

# Analysis of Crosslinking in Amine-Cured Epoxy Systems: The One-to-One Relationship Between $T_g$ and Conversion

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## SYNOPSIS

Network formation, in a system such as a tetrafunctional aromatic diamine cured with a difunctional epoxy, is considered on the basis of only interconnected trifunctional crosslinking sites. The number-average molecular weight, the crosslinking density, and the gel point, and also the vitrification contours of the time-temperature-transformation (TTT) isothermal cure diagram, are related to the ratio of the reaction rate constants,  $k_2/k_1$ , of the competing reactions of epoxy with secondary amine group ( $k_2$ ) and with primary amine group ( $k_1$ ). It is considered that the glass transition temperature,  $T_g$ , is related uniquely to conversion on the basis that the number-average molecular weight and crosslinking density are insensitive to the ratio,  $k_2/k_1$ . Experimental data support the theoretical result. The potential influences of chemical structure and physical aging on  $T_g$  are discussed.

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## INTRODUCTION

Polymerization of low-molecular-weight multifunctional monomers leads to higher-molecular-weight branched structures with branching sites and, eventually, to an infinite network structure with crosslinking sites. The theory of crosslinking systems in stepwise network polymerization was introduced by Flory<sup>1-3</sup> and has been developed by many scientists.<sup>4-11</sup> The common method used to analyze the concentration of effective crosslinking units is described as follows (see Fig. 1):

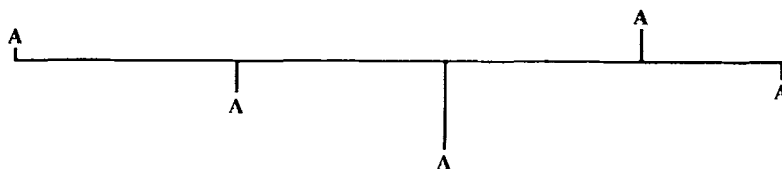
For a monomer residue,  $A_f$ , that has  $f$  arms each ending with a functional group A, as in Figure 1, if 3 of its A functional groups lead to an infinite structure, then it is a trifunctional crosslinking unit. If  $j$  arms ( $3 \leq j \leq f$ ) of  $A_f$  connect with the infinite network, then the functionality of the crosslinking unit is considered to be  $j$ , and is represented as in Figure 2 ( $j = 3, 4, 6, 8$ ). Accordingly, the crosslinking density<sup>3,6</sup>

$$X_{dc} = \frac{N_f}{W} \sum_{j=3}^f P_j^{(gel)} \quad (1)$$

where  $N_f$  = moles of  $A_f$  monomer residues,  $W$  = bulk mass, and  $P_j^{(gel)}$  = the probability of  $j$  arms of functional groups A in one  $A_f$  unit leading to an infinite structure. According to Flory's method, the segments between two neighboring A functional groups (Fig. 1) in the same  $A_f$  unit are neglected, i.e., the curing agent is considered to be a point with several arms (Fig. 2). However, a  $j$ -crosslinking point with  $j$  large does not exist in most practical thermosetting systems. It follows that there are defects in the general treatment of crosslinking.

In recent work by Wisanrakkit, et al.,<sup>12</sup> a stoichiometric tetrafunctional aromatic diamine-cured difunctional epoxy resin system was studied, the chemical reactants for which are shown in Figure 3. It is noted that the length of the segment between the two primary amine groups in trimethylene glycol di-*p*-aminobenzoate (TMAB) is similar to that between the two epoxy groups in the diglycidyl ether of bisphenol A (DGEBA). It was found that it was difficult to use Flory's theory [eq. (1)] directly to relate  $T_g$  to fractional conversion for the curing sys-

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**Figure 1** A generalized  $A_f$  monomer, with  $f$  arms each with a functional group A, and with segments between nearest pairs of functional groups ( $f = 5$ , number of segments = 4).

tem. However, the experimental data fitted the theoretical model better using the assumption that the efficiency of a tetrafunctional crosslinking unit is twice that of a trifunctional crosslinking unit.

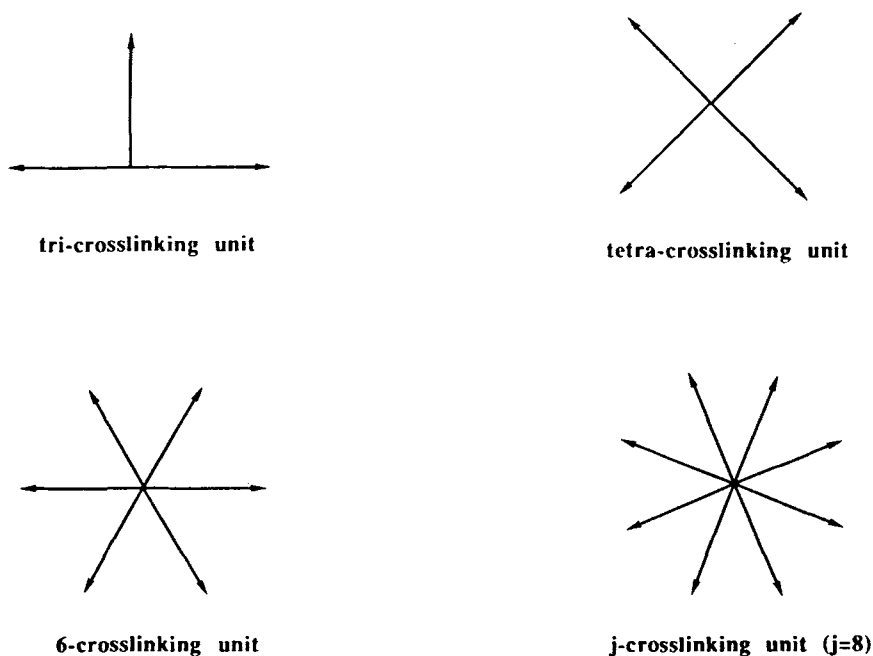
In this study, French's<sup>10,11</sup> tri-branch point concept, combined with Luo's network model,<sup>13</sup> and kinetic equations are used to treat the same crosslinking reaction.<sup>12</sup> The one-to-one relationship between  $T_g$  and conversion, which was developed by Wisanrakkit for the present system,<sup>12</sup> is discussed in terms of the influence of the ratio ( $k_2/k_1$ ) of the rate constants of the competing secondary amine group and primary amine group reactions with epoxy on the number-average molecular weight and on the crosslinking density of the curing system. The re-

sults are also used to predict the effect of the ratio ( $k_2/k_1$ ) on gelation, the fraction of branching units, and on the vitrification contour of the isothermal time-temperature-transformation (TTT) cure diagram.<sup>12</sup> A preliminary report on this research has been published.<sup>14</sup>

## THEORETICAL TREATMENT

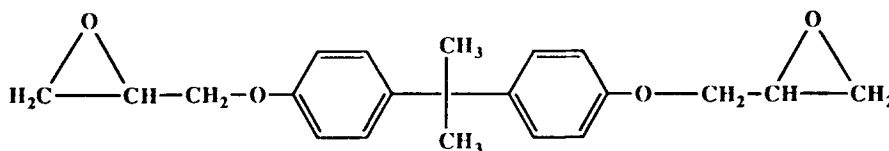
### Crosslink Density

Consider an  $a$ -multifunctional epoxy monomer whose  $a$  chain ends are each terminated by a reactive epoxide group (A) that reacts with a crosslinking monomer such as a multiprimary amine. At the

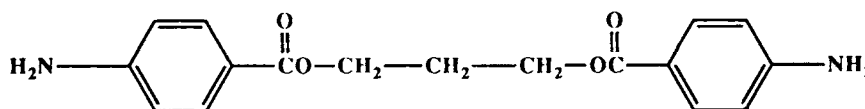


**Figure 2** Types of crosslinking unit according to Flory's method. The crosslinking site is assumed to be a point with several arms each connected to an infinite structure.

## CHEMICAL REACTANTS



Diglycidyl Ether of Bis-phenol A



Trimethylene Glycol Di-p-aminobenzoate

**Figure 3** The structures of the difunctional epoxy and the tetrafunctional diamine used in earlier research.<sup>12</sup>

stoichiometric equivalent ratio (i.e., one epoxy group/one amine hydrogen atom) and with the branch points uniting no more than three chain ends, the value of the network crosslinking density,  $X_{df}$ , in mol/g in the fully cured material is<sup>10,11,13</sup>

$$X_{df} = \frac{N_a(a-2) + N_b(2b-2)}{W_a + W_b} \quad (2)$$

Here  $N_a$  = moles of epoxy monomer,  $W_a$  = weight of epoxy monomer, and  $a$  = number of functionalities in one epoxy monomer. Similarly,  $N_b$  = moles of amine monomer,  $W_b$  = weight of amine monomer, and  $b$  = number of primary amine functional groups in one amine monomer.

