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Exploring the Scope of Possible Microstructures Accessible from Polymerization of Ethylene by Late Transition Metal Single-Site Catalysts. A Theoretical Study

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ABSTRACT: The stochastic simulations of the polymer growth under different reaction conditions (temperature and pressure) have been performed for the ethylene polymerization processes catalyzed by late transition metal complexes. The processes catalyzed by the real Pd-based diimine catalyst have been studied on the basis of the energetics of elementary reactions (DFT-calculated and experimental). The simulations with systematically changed insertion barriers have also been performed to model the influence of different catalysts, going beyond diimine systems. In the case of diimine catalysts, the simulations reproduce the experimentally observed average number of branches as well as the temperature and pressure dependencies of the branching numbers. The results explain the microscopic origin of an opposite temperature effect observed for ethylene and propylene polymerization. Further, the simulations allow one to understand the different pressure effect observed for Pd- and Ni-based diimine catalysts. The model simulations give insight into the role of particular factors controlling the polyethylene branching. It has been found that an energy difference between the activation barriers for the primary and secondary insertions strongly influences the polymer microstructure. The results demonstrate that a wide range of polymer topologies can be potentially obtained from ethylene polymerizations with various single-site catalyst characterized by different energetics of the catalytic cycle. Thus, it seems to be possible to rationally design a catalyst producing a desired polyethylene microstructure.

Introduction

There has been an increasing interest in macromolecules with hyperbranched tridimensional architectures,[1−7] such as perfectly regular dendrimers and highly branched polymers with random topologies. Dendric macromolecules, possess unusual properties compared to linear polymers and have found applications in different areas, ranging from catalysis to medicine.[1−4] Highly symmetric dendrimers with perfect topologies are obtained in a tedious, iterative synthesis, which is a major drawback for their widespread use. Therefore, a polymer approach to dendric materials is attractive, as it involves one-step synthesis.[7] Thus, controlled generation of highly branched polymers with specific microstructures is one of the new challenges in polymerization chemistry.

In traditional approaches branching is introduced via monomers with complex structures.[7] In contrast, hyperbranched polymers are obtained[8−12] in the polymerizations of simple monomers such as ethylene and linear α-olefins, catalyzed by Ni− and Pd−diimine catalysts.[12−14] Branches in these polyolefins form as a result of fast chain isomerization reactions. The topology of the polymers is strongly affected by the olefin pressure: under low pressure highly branched structures are obtained, whereas high pressure gives rise to structures with linear side chains. Interestingly, in the polymerization catalyzed by Pd−diimine complexes the average number of branches is pressure independent, while for the Ni-based system it is strongly affected by the pressure. Branching in olefin polymerization catalyzed by diimine complexes can be controlled also to some extent by the polymerization temperature and the substituents on the catalyst. The questions that naturally arise are (i) to what extent can the various structures of polyethylenes differ from each other and (ii) whether it is possible to rationally design a single-site catalyst that would produce a polymer with a specific, desired microstructure. In this theoretical study, we address these questions.

Scheme 1 shows the basic steps of chain propagation/chain isomerization in the ethylene polymerization processes catalyzed by late-transition metal complexes. The catalyst resting state is an olefin π-complex, **B**/**B′**/**B″**,[12,13] formed from a β-agostic alkyl complex, **A**/**A′**/**A″**, by monomer capture. An insertion of ethylene (**B**/**B′**/**B″** → **C**/**C′**/**C″**) starts from the π-complex and gives rise to an alkyl complex with the primary carbon atom attached to the metal of the catalyst (**C**/**C′**/**C″**, **A**). The primary alkyl complex (**A**) may capture and insert the next ethylene molecule (**A** → **B** → **C**), or it may isomerize (**A** → **A′**) to a more stable complex with the secondary carbon attached to the metal (**A′**), thus producing a methyl branch. Prior to the next insertion (**A′**→**B′**→**C′**), such an isomerization reaction may proceed further (**A′** → **A″** → ...), elongating the branch and "moving the insertion point" along the polymer chain ("chain walking"). Hyperbranched structures are formed if the ethylene insertion into the M−C bond involving the secondary carbon is possible and if the isomerization is able to "pass" the tertiary carbon in the polymer chain. It should be emphasized here that the isomerization reactions favor formation of branches, as the stability

