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Polymerization of 1-hexene using α-diimine nickel catalysts: Stochastic simulation of branch distribution

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Abstract

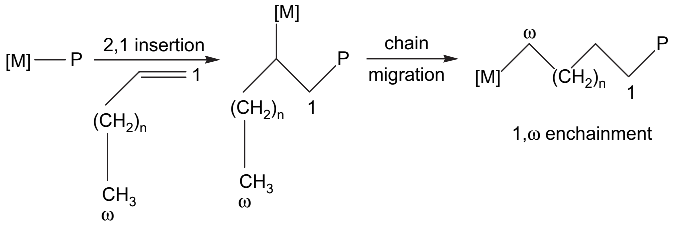
This work presents a new stochastic model to simulate the chain-walking mechanism during the polymerization of 1-hexene with α-diimine nickel catalysts based on the kinetic mechanism and branching data provided in the literature. Poly(1-hexene)s produced present short-chain branches such as methyl and butyl as well as longer chain branches showing very good agreement with the experimental branching data available. The new stochastic model is capable to cope with regioselective insertions of α-olefins and typical occurrence of 1,ω enchainment leading to the formation of longer chain branches and allows the calculation of molar mass and branching distributions. Another important result is that model simulations were able to unveil deficiencies for the kinetic mechanism to accurately predict the branching distribution at low temperatures. It is also shown that model probabilities may be interpreted in kinetic terms and properly correlated to the reaction polymerization temperature.

Keywords: 1-Hexene; Nickel catalyst; Stochastic modeling

1. Introduction

α-Diimine nickel and palladium catalysts produce poly(α-olefin)s with structural properties very different from those of polymers obtained with conventional Ziegler–Natta or metallocene catalysts [1]. For example, polypropylenes obtained with α-diimine palladium catalysts present amorphous and elastomeric structures characteristic of rubbers obtained by copolymerization of ethylene and propylene [2,3].

Polypropylenes produced with α-diimine nickel catalysts have fewer methyl branches than those obtained with conventional catalysts [2,4]. This reduction can be explained through 2,1 α-olefin insertion and, after migration of the active site to the terminal carbon (ω), there may be subsequent insertions resulting in a phenomenon called 1,ω enchainment of α-olefins [2], as shown in Scheme 1. The motion of the active site [M], also shown in Scheme 1, is referred to as chain-walking. This phenomenon, which occurs when β-hydrogen elimination takes place instead of monomer addition [5], explains the appearance of unbranched segments in these polymers, resulting in crystalline domains. Increase in the length of these unbranched segments result in larger melt transition temperatures in these semicrystalline polymers [5].



Scheme 1. Illustration of the chain-walking mechanism in α-olefin polymerization.

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Many articles discuss the influence of variables such as temperature, pressure, monomer concentration, and catalyst structure on polymerization using α-diimine Ni(II) [6–8] catalysts. In spite of the large interest in these catalysts, few articles propose and validate kinetic models. The first models proposed to predict branch distribution in polymers synthesized using α-diimine Ni(II) catalysts were based on stochastic simulations [9]. These simulations used random numbers to decide about the outcome of the steps postulated for the kinetic mechanism of the system under study. The first model developed to simulate the chain-walking mechanism described ethylene polymerization using α-diimine Ni(II) catalysts [9]. The model used five parameters related to the probability of events in the chain-walking mechanism, such as β-hydrogen elimination, isomerization (hydrogen re-insertion in the polymer chain with opposite regiochemistry), forward chain-walking, preferential appearance of methyl groups, and chain transfer. This stochastic model provided a good description of the experimental data. In order to expand the predictive capabilities of the model, the parameters were later written as functions of monomer concentration and temperature using empirical correlations [8]. A stochastic model was also proposed to simulate the formation of branched polyethylenes with the α-diimine Pd(II) catalyst, and the conformational properties of these polymers were predicted by molecular simulation [10]. Other methods have been used to model polymer microstructures, such as population balances, and describe branching distributions in these polymers [11].

Poly(1-hexene)s have been obtained from α-diimine Ni(II) and other related catalytic systems [12–16]. Subramanyam et al. [12] have been the first to report a detailed experimental study on this system and propose a mechanistic kinetic explanation for the polymerization. ^{13}C NMR spectra of poly(1-hexene) samples obtained by Subramanyam et al. [12] presented several structures, such as methyl, butyl, and longer chain branches whereas formation of ethyl and propyl branches were not observed. Besides, complete 1,6 enchainment due to chain-walking was found to be responsible for the formation of runs of methylene units in the polymer backbone.

This work presents a new stochastic model to simulate the chain-walking mechanism in the homopolymerization of 1-hexene with an α-diimine nickel catalyst/MAO (methylaluminumoxane) system, as used by Subramanyam et al. [12]. In 1-hexene polymerization, the active site is assumed to be a cationic ligand of type α-diimine Ni(II), which is connected to a 1-hexene molecule and to a growing chain. Unlike ethylene polymerization using the same catalytic system, 1-hexene insertions alone are capable of promoting not only chain growth but also the formation of branches. The new stochastic model is capable to cope with regioselective insertions of α-olefins and allows the calculation of molar mass and branching distributions. It is shown that model predictions present very good agreement with the experimental branching data available and that model simulations were able to unveil deficiencies for the kinetic mechanism to accurately predict the branching distribution at low temperatures. It is also shown that model probabilities may be interpreted in kinetic terms and properly correlated to the reaction polymerization temperature.

