Curing of Diepoxides with Tertiary Amines: Influence of Temperature and Initiator Concentration on Polymerization Rate and Glass Transition Temperature

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SYNOPSIS

The cure of an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), with benzyldimethylamine (BDMA), was investigated using differential scanning calorimetry. The kinetics showed a first-order behavior with respect to both epoxy and tertiary amine concentrations and a non-Arrhenius dependence on temperature. An activation energy could be defined only in the low-temperature range, i.e., from 80 to 120°C. Its value ($E = 24.2$ kJ/mol = 5.8 kcal/mol) indicates a very slight dependence on temperature. The glass transition temperature of epoxy networks decreased with an increase in both the tertiary amine concentration and the cure temperature. These effects are attributed to plastification by the free amine and to the decrease in the average length of polyether chains, which, in turn, increases the number of network defects.

INTRODUCTION

Tertiary amines are important curing agents of technical epoxy resins. They may be used as independent curing agents or as catalysts in the reaction of epoxides with alcohols, phenols, and carboxylic acids and their anhydrides. Triethylamine (TEA) and benzyldimethylamine (BDMA) are the tertiary amines most frequently used. Experimental work has been carried out on model systems, i.e., monoepoxides like phenyl glycidyl ether (PGE) or p-cresyl glycidyl ether (CGE), that give a distribution of linear oligomers as polymerization products. These studies led to our present knowledge of the reaction mechanism.[1,2] Figure 1 shows possible reactions for the curing of an epoxy monomer with BDMA, whereas Figure 2 shows the structure of different epoxy monomers mentioned in the text.

The initiation step consists in the formation of a quaternary ammonium alcoholate that is the active

propagating site in the anionic polymerization. The presence of the proton–donor compound, R′OH, is necessary to start the reaction.[1,3] The formation of the initiating complex is supported by the existence of an induction period in these polymerizations, first observed by Tanaka and Kakiuchi.[4]

Most of the oligomers resulting from glycidyl ether polymerizations have been characterized as having one C=C double bond and one OH at the ends of a primary chain.[1,2,5-8] These species may result from the alkoxide (3b) or phenoxide (3c) eliminations by intramolecular chain transfer in the propagating anion. They may also be generated via termination by hydrogen abstraction from the counterion[1] (Hoffman elimination) if the enol form of the reaction product enters rapidly in the reaction scheme through steps (1) or (3a).

Although always present, the chain transfer reaction (3a) has a particular significance at the beginning of the polymerization. Chain transfer is favored by an increase in the acidic character of the hydroxyl group. Water, present as an impurity, is the most acidic species present in the initial stages of the reaction. Chain transfer to water occurs almost quantitatively,[1] resulting in the formation of diol species. The rate of addition of epoxide to the
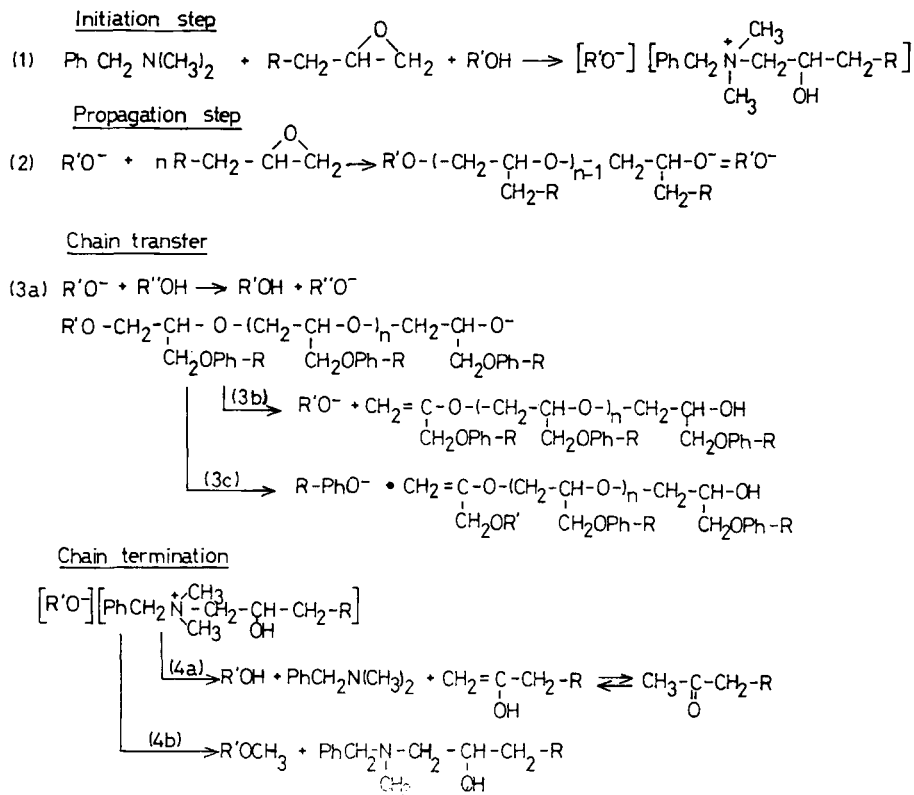
Figure 1 Proposed reaction mechanism for the curing of an epoxy monomer with benzyldimethylamine.

conjugate base of R"OH is higher the lower the acidity of the hydroxyl group. The reactivity of the conjugate base decreases in the sequence alkoxide > hydroxide > phenoxide. Then, transformation of hydroxides in the more reactive alkoxides by propagation leads to an increase in the reaction rate and may add to the appearance of an induction period at the start of the reaction. The phenoxide anion generated in step (3c) is the conjugate base of a highly acidic phenol. This means that it would have a lower rate of further epoxide addition than that of alkoxide, introducing a retardation effect.

