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KINETICS, CATALYSIS, AND REACTION ENGINEERING

Calorimetric and Kinetic Analysis of the Diglycidyl Ether of the Bisphenol A/Tetrabromobisphenol A Reaction for the Production of Linear Brominated Epoxy Resins

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The reaction process of diglycidyl ether of bisphenol A (DGEBA) with tetrabromobisphenol A (TBBA) to yield linear brominated epoxy resins was studied by calorimetric techniques and quantitative IR analysis. A wide range of DGEBA/TBBA molar ratios and of catalyst concentrations was investigated, including those typical of industrial processes. The study was focused on the thermal effects and overall reaction kinetics of the DGEBA/TBBA linear polymerization process. The influence of secondary reactions was proven to be negligible under the experimental conditions considered. The kinetic parameters of the reaction process were evaluated by an Arrhenius single-step model. The kinetic and calorimetric parameters estimated may be used for a preliminary indication of process conversions and reaction rates and for the safety analysis of the DGEBA/TBBA industrial reaction processes.
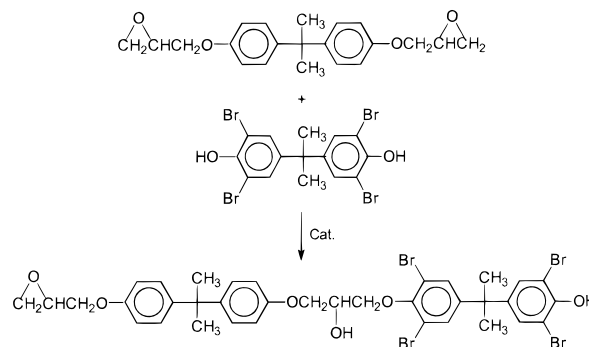
Introduction

Brominated epoxy resins are widely used for the manufacture of electronic equipment, in particular of computer-printed circuit boards. The production of solid resins is usually performed by a two-step process: in the first stage, called "advancement process", high molecular weight linear brominated epoxy resins are produced; in the second stage, cross-linked resins are obtained by curing.[1]

Reactive brominated flame retardants are used in the formulation of the epoxy resins to enhance the flame resistance of the final product. Products containing more than 20% of bromine by weight are commonly used for the production of computer-printed circuit boards.

In recent years, at least two runaway accidents have been reported involving batch reactors during the production of these brominated epoxy resins.[2] In both cases, the runaway caused the explosion of the vessel. The presence of bromine in the chemical system resulted in the release of a cloud of toxic products, possibly hydrogen bromide, bromophenols, and other hazardous brominated compounds. The suspected cause of the accidents was probably the lack of knowledge of both the reactoristic and the thermokinetic aspects of the process. As a matter of fact, scarce data are available

Scheme 1

Scheme 2
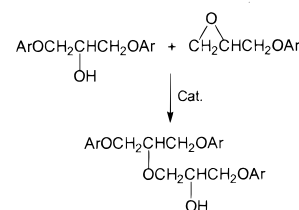
in the literature on the reaction kinetics and the thermal effects of brominated epoxy resin production and, in particular, of the linear polymerization process.

Linear brominated epoxy resins are obtained by the polyaddition reaction of the diglycidyl ether of bisphenol A (DGEBA) with tetrabromobisphenol A (TBBA).[1] The

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chain-lengthening step is based on the nucleophilic attack of the phenolic group of TBBA to the less substituted carbon atom of the oxirane ring of DGEBA, which leads to ring-opening formation of an ether link and generation of a secondary hydroxilic group (Scheme 1). An important side reaction of the process is the addition of the generated secondary hydroxilic group to another epoxide (Scheme 2). Because this process leads to chain branching and eventually to cross-linking, it should be minimized during the advancement process, where linear epoxy resins are the desired product.

The analysis of the DGEBA/TBBA reaction process is thus concerned with two problems: the kinetics of the main reaction process and the influence of secondary reactions. Although kinetic data are reported in the literature for the DGEBA/bisphenol A (BA) reaction,[3,4] less information is available on the reaction of tetrabromobisphenol A with DGEBA. Previous studies mainly investigated the reaction mechanism[5] and catalyst selectivity[6] but did not explore the thermal effects of the reaction and the reaction kinetics dependence on the catalyst concentration and reactant ratio.

The present study was focused on the thermal effects and overall reaction kinetics of the DGEBA/TBBA linear polymerization process. Calorimetric techniques and IR quantitative analysis were used to obtain information on heat generation and reactant conversion during the reaction process. The influence of secondary reactions and of polymer chain growth on reaction rate was also investigated. The study was oriented to the achievement of calorimetric and kinetic data to be used in process optimization and safety analysis.[7-10]

Experimental Section

Materials. The following compounds were used for the study: Epikote 828 epoxy grade diglycidyl ether of bisphenol A [CAS 1675-54-3], supplied by Shell and tetrabromobisphenol A [CAS 79-94-7], 2,6-dibromo-4-methylphenol (DBMP) [CAS 2432-14-6], and 1-phenoxy-2-propanol (POP) [CAS 770-35-4] supplied by Aldrich. Ethyltriphenylphosponium iodide (ETPPI) [CAS 4736-60-1], supplied by Aldrich, was used as a catalyst.

Techniques. The reaction kinetics was studied using combined methods based on differential scanning calorimetry (DSC) and FT-IR analysis.

DSC experimental data were collected using a Mettler DSC-25 calorimeter. Constant heating rate (35–250 °C, 1–2.5 °C/min) and isothermal (120–170 °C) experimental runs were performed using nitrogen as the purge gas (300 mL/min). Typical total sample weights of 15–25 mg were used. The isothermal DSC data were obtained by inserting the sample in the DSC cell preheated to the temperature chosen for the run. DSC data were collected until negligible further heat flow occurred.

Sample conversion at the end of either constant heating rate or isothermal runs was estimated by FT-IR analysis. FT-IR measurements were performed using a Bruker Equinox 55 FT-IR analyzer. Samples for FT-IR analysis were prepared as thin films between sodium chloride disks.

