Monte Carlo Simulation of Polymer Network Formation with Complex Chemical Reaction Mechanism: Kinetic Approach on Curing of Epoxides with Amines

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ABSTRACT: A new algorithm of Monte Carlo (MC) simulation has been developed for network formation by a kinetic approach. This method is very general and can be directly applied to various systems with a complex chemical reaction mechanism. The strategy of the MC method is divided into two steps, selecting the type of the reaction mechanism and then choosing the reacting molecules. This makes it possible to accomplish the simulation in a reasonable time. Then the systems of epoxy resins cured with primary amines with a substitution effect and etherification were analyzed by this method. The changes of the structure, such as the molecular weight distribution of polymers, gel fraction, and cycle rank, were calculated, and the gel point was determined by the method of reduced average molecular weight. It is found that, if the effect of topology is not taken into account, very few times of the intramolecular reactions occur before gelation for a large finite system. The gel point and the average molecular weight profiles simulated are well consistent with those by another kinetic approach and experimental data, and the changes of the molecular weight distribution (MWD) depend on the rate of etherification.

1. Introduction

There are several theories of network formation, including statistical and kinetic methods,[1-11] and simulation in n-dimensional space,[12-15] such as the percolation method,[16] to describe the relations among the molecular weight of polymers and the conversion or reaction time during cure. For a polyfunctional system with equal reactivities of groups and without substitution effects, i.e., random polymerization, the molecular weight distribution (MWD) can be obtained by either the kinetic approaches or the statistical methods.[1,2,17]

Furthermore, many researchers have developed various methods to analyze nonrandom cases, such as epoxy resins cured with amines. Dusek et al.[18] study the effect of the unequal reactivities of the two hydrogens in primary amine, i.e., the first shell substitution effect (FSSE)[19] on the curing reaction of epoxy resins, by the theory of branching processes (TBP). Tsou and Peppas[20] combined TBP with kinetic theory to the system with etherification (living polymerization). The other two groups, Bokare and Gandhi[21] and Riccardi and Williams,[22] also used various combined models, expectation theory[5] and statistical structural model, respectively, to study the curing of a diglycidyl ether Bisphenol A (DGEBA) based epoxy resin with a bis(4-aminophenyl)sulfone (DDS). Recently, Gupta and Macosko[23] and Riccardi and Williams[24] made comparisons of rigorous and approximate models for the formation of epoxy-amine networks with etherification. However, the kinetic method directly accounts for the history of network formation; thus, we have derived a general kinetic method, which can be directly used with the systems of epoxy resins cured with mixed amines before gelation.[25]

Those combined methods were successfully applied to the complex systems for calculating the average molecular weight of polymer as a function of conversion, but the deriving procedures are case by case and very complicated. Moreover, the MWD cannot be obtained by the combined methods, though a full MWD will provide more insight information on network formation. On the other hand, a Monte Carlo (MC) simulation can provide detailed insight information about the structure of the reaction system, such as the full MWD of the polymers. On the basis of MC simulation, Mikes and Dusek studied the kinetic process of the stepwise polymerization with FSSE[26] and Tobita analyzed the MWD in free-radical cross-linking copolymerization.[27]

In this work, according to the kinetic theory, we developed a quite general algorithm of MC simulation for network formation with a complex kinetic mechanism, and the curing of epoxides with amines, in which both stepwise and living polymerizations take place simultaneously, were taken as examples. The results of the average molecular weight of polymers were compared with those by another numerical method and experimental data before gelation, and the changes of the MWD were calculated for the reaction dominated by the etherification or not.

2. Monte Carlo Simulation

I. Modeling. First, we define a finite polymerization system consisting of N_p molecules MOL(I), $I = 1, ..., N_p$, in which N_p is the number of molecules of the system. The composition of a molecule, MOL(I), is characterized by a vector, $\langle n(I,1), n(I,2), ..., n(I,N_g), W(I)\rangle$, in which $n(I,J)$ denotes the number of the independent reacting or resultant group $A(J)$ of MOL(I), N_g is the number of types of the independent groups involved in the reaction, and $W(I)$ is the molecular weight of molecule MOL(I). Note that $A(J)$, $J = 1, ..., N_g$, is an independent group; that is, if J' is not equal to J'', $A(J')$ is different from $A(J'')$.

According to the kinetic theory, this polymerization system is simulated by choosing a pair of reacting functional groups of molecules and combining the reacting molecules into a larger one, and an intramolecular reaction is also involved. The system considered consists of m irreversible elementary reactions without condensation byproducts. These elementary reactions take place among reacting groups of molecules as follows:

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$$A(b_{i1}) + A(b_{i2}) \xrightarrow{k_i} A(b_{i3}) + A(b_{i4})$$
$$\text{for } i\text{th reaction } R_i \ (i = 1, ..., m) \quad (1)$$

where $A(b_{i1})$ and $A(b_{i2})$ are the reacting groups, $A(b_{i3})$ and $A(b_{i4})$ are the resultant groups, in which $b_{ij} = J$, if $A(b_{ij})$ is the same as $A(J)$, and k_i denotes the reaction rate constant. Then the reaction rate equation could be expressed as

$$r(R_i) = k_i'[A(b_{i1})][A(b_{i2})] \quad (2)$$

where $[A(b_{ij})]$ is the concentration of the group $A(b_{ij})$, $r(R_i)$ is the reaction rate of the ith reaction R_i, and $k_i' = k_i/2$, if $A(b_{i1})$ is the same as $A(b_{i2})$ or $k_i' = k_i$, if $A(b_{i1})$ is different from $A(b_{i2})$.

The polymerization is simulated by choosing cycles accomplished by the Monte Carlo (MC) method. First, select the reaction type in eq 1. The probability of the reaction R_i occurring at each cycle is proportional to the value of $r(R_i)$. Second, choose the molecules or molecule containing the reacting groups of the selected reaction type for entering this reaction. Then these two smaller molecules become a larger one, or a cyclization forms.

