

Polymer Networks including Ring Forming Parameter in the Cure of Diglycidyle Ether of Bisphenol A and Propylene Glycol Diamino Ether

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A molecular model was constructed for the network formation through the polymerisation of RA₄ + RB₂ type reaction. The model was intended to be applied for the gel point prediction in the curing of diglycidyle ether of bisphenol A and propylene glycol diamino ether which correspond with RA₄ and RB₂ respectively. The ring forming parameter was incorporated into the model to improve the classical gelation theory; the parameter is the ratio of internal and external reactant groups, and was used to measure the competition between inter- and intramolecular reaction. Specific reactions of RA₄ and RB₂ were considered to give the internal concentration of reactant groups.

Key words: ring structure, network formation, molecular model, gel point, epoxy, cure

1. INTRODUCTION

An experimental research work has so far been carried out in our Laboratory on the polymerisation of diglycidyle ether of bisphenol A (DGEBA) and propylene glycol diamino ether (PPG diamine) in terms of network formation and gel point estimation.[1] Polymerisation of diamine and diepoxy molecules has been extensively researched by many research groups.[2-5]

In order to make better interpretation on our experimental results, it was shown to be essential to estimate the quantity of the ring structures which do not contribute to the elasticity but exist in the network formed by the polymerisation.[6] The quantity of the ring structures mean the lengths and the numbers of the polymer chains forming them. Although this estimation is considered to be very difficult, to build up a suitable model will help to carry it out.[7] A summary of the previous study was shown below.

(1) According to the proceeding of the reaction, H atoms of the amine group were categorised as H1, H2, HR, where the atoms which belong to the unreacted amine groups were defined as H1. The unreacted hydrogen atoms which belong to the semireacted amine groups were defined as H2. The reacted hydrogen atoms were defined as HR. The progress of the reaction was expressed by the fraction of these H atoms, p_{H1} , p_{H2} and p_{HR} , where $p_{H1}=(C_{H1}/C_{H1}^0)$, $p_{H2}=(C_{H2}/C_{H1}^0)$ and $p_{HR}=(C_{HR}/C_{H1}^0)$; C_{H1} , C_{H2} , C_{HR} and C_{H1}^0 are the concentration of H1, H2, HR and H1 before reaction respectively. Similarly p_{EP} was defined as (C_{EP}/C_{EP}^0) , where C_{EP} and C_{EP}^0 are the concentration before and after the reaction starts. Note that practically p_{HR} is equivalent with the extent of reaction measured by FT-IR method.[1]

(2) As the reaction proceeds the state of PPG diamine unit varies. The state was classified into six as shown schematically in Figure 1.

(3) Using the probability, γ_a and γ_b , the equation for gelation was written as $\gamma_a \times \gamma_b = 1$ (The definition of γ_a and γ_b was written in detail below.), where ring forming parameters were not incorporated. The result derived from this equation was that $p_{HR} = (1/\sqrt{3})$. It is

consistent with the gel point of the classical Flory-Stockmayer theory, which proves the validity of the molecular model shown in previous study.

As a further consideration to these remarks, this study discusses the network formation model including the ring forming parameter.

2. PROBABILITY OF PATH CONTINUATION

Concerning the classification for the states of PPG diamine unit shown in Figure 1, X_i can be expressed as a function of p_{H1} , p_{H2} and p_{HR} , where the mole fractions of these six states were written as X_i ($i=1-6$). X_i finally become functions of p_{HR} , because p_{H1} and p_{H2} can be given as functions of p_{HR} .

$$\begin{aligned} X_1 &= p_{H1}^2 & X_2 &= 4p_{H1}p_{H2} \\ X_3 &= 2p_{H1}(p_{HR} - p_{H2}) & X_4 &= 4p_{H2}^2 \\ X_5 &= 4p_{H2}(p_{HR} - p_{H2}) & X_6 &= (p_{HR} - p_{H2})^2 \end{aligned} \quad (1-6)$$

State 1	State 2	State 3
State 4	State 5	State 6

Figure 1. Classification of PPG diamine unit.