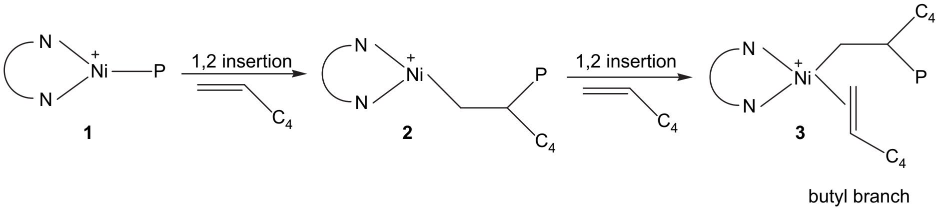
This article is organized as follows. The Section 2 describes the kinetic mechanism proposed in the literature [12] for the polymerization of 1-hexene, which explains the formation of the typical branches in poly(1-hexene)s obtained with the α-diimine Ni(II) catalyst. Then, the Section 3 presents the stochastic polymerization model along with a detailed explanation of it's probabilistic parameters as well as the polymerization rules adopted. The Section 4 presents a comparison between experimental and calculated branching data provided for model validation. A sensitivity analysis is also performed in order to allow for a full evaluation of the model parameters upon the branching distributions. Besides, this section also provides a kinetic interpretation of the temperature dependency of model parameters with the polymerization temperature. This article ends with the Section 5 where the main contributions of this research are presented.

2. Polymerization kinetic mechanism

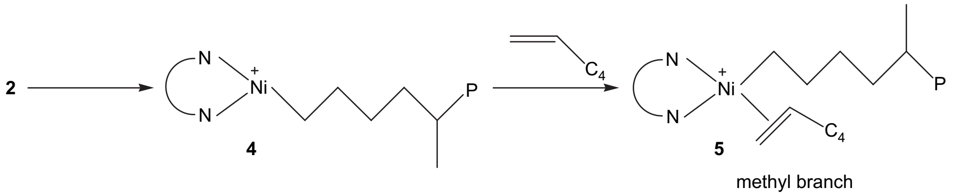
A detailed study of the microstructure of poly(1-hexene)s obtained using the α-diimine Ni(II) catalyst has been recently reported [12]. This polymer has several structures, such as methyl, butyl, and longer chain branches, which can be explained by several polymerization rules, as will be described here. Although the kinetic mechanisms of the catalytic system investigated in this work have been already reported and discussed in the literature [12], they are presented here for the sake of completeness and to provide a sound basis for the model development and analysis.

2.1. Butyl branches

Butyl branches form when 1,2 insertion of 1-hexene takes place between the nickel–carbon bond in species **1**, resulting in species **2**, as shown in Scheme 2. Another 1,2 insertion in



Scheme 2. Formation of butyl branches.



Scheme 3. Formation of methyl branches.

species **2** leads to species **3**, forming a butyl branch in the chain.

2.2. Isolated methyl branches

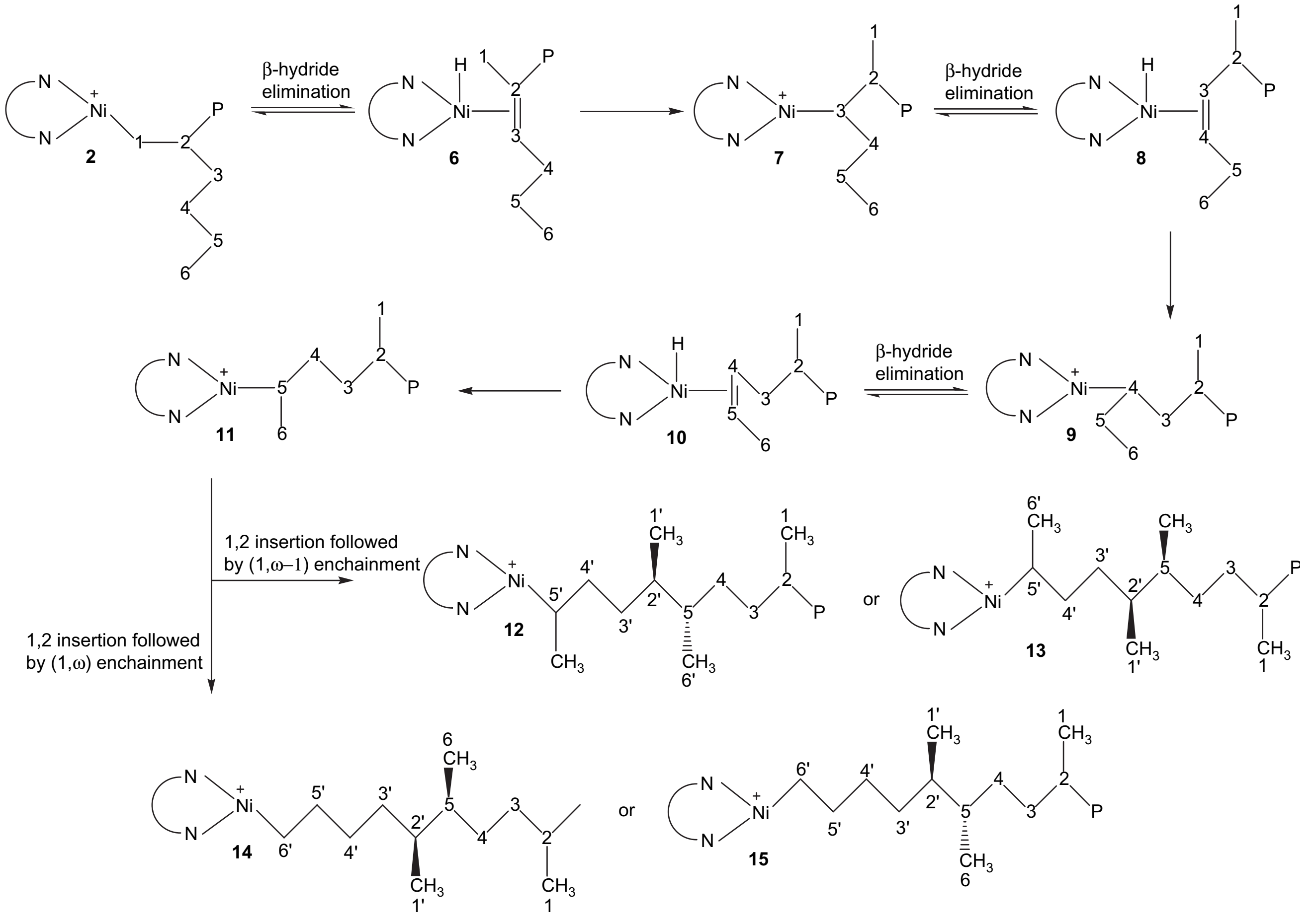
Isolated methyl branches appear when the active site of species **2** moves to the terminal carbon atom (ω) resulting in species **4**, as shown in Scheme 3. Subsequent insertions of 1-hexene introduce methyl branches in the growing chain.

