Comparing Long Chain Branching Mechanisms for Ethylene Polymerization with Metallocene Catalysts: What Simulated Microstructures Can Teach Us

By

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Abstract

The versatility of polyethylene stems from the diversity of its microstructure that can be characterized by its molecular weight averages and distribution, long chain branching, and short chain branching. In an ideal scenario, one would want to predict the polymerization parameters needed to produce a polyethylene with the microstructure required to meet specific application demands. Employing various mathematical and statistical models usually gives insights for the good design of polyethylenes.

Long chain branching is one of the important microstructural properties that influences polyethylene processability and mechanical properties. It is widely accepted that long chain branches (LCB) in polyethylene made with coordination catalysts are formed via terminal branching, which is a random intermolecular incorporation pathway for in-situ produced macromonomers. However, some publications in the literature have claimed that this mechanism disagrees with certain experimental observations, especially for slurry and gas phase polymerization processes. As a result, alternative mechanisms have been proposed to reconcile these differences.

We have chosen two alternative mechanisms for LCB formation: 1) carbon-hydrogen bond (C-H) activation, and 2) intramolecular branching pathway, to be compared with the conventional terminal branching mechanism. We developed simulation models for all three mechanisms in two different polymerization systems: semi-batch and continuous polymerizations. The main aim of this approach was to find out how the different long chain branching mechanisms were reflected in the microstructures of the formed polyethylene chains. Several researchers have proposed alternative mechanisms for this process, but

surprisingly none of them asked the question: If this mechanism is valid, how would if affect the microstructure of the formed polyethylene under different polymerization conditions?

Increasing the ethylene concentration in the semi-batch simulations led to a decrease in LCB frequencies for the terminal branching and intramolecular mechanisms, whereas no effect was observed on the C-H activation mechanism, which disagrees with most previous literature data. Another observation of importance was the evolution of LCB parameters with time and conversion, where the intramolecular mechanism showed almost no dependence on time or ethylene conversion. This is also in disagreement with the published experimental data for these systems.

For the simulation of continuous polymerization processes, an important observation was the comparison of the polydispersity (PDI) dependence on LCB parameters. Data reported in the literature showed that simulations based on the terminal branching mechanism follow the data much more adequately, whereas the C-H activation results follows the experimental data below a certain LCB frequency, but then completely deviates from it. The intramolecular simulation results have shown a poorer comparison than terminal branching, but better than C-H activation.

Therefore, our detailed simulations confirm that the terminal branching mechanism is indeed the most likely mechanism for LCB formation with ethylene when polymerized with coordination catalysts.

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Life is nothing but a bundle of experiences that we go through; sometimes we enjoy a certain experience, and other times we may not. This last one year and eight months have been the most enjoyable and rich experience in my life in all aspects, especially the research work and the great sense of curiosity and exploration that comes with it.

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Chapter 1: Introduction

1.1 Motivation

Some metallocene catalysts can make polyethylene with long chain branches (LCB).[1–7] Terminal branching, illustrated in Figure 1-1, is the most widely accepted mechanism for LCB formation with these catalysts. This mechanism assumes that macromonomers, generated via β-hydride elimination or transfer to monomer, are randomly incorporated onto the growing polymer chains, creating a LCB. Several polymerization mathematical models have been developed in the literature assuming the terminal branching mechanism for ethylene polymerization.

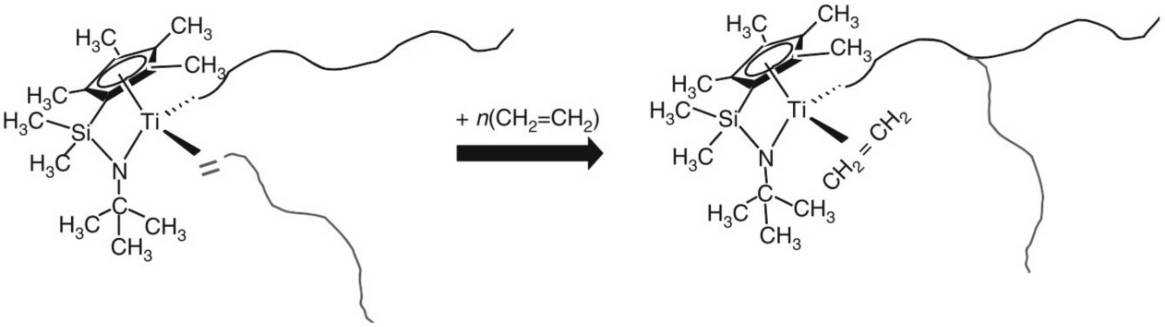

Figure 1-1. Long chain branch formation via terminal branching.[8]

However, some discrepancies between experimental data and predictions based on the terminal branching mechanism have been reported in literature. For instance, the reactivity of the macromonomers with respect to ethylene would need to be higher than those of shorter α-olefins[9] to fit the experimental data, which disagrees with the consensus that the reactivity ratios of α-olefins with respect to ethylene decrease as the α–olefin molecule becomes longer. (Notice that a macromonomer is simply a long α-olefin, see Figure 1-1.)[9,10]

Some of the hypotheses proposed in literature to explain this discrepancy include LCB formation via the chain walking mechanism,[11] C-H activation,[12] intramolecular random incorporation mechanism,[13,14] and micro-mixing effects.[9] The first three hypotheses involve chemical mechanisms, whereas the last one is based on a purely physical phenomenon: it has been proposed that the local concentration of macromonomers is higher in the vicinity of the active site, due to the slow mass transfer rate of the formed macromonomer, than in the bulk solution.[9] The intramolecular random incorporation mechanism was proposed mainly for slurry and gas phase polymerizations, as it was claimed that the terminal branching mechanism was not plausible for these processes due to the limited mobility of macromonomers in the solid polymer matrix surrounding the active sites.[13,14] The C-H activation mechanism has been proposed as a general alternative for LCB formation during ethylene polymerization with metallocene catalysts, while chain walking has been proven to be extremely unlikely to form LCB in these systems[15].

In this thesis, we used the commercial software PREDICI® to compare the three most relevant mechanisms for LCB formation during solution polymerization: terminal branching, the carbon-hydrogen bond activation (CH), and the intramolecular random incorporation mechanism (IM). Our main objective was to find out which polymer molecular structure would result from each LCB-formation mechanism under different semi-batch and continuous polymerization conditions.

1.2 Research Objectives

The main objective of this thesis is to differentiate between the possible long chain branching mechanisms using mathematical modelling. We used the commercial software PREDICI® for the development of all the simulation models in this thesis. In order to achieve our main objective, the following several objectives had to be achieved:

- Developing a simulation model for the terminal branching mechanism for ethylene polymerization using metallocene catalysts in semi batch and continuous processes.
- Developing a simulation model for the C-H activation mechanism for ethylene polymerization using metallocene catalysts in semi batch and continuous processes.
- Developing a simulation model for the intra-molecular mechanism for ethylene polymerization using metallocene catalysts in semi batch and continuous processes.
- Contrast the resulting polymer LCB structures resulting from these long chain branching mechanisms upon varying polymerization conditions for semi-batch and continuous processes.
- Verify some of the simulation results with literature experimental data in order to be able to understand the dominating long chain branching mechanism for metallocene catalysts.

1.3 Thesis Outline

This thesis consists of five chapters that are arranged as follows:

Chapter 1 includes the introduction, thesis objectives, and thesis outline. Chapter 2 reviews the relevant literature related to this research. Semi-batch simulation results are discussed in Chapter

3 under two main sections: the effect of reaction rate constants variation, and the effect of polymerization conditions on the molecular structure of the polymer: molecular weight averages, polydispersity index, and long chain branching parameters. Chapter 4 details the continuous process simulation results and is divided in two sections: effect of the average residence time on molecular structure, and PDI dependence on long chain branching parameters. Finally, chapter 5 will include our conclusions and recommendations for future research.

Chapter 2: Literature Review

2.1 Polyethylene

Polyethylene is one of the most produced thermoplastics in the world due to its versatility in terms of properties and applications. Since the discovery of Ziegler-Natta catalysts, which allowed for the production of linear polyethylene, the demand for this polymer have been increasing continuosly.[16] The versatility of polyethylene stems from the diversity of its microstructure that can be quantified with the following parameters: molecular weight averages and distribution, long chain branching frequency and topology, and short chain branching average and distribution. In an ideal situation, one would want to determine a priori the polymerization parameters are needed to produce a polyethylene grade with the specific microstructure needed to meet a desired application performance. Such predictions can be achieved using mathematical models using the method of moments, population balances, or Monte Carlo simulations. An essential input for all these modelling methods is the polymerization mechanism taking place during the production of polyethylene. The main steps in the polymerization mechanisms of olefins with metallocene catalysts are fairly well understood, but some steps still remain controversial.[17]

2.2 Long Chain Branching in Polyethylene

One of the important microstructural characteristics of polyethylene is long chain branching, because the presence of even small amounts of LCBs can drastically affect the properties of polyethylene. As mentioned in Chapter 1, the most accepted mechanism for the formation of LCBs in polyethylenes is terminal branching mechanism, illustrated in Figure 1-1. However, some experimental discrepancies reported in literature seem to contradict this mechanism. Nele and Soares[9] have compared the reactivity ratios of macromonomers and α-olefins to ethylene, as shown in Figure 2-1. Terminal branching is the random intermolecular incorporation of very long α-olefins, which is the same mechanism for short α-olefin copolymerization. The reactivity of α-olefins decreases as the number of carbons in the molecule increase.[3] Consequently, one would think that the reactivity of macromonomers (that are responsible for the formation of LCBs) should follow the same trend. However, this is not what has been observed, as shown in Figure 2-1 for a limited number of experimental results. Proposed explanations for this discrepancy are either the existence of C-H activation reactions that lead to LCB formation, or micro-mixing effects that make the local concentration of macromonomers near the active site to be much higher than their bulk concentration in the reactor.

