

The Relationship between Catalyst Precursors and Chain End Groups in Homogeneous Propene Polymerization Catalysis

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ABSTRACT: The chain transfer to monomer reactions promoted by primary and secondary growing chains in the propene polymerization promoted by *ansa*-zirconocenes and postmetallocene precursors are studied by using DFT methods. From the theoretical results it comes out that the prevalence of propene insertion over β -hydrogen transfer to the monomer decreases drastically in the presence of a secondary chain. Furthermore, we explained the reason why C_2 -symmetric metallocene catalysts promote the *selective* formation of *cis* but-2-enyls end group after a 2,1 inserted unit whereas for octahedral bis(phenoxy-imine)titanium-based catalysts, chain release promotes

exclusively the formation of allyl terminated chain end. These results might be useful to design ligand precursors able to obtain not only high M_n PP polymers but also tuned chain end groups to build new polymer architectures. Overall, a more general picture of the enantioselectivity of the chain transfer to monomer processes is reported. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 699–708, 2010

KEYWORDS: metallocene catalysts; molecular modeling; poly(propylene) (PP); Ziegler-Natta polymerization

INTRODUCTION The enantioselective α -olefin polymerization process promoted by metallocene single-site catalysts is still one of the catalytic processes more studied in detail, both from experimental and theoretical point of view.¹ The insights reached into the ligand architecture/polymer microstructures relationship achieved, specifically in the case of propene polymerization, has been successfully expanded also to postmetallocene catalysis.^{2,3} In the last decade, the scope of ligand design has been shifted to molecular weight control, as practical applications require high molecular weight for polypropylenes of any microstructure. A pioneering success of this strategy can be found in the synthesis of sterically congested 2,2'-substituted *rac*-bis(benz[e]indenyl) *ansa*-zirconocenes systems reported by Brintzinger and co-workers.⁴ The simple 2,2' methyl substitution suppress in such extent the β -hydrogen transfer from the growing polymer chain to the incoming monomer molecule increasing the polymer average molecular mass. Computational methods, mainly the ones rooted in Density Functional Theory (DFT), have been extensively applied to study the geometry of the transition state (TS) for the propene insertion and for the β -hydrogen transfer to the monomer (BHT).⁵ These two TSs have different space requirements, and therefore react differently to ancillary ligand substitution. The former process has a compact four-center TS, with the reacting atoms spanning an angle of about 90°, the latter, instead, has a larger six-cen-

ter TS spanning an angle of about 125° that may be destabilized by nonbonded contacts of substituents suitably located in the ligand framework (e.g., 2,2' position, see Fig. 1). This simple evidence can be recognized as a sort of "design principle,"^{5(a)} and theoretical results suggest⁶ that this principle can be expanded to postmetallocene⁷ systems like octahedral amine-phenolate⁸ and bis(phenoxy-imine) catalysts.⁹ Finally, more recently, computational studies of a variety of polymerization catalyst models has revealed an unexpected fluidity in chain termination mechanism pointing out the existence of an additional new pathway involving a direct hydrogen transfer without a strong metal hydrogen bonding interaction TS for the BHT.¹⁰

As a matter of fact, almost all these theoretical studies^{1,3,5} focused on the BHT promoted by a primary chain growth, despite the fact that it is well known that a secondary chain growth formed by an occasional secondary (or 2,1) propene inserted unit might affect dramatically the polymerization kinetics of metallocene systems, as well as the molecular weight of the polypropylenes.^{1(a),11} Experimentally, chain release by BHT after a 2,1 insertion is often observed when the catalyst is not fully regioselective, and the low molecular weight obtained has been ascribed to a higher frequency of such secondary insertions.¹² A thorough experimental review on the influence of the secondary chain on the termination reactions can be found in the literature.¹³

Additional Supporting Information may be found in the online version of this article. Correspondence to: L. Caporaso (E-mail: lcaporaso@unisa.it)
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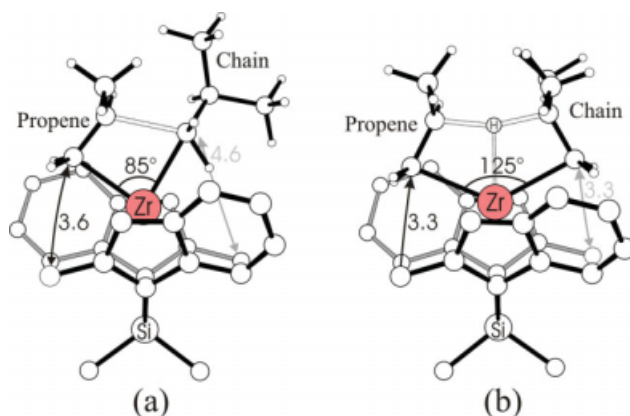


FIGURE 1 TS structures obtained by DFT methods for the propene insertion with the right enantioface (a) and for the BHT by a primary chain to the incoming propene with the 1,2 *re* enantiofaces (b) promoted by $\text{Me}_2\text{Si}(2\text{-Melnd})_2\text{Zr}$ system. Distance in Å and angles in degree. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

A general overview of the termination reactions and the corresponding chain end groups is reported in the Schemes 1a and 1b for the primary and secondary polypropylene chain growths, respectively.

