

Epoxy–Amine Oligomer Production

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Synopsis

The production of an adduct epoxy–polyetheramine with free epoxy groups is analyzed. Differential scanning calorimetry (DSC), infrared spectroscopy (IR), titration of functional groups, and gel permeation chromatography (GPC) were used to study the reaction of bisphenol A diglycidyl ether (DER 332) with an aliphatic hindered polyether–amine (Jeffamine D-2000). The general kinetic model derived by Riccardi and Williams¹ is extended to generate equations for nonstoichiometric epoxy–amine systems. The parameter N , which gives the reactivity ratio between the secondary and primary amine groups, was obtained from a linear regression obtained at various temperature levels. The activation energies of the epoxy amine reaction catalyzed by OH groups and the noncatalytic one were determined. According to experimental evidence, the etherification reaction may be neglected. From dynamic experiments in DSC a heat of reaction of 25 kcal/eq was obtained. The weight average molecular weight of different epoxy–amine oligomers with high ratio of epoxy–amine were compared with those theoretically predicted using an statistical structural model (SSM). This model utilizes a kinetic scheme and a recursive method to determine statistical parameters and it was applied before to phenolic resins^{2,3} and epoxy–amine systems.⁴ Depending on the required oligomer characteristics, the best production policy can be established using the data supplied in this report.

INTRODUCTION

The flexibility and toughness of epoxy systems are usually enhanced by including polyether–amine products. The physical and morphological properties of epoxies cured with hindered and unhindered amines may be different because of their inherent reactivity differences. As well, the extent to which the etherification reaction [epoxy–(OH) groups] takes place depends on the particular system under consideration. In order to prepare low molecular weight epoxy oligomers for processing in reaction injection molding (RIM), a kinetic study of the reaction of commercial hindered polyether–amine modifiers with bisphenol A diglycidyl ether was carried out. Different aspects related to kinetic studies of hindered amine–epoxy systems by DSC technique are discussed. The modeling of the production of this oligomer will permit easier modification of the adduct characteristics in order to handle further crosslinking reactions, phase separation, and final product properties in the RIM process.

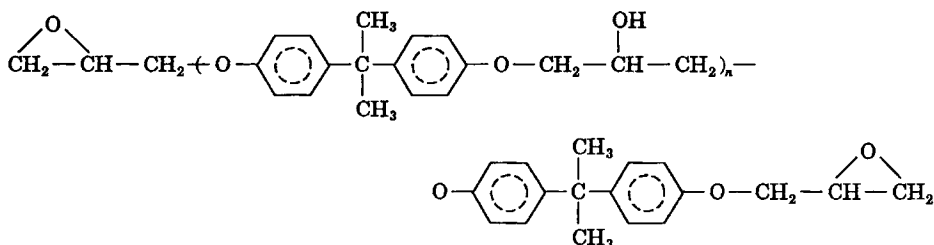
The aim of this paper is to establish the way to select the appropriate policy of production of different epoxy–amine adducts. The kinetic study and the statistical analysis of the oligomer formation permit the prediction of weight

average molecular weights arising from different process conditions that are in good agreement with experimental results.

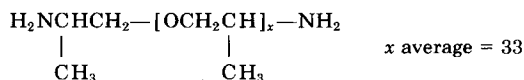
EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (DGEBA), DER 332 (Dow Chemical) with the following structure:



The epoxy content was 5.69 eq/kg as determined by titration (weight per equivalent, WPE = 175.84 g/eq, Technique V.b). This corresponds to $n = 0.04056$ in the structural formula. The resin was degassed at 85°C (oil bath) under vacuum (30 mm Hg) before use. The amine was a polyether-amine, Jeffamine D-2000, provided by Texaco, $M_n = 1840$, $D = 1.08$, and WPE = 526 g/eq. The supplier data shows the following formula:



A small amount of residual (OH) groups and unsaturations are present in Jeffamine D-2000. The production process involves the exchange of secondary hydroxyl groups of polypropylene oxide for amine groups. Typical commercial polypropylene oxides diols have unsaturations and a functionality of 1.9. Then, the final product is 90% capped with $\dot{\text{N}}\text{H}_2$ groups. This chemical was degassed at 45°C under vacuum before use. DER 332 is considered to be difunctional and the equivalent ratio r will be defined by: eq epoxy/eq hydrogen in the amine.

Techniques

Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter DuPont 910 with a DuPont 2000 computer/thermal analyzer system have been used to measure heat of reaction, residual heat, and heat capacity of reactants and products.

Two methods were applied: Isotrack and Scan. Both work with hermetic pans and sample mass in the range of 5–10 mg. The Isotrack technique permits a good control of constant temperature of the sample itself and a simultaneous plot of reaction rate and sample temperature vs. time (see Fig. 1).

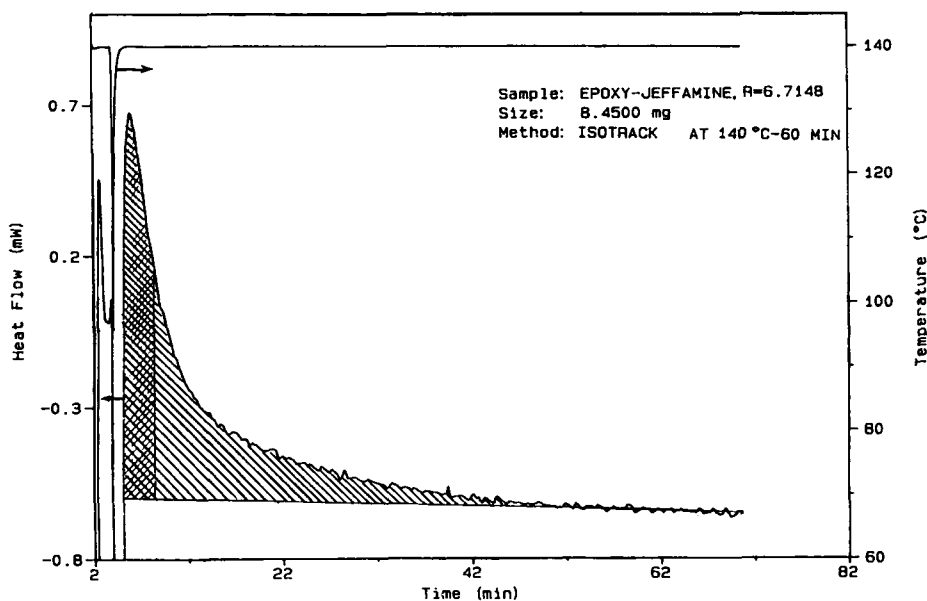


Fig. 1. Reaction of epoxy resin with Jeffamine D-2000 using Isotrack mode of the DSC at 140°C.

The cell was stabilized at the required temperature. The sample contained in a hermetic capsule was positioned and the run started. This procedure diminished the extent of premature reaction which took place during the stabilization period when the sample was placed before the initial heating up.

For a given time the conversion was calculated using

$$x = A(t)/A(\infty)$$

where $A(t)$ is the heat of reaction calculated from the area under the peak and $A(\infty)$ represent the total heat of reaction arising from isothermal runs at 140°C. Considering the heat evolved in the reaction between epoxy and amine groups, the overall kinetics of epoxy consumption is obtained from calorimetric information.

The reaction rate arises from

$$dx/dt = (dH/dt)/A(\infty)$$

where x = epoxy conversion, dH/dt = heat flow, DSC signal (mW) (Fig. 1), and $A(\infty)$ is expressed in energy units. Due to the big difference in reactivity between primary and secondary amine for the kinetic study the ISOTRACK technique was applied only at 130 and 140°C. Below this range of temperature the conversion of epoxy groups was followed by titration.

The equipment was calibrated in the temperature range of 20–250°C by determining heat of fusion, heat capacity, and transition peak temperatures of Indium, Al₂O₃ and ammonium thiocyanate, respectively. The transition of am-

monium thiocyanate from monoclinic to rhombic (92°C) and the melting point (149.6°C) permit a two-point calibration.

