JOURNAL OF CATALYSIS 77, 32–42 (1982)

Steric Control in Ziegler–Natta Catalysts: An Analysis of Nonbonded Interactions at Model Catalytic Sites

PAOLO CORRADINI,* VINCENZO BARONE,* ROBERTO FUSCO,* AND GAETANO GUERRA†

Istituto Chimico, Università di Napoli, Via Mezzocannone 4, 80134 Napoli, Italy, and †Istituto Donegani, Centro Ricerche Napoli, Via Nuova delle Brecce 150, 80147 Napoli-Barra, Italy

Received June 18, 1981; revised March 15, 1982

The stereospecificity of Ziegler–Natta heterogeneous catalysts is analyzed in terms of nonbonded interactions at the simplest model catalytic sites, which still retain the essential characteristics of chirality. The energetic calculations described show that model catalytic sites, comprising only three titanium atoms, may lead to a reasonable explanation of the stereospecificity in the polymerization of propene. Active sites of this type could be present in all the layered modifications of $TiCl_3$. As well as in the more complex catalytic surfaces examined in previous papers, the main factor in determining the stereospecific behavior of such sites is the fixed, chiral orientation into which the growing polymeric chain appears to be forced. The possible factors favoring the primary insertion of the olefin are also discussed.

INTRODUCTION

The stereospecificity of Ziegler–Natta catalysts in the polymerization of olefins is due, according to most authors, to interactions between nonbonded atoms at the catalytic site. These interactions have been examined in detail, but qualitatively, first by Cossee (*1–4*) and subsequently by Allegra (*5*) for slightly different models of the catalytic surface. In previous papers (*6, 7*) we have reported extensive energy calculations examining these models, together with other suitable faces and edges of the layered modifications of $TiCl_3$. In the present paper we shall discuss the essential factors determining the stereospecificity and regiospecificity which could emerge from nonbonded interactions, by considering the simplest models of catalytic sites which still retain the essential characteristics of chirality.

1. BASIC ASSUMPTIONS ON THE POLYMERIZATION MECHANISM

The essential features of the reaction mechanism which provide a general framework for our studies are as follows. (i) The mechanism is monometallic (*3, 4*): a Ti atom at the surface (on a lateral cut of a $TiCl_3$ layer, as shown in Fig. 1) becomes "active" when a nonbridged chlorine atom is substituted by an alkyl group (Fig. 2). (ii) The propagation reaction occurs through a two-stage mechanism (*4, 8, 9*): coordination of the olefin and its subsequent insertion (through *cis*-opening) in the Ti-polymer (Ti-*p*) bond. (iii) The situations suitable for the insertion step are characterized by an orientation of the double bond of the olefin parallel or nearly parallel to the Ti-*p*-bond (*3, 4*). (iv) The insertion step occurs according to "the least nuclear motion" (*10*) as described by Cossee (*4*) and schematically shown in Fig. 3. This implies an orientation of the first C–C bond of the growing chain corresponding to $\theta_1 \simeq \pm 90°$ (Fig. 4). Moreover, we assume that only in cases such as *a* and *d* of Fig. 4 are the relative orientations of the methyl group of the monomer and the second carbon atom of the polymeric chain (on opposite sides in respect to the plane defined by CH_2–Ti–(center of the double bond)) suitable for the successive insertion of the olefin. In cases *b* and *c* the short distance between the methyl group of the monomer and the second carbon atom of the polymeric chain (protrud-

0021-9517/82/090032-11$02.00/0

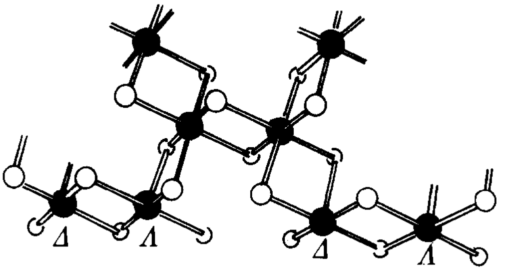

FIG. 1. Perspective drawing of a lateral cut of $TiCl_3$ layer. The chirality of the exposed Ti atoms is also indicated.

ing on the same side of the plane defined above) gives rise to relevant steric repulsions in an insertion step analogous to that reported in Fig. 3.

2. ASPECTS OF CHIRALITY IN THE ZIEGLER–NATTA POLYMERIZATION

It has been shown that, upon coordination, a prochiral olefin, such as propylene, may obtain not superposable re–re or si–si coordinations (*11*) (Fig. 4). The formation of an isotactic polymer according to the mechanism discussed in Section 1 necessarily implies that, for a long series of additions, the olefin is coordinated always in the same way.

A second element of chirality is related to the local situation of the Ti atoms. Neighboring Ti atoms (bridged by two Cl atoms) have opposite Λ or Δ chirality (*5*, *12*) (Fig. 1). A third element of chirality is given by the growing chain, whose tertiary carbon atoms are asymmetric. We point out that whatever the chirality of the growing chain is, almost identical minima are found, though for different values of θ_2, θ_3 as defined in Fig. 2.

We assume that the stereospecificity of the Ziegler–Natta polymerization is connected with the energetic differences between the diastereoisomeric situations which originate from the combination of two or more of the above elements of chirality.

3. METHOD OF COMPUTATION

The method of calculation and the parameters for the nonbonded potential functions have been previously described (*6*, *7*). Figure 2 illustrates the main structural parameters assumed and the dihedral angles varied in most of the reported calculations. The slight modifications with respect to Ref. (*6*) (larger $\hat{HCH}$ and $\hat{HCH_3}$ angles of the olefin) allow a better compromise between bending deformations and nonbonded interactions. As a consequence the nonbonded energy maps reported here are not strictly comparable to those presented in the earlier studies (*6*, *7*); however, the general conclusions previously drawn still remain valid. For purposes of illustration we shall compare in all cases only some specific sections $E(\theta_0, \theta_1)$ of the multidimensional energy surface for values of θ_2 corresponding to energetic minima (which generally occur at $\theta_2 = -70°$ or $\theta_2 = -160°$). The conclusions arise, however, from the complete set of calculations.

