Epoxy Resins Based on Trimethylolpropane. II. Kinetic and Thermodynamic Parameters of Cure with *m*-XDA

M. PAZOS PELLÍN,[1] L. NÚÑEZ REGUEIRA,[2] A. LOPEZ QUINTELA,[3] P. PASEIRO LOSADA,[4] J. SIMAL GÁNDARA,[5] and S. PAZ ABUÍN[1,*]

[1]Department of Research, Gairesa, 15551 Lago-Valdoviño, La Coruña, Spain, [2]Department of Applied Physics, Santiago University, Spain, [3]Department of Physical-Chemistry, Santiago University, Spain, [4]Department of Analytical Chemistry, Nutrition and Bromatology, Santiago University, Spain, and [5]Department of Nutrition and Bromatology, Vigo University, Spain

SYNOPSIS

A study of cure of an epoxy resin based on trimethilolpropane (TMP) used as supplied and in purified form and *m*-xylylenediamine (*m*-XDA), as curing agent has been carried out. Thermodynamic functions such as activation energy, activation entropy, activation enthalpy, and free energy of activation were determinated. From kinetic study we have observed that there are two competitive mechanisms; autocatalyzed and *n* order, with the values of activation energy ranging between 52.9 and 64.6 kJ/mol. The overall order of reaction is found to be 2.5, and the order of reaction with respect to the hydroxyl group is clearly determined and equal to 1. Gelation study was carried out under two conditions: isothermal and adiabatic. From isothermal study we obtained the values of functionality of the resins (approximately two) and the apparent activation energy of the process. The adiabatic study allowed us the determination of the pot-life taking into account the theoretical model used, with reasonable theoretical/experimental agreements. The importance of *n*-order path for this kind of resins (with high OH contents) is well demonstrated through kinetic and thermodynamic parameters. The thermodynamic functions showed themselves as very sensitive parameters for the following and evolution of the reaction. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The reaction rate for an epoxy system can be expressed by the sum of all partial reaction rates involved in the mechanism. If we suppose, as has been widely showed,[1-4] that in this kind of reaction there exist two mechanisms—*n* order and autocatalyzed—the general equation of rate will be

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{n\text{-order}} + \left(\frac{d\alpha}{dt}\right)_{\text{aut}} \tag{1}$$

For materials that follow *n*-order kinetics, the rate of conversion, $(d\alpha/dt)_{n\text{-order}}$, is given by the expression

$$\left(\frac{d\alpha}{dt}\right)_{n\text{-order}} = K_{n\text{-order}}(1 - \alpha)^n$$

The autocatalyzed reactions take place when one of the products of the reaction is a reactant in the same or a coupled reaction. The rate of conversion $(d\alpha/dt)_{\text{autocat.}}$ can be expressed by

$$\left(\frac{d\alpha}{dt}\right)_{\text{aut}} = K_{\text{aut}}\alpha^m(1 - \alpha)^n$$

which lead to the general form of reaction rate:

$$\frac{d\alpha}{dt} = (K'_1 + K_1\alpha^m)(1 - \alpha)^n \tag{2}$$

This is a very well known equation of rate when the reactants are in stoichiometric relations, and all amine hydrogens have the same reactivity,[1] being

---

* To whom correspondence should be addressed.

K'_1 and K_1 the rate constants for the n order and autocatalytic path, n and m are the reaction orders, respectively.

By application of transition stage theory[5,6] and from K'_1 and K_1, it is possible to evaluate the basic thermodynamic functions; activation entropy $(\Delta S^{\neq})$, activation enthalpy $(\Delta H^{\neq})$, and Gibbs free energy of activation $(\Delta G^{\neq})$. This theory supposes the formation of an activated complex $(X^{\neq})$ in equilibrium with the reactants (A, B) before reaching the formation of product (P).

$$A + B \overset{K^{\neq}}{\rightleftharpoons} X^{\neq} \overset{k}{\to} P$$
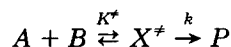
The constants, $K^{\neq}$ and k, are related through Eq. (3).

$$k = \frac{k_B T}{h} K^{\neq} \tag{3}$$

where k is the rate constant, k_B is the Boltzmann's constant, h the Planck's constant, and $K^{\neq}$ the equilibrium constant of activated complex. If we relate the equilibrium constant to the Gibbs free energy by using the van't Hoff equation,

$$\Delta G^{\neq} = -RT \ln K^{\neq} \quad \text{or} \quad K^{\neq} = e^{-\Delta G^{\neq}/RT}$$

Eq. (3) will take the form

$$k = \frac{k_B T}{h} e^{-\Delta G^{\neq}/RT}$$

Taking into account the thermodynamic relation among ΔG, ΔH, and ΔS:

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \tag{4}$$

then,

$$k = \frac{k_B T}{h} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/T} \tag{5}$$

this equation can be written as:

$$\frac{k}{T} = \left(\frac{k_B}{h} e^{\Delta S^{\neq}/R}\right) e^{-\Delta H^{\neq}/RT} \tag{6}$$

taking natural logarithms,

$$\ln \frac{k}{T} = \text{const} - \frac{\Delta H^{\neq}}{RT} \tag{7}$$

Plotting the first term against $1/T$, we will obtain $\Delta S^{\neq}$ and $\Delta H^{\neq}$ from the intercept, and the slope $\Delta G^{\neq}$ is obtained from Eq. (4).

