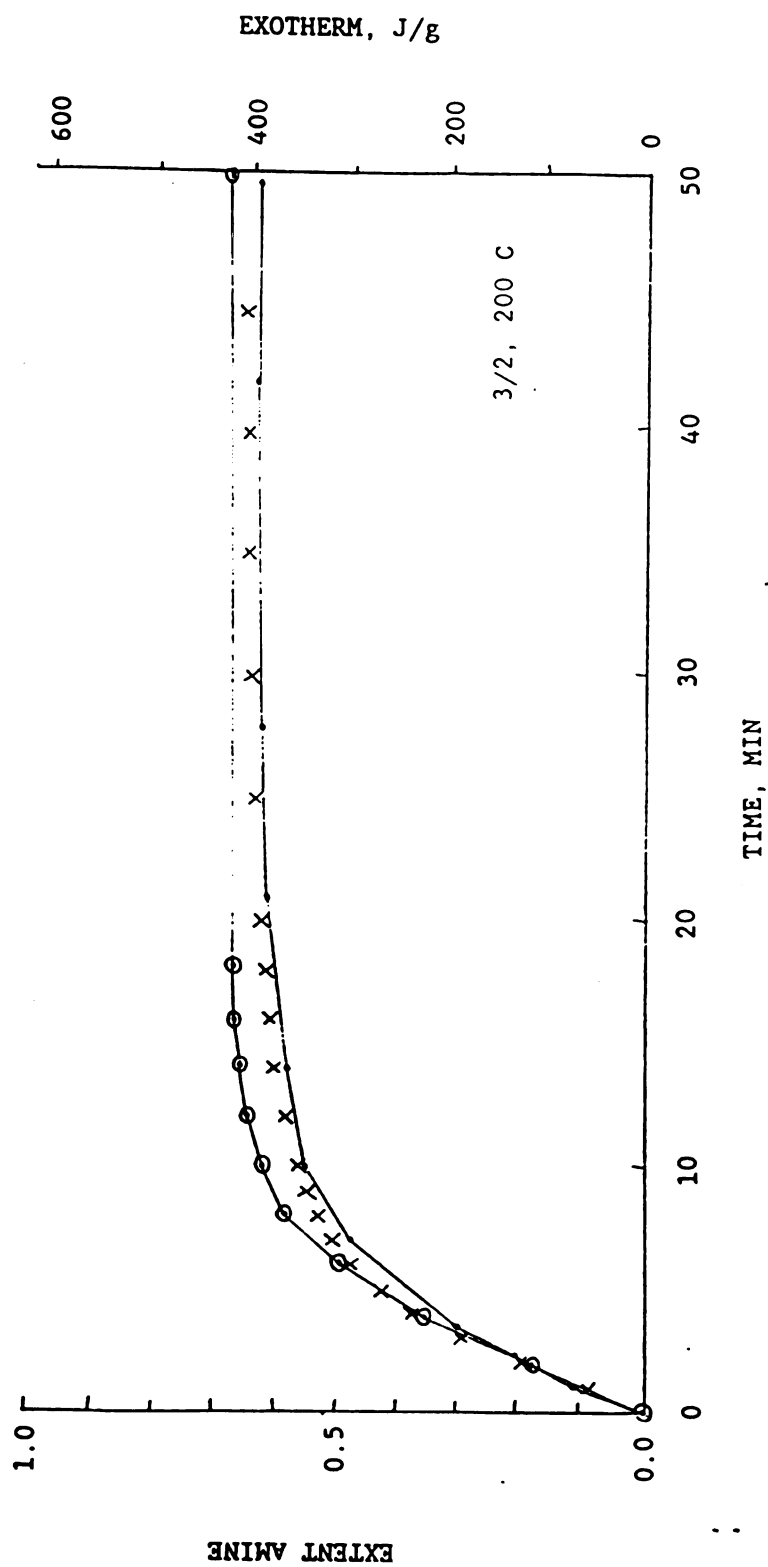


Figure 20. Extent amine and DSC exotherm vs. time (3/2, 200 C).
FTIR (—○—), DSC (---×---), theory (x).

isothermal experiments are integrated. This enables the zero-extent rate constant to be determined as something other than zero.

Dynamic scans in order to determine the glass transition temperature were also conducted. These scans involved using the Ramping temperature program of the Model 9900. The program used in all cases was 10 deg C/min to 270 C. The results of these scans are shown in Table 4. The glass transition temperature is defined as the point where the DSC scan has its first inflection point.

Table 4. Results of T_g Measurements

Formulation	Cure Temperature, deg C	T_g , deg C
1/2	140	--
	160	53.2
	180	55.1
	200	54.2
2/2	140	163.2
	160	182.1
	180	204.5
	200	221.9
3/2	140	167.5
	160	178.6
	180	177.9
	200	180.7

There is no result for the 1/2, 140 C scan due to the fact that there was no inflection point in the DSC trace. The T_g of the mixture is probably less than room temperature. Upon completion of the isothermal DSC scan, the sample was reused for the dynamic

scan. Regardless of whether the scan was dynamic or isothermal, all scans were repeated twice. Since three different formulations were used in conjunction with four different isothermal temperatures, twenty-four isothermal scans (and therefore twenty-four dynamic scans) were conducted using the DSC.

The percentage error associated with the exotherm and heat flux methods is given by the manufacturer as 10 %. The heat fluxes measured are not large and it is difficult to locate the samples in the same position in the calorimeter time after time. The more sample used the less the error. Measurements at large temperatures deviate more due to the fact that there is greater heat loss from the calorimeter to the environment. Also, the baselines used in the isothermal experiments may not always be exactly horizontal. Figure 44 shows an example of how this effect may show up in experiments with very low heat fluxes (1/2, 140 C). The measured flux decreases and subsequently increases; this does not occur in any other case. The baseline is probably not exactly straight but curves a little downward before leveling off. The largest measured heat flux was about 8 mW (1.0 W/g) which occurred for the 3/2, 200 C mixture. The lowest heat flux which can be detected by the instrument is 0.01 mW.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier Transform Infrared Spectroscopy was used in order to monitor the concentrations of two different reactive species as a function of temperature and time. Concentrations of reactive groups were found to depend on the peak areas. These results are

compared to those of DSC in order to elucidate reaction pathways in greater detail. The two species monitored in these experiments were epoxide and amine hydrogen.

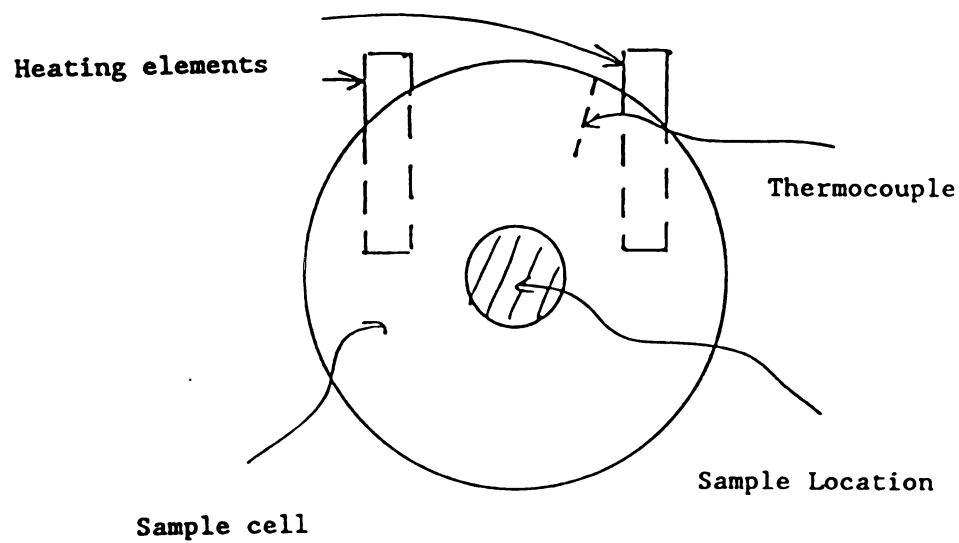
Sample preparation for FTIR involved the same formulations that were used for the DSC experiments. However, since a much smaller amount of sample is required for an FTIR analysis, heating of the sample in order to facilitate mixing is not required. Rather, a mixture of unreacted epoxy and DDS powder was dissolved in acetone in a ratio of 100 ml acetone per gram of DDS. Three drops of the resulting solution was placed on a potassium bromide (KBr) window 1 cm in diameter. These were then placed out in the open air so that the acetone could evaporate, leaving a thin film of epoxy/amine mixture on the KBr disc. This resulted in a film thickness of 10-20 microns. Once the acetone was evaporated, another KBr window was placed on top making an epoxy/amine-KBr sandwich.

The KBr windows had to be manufactured in the laboratory for use in these experiments. Each window required 0.3 g of KBr powder. A Spectra-Tech KBr Die Model 129 was used in conjunction with a Carver Laboratory Press (Model SP-F 6030) in order to produce the windows. The pressure cycle used was 15000 psi for 5 minutes at a time repeated thrice. During the course of this work it was found that operating the press at 70 C reduced the opacity of the windows. The KBr window resulting from this procedure was generally 1 mm in thickness and 1 cm in diameter. A white powder was transformed into a clear crystalline substance essentially transparent to infrared radiation.

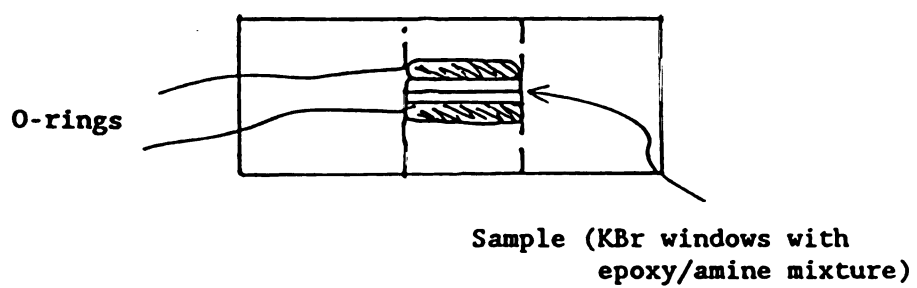
The FTIR instrument used was a Perkin-Elmer Model 1800 Spectrophotometer with CDS-3 applications software. The scans were from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 1 cm^{-1} and required 40 seconds to complete. Since the scans were conducted at elevated temperatures a Widmer Hot Cell was used to house the samples. A drawing of the hot cell along with the sample placement is shown in Figure 21. A Cole-Parmer Digisense temperature controller (Model 2168-70) was used along with heating elements and a thermocouple in order to control the temperature of the hot cell. The FTIR instrument software was modified to include a program named HOTCELL which automated scanning so that the scans could be repeated as often as the operator wished with preselected time intervals. A maximum of 37 scans per run could be carried out, limited by the capacity of the floppy discs used for storing the spectra. Information regarding the scans is given in Table 5. As in the DSC experiments, each run was repeated twice.

Table 5. Parameters for FTIR Scans

Formulation	Temp., C	# Scans	Time/Scan	Total Time
1/2	140	33	30 min	960 min
	160	37	20 min	720 min
	180	31	15 min	450 min
	200	37	10 min	360 min
2/2	140	33	15 min	480 min
	160	33	15 min	480 min
	180	26	10 min	250 min
	200	25	5 min	120 min
3/2	140	37	5 min	180 min
	160	25	5 min	120 min
	180	31	3 min	90 min
	200	31	2 min	60 min



Front view



Side view

Figure 21. Sample with hot cell used in FTIR experiment.

There were three IR bands in each spectra which were analyzed. Two of them have been used extensively by other investigators (see Background section). These were the epoxide band at 915 cm^{-1} and the C-H aromatic stretch at 1510 cm^{-1} which is used as a reference since it does not participate in the reaction. The instrument software has the capability to integrate these bands in order to determine their area. Extent epoxide consumed is determined using the following formula

$$\alpha_E(t) = 1 - \frac{(A_{915}/A_{1510})_t - t}{(A_{915}/A_{1510})_t - 0} \quad (83)$$

The integration limits used were from 885 to 940 cm^{-1} for epoxide and 1480 to 1550 cm^{-1} for the C-H stretch. The results of this calculation are shown in Figures 23-34 for each run.

The third band is a doublet which occurs around 695 cm^{-1} . Consideration of a number of spectra revealed that this band disappeared with time. This band was integrated from 675 to 735 cm^{-1} and was compared to the C-H stretch in the same fashion as the epoxide band.

$$\alpha_A(t) = 1 - \frac{(A_{695}/A_{1510})_t - t}{(A_{695}/A_{1510})_t - 0} \quad (84)$$

This ratio was equal to approximately $2/3$ for a complete reaction of the $3/2$ (excess amine) mixture. This corresponds to complete

Table 6. Comparison of FTIR and DSC Results

Formulation	Temp, C	Exotherm	α_{695}	equiv/g epoxide/amine	Kcal/eq amine
1/2	140	229.7	0.826	.004902/.002451	27.12
	160	269.9	0.990		26.58
	180	273.3	0.996		26.76
	200	254.9	0.996		24.96
2/2	140	319.3	0.728	.004255/.004255	24.64
	160	396.7	0.756		29.47
	180	437.7	0.776		31.68
	200	339.0	0.852		22.35
3/2	140	368.1	0.529	.003759/.005639	29.49
	160	391.5	0.679		24.44
	180	338.0	0.736		19.62
	200	390.8	0.685		24.18

reaction of epoxy with amine with 1/3 of the total amine remaining. The band completely disappeared when epoxy was in excess. This leads to the hypothesis that this band represents amine hydrogen. Using this hypothesis as a basis, Table 6 (see next page) is constructed. (α_{695} represents the above quantity.) Averaging the results in the right hand column gives an average exotherm of 25.94 Kcal/eq amine for the epoxy/amine hydrogen reaction. Consideration of the bond energies (cf. Figure 2) gives an estimate of 25.7 Kcal/mol. Values in the literature range from 24.5 to 26.0 Kcal/eq epoxy (24).

This value of 25.94 Kcal/mol is used to scale the plots in Figures 9-20. Assuming that all available amine hydrogen reacts, the following maximum theoretical exotherms would result.

Table 7. Theoretical Maximum Sample Exotherms

Formulation	Exotherm, J/g
1/2	266.0
2/2	461.8
3/2	612.0

This is how the scales for the right-hand axis in Figures 9-20 were selected. The left-hand axis corresponds to the extent calculated from FTIR results. Placing the FTIR amine hydrogen extents on the same plots used for DSC evolved exotherms enables comparison of the two methods.

Comparing Figures 23-34 (FTIR epoxide) with Figures 9-20 (FTIR and DSC amine hydrogen) shows that epoxide continues to disappear via reaction long after no amine hydrogen is left and there is no longer an exothermic contribution to the reaction.

This indicates that the reaction proceeds by more than one pathway. This effect is most pronounced for the runs at 140 C and especially for the runs with the amine deficient formulation (Figures 9-12 and 23-26).

Figure 22 plots the initial intensity ratios for the bands at 915 and 695 cm^{-1} for each formulation as a function of initial reactant concentration. The linearity of these plots shows that the intensity ratios correspond to the reactant concentrations and that the Beer-Lambert law is valid. The fact that this behavior is exhibited is due to the thinness of the reactant films used in the FTIR experiment.

The error associated for measurement of concentration using this method is also given by the manufacturer as 10 % for this instrument. The chief deviation which is not a function of the instrument is probably due to variations in quality of the KBr windows. Combining the percent errors for FTIR and DSC, a 15 % error can be expected when the two are used in concert. One example of this is the calculation of the exotherm of 25.94 Kcal/eq amine above. The 15 % error corresponds to approximately plus or minus 4 Kcal/eq. Ten out of twelve measurements fall within this range, while the definition of standard deviation predicts 68 % or eight out of twelve.

The above discussion of methods and results from the FTIR experiments involves a certain amount of interpretation. There is no evidence in the literature that the band at 695 cm^{-1} has ever been used for this analysis. It has already been mentioned that primary and secondary amine bands (1615 and 3400 cm^{-1}

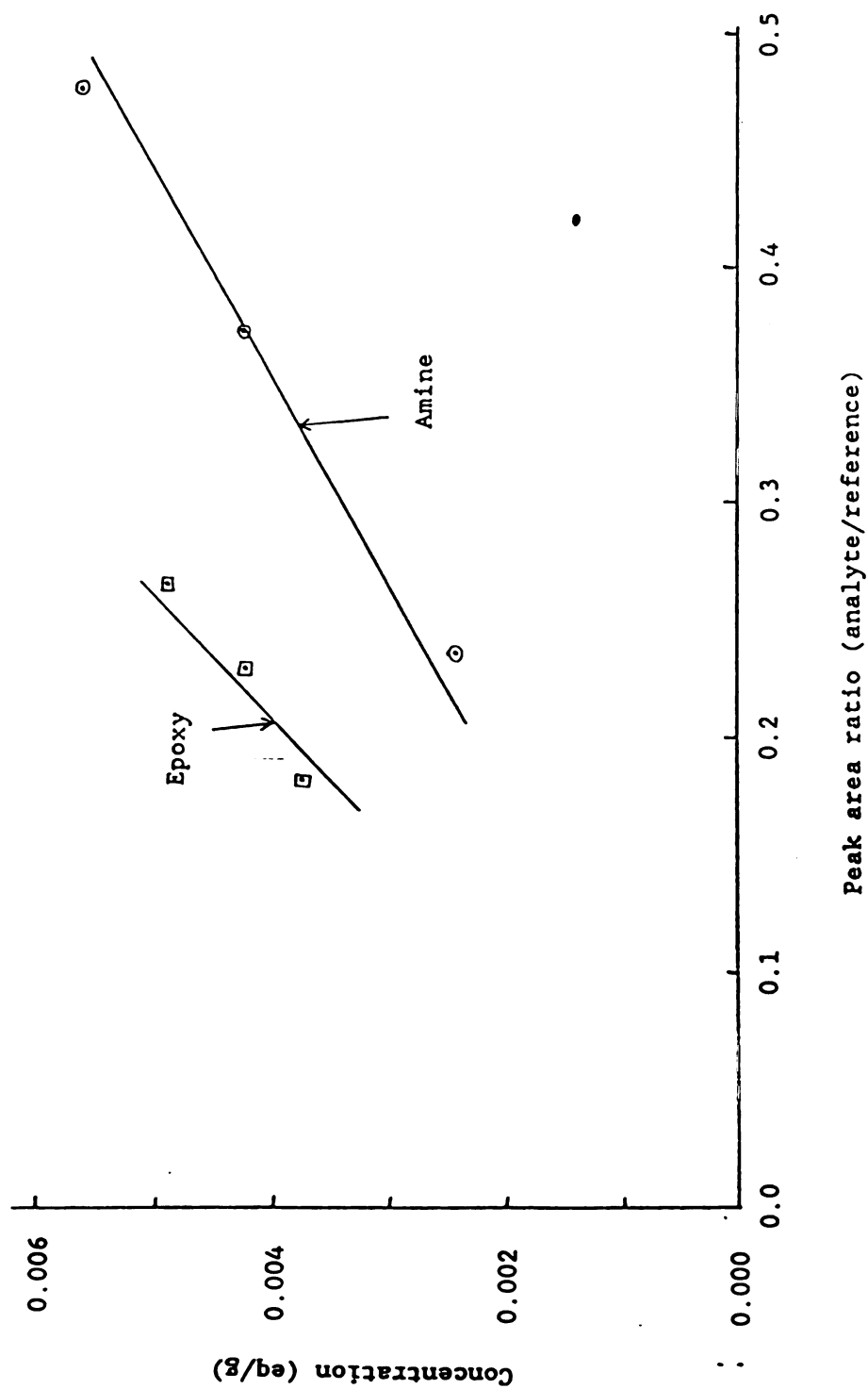


Figure 22. Peak area ratio for epoxy and amine (FTIR) vs. concentration.

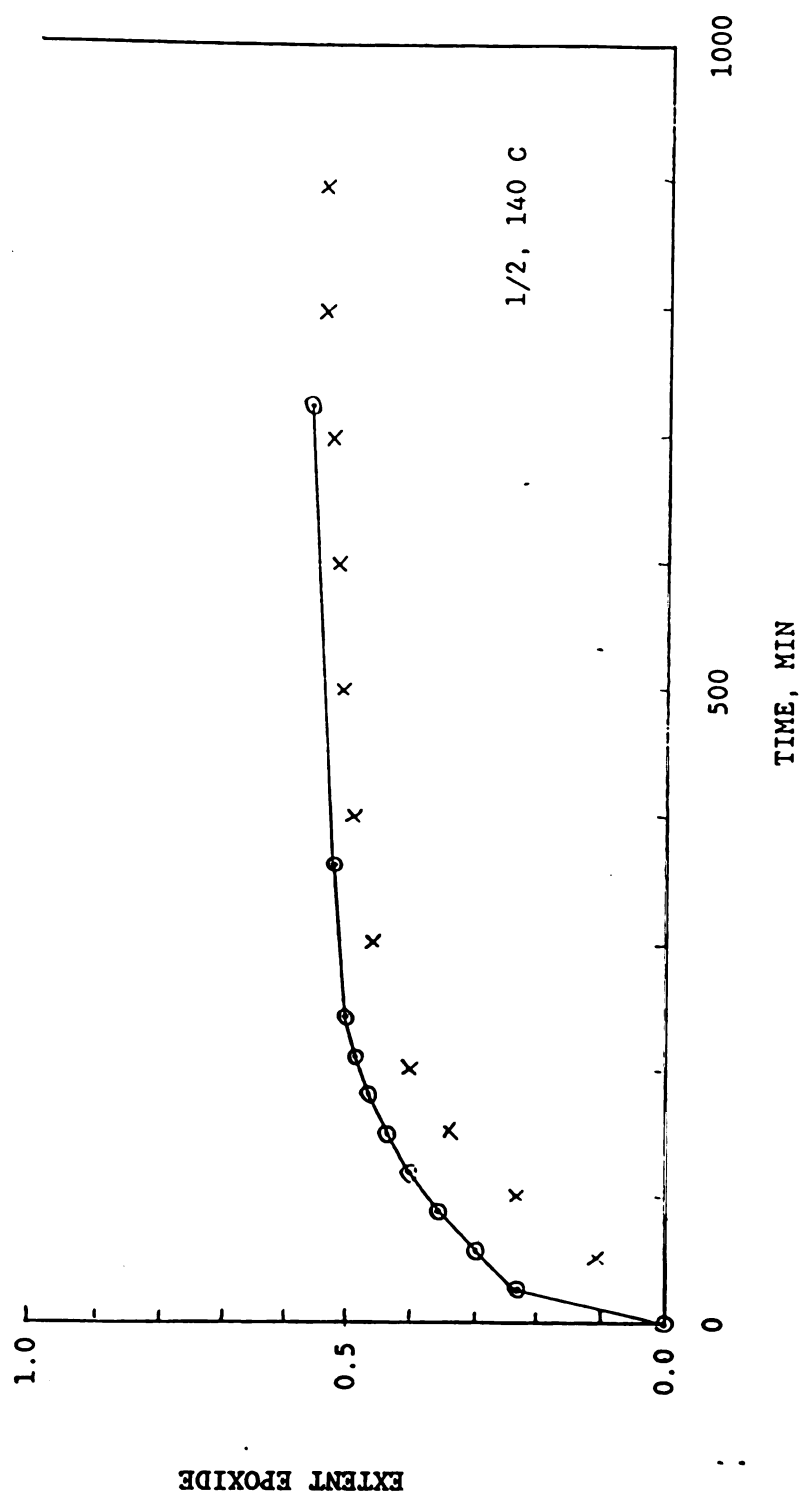


Figure 23. Extent epoxide vs. time (1/2, 140 C).
FTIR (—○), theory (x).

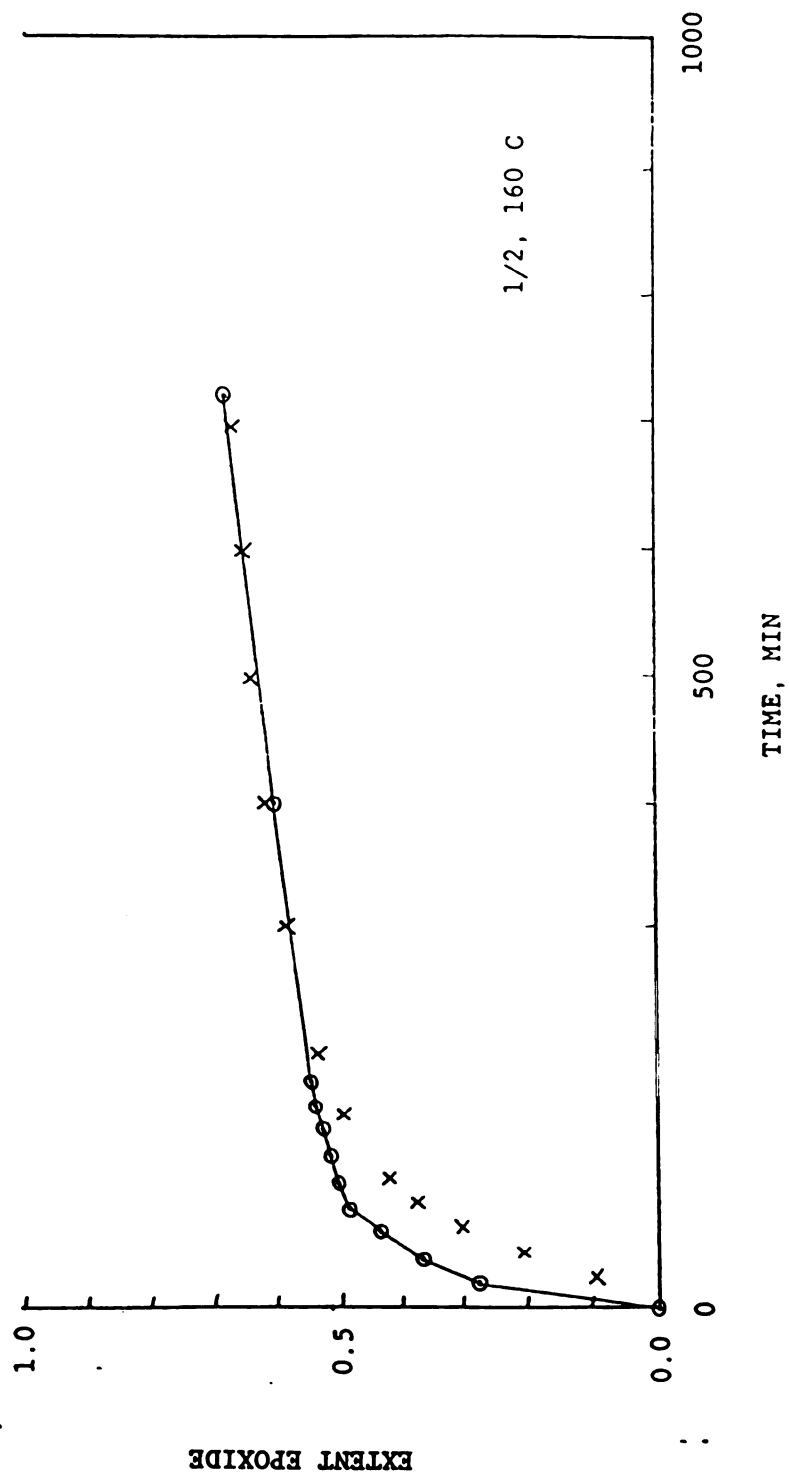


Figure 24. Extent epoxide vs. time (1/2, 160 C).
FTIR (—○—), theory (x).

