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A theoretical study of ethylene–styrene copolymerization by using half-sandwich Cp-based titanium catalysts

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Abstract

In this work we present the first attempt to study the copolymerization process of ethylene with styrene by computer simulation. Density functional theory calculations have been carried out on the detailed mechanism of ethylene–styrene copolymerization using non-bridge half-sandwich cationic species, generated by the system $CpTiCl_3$ activated with the methylaluminoxane cocatalyst. The goal of the study is to examine how the different active oxidation states of the transition metal can influence their abilities to produce a variety of polymers. This is of particular interest when considering that under the polymerization conditions Ti(IV) can be reduced to Ti(III) catalytic species. The theoretical calculations are in good agreement with the experimentally published results. It could be shown that the cationic species $[CpTiMe_2]^+$ produces a mixture of ethylene homopolymer and ethylene–styrene copolymer whereas the active species $[CpTiMe]^+$ is responsible for promoting only styrene homopolymerization. For the Ti(IV) catalytic system, the activation energy for the first ethylene monomer insertion is 2.9 kcal/mol, while for the styrene monomer is notably higher, being 10.4 and 9.4 kcal/mol for the 2,1 secondary and 1,2 primary insertion, respectively. The position of the phenyl ring of the styrene monomer plays a very important role in the polymerization reaction. Thus, in the 1,2 primary styrene insertion, the phenyl ring strongly interacts with the active site, blocking the active centers and avoiding the polymerization, whereas in the 2,1 secondary styrene insertion the interaction leaves one position free so that the polymerization can carry on. The monomer complexation energies after the 2,1 secondary styrene insertion is -0.9 kcal/mol for the ethylene and 0.8 and -3.3 kcal/mol for the 1,2- or 2,1-styrene monomer. On the other hand the energy barriers for monomer insertions are 3,3 kcal/mol for the ethylene and 20.6 kcal/mol for the 2,1 secondary styrene insertion. When the two monomers are competing for the Ti(III) catalytic species the energy barrier for the first monomer insertion is very high for the ethylene (18.2 kcal/mol) and 9.7 kcal/mol for the styrene monomer. Once the initial styrene insertion has taken place further ethylene insertion has also a very high energy barrier of 15.5 kcal/mol as compared to 5.8 kcal/mol for the styrene. Therefore, styrene polymerization is far more likely to occur than ethylene polymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymerization; Ethylene–styrene; Computational methods

1. Introduction

Over last decades many attempts have been made to synthesize ethylene (E)–styrene (S) copolymers. The reason behind these efforts lies in the interest to produce new materials by combining properties of flexible polymers having glass transition temperature far below ambient temperature with polymers exhibiting glassy behavior at the latter temperature.

Traditional Ziegler–Natta catalysts, which are able to polymerize ethylene as well as styrene separately, are rather inefficient for producing E–S copolymers due to the low activity, giving in general a mixture of ethylene homopolymer, polyethylene with low content of styrene comonomer (less than 1.0 mol%) and styrene block copolymers products [1–4]. In the recent years with the discovery of single-site metallocene catalysts intensive activities of research have been carried out in order to produce new E–S based copolymers. Thus, E–S copolymers with a wide range of compositions and structures have been synthesized using single-site homogeneous catalysts, including non-metallocene catalytic systems [5–10]. Some of the most investigated metallocene catalysts for the E–S copolymerization are those based on a variety of soluble titanium

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organometallic compounds in different oxidation states [11–14].

Based on the ability of the non-bridged half-sandwich $CpTiCl_3$ to polymerize either ethylene or styrene monomers, Longo et al. [15] reported for the first time that this catalyst could also promote the ethylene–styrene copolymerization when activated with methylaluminoxane (MAO) as cocatalyst. The composition of the copolymer strongly depends on the $CpTiCl_3$/MAO mole ratio. At high Al/Ti ratio a mixture of polyethylene and polystyrene is produced while at low Al/Ti ratio, E–S copolymers are obtained. These results were explained by assuming that the reaction between $CpTiCl_3$ and MAO could give rise to different active species that in turns produces either homopolymers or E–S copolymers. On the contrary, Aaltonen and Seppälä [16] found no formation of E–S copolymer during the polymerization of ethylene and styrene monomers in the presence of $CpTiCl_3$/MAO catalyst. A mixture of polystyrene and linear polyethylene was rather obtained. These results could be explained due to the formation of a variety of active species of Ti having different oxidation states. Indeed, by electron spin resonance studies on the oxidation state of different titanocene catalytic systems, several authors [17–19] have shown that under normal polymerization conditions the tetravalent Ti(IV) catalyst can undergo reduction to the trivalent state Ti(III). Furthermore, it has been suggested that the trivalent $[CpTiR]^+$ cation is the active species for the styrene polymerization while the Ti(IV) is responsible for the homopolymerization of ethylene and the ethylene–styrene copolymerization.

As pointed out by Brintzinger et al. [5], the copolymerization mechanism with half-sandwich titanocene catalysts is very complex and needs to be clarified. This paper deals with the theoretical modeling of the ethylene and styrene copolymerization with $CpTiCl_3$ catalyst. Special attention is paid to the oxidation state of the transition metal, particularly when considering that under normal polymerization conditions Ti(IV) can be easily reduced to Ti(III), as it has been mentioned before. On the other hand, it should be pointed out that despite the great amount of publications on the theoretical modeling of polymerization by metallocene catalysts none has appeared dealing with ethylene–styrene copolymerization.

2. Computational methods

Energy calculations were performed within the density functional theory formalism selecting the gradient corrected or non-local functionals of Becke [20] for exchange and Perdew [21] for correlation.

The LACV3P* basis set was used for all the calculations. It is an effective core potential basis set developed at Los Alamos National Laboratory [22]. LACV3P includes the outermost set of core orbitals, e.g. 3s and 3p for titanium, along with a triple zeta contraction for the valence orbitals for every element and polarization functions for non-hydrogen atoms.