Gel Permeation Chromatography (GPC)

GPC was used to determine the molecular weight of reactants and products. The equipment was a Waters Model 590 chromatograph with tetrahydrofuran (THF) as the mobile phase and a flow rate of 1 mL/min. The high initial epoxy-amine equivalent ratio used in the production of the oligomers and the high molecular weight of the amine permitted neglect the solvation effects caused by hydrogen bridges between the oxygen of THF and the hydroxyl groups in the polymeric chain were not considered. The GPC calibration was based on standard polystyrene. A column set Waters Styragel 100, 500, 1000, and 10,000 A dual detection by UV spectrophotometer (23°C, 250 nm) and a differential refractometer (40°C) were employed.

Viscometry

In order to measure the dynamic viscosity of the oligomer produced a viscometer Rheomat 30, rotor C4, thermally controlled in a silicon oil bath, was used (see Fig. 2).

Infrared Spectrophotometry (IR)

A Unicam SP1000 spectrophotometer and different sampling methods, KBr pellets, capillary films on ClNaA monocrystals and quartz windows were applied.

The Jeffamine contribution to the ether band at 1120 cm^{-1} and the overlapping of peaks in the area of epoxy groups at 910 cm^{-1} limited the qualitative analysis to the range 2000–4000 cm^{-1} (hydroxyl and amine groups).

Determination of Epoxy Groups Content (eq/100 g Sample)

(a) Argentimetric method for analysis of epoxides containing amines.⁵ This method involves a hydrochlorination reaction followed by measuring the consumption of chloride ions.

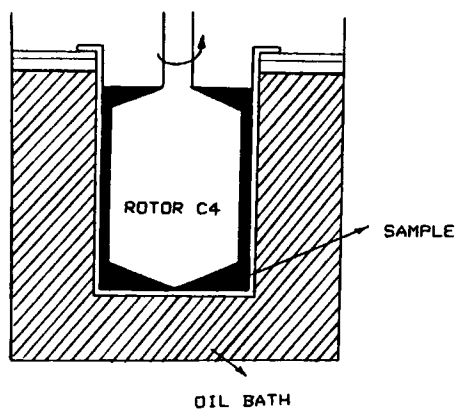


Fig. 2. Viscometer Rheomat 30.

(b) Hydrochlorination reaction (0.2N ClH in dioxane). The acid in excess is determined by titration with standard alkali (0.1N NaHO).

Determination of Amine Content

For primary and total amine the methods ST 5.34 and ST 5.22 developed by Texaco were applied.⁶ The content of tertiary amino groups was determined by direct titration with perchloric acid after acetylation of primary and secondary groups with acetic anhydride.⁷

RESULTS

Heat of Reaction

A DSC scan at 20°C/min of a freshly mixed sample ($r = 5.882$) is shown in Figure 3. The two exothermic peaks represent the primary and secondary amine hydrogen reactions. Similar behavior was reported by Sabra and Pascault⁸ for the epoxy-cycloaliphatic diamine (menthane diamine, MNDA) system. Donellan and Roylance⁹ have found that the primary hydrogen of MNDA reacts slowly at room temperature to form a linear polymer. Iso-track experiments with fresh mixtures at 140°C showed negligible reaction after 45 min (Fig. 1). The residual heat measured after 1.5 and 2.5 h at this temperature was equal to 10% of the total heat evolved in the isothermal run.

Titration of functional groups showed a complete epoxy-amine reaction at 140°C. The residual reaction is associated with a controlled consump-

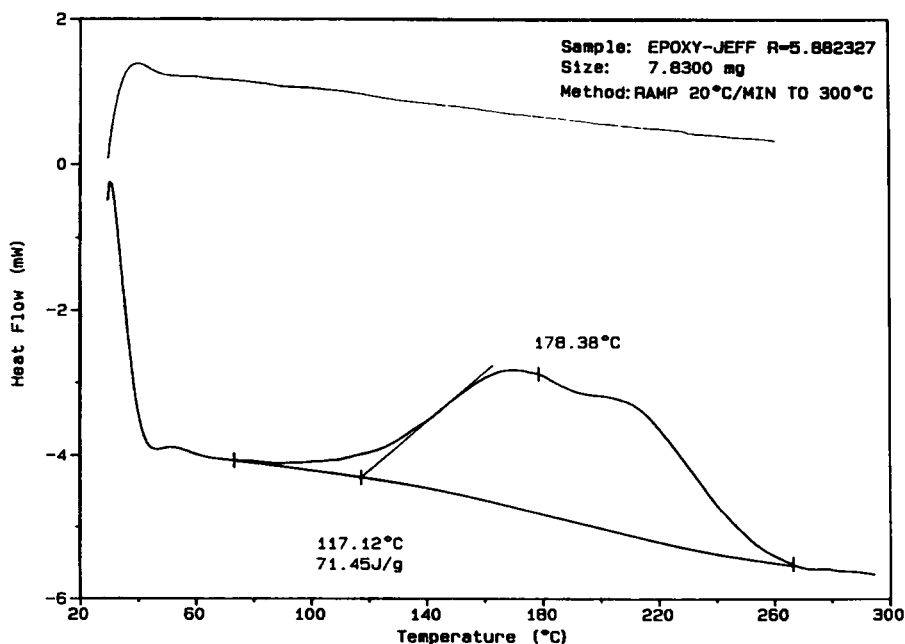


Fig. 3. Reaction of epoxy resin with Jeffamine D-2000 using the dynamic mode of the DSC. Heating rate: 20°C/min.

tion of epoxy groups and a small increase of the weight average molecular weight (GPC). This behavior seems to be related to a reaction of the epoxy group with another functional group present in the Jeffamine product. The average heat of reaction arising from the area under the peaks (isothermal and dynamic experiments at 20°C/min) was 25 ± 0.5 kcal/eq. This value is in good agreement with results reported for several epoxy-amine systems.^{1,10-12} Horie et al. have reported a value of $24.5 + 0.6$ kcal/eq for the reaction of phenyl glycidyl ether with butylamine taken as a model system.¹³

Figure 4 shows the predicted adiabatic increase in temperature vs. equivalent ratio. The results are based on heat capacity (C_p) measurements, DSC technique, $C_p = 1.84$ J/g °C. Figures 5 and 6 show DSC curves obtained at 10°C/min. Two more runs were performed with the same sample, which was quench-cooled after each run in order to stop the chemical reaction. No residual heat appeared in the second run at 5°C/min. The peaks of the epoxy amine reaction are overlapped by another small one originating in the reaction of epoxy with another functional group present in the amine reactant. According to the results obtained from different runs, the calorimetric information is a function of the heating rate range of 5–20°C/min. At 5°C/min or lower program rates, no residual heat appeared in the second run. The residual heat increase with the program rate applied in the first run. Above 20°C/min, the residual heat was a constant value close to 10% of the total heat expected for the epoxy-amine reaction. Evaluation of residual heat (technique 1) in samples of different equivalent ratios, reacted 7 days at 75°C and 2 h at 140°C, showed it to be 10% of the total heat expected for the epoxy-amine reaction (Fig. 7).

Weight Average Functionality of the Amine

The adduct is obtained by copolymerization of DER 332 (E2) with Jeffamine D-2000 (A). Defining

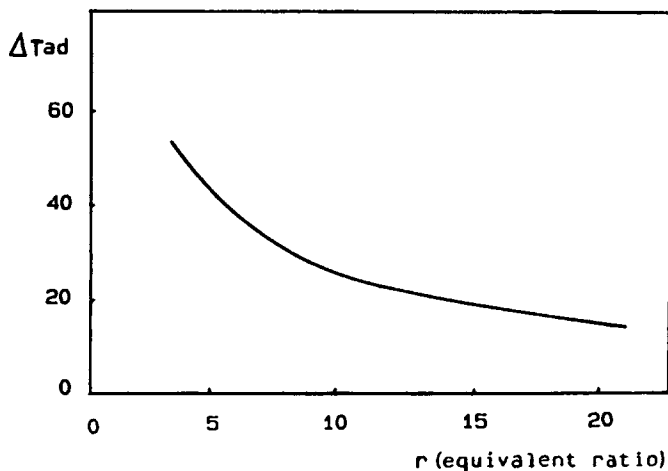


Fig. 4. Adiabatic temperature increase (ΔT_{ad}) predicted for the epoxy-Jeffamine formulation vs. equivalent ratio.

