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Stereoselectivity and chemoselectivity in Ziegler–Natta polymerization of conjugated dienes. 2. Mechanism for 1,2 syndiotactic polymerization of diene monomers with high energy s-*cis* η^4 coordination

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Abstract

Possible mechanisms of Ziegler–Natta polymerizations of conjugated dienes have been investigated by density functional methods, by considering η^2 or η^4 (both *cis* and *trans*) coordination of the monomer and η^1 or η^3 (*syn* or *anti*) allyl coordination of the growing chain. In agreement with previous studies, for diene monomers presenting a low s-*cis*-η^4 coordination energy (like butadiene), the favored insertion reaction would involve a s-*cis*-η^4 monomer coordination and an *anti* η^3 allyl coordination of the growing chain (mechanism I). On the other hand, for diene monomers presenting high s-*cis*-η^4 coordination energy (like (*Z*)-pentadiene and 4-methyl-pentadiene), the favored insertion reaction would generally involve a 5-*trans* η^2 monomer coordination and a back-biting *syn* allyl (η^3–η^2) coordinated growing chain (mechanism II). However, these monomers would present an s-*cis*-η^4 coordination whenever the formation of the back-biting of the penultimate unit of the growing chain would be unfeasible, as for initiation steps as well as for insertion steps following an ethylene insertion. A switch from mechanism II toward mechanism I is able to rationalize the correspondingly observed loss of chemoselectivity. Mechanism II is also able to account for the high stereoselectivity in favor of 1,2 syndiotactic polymerization which has been observed for these dienes. The chain end stereocontrol would be dictated by the chirality of coordination of the *syn* allyl terminal of the back-biting growing chain.

Keywords: Ziegler–Natta diene polymerizations

1. Introduction

Several experimental facts [1–10], relative to polymerization of conjugated dienes with transition metal catalytic systems, have been rationalised in terms of different π-allyl insertion mechanisms, depending on the nature of the catalytic systems and of the diene monomer, mainly by the extensive work of Porri and co-workers, as reviewed in Refs. [8,9], and Taube and co-workers, as reviewed in Ref. [10]. A widely accepted scheme for *cis*-1,4 and 1,2 polymerizations of conjugated dienes is reported in Scheme 1 (mechanism I) [8–12]. In particular, it has been suggested that 1,2 units and *cis*-1,4 units can derive from an intermediate involving a s-*cis*-η^4 coordinated diene monomer as well as a η^3 coordinated allyl terminal of the growing chain presenting an *anti* structure [7–9]. This kind of arrangement of the ligands would give rise to *cis*-1,4 or to 1,2 units, depending on whether the incoming monomer reacts at the terminal C4′, or internal C2′ allyl carbon, respectively. The labels for the carbon atoms presented in Scheme 1 and used in the rest of the paper should help to visualize 1,4 and 1,2 enchainments.

This polymerization scheme has been also used in our previous density functional study (the first part of this series study) to rationalize the chemoselectivities and the stereoselectivities for monomers having a low s-*cis*-η^4 coordination energy [11]. It is worth noting that the s-*cis*-η^4 coordination of the diene monomer is energetically favorable (and, in fact, it has been observed in several metal complexes [13]) for the case of several dienes like butadiene, isoprene, (*E*)-pentadiene, 2,3-methyl-butadiene. This kind of coordination is instead of much higher energy, and has not been observed for stable metal complexes of

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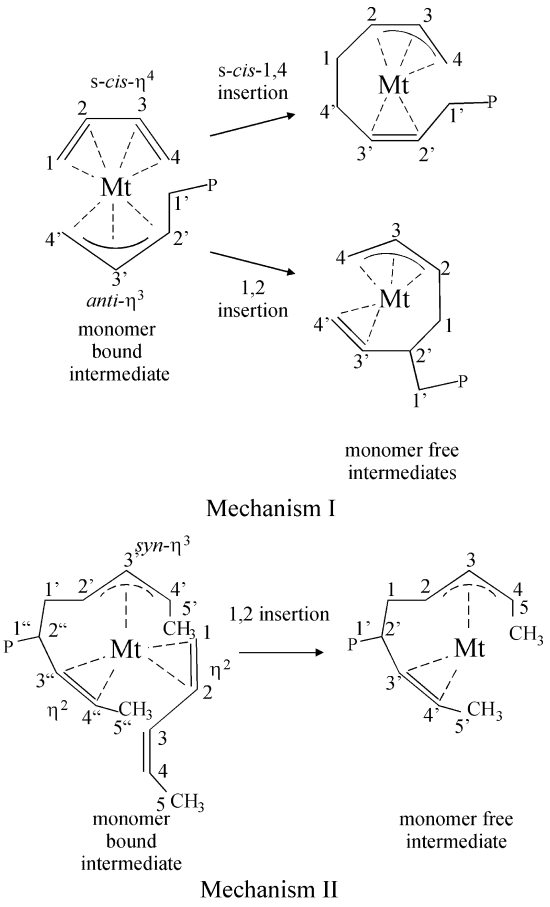


Scheme 1.

(*Z*)-pentadiene and 4-methyl-pentadiene, due to non-bonded intramolecular interactions between the methylenic group and a methyl group. Moreover, for the latter monomers this kind of non-bonded repulsive interactions would be present also in the resulting *anti*-η^3 allyl group.

Besides these simple geometrical considerations, several experimental data, relative to diene polymerization catalyzed by CpTiCl$_3$-MAO system, clearly indicate that, for monomers with high energy s-*cis*-η^4 coordination, a different mechanism should occur. In fact, this catalytic system promotes 1,4-*cis* polymerization of butadiene and 1,2 syndiotactic polymerization of 4-methyl pentadiene, with faster polymerization rate for the latter bulkier monomer [14]. The behavior of this catalytic system with (*E*) and (*Z*) isomers of 1,3-pentadiene is also intriguing. Actually, (*E*)-pentadiene affords at any temperature an irregular product containing substantial amounts of both 1,4-*cis* and 1,2 units while (*Z*)-pentadiene is stereospecifically polymerized to 1,4-*cis* isotactic polymer at temperatures higher than 20 °C [15,16] and to 1,2 syndiotactic polymer at −20 °C or less [14,16–19]. Furthermore, the polymerization rates are higher for 1,2-syndiotactic polymerizations, which are conducted at lower temperatures [16, 19]. These experimental data are collected in Scheme 2.

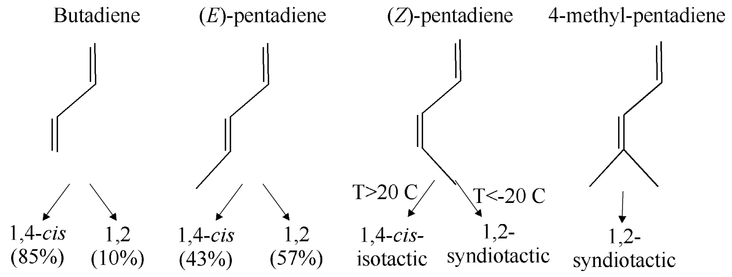
Several experimental data obtained by Zambelli and co-workers clearly indicate that polymerizations of (*Z*)-pentadiene and of 4-methyl-pentadiene involve a relevant role of the growing chain in determining the chemoselectivity of the insertion of the incoming monomer [19–21]. In fact, the 1,2 chemoselectivity disappears for monomer insertion steps involving an attack to an allyl growing chain which does not present a double bond in the penultimate inserted unit. In particular, the study of the initiation step for the polymerization of 4-methyl-pentadiene (in presence of a catalytic system prepared with CpTiCl$_3$-MAO and Al(^{13}CH$_3$)$_3$) showed that the first monomeric unit can be both 1,2 and 1,4 inserted [20]. Moreover, copolymerization with ethylene of (*Z*)-pentadiene at −20 °C [19] as well as of 4-methyl-pentadiene [21] give irregular copolymers containing substantial amounts of *cis*-1,4 units adjacent to ethylene inserted units.

Reaction intermediates involving a back-biting coordination of the growing chain (that is the simultaneous coordination of the allyl terminal of the growing chain and of the double bond of the penultimate monomer unit) have been suggested, for a possible rationalization of these data [19]. In this paper, possible polymerization mechanisms, in the presence of the catalytic system CpTiCl$_3$-MAO, for butadiene and for monomers with high energy s-*cis*-η^4 coordination (like (*Z*)-pentadiene and 4-methyl-pentadiene) are compared. In particular, intermediate metal complexes with diene monomers η^2 or η^4 (*trans* or *cis*) coordinated as well as with terminal allyl groups of the growing chain η^1 or η^3 (*syn* or *anti*) coordinated are considered. For different growing chain coordinations, the possible formation of a back-biting bond with the metal of the last double bond of the growing chain is also considered.

2. Models and computational details

2.1. Models

The considered models correspond to both monomer free and monomer bound intermediates. The occurrence of both kinds of intermediates is widely accepted in the literature, and is based on NMR and X-ray diffraction characterizations of π-allyl complexes [13,22–25]. The chirality of coordination of double bonds and of the allyl group of the considered models is defined according to Ref. [26]. Both monomer free and monomer bound intermediates have been labeled as *trans*-1,4-*like*, *trans*-1,4-*unlike*, *cis*-1,4-*like*, 1,2-*like*, or 1,2-*unlike*. Of course, 1,4 and 1,2 refer to the constitution of diene units and *cis* or *trans* refer to the configuration of double bonds along the chain in 1,4 units. As for the *like* and *unlike* nomenclature, it indicates that the corresponding intermediate would possibly lead to isotactic and syndiotactic units, respectively. In particular, isotactic and syndiotactic stereoregularity could occur for all diene monomers in case of 1,2 polymerization, while it would occur only for 4-alkyl substituted and 1,4 alkyl disubstituted



Scheme 2.

dienes in case of 1,4 polymerization. For the sake of comparison with the conformational analysis of Ref. [27], the dihedral angles relative to the backbone of the growing chain have been labeled (σ_2-σ_5), as in that paper.

As usual for molecular modeling studies on insertion polymerization catalysts only the internal energy has been evaluated.

2.2. Computational details

Stationary points on the potential energy surface were calculated with the Amsterdam Density Functional (ADF) program system developed by Baerends et al. [28,29]. The electronic configurations of the molecular systems were described by a triple-ζ STO basis set on Ti for 3s, 3p, 3d, 4s, and 4p. Double-ζ STO basis sets were used for C (2s, 2p) and H (1s). The basis sets on C is augmented with a single 3d polarization function except for H, where a 2p function was used. The $1s^22s^22p^6$ configuration on titanium and $1s^2$ configuration on carbon were assigned to the core and treated within the frozen core approximation. Energetics and geometries were evaluated by using the local exchange-correlation potential by Vosko et al. [30] augmented in a self-consistent manner with Becke's [31] exchange gradient correction and Perdew's [32] correlation gradient correction. First-order scalar relativistic corrections were added to the total energy, since a perturbative relativistic approach is sufficient for 3d metals. Due to the open-shell character of the systems under study an unrestricted formalism has been used.

