Kinetic and Thermodynamic Studies of an Epoxy System Diglycidyl Ether of Bisphenol-A/1,2 Diamine Cyclohexane

LISARDO NÚÑEZ,* F. FRAGA, L. FRAGA, A. CASTRO

Research Group TERBIPROMAT, Department Física Aplicada, Universidad de Santiago, 15706 Santiago, Spain

ABSTRACT: The curing reaction of a system consisting of a purified diglycidyl ether of bisphenol-A (BADGE, $n = 0$) and 1,2 diamine cyclohexane (DCH) was studied with a differential scanning calorimeter. The objective of this article was twofold: a kinetic study from which parameters such as reaction orders, rate constants, and activation energies were determined; and a thermodynamic study where values of enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$), and Gibbs free energy ($\Delta G^{\#}$) changes were calculated. This second study showed that an n-order path reaction mechanism was more favored than the autocatalyzed mechanism above 338 K. This fact was also checked when plotting rate constant ratio against temperature. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 635–641, 1997

INTRODUCTION

The use of materials derived from epoxy resins has grown considerably since they were first commercialized in the late 1940s. Epoxy resins find thousands of practical applications because they offer great versatility, low shrinkage, good chemical resistance, and outstanding adhesion. From the economic point of view, the use of these resins provides low manufacturing cost materials.

For this study we chose a system consisting of a purified epoxy resin,[1] diglycidyl ether of bisphenol-A (BADGE, $n = 0$) and 1,2 diamine cyclohexane (DCH) as the curing agent. This selection was made because of the high reactivity of the mixture and also the absence of available data on it.

The kinetic model was that given by Horie et al.,[1] assuming equal reactivity for all amine hydrogens. Hydroxyl groups generated during the reaction and the presence of initial impurities such as water, glycol, solvent, etc., markedly accelerated the course of the epoxy-amine reaction. This model was successfully used in a previous study.[2]

EXPERIMENTAL

Materials

BADGE was the epoxy resin used ($n = 0$, Resin 332, Sigma Chemical, Co.) and 1,2 diamine cyclohexane (DCH; Fluka) was the curing agent. The epoxide equivalent weight of the resin after purification was 173.6 and that of the diamine was taken as 28.5. The epoxide equivalent of BADGE was determined by wet analysis following procedures described elsewhere.[3,4] Some of its properties are listed in Table I.

Sample Preparation

The size of the samples was 4–7 mg. The materials were carefully mixed under a nitrogen atmosphere inside a microcalorimeter dry box at about 5°C. They were sealed, using a press, in aluminum pans before introducing them into the calorimeter.

Differential Scanning Calorimetry (DSC)

Calorimetric measurements were performed using a Perkin–Elmer DSC7. Owing to the wide range of temperature (−30–250°C) necessary for

---

Table I   Data from Wet Analysis of Resin

	Commercial	Purified
Epoxide g equiv resin/ g equiv epoxy	181	173.6
OH content equiv/ 100 g resin	5.20%	3.01%
Hydrolyzable chlorine (ppm)	647	241

this study, the calorimeter was calibrated using two standards (indium and bidistilled water). For determination of the different kinetic parameters, the calorimeter was operated in isothermal and dynamic modes, considering the combination of these methods very valuable for this kind of study.[2]

For isothermal measurements, the temperature was raised from 5°C to the curing temperature at the rate of 150°C/min. This heating rate value is higher than those used by some authors.[2,5,6] In this way, we attempted to minimize heat losses arising from the time necessary to send the sample from 5°C to the selected temperature. One other improvement was to stabilize the calorimeter (at about −20°C) after introducing the sample to allow an increase in the data collection by the computer (1020 Perkin–Elmer), which makes the calculation of the enthalpy changes of the system easier.

RESULTS AND DISCUSSION

Kinetic Study

In the first step, the optimum BADGE/DCH ratio was determined. This method was based on the search for the maximum enthalpy change.[2] To obtain this value, necessary for a subsequent isothermal study, a dynamic study was carried out. Different values of the epoxy/curing agent ratio were used. Table II shows values of ΔH corresponding to the different ratios tried. It was found that the maximum enthalpy change was $\Delta H = -411.4$ J/g, corresponding to the stoichiometric ratio, 100 : 16.3. The values of the glass transition temperature (T_g) for the different mixtures are also reported. T_g was taken as the temperature at the midpoint between the initial and final heat capacity curves on samples heated at 10°C/min. The maximum value of the T_g corresponded to the same epoxy/diamine ratio. This fact confirmed

100 : 16.3 as the optimum value to be used in subsequent isothermal experiments.