Geometry optimizations were carried out with the following convergence criteria: 4.5×10^{-4} hartrees/bohr as the maximum element of gradient, 3.0×10^{-4} hartrees/bohr as the rms of gradient elements, 1.8×10^{-3} bohrs as the maximum element of nuclear displacement. 1.2×10^{-3} bohrs as the rms of nuclear displacement and 5.0×10^{-5} hartrees as the energy difference between consecutive iterations.

Complexation energies were calculated as the difference between the optimized π-complex on one hand and cationic species and monomer on the other. Activation or insertion barriers were estimated as the difference between transition state structures and π-complex reactants.

The whole set of calculations were done with the Titan 1.0.5 software in Pentium 4-based PCs.

3. Results and discussion

It is well known that Ti(IV) catalysts system can be reduced to Ti(III) species under the conditions usually given during olefin polymerization. Therefore, for the study of these catalytic systems, the oxidation states of the transition metal should be considered. This section is divided into two parts, one dealing with the Ti(IV) catalytic system and the other one with the Ti(III) half-sandwich titanocene complex.

The Cossee–Arlman [23] and Brookhart–Green [24] mechanisms are the most accepted one for the olefin polymerization by transition metal catalysts. The key steps of these mechanisms are: (1) olefin coordination to the vacant site of the Ti atom and (2) olefin insertion into the Ti–C bond through a four-member cyclic transition state. Once the insertion has been produced, the system comes to the initial catalytic step, and a new cycle begins towards a new insertion. These mechanisms will be used here for the study of the titanium catalytic system.

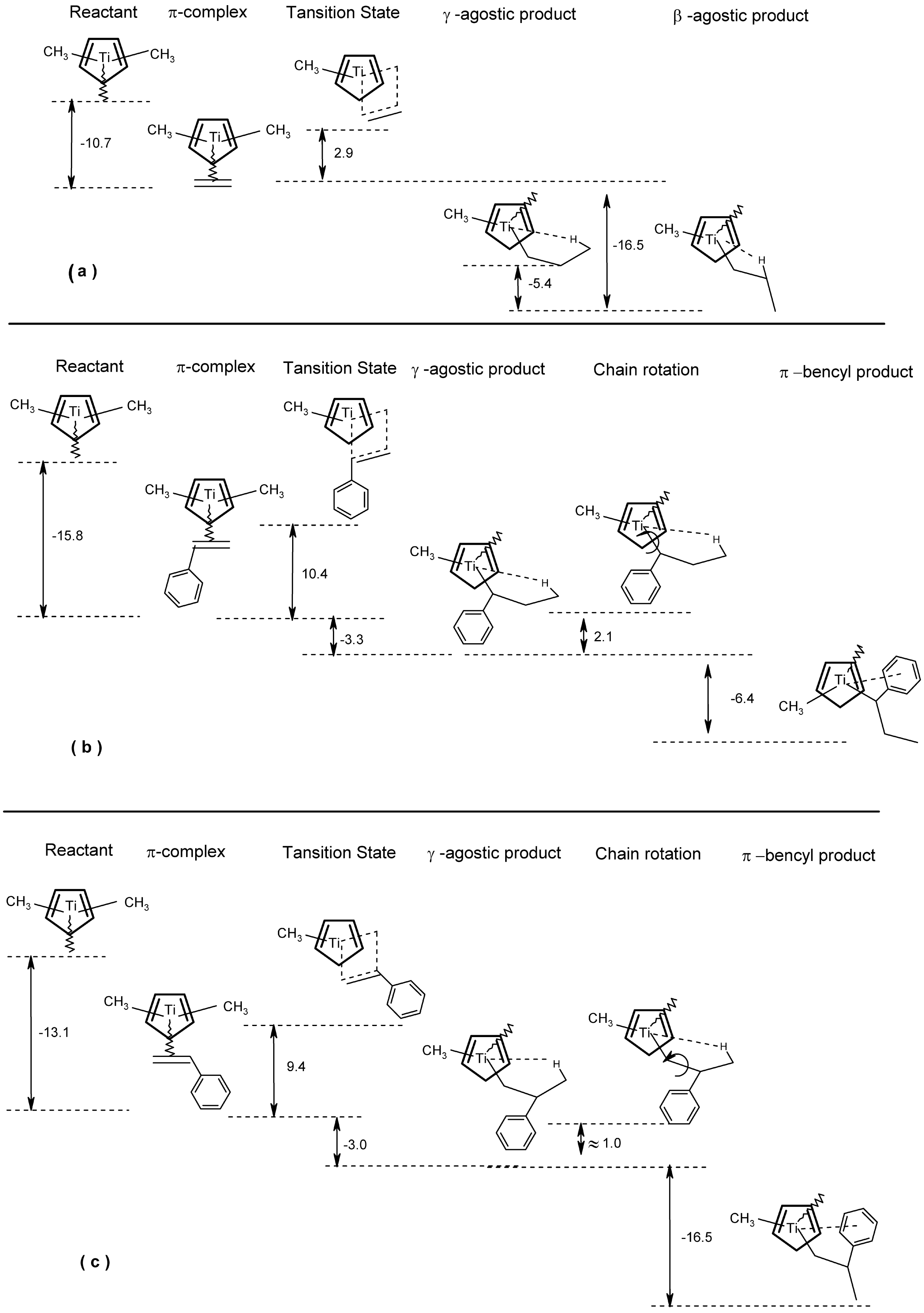
3.1. Ti(IV) catalytic system

It has been established that the whole polymerization process comprises two main steps: initial monomer insertion followed by subsequent polymer chain growth. Both processes will be treated in detail.