If  $E_a$ ,  $E_b$  are the corresponding equivalent weights of epoxy and primary amine in the monomers, eq. (2) becomes

$$X_{df} = \frac{N_a(a-2) + N_b(2b-2)}{aN_aE_a + 2bN_bE_b} \quad (3)$$

For an incompletely cured system, the number of unreacted epoxy groups, in mol/g, in the gel fraction is

$$\frac{(1-S_a)aN_a}{aN_aE_a + 2bN_bE_b} (1-P_{Ag}) \quad (4)$$

where  $P_{Ag}$  is the epoxide fractional conversion in the gel.  $S_a$  is the weight fraction of unreacted and reacted epoxy monomer residues  $A_a$  in the sol.

If  $G_a$  represents the weight fraction of epoxy monomer residues  $A_a$  in the gel (i.e.,  $G_a + S_a = 1$ ), and  $P_{As}$  is the epoxide fractional conversion in the sol, then the overall fractional conversion of epoxide,

$$P_A = S_aP_{As} + G_aP_{Ag} = S_aP_{As} + (1-S_a)P_{Ag} \quad (5)$$

From eq. (5),

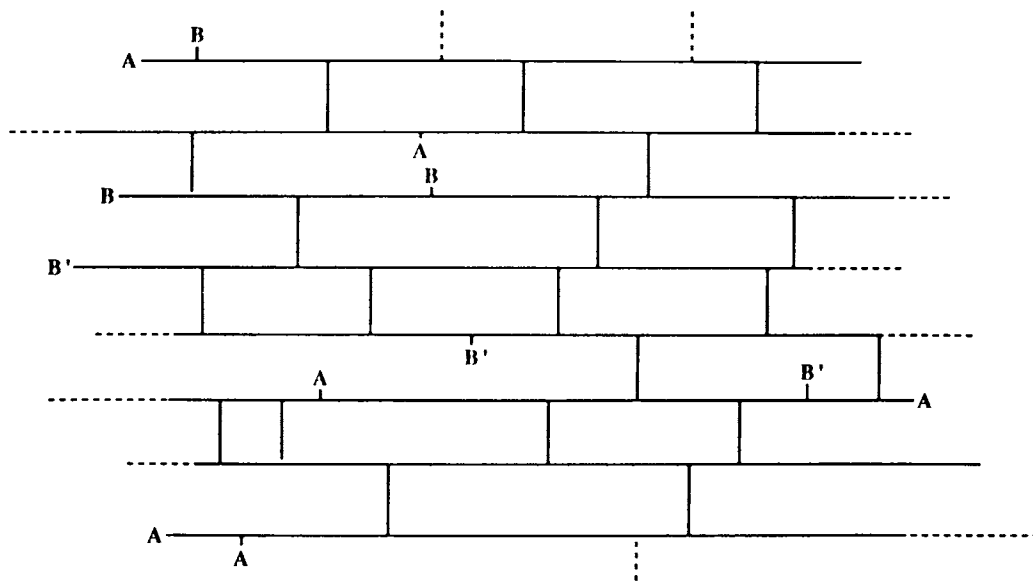
$$P_{Ag} = \frac{P_A - S_aP_{As}}{1-S_a} \quad (6)$$

Substituting for  $P_{Ag}$  in eq. (4), the number of unreacted epoxide groups, in mol/g, in the gel fraction is

$$\frac{(1-P_A) - S_a(1-P_{As})}{E_a + 2r_bE_b} \quad (7)$$

where  $r_b = bN_b/aN_a (= \frac{1}{2}$  for a stoichiometric system).

Note that every unreacted epoxy group in the gel fraction will diminish the number of crosslinking units by two<sup>13</sup> relative to the fully developed network



**Figure 4** A generalized incompletely reacted infinite network model,<sup>13</sup> with branching points, dangling chains, crosslinking points, unreacted epoxide A, unreacted primary amine B, and unreacted secondary amine B'.

(Fig. 4). That is, the number of the crosslink units that have not formed due to incomplete reaction of epoxide in the gel will be

$$2 \frac{(1 - P_A) - S_a(1 - P_{As})}{E_a + 2r_b E_b} \quad (8)$$

The number of crosslinking units in the system during cure,  $X_{dc}$ , should be the number of crosslinking units at 100% conversion in the gel fraction,  $GX_{df}$ , minus the number of crosslinking units that do not form because of incomplete reaction of epoxide in the gel

$$X_{dc} = \frac{N_a(a - 2) + N_b(2b - 2)}{aN_a E_a + 2bN_b E_b} \times (1 - S) - 2 \frac{(1 - P_A) - S_a(1 - P_{As})}{E_a + 2r_b E_b} \quad (9)$$

where  $G$  is the gel weight fraction, and  $S$  is the sol weight fraction ( $S + G = 1$ ). Eq. (9) can be readily modified to apply to non-stoichiometric systems. The advantages of this approach are discussed in Appendix A.

The result is similar to that derived by French,<sup>10</sup> except for his assumption that the overall fractional conversion,  $P_A$ , equals the fractional conversion in the gel (i.e.,  $P_{Ag} = P_A$ ), which is not valid. It is emphasized that the segments between two functional

groups in the reactant molecules have been considered in developing eq. (9). If  $P_A$ ,  $P_{As}$ , and  $S_a$  can be measured by experiment, the crosslink density can be calculated by means of eq. (9). However, to a good approximation, the relationship between  $P_A$ ,  $P_{As}$ , and  $S_a$  can be obtained from Flory's theory<sup>3</sup>, as follows in the next section, because the fraction of intramolecular reactions in the sol is small.

### Sol-Gel Fraction

A, B, and B' are defined as epoxy, primary, and secondary amine groups, respectively. The secondary amine is generated by reaction between primary amine group and epoxide group.  $P_A$ ,  $P_B$ , and  $q_{B'}$ , are defined as the corresponding fractional conversions of epoxide, primary, and secondary amine groups.

For an  $A_a$  monomer residue, consisting of  $a$  arms of functional group A in its chemical structure, the probability for the event that an  $A_a$  unit is only in the sol is<sup>7,8</sup>

$$S_a = [A(S)]^a$$

$A(S)$  is the probability of one of the  $A_a$  functional groups being in the sol;  $[A(S)]^a$  is the probability of all arms of the  $A_a$  monomer residue being in the sol. The probability,  $A(S)$ , involves the sum of the probabilities of two events<sup>7,8</sup>: (1) the group A is un-

reacted, and (2) the group A is reacted, but the reaction keeps A in the sol; thus

$$A(S) = 1 - P_A + P_A \left[ r_b \frac{P_B}{P_A} [A^*(S)] + r_b \frac{P_B q_{B'}}{P_A} [A'^*(S)] \right] \quad (10)$$

where  $r_b P_B/P_A$  and  $r_b P_B q_{B'}/P_A$  are the weight coefficients of reactions of A with B and B', respectively;  $A^*(S)$  = the probability of an A unit reacted with B in the sol;  $A'^*(S)$  = the probability of an A unit reacted with B' in the sol.

For the  $B_b(B'_b)$  monomer, which has  $b$  arms of functional group B (each of which becomes B' after reacting with A), the probability  $B(S)$ , for one B group being in the sol, is the sum of the probabilities

of no reaction and of reaction that keeps B in the sol:

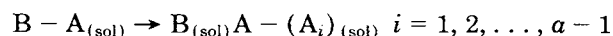
$$B(S) = 1 - P_B + P_B [B^*(S)] \quad (11)$$

where  $B^*(S)$  is the probability of a B group reacted with A in the sol. In the same way, the probability of the secondary amine (B') in the sol,  $B'(S)$ , is