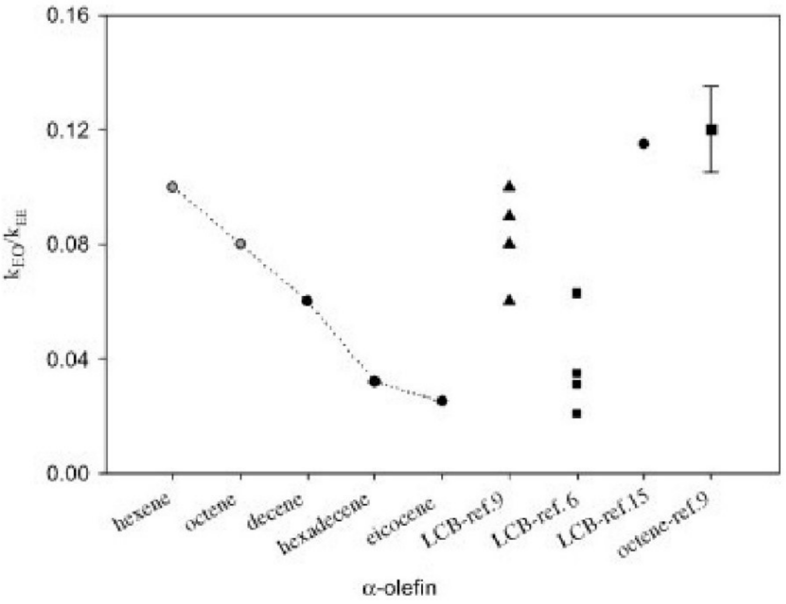

Figure 2-1. Reactivity ratios of α-olefins and macromonomers (LCBs) to ethylene.[9]

Due to the fact that higher levels of long chain branching has been reported in literature in slurry and gas phase polymerization,[18–20] an intramolecular long chain branching mechanism has also been proposed.[13,14]

Another observation that disagrees with the terminal branching mechanism is that the crossover of macromonomers when using two catalysts during the polymerization has not been observed in some investigations.[11] In addition to the C-H activation and intramolecular mechanisms, chain walking has also been proposed as an alternative mechanism to explain LCB formation in these systems.[11]

2.3 Proposed Long Chain Branching Mechanisms

In this section, we will review all proposed mechanism for LCB formation during the polymerization of ethylene with coordination catalysts: terminal branching, C-H activation, intramolecular branching, and chain walking.

2.3.1 Terminal Branching

The first polyethylene containing LCBs made with a metallocene catalyst was reported by Dow Chemical[21] and Exxon Chemical[22] using constrained geometry catalysts (CGC). Shortly thereafter, Zhu[2,23] and Soares[7,24] research groups started synthesising and characterizing long chain branched polyethylenes. All polymerization kinetics models for long chain branched polyethylene in the literature assume that LCBs are made via terminal branching, as shown in

Figure 2-2. Several reaction mathematical models were developed by Soares and coworkers,[9,25] as well as Zhu and coworkers.[2] An algebraic solution for the model describing long chain branching with such catalysts has also been developed by Soares.[26] The terminal branching mechanism follows an intermolecular random incorporation pathway of the in-situ formed macromonomers. Macromonomers are generated mainly by two chain transfer mechanisms: transfer to monomer, and β-hydride elimination. A more detailed explanation of this mechanism will be provided later in this thesis.

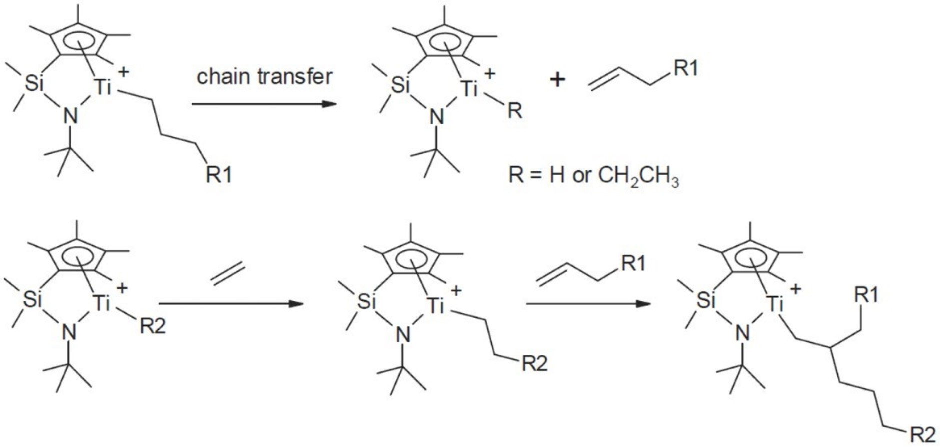

Figure 2-2. LCB formation via terminal branching for CGC catalysts.[27]

2.3.2 C-H Activation Mechanism

The C-H activation mechanism assumes that the carbon-hydrogen bonds on the growing (intramolecular) or dead (intermolecular) polymer chains can be activated by coordination to the metal active site, causing the active site to migrate to growing or dead chains. Monomer propagation continues from the “migrated” active site. Since the active site is no longer placed at the end of the polymer chain, but rather in a random position along its backbone, propagation from that site will lead to formation of a LCB. This mechanism was originally proposed for the LCB with vanadium coordination catalysts.[12] Figure 2-3 illustrates the C-H activation reaction scheme.

Karimkhani et al. have discussed the possibility of such reaction happening with metallocene catalysts, and concluded that it could not be excluded as a possible pathway for LCB formation, but have also doubted such reaction would take place on a dead aliphatic polymer chain.[28]

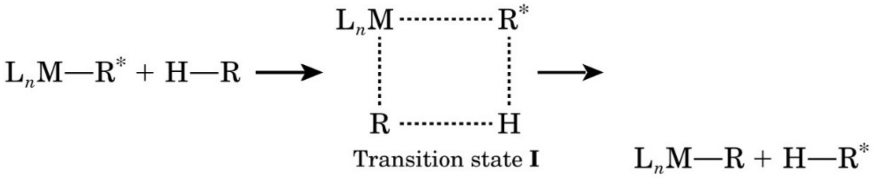

Figure 2-3. C-H Activation mechanism reaction scheme. [12]

2.3.3 Intra-Molecular Mechanism

The intramolecular mechanism for LCB formation was proposed mainly for slurry polymerization processes. The mechanism assumes that each active site incorporates its own produced macromonomers, which is mainly determined by the ability of the active site to keep the macromonomer coordinated to itself after a chain transfer step, as illustrated in Figure 2-4.

Experimental results supporting this mechanism have been reported by Jensen M et al.[14] However, it has also been shown that the predominant mechanism for LCB formation in slurry polymerizations is still the widely accepted terminal branching.[28]

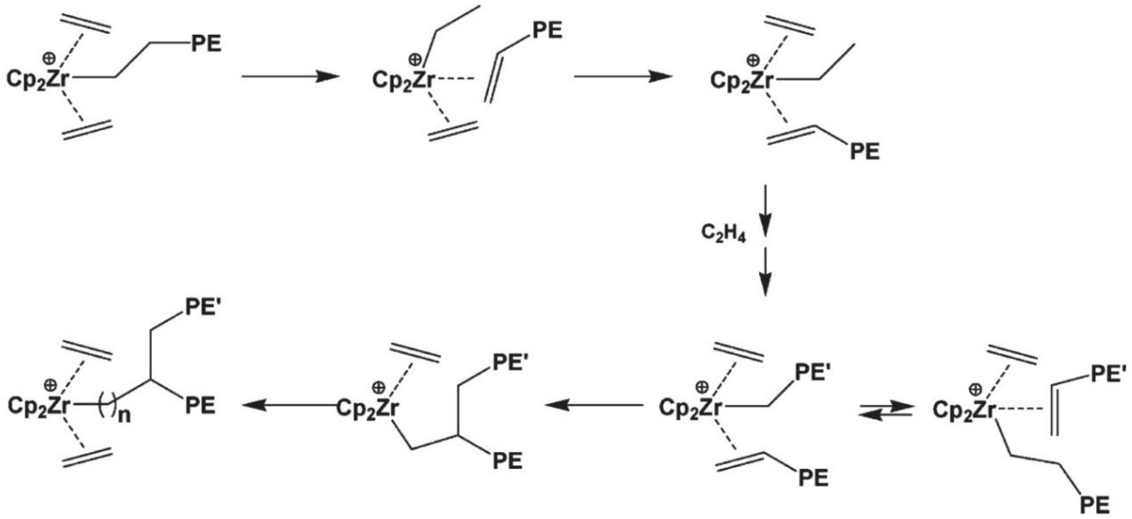

Figure 2-4.Reaction scheme of the intramolecular mechanism.[13]

2.3.4 Chain Walking Mechanism

The chain walking mechanism is the based on the assumption that the metal active site may move along the backbone of a living polymer chain, as displayed in Figure 2-5.

Soares and co-workers have argued against the chain walking mechanism as a formation pathway for LCBs as chain walking is a random process that can only lead to the formation of short chain branches.[29–31] Stadler and co-workers also concluded that such reaction is not likely to account for LCBs, especially during slurry polymerization, but may be possible in solution polymerization.[28]

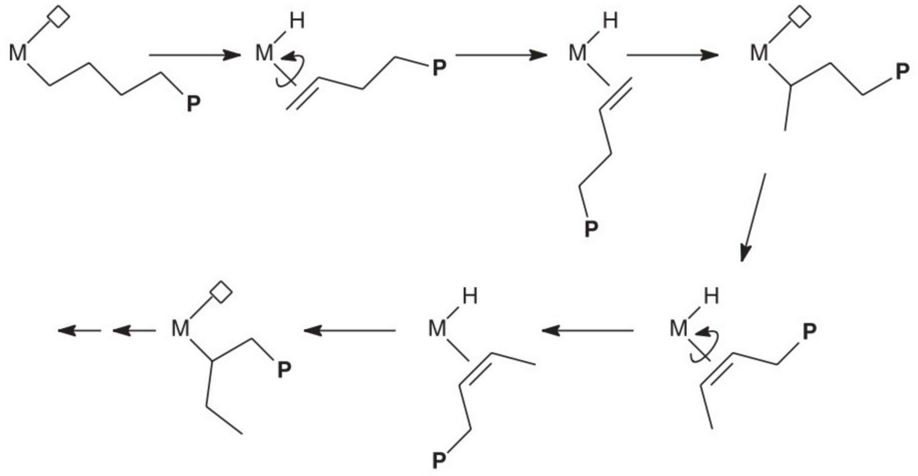

Figure 2-5. Chain walking reaction pathway.[11]

Chapter 3: Comparing Long Chain Branching Mechanisms in Semi-Batch Reactors using PREDICI®

3.1 Introduction

Most laboratory-scale ethylene polymerizations are conducted on semi-batch reactors, even though commercial processes use of continuous reactors. Semi-batch reactors are preferred for laboratory-scale experiments because they are easier and cheaper to run than continuous reactors, but the large-scale production of commodity polyethylenes can only be achieved with continuous reactors. Understanding how polymerization in semi-batch reactors is, therefore, essential to build realistic predictive models to tailor the properties of polyethylenes. In a semi-batch ethylene polymerization reactor set up, ethylene is fed on demand to keep a constant concentration in solution by compensating the reaction consumption. All other reagents/catalyst components are fed in batch mode at the beginning of the polymerization.

