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Prediction of the Molecular and Polymer Solution Properties of LDPE in a High-Pressure Tubular Reactor Using a Novel Monte Carlo Approach.

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Abstract

In the present work, a novel kinetic/topology Monte Carlo algorithm is developed for the prediction of molecular, topological and solution properties of highly-branched low-density polyethylene (LDPE), produced in a high-pressure multi-zonal tubular reactor. It is shown that the combined kinetic/topology MC algorithm can provide comprehensive information regarding the distributed molecular and topological properties of LDPE (i.e., molecular weight distribution, short- and long-chain branching distributions, joint molecular weight-long chain branching distribution, branching order distribution, seniority/priority distributions, etc.) The molecular/topological results obtained from the MC algorithm are then introduced into a random-walk molecular simulator to calculate the solution properties of LDPE (i.e., the mean radius of gyration, R_g , and the branching factor, g) in terms of the chain length of the branched polyethylene. The validity of the commonly applied approximation regarding the random scission of highly-branched polymer chains is assessed by a direct comparison of the average molecular properties of LDPE (i.e., number and weight average molecular weights), calculated by the combined kinetic/topology MC algorithm, with the respective predictions obtained by the commonly applied method of moments (MOM). Through this comparison it is demonstrated that the ambiguous implementation of the random scission reaction in the MOM formulation can result in erroneous predictions of the weight average molecular weight and MWD of LDPE. Finally, the effects of two key process parameters, namely, the polymerization temperature profile and the solvent concentration, on the molecular, topological and polymer solution properties of LDPE produced in a multi-zonal tubular reactor are investigated.

Keywords: Monte Carlo, low-density polyethylene, molecular properties, topological architecture, branched polymers, free-radical polymerization, tubular reactors.

Introduction

In the past fifty years, a great number of studies have been published on the prediction and control of “polymer quality” in polymerization reactors. The term “polymer quality” includes all the molecular properties (e.g., molecular weight distribution (MWD), copolymer composition distribution (CCD), sequence length distribution (SLD), long and short chain branching distributions (LCB, SCB), etc.), and morphological properties (e.g., particle size distribution, (PSD), pore size distribution, density, etc.) of a particulate polymer product (Kiparissides, 2006). Based on the general framework of molecular species population balances in a polymerization system, a number of deterministic and probabilistic models have been developed dealing with the prediction of molecular properties of linear and branched polymers. The various modelling approaches have been presented and reviewed in a series of recent publications by Kiparissides and his co-workers (Kiparissides, 2006; Meimaroglou et al., 2007 & 2008; Saliakas et al., 2007; Krallis and Kiparissides, 2007; Krallis et al., 2008).

Presently, a number of distributed molecular properties (e.g., MWD, SCBD, LCBD, CCD, SLD, etc.) as well as some important average molecular properties (e.g., number and weight average molecular weights, number and weight average degree of branching, etc.) can be predicted by solving the governing dynamic molecular species population balance equations (PBEs) for the “live” and “dead” polymer chains, via the implementation of advanced numerical methods (e.g., Orthogonal Collocation on Finite Elements (OCFE), Fixed Pivot Technique (FPT), etc.). Moreover, in two recent publications (Meimaroglou et al., 2007 and 2008), a novel stochastic Monte Carlo (MC) method was proposed for solving the governing PBEs. It was shown that stochastic MC simulations could successfully deal with multi-dimensional population balance problems (e.g., two- and/or higher-dimensional) in a simple and efficient way, making them an ideal computational tool for the calculation of multi-dimensional distributed molecular properties (i.e., joint MW-LCB distribution, joint MW-CC distribution, etc.) in dynamic polymerization systems. The present work

is focused on the prediction of the molecular and solution properties of low-density polyethylene (LDPE), produced in high-pressure tubular reactors, via the implementation of a combined kinetic and chain topology stochastic approach (Meimaroglou and Kiparissides, 2010).

LDPE and its copolymers have been commercially produced in high-pressure reactors for more than five decades (Kiparissides et al., 2005). The present strong market demand for LDPE underlines its commercial importance since a large number of applications in packaging, adhesives, coatings, films, etc. largely depend on the unique molecular and rheological properties of LDPE. In principle, two reactor technologies, (i.e., tubular reactors and autoclaves) are employed in the high-pressure free-radical polymerization of ethylene. The polymerization is commonly carried out at very high temperatures (140-300 °C) and pressures (1500-3000 atm), in the presence of a mixture of thermally decomposed chemical initiators (e.g., peroxides and azo compounds).

A high-pressure LDPE tubular reactor typically consists of a spiral-wrapped metallic pipe, having a length-to-diameter ratio larger than 10^4 . The total length of the reactor ranges from 500 to 1500 m, while its internal diameter does not exceed 70-80 mm. With respect to the process heat transfer requirements, the tubular reactor can be divided into a number of zones (i.e., preheating, reaction and coolant zones). The inlet temperatures or/and flow rates of the coolant streams into the multi-zone reactor jackets are employed to control the reactor temperature profile along the tube. A detailed description of the high-pressure LDPE process can be found in the publication of Kiparissides et al. (2005).

The importance of the high-pressure tubular technology has led to a great number of modeling studies over the past 40 years (Agrawal and Han, 1975; Chen et al., 1976; Donati et al., 1982; Kiparissides and Mavridis, 1985; Brandolin et al., 1996). In these publications, a number of important issues regarding the physical state of the reaction mixture, the kinetic mechanism, the kinetic rate constants etc., are addressed. In addition, a number of papers have been published dealing with the prediction of the average and distributed molecular properties of LDPE (Feucht et

al., 1985; Nordhus et al., 1997; Pladis and Kiparissides, 1998; Iedema et al., 2000; Tobita, 2001; Kiparissides et al., 2005; Krallis et al., 2007). However, the prediction of the exact topological architecture of highly-branched polymers, in terms of the kinetic mechanism and reactor operating conditions, has not been dealt satisfactorily despite its importance for predicting the rheological behavior of LDPE melts (Inkson et al., 1999; Park and Larson, 2005; Park et al., 2005; Das et al., 2006).

The first notable attempt to predict the molecular architecture of highly-branched polymer chains was reported by Tobita (Tobita, 1993) who employed a ‘random sampling technique’ to generate long polymer chains via the successive connection of linear chain segments (also called ‘primary polymers’). The random segment connection principle was also utilized by other researchers in the field (Iedema and Hoefsloot, 2001; Inkson et al., 2006). However, Tobita’s approach requires some prior knowledge of the analytical functions regarding the segment length and branching density distributions as well as the application of a number of simplifying assumptions (e.g., time invariant polymerization conditions, the Quasi Steady-State Approximation (QSSA) for the “live” polymer chains, etc.) that largely limit its general applicability and predictive capabilities. In a recent publication by Meimaroglou and Kiparissides (2010), it was demonstrated that the exact topological architecture of a large ensemble of highly-branched polymer chains (i.e., 10^4 - 10^5) can be accurately monitored, in a dynamic polymerization system, in terms of the polymerization kinetic mechanism and the time varying polymerization conditions. It should be noted that the proposed MC approach does not require the use of any type of simplifying assumptions regarding the functional forms of “live” and “dead” polymer chain distributions. In the proposed kinetic/topology stochastic algorithm, the evolution of the non-linear polymer chains is considered to occur in time via a series of kinetic reaction steps by taking into account the various diffusional phenomena associated with termination and propagation reactions (i.e., gel- and glass-effect).

In the present publication, our novel kinetic/topology MC algorithm (Meimaroglou and Kiparissides, 2010) is applied to an industrial high-pressure LDPE tubular reactor to calculate the exact topological architecture of the polymer chains formed in the different reaction zones of a multi-zonal reactor configuration. Moreover, the effects of the reactor temperature profile and solvent concentration on the distributed molecular and rheological properties of LDPE are investigated. Finally, the validity of the commonly applied approximation regarding the random scission of highly-branched polymer chains (Ariola, 1989; Pladis and Kiparissides, 1998) is assessed by a direct comparison of the average molecular properties of LDPE (i.e., number and weight average molecular weights), calculated by the combined kinetic/topology MC algorithm, with the respective predictions obtained by the commonly applied method of moments (MOM) (Kiparissides et al., 2005).

The Polymerization Kinetic Mechanism

To describe the formation of both linear and highly-branched polymer chains in the free-radical polymerization of ethylene, the following general kinetic mechanism was employed.

Initiator decomposition



Chain initiation



Propagation



Chain transfer to monomer



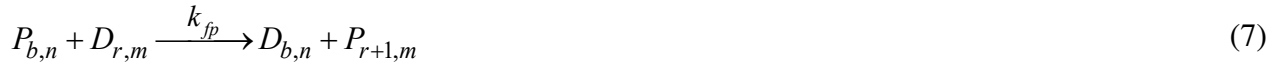
Chain transfer to solvent (chain transfer agent)



Intramolecular transfer (short chain branching)



Chain transfer to polymer



Random scission



Termination by combination



Termination by disproportionation



The symbols $P_{b,n}$ and $D_{b,n}$ denote the respective “live” and “dead” polymer chains with ‘b’ long chain branches and a total chain length equal to ‘n’. Note that the “live” polymer chains $P_{b,n}$ and $P_{b,n}^*$ in Eq.(6) differ by one short chain branch. The above kinetic mechanism has been extensively employed in the literature (Zabisky et al., 1992; Kiparissides et al., 1993; Pladis and Kiparissides, 1998) to describe the free-radical polymerization of ethylene. The above mechanism does not include formation of polyradicals or/and intramolecular double bond reactions. Moreover, the intramolecular transfer reaction (Eq.(6)) is assumed to exclusively produce butyl-type of short-chain branches (i.e., via a hydrogen abstraction reaction from the fifth methylene group of the free-radical chain end) (Roedel, 1953; Odian, 1981). Any other reactions that may lead to the formation of different carbon groups (i.e., ethyl, vinyl, amyl, etc.) have not been included in the present study.

However, as clearly discussed in a recent publication by Meimaroglou and Kiparissides (2010), additional reactions can be easily implemented provided that the numerical values of the relevant kinetic rate constants are known.

The Stochastic Kinetic/Topology Algorithm

In a series of publications (Meimaroglou et al., 2007; Krallis et al., 2008), the development and application of a computationally efficient kinetic Monte Carlo (MC) algorithm to various time-varying free-radical polymerization systems was demonstrated. In particular, the kinetic MC algorithm can be successfully employed to predict the average and distributed molecular properties of polymer chains produced in a dynamic polymerization system. Recently, a new kinetic/topology MC algorithm was developed (Meimaroglou and Kiparissides, 2010) to predict the exact topological features of highly-branched polymer chains. The new kinetic/topology MC algorithm provides detailed information regarding the characteristics of non-linear polymer chains (e.g., short- and long-chain branching length distributions, branching order distributions, seniority/priority distributions, radius of gyration, etc.). In the present work, this novel kinetic/topology MC algorithm is applied to an industrial high-pressure LDPE tubular reactor to predict the exact topological features of highly-branched polymer chains formed along the reactor length. Prior to the detailed description and application of the kinetic/topology MC algorithm to the tubular reactor, the main features of the proposed kinetic/topology MC formulation are briefly reviewed.

According to the postulated kinetic and chain topology stochastic algorithm (Meimaroglou and Kiparissides, 2010), every branched polymer chain in the polymerization medium is assumed to consist of a backbone linear sequence of carbon atoms and a number of branches attached either to the backbone chain or to any other branch of the polymer chain via a number of branching points (see Figure 1). The size (length) of any segment in a highly-branched polymer chain is characterized by the number of its constituting monomer units (i.e., its degree of polymerization).

Each monomer unit in a highly-branched polymer chain is uniquely identified by a specific number (i.e., varying from one to the total degree of polymerization), following an elaborated numbering system that accounts for the exact position of each monomer unit in a polymer chain (see Figure 1).

All the topological information necessary to fully characterize a polymer chain is stored in the respective *topology column* in the overall *topology array* of the polymerization system. Each topology column is directly associated with a specific branched polymer chain, following a comprehensive renumeration system of all the constituting monomer units, branches, branching points, etc. For example, the top three entries of a topology column contain information regarding the total chain length of the branched polymer chain (i.e., degree of polymerization), the length of its linear “backbone” carbon sequence and its total number of branches. The subsequent rows of the topology column contain relevant information regarding the length (i.e., the number of monomer units in a branch) and the exact position of all the chain branches (i.e., the number of the carbon atom to which a specific branch is attached to). These specific branch characteristics are stored in consecutive pairs in the topology column following the order of branch appearance in a polymer chain. Thus, when a new branch is formed in a polymer chain (i.e., due to a chain transfer to polymer reaction), the respective branch features (i.e., the branch length and the number of carbon atom to which the branch is attached to) are stored into predetermined rows of the relevant topology column of the branched polymer chain.

The proposed kinetic/topology MC algorithm is capable of efficiently tracking all the stochastically occurring reactions of the kinetic mechanism (i.e., Eqs.(1)-(10)) and, thus, it can follow all the topological molecular changes of “live” and “dead” polymer chains in a dynamic polymerization system.