All the structures that will follow are stationary points on the potential energy surface. Geometry optimizations were terminated if the largest component of the Cartesian gradient was smaller than 0.002 au. Minimum energy intermediates of monomer bound species, for *anti* allyl growing chain relative to butadiene, (*Z*)-pentadiene and 4-methyl-pentadiene, have been located starting from models of Ref. [11], Fig. 2. A preliminary molecular mechanical study to select the conformational minimum energy for the modeled growing chain, followed by an optimisation made with DFT methods.

A considerable amount of related computational studies have contributed to the comprehension of fine details of olefins polymerizations with both early and late transition metals [33], of styrene polymerization with Cp-based titanium catalysts [34], and of butadiene polymerization with Ni(II) based catalysts [35–38] and, finally, butadiene polymerization with $CpTiCl_3$-MAO in our previous paper [11]. Furthermore, a comparative study has shown that DFT functional we have chosen is in excellent agreement with one of the best wavefunction-based methods available today to investigate polymerization reactions with Ziegler–Natta catalysts [39].

3. Results

In this section we discuss geometry and relative energies of monomer free and monomer bound intermediates.

3.1. Preliminary screening between possible polymerization mechanisms

Possible mechanisms for 1,2 polymerization of (*Z*)-pentadiene were preliminary screened by comparing the energy of the possible monomer bound intermediates leading to 1,2-*unlike* (syndiotactic) insertion (structures **1a–1d** of Fig. 1). Besides the usually assumed intermediate **1a**, presenting a s-*cis*-η^4 coordination of the diene and an *anti*-η^3 coordination of the growing chain, typical of dienes with low energy η^4 coordination [8,10–12], we located three more coordination intermediates of similar or lower energy. Intermediate **1b**, with a η^2 coordinated monomer and a *syn*-η^3 coordination of the chain—originally suggested by Porri and co-workers [15]—is very close in energy to the classical s-*cis*-η^4/*anti*-η^3 intermediate **1a**. Intermediate **1c**—suggested by some of us in a previous paper [18]—is characterized by a η^2 coordination of the monomer, a η^1 coordination of the growing chain, and a η^2 coordination of the double bond of the penultimate inserted unit and is substantially more stable than intermediate **1a**. Finally, intermediate **1d**, presenting a η^2 coordination of the monomer, a *syn*-η^3 coordination of the growing chain (as for **1b**) and a η^2 back-biting coordination of the growing chain (as for **1c**) is by far the more stable intermediate.

On the basis of this preliminary analysis, we confined our study to a detailed comparison between the traditional polymerization mechanism sketched in the upper part of Scheme 1, involving monomer bound intermediates like **1a** (mechanism I), and an alternative mechanism compatible

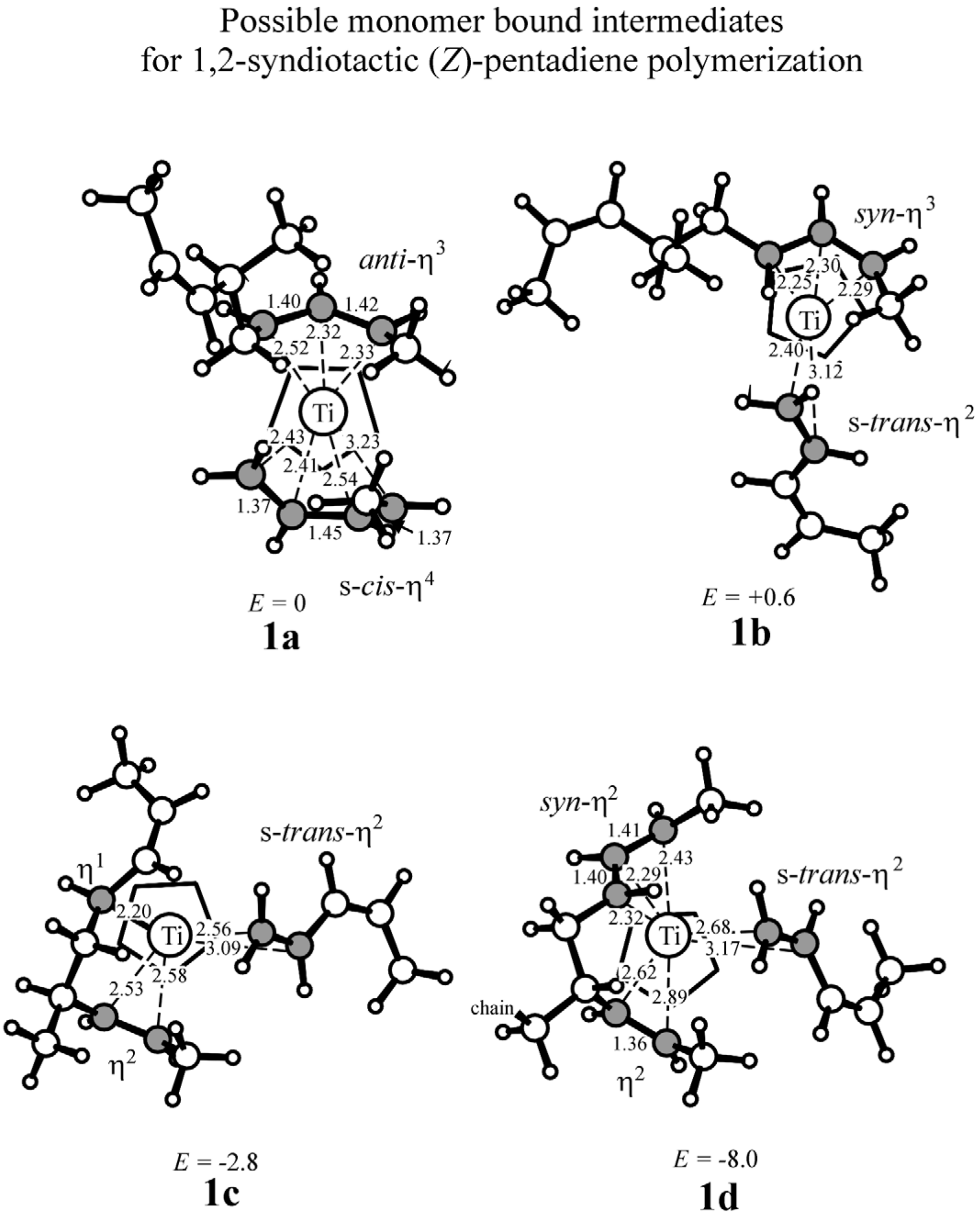


Fig. 1. Minimum energy geometries of possible monomer bound intermediates, which could lead to 1,2-*unlike* (syndiotactic) insertion. **1a** presents a s-*cis*-η^4 coordination of the diene monomer and an *anti*-η^3 allyl coordination of the growing chain, **1b** presents an η^2 monomer coordination and a *syn*-η^3 allyl coordination of the growing chain, **1c** presents η^2 coordination of the monomer and (η^1,η^2) back-biting growing chain and **1d** presents an η^2 coordination of the monomer and (η^3,η^2) back-biting growing chain. Distances are in Å and energies are in kcal/mol.

with the monomer bound intermediate **1d** (mechanism II), sketched in the lower part of Scheme 1. This comparison will be performed for butadiene, (*Z*)-pentadiene and 4-methyl-pentadiene.

3.2. Comparison between mechanisms I and II: monomer free intermediates

Conformational requirements for a back-biting of a syn-η^3-allyl growing chain. A full analysis of the conformations of diastereomeric monomer free intermediates showed that the conformational requirements for the back-biting of a *syn*-η^3 chain are very strict [27]. As for $[\mathrm{CpTi(C_7H_{11})}]^+$ (Fig. 2), we found two minimum energy conformations for each chirality of coordination of the allyl group: (2b,2c) and (2b,2d) for the R and S chirality of the internal allyl carbon, respectively.

The models of low energy (**2a** and **2b**) involve the η^2 back-biting double bond roughly parallel to the Cp plane, whereas the models of high energy (**2c** and **2d**) show the η^2 back-biting double bond roughly orthogonal to the Cp plane. The higher energy of **2c** and **2d** is associated with the

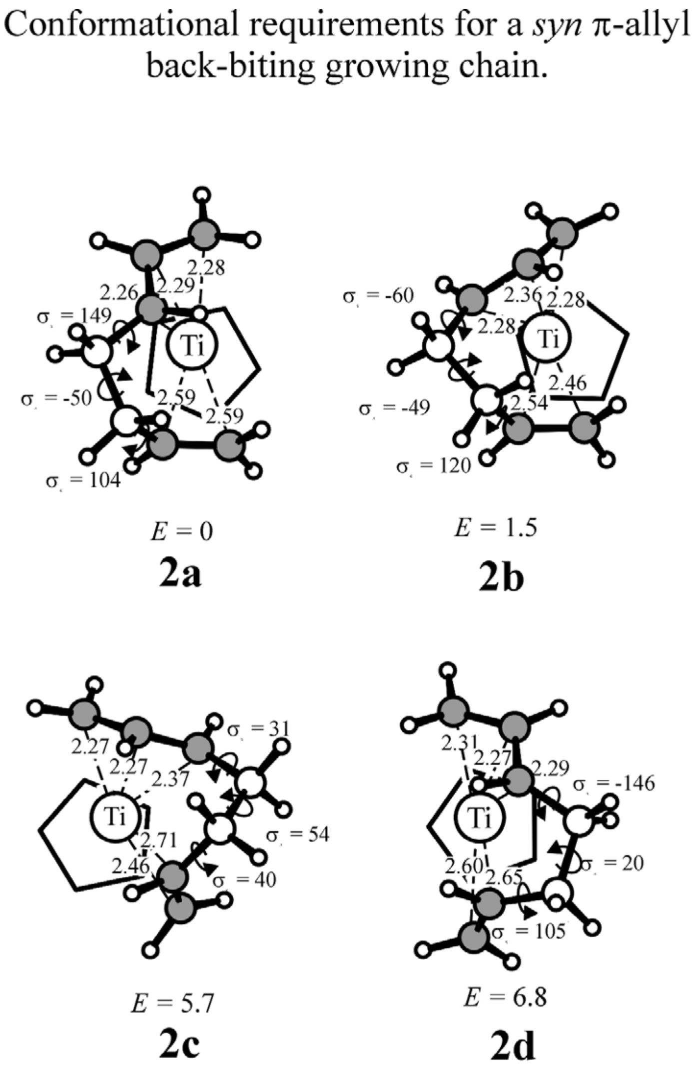


Fig. 2. Minimum energy conformations of a back-biting *syn* π-allyl growing chain for a monomer free intermediates presenting a Cp ligand. Distances are in Å and energies are in kcal/mol. The dihedral angles σ_3, σ_4 and σ_5 are defined as in Ref. [23b].

orientation of the η^2 back-biting double bond, since similar calculations on a simplified model coordinating to a Ti atom an ethylene molecule, a Cp ring and an allyl group showed that an ethylene orientation nearly parallel to the Cp plane (as for **2a** and **2b**) is favored of about 5 kcal/mol in comparison to an ethylene nearly orthogonal with respect to the Cp plane (as for **2c** and **2d**) [11].

