

Possible model for chain end control of stereoregularity in the isospecific homogeneous Ziegler–Natta polymerization

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A conformational study of a possible model for chain end control in the homogeneous isotactic specific Ziegler–Natta polymerization is presented. The model site consists of a complex with two ligands (olefin and growing chain) besides two cyclopentadienyl ligands. The geometries corresponding to the located energy minima are very similar to those of the chiral model previously proposed by us for the site control in the homogeneous isospecific Ziegler–Natta polymerization. In this case the diastereoisomeric intermediates for isotactic and syndiotactic propagation are energetically similar but, according to our assumptions, the insertion path for the propene would be easier in the case of isotactic propagation.

(Keywords: homogeneous Ziegler–Natta polymerization; isospecificity; chain end control; catalytic model; conformational analysis, insertion mechanism)

INTRODUCTION

The isospecific polymerization of 1-alkenes in the presence of homogeneous catalysts based on the group 4a metallocene/methylalumoxane systems, has been recently reported^{1–3}. In particular, for catalysts based on stereorigid chiral metallocenes (highly isotactic specific), a chiral site control of the stereospecificity was pointed out^{1,2,4}, while for the catalyst based on the bis(cyclopentadienyl) titanium diphenyl (partially isotactic specific) the stereochemistry of the monomer insertion is controlled by the configuration of the last tertiary carbon atom of the growing chain (chain end controlled)^{1,2,5}.

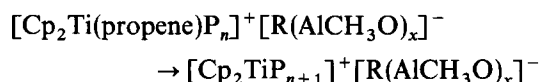
The stereospecific behaviour of this system is strongly dependent on the considered monomer. In particular, the probability of isotactic stereochemical dyads is close to 0.9 for propene, to 0.6 for butene and to 0.5 (almost completely stereo-irregular) for 4-methyl-pentene^{5,6}.

In previous papers conformational studies for a possible chiral model which gives site control in the homogeneous isospecific Ziegler–Natta polymerization have been presented^{7,8}. In this paper an achiral model which could account for the chain end control in the isospecific homogeneous polymerization is presented.

CATALYTIC MODEL, NOTATION AND COMPUTATION METHOD

The model catalytic site assumed by us consists of a complex with two ligands (olefin and growing chain) besides two cyclopentadienyl ligands. As discussed in previous papers^{7,8} as well as in a recent review⁹, this could be possible, for instance, if the active catalyst has an

ion-pair nature:



where Cp = cyclopentadienyl group and P = polymeric chain.

The geometry of the site was constructed by analogy to the crystal structure of the bis(cyclopentadienyl) titanium dichloride complex¹⁰, by substituting (at appropriate distances, see *Table 1*) the two chlorine atoms with the first carbon atom of the growing chain and with the centre of the double bond of the coordinated olefin. Since in the crystal structure an almost perfect local C₂ symmetry axis is present, the coordinates of the atoms of the cyclopentadienyl ligands have been averaged in such a way as to provide a perfect local C₂ symmetry axis in the catalytic model site. Moreover a perfect C₅ symmetry for the two cyclopentadienyl groups has been imposed.

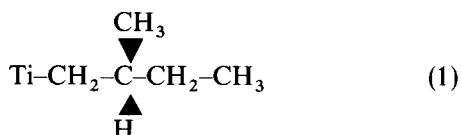
Table 1 Geometrical parameters assumed for our models

	Bond lengths Å
Ti–C (alkyl)	2.15
Ti–C (olefin)	2.16
Ti–Cp centre	2.06
C=C (olefin)	1.438
C–C (ring)	1.40
=C–H (olefin)	0.985
=C–C (olefin)	1.50
	Bond angles
Cp–Ti–Cp	131°
Ti–C–C	118.6°
Ti–C–H	109.0°
C=C–H	114.5°
C=C–C	114.5°
H–C(olefin)–H	119.2°
H–C(olefin)–C	119.2°

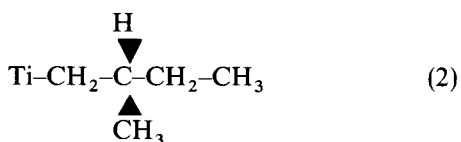
The essential features of the reaction mechanism that provide the general framework of our studies have been previously discussed⁷ and are not reported here. We only recall that, upon coordination, a prochiral olefin such as propene may give rise to non-superposable *re* and *si* coordinations¹¹. The formation of an isotactic polymer, according to the assumed mechanism, implies that successive (constantly *cis*) monomer insertions correspond to coordinations of equal chirality.

In the model for the growing chain coordinated to the titanium (Ti), two different alkyl groups are considered in our computations: the ethyl group and the 2-methyl-butyl group.

For the longer alkyl group the chirality of the tertiary carbon atom can be R or S. In particular the R chirality



could be obtained by a *cis* primary insertion of a *si*-coordinated propene into an ethyl-Ti bond and the S chirality



could be obtained by a *cis* primary insertion of a *re*-coordinated propene. For this reason, models (1) and (2) will be named hereafter *si*-ending model chain (or more briefly *si*-chain) and *re*-ending model chain (or more briefly *re*-chain), respectively. Without loss of generality, our calculations refer to a *si*-ending model chain.

