Modelling of condensation reactions in an amine-cured epoxy system with groups of unequal reactivity*

Anoop Agrawal
Donnelly Corp., 414 E. 40th St., Holland, MI 49423, USA

and Donald R. Uhlmann
Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA

(*Received 24 May 1989; accepted 19 January 1990*)

A simple model is presented to simulate the process of network formation involving bifunctional epoxies and amines. This model takes account of different reaction rates of the primary and the secondary amines. At the start of the reaction, the amine could either be a mixture of primary and secondary amines or only primary amine, but as a hydrogen of a primary amine is consumed during the reaction, the other hydrogen becomes secondary. The principal effects of the higher reactivity of the primary amines are: (a) increased extents of reaction are required to reach the gel point, with this extent being dependent on the initial stoichiometry; and (b) increased number of less branched species are generated during the reaction.

(Keywords: epoxy; amine curing agent; polycondensation; gelation)

INTRODUCTION

The basic requirements for the formation of three-dimensional polymer networks were suggested by Carothers, Flory and Stockmayer[1–7]. Their models rest on two basic assumptions: (1) all the functional groups undergoing reaction have equal reactivity; and (2) all the reactions are intermolecular. A number of other methods have also been proposed to analyse the process of network formation. These include percolation theory[8,9], stochastic branching processes[10–17] and treatments including the recursive nature of chain branching[18,19]. A few of these methods have been applied for polycondensation reactions with groups having unequal reactivity[16,17,19–22]; and some of them have been used to describe epoxy/primary amine reactions[15,16,20].

The approach described here is particularly aimed at amine-cured epoxy resins, where the amine may have both primary and secondary groups and the reactivities of primary and secondary amines may differ significantly. As the primary amines react (when one of the primary hydrogens is consumed), secondary amines are generated. Although the model proposed here is for epoxy/amine reactions, it can be adopted for any general polycondensation reaction. Compared with the other methods, the approach does not require mathematical rigour and abstractness to evaluate the gel point or to obtain insight into the species present at different stages of the reaction. In addition, the method can easily be adapted to systems where there are more than two levels of reactivity.

Just as with the Flory–Stockmayer (FS) theory, the present model can be criticized on the grounds that it does not take into account the occurrence of closed rings when large molecular structures are formed during the course of the reaction. This prohibition against closed rings is probably not serious in the early stages of the reaction, but may become important in later stages, close to gelation. This drawback also persists when the problem is analysed by stochastic branching (or percolation on a Bethe lattice)[9], where it results in a growth of the surface density of the lattice without limit. The problem of overcrowding at the surface can be overcome by assuming the lattice grows in an infinite-dimensional space. However, the problem of the intramolecular reactions may be addressed by a three-dimensional percolation model only by incorrectly assuming that each of the crosslinking monomers (amine molecules in this case) is located at a lattice site that is stagnant throughout the reaction.

The method suggested here embraces the same principles as in FS theory, but with the removal of the equal reactivity constraint, and thus retains the simplicity and the constraints of a mean-field approach.

MODEL

This model considers the reaction between a bifunctional epoxy (species B) and a multifunctional amine (species A). Only intermolecular reactions are permitted between A and B. When the reaction between epoxy/amine nears completion, there is the possibility of condensation of –OH groups generated during the normal epoxide/amine reaction. However, these reactions are not important and may only occur to a small extent after gelation[15,17,23–26]. Further, the discussion here should be limited up to the point of gelation, as steric factors have not been considered.

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* Based on a thesis submitted by A. Agrawal in partial fulfilment of the requirements for the Sc.D. degree, Massachusetts Institute of Technology

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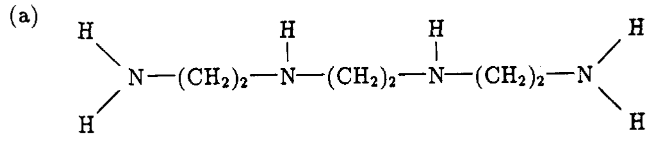
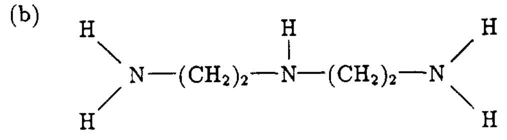
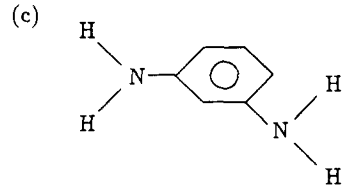


