# Kinetics of Curing Reaction of Epoxide Catalyzed by Tertiary Amine

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## SYNOPSIS

The kinetic study of the curing reaction of epoxide catalyzed by tertiary amine was carried out through thermal analysis of the reaction by differential scanning calorimetry (DSC). Using infrared spectroscopy (IR) and neutron magnetic reasonance (NMR) analysis, a reaction mechanism for this reaction was proposed. The reaction proceeded to anionic polymerization. An autocatalytic reaction was induced at high concentration of the tertiary amine catalyst. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Epoxy resin is one of the most important products widely used in the polymer industry for coating, adhesive, insulating materials, composites, etc.[1] Amine has been an important curing agent for the curing reaction of epoxide for many years. Basically, primary and secondary amines play the same role in the curing reaction, but tertiary amines will function differently.[2] According to studies on the epoxy reaction with primary or secondary amines,[3-7] the hydroxyl group is first formed after the ring-opening reaction of the epoxide group, where a proton is transferred from the primary or secondary amines to the oxygen atom of the epoxide group. Then, this hydroxyl group catalyzed the unreacted epoxide group to propagate the reaction. This is the so-called autocatalytic reaction. Fricke proposed the kinetic equation

$$d\alpha/dt = k\alpha^m(1-\alpha)^n$$

to describe this autocatalytic reaction,[8] where $k$ and $\alpha$ are the reaction constant and conversion, respectively, and $m$ and $n$ are reaction orders. On the other hand, the reaction mechanisms proposed by many researchers for the epoxy reaction catalyzed by tertiary amine are different, but the presence and increase of double bonds and the hydroxyl group (unsaturated alcohol) during the reaction have been confirmed in all the studies.[9-14] This article studies the kinetic equations for various types of epoxy catalyzed by the tertiary amine, benzyldimethylamine (BDMA), through thermal analysis of differential scanning calorimetry (DSC). The reaction mechanism will be proposed by the analysis of infrared spectroscopy (IR) and neutron magnetic reasonance (NMR).

## EXPERIMENTAL

### Materials

The epoxies used for this experiment are phenylglycidyl ether (PGE) and diglycidyl ether of bisphenol A (DGEBA, DER331, Dow Chemical Co.). They were degassed in vacuum at 60°C overnight before use. Benzyldimethylamine (BDMA) served as a tertiary amine catalyst and was used as received.

### Conversion Measurement from DSC[15-20]

The epoxy resin was kept in vacuum at 60°C for about 12 h to remove gas or moisture in the epoxy. Then, the mixture of about 10 mg of known weight of the epoxy with a suitable amount of BDMA was put into an aluminum pan and covered for DSC measurement. The DSC was calibrated with indium

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metal before the test. Dynamic scanning DSC was performed at a heating rate of 1.25°C/min and a temperature range from 30 to 250°C. The same procedure performed in isothermal DSC was used to measure the total heat of isothermal reaction ($\Delta H_T$) at constant temperature. The area under this isothermal DSC curve up to any time $t$ represents the $\Delta H_t$. After the isothermal test, the sample pan was quenched and then the residual heat of the reaction ($\Delta H_r$) was determined by dynamic scanning DSC. The area under this dynamic DSC curve represents the value of the $\Delta H_r$. The sum of the residual heat of reaction ($\Delta H_r$) and the total heat of the isothermal reaction ($\Delta H_T$) was the total heat of reaction ($\Delta H$). Thus, the conversion ($\alpha$) at time $t$ and temperature $T$ could be calculated by $\alpha(t, T) = \Delta H_t/\Delta H$. The changes of functional groups during the reaction were detected by infrared spectrum (IR) of the reaction mixture that was dabbed onto the KBr pellet. The proton transfer during the reaction was detected by NMR analysis. $CDCl_3$ was used as solvent for the NMR analysis.

