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Estimation of Gel Point in the Sol – Gel Transition : A molecular model for the network formation of Diglysidyle Ether of Bisphenol A and Propylene Glycol Diamino Ether

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A molecular model was constructed to understand the experimental results for the network formation by the polymerisation of Diglysidyle ether of bisphenol A and Propylene glycol diamino ether. In the experiments FT-IR spectroscopy and viscoelastic measurements have been carried out to obtain the extent of reaction at the gel point. To build up the model, at first, the hydrogen atoms in the amine group were sorted out as H1, H2, HR to express the state of the amine group. Next, the state of PPG diamine was divided into six kinds according to the extent of reaction. The condition of the infinite network containing no ring structure was obtained by considering the probability to form the network, which could be expressed as a function of the extent of reaction. This condition was in good agreement with the classical theory. For the better understanding of the experimental results, it is necessary to estimate the ring structure. Although the model presented here is limited to that containing no ring structure, it is likely to improve to the model capable of analysing the ring formation. A rough idea was shown for the improvement.

Key words: diamine, diepoxy, molecular model, network, gel point

1. INTRODUCTION

An experimental research work has so far been carried out in our Laboratory on the polymerisation of diglysidyle 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 was been extensively researched by many research groups.[2-5]

The experimental work carried out in our laboratory contained both FT-IR spectroscopy and viscoelasticity measurement; in the course of reaction the absorbance was measured against reaction time and the extent of reaction was obtained from the absorption peak ($4530\mathrm{cm}^{-1}$) of the epoxy group. The storage modulus and loss modulus was measured by the multiple wave technique in the course of reaction. The gelation time was determined using the method proposed by H. H. Winter.[6] Using these technique the extent of reaction at the gel point was obtained for the solution of DGEBA and PPG diamine of several concentration. The gel point obtained did not agreed with the value predicted by the classical Flory-Stockmayer theory. It can be considered that the disagreement comes from the existence of ring in the network formation

Therefore, for the better interpretation of the experimental results, it is essential to estimate the quantity of the ring structure which does not contribute to the elasticity but exist in the network formed by the polymerisation. The quantity of the ring structure means the length and the number of the polymer chain forming it. Although this estimation is considered to be very difficult, to build up a suitable model will help to carry it out.[7] This paper deals with the model of network formation for the reaction of DGEBA and PPG diamine. The model presented here is limited to that of no ring formation. However, as described later, it is comparatively easy to introduce the probability of ring formation in this model, it has much potential to be a powerful tool in developing the analysis of ring structure.

2. Reaction Model

Before going to the description of the model built up in this study the definition must be given for the reaction of DGEBA and PPG diamine. It is possible to categorise this reaction as RA_4 + RB_2 type polycondensation.[8]

In the course of network formation, the primary amine and an epoxy group react as shown schematically in the formula (1) (see Figure 1) with a rate constant of k_1; hydrogen atoms were sorted out as H1, H2 and HR according to the reactions. That is, the atoms which belong to the unreacted amine group were defined as H1. The unreacted hydrogen atom which belongs to the semireacted amine group was defined as H2. The reacted hydrogen atom was defined as HR. During this reaction two H1 atoms decrease, then one H2 atom and one HR atom increase. The secondary amine and an epoxy group react to form the tertiary amine as shown in formula (2) with the rate constant of k_2, where one H2 atom decreases and one HR atom increases.

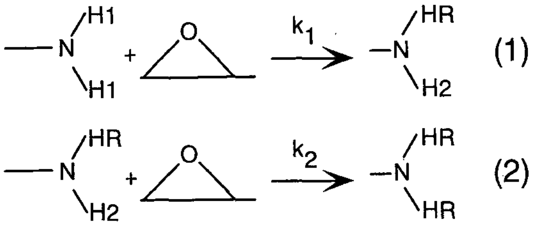

Figure 1. Schematic representation for the reaction of DGEBA and PPG ether with the rate constants of k_1 and k_2.