Comparing the two Schemes, one can visualize how variegated might be the termination process promoted by a growing chain with a 2,1 propene last inserted unit. This promotes an internal double bond with *cis* or *trans* conformation or an allylic end group when the H atom is transferred from the methylene or the terminal methyl, respectively. Interestingly, in the propene polymerization promoted by tetrahedral C_2 -symmetric zirconocene catalysts the *selective* formation of *cis* but-2-enyls end group has been reported for the BHT after a 2,1 unit,¹⁴ whereas in the case of octahedral bis(phenoxy-imine)titanium catalysts, Coates and coworkers reported that chain release occurs exclusively by the H-transfer from the terminal methyl¹⁵ generating an allylic end group, as shown in Scheme 1b. It is worth to note that the presence of vinyl-terminated macromolecules¹⁶ are often preferred for some chain end functionalizations or in copolymerizations because they are generally more reactive than other types of unsaturated chain ends yielding a macroinitiator with sufficiently high chain-end functionality to successfully form block copolymers, for example, by using combined techniques (e.g., via ATRP).¹⁷

It appears that a rationalization of chain transfer step/ligand framework might be useful to obtain not only high M_n PP polymers but also to tune the chain end forming novel building blocks for the synthesis of new polymer architectures.¹⁸

In this article we are trying to explain the above experimental facts by using computational methods. For the sake of readability, the results have been separated into three sections: in the Chain Effect section we will compare the termination reactions promoted by a secondary chain with respect

to the one promoted by a primary chain, for the prototypical C_2 symmetric catalyst (system 1 of Chart 1, where X and Y indicate the two available positions for the monomer and the growing chain), where a large body of experimental data is reported.

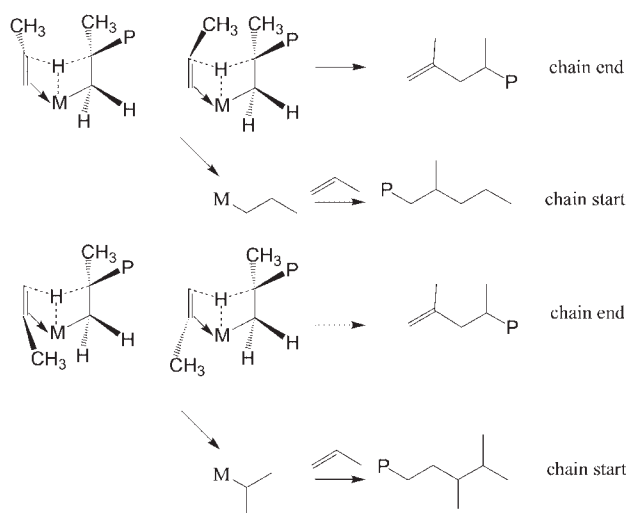
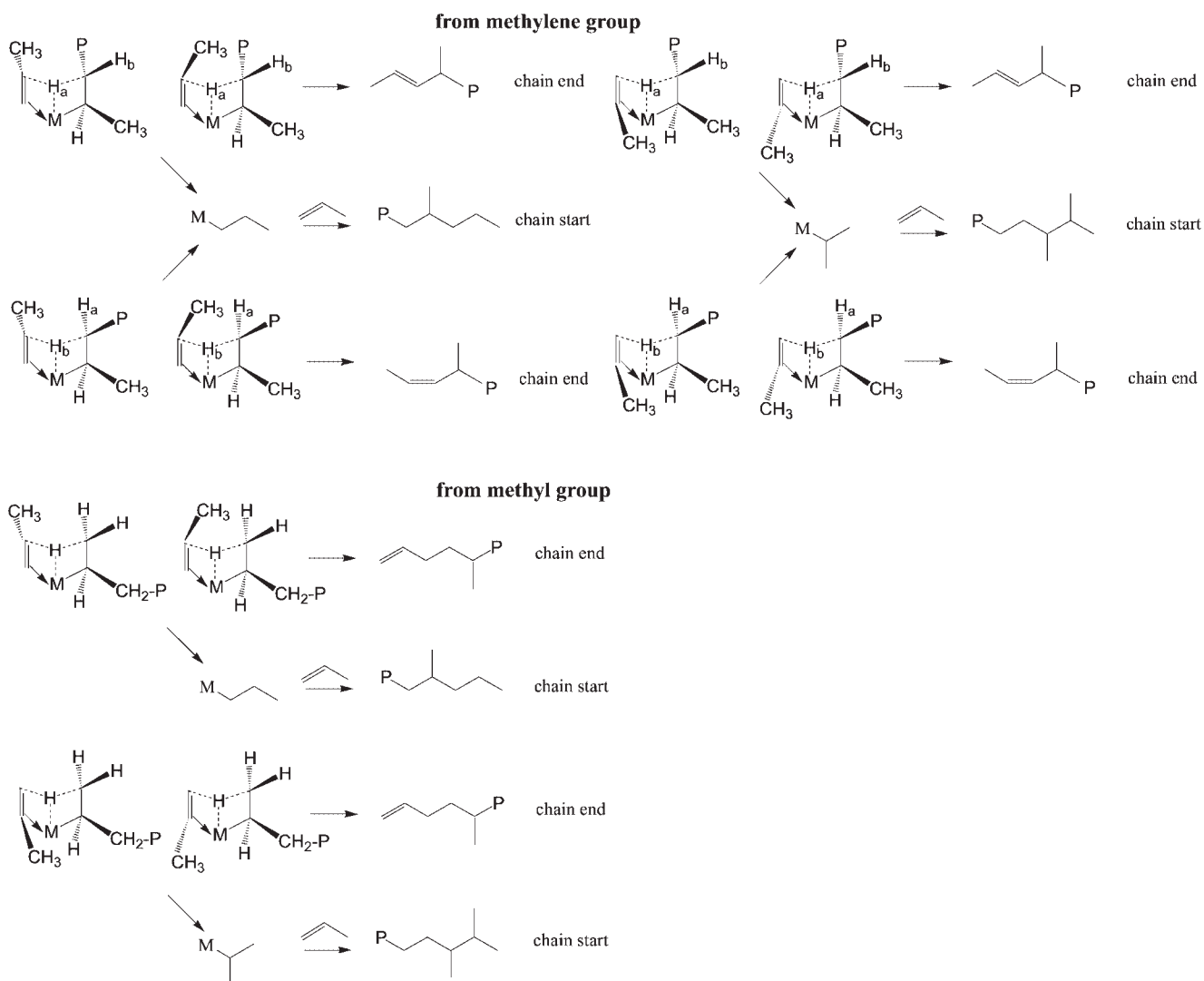
In the Substituents Effect section we will analyze the results of the modified system 1 with methyl substituents in the 2,2' position (see system 2 in Chart 1) to verify the consistency of the “design principle” when applied to secondary chain, and the propensity of the growing chain to undergo β -H transfer to the monomer.