As far as the orientation of the polymeric chain is concerned, and also assumed for the previous catalytic models^{7,12,13}, the second chain carbon atom should be as near as possible to the olefin compatibility with steric repulsions, in order that the insertion occurs through a 'least nuclear motion' process¹⁴⁻¹⁶. In particular, conformations in which the second carbon atom of the growing chain is on the opposite side ($\vartheta_1 \simeq 180^\circ$, instead of $|\vartheta_1| \simeq 60-90^\circ$ (see later) with respect to the olefin are considered not suitable for insertion.

The main internal coordinates, which have been varied in our calculations are sketched in Figure 1: the angle α between the local C_2 axis and the axis connecting the metal and the centre of the double bond, the angle β between the local C_2 axis and the metal-carbon bond of the growing chain (the α and β angles have been both confined in the plane defined by the Cl-Ti-Cl bonds in the crystal structure of ref. 9); the dihedral angle ϑ_0 associated with the rotation of the olefin around the axis connecting the metal to the centre of the double bond; the internal rotation angles of the growing chain ($\vartheta_1, \vartheta_2, \vartheta_3 \dots$); the dihedral angles σ_1 and σ_2 which rotate the cyclopentadienyl groups around the local C_5 symmetry axes, which have, of course, a period of 72° .

Near to $\vartheta_0 \simeq 0^\circ$ the propene is oriented in a way suitable for primary insertion, while $\vartheta_0 \simeq 180^\circ$ corresponds to an orientation suitable for secondary insertion. $\vartheta_1 = 0^\circ$ corresponds to the metal-C-C(chain) moiety *cis* to the olefin while the conformation with $\vartheta_1 = 180^\circ$ presents the second carbon atom of the growing chain on the opposite

side with respect to the olefin. The dihedral angles $\vartheta_2, \vartheta_3 \dots$ are measured according to the IUPAC rules¹⁷. For our purposes it is convenient to refer ϑ_2 to the H atom bound to the tertiary carbon atom. In that case the dihedral angle will be explicitly indicated as ϑ_{2H} .

The main structural parameters assumed in our computations are reported in Table 1; more details are given in ref. 7.

The reported energy maps refer to fixed values for α, β ($\alpha = 39^\circ, \beta = 55^\circ$) which minimize the energy for the case of coordination of the olefin and of the ethyl group. These α and β values are very close to those found in the crystal structure of the analogous bis(cyclopentadienyl)ethyl-(ethylene) niobium complex¹⁸. Different choices (i.e. $\alpha = \beta = 46^\circ$) do change the numerical results but not the general conclusions that can be drawn.

The method of calculation of the non-bonded potential energy has been previously described¹⁹. The results reported in this paper have been obtained using the potential functions parameters proposed by Flory²⁰, treating the CH_2 and CH_3 groups as well as the CH groups of the cyclopentadienyl as spherical domains²¹. In order to test the dependence of our results on the particular choice of these parameters, the computations were also performed avoiding the assumption of spherical domains and/or by using the parameters reported by Hopfinger²². Even if some differences are observed (non-bonded energies are generally smaller when the Hopfinger's parameters are used), the overall trends and the location of the minima remain substantially unchanged.

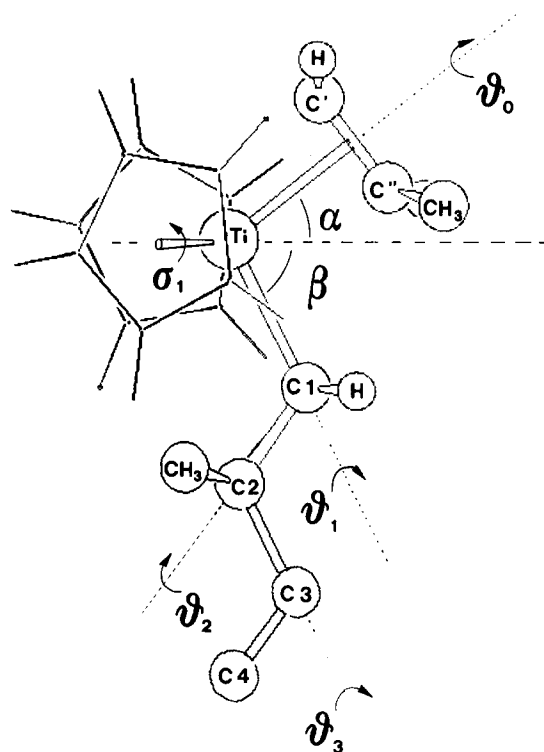


Figure 1 The model catalytic site used in our computations comprises two cyclopentadienyl groups (related by a local C_2 axis, dashed) a propene molecule (shown for the *re*-coordination) and an alkyl group simulating a growing chain. The main internal coordinates which have been varied in the present calculations are indicated. The conformation depicted corresponds to $\vartheta_0 = 0^\circ, \vartheta_1 = \vartheta_2 = \vartheta_3 = 180^\circ$. The atom labels used in the text, as well as in the following figures, are also specified

