

# Theoretical studies on the polymerization and co-polymerization processes catalyzed by the late-transition-metal complexes

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## INTRODUCTION

Although the early-transition-metal-based catalysts presently dominate industrial polymerization processes, there has been an increasing interest in development of catalytic systems based on the late-transition-metal complexes.<sup>1</sup> Similarly to the early-metal-based systems, the late-metal-complexes can yield high molecular-weight polymers. Moreover, they can lead to polyolefins with different microstructures, varying with different catalysts and potentially controlled by changes in the reaction conditions (temperature, olefin pressure).<sup>1-5</sup> Unlike the heterogeneous catalysts and the early-metal-complexes, the late-metal-based systems exhibit substantial tolerance toward polar groups, and as such they may be useful for the co-polymerization of  $\alpha$ -olefins with polar monomers.<sup>6-8</sup>

In the present study we address two aspects of the polymerization processes catalyzed by the late-transition-metal complexes:

- (i) influence of the catalyst structure and the reaction conditions (temperature and olefin pressure) on the polyolefin microstructure;
- (ii) co-polymerization of  $\alpha$ -olefins with the oxygen-containing monomers.

The combined DFT/stochastic approach has been applied for ethylene and propylene polymerization catalyzed by Pd-based diimine catalysts with different ligands. Further, the influence of the catalyst has been modeled by changing the crucial insertion barriers. The major goal of this study was to understand the relationship between the catalyst/reaction conditions (T,p) and the polymer microstructure.

A design of an efficient catalyst for the copolymerization of olefins with oxygen containing monomers is one of the challenges for the polymerization chemistry.<sup>1,6-8</sup> The studies in (ii) have been focused on understanding the factors responsible for the differences between the Pd-(active catalyst for ethylene-acrylate copolymerization)<sup>1,7,8</sup> and Ni-diimine (inactive) catalyst. The mechanism of the polar co-polymerization involves a competition between olefin and the polar monomer insertion. The latter can be bound either by its olefinic functionality (to form the  $\eta^2$ - $\pi$ -complex), or by the oxygen atom (to form the  $\eta^1$ -O-complex); formation of the  $\pi$ -complex is required for the insertion. The insertion of the polar monomer is followed by formation of the chelated structures; the chelate is opened by the next olefin molecule. The full mechanistic DFT studies, involving static calculations and molecular dynamic (MD) simulations have been performed for both Ni- and Pd-based systems.

## COMPUTATIONAL DETAILS

**Stochastic modeling of the polymer growth and branching.** A model for performing the stochastic simulations for the polymer growth and isomerization has been developed. The model uses the energetics of elementary reactions in the catalytic cycle, and is based on the assumption that the relative probabilities of the reactive events are equal to the relative reaction rate (macroscopic); this assumption allows us to discuss the effects of the temperature and olefin pressure. The details of the model has been described elsewhere.<sup>9</sup> The ethylene and propylene polymerization catalyzed by Pd-diimine catalysts have been modeled with the use of both, experimental<sup>1,10</sup> and computed<sup>11,12</sup> reaction barriers and stabilities of the intermediates in the catalytic cycle. To further model the influence of the catalyst, by going beyond the diimine systems, a set of simulations has been performed with changing the barriers for the insertion into the Me-C bond involving primary and secondary carbon (between 1 and 9 kcal/mol, relative to the  $\beta$ -agostic complex).

**Polar co-polymerization.** The details of the static DFT studies on the polar monomer binding mode performed with the ADF program<sup>13</sup> have been presented elsewhere.<sup>14</sup> In addition, the unconstrained MD simulations at T=300K have been performed to investigate the stability of the methyl

acrylate  $\pi$ - and O-complexes with the Pd- and Ni-diimine catalysts, modeled by N<sup>\*</sup>N-Me, with N<sup>\*</sup>N=NH-CH-CH-NH. Further, the constrained slow-growth MD simulations have been performed to model the interconversion between the  $\pi$ - and O-complexes; the substitution constraint  $R(\text{Me-C}) - R(\text{Me-O}) = \text{const.}$  was used, with the initial/final constraint value corresponding to the distances in the  $\pi$ - and O-complexes.

