

A Kinetic Scheme for Anhydride Curing of Diglycidyl Ester with Tertiary Amine as Catalyst

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SYNOPSIS

A kinetic model has been developed on the basis of reaction mechanisms proposed for the anhydride curing of diepoxides, using tertiary amine as catalyst. The model has been tested for the cure reaction of a diglycidylester model compound, bis-(2,3-epoxypropyl)-1,3-benzenedicarboxylate, with hexahydrophthalic anhydride as the curing agent and benzyldimethylamine as the catalyst, over the temperature range 100–120°C, the rate being measured by means of differential scanning calorimetry, using an isothermal approach. The rate expressions derived for the model are half order and first order, with respect to reacted and unreacted functional groups, respectively, in the initial stage. For the later stage of curing, up to the point of vitrification, the model indicates a 1.5 order with respect to the unreacted functional groups. These are in good agreement with the kinetic orders of 0.5 and 1.5, with respect to reacted and unreacted functional groups, respectively, reported earlier from a phenomenological approach for the whole range of curing prior to the onset of vitrification. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Anhydride curing agents are used in most of the important applications of epoxy resins, particularly in casting and laminates. Strong bases, such as tertiary amines, are commonly used to catalyze the curing reaction. Chemical reactions that take place during cure determine the properties of the cured thermoset. The understanding of the mechanism and kinetics of cure is thus the first essential step in the evaluation of processing–property relationships. The chemistry of catalyzed epoxy curing is complex and the cure kinetics are not easily elucidated. Moreover, phenomena, such as autocatalysis in the early stages and onset of gelation in the later stages of curing, further complicate the kinetic modeling.

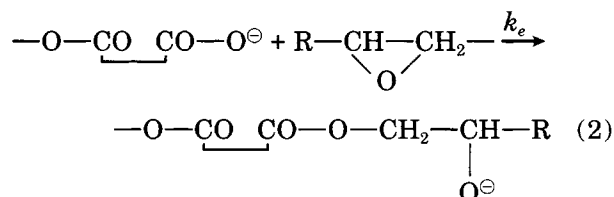
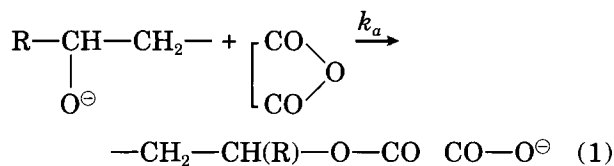
The uncatalyzed cure of epoxy resins with cyclic anhydrides is well understood.^{1,2} The mechanism involves the attack of hydroxyl groups of the epoxy resin on the anhydride molecules to form a monoester having a free carboxyl group. The monoester

then reacts with the epoxide to yield a diester and a new secondary hydroxyl group, thus perpetuating cure. These reactions were confirmed by the evidence that the amounts of mono- and diester that are produced are stoichiometrically equivalent to the amount of anhydride that disappears and the evidence that, at least up to gelation, there was no significant difference in the consumption of epoxide and anhydride.³ The observation that, at higher conversions, the epoxy group decreased faster than the increase in diester group was attributed to the etherification reaction between the epoxy and hydroxyl groups, which constitutes a significant side reaction.

The mechanisms become less definitive if the epoxide–anhydride reaction is catalyzed by strong bases, such as tertiary amines. Most authors, however, agree that the mechanism is an anionic one. According to Fischer,⁴ the reaction is initiated by a zwitterion. The anhydride reacts with the tertiary amine creating a carboxylate $R_3N^{\oplus}-CO-CO-O^{\ominus}$ which can undergo reaction with epoxide. However, according to Tanaka and Kakiuchi,⁵ the tertiary amine forms a zwitterion with the epoxide forming a hydroxylate, $R_3N^{\oplus}CH_2-CH(CH_2R')O^{\ominus}$, which can react with anhydride.

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The mechanism in either case represents an anionic living polymerization, in which propagation proceeds via two reactions involving acylation and esterification in sequence:



Generally, acylation is much faster⁶ than the reaction between epoxide and carboxylate, so that $k_a \gg k_e$.

Besides the above ionic mechanism, two other mechanisms have been suggested, based on initiation by tertiary amine with the participation of (1) a preexisting proton donor⁷ and (2) a proton donor formed during the reaction.⁵ All of these mechanisms indicate that the reaction mechanism has not been fully elucidated. The study of the mechanism is usually based on reaction kinetics, but the kinetic course of the reaction between epoxide and anhydride has not yet been reliably determined. Various authors report kinetic orders, ranging from zero to four, which include a change in the order during cure.⁸

Most of the investigations on anhydride curing of epoxy resins, reported in literature, have been on bisphenol A diglycidyl ether or model compounds, such as phenyl glycidyl ether, but little is known about the anhydride curing of diglycidyl esters, which are important for the fabrication of elec-

troinsulators. This lack of knowledge prompted Steinmann⁹ to study the kinetics and the mechanism of the anhydride curing of a diglycidyl ester. We have investigated a diglycidyl ester-cyclic anhydride-tertiary amine system and have studied¹⁰ the reaction of the model compound isophthalic diglycidyl ester (IPDGE) with hexahydrophthalic anhydride (HHPA), catalyzed by benzyldimethylamine (BDMA).

To describe the autocatalytic cure of the resin, observed by the DSC technique, a phenomenological equation of the type proposed by Kamal¹¹ was employed:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (3)$$

where α is the extent of conversion of epoxy groups, k_1 and k_2 are the specific rate constants, and m and n are reaction orders. The empirical equation provided a good fit to the experimental data, up to the point of vitrification.¹⁰ The orders m and n , determined without imposing any constraints, over the temperature range 100–135°C, averaged to a value of 0.5 and 1.5, respectively.