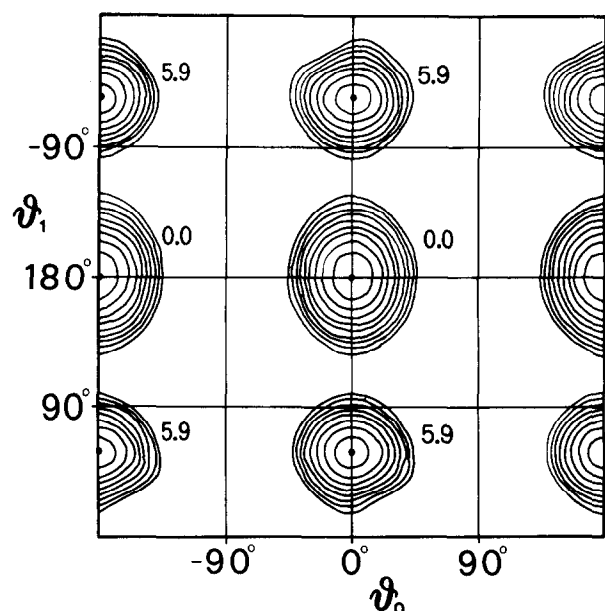


Figure 2 Map $E(\vartheta_0, \vartheta_1)$ for the catalytic model with an ethene monomer and an ethyl group coordinated to the metal. The isoenergetic curves correspond to 5, 10, 15, 20, 25, 30, 35, 40 and 45 kcal/mol

For ϑ_{2H} and ϑ_3 intrinsic torsional potentials of the form

$$E(\vartheta_i) = E_0/2[1 + \cos(3\vartheta_i)]$$

with $E_0 = 2.8$ kcal/mol, are included. The torsional potentials for the rotations ϑ_0 and ϑ_1 are not known and therefore not included. While we expect such energy contribution to be low for ϑ_1 , this may be not true for ϑ_0 . Because deep energy minima for the non-bonded interactions are found only for $\vartheta_0 \approx 0^\circ$, the inclusion of a torsional potential for ϑ_0 would not change our conclusions.

We are aware of the fact that the numerical results cannot be trusted as such, especially in energy regions far from the minima, because of inaptitude of the energy functions in such regions and because of the simplifying assumption of constancy (instead of near-constancy) of most internal coordinates. We believe, however, that all the results that we present can be trusted in a semiquantitative way.

RESULTS AND DISCUSSION

As for the previously proposed models^{7,12,13}, we have assumed that the propagation reaction occurs through a two-stage mechanism: coordination of the olefin on a deficient site and its subsequent insertion into the metal-polymer bond.

In a first section, conformational energy minima for various possible diastereoisomeric Ti complexes are located and those closer to possible transition states are selected. In a second section, starting from the energy minima located in the first section, models corresponding to other significant points of the reaction paths are considered. On the basis of a comparison of these models, an evaluation of the diastereoisomeric situations more suitable for chain propagation is attempted.

Minimum energy conformations for possible diastereoisomeric complexes

Let us first consider a simplified model with an ethene

monomer and an ethyl group coordinated to the metal. The corresponding energy map $E(\vartheta_0, \vartheta_1)$ in which the energies are minimized with respect to σ_1 and σ_2 is shown in Figure 2.

As for the analogous case of the chiral model site⁷, deep energy minima are found only for the region with $\vartheta_0 \approx 0^\circ$ (or the equivalent region with $\vartheta_0 \approx 180^\circ$) and for $\vartheta_1 \approx \pm 60^\circ$ or 180° . The energy minima at $\vartheta_1 \approx +60^\circ$ and $\vartheta_1 \approx -60^\circ$ (energetically equivalent due to the absence of chirality) are higher than the minimum at $\vartheta_1 \approx 180^\circ$.

Analogous maps $E(\vartheta_0, \vartheta_1)$ for the *si* and *re* coordinations of propene in the presence of an ethyl group are reported in Figures 3a and 3b, respectively. As for the chiral site described in ref. 7, the minima at $\vartheta_0 \approx 0^\circ$ (orientation suitable for primary insertion) are deeper than the minima at $\vartheta_0 \approx 180^\circ$ (orientation suitable for the secondary insertion). Moreover, besides the lowest minimum at $\vartheta_1 \approx 180^\circ$, for the *si*-coordination of the