From the isothermal experiments performed around $T_g = 146$°C, a range of 60–100°C was selected based on the fact that temperatures above and just below T_g lead to very low conversions (less than 0.30).

Enthalpy changes corresponding to the different selected temperatures were measured. From the values obtained and the kinetic model used, values of reaction orders were determined.

A general expression for fractional conversion, α, is

$$\alpha = \frac{\Delta H_t}{\Delta H_0},\qquad(1)$$

where ΔH_t is the heat evolved up to a certain time and ΔH_0 the total heat of reaction. The reaction rate, $d\alpha/dt$, was determined from DSC experiments using the equation,

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0},\qquad(2)$$

assuming its proportionality to the rate of heat generation dH/dt.

The reaction rate of an epoxy system can be expressed by the sum of all reaction rates involved in the mechanism. Assuming, as has been widely shown, that in this kind of reaction two mechanisms exist, nth order and autocatalyzed, and assuming stoichiometric relations and the same reactivity for all amine hydrogens, a general form of reaction rate is derived:

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha^m)(1 - \alpha)^n,\qquad(3)$$

where K_1 and K_1' are constants related to the rate constants of the two reactions and m and n are

Table II   Values of Enthalpy Changes and Glass Transition Temperatures at Different Epoxy/Diamine Ratios from DSC Measurements

Epoxy/Diamine Ratio	ΔH_0 (J/g)	T_g (°C)
100 : 15	−400.9	137
100 : 16.3	−411.4	146
100 : 18	−396.5	141
100 : 22	−350.7	120

parameters related to reactions orders for auto-catalytic and nth order paths, respectively.[7]

The reduced rate is defined as

$$\alpha^0 = \frac{d\alpha/dt}{(1-\alpha)^n} = K_1' + K_1\alpha^m. \qquad (4)$$

To check the validity of the kinetic model used, plots of the reduced rate α^0 against the extent of cure α at different temperatures were made. The method is based on the search values of m and n best fitting a linear relationship between experimental and theoretical data.

Values of the reaction order n, corresponding to the nth path mechanism, can be derived using the first part of eq. (4), $\alpha^0 = d\alpha/dt/(1-\alpha)^n$. Values of $d\alpha/dt$ and α can be obtained from the experimental curves recorded during the DSC experiments. Substitution of these values in this last equation gives values of α^0 that depend on n. Different values of n were tried in order to obtain the best linear fitting of the experimental results. Figure 1(a–c) shows plot of α^0 versus α at 100, 80, and 60°C, respectively. These figures show curves corresponding to $n = 1.5$ and 2. It can be seen that $n = 2$ satisfies our requirements because it leads to higher conversions. Once this value was found, the second part of eq. (4), $\alpha^0 = K_1' + K_1\alpha^m$, was used to determine values of K_1' and K_1, assuming an overall reaction order $m + n = 3$. This value was pointed out by Barton[7] for curing kinetics of stoichiometric mixtures of BADGE/diamine. From the straight lines resulting from linear fitting, values of K_1' and K_1 can be derived. Values of these constants, at the various temperatures used in our isothermal experiments, are listed in Table III. A sudden decrease in reduced rate at 55–90%, depending on the isothermal temperature, may have been caused by the onset of rate control by the diffusion process of the reactants due to the increased viscosity of the system.[1,8,9]

The activation energies corresponding to the two kinetic mechanisms were obtained from the Arrhenius plots in Figure 2 (correlations in the range 0.991–0.999). Values of these activation energies are shown in Table IV. As expected, activation energy corresponding to the autocatalyzed reaction was lower than that corresponding to the nth order path. The difference between both activation energies was higher than those observed for some other systems. However, this cannot be taken as definitive proof that one mechanism was predominant over the other.

