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Computational Insight into Catalytic Control of Poly(ethylene−methyl acrylate) Topology

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Drent et al. have recently reported on a neutral Pd(II)-based complex with a bidentate sulfonate ligand that is able to copolymerize ethylene (E) and methacrylate (MA) into linear EMA polymers. We report here on a theoretical study that examines the Drent system and compares it to the cationic Brookhart catalyst, which affords branched EMA polymers with MA units at the end of the branches.

Introduction

The copolymerization of polar and nonpolar monomers in the presence of late-transition-metal systems is an area of ever-increasing interest, as reflected in the number of patents and research papers.[1] Researchers have focused on finding catalysts that can provide the means to make a wide variety of polymer architectures with increasingly more precise control and greater complexity.[2−5] Defects in polymer microstructure that result from random branching induced by chain transfer reactions are known to have a significant effect on the polymer's crystallization and melting behavior (melting points are depressed with increasing steric bulk of such imperfections).[6−8] Theoretical studies performed on the already known catalytic systems can help in tailoring the coordination environment of the metal center in such a way as to obtain control over the molecular weight, molecular weight distribution, comonomer incorporation, and copolymer topology.

Among different catalysts proposed for the copolymerization of acrylates with olefins, the cationic diimine Brookhart systems (see **1b** of Figure 1) are thought to be particularly promising.[2] Nevertheless, in their presence, the amount of incorporated acrylates is rather low and the resulting copolymers, depending on copolymerization conditions, show moderately branched to hyperbranched topology with the polar groups situated at the end of the branches. According to many mechanistic experimental[2] and theoretical[9−11] studies on the system, formation of branches in the ethylene−methacrylate (EMA) copolymers is essential for the copolymerization process to occur, as incorporation of methacrylate into the growing polyethylene leads to the formation of strong chelates in which an oxygen atom from the coordinated polymer chain binds to the metal, hindering coordination of the next monomer.

After the success of Brookhart in copolymerizing ethylene with methacrylate, highly branched versions of EMA copolymers were reported in 2001 by Killian et al.[1] To reach control over copolymer microstructure, their interest has further been directed toward obtaining a more linear topology of the EMA copolymer. The first successful catalyst to achieve the goal was reported 1 year later, by Drent et al.[3] The authors demonstrated that Pd(II) complexes containing anionic bidentate sulfonate coligands (see **1a** of Figure 1) provide EMA copolymers with methacrylate incorporated into a linear polyethylene. The content of methacrylate within the formed copolymers was similar to that obtained with the classical Brookhart systems ($<$20%), but differences in their architectures were evident.

The unusual behavior of the Drent complexes has stimulated the computational investigation reported here into the elementary processes involved in the ethylene/methacrylate copolymerization. Given the importance of functional olefin copolymers and the dependence of polymer properties upon topology, it is both of fundamental and practical importance to explore how the catalytic systems function. Particular attention is given to competitions between the chain propagation and the catalyst "chain-walking" processes. The latter phenomenon, first discussed by Brookhart,[12] allows one to introduce branching by the catalyst instead of by monomer structure, since the catalytically active center can control the position for the next monomer addition.

We shall explain why the Drent catalyst offers linear EMA copolymers with a low incorporation of methacrylate. Our explanation will invoke that the insertion of methacrylate catalyzed by the Drent system is reversible, just as the

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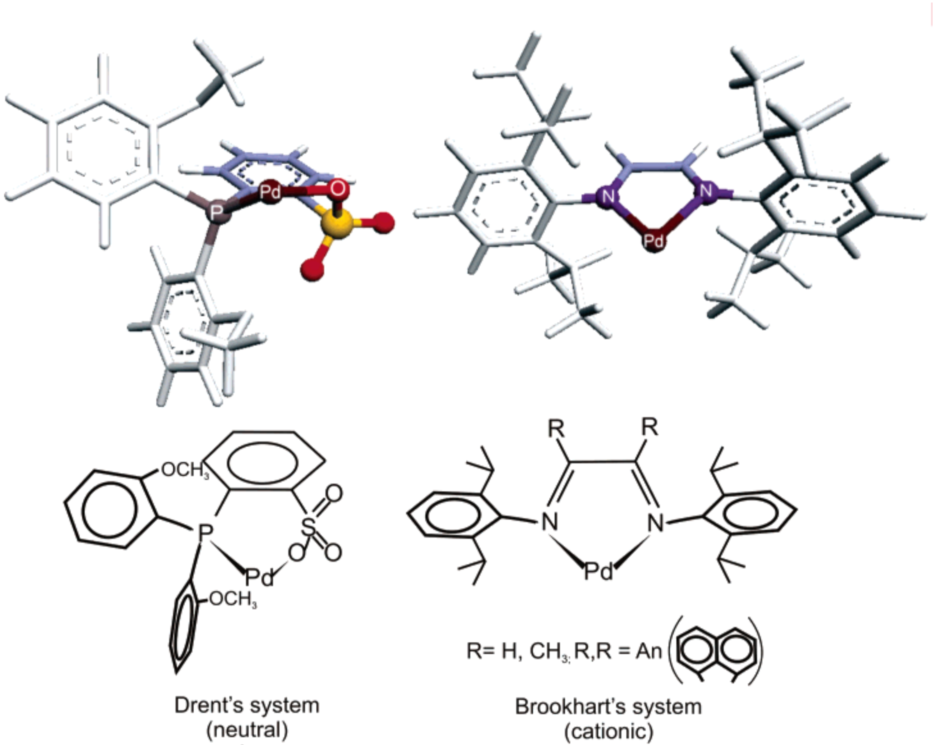

