

Effects of unequal reactivity of functional groups on gelation phenomena in polyurethane systems

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A model to describe the effect of unequal reactivity on curing of a diisocyanate with water, polyol and a diol was developed. The model predicts whether a given initial composition would gel or not and the fractional conversions of functional groups at the gel point. It has been shown that the relative speeds of reaction of water and hydroxyl groups can be used to classify water's behaviour as that of a (i) nonreactive diluent (ii) monofunctional blocking agent and (iii) chain extender capable of connecting branch points.

(Keywords: unequal reactivity; gelation; urethanes)

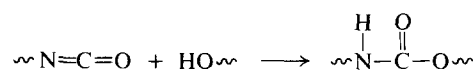
INTRODUCTION

The condensation of a polyfunctional monomer with another bifunctional or polyfunctional monomer can lead to the formation of macroscopic dimensional infinite networks or gels. Flory¹ provided the theoretical basis for calculating the fractional conversions of functional groups at which gelation occurs. In this pioneering work, he assumed that all the functional groups of the monomers are equally reactive. However, this assumption is not valid for many industrially important reactions such as those between epoxies and amines², isocyanates and alcohols³, phenol and formaldehyde^{3,4}, etc. Three basic types of unequal reactivity have been identified. Structural asymmetry⁵ or asymmetry⁶ refers to the situation where the different functional groups, which are chemically similar react at different rates. Those cases where the reactivities of all the functional groups of a monomer are equal but different from that of the very same functional groups present at the end of a polymer chain have been termed induced asymmetry⁶ or first shell substitution effects⁷. Cyclic monomers⁶ which generate a chemically equivalent group after reaction constitute the last category of unequal reactivity. It is possible that a monomer may simultaneously possess one or more of these basic unequal reactivity characteristics. Miller and Macosko presented a procedure for calculating the gel points where the monomers have either structural asymmetry⁵ or exhibit first shell substitution effect⁸. Bokare and Gandhi⁹ analysed the gelation behaviour in epoxy-amine systems accounting for the simultaneous influence of first shell substitution effect and the side reaction between the epoxy and the secondary hydroxyl group which is created as a product during the reaction.

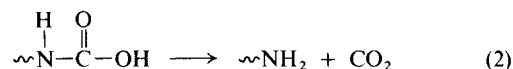
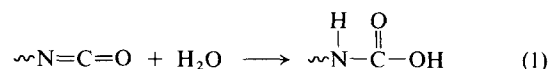
Isocyanate monomers can exhibit a very complex behaviour. Several monomers show the simultaneous

presence of structural asymmetry and first shell substitution effect^{3,10}. In the present work, the theory of curing of such monomers will be considered.

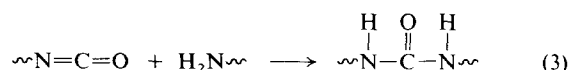
Polyurethanes can be produced by the prepolymer method or one-shot process. In the latter process, which is commonly used in industry, a diol and a polyol are reacted with a diisocyanate. Water and or another foaming agent can also be added to the above mixture if a foam is the desired product¹¹. The diol may be a hydroxyl terminated polyether or polyester while the commonly used diisocyanates are tolylene diisocyanate or methylene diphenyl diisocyanate. The polyol could be a compound like glycerol. The reaction between hydroxyl group and isocyanate group produces the urethane linkage.



The reactions between water and isocyanate group are



The gaseous CO₂ liberated in the second reaction acts as the foaming agent. The amine generated in the second reaction can react with isocyanate group producing polyurea linkages:



In this work, gel points will be calculated for a one-shot batch process employing reaction mixtures containing a diisocyanate, a diol, a polyol and water. The diisocyanate monomer will be assumed to exhibit structural asym-

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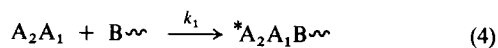
metry as well as first shell substitution effects. The hydroxyl groups of the diol and polyol will be assumed to be equally reactive.

MODEL OF THE SYSTEM

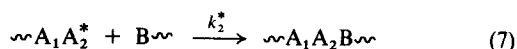
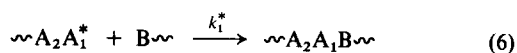
In polyurethane foam production, apart from the urethane formation and reactions (1) to (3), allophanate and biuret linkages are also formed. Such linkages can contribute to chain branching and crosslinking. While some catalyst systems may promote these side reactions, generally their effect can be ignored except at high temperatures^{10,11}. In the present work, these side reactions will be assumed to be absent.

Urethane formation

Let us denote the diisocyanate monomer as A_1A_2 thereby explicitly recognizing that the two monomeric isocyanate groups will react at different rates. Let us denote the diol by B_2 and the polyol by B_f . The same symbol B is being assigned to all hydroxyl groups as all of them have been assumed to be equally reactive. The structural asymmetry of the diisocyanate monomer can be represented by the following equations:



The A_1 and A_2 present at the end of a polymeric chain have been clearly distinguished by a star as they will react at a rate different from that of the corresponding monomeric group due to first shell substitution effects. The first shell substitution effect can be modelled as



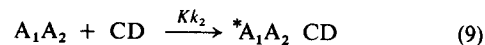
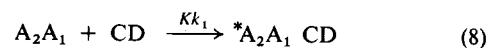
Linear polymerization of such A_1A_2 monomer with only B_2 monomer has been analysed by Gandhi and Babu¹² and their results can be applied to analyse urethane formation by reactions (4) to (7).

Reactions with water

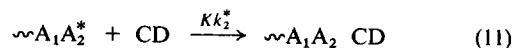
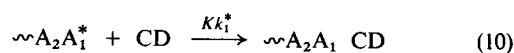
Since reaction (2) is very fast, it will be assumed to occur instantaneously. Then a water molecule reacts with one isocyanate group and, in effect, generates the amine group directly. The amine group can then react with one isocyanate group by reaction (3). Such a sequence of reactions is similar to those of a cyclic monomer and in particular those between an anhydride and hydroxyl group. In other words water can be modelled as a cyclic monomer. Let us symbolically denote water by CD. The C group reacts first consuming one isocyanate group and generates a D group (amino group). The D group does not exist in the monomer and hence cannot react until the 'adjoining' C group reacts. Therefore the D group can be present only at the end of a chain while the C group cannot form the end of a chain. The D group can then react with one isocyanate group. The C and D groups can react with the isocyanate groups at different rates. For simplicity we will assume that the asymmetric characteristics of A_1A_2 monomer are inherent to the A_1A_2 monomer

and the same characteristics used in urethane formation are applicable here also.

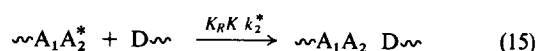
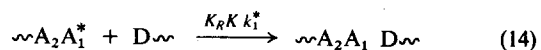
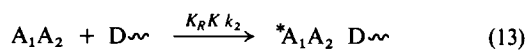
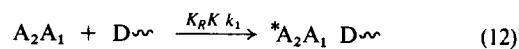
In other words we are assuming that the relative reactivities of polymeric and monomeric A_1 and A_2 groups are unaltered irrespective of the group with which they react though their absolute reactivities may be different. The reactions with water may then be written as follows:



The A_1 and A_2 groups of the products of reactions (8) and (9) are polymeric in character. Thus we will write



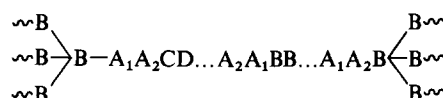
The D (amino) group reactions are



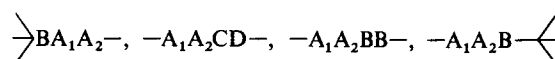
Reactions (4) to (15) then form the basic model of the system.

PROBABILITY OF NETWORK FORMATION

Initially let only monomers A_1A_2 , B_2 , B_f , CD be present. For the system being considered, gelation occurs through formation of structures like



If the probability of occurrence of the above structure regardless of the number of intervening bifunctional CD and BB units, or the branching coefficient¹³, can be calculated, the gel point can be predicted following Flory¹³. The probabilities of finding structures of the type



are needed to calculate the branching coefficient. All such probabilities have been shown^{5-9,12} to be related to the fraction of the total number of the various groups that have been consumed in direct reaction. The probabilities and their interrelations can be calculated once the kinetics of the reactions are known. An example of such a calculation is given in Appendix I.

