Kinetic Models of Pregelation Stages for Epoxy Resins Cured with Mixed Amine Systems

Kuo Chung Cheng and Wen Yen Chiu*

Department of Chemical Engineering, National Taiwan University,
Taipei, Taiwan, Republic of China 106

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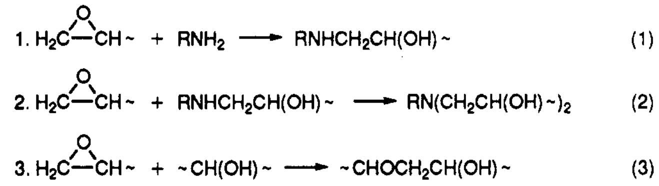
ABSTRACT: The systems of epoxy resins cured with primary amines with the substitution effect and etherification have been analyzed by the kinetic method. The average molecular weight, which changed with reaction time or conversion, and the gel time were calculated, and the results agree well with those by another combined kinetic and statistical theory and experimental data. Then a more complex system, epoxy resins cured with mixed amines, was analyzed for various reactivity ratios of two kinds of amines. For a system in which the reactivity of one kind of amine unit is rather higher than another, the average degree of polymerization profile versus epoxy conversion is close to those systems with only one kind of amine and excess epoxy units.

1. Introduction

The curing reaction of epoxy resins with amines has been studied by many researchers.[1,2] According to the literature,[3] the three main reactions between an epoxide and a primary amine are



There are several statistical methods applied to describe the relations among the molecular weight of polymers and conversion during cure. Dusek et al.[4] analyzed the effect of the unequal reactivities of the two hydrogens in primary amine, i.e., the first-shell substitution effect (FSSE)[5] on the curing reaction of epoxy, by the theory of branching processes (TBP).[6] Tsou and Peppas[7] extended this method by combining with kinetic theory to the system with etherification (eq 3), which is significant especially for aromatic amines, at high temperature or with an initial excess of epoxides.[8] The other two groups, Bokare and Gandhi[9] and Riccardi and Williams,[10] also used various combined model, expectation theories[11] and statistical structural models, respectively, to study the curing of a diglycidyl ether Bisphenol A (DGEBA) based epoxy resin with a 4,4′-diaminodiphenyl sulfone (DDS).

Those combined methods were successfully applied to many systems for calculating molecular weight as a function of conversion, but the deriving procedures are case by case and very complicated. In our previous work, a very general kinetic method has been developed.[12] In this work, the general kinetic method is applied to the reactions of epoxy resins with amines before gelation. Both the FSSE of amine and etherification are taken into account.

2. Kinetic Approach

Consider a polymerization system in which m irreversible elementary reactions occur between units of molecules. It can be expressed as follows:

$$A_{i1} + A_{i2} \xrightarrow{k_i} A_{i3} + A_{i4} + C_i \quad (4)$$

$$\langle \mathbf{P}' \rangle + \langle \mathbf{P}'' \rangle \xrightarrow{k_i} \langle \mathbf{P}' + \mathbf{P}'' + \mathbf{L}_i \rangle + C_i$$

for the ith reaction ($i = 1, 2, ..., m$) (5)

Equation 4 describes the reaction between units A_{i1} and A_{i2} to form reactant units A_{i3} and A_{i4} and a condensation byproduct C_i, and k_i is the reaction rate constant for the ith reaction. In eq 5, $\langle \mathbf{P}' + \mathbf{P}'' + \mathbf{L}_i \rangle$ is the product molecule formed from molecule $\langle \mathbf{P}' \rangle$ and $\langle \mathbf{P}'' \rangle$ in the ith reaction, in which $\mathbf{P}$ is a matrix used to characterized the molecule $\langle \mathbf{P} \rangle$,

$$\mathbf{P} = \begin{bmatrix} p_{11} & p_{12} & p_{13} & p_{14} & p_{15} \\ p_{21} & p_{22} & p_{23} & p_{24} & p_{25} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ p_{m1} & p_{m2} & p_{m3} & p_{m4} & p_{m5} \\ p_w & 0 & 0 & 0 & 0 \end{bmatrix} \quad (6)$$

