

# The Effect of Epoxy Excess on the Kinetics of an Epoxy–Anhydride System

A. N. MAURI, C. C. RICCARDI

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Av. J. B. Justo 4302, B7608FDQ Mar del Plata, Argentina

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**ABSTRACT:** The uncatalyzed cure of a commercial tetrafunctional epoxy monomer TGDDM (*N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane) with hexahydrophthalic anhydride (HHPA), using variable stoichiometric ratios is reported. The reaction was followed by differential scanning calorimetry (DSC). Two kinds of experiments were performed: (1) fresh samples were run at several heating rates, and (2) samples, precured a certain time in an oil bath at constant temperature (i.e., 80 to 120°C), were run at 10°C/min. Two peaks were observed in the case of the epoxy excess but only one for the stoichiometric formulation: the peak at low temperature was attributed to the epoxy copolymerization with the anhydride while the peak at high temperature was attributed to the epoxy homopolymerization. The catalytic effect of the OH groups present in the epoxy monomer on the copolymerization reaction was demonstrated by the decrease in the activation energy of the propagation step when increasing the epoxy excess. There is a catalytic effect of the copolymerization product on the homopolymerization reaction. Our simplest model, proposed previously for a catalyzed epoxy/anhydride system [*J. Polym. Sci. Part B: Polym. Phys. Ed.*, **37**, 2799 (1999)], can be used to fit both isothermal and dynamical kinetic data. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2342–2349, 2002

## INTRODUCTION

A simple kinetic model was recently proposed to study epoxy/anhydride polymerization initiated by tertiary amines.<sup>1</sup> It enabled us to provide an explanation of the inconsistencies found in previous kinetic studies. These inconsistencies may be summarized as follows: (a) first-order kinetics can fit both dynamic and isothermal differential scanning calorimetry tests, but with significantly different values of the apparent activation energy,<sup>2–5</sup> and (b) phenomenological autocatalytic kinetic expressions with different orders can also be used to fit kinetic results under both isothermal

and nonisothermal conditions, using a single value of the apparent activation energy.<sup>6–8</sup> The simplest polymerization model consists of two relevant steps: a reversible reaction transforming an inactive species (*i*) into an active one (*i*\*), and the usual propagation step where the monomer, *m*, reacts with the active specie. In this case *m* represents a couple of epoxy and anhydride groups because, once formed, the active epoxides at chain ends react almost immediately with anhydride monomers.<sup>9,10</sup> It was also assumed that the chain transfer step regenerated the active species.

In a previous study of a tetrafunctional epoxy monomer with hexahydrophthalic anhydride (HHPA), it was pointed out that OH groups, present as impurities in the technical epoxy, catalyze the epoxy–anhydride copolymerization, and that the epoxy homopolymerization reaction be-

Correspondence to: C. C. Riccardi (criccard@fi.mdp.edu.ar)

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comes significant in formulations containing epoxy excess. Although first-order kinetics can fit both isothermal and nonisothermal experiments, there was no coincidence between the calculated activation energy values.<sup>11</sup>

The aim of this article is to present and discuss experimental results related to the cure of a commercial tetrafunctional epoxy monomer with HHPA anhydride, using variable stoichiometric ratios, applying the model previously described and introducing the homopolymerization reaction in the kinetic model.

## EXPERIMENTAL

### Materials

The epoxy monomer used consisted mainly of *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM, Ciba-Geigy MY-720). The mass per epoxy group was 120.1 g, as determined by titration with perchloric acid. The theoretical value for pure TGDDM was 105.5 g, meaning that a significant amount of impurities is present in the commercial product. These have been identified as chlorohydrins, glycols, dimers, trimers, and higher oligomers.<sup>12,13</sup> The presence of a broad band at 3500 cm<sup>-1</sup> in the FTIR spectra showed that the product contains a significant concentration of OH groups. The mass per epoxy equivalent is 60.05 g/equiv.

The commercial anhydride used in this study was hexahydrophthalic anhydride (HHPA, Fluka) that had a melting point of 30–32°C and a theoretical mass per anhydride equivalent equal to 77 g/equiv.