The choice mentioned above is random in space; thus, the topological effect is neglected.

II. Algorithm. (1) Initial conditions. According to the compositions of the added monomers, set the values $n(I,J)$ and $W(I)$ for each molecule MOL(I), in which $I = 1, ..., N_p$ and $J = 1, ..., N_g$.

(2) Choice of the reaction type R_x. From the sample space $\{S(R_1), S(R_2), ..., S(R_m)\}$, in which $S(R_i)$ is the event of the reaction R_i, search for the entering reaction type R_x, $x = 1, ...,$ or m, by using the piecewise fitting method:[26]

$$\sum_{i=1}^{x-1} r(R_i) < \epsilon_R \sum_{i=1}^{m} r(R_i) \le \sum_{i=1}^{x} r(R_i) \quad (3)$$

where ϵ_R is a uniformly distributed random number in the interval (0,1).

(3) Choice of the reaction molecule. The opportunity of the molecule MOL(I) entering this reaction, R_x, is proportional to the number of the reacting groups $A(b_{x1})$ or $A(b_{x2})$ of MOL(I), $n(I,b_{x1})$ or $n(I,b_{x2})$. Thus, according to the following rules, search for the reaction molecules MOL(Y) and MOL(Z), which contain reacting group $A(b_{x1})$ or $A(b_{x2})$ by the piecewise fitting method:

$$\sum_{I=1}^{Y-1} n(I,b_{x1}) < \epsilon_1 \sum_{I=1}^{N_p} n(I,b_{x1}) \le \sum_{I=1}^{Y} n(I,b_{x1}) \quad (4)$$

$$\sum_{I=1}^{Z-1} n(I,b_{x2}) < \epsilon_2 \sum_{I=1}^{N_p} n(I,b_{x2}) \le \sum_{I=1}^{Z} n(I,b_{x2}) \quad (5)$$

where ϵ_1 and ϵ_2 are random numbers in the interval (0,1).

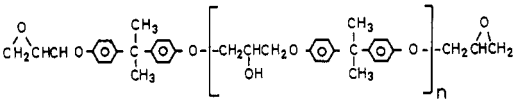
(4) Bookkeeping. For each cycle, consume one reacting group $A(b_{x1})$ and one $A(b_{x2})$ and produce one resultant group $A(b_{i3})$ and one $A(b_{x4})$. There are two different cases as follows:

Case 1. Intermolecular reaction (if $Y \neq Z$, combine MOL(Y) and MOL(Z) to a larger one).

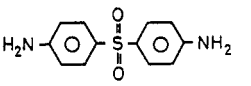
$$n(Y,J) \leftarrow n(Y,J) + n(Z,J), \quad J = 1, ..., N_g$$

$$W(Y) \leftarrow W(Y) + W(Z)$$

(a) diglycidyl ether bisphenol A (DGEBA) based epoxy resin (DER 332)



(b) 4,4'-Diaminodiphenyl Sulfone (DDS)



(c) 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (3DCM)

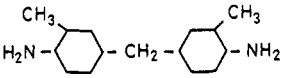


Figure 1. Structural formulas of (a) DGEBA based epoxy resin (DER 332), (b) DDS, and (c) 3DCM.

$$n(Y,b_{x1}) \leftarrow n(Y,b_{x1}) - 1$$

$$n(Y,b_{x2}) \leftarrow n(Y,b_{x2}) - 1$$

$$n(Y,b_{x3}) \leftarrow n(Y,b_{x3}) + 1$$

$$n(Y,b_{x4}) \leftarrow n(Y,b_{x4}) + 1$$

$$n(Z,J) \leftarrow n(N_p,J), \quad J = 1, ..., N_g$$

$$W(Z) \leftarrow W(N_p)$$

$$N_p \leftarrow N_p - 1$$

Case 2. Intramolecular reaction (if $Y = Z$, molecule MOL(Y) reacts with itself).

$$n(Y,b_{x1}) \leftarrow n(Y,b_{x1}) - 1$$

$$n(Y,b_{x2}) \leftarrow n(Y,b_{x2}) - 1$$

$$n(Y,b_{x3}) \leftarrow n(Y,b_{x3}) + 1$$

$$n(Y,b_{x4}) \leftarrow n(Y,b_{x4}) + 1$$

$$N(\text{intra}) \leftarrow N(\text{intra}) + 1$$

where N(intra) denotes the times of the intramolecular reaction occurring, i.e., the cycle rank.

(5) Calculation of the average molecular weight and conversion.

$$\bar{M}_N = \sum_{I=1}^{N_p} W(I)/N_p \quad (6)$$

$$\bar{M}_W = \sum_{I=1}^{N_p} W^2(I) / \sum_{I=1}^{N_p} W(I) \quad (7)$$

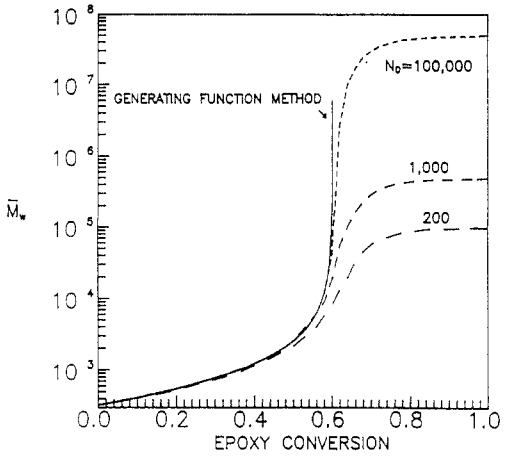


Figure 2. Size effect on the weight-average molecular weight versus epoxy conversion.