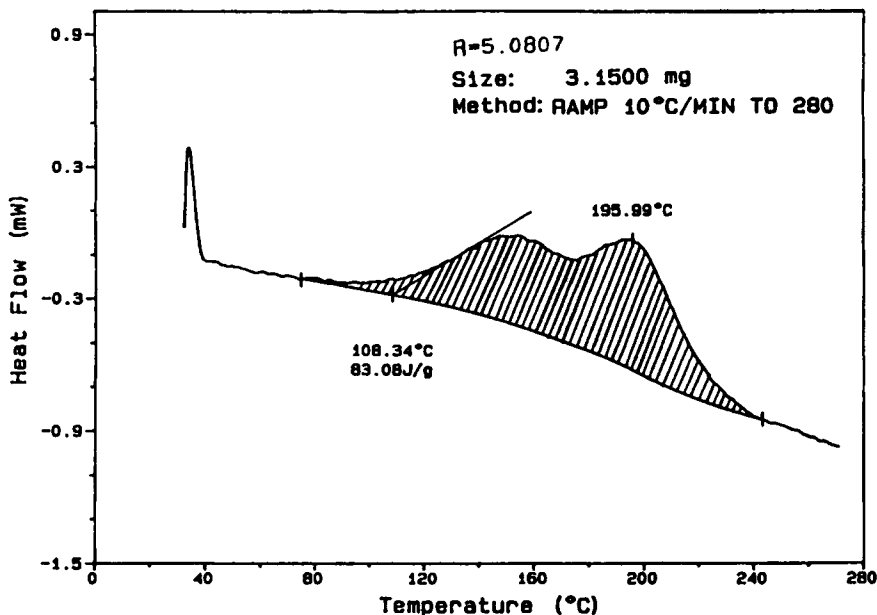


Fig. 5. Reaction of epoxy resin with Jeffamine using dynamic mode of the DSC. Heating rate: 10°C/min.

$$r = \text{initial equivalent ratio} = E_0/A_0$$

$$p_a = r * p_e = \text{fraction of } A_0 \text{ reacted} = (A_0 - A)/A_0$$

the polymerization of a mixture E_2 -A with $r \geq 1$ to $p_a = 1$ will give a solution of molecules (polyfunctional and polydisperse) with residual epoxy groups unreacted.

Following the Macosko-Miller statistical approach,¹⁴⁻¹⁶ one can obtain the critical equivalent ratio to produce a gel:

$$r_{\text{gel}} = (f - 1) * (g - 1)$$

where f and g are the weight average functionalities of amine and epoxy, respectively.

It was assumed that the above system fulfilled the main assumptions of the statistical treatment:

- The reactivity of the epoxy groups in DER 332 and the amino groups in Jeffamine can be regarded as independent.
- No cyclization.
- Due to the complete reaction of the amine groups the unequal reactivity—termed induced asymmetry of first shell substitution effect (FSSE)—does not affect the results.

Samples with different equivalent ratio ($2 < r < 4$) were degassed and reacted at 75°C for 9 days in sealed glass tubes. The sol fraction was extracted with a

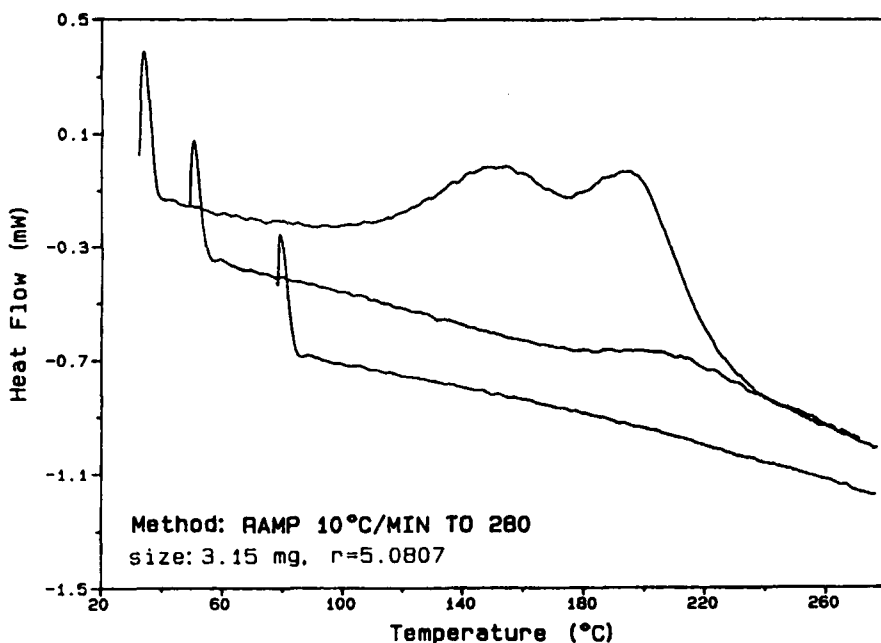


Fig. 6. Reaction of epoxy resin with Jeffamine and residual heat evaluation using dynamic mode of the DSC. Heating rate: 10°C/min.

mixture toluene-isopropyl alcohol (3/2 v/v) or dioxane. Both solvents gave the same results. The lower and upper equivalent ratio values found for gel and completely soluble samples were 2.65 and 2.70. From r_{gel} the weight average functionality of the amine is found to be $f = 3.68$. Assuming etherification and cyclization negligible, the weight average functionality of the adduct, g_w , at full conversion of amine groups can be predicted from

$$g_w = (r - 1) * g / [r - (f - 1) * (g - 1)]$$

According to the previous results, adducts have been prepared from mixtures with $r > 2.68$.

KINETIC STUDY

Experimental

Samples with different equivalent ratio, $4 < r < 24$, were reacted at constant temperature following two different methods selected according to the temperature level analyzed.

Method I: Temperature Range 70–110°C

After preheating reactants, ampoule experiments were carried out under stirring, and either vacuum conditions (30 mm Hg) or N_2 atmosphere. Due to the low adiabatic temperature increase possible for this high epoxy-amine

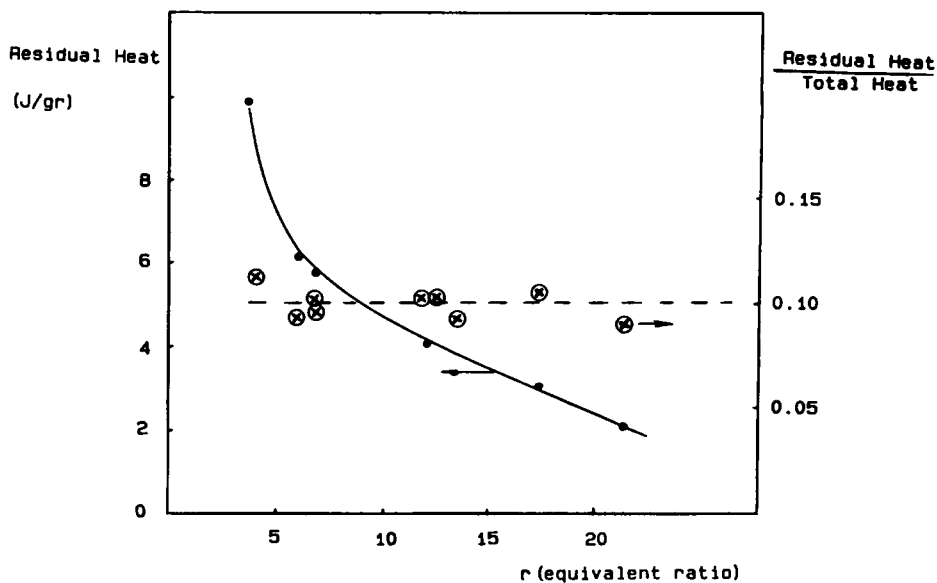


Fig. 7. Residual heat (DSC, 5°C/min) in samples reacted 7 days at 75°C and 2 h at 140°C. Total heat = heat of reaction epoxy-amine.

equivalent ratio system and the characteristic step reactions, the samples were at constant temperature along the experiments. Mixtures of 100 mL were reacted at constant temperature with the glass container immersed in an oil bath. The conversion of functional groups was followed by titration.