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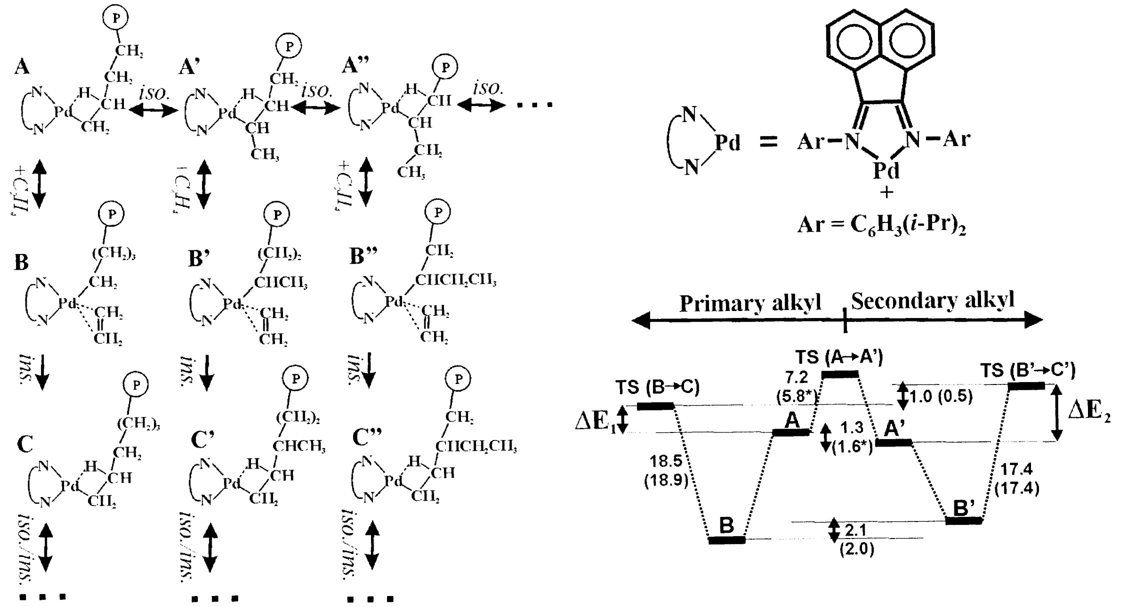
Scheme 1. Chain Propagation/Chain Isomerization Steps in the Mechanism of Ethylene Polymerization Catalyzed by Late Transition-Metal Complexes (Left) and the Energy Profile (Bottom Right) for Ethylene Polymerization Catalyzed by a Pd-based Diimine Complex (Top Right)[a]



[a] The experimental[17−19] and theoretical[15,16] (in parentheses) values for the insertion and isomerization barriers are presented in the energy profile (bottom right). The calculated energies for chain isomerizations (values marked with an asterisk) were obtained for the simplified model of the catalyst, N∧N−Pd, N∧N = [−NH=CH−CH=NH−],[15] while the calculated insertion data are for the real catalyst[16,23] shown in the figure.

of alkyl complexes changes in the following order: tertiary > secondary > primary. However, the stability order of the resuling olefin complexes is opposite (primary > secondary > tertiary).[15−19] Also, an additional branch can be introduced only as a result of "secondary" insertion. The "primary" insertion (at the chain ends) can only extend existing branches. Thus, the branching/microstructure of polyolefins is controlled by many (opposing) factors. Consequently, to model polymer growth one has to consider all possible elementary reactions and the presence of different alkyl species (primary, secondary, tertiary) in the polymerization cycle.

Quantum chemistry has establish itself as 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 topology of the resulting polymer, as well as on the influence of the reaction conditions are not practical without the aid of statistical methods. We have to this end proposed a combined approach in which quantum chemical methods are used to provide information on the microscopic energetics of elementary reactions in the catalytic cycle, that is required for a "mesoscopic" stochastic simulations of polymer growth. A model for performing the stochastic simulations has been developed.[22] The model is based on the assumption that the relative probabilities of reactive events are equal to the relative reaction rates (macroscopic); this assumption allows us to discuss the effects of temperature and olefin pressure. The details of the model and its application to the propylene polymerization catalyzed by Pd−diimine complexes have been described elsewhere.[22] We would like to point out only that the proposed approach allows one to understand the microscopic origin of the influence of both, the catalyst and the reaction conditions (T, p) on the polymer topology. In the course of a single stochastic simulation, a polymer structure is generated that can be directly analyzed in terms of branches as well as its microstructure. This can be very useful as a suplement to experimental studies, since precise experimental characterization of polymer topology represents a major problem.[7]