Therefore, we have the following equations;

$$dC_{H1}/dt = -2k_1 \times C_{H1} \times C_{EP} \qquad \text{(eq.1)}$$

$$dC_{H2}/dt = k_1 \times C_{H1} \times C_{EP} - k_2 \times C_{H2} \times C_{EP} \qquad \text{(eq.2)}$$

$$dC_{HR}/dt = k_1 \times C_{H1} \times C_{EP} + k_2 \times C_{H2} \times C_{EP} \qquad \text{(eq.3)}$$

where C_{H1}, C_{H2}, C_{HR} and C_{EP} are the concentration of H1, H2, HR atom and epoxy group, respectively. Let the concentration of H1 and epoxy group before the reaction(i.e. t=0) be $C^0{}_{H1}$, $C^0{}_{EP}$, then we have the extent of reaction;

$$p_{HR} = \frac{C_{HR}}{C^0_{H1}} \ .$$

It is noted that the values of p_{HR} and $C^0{}_{H1}$ are directly measured in the FT-IR spectroscopy. p_{H1}, p_{H2} and p_{EP} , these values can similarly be defined. The stoichiometric ratio, r, can be written as;

$$r = \frac{C^0_{EP}}{C^0_{H1}}$$

where, r=1 in this experimental work.[1] Furthermore, the experimental condition shows that;
$C_{H1}=C^0{}_{H1}$, $C_{H2}=0$, $C_{HR}=0$ before the reaction starts, $C_{HR}=C^0{}_{H1}-C_{H1}-C_{H2}$, $p_{HR},=r \times p_{EP}$ in the course of reaction.[9] Therefore, the solution of the equations (1-3) can be obtained as follows;

$$C_{H2} = \frac{1}{\rho - 2}(A \times C_{H1}^{(\rho/2)} + C_{H1})$$

$$C_{HR} = \frac{(-2\rho + 2)}{2(\rho - 2)} C_{H1} - \frac{A}{(\rho - 2)} C_{H1}^{(\rho/2)} + B$$

where, $A = -C^0{}_{H1}^{(1-\rho/2)}$, $B = C^0{}_{H1}$, ρ is the rate constant ratio, $\rho=k_2/k_1$. Thus, the behaviour of p_{H1} and p_{H2} can be calculated as a function of p_{HR}.

The results of the calculation for the relations of p_{H1} and p_{HR}, p_{H2} and p_{HR} were shown in Figure 2 for a limited condition of ρ=1.

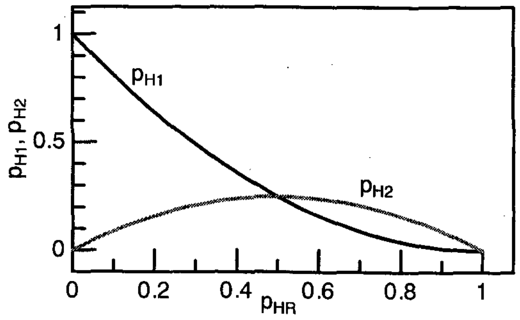

Figure 2 The behaviour of p_{H1} and p_{H2} calculated as a function of p_{HR} for a limited condition of ρ=1.

After the H2 atom is produced in the reaction of Figure 1(1), the consumption will follow. So that the relation of p_{H2} and p_{HR} showed a maximum. The meaning of ρ variation will be described here shortly; ρ=1 means $k_1=k_2$. H1 atom decreases as the reaction proceeds, also H2 atom decreases by the k_2 reaction. However, H2 increases more than it by the k_1 reaction. These occurs until p_{HR} becomes near 0.5. When H1 atom became lessened, k_1 reaction became less, so that H2 atom turns to decrease. The decrease in ρ means the increase in k_1 and the decrease in k_2. The fraction of k_1 reaction is more than that of ρ=1 because of the increase in k_1. The decrease in H1 atom becomes more pronounced than that of ρ=1. The k_2 reaction, that is, the reaction of H2 atom expenditure, is less than that of ρ=1, therefore p_{H2} of lower ρ value is higher than p_{H2} of ρ=1.

3. Variation of the state of diamine units.

In the course of the reaction of DGEBA and PPG diamine, the state of the diamine unit can be classified into six according to the extent of reaction as shown schematically in Figure 3. When we represent the mole fractions of these six states by X_i (i=1 – 6), X_i can be expressed as a function of p_{H1}, p_{H2} and p_{HR} from the reason described below. That is to say, the variation of X_i in the course of the reaction can be expressed by the experimentally observable value of p_{HR}.

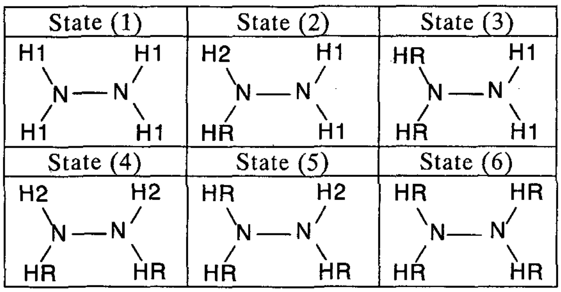

Figure 3 Classification for the states of the diamine units in the course of the reaction.