Method II: Temperature Range 130–140°C

Small samples were hand mixed and 5–10 mg were placed in hermetic pans. DSC technique in Isotrack control was applied. The sample was introduced once the desired temperature was established.

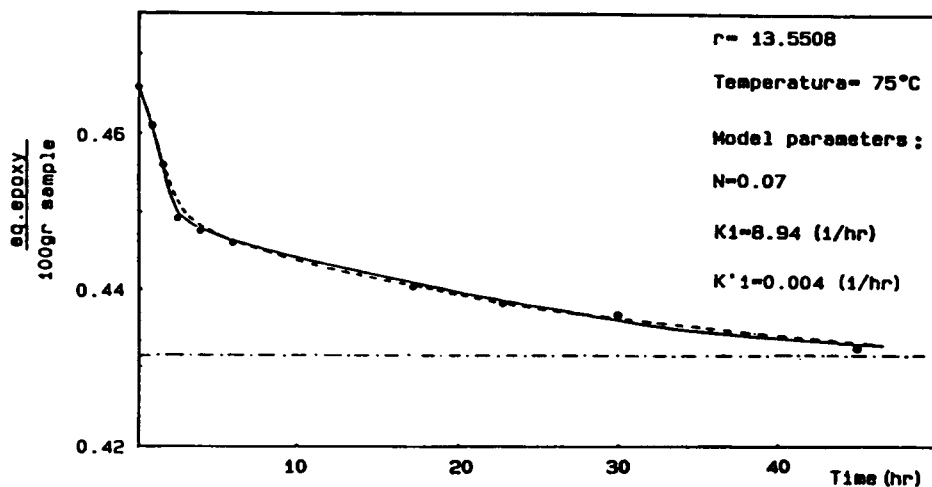
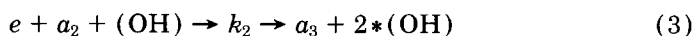
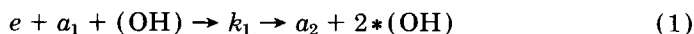


Fig. 8. Concentration of epoxy groups at constant temperature vs. time: (—) experimental, titration technique; (---) predicted by the statistical structural model.

The conversion was estimated using technique 1 (Fig. 1). Total and fractional areas were estimated by weighing paper of uniform thickness. Figures 8, 9, and 10 show typical results of concentration of epoxy groups (eq epoxy/100 g sample) vs. time. The dashed line at the bottom is the lower value expected for a full conversion of amine without etherification reaction.

Kinetic Model

The general kinetic model derived by Riccardi and Williams¹ was extended to generate equations for nonstoichiometric epoxy-amine systems. Given the following scheme of reactions:



where e = concentration of epoxy, a_1 = concentration of primary amine hydrogens, a_2 = concentration of secondary amine hydrogens, k = specific constant for the catalytic reaction rate, and k' = specific constant for the noncatalytic

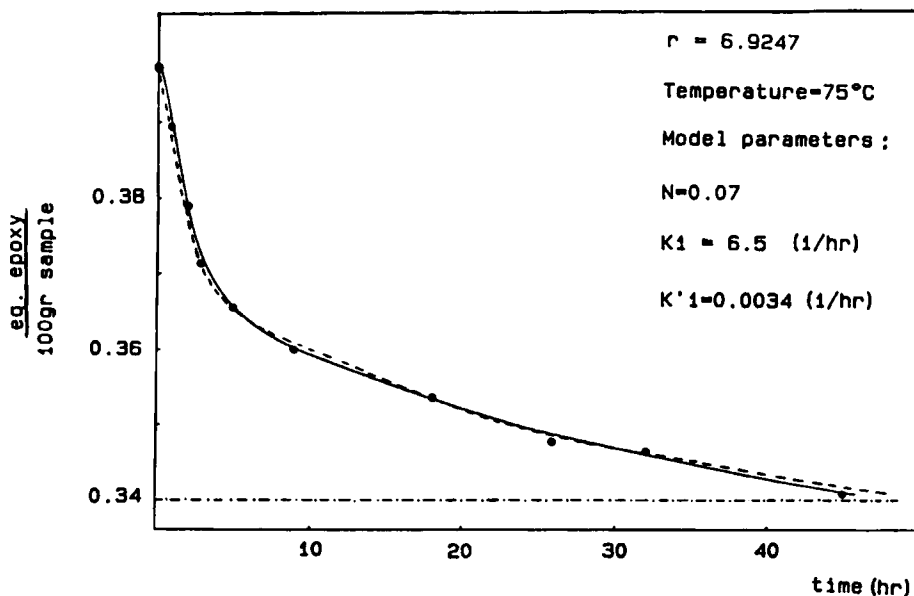


Fig. 9. Concentration of epoxy groups at constant temperature vs. time: (—) experimental, titration technique; (---) predicted by the statistical structural model.

reaction rate (subscripts 1, 2, and 3 indicate the possible reaction paths). Defining

$$N = [k'_2 + k_2 * (\text{OH})] / [k'_1 + k_1 * (\text{OH})] \quad (7)$$

$$L = [k'_3 + k_3 * (\text{OH})] / [k'_1 + k_1 * (\text{OH})] \quad (8)$$

$$K'_1 = k_1 * e_0 \quad (9)$$

$$K_1 = k_1 * e_0^2 \quad (10)$$

$$x = (e - e_0) / e_0 \quad (11)$$

$$\alpha = a_1 / a_{10} \quad (12)$$

$$r = e_0 / a_{10} > 2.68 \quad (13)$$

the following kinetic equations may be written:

$$-de/dt = e * (k'_1 + k_1 * (\text{OH})) * [a_1 + N * a_2 + L * (\text{OH})] \quad (14)$$

$$-da_1/dt = 2 * a_1 * e * [k'_1 + k_1 * (\text{OH})] \quad (15)$$

$$da_2/dt = [k'_1 + k_1 * (\text{OH})] * e * (a_1 - N * a_2) \quad (16)$$

$$d(\text{OH})/dt = [k'_1 + k_1 * (\text{OH})] * e * (a_1 + N * a_2) \quad (17)$$

