

Cure of Epoxy Novolacs with Aromatic Diamines.

I. Vitrification, Gelation, and Reaction Kinetics

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SYNOPSIS

The cure reaction of a commercial epoxidized novolac with 4,4' diaminodiphenylsulfone (DDS) was studied at constant cure temperatures in the range 120–270°C, as well as at constant heating rates (differential scanning calorimetry, DSC). Stoichiometric formulations did not attain complete conversion due to the presence of topological restrictions. The limiting conversion was $x_{\max} = 0.8$. Samples containing an amine excess ($\geq 20\%$) could be completely reacted, whereas this was not possible for formulations containing an epoxy excess. Samples containing a 20% amine excess showed the maximum value of the glass transition temperature (T_g 230°C). Cure took place by epoxy-amine hydrogen reactions catalyzed by (OH) groups. A reactivity ratio of secondary to primary amine hydrogens equal to 0.2 was found. The activation energy was $E = 61$ kJ/mol, as arising from T_g versus time shift factors and time to gel measurements. A unique relationship between T_g and x could be obtained. Gelation took place at $x_{\text{gel}} = 0.45$ and the maximum T_g for the stoichiometric system was $T_{g\max} = 215^\circ\text{C}$ for $x = 0.8$. A conversion versus temperature transformation diagram was used to represent conditions where gelation, vitrification, degradation, and topological limitations took place. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy novolacs is a generic term designating epoxidized products derived from phenol- or cresol-formaldehyde novolacs. They constitute the basis of several high- T_g thermosetting materials such as adhesives, coatings, and encapsulants for integrated circuits.¹ Usual hardeners are novolacs or aromatic diamines. The former have been used since the early 1970s in silica-filled (70% wt) formulations for the encapsulation of integrated circuits. Therefore, some fundamental studies may be found in the literature concerning the reaction between epoxy novolacs and phenols.^{2–6} However, except for a preliminary report,⁷ no fundamental studies have been published on the reaction between epoxy novolacs and aromatic diamines.

The aim of this work is to study the cure reaction of a commercial epoxy novolac, derived from a phenol-formaldehyde novolac resin, with 4,4'di-

aminodiphenylsulfone (DDS), which is a common aromatic diamine used in high- T_g formulations. This first part deals with the analysis of transformations occurring during network formation such as vitrification, gelation, and thermal degradation, the reaction kinetics and the presence of topological restrictions to reach complete conversion. A second part of the study will focus on the explanation of some of the observed trends through a statistical model of network formation.

EXPERIMENTAL

Materials

Figure 1a shows the structure of the commercial epoxidized novolac (EPN 1138, Ciba-Geigy), as reported by the supplier. This structure assumes a 100% efficiency in the transformation of phenolic hydroxyls into phenyl glycidyl ethers. That this does not correspond to the actual structure is evident from the specified weight per epoxy equivalent, WPE

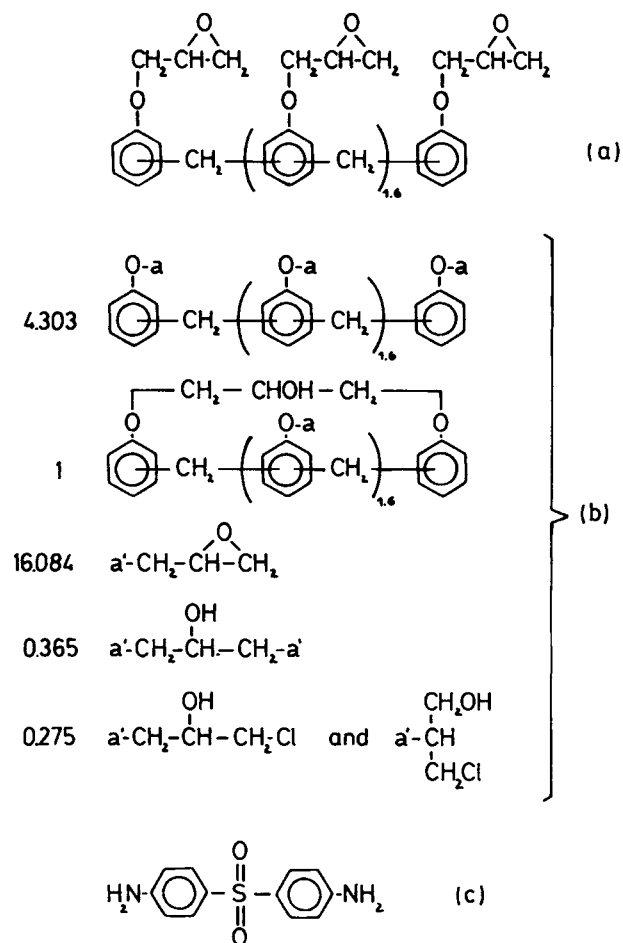


Figure 1 (a) Molecular structure of the commercial epoxidized novolac (EPN 1138, Ciba-Geigy), as specified by the supplier; (b) Proposed molecular structure of the same epoxidized novolac, derived from its characterization; (c) Structure of 4,4'-diaminodiphenylsulfone (DDS).

176–181 g eq⁻¹, which is significantly higher than the one arising from the proposed structure (WPE 158.7 g eq⁻¹). A detailed analysis of the epoxidation of bisphenol A and phenolic novolacs has been reported elsewhere.⁸ The difference between actual and proposed structures for epoxidized novolacs is mainly ascribed to both intra- and intermolecular glycerol groups (—CH₂—CHOH—CH₂—), arising from epoxy-ArOH reactions.