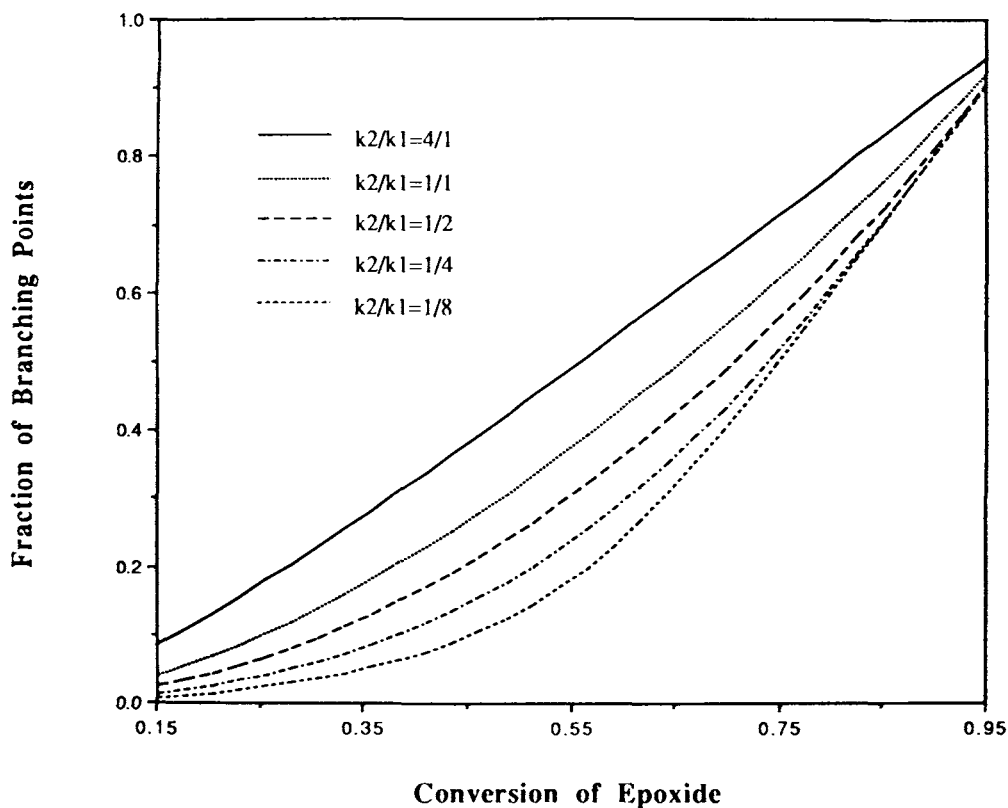
$$B'(S) = 1 - q_{B'} + q_{B'} [B'^*(S)] \quad (12)$$

where  $B'^*(S)$  is the probability of a B' group reacted with A in the sol.

For a reaction of B with one of the arms of a monomer residue  $A_a$  in the sol that keeps the unit (BA) in the sol, the other  $(a - 1)$  arms of the  $A_a$  monomer residue must also be in the sol:



**Effect of Kinetic Ratio on the Number of Branching-Points**



**Figure 5** Effect of the kinetic ratio on the number of branching points ( $P_B q_B$ ); obtained from a model calculation with  $a = 2$ ,  $b = 2$ , and  $r_b = 0.5$  (see Appendix B).

Therefore  $B^*(S)$  equals the probability of the  $(a - 1)$  arms of the  $A_a$  molecule being connected with B in the sol,<sup>7,8</sup> and

$$B^*(S) = [A(S)]^{a-1} \quad (13)$$

where  $A(S)$  is the probability of one A group being only in the sol. In the same way

$$B'^*(S) = [A(S)]^{a-1} \quad (14)$$

$$A^*(S) = [B(S)]^{b-1}[B'(S)]^b \quad (15)$$

$$A'^*(S) = [B(S)]^b[B'(S)]^{b-1} \quad (16)$$

Because the reaction of the group B with group A can occur both in the sol and the gel, the probability of one group B only reacting with A in the sol,  $B^*(S)$ , should be the ratio of the concentration of group A in the sol to that in the total system<sup>3</sup>:

$$B^*(S) = S_a \frac{1 - P_{As}}{1 - P_A} \quad (17)$$

where  $P_{As}$  is the conversion of group A in the sol fraction.  $P_A$  is the total conversion of group A. The relationship between  $P_A$ ,  $P_{As}$ , and  $P_{Ag}$  is given in eq. (5), i.e.,

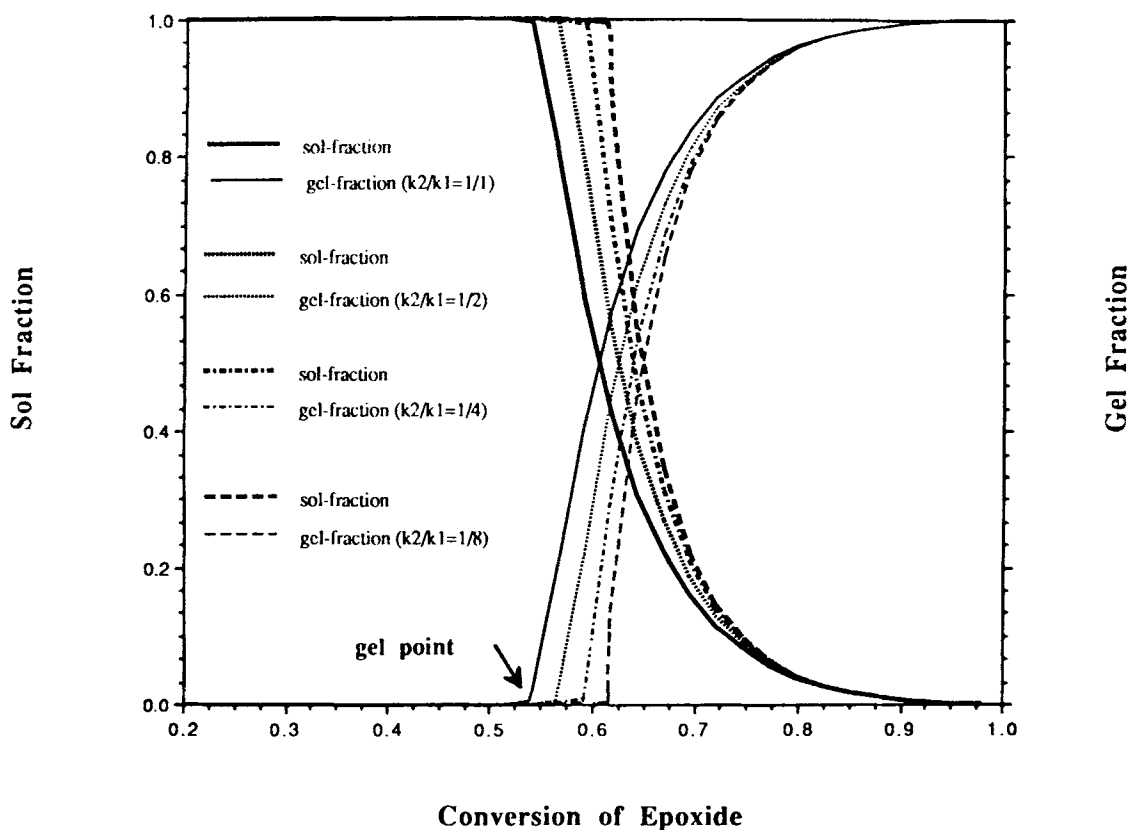
$$P_A = S_a P_{As} + G_a P_{Ag} = S_a P_{As} + (1 - S_a) P_{Ag}$$

where  $S_a$  is the fraction of  $A_a$  monomer residues in the sol, and

$$S_a = [A(S)]^a \quad (18)$$

where, again,  $[A(S)]^a$  is the probability of all of the arms of a monomer  $A_a$  being in the sol.

For the amine-cured epoxy reaction,



**Figure 6** Effect of the kinetic ratio on the sol-gel fraction and gel point; obtained from a model calculation with  $a = 2$ ,  $b = 2$ ,  $r_b = 0.5$ ,  $E_a = 174$  g/eq, and  $E_b = 157$  g/NH<sub>2</sub> [results calculated from eq. (25);  $G + S = 1$ ].

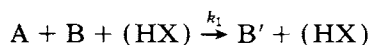
$$P_A = r_b P_B + r_b P_B q_{B'} \quad (19)$$

To solve eqs. (10)–(19), the kinetic equations that govern the conversions of epoxide, primary amine, and secondary amine are used.

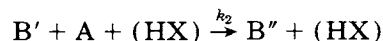
**Kinetics**

The reactivities of primary amine and secondary amine with epoxide are different, as has been shown in many papers<sup>15–23</sup> and also in our recent work.<sup>24</sup> Generally, the reactions of diamine-cured epoxy resins can be modeled as follows.

First step: primary amine reaction with epoxide that generates secondary amine.