It is worth noting that the minimum energy model **2a** presents the chiralities of coordination of the allyl group and of the double bond as observed in the X-ray structure of a Pd(II) geranyl complex [24]. Moreover, the sequence of the dihedral angles of **2a** is similar to that of the geranyl complex ($\sigma_2 = 162°$, $\sigma_3 = 121°$, $\sigma_4 = -57°$, $\sigma_5 = 126°$). We found similar conformations also for the monomer free intermediates **3a**, **3b**, **4a**, **4b**, **5a** and **5b**, that will be discussed in the following.

Monomer free intermediates with polybutadienyl growing chains. The minimum energy diastereoisomeric monomer free intermediates for complexes with a Cp ligand and a back-biting *syn*-η^3 polybutadienyl growing chain (where also the penultimate unit has been obtained from a *syn*-η^3 polybutadienyl chain) are shown in Fig. 3(a)–(d), and their energies are reported in Table 1. Structures **3a** and **3b** correspond to *trans*-1,4-like and 1,2-unlike enchainments, respectively, and were obtained from structure **2a** by suitable positioning of the growing chain. Structures **3c**

Table 1

Mechanisms	Butadiene					
	Monomer free intermediates			Monomer bound Intermediates		
II	**3a**	*trans*-1,4-*like*	1.2	**6a**	*trans*-1,4-*like*	1.5
	3b	1,2-*unlike*	0	**6b**	1,2-*unlike*	1.1
	3c	*trans*-1,4-*unlike*	3.3	**6c**	*trans*-1,4-*unlike*	0.1
	3d	1,2-*like*	1.9	**6d**	1,2-*like*	0
I	**3e**	*cis*-1,4-*like*	−3.5	**6e**	*cis*-1,4-*like*	−1.0
	3f	1,2-*unlike*	−2.8	**6f**	1,2-*unlike*	2.0

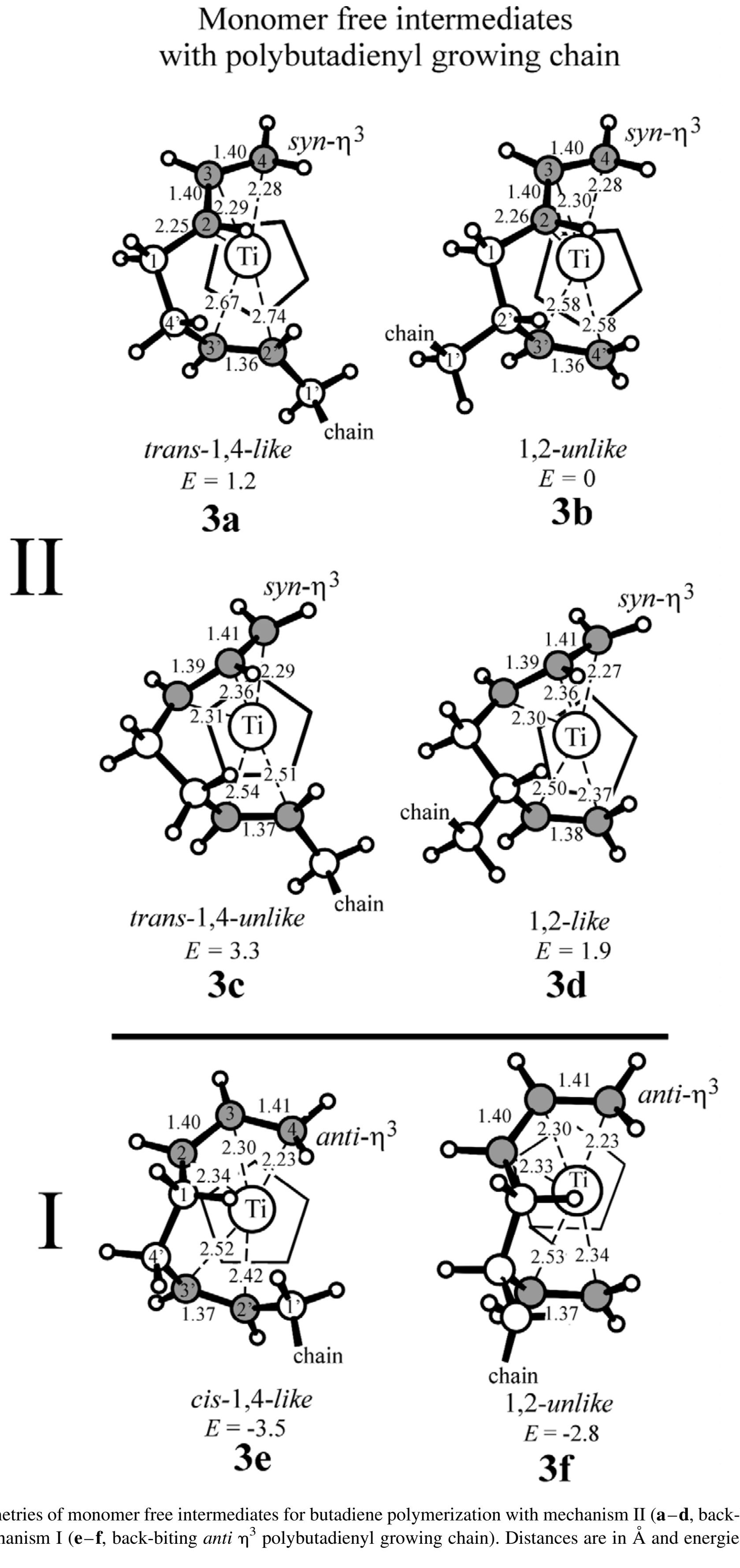


Fig. 3. Minimum energy geometries of monomer free intermediates for butadiene polymerization with mechanism II (**a**–**d**, back-biting *syn* η^3 polybutadienyl growing chain) and with mechanism I (**e**–**f**, back-biting *anti* η^3 polybutadienyl growing chain). Distances are in Å and energies are in kcal/mol.

and **3d**, instead, correspond to *trans* 1,4-*unlike* and 1,2-*like* enchainments, respectively, and were obtained from structure **2b** in a similar way.

The lower energy of **3a** and **3b** relative to **3c** and **3d** substantially reflects the lower energy of **2a** relative to **2b**. Moreover, the higher energy of the 1,4 enchainments (**3a** and **3c**) relative to the corresponding 1,2 enchainments (**3b** and **3d**) can be related to the position of the added methyl group, $\mathrm{C1'}$, which simulates the remaining of the growing chain. It sterically interacts with the Cp ring in the 1,4 enchainments, whereas it is external with respect to the catalytic site in the 1,2 enchainments. In fact, in **3a** and **3c** the shortest distances between the methyl group and the Cp ring are close to 3.3 Å. This interaction also induces a worse coordination of the double bond in **3a**, as evidenced by the relatively longer Ti-$\mathrm{C2'}$ and Ti-$\mathrm{C3'}$ distances in **3a** relative to **3b**–**3d**.

In the framework of mechanism I, the minimum energy monomer free intermediates **3e** and **3f**, characterized by a back-biting *anti*-η^3 polybutadienyl growing chain (where also the penultimate unit has been obtained from an *anti*-η^3 chain), correspond to a *cis*-1,4-*like* and to a 1,2-*unlike* enchainments, respectively [11]. Both intermediates present the methyl group simulating the growing chain in the opposite direction with respect to the Cp ring. Despite the generally higher energy of *anti*-allyl group with respect to the *syn*-allyl group, **3e** and **3f** and are of quite lower energy relative to the *syn* allyl intermediates **3a**–**3d**. On the basis of our previous studies [11], this energetical preference could be related to a more favorable orientation and, hence of coordination, of the *anti*-allyl group with respect to the Cp ring.

Monomer free intermediates with poly-(Z)-pentadienyl growing chains. The minimum energy diastereoisomeric monomer free intermediates, for complexes presenting a back-biting *syn*-η^3 poly-(*Z*)-pentadienyl chain are shown in Fig. 4(a)–(d), and their energies are reported in Table 2. Similarly to the butadiene intermediates of Fig. 3, structures **4a**, **4b**, **4c** and **4d** correspond to *trans*-1,4-*like*, 1,2-*unlike*, *trans*-1,4-*unlike* and 1,2-*like* enchainments, respectively.

Energy differences are amplified relative to the corresponding intermediates of Fig. 3, since structures **4a** and **4b**, derived from **2a**, are of remarkably lower energy relative to structures **4c** and **4d**, derived from structure **2b**. The high energy of **4c** and **4d** can be traced to the different position of the methyl group of the last inserted (*Z*)-pentadiene unit indicated as C5. The short distances between this methyl group and the Cp ring, below 3.2 Å for **4c** and **4d**, are indicative of repulsive steric interactions that also cause a worse coordination of the allyl group, as evidenced by the longer Ti-C4 distances in **4c** and **4d** compared to **4a** and **4b**.

Energy differences between 1,4 and 1,2 enchainments are amplified by the presence of the methyl group, ($\mathrm{C5'}$), of the penultimate inserted unit, which has a nearly *cis* conformation with respect to $\mathrm{C2'}(\mathrm{C5'}-\mathrm{C4'}-\mathrm{C3'}-\mathrm{C2'} = 20^\circ$ and 8.1° for **4a** and **4c**, respectively).

As for butadiene, the minimum energy monomer free intermediates **4e** and **4f**, characterized by a back-biting *anti*-η^3 poly-(*Z*)-pentadienyl growing chain correspond to a *cis*-1,4-like and to a 1,2-unlike enchainments, respectively [11]. Although the growing chain is bonded to two different positions, models **4e** and **4f** are identical since the growing chain has been simply simulated by a methyl group. Differently from butadiene, intermediates as **4e** and **4f**—charaterized by an *anti*-η^3 coordinated chain and thus consistent with mechanism I—are not the most stable structures since they are destabilized by the *cisoid anti* allyl group (both C5 and C1 are *anti* with respect to the allyl group). Thus, for (*Z*)-pentadiene the monomer free intermediate **4b**, with a back-biting *syn*-η^3 chain and leading through mechanism II to a 1,2-unlike enchainment, is by far the lowest energy structure.

Monomer free intermediates with poly-4-methyl-pentadienyl growing chains. The minimum energy diastereoisomeric monomer free intermediates, for complexes presenting a back-biting *syn*-η^3 poly(4-methyl-pentadienyl) chain are shown in Fig. 5(a)–(d), and their energies are reported in Table 3. Similarly to the butadiene and (*Z*)-pentadiene, structures **5a**, **5b**, **5c** and **5d** correspond to *trans*-1,4-like, 1,2-unlike, *trans*-1,4-unlike and 1,2-like enchainments, respectively.