3.2 Objectives

The main objectives of the simulations described in the chapter are:

- To investigate the effect of ethylene pressure during semi-batch polymerization on molecular weight averages, polydispersity index, molecular weight distributions, and long chain branching of polyethylene made with the three mechanisms compared in this thesis: terminal branching, C-H activation, and intermolecular mechanism.

- To observe the long chain branching evolution with polymerization time and ethylene conversion.
- To compare the simulation results, when applicable to experimental data from literature in order to make meaningful conclusions regarding which mechanism is more likely to be responsible for the formation of LCB in polyethylene.

3.3 LCB Formation Mechanisms

In this section, we will list all elementary steps for the three LCB formation mechanisms that were used to build the simulation models.

3.3.1 Terminal Branching Mechanism

The main steps for the terminal branching mechanism are listed in Table 3-1: initiation, propagation, LCB formation, chain transfer, β-hydride elimination, and deactivation. In the initiation step, Equation (3.1), the monomer (M) coordinates to the active site (C) to make a living polymer chain ($P_{1,0}$) with a chain length of 1 and 0 LCB. This active species may propagate by monomer insertion in the metal-carbon bond on the active site, Equation (3.2), where r is the chain length and i is the number of LCBs. When a macromonomer, which is a dead chain with a terminal reactive double bond ($D^{=}_{q,j}$) of chain length q having j LCB, is inserted onto a living chain, a new LCB is formed, Equation (3.3). In the transfer step, Equation (3.4), a chain transfer agent (CTA) terminates polymer growth, producing a saturated dead chain ($D_{r,i}$) with chain length r and i LCBs, and an active species that can keep reacting with monomer. The abstraction of the hydrogen atom attached to the β carbon in the living polymer chain makes a macromonomer (that is, dead chain with a terminal double bond, $D^{=}_{r,i}$) of chain length *r* and *i* LCBs, and an active species, Equation (3.5). The last step in this mechanism, the spontaneous deactivation of catalyst or living chains, yield a dead catalyst site (DC), Equation (3.6), or a dead chain and a dead catalyst site, Equation (3.7).

Table 3-1. Terminal branching mechanistic steps.

Terminal Branching	
Initiation Reaction	
$C + M \overset{k_i}{\rightarrow} P_{1,0}$	(3.1)
Propagation	
$P_{r,i} + M \overset{k_P}{\rightarrow} P_{r+1,i}$	(3.2)
Long chain branching	
$P_{r,i} + D^{=}_{q,j} \xrightarrow{k_{LCB1}} P_{r+q,i+j+1}$	(3.3)
Chain transfer reactions	
$P_{r,i} + CTA \xrightarrow{k_{CTA}} D_{r,i} + P_{1,0}$	(3.4)
β-H Elimination	
$P_{r,i} \overset{k_\beta}{\rightarrow} D^{=}_{r,i} + P_{1,0}$	(3.5)
Deactivation Reactions	
$C \overset{k_d}{\rightarrow} DC$	(3.6)
$P_{r,i} \overset{k_d}{\rightarrow} D_{r,i} + DC$	(3.7)

3.3.2 C-H Activation Mechanism

All steps shown in Table 3-2 for the C-H activation mechanism are the same as the ones for terminal branching, with the exception of the LCB formation step. In the C-H activation mechanism, LCBs are formed in a step similar to transfer to polymer in free radical polymerization. These reactions may occur via intermolecular or intramolecular (similar to backbiting in free radical polymerization) pathways. The latter, however, will be ignored in this study, as it is more likely to form short chain branches, not LCBs. Long chain branches may be formed when the C-H bond of a dead chain (saturated, Equation (3.10), or unsaturated Equation (3.11)) is activated and coordinates with an active site, forming a dead chain, and producing a living chain in which the active site is randomly located along its backbone. Upon monomer propagation, a LCB will be formed.

Table 3-2. C-H activation mechanistic steps.

C-H Activation

Initiation Reaction

$$C + M \overset{k_i}{\rightarrow} P_{1,0} \tag{3.8}$$

Propagation

$$P_{r,i} + M \overset{k_P}{\rightarrow} P_{r+1,i} \tag{3.9}$$

Long chain branching

$$P_{r,i} + D_{q,j} \xrightarrow{k_{LCB2}} D_{r,i} + P_{q,j+1} \tag{3.10}$$

$$P_{r,i} + D_{q,j}^{=} \xrightarrow{k_{LCB3}} D_{r,i} + P_{q,j+1} \tag{3.11}$$

Chain transfer reactions

$$P_{r,i} + CTA \xrightarrow{k_{CTA}} D_{r,i} + P_{1,0} \tag{3.12}$$

β-H Elimination

$$P_{r,i} \overset{k_\beta}{\rightarrow} D_{r,i}^{=} + P_{1,0} \tag{3.13}$$

Deactivation Reactions

$$C \overset{k_d}{\rightarrow} DC \tag{3.14}$$

$$P_{r,i} \overset{k_d}{\rightarrow} D_{r,i} + DC \tag{3.15}$$

3.3.3 Intra-Molecular Branching Mechanism

The intramolecular mechanism is based on the assumption that an active site can coordinate to three species at the same time: the growing polymer chain, the propagating monomer, and the macromonomer. This mechanism assumes that the macromonomer may stay coordinated to the active site after being terminated, and may insert again at a later time, creating a LCB. This implies that every active site produces and incorporates its own macromonomers to form LCBs.[13,14] All the steps involved in this mechanism are shown in Table 3-3. Like the other two mechanisms, the first step is the initiation of the active site with a monomer. The next step is the trigger step, Equation (3.17), where a second monomer coordinates to the active site creating species $PM_{r,i}$ of chain length *r* and *i* LCBs.

In this mechanism, the transfer step, Equation (3.20), is essential because the terminated living chain (macromonomer) stays coordinated to the active site, leading to the species $PL_{1,0}.D_{r,i}$ which represents an active site that is coordinated to a monomer, hence, chain length of 1 and 0 LCB, and a vinyl-terminated coordinated dead chain (macromonomer) of chain length *r* and *i* LCB. This species can keep reacting with monomer in further propagation steps, but the LCB reaction happens when the coordinated dead chain inserts back into the living chain (3.21), creating species $P_{q+r,j+i+1}$, where q and r are chain lengths, and *i* and *j* are the number of LCBs in the chain. This species needs to be triggered to propagate again. Two other important reactions are the displacement of the coordinated dead chain by a monomer, Equation (3.22), or the spontaneous dissociation of that dead chain, Equation (3.23). The last three reactions, Equation (3.24) to Equation (3.26), are just normal monomolecular deactivation reactions.

Table 3-3. Intramolecular mechanism steps.

Intra-Molecular Branching	
Initiation Reaction	
$C + M \overset{k_i}{\rightarrow} P_{1,0}$	(3.16)
Trigger Reactions	
$P_{r,i} + M \xrightarrow{k_{mt}} PM_{r,i}$	(3.17)
Propagation	
$PM_{r,i} + M \overset{k_P}{\rightarrow} PM_{r+1,i}$	(3.18)
$PL_{q,j}.D_{r,i} + M \overset{k_P}{\rightarrow} PL_{q+1,j}.D_{r,i}$	(3.19)
Transfer Reaction	
$PM_{r,i} \xrightarrow{k_{BHT}} PL_{1,0}.D_{r,i}$	(3.20)
Long chain branching	
$PL_{q,j}.D_{r,i} \xrightarrow{k_{LCB4}} P_{q+r,j+i+1}$	(3.21)
Macromonomer Displacement	
$PL_{q,j}.D_{r,i} + M \xrightarrow{k_{mt}} PM_{q,j} + D_{r,i}$	(3.22)
Macromonomer Dissociation	
$PL_{q,j}.D_{r,i} \xrightarrow{k_{dis}} P_{q,j} + D_{r,i}$	(3.23)
Deactivation Reactions	
$C \overset{k_d}{\rightarrow} DC$	(3.24)
$PM_{r,i} \overset{k_d}{\rightarrow} D_{r,i} + DC$	(3.25)
$PL_{q,j}.D_{r,i} \overset{k_d}{\rightarrow} D_{q,j} + D_{r,i}$	(3.26)

3.4 Models Development

The commercial software PREDICI®11 was used for the simulations discussed in the subsequent sections. PREDICI can calculate the dynamic evolution of polymer MWD when the polymerization kinetics steps are specified using the Galerkin h-p method.[32]

The following assumptions have been made during model development:

1. The only chain transfer agents present in the reactor were ethylene and the co-catalyst.
2. The models were developed to simulate polymerization kinetics in a solution process in the absence of mass transfer limitations.
3. The values of most polymerization kinetic constants for the three mechanisms, as seen in Table 3-5, were derived from the terminal branching mechanism based on experiments reported by Mehdiabadi and Soares[7], except for some steps for which the constants were adjusted. For example, for the LCB formation step in the C-H activation mechanism, the constants were estimates to make a polymer with the same average LCB that would be predicted with the terminal branching mechanism at the same polymerization conditions. A similar approach was adopted for the intramolecular branching mechanism. These adjustments were needed to make meaningful comparisons among the three LCB formation mechanism.
4. The ethylene concentration in the semi-batch reactor was kept constant by feeding ethylene under the control of a PID feedback control loop that monitored the concentration evolution of ethylene in the solution where the reaction takes place. This approach was favored instead of forcing the rate of change of ethylene concentration to be zero, which sometimes lead numerical instabilities in PREDICI.