EXPERIMENTAL

Materials

The resin used was a diglycidyl ether of trimethilolpropane (TMP) (TRIEPOX GA from Gairesa, Spain) and m-xylylenediamine (m-XDA) (Aldrich Chemical Co., 99% pure) as curing agent. The resin was used as supplied and purified (as described in Part I).[7]

All mixtures (resin–curing agent) were done in stoichiometric relations, taking the values of epoxy[7] and amine[8] equivalents (150 g/eq and 136 g/eq for the resins in supplied and purified forms, respectively, and 34 g/eq for the curing agent), 100/22.6 for the resin in supplied form and 100/25 for the purified resin "soluble fraction."

Techniques

Differential Scanning Calorimetry (DSC) Study

The calorimetric study was carried out using a Perkin-Elmer DSC7 coupled to a 7700 personal computer with isothermal, dynamic, and specific heat software. Due to the range of cure temperatures taken for isothermal tests (from +30 to 65°C), a cryogenic device was necessary. More details about calibration procedure and thermal conditions can be found elsewhere.[4,8]

Gelation Study

Gelation was followed under two thermal conditions: isothermal and adiabatic. The isothermal study was carried out in a thermostatted water bath. To determinate the gel point, we weighed about 10 g of sample of a well-known epoxy system (based on a purified epoxy resin of bisphenol A and m-XDA).[8] The sample was introduced into an aluminum container (7 cm diameter and 5 cm height). At different times and degrees of insolubility it was taken out from the container and dissolved in tetrahydrofuran (THF). At the same time the conversion was determined by FTIR (internal ratio of absorbances at 916 and 1610 cm^{-1}),[8] and DSC (by measurement of residual heat). After several tests when we obtained the value of the extension of reaction equal to 0.58 (value corresponding to the gel point[9]), we identified the gel under organoleptic point of view as a non-

THF soluble and nonflowing fiber formed when a glass rod is introduced in the epoxy system and it is lifted perpendicular to the bottom of the container. Once identified, we took this organoleptic reference as our standard for further determinations on unknown systems. DSC was used for determinations of conversion (for the case under study FTIR measurement was not a useful method owing to the difficulty in finding a reliable reference band). Before starting the DSC measurement, the samples from the aluminum container were weighed in closed aluminum pans and cooled with liquid nitrogen to stop the reaction.

For adiabatic determinations we used a gel timer, Tecam Gel Timer GT3 (TECHNE). One hundred grams of resin–curing agent blend were weighed in a thermal isolated container. The plunger of the gel timer is moved up and down in the resin system. When the resin exerts the required resistence on the plunger, the gel timer switches off automatically and the gel time is recorded. We were not able to determine with good accuracy the conversion at this point because the evolution of reaction is very fast. However, and owing to this fact, the experimental error in the time must be small because in only a few seconds the temperature increases 40–50°C. The specific heat, c, necessary for the theoretical esti-

mations was evaluated taking into account its dependence with the temperature and the enthalpy of reaction.[10,11] For the calculations we took a constant value of $c = 1.90$ J/g °C just above T_g at 50°C where the variations with the temperature are small and the evolution of reaction happen predominantly at high temperatures.[10]

RESULTS AND DISCUSSION

Kinetic Parameters

Following the same procedure to obtain the kinetic parameters already stated in other studies,[4,8] Table I shows the differences between both epoxy systems studied: Triepox GA as supplied/m-XDA (TEX$_s$) and Triepox GA purified or soluble fraction/m-XDA (TEX$_p$). The activation energies range between 48.3 (11.6) and 60.4 kJ/mol (14.5 kcal/mol) in the same order as other epoxy–amine systems.[1,4,8] The ratio of the rate constants K_1/K'_1 (Fig. 1) indicates that both resins have a similar behavior (if we take into account that the values are between 1.1 and 1.4, a narrow interval with respect to other epoxy systems as we will see); practically both mechanisms are superimposed and only the purified resin exhibits a
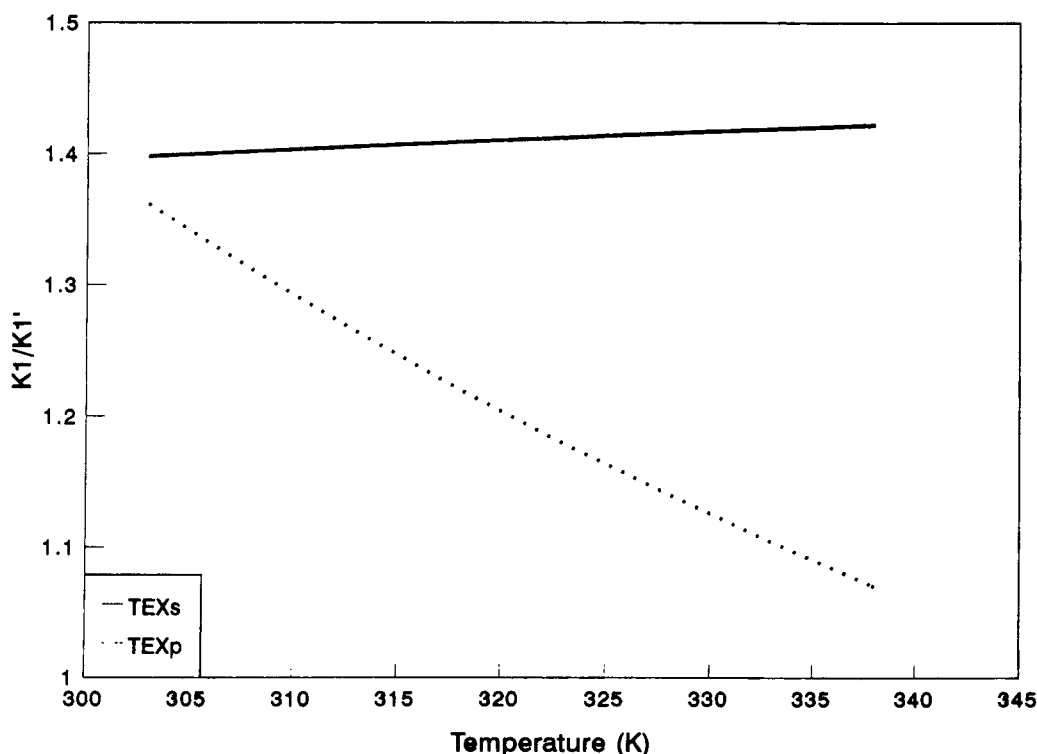