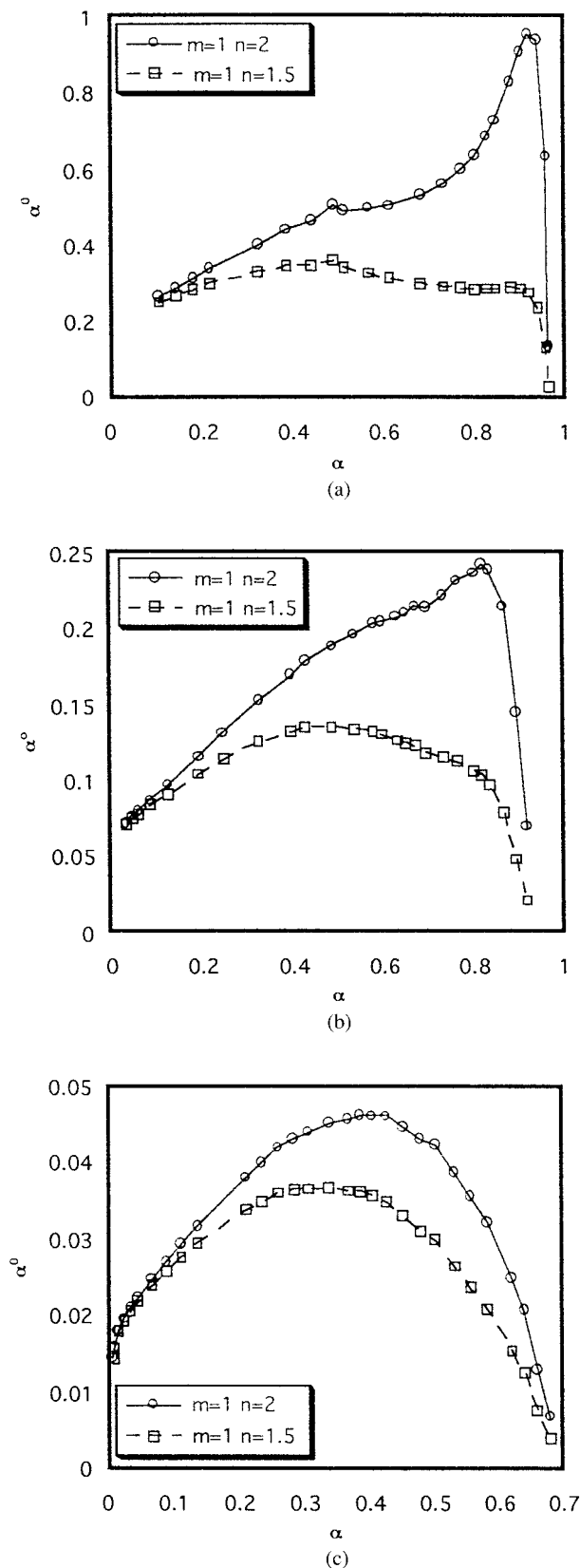Figure 3 shows plots of reaction rate versus

Figure 1 Plots of reduced rate, α^0, vs. conversion, α, for $m = 1$, $n = 2$, and $m = 1$, $n = 1.5$ at (a) 100°C, (b) 80°C, (c) 60°C.

Table III Values of K_1' and K_1 Obtained from α^0 vs. α Plots

T (°C)	nth Order K_1' (min^{-1})	Autocatalyzed K_1 (min^{-1})
100	0.20	0.61
90	0.11	0.34
80	0.064	0.27
70	0.039	0.14
60	0.018	0.09

time at 100, 80, and 60°C, respectively, where experimental data and those predicted through the kinetic model used are compared. There was excellent agreement at 100°C, which worsened with decreasing temperatures. Plots of reaction rates n-path/autocatalyzed ratio versus degree of conversion are shown in Figure 4. The mechanism of reaction was conversion dependent up to 60%. All the curves show similar shape.