Table 3-4. Polymerization conditions for semi-batch simulations.

Parameter	Value
Polymerization Time (s)	900
Ethylene Concentration (mol/L)	0.400
Catalyst Concentration (mol/L)	1.0x10^{-6}
Co-catalyst Concentration (mol/L)	3.0x10^{-2}
Reaction Volume (L)	0.150
Temperature (°C)	120

Table 3-5. Rate constants for the three LCB formation mechanisms.

Rate Constant	TB	CH	IM
$\boldsymbol{k_i}$ (s^{-1})	5.0x10^4	5.0x10^4	5.0x10^4
$\boldsymbol{k_P}$ (L.mol^{-1}.s^{-1})	5.0x10^4	5.0x10^4	5.0x10^4
$\boldsymbol{k_{LCB1}}$ (L.mol^{-1}.s^{-1})	5.0x10^3	-	-
$\boldsymbol{k_{CTA}}$ (L.mol^{-1}.s^{-1})	7.0	7.0	7.0
$\boldsymbol{k_\beta}$ (s^{-1})	4.0	4.0	4.0
$\boldsymbol{k_d}$ (s^{-1})	3.6 x10^{-3}	3.6 x10^{-3}	3.6 x10^{-3}
$\boldsymbol{k_{LCB2}}$ (L.mol^{-1}.s^{-1})	-	1.7	-
$\boldsymbol{k_{LCB3}}$ (L.mol^{-1}.s^{-1})	-	1.7	-
$\boldsymbol{k_{LCB4}}$ (L.mol^{-1}.s^{-1})	-	-	5.0x10^4
$\boldsymbol{k_{mt}}$ (s^{-1})	-	-	5.0x10^4
$\boldsymbol{k_{BHT}}$ (L.mol^{-1}.s^{-1})	-	-	4.0
$\boldsymbol{k_{dis}}$ (s^{-1})	-	-	3.6 x10^{-3}

3.5 Results and Discussion

In the first part of this section, we will investigate the effect of changing ethylene concentration on the microstructure of polyethylene made with the three different LCB formation mechanism. In the second part, will focus on the evolution of LCB topology as a function of polymerization time and ethylene conversion.

3.5.1 Effect of Ethylene Concentration

Ethylene concentration is an experimental parameter that can be easily manipulated to track how it affects polymer molecular weight and long chain branching. The effect of changing Ethylene concentration from 0.1 to 1.0 mol/L with the three mechanisms, terminal branching (TB), C-H activation (CH), and the intramolecular branching (IM) on the polymer number average molecular weight (M_n), is shown in Figure 3-1. Not surprisingly, the M_n value increases with ethylene concentration for all mechanisms: higher ethylene concentration leads to higher polymerization rates, and since the transfer rate is not controlled by transfer to ethylene, M_n increases with ethylene concentration. Therefore, the effect of ethylene pressure on polymer M_n is not adequate to discriminate among the three branching models.

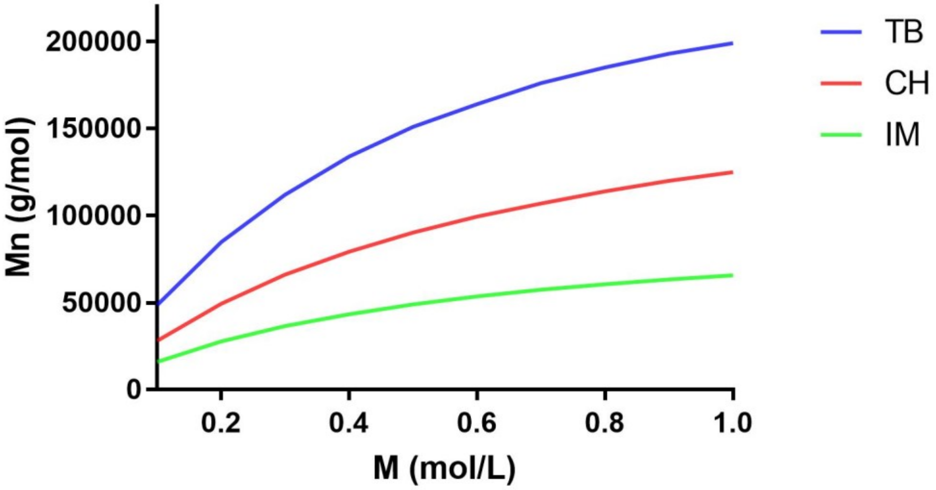

Figure 3-1. Effect of ethylene concentration on M_n.

Similarly, the weight average molecular weight (M_w) of polymer made with all mechanisms increases with ethylene concentration, as shown in Figure 3-2, but the rate of increase for the intramolecular mechanism is lower than for the other two mechanisms, because in the intramolecular mechanism the ethylene concentration affects both trigger steps described in Equations (3.17) and Equation (3.22).

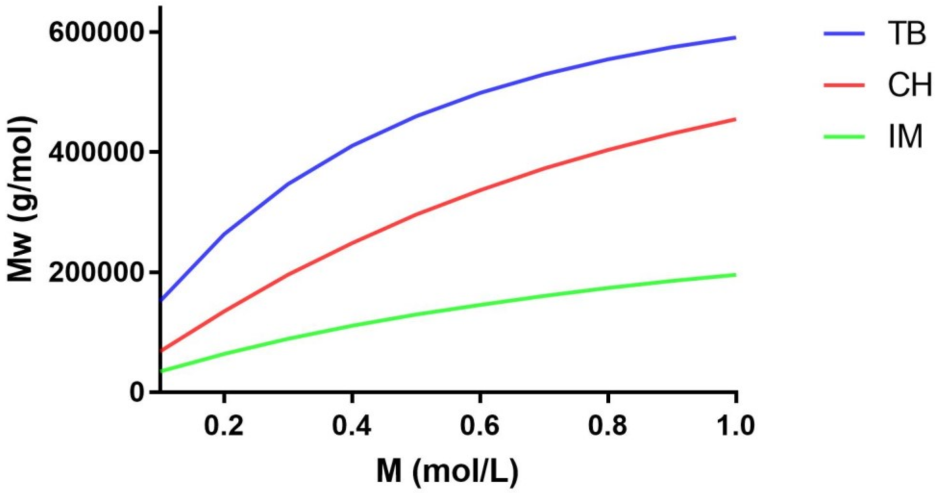

Figure 3-2. Effect of ethylene concentration on M_w.

An important difference among the three mechanisms can be seen in Figure 3-3, which shows the effect of the ethylene concentration on the polydispersity index (PDI = M_w/M_n). The value of PDI increases with ethylene concentration for the C-H activation and intramolecular mechanisms, whereas it decreases for terminal branching. For the terminal branching mechanism, the rate of LCB formation is higher at lower ethylene concentrations, since macromonomer and ethylene compete for insertion into the growing chain. As a consequence, M_w increases at a lower rate than M_n when ethylene concentration increases due to the lower rate of LCB formation, causing PDI to drop. For the C-H activation mechanism, LCB formation is independent of ethylene concentration; rather, when the ethylene concentration increases in the reactor, more polymer chains are made, and more C-H bonds become available for activation. This makes PDI increase with ethylene concentration. For the intramolecular mechanism, the PDI increases slightly, but this increase is uncorrelated to higher long chain branching in the polymer; instead, it is due to a competition among the rate of displacement, dissociation, and trigger (Equations (3.17), (3.22), and (3.23), respectively). When the concentration of ethylene increases, the concentration of the polymer population $P_{r,i}$ decreases, which lowers M_n slightly, leading to the observed increase in PDI.

These observations from the simulation results can be easily monitored experimentally, and could be used to differentiate the terminal branching mechanism from the C-H and intramolecular mechanism. Most data in literature cannot be directly correlated to our findings, as these studies did not systematically compare the PDI of polyethylenes made at different ethylene pressures/concentrations However, data in Table 3-6, reported by Kokko et al.,[4] describes the effect of changing ethylene pressure (which is directly correlated with the ethylene concentration in the reactor) on polyethylene PDI. These experimental findings show that decreasing ethylene pressure make the PDI of polyethylene to increase, which is in complete agreement with the reported simulation findings for the terminal branching mechanism. The increase observed in PDI is correlated to an increase in LCB frequency, as the next figures in this chapter illustrate.[4]

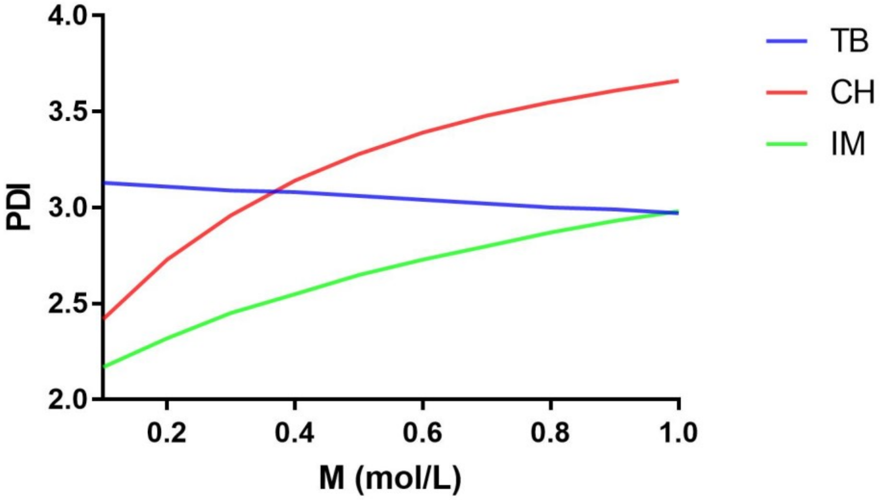

Figure 3-3. Effect of ethylene concentration on PDI.