A batch of EPN 1138 was characterized by determining the weight per epoxy equivalent (WPE), the weight per epoxy plus OH equivalent (WPE + OH), the residual chlorine and the number average molecular weight.⁸ The following values were obtained: WPE = 184.2 g eq⁻¹, WPE + OH = 172 g eq⁻¹, %Cl = 0.33, M_n = 600 g mol⁻¹. These values lead to the actual structure of the epoxidized novolac, shown in Figure 1b. Instead of showing an average

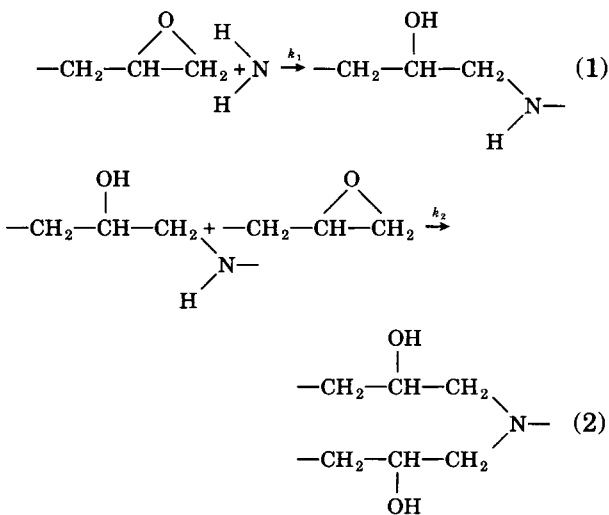
chemical formula, the structure is fragmented into the distinct units shown in Figure 1b. Sites where the structure was cut are labelled with letters *a* and *a'*. The average chemical structure may be rebuilt by randomly joining bonds labelled with the letter *a* with those marked with the letter *a'*. A cyclic structure (without any cut) is also shown.

The epoxidation efficiency is 84.3% (16.084 epoxy groups for 5.303 × 3.6 phenolic rings); the remaining phenolic hydroxyls are consumed in the formation of intramolecular cycles (10.5%; i.e., 2 of the initial 5.303 × 3.6 phenolic rings), chain extension (3.8%; i.e., 2 × 0.365 of the initial 5.303 × 3.6 phenolic rings), and production of chlorine-containing residues (1.4%; i.e., 0.275 of the initial 5.303 × 3.6 phenolic rings). Although the actual structure is not relevant for the conclusions to be derived in this part of the series, it is of major importance for the statistical description of network formation, to be discussed in the next part of the study.

The hardener was 4,4'-diaminodiphenylsulfone (DDS, HT 976, Ciba-Geigy). Its structure is shown in Figure 1c. It has a melting point close to 176°C, a density of 1.38 g cm⁻³ (20°C) and a theoretical equivalent weight of 62 g eq⁻¹ (functionality = 4).

Reactions/Mixing Procedure

The following main reactions take place between the epoxy novolac and the aromatic diamine:



Such secondary reactions as the epoxy secondary hydroxyl polyetherification and the epoxy homopolymerization may be considered negligible in this particular system, as will be discussed in following sections. The reactivity of a secondary amine hy-

drogen normally is smaller than that of a primary amine hydrogen.

As no catalyst was added, the polymerization was thermally activated. This made it possible to select a particular temperature where a good mixing was performed without advancing the chemical reaction. The following procedure was selected: the epoxy novolac was kept at 135°C and the specified amount of DDS added while stirring continuously. After 1–2 min a clear homogeneous solution resulted. Fresh samples were always prepared.

Techniques

Heats of reaction for different stoichiometric ratios, were determined using differential scanning calorimetry (DSC, Du Pont 990 provided with a 910 DSC cell). Runs were carried out at 10°C/min under a nitrogen flow. After quenching to room temperature, samples (contained in the same sealed pans) were rescanned at the same rate to obtain the glass transition temperature. T_g appeared as an endothermic shift over a broad temperature interval in the DSC scan (Fig. 2). It was defined as the midpoint of the step transition.

The increase in the glass transition temperature as a function of time, was determined at eight different temperatures: 140, 160, 180, 200, 220, 240, 260, and 270°C. Samples were cured inside the DSC cell isothermally under continuous N₂ flow for prespecified times. After cooling to room temperature, samples were subjected to a temperature scan at 10°C/min to determine the T_g of the material after the partial cure and the residual exotherm, ΔH_r , of the remaining reaction. A typical DSC scan is shown in Figure 2. Vitrification was attained when $T_g = T_{cure}$. After this time, polymerization continued at a very slow rate together with sub- T_g physical annealing. This last process gives place to an endothermic relaxation peak just before the residual exotherm, which complicates the measurement of

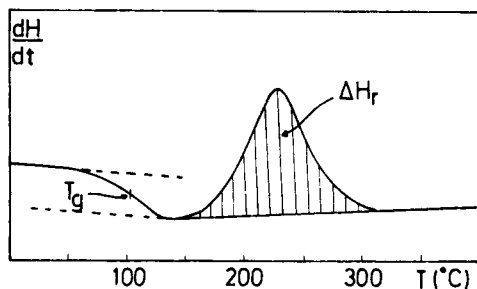


Figure 2 Typical DSC scan of a partially cured sample (28 min at 160°C).

ΔH_r . The effect of physical annealing can be erased by heating to a temperature just above the endothermic peak, quenching, and rescanning.^{3,9-11} However, this procedure was not necessary because the analysis was restricted to results in the range of $T_g \leq T_{cure}$.

Conversions were defined as:³

$$x = (\Delta H_u - \Delta H_r) / \Delta H_T \quad (3)$$

where ΔH_u is the maximum heat that can be detected from reacting samples in the DSC at 10°C/min, ΔH_r is the residual heat of reaction (Fig. 2), and ΔH_T is the total heat evolved by an epoxy-amine reaction, determined from the literature to be 105 kJ/eq.¹²⁻¹⁹ Whereas $\Delta H_u = \Delta H_T$ for the cure of epoxy resins based on diglycidylether of bisphenol A (DGEBA) with diamines, $\Delta H_u / \Delta H_T$ is less than unity for systems based on epoxy novolacs.³

Gelation times were measured by curing samples at six different temperatures: 120, 130, 140, 150, 160, and 170°C, for prespecified times, and determining the solubility in tetrahydrofuran (THF). Gelation was ascribed to the incipient formation of an insoluble fraction.