Figure 1 Variation of the ratios of rate constants against temperature (K).

tendency to n order with the temperature. With respect to the liquid aromatic epoxy resins where the OH_0 (initial OH content) content is low (about 0.06 Eq/100), the resins studied have much greater initial values of (OH_0) and OH_0/e_0 (e_0, initial epoxy content); $(OH_0/e_0)TEX_s = 0.54$, $(OH_0/e_0)TEX_p = 0.47$ while the (OH_0/e_0) values for an aromatic system are between 0.1 and 0.015.[3,8,12] This fact alone explains the differences in the quotient of constant rate of these systems with respect to the aromatic resins, where rate constants K_1/K_1' are above 5[8] and even much greater.[2] Obviously and conversely to the bisphenol A resins, the path n order is very important, as pointed out in Table I, where we can see that the theoretical values of $(d\alpha/dt)_{max}$ correspond to K_1', theoretical case for n-order reactions. If we plot the ratio of reaction rates $(d\alpha/dt)_{n-order} = K_1'(1 - \alpha)^{1.5}$ and $(d\alpha/dt)_{aut} = K_1\alpha(1 - \alpha)^{1.5}$ against conversion, α, we can observe the result (Fig. 2). Again this figure shows the behavior very well. At low conversions the path is clearly n order, and it looses its effect with respect to autocatalytic path with the conversion, being practically constant and equal to 1 for values of conversion above 0.55. This fact agrees very well with that already stated for the ratio of rate constants where the quotients are close to 1 (not conversion dependent, but temperature dependent; high temperatures imply high conversions). According to that, the reaction is catalyzed by the OH group content in the resin; these groups are consumed very quickly and the reaction continues to be catalyzed by the OH generated. It is very important to remark that the same result (Fig. 2) was practically obtained for both formulations in all temperature ranges studied.

Figure 3 shows a plot of the logarithm expression as the ratio of reaction rates against conversion. The value of the slope of this straight line is exactly -1 (correlation 0.99999). Therefore, if

$$\frac{\Delta \ln[(d\alpha/dt)_{n\text{-order}}/(d\alpha/dt)_{aut}]}{\Delta \ln \alpha} = -1$$

it implies that $m = 1$ and, of course, the order of reaction with respect to OH is one. Again we obtained such excellent fit for both resins in all temperature tests with practically the same correlations.

Once we confirmed the value $m = 1$, we again started our study for values of $m = 1$ and $n = 2$. We found good agreements for $m = 1$ and $n = 2$ in some cases. However, at 50°C and for (TEX_p) the reduced rate[2,8] markedly increased with the conversion after the onset of vitrification. Under our point of view
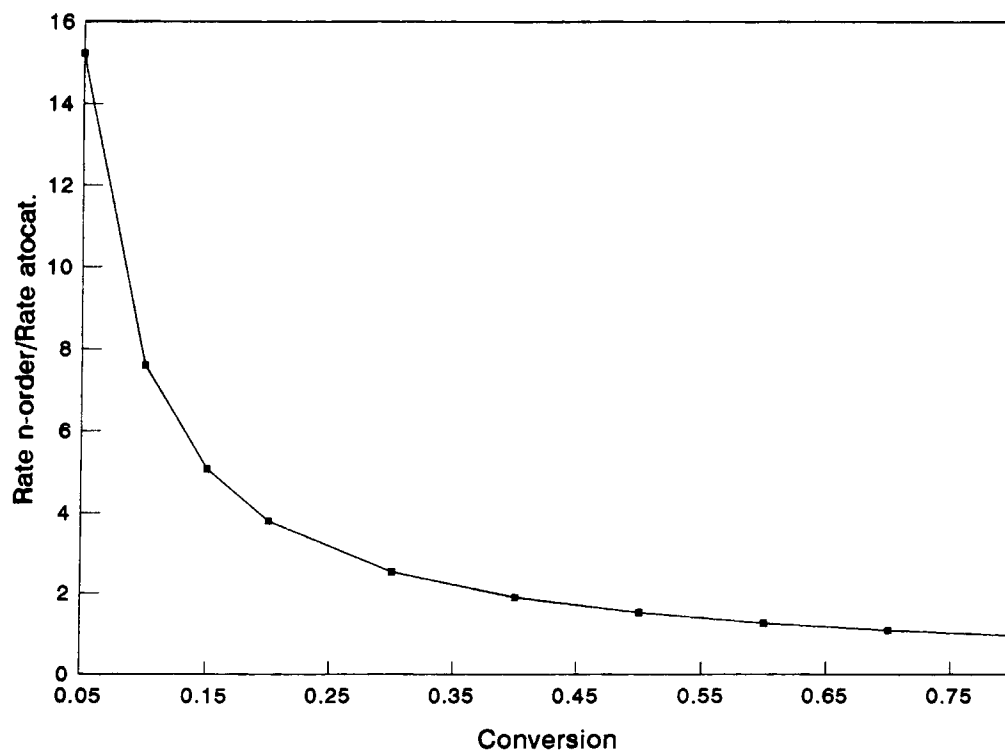

