

Kinetic Parameters in Non-Stoichiometric Epoxy-Resin/*m*-Xylylenediamine Reactions

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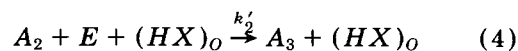
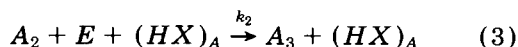
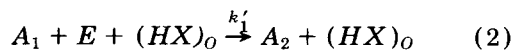
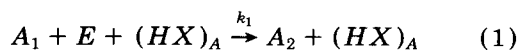
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SYNOPSIS

The curing reaction of bisphenol A epoxy resin has been widely studied. We have found that when initial reactants are highly pure the reaction epoxy resin/*m*-xylylenediamine follows a predominantly autocatalytic path independent of the temperature. The purpose of this study was to discern if the kinetic model is applicable at high values of amine/epoxy equivalent ratio. Because of the nature and reactivity of *m*-xylylenediamine (*m*-XDA), the studies were carried out at low temperatures. Also, in order to obtain information about the formation mechanism of the system, different parameters such as reaction orders, activation energies, and reaction rate variation with concentration have been studied at different (1.5 : 1, 2 : 1, and 3 : 1) amine/epoxy equivalent ratios. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

For the reaction under study, Horie et al.¹ propose a reaction scheme



here *E*, *A*₁, *A*₂, and *A*₃ represent epoxide, primary amine, secondary amine produced by addition to an epoxy group, and tertiary amine as a final product, respectively. (*HX*)_A and (*HX*)_O represent the reaction products having hydroxyl groups and the initial impurities or external catalyst.

From these equations, and taking into account some considerations that we will present, the reaction rate, $d\alpha/dt$, becomes

$$\frac{d\alpha}{dt} = (K'_1 + K_1\alpha^m)(1 - \alpha)^a(B - \alpha)^b \quad (5)$$

and the reduced rate α° defined as

$$\alpha^\circ = \frac{\frac{d\alpha}{dt}}{(1 - \alpha)^a(B - \alpha)^b} = K'_1 + K_1\alpha^m \quad (6)$$

where *m*, *a*, and *b* are the reaction orders related to hydroxyl, epoxy, and amine, respectively, and *B* the amine/epoxy equivalent relation.

This model does not take into account other different possible reactions such as etherification and homopolymerization, even when the first may happen at high curing temperatures.² However, we think that for this diamine the reaction is highly improbable, even more so using high values for the amine/epoxy ratio.^{3,4,5} The anionic homopolymerization reaction has not been considered due to its small significance,⁶ but as will be seen, is not quite discarded for amine/epoxy ratio 3 : 1, owing to the existence of relatively low molecular weight tertiary amines. If *B* increases, the chemical structure changes from a highly crosslinked polymer (*B* = 1)

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to a linear structure polymer⁷⁻⁹ for values over the critical ratio, a_0/e_0 , where a_0 and e_0 correspond to the initial concentration values of amine and epoxy, respectively.

It is very important to follow the tertiary amine concentration in order to control the reaction. It decreases when B increases and leads to a soluble polymer when $B > a_0/e_0$ and $[A_3] \rightarrow 0$.

From the Horie model, eq. (5) can be derived by following two different methods.

1. Including the formation of tertiary amines, eqs. (1), (2), (3), and (4).¹⁰

$$\frac{dx}{dt} = k_1 a_1 e x + k'_1 a_1 e c_0 + k_2 a_2 e x + k'_2 a_2 e c_0$$

(a_1 , e , c_0 , a_2 , and x represent primary amine, epoxy, external catalizer, secondary amine concentrations, and the epoxide consumed).

Taking $e = e_0 - x$ and assuming $k_2/k_1 = k'_2/k'_1 = n$ and equal reactivity for all hydrogen amines

$$a_1 + (a_2/2) = a_0 - (x/2)$$

and introducing the reduced variable $\alpha = x/e_0$

$$\frac{d\alpha}{dt} = \frac{1}{2}(k_1 e_0^2 \alpha + k'_1 e_0 c_0)(1 - \alpha)(2a_0/e_0 - \alpha)$$

this equation for $m = a = b = 1$, leads to

$$\frac{d\alpha}{dt} = (K_1 \alpha + K'_1)(1 - \alpha)(B - \alpha). \quad (7)$$

Here

$$K_1 = \frac{1}{2} k_1 e_0^2$$

$$K'_1 = \frac{1}{2} k'_1 e_0 c_0$$

$$B = 2a_0/e_0.$$

2. Excluding the formation of tertiary amine. The reaction scheme is reduced to eqs. (1) and (2).

$$\frac{dx}{dt} = k_1 a_1 e x + k'_1 a_1 e c_0.$$

Taking $e = e_0 - x$ and $a_1 = a_0 - x$

$$\frac{d\alpha}{dt} = (K_1 \alpha + K'_1)(1 - \alpha)(B/2 - \alpha) \quad (8)$$

where

$$K_1 = k_1 e_0^2 \quad \text{and} \quad K'_1 = k'_1 e_0 c_0.$$

According to this and, in absence of other reactions, assuming that the whole crosslinking is due to the formation of tertiary amines, the epoxy-amine reaction could be followed by simple (K_1) non-stoichiometric/(K_1) stoichiometric and (K'_1) non-stoichiometric/(K'_1) stoichiometric ratios inside the values 2-1, with crosslinked structure next to 1 and non-crosslinked structure close to 2.

