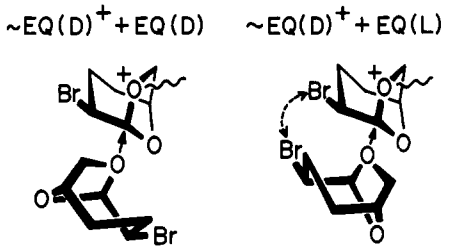
Scheme III
Possible Mode of the Enantiomer Selection at the Growing Chain End in the Polymerization of 4(e)-BrDBO (EQ)



ion of the D-enantiomeric unit in such a way that the dipole moments of the two tetrahydropyran rings are oriented in the opposite direction, there is relatively small electronic repulsion between the bromine atom of the incoming monomer and the lone pair orbital of the oxygen atom of the terminal unit. On the other hand, when the L enantiomer attacks the oxonium ion of the D-enantiomeric unit, there occurs repulsion between the bromine atom of the incoming monomer and the bromine atom of the terminal unit. When the monomer approaches the active center in such a way as to avoid the repulsion, alternative electronic repulsion between the bromine atom of the incoming monomer and the lone pair orbital of the oxygen atom of the terminal unit becomes unavoidable. Therefore, the propagation between the monomer and the terminal unit of the same chirality should occur more readily than the propagation between the monomer and the terminal unit of the opposite chirality, thus producing a stereoregular polymer that is rich in isotactic dyad.

In conclusion, the polymerization of 4(e)-BrDBO proceeds through an oxonium ion intermediate at low temperatures to give stereoregular polymers consisting entirely of α-form units and being rich in isotactic sequences of their D,L-enantiomeric units. In contrast, the polymerization of stereoisomer mixtures of 4(a)-BrDBO and 4(e)-BrDBO gives rise to stereoirregular polymers composed of both α-form and β-form units even at −90 °C due to the participation of the bromonium ion intermediate of a 4(a)-BrDBO terminal unit in the propagation.

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Steric Control in the First Step of the Isospecific Ziegler–Natta Polymerization of Propene

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ABSTRACT: Our recent model of the catalytic site in heterogeneous Ziegler–Natta catalysts has been employed to study the first step in the polymerization of propene when the alkylating group is CH_3, C_2H_5, or i-C_4H_9. The computations indicate, in agreement with experimental data obtained by Zambelli and co-workers, that the placement of the first group is stereoirregular in the case of CH_3, but becomes partially stereospecific in the case of C_2H_5 and is totally isospecific in the case of i-C_4H_9. This trend is due to the fixed chiral orientation of the first C–C bond of alkyl groups bulkier than CH_3 induced by steric interactions with the local environment of the catalytic site. That orientation, in fact, determines different nonbonded interactions depending on the presented monomer face.

Introduction

In previous papers[1-3] we have studied, through extensive computations the role played by nonbonded interactions at model catalytic sites in determining the stereospecificity and regiospecificity of heterogeneous Ziegler–Natta catalysts. We concluded that, in the framework of the model, the isospecificity of the reaction is mainly due to the fixed chiral orientation of the first C–C bond of the reactive end of the growing polymeric chain. Although some specific features of the isotactic steric control depend on the

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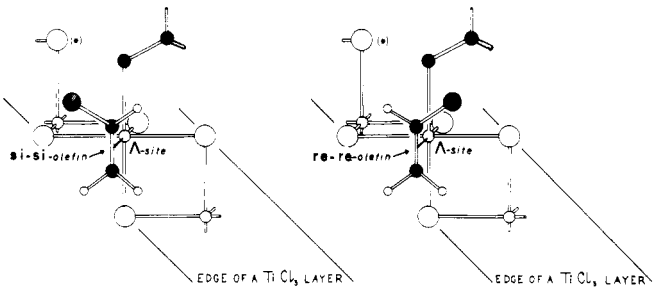

Figure 1. Schematic drawing of the local environment of a catalytic site located at a relief of the lateral surface of $TiCl_3$.

particular location of the site on the catalyst surface, the above effect is completely general irrespective of the particular model adopted for the disposition of further apart surface atoms in the neighborhood of the catalytic site.