## KINETIC EQUATIONS

At a low concentration of tertiary amine, the rate equation of curing of epoxide catalyzed by tertiary amine is proposed as follows:

$$-d[Ep]/dt = k[BDMA]_0^l[Ep]^n \qquad (1)$$

$$k = A\exp(-Ea/RT) \qquad (2)$$

where $[Ep]$ and $[BDMA]_0$ are the concentration of epoxy and initial concentration of BDMA, respectively; $[Ep]_0$, $k$, $Ea$, and $A$, the initial concentration of epoxy, rate constant, activation energy, and frequency factor, respectively; and $n$ and $l$, the reaction orders for the components. Equation (1) can be substituted by the conversion $\alpha = ([Ep]_0 - [Ep])/[Ep]_0$ and becomes

$$d\alpha/dt = k'(1-\alpha)^n, \qquad (3)$$

where

$$k' = k[BDMA]_0^l[Ep]_0^{n-1} \qquad (4)$$

Taking the logarithm on both sides of eq. (3), we obtain

$$\ln(d\alpha/dt) = n\cdot\ln(1-\alpha) + \ln k' \qquad (5)$$

Thus, $n$ and $k'$ can be determined from the interception and the slope, respectively, of the plot of $\ln(d\alpha/dt)$ vs. $\ln(1-\alpha)$. The $\alpha$ and $(d\alpha/dt)$ values are computed from the DSC data of the reaction according to the method described in the second part of the Experimental section. Moreover, $k$ and $l$ can be determined from eq. (6) with more than three sets of various concentrations of BDMA related to their $k'$ values:

$$\ln k' = l\cdot\ln BDMA]_0 + \ln k[Ep]_0^{n-1} \qquad (6)$$

The $A$ and $Ea$ can be obtained from eq. (7) with $k$ values at different temperatures:

$$\ln k = \ln A - (Ea/R)\cdot\left(\frac{1}{T}\right) \qquad (7)$$

In the system with a high concentration of tertiary amine, due to the presence of unsaturated alcohol, which can be a proton donor in the reaction of epoxy catalyzed by tertiary amine, the autocatalytic equation is thus proposed as follows:

$$-d[Ep]/dt = ka[Ep]^{n'}[BDMA]^{l'} \times([Ep]_0 - [Ep])^{m'} \qquad (8)$$

$$ka = A'\exp(-Ea'/RT) \qquad (9)$$

where $[Ep]$ and $[BDMA]_0$ are the concentrations of epoxy and the catalyst, BDMA, respectively; $[Ep]_0$, $ka$, $E'_a$, and $A'$ are the initial concentration of epoxy, rate constant, activation energy, and frequency factor, respectively; and $n'$, $l'$, and $m'$ are the reaction orders for the components. Equation (8) can be substituted by the conversion $\alpha = ([Ep]_0 - [Ep])/[Ep]_0$ and becomes

$$d\alpha/dt = k'_a\alpha^{m'}(1-\alpha)^{n'} \qquad (10)$$

where

$$k'_a = k_a[BDMA]^{l'}[Ep]_0^{n'+m'} \qquad (11)$$

Both sides of eq. (10) can be differentiated by $\alpha$ and then divided by eq. (10) to obtain

$$\left[\frac{d(d\alpha/dt)}{d\alpha}\bigg/\left(\frac{d\alpha}{dt}\right)\right]\cdot\alpha = m' - n'\left(\frac{\alpha}{1-\alpha}\right) \qquad (12)$$

Thus, $m'$ and $n'$ can be determined from the interception and the slope, respectively, of the plot of $\{[d(d\alpha/dt)/d\alpha]/(d\alpha/dt)\}\cdot\alpha$ vs. $[\alpha/(1-\alpha)]$. The $\alpha$, $(d\alpha/dt)$, and $[d(d\alpha/dt)/d\alpha]$ values are computed from the DSC data of the reaction according to the method described in the second part of the Experimental section. The $k_a'$ value in eq. (10) can be calculated from the following equation:

$$k_a' = \frac{(d\alpha/dt)_p}{\alpha_p^{m'}(1-\alpha_p)^{n'}} \tag{13}$$

at the peak value (i.e., maximum conversion rate) of the isothermal DSC[4] data. Moreover, $ka$ and $l'$ can be determined by eq. (14) with more than three sets of various concentrations of BDMA related to their $ka'$ values:

$$-\ln\left(\frac{k_a'}{[Ep]_0^{n'+m'+1}}\right) = \ln ka + l' \ln[BDMA] \tag{14}$$

