Model Catalytic Sites for Olefin Polymerization and Diastereoselectivity in the Cyclopolymerization of 1,5-Hexadiene

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ABSTRACT: The diastereoselectivity of the cyclization step in the cyclopolymerization of 1,5-hexadiene with homogeneous catalysts based on zirconocene/methylalumoxane systems is investigated through the analysis of the nonbonded interactions on model catalytic sites analogous to those proposed for α-olefin polymerizations. A model which does not include any cyclopentadienyl ring presents a small trans specificity: the minimum energy intermediate brings the formation of trans rings and resembles a cyclohexane chair in which the growing chain occupies a pseudoequatorial position (trans-chair conformation). The addition of two cyclopentadienyl rings to the Zr atom, due to interactions with the growing chain which occupies a pseudoaxial position, disfavors the two most stable cis conformations (a cis-chair and a cis-boat). As a consequence, the model with two cyclopentadienyl rings shows a higher trans specificity than the "bare" model. In the presence of two pentamethylcyclopentadienyl rings, the steric interactions of the aromatic ligands tend to disfavor the trans-chair with respect to a cis-twist conformation and the model becomes cis-specific. A good qualitative agreement between the modeling and polymerization results is observed.

Introduction

Homogeneous Ziegler–Natta catalysts based on group 4 metallocenes exhibit remarkable activity and stereospecificity in the polymerization of α-olefins. Results to date have been truly impressive: both isospecific (site-controlled[1,2] and chain-end-controlled[1]) and syndiospecific[3] polymerizations of 1-alkenes have been reported.

One of the most exciting features of these homogeneous catalysts is that the structure of the catalyst precursors can be accurately determined and the influence of the ligand geometry on the stereospecificity of the polymerization reactions can be studied in detail. Correlations of the polymer microstructure with the structure of the catalyst precursor have revealed an extraordinary amount of information on the polymerization mechanism and the origin of stereodifferentiation for these homogeneous polymerization reactions.[4] To the extent that stereodifferentiation is related to steric nonbonded interactions in the transition state (disregarding for the moment electronic effects and potential agostic interactions[5]), conformational analysis can provide considerable insight into the origin of stereocontrol with these homogeneous polymerization reactions.

Previous studies from our group in Naples have led to conformational models to interpret the isospecific polymerization of α-olefins under enantiomorphic site control,[6,4a] and chain-end control[7] with homogeneous catalysts. Furthermore, the aspecific behavior of racemic ethylenebis(3-methyl-1-indenyl)[8] and isopropylidene(cyclopentadienyl)(1-indenyl)[9] ligands and the hemisotactic behavior of isopropylidene(9-fluorenyl)(3-methylcyclopentadienyl)[8,10] ligands were readily interpreted in terms of conformational models developed in our laboratories.[6b,c]

For all these model sites a common mechanism for the enantioselectivity has been suggested, analogous to that previously proposed for the traditional heterogeneous Ziegler–Natta catalysts,[11] and based on the chiral orientation of the growing chain.

The basic assumptions about the polymerization mechanism, common to the proposed models, are as follows: (i) the mechanism is monometallic, and the active center is a transition metal–carbon bond;[12–15] (ii) the mechanism is in two stages, the coordination of the olefin to the catalytic site, followed by the insertion into the metal–carbon bond through a cis opening.[13,16,17]

Geometries of coordination of the aromatic ligands, similar to those observed in the crystal structures of the precursor metallocenes and of cationic zirconocenes, have been assumed in our monometallic model catalytic sites. In addition to the aromatic ligands of the precursor metallocenes, also an incoming monomer molecule and an alkyl group (to simulate the growing polymer chain) are coordinated to the metal in the models for the stage preceding monomer insertion.

Calculations of the nonbonded interactions for these models have suggested that the coordination of a further ligand is sterically unfeasible, and have forced us to assume a four-coordinate cationic model for the active site. The cationic hypothesis for the active site, proposed as long ago as 1961,[18] has recently been confirmed by the synthesis of a wide series of group 4 metallocene cations able to polymerize ethylene and propylene without any aluminum cocatalyst.[19] The finding by Ewen that ethylenebis(1-indenyl)$ZrCl_2$/methylalumoxane and ethylenebis(1-indenyl)$ZrCH_3^+B(C_6F_5)_4^-$ produce isotactic polypropylene with the same microstructural defects is the best available proof for the cationic nature of the active species.[9]

In this paper, we present conformational calculations on the diastereoselective cyclopolymerization of 1,5-hexadiene, recently reported by Resconi and Waymouth for homogeneous Ziegler–Natta catalysts.[20]

Cyclopolymerization of 1,5-hexadiene was first reported by Marvel and co-workers,[21] and further investigated by