In the conformational maps the regions corresponding to orientations of the mono-

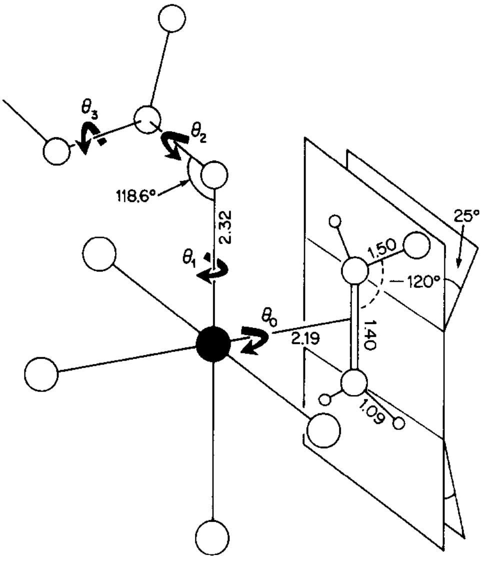

FIG. 2. Model showing the coordination of the monomer and the growing chain at the same Ti atom and the dihedral angles which have been varied in our computations. θ_0 defines the orientation of the olefin, while θ_1, θ_2, θ_3, . . . define the orientation of the chain. The most relevant bond lengths (in Å) and valence angles (in degrees) are also reported.

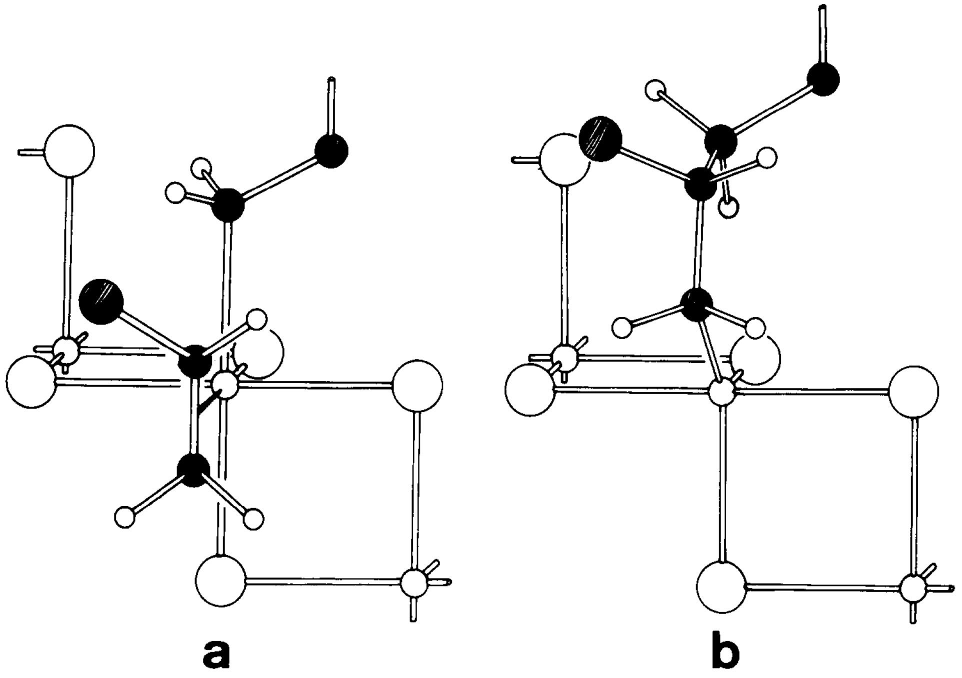

FIG. 3. A possible reaction mechanism for the insertion of the monomer in the Ti-chain bond according to the "least nuclear motion" principle. The initial stage (for an olefin coordinated si–si and a conformation of the chain corresponding to $\vartheta_1 = +90°$) is shown in (a), while the final situation (with the chain in an intermediate position between the two free octahedral positions at a Ti atom) is shown in (b).

mer and the chain suitable for a primary insertion (see Section 1) are indicated by squares. On the bottom of the maps, we report a schematic drawing of the corresponding model of the catalytic site and the relative positions of the monomer (m) and the growing chain (p). Re–re coordination of the monomer is denoted by mR and si–si coordination by mS. The active titanium atom has always Λ chirality.

4. INFLUENCE OF THE LOCAL ENVIRONMENT ON THE CONFORMATIONAL ENERGY OF DIASTEREOISOMERS AT THE CATALYTIC SITE

Let us consider the simplified model of catalytic site reported in Fig. 5. It involves only three Ti atoms and all the atoms directly bonded to them. The terminal Ti atoms are bridge-bonded (through pairs of Cl atoms) to the active Ti atom, to which both the polymeric chain and the monomer are coordinated. It is to be noted that this is the simplest model of catalytic surface in which the active Ti atom retains its Λ or Δ chirality.

In Fig. 5 we report only the chlorine atoms which show relevant steric interactions with the chain and the olefin coordinated at the positions *i* and *o*. The resulting catalytic model is characterized by a twofold symmetry axis relating, in particular, the *i* and 1 positions with the *o* and 2 positions, respectively.

