A Possible Model for the Stereospecificity in the Syndiospecific Polymerization of Propene with Group 4A Metallocenes

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ABSTRACT: The techniques of conformational analysis to investigate the factors that determine the stereospecificity, previously applied to stereorigid model sites for the homogeneous isospecific Ziegler–Natta catalysis, are now extended to other stereorigid cationic model sites. For a model site including an isopropyl(cyclopentadienyl-1-fluorenyl) ligand, a precise definition of the interactions that determine its enantioselectivity at the molecular level is presented. For other model sites including an isopropyl(cyclopentadienyl-1-indenyl) or an isopropyl(1-fluorenyl-3-methylcyclopentadienyl) ligand, on the basis of energy calculations, predictions of their stereospecific behavior are presented, which are in a qualitative agreement with the available experimental information.

Introduction

It has been recently shown[1-3] that stereorigid chiral compounds belonging to the class of group 4A metallocenes may behave, in the presence of methylalumoxane, as catalysts for the isospecific or for the syndiospecific polymerization of 1-alkenes, depending on the nature of the aromatic ligand.

In particular, highly isotactic polypropylene has recently been obtained with the racemic ethylenebis(1-indenyl) ligand,[1] while highly syndiotactic polypropylene has been obtained with the isopropyl(cyclopentadienyl-1-fluorenyl) ligand[3] (shortly, IpCpFlu in the following).

In the hypothesis that the stereochemical behavior is mainly related to the nonbonded interactions active in the transition state, we have applied, in previous papers,[4-6] the techniques of conformational analysis to investigate the factors that determine the stereospecificity of the isospecific stereorigid catalysts. As a result, we have been able to develop a model for the site control of the isospecificity that is in agreement with all the presently available experimental information on the stereochemical behavior of these systems.

As in the case of the Ziegler–Natta heterogeneous catalysts,[7,8] the growing chain plays an essential role. According to the model, the nonbonded interactions with the chelating ligand force the growing chain to choose one of two possible chiral orientations, depending on the (*R*,*R*) or (*S*,*S*) coordination chirality of the ligand. As a consequence, one of the two possible chiral coordinations (*re* or *si*) of a propene molecule is strongly disfavored with respect to the other by selective repulsive interactions of the propene methyl group with atoms of the growing chain.

The two coordination positions available for the incoming monomer and for the growing chain are related in this model by the same local 2-fold symmetry axis that characterizes the coordinated racemic ethylenebis(1-indenyl) ligand. For this reason, identical situations are obtained after each insertion step, whatever the relative positions of the chain and of the monomer. This results in the preferential insertion of monomers having always the same chirality at a given site and explains the high isospecificity of the catalytic systems.

In agreement with experimental findings,[9] the model predicts that the insertion of *re*- and *si*-coordinated propene is favored for the (*R*,*R*) and (*S*,*S*) coordination of the ethylenebis(1-indenyl) ligand, respectively.[4,6] Moreover, for the initiation step at a Ti–CH_3 bond, the model predicts[5] a nonstereospecific behavior for the insertion of propene and a partial enantioselectivity for the insertion of 1-butene. Both these predictions are in agreement with the experimental results of Zambelli and co-workers.[10] Similar calculations performed for other stereorigid model complexes predicted[6] the highly isospecific behavior experimentally observed in the presence of the racemic ethylenebis(3-methylcyclopentadienyl) ligand[11] and confirmed the almost complete absence of stereospecificity observed in the presence of the racemic ethylenebis(3-methyl-1-indenyl) ligand.[12]

In this paper, we apply the same methods to investigate the stereochemical behavior of a stereorigid cationic model containing the IpCpFlu ligand. In this model, a local symmetry plane characterizes the coordinated bridged IpCpFlu ligand and relates also the two coordination positions available for the incoming monomer and for the growing chain. This implies that the two possible situations, obtained by exchanging the coordination positions of the monomer and of the chain, are enantiomeric. According to the generally accepted mechanism for the Ziegler–Natta polymerization,[13] the metal carbon bond of the growing chain moves, during each insertion step, to the other available coordination position (previously occupied by the coordinated monomer). Hence, for the IpCpFlu model, if no rearrangement of the catalyst occurs before the coordination of a new monomer molecule, the chirality of the metal atom in the model catalytic intermediate is inverted at each insertion step. As a consequence, if some enantioselectivity exists, the IpCpFlu model is syndiospecific.