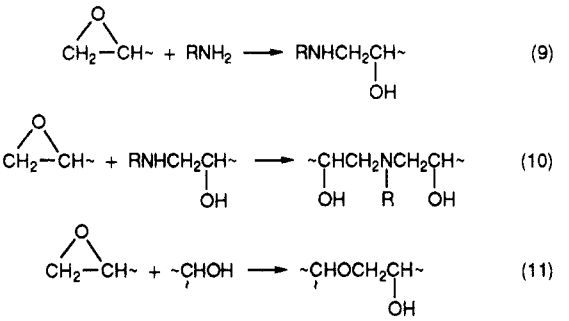
$$\text{conversion of the group } A(J) = 1 - \sum_{I=1}^{N_p} n(I,J)/N(J,t=0) \quad (8)$$

where $\bar{M}_W$ and $\bar{M}_N$ are the weight-average and number-average molecular weights of the polymers, respectively, and $N(J,t=0)$ is the initial total number of the group $A(J)$ of the system.

(6) Repeat procedures 2–5 until the total reaction rate, $\sum_{i=1}^{m} r(R_i)$, becomes zero.

The flowchart of this simulation algorithm is plotted in the appendix.

III. Kinetic Model of Epoxides Cured with Amines. According to the literature,[28,29] the three main elementary reactions for the epoxy cured with a primary amine system are



In terms of the reacting and resultant groups, these reactions can be written as

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

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

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

where EP, PA, SA, TA, ET, and OH are defined as the epoxy, primary amine, secondary amine, tertiary amine,

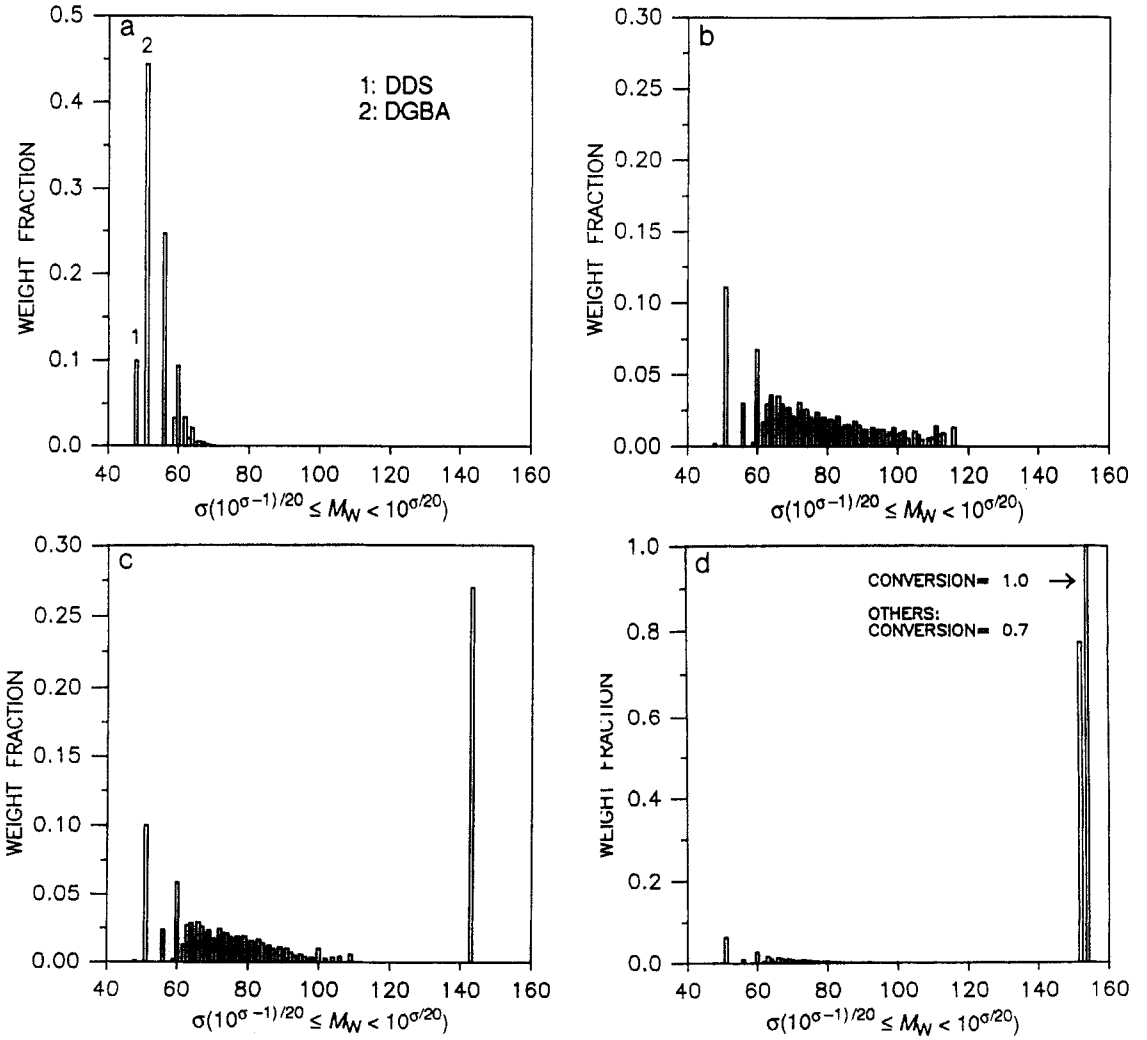


Figure 3. Molecular weight distribution as function of epoxy conversion: α(EP) = (a) 0.2; (b) 0.6; (c) 0.62; (d) 0.7 or 1.0 (R = 1, b = 0, N_0 = 100 000).

ether, and hydroxyl containing groups, respectively, and

$$k_i = k_i' + k_i''[\mathrm{OH}] \qquad i = 1, 2, 3 \tag{15}$$

where k_i' and k_i'' denote noncatalytic and catalytic rate constants, respectively, and [OH] is the concentration of the hydroxyl group. The ratios of rate constants are assumed to be as follows:[30]

$$k_2/k_1 = k_2'/k_1' = k_2''/k_1'' = a \tag{16}$$

$$k_3/k_1 = k_3'/k_1' = k_3''/k_1'' = b \tag{17}$$

where a and b are assumed to be constants and independent of the extent of reaction and curing temperature.