Isothermal reaction runs were also carried out in a laboratory oven using temperatures between 130 and 150 °C. A total of 20–40 crucibles were prepared, each containing about 40 mg of the reaction mixture. At the beginning of the run, all of the samples were
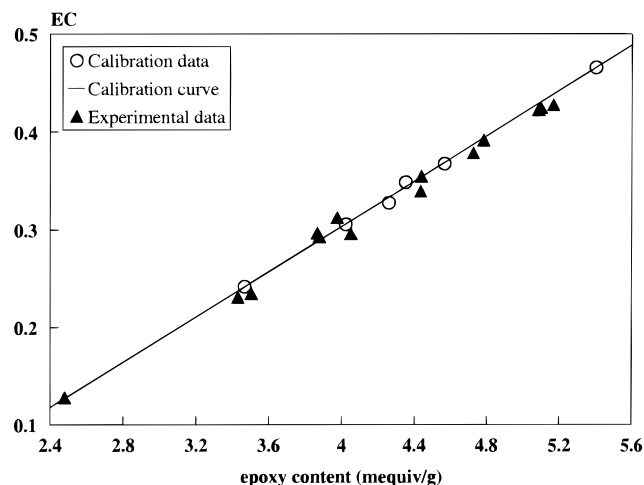

Figure 1. Experimental epoxy content of DGEBA/TBBA/ETPPI samples (EC) at the end of the DSC runs with respect to theoretical value assuming 100% conversion.

positioned in the oven preheated to the desired temperature. At regular time intervals (3–10 min, depending on the temperature of the oven) a sample was taken out and quenched to ambient temperature with cold acetone, to stop the reaction. The FT-IR analysis of the sample was then carried out, allowing the determination of the sample epoxy content and thus of epoxy conversion.

Determination of Epoxy Content. To estimate the conversion of samples in DSC runs, the epoxy content of the samples was measured by quantitative IR analysis. The epoxy content was defined as the ratio of the number of epoxy groups to the initial weight of DGEBA and was expressed as milliequivalents per gram (mequiv/g).

The epoxy content of the samples was evaluated using the value of EC, defined as the ratio between the area of the epoxide IR absorption band at 916 cm^{-1} and the total area of the aromatic absorption peaks at 1608 and 1582 cm^{-1} (internal standard).

Following the procedures given in the literature to obtain reliable quantitative IR measurements of the epoxy content, an experimental calibration curve was used.[11] Six samples were analyzed having the following epoxy contents: 3.47, 4.02, 4.26, 4.35, 4.56, and 5.40 mequiv/g. The linear calibration curve shown in Figure 1 was obtained from the analysis of the calibration samples.

Preparation of Samples for DSC Experiments. The DSC crucibles have a volume of 40 μL, thus allowing the use of quite limited amounts of sample (less than 30 mg of the initial reaction mixture). The preparation of representative and homogeneous samples thus required the development of procedures for the preliminary mixing of the reactants before the DSC runs. An additional difficulty was given by the limited solubility of TBBA and ETPPI in DGEBA at ambient temperature.

Two different procedures were used to prepare DGEBA/TBBA/ETPPI mixtures. Method A consisted of the preparation of separate TBBA/DGEBA and ETPPI/DGEBA solutions. The two solutions were mixed directly in the DSC crucible immediately before the experiment. Alternatively, DGEBA, TBBA, and the catalyst were dissolved at ambient temperature in acetone. The solution was stored at 0 °C. Immediately before the run, the acetone was evaporated at ambient
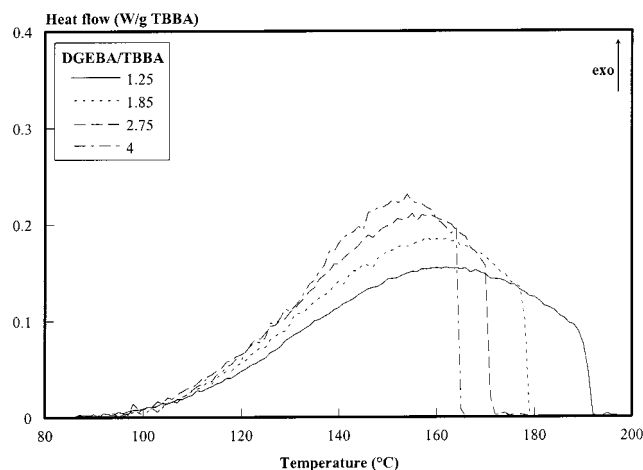
Figure 2. Results of constant heating rate (2 °C/min) DSC runs on reaction mixtures with different DGEBA/TBBA molar ratios and a catalyst concentration of 8.5×10^{-4} mol/kg.

Table 1. Reactants and Catalyst Concentration Ranges Used for the Kinetic Study of the DGEBA/TBBA Polymerization

DGEBA/TBBA (mol/mol)	C_d (mol/kg)	C_t (mol/kg)	C_c (mol/kg)
1–23	1.09–2.53	0.11–1.09	2.9×10^{-4}–4.7×10^{-3}

temperature under vacuum (method B). Method A was used to obtain samples with different catalyst concentrations, while with method B, because of the presence of acetone as a solvent, a wide range of DGEBA/TBBA ratios were achieved at constant catalyst concentration.

DGEBA/POP/ETPPI and DGEBA/DBMP/ETPPI mixtures were prepared using method A.

Results and Discussion

DSC Experimental Data. DSC runs were carried out in order to explore the thermal effects and the kinetics of the DGEBA/TBBA/ETPPI reaction process. Constant heating rate and isothermal DSC runs were performed. The concentration ranges of the reactants and catalyst used in experimental runs are reported in Table 1. Most of the experimental runs were carried out using an excess of DGEBA and catalyst concentrations on the same order of magnitude as those typical of the industrial processes.

Figure 2 shows the results obtained from dynamic DSC runs carried out on DGEBA/TBBA mixtures having different reactant molar ratios and the same catalyst concentration (8.5×10^{-4} mol/kg). In the following, the DGEBA/TBBA mixtures used in the experimental runs will be identified by the molar ratio of DGEBA to TBBA.