1a **1b**

Figure 1. Schematic views of the neutral Drent system (**1a**) and the cationic diimine Brookhart system (**1b**).

corresponding CO insertion catalyzed by the Drent system was shown to be reversible in a previous study.[13,14] This is, to our knowledge, the first time where a strong case can be made for the reversibility of olefin insertion into a metal−alkyl bond.

Computational Details

Structures and energies of reactants, transition states, and intermediates for the investigated reaction pathways were obtained from density functional calculations using the Amsterdam density functional (ADF) program package.[15] All stationary points were optimized without any geometry constraints using the procedure developed by Versluis and Ziegler.[16,17] The real Drent catalyst (**1a**) was modeled by a hybrid QM/MM potential,[18] in which the benzenesulfonate coligand was treated quantum mechanically, whereas the rest of the system (i.e., the bulky side groups) was approximated by the MM force field. For all of the atoms in the QM region, use was made of the local density approximation augmented with the gradient corrections of Becke (exchange) and Perdew (correlation)[19−21] for both energies and structures. A triple-ζ STO basis set with polarization function was employed for Pd, while all other atoms were described by a double-ζ plus polarization STO basis. The frozen core approximation was employed for the 1s electrons of the C and O atoms, up to and including the 2p electrons of the P and S atoms and the 3d electrons of Pd. Finally, first-order scalar relativistic corrections were added to the total energy of the system.[22−24] The atoms in the MM region were approximated by the Sybyl force field. Electrostatic interactions were not included in the molecular mechanistic potential, in order to save computational time. This approximation seems to be justified, on the basis of the recent experimental studies by Nozaki et al.[25] According to the experimental data reported by the authors, the presence of *o*-methoxy substituents on the aryl rings has no impact on the topology of EMA copolymers, since the linear copolymer is obtained even with unsubstituted aryls.

Results and Discussion

To analyze the copolymerization of ethylene and methacrylate mediated by the complexes proposed by Drent,[3] it was necessary to take into account a possible migration of the catalyst along the growing polymer chain (see Scheme 1).

This migration or "chain-walking" can lead to chain branching if the rate of migration is larger than that of chain propagation. The relative rates of the two processes can be influenced by temperature,[26] monomer pressure,[26] and ligand design.[27] Chain-walking is not a desired process for copolymerization of ethylene with methacrylate where linear EMA copolymer is the target.

Ethylene Homopolymerization. In Scheme 2 and Table 1, we present enthalpic changes for different reactions involving a Pd−R complex, where R is an alkyl group consisting of three or more carbon atoms.

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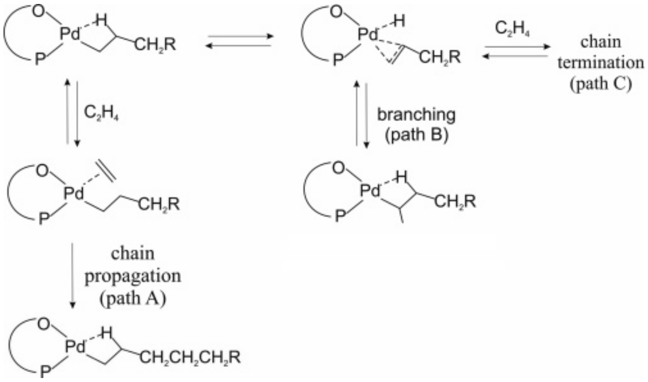
Scheme 1. Competitions between Different Possible Alkyl Fates during Homopolymerization of Ethylene



Scheme 2. Enthalpic Changes during the Ethylene Homopolymerization (Solid Line) and Isomerization (Dashed Line) Processes