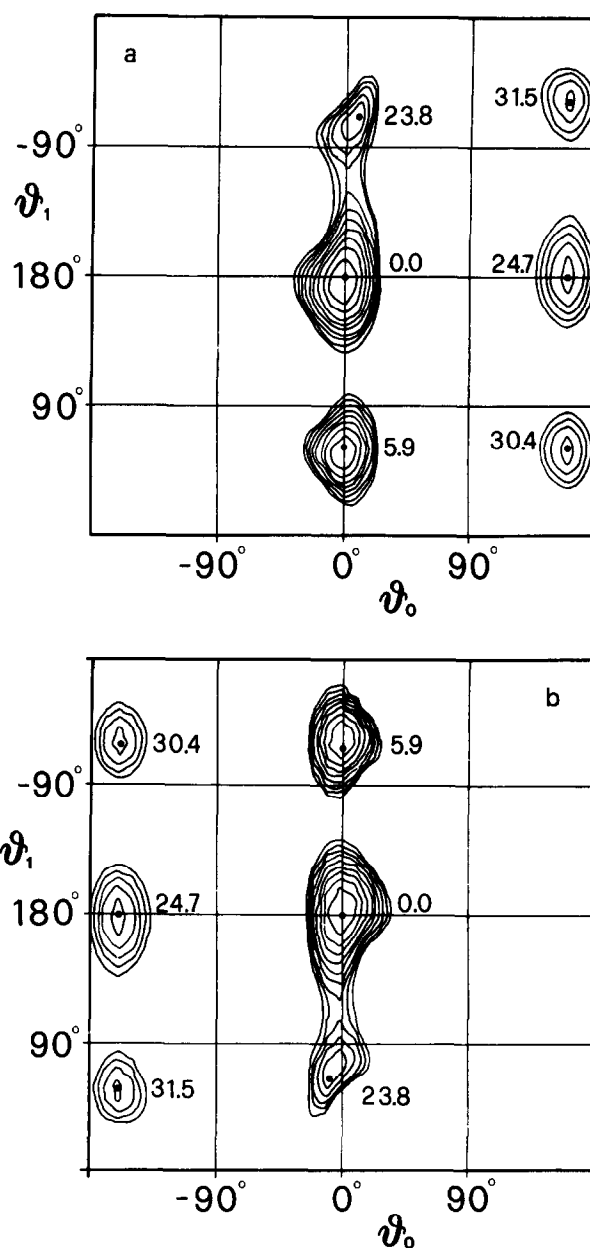


Figure 3 Maps $E(\vartheta_0, \vartheta_1)$ for the models with an ethyl group and an *si* (a) or an *re* (b) propene coordinated. The isoenergetic curves correspond to 5, 10, 15, 20, 25, 30, 35, 40 and 45 kcal/mol

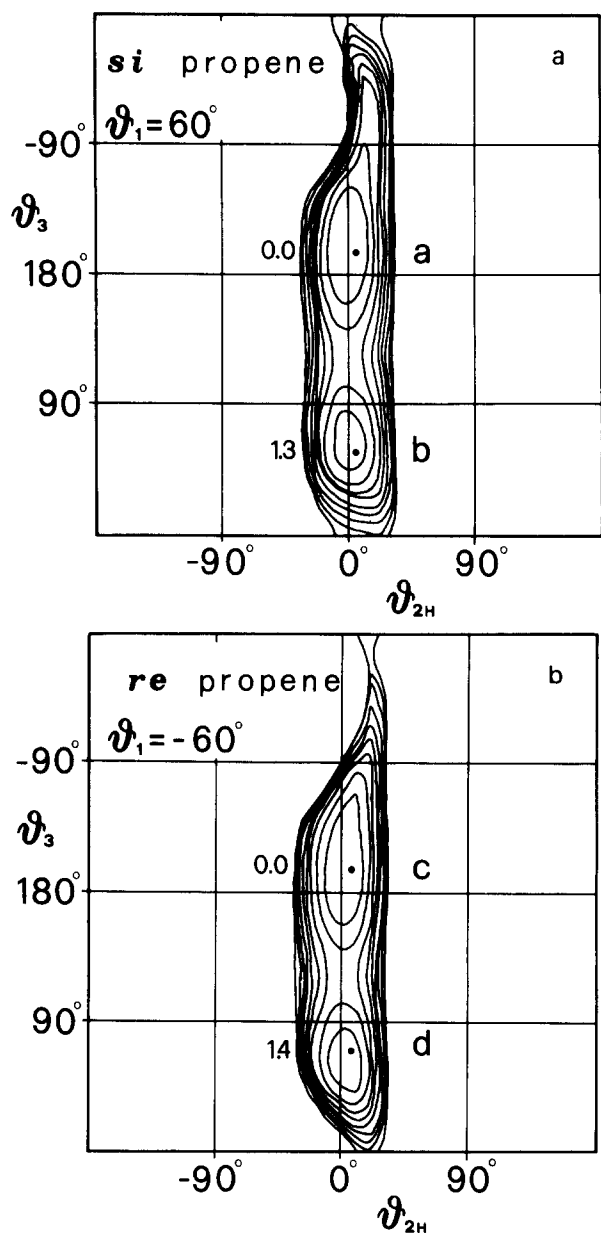


Figure 4 Maps $E(\vartheta_{2H}, \vartheta_3)$ for the models with the alkyl group as in the scheme 1 (*si*-chain) and an *si* (a) or an *re* (b) propene coordinated. The fixed ϑ_0 and ϑ_1 values ($\vartheta_0 = 0^\circ$; $\vartheta_1 = +60^\circ$ for the *si* monomer and $\vartheta_1 = -60^\circ$ for the *re* monomer) correspond to the energy minima of Figure 3. The isoenergetic curves correspond to 5, 10, 15, 20, 25, 30, 35, 40 and 45 kcal/mol. For easier identification, the minima of the maps are labelled (a, b, c, d)