In the Ligand Effect section the BHTs promoted by octahedral bis(phenoxy-imine)titanium catalysts (FI-type,⁹ see system 3 in Chart 1) with suitable R^1 substituents (systems 3a and 3b with $R^1 = \text{H}$ and $t\text{Bu}$, respectively) will be compared with the ones obtained by metallocene systems 1 and 2 to explain the experimental data reported in literature (ligand effect).

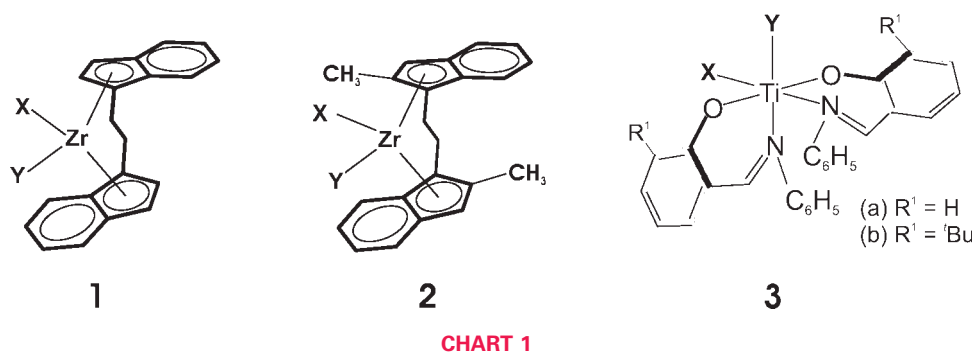
For any systems discussed in the text we have also analyzed, for the first time, the enantioselectivity of both insertion and chain transfer steps.

Computational Methods

All geometries were fully optimized as transition state saddle points using DFT computational methods. Calculations were performed with the B3LYP¹⁹ functional, in combination with the SVP²⁰ basis set (LANL2DZ basis and pseudopotential²¹ at first and second-row transition metals) using Gaussian03 program.²² Stationary points were characterized using vibrational analyses, and these analyses were also used to calculate zero-point energies and thermal (enthalpy and entropy) corrections (298.15K, 1 bar); the complete set of data is reported in the Supporting Information. Test calculations with improved electronic energies were obtained from single-point calculations using a TZVP basis set²³ (SDD basis and pseudopotential²⁴ at the metal; for Zr, an *f* function with exponent 0.5 was added) obtaining similar results. This computational methodology has already been compared with experimental data and found reliable although without using counterion and solvent effects.²⁵ In the following, we will define the stereoselectivity of the propene insertion ($\Delta E_{\text{stereo}}^\ddagger$) as the energetic difference between the TSs for the two primary insertions with opposite enantiofaces; the regioselectivity ($\Delta E_{\text{regio}}^\ddagger$) as the difference of the most stable TSs for both 2,1 and 1,2 propene insertion. Assuming that the average polymer molecular mass is dictated by the competition between the favored propene insertion and propene-induced chain transfer, we computed the internal energy difference ($\Delta E_{\text{T-P}}^\ddagger$) between the corresponding two transition states. For a correct comparison with the experimental results we will report also the ($\Delta H_{\text{T-P}}^\ddagger$).^{25,26} Finally, a “measure” of the enantioselectivity of the BHT processes will be reported assuming $\Delta E_{\text{BHTstereo}}^\ddagger$ as the energetic difference between the TS for the BHT to the incoming monomer with opposite enantiofaces, and $\Delta E_{\text{BHTregio}}^\ddagger$ as the difference between the transfer to the incoming monomer with the lower 1,2 and 2,1 propene insertion modes. Positive

(a) **Bimolecular β -H Transfer from primary chain**(b) **Bimolecular β -H Transfer from secondary chain**

SCHEME 1



numbers for $\Delta E_{\text{regio}}^{\ddagger}$, $\Delta E_{\text{T-P}}^{\ddagger}$, and $\Delta E_{\text{BHTregio}}^{\ddagger}$ means that primary is favored over secondary insertion, propagation over termination, and BHT transfer to 1,2 favored over 2,1 propene orientations.

We selected the (*R,R*) chirality of coordination of the bridged π -ligand for the systems **1** and **2** and a Λ chirality for the system **3**. The various reactions were computed by using $(-\text{CH}_2\text{CH}(\text{CH}_3)_2)$ group as a model of primary chain growth/termination in propene polymerization and $(-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3)$ group for the secondary chain formed by a 2,1 propene last inserted unit. We verified that the use of longer groups both for the primary and secondary growing chains modify the ΔE^{\ddagger} values within 1 kcal/mol.

