Polymer Chain Buildup and Network Formation of Imidazole-Cured Epoxy/Phenol Resins

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ABSTRACT: A new algorithm of Monte Carlo (MC) simulation has been proposed for the imidazole/epoxy/phenol resin system. The strategy of the MC method is divided into two steps: the first is deciding the type of reaction mechanism, and then choosing the reacting functional groups. The structural properties corresponding to the conversion change, such as the average molecular weight, the molecular weight distribution, the sol−gel fraction, and the branch point distribution of the sol part can be simulated by this method. The BPA molar ratio seems the most important factor in this system. Because it dominates the final structure of the cured resins, either linear or branched. The theoretical results were compared and verified by the gel permeation chromatography and the sol extraction analysis. Both theoretical and experimental results coincide with each other very successfully.

Introduction

In recent years, there has been a great increase in the number of application of epoxy-phenol resins, especially in the electronics industry as encapsulating and packing materials.[1−3] Nowadays the chip sizes have become larger, while the dimensions of devices inside the chip have become smaller and the structure of the chip has become more delicate. Encapsulants formulated out of epoxy/phenol resins are transfer-molded to form the protective shell outside the integrated circuits. During the polymerization, the molecular weight increases and the cross-linked structure builds up, which governs the rheological and mechanical properties of the cured resins. The polymerization of diglycidyl ether of bisphenol A (DGEBA) cured with bisphenol A (BPA) and 2 ethyl-4-methylimidazole (2,4EMI), forming a liner structure or a densely cross-linked network, is controlled by the molar ratio between DGEBA and BPA. There have been some studies on the reaction kinetics.[4−9] However, a theoretical treatment on the chain buildup and network formation governed by these apparent complicated reaction mechanisms is still lacking.

The theories of network formation during the curing of epoxy resin can be divided into two major fields: One is based on the Flory−Stockmayer off-lattice theory,[10−14] i.e., the graphlike model, including the statistical and kinetic methods. The other is the network simulation in *n*-dimensional space, such as the percolation method.[15] For the statistical method, one can theoretically establish the branched or cross-linked structures by the combination of monomer (or other) units in different reaction states. These combinations are based on the first-order Markovian chain rules, which, in the theory of branching process[16] (TBP) is mathematically transferred into cascade substitution[17−19] and yields recurrent equations for the structure propagation probabilities. The history of the network formation is reflected only through the time evolution of the distribution of units in different reaction states. No information about how these units are combined in the sequence. For the kinetic method,[20−23] every molecule, including the gel, is considered as individual component, and the structure buildup vs time (or conversion) is described by an infinite set of differential equations. These kinetic equations are a degenerated case of Smoluchowski coagulation equations. The reactivity of functional group can depend on the size and structure of molecules. Besides, there are other statistical models, including the expectation theory of Miller and Macosko[24,25] and the branching theory proposed by Durand et al.[26,27] They are the same as cascade theory but use somewhat different mathematical representations.

All of the methods surveyed above were successfully applied to the complex systems for calculating the structural properties of polymer as a function of conversion. But the derived mathematical formula is case by case and very complicated. Moreover, only average properties can be obtained by these methods.

Besides the average properties by the conventional methods, the Monte Carlo (MC) method[28] can provide very detailed insight information about the structural evolution of polymer chains, such as the molecular weight distribution, the branch point distribution, and the loop structure inside the chains. This detailed information is very important for the understanding of the chemorheological properties due to the evolution of branched or cross-linked structure inside the polymers.

In this work, we develop a quite general algorithm of MC simulation for network formation with complex kinetic mechanisms. The polymer chain buildup properties, such as the molecular weight of the sol, the sol−gel fraction, and the branch point distribution of sol were studied by the MC method. To verify the theoretical results, the experimental data by gel permeation chromatography (GPC) and the sol extraction analysis

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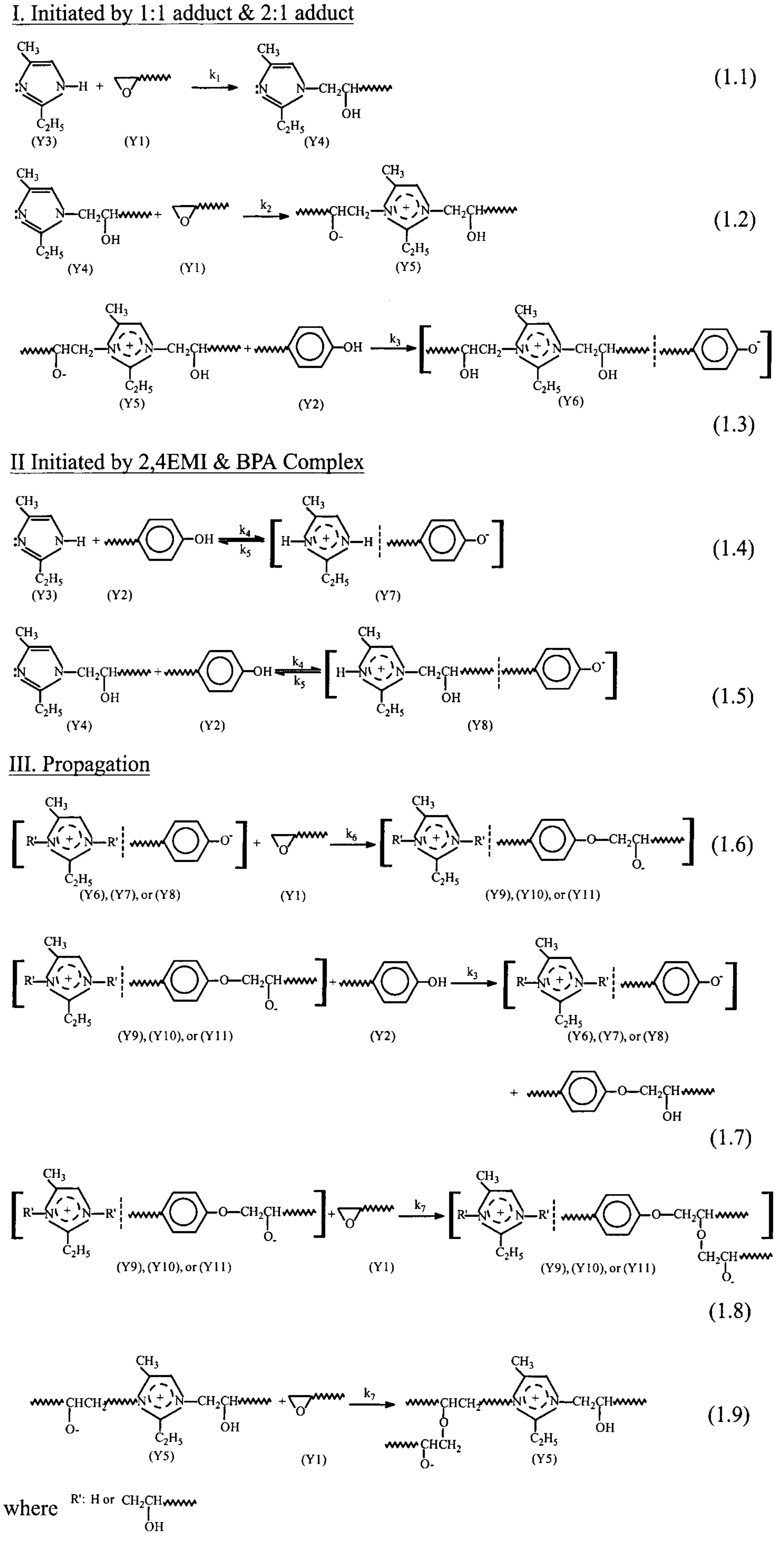

Figure 1. Proposed reaction mechanisms.

