

# Cure Kinetics of Diglycidylether of Bisphenol A–Ethylenediamine Revisited Using a Mechanistic Model

C. C. RICCARDI,<sup>1</sup> F. FRAGA,<sup>2</sup> J. DUPUY,<sup>3</sup> R. J. J. WILLIAMS<sup>1</sup>

<sup>1</sup> Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina

<sup>2</sup> Facultad de Ciencias, Universidad de Santiago de Compostela, Campus de Lugo, 27002 Lugo, Spain

<sup>3</sup> Laboratoire des Matériaux Macromoléculaires, UMR CNRS N° 5627, INSA de Lyon, 20 Av. Albert Einstein, 69621 Villeurbanne Cedex, France

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**ABSTRACT:** The polymerization kinetics of the reaction between diglycidylether of bisphenol A (DGEBA) and ethylenediamine (EDA) was analyzed, using dynamic scanning calorimetry, in both isothermal and programmed heating-rate modes. A simple mechanistic model, consisting of an equilibrium reaction generating an epoxy–hydroxyl complex, and including two possible mechanisms for the consumption of amine hydrogens [(1) with free epoxy groups, (2) with the epoxy–hydroxyl complex], provided a reasonable fitting of the whole set of experimental results. It was found that the equilibrium constant decreased with temperature, making less important the reaction mechanism involving the epoxy–hydroxyl complex. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2319–2325, 2001

**Key words:** epoxy–amine kinetics; DGEBA–EDA kinetics; mechanistic kinetic models

## INTRODUCTION

Mechanistic kinetic models for epoxy–amine systems arose from an early study by Schechter et al.,<sup>1</sup> in which the kinetics of epoxy–amine reactions was investigated using model compounds. They found that the rate was markedly accelerated by hydroxyl groups generated during the reaction or provided by the addition of alcohols. Smith<sup>2</sup> proposed a third-order kinetic expression (rate proportional to the concentration of epoxides, amine hydrogens, and hydroxyls), which was

consistent with the results of Schechter et al. Horie et al.<sup>3</sup> assumed that external catalysts, including impurities initially present in the system, could also act as catalysts of this reaction. The resulting kinetic expression was verified by several epoxy–amine systems, at least in limited ranges of conversion and temperature.<sup>4–9</sup>

The next improvement of mechanistic approaches was the incorporation of the following alternatives to the reaction scheme: (1) the reactivity of secondary amine hydrogens is different (usually less) from the reactivity of primary amine hydrogens, and (2) epoxy groups may homopolymerize through different mechanisms. Sets of kinetic equations considering these possibilities were proposed by Zukas et al.,<sup>10</sup> Riccardi and Williams,<sup>11</sup> Chiao,<sup>12–14</sup> Cole,<sup>15</sup> and Gupta et al.<sup>16</sup> A reasonable fitting of these extended mech-

Correspondence to: R. Williams (williams@fi.mdp.edu.ar).  
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anistic models was shown for several epoxy-amine systems.<sup>10,11,13,14,17-24</sup>

However, there is also a parallel series of studies showing that the extended mechanistic models are not able to fit the experimental results obtained for several epoxy-amine systems. Many authors have used different types of phenomenological equations to fit their experimental data,<sup>25-47</sup> the most popular one of which is Kamal's equation, so-called.<sup>31-33</sup>

Results arising from phenomenological equations cannot be extrapolated to account for changes in the initial formulation or in the range of conversions and temperatures at which experimental data were determined. In this regard, mechanistic models offer more flexibility. Chiao et al.<sup>13,14,17</sup> showed the predictive capability of mechanistic models and the way in which they can account for variations in the initial formulations. Moreover, they provide an insight into the network structure, given that the different possible reactions are accounted for. This is particularly useful to predict the evolution of different statistical parameters during network formation.<sup>48,49</sup> Therefore, the search for better mechanistic models is ongoing.

An improvement of mechanistic models arose from the consideration that different hydrogen-bonded transition complexes may be formed, whose formation and dissociation during the reaction control the kinetics.<sup>50</sup> Mijovic et al.<sup>51,52</sup> studied the reaction kinetics of epoxy-amine model systems and proposed the existence of three intermediate hydrogen-bonded transition complexes: (1) epoxy-amine, (2) epoxy-hydroxyl, and (3) amine-hydroxyl. These three transition complexes may react with amine hydrogens and also complexes (2) and (3) are allowed to react between themselves. This general kinetic scheme was employed by Flammersheim<sup>53</sup> to model experimental results obtained for different epoxy-amine systems. Kinetic parameters were obtained by multivariate nonlinear regression analysis. However, as pointed out by the author, the high number of adjustable parameters led to a high correlation among them, making their use unreliable under different experimental conditions. Therefore, the flexibility of mechanistic models is partially lost.