### Techniques

#### Sample Preparation

Before mixing with anhydride, the epoxy monomer was degassed under vacuum for about 10 min at 50°C. The stoichiometric ratio was defined as:

$$r = \text{anhydride equiv/epoxy equiv}$$

Samples with *r* equal to 1, 0.7, 0.5, and 0.1 were analyzed. TGDDM-HHPA samples were prepared by mixing both components for about 10 min at 50°C. The solution remained homogeneous at room temperature, meaning that HHPA crystallization was inhibited upon cooling. It was veri-

fied that the reaction was not advanced during the mixing period.<sup>11</sup>

#### Differential Scanning calorimetry (DSC)

DSC measurements were performed under nitrogen atmosphere with a Shimadzu DSC-50, calibrated by standard procedures. Two kinds of experiments were performed: (1) fresh samples were run at different heating rates, *q*, varying between 0.5 and 20°C/min, and (2) samples with *r* equal to 0.5 and 0.7 precured a certain time in and oil bath at constant temperature (i.e., 80 to 120°C), were run at 10°C/min. Total and residual heat were obtained from these thermograms. Also, in both cases, the glass transition temperature, *T<sub>g</sub>*, was measured in a second scan at 10°C/min.

#### Dynamic-Mechanical Thermal Analysis (DMTA)

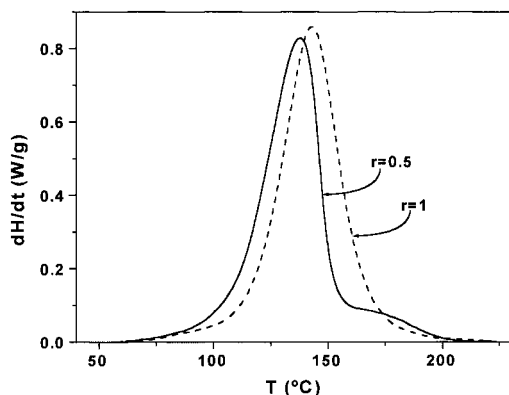
Plaques for subsequent dynamic mechanical characterization were obtained in a mold consisting of two glass plates coated with siliconized paper, spaced by a 2.5 mm rubber cord, and held together with clamps. The cure cycle employed was 2 h at 120°C and 2 h at 200°C. Specimens with dimensions 20 × 3.3 × 2.5 mm, were machined from the plaques. Dynamic mechanical spectra were obtained with a Perkin-Elmer DMA-7 system, operating at 1 HZ in the three-point mode at a heating rate of 10°C/min.

#### Fourier-Transformed Infrared Spectra (FTIR)

Filings of the plaques obtained for dynamic mechanical characterization were used to prepare KBr pellets of materials with *r* ≤ 1. Fourier-transformed infrared spectra were obtained in a Mattson Genesis II device in the 400–4000 cm<sup>-1</sup> range with a resolution of 2 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

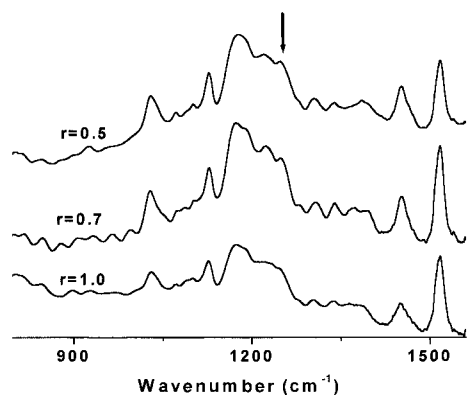
DSC scans of fresh samples prepared with different *r* ratios were made at several heating rates. Thermograms of samples prepared with epoxy excess (*r* < 1) and cured at *q* < 10°C/min show a shoulder at high temperatures. Figure 1 allows us to compare the symmetric aspect of the curve corresponding to the stoichiometric sample with the two peaks scan obtained with the epoxy excess. Bouillon et al. observed two peaks in the case of the epoxy excess but only one for *r* ≥ 1, in