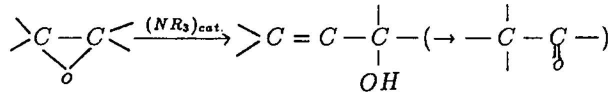
Finally, $A'$ and $Ea'$ can be obtained by eq. (15) with $ka$ values at different temperatures:

$$\ln ka = A' - (Ea'/R)\cdot\left(\frac{1}{T}\right) \tag{15}$$

## RESULTS AND DISCUSSION

### IR and NMR Analysis

The IR analysis of the BDMA/PGE reaction system is shown in Figures 1 and 2. For the system with a low concentration of BDMA, the epoxide group intensity at 916 cm$^{-1}$ of IR decreased with the reaction time and did not show a double-bond peak of olefin (1650 cm$^{-1}$) (see Fig. 1). On the contrary, for the PGE or DGEBA system with a high concentration of BDMA, the epoxide group intensity of IR decreased with the reaction time and obviously exhibits a double bond peak of olefin at 1650 cm$^{-1}$ (see Figs. 2 and 3), which was due to the formation of the allyl alcohol[1]:



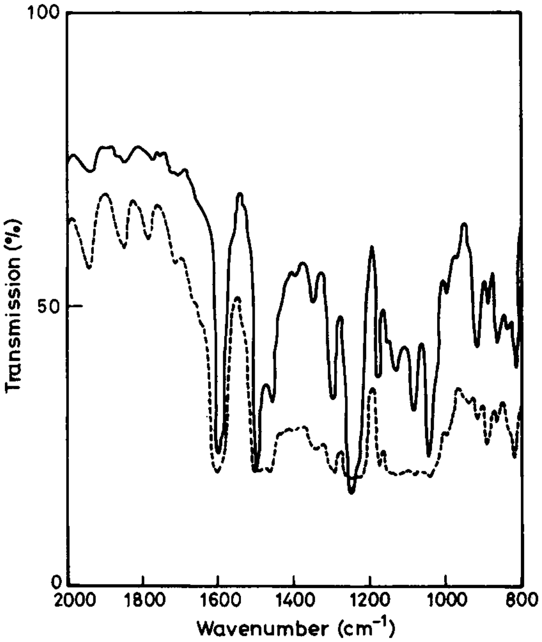


**Figure 1** Infrared spectrum for the reaction of PGE catalyzed by BDMA (5 phr) at 50°C at various reaction times: (——) 0 h; (– – –) 1.35 h.

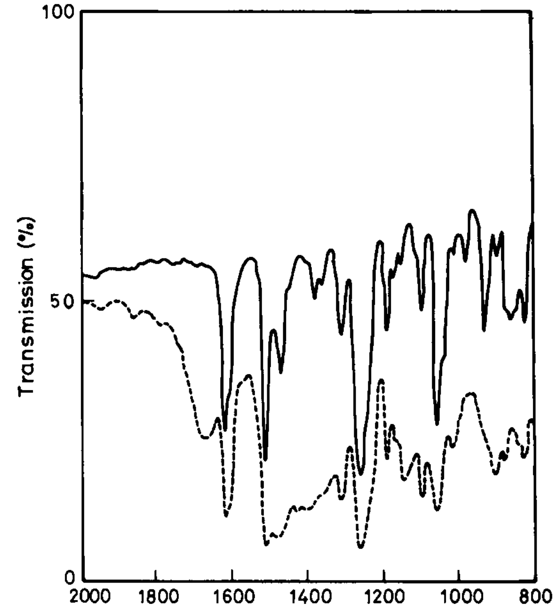


**Figure 2** Infrared spectrum for the reaction of PGE catalyzed by BDMA (70 phr) at 80°C at various reaction times: (——) 0 h; (– – –) 1.4 h.

In addition, the NMR analysis of the reaction system of DGEBA at a high concentration of BDMA is shown in Figures 4 and 5. No double-bond peak of olefin was observed initially for the reaction in $CDCl_3$ solvent at 65°C. After 3 h, the double-bond peaks of olefin at $\delta = 5$ ppm and the $CHCl_3$ peak at $\delta = 7.25$ ppm appeared. For this reason, the proton of the hydroxyl group of allyl alcohol was shown to occur via deuterium exchange with the deuteron of $CDCl_3$. Therefore, the peak intensity of the $CHCl_3$ increased with the reaction time (see Fig. 5). In summary, the concentration of BDMA would affect the reaction mechanism of epoxide curing.