RESULTS AND DISCUSSION

ΔH_u vs. Stoichiometric Ratio: Topological Limitations

Figure 3 shows heats of reaction, ΔH_u , obtained in DSC scans at 10°C/min, as a function of the stoichiometric ratio, $r = \text{amine eq./epoxy eq.}$. As values of ΔH_u are calculated on the basis of the reactant that is deficient in the formulation, every value should lie in the range of theoretical values (i.e., 105 ± 5 kJ/eq). However, the actual situation is completely different. Only for 20–60% amine excesses ($r = 1.2$ – 1.6) are expected values obtained within experimental error. This means that, in these conditions, $\Delta H_u = \Delta H_T$ and epoxides were completely reacted. However, when the diamine is deficient ($r < 1$), complete reaction could not be attained.

To decide whether incomplete reaction was the result of kinetic or topological limitations,^{3,20} the stoichiometric mixture was subjected to prolonged isothermal heating at temperatures $T > T_{g_{max}}$ (see following sections). Only an almost negligible advance in conversion could be inferred from the fact that T_g increased from 210°C (obtained after the first DSC scan) to 215°C ($T_{g_{max}}$ of the stoichiometric sample). The conversion after the first DSC scan

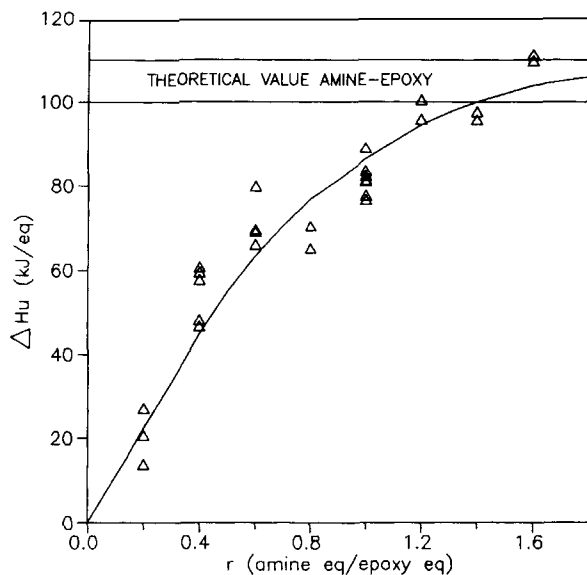


Figure 3 Heats of reaction, ΔH_u (expressed per equivalent of the reactant deficient in the formulation), obtained in DSC scans at $10^\circ\text{C}/\text{min}$, as a function of the stoichiometric ratio, $r = \text{amine eq./epoxy eq.}$

was close to $x = 0.8$. This means that for $x > 0.8$ topological limitations are operative. The origin of this restriction in the network build up may be that it is not possible to bind every diamine by its four arms due to the stiffness of both monomers. Thus, if only three amine hydrogens can enter reaction without steric restrictions, the conversion at which topological limitations would appear is $x = 0.75$ (i.e., close to the experimental value).

Topological limitations were also observed by Hale et al.³ in the cure of epoxy novolacs with cresol novolacs. The highest value of conversion recorded on a stoichiometric mixture after a DSC scan at $20^\circ\text{C}/\text{min}$, was close to 80%, that is the same value as the one arising for the epoxy novolac-aromatic diamine cure. The presence of a significant amount of unreacted epoxy was qualitatively supported by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Therefore, it may be concluded that when epoxy novolacs are cured with a stoichiometric amount of a rigid hardener, a limiting conversion will be attained due to topological limitations.

The branch of ΔH_u versus r (Fig. 3), for $r < 1$, will be examined now. Again, in order to analyze the presence of kinetic limitations, DSC scans at different heating rates were carried out for a sample with $r = 0.4$. Table I shows the resulting experimental values. Kinetic limitations are evident, possibly derived from the slower reaction rate of the secondary amine compared to the primary one. This

will be discussed in more detail in the section dealing with kinetics. Also of interest is the fact that the maximum conversion attained for the slowest scanning rate is $x = 80/105 = 0.76$, which is very close to the limiting conversion arising from topological limitations.

Another result which is implicit in Figure 3, is the absence of such secondary reactions as epoxy-OH or the homopolymerization of epoxy groups, at least in the time scale of our experiences (no reaction at all is observed for a system devoid of hardener). Should these reactions be present, no limitation for the maximum extent of reaction of epoxy groups could be expected, due to the flexibility of polyether chains. In fact, it was shown that the reaction between epoxy novolacs and secondary hydroxyls proceeds only when a catalyst (i.e., an imidazole) is present in amounts higher than a critical value.¹

T_g vs. Stoichiometric Ratio: Maximum T_g

Figure 4 shows glass transition temperatures obtained after a first scan at $10^\circ\text{C}/\text{min}$, as a function of the stoichiometric ratio. The maximum T_g is obtained for samples with a 20% amine excess (i.e., $T_g(r_{1.2}) = 230^\circ\text{C}$). This value is greater than the maximum T_g obtained for the stoichiometric system reacted to its limiting conversion ($T_{g_{\text{max}}} = 215^\circ\text{C}$). Both networks have different structures. The stoichiometric system has 20% of unreacted epoxides and amines, while the system with $r = 1.2$ has its epoxides almost completely reacted and a 20% free amine hydrogens (possibly free secondary amines). This last network shows the higher T_g .