2.3. Adjacent methyl branches

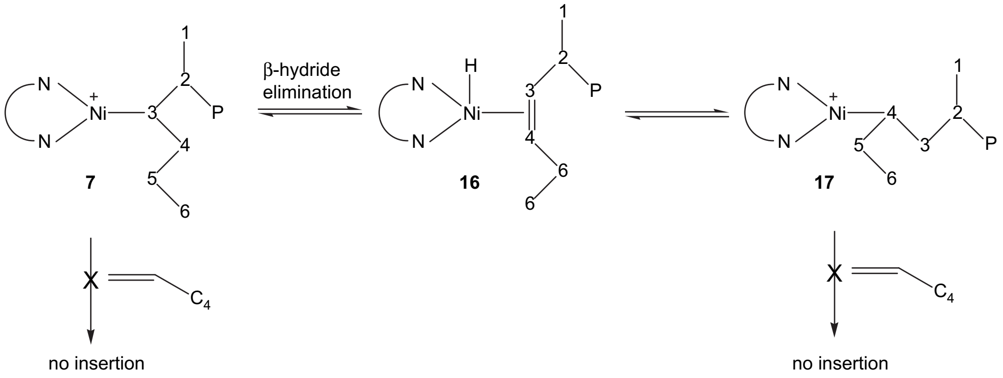
The appearance of adjacent methyl branches is explained according to Scheme 4. It is shown that the formation of species **12–15** is supposed to appear according to the following sequence:

i an insertion of type 1,2 (species **2**);
ii migration of the active site to carbon (ω-1) with formation of species **11**;
iii in species **11** 1,2 insertion of 1-hexene results either in species **12** and **13** when followed by (1,ω-1) enchainment, or species **14** and **15** when followed by (1,ω) enchainment.

The formation of adjacent methyl branches is possible only when 1,2 insertion of 1-hexene takes place and the catalytic site is located in secondary carbon atoms. It is intriguing that ethyl and propyl branches have not been observed experimentally as the migration of the active site along the chain may reach (ω-2) and (ω-3) carbons. However, ^{13}C NMR observations of Subramanyam et al. [12] indicate that whenever the metal is located at positions (ω-2) and (ω-3), it prefers to migrate rather than to insert another monomer unit, as shown



Scheme 4. Formation of adjacent methyl branches.



Scheme 5. Monomer insertion at nickel–adjacent carbon.

in Scheme 5. Subramanyam et al. [12] points out that positions 1, (ω-2) and (ω-3) are stable enough to allow monomer insertion, as opposed to positions (ω-2) and (ω-3). This behavior was also observed for the polymerization of 1-octene, 1-decene and 1-tetradecene, using the same catalyst as with 1-hexene [12]. However, a detailed investigation of this topic is still missing and, for this reason, formation of ethyl and propyl branches are prohibited in the kinetic mechanism.

2.4. Longer chain branches

Starting from species **4**, shown in Scheme 3, species **18** is formed after an 2,1 insertion, and the active site migrates and forms species **19**, thereby forming a longer chain branch, C_{10}. Repetition of this process causes the formation of branches longer than C_{10}, as shown in Scheme 6.