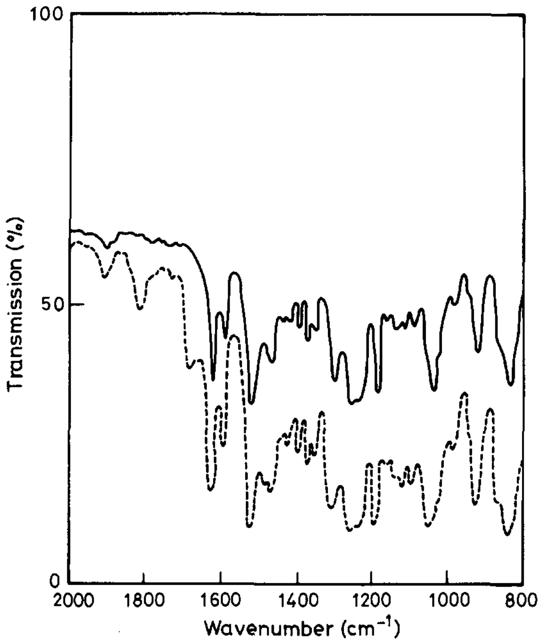


**Figure 3** Infrared spectrum for the reaction of DGEBA catalyzed by BDMA (10 phr) at 70°C at various reaction times: (——) 0 h; (– – –) 1.5 h.

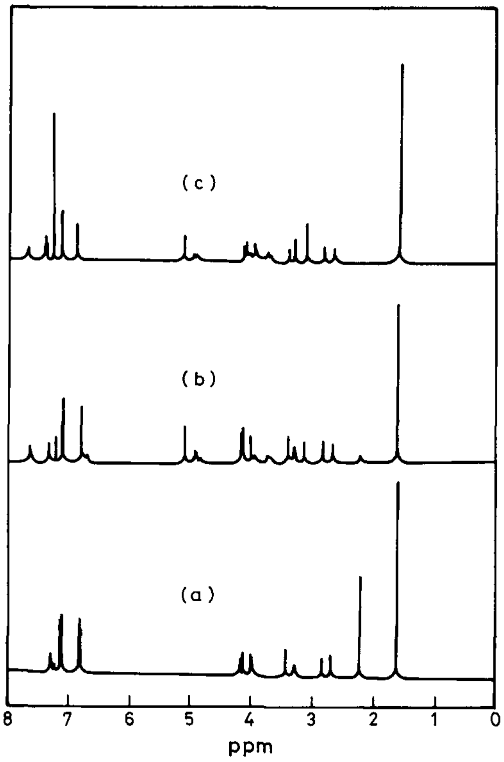


**Figure 5** NMR spectrum for the reaction of DGEBA catalyzed by BDMA (10 phr) at 70°C at various reaction times: *(a) initial reaction; (b) 0.5 h; (c) 1.5 h.*

## Reaction Mechanism[9,21,22]

The temperature values of dynamic DSC peaks of the epoxide catalyzed by tertiary amine (BDMA) at various concentration ratios are listed in Table I. The peak temperature of the curing reactions was rather different for the high and low concentrations of the tertiary amine (BDMA) catalyst.

The isothermal DSC curve of the PGE/BDMA (or DGEBA/BDMA) reaction system is shown in Figure 6. The figure shows different reaction types between high and low concentrations of the tertiary amine catalyst.

From the aforesaid IR and NMR analysis, the different mechanisms between the high-concentration tertiary amine-catalyzing epoxide and the low-concentration amine-catalyzing epoxide reactions

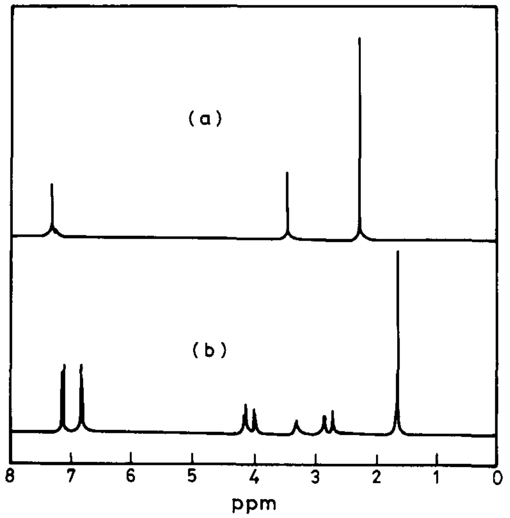


**Figure 4** NMR spectrum for pure component: (a) BDMA (b) DGEBA.

**Table I Peak Temperatures of Dynamic DSC Curves for the Reaction of Tertiary Amine with Epoxide Groups at Various Concentrations at a Scanning Rate of 1.25°C/Min**

| BDMA/PGE | | BDMA/DGEBA | |
|---|---|---|---|
| BDMA (phr) | Peak Temp (°C) | BDMA (phr) | Peak Temp (°C) |
| 3 | 119 | 0.3 | 113 |
| 5 | 116 | 0.5 | 112 |
| 7 | 118 | 0.7 | 112 |
| 70 | 94 | 10.0 | 94 |
| 80 | 93 | 13.0 | 93 |
| 90 | 93 | 15.0 | 93 |