The general features of this syndiospecific mechanism have been proposed by Ewen and co-workers on the basis of the stereosequence defects observed in the syndiotactic polypropylene obtained with this catalytic system.[3] Our calculations tend to a more precise definition of the model and of the interactions that determine its enantioselectivity at the molecular level. We also report energy calculations for the models containing the isopropyl(cyclopentadienyl-1-indenyl) or the isopropyl(1-fluorenyl-3-methylcyclopentadienyl) ligand (referred in the following as IpCpInd and IpFluMCp ligands, respectively), in order to make a prediction of their possible stereospecific behavior. As in all our previous works on this subject, we make the fundamental assumption that the model sites are reasonably similar to the transition state of the insertion step. The ability of our calculations to predict behaviors in substantial agreement with experiments can

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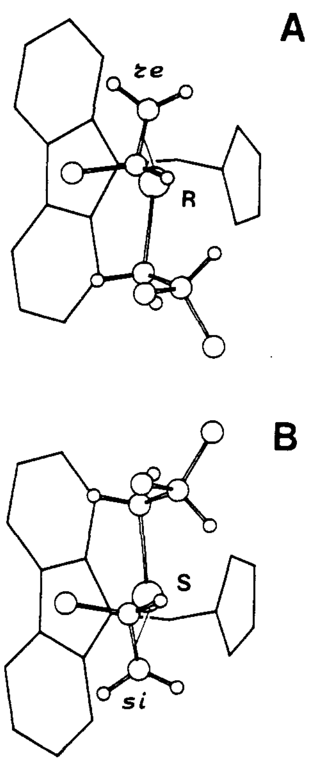

Figure 1. Enantiomeric minimum energy conformations of the (propene)(isobutyl)(IpCpFlu) model sites with *R* and *S* chirality at the metal atom. For the sake of clarity, for the aromatic ligand only the C–C bonds are sketched, and the carbon atoms of the methyl groups of the isopropyl bridge are omitted.

be taken as an indication of the approximate validity of this approach.

Models and Methods

The basic models of the catalytic site considered in this paper are metal complexes containing three ligands, that is, a π-coordinated ethene or propene molecule, a σ-coordinated methyl or isobutyl group, and a chelating IpCpFlu, IpCpInd, or IpFluMCp ligand. In order to simplify the description of our calculations and results, model sites containing the IpCpFlu, IpCpInd, or IpFluMCp ligand are identified in the following as (olefin)(alkyl group)IpCpFlu, (olefin)(alkyl group)IpCpInd, (olefin)(alkyl group)IpFluMCp sites, respectively. For instance, the notation (*re*-propene)(isobutyl)IpCpFlu identifies a model site containing the IpCpFlu ligand, a propene molecule coordinated *re* to the metal atom, and the growing chain simulated by an isobutyl group.

For all the models the metal atom is chiral, and its chirality can be labeled with the notation *R* or *S* by the extension of the Cahn–Ingold–Prelog rules[14,15] to the metal centers as proposed by Stanley and Baird[16] and accepted and employed by several researchers.[17,18]

The coordination of the IpCpInd and IpFluMCp ligands is also chiral and can be labeled with the notation (*R*) or (*S*) (in parentheses), according to the rules of Cahn–Ingold–Prelog[14,15] extended to chiral metallocenes as outlined by Schlögl.[19] The symbols (*R*) and (*S*) indicate the absolute configuration of the bridgehead carbon atom of the Ind group in the first case and of the MCp group in the second case. Without loss of generality, all the reported calculations refer to the (*R*) coordination of the IpCpInd and of the IpFluMCp ligands. No chirality of coordination exists, on the contrary, for the IpCpFlu ligand. Schematic representations of two enantiomeric model complexes of the kind (propene)(isobutyl)IpCpFlu, having *R* and *S* chirality, are shown in parts A and B of Figure 1, respectively.

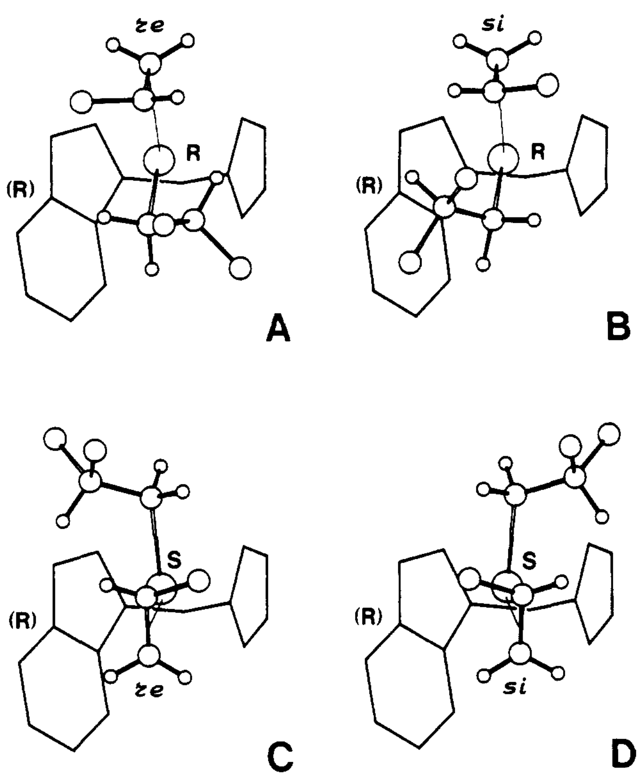

Figure 2. Diastereoisomeric minimum energy conformations of the (propene)(isobutyl)(IpCpInd) model sites having *re*,*R*,(*R*), or *si*,*R*,(*R*), *re*,*S*,(*R*), or *si*,*S*,(*R*) chirality. The chirality of coordination of the Ind ligand is (*R*) for all the models; the chirality at the metal atom is *R* for A and B and *S* for C and D. The symbol *re* or *si* refers to the chirality of coordination of propene. For the sake of clarity, for the aromatic ligand only the C–C bonds are sketched, and the carbon atoms of the methyl groups of the isopropyl bridge are omitted.