Three different situations are considered: (a) both positions 1 and 2 are vacant; (b) only one of the positions 1 and 2 is occupied by a chlorine atom (irrespective of the specific position occupied because they are symmetry related); (c) both positions 1 and 2 are occupied by chlorine atoms. Our computations for case (b) refer to a chlorine

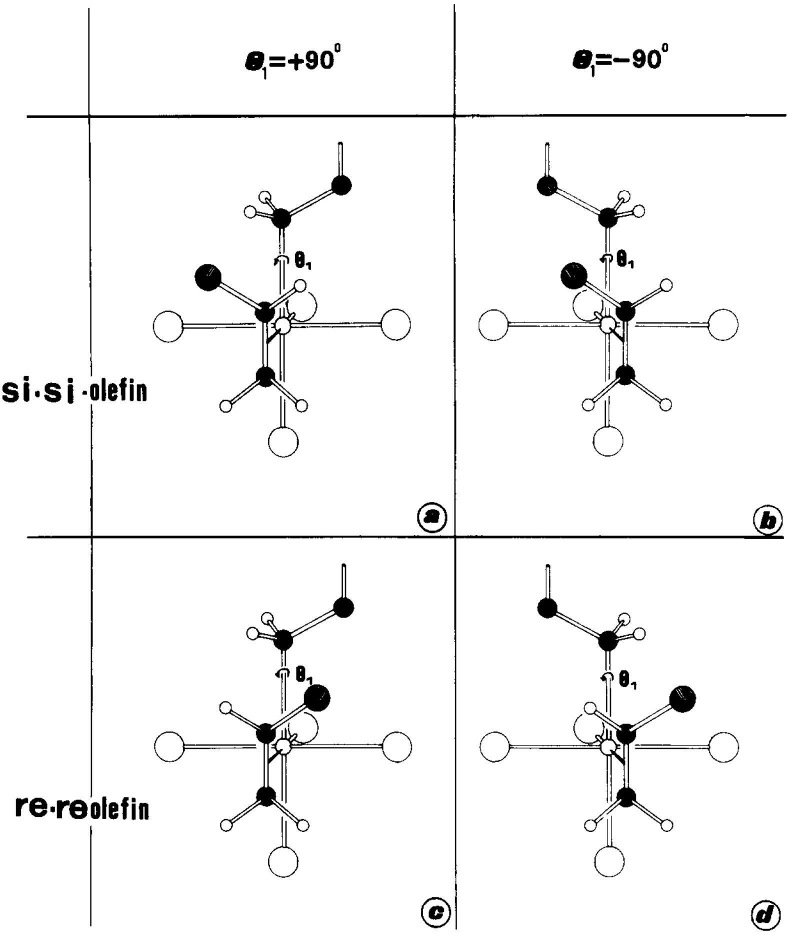

FIG. 4. The two possible coordinations of propene (re–re and si–si) suitable for a primary insertion are shown in connection with the two conformations of the polymeric chain corresponding to $|\theta_1| = 90°$.

atom in position 1. This atom destroys the symmetry of the whole catalytic model and hence, contrary to other cases, the two possible relative dispositions of the growing chain and the monomer (chain coordinated at the *i* or *o* position, respectively) give rise to different conformational maps.

Typical energy maps relative to case (a) are reported in Fig. 6. Similar energy minima are found in the whole range of ϑ_0 for the re–re and si–si coordinations of the olefin. However, it is interesting to note that, in the region of $\vartheta_0 \simeq 0°$, energy minima are found at $\vartheta_0 \leq 0°$ for the re–re coordination of the olefin and at $\vartheta_0 \geq 0°$ for the si–si coordination. These slight adjustments allow one to minimize the steric interactions between the methyl group of the olefin and the growing polymeric chain. The growing polymeric chain has a great conformational freedom and for both re–re and si–si coordinations the energies are similar inside the squares corresponding to situations suitable for primary insertion (possibly at different values of ϑ_2). As a consequence this model does not show any evidence of stereospecificity.

Next we consider case (b). As previously pointed out, in this case the energy maps relative to *i* and *o* coordinations of the monomer are different. For an *o* coordination of the monomer (Figs. 7 and 8) the

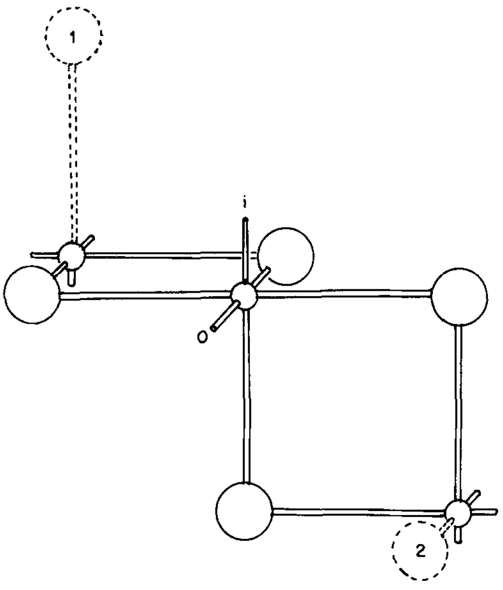

FIG. 5. Different local environments of an "exposed" titanium atom (catalytic site) are obtained if none, one, or both positions 1 and 2 are vacant.

presence of a chlorine atom in position 1 strongly limits the conformational freedom of the growing chain, but for the allowed values of ϑ_1, the energy minima are not increased with respect to case (a). In the region of $\vartheta_0 \simeq 0°$ the orientation of the growing chain becomes chiral, as low energy minima are found only in the region of ϑ_1 delimited by values of 90 and 150°. Re–re and si–si coordinated olefins show a similar energy behavior in the whole surface (ϑ_0, ϑ_1), but the orientation of the polymeric chain is favorable only for the insertion of a si–si coordinated olefin (cf. cases (a) and (c) of Fig. 4). As a consequence we consider this model stereospecific as far as the insertion step is concerned.