The present work is concerned with the development of kinetic models, based on the reaction mechanisms, to explain the observed rate data of the tertiary-amine catalyzed epoxy-anhydride reaction, over the entire range of cure. The rate expressions can then be compared to those obtained earlier, using a phenomenological approach.

EXPERIMENTAL

Materials and Procedure

The epoxy compound, bis-(2,3-epoxypropyl)-1,3-benzenedicarboxylate (IPDGE; Fig. 1), used for studying the cure kinetics by differential scanning calorimetry (DSC), was synthesized by the Schotten-Baumann reaction, using isophthaloyl dichloride (Aldrich, 98%) and glycidol (Aldrich, 96%). The detailed method and the product characteristics are described elsewhere.¹⁰ The curing agent, hexahydrophthalic anhydride (HHPA) (Ciba-Geigy, mp 35–36°C), and the catalyst, benzyldimethylamine (BDMA) (Aldrich, 99%), were used as received.

The Rigaku 8230 calorimeter, coupled with the TAS 100 data storage station, were used for data acquisition. Details of the experimental procedure and the method for obtaining the reaction rate,

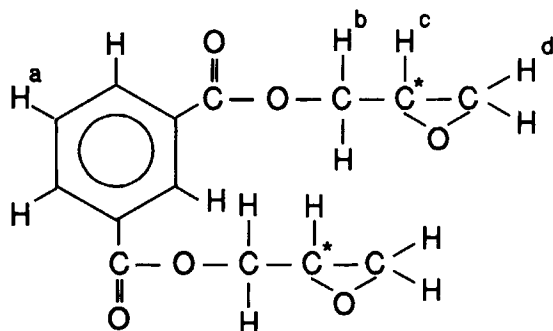


Figure 1 Structure of bis-(2,3-epoxypropyl)-1,3-benzenedicarboxylate, (IPDGE).

which involves conversion data from the DSC thermograms, have been described previously.¹⁰ Typical plots of reaction rate vs. conversion are shown in Figure 2 and those of conversion vs. time are shown in Figure 3.

DISCUSSION

Phenomenological Model

As shown in Figures 2 and 3, eq. (3), with $m = 0.5$ and $n = 1.5$, fit the experimental data well up to about 65% conversion. At higher conversions, significant deviations were observed, which could be attributed to the onset of vitrification. Thus the same equation with the rate constants modified by a suitable diffusion factor^{12,13} fit well the experimental data also in the postvitrification region.

The k_1 values, obtained experimentally, were negligibly small as compared to the k_2 values estimated using Marquardt's¹⁴ regression technique in the temperature range 100–120°C. So, eq. (3), for the present system, could be approximated by

$$\frac{d\alpha}{dt} = k_2 \alpha^{0.5} (1 - \alpha)^{1.5} \quad (4)$$

yielding half order with respect to the reacted functional groups and 1.5 order with respect to unreacted functional groups. This equation, as in eq. (3), pro-

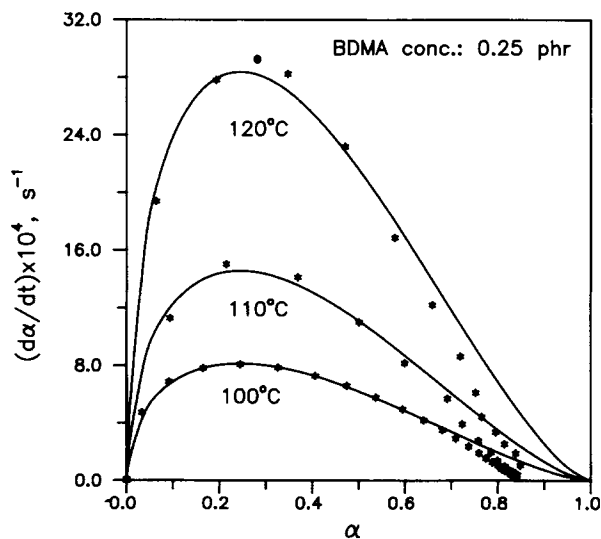


Figure 2 Comparison of experimental data with model eq. (3): reaction rate vs. conversion. (***) experimental, (—) model eq. (3).

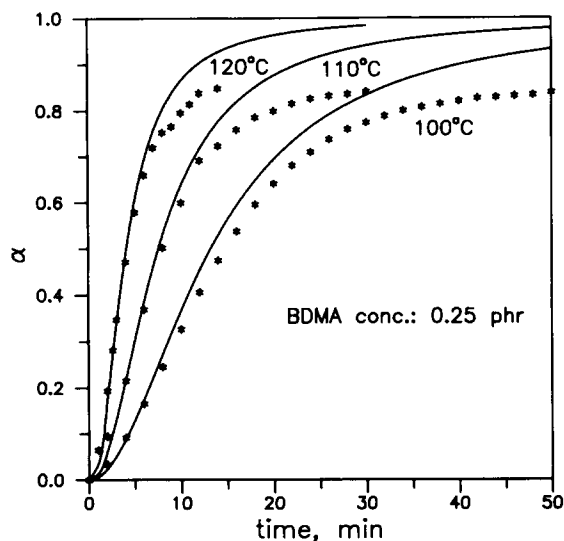


Figure 3 Comparison of experimental data with model eq. (3): conversion vs. time. (***) experimental, (—) model eq. (3).

