

Stochastic Simulations of Polymer Growth and Isomerization in the Polymerization of Propylene Catalyzed by Pd-Based Diimine Catalysts

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Abstract: A model is presented that employs a stochastic approach to the simulation of polyolefin chain growth and isomerization. The model is applied to propylene polymerization catalyzed by Pd-based diimine catalysts. The stochastic approach links the microscopic (quantum chemical) approach with modeling of the macroscopic systems. The DFT calculated energies of the elementary reactions and their barriers have been used as input parameters for the simulations. The influence of the catalyst's steric bulk, as well as polymerization temperature and olefin pressure on the polymer branching and its microstructure, is discussed. The results are in good agreement with available experimental data. In the propylene polymerization catalyzed by Pd(II) complexes with methyl backbone- and -Ph-Pr₂ imine substituents a number of branches of 238 branches/1000 C have been obtained. An increase in polymerization temperature leads to a decrease in the number of branches. Change in olefin pressure does not affect the global number of branches, while it strongly affects the polymer microstructure, leading to hyperbranched structures at low pressures. Further, the simulations confirm the experimental interpretation of the mechanistic details for this process: (1) both 1,2- and 2,1-insertion happen with the ratio of ca. 7:3; (2) there are no insertions at the secondary carbons; and (3) most of the 2,1-insertions are followed by a chain straightening isomerization. Thus, for this catalyst the total number of branches is controlled exclusively by the 1,2-/2,1-insertion ratio. For the catalysts with different substituents the branching can be controlled by a 1,2-/2,1-insertion ratio as well as the fraction of the insertions at the secondary carbons. The results of the present studies demonstrate that a stochastic approach can be successfully used to model the polyolefin microstructures and their catalyst, temperature, and pressure dependence. Further, it can also facilitate interpretation of the experimental results, and can be used to draw general conclusions about the influence of the specific elementary reaction barriers on the polymer structures; this can be helpful for a rational design of the catalysts producing a desired microstructure.

Introduction

A new challenge in polymerization chemistry is the controlled generation of polymer materials with a specific microstructure. This challenge is driven by the need to create polymers with unusual properties. Of special interest are the dendritic and hyperbranched polymers: structures in which the complex branch-on-branch patterns are present, i.e., not all branching points can be crossed in a single "walk" along the chain.¹ In most of the studies, the branches in such polymers have been introduced by the structure of the monomer, e.g. in the condensation of the AB₂-type monomers, or the "self-condensing" approach.¹⁻⁸ Recently,⁹⁻¹² the hyperbranched polymers

have been obtained with Ni- and Pd-based diimine catalysts¹³⁻¹⁷ in polymerization processes under low olefin pressure, as a result of fast chain isomerization reactions in this system. Interesting

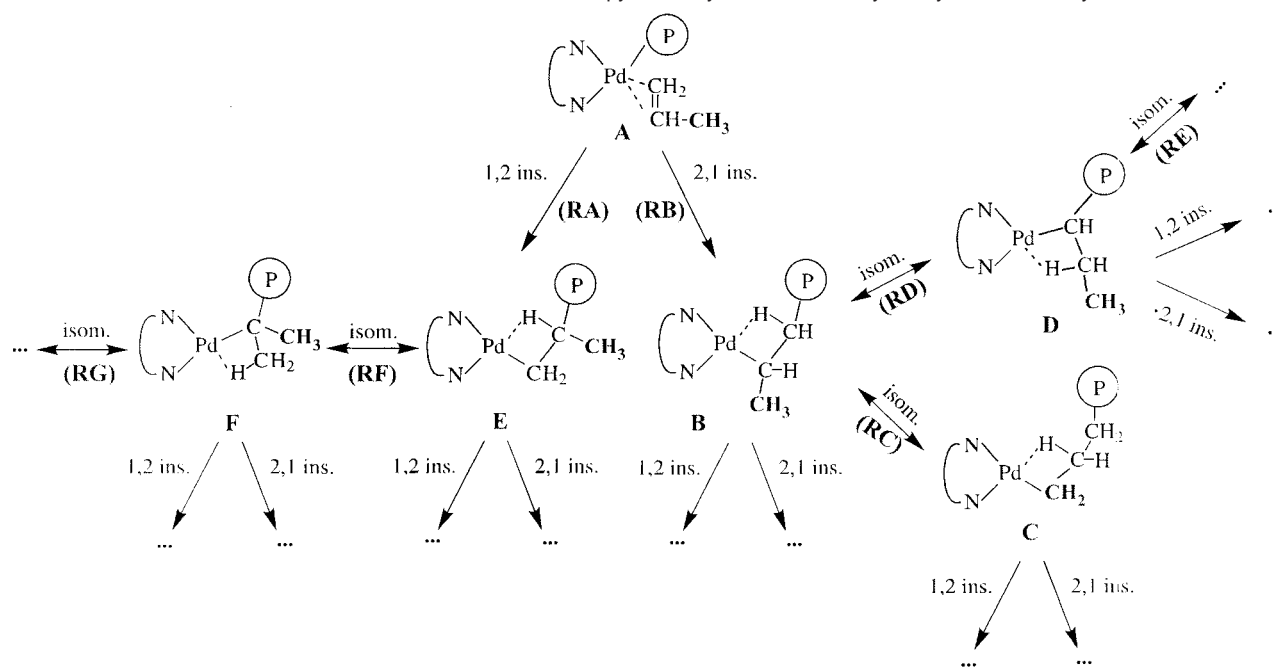
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Scheme 1. Chain Growth and Isomerization Reactions in the Propylene Polymerization Catalyzed by Diimine Catalysts

is also the fact that, unlike its Ni analogue, the Pd-based catalyst produce polymers characterized by a pressure-independent number of branches.^{9–13} The microstructure of the polymer, however, is strongly affected by the olefin pressure: hyperbranched structures are obtained under low pressure, and structures with linear side chains under high olefin pressure.^{9–13} The low molecular weight, hyperbranched polymers were also obtained in ethylene polymerization catalyzed by other early and late transition-metal-based systems.^{18,19} However, a mechanism of formation of these structures remains to be investigated; it may be different than that in diimine systems. Methods for the preparation of macromolecules with hyperbranched structures have been reviewed in a recent article by Frey et al.¹

Quantum chemistry has been proven to be a valuable tool in the studies of polymerization processes.^{20,21} However, direct quantum chemical studies on the relationship between the catalyst structure and the microstructure of a polymer, as well as the influence of the reaction conditions, are not practical without the aid of statistical methods. One such approach is a “mesoscopic” scheme, in which the results of the DFT calculations performed for the reaction intermediates are used as input parameters for a stochastic modeling of a polymer growth. In the present investigation we present an example of such a procedure.