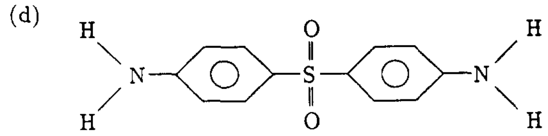
Triethylenetetramine



Diethylenetriamine



m - Phenylenediamine



p - p′ - diaminodiphenylsulfone

Figure 1 Typical curing agents used for epoxides: (a) and (b) represent those curing agents that contain a mixture of primary and secondary amines; (c) and (d) are tetrafunctional curing agents with only primary amines

A typical amine, which consists of both secondary and primary amines, is triethylenetetramine (TETA). This is shown schematically in *Figure 1*. TETA has two primary amine groups and two secondary amine groups. In amine curing agents the reactivities of the primary and secondary amines can differ by a factor of 2 to 5, and even by as much as 60, depending on the system[27–30]. As one of the hydrogens of the primary amine reacts, the other hydrogen becomes secondary. Hence, in these reactions, not only are the reactivities of the groups initially different, but also, as the reaction proceeds, the reactivities of the groups change.

Another commonly used curing agent that has a mixture of primary and secondary hydrogens is diethylenetriamine (*Figure 1*). Also shown in *Figure 1* are two other amines that are tetrafunctional. These hardeners have only primary amines, but no secondary amines. However, as a hydrogen of a primary amine reacts, the other hydrogen linked to the same nitrogen becomes secondary.

A model will be presented where a bifunctional epoxy reacts with an amine containing both primary and secondary amines (the secondary amines present at the start of the reaction will be labelled as original in the text).' Later it will be simplified to show how it is applicable to systems containing only primary amines. In this model, the reactivity of the secondary groups present initially and those generated due to the reaction of the primary amines is assumed to be the same.

First, a relationship is developed to describe the numbers of primary groups (x) and secondary groups (y) at any stage of the reaction. This relationship will clearly depend on the reactivity ratios of the primary and the secondary groups. In the second step, the extent of reaction needed for gelation will be determined. From this value, the fraction of primary and secondary groups consumed at the gel point will be estimated.

Consider an epoxy/amine reaction where the initial conditions are:

$$\text{number of primary nitrogens} = A_0$$

$$\text{number of secondary nitrogens} = B_0$$

$$\text{number of tertiary nitrogens} = C_0 = 0$$

$$\text{number of epoxy groups} = E_0$$

The initial stoichiometry (r_0)* for TETA with a bifunctional epoxy is then given by:

$$r_0 = (2A_0 + B_0)/E_0 \qquad (1)$$

The initial number of moles of TETA would be $A_0/2$ or $B_0/2$ and for the epoxy $E_0/2$. Similarly for a tetrafunctional curing agent containing two primary amines, the initial number of moles of amine is $A_0/2$; and since $B_0 = 0$, the initial stoichiometry r_0 is $2A_0/E_0$.

The following are defined at any stage of the reaction:

$$\text{number of primary nitrogens reacted} = x$$

$$\text{number of primary nitrogens remaining} = A = A_0 - x$$

$$\text{number of secondary nitrogens reacted} = y$$

$$\text{number of secondary nitrogens remaining} = B = B_0 + x - y$$

$$\text{number of epoxy groups remaining} = E$$

At all times, $A + B + C$ is constant, where C is the concentration of the tertiary groups during the reaction. The kinetic equations for the reaction can be written as

$$\mathrm{d}x/\mathrm{d}t = -2K_1AE \qquad (2)$$

$$\mathrm{d}y/\mathrm{d}t = -K_2BE \qquad (3)$$

Here K_1 and K_2 are the rate constants for reaction of the primary and secondary amino hydrogens with the epoxy. The factor of 2 arises in equation (2) because there are two hydrogens for each primary nitrogen. Dividing equation (2) by equation (3) and substituting $K = 2K_1/K_2$, one obtains:

$$\frac{\mathrm{d}x}{\mathrm{d}y} = \frac{2K_1A}{K_2B} = \frac{K(A_0 - x)}{B_0 + x - y} \qquad (4)$$

or

$$\frac{\mathrm{d}y}{\mathrm{d}x} + \frac{y}{K(A_0 - x)} = \frac{B_0 + x}{K(A_0 - x)} \qquad (5)$$