EXPERIMENTAL

Materials

Following the procedure described¹¹ the resin used was Epikote 828 (from Shell), purified by distillation and further crystallizations in methanol; *m*-XDA (from Aldrich Chemical Co.) was used as supplied, 99.2% pure.

In order to prevent premature reaction, all the mixtures for different values of B were made at 10°C, by weighing epoxy/*m*-xylylenediamine amounts based on $B = 1$ (100/19.5).

Techniques

DSC Study

The kinetic study was carried out using a Perkin-Elmer DSC7 coupled to a 3700 Data Computer with isothermal and dynamic software. Owing to the initial temperature range from 20°C, a cryogenic device was used. In all the cases run start temperature was fixed at 0°C, and the scan rate varied from 50–200°C/min, depending on the difference between the initial and final temperatures (isothermal). The dynamic experiments were carried out between 0°C and 200°C at 10°C/min. The results obtained from those experiments were used to calculate α and $d\alpha/dt$, in combination with the isothermal results.¹¹

It took 3–4 h to stabilize the equipment and to reach thermal equilibrium. In order to do this, liquid nitrogen with a flow rate controlled by a cooling external device thermostated at –20°C, necessary to reach thermal equilibrium at 0°C, was used. Other devices, such as an externally connected refrigerator, did not lead to reproducible results. The isothermal temperature ranges were 45–90°C for $B = 1$, 45–80°C for $B = 2$, and 20–45°C for $B = 3$. These iso-

thermal ranges were considered the most appropriate for each reaction, taking into account the previous dynamic experiments and following the same criteria explained in our previous paper.¹¹

Analytical Techniques for Tertiary Amine Determination

Tertiary amine determination was carried out using different analytical techniques, wet analysis,¹² potentiometric titration,¹³ and UV-visible spectrophotometry,¹⁴ the last producing the best results.¹⁵ This technique permits the measurement of the formation of a colored product because of the cycling reaction between malonic acid and acetic anhydride in the presence of tertiary amines. The resultant yellow color can be measured at 390 nm.

UV-Visible Study

The UV-visible spectrophotometer used was the double beam model 100-60 from HITACHI, with a wolfram lamp as source and a pair of 1 cm path length quartz cells QS-281 for measurements.

Reagents.

1. Malonic acid (99%). Aldrich, Cat. No. M129-6.
2. Acetic anhydride (99%). Aldrich, Cat. No. 11.004-3.
3. Tetrahydrofuran, HPLC grade. Scharlau, Te 225.
4. Ashless filter paper. Whatman, Ref. 42.

Sample Preparation. After adding 30 mL of tetrahydrofuran, 500 mg of the 3 : 1 *m*-XDA/BADGE equivalent ratio amine/epoxy formulation, previously scratched, was weighed and heated at 40°C for some minutes for total dissolution, filtered after cooling through filter paper into a 50 mL volumetric flask, washed with tetrahydrofuran and also filter washings. Finally, tetrahydrofuran was added to mark. Fifteen to 50 mL was first diluted with tetrahydrofuran and then 10 mL of this new solution was diluted with tetrahydrofuran to 50 mL. The solution for spectrophotometry was obtained by taking 10 mL and brought up to 25 mL with the color reagent. The color measurement was carried out after remaining at room temperature for 30 min.

Color Reagent. The color reagent was prepared as follows: 8 g of malonic acid previously desiccated at 110°C was weighed and dissolved in acetic anhydride to 200 mL by stirring in an ultrasonic bath.

DSC Results

Kinetic model eq. (5) was checked for different values of m , a , and b , in all the three cases studied; α° was plotted against α obtaining the best results for $m = 1$, $a = 1$, $b = 0.5$ (correlations better than 0.996). From the slope and the ordinate intercept of the linear part of the reduced rate curve, K_1 and K'_1 were determined.

Activation energies corresponding to the autocatalytic reaction Ea_1 , and to the n -order path Ea'_1 , as well as the exponential prefactors for the three cases were obtained using Arrhenius plots (correlations between 0.990, for $B = 3$, and 0.999 for $B = 1.5$). Figures 1–3 show experimental–theoretical values of the rate, $d\alpha/dt$, versus conversion α at different temperatures.

Spectral Results

Absorbance of the formed yellow color was measured at 390 nm with a 2 nm bandwidth, after fitting the 0–100% T range of the spectrophotometer and then the sample and reference beams to a 0.000 absorbance with a blank for each of them. The visible spectrum obtained is presented in Figure 4.