Scheme 1 presents the mechanism of the propylene polymerization catalyzed by diimine catalysts.^{13–17,22,23} In this process, the resting state of the catalyst is an olefin π-complex, **A**, from which the polymer chain may grow via 1,2- (**RA**) or

2,1-insertion (**RB**). Both insertion paths introduce one methyl branch. Thus, if they were the only reactions in the polymerization, a polypropylene chain would have a regular number of 333 methyl branches per 1000 carbon atoms. It has been found experimentally^{13–17} that in the propylene polymerization catalyzed by Ni- and Pd-based diimine complexes the number of branches is much lower, and varies between 150 and 300. The “chain straightening” reaction (**RC**) is responsible for the removal of a branch; this isomerization reaction may follow the 2,1-propylene insertion. However, the isomerization reactions may also elongate branches, when they proceed in the opposite direction (**RD**, **RE**, etc.). Another isomerization reaction that may follow the 1,2-insertion introduces an additional methyl branch, and also may proceed further (**RF**, **RG**, etc.). Thus, in the polymerization cycle, many different alkyl species are present (**B–F**), in which the metal atom forms a bond with primary, secondary, or tertiary carbon atoms; each of them can capture the next monomer and give rise to a subsequent insertion. It is thus clear that one must consider all these elementary reactions to understand the influence of the catalyst and the reaction conditions on the polymer microstructure.

In recent papers^{22,23} we reported the results of computational (DFT) studies on the elementary reactions in ethylene and propylene polymerization catalyzed by Pd-based diimine catalysts with different substituents. These studies explained many details of the substituent effects in the polymerization process and gave the energetics of the elementary reactions. However, no attempt was made to relate these results to the polyolefin microstructure.

In this article we present a simple model for performing stochastic simulations of the polymer growth. With the DFT-calculated energetics of the elementary reactions as an input, a stochastic model is applied in the propylene polymerization

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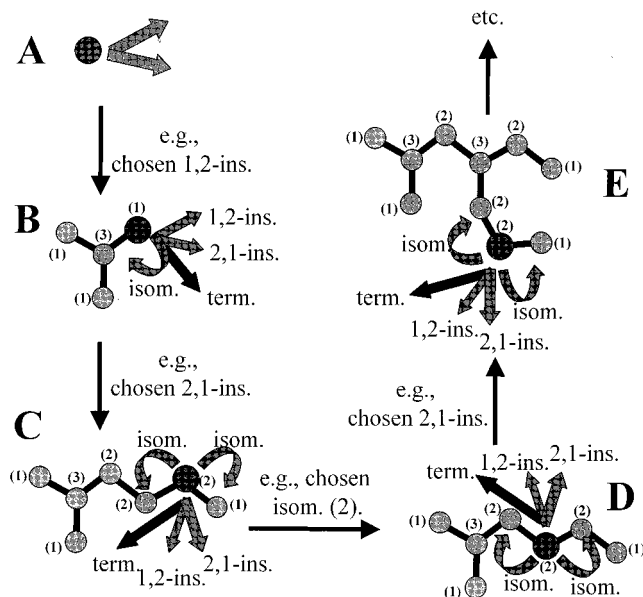


Figure 1. Stochastic simulations. In the starting structure (A) one C atom is attached to the catalyst; only two events are possible: propylene capture followed by the 1,2- or 2,1-insertion. For structure B four events are taken into account: isomerization to the tertiary carbon, 1,2- and 2,1-insertions, and a termination. For structures C, D, and E five events are considered: two isomerizations, two insertions, and a termination. The probabilities of these events are equal for structures C and E (in both cases two different isomerizations lead to a primary or secondary carbon at the metal), and different for structure D (for which both isomerizations lead to the structure with a secondary carbon attached to the metal). For clarity, the numbers [(1), (2), and (3)] labeling different atom types (primary, secondary, and tertiary, respectively) are shown.

catalyzed by the Pd-based diimine catalysts. The effect of the catalyst substituents and the reaction conditions (temperature, olefin pressure) on the number of branches and the polymer microstructure will be discussed.

Model for Stochastic Simulations

In the present studies the polymer growth and branching has been modeled by a number of stochastic simulations, from which a set of polymer structures was obtained. A few initial steps in a typical simulation are presented in Figure 1. Initially, one carbon atom (a methyl group) is attached to the metal of the catalyst (A in Figure 1). In the first step, it will capture and insert a propylene molecule via either the 1,2- or 2,1-insertion route. Thus, one of these insertion events is stochastically chosen; this choice, however, is not totally random but weighted by the probabilities of the two reactions. Now, let us assume that the 1,2-insertion has happened in the first step, i.e., the isobutyl group is attached to the catalyst (B) after insertion. At this stage four different elementary events are possible: two alternative insertion routes (1,2- and 2,1-insertion) preceded by the capture of olefin, the termination reaction, and the isomerization reaction that would lead to a *tert*-butyl group attached to the metal center. If, for instance, the 2,1-insertion happened, a heptyl group would be attached to the catalyst by its secondary carbon atom (C); thus, five reactive events would be possible (two insertions, a termination, and two isomerizations), one of them would be stochastically chosen in the next step, etc.

In this model we assign different probabilities for similar events starting from or/and leading to structures with a carbon

atom of different character being attached to a metal. For example, the 1,2-insertion starting from a primary carbon is not equivalent to the 1,2-insertion starting from the secondary carbon. Similarly, the isomerizations starting from a primary, secondary, and tertiary carbon are not equivalent in general, and also the two isomerizations starting from a secondary carbon may be inequivalent, e.g. if one of them leads to a primary and another to a secondary or tertiary carbon at the metal (as at stage C and E). In other words, we take into account in this model three different 1,2- insertions, three different 2,1- insertions, three different terminations (each starting from 1°, 2°, and 3°-carbon), and nine different isomerizations (starting from and leading to 1°, 2°, and 3°-carbon).

It should be emphasized here as well that at different stages the *absolute* probabilities of equivalent events may be different, since they depend on the probabilities of all the other events (because of the probability normalization). For example, at stages C and D in Figure 1, the secondary carbon is attached to the metal, and five reactive events are possible. However, at stage C the isomerization reactions are inequivalent (one leads to the primary carbon and another to the secondary carbon), while at stage D they are equivalent. As a result, the *absolute* probabilities of *all the events* at stage C will differ from those at stage D.