The solution to this equation yields a relationship between x and y. For $K = 1$:

$$y = (B_0 + x) + (A_0 - x)\ln(A_0 - x) - \frac{(A_0 - x)(B_0 + A_0 \ln A_0)}{A_0} \qquad (6)$$

For $K \neq 1$:

$$y = (B_0 + x) + \frac{K(A_0 - x)}{K - 1} - \frac{KA_0 + B_0}{(K - 1)}\left(\frac{A_0 - x}{A_0}\right)^{1/K} \qquad (7)$$

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* The initial stoichiometry is defined as the ratio of the number of reactive groups on the amine to the number of reactive groups on the epoxy for the initial mixture

Before the condition for gelation is applied, the probabilities for the reaction of the various groups will be defined at any stage of reaction. We denote by y_p the number of nitrogens that were primary at the start of the reaction and now have reacted to yield tertiary nitrogens. Then:

probability that a primary hydrogen has reacted $= q_1 = x/A_0$

probability that a secondary hydrogen (formed from a primary nitrogen) has reacted $= q'_1 = y_p/x$

probability that an original secondary hydrogen has reacted $= q_2 = (y - y_p)/B_0$

probability that both the primary hydrogen and the secondary formed due to this reaction have reacted (converted to a tertiary) $= q_3 = q'_1 q_1 = y_p/A_0$

probability that an epoxy group has reacted $= p = E/E_0 = (x + y)/E_0$

By definition, gelation occurs[6] when one junction (amine molecule in this case) being reached leads to another junction with certainty. As shown in *Figure 2*, there are three distinct ways to achieve this for TETA, and two for tetrafunctional primary amines. These differences depend on the reactive site of the junction that is reached, since the other sites through which the crosslinking occurs will have in general different reactivities. For TETA, the three possibilities are as follows:

(1) When the junction is reached by a primary hydrogen (*Figure 2a*), then three secondary and two primary sites are available to lead to another junction.

(2) When the junction is reached by a secondary site that was formed when one of the primaries had reacted, then for reaching another junction, two primary and two secondary groups are available (*Figure 2b*). Note that crosslinking can also occur through the other end of the epoxy molecule that had reacted with the primary group. This epoxy end has been shown as unreacted because by the definition of gel point (given above) this is one of the possible but not a definite route to lead to another junction. This possibility specifically arises because, as a primary hydrogen reacts, the reactivity of the other hydrogen attached to the same nitrogen changes.

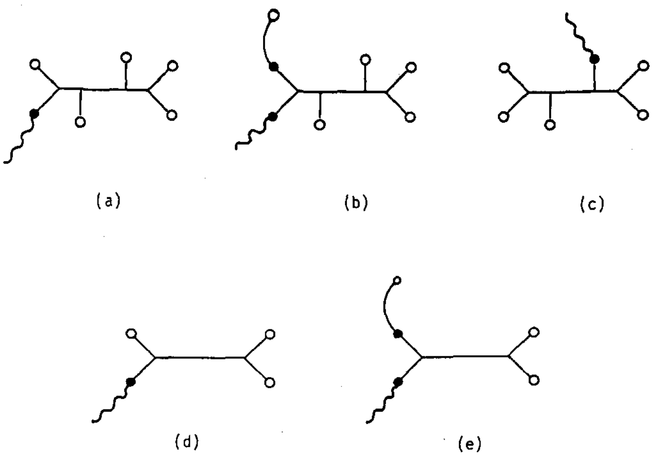

Figure 2 Three distinct ways (a), (b) and (c) TETA and two ways (d) and (e) a tetrafunctional junction would appear when reached by a chemically bonded chain. Solid ends indicate that they are reacted

(3) When the junction is reached by a secondary site (*Figure 2c*), then one secondary and four primary groups are available to form a link with another junction.

For a tetrafunctional primary amine curing agent, only the first two possibilities exist as shown in *Figures 2d* and *2e*.