Geometries and energy differences are similar to those of the corresponding monomer free intermediates for (*Z*)-pentadiene polymerization and reported in Fig. 4. However, the 1,2-unlike intermediate **5b** presents a worse coordination of the back-biting double bond relative to **4b** (longer

Table 2

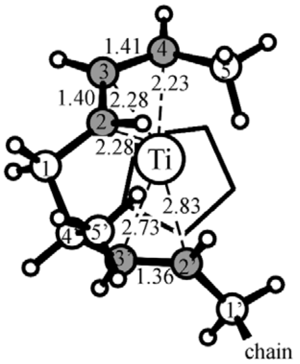
Mechanisms	(*Z*)-Pentadiene					
	Monomer free intermediates			Monomer bound Intermediates		
II	**4a**	*trans*-1,4-*like*	5.3	**7a**	*trans*-1,4-*like*	3.5
	4b	1,2-*unlike*	0	**7b**	1,2-*unlike*	0.2
	4c	*trans*-1,4-*unlike*	17.6	**7c**	*trans*-1,4-*unlike*	3.2
	4d	1,2-*like*	10.4	**7d**	1,2-*like*	0
I	**4e**	*cis*-1,4-*like*	5.8	**7e**	*cis*-1,4-*like*	8.1
	4f	1,2-*unlike*	5.8	**7f**	1,2-*unlike*	8.2

Table 3

Mechanisms	4-Methyl-pentadiene					
	Monomer free intermediates			Monomer bound Intermediates		
II	**5a**	*trans*-1,4-*like*	2.8	**8a**	*trans*-1,4-*like*	3.6
	5b	1,2-*unlike*	0	**8b**	1,2-*unlike*	1.0
	5c	*trans*-1,4-*unlike*	15.4	**8c**	*trans*-1,4-*unlike*	6.0
	5d	1,2-*like*	10.0	**8d**	1,2-*like*	0
I	**5e**	*cis*-1,4-*like*	5.7	**8e**	*cis*-1,4-*like*	11.2
	5f	1,2-*unlike*	4.7	**8f**	1,2-*unlike*	6.7

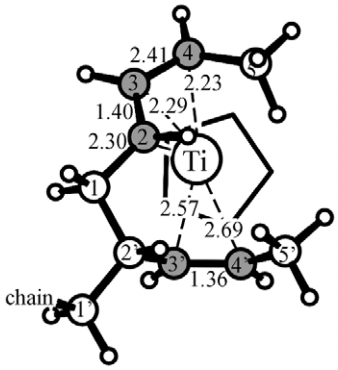
Monomer free intermediates
with poly-(Z)-pentadienyl growing chain

II



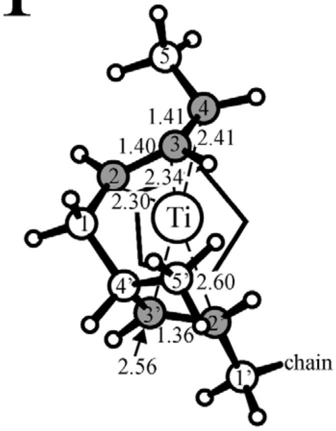
trans-1,4-*like*
E = 5.3

4a



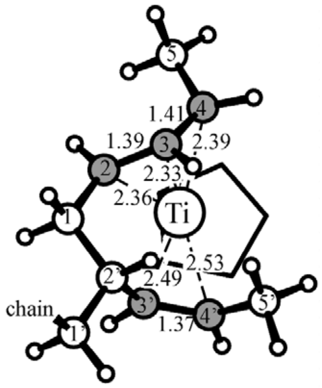
1,2-*unlike*
E = 0

4b



trans-1,4-*unlike*
E = 17.6

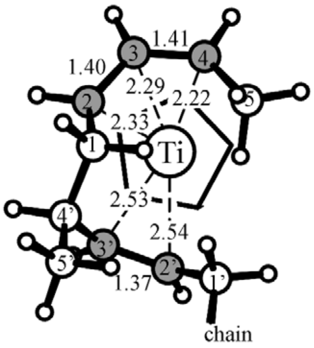
4c



1,2-*like*
E = 10.4

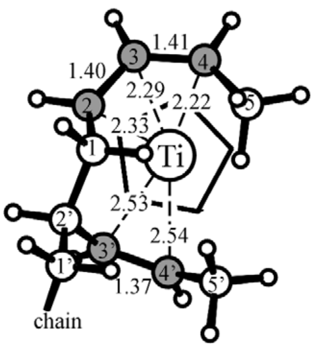
4d

I



cis-1,4-*like*
E = 5.8

4e



1,2-*unlike*
E = 5.8

4f

Ti-C3$'$ and Ti-C4$'$ distances). Moreover, the **5c** *trans*-1,4-*unlike* and **5d** 1,2-*like* intermediates present a worse coordination of the allyl group relative to the corresponding **4c** and **4d** (*Z*)-pentadiene intermediates (longer Ti–C4 distances). The minimum energy monomer free intermediates **5e** and **5f**, with a back-biting *anti*-η^3 allyl terminal of the growing chain, correspond to *cis*-1,4-like and 1,2-unlike enchainments. As for (*Z*)-pentadiene, and differently from butadiene, these intermediates are of remarkably high energy due to the *cisoid anti* allyl group. Thus, as for (*Z*)-pentadiene the monomer free intermediate **5b**, with a back-biting *syn*-η^3 chain and leading through mechanism II to a 1,2-unlike enchainment, is by far the lowest energy structure.

3.3. Comparison between mechanisms I and II: monomer bound intermediates

Butadiene monomer bound intermediates. In the framework of mechanism II monomer bound intermediates are obtained by adding a *trans*-η^2 monomer in the metal coordination sphere of the monomer free intermediates **3a**–**3d**. The minimum energy monomer bound intermediates for *trans* 1,4-*like*, 1,2-*unlike*, *trans* 1,4-*unlike* and 1,2-*like* enchainments are reported in Fig. 6(a)–(d), respectively, while their energies are reported in Table 1.

Structures **6a** and **6b** are of slightly higher energy relative to **6c** and **6d** due to a worse coordination of the butadiene monomer, as suggested by the substantially longer Ti-butadiene distances in **6a** and **6b**. It is worth noting that in monomer bound intermediates **6a**–**6d** the conformation of the growing chain remains close to the corresponding monomer free intermediates **3a**–**3d**.

Low energy monomer bound intermediates involving a s-*cis*-η^4 coordinated monomer and an *anti*-η^3 coordinated terminal of the growing chain, corresponding to *cis-1,4-like* and 1,2-*unlike* enchainments, are shown in Fig. 6(e) and (f), respectively. These models are similar to those of Fig. 2 of Ref. [11]. However, to get a quantitative comparison with the other models of Fig. 6, a monomer unit has been added to the growing chain. Intermediate **6e** presents an energy slightly lower than all the *syn* allyl structures (− 1.0 kcal/mol with respect to structure **6d**). The energy difference could be attributed to a better orientation of the allyl group with respect to the Cp ring [11], and to a reduction of the steric hindrance, due to the removal of the back-biting, which allows to extend the rest of the growing chain out of the metal coordination sphere. Moreover, the removal of the back-biting is electronically compensated by the η^4 instead of η^2 coordination of the monomer.

As for the monomer coordination energies, ΔE_{coord}, the back-biting *syn* allyl intermediate **6b**, which corresponds to the monomer free intermediate of lowest energy, presents a $\Delta E_{\text{coord}} = -8.7$ kcal/mol, while intermediate **6d**, which is the lowest energy monomer bound intermediate with a *syn* allyl terminal of the growing chain, presents a $\Delta E_{\text{coord}} = -11.7$ kcal/mol. As reported in Ref. [11], in the framework of mechanism I the *cis*-1,4-*like* enchainment presents a $\Delta E_{\text{coord}} \approx -5$ kcal/mol. The lower coordination energy for *cis*-1,4-*like* is due to the loss of the back-biting in the monomer bound intermediate. Of course, less negative or even positive ΔG_{coord} are expected as a consequence of the reduction of entropy associated with monomer coordination [11].

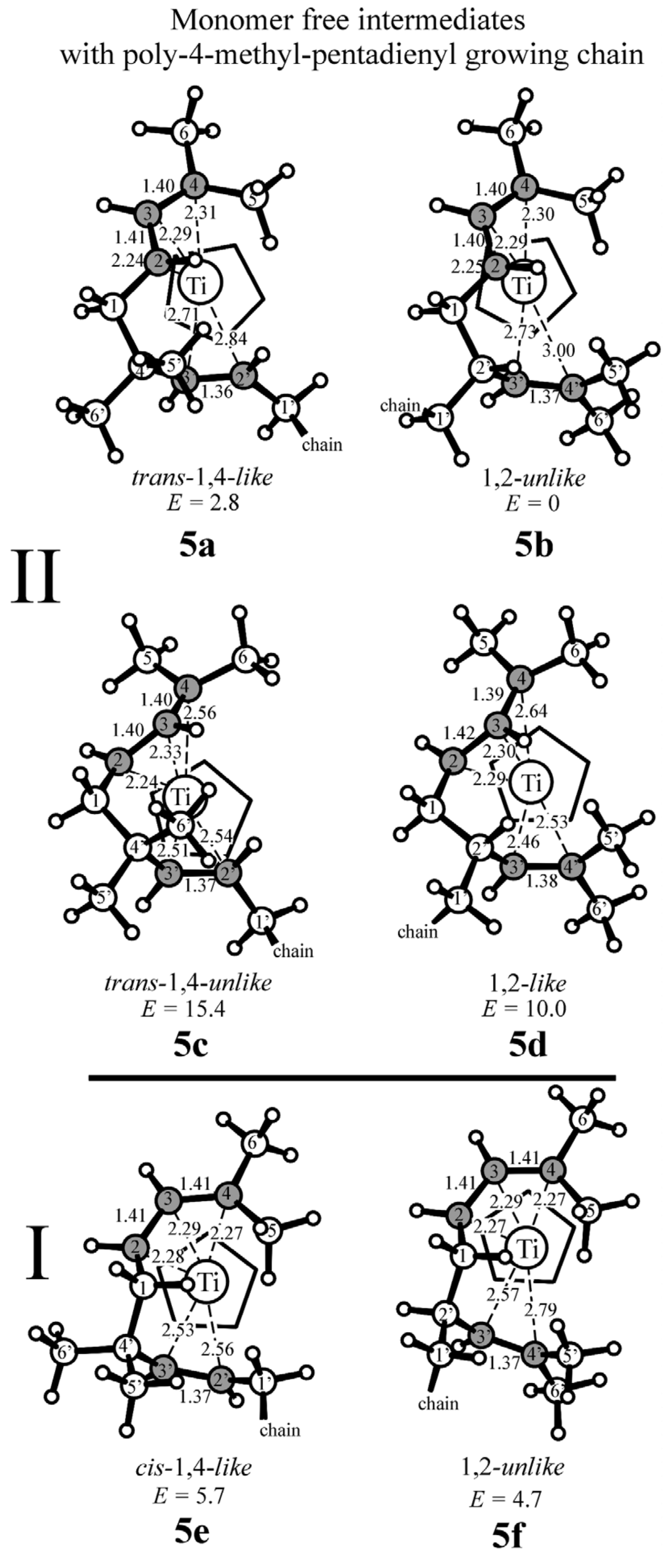
(Z)-pentadiene monomer bound intermediates. Monomer bound intermediates are obtained by adding a *trans*-η^2 monomer in the metal coordination sphere of the monomer free intermediates **4a**–**4d**. The minimum energy monomer bound intermediates for *trans* 1,4-*like*, 1,2-*unlike*, *trans* 1,4-*unlike* and 1,2-*like* enchainments are reported in Fig. 7(a)–(d), respectively, while their energies are reported in Table 2.