For the system **3** which promotes the propene polymerization through secondary monomer insertion, the chiral $(-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2)$ group has been used to model the secondary polymer chain. Finally, we verified that the BHT TSs reported here show lower energies compared with the alternative BHTs reported in literature.¹⁰

RESULTS AND DISCUSSION

Chain Effect

Let us start the discussion comparing the TS structures for the propene insertion and BHT promoted by a primary chain with the system **1**. For the sake of readability only the preferred propene insertion in the 1,2 mode has been reported (see Fig. 2a), whereas for the BHT the TSs corresponding to

H transfer from the growing chain to the primary and secondary incoming propene with two different enantiofaces (1,2*re*, 1,2*si*, and 2,1*si*,²⁷ respectively), are also reported [see Fig. 2(b-d)]. The results in Table 1 indicate that the lowest energy pathway of β -H transfer to propene involves the latter in 1,2 orientation consistently with the experimental data of chain end-group analysis reported in literature (Scheme 1a). At the same time, according to the calculations, the BHT coming from a primary chain is *not* strongly enantioselective and only slightly regioselective [see the $\Delta E_{\text{BHTstereo}}^{\ddagger}$ and $\Delta E_{\text{BHTregio}}^{\ddagger}$ values of 0.2 and 1.0 kcal/mol, respectively, in Table 1, and the Fig. 2(b-d)]. Interestingly, this is the opposite trend found for the propene insertion promoted by the C_2 -symmetric catalysts and reported in Table 1 (compare the values of $\Delta E_{\text{stereo}}^{\ddagger}$ and $\Delta E_{\text{regio}}^{\ddagger}$ with $\Delta E_{\text{BHTstereo}}^{\ddagger}$ and $\Delta E_{\text{BHTregio}}^{\ddagger}$, respectively). In the insertion step the site chirality is able to impose a chiral orientation of the growing chain, which selects between the two enantiofaces of the inserting propene molecule,²⁹ whereas this effect is partially lost in the larger six-center TS of the BHT, where the ligand framework is not able to impose any chirality to the chain and, only slightly, to the monomer (see Fig. 2). As a matter of fact, it has to be recalled that the stereochemistry of BHT steps has little practical relevance since we are creating always *n*-Pr groups. In any case this might be useful to give us insights on the factors determining the stereoselectivity in general and, in this specific case, the direct (weak) *ligand-monomer* interactions, which are the main responsible for the $\Delta E_{\text{BHTstereo}}^{\ddagger}$ and $\Delta E_{\text{BHTregio}}^{\ddagger}$ values.

TABLE 1 Calculated ΔE^{\ddagger} (ΔH^{\ddagger} in parenthesis) in kcal/mol for the Insertion and BHT Reactions Promoted by the Systems **1** and **2** of Chart 1 (for the definitions, see text)

Chain	System	$\Delta E_{\text{stereo}}^{\ddagger}$	$\Delta E_{\text{regio}}^{\ddagger}$	$\Delta E_{\text{T-P}}^{\ddagger}$ ^b	$\Delta E_{\text{BHTstereo}}^{\ddagger}$	$\Delta E_{\text{BHTregio}}^{\ddagger}$
Primary	1	3.3 ^a	3.2	9.3 (6.5)	0.2	1.0
Secondary BHT from CH ₂	1	0.8	1.1	1.9 (-0.6) ^b	2.3	3.7
BHT from CH ₃				10.4 (8.1) ^b	0.8	3.8
Primary	2	3.4 ^a	3.6	10.0 (7.8)	0.3	2.3
Secondary BHT from CH ₂	2	0.6	3.1	3.8 (1.9) ^b	3.1	5.5
BHT from CH ₃				11.1 (8.4) ^b	0.8	6.0

^a We found that for the systems **1** and **2**, the preferred stereomistake is due to the *syn* propene insertion to the growing polymer chain.²⁸

^b All numbers are relative to the lower TS insertion.

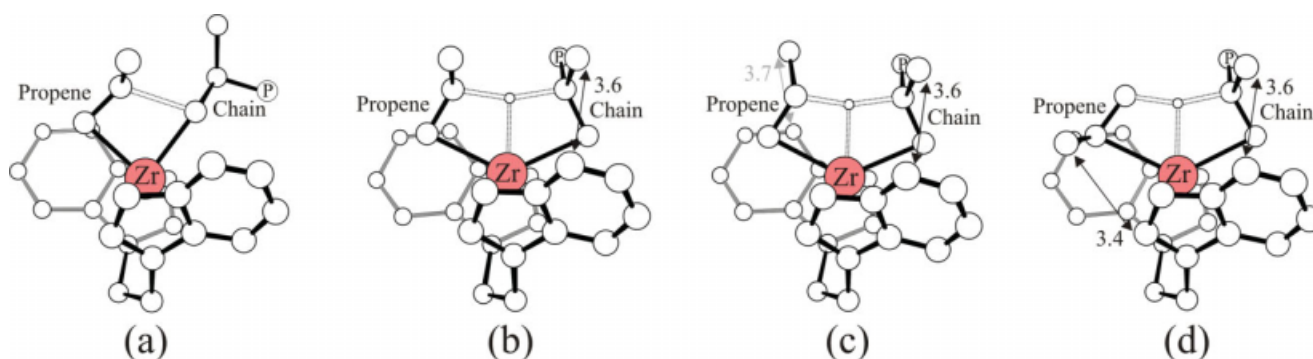


FIGURE 2 TS structures obtained by DFT methods for the propene insertion with the right enantioface (a) and for the BHT promoted by a primary chain to the incoming propene with the 1,2 *re* (b), 1,2 *si* (c) and 2,1 *re* (d) enantiofaces, respectively. H atoms are omitted for clarity and P = polymeryl chain. Distance in Å. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The situation is more variegated with a growing polymer chain with a last 2,1 propene inserted unit (see Scheme 1b). The BHT starting from a secondary ($-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$) moiety shows, in principle, more alternative routes than ($-\text{CH}_2\text{CH}(\text{CH}_3)_2$). As a matter of fact, two different BHT are possible; they correspond, indeed, to the H-transfer coming from the methylene group ($-\text{CHCH}_3-\text{CH}_\beta\text{H}-\text{CH}_3$) and from the methyl group ($-\text{CH}-\text{CH}_\beta\text{H}_2-\text{CH}_2\text{CH}_3$). In addition, considering the transfer from methylene group, two structures producing 2-butenyl end groups are possible, in configuration *cis* or *trans*, respectively. Figure 3 shows the corresponding TS structures involved in the mechanism. In particular, we reported in Figure 3(a) the preferred TS for the propene insertion into the growing chain with the favored 2,1 last inserted unit, in Figures 3(b-c) the BHT coming from the methylene with a *cis* and *trans* chain conformation, respectively, and finally, in Figure 3d the BHT coming from the terminal methyl group.^{30,31}