For an *i* coordination of the monomer (Figs. 9 and 10) the presence of the chlorine atom in position 1 does not sensibly restrict the range of possible values of θ_1, but strongly increases the steric interactions (for any orientation of the monomer) with respect to case (a). In the region of $\vartheta_0 \simeq 0°$, positive values of ϑ_0 are unfavorable because of interactions between the chlorine atom in position 1 and the CH_2 group of the olefin. On the other hand, as previously discussed for case (a), negative values of ϑ_0 cause higher interactions between the methyl group of propene and the growing chain, upon si–si coordination. As a consequence, re–re coordination is strongly favored. Since the growing polymeric chain can assume orientations suitable for the primary insertion of a re–re coordinated olefin ($\theta_1 \simeq 90°$), also this model shows a stereospecific behavior.

Summarizing, our computations indicate that on model (b) the two possible relative positions of the monomer and the polymeric chain (*o–i* and *i–o*, respectively) lead to different situations (preferential insertion of the si–si coordinated olefin in the former case and preferential coordination of the re–re coordinated olefin in the latter). Hence the formation of a highly isotactic polymer demands a significant energy difference between the two situations. According to our results, the coordination of the less bulky terminal CH_2 group of the growing chain in the more hindered position *i* is favored by 2.7 kcal mol^{-1} in respect to the *i* coordination of the monomer.

Typical energy maps relative to case (c) are reported in Fig. 11. In this model, both the growing chain and the olefin experience repulsive interactions with the two chlorine atoms added with respect to case (a). Thus the steric interactions are strongly increased for any orientation of the monomer and, contemporary with this, the conformational freedom of the growing chain is severely limited. In the region of $\theta_0 \simeq 0°$, the lowest energy minimum (7.4 kcal mol^{-1}) is found for a re–re coordination of the olefin, but the orientation of the polymeric chain ($\theta_1 \simeq 90°$) is not favorable for the insertion step. Other minima (in the region of $\theta_0 \simeq 0°$) are above 10 kcal mol^{-1}.

Next we analyze which sites belonging to lateral surfaces experience a local environment similar to that of the previous simplified models.

The local environment corresponding to model (a) is likely to occur in very specific

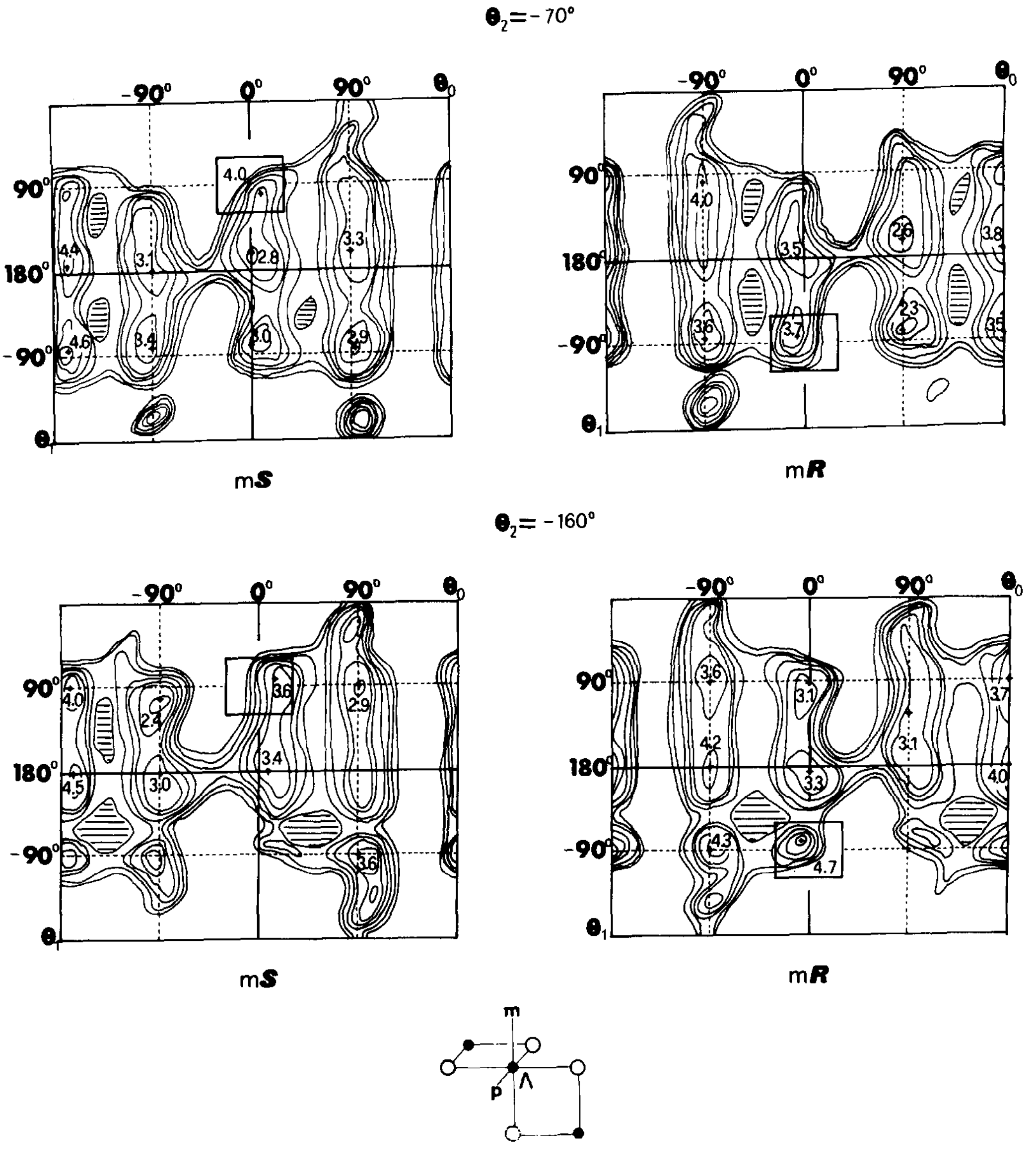

FIG. 6. Sections $E(\theta_0,\theta_1)$ of the multidimensional energy surface for a situation corresponding to the model of Fig. 5 when both positions 1 and 2 are vacant. The values of θ_2 correspond to energy minima and the isoenergetic curves correspond to 5, 7, 9, 11, 13, and 15 kcal mol^{-1}.