where p_{ij} ($i = 1, 2, ..., m$; $j = 1, 2, 3, 4$) denotes the number of units A_{ij}, p_{i5} is the number of times the ith reaction occurs, and p_w is the weight of $\langle \mathbf{P} \rangle$ if no byproduct forms, and

$$\mathbf{L}_i = \begin{bmatrix} l_{11} & l_{12} & l_{13} & l_{14} & l_{15} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ l_{m1} & l_{m2} & l_{m3} & l_{m4} & l_{m5} \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (7)$$

here $-l_{i1} = -l_{i2} = l_{i3} = l_{i4} = l_{i5} = 1$, and the other elements of $\mathbf{L}_i$ are equal to zero.

First, we assume elements p_{ij} are independent of each other, and this assumption will be released in the final. According to eq 5, the reaction rate equation can be expressed as

$$\frac{\mathrm{d}[\mathbf{P}]}{\mathrm{d}r} = \sum_{i=1}^{m} k_i^* \left\{ \sum_{\substack{\text{all } \mathbf{P}', \mathbf{P}'' \\ \text{that } \mathbf{P} = \mathbf{P}' + \mathbf{P}'' + \mathbf{L}_i}} [\mathbf{P}'][\mathbf{P}'']p'_{i1}p''_{i2} - [\mathbf{P}]p_{i1} \sum_{\text{all } \mathbf{P}'''} [\mathbf{P}''']p'''_{i2} - [\mathbf{P}]p_{i2} \sum_{\text{all } \mathbf{P}'''} [\mathbf{P}''']p'''_{i1} \right\} \quad (8)$$

where $\Sigma_{\text{all } \mathbf{Q}}$ denotes the summation over all possible matrix $\mathbf{Q}$ ($\mathbf{Q} = \mathbf{P}, \mathbf{P}', \mathbf{P}''$, or $\mathbf{P}'''$), and

$$[\mathbf{P}] = N(\mathbf{P})/N_0 \quad (9)$$

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* Author to whom correspondence should be addressed.

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$$\tau = t k_0 N_0 / V_0 \qquad (10)$$

$$k_i^* = (k_i/k_0)(V_0/V) \qquad (11)$$

in which $N(\mathbf{P})$ is the number of molecules $\langle \mathbf{P} \rangle$, t is the reaction time, V is the volume of this system, and N_0, K_0, and V_0 are arbitrary reference number, reaction rate constant, and volume, respectively.

Equation 8 cannot be solved directly but can be transformed into finite ordinary differential equations for moments by a generating function, and then the average molecular weight of polymers may be obtained from the generating function by using a numerical method. For the reaction of epoxides with amines (eqs 1–3), no condensation byproducts form during cure. Unit A_{ij} may be the same as A_{uv}, though (i,j) is not equal to (u,v), such as unit A_{ij} is the epoxy group; thus, the elements p_{ij} in matrix $\mathbf{P}$ may not be independent. In order to solve this problem, matrix $\mathbf{P}$ is transformed into a vector $\mathbf{E}$ consisting of independent elements. These procedures and the algorithm for calculating $\bar{M}_w$ and $\bar{M}_n$ were described in detail in ref 12.

3. Results and Discussion

I. Epoxy Resin Cured with Primary Amine. First, our kinetic approach was applied to the tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM)/4,4′-diaminodiphenyl sulfone (DDS) system, in which TGDDM is assumed to contain four epoxy groups, and DDS contains two primary amine groups.