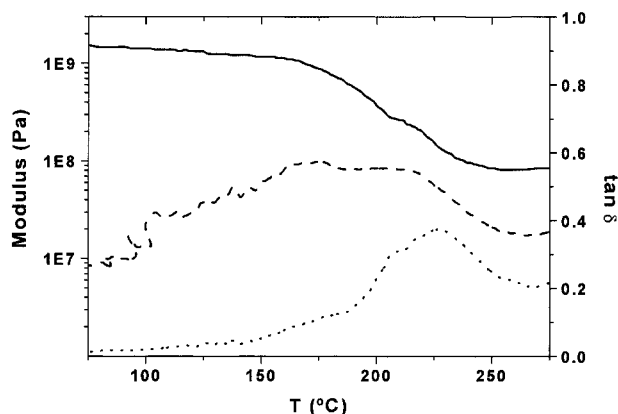
**Figure 1** DSC scans obtained at  $q = 5^\circ\text{C}/\text{min}$  for samples prepared with:  $r = 1$  (—) and  $r = 0.5$  (---).

thermograms of an epoxy/anhydride polymerization catalyzed by tertiary amines or by imidazoles. They attributed the peak at low temperature to the epoxy copolymerization with the anhydride and the one at high temperature to the epoxy homopolymerization.<sup>14</sup> The same effect was shown, for the system that is studied in this article, in dynamic scans of samples prepared with  $r = 0.5$  and precured at constant temperatures.<sup>11</sup>

Figure 2 shows the FTIR spectra for samples with  $r \leq 1$ . There is no evidence of the ether band expected at  $1150\text{--}1070\text{ cm}^{-1}$  for samples prepared with epoxy excess.<sup>15</sup> Steinmann, in her investigations on the curing of epoxy resins with HHPA, detected very small amounts of ether groups in  $^{13}\text{C}$ -NMR spectrum, but these groups, arising from the homopolymerization reaction, could not be detected by FTIR spectroscopy due to overlapping of the ether band with the ester peak at  $1120\text{ cm}^{-1}$ .<sup>16,17</sup> The main difference in the spectra is that the peak at  $1250\text{ cm}^{-1}$  is highest for the



**Figure 2** FTIR spectra for samples with  $r \leq 1$ .



**Figure 3** DMTA spectra for a sample prepared with  $r = 0.7$ : storage modulus (—), loss modulus (---) and  $\tan \delta$  (·····).

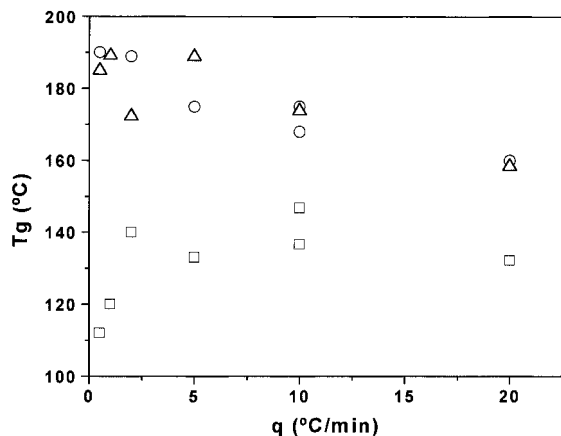
epoxy excess case as in the pure TGDDM spectra. Field et al.<sup>18</sup> studied several epoxy compounds, and concluded that this band corresponds to the epoxy group, implying that the homopolymerization reaction was not complete.

The dynamic mechanical spectra obtained for a fully cured sample, prepared with  $r = 0.7$ , is shown on Figure 3. Two glass transition temperatures can be observed in the storage and loss modulus and  $\tan \delta$  curves. They correspond to the copolymerization and the homopolymerization products. Curves of samples with  $r = 0.5$  have the same aspect, but those from the stoichiometric one show a single  $T_g$  value. Although in a second DSC scan at  $10^\circ\text{C}/\text{min}$  it is not possible to distinguish positively two  $T_g$ s, the values for formulations containing epoxy excess are higher than those corresponding to the stoichiometric system. The results shown in Figure 4 are in accord with the fact that the maximum  $T_g$  for epoxy anhydride formulations is usually reported for  $r < 1$ .<sup>14,19</sup> Within experimental error it is possible to notice that  $T_g$  values are constant for the stoichiometric formulation if  $q \geq 1$ , and that the highest  $T_g$  values for formulations containing an epoxy excess are measured for the smaller heating rates.