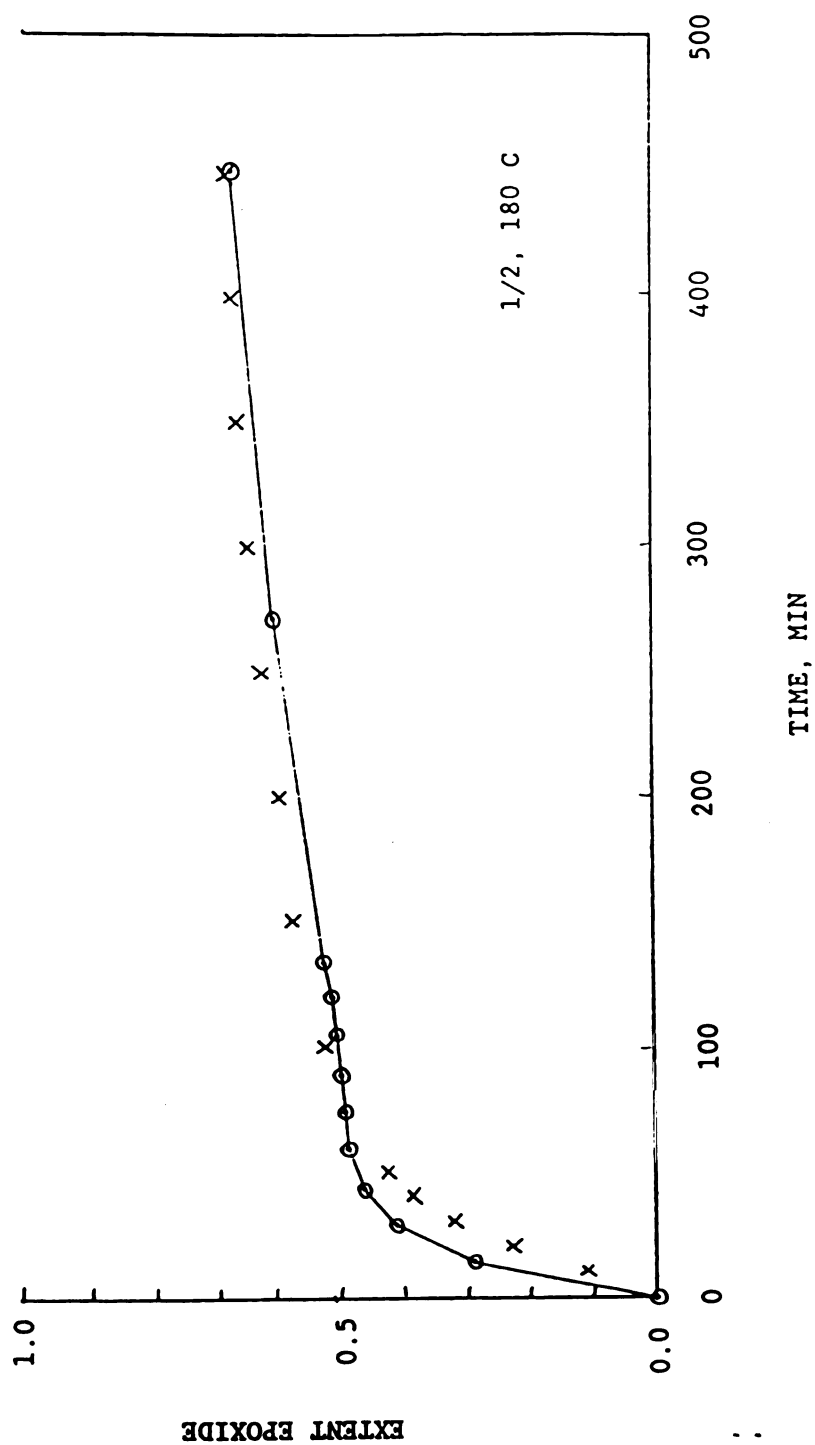


Figure 25. Extent epoxide vs. time (1/2, 180 C).
FTIR (—○—), theory (x).

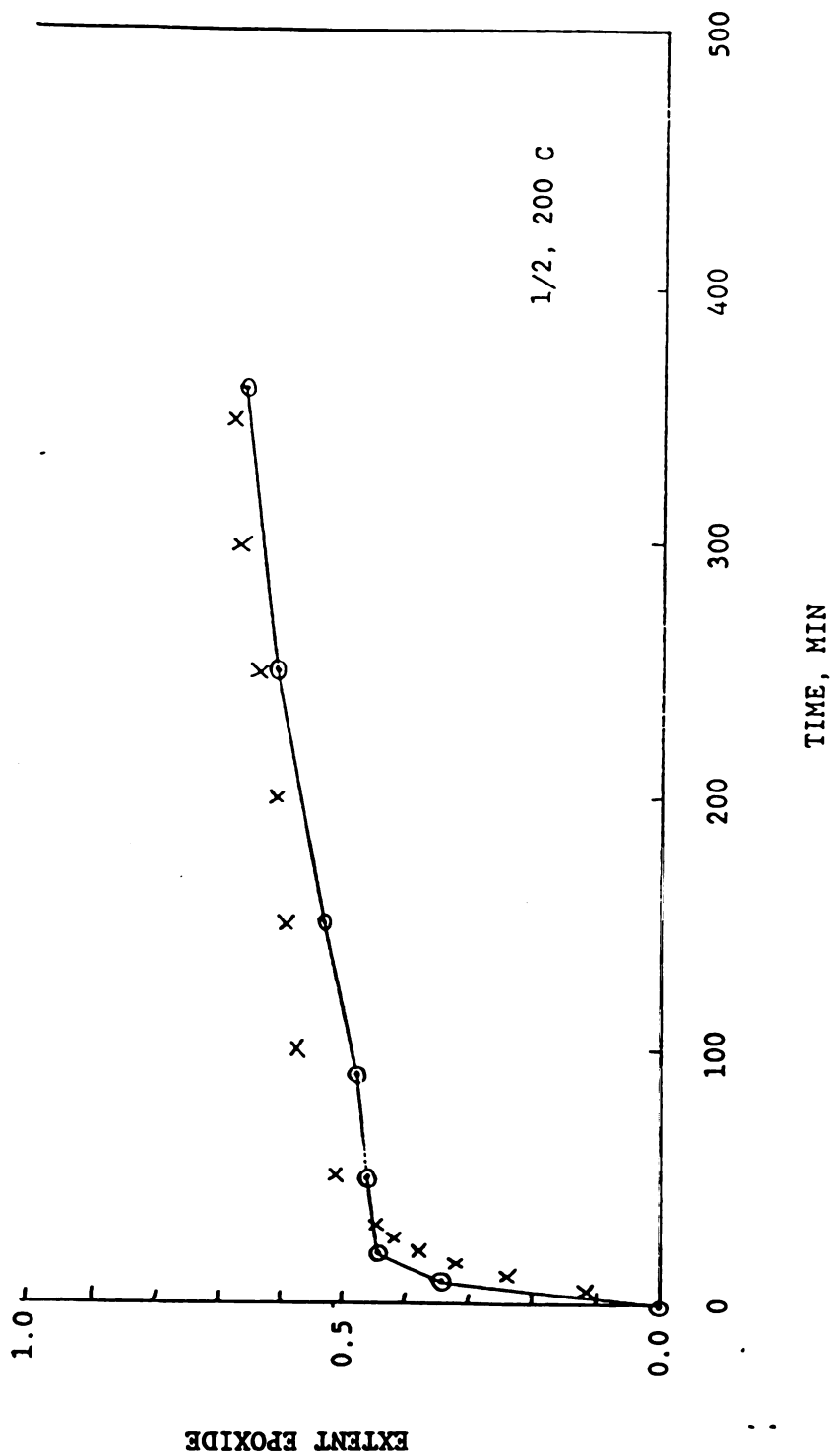


Figure 26. Extent epoxide vs. time (1/2, 200 C).
FTIR (—○), theory (x).

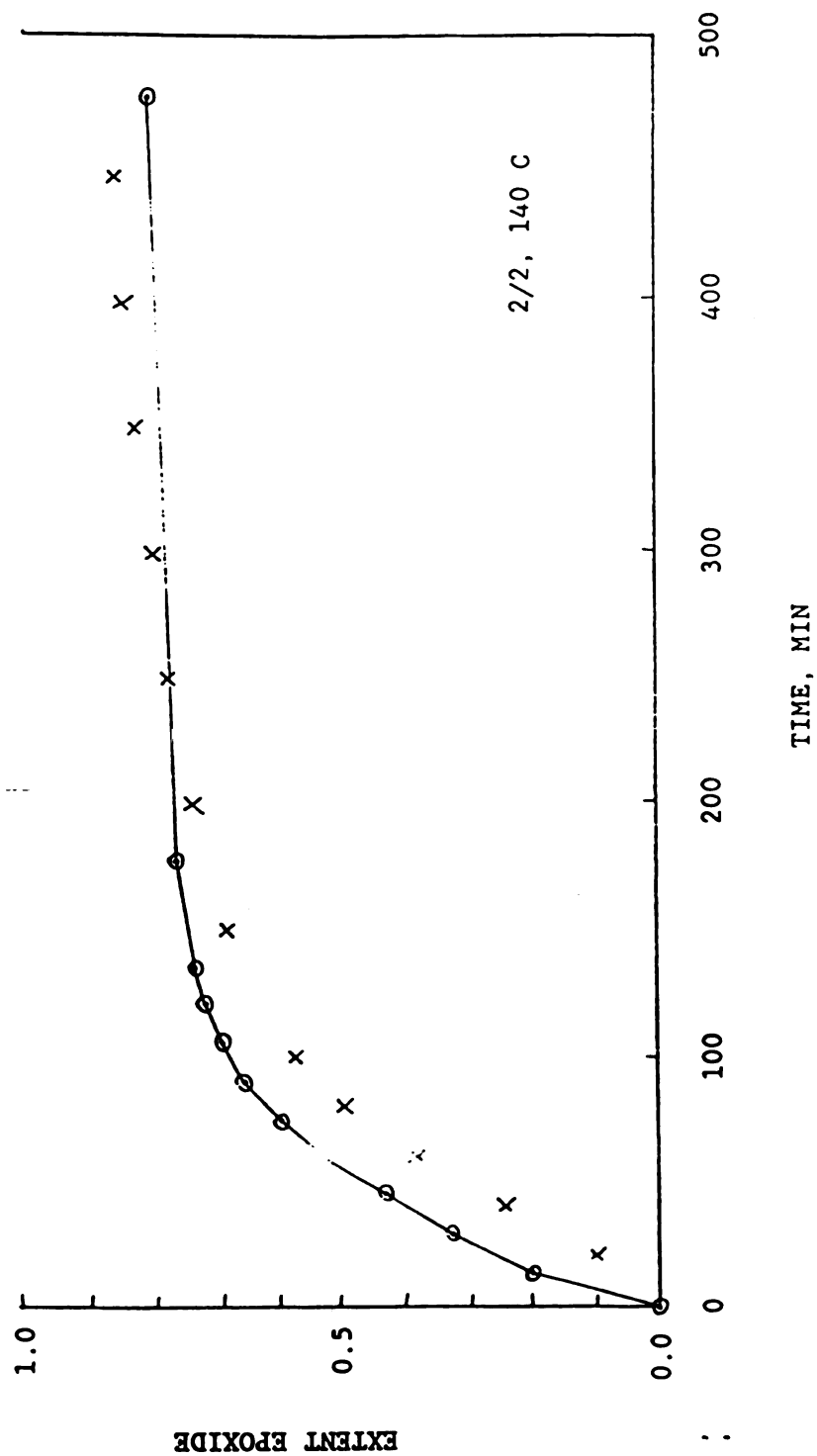


Figure 27. Extent epoxide vs. time (2/2, 140 C).
FTIR (—○—), theory (x).

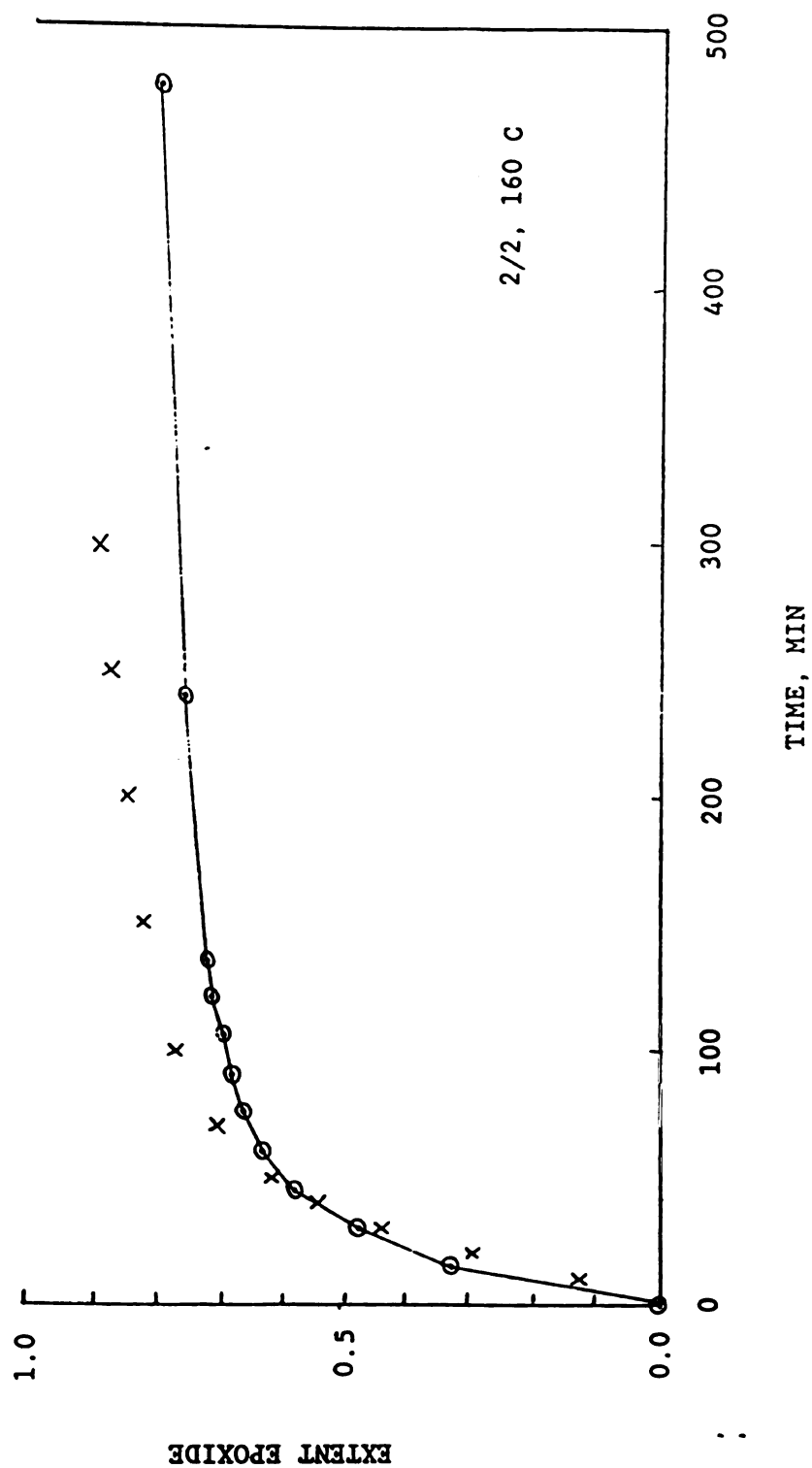


Figure 28. Extent epoxide vs. time (2/2, 160 C).
FTIR (—○), theory (x).

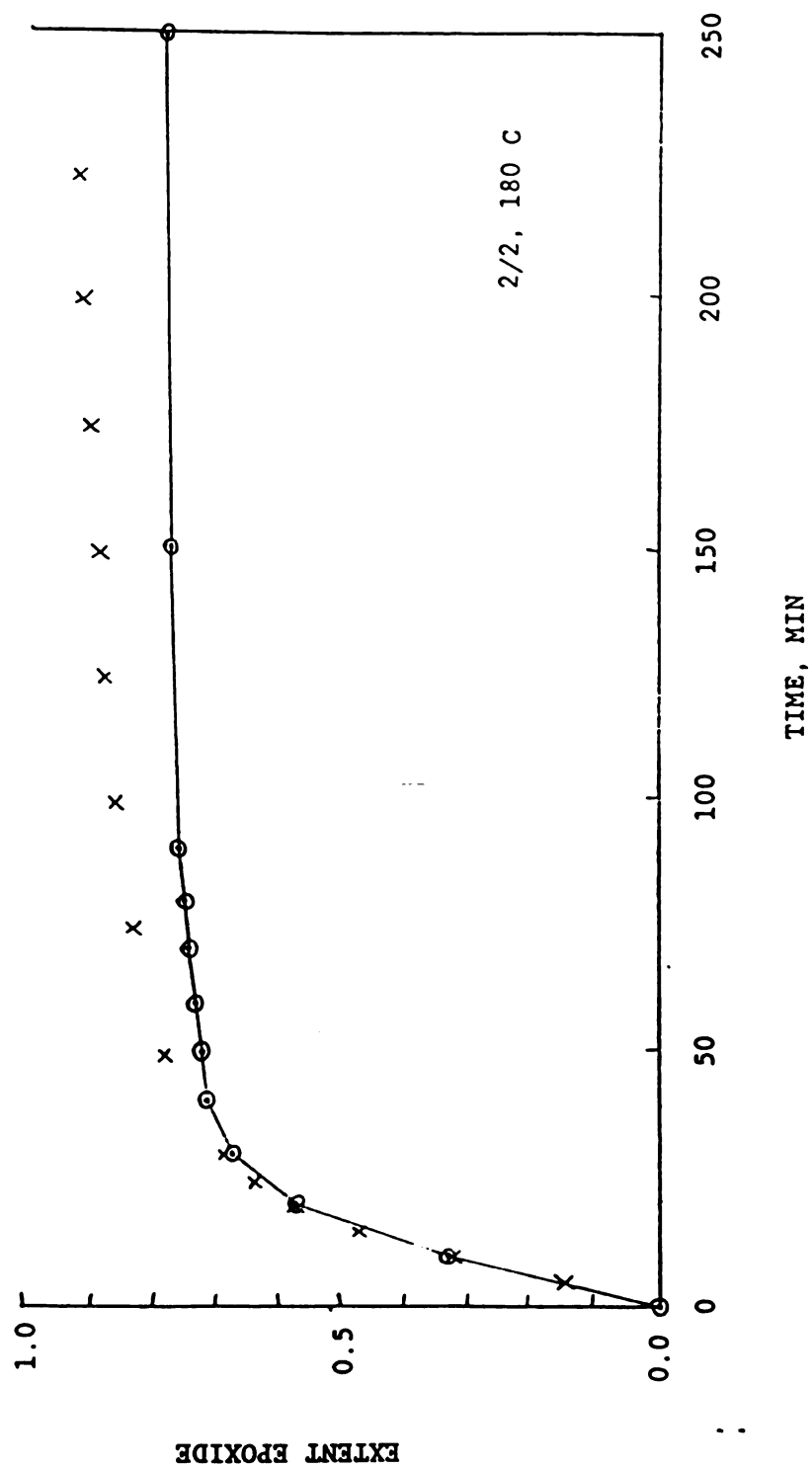


Figure 29. Extent epoxide vs. time (2/2, 180 C).
FTIR (—○—), theory (X).

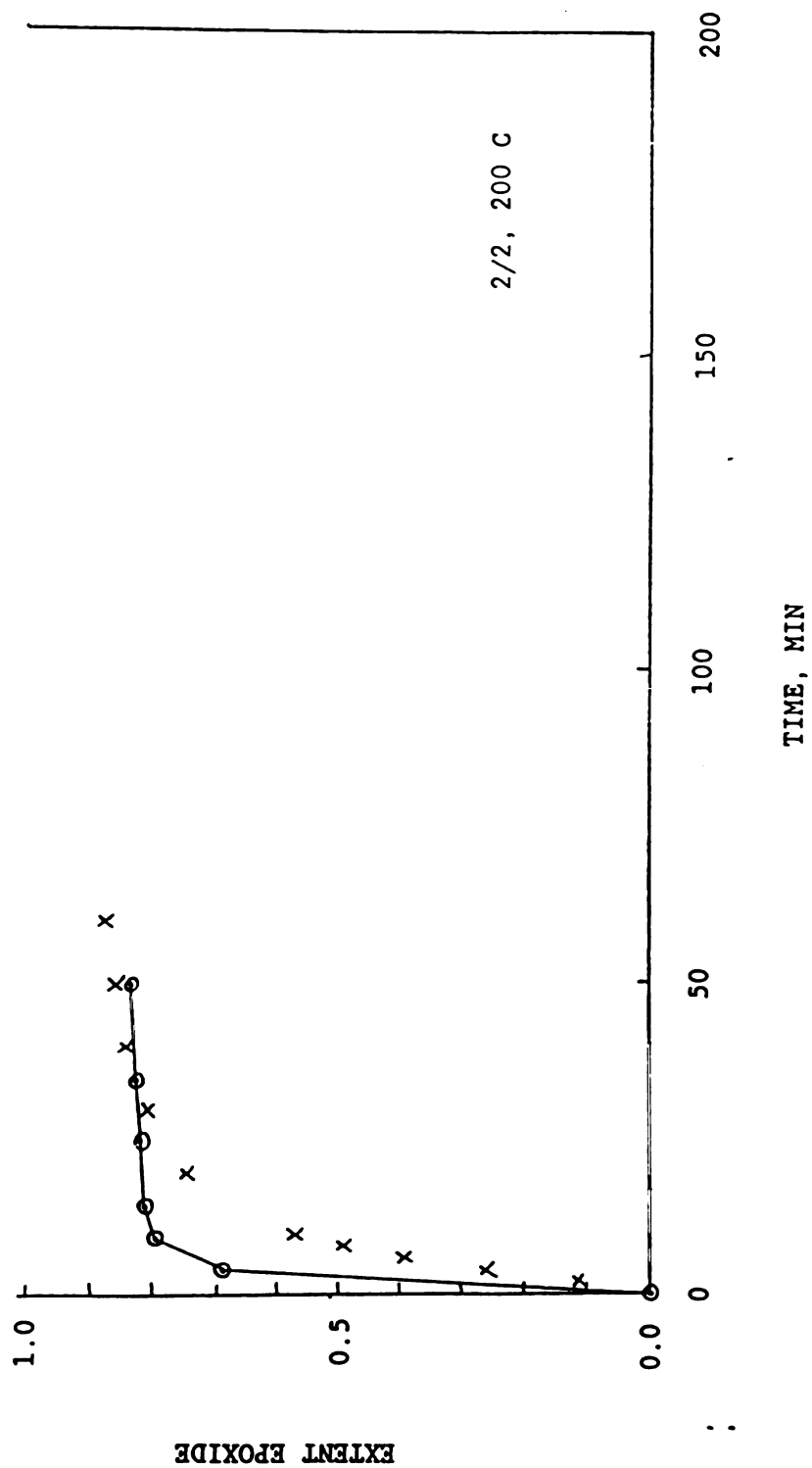


Figure 30. Extent epoxide vs. time (2/2, 200 C).
FTIR (—○—), theory (x).

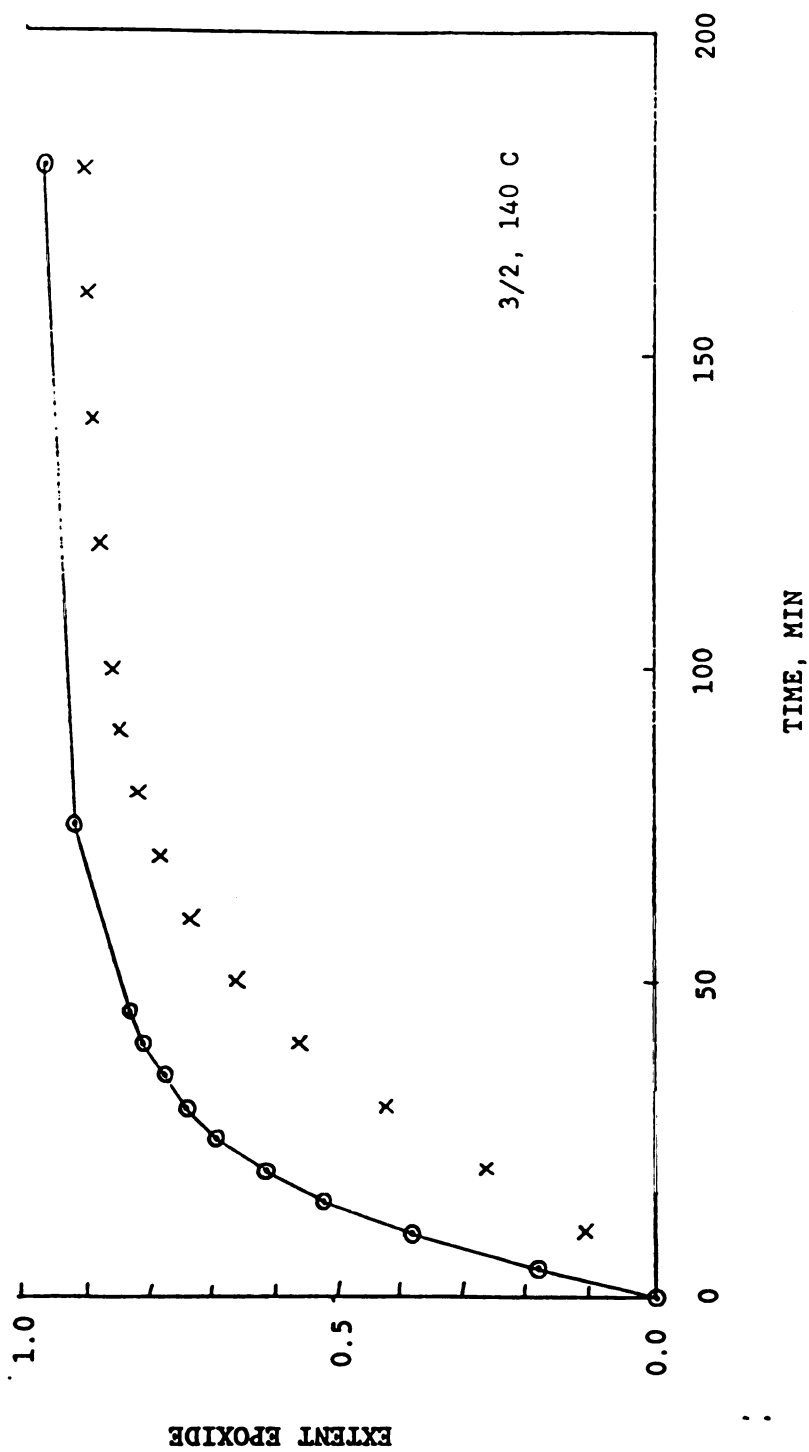


Figure 31. Extent epoxide vs. time (3/2, 140 C).
FTIR (—○—), theory (X).

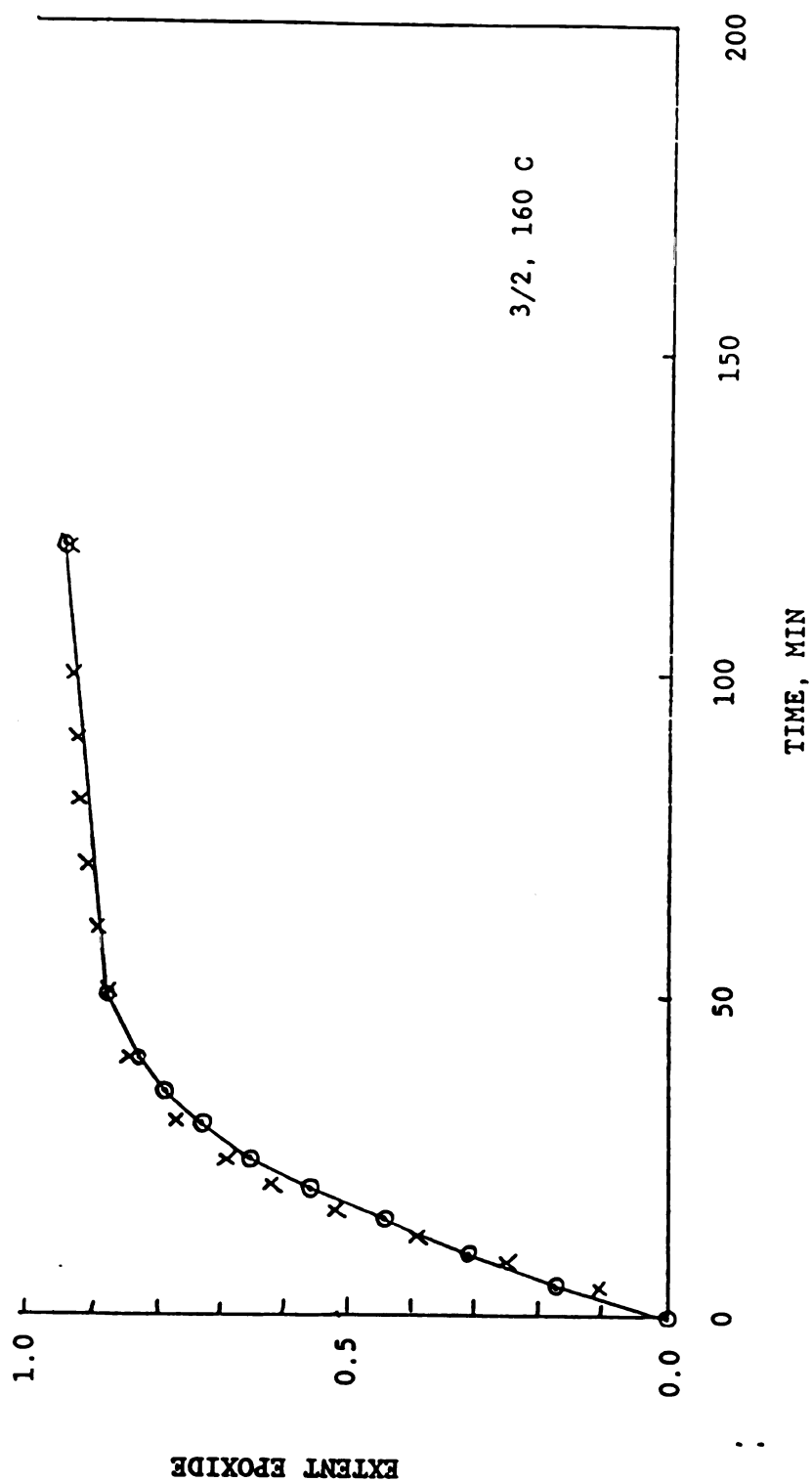


Figure 32. Extent epoxide vs. time (3/2, 160 C).
FTIR (—○—), theory (x).