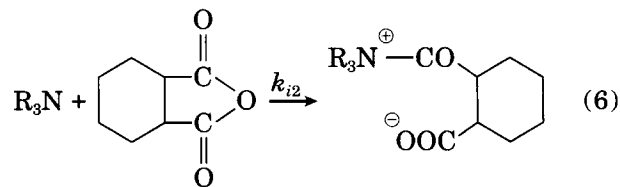
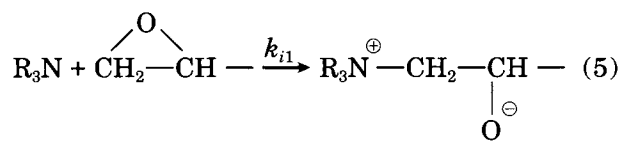
vided a good fit to the experimental data until the onset of gelation.

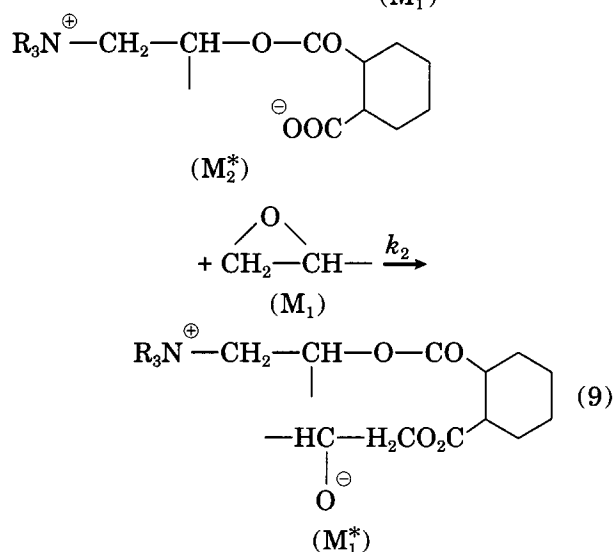
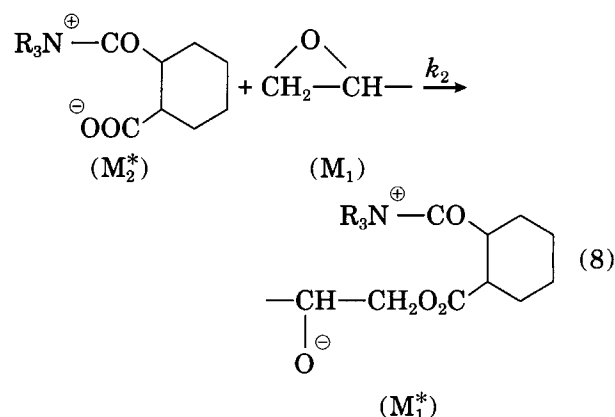
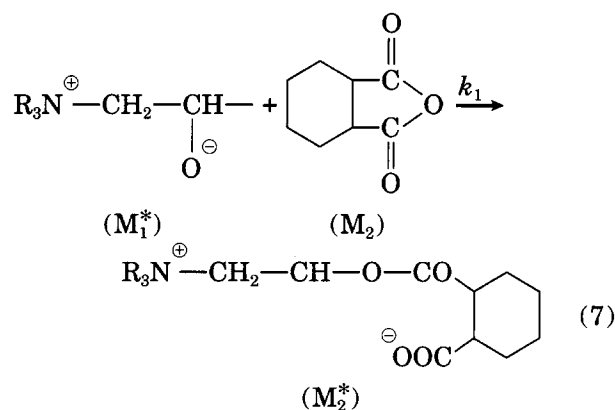
Kinetic Model

For developing a kinetic model for the present tertiary amine catalyzed epoxy-anhydride system, the entire curing period is divided into three stages: initial, intermediate, and final.

Initial Stage

The curing mechanism in the initial stage consists mainly of two steps, viz., (i) initiation by reaction of tertiary amine with epoxy or anhydride and (ii) propagation by reaction of active species with anhydride and epoxide, successively. The reactions in the initial stages may therefore be visualized as:





Equations (5)–(9) indicate that monomer consumption occurs in two ways: the reaction of the monomer with tertiary amine and the reaction of the monomer with the active species. However, the number of monomer molecules involved in the initiation step is fewer than those involved in the propagation step. The rates of disappearance of M_1 and M_2 at the initial stage can then be closely approximated and expressed as

$$\frac{d[M_1]}{dt} = -k_2[M_1][M_2^*] \quad (10)$$

$$\frac{d[M_2]}{dt} = -k_1[M_2][M_1^*] \quad (11)$$

$$\frac{d[M_1^*]}{dt} = -k_1[M_2][M_1^*] + k_2[M_1][M_2^*] \quad (12)$$

$$\frac{d[M_2^*]}{dt} = k_1[M_2][M_1^*] - k_2[M_1][M_2^*] \quad (13)$$

Matejka et al.⁶ examined the epoxy anhydride curing mechanism by using a model reaction between phenylglycidyl ether and benzoic acid anhydride, base catalyzed by BDMA. Using NMR spectroscopy, which in particular provided information about the initiation of the reaction, they observed a rapid initial fall in the concentration of BDMA. For fast initiation through the epoxy–amine reaction [eq. (5)], the initial conditions can thus be written as

$$\left. \begin{array}{l}
 [M_1^*] \simeq [C]_o \\
 [M_2^*] = 0 \\
 [M_1] \simeq [M_1]_o
 \end{array} \right\} \quad (14)$$

where $[C]_o$ is the initial concentration of the tertiary amine catalyst. Dividing eq. (13) by eq. (10), one obtains,

$$\frac{d[M_2^*]}{d[M_1]} = -\frac{k_1[M_1^*][M_2]}{k_2[M_2^*][M_1]} + 1 \quad (15)$$