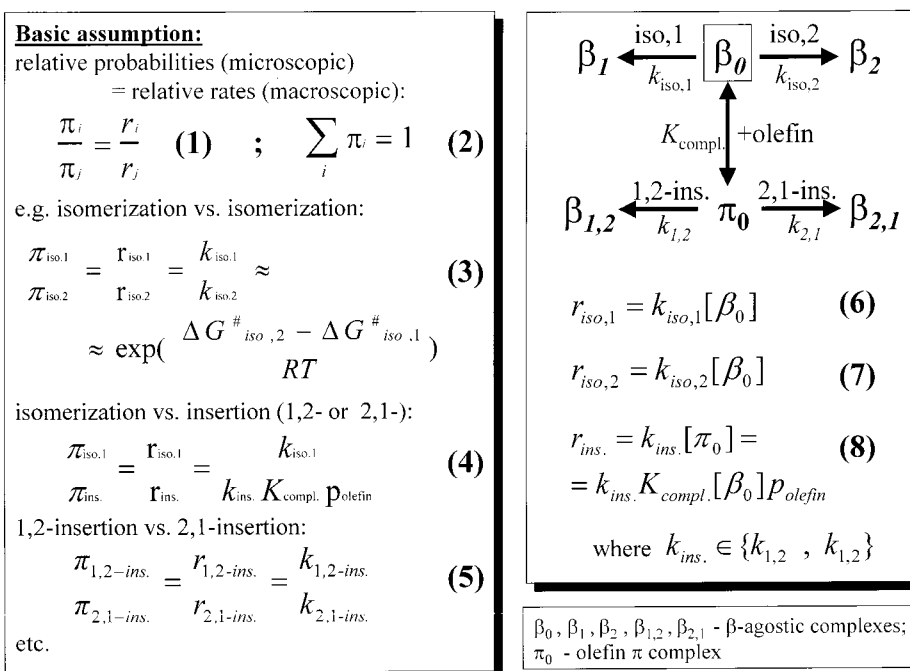
In Scheme 2 we summarize a way to obtain probabilities of the events applied in this study. The basic assumption here is that the *relative* probabilities of elementary reactions at the microscopic level, π_i/π_j , are equal to their *relative* reaction rates (macroscopic), r_i/r_j . Thus, the *relative* reaction rates (eq 1) for all pairs of the considered reactive events together with the probability normalization condition (eq 2) constitute the system of equations that can be solved for the *absolute* probabilities of all the events at a given stage. With this assumption, one can use the experimentally determined reaction rates or the theoretically calculated relative rate constants, obtained from the energetics of the elementary reactions with the standard Eyring exponential equation. The Eyring equation introduces as well a temperature dependence of all the relative probabilities (as in eq 3).

Let us now have a closer look at the three basic types of relative probabilities appearing in the model: an isomerization vs another isomerization, the 1,2-insertion vs 2,1-insertion, and an isomerization vs an insertion. The right-hand part of the Scheme 2 summarizes the equations for the macroscopic reaction rates for the alternative reactive events starting from an alkyl complex β_0 ; let us assume that the secondary carbon atom is attached to the metal, so that two isomerization reactions have to be considered.

The isomerization reactions are first order in concentration of the initial alkyl complex, $[\beta_0]$ (eqs 6 and 7). Thus, the relative probability for the two isomerizations (eq 3) is given by the ratio of their rate constants, $k_{\text{iso},1}/k_{\text{iso},2}$ (as equal to the relative rate, $r_{\text{iso},1}/r_{\text{iso},2}$), and at given temperature it can be calculated from the isomerization barriers $\Delta G_{\text{iso},1}^\ddagger$ and $\Delta G_{\text{iso},2}^\ddagger$, as in eq 3.

From alkyl complex β_0 , the olefin can be captured to form the π -complex π_0 , and inserted via the 1,2- or 2,1-insertion route. In the model applied here we consider the olefin capture and its insertion as one reactive event, i.e., we assume a preequilibrium between the alkyl and olefin complexes, de-

Scheme 2. Basic Equations Used in the Stochastic Model



scribed by an equilibrium constant $K_{\text{compl.}} = [\pi_0]/[\beta_0] = \exp(\Delta G_{\text{compl.}}/RT)$. This corresponds to neglecting the barrier for the monomer capture. Such an approach is valid for the late transition metal complexes, e.g. the diimine catalysts studied in the present work, where the resting state of the catalyst is a very stable olefin π -complex and the olefin capture barrier and the related π -complex dissociation barrier are much lower than the insertion barriers. This assumption allows one to speed up the simulation: otherwise many olefin capture/dissociation steps, not important for the final result of the simulation, would be happening before insertion takes place. It follows from the above considerations that the insertion rate is given by eq 8, and the equation for the isomerization vs insertion relative probability (eq 4) includes the isomerization and insertion rate constants, the equilibrium constant, $K_{\text{compl.}}$, and the olefin pressure, p_{olefin} . Finally, the relative probability for the two alternative insertions is given by eq 5, which depends on the ratio of the two rate constants only.

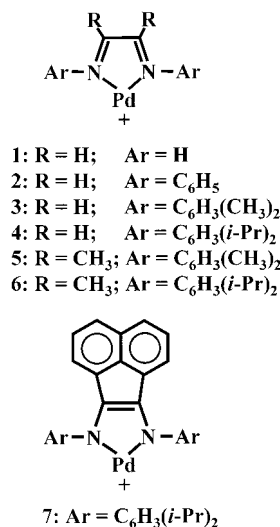
We would like to emphasize here that the model in such a form allows one to simulate the influence of the reaction conditions. The temperature dependence of all the relative probabilities appears in the exponential expressions for the rate constants and the equilibrium constants. The olefin pressure influences the isomerization–insertion relative probabilities. As a result, both temperature and olefin pressure influence the values of the *absolute* probabilities for *all* the reactive events considered.

In this study, we use the energies of the elementary reactions and their barriers obtained from our previous DFT calculations.²³ Thus, we neglect the entropic contributions to the corresponding free energies. We would like to briefly discuss possible implications of this approximation now. The entropic contribution to the insertion barriers is small and comparable for 1,2- and 2,1-insertion, so it is canceled in the expression for the 1,2- vs 2,1-insertion *relative* probabilities (eq 5). Similarly, it can be expected that the isomerization vs isomerization relative probabilities (eq 3) will not be affected by the entropic

contribution either. However, the entropic contribution to the olefin complexation free energy is known to be strongly destabilizing ($-T\Delta S = 9\text{--}13$ kcal/mol, at 300 K, for different systems).²⁴ Thus, it strongly influences the complexation equilibrium constants $K_{\text{compl.}}$, used in the expressions for the isomerization vs insertion relative probabilities (eq 4). However, the relative probability of eq 4 depends on the product $K_{\text{compl.}}p_{\text{olefin}}$, and the error in $K_{\text{compl.}}$ can be counterbalanced by the change in the olefin pressure, p_{olefin} . As a consequence, in this study the olefin pressure is expressed in arbitrary units, and the values of p_{olefin} cannot be related to the absolute values of the real olefin pressure in the polymerization process. Only the product $K_{\text{compl.}}p_{\text{olefin}}$ can be related to the corresponding experimental value. Further, since our $K_{\text{compl.}}$ is overestimated, it can be expected that the experimental conditions correspond to a low value of our p_{olefin} parameter, $p_{\text{olefin}} \ll 1$. It should be emphasized, however, that this still allows one to qualitatively investigate the pressure influence on the polymer microstructure, since the physical meaning of the p_{olefin} parameter remains the same, regardless of its absolute value.