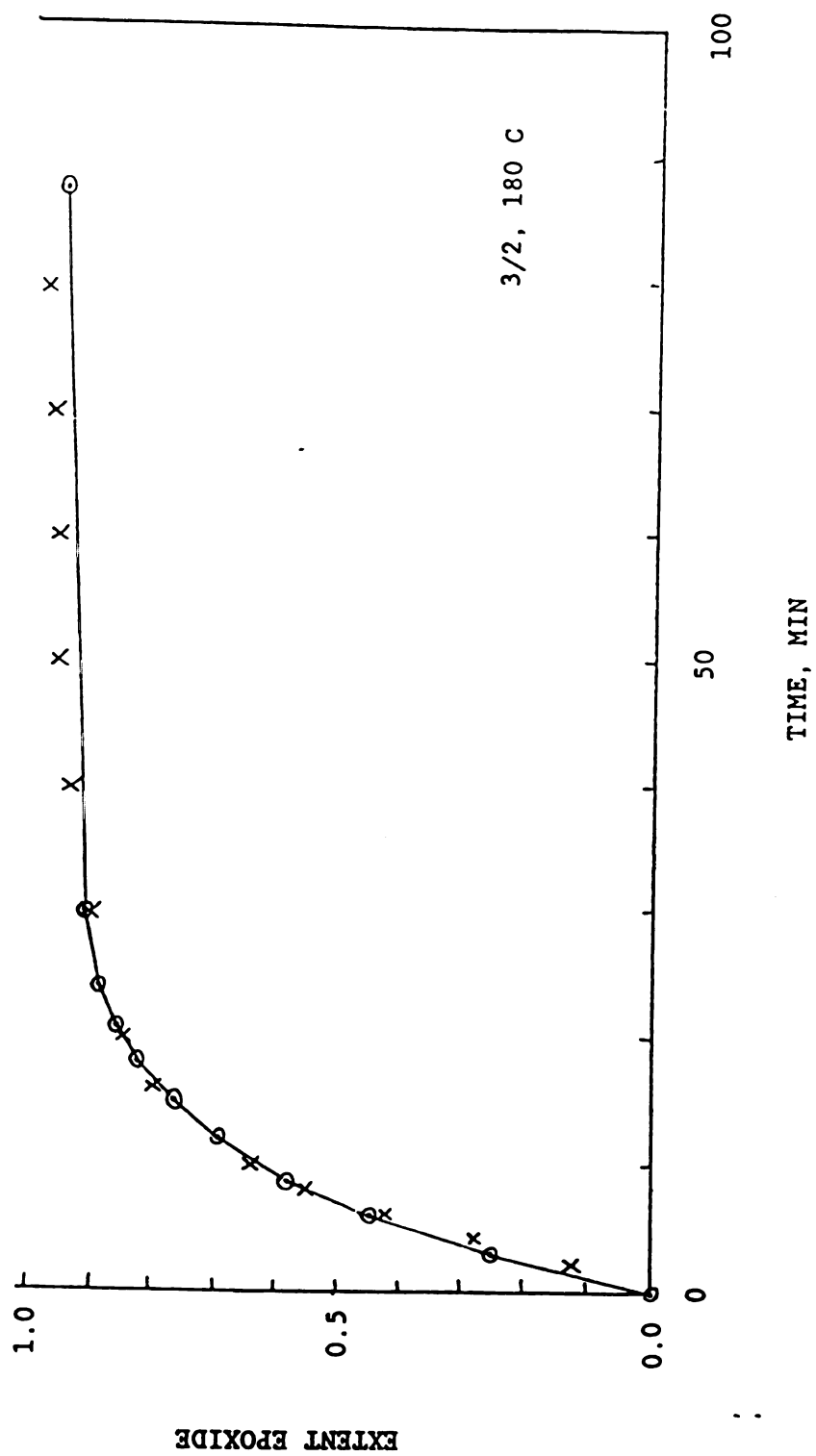


Figure 33. Extent epoxide vs. time (3/2, 180 C).
FTIR (—○), theory (x).

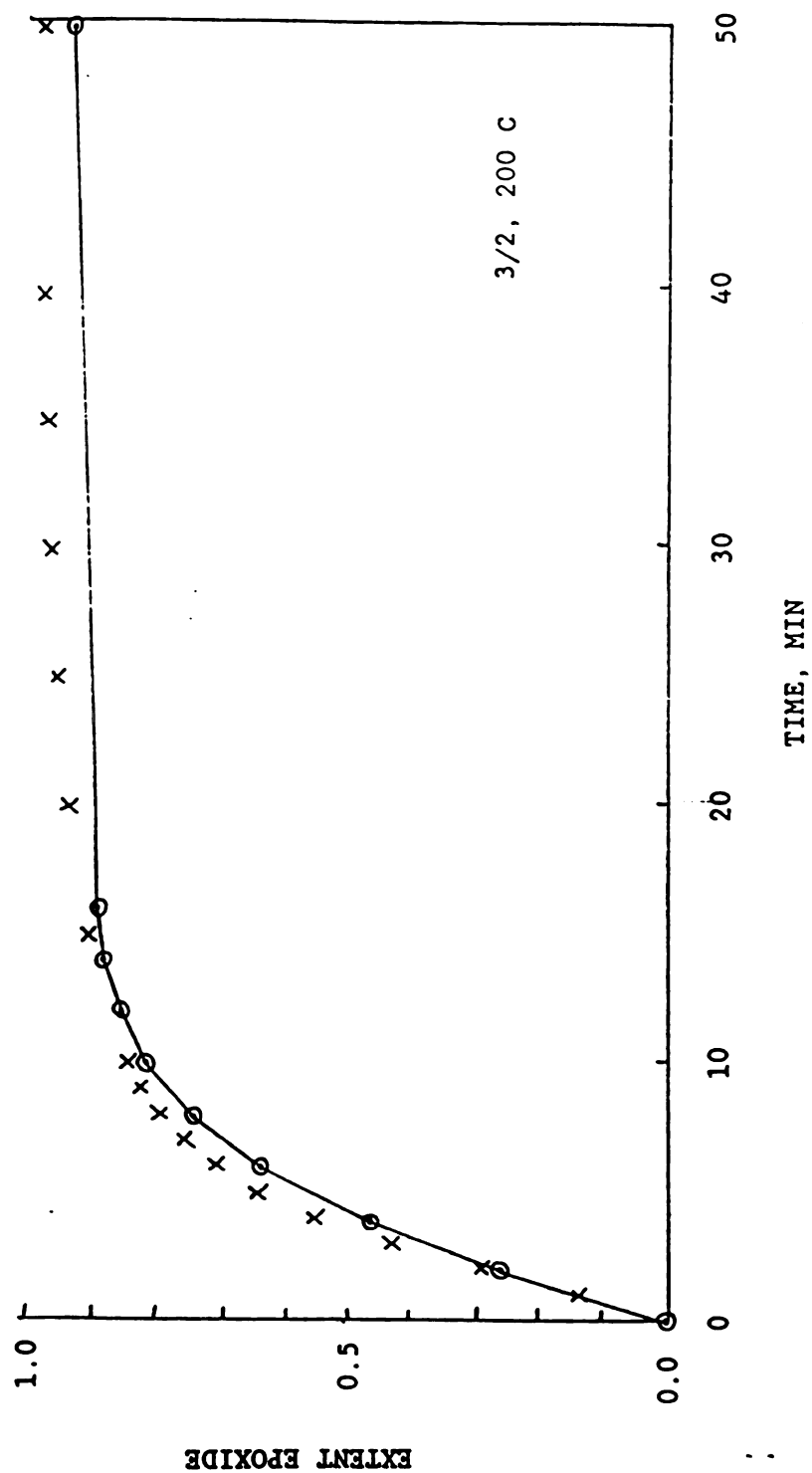


Figure 34. Extent epoxide vs. time (3/2, 200 C).
FTIR (—○), theory (x).

respectively) have been used for analysis as well as the hydroxide band (3500 cm^{-1}). It is the opinion of this investigator that these bands are all too closely merged with other bands to be considered accurate. The progress of hydroxide formation, for instance, can be more closely followed by monitoring the consumption of amine hydrogen since one mole of amine hydrogen is consumed for every mole of hydroxide formed. If it is assumed that the reactivity of primary and secondary amine hydrogen is equivalent the evolution of these species may be calculated from the rate law.

CARBON-13 NUCLEAR MAGNETIC RESONANCE

This method was employed in a slightly different fashion than the above two methods. The NMR experiments described herein are all static, which is to say that they are all done on fully-cured samples as opposed to the FTIR and DSC experiments which are time-dependent. Only selected samples were prepared for analysis, particularly the amine-deficient 1/2 mixtures. The chemical shifts for DGEBA cured with amine are in the literature (13). Since it is believed that different species form when the formulation is amine-deficient chemical shifts should appear which have not been previously observed.

Five solid and one liquid sample were prepared for analysis. The five solid samples were cured using the following formulations, temperatures, and cure times. Cures were carried out in an oven using a dogbone mold. The samples were mixed first in the same manner as that used for DSC.

Table 8. Sample Preparation for NMR Experiments

Formulation	Temperature, C	Time, hr
1/2	140	12
1/2	160	10
1/2	180	8
1/2	200	6
3/2	200	2

The first four samples are all of course amine-deficient while the fifth sample is selected because the side reaction is not favored under these conditions and therefore should not be observed. The samples were ground to a fine powder using a Crescent Wig-L-Bug. Approximately 0.3 g of sample are required for a C-13 NMR scan.

The liquid sample was prepared from 10 g of unreacted epoxy/amine mixture (1/2 formulation) dissolved in 10 ml deuterated acetone. This solvent was used since it does not show up in the spectra. This sample was chosen so that it could be compared with the spectra of the reacted mixtures. Approximately 1 ml of this mixture was used in the spectrometer.

The solid samples were analyzed using a Varian VXR-400 NMR with a Bruker CP-MAS (Cross Polarization-Magic Angle Spinning) probe. Magic Angle Spinning is a technique which reduces anisotropy in a solid sample; without it, the resulting spectral bands are too broad to be useful. The granulated samples are placed in a 7 mm zirconia rotor (Doty Scientific Co.) and spun in the NMR instrument at a rate of 4800 Hz. The larger the spinning rate the more narrow the bands. The spinning is accomplished using a pneumatic mechanism so that the rotor never touches the instrument. If the sample is not granulated enough, high spin

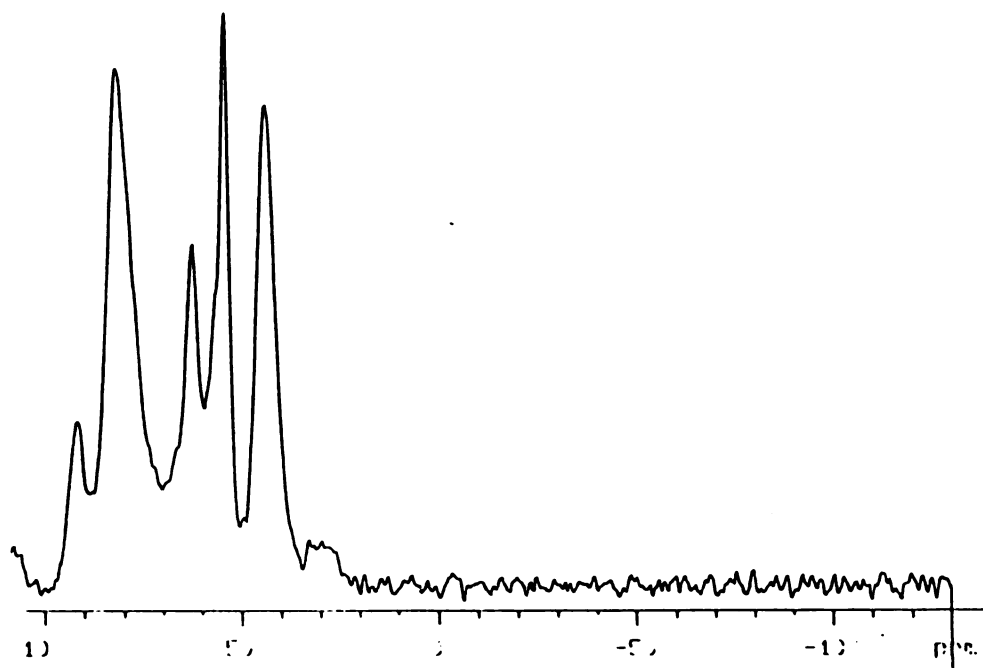


Figure 35. C-13 NMR scan (1/2, 140 C, 4880 Hz).

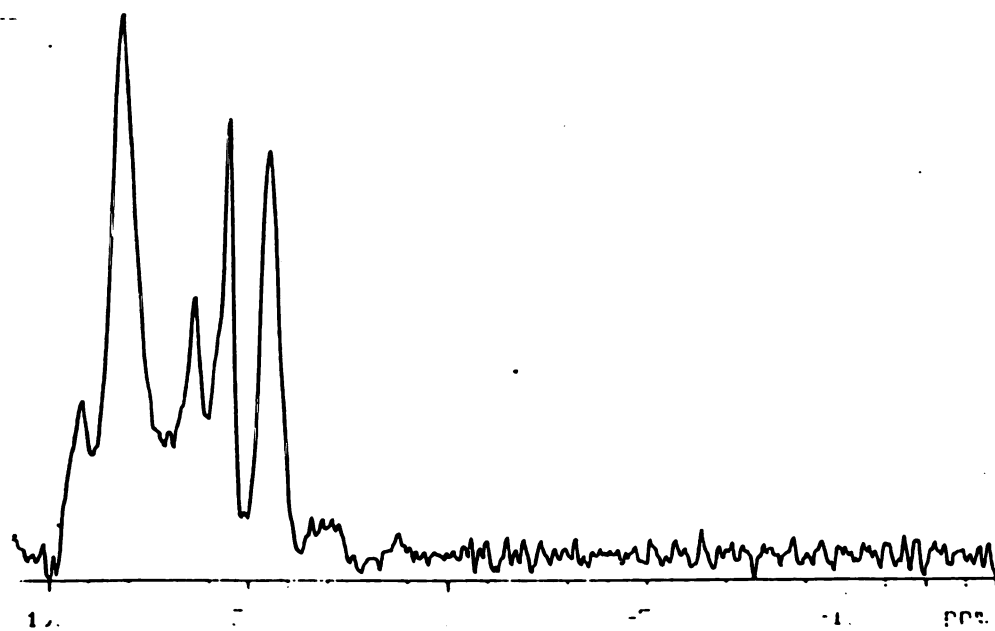


Figure 36. C-13 NMR scan (1/2, 160 C, 4880 Hz).

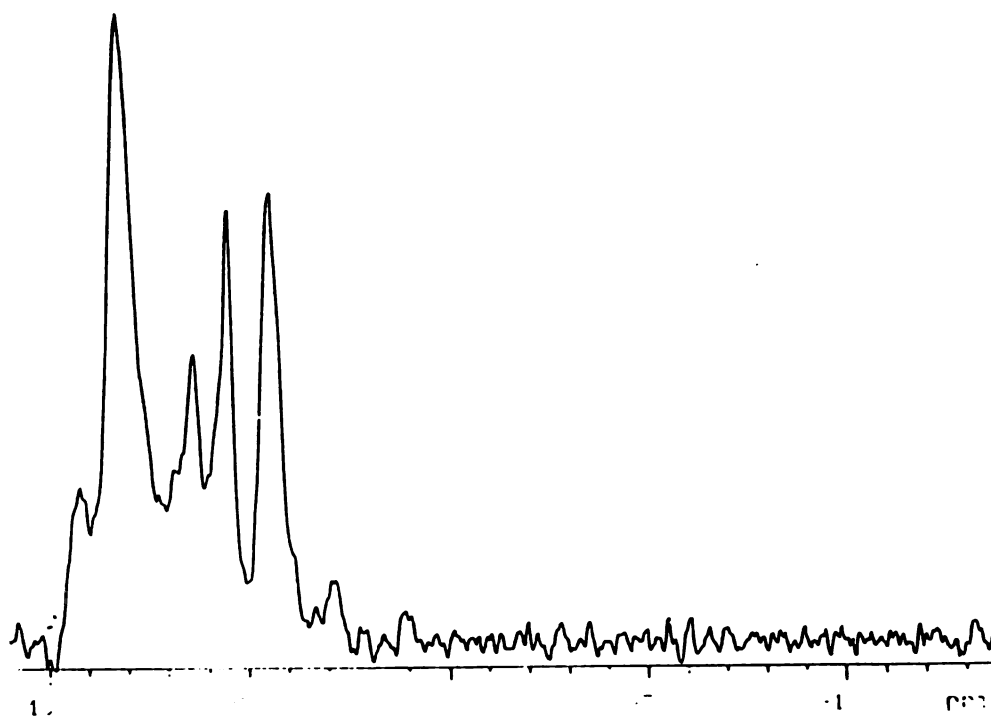


Figure 37. C-13 NMR scan (1/2, 180 C, 4880 Hz).

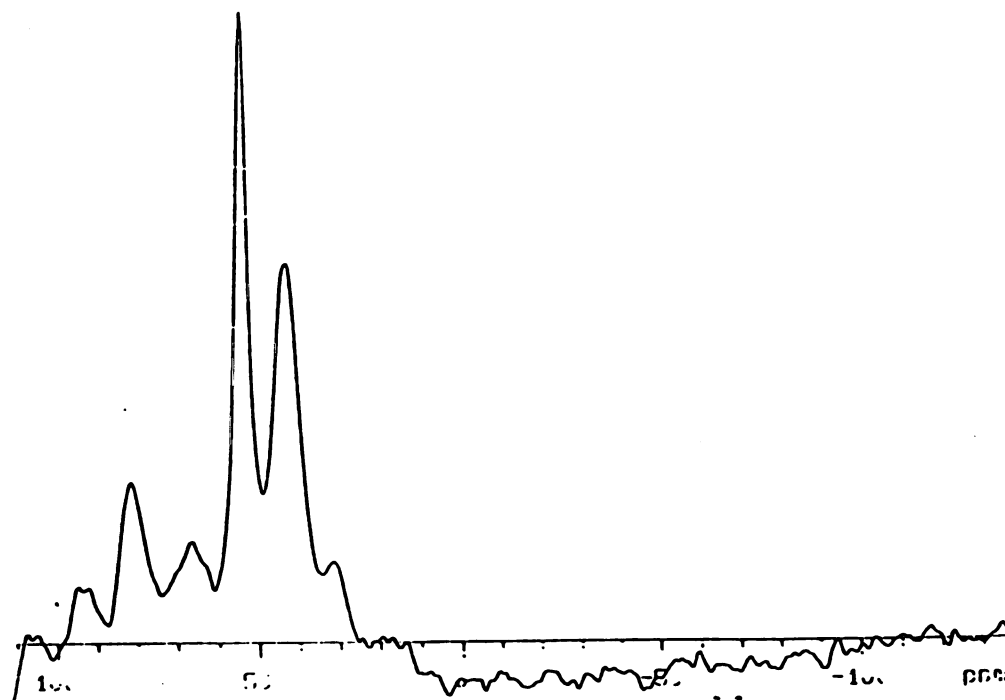


Figure 38. C-13 NMR scan (1/2, 200 C, 1100 Hz).

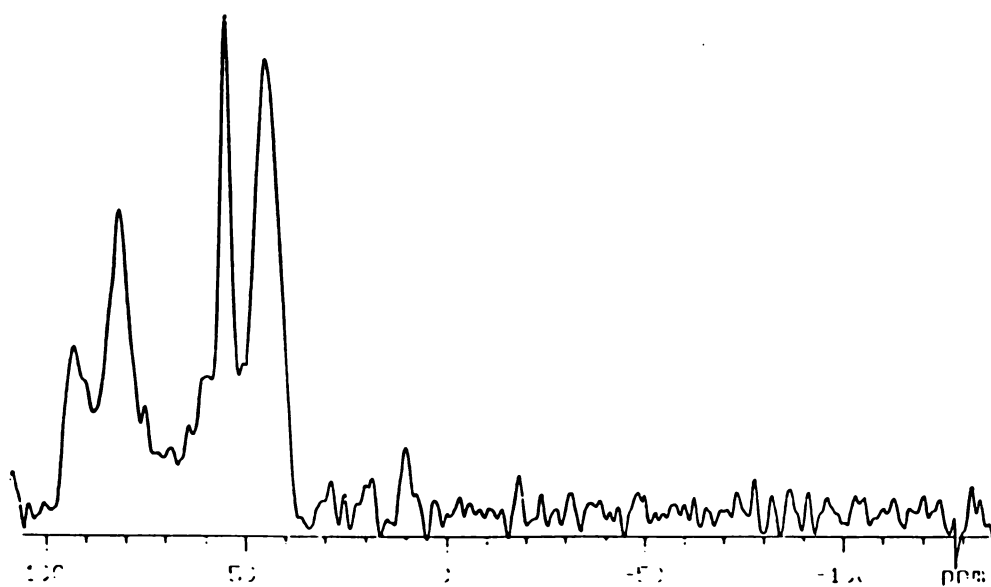


Figure 39. C-13 NMR scan (3/2, 200 C, 4880 Hz).

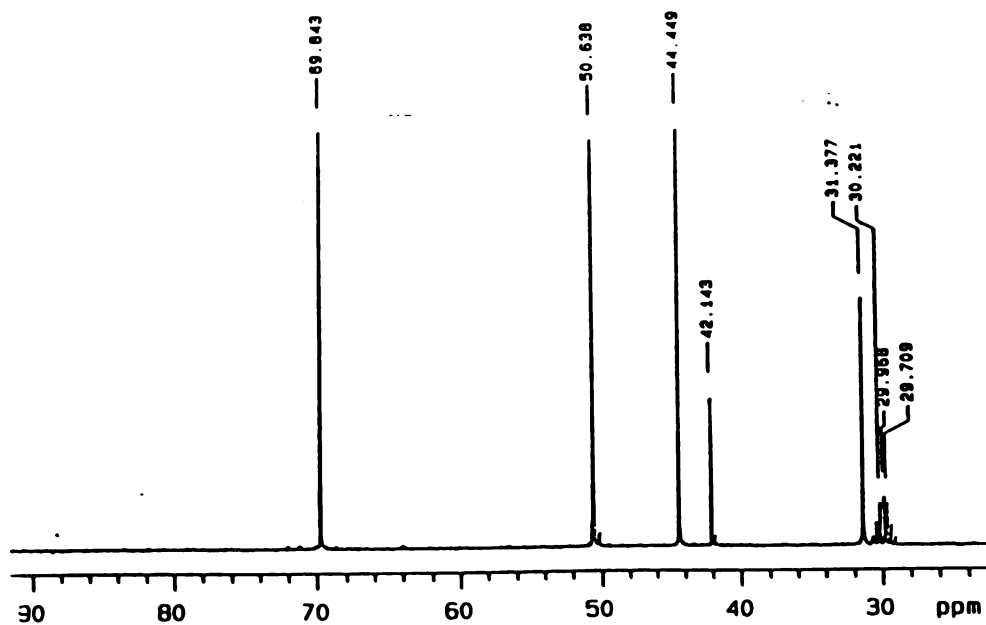


Figure 40. C-13 NMR scan (1/2, unreacted liquid).

rates cannot be achieved; as an example, the 1/2, 200 C sample was spun at a rate of only 1100 Hz. The liquid spectrum was taken with a Varian VXR-300 using proton-decoupling. Magic Angle Spinning is not necessary for the liquid experiment because the bands are narrow enough without it. The solid experiments used an excitation frequency of 100 MHz while the liquid experiment was carried out at 77 MHz.

Figures 35-40 show the spectra resulting from these experiments. As mentioned in the background section, the aliphatic regions of the spectra (0-100 ppm) are the regions of interest so they are reproduced here. Interpretation of these results is saved for the Discussion section. The spin rates for the rotor are given where applicable. Note that spinning the sample causes the creation of bogus bands known as spinning sidebands. These arise since the spin rate is added to the spin rate of the carbon-13 nucleus, creating an artificial addition to the chemical shift.

MODELING OF CURE REACTIONS

Central to the modeling of the experimental results is the determination of the rate law. As it turns out, a model for the determination of the glass transition temperature is necessary for evaluation of the diffusion-limited nature of the reaction kinetics. An already existing equation (DiBenedetto Equation) was used to fit the data. Modeling of the dielectric properties involved determining how the relaxation times change with temperature for a single-relaxation-time model. Equations in the

Background section are simplified by making a few well-chosen assumptions.

Rate laws for the reaction system involve time dependent expressions for epoxide, primary, secondary, and tertiary amine groups, hydroxide, and the quaternary ammonium ion. Therefore, six equations are required. It is assumed that the reactivities of primary and secondary amine hydrogens are equivalent. Based upon the postulated reaction mechanism the equations are as follows

$$-dC_{AP}/dt = 2k_a C_{AP} C_E^f \quad (85)$$

$$-dC_{AS}/dt = -2k_a C_{AP} C_E^f + k_a C_{AS} C_E^f \quad (86)$$

$$-dC_{AT}/dt = -k_a C_{AS} C_E^f + k_s C_{AT} C_E \quad (87)$$

$$dC_{AQ}/dt = k_s C_{AT} C_E \quad (88)$$

$$dC_{OH}/dt = 2k_a C_{AP} C_E^f + k_a C_{AS} C_E^f \quad (89)$$

$$-dC_E/dt = 2k_a C_{AP} C_E^f + k_a C_{AS} C_E^f + k_s C_{AT} C_E \quad (90)$$

Note that the rate of primary amine disappearance differs from that of the secondary amine by a factor of two. This is due to the fact that the primary amine contains two amine hydrogens as opposed to only one in the case of secondary amine. The rate constant k_a refers to the reaction of epoxide with amine hydrogen. The "f" in the equations above refers to the diffusion-limited parameter for the reaction to be described later. This quantity

varies from one to zero. The rate constant k_s is that associated with the side reaction forming quaternary ammonium ion. Note that there is no diffusion limited parameter associated with this rate constant. This reaction is not diffusion-limited but possibly equilibrium-limited as will be discussed later.

The rate constant k_a is further broken down into uncatalyzed and autocatalyzed parts as already described. The influence of the autocatalyzed part is of course dependent on the hydroxide concentration. In the equation below, k_u refers to the uncatalyzed part and k_c refers to the autocatalyzed part.

$$k_a = k_u + k_c C_{OH} \quad (91)$$

The rate laws for disappearance of amine hydrogen therefore involve a combination of second- and third-order terms. Formation of quaternary ammonium ion is characterized by a second-order expression.

The individual rate constants themselves depend upon temperature in an Arrhenius-like fashion.

$$k = A \exp(-E_a/RT) \quad (92)$$

The factor "f" regarding the diffusion-limited nature of the reaction is dependent on the glass transition temperature in a manner similar to the WLF equation.

$$f = \exp \left[B \left[\frac{T + T_{g0}}{C + T - T_{g0}} + \frac{T - T_g}{C + T - T_{g0}} \right] \right] \quad (93)$$

Here, B and C are parameters determined by experiment. As can be seen, when T_g is equal to T_{g0} the factor f is equal to one. As $(T - T_g)$ approaches C, the argument of the exponential blows up negative and f falls off to zero. T_{g0} is the glass transition temperature for an unreacted mixture while T is the reaction temperature.

The exact value of the rate constant k_a as a function of temperature, hydroxide concentration, glass transition temperature, and formulation is determined as follows. DSC experiments give the amine hydrogen concentration and the epoxide/amine hydrogen reaction rate at each temperature and formulation. The DSC heat flux is divided by the reaction exotherm (25.9 Kcal/mol determined experimentally). The extent of amine consumption (and therefore hydroxide production) is determined by dividing the evolved exotherm by the maximum possible exotherm and multiplying by the initial amine concentration. The epoxide consumption is measured by FTIR.

$$k_a = \frac{\text{FLUX}/(25.9)(4.184)}{C_{AO}C_{EO}(1 - \alpha_A)(1 - \alpha_E)} \quad (94)$$

Since the initial few points (low extents) are assumed to be independent of the diffusion limit, they are used to find the

hydroxide dependency. A simple linear expression sufficed to fit this data.

$$k_a = k_u + C_{OH} k_c \quad (95)$$

This results in a set of second- and third-order rate constants that depend upon temperature and formulation. Each set of rate constants (involving uncatalyzed and autocatalyzed parts) for a given formulation is plotted using an Arrhenius equation to fit data. Figures 41 and 42 show the results of this for the uncatalyzed and autocatalyzed rate constants, respectively. The data for each formulation is analyzed for the activation energy. At this point a constraint is added to the model such that the activation energy for the uncatalyzed and autocatalyzed rate constants is independent of formulation. The three activation energies (one for each formulation) are averaged yielding one value. The resultant E_a 's have the values of 16.55 kcal/mol (uncatalyzed) and 13.72 kcal/mol (autocatalyzed). Data for each formulation is then fit in order to find the frequency factor for each formulation. The following table gives these values ($\ln A$).