State (1) consists of two unreacted amine groups. Let the mole fraction of the unreacted amine group be X_u, then we have $X_1=X_u{}^2$. State (2) consists of a semireacted amine group and an unreacted amine group. When the mole fraction of the semireacted amine group is written as X_s, then $X_2=2X_u X_s$. State (3) consists of a fully reacted amine group and an unreacted amine group. Similarly, if we define the mole fraction of the fully reacted group, X_R then $X_3=2X_uX_R$, $X_4=X_s{}^2$, $X_5=2X_sX_R$, $X_6=X_R{}^2$. Also obviously, $X_u+X_s+X_R = 1$.

Now, to count the number of H1 atom, it gives four in State (1), two in State (2) and two in State (3). Further, to count the number of H2 atom, it gives one in State (2), two in State (4), one in State (5); also we can count the number of HR atom in each State. Thus,

$C_{H1}= (4X_1 + 2X_2 + 2X_3) \times C^0{}_{H1}$

$C_{H2}= (X_2 + 2X_4 + X_5) \times C^0{}_{H1}$

$C_{HR}=(X_2 + 2X_3+2X_4+3X_5+4X_6) \times C^0{}_{H1}$.

Ultimately we have the following three relations;

$p_{H1}=X_u{}^2+X_uX_s+X_uX_R$

$\quad =X_u{}^2+X_u(X_s+X_R)=X_u{}^2+ X_u(1-X_u)$

$2 \times p_{H2}= X_uX_s+ X_s{}^2 +X_sX_R$

$2 \times p_{HR}= X_uX_s+2X_uX_R+X_s{}^2+3X_sX_R+2X_R{}^2$.

These manipulations give the relation between X_i and the extents of reaction.

$$X_1=p_{H1}{}^2 , \qquad X_2=4p_{H1}p_{H2} \ .$$
$$X_3=2p_{H1}(p_{HR} - p_{H2}) \qquad X_4=4p_{H2}{}^2 \ .$$
$$X_5=4p_{H2}(p_{HR} - p_{H2}) \qquad X_6 =(p_{HR} - p_{H2})^2 \ . \qquad \text{(eqs.4–9)}$$

The calculation of X_i (i=1 – 6) was carried out as a function of p_{HR} . The results were shown in Figure 4.

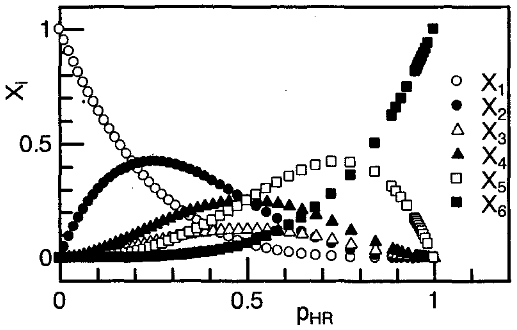

Figure 4 Results of calculation for the mole fraction of each state of diamine unit.

4. Network Formation Model

Next, we will go on to the condition for forming the infinite network in the development of six States. To consider the role of each states gives that; State (1) is not included in a polymer chain. State (2) is at the end of a polymer chain. States (i), i=3 – 6, these are constituent parts of a polymer chain. In particular, for i=5 and 6 the branching takes place.

This condition can clearly be described by giving the probability of continuing path; that is, when a unit in a polymer is randomly chosen, either a diamine or a diepoxy unit, the probability that the unit has at least one path which continues to the infinite network. To prepare this, let's consider γ_a; the probability of continuing path out of the diamine unit attached to a randomly chosen H atom, either reacted or unreacted. Also γ_b can be considered; the probability out of the diepoxy unit attached to a randomly chosen epoxy group, either reacted or unreacted. So, $\gamma_a \times \gamma_b = 1$, this is the condition of infinite network.

In order to obtain γ_a, at first, we must make an equation for finding H1, H2 and HR atoms in the amine unit of State (i), i=1 – 6. For example, because there are four H1 atoms in State (1), two in State (2) and (3), the total number of H1 atom is six. Then, $Q_{H1,i}$, the probability of finding H1 atom in the diamine unit can be written as;

$$Q_{H1,i=1}=\frac{4X_1}{4X_1+2X_2+2X_3},\quad Q_{H1,i=2}=\frac{2X_2}{4X_1+2X_2+2X_3},$$

$$Q_{H1,i=3}=\frac{2X_3}{4X_1+2X_2+2X_3},$$

$Q_{H1,i=4}=Q_{H1,i=5}=Q_{H1,i=6}=0$.