In the network model without ring forming parameter the probabilities of Q_{H1} , Q_{H2} and Q_{HR} were introduced to express those of finding H1, H2 and HR in PPG diamine unit; some examples of them were shown below.

$$\begin{aligned} Q_{H1,i=1} &= \frac{4X_1}{4X_1 + 2X_2 + 2X_3}, & Q_{H1,i=4} &= 0 \\ Q_{H1,i=2} &= \frac{2X_2}{4X_1 + 2X_2 + 2X_3}, & Q_{H1,i=5} &= 0, \\ Q_{H1,i=3} &= \frac{2X_3}{4X_1 + 2X_2 + 2X_3}, & Q_{H1,i=6} &= 0. \end{aligned} \quad (7-12)$$

Furthermore, in the PPG diamine unit, β_i , the number of way out to go from a reacted H atom to a next diepoxy unit was counted, so that the probabilities, γ_a and γ_b could be given. γ_a stands for the probability of path

continuation out of PPG diamine unit attached to a randomly chosen H atom, either reacted or unreacted. Similarly, γ_b stands for the probability out of DGEBA unit attached to a randomly chosen epoxy group, either reacted or unreacted. (These descriptions will appear again in Section 3.)

There are three kinds of contributions to γ_a ; namely, those come from Q_{H1} , Q_{H2} and Q_{HR} . If we regard S_{H1} as the contribution from H1 to γ_a , then S_{H1} means the probability of path continuation from H1 atom to the next DGEBA unit on condition that randomly chosen H atom was H1 atom. Similar definitions can be given for the probabilities S_{H2} and S_{HR} . Therefore we have,

$$\gamma_a = S_{H1} + S_{H2} + S_{HR} \quad (13)$$

On the other hand, the probability to chose H1 atom from all of H atoms is p_{H1} which can be determined by the experiment. Now, S_{H1} can be obtained as follows;

$$S_{H1} = p_{H1} \times \sum_{i=1}^6 Q_{H1,i} \times \beta_i \quad (14)$$

where $\beta_1 = \beta_4 = \beta_5 = \beta_6 = 0$, $\beta_2 = 1$, $\beta_3 = 2$. These β_i values can be determined by counting the number of H1 and HR atoms.

Similarly, the expressions for $Q_{H2,i}$ and β_i , as well as those for $Q_{HR,i}$ and β_i ($i=1\sim 6$) can be written using X_i . Therefore, γ_a can be calculated. Furthermore, γ_b can be calculated as a function of p_{HR} , consequently $\gamma_b = p_{HR}$ holds.

3. RING FORMING PARAMETER

In order to modify classical gelation theory, the ring forming parameter was introduced into the network formation model used in this study. The ring forming is illustrated in Figure 2 to show the competition between inter- and intramolecular reaction occurring throughout a polymerisation.[8-10] In the illustration, A means a H atom in PPG diamine, B is an epoxy group. The \square group is about to react with an epoxy group. $C_{b,int}$ is the total effective concentration of B groups from the same molecule around \square . $C_{b,ext}$ is the concentration of B groups from other molecules. ν is the number of bonds in the chain forming the smallest ring structure.

It is assumed first that the intrinsic rate of reaction between A and B group is insensitive to whether inter- or intramolecular reaction is occurring, and second that the probabilities of inter- and intramolecular reactions are directly proportional to concentrations. The first assumption neglects any orientation effects which may be prevalent in intramolecular reaction, and the second neglects the fact that the reaction between the amine and the epoxy groups may have a complex mechanism and the expression for the rate of reaction may not be simply factorisable in terms of concentrations.

The ring forming parameter λ_b is given concerning B group as;

$$\lambda_b = \frac{C_{b,int}}{C_{b,int} + C_{b,ext}} \quad (15)$$

Similarly, λ_a , $C_{a,int}$, and $C_{a,ext}$ can be defined when a B group is about to react with A groups.

As a next step, the size of ring structure was given; for example, the smallest ring structure is comprised of a PPG diamine and a DGEBA unit. This structure is regarded as that of $j=1$. The second smallest ring consists of two of each unit and was regarded as the

structure of $j=2$. In consequence, $C_{b,int}$ shown in Figure 2 is the total of the concentration of each size.