For TETA, the probabilities of its being connected with another TETA molecule via each of these routes are j_1, j_2 and j_3:

$$j_1 = (q'_1 + 2q_2 + q_1 + q_3)p \tag{8}$$

$$j_2 = (1 + q_1 + q_3 + 2q_2)p \tag{9}$$

$$j_3 = (q_2 + 2q_1 + 2q_3)p \tag{10}$$

All these probabilities have been multiplied by p since the other end of the epoxy has to react to form the link between the two junctions. In equation (9), the term of 1 arises because the link by which the junction is reached is secondary; and as shown in *Figure 2b*, this was formed by the previous reaction of a primary hydrogen. Combining j_1, j_2 and j_3 with their respective frequencies of occurrence will give α, the overall probability of connection to another TETA molecule:

$$\alpha = j_1 \frac{x}{x+y} + j_2 \frac{y_p}{x+y} + j_3 \frac{y-y_p}{x+y} \tag{11}$$

Note that the sum of the weights for j_1, j_2 and j_3 is 1. Similarly for the tetrafunctional primary amine curing agent discussed above:

$$\alpha = j_1 \frac{x}{x+y_p} + j_2 \frac{y_p}{x+y_p} \tag{12}$$

where j_1 and j_2 for this case are defined as:

$$j_1 = (q'_1 + q_1 + q_3)p \tag{13}$$

$$j_2 = (1 + q_1 + q_3)p \tag{14}$$

Gelation is defined by the condition $\alpha = 1$. The values of x and y at gelation can be obtained by simultaneously solving equation (6) with equation (11) or equation (12) or equation (7) with equation (11) or equation (12) (according to the value of K and the nature of the curing agent) and then setting $\alpha = 1$.

As these equations were too cumbersome to handle analytically, they were solved by writing a simple program on a personal computer. The reaction was simulated by increasing in small increments the extent of the epoxide or the amine consumed. For example, for a bifunctional epoxy and TETA, a small percentage of the initially present primary hydrogens is assumed to react (x). Then from equation (6) or equation (7) (depending on K) the value of y is evaluated. Then all the probabilities listed above are calculated. These are then substituted in equations (8) through (10) to obtain j_1, j_2 *and* j_3, which are in turn substituted into equation (11) to obtain the value of α. To evaluate y_p, a parallel calculation is done at each x assuming that $B_0 = 0$ (i.e. by substituting $B_0 = 0$ in equation (6) or equation (7)). The value of y obtained in this way is y_p.

The results of these calculations at the gel point for TETA/epoxy and a tetrafunctional primary amine/epoxy as a function of K and the initial stoichiometry are shown in *Table 1*. The results show that the effect of the unequal

Table 1 Gel point (fraction of epoxide reacted) as a function of initial stoichiometry and reactivity ratio. The figures in round parentheses have been calculated from Flory's equal reactivity results, and the ones in square brackets are from Kakurai *et al.*[20]. Dusek *et al.*'s[16] results derived by the stochastic branching model are identical to those of Kakurai *et al.*

(a) DGEBA/TETA system

Stoichiometry	Epoxide reacted (%) for $K =$		
$(A/E)^a$	1	2	5
0.5	0.316 (0.316)	0.322	b
1	0.449 (0.447)	0.458	0.474
2	0.633 (0.632)	0.653	0.67

(b) DGEBA/tetrafunctional (primary) amines

Stoichiometry	Epoxide reacted (%) for $K =$		
$(A/E)^a$	1	2	5
0.5	0.411 (0.408)	0.416	b
1	0.578 (0.577) [0.58]	0.597 –	0.615 [0.61]
2	0.815 (0.817)	0.859	0.908

[a] A/E represents the ratio of initial amine hydrogens to the initial epoxide groups

[b] Even after all the primary amine was exhausted, the gel point was not reached

reactivity is to increase the extent of the reaction at the gel point. The differences among the extents of reaction at the gel point over the range of K values considered is, however, small. The difference is seen to increase when the initial mix is richer in initial amine content. If K is not known for a system, then this could be extracted from the shift in gel point, but the extent of reaction has to be monitored with good precision.

Table 1 also compares the predictions of the present model with those of the Flory–Stockmayer relation when $K = 1$ and with the results of Kakurai *et al.*[20] and Dusek *et al.*[16] for $K = 1$ and $K = 5$. It is seen that the predictions of the present model are in close agreement with those of Kakurai *et al.* and Dusek *et al.* *Figure 3* (for the TETA/epoxy system) shows the fraction of the primary amine reacted as a function of the extent of reaction for different values of K and the initial stoichiometry. Although the extent of the consumption of epoxy due to the reactivity differences is small at the gel point, there are large differences in the extent to which the primary amine is consumed. This difference shows that the network structure at the gel point will be strongly influenced by the differences in the reactivity of primary and secondary amines.