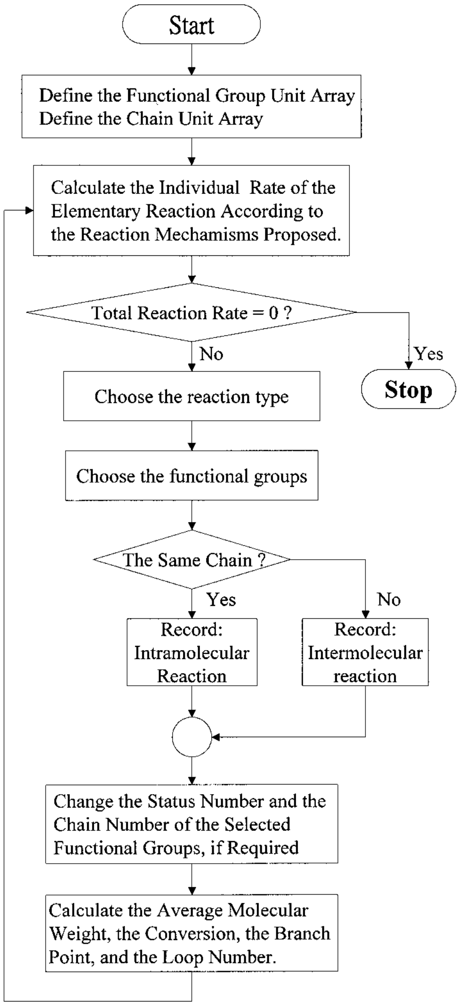

Figure 2. Concise flowchart of the Monte Carlo simulation.

Table 1. Reaction Rate Constants[9] Used in MC Simulation

k_1 and k_2 (L/(mol s))		k_3 ((L/mol s))	
ln(*A*)	E_a (kJ/mol)	ln(*A*)	E_a (kJ/mol)
18.33	74	13.52	38.35

k_4 (L/(mol s))	k_5 (1/s)
5×10^{-2}	10^{-7}

molar ratio DGEBA/ BPA/2,4EMI	k_6 (L/(mol s))			K_7 (L/(mol s))		
	ln(*A*)	E_a (kJ/mol)	*R*	ln(*A*)	E_a (kJ/mol)	*R*
100/40/6	20.40	79.81	−0.998	21.46	80.07	−0.997
100/40/4	20.62	80.18	−1.000	20.73	77.36	−0.992
100/80/4	21.35	81.42	−0.998	21.35	81.42	−0.998
100/100/6	20.68	79.34	−0.998	20.68	79.34	−0.998
100/100/4	20.69	79.30	−0.997	20.69	79.30	−0.997

were also studied. Both theoretical and experimental results coincided with each other very successfully.

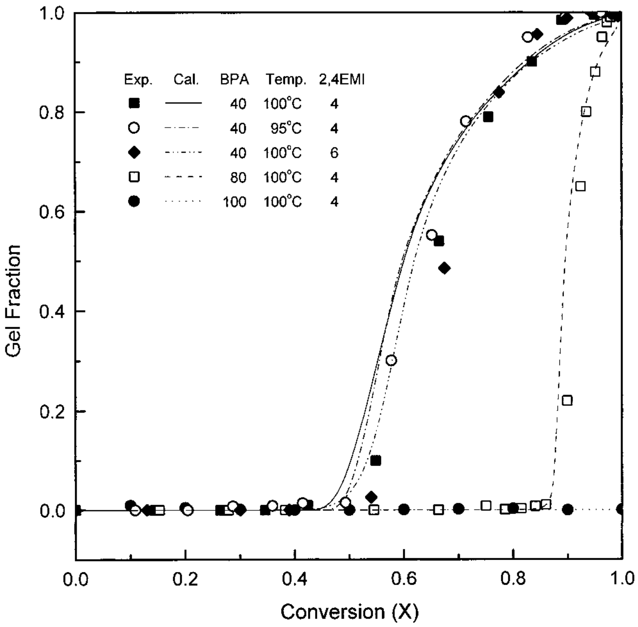

Figure 3. Gel fraction profile vs conversion for DGEBA cured with different BPA molar ratio, different 2,4EMI molar ratios, and reaction temperatures.

Table 2. Molecular Weight of Materials Used in MC Simulation

material	molecular weight
DGEBA (*n* = 0)	340
DGEBA (*n* = 1)	624
BPA	228
2,4EMI	110

Experimental Section

Materials. The epoxy resin (DER332), a nearly pure form of the diglycidyl ether of bisphenol A(DGEBA), was supplied by the Dow Chemicals Co. The epoxide equivalent weight (EEW) of DER332, determined by titration, was 174 g/mol-epoxide. The difunctional phenol, bisphenol A (BPA) with a purity >99%, was obtained from the Tokyo Chemical Industry Co. The imidazole, 2-ethyl-4-methyl-imidazole (2,4EMI) with a purity >99%, was obtained from Acros Organics. All materials were stored in a desiccator and used as received without further purification.

Sample Preparation. Different molar ratios of BPA/epoxide and 2,4EMI were dissolved separately in spectrometric grade acetone. Both of the solutions were added and mixed well by rigorous stirring, and the acetone was evaporated under vacuum at 30 °C for 10 min. The resultant mixture was immersed in ice-cold water immediately to minimize further cure reaction before kinetics studies and other experiments. The prepared samples were surveyed from room temperature to 320 °C by thermogravimetric analysis (TGA). The results of TGA showed that the total weight loss caused by residual acetone loss and thermal degradation of resultant mixture is less than 1%.

Polymerization and Sol Extraction. The prepared samples (ca. 5 g) were added into empty glass tubes and sealed well. All sample tubes were immersed into the isothermal silicon oil bath, and then further reaction was restarted at the setting temperature. Sample tubes were removed from the silicon oil bath at various reaction time intervals and immediately quenched, and the sample was pulverized in liquid nitrogen. Then tetrahydrofuran (THF) was added into the sample tube to extract the soluble portion from the cured sample. All sample tubes were fixed on a shaker water bath and kept at 15 °C during the extraction experiments. The sample was extracted for at least 2 days and the solvent was replaced with fresh THF every 6 h. The sol fraction was determined from the difference between the initial and final weights of the cured sample.

Gel Permeation Chromatography (GPC) Analysis. A Waters Associates Chromatograph (model 6000A pump) was equipped with three columns, one Polymer Laboratories