Probability of finding unreacted A_1A_2 monomer

This can be simply defined as the ratio of unreacted monomer concentrations at any given time and initially.

$$\alpha = [A]/[A]_0$$

Probabilities of reaction of A groups

During the course of reaction monomeric A_1 groups are lost by reaction (4) as well as by (5). Reaction (4) consumes a monomeric A_1 group by direct reaction whereas reaction (5) converts a monomeric A_1 group to a polymeric A_1 group. Let A_1^r be the moles of monomeric A_1 groups that have been consumed by reaction (4) per unit volume at any time. Following Gandhi and Babu¹² let us define the probability that a monomeric A_1 groups has reacted as

$$\alpha_1 \equiv \frac{A_1^r}{[A] + A_1^r} \quad (16)$$

Such a definition has the advantage that it reaches a value of unity at the end of the reaction when A_1A_2 monomer is in stoichiometric deficiency. Similarly the probability that a monomeric A_2 group has reacted is

$$\alpha_2 \equiv \frac{A_2^r}{[A] + A_2^r} \quad (17)$$

Note that

$$[A]_0 = [A] - A_1^r - A_2^r \quad (18)$$

When A_2^r moles of monomeric A_2 groups have reacted, the same number of polymeric A_1 or A_1^* groups have been created. If $[A_1^*]$ is the concentration of unreacted polymeric A_1 groups at any time, then $A_2^r - [A_1^*]$ number of polymeric A_1^* groups have reacted by reaction (6). Hence, the probability of reaction of polymeric A_1 groups can be defined as

$$\alpha_1^* \equiv \frac{A_2^r - [A_1^*]}{A_2^r} \quad (19)$$

Similarly, the probability of reaction of polymeric A_2 groups is defined as

$$\alpha_2^* \equiv \frac{A_1^r - [A_2^*]}{A_1^r} \quad (20)$$

Probabilities of reaction of B groups

Let $[B_f]_0$ and $[B_2]_0$ represent the initial concentrations of the polyol and diol respectively. Let $[B]$ be the concentration of unreacted B ends present at any time. The probability that a randomly selected B group has reacted is defined as

$$\beta \equiv 1 - \frac{[B]}{f[B_f]_0 + 2[B_2]_0} \quad (21)$$

Probabilities of reaction of CD units

Let $[C]_0$ and $[C]$ respectively represent the concentrations of the CD monomer initially and at any time. Let $[D]$ represent the concentration of unreacted D ends at any time. The number of CD units that have reacted per unit volume is $[C]_0 - [C]$. Hence the probability of finding a CD unit where C group has reacted can be defined as

$$\gamma \equiv \frac{[C]_0 - [C]}{[C]_0} \quad (22)$$

During the course of reaction, $[C]_0 - [C]$ moles of CD monomer units have reacted and hence that many moles of D ends have been created per unit volume. Out of these only $[D]$ moles per unit volume of unreacted D ends are present. Hence the moles per unit volume of CD units in which both C and D groups have reacted is equal to $[C]_0 - [C] - [D]$. The probability of finding a CD unit where both C and D have reacted can be defined as

$$\delta \equiv \frac{[C]_0 - [C] - [D]}{[C]_0} \quad (23)$$

Again note that β, γ and δ will attain unity at the end of the reaction if A_1A_2 monomer is in stoichiometric excess.

Stoichiometric relationship

The total number of A groups that have reacted must be equal to the total number of B, C and D groups that have reacted. Hence

$$S \equiv A_1^r(1 + \alpha_2^*) + A_2^r(1 + \alpha_1^*) \\ = \{f[B_f]_0 + 2[B_2]_0\}\beta + [C]_0(\gamma + \delta)$$

In terms of the above defined probabilities, the first equality reduces to

$$S = \alpha \{ \alpha_1(1 - \alpha_2)(1 + \alpha_2^*) + \alpha_2(1 - \alpha_1)(1 + \alpha_1^*) \} [A]_0 / \\ \{ (1 - \alpha_1)(1 - \alpha_2) \} \quad (24)$$

Let us define the fraction of polyfunctional groups, ρ ,

$$\rho \equiv \frac{f[B_f]_0}{f[B_f]_0 + 2[B_2]_0 + 2[C]_0} \quad (25)$$

and fraction of hydroxyl groups contributed by the diol, d ,

$$d \equiv \frac{2[B_2]_0}{f[B_f]_0 + 2[B_2]_0} \quad (26)$$

and the fraction of blowing agent groups, b ,

$$b \equiv \frac{2[C]_0}{f[B_f]_0 + 2[B_2]_0 + 2[C]_0} \quad (27)$$

The above three quantities are related through

$$\rho = (1 - d)(1 - b) \text{ or } b(1 - d) = 1 - \rho - d \quad (28)$$

Further let us define the stoichiometric ratio, R , as the ratio of initial concentrations of A groups and the concentrations of all the groups with which A can react

$$R \equiv \frac{2[A]_0}{f[B_f]_0 + 2[B_2]_0 + 2[C]_0} \quad (29)$$

Then using relationships (25) to (29), the total B, C, D groups that have reacted, S , is given by

$$S = \frac{[A]_0}{R(1 - d)} [2\rho\beta + (1 - d - \rho)(\gamma + \delta)] \quad (30)$$

Probability of a structure of the type $-A_1A_2BB-$

The structure being considered can be formed in four ways:

(i) Monomeric A_1 group reacts, then the polymeric A_2 group reacts with a B_2 unit and the B end reacts subsequently, so that $-A_1A_2^*BB-$ can represent such a structure. (ii) Monomeric A_2 group reacts, the polymeric A_1 group reacts with a B_2 unit and the B end reacts afterwards. $-A_2A_1^*BB-$ represents this type of structure. (iii) One B group of a B_2 unit can react, the other B end can then react with monomeric A_1 group and the polymeric A_2 group can react thereafter. $-A_2^*A_1BB-$ symbolises this type of formation (read from left to right). (iv) A B_2 unit can react, monomeric A_2 reacts with the other B end and then polymeric A_1 group reacts. $-A_1^*A_2BB-$ is the representation of this type of formation. The total probability of formation of $-A_1A_2BB-$ type of unit, irrespective of the internal arrangements of A_1A_2 or the ways in which the unit was formed, is the sum of the probabilities of occurrence of the four types of sequences of events listed above.

The probability of occurrence of the first of the above sequences will be calculated as an example. The probability is given by

$$\left(\begin{array}{l} \text{probability of finding} \\ \text{a monomeric } A_1 \text{ reacted} \\ \text{group next to a bond} \end{array} \right) \left(\begin{array}{l} \text{probability that} \\ \text{polymeric } A_2 \text{ reacts} \\ \text{with a BB unit} \end{array} \right) \left(\begin{array}{l} \text{probability that} \\ \text{the B end has} \\ \text{reacted} \end{array} \right)$$

$$= \left(\frac{A_1^r}{S} \right) \left(\alpha_2^* \frac{2[B_2]_0\beta}{S} \right) (\beta)$$

Similarly the probability of the second, third and fourth sequences can be calculated to be, respectively,

$$\frac{A_2^r}{S} \cdot \alpha_1^* \frac{2[B_2]_0\beta}{S} \cdot \beta, \quad \frac{2[B_2]_0\beta}{S} \cdot \beta \cdot \frac{A_1^r}{S} \cdot \alpha_2^*,$$

$$\frac{2[B_2]_0\beta}{S} \cdot \beta \cdot \frac{A_2^r}{S} \cdot \alpha_1^*$$

Hence the total probability of finding $-A_1A_2BB-$ unit P_{BB} is given by

$$P_{BB} = 2 \frac{A_1^r \alpha_2^* + A_2^r \alpha_1^*}{S} \cdot \frac{2[B_2]_0\beta^2}{S}$$

After substitution of relationships (24) and (30)

$$P_{BB} = 4 \frac{\alpha_1 \alpha_2^* (1 - \alpha_2) + \alpha_2 \alpha_1^* (1 - \alpha_1)}{\alpha_1 (1 - \alpha_2) (1 + \alpha_2^*) + \alpha_2 (1 - \alpha_1) (1 + \alpha_1^*)} \cdot \frac{\rho \beta^2}{2\rho\beta + (1 - d - \rho)(\gamma + \delta)} \quad (31)$$

Probability of a structure of the type $-A_1A_2CD-$

Using a similar analysis to the previous section, there are eight ways in which the structure being considered can be formed. Using a notation similar to the earlier section these eight ways can be listed as: $-A_1A_2^*CD-$, $-A_1A_2^*DC-$, $-A_2A_1^*CD-$, $-A_2A_1^*DC-$, $-A_1^*A_2CD-$, $-A_1^*A_2DC-$, $-A_2^*A_1CD-$, $-A_2^*A_1DC-$. As an example, the fifth structure may be interpreted to have formed when a monomeric A_2 group reacts with CD monomer and subsequently the polymeric A_1 group and D group

generated react. Following the method employed in the earlier section, the probabilities of the above eight structures can be calculated and are given by

$$\frac{A_1^r}{S} \cdot \alpha_2^* \frac{C_0\delta}{S}, \quad \frac{A_1^r}{S} \cdot \alpha_2^* \frac{C_0\delta}{S}, \quad \frac{A_2^r}{S} \cdot \alpha_1^* \frac{C_0\delta}{S}, \quad \frac{A_2^r}{S} \cdot \alpha_1^*,$$

$$\frac{C_0\delta}{S}, \quad \frac{C_0\delta}{S} \frac{A_2^r}{S} \cdot \alpha_1^*, \quad \frac{C_0\delta}{S} \frac{A_2^r}{S} \cdot \alpha_1^*, \quad \frac{C_0\delta}{S} \frac{A_1^r}{S} \cdot \alpha_2^*, \quad \frac{C_0\delta}{S} \cdot \frac{A_1^r}{S} \cdot \alpha_2^*$$

respectively. The total probability of finding $-A_1A_2CD-$ structure irrespective of the internal arrangements of the A_1A_2 and CD units P_{CD} is then the sum of all the above eight probabilities or

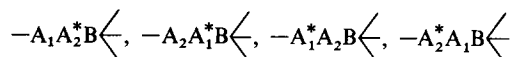
$$P_{CD} = 4 \frac{A_1^r \alpha_2^* + A_2^r \alpha_1^*}{S} \cdot \frac{C_0\delta}{S}$$

In terms of probabilities and other definitions adopted earlier

$$P_{CD} = 4 \frac{\alpha_1 \alpha_2^* (1 - \alpha_2) + \alpha_2 \alpha_1^* (1 - \alpha_1)}{\alpha_1 (1 - \alpha_2) (1 + \alpha_2^*) + \alpha_2 (1 - \alpha_1) (1 + \alpha_1^*)} \times \frac{(1 - d - \rho)\delta}{2\rho\beta + (1 - d - \rho)(\gamma + \delta)} \quad (32)$$