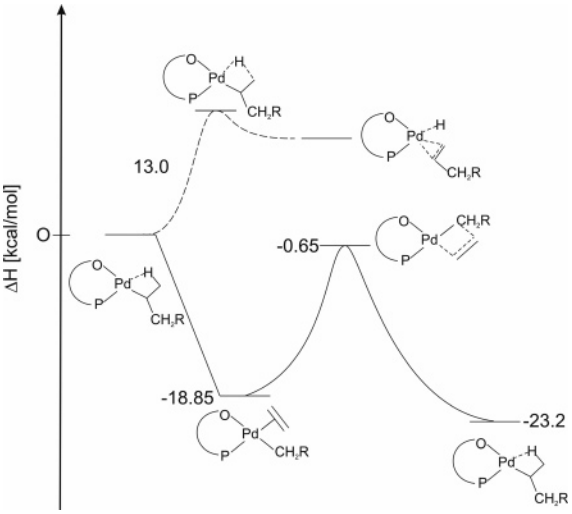


Table 1. Ethylene Complexation Energies and Activation Parameters for Ethylene Insertion and Catalyst Isomerization with Respect to the Studied Neutral Drent Complex, 1a, and the Cationic Diimine Brookhart Catalyst, 1b

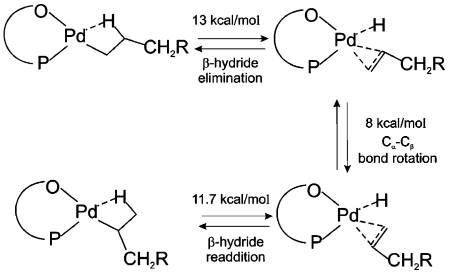
cat.	π complex (kcal/mol)	TS_{ins} (kcal/mol)	TS_{iso} (kcal/mol)
(dppbs)Pd + *o*-methoxy	−18.85	18.2	13.0
diimine Pd(II)	−18.91[a] (−17.2)	18.93[a] (−17.8)	5.8[b]

[a] Taken from ref 28. Values in parentheses correspond to theoretical values from ref 10. [b] Taken from ref 29.

With a β-H agostic complex, the thermodynamic product of ethylene insertion, as the starting point, one can expect either coordination of another ethylene from the reaction mixture or formation of an olefin hydride complex by β-hydrogen elimination. We shall in this section discuss the possible reactions involving the π complex. The processes due to the olefin hydride complex will be discussed in the next section.

Due to the asymmetry of the Drent ligand (see Figure 1), there are two possible modes of monomer coordination to the Pd−alkyl species with ethylene either cis or trans relative to the chelating oxygen. However, it is significantly easier for an incoming ethylene molecule to attack cis to oxygen, as the trans position is sterically crowded by the large phenyl groups attached to phosphorus. This conformation is also favored by having the alkyl group experiencing the less trans-directing oxygen atom. The complex with ethylene residing cis to the O atom is calculated to be the more stable configuration by 5.1 kcal/mol. Further, the ethylene complexation energy was found to be ca. 19 kcal/mol for the more stable π complex (see Table 1).

Scheme 3. Key Steps Involved in the Catalyst Walking from Carbon α to Carbon β[a]



[a] R represents the remaining part of the coordinated copolymer chain.

After complexation, ethylene can now undergo insertion into the Pd−alkyl bond. We find, in agreement with previous studies,[26] that the barrier of insertion with olefin trans to oxygen is lower than the insertion from the more stable π complex with olefin cis to oxygen. Further, the most facile chain propagation step involves cis/trans isomerization of the olefin complex followed by insertion. We shall discuss isomerization later and note here that the insertion step is rate determining with a barrier of 18.2 kcal/mol relative to the most stable π complex (Scheme 2). After the insertion TS is passed, a new β-agostic Pd−alkyl species is formed with a reaction enthalpy of −23.2 kcal/mol relative to free ethylene and the original Pd−alkyl complex (Scheme 2). It is possible for the π complex to undergo a transfer of a β-hydrogen on the alkyl chain to the olefin.[28] Such a process might eventually lead to chain termination.[28] We shall not discuss the process further here, as we primarily are interested in the relative rates of chain propagation and chain branching.

Chain Isomerization. In this section we discuss the other process involving the Pd−alkyl complex, namely β-hydrogen elimination, which can lead to chain isomerization.