Energy differences are lower with respect to those of the corresponding monomer free intermediates. 1,2 Enchainments remain favored with respect to 1,4 enchainments, but intermediates **7b** and **7d** corresponding to the 1,2-*unlike* and 1,2-*like* enchainments are now of similar energy. Of course, this corresponds to a much higher coordination energy for the 1,2-*like* pathway than for 1,2-*unlike* pathway ($\Delta E_{\text{coord}} = -11.9$ and -1.3 kcal/mol, respectivley) and in remarkably shorter Ti-monomer distances in **7d** relative to **7b**. Moreover, steric interactions between the monomer and the C5$'$ methyl group of the allyl chain in **7b** slightly push away the C4$'$ atom of the allyl chain from the metal, compared to the corresponding monomer free intermediate **4b**. As for butadiene, entropy contributions will reduce the corresponding ΔG_{coord}.

Low energy monomer bound intermediates involving a s-*cis*-η^4 coordinated monomer and an *anti*-η^3 coordinated terminal of the growing chain, corresponding to *cis*-1,4-*like* and 1,2-*unlike* enchainments, are shown in Fig. 7(e) and (f), respectively. Differently from butadiene, these intermediates are of substantially higher energy than all the *syn* allyl intermediates **7a**–**7e**. The high energy difference with respect to **7d** is probably due to the *cisoid anti* allyl group (both C5$'$ and C1$'$ are *anti* with respect to the allyl group) as well as to the high energy s-*cis* conformation of the (*Z*)-pentadiene monomer. This determines also an unfavorable coordination energy ($\Delta E_{\text{coord}} = +0.7$ kcal/mol for **7e**).

4-Methyl-pentadiene monomer bound intermediates. Monomer bound intermediates are obtained by adding a *trans*-η^2 monomer in the metal coordination sphere of

Fig. 4. Minimum energy geometries of monomer free intermediates intermediates for (*Z*)-pentadiene polymerization with mechanism II (**a**–**d**, back-biting *syn* η^3 poly-(*Z*)-pentadienyl chain) and with mechanism I (**e**–**f**, back-biting *anti* η^3 poly-(*Z*)-pentadiene growing chain). Distances are in Å and energies are in kcal/mol.


Monomer free intermediates
with poly-4-methyl-pentadienyl growing chain
II
1.40
2.31
1.41
2.29
2.24
2.71
2.84
1.36
chain
trans-1,4-like
E = 2.8
5a
1.40
2.30
1.40
2.29
2.25
2.73
3.00
1.37
chain
1,2-unlike
E = 0
5b
1.40
2.56
1.40
2.33
2.24
2.54
2.51
1.37
chain
trans-1,4-unlike
E = 15.4
5c
1.39
2.64
1.42
2.30
2.29
2.53
2.46
1.38
chain
1,2-like
E = 10.0
5d
I
1.41
1.41
2.29
2.27
2.28
2.53
2.56
1.37
chain
cis-1,4-like
E = 5.7
5e
1.41
1.41
2.29
2.27
2.27
2.57
2.79
1.37
chain
1,2-unlike
E = 4.7
5f
Ti

the monomer free intermediates **5a–5d**. The minimum energy monomer bound intermediates for *trans*-1,4-*like*, 1,2-*unlike*, *trans*-1,4-*unlike* and 1,2-*like* enchainments are reported in Fig. 8(a)–(d), respectively, while their energies are reported in Table 3.

Geometries and energy differences are very similar to those reported for (*Z*)-pentadiene, suggesting that the additional methyl group in position 4 of the monomer does not interact repulsively with the other intermediates. Also the monomer coordination energies are rather similar to those calculated for (*Z*)-pentadiene. For example, we calculated a $\Delta E_{\mathrm{coord}}$ of -2.6 and -13.6 kcal/mol in **8b** and in **8d**, to be compared with the values of -1.3 and -11.9 kcal/mol in **7b** and **7d**, respectively.

Low energy monomer bound intermediates involving a s-*cis*-η^4 coordinated monomer and an *anti*-η^3 coordinated terminal of the growing chain, corresponding to *cis*-1,4-*like* and 1,2-*unlike* enchainments, are shown in Fig. 8(e) and (f), respectively. As for (*Z*)-pentadiene, and differently from butadiene, these intermediates are of substantially higher energy than all the *syn* allyl intermediates **7a–7e**.

4. Discussion

4.1. Polymerization mechanism for butadiene: the poorly chemoselective Mechanism I

According to the calculations reported in the previous sections for the $CpTiCl_3$-MAO catalytic system, monomer free and monomer bound intermediates for butadiene polymerization presenting a back-biting *syn* allyl terminal of the growing chain are always unfavored with respect to corresponding intermediates presenting an *anti* allyl terminal of the growing chain (Fig. 3 and Table 1). Moreover, the intermediates corresponding to *cis*-1,4-*like* (**3e**) and 1,2-*unlike* (**3f**) insertions present similar energies.

Hence, the present more complete calculations confirm that for butadiene, as well as for other diene monomers with low energies of s-*cis*-η^4 coordination like isoprene and (*E*)-pentadiene, the lowest energy insertion pathways would correspond to *cis*-1,4-*like* and 1,2-*unlike* in the framework of mechanism I, as described in Fig. 10 of Ref. [11]. Of course, these results are able to account for the poor chemoselectivity of the polymerization of these diene monomers in the presence of the $CpTiCl_3$–MAO catalytic system.

4.2. Polymerization mechanism for (Z)-pentadiene and 4-methyl pentadiene: the highly chemoselective Mechanism II

According to the calculations reported in the previous sections for the $CpTiCl_3$–MAO catalytic system, as for (*Z*)-pentadiene and 4-methyl-pentadiene, monomer free intermediates presenting a back-biting *syn* allyl terminal of the growing chain and leading to a 1,2-*unlike* enchainment (**4b** and **5b**, respectively) are largely favored with respect to all the other monomer free intermediates (see Tables 2 and 3). Moreover, monomer bound intermediates presenting a back-biting *syn* allyl terminal growing chain and a *trans* η^2 coordinated monomer and leading to 1,2 enchainments (**7b**,**d** and **8b**,**d**, respectively) are favored with respect all the other monomer bound intermediates.

Hence, diene monomers with high energy of s-*cis* η^4 coordination, like (*Z*)-pentadiene and 4-methyl-pentadiene, would preferably react according to mechanism II and correspondingly the polymerization would be highly chemoselective and stereoselective in favor of 1,2-syndiotactic propagation.

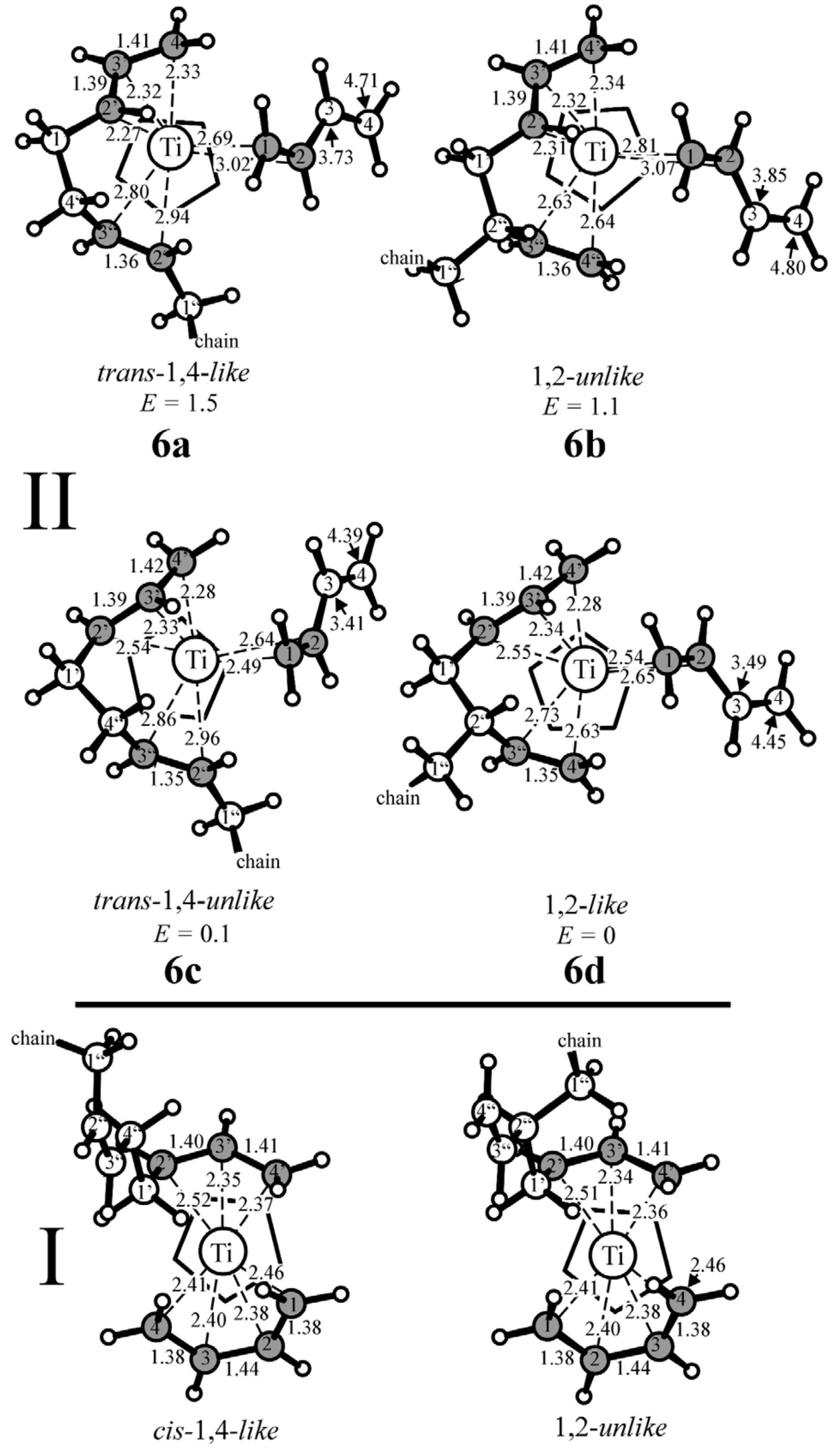
These results account for the high syndiotacticity of the 1,2 polydienes obtained by polymerization of 4-methyl-pentadiene [14] and by low temperature polymerization of (*Z*)-pentadiene [14,16–19].

The monomer bound intermediate of mechanism II (Scheme 1), presenting a close back-biting of the growing chain, becomes, of course, unfeasible, if the penultimate inserted unit does not present a double bond. This occurs, for instance, for the first monomer insertion or for diene inserted units following an ethylene insertion. The lack of a possible back-biting could lead to a switch, for that particular insertion step, from the η^2 monomer coordination (mechanism II) toward the s-*cis*-η^4 coordination (mechanism I). This change of mechanism can easily rationalize the low chemoselectivity which has been observed after an ethylenic unit [19,21], as well as for the first insertion step [21] (Scheme 3).