For the polymerization of propylene, the stochastic simulations[22] based on the DFT-calculated[15,16] energetics of elementary reactions reproduced the experimental observations and supported the interpretation of the branching mechanism.[11,12] In this study, we will discuss the results of stochastic simulations for the ethylene polymerization catalyzed by Pd−diimine complexes, based on both with the theoretical[15,16] and experimental[17−19] reaction energetics (Scheme 1). Further, we will present the results of the simulations performed with systematically changed insertion barriers, to model the influence of catalyst, going beyond the diimine systems.

Computational Details

The stochastic simulations of the polymer growth and isomerization were performed using the approach described in a recent paper[22] and implemented in our own code. This method uses as input data the energies/activation energies of the elementary reactions in the process and is based on the assumption that the relative probablilities of two reactive events (microscopic), π_i and π_j, are equal to their relative reaction rates (macroscopic), $\pi_i/\pi_j = r_i/r_j$; with the probability normalization constraint, $\sum_i \pi_i = 1$. Such an approach makes it possible to model the temperature and pressue effects. More specifically, the temperature dependence appears in the probabilities for all the events through the rate constants and equilibrium constatnts (Arrhenius/Eyring equations). The pressure affects directly the relative probabilities for unimolecular (isomerization)/bimolecular (ethylene capture + insertion) reactive events, and indirectly it influences all the probabilities because of probability normalization. Namely, the relative isomerization/insertion probability is given by[22]

$$\pi_{iso}/\pi_{ins} = r_{iso}/r_{ins} = k_{iso}/(k_{ins}Kp) \qquad (1)$$

where k_{iso} and k_{ins} are the insertion and the isomerization rate constants, K denotes the ethylene complexation equilibrium constant, and p stands for the olefin pressure.[24]

First, the simulations were performed for ethylene polymerization catalyzed by the Pd−diimine catalyst (see Scheme 1). The DFT-calculated energetics[15,16,23] and the corresponding experimental values,[17−19] respectively (see Scheme 1), were used as data for two sets of independent simulations. The temperature and pressure effects were studied by performing the simulations for T in the range of 48−498 K with an increment of 50 K and $p = 10^n$, $n = -4, -3, ..., 0$, respectively. In the next stage, we carried out simulations in which the barriers for the primary and secondary insertions were systematically changed, ΔE_1, $\Delta E_2 = 1-9$ kcal/mol (see Scheme 1), again for different pressure values, $p = 10^n$, $n = -4, -3, ..., 0$.[24]

For each system under a given set of reaction conditions (T, p), 500 independent simulations were performed; in each case a polymer chain of 1000 C atoms was produced. 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, secondary, tertiary*, etc. (starting from the main chain, primary branches, secondary branches, etc., respectively). 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 simulations performed for ethylene polymerization catalyzed by the Pd-dimine catalyst, and then the results obtained for different sets of insertion barriers. The latter results will allow us also to explain the different pressure effect observed for the Pd- and Ni-based diimine catalysts.

Polymerization of Ethylene Catalyzed by Pd(II)—Diimine Catalyst. The simulations performed for the ethylene polymerization catalyzed by the Pd-based diimine catalyst (Scheme 1) with the theoretically determined energetics for the elementary reactions give the average branching number of 131 branches/1000 C. This is in a reasonable agreement with the experimental value[9] of 122 br/1000 C obtained for a closely related system with methyl backbone substituents on the catalyst [N∧N−Pd, N∧N = −N(Ar)=CR−CR=N(Ar)−; Ar = $-C_5H_3(o\text{-}^iPr)_2$; R = $-CH_3$)], although it is slightly above the experimental range of 90−122 br/1000 C observed for various diimine systems[8−14.] To further validate our model, we performed the simulations with the experimental values[17−19] of the reaction barriers and stabilities of intermediates (see Scheme 1). We obtained the value of 121 br/1000 C, in very good agreement with experiment.[9] The fact that the simulations based on the theoretical data overestimate the number of branches comes as a result of the theoretically obtained energy difference between the transition states for primary and secondary insertions that is slightly underestimated (0.5 kcal/mol), compared to the experimental value of 1.0 kcal/mol.[23] This leads to an overestimation of the fraction of “secondary” insertions and, consequently, to an excess in the average number of branches.