If r is increased beyond 1.2, a decrease in T_g is observed because no extra gain is obtained in the extent of reaction but more imperfections are introduced (a decrease in the concentration of elastically active chains and an increase in the concentration of pendant chains).²¹ Thus, to obtain the maximum

Table I Heats of Reaction, ΔH_u ,^a Obtained in DSC at Different Heating Rates, for Samples with a Stoichiometric Ratio, $r = 0.4$

Heating Rate ($^\circ\text{C}/\text{min}$)	ΔH_u (kJ/eq)
2	80
5	67
10	61
20	46

^a Expressed per equivalent of the reactant deficient in the formulation.

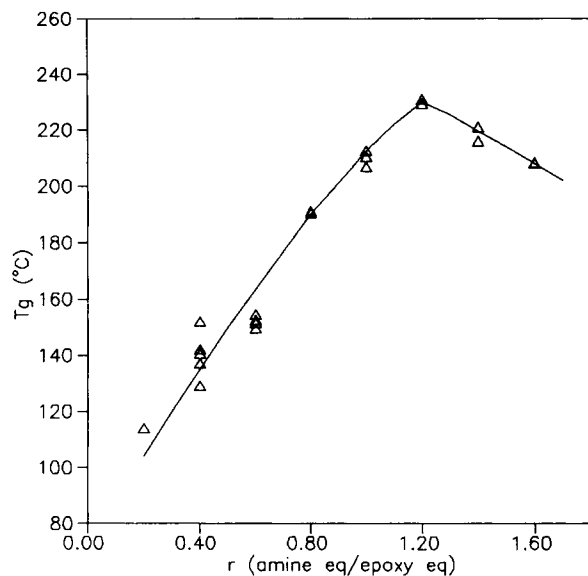


Figure 4 Glass transition temperatures obtained after a first scan at 10°C/min, as a function of the stoichiometric ratio, $r = \text{amine eq./epoxy eq.}$

T_g possible in these systems, formulations with a 20% amine excess must be selected.

DGEBA-based systems always show a maximum in T_g for the stoichiometric formulation ($r = 1$).²¹ This general empirical observation may be justified on theoretical grounds.²¹ Some exceptional reported departures must be ascribed to an error in the equivalent weight assigned to one of the reactants.²² However, when topological limitations are present, as seems to be the case in the cure of epoxy novolacs with rigid hardeners, a shift in the maximum of T_g versus r can arise.

In what follows, only results for stoichiometric systems will be discussed.

T_g vs. Time: Time-Temperature Shift

The increase in T_g with time for the eight isothermal cure temperatures is shown in Figure 5. Vitrification times for cure temperatures lower than $T_{g_{\max}}$ are marked by arrows (at 140°C vitrification was not attained during the cure period). The initial solution of monomers had a $T_{g_0} = 40^\circ\text{C}$.

The maximum glass transition temperature that could be attained was $T_{g_{\max}} = 215^\circ\text{C}$, in agreement with results reported by Mohanty et al.⁷ for a similar system. The cure at $T > T_{g_{\max}}$ did not increase this limiting value. Therefore, an explanation for arresting the polymerization in the rubbery region (at conversions close to $x_{\max} = 0.8$), is the presence of topological limitations, as discussed in previous sec-

tions. Moreover, when the cure at 270°C was continued for more than 2 h, thermal degradation took place as revealed by the decrease in T_g . Chemical reactions involved in thermal degradation of epoxy novolacs have been discussed by Sullivan.⁶

By assuming that the reactivity ratio of secondary to primary amine hydrogens, k_2/k_1 , does not depend on temperature, a unique relationship between conversion and network structure, or its characteristics T_g , must exist. In turn, this leads to the possibility of making a time-temperature superposition of experimental results.^{9-11,23,24}

The increase in conversion in the region where the polymerization is kinetically controlled (e.g., for $T_g < T_{\text{cure}}$) may be expressed by a constitutive equation of the type

$$dx/dt = Af(x)\exp(-E/RT) \quad (4)$$

where E is the activation energy of the epoxy-amine reaction catalyzed by OH groups.²⁵

Integrating eq. (4) at constant temperature, and taking natural logarithms, it results

$$\ln\left(\int_0^x dx/f(x)\right) = \ln A - E/RT + \ln t \quad (5)$$

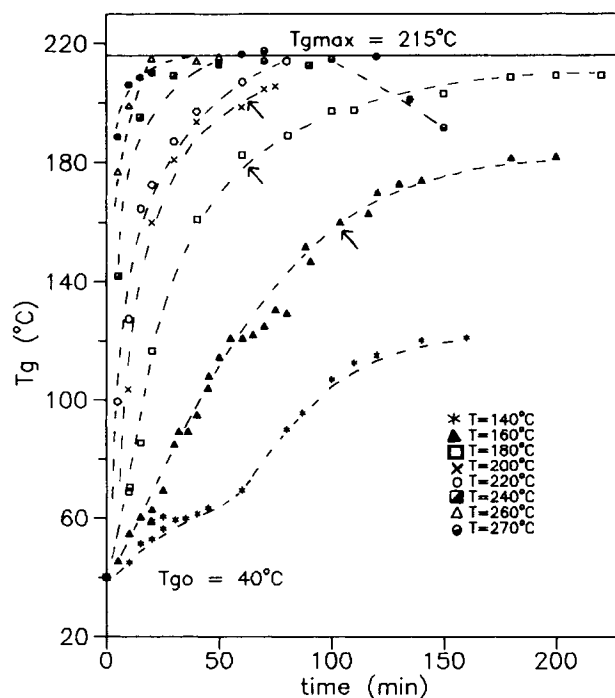


Figure 5 Glass transition temperature vs. time at different cure temperatures. Vitrification points for three cure temperatures are marked by arrows.