Probability of a structure of the type $-A_1A_2\leftarrow$

There are four ways in which this structure can form:



The probabilities of these four structures respectively are:

$$\frac{A_1^r}{S} \cdot \alpha_2^* \frac{f[B_f]_0\beta}{S}, \quad \frac{A_2^r}{S} \cdot \alpha_1^* \frac{f[B_f]_0\beta}{S},$$

$$\frac{f[B_f]_0\beta}{S} \cdot \frac{A_2^r}{S} \cdot \alpha_1^*, \quad \frac{f[B_f]_0\beta}{S} \cdot \frac{A_1^r}{S} \cdot \alpha_2^*$$

The total probability of finding this structure P_{B_r} is given by

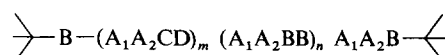
$$P_{B_r} = 2 \frac{A_1^r \alpha_2^* + A_2^r \alpha_1^*}{S} \cdot \frac{f[B_f]_0\beta}{S}$$

and after substitution of earlier definitions

$$P_{B_r} = 4 \frac{\alpha_1 \alpha_2^* (1 - \alpha_2) + \alpha_2 \alpha_1^* (1 - \alpha_1)}{\alpha_1 (1 - \alpha_2) (1 + \alpha_2^*) + \alpha_2 (1 - \alpha_1) (1 + \alpha_1^*)} \times \frac{\rho(1 - d)\beta}{2\rho\beta + (1 - d - \rho)(\gamma + \delta)} \quad (33)$$

Branching coefficient

Consider the following structure



The probability of the above structure is simply given by

$$\beta \cdot (P_{CD})^m (P_{BB})^n \cdot P_{B_f}$$

However the $-A_1A_2CD-$ and $-A_1A_2BB-$ units can be interchanged and it will lead to $(m+n)!/(m!n!)$ number of structures with the same probability. Hence the total probability of finding such a structure irrespective of the internal rearrangements is

$$\frac{(m+n)!}{m!n!} P_{B_f} (P_{CD})^m (P_{BB})^n$$

Branching coefficient is equal to the probability that a B group selected at random from one of the B_f units will lead to a B group of another B_f unit regardless of the number of connecting bifunctional units. Thus branching coefficient is given by

$$\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \beta P_{B_f} \frac{(m+n)!}{m!n!} (P_{CD})^m (P_{BB})^n$$

or

$$\frac{\beta P_{B_f}}{1 - P_{CD} - P_{BB}}$$

Following arguments of Flory¹³, the gel point occurs when

$$\text{when } (f-1) \frac{\beta P_{B_f}}{1 - P_{CD} - P_{BB}} \geq 1 \quad (34)$$

The above criteria along with kinetics of the reactions can be used to predict the fractional conversions at which gelation will occur. The inter-relations between probabilities have been derived in Appendix I assuming second order kinetics. The gel criteria then simplifies to

$$(f-1) \frac{4\beta^2 \rho (\alpha_2^* + K_A \alpha_1^*) (1-d)}{[1 + \alpha_2^* + K_A (1 + \alpha_1^*)][2\rho\beta + (1-d-\rho)(\gamma + \delta)] - 4(\alpha_2^* + K_A \alpha_1^*)[(1-d-\rho)\delta + \rho d\beta^2]} \geq 1 \quad (35)$$

The above criteria must be simultaneously satisfied along with the stoichiometric relation which now reduces to

$$\frac{\alpha_1}{1 + K_A \alpha_1} [1 + \alpha_2^* + K_A (1 + \alpha_1^*)] = \frac{1}{R(1-d)} [2\rho\beta + (1-d-\rho)(\gamma + \delta)] \quad (36)$$

Both these equations are proved in the Appendix I.

RESULTS AND DISCUSSION

The gelation criteria given by relationship (34) can be used to predict whether a particular initial composition specified by R , ρ and d will lead to the formation of an infinite network or not. Further if a gel were to form, the fractional decrease in the initial functional group concentrations required before gelation can occur can also be predicted by relationship (34). Results have been obtained in this paper for reaction of a diisocyanate with a triol ($f=3$), a diol and water.

Recovery of appropriate limits

Under appropriate restrictions, the present model must reduce to those developed by earlier workers. A few such examples are given to demonstrate the validity of the present model. The kinetics presented in the Appendix I will be used as and when necessary.

(i) *Limit of equal reactivity.* When $k_2/k_1 \equiv K_A = 1$, $k_1^*/k_1 \equiv K_1 = 1$ and $k_2^*/k_2 \equiv K_2 = 1$, both the functional groups, A_1 and A_2 , are equally reactive in their monomeric as well as polymeric forms. Further if $K=2$ and $K_R=0.5$, the CD monomer behaves like a B_2 monomer⁶. Flory's¹³ equal reactivity limit must be recovered with these restrictions. The following relationships can be easily established from the Appendix with the above restrictions:

$$\gamma = 2\beta - \beta^2, \delta = \beta^2, \alpha_1 = \alpha_2, \alpha_1^* = \alpha_2^*, 1 - \alpha_1^* = \frac{1 + \alpha_1}{\alpha_1} \left[\frac{1 - \alpha_1}{1 + \alpha_1} - \sqrt{\frac{1 - \alpha_1}{1 + \alpha_1}} \right] \quad (37)$$

If p_A is defined as the fraction of total A groups that have reacted, then

$$p_A = \frac{A_1^*(1 + \alpha_2^*) + A_2^*(1 + \alpha_1^*)}{2[A]_0} = \frac{\alpha_1}{1 + \alpha_1} (1 + \alpha_2^*) \quad (38)$$

From relationships (37) and (38), it can be shown that

$$\frac{\alpha_1}{1 + \alpha_1} = \frac{p_A(2 - p_A)}{2} \quad \text{and} \quad \alpha_1^* = \frac{p_A}{2 - p_A}$$

Similarly if p_B is defined as the fraction of B, C and D

groups that have reacted, then, it can be shown that

$$p_B = \frac{\{f[B_f]_0 + 2[B_2]_0\}\beta + [C]_0(\gamma + \delta)}{f[B_f]_0 + 2[B_2]_0 + 2[C]_0} = \beta \quad (39)$$

If all the above results are substituted in the stoichiometric relationship (36), it reduces to $Rp_A = p_B$ and the gelation criteria (35) reduces to

$$(f-1) \frac{\rho p_A p_B}{(1 - (1 - \rho)p_A p_B)} \geq 1 \quad (40)$$

Both these results are identical to that given by Flory¹³. Note that Flory's r is $1/R$ and BB monomer in Flory's reference is the AA monomer of this paper.

(ii) *Limit of only first shell substitution effect.* This limit is obtained when $K_A = 1$, $K_1 = K_2$. To make CD equivalent to B_2 , we let $K=2$ and $K_R=0.5$. Hence $\alpha_1 = \alpha_2$, $\alpha_1^* = \alpha_2^*$, $\gamma = 2\beta - \beta^2$, $\delta = \beta^2$. Miller and Macasko⁸ considered gelation of A_g with B_2 where A_g exhibits first shell substitution effect. To compare therefore we

have to put $g=2$ in their results and $f=2$, $\rho=1$, $d=0$, $b=0$ in ours. Miller and Macosko⁸ define p_i to be the fraction of the initial A_g units in which i number of A groups have reacted. It is easy to show that

$$p_0 = \frac{[A]}{[A]_0} = \frac{1 - \alpha_1}{1 + \alpha_1}, p_1 = \frac{2[A_1^*]}{[A]_0} = \frac{2\alpha_1(1 - \alpha_2^*)}{1 + \alpha_1}$$

and

$$p_2 = \frac{2A_1^* \alpha_2^*}{[A]_0} = \frac{2\alpha_1 \alpha_2^*}{1 + \alpha_1}$$

If these results are substituted in the gel criteria given by Miller and Macosko, it reduces to $2R\alpha_1\alpha_2^*/(1 + \alpha_1) = 1$. For the case being considered, the stoichiometric relation (36) simplifies to $R\alpha_1(1 + \alpha_2^*)/(1 + \alpha_1) = \beta$ and the gel criteria (35) is given by $2\beta\alpha_2^*/(1 + \alpha_2^*) = 1$. When these two are combined the gel criteria is identical to that given by Miller and Macosko⁸.

Bokare and Gandhi⁹ considered the crosslinking of f functional epoxides with $g/2$ functional primary amines, where the amine hydrogens exhibit first shell substitution effect. They also considered the side reaction of the epoxide group with the secondary hydroxyl group generated. If the hydroxyl group is considered to be non-reactive and if $g=2$, their results are for the reaction between A_1A_2 with B_f where A_1A_2 has only first shell substitution effect. As hydroxyl groups are not reactive only secondary amine S_1 and tertiary amine T_2 (defined in ref. 9) exist and gel criteria given by them⁹ reduces to $2(f-1)T_2/e_0 = 1$. T_2 is the number of tertiary amine units or in our notation, A_1A_2 units in which both A_1 and A_2 have reacted. Hence,

$$\frac{T_2}{e_0} = \frac{2A_1^* \alpha_2^*}{f[B_f]} = R \frac{\alpha_1 \alpha_2^*}{1 + \alpha_1}$$

and gel criteria given is equivalent to $2(f-1)R\alpha_1\alpha_2^*/(1 + \alpha_1) = 1$. This is identical to that predicted by relationships (35) and (36). Note $d=b=0$ since the reaction is between A_1A_2 and B_f only.