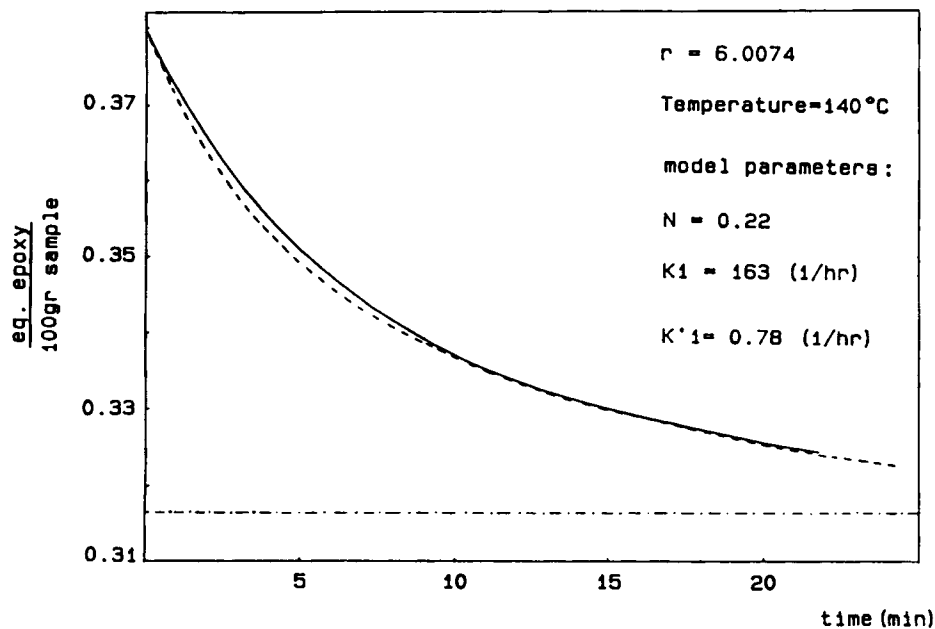


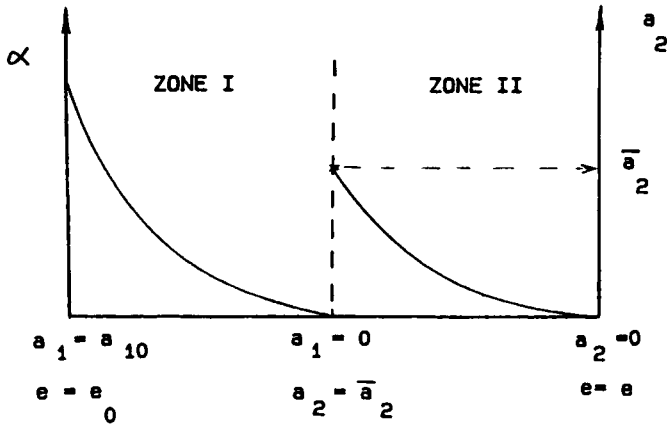
Fig. 10. Concentration of epoxy groups at constant temperature vs. time: (—) experimental, Isotrack DSC technique; (---) predicted by the statistical structural model.

From eqs. (15)–(17) we get

$$d(\text{OH})/dt = -da_1/dt = da_2/dt \quad (18)$$

$$(\text{OH}) = (\text{OH})_0 + (a_{10} - a_1) + (a_{20} - a_2) \quad (19)$$

In order to solve the system, we considered two zones as shown in the following scheme:



ZONE I. Dividing eq. (16) by (15) and integrating, we get

$$(a_1/a_{10})^{N/2} = (2 - N) * (a_2/a_{10}) + (a_1/a_{10}) \quad (20)$$

Replacing eqs. (9)–(12) and eq. (20) in eq. (14),

$$dx/dt = (1 - x) * (K'_1 + K_1 * \text{FC}) * \text{FM} \quad (21)$$

where

$$\text{FM} = (\alpha/r) + \{N/[r * (2 - N)]\} * (\alpha^{N/2} - \alpha) + L * \text{FC} \quad (22)$$

$$\text{FC} = [(\text{OH})_0/e_0] + (1/r) - (\alpha/r) - (1/r) * (\alpha^{N/2} - \alpha) * (1/(2 - N)) \quad (23)$$

The relationship between α and x may be obtained by introducing eq. (12) in eq. (15), dividing by eq. (21) and integrating; this leads to

$$x = [(N - 1) * (\alpha - \alpha^{N/2}) / [(2 - N) * r] + (1/r) - (L/2)] \\ \times [(N + 1) / (r * N)] - (L/2) * \{ [((\text{OH})_0/e_0) + (1/r)] * \ln \alpha \\ + \{1/[r * (2 - N)]\} * [(N - 1) * \alpha - (2/N) * \alpha^{N/2}] \} \quad (24)$$

ZONE II.

$L = 0$: When $a_1 = 0$,

$$-de/dt = e[k'_1 + k_1 * (\text{OH})] * N * a_2 \quad (25)$$

$$a_2 = a_{10} - e_0 - e \quad (26)$$

$$(\text{OH}) = x * e_0 + (\text{OH})_0 \quad (27)$$

Then

$$dx/dt = (1 - x) * (K'_1 + K_1 * \text{FC}) * \text{FM} \quad (28)$$

where

$$\text{FC} = x + (\text{OH})_0 / e_0 \quad (29)$$

$$\text{FM} = N * [(a_{10} / e_0) - x] \quad (30)$$

If $L \neq 0$, the integration constants $\bar{a}_2 = a_2$ ($a_1 = 0$) and $\bar{x} = x$ ($a_1 = 0$) are obtained as follows: Assuming high frequency of data, we can express a_2 in terms of the previous step (Runge-Kutta method). When $a_1 = 0$, step i,

$$-de/dt = e * [k'_1 + k_1 * (\text{OH})] * [N * a_2 + L * (\text{OH})] \quad (31)$$

$$(\text{OH}) = a_{10} - a_2 + (\text{OH})_0 \quad (32)$$

$$da_2/dt = -[k'_1 + k_1 * (\text{OH})] * e * N * a_2 \quad (33)$$

$$dx/dt = (1 - x) * \text{FM} * (K'_1 + K_1 * \text{FC}) \quad (34)$$

where

$$\text{FC} = [a_{10} - a_2 + (\text{OH})_0] / e_0 \quad (35)$$

$$\text{FM} = N * a_2 / e_0 - L * \text{FC} \quad (36)$$

The relationship between a_2 and x may be obtained from

$$dx/da_2 = [(L/N) - 1] * (1/e_0) - [L/(N * a_2)] * \{ (1/r) + [(\text{OH})_0 / e_0] \} \quad (37)$$

integrating

$$x = \bar{x} + [1 - (L/N)] * [(\bar{a}_2 - a_2) / e_0] + (L/N) * \{ (1/r) + [(\text{OH})_0 / e_0] \} * \ln(\bar{a}_2 / a_2) \quad (38)$$

where

$$\bar{a}_2 = a_2(i) = [(\alpha_{i-1}^{N/2} - \alpha_{i-1}) / (2 - N)] * a_{10}$$

and

$$\bar{x} = x(i)$$

In order to check the fitting of the kinetic scheme with experimental results we express:

$$Y = (dx/dt)/[(1-x)*FM] = K_1' + K_1*FC \quad (39)$$

where FC and FM have different expressions [eqs. (22), (23), (29), (30), (35), and (36)] depending on the zone and value of L .

Side Reactions

The homopolymerization of epoxy groups require the presence of Lewis bases (i.e., tertiary amines), inorganic bases (i.e., NaOH), or Lewis acid catalysts (i.e., F_3B complexed with an amine).¹⁷ As the tertiary amine arising from the reaction epoxy-amine is sterically hindered its catalytic effect towards the homopolymerization reaction will not be significant. However, the relevance of the etherification reaction [eqs. (5) and (6)] with respect to the epoxy-amine reactions depends on the nature of the amine, the equivalent ratio, and the reaction temperature. The kinetic analysis of these polyaddition reaction without termination is of practical interest in order to know the possible changes of oligomer characteristics and to avoid gelation.

Experimental

Samples of epoxy-amine with different equivalent ratio were reacted at 75°C for 7 days. Later, these oligomers were placed in sealed glass containers and post-reacted at 200°C. The consumption of epoxy groups was followed by titration (Fig. 11) and the evolution of M_w by GPC (Fig. 12). Assuming that only the etherification reaction took place, we can write

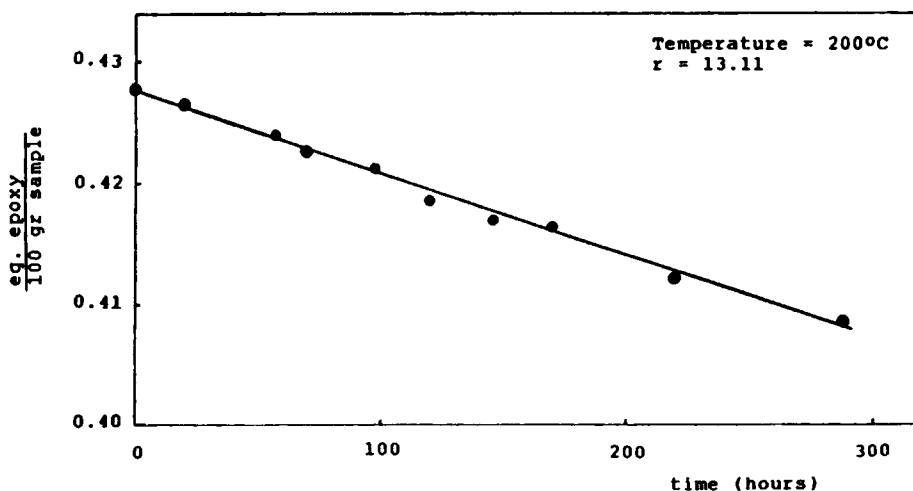


Fig. 11. Concentration of epoxy groups vs. time. Post-etherification reaction at 200°C, $r = 13.11$ reacted 7 days at 75°C.