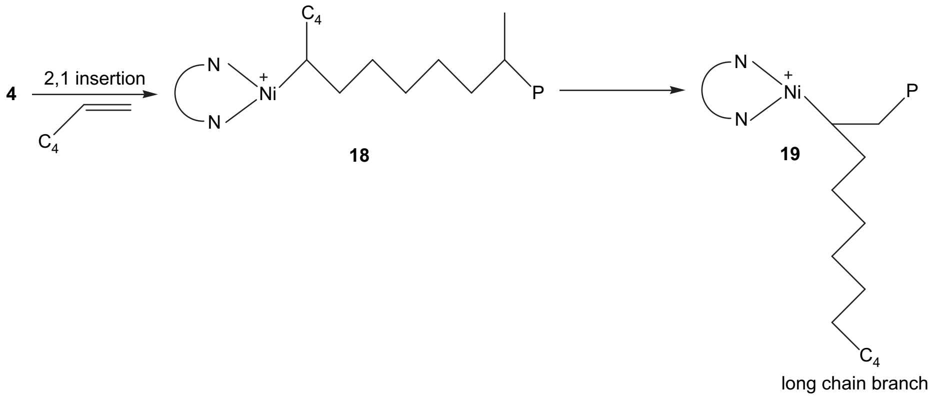
3. Model and simulation techniques

A new stochastic model was developed to simulate the distribution of branches in polymers obtained during the polymerization of 1-hexene with the α-diimine Ni(II) catalyst, based on the use of probabilistic parameters, as previously performed in order to describe the homopolymerization of ethylene [9]. The new stochastic model differs from previous models of polymerization through chain-walking mechanisms as it is capable to cope with regioselective insertions of α-olefins and typical occurrence of 1,ω enchainment leading to the formation of longer chain branches.

The stochastic model has five parameters, namely: r_n (average number of insertions); P_β (probability of transfer); P_i (isomerization probability); P_f (probability of forward walking); P_{12} (probability of 1,2 insertion).

Parameter r_n is not directly related to the chain length of the polymer but it only regulates the maximum number of insertions allowed for the chains, i.e., parameter r_n is related to the chain molar mass. Parameter r_n affects the polymer molar mass but not the branching distribution, as the probability of branching formation is very much affected by other stochastic parameters.

Parameter P_β is the probability of β-hydrogen elimination from the active site [7]. This parameter does not increase the number of branches as in ethylene polymerization [9] but, combined with parameters P_i and P_f, promotes the mechanism of chain-walking. This mechanism requires an isomerization step without chain transfer [8]. Parameter P_i represents this step. Parameter P_f is the probability that an active site moves from the chain end to an internal position. A new parameter, P_{12}, determines whether monomer insertions are of the type 1,2 or 2,1 [17], and it's effect on branch distribution is critical. The probability of chain termination, P_t, was obtained from parameter r_n [9]:



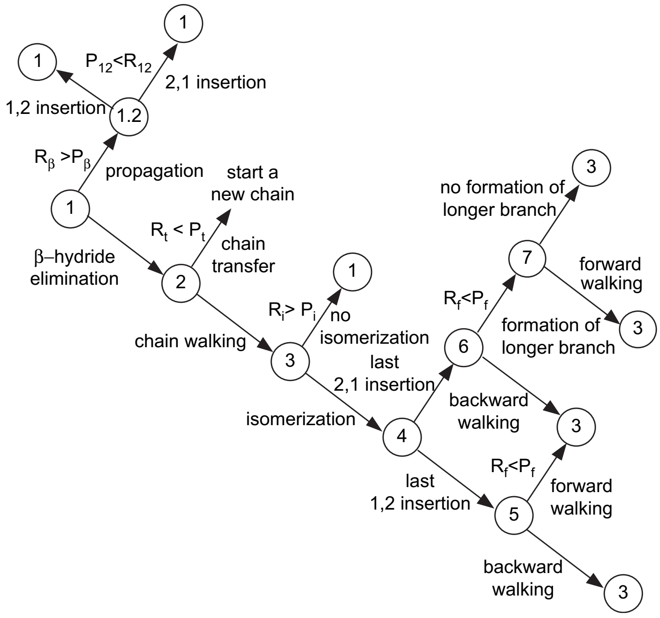
Scheme 6. Formation of longer chain branches.

$$P_t = \frac{1}{P_\beta r_n} \qquad (1)$$

Scheme 7 shows a simplified flowchart that describes the model to simulate the mechanism of 1-hexene homopolymerization with the α-diimine Ni(II) catalyst. The procedure uses random numbers with uniform distribution between 0 and 1 to decide between two options at each step of the kinetic mechanism, by comparison with the corresponding probabilistic parameter of the model. A L'Ecuyer random number generator of long period ($>2 \times 10^{18}$) with shuffling was used [18]. In the discussion that follows, we denote these random numbers by R with a subscript that identifies the step in which they were drawn.

If $R_\beta > P_\beta$, a monomer is inserted, and the insertion type is chosen by comparison of parameter P_{12} with a new random number. If $R_{12} \le P_{12}$, monomer insertion will be of type 1,2; otherwise, the insertion will be of type 2,1.