In Figure 2, the kinetic/topological simulation of a propagation reaction is schematically depicted. In this case, the length of the linear “backbone” carbon sequence increases by one monomer unit and so does the total length of the branched polymer chain. These topological changes are

accounted by changing the values of the relevant entries (i.e., in rows 2 and 1) in the corresponding topology column of the specific branched polymer chain as well as the value of the corresponding entry in row 7 (i.e., from 8 to 9), representing the carbon atom position to which the branch is attached to (see Figure 2). It should be pointed out that the topological simulation of certain reactions often requires the re-numbering of all the carbon atoms in a polymer chain. For example, in Figure 3, the topological simulation of chain transfer to polymer reaction is depicted. As can be seen, the transfer of radical activity from a “live” polymer chain to an internal carbon atom of a “dead” polymer chain results in the formation of a new “live” polymer chain that makes necessary the renumbering of all its carbon atoms and branches.

Application of the Kinetic/Topology Algorithm to a Simulated Tubular Reactor Model

To predict the molecular architecture (i.e., distributed and topological molecular properties) of branched polyethylene chains produced in a high-pressure multi-zonal tubular reactor, the above described comprehensive kinetic/topology stochastic algorithm was applied to a simulated industrial tubular reactor model. More specifically, it was assumed that a differential reaction volume, ΔV , moves along the tube length at a variable velocity, $u(z)$ (see Figure 4). Following the fundamental developments of the kinetic (Meimaroglou et al., 2007) and kinetic/topology (Meimaroglou and Kiparissides, 2010) MC algorithms, all the molecular and topological changes taking place in the reaction volume, ΔV , were stochastically simulated along the tube length (i.e., from the reactor inlet to the outlet). All the necessary information regarding the polymerization temperature, pressure and velocity of the reaction mixture at a given reactor length, z , (i.e., $T(z)$, $P(z)$ and $u(z)$) were introduced into the stochastic algorithm externally by solving a mathematical model simulating the operation of a real industrial reactor (Kiparissides et al., 2005).

The ethylene conversion, $x(z)$, in the moving differential volume, ΔV , was explicitly calculated by the stochastic algorithm and served as a key variable, providing the dynamic connection between

the stochastic simulator and the externally introduced operating conditions (i.e., $T(z)$, $P(z)$ and $u(z)$). Thus, by comparing the externally calculated ethylene conversion along the reactor length, $x(z)$, (i.e., obtained from the simulated reactor model) with the ethylene conversion explicitly calculated by the stochastic algorithm, it was possible to determine the exact position of the moving reaction volume, ΔV , in the tube and, thus, to import into the stochastic simulator the appropriate values of the operating conditions ($T(z)$, $P(z)$ and $u(z)$). A schematic representation of the MC algorithm, as was applied to the moving reaction volume ΔV , is depicted in Figure 5.

The differential time interval, Δt , required for the reaction volume, ΔV , to move from z_i to z_{i+1} in the tube was calculated by the following equation:

$$\Delta t_i = (z_{i+1} - z_i) / \bar{u}(z_i) \quad (11)$$

where $\bar{u}(z_i)$ is the average velocity of the reaction mixture in the length interval (z_i to z_{i+1}):

$$\bar{u}(z_i) = (u(z_i) + u(z_{i+1})) / 2 \quad (12)$$

From Eqs. (11) and (12) it is evident that the accuracy of the time-interval calculation, Δt_i , depends on the discretization length, Δz_i . Thus, the externally introduced values of $T(z)$, $P(z)$ and $u(z)$ into the kinetic/topology stochastic algorithm were provided at a very high discretization rate (i.e., $\Delta z_i = 6.25 \times 10^{-4} L$, where L is the total reactor length). However, it was found that, for values of $\Delta z_i < 10^{-3} L$, the overall accuracy of the stochastically calculated results did not significantly vary with respect to the discretization length, Δz_i .

Results and Discussion

The kinetic/topology MC algorithm was applied to a simulated model of a real industrial reactor of a total length of 1040 m. The tubular reactor had three initiator injection points and, thus, three reaction zones. The reaction pressure at the reactor inlet was equal to 2700 atm. The gel-effect model of Buback (1990) was employed to describe the dependence of the termination rate constant

on ethylene conversion. The numerical values of all the kinetic rate constants, used in the present work, can be found in a recent publication by Meimaroglou and Kiparissides (2010). The sample population employed in the kinetic/topology MC simulations initially contained 1.7×10^8 to 5.8×10^8 monomer units and 5.6×10^5 to 1.9×10^6 chain transfer molecules, depending on the simulated case. The total simulation time in a 2.21 GHz dual core processor (AMD Athlon™ 64 X2, 4200+) ranged from 35 to 260 mins. It should be noted that all the average molecular properties and distributions reported in this work represent the average values of five MC simulation runs per case (Meimaroglou and Kiparissides, 2010).

In order to study the effects of the reactor temperature profile and solvent concentration on the molecular and topological characteristics of the PE chains, a total number of seven LDPE grades were simulated. The selected reactor operating conditions for each LDPE grade are reported in Table 1. In Figure 6, the simulated temperature profiles along the reactor tube are depicted for grades 1-4. In Figure 7, the variation of the number and weight average molecular weights (i.e., M_n and M_w) of LDPE, as calculated by the classical method of moments (MOM) (Kiparissides et al., 2005), the kinetic MC method (Meimaroglou et al., 2007) and the combined kinetic/topology MC method (Meimaroglou and Kiparissides, 2010), is depicted for the LDPE grade 3. It is apparent that all tested methods (i.e., MOM, kinetic MC and kinetic/topology MC) provide almost identical predictions for the variation of M_n along the reactor length. However, significant deviations are observed among the respective values of M_w due to the inherent approximations required by the method of moments and the kinetic MC method.

More specifically, in the MOM the mathematical description of chain transfer to polymer (Eq.(7)) and random scission (Eq.(8)) reactions requires the application of three simplifying kinetic assumptions, namely, i) the QSSA for the “live” polymer chains, ii) the use of an approximation for the closure of higher moments and, iii) all possible chain length fractions (e.g., (0.1-0.9), (0.2-0.8), (0.5-0.5), etc.), resulting from the random scission of a “dead” polymer chain (see Eq.(8)), are

assumed to be equally probable. However, as clearly explained in the publications of Ariola (1989) and Pladis and Kiparissides (1998), the above three assumptions will be approximately correct only for linear or/and low degree of branching polymer chains. This means that for highly-branched polymer chains the MOM will not be strictly applicable since it cannot handle correctly internal scission reactions.

On the other hand, in the simple kinetic MC algorithm, although the first two of the above simplifying assumptions are not applied, the internal scission reaction is still handled by a similar way to the MOM. Thus, in the calculated values of M_w by the MOM and the kinetic MC algorithm, a difference of approximately 4% is observed for grade 3 (see Figure 7). Note that this difference increases as the LCB content in the LDPE chains increases (see Figure 8).

On the other hand, in the combined kinetic/topology stochastic algorithm none of the above approximations is required that makes possible a more realistic simulation of the internal scission and transfer to polymer reactions. The observed deviation in the calculated values of M_w by the kinetic MC and the combined kinetic/topology MC method is due to the different treatment of the random scission reaction (see Eq.(8)) by the two methods. As described earlier, in the simple kinetic MC method of Meimaroglou et al. (2007), the stochastic simulation of the random scission of a “dead” polymer chain, $D_{r,m}$, (see Eq.(8)) results in the formation of two new polymer chains (i.e., $P_{x,z}$ and $D_{r-x,m-z}$) with respective total chain lengths of “z” and “m-z”. The corresponding total chain lengths of the generated polymer chains (i.e., $P_{x,z}$ and $D_{r-x,m-z}$) are assumed to be uniformly distributed in the range $[0,m)$ and $[m,0)$, respectively, following the outcome of a random (pseudo-random) number generator in the range $[0,1)$ (Rubinstein, 1981). On the other hand, in the combined kinetic/topology MC method of Meimaroglou and Kiparissides (2010), a random (or pseudo-random) number generator is employed only to determine the exact position of the carbon-carbon bond in the polymer chain, $D_{r,m}$, at which a bond scission reaction can occur. This results in a uniform distribution of all possible scission points in a polymer chain (i.e., all potential carbon

atoms in a polymer chain are equally probable for a scission reaction to occur). Note that, the two distributions, in relation to a scission reaction (i.e., the chain length fraction distribution in the kinetic MC approach and the distribution of all potential carbon scission points in a polymer chain in the kinetic/topology MC approach), will be identical only in the case of linear polymer chains. On the other hand, for highly-branched polymer chains, the two distributions will be significantly different.

The last observation is clearly illustrated in Figure 8, where the values of M_w as calculated by the kinetic and the kinetic/topology MC methods are plotted for three LDPE grades (i.e., 2-4 in Table 1). In the inserted Figure, the average values of long- and short-chain branches per 1000 carbon atoms, as calculated by the two stochastic methods (i.e., the kinetic MC and the kinetic/topology MC), are also presented. As can be seen, the predicted average values for long- and short-chain branches per 1000 carbon atoms by both stochastic methods are in very good agreement for the three simulated LDPE grades (2-4). On the other hand, as the number of LCBs per 10^3 C increases (i.e., from grade 2 to grade 4) the observed deviation in the calculated values of M_w by the two methods increases.

It should be noted that the simulation of a purely “kinetic” (i.e., as applied in the kinetic MC method) or “topological” (i.e., as applied in the kinetic/topological MC method) random scission event is an issue that has been addressed by several investigators (Giudici and Hamielec, 1996; Tobita, 2001; Iedema and Hoefsloot, 2001). It is worth noting that, in the commonly employed “random segment connection” approach (Iedema and Hoefsloot, 2001), the simulation of a random scission reaction requires the use of some approximation functions regarding the fragment length and branching distributions. On the other hand, in the present kinetic/topological MC approach, the simulation of a random scission reaction for highly-branched polymer chains does not require the use of any kind of simplifying assumptions.

In Figures 9a and 9b, the bivariate long-chain branching – molecular weight (LCB-MW) distribution (Figure 9a) and the short-chain branching – molecular weight (SCB-MW) distribution (Figure 9b) are plotted, at the reactor exit, for the LDPE grade 4. The observed long tails at high molecular weights for both distributions reveal the presence of PE chains with a high content in LCB and SCB.

The branching structure of highly-branched polymer chains can be alternatively characterized by the number of consecutive ‘branching order levels’. In the present study, every branch that is directly attached to the main carbon backbone chain is defined as zero-order branch. A branch attached to a zero-order branch is characterized as a first-order branch while a branch of order ‘ $n+1$ ’ is a branch attached to an ‘ n ’ order branch. In Figure 10, the bivariate branching order – branch molecular weight (BO-BMW) distribution of LCBs is plotted for the simulated LDPE grade 4, at the reactor exit. The distribution provides detailed information on the molecular weight of the PE long-chain branches as well as on their branching order with respect to the linear “backbone” carbon sequence. As can be seen, the “branching order levels” of the majority of long-chain branches are in the range of 0-3.

In a number of recent publications (Inkson et al., 1999; Park and Larson, 2005; Park et al., 2005) it has been shown that the topology of branched polymer chains is directly linked with the rheological behavior of the polymer melt. In fact, Read and McLeish (2001) were among the first ones who used the terms seniority and priority to characterize the branching topology of a branched polymer chain. A detailed description of the definition and significance of the seniority and priority distributions can be found elsewhere (Read and McLeish, 2001; Meimaroglou and Kiparissides, 2010). In Figures 11a and 11b, the seniority-priority distribution for the LDPE grade 3 is depicted, at the first and third reactor temperature peak, respectively, along with the theoretical seniority-priority distributions that correspond to the pure comb (upper curve) and ideal star (lower curve) polymer chain architectures. It can be seen that during the early stages of polymerization (i.e., at the

first peak), the seniority-priority distribution is closer to the upper curve, indicating that the branched polymer chains exhibit a structure similar to that of a pure comb polymer chain. On the other hand, as the polymerization progresses (i.e., at the third peak), more long-chain branches are formed that result in the shift of the seniority-priority distribution closer to a more star-like branching structure (lower curve in Figure 11b).

Effect of Temperature Profile on the Molecular Properties of LDPE

In Figures 12a and 12b, the effect of polymerization temperature profile (see Figure 6) on the average number and length of long-chain branches is depicted for the four simulated LDPE grades (i.e., 1-4 in Table 1). As can be seen, an increase in the polymerization temperature results in a respective increase of the average number of LCB/ 10^3 carbon atoms (see Figure 12a), due to the increase of the transfer to polymer kinetic rate constant. On the other hand, an increase in the polymerization temperature results in a decrease of the average length of LCBs due to the combined effects of propagation, chain transfer to solvent and termination reactions (Konstadinidis et al., 1992; Achilias and Kiparissides, 1992), as shown in Figure 12b.

Effect of Solvent Concentration on the Molecular Properties of LDPE

In Figures 13-15, the effect of solvent (chain transfer agent) concentration on the molecular properties of LDPE is depicted for grades 5-7 (see Table 1). In Figure 13, the molecular weight distribution of LDPE is depicted at the reactor exit for grades 5-7. In the inset scheme, the simulated temperature profile along the reactor tube is depicted for these grades (i.e., 5-7). It is evident that, as the initial solvent concentration increases, the distribution moves to lower molecular weights caused by the increase in the rate of transfer to solvent reaction (Eq.(5)).