Let us examine in detail the two β -hydrogen TS structures coming from the methylene [see Fig. 3(b-c) and Scheme 1(b)] first. According to the calculations, the TS for the structure leading to a *cis*-2-butene end group [Fig. 3(b)] is

lower in energy than the one leading to a *trans*-2-butene end group [Fig. 3(c)] for about 2.3 kcal/mol (see Table 1).³² We attributed this difference mainly to a direct *chain-ligand* interaction because of the steric effects of the chain in *trans* conformation, which points toward the indenyl moieties.³³

We already addressed that a β -H transfer might also come from the terminal methyl group [see Fig. 3(d)]. This termination reaction produces an allyl terminal chain end (see Scheme 1b), which are often desired for chain end functionalizations or in copolymerizations because they are generally more reactive than other types of unsaturated chain ends (e.g., vinylidene, trisubstituted, and vinylene). Polymer chains containing allyl chain-ends may serve as macromonomers in copolymerizations with α -olefins to give branched polymers.³⁴ However, our calculations revealed that, for the metallocene system considered, the lower energetic TS is the one coming from the methylene group (for about 8 kcal/mol, see the relative difference of $\Delta E_{\text{T-P}}^\ddagger$ values in Table 1). The considerably high energetic difference is related to a clear steric hindrance in the TS for the BHT coming from the CH_3 (compare structures b and d in Fig. 3).³⁵ This is in

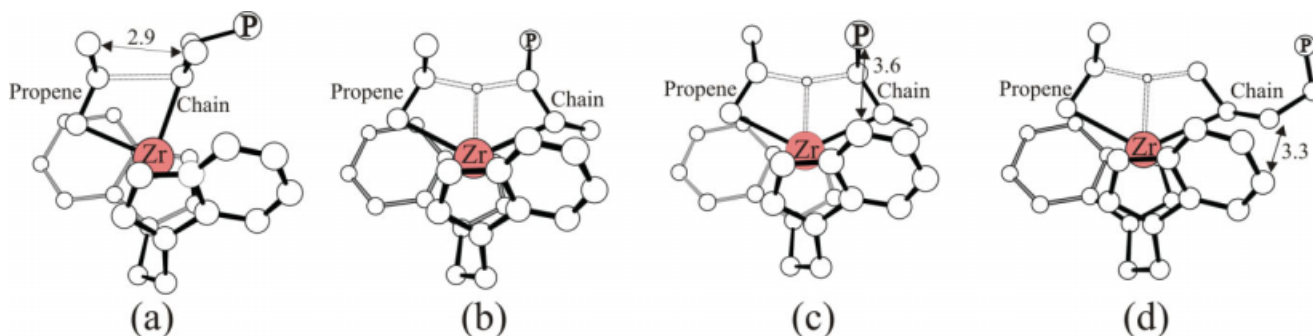


FIGURE 3 TS structures obtained by DFT methods for the propene insertion (a) and for the β -H transfer promoted by a growing chain with a 2,1 last inserted unit to the incoming propene with the 1,2 *re* (b), 1,2 *si* (c) and 2,1 *re* (d) enantiofaces, respectively. H atoms are omitted for clarity and P = polymeryl chain. Distance in Å. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

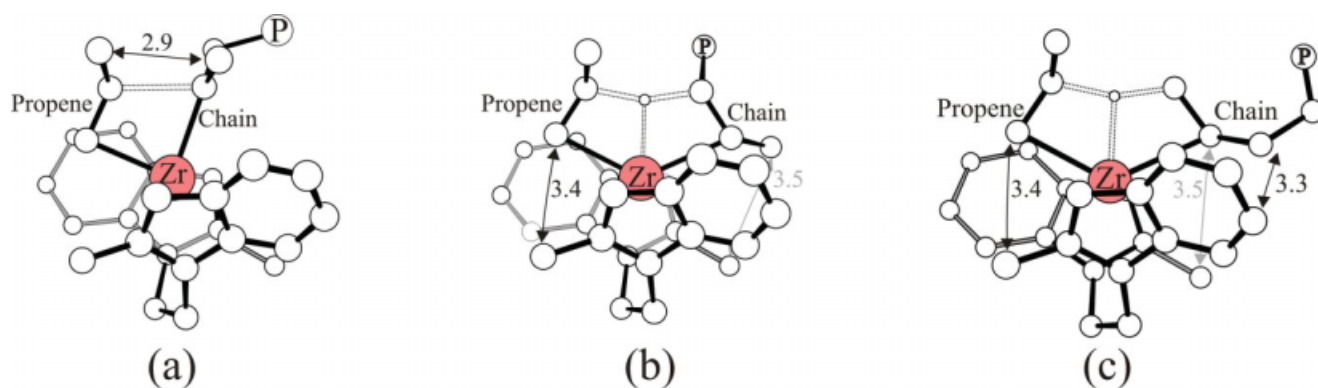


FIGURE 4 TS structures obtained by DFT methods for the propene insertion (a) and BHT from CH_2 (b) and CH_3 (c), on a growing chain with a 2,1 last inserted unit promoted by the system **2**. H atoms are omitted for clarity and P = polymeryl chain. Distance in Å. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

agreement with the experimental end group analysis where in practice only the internal vinylene, the *cis* 2-butenyl group, has been observed for termination reaction after a secondary unit in the propene polymerization.^{12,36}

Concerning the enantioselectivity of the BHT reactions promoted by the methylene group of the secondary chain, we note that, similarly to the primary chain, the preferred H transfer is to the incoming monomer in the 1,2 mode, with a $\Delta E_{\text{BHTregio}}^{\ddagger}$ of 3.7 kcal/mol. However, contrarily to the primary chain, this transfer is also stereoselective (see the $\Delta E_{\text{BHTstereo}}^{\ddagger}$ of 2.3 and 0.2 kcal/mol, respectively).³² This effect is in turn absent in the BHT reactions promoted by the terminal methyl group, which are instead remarkably regioselective.