If $R_\beta \le P_\beta$, the step of β-hydrogen elimination begins and a new random number is generated in order to decide between the next two steps. If $R_t \le P_t$, growth of the polymer chain terminates and all information about it's microstructure is stored; a new chain then begins, until the specified total number of chains is generated. If $R_t > P_t$, the chain-walking mechanism may occur. To start this mechanism, it is necessary to overcome the isomerization barrier. A new random number is generated to test the isomerization probability. If $R_i > P_i$, isomerization will not occur and the procedure returns to the step in which it decides about monomer insertion; otherwise, the active site can move either forward or backward. However, before taking this decision, it is necessary to verify whether the last insertion was either 1,2 or 2,1. If it was of type 2,1, a new random number is generated and compared with parameter P_f. If $R_f < P_f$, the chain may be about to form longer chain branches and, if there is space in the chain, the active site moves one position forward. In this case, the active site should be located in the first carbon atom or between this atom and the first tertiary carbon atom that links chain P to the methyl group, as shown in Scheme 6. If site M is on the tertiary carbon and moves forward, it would occupy a methyl position and not the carbon atoms that belonged to part P in the chain (Scheme 6). If $R_f \ge P_f$, the active site moves back one carbon atom, i.e., the site should be located on the methyl group or between the methyl group and the first carbon atom in the chain.



Scheme 7. Simplified flowchart of the stochastic procedure developed to simulate 1-hexene polymerization.

If the previous insertion was of type 2,1 and formation of longer chain branches was not possible (i.e., the kinetic sequence 1,2 insertion, chain-walking to carbon ω, and 2,1 insertion did not occur), then the active site was not allowed to move forward after the 2,1 insertion. This restriction was used to facilitate the chain-walking mechanism and to prevent violation of the mechanisms suggested into literature [12] for branch formation. If the previous insertion was of type 1,2, the direction of the active site movement is tested; if $R_f < P_f$, the active site moves forward if there is space, i.e., the active site should be located at the first carbon atom or between this atom and carbon ω. Scheme 4 illustrates the active site motion in the transformations from species **2** to **11**. Otherwise, the active site moves back one carbon atom. In this case, the active site should be located in carbon ω or in any carbon atom other than the first one in the chain (Scheme 4).

For model validation, probabilistic parameters were determined by trial and error for a good match with experimental data. This stochastic algorithm to simulate 1-hexene polymerization was implemented in Fortran 90. The simulations were executed in a personal computer with an Intel 32-bit Pentium IV processor, 2.0 GHz, and 256 MB of RAM. For each simulation 1×10^6 poly(1-hexene)s chains were generated. Branch distributions were calculated by dividing the individual number of branches (INB) by the total number of branches (TNB) for all generated chains, i.e., the summation is performed over all generated chains. In all simulations reported in the next section, parameter r_n was set equal to 5000.

4. Results and discussion

4.1. Stochastic model validation

Table 1 compares experimental values of branch distributions with model predictions, in terms of the ratio of the individual number of branches of a given type and the total number of branches in the generated chains (i.e., in a number percent basis), as reported experimentally [12], using the parameters reported in Table 2. At some temperatures, the branching data found in the literature provided relative amounts of branches whose summation did not equal 100% due to the ^{13}C NMR calculation procedures used. Therefore, in order to compare experimental and simulated data appropriately, experimental branching data were normalized to sum 100% at all temperatures.

Table 1
Branch distribution in poly(1-hexene)s produced with the α-diimine Ni(II) catalyst and experimental ^{13}C NMR data [12] ((INB/TNB) × 100%)

Type of branch	^{13}C NMR	Simulation	^{13}C NMR	Simulation
	Experiment 1 ($T = 70$ °C)		Experiment 2 ($T = 60$ °C)	
Methyl	78.4	80.3	78.4	80.3
Butyl	13.7	12.5	14.7	12.5
Hexyl+	7.8	7.1	6.9	7.1
	Experiment 3 ($T = 35$ °C)		Experiment 4 ($T = 5$ °C)	
Methyl	73	73.6	38.2	41.1
Butyl	21	20.0	58.8	58.5
Hexyl+	6	6.3	2.9	0.4
	Experiment 5 ($T = -7$ °C)			
Methyl	33.7	34.8		
Butyl	64.3	65.1		
Hexyl+	1.9	0.2		

At high temperatures, the stochastic model gives a satisfactory description of the experimental data, as can be observed in experiments 1, 2, and 3. In fact, experimental results are similar at 60 and 70 °C and the same set of parameter values was used at these two temperatures. At low temperatures, prediction of methyl and butyl branching is also satisfactory, but larger deviations from the experimental data are observed in the description of longer chain branches. Formation of longer branches requires repeated 2,1 insertions followed by full chain-walking past a butyl branch, as depicted in Scheme 6. Subramanian et al. [12] point out that 2,1 insertions are less frequent at low temperatures once the sequences of methylene units are shorter at these conditions, as analyzed from the ^{13}C NMR spectra of the polymer samples available. This explains the decrease in the number of longer branches as temperature decreases, but not the discrepancies of the model simulations. It is clear that the literature mechanism alone is not enough to justify the formation of longer branches at low temperatures. More information could be obtained from a detailed investigation of this catalytic system at these conditions with emphasis on the postulation of alternative mechanisms to produce longer chain branches. Overall, model results are in good agreement with experimental data, suggesting that the major steps of the polymerization mechanism are correctly described and that the mechanistic rules implemented represent quite satisfactorily the physico-chemical system.