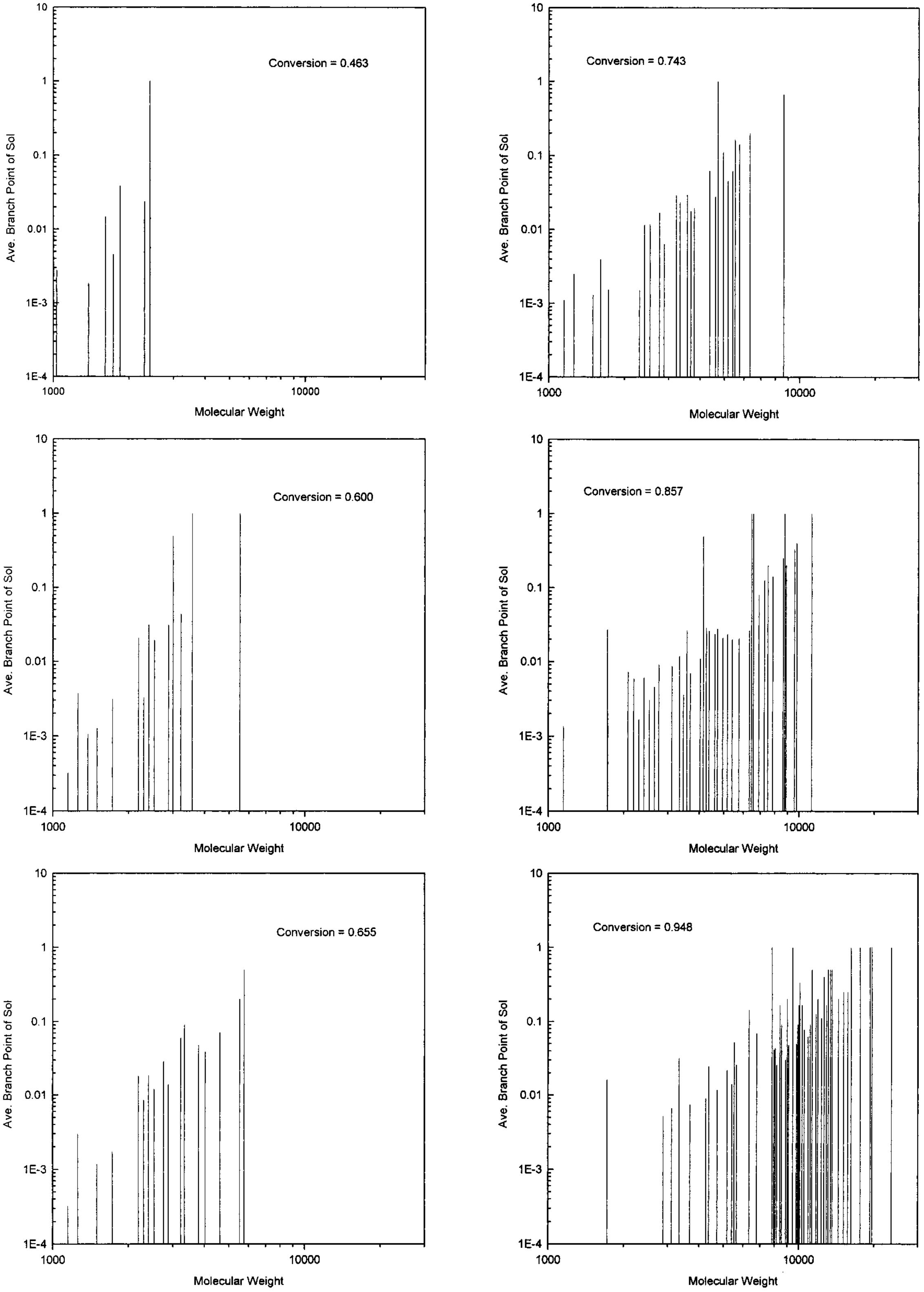

Figure 4. Branch point profiles at different conversions for the molar ratio of DGEBA/BPA/2,4EMI 100/100/4, at 100 °C.

Mixed-C, and two American Polymer Standard 100 Å in series, connected to the Shodex RI-71 refractive index detector. The analytical pure THF was used as eluent, and the flow rate was set to 1 mL/min. The average molecular weights were determined from the calibration curve established by means of polystyrene standards (Polymer Laboratories) with normal molecular weights 162, 580, 2100, 3250, 9200, 28500, 66000, 156000, 330000, 1030000, and 3040000.

Theoretical Approach

Reaction Mechanisms. On the basis of our previous studies,[9] the proposed reaction mechanisms are shown

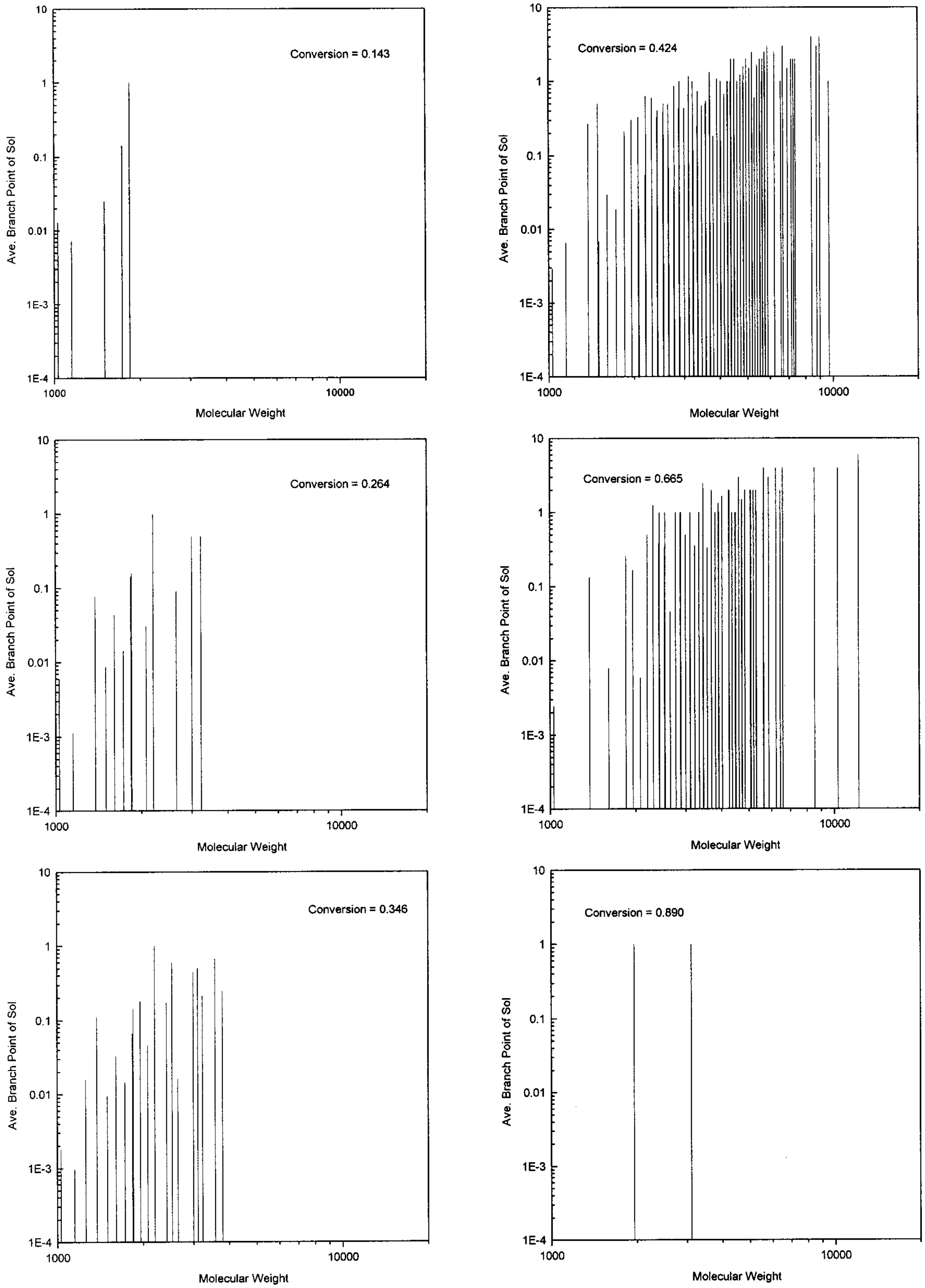

Figure 5. Branch point profiles of the sol part at different conversions for the molar ratio of DGEBA/BPA/2,4EMI: 100/40/4, at 100 °C.