As a final remark, comparing the TS energies for the preferred insertion and BHT steps with a secondary chain, we note the large effect of a secondary last inserted unit on the $\Delta E_{\text{T-P}}^{\ddagger}$ and $\Delta H_{\text{T-P}}^{\ddagger}$ values (see the positive value of 6.5 kcal/mol for a primary and the negative value of -0.6 kcal/mol for the secondary). This is due to the higher energies of the insertion step, because of the close contact of the two methyl groups, which belong to the chain and the monomer [see Fig. 3(a)]. The reported data are fully consistent with (and at the same time explain) the experimental observation that the

frequencies of secondary insertion might affect the molecular weight of the polymers.¹³

Substituents Effect

As stated in the Introduction the methyl substitution on the 2,2' position of zirconocenes increase experimentally the average polymer mass (see e.g., Fig. 1).

Our results on the system **2** are in line (see $\Delta E_{\text{T-P}}^{\ddagger}$ values for the system **2** in Table 1) with this expectation and with theoretical results reported in literature for related systems.^{4,5} However, we found that this effect is verified also for the secondary chain. In fact, looking at the results in Table 1 we have noted that the 2,2' position increases the $\Delta H_{\text{T-P}}^{\ddagger}$ for both primary and secondary chains compared with the system **1** (by 1.3 and 2.5 kcal/mol, respectively).³⁷ A better overview is reported in Figure 4 where the TSs for the insertion and BHT are compared. The methyl groups affect sterically both the monomer and the growing chain increasing the $\Delta E_{\text{T-P}}^{\ddagger}$ value (compare the structures **a** and **b** in Fig. 4). Interestingly, the 2,2' substitution plays a similar role also in the TS for the H transfer coming from the CH_3 [see Figs. 4(c)]. As a consequence, the preference for β -H transfer coming from the CH_2 with respect to the one coming from the CH_3 is substantially unaffected. Finally, the main

TABLE 2 Calculated ΔE^{\ddagger} (ΔH^{\ddagger} in parenthesis) in kcal/mol for the Insertion and BHT Reactions Promoted by the Systems **3a** and **3b** of Chart 1 (see text)

Chain	System	$\Delta E_{\text{stereo}}^{\ddagger}$	$\Delta E_{\text{regio}}^{\ddagger}$	$\Delta E_{\text{T-P}}^{\ddagger}$	$\Delta E_{\text{BHTstereo}}^{\ddagger}$	$\Delta E_{\text{BHTregio}}^{\ddagger}$
Primary	3a	0.0 ^a	1.6	7.3 (4.7)	0.3	-0.3
Secondary BHT from CH_2	3a	0.0 ^a	-1.5 ^b	11.0 (8.9) ^c	0.3	2.8
BHT from CH_3				8.4 (6.0)	0.8	2.3
Primary	3b	3.3 ^a	0.4	10.4 (8.1)	1.3	-1.9
Secondary BHT from CH_2	3b	0.8 ^a	-2.2	12.4 (10.0)	0.1	0.9
BHT from CH_3				3.2 (0.5)	1.6	0.9

^a The syndiospecific mechanism of stereoselectivity has been already addressed elsewhere.^{2,43}

^b Negative numbers means that the favourite propagation is secondary and the preferred BHT is to a secondary propene molecule (see text).

^c Here the *trans* arrangement is preferred to the *cis* for about 0.8 kcal/mol.

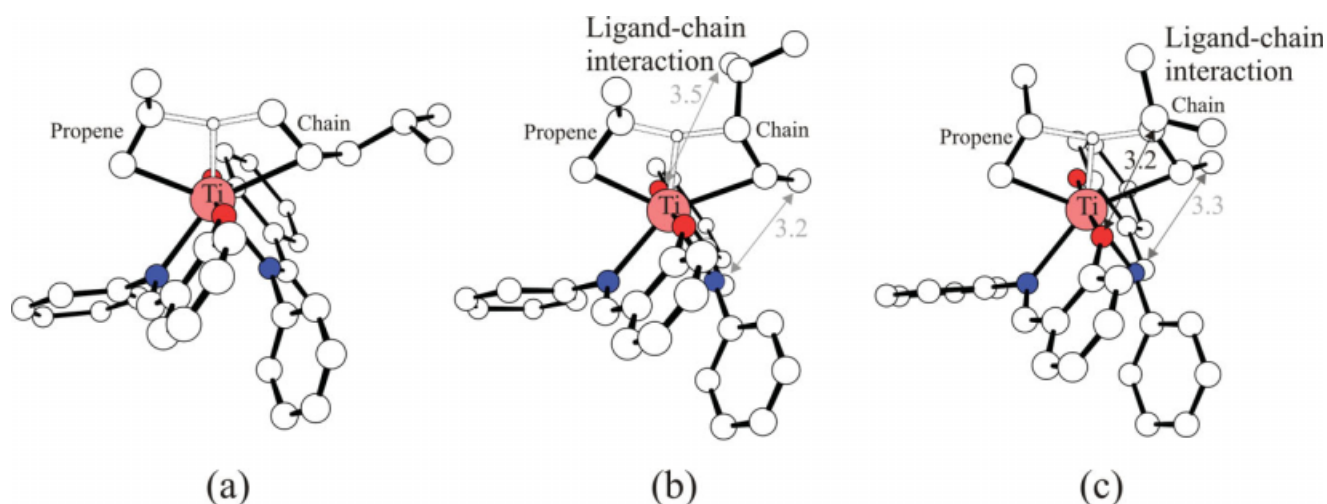


FIGURE 5 TS structures obtained by DFT methods for the BHTs promoted by a secondary chain to the 1,2 incoming propene promoted by the system **3a**. They correspond to the H transfer coming from the terminal CH₃ group (a) and from the methylene with a *cis* (b) and *trans* (c) chain configuration (see text). H atoms are omitted for clarity. Distance in Å.