For thermosets that follow nth order kinetics, the reactions rate is usually expressed as

$$\left(\frac{d\alpha}{dt}\right)_{n\text{th}} = k_1'(1 - \alpha)^n. \tag{5}$$

The reaction rate for cure reactions that are autocatalyzed is described by relations such as

$$\left(\frac{d\alpha}{dt}\right)_{\text{auto}} = k_1\alpha^m(1 - \alpha)^n, \tag{6}$$

giving a quotient
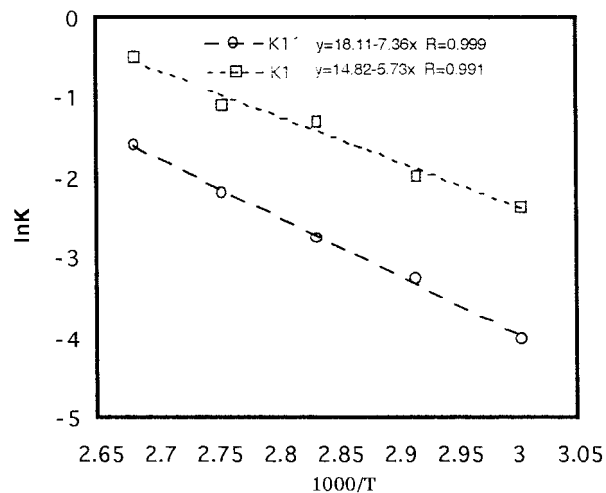
Figure 2 Arrhenius plot, $\ln k$ vs. $1000/T$ from which activation energies for the nth order and autocatalyzed path can be obtained.

Table IV Values of Activation Energies from Arrhenius Plot

	nth Order (kJ/mol)	Autocatalyzed (kJ/mol)
E_a	61.19	47.67

$$\frac{(d\alpha/dt)_{n\text{th}}}{(d\alpha/dt)_{\text{auto}}} = (k_1'/k_1)\alpha^{-m}, \tag{7}$$

and taking natural logarithms

$$\ln\left[\frac{(d\alpha/dt)_{n\text{th}}}{(d\alpha/dt)_{\text{auto}}}\right] = \ln(k_1'/k_1) - m \ln \alpha. \tag{8}$$

In Figure 5 it can be seen that plots of $\ln[(d\alpha/dt)_{n\text{th}}/(d\alpha/dt)_{\text{auto}}]$ versus $\ln \alpha$ give straight lines with a slope m and intercept on the y axis $\ln(k_1'/k_1)$. These plots show a value $m = 1$ at all the temperatures used in this study. It can be seen also that at low conversions, the n-path mechanism was dominant and lost its effects with conversion.

Thermodynamic Study

Changes of entropy, enthalpy, and Gibbs free energy for an epoxy-diamine curing reaction can be evaluated by application of the transition state theory.[10,11] This theory assumes the formation of an activated complex $(AB^\#)$ in equilibrium with reactants (A and B) before the formation of the eventual product (P). The scheme is as follows:

$$A + B \overset{K^\#}{\leftrightarrow} (AB)^\# \overset{k}{\rightarrow} P. \tag{9}$$
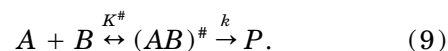
The equilibrium constant $K^\#$ for the formation of the transition state can be written as

$$K^\# = \frac{[AB]^\#}{[A][B]}, \tag{10}$$

where $[A]$, $[B]$, and $[AB]^\#$ represent concentrations of A, B, and the activated complex, respectively.