Results of constant heating rate DSC runs as those reported in Figure 2 showed an exothermic process at temperatures between 80 and 200 °C. The precise temperature range of the reaction mainly depends on the catalyst concentration, while the overall value of the heat generated was mainly influenced by reactant concentrations and ratios.

These preliminary results were confirmed by the isothermal DSC runs. DSC curves obtained from isothermal runs on DGEBA/TBBA mixtures with a constant catalyst concentration are compared in Figure 3. Figure 3a shows isothermal DSC curves obtained for the same reaction mixture at temperatures ranging between 130 and 170 °C, while Figure 3b shows the results obtained
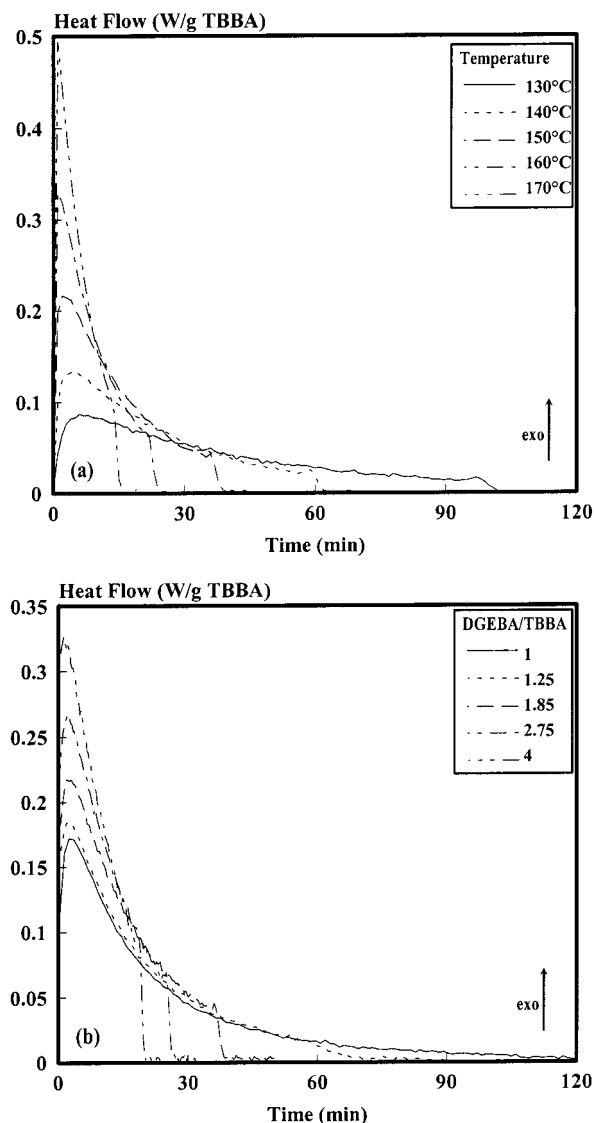

Figure 3. Results of isothermal DSC runs on reaction mixtures with a catalyst concentration of 8.5×10^{-4} mol/kg. (a) Runs at different temperatures for samples with a 1.85 DGEBA/TBBA molar ratio. (b) Runs at 150 °C for samples with different DGEBA/TBBA molar ratios.

at 150 °C for different mixtures. It can be observed that, for a constant catalyst concentration, the reaction rate increases if the DGEBA/TBBA ratio is increased and, as expected, if the reaction temperature is raised.

To use the DSC data for the analysis of reaction kinetics, it was necessary to obtain additional information on the conversion of the samples at the end of DSC runs and on the possible presence of secondary reactions in the temperature range used for the experimental runs.

Sample conversion at the end of the DSC runs was evaluated by quantitative FT-IR analysis of the epoxy group concentration, using the method described in the Experimental Section. The experimental value of EC obtained for a few samples at the end of the DSC runs is plotted in Figure 1 versus the theoretical final epoxide concentration calculated assuming 100% conversion of the limiting reactant. The results clearly show that the sample conversion can be considered almost complete in all experimental runs.

The epoxy content was also monitored during the isothermal reaction runs carried out in a laboratory oven. These experimental runs were aimed to compare
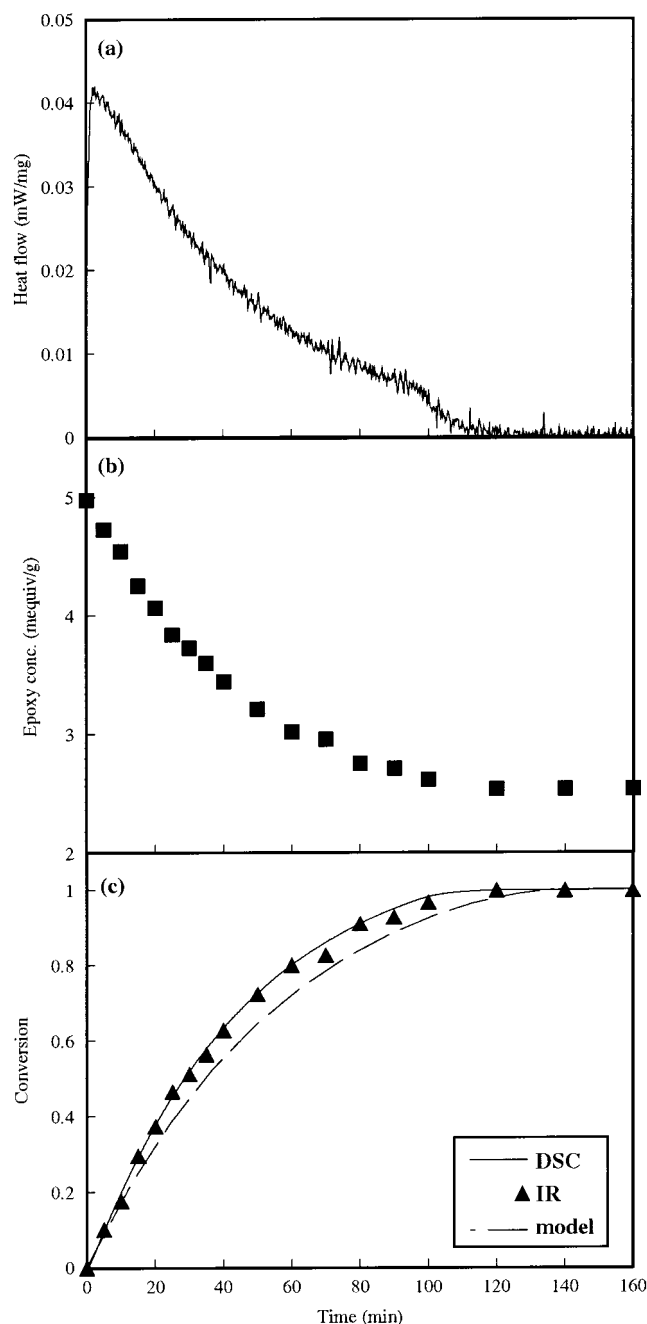
Figure 4. Conversion with respect to time at 130 °C of samples with a 1.85 DGEBA/TBBA molar ratio and catalyst concentration of 8.5×10^{-4} mol/kg. (a) Results of an isothermal DSC run. (b) Epoxy content of samples reacted in a laboratory oven. (c) TBBA conversion calculated from DSC data, IR data, and kinetic model.