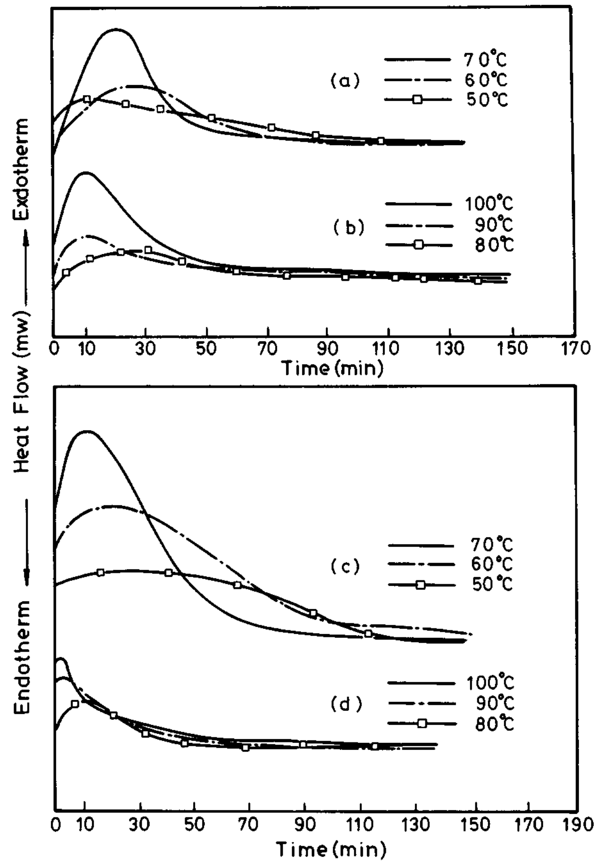
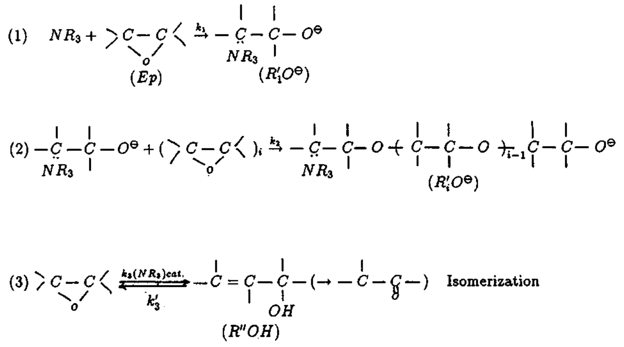
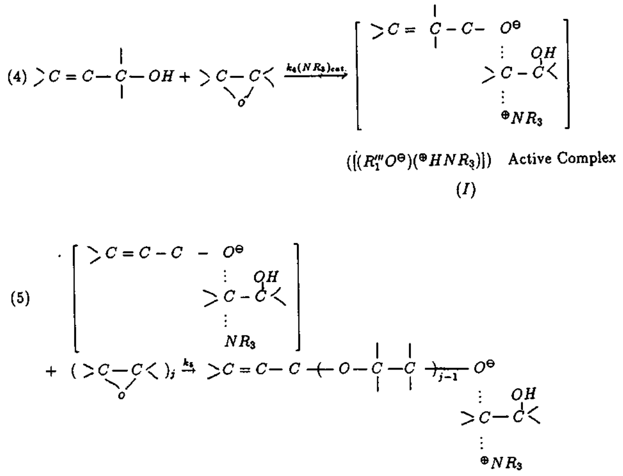


**Figure 6** Isothermal DSC curves for the reaction of the epoxide group with tertiary amine (BDMA): (a) PGE/BDMA (70 phr); (b) PGE/BDMA (7 phr); (c) DGEBA/BDMA (10 phr); (d) DGEBA/BDMA (0.5 phr).

were shown. When allyl alcohol formed at the high concentration of the tertiary amine-catalyzing epoxide reaction system, it acted as a proton donor to catalyze the ring-opening reaction. Therefore, the overall reaction was like an autoacceleration reaction.