Furthermore, the rate equation of the epoxy groups could be described as follows:

$$-\mathrm{d[EP]}/\mathrm{d}t = 2k_1[\mathrm{EP}][\mathrm{PA}] + k_2[\mathrm{EP}][\mathrm{SA}] + k_3[\mathrm{EP}][\mathrm{OH}] = r_{\mathrm{ep}}(t) \tag{18}$$

$$\mathrm{d}\alpha(\mathrm{EP})/\mathrm{d}t = r_{\mathrm{ep}}(t)/[\mathrm{EP}]_0 = r^*(t) \tag{19}$$

where $r_{\mathrm{ep}}(t)$ denotes the total reaction rate of the epoxy groups at time t, $[\mathrm{EP}]_0$ is the initial concentration of the epoxy group, and $\alpha(\mathrm{EP})$ is the epoxy conversion. According the trapezoid rule, the time interval Δt between $\alpha(\mathrm{EP})_t$ and $\alpha(\mathrm{EP})_{t+\Delta t}$ can be calculated by the following equation:

$$\Delta t = 2[\alpha(\mathrm{EP})_{t+\Delta t} - \alpha(\mathrm{EP})_t]/[r^*(t) + r^*(t+\Delta t)] \tag{20}$$

Thus, we can get the time interval Δt for each cycle of the MC simulation.

3. Results and Discussion

I. DER 332/DDS System. This method was first applied to the diglycidyl ether Bisphenol A (DGEBA) based epoxy resin DER 332 cured with the bis(4-aminophenyl) sulfone (DDS). The structural formulas of DER 332 and DDS are shown in Figure 1. In this case, the average value of n is equal to 0.03,[31] thus, the epoxy prepolymer, DER 332, is assumed to be a mixture having 97 mol % pure DGEBA (n = 0) and 3 mol % second hydroxyl containing DGEBA based epoxide (n = 1). The parameters of this simulation are as follows:

$$a = 0.4 \qquad b = 0 \text{ or } 0.1$$

molecular weight of epoxide (n = 0) = 340

molecular weight of epoxide (n = 1) = 624

molecular weight of DDS = 248

$$R = 1/2,\ 1/1,\ \text{or}\ 1/0.6$$

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

Figure 2 shows the weight-average molecular weight of polymers, $\bar{M}_W$, versus the epoxy conversion, $\alpha(\mathrm{EP})$, for various finite sizes based on the initial number of the epoxy prepolymers, N_0. As the size increased, the profiles approach the result calculated by the generating function method,[25] of which the system is considered as an infinite size.

The molecular weight distributions are shown in the Figure 3a–d. The weight fractions of smaller molecules decrease with the epoxy conversion for forming the larger molecules, whereas the molecular weight of the largest one, M_W(largest), increases with the conversion. After the critical conversion, about 0.6 in this case, the value of M_W(largest) rises much higher than the other ones (see parts c and d of Figure 3). The profiles of molecular weight of the largest and second-largest molecule are plotted in Figure 4. The molecular weight of the largest one rises sharply near the gel point. On the other hand, increasing with the conversion, the molecular weight of the second-

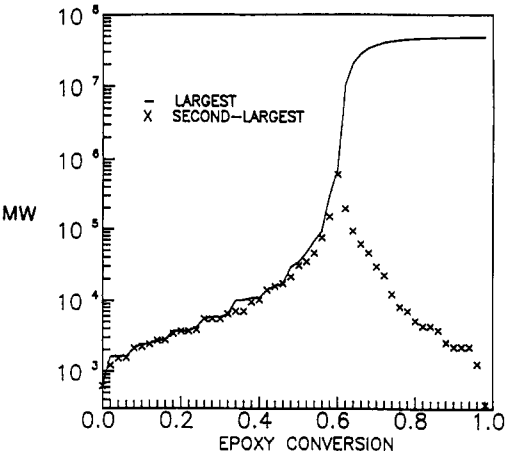


Figure 4. Molecular weights of the largest and second-largest molecules versus epoxy conversion (R = 1, b = 0, N_0 = 100 000).

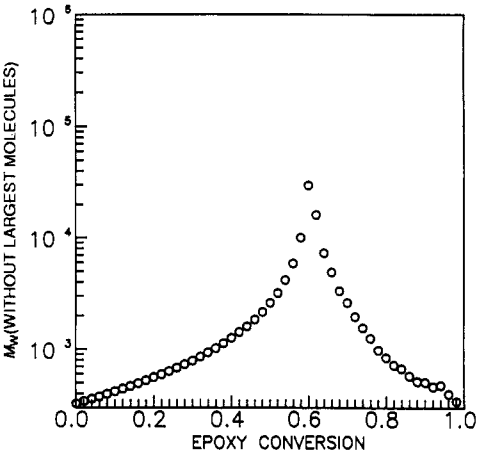


Figure 5. Reduced weight-average molecular weight of polymers versus epoxy conversion (R = 1, b = 0, N_0 = 100 000).

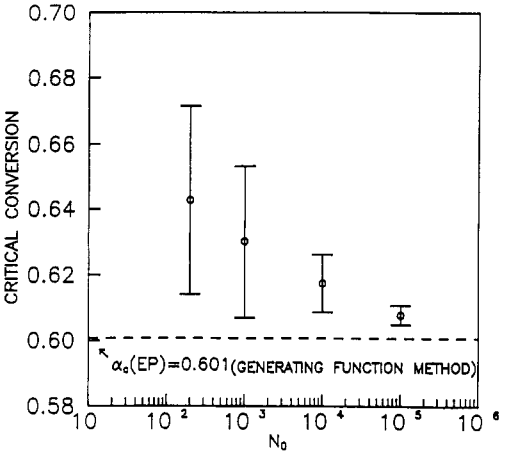


Figure 6. Size effect on the critical epoxy conversion (R = 1, b = 0). Error bars: standard deviation with at least 5 times the independent MC experiments.