3.1.1. Initial monomer insertion

In principle, each active species $Ti(IV)Cp(CH_3)_2^+$ can initiate a polymer chain by inserting ethylene or styrene monomers in one of the two titanium–methyl bonds.

The π-complex formation is an exothermic process. In the case of ethylene complexation, the calculated energy was -10.7 kcal/mol (see Scheme 1(a), part a). This energy is of the order of that found for metallocene catalysts [25]. However, for the styrene monomer two possibilities should



Scheme 1. First monomer insertion paths into the Ti^{IV} species. (a) Ethylene insertion; (b) secondary styrene insertion; (c) primary styrene insertion. The point of view for the schematized structures is located above the Cp ring along the metal–Cp centroid axis. The active site location is indicated by a sinusoidal line. π-Benzyl interaction is indicated by a line joining the metal and the phenyl centroid.

be considered, the 2,1 secondary insertion or 1,2 primary insertion (Scheme 1(b) and (c), respectively). The complexation energy for these two alternative processes are −15.8 and −13.1 kcal/mol, respectively. Therefore, the 2,1-styrene π-complex is slightly more stable than the 1,2-form. The π-complex formation energy difference between ethylene and styrene monomers could be attributed to the phenyl group of the styrene which tends to stabilize the π-complex rather than ethylene for the first olefin insertion. However, in both cases the π-complex are formed through a η^2 interaction with the metal atom. It is very surprising that for the Ti(IV) catalytic system the phenyl group has no direct interaction with the metal atom (Fig. 1). This situation is very different to that found for the Ti(III) catalyst as reported below. Several attempts were performed to locate structures with stronger π-benzyl interaction, but geometry optimizations yielded to the above mentioned geometries in all cases.

As commented in Section 2, the activation energy is calculated as the difference between transition state and π-complex energies. The located transition state consists of the well-known four center pseudo-ring formed by the metal atom, the C atom of the methyl group and both C atoms of the ethylene monomer [26]. For the insertion process an activation energy of 2.9 kcal/mol was found for the ethylene monomer (Scheme 1(a)). This corresponds to a typical value for ethylene polymerization using metallocene catalysts. The energy barriers for the secondary and primary insertions of the styrene monomer are somewhat higher compared to ethylene, being 10.4 and 9.4 kcal/mol, respectively (Scheme 1(b) and (c)). The corresponding transition states exhibit similar features to those found for ethylene insertion (Fig. 2(a)). Particularly, the formation of the four-member pseudo-ring presents less planarity for the secondary insertion than for the primary insertion. In the secondary insertion transition state a η^3 interaction could be observed when considering the distances between the Ti atom and C1 (2.471 Å), C2 (2.211 Å) and C3 (2.578 Å) of the styrene monomer (Fig. 2(b)). This η^3 interaction should in principle decrease the energy barrier in the secondary insertion. The reason for the higher activation energy is due to the steric hindrance of the phenyl group in the secondary in comparison to the primary insertion. The primary styrene insertion transition state shows a η^2 interaction along with a planarity of the four-member ring similar to that found for the ethylene case (Fig. 2(c)).

The resulting products present the characteristic γ-agostic interaction. However, they are not the most stable structures that can be formed as it is possible to find lower energy conformers by rotating some bonds of the growing polymer chain. For the ethylene polymerization the β-agostic structure is 5.4 kcal/mol more stable than the γ-agostic one (Scheme 1(a)), which is in agreement with the usual results found in the literature [26,27].

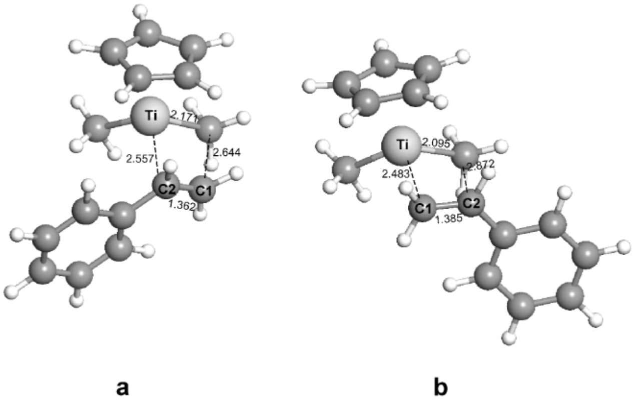


Fig. 1. π-Complexes for (a) secondary styrene insertion and (b) primary styrene insertion into the $CpTi^{IV}(CH_3)^+$ species. Interatomic distances in angstrom.

The secondary styrene insertion yields a γ-agostic product with an energy of 3.3 kcal/mol lower than the reactant. The growing chain can rotate around the Ti–Cα bond to form a similar Ti–phenyl interaction structure which is 6.4 kcal/mol more stable than the γ-agostic product (Fig. 3(a)) giving rise finally to a η^3 interaction. The energy barrier for the rotation around the Ti–Cα bond is 2.1 kcal/mol. Similarly, for the primary styrene insertion the γ-agostic product is 3.0 kcal/mol more stable than the π-complex reactant. This structure can be rearranged to a

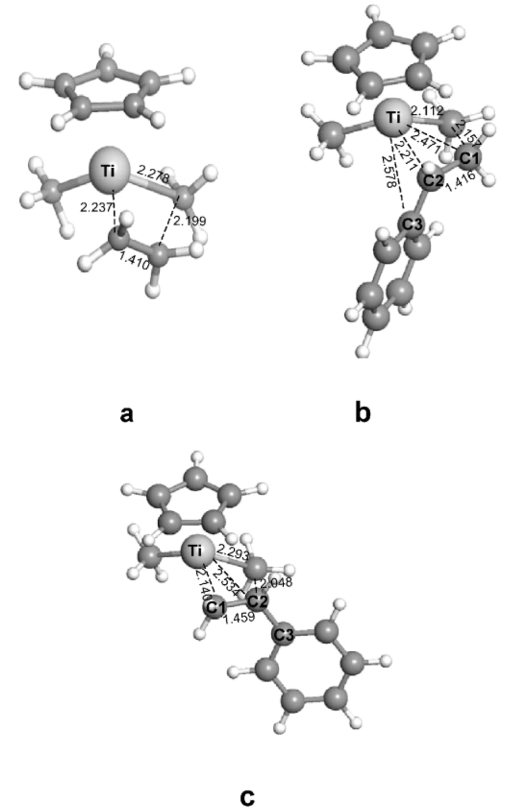


Fig. 2. Transition states for (a) ethylene insertion, (b) secondary styrene insertion and (c) primary styrene insertion into the $CpTi^{IV}(CH_3)^+$ species. Interatomic distances in angstrom.