The details of the static DFT calculations for all the mechanistic steps in the ethylene-methyl acrylate co-polymerization catalyzed by the Pd-diimine catalysts have been presented elsewhere.<sup>15</sup> Similar calculations with the ADF program<sup>13</sup> have been performed for the generic Ni-based system. For both, Ni- and Pd-catalysts the chelate opening reactions were further investigated by the slow-growth MD simulations. Here, considered have been the ethylene insertions starting from the most stable, chelated  $\pi$ -complex, as well as the insertions starting from the higher energy complexes without the chelating Me-O bond. The latter correspond to the two-step chelate opening mechanism proposed in the recent paper; the slow-growth MD simulations have been performed for the Me-O bond-breaking step of this mechanism as well.

All MD results were obtained with the Car-Parrinello projector augmented wave (PAW) code,<sup>16,17</sup> with the computational settings as in other MD studies of ours<sup>18</sup> (BP XC functional, energy cutoff of 30 Ry; frozen core approximation, periodic boundary conditions, Blöchl charge separations scheme). The standard warm-up/equilibration procedure (10000 timesteps) has been applied prior to each simulation (25000 timesteps).

## DISCUSSION

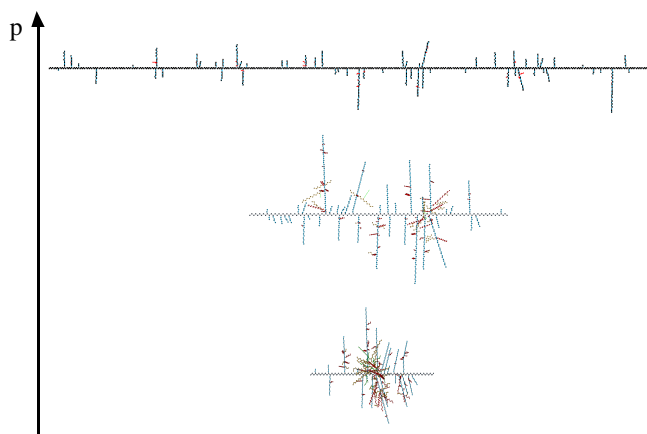
**Catalyst/T/p influence on the polymer microstructure.** The results for the propylene and ethylene polymerization with the Pd-based diimine catalyst are in very good agreement with experimental data.

In the Pd-catalyzed propylene polymerization the number of branches of 238 br./1000 C obtained here is only slightly larger than the experimental value of 213 br./1000.<sup>1</sup> Also, the temperature and pressure dependence of the number of branches and the polymer microstructure are in-line with experimental observations:<sup>1-5</sup> 1) an increase in polymerization temperature leads to a decrease in the number of branches; 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: 1) both 1,2- and 2,1-insertion happen with the ratio of c.a. 7:3; 2) there are no insertions at the secondary carbons; 3) most of the 2,1-insertion are followed by a chain straightening isomerization. Thus, for the Pd-diimine 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 1,2-/and 2,1-insertion ratio as well as by the fraction of the insertions at the secondary carbons. Also, the results for the model catalyst with unsubstituted phenyl rings demonstrate that the reversed preference of the insertion regioselectivity (2,1-insertion preferred instead of the 1,2-insertion) can lead to a dramatic change in the polymer branching (decreased to 122 br/1000C) and its microstructure.

For ethylene polymerization with the Pd-based diimine system the experimentally observed number of branches of 121 br./1000C was obtained from the simulations. As for propylene, the number of branches is pressure-independent. However, change in olefin pressure dramatically affects the polymer microstructure, leading to the hyperbranched structures at low ethylene pressures (see Figure 1). This is in agreement with experimental results<sup>1-5</sup>. The temperature effect is also in agreement with experimental observations: an increase in T leads to an increase in the number of branches.<sup>1-5</sup>

The results of the model simulations, in which the barriers for the insertion into the Me-C bond involving the primary and secondary carbon were systematically changed, reveal that: 1) for each catalyst there exist a range of pressures for which the number of branches is pressure independent; 2) the faster are the isomerizations (relative to the insertions), the more extended is this range. This explains the origin of the experimentally observed difference between the Pd- and Ni-based systems: in the polymerization processes catalyzed by the latter the pressure-dependent branching number was observed.<sup>1-5</sup> It is known,<sup>1</sup> that in the processes catalyzed by the Ni-catalyst, the isomerizations are relatively slower than for the Pd-based complexes; thus, for the Ni-catalyst

the number of branches is pressure-dependent in the experimental range of pressures.