As x and T_g are uniquely related, eq. (5) may be rewritten as

$$F(T_g) = \ln A - E/RT + \ln t \quad (6)$$

Figure 6 represents the increase in T_g as a function of $\ln t$ in the region where the polymerization is kinetically controlled ($T_g < T_{cure}$).

Equation (6) may be written for an arbitrary reference temperature, T_r , as:

$$F(T_g) = \ln A - E/RT_r + \ln t(T_r) \quad (7)$$

By subtracting eq. (6) from eq. (7), a shift factor may be defined as:

$$a_T = \ln t(T_r) - \ln t(T) = E/RT_r - E/RT \quad (8)$$

The selected reference temperature was $T_r = 180^\circ\text{C}$ and the best a_T factor was determined for all other temperatures (Table II), to produce the superposition shown in Figure 7. The excellent superposition of T_g versus $\ln(\text{time})$ curves confirms that the network structure is determined exclusively by the conversion level attained in the polymerization, independently of the selected cure temperature. This also gives us an indirect evidence that secondary reactions are not significant in the selected experimental conditions.

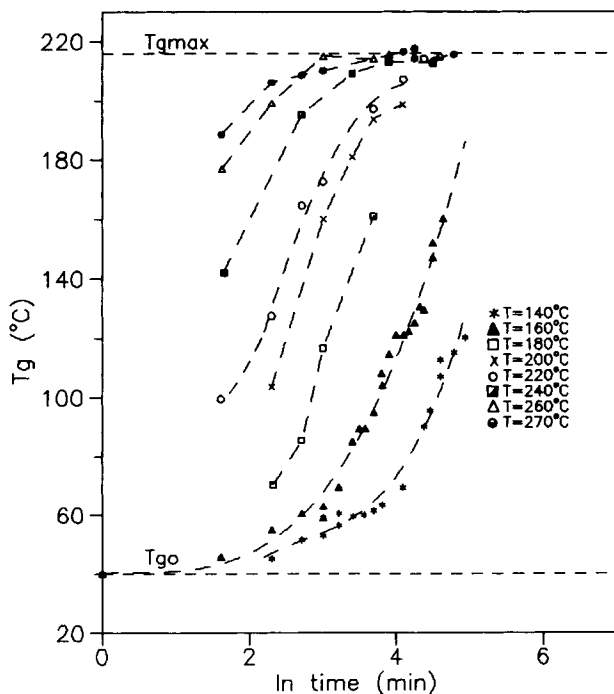


Figure 6 Glass transition temperature vs. \ln time (min) for the kinetically controlled polymerization ($T_g < T_{cure}$).

Table II Shift Factor (a_T) in the \ln (Time) Scale Used in the Construction of the Master Curve at 180°C

Cure Temperature ($^\circ\text{C}$)	Shift Factor $\ln t(180^\circ\text{C}) - \ln t(T)$
140	-1.711
160	-0.912
200	0.657
220	1.050
240	1.770
260	2.340

Activation Energy of the Polymerization

By plotting shift factors shown in Table II as a function of $(1/T)$, the activation energy of the polymerization may be obtained [eq. (8)]. Figure 8 shows such a plot which leads to $E = 61.3$ kJ/mol. This value is typical of an epoxy-amine reaction catalyzed by OH groups.^{12,15} In particular, activation energy values reported for the reaction between DDS and DGEBA-based epoxy resins are: $E = 61.9$ kJ/mol (Riccardi and Williams¹⁸), $E = 60$ kJ/mol (Sung et al.²⁶), $E = 63$ kJ/mol (Harran and Grenier-Loustalot²⁷), $E = 53$ kJ/mol (Grillet et al.¹⁹).

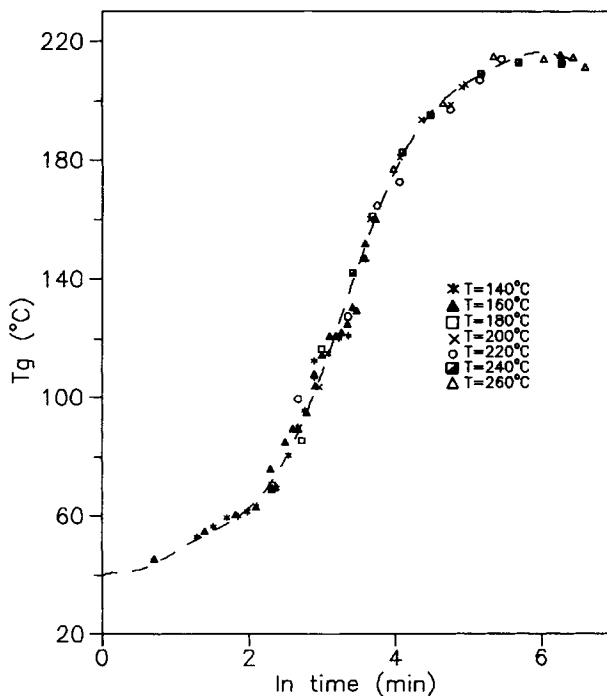


Figure 7 Superposition of the T_g vs. \ln (time) data to form a master curve at 180°C .