DISCUSSION

Our results (Table I) show that the kinetic equations are similar and do not depend on the amine/epoxy ratio. Activation energies show practically the same values in all cases with an anomalous behavior for $B = 2$. In this case the activation energy corresponding to the autocatalytic path Ea_1 is higher than that corresponding to the n -order Ea'_1 . As a consequence of these results a special study was carried out repeating all DSC tests in different experimental conditions. Starting temperature (0°C) was changed and it was observed that when starting at 25°C, absolute values of K_1 and K'_1 were very similar while the difference between activation energies markedly increased.

As previously mentioned, isothermal runs were carried out in the most appropriate temperature ranges, different for each formulation. In some cases only 5–6 isothermal curves could be obtained at intervals of 5°C. At low temperatures it is very difficult to obtain reproducible results because experimental errors (noise, water condensation, etc.) become important, especially when the measurements are influenced by baseline slope variations even in isothermal experiments. For example in the case B

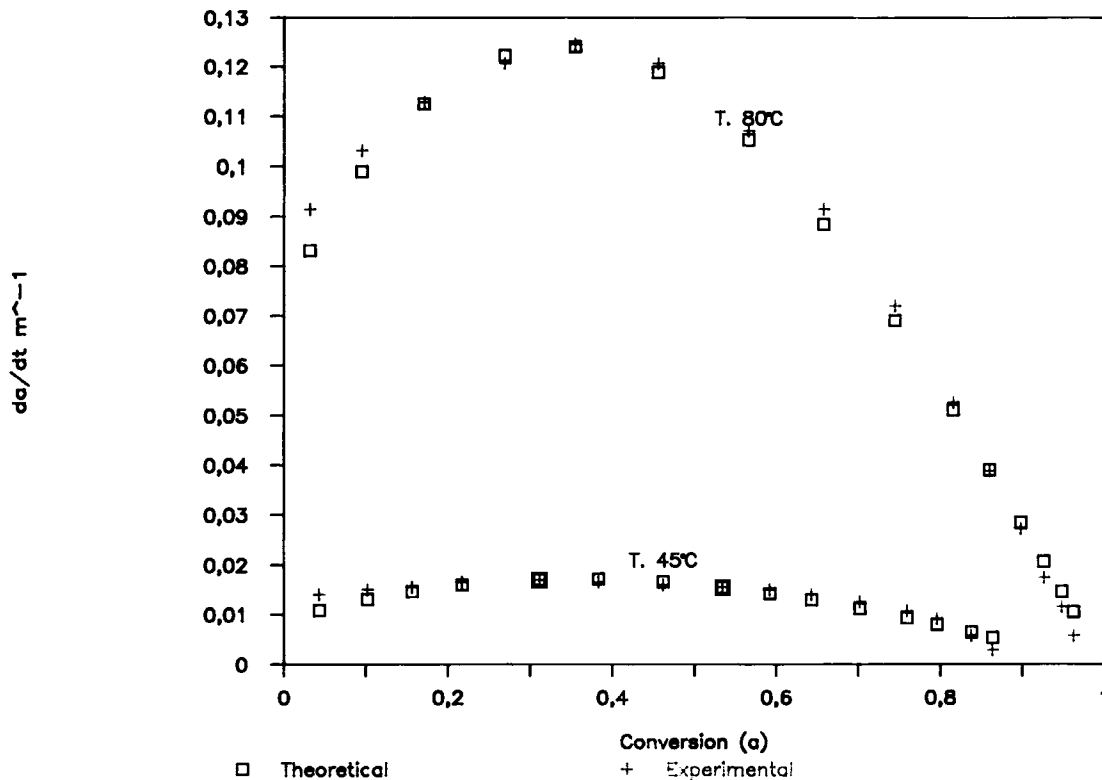


Figure 1 Rate of reaction against conversion: at 80°C and 45°C , $B = 1.5$.