(iii) *Limit of only structural asymmetry.* This limit is obtained when $K_1=K_2=1$, $K=2$, $K_R=0.5$. Hence $\alpha_1^*=\alpha_2^*$, $\gamma=2\beta-\beta^2$, $\delta=\beta^2$. For this case Miller and Macosko⁵ have given the gelation criteria to be $r=q_1q_2[1+(f-2)a_f]$. q_1 and q_2 are the fraction of A_1 and A_2 groups consumed and are easily shown to be given by $\alpha_1(1+K_A\alpha_1^*)/(1+K_A\alpha_1)$ and $\alpha_2(K_A+\alpha_2^*)/(1+K_A\alpha_1)$ respectively. Noting that $r=1/R$ and $a_f=\rho$, the gelation criteria of Miller and Macosko reduces to $R\alpha_1\alpha_2^*(K_A+1)[1+(f-2)\rho]/(1+K_A\alpha_1) = 1$. Simplifying relations (35) and (36) it can be shown that relationship (35) is identical with that of Miller and Macosko.

Gelation envelope

For a given system, the reaction rate constants are fixed and relation (35) can predict the fractional conversions at which gelation will occur once R , ρ and d are specified. However, the maximum possible conversion is complete conversion of those groups which are in stoichiometric deficiency. For example when $R < 1$, gel can form only when all $\alpha \leq 1$. Hence for a given ρ and d , by gelation condition and stoichiometry, a value R_{\min} exists, which is a

minimum value of stoichiometric ratio, at which gelation can occur when all $\alpha = 1$. For any $R < R_{\min}$, gelation is not possible for the same value of ρ and d because, before the required amounts of polyfunctional B groups can react A_1A_2 monomer would be exhausted. Similarly there will be a R_{\max} such that for $R > R_{\max}$, gelation will not occur. To illustrate this point consider as an example gelation of AA with B_3 and B_2 . The system is one of equal reactivity and $d=(1-\rho)$ since $b=0$. The gel criteria has been shown to be

$$\frac{2\rho p_A p_B}{1 - (1-\rho)p_A p_B} \geq 1 \quad (41)$$

and the stoichiometric equation is given by $Rp_A = p_B$. For $R < 1$, the maximum value p_A can attain is 1 while p_B is always less than 1. Using stoichiometry, the gelation criteria simplifies to

$$\frac{2\rho R p_A^2}{1 - (1-\rho)R p_A^2} \geq 1 \quad \text{or} \quad R \geq \frac{1}{p_A^2(1+\rho)}$$

Thus when $p_A = 1$, R takes its minimum possible value: $R_{\min} = 1/(1+\rho)$. Clearly gelation cannot occur at the same ρ if $R < R_{\min}$ since that would require $p_A > 1$. If $R > R_{\min}$ gelation can occur but for $p_A < 1$. Similarly if $R > 1$, the maximum value possible for p_B is 1 while $p_A < 1$. Now the gelation criteria will reduce to

$$\frac{2\rho p_B^2}{(R - (1-\rho)p_B^2)} \geq 1 \quad \text{or} \quad R \geq (1+\rho)p_B^2$$

Hence the maximum value of the stoichiometric ratio, R_{\max} , at which gelation can occur is given by $(1+\rho)$ when p_B has been equated to one. Gels will form only if $R \leq R_{\max}$ and for $R < R_{\max}$, $p_B > 1$ at the gel point. Thus gelation is possible only if $R_{\min} \leq R \leq R_{\max}$ for a given ρ . These two limits then define the boundaries of the gelation envelope and it is shown in Figure 1 for an equal reactivity case. Gelation will occur only if the initial composition falls inside the envelope. The plots of R_{\min} vs. ρ and R_{\max} vs. ρ will be referred to as the lower and upper boundaries of the envelope respectively. The gelation envelopes for different parametric values of the reaction rate constants and d will be presented in this section. First we shall consider the case when $d=0$ for simplicity.

Gelation envelope in the absence of bifunctional monomer

(i) R_{\min} versus ρ . This gives us the lower boundary of the gelation envelope. R_{\min} would be less than unity and therefore A_1A_2 monomer is in stoichiometric deficiency. The value of R_{\min} is obtained when all A groups have been consumed or when $\alpha_1 = \alpha_2 = \alpha_1^* = \alpha_2^* = 1$. Then relationship (35) reduces to

$$\frac{4\beta^2 \rho}{2\rho\beta + (1-\rho)(\gamma-\delta)} \geq 1 \quad \text{or} \quad \rho[4\beta^2 - 2\rho\beta + (\gamma-\delta)] \geq (\gamma-\delta) \quad (42)$$

and relationship (36) reduces to

$$2R = 2\rho\beta + (1-\rho)(\gamma+\delta) \quad (43)$$

In the above we have taken $f=3$ and $d=0$. By definition $\gamma-\delta$ is always positive and $0 \leq \rho \leq 1$. Then relationship

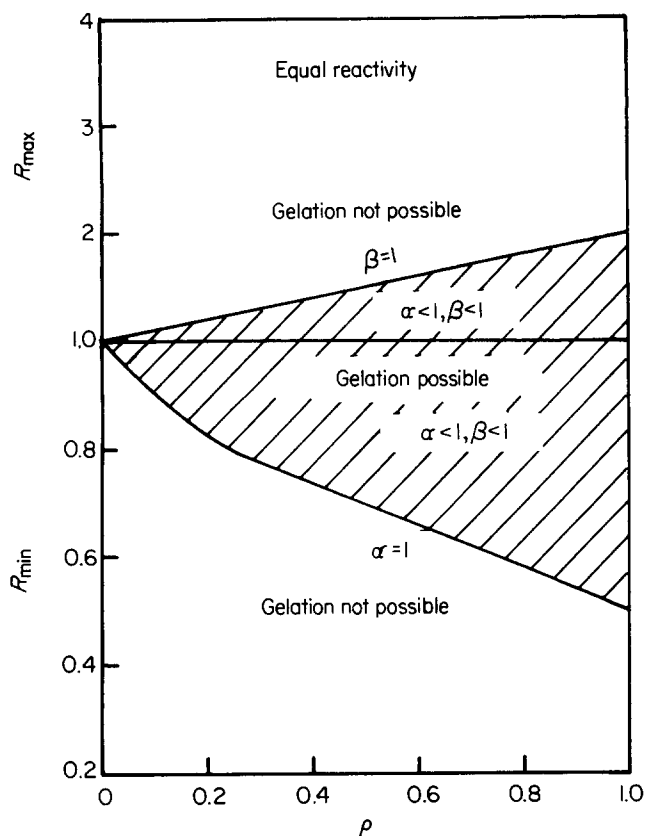


Figure 1 Gelation envelope for the case of equal reactivity ($K=2$, $K_R=1/2$, $K_A=K_1=K_2=1$)

(42) can be rearranged to get

$$\rho(4\beta^2 - 2\beta) \geq (1 - \rho)(\gamma - \delta)$$

and hence the minimum value that β must attain before gelation can occur is given by

$$4\beta^2 - 2\beta \geq 0 \quad \text{or} \quad \beta \geq 0.5$$

Further note that gelation will occur at $\beta=0.5$ if $\rho=1$ regardless of the values of the reaction rate constants. The value of R_{\min} at $\rho=1$ therefore is obtained from relationship (43) to be 0.5 and this result is common to all gelation envelopes.

If gelation were to occur at $\beta=1$ and since $\beta=1$ also means that $\gamma=\delta=1$, the only value possible for R_{\min} is unity by relationship (43). Conversely when $R_{\min}=1$, $\beta=\gamma=\delta=1$ and any value of $\rho \geq 0$ will lead to gelation by relationship (42). But when $\rho=0$ only $R_{\min}=1$ will satisfy relationships (42) and (43). Therefore, $R_{\min}=1$ when $\rho=0$ forms a common point for all gelation envelopes.

Since A_1A_2 monomer is completely consumed, only the time required for gelation and not the lower boundary of the gelation envelope is affected by the reaction rate constants' ratios K_A , K_1 and K_2 . Only the reactivity ratios K and K_R , which describe the effect of the behaviour of the blowing agent, influence the results.

Effect of K . This parameter indicates the effect of the relative reactivity of the C group. Let us first consider the two obvious limits given by $K=0$ and $K \rightarrow \infty$. When $K=0$, the blowing agent is nonreactive and hence acts simply as a diluent. Both γ and δ are therefore zero and relationship (42) predicts that gelation will occur as soon

as β reaches 0.5 and hence from relationship (43), $R_{\min} = \rho/2$. This result indicates that as ρ is increased, more AA monomer is required for gelation. It is an expected result since as ρ is increased, the fraction of the reactive B_f monomer increases while the fraction of nonreactive blowing agent decreases. As $K \rightarrow \infty$ the blowing agent CD reacts instantaneously and completely before any B groups can be consumed. Hence $\gamma = \delta = 1$ and therefore gelation will again occur as soon as $\beta=0.5$. From relationship (43) therefore $R_{\min} = 1 - 0.5\rho$. First this result shows that for the same value of ρ , R_{\min} required for $K=0$ is less than that for $K \rightarrow \infty$. This is to be expected since CD does not consume any A_1A_2 when $K=0$ while CD requires stoichiometrically equivalent of A_1A_2 when $K \rightarrow \infty$. Secondly the above result shows that, unlike when $K=0$, as ρ is increased, A_1A_2 required for gelation decreases. This can be understood since CD monomer consumes A_1A_2 monomer at the beginning itself forming -AACD- type prepolymer but not resulting in cross-linking. Hence as ρ is increased, the CD monomer fraction decreases and thus the requirement of A_1A_2 is reduced.