In terms of the reacting and resultant units, the reactions corresponding to eqs 1–3 can be written as

$$\mathrm{EP} + \mathrm{PA} \xrightarrow{2k_1} \mathrm{SA} + \mathrm{OH} \qquad (12)$$

$$\mathrm{EP} + \mathrm{SA} \xrightarrow{k_2} \mathrm{TA} + \mathrm{OH} \qquad (13)$$

$$\mathrm{EP} + \mathrm{OH} \xrightarrow{k_3} \mathrm{ET} + \mathrm{OH} \qquad (14)$$

where EP, PA, SA, TA, ET, and OH are defined as epoxy, primary amine, secondary amine, tertiary amine, ether, and hydroxyl containing units, respectively, and

$$k_i = k_i' + k_i'' C(\mathrm{OH}) \qquad i = 1, 2, 3 \qquad (15)$$

where k_i' and k_i'' denote noncatalytic and catalytic rate constants, respectively, and $C(\mathrm{OH})$ is the concentration of the hydroxyl group. The ratios of rate constants are assumed as follows:

$$k_2/k_1 = k_2'/k_1' = k_2''/k_1'' = a \qquad (16)$$

$$k_3/k_1 = k_3'/k_1'' = k_3''/k_1' = b \qquad (17)$$

where a and b are assumed as constants and independent of the extent of the reaction and temperature.

Figures 1 and 2 show the weight-average and number-average molecular weights of polymers, $\bar{M}_w$ and $\bar{M}_n$, versus the epoxy conversion, $\alpha(\mathrm{EP})$ for the TGDDM/DDS system. The parameters of this calculation are as follows:

$$a = 0.4$$

$$b = 0 \text{ or } 0.11$$

$$\text{molecular weight of TGDDM} = 422$$

$$\text{molecular weight of DDS} = 248$$

$$r = 0.5, 1.0, \text{ or } 2.0$$

where r is the initial molar ratio of the amine hydrogen to the epoxy group.

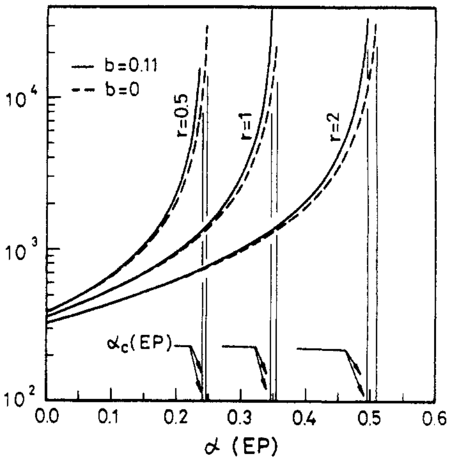

Figure 1. Weight-average molecular weight versus epoxy conversion for various r.

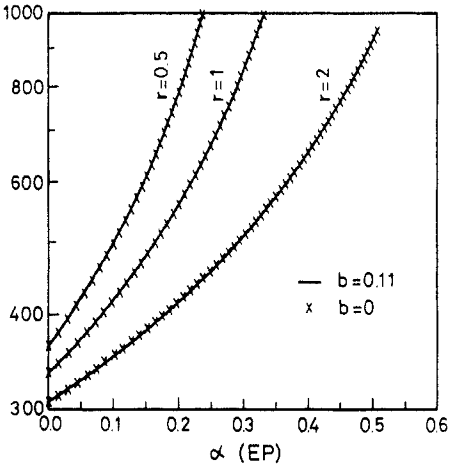

Figure 2. Number-average molecular weight versus epoxy conversion for various r.

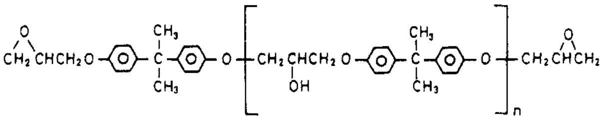

Figure 3. Structural formula of DGEBA based epoxy resin (DER 332).

It is shown that the etherification reaction (eq 14) generates the extra branching and leads to the lower critical epoxy conversion, $\alpha_c(EP)$, at which gelation occurs. The value of $\alpha_c(A)$ increases with increasing the initial molar ratio of the amine hydrogen to the epoxy group, r, as shown in Figure 1. These calculated results are identical to those by the combined model deveoped by Tsou and Peppas.[7] On the other hand, the profiles of $\bar{M}_n$ versus $\alpha(EP)$ are independent of the value of b, shown in Figure 2, because the decreasing rate of the number of molecules in the reaction system is equal to the decreasing rate of the number of epoxy units.