situations only (corners of cuts parallel to the **a–b** vector of the reference cell (*13*) or some sites on a zig-zag cut (*5*)). Since model (a) does not show a stereospecific behavior as regards both the coordination and the insertion step, these situations could give rise to the small amount of atactic polymer which is always present even in highly isotactic polymers.

With reference to the lateral surfaces of $TiCl_3$ (figure 1) the positions *i* and *o* of figure 5 correspond to the non-equivalent "inward" and "outward" positions previously defined (*6, 7*). The models (b) and (c) can then represent catalytic sites residing on structural layers protruding above both the neighbouring layers (*e.g.* reliefs) because, in this case, the atoms not explicitly in-

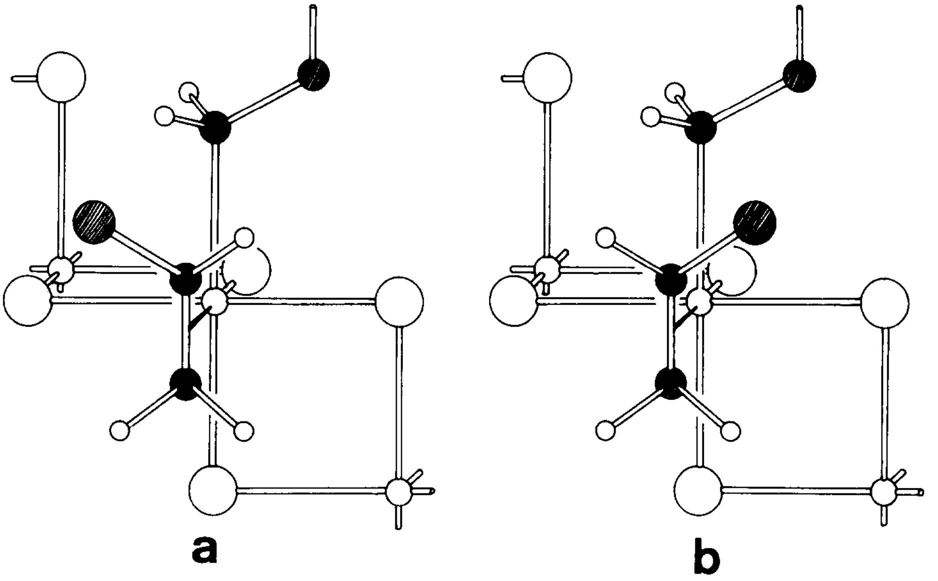

FIG. 7. Perspective drawing of the two possible enantiomeric coordinations of propene suitable for a primary insertion in connection with an appropriate conformation of the polymeric chain. The catalytic site corresponds to the model of Fig. 5 when only position 1 is occupied by a chlorine atom and the polymeric chain is coordinated in the *i* position.

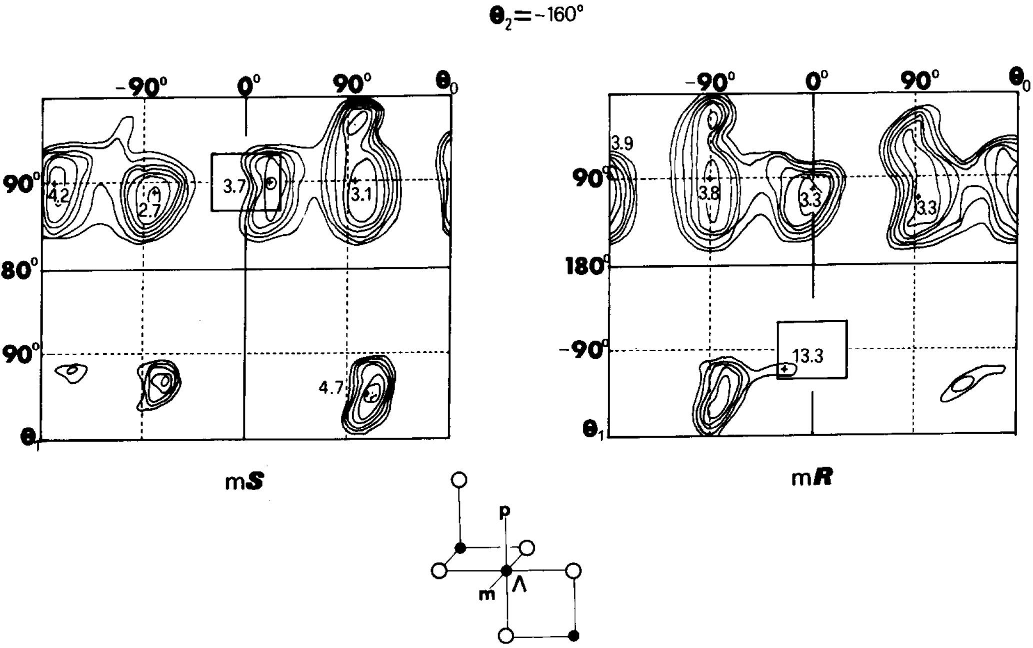

FIG. 8. Sections $E(\theta_0, \theta_1)$ of the multidimensional energy surface for a situation corresponding to the model of Fig. 5. The isoenergetic curves are the same as in Fig. 6.