in Figure 1. It contains two initiation mechanisms: the first one starts with the adduct ion of the pyridine-type nitrogen with epoxy (1.1, 1.2). The second results from the ionic nature of the 2,4EMI-phenol interaction (1.4, 1.5). And the following propagation steps consist of three main reaction mechanisms: the epoxide/phenol reaction 1.6, the acid–base reaction (1.3, 1.7), and the epoxide/R–O^- reaction (1.8, 1.9). And the corresponding mathematical scheme can be expressed as (where "y_i" are identified in Figure 1)

$$\frac{dy_1}{dt} = -k_1y_1y_3 - k_2y_1y_4 - k_6y_1(y_6 + y_7 + y_8) - k_7y_1(y_5 + y_9 + y_{10} + y_{11}) \quad (1)$$

$$\frac{dy_2}{dt} = -k_3y_2y_5 - k_4y_2(y_3 + y_4) + k_5(y_7 + y_8) - k_3y_2(y_9 + y_{10} + y_{11}) \quad (2)$$

$$\frac{dy_3}{dt} = -k_1y_1y_3 - k_4y_2y_3 + k_5y_7 \quad (3)$$

$$\frac{dy_4}{dt} = k_1y_1y_3 - k_2y_1y_4 - k_4y_2y_4 + k_5y_8 \quad (4)$$

$$\frac{dy_5}{dt} = k_2y_1y_4 - k_3y_2y_5 \quad (5)$$

$$\frac{dy_6}{dt} = k_3y_2(y_5 + y_9) - k_6y_1y_6 \quad (6)$$

$$\frac{dy_7}{dt} = k_4y_2y_3 - k_5y_7 - k_6y_1y_7 + k_3y_2y_{10} \quad (7)$$

$$\frac{dy_8}{dt} = k_4y_2y_4 - k_5y_8 - k_6y_1y_8 + k_3y_2y_{11} \quad (8)$$

$$\frac{dy_9}{dt} = k_6y_1y_6 - k_3y_2y_9 \quad (9)$$

$$\frac{dy_{10}}{dt} = k_6y_1y_7 - k_3y_2y_{10} \quad (10)$$

$$\frac{dy_{11}}{dt} = k_6y_1y_8 - k_3y_2y_{11} \quad (11)$$

Monte Carlo Procedure. The strategy of the MC method is divided into two steps: the first is to decide the type of the reaction mechanism, and the second is to select the reacting functional groups. The concise flowchart is sketched in Figure 2.

All parameters used in Monte Carlo simulation are listed in Table 1. Since the average value of n of DER332 is 0.028, the epoxy prepolymer, is assumed to be a mixture having 97.2 mol % of pure DGEBA ($n = 0$) and 2.8 mol % of DGEBA ($n = 1$). And their molecular weights are listed in Table 2.

According to the method of reduced average molecular size,[29] the critical conversion (or the gel point) is defined as the conversion at which the weight-average molecular weight, excluding the largest molecule, reaches the maximum value.

In the following simulations, the dimension size of epoxide group is set as 100 000 and the numbers of BPA and 2,4EMI are depended on the molar ratios to epoxide group for different initial conditions. The results of MC simulation shown in figures are the mean values with at least five independent MC calculations.

Results and Discussion

In the following discussion, the molar ratio of BPA and 2,4EMI is relative to that of DGEBA.

Sol–Gel Fraction. In the MC simulation, the calculated gel fraction is defined as the weight of the first largest molecule over the total weight of the curing system. The comparison of the theoretical and experimental gel fraction vs conversion is shown in Figure 3.

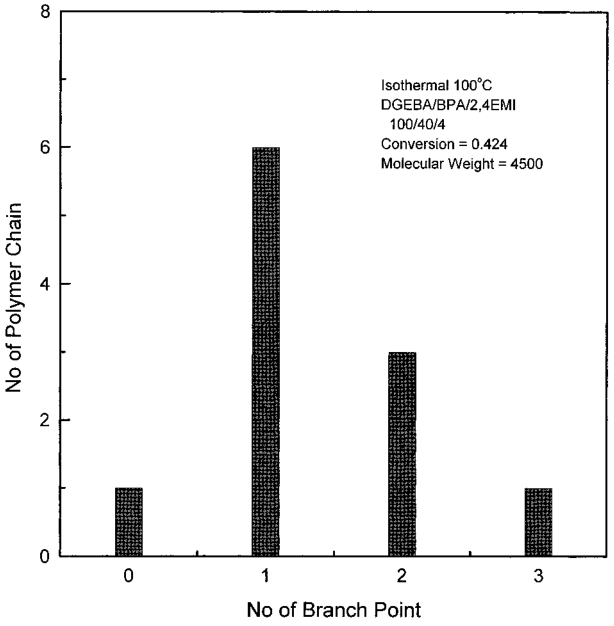

Figure 6. Branch point distributions at the molecular weight 4500, as the conversion is 0.424. Molar ratio of DGEBA/BPA/2,4EMI: 100/40/4, at 100 °C.

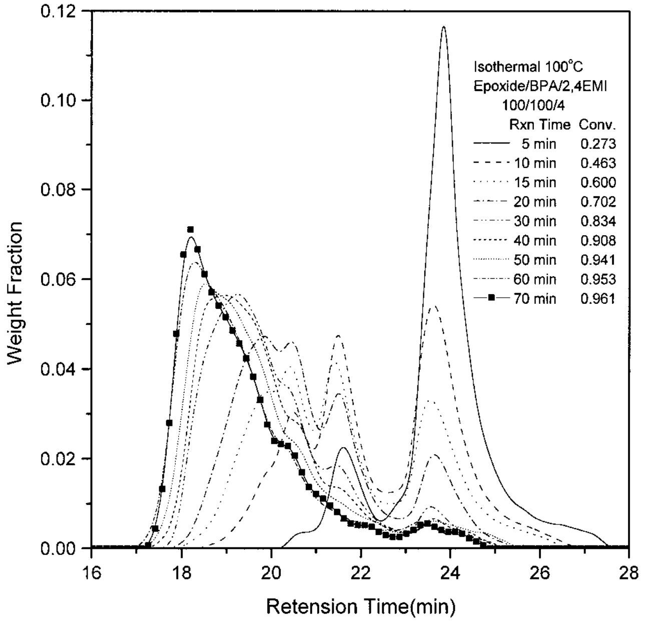

Figure 7. Normalized weight fraction profile at different time intervals by GPC for DGEBA cured with 100% molar ratio of BPA and 4% molar ratio of 2,4EMI at 100 °C.

If the BPA molar ratio was 100%, no gel part is found at any reaction temperature or molar ratio of 2,4EMI. Both theoretical and experimental results agree with each other. When the BPA molar ratio is less than 100%, the gel part forms after the phenol groups are nearly consumed and the weight fraction of the gel part raises up sharply. The profiles of gel fraction are a strong function of the BPA molar ratio. If the less molar ratio of BPA is used initially, the BPA molecules are depleted earlier and the gel point will happen at a lower epoxide conversion. Also it is found that either the reaction temperature or the molar ratio of 2,4EMI has only a slight influence on the profiles of gel fraction.