Table 9. Frequency Factors for Rate Constants

Formulation	$\ln A_c$	$\ln A_u$
1/2	14.06	15.59
2/2	15.03	15.90
3/2	15.62	16.50

The calculated rate constants are also plotted in Figures 41 and 42. The experimentally determined values and the model results are given in the following Table 10 for reference. The value on the left in all cases is the experimentally determined value.

Table 10. Values of Rate Constants - Theory vs. Experiment

Uncatalyzed (g/eq-sec)						
Temperature	1/2		2/2		3/2	
140	.00923	.0105	.0153	.0136	.0251	.0248
160	.0292	.0260	.0327	.0351	.0582	.0638
180	.0569	.0646	.0750	.0871	.146	.158
200	.130	.132	.172	.178	.359	.324

Autocatalyzed ($\text{g}^2/\text{eq}^2\text{-sec}$)						
Temperature	1/2		2/2		3/2	
140	22.6	27.9	42.2	43.7	60.9	59.6
160	60.2	61.7	117.5	95.5	136.5	131.8
180	138.0	124.5	275.4	190.5	251.2	263.0
200	288.4	251.2	524.8	375.8	338.8	524.8

Determining how the rate constant changes with the diffusion limit involves use of the DiBenedetto Equation in conjunction with the WLF Equation. The DiBenedetto Equation is fit to data already described and the results plotted in Figure 43. The values of ϵ_x/ϵ_0 and c_x/c_0 are assumed independent of formulation since the segments of the crosslinking polymers are the same. Therefore, once ϵ_x/ϵ_0 and c_x/c_0 are found adjustments to fit data for a non-stoichiometric mixture involve only the variation of T_{g0} .

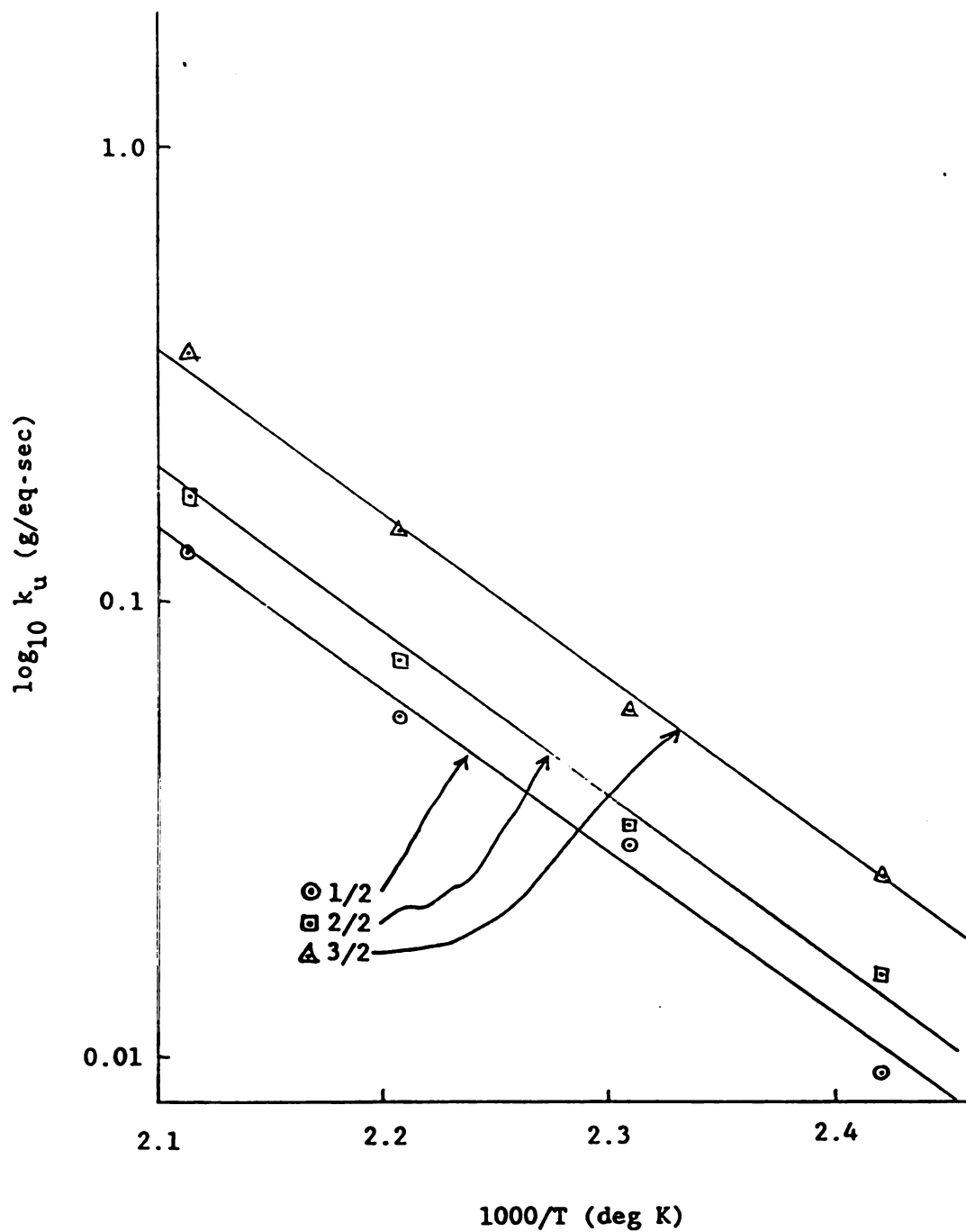


Figure 41. Uncatalyzed rate constant vs. $1000/T$

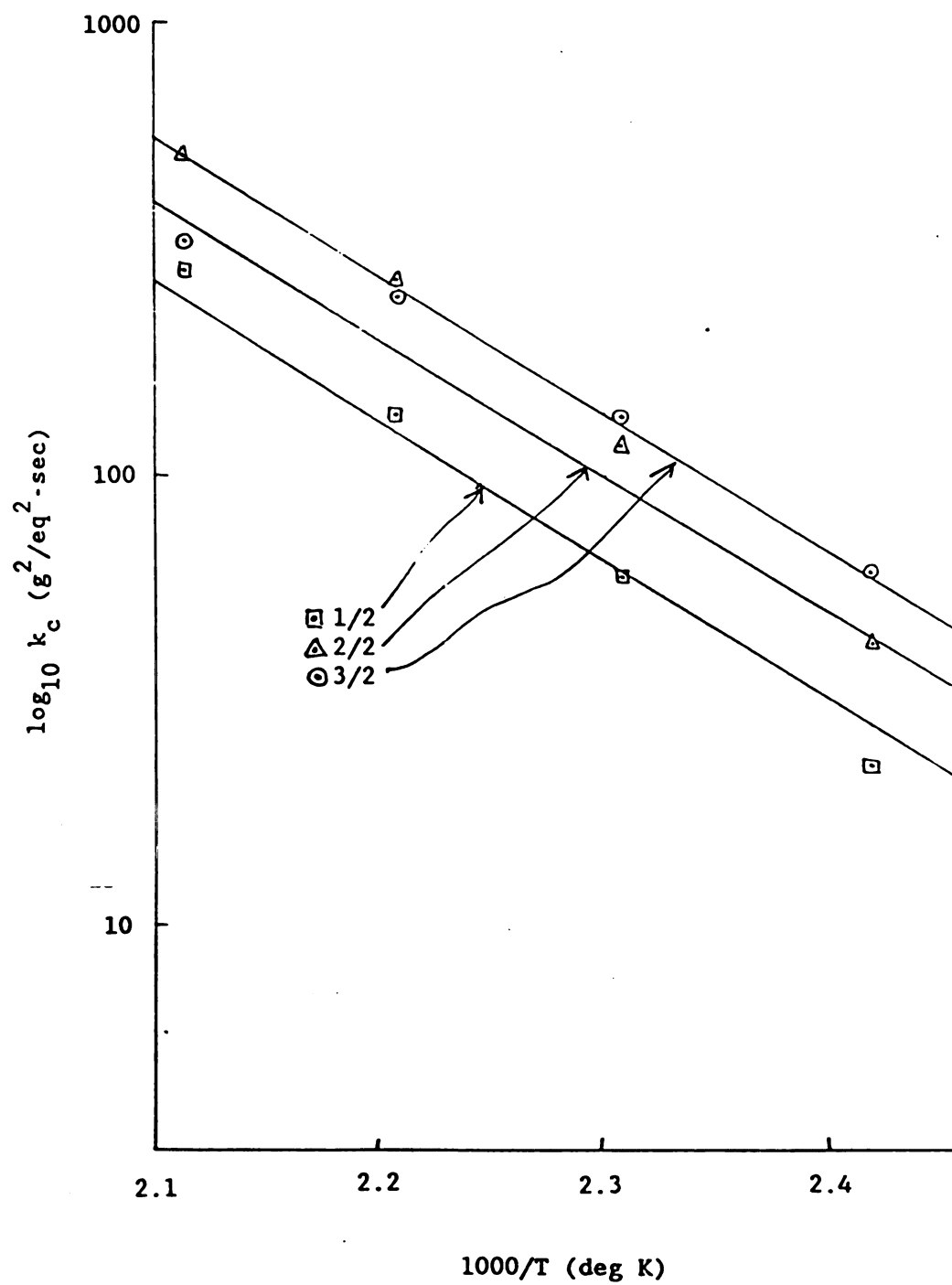


Figure 42. Autocatalyzed rate constant vs. $1000/T$

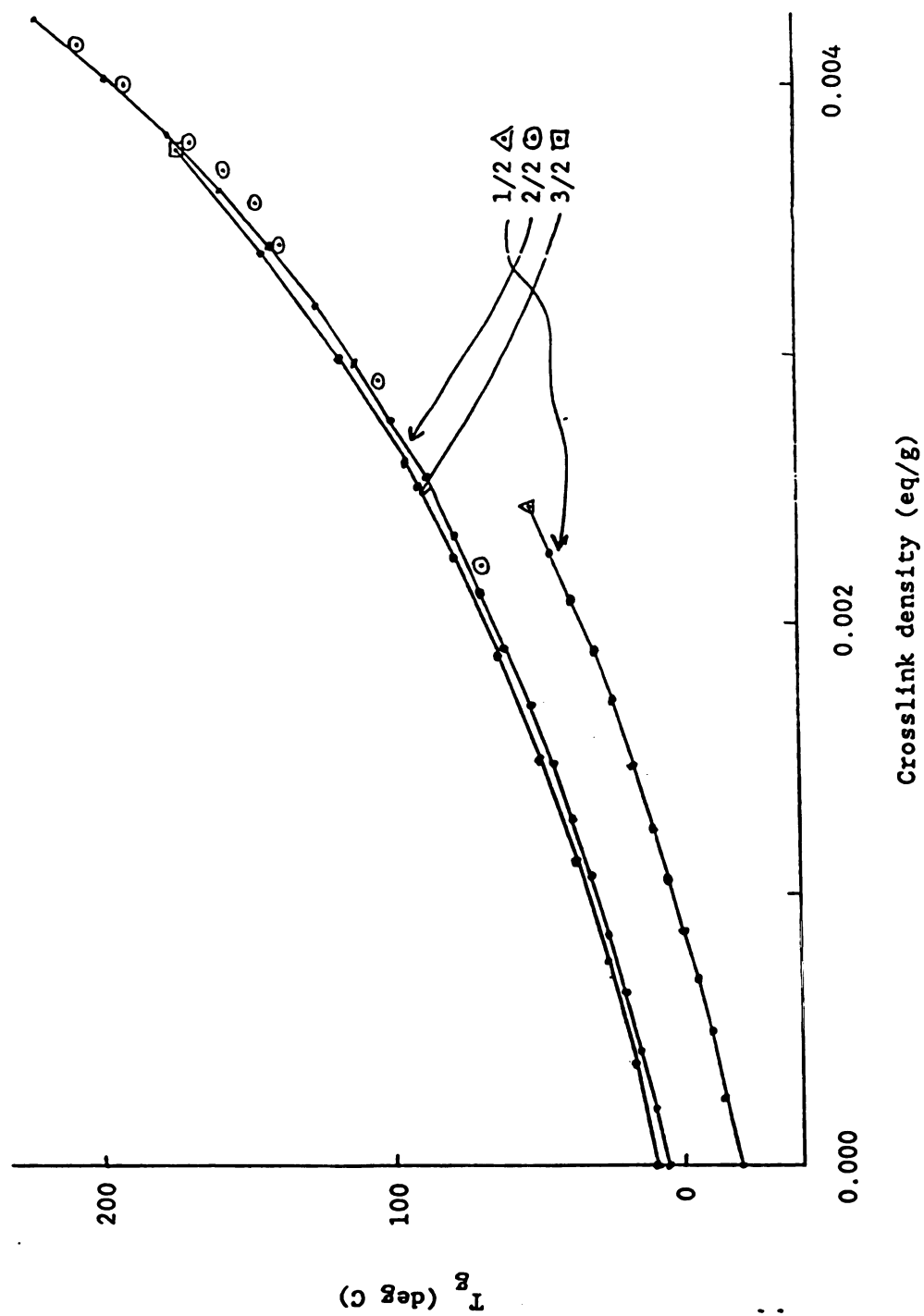


Figure 43. Glass transition temperature vs. crosslink density (DiBenedetto Equation results —•—).

$$\frac{T_{gx} - T_{g0}}{T_{g0}} = \frac{(\epsilon_x/\epsilon_0 - c_x/c_0)\rho}{1 - (1 - c_x/c_0)\rho} \quad (96)$$

Ordinarily, the equation above as it is applied in the literature is in extent instead of reduced crosslinking density. The maximum possible epoxide/amine crosslinking density for the DER 332/DDS system is .004255 mole crosslinks/g. Any variation of formulation away from the stoichiometric mixture will reduce the concentration of either epoxide or amine, therefore reducing the maximum concentration of crosslinks. The value of ϵ_x/ϵ_0 is found equal to 0.751 with the value of c_x/c_0 being equal to 0.419. The value of T_{g0} are given below.

Table 11. Zero Extent Glass Transition Temperatures (Calculated)

Formulation	T_{g0}
1/2	- 17 C
2/2	+ 5 C
3/2	+ 8 C

When the above equation is used it must be remembered that crosslinking density is a function of the extent of the epoxy/amine hydrogen reaction. The initial amine hydrogen concentration multiplied by the extent yields the crosslinking density.

The WLF Equation is then used with the calculated T_g 's in mind. In all cases, the values of k_a determined from experimental data as described above fall off to zero. A value of T_g is calculated for the extent of reaction at which this point occurs

and compared to the reaction temperature in order to estimate the parameter C . It is assumed that there is only one value of C for each formulation. These values are given in the following table.

Table 12. WLF Equation Parameters

Formulation	C , deg C
1/2	- 105
2/2	+ 25
3/2	+ 15

As can be seen from these values the reaction ceases at a point well above T_g for the 1/2 formulation while it ceases below T_g for the 3/2 and 2/2 formulations. The value for the 2/2 formulation corresponds to that found in the literature (14). Once a value for C is known the value of B is determined by trial and error. These values are given in the following table.

Table 13. Additional WLF Equation Parameters

Temperature	1/2	2/2	3/2
140	-0.083	4.878	1.704
160	-0.176	5.330	3.400
180	-0.333	6.216	4.924
200	-0.667	6.900	6.939

When taken together, the above parameters estimate the rate constant k_a for the reaction of epoxide with amine hydrogen. The rate constant therefore depends on hydroxide concentration, formulation, temperature, and proximity of the reaction temperature to the glass transition temperature.

The rate constant for the side reaction is estimated in the

hydrogen is no longer reacting. In these regions concentration of unreacted epoxy is experimentally determined while the concentration of tertiary amine is theoretically estimated. This is done using the following equations which balance the maximum following manner. For all of the 1/2 formulations as well as for the 2/2 formulation at 140 C, there is a region in the extent curves where epoxide continues to be consumed even while amine tertiary amine concentration possible

$$C_{ATmax} = C_{AO} \alpha_A^2 \quad (97)$$

with the amount reacted with epoxide

$$C_{AT} = C_{ATmax} - [(C_{EO} - C_E) - (C_{AO} - C_A)] \quad (98)$$

in order to find the amount present. The rate of epoxide consumption in these regimes is estimated by finding the slope of the epoxide consumption curve at that point. The rate constant k_s is then found using the following formula

$$k_s = (dC_E/dt)/(C_{AT}C_E) \quad (99)$$

The values thus determined remain constant over the entire range of the data used and are given in the following table. The rate constants are second order. No value for the 3/2 case is given because the data was unreliable.

Table 14. Values of Side Reaction Rate Constant k_s

Formulation	Rate Constant k_s (g/eq-sec)			
	140 C	160 C	180 C	200 C
1/2	.027	.030	.033	.037
2/2	.027	-	-	-

The values for the 1/2 case will be used for all formulations. It is assumed that the values are independent of formulation since the values of the 1/2 case and the 2/2 case at 140 C are equivalent. The values appear to be weakly temperature dependent with an activation energy of 2.2 Kcal/mol.

The values of the rate constants are then integrated using a first-order Runge-Kutta predictor-corrector algorithm (67). Extents of amine hydrogen reaction thus calculated are plotted in Figures 9-20 while the epoxide curves are plotted in Figures 23-34. The rate of amine hydrogen consumption is multiplied by the exotherm in order to model the DSC curves. The results of this calculation are plotted in Figures 44-55. The calculated amine mole fractions of primary, secondary, and tertiary amines (a_p , a_s , and a_t), quaternary ammonium ion (a_q), as well as calculated final extents of reaction for amine hydrogen and epoxy (α_A and α_E) are shown in the table on the following page. The FORTRAN algorithm used as well as instructions for its use is the makeup of the Appendix.

Table 15. Results of Numerical Integrations

1/2	a_p	a_s	a_t	a_q	α_A	α_E
140	.0426	.3276	.0298	.6001	.7936	.5471
160	.0016	.0765	.1198	.8021	.9602	.6809
180	.0000	.0019	.2296	.7685	.9991	.6919
200	.0000	.0000	.2563	.7437	1.0000	.6862
2/2						
140	.0599	.3697	.3359	.2346	.7553	.8728
160	.0361	.3078	.4745	.1816	.8100	.9010
180	.0206	.2459	.5825	.1510	.8565	.9322
200	.0161	.2216	.6867	.0755	.8731	.9111
3/2						
140	.1571	.4785	.3180	.0464	.6036	.9405
160	.1422	.4698	.3620	.0260	.6230	.9542
180	.1256	.4576	.4006	.0162	.6456	.9807
200	.1169	.4500	.4235	.0096	.6581	.9945

Note that

$$\alpha_A = (a_q + a_t) + 1/2a_s \quad (100)$$

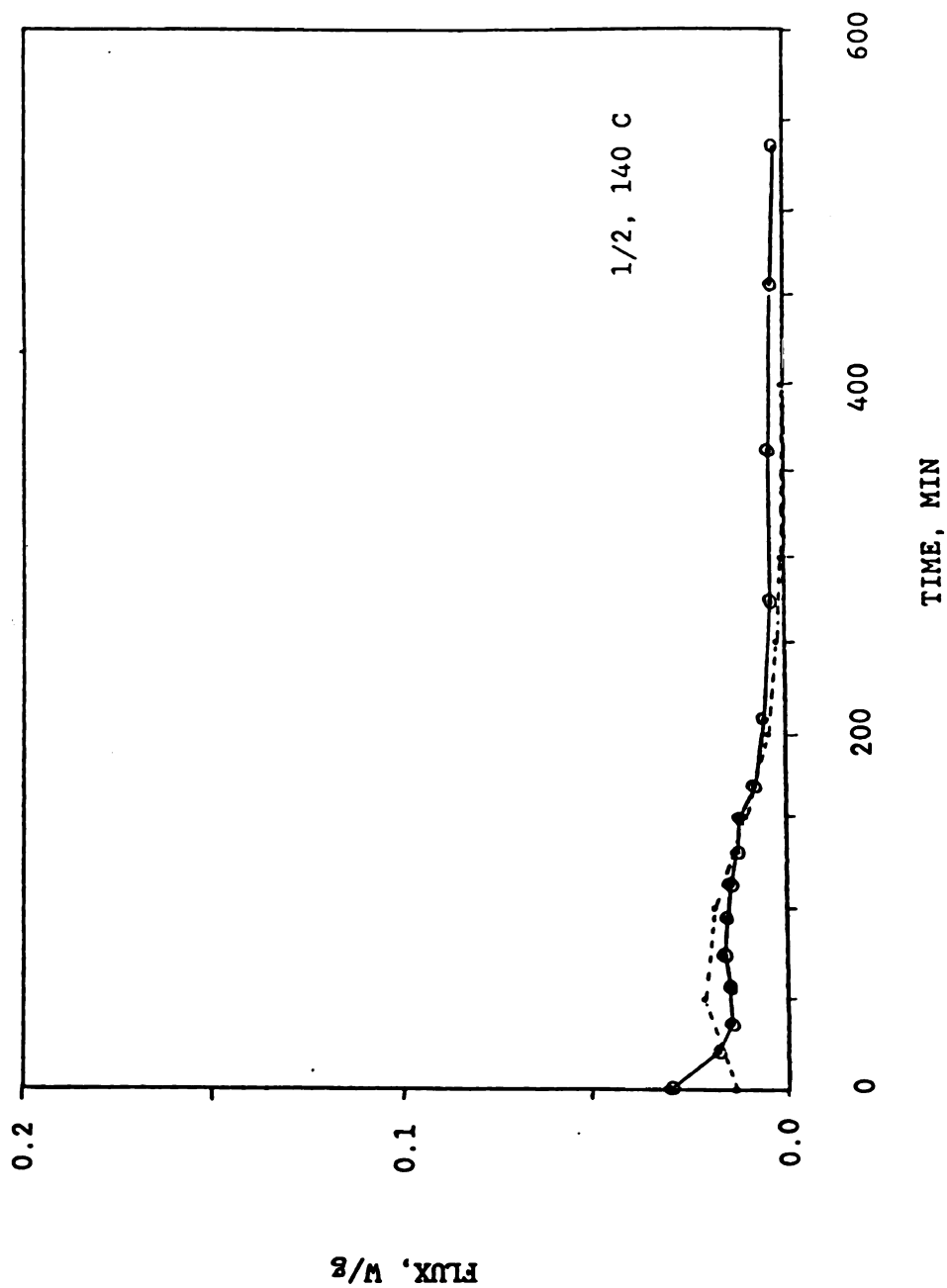


Figure 44. Isothermal DSC scan (1/2, 140 C).
Experiment (—○—), theory (---○---).

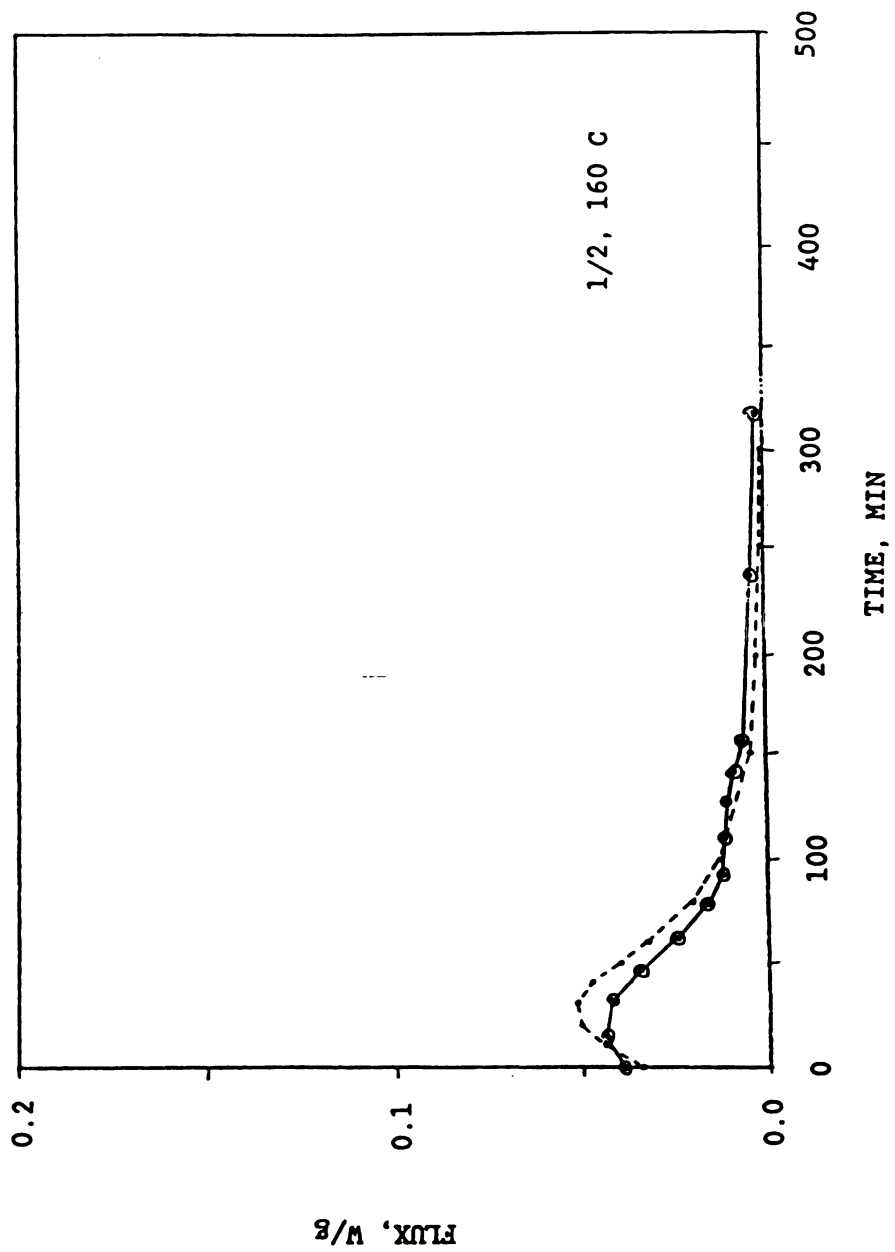


Figure 45. Isothermal DSC scan (1/2, 160 C).
Experiment (—○), theory (---).

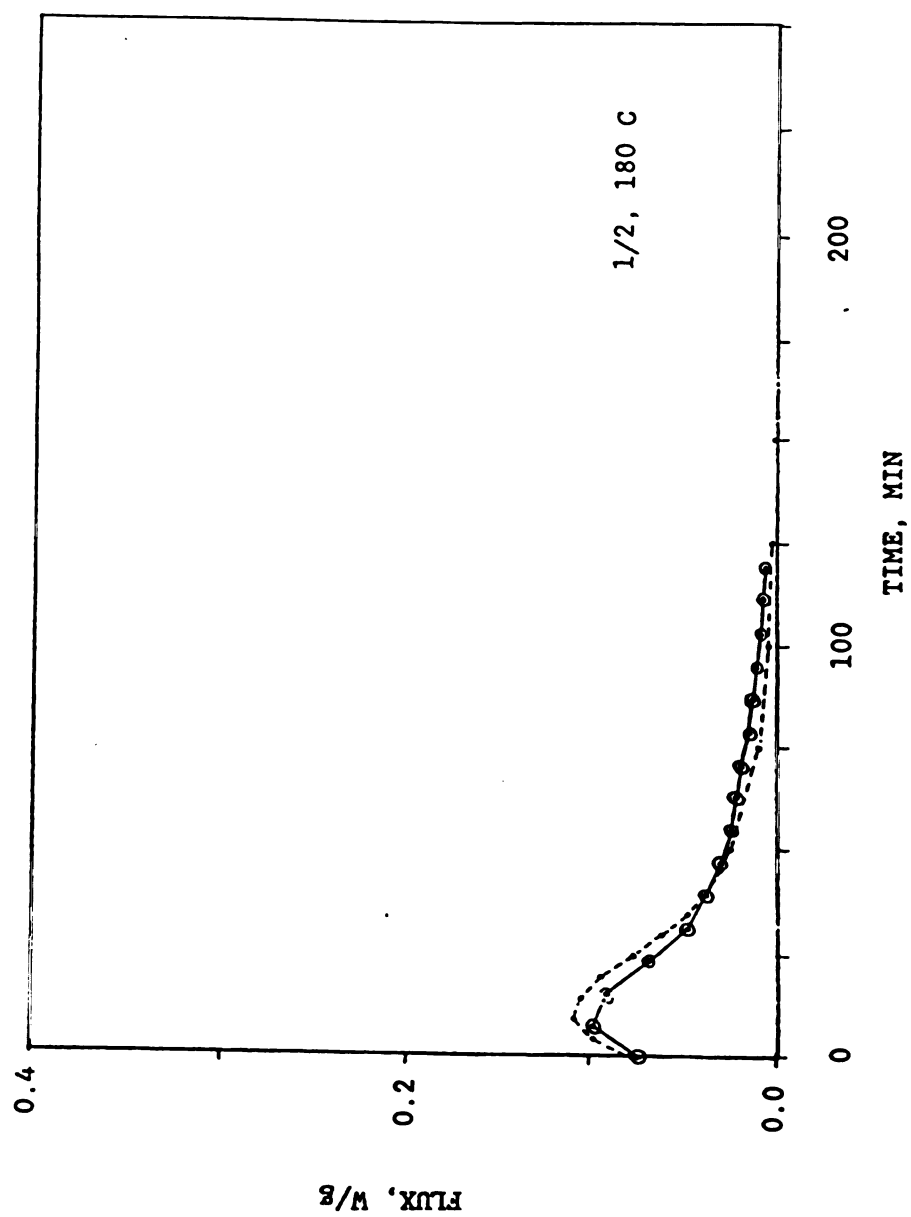


Figure 46. Isothermal DSC scan (1/2, 180 C).
Experiment (—○), theory (---).

