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Simulation of Gel Permeation Chromatography Measurement for Long Chain Branched Metallocene Polyethylene

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Summary: The research about the polymerization reaction mechanism of long chain branched polymer provides a method to simulate the generation of LCB mPE (long chain branched metallocene polyethylene). [1-3] In this work, after simulating the generation of one million LCB mPE molecules, we calculate the sizes (i.e. radii of gyration) of molecules in good solvents to obtain the molecular size distributions. Then we simulate the fractionation in GPC (gel permeation chromatography) measurement and the different GPC detector responses to obtain simulated GPC MWDs (molecular weight distributions). The simulated MWDs are compared to the real GPC results provided by the Dow Chemical Company.

Keywords: branch; gel permeation chromatography; metallocene polyethylene; molecular weight distribution; radius of gyration

Introduction

Long chain branched metallocene polyethylene (LCB mPE) is a new polymer material which is produced by single-site metallocene catalysts. Contrary to Ziegler-Natta catalyst polyethylene, it has narrower molecular weight distribution (MWD) with polydispersity indexes of approximately 2. This material contains both linear chains, the majority, and branched chains. The metallocene catalysts produce low levels of long chain branching so as to improve the processability without impacting the physical properties seriously.

To fully understand the properties of LCB mPE, we need to understand its molecular structure and MWD. Gel permeation chromatography (GPC) is the most important and widely applied technique to measure the MWD. In this analytical technique, polymer molecules are fractionated by their hydrodynamic volume (i.e. the sizes of polymer molecules in good solvents). This work is focused on the simulation of GPC for the MWD of LCB mPE.

Soares and Beigzadeh[3] described the reaction mechanism of long chain branched polyethylene via

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single-site metallocene catalysis and developed an algorithm to simulate the generation of LCB mPE molecules. Two generation probabilities are taken into account in their simulation: the propagation probability (pp) and the monomer selection probability (lp). The values of pp and lp can be derived from two experimental parameters: weight-average molecular weight (M_w) and average branch point density per 10^3 C (λ). The former can be measured by light scattering and the latter can be measured by ^{13}C nuclear magnetic resonance. In this work the algorithm is used and the structure of each molecule is recorded in the simulation to calculate the size.

Calculation of the sizes of LCB mPE molecules

The information about the materials simulated in this study is shown in Table 1.

Table 1. Measured average molecular parameters of materials HDB1-3

Materials	Weight-average molecular weight (M_w)	Average branch point density per 10^3 C (λ)
HDB1	80,000	0.026
HDB2	84,000	0.037
HDB3	85,000	0.042

Based on these parameters, simulations were performed to generate one million molecules for each material to study its constitution. The results for material HDB3 are presented in Tables 2 to illustrate.

Table 2. Constitution of Material HDB3 (The proportion is number fraction)

Linear Molecules	90.6726%
Molecules with 1 branch	7.67859%
Molecules with 2 branches	1.29834%
Molecules with 3 branches	0.261512%
Molecules with 4 branches	0.066484%
Molecules with 5 branches	0.017082%
Molecules with 6 branches	0.003810%
Molecules with 7 branches	0.001352%
Molecules with 8 branches	0.000246%
Molecules with 9 branches	0%

GPC fractionates the polymer molecules in terms of their sizes. To simulate the fractionation of GPC, it is a prerequisite to calculate their sizes (i.e. radius of gyration). In a good solvent the radius of gyration of a linear polyethylene molecule, $\left\langle R_g^2 \right\rangle_l$, is related to its molecular weight, M, as[4]

$$\left\langle R_g \right\rangle_l = C \cdot M^{0.6} \tag{1}$$

A linear metallocene polyethylene sample was used in the Triple-Detector GPC with MALLS measurement by the Dow Chemical Company (the good solvent used was 1,2,4-trichlorobenzene, the operation temperature was 145 °C). The measurement result shows that the value of C is 0.02 which can be used for linear molecules in LCB mPE.