Branch Point of Sol. According to the reaction mechanisms proposed, the aliphatic ether linkage (R–

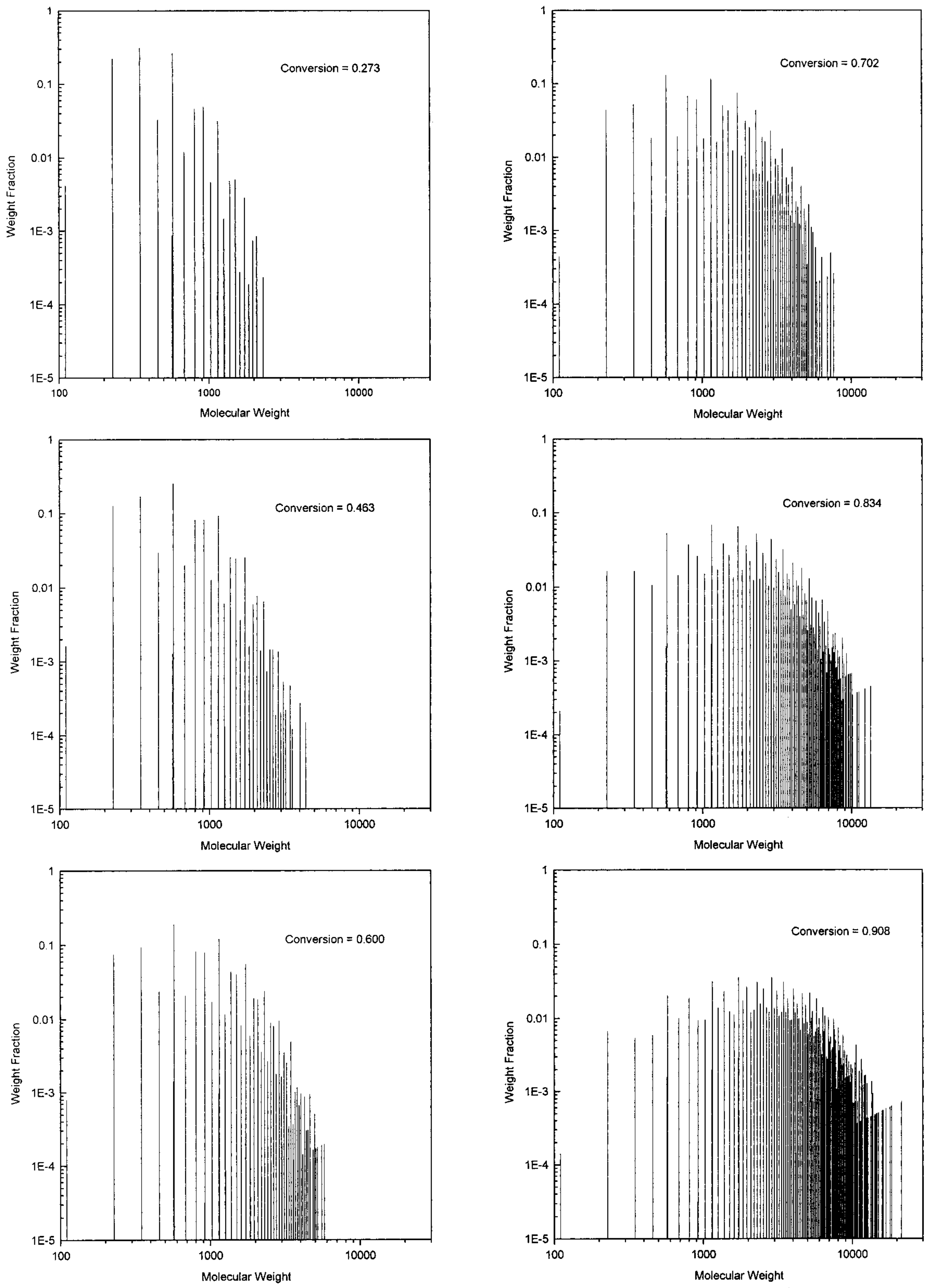

Figure 8. MC simulation of the molecular weight distribution of the sol part at different conversions for the molar ratio of DGEBA/BPA/2,4EMI: 100/100/4 at 100 °C.

O−R) is formed through the epoxide/R−O$^-$ reaction and this linkage possesses three active sites for further propagation. Based on Flory's works,[10] the built-up aliphatic ether linkage is termed as the "branch point" in the studies. Hence the branch point number of each polymer chain can be seemed as the chance of epoxide/R−O$^-$ reaction on itself. Also, the "loop" is defined as the structure formed by the intrachain reaction. According to the simulation results, very few loop structures were found in the sol part during the MC calculation, no matter what initial conditions were chosen. These results are consistent with the studies of Falk and Thomas.[30]

The branch point distributions of the sol part vs molecular weight at different epoxide conversion are showed in Figures 4 and 5. Every discrete spectra line describes the number-average value of branch point at any specific molecular weight. If the BPA molar ratio is 100%, the calculated values of the average branch point are very small as shown in Figure 4. The results agree with our hypothesis: if the BPA molar ratio is 100%, there are enough phenol groups to react with epoxide groups, which results in a linear aromatic ether linkage, Ar−O−C. And no gel part was found through the entire reaction. Figure 5 depicts the branch point profile that the gel part is built up if the conversion is above the critical value ($X = 0.512$). Before the gel point, the number of branched molecule increases with increasing conversion. Hence, the number of discrete spectra line increases and the profile of branch point distribution shifts from the low molecular weight region into the high one with increasing conversion. When the conversion is above the critical value, large molecules presented in the sol part are much easier to connect onto the gel part. Therefore, it is found that the branch point profile moves back to the low molecular region and the number of spectra line decreases.

Moreover, the MC method can also scrutinize into the number of branch point on any individual polymer chain with a particular molecular weight, at a specific conversion. For example, at a conversion of 0.424 (BPA,40 mol %; 2,4EMI, 4 mol %; $T = 100$ °C), there are 11 polymer chains which have the same molecular weight of 4500 but, however, contain different numbers of branch points as shown in Figure 6. Therefore, the number-average branch point of the specific molecular weight 4500 is 1.364. This average value is depicted as one discrete spectrum in Figure 5.

Molecular Weight. As the BPA molar ratio is 100%, the normalized weight fraction profiles by GPC at different conversions are depicted in Figure 7. The profiles of weight fraction will move to the smaller elution time interval as the conversion increases, i.e., the average molecular weights of the cured resins grow up. For the same BPA molar ratio, the theoretical results calculated by the MC method are shown in Figure 8. There is no gel part found through the whole MC simulation, which is consistent with the experimental results. The weight fraction profiles of the sol part move form the low molecular weight region into the high one as the conversion increases. And the range of molecular weight distribution becomes larger. When the BPA molar ratio is lowered to 40%, the profiles of the normalized weight fraction by GPC and the MC method are plotted in Figures 9 and 10. Since the gel part would be formed after the critical conversion, the profiles of the sol part shift to small elution time region at first, and then move backward to high elution time region as shown in Figure 9. Also the simulation results depicted in Figure 10 indicate that the weight fraction distribution shifts form low molecular weight region into high one before the gel point. After the critical conversion, the weight fraction profile of the sol part moves back form high molecular weight into low one because large molecules are much easier to connect onto the gel part than small ones.

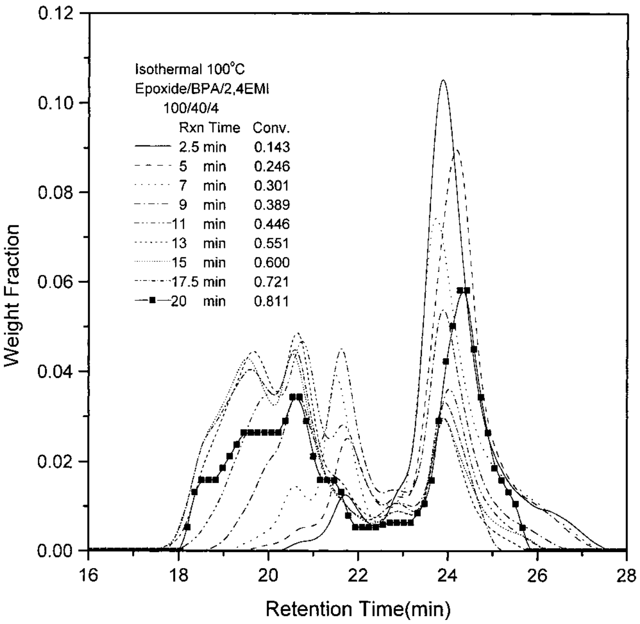

Figure 9. Normalized weight fraction profile at different time interval by GPC for DGEBA cured with 40% molar ratio of BPA and 4% molar ratio of 2,4EMI at 100 °C.