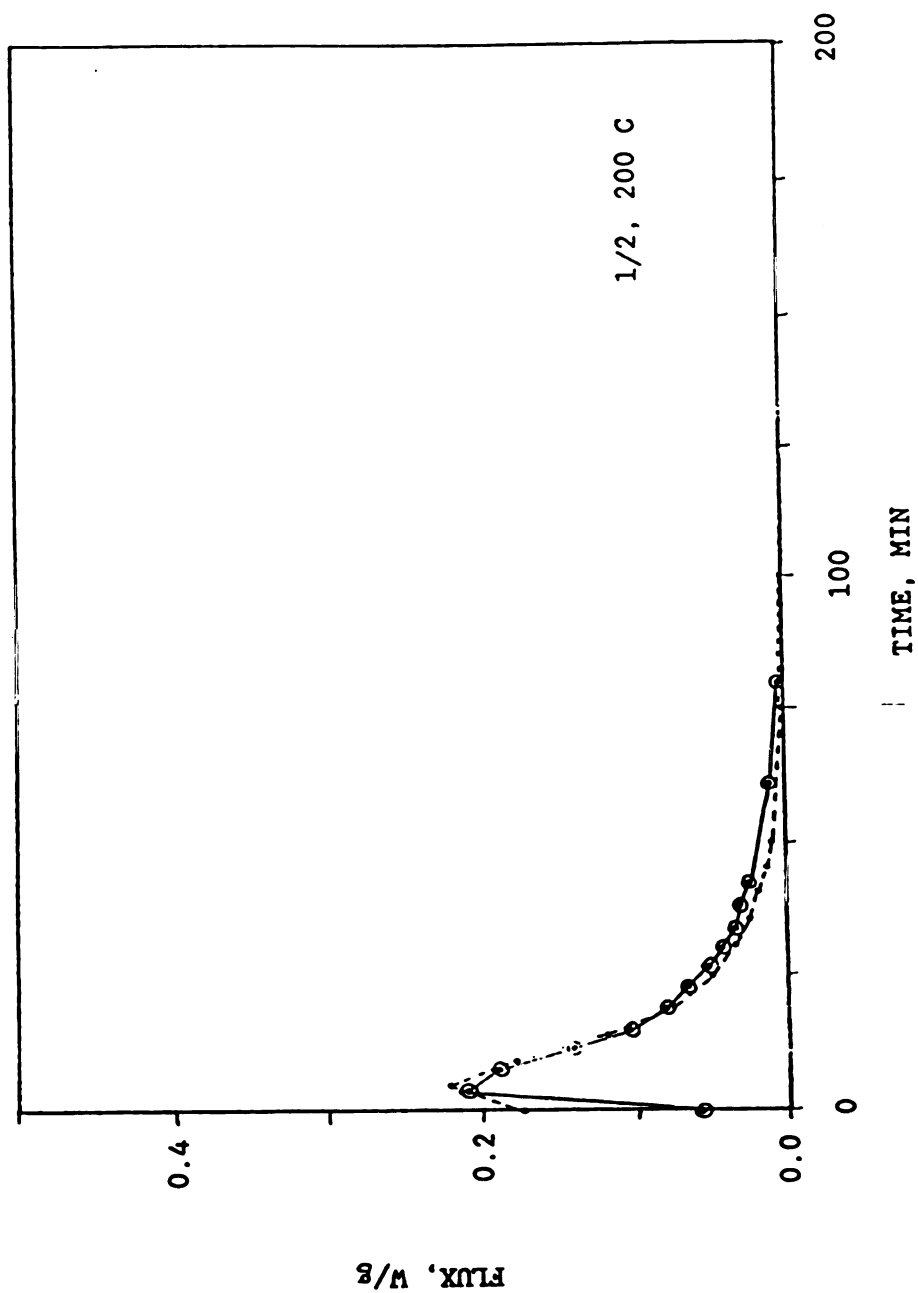


Figure 47. Isothermal DSC scan (1/2, 200 C). Experiment (—○—), theory (---).

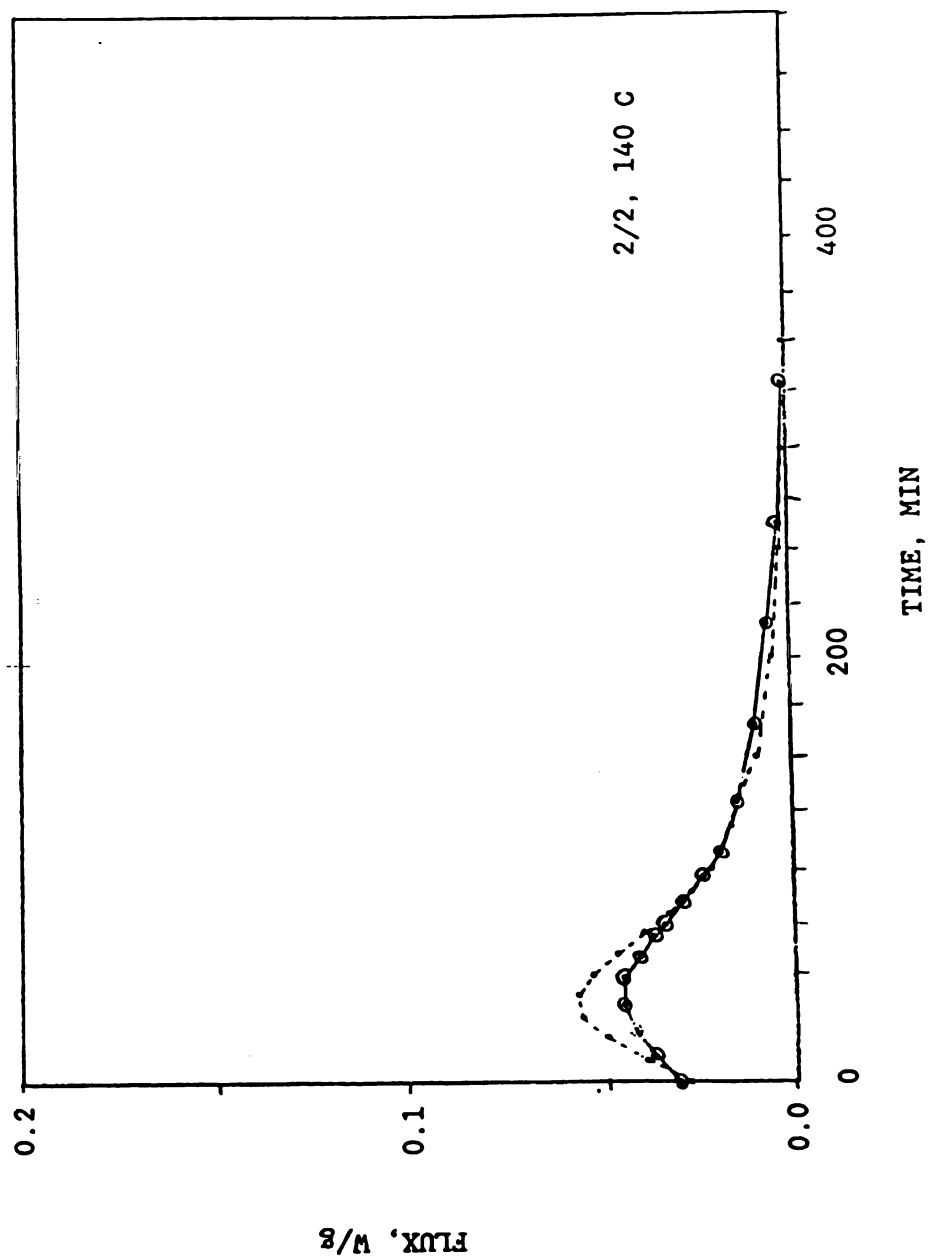


Figure 48. Isothermal DSC scan (2/2, 140 C).
Experiment (—○—), theory (---).

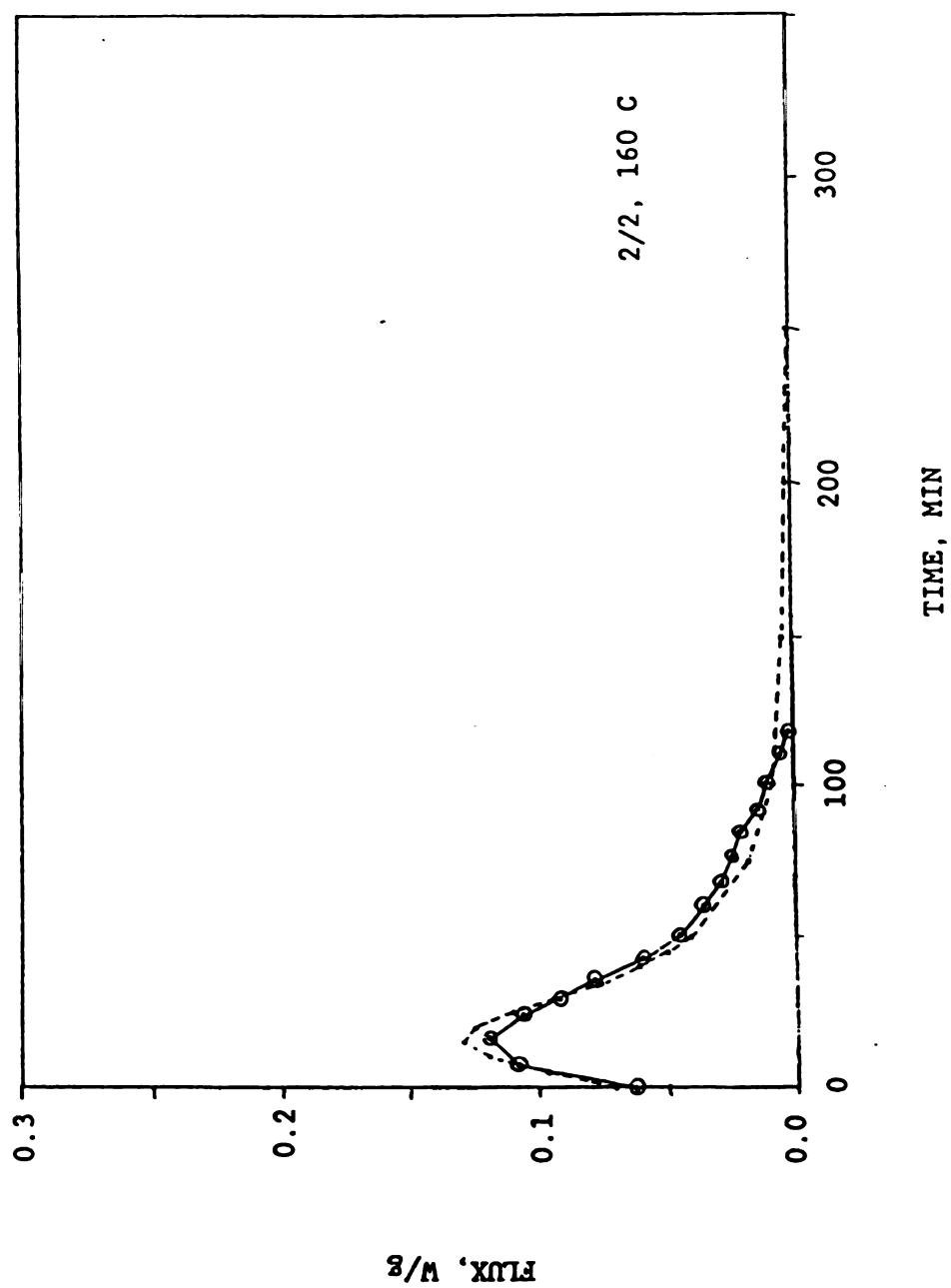


Figure 49. Isothermal DSC scan (2/2, 160 C).
Experiment (—○), theory (---).

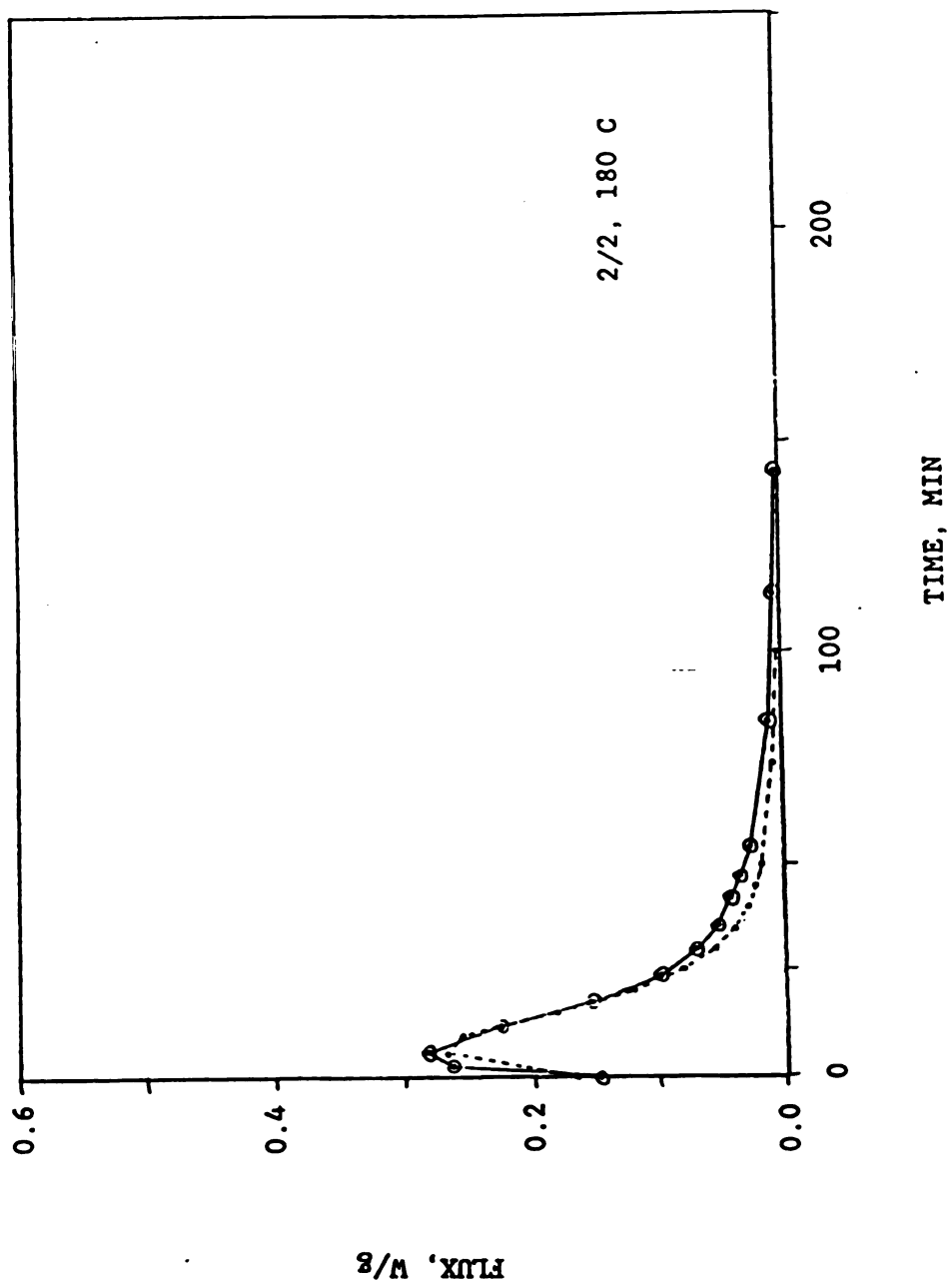


Figure 50. Isothermal DSC scan (2/2, 180 C).
Experiment (—●—), theory (---).

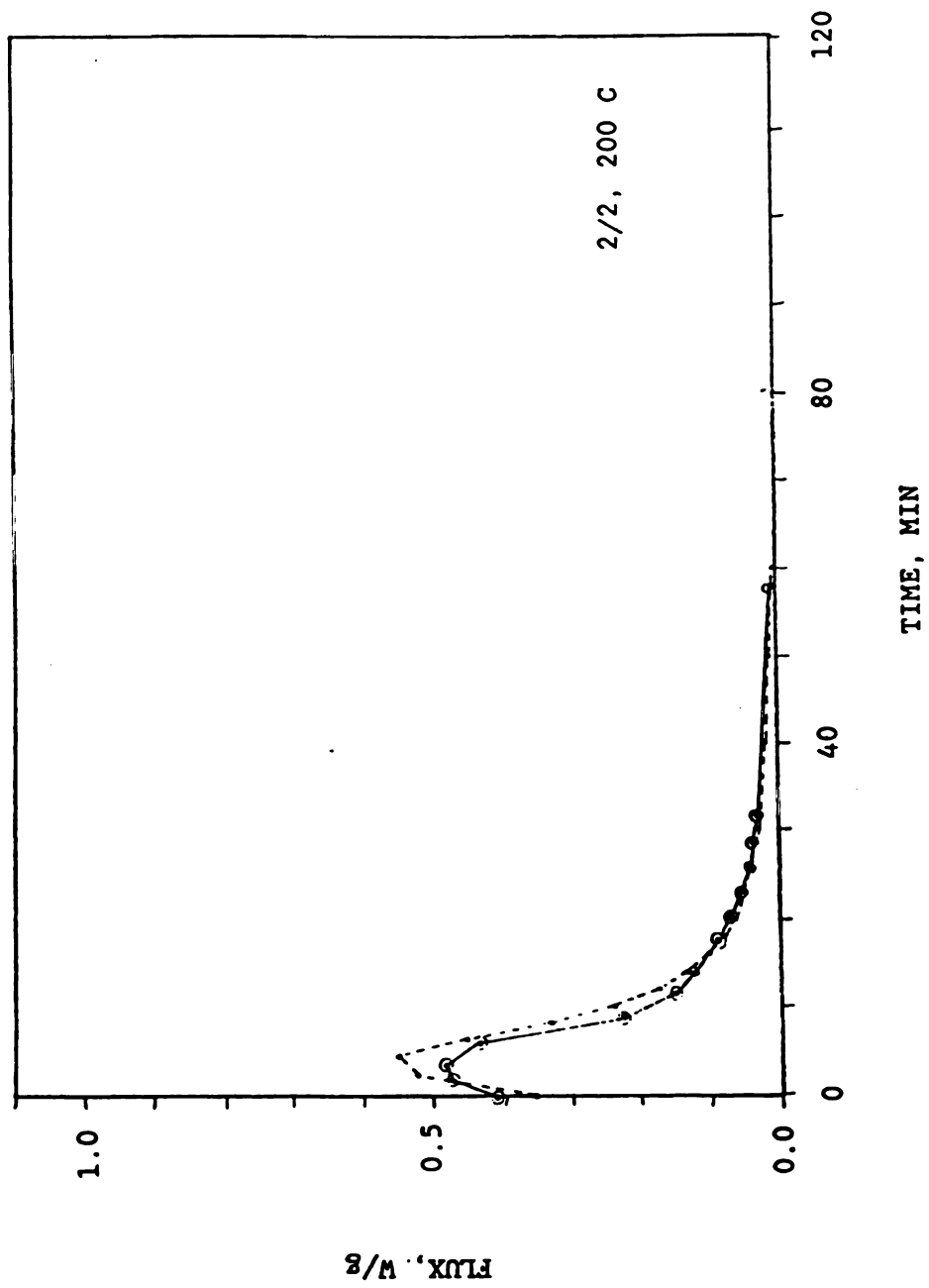


Figure 51. Isothermal DSC scan (2/2, 200 C).
Experiment (—○), theory (---○).

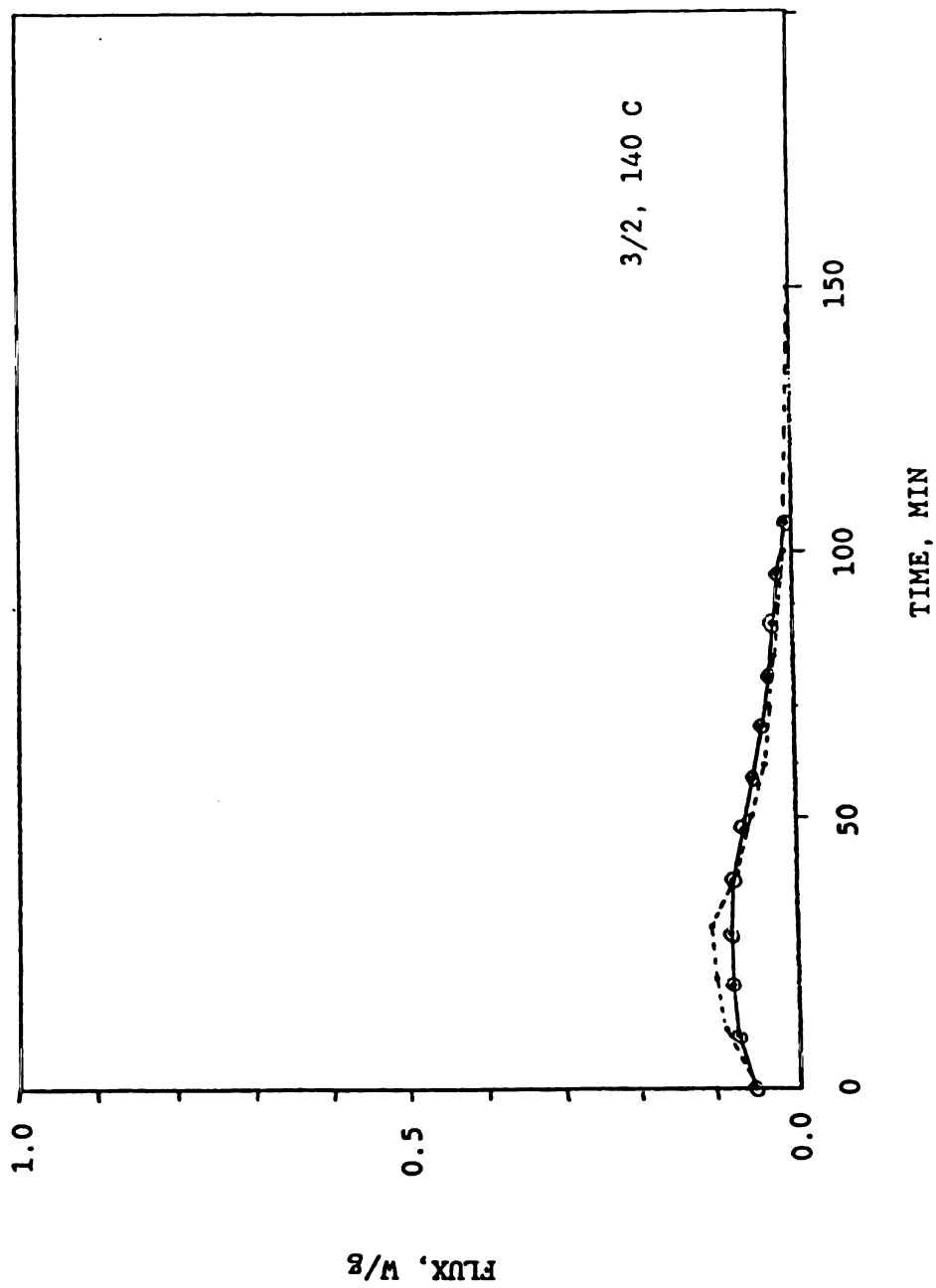


Figure 52. Isothermal DSC scan (3/2, 140 C).
Experiment (—○—), theory (---).

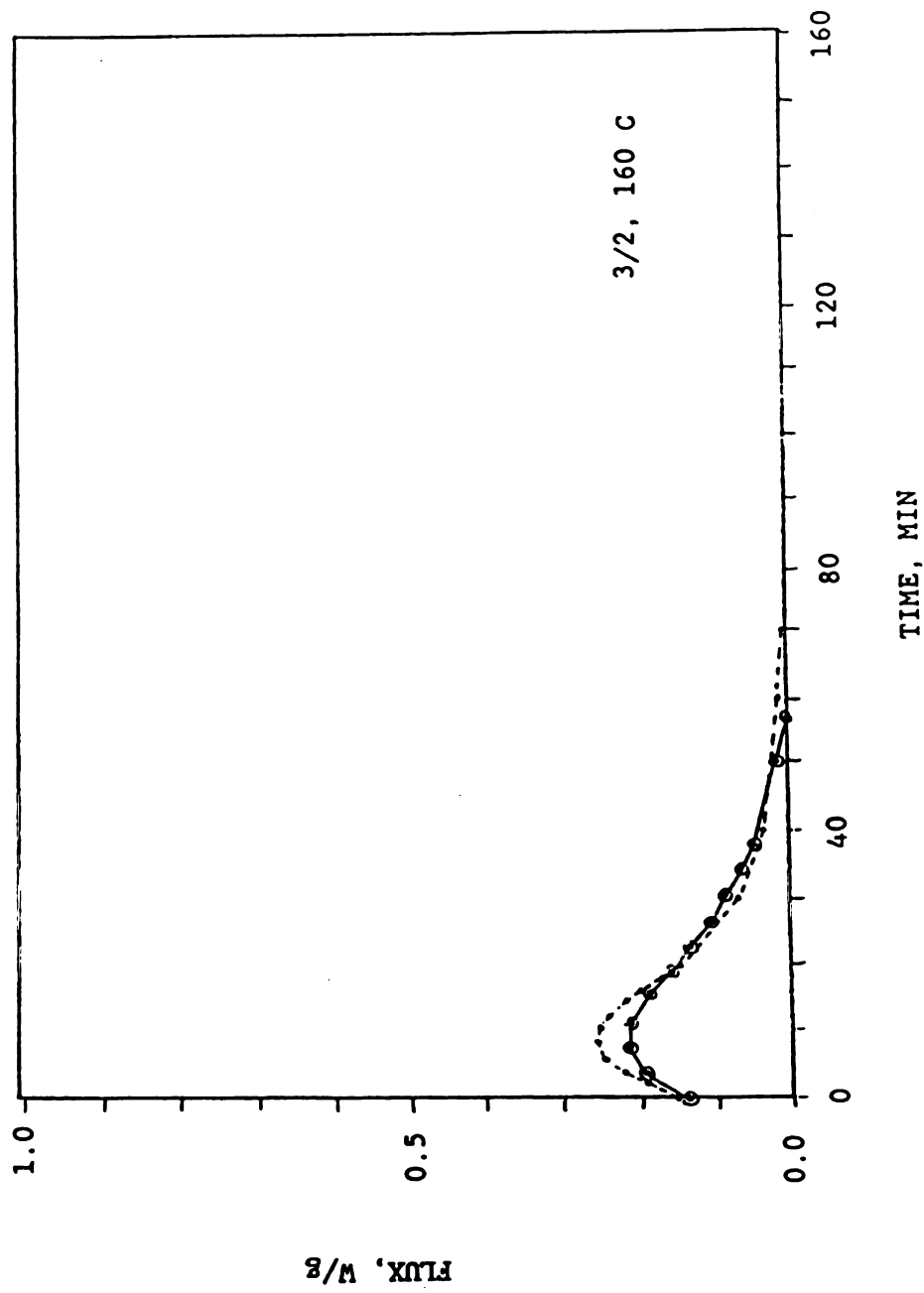


Figure 53. Isothermal DSC scan (3/2, 160 C).
Experiment (—○), theory (---).