In accordance with the above observation, the following reaction mechanism was proposed:





At a high concentration of tertiary amine, step (3) was important. The epoxide group could be catalyzed by tertiary amine for isomerization to occur and also to form allyl alcohol, which acted as a proton donor. Then, the allyl alcohol, tertiary amine, and epoxide group reacted together to form an active complex [step (4), see structure (**I**)] and to proceed to anionic polymerization through step (5). In contrast, at a low concentration of the tertiary amine, steps (3)–(5) could be negligible.

According to the above mechanism, the consumption rate of the epoxide group was written as

$$-d[Ep]/dt = k_1[NR_3][Ep] + k_2[Ep]\sum_i [Ri'O^{\ominus}] + k_3[Ep] - k_3'[R''OH] + k_4[R''OH][Ep] + k_5[Ep]\sum_j [(R_j'''O^{\ominus})(^{\oplus}HNR_3)] \quad \text{(a)}$$

Assuming that step (3) reached equilibrium, $[R''OH] = (k_3/k_3')[Ep]$, the equation (a) became

$$-d[Ep]/dt = k_1[NR_3][Ep] + k_2[Ep]\sum_i [R_i'O^{\ominus}] + k_4(k_3/k_3')[Ep]^2 + k_5[Ep]\sum_j [(R_j'''O^{\ominus})(^{\oplus}HNR_3)] \quad \text{(b)}$$

When the concentration of tertiary amine was low, then only steps (1) and (2) reactions were important. Thus, eq. (b) became

$$-d[Ep]/dt = k_1[NR_3][Ep] + k_2 \times [Ep]\sum_i [R_i'O^{\ominus}] \quad \text{(c)}$$

The mass balance of the tertiary amine was

$$\sum_i [RiO^{\ominus}] = [NR_3]_0 - [NR_3] \qquad (c')$$

where $[NR_3]_0$ = initial concentration of the tertiary amine. Substituting eq. (c′) into eq. (c),

$$-d[Ep]/dt = (k_1 - k_2)[NR_3] + k_2[NR_3]_0[Ep]$$

Because $[NR_3]$ was small enough to be neglected, hence

$$-d[Ep]/dt = k_2[NR_3]_0[Ep] \qquad (d)$$

The consumption rate of the epoxide group was proportional to both the initial concentration of BDMA and the concentration of the epoxide group when BDMA was in a low concentration level.

When the concentration of the tertiary amine was high enough to initiate steps (3) and (4), eq. (b) became

$$-d[Ep]/dt = k_4(k_3/k_3')[Ep]^2 + k_5[Ep]\sum_j[(R_j'''O^{\ominus})(^{\oplus}HNR_3)]$$

where steps (1) and (2) were neglected in comparison with the reaction rates of steps (3)-(5). Step (5) was the propagation reaction of the anionic polymerization, $k_5 \gg k_4$, and $(R_j'''O^{\ominus})(^{\oplus}HNR_3)$ was the propagation center. The concentration of $\sum_j[(R_j'''O^{\ominus})(^{\oplus}HNR_3)]$ was a function of the consumption of the epoxide group; thus, it was assumed that