Because the GPC columns are calibrated by polystyrene (PS) standards, some transformation is needed in order to compare the theoretical and experimental results. At first, the prepolymer DER331 is selected as the converted standard. There are three main compositions of DER331, i.e., DGEBA $n = 0$, 1, and 2, and their corresponding true molecular weight (M_{GPC}) are 340, 624 and 908, respectively. After the separation process by GPC, three main peaks are shown and their corresponding calculated molecular weights (M_{cal}) are obtained, relative to the PS standards. Then the converted factor (α) is defined as below:

$$\alpha = M_{\mathrm{cal}}/M_{\mathrm{GPC}} \tag{12}$$

It is found that the average value of α is 1.17. Because the main chain structure of DGEBA is more rigid than that of PS, the radius of gyration of DGEBA would be larger than that of PS, if both of them have the same molecular weight.[31] In other words, the calculated molecular weight of DGEBA will be overestimated, relative to the PS standard. In the following experimental results, all the GPC data (M_{cal}) are divided by the converted factor (α) and transformed into the true molecular weight (M_{GPC}).

Another important factor that should be considered here is the deviation caused by the structural difference; i.e., linear or branched. In the pioneering papers, Stockmayer,[32] Zimm,[33−34] and Fixman[35] proposed a concept of shrinking factor to correct the size deviation between different structure of polymer chains. On the basis of the cascade theory, Burchard[36−40] derived the shrinking factors for the star polymers, which are consisted of the regular-star model for a star polymer with uniform arm length and the polydisperse-star model for a star polymer with a specific distribution of arm length. The influences of chain stiffness and the core size of the star center can also be considered by his theoretical derivation.

As far as the imidazole cured epoxy/phenol reaction system is considered, the branched structure is resulted from the aliphatic ether linkage (R−O−R). Since there is only a short aliphatic ether linkage between two branch points, this branched structure can be idealized and simplified as a starlike polymer, and the representation structure is shown in Figure 11. The relationship between the branch point “Br” and the functionality “f” of the starlike polymer is $f = \mathrm{Br} + 2$.

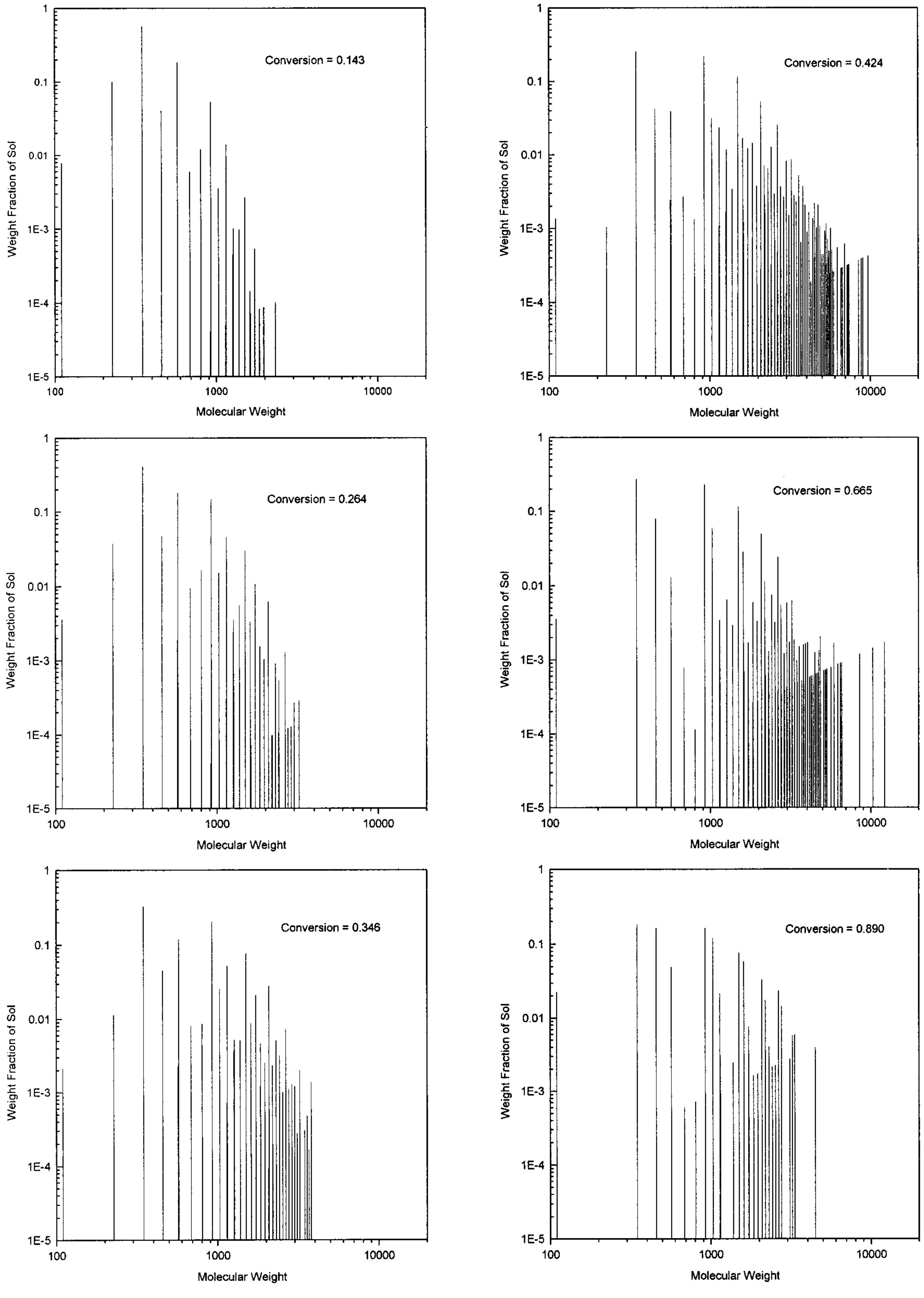

Figure 10. MC simulation of the molecular weight distribution of the sol part at different conversion for the molar ratio of DGEBA/BPA/2,4EMI: 100/40/4 at 100 °C.

According to Burchard's works, the shrinking factor for polydisperse star (PDS) model is defined as

$$g_{\mathrm{pds}} = \frac{\langle S^2\rangle_{Z,\mathrm{poly,branch}}}{\langle S^2\rangle_{Z,\mathrm{mono,linear}}} = \frac{6f}{(f+1)^2} \tag{13}$$

where g_{pds} represents the shrinking factor of the chain size that converts a star polymer with the most probable distribution of arm lengths to a linear monodisperse polymer, with the same molecular weight.

Using the above shrinking factor, we can transform the absolute molecular weight (M_w) of a branched polymer, which is calculated by the MC method, into an equivalent molecular weight of a linear phantom

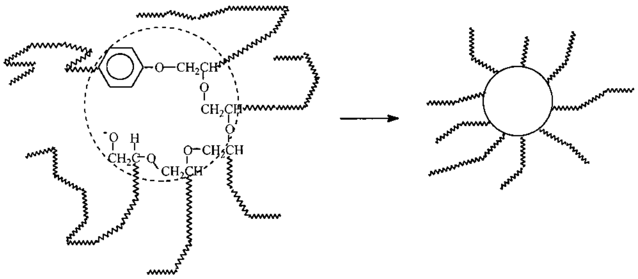

Figure 11. Representation of the idealized starlike polymer.