The blowing agent can therefore act in two opposing ways: as a nonreactive diluent and as a chain extending consumer of AA. As ρ is increased, the former effect tends to increase R_{\min} while the latter effect tends to decrease R_{\min} . The values of K and ρ determine the effect that dominates. It is pertinent here to point out that, had CD been assumed to be equally reactive as B_f , the theory would predict a monotonic decrease in R_{\min} as ρ is increased. Numerical results illustrating the effect of K are presented in Figure 2 for $K_R=1$. For $K > 2$, the diluent effect is not there at all and R_{\min} monotonically decreases with increasing ρ . However when K is sufficiently low, such as 0.1, very interesting behaviour that reflects a balance of the two effects already described is observed. At such a low value of K , the blowing agent reacts very slowly and should behave like a diluent. But at low values of ρ , large amounts of CD are present and thus the low reactivity is compensated for by the high concentration. As a result, a significant amount of AA is consumed in chain extension.

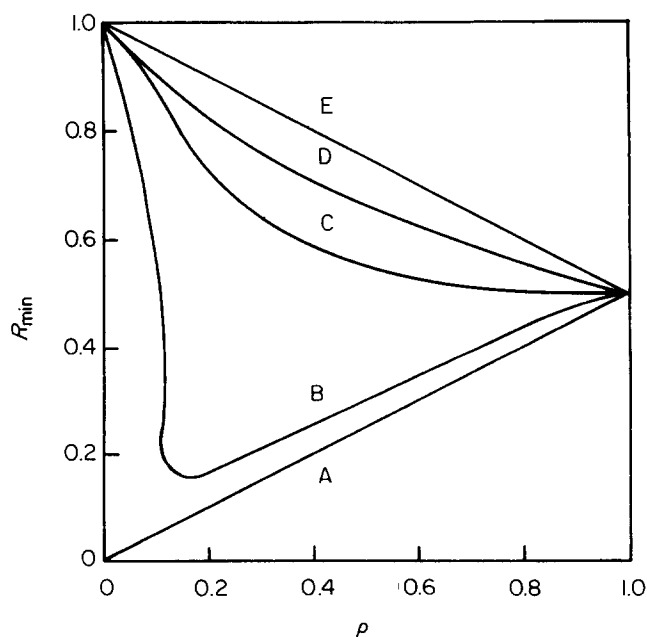


Figure 2 Effect of K on R_{\min} . The curves A-E are for $K=0$, 0.1, 1, 2 and ∞ respectively with $K_R=1$

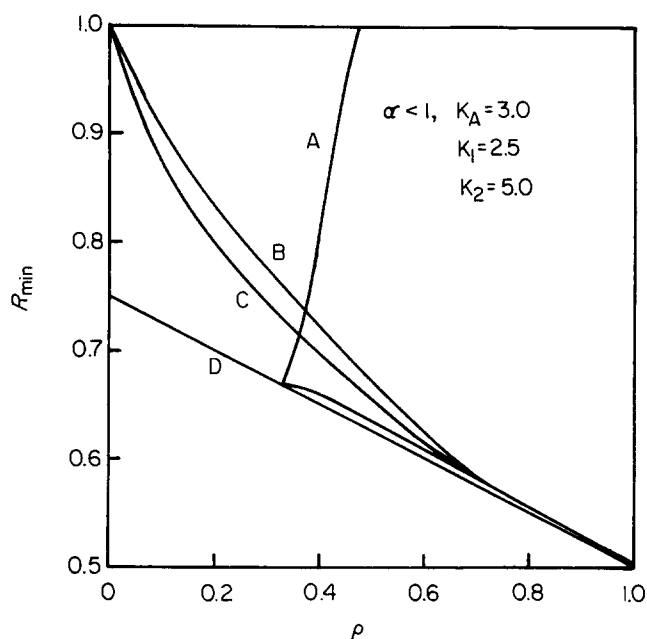


Figure 3 Effect of K_R on R_{\min} . Curves A–D are for $K_R=0, 0.1, 0.5$ and ∞ respectively with $K=2$

Hence at low values of ρ , the blowing agent behaves like a chain extending agent and increased values of ρ cause a decrease in R_{\min} . However, at sufficiently high values of ρ , large amounts of fast reacting B groups are present to consume AA monomer leaving the blowing agent essentially unreacted. The blowing agent now essentially plays the role of a diluent and hence increased ρ results in an increased R_{\min} . This conclusion is confirmed by calculations which show that $\gamma \simeq \delta \simeq 0$ in curve B till the minima is reached. To the left of the left boundary of this curve, gelation will not take place since too few B_3 molecules are there to create sufficient number of connected branch points. No gelation is possible to the right of the right boundary since excess of B_3 monomer is present leading to too many unconnected B groups.

All the curves of *Figure 2* indicate, as expected, that at constant ρ an increased value of K would mean more consumption of AA by CD or larger chain lengths between branch points and hence increased R_{\min} . Another conclusion we can draw from these curves is that, if R is fixed, gels can be formed even if large amounts of blowing agent are added if a retarding agent for its reaction is found.

Effect of K_R . Again, it will be fruitful to investigate the two limits of $K_R=0$ and $K_R \rightarrow \infty$. When $K_R=0$, the D group is unreactive and hence CD acts like a monofunctional blocking agent and $\delta=0$. The gel criteria now reduces to

$$\rho \geq \frac{R_{\min}}{2\beta^2} \quad (44)$$

and stoichiometric relation is given by

$$2R = 2\rho\beta + (1-\rho)\gamma \quad (45)$$

When $\beta=1$, γ is also equal to unity and $R=1+0.5\rho$ (from relationship (45)). We can therefore infer from relationship (44) that gelation will occur only if $\rho \geq 1/3$. This is shown

in *Figure 3* in curve A. The top portion of curve A was obtained for $\alpha < 1$ and $\beta < 1$ for the indicated values of the parameters. The relationships (44) and (45) cannot be combined into one analytical expression and numerical results can be presented only after assuming a value for K . The portion of the curve A for $1/3 \leq \rho \leq 1$ has been calculated for $K=2$. As ρ is increased, the fraction of blowing agent is decreased and the amount of AA monomer wastefully consumed and blocked decreases. Thus R_{\min} decreases as ρ is increased as seen in *Figure 3*.

When $K_R \rightarrow \infty$ the D group reacts instantaneously or in effect each C group that reacts consumes two A groups. Thus $\gamma = \delta$ and therefore gelation occurs as soon as $\beta = 0.5$. Stoichiometry requires that

$$R = \rho\beta + (1-\rho)\gamma = \rho\beta + (1-\rho)[1 - (1-\beta)^K]$$

and therefore

$$R_{\min} = \frac{\rho}{2} + (1-\rho) \left[1 - \left(\frac{1}{2} \right)^K \right]$$

Results of this limit are represented by curve D of *Figure 3* for $K=2$. Note that at $\rho=0$, $\beta=0.5$ is a meaningless criteria and hence gel will form only if $R_{\min}=1$. In this limit also, like in the limit of $K_R \rightarrow 0$, as the value of ρ is increased, R_{\min} decreases and this is to be expected as the blowing agent behaves like a chain extending agent.

The effect of increasing K_R on R_{\min} at constant ρ is quite unexpected as R_{\min} increases at first and decreases later. This can be observed from *Figure 3*. At low values of K_R , the D group does consume A groups but at such slow rates that CD monomer essentially behaves like a blocking agent. Hence, increasing K_R from zero effectively leads to increased consumption of A groups but not to effective chain extension as long as K_R is sufficiently low. Thus initial increases in K_R from zero will increase R_{\min} . However as K_R is increased further the blocking effect vanishes and CD will now participate in effective chain extension or connecting branch points. This effect will then decrease the requirements of A groups and hence R_{\min} will decrease. Another useful conclusion from these results is that if K_R is increased to sufficiently high values by catalysis, gels can still be obtained by addition of larger amounts of blowing agent at constant R .

Figures 4 and 5 display the combined effects of K and K_R for different sets of values.

(ii) R_{\max} versus ρ . This gives us the upper boundary of the gelation envelope. R_{\max} will be greater than unity or the A groups are in stoichiometric excess and hence the upper boundary is obtained when $\beta = \gamma = \delta = 1$. The only parameters of significance therefore are K_A , K_1 and K_2 as relationships (35) and (36) now simplify to

$$\rho \geq \frac{1}{2} \frac{1+K_A}{\alpha_2^* + K_A \alpha_1^*} - \frac{1}{2} \leq 1 \quad (46)$$

and

$$\frac{\alpha_1}{1+K_A \alpha_1} [1 + \alpha_2^* + K_A(1 + \alpha_1^*)] = \frac{2}{R} \quad (47)$$

In particular note that d does not have any effect. The only point common to all gelation envelopes is $\rho=0$ and