Since $[M_1]_o = [M_2]_o$, and it is a case of step addition reaction, $[M_1] \simeq [M_2]$ [eq. (15)] thus reduces to

$$\frac{d[M_2^*]}{d[M_1]} = -\frac{k_1[M_1^*]}{k_2[M_2^*]} + 1 \quad (16)$$

Since each mole of M_1^* and M_2^* contains one mole of the tertiary amine catalyst,

$$[M_1^*] + [M_2^*] = [C]_o \quad (17)$$

Combining eqs. (16) and (17), and rearranging, one obtains

$$\frac{1}{k'[C]_o} \left[\frac{d[M_2^*]}{K - 1/[M_2^*]} \right] = d[M_1] \quad (18)$$

where

$$k' = k_1/k_2 \quad (19)$$

and

$$K = (1 + k')/k'[C]_o \quad (20)$$

Integration of eq. (18) yields

$$\frac{1}{k'[C]_o} \left[\frac{[M_2^*]}{K} + \frac{1}{K^2} \ln(1 - [M_2^*]K) - \frac{\ln K}{K^2} \right] = [M_1] + \text{constant} \quad (21)$$

Since the acylation reaction is generally faster than the carboxylate-epoxide reaction,⁶ $k_1 \gg k_2$ and $[M_2^*]K$ can be approximated by $[M_2^*]/[C]_o$. In view of eq. (17), the latter ratio is always less than 1. Expanding $\ln(1 - [M_2^*]K)$ and neglecting higher order terms, eq. (21) then simplifies to

$$-\frac{[M_2^*]^2}{2k'[C]_o} - \frac{\ln K}{k'[C]_o K^2} = [M_1] + \text{constant} \quad (22)$$

Using the initial conditions, eq. (14), to evaluate the constant, eq. (22) further simplifies to

$$[M_2^*] = \sqrt{2k'[C]_o([M_1]_o - [M_1])} \quad (23)$$

The substitution of eq. (23) in eq. (10) then yields

$$\frac{d[M_1]}{dt} = -K^I[M_1]\sqrt{[M_1]_o - [M_1]} \quad (24)$$

where $K^I = \sqrt{2k_1k_2[C]_o}$.

Defining epoxy conversion α by

$$\alpha = \frac{[M_1]_o - [M_1]}{[M_1]_o} \quad (25)$$

eq. (24) can be rewritten as

$$\frac{d\alpha}{dt} = K^{II}\sqrt{\alpha}(1 - \alpha) \quad (26)$$

where

$$K^{II} = K^I[M_1]_o^{1/2} = \sqrt{2k_1k_2[C]_o[M_1]_o} \quad (27)$$

Equation (26) relates to initial stage curing when initiation is by tertiary amine-epoxy reaction. If, however, initiation involves tertiary amine-anhydride reaction, represented by eq. (6), the initial conditions can be written as

$$\left. \begin{aligned} [M_1^*] &= 0 \\ [M_2^*] &\simeq [C]_o \\ [M_1] &\simeq [M_1]_o \end{aligned} \right\} \quad (28)$$

The application of the above procedure then leads to

$$\frac{d\alpha}{dt} = K^I(1 - \alpha) \sqrt{\alpha[M_1]_o + \frac{[C]_o}{2k'}} \quad (29)$$

Since the catalyst concentration, $[C]_o$, employed is small (3.6×10^{-3} to 1.7×10^{-2} mmol/g), and $k' = k_1/k_2 \gg 1$, eq. (29) can be simplified to

$$\frac{d\alpha}{dt} = K^{II}\sqrt{\alpha}(1 - \alpha)$$

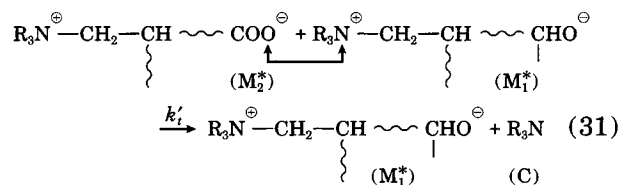
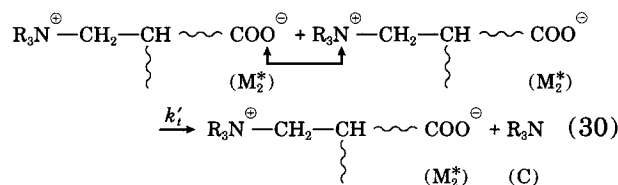
which is identical to eq. (26). It is therefore not possible to distinguish between the two initiation mechanisms on the basis of conversion rate data alone.

Intermediate Stage

After the initial stage, when the concentrations of the active species M_1^* and M_2^* build up, termination reactions involving these active species assume significance. According to the mechanism proposed by Tanaka and Kakiuchi,³ such termination reactions lead to a regeneration of the tertiary amine catalyst.