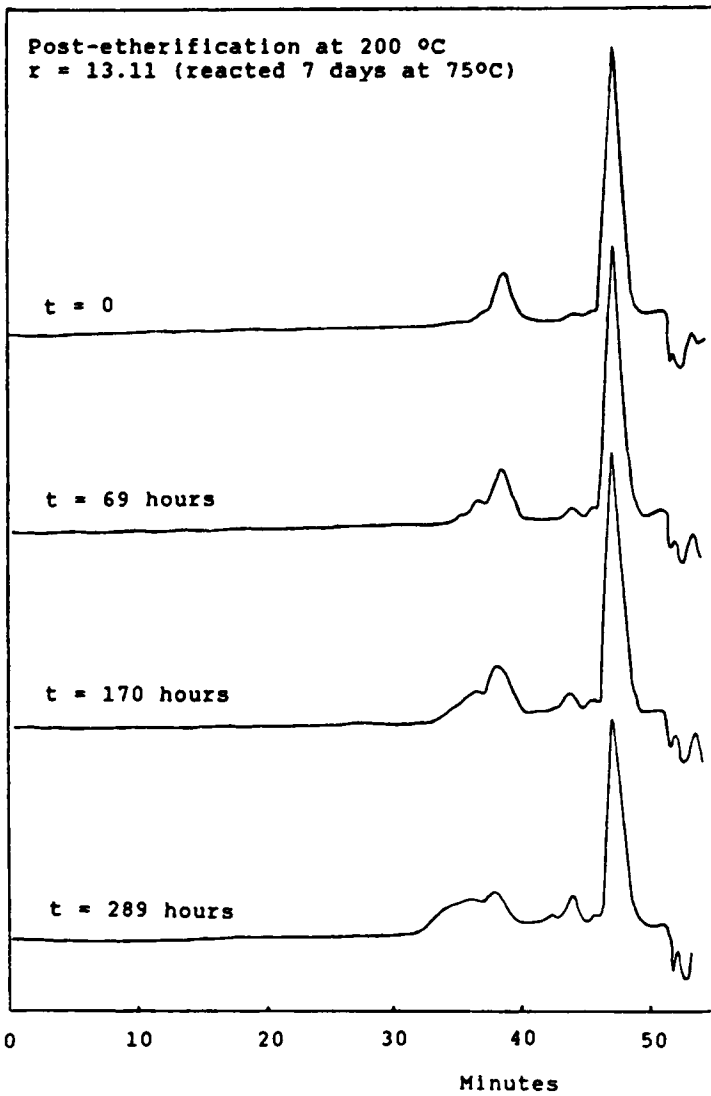


Fig. 12. GPC chromatograms obtained at different times when the etherification reaction proceeds at 200°C.

$$-de/dt = k_e * (\text{OH}) * e \quad (40)$$

Defining

e_f = concentration of epoxy groups at the beginning

of the post-treatment at 200°C

then

$$\ln e/e_f = -(\text{OH}) * k_e * t = \text{constant} * t \quad (41)$$

TABLE I
Kinetic Parameters Arising from the Best Linear Regression

T (°C)	r	N	K_1 (h ⁻¹)	K'_1 (h ⁻¹)
75	6.925	0.07	6.5	—
75	13.551	0.07	8.94	—
105	6.996	0.14	35	0.05 ± 0.01
130	8.558	0.20	143	0.42
140	6.0074	0.22	160	0.78
140	6.7148	0.22	175	0.8

where

$$k_e = k'_3 + k_3*(OH) = L*[k'_1 + k_1*(OH)]$$

From the plot $\ln e/e_f$ vs. time at 200°C we obtained the k_e value. It was 3.5×10^{-3} (100 g sample/h eq). Then, a negligible L value can be expected at temperatures in the range 75–140°C. In order to obtain the specific rate constants for the reaction of epoxy-amine, the kinetic model was applied assuming $L = 0$.

Results

Table 1 shows the kinetic parameters and the N value arising from the best linear regression [eq. (39), regression coefficient > 0.997]. In order to test the influence of temperature on the N value, several samples with an excess of amine ($r < 1$) were degassed and reacted at 75, 105, and 140°C, finding the critical ratio leading to gelation at full conversion of epoxy groups. Evaluation of the soluble fraction gave the results shown in Table II. The activation energy of the epoxy–primary amine reaction catalyzed by hydroxyl groups obtained from the Arrhenius plot, depicted in Figure 13, was 14.43 kcal/mol. This value is in excellent agreement with corresponding values reported for curing of aliphatic diamines.^{13,18}

The low significance of the noncatalytic mechanism made impossible the regression in the total temperature range. Considering the results obtained at high temperature, we estimated an activation energy ($E_a = 23.5$ kcal/mol). This value was accepted in order to estimate the specific constant for the noncatalytic reaction rate at low temperature when the theoretical model was analyzed.

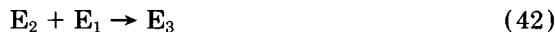
TABLE II
Critical Equivalent Ratio at Different Temperature

T (°C)	r_{gel}	r_{solube}
75	0.4785	0.4608
105	0.4587	0.4504
140	0.4444	0.433

Prediction of the Weight Average Molecular Weight and Conversion of Epoxy Groups vs. Time

In order to predict the weight average molecular weight, the statistical structural model developed by Riccardi and Williams⁴ was applied. The model is based on a combination of kinetic schemes accounting for the evolution of all possible fragments that may be generated from the macromolecules structure, together with a simple expectation theory. This approach has been previously used for the build up of phenolic resin networks^{2,3} and epoxy-diamino diphenyl sulfone ones.⁴

According to the previous kinetic characterization, during the reaction of epoxy-Jeffamine different structural elements would be present (see Fig. 14). Different structural fragments that may be distinguished as the reaction proceeds are shown in Figure 15. Note that arrows are joined to arrows and segments to segments. Based on the number average functionality we assumed that $(E_5)_0 = 0.13 * (E_1)_{0j} = 0.13 * [(E_2)_0 / (2 * r)]$. In terms of structural fragments, the reaction scheme may be written as



Masses of the structural fragments will be denoted by M_1 - M_5 . The ratio of amine/epoxy equivalents is given by

$$r = (E_2)_0 / [2 * (E_1)_0] \quad (44)$$

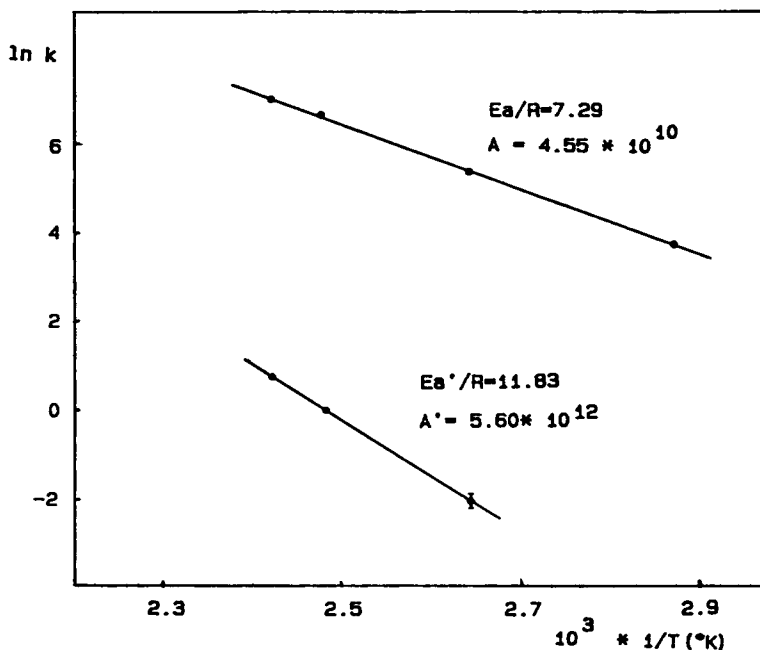


Fig. 13. Arrhenius plot of the specific constants for the epoxy-amine reaction.