For branched molecules in LCB mPE, a so called g-factor which is applied to compute the mean square radii of gyration of branched molecules is defined by the following equation:

$$g = \frac{\left\langle R_g^2 \right\rangle_{br}}{\left\langle R_g^2 \right\rangle_l} \tag{2}$$

where $\left\langle R_g^2 \right\rangle_{br}$ is the mean square radius of gyration of a branched molecule which has the same molecular weight as a linear one with $\left\langle R_g^2 \right\rangle_l$. The g-factor depends on the chain topology and its value is necessary to obtain the radius of gyration. During the reaction, there are different ways to construct branched molecules. For example, there are two ways to construct a molecule with two branches: two linear branches attach to a same linear chain or a chain with one branch attaches to another linear chain. Actually they have identical structure dispite the different topologies. The number of possible ways a molecule can be generated in the polymerization process is known as the Catalan number $C(n)$[2],

$$C(n) = \frac{(2n)\,!}{n!(n+1)\,!} \tag{3}$$

where n is the number of branches.

The topologies of molecules with branches no more than 3 are shown in Figure 1:

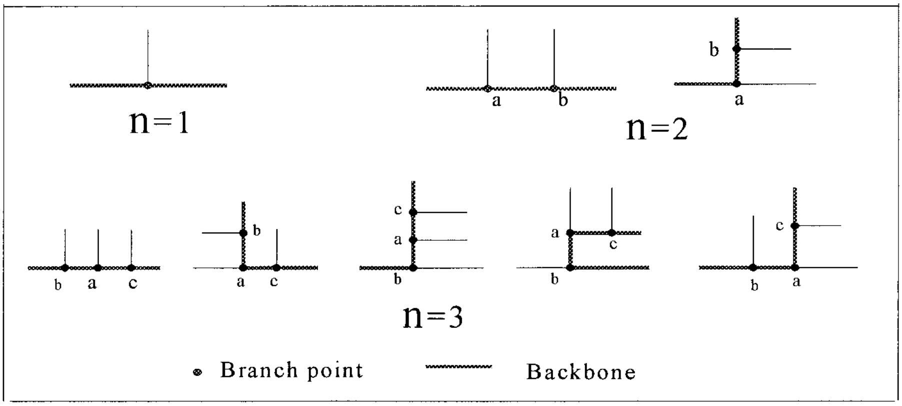

Figure 1 Topologies of molecules with n ≤ 3 (n is the number of branches)

Since the proportion of molecules with n≤ 3 for LCB mPE materials HDB1-3 is more than 99.9%, the detailed topologies of those molecules are recorded in the simulation. Zimm and Stockmayer[5] deduced the formulae to calculate the g-factor for branched molecules. In this work, we found that there were mistakes in the published formulae for molecules with n≤ 3. The corrected formulae are given below.

For molecules with n = 1

$$g = \frac{6}{N_{total}^{2}} \sum_{v} \left[\frac{N_v^2}{2} - \frac{N_v^3}{3N_{total}} \right] \tag{4}$$

For molecules with n = 2

$$g = \frac{6}{N_{total}^{2}} \left[\sum_{v} \left(\frac{N_v^2}{2} - \frac{N_v^3}{3N_{total}} \right) + \frac{N_{ab}}{N_{total}} \left(\sum_{va} N_{va} \right) \left(\sum_{vb} N_{vb} \right) \right] \tag{5}$$

For molecules with n = 3

$$g = \frac{6}{N_{tatal}^{2}} \left[\begin{array}{l} \sum_{v} \left(\frac{N_v^2}{2} - \frac{N_v^3}{3N_{total}} \right) + \frac{N_{ab}}{N_{tatal}} \left(\sum_{va} N_{va} + \sum_{vc} N_{vc} + N_{ac} \right) \left(\sum_{vb} N_{vb} \right) \\ + \frac{N_{ac}}{N_{total}} \left(\sum_{va} N_{va} + \sum_{vb} N_{vb} + N_{ab} \right) \left(\sum_{vc} N_{vc} \right) \end{array} \right] \tag{6}$$

where N represents the number of segments, the index $total$ means the total number of segments in the whole molecule, the index v is for free arms and inner backbones; the index of the inner backbone between branch points a and b is ab, between branch points a and c is ac; the index of free arms growing from a is va, growing from b is vb, and growing from c is vc.