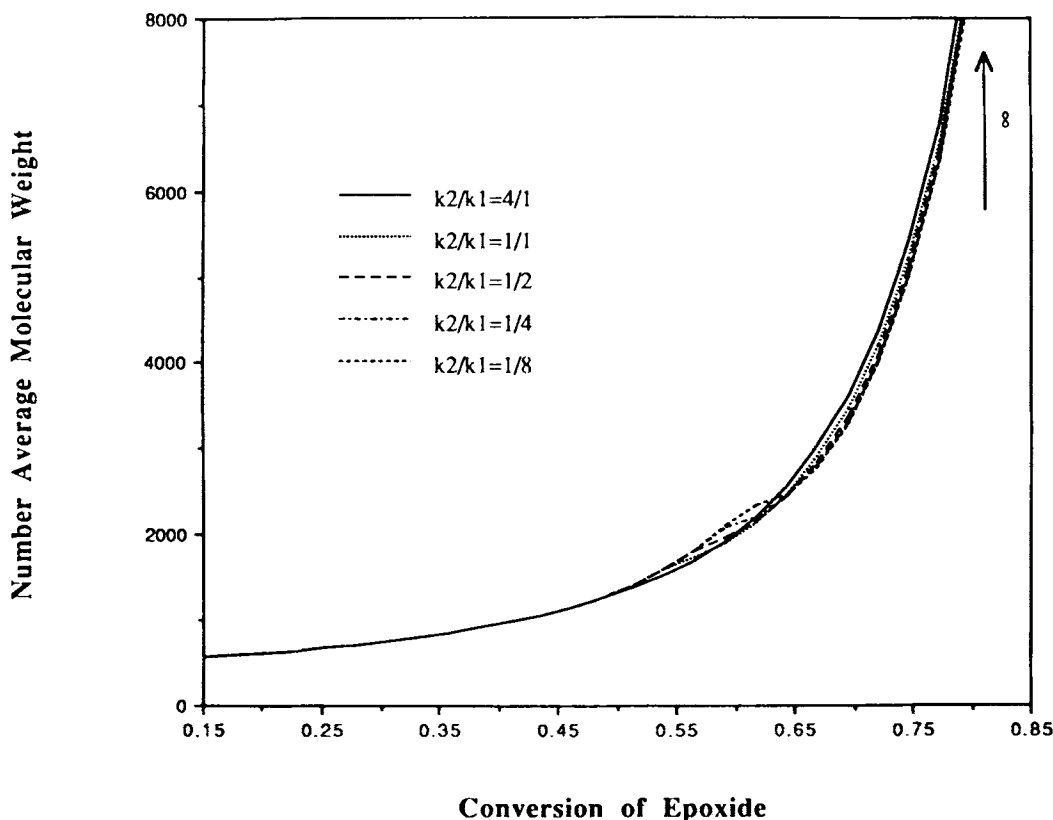
Second step: secondary amine reaction with epoxide that generates tertiary amine



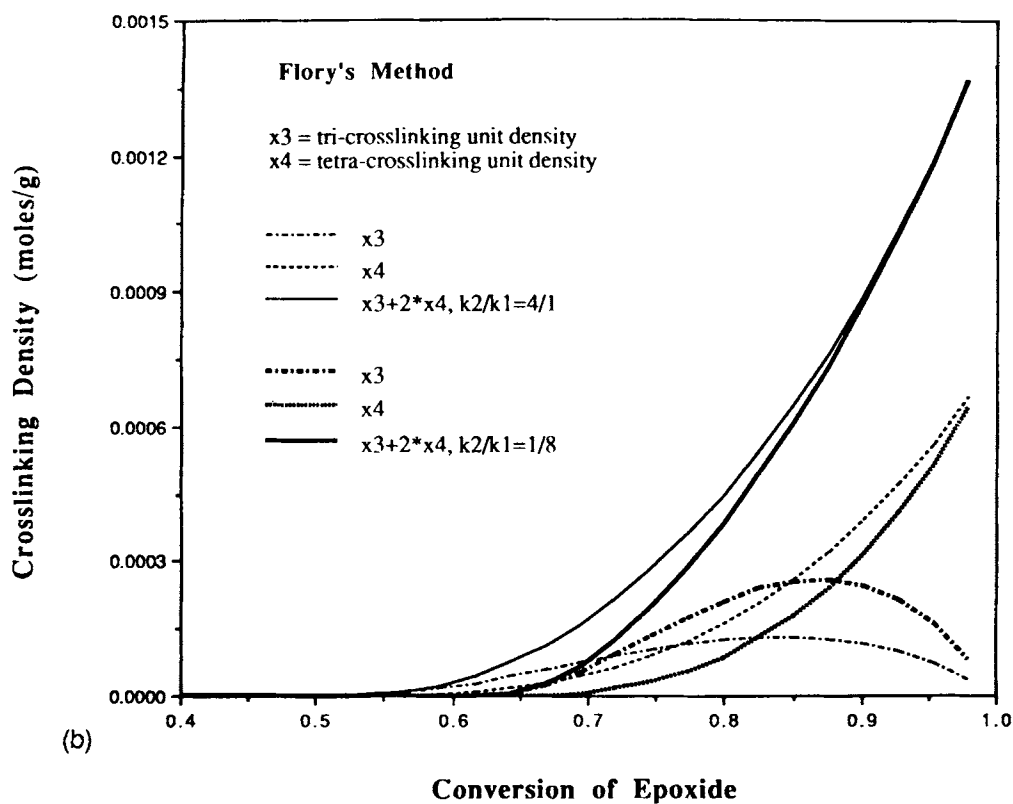
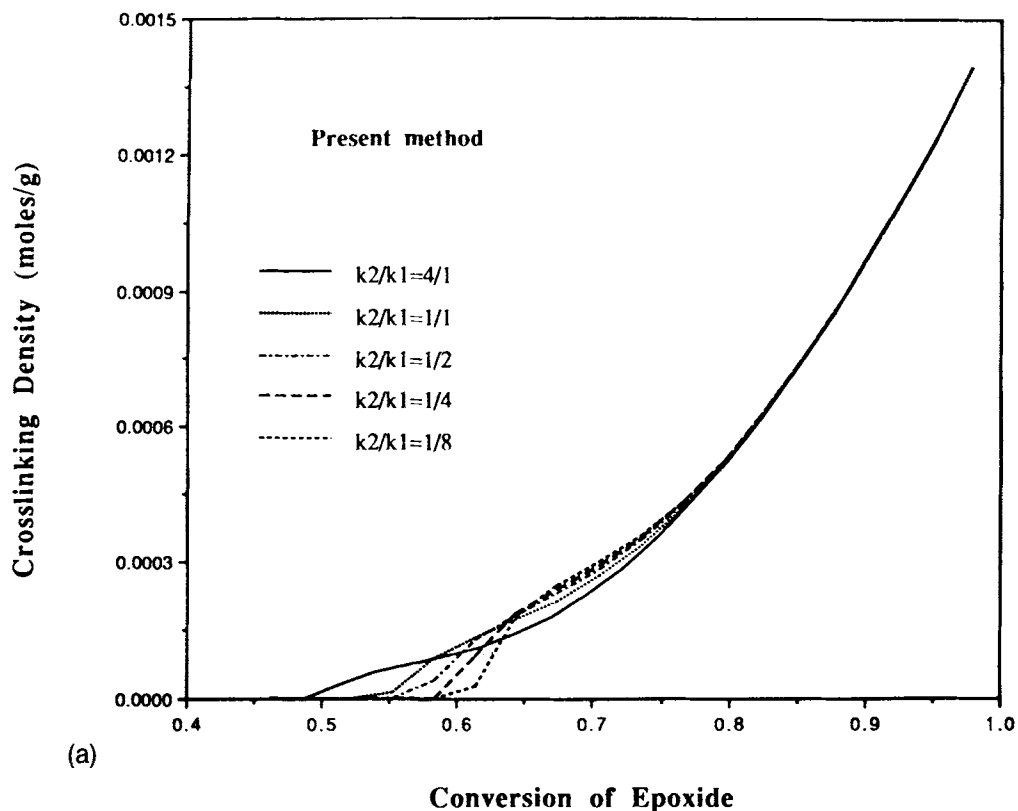
where A, B, B', and B'' represent the epoxy, primary amine, secondary amine, and tertiary amine groups, respectively. (HX) relates to catalyst in the amine-cured epoxy process, for example, hydroxyl groups. Let  $P_A$ ,  $P_B$ , and  $q_{B'}$  represent the corresponding fractional conversions of epoxy group, primary amine, and secondary amine groups, and let [OH] represent the concentration of hydroxyl group in the curing system. The kinetic equations can be written as follows<sup>24</sup>:

For rate of consumption of primary amine:

$$\frac{dP_B}{dt} = k_1 A_0 (1 - P_A) (1 - P_B) [OH] \quad (20)$$



**Figure 7** Effect of the kinetic ratio on  $\bar{M}_n$ ; obtained from a model calculation (including intramolecular reactions) with  $a = 2$ ,  $b = 2$ ,  $r_b = 0.5$ ,  $E_a = 174$  g/eq, and  $E_b = 157$  g/NH<sub>2</sub> [results calculated from eq. (26)].



**Figure 8** Effect of the ratio  $k_2/k_1$  on the crosslinking density using the branching method suggested by French.<sup>10,11</sup> Results calculated from eq. (9) [Fig. 8(a)], and by Flory's method [Fig. 8(b)], with  $a = 2$ ,  $b = 2$ ,  $r_b = 0.5$ ,  $E_a = 174$  g/eq, and  $E_b = 157$  g/NH<sub>2</sub> (see text).