Absolute reaction rate theory that has shown

$$k[A][B] = [AB]^\# \frac{k_B T}{h}, \tag{11}$$
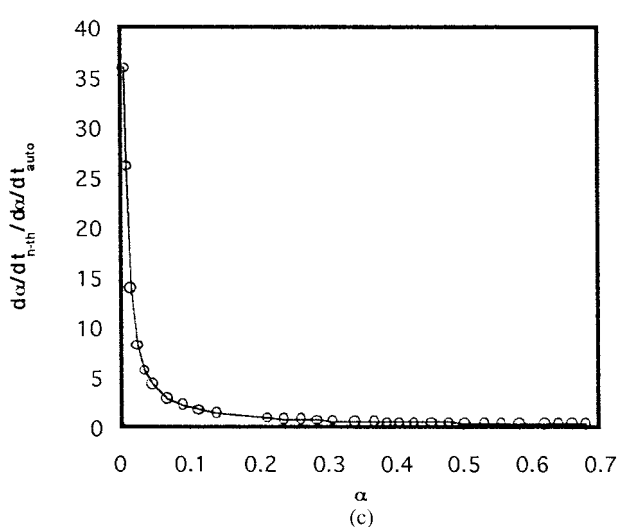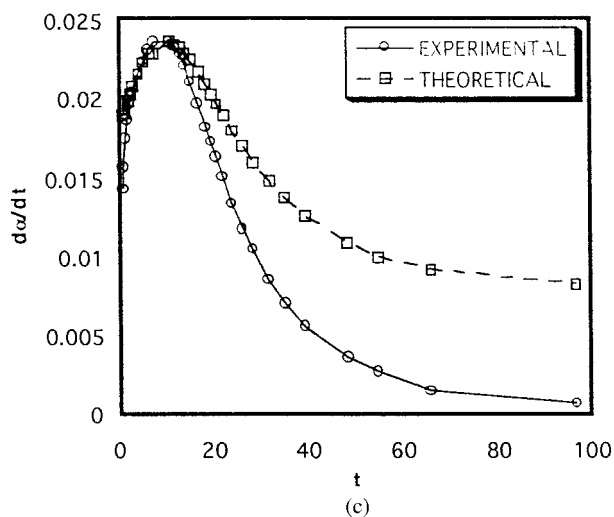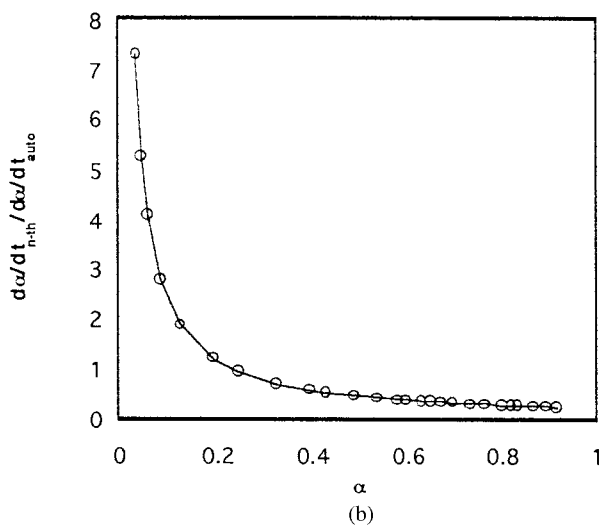
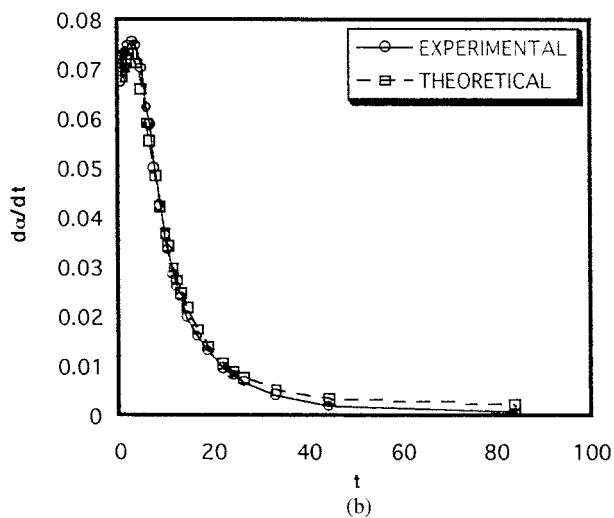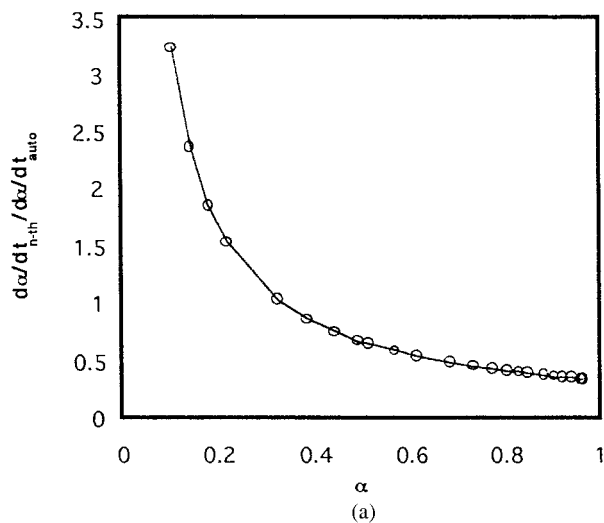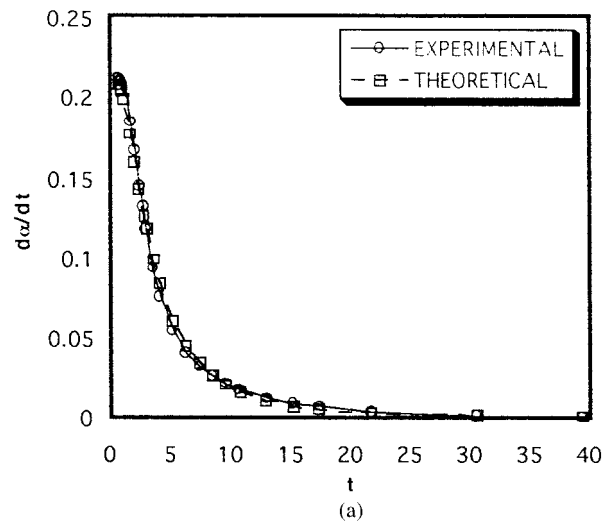where k is the specific reaction rate to form the