Schematic representations of the diastereoisomeric model complexes of the kind (propene)(isobutyl)IpCpInd having *re*,*R*,(*R*), *si*,*R*,(*R*), *re*,*S*,(*R*), and *si*,*S*,(*R*) chirality are shown in parts A–D of Figure 2, respectively. Schematic representation of the diastereoisomeric model complexes of the kind (propene)(isobutyl)IpFluMCp with the above chiralities are shown in Figure 3.

An important aspect of the study of these catalytic models concerns the best geometry of coordination of a growing chain at the site in the absence of a coordinated monomer and the problem of the stability of such geometry before the coordination of a new monomer molecule.

According to quantum-mechanical considerations by Hoffman and co-workers for d^0, d^1, d^3, or low spin d^2 complexes of the kind MeCp′Cp″L,[20] the best coordination of L may not be the one (most symmetrical and presumably sterically most favorable) along the symmetry axis, which relates the two bent cyclopentadienyl rings. Energy minimum situations for a d^0 complex and for L = H would correspond to angular deviations $\alpha \approx \pm 65°$ from the symmetry axis. However, the involved quantum-mechanical energy differences are not high and could be overcome by nonbonded interactions in the case of a bulky L group. On the other hand, an additional stabilization of a geometry with $\alpha \neq 0°$ at the strongly unsaturated metal center could occur because of an agostic interaction of a hydrogen in the γ-position (see scheme in Figure 4), analogous to that postulated by Brookhart and Green,[21] and/or because of some other type of interaction. Of course, we expect that α is different from 0° whenever a solvent or monomer molecule gets coordinated in the equatorial belt of the bent metallocenic cation, together with the polymeryl group. Note that a geometry with $\alpha \neq 0°$ makes the metal

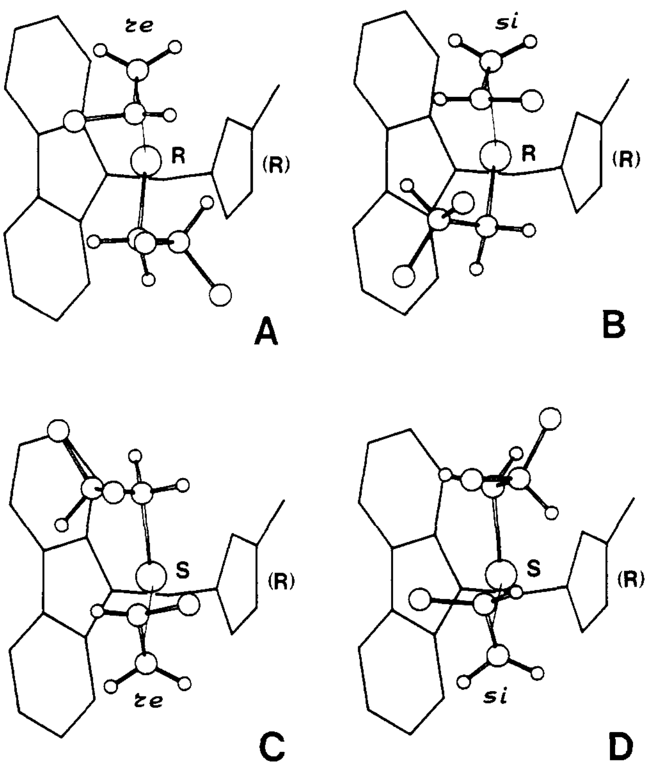

Figure 3. Diastereoisomeric minimum energy conformations of the (propene)(isobutyl)(IpFluMCp) model sites having *re*,*R*,(*R*), *si*,*R*,(*R*), *re*,*S*,(*R*), or *si*,*S*,(*R*) chirality. The chirality of coordination of the MCp ligand is (*R*) for all the models; the chirality at the metal atom is *R* for A and B and *S* for C and D. The symbol *re* or *si* refers to the chirality of coordination of propene. For the sake of clarity, for the aromatic ligand only the C–C bonds are sketched, and the carbon atoms of the methyl groups of the isopropyl bridge are omitted.

atom chiral in $(MeCp'Cp''L)^+$, if the two cyclopentadienylic ligands Cp′ and Cp″ are different.