the conversion values measured by the IR technique to those obtained from the analysis of DSC data. Isothermal reaction runs in the laboratory oven and isothermal DSC runs were thus performed on the same reaction mixtures at the same temperatures. The results obtained at 130 °C for a 1.85 DGEBA/TBBA mixture are reported in Figure 4. The heat flow measured in the DSC run and the epoxy groups concentration calculated from IR data using the procedure described in the Experimental Section are plotted versus time in parts a and b of Figure 4, respectively. From the analysis of Figures 1 and 4, it may be concluded that (i) the heat generated during the DSC experiments is related to the conversion of epoxy groups and (ii) the conversion of
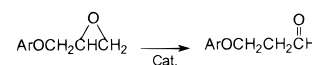
Scheme 3
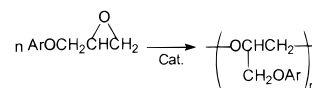
Scheme 4

Table 2. Reactants and Catalyst Concentration Ranges, Temperature, and Heat of Reaction of DGEBA/POP Reaction

DGEBA/POP (equiv/equiv)	C_{POP} (mol/kg)	C_c (mol/kg)	$T_i - T_f$ (°C)	ΔH (kJ/mol of −OH)
4.7	0.97	6.9×10^{-3}	−	−
10.5	0.47	1.9×10^{-2}	−	−
12−13.5	0.37−0.40	$6.1 \times 10^{-2}-$ 6.7×10^{-2}	130−205	−75

epoxy groups present in the sample is compatible with a 100% conversion of the limiting reactant during DSC runs under the experimental conditions used in the present work.

However, the characteristics of the DGEBA/TBBA chemical system do not allow the direct measurement of the TBBA concentration by the IR technique. Because secondary reactions of the epoxy group are possible, an investigation of the influence of these secondary processes under the experimental conditions used in the present work was necessary in order to allow further quantitative analysis of DSC data.

Secondary Reactions. Several side reactions are possible in the DGEBA/TBBA chemical system. A number of workers have reported the reaction between epoxide and secondary hydroxilic groups (Scheme 2). The extent of the reaction depends on the temperature, nature, and concentration of the catalyst employed.[12−15] However, available data suggest that the reaction with secondary alcohols is significantly slower than that with phenolic groups. Furthermore, ETPPI has been shown to have a high selectivity toward the primary reaction process.[6] Moreover, the secondary hydroxilic groups present in the polymeric chains are expected to exhibit a decreased reactivity due to restricted mobility. Nevertheless, to assess the possible influence of this reaction under the experimental conditions used for DSC runs, a model compound was used. The ETPPI-catalyzed reaction of DGEBA with POP was analyzed in order to study the chain-branching process in the DGEBA/TBBA reaction. POP is supposed to be representative of the secondary hydroxilic groups present in the linear epoxy chains formed by the advancement process. Constant heating rate DSC runs were performed using different catalyst concentrations. The results obtained are reported in Table 2. The data in the table were obtained as the mean of at least three different experimental runs. As shown in the table, no reaction could be observed in the DSC runs performed using catalyst concentrations in the range of those used to study the DGEBA/TBBA reaction. A reaction could be observed from DSC data only at larger catalyst concentrations, about 2 orders of magnitude higher. These results are in agreement with previous findings reported in the literature,[13] where the reaction of secondary alcohols was shown to have a rate about 2 orders of magnitude lower than the reaction of phenolic groups.

Table 3. Catalyst Concentration, Temperature, Conversion, and Heat of Reaction of DGEBA Secondary Reactions

C_c (mol/kg)	$T_i - T_f$ (°C)	Q (kJ/ mol of epoxy)	epoxy conversion (%)	ΔH (kJ/ mol of epoxy)
0	—	—	—	—
7.8×10^{-4}	—	—	—	—
7.9×10^{-3}	145−225	−1.5	4	−38
4.8×10^{-2}	145−225	−6.5	18	−36
9.6×10^{-2}	145−230	−14.5	46	−32

There is considerable evidence in the literature that several agents can also catalyze the homopolymerization of epoxy groups[12,16−25] (Scheme 3). In addition to polymerization, Morgan and Mones[26] report the isomerization of epoxy groups to carbonyl groups (Scheme 4). These reactions are generally strongly influenced by the catalyst concentration and the reaction temperature. Pure DGEBA and mixtures of DGEBA with ETPPI were used in order to estimate the importance of these side reactions of the epoxy groups. Constant heating rate DSC runs were performed. The samples obtained at the end of the DSC runs were investigated by FT-IR in order to evaluate epoxy conversion. The results are reported in Table 3. The data shown in the table were obtained as the mean of at least three experimental runs. At high catalyst concentration, the infrared analysis revealed the simultaneous increase of the ether band intensity (1120 cm^{-1}) and the appearance of a carbonyl band (1720−1740 cm^{-1}) upon epoxide consumption. The most convincing explanation of FT-IR observations is that epoxide homopolymerization and isomerization take place. However, also in this case a reaction could be observed only at catalyst concentrations of about 1 order of magnitude higher than those typical of the industrial processes and used in the present study.