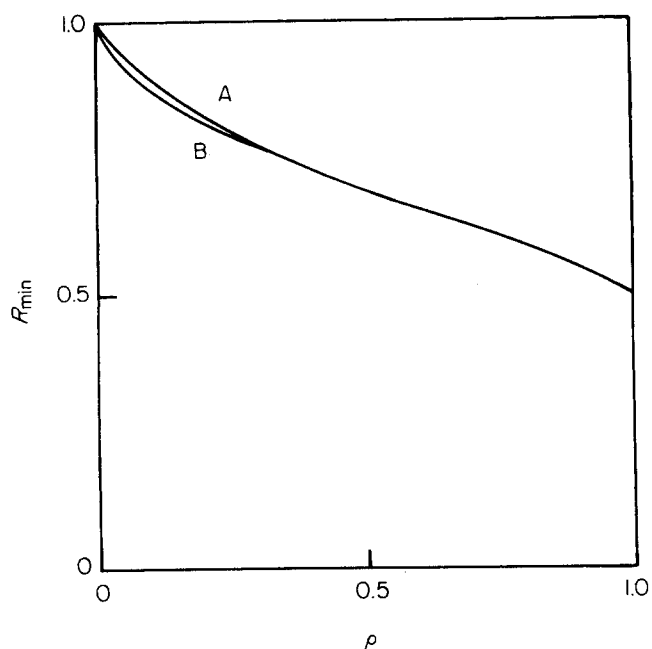


Figure 4 Effect of K_R on R_{\min} . K_R for the curves A and B are 0.1 and 5 respectively with $K=5$

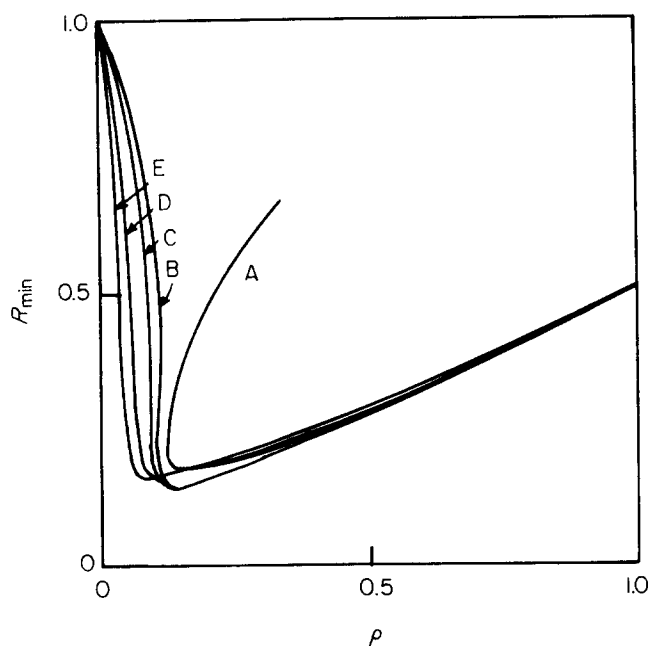


Figure 5 Effect of K_R on R_{\min} . Curves A-E are for $K_R=0, 2, 2.5, 5$ and 7.5 respectively with $K=0.1$

$R_{\max} = 1$. This can be seen from relationship (46) since if $\rho = 0$, relationship (46) can be satisfied only if $\alpha_1^* = \alpha_2^* = 1$ which in turn implies that $\alpha_1 = \alpha_2 = 1$. Numerical results illustrating the effect of K_A , K_1 and K_2 are shown in Figure 6.

Effect of K_A . Note that $K_A \geq 1$ since labelling of 1 and 2 on A groups is arbitrary. For simplicity let us first consider the case when $K_1 = K_2 = 1$. If the value of K_A is greater than unity, A_2 reacts faster than A_1 and hence if large amounts of A_1A_2 monomer are present, all B groups are consumed by A_2 groups leaving A_1 groups unreacted. To promote crosslinking, the A_1 groups have to be forced to react and this can be achieved only by decreasing R at

constant ρ . Thus the effect of increased value of K_A is to decrease R_{\max} , as shown in Figure 6 by curve B.

Effect of K_1 or K_2 . First consider the case when $K_A = 1$ and $K_1 = K_2$. If K_1 or K_2 is greater than unity the polymeric A groups react faster than monomeric A groups or the processes of connection of branch points and chain extension are promoted. Hence larger amounts of AA monomer can be utilized or R_{\max} is increased at constant ρ . This is shown by curve C of Figure 6.

At constant ρ therefore the effects of increased K_A and K_1 (or K_2) on R_{\max} are in the opposite directions. The net effect is determined by the numerical magnitudes of these constants. This is illustrated in Figure 6 by the other curves.

It is observed in all these curves that as ρ is increased R_{\max} increases. When ρ is increased the fraction of B_f increases. Gelation will not occur if A_1A_2 monomer terminates all B, C, D groups without linking two branch points and this happens when A_1A_2 is in excess of R_{\max} . However the chances of two branch points being connected are increased when the fraction of the polyfunctional groups or ρ is increased and therefore more A_1A_2 monomer can be tolerated by the reaction mixture. Hence as ρ is increased R_{\max} also increases.

Gelation envelope in the presence of difunctional monomer

The broad principles discussed in the previous sections will still hold in explaining the influence of the presence of B_2 monomer or when $d \neq 0$. Firstly it has already been noted that the R_{\max} vs. ρ curve is not influenced by d and hence we need to discuss only R_{\min} vs. ρ . The relevant

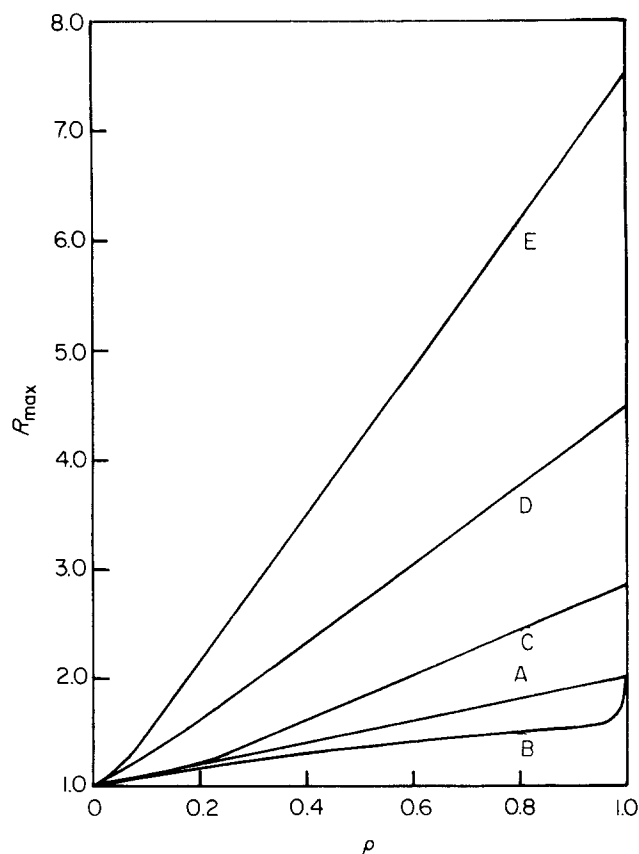


Figure 6 Effect of K_A , K_1 and K_2 on R_{\max} . The values of the above parameters for the various curves are: A: 1, 1, 1; B: 5, 1, 1; C: 1, 4, 4; D: 10, 10, 10 and E: 2.5, 10, 10

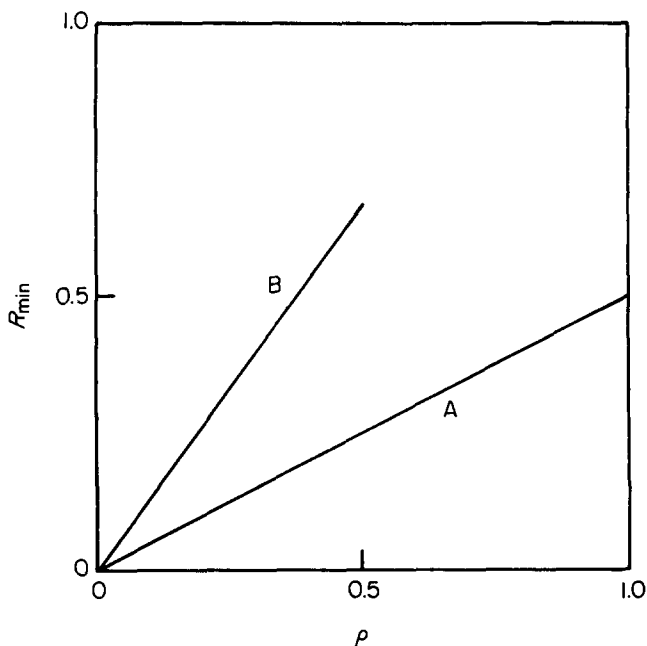


Figure 7 Effect of the addition of the difunctional monomer on R_{\max} for $K=0$. Curves A and B represent $d=0$ and 0.5 respectively

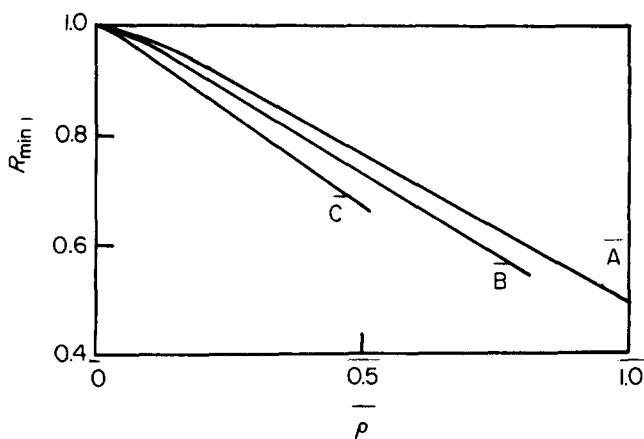


Figure 8 Effect of addition of the difunctional monomer on R_{\min} for $K=\infty$ the curves A-C are for $d=0, 0.2$ and 0.5 respectively

parameters therefore are K and K_R only. The limiting results for K and $K_R \rightarrow 0$ and ∞ can easily be derived and will not be presented. Moreover, the effects of K and K_R are unaltered by the presence of B_2 and hence need not be discussed. We shall focus our attention on the effects of d . It is convenient to recall that $\rho = (1-d)(1-b)$ by relationship (28). Firstly it should be noted that the maximum permissible value for ρ is $(1-d)$ when $b=0$. Further if d is increased while ρ is kept constant, it implies a decrease in the concentration of the blowing agent in the reaction mixture. The results therefore can be understood in terms of the relative effectiveness of B_2 and CD in creating connections between branch points. In the following discussion it is assumed that ρ is kept constant.