For rate of yield of tertiary amine:

$$\frac{d(P_B q_{B'})}{dt} = k_2 A_0 (1 - P_A) P_B (1 - q_{B'}) [\text{OH}] \quad (21)$$

where  $A_0$  is the initial concentration of epoxide. Dividing eq. (21) by eq. (20),

$$\frac{d(P_B q_{B'})}{dP_B} = \frac{k_2 P_B - (P_B q_{B'})}{k_1 (1 - P_B)} \quad (22)$$

Integrating eq. (22) from 0 to  $P_B$  yields eqs. (23) and (24), corresponding to the two types of the ratio  $K (= k_2/k_1, \text{ where } k_2 \text{ is usually less than } k_1)$  (see Appendix B):

$$\frac{1 - P_B q_{B'}}{1 - P_B} = \frac{K - (1 - P_B)^{K-1}}{K - 1} \quad K \neq 1 \quad (23)$$

$$\frac{1 - P_B q_{B'}}{1 - P_B} = 1 - \ln(1 - P_B) \quad K = 1 \quad (24)$$

It should be noted that eqs. (23) and (24) apply to any order of reaction as long as the exponents for the amine concentrations in eqs. (20) and (21) are one. Eqs. (23) and (24) apply with and without catalyst. Eqs. (10)–(24) apply to non-stoichiometric and to stoichiometric systems.

## DISCUSSION

The ratio  $k_2/k_1$ , which is designated the kinetic ratio and also as  $K$ , may have consequences that are related to the gelation point, the average molecular weight and molecular weight distribution, and the structure of the network including the branching point concentration and the crosslinking density.

In a tetrafunctional diamine-cured difunctional epoxy system, the branching points arise from the reaction between secondary amine and epoxide. The kinetic ratio  $k_2/k_1$  influences the branching point concentration [see eq. (B23) in Appendix B for the definition], as shown in Figure 5. The fraction of branching points increases with increase of the kinetic ratio at the same conversion of epoxide, which implies that the kinetic ratio significantly affects the molecular structure.

The weight fraction of sol is

$$S = \omega_{A_a} S_a + \omega_{B_b(B'_b)} S_b \quad (25)$$

where  $\omega_{A_a}$  is the weight fraction of epoxy monomer

( $A_a$ ) residue in the system,  $\omega_{B_b(B'_b)}$  is the weight fraction of multiprimary amine [ $B_b(B'_b)$ ] monomer residue in the system, and

$$S_a = [A(S)]^a \quad \text{and} \quad S_b = [B(S)]^b [B'(S)]^b$$

The weight fraction of the gel  $G = 1 - S$ .

The gel point occurs as  $G$  approaches zero with decreasing conversion. The results from the model calculations also show that the gel point is affected by the ratio  $k_2/k_1$  (Fig. 6). The higher the ratio; the lower the conversion at the gel point. The gel point is 0.58 (based on the conversion of epoxide) in the system when the ratio  $k_2/k_1$  is  $\frac{1}{2}$ . (Note that the present definition of the rate constants is based on the secondary and primary amine groups; however, on the basis of the amino hydrogen atoms, the ratio  $k_2/k_1$  would be  $\frac{1}{4}$ .) When the ratio decreases to  $\frac{1}{8}$ , the gel point conversion increases to 0.62. It should be noted that this change of the gel point is only 8% even though the change of the kinetic ratio is about 75%. Therefore, using the gel point to study the kinetic ratio ( $k_2/k_1$ ) is insensitive. The higher the ratio, the higher the gel fraction and the lower the sol fraction at the same conversion (Fig. 6.)

The number-average molecular weight,  $\bar{M}_n$ , of the total curing system is

$$\bar{M}_n = \frac{N_a m_a + N_b m_b}{N_a + N_b - (a N_a P_a - N_{\text{in.r}})} \quad (26)$$

where  $N_a m_a + N_b m_b$  is the total weight of the system;  $m_a$  and  $m_b$  are the molecular weights of monomers  $A_a$  and  $B_b(B'_b)$ . The parameter  $a N_a P_a$  is the total number of epoxy groups reacted. The parameter  $N_{\text{in.r}}$  is the number of intramolecular reactions, which does not influence the number of molecules. Therefore,  $a N_a P_a - N_{\text{in.r}}$  is the number of intermolecular reactions (one intermolecular reaction reduces the number of molecules by one). Intramolecular reactions are considered to become important after the gelation point, especially in the gel. The crosslinking points arise from the intramolecular reactions in the gel. In Figure 4, one intramolecular reaction is seen to introduce on average two trifunctional crosslinking points; thus

$$N_{\text{in.r}} = \frac{1}{2} X_{\text{dc}} W \quad (27)$$

where  $W = a N_a E_a + b N_b E_b$ . Other symbols have already been defined. Figure 7 shows that  $\bar{M}_n$  versus conversion is only weakly influenced by the kinetic ratio.

The results of crosslinking density versus fractional conversion of epoxide from the present method and from Flory's method are presented in Figures 8(a) and 8(b), respectively. Figure 8(a) shows that the crosslinking density after the gel point is insensitive to the kinetic ratio  $k_2/k_1$  according to the definition that the system is composed to only tri-crosslinking sites. However, the results from Flory's method,<sup>3,6</sup> which distinguishes between tetra- and trifunctional crosslinking sites, show that each type is inversely influenced by  $k_2/k_1$  [Fig. 8(b)]. If a tetrafunctional crosslinking site is considered to be two trifunctional crosslinking sites,<sup>12</sup> the sum of the crosslinking sites is insensitive to the kinetic ratio at high conversions.

In summary, the average postgel properties of the curing system, number-average molecular weight ( $\bar{M}_n$ ) and crosslinking density ( $X_{dc}$ ), are not sensitive to the kinetic ratio of the competing reactions.

The physical properties of a thermosetting system can be divided into two groups: (1) "long-range"

relaxation properties, for example, yield stress and strain, and energy to break at high deformation; (2) "short-range" relaxation properties, such as the glass transition and dynamic modulus at low deformation. The long-range relaxation properties of curing systems are determined by the distribution of molecular weight, network mesh size concentrations and distributions, and the sol-gel fraction, because these parameters are related to the friction between molecular segments and the change in the shape of the network. However, the properties of short-range relaxations are mainly determined by average parameters, such as number-average molecular weight ( $\bar{M}_n$ ) of the total system and crosslinking density ( $X_{dc}$ ). According to Fox's theory,<sup>25</sup>  $T_g$  of a crosslinking system can be described by the following equation:

$$T_g = C_1 + \frac{C_2}{\bar{M}_n} + C_3 X_{dc} \quad (28)$$

Arrhenius Plot of Ratio  $k_2/k_1$  vs. Temperature  
(100~160°C by FTIR Analysis)

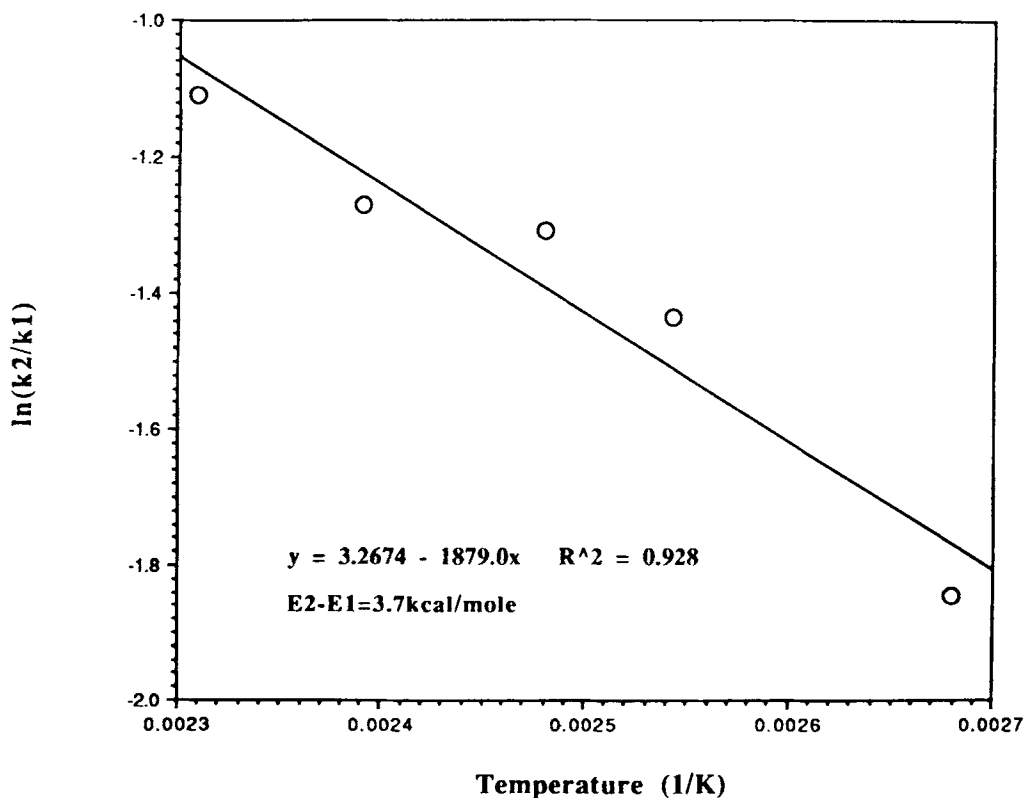


Figure 9 Infrared data<sup>24</sup> show that the kinetic ratio  $k_2/k_1$  changes with cure temperature.

where  $C_1$ ,  $C_2$ , and  $C_3$  are constants. Therefore, from the results of Figures 7 and 8(a), which show the insensitivity of  $\bar{M}_n$  and  $X_{dc}$  to the kinetic ratio,  $k_2/k_1$ , it is predicted that the relationship between  $T_g$  and epoxide conversion is one-to-one and not influenced by the kinetic ratio.