For highly branched polymer chains (n>3), it is unwieldy to calculate the g-factor for all possible topologies. In this work, a methodology to calculate the average g-factor for constant n is proposed. First, the g-factors for individual isomeric structures should be calculated. Bonchev et al.[6] derived a formula which can be used to compute the g-factor of isomeric structures based on the theory of the *Wiener Number* which is a topological descriptor:

$$g=\frac{6n\cdot(f^2-1)+6+(f-1)^2[n\cdot(n-1)(n+7)-6\sum_{i=j}^{t}n_i(i-1+\sum_{s=j-1}^{i-1}n_s)(n-i-\sum_{s=j}^{i}n_s)]}{[n\cdot(f-1)+1]\,[n\cdot(f-1)+2]\,[n\cdot(f-1)+3]} \qquad (7)$$

where n is the number of branch points, f is the number of functionality, the position of the branches along the main chain are denoted by $i, j, k, \ldots, t$, respectively, $n_i, \ldots, n_s$ denote the number of branched units in the respective branched branches $i, \ldots, s$.

For long chain branched polyethylene, $f = 3$, Equation 7 yields

$$g=\frac{48n+6+4[n(n-1)(n+7)-6\sum_{i=j}^{t}n_i(i-1+\sum_{s=j-1}^{i-1}n_s)(n-i-\sum_{s=j}^{i}n_s)]}{[2n+1][2n+2][2n+3]} \qquad (8)$$

Second, the number of different ways that each structural isomer can be produced, $C_i(n, i)$, is obtained by statistics. Then the probability of producing each isomeric structure is calculated from $C_i(n,i)/C(n)$. With the g-factor for each isomeric structure calculated from Equation 8, the average g-factor, g(n), can be obtained as a function of n only:

$$g(n)=\sum_{i=1}^{J(n)}g_i\,\frac{C_i(n,i)}{C(n)} \qquad (9)$$

For instance, the calculation procedure for n= 8 is described in Figures 2.

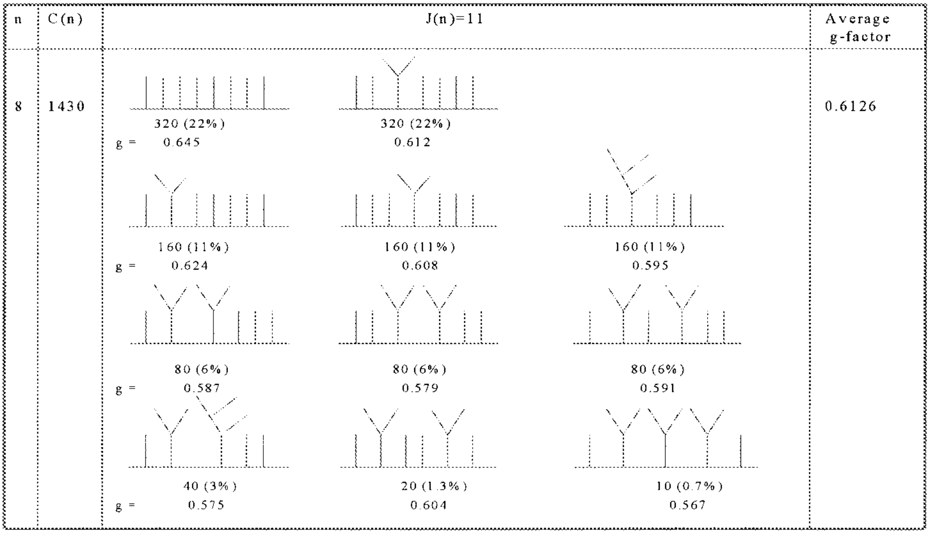

Figure 2 Calculation of the average g-factor for branched molecule with n = 8

For isomers with a comb-like structure, the number of possible topologies, C(n, comb), can be calculated with