A tentative polymerization scheme is reported in Figure 4. For the assumed metallocene-based catalytic models and on the basis of a polymerization mechanism like the one reported in Figure 4, at the end of each polymerization step the chain occupies the coordination site, previously occupied by the alkene monomer. Hence, if the rate of rearrangement of the ligands is much lower than the rate of insertion of a new monomer molecule, most consecutive polymerization steps correspond to models obtained by exchanging the relative positions of the growing chain and of the incoming monomer. This is extremely relevant for the stereospecific behavior of the models since if a chirality at the central metal atom exists, it is inverted at each polymerization step, as shown in the scheme reported in Figure 4.

The geometries of the model sites have been constructed by using the internal parameters listed in Table I, which are averages of values observed in the crystal structures of methylenebis(cyclopentadienyl)titanium dichloride[22] or isopropyl(cyclopentadienyl-1-fluorenyl)hafnium dichloride.[3] As in ref 4, the geometric parameters relative to the coordinated olefin have been derived from the crystal structure of bis(pentamethylcyclopentadienyl)(ethene)titanium.[23] The distance Hf–C(chain) has been assumed to be 2.24 Å, as observed in some σ-alkyl Hf complexes,[24] while the distance Hf–C(olefin) has been set equal to 2.27 Å, that is, 0.03 Å bigger than the distance Hf–C(chain), to be consistent with the analogous distances observed in titanium complexes.[23,25–27]

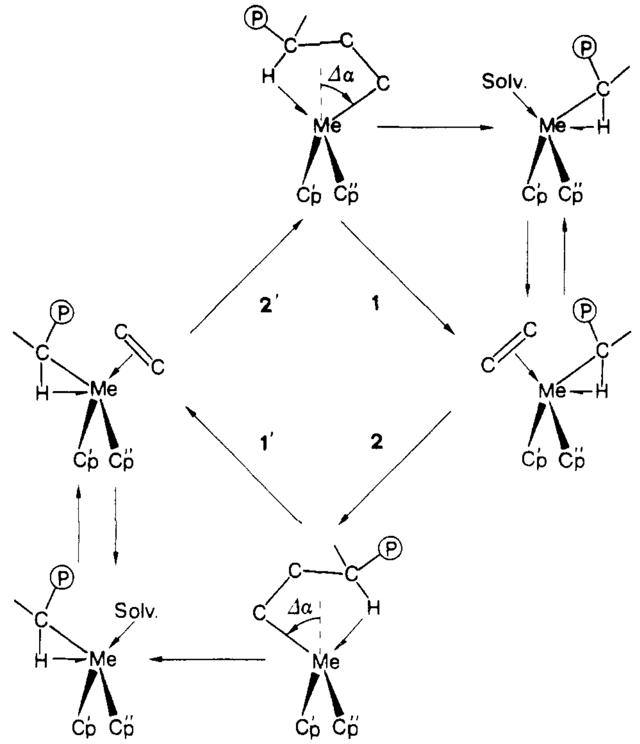

Figure 4. Scheme of a possible mechanism of polymerization: (1,1′) Electrophilic attack of the metal atom to the monomer molecule; (2,2′) Insertion of the monomer molecule into the metal carbon bond. The possible formation of agostic Me–H bonds is indicated by half-arrows.

Table I
Selected Values of Some Distances (in Angstroms) and Angles (in Degrees), Used in the Construction of the Model Sites Geometry

atoms[a]	distances	ref	atoms[a]	angles	ref
Hf–C1	2.42	3	Cn_{Flu}–Hf–Cn_{Cp}	119.4	3
Hf–C2	2.50	3	Hf–Cn_{Flu}–C1	83.0	22
Hf–C3	2.64	3	Hf–Cn_{Cp}–C6	87.5	22
Hf–C4	2.64	3	C1–C11–C6	100.9	3
Hf–C5	2.50	3			
Hf–C6	2.43	22			
Hf–C7	2.46	22			
Hf–C8	2.51	22			
Hf–C9	2.51	22			
Hf–C10	2.46	22			
Hf–Cn_{Flu}	2.24	3			
Hf–Cn_{Cp}	2.16	3			

[a] Cn denotes centroid of a C-5 ring.

The main internal coordinates that have been varied in our calculations (see Figure 5B) are defined in analogy with our previous papers.[4–6] The angles α and β have been confined in the plane defined by the two metal chlorine bonds in the crystal structures of refs 3 and 22 and referred to the intersection of this plane with the local symmetry plane of the chelating ligand (dashed line in Figure 5B). In particular, the angle α is defined by this axis and the axis connecting the metal to the center of the double bond, while the angle β is defined by this axis and the metal carbon bond of the growing chain. Other internal coordinates that have been varied in the calculations are as follows: the dihedral angle θ_0 associated with rotations of the olefin around the axis connecting the metal to the center of the double bond; the internal rotation angles θ_1 and θ_2, associated with rotations around the two bonds between the metal atom and the first carbon atom of the growing chain and between the first and the second carbon atoms of the growing chain, respectively. While the angles α and β are varied, their sum is forced to remain in the experimentally observed range 91–99°.[20,28,29] In particular, various sets of calculations have been performed with α