Figure 5 shows the reaction heat (expressed per anhydride equivalent) calculated from DSC thermograms. The average values obtained, over all heating rates, follow a linear relationship with the stoichiometric ratio:

$$\Delta H(\text{kJ/eq}) = 87.66 - 38.97r \quad (1)$$

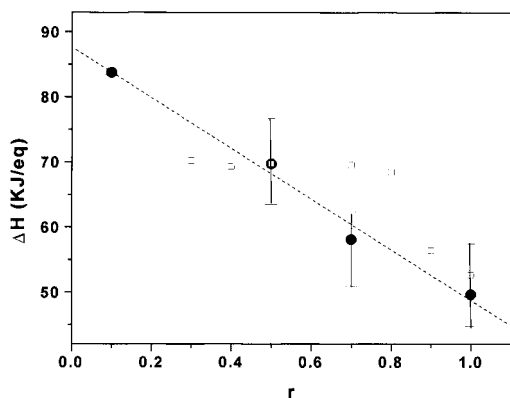
The extrapolated values obtained for homopolymerization ( $r = 0$ ), i.e.,  $87.66\text{ kJ/Eq}$  and for copo-



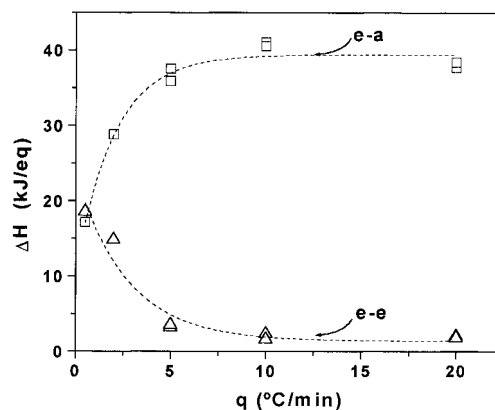
**Figure 4** Glass transition temperatures determined by calorimetry at 10°C/min for formulations with  $r$ : 1 ( $\square$ ), 0.7 ( $\circ$ ), and 0.5 ( $\triangle$ ).

lymerization ( $r = 1$ ), i.e., 48.69 kJ/Eq are very close to the values previously reported in the references.<sup>11,14,20,21</sup> This linear trend was also observed by Buillon et al. for samples prepared either with epoxy or anhydride excess.<sup>14</sup> The difference from our previous results could be due to the amount of impurities in the TGDDM batch or due to the number of scans made.<sup>11</sup>

The knowledge of total heat for each reaction lets us analyze the deconvolution of DSC scans made. Figure 6 shows heats of reaction for both the copolymerization (e-a) and the homopolymerization (e-e) reactions as a function of the heating rate in a material with  $r = 0.7$ . The homopolymerization reaction appears to be more signifi-



**Figure 5** Reaction heat (expressed per anhydride equivalent), as a function of the stoichiometric ratio. Closed symbols represent the arithmetical mean obtained with different heating rates. Open symbols correspond to ref. 11.



**Figure 6** Reaction heats for both the copolymerization (e-a) and the homopolymerization (e-e) reactions as a function of the heating rate in a material with  $r = 0.7$ .

cant at lower heating rates, and it seems that the copolymerization reaction is complete for  $q \geq 5^\circ\text{C}/\text{min}$  in accordance with results shown in Figure 4. Similar results are obtained for samples prepared with  $r = 0.5$ , but only two scans were made for samples with  $r = 0.1$  corresponding to heating rates of 2 and 10°C/min. Table I shows the average epoxy conversions,  $x$ , due to the e-e reaction, when it can be assumed that the e-a reaction is complete. The last column shows a similar percentage of epoxy excess that reacts by the homopolymerization reaction for stoichiometric ratios of 0.5 and 0.7: the material prepared with  $r = 0.1$  has a lower value. This result is in accord with the fact that, as was demonstrated with FTIR spectra (see Fig. 2), the homopolymerization reaction is not complete. Stevens had proved that hydroxyl groups catalyze this reaction,<sup>15</sup> and when the copolymerization reaction occurs, there are two sources of OH: the impurities in the technical-grade epoxy and the OH produced by the formation of a monoester intermediate in the copolymerization reaction.<sup>11</sup> Although the OH

**Table I** Epoxy Excess Reacted by the Homopolymerization Reaction

$r$	$x_{e-e}$	Epoxy Excess Reacted (%)
1.0	0	0
0.7	0.064	21.5
0.5	0.109	21.9
0.1	0.037	4.1

**Table II** Activation Energy for the Copolymerization Reaction

$r$	$E_{e-a}$ (kJ/mol)	Regression Coefficient
1.0	69.44	0.999
0.7	58.25	0.997
0.5	52.64	0.998

groups coming from the TGDDM are increased with the epoxy excess, those belonging to the monoester increase with the stoichiometric ratio, implying a strong catalytic effect of the e-a product on the homopolymerization reaction.