In tetrafunctional aromatic diamine-cured difunctional epoxy resin systems, such as the TMAB-cured DGEBA system, results from infrared experiments<sup>24</sup> show that the reactivities of primary amine and secondary amine are different. The ratio  $k_2/k_1$  for the system changes with temperature with a difference in activation energy of 3.7 kcal/mol according to the Arrhenius equation<sup>24</sup> (Fig. 9). However, the  $T_g$  versus epoxy conversion relationship is not affected by the cure temperature according to the experimental data of Wisanrakkit<sup>12</sup> (Fig. 10), which provides experimental support for the present theoretical results.

The above analysis considers only geometric factors of the developing network. However, it might be expected that the change in chemical structure that arises from the temperature dependence of  $k_2/k_1$  could affect  $T_g$ . Figure 5 shows that the kinetic

ratio significantly affects the tertiary amine concentration. Therefore, it is expected for the amine/epoxy system that there would be a difference of polarity of the system for a given conversion ( $P_A < 1$ ) with different cure paths, and that polarity would affect  $T_g$ . In this system, since experimental results show that there is a one-to-one relationship between  $T_g$  and conversion and the theoretical analysis reveals that  $\bar{M}_n$  and  $X_{dc}$  are insensitive to the kinetic ratio [Figs. 7 and 8(a)],  $T_g$  is mainly governed by the parameters  $\bar{M}_n$  and  $X_{dc}$  and is insensitive to chemical structure (or polarity) in the system. In most thermosetting systems, the polarity is proportional to the chemical conversion.

Another factor that could be important in affecting the  $T_g$  value is the physical aging that occurs when a sample is in the glassy state. The glassy state is usually considered to be far from the equilibrium state. A procedure to obtain the value of  $T_g$  that is unaffected by physical aging is to obtain  $T_g$  on cooling the specimen from an equilibrium state ( $T > T_g$ ) through the glass transition.

It should be noted that the theory presented here can be easily introduced into other thermosetting

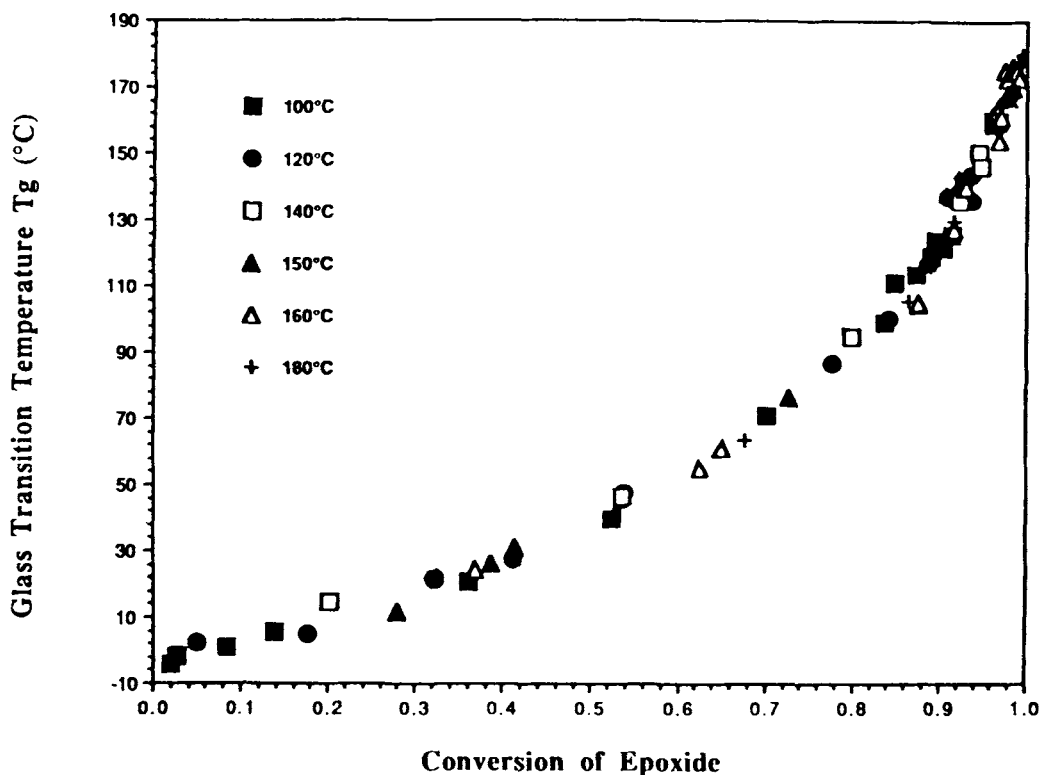


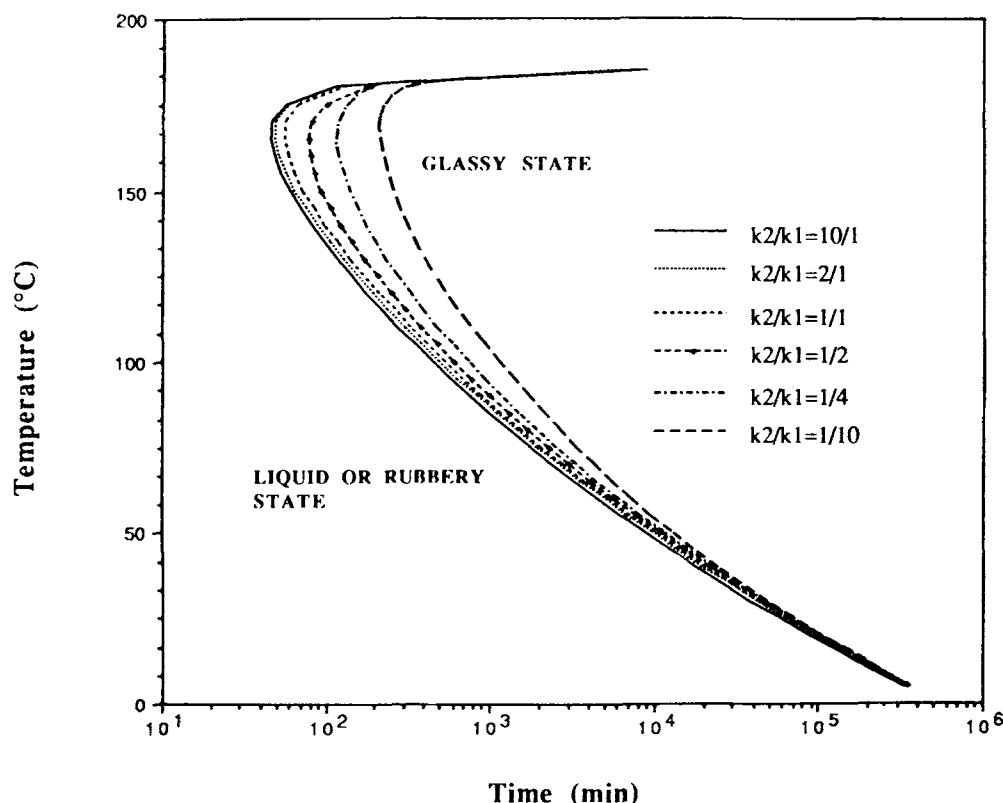
Figure 10  $T_g$  versus epoxy conversion.<sup>12</sup> The relationship is independent of the temperature of reaction and the ratio  $k_2/k_1$ .

polymer systems, and that the result of the insensitivity of the  $T_g$  versus conversion relationship on the ratio ( $k_2/k_1$ ) is considered to be common. The glass transition temperature is a good index for monitoring conversion in high- $T_g$  thermosetting systems during cure regardless of the ratio  $k_2/k_1$ . However, using the  $T_g$  to study the kinetics of curing systems needs caution because of the insensitivity of  $T_g$  to the ratio.