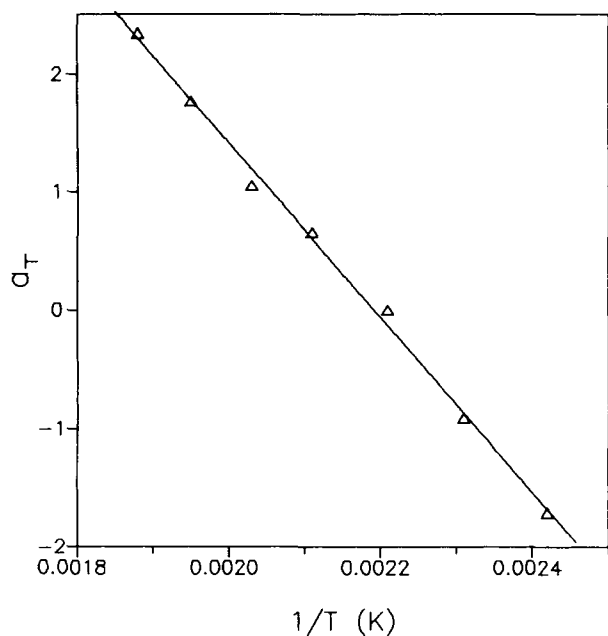


Figure 8 Arrhenius plot of the shift factor, a_T .

Therefore, it may be inferred that the same catalytic mechanism (e.g., catalysis by hydroxyls) is operative in DGEBA-based epoxies and novolac epoxies in their reaction with aromatic diamines.

Glass Transition Temperature vs. Conversion Relationship

Figure 9 shows glass transition temperatures measured in the kinetically controlled polymerization ($T_g < T_{\text{cure}}$), plotted as a function of conversion [calculated from eq. (3)]. Within the scattering of experimental results, particularly at high conversions, a unique relationship between T_g and conversion is apparent.

The influence of the network structure on the T_g versus x functionality will be discussed in part 2.

Constitutive Equation for the Polymerization Kinetics

Using the shift factors shown in Table II, conversion versus time curves obtained at different temperatures may be superposed in a master curve at the reference temperature (180°C). Figure 10 shows such a plot in linear scale of conversions and times.

As there is a significant initial amount of (OH) groups in the epoxy novolac, $[\text{OH}]_0/e_0 = 0.1$ (Fig. 1b), a pure autocatalytic mechanism may be proposed.^{15,25} The following kinetic equations may be written

$$-de/dt = k_1[\text{OH}]e(a_1 + Na_2) \quad (9)$$

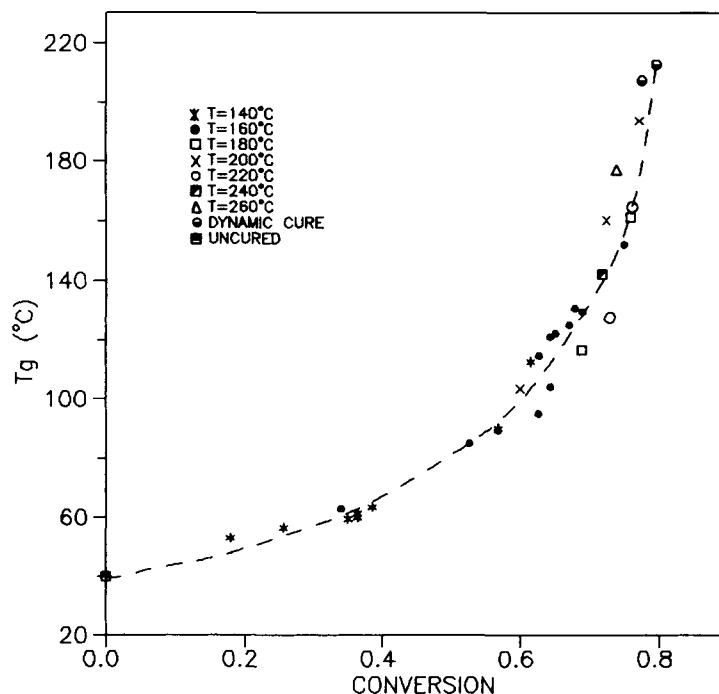


Figure 9 Glass transition temperature as a function of conversion.

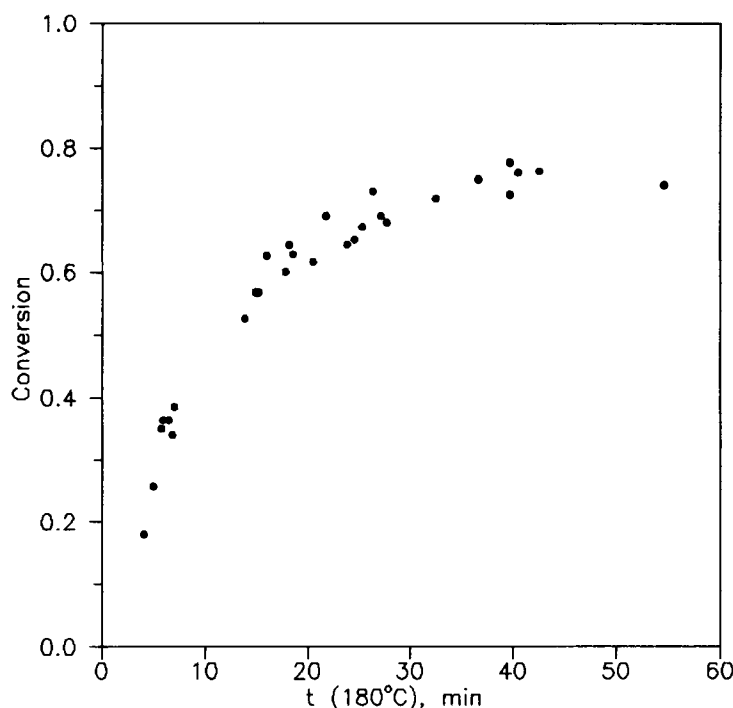


Figure 10 Superposition of conversion vs. time data, at a reference temperature of 180°C, for the kinetically controlled region ($T_g < T_{cure}$).

$$-da_1/dt = 2k_1[OH]ea_1 \quad (10)$$

$$da_2/dt = k_1[OH]e(a_1 - Na_2) \quad (11)$$

where e is the concentration of epoxy equivalents, a_1 is the concentration of primary amine hydrogens, a_2 is the concentration of secondary amine hydrogens, N is the k_2/k_1 (reactivity ratio of secondary to primary amine hydrogens). The factor 2 in eq. (10) accounts for the fact that the reaction of a primary amine hydrogen automatically converts the remaining hydrogen into a secondary amine one.