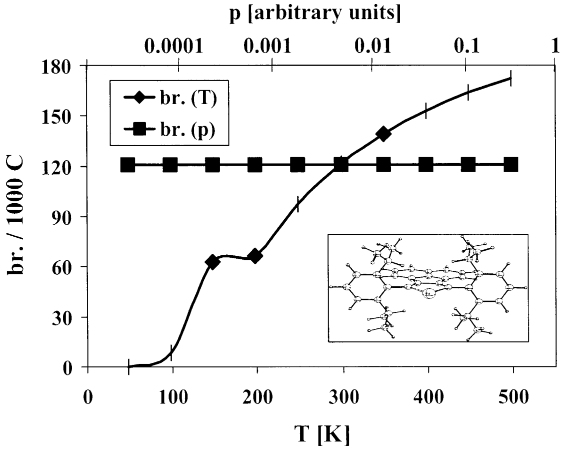


Figure 1. Pressure and temperature dependence of the average number of branches in the ethylene polymerization catalyzed by the Pd-based diimine catalyst obtained from the stochastic simulations based on experimental energetics (see Scheme 1).

Figure 1 presents results from simulations in which different reaction conditions (p, T) have been modeled. The temperature dependence of the average number of branches/1000 C clearly indicate an increase in the number of branches with an increase of temperature, in agreement with experimental observations.[8−12] Obviously, from the experimental point of view only a narrow range of temperatures is interesting. However, the simulations for a much wider range of T values demonstrate a trend very clearly and allows us to explain its microscopic origin. This trend can be understood from the energetics of the catalytic cycle. The TS for secondary insertion is higher in energy (by 1 kcal/mol) than the TS for the primary insertion. Thus, at low temperatures there is practically no secondary insertions and only primary insertions (elongating the main chain or existing branches) may happen. With an increase in temperature, the fraction of the secondary insertions (producing new branches) increases. Thus, as a result the average number of branches increases with temperature. However, it is worth mentioning that the average number of branches does not increase monotonically: there exist a very shallow minimum at T = 198 K (Figure 1). This indicates that the temperature dependence is not exclusively controlled by the primary/secondary insertion ratio; obviously, the insertion/isomerization ratio plays a role as well, and it is responsible for the local minimum observed at T = 198 K. We would like to point out here that, in a general case, depending on the values of all the parameters (insertion/isomerization ratio; primary/secondary insertion ratio), the temperature effect may be more complex than that observed here. However, it may be concluded that in the case of ethylene polymerization catalyzed by the Pd−diimine catalysts, the major factor controlling the temperature dependence of the branching number is the primary/secondary insertion ratio.

The pressure effect was studied by performing simulations for $p = 10^n$, $n = -4, ..., 0$.[24] As the plot in Figure 1 shows, within the wide range of pressures the simulations give a constant average number of branches. The microstructure of the polymer, however, is strongly affected by the pressure. Examples of the polymer structures obtained from the simulations are shown in

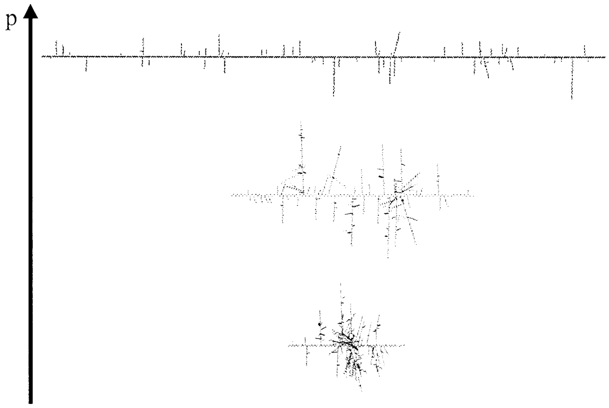


Figure 2. Influence of pressure on the polymer topology in the polymerization of ethylene catalyzed by the Pd−diimine catalyst. In each case a chain of 1000 carbon atoms is shown. For each structure the main chain of the polymer (longest chain) is projected along the horizontal axis. Different atoms shadings are used to mark different types of branches (primary, secondary, etc.).