Table 2
Estimated probabilistic simulation parameters

Entry	Probabilistic simulation parameters			
	P_β	P_i	P_f	P_{12}
1	0.2	0.99	0.99	0.74
2	0.2	0.99	0.99	0.74
3	0.2	0.65	0.75	0.65
4	0.18	0.58	0.45	0.3
5	0.15	0.56	0.42	0.25

Table 3
Molar mass distributions' averages

Temperature (°C)	$\overline{M}_w$ (g/mol)	$\overline{M}_n$ (g/mol)	PI
5	14,743	7528	1.96
35	21,360	10,778	1.98
60	37,699	18,912	1.99
70	37,699	18,912	1.99

Note: $\overline{M}_w$ = weight-average molar mass; $\overline{M}_n$ = number-average molar mass; PI = $\overline{M}_w/\overline{M}_n$ = polydispersion index.

Table 3 shows the average polymer molar masses, as predicted by the stochastic simulations. Regarding this topic, it is important to notice that the growth of a polymer chain is determined by steps 1 and 2 of Scheme 7, where competition between chain growth and termination is observed. If no other parameter would interfere on the chain molar mass, then, for fixed P_β, all chains would present the same molar mass. However, it is important to realize that there are forbidden carbons in the polymer chain, as the formation of ethyl and propyl branches is not allowed (cf. Scheme 5). The larger the value of parameter P_i, the greater the chances of repeated chain-walking to occur, according to Scheme 7 , which increases the chances for the metal to be located in a favorable position for insertion. On the other hand, the lower the value of P_i, the lower will be the chances of repeated chain-walking to occur, increasing the chances for the metal to be attached to intermediate carbons, where insertion is prohibited (cf. discussions about Scheme 5). Therefore, when the metal is attached to a non-favorable carbon, the stochastic procedure drives the system to step 2, where termination may be possible. In other words, parameter P_i affects the molar mass of the chain by increasing the chances for termination.

As the temperature increases, the model predicts an increase in the degree of polymerization, as parameter P_i reaches it's maximum in Table 2. The distributions predicted by the stochastic simulations are reported in Fig. 1. Unfortunately, there is no experimental information available for this system for comparison. However, the molar mass distributions present expected polydispersion indices approximately equal to two, as they are known to be described by Flory–Schultz distributions [7–9].

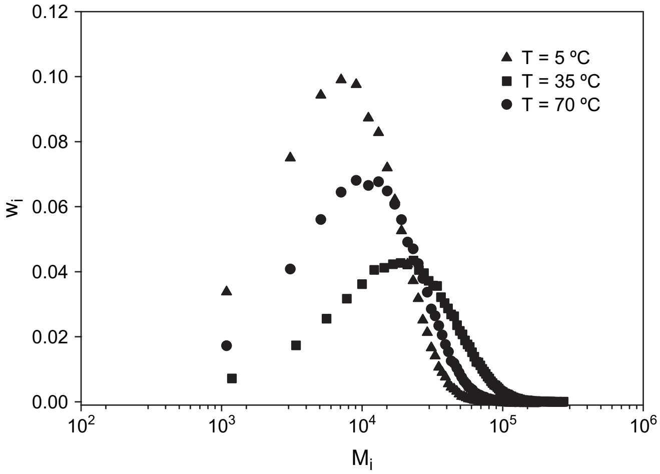


Fig. 1. Simulated molar mass distributions of poly(1-hexene)s at different temperatures.

4.2. Model sensitivity analysis

A sensitivity analysis was performed in order to evaluate the effect of the model parameters on the branching distributions. Table 3 shows that most parameters, except P_β, are required to assume a wide range of values in order to describe the experimental range of reaction conditions. For this reason, in the sensitivity analysis presented, parameter P_β was kept constant with the value 0.2. Besides, because larger deviations of model predictions were found at the lower temperature experiment (i.e., experiment 4), parameters P_i, P_f, and P_{12} were allowed to vary within approximately their corresponding values used to describe experiments 1−3.

Table 4 presents the parametric sensitivity data generated by model simulations. An overall look at the reported simulation data allows one to notice that, for a given value of the probabilistic forward walking parameter P_f, the larger the value of the isomerization parameter P_i, the larger is the expected relative amount of methyl branches and, consequently, the lower is the relative amount of butyl branches, as the number of longer chain branches is significantly smaller when compared to the other types of branches. This behavior is explained by considering the kinetic mechanisms presented in Schemes 2−4. It is clear that there is significant competition between formation of methyl and butyl branches. Butyl branches are favored when 1,2 insertions are dominant or, in other words, when isomerization is less probable to occur (cf. Scheme 2). As isomerization probabilities are enhanced, the mechanisms presented in Schemes 3 and 4 are predominant and methyl branches are relatively more abundant.