$$C(n, comb) = (n+2) * 2^{n-3} \tag{10}$$

Combined with Equation 3, for other isomers with non-comb-like structure, the number of possible topologies, C(n, non-comb), is given by

$$C(n, non-comb) = \frac{(2n)\,!}{n\,!\,(n+1)\,!} - (n+2) \cdot 2^{n-3} \tag{11}$$

The values of average g-factor, g(n), which are calculated from the procedure above, agree with the results from Zimm-Stockmayer Equation B15[5]:

$$g_f(n) = 3\,\frac{n!\,(fn-2n+2)\,!}{(fn-n+3)\,!}\sum_{i=0}^{n}\binom{fn-2n+2+i}{i}(f-1)^{n-i} \tag{12}$$

where f is the functionality of polymer chain. For LCB mPE, $f = 3$, from the equation 12, it is obtained:

$$g_3(n) = 3\,\frac{n!\,(n+2)\,!}{(2n+3)\,!}\sum_{i=0}^{n}\binom{n+2+i}{i}2^{n-i} = 3\,\frac{n!}{(2n+3)\,!}\sum_{i=0}^{n}\frac{(n+2+i)!}{i\,!}\,2^{n-i} \tag{13}$$

After the calculation of the sizes of molecules in good solvents, the molecular size distributions for materials HDB1-3 are obtained (Figure 3 to 5).

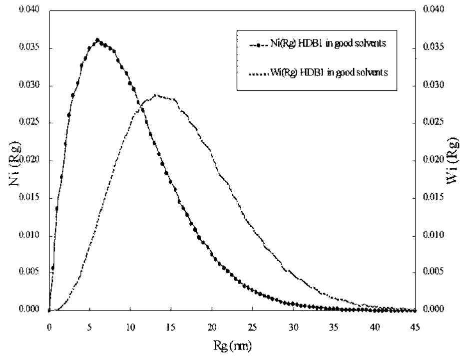

Figure 3 Molecular Size Distribution of HDB1

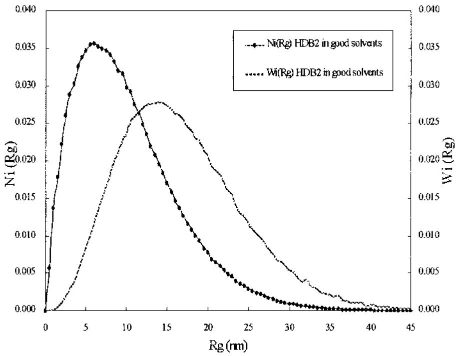

Figure 4 Molecular Size Distribution of HDB2

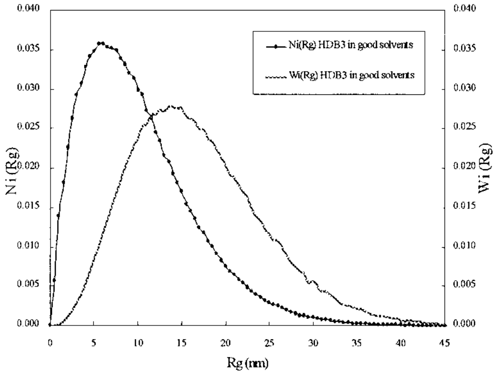

Figure 5 Molecular Size Distribution of HDB3

Simulation of the fractionation of GPC

In experiments, the product of intrinsic viscosity $[\eta]$ of a solvated polymer molecule and its molecular weight, $[\eta]M$, is normally used as a measure of hydrodynamic volume. So in this method all the molecules are fractionated in terms of $[\eta]M$.