Table 3-6. Experimental data on the effect of ethylene pressure and polymerization time on PDI, table was reproduced with permission.[4]

Ethylene Pressure (bar)	Polymerization Time (min)	PDI
5	10	1.9
5	25	1.9
3	10	2
1	10	2.2
1	20	2.4
0.5	25	2.8
0.25	30	3.2

Figure 3-4 shows how the LCB frequency varies with ethylene concentration in the reactor. For both terminal branching and intramolecular mechanisms, LCB decreases with increasing ethylene concentration, but it hardly depends on ethylene concentration for the C-H activation mechanism. This response can also be used to differentiate the C-H activation mechanism from the other two. Figure 3-5 shows how the LCB frequency varies as a function of ethylene concentration for two different metallocene catalysts, as reported by Jensen M et al.[14] These experimental results show that both terminal branching and intramolecular mechanisms can satisfy the observed trend, but not the C-H activation mechanism. More supporting evidence on the decrease of LCB at higher ethylene concentrations has been reported by Kokko et. al.,[4] Kolodka et al.,[33] and Soares and coworkers.[7]

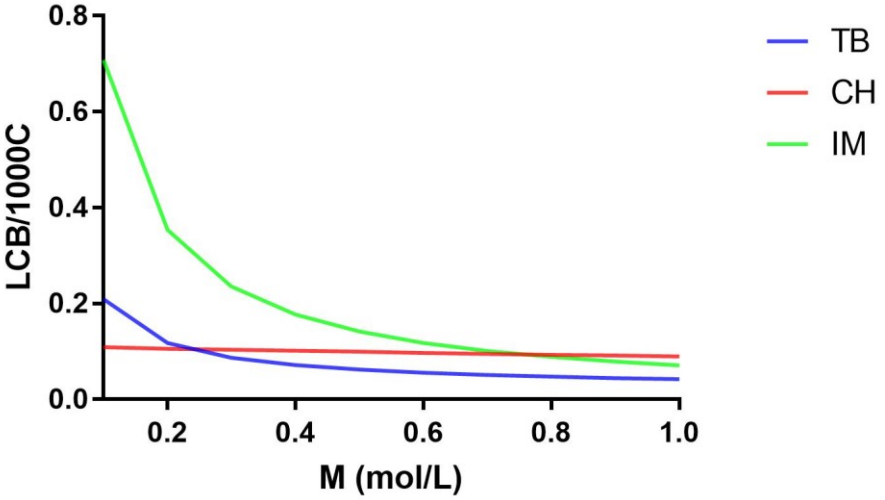

Figure 3-4. Effect of ethylene concentration on LCB/1000C.

The dependency of the average number of LCBs per chain on ethylene concentration for the three mechanisms is compared in Figure 3-6. In both terminal branching and intramolecular mechanisms, LCB/chain decreases at higher ethylene concentration, but the response is linear only for terminal branching. In the C-H activation mechanism, LCB/chain increases with ethylene concentration in the reactor, because higher ethylene concentrations produce more polymers, making more C-H bonds available for activation.

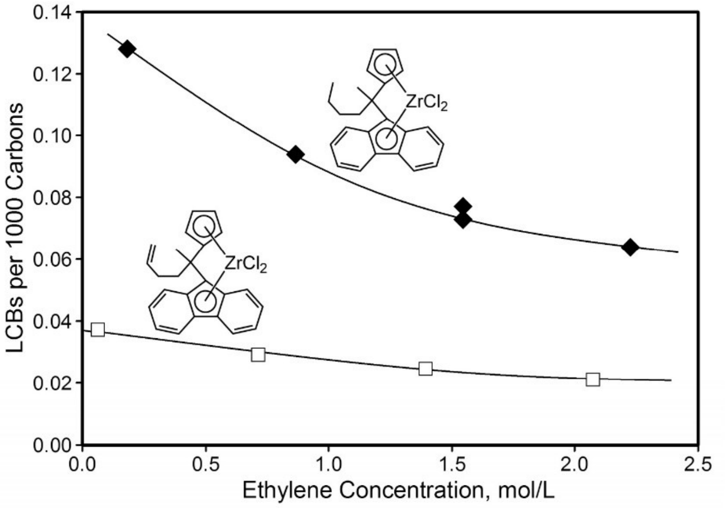

Figure 3-5. Experimental results showing the effect of ethylene concentration on LCB/1000 C.[14]

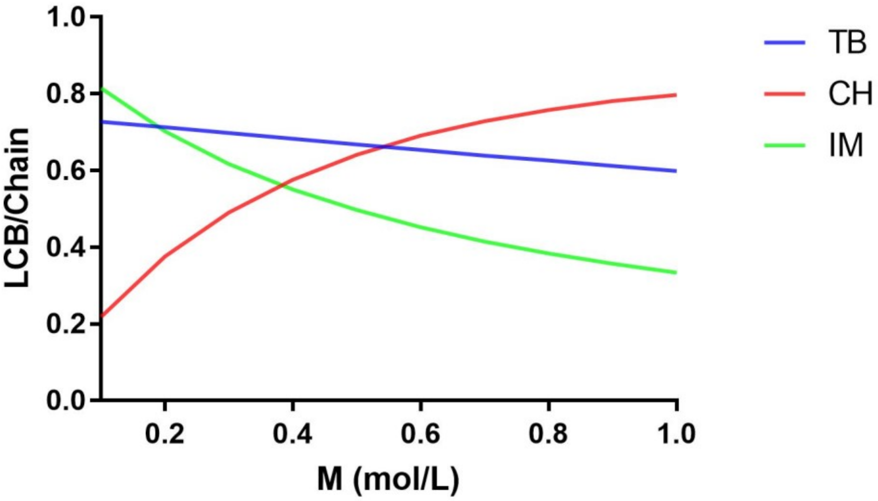

Figure 3-6. Effect of ethylene concentration on LCB/chain.

Figure 3-7 to Figure 3-9 show molecular weight distributions (MWD) for polyethylenes simulated with the three mechanisms at different ethylene concentrations: 0.1, 0.5, and 1.0 mol/L. Both terminal branching and intramolecular mechanisms make polyethylene with very similar MWDs. The MWDs of polymer simulated with the terminal branching mechanism get narrower and shift to higher molecular weight averages as ethylene concentration increases (Figure 3-7). For the intramolecular mechanism, however, MWDs shift to higher molecular weight averages, but also broaden very slightly (Figure 3-9). The reason for the slight MWD broadening, as explained above, is that the M_n responds to changes in ethylene concentration at a lower rate than M_w, due to the existence of many active species in the intramolecular mechanism, one of which, $P_{r,i}$, does not deactivate and is affected by the competitive reaction rates of trigger, macromonomer displacement, and dissociation. For the C-H activation mechanism, on the other hand (Figure 3-8), MWD broadens and shifts to higher averages significantly as the ethylene concentration increases. The quite noticeable broadening is due to the higher levels of LCB formation as the ethylene concentration is increased, causing more polymer chains to be formed, and more C-H bonds to become available for activation in the reactor. The increment of shift in the MWD for all mechanisms corresponds to the increment of change in ethylene concentration.

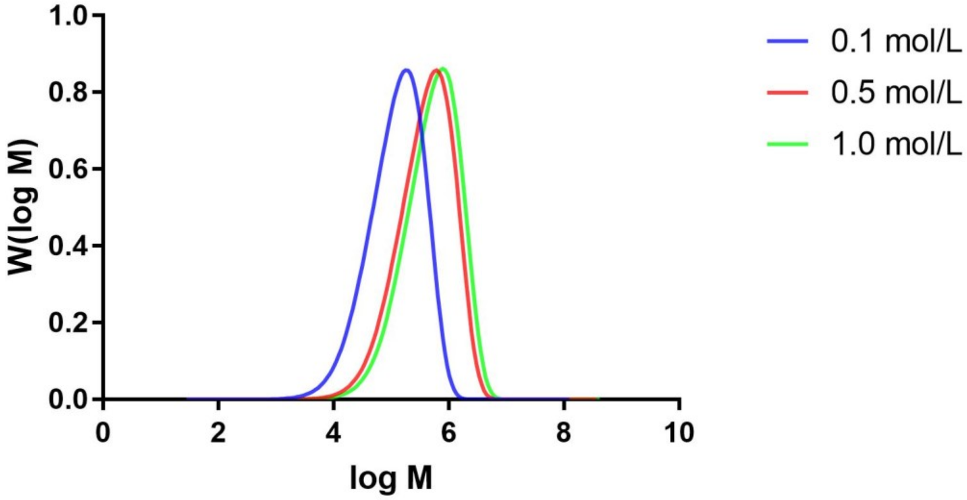

Figure 3-7. MWD for polyethylene simulated with the terminal branching mechanism at different 3 different ethylene concentrations.

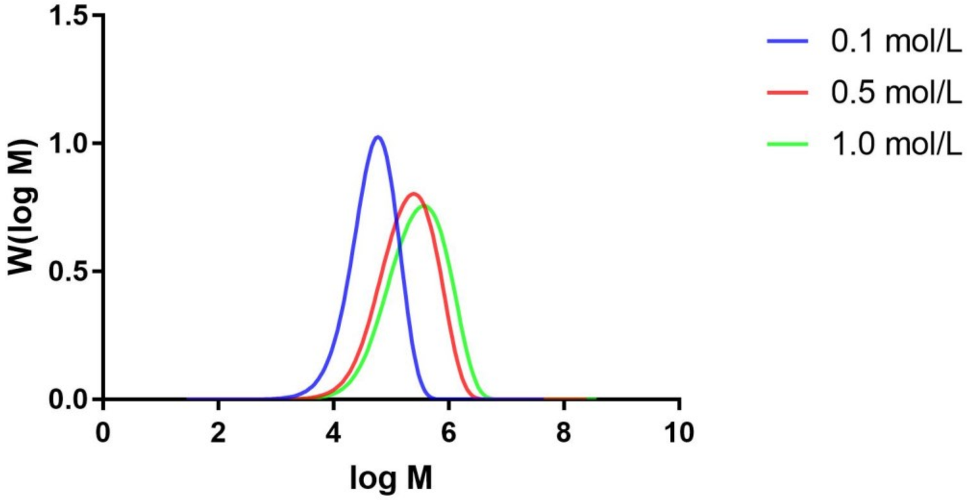

Figure 3-8. MWD for polyethylene simulated with the C-H activation mechanism at 3 different ethylene concentrations.