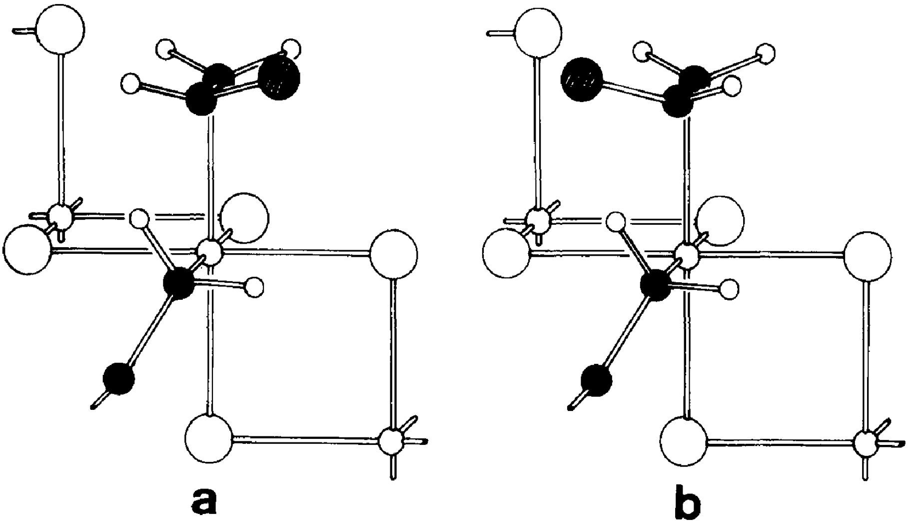

FIG. 9. Perspective drawing of the two possible enantiomeric coordinations of propene suitable for a primary insertion in a situation corresponding to an *o* coordination of the polymeric chain for the model of catalytic site of Fig. 5 when only position 1 is occupied by a chlorine atom.

cluded in the models do not show further appreciable interactions with the catalytic site. This demands only that the nonbridged chlorine atoms occupy an intermediate position between the two free octahedral sites at their respective Ti atoms.

Model (b) deserves special consideration because it shows a stereospecific behavior

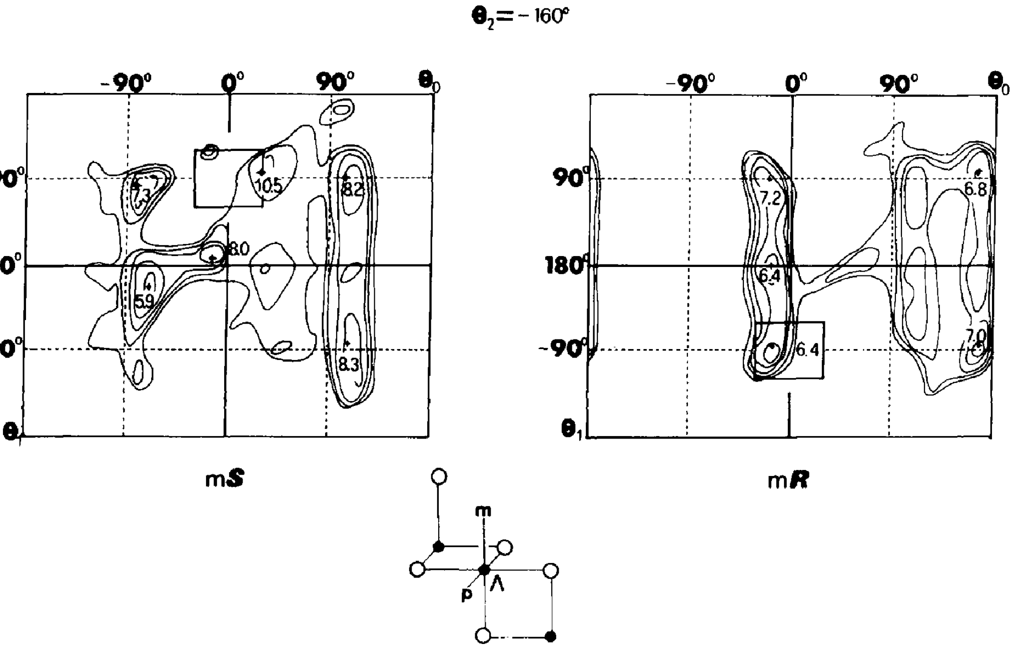

FIG. 10. Sections $E(\theta_0,\theta_1)$ of the multidimensional energy surface for a situation corresponding to the model of Fig. 5. The isoenergetic curves correspond to 7, 9, 11, 13, and 15 kcal mol^{-1}.