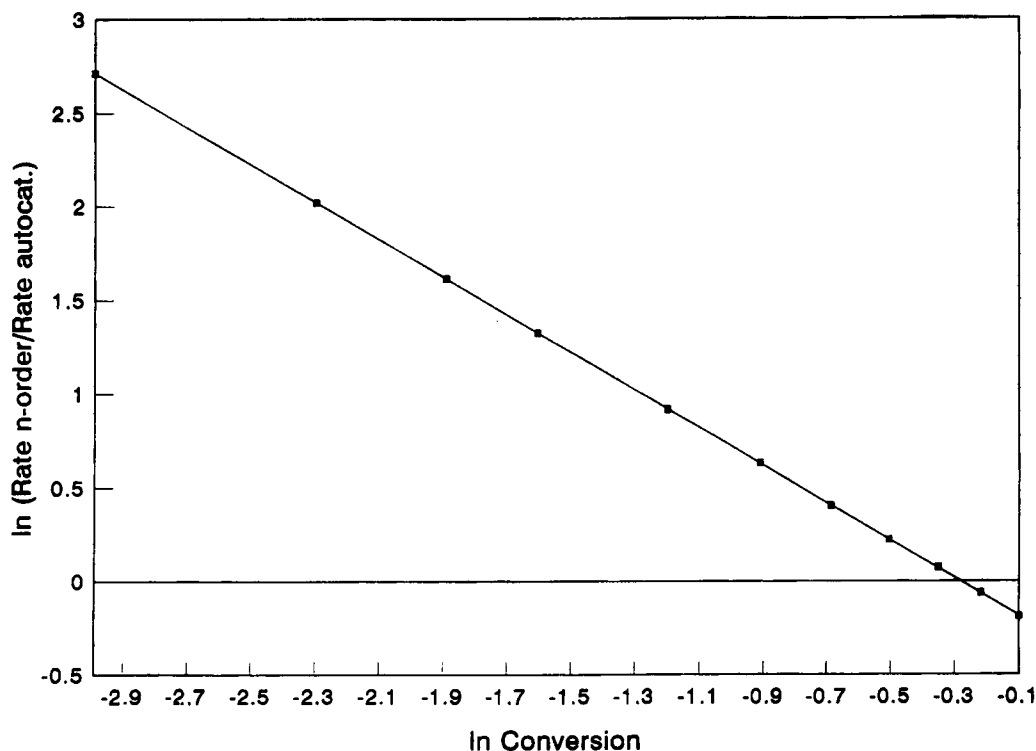**Figure 2** Ratio of reaction rates against conversion.

Figure 3 In ratio of reaction rates against ln conversion.

and unless the ratio of rate constants for the formation of primary and secondary amines change at different temperatures[13] (taking different values of 1, a fact that for this amine does not seem probable as we stated[4]), we believe that the reduced rate cannot increase its value after vitrification. So this reaction is well expressed for $n = 1.5$ and $m = 1$. It is important to point out that we obtained very good theoretical/experimental kinetic agreements (e.g., rate of reaction/time, conversion/time) in all tests.[10]

Gelation Results

Isothermal

As we stated, the gelation was followed by DSC (conversion) after determinations of the solubility in THF. We obtained values for $\alpha_g TEX_s = 0.61 \pm 0.01$ and $\alpha_g TEX_p = 0.58 \pm 0.01$. From the gel expression and through Eq. (8),[14,15] we can estimate the functionality of both resins:

$$\alpha_g = \sqrt{\frac{B}{(f-1)(g-1)}} \qquad (8)$$

where f and g are the functionalities of the resin and amine, and B the amine–epoxy equivalent relation (1 in our case, as stated).

By applying Eq. (8), we obtained the values of functionality for both resins; $f_{TEX_s} = 1.90$ and $f_{TEX_p} = 2.00$. The value of TEX_s compares very well with that result estimated from molecular considerations.[7] This is not the same case for the resin in the as-supplied form, for which we obtained a value of $f = 2.15$. But, as we explained in the previous study,[7] this result is not quite correct owing to the fact that it implies species with functionality $f = 3$ of which we have not any experimental evidence. The value of 1.90 is much more probably taking into account that in this resin we observed the presence of some products of functionality equal to 1. (See mass spectrum, Fig. 3 part I, m/z at 283).