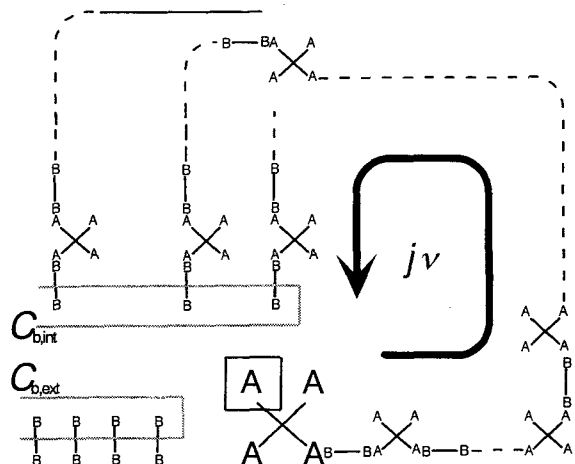


Figure 2. Schematic representation of the competition between inter- and intramolecular reaction. See text in detail.

$$C_{b,int} = \sum_{j=1}^{\infty} C_{b,int,j} \quad (16)$$

In counting the concentration $C_{b,int,j}$, a specific feature was given below; that is, the ring structure can be regarded as a chain which end-to-end distance is equal to zero.[11] It is then, assumed that the distribution of end-to-end distance can be written by independent Gaussian sub-chain statistics of eq.(17) for the polymer chain including PPG diamine and DGEBA.

$$P(\bar{r}, j\nu) = \sqrt{\left(\frac{3}{2\pi \langle r^2 \rangle}\right)^3} \exp\left(-\frac{3\bar{r}^2}{2 \langle r^2 \rangle}\right) \quad (17)$$

$$\langle r^2 \rangle = \nu j b^2 \quad (18)$$

\bar{r} is end-to-end vector. b is the effective bond length of the chain of νj bonds. In particular, if a definition is given on P_{ab} with dividing by Avogadro constant, N_{AV} and substituting $\bar{r} = 0$ and $j=1$, then it is a useful parameter in counting the concentration of $C_{a,int,j}$ and $C_{b,int,j}$.

$$P_{ab} = \frac{1}{N_{AV}} \sqrt{\left(\frac{3}{2\pi \langle r^2 \rangle}\right)^3} \quad (19)$$

Once the molecular structure of the monomer is given, values of ν and b can in principle be estimated. P_{ab} means the concentration of intramolecular B groups of $j=1$ around the A group; it can also be said that P_{ab} means the concentration of intramolecular A groups of $j=1$ around the B group. Equation (19) neglects any effects of the connectivity of the branch units on the statistics governing the mutual separations of pairs of end groups in a branched chain. Consequently, eq.(16) can be calculated as follows;

$$C_{b,int} = \sum_{j=1}^{\infty} \frac{1}{N_{AV}} \sqrt{\left(\frac{3}{2\pi \langle r^2 \rangle}\right)^3} = \frac{1}{N_{AV}} \sum_{j=1}^{\infty} \sqrt{\left(\frac{3}{2\pi \nu j b^2}\right)^3} = P_{ab} \sum_{j=1}^{\infty} \left(\frac{1}{j}\right)^{3/2} = 2.61 P_{ab}$$

In the above calculation Truesdell function was taken into account.[12] Its use allows ring structures of all sizes ($j=2, 3, \dots$) to be accounted for. With these preparations, now λ_a and λ_b become solvable. The outline to find P_{ab} , which is the final target in our research work, is; first, to give $(\gamma_a \times \gamma_b)$ as a

function of P_{ab} and p_{HR} , then put p_{HR} value at gel point obtained from experiments to the equation of gelation, $(\gamma_a \times \gamma_b) = 1$.

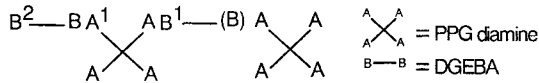


Figure 3. Schematic representation for the chain growth in the polymerisation of DGEBA and PPG diamine.

It should be noted for γ_a and γ_b using the schematic representation of Figure 3 for the chain growth in a polymerisation. Imagine that the chain grows from right to left, specifically the growth from B^1 to B^2 was considered in the following sections. γ_b is the probability that B^1 reacts with PPG diamine of the left side, γ_a is the probability that A^1 reacts with DGEBA of left side.

4. INTERNAL CONCENTRATION OF H ATOM

In order to count the number of A group around B^1 , the H atom reacted with (B) which is paired with B^1 was considered, then $C_{a,int,j}$ became countable. The probability that the PPG diamine is in i -th state ($i=1\sim 6$) is equivalent to $Q_{HR,i}$, because $Q_{HR,i}$ was the fraction of i -th state on condition that the reacted H atom had been chosen. Obviously we have the following equation.

$$Q_{HR,i=2} + Q_{HR,i=3} + Q_{HR,i=4} + Q_{HR,i=5} + Q_{HR,i=6} = 1 \quad (21)$$

The number of the intramolecular A groups around B^1 was counted in order of j when PPG diamine was in i -th state in the estimation of $C_{a,int,j}$. Note that $C_{a,int,j}$ was written hereafter with abbreviating the subscript of i to make it simple. It can be expressed as;

$$[\text{intramolecular A groups}] = Q_{HR,i} C_{a,int,j} \times [\text{unreacted A groups}] \quad (22)$$

Square brackets mean the concentration. Estimation of $C_{a,int,i}$ was described below concerning $i=1\sim 6$ on the basis of this equation.