When $x = (e_0 - e)/e_0$, $\alpha = a_1/e_0$, and $K_1 = k_1e_0^2$ are defined and the relationships between a_1 and e [integrating the ratio of eqs. (9) and (10)] and a_1 and a_2 [integrating the ratio of eqs. (10) and (11)] are found,¹⁸ kinetics for a stoichiometric system may be finally expressed by²⁵

$$dx/dt = K_1 \{ [OH]_0/e_0 + x \} (1 - x) \times \{ \alpha + [N/(2 - N)](\alpha^{N/2} - \alpha) \} \quad (12)$$

$$x = 1 - [\alpha(1 - N) + \alpha^{N/2}]/(2 - N) \quad (13)$$

Figure 11 shows the fitting of the proposed kinetic model with experimental results. The best fitting was obtained for $N = 0.2$ and $K_1 = 0.42 \text{ min}^{-1}$ (at

180°C). Taking into account the value of the activation energy calculated from Figure 8, the following relationship between K_1 and T (K) may be obtained:

$$K_1 (\text{min}^{-1}) = 4.984 \times 10^6 \exp(-7379/T) \quad (14)$$

The low value of the reactivity ratio, N , gives us a qualitative explanation for the increase in the final conversion which was observed when decreasing heating rate in DSC scans, for formulations containing an epoxy excess (Table I). N values reported for the reaction between DDS and DGEBA-based epoxy resins are in the range 0.2–0.6^{18,28–31} (N is defined in such a way that $N = 1$ represents the ideal polymerization without substitution effects). In particular, our $N = 0.2$ agrees with the value reported by Bidstrup and Macosko.³¹ It seems that a similar substitution effect is operative in the reaction of DDS with epoxy novolacs or with DGEBA-based epoxies.

Gelation

Gel times, t_{gel} , were defined as the cure time at constant temperature leading to an incipient gel in tetrahydrofuran. As the network structure is a unique function of conversion, x_{gel} may be considered con-

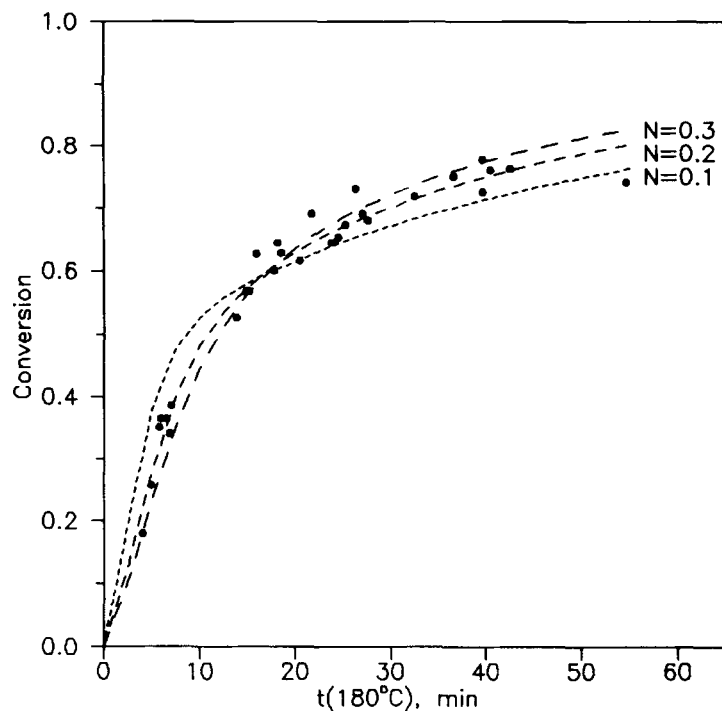


Figure 11 Fitting of the proposed kinetic model with experimental results for different values of the reactivity ratio, $N = k_2/k_1$.

stant and independent of temperature. Then, integrating eq. (4) from $x = 0$ to $x = x_{\text{gel}}$, it results

$$\ln t_{\text{gel}} = \left(\int_0^{x_{\text{gel}}} dx / f(x) \right) - \ln A + E/RT$$

$$= \text{const.} + E/RT \quad (15)$$

Figure 12 shows experimental values of $\ln t_{\text{gel}}$ plotted as a function of $(1/T)$. From the slope of the straight line an activation energy equal to $E = 60.4 \text{ kJ/mol}$ resulted, in excellent agreement with the value arising from T_g versus $\ln t$ shift factors.

The straight line shown in Figure 12 may be extrapolated to obtain t_{gel} at any cure temperature. Table III shows values of t_{gel} at different temperatures, as well as x_{gel} calculated from the kinetic equation. Gelation takes place at $x_{\text{gel}} = 0.45 \pm 0.01$. In part 2, this value will be compared with statistical predictions obtained using a fragment model to describe network formation.³²

Transformation Diagram

The different transformations observed during the cure of the epoxy novolac with a stoichiometric amount of DDS may be illustrated in a conversion versus temperature transformation diagram (Fig.