Basically, the chain isomerization includes three key steps that allow the catalytic site (active growing site) to migrate on the polymer chain during propagation. As a consequence, the next monomer unit is assembled onto any part of the polymer backbone instead of at the end (see Scheme 3). It starts with partial transfer of H_β to the metal: i.e., partial β-hydride elimination. The estimated barrier for the process amounts to 13 kcal/mol (see Scheme 2 and Table 1) relative to the most stable alkyl complex. This value is significantly higher than the barrier observed in the case of the cationic (diimine)Pd Brookhart system (ca. 6 kcal/mol).[12] The fate of the formed olefin hydride complex is now essentially twofold. A displacement of the coordinated olefin by the next monomer would terminate the chain. Previous calculations have shown that such a termination process is unlikely, due to the strong π-complexation energy of the new olefin unit.[29,30] Alternatively, the hydride olefin complex might revert back to the primary β-agostic complex or it might transform into a new β-agostic complex with a secondary carbon atom coordinated to the active metal center. In the latter case the olefin of the hydride olefin complex undergoes a relative rotation around the olefin $C_\alpha-C_\beta$ bond, as shown in Scheme 3. The olefin rotation requires an energy of 8 kcal/mol in order to take place and is similar to that reported

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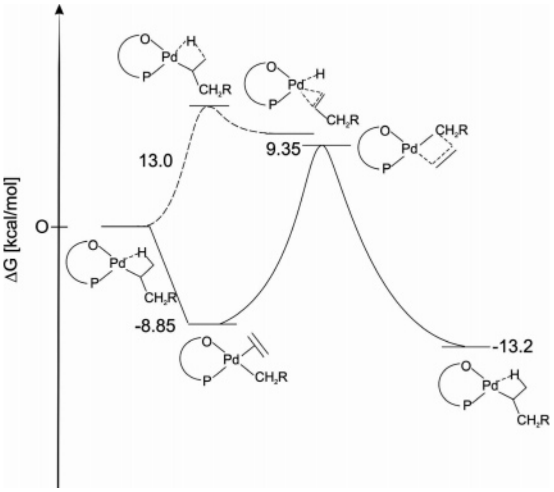
Scheme 4. Free Energy Changes during the Ethylene Homopolymerization Process



for the classical Brookhart catalyst (ca. 8 kcal/mol). Thus, the C−C bond rotation is a lower energy process than β-H elimination for the studied neutral catalyst. To complete the isomerization, transfer of the hydrogen back to the olefin occurs, resulting in a structure with the metal bound to a secondary carbon. The β-agostic hydride complex with a secondary carbon atom is more stable than the starting primary carbon β-agostic hydride by ca. 3 kcal/mol. The isomerization can be repeated several times as the metal moves along the chain.

Solely on the basis of the enthalpic energy differences presented in Scheme 2, it would seem that propagation is favored over isomerization to such a degree that the Drent system should produce only linear polymers in homo-olefin polymerization. A similar conclusion could be reached from the enthalpic data published[29] for the cationic Pd(II)-based Brookhart system, although the Brookhart system can produce branched polymers. What is missing in the considerations is the fact that olefin uptake is a bimolecular reaction for which entropy must be taken into account.

Free Energy Changes. Scheme 4 provides an approximate free energy profile in which we have adopted an entropic contribution ($-T\Delta S$) to the olefin complexation of 10 kcal/mol. The chosen value is in the typical range for olefin complexation to Pd−alkyl complexes reported experimentally.[26,31] It is relatively easy to obtain the entropy of olefin complexation in the gas phase from standard statistical mechanical methods based on frequency calculations. However, we are not aware of reliable methods that take into account solvation. We must for this reason rely on experimental estimates. The contributions from ΔS to the free energy of any intramolecular reaction were neglected in Scheme 2.

It follows from Scheme 4 that including the entropic contribution to the ethylene complexation energy raises significantly the energy of the π complex relative to the alkyl complex, such that the β-hydride elimination step now appears much more probable. Nevertheless, in the case of the Drent system the isomerization process is still less feasible than the normal chain propagation. If we assume that association of ethylene to Pd−alkyl is much faster than β-hydride elimination, then the migratory insertion path to unbranched polymers from the Pd−alkyl species should have a lower barrier than combined barriers for β-hydride elimination and the associative isomerization to a Pd−alkyl complex with a secondary carbon atom.

In the case of the classical Brookhart system, according to the published theoretical results by Michalak et al.,[29] the enthalpic energy profile differs only in the barrier for β-hydride elimination, which is ca. 7 kcal/mol lower in energy than that found for the Drent system (see Table 1). As a consequence, the barrier height for ethylene migratory insertion on the free energy diagram is higher by ca. 5 kcal/mol than for the β-hydride elimination for the cationic (diimine)palladium species. The low-energy route to secondary (alkyl)palladium intermediates is consistent with the extensive branching found for polymerization with the classical Brookhart palladium catalysts. It should be noted that another neutral catalyst, namely that of Grubbs, was found to have a barrier for β-hydrogen elimination similar to that of the Drent system.[32]

Incorporation of Methacrylate. To complete our analysis of the ethylene/methacrylate copolymerization, we now turn to the insertion of MA into the Pd−alkyl bond, as illustrated in Scheme 5.