By Arrhenius analogy $t_g = t_0 e^{E_a/RT}$ we can reckon the gel times at different temperatures, where t_g is the time to reach the gelation, t_0 the preexponential factor, E_a the overall apparent activation energy, and T the absolute temperature. Figure 4 shows an Arrhenius plot for both systems at different test temperatures. The values of activation energy comprised between $(E_a)_{TEX_s} = 64.6$ kJ/mol and $(E_a)_{TEX_p} = 52.9$ kJ/mol compare well with other values for different epoxy–amine systems.[2,16]
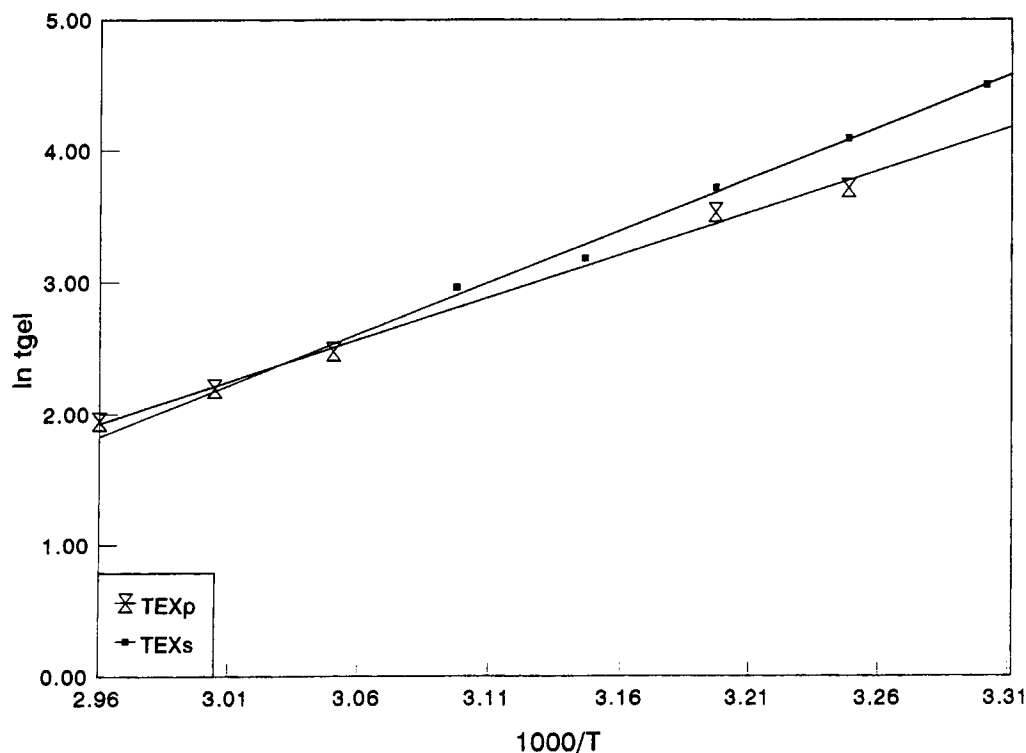
Figure 4 Gel time. Arrhenius plot.

Adiabatic

The study of adiabatic gelification is very interesting from a practical point of view. Because of the low thermal conductivity of the resin, the thermal behavior is similar to a semiadiabatic reactor and in this sense it is the pot-life measurement, a very important feature for epoxy resins when the cure is carried out at room temperature.

Theoretically and for an isolated system,

$$T_f - T_0 = -\alpha \frac{\Delta H}{c}$$

where T_f and T_0 are the final and initial temperatures, α is the conversion which corresponds to the thermal evolution of the reaction, c the specific heat, and ΔH the total enthalpy of reaction (defined as negative for an exotermic reaction). Therefore the final temperature T_f where α_f is reached,

$$T_f = T_0 - \alpha_f \frac{\Delta H}{c} \qquad (9)$$

if we differenciate this expression with respect to time,

$$\frac{dT}{dt} = -\frac{\Delta H}{c} \frac{d\alpha}{dt} \qquad (10)$$

where $d\alpha/dt$ is the general expression of rate from Eq. (2). Substituting this equation into Eq. (10) and taking the values for K_1 and K_1' we obtain the integral form:

$$\int_0^{t_f} dt = -\frac{c}{\Delta H}$$

$$\times \int_{T_0}^{T_f} \frac{dT}{\left[A_1' e^{-E_a/RT} + A_1 e^{-E_{a_1}/RT} \left(-\frac{c(T_f - T_0)}{\Delta H} \right) \right]}$$

$$\times \left[1 + \frac{c(T_f - T_0)}{\Delta H} \right]^{1.5} \qquad (11)$$

For the evaluation of this expression we need the previous knowledge of the T_f and c. In our case T_f is T_g' (temperature at gel point) so that Eq. (9) $T_g' = T_0 - \alpha_g(\Delta H/c)$. We know that α_g is equal to 0.61, a value taken from isothermal experiments (for TEX$_s$). In this way we can evaluate the integral [Eq. (11)] if c has been previously determinated, ΔH is the value of enthalpy of reaction, $\Delta H_0 = -547$ J/g

(Table I) and t_f is t_g. Figure 5 shows the differences between theoretical Eq. (11) and experimental results at different mixing temperatures (20, 30, 40, and 50°C). We consider this an acceptable agreement because the differences are relatively small if we take into account the approaches. We did not consider the loss of heat, we took the value of specific heat as constant, which is not exact (it varies between 1.9 J/g °C at 50°C and 2.50 J/g °C at 175°C), and the conversion α_g can be inexact because the gel timer stops without any previous α_g calibration due to the inherent difficulties already stated. However, this procedure allows us to have a good approach to estimate the pot-life and show the validity of kinetic model. The shape of the curves are very similar, and so the mathematic functions must be too. The DSC is not an adiabatic calorimeter, but through this procedure it is possible to estimate adiabatic values.

Thermodynamic Results

From Table I we can see the thermodynamic results for $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G_0^{\neq}$ (standard conditions at 298.16 K) obtained by plotting the values of K_1/T and K_1'/T according to Eqs. (7) and (4). Figure 6 shows the representation of $\ln K_1/T$ and $\ln K_1'/T$ against $1000/T$ for TEX_s.

The values of $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ found by us for the resin as-supplied form are very similar for both rate constants while for the purified one there are differences among all thermodynamic functions. $\Delta H^{\neq}$ is greater and $\Delta S^{\neq}$ is lower for the autocatalytic path than for the n order, which indicates that the formation of activated complex is more favorable through n-order mechanism. This fact is better reflected by the Gibbs free energy of activation where $\Delta G_0^{\neq} > 0$. On the other hand, Figures 7 and 8 show the variations with the temperature of $\Delta G^{\neq}$ for both systems and rate constants. Again we can see that the formation of activated complex is not favorable for TEX_p from 285 K (Fig. 7) and the reaction goes through n-order process. This is not the same case for TEX_s (Fig. 8) where the high values (negative values) of $\Delta G^{\neq}$ for both rate constants indicate that the mechanism of reaction is competitive and take into account both paths with the same significance.