The chain termination step (4b) seems to be relevant only at high temperatures[1] (420 K or so) and explains the presence of nitrogen in the polymer when curing in these conditions.

(DGEBA-based epoxy resin)
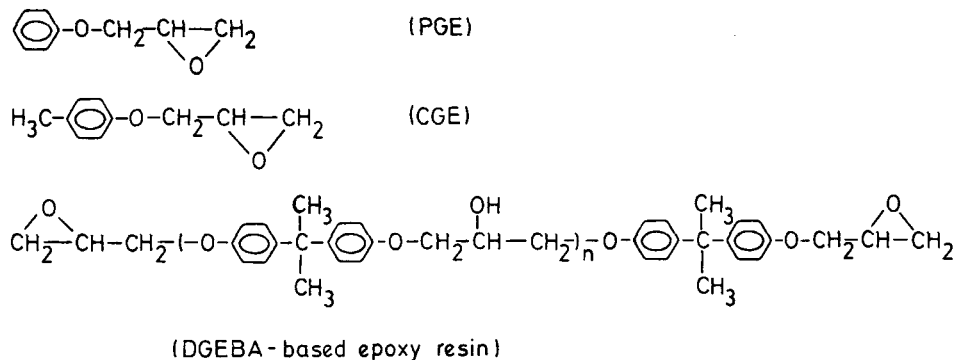
Figure 2 Chemical structures of different epoxy monomers.

The reaction mechanism shown in Figure 1 will be used as a frame of reference for a qualitative interpretation of experimental results that will be shown in what follows. It is not our intention to contribute to the analysis of the polymerization mechanism, but instead results of practical value will be discussed. They include the effect of cure temperature and tertiary amine concentration on the polymerization rate and glass transition temperatures of the resulting networks.

EXPERIMENTAL

A commercial epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) was used (Ciba-Geigy GY-250). The epoxide equivalent weight determined by titration, was 190 g/equiv epoxide. This gives n = 0.14 in the chemical structure shown in Figure 2. The resin was carefully dehydrated by heating under vacuum before use. Benzyldimethylamine (BDMA), from Sigma, was used without further purification. Formulations were prepared using variable BDMA concentrations defined as mol % BDMA = mol BDMA/100 equiv epoxide.

Differential scanning calorimetry (DSC) was used to follow the polymerization rate. Its use in complex polymerizations of this type requires that most of the epoxy consumption results from the propagation step. Recently, Pascault and co-workers[9] proved that conversions arising from DSC are the same as those determined from GPC (following the peak of DGEBA[10]), for cationic chain-wise epoxy polymerizations initiated by trifluoride–amine complexes.

Isothermal and temperature ramp studies were carried out using a DuPont 990 thermal analyzer provided with a 910 DSC cell. Conversions were determined from isothermal thermograms dividing the heat evolved up to a given time by the total heat evolved at complete reaction. The glass transition temperature (T_g) and the residual reaction heat were determined using a scanning rate of 10°C/min. The T_g value was taken as the onset of the endothermic deflection of the base line.

The residual amount of free epoxy groups in cured samples was determined using NIR spectroscopy (Cary 2300, Varian). The absorbance of the epoxide at 2207 nm was monitored, taking the peak at 2138 nm as internal reference. As both the epoxy and reference peaks are very "clean" in near-infrared spectroscopy, their relative concentrations may be determined with a high precision.

RESULTS AND DISCUSSION

Curing with a Temperature Ramp

The most relevant result from dynamic DSC runs carried out at 2°C/min up to 220°C was the impossibility of curing samples to complete conversion. Subsequent scans always showed the presence of a residual reaction heat. Indirectly, this means that the temperature dependence of the overall polymerization rate does not follow the usual Arrhenius law. Therefore, the maximum reaction heat could not be obtained from these runs.

Another interesting fact arising from dynamic runs was the roughly linear proportionality between the reaction heat evolved in the first scan and the tertiary amine concentration, as shown in Figure 3. This effect, which has been previously reported by Galy et al.,[3] is a consequence of the reaction rate being directly proportional to the tertiary amine concentration.