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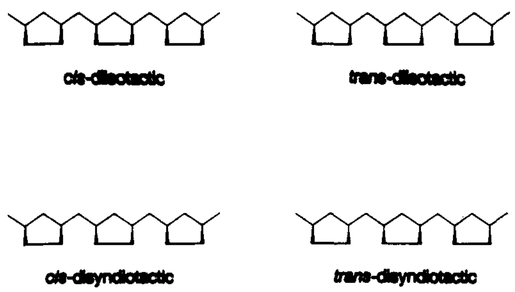
Chart I



Makowski.[22] Using catalysts derived from $TiCl_4/Al\text{-}i\text{-}Bu_3$ and $TiCl_4/AlEt_3$, respectively, both groups reported low activities and incomplete cyclization of the diolefin. More recently, Cheng[23] reported the cyclopolymerization of 1,5-hexadiene using a $TiCl_3/AlEt_2Cl$ catalyst. ^{13}C NMR analysis of the resulting polymer indicated complete cyclization and a nearly 1:1 ratio of trans and cis cyclopentane rings in the polymer.

For this polymer, poly(methylene-1,3-cyclopentane), four microstructures of maximum order are possible (Chart I).[24]

There are two distinct stereochemical events for these cyclopolymerizations: olefin insertion and olefin cyclization. The enantioselectivity of the olefin insertion determines the tacticity of the polymer (the relative stereochemistry between the rings), and the diastereoselectivity of the cyclization step determines whether cis or trans rings are formed.

Recently, some of us have been investigating group 4 metallocene/methylalumoxane catalysts for the polymerization of 1,5-hexadiene,[20] finding that cyclization is complete also in the case of these homogeneous catalysts.

With achiral zirconocenes, the cis/trans selectivity can be controlled, leading to the first examples of atactic *trans*- and atactic *cis*-poly(methylene-1,3-cyclopentane).[20] The prevailingly trans polymer is obtained in the presence of Cp_2MeX_2 (Cp = cyclopentadienyl; Me = Zr, Hf; X = Cl, CH_3); the prevailingly cis polymer is obtained in the presence of the more sterically hindered $Cp_2{}^*MeX_2$ (Cp* = pentamethylcyclopentadienyl).

In this paper the diastereoselectivity of the cyclization step will be investigated through the analyses of the nonbonded interactions on model catalytic sites analogous to those proposed for the 1-alkene polymerizations.

In particular, sites with two Cp rings or with two Cp* rings are compared, in order to try to explain the opposite diastereoselectivities of the two corresponding systems.

For a comparison with the results of the modeling, some recent polymerization results for different catalytic complexes, in similar experimental conditions, are also reported.

Table I
Polymerization of 1,5-Hexadiene with Different Metallocenes[a]

metallocene	T_p (°C)	% cis	toluene (mL)	1,5-hexadiene (mL)
$CpZrCl_3$	20	20.0	1	2
Cp_2ZrCl_2	21	21.5	30	10
$Me_2SiCp_2ZrCl_2$	20	35.7	5	20
Cp^*ZrCl_3	17	48.6	30	10
$Me_2Si(Me_4Cp)_2ZrCl_2$	17	55.6	30	10
$Cp^*{}_2ZrCl_2$	20	83.7	3	20

[a] MAO as cocatalyst, Al/Zr ≈ 1000. Percent cis rings determined from the ratio of the ^{13}C NMR resonances at 33.7 and 32.4 ppm (ODCB, 100 °C, reference TMS = 0).

Experimental Section

All polymerizations were carried out in a Schlenk tube equipped with a side arm for the nitrogen inlet and a magnetic stirring bar, thermostated with a water bath.

Toluene (Carlo Erba) was purified by refluxing over $Al\text{-}i\text{-}Bu_3$ and subsequent distillation under nitrogen. 1,5-Hexadiene (Fluka, 97%) was distilled on a Todd fractional distillation apparatus, collecting the fraction boiling at 59.8–60.2 °C, which resulted in a 99.3% pure sample (GC); this fraction was subsequently vacuum-transferred from CaH_2 and stored under nitrogen. Cp_2ZrCl_2 (Aldrich), $CpZrCl_3$, $Cp^*{}_2ZrCl_2$, and Cp^*ZrCl_3 (Strem) were used as received. $Me_2SiCp_2ZrCl_2$[25] and $Me_2Si(Me_4Cp)_2ZrCl_2$[26] were prepared according to known procedures.

The experimental polymerization conditions and the percent cis rings for the obtained polymers are reported in Table I.

Models and Calculation Methods

Cyclopolymerization Mechanism. Two mechanisms have been proposed for the cyclopolymerization of nonconjugated dienes.