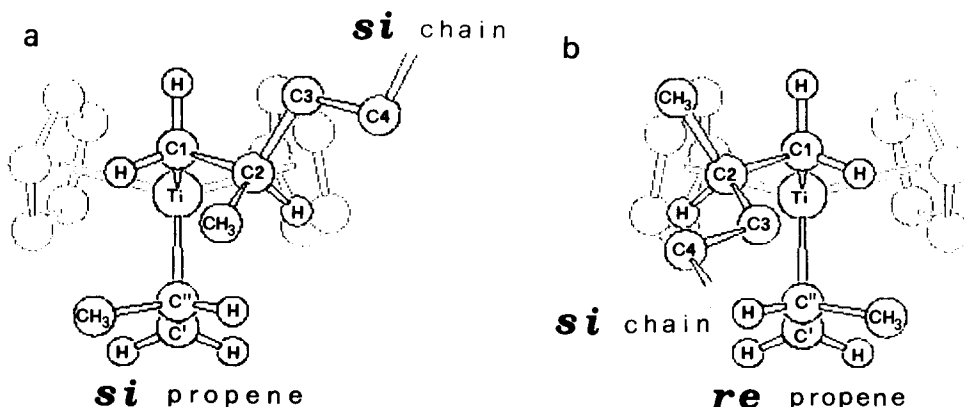


Figure 5 The two diastereoisomeric situations corresponding to the energy minima a and c of Figure 4. For the model corresponding to subsequent isospecific propagation (a) the chain (atoms C3, C4...) points away from the olefin, while for the model corresponding to subsequent syndiospecific propagation (b) it points toward the olefin

monomer a deep minimum is present only for $\vartheta_1 \approx +60^\circ$ (for the *re*-coordination at $\vartheta_1 \approx -60^\circ$).

The only element of chirality of this complex arises from the coordination of the prochiral olefin, as a consequence the situations (*si*-propene, $\vartheta_1 \approx +60^\circ$ and *re*-propene, $\vartheta_1 \approx -60^\circ$) are enantiomeric and hence energetically equivalent.

Diastereoisomeric, rather than enantiomeric, situations are instead obtained by introducing a second element of chirality: a tertiary carbon atom in the growing chain, as for the alkyl groups of schemes (1) and (2).

For the case of a *si*-ending chain (scheme 1), maps $E(\vartheta_{2H}, \vartheta_3)$, for the *si* and *re* coordinations of propene, are reported in Figures 4a and 4b, respectively. For the construction of the maps ϑ_0 was fixed equal to zero and ϑ_1 equal to $+60^\circ$ for *si*-coordination and to -60° for *re*-coordination because the minima with $\vartheta_1 \approx 180^\circ$, as discussed in the previous section, were considered not to be suitable for the insertion. All energy minima, both for the *si* and *re* coordinations of propene, are located in regions with $\vartheta_{2H} \approx 0^\circ$. Moreover, for corresponding ϑ_3 values, the minima for *si*-coordination (a and c in Figure 4a) are energetically very close to the minima for *re*-coordination (c and d in Figure 4b).

The two diastereoisomeric situations corresponding to the energy minima at $\vartheta_{2H} \approx 0^\circ$ and $\vartheta_3 \approx 180^\circ$, with $\vartheta_1 = +60^\circ$ for *si*-propene and $\vartheta_1 = -60^\circ$ for *re*-propene (the minima a and c in Figure 4), are sketched in Figures 5a and 5b, respectively. The two situations are clearly different, in fact, being $\vartheta_{2H} \approx 0^\circ$, the conformation with $\vartheta_1 = +60^\circ$ (Figure 5a), which corresponds to an isotactic propagation, has a methyl group pointing toward the olefin while the conformation with $\vartheta_1 = -60^\circ$ (Figure 5b), which corresponds to a syndiotactic propagation, points the rest of the chain toward the olefin.

This difference suggests that although diastereoisomeric situations like the two of Figure 5, have almost identical energies, the enantioselectivity could be associated with different energies at subsequent points of the insertion path.

Mechanism of monomer insertion

Diastereoisomeric situations like those corresponding to the energy minima of Figures 4a and 4b may be taken as starting situations for possible reaction paths for monomer insertion.