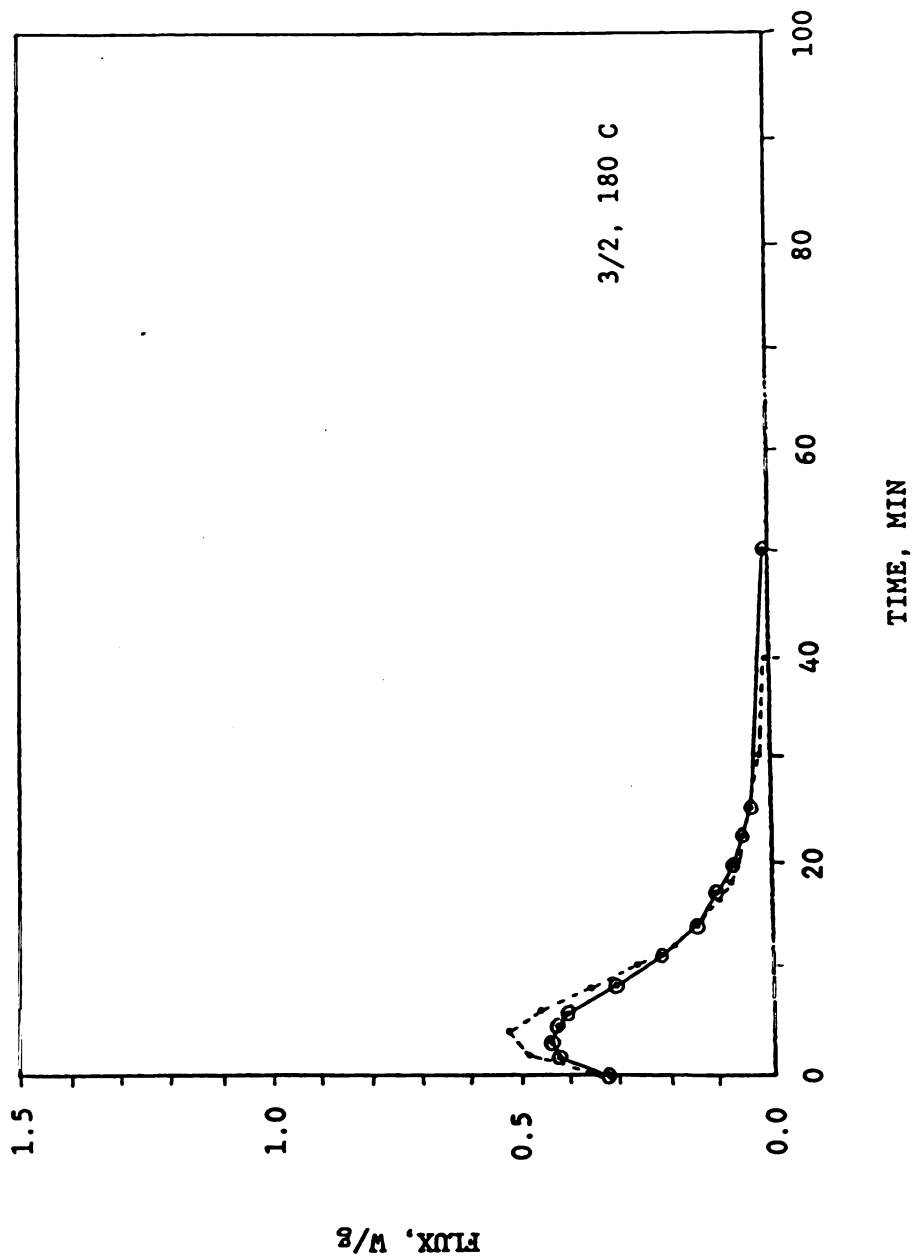


Figure 54. Isothermal DSC scan (3/2, 180 C).
Experiment (—○), theory (---).

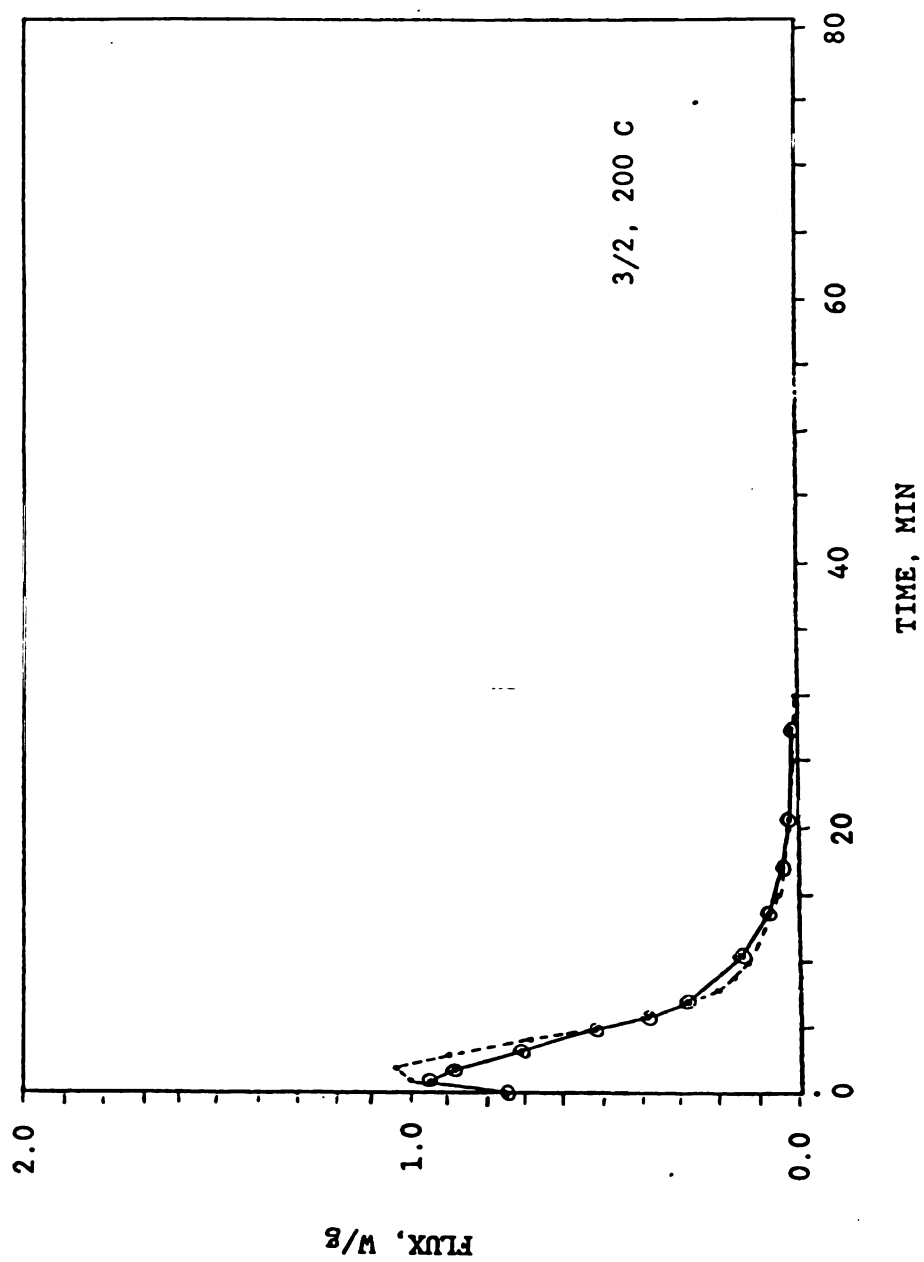


Figure 55. Isothermal DSC scan (3/2, 200 C).
Experiment (—○—), theory (---).

MODELING OF DIELECTRIC PROPERTIES

Modeling of the dielectric properties of stoichiometric mixtures as a function of DSC extent is made much easier with a few simplifying assumptions. Recall the forms of the equations for dielectric constant and loss tangent given at the end of the discussion regarding dielectric properties in the background section. If one assumes that α is equal to one and that $\omega\tau$ is large they can be reduced to the following

$$\epsilon' - \epsilon_{\infty} = \frac{(\epsilon_0 - \epsilon_{\infty}) \sin \phi}{(1 + 2(\omega\tau)^{\beta} \cos (\beta\pi/2) + (\omega\tau)^{2\beta})^{1/2}} \quad (101)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty}) \cos \phi}{(1 + 2(\omega\tau)^{\beta} \cos (\beta\pi/2) + (\omega\tau)^{2\beta})^{1/2}} \quad (102)$$

$$\tan \phi = \frac{\sin (\beta\pi/2)}{\cos (\beta\pi/2)} \quad (103)$$

$$\phi = \beta\pi/2 \quad (104)$$

It can be seen that the $\tan \phi$ term depends only upon the distribution parameter β for large $\omega\tau$. Therefore, the distribution parameter can be found by considering the ratio of the susceptibility and assuming the ratio to be independent of temperature.

$$\tan \phi = \frac{\epsilon''}{\epsilon' - \epsilon_{\infty}} \quad (105)$$

Additionally, this determines the infinite-frequency dielectric constant as a function of the extent of cure. Once the distribution parameter is obtained, the relaxation times as a function of temperature can be determined. The zero frequency dielectric constant is found by fitting the curves to the experimental data in Figures 58 and 59.

A plot of $\ln \epsilon''$ vs. $1/T$ should yield a straight line if the assumption of a single relaxation is correct. Figure 56 shows that this is indeed the case. The slope of this line yields what is termed the "apparent" activation energy in the literature (46,47). The true activation energy is the apparent activation energy divided by the distribution parameter. Table 16 (next page) shows how the distribution parameter, the infinite frequency dielectric constant, and the apparent and true activation energies vary with the extent of cure.

The relaxation times as a function of the extent of cure are determined by an iterative process, first by assuming a value of the oscillator strength ($\epsilon_0 - \epsilon_{\infty}$) based on literature values for these materials (34) and backing out the value of τ . The expressions thus determined for τ are then used to calculate the oscillator strength more precisely. The iterations are performed until the solution is consistent. Plots of $\ln \tau$ vs. $1/T$ for each extent are shown in Figure 57. The results of the calculation are

Table 16. Dielectric Relaxation Parameters

% EXTENT	β	ϵ_{∞}	E_a (app)	E_a (true), kcal/mol
0	0.236	3.556	5.558	23.55
4	0.171	3.352	4.294	25.11
14	0.170	2.961	4.065	23.91
37	0.145	3.032	2.607	17.98
44	0.103	2.839	1.933	18.77
46	0.124	2.824	1.859	14.99
57	0.126	2.640	1.200	9.52

Table 17. Additional Dielectric Relaxation Parameters

% EXTENT	$(\epsilon_0 - \epsilon_{\infty})$	$\ln A$	E_a (true), kcal/mol
0	13.846	-49.34	23.55
4	13.902	-48.18	25.11
14	13.906	-45.11	23.91
37	13.984	-30.22	17.98
44	14.004	-24.55	18.77
46	13.925	-19.80	14.99
57	13.978	-11.24	9.52

shown in Table 17.

An oscillator strength of 13.934 gives excellent agreement with experiment. Note that there is only one oscillator strength which fits the data regardless of extent. Figures 58 and 59 show the agreement of the model with the experimental results. The excellent agreement of theory with experiment is apparent. The model predicts a peak in the absorption at around 185 C for the unreacted mixture. It would be difficult to verify this experimentally because the reaction progresses extremely rapidly under these conditions and maintenance of constant sample composition would be difficult.

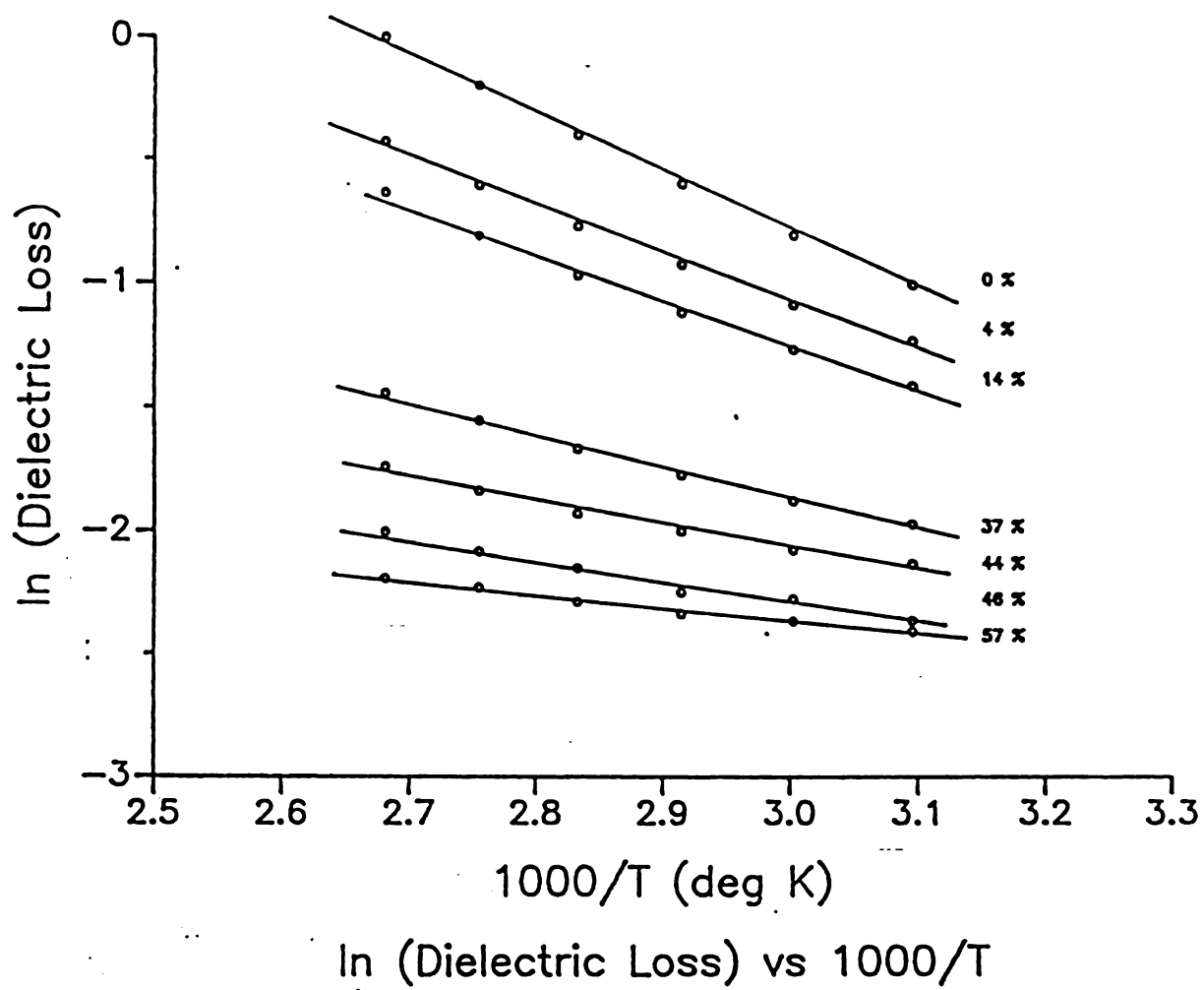
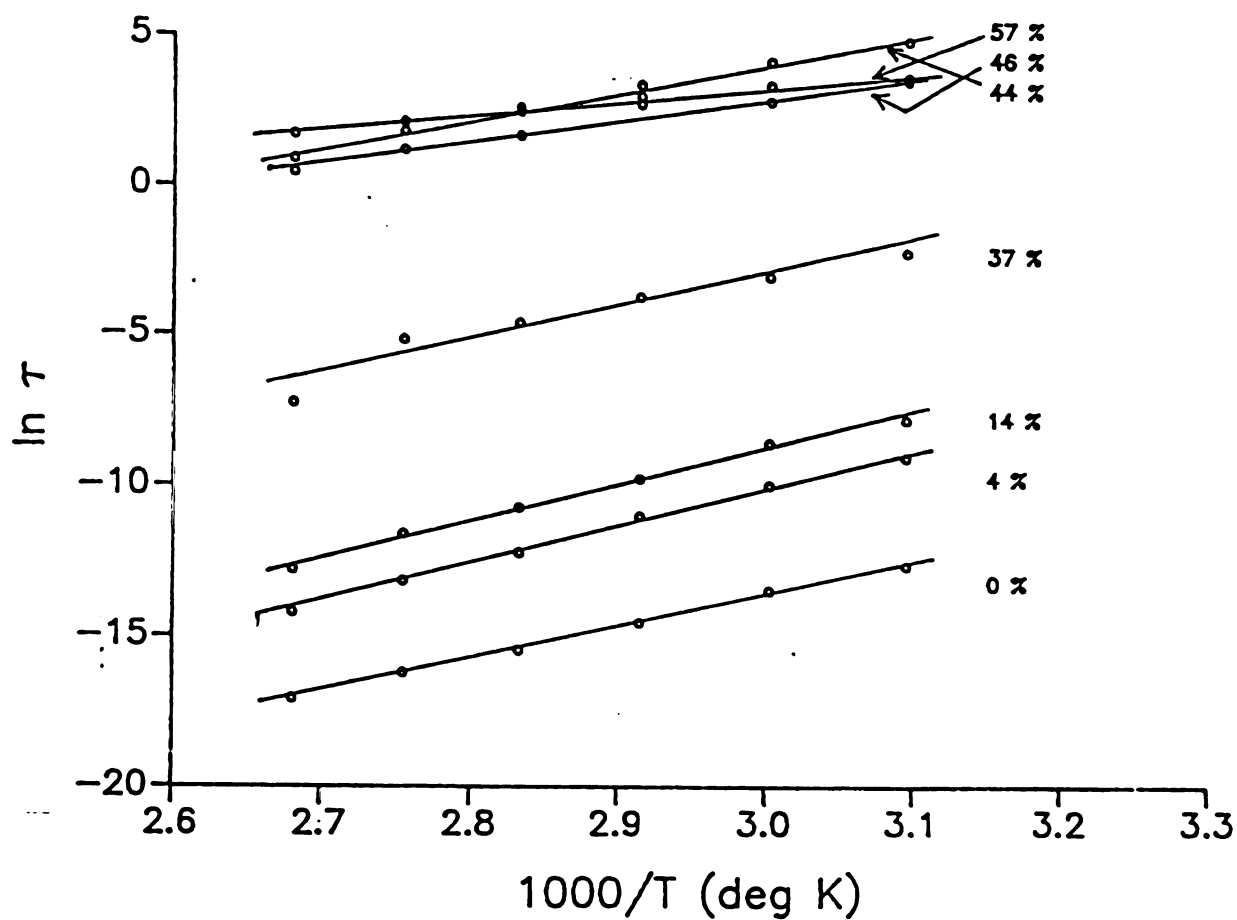
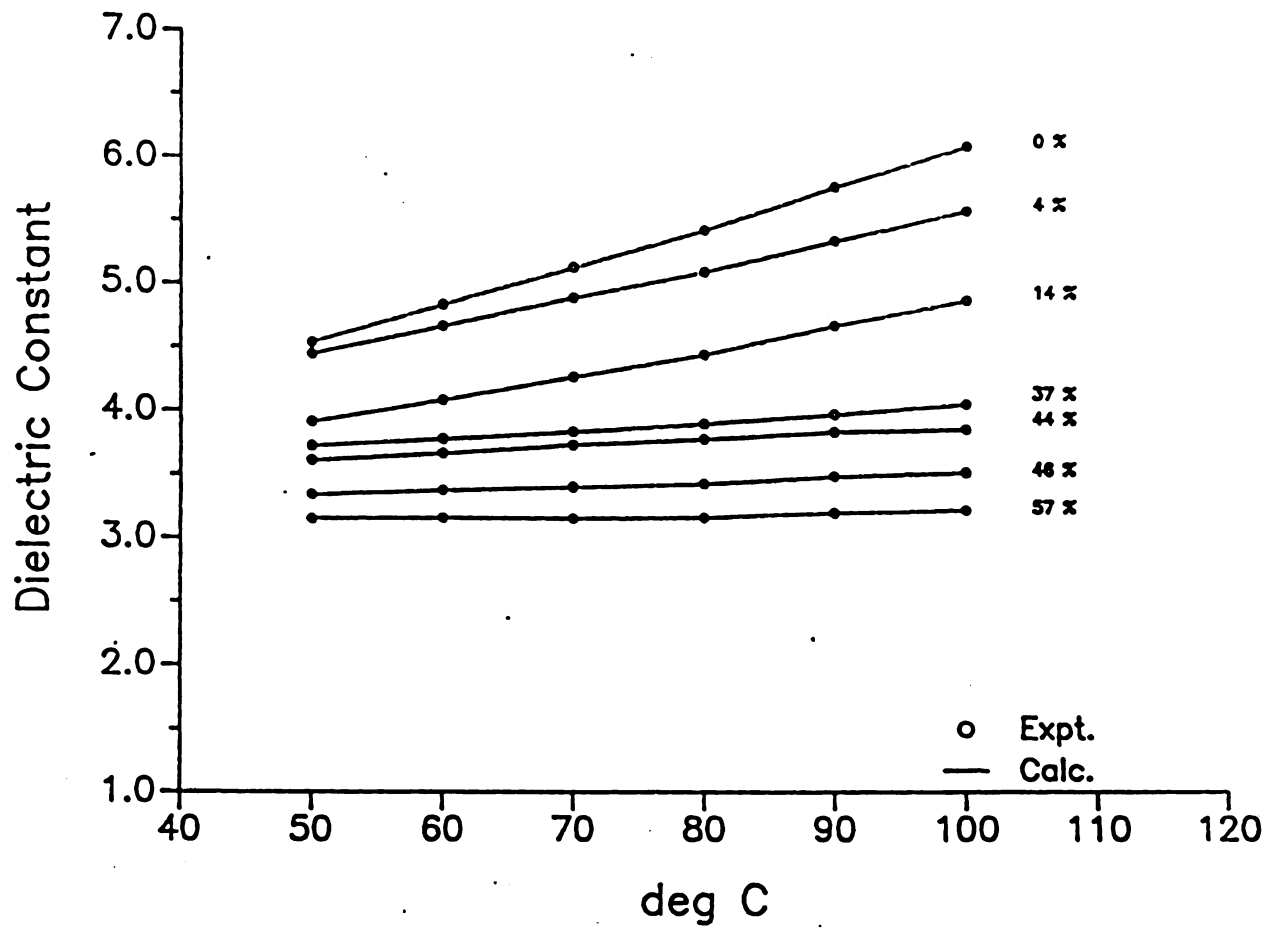


Figure 56. Logarithmic plot of loss factor vs. $1000/T$ for various extents. (DER 332/DDS, 2.45 GHz).



$\ln \tau$ vs $1000/T$ and extent of cure

Figure 57. Logarithmic plot of mean relaxation time vs. $1000/T$ for various extents (DER 332/DDS, 2.45 GHz).



Dielectric Constant vs Temperature and Extent

Figure 58. Dielectric constant for a variety of extents (DER 332/DDS) as a function of temperature (experiment vs. theory, 2.45 GHz).

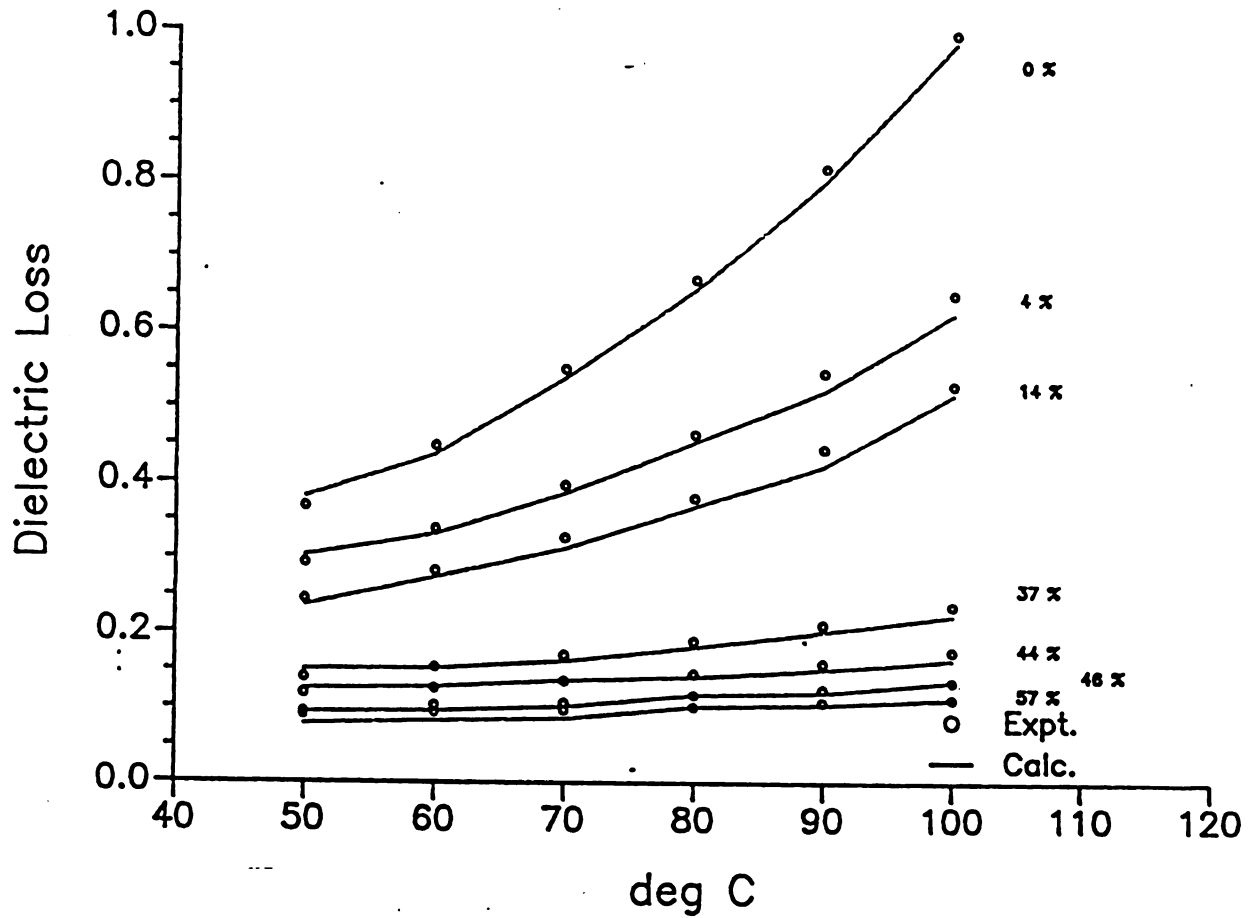


Figure 59. Loss factor for a variety of extents (DER 332/DDS) as a function of temperature (experiment vs. theory, 2.45 GHz).

DISCUSSION

The experimental evidence supports the three-step reaction mechanism. Consideration of the FTIR data shows no appreciable evidence of the formation of ether linkages. As an example of this, two sample FTIR spectra are shown in Figures 60 and 61. The first spectra is of an unreacted 1/2 sample used for a run at 180 C. The bands used in the analysis (epoxide at 915 cm^{-1} , amine hydrogen doublet around 695 cm^{-1} , and the aromatic C-H reference band at 1510 cm^{-1}) are plainly visible. The primary amine band that appears as a shoulder at 1615 cm^{-1} is also apparent. The second spectra is the same sample after 250 minutes time has elapsed. If aliphatic ether linkages were formed there would be a band at around 1100 cm^{-1} . It appears that a small amount of ether linkages are formed since the band that is already there is broadened somewhat. The intensity of the absorption hardly changes, however, indicating that even though there is some formation of ether linkages, the influence of this reaction pathway can be neglected in this analysis. The amine hydrogen doublet is diminished considerably as is the epoxide band. The primary amine band is completely gone. Hydroxide formation appears as a broad absorption at around 3500 cm^{-1} . Absorptions tend to broaden slightly in the reacted sample. This may be due to the fact that the temperature of the KBr window lags behind that of the thermocouple. It is not unusual for thermal broadening of absorption bands to occur. This phenomena requires that some care be exercised in the selection of the integration limits when the spectra are analyzed. It is also possible that the broadening of

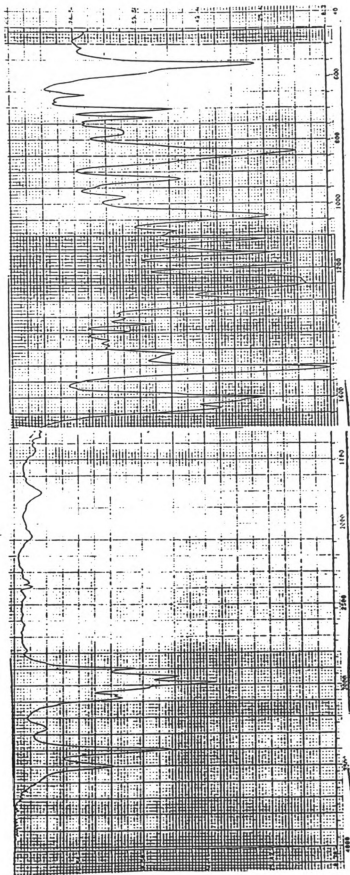


Figure 60. 1/2, 180 C sample (FTIR, 4000 to 450 cm^{-1}), unreacted.