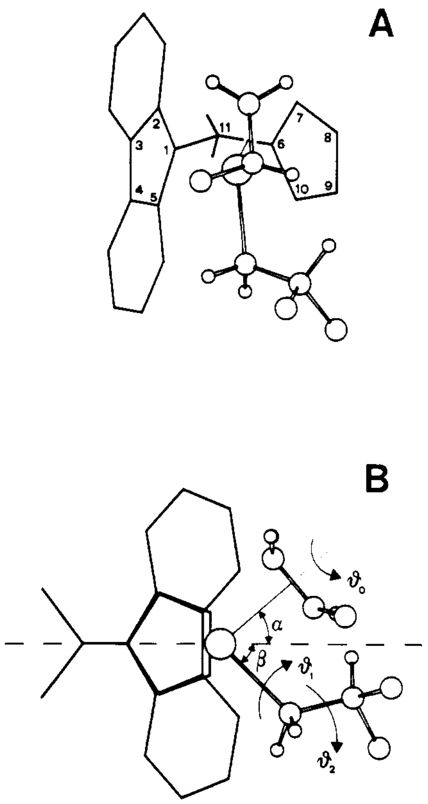

Figure 5. Different views of the (*re*-propene)(isobutyl)(IpCpFlu) model site, with *R* chirality at the metal atom. Part A shows the numerical labels for the atoms of the ligands used in Table I. Part B shows a projection of the local symmetry plane, which characterizes the IpCpFlu ligand (dashed line), and the main internal coordinates, which have been varied. The depicted conformation corresponds to $\theta_0 = 0°$, $\theta_1 = -40°$, and $\theta_2 = -20°$. For the sake of clarity, for the chelating ligand only the C–C bonds are sketched.

+ β = 91°, 93°, 95°, 97°, and 99°, respectively. At θ_0 = 0° the olefin is oriented in a way suitable for primary insertion, while θ_0 = 180° corresponds to an orientation suitable for secondary insertion. θ_1 = 0° corresponds to the conformation having the first C–C bond of the growing chain eclipsed with respect to the axis connecting the metal atom to the center of the double bond of the olefin. θ_2 = 0° corresponds to the conformation having the Hf–C bond of the growing chain eclipsed with respect to the C–H bond on the second carbon atom of the growing chain. The torsional potential for the rotations θ_0 and θ_1 are not known and therefore are not included. While we expect such energy contribution to be small for θ_1, it may not be so for θ_0. Since deep energy minima are found only for $\theta_0 \approx 0°$, the inclusion of such a torsional potential would not change our conclusions. For the rotation θ_2, the torsional potential reported in ref 30 is included.

The bond angles centered on the first and the second carbon atoms of the growing chain have been optimized in each calculation, arbitrarily assuming the bending potential for the Hf–C–C and Hf–C–H angles equal to the potential for the C–C–C and C–C–H angles. The bending contribution to the total energy has been evaluated according to ref 30. The method of calculation of the nonbonded potential energy has been previously described[31] and is not reported here. The results presented in this paper are obtained with the parameters proposed by Scheraga,[32] treating the CH_3 group of the propene and the CH_3 groups of the isobutyl group as spherical domains.[33] The energy parameters for the CH_3 groups treated as spherical domain were derived assuming for the domain the polarizability α = 1.77 Å^3 and the effective number of electrons $N_e = 7$, as suggested in ref 33, with a van der Waals radius 1.9 Å. In order to test the dependence of the results on the particular choice of the parameters in the potential functions, some calculations have also been performed by using the parameters proposed by Flory[30,33,34] and/or avoiding the approximation of the spherical domains. Although the results are different from the quantitative point of view, the overall trends as the location of the energy minima are practically unchanged.

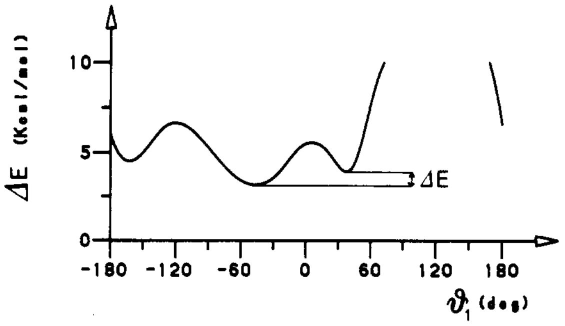

Figure 6. Minimized energy (see text) of the (ethene)(isobutyl)(IpCpFlu) model site, as a function of θ_1, for a model site presenting *R* chirality at the metal atom.

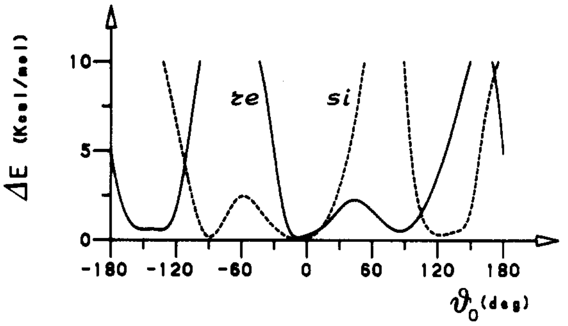

Figure 7. Minimized energy (see text) of the (propene)(methyl)(IpCpFlu) model site, as a function of θ_0, for a model site presenting *R* chirality at the metal atom. The full and the dashed lines refer to *re*- and *si*-coordinated propene, respectively.