We consider that it is important to point out the good concordance between kinetic and thermodynamic results. Figure 1 shows the tendency to n order when the temperature rises (TEX_p). Figure 7 shows this same fact, which stands out much more. Also

Table I Thermodynamic and Kinetic Parameters

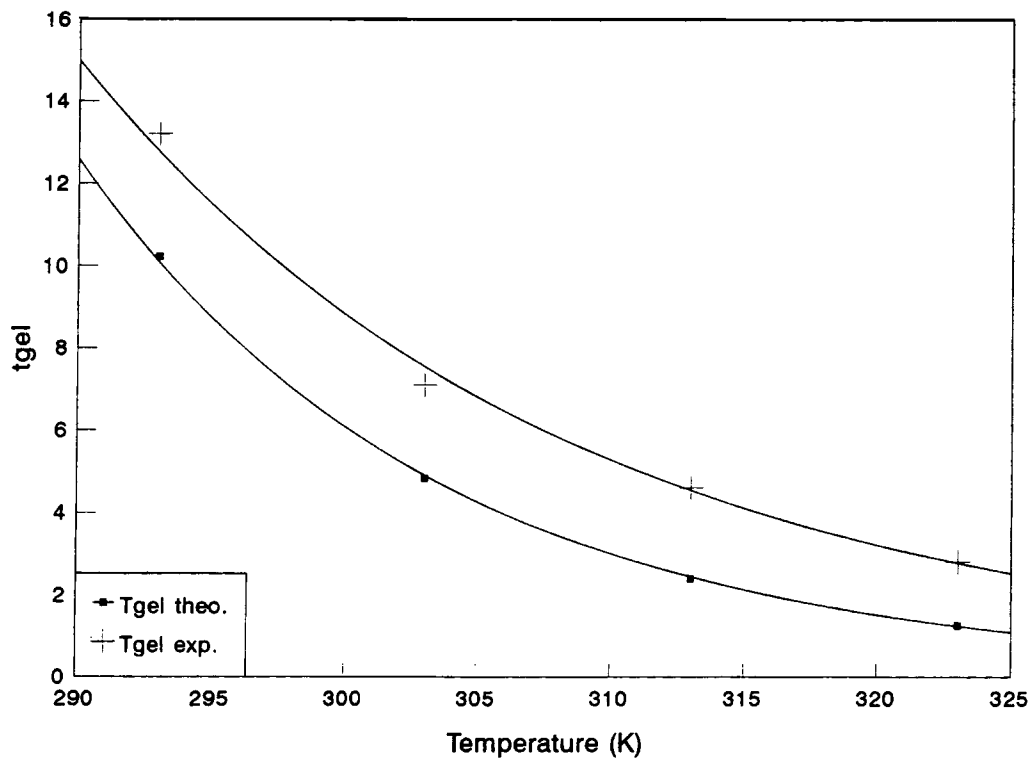| Parameters	TEX Supplied		TEX Purified	
ΔH_0 (J/g)	-547		-567	
$\Delta H^{\neq}$ (kJ/mol)	K_1	K_1'	K_1	K_1'
	-58.0	-57.5	-45.8	-51.4
$\Delta S^{\neq}$ (J/mol K)	K_1	K_1'	K_1	K_1'
	-122.9	-127.0	-160.5	-143.9
$\Delta G_0^{\neq}$ (kJ/mol) at 298.16 K	K_1	K_1'	K_1	K_1'
	-21.4	-19.6	$+2.1$	-8.5
$T_{g\infty}$ (°C)	35		33	
α_{max} theoretical	$\rightarrow 0$		$\rightarrow 0$	
α_{max} experimental	0.033 (50°C)		0.085 (65°C)	
K_1 (min^{-1})	$3.78 \times 10^8 \times e^{-14.5/RT}$		$4.10 \times 10^8 \times e^{-11.6/RT}$	
K_1' (min^{-1})	$2.29 \times 10^8 \times e^{-14.4/RT}$		$3.08 \times 10^7 \times e^{-13.0/RT}$	
$(d\alpha/dt)_{max}$ theoretical (min^{-1})	$\rightarrow K_1'$		$\rightarrow K_1'$	
$(d\alpha/dt)_{max}$ experimental (min^{-1})	0.039 (50°C)		0.11 (65°C)	
Time to reach (min) $(d\alpha/dt)_{max}$ theoretical	$\rightarrow 0$		$\rightarrow 0$	
Time to reach (min) $(d\alpha/dt)_{max}$ experimental	1.08		1	
α_{gel} experimental	0.61		0.58	
t_{gel} isothermal	$5.56 \times 10^{-10} \times e^{15.5/RT}$		$4.10 \times 10^{-8} \times e^{12.7/RT}$	
Order				
OH	1		1	
Order amine + epoxy	1.5		1.5	
Overall order	2.5		2.5	