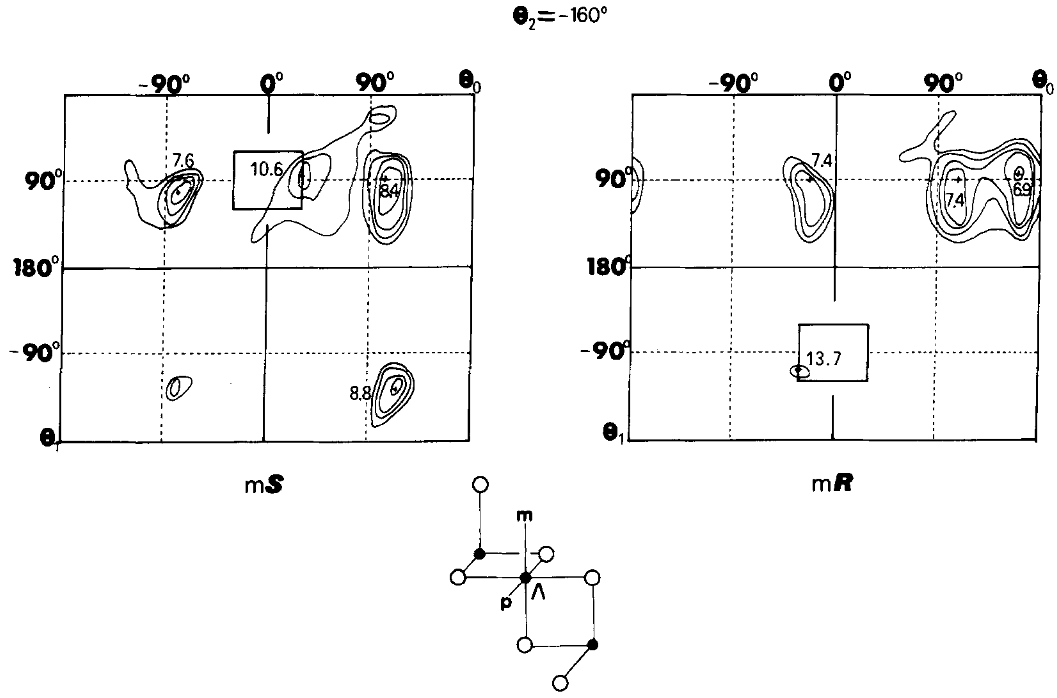

FIG. 11. Sections $E(\theta_0,\theta_1)$ of the multidimensional energy surface for a situation corresponding to the model of Fig. 5 when both positions 1 and 2 are occupied by chlorine atoms. The isoenergetic curves are the same as in Fig. 10.

coupled with low steric hindrances.

Model (c), although stereospecific, gives rise to much higher steric hindrances. However, models similar to it need consideration if the surface Ti atoms are hexacoordinated (e.g., bridge-bonded to aluminum atoms) even when not directly involved in the polymerization.

Catalytic sites residing on structural layers protruding above only one of the neighboring layers (e.g., steps or edges), or normally piled up, require the inclusion of further atoms in the calculations.

In the former case, the energy difference favoring the coordination of the polymeric chain in the more hindered position becomes even higher. This, in turn, determines a fixed, chiral orientation of the growing chain, which remains the main factor in determining the stereospecificity (*7*). In the latter case, the catalytic sites (residing in the bulk of the lateral surfaces) turn out to be too crowded, giving rise to very high coordination energies (*6*); furthermore their hypothetical catalytic behavior is not independent, in disagreement with experimental data (*14, 15*), on the particular crystalline modification of $TiCl_3$.

5. ORDER OF MAGNITUDE OF THE ENERGIES IMPLIED IN DETERMINING THE REGIOSPECIFICITY

In the models discussed in Section 4 and in most of the ones treated in our previous papers (*6, 7*) we did not find any evidence of regiospecificity in the coordination step (deep energy minima are found also for $\vartheta_0 = 180°$). Since the regiospecificity of Ziegler–Natta catalysts has a sound experimental basis (*16–19*) we think it worthwhile to discuss this problem in some detail. The problem of regiospecificity can be treated by formally considering the copolymerization of a monomer $CH_2 = CHR$ (entering the chain through primary insertion Me–CH_2–CHR–P, index 1) with a monomer $CHR' = CH_2$ (entering the chain through secondary insertion Me–CHR′–CH_2–P, index 2). Of course, in the case of the polymerization of propene, R = R′ = CH_3. Let us call p_{ij} the probability that a monomeric unit having constitution j is inserted in a chain bonded to the metal through a monomeric unit having constitution i and let us call E_{ij} the corresponding molar activation energy. Then:

$$\Delta E_1 = E_{12} - E_{11} = RT \ln \frac{p_{11}}{p_{12}}$$

and

$$\Delta E_2 = E_{21} - E_{22} = RT \ln \frac{p_{22}}{p_{21}}.$$

In the case of the homogeneous polymerization of propylene with vanadium catalysts, the different insertion probabilities p_{ij} have been obtained by Doi (*20*); from these values it is possible to calculate:

$$\Delta E_1(\text{homo}) = 0.45 \text{ kcal mol}^{-1}$$

$$\Delta E_2(\text{homo}) = 1.39 \text{ kcal mol}^{-1}.$$

In the case of the isospecific catalysis, however, the amount of secondary insertions is so low (of the order of 1% or, even, 0.1%) that it has not yet been possible to determine the different insertion probabilities. Nevertheless, it is possible to evaluate their order of magnitude assuming that, in the case of the heterogeneous catalysis, an extra energy term exists, which disfavors the secondary insertion. For the sake of simplicity we assume that both terms E_{12} and E_{22} are increased by the same amount α, so that:

$$\Delta E_1(\text{hetero}) = \Delta E_1(\text{homo}) + \alpha$$

$$\Delta E_2(\text{hetero}) = \Delta E_2(\text{homo}) - \alpha.$$

From simple calculations it results that, at room temperature, an energy term α of the order of 2.5 kcal mol^{-1} (or 4 kcal mol^{-1}), respectively, would lead to a fraction of secondary insertion lower than 1% (or 0.1%), respectively.