Table 1. Comparison of the Critical Conversion for a DGEBA/DDS System[a]

	$R = [AM]_0/[EP]_0$ with $k_3/k_1 = 0$		
	1/2	1/1	1/0.6
critical conv I	0.419	0.608	0.803
critical conv II	0.411	0.601	0.793
difference (I − II)	0.008	0.007	0.010
	$R = [AM]_0/[EP]_0$ with $k_3/k_1 = 0.1$		
	1/2	1/1	1/0.6
critical conv I	0.408	0.592	0.780
critical conv II	0.398	0.584	0.771
difference (I − II)	0.010	0.008	0.009

[a] I: Monte Carlo method (N_0 = 100 000). II: Generating function method.

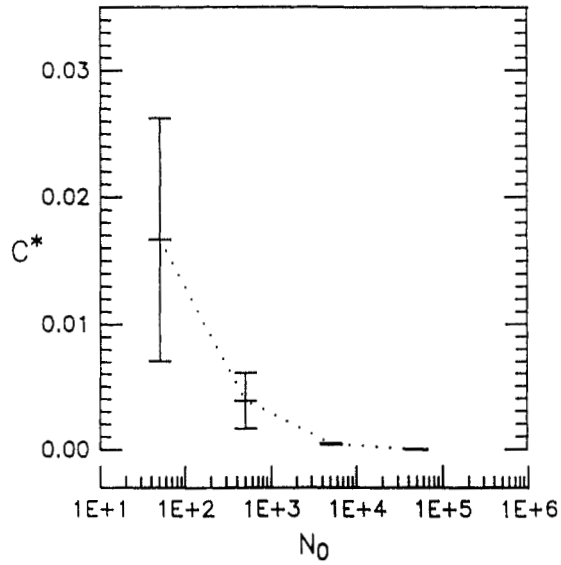


Figure 7. Size effect on the value of C^*, the cycle rank over the number of bonds (R = 1, b = 0). Error bars: standard deviation with at least 3 times the independent MC experiments.

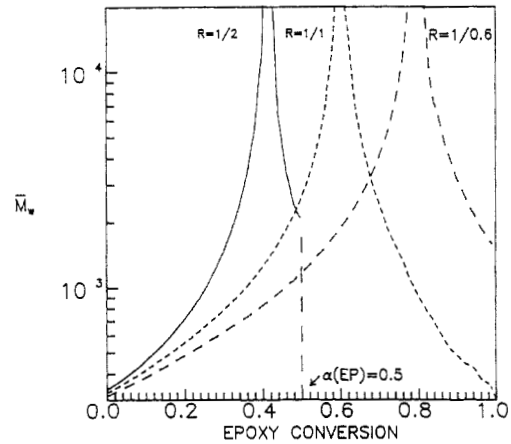


Figure 8. Weight-average molecular weight of the sol phase versus epoxy conversion for various R (b = 0, N_0 = 100 000).

largest molecule follows closely the largest one until near the gel point and then decreases after the gel point. It can be explained by the kinetic theory. Near the gel point, the probability of a combination of the largest molecule with the second-largest molecule is much higher than the other ones, for the larger molecules contain a higher number of unreacted groups.

Table 2. Number of Intramolecular Reactions as a Function of Epoxy Conversion (R = 1, b = 0, N_0 = 100 000)

α(EP)	N(intra)	α(EP)	N(intra)	α(EP)	N(intra)	α(EP)	N(intra)
0.00	0	0.60	5	0.52	1	0.70	3156
0.20	0	0.62	33	0.54	2	0.80	15104
0.40	0	0.64	260	0.56	2	0.90	31983
0.44	1	0.66	850	0.58	4	1.00	51547
0.50	1	0.68	1809				

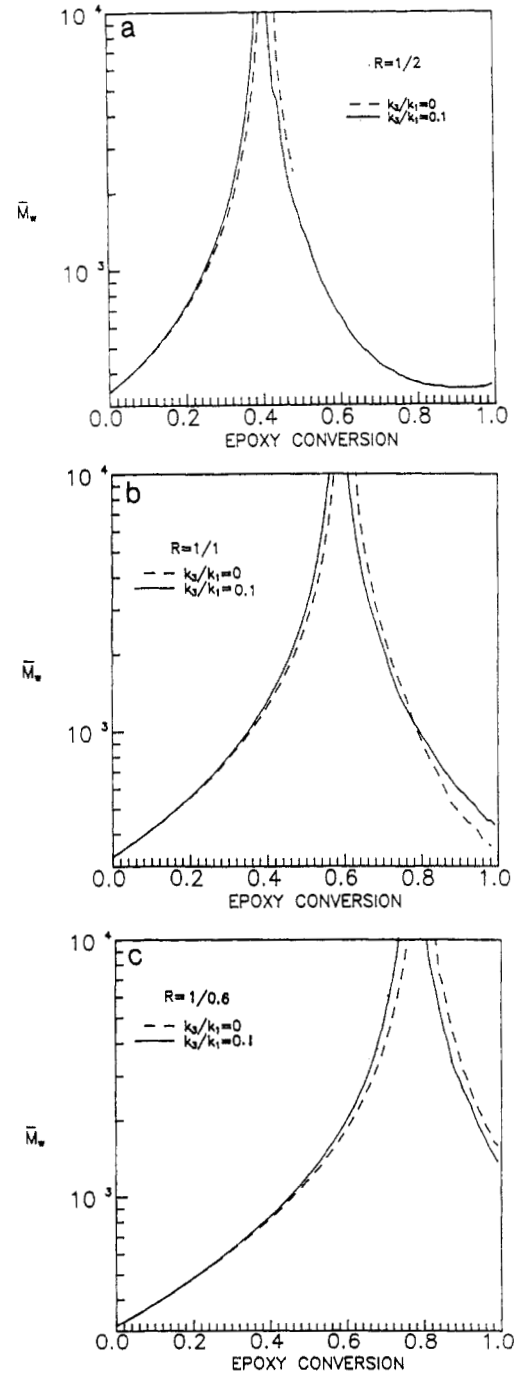


Figure 9. Effect of etherification on the weight-average molecular weight of the sol phase versus epoxy conversion for various R: (a) 1/2; (b) 1/1; (c) 1/0.6 (N_0 = 100 000).