enantioselectivity features for the BHT process discussed for the system **1** are maintained for the system **2** with higher values for the regioselectivity.

It appears from our analysis that a suitable tuning of the zirconocenes can increase the M_n of the resulting polypropylenes, in part avoiding the termination reaction after a 2,1 last inserted unit (see system **1** and **2** results). However, it is difficult to obtain exclusively allyl terminated chain end for building new polymer architectures within the tetrahedral metallocene ligand framework.³⁸ The fact that the C_2 -symmetric catalysts prefer selectively one of the two possible 2,1 propene unit, which force the chain to a direct contact with the indenyl-ligand [independently of the substituents, see Figs. 3(d) and 4(c)] seems to rule out the use of C_2 *ansa*-zirconocenes to obtain allylic chain-ends.

Ligand Effect

The situation depicted above changes as soon as we considered the new class of C_2 -symmetric Group 4 metal catalysts bearing two phenoxy-imine ligands.⁹ These systems have attracted much attention for the possibility to polymerize ethene and propene in a “living” manner when *ortho*-F-substituted phenyl ring on the N are present.³⁹ Several papers attempted to explain this *ortho*-F effect⁴⁰ as well as the predominantly secondary insertion mode^{41,42} and the syndio-specific mechanism of polymerization.^{2,43} However, Ti based-catalysts (see system **3** in Chart 1) afford propene polymers with secondary chain growth of relatively low average molecular mass with chain release occurring exclusively by β -hydride transfer from the terminal methyl.^{39,44} This generates an allylic end group⁶ as shown in Scheme 1, and it has

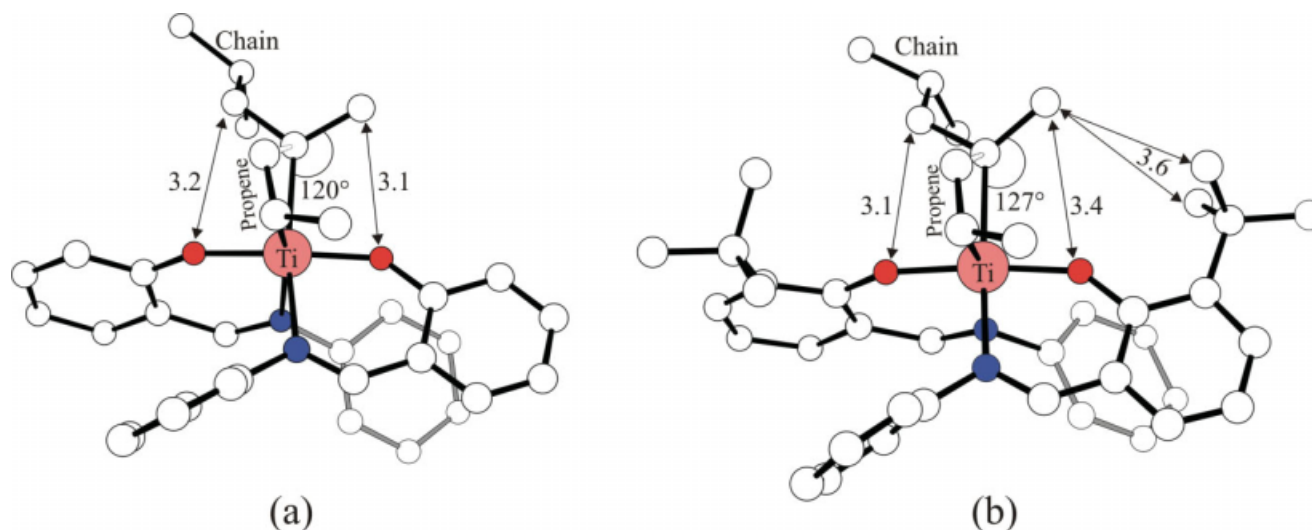


FIGURE 6 TS structures obtained by DFT methods for the propene insertion on a secondary chain promoted by the system **3a** (a) and **3b** (b). H atoms are omitted for clarity. Distance in Å and angles in degree.

been utilized by Coates and coworkers to produce functionalized syndiotactic propylene oligomers.¹⁵

To find a rationalization for this effect we modeled the system with $R^1 = H$ at the first, (see Table 2). Interestingly, the lowest energy pathway of β -H transfer to propene involves the monomer in a 2,1 orientation for the primary and in a 1,2 orientation for the secondary chains, respectively, (see the negative and positive numbers for $\Delta E_{\text{BHTregio}}^\ddagger$ in Table 2). However, the more intriguing aspect is that the lower path for the β -H transfer moving from a secondary chain is the one coming from the terminal methyl. In Figure 5 we report the TS geometries for the three types of H transfer, moving from CH_3 , and CH_2 with the *cis* and *trans* chain arrangements, respectively.⁴⁵ From the TS geometries we note that the structure 5a shows the growing chain quite far from the ligand skeleton, whereas close contacts between chain and the octahedral ligand framework are present in Figures 5(b,c). This effect increases dramatically as soon as we consider the real system with bulky R^1 substituents (see system 3b and Table 2).