A significant steric contribution to α is suggested by the following considerations. Let us suppose that the catalytic sites responsible for the homogeneous polymerization have a trigonal bipyramidal coordination (*21*). On the other hand, the catalytic sites responsible for the heterogeneous polymerization should have an octahedral coordination. During the reaction path leading to a secondary insertion, the lateral group (CH_3 for propene) of the entering unit must experience a distance from a chlorine atom (also bonded to the metal), which is significantly shorter than the van der Waals contact distance for an octahedral catalytic site, while this is not the case if the coordination at the catalytic site is the (looser) trigonal bipyramidal one. Using the previously described geometrical parameters and nonbonded energy functions (*6*, *22*, *23*) we obtain a not negligible difference between primary and secondary insertion even for the final state (i.e., CH_2–$CH(CH_3)$–P vs $CH(CH_3)$–CH_2–P chains coordinated in an intermediate position between the two free octahedral positions at a Ti atom (see Fig. 3)). Assuming linear variations of internal coordinates between the initial and final states of Fig. 3, an approximate transition state for secondary insertion leads to a methyl–Cl distance of about 3 Å, i.e., to an increase of the interaction (repulsive) energy of about 2–3 kcal mol^{-1} with respect to primary insertion.

All other possible effects (e.g., electronic) being equal, it follows that in the heterogeneous polymerization both E_{12} and E_{22} are increased by at least 2 kcal mol^{-1} with respect to their values in the homogeneous polymerization. From the above arguments we suggest that the octahedral catalytic sites involved in the heterogeneous polymerization need not prohibit per se the coordination of the olefin at $\theta_0 \simeq 180°$ in order to give rise to a regiospecific reaction; it is actually sufficient that the activation energy for the secondary insertion on these sites be sensibly higher than on homogeneous sites. This effect could originate, inter alia, from different steric interactions.

CONCLUSIONS

The energy calculations described in this paper show that model catalytic sites, comprising only three titanium atoms, may lead to a reasonable explanation of the stereospecificity of Ziegler–Natta catalysts in the polymerization of propene.

Sites of the described type are a reasonable representation of the catalytic sites which could be present on reliefs or edges of lateral surfaces of the $TiCl_3$ lamellar crystals; in respect to other catalytic sites, which could be considered as well in a monometallic mechanism, they show lower steric hindrances in the coordination of the olefin and of the growing chain, while still retaining a high stereospecificity. The model catalytic sites which we have described do not prohibit per se a coordination of propene suitable for its secondary insertion. The regiospecificity of the isospecific polymerization could, however, be explained by considering that the activation energy for the secondary insertion on solid catalysts is considerably higher than on soluble catalysts.

Of the three elements of chirality occurring on the site, namely, Δ or Λ configuration of the metal atom, re–re or si–si coordination of the olefin and R or S configuration of the tertiary carbon atoms of the growing chain, this last one does not play an important role, while a Δ (Λ) configuration of the metal atom forces the growing chain to a chiral orientation (Fig. 6) which favors the successive preferential insertion (through *cis*-opening) of the olefin with re–re (si–si) coordination. It is known that all the layered modifications of $TiCl_3$ and also the catalysts supported on $MgCl_2$ show stereospecific behaviors which are similar in the polymerization of propene. Active sites of the simple type described could be present on the lateral faces of the crystals of all the above-mentioned catalysts, giving rise to polymers with stereoregular structure.

ACKNOWLEDGMENT

This work has been supported by the "Progetto Finalizzato del CNR Chimica Fine e Secondaria."

REFERENCES

1. Cossee, P., *Tetrahedron Lett.* **17,** 12 (1960).
2. Cossee, P., *J. Catal.* **3,** 80 (1964).
3. Arlman, E. J., and Cossee, P., *J. Catal.* **3,** 99 (1964).
4. Cossee, P. *in* "The Stereochemistry of Macromolecules" (A. D. Ketly, Ed.), Vol. 1, Chap. 3. Marcel Dekker, New York, 1967.
5. Allegra, G., *Makromol. Chem.* **145,** 235 (1971).
6. Corradini, P., Barone, V., Fusco, R., and Guerra, G., *Eur. Polym. J.* **15,** 1133 (1979).
7. Corradini, P., Guerra, G., Fusco, R., and Barone, V., *Eur. Polym. J.* **16,** 835 (1980).
8. Natta, G., Danusso, F., and Sianesi, D., *Makromol. Chem.* **30,** 238 (1959).
9. Avdeev, V. J., Zakharov, I. I., Zakharov, V. A., Bukatov, G. D., and Ermakov, Y. I. *Zh. Strukt, Khimii* **18,** 525 (1977).
10. Hine, J., J. Org. Chem., *31,* 1236 (1966); *Adv. Phys. Org. Chem.* **15,** 1 (1977).
11. Hanson, K. R., *J. Amer. Chem. Soc.* **88,** 2731 (1966).
12. Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.* **28** (1971).
13. Allegra, G., *Nuovo Cimento* **23,** 502 (1962).
14. Natta, G., Pasquon, J., Zambelli, A., and Gatti, G., *J. Polym. Sci.* **51,** 387 (1961).
15. Torquist, E. G. M., *Ann. N.Y. Acad. Sci.* **155,** 447 (1969).
16. Zambelli, A., Tosi, C., and Sacchi, M. C., *Macromolecules* **5,** 649 (1972).
17. Bovey, F. A., Sacchi, M. C., and Zambelli, A., *Macromolecules* **7,** 752 (1974).
18. Zambelli, A., Locatelli, P., and Rigamonti, E., *Macromolecules* **12,** 156 (1979).
19. Natta, G., Pino, P., Mantice, E., Danusso, F., Mazzanti, G., and Peraldo, M., *Chim. Ind.* **38,** 124 (1956).
20. Doi, Y., *Macromolecules* **12,** 248 (1979).
21. Zambelli, A., and Allegra, G., *Macromolecules* **13,** 42 (1980).
22. Hopfinger, A. J., *in* "Conformational Properties of Macromolecules." Academic Press, New York, 1973.
23. Kadymova, F. A., *Theor. Chim. Acta.* **35,** 93 (1974).