Figure 3 Plots of reaction rate, $d\alpha/dt$, vs. time, t. Comparison of experimental data with model predictions at (a) 100°C, (b) 80°C, (c) 60°C.

Figure 4 Plots of (reaction rate)$_{n\,\text{th order}}$/(reaction rate)$_{\text{autocatalyzed}}$, $(d\alpha/dt)_{n\,\text{th}}/(d\alpha/dt)_{\text{auto}}$, ratio vs. conversion, α, at (a) 100°C, (b) 80°C, (c) 60°C.
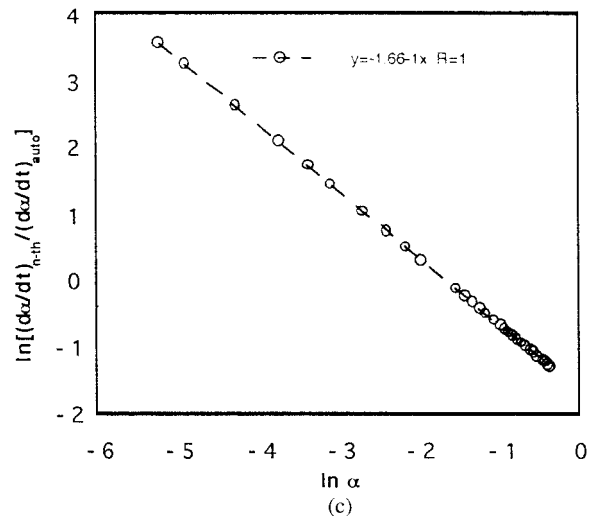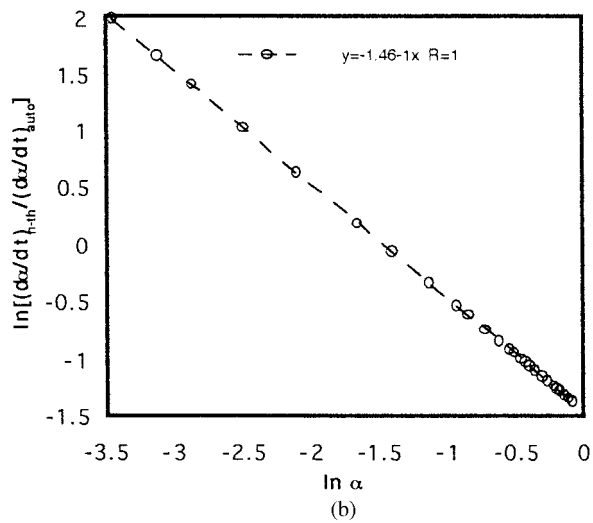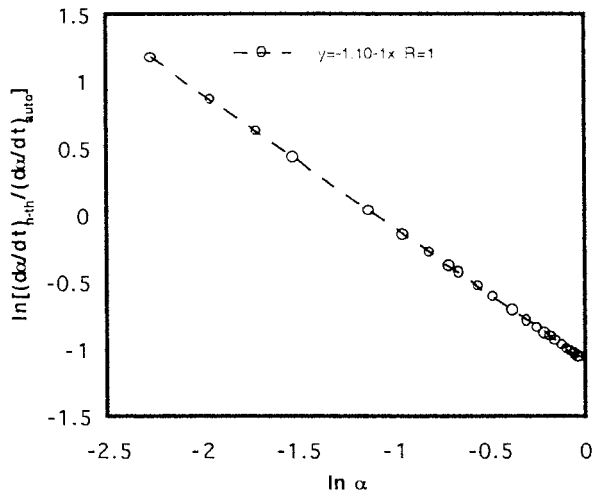
(a)