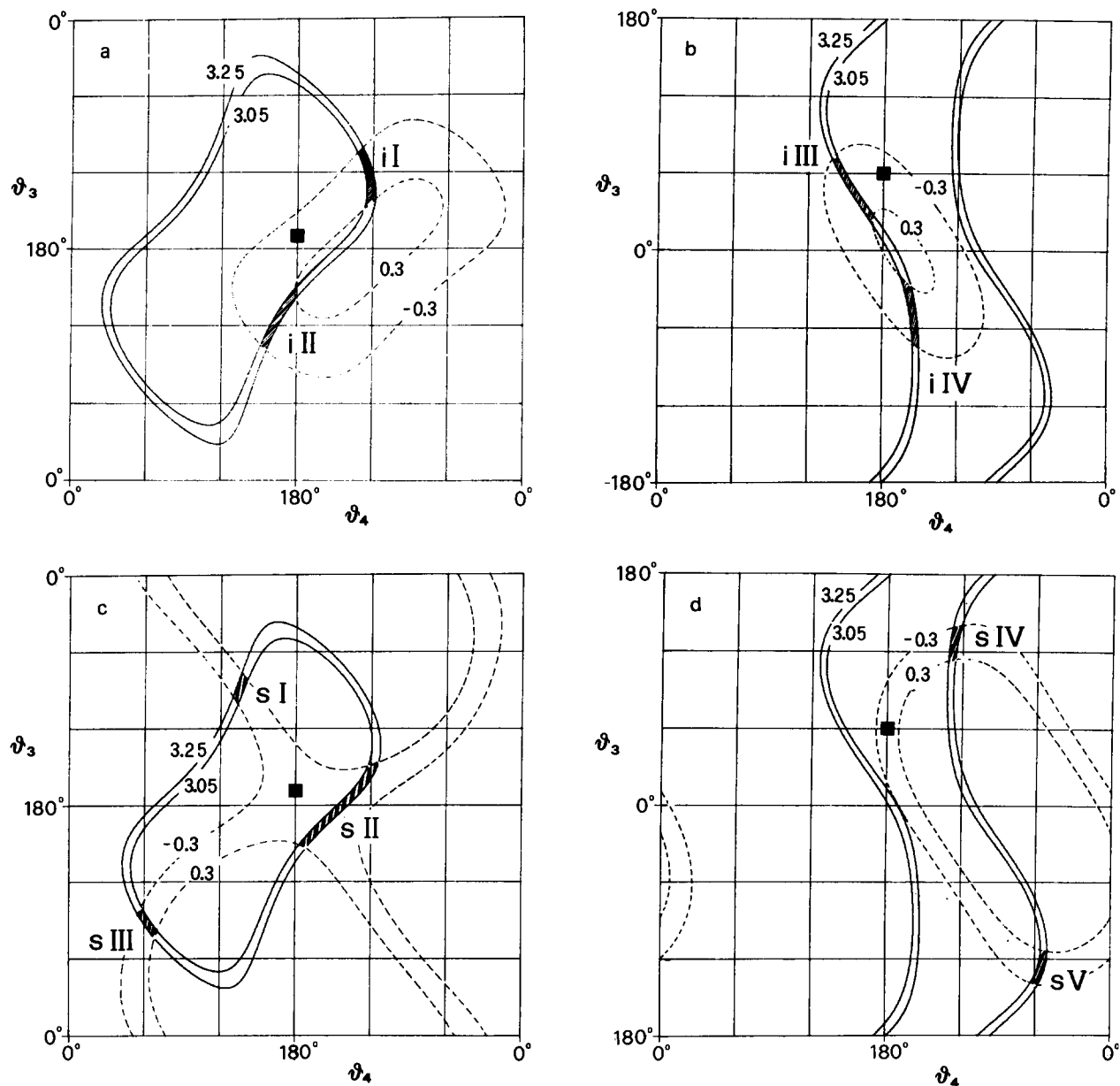


Figure 6 Maps $z(\vartheta_3, \vartheta_4)$ (dashed lines) and $d(\vartheta_3, \vartheta_4)$ (full lines) for the starting models corresponding to the minima a (a), b (b), c (c) and d (d) of Figure 4. The conformational regions for which z is in the range $-0.3, +0.3 \text{ \AA}$ and d is in the range $3.05, 3.25 \text{ \AA}$ corresponding to possible 'prefinal' models (see text) are dashed and labelled. The labels *i* and *s* stand for isotactic and syndiotactic propagation, respectively. The black squares indicate the ϑ_3 and ϑ_4 values of the starting models

According to the viewpoint of Hine^{15,16} and Cossee¹⁴, feasible mechanisms should fulfil the condition that in the rate-determining step the positions of the nuclei before and after the rearrangement should resemble each other as closely as possible. Following this general principle and with the purpose of simplifying our calculations, let us assume that in the transition state for the reaction of monomer insertion the positions of the nuclei of the growing chain, with the exception of a few atoms close to the metal, should not change. We also assume that the two carbon atoms of the inserting olefin (C' and C'') and the first carbon atom of the chain (C1) should roughly remain in the same plane (π) which they define in the starting models.

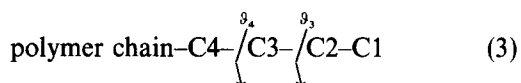
This latter assumption is also based on the electronic considerations presented by Hoffmann and coworkers^{23,24} for the insertion mechanism of coordinated olefins in cyclopentadienyl metal complexes and it was already

made in previous studies on the mechanism of Ziegler-Natta polymerization^{14,25,26}.