The usefulness of the present treatment can also be extended to analyse the distributions of species present at each stage of reaction. As an example, if the value of K is large, then in the initial stages only the primary amines will react (*Figure 3*); and this will lead to the formation of long linear chains before branching occurs.

In describing the distributions of species, note that any junction (TETA molecule) in the reaction mix can consist of primary nitrogen(s) (P), secondary nitrogen(s) (S) or tertiary nitrogen(s) (T). For example, in case of TETA the first or the fourth nitrogen could be P, S or T; whereas for the second or the third nitrogen the possibilities are S and T. The designation of a species N1P1S indicates that one primary and one secondary have reacted. All the combinations of the possible species are shown in *Figure 4*. An abundance of the species N2P0S in a reaction would indicate that there is a preference towards the formation of linear chains. N0P0S is unreacted TETA. *Figure 5* lists these species for a tetrafunctional curing agent. For TETA, the fraction of each of these can be calculated after defining the following probabilities:

first or last nitrogen is primary $= FPN = (A_0 - x)/A_0$

first or last nitrogen is secondary $= FSN = (x - y_p)/A_0$

first or last nitrogen is tertiary $= FTN = y_p/A_0$

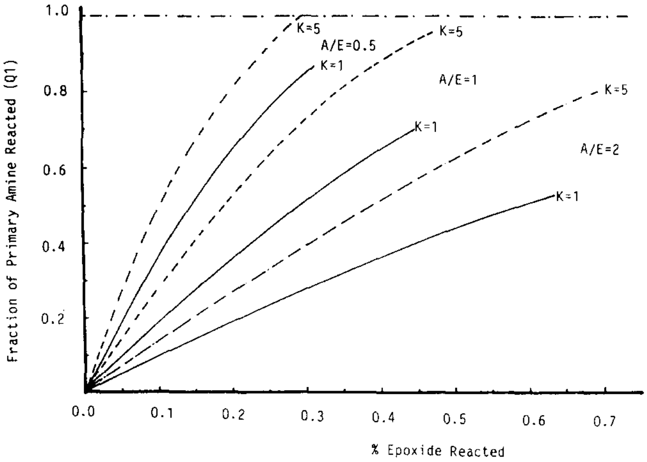

Figure 3 Fraction of primary amine reacted with increasing consumption of epoxide. These results are plotted either up to the gel point or to the point at which the primary amines are exhausted

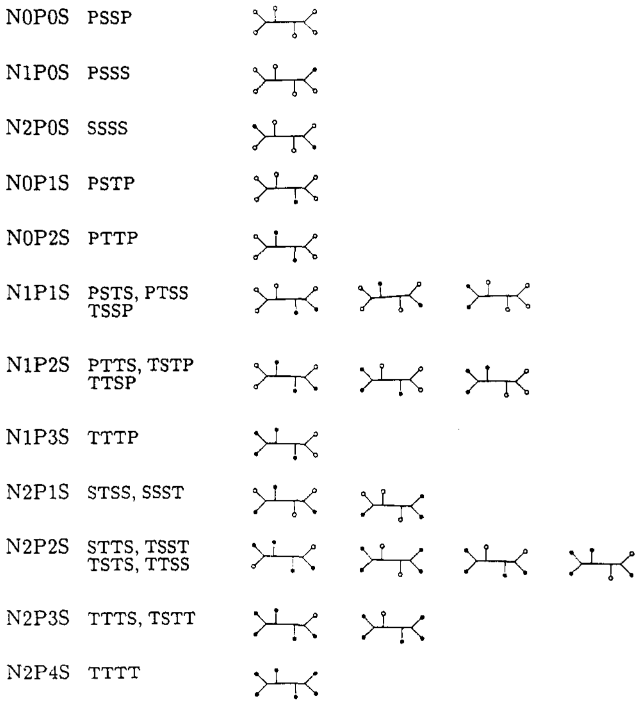

Figure 4 Different types of species generated for TETA. Species N0P1S indicates zero primary and one secondary have reacted. This can also be written as PSTP, i.e. the first nitrogen is primary, the second is secondary, the third is tertiary and the last one is primary. The schematics show TETA molecules. A solid end indicates that it is reacted

second or third nitrogen is secondary $= SNS = (B_0 + yB_0 - y)/B_0$

second or third nitrogen is tertiary $= SNT = (y - y_p)/B_0$

Once these probabilities are known, the sets of equations in *Tables 2* and *3* (which correspond to *Figures 4* and *5* respectively) are used to calculate the probabilities of these species. At any epoxide conversion, the average number of hydrogens in an amine molecule that have reacted (ρ) is given by:

$$\rho = \sum_i N_i P_i \tag{15}$$

The summation is carried over all the species i. N_i is the number of hydrogens reacted in the ith species and P_i is the probability of finding it at a particular conversion as calculated in *Tables 2* and *3*. Calculation of ρ provides a quick check on these calculations since it can also be computed by dividing the extent of reaction $(x + y)$ by the initial number of TETA molecules $(A_0/2)$.