Furthermore, the number of way out must be counted as shown below. There is not HR atom in State (1) but one HR atom in State (2). The existence of HR atom means the continuity with the next diepoxy unit. That is, to evaluate γ_a is to give the probability of continuity. The number of HR atom which continues to the next unit like this can be defined as β_i, the number of way out. Then, the sum of $(Q_{H1,i} \times \beta_i)$ of i = 1 – 6, is equal to the probability that a path continues from H1 atom to the next diepoxy unit. Obviously, there are three kinds of contributions to γ_a, from H1, H2 and HR atoms. The contribution from H1 atom, S_{H1}, means the probability of continuity on condition that randomly chosen H atom was H1 atom. The probabilities, S_{H2}, S_{HR} can also be defined similarly. Hence,

$\gamma_a = S_{H1}+S_{H2}+S_{HR}$. (eq.10)

On the other hand, the probability to chose H1 atom from all of H atoms is p_{H1} which comes originally from the experimental condition. Therefore,

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

Where $\beta_1=\beta_4=\beta_5=\beta_6=0$, $\beta_2=1$, $\beta_3=2$.

Similarly, we now can give $Q_{H2,i}$ and β_i as follows;

$$Q_{H2,i=1}=0,\quad Q_{H2,i=2}=\frac{X_2}{X_2+2X_4+X_5},\quad Q_{H2,i=3}=0,$$

$$Q_{H2,i=4}=\frac{2X_4}{X_2+2X_4+X_5},\quad Q_{H2,i=5}\frac{X_5}{X_2+2X_4+X_5},$$

$Q_{H2,i=5}=0$.

$\beta_1=\beta_3=\beta_6$, $\beta_2=1$, $\beta_4=2$, $\beta_5=3$.

Then, S_{H2} can be obtained. Next, for $Q_{HR,i}$ and β_i

$$Q_{HR,i=1}=0,\quad Q_{HR,i=2}=\frac{X_2}{X_2+2X_3+2X_4+3X_5+4X_6},$$

$$Q_{HR,i=3}=\frac{2X_3}{X_2+2X_3+2X_4+3X_5+4X_6},$$

$$Q_{HR,i=4}=\frac{2X_4}{X_2+2X_3+2X_4+3X_5+4X_6},$$

$$Q_{H2,i=5}=\frac{3X_5}{X_2+2X_3+2X_4+3X_5+4X_6},$$

$$Q_{HR,i=6}=\frac{4X_6}{X_2+2X_3+2X_4+3X_5+4X_6},$$

$\beta_1=\beta_2=0$, $\beta_3=1$, $\beta_4=1$, $\beta_5=2$, $\beta_6=3$.

Then, S_{HR} can be obtained and γ_a can be calculated as a function of p_{HR} .

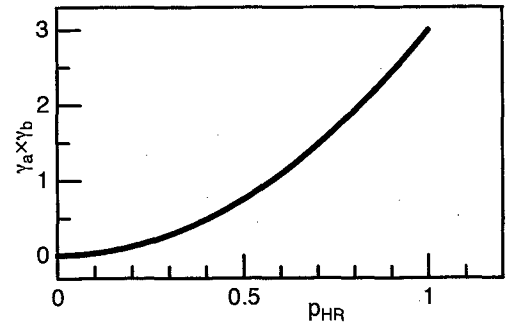

Figure 5 Results of calculation for the probability of continuing path.

Similarly, we can express γ_b as a function of p_{HR}. In the course of the reaction, the state of the diepoxy unit can be classified into three according to the extent of reaction; that is, EP – EP (Z_1), EP$_R$ – EP (Z_2), EP$_R$ – EP$_R$ (Z_3), where EP and EP$_R$ are an unreacted and reacted epoxy groups, respectively. Z_i, i=1 – 3, is the mole fraction of each state;

$Z_1=(1-P_{EP})^2$, $Z_2=2\times P_{EP}(1-P_{EP})$, $Z_3=P_{EP}^2$ (eqs.11 -13).

The first state includes two unreacted epoxy groups, the second group has both unreacted and reacted groups and the third group has two reacted epoxy groups. Therefore, the total number of unreacted epoxy group is $(2Z_1+Z_2)$, that of reacted group is (Z_2+2Z_3). Now γ_b

can be represented using equations (11 –13) as;

$$\gamma_b = (1 - P_{EP})\frac{Z_2}{2Z_1 + Z_2} + P_{EP}\frac{2Z_3}{Z_2 + 2Z_3} \qquad \text{(eq.14)}$$

The calculation of (eq.14) showed $\gamma_b = P_{EP}$, that is, it is equal to P_{HR} .