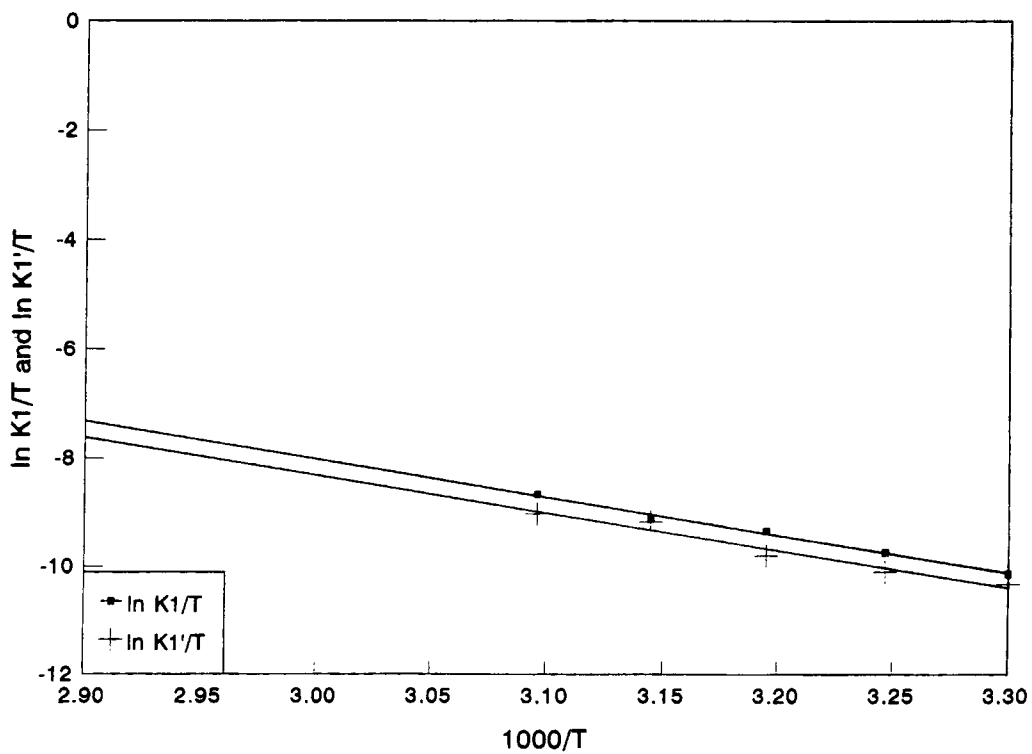**Figure 5** Adiabatic gel time against mixing temperatures (K); TEX$_s$.

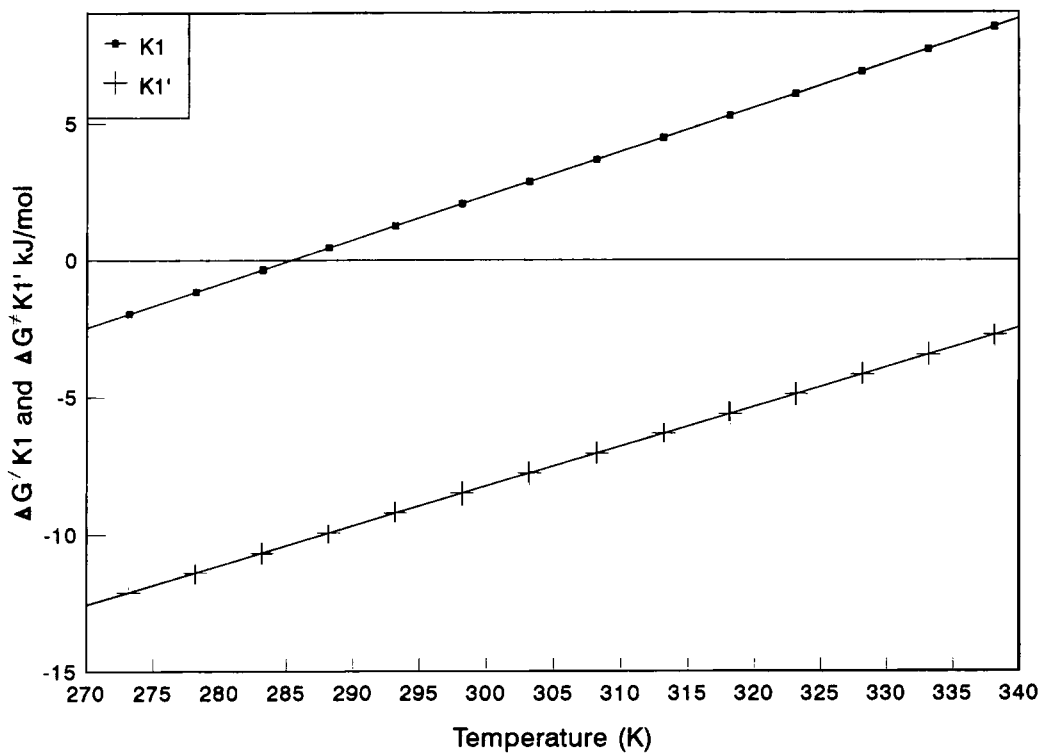**Figure 6** ln K_1/T and ln K'_1/T against $10^3/T$.