Our interest in this study is to investigate whether one of the most simple kinetic models of this new generation, for example, the one based on the existence of the epoxy-hydroxyl complex as the only intermediate species,<sup>54</sup> may be used to

fit experimental results obtained by differential scanning calorimetry (DSC) for the diglycidylether of bisphenol A (DGEBA)-ethylenediamine (EDA) system, under both isothermal and constant heating-rate conditions. In a previous study<sup>4</sup> we found that kinetic equations obtained from programmed heating-rate experiments and those from isothermal curing were different. It was proposed that the autocatalytic mechanism could vanish at the high temperatures of the dynamic runs, probably as a result of the difficulty of forming the ternary transition complex. We attempt to verify this assessment by introducing the equilibrium constant for the formation of the epoxy-hydroxyl complex in the kinetic scheme.

## KINETIC MODEL

Let us consider a stoichiometric DGEBA-EDA system and assume equal reactivities of primary and secondary amine hydrogens.<sup>4</sup> By denoting E = epoxy group, AH = amine hydrogen, E-OH = complex between epoxy and hydroxyl groups, and e, aH, e-OH, and OH, the corresponding molar concentrations, the following reaction scheme may be written:



It is assumed that the equilibrium represented by eq. (1) is achieved at a very fast rate, so that the concentrations e, OH, and e-OH are always related through the equilibrium constant  $K'$ . The specific rate constant  $k'_1$  corresponds to the reaction catalyzed by impurities initially present in the formulation (e.g.,  $\alpha$ -glycols present in the epoxy monomer<sup>28</sup>); the specific rate constant  $k'_2$  indicates the reaction of the epoxy-hydroxyl complex with amine hydrogens.

The concentration of different groups along the reaction is given by

$$aH = e + e-OH = e_0(1 - x) \quad (4)$$

$$OH + e-OH = (OH)_0 + xe_0 \quad (5)$$

where  $x$  is the conversion and

$$K' = e\text{-OH}/(e)(\text{OH}) \quad (6)$$

By defining  $K = K'e_0$  (dimensionless),  $k_1 = k'_1e_0$  ( $\text{time}^{-1}$ ),  $k_2 = k'_2e_0$  ( $\text{time}^{-1}$ ),  $(\text{OH})_0/e_0 = c_0$ , and  $y = e\text{-OH}/e_0$ , the reaction kinetics is determined by the following set of equations:

$$dx/dt = (1 - x)[k_1(1 - x - y) + k_2y] \quad (7)$$

$$K = y/[(1 - x - y)(c_0 + x - y)] \quad (8)$$

Equation (8) may be analytically solved to give

$$y = 0.5\{A - (A^2 - 4[c_0 + x(1 - c_0) - x^2])^{0.5}\} \quad (9)$$

with

$$A = 1 + c_0 + 1/K \quad (10)$$

To fit the experimental curves,  $k_1$ ,  $k_2$ , and  $K$  are expressed as a function of temperature in terms of an Arrhenius equation.

The proposed kinetic model verifies that  $dx/dt = f(x, T)$ , meaning that for any pair of values of conversion and temperature a unique value of the reaction rate, which does not depend on the particular history to attain this point, may be defined in the system. This statement may be violated by simply assuming that the complex formation, eq. (1), is out of equilibrium. In this case, rate equations for the forward and backward reactions represented by eq. (1) have to be stated. Therefore, before attempting to fit the proposed kinetic model, one must determine whether a unique relationship exists between  $dx/dt$  and  $(x, T)$  values obtained in isothermal and in programmed heating-rate experiments.

## EXPERIMENTAL

The epoxy monomer, based on diglycidylether of bisphenol A (DGEBA; MY 790, Ciba, Summit, NJ), had an epoxy equivalent weight of 173.8 g/mol, as determined by acid titration. The ratio  $c_0 = (\text{OH})_0/e_0$  was equal to 0.015. It was dried under vacuum before use. Ethylenediamine (EDA; Sintorgan, Buenos Aires, Argentina), was used in a stoichiometric proportion giving a solution with  $e_0 = 6.04$  mol/L. A fresh sample was prepared before every experimental determination.