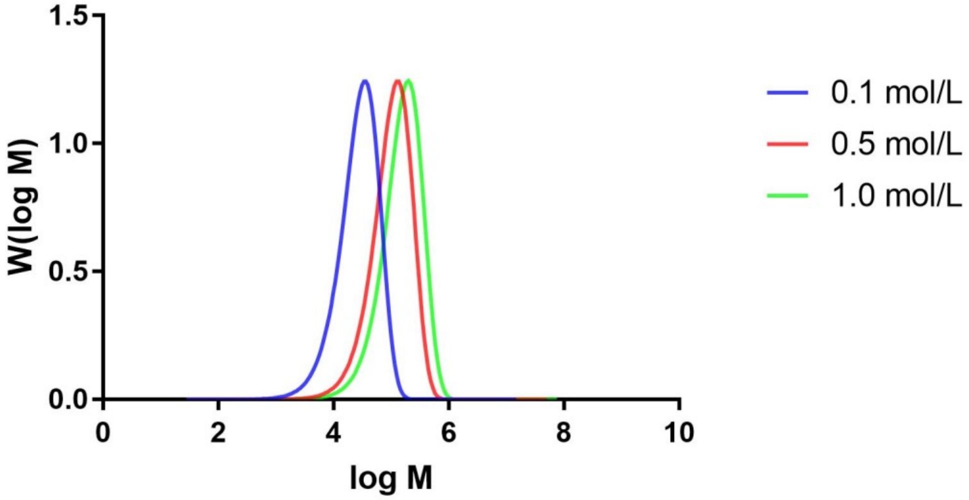

Figure 3-9. MWD for polyethylene made with the intramolecular mechanism at 3 different ethylene concentrations.

These simulations show that relating how M_n, M_w, PDI and LCB frequencies vary as a function of ethylene concentration (or pressure) in the reactor can be used to differentiate among the three studied LCB formation mechanisms. Based on the relatively scarce experimental results available in the literature, it seems that terminal branching is the most likely mechanism, followed by the intramolecular mechanism. The available experimental data does not support the C-H mechanism as a viable route for the formation of LCB in polyethylenes made with coordination catalysts.

3.5.2 LCB Evolution

Another important polymer parameter that can be experimentally traced in relation to the mechanisms investigated in this thesis is how the LCB frequency changes with polymerization time in a semi-batch reactor. It is the common understanding that to attain higher LCB levels, longer polymerization times are required. Some data in the literature support this conclusion:

for instance, Table 3-6 shows that for the same ethylene pressure, increasing polymerization time increases PDI, which is correlated to higher level of long chain branching.[4]

Figure 3-10 tracks the evolution of the LCB frequencies for polymers simulated with the three mechanisms. For the intramolecular mechanism, the LCB frequency reaches its highest value at the very beginning of the polymerization and remains practically constant for the rest of the polymerization. The other two mechanisms, however, predict that LCB frequencies will increase steadily as a function of polymerization time, as usually observed experimentally, at least for solution polymerizations.

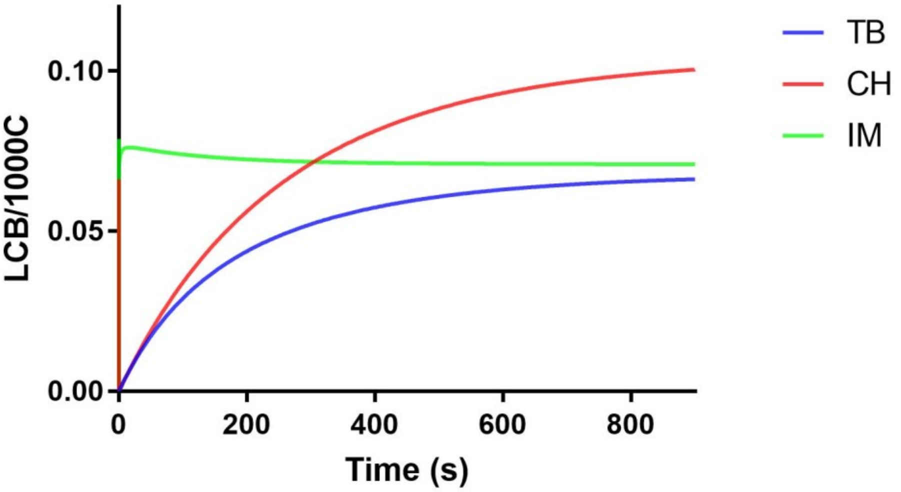

Figure 3-10. LCB/1000C evolution with polymerization time.

A similar response is seen for the LCB/chain plots in Figure *3-11*. To the best of our knowledge, no experimental evidence exists to support the behavior predicted by the intramolecular model (quick increase in LCB frequency followed by a near plateau value).

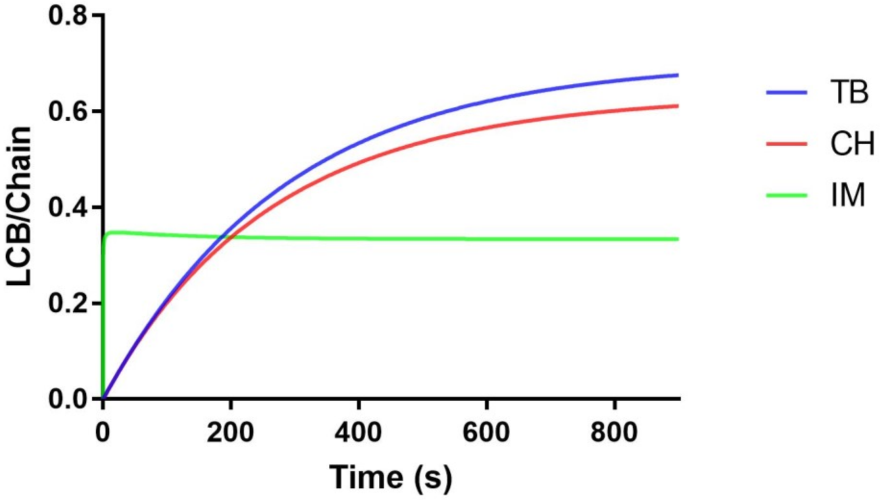

Figure 3-11. LCB/Chain evolution for the three mechanisms

Two other relevant simulation predictions are the dependencies of LCB frequency and average LCB per chain as a function of ethylene conversion, as shown in Figure 3-12 and Figure 3-13, respectively. Both terminal branching and C-H activation mechanisms predict that high conversions are required to make polymer with high long chain branching levels, with an exponential increase towards very high conversions. On the other hand, high levels of long chain branching are attained at very low conversions in the intermolecular mechanism. This is related to the high ethylene conversions mean high macromonomer/polymer and low ethylene concentrations, which both favour LCB formation via the terminal branching or C-H activation mechanisms, but have little influence on the intramolecular mechanism, since in the latter the rate of LCB formation only depends on the coordination of a locally terminated macromonomer, not on the overall concentrations of macromonomer/polymer or ethylene in the reactor.[27]

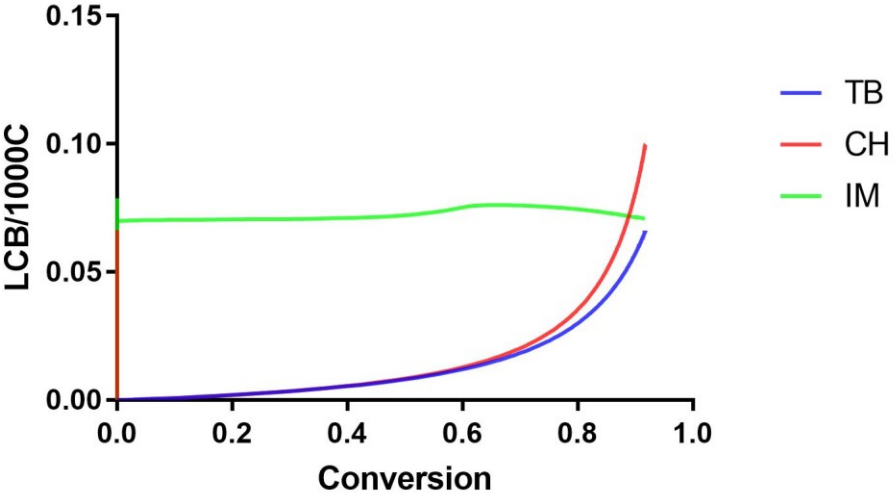

Figure 3-12. LCB/1000C as a function of ethylene conversion.

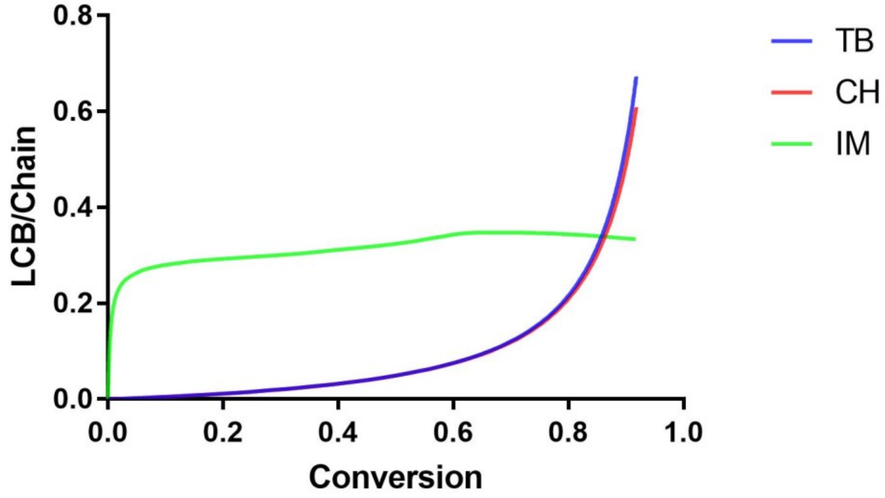

Figure 3-13. LCB/chain as a function of ethylene conversion.