Table 4
Parametric sensitivity data generated by model simulations

Entry	Simulation parameters			(INB/TNB) × 100%		
	P_i	P_f	P_{12}	Methyl	Butyl	Hexyl+
1	0.6	0.5	0.8	52.3	47.2	0.67
2	0.8	0.5	0.8	59.0	40.4	0.65
3	0.99	0.5	0.8	64.0	35.1	0.81
4	0.6	0.8	0.8	81.7	14.2	4.12
5	0.8	0.8	0.8	85.2	10.1	4.64
6	0.99	0.8	0.8	87.5	7.5	4.98
7	0.6	0.99	0.8	73.5	22.2	4.31
8	0.8	0.99	0.8	81.6	13.5	4.94
9	0.99	0.99	0.8	86.5	7.6	5.81
10	0.6	0.5	0.9	52.6	47.1	0.27
11	0.8	0.5	0.9	59.7	40.0	0.35
12	0.99	0.5	0.9	64.9	34.6	0.39
13	0.6	0.8	0.9	84.3	13.5	2.17
14	0.8	0.8	0.9	88.0	9.6	2.37
15	0.99	0.8	0.9	90.3	7.2	2.53
16	0.6	0.99	0.9	83.8	13.6	2.55
17	0.8	0.99	0.9	87.6	9.7	2.70
18	0.99	0.99	0.9	89.8	7.2	2.95
19	0.6	0.5	0.99	52.8	47.2	0.03
20	0.8	0.5	0.99	60.1	39.8	0.04
21	0.99	0.5	0.99	65.5	34.4	0.04
22	0.6	0.8	0.99	86.3	13.4	0.23
23	0.8	0.8	0.99	90.2	9.5	0.25
24	0.99	0.8	0.99	92.6	7.1	0.25
25	0.6	0.99	0.99	88.6	11.1	0.27
26	0.8	0.99	0.99	91.1	8.6	0.29
27	0.99	0.99	0.99	92.6	7.1	0.30

Entries 1−9 of Table 4 report branching distributions for $P_{12} = 0.8$. It is possible to observe that, for a given value of parameter P_i, the relative amount of methyl branches is also favored by the forward walking parameter P_f, as this parameter enhances the probabilities for chain-walking by moving the active site to positions where the formation of methyl branches takes place (cf. Schemes 3 and 4). An opposite effect is observed for the butyl branches. One may also see that a maximum effect upon the methyl branching distributions (opposite effect for the butyl branching distributions) is obtained for intermediate values of P_f. The kinetic mechanisms presented in Schemes 2−6, alone, are not enough to explain this behavior. It is important to emphasize that though, the mechanism developed in the literature [12] to explain the appearance of different types of branches are based on the interpretation of ^{13}C NMR spectra of the polymer samples available at different temperatures, and can thus provide only qualitative information regarding the mechanistic pathways that may actually exist for this system. Other kinetic routes may be postulated to explain the appearance of branches, provided that there are no insertions in forbidden positions and there is no violation of steric limitations. It is, therefore, possible that there exists a set of reaction pathways not described in the experimental study that may explain the maximum formation of methyl branches at intermediate values of P_f.

One may observe that the interesting behavior described above for the variation of parameter P_f is attenuated and eventually disappears when parameter P_{12} is increased, as shown from entries 10−18 and 19−27 of Table 5, respectively. As shown in Table 3 , the largest values of P_{12} were estimated for the high temperature experiments, where deviations of the experimental branching distributions from model predictions were very low. This seems to indicate that at low temperatures there may be some alternative kinetic pathways that were not detected based solely on the qualitative analysis of the ^{13}C NMR spectra of the polymer samples.

The last point regards the effect of model parameters on the formation of longer chain branches. Initially, the effect of parameter P_i is analyzed. For any given combination of parameters P_f and P_{12} (e.g., entries 1−3, 4−6 etc.) it is possible to observe that the isomerization parameter P_i has minimal effect on the number of longer chain branches. Despite being small, the effect of increasing P_i points towards the increase of the relative amount of longer chain branches, which is in

Table 5
Parameter estimation results for the temperature dependency of the probabilistic parameters

Parameter in Eq. (6)	Probabilistic parameter			
	P_β	P_i	P_f	P_{12}
A	−1.6463	−0. 4816	−0. 3551	−0. 5755
B (K)	10.947	823.982	1195.740	900.000

accordance with the mechanism presented in Schemes 2, 3 and 6. The higher the isomerization probabilities, the higher the chances of chain-walking to occur, resulting preferably in species **4** (cf. Scheme 3) and species **18** (cf. Scheme 6), with potential to form longer chain branches.

Forward walking parameter P_f has a positive effect upon the formation of longer chain branches. Entries 1, 4, and 7, or 10, 13, and 16, or 19, 22, and 25 of Table 5 , for instance, show that, given constant values of the pair of parameters P_i and P_{12}, the increase of P_f is capable to produce a one-fold increase in the relative amount of longer chain branches. This behavior is in consonance with the kinetic mechanisms used to explain the effect of P_i, in the previous paragraph. Larger values of P_f imply larger rate of chain-walking, thus favoring the formation of longer chain branches, as shown in Schemes 2, 3 and 6.

On the other hand, the isolated effect of increasing parameter P_{12} (e.g. entries 1, 10 and 19 or 5, 14, and 23) is a dramatic decrease of the relative amount of longer chain branches. This behavior is explained by the fact that higher values of P_{12} imply higher probabilities of 2,1 insertions to occur, decreasing the rate of formation of species **4** (cf. Scheme 3). This negative effect of increasing P_{12} on the longer chain branches distribution is enhanced at low values of parameters P_i and P_f due to the reasons already discussed in the previous paragraphs. To summarize, the maximum relative amount of longer chain branches may only be attained at the highest probabilities of chain-walking (P_i and P_f) and minimal probability of 1,2 insertion (P_{12}).