Peak temperatures,  $T_p$ , determined during peak deconvolution, were used to obtain the activation energy for each reaction by applying the Kissinger method.<sup>22</sup> In this method the activation energy,  $E$ , is determined from the slope of the following equation:

$$\ln \frac{q}{T_p^2} = C - \frac{E}{R T_p} \quad (2)$$

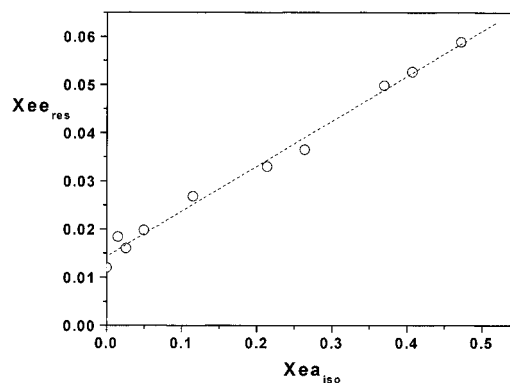
where  $C$  is a constant and  $R$  is the ideal gas constant. The error in the activation energy has been proved not to exceed 5%.<sup>23</sup> The corresponding plots of eq. (2) for each peak lets us obtain the activation energy values for the copolymerization,  $E_{e-a}$  and the homopolymerization,  $E_{e-e}$ . The results are shown in Table II. The increase in the epoxy excess diminishes  $E_{e-a}$ , showing the catalytic effect of the OH groups present in the commercial epoxy monomer. This trend was previously observed in the  $E_{e-a}$  values determined from the times to gel for formulations with  $r$  varying between 0.3 and 0.7 of this particular system; values are of the same magnitude.<sup>11</sup> For the homopolymerization reaction experimental points of  $r = 0.7$  and  $r = 0.5$  are more or less on a unique straight line and lead to an activation energy of 30.3 kJ/mol. This value is closest to the value for  $E_{e-e}$ , i.e., 24.5 kJ/mol, reported for the epoxy homopolymerization catalyzed with a tertiary amine.<sup>21</sup> The reality, that  $E_{e-a}$  is higher than  $E_{e-e}$ , and that the homopolymerization reaction takes place at the highest temperatures, is in accord with the catalytic effect of the e-a product.

The cure at low temperatures was analyzed to separate the epoxy/anhydride reaction from the epoxy homopolymerization. Formulations with stoichiometric ratios of 0.5 and 0.7 were precured

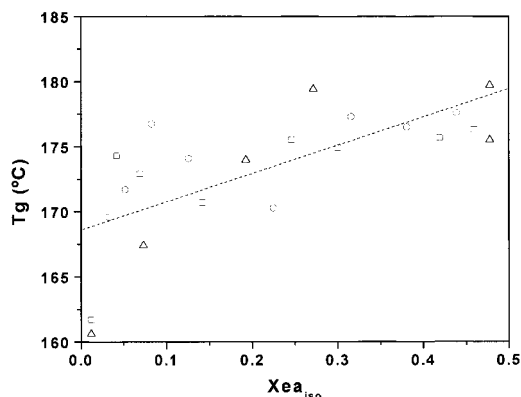
a certain time in an oil bath at constant temperature in the 80–120°C range. Residual reaction heats were obtained by calorimetry at 10°C/min.. After the deconvolution of the peaks, the epoxy conversions were obtained by assuming that the homopolymerization reaction is negligible during the isothermal cure. Figure 7 shows the epoxy conversion due to the homopolymerization reaction produced in the second step,  $xe-e_{res}$  vs. the epoxy conversion attained during the isothermal cure due to the copolymerization reaction,  $xe-a_{iso}$ , for a formulation with  $r = 0.5$  precured at 80°C. The extent of the homopolymerization reaction was obviously increased due to increased copolymerization reaction during the first cure step. It also suggests that the e-a products catalyze the homopolymerization reaction. The glass transition temperatures measured in subsequent DSC scan at 10°C/min shows the same trend as shown in Figure 8 for formulations with  $r = 0.5$ .