The mechanism proposed by Boor[15] is a concerted one-step addition, which in the transition state involves the coordination of both the double bonds. Marvel and Garrison proposed a stepwise mechanism[21] involving a sequential insertion cyclization sequence as shown in Scheme I. In light of the observed dependence of the cis/trans stereoselectivity on reaction conditions and catalyst structure, the mechanism of Marvel and Garrison has come to be accepted as the most reasonable mechanism for these cyclopolymerization reactions.[23,27]

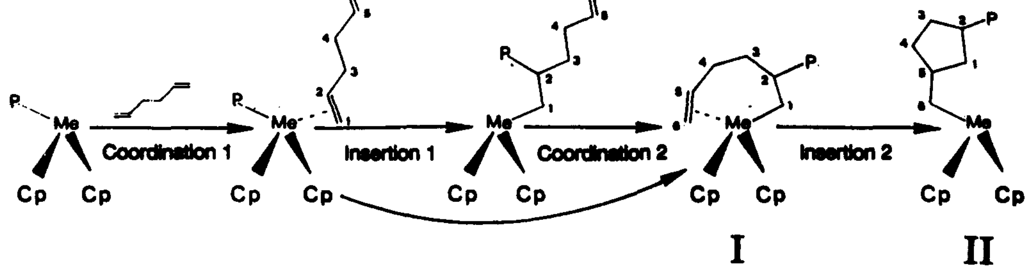
In the framework of our catalytic models, the mechanism of Marvel and Garrison is the only one that is energetically feasible, since, due to the bulkiness of the aromatic ligands, there is not sufficient space for the contemporary coordination of the growing chain and of the two double bonds of the monomer molecule.

In this paper we confine our analysis to the cyclization step and, in particular, to a conformational analysis on the catalytic intermediate I (Scheme I), in which the primary insertion of one double bond has already occurred and the second double bond would be π-coordinated to the metal.

It is worth noting that in the framework of the assumed mechanism the cyclization step is strictly analogous to the cyclization of 5-hexen-1-yl compounds.[28]

Model for the Catalytic Intermediates. The basic models of the catalytic intermediate I (Scheme I) considered in this paper are zirconium complexes containing three ligands, that is, a σ,π-

Scheme I



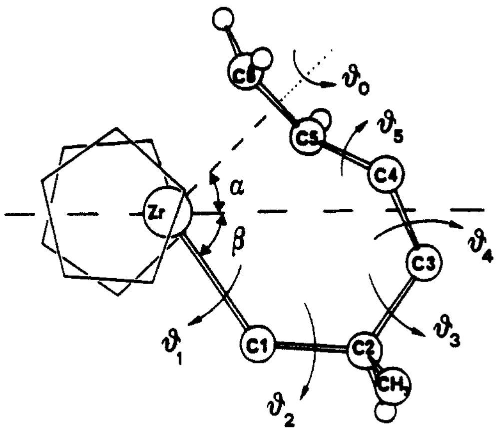


Figure 1. Schematic drawing of the model comprising two Cp rings and an (*R*)-2-methyl-5-hexenyl group, coordinated to a Zr atom. The main internal coordinates, varied in the calculations, are indicated. The depicted conformation corresponds to the cis-chair of Table III.

coordinated 5-hexenyl or 2-methyl-5-hexenyl group (the methyl group simulates the growing chain P of the intermediate I in Scheme I) and two Cp or Cp* rings.

For the chirality of coordination of the double bonds the *R*,*S* notation (as defined for double or triple bonds π-bonded to a metal atom[29] and used by us in ref 11[a]) is adopted in this paper for the coordination of the 1-alkenes rather than the *re*,*si* notation suggested for specifying heterotopic half-spaces[30] (used by us in refs 6, 7, and 11[e]) or the *Re*,*Si* notation for reflection-variant units[31] (used by Pino and co-workers in ref 32). The reason is that, at variance with the *R*,*S* notation, the symbol for a given enantioface of a 1-alkene molecule changes with the bulkiness of the substituent in position 1.

For the models containing the 2-methyl-5-hexenyl substituent, C2 (see Scheme I) is stereogenic. The absolute configuration of this center can be denoted *R* or *S*, and is determined by the stereofacial coordination of 1,5-hexadiene in the insertion step of the first double bond of the diene (insertion step 1). Without loss of generality, all the reported calculations refer to the *R* configuration for C2 as deriving from the insertion of an *S*-coordinated double bond. As implied by the chosen model, the diastereoisomeric complexes corresponding to an *R* or an *S* coordination of the double bond of the 2-methyl-5-hexenyl substituent would produce, according to the reaction Scheme I, cis or trans cyclopentane rings along the chain, respectively. For the sake of immediacy, we will refer hereafter cis or trans the complexes which produce in our framework cis or trans cyclopentane rings, respectively.