The results obtained here show that the short-range relaxation properties, which are dependent on the average parameters of the network, are insensitive to the kinetic ratio; however, this does not imply that there is no effect of the kinetic ratio on the long-range relaxation properties, e.g., the yield stress and strain, and the energy to break at high deformation. It is predicted that the ratio will affect the distribution of the network mesh size, the distribution of the length of dangling chains, etc., and therefore the long-range properties.

The transformation occurring in a thermosetting

polymerization may lead to two distinct transitions: (1) the change of sol to gel and (2) the change of rubber (or liquid) to glass. A current method for analyzing the phenomena is the time-temperature-transformation (TTT) isothermal cure diagram.<sup>12</sup> Generally, the time to vitrification is determined from the isothermal time-conversion curve [using eqs. (20) and (21)] at the conversion when  $T_g = T_{cure}$  [using the conversion- $T_g$  relationship (Fig. 10)]. Vitrification contours calculated for different  $k_2/k_1$  kinetic ratio are shown in Figure 11. At low temperatures, the vitrification point is relatively insensitive to the ratio. However, at higher temperatures, the ratio significantly influences the relative times to vitrify. When the ratio  $K$  decreases ( $K < 1$ ), which implies that the cure kinetics are controlled mainly by the reaction of secondary amine with epoxide, the time for the curing system to reach the vitrification point increases. When the ratio  $K$  increases, the opposite occurs. If the ratio  $K$  is larger than 10/1, which implies that the cure kinetics are



**Figure 11** Effect of the ratio  $k_2/k_1$  on the time-to-vitrify contour of the isothermal time-temperature-transformation (TTT) cure diagram.<sup>24</sup> Results calculated from the kinetic equations, [(B21) and (B22)] and the conversion versus  $T_g$  relationship, Figure 10, with  $r_b = 0.5$ ,  $k_1 = 3.5 \times 10^7 \exp(-7.6 \times 10^3/T)$ .<sup>12</sup>

virtually controlled by the first step, there is almost no dependence of the vitrification contour on the ratio.

## CONCLUSIONS

Theoretical analysis of the crosslinking of a tetrafunctional diamine/difunctional epoxy high- $T_g$  thermosetting system shows that the  $T_g$  versus conversion relationship is insensitive to the kinetic ratio,  $k_2/k_1$ , of the competing epoxy/secondary amine and epoxy/primary amine reaction rate constants. This implies that the  $T_g$  versus conversion relationship is independent of cure path. The reason is that the number-average molecular weight and the crosslinking density are insensitive to the ratio. Experimental data for  $T_g$  versus conversion support the theoretical results. Therefore  $T_g$  is an appropriate parameter for measuring the chemical conversion in high- $T_g$  thermosetting epoxy systems during cure regardless of the kinetic ratio of competing reactions. This is important in practice since  $T_g$  is easily measured, changes through a wide range, is directly relevant to material thermo-mechanical behavior, and has increased sensitivity at high conversion because of the nonlinear relationship between  $T_g$  and conversion. The underlying principles of the theory and the derived relationships between molecular and macroscopic parameters, and the consequences are considered to be general for highly crosslinked systems.

## APPENDIX A

### Number of Crosslinking Units Formed Per Intramolecular Reaction in the Gel

In practice, adhesives, coatings, and sealants are commonly made by reaction of low-molecular-weight crosslinking agents with polyfunctional prepolymers that generally have a wide distribution of functionality and molecular weight, e.g., polyfunctional epoxy.

For an epoxy prepolymer molecule,  $A_{a_i}$ , which has  $a_i$  arms each ending with a functional epoxy group A, the number of the prepolymer molecules,  $A_{a_i}$ , in a curing system, is  $N_{a_i}$ . Therefore, the polyfunctional epoxy, prior to reaction, is a mixture of  $A_1$ ,  $A_2$ ,  $A_3$ ,  $\dots$ ,  $A_{a_i}$ ,  $\dots$  molecules ( $a_i = 1, 2, 3, \dots$ ). For this epoxy cured with tetrafunctional diamine, according to Flory's method, the crosslinking density during cure should be

$$X_{dc} = \frac{1}{W} \left( \sum_{a_i} N_{a_i} \sum_{j=3}^{a_i} P_{j(A)}^{gel} + N_b \sum_{j=3}^{2b} P_{j(B)}^{gel} \right) \quad (A1)$$

where  $P_{j(A)}^{gel}$  = the probability of  $j$  arms of epoxy groups A in a prepolymer molecule residue  $A_{a_i}$  leading to an infinite structure,  $P_{j(B)}^{gel}$  = the probability of  $j$  hydrogens in an amine monomer residue leading to an infinite structure,  $W$  = bulk mass,  $N_b$  = moles of amine monomer, and  $b$  = number of primary amine functional groups in one amine monomer. It is noteworthy that using eq. (A1) to treat practical systems is limited since the distribution of  $N_{a_i}$  versus  $a_i$  is unmeasurable for most polyfunctional prepolymers.

However, the theoretical treatment of crosslinking presented herein deals rather easily with the problem of not knowing the distribution of the functionality in a given prepolymer. Considering that the network structure consists of only trifunctional crosslinking units (which is usually true for most thermosetting systems), the number of crosslinking units in the system during cure,  $X_{dc}$  should be the number of crosslinking units at 100% conversion in the gel fraction,  $GX_{dc}$ , minus the number of crosslinking units that do not form because of incomplete reaction of epoxide in the gel<sup>10,11,13</sup>

$$X_{dc} = \frac{\sum N_{a_i}(a_i - 2) + N_b(2b - 2)}{aN_a E_a + 2bN_b E_b} \times (1 - S) - 2 \frac{(1 - P_A) - S_a(1 - P_{As})}{E_a + 2r_b E_b} \quad (A2)$$

since

$$N_a = \sum_{a_i} N_{a_i} \quad \bar{a}N_a = \sum_{a_i} N_{a_i} a_i = \frac{W_a}{E_a}$$

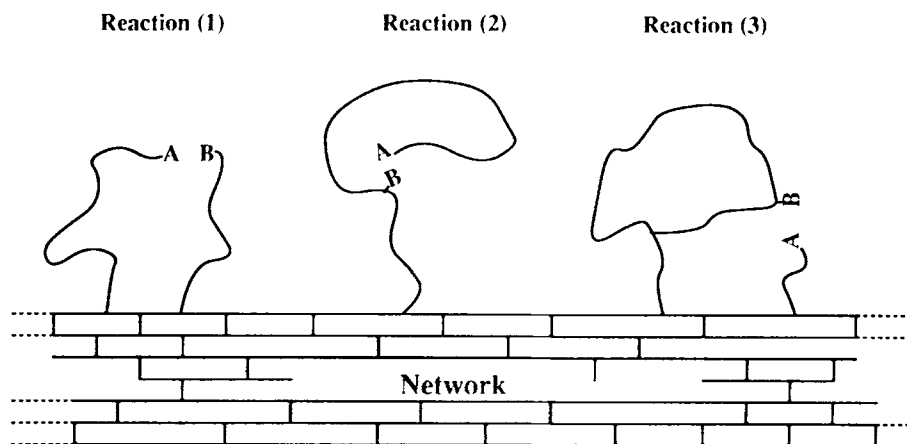
and

$$\bar{a} = \frac{W_a}{E_a N_a} = \frac{\bar{M}_n}{E_a}$$

Eq. (A2) is simplified to

$$X_{dc} = \frac{N_a(\bar{a} - 2) + N_b(2b - 2)}{W_a + W_b} \times (1 - S) - 2 \frac{(1 - P_A) - S_a(1 - P_{As})}{E_a + 2r_b E_b} \quad (A3)$$

where  $\bar{a}$  is the number average value of the func-



**Figure 12** Intramolecular reactions between reactive groups of dangling chains in a network structure (see Appendix A).

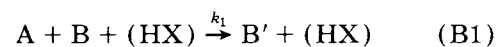
tionality of the epoxy prepolymer. The parameters  $P_A$ ,  $P_{A_s}$ , and  $S_a$  are experimentally measurable.  $E_a$  and  $\bar{M}_n$  are given parameters for commercial products.

In the developing network structure, intramolecular reactions become important during cure. Intramolecular reactions may occur between reactive groups of different dangling chains and also between reactive groups of the same dangling chain, the latter being difficult to handle by other theories. Figure 12 shows that reaction (1), which occurs between two independent dangling chains in the gel, gives two crosslinking units; that reaction (2), which occurs between reactive groups in the same dangling chain in the gel, gives a mono-cyclic structure without having created crosslinking units; and that reaction (3), which occurs in the gel, gives four crosslinking units. The average number of crosslinking units formed due to one intramolecular reaction in the gel is considered to be two, which appears in front of the second term of eq. (A3) and in eq. (9) of the main text.