### Curing at Constant Temperature

A typical isothermal DSC thermogram is shown in Figure 4. A maximum in polymerization rate located at very low conversions is observed. Several hours were usually necessary for attaining a constant base line. The reaction heat determined as the area under the DSC thermogram varied in the range $(-\Delta H)$
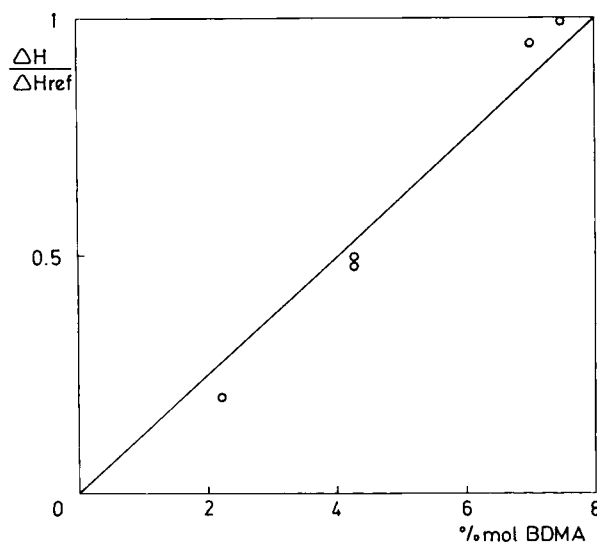
Figure 3 Relative reaction heat in dynamic DSC runs at 2°C/min as a function of the tertiary amine concentration; ΔH_{ref} = experimental value for the sample containing 7.5 mol % BDMA.
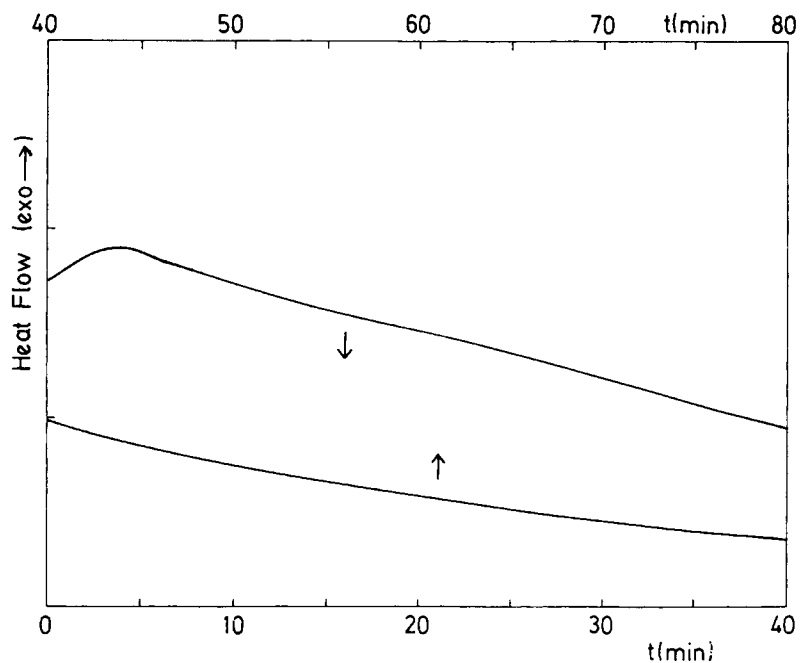
Figure 4 Isothermal DSC thermogram at 110°C, for a sample containing 4 mol % BDMA.
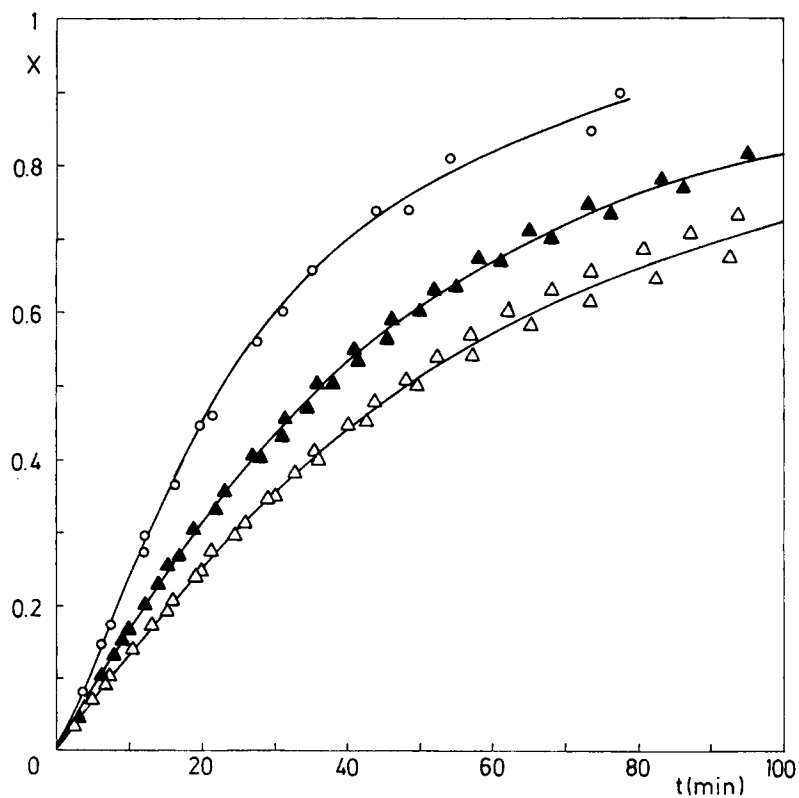
Figure 5 Conversion vs. time curves arising from isothermal DSC runs carried out at 110°C, for samples containing different BDMA concentrations; (△) 3 mol %; (▲) 4 mol %; (○) 6 mol %. Two different runs are plotted for each concentration.