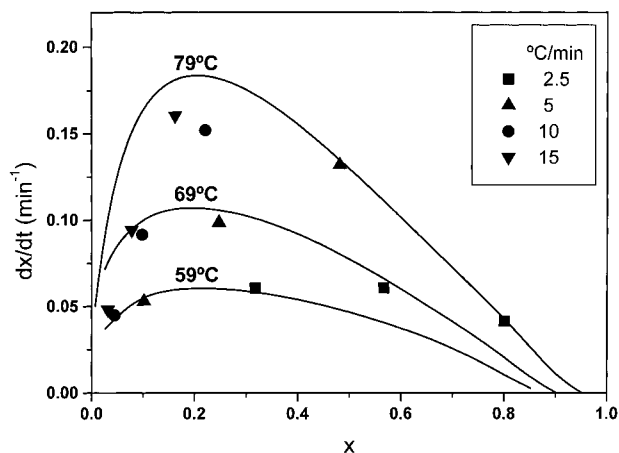
The cure kinetics was studied by differential scanning calorimetry (DSC; Shimadzu DSC-50, Shimadzu, Japan), both in the isothermal mode (59, 69, 79°C) and in the programmed heating-rate mode (2.5, 5, 10, and 15°C/min), under nitrogen. Both the rate of heat generation  $dH/dt$  and temperature  $T$  were continuously recorded. A consistent constant value of the maximum reaction heat,  $(\Delta H)_{\text{max}} = 105 \pm 2$  kJ/mol, was obtained for dynamic runs and for the sum of the isothermal heat of reaction and the residual heat obtained in a subsequent scan. This is in close agreement with many values reported in the literature. The constancy of the experimental value of  $(\Delta H)_{\text{max}}$  under different cure conditions furnishes indirect support that the amine volatilization during the reaction was not significant.

Conversion was defined as the ratio of the partial reaction heat over the maximum reaction heat,  $x = (\Delta H)/(\Delta H)_{\text{max}}$ ; the reaction rate was obtained as  $dx/dt = (dH/dt)/(\Delta H)_{\text{max}}$ . The maximum glass-transition temperature of the DGEBA-EDA system is  $T_{g\infty} = 111^\circ\text{C}$ .<sup>55</sup> Therefore, vitrification takes place in the course of isothermal runs carried out at temperatures lower than  $T_{g\infty}$ . For these runs the fitting of the kinetic model was performed for conversions lower than the vitrification conversion,<sup>4</sup> to avoid the onset of diffusion control on the reaction rate. For dynamic runs, complete conversion was attained without traversing the vitrification region. These runs enabled us to test the fitting of the kinetic model in the whole conversion range.

## RESULTS AND DISCUSSION

Figure 1 shows the results of isothermal runs plotted as reaction rate as a function of conversion. The autocatalytic nature of the reaction is clearly evidenced. Values of reaction rates, obtained at the same temperature in the course of dynamic runs, are also indicated. Within the error of the experimental curves, the agreement may be considered reasonable, which means that a unique function  $dx/dt = f(x, T)$  may be searched to fit the experimental data.

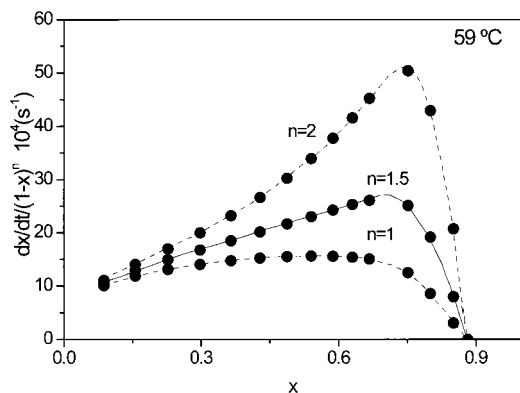
Figure 2 shows experimental values of reaction rates at 59°C plotted as  $(dx/dt)/(1 - x)^n$  versus  $x$ , for  $n = 1, 1.5$ , and 2. The value of  $n = 2$  (Horie's model) gives a very good fitting in a limited conversion range, as previously shown by Riccardi et al.<sup>4</sup> The fit is even better for  $n = 1.5$ , as pointed out by Carrozzino et al.<sup>27</sup> for a similar system.



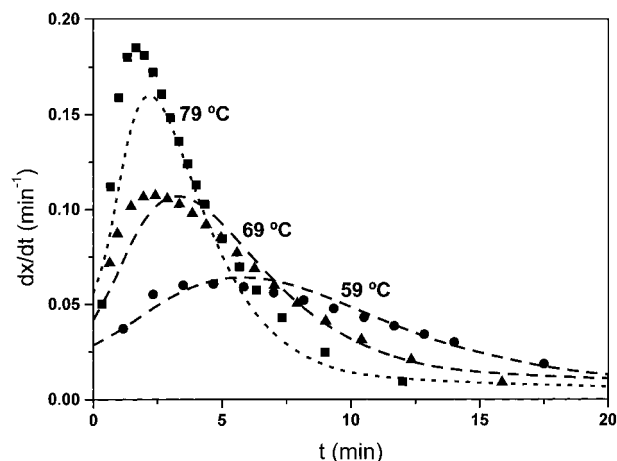
**Figure 1** Reaction rate as a function of conversion at constant temperatures; curves represent the data arising from isothermal DSC runs at 59, 69, and 79°C, whereas the points indicate the reaction rates obtained for the same temperature in dynamic runs.