In the following we shall present the results for the propylene polymerization catalyzed by the Brookhart Pd-based diimine catalysts with different substituents. The seven models for the catalysts considered are presented in Scheme 3. As we have already mentioned, three values for the barriers for each of two alternative insertions and nine isomerization barriers are required as model parameters for the simulations. All these values were computed for the *generic catalyst model* only, in which the bulky diimine substituents were replaced by hydrogen atoms ($R = H, Ar = H$).²² The results of these studies show that π -complex stabilization energies are very small for the system involving tertiary alkyl, and the corresponding insertion barriers are much higher than those for the systems with primary and secondary alkyl. Thus, it seems reasonable to assume that the insertion into the Pd–C bond involving tertiary carbon does not happen

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Scheme 3. Pd-Based Diimine Catalysts Considered in the Present Work

at all. Further, the recent DFT calculations²³ for all the remaining “real” catalysts (with the diimine substituents considered) were performed for the alkyl complexes and the π -complexes with the primary and secondary alkyl, but the 1,2- and 2,1-insertion barriers were evaluated only for the systems with the primary alkyl. Therefore, in the present simulations we use all the available results from the DFT studies,^{22,23} and we assume that the insertion barriers into the Pd–C bond with secondary carbons are 1 kcal/mol higher than those with primary carbon, as they are for the generic catalyst.²² In all the simulations we use the isomerization barriers calculated for the generic catalyst, since the corresponding barriers for the real catalyst have not been computed. This seems reasonable, since the isomerization barriers are not much affected by the steric bulk: the experimental data for the *real catalysts* ($\Delta H^\ddagger = 6.1$ kcal/mol, $\Delta G^\ddagger = 7.2$ kcal/mol)²⁷ are close to the barriers computed for the *generic catalyst* ($\Delta H^\ddagger = 5.8$ kcal/mol, $\Delta G^\ddagger = 6.8$ kcal/mol).²² Further, we neglect termination in the present studies, since it does not affect the polymer branching and microstructure, but only their molecular weights.

For each system under a given set of reaction conditions (temperature and pressure) 500 independent simulations were performed. All the simulations were carried out until the polymer chain reached 1000 carbon atoms. We would like to point out here, however, that the structure obtained from the single simulation already represents an ensemble averaged structure, because of the basic assumption of the model and the use of the macroscopic parameters (T , p). Thus, the average values from 500 simulations, that each produces a chains of 1000 C, correspond to the result of a simulation that produces a chain of 500 000 C. Since the analysis of branched high-mass polymers is computationally expensive, it is more efficient to perform many simulations producing shorter chains.

The resulting structures were analyzed by calculating the average number of branches. For each structure the main chain was identified as the longest chain in the structure; after that, the branches were classified as primary branches (starting from

the main chain), secondary branches (starting from the primary branches), tertiary branches (starting from secondary branches), etc. All the branches were measured and the average lengths were calculated for all different types of branches.

Results and Discussion

In the following we will first discuss the results of the propylene polymerization simulations performed with the Brookhart Pd-based diimine catalyst for different substituents and at the same reaction conditions ($T = 298$ K, $p = 1$); the results are summarized in Figure 2. Later, the effect of the temperature (Figure 3) and the olefin pressure (Figures 4–6) will be discussed.

Influence of the Catalyst Substituents. In Figure 2 the examples of the polymer structures together with the values characterizing the structure (number of branches/1000 C; percent of atoms in the main chain; percent of atoms in primary branches; average ratio of isomerization and insertion events) are listed for catalysts 1–7 (for numbering see Scheme 3), while Table 1 collects the values of probabilities of the reactive events at the selected stages of polymer growth. Let us first discuss the results of the simulations for the propylene polymerization catalyzed by the Pd-based diimine catalyst with $R = \text{CH}_3$, $\text{Ar} = \text{C}_6\text{H}_3(i\text{-Pr})_2$ (6), as for this system there exist experimental data.^{12–14} At $T = 298$ K and for $p = 1$ (arbitrary units) the simulations lead to the structure characterized by an average number of 238 branches/1000 C atom in the chain. The experimentally determined value for this catalyst is 213 branches/1000 C.¹⁴ Thus, the agreement between the two values seems to be quite good, especially when one takes into account the simplicity of the model, and notices that the “ideal” polymerization without isomerizations would produce 333.3 branches/1000 C.

In the structures obtained from the simulations ca. 61.7% of the carbon atoms belong to the main chain and ca. 36.5% to the primary branches, i.e., less than 2% appears in the branches of higher order. The lengths of the longest observed primary, secondary, and tertiary branches are 28, 11, and 7, respectively. However, the average lengths of those branches are much shorter: 1.6, 2.3, and 0.3. Only one quaternary methyl branch was obtained in all the simulations.

The polymerization process is characterized by an average probability ratio of isomerization vs insertion steps of 2.6. A closer look at the simulation results shows that for this catalyst the insertions practically occur only at the primary carbon, the insertion from the secondary carbon happening very rarely. To illustrate this point, the values of the probabilities of alternative events may be helpful. If the primary carbon is attached to the metal, the probabilities of the 1,2-insertion, 2,1-insertion, and the isomerization (to secondary or tertiary carbon) are 0.700, 0.286, and 0.014, respectively. If the secondary carbon, neighboring with the two secondary carbon atoms, is attached to the metal, the corresponding values are 0.002 (1,2-insertion), 0.001 (2,1-insertion), and 0.499 (two equivalent isomerizations). And if the secondary carbon, neighboring with one primary C and one secondary C, is at the Pd center, the probabilities are: 0.002 (1,2-insertion), 0.001 (2,1-insertion), 0.265 (isomerization to primary C), and 0.731 (isomerization to secondary C).