(b)

(c)

Figure 5 Plots of natural logarithm reaction rates ratio, $\ln[(d\alpha/dt)_{n\,\text{th}}/(d\alpha/dt)_{\text{auto}}]$ vs. natural logarithm of conversion, $\ln\alpha$, at (a) 100°C, (b) 80°C, (c) 60°C.
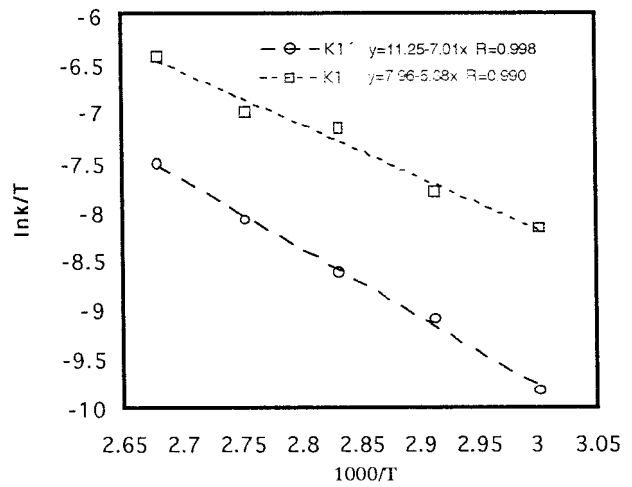

Figure 6 Arrhenius plot $\ln k/T$ vs. $1000/T$ from where $\Delta H^{\#}$ and $\Delta S^{\#}$ can be obtained.

product, k_B is Boltzmann constant, h is Planck's constant, and T is the absolute temperature. From the last two equations

$$k = \frac{k_B T}{h} K^{\#}. \tag{12}$$

On the other hand, the equilibrium constant $K^{\#}$ is related to the activation free energy change $\Delta G^{\#}$ as follows:

$$\Delta G^{\#} = -RT \ln K^{\#} = \Delta H^{\#} - T\Delta S^{\#}, \tag{13}$$

where $\Delta H^{\#}$ is the activation heat of reaction, $\Delta S^{\#}$ the entropy change of activation, and R the gas constant.

$\Delta G^{\#}$ can also be written as

$$\Delta G^{\#} = -RT \ln \frac{kh}{k_B T} = \Delta H^{\#} - T\Delta S^{\#}. \tag{14}$$

Solving for k,

$$k = \frac{k_B T}{h} e^{-\Delta G^{\#}/RT}, \tag{15}$$

or

$$k = \frac{k_B T}{h} e^{\Delta S^{\#}/R} e^{-\Delta H^{\#}/RT}. \tag{16}$$

This last equation can be written as

Table V   Values of Activation Enthalpy and Activation Entropy Changes

	$\Delta H\#$ (kJ/mol)	$\Delta S\#$ (J/mol K)
nth order path	−58.3	−104.1
Autocatalyzed path	−44.7	−131.4

$$\frac{k}{T} = \frac{k_B}{h} e^{\Delta S^{\#}/R} e^{-\Delta H^{\#}/RT}. \quad (17)$$

Taking natural logarithms

$$\ln \frac{k}{T} = \ln\left(\frac{k_B}{h} e^{\Delta S^{\#}/R} \right) - \frac{\Delta H^{\#}}{RT}. \quad (18)$$

The plot of $\ln k/T$ against $1/T$ (Fig. 6) gives a straight line with a slope $\Delta H^{\#}/R$ and intercept on the y axis $\ln(k_B e^{\Delta S^{\#}/R})$ from whence $\Delta H^{\#}$ and $\Delta S^{\#}$ can be determined. Values of $\Delta H^{\#}$ and $\Delta S^{\#}$ are given in Table V.