The C–C bond distance has been set equal to 1.40 Å for the Cp rings,[33] and equal to 1.42 Å for the Cp* rings.[33] The bond distance C–CH_3 in the Cp* ligands has been set equal to 1.51 Å,[33] while the out-of-plane bending angle γ has been assumed to be 10°, which is an average value for sterically crowded complexes.[34]

The distance of the center of the Cp and Cp* rings from the Zr atom has been set equal to 2.24 Å,[33] while the angle ϕ defined as ring center–metal–ring center has been set equal to 129° for the Cp_2Zr system, and equal to 136° for the $Cp_2{}^*Zr$ system, which are averages of some observed experimental values.[35] Strictly analogous results have been obtained with this distance set equal to 2.22 Å, which is an average of the values observed in cationic zirconocene complexes.[19c,e,36]

The distance Zr–C1 (chain) has been assumed to be 2.27 Å, as observed in some σ-alkylzirconium complexes.[37] Test calculations have been performed by assuming Zr–C1 equal to 2.24 and 2.26 Å for the systems with the Cp and Cp* rings, respectively, which are averages of the values observed in cationic zirconocene complexes.[19c,e,36]

The distance between the metal atom and the olefinic carbon atoms (Zr–C5 and Zr–C6), hereafter denoted as *d*, has been set equal to 2.30 Å, which is 0.03 Å bigger than the distance Zr–C1, to be consistent with the analogous distances observed in titanium complexes.[38] As described in the following test calculations have been performed with different values for the distance *d*, to account for the larger values observed for this parameter in the structure of $Cp_2Zr(C_2H_4)(PMe_3)$.[39]

The main internal coordinates that have been varied in our calculations (see Figure 1) are defined in analogy with our previous papers.[6,7] The angles α and β have been confined in the local symmetry plane which passes through the Zr atom and relates the two Cp or Cp* rings (when eclipsed), and referred to the intersection of this plane with the plane containing the Zr atom and the centers of the rings (dashed line In Figure 1). 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 our 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, and the internal rotation angles θ_1, θ_2, θ_3, θ_4, and θ_5, associated with rotations around the bonds of the hexenyl group.

While the angles α and β are varied, their sum is forced to remain in the range 91–99° experimentally observed for analogous organometallic compounds.[38e,40] Test calculations have also been performed without any constraint for α and β. For all the minimum energy situations the sum of α and β results in the range 90–105°. Although the results are slightly different from the quantitative point of view, the overall trends as well as the location of the energy minima are practically unchanged. At $\theta_0 = 0°$ the olefin is oriented in a way suitable for primary insertion, while $\theta_0 = 180°$ corresponds to an orientation suitable for secondary insertion. $\theta_1 = 0°$ 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. The torsional potentials 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. For this reason, besides energy minimizations without any constraint on θ_0, also minimizations with θ_0 in the range −20 to +20°, which is also most suitable for the cyclization, have been performed. For the rotations θ_2, θ_3, and θ_4, and for the rotation θ_5 standard 3-fold and 2-fold torsional potentials, respectively, have been included.[41,42]

The bond angles centered on sp^3 carbon atoms of the monomer have been optimized in each calculation; the bending potential for the Zr–C–C angle has been arbitrarily assumed to be equal to the potential for the C–C–C angle.[41] The method of calculation of the nonbonded potential energy has been previously described[42] and is not reported here. The results proposed in this paper are obtained with the parameters proposed by Scheraga,[43] treating the CH_2 and CH_3 groups as spherical domains. The energy parameters for these groups have been set equal to those described in ref 6c.

The results of the nonbonded energy calculations relative to the catalytic intermediate I (Scheme I) depend, of course, on the connectivity of the complex, that is, on the bonds which are assumed between the atoms. Possibly, in the transition state of the cyclization reaction (insertion 2 in Scheme I) the connectivity is intermediate between that of the intermediates I and II. Hence, for the sake of simplicity, we have performed two sets of calculations of nonbonded interactions on the intermediate I, with the connectivities of the intermediate I, or of the intermediate II. Since the results of the calculations are analogous for both sets, only the calculations with the connections of intermediate I are reported here.

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 conclusion. As far as the results of our calculations are in qualitative, or perhaps semi-

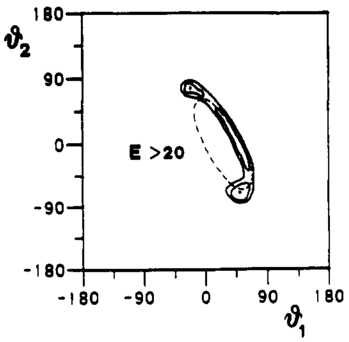


Figure 2. Map $E(\theta_1,\theta_2)$ for the model comprising a 5-hexenyl group coordinated to a Zr atom. The energy curves correspond to 10 and 20 kcal/mol. The dashed curve is the locus of points with the bond distance C3–C4 equal to 1.53 Å.

quantitative, agreement with all the experimental findings, we also believe that such calculations can be used in a predictive way.

Location of the Minimum Energy Conformations for the Intermediate I. To sample the likely low-energy conformations, we first considered an unsubstituted 5-hexenyl chain on a zirconium atom lacking ancillary ligands. The conformation of the cyclic olefin adduct can be considered as determined by the positions of seven points, the carbon atoms C1, C2, C3, C4, and C5, the fictitious atom positioned in the center of the double bond, and the Zr atom (see Figure 1). Hence, 15 independent variables ($3N - 6$) have to be used to determine the cycle conformation. The 15 independent parameters chosen in our analysis are six bond distances (all the bond distances present in the cycle, with the exception of the bond distance C3–C4), the five included bond angles, and the four included torsion angles. The distance C3–C4, the two bond angles centered on the C3 and C4 atoms, and the three torsion angles including both the C3 and C4 atoms are thus defined by the values assumed by the 15 parameters indicated above.