These results strongly suggest that the importance of the possible secondary reactions in the catalyst concentration range used in the present study is negligible, at least if temperature−time profiles are comparable to those used in the DSC runs.

Kinetic Analysis. The results obtained with respect to the analysis of secondary reactions and the conversion of epoxy groups at the end of the DSC runs allowed the following assumptions in the further analysis of DSC data: (i) negligible influence of secondary reactions; (ii) 100% conversion of the limiting reactant; and (iii) heat of reaction constant and independent of conversion.

The heat generated in the reaction could be evaluated from the integration of DSC curves. A mean value of 72.5 kJ/mol of −OH was obtained.

The DSC data were correlated to the reaction rate using the following expression:

$$\frac{dC}{dt} = -\frac{q}{2(-\Delta H)}\frac{1}{W} \tag{1}$$

where q is the heat flow recorded by the DSC, ΔH the heat of reaction as defined above, W the sample weight, and C the concentration of the limiting reactant (moles per total weight). The numerical integration of eq 1 with respect to time was used to obtain concentration values. The relationship between the conversion and concentration of the limiting reactant is

$$\xi = 1 - C\frac{W}{N_0} \tag{2}$$
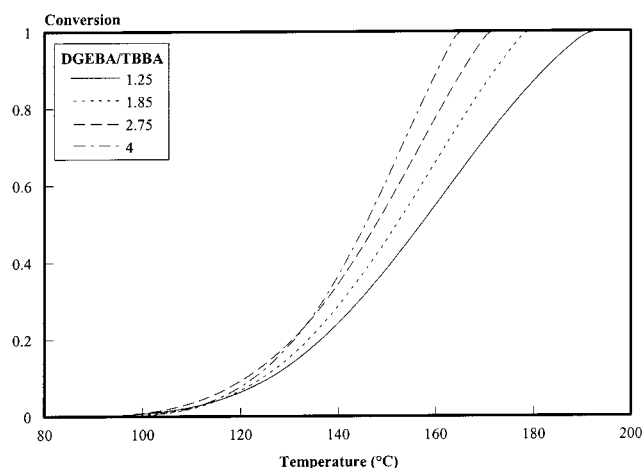
Figure 5. TBBA conversion calculated for the DSC curves reported in Figure 2.

where ξ is the molar conversion and N_0 the initial number of moles of the limiting reactant. Figure 4c reports a comparison of the conversion−time curve obtained from an isothermal DSC run to the results obtained from IR analysis. A satisfactory agreement is present between the two sets of data. Conversion vs temperature curves obtained from the DSC runs shown in Figure 2 are reported in Figure 5.

The kinetic analysis was developed assuming that TBBA was the limiting reactant, as in most of the experimental runs performed. Kinetic data were obtained assuming a single-step Arrhenius kinetic scheme:

$$\frac{dC_t}{dt} = -K(T)C_d^m C_t^n = -Ae^{-E_a/RT}C_c^p C_d^m C_t^n \tag{3}$$

where K is an apparent kinetic constant, A is a preexponential factor, E_a is the activation energy, R is the universal gas constant, C_t is the TBBA concentration, C_d is the DGEBA concentration, C_c is the concentration of the catalyst, and m, n, and p are the reaction orders with respect to reactant and catalyst concentrations. An apparent preexponential factor may also be defined for each catalyst concentration:

$$A' = AC_c^p \tag{4}$$

The apparent kinetic constant may be easily evaluated from the experimental DSC data using the following relation, derived from eq 3:

$$K(T) = -\frac{\dfrac{dC_t}{dt}}{C_d^m C_t^n} \tag{5}$$

The derivative of concentration with respect to time was obtained from the experimental data using eq 1. Numerical integration of eq 1 yields C_t, while C_d can be obtained from a molar balance. In the analysis of constant heating rate DSC runs, the entire DSC curve was considered, while the values of K at $C_t = 0.5 C_t(t=0)$ were calculated from isothermal runs.

No data are reported in the literature on the reaction order of the DGEBA/TBBA reaction with respect to reactant conversion. However, several authors[4,14,27] reported a linear dependence on epoxy group concentration in the reaction between DGEBA and BA. Therefore,
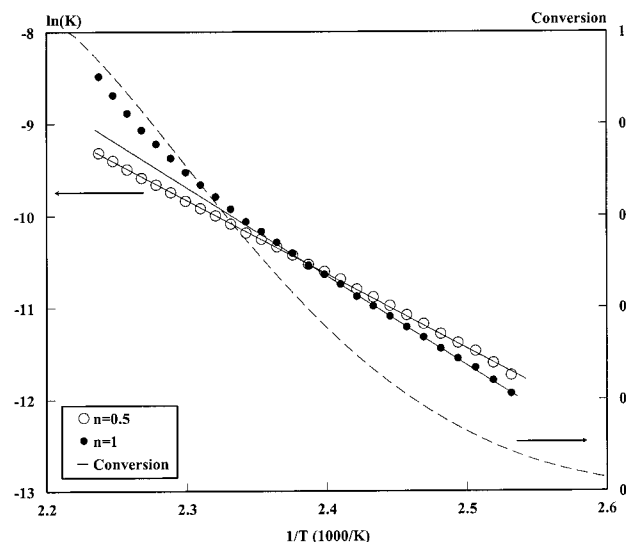
Figure 6. Conversion and Arrhenius plot for a constant heating rate (2 °C/min) DSC run on a DGEBA/TBBA/ETPPI mixture ($C_c = 8.5 \times 10^{-4}$ mol/kg; $C_d = 1.504$ mol/kg; $C_t = 0.813$ mol/kg) obtained considering only data up to 50% TBBA conversion. Dots: experimental data. Lines: kinetic model predictions.

the reaction order for DGEBA concentration was assumed $m = 1$ in the present analysis. It must be remarked that most of the experimental runs were carried out using high excess concentrations of DGEBA. Thus, only limited changes in the value of the DGEBA concentration, C_d, take place during DSC experiments. This results in a limited influence of m on the value of the apparent kinetic constant K in eq 5.