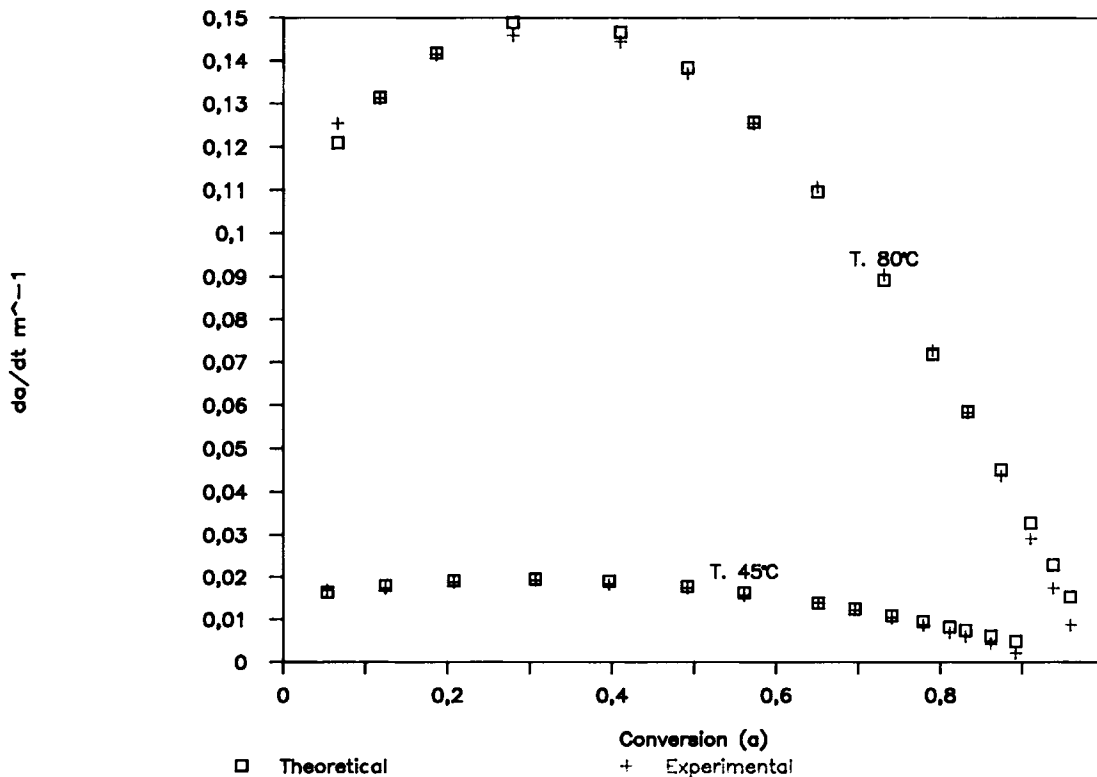


Figure 2 Rate of reaction against conversion: at 80°C and 45°C , $B = 2$.

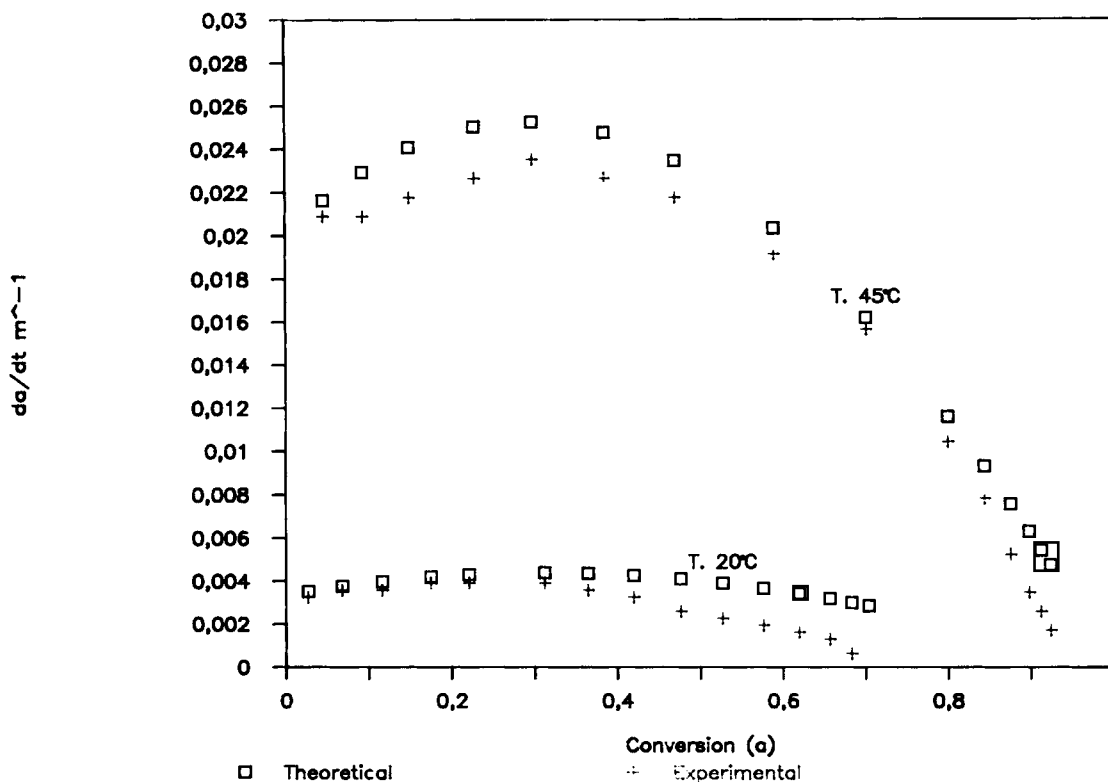


Figure 3 Rate of reaction against conversion: at 45°C and 20°C, $B = 3$.

= 3 at 20°C, the experiment took 500 min and maximum value of dH/dt recorded was less than 0.230 mW.