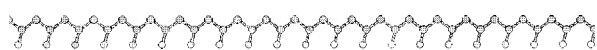
Thus, the isomerization is not likely to happen after 1,2-insertion (when the primary carbon is attached to the catalyst),

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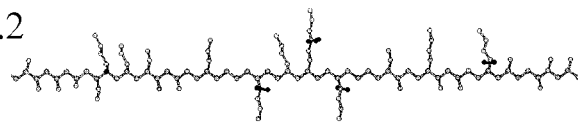
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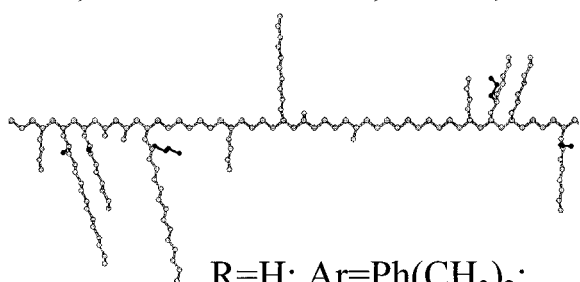
R=H; Ar=H: 331.6 br.; 66.7% 33.3%; 0



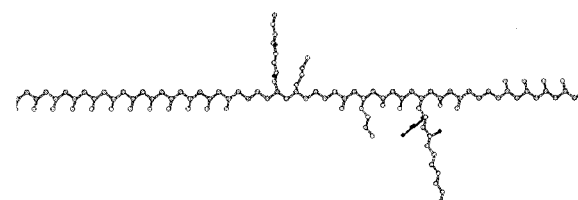
R=CH₃; Ar=Ph(CH₃)₂:
251.0 br.; 59.7%; 38.7%; 0.93



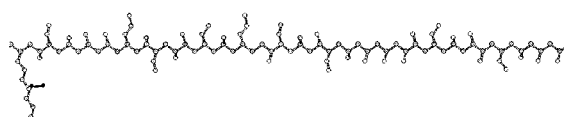
R=H; Ar=Ph: 122.5 br.; 51.7%; 40.1%; 14.2



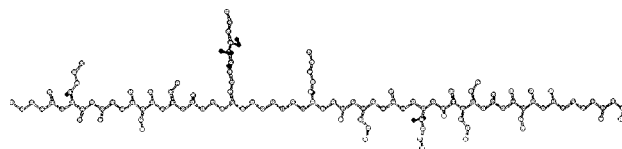
R=CH₃; Ar=Ph(*i*-Pr)₂:
238.2 br.; 61.7%; 36.5%; 2.6



R=H; Ar=Ph(CH₃)₂:
269.6 br.; 60.9%; 38.1%; 0.89



R=An; Ar=Ph(*i*-Pr)₂:
255.6 br.; 59.9%; 38.5%; 1.35



R=H; Ar=Ph(*i*-Pr)₂:
269.6 br.; 60.9%; 38.1%; 1.37

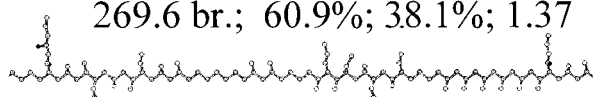


Figure 2. Examples of the polymer structures obtained with different catalysts ($T = 298\text{ K}$, $p = 1$). The values above the plots denote the average number of branches/1000 C, % of atoms in the main chain, % of atoms in the primary branches, and the ratio between the number of isomerization and insertion steps. Different atom shadings are used to mark different types of branches (primary, secondary, etc.).

Table 1. The Probabilities of the Reactive Events at Selected Stages of the Polymer Chain Growth

catalyst	probabilities									
	Pd-CH ₂ ... ^a			CH ₂ -CH(Pd)-CH ₂ ... ^b				...-CH ₂ -CH(Pd)-CH ₂ ... ^c		
	1,2-insert.	2,1-insert.	isomer.	1,2-insert.	2,1-insert.	isom. to 1° C	isom. to 2° C	1,2-insert.	2,1-insert.	both isom.
1	0.003	0.969	0.001	0.001	0.994	0.001	0.003	0.992	0.001	0.006
2	0.301	0.582	0.117	0.001	0.002	0.266	0.731	0.001	0.002	0.998
3	0.102	0.898	0.001	0.050	0.445	0.134	0.369	0.041	0.360	0.600
4	0.046	0.954	0.000	0.019	0.403	0.154	0.424	0.015	0.317	0.666
5	0.057	0.943	0.000	0.017	0.502	0.128	0.352	0.014	0.410	0.574
6	0.700	0.286	0.014	0.002	0.001	0.265	0.731	0.002	0.001	0.998
7	0.272	0.727	0.001	0.090	0.238	0.179	0.493	0.068	0.181	0.750

^a Primary carbon attached to the catalyst. ^b Secondary carbon neighboring with a primary and secondary carbon attached to the catalyst. ^c Secondary carbon neighboring with two secondary carbons attached to the catalyst.

and usually occurs after 2,1-insertion (when the secondary carbon is at the catalyst). In any case, when the alternative isomerizations are considered, the one going along the chain is always preferred, compared to the isomerization leading to the primary carbon. However, the latter isomerization occurs often, since there is no insertion at the secondary carbon and its probability is quite high (0.265). This explains the relatively large ratio for isomerization/insertion steps of 2.6.

The above results lead to the conclusion that for this catalyst the overall number of branches is exclusively controlled by the relative ratio of 1,2- and 2,1-insertions; the first one always produces the branch, and the second one is always followed by chain running, eventually leading to a removal of one of the existing branches. Thus, from the probabilities of 1,2- and 2,1-insertions one can expect a removal of 28.6% of the branches (95.3 branches/1000 C), i.e., the expected overall number of

branches is 238, as observed from the simulations. The results presented here are in very good qualitative agreement with the experimental data: it has been concluded from the NMR analysis of the polypropylenes that for this catalyst insertion happens only at the primary carbons, all the 2,1-insertions lead to the removal of a branch, and 1,2-insertion is the main route for polymer growth.¹²

Let us now discuss the influence of the catalyst substituents on the polymer branching and its microstructure. To understand the influence of the steric bulk, the simulations have been performed for all the remaining catalysts of Scheme 3. It should be mentioned here, however, that the less bulky catalysts, **1** and **2**,²⁸ are not capable of polymerizing olefins. The termination barriers for these systems are very low, due to the lack of steric

(28) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65.

bulk. Thus, the results obtained for catalysts **1** and **2** are of purely theoretical character. They are useful, however, for understanding how the steric bulk can control the polyolefin branching. They also demonstrate how the microstructures can change with small modifications in the energetics of the polymerization cycle.