The monomer bound intermediates of mechanism II are expected to be entropically unfavored with respect to those of mechanism I, due to the strong reduction of conformational freedom associated with the back-biting double bond. This could suggest that also the change of chemoselectivity, which has been observed for (*Z*)-pentadiene by increasing the temperature, could be associated with a change from mechanism II to mechanism I.However, according to our calculations, the similar energies of the monomer bound intermediates **7e** and **7f**, as well as the similar energies of the corresponding monomer free intermediates **4e** and **4f** (see Table 2), show that the

Fig. 5. Minimum energy geometries of monomer free intermediates for 4-methyl-pentadiene polymerization with mechanism II (**a–d**, back-biting *syn* η^3 poly-4-methyl-pentadienyl chain) and with mechanism I (**e–f**, back-biting *anti* η^3 poly-4-methyl-pentadiene growing chain). Distances are in Å and energies are in kcal/mol.

Butadiene monomer bound intermediates



trans-1,4-*like*
$E = 1.5$
6a

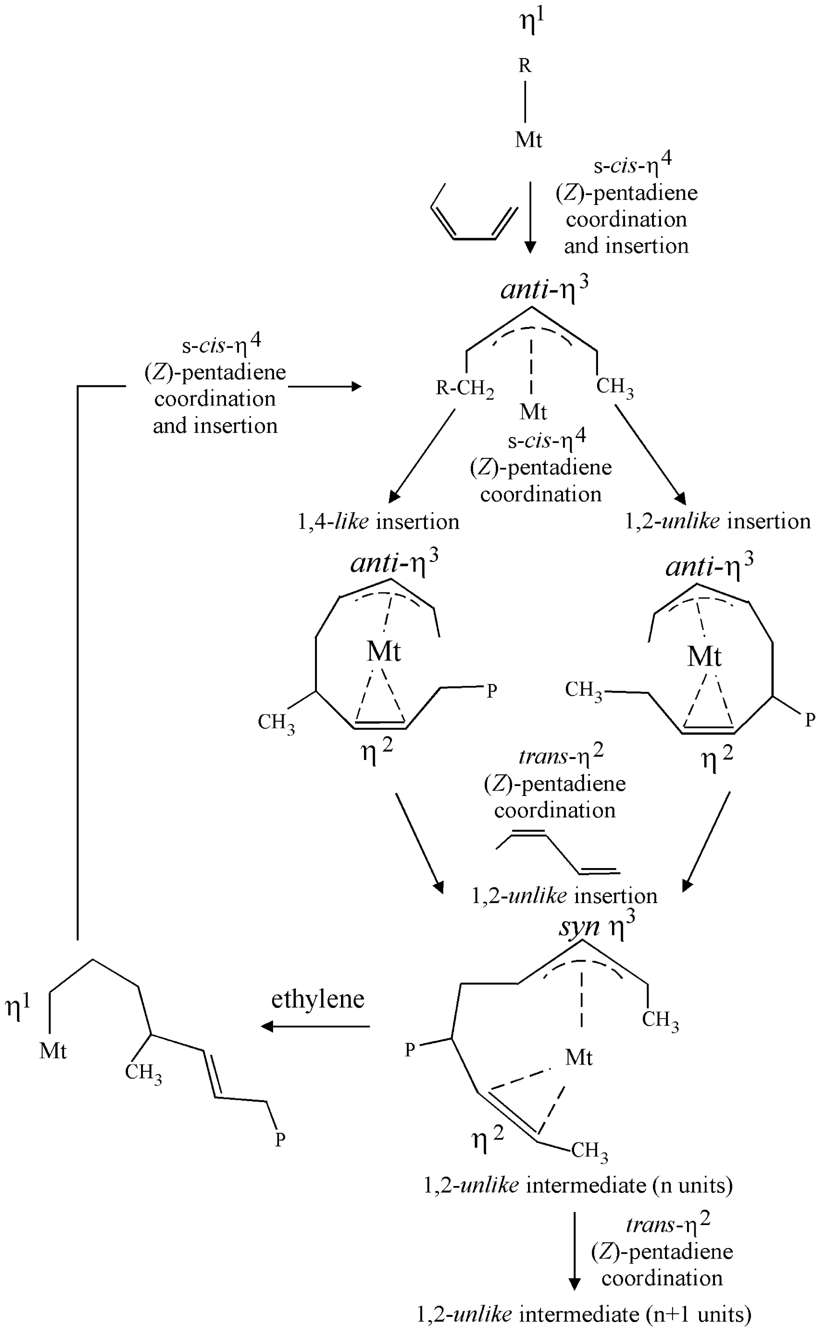
1,2-*unlike*
$E = 1.1$
6b

trans-1,4-*unlike*
$E = 0.1$
6c

1,2-*like*
$E = 0$
6d

cis-1,4-*like*
$E = -1.0$
6e

1,2-*unlike*
$E = 2.0$
6f

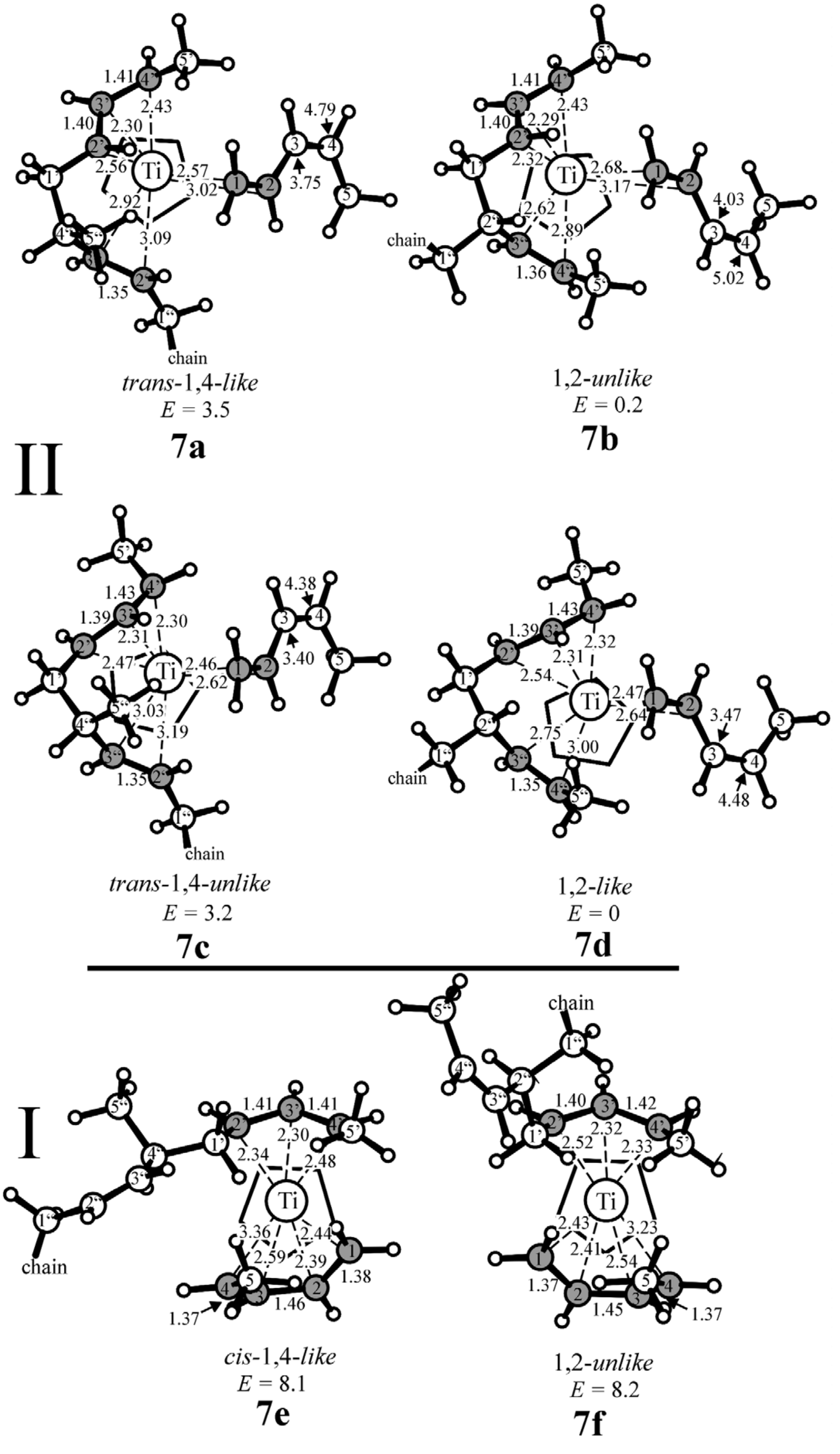


Scheme 3.

mechanism I is anyway expected to be poorly chemoselective. This is especially true for (*Z*)-pentadiene whose *anti* allyl terminal of the growing chain presents similarly hindered internal and terminal carbon atoms (see, e.g. atoms 2′ and 4′ in Fig. 7(e) and (f)). Hence a possible switch from mechanism II to mechanism I, for (*Z*)-pentadiene as a consequence of temperature increase, seems unsuitable to account for the high 1,4 *cis* isotactic chemo and stereoselectivity, which is observed for this monomer in the temperature range 20–70 °C. Further modeling studies are in progress in the attempt to find a possible rationalization of this high temperature chemo and stereoselectivity.

Fig. 6. Minimum energy geometries of monomer bound intermediates for butadiene polymerization with mechanism II (**a**–**d**, *trans* η^2 coordinated butadiene and back-biting *syn* η^3 polybutadienyl chain) and with mechanism I (**e**–**f**, s-*cis* η^4 coordinated butadiene and *anti* η^3 polybutadienyl growing chain). Distances are in Å and energies are in kcal/mol.

(*Z*)-pentadiene monomer bound intermediates



4.3. Molecular origin of stereoselectivity for 1,2 syndiotactic polymerization in the framework of Mechanism II

In this section we investigate in detail mechanism II, aiming to establish the molecular factors determining its syndiospecificity. Models and schematic energy plots corresponding to coordination and subsequent insertion, on the minimum energy monomer free intermediate, of both enantiofaces of the η^2 coordinated (*Z*)-pentadiene monomer are shown in Fig. 9.

The free energy profiles have been sketched in the rough assumption that the loss of entropy associated with monomer coordination is of 10 kcal/mol. It seems reasonable to assume that the $-T\Delta S$ contribution to the free energy of diene complexation to a group 4 metal atom in these catalysts is at least equal to 10 kcal/mol, that is the value observed [40] as well as calculated [41] at 300 K for olefin coordination to Ni and Pd compounds.

First of all it is worth noting that, for a growing chain presenting an allyl coordination to the metal associated with a back-biting of the double bond of the penultimate inserted unit, minimum energy intermediates correspond to an *endo* coordination of the allyl group with respect to the ancillary ligand (in our case the Cp). This is true for polydienic growing chain presenting both *syn* (see, e.g. models **3b**, **4b** and **5b**) and *anti* (see, e.g. models **3e** and **3f**) coordinated allyl groups, independently of the considered diene monomer. In particular, for the case of (*Z*)-pentadiene the minimum energy free intermediate (**4b**), presents an *endo syn* allyl coordination of the growing chain. Without loss of generality, let us consider only the monomer free intermediate which presents a *R* chirality [26] of the internal allyl carbon, shown in the left side of Fig. 9.