$= 88 \pm 3$ kJ/equiv for samples containing 4 mol % BDMA or more and cured at a constant temperature in the 110–150°C range. The maximum reaction heat was taken as $(-\Delta H) = 92$ kJ/equiv according to Klute and Viehmann.[11] The fact that samples cured in the DSC did not attain complete conversion will be evidenced when discussing glass transition temperatures.

Figures 5 and 6 show the influence of BDMA concentration and curing temperature on conversion vs. time curves arising from isothermal DSC thermograms. Although the effect of the tertiary amine concentration is relevant, temperature shows a very slight influence on kinetics. Moreover, in the 130–150°C temperature range, there is no measurable effect at all within experimental error. These trends are identical to those found for the polymerization of monoepoxides.[2]

Figures 7 and 8 show first-order regressions of conversion vs. time curves plotted in Figures 5 and 6. Except in the very low conversion range, where a maximum in reaction rate had been observed, a reasonable correlation is shown for most runs, i.e., a first-order dependence of polymerization rate on

epoxide concentration is apparent. A linear relationship between specific rate constants, determined from the slopes of straight lines of Figure 7, and the tertiary amine concentration is shown in Figure 9. Thus, the polymerization rate is indeed directly proportional to the BDMA concentration, as previously inferred from Figure 3.

The dependence of polymerization rate on temperature is more complex. Figure 10 shows an Arrhenius plot for the apparent specific rate constants calculated from Figure 8. An activation energy may be defined for the low-temperature range, i.e., from 80 to 120°C. The following value results: $E = 24.2$ kJ/mol (5.8 kcal/mol). Thus, even in the low-temperature range, the homopolymerization of epoxy resins initiated by tertiary amines shows a slight dependence on temperature. A similar effect has been shown for the polymerization of p-cresyl glycidyl ether initiated by BDMA.[2]