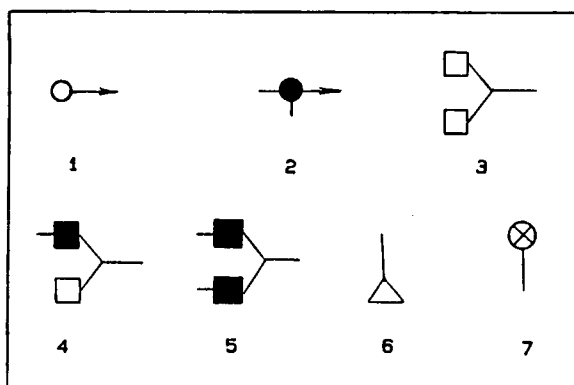


Fig. 14. The structural elements present during the reaction epoxy-amine. (1) unreacted epoxy; (2) reacted epoxy; (3) unreacted amine; (4) partially reacted amine; (5) completely reacted amine; (6) hydroxy group; (7) another residual group present in the amine reactant.

The conversion of epoxy groups may be written as

$$X_e = (E_3 + 2 \cdot E_4) / (E_2)_0 \quad (45)$$

A knowledge of the kinetics of reactions will permit one to find the evolution of the different fragments as a function of conversion. The rate of disappearance of epoxy groups may be written as

$$-dE_2/dt = E_2 \cdot (k'_1 \cdot 2 \cdot E_1 + k_1 \cdot (\text{OH}) \cdot 2 \cdot E_1 + k'_2 \cdot E_3 + k_2 \cdot (\text{OH}) \cdot E_3) \quad (46)$$

Defining

$$M = k'_1 / [k_1 \cdot (E_2)_0] = k'_2 / [k_2 \cdot (E_2)_0] \quad (47)$$

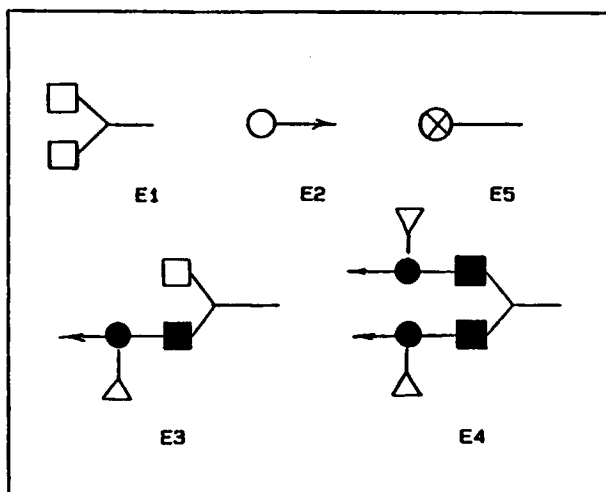


Fig. 15. Structural fragments present during the reaction epoxy-amine.

$$E_i\# = E_i/(E_2)_0, \quad i = 1-5 \quad (48)$$

$$(\text{OH})\# = E_3\# + 2 \cdot E_4\# + [(\text{OH})_0/(E_2)_0] \quad (49)$$

$$E\# = E_2\# \cdot [M + (\text{OH})\#] \quad (50)$$

$$t\# = k_1 \cdot (E_2)_0^2 \cdot t \quad (51)$$

We get

$$-dE_2\#/dt = E\# \cdot (2 \cdot E_1\# + N \cdot E_3\#) \quad (52)$$

Similarly, the rates of variation of the other structural fragments are given by

$$-dE_1\#/dt = E\# \cdot 2 \cdot E_1\# \quad (53)$$

$$dE_3\#/dt = E\# \cdot (2 \cdot E_1\# - N \cdot E_3\#) \quad (54)$$

$$dE_4\#/dt = E\# \cdot N \cdot E_3\# \quad (55)$$

The system of eqs. (52)–(55) is solved using a fourth-order Runge–Kutta method. From eq. (45) we calculated the epoxy conversion vs. time. Figures 8–10 show the experimental conversion–time curves (solid line) and the predicted ones (dashed line). An example of the fragments evolution is shown in Figure 16.

In order to calculate the weight average molecular weight M_w , the average weight hanging from an arrow (Y) and a segment (Z) must be determined. They are obtained from

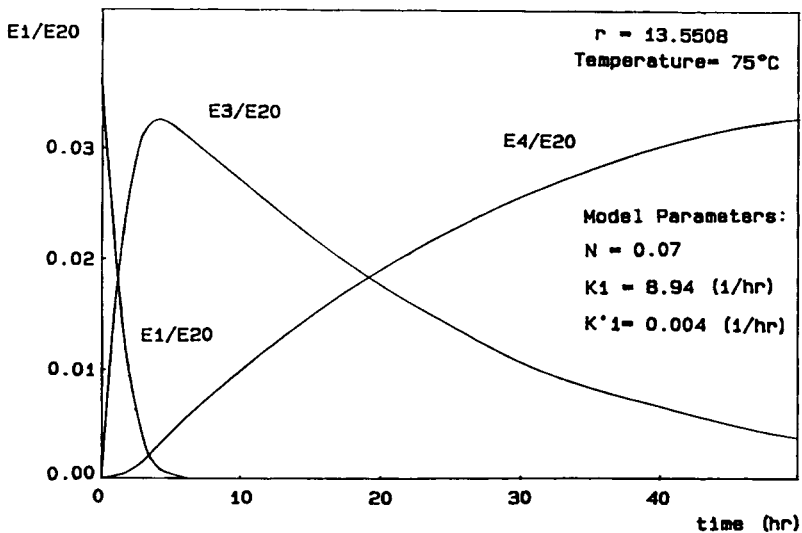


Fig. 16. Fragments evolution predicted by the statistical structural model.

$$Y = [E_2 * M_2 + E_3 * (M_3 + Z) + 2 * E_4 * (M_4 + Y + Z)] / (E_2)_0 \quad (56)$$

$$Z = [E_1 * M_1 + E_3 * (M_3 + Y) + E_4 * (M_4 + 2 * Y) + E_5 * M_5] / [1.13 * (E_2)_0 / (2 * r)] \quad (57)$$

This system may be solved as a function of the reaction extent. The average hanging from each fragment is written as

$$M_{t1} = M_1 + Z$$

$$M_{t2} = M_2 + Y$$

$$M_{t3} = M_3 + Y + Z$$

$$M_{t4} = M_4 + 2 * Y + Z$$

$$M_{t5} = M_5 + Z$$

where $M_1 = 920$, $M_2 = 175.84$, $M_3 = M_2 + M_1$, $M_4 = M_1 + 2 * M_2$, and $M_5 = M_1$. The mass fraction of each structural fragment is given by

$$W_i (i = 1-5) = (E_i * M_i) / \{ (E_2)_0 * [M_2 + (M_1 / (2 * r))] + M_5 * (0.13 / (2 * r)) \} \quad (58)$$

The weight average molecular weight is defined as

$$M_w = \sum W * M_{t(i)} \quad (59)$$

Figure 17 shows the M_w evolution predicted according to the reaction shown in Figure 16. Assuming that no cyclization reaction takes place, the number average molecular weight M_n may be calculated as follows:

$$M_n = \text{total mass / number of moles} = (M_2 + M_1 / (2 * r) + M_5 * 0.13 / (2 * r)) / (0.5 + 0.785 / r - X_e) \quad (60)$$

Equation (60) assumes that each time an epoxy reacts the number of molecules diminishes in one unit (no intramolecular reactions). In order to compare molecular weight predictions with experimental values, several samples with different equivalent ratio were reacted at temperatures in the range 75–140°C. Table III shows molecular weight predicted by Eqs. (59) and (60) and those measured (GPC) in samples reacted 7 days at 75°C. w_1 is the mass fraction of epoxy DER 332 free ($M_{w1} = 340$). g_w is the oligomer weight average functionality predicted assuming etherification reaction and cyclization negligible.