(1) $C_{a,int,i=2}$: (B) reacts with the 2nd state.

B^1 forms a ring of $j=1$. Because the forming has three ways, the concentration of A groups of $j=1$ is $C_{HI}^0 \times p_{EP} Q_{HR,i=2} C_{a,int,j=1} \times 3$; where, p_{EP} comes from the condition that the reaction of (B) is necessary for PPG diamine to be the 2nd state.

The ring formation of $j>2$ is impossible when the PPG diamine is in the 2nd state. Therefore we have the following equation.

$$C_{a,int,i=2} = C_{HI}^0 \times p_{EP} Q_{HR,i=2} C_{a,int,j=1} \times 3$$

$C_{a,int,j=1} = P_{ab}$ holds when there are no chains of $j>2$. Moreover, we have $p_{EP} = p_{HR}$ when the stoichiometric ratio is unity. Therefore, the internal concentration can be given as;

$$C_{a,int,i=2} = C_{HI}^0 \times 3 p_{HR} Q_{HR,i=2} P_{ab} \quad (23)$$

(2) $C_{a,int,i=3}$: (B) reacts with the 3rd state.

B^1 forms a ring of $j=1$. Because the forming has two ways, the concentration of A group of $j=1$ is $C_{HI}^0 \times p_{EP} Q_{HR,i=3} C_{a,int,j=1} \times 2$. p_{EP} comes from the same reason as the situation of $i=2$. The concentration of $j=2$ is $C_{HI}^0 \times p_{EP} Q_{HR,i=3} C_{a,int,j=2} \times 2(1-p_{HR})$. The factor $2(1-p_{HR})$ is the number of opportunities of forming a ring structure, that is, the number of unreacted A groups on

PPG diamine unit of $j=2$. The same expressions can be obtained for the concentration of $j=3, 4, \dots$. The total internal concentration on condition that the reacted PPG diamine was in the 3rd state can be obtained from the sum over $j=2, 3, 4, \dots$.

$$C_{a,int,i=3} = C_{HI}^0 \times 2 p_{HR} Q_{HR,i=3} P_{ab} (2 + 3.22(1-p_{HR})) \quad (24)$$

(3) $C_{a,int,i=4}$: (B) reacts with the 4th state.

B^1 forms a ring of the same structure as that considered in $C_{a,int,i=3}$. Therefore $C_{a,int,i=4}$ can be given by the following equation.

$$C_{a,int,i=4} = C_{HI}^0 \times 2 p_{HR} Q_{HR,i=4} P_{ab} (2 + 3.22(1-p_{HR})) \quad (25)$$

(4) $C_{a,int,i=5}$: (B) reacts with the 5th state.

B^1 forms a ring of $j=1$ in only one way. The concentration of A group of $j=1$ is $C_{HI}^0 \times p_{EP} Q_{HR,i=5} C_{a,int,j=1}$. The concentration of $j>2$ can be derived in the same way as that of $C_{a,int,i=3}$. Because there is bifurcation it becomes twice as large as the concentration when (B) reacts with 3rd state. Thus, the following can be given.

$$C_{a,int,i=5} = p_{EP} Q_{HR,i=5} C_{a,int,j=1} + 2 \sum_{j=2}^{\infty} p_{EP} Q_{HR,i=5} C_{a,int,j} \times 2(1-p_{HR})$$

$$= C_{HI}^0 \times p_{EP} Q_{HR,i=5} P_{ab} [1 + 4(\phi(1,3/2) - 1)(1-p_{HR})]$$

$$= C_{HI}^0 \times p_{HR} Q_{HR,i=5} P_{ab} [1 + 6.44(1-p_{HR})] \quad (26)$$

(5) $C_{a,int,i=6}$: (B) reacts with the 6th state.