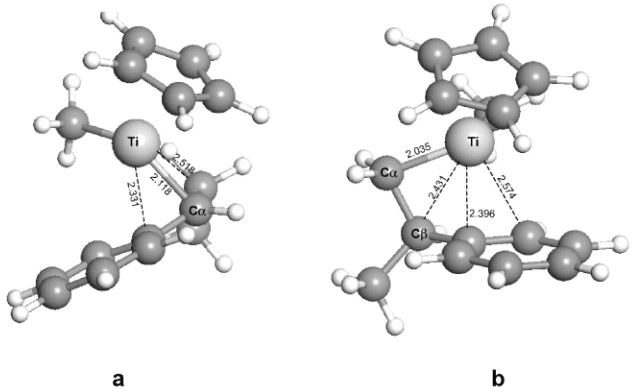


Fig. 3. Most stable products after (a) secondary styrene insertion and (b) primary styrene insertion into the $CpTi^{IV}(CH_3)^+$ species. Interatomic distances in angstrom.

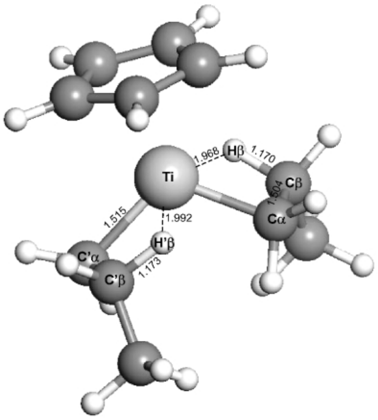


Fig. 4. Resting state after ethylene polymerization in both alkyl chains.

conformation with a strong Ti–phenyl interaction by rotation around the Cα–Cβ bond. The resulting geometry is 16.5 kcal/mol more stable than the γ-agostic product (Fig. 3(b)). The energy barrier calculated for the rotation about the Cα–Cβ bond is less than 1 kcal/mol. The π-benzyl product for the 1,2-insertion is much more stable than for the 2,1-insertions, since in the former case the phenyl ring can adopt a more appropriate position for a stronger interaction with the metal atom, giving rise then to a η^4 interaction.

The relative energies of the complete process from reactants to the most stable products are given in Scheme 1. It can be seen that ethylene insertion is more feasible than the styrene case. Furthermore, the probabilities of a primary or a secondary styrene insertion are not very different for the Ti(IV) oxidation state of the catalyst. However, secondary styrene insertions are the preferred ones, specially in those cases where the metal and phenyl group have the possibility of stronger interaction, as it is for the Ti(III) catalyst that will be discussed later.

3.1.2. Growing polymer chain

This section is divided into three different parts according to the previous monomer insertion steps.