The results of these calculations for a TETA/epoxy system as a function of K and the initial stoichiometry are shown in *Tables 4* through *9*. Similarly, the fractions of the epoxy molecules at the different stages of the reaction are given by:

$$\text{both ends of the epoxide unreacted} = (1 - p)^2 \tag{16}$$

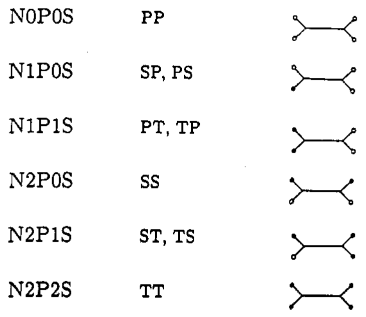

Figure 5 Different species generated when a tetrafunctional curing agent is used

Table 2 Probabilities for calculating the fractions of species shown in *Figure 4*

N0P0S = $FPN^2.SNS^2$
N1P0S = $2.FPN.FSN.SNS^2$
N2P0S = $FSN^2.SNS^2$
N0P1S = $2.FPN^2.SNS.SNT$
N0P2S = $FPN^2.SNT^2$
N1P1S = $4.FPN.SNS.SNT.FSN + 2.FPN.SNS^2.FTN$
N1P2S = $2.FPN.SNT^2.FSN + 4.FPN.SNT.SNS.FTN$
N1P3S = $FPN.SNT^2.FTN$
N2P1S = $2.FSN^2.SNT.SNS + 2.FTN.SNS^2.FSN$
N2P2S = $FSN^2.SNT^2 + FTN^2.SNS^2 + 4.FTN.SNS.SNT.FSN$
N2P3S = $2.FTN.SNT^2.FSN + 2.FTN^2.SNS.SNT$
N2P4S = $FTN^2.SNT^2$

Table 3 Probabilities for calculating the fractions of species shown in *Figure 5*

N0P0S = FPN^2
N1P0S = $2.FPN.FSN$
N1P1S = $2.FPN.FTN$
N2P0S = FSN^2
N2P1S = $2.FSN.FTN$
N2P2S = FTN^2

Table 4 Percentages of different species at increasing epoxide conversion (EPON/TETA): $K = 1$, $r_0 = 0.5$

	Epoxide conversion (%)		
Type of species	8.2	18.4	34.2
N0P0S	34.3	6.4	0.25
N1P0S	26.8	14.9	1.72
N2P0S	5.23	8.65	2.95
N0P1S	13.4	7.44	0.86
N0P2S	1.31	2.16	0.74
N1P1S	13.1	21.6	7.4
N1P2S	2.04	10.05	10.1
N1P3S	0.10	1.46	4.32
N2P1S	3.06	15.1	15.1
N2P2S	0.648	9.49	28.1
N2P3S	0.058	2.54	22.2
N2P4S	0.002	0.247	6.3
ρ^a	1.03	2.21	3.79

^{a} ρ is the average number of functionalities reacted for a TETA molecule

Table 5 Percentages of different species at increasing epoxide conversion (EPON/TETA): $K = 1$, $r_0 = 1$

	Epoxide conversion (%)				
Type of species	7.8	16.3	25.8	36.7	44.9
N0P0S	61.4	34.3	16.6	6.4	2.81
N1P0S	20.8	26.8	23.2	14.9	9.14
N2P0S	1.76	5.23	8.1	8.7	7.44
N0P1S	10.4	13.4	11.6	7.43	4.57
N0P2S	0.44	1.31	2.02	2.16	1.86
N1P1S	4.4	13.1	20.2	21.6	18.6
N1P2S	0.3	2.04	5.6	10.05	12.1
N1P3S	0.006	0.10	0.49	1.46	2.46
N2P1S	0.45	3.06	8.4	15.1	18.2
N2P2S	0.041	0.65	3.2	9.49	16.0
N2P3S	0.002	0.058	0.51	2.54	6.01
N2P4S	0	0.002	0.03	0.25	0.82
ρ^a	0.47	0.98	1.55	2.21	2.69