Now we can calculate ($\gamma_a \times \gamma_b$), the results were shown in Figure 5. Although the results of ρ=1 was shown here taking account of the experiments in this study, it is possible to calculate for various ρ values. Interestingly, the relation between ($\gamma_a \times \gamma_b$) and p_{HR} showed a same smooth curves for various ρ values .

The processes written above show that p_{HR}=0.577 could be seen as the condition of infinite network containing no ring structure. This value is equal to that obtained from the classical Flory-Stockmayer theory, where the gel point is expressed as;

$$p_a \times p_b \times (f_a - 1)(f_b - 1) = 1$$

for the polymerisation of (RA_{fa} + RB_{fb}) type. To apply the experimental condition of this study, f_a= 4, f_b= 2, p_a=p_b, gives the gel point of p_a=0.577. Therefore, it can be said that the network formation model shown here is suitable to consider the gelation condition.

5. Development of Network Formation Model.

We must go on to the model containing ring structures. For this purpose, the growth of polymer chain was considered as shown schematically in Figure 6; the chain grows from right to left. In particular, let's focus on the growth from B^1 to B^2.

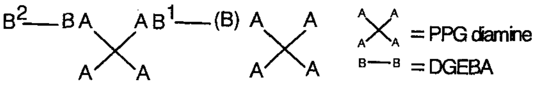

Figure 6 Schematic representation for the chain growth in the polymerisation of DGEBA and PPG diamine.

At first, the diamine unit which was going to reacts on B^1 was divided into two kinds, external and internal diamines. The external diamine is not included in the same chain as B^1 is, while the internal diamine is. When an external diamine reacts, the ring forms. Let the concentration of internal diamine unit be $C_{a,\,int}$ and the external diamine molecule be $C_{a,\,ext}$, then we can define the value shown below as the probability of the ring formation.

$$\lambda = \frac{C_{a,\text{int}}}{C_{a,\text{int}} + C_{a,ext}}$$

The probability of ring formation at the gel point can be obtained by applying the experimental results, that is, the extent of reaction at the gel point, provided that both $C_{a,\,int}$ and $C_{a,\,ext}$ can be expressed as a function of p_{HR}. This analysis will hopefully be carried out in the future study.

7. Concluding Remarks

A molecular model was constructed to understand the experimental results concerning the network formation by the polymerisation of DGEBA and PPG diamine. The state of PPG diamine was divided into six kinds according to the extent of reaction. The variation of the mole fraction of each state could be expressed as a function of p_{HR} which is directly observable in the FT-IR spectroscopy. The condition of the infinite network containing no ring structure was obtained by considering the probability to form the network, which could be expressed as a function of p_{HR} . This condition was in good agreement with the classical theory. A rough idea was shown to expand this model to that containing ring structures.

REFERENCES and NOTES

[1] Y. Tanaka, Polym. Prep. 53, (2) 3265(2004); ibid, 53, (1), 957(2004)

[2] K. Dusek, American Chem. Soc. Symp. Ser., 208, 3-14(1984)

[3] J. P. Eloundou, M. Feve, D. Harran, J. P. Pascault, Ang. Makromol. Chem, 230, 13-46(1995)

[4] K. Dusek, J. Plestil, F. Lednicky, S. Lunak, Polymer, 19, 393-397(1978)

[5] J. P. Eloundou, M. Feve, J. F. Gerard, D. Harran, J. P. Pascault, Macromolecules, 29, 6907-6916(1996); J. P. Eloundou, J. F. Gerard, D. Harran, J. P. Pascault, ibid, 6917-6927(1996)

[6] H. H. Winter, Adv. Polym. Sci., 134, 165-234(1997)

[7] M. Gordon and S.B. Ross-Murphy, Pure Appl. Chem., 43, 1-26(1975)

[8] The reaction between primary amine and epoxy gives the secondary amine containing hydroxyl group. It is necessary to consider whether this hydroxyl group reacts further with an epoxy group or not. It was reported that the hydroxyl group hardly reacts under a normal condition. Thus, the effect of this reaction was negated here. See for reference, H. Dannenberg, SPE Trans, 3, 78(1963).

[9] It is necessary to define the concentration of reacted epoxy group to give p_{EP} value. This concentration is obviously equal to C_{HR}.

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