The Mark-Houwink equation for linear polyethylene in the solvent of interest is[7]

$$[\eta]_l = 3.8\times10^{-4}M^{0.73} \tag{14}$$

where $[\eta]$ is the intrinsic viscosity and M is weight-average molecular weight. Therefore $[\eta]$M of linear PE molecules can be expressed as

$$[\eta]_l M = 3.8\times 10^{-4} M^{1.73} \qquad (15)$$

For branched molecules, similar as the definition of g-factor, a g'-factor is defined as the ratio in intrinsic viscosity of branched molecules to linear molecules with the same molecular weight[8]:

$$g' \equiv \frac{[\eta]_{br}}{[\eta]_l} \qquad (16)$$

The two factors g and g' are related by:

$$g' = g^d \qquad (17)$$

where d=0.5 for randomly branched polymers.[8] Combination of Equations 14, 16 and 17 gives the expression for the hydrodynamic volume of branched molecule:

$$[\eta]_{br} M = 3.8\times 10^{-4} g^{0.5} M^{1.73} \qquad (18)$$

Simulation of GPC with DRI detector

The conventional GPC measurement uses the DRI (differential refractive index) detector to determine the relative concentration of each fraction, and a set of linear polymer standards is used to establish the relationship between elution volume and molecular weight. This technique can appropriately evaluate the MWD of linear polymers but it underestimates the molecular weights of branched polymers.

Consider the molecular weight and the intrinsic viscosity of a branched molecule are M and $[\eta]_{br}$, the molecular weight and the intrinsic viscosity of a linear molecule whose elution volume is the same as the branched one are M^* and $[\eta]^*$, by using the Universal Calibration, we have[8]:

$$M^*[\eta]^* = M[\eta]_{br} \qquad (19)$$

Then with the Mark-Houwink equation:

$$[\eta]^* = K(M^*)^a \qquad (20)$$

$$[\eta]_l = K\, M^a \qquad (21)$$

Combining the Equations 19, 20, 21 with Equations 16, 17, M and M* are related by

$$\frac{M}{M^*} = \frac{[\eta]^*}{[\eta]_{br}} = \frac{[\eta]^*/[\eta]_l}{[\eta]_{br}/[\eta]_l} = \frac{\left(\frac{M^*}{M}\right)^a}{g^d} \tag{22}$$

Equation 22 can be reduced to [8]

$$M^* = g^{\frac{d}{a+1}}\ M \tag{23}$$

where $a = 0.73$, $d = 0.5$ refer to the preceding explanation. Then Equation 23 yields

$$M^* = g^{0.29}\ M \tag{24}$$

For linear molecules, M* = M since g = 1; for branched molecules, M* < M since g < 1. This explains why the conventional GPC measurement underestimates the molecular weights of branched polymers.

The simulated MWD for HDB1compared with GPC experimental results for HDB1 is presented in Figures 6.

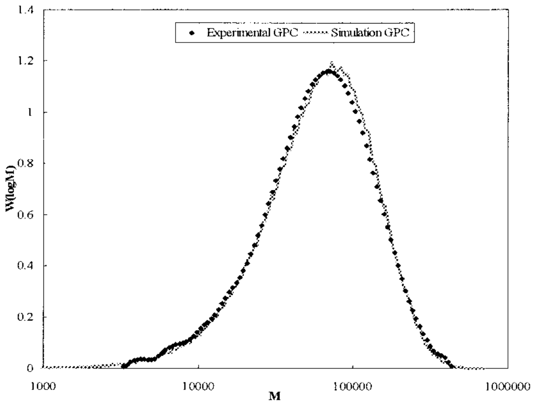

Figure 6 Simulated and Experimental Conventional GPC MWD for HDB1

Simulation of GPC with Triple Detectors

In advanced GPC measurement, three detectors (i.e. DRI detector, viscometer detector and low angle laser light scattering detector) are applied simultaneously to measure the MWD. For each fraction, the result of the DRI detector provides the weight fraction, the result of the viscometer detector provides the intrinsic viscosity and the result of the low angle laser light scattering detector provides weight-average molecular weight. Hence the actual weight-average molecular weight in each fraction is calculated in the simulation. The simulated MWD for HDB3 is compared with the experimental results in Figures 7. When raw experimental data of HDB3 from the Dow Chemical Company are compared with the simulation results, although the experimental data are noisy in the low molecular weight range due to the measuring deviation, a good agreement over the whole range is achieved.