On the other hand, the apparent reaction order with respect to TBBA, that is usually the limiting reactant under the experimental conditions used in the present work, was estimated by a best fit technique. It is clear from eq 3 that, using an Arrhenius kinetic model, if the catalyst concentration is constant, the logarithm of K must show a linear dependence on the reciprocal of the temperature:

$$\ln(K(T)) \cong a\frac{1}{T} + b \qquad (6)$$

where $a = -E_a/R$ and $b = \ln(A')$. To estimate the best-fit value of the order of reaction n with respect to TBBA concentration, tentative values of 0, 0.5, 1, 1.5, and 2 where assumed and the parameters a and b in eq 6 were calculated for each value of n using a linear least-squares method. Thus, it was possible to estimate the value of n that minimized the model error with respect to the values of $\ln(K)$ calculated from experimental data. The best-fit value of n obtained with this procedure resulted in $n = 0.5$. Figure 6 confirms these results. The figure was obtained using constant heating rate DSC data up to 50% sample conversion in the best-fit procedure. The DSC data were obtained for a DGEBA/TBBA/ETPPI mixture produced by method A. The figure clearly shows that a first-order reaction is inadequate to model the reaction kinetics over the entire range of conversion values, because a deviation from linearity takes place at conversions greater than 0.6. On the other hand, assuming a reaction order of $n = 0.5$ minimizes model errors over the entire range of conversion values.

Figure 7 shows the Arrhenius plot obtained for several DSC runs assuming $n = 0.5$. The plots of the experimental data are almost parallel, thus showing a constant activation energy. The different values of the apparent kinetic constant shown by the different DSC runs in the figure are due to different catalyst concentrations. From the best-fit values of the parameters a and b in eq 6 calculated assuming $n = 0.5$, it was possible to evaluate the apparent preexponential factor A' and the activation energy E_a for each DSC constant heating rate run. As shown in Figure 7, the limited differences (5%) found between the values of the activation energy obtained for the samples at different catalyst concentrations suggested the assumption in the present analysis of a mean activation energy value, E_a, of 68.3 kJ/mol.

The use of a common value of the activation energy required the recalculation of the corresponding best-fit
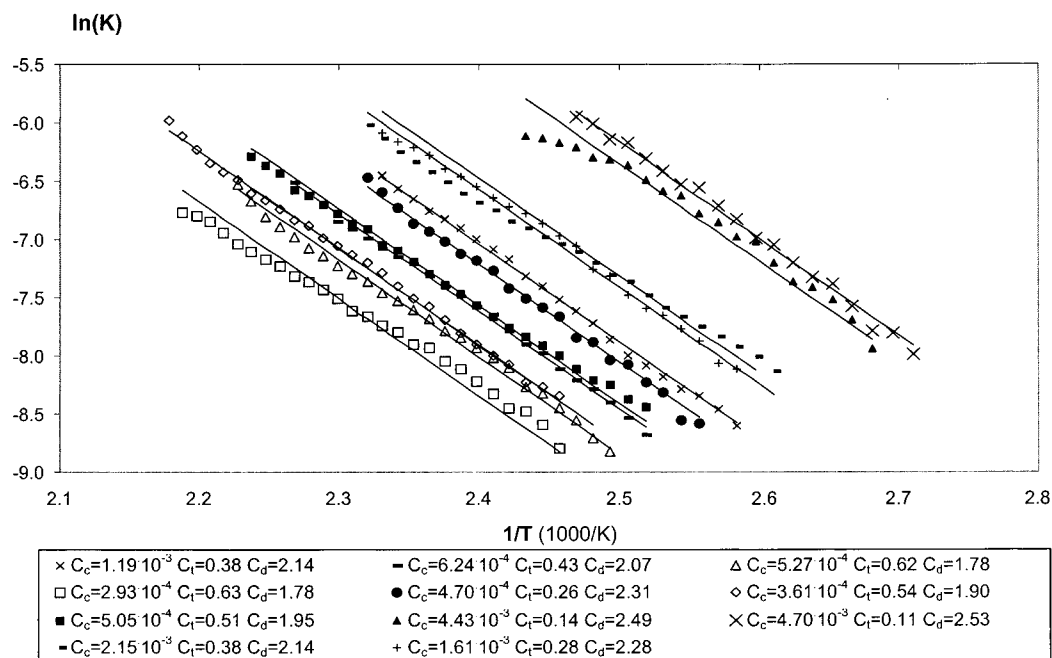

Figure 7. Arrhenius plot for different DGEBA/TBBA/ETPPI reaction mixtures obtained from constant heating rate (2 °C/min) DSC runs. Dots: experimental data. Lines: kinetic model predictions.
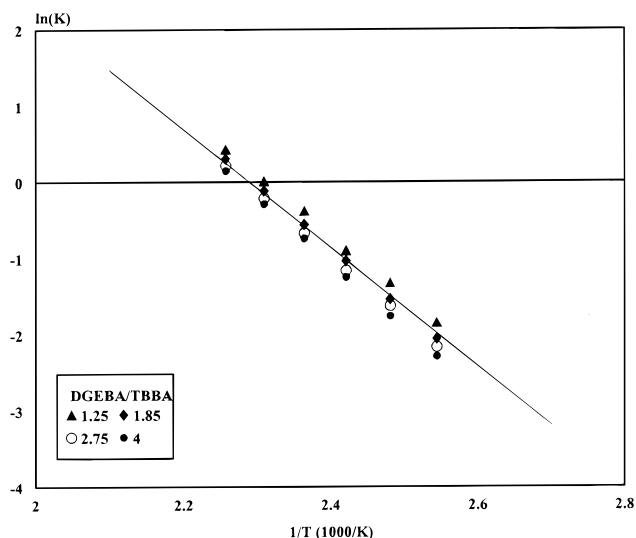
Figure 8. Arrhenius plot obtained from isothermal DSC data on samples of different DGEBA/TBBA molar ratio and catalyst concentration of 8.5×10^{-4} mol/kg.