## APPENDIX B

### Effect of Kinetic Ratio on Number of Branching Points

Let  $A$ ,  $B$ ,  $B'$ , and  $B''$  represent epoxy, primary amine, secondary amine, and tertiary amine groups, respectively, and  $(HX)$  relates to hydroxyl; then, the hydroxyl-catalyzed epoxy/amine reactions can be represented as follows:



The rate of consumption of primary amine

$$\frac{dP_B}{dt} = k_1[A]_0(1 - P_A)(1 - P_B)[OH] \quad (B3)$$

The rate of yield of tertiary amine

$$\begin{aligned} \frac{d(P_B q_{B'})}{dt} \\ = k_2[A]_0(1 - P_A)P_B(1 - q_{B'})[OH] \end{aligned} \quad (B4)$$

where  $[OH]$  is the concentration of hydroxyl in the curing system;  $P_A$ ,  $P_B$ , and  $q_{B'}$  represent the fractional conversions of epoxide, primary amine, and secondary amine, respectively, and are defined as follows:

$$P_A = \frac{[A]_0 - [A]}{[A]_0} \quad (B5)$$

$$P_B = \frac{[B]_0 - [B]}{[B]_0} \quad (B6)$$

$$q_{B'} = \frac{[B]_0 - [B] - [B']}{[B]_0 - [B]} = \frac{[B'']}{[B]_0 - [B]} \quad (B7)$$

$[A]_0$  and  $[B]_0$  are the initial concentrations of epoxide and primary amine groups, respectively;  $[B]$ ,  $[B']$ , and  $[B'']$  are the concentrations of primary

amine, secondary amine, and tertiary amine groups during cure, respectively.

Dividing eq. (B4) by (B3) yields

$$\frac{d(P_B q_{B'})}{dP_B} = \frac{k_2 P_B - (P_B q_{B'})}{k_1 (1 - P_B)} \quad (B8)$$

Let

$$y = \frac{1 - P_B q_{B'}}{1 - P_B} \quad (B9)$$

$$x = P_B \quad (B10)$$

Rearranging eqs. (B9) and (B10):

$$P_B q_{B'} = 1 - y(1 - x) \quad (B11)$$

$$P_B = x \quad (B12)$$

Substituting  $P_B q_{B'}$  and  $P_B$  of eqs. (B11) and (B12) into eq. (B8), the nonlinear differential eq. (B8) becomes

$$-(1 - x) \frac{dy}{dx} + y = K(y - 1) \quad (B13)$$

where  $K = k_2/k_1$ . Equation (B13) depends on the value of the ratio  $K$ , i.e.,

$$dy = \frac{dx}{1 - x} \quad K = 1 \quad (B14)$$

and

$$\frac{dy}{(K - 1)y - 1} = - \frac{dx}{1 - x} \quad K \neq 1 \quad (B15)$$

Integrating eqs. (B14) and (B15) from 0 to  $x$  yields

$$y = [1 - \ln(1 - x)] \quad K = 1 \quad (B16)$$

and

$$y = \frac{K - (1 - x)^{K-1}}{K - 1} \quad K \neq 1 \quad (B17)$$

Substituting  $y$  and  $x$  of eqs. (B9) and (B10) into eqs. (B16) and (B17) gives

$$\frac{1 - P_B q_{B'}}{1 - P_B} = 1 - \ln(1 - P_B) \quad K = 1 \quad (B18)$$

and

$$\frac{1 - P_B q_{B'}}{1 - P_B} = \frac{K - (1 - P_B)^{K-1}}{K - 1} \quad K \neq 1 \quad (B19)$$

Let  $r_b = [\text{initial primary amino groups}]/[\text{initial epoxide groups}]$ . It follows for the reactions in the amine-cured epoxy system that

$$P_A = r_b P_B + r_b P_B q_{B'} \quad (B20)$$

Substituting  $P_B q_{B'}$  of eq. (B20) into eqs. (B18) and (B20) yields

$$\begin{aligned} \frac{1 - [(P_A - r_b P_B)/r_b]}{1 - P_B} \\ = \frac{K}{K - 1} - \frac{1}{K - 1} (1 - P_B)^{K-1} \quad K \neq 1 \quad (B21) \end{aligned}$$

and

$$\begin{aligned} \frac{1 - [(P_A - r_b P_B)/r_b]}{1 - P_B} \\ = [1 - \ln(1 - P_B)] \quad K = 1 \quad (B22) \end{aligned}$$

The parameter

$$\begin{aligned} P_B q_{B'} &= \frac{[B]_0 - [B]}{[B]_0} \frac{[B]_0 - [B] - [B']}{[B]_0 - [B]} \\ &= \frac{[B'']}{[B]_0} \quad (B23) \end{aligned}$$

which is the ratio of the tertiary amine concentration to the initial concentration of primary amine. Therefore,  $P_B q_{B'}$  is defined as the fraction of branch points. The effect of the kinetic ratio on the number of branching points is calculated from eqs. (B18), (B19), and (B20) with various values of  $K$  (i.e.,  $K = 1, \frac{1}{2}, \frac{1}{3}, \dots$ ).

### SYMBOLS

A	epoxy group.
$A_a$	epoxy monomer residue with $a$ arms of reactive groups.
$A_f$	monomer with $f$ arms each with functional groups A.

$A(S)$	probability of functional group A only in sol.	$N_a$	moles of epoxy monomer each with $a$ epoxy groups.
$A^*(S)$	probability that any functional group A reacts with B in sol.	$N_b$	moles of multiprimary amine each with $b$ primary amine groups.
$A'^*(S)$	probability that any functional group A reacts with B' in sol.	$N_f$	moles of $f$ -functional monomer.
$[A]_0$	initial concentration of epoxide group.	$N_{in,r}$	number of intramolecular reactions.
$a$	number of functionalities in one epoxy monomer residue.	$[OH]$	concentration of hydroxyl in curing system.
B	primary amine group.	$P_A$	fractional conversion of epoxy groups.
B'	secondary amine group which is formed by the reaction between primary amine and epoxide.	$P_B$	fractional conversion of primary amine groups.
B''	tertiary amine group which is formed by the reaction between secondary amine and epoxide.	$P_{As}, P_{Ag}$	fractional epoxide conversion in sol and gel, respectively.
B(S)	probability of functional group B only in sol.	$P_j^{(gel)}$	probability of $f$ arms (each with functional group A) in one $A_f$ monomer residue leading to an infinite structure.
B'(S)	probability of functional group B' only in sol.	$q_{B'}$	fractional conversion of secondary amine groups.
B*(S)	probability that any functional group B reacts with A in sol.	$r_b$	$bN_b/aN_a$ .
B'*(S)	probability that any functional group B' reacts with A in sol.	$S$	sol weight fraction of total system.
[B], [B'], [B'']	concentrations of primary amine, secondary amine, and tertiary amine groups during cure, respectively.	$S + G$	1.
$[B]_0$	initial concentration of primary amine group.	$S_a$	sol weight fraction of epoxy monomer residue $A_a$ .
$B_b(B'_b)$	amine monomer residue originally with $b$ arms of primary amine groups; each group B has the possibility to generate a secondary amine group B' when reacting with epoxide.	$S_b$	sol weight fraction of amine monomer residue $B_b(B'_b)$ .
$b$	number of primary amine functional groups in one amine monomer residue.	$T_g$	glass transition temperature of curing system.
$E_a, E_b$	equivalent weight of epoxy and multiprimary amine monomers.	$W$	bulk weight.
$G$	gel weight fraction of total system.	$W$	$W_a + W_b$ .
$G_a$	gel weight fraction of monomer residue $A_a$ .	$W_a$	initial weight of epoxy monomer in the system.
(HX)	catalyst in the amine-cured epoxy system.	$W_b$	initial weight of amine monomer in the system.
$K$	$(k_2/k_1)$ .	$\omega_{A_a}$	weight fraction of the epoxy monomer residue in the system.
$k_1$	kinetic rate constant of epoxide reaction with primary amine group.	$\omega_{B_b(B'_b)}$	weight fraction of amine monomer residue in the system.
$k_2$	kinetic rate constant of epoxide reaction with secondary amine.	$X_{dc}$	network crosslinking density in mol/g, for incompletely cured system.
$\bar{M}_n$	number-average molecular weight of the total system during cure.	$X_{df}$	network crosslinking density, in mol/g, for fully cured system.
$m_a$	molecular weight of $A_a$ .		
$m_b$	molecular weight of $B_b(B'_b)$ .		

Financial support has been provided by Hercules Inc.

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Received September 9, 1991

Accepted October 30, 1991