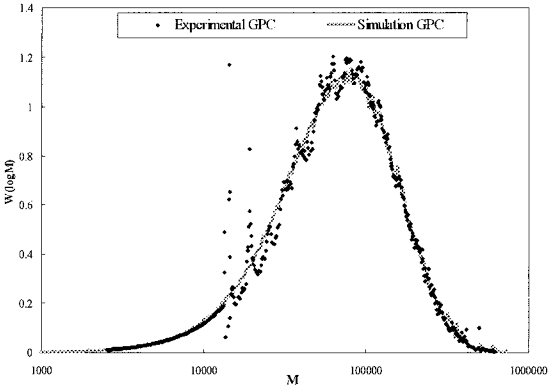

Figure 7 Simulated and Experimental Triple-Detector GPC MWD for HDB3

Simulation of GPC with MALLS Detectors

When multi-angle laser light scattering (MALLS) detectors are combined, not only the molecular weights but also the average radius of gyration of the molecules in each fraction can be measured. The MALLS measurement was performed for HDB2 giving the relationship between the molecular weight and the radius of gyration. The simulation results for HDB2 and experimental MALLS data are presented in Figure 8. At the very low and very high molecular weight range, the experimental data are scattered due to the experiment error. Except for the scattered experimental data, the comparison shows that the simulation results are in a good agreement with the experimental data through the reliable measuring range.

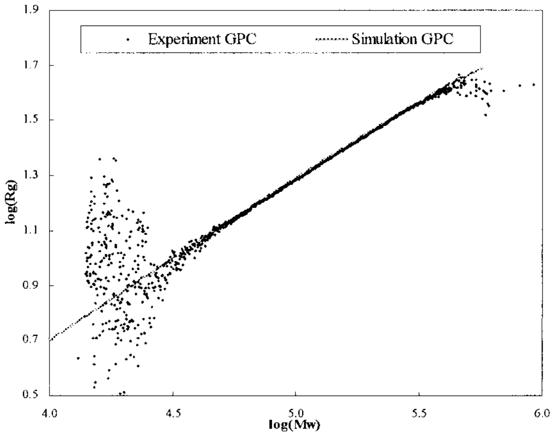

Figure 8 Simulated and Experimental Results of GPC with MALLS Detectors for HDB2

Application of the Simulation

For the materials of LCB mPE studied in this work, there is a theoretical MWD function which presents the actual MWD[2]:

$$w(M)=\frac{\sqrt{1+\beta^{-1}}}{M_N}\exp\left[-(2\beta+1)\frac{M}{M_N}\right]I_1\left(2\sqrt{\beta(\beta+1)}\frac{M}{M_N}\right) \tag{25}$$

where β is the average number of branches per molecule, M_N is number-average molecular weight, I_1 is the modified Bessel function of the first kind of order 1, which can be presented as:

$$I_1(x)=\sum_{n=0}^{\infty}\frac{(x/2)^{2n+1}}{n!(n+1)!} \tag{26}$$

The comparisons between the MWD from the Simulated Triple-Detector GPC and from the theoretical function above for material HDB1 and HDB2 are shown in Figures 9 and 10. The comparisons show that the simulated GPC MWD is consistent with the actual MWD from the theoretical function.

As shown before, the simulated GPC MWD gives a good agreement with experimental GPC data. Thus, the simulation relates the theoretical MWD of LCB mPE to the measured MWD by GPC and confirms the theoretical function. It also verifies that the Triple-Detector GPC measurement provides good evaluation for MWD of LCB mPE.