Therefore, the analysis of long chain branching time/conversion evolution does not support the intramolecular mechanism as a viable LCB formation route for these polymerization systems.

3.6 Conclusions

This chapter investigated two main factors that affect LCB formation during ethylene polymerization with coordination catalysts: 1) ethylene pressure/concentration, and 2) polymerization time/ethylene conversion. Both variables are easy to be followed experimentally, and their effects on the polymer microstructure can be used to evaluate the likelihood of each of the three LCB-formation mechanism compared in this thesis.

As ethylene concentration in the reactor increases, lower LCB frequencies were predicted with both terminal branching and intramolecular mechanisms, whereas higher values were simulated with the C-H activation mechanism. These predictions were compared to experimental data from literature. Based on this comparison, the C-H activation mechanism can be ruled out as the pathway for LCB formation with coordination catalysts.

The intramolecular mechanism predicted that LCB levels should not depend significantly on polymerization time or ethylene conversion, in opposition to the terminal branching and C-H activation mechanisms which predict that LCB rises sharply for high polymerization times and ethylene conversions. Unfortunately, there are no systematic studies in the literature that specifically investigate this phenomenon, but it can be indirectly inferred from some of the results reported in literature that LCB increases with polymerization time/ethylene conversion for solution polymerizations of ethylene with coordination catalysts (no data is available for slurry or gas phase polymerizations).

Therefore, the semi-batch simulations with the three LCB-formation mechanisms seem to indicate that C-H activation mechanism is invalid, the intramolecular mechanism is a less likely alternative (at least for solution processes), but that the terminal branching mechanism is the most likely pathway for LCB formation in these systems.

Chapter 4: Comparing Long Chain Branching Mechanisms in a Continuous Stirred Tank Reactor using PREDICI®

4.1 Introduction

All commercial LCB polyethylenes made with coordination catalysts are produced in CSTRs operated at steady state. Therefore, it is important to compare the three proposed LCB formation mechanism under conditions that are close to those used in the industry. In this chapter, we will discuss the objectives, model development, and the results for the continuous polymerization system.

4.2 Objectives

There are mainly two objectives for the simulation models discussed this chapter:

- To investigate the effect of average residence time on polymer PDI and on average long chain branching per chain.

- To compare the polymer PDI dependence on long chain branching parameters with experimental data published in the literature.

4.3 Model Development

The models in this chapter simulate the behavior of polyethylene using the three different mechanisms in a CSTR. Catalyst, co-catalyst, and ethylene are fed constantly to the reactor. The residence time is controlled by the inlet stream flow rate. All the results reported in this chapter were obtained after the CSTR reached steady state. Process conditions are shown in Table 4-1.

Table 4-1. Polymerization conditions for CSTR simulations.

Parameter	Value
Average Residence Time (s)	1800
Ethylene Feed Concentration (mol/L)	0.400
Catalyst Feed Concentration (mol/L)	$1.0\text{x}10^{-6}$
Co-catalyst Feed Concentration (mol/L)	$3\text{x}10^{-3}$
Reaction Volume (L)	0.150
Temperature (°C)	120

The three LCB-formation models compared in the chapter were described in details in Chapter 3. The only difference between the simulations in this chapter is that the polymerizations were considered to take place in a continuous, not semi-batch, reactor. Isothermal, ideal CSTR (perfect mixing) behaviour was also assumed in all simulations.

For the second objective of this chapter, comparing how PDI varied with LCB levels for the simulated mechanisms and experimental data published in the literature, we have chosen reaction rate constants that are involved in the rate of formation of LCB as the manipulated variables. From the analytical solution for the LCB in the terminal branching mechanism by Soares and Mckenna[8], the following equations were derived:

$$\lambda = 500\frac{\alpha}{r_n} \qquad (4.1)$$

Where λ is the LCB frequency, α is lump of parameters that will be defined in the subsequent equation (4.3), and r_n is the number average chain length.

$$n_{LCB} = \frac{\alpha}{1-\alpha} \qquad (4.2)$$

where n_{LCB} is the average number of LCB per chain.

$$\alpha = \mu f \qquad (4.3)$$

f is the molar fraction of macromonomers in the reactor, and μ is defined in equation (4.4):

$$\mu = \frac{1}{1+\frac{s}{k_{LCB}Y_0}} \qquad (4.4)$$

Where s is the reciprocal of average residence time, k_{LCB} is the reaction rate constant of LCB, and Y_0 is the zeroth living polymer moment. Both LCB parameters in equations (4.1) and (4.2) are correlated to α which is directly correlated to PDI according to equation (4.5).

$$PDI = \frac{2}{1-\alpha} \qquad (4.5)$$

From the above equations for the terminal branching, we can see how many parameters can affect the relation between PDI and LCB parameters. We have chosen to manipulate the rate of LCB formation, equations (4.6) to (4.9) for the three mechanisms respectively, by changing the LCB reaction rate constant at the same ratio to the propagation constant for all the three mechanisms, as shown in Table 4-2.

The LCB formation rates (R_{LCB}) for the three mechanisms are described by the following equations:

$$R_{LCB1} = k_{LCB1}[D^{=}] \qquad (4.6)$$

$$R_{LCB2} = k_{LCB2}[D^{=}] * r \qquad (4.7)$$

$$R_{LCB3} = k_{LCB3}[D] * r \qquad (4.8)$$

$$R_{LCB4} = k_{LCB4}[PL_0 D] \qquad (4.9)$$

Where $D^{=}$ is the concentration of vinyl terminated dead chains, D is the concentration of saturated end dead chains, r is the chain length, and PL_0 is the zeroth moment of the population of the species that has a macromonomer coordinated to the active site. Varying the LCB reaction rate constants will vary the LCB levels leading to the observed effect on PDI that is correlated for the terminal branching by equations (4.1) to (4.5), whereas no analytical solution has been proposed for the other mechanisms.

Table 4-2. Predicted LCB-PDI dependency for terminal branching, C-H bond activation, and intermolecular incorporation

k_{LCB}/k_p	LCB/1000C			LCB/Chain			PDI		
	TB	**CH**	**IM**	**TB**	**CH**	**IM**	**TB**	**CH**	**IM**
0.2	0.069	0.022	0.000	0.199	0.057	0.000	2.398	2.120	2.000
0.4	0.137	0.109	0.097	0.365	0.285	0.488	2.730	2.793	2.082
0.6	0.240	0.218	0.216	0.568	0.569	0.649	3.135	4.582	2.109
0.8	0.343	0.324	0.374	0.731	0.844	0.733	3.460	10.984	2.124

4.4 Results and Discussion

Two main case studies were investigated in this chapter. Firstly, we discussed the effect of varying reactor residence time on the polymer PDI and average LCB per chain. In the second case study, we compared how PDI depended on LCB values using experimental data reported in literature.

4.4.1 Effect of Average Residence Time

Figure 4-1 shows the effect of changing the average reactor residence time from 1 800 to 3 600 seconds on the PDI of polyethylene simulated with the three mechanisms. The primary y-axis shows the response for the terminal branching and intramolecular mechanisms, whereas the C-H activation mechanism response is shown on the secondary y-axis because it predicted widely different values for PDI. PDI does not depend on the average reactor residence time for the intramolecular mechanism because the LCB formation reaction does not depend on conversion (or macromonomer concentration in the bulk phase of the reactor), only whether or not a macromonomer is associated with the active site (see Equation (3.21) in Table 3-1). For this mechanism, the main parameter that affects LCB formation is the transfer step that forms a macromonomer coordinated to the active site: the higher the transfer rate, the higher the probability of forming LCBs. Another important observation from Figure 4-1 is that PDI increases very fast with reactor residence time for the C-H activation mechanism, but no commercial substantially linear polyethylenes[1] have even been reported with such large PDI values.

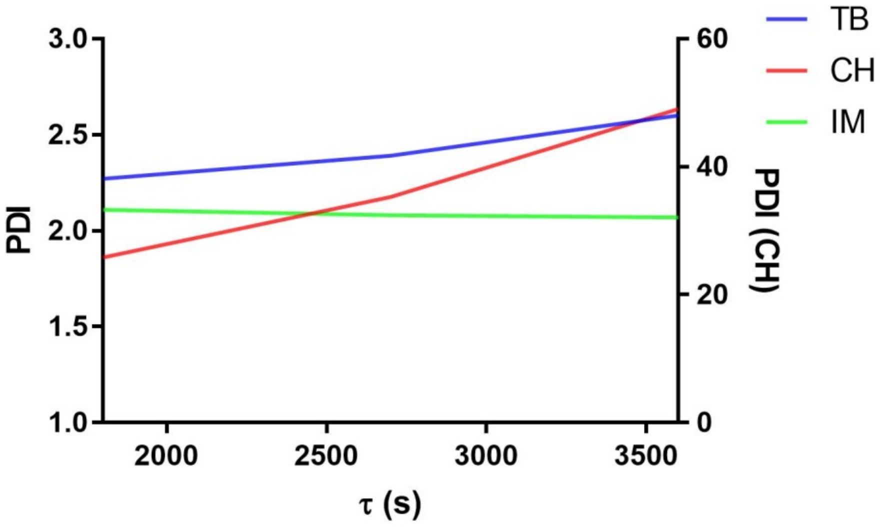

Figure 4-1. Effect of average reactor residence time on PDI.