### Modeling the Kinetic Data

As was noted in the introduction section, there is a simple model that can fit both dynamic and isothermal data for the epoxy/anhydride copolymerization initiated by tertiary amines and that can explain the inconsistencies found in the literature.<sup>1</sup> In this work, the model was applied to the uncatalyzed system, taking into account the homopolymerization reaction. The steps taken into account are: (1) a reversible reaction transforming an inactive species of an initiator ( $i$ , i.e., the OH groups initially presents as impurities in the epoxy monomer) into an active one ( $i^*$ ), (2) the



**Figure 7** Epoxy conversion due to the homopolymerization reaction,  $xe-e_{res}$  vs. the epoxy conversion attained during the isothermal cure,  $xe-a_{iso}$ , at 80°C for formulations with  $r = 0.5$ .



**Figure 8** Glass transitions temperatures of samples with  $r = 0.5$  precured isothermally at  $T$ : 80 (□), 100 (○), and 120°C (△), and postcured at a constant heating rate of 10°C/min.

propagation step in which both the anhydride (**a**) and the epoxy (**e**) monomer react as a couple, and (3) a reversible homopolymerization reaction catalyzed by the **e**-**a** product. The third step was defined as reversible to consider the possibility of regeneration steps. The following kinetics equations result from this model:

$$\frac{di}{dt} = -k_1 i + k_1 i^* \quad (3)$$

$$\frac{di^*}{dt} = k_1 i - k_1 i^* \quad (4)$$

$$\frac{da}{dt} = -k_2 i^* a \quad (5)$$

$$\frac{de}{dt} = -k_2 i^* a - k_3 (a_0 - a)e + k_3 p \quad (6)$$

where the subindex 0 means initial condition and  $p$  is the homopolymerization product; its concentration can be calculated with the molar balance:

$$p = e_0 - e - a_0 + a \quad (7)$$

For formulations containing the stoichiometric epoxy/anhydride ratio only the steps (1) and (2) must be taken into consideration. Figure 9 shows results fitting the dynamic differential scanning calorimetry runs, expressed as epoxy conversion versus temperature. The agreement between the experimental points and the model is good except

for high conversions ( $x > 0.85$ ); these may be explained by diffusional restrictions associated to vitrification.<sup>11</sup> The resulting dimensionless constants are:

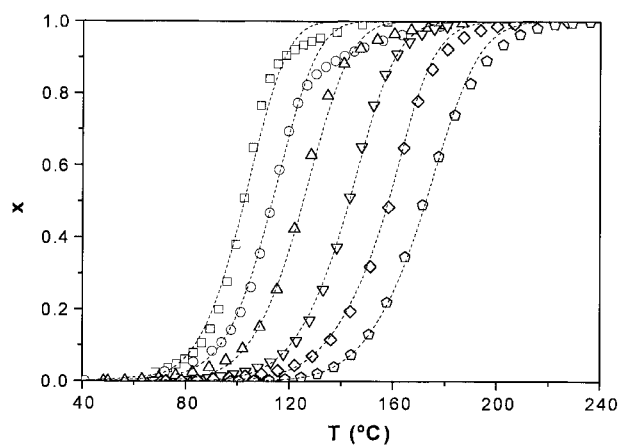
$$\ln k_1 = 12.20 - \frac{7034.83}{T} \text{ s}^{-1} \quad (8)$$

$$\ln k_1' = -6.27 - \frac{900.04}{T} \text{ s}^{-1} \quad (9)$$

$$\ln k_2 = 14.27 - \frac{8193.27}{T} \text{ s}^{-1} \quad (10)$$

The activation energies corresponding to the reversible first step are 58.48 and 7.47 kJ/mol, and are in agreement with those reported for the epoxy/anhydride copolymerization initiated by tertiary amine.<sup>1</sup> The value of the activation energy for the second step, i.e., the propagation one, is 68.12 kJ/mol, very close to that determined with Kissinger's method (see Table II).