The results presented in Figure 2 demonstrate that for the generic catalyst model **1** ($R = H$, $Ar = H$) the chain grows by a regular sequence of 2,1-insertions. There is practically no isomerization, the average number of branches is 331.6 branches/1000 C, and 66.7% of C belongs to the main chain and the rest to the methyl branches. This comes from the fact that for the generic catalyst the 2,1-insertion is strongly preferred and the insertion barriers (calculated with respect to the separated reactants) are low compared to the isomerization: the probabilities of the 2,1-insertion at the primary and secondary C are 0.969 and 0.992–0.994, respectively.

Catalyst **2** is located on the opposite side of the range of branching patterns. Here, the lowest average number of branches of 122.5 branches./1000 C is obtained. Only 51.7% of atoms belong to the main chain, and 40.1% to the primary branches, i.e., 8% of the carbon atoms are located in the branches of higher order. As in the example structure shown in Figure 2, the branches produced here are relatively long and are often separated by a few methylene units. The longest observed primary, secondary, tertiary, and quaternary branches are built of 75, 28, 13, and 8 carbon atoms, while the average lengths of the primary, secondary, and tertiary branches are 4, 4, and 2.5, respectively. Thus, the structure obtained for catalyst **2** is quite different from those for systems **6** and **1**. Also, the average ratio of isomerization vs insertion steps of 14.2 is the largest observed, and distinctly larger than those obtained for the remaining systems.

A comparison of the probabilities of the events (Table 1) for catalysts **2** and **6** reveals that the basic difference between them is the reversed insertion regioselectivity: the 2,1-insertion is preferred for **2**, and the 1,2-insertion for **6**. In both cases the insertions happen only at the primary carbons, and in both cases the isomerization starting from the primary carbon has much lower probability than any insertion. Therefore, it comes as no surprise that the observed number of branches is that low for system **2**, since it is controlled only by the 1,2-/2,1-insertion ratio, as in system **6**. However, it is quite surprising and hard to predict without simulations that the average isomerization/insertion ratio and especially the resulting microstructures of the polymers are so different for the two systems, just because of the reversed insertion regioselectivity!

A comparison of the results for catalyst **3–7** (see Figure 2) shows that the increased steric bulk leads to a slight decrease in the global number of branches, and the increase in the insertion/isomerization ratio. For systems **3** and **4** (with $R = H$) the average number of branches and the structural characteristics are almost identical. This arises from the fact that the energetics of the polymerization cycle is quite similar. This can be understood by observing that hydrogens as the backbone substituent give the aryl rings flexibility to adjust their orientation and minimize a steric repulsion, when their substituents are increased in size.²³ For the two systems with methyl backbone and different aryl substituents (catalysts **5** and **6**) the

difference in the number of branches is more pronounced (251.0 branches/1000 C for **5**, and 238.3 branches/1000 C for **6**).

The observed trend—a decrease in the number of branches with increased steric bulk—is quite surprising. One could expect the opposite trend, since the steric effects increase the ratio between 1,2- and 2,1-insertions, and intuitively, this should lead to an increase in the number of branches (fewer 2,1-insertions—fewer removed branches). However, for systems **3**, **4**, **5**, and **7** the insertions at the secondary carbons happen with relatively large frequencies: for systems **3**, **4**, and **5** the probabilities of the insertion starting from the secondary carbon are ca. 0.4–0.5, and for system **7** ca. 0.25–0.33. Since every insertion into the secondary carbon by definition adds a branch, the global number of branches for systems **3–5** and **7** is larger than that for the more bulky catalyst **6**, for which there are practically no insertions from the secondary carbons. An increase in the steric bulk leads to a decrease in the secondary-insertion probability, and eventually to a decrease in a number of branches, despite the larger fraction of 1,2-insertions. Thus, the results show that for systems **3–5** and **7** the branching is controlled by both the 1,2-/2,1-insertion ratio and the ratio between the isomerization and insertions starting from the secondary carbon. This leads to the surprising results mentioned above. We would like to point out here again that, due to the lack of experimental/theoretical results, the secondary insertion barriers for the real catalysts were *assumed* to be 1 kcal/mol higher than the primary insertion barriers (as *calculated* for the generic system). For catalyst **6** this is a posteriori validated by the good agreement with experimental results. Unfortunately, there are no clear experimental data for propylene polymerization with the Pd-based catalyst for different substituents. For the related Ni-based systems, the reversed trend has been observed experimentally:¹² an increase in the number of branches with an increase in the steric bulk, as could be expected from the increased 1,2-insertion fraction. However, the Ni- and Pd-based systems are known to be very different concerning the branching and the polymer microstructures.^{9–13} Therefore, no conclusions can be drawn from those experimental data about the validity of our assumption.

Temperature Effect. The temperature effect in the propylene polymerization was investigated by performing a set of simulations in the temperature range of 48–498 K, with increments of 50 K, for catalyst **6**. Obviously, from the experimental point of view only a narrow range of temperatures in the vicinity of 300 K are interesting. However, to clearly see and understand the trends we performed the simulations for a much wider range of temperatures.

The average number of branches as a function of temperature together with examples of the polymer structures are plotted in Figure 3. The trend is clear, the number of branches decreases with an increase in temperature, going from the “ideal” number of 333 branches/1000 C at 0 K down to 229 branches/1000 C at 498 K. This trend is easy to understand: at 0 K only 1,2-insertions happen, as the preferred insertion path, so no branches can be removed in any way. With an increase in temperature, the fraction of the 2,1-insertion increases and the branches introduced by the 2,1-insertions are removed. Since in the studied range of temperatures there are practically no insertions into the Pd–C bonds involving secondary carbon, the branching is controlled by the ratio between the 1,2- and 2,1-insertion. At