When (B) reacts with PPG diamine of the 6th state the ring structure of $j=1$ does not form. Concerning the ring of $j=2$, the derivation used when $C_{a,int,i=3}$ was counted can be applied to give $C_{a,int,j=2}$. The 6th state causes three-ways branching in comparison with the 3rd state.

$$C_{a,int,i=6} = C_{HI}^0 \times 3 \sum_{j=2}^{\infty} p_{EP} Q_{HR,i=6} C_{a,int,j} \times 2(1-p_{HR})$$

$$= C_{HI}^0 \times 6 p_{EP} Q_{HR,i=6} P_{ab} (\phi(1,3/2) - 1)(1-p_{HR})$$

$$= C_{HI}^0 \times 9.66 p_{HR} Q_{HR,i=6} P_{ab} (1-p_{HR}) \quad (27)$$

As shown in equations (23-27), $C_{a,int,i}$ could be counted for $i=1\sim 6$. It should be noted that $C_{a,int,i}$ is expressed by three variables of p_{HR} , $Q_{HR,i}$ and P_{ab} . Further, the value of $Q_{HR,i}$ is fixed if p_{HR} is determined. Consequently the expression of λ_a can be written using p_{HR} and P_{ab} .

5. INTERNAL CONCENTRATION OF EPOXY GROUP

Next, the probability of the intramolecular reaction is calculated when A^1 is on the point of reacting with DGEBA of left side as shown in Figure 3. That is, we are going to count $C_{b,int,i}$ with the manner used in counting $C_{a,int,i}$. It follows that, at first a PPG diamine unit including A^1 is classified according to $i=1\sim 6$, then the internal concentration of epoxy group is counted for j using the same idea of eq. (22).

It obviously cannot happen that the PPG diamine is in the 1st state because the PPG diamine unit is presupposed to react with B^1 . In addition, ring formation is impossible when the PPG diamine is in the 2nd state. Thus, $C_{b,int,i=1,2} = 0$.

(1) $C_{b,int,i=3}$: A^1 is included in the 3rd state.

Specific reactions of the PPG diamine in the 3rd state were considered. A^1 forms a ring structure of $j=1$ only when (B) is unreacted. The concentration of (B) is $C_{HI}^0 \times Q_{HR,i=3} \times C_{b,int,j=1} (1-p_{EP})$.

Concerning the ring structure of $j=2$, the internal concentration of B can be written as $C_{H1}^0 \times Q_{HR,i=3} \times p_{EP} \times C_{b,int,j=2} \times 2p_{HR}(1-p_{EP})$. p_{EP} preceding $C_{b,int,j=2}$ was placed because the reaction of (B) is necessary to become a ring of $j=2$. p_{HR} was placed because the reaction of PPG diamine at the right side of (B) is necessary to become a ring of $j=2$. The concentration of B groups of $j>3$ can be counted similarly. The result of addition over $j=1, 2, 3, \dots$ will be given below.

$$C_{b,int,i=3} = C_{H1}^0 \times Q_{HR,i=3} \times C_{b,int,j=1} (1-p_{EP}) + C_{H1}^0 \times \sum_{j=2}^{\infty} Q_{HR,i=3} \times p_{EP} C_{b,int,j} \times 2p_{HR} (1-p_{EP}) = C_{H1}^0 \times Q_{HR,i=3} P_{ab} (1-p_{HR}) (1+3.22p_{HR}^2) \quad (28)$$

(2) $C_{b,int,i=4}$: A^1 is included in the 4th state.

A^1 forms a ring of the same structure as that considered in $C_{b,int,i=3}$. Therefore $C_{b,int,i=4}$ can be given by the following equation.

$$C_{b,int,i=4} = C_{H1}^0 \times Q_{HR,i=4} P_{ab} (1-p_{HR}) (1+3.22p_{HR}^2) \quad (29)$$

(3) $C_{b,int,i=5}$: A^1 is included in the 5th state.

To divide the situation into two whether (B) is reacted or unreacted will help to consider the concentration of intramolecular B group. If (B) is unreacted the ring structure will be $j=1$, which forms in two ways. Thus the concentration is $C_{H1}^0 \times 2Q_{HR,i=5} \times C_{b,int,j=1} (1-p_{EP})$. If (B) is reacted then the ring structure will be that of $j>2$, and there are two ways to form it. For $j=2$, the concentration is $C_{H1}^0 \times Q_{HR,i=5} \times p_{EP} C_{b,int,j=2} \times 2p_{HR} (1-p_{EP})$ in each way, then the total is double the concentration. Similar expression can be obtained for $j=3, 4, \dots$; $C_{b,int,i=5}$ can be given by the sum over $j=1, 2, 3, \dots$.

$$C_{b,int,i=5} = C_{H1}^0 \times 2Q_{HR,i=5} C_{b,int,j=1} \times (1-p_{EP}) + 2 \sum_{j=2}^{\infty} Q_{HR,i=5} p_{EP} C_{b,int,j} \times 2p_{HR} (1-p_{EP}) = C_{H1}^0 \times 2Q_{HR,i=5} P_{ab} (1-p_{HR}) (1+3.22p_{HR}^2) \quad (30)$$

(4) $C_{b,int,i=6}$: A^1 is included in the 6th state.