Only the steps (1) and (2) must be taken into consideration for materials cured isothermally at low temperature, providing that the homopolymerization reaction is negligible. The fitting for formulations with epoxy excess was made with the  $k_1$  and  $k_1'$  reported for the stoichiometric formulation and given by eqs. (8) and (9). The excellent concordance of the model with the experimental points is shown in Figure 10 for a material formulated with  $r = 0.7$ ; similar fitting results were obtained for a system made with  $r = 0.5$ . The dimensionless  $k_2$  expressions for  $r = 0.7$  and



**Figure 9** Epoxy conversion,  $x$ , vs. temperature in the stoichiometric system at different  $q$ : 0.5 (□), 1 (○), 2 (△), 5 (▽), 10 (◇), and 20°C/min (pentagon shaped).

$r = 0.5$  are given by eqs. (11) and (12), respectively

$$\ln k_2 = 12.46 - \frac{7178.75}{T} \text{ s}^{-1} \quad (11)$$

$$\ln k_2 = 11.35 - \frac{6641.94}{T} \text{ s}^{-1} \quad (12)$$

and the corresponding activation energies are 59.68 and 55.21 kJ/mol. These values agree with the trend shown in Table II due the catalytic effect of the OH groups present in the epoxy monomer.

In the fitting analysis of DSC scans of samples, precured isothermally and those of fresh samples run at several heating rates, for formulations containing epoxy excess, the three steps of the model must be taken into consideration. From the residual reaction heat data the dimensionless  $k_3$  and  $k_{3'}$  expressions for  $r = 0.7$  are:

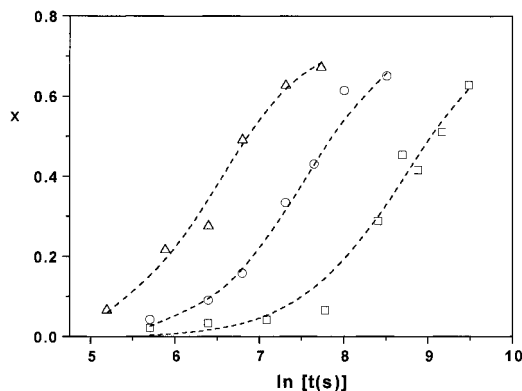
$$\ln k_3 = -0.65 - \frac{3493.656}{T} \text{ s}^{-1} \quad (13)$$

$$\ln k_{3'} = 10.17 - \frac{7767.391}{T} \text{ s}^{-1} \quad (14)$$

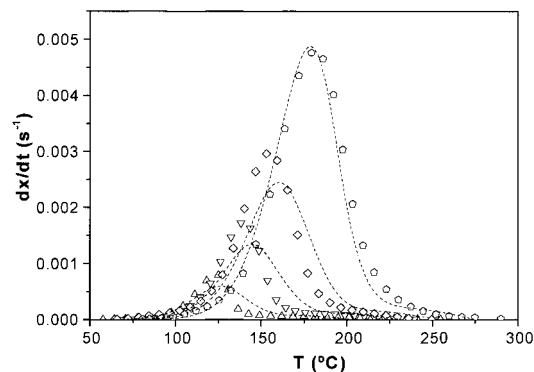
and the corresponding expressions for  $r = 0.5$  are:

$$\ln k_3 = 0.10 - \frac{3606.78}{T} \text{ s}^{-1} \quad (15)$$

$$\ln k_{3'} = 13.41 - \frac{9080.95}{T} \text{ s}^{-1} \quad (16)$$



**Figure 10** Epoxy conversion,  $x$ , vs. the natural logarithm of curing time,  $t$ , of samples with  $r = 0.7$  precured isothermally at  $T$ : 80 ( $\square$ ), 100 ( $\circ$ ), and 120°C ( $\triangle$ ).



**Figure 11** Dash lines represents the model prediction for the experimental points obtained with  $r = 0.7$  at different  $q$ : 2 ( $\triangle$ ), 5 ( $\nabla$ ), 10 ( $\diamond$ ), and 20°C/min (pentagon shaped).

The calculated activation energies for the homopolymerization direct reaction, for systems having  $r = 0.7$  and  $r = 0.5$ , are 29.04 and 29.99 kJ/mol, respectively. These values are very close to that arising from the Kissinger method (see Table II). The calculated activation energies for the reverse reaction are 64.57 and 75.50 kJ/mol, but do not provide proof for this mechanism considering the small extent of the homopolymerization reaction shown in Figure 7.