Kinetic Model

The most striking feature of this polymerization is the fact that, in spite of its complex mechanism, the
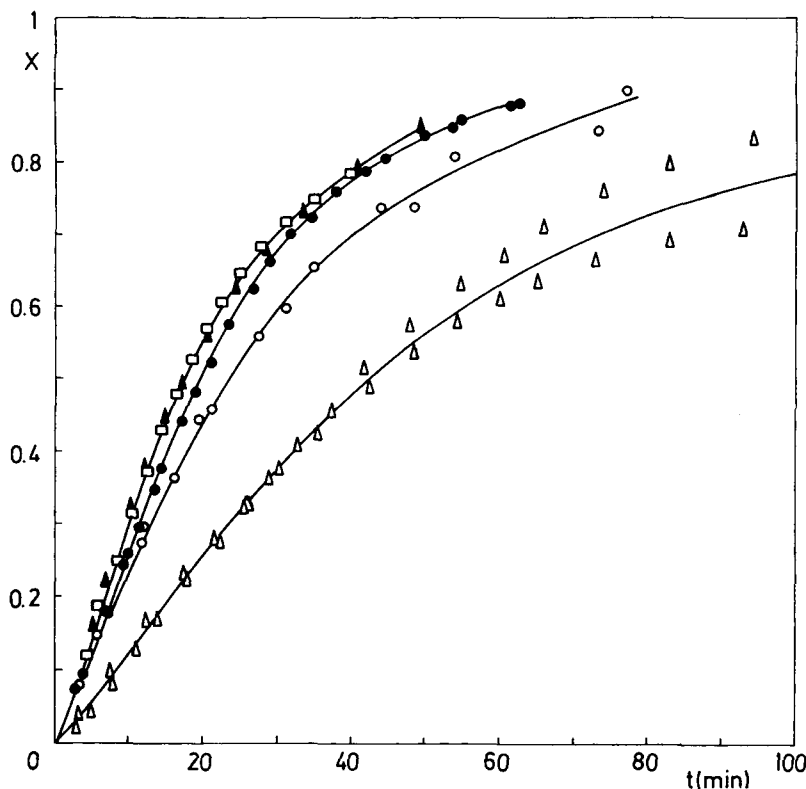
Figure 6   Conversion vs. time curves arising from isothermal DSC runs carried out at different temperatures for samples containing 6 mol % BDMA: ($\triangle$) 80°C; ($\bigcirc$) 110°C; ($\bullet$) 120°C; ($\square$) 130°C; ($\blacktriangle$) 150°C. Two different runs are plotted for 80, 110, and 120°C.
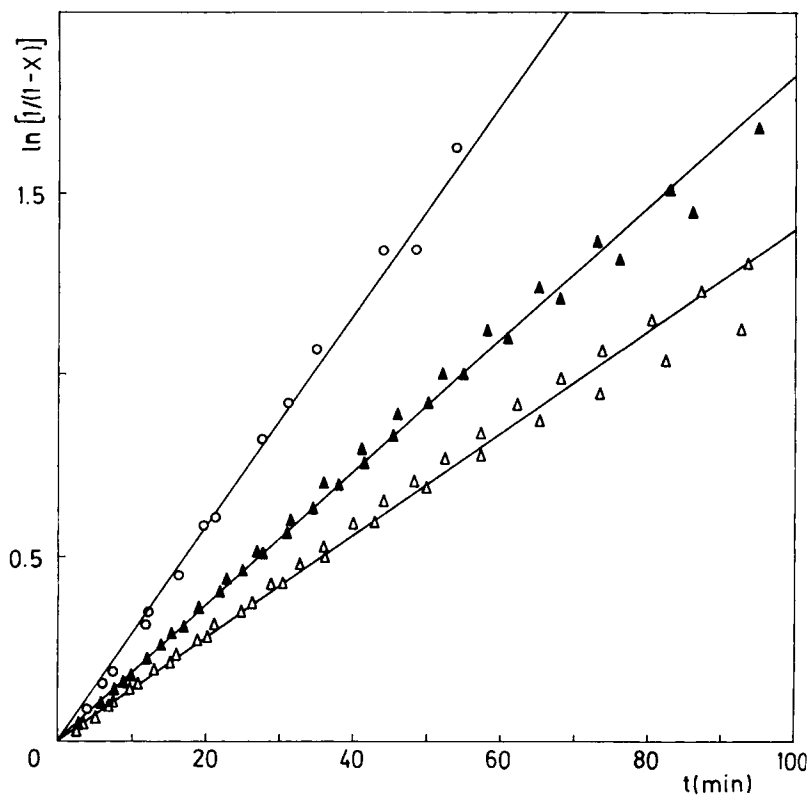
Figure 7   First-order regressions for runs shown in Figure 5, with the same notation.
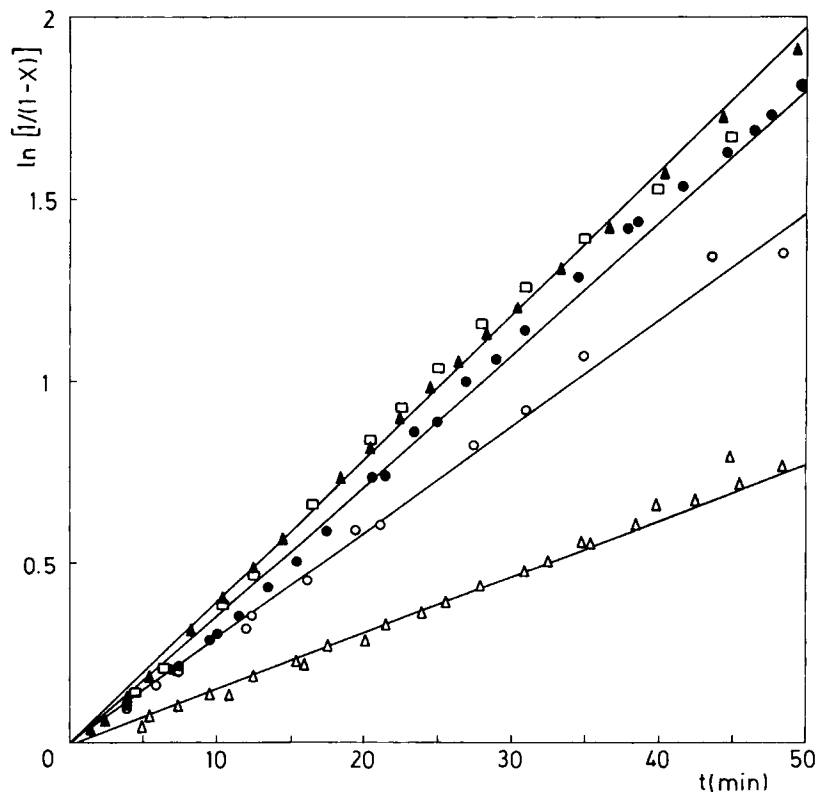

Figure 8   First-order regressions for runs shown in Figure 6, with the same notation.
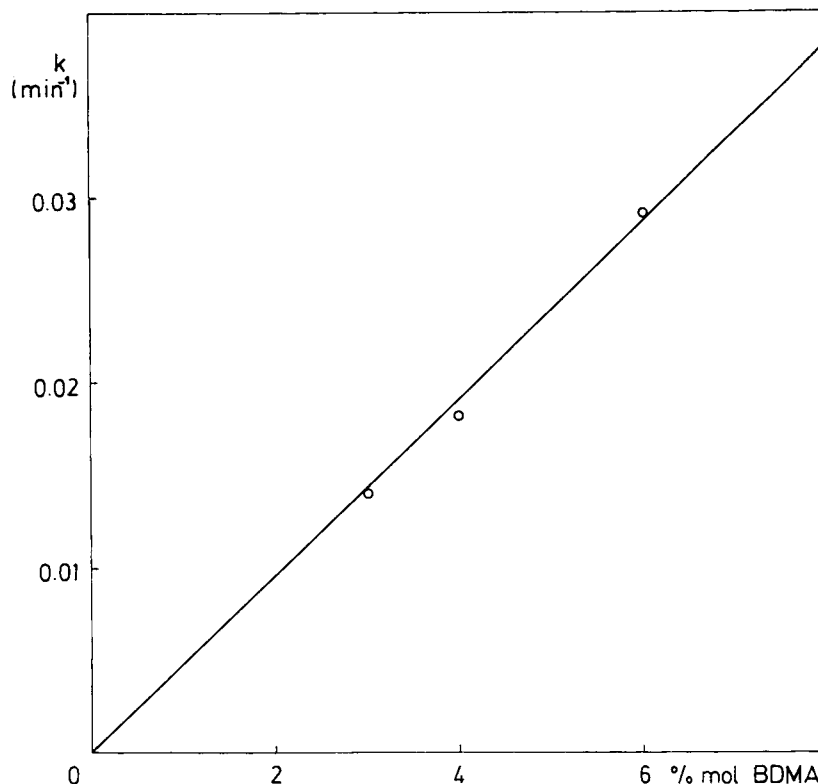
Figure 9   Apparent specific rate constant at 110°C as a function of mol % BDMA.