It should be noted at this point that bulky R^1 substituents are important also for the regiochemistry of propagation (see $\Delta E_{\text{regio}}^\ddagger$ column). In fact, differently from the system 3a, we calculated a very low value for the regiochemistry on a primary chain for the system 3b (see the $\Delta E_{\text{regio}}^\ddagger$ values of 1.6 and 0.4 kcal/mol, respectively, in Table 2) which increases consistently as soon as the first 2,1 propene molecule is inserted (see $\Delta E_{\text{regio}}^\ddagger$ of -2.2 kcal/mol in Table 2). This means that after a 2,1 insertion, secondary propagation is maintained because it does not require the formation of a sterically demanding head-to-head enchainment,⁴² in agreement with the experimental results.^{9,15,18}

A last important remark of the data reported in Table 2 is the large decrease of the $\Delta E_{\text{T-P}}^\ddagger$ going from the system 3a to the 3b for the secondary propagation. This is an unusual behavior, considering our previous results obtained on the systems 1 and 2. Furthermore, it is well known that restricting space around the metal by using bulky substituents on octahedral species lead to suppression of BHT and higher molecular weights.³ This is, in turn, confirmed by our data on the primary chain where $\Delta E_{\text{T-P}}^\ddagger$ increases by 2 kcal/mol (going from 7 to 10). A deeper examination of the TS propene insertion geometries promoted by the systems 3a and 3b (see Fig. 6) may be revealing. The secondary chain shows, indeed, two C atoms in β position, one which belong to the chain and the other forming the terminal methyl. The presence of the ^tBu substituents on the bis(phenoxy)imine systems is pushing out the C atom of the terminal methyl forcing to assume a larger Ti—C—C angle [127°, in a place of 120° see Fig. 5(b)]. This effect is avoided on the BHT coming from the CH_3 [see Fig. 5(a)], which has a single C atom in β position far from the R^1 substituents.

CONCLUSIONS

In this article, we have investigated in detail the BHT reactions promoted by primary and secondary propene growing chains by using DFT methods. The whole mechanism of

enantioselectivity of these reactions has been sorted out and compared with the propene propagation.

The main conclusion can be summarized:

1. A secondary propene last inserted unit as well as a secondary chain has a large effect on the $\Delta E_{\text{T-P}}^\ddagger$ decreasing drastically the difference between propagation and termination processes in the propene polymerization.
2. Suitable ligand substitution in the metallocene framework, like the 2,2' position, increases the $\Delta E_{\text{T-P}}^\ddagger$ both for primary and secondary chains.
3. Among several β -H transfer available from a secondary chain, we found that *ansa*-zirconocene systems prefer the BHT coming from the CH_2 with a *cis* arrangement of the growing polymer chain with respect to the one coming from the CH_3 . The high preference calculated seems to be related to an intrinsic feature of C_2 *ansa*-metallocene skeletons and appears to be independent of ligand substitution.
4. The enantioselectivity studies of the BHT processes allowed us to distinguish several factors determining the mechanism of stereoselectivity in general, which can be summarized as *monomer-ligand*, *chain-ligand*, and *monomer-chain* interactions (with the former important for the primary and the latter for the secondary chains, respectively).
5. Tuned chain ends with the formation of allyl-end group can be obtained in the place of vinyl or vinylidene by using octahedral ligand precursors.
6. Bulky R^1 substituents on the octahedral framework increase the $\Delta E_{\text{T-P}}^\ddagger$ values in the case of primary propagation but decrease the $\Delta E_{\text{T-P}}^\ddagger$ for the secondary propagation.

We feel that these results might be useful from application standpoint to obtain polypropylenes with higher molecular mass and to select suitable ligand catalysts, which promote selective chain end groups to create new polymer architecture.

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- 26 (a) The zero-point corrections must be calculated when comparing the TS energies of insertion and BHT because they show different values in a relative sense, see e.g. ref. 25; Talarico, G.; Budzelaar, P. H. M.; Barone, V.; Adamo, C. *Chem Phys Lett* 2000, 329, 99–105.
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- 30 (a) It is important to note that the chirality at the chain alpha-carbon in Figure 3 is fixed by the enantioselectivity of the previous (2,1) regioirregular placement. The low-energy pathway for secondary and primary insertions promoted by C_2 -symmetric catalysts correspond to opposite monomer enantiofaces, see e.g. (b) Guerra, G.; Cavallo, L.; Moscardi, G.; Vaccatello, M.; Corradini, P. *J Am Chem Soc* 1994, 116, 2988–2995; (c) Guerra, G.; Longo, P.; Cavallo, L.; Corradini, P.; Resconi, L. *J Am Chem Soc* 1997, 119, 4394–4403.
- 31 In Figure 3 and Table 1 we reported only the lower TS. The complete set of energetic data is reported in the Supporting Information.
- 32 The difference between the *cis* and *trans* TS structures correspond to the $\Delta E_{\text{BHT}^{\text{stereo}}}^{\ddagger}$ because they prefer opposite monomer enantiofaces in order to minimize the direct *syn monomer-chain* interaction, see Figure S1 of the Supporting Information.
- 33 The kinetic products of the two BHTs lead to a *cis* and a *trans*-2-butene coordinated on LM-CH₂CH₂CH₃ chain, respectively, with the former more stable than the latter of 2.7 kcal/mol.
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contact of the F-substituted rings with the growing polymer chain and an incoming propene molecule has been reported in reference 6.

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44 In reference 6 has been reported that the amount of allyl terminated chain end in the polypropylene chains turned out to be independent of propene concentration within the experimental uncertainty, which implies that chain propagation and β -H transfer have the same reaction order on the monomer.

45 Here the results are non dependent to the chirality of the alpha-carbon.