The η^2 coordination of a diene monomer is chiral. In fact, as shown by the monomer bound intermediates which are presented in the middle of Fig. 9, the η^2 diene coordination can occur with one of its two possible enantiofaces which also can be indicated through the *R* or *S* chirality of the internal carbon atom of the coordinated double bond [26]. Of course, since the considered growing chain coordination is also chiral, this generates two diastereoisomeric monomer bound intermediates. Our energy analysis clearly indicates that the monomer coordination step is poorly enantioselective. For instance, for the case of (*Z*)-pentadiene the energy difference between the monomer bound intermediates, which are shown in Fig. 9, is close to 1 kcal/mol.

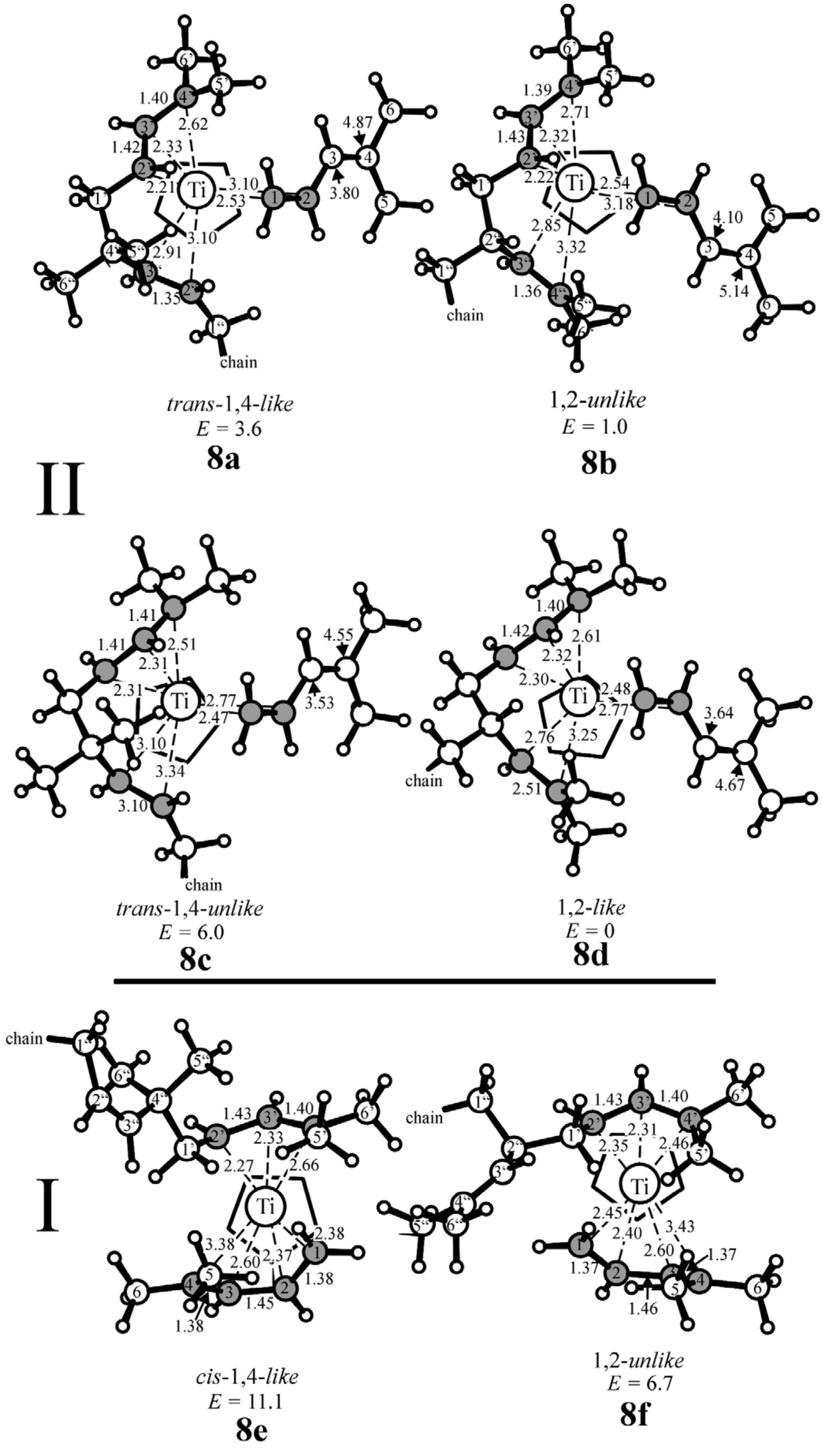
Large energy differences, instead, occur in favor of the 1,2 insertion of the η^2 *R* coordinated diene, which eventually leads to a new monomer free intermediate which present opposite chirality of coordination of the allyl with respect to the starting one. In fact, as shown by the darker model on the right side of Fig. 9, the new monomer free intermediate presents an allyl group again *endo* coordinated to the metal but with a *S* chirality at the internal allyl carbon. The 1,2 insertion of a *S* coordinated diene leads to the monomer free intermediate (lighter model on the right side of Fig. 9), which presents the allyl group coordinated to the metal with a *R* chirality. This insertion pathway is energetically unfavored since the resulting monomer free intermediate (as well as the corresponding transition state) is not able to assume the low energy *endo* allyl coordination, if associated with a back-biting of the double bond of the penultimate inserted unit. A sequence of insertion steps like that one corresponding to the minimum energy pathway (continuous line) of Fig. 9 leads to 1,2 syndiotactic polymerization, whose stereocontrol is dictated by the chirality of coordination of the *syn* allyl terminal of the back-biting growing chain.

It is worth adding that the starting monomer free intermediate of Fig. 9 corresponds to a penultimate unit which has been obtained by a 1,2 *unlike* insertion. However, all considerations previously done on the mechanism of Fig. 9 also hold for penultimate units which would have been accidentally obtained by 1,2-*like* or 1,4-*cis* or 1,4-*trans* insertion steps. This indicates that the 1,2-syndiotactic chemo- and stereoselectivity of mechanism II is maintained independently of the constitution and configuration of the previously inserted monomeric unit, when it was obtained by insertion of a conjugated diolefin monomer. Hence, this model corresponds to a chain end stereocontrol with a first order Markovian statistics, as for the configuration of the tertiary carbon atoms of the 1,2 enchained polydienes [42]. On the other hand, as discussed in detail in the previous section, the high stereoselectivity would be lost when the previously inserted monomer unit was obtained by insertion of an olefin monomer, due to a switch from mechanism II to mechanism I.

It is also worth noting that, as it often occurs for models for stereospecific polymerization of olefins (both chiral site controlled C_2 and C_s symmetric metallocene catalysts [43–45] as well as for chain-end controlled catalysts [45, 46]), the discrimination between the monomer enantiofaces would not occur in the coordination step but would be associated with the monomer insertion step. However, for the present mechanism of syndiospecific polymerization of dienes, large energy differences would be not only present between diastereoisomeric transition states but also between diastereoisomeric monomer free intermediates corresponding to the completion of the monomer insertion reaction. These large energy differences can contribute to rationalize the extremely high level of stereoselectivity, which can be

Fig. 7. Minimum energy geometries of monomer bound intermediates for (*Z*)-pentadiene polymerization with mechanism II (**a**–**d**, *trans* η^2 coordinated (*Z*)-pentadiene and back-biting *syn* η^3 poly-(*Z*)-pentadienyl chain) and with mechanism I (**e**–**f**, s-*cis* η^4 coordinated (*Z*)-pentadiene and *anti* η^3 poly-(*Z*)-pentadienyl growing chain). Distances are in Å and energies are in kcal/mol.

4-methyl-pentadiene monomer bound intermediates



trans-1,4-*like*
E = 3.6
8a

1,2-*unlike*
E = 1.0
8b

trans-1,4-*unlike*
E = 6.0
8c

1,2-*like*
E = 0
8d

cis-1,4-*like*
E = 11.1
8e

1,2-*unlike*
E = 6.7
8f

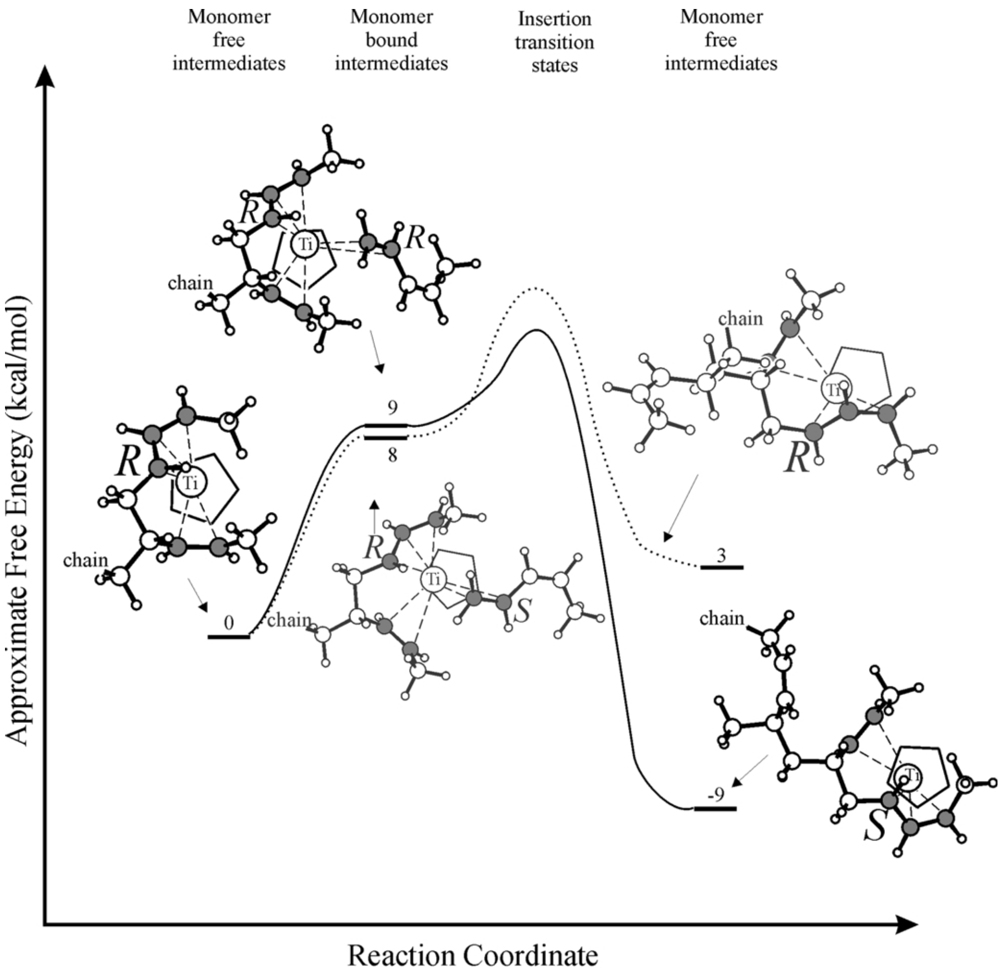


Fig. 9. Models and schematic energy plots corresponding to coordination and subsequent insertion, on the minimum energy monomer free intermediate (**4b**, with a *R* chirality of coordination of the back-biting allyl group), of both enantiofaces (*R* and *S*) of the η^2 coordinated (*Z*)-pentadiene monomer (mechanism II). The minimum energy pathway (continuous line and darker models) leads to an intermediate with *S* chirality of coordination of the back-biting allyl group and hence corresponds to a 1,2 syndiotactic polymerization.

reached for some diene polymerizations although the only elements of chirality are the coordination of the prochiral allyl terminal of the growing chain and the coordination of the prochiral monomer. Let us recall that the olefin polymerizations, when the stereocontrol is only dictated by the chirality of the growing chain, generally lead to much lower stereoselectivities [47]. This higher chain end stereocontrol for diene polymerizations, according to minimum energy intermediates calculated in this paper (Fig. 9), would be due to the geometrical constrain associated with the presence of the back-biting of the double bond of the penultimate monomer unit, for both monomer free and monomer bound intermediates.