From an experimental point of view, it has been recently shown by Zambelli and co-workers[4] that in the catalytic system $TiCl_3$–$Al(CH_3)_3$, the placement of the $^{13}CH_3$ end group is stereoirregular, although the stereoregularity of the inner monomer units of the macromolecule remains very high. The placement of the end groups becomes partially isospecific for an alkylation of the catalyst by $Al(C_2H_5)_2Cl$ (i.e., with ethyl groups) and becomes totally isospecific in the case of the isobutyl group. These results were taken as indicating that the isotactic steric control requires (together with the chirality of the active site) the presence of an alkyl ligand bulkier than CH_3, i.e., the presence in the alkyl group of a C–C bond.

On these grounds, we thought it would be interesting to examine by our previous model the first step in the polymerization of propene when the catalytic Ti atom is coordinated to a CH_3, C_2H_5 or isobutyl group. The consideration of small alkyl ligands coordinated at very simple models of catalytic sites (but still retaining the essential characteristics of chirality) would allow a clear-cut analysis of the intrinsic characteristics of the active center and of the modifications induced by bulkier alkyl ligands and/or by the inclusion of further surface atoms.

Model, Structure, and Method

The essential features of the reaction mechanism that provide the general framework of our studies have been previously discussed[1,3] and are not reported here. We only recall that upon coordination a prochiral olefin such as propene may produce nonsuperposable *re–re* or *si–si* coordinations[5,6] (Figure 1). The formation of an isotactic polymer according to the adopted reaction mechanism necessarily implies that for a long series of additions the olefin is coordinated always in the same way. Furthermore, the (octahedral) catalytic site is chiral, and the two enantiomeric situations will be designated by the symbols Λ and Δ.[7]

As far as the structure of the active center is concerned, we have previously suggested that isospecific sites are most probably located at defective sites (e.g., reliefs) of $TiCl_3$ crystals. These sites show, of course, the same catalytic characteristics for all the layered modifications of $TiCl_3$ and are characterized, according to our computations, by a highly stereospecific behavior coupled with lower steric hindrances than on nondefective sites. The local environment of the defective sites is well represented by the simple model shown in Figure 1.[3] Also for this model (as for larger models[1,2]) lower steric repulsions are obtained for a coordination of the monomer in the (less hindered) outward position.

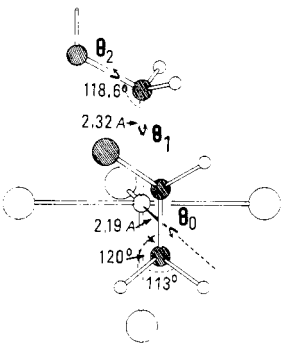

Figure 2. Model showing the coordination of the monomer and the growing chain at the same Ti atom and the dihedral angles that have been varied in our computations. The most relevant bond lengths (in Å) and valence angles (in degrees) are also reported. the values of the dihedral angles are $\vartheta_0 \simeq 0°$, $\vartheta_1 \simeq -90°$, and $\vartheta_2 = 180°$.

The method of calculation and the parameters for the nonbonded potential functions have been previously described[1] and are not reported here. Figure 2 shows the main structural parameters adopted[3,8] and the dihedral angles varied in this study. The dihedral angles are defined so that $\vartheta_0 = 0°$ corresponds to an orientation of the olefin suitable for primary insertion (while at $\vartheta_0 = 180°$ the olefin is oriented in a way suitable for secondary insertion); $\vartheta_1 = 0°$ corresponds to the Ti–C–C(chain) moiety cis to the olefin and $\vartheta_2 = 0°$ corresponds to the second C–C(chain) bond eclipsed with respect to the Ti–C bond. According to the IUPAC rules[9] the dihedral angles ϑ_i increase by counterclockwise rotations (as indicated by arrows in Figure 2) and values in the range $180° < \vartheta_i < 360°$ are taken as $\vartheta_i' = \vartheta_i - 360°$.

For alkyl groups different from CH_3 we shall compare for purposes of illustration only some specific sections $E(\vartheta_0,\vartheta_1)$ of the multidimensional energy surface. The corresponding value of ϑ_2 is reported on the top of the maps (Figures 4 and 5). The conclusions arise, however, from the complete set of computations.