If (B) is unreacted, the ring of $j=1$ forms in three ways. Thus, the internal concentration of B around A^1 is $C_{H1}^0 \times 3Q_{HR,i=6} \times C_{b,int,j=1} (1-p_{EP})$. If (B) is reacted then it forms the ring structure of $j>2$ in three ways. As a consequence;

$$C_{b,int,i=6} = C_{H1}^0 \times 3Q_{HR,i=6} \times C_{b,int,j=1} \times (1-p_{EP}) + C_{H1}^0 \times 3 \sum_{j=2}^{\infty} Q_{HR,i=6} p_{EP} C_{a,int,j} \times 2p_{HR} (1-p_{EP}) = C_{H1}^0 \times 3Q_{HR,i=6} P_{ab} (1-p_{HR}) (1+3.22p_{HR}^2) \quad (31)$$

As shown in equations (28–31), $C_{b,int,i}$ could be counted for $i=1-6$.

6. THE INCORPORATION OF RING FORMING PARAMETER INTO γ_a AND γ_b

As can be seen in Section 4, $C_{a,int,i}$ could be counted. It is necessary to show the relation between $C_{a,int,i}$ and λ_a as well as λ_a and γ_b . It is also necessary to show the relation of $C_{b,int,i}$, λ_b and γ_a in order to accomplish the equation for network formation including the ring forming parameter.

Then, λ_a' was defined as shown in the following equation, to give the relation between $C_{a,int,i}$ and λ_a .

$$\lambda_a' = C_{a,int} / C_{a,ext} = \sum_{i=1}^6 C_{a,int,i} / C_{H1}^0 (1-p_{HR}) \quad (32)$$

The relation between λ_a and λ_a' is;

$$\lambda_a = (\lambda_a' / (1 + \lambda_a')) \quad (33)$$

The calculation of γ_b was mentioned briefly in Section 2; the number of way out must be counted in this calculation. The number of way out to continue to next PPG diamine through the intermolecular reaction is $(1-\lambda_a)$ taking account of the ring formation. Therefore the expression for γ_b can be obtained as; [6]

$$\gamma_b = (1-p_{EP}) \frac{Z_2}{2Z_1 + Z_2} (1-\lambda_a) + p_{EP} \frac{2Z_3}{Z_2 + 2Z_3} (1-\lambda_a) \quad (34)$$

On the other hand, $\lambda_{b,i}$ can be expressed using $C_{b,int,i}$ derived in Section 6 for $i=1 \sim 6$ as;

$$\lambda_{b,i} = C_{b,int,i} / (C_{b,int,i} + C_{b,ext}) \quad (35)$$

The same idea as used in eq. (34) can be applied for $\lambda_{b,i}$ in incorporating it into γ_a . Thus;

$$\gamma_a = p_{H1} \times \sum_{i=1}^6 Q_{H1,i} \times \beta_i (1-\lambda_{b,i}) + p_{H2} \times \sum_{i=1}^6 Q_{H2,i} \times \beta_i (1-\lambda_{b,i}) + p_{HR} \times \sum_{i=1}^6 Q_{HR,i} \times \beta_i (1-\lambda_{b,i}) \quad (36)$$

Although eqs. (34) and (36) appear to include a lot of variables, in fact, they comprise only two variables of p_{HR} and P_{ab} . Therefore, if p_{HR} was given at the gelation point from the experimental result, P_{ab} can be obtained.

7. CONCLUDING REMARKS

Gelation process of the cure of DGEBA and PPG diamine could be analysed with the extent of reaction of p_{HR} . A molecular model including the ring forming parameter was constructed to be applied for the gelation process. The classification of PPG diamine was carried out according to the reaction state; that was crucial in incorporating the ring forming parameter into the model.

The comparison of p_{HR} values between those determined by this theory and measured experimentally is now under the process of carrying out.

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