Because the structures of the transition states are highly hypothetical, we confined our analysis to the study (for different starting situations) of the geometrical feasibility of prefinal structures. We consider as 'prefinal' structures, those structures in which the monomer insertion is already completed but the assumptions discussed would be still valid (that is those structures, closest to the transition states, where conformational rearrangements of the chain did not yet occur).

The number of possible 'prefinal' models becomes very high when the movement, in the rate determining step, of many chain atoms is allowed. For this reason in the following we will consider only 'prefinal' models which present the chain atoms C3, C4, C5 ..., in the same position as in the starting models (corresponding to a very rigid interpretation of the first assumption). These are

constructed by changing the dihedral angles ϑ_3 and ϑ_4 in the starting models



which move only the backbone carbon atoms C2 and C1.

This assumption is rather drastic but convenient for the purpose indicated above and it is justifiable in so far as mechanisms which move the whole growing chain in the rate determining step, are not acceptable. This hypothesis is possibly acceptable for the case of propene polymerization where the bulkiness of the side substituent (a methyl group) is small with respect to the local bulkiness of the chain, but is, of course, less acceptable for the case of bulkier side substituents (as for the butene or 4-methyl-pentene polymerization).

Let us define $d(\vartheta_3, \vartheta_4)$ the distance of the atom C1 from the titanium atom and $z(\vartheta_3, \vartheta_4)$ the distance of C1 from the plane π .

In the 'prefinal' models the second assumption is satisfied if $z=0$ and $d=3.15 \text{ \AA}$ (the latter condition follows also from the assumption that bond lengths and

bond angles for the new chain:



are equal to those of the atoms with similar constitution in the starting chain (see Table 1)).

In order to avoid any possible confusion, the dihedral angles in the starting models and in the 'prefinal' models will be labelled with different symbols. In particular, for the 'prefinal' models the dihedral angle defined by the atoms C3, C2, C1, C' will be named ϑ'' , and the dihedral angles defined by the atoms C2, C1, C'', C' will be named ϑ' .

Conformational regions for which the distance $d(\vartheta_3, \vartheta_4)$ is in the range (3.05, 3.24 Å) and the distance $z(\vartheta_3, \vartheta_4)$ is in the range (-0.3, +0.3 Å) are shown in Figure 6. The maps A, B, C and D refer to starting models corresponding to the four minima a, b, c and d of Figure 4. Maps A and B correspond to the isotactic propagation while maps C and D correspond to the syndiotactic propagation.

The conformational regions in which both requirements are satisfied are dashed and labelled with a letter and a roman number in Figure 6 for easier identification in the subsequent analysis.

The models corresponding to these regions present, by construction, all bond lengths and bond angles typical of a polyolefinic chain, except the bond angle C''-C1-C2(τ) which is not prefixed and can also assume unrealistic values in the models.

The values of the bond angle τ and of two relevant dihedral angles (ϑ' , ϑ'') for the models corresponding to the central points of the labelled regions are, for instance, reported in Table 2. It is immediately apparent that in all cases the values of τ are more suitable (i.e. closer to nearly tetrahedral values) for the models corresponding to an isotactic propagation than for the models corresponding to a syndiotactic propagation. For the models corresponding to isotactic propagation τ values close to 113° can be obtained by simply considering different points in

Table 2 Values of the ensuing bond angle τ and dihedral angles ϑ' and ϑ'' (see text) for the models corresponding to the central points of the conformational regions labelled in Figure 6

	τ	ϑ'	ϑ''
i I	132°	-138°	104°
i II	98°	-61°	-153°
i III	100°	-102°	155°
i IV	110°	-50°	-34°
s I	143°	44°	163°
s II	60°	131°	11°
s III	167°	120°	71°
s IV	139°	0.7°	162°
s V	160°	-15°	-14°