Second, a diglycidyl ether Bisphenol A (DGEBA) based epoxy resin (DER 332) cured with 4,4′-diamino-3,3′-dimethyldicyclohexylmethane (3DCM) was treated by our kinetic approach. The structural formula of DER 332 is shown in Figure 3. In this case, the average value of n is equal to 0.03; thus, the epoxy prepolymer, DER 332, is assumed as a mixture consisting of 97 mol % pure DGEBA ($n = 0$) and 3 mol %, secondly, hydroxyl containing DGEBA based epoxide ($n = 1$), and both the noncatalytic mechanism and etherification are neglected. The parameters of this system for calculation are:

$$k_1' = k_2' = k_3' = 0$$

$$a = 0.4$$

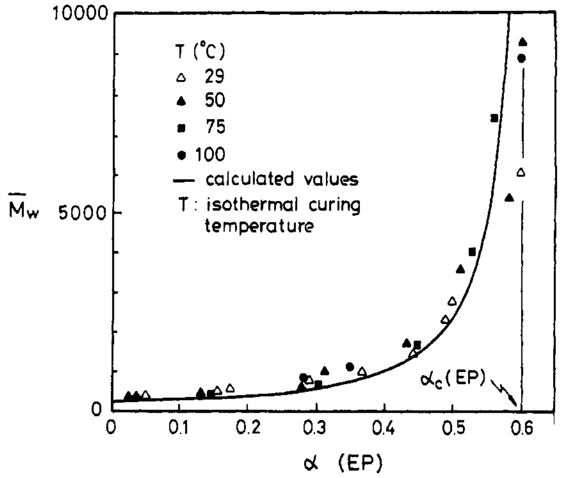

Figure 4. Weight-average molecular weight versus epoxy conversion for the DER 332/3DCM system ($r = 1$, experimental data from ref 13).

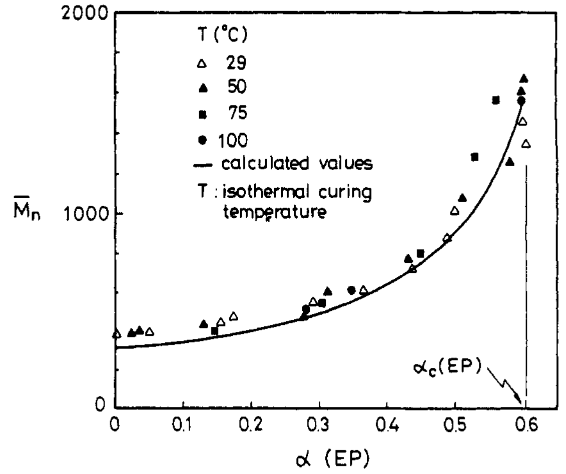

Figure 5. Number-average molecular weight versus epoxy conversion for the DER 332/3DCM system ($r = 1$, experimental data from ref 13).

$$b = 0$$

molecular weight of epoxide ($n = 0$) = 340

molecular weight of epoxide ($n = 1$) = 624

molecular weight of 3DCM = 238

$$r = 1$$

Figures 4 and 5 show the calculated weight-average and number-average molecular weights of polymers, $\bar{M}_w$ and $\bar{M}_n$, versus the epoxy conversion, respectively. In our calculations, the value of a is assumed to be independent of curing temperature; thus, the average molecular weight profiles versus $\alpha(EP)$ are the same for various curing temperatures. It is shown that the calculated values agree well with the experimental measurements.[13]

II. Epoxy Resin Cured with Mixed Amines. Furthermore, we considered a more complex system consisting of one kind of epoxy and two different kinds of primary amine monomers, and the epoxide contains four epoxy groups, and both of the amines contain 2 primary amine groups. The reactions between units are assumed as follows:

$$\mathrm{EP} + \mathrm{PA}_1 \xrightarrow{2k_{11}} \mathrm{SA}_1 + \mathrm{OH} \qquad (18)$$

$$\mathrm{EP} + \mathrm{SA}_1 \xrightarrow{k_{12}} \mathrm{TA}_1 + \mathrm{OH} \qquad (19)$$