Figure 5 shows the behavior of α_{max} as a function of the temperature. It may be observed that α_{max} decreases with the temperature for $B = 1.5$ and B

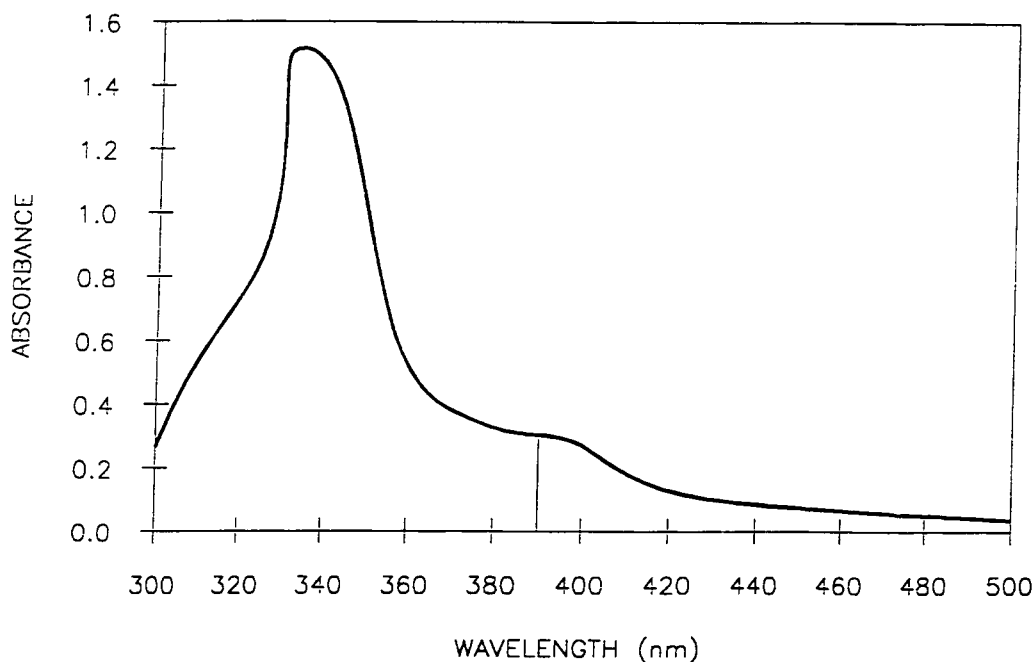


Figure 4 Visible spectrum for $B = 3$.

Table I Thermodynamic and Kinetic Parameters

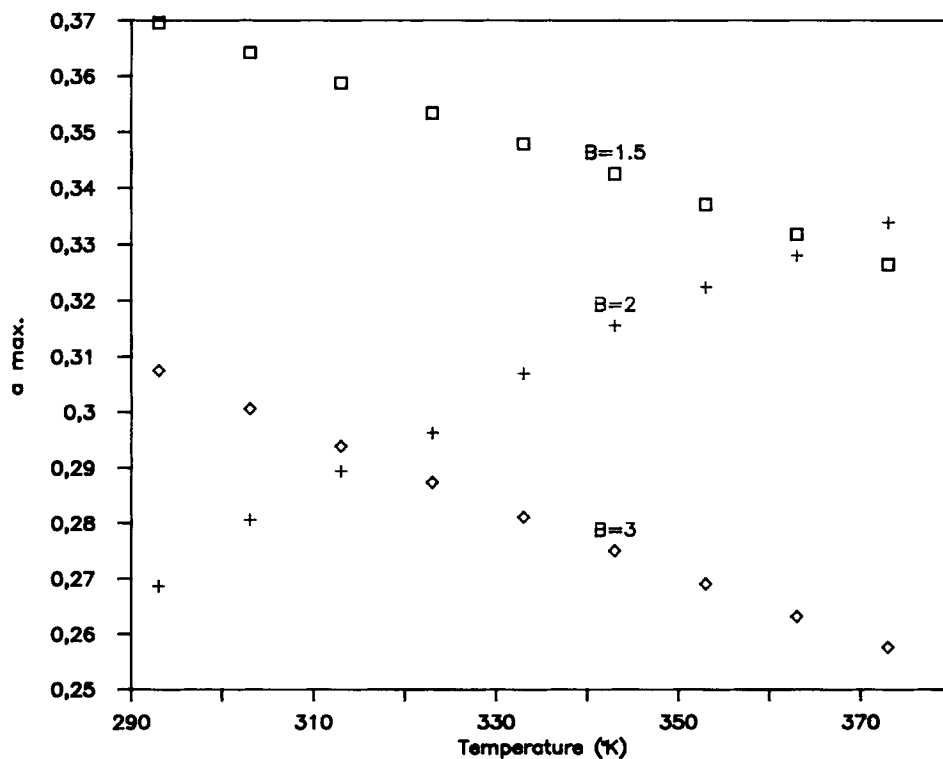
	1 : 1.5	1 : 2	1 : 3
ΔH_T (J/g)	543	512	489
Varies with temperature			
α_{\max} theoretical	0.33 (90°C)	0.32 (80°C)	0.29 (50°C)
α_{\max} experimental	0.34 (90°C)	0.28 (80°C)	0.30 (50°C)
Tg_{∞} °C	91	65	26
K_1 (min^{-1})	$1.20 \cdot 10^7 \cdot e^{-12.20/RT}$	$6.43 \cdot 10^7 \cdot e^{-13.45/RT}$	$1.60 \cdot 10^7 \cdot e^{-12.60/RT}$
K'_1 (min^{-1})	$1.30 \cdot 10^7 \cdot e^{-13.45/RT}$	$3.04 \cdot 10^6 \cdot e^{-12.30/RT}$	$1.61 \cdot 10^7 \cdot e^{-13.30/RT}$
$(d\alpha/dt)_{\max}$			
Theoretical (min^{-1})	0.20 (90°C)	0.15 (80°C)	0.034 (50°C)
Experimental (min^{-1})	0.20 (90°C)	0.14 (80°C)	0.036 (50°C)
Time to reach (min)			
$(d\alpha/dt)_{\max}$ theoretical	1.92 (90°C)	2.13 (80°C)	9.60 (50°C)
$(d\alpha/dt)_{\max}$ experimental	1.93 (90°C)	1.75 (80°C)	10.00 (50°C)
Order			
OH	1	1	1
Amine	0.5	0.5	0.5
Epoxy	1	1	1
Overall	2.5	2.5	2.5