The conformational analysis for the location of the minimum energy conformations of the coordinated 5-hexenyl group has been performed by minimizing the energy with respect to the torsional angle θ_0, in the range -30° to +30°, and by varying the angles θ_1 and θ_2 in the range -180° to + 180°, by steps of 10°. All the energy contributions of the 5-hexenyl cycle have been considered during the search. To constrain the bond distance C3–C4 to reasonable values, a parabolic energy contribution of the type $E = 0.5K(R - R_0)^2$ (with $K = 100$ kcal/mol and $R_0 = 1.53$ Å) has been added. The resulting energy map $E(\theta_1,\theta_2)$ is plotted in Figure 2.

Energy minimizations, with respect to all the variables indicated in Figure 1, now fixing the bond distances C3–C4 at 1.53 Å, have been performed starting from several conformations along the narrow domain of minimum energy of Figure 2. This procedure led to the location of only four minimum energy conformations (whose geometries are reported in Table II), which present an energy in the range of 5 kcal/mol with respect to the absolute minimum.

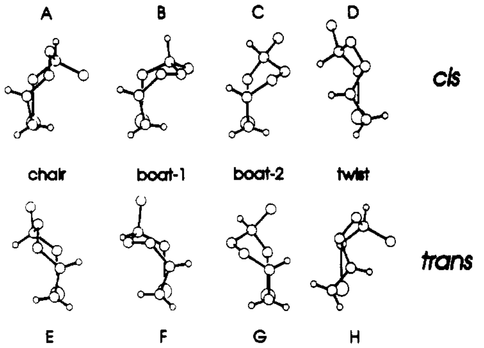


Figure 3. Minimum energy conformations of the model comprising an (*R*)-2-methyl-5-hexenyl group coordinated to a Zr atom. The cis (A–D) and the trans (E–H) conformations (Table III) correspond to the *R* and *S* coordinations of the double bond, respectively.

The geometries of the various minimum energy conformations are scarcely dependent on the calculation method (e.g., presence of constraints for α and β, or for θ_0, or different connectivities). The energy minimum geometries are reported in Table II, and are named according to IUPAC nomenclature for the conformations of six-membered saturated ring compounds[44] (considering the ring being formed by the carbon atoms C1–C5 and by the metal atom). They approximately correspond to a pseudochair, two pseudoboat, and a pseudotwist conformation (chair, boat-1, boat-2, and twist, respectively, in the following), and the most stable conformation is the chair.

The thus selected conformations represent the starting points for all the calculations subsequently performed.

Results and Discussion

Conformational Analysis. We have started our conformational analysis on the catalytic intermediate I, for the cyclization reaction, by ignoring the cyclopentadienyl rings.

The values of the most relevant geometrical parameters, obtained by energy minimization of the (*R*)-2-methyl-5-hexenyl group coordinated to the bare Zr atom are reported in Table III. In this case, since C2 is stereogenic, both diastereoisomeric situations with *R*- and *S*-coordinated olefins have been considered.

Table II
Relevant Dihedral Angles and the Energy for the Located Minimum Energy Conformations of the Model Comprising a 5-Hexenyl Group Coordinated to a Bare Zr Atom

conformn	θ_0 (deg)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	θ_4 (deg)	θ_5 (deg)	E (kcal/mol)
chair	11.6	54.0	-71.7	67.0	-65.1	149.9	0.0
boat-1	14.1	58.1	-19.2	-60.1	68.3	84.8	2.1
boat-2	4.7	35.8	19.9	-83.4	51.3	109.7	3.3
twist	30.0	-35.6	73.6	-44.7	-33.7	157.5	3.8

Table III
Relevant Dihedral Angles and the Energy for the Located Minimum Energy Conformations of the Model Comprising an (*R*)-2-Methyl-5-hexenyl Group Coordinated to a Bare Zr Atom

conformn	θ_0 (deg)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	θ_4 (deg)	θ_5 (deg)	E (kcal/mol)	E'^a (kcal/mol)
cis-chair	11.8	54.9	-70.6	65.4	-63.2	147.7	1.1	1.1
cis-boat-1	14.5	58.1	-19.4	-60.9	69.6	85.0	2.2	2.2
cis-boat-2	4.0	35.6	19.7	-84.4	51.3	110.8	2.8	2.8
cis-twist	30.8	-36.5	75.4	-47.8	-32.3	156.3	2.7	3.1
trans-chair	-13.1	-52.9	71.7	-68.8	66.7	-149.1	0.0	0.0
trans-boat-1	-16.7	-58.2	22.2	57.4	-69.4	-83.1	2.8	2.8
trans-boat-2	-3.2	-36.0	-17.4	78.9	-45.9	-114.8	5.0	5.1
trans-twist	-41.0	47.3	-74.4	37.0	42.3	-153.0	3.3	5.4

[a] Energy computed with θ_0 restricted in the range -20° to +20°.