It can be seen that $\Delta S^{\#}$ is less negative for the nth order path, while $\Delta H^{\#}$ is less negative for the autocatalytic one. This means that the nth order path is dominant for the formation of the activated complex. Table VI gives values of the $\Delta G_{n\text{-path}}$ and ΔG_{auto} at various temperatures. It can be seen that the nth order mechanism is predominant above 348 K ($\Delta G_{auto} > 0$). This behavior is in good agreement with that shown by some other systems.[9,12]

CONCLUSIONS

A good agreement between kinetic and thermodynamic data was found. Plots of K_1'/K_1 ratio (Fig.

Table VI   Gibbs Activation Free Energy Changes Corresponding to nth Order and Autocatalyzed Mechanisms

T (K)	$\Delta G_{n\text{th Path}}$ (kJ/mol)	ΔG_{auto} (kJ/mol)
298.15	−27.24	−5.57
308.15	−26.20	−4.25
318.15	−25.16	−2.94
328.15	−24.12	−1.62
338.15	−23.08	−0.31
348.15	−22.04	1.00
358.15	−21.00	2.32
368.15	−19.96	3.63
378.15	−18.92	4.95
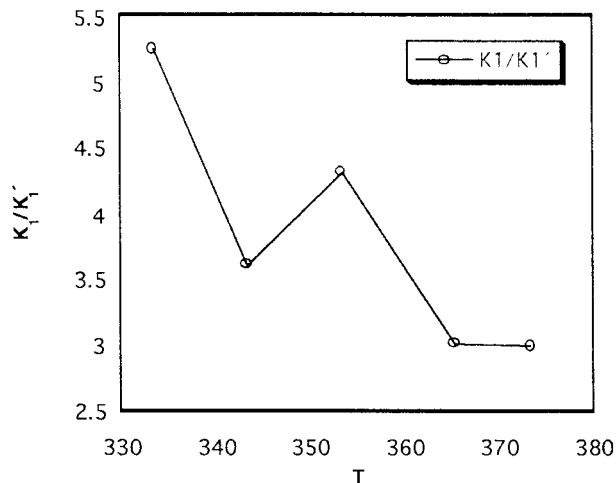
Figure 7   Plot of rate constants ratio, K_1/K_1', vs. temperature, T.

7) and values of the Gibbs free energy changes for the nth path and autocatalytic mechanisms strongly suggested a trend to the nth path mechanism with increasing temperatures.

Because of its high reactivity in a wide range of temperatures, the epoxy system studied here would be very useful for application in many different industries.

REFERENCES

1. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci.,* **8,** 1357 (1970).
2. L. Núñez, F. Fraga, L. Fraga, T. Salgado, and J. Rodriguez Añón, *Pure Appl. Chem.,* **67,** 1091 (1995).
3. H. Lee and K. Neville, *Handbook of Epoxy Resin,* McGraw−Hill, New York, 1967.
4. C. A. May, *Epoxy Resins: Chemistry and Technology,* Marcel Dekker, New York, 1988.
5. S. Wasserman and G. P. Johari, *J. Appl. Polym. Sci.,* **53,** 331 (1994).
6. R. Podgaiz, C. C. Riccardi, and R. J. J. Willians, *Polym. Eng. Sci.,* **32,** 836 (1992).
7. J. M. Barton, *Adv. Polym. Sci.,* **72,** 111 (1985).
8. S. Sourour and M. R. Kamal, *Thermochim. Acta,* **14,** 41 (1976).
9. C. C. Riccardi, H. E. Adabbo, and R. J. J. Willians, *J. Appl. Polym. Sci.,* **29,** 2481 (1984).
10. H. Eyring, *J. Chem. Phys.,* **3,** 107 (1935).
11. M. G. Evans and M. Polyani, *Trans. Faraday Soc.,* **31,** 875 (1935).
12. M. Pazos Pellín, L. Núñez, A. López Quintela, P. Paseiro, J. Simal, and S. Paz, *J. Appl. Polym. Sci.,* **55,** 1507 (1995).