According to Cossee[10] the primary insertion of the monomer through the "least nuclear motion" implies an orientation of the monomer and the chain corresponding to $\vartheta_0 \simeq 0°$ and $\vartheta_1 \simeq \pm 90°$, respectively. We have assumed[1-3] that lower activation energies are obtained for situations (evidenced by squares on some of the reported conformational maps) where the methyl group of the monomer and the second carbon atom of the polymeric chain are on *opposite* sides with respect to the plane defined by the CH_2Ti center of the double bond (i.e., at $\vartheta_1 \simeq +90°$ for a *si–si* coordination and at $\vartheta_1 \simeq -90°$ for a *re–re* coordination). In fact, if the methyl group of the monomer and the second carbon atom of the polymeric chain are on the *same* side with respect to the above-defined plane (i.e., at $\vartheta_1 \simeq -90°$ for a *si–si* coordination and at $\vartheta_1 \simeq +90°$ for a *re–re* coordination of the monomer), they would give rise to a strong repulsive nonbonded interaction during the addition step.

On the bottom of the reported conformational maps we show a schematic drawing of the catalytic site and the structure of the alkyl ligand. The propene is denoted by m (monomer); its *re–re* coordination is labeled m*R* and its *si–si* coordination m*S*. The active Ti atom has always Λ chirality.

Results and Discussion

Figure 3 shows conformational maps for both *re–re* and *si–si* coordination of propene when the coordinated alkyl group is CH_3. The results show, of course, a periodicity

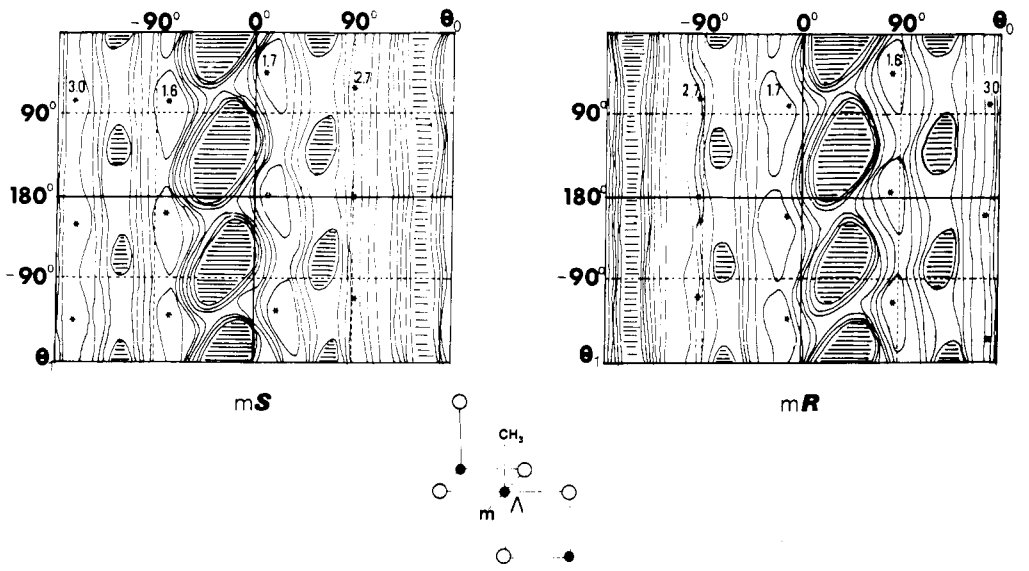

Figure 3. Sections $E(\vartheta_0,\vartheta_1)$ of the multidimensional energy surface for a CH_3 alkylating group. The isoenergetic curves are spaced 2 kcal/mol until 9 kcal/mol.