**Figure 1.** An influence of the ethylene pressure on the polymer microstructure in the polymerization catalyzed by the Pd-diimine catalyst; for each structure a chain of 1000 C is shown.

The model simulations further demonstrate that by change of the catalyst (corresponding to the change of the barriers in the simulations) one can obtain a variety of polymers characterized by different microstructures and branching numbers (pressure-dependent or independent). This leads to the conclusion that a rational design of the catalysts producing desired microstructures is potentially possible.

The results of the present studies also 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.

**Polar copolymerization.** The results of the static DFT calculations on the polar monomer binding mode<sup>14</sup> clearly indicate that in the case of the Ni-based diimine catalyst the polar monomers are bound by the carbonyl oxygen atom, while in the Pd-systems the  $\pi$ -complexes are preferred. These preferences are independent of the steric bulk on the catalysts. The difference between the Ni- and Pd-systems has mainly a steric (electrostatic + Pauli repulsion) origin; there is practically no difference in the orbital-interaction contribution to the binding energy, as far as a comparison between the two binding modes is concerned. In the case of the fluorinated polar monomers, the complexation energies of both, the  $\pi$ - and O-complexes are decreased in comparison to methyl acrylate and vinyl acetate. Thus, in a prospective co-polymerization with fluorinated compounds, the incorporation of the polar monomer into a polyolefin chain would be relatively small. The use of neutral catalysts seems to be more promising. The results for Ni- and Pd-based systems with Grubbs ligands show that for both metals the  $\pi$ -complexes are strongly preferred over the O-complexes; the binding energies of the  $\pi$ -complexes are comparable with the corresponding systems involving the diimine catalysts.

The results of the MD simulations at 300 K show that all the complexes are stable on the free-energy surfaces and do not exhibit any tendency toward a spontaneous inter-conversion. In the Ni-case the O  $\rightarrow$   $\pi$  inter-conversion reaction is difficult and leads first to another 'inactive' intermediate, the  $\eta^2$ - complex in which the monomer is bound by the O- and one of the C atoms (1,4-binding).

A comparison of Ni- and Pd-diimine systems leads to the conclusion that the theoretical analysis of the polar co-monomer binding mode can be used as a screening test to select the best prospective catalytic candidates for the co-polymerization: the complexes with preference of the O-complexes can be excluded from further studies.

The static DFT calculations for the ethylene-methyl acrylate copolymerization catalyzed by the Pd-complex give the acrylate insertion barrier of 12.1 kcal/mol, in excellent agreement with the experimental value.<sup>8</sup> For the Ni-based catalyst the calculated acrylate insertion barrier is

lower by c.a. 3 kcal/mol than for the Pd-catalyst. Further, the static and dynamic studies reveal that the two-step mechanism of the chelate opening must be assumed in order to explain the difference between the Ni- and Pd-based systems. Namely, in the most stable ethylene complexes resulting from the chelates, the chelating M-O bond is still present in the axial position. The ethylene insertions starting from such structures have a very high barriers (ca. 30 kcal/mol for the 6-membered chelate with the generic Pd-catalyst). Much lower barriers, comparable to those of ethylene homopolymerization<sup>11,12</sup> (c.a. 18 kcal/mol for a generic Pd-catalyst) have been obtained for the insertions starting from the higher energy isomers in which the chelating bond has been broken. In both cases the insertion barriers computed for the Ni-catalyst are lower than for the Pd-system. However, the opening of the chelate prior to ethylene insertion has substantially lower barrier for Pd- (c.a. 9 kcal/mol) than for Ni-catalyst (an upper estimate of 19 kcal/mol appears to be larger than the corresponding insertion barriers).

Thus, the result of the static and dynamic DFT calculations suggest that there are two factors inhibiting the polar co-polymerization in the Ni-catalyst case: (1) the initial O-complex formation; (2) a difficult chelate opening by prior to insertion of the next monomer. These two reactions can be used as a theoretical screening test in a search for an active copolymerization catalyst.

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