In order to determine the gel point, for a finite curing system, the method of reduced average molecular size was used.[32] Figure 5 shows the reduced weight-average molecular weight, the average molecular weight of the system without the largest one, as function of the epoxy conversion. The critical conversion is determined by the conversion at which the reduced weight-average molecular

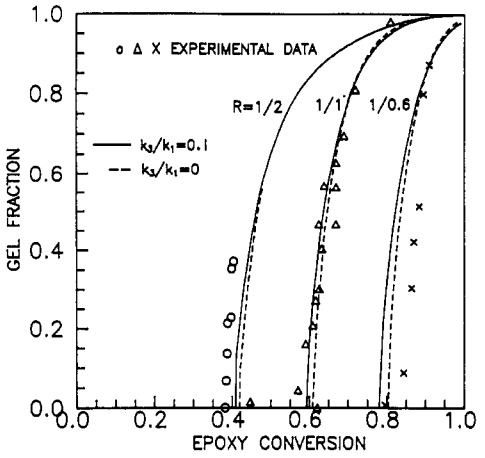


Figure 10. Comparison of the gel fraction by the MC simulation (N_0 = 100 000) to the experimental data from ref 34.

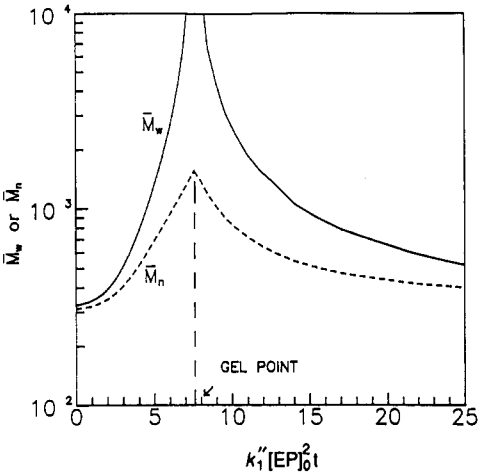


Figure 11. Average molecular weights, $\bar{M}_W$ and $\bar{M}_N$, of the sol phase versus reaction time for a DER 332/3DCM system (N_0 = 100 000).

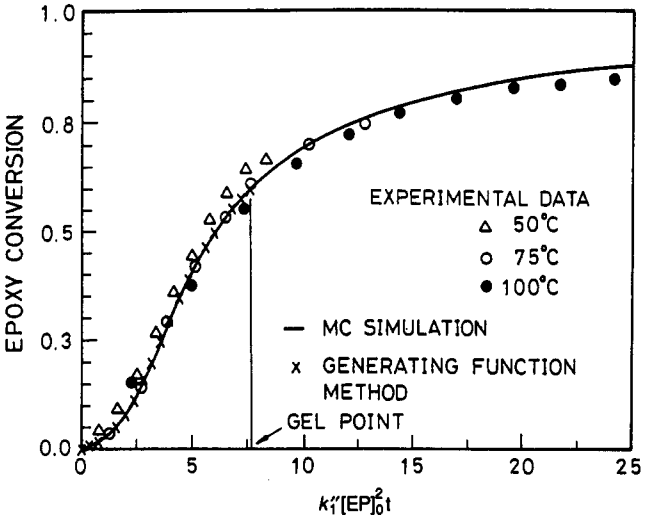


Figure 12. Comparison of the epoxy conversion versus time by the MC simulation (N_0 = 100 000) to the generating function method and the experimental data determined by DSC.

weight reaches the maximum value.

The size effects on the critical epoxy conversion, α_c(EP), are shown in Figure 6. It is found that, if the size, N_0, is larger, the critical conversion of the finite system is closer to the infinite one obtained by the generating

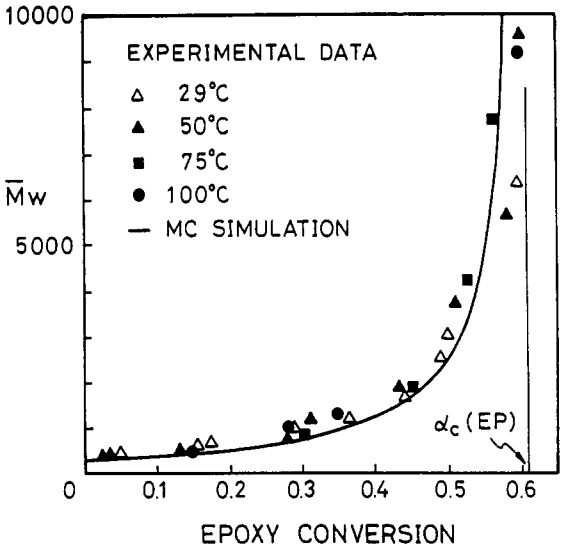


Figure 13. Weight-average molecular weight versus epoxy conversion for a DER 332/3DCM system (experimental data from ref 31).