Again, there are several possibilities for the coordination of MA to the Pd−alkyl species. Due to the asymmetric character of the Drent ligand, the olefin can be coordinated either cis or trans relative to the ligated oxygen. Moreover, it can form a π complex, which is a prerequisite for the following migratory insertion step, or it can form a σ complex via oxygen complexation. The latter mode is undesirable, as it would deactivate the catalyst. Fortunately, the π complex is calculated to be ca. 3 kcal/mol lower in energy than the most stable σ complex. An interesting observation here is that the polar olefin forms a weaker π complex with the catalyst than does ethylene (by ca. 1.5 kcal/mol).

After the complexation step, there are two possible routes for the insertion of MA: i.e., the 1,2-insertion and the 2,1-insertion. The 2,1-insertion, where the migrating group ends up on the unsubstituted carbon of the monomer, is preferred by ca. 7 kcal/mol. The preference for a 2,1-insertion over the 1,2-insertion path is in part due to a reduction in the steric repulsion between the migrating group and the substituent on the olefin. Electronic factors might also play a role, as explained by Michalak et al.[29] The energy barrier for the following MA insertion step is predicted to be 13 kcal/mol, which is significantly lower than for the ethylene insertion (ca. 18 kcal/mol; see Table 1). Taking into account that only small amounts of polar groups were successfully incorporated into the EMA copolymer even if an excess amount of MA was used in the reaction, the low barrier for methacrylate insertion is quite surprising and we shall return to the point shortly. After the insertion of methyl acrylate into the Pd−alkyl bond in a 2,1-fashion, rearrangements of the kinetic γ-agostic product occur to form several intermediates in which an empty coordination site at the palladium is occupied by the oxygen from the coordinated polymer chain (see Scheme 6).

For comparison, we cite the corresponding energy values for the cationic palladium diimine system reported by Michalak et al.[9,29] It is worth noting that the five-membered chelate is predicted to be more stable than the kinetic product by 6.5 kcal/mol, whereas in the case of the cationic Brookhart system the six-membered chelate is the most stable configuration, being lower in energy than the kinetic product by 21 kcal/mol. This complexation inhibits any subsequent monomer addition to the catalyst and is consistent with the Brookhart observation that methyl acrylate appears at the end of chain branches. This is in contrast to the Drent system, where methyl acrylate insertion

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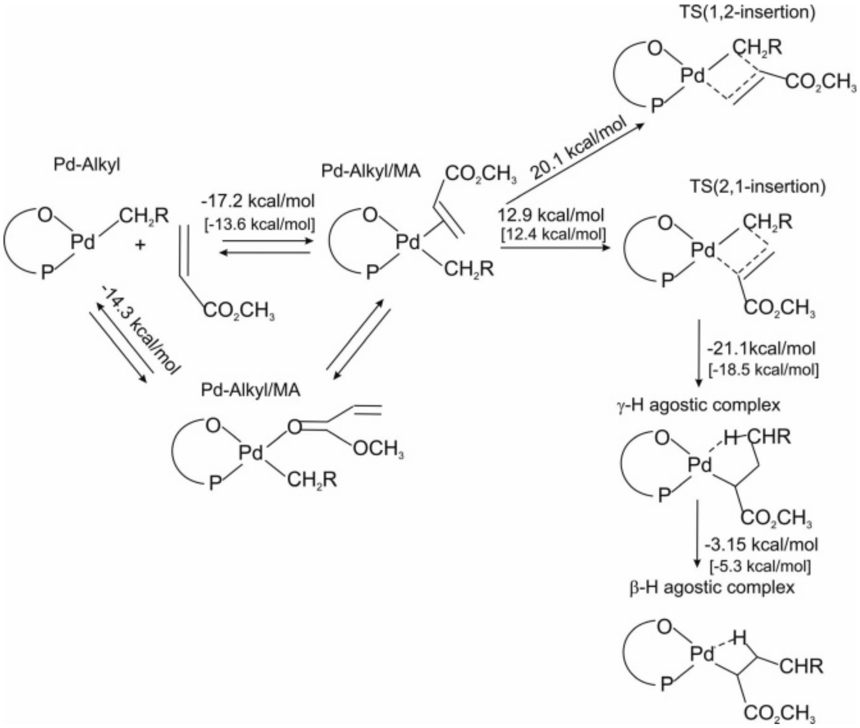
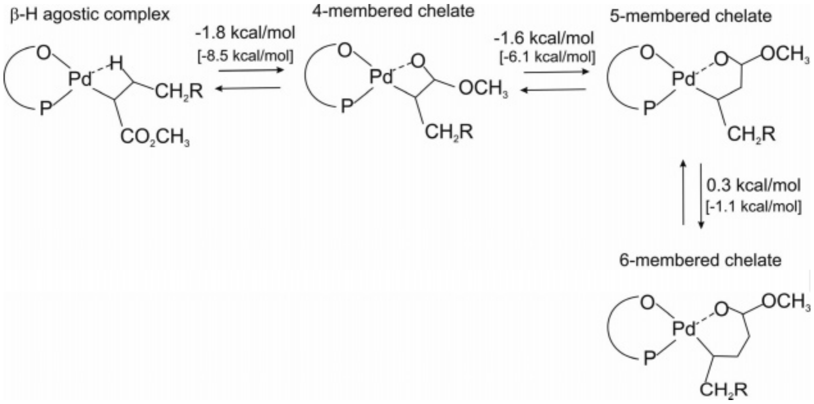
Scheme 5. Enthalpic Changes during the Incorporation of Methacrylate into Polyethylene[a]