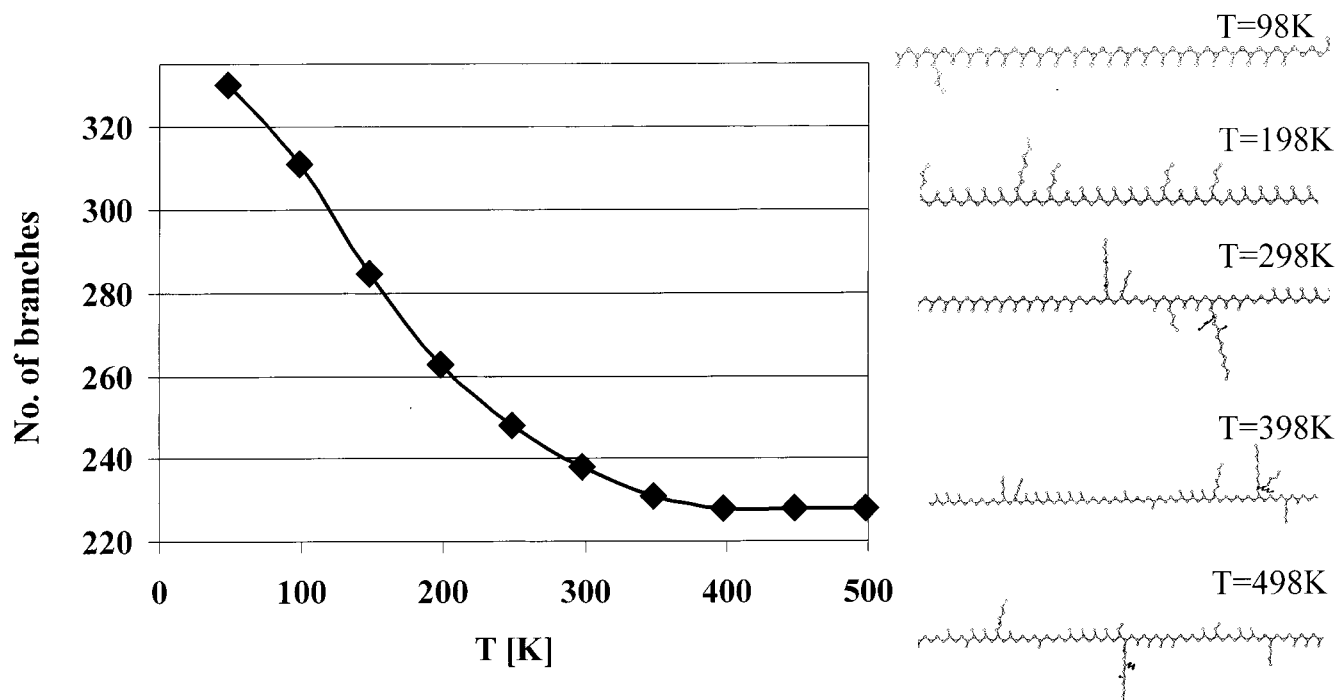


Figure 3. Effect of temperature on the average number of branches/1000 C in the propylene polymerization catalyzed by the catalyst with R = CH₃ and Ar = Ph(*i*-Pr)₂. Examples of the structures obtained at selected temperatures are shown in the right-hand part of the figure. Different atom shadings are used to mark different types of branches (primary, secondary, etc.).

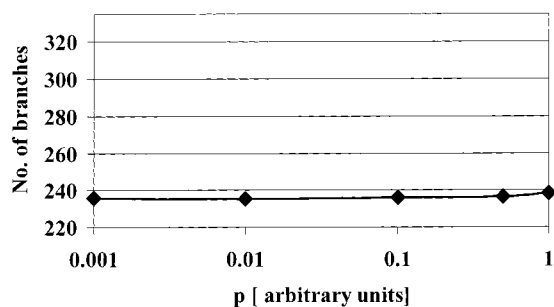


Figure 4. Effect of the olefin pressure on the average number of branches/1000 C.

infinite temperature, however, the probabilities of all the events must become equal, and therefore the asymptotic number of branches is 211.1 branches/1000 C (one-third of the branches removed). The trend observed here is in good agreement with the experimentally observed temperature dependence of polypropylene branching for the analogous Ni-based catalyst.¹² Certainly, the change in polymerization temperature affects not only the number of branches, but also the polymer microstructure. As shown by the structures of Figure 3, the increase in temperature results in an increase in the length of branches and formation of higher order branches. However, the effect is not dramatic. In the experimentally available range of temperatures it can hardly be observed.

Effect of Olefin Pressure. Let us finally discuss the influence of olefin pressure on the polypropylene microstructure. Sets of simulations at different olefin pressures were performed for the real catalyst **6**. The results presented in Figure 4 clearly demonstrate that a decrease in olefin pressure does not affect the number of branches: within $\frac{1}{2}$ a branch the value stays close to 238 even for $p = 0.0001$. The microstructure of the polymer, however, is strongly affected by changes in p_{olefin} . The

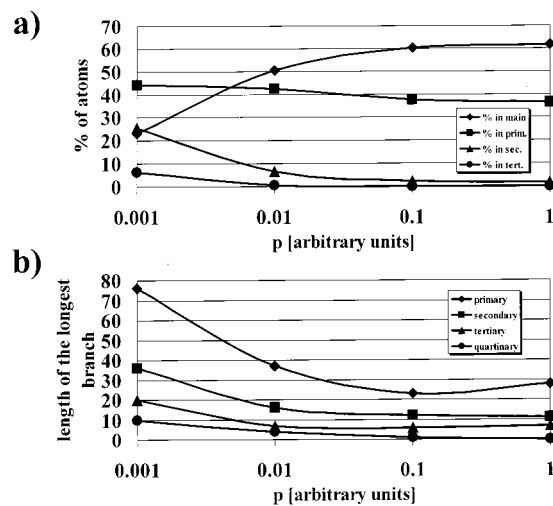


Figure 5. Effect of the olefin pressure on the polymer microstructure, characterized by the percentage of the atoms in the main chain and different branches (panel a) and the number of carbons in the longest branches of different types (panel b).

results presented in Figure 5 indicate that at lower p_{olefin} the branches are elongated, and the formation of higher order branches becomes common. The percentage of the atoms in the main chain decreases from 62% at $p_{\text{olefin}} = 1$ down to 23% at $p_{\text{olefin}} = 0.001$, while the percentage of atoms in branches increases: at $p_{\text{olefin}} = 0.001$ 25% of the atoms are located in secondary and 8% in tertiary branches. The lengths of the longest observed primary, secondary, tertiary, and quaternary branches are 76, 28, 19, and 10, respectively. In Figure 6 we show examples of the polymer structures obtained for different olefin pressure. They clearly support the results of Figure 5 and demonstrate a tendency for forming hyperbranched structures at low olefin pressure.