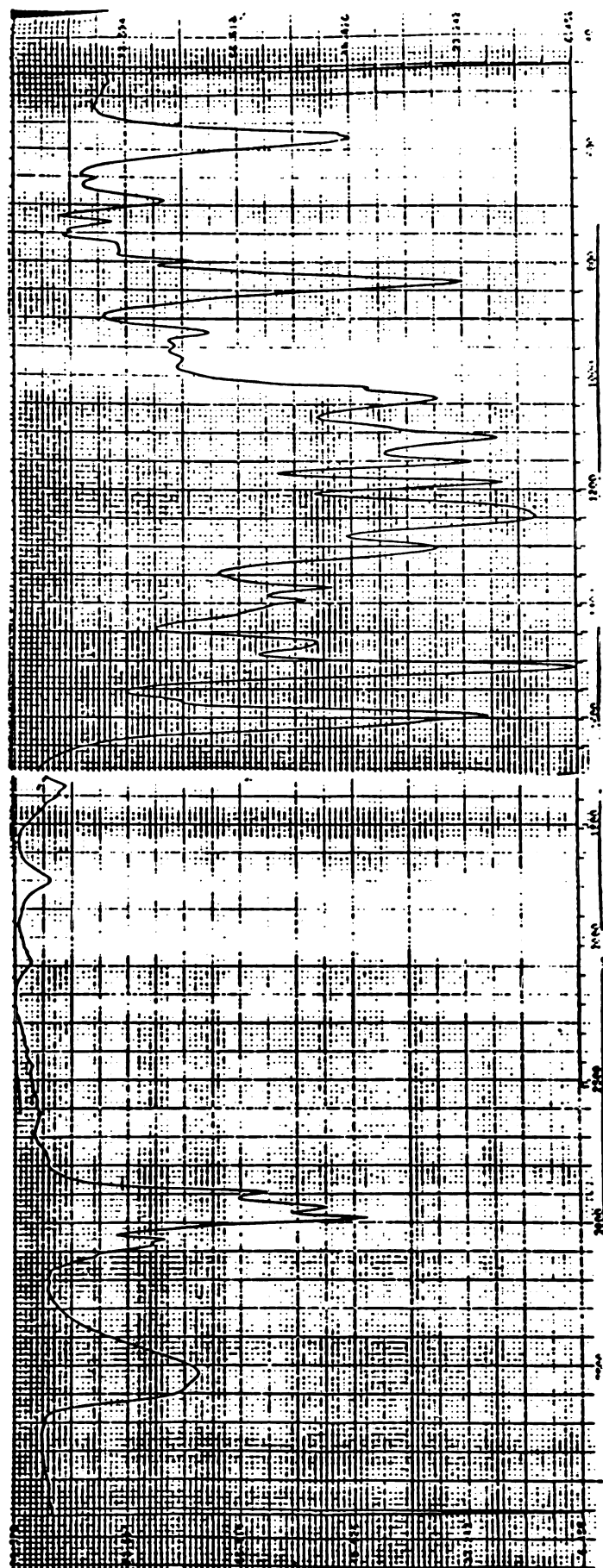


Figure 61. 1/2, 180 C sample (FTIR, 4000 to 450 cm^{-1}), reacted (250 min).

the ether bands with time described above could be attributed to this effect.

It has already been mentioned that a large amount of epoxide consumption occurs with no exotherm in the case of the 1/2 samples. The etherification reaction has an appreciable exotherm, whether determined by evaluation of bond energies (22.6 Kcal/mol) or experimentally (20 Kcal/mol from Reference (9)) and would therefore show up in the DSC traces in the experiments involving the 1/2 samples since a large amount of epoxide consumption occurs even though the amine is completely gone. Since the DSC traces completely vanish subsequent to the disappearance of amine hydrogen it is not likely that etherification is the preferred pathway. The formation of the quaternary ammonium ion is the pathway which occurs in this epoxy/amine reaction. Since the formation of the quaternary ammonium ion species occurs along with the formation of an alkoxide ion, it is possible that alkoxide ion formed could react with epoxide to form another alkoxide ion and an ether linkage via an anionic polymerization mechanism. The FTIR spectra, however, indicate that this does not occur to any significant extent.

The formation of quaternary ammonium ion is borne out by the C-13 NMR experiments. Quaternary ammonium ion would be expected to be formed in appreciable amounts only when there is a deficiency of amine. Circumstances favoring its formation include the fact that the reaction rate constant for the epoxy/amine reaction is lowest in the 1/2 case. Additionally, there is an appreciable amount of tertiary amine compared with secondary or

primary amine. Conditions of excess amine would tend to inhibit its formation. The scans for the 1/2 solid reacted samples show a band at about 60-65 ppm which does not appear in the scan for the 3/2 sample. A carbon adjacent to a quaternary ammonium species is expected to absorb at 65 ppm (31). The other bands in the aliphatic region of the NMR spectra are the same. Figure 62 (taken from Reference (13)) gives detailed assignments for NMR bands in an epoxy/amine system (the symbology used in the Figure is not in French even though the article from which it is taken was, making translation relatively simple.) The band around 45 ppm is a merging of epoxide carbon and the diphenyl-methyl carbon. The band at 50-55 ppm is the carbon adjacent to the secondary or tertiary amine species. The band at 80-85 ppm is most likely the carbon adjacent to an oxide-type species. The band at 90 ppm is a spinning sideband resulting from the band at 45 ppm. The liquid spectra (Figure 40) is exactly the same as one found in the literature for an unreacted system (26).

One can only speculate on what would occur if there were a catalyst included in this system so that etherification would be a possible reaction pathway. Since the value of the exotherm for this reaction is similar to that of the main epoxy/amine hydrogen reaction, it would be expected that the DSC results would be similar to the FTIR results over a larger range than if there were no catalyst present. If the etherification pathway would be preferred to the formation of quaternary ammonium ion, the FTIR epoxide data would be expected to mirror the DSC data more closely. FTIR would become much more important in the separation

GRENIER-LOUSTALOT ET GRENIER

TABLEAU IV*
Déplacements Chimiques ^{13}C et ^{15}N (ppm) Relevés lors de l'Étude du Système
DGEBA/mPDA à $T = 100^\circ\text{C}$

Carbones de la résine DGEBA*		C oligomères linéaires		C amines tertiaires réticulation	C expérience B
C	DGEBA				
1	44,1 ₁	1'	47,4 ₁	1" 53,4 ₂ -52,4 ₂	1° 63,6 ₂
2	50,1 ₁	2'	68,6 ₁	2" 68,0 ₁ -67,9 ₁	2° 70,5 ₁
3	69,1 ₁	3'	71,1 ₁		3° 71,4 ₁
4	156,7 ₁	4'	{157,0 ₁ 157,1 ₁	4" 157,1 ₁	
5	114,7 ₁		114,7 ₁		
6	127,7 ₁		127,7 ₁		
7	143,6 ₂		{143,2 ₁ 143,7 ₁	7" 143,3 ₁	
8	41,7 ₁		41,7 ₁		
9	31,0 ₁		31,0 ₁		

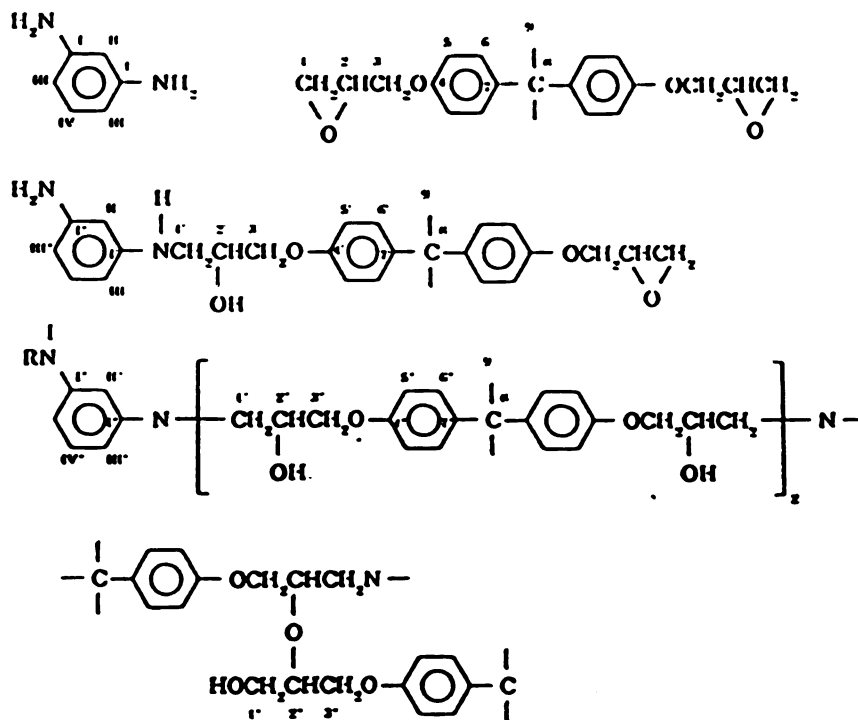


Figure 62. Chemical shifts of carbon-13 nuclei (DGEBA/mPDA), aliphatic region (unreacted DGEBA/secondary/tertiary/ether).

of the reaction data into the epoxy/amine and the epoxy/hydroxide pathways. The reaction system would of course become more complicated. It would be an interesting study to determine if the glass transition temperature would change if there were more than one type of crosslink. Activation energies of the reactions would of course be lowered with a catalyst present, making the reaction more rapid at lower temperatures. This would tend to inhibit the formation of the quaternary ammonium species at the expense of the other pathways. The catalyst concentration would also have to be varied in order to assess its effect on the reaction mechanism. If this work were to be repeated for a system including catalyst, the only facet which would not be appreciably different would be the method used to analyze the dielectric results. In fact, the results themselves might be expected to be similar since the overall concentration of polar groups would not be appreciably changed.

The activation energies found for the uncatalyzed and autocatalyzed reaction are consistent with those found in the literature for previous investigations of systems of this nature (cf. Background section). It is interesting to note that when a rate law involving a fit of an n -th order equation with only one rate constant is used (16,18), the value of the activation energy obtained is similar to the value of the one obtained from these experiments for the autocatalyzed reaction (around 13 Kcal/mol). This implies that the autocatalyzed reaction dominates over most of the reaction extent. For both the uncatalyzed and autocatalyzed reaction the frequency factor increases in a manner

roughly proportional to the initial concentration of amine. This is consistent with the mechanism postulated by Hagnauer et.al. (15) which fits initial rate data for an epoxy/amine system (albeit on involving TGMDA rather than DGEBA). The rate equation in this case is

$$-d[\text{TGMDA}]/dt = k[\text{TGMDA}][\text{DDS}]^2 \quad (106)$$

It is simple to translate this equation into a second-order equation by using the associative law.

$$-d[\text{TGMDA}]/dt = (k[\text{DDS}])[\text{TGMDA}][\text{DDS}] \quad (107)$$

$$= k'[\text{TGMDA}][\text{DDS}] \quad (108)$$

Note that now the rate constant is a function of initial amine concentration. This effect does not manifest itself to an appreciable extent in the rate constant for the side reaction. While there is only one set of rate constants available for the basis of comparison (1/2 and 2/2 mixtures at 140 C), the assumption that the side reaction rate constant does not change with formulation is borne out by the fact that the rate equations fit the data pretty well for these mixtures. The most glaring difference between the experimentally determined rate constants and those predicted by the reaction model occurs for the autocatalyzed rate constant at 200 C for the 2/2 and 3/2

formulations. Even still, the rate laws when integrated compare favorably with the experimental results. The reader is again referred to Figures 9-20 and Figures 23-34 in order to judge for themselves whether experiment and modeling agree. The largest differences between DSC and FTIR determinations of amine hydrogen occur for the 2/2 and 3/2 formulations at 180 C (nearly a 20% difference).

The experimentally determined activation energies and exotherms can be used to construct potential energy diagrams for the three reaction pathways postulated to be important in this system. These are shown in Figure 63. The chief difference in the pathways is apparent. It is possible that the side reaction is reversible and involves the setting up of an equilibrium while the epoxy/amine hydrogen reaction appears most definitely irreversible. The side reaction does not appear to have a great deal of effect on T_g . A probable explanation of this phenomena is that the reaction involving formation of this crosslink is indeed reversible. Another explanation of this is that the formation of a third crosslink where two already exist does not increase the rigidity of the molecular network. The strength of the chemical bond formed is definitely weaker than that formed in the primary reaction regardless of whether the reaction is reversible or not. Different chain linkages or bond types have predictable effects on glass transition (59-63). The crosslinking density in the DiBenedetto Equation applied to this system fits data if only the epoxy/amine linkages are considered. Consideration of Figure 43 (particularly the data point for the 1/2 formulation) bears this

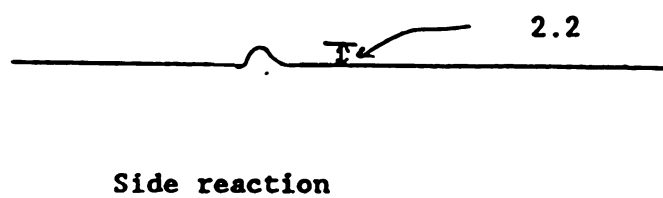
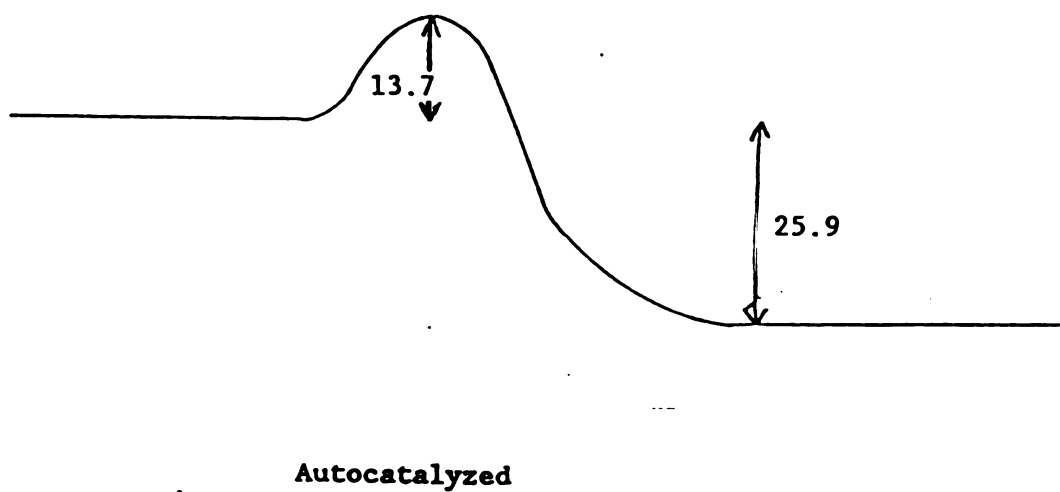
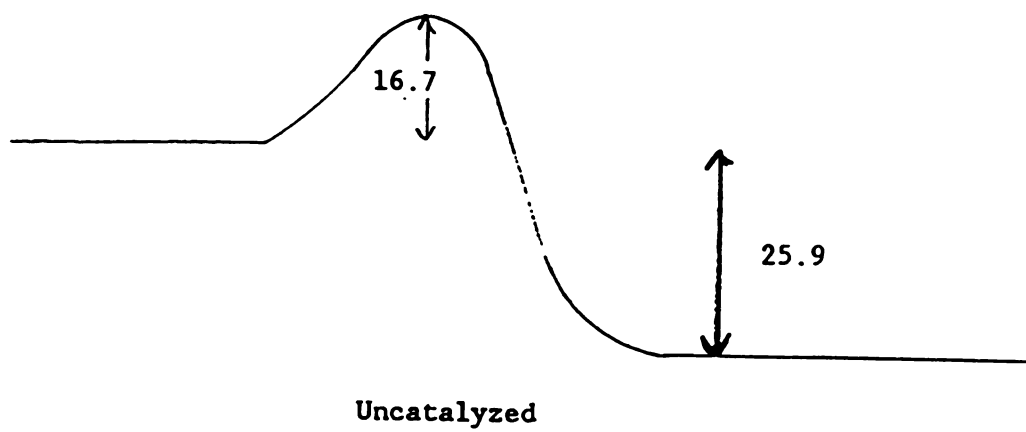


Figure 63. Potential energy surfaces (in Kcal/mol).

out. If the epoxy/quaternary ammonium linkages had the same effect on T_g as the epoxy/amine hydrogen linkages, a crosslinking density of .0036 eq/g would be associated with a T_g of 54 C. Refitting this data point would involve a radical change in T_{g0} , ϵ_x/ϵ_0 , and c_x/c_0 . The lattice energy and mobility ratios are parameters which do not change with formulation. Based upon the fact that the side reaction has a deleterious effect on the glass transition temperature, it would make sense to run the reaction under conditions which would tend to make the side reaction a less favorable pathway. A slight excess in amine for a near stoichiometric mixture at a high temperature would possibly increase T_g over that of an exactly stoichiometric mixture.

Figures 64-66 show how the experimentally determined epoxy/amine rate constants vary with extent for each formulation and compare the experimental results with the model results. The diffusion limited nature of the reaction is apparent since the rate constant falls off to zero at high extents in all cases. The rate constants are linear with respect to amine extent (hydroxide concentration) at low extents of reaction which is consistent with the autocatalyzed nature of the reaction. The gel point for each formulation (determined by the Flory relationship $\alpha_A \alpha_E = 1/3$) is also included on these graphs. It can be seen that the diffusion limit reduces the value of the rate constant by a factor of approximately 50 % at the gel point.

The rate equations for this system can be rewritten in a dimensionless manner similar to those written by Dusek (14). They are written in terms of primary amine mole fraction (with respect

1/2

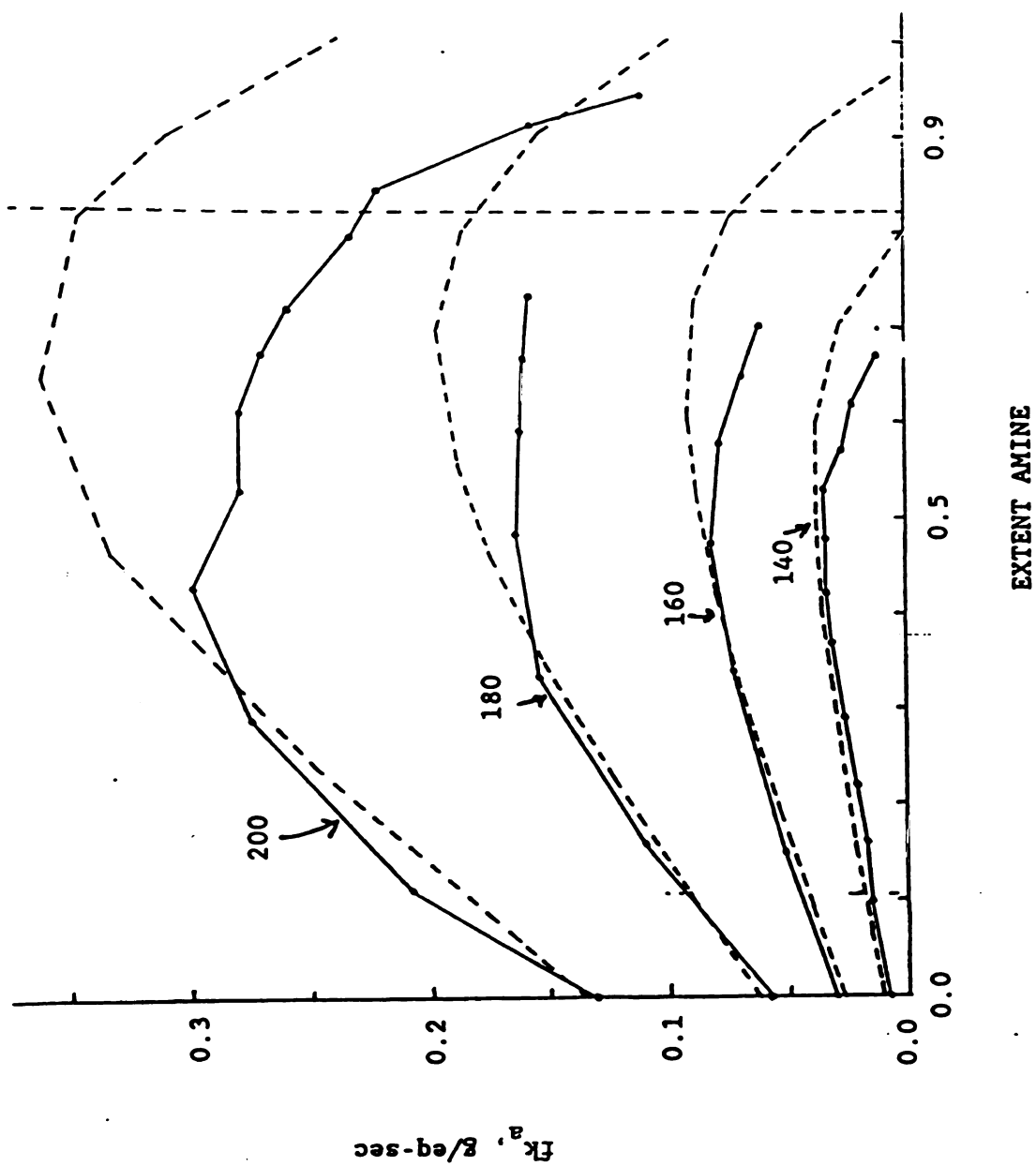


Figure 64. Epoxide/Amine Hydrogen Rate Constants vs. Extent Amine (second order, 1/2 formulation). --- theory, —●— expt.

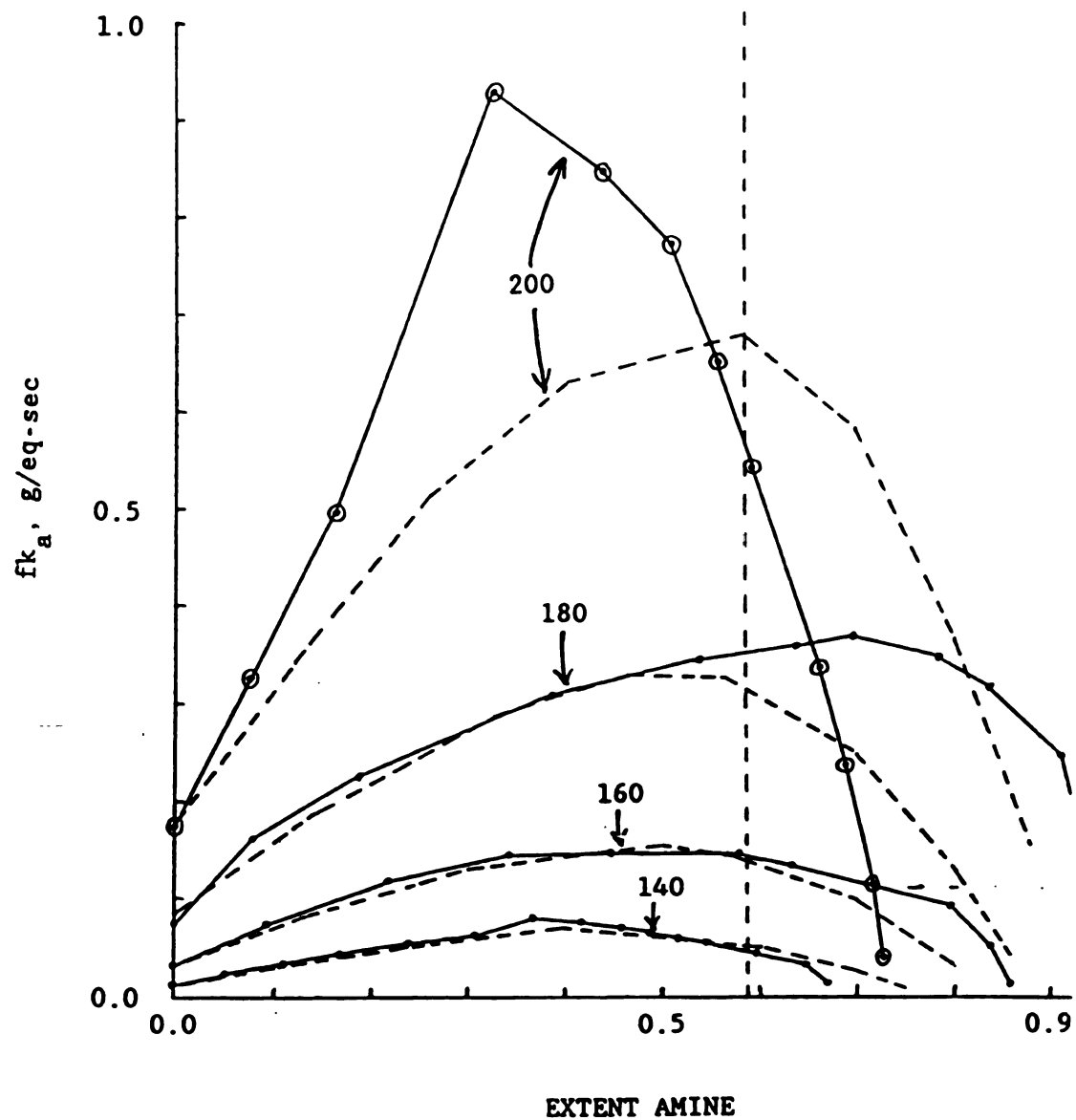


Figure 65. Epoxide/Amine Hydrogen Rate Constants vs. Extent Amine (second order, 2/2 formulation).--- theory, —● expt. $\odot$

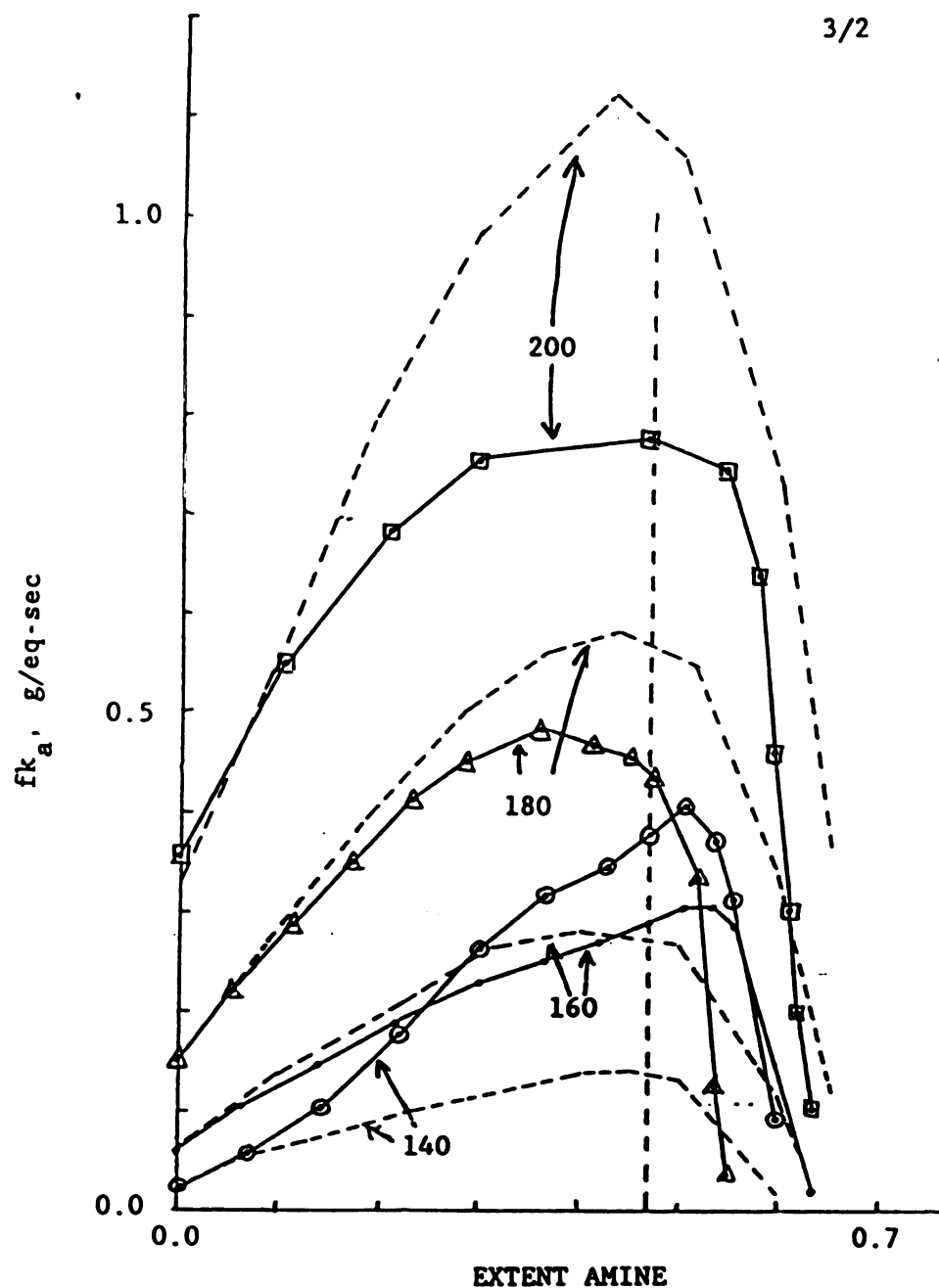


Figure 66. Epoxide/Amine Hydrogen Rate Constants vs. Extent Amine (second order, 3/2 formulation) ---- theory, —●— expt.



to total amine only) as follows

$$da_p/da_p = 1 \quad (109)$$

$$da_s/da_p = 0.5(a_s/a_p) - 1 \quad (110)$$

$$da_t/da_p = -0.5(a_s/a_p) + (k_s/2k_a)(a_t/a_p) \quad (111)$$

$$da_q/da_p = -(k_s/2k_a)(a_t/a_p) \quad (112)$$

A problem that arises when these equations are numerically integrated is that the primary amine can disappear before the reaction is complete so that the information developed by the integration of these rate equations is not available over the entire extent of reaction. In order to complete the integration, the equations are integrated with respect to the quaternary ammonium ion fraction once the primary amine is totally consumed.