Figure 18 shows the relationship predicted by the statistical structural model between r and time of production (h) at constant temperature (°C) and to 99% of conversion of epoxy groups. The dynamic viscosity of the oligomers produced was measured by Technique III described earlier. The results obtained at 105°C and shear rate 715 (1/sec) are shown in Figure 19.

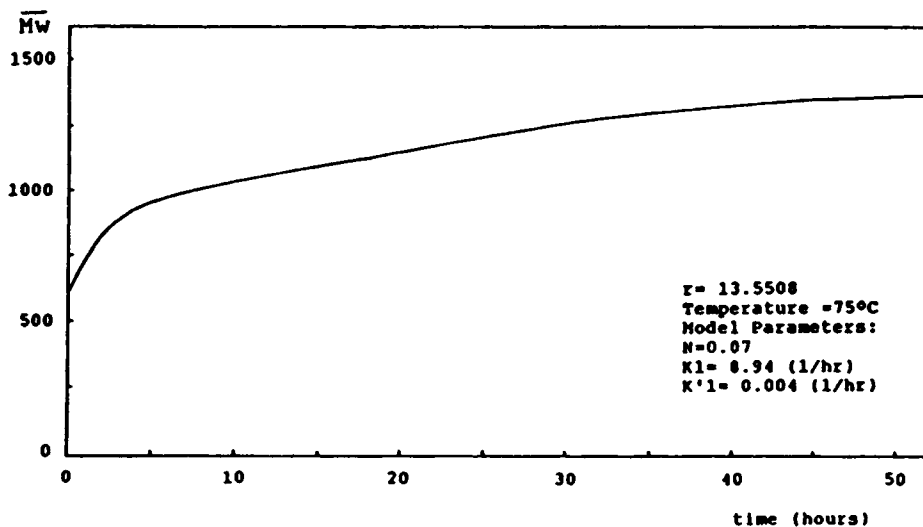


Fig. 17. Weight average molecular weight evolution predicted by the statistical structural model.

Table IV shows the effect of varying the Jeffamine D-2000 content in order to exert control over the soft domain size. M_w and M_n are the copolymer molecular weights associated with the first peak in the chromatograms in Figure 12.

The subject of current research is to measure the alternate product properties (such as the mechanical ones) which are achieved by not only varying the Jeffamine D-2000 content, but by introducing other Jeffamines from the available series.

CONCLUSIONS

Analysis of the reaction epoxy-amine below 140°C showed the following facts:

TABLE III
Experimental and Predicted Molecular Weights

r	w_1	M_w	M_n	Predicted		
				M_w	M_n	g_w
3.8612	0.378	8232.5	832.4	8229.62	984	4.84
6.9247	0.560	2644.8	571	2707.39	631.8	2.79
12.208	0.723	1522	455	1486.43	494.5	2.35
17.572	0.795	1125.15	438.14	1105.7	447.1	2.23
21.64	0.828	964.87	403	954.33	427.9	2.17

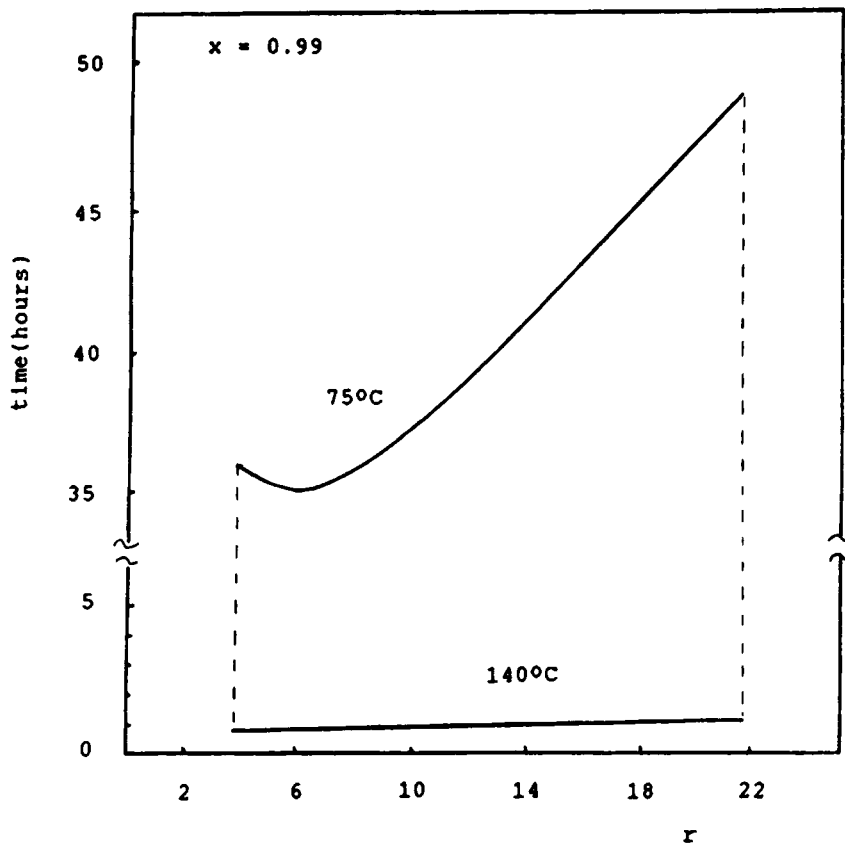


Fig. 18. Time of reaction to get 99% of epoxy group conversion at constant temperature.

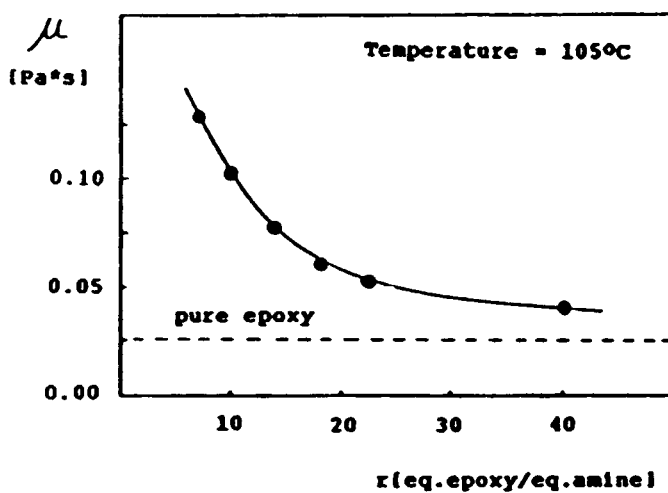


Fig. 19. Dynamic viscosity of oligomers with different equivalent ratio. Temperature = 105°C; shear rate = 715 (1/sec).

TABLE IV
Soft Region Content and Domain Size

r (eq. ratio)	3.8	6.9	12.2	17.6	21.6
Jeffamine (mass %)	43.6	30.16	19.7	14.54	12.10
M_w	13000	5578	4610	4170	3973
M_n	7000	4200	3883	3668	3566

- The reaction proceeds mainly by an autocatalytic mechanism characterized by an activation energy $E_a = 14$ kcal/mol.
- The experimental evidence indicated that the etherification reaction may be neglected.
- The heat evolved from dynamic DSC runs depends on the heating rate. At 5°C the consumption of epoxy groups is associated with the reaction with amine and with another functional group present in the Jeffamine reactant.
- Dynamic DSC evaluation of residual heat after complete reaction epoxy-amine at constant temperature below 140°C showed it to be 10% of the total heat evolved in the previous isothermal run.
- The rate of reaction of primary hydrogen was lower than the rate found in another aliphatic amine¹ due to the steric hindrance of the nearby methyl group.
- The low reactivity ratio between secondary and primary amino groups obtained from the fitting of the kinetic model to experimental data is in good agreement with the previous values reported using hindered amines.^{8,12}
- In order to produce oligomers from epoxy and Jeffamine D-2000, the interrelationship between equivalent ratio-temperature-time of reaction was established.
- The previous kinetic study of this epoxy-amine system permitted good prediction of product molecular weights when the statistical structural model was applied.

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