This in turn results in a respective decrease of the M_n and M_w values of LDPE. In Figure 14, the average number of long- and short-chain branches per 1000 carbon atoms are plotted for the three

LDPE grades (i.e., 5-7). As can be seen, both quantities do not change with the solvent concentration. On the other hand, as the solvent concentration increases, the average length of the long chain branches decreases, as clearly shown in Figure 15.

Effect of Branching Content on the Polymer Solution Properties

On the basis of the calculated topologies of the branched polymer chains, one can easily reconstruct their respective 3-D spatial configurations using standard random-walk molecular simulations, as described in a recent publication by Meimaroglou and Kiparissides (2010). Accordingly, a number of important properties, associated with the volume occupied by a polymer chain (i.e., the radius of gyration, R_g , the branching factor, g , etc.), can be calculated.

In the present work, the radius of gyration, R_g , and the branching factor, g , were calculated for the LDPE grades 2 and 4, via the application of a standard random-walk molecular simulator, under Θ -solvent conditions (Meimaroglou and Kiparissides, 2010). The molecular simulations were carried out in a 1.6 GHz Intel Xeon 5110 quad core processor and required approximately 50 h of simulation time using a sample population of 87.8×10^4 and 118.5×10^4 branched polymer chains for the respective grades 2 and 4. Note that the chain length of the polymer chains ranged from 10^2 to 7.7×10^4 monomer units and their total branching content reached up to 2×10^3 branches per polymer chain. The predicted properties (i.e., R_g and g) were calculated by averaging the respective values of ten successive molecular simulations per polymer chain.

In Figures 16 and 17, the computed values for the radius of gyration, R_g , of the branched polymer chains (triangles) are plotted for the LDPE grades 2 and 4, respectively. Each point in the Figures represents the respective R_g value (averaged over ten simulation runs) of an individual polymer chain in the sample population while the continuous lines represent the calculated average R_g curves. The open circles in the two Figures represent the corresponding R_g values for the respective linear polymer chains of the same molecular weight (i.e., with zero branches). As expected, the

calculated average R_g values for the linear polymer chains are higher than those calculated for the branched polymer chains of the same molecular weight (i.e., the R_g value decreases as the LCB content in a polymer chain increases, at constant molecular weight).

A comparison between the calculated R_g values for the above two LDPE grades (see Figures 16 and 17) reveals that the calculated average R_g values for the branched polymer chains for the LDPE grade 4 are higher than the respective R_g values of the branched polymer chains for the LDPE grade 2. This is attributed to the different polymerization temperature profiles (see Figure 6). As a result, as the polymerization temperature decreases the average LC branching content decreases (see inset scheme in Figure 8) which shifts the R_g curve (blue broken line) closer to that of linear polymer chains.

Another parameter that reflects the extent of long-chain branching in LDPE, which is strongly related with the rheological behavior of LDPE melts, is the branching factor, g , (Drott and Mendelson, 1970):

$$g = \left(\frac{\overline{R_{g \text{ br}}^2}}{\overline{R_{g \text{ lin}}^2}} \right)_M \quad (13)$$

The terms $\overline{R_{g \text{ br}}^2}$ and $\overline{R_{g \text{ lin}}^2}$ denote the respective mean square values of the radius of gyration of branched and linear polymer chains of the same molecular weight. In Figure 18, the variation of the branching factor, g , is depicted for the LDPE grade 2 (red circles and red curve) and grade 4 (blue circles and blue curve) with respect to the PE chain length. Each point in the Figure 18 represents the value of g , calculated via Eq.(13) for a given value of the PE chain length. The continuous lines represent the average g curves for each grade. As can be seen, an increase in the polymerization temperature (see Figure 6) results in an increase of LCB content that brings about a decrease in the average branching factor, g . To our knowledge this is the first time that the variation of the

branching factor, g , w.r.t. the molecular weight of LDPE is predicted based on a kinetic/topological simulation of ethylene polymerization in a high-pressure industrial tubular reactor.

Conclusions

In the present publication, a novel kinetic/topology MC algorithm (Meimaroglou and Kiparissides, 2010) was applied to an industrial high-pressure LDPE process to predict the exact topological architecture of the LDPE chains produced in a multi-zonal tubular reactor configuration. The average molecular properties of LDPE (i.e., number and weight average molecular weights) as calculated by the combined kinetic/topology MC algorithm, were compared with the respective predictions obtained by the well-established method of moments (MOM) (Kiparissides et al., 2005) to assess the validity of the commonly applied approximation for random scission of highly-branched polymer chains. Through this comparison it was demonstrated that the ambiguous implementation of the random scission reaction in the MOM formulation can result in erroneous predictions of the weight average molecular weight and MWD of LDPE.

The effects of two key process parameters, namely, the polymerization temperature profile and the solvent concentration, on the final molecular, topological and solution properties of the LDPE produced in a multi-zonal tubular reactor were investigated. It was found that an increase in the reactor temperature results in the production of branched polymer chains with a higher number of long-chain branches of shorter length. On the other hand, an increase in the solvent concentration results in a decrease of the average length of the long-chain branches but does not affect their total number.

Finally, the effect of the above process parameters on the polymer solution properties of LDPE (i.e., R_g and g) was investigated via the employment of a random-walk molecular simulator, based on the calculated topologies of a large ensemble of polymer chains. It was found that an increase in the reactor temperature results in the formation of polymer chains characterized by lower values of R_g and g , due to their increased LCB content. To our knowledge, this is the first time that the

solution properties of highly-branched LDPE chains, produced in an industrial high-pressure multi-zonal tubular reactor, can be predicted in terms of their exact molecular and topological features.

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Figure Captions

- Figure 1.** Schematic representation of the topological characteristics of a “live” branched polymer chain.
- Figure 2.** Stochastic topological simulation of a propagation reaction.
- Figure 3.** Stochastic topological simulation of a transfer to polymer reaction.
- Figure 4.** Schematic representation of the tubular reactor.
- Figure 5.** Implementation of the kinetic/topology MC algorithm to a tubular reactor (f: sampling factor, N_A : Avogadro number).
- Figure 6.** Calculated reactor temperature profiles for the four simulated LDPE grades 1-4 (see Table 1).
- Figure 7.** Number and weight average molecular weights of the LDPE grade 3 as calculated by the MOM (solid lines), the kinetic MC method (green solid dots) and the kinetic/topology MC method (green open circles).
- Figure 8.** Weight average molecular weight of LDPE as calculated by the kinetic (solid lines) and the kinetic/topology (broken lines) MC methods for the LDPE grades 2-4. Inset Figure: Number of long- and short-chain branches per 1000 carbon atoms of LDPE as calculated by the kinetic MC (solid lines) and the kinetic/topology MC (dots) methods for the LDPE grades 2-4.
- Figure 9.** Calculated 2-D joint (LCB-MW) distribution **(a)** and 2-D joint (SCB-MW) distribution **(b)** of LDPE at the reactor exit (simulation grade 4 in Table 1).
- Figure 10.** Calculated 2-D joint (BO-BMW) distribution of LDPE at the reactor exit (simulation grade 4 in Table 1).
- Figure 11.** Calculated seniority-priority distributions of LDPE at the first **(a)** and third **(b)** reactor temperature peak (simulation grade 3 in Table 1).

- Figure 12.** Number of LCBs per 10^3 carbon atoms **(a)** and average LCB length **(b)** as calculated by the kinetic/topology MC algorithm at the reactor exit for the four LDPE grades 1-4 (see Table 1).
- Figure 13.** Effect of the initial solvent (CTA) concentration on the molecular weight distribution of LDPE as calculated by the kinetic/topology MC algorithm at the reactor exit for the LDPE grades 5-7 (see Table 1).
- Figure 14.** Effect of the initial solvent (CTA) concentration on the numbers of long- and short-chain branches per 10^3 carbon atoms as calculated by the kinetic/topology MC algorithm at the reactor exit, for the LDPE grades 5-7 (see Table 1).
- Figure 15.** Variation of the average LCB length with respect to the reactor length for different initial solvent concentrations as calculated by the kinetic/topology MC algorithm for the LDPE grades 5-7 (see table 1).
- Figure 16.** Calculated values of the mean radius of gyration, R_g , for the LDPE grade 2, using a random-walk molecular simulator and a sample population of 8.98×10^4 branched polymer chains.
- Figure 17.** Calculated values of the mean radius of gyration, R_g , for the LDPE grade 4, using a random-walk molecular simulator and a sample population of 1.18×10^5 branched polymer chains.
- Figure 18** Variation of the branching factor, g , with respect to the PE chain length for two LDPE grades (2 and 4), using a sample population of 8.98×10^4 and 1.18×10^5 branched polymer chains, respectively.