= 3, while it increases for $B = 2$. Even though an autocatalytic path is clear for all three formulations, $B = 2$ shows again an anomalous behavior possibly indicating an autocatalytic process favored by the temperature increase.

Examination of Figure 6 shows constants rate ratio K_1/K'_1 as a function of the temperature (to help

the discussion $B = 1$ is also included¹¹). It can be seen that $B = 1.5$ and $B = 3$ differ from the stoichiometric reaction in their tendency to n -order path with temperature, while $B = 2$ tends to an autocatalytic path.

Deviation of $B = 1.5$ from $B = 1$, may be explained considering that the excess of RNH_2 groups produce

**Figure 5** α_{\max} against temperature ($^{\circ}\text{K}$).

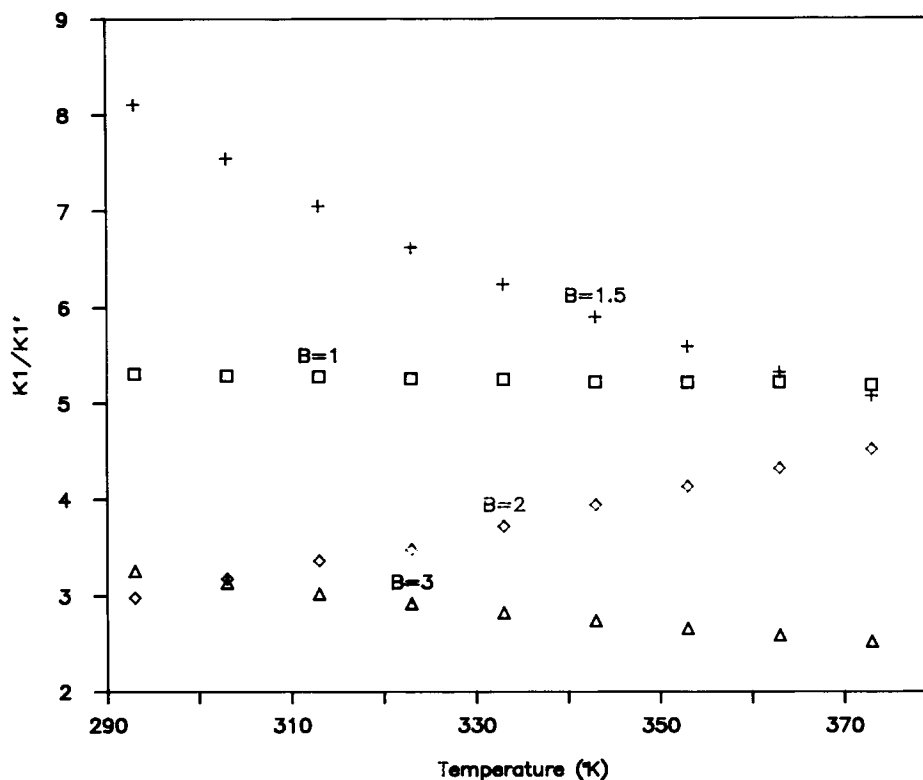


Figure 6 Variation of the ratios of the rate constants against temperature ($^{\circ}\text{K}$).

a displacement in eq. (2) because of the concentration increase of one of the reagents. The autocatalytic process, eq. (1), is disfavored because of the necessity of forming intermediate complex molecules from the OH^- produced during the epoxy-amine reaction.¹⁶

Reaction $B = 3$, shows a quasi-linear behavior with temperature. Both processes compete simultaneously, but as previously appointed, the autocatalytic path loses part of its significance.