Amine-Epoxy Initiation

According to the mechanism of Tanaka and Kakiuchi,³ for the case in which the initiation is through the tertiary amine-epoxy reaction, the regeneration steps can be written as



The curing in the intermediate stage is assumed to involve initiation, propagation, and termination, the rates of which are given by

$$R_i = k'_{i1}[C][M_1] \quad (32)$$

$$R_p = k_1[M_1^*][M_2] + k_2[M_2^*][M_1] \quad (33)$$

$$R_t = k'_t[M_2^*]^2 + k'_t[M_1^*][M_2^*] \quad (34)$$

where $[C]$ is the concentration of the tertiary amine catalyst at any time t . It may be noted that k'_{i1} , of eq. (32), is likely to be different from k_{i1} of eq. (5), since the former relates to reaction of the tertiary amine with the epoxide group of species, which are much larger than the monomer IPDGE. It is further assumed that there is steady state for the total concentration of active species, that is,

$$\frac{d([M_1^*] + [M_2^*])}{dt} = 0 \quad (35)$$

and that the rates of interconversion of M_1^* and M_2^* are equal, that is,

$$k_1[M_1^*][M_2] = k_2[M_2^*][M_1] \quad (36)$$

Equation (35) is qualitatively in accord with the reported observation⁶ that $k_1 \gg k_2$, $[M_2^*] \gg [M_1^*]$ and $[M_1] \simeq [M_2]$ for equimolar epoxy and anhydride in the feed. By mass balance on the catalyst, we now have

$$[C]_o = [M_1^*] + [M_2^*] + [C] \quad (37)$$

The steady state assumption of eq. (35) therefore implies that $[C]$ is constant. Moreover, since

$$\frac{d[M_1^*]}{dt} = k'_{i1}[C][M_1] - k_1[M_1^*][M_2] + k_2[M_2^*][M_1] \quad (38)$$

$$\frac{d[M_2^*]}{dt} = k_1[M_1^*][M_2] - k_2[M_2^*][M_1] - k'_t([M_2^*]^2 + [M_1^*][M_2^*]) \quad (39)$$

the application of eqs. (35) and (36) leads to,

$$k'_{i1}[C][M_1] = k'_t([M_2^*]^2 + [M_1^*][M_2^*]) \quad (40)$$

Since the initial molal concentrations of M_1 and M_2 are equal, and they are consumed at equal rates in alternating-type step polymerization reactions, it follows that $[M_1] \simeq [M_2]$ during the course of reaction. Equation (36) thus yields

$$[M_1^*] \simeq k_2[M_2^*]/k_1 \quad (41)$$

Substituting for $[M_1^*]$ in eq. (40), one obtains

$$[M_2^*] = \sqrt{\frac{k'_{i1}[C][M_1]}{k'_t(1 + k_2/k_1)}} \quad (42)$$

A combination of eqs. (33), (35), and (36) yields

$$R_p = -\left(\frac{d[M_1]}{dt} + \frac{d[M_2]}{dt}\right) = 2k_2[M_2^*][M_1] \quad (43)$$

Considering that M_1 and M_2 are consumed by alternating copolymerization, a substitution for $[M_2^*]$ from eq. (40) then yields

$$-2\frac{d[M_1]}{dt} = 2k_2[M_1]^{1.5} \sqrt{\frac{k'_{i1}[C]}{k'_t(1 + k_2/k_1)}} \quad (44)$$

Equation (44) can be rewritten in terms of conversion α as

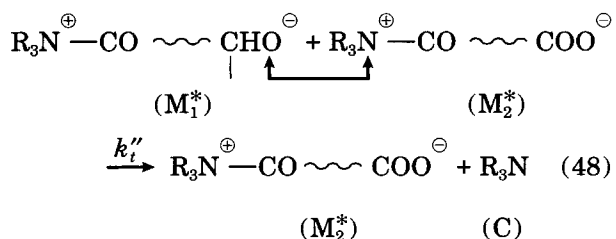
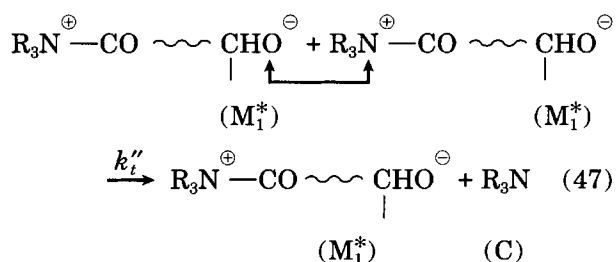
$$\frac{d\alpha}{dt} = K^{III}(1 - \alpha)^{1.5} \quad (45)$$

where

$$K^{III} = k_2 \sqrt{\frac{k'_{i1}[C][M_1]_o}{k'_t(1 + k_2/k_1)}} \quad (46)$$

Amine-Anhydride Initiation

If initiation occurs by the reaction of tertiary amine with anhydride, the termination reactions regenerating the catalyst, according to the mechanism of Tanaka and Kakiuchi,³ will be represented by



The rates of initiation, propagation, and termination are then given by

$$R_i = k'_{i2}[C][M_2] \quad (49)$$

$$R_p = k_2[M_1][M_2^*] + k_1[M_2][M_1^*] \quad (50)$$

$$R_t = k_t''[M_1^*]^2 + k_t'[M_1^*][M_2^*] \quad (51)$$

Proceeding in the same way as in the previous section, we obtain

$$\frac{d\alpha}{dt} = K^{IV}(1 - \alpha)^{1.5} \quad (52)$$

where

$$K^{IV} = k_1 \sqrt{\frac{k'_{i2}[C]}{k_t''(1 + k_1/k_2)}} \quad (53)$$

Since both eqs. (45) and (52) are of similar form, it is not feasible, as in the initial stage of curing, to distinguish between the two initiation mechanisms from the conversion data alone.