Figure 7 Variation of the Gibbs free energy of activation with the temperature (K); TEX_p.
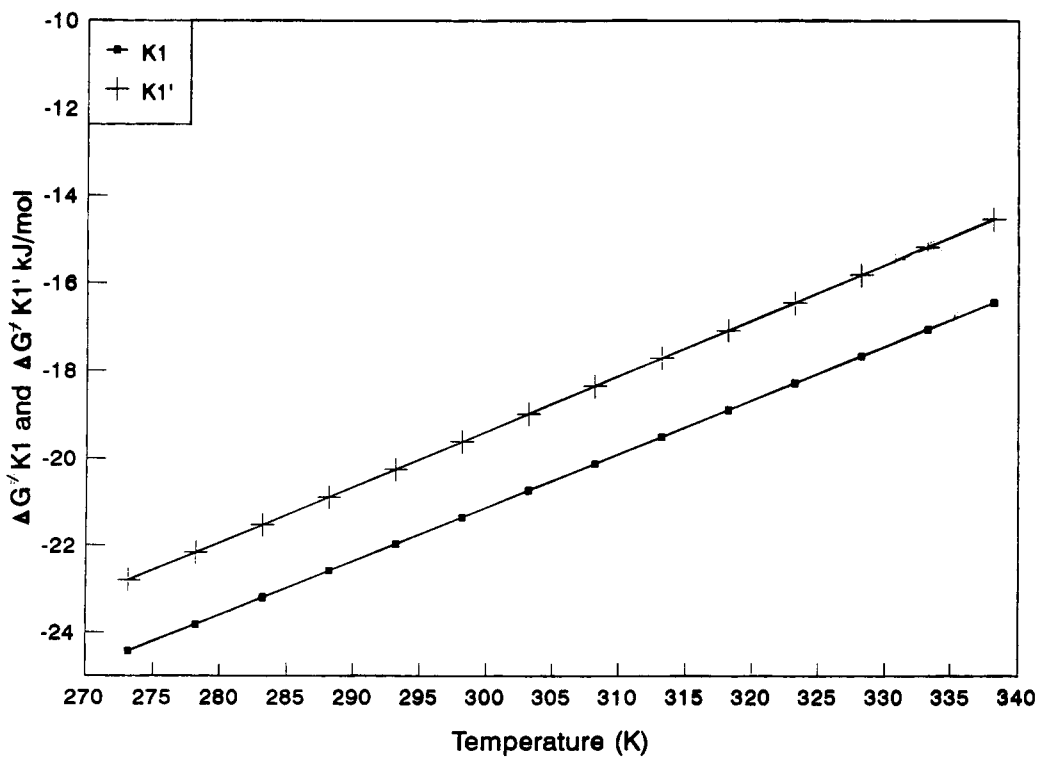

Figure 8 Variation of the Gibbs free energy of activation with the temperature (K); TEX_s.

Figure 1 indicates that both paths are superimposed and practically constant with the temperature (TEX_s).

Again this fact can be observed in Figure 8 where the variations of $\Delta G^{\ne} K_1$ and $\Delta G^{\ne} K_1'$ are shown as two straight lines, and its values are close for both paths; the formation of activated complex needs both mechanisms.

This study indicates that the entropic term ($T \Delta S^{\ne}$) can be of great significance in epoxy resin reactions. From a thermodynamic point of view the roll of n-order path is shown as markedly important for formulations with high OH content.

CONCLUSION

Through this work we showed the kinetic and thermodynamic parameters of cure obtained for two epoxy systems. It is clear than the resins with high initial OH content, even aliphatic structures, can be very fast systems if we compare them with the bisphenol A epoxy resins. Owing to the low T_g of these systems, high conversions can be reached at temperatures close to room temperature. The kinetic and thermodynamic parameters show a great tendency to n order of reaction. The order with respect to OH is clearly well stated to be 1, and the overall order for this reaction seems to be 2.5. The kinetic model compares well with the experimental results, including the pot-life measurements where we took the isothermal DSC results to obtain adiabatic approaches.

The functionality of this resin (basically 2) is determined through the gelation theory and compares well with the results obtained by molecular considerations. The basic thermodynamic functions $\Delta H^{\ne}$, $\Delta S^{\ne}$, and $\Delta G^{\ne}$ appear as very sensitive parameters to follow up and to control an epoxy–amine reaction.

REFERENCES

1. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci. A-1*, **8**, 1357 (1970).
2. S. Sourour and M. R. Kamal, *Termochim. Acta*, **14**, 41 (1976).
3. C. C. Ricardi, H. E. Adabbo, and R. J. J. Williams, *J. Appl. Polym. Sci.*, **29**, 2481 (1984).
4. S. P. Abuín, M. P. Pellín, L. Nuñez, J. S. Gandara, and P. P. Losada, *J. Appl. Polym. Sci.*, **47**, 533 (1993).
5. H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).
6. M. G. Evans and M. Polyani, *Trans. Faraday Soc.*, **31**, 875 (1935).
7. M. P. Pellín, L. Nuñez, J. S. Gandara, P. P. Losada, C. P. Lamela, and S. P. Abuín, *J. Appl. Polym. Sci.*, **55**, 225 (1995).
8. S. P. Abuín, M. P. Pellín, and L. Nuñez, *J. Appl. Polym. Sci.*, **41**, 2155 (1990).
9. P. L. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY, 1953, Chap. IX.
10. M. P. Pellín, Ph.D. Thesis, University of Santiago, Spain (1994).
11. W. P. Brennan, B. Miller, and J. C. Whitwell, *Ind. Eng. Chem. Fundam.*, **8**, 314 (1969).
12. D. Verchere, H. Santereau, J. P. Pascault, C. C. Riccardi, S. M. Moschiar, and R. J. J. Williams, *Macromolecules*, **23**, 725 (1990).
13. J. M. Barton, *Brit. Polym. J.*, **18**, 1 (1986).
14. D. R. Miller, E. Valles, and C. W. Macosko, *Polym. Eng. Sci.*, **19**, 272 (1979).
15. C. W. Macosko and D. R. Miller, *Macromolecules*, **9**, 199 (1976).
16. P. A. Oyanguren and R. J. J. Williams, *J. Appl. Polym. Sci.*, **47**, 1361 (1993).