^{a} ρ is the average number of functionalities reacted for a TETA molecule

$$\text{one end of the epoxide reacted} = 2(1 - p)p \tag{17}$$

$$\text{both ends of the epoxide reacted} = p^2 \tag{18}$$

The species in *Tables 4* through *9* that would give rise to linear chains would be N2P0S, N0P2S and N1P1S, and the species that may give rise to the dimers are N1P0S and N0P1S. The other species would be branched. As the reaction proceeds, in all cases unreacted TETA (N0P0S) decreases steadily. When $K = 1$ (*Tables 4–6*) then:

(1) In the initial stages, a large number of species with only one reacted end are formed. The number of N1P0S is twice the number of N0P1S since there are twice the number of primary hydrogens at the start of the reaction. They reach a high concentration during the reaction and then decrease.

(2) The species giving rise to the linear chains also reach a maximum in the intermediate stages. The most abundant of these species are N2P0S and N1P1S. The species N0P2S are few in number at all stages of the reaction.

(3) At gelation, the nature of the species present is strongly influenced by the initial stoichiometry (r_0). When $r_0 = 1$, a large proportion of the crosslinking is due to the

Table 6 Percentages of different species at increasing epoxide conversion (EPON/TETA): $K = 1$, $r_0 = 2$

	Epoxide conversion (%)						
Type of species	7.64	15.6	23.9	32.7	42	62.2	63.2
N0P0S	79.1	61.4	46.5	34.3	16.6	10.72	10.22
N1P0S	12.6	20.8	25.3	26.8	23.2	19.33	18.9
N2P0S	0.5	1.76	3.44	5.23	8.08	8.72	8.74
N0P1S	6.29	10.4	12.7	13.4	11.6	9.67	9.45
N0P2S	0.125	0.44	0.86	1.31	2.02	2.18	2.19
N1P1S	1.25	4.4	8.6	13.1	20.2	21.8	21.9
N1P2S	0.04	0.3	0.94	2.04	5.63	7.86	8.09
N1P3S	0	0.006	0.032	0.10	0.49	0.886	0.935
N2P1S	0.06	0.447	1.4	3.06	8.44	11.8	12.13
N2P2S	0.03	0.041	0.207	0.65	3.19	5.76	6.08
N2P3S	0	0.002	0.013	0.058	0.512	1.20	1.3
N2P4S	0	0	0	0.002	0.03	0.09	0.1
ρ^a	0.23	0.47	0.73	0.98	1.55	1.87	1.90

[a] ρ is the average number of functionalities reacted for a TETA molecule

Table 7 Percentages of different species at increasing epoxide conversion (EPON/TETA): $K = 5$, $r_0 = 0.5$

Type of species	Epoxide conversion (%)			
	5.7	12	20.6	29.7[b]
N0P0S	45.6	13.3	0.63	0.001
N1P0S	38.4	37.9	9.7	0.168
N2P0S	8.07	27	37.6	13.37
N0P1S	3.31	2.56	0.33	0.001
N0P2S	0.06	0.122	0.042	0
N1P1S	3.52	9.32	6.66	0.344
N1P2S	0.104	0.74	1.49	0.232
N1P3S	0.001	0.019	0.109	0.032
N2P1S	0.89	8.08	32	34.9
N2P2S	0.036	0.88	10	34
N2P3S	0.001	0.042	1.38	14.6
N2P4S	0	0.001	0.07	2.34
ρ^a	0.68	1.45	2.47	3.56

[a] ρ is the average number of functionalities reacted for a TETA molecule

[b] At 29.7% of epoxide conversion, all primary amine was exhausted and the gel point was not reached ($\alpha = 0.84$)

highly branched species such as N2P2S and N2P3S. When $r_0 = 2$, most of the species are only linear (N1P1S); and it seems that the gelation occurred due to N1P2S. Also a large amount of the unreacted TETA is left in the amine-rich systems.

Comparing these results for $K = 5$ (*Tables 7–9*), we have:

(1) Again, as in the previous case, many species with only one reacted functionality are formed at the start of the reaction. However, the important species is N1P0S and the fraction of N0P1S is small.