(i) $K=0$: Here CD is a nonreactive diluent. Thus if d is increased, the fraction of B_2 monomer, which consumes A groups, is increased. We can therefore expect R_{\min} to increase. This is shown in Figure 7.

(ii) $K \rightarrow \infty$: Here CD is an instantaneously reacting blowing agent and hence consumes more A groups than B_2 monomer. Hence as d is increased, the slow reacting B_2

replaces the fast reacting CD resulting in a decreased R_{\min} . This is shown in Figure 8.

(iii) $K_R=0$: The CD monomer is a monofunctional blocking agent which consumes A groups wastefully. Thus as d is increased we expect R_{\min} to decrease as B_2 does not have any blocking effect. This is shown in Figure 9.

(iv) $K_R \rightarrow \infty$: Here the CD monomer is more effective in chain extension and providing linkages than the B_2 monomer, due to the fact that the D group reacts at a faster rate than a B group. Hence we can expect R_{\min} to increase as d is increased. This is shown in Figure 10.

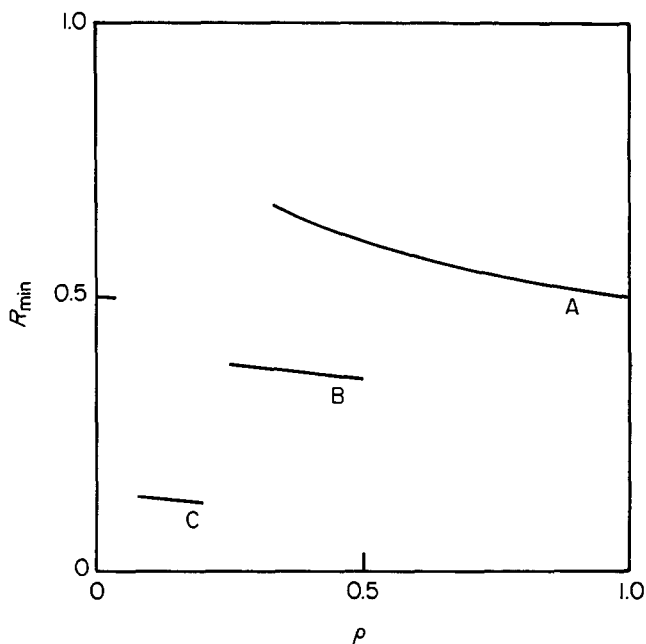


Figure 9 Effect of addition of the difunctional monomer on R_{\min} for $K_R=0$. The curves A-C are for $d=0, 0.5$ and 0.8 respectively

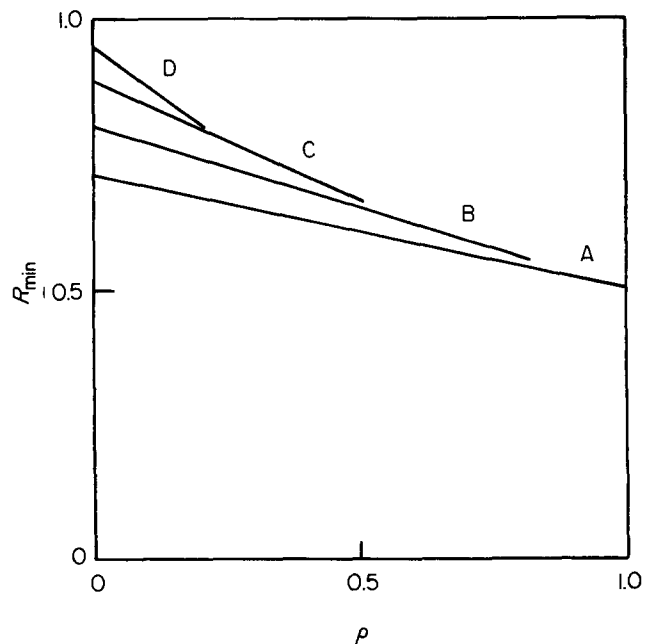


Figure 10 Effect of addition of the difunctional monomer on R_{\min} for $K_R=\infty$. The curves A-D are for $d=0, 0.2, 0.5$ and 0.8 respectively

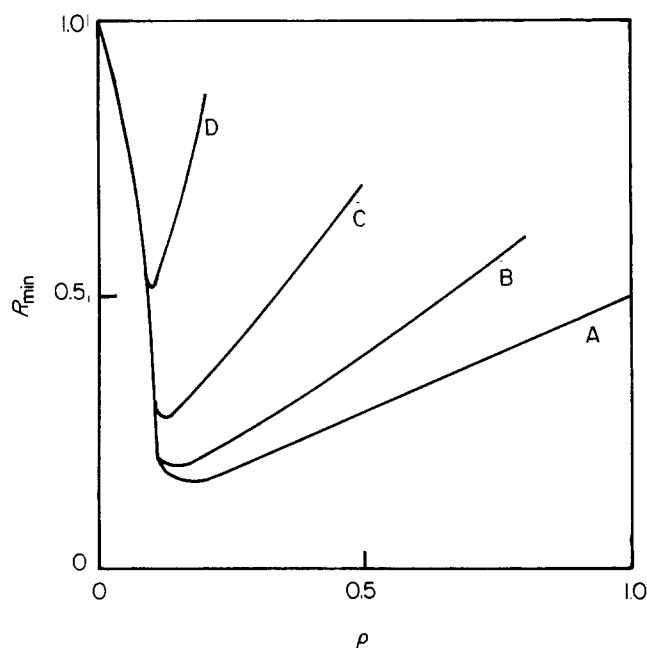


Figure 11 Effect of addition of the difunctional monomer on R_{\min} for $K=0.1$ and $K_R=1$. The curves A–D are for $d=0, 0.2, 0.5$ and 0.8 respectively

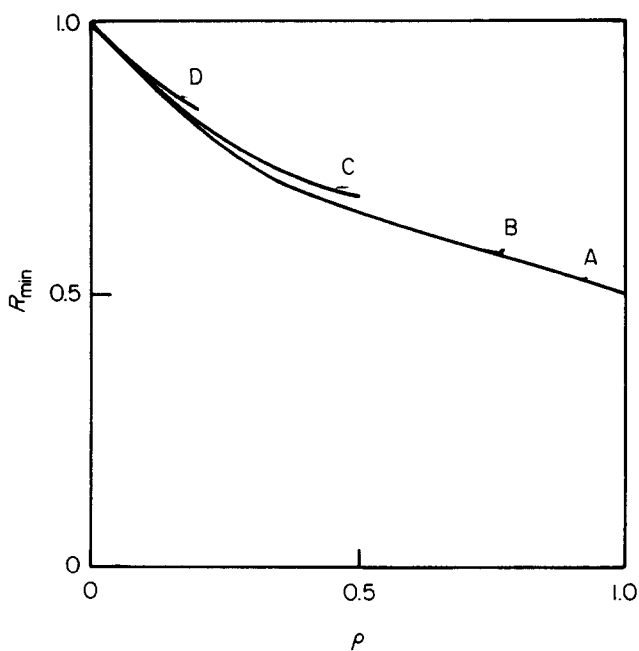


Figure 12 Effect of difunctional monomer concentration on R_{\min} for $K=2$ and $K_R=0.1$. Curves A–D are for $d=0, 0.2, 0.5$ and 0.8 respectively

For values of K and K_R in between the above discussed limits, the behaviour is illustrated in *Figures 11* and *12* and can be explained along lines similar to the ones used above and in the previous sections.