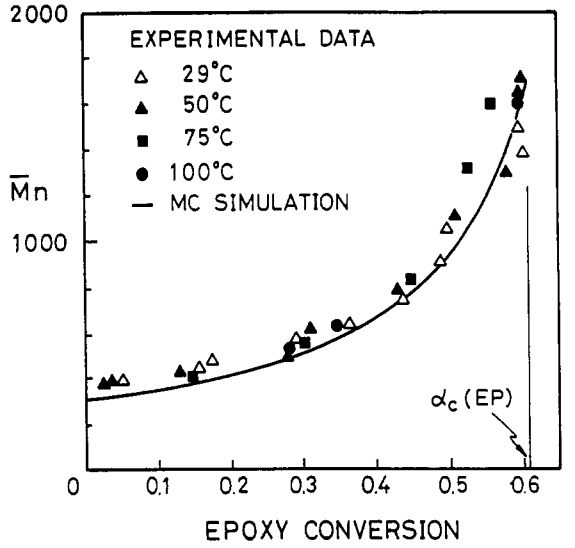


Figure 14. Number-average molecular weight versus epoxy conversion for a DER 332/3DCM system (experimental data from ref 31).

Table 3. Comparison of the Critical Conversion for Various Models ($b = k_3/k_1 = 10$, $N_0 = 50\,000$)

	MC method		combined model[a]		PRM[b]	
R	α_c(EP)	α_c(H)[c]	α_c(EP)	α_c(H)[c]	α_c(EP)	α_c(H)[c]
0.25	0.20	0.29	0.19	0.28	0.53	0.47
0.5	0.29	0.24	0.26	0.23	0.56	0.34
1	0.37	0.18	0.35	0.18	0.63	0.25
2	0.52	0.14	0.47	0.13	0.74	0.18

[a] Rigorous model.[23] [b] Primitive random model (approximate model).[23] [c] α_c(H): critical amine hydrogen conversion.

function method[25] and the standard deviation becomes narrower. Table 1 shows the differences between these two methods for various systems, and all of the differences of the critical conversions are not larger than 0.01.

Although the cyclizations in our MC simulations are allowed either before or after the gel point, only a very few times of the intramolecular reactions occur before the gel point for a large finite system (see Table 2). Figure 7 shows the size effects on the cycle rank at α(EP) = 0.6,

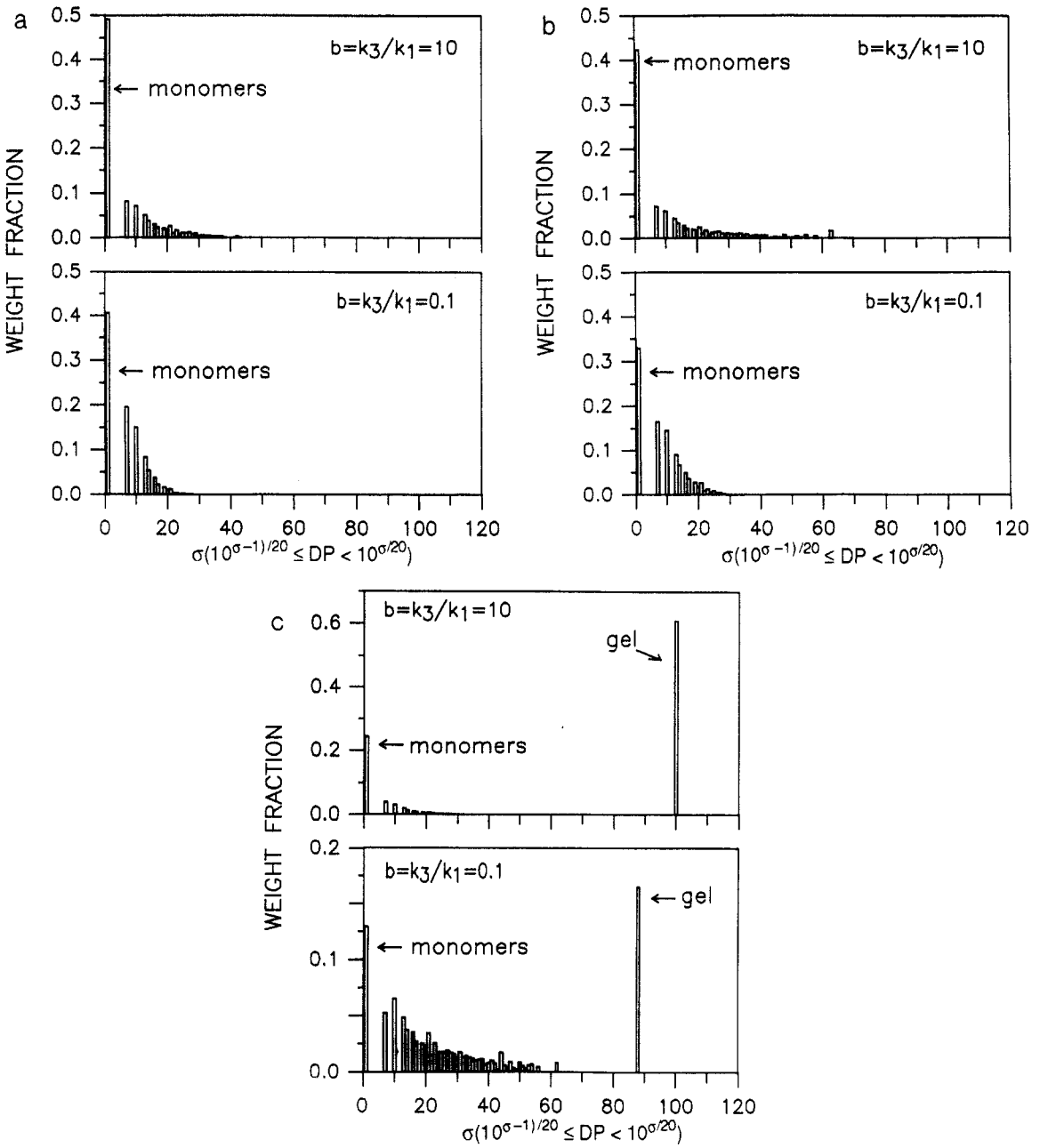


Figure 15. Distribution of the degree of polymerization: α(EP) = (a) 0.3; (b) 0.36; (c) 0.56 (R = 1, b = 10 or 0.1, N_0 = 50 000).