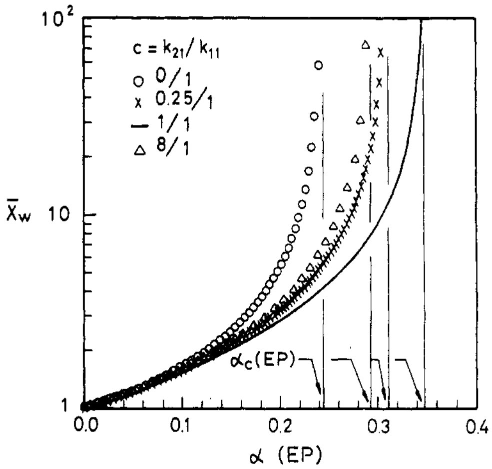

Figure 6. Weight-average degree of polymerization versus epoxy conversion for epoxy resin cured with mixed amines.

$$\mathrm{EP} + \mathrm{PA}_2 \xrightarrow{2k_{21}} \mathrm{SA}_2 + \mathrm{OH} \qquad (20)$$

$$\mathrm{EP} + \mathrm{SA}_2 \xrightarrow{k_{22}} \mathrm{TA}_2 + \mathrm{OH} \qquad (21)$$

$$\mathrm{EP} + \mathrm{OH} \xrightarrow{k_3} \mathrm{ET} + \mathrm{OH} \qquad (22)$$

where the subscripts "1" and "2" on PA, SA, or TA denote the amine units of the first and second kind of primary amine monomers, respectively, and

$$k_{ij} = k'_{ij} + k''_{ij}C(\mathrm{OH}) \qquad i, j = 1 \text{ or } 2 \qquad (23)$$

$$k_3 = k'_3 + k''_3 C(\mathrm{OH}) \qquad (24)$$

where k'_{ij} (or k'_3) and k''_{ij} (or k''_3) denote noncatalytic and catalytic reaction rate constants, respectively, and $C(\mathrm{OH})$ is the concentration of the hydroxyl unit.

The ratios of rate constants are assumed as follows:

$$k_{12}/k_{11} = k'_{12}/k'_{11} = k''_{12}/k''_{11} = a \qquad (25)$$

$$k_3/k_{11} = k'_3/k'_{11} = k''_3/k''_{11} = b \qquad (26)$$

$$k_{21}/k_{11} = k_{22}/k_{12} = c \qquad (27)$$

where a, b, and c are also assumed as constant and independent of the extent of the reaction. The parameters for the calculation are as follows:

$$a = 0.4$$

$$b = 0.14$$

$$k''_{ij}C_0(\mathrm{EP})/k'_{ij} = 20, \quad i, j = 1 \text{ or } 2$$

$$k''_{ij}C_0(\mathrm{EP})/k'_3 = 20$$

$$r = 1$$

$$C_0(\mathrm{PA}_1)/C_0(\mathrm{PA}_2) = 1$$

$$\tau = k'_{11}C_0(\mathrm{EP})t$$

where $C_0(\mathrm{EP})$ is the initial concentration of the epoxy unit, $C_0(\mathrm{PA}_1)$ and $C_0(\mathrm{PA}_2)$ are the initial concentrations of the first and second kinds of primary amine units, respectively, and t is the reaction time.

Figures 6 and 7 give the weight-average and number-average degree of polymerization, $\bar{X}_w$ and $\bar{X}_n$, versus epoxy conversion, respectively. It is found that the $\bar{X}_w$ profile depends on the value of c, but the $\bar{X}_n$ profile is not affected by the reactivity ratio c before gelation. Figure 8 shows the profiles of $\bar{X}_w$ versus scaled time, τ. Increasing the value of c, the rising rate of $\bar{X}_w$, $d\bar{X}_w/d\tau$, increases and the gel time decreases.