Table 4. Kinetic and Calorimetric Parameters Obtained for the DGEBA/TBBA/ETPPI and DGEBA/DBMP/ETPPI Reaction

	E_a (kJ/mol)	A (mol$^{-1.5}$ kg$^{1.5}$ s^{-1})	m	n	p	ΔH (kJ/mol of $-OH$)
DGEBA/TBBA	68.3	1.57×10^8	1	0.5	1	−72.5
DGEBA/POP	71.5	1.30×10^8	1	0.5	1	−80.0

preexponential factors, A'. The values obtained were employed to estimate the "true" preexponential factor, A, and the reaction order p with respect to catalyst concentration by eq 4. Assuming $p = 1$ and calculating A by a linear regression yielded a value of the preexponential factor of 1.57×10^8 mol$^{-1.5}$ kg$^{1.5}$ s^{-1} and a regression coefficient of 0.91.

The value of the regression coefficient is sufficiently close to unity; thus, the linear dependence of the reaction rate on catalyst concentration seems to be confirmed by the experimental data.

A further confirmation comes from the Arrhenius plot obtained by the analysis of isothermal DSC data, reported in Figure 8. In the figure, a good agreement is observed between the experimental data and the kinetic model.

The kinetic parameters obtained from the present analysis for the DGEBA/TBBA/ETPPI process are summarized in Table 4. It is obvious that the values reported in the table are only the overall apparent kinetic parameters of the process, because a single-step kinetic model probably oversimplifies the actual reaction mechanism. Nevertheless, in Figure 9 the results of isothermal DSC runs carried out at 130, 150, and 170 °C for three different DGEBA/TBBA ratios are compared to the predictions of the kinetic model. A satisfactory agreement is shown by experimental DSC data and model predictions.

Little data are reported in the literature for the kinetics of the DGEBA/TBBA reaction. The studies concerning brominated epoxy resins synthesis were mainly focused on catalyst selectivity[6] and on the reaction mechanism.[5]

On the other hand, more data are present for the reaction of BA with DGEBA to produce the nonbromin-
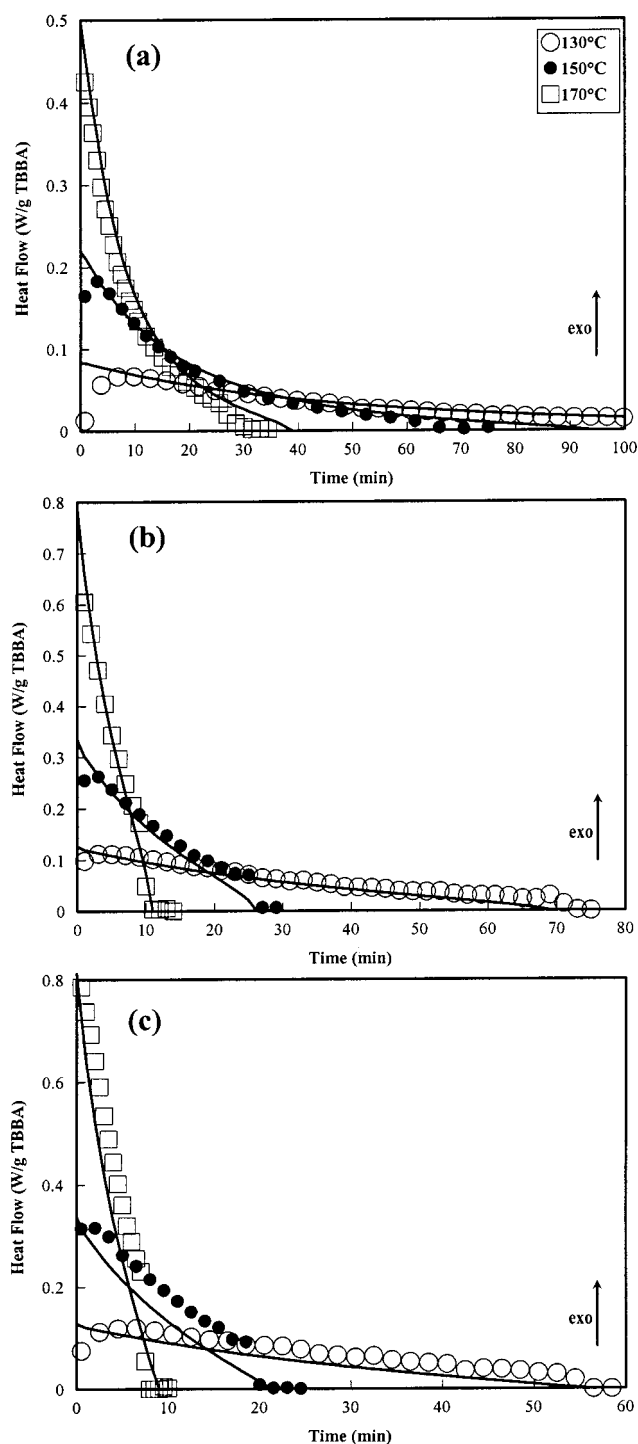

Figure 9. Results of isothermal DSC runs for reaction mixtures with DGEBA/TBBA ratios of 1.25 (a), 2.75 (b), and 4 (c) and a catalyst concentration of 8.5×10^{-4} mol/kg. Dots: experimental data. Lines: kinetic model predictions.

ated resins. An activation energy in the range of 80−100 kJ/mol was found by Ishida and Smith[4] for the DGEBA/BA reaction catalyzed by a urea-derived compound. The actual value of the activation energy turned out to be dependent on kinetic model assumptions and, in particular, on the reaction order with respect to DGEBA concentration. Other studies report an activation energy of 70 kJ/mol for the curing reaction of DGEBA with anhydrides catalyzed by quaternary phosphonium compounds.[19] These values are close to those obtained in the present study.

No data are available in the literature for the reaction order with respect to TBBA or BA concentration. Previous studies only considered the influence of the epoxide concentration on the reaction rate. Even if BA or TBBA were the limiting reactant,[3,4] the influence of phenolic groups on the reaction rate was never explored.