The numerical results of our calculations cannot be trusted as such. This is especially true for conformations far from the energy minima, because of the inaptitude of the energy functions in such regions and because of the simplifying assumption of constancy (rather than near-constancy) of most internal coordinates. However, we believe that the trends suggested by our results are realistic, in the sense that conformations having low energy according to our calculations are not likely to be substantially different from those of low energy in the catalytic system. Furthermore, although the numerical values of the energy differences depend on the exact geometry and on the energy parameters adopted in the calculations, no reasonable adjustment of these parameters can modify our conclusions. As far as the results of our calculations are in qualitative, or perhaps semiquantitative, agreement with all the experimental findings, we also believe that such calculations can be used in a predictive way.

Results and Discussion

Figure 6 plots as a function of θ_1 the energy, minimized with respect to all the variables depicted in Figure 5B, for the (ethene)(isobutyl)IpCpFlu model with *R* chirality at the metal atom. The growing chain tends to prefer values of θ_1 close to −50°, while positive values of θ_1 are disfavored. Already on inspection of the model of Figure 1A, it is apparent that this is due to the nonbonded interactions between the growing chain and a six-membered ring of the fluorenyl ligand.

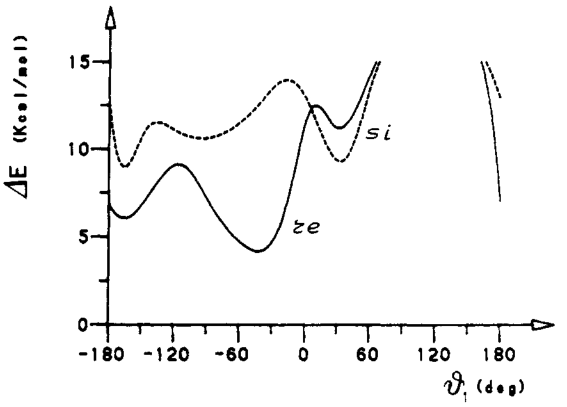

Figure 8. Minimized energy (see text) of the (propene)(isobutyl)(IpCpFlu) model site, as a function of θ_1, for a model site presenting *R* chirality at the metal atom. The full and the dashed lines refer to *re*- and *si*-coordinated propene, respectively.

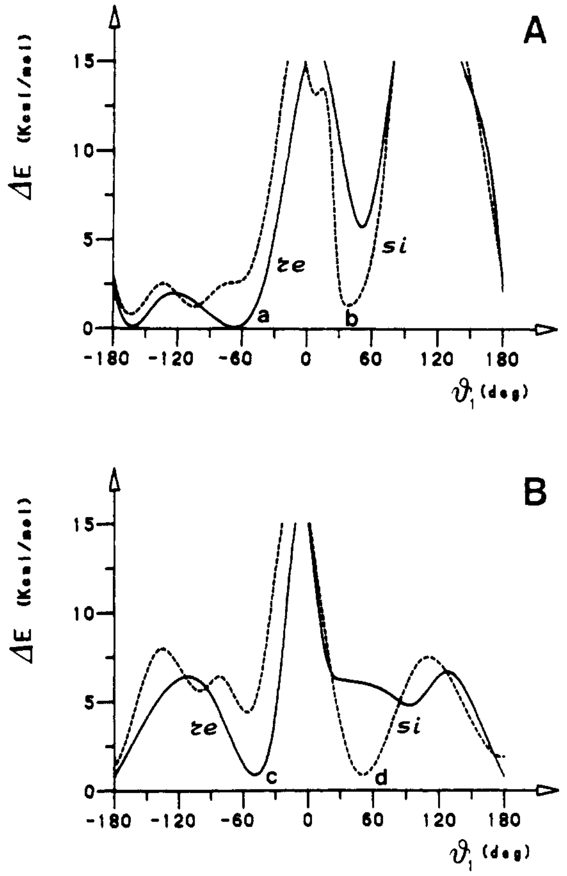

Figure 9. Minimized energy (see text) of the (propene)(isobutyl)(IpCpInd) model site as a function of θ_1, for the diastereoisomers (A) *R*,(*R*) and (B) *S*,(*R*). The full and the dashed lines refer to *re*- and *si*-coordinated propene, respectively. The conformation corresponding to the energy minima a–d are sketched in parts A–D of Figure 2, respectively.