overall rate follows a simple first-order dependence with respect to both tertiary amine and epoxide concentrations. The obvious explanation is to assume that (1) the rate of epoxy consumption is equal to the propagation rate and (2) the concentration of the propagating species attains a constant value after the initial induction period. Thus,

$$-d[ep]/dt = k_p[\text{R'O}^-][ep] \qquad (1)$$

$$[\text{R'O}^-] = k'[\text{R}_3\text{N}]_0 \qquad (2)$$

The constant k' possibly includes initiation, chain transfer, and chain termination rate constants. Although not supported by specific experimental evidence, it may be assumed that the constancy of $[\text{R'O}^-]$ derives from the attainment of a steady state between initiation (**1**) and termination (**4a,b**) and/or chain transfer step (**3c**), assuming that the phenoxide anion propagates the chain at a slower rate than does the alkoxide. The fact that polymerization is hardly dependent on temperature in the high-temperature range may be explained by the fact that one of the mentioned steps has a high activation energy, becoming relevant only at high temperatures. This makes the values of k' to go through a broad maximum as temperature is increased. In fact,

there is experimental evidence indicating that step (**4b**) takes place at high temperatures.[1] If this picture of the reaction is correct, the constant k' may be written as

$$k' = \frac{k_i}{k_{t1} + k_{t2}} \qquad (3)$$

where k_i, k_{t1}, and k_{t2} are, respectively, specific rate constants characterizing initiation, low-activation-energy termination, and high-activation-energy termination.
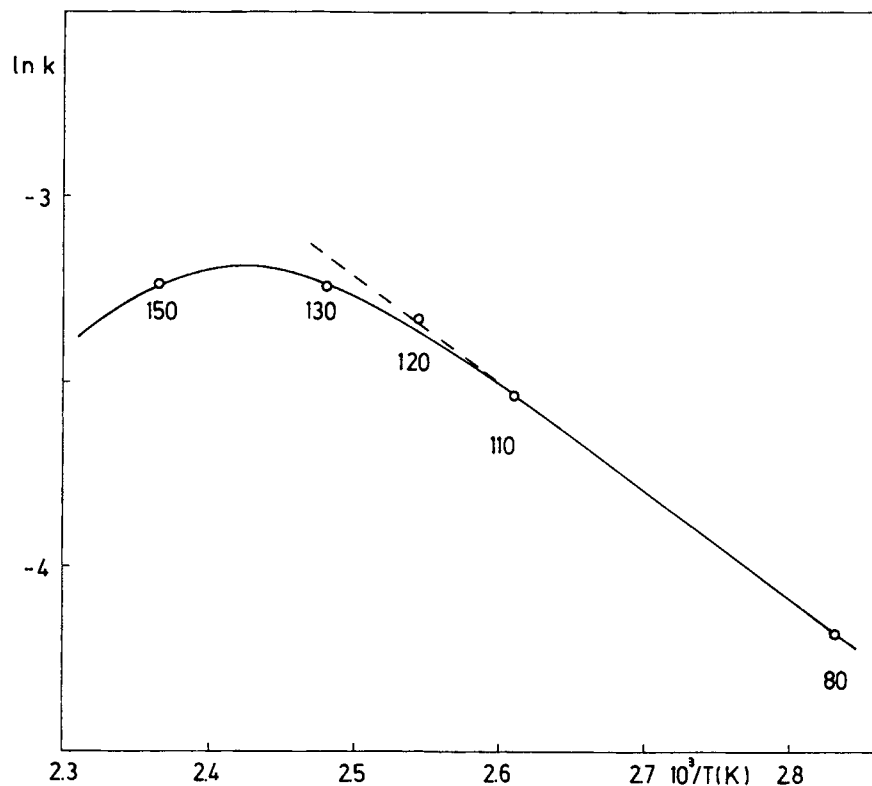
The first-order specific rate constant for epoxy consumption may be, then, written as

$$k = \frac{k_p k_i}{k_{t1} + k_{t2}} [\text{R}_3\text{N}]_0 \qquad (4)$$

The k vs. T dependence experimentally observed may be explained by accepting that the activation energies are such that

$$E_{t1} < E_p + E_i \qquad (5)$$

$$E_{t2} > E_p + E_i \qquad (6)$$

Figure 10   Arrhenius plot for the apparent specific rate constants. The temperature, in °C, is also indicated.