13).^{33,34} The temperature at which vitrification and gelation take place simultaneously is gel, $T_g 65^\circ\text{C}$. In order to avoid a quenching of the chemical reaction by vitrification, a cure cycle for these mate-

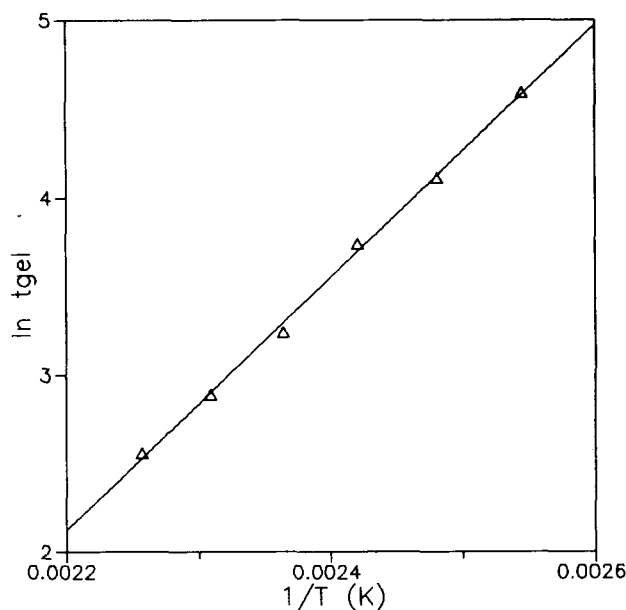


Figure 12 Natural logarithm of the gel time as a function of $(1/T)$.

Table III Gel Times and Gel Conversions at Different Cure Temperatures

T ($^{\circ}\text{C}$)	t_{gel} (min)	x_{gel}
100	269	0.44
120	98	0.44
140	42	0.45
160	18	0.45
180	9	0.46
200	4.5	0.45

rials must include a final step at $T \geq 215^{\circ}\text{C}$. However, it is not convenient to go beyond 270°C because chemical degradation may occur leading to a decrease in the final T_g . Although the degradation temperature was arbitrarily fixed at 270°C , it must be taken into account that the observed degradation depends on the exposure time (e.g., 2 h for 270°C). The most significant finding for the cure of epoxy novolacs is the relatively low conversion at which topological restrictions limit the maximum extent of reaction (e.g., $x_{\text{max}} = 0.8$). A similar value was reported by Hale et al., for the cure of epoxy novolacs with novolacs derived from *o*-cresol.^{2,3}

CONCLUSIONS

Epoxy novolacs cured with stoichiometric amounts of aromatic diamines like DDS do not reach complete conversion due to the presence of topological

restrictions. A limiting conversion equal to $x_{\text{max}} 0.8$, could be attained even by prolonged heatings at high temperatures. A 2 h heating at 270°C lead to chemical degradation as revealed by a decrease in T_g . Samples containing an amine excess over stoichiometry ($\geq 20\%$), could be completely reacted while this was not possible for formulations containing an epoxy excess. It may be inferred that topological limitations arise from steric restrictions involved in the reaction of the 4 amine hydrogens of DDS with the epoxy novolac. Due to the possibility of attaining an almost complete conversion, samples containing a 20% amine excess ($r 1.2$) showed the maximum value of T_g for different stoichiometries ($T_g 230^{\circ}\text{C}$).

Reactions involved in the cure of epoxy novolacs with aromatic diamines are: epoxide-primary amine hydrogen (specific rate constant k_1) and epoxide-secondary amine hydrogen (specific rate constant k_2). Both reactions are catalyzed by OH groups initially present and generated during the polymerization (autocatalytic system). A reactivity ratio $N = k_2/k_1 = 0.2$ was found. Secondary reactions (epoxy-hydroxyl polyetherification or epoxy homopolymerization) were negligible, at least in the time scale used in our experiences and in the absence of specific catalysts. The activation energy for the epoxy-amine reaction catalyzed by (OH) groups was $E = 61 \text{ kJ/mol}$, as arising from T_g vs time shift factors and time-to-gel experiences. This agrees with most of E values reported in the literature for the catalytic mechanism of the epoxy-amine reaction.

A unique relationship between T_g and conversion could be obtained. This suggests that the reaction

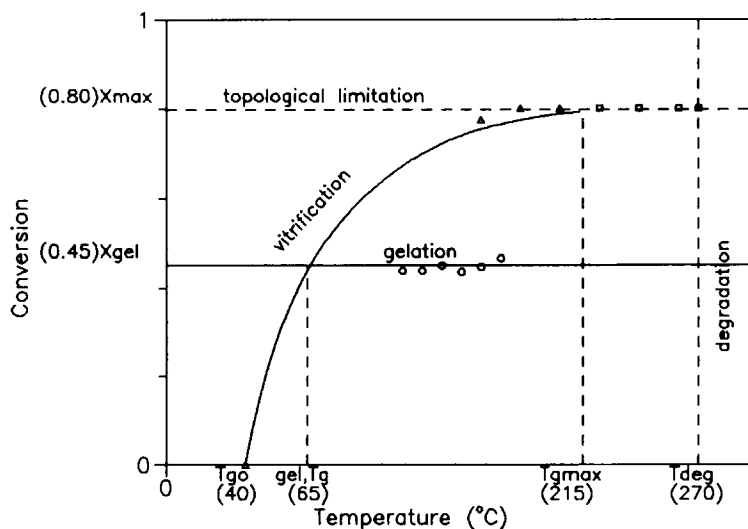


Figure 13 Conversion vs. temperature transformation diagram showing conditions where gelation, vitrification and chemical degradation take place, as well as restrictions arising from topological limitations.

path and the relative reaction rates were the same, independently of the cure temperature. The maximum T_g for the stoichiometric system was $T_{g_{max}}$ 215°C, for a formulation cured to its limiting conversion, x_{max} 0.8. Gelation took place at x_{gel} 0.45 ± 0.01 and temperature at which gelation and vitrification took place simultaneously was gel, T_g 65°C. Gelation, vitrification, degradation, and topological limitations were conveniently represented in a conversion versus temperature transformation diagram, which may be used to design cure cycles for these materials.

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