The rate constants K^{II} and K^{III} , in eqs. (26) and (45), respectively, are estimated using the nonlinear regression technique.¹⁴ Figures 4 and 5 present typical comparisons between experimental data and

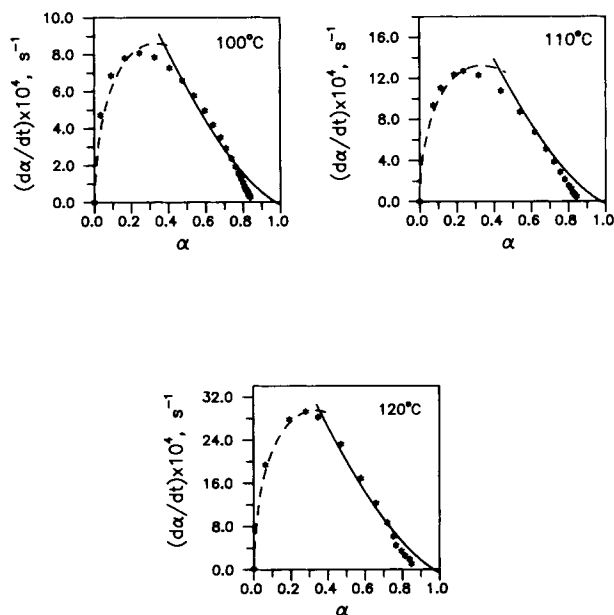


Figure 4 Comparison of experimental data with model eqs. (26) and (45) for BDMA concentration of 0.25 phr: reaction rate vs. conversion. (***) experimental, (---) model eq. (26), (—) model eq. (45).

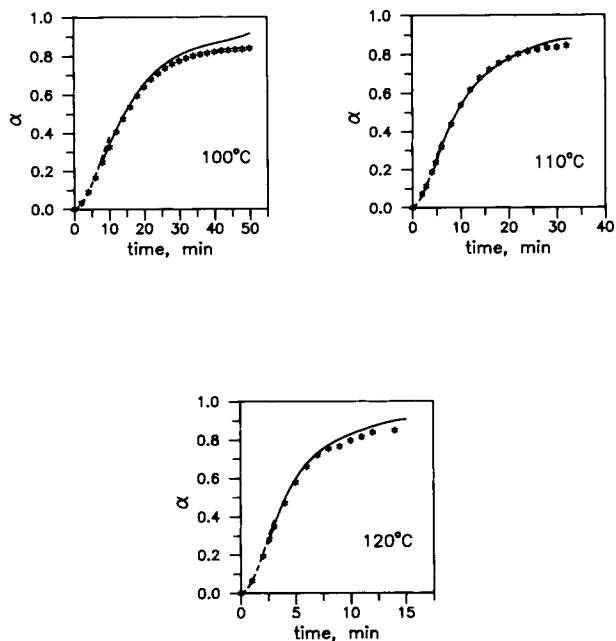


Figure 5 Comparison of experimental data with model eqs. (26) and (45) for BDMA concentration of 0.25 phr: conversion vs. time. (***) experimental, (---) model eq. (26), (—) model eq. (45).

model predictions for the initial and intermediate stages of cure. Equation (26) fits the experimental data reasonably well up to 25% conversion and eq. (45) fits over the conversion range of approximately 35–70%. Similar agreement is also observed with the DSC data at other concentrations of BDMA. Moreover, according to eq. (27), K^{II} for the initial stage should be proportional to $\sqrt{[C]_0}$. This is supported by the results plotted in Figure 6.

Figures 7 and 8 show the Arrhenius plots of K^{II} for the initial stage and K^{III} for the intermediate stage of curing. In both cases, no significant differences are observed between the results for BDMA concentrations of 0.25 and 0.5 phr. The activation energies obtained are 71.8, 75.2 kJ/mol in the initial stage of curing and 68.9, 71.2 kJ/mol in the intermediate stage of curing. The first and second values in each case relate to BDMA concentrations of 0.1 and 0.25 phr, respectively.

Postvitrification Stage

As is shown in Figures 4 and 5, both rate and conversion plots, according to the model in eq. (45), deviate from the experimental data beyond 70% conversion. This could be attributed to the onset of gelation in the system. As the cure progresses and the resin crosslinks, the glass transition tempera-

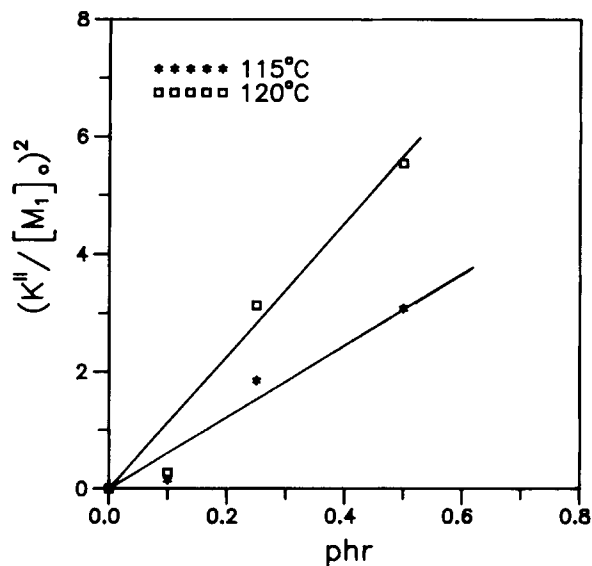


Figure 6 Plot of $(K''/[M_1]_o)^2$ vs. BDMA concentration.

ture, T_g , of the system rises. When T_g approaches the curing temperature, the resin passes from a rubbery state to a glassy state. In this state, the mobility of the reacting groups is hindered and the rate of reaction is controlled by diffusion rather than by chemical factors. This necessitates the modification of the model equation for the intermediate region by inclusion of a diffusion term.