Figure 2. It is clearly seen that at high pressures the polymer is mostly “linear” with a large fraction of atoms located in the main chain, and with relatively short and mostly linear side chains. With a decrease in pressure, the hyperbranched structures are formed, the number of atoms in the main chain decreases, while the length of branches and number of branch-on-branch structures increase. Both, the pressure independence of the average number of branches and the pressure influence on the polymer topology are in agreement with experimental results obtained for Pd−diimine catalysts.[8−12]

We would like to emphasize here, that the branching of polyethylene is controlled by different factors than that of polypropylene. Here, the primary/secondary insertion ratio is crucial, whereas in the case of propylene polymerization catalyzed by diimine catalysts, the ratio between the two alternative insertion pathways (1,2- and 2,1-) is more important.[22] As a result, an opposite temperature effect has been observed for ethylene (increase in branching number with T) and propylene (decrease in branching number with T).

Effect of Different Energetics of the Elementary Reactions (Catalyst Variation). To model branching features of the ethylene polymerization processes catalyzed by different single-site catalysts, we performed a set of simulations in which the barriers for the primary and secondary insertions were systematicaly changed, ΔE_1, $\Delta E_2 = 1-9$ kcal/mol (see Scheme 1). A change of the two insertion barriers corresponds to a change of the catalyst, as the processes catalyzed by different transition metal systems with different ligands are characterized by different free energy profiles. Certainly, in the real processes catalyzed by different transition metal complexes, the isomerization barriers and the relative stabilities of all intermediates are also different. However, a variation in the isomerization barrier affects the relative probabilities of isomerization vs insertions (both primary and secondary), giving the same result as the change in the respective insertion barriers for a constant isomerization barrier. Therefore, in the *model* simulations presented here, we used the constant isomerization barriers for the Brookhart catalyst (Scheme 1).

Figure 3 presents the pressure dependence of the average number of branches for different sets of the insertion barriers. The curves of Figure 3 can be understood when one notices the following: (i) In the limit of $p \to \infty$ (cf. Equation 1), the number of branches must be zero for each catalyst, as the ethylene π-complexes would be formed immediately after the insertion and there would be no isomerization reactions whatsoever. (ii) In the limit of $p \to 0$ chain walking would be infinitely fast compared to insertions (cf. Equation 1), and then the number of branches would be controlled exclusively by the ratio of primary vs secondary insertions (i.e., the insertion /isomerization ratio would not play a role). Thus, in the low-pressure range, the curves of Figure 3 converge to the average number of branches characteristic for a given pair of [ΔE_1, ΔE_2], while in the high-pressure regime they decay to zero. Consequently, for each catalyst there exist a range of (low) pressure values, for which the average number of branches is pressure independent. With an increase of the insertion barriers this range extends toward high-pressure values; for example, in Figure 3 all the branching numbers corresponding to $\Delta E_1 = 6$ kcal/mol are practically pressure independent.