[a] Numbers in parentheses correspond to the stabilization energies for the cationic diimine palladium Brookhart catalyst reported in refs 9 and 27.

Scheme 6. Rearrangements of the γ-Agostic Product of Methacrylate Insertion into the Pd−Alkyl Bond[a]



[a] Numbers in parentheses correspond to the stabilization energies for the cationic diimine palladium Brookhart catalyst reported in ref 9.

leads to products with weak interaction between the carbonyl oxygen and metal. This is consistent with the experimental observation that methacrylate insertion is slow but allows for continuous MA/ET copolymerization. We find the barrier of ethylene insertion into the Pd−$CH(CO_2CH_3)CH_2R$ bond to be ca. 12 kcal/mol higher than the barrier (18 kcal/mol) for insertion into the Pd−CH_2CH_2R bond. This might explain the low incorporation of MA as well as the slow rate of MA/ethylene copolymerization.

Cis−Trans Isomerization. The asymmetric character of the **1a** ligand (see Figure 1) might have important consequences on the studied copolymerization process, as it requires prior isomerization of coordinated monomer from the more stable to the less stable coordination mode in order to lower the reaction barrier for monomer insertion. If the barrier of cis/trans isomerization is low relative to the barrier heights for the monomer insertion process, one may assume fast equilibrium between the cis and trans monomer complexes. As a consequence, the energy barrier for monomer insertion is calculated as the difference in the energy of the more stable conformer and the lower insertion transition state. We provide in the following some additional justification for the procedure.

In all studied cases, the barrier of cis/trans isomerization was found to be significantly lower than the barrier heights for monomer insertion from the two possible coordination modes. The computed energy barriers for the cis−trans isomerization processes were found to be relatively low (ca. 12 kcal/mol) for the Pd−propyl/C_2H_4, Pd−propyl/methacrylate, and Pd−$CH(CO_2CH_3)CH_2CH_2CH_3/C_2H_4$ complexes. In all isomerization transition state structures both the coordinated polymer chain and the monomer molecule are rotated in a concerted manner by about 90° into two axial positions. As an example, the transition state of the cis−trans isomerization of methacrylate within the Pd−propyl/MA complex is displayed in Figure 2.

The rotation of the coordinated monomer and polymer chain is facilitated by the hard donor character of the chelating oxygen atom that is only weakly bounded to the metal center, thus allowing some flexibility of the Drent ligand.

Kinetics of Methacrylate/C_2H_4 Copolymerization. As mentioned previously, the amount of incorporated methacrylate