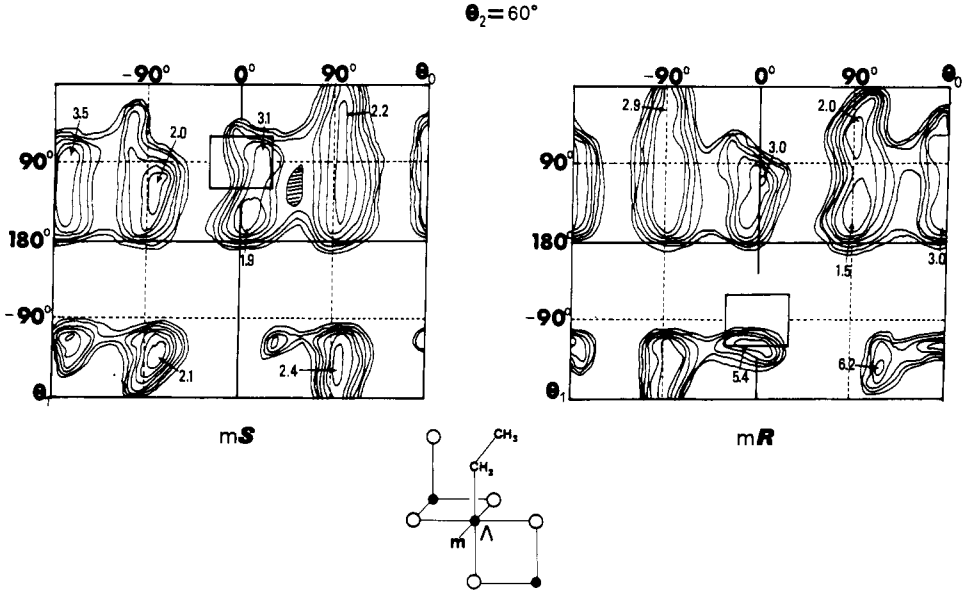

Figure 4. Sections $E(\vartheta_0,\vartheta_1)$ of the multidimensional energy surface for a C_2H_5 alkylating group. The value of ϑ_2 corresponds to an energy minimum and the isoenergetic curves are spaced 2 kcal/mol until 15 kcal/mol.

of 120° on ϑ_1, but we have reported the whole maps in order to facilitate comparison with successive computations.

Similar energy minima are found over the whole range of ϑ_0 for the *re–re* and *si–si* coordinations of the propene, in particular for situations suitable for a primary insertion ($\vartheta_0 \simeq 0°$). As a consequence our model does not show any evidence of stereospecificity in the coordination of the olefin when the alkylating group is CH_3. This first computation is also interesting as the monomer occupies an exposed position and only feels steric interactions with the methyl group and the chlorine atoms directly bonded to the active titanium atom. Figure 3 clearly shows that in this situation the double bond of the olefin tends to assume orientations nearly parallel to the four octahedral bonds normal to the axis Ti center of the double bond. Distinct minima are present for values of ϑ_0 of about 180°, −90°, 0°, and 90°. It is interesting to note that this general pattern is retained also in more complicated models, although each particular minimum is modified by the further interactions added to the catalytic site. A second comment is in order about the differences between these four minima. The adopted parameters for the nonbonded potential functions are such that the steric hindrance of a methyl group is lower than that of a chlorine atom. As a consequence deeper minima are found when the methyl group of propene interacts with the coordinated methyl group (e.g., $\vartheta \simeq 0°$) rather than with a chlorine atom of the surface (e.g., $\vartheta_0 \simeq 180°$). However, the energy difference is so small that an explanation of the high regiospecificity of the heterogeneous polymerization demands different considerations concerning the addition step.[3]

Figure 4 shows typical energy maps for an ethyl ligand. In order to allow a better comparison with the following results concerning the isobutyl group, in this computation the CH_3 group of C_2H_5 retains its structure (i.e., it has not been simulated by a spherical pseudoatom). The four distinct conformational minima of ϑ_0 previously found are again present, but now the presence of the chlorine atom marked with an asterisk in Figure 1 leads to a chiral orientation or the C–C bond of the ethyl group. As a matter of fact positive values of ϑ_1 are always favored. In the