near the gel point α_c(EP) = 0.601, in which C^* denotes the cycle rank over the total number of bonds of the system. As N_0 increases, the value of C^* tends to be zero, and this result is consistent with the random stepwise polymerization studied by Falk and Thomas.[33]

After the critical conversion, the largest molecule is taken as the gel phase, and the other molecules, all of which are far smaller than the largest one, are taken as the sol phase. Figure 8 illustrates the weight-average molecular weight of the sol phase versus epoxy conversion. The profiles are shifted from left to right as the values of R, $[AM]_0/[EP]_0$, increase. If the etherification (eq 14) is neglected, i.e., k_3 = 0, the reaction of the system with excess epoxy, R = 0.5, stops at the epoxy conversion of 0.5, for the amine groups are exhausted, whereas if the etherification is taken into account, the reaction progresses until all of the epoxy groups are reacted (Figure 9a), because the etherification is a living polymerization, and the hydroxyl groups are not consumed by this reaction. Furthermore, the etherification generates the extra branching and leads to a lower critical epoxy conversion, α_c(EP). These results are shown in Figure 9a–c and Table 1. Figure 10 shows the results of the MC simulation for the gel fraction, and the calculated values agree well with the experimental data.[34]

II. DER 332/3DCM System. Another system studied is the diglycidyl ether Bisphenol A (DGEBA) based epoxy resin DER 332 cured with the bis(4-amino-3-methylcyclohexyl)methane (3DCM), of which the structural formula is shown in Figure 1. In this calculation, the noncatalytic reactions and etherification are neglected, and the parameters of this model are[31]

$$k_1' = k_2' = 0 \qquad a = 0.4 \qquad b = 0$$

molecular weight of epoxide (n = 0) = 340

molecular weight of epoxide (n = 1) = 624

molecular weight of 3DCM = 238

$$R = 1$$

According to eq 20, we can obtain the average molecular weight of the sol phase versus the reaction time in Figure 11 and the epoxy conversion as function of the reaction time in Figure 12. The simulated result in Figure 12 is consistent with the experimental data determined by DSC.[31] Before gelation, the conversion profile can also be calculated by the generating function method,[25] shown with symbol "×" in Figure 12, which coincides well with the curve by the MC method. Figures 13 and 14 show the calculated weight-average and number-average molecular weights of the polymers, $\bar{M}_W$, and $\bar{M}_N$, versus the epoxy conversion, respectively, and the profiles predicted by the MC simulation agree fairly well with the experimental measurements.[31]

III. Comparison of the Gel Point Determined by Different Models. Table 3 shows the comparison of the critical conversion determined by various models in the effect of etherification for a diepoxy cured with a difunctional diamine.[23] In this study, the substitution effect is ignored; that is, the parameter $a = 1$. For the reaction dominated by the etherification, $b = 10$, the results calculated by the MC method are closer to the combined model (rigorous model) than the approximate one, which ignores some nonrandom combinations.[23] The size effect of the finite system mentioned above results in the differences between the values of α_c obtained by the MC method and the rigorous model.

Furthermore, the MWD was inspected by the MC simulation for two cases, $b = 10$ and 0.1. As shown in Figure 15, in the pregelation stage, the distribution of the degree of polymerization (DP) of the system with a fast rate constant of etherification ($b = 10$) is broader than that of the system with $b = 0.1$ at the same conversion. Because, for the etherification dominated system, the reacted molecule with a larger number of –OH groups is easily combined with other molecules containing epoxy groups and then forms a larger molecule, this causes a high-DP tail on the distribution and leads to a lower critical conversion. Moreover, the consumption of monomers of the case $b = 0.1$ is faster than that of the case $b = 10$.

4. Conclusion

A very general Monte Carlo method has been developed for various simulating network formations with a complex chemical reaction mechanism. This method was applied to the systems of epoxides cured with primary amines in this work. The relationships among the structure, such as the molecular weight, gel fraction, and conversion or reaction time, can be obtained by the MC simulation.

It is shown that the etherification (living polymerization) leads to the lower critical epoxy conversion, and the distribution of the degree of polymerization (DP) of the system dominated by living polymerization is broader than stepwise polymerization before gelation. If the effect of topology is not considered, very few times of the intramolecular reactions occur before gelation for the large finite system. The gel point determined by this MC method varies with changing the finite size of the simulation system, and the size is larger when the critical conversion of the finite system is closer to the infinite one obtained by the generating function method.

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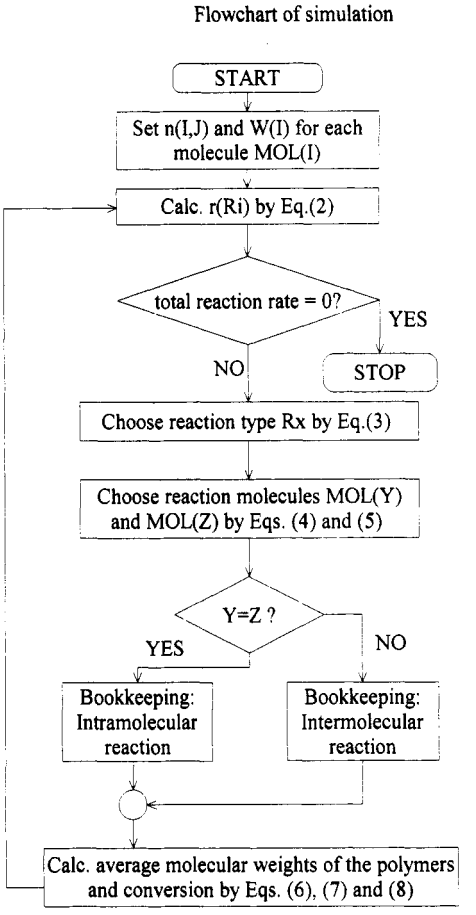
Appendix



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