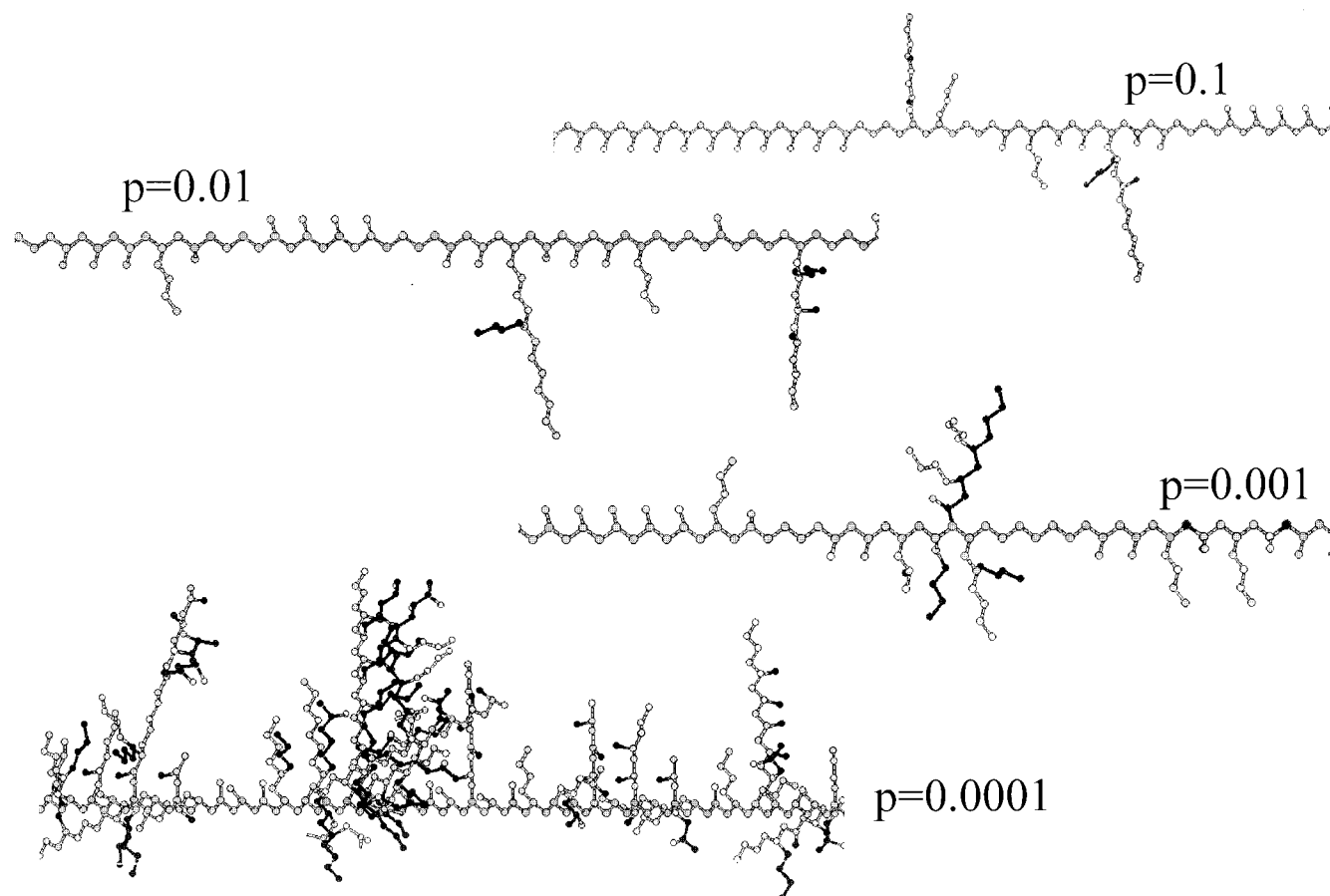


Figure 6. Examples of the structures obtained from simulations with different olefin pressures in the propylene polymerization catalyzed by the catalyst with $R = \text{CH}_3$ and $\text{Ar} = \text{Ph}(i\text{-Pr})_2$ [$T = 298 \text{ K}$]. All the structures are characterized by the same global number of 238 branches/1000 C. Different atom shadings are used to mark different types of branches (primary, secondary, etc.).

The origin of the results obtained here for the polypropylene polymerization catalyzed by **6** is quite clear. As we have already discussed, for this system the branching number is determined by the 1,2-/2,1-insertion ratio, which is pressure independent (see Scheme 2). A decrease in olefin pressure leads to an increase in the isomerization/insertion ratio. For low pressures the number of isomerization steps between two insertions becomes large; as a result of extensive chain running every random branch can grow and this leads to the formation of hyperbranched polymers.

The results of the present simulations are in perfect qualitative agreement with the experimental findings: it is known that with Pd-based diimine catalyst changes in olefin pressure strongly affect the polymer microstructures, while the global branching numbers practically remain constant.^{9–13}

Concluding Remarks

In the present article we have presented the model and the result of stochastic simulations of the polymer growth and isomerization in the propylene polymerization catalyzed by Pd-based diimine catalysts. The DFT calculated energies of the elementary reactions and their barriers^{22,23} have been used as input parameters for the simulations. The simulations for a variety of catalysts with different substituents and for different reaction conditions have been performed in order to understand the influence of the catalyst steric bulk, as well as polymerization

temperature and olefin pressure, on the polymer branching and its microstructure.

The results are in very good agreement with available experimental data.^{9–14} In the propylene polymerization catalyzed by **6** the number of branches of 238 branches/1000 C obtained here is slightly larger than the experimental value of 213 branches/1000 C.¹³ However, the temperature and pressure dependence of the number of branches and the polymer microstructure are in-line with experimental observations:^{9–13} (1) an increase in polymerization temperature leads to a decrease in the number of branches and (2) changes in olefin pressure do not affect the global number of branches, but strongly affect the polymer microstructure, leading to hyperbranched structures at low pressures. Further, the simulations confirm the experimental interpretation of the mechanistic details of the process with catalyst **6**:¹² (1) both 1,2- and 2,1-insertion happen with the ratio of ca. 7:3; (2) there are no insertions at the secondary carbons; and (3) most of the 2,1-insertions are followed by a chain straightening isomerization. Thus, for this catalyst the total number of branches is controlled exclusively by the 1,2-/2,1-insertion ratio.

For the catalysts with different substituents the branching can be controlled by the 1,2-/2,1-insertion ratio as well as the fraction of the insertions at the secondary carbons. We have demonstrated that the reversed preference of the insertion regioselectivity (as observed for catalysts **2** and **6**) can lead to a

dramatic change in the polymer branching and microstructure. Further, due to a significant fraction of secondary insertions, with an increase of the catalyst steric bulk, the number of branches slightly decreases. This trend is opposite to the experimentally determined trend for the analogous Ni-based catalysts;¹² it is known that the mechanistic details for Ni- and Pd-based systems are quite different.

The results of the present studies demonstrate that a stochastic approach bridging the microscopic, quantum chemical calculations with modeling of the macroscopic systems can be successfully used to simulate the polyolefin microstructures and their dependence on catalyst, temperature, and pressure. Further, the approach makes it possible to understand the mechanistic details determining the experimentally observed trends. Also, the stochastic simulations can be used to facilitate an interpreta-

tion of the experimental results, and to draw general conclusions about the influence of the specific elementary reaction barriers on the polymer structures; this can be helpful for a rational design of the catalyst producing a desired microstructure. In future simulations we will address these aspects in connection with ethylene polymerization.

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