Table IV
Relevant Dihedral Angles and the Energy for the Located Minimum Energy Conformations of the Model Comprising Two Cp Rings and an (*R*)-2-Methyl-5-hexenyl Group Coordinated to a Zr Atom

conformn	θ_0 (deg)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	θ_4 (deg)	θ_5 (deg)	*E* (kcal/mol)	E'^a (kcal/mol)
cis-chair	17.0	38.8	−54.9	61.6	−74.2	156.5	5.1	5.1
cis-boat-1	converged to boat-2							
cis-boat-2	5.9	17.0	41.9	−85.7	33.7	125.2	2.3	2.3
cis-twist	21.9	−24.9	71.5	−55.8	−21.6	155.9	2.0	2.0
trans-chair	−14.9	−49.0	68.6	−68.8	70.3	−151.3	0.0	0.0
trans-boat-1	−25.5	−52.8	22.7	52.0	−69.8	−76.0	4.9	5.2
trans-boat-2	−6.3	−30.9	−21.1	74.7	−39.7	−117.6	5.6	5.6
trans-twist	−21.4	22.1	−63.8	46.9	26.3	−157.3	5.0	5.0

[a] Energy computed with θ_0 restricted in the range −20° to +20°.

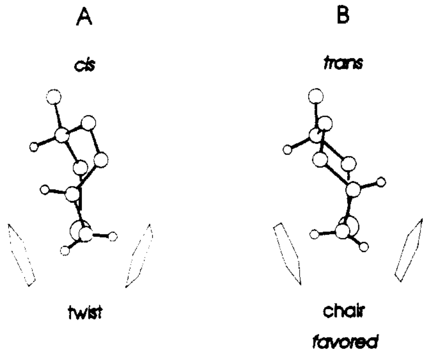


Figure 4. Minimum energy conformations of the model comprising two Cp rings and an (*R*)-2-methyl-5-hexenyl group coordinated to a Zr atom. The cis-twist (A) and the trans-chair (B) conformations (Table IV) correspond to the *R* and *S* coordinations of the double bond, respectively.

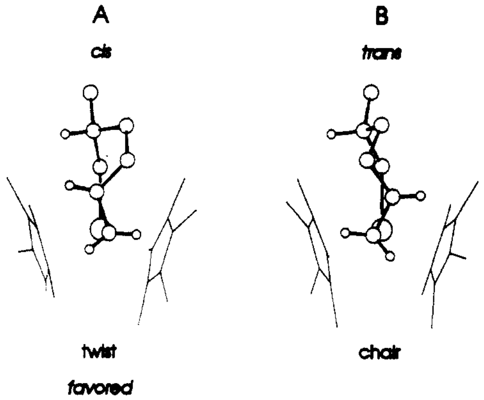


Figure 5. Minimum energy conformations of the model comprising two Cp* rings and an (*R*)-2-methyl-5-hexenyl group coordinated to a Zr atom. The cis-twist (A) and the trans-chair (B) conformations (Table V) correspond to the *R* and *S* coordinations of the double bond, respectively.

The energy minimum geometries reported in Table III are sketched in parts A–D and E–H of Figure 3 for the *R* and *S* coordinations of the (*R*)-2-methyl-5-hexenyl group (corresponding to cis and trans cyclizations), respectively. The most stable conformation is the trans-chair (Figure 3E), which brings the methyl group which simulates in the model the growing chain, in a pseudoequatorial position. As far as the cis conformations are concerned the most stable are the cis-chair and the cis-boat-1.

The energetically favorable coordination of the metal atom with a C5–C6 π bond leading to a transition state resembling a cyclohexane chair, in which a substituent preferentially occupies a pseudoequatorial position, has also recently been found by ab initio and molecular mechanics calculations, for substituted 5-hexen-1-yllithiums. The model accounts for the corresponding stereoselectivity of cyclizations[45] and in particular for the trans specificity of cyclization of the 2-methyl-substituted hexenyl ligand.

The addition of cyclopentadienyl substituents to the metal center results in a number of changes in the energies of the various conformations. The values of the most relevant geometrical parameters, obtained by energy minimization of the (*R*)-2-methyl-5-hexenyl group coordinated to the Zr atom in the presence of two Cp rings, are reported in Table IV, for both the *R* and *S* coordinations of the double bond. The energy minimum geometries for cis and trans cyclization, reported in Table IV, are sketched in parts A and B of Figure 4, respectively.