Figure 7 plots as a function of θ_0 the energies, minimized with respect to α and β, of the (propene)(methyl)IpCpFlu model. The full and dashed lines refer to *re*- and *si*-coordinated propene, respectively. As previously found for other proposed stereospecific models,[4-6] in the presence of a methyl group the two chiral coordinations of propene are nearly isoenergetic. This indicates that also in this case the chirality of the model, in the absence of alkyl groups longer than a methyl, is unable to generate enantioselectivity in the olefin coordination step. In other words, at least in the coordination step, the difference in steric hindrance between the cyclopentadienyl and the fluorenyl ligands is able to influence directly the conformation of the growing chain but is not able to influence directly the chirality of coordination of propene.

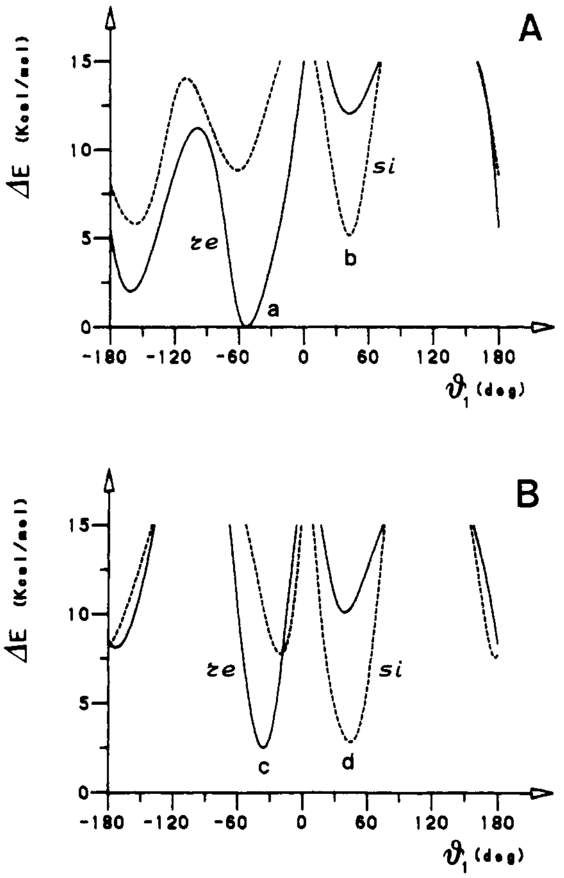

Figure 10. Minimized energy (see text) of the (propene)(isobutyl)(IpFluMCp) model site as a function of θ_1, for the diastereoisomers (A) *R*,(*R*) and (B) *S*,(*R*). The full and the dashed lines refer to *re*- and *si*-coordinated propene, respectively. The conformation corresponding to the energy minima a–d are sketched in parts A–D of Figure 3, respectively.

Figure 8 plots, as a function of θ_1, the minimized energy of the (propene)(isobutyl)IpCpFlu model. As in Figure 7 the full and the dashed lines refer to *re*- and *si*-coordinated propene, respectively. It is apparent that the model complex, in the presence of an alkyl group longer than a methyl, is enantioselective. However, this is not due to direct interactions of the IpCpFlu ligand with the monomer but to the interactions of the IpCpFlu ligand with the growing chain, determining its chiral conformation ($\theta_1 \approx -50°$, preferred to $\theta_1 \approx +50°$), which, in turn, discriminates between the two prochiral faces of the propene monomer. In fact, already on inspection of the model with *R* chirality at the metal atom in the evaluated minimum energy situation (Figure 1A), it is apparent that the coordination and the insertion of a *re* olefin minimizes the interactions between the growing chain (at $\theta_1 \approx -50°$) and the methyl group of the incoming monomer.

After the insertion of the monomer and the coordination of a new monomer molecule, in our assumptions, a model complex with *S* chirality at the metal atom is obtained. Of course, the evaluated minimum energy situation for this model complex (Figure 1B) corresponds to $\theta_1 \approx +50°$ and to a *si* coordination of the monomer. A regular alternation of insertion steps in models likes those of parts A and B of Figure 1 assures the syndiospecific behavior of the model.

Figures 9 and 10 plot, as a function of θ_1, the minimized energy of the diastereoisomeric models of the kind (propene)(isobutyl)IpCpInd and (propene)(isobutyl)IpFluMCp, sketched in Figures 2 and 3, respectively.

Table II
Minimized Energy Differences between the *si* and *re* Coordinations of the Propene ($E_{si} - E_{re}$) for the Stereorigid Model Sites of the Kind (Propene)(isobutyl)(ligand)[a]

	chelating ligand and chirality of coordination[b]	metal atom	metal chirality	$E_{si} - E_{re}$
a	(*R*),(*R*)-ethylenebis(1-indenyl)	Ti		18.4
b	(*R*),(*R*)-ethylenebis(1-indenyl)	Zr		7.2
c	(*R*),(*R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)	Ti		18.7
d	(*R*),(*R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)	Zr		8.2
e	(*R*),(*R*)-ethylenebis(3-methylcyclopentadienyl)	Ti		17.4
f	(*R*),(*R*)-ethylenebis(3-methyl-1-indenyl)	Ti		1.3
g	isopropyl(cyclopentadienyl-1-fluorenyl)	Hf	*R*	4.1
			S	−4.1
h	(*R*)-isopropyl(cyclopentadienyl-1-indenyl)	Hf	*R*	1.1
			S	0.1
i	(*R*)-isopropyl(1-fluorenyl-3-methylcyclopentadienyl)	Hf	*R*	6.2
			S	0.2

[a] The chirality of coordination of the chelating ligand (if any), the kind of metal atom (Ti, Zr, or Hf, which corresponds to different metal–carbon distances), and the chirality at the metal atom (if any), is indicated. An alphabetical label for the model sites, for an easier identification in the text, is also indicated. [b] The chirality of coordination is stable during the polymerization. [c] The chirality of the metal atom is changing at each insertion step.