However, these kinetic expressions could not fit the cure rates obtained under programmed heating-rate conditions.<sup>4</sup>

The fitting of the proposed kinetic model [eqs. (7) to (10)] with experimental data was made using the following procedure. Tables of  $dx/dt$ ,  $x$ , and  $T$ , using 20–25 conversion values evenly distributed in the conversion range, were built up from every experimental curve. In isothermal runs the experimental recorded values of temperature were selected for every point (they were almost constant, except in the initial 0–0.1 conversion range). An initial set of  $K(T)$ ,  $k_1(T)$ , and  $k_2(T)$  functions of the Arrhenius type was se-



**Figure 2** Experimental values of reaction rates at 59°C plotted as  $(dx/dt)/(1-x)^n$  versus  $x$ , for  $n = 1, 1.5$ , and 2.



**Figure 3** Fit of the kinetic model (continuous curves) with experimental values (squares) for isothermal DSC runs at 59, 69, and 79°C.

lected. Predicted  $dx/dt$  values were generated using eqs. (7), (9), and (10). The following summation, including every selected experimental point of isothermal and dynamic runs, was calculated:

$$S = \sum [(dx/dt)_{\text{exp}} - (dx/dt)_{\text{model}}]^2 / [(dx/dt)_{\text{max}}]^2 \quad (11)$$

where  $(dx/dt)_{\text{max}}$  is the maximum reaction rate for every subset of points pertaining to an isothermal or dynamic run. A minimum of the  $S$  function was searched using an optimization program that operates over the adjustable functions:  $K(T)$ ,  $k_1(T)$ , and  $k_2(T)$ . The best set obtained using this fitting procedure is as follows:

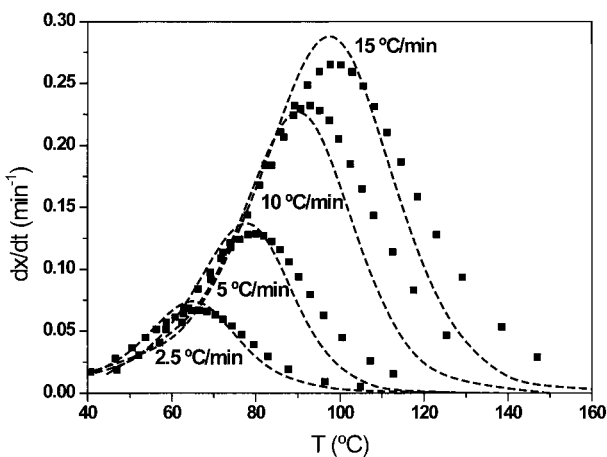
$$\ln K = -13.440 + 4854.0/T \quad (12)$$

$$\ln k_1(\text{min}^{-1}) = 12.337 - 5273.5/T \quad (13)$$

$$\ln k_2(\text{min}^{-1}) = 21.837 - 7567.4/T \quad (14)$$

Figures 3 and 4 show, respectively, the fit of experimental curves with the kinetic model for isothermal and dynamic scans. Taking into account the broad range of experimental conditions, the agreement may be considered satisfactory. Attempts to improve the fitting, by adding different possible equilibria to the reaction scheme,<sup>51–53</sup> were limited by the accuracy of the experimental information.

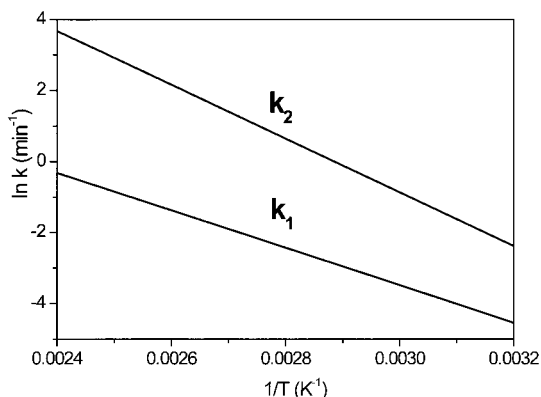
Figure 5 shows Arrhenius plots of the specific rate constants  $k_1$  and  $k_2$ . The specific rate constant for the reaction of E–OH with AH ( $k_2$ ) is