A typical approach¹⁵ for mathematical treatment of the above type of diffusion phenomenon is to express T_g in terms of α and then to express the dif-

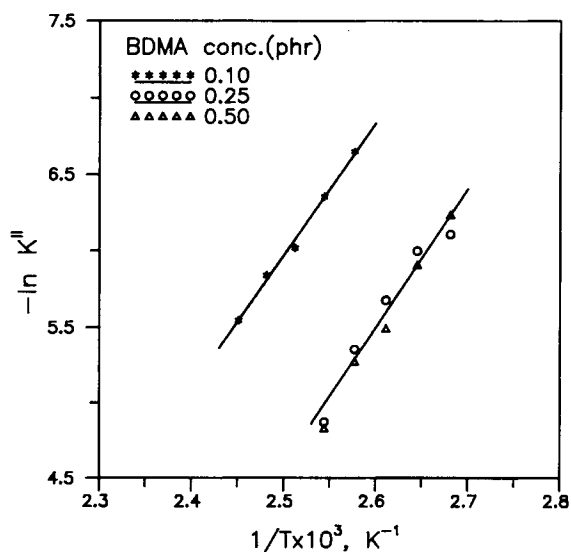


Figure 7 Arrhenius plot of rate constant K'' .

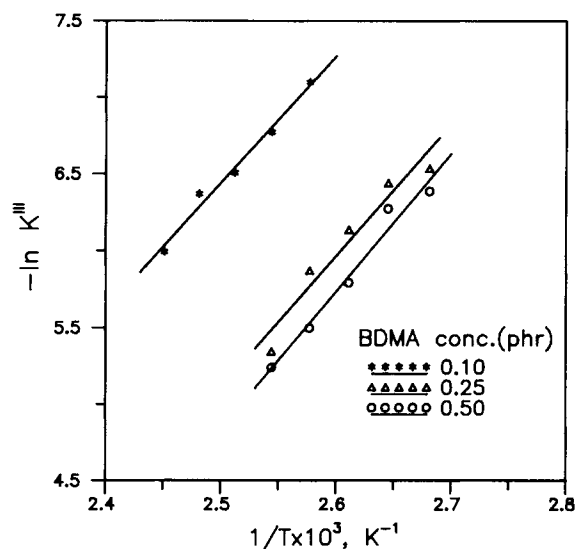


Figure 8 Arrhenius plot of rate constant K''' .

fusion controlled rate constant in terms of $T-T_g$ by a William-Landell-Ferry type of equation. This, however, leads to a complex relationship. A somewhat simpler semiempirical relationship, based on free-volume considerations to explain the diffusion control in cure reactions, was proposed by Chern and Pohlein.¹² It relates the diffusion-controlled rate constant, k_d , to the chemical rate constant, k_c , by the expression

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \quad (54)$$

where C is a constant and α_c is the critical conversion. Equation (54), however, corresponds to an abrupt onset of diffusion control at $\alpha = \alpha_c$, while, in reality, the onset is gradual and there is a region where both chemical and diffusion factors are controlling. According to Rabinowitch,¹³ an overall effective rate constant, k_e , can be expressed in terms of k_d and k_c by the relation

$$\frac{1}{k_e} = \frac{1}{k_c} + \frac{1}{k_d} \quad (55)$$

Combining equations (54) and (55), a diffusion factor $f(\alpha)$ can be defined as

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (56)$$

For $\alpha \ll \alpha_c$, $f(\alpha)$ approximates unity and the effect of diffusion is negligible. As α approaches α_c , $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$

and zero as α increases beyond α_c . The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$.

Among the four rate constants involved in eq. (45) only k_1 , k_2 , and k'_t will be expected to be significantly affected by diffusional effects. Since initiation involves reaction with smaller catalyst molecules, the diffusional effect on k'_{i1} may be ignored for simplicity. It may further be assumed, with reasonable approximation, that the propagation rate constants k_1 and k_2 are affected in the same way. Replacing k_1 , k_2 , and k'_t in eq. (45) by the corresponding effective rate constants, according to eq. (56), and simplifying, one obtains

$$\frac{d\alpha}{dt} = k_2 \sqrt{\frac{k'_{i1}[C][M_1]_0}{k'_t(1+k_2/k_1)}} \frac{\sqrt{1 + \exp[C_2(\alpha - \alpha_c)]}}{1 + \exp[C_1(\alpha - \alpha_c)]} \times (1 - \alpha)^{1.5} \quad (57)$$

where C_1 is the diffusional constant for k_1 and k_2 , and C_2 is that for k'_t .

The parameters in eq. (57) were estimated using the nonlinear regression technique.¹⁴ The equation is fitted to the experimental data of rate vs. conversion in Figure 9 and conversion vs. time in Figure 10.