The energy curves of Figures 9A and 10A refer to the *R*,(*R*) diastereoisomers and are qualitatively similar to those of the *R* enantiomer of the IpCpFlu model (Figure 8). Negative values of θ_1 ($\theta_1 \approx -50°$) are favored, which produce energy differences in favor of the *re* coordination of the monomer. However, this energy difference is similar for the *R*,(*R*)-IpFluMCp and the *R*-IpCpFlu models and much lower for the *R*,(*R*)-IpCpInd model (in our calculations 6.2, 5.7, and 1.1 kcal/mol, respectively).

Schematic representations of the minimum energy conformations for the *R*,(*R*) diastereoisomers, both for *re* and *si* coordinations of the monomer, are shown in parts A and B of Figure 2, for the IpCpInd sites, and in parts A and B of Figure 3 for the IpFluMCp sites.

The energy curves of Figures 9B and 10B refer to the *S*,(*R*) diastereoisomers of the IpCpInd and IpFluMCp sites, respectively. The two orientations of the growing chain with $\theta_1 \approx +50°$ and $\theta_1 \approx -50°$ are substantially equivalent, and for both models only small minimum energy differences for the *re* and *si* coordinations of propene are observed.

Schematic representations of the minimum energy conformations for the *S*,(*R*) diastereoisomers, both for *re* and *si* coordinations of the propene, are shown in parts C and D of Figure 2, for the IpCpInd site, and in parts C and D of Figure 3, for the IpFluMCp site. A polymerization mechanism analogous to that hypothesized for the IpCpFlu model (which assumes that, after each insertion step, the catalyst does not rearrange before the coordination of a new monomer molecule) implies, for the IpCpInd and IpFluMCp sites, a regular alternance of *R*,(*R*) and *S*,(*R*) diastereoisomers. In particular, for the IpFluMCp site, the high enantioselectivity of the *R*,(*R*) diastereoisomer implies, in agreement with very recent experimental results,[35] the production of a hemiisotactic polypropylene (that is, a polymer for which isotacticity exists only for alternating tertiary carbon atoms.[36,37]) On the other hand, the low enantioselectivity of the *R*,(*R*) diastereoisomer and the very low enantioselectivity of the *S*,(*R*) diastereoisomer of the IpCpInd model is in qualitative agreement with the experimentally observed production of prevailingly atactic polymer[38] and of hemiisotactic polymer at low temperatures.[39]

Conclusions

The energy differences between the *si* and *re* coordinations of the monomer (enantioselectivity) calculated and minimized as described in the Models and Methods section, for several stereorigid model sites of the kind (propene)(isobutyl)(ligand), are collected in Table II.

As also discussed in previous papers,[4-6] it is apparent that the isospecific model sites a–e are highly enantioselective, while a nearly complete absence of enantioselectivity is predicted for site f.

According to the present calculations, and in agreement with experimental observations on catalysts including the corresponding chelating ligands,[1-3,11,12,35,38] the alternation of model sites g (*R* and *S*) during the polymerization should give rise to syndiospecificity, while the model sites h should behave as almost aspecific and the model sites i should behave as hemiisospecific. According to the calculations, the enantioselectivity should be smaller for the syndiospecific model than for the isospecific models. We note in this respect that the stereoregularity of the syndiotactic polypropylene obtained with this catalytic system[3] is lower than that of the corresponding isotactic polypropylene.[1,2]

Another relevant result of our calculations is that, if a methyl group substitutes the isobutyl group, all the considered stereospecific model sites become substantially nonenantioselective as already cited; this prediction of the models has been confirmed, at least in one case, by the analysis of the stereochemical structure of the ^{13}C-enriched end groups of the isotactic polypropylene obtained with a catalyst based on the ethylenebis(1-indenyl).

The origin of the enantioselectivity for the stereorigid models considered in this work (isospecific, syndiospecific, hemiisospecific) is essentially the same. The chiral environments of the models, which are generally unable to influence directly the chirality of coordination of propene, are instead able to force the growing chain to choose one of two possible chiral orientations ($\theta_1 \approx +50°$ or $\theta_1 \approx -50°$). As a consequence, one of the two possible chiral coordinations (*re* or *si*) of a propene molecule is strongly disfavored with respect to the other by selective repulsive interactions of the propene methyl group with atoms of the growing chain.

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