The PDI responses shown in Figure 4-1 reflect changes in LCB/chain, depicted in Figure 4-2. For the intramolecular mechanism, LCB/chain is almost independent of the average reactor

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[1] Branched polyethylenes made with metallocene catalysts are called "substantially linear polyethylenes" to indicate that most of their polymer molecules are linear, that is, have no LCBs.

residence time, while for the C-H activation mechanism, the rate of increase is quite significant in comparison to the terminal branching mechanism.

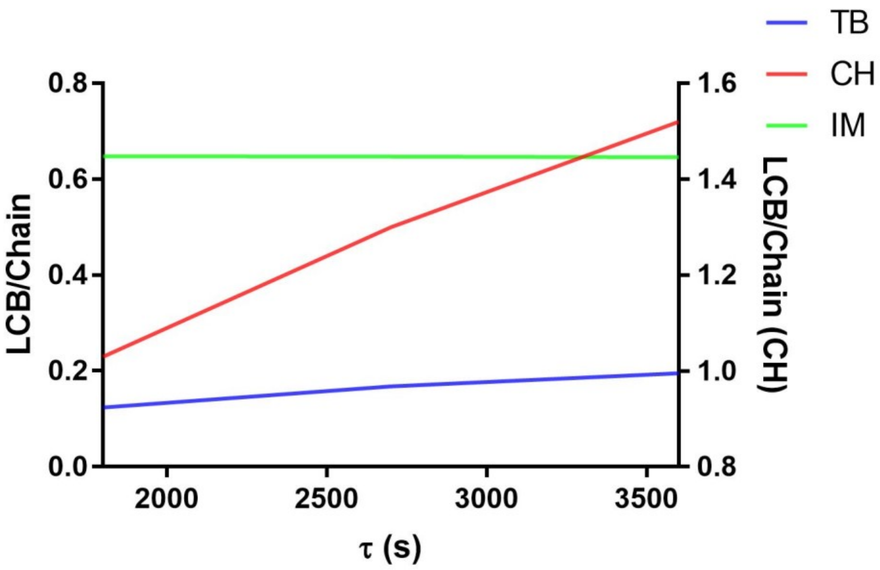

Figure 4-2. Effect of average reactor residence time on LCB/chain.

4.4.2 PDI dependence on LCB

In Chapter 3 we explained how PDI values were correlated to LCB frequencies: the higher the LCB frequency, the higher the PDI and the broader the MWD. In this section, we compared this correlation to experimental data reported by Soares and Mckenna[8], shown in Table 4-3, for polyethylenes made in a CSTR (solution polymerization) containing different LCB frequencies. Table 4-2 shows the varied parameter and the results illustrated in Figure 4-3 and Figure 4-4. Both LCB/1000 C and LCB/chain increase as the PDI increases. We have extracted similar data points from the simulations with the three LCB-formation mechanism to compare model predictions with experimental data.

Table 4-3. PDI dependence on LCB levels. The first two columns were reproduced from Polyolefin Reaction Engineering[8].

PDI	LCB/1000C	LCB/Chain
2.13	0.026	0.0671
2.20	0.037	0.0985
2.23	0.042	0.1160
2.45	0.080	0.2240
2.50	0.090	0.2030
2.80	0.190	0.3300
3.10	0.330	0.5320

Figure 4-3 shows that how PDI varies with LCB/1000C according to the three mechanisms in comparison with the experimental data. The terminal branching mechanism agrees with the data much better than the other two mechanisms. The C-H activation mechanism provides the worst comparison and can be easily ruled out as a significant mechanism for LCB formation for the assumed system. The intramolecular mechanism predicts the right trend, but the comparison is not as good as the terminal branching mechanism. One important observation is that the PDI dependence on LCB for the intramolecular mechanism is very small, that is, large LCB frequencies can be attained without changing the polymer PDI significantly. Similar conclusions can be drawn from Figure 4-4, showing the how LCB/chain is related to polymer PDI.

Table 4-4. LCB-PDI dependency data for all the mechanisms

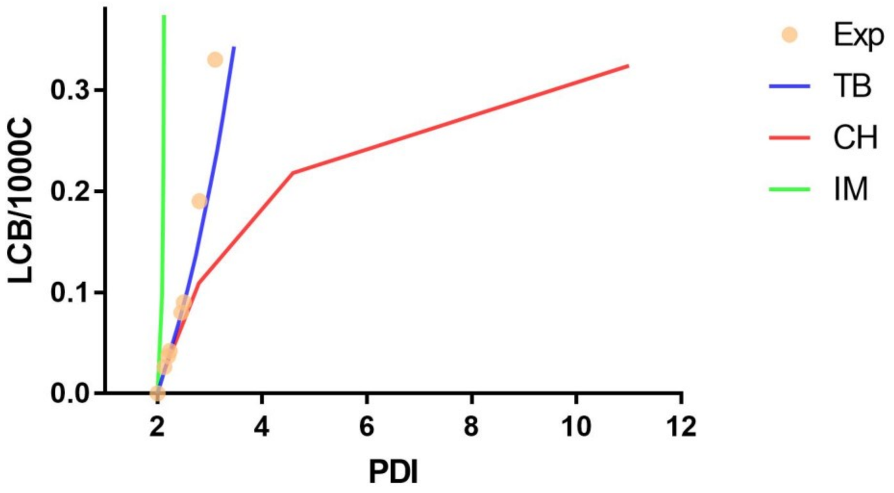

Figure 4-3. LCB/1000 C dependence on PDI: Comparison of experimental results with model predictions.

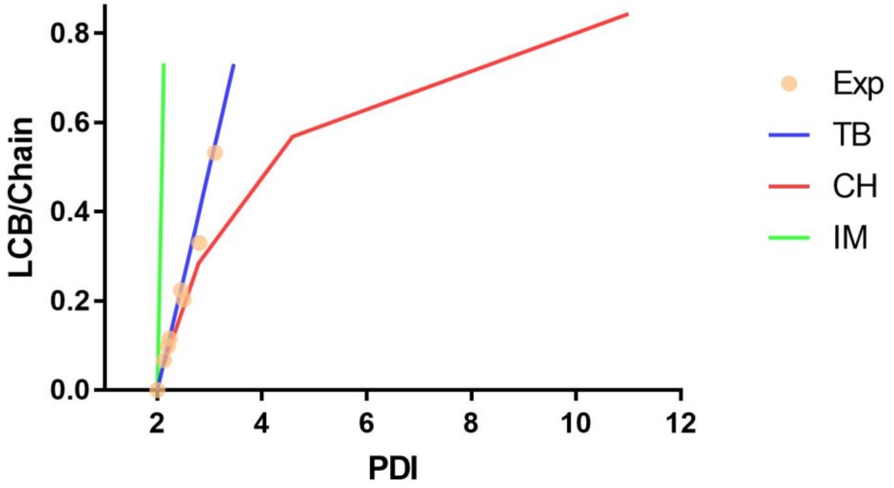

Figure 4-4. LCB/chain dependence on PDI: Comparison of experimental results with model predictions.

Therefore, even though all three mechanisms agree that LCB levels should increase with increasing polymer PDI, only the terminal branching mechanism could follow the experimental data adequately.

4.5 Conclusions

The simulations in this chapter show that increasing the average reactor residence time in a CSTR increases PDI drastically for the C-H activation mechanism to values that were never observed for substantially linear polyethylenes. This observation, in combination of those reported in Chapter 3, invalidate this mechanism of LCB formation for polyethylenes made with coordination catalysts.

The intramolecular mechanism predicts a correct trend between PDI and LCB frequencies, but the dependency of PDI of LCB is much smaller than that reported experimentally.

Finally, the terminal branching mechanism followed the experimental data for branched polyethylene made by solution polymerization with a coordination catalyst in a CSTR very well. Therefore, it seems to be the most adequate mechanism for LCB formation in this process.

Chapter 5: Conclusions and Future Work

Simulation models have been developed for LCB formation during ethylene polymerization with a coordination catalyst considering terminal branching, C-H activation, and intramolecular mechanism. The three models were used to investigate how polymerization conditions altered the microstructure of polyethylene made in semi-batch and continuous polymerization reactors. The main objective of the thesis was to discriminate between the three LCB-formation mechanisms by observing changes in polymer molecular structure upon variations in some selected polymerization conditions.

From the semi-batch simulation models, we have shown the effect of ethylene concentration on molecular weight averages, polydispersity index, molecular weight distributions, and long chain parameters. As ethylene concentration increases, lower LCB frequencies were predicted with both terminal branching and intramolecular mechanisms, whereas higher values were observed with the C-H activation mechanism. These results were compared to experimental data from literature. This comparison ruled out the C-H activation mechanism as the pathway for LCB formation in this system.

Additionally, we have presented simulation results on how LCB frequencies evolved with time and conversion during polymerization. The important highlight was that the intramolecular mechanism showed no significant dependence on polymerization time or ethylene conversion, in opposition to the trends predicted by the other two mechanisms that required higher polymerization times/ethylene conversions to reach higher LCB frequencies.

We have also shown that an important discriminating factor among these three mechanisms is the LCB frequency dependence on PDI for polymers made in a CSTR at steady state. The terminal branching mechanism provided the best comparison to the available experimental data, while the C-H activation did not follow the experimental trend. The intramolecular mechanism did not follow the data adequately either.

In conclusion, at least for the solution polymerization of ethylene with a single-site metallocene catalyst, the simulations clearly indicate that the terminal branching mechanism is the best option to describe the LCB formation process.

This thesis focused on comparing different LCB-formation mechanisms to find insights about the studied system, and relied on the scarce publish data to make conclusions regarding the most likely pathway to LCB generation. Systematic experimental designs to support our findings would be the logical second step. Below find our recommendations for future work in this area of research:

- Perform ethylene solution polymerizations in a semi-batch reactor where the only changing variable is polymerization time, and measure how LCB frequencies, M_n, and PDI vary as a function of time.
- Test the same catalyst under different processes conditions (solution, slurry, and gas phase) and observe how polymerization time and conditions affects LCB frequencies, M_n, and PDI.
- Control macromonomer diffusion rates during polymerization by changing the viscosity of the polymerization medium by changing the polymerization solvent. This would help understand the effect (if any) of micro-mixing effects on LCB formation.

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