The results obtained for the reaction order ($n = 0.5$) may suggest the presence of diffusional limitations at a high degree of conversion. This is also suggested by the sudden drop in heat flow observed at high conversions in DSC experiments. Moreover, the analysis of most of the constant heating rate DSC runs showed that the first-order assumption for TBBA reaction order holds up to 60% conversion. An example is given in Figure 6, where the Arrhenius plots obtained for a single DSC run using $n = 0.5$ and $n = 1$ are compared.

The apparent decrease in the reaction order, shown by an increase of the experimental vs predicted kinetic constant at conversion values higher than 60% in Figure 6, was observed also for the DGEBA/BA system.[4] A possible influence of secondary reactions of aliphatic hydroxilic groups and of epoxide polymer on the reaction rate can be excluded on the basis of the results discussed above and of the data reported in the literature.[13] Thus, the influence of diffusional limitations due to polymeric chain growth or of a change in the reaction mechanism was identified as the possible cause of the observed behavior.

However, the apparent reaction order of 0.5 resulted even from experimental runs on mixtures with a DGEBA/TBBA molar ratio of 20, thus with a large excess of DGEBA. The formation of high molecular weight polymeric chains seems unlikely under these conditions. Thus, the apparent reaction order with respect to TBBA concentration is more probably the result of the actual reaction mechanism.

Nevertheless, to check if diffusional limitations due to polymer chain growth may play a role on the apparent reaction order with respect to phenolic group concentration at high conversion values, the DGEBA reaction with DBMP was also studied. DBMP was chosen to serve as a model compound for TBBA because the aromatic ring of DBMP has the phenolic group and the bromine atoms in the same positions as TBBA. Therefore, the reaction mechanism and kinetics of the DGEBA/DBMP reaction should be very similar to that of epoxy groups with TBBA. However, DBMP has a single phenolic group; thus, the DGEBA/DBMP reaction does not result in the formation of polymeric chains. In the absence of chain formation, the effect of increasing temperature during constant heating rate DSC runs should enhance the diffusivity of the reactants and reduce the viscosity of the system.

The DSC experimental runs on the DGEBA/DBMP system were carried out under the same conditions as those used to study the DGEBA/TBBA system. ETPPI was used as a catalyst, and the epoxy/phenol ratios and concentrations were of the same order as those used for the study of the DGEBA/TBBA reaction.

The kinetic analysis of the DSC data was performed with the same assumptions as those used for the analysis of DGEBA/TBBA data. The heat generated in the reaction is 80 kJ/mol of $-$OH. Again, eq 5 was used to calculate the apparent kinetic constant from the experimental data. Also in this case, the reaction order with respect to DGEBA concentration was assumed to be $m = 1$. The best-fit procedure described above was

repeated in order to evaluate the activation energy and the reaction order with respect to DBMP, that was the limiting reactant in the conditions used for the experimental DSC runs. The reaction order resulted in $n = 0.5$. The mean value of the activation energy is of 71.5 kJ/mol ($\pm 4\%$).

Also in this case a linear regression ($p = 1$) was used to estimate the value of the "true" preexponential factor from the values of A' obtained from eq 6 for the different constant heating rate DSC runs. The value of A is 1.3×10^8 mol$^{-1.5}$ kg$^{1.5}$ s^{-1}, and the regression coefficient is 0.97.

The kinetic and calorimetric parameters obtained from the present analysis for the DGEBA/DBMP/ETPPI reaction are summarized in Table 4. The similar values of the heat of reaction and of the overall activation energies shown in Table 4 suggest that the DGEBA/TBBA and the DGEBA/DBMP reaction processes are quite similar and support the hypothesis that the reactivity of the phenolic groups of TBBA and DBMP are very similar.

On the other hand, the same apparent reaction order with respect to phenolic group concentration was found for the two reactants, despite the formation of polymeric chains in the DGEBA/TBBA process that increases the system viscosity.

Thus, the value of the reaction order ($n = 0.5$) may result from the actual reaction mechanism of the phenolic groups with the epoxy groups of DGEBA or may be the result of a change in the reaction mechanism, possibly related to the depletion in the phenolic group concentration at high conversion degrees. However, the results discussed above suggest that the increase in viscosity due to polymer chain growth plays only a minor role on the apparent reaction kinetics.

Conclusions

The DGEBA/TBBA/ETPPI reaction process was studied by calorimetric techniques and quantitative IR analysis. A wide range of DGEBA/TBBA molar ratios and of catalyst concentrations was studied, including those typical of industrial processes.

The influence of secondary reactions, such as DGEBA homopolymerization or isomerization, and of secondary hydroxilic group reaction with DGEBA was proven to be negligible under the experimental conditions used in the present study.

The kinetic parameters of the reaction process were evaluated using a single-step Arrhenius kinetic model. Although the model used to analyze the experimental data is probably oversimplified compared to the actual reaction mechanism, the kinetic data obtained may be useful at least for a preliminary evaluation of process conversions and reaction rates. The kinetic and calorimetric parameters estimated may also be a starting point for the safety evaluation of chemical reaction hazards in DGEBA/TBBA industrial reaction processes, because in general the temperature range and temperature$-$time profiles of these processes are similar to those considered in the present study.

Nomenclature

A = preexponential factor (s^{-1} (mol/kg)$^{1-m-n-p}$)

A' = apparent preexponential factor (s^{-1} (mol/kg)$^{1-m-n}$)

C_c = catalyst concentration (mol/kg)

C_d = DGEBA concentration (mol/kg)

C_t = TBBA concentration (mol/kg)

E_a = activation energy (kJ/mol)

EC = ratio between the area of the epoxide IR absorption band at 916 cm^{-1} and the total area of the aromatic absorption peaks at 1608 and 1582 cm^{-1}

K = kinetic constant (s^{-1} (mol/kg)$^{1-m-n}$)

m = reaction order with respect to DGEBA concentration

n = reaction order with respect to TBBA concentration

N_0 = initial moles of the limiting reactant (mol)

p = reaction order with respect to catalyst concentration

q = heat flow (W)

Q = global reaction heat (J)

R = universal gas constant (8.31 J/mol K)

t = time (s)

T = temperature (K)

W = sample weight (kg)

ΔH = heat of reaction (J/mol of $-$OH)

ξ = molar conversion of the limiting reactant

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