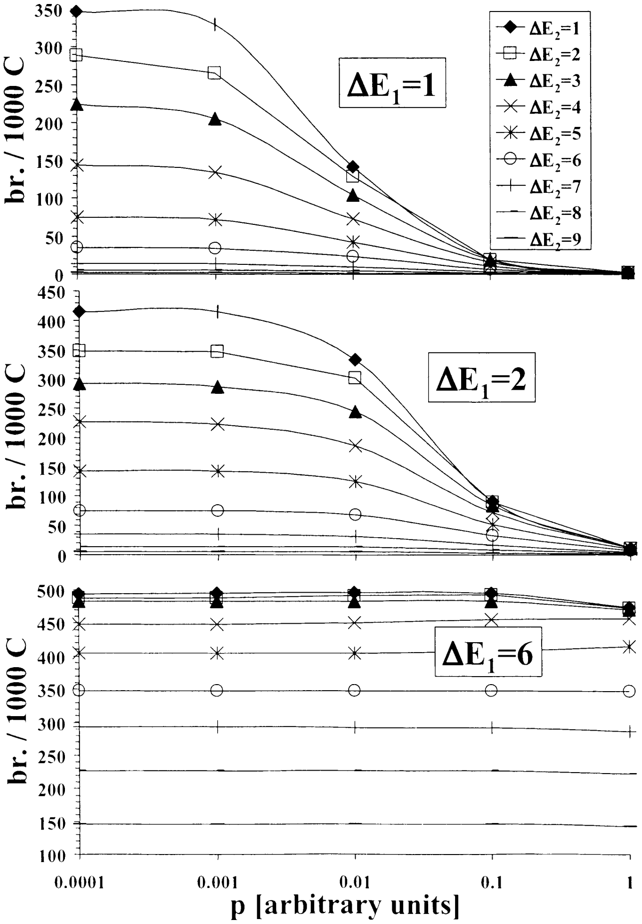


Figure 3. Pressure dependence of the average number of branches obtained from the model stochastic simulations with different primary and secondary insertion barriers, ΔE_1 and ΔE_1 (see Scheme 1).

It may be concluded from the results of Figure 3 that the faster chain walking is compared to insertions, the more extended is the range of pressures for which the average number of branches is constant. This allows us to qualitatively explain the difference between the Pd- and Ni-based diimine catalysts: it is known that the polymerizations of α-olefin catalyzed by the former are characterized by much lower chain isomerization barriers (ca. 7 kcal/mol) than those catalyzed by the latter

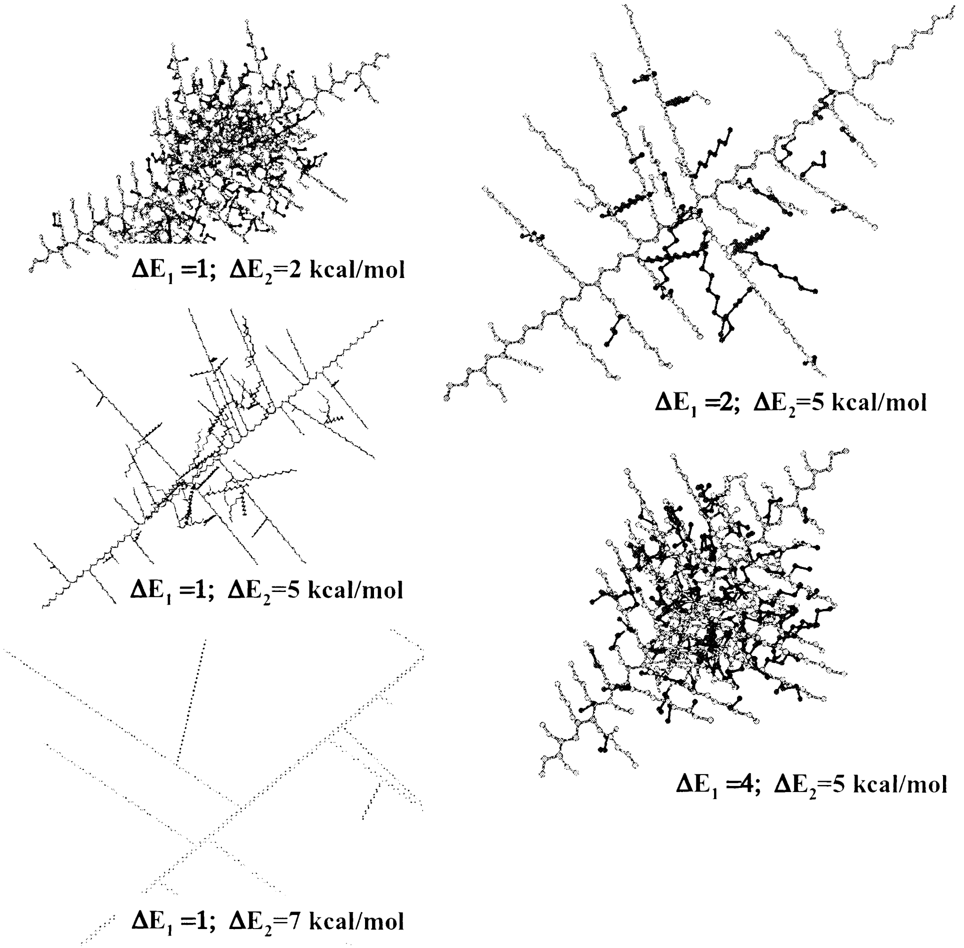


Figure 4. Examples of polymer structures obtained from the model stochastic simulations with different primary and secondary insertion barriers, ΔE_1 and ΔE_1 (see Scheme 1). Different atoms shadings are used to mark different types of branches (primary, secondary, etc.).