These equations are as follows

$$da_p/da_q = -(2k_a/k_s)(a_p/a_t) \quad (113)$$

$$da_s/da_q = (2k_a/k_s)(a_p/a_t) - 2(a_s/a_t) \quad (114)$$

$$da_t/da_q = 2(a_s/a_t) - 1 \quad (115)$$

$$da_q/da_q = 1 \quad (116)$$

Primary and quaternary mole fractions are chosen for this since they are involved in the steps involving only disappearance or consumption of reactants which make the dimensionless reformulation of the equations much easier.

These mole fractions can be used to estimate the glass transition temperature of a crosslinking material in far greater detail than has been done up to this point. First the fraction of each type of monomer must be estimated. This can be done using the appropriate combinations of a_i 's and e_i 's. For instance, the mole fraction of unreacted amine would be expressed as $a_0 a_0$ or a_{00} . This is referenced to concentration of total amine. The section on Network Modeling in the Background section has examples of these types of equations. Next, the characteristic glass transition temperature T_g^* for each monomer unit must be multiplied by the mole fraction of each monomer. This can be done if the assumption of mole fraction contributions to the reduction in chain mobility and lattice energy with crosslinking is valid. Summing over the T_g^* 's and mole fractions yields an estimate of T_g . The fitting of data to such a model would require measurements of T_g versus extent epoxide and amine and would have to be compared to a network calculation. Four different possible chain ending groups imply ten different amine monomers while three different end groups on the epoxide chains imply six different monomers making sixteen possible contributions to the sum. The fitting of data using this method is not as difficult as it would seem and is currently under investigation. This method is based somewhat loosely on the DiBenedetto Equation in its newer form (63).

Another way these equations can be applied is to speculate upon the nature of microwave versus thermal curing and the possible effects that microwave curing would have upon network

formation and material properties. Results taken in our laboratory (38) indicate that curing an epoxy/amine system electromagnetically increases T_g compared to the value resulting from thermal curing. It may be recalled at this point in the discussion that the glass transition temperature of a thermoset depends upon crosslinking in a manner predicted by the reduction in chain mobility caused by the reaction of end groups (61). Therefore a tetrafunctional diamine molecule would have a greater effect on T_g if there was a crosslink at each end rather than two crosslinks at one end. The formation of a second crosslink at an amine group would not have as great an effect as the formation of the first.

It is well known that microwaves excite the rotation of dipolar groups in molecules. The reaction of epoxide with primary amine occurs between two dipolar species at the end of polymer chain molecules which can be expected to exhibit molecular rotation. On the other hand, the reaction of epoxide with secondary amine occurs between one chain-ending dipole and another species which exists as a member of a polymer chain. It is possible that the preferential absorption of microwaves by easily-rotating polymer end groups would increase the amount of energy available for promotion of chemical reaction of these species. If this is the case, the rate constants would be increased by the use of microwave curing. The reaction of primary amine with epoxide would be expected to be increased to a larger degree than the reaction of secondary amine with epoxide since there are two end groups reacting in the former and one in the latter.

Consideration of the magnitudes of the partition functions for rotation and vibration indicate that energy transfer from rotational to vibrational modes (and the reaction transition state) is not thermodynamically favored (40). The N-H stretching vibration occurs at 1614 cm^{-1} which corresponds to the formation of an excited vibrational state 4.612 Kcal/mol above the ground state. Assuming an activation energy of 15 Kcal/mol and utilizing the Boltzmann distribution indicates that the excited vibrational state must be populated three times as heavily in order to double the rate constant. This also assumes the frequency factor of the rate constant is the same. This excess population of the excited vibrational state implies a system vibrational temperature above that of the ambient (translational) temperature so that the system is not in thermal equilibrium. In order to increase the rate constant with microwave radiation, a condition would therefore have to be set up in the system where the rotational and vibrational modes would not be in a condition of thermal equilibrium. Pumping the dipolar groups with microwave energy and the consequent rotational excitation might be a way of accomplishing this.

A speculative calculation can be conducted where the primary amine rate constant is doubled over the primary amine rate constant determined by the experimental results. Of course, all of the work in this thesis involves thermal curing. If the key to increasing the glass transition temperature is the reaction of all amine end groups, the calculation should determine how many of these groups are present if this doubling of the rate constant is

assumed. Table 18 shows the primary amine mole fractions (a_p) and the mole fraction of amine molecules with no linkages at all (a_0) for both the thermal and the "microwave" case assuming microwaves double the value of the rate constant for the epoxy/primary amine reaction while leaving the value of the secondary amine rate constant unchanged. The values in the table correspond to complete reaction up the point where the diffusion limit quenches the reaction. The diffusion limit is assumed to be unchanged. This results in the epoxy and amine extents being essentially the same for thermal and microwave cure as a consequence of the calculation. If microwave curing results in higher extents of reaction, the values for the microwave case (x_2) would be even lower.

As can be seen, doubling the primary amine rate constant reduces the total concentration of free end groups, which would therefore result in an increase in T_g . There is of course an increased initial rate of reaction although the overall cure time is not decreased that much due to the fact that the diffusion limited region is reached more quickly as a consequence of the initial rate increase. The onset of gelation occurs more quickly. Table 19 below shows the total gel time for the thermal and (x_2) cases. Note that gelation does not occur for the (1/2, 140 C) case. The glass transition temperature of this system was below room temperature.

Wang and Gillham in an as yet unpublished article (68) carry out a study which further suggests a possible rate enhancement by using microwave curing. They study a trimethylene glycol di-p-

Table 18. Additional Results of Network Calculation

Formulation	Temperature	a_p		a_0	
		--	x2	--	x2
1/2	140	0.0426	0.0086	0.0018	0.0001
	160	0.0016	0	0	0
	180	0	0	0	0
	200	0	0	0	0
2/2	140	0.0599	0.0143	0.0036	0.0002
	160	0.0301	0.0056	0.0013	0
	180	0.0206	0.0019	0.0004	0
	200	0.0161	0.0011	0.0003	0
3/2	140	0.1571	0.0884	0.0247	0.0078
	160	0.1422	0.0730	0.0202	0.0053
	180	0.1256	0.0599	0.0158	0.0036
	200	0.1169	0.0538	0.0137	0.0029

Table 19. Total Gel Time (min).

Formulation	Temperature	$t_{gel} (x2)$	t_{gel}
		---	---
1/2	140	---	---
	160	80	110
	180	35	50
	200	20	25
2/2	140	70	110
	160	30	45
	180	15	25
	200	8	12
3/2	140	35	55
	160	16	26
	180	8	12
	200	4	6

aminobenzoate/DGEBA system and find that k_2/k_1 increases with temperature by a factor of 2 over the temperature range 100 to 160 C. This implies that the secondary amine rate constant is much greater at even higher temperatures and would imply that the reaction would occur at high extents (during vitrification) more easily. Since microwave reactions can be carried out at extremely high temperatures (36-38) this would mean that higher extents of cure could be realized using microwaves. This author, however, has a problem with the reaction mechanism as postulated in this paper since only the autocatalyzed step is assumed to occur. The ratio k_2/k_1 is lower than 0.5 which is in contradiction to the conclusions of other investigators for DGEBA/diamine systems (14,19,22). It is possible that this is due to the incorrect mechanism being used. One wonders how, if only the autocatalyzed step occurs, how the reaction can initiate with no hydroxyl present at the outset.

It is a possibility that true network formation does not occur in the 1/2 case. Instead, the crosslinking density may be unevenly distributed with regimes having a high crosslink concentration alternating with regimes containing no crosslinks at all. Crosslinking density would be highest at the location of the deficient reactant (amine) with all four amine linkages showing branches if the reaction is complete. Therefore, networks would form but would not be evenly distributed throughout the cured thermoset.

Cyclization is the name attributed to the phenomenon where epoxy groups react with pendant hydroxide groups of the same epoxy

molecule. The work most often cited is that of Rozenberg (69). It is more common in TGMDA systems than in DGEBA systems due to the proximity of the epoxide and the hydroxide. It is not expected to be important in this system since the etherification reaction (which is associated with cyclization) does not occur in an epoxy/amine cure without catalyst present.

It is interesting to note that the oscillator strength remains constant while the other relaxation parameters change as the extent of cure progresses. This indicates that it is primarily the dipolar environments and not the dipoles themselves which exert the primary influence on dielectric relaxation in these systems. The value of the oscillator strength corresponds to that used to fit low frequency data in the literature (1,31,34). The values of ϵ_0 and ϵ_∞ change in a manner consistent with one another so that the oscillator strength remains fairly constant.

The magnitudes of the activation energies move from those associated with α -relaxations involving large chain segments (25-40 Kcal/mol) to those involving smaller chain segments (10-15 Kcal/mol). These are referred to as β or γ -relaxations in the literature. The distribution of relaxation times widens as the segments involved become smaller (46,47,64). At low extents of cure it can be seen, by considering the values of the activation energies, that the α -type predominates, while the β - or γ -type mechanisms predominate at higher extents. It is believed that the mechanism at higher extents of cure proceeds primarily via a crankshaft-type mechanism (64), possibly involving the motion of a hydroxyether group (70). In order to combine the dielectric

modeling with a process model, the results for the various discrete extents would have to be made continuous. How this might be accomplished might be combined with a network analysis. This would involve assigning a characteristic mean relaxation time for each type of species in the network along with a distribution parameter. The reduced concentration of end groups associated with the theoretical nature of microwave curing described above would reduce the loss factor and the absorption of these systems as cure progresses beyond the reduction of this parameter with extent associated with thermal cure. These concerns are discussed in a paper recently prepared by this author (among others) which has been accepted for publication (71).

CONCLUSION

In the absence of a catalyst, the reaction between DGEBA epoxy resins and amine curing agents primarily involve a reaction between epoxide and amine hydrogen. A side reaction occurs where epoxide reacts with tertiary amine formed in the reaction to form a quaternary ammonium/oxide ion pair. The main reaction has a large exotherm while the side reaction proceeds with essentially no exotherm. The side reaction is favored when there is a deficiency of amine or when the reaction temperature is low. It is possible that the side reaction is reversible and that this property lowers the T_g of systems where the side reaction occurs.

Rate constants for the main reaction are functions of hydroxyl formation, glass transition, temperature, and initial amine concentration. The reactions are all second-order. The main reaction involves an uncatalyzed and an autocatalyzed part involving hydroxide. Etherification is not believed to be important in this system because there is no species that catalyzes its formation. It is possible to find a rate constant which is valid over the entire extent of reaction rather than over only a small part of the cure process. DSC, FTIR, and NMR combined yield information and a potential for interpretation greater than that possible by using only one experimental technique.

Etherification would be expected to occur in the presence of a catalyst. While the addition of a catalyst would not be expected to have a great deal of effect on the 2/2 or 3/2 results since

these conditions favor the main reaction, the 1/2 results would be changed. There would be more crosslinks and a higher T_g as well as a larger exotherm since the etherification reaction is much more exothermic than the tertiary amine reaction. In fact, since epoxide concentration is highest in the 1/2 mixture it would follow that the reaction exotherm would be highest of all for this formulation. It would be interesting to apply a combined DSC and FTIR program to a catalyzed system and measure the kinetics and glass transition temperatures. The FTIR interpretation would be much more important since DSC could not be used to separate epoxy/amine reactions from etherification reactions since their exotherms are so similar.

Changes in the system dielectric properties with increasing extent of cure are caused by widening of the distribution of relaxation times as the system relaxations involve shorter and shorter segments. The oscillator strength is constant regardless of the extent of cure. The zero- and infinite frequency dielectric constants decrease with increasing extent of cure. Modeling dielectric data obtained in other experiments indicates that there would be a peak in the absorption at 185 C at 2.45 GHz for an unreacted stoichiometric mixture.

FUTURE WORK

The combined FTIR/DSC approach can be applied to any thermoset system where there is more than one pathway and more than one exotherm. The experimental program could be repeated with catalyst added to check for etherification. A model compound study could be conducted using a tertiary amine species to test hypotheses regarding the side reaction. The etherification reaction could be studied by examination of a epoxy/catalyst system with no amine present. The group contribution model could be utilized in conjunction with network calculations in order to model glass transition as a function of extent and formulation. The hypothesis that a formulation with amine slightly in excess would have an increased T_g could be investigated. The dielectric data could be modeled in such a way that the dependence on extent is continuous rather than discrete so that it could be used to model microwave processing. The dependence of dielectric parameters on network formation could be investigated and modeled. The dielectric properties of non-stoichiometric mixtures could be investigated. A way could be found to rapidly measure dielectric properties so that fast-reacting systems such as the unreacted mixture at 185 C could be experimentally investigated.

APPENDIX

FORTTRAN Program for Numerical Integration of Rate Equations

The following section details the use of the FORTRAN program which integrates the rate equations for the epoxy/amine reaction. The algorithm used is a first-order Runge-Kutta method (predictor-corrector) which integrates a set of five differential equations. The time-dependent quantities calculated in this manner are

	Initial Values		
	1/2	2/2	3/2
c(1) - primary amine	.001226	.002128	.002820
c(2) - secondary amine	0	0	0
c(3) - tertiary amine	0	0	0
c(4) - quaternary ammonium	0	0	0
c(5) - epoxide	.004902	.004255	.003759

The concentrations listed in the initial conditions are in units of eq/g. These units are chosen because they are volume-independent and avoid having to consider the effects of thermal expansion. Hydroxide concentration is not integrated because it can be determined simply by considering the amine extent. The program also calculates the glass transition temperatures, the diffusion-limited parameter f , the rate constants, and DSC heat fluxes.

The main program is called "fluxclc" while the subroutine is

called "dcalc". A key variable is the mole fractions associated with the various amine species. They are a_p (primary), a_s (secondary), a_t (tertiary), and a_q (quaternary). DSC fluxes are determined in an unusual manner to make plotting of the results easier. A DSC plot on the Model 9300 measures 15.0 cm vertical (heat flux) by 20.7 cm horizontal (time). The program calculates the results in cm so that the calculated results can be compared directly with the plots.

The variable "numdat" refers to the total number of data sets (three formulations and four temperatures implies twelve of them). An example of data input is shown below (this one is for the 1/2, 140 C mixture).

```

05  10.000      096  060      0.2      -0.083
15.591  14.060   413.      12.140   254.      308.      0.027
0.001226
0.
0.
0.
0.004902

```

Line by line, this means:

First line	- numvar	number of variables (ALWAYS five)
	tstep	time increment of integration (in seconds)
	imax	number of outputs
	niter	iterations per output
	range	vertical range of DSC plot (W/g)
	b7	B for WLF equation
Second line	- blu	$\ln A_u$
	blc	$\ln A_c$
	b2	temperature
	b3	"12.140" means 1/2, 140 C
	b4	T
	b5	C^g for WLF equation
	b6	side reaction rate constant

Third line - cinit(1) c(1) initial value

Fourth line - cinit(2) c(2) initial value

Fifth line - cinit(3) c(3) initial value

Sixth line - cinit(4) c(4) initial value

Seventh line - cinit(5) c(5) initial value

An example of a few lines of output is shown below.

12.140

0.0	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.01	0.0103
10.0	0.9356	0.0634	0.0010	0.0000	0.0328	0.0164	1.17	0.0126
20.0	0.8645	0.1306	0.0047	0.0002	0.0702	0.0352	1.32	0.0151
30.0	0.7884	0.1990	0.0117	0.0008	0.1121	0.0563	1.46	0.0178
40.0	0.7094	0.2657	0.0228	0.0021	0.1577	0.0794	1.57	0.0207
50.0	0.6299	0.3275	0.0383	0.0043	0.2063	0.1043	1.65	0.0237
60.0	0.5526	0.3816	0.0583	0.0076	0.2567	0.1303	1.69	0.0267
70.0	0.4795	0.4259	0.0822	0.0124	0.3076	0.1569	1.69	0.0296
80.0	0.4124	0.4596	0.1094	0.0187	0.3578	0.1837	1.65	0.0322
90.0	0.3524	0.4825	0.1386	0.0266	0.4064	0.2099	1.57	0.0344
100.0	0.2999	0.4955	0.1686	0.0360	0.4524	0.2353	1.48	0.0361

The first line of the output is the "12.140" described above. The next line denotes (reading across left to right) time in minutes (time), a_p , a_s , a_t , a_q , α_A , α_E , flux (in cm on DSC plot), and k_a (the main reaction rate constant). All of the output generated is not given here simply for the sake of brevity. Thanks to Dr. Charles Petty for suggesting the above format a long time ago in CHE 801.

Following is the program used for this calculation. It was run on the MSU VAX at node "Grumpy".

```

program fluxclc
dimension c(10),cl(10),cr(10),cinit(10)
dimension dc(10),dcdtr(10),dcdtl(10)
common blu,blc,b2,b4,b5,b6,xa,cinit
open (60,file='blood.dat.',status='old')
open (61,file='money.dat.',status='new')
read (60,11) numdat
11 format (i2)
do 1000 lust=1,numdat
read (60,1) numvar,tstep,imax,niter,range,b7
1 format (i2,3x,f10.4,2x,i3,2x,i3,5x,f5.3,5x,f10.4)
read (60,3) blu,blc,b2,b3,b4,b5,b6
3 format (7f10.4)
do 1001 n=1,numvar
read (60,2) cinit(n)
2 format (f10.6)
1001 continue
do 666 n=1,numvar
c(n)=cinit(n)
666 continue
write (61,20) b3
20 format (////f10.3)
do 100 iprint=1,imax,1
do 150 iter=1,niter
do 160 n=1,numvar
cl(n)=c(n)
160 continue
ap=cl(1)/cinit(1)
as=cl(2)/cinit(1)
at=cl(3)/cinit(1)
aq=cl(4)/cinit(1)
xa=0.5*as+at+aq
xe=(cinit(5)-cl(5))/cinit(5)
call dcalc (cl,dcdtl,b7,f2,tg,akt,clink)
if (iter.ne.1) go to 210
aprint=iprint-1.
time=aprint*tstep
flux=108365.6*(2.*cl(1)+cl(2))*akt*cl(5)*(15.0/range)
write (61,10) time,ap,as,at,aq,xa,xe,flux,akt
10 format (5x,f6.1,6(f7.4),f5.2,f7.4)
210 continue
do 170 n=1,numvar
cr(n)=cl(n)+dcdtl(n)*tstep
170 continue
ap=cr(1)/cinit(1)
as=cr(2)/cinit(1)
at=cr(3)/cinit(1)
aq=cr(4)/cinit(1)
xa=0.5*as+at+aq
xe=(cinit(5)-cr(5))/cinit(5)
call dcalc (cr,dcdtr,b7,f2,tg,akt,clink)
do 180 n=1,numvar
dc(n)=(dcdtr(n)+dcdtl(n))/2.
c(n)=cl(n)+dc(n)*tstep

```

```

180  continue
150  continue
100  continue
1000 continue
      close (60)
      close (61)
      end

```

```

subroutine dcalc (c,dcdt,b7,f2,tg,akt,clink)
dimension c(10),dcdt(10),cinit(10)
common blu,blc,b2,b4,b5,b6,xa,cinit
clink=xa*cinit(1)*2.
tg=(.332*b4*clink)/(.004255-(.581*clink))+b4
if (tg.lt.b5) then
f1=b7*((b4-b2)/(b5-b4))+((b2-tg)/(b5-tg))
if (abs(f1).gt.20.5) then
f2=0.
else
f2=exp(f1)
endif
else
f2=0.
endif
aku=blu-8327.5/b2
akc=blc-6906.6/b2
aku=exp(aku)
akc=exp(akc)
akt=f2*(aku+xa*akc)
dcdt(1)=-akt*2.*c(1)*c(5)
dcdt(2)=-dcdt(1)-akt*c(2)*c(5)
dcdt(3)=akt*c(2)*c(5)-b6*c(3)*c(5)
dcdt(4)=b6*c(3)*c(5)
dcdt(5)=-akt*2.*c(1)*c(5)-akt*c(2)*c(5)-b6*c(3)*c(5)
return
end

```

REFERENCE LIST

- (1) Bidstrup, S. A., N. F. Sheppard, and S. D. Senturia. Proc. Soc. Plas. Eng. 45, (1987).
- (2) Neville, K. and H. Lee. Handbook of Epoxy Resins. New York, McGraw Hill (1967).
- (3) Benson, S. Thermochemical Kinetics. Wiley, New York (1976).
- (4) McGrath, J., ed. Ring Opening Polymerization. American Chemical Society (1985).
- (5) Swain, C. G. J. Am. Chem. Soc. 70, (1948), 1119.
- (6) Shechter, L., J. Wynstra, and R. P. Kurkijy. Ind. Eng. Chem. 48, (1956), 94.
- (7) Smith, I. T. Polymer 2, (1961), 95.
- (8) Narracot, E. S. Brit. Plast. 26, (1953), 120.
- (9) Hale, A. Ph. D. Thesis, Univ. of Minnesota, (1988).
- (10) Tsou, A. H. and N. A. Peppas. Polym. Mat. Sci. Eng. 58, (1988), 1099.
- (11) Morgan, R. J. Adv. Polym. Sci. 78, (1986).
- (12) Smith, R. E., F. N. Larsen, and C. L. Long. J. Appl. Polym. Sci. 29, (1984), 3713.
- (13) Grenier-Loustalt, M. F. and P. Grenier. J. Polym. Sci. Polym. Chem. Ed. 22, (1984), 4011.
- (14) Dusek, K. Adv. Polym. Sci. 78, (1986).
- (15) Hagnauer, G. L., P. J. Pearce, B. R. LaLiberte, and M. F. Roylance. ACS Symp. Ser. 227, (1983), 25.
- (16) Acitelli, M. A., R. B. Prime, and E. Sacher. Polymer 12, (1971), 335.
- (17) Sourour, S. and M. R. Kamal. Thermochemica Acta 14, (1976), 41.
- (18) Moroni, A., J. Mijovic, E. M. Pearce, and C. C. Foun. J. Appl. Polym. Sci. 32, (1986), 3761.
- (19) Charlesworth, J. M. J. Polym. Sci. Polym. Chem. Ed. 25, (1987), 731.

- (20) Sung, C. S. P., I. J. Chin, and W. C. Yu. *Macromolecules* 18, (1985), 1510.
- (21) Chin, I. J., and C. S. P. Sung. *Macromolecules* 17, (1984), 2603.
- (22) Sung, C. S. P., E. Pyun, and H. L. Sun. *Macromolecules* 19, (1986), 2922.
- (23) Carrozino, S., G. Levita, P. Rolla, and E. Tombari. *Polym. Eng. Sci.* 30, (1990), 366.
- (24) Turi, E. R., ed. *Thermal Characterization of Polymeric Materials*. Academic Press, New York (1981), Chapter 5.
- (25) Lee, W. I., A. C. Loos, and G. S. Springer. *J. Composite Materials* 16, (1982), 510.
- (26) Mertz, E., and J. L. Koenig. *Adv. Polym. Sci.* 78, (1986).
- (27) Moacanin, J., M. Cizmecioglu, S. D. Hong, and A. Gupta. *ACS Symp. Ser.* 227, (1983), 83.
- (28) Schiering, D. W., J. E. Katon, L. T. Drzal, and V. B. Gupta. *J. Appl. Polym. Sci.* 34, (1987), 2367.
- (29) Perkin-Elmer Model 1800 Applications Manual, Order # IR-47 (prepared by N. B. Colthup, "Spectra-Structure Correlations").
- (30) Breitmayer, E. ¹³C NMR Spectroscopy. A Working Manual With Exercises. Harwood Academic, New York, (1984).
- (31) Bates, R. B. *Carbon-13 NMR Spectral Problems*. Humana Press, Clifton, New Jersey, (1981).
- (32) Sheppard, N. F., and S. D. Senturia. *Proc. Soc. Plas. Eng.* 43, (1985).
- (33) Day, D. R. *Polym. Eng. Sci.* 26, (1986), 362.
- (34) Senturia, S. D., and N. F. Sheppard. *Adv. Polym. Sci.* 80, (1986).
- (35) Lane, J. W., J. C. Seferis, and M. J. Bachmann. *Polym. Sci. Eng.* 26, (1986), 346.
- (36) Jow, J., M. C. Hawley, M. Finzel, J. Asmussen, H. H. Lin, and B. Manring. *IEEE Trans. Mic. Thy. Tech.* MTT-35, (1987), 1435.
- (37) Jow, J., M. C. Hawley, M. Finzel, and T. Kern. *Polym. Sci. Eng.* 28, (1988), 1450.

- (38) Jow, J. Ph. D. Thesis, Michigan State University, (1988).
- (39) Debye, P. Polar Molecules. Dover, New York, (1945).
- (40) McQuarrie, D. A. Statistical Mechanics. Harper and Row, New York, (1976).
- (41) Kauzmann, W. Rev. Mod. Phys. 14, (1942), 12.
- (42) Eyring, H. J. Chem. Phys. 4, (1936), 283.
- (43) Havriliak, S., and S. Negami. Polym. Symp. 14, (1966), 99.
- (44) Cole, R. H. J. Phys. Chem. 23, (1955), 493.
- (45) Cole, K. S., and R. H. Cole. J. Phys. Chem. 9, (1941), 341.
- (46) Ngai, K. L., A. K. Jonscher, and C. T. White. Nature 277, (1979), 185.
- (47) Jonscher, A. K. Nature 267, (1978), 673.
- (48) Finzel, M. C. M. S. Thesis, Michigan State University, (1985).
- (49) Flory, P. J. J. Am. Chem. Soc. 63, (1941), 3083.
- (50) Flory, P. J. J. Am. Chem. Soc. 63, (1941), 3091.
- (51) Flory, P. J. J. Am. Chem. Soc. 63, (1941), 3096.
- (52) Macosko, C. W., and D. R. Miller. Macromolecules 9, (1976), 199.
- (53) Miller, D. R., and C. W. Macosko. Macromolecules 9, (1976), 206.
- (54) Miller, D. R., and C. W. Macosko. Macromolecules 11, (1978), 656.
- (55) Miller, D. R., and C. W. Macosko. Macromolecules 13, (1980), 1063.
- (56) Gordon, M. Proc. Roy. Soc. London A268, (1962), 240.
- (57) Gordon, M., and G. N. Malcolm. Proc. Roy. Soc. London A295, (1966), 29.
- (58) Kuchanov, S. I. Methods of Kinetic Calculations in Polymer Chemistry. Khimaya, Moscow, (1978).
- (59) Hayes, R. A. J. Appl. Polym. Sci. 5, (1961), 318.

- (60) Kaelble, D. ACS Org. Coat Appl. Polym. Sci. Proc. 46, (1982), 241.
- (61) Nielsen, A. J. Macromol. Sci. J. Macromol. Chem. C3, (1969), 69.
- (62) DiBenedetto, A. T., personal communication, (1990).
- (63) DiBenedetto, A. T. J. Polym. Sci. B25, (1987), 1949.
- (64) McCrum, N. G., B. E. Read, and G. Williams. Anelastic and Dielectric Effects in Polymeric Solids. Wiley, London, (1967).
- (65) Doolittle, A. K. J. Appl. Phys. 23, (1952), 236.
- (66) Williams, M. L., R. F. Landel, and J. D. Ferry. J. Am. Chem. Soc. 77, (1955), 3701.
- (67) Carnahan, B., H. A. Luther, and J. O. Wilkes. Applied Numerical Methods. Wiley, New York, (1969).
- (68) Wang, X., and J. K. Gillham. J. Appl. Polym. Sci., (1991), in press.
- (69) Rozenberg, B. A. Adv. Polym. Sci. 75, (1985), 113.
- (70) Pangrle, S., C. S. Wu, and P. H. Geil. Polym. Composites, (1990), in press.
- (71) Finzel, M. C., J. Jow, and M. C. Hawley. Polym. Eng. Sci., (1991), in press.

MICHIGAN STATE UNIV. LIBRARIES



31293009041231