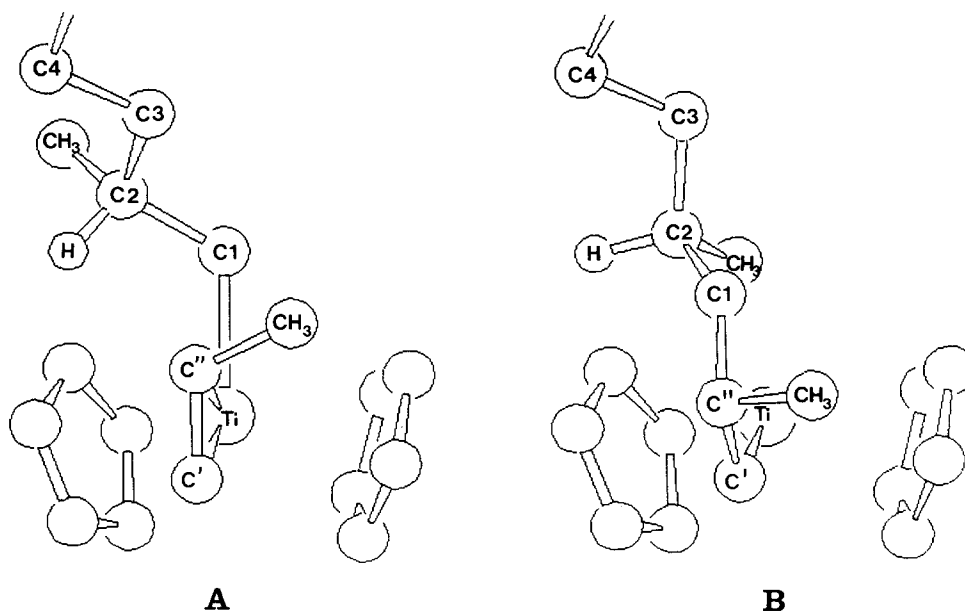


Figure 7 A possible mechanism for isotactic propagation with fixed positions for C3, C4 and the following chain atoms. (a) Starting model corresponding to the energy minimum a of Figure 4. (Figure 5a shows a different view); (b) the 'prefinal' model corresponding to the central point of the conformational region ii of Figure 6a.

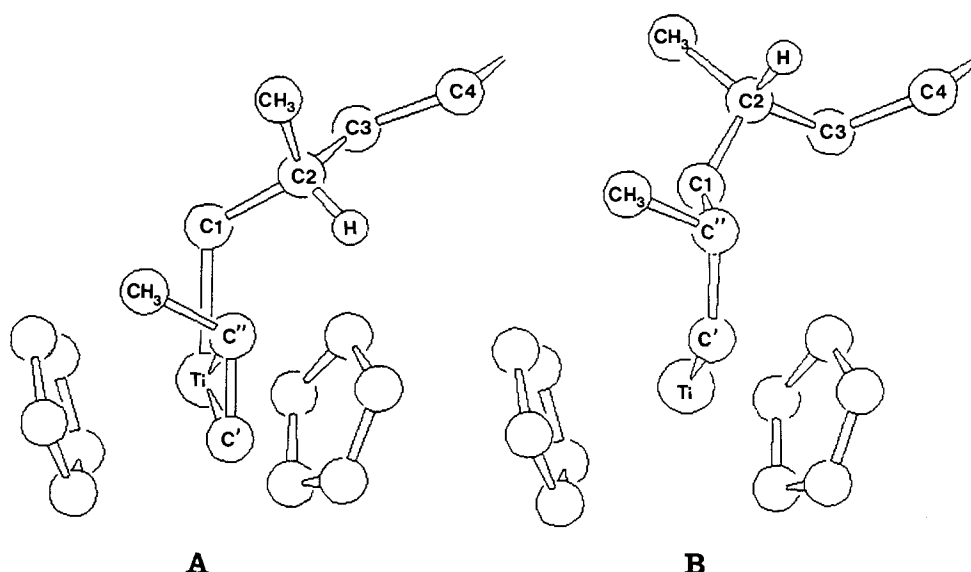


Figure 8 A possible path for syndiotactic propagation which assumes fixed positions for C3, C4 and the following chain atoms. (a) Starting model corresponding to the energy minimum c in Figure 4 (Figure 5b shows a different view); (b) the 'prefinal' model corresponding to the central point of the conformational region sI of Figure 6c

the dashed regions rather than the central point. The model corresponding to the situation II is, for instance, shown in Figure 7 together with the corresponding starting model.

For some of the models corresponding to syndiotactic propagation (sII, sIII, sV) the τ values are highly unrealistic and no significant adjustment seems to be possible. Moreover for some models (sII, sIV) the presence of high energy nearly *cis* conformations is indicated in Table 2.

The 'prefinal' model for syndiotactic propagation which seems less unrealistic on the basis of the data of Table 2 (sI) is shown in Figure 8 together with the corresponding starting model. Under the assumed restrictions, it brings the methyl group, bonded to the C2 atoms, close to the metal and hence it appears also to correspond to a higher energy pathway.

An analogous analysis for starting situations presenting $\vartheta_1 \approx 180^\circ$ generates only highly unrealistic 'prefinal' models (e.g. τ values of $\approx 45^\circ$). This supports the hypotheses that conformations with $\vartheta_1 \approx 180^\circ$ are not suitable for monomer insertion, as assumed in the previous section as well as in previous papers^{7,12-14}.

CONCLUSIONS

In summary, we have made calculations of the non-bonded energy for various hypothetical intermediates in the polymerization of propene with achiral bis(cyclopentadienyl) titanium diphenyl. This is a continuation of our previous work on similar, but chiral, systems^{7,8}.

According to our assumptions, although possible diastereoisomeric intermediates for isotactic or syndiotactic propagation are energetically similar, reasonable insertion mechanisms which are lower in energy could occur for the isotactic propagation in the case of the polymerization of propene. Suitable insertion mechanisms for the syndiotactic propagation seem to require that the positions of a higher number of nuclei of the growing chain are changed in the rate-determining step. This could

correspond to the occurrence of internal energy as well as of entropy differences between the transition states, which could give rise to the observed preference for the chain end controlled isotactic propagation.

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