The most stable conformation is again the trans-chair (Figure 4B), while the cis-boat-1 does not represent anymore a stable minimum, in fact, the energy minimization using as starting point this conformation brings to the minimum cis-boat-2; also the conformation cis-chair is strongly disfavored by the presence of the Cp rings. On the other hand, the conformations which less interact with the Cp rings are the cis-twist and cis-boat-2, and the first one (Figure 4A) becomes of minimum energy for the cis cyclization. This is, of course, due to the fact that the cis-chair and the cis-boat-1 conformations bring the methyl substituent (simulating the growing chain) in a pseudoaxial position. The overall effect is an increase of the trans specificity of the model, in the presence of Cp groups, in qualitative agreement with the experimental results.[20]

The addition of Cp* ligands to the transition-metal center dramatically limits the number of allowed conformations for the hexenyl ring. The values of the most relevant geometrical parameters, obtained by energy minimization of the (*R*)-2-methyl-5-hexenyl group coordinated to a Zr atom in the presence of two Cp* rings are reported in Table V, for both the *R* and *S* coordinations of the double bond. Only two conformations now present reasonable low-energy values: the trans-chair and the cis-twist, whose geometries are sketched in Figure 5. However, the most stable conformation is now the cis-twist (Figure 5A), which has minimum interactions with the Cp* rings. The larger interactions of the trans-chair conformation with the Cp* rings are also indicated by the larger deviations observed for the dihedral angles (compare for instance the values of θ_0 and θ_1 in Tables III–V, or the sketches of Figures 3E, 4B, and 5B). Thus, according to our model, in the presence of the Cp* rings a cis closure of the ring is slightly favored with respect to a trans closure, again in qualitative agreement with the experimental results.[20]

In order to verify the influence of the main geometrical parameters which have been kept fixed during the above calculations, some test calculations have been performed by varying the distance *d* as well as the angles φ and γ.

These calculations are only aimed to show that the previous general conclusions are not modified by reasonable adjustments of the assumed geometrical parameters.

The energy differences between the minimum energy cis and trans intermediates $E_{cis} - E_{trans}$, as a function of

Table V
Relevant Dihedral Angles and the Energy for the Located Minimum Energy Conformations of the Model Comprising Two Cp* Rings and an (*R*)-2-Methyl-5-hexenyl Group Coordinated to a Zr Atom

conformn	θ_0 (deg)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	θ_4 (deg)	θ_5 (deg)	E (kcal/mol)	E'^a (kcal/mol)
cis-chair	28.1	6.3	−21.5	50.4	−84.2	162.9	8.0	9.7
cis-boat-1					converged to twist			
cis-boat-2					converged to twist			
cis-twist	18.0	−11.9	64.6	−69.9	1.4	143.3	0.0	0.0
trans-chair	−26.6	−30.2	57.3	−70.3	83.3	−155.0	0.1	1.8
trans-boat-1					converged to boat-2			
trans-boat-2	−16.9	−6.6	−43.7	73.2	−25.6	−125.0	6.9	6.9
trans-twist					converged to boat-2			

[a] Energy computed with θ_0 restricted in the range −20° to +20°.

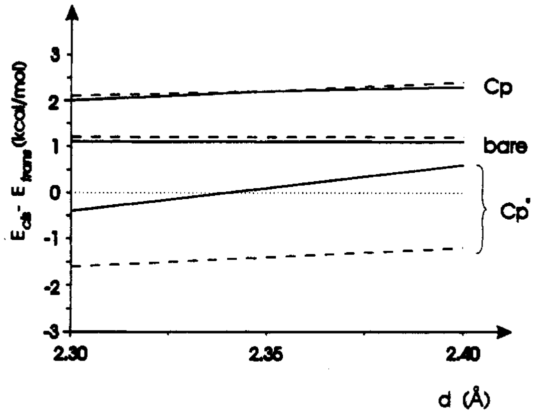


Figure 6. Energy difference between the cis and the trans minimum energy conformations as a function of the Zr–C5 and Zr–C6 distance d, for the model with a bare Zr atom or with two Cp or two Cp* rings. Continuous lines correspond to results without constraints on θ_0; dashed lines correspond to results with $-20° < \theta_0 < +20°$.

the distance Zr–C5 and Zr–C6 of the olefinic carbon atoms, d, are reported in Figure 6, with the distance Zr–C1 (chain) set equal to 2.27 Å. Continuous lines correspond to minimizations without constraints on θ_0, while dashed lines correspond to minimizations with θ_0 in the range −20° to +20°, which is most suitable for the cyclization.

It is apparent that, independently of the calculation method and parameters, the system with the Cp rings is the most trans favoring, and the system with the Cp* rings is the most cis favoring, while the bare system is intermediate and slightly trans favoring. Strictly analogous results have been obtained with the Zr–C1 distance set equal to 2.24 or 2.26 Å, for the systems with the Cp or Cp* rings, respectively (average of the values observed in cationic zirconocene complexes).[36]

Figure 7A reports the energy difference between the minimum energy cis and trans intermediates $E_{cis} - E_{trans}$, as a function of the ring center–metal–ring center angle ϕ in the ranges of ±5° around the values assumed in the previously reported calculations. It is apparent that, according to the calculations, the model with two Cp is always trans specific, while the model with two Cp* is always cis specific.