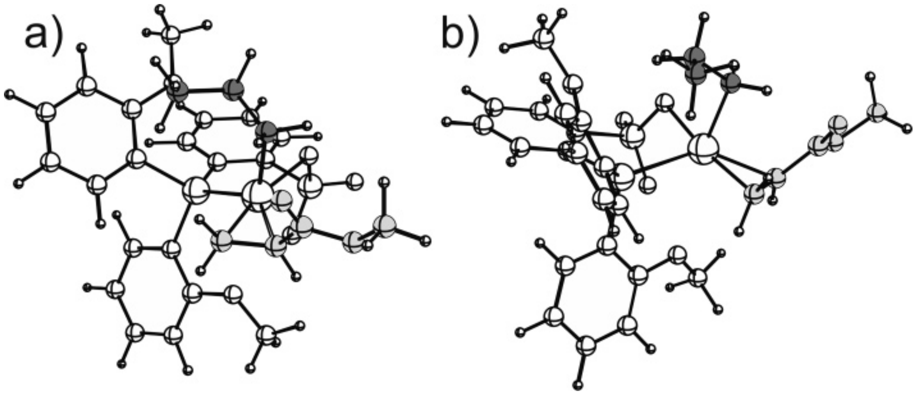
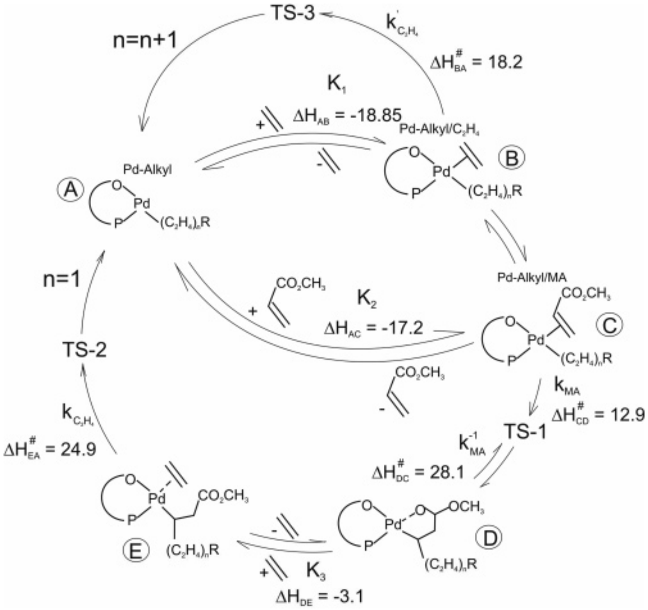


Figure 2. Transition state for the cis−trans isomerization of coordinated methacrylate to the Pd−propyl complex: (a) front view; (b) back view. The coordinated methacrylate is represented by the bright gray spheres and the coordinated propyl chain by the dark gray spheres.

Scheme 7. Catalytic Cycle of the Methacrylate−Ethylene Copolymerization in the Presence of 1a



observed experimentally seems low, in view of the fact that methacrylate insertion into the Pd−propyl species is favored over ethylene insertion by 5.3 kcal/mol. To understand this discrepancy and to complete the analysis of the ethylene/methacrylate copolymerization, we shall in the following formulate a kinetic scheme including all processes involved in the ethylene/methacrylate propagation step (see Scheme 7).

The catalytic cycle starts with the Pd−propyl complex (structure A) followed by complexation of ethylene (path A → B) and methacrylate (path A → C) to this species. Next, migratory insertion of ethylene (path B → A) and methacrylate (path C → D) into the Pd−propyl bond takes place, with the latter process being the fastest. After methacrylate insertion, the kinetic product, i.e., the γ-agostic complex, undergoes some rearrangements with the formation of a five-membered chelate (structure D) that is thermodynamically preferred over the γ-H agostic complex by ca. 5.5 kcal/mol. A complexation of ethylene to the thermodynamic product of the prior methacrylate insertion (path D → E) is exothermic by only 3.1 kcal/mol. As a final step, the E complex undergoes migratory insertion of ethylene (path E → A) after overcoming the barrier height of ca. 24.9 kcal/mol. The possibility of methacrylate coordination to the D complex and its subsequent insertion is neglected, due to the lack of consecutive methacrylate units in the experimental spectrum of the formed copolymer chain.

The final expression for the ratio of the global rates for nonalternating, r_{na}, and alternating pathways, r_a, takes the form

$$f_{na} = \frac{r_{na}}{r_a} = \left(\frac{k'_{C_2H_4}}{k_{MA}}\frac{[C_2H_4]}{[MA]}\frac{K_1}{K_2}\right)\left(\frac{K_3k_{C_2H_4}[C_2H_4]}{K_3k_{C_2H_4}[C_2H_4] + {k_{MA}}^{-1}}\right) \quad (1)$$

This equation consists of two main components and is analogous to the equation describing copolymerization of ethylene with CO discussed in detail elsewhere.[13,14] The first component, i.e.

$$\frac{r_{na}}{r'_a} = \frac{k_{C_2H_4}}{k_{MA}}\frac{[C_2H_4]}{[MA]}\frac{K_1}{K_2} = F_B \quad (2)$$

is based on the assumption that the degree of alternation can be explained in terms of the competition between MA and ethylene insertion into the Pd−alkyl bond. The second part of eq 1

$$F_{cor} = \frac{K_3k_{C_2H_4}[C_2H_4]}{K_3k_{C_2H_4}[C_2H_4] + {k_{MA}}^{-1}} \quad (3)$$

is a function of the following rate and equilibrium coefficients: (i) the rate of MA deinsertion (${k_{MA}}^{-1}$); (ii) the equilibrium constant for the formation of the ethylene complex E from D and free ethene (K_3); (iii) the rate of insertion of ethylene into the product of the prior 2,1-insertion of methacrylate into the Pd−alkyl bond of E ($k_{C_2H_4}$).