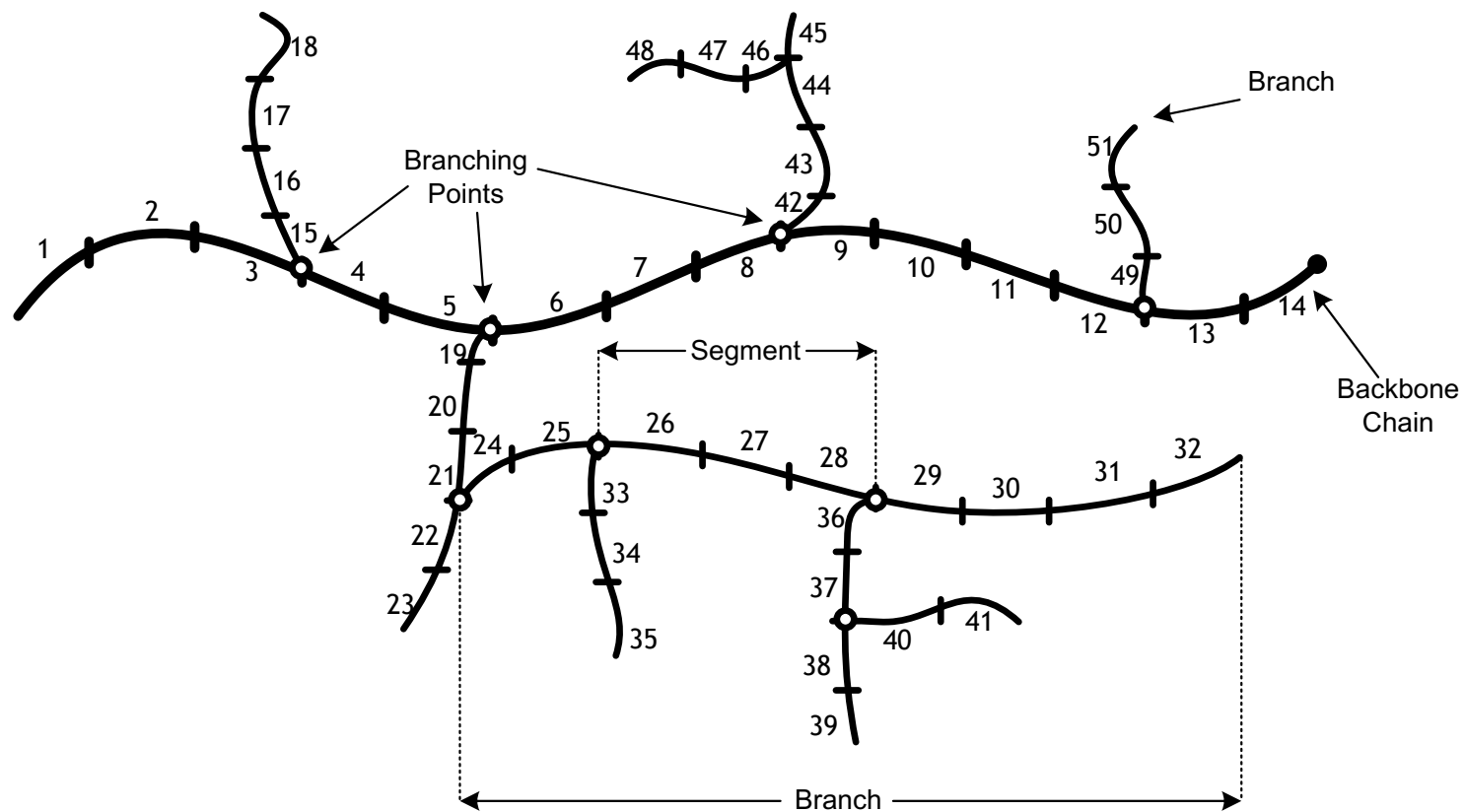


FIGURE 1

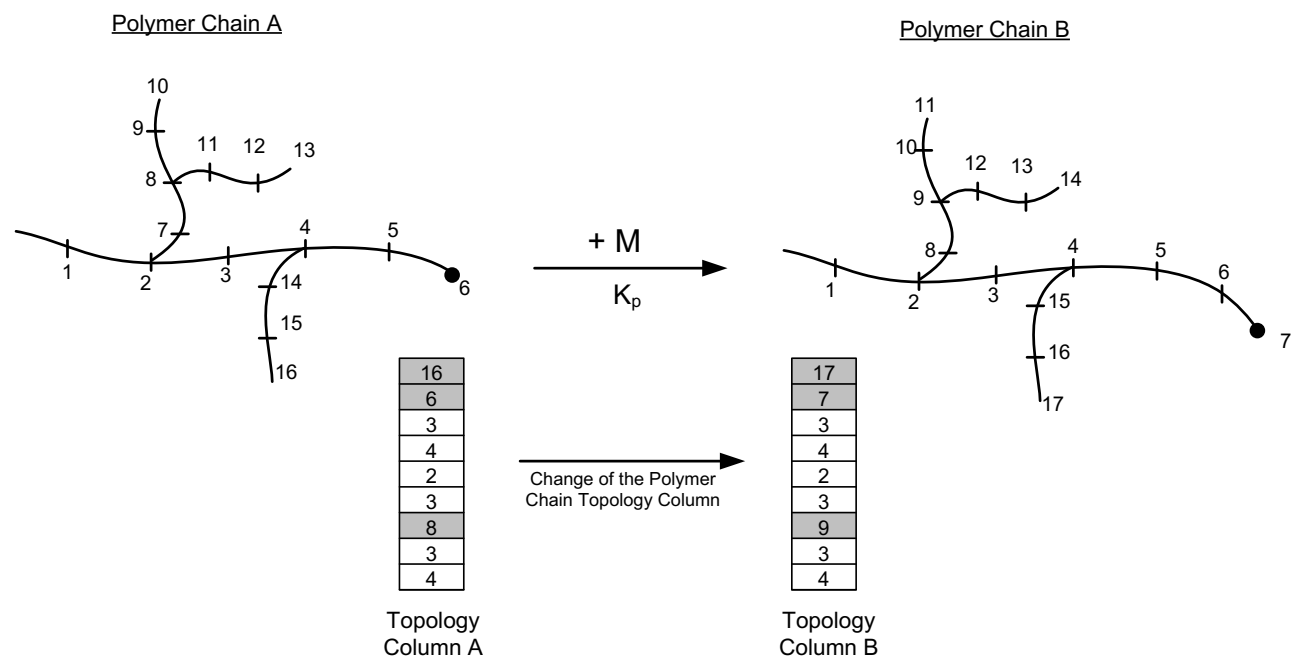


FIGURE 2

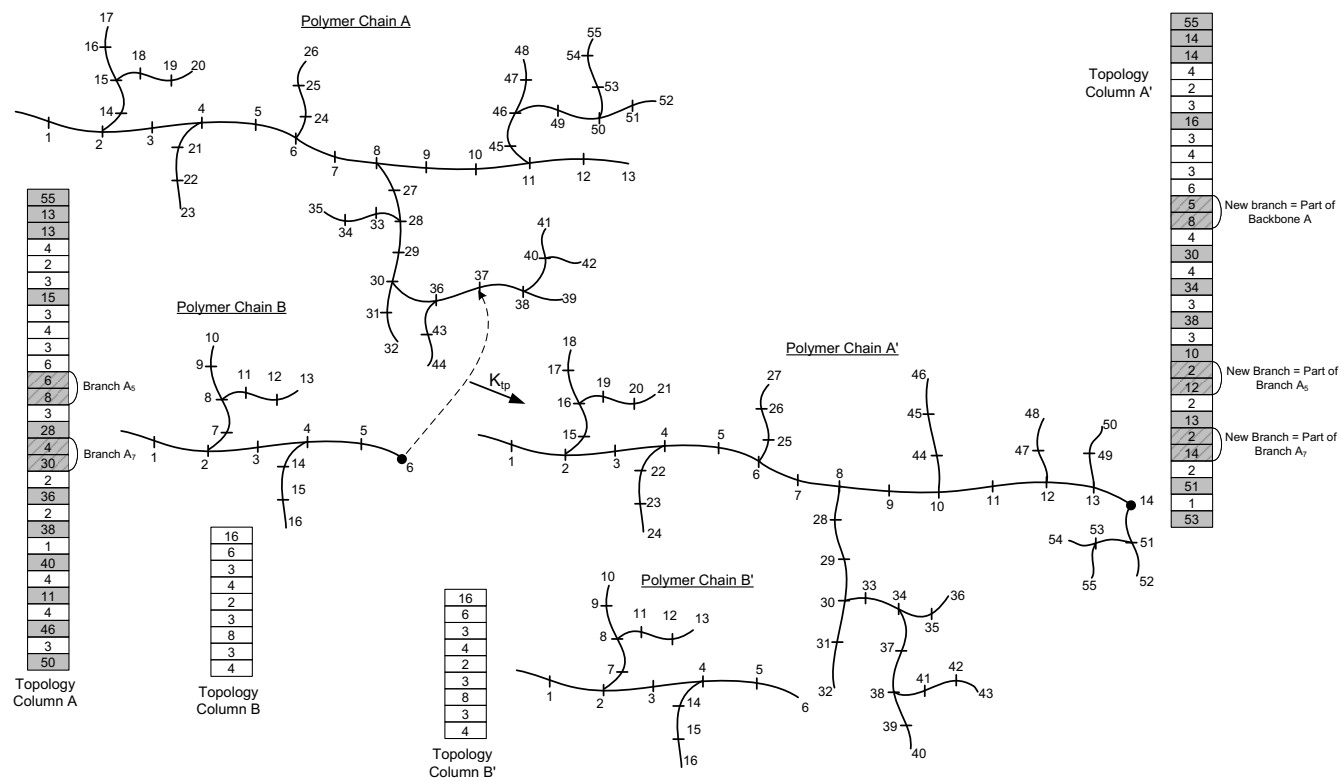


FIGURE 3

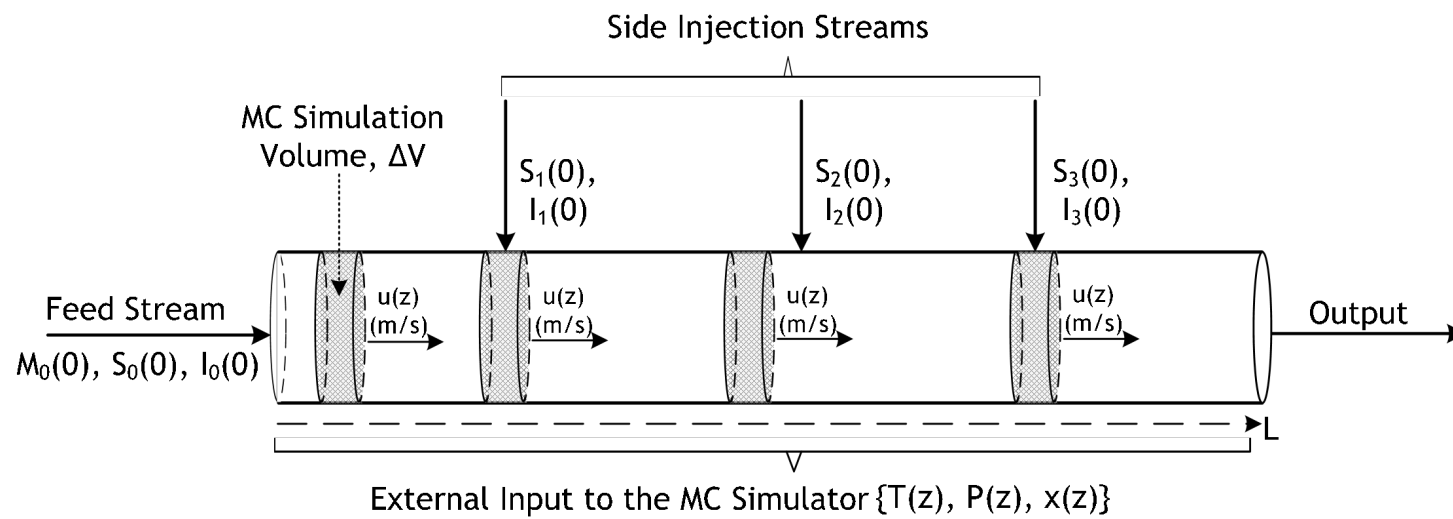


FIGURE 4

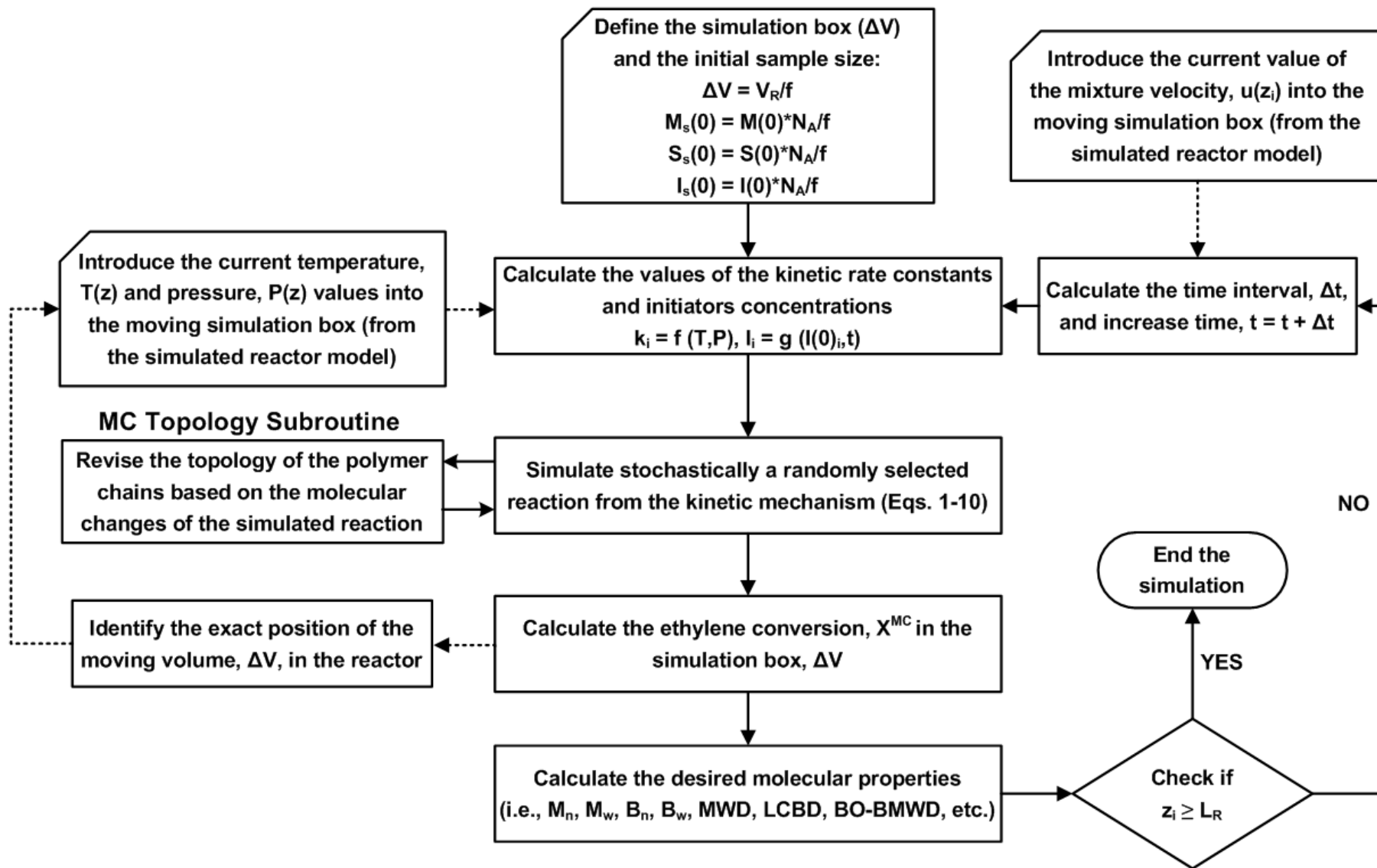