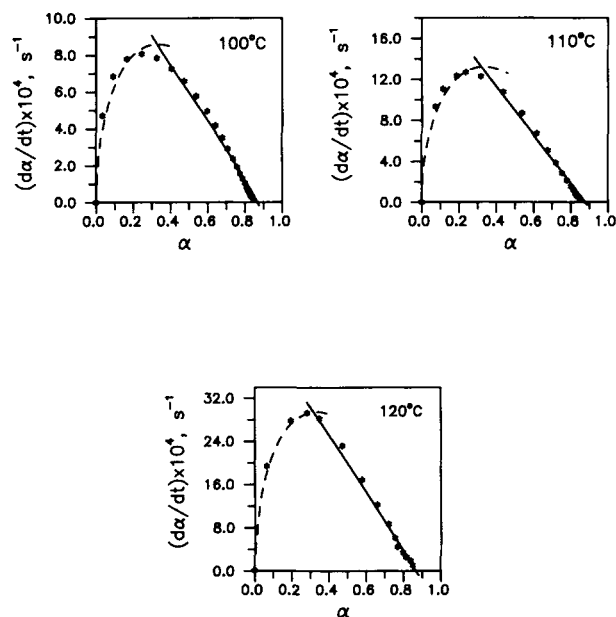


Figure 9 Comparison of experimental data with model eqs. (26) and (57) for BDMA concentration of 0.25 phr: reaction rate vs. conversion. (***) experimental, (- - -) model eq. (26), (—) model eq. (57).

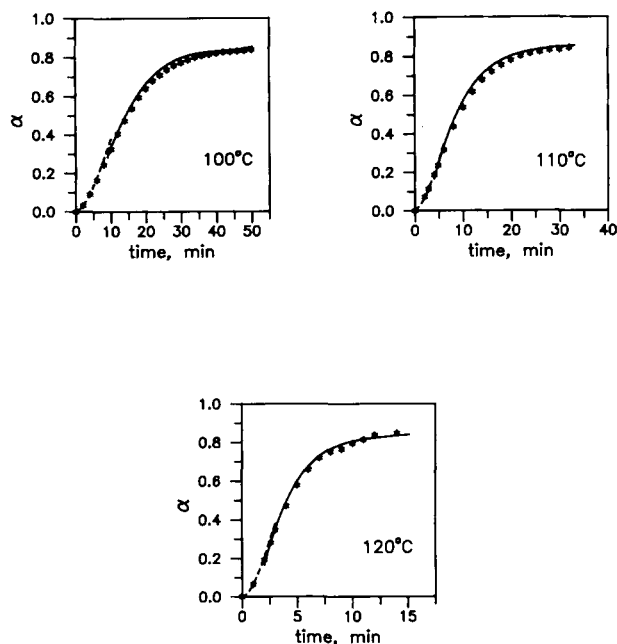


Figure 10 Comparison of experimental data with model eqs. (26) and (57) for BDMA concentration of 0.25 phr: conversion vs. time. (***) experimental, (- - -) model eq. (26), (—) model eq. (57).

10. Equation (57) fits the experimental data well, both in the intermediate and postvitrification stages of curing. The values of C_1 , C_2 , and α_c , estimated for different concentrations of BDMA and temperatures, are shown in Table I. The value of α_c agrees with the conversion at which the model eq. (45) is found to deviate from the experimental curve, indicating the onset of vitrification.

Equation (57) indicates that the rate of conversion is more sensitive to a decrease of k_1 and k_2 than to a decrease of k'_t , due to diffusional effects. The values obtained for C_1 and C_2 (Table I) also indicate that the propagation rate constants, k_1 and k_2 , are more strongly affected by diffusion than is the ter-

Table I Values of C_1 , C_2 , and α_c at Different Temperatures and Various BDMA Concentrations

Temperature (°C)	BDMA Concentration					
	0.25 phr			0.5 phr		
	C_1	C_2	α_c	C_1	C_2	α_c
100	36.28	3.90	0.803	39.34	5.19	0.845
110	29.61	3.59	0.805	40.71	3.79	0.842
120	31.03	3.47	0.786	39.28	4.28	0.883

mination rate constant k'_t . This is contrary to gelation effects in radical polymerization. Both C_1 and C_2 are found to be insensitive to temperature. Chern and Pohlein¹² also observed that the effect of temperature was more pronounced on the curing reactions than on the diffusional effects.

CONCLUSIONS

Kinetic mechanisms are proposed and rate expressions are derived for the anhydride curing of diepoxides, catalyzed by a tertiary amine. The cure reaction is divided into three steps, namely, the initial, intermediate, and postvitrification stages. The models are tested with DSC data on isophthalic diglycidyl ester/hexahydrophthalic anhydride/benzyltrimethylamine system. In the initial stages of curing, the main reactions are considered to be propagation by reaction of alkoxylate and carboxylate active species with anhydride and epoxy, respectively. This is preceded by a fast initial reaction of tertiary amine with either epoxy or anhydride, producing the active species. The rate expressions so derived are half order with respect to reacted functional groups and first order with respect to unreacted functional groups, for the initial stage. In the intermediate stage of curing, the propagation reactions are coupled with termination reactions, regenerating the tertiary amine catalyst. Steady state is assumed for the total concentration of active species to derive an expression for the rate of epoxy conversion. This rate is 1.5 order with respect to unreacted functional groups.

The above rate expressions bear a close analogy to the semiempirical model, reported by us earlier,¹⁰ yielding 0.5 and 1.5 orders with respect to reacted and unreacted functional groups, respectively. These rate expressions provide good fit to experimental data in the initial and intermediate stages of curing up to the point of vitrification. To describe the cure in the postvitrification region, the kinetic model of the intermediate stage has been modified by introducing a diffusion factor, by combining equations

proposed by other workers.^{12,13} The modified equation fits the experimental rate data well, both in the intermediate and postvitrification stages of curing. The evaluation of diffusion factors indicates that, unlike in radical chain polymerization, the propagation rate constants are affected by diffusion more than the termination rate constant.

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