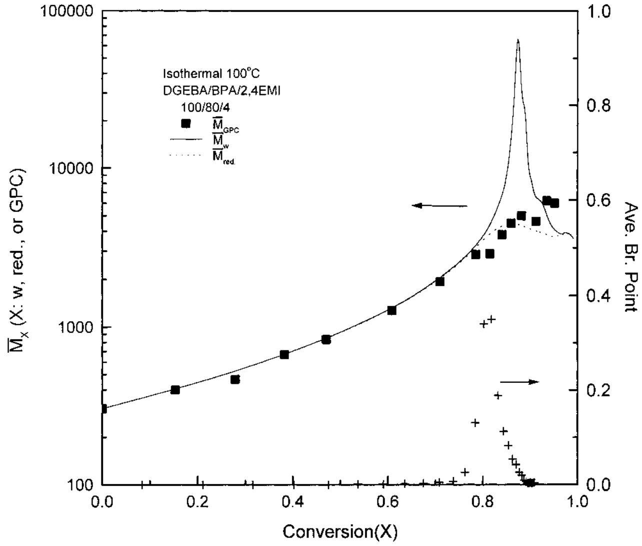

Figure 12. Comparison of the $\bar{M}_{GPC}$, $\bar{M}_w$, and $\bar{M}_{red}$, and the average branch point vs conversion for DGEBA cured with 80% molar ratio of BPA and 4% molar ratio of 2,4EMI at 100 °C.

polymer that possesses the same hydrodynamic volume as the branched one. This equivalent molecular weight of the linear phantom polymer is termed as the reduced molecular weight (M_{red}), and used in the following comparison between the theoretical prediction and experimental results. For example, if there is a branched polymer whose absolute molecular weight (M_w) is 4000 and it contains four branch points, the functionality "f" is calculated as 6. Substituting "f" into eq 2, the shrinking factor g_{pds} is found as 0.735. By the following equation

$$M_{red} = g_{pds}M_w \tag{14}$$

the reduced molecular weight (M_{red}) of the linear phantom polymer is calculated as 2939.

Figure 12 shows the profile of the calculated number-average branch point, the absolute molecular weight, the reduced molecular weight, and the experimental data by GPC for the sol part when the BPA molar ratio is 80%. The calculated absolute molecular weight of sol part increases rapidly around the gel point ($X = 0.85$), reaches a maximum value, and then levels off. In the meanwhile, the profile of number-average branch point of the sol part has a maximum value near the gel point also. As far as the shrinking factor is considered, it is found that PDS model can effectively compensate for the deviation between the theoretical prediction by MC simulation and the GPC results, especially around the gel point region. In the low epoxide conversion region, there are enough phenol molecules to react with epoxide groups and a linear aromatic ether linked structure is formed. No obvious deviation is found among the absolute molecular, the reduced molecular weight, and the GPC data. As the epoxide conversion increases, the quickly disappearing phenol groups no more dominate the reaction with epoxide, and a lot of branched structures are constructed by the epoxide/R—O$^-$ reaction. Hence the average value of branch point grows up quickly near the gel point. From the branch point distribution of the MC simulation, it is found that the large molecules contain more branch points than the small molecules. Substituting the detailed information on branch points profile into the shrinking factor correlation, the absolute molecular weight of the branched polymer can be transform into, chain by chain, the reduced molecular weight of the linear phantom polymer. The difference between the absolute molecular weight and the reduced molecular weight of the polymer chain is getting large as the number of branch point of the polymer chain increases.

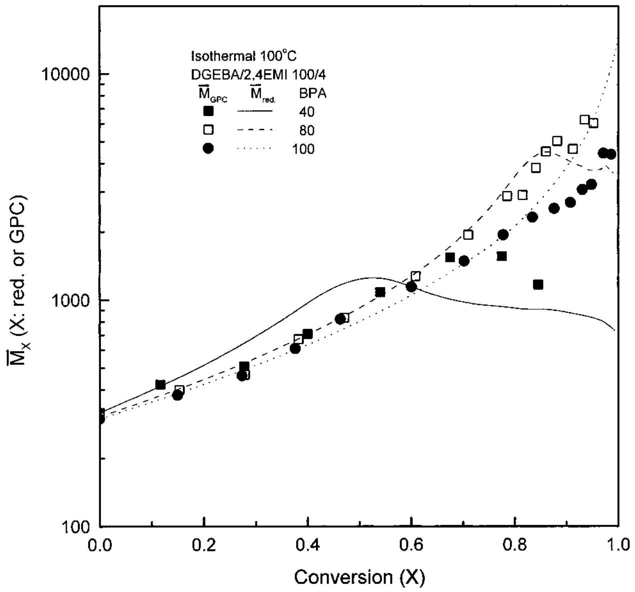

Figure 13. Comparison of $\bar{M}_{GPC}$ and $\bar{M}_{red}$ vs conversion for DGEBA cured with 4% molar ratio of 2,4EMI and different BPA molar ratios at 100 °C.

The influence of BPA molar ratio on the molecular weight profile of the sol part is shown in Figure 13. The BPA molar ratio seems the most effective factor dominating the molecular weight profiles, since the BPA molar ratio controls the beginning of gel formation, the structural type of polymer chains, i.e., linear or branched. Both the MC simulation and the experimental data coincide with each other very well before the diffusion effect becomes serious.

Figure 14 shows the accumulated molecular weight distribution at different epoxide conversions as the BPA molar ratio is 100%. The results of MC simulation agree with the experimental data by GPC well. It is found that only a slight difference comes if the diffusion effect becomes important, i.e., the conversion increases over 80%.

When the BPA molar ratio is lowered to 80%, the comparisons of MC simulation and the GPC results are shown in Figure 15. As the conversion is below 70%, the number-average branch point is quite small. So the accumulated profile of the absolute molecular weight and that of the reduced molecular weight are very similar. Both of them coincide with the experimental