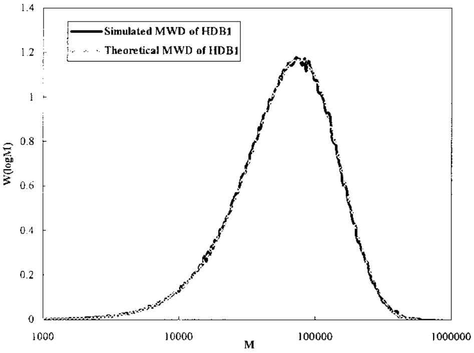

Figure 9 Simulated GPC MWD and MWD from Theoretical Function for HDB1

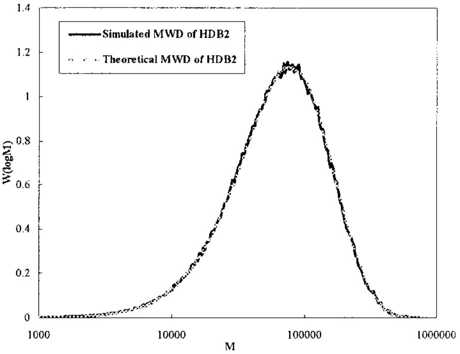

Figure 10 Simulated GPC MWD and MWD from Theoretical Function for HDB2

Prediction of the MWD of highly branched metallocene polyethylene

The LCB mPE samples measured by the Dow Chemical Company have low levels of long chain branching. However, the simulation used in this work can be applied to predict the GPC results of highly branched polymers. For example, the simulation results for two hypothetical highly branched materials with $\lambda = 0.5$ and $\lambda = 2$ (i.e. average branch density per 10^3 carbon), Mw=84,000 (i.e. weight-average molecular weight) are shown in Figures 11 and 12. These results are consistent with the actual MWDs which are obtained from the theoretical MWD function. This indicates that Triple-Detector GPC can be expected to yield accurate results even for quite highly branched metallocene polyethylene.

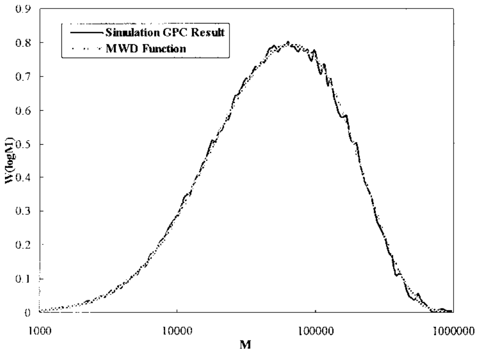

Figure 11 The MWD of highly branched material with $\lambda = 0.5$ and $M_w = 84{,}000$

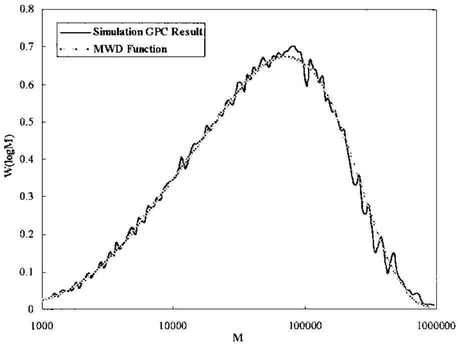

Figure 12 The MWD of highly branched material with $\lambda = 2$ and $M_w = 84{,}000$

Conclusions

The simulation in this work is based on the reaction mechanism of LCB mPE. The agreement of simulated GPC results with experimental GPC results not only confirms the quality of the GPC measurement but also confirms the theoretical MWD function of LCB mPE conversely.

This simulation develops a technique for calculating the distribution of radii of gyration of branched molecules. The obtained simulation GPC results can be use to interpret experimental GPC results or detect the deviation of GPC measurements. It also can predict the GPC results for highly branched metallocene polyethylene.

Simulation methods are important because GPC measurement requires expensive devices and experienced operation. So we recommend to apply the simulation of GPC to other polymers, such as polypropylene and copolymers as long as the reaction mechanism and the molecular topology are known.

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