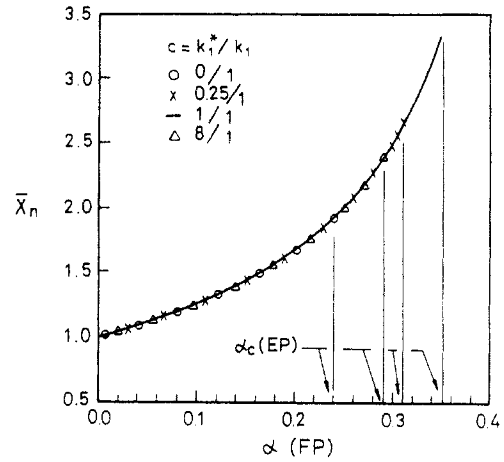

Figure 7. Number-average degree of polymerization versus epoxy conversion for epoxy resin cured with mixed amines.

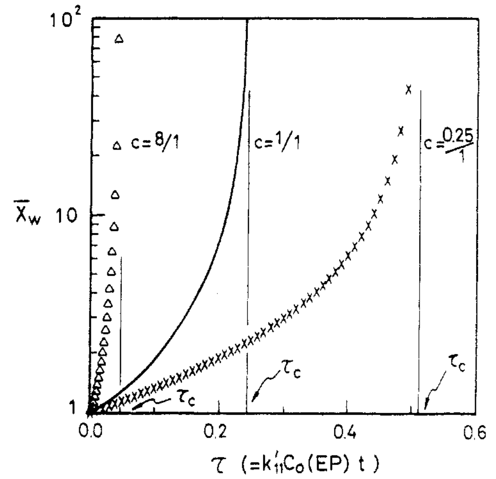

Figure 8. Weight-average degree of polymerization versus scaled time τ for epoxy resin cured with mixed amines.

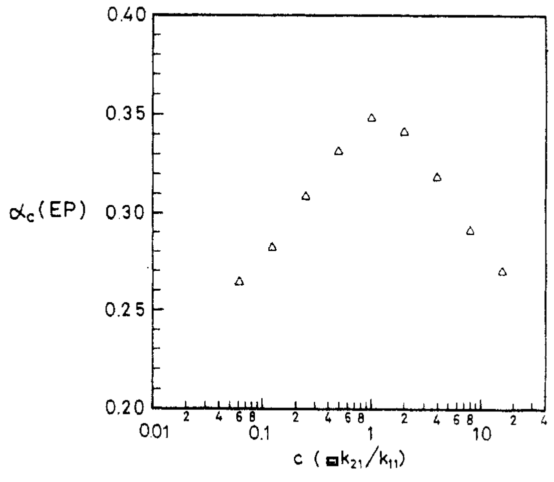

Figure 9. Dependence of critical epoxy conversion on the value of c.

On the other hand, the dependence of critical conversion of the epoxy unit, α_c(EP), at which gelation occurs, on the value of c is shown in Figure 9. The maximum α_c(EP) occurs at about $c = 1$, and the critical conversion decreases with increasing the difference between k_{21} and k_{11}. On the basis of the assumptions of eqs 25–27, if the reactivity of one kind of amine unit is rather higher than another one, for example, $k_{21}/k_{11} = 0.0625/1$ or $k_{21}/k_{11} = 16/1$, the reaction system will be dominated by the amine unit with higher reactivity, and the consumption of the amine units with lower reactivity is very few (see Figures 10 and 11).

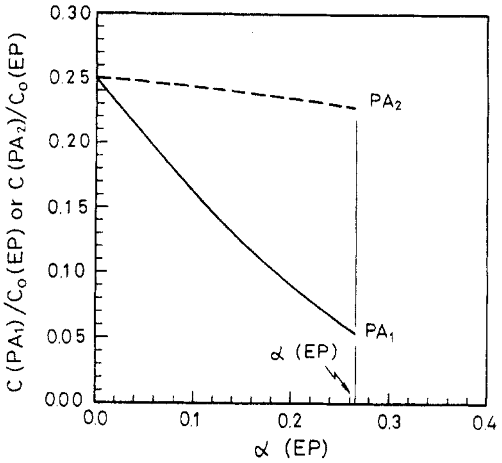

Figure 10. Concentrations of primary amine units versus epoxy conversion (c = 0.0625/1).