FIGURE 5

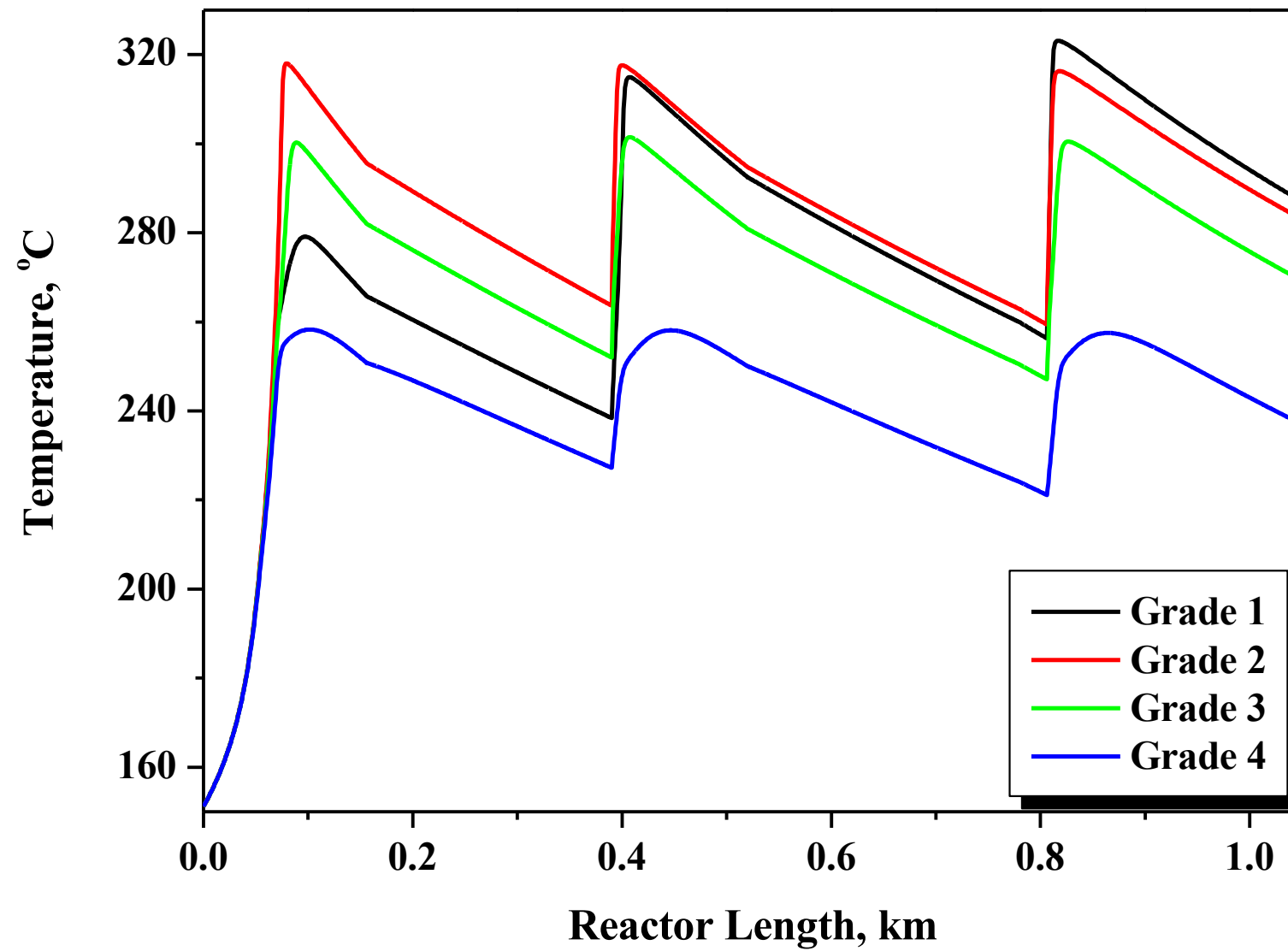


FIGURE 6

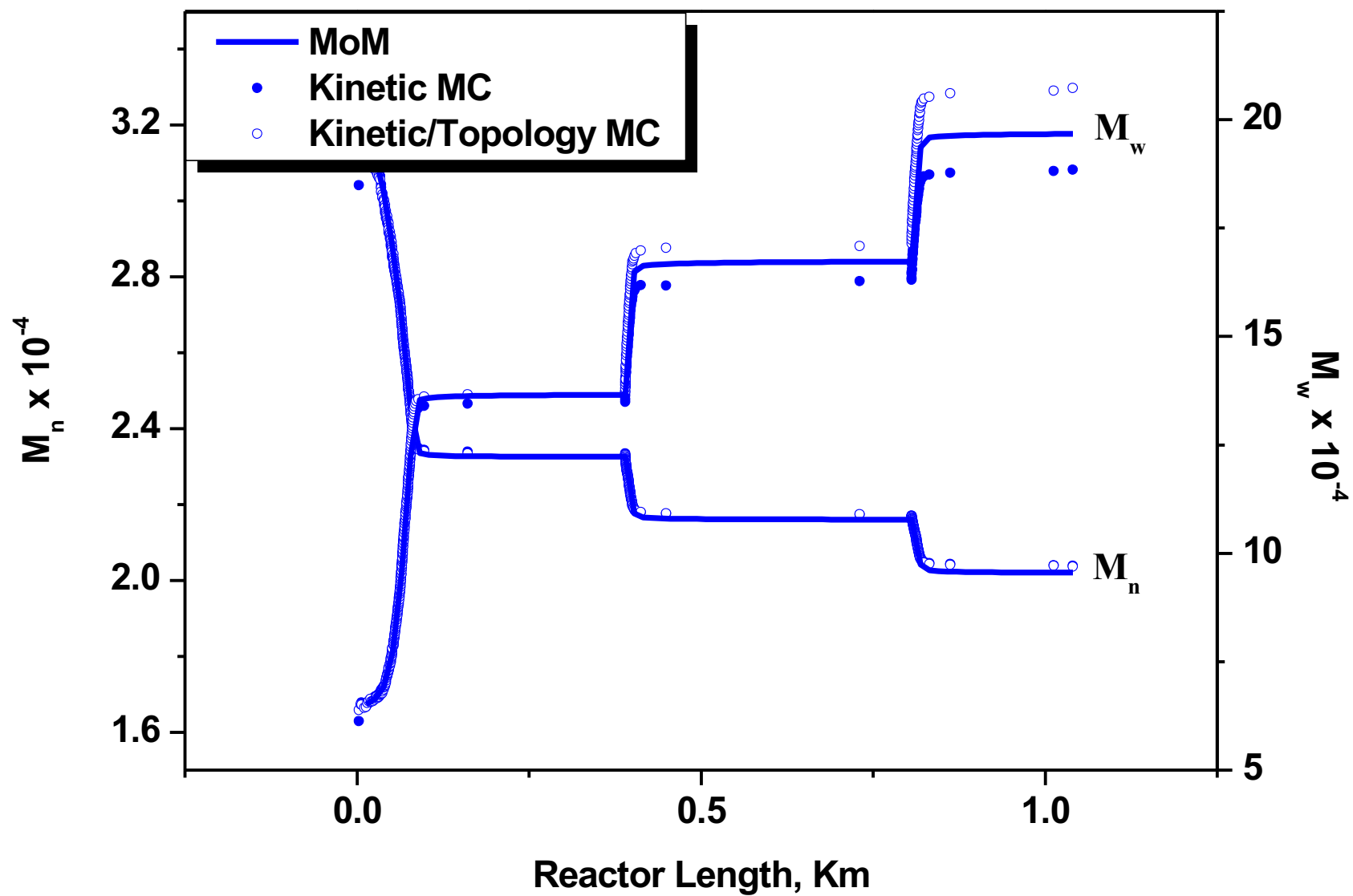


FIGURE 7

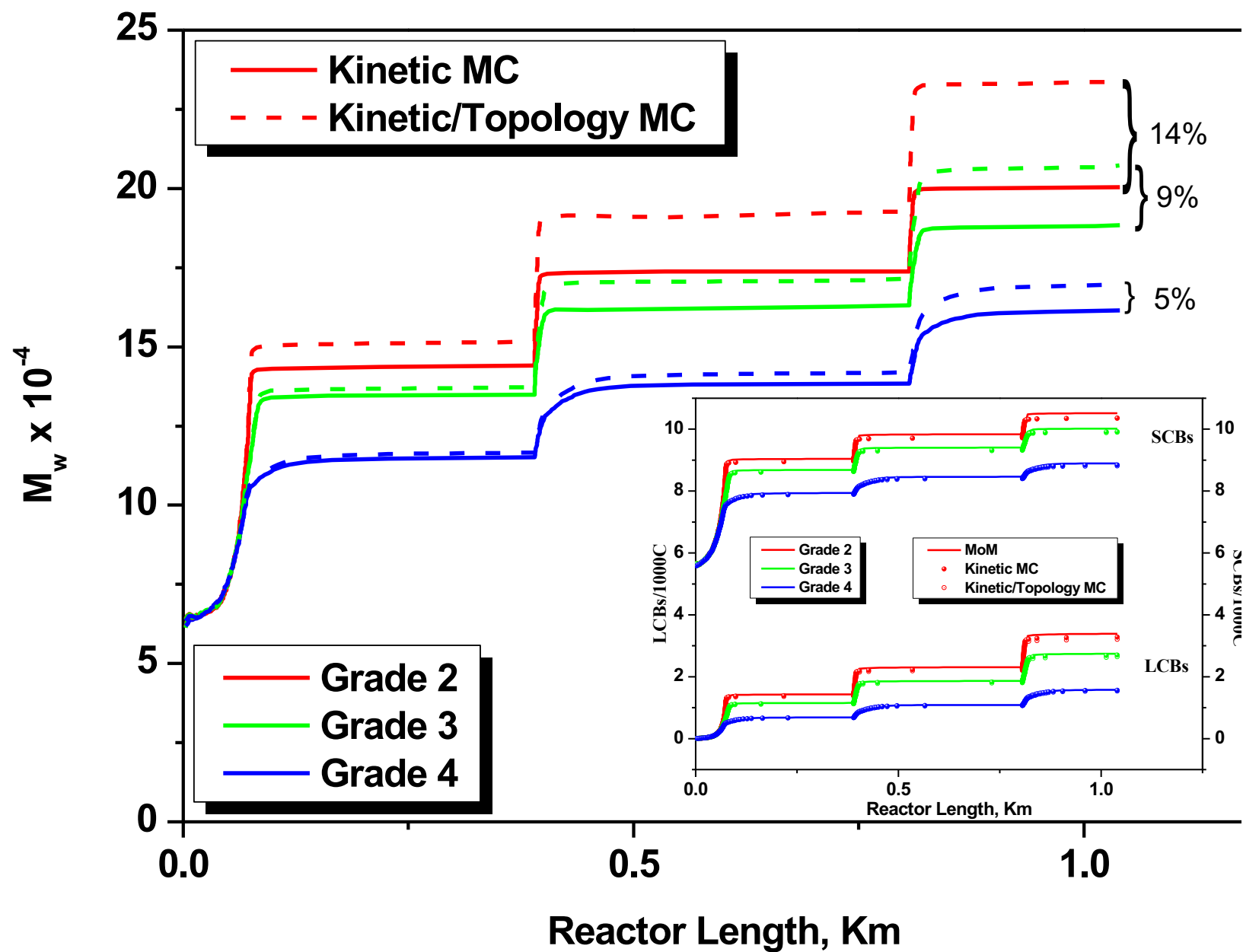


FIGURE 8

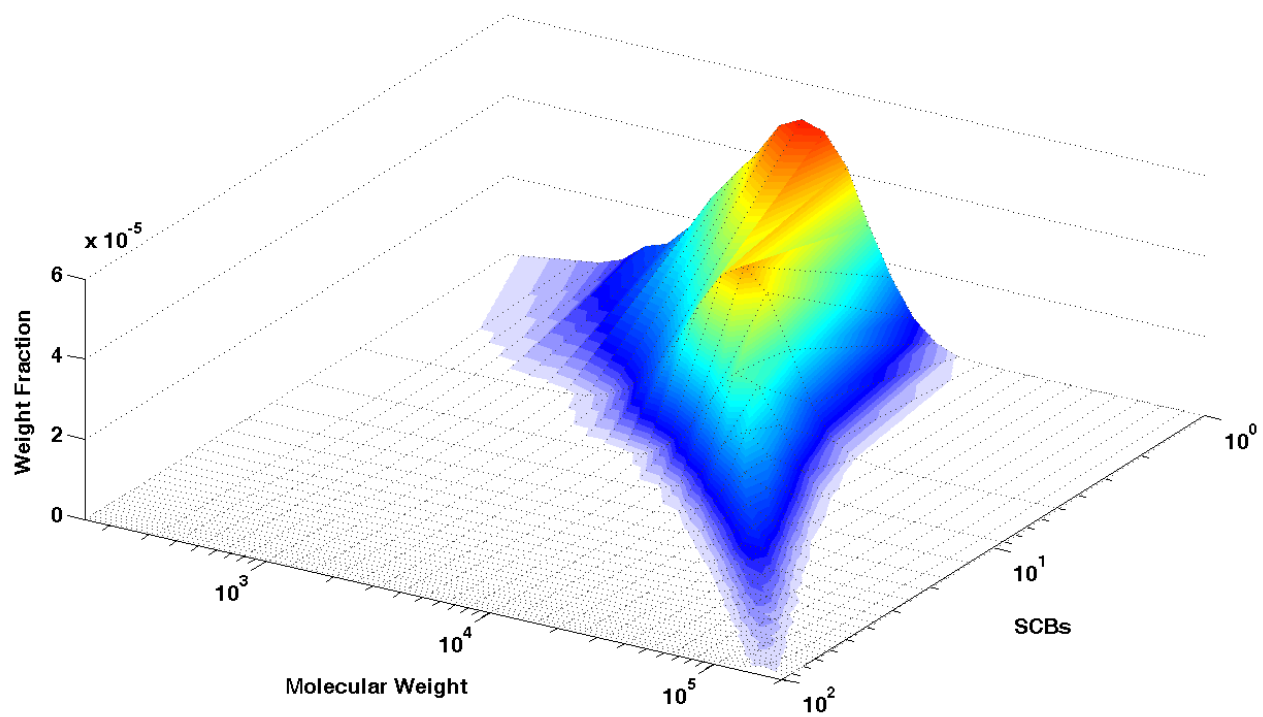
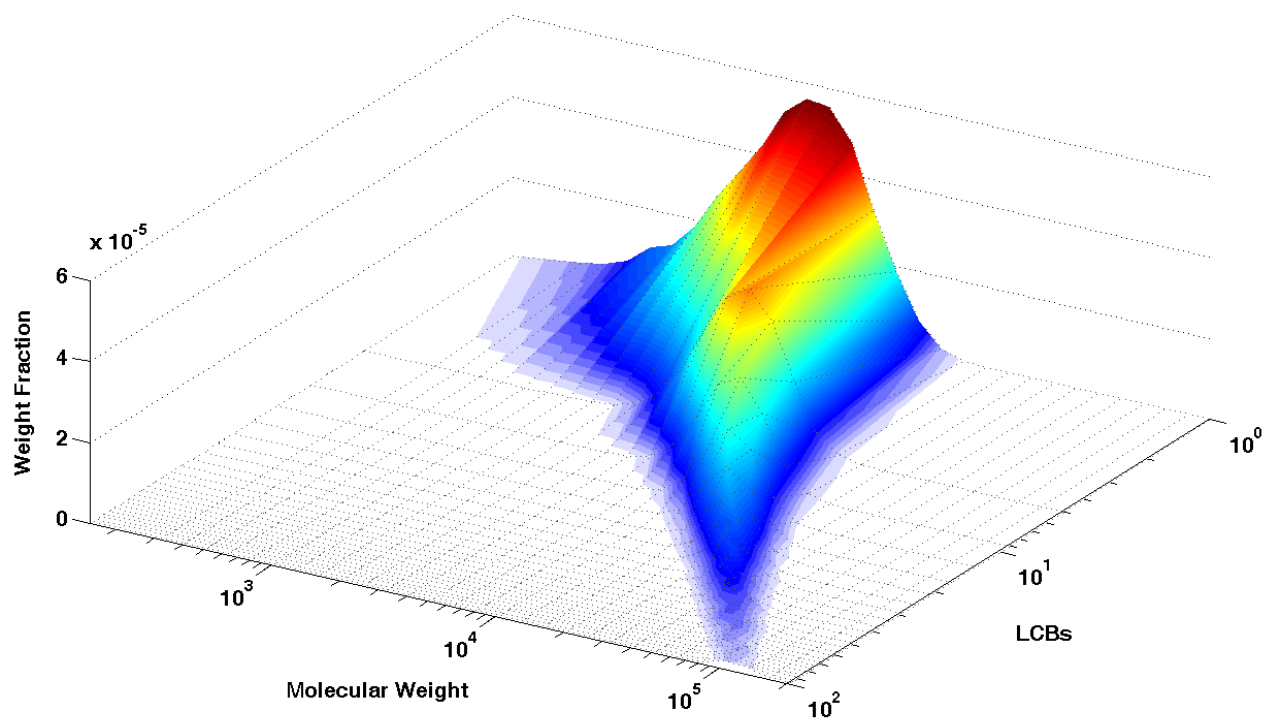