Figure 7B reports the $E_{cis} - E_{trans}$ as a function of the out-of-plane bending angle γ and of the hydrogens (methyl groups) of the Cp (Cp*) rings in the range 0–4° for the Cp_2Zr system and in the range ±4° around the assumed value of 10° for the $Cp_2{}^*Zr$ system. The figure shows that for the system with the Cp* rings the value assumed by this angle largely modifies the numerical value of the energy differences (and hence the selectivity of the model). However, again, the model with two Cp rings is always trans-specific, while the model with two Cp* rings is always cis-specific.

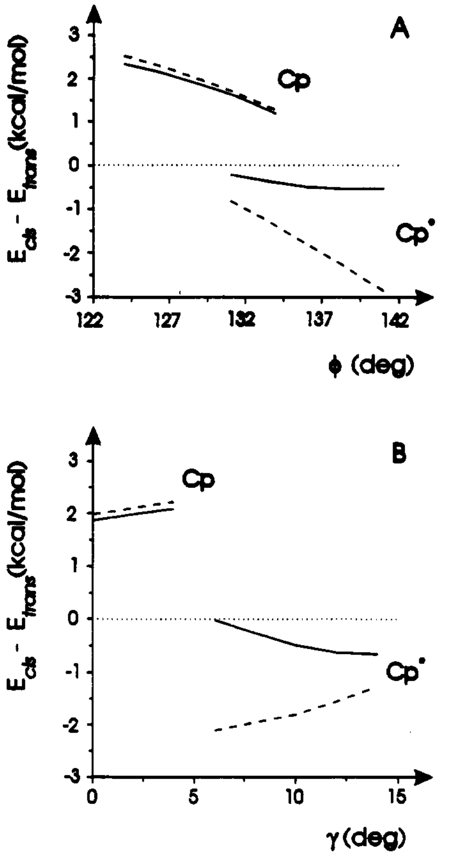


Figure 7. Energy difference between the cis and the trans minimum energy conformations as a function of the ring center–metal–ring center angle ϕ (A) and of the out-of-plane bending angle of the cyclopentadienyl substituents γ (B) for the model with two Cp or two Cp* rings. Continuous lines correspond to results without constraints on θ_0; dashed lines correspond to results with $-20° < \theta_0 < +20°$.

Experimental Results. A series of experimental investigations were carried out to compare the trends predicted from the calculations. These results are presented in Table I for a variety of cyclopentadienyl derivatives. The experimentally observed trends are generally in good agreement with the selectivities predicted from the theoretical model.

The Cp derivatives exhibit a trans selectivity and the Cp* derivatives a cis selectivity. The monocyclopentadienyl derivatives are intermediate in behavior; the $CpZrCl_3$ precursor shows almost the same trans selectivity as that of Cp_2ZrCl_2 whereas the Cp^*ZrCl_3 precursor shows almost no selectivity.

A simplistic application of the model to interpret possible changes in selectivity when a $Me_2Si<$ group bridges the two aromatic ligands fails in the case of the Cp derivatives. The calculations presented in Figure 7 would predict that, for the Cp derivatives, the trans selectivity should increase as the Cp–M–Cp angle ϕ decreases. In contrast, the Cp_2ZrCl_2 precursor ($\phi \approx 130°$)[37f] shows a higher trans selectivity than the $Me_2SiCp_2ZrCl_2$ precursor ($\phi \approx 125°$).[46] In this case, the increased rigidity imparted by the silicon bridge may not be adequately accounted for in a simple extrapolation of the present model. Nevertheless, for the Cp* derivatives, the experimental selectivities are in agreement with the calculations as the $Me_2Si(Me_4Cp)_2ZrCl_2$ precursor (possibly $\phi \approx 125°$) exhibits a lower cis selectivity than the $Cp^*{}_2ZrCl_2$ precursor ($\phi \approx 135°$ for $Cp^*{}_2ZrCH_2Si(CH_3)_3$[36a]).

Conclusions

The above analyses, based on the nonbonded interactions in model sites for the cyclization step of the 1,5-hexadiene cyclopolymerization (intermediate I of Scheme I), indicate the presence of several minimum energy conformations. In particular, the analysis with the (*R*)-2-methyl-5-hexenyl group on a bare metal atom suggests that the trans-chair conformation, that is, the intermediate resembling a cyclohexane chair in which the substituent (growing chain) occupies a pseudoequatorial position, is slightly favored. The presence of Cp rings tends to disfavor the most stable cis conformations, that is, the cis-chair and the cis-boat-1 conformations (in which the polymeryl group occupies a pseudoaxial position), and as a consequence tends to increase the trans specificity with respect to the "bare" model. In the presence of the Cp* rings the steric interactions of the ligands tend to disfavor the trans-chair with respect to the cis-twist conformation which becomes the most stable. As a consequence the model becomes cis-specific.

These results are in a qualitative agreement with the available experimental results.

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