3.1.2.1. Growing polymer chain after ethylene insertion

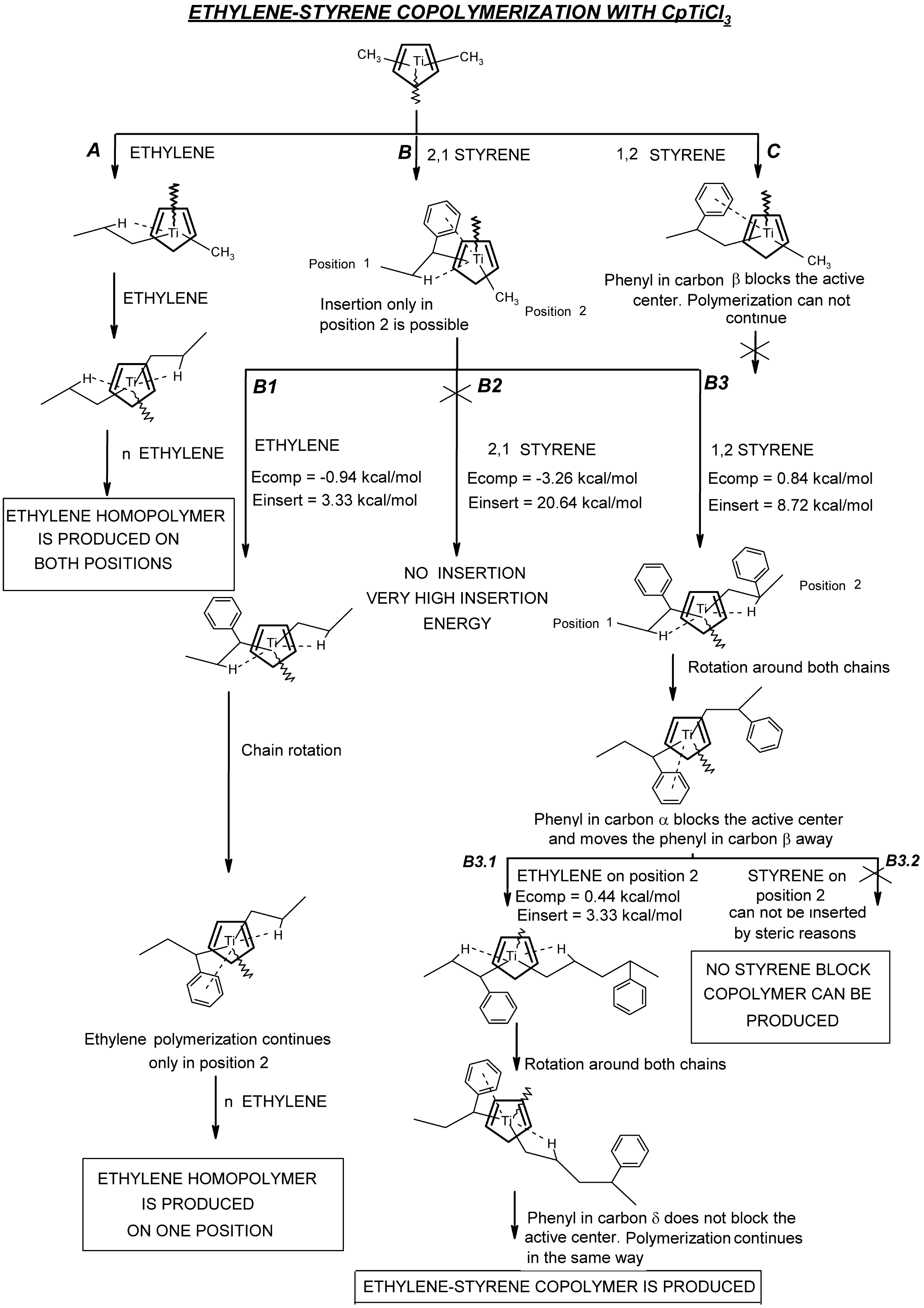
The first ethylene insertion gives rise to a product with a β-agostic interaction as it was discussed before. The second monomer could be inserted either in this product with the β-agostic interaction or in the still remaining CH_3 alkyl group. It was found that the subsequent monomer complexation and insertion is more favorable in the still available Ti–methyl bond than in the already started β-agostic growing chain. The energy obtained for such complexation and insertion is equivalent to that obtained for the first olefin monomer insertion step. The new resulting structure presents now two β-agostic interactions corresponding to C–H groups in both growing chains (Ti–H_β 1.968 Å and Ti–H'_β 1.992 Å) which are placed on opposite sides, i.e. anti (Fig. (4)). Following this procedure, ethylene can be inserted alternatively in both positions giving rise to two growing polyethylene chains (see route A in Scheme 2). The situation is different when the styrene is the monomer to be inserted into the cationic species as it will be shown later.

3.1.2.2. Growing polymer chain after primary styrene insertion

The structure obtained after 1,2-styrene insertion presents a strong π-benzyl interaction blocking the subsequent insertion into the active site (Fig. 3(b)), due to a η^4 interaction with the transition metal atom. Several attempts to coordinate any monomer to that complex from different positions were found unsuccessful. The best result was obtained when the ethylene monomer was placed between the methyl group and the blocking phenyl group. However, the ethylene monomer is still too far away (3.155 Å) to be part of the Ti coordination sphere and therefore to be inserted. The complexation process is endothermic with an energy of 14.0 kcal/mol, and therefore it is a non-feasible process In conclusion, the 1,2 primary styrene insertion produces a cationic species with the active site blocked in such a way that polymerization is not possible at any of the two available Ti–C bonds (see route C in Scheme 2).

3.1.2.3. Growing polymer chain after secondary styrene insertion

In the case of the secondary styrene insertion the resulting product gives rise to a structure with a phenyl group–titanium interaction weaker than in the primary styrene insertion (see route B in Scheme 2 and Fig. 3(a)). The hapticity is η^3 for the secondary insertion (Fig. 3(a)) as compared to η^4 for the primary styrene insertion (Fig. 3(b)). This π-benzyl complex blocks also one of the active site, but leaving the other CH_3 available for the monomer insertion. Table 1 shows the complexation and insertion energies for the different monomers, ethylene, 1,2-styrene and 2,1-styrene, after secondary styrene insertion. The complexation energy for any of the three π-complexes is



Scheme 2. Possible routes for ethylene/styrene copolymerization with CpTiCl3 catalyst. The same point of view is selected as in Scheme 1.

Table 1
Relative complexation and insertion energies after secondary styrene insertion into the $CpTi^{IV}(CH_3)^+$ catalyst

Monomer insertion	Complexation energy (kcal/mol)	Insertion barrier (kcal/mol)
Ethylene	−0.94	3.33
1,2-styrene	0.84	8.72
2,1-styrene	−3.26	20.64

significantly smaller (−0.94, 0.84 and −3.26 kcal/mol, respectively). Even a slightly endothermic process was found for the case of the primary styrene complex (0.84 kcal/mol, see also route B3 in Scheme 2). This is due to the presence of the blocking phenyl group of the already inserted styrene monomer which hinders somehow the approach of any incoming monomer. In fact, for the case of a new secondary styrene insertion, the aromatic ring of the monomer adopts a *syn* position with respect to the cyclopentadienyl ring most probably due to a steric repulsion with the phenyl group of the already inserted secondary styrene (Fig. 5(a), and route B2 in Scheme 2). The insertion barriers for ethylene and 1,2-styrene are similar to those values found for the first monomer insertion (3.33 and 8.72 kcal/mol, respectively, see Table 1 and routes B1 and B3 in Scheme 2). However, for the secondary insertion of a styrene monomer a large activation barrier of 20.6 kcal/mol was obtained. This result can be explained by the fact that both phenyl rings are mutually hindered in the transition state so that the interaction between the Ti atom and the phenyl group of the growing chain is weakened (Fig. 5(b)). This can be deduced from the increase of the Ti–phenyl centroid distance that goes from 3.331 to 3.636 Å and the Ti–Cα–C1 angle from 80.9 to 88.2° (Fig. 5).