FIGURE 9

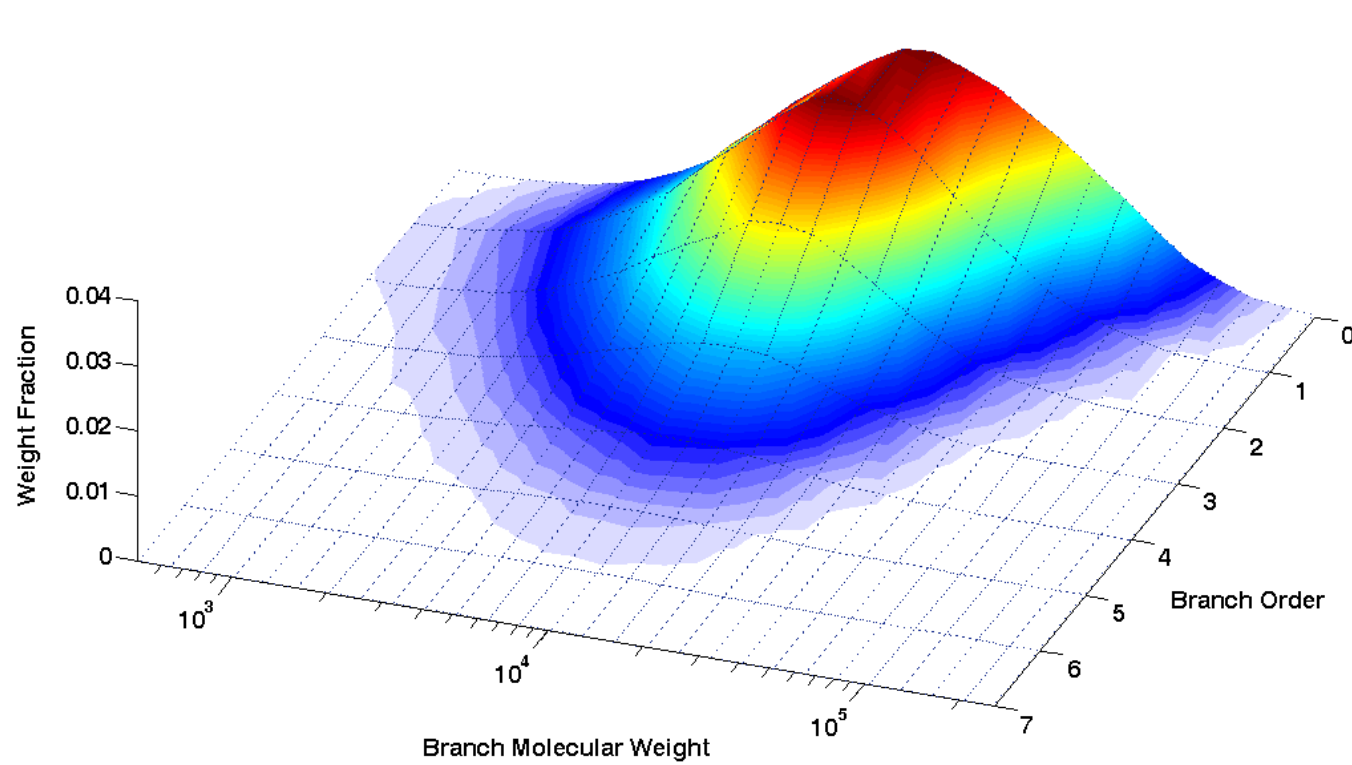


FIGURE 10

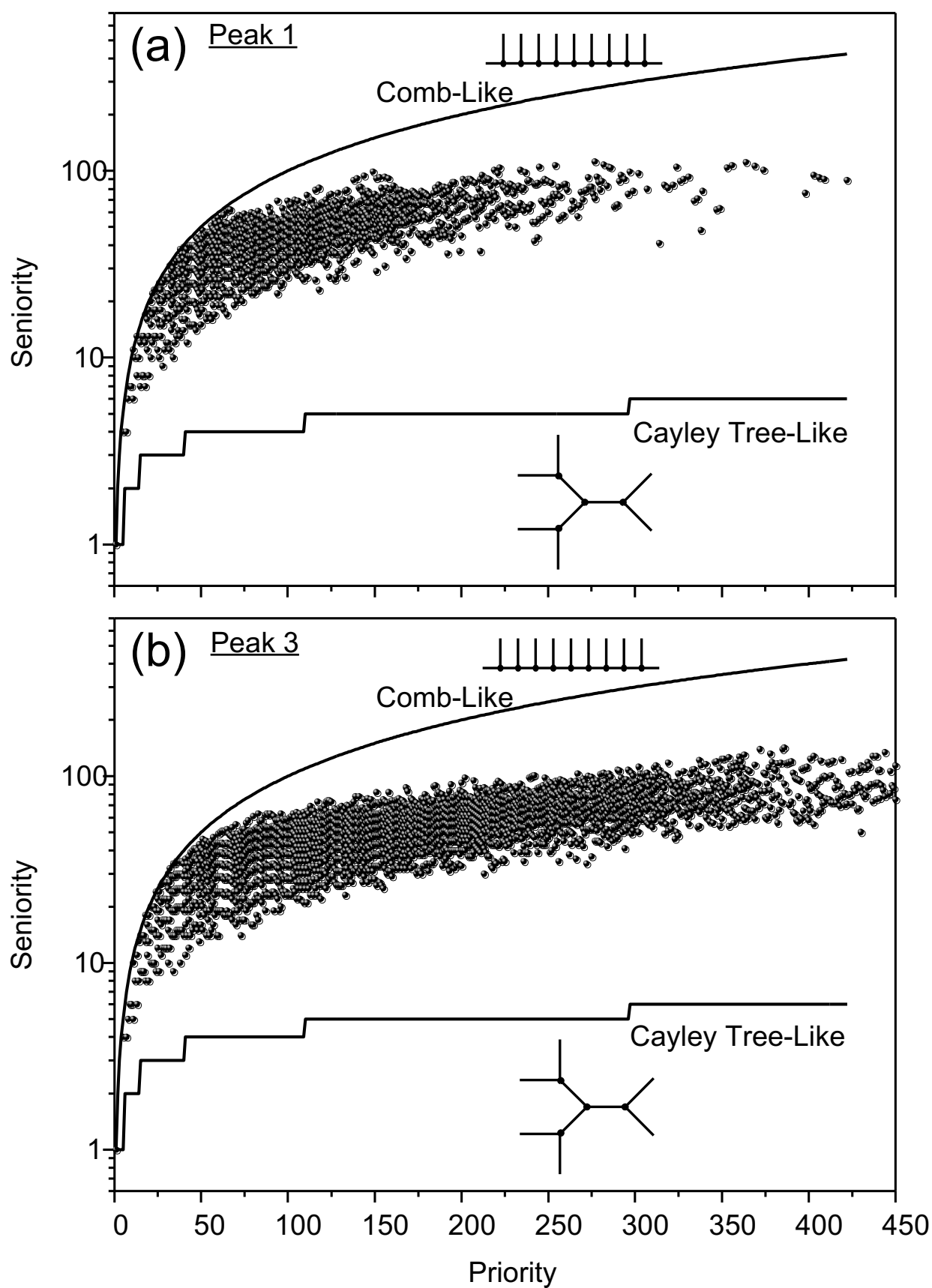


FIGURE 11

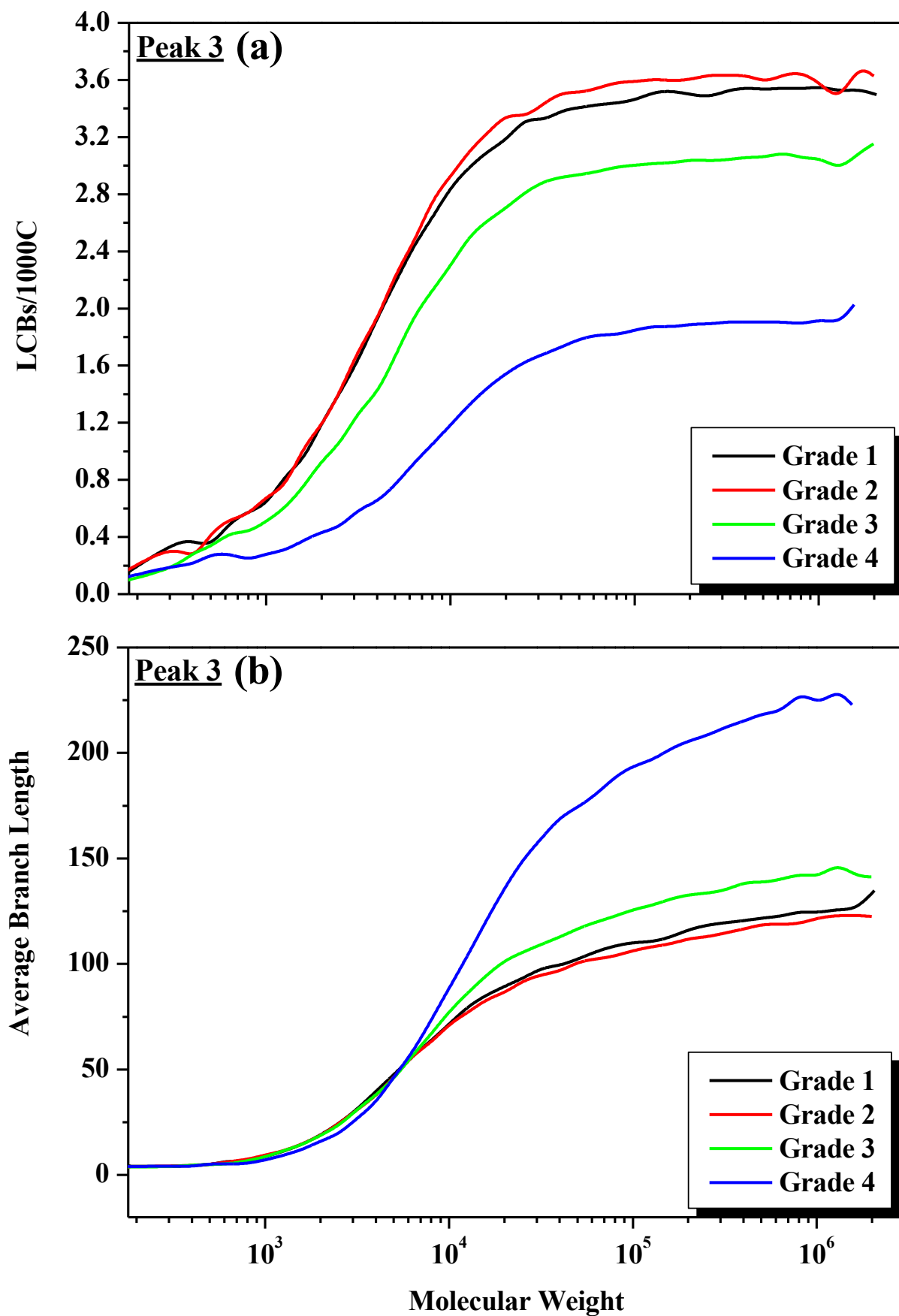


FIGURE 12

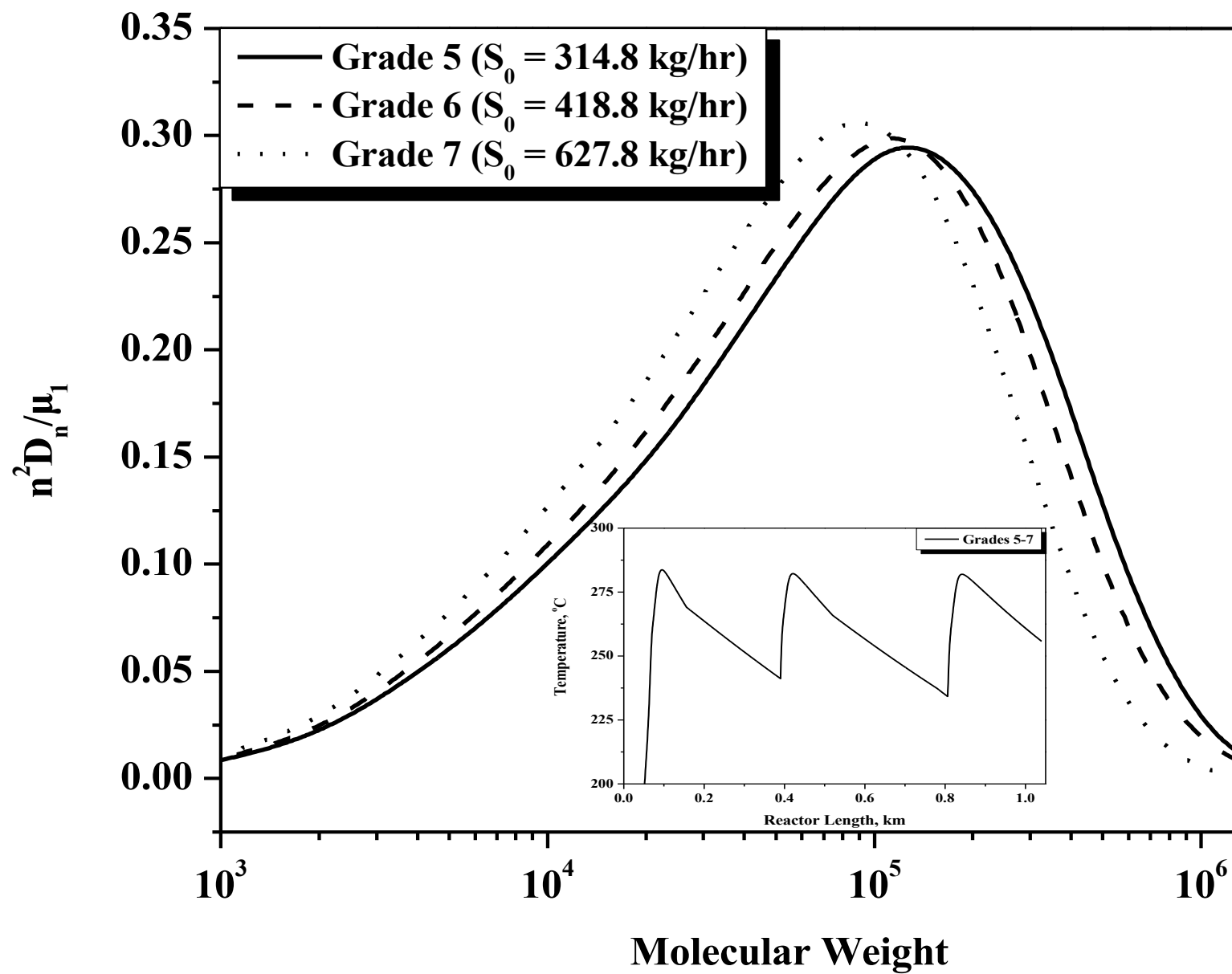


FIGURE 13

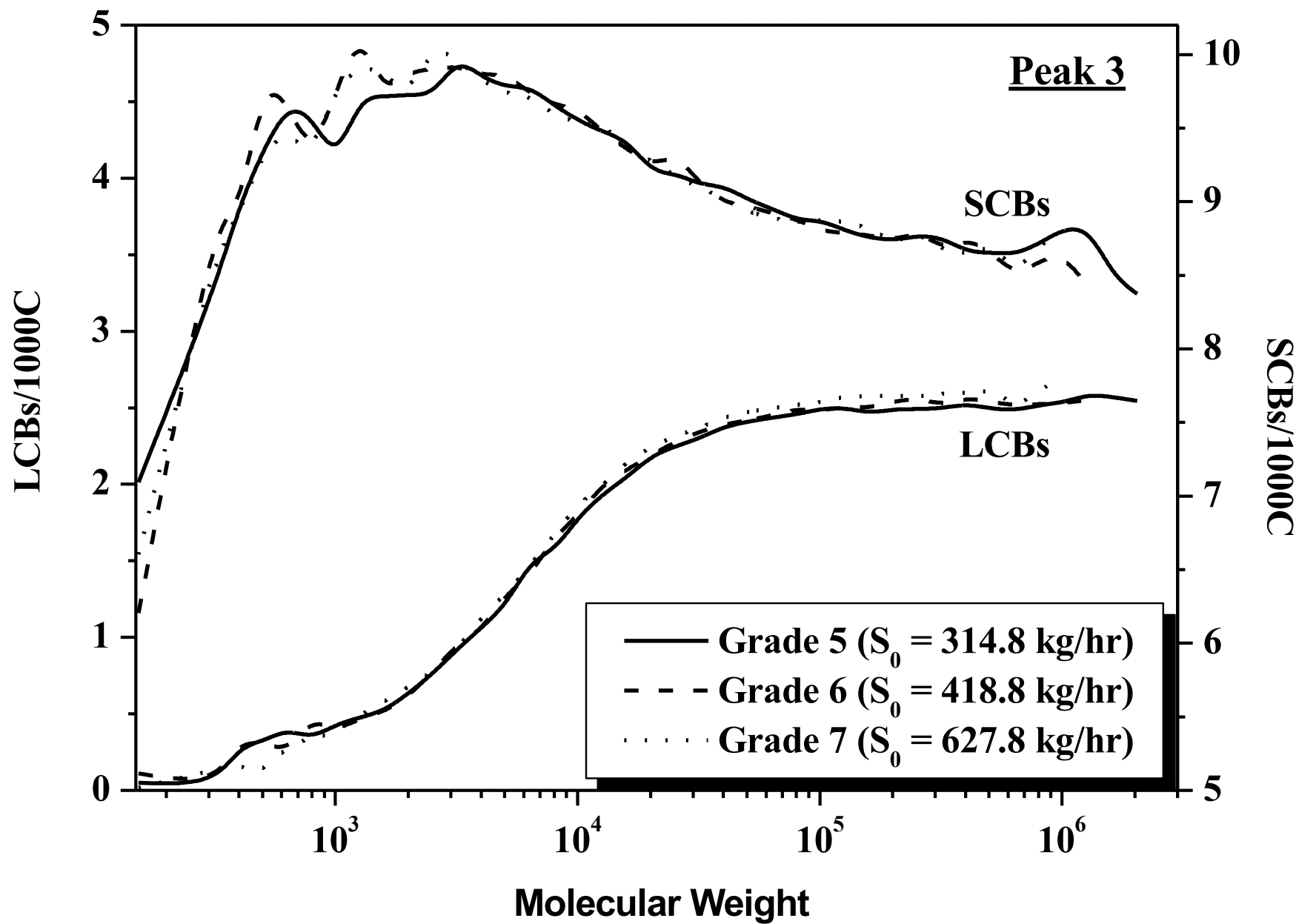


FIGURE 14

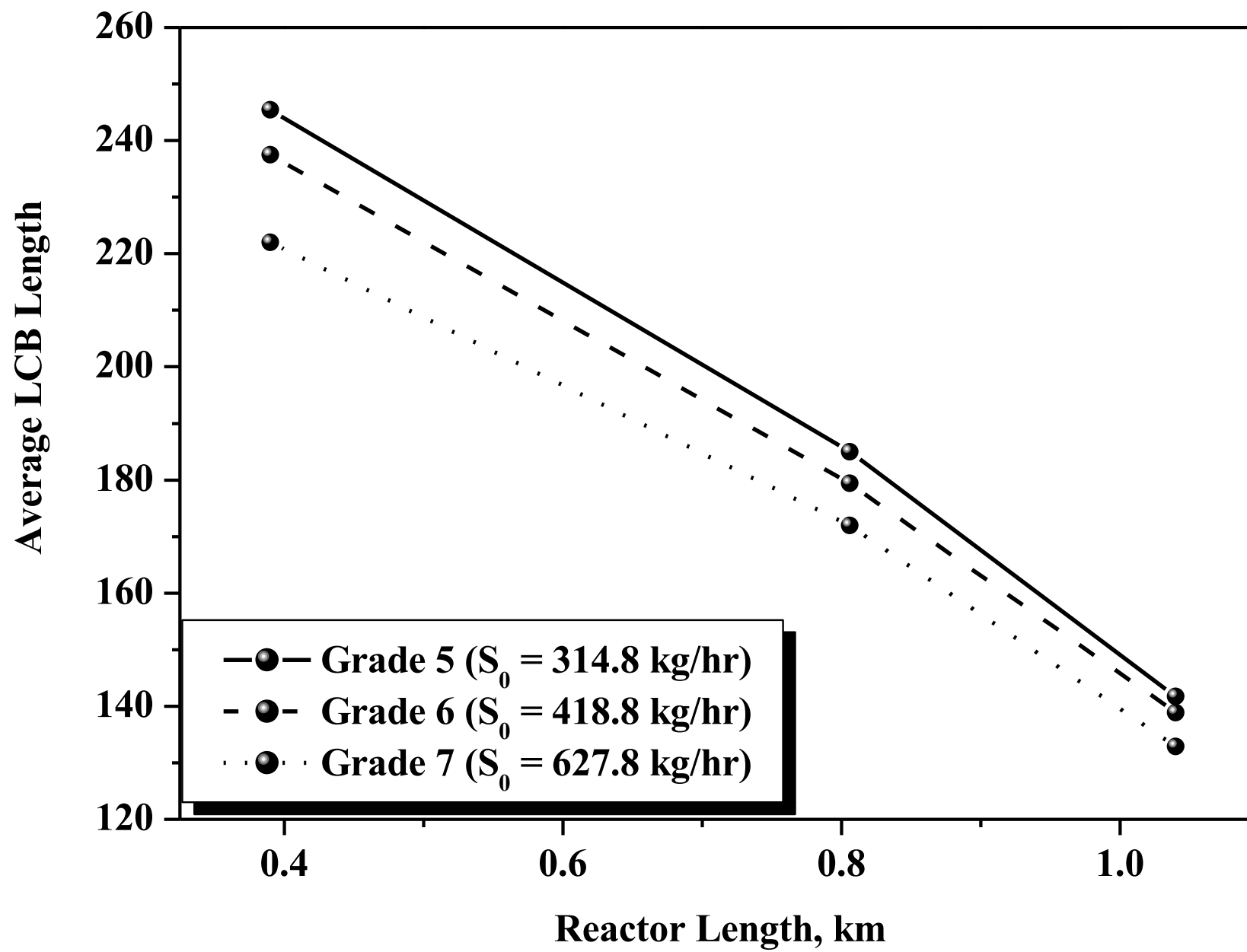


FIGURE 15

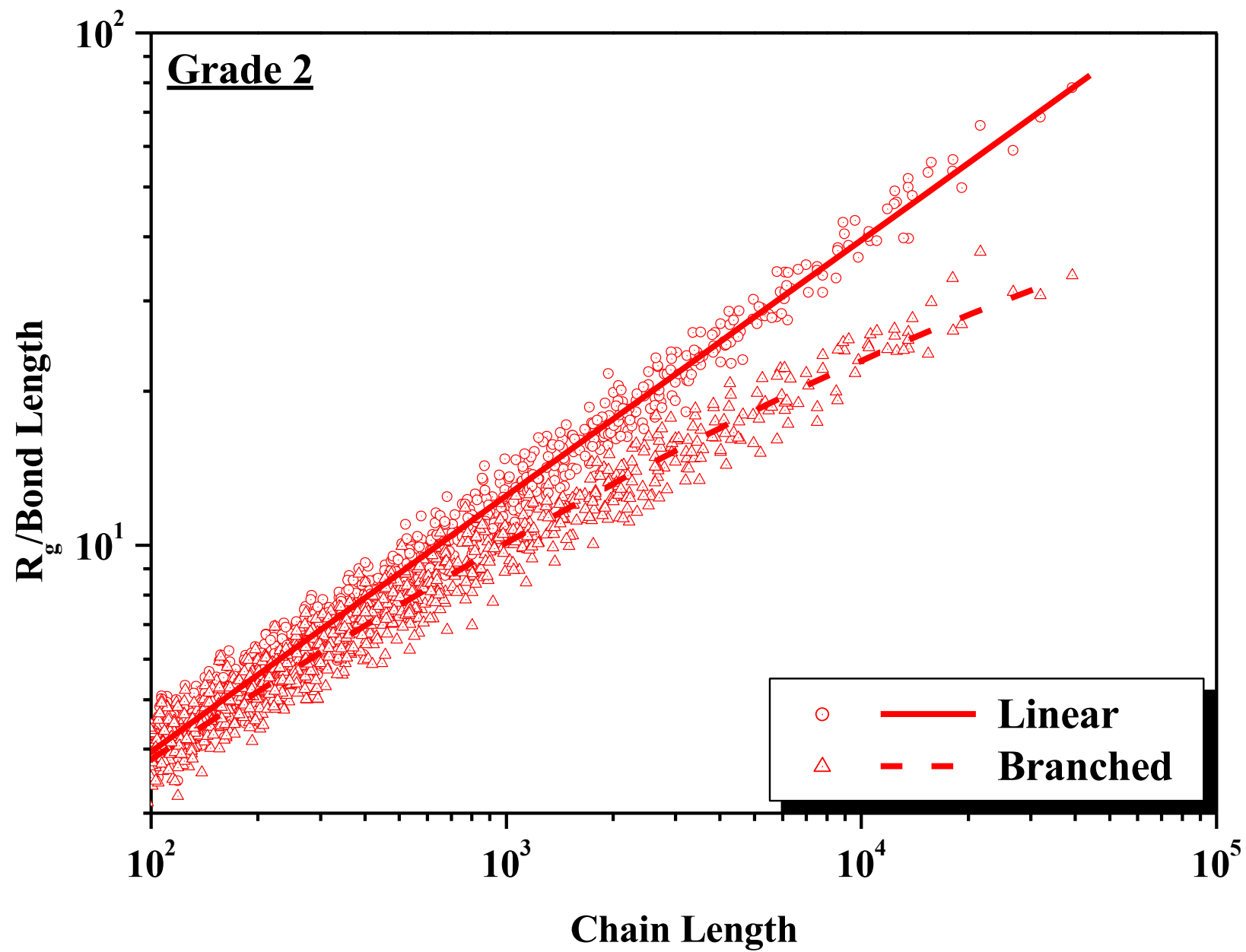


FIGURE 16

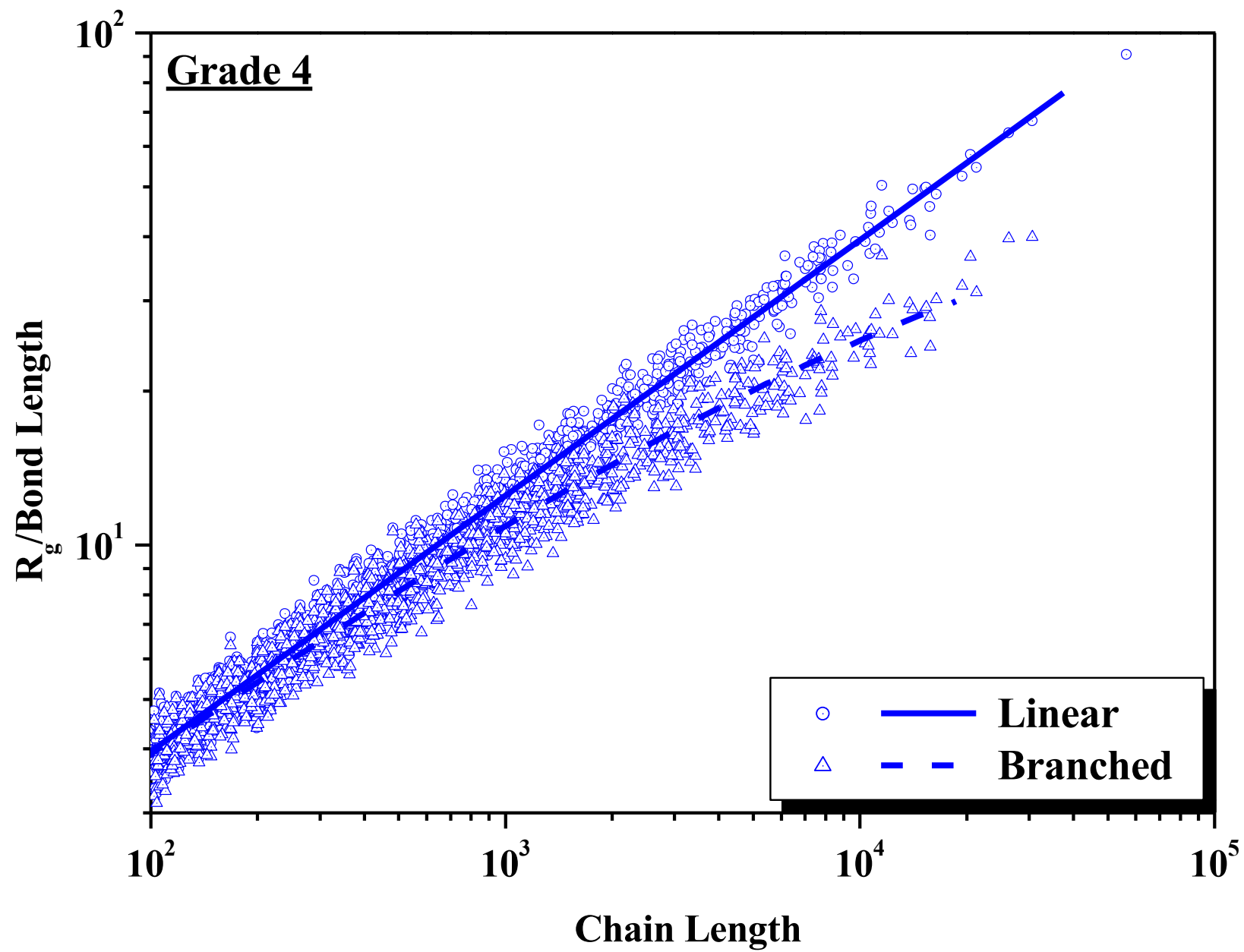


FIGURE 17

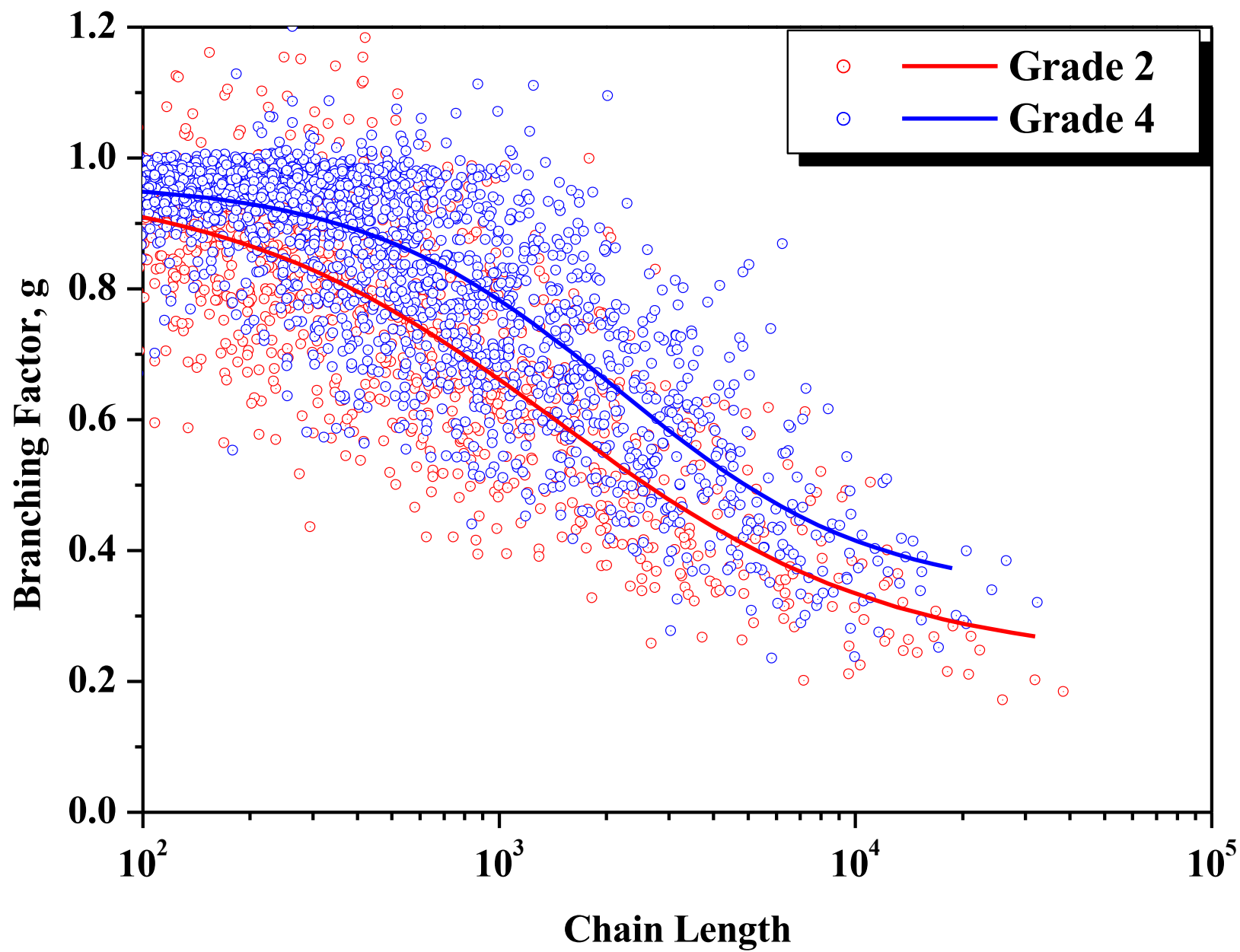


FIGURE 18

Table 1. Reactor operating conditions for the seven simulated LDPE grades.

Mass Flowrates of Feed and Side Streams				
	Feed Stream	Injection 1	Injection 2	Injection 3
Simulation Grade 1 – (Base Case)				