This analysis indicates that multiple ethylene insertions in eq 1 can be enhanced, provided that F_{cor} is large enough. This can happen if the rate of methacrylate deinsertion (${k_{MA}}^{-1}$) from D is larger than the effective propagation rate $K_3k_{C_2H_4}[C_2H_4]$ for ethylene insertion into the Pd−CH(CO$_2$CH$_3$)CH$_2$CH$_2$CH$_3$ bond of D. This is in fact what is observed in the present computational study. We note also that the effective rate of ethylene insertion will decrease with temperature as K_3 due to entropy effects decreases. Thus, MA incorporation is predicted to decrease with increasing T (Table 2), in agreement with experimental observations.[3] This is, to the best of our knowledge, the first time that a polar monomer other than CO has been implicated in deinsertion. Kinetic data obtained according to eq 1 by assuming 1:1 concentration of comonomers are given in Table 2.

Conclusions and Outlook

Nonlocal DFT calculations were performed on the ethylene/methacrylate copolymerization catalyzed by the neutral Pd(II)

Table 2. Kinetics of the Ethylene/Methacrylate Copolymerization in the Presence of 1a

T (°C)	K_1/K_2	$k'_{C_2H_4}/k_{MA}$	F_B	K_3	$k_{C_2H_4}$	k_{MA}^{-1}	F_{cor}	f_{na}
25	16.2	1.3×10^{-4}	2.1×10^{-3}	2.5×10^{-6}	5.5×10^{-6}	1.6×10^{-8}	1.777×10^{4}	37.5
80	10.5	5.2×10^{-4}	5.5×10^{-3}	1.1×10^{-6}	2.9×10^{-3}	3.0×10^{-5}	9.309×10^{4}	513.0

complexes designed by Drent et al.[3] The analyzed processes included chain propagation via homopolymerization of ethylene and its copolymerization with methacrylate, as well as formation of a olefin hydride complex that is a prerequisite to catalyst isomerization along the growing polymer chain. To put the calculated energy profiles for the studied *o*-methoxy substituted Drent system into perspective, the results were compared with published theoretical data on the classical Pd(diimine) Brookhart catalysts, which provide highly branched EMA copolymers with a similar amount of incorporated polar monomers.

The energy diagrams for the ethylene homopolymerization in the presence of both catalytic systems reveal significant differences in the energy barriers for β-hydride elimination: i.e., the first step in the catalyst migration along the formed copolymer chain (ca. 13 kcal/mol for the Drent system and ca. 6 kcal/mol for the Brookhart diimine catalyst). Both the ethylene complexation energies and the barriers for ethylene insertion into the Pd−alkyl bond are comparable in both cases and point to the formation of stable π complexes as resting states. However, β-hydride elimination and subsequent chain branching was found only to be competitive with insertion for the Brookhart system. The generation of branches during the ethylene homopolymerization is necessary for continuous ethylene/methacrylate copolymerization catalyzed by the diimine Brookhart system, since the catalyst forms, after the MA incorporation into the Pd−alkyl bond, strong six-membered chelates in which oxygen from the coordinated polymer chain interacts with the catalytically active center. Different from the Brookhart system, for which the thermodynamic six-membered product is favored over the kinetic γ-agostic product by ca. 21 kcal/mol, rearrangements of the γ-agostic complex in the presence of the Drent catalyst are associated with a low energy gain (ca. 6.5 kcal/mol). This is consistent with the fact that the catalyst allows for continuous copolymerization after incorporation of MA into a linear polyethylene but only a small amount of the polar monomer is observed in the resulting polymer. The low incorporation of MA is attributed to the rate of ethylene insertion into D compared to deinsertion of MA from D, especially at higher temperatures. To the best of our knowledge, this is the first time that deinsertion of a polar monomer other than CO has been implied.

In conclusion, it is evident that the neutral Drent complex is prone to catalyze the formation of linear polymers, due to the high-energy barrier for isomerization to secondary (alkyl)-palladium intermediates. Furthermore, the catalyst is able to copolymerize ethylene with methacrylate in a continuous fashion without generation of branches, as the oxo chelates formed after methacrylate insertion into the Pd−alkyl bond are considerably destabilized relative to the analogous complexes formed with the cationic Brookhart systems. Work is underway to improve the amount of incorporated polar monomers as well as the activity. Attention will also be given to the incorporation of other polar monomers.

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