Finally $B = 2$ shows an anomalous behavior with respect to the previous two opposed to our previous reasoning. We have not arguments enough to justify this fact, nor experimental tests capable of doing it. However, values of the reaction rates at different temperatures settle it in an intermediate place between $B = 1.5$ and $B = 3$ (Fig. 7).

Study of the reaction order was carried out by measuring the reduced rate at different values of m , a , and b [eq. (6)], the best results being $m = 1$, $a = 1$, $b = 0.5$ (correlations better than 0.996). Good correlations were also found for $a = 1$ and $b = 1$ at high temperatures and high equivalent ratios ($B = 2$, $B = 3$). On the other hand, $a = 0.5$ and $b = 1$ never happen and m remains constant throughout the whole study. These facts support the suggestion of termolecular mechanism, that is, first order respect to OH , first order respect to epoxy and

0.5 related to the amine. However, a tendency to an overall order 3 cannot be discarded in the previously marked conditions.

Figure 8 represents the quotient of the constants K_1 and K_1' for the different equivalent ratios with respect to the constant of stoichiometric reaction ($B = 1$) at different temperatures.

These values, as appointed, are close to the range 1–2, depending on the crosslinked or non-crosslinked structures originated. Deviation of these values have no physical meaning, unless the rate constants K_1 and K_1' , in the case $B = 1$, are from a system with 100% conversion into tertiary amines. In this case, and in stoichiometric conditions, a polymer 100% crosslinked would be obtained, which does not happen because the polymer has a well-defined glass transition temperature at 109°C and, as is usual with this kind of polymers, the degree of crosslinking above 60–65% very seldom occurs.¹⁷ In our opinion this figure is very important from the practical point of view. It suggests the formation of tertiary amines in the process $B = 3$, which should not happen being a product soluble in organic solvents (ketone, tetrahydrofuran, chloroform, etc.). This formation would take place due to the autocatalytic mechanism (values close to 1 with the temperature increase), while n -order path would mean the opposite. $B = 1.5$ would follow the same

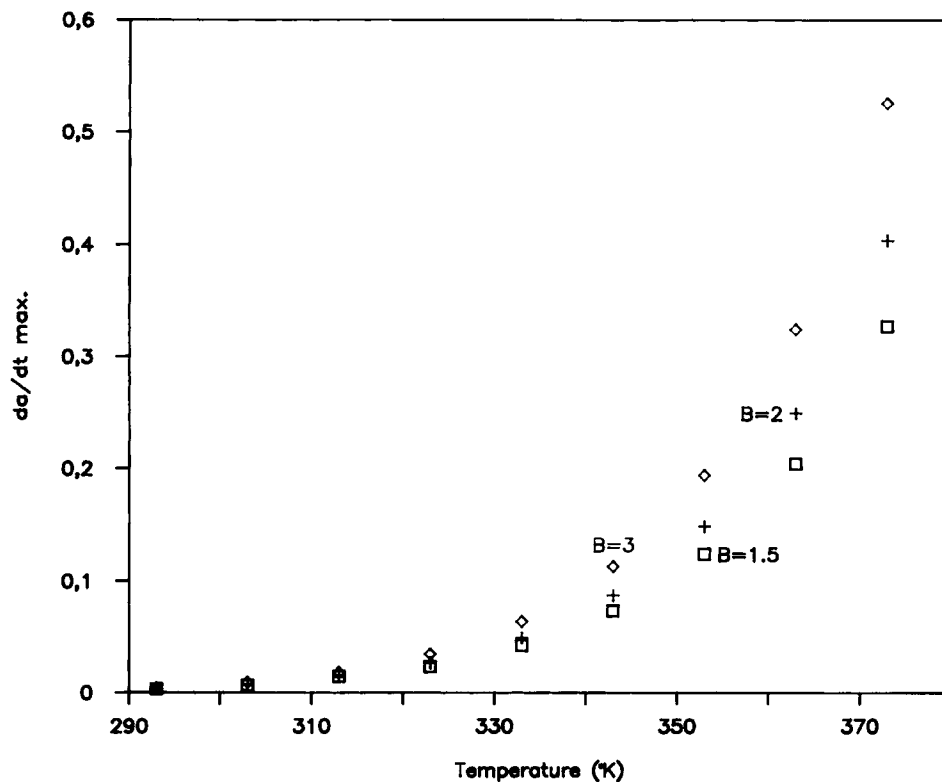


Figure 7 da/dt_{max} against temperature ($^{\circ}K$).