According to the complexation energy (−0.94 kcal/mol) and insertion barrier (3.33 kcal/mol) calculated for the ethylene, this monomer can be easily polymerized in the available $Ti-CH_3$ position due to the fact that the other position is blocked by the phenyl group as mentioned before (see route B1 in Scheme 2).

Once the 1,2-styrene insertion has taken place the interaction between its phenyl group attached to Cβ and the Ti atom cannot be formed (Ti–phenyl centroid distance is too large, 5.088 Å). This could be explained by assuming that the phenyl group in the Cα position of the former 2,1 already inserted styrene monomer is avoiding its approach to the Ti atom (Fig. 6(a)). Therefore, polymerization can only proceed in position 2 where an 1,2-styrene monomer has been inserted (see route B3 in Scheme 2). In fact, the ethylene monomer can be complexed in position 2 with a slight energetic cost of 0.44 kcal/mol (Fig. 6(b) and route B3.1).

The ethylene or styrene complexation was attempted to the growing polymer chain in position 1, where the phenyl group attached to the Cα has a strong interaction with the Ti atom (Ti–phenyl centroid distance, 3.058 Å). For these processes a complexation energy of 10 and 15 kcal/mol, respectively, was found. Therefore, it could be considered a very improbable mechanism and no further work was performed.

In conclusion, in Scheme 2 the different possibilities for the ethylene/styrene copolymerization with the $CpTi^{IV}(CH_3)_2^+$ system have been summarized taking into consideration the different processes described above. It is possible to identify two different species that could exist along the copolymerization process. First, one structure that can give ethylene homopolymer on both positions (route A) and second, another structures formed after secondary styrene insertion which can give rise to either ethylene homopolymer (route B1) or to styrene/ethylene copolymer only on one of the two possible positions of the growing polymer chain (route B3.1). The ethylene/styrene copolymer that can be produced is formed by isolated styrene monomer units.

3.2. Ti(III) catalytic system

The study of the polymerization mechanism with the Ti(III) half-sandwich catalyst has been also divided into two parts: initial monomer insertion and growing polymer chain.

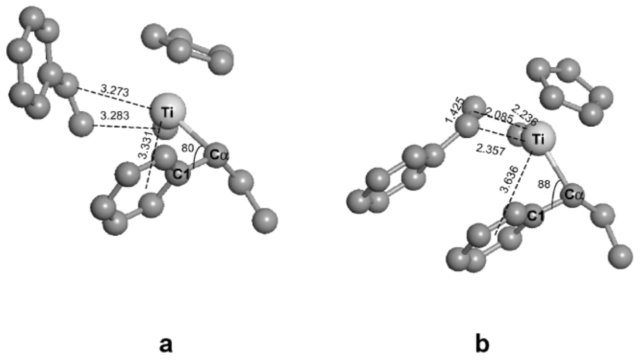


Fig. 5. π-Complex (a) and transition state (b) of secondary styrene insertion in chain 2 after a previous secondary styrene insertion in position 1. See text for details. Hydrogen atoms are omitted for the sake of clarity.

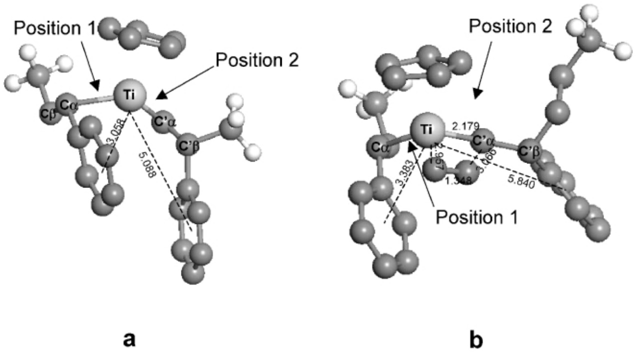


Fig. 6. (a) Competitive blocking and interaction of phenyl rings in different C atoms with the metal centre and (b) ethylene complexation in that structure. π-Benzyl interaction is indicated by a line joining the metal centre and the phenyl centroid.

3.2.1. Initial monomer insertion

Both monomers coordinate to the CpTi(III)CH_3^+ catalyst forming very stable π-complexes with complexation energies of −30.9 kcal/mol for ethylene and −45.2 kcal/mol for styrene. The ethylene π-complex shows the monomer coordinated to the metal atom perpendicular to the Ti–CH_3 bond in a position which is typical in metallocene systems (Fig. 7(a)). In case of the styrene monomer the π-complex shows a η^4 coordination with the metal center due to the large room available in the active site (Fig. 7(b)). This situation is different to that found in case of the Ti(IV) active species as it was seen before. Now, the position of the styrene monomer enables a secondary insertion into the Ti–alkyl bond to take place. In fact, initial geometries built with styrene oriented towards a primary insertion converged, after geometry optimization, to a structure with the monomer oriented to a secondary insertion (see also Fig. 7(b)).

For the ethylene insertion the energetic barrier obtained is very high (18.2 kcal/mol), which is in agreement with experimental findings indicating that Ti(III) catalyst are inefficient for ethylene polymerization. Also this energy barrier is much larger than that of the same process with the Ti(IV) catalyst (2.9 kcal/mol). The structure of the transition state shows two significant differences with respect to the Ti(IV) system and to the usual findings for metallocene catalysts. First, the planarity of the four-center pseudo-ring is lost, and secondly the characteristic α-agostic interaction between the Ti atom and the methyl group disappears (Fig. 8(a)). In the case of the styrene monomer insertion we found an energy barrier of 9.7 kcal/mol. This insertion barrier is similar to that found for the Ti(IV) system and is in agreement with the value given for a similar system reported by Minieri et al. [28]. The structure at the saddle point preserves the η^4-coordination to the metal atom and the analysis of distances in the four-center ring suggests an early transition state (Fig. 8(b)).