The predictions of the model for the kinetic data from of DSC scans of fresh samples, and calculated with constants given with eqs. (8)–(16), show reasonable agreement with the experimental points considering the differences between the two kinds of experimental procedures. Figure 11 shows these results for the  $r = 0.7$  formulation.

## CONCLUSIONS

This study of the uncatalyzed cure of a commercial tetrafunctional epoxy monomer with HHPA anhydride, using variable stoichiometric ratios, revealed the following features:

1. The catalytic effect of the OH groups present in the epoxy monomer on the copolymerization reaction was demonstrated by the decrease in the activation energy of the propagation step when increasing the epoxy excess.
2. The homopolymerization reaction takes place in formulations with epoxy excess at high temperatures, which do not go to completion.

3. The copolymerization products produce a catalytic effect on the homopolymerization reaction.
4. The reaction heat, expressed per anhydride equivalent, follows a linear relationship with the stoichiometric ratio.
5. The simplest model proposed previously for a catalyzed epoxy/anhydride system, can be used to fit both isothermal and dynamical kinetic data for a noncatalyzed epoxy/anhydride system.<sup>1</sup>
6. It is necessary to continue the study with higher epoxy excess to clarify the mechanism of the homopolymerization reaction, due to the low etherification extent produced in this system.

## REFERENCES

1. Riccardi, C. C. Dupuy, J.; Williams, R. J. J. *J Polym Sci Part B Polym Phys Ed* 1999, 37, 2799.
2. Mauri, A. N.; Galego, N.; Riccardi, C. C.; Williams, R. J. J. *Macromolecules* 1997, 30, 1616.
3. Galante, M. J.; Oyanguren, P. A.; Andromaque, K.; Frontini, M. P.; Williams, R. J. J. *Polym Int* 1999, 48, 642.
4. Fava, R. A. *Polymer* 1968, 9, 137.
5. Peyser, P.; Bascom, W. D. *J Appl Polym Sci* 1977, 21, 2359.
6. Montserrat, S.; Málek, J. *J Thermochim Acta* 1993, 228, 47.
7. Montserrat, S.; Flaqué, C.; Pagés, P.; Málek, J. *J Appl Polym Sci* 1995, 56, 1413.
8. Montserrat, S.; Flaqué, C.; Calafell, M.; Andreu, G.; Málek, J. *J Thermochim Acta* 1995, 269/270, 213.
9. Matejka, L.; Lovy, J.; Pokorny, S.; Bouchal, K.; Dušek, K. J. *J Polym Sci Polym Chem Ed* 1983, 21, 2873.
10. Dušek, K. J. *Adv Polym Sci* 1986, 1, 78.
11. Corcuera, M. A.; Mondragón, I.; Riccardi, C. C.; Williams, R. J. J. *J Appl Polym Sci* 1997, 64, 157.
12. Dobás, I.; Lunák, S.; Podzimek, S.; Mach, M.; Spacek, V. In *Crosslinked Epoxies*; Sedláček, B.; Kahovec, J., Eds; de Gruyter: Berlin, 1987, p. 81.
13. Hagnauer, G. L.; Pearce, P. J. In *Epoxy Resins Chemistry II*; Bauer, R. S., Ed.; ACS Symp Series 221; American Chemical Society: Washington, DC, 1983, p. 193.
14. Bouillon, N.; Pascault, J. P.; Tighzert, L. *J Appl Polym Sci* 1989, 38, 2103.
15. Stevens, G. C. *J Appl Polym Sci* 1981, 26, 4259.
16. Steinmann, B. *J Appl Polym Sci* 1989, 37, 1753.
17. Steinmann, B. In *Crosslinked Epoxies*; Sedláček, B.; Kahovec, J., Eds.; Walter de Gruyter: Berlin, 1987, p. 117.
18. Field, J. E.; Cole, J. O.; Woodford, D. E. *J Chem Phys* 1950, 18, 1298.
19. Guerrero, P. E.; De la Caba, K.; Valea, A.; Corcuera, M. A.; Mondragón, I. *Polymer* 1996, 37, 2195.
20. Klute, C. H.; Viehmann, W. *J Appl Polym Sci* 1961, 5, 86.
21. Vazquez, A.; Bentaleb, D.; Williams, R. J. J. *J Appl Polym Sci* 1991, 43, 967.
22. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
23. Criado, J. M.; Ortega, A. *J Non-Cryst Solids* 1986, 87, 302.