In particular, the full curve fitting the experimental points in Figure 10 is described by

$$k(\text{min}^{-1}) = 1/[A_1 \exp(-E_1/RT)$$
$$+ A_2 \exp(-E_2/RT)] \quad (7)$$

where

$$A_1 = 1.674 \times 10^{-2} \text{ min}$$

$$A_2 = 3.193 \times 10^{13} \text{ min}$$

$$E_1 = E_{t1} - E_p - E_i = -24.2 \text{ kJ/mol}$$

$$= -5.8 \text{ kcal/mol}$$

$$E_2 = E_{t2} - E_p - E_i = 101.7 \text{ kJ/mol}$$

$$= 24.3 \text{ kcal/mol}$$

In the low-temperature range, $k_{t1} \gg k_{t2}$, and the Arrhenius law is verified (activation energy equal to $E_p + E_i - E_{t1} = -E_1$).
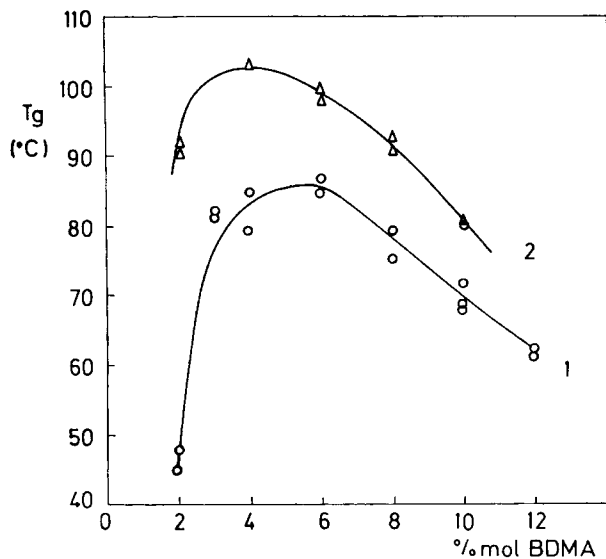
Glass Transition Temperatures

Figure 11 shows T_g as a function of the tertiary amine concentration for samples cured at 110°C.

The lower curve represents the results obtained immediately after the DSC isothermal run (cooling and rescanning at 10°C/min), whereas the upper one indicates the values obtained after 7 days at 110°C. The maximum glass transition temperature of the polymer network, i.e., $T_{g\infty}$, is very sensitive to the final reaction extent in the region of high conversions. This is due to the steep increase in the concentration of the cross-linking units of highest functionality by the end of the reaction.[12] Then, a small advance in the final reaction extent explains the increase in T_g values after the prolonged heating at 110°C. Formulation containing 2% BDMA polymerized very slowly. Even after 7 days at 110°C, the reaction extent was $X = 0.98$ as determined from NIR, i.e., the $T_{g\infty}$ was not attained. All the other formulations pertaining to curve 2 were completely cured within the experimental error of NIR spectroscopy.

The decrease of $T_{g\infty}$ with an increase in the tertiary amine concentration may be expected from the fact that most of the BDMA is not attached to the polymer network. Then, it may act as a plastifier of the final network. For practical purposes, it is convenient to use the least amount of tertiary amine compatible with a convenient polymerization rate.

Figure 11 Glass transition temperature as a function of mol % BDMA for samples cured at 110°C: (1) immediately after the DSC isothermal run; (2) after 7 days at 110°C.

In this sense, the curing with BDMA is different from the one produced by 1-unsubstituted imidazoles[13] or secondary amines as piperidine,[14] which remain covalently bonded to the network by the end of reaction. It may also be argued that the decrease of $T_{g\infty}$ is produced by the increase in the concentration of initiators (RO⁻) and the corresponding decrease of the average chain length. However, Berger and Lohse[2] showed that the av-

erage chain length does not depend on the tertiary amine concentration for the p-cresyl glycidyl ether polymerization initiated by BDMA.

Figure 12 shows the heat evolved in isothermal DSC runs and the T_g values determined after the runs for specimens containing 6 mol % BDMA and cured at different temperatures. Samples cured at 80 and 90°C could not reach the same conversion level as did the other ones—as measured from the $(-\Delta H)$ value—because they vitrify during polymerization, i.e., $T_g > T_{cure}$ by the end of the reaction. Figure 13 shows the residual reaction heat evolved after devitrification for a sample previously cured at 80°C. In spite of this fact, T_g values decrease with increasing curing temperature. Again, T_g shows a very high sensitivity on the network structure. Increasing the polymerization temperature reduces the average length of primary polyether chains due to the increase in the rate of termination reactions, as discussed in relation to the kinetic model. This introduces more chain ends as network defects and explains the observed decrease of the glass transition temperature. In fact, experimental results showed that average chain length of monofunctional epoxides homopolymerized using tertiary amines decreased by increasing the reaction temperature.[2]