Ethylene	3×10^4 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹
Solvent ^a	209.8 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹
Initiator 1 ^a	0.0 kg hr ⁻¹	2.194 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹
Initiator 2 ^a	0.0 kg hr ⁻¹	1.615 kg hr ⁻¹	0.768 kg hr ⁻¹	1.230 kg hr ⁻¹
Initiator 3 ^a	0.0 kg hr ⁻¹	0.088 kg hr ⁻¹	1.135 kg hr ⁻¹	1.826 kg hr ⁻¹
Simulation Grade 2^b				
Initiator 3 ^a	0.0 kg hr ⁻¹	0.75 kg hr ⁻¹	0.8 kg hr ⁻¹	1.126 kg hr ⁻¹
Simulation Grade 3^b				
Initiator 2 ^a	0.0 kg hr ⁻¹	1.415 kg hr ⁻¹	0.708 kg hr ⁻¹	0.9 kg hr ⁻¹
Initiator 3 ^a	0.0 kg hr ⁻¹	0.330 kg hr ⁻¹	0.4 kg hr ⁻¹	0.6 kg hr ⁻¹
Simulation Grade 4^b				
Initiator 2 ^a	0.0 kg hr ⁻¹	1.215 kg hr ⁻¹	0.668 kg hr ⁻¹	1.330 kg hr ⁻¹
Initiator 3 ^a	0.0 kg hr ⁻¹	0.02 kg hr ⁻¹	0.045 kg hr ⁻¹	0.046 kg hr ⁻¹
Simulation Grade 5^b				
Initiator 3 ^a	0.0 kg hr ⁻¹	0.12 kg hr ⁻¹	0.145 kg hr ⁻¹	0.226 kg hr ⁻¹
Solvent ^a	314.8 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹
Simulation Grade 6^b				
Initiator 3 ^a	0.0 kg hr ⁻¹	0.12 kg hr ⁻¹	0.145 kg hr ⁻¹	0.226 kg hr ⁻¹
Solvent ^a	418.8 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹
Simulation Grade 7^b				
Initiator 3 ^a	0.0 kg hr ⁻¹	0.12 kg hr ⁻¹	0.145 kg hr ⁻¹	0.226 kg hr ⁻¹
Solvent ^a	627.8 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹	0.0 kg hr ⁻¹

^a Undisclosed information due to confidentiality reasons.^b Only the differences from the base case are reported.