4.3. Temperature dependence of probabilistic parameters

The sets of probability parameters reported in Table 3 were obtained at different polymerization temperatures. In order to expand the predictive capabilities of the model, the probabilistic parameters were correlated to the polymerization temperature. The approach adopted here aims at minimizing the parameter estimation computational costs [8] as well as providing a kinetic interpretation of each step of the probabilistic model describing the polymerization of 1-hexene.

During the α-diimine Ni(II) catalyzed 1-hexene polymerization, each possible kinetic pathway may be interpreted as a competition between two possible reactions and the probabilistic factors used to describe this competition depend upon the ratio of the specific reaction velocities for each possible reaction. Let r_1 and r_2 represent the specific reaction velocities of the two possible reactions, 1 and 2, in a given polymerization step, respectively:

$$r_1 = \alpha_1 \exp\left(\frac{-B_1}{T}\right), \tag{2}$$

$$r_2 = \alpha_2 \exp\left(\frac{-B_2}{T}\right), \tag{3}$$

where explicit dependence upon temperature is presented.

The ratio between Eqs. (3) and (2) is given by:

$$\frac{r_2}{r_1} = \frac{\alpha_2}{\alpha_1} \exp\left(-\frac{(B_2 - B_1)}{T}\right) = \alpha \exp\left(-\frac{B}{T}\right), \tag{4}$$

where $\alpha = \alpha_2/\alpha_1$ and $B = B_2 - B$.

It is now assumed that the probability for reaction 2 to occur is proportional to the kinetic ratio given by Eq. (4), i.e.:

$$P = c\frac{r_2}{r_1} = c\alpha \exp\left(-\frac{B}{T}\right) = A \exp\left(-\frac{B}{T}\right), \tag{5}$$

where c is proportionality constant which may be grouped with parameter α to form a new parameter A. Therefore, Eq. (5) may be used to express the dependence of the probabilistic model parameters P_β, P_i, P_f and P_{12} to the polymerization temperature. However, literature [19] points out that, in order to minimize the statistical correlation between parameters A and B during parameter estimation procedures, Eq. (5) should be rearranged as follows:

$$P_j = \exp\left(A_j - B_j\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right), \tag{6}$$

where $j = \beta, \text{i}, \text{f}, \;\; 12$ and T_{ref} is a given reference temperature.

Eq. (6) was used to estimate parameters A and B for each one of the probabilistic parameters of the model from the experimental branching data presented in Table 1 , although only a few experimental data are available for parameter estimation. In order to perform the parameter estimation, a least squares method was used as implemented in the literature [20]. According to the least squares procedure, the best parameter estimates are those which allow the minimization of the following objective function (OF):

$$\text{OF} = \sum_{i=1}^{N_{\text{exp}}} \left(y_i^{\text{exp}} - y_i^{\text{calc}}\right)^2, \tag{7}$$

where y_i is the percent amount of a certain type of branch obtained either experimentally (exp) or calculated (calc) at the

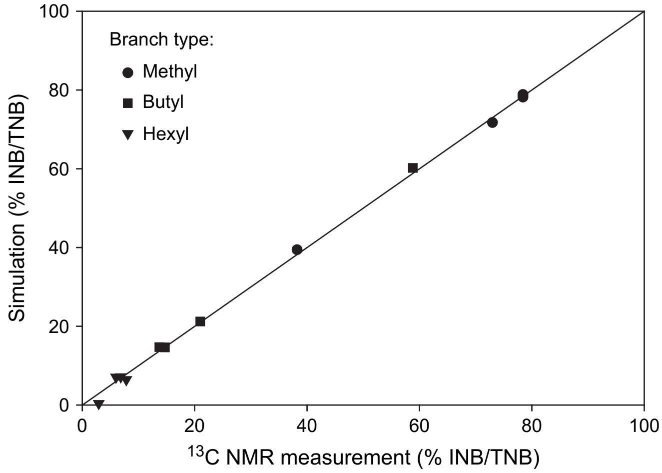


Fig. 2. Comparison of experimental and calculated branching data after temperature dependence parameter estimation.

experiment point i, and $N_{\exp}$ is the number of experimental data available.

Parameter estimates are presented in Table 4 and Fig. 2 presents the comparison between experimental and calculated branching data. One may notice that, despite the relatively few data provided for the parameter estimation, results present a very good coincidence between experimental and simulated branching values. The proposed correlation given by Eq. (5) was able to capture appropriately the temperature dependence of the probabilistic parameters quite satisfactorily as well as provide a kinetic interpretation for them.

5. Conclusions

A stochastic model was proposed to simulate the distribution of branches in poly(1-hexene)s obtained with α-diimine nickel catalysts. The stochastic simulations could reproduce the formation of methyl, butyl, and longer chain branches, which are typical for this polymerization system. This information about polymer microstructure generated by the simulations reported herein can be useful in molecular simulation studies to determine conformational properties based on the Monte Carlo and molecular dynamics methods. Model simulations showed that, at low temperature, the kinetic mechanism presented in the literature [12] for the polymerization of 1-hexene with α-diimine nickel catalysts is not enough, alone, to explain the polymer microstructure obtained experimentally. Therefore, the modeling approach used here may be used as a tool to provide directions for experimental investigations in these catalytic systems. Finally, the proposed temperature dependence of the probabilistic parameters was able to provide a kinetic interpretation to the stochastic model as well as a straightforward way to successfully estimate the temperature dependent parameters.

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