(2) The species giving rise to the linear chains are also formed at the intermediate stages of the reaction. The important one is N2P0S as opposed to N1P1S. Even at the gel point, the proportion of these is large.

(3) At gelation, the nature of species present is also influenced by the initial stoichiometry; but in all cases, the amount of unreacted TETA is negligible. The shift in the gel point (as compared to the case when $K = 1$) is larger in the amine-rich systems. The species through which most of the crosslinking occurs appears to be

Table 8 Percentages of different species at increasing conversion (EPON/TETA): $K = 5$, $r_0 = 1$

	Epoxide conversion (%)						
Type of species	5.6	11.3	17.4	23.9	31.3	41.1	47.4
N0P0S	69.9	45.6	26.8	13.32	4.74	0.631	0.10
N1P0S	24.5	38.4	42.5	37.9	26.1	9.74	3.5
N2P0S	2.14	8.1	16.8	27	36	37.6	31.1
N0P1S	2.3	3.31	3.31	2.56	1.41	0.33	0.073
N0P2S	0.02	0.06	0.102	0.123	0.105	0.042	0.013
N1P1S	1.01	3.52	6.65	9.32	10.1	6.66	3.48
N1P2S	0.013	0.103	0.34	0.74	1.26	1.49	1.13
N1P3S	0	0.001	0.005	0.019	0.051	0.109	0.121
N2P1S	0.106	0.89	3.19	8.08	17.04	32	38.7
N2P2S	0.002	0.036	0.22	0.884	2.95	10.0	17.9
N2P3S	0	0.001	0.001	0.042	0.222	1.38	3.63
N2P4S	0	0	0	0.001	0.006	0.07	0.273
ρ^a	0.34	0.68	1.04	1.44	1.89	2.47	2.84

[a] ρ is the average number of functionalities reacted for a TETA molecule

Table 9 Percentages of different species at increasing epoxide conversion (EPON/TETA): $K=5$, $r_0=2$

	Epoxide conversion (%)						
Type of species	5.54	11.2	16.9	28.7	41.2	54.9	69
N0P0S	84.2	69.9	57.1	35.6	19.4	8.44	2.73
N1P0S	13.6	24.5	32.7	41.6	41.2	32.8	20.4
N2P0S	0.55	2.14	4.68	12.2	21.9	31.9	38.1
N0P1S	1.32	2.29	2.95	3.4	3.01	2.01	0.97
N0P2S	0.005	0.019	0.038	0.082	0.12	0.119	0.086
N1P1S	0.266	1.01	2.13	5.07	8.12	10.04	9.45
N1P2S	0.002	0.013	0.044	0.199	0.517	0.997	1.43
N1P3S	0	0	0	0.002	0.010	0.032	0.069
N2P1S	0.013	0.11	0.367	1.793	5.23	11.94	21.8
N2P2S	0	0.002	0.010	0.096	0.457	1.64	4.57
N2P3S	0	0	0	0.002	0.017	0.097	0.417
N2P4S	0	0	0	0	0	0.002	0.014
ρ^a	0.17	0.34	0.51	0.86	1.24	1.65	2.07

$^a\rho$ is the average number of functionalities reacted for a TETA molecule

N2P1S. This seems not to be the case when $r_0=0.5$ because all the primary hydrogens are consumed before gelation, and only the secondary hydrogens are left to react (*Table 7*).

CONCLUSIONS

The gel point for reactions between a bifunctional epoxy and amines can be estimated by a simple method when the reactivities of the primary and secondary amines are not the same. The primary effects due to the different reactivities of secondary and primary amines are:

(1) The gel point shifts to a higher extent of reaction, and this difference is greater in amine-rich systems.

(2) The amount of the unreacted amine curing agent at the gel point is smaller.

(3) The number of linear chains formed by the reaction of the primary groups increases rapidly at the intermediate stages of the reaction. At the gel point, the amount of the primary amine consumed is strongly influenced by the reactivity ratio, which in turn governs the nature of the network produced.

The most interesting aspect of the present model is the simple fashion in which the concepts of the Flory–Stockmayer network formation theory can be extended to include differences in unequal reactivity and the capability that it provides for obtaining insight into the species present at different stages of reaction.

ACKNOWLEDGEMENTS

Financial support for the present work was provided by the Air-Force Office of Scientific Research. This support is gratefully acknowledged.

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