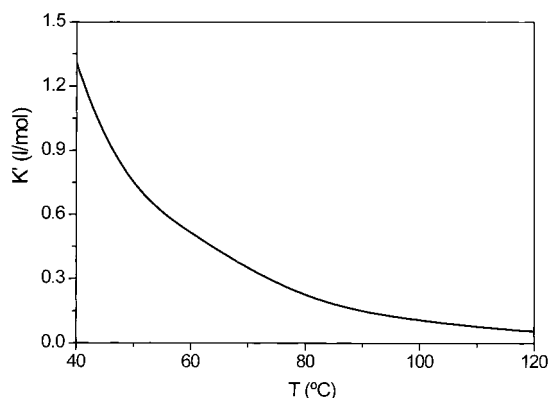
**Figure 4** Fit of the kinetic model (continuous curves) with experimental values (squares) for dynamic DSC runs at 2.5, 5, 10, and 15 °C/min.

significantly higher than the reaction of E with AH catalyzed by impurities ( $k_1$ ), in the temperature range of interest. However, the activation energy of the former ( $E_2 = 62.9$  kJ/mol) is higher than that of the latter ( $E_1 = 43.8$  kJ/mol).

Figure 6 represents the equilibrium constant for the formation of the E–OH complex,  $K'$  (L/mol) =  $K/e_0$ , as a function of temperature. An increase in temperature leads to a significant decrease in the concentration of the E–OH complex. Flamersheim<sup>54</sup> reported values of  $K' = 0.45$  L/mol at 90 °C for the phenyl glycidyl ether/cyclohexanol system, and  $K' = 1.05$  L/mol at 90 °C for the phenyl glycidyl ether/benzyl alcohol system. For the DGEBA/aniline system he used a value of  $K' = 0.7$  L/mol as an average in the 70–150 °C range.<sup>53</sup> Values shown in Figure 6 are somewhat



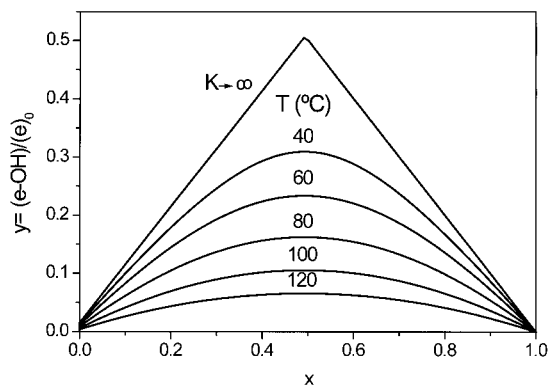
**Figure 5** Arrhenius plots of the specific rate constants  $k_1$  and  $k_2$ .



**Figure 6** Equilibrium constant for the formation of the E–OH complex,  $K'$  (L/mol) =  $K/e_0$ , as a function of temperature.

lower but still in the same range that those reported in the literature. However, we found that, to provide a reasonable fitting with experimental kinetic data,  $K'$  should decrease significantly with temperature.

Figure 7 shows the concentration of the epoxy–hydroxyl complex as a function of conversion, for several temperatures in the 40–120 °C range. The presence of a maximum is attributed to the competence between the increase in the concentration of total OH groups and the decrease in the concentration of total epoxy groups, with conversion. Increasing temperature leads to a significant decrease in the complex concentration and on the participation of the mechanism involving this complex in the overall reaction rate. The hypothetical curve for  $K \rightarrow \infty$  is indicated in Figure 7, representing the maximum possible concentration of E–OH complex as a function of conversion.



**Figure 7** Concentration of the epoxy–hydroxyl complex as a function of conversion for several temperatures. The limiting case of  $K \rightarrow \infty$  is indicated.

## CONCLUSIONS

A simple kinetic model consisting of an equilibrium reaction, generating an epoxy–hydroxyl complex and including two possible mechanisms for the consumption of amine hydrogens [(1) with free epoxy groups, (2) with the epoxy–hydroxyl complex], provided a reasonable fitting of calorimetric results obtained for a DGEBA–EDA system in isothermal and programmed heating-rate experiments. Horie's model was not able to provide such a fit.<sup>4</sup>

The fitting of experimental results required that the equilibrium constant decreases with temperature. This trend should be checked by independent measurements of the epoxy–hydroxyl equilibrium in nonreactive systems. The presence of other types of equilibria, as proposed by Mijovic et al.,<sup>51,52</sup> should not be discarded. But their inclusion in kinetic models requires the availability of accurate experimental information regarding the evolution of the concentration of every relevant species with conversion.

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