(ca. 12−15 kcal/mol).[12,25−28] Further, the insertion barriers for the Pd catalysts are substantially higher (by 4−5 kcal/mol) than those for the Ni-based systems.[12] Thus, for the Pd−diimine catalysts the isomerization is much faster compared to insertion than for Ni complexes. As a result, for the Pd systems, the number of branches is constant in the experimental range of pressure values, while for the Ni complexes the number of branches depends on the pressure in this range (and would be pressure independent for much lower pressures).[8−12] It should be pointed out that the above discussion is consistent with the kinetic arguments given by Guan et al.[8] for the Pd−diimine catalyst.

Let us now discuss the influence of the pressure on the polymer topology. Figure 4 displays examples of the polymer structures obtained for different combinations of ΔE_1 and ΔE_2, for $p = 0.0001$. To provide quantitative insight, Figure 5 presents the average length of different branches as a function of ΔE_2, determined for constant $\Delta E_1 = 1$ kcal/mol. Although all the structures of Figure 4 are practically hyperbranched, the topology varies to a large extent. As we discussed above, in the low-pressure regime the branching is controlled by the ratio of primary and secondary insertions. Thus, the difference between the barriers for the primary and secondary insertions controls the polymer topology. For small values of $\Delta E_{2,1} = \Delta E_2 - \Delta E_1$ branches are formed as a result of both, the primary and secondary insertions with comparable probablilities. With an increase in $\Delta E_{2,1}$, the probability of secondary insertions decreases and insertions at ends of branches happen more often; as a result an increase in the length of the linear segments can be observed. This is clearly seen in the plots of Figure 5: the average length of primary branches increases monotonically with an increase in ΔE_2; for the higher-order branches, local maxima can be observed, reflecting a tendency toward elongation of the main chain and primary branches for larger $\Delta E_{2,1}$.

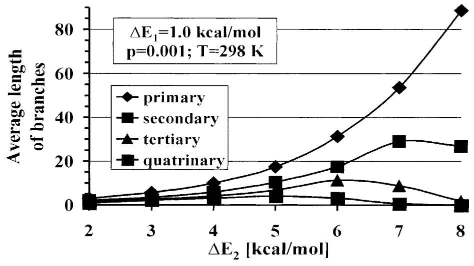


Figure 5. Average number of C atoms in different branches as a function of the secondary insertion barrier, ΔE_2.

Concluding Remarks

The results presented here demonstrate that the design of polyethylene materials with a specific microstructures is potentially possible. By use of various single-site catalysts characterized by different sets of insertion/isomerization barriers, one can control the average number of branches as well as the polymer topology. The question that naturally arises is how practical are the conclusions presented here. It should be pointed out that usually all the barriers of elementary reactions and the stabilities of the intermediates in the polymerization cycle are strongly coupled; i.e., each change of the catalyst structure will result in some changes of all of them. However, to some extent one can control the parameters that are crucial for the polymer branching/topology such as insertion/isomerization ratio and the relative probabilities of primary and secondary insertions. For example, the latter can be strongly influenced by the steric bulk on the catalyst ligands, which practically does not affect the former.[18,19] Also, there are hundreds of known transition metal complexes capable of polymerizing ethylene/α-olefins;[12,29] practically in each family of compounds, some variation of the ligands is possible without affecting the polymerization activity. Detailed mechanistic studies, both experimental[12,17−19] and theoretical,[15,16,20,21,25−28] have rationalized relationships between the structure of the catalyst and the energetics of the elementary reactions in the polymerization processes. Therefore, a rational design of single-site catalysts that would produce specific polyolefin microstructures should be possible.

The results obtained for the real Pd-based diimine catalyst reproduced the experimentally observed effects of reaction conditions on the polymer microstructure. Further, the simulations allow us to understand the microscopic origin of differences between the polymerization of ethylene and propylene (opposite temperature effect), as well as a difference in the pressure effects observed for Pd- and Ni-based catalysts. This demonstrates that a stochastic approach bridging the microscopic, quantum chemical calculations with modeling of the macroscopic systems can be successfully used to simulate polyolefin microstructures and their dependence on the reaction conditions. The approach makes it possible to understand the mechanistic details determining the experimentally observed trends.

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