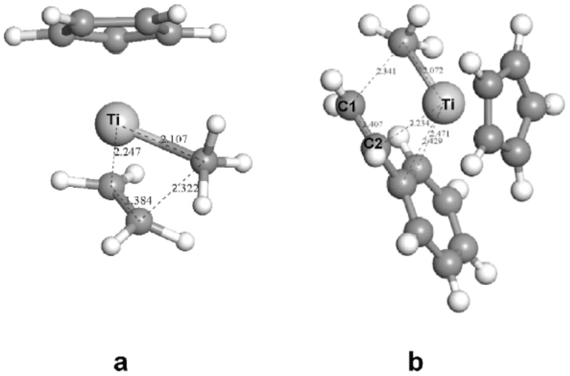


Fig. 8. Transition states for monomer insertion into the $CpTI^{III}CH_3^+$ species: (a) ethylene and (b) styrene.

The ethylene insertion product gives rise to the well-known γ-agostic compound which is 8.7 kcal/mol lower in energy than the π-complex (Fig. 9(a)). The β-agostic conformer is, however, less stable than the direct γ-agostic product by 4.8 kcal/mol, in contrast to the usual result published in the literature. It has been reported that the structure containing the β-agostic interaction is the conformer with the lowest energy. The product obtained by styrene insertion consists of a η^7-coordinated compound showing a strong π-benzyl interaction with the metal atom (Fig. 9(b)). This geometry is equivalent to that reported in the literature [28], and is 19.2 kcal/mol lower than the π-complex energy.

3.2.2. Growing polymer chain

The results described in Section 3.2.1 clearly indicate that when the two monomers are competing for the same active center the initial insertion of styrene is by far more likely to occur than ethylene insertion. Once the styrene monomer has been inserted, two possibilities can be considered: either a further ethylene or a subsequent styrene insertion. Once the initial styrene insertion has taken place, the ethylene can coordinate to give a structure with an exothermic complexation energy of −9.1 kcal/mol. The optimized structure still shows the characteristic η^7-coordination of the phenyl group in the growing chain to the Ti atom. The ethylene monomer is approaching the metal center forming the usual π-complex structure (Fig.

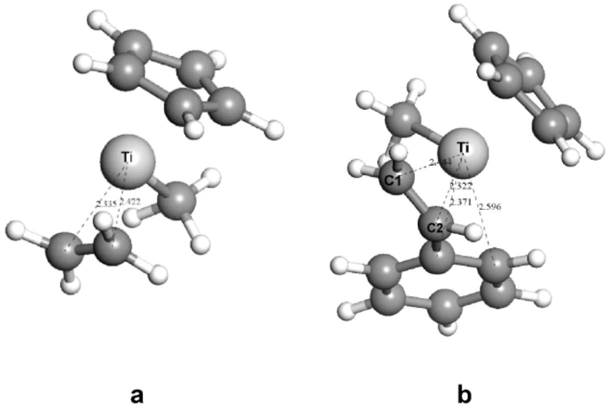


Fig. 7. π-Complexes for monomer insertion into the $CpTI^{III}CH_3^+$ species. (a) ethylene complex and (b) styrene complex.

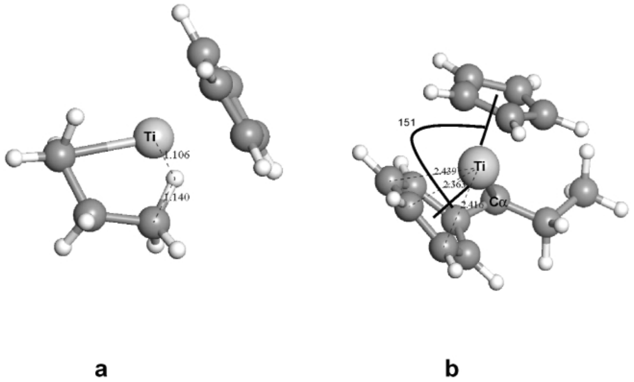


Fig. 9. Products for monomer insertion into the $CpTI^{III}CH_3^+$ species: (a) ethylene and (b) styrene. In the styrene case not all interactions between the phenyl ring and the metal atom are showed for clarity.

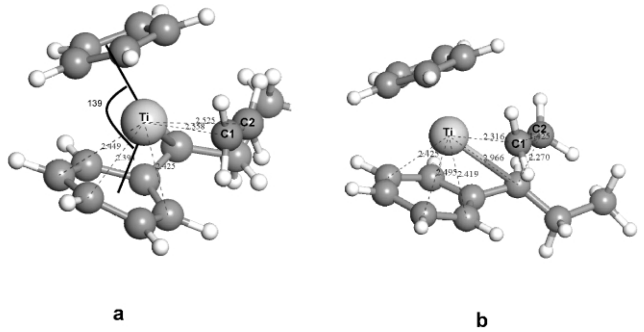


Fig. 10. Ethylene insertion into the CpTI^{III}CH$_3^+$ species after styrene insertion. (a) π-Complex, (b) transition state. Not all interactions between the phenyl ring and the metal atom are showed for clarity.

10). The angle Cp centroid–Ti–benzyl centroid decreases from 151° in the cationic precursor (Fig. 9(b)) to 139° in the π-complex (Fig. 10(a)) providing the necessary space for the accommodation of the monomer. Insertion of ethylene into the Ti–Cα bond was tried by performing a linear synchronous transit following the distance between the Cα and the nearest ethylene C atom. This allows one to identify a transition state for the ethylene insertion with an energy barrier of 15.5 kcal/mol (Fig. 10(b)). This clearly indicates that ethylene insertion is an unlike process with this catalytic species.