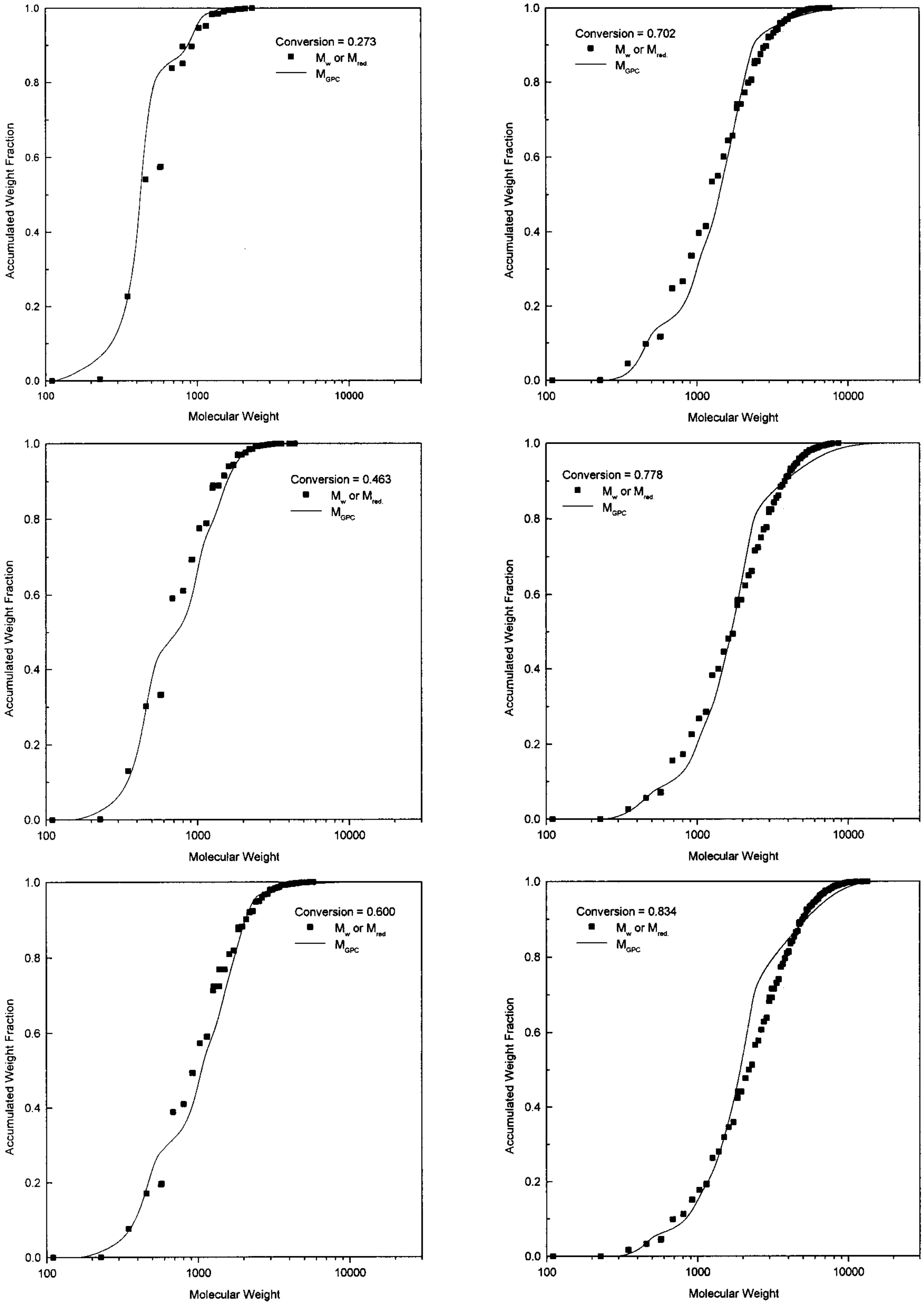

Figure 14. Comparison of accumulated weight fraction profile at different conversions for DGEBA cured with 100% molar ratio of BPA and 4% molar ratio of 2,4EMI at 100 °C.

results by GPC very well. As the conversion increases near the gel point ($X = 0.85$), an obvious deviation is found between the experimental data and the theoretical predicted values. However, the profiles of reduced molecular weight modified by PDS model seem better than that without any modification.

Conclusion

A very general Monte Carlo method has been developed and used in the imidazole cured epoxy/phenol reaction system. The evolution of structural profiles, such as the average molecular weight, the molecular weight distribution of the sol, the sol–gel fraction, and

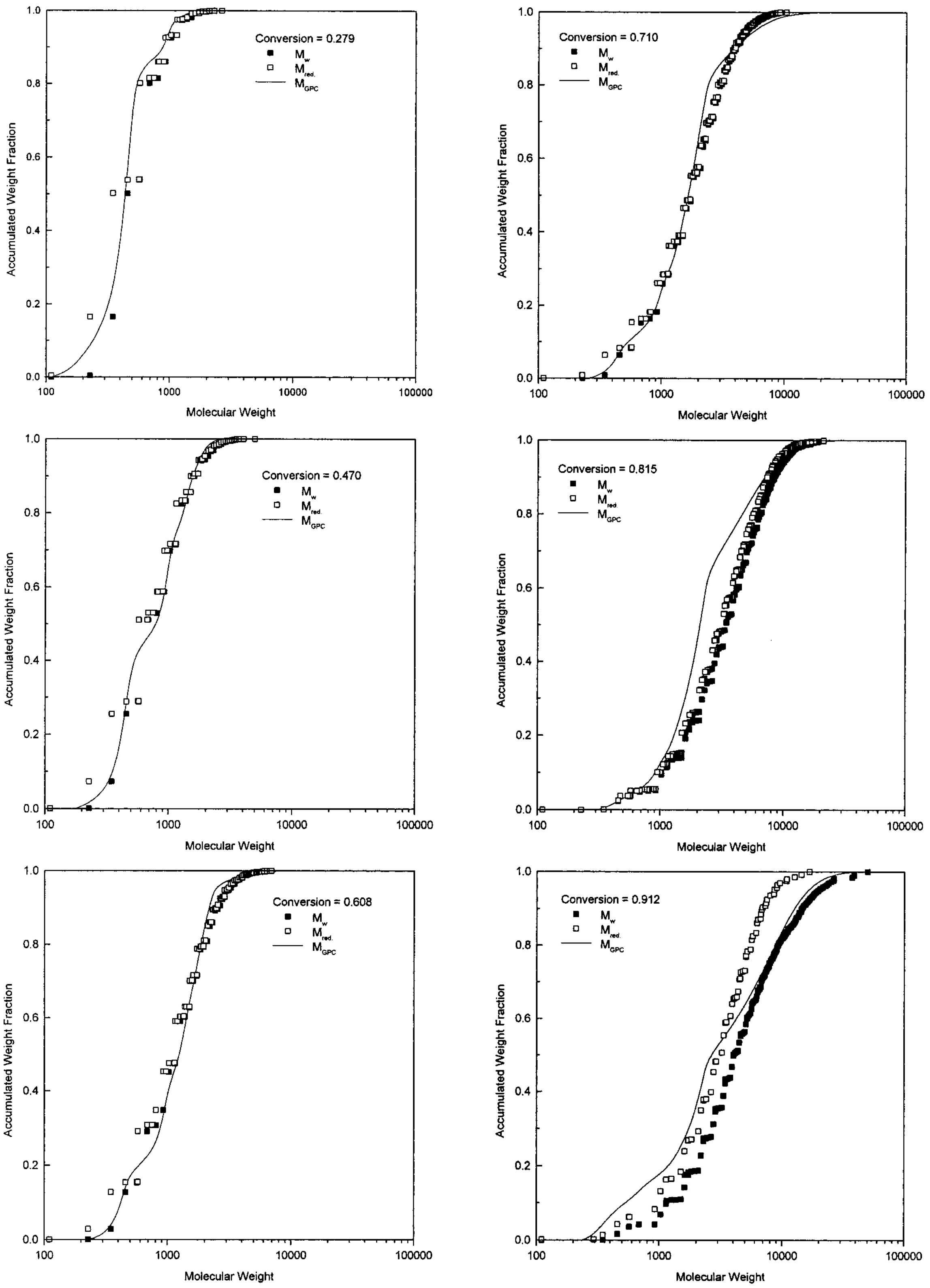

Figure 15. Comparison of accumulated weight fraction profile at different conversions for DGEBA cured with 80% molar ratio of BPA and 4% molar ratio of 2,4EMI at 100 °C.

branch point distribution of the sol, can be simulated by this MC method, and these structural properties are compared and verified by the experimental data.

As the sol extraction is considered, it seems that the BPA molar ratio is the most important factor because it dominates the types of the polymer chain constructed. If 100% molar ratio of BPA is used, there are enough phenol groups to react with epoxide groups and form the linear aromatic ether linked (Ar—O—C) structure. Hence no gel part was found either by the MC simulation or by the sol extraction test. As the BPA molar ratio is lowered, the unreacted epoxide groups polymerize through the epoxide/R−O$^-$ reaction and construct the branched aliphatic ether linked structure, accompanying with the formation of the gel part. The other controlled factors, such as the reaction temperature or the 2,4EMI molar ratio, seem not to be a significant influence on the calculated results. The MC results coincide with the experimental data of sol extraction very well.

To compare the theoretical molecular weights with the GPC results, two modifications are used. One is the correction of size deviation resulted from the rigidity of polymer chains. The other is the correction to compensate the deviation of hydrodynamic volume between the linear and branched structure. The shrinking factor of the PDS model proposed by Burchard is selected in this work to transform the calculated absolute molecular weight of a branched polymer into the reduced molecular weight of a linear phantom polymer that has the same hydrodynamic volume as the branched one. Combining these modifications with the results of MC simulation, the theoretical predicted profiles, including the average molecular weight and the molecular weight distribution, conform well with the GPC data for either linear structure resins or branched ones.

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