Gel point calculation for incomplete conversions

The curves for incomplete conversions will lie inside the gelation envelope. If a value of α_1 (< 1) is fixed, all the other values of $\alpha_2, \alpha_1^*, \alpha_2^*, \beta, \gamma$ and δ can be calculated from the kinetic parameters. For these probabilities, the values of R, ρ and d that will satisfy relationships (35) and (36) can be determined and plots of R versus ρ can be generated. It

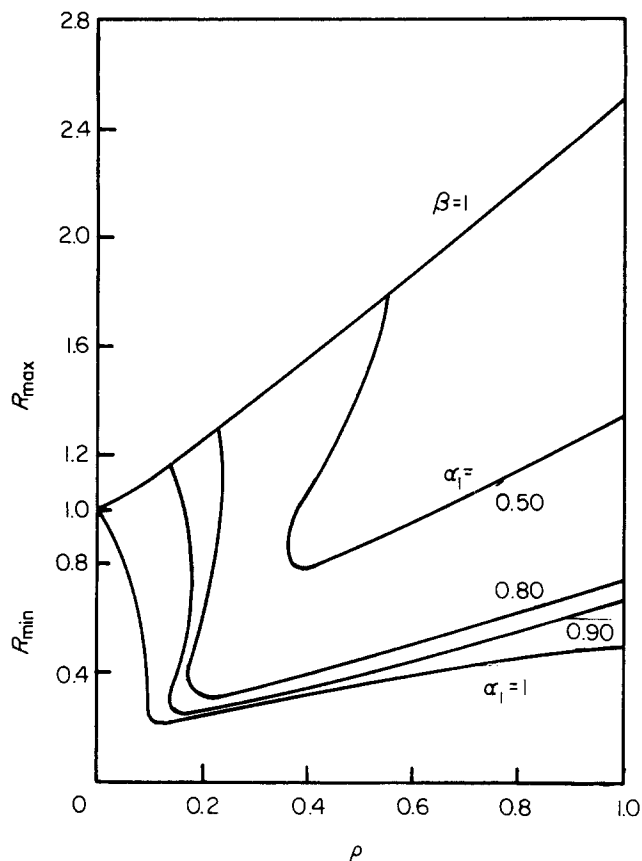


Figure 13 Gelation envelopes for incomplete conversion of all the monomers. The Figure is for $K=0.1, K_R=2, K_A=2.0, K_1=1.5$ and $K_2=3.0$

was found that the effect of rate constants on such plots was similar to that observed on gelation envelopes. A typical plot is shown in *Figure 13*. The curves start inside the lower half of the gelation envelope. To start with $\beta > 0.5$ and it steadily increases as R is changed. At some value of R, β attains a value of unity. This particular value of R will lie on R_{\max} vs. ρ curve. Such parametric curves give an indication of the extents of conversion attained when gelation occurs for any initial composition specified by R, ρ and d lying inside the gelation envelope.

CONCLUSIONS

A model for describing the curing behaviour of a monomer with structural asymmetry as well as first shell substitution effects has been developed and was applied to systems consisting of a diisocyanate (A_1A_2), a polyol (B_f), a diol (B_2) and foaming agent water (CD). The gelation condition was derived and it predicts (i) whether a given initial composition of the reaction mixture will lead to a gel or not and (ii) the fractional conversions of functional groups required before gelation can occur.

Gel formation at complete conversion of the groups in stoichiometric deficiency defines the boundaries of gelation envelope and only those initial compositions which lie inside the envelope can lead to the formation of infinite networks. The boundaries of the gelation envelope have been presented as a plot of the ratio of the concentration of A groups and the concentrations of groups with which A can react, R_{\max} or R_{\min} , versus the fraction of the polyfunctional groups ρ .

Water can influence gelation behaviour in three ways

by acting like a non-reactive diluent, a monofunctional blocking agent and an effective chain extender linking branch points. As the water content in the reaction mixture is decreased, R_{\min} would increase if it were to operate like a nonreactive diluent and R_{\min} would decrease if the other two ways were operative. The total behaviour is a combination of all the three aspects and is determined by the relative speeds of reaction of water and hydroxyl groups.

The asymmetric characteristics of the A_1A_2 monomer can either promote or retard chain extension. Structural asymmetry retards chain extension. A first shell substitution effect that makes polymeric A ends to react faster than monomeric A ends promotes chain extension. At a constant ρ , R_{\max} was found to increase if the overall effect of structural asymmetry and first shell substitution effect was to promote chain extension.

Calculation of conversions at which infinite networks form for compositions which lie inside the gelation envelope has also been illustrated.

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APPENDIX I

If it is assumed that reactivity of an end group is unaffected by chain length and that second order kinetics apply, the following equations can be written.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A]\{[B] + K[C] + KK_R[D]\} \quad (A1)$$

$$\frac{dA_1^*}{dt} = k_1[A]\{[B] + K[C] + KK_R[D]\} \quad (A2)$$

$$\frac{dA_2^*}{dt} = k_2[A]\{[B] + K[C] + KK_R[D]\} \quad (A3)$$

$$-\frac{d[A_1^*]}{dt} = -\frac{dA_1^*}{dt} + k_1^*[A_1^*]\{[B] + K[C] + KK_R[D]\} \quad (A4)$$

$$-\frac{d[A_2^*]}{dt} = -\frac{dA_2^*}{dt} + k_2^*[A_2^*]\{[B] + K[C] + KK_R[D]\} \quad (A5)$$

$$-\frac{d[C]}{dt} = K[C]\{(k_1 + k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\} \quad (A6)$$

$$-\frac{d[D]}{dt} = \frac{d[C]}{dt} + KK_R[D]\{(k_1 + k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\} \quad (A7)$$

$$-\frac{d[B]}{dt} = [B]\{(k_1 + k_2)[A] + k_1^*[A_1^*] + k_2^*[A_2^*]\} \quad (A8)$$

Since initially only monomer is present, $A_1^* = A_2^* = 0$ initially¹². Dividing relationship (A3) by relationship (A2) and integrating with the above initial condition

$$A_2^* = K_A A_1^* \quad (A9)$$

where $K_A = k_2/k_1$. Combining this with relationships (16) and (17) it is easy to show that

$$\frac{\alpha_2(1 - \alpha_1)}{\alpha_1(1 - \alpha_2)} = K_A \quad (A10)$$

Initially $[A_1^*] = [A_2^*] = 0$ and these are the initial conditions for relationships (A4) and (A5)¹². Substituting relationship (A3) into relationship (A4) and dividing the resulting equation by relationship (A1),

$$\frac{d[A_1^*]}{d[A]} = -\frac{k_2}{k_1 + k_2} + \frac{k_1^*}{k_1 + k_2} \frac{[A_1^*]}{[A]}$$

The initial A_1A_2 monomer concentration is $[A]_0$. Hence the above can be integrated¹² with the condition that $[A_1^*] = 0$ when $[A] = [A]_0$. The result is

$$\frac{[A_1^*]}{[A]_0} = \frac{K_A}{K_1 - 1 - K_A} \left[\frac{[A]}{[A]_0} - \left(\frac{[A]}{[A]_0} \right)^{K_1} \right] \quad (A11)$$

where $K_1 = k_1^*/k_1$. Similarly substituting relationship (A2) into (A5), dividing by relationship (A1) and integrating

$$\frac{[A_2^*]}{[A]_0} = \frac{1}{K_A K_2 - K_A - 1} \left[\frac{[A]}{[A]_0} - \left(\frac{[A]}{[A]_0} \right)^{K_A K_2} \right] \quad (A12)$$

where $K_2 = k_2^*/k_2$. These results are identical to those given in ref. 12 and hence equations (20), (23) and (24) of that reference, reproduced below, are also valid

$$\alpha = \frac{[A]}{[A]_0} = \frac{1 - \alpha_1}{K_A \alpha_1 + 1} = \frac{K_A(1 - \alpha_2)}{\alpha_2 + K} \quad (A13)$$

$$1 - \alpha_1^* = \frac{K_A \alpha_1 + 1}{\alpha_1(K_1 - 1 - K_A)} \left\{ \frac{1 - \alpha_1}{K_A \alpha_1 + 1} - \left(\frac{1 - \alpha_1}{K_A \alpha_1 + 1} \right)^{K_1} \right\} \quad (A14)$$

$$1 - \alpha_2^* = \frac{K_A \alpha_1 + 1}{\alpha_1(K_A K_2 - 1 - K_A)} \left\{ \frac{1 - \alpha_1}{K_A \alpha_1 + 1} - \left(\frac{1 - \alpha_1}{K_A \alpha_1 + 1} \right)^{K_A K_2} \right\} \quad (A15)$$

The above can be easily obtained by combining relationships (16) to (20) with relationships (A9) to (A12).

For the other groups, the initial conditions are $[C]=[C]_0$, $[D]=0$ and $[B]=[B]_0=f[B_f]_0+2+[B_2]_0$. Dividing relationship (A6) by (A8) and integrating after using relationships (21) and (22)

$$(1-\gamma)=(1-\beta)^K \quad (\text{A16})$$

Dividing relationship (A7) by (A6) and integrating after using (22) and (23)

$$\delta=\gamma-\frac{1-\gamma}{K_R-1}[1-(1-\gamma)^{K_R-1}] \quad (\text{A17})$$

Substituting these relations in (24) and equating it to (30) it is easy to show that stoichiometric relation reduces to

$$\frac{\alpha_1}{K_A\alpha_1+1}[1+\alpha_2^*+K_A(1+\alpha_1^*)]=\frac{1}{R(1-d)}[2\rho\beta+(1-d-\rho)(\gamma+\delta)]$$

which is equation (36).

Similarly it is easy to show that

$$P_{BB}=4\frac{\alpha_2^*+K_A\alpha_1^*}{1+\alpha_2^*+K_A(1+\alpha_1^*)}\frac{\rho d\beta^2}{2\rho\beta+(1-d-\rho)(\gamma+\delta)}$$

$$P_{CD}=4\frac{\alpha_2^*+K_A\alpha_1^*}{1+\alpha_2^*+K_A(1+\alpha_1^*)}\frac{(1-d-\rho)\delta}{2\rho\beta+(1-d-\rho)(\gamma+\delta)}$$

$$P_{B_f}=4\frac{\alpha_2^*+K_A\alpha_1^*}{(1+\alpha_2^*)+K_A(1+\alpha_1^*)}\frac{\rho(1-d)\beta}{2\rho\beta+(1-d-\rho)(\gamma+\delta)}$$

These relationships can be substituted into the gelation condition (34) to obtain (35). Further if any one probability is known the rest can be calculated for a given initial composition specified by R , ρ and d . For example if α_1 is known, α , α_1^* and α_2^* can be calculated by relationships (A13), (A14) and (A15) respectively. γ and δ are related to β and hence the stoichiometric relationship (36) can be used to obtain β . The value of α_1 at any time can be obtained by integration of (A2) as indicated earlier¹².