CONCLUSIONS

The buildup of epoxy networks from diepoxides–tertiary amine systems was studied by differential scanning calorimetry. The polymerization rate
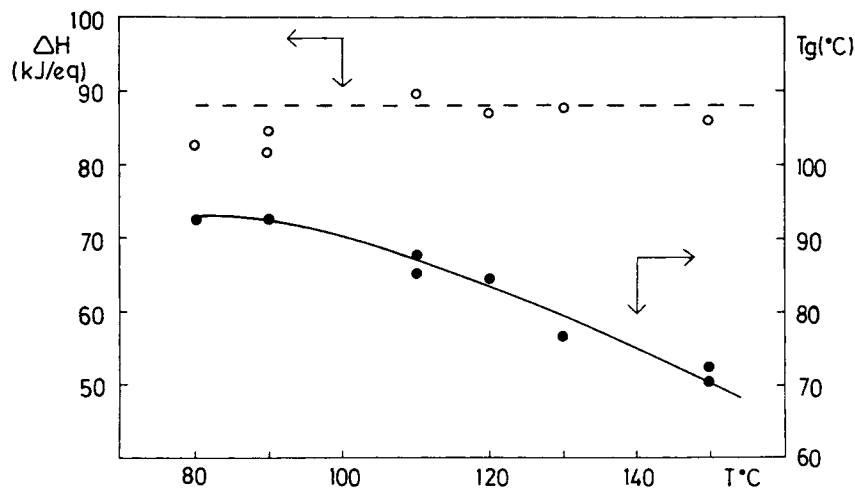
Figure 12 Reaction heat evolved in isothermal DSC runs and glass transition temperatures determined after the runs for samples containing 6 mol % BDMA and cured at different temperatures.
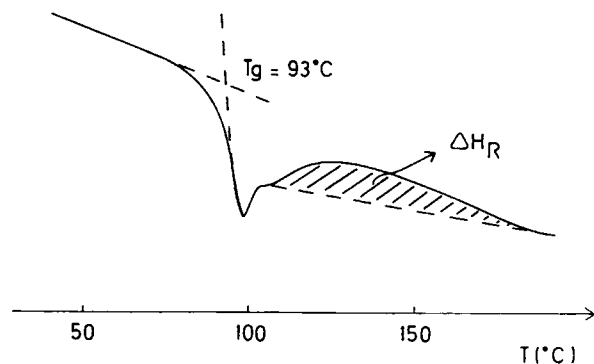
Figure 13 Dynamic DSC run carried out at 10°C/min for a sample containing 6 mol % BDMA previously cured at 80°C.

showed a first-order behavior with respect to both epoxide and tertiary amine concentrations and a complex dependence on temperature. In the low-temperature region (i.e., from 80 to 120°C), an Arrhenius behavior was observed with a very small activation energy, i.e., $E = 24.2$ kJ/mol (5.8 kcal/mol), whereas at high temperatures (i.e., from 130 to 150°C), no sensitivity of reaction rate with respect to temperature could be detected. This is attributed to the presence of termination steps with high activation energies that are only significant at high temperatures.

On the other hand, factors affecting the maximum attainable T_g value were discussed. It was shown that decreasing both the tertiary amine concentration and the reaction temperature led to an increase in the T_g value of the resultant network. The effect of tertiary amine is explained through the fact that it is not bounded to the network and, consequently, acts as a plastifier. The effect of a temperature increase is to reduce the average length of polyether chains. This increases the relative amount of chain ends and reduces the value of $T_{g\infty}$.

REFERENCES

1. B. A. Rozenberg, *Adv. Polym. Sci.*, **75**, 113 (1986) and references therein.
2. J. Berger and F. Lohse, *Eur. Polym. J.*, **21**, 435 (1985).
3. J. Galy, A. Sabra, and J. P. Pascault, *Polym. Eng. Sci.*, **26**, 1514 (1986).
4. Y. Tanaka and H. Kakiuchi, *J. Polym. Sci. A*, **4**, 109 (1966).
5. A. Eastham, *Can. J. Chem.*, **29**, 575 (1951).
6. A. Eastham, *Can. J. Chem.*, **29**, 585 (1951).
7. E. S. Narracot, *Br. Plast.*, **26**, 120 (1953).
8. M. S. Lidarik, *Vysokomolek. Soedin.*, **5**, 1738 (1963).
9. N. Bouillon, L. Tighzert, and J. P. Pascault, unpublished results.
10. D. Verchère, H. Sautereau, J. P. Pascault, C. C. Riccardi, S. M. Moschiar, and R. J. J. Williams, *Macromolecules*, **23**, 725 (1990).
11. C. H. Klute and W. Viehmann, *J. Appl. Polym. Sci.*, **5**, 86 (1961).
12. R. J. J. Williams, in *Developments in Plastics Technology-2*, A. Whelan and J. Craft, Eds., Elsevier, Barking, UK, 1985, p. 339.
13. M. S. Heise and G. C. Martin, *Macromolecules*, **22**, 99 (1989).
14. T. R. Cuadrado, A. Almaraz, and R. J. J. Williams, in *Crosslinked Epoxies*, B. Sedláček, and J. Kahovec, Eds., de Gruyter, Berlin, 1987, p. 179.