For the styrene monomer, the complexation is also exothermic with −16.5 kcal/mol. The structure of this adduct is equivalent to the structure found by Minieri et al. [28] (Fig. 11(a)). The styrene molecule already inserted in the chain remains η^7 coordinated to the metal atom, while the entrant monomer adopts a η^2 coordination (Fig. 11(a)). The fluxional behavior described by these authors has also been observed in this work, the change from η^7 to η^3-coordination for the phenyl ring in the growing polymer chain is accomplished by the coordinated styrene monomer changing from η^2 to η^4-coordination to the metal center (Fig. 11(c)). This structure is 3.5 kcal/mol above the structure in Fig. 11(a). Between these two π-complex geometries a transition state was located at 6.1 kcal/mol above the mentioned structure given in Fig. 11(a). This transition state shows a η^3-coordination for both phenyl groups, the one inserted in the growing chain and the other in the incoming styrene monomer (Fig. 11(b)). The structure given in Fig. 11(c) is really a transient complex in the insertion process. The transition state between the previous structure and the final product has an energy barrier of 5.8 kcal/mol. The structure of this transition state has the following features: (i) the four-center pseudo-ring has a planar geometry with an α-agostic interaction with the Ti, (ii) the phenyl ring of the incoming monomer is η^4-coordinated to the metal atom while the phenyl group of the inserted styrene monomer is η^3-coordinated, (iii) a slight rotation of the inserted styrene monomer around the Ti–Cα bond was observed which allows more room for the incoming monomer. These results were in agreement with those found by Minieri et al. [28], for styrene homopolymerization.

The styrene monomer is inserted in the growing polymer chain by a 2,1 secondary insertion. As a result the Ti(III) half-sandwich catalyst preferably produces styrene

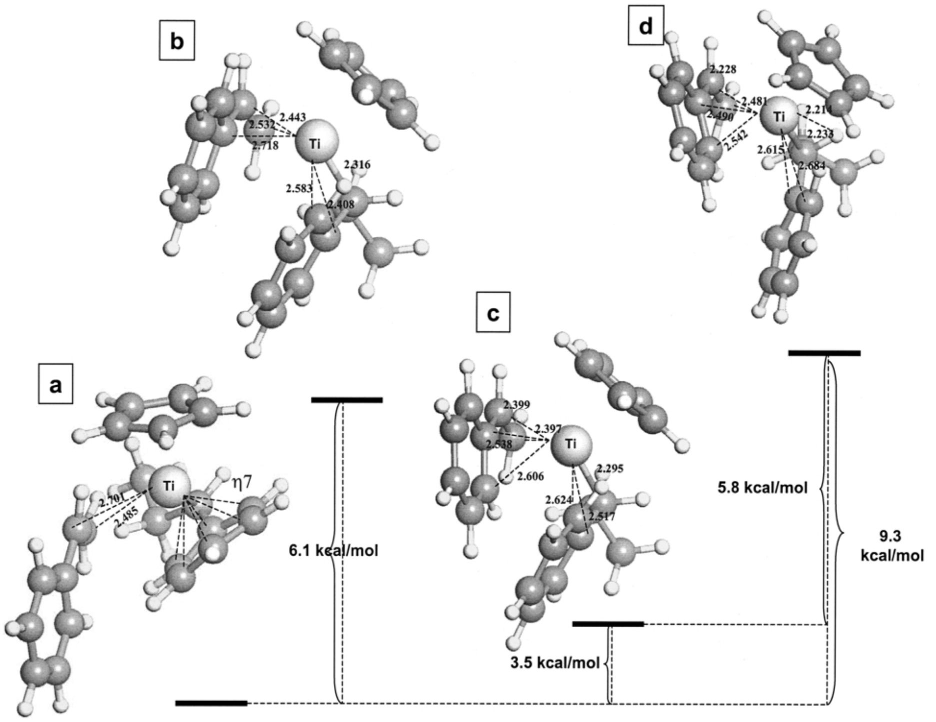


Fig. 11. Styrene insertion into the CpTI^{III}CH$_3^+$ species after styrene insertion: (a) initial π-complex, (b) transition state between π-complexes, (c) transient π-complex, (d) transition state for the insertion process. Not all interactions between the phenyl ring and the metal atom are shown for clarity in part (a).

homopolymer as the ethylene insertion has an energy barrier much larger (15.5 kcal/mol) than the styrene monomer insertion (9.3 kcal/mol).

4. Conclusions

Ethylene/styrene copolymerization with monocyclopentadienyl titanium catalytic systems is largely influenced by the oxidation state of the metal atom. The Ti(IV) species tends to give a mixture of ethylene homopolymer with ethylene/styrene copolymer having isolated styrene monomers along the polymer chain. On the other hand Ti(III) species gives rise preferably to a styrene homopolymer. Therefore, the experimental results published in the literature reporting the formation of a complex mixture of polyethylene and polystyrene with ethylene/styrene copolymer can be only explained by assuming that the Ti(IV)Cp$(CH_3)_3$ catalyst is reduced from Ti(IV) to Ti(III) during polymerization.

Ethylene can be easily polymerized with the Ti(IV) half-sandwich metalocene catalyst due to the relative low activation and complexation energies while in the case of the Ti(III) catalyst ethylene insertion has a high energy barrier due to the fact that the transition state is not stabilized by the agostic interaction. For the styrene polymerization, the result can be explained by the role played by the phenyl ring of the styrene molecule which interacts differently with the metal atom depending on the oxidation state. In case of Ti(III) the absence of one ligand compared to Ti(IV) provides more space for a stronger π-benzyl interaction between the metal and the phenyl ring of the incoming monomer compared to the Ti(IV) catalyst. This situation makes the styrene polymerization more feasible.

Finally, Ti(IV) is the only catalytic species that can copolymerize ethylene with styrene only when styrene is inserted in 2,1-position. This is due to the fact that in the 2,1-insertion the phenyl ring does not block the active center.

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