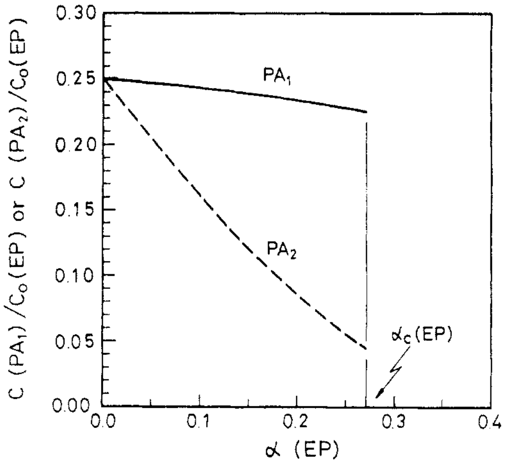

Figure 11. Concentrations of primary amine units versus epoxy conversion (c = 16/1).

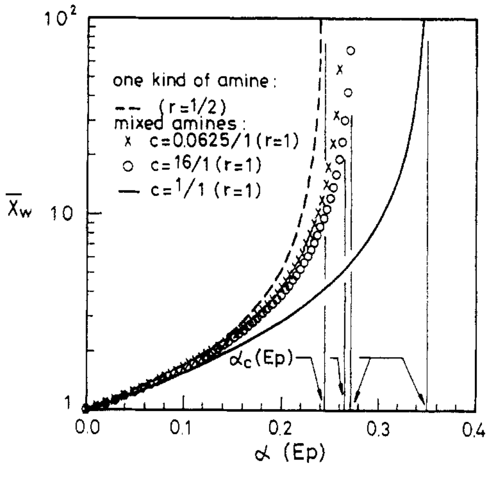

Figure 12. Weight-average degree of polymerization versus epoxy conversion for epoxy resin cured with one kind of amine or mixed amines.

Thus, the $\bar{X}_w$ profile of this system is close to the system with only one kind of amine and excess epoxy unit as shown in Figure 12.

4. Conclusion

The kinetic approach developed by us before has been applied to the systems of epoxy cured with primary amines in this work. The relationships between the average molecular weight and the reaction time or conversion can be directly obtained even for a complex system.

It is shown that the etherification reaction leads to the lower critical epoxy conversion. For the curing of an epoxy with mixed amines, the average molecular weight profiles and gel point are affected by the reactivity ratio of different kinds of amines. If the reactivity of one kind of amine unit is rather higher than another one, the epoxy critical conversion and the profile of the average degree of polymerization versus epoxy conversion are close to those systems consisting of only one kind of amine and excess epoxy units.

References and Notes

(1) Rozenberg, B. A. *Adv. Polym. Sci.* **1985**, *75*, 113.
(2) Dusek, K. *Adv. Polym. Sci.* **1986**, *78*, 1.
(3) Schechter, L.; Wynstra, J.; Kurkjy, R. P. *Ind. Eng. Chem.* **1956**, *48*, 94.
(4) Dusek, K.; Ilavsky, M.; Lunak, S. *J. Polym. Sci., Polym. Symp. Ed.* **1975**, *53*, 29; *Makromol. Chem., Suppl.* **1979**, *2*, 35.
(5) Gordon, M.; Scantlebury, G. R. *Proc. R. Soc. London, Ser. A* **1966**, *A292*, 380.
(6) Gordon, M. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 240.
(7) Tsou, A. H.; Peppas, N. A. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2043.
(8) Riccardi, C. C.; Williams, R. J. J. *J. Appl. Polym. Sci.* **1986**, *32*, 3445.
(9) Bokare, U. M.; Gandhi, K. S. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 857.
(10) Riccardi, C. C.; Williams, R. J. J. *Polymer* **1986**, *27*, 913.
(11) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 199.
(12) Cheng, K. C.; Chiu, W. Y. *Macromolecules* **1993**, *26*, 4658.
(13) Verchere, D.; Sautereau, H.; Pascault, J. P.; Riccardi, C. C.; Moschiar, S. M.; Williams, R. J. J. *Macromolecules* **1990**, 23, 725.