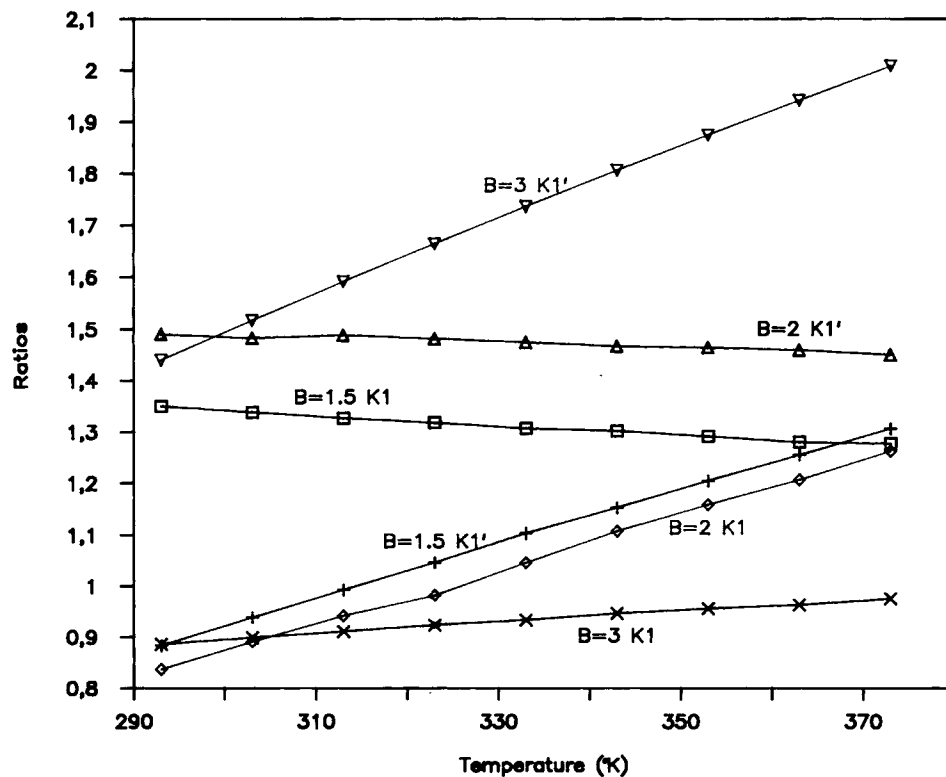


Figure 8 Variation of the ratios of $(K_1, K_1') B \neq 1 / (K_1, K_1') B = 1$ against temperature ($^{\circ}K$).

path, and the opposite path would happen, as expected, for $B = 2$.

The existence of tertiary amines without the formation of a three-dimensional structure is very important in order to prove the validity of the kinetic model used at high amine/epoxy ratios. For this reason the searching of these amines was one of our main objectives. Because of low sensitivity due probably to their high equivalent weight and low basicity, potentiometry was not valuable. They were detected, as stated, through UV-visible spectrophotometry at 390 nm (Fig. 4). With the use of positive ion mass spectra in FAB mode in a Kratos MS9/50TC mass spectrometer using fast xenon bombardment (5–8 keV) m/z were obtained at 612 and 1088 a.m.u. These molecular weights correspond to the reaction $2x$ m -XDA + $1x$ epoxy resin and $3x$ m -XDA + $2x$ epoxy resin, respectively. In this last reaction and assuming equal reactivity for all the hydrogen amines of the m -XDA, the production of —N— is highly probable. Also, some other sim-

ilar molecules may be formed but, because of the equipment mass range, were not detected. Perhaps their existence is related to the vicinity of the equivalent rate ($B = 3$), used to the obtained critical ratio, 2.97.

CONCLUSIONS

From the results obtained it is very important to distinguish:

1. The reaction epoxy/ m -XDA is first order with respect to OH concentration, first order related to epoxy, and 0.5 for the amine.
2. Reactions follow a termolecular mechanism with an overall 2.5 order, even when order 3 may be found at high temperatures and high equivalent relations. However, the order is practically independent of the amine/epoxy ratios.
3. The kinetic model used is valid for the study of the epoxy/ m -XDA reaction, at different equivalent relations, providing tertiary amines exist. The differences theoretical–experimental for $B = 3$, at low temperatures, may be assigned to difficulties inherent to the experimental procedure rather than to the kinetic model used.
4. In all the relations studied a double autocatalytic/catalytic mechanism coexists, the second being more important with temperature increase. However, this fact cannot be generalized for all the different ratios.
5. Even when a possible anomalous behavior for $B = 2$ exists, activation energies (Ea_1 and Ea'_1) have values inside the range 12–14 Kcal/mol.
6. The existence of tertiary amines, for equivalent relations in the proximity of the critical ratio value, was experimentally checked.
7. For the reaction $B = 3$ and probably due to the practically equal reactivity of the hydrogen amines, both non-crosslinked polymers and low molecular weight tertiary amines may be obtained.
8. In the absence of other reactions such as etherification and/or anionic homopolymerization the quotients of the rate constants non-stoichiometric/stoichiometric are very close to 2/1.

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