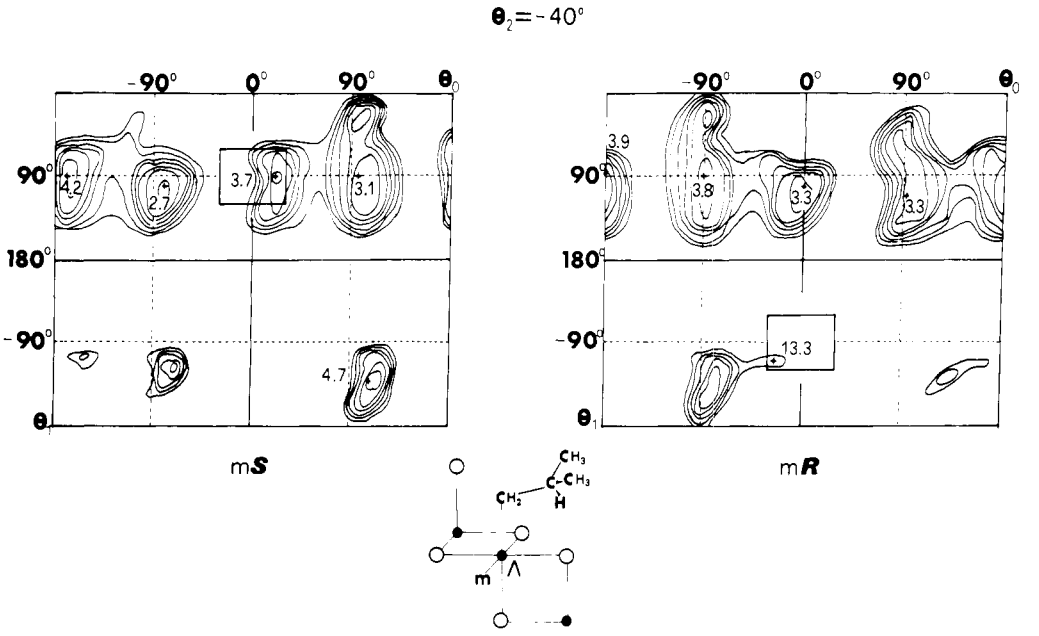

Figure 5. Same as Figure 4 for an i-C_4H_9 alkylating group.

region of $\vartheta_0 \simeq 0°$ low-energy minima are always found at $\vartheta_1 \simeq 90°$ (the most suitable situation for the primary insertion of a *re–re* coordinated olefin). Furthermore, the minima at $\vartheta_1 \simeq 90°$ are much steeper. An evaluation of the isospecific steric control demands an analysis of the partition functions in order to take into account the conformational freedom of the ϑ_2 dihedral angle. At room temperature our results suggest a ratio between *si–si* and *re–re* coordinations ranging from 10 to 50, depending on the geometrical parameters adopted for the ethyl group (Ti–C bond length between 2.2 and 2.32 Å and TiCC bond angle between 115° and 119°).

Typical energy maps for the isobutyl group are reported in Figure 5. The greater bulkiness of the isobutyl group further reduces the number of allowed conformations for the alkyl ligand. As a matter of fact ϑ_1 is constrained between 90° and 180° and ϑ_2 (measured relative to the C–H bond) can assume only values in the neighborhood of 50° or −40°. However, for the allowed values of ϑ_1 and ϑ_2 the energy minima are not strongly increased with respect to simpler alkylating agents. *re–re* and *si–si* coordinated olefins show a similar energy behavior over the whole surface (ϑ_0, ϑ_1), but the orientation of the first C–C bond of the alkyl group is favorable only for the insertion of a *si–si*-coordinated olefin. As a consequence, we consider this model highly stereospecific as far as the insertion step is concerned.

Summarizing, our computations indicate that isotactic steric control in the $TiCl_3$–AlR_3 system requires, in addition to the chirality of the active site, the presence of a primary alkyl group bulkier than CH_3. In fact, for a methyl ligand, the nonbonded interactions between the incoming monomer and the catalytic site are the same, whatever the monomer presentation. On the other hand, the first C–C bond of bulkier alkyl ligands is forced (by steric interactions with the local environment of the catalytic site) to assume a fixed chiral orientation. This orientation, in turn, determines different nonbonded interactions (especially in the insertion step) depending on the presented monomer face. Since the reactive end of the polypropylene chain is well simulated by an isobutyl group,[1-3] the results of Figure 5 indicate that on a catalytic site as described the stereoregularity of the monomeric units of the macromolecule beyond the first polymerized monomer is very high, whatever the alkylating agent.

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