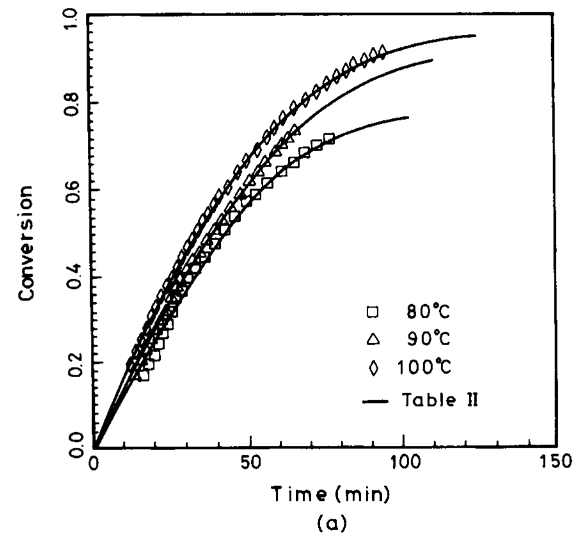


**Figure 7** Conversion–time relation for the reaction of PGE with low concentration of BDMA (3 phr).

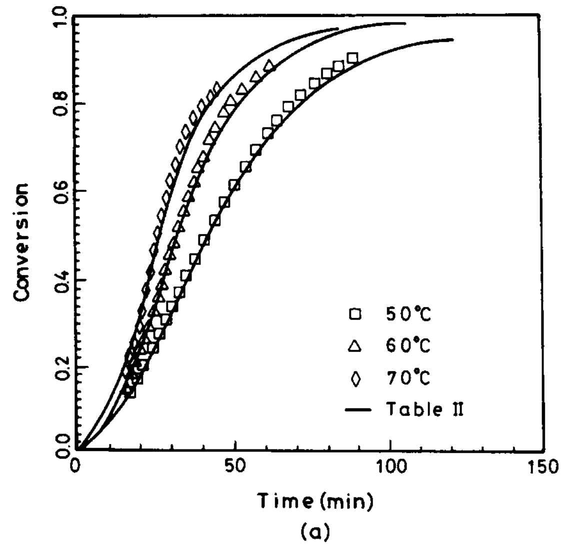


**Figure 8** Conversion–time relation for the reaction of PGE with a high concentration of BDMA (70 phr).

$$\sum_j[(R_j'''O^{\ominus})(^{\oplus}HNR_3)] = f([Ep]_0 - [Ep]) = constant \times ([Ep]_0 - [Ep])^n, \quad n < 1 \qquad (e)$$

($[Ep]_0$ = initial concentration of the epoxide group). Then, eq. (e) became

$$-d[Ep]/dt = K[Ep]([Ep]_0 - [Ep])^n \quad n < 1$$

where $K = k_5 \times constant$.

Therefore, this reaction was similar to an autoacceleration reaction when BDMA was in the high concentration level. But the order $n$ was smaller than unity. The epoxide groups would react through three ways: first, by the general reactions of steps (1) and (2); second, by the isomerization of step (3); and third, by the autocatalytic reactions of steps (4) and (5). The $(R_j'''O^{\ominus})(^{\oplus}HNR_3)$ could form only through the third way. Thus, the $n$ value was smaller than unity.

## Reaction Kinetics

The reaction kinetics was studied by DSC; the relation between reaction heat and conversion was defined as

$$\alpha = \Delta H_t/\Delta H$$

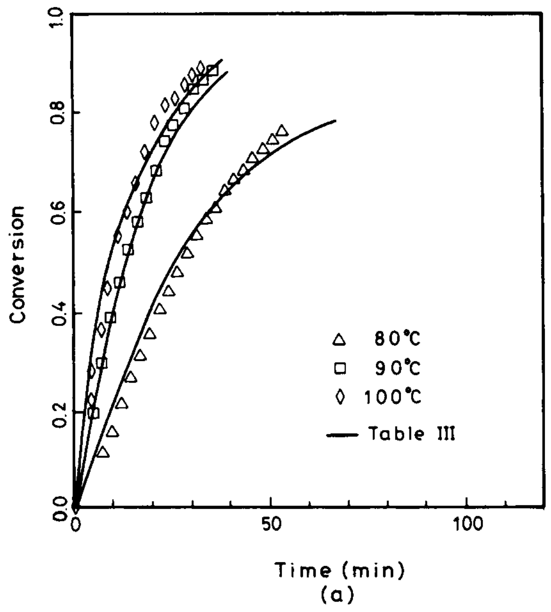


**Figure 9** Conversion–time relation for the reaction of DGEBA with a low conversion of BDMA (0.3 phr).

where $\Delta H = \Delta H_T + \Delta H_r$ = total heat of reaction; $\Delta H_t$ = heat of isothermal reaction at time $t$; $\Delta H_T$ = total heat of isothermal reaction; and $\Delta H_r$ = residual heat of isothermal reaction.

The conversion–time data for both low-concentration BDMA and high-concentration BDMA in PGE (or DGEBA) reaction systems are shown in Figures 7 and 8 (or Figs. 9 and 10). According to the method described under Kinetic Equations, the reaction rate equations are summarized as follows:

At a low concentration of BDMA:

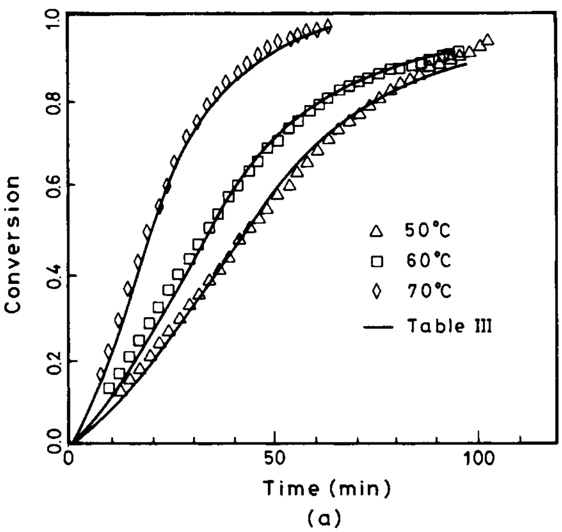


**Figure 10** Conversion–time relation for the reaction of DGEBA with a high conversion of BDMA (10 phr).

$$-[PGE]/dt = k[BDMA]_0^l[PGE]^n \qquad (16)$$

$$(or - [DGEBA]/dt = k[BDMA]_0^l[DGEBA]^n) \qquad (17)$$

where $k = A\exp(-Ea/RT)$.

At a high concentration of BDMA:

$$-d[PGE]/dt = k_a[BDMA]_0^{l'}[PGE]^{n'}([PGE]_0 - [PGE])^{m'} \qquad (18)$$

$$(or - d[DGEBA]/dt = k_a[BDMA]_0^{l'}[DGEBA]^{n'} \times ([DGEBA]_0 - [DGEBA])^{m'} \qquad (19)$$

**Table II Parameters for the Reaction Kinetics at High and Low Concentrations of BDMA Catalyst**

BDMA Low Concentration

| | Parameter | | | |
|---|---|---|---|---|
| Reaction System | *l* | *n* | *A* | *Ea* (kcal/mol) |
| BDMA/PGE | 1.040 | 0.969 | $3.173 \times 10^{13}$ | 13.778 |
| BDMA/DGEBA | 0.617 | 1.046 | $1.968 \times 10^{10}$ | 13.510 |

BDMA High Concentration

| | Parameter | | | | |
|---|---|---|---|---|---|
| | *l'* | *n'* | *m'* | *A* | *Ea* (kcal/mol) |
| BDMA/PGE | 0.958 | 1.080 | 0.564 | $2.202 \times 10^{14}$ | 6.892 |
| BDMA/DGEBA | 0.633 | 0.633 | 0.337 | $1.642 \times 10^{13}$ | 11.204 |

**Table III Reaction Order of Kinetic Rate Equation for BDMA/DGEBA Reaction System at High Temperature Below 30% Conversion**

| BDMA Concentration | Parameter | | |
|---|---|---|---|
| | $l$ (or $l'$) | $n$ (or $n'$) | $m'$ |
| Low (100°C) | 0.810 | 1.038 | — |
| High (100°C) | 0.798 | 0.861 | 0.517 |

where $k_a = A'\exp(-Ea'/RT)$. The $l$, $n$, $A$, and $Ea$ (or $l'$, $n'$, $m'$, $A'$, and $Ea'$) parameters are listed in Table II. The correlations between these equations [see eqs. (16)-(19)] and the experimental data are shown in Figures 7-10, respectively. Most of the experimental data conformed well with the equations.

The deviation of the reaction order of the rate equation [comparing eqs. (d) and (g) with eqs. (18) and (19)] was rather large. One of the reasons might be that the reactivity of bifunctional epoxide groups was not uniform in the DGEBA/BDMA reaction system. The other reason might be the high viscosity of this system that induces the diffusion effect on the reaction. From the data in Table III, when the DGEBA/BDMA reaction system was under a high-temperature condition (i.e., low viscosity and low diffusion effect), the reaction order was more approximate to that in the equation. In addition, in the system, a heterogeneous reaction might occur near the gelation point. Therefore, the conversion deviated largely from the equation at the high conversion of the reaction.

## CONCLUSION

The concentration of tertiary amine affects the reaction mechanism of epoxide curing in the PGE/BDMA or DGEBA/BDMA system. At low concentration, the tertiary amine opened the epoxide ring to form Zwitterion and then it underwent polymerization. Thus, the consumption rate of the epoxide group was proportional to the first order of the epoxide group. But at high concentration, the tertiary amine could catalyze the epoxide ring, upon rearrangement, to form allyl alcohol (proton donnor). The allyl alcohol, tertiary amine, and epoxide group then formed an actived complex and proceeded to anionic polymerization. This system was like an autoacceleration reaction.

From IR and NMR analysis, the formation of allyl alcohol during the reaction was confirmed when the concentration of tertiary amine was high, but no allyl alcohol was found in the case of a low concentration of tertiary amine.

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