5. Conclusions

The results obtained for the $CpTiCl_3$–MAO catalytic system can be summarized as follows.

Diene monomers with low energies of s-*cis*-η^4 coordination, like butadiene, isoprene and (*E*)-pentadiene would react following the mechanism I and the polymerization generally would be poorly chemoselective. On the other hand, diene monomers with high energy of s-*cis*-η^4 coordination, like (*Z*)-pentadiene and 4-methyl-pentadiene, would preferably react according to mechanism II and correspondingly the polymerization would be highly chemoselective and stereoselective in favor of 1,2-syndiotactic propagation.

Fig. 8. Minimum energy geometries of monomer bound intermediates for 4-methyl-pentadiene polymerization with mechanism II (**a**–**d**, *trans* η^2 coordinated 4-methyl-pentadiene and back-biting *syn* η^3 poly-4-methyl-pentadienyl chain) and with mechanism I (**e**–**f**, s-*cis* η^4 coordinated 4-methyl-pentadiene and *anti* η^3 poly-4-methyl-pentadienyl growing chain). Distances are in Å and energies are in kcal/mol.

The monomer bound intermediate of mechanism II (Scheme 1), presenting a close back-biting of the growing chain, becomes, of course, unfeasible, if the penultimate inserted unit does not present a double bond. This occurs, for instance, for the first monomer insertion or for diene inserted units following an ethylene insertion. The lack of a possible back-biting would lead to a switch, for that particular insertion step, from the η^2 monomer coordination (mechanism II) toward the s-*cis*-η^4 coordination (mechanism I). This change of mechanism can easily rationalize the low chemoselectivity which has been observed after an ethylenic unit [19,21], as well as for the first insertion step [20] (Scheme 3).

The high chemoselectivity and chain end controlled stereoselectivity in favor of 1,2-syndiospecific polymerization, in the presence of mechanism II, would be due to the geometrical constrain associated with the back-biting of the growing chain (that is the simultaneous coordination of the allyl terminal of the growing chain and of the double bond of the penultimate monomer unit) which generates large energy differences, also between diastereoisomeric monomer free intermediates. In particular, this 1,2-syndiospecific stereocontrol would be dictated by the chirality of coordination of the *syn* allyl terminal of the back-biting growing chain.

The geometrical constrain dictated by the back-biting of the growing chain in both monomer free and monomer bound intermediates has been already indicated as the essential factor determining the high 1,4-*cis* selectivity for butadiene polymerization by Ni(II) catalysts [11,35–38]. In particular, the *cis*-1,4-*unlike* (syndiospecific for 4-monosubstituted or 1,4 disubstituted monomers) stereocontrol would be dictated by the chirality of coordination of the *anti* allyl terminal of the back-biting growing chain [11].

A possible working hypothesis based on the present and previous calculations [11] is that, more in general, this back-biting constrain could be essential to rationalize the high chemoselectivity and stereoselectivity of the industrially relevant catalytic systems for conjugated diene polymerization.

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References

[1] Porri L, Natta G, Gallazzi MC. Chim Ind (Milan) 1964;46:428–9.
[2] Natta G, Porri L, Carbonaro A, Greco A. Makromol Chem 1964;71:207–11.
[3] Wilke G, Bogdanovich B, Hardt P, Heimbach P, Keim W, Kromer M, Oberkirch W, Tanaka K, Steinrucke E, Walter D, Zimmermann H. Angew Chem Int Ed Engl 1966;5:151–64.
[4] Marconi W. In: Ketley AD, editor. The stereochemistry of macromolecules, vol. 1. New York: Dekker; 1967. p. 239.
[5] Natta G, Porri L. Polymer chemistry of synthetic elastomers. In: Kennedy JP, Tornquist E, editors. Wiley-Interscience; 1969. p. 597. Part II.
[6] Teyssie P, Dawans F. In: Saltman WM, editor. The stereo rubbers. New York: Wiley; 1977. p. 79.
[7] Porri L. In: Ciardelli F, Giusti P, editors. Structural order in polymers. Oxford, UK: Pergamon Press; 1981. p. 51.
[8] Porri L, Giarrusso A. In: Eastmond GC, Ledwith A, Russo S, Sigwalt P, editors. Comprehensive polymer science, 4. Oxford, UK: Pergamon Press; 1989. p. 53. Part II.
[9] Porri L, Giarrusso A, Ricci G. Prog Polym Sci 1991;16:405–41.
[10] Taube R, Windisch H, Maiwald S. Macromol Symp 1995;89:393–409.
[11] Costabile C, Milano G, Cavallo L, Guerra G. Macromolecules 2001;23:7952–60.
[12] Guerra G, Cavallo L, Corradini P, Fusco R. Macromolecules 1997;30:677–84.
[13] Erker G, Berg K, Krüger C, Müller G, Angermund K, Benn R, Schroth G. Angew Chem Int Ed Engl 1984;96:445–6.
[14] Longo P, Oliva P, Proto A, Zambelli A. Gazz Chim Ital 1996;126:377–82.
[15] Oliva L, Longo P, Grassi A, Ammendola P, Pellecchia C. Makromol Chem Rapid Commun 1990;11:519–24.
[16] Ricci G, Porri L, Giarrusso A. Macromol Symp 1995;89:383–92.
[17] Ricci G, Italia S, Porri L. Macromolecules 1994;27:868–9.
[18] Longo P, Proto A, Zambelli A. Macromol Chem Phys 1995;196:3015–29.
[19] Longo P, Guerra G, Grisi F, Pizzuti S, Zambelli A. Macromol Chem Phys 1998;199:149–54.
[20] Longo P, Proto A, Oliva P, Zambelli A. Macromolecules 1996;29:5500–1.
[21] Longo P, Grisi F, Proto A. Macromol Rapid Commun 1997;18:183–90.
[22] Natta G, Giannini U, Pino P, Cassata A. Chim Ind (Milan) 1965;47:524–5.
[23] Taube R, Wache S, Sieler J. J Organomet Chem 1993;459:335–47.
[24] Ciajolo R, Jama MA, Tuzi A, Vitagliano A. J Organomet Chem 1985;295:233–8.
[25] Allegra G, Lo Giudice F, Natta G, Giannini U, Fagherazzi G, Pino P. Chem Commun 1967;24:1263–5.
[26] Hanson KR. J Am Chem Soc 1966;88:2731–42.
[27] Corradini P, Guerra G, Jama MA, Zhi G, Tuzi A. Polym Commun 1985;26:175–8.
[28] Baerends EJ, Ellis DE, Ros P. Chem Phys 1973;2:41–51.
[29] Baerends EJ, Ros P. Chem Phys 1973;2:52–9.
[30] Vosko SH, Wilk L, Nusair M. Can J Phys 1980;58:1200–11.
[31] Becke AD. Phys Rev B 1986;34:7406.
[32] Perdew JP. Phys Rev 1988;38:3098.
[33] (a) Lohrenz JCW, Woo TK, Ziegler T. J Am Chem Soc 1995;117:12793–800. (b) Deng L, Woo TK, Cavallo L, Margl PM, Ziegler T. J Am Chem Soc 1997;119:6177–86. (c) Cavallo L, Guerra G, Corradini P. J Am Chem Soc 1998;120:2428–36. (d) Margl PM, Deng L, Ziegler T. J Am Chem Soc 1998;120:5517–25. (e) Guerra G, Longo P, Corradini P, Cavallo L. J Am Chem Soc 1999;121:8651–2. (f) Milano G, Guerra G, Pellecchia C, Cavallo L. Organometallics 2000;19:1343–9. (g) Longo P, Grisi F, Guerra G, Cavallo L. Macromolecules 2000;33:4647–59.
[34] (a) Minieri G, Corradini P, Zambelli A, Guerra G, Cavallo L. Macromolecules 2001;34:2459–68. (b) Minieri G, Corradini P, Zambelli A, Guerra G, Cavallo L. Macromolecules 2001;34:5379–85.
[35] Tobisch S, Bögel H, Taube R. Organometallics 1996;15:3563–71.

[36] Tobisch S, Bogel H, Taube R. Organometallics 1998;17:1177–96.

[37] Tobisch S, Taube R. Organometallics 1999;18:5204–18.

[38] (a) Tobisch S, Taube R. Organometallics 1999;18:3045–60. (b) Tobisch S. Acc Chem Res 2002;96–104.

[39] Jensen VR, Borve KJ. J Comput Chem 1991;19:94.

[40] Rix FC, Brookhart M, White PS. J Am Chem Soc 1996;118:4746–64.

[40] (a) Margl PM, Deng L, Ziegler T. Organometallics 1998;17:933–46. (b) Musaev DG, Froese RDJ, Svensson M, Morokuma K. J Am Chem Soc 1997;119:367–74.

[42] Zambelli A, Tosi C. Fortschritte der Hochpolymeren-Forschung 1974; 15:31–60.

[43] Guerra G, Cavallo L, Moscardi G, Vacatello M, Corradini P. J Am Chem Soc 1994;116:2988–95.

[44] Cavallo L, Guerra G, Vacatello M, Corradini P. Macromolecules 1991;24:1784–90.

[45] Corradini P, Cavallo L, Guerra G. In: Scheirs J, Kaminsky W, editors. Metallocene based polyolefins, properties and technology, vol. 2. Chichester: Wiley; 2000. p. 3.

[46] (a) Venditto V, Guerra G, Corradini P, Fusco R. Polymer 1990;31: 530–7. (b) Milano G, Fiorello G, Guerra G, Cavallo L. Macromol Chem Phys 2002;203:1564–72.

[47] (a) Zambelli A, Tosi C. Adv Polym Sci 1974;31. (b) Resconi L, Abis L, Franciscono G. Macromolecules 1992;25:6814–7. (c) Erker G, Fritze C. Angew Chem Int Ed Engl 1992;31:199–202.