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Stereoselectivity of the Model Catalytic Site Proposed for the Isospecific Ziegler–Natta Polymerization of the α-Olefins

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ABSTRACT: The coordination of C-3 branched α-olefins to the model catalytic site, proposed by some of us for the isospecific Ziegler–Natta polymerization, is considered. We point out that the model is able to account for the stereoselectivity of the catalyst in the presence of a chiral monomer (3-methyl-1-pentene). The model would be also able to account for the relative reactivities of the C-3 branched monomers in the polymerization initiation steps.

Introduction

In previous papers,[1-5] a model for the catalytic site for the Ziegler–Natta polymerization of the α-olefins, which accounts for the observed isospecific behavior, has been proposed. Such a model is able to explain a large number of factual observations (e.g., type of tacticity errors along a mainly isotactic chain,[1] maintenance of isotacticity after an ethylene insertion,[1] similarity of the general behavior of $TiCl_3$ and $MgCl_2$–Lewis base supported catalysts[4]) and above all was able to give correct predictions[1,3] relative to the stereospecificity of polymerization initiation steps (when the alkylating groups are CH_3, C_2H_5, or i-C_6H_9), confirmed by the experimental data obtained by Zambelli and co-workers.[6]

It is well-known that the isospecific catalysts are also partially stereoselective: in the presence of racemic monomers, polymers are obtained, which can be partially resolved into optically active fractions.[7-10] Recently a detailed study relative to the isotactic polymerization of (*RS*)- and (*S*)-3-methyl-1-pentene has been published.[11] In particular, quantitative data have been reported relative to the initiation step on Ti–methyl bonds, which was characterized as nonenantioselective but partially diastereoselective. In other words both *si* and *re* attack of the

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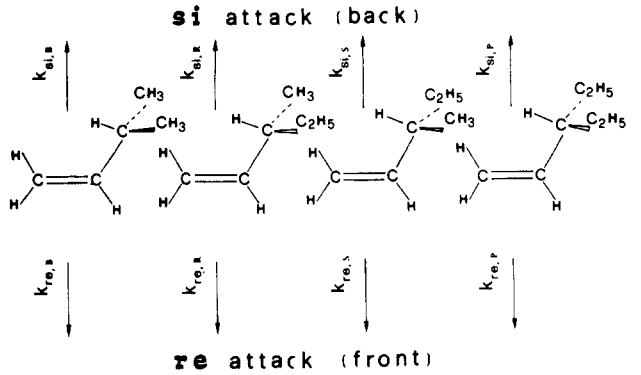

Figure 1. Upon coordination a prochiral olefin may get nonsuperposable *re* or *si* configurations.[12] With reference to the figure, *si* (*re*) coordination or attack is characterized by the coordination centers below (above) the plane of the sheet. The *K*'s are the rate constants of the initiation steps of the faces of the considered C-3 branched monomers; B and P stand for 3-methyl-1-pentene and 3-ethyl-1-pentene; R and S indicate the chirality of the two enantiomers of 3-methyl-1-pentene.

olefin are allowed (see definition in Figure 1), but in the case of a *si* attack (*re* attack) the reactivity of the *S* enantiomer (*R* enantiomer) is 2 times the reactivity of the *R* one (*S* one).

The chain propagation steps, which are highly enantioface discriminating (isotactic polymer indeed is obtained), would present an analogous diastereoselectivity.[11]

By copolymerization of different C-3 branched α-olefins (both chiral and achiral) in the presence of ^{13}C-enriched end groups of the resulting copolymers, the relative reactivities in the initiation steps (defined in Figure 1) of the faces of 3-methyl-1-pentene (3MP1), 3-methyl-1-butene (3MB1), and 3-ethyl-1-pentene (3EP1) have been experimentally determined.[13]

The trend of the reactivities as a function of the structure of the monomers was tentatively accounted for by assuming that the *si* (*re*) attacks of the olefins should be possible only from the H-skew − (H-skew +) conformations[13] (Figure 2).

In a recent paper[14] by some of us, a conformational analysis of the cited C-3 branched monomers has been reported. The comparison between the calculated populations of the H-skew − conformers and the experimental relative reactivities of the *si* attacks seems to support the previous hypothesis. However, a quantitative agreement between experimental and calculated data is reached only by assuming somewhat different activation energies (but in all cases differences less than 0.9 kcal/mol) for the attacks of the different monomers.

In this paper the coordination of the cited C-3 branched monomers, to the previously proposed model catalytic site, is considered. The aim is to elucidate whether the model is able to account for, at least qualitatively, the stereoselectivity of the isospecific polymerization and possibly the relative reactivities of the monomers in the cited initiation steps.

Model, Structure, and Method

The essential features of the reaction mechanism that provide the general framework of our studies have been previously discussed[1,2] and are not reported here. We only recall that the formation of an isotactic polymer according to the adopted reaction mechanism necessarily implies that for a long series of additions the olefin reacts always with the same prochiral face (*si* or *re*). Furthermore, the (octahedral) catalytic site is chiral, and the two enantiomeric situations will be designated by the symbols Λ and Δ.[15] In

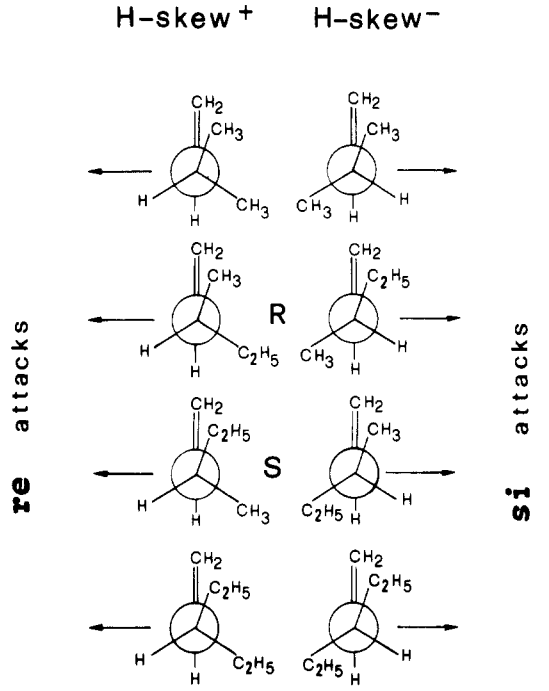

Figure 2. Newman projections of the H-skew + and H-skew − conformations of 3MB1, (*R*)-3MP1, (*S*)-3MP1, and 3EP1. Only on the basis of reactivity data of the monomer faces it was supposed that *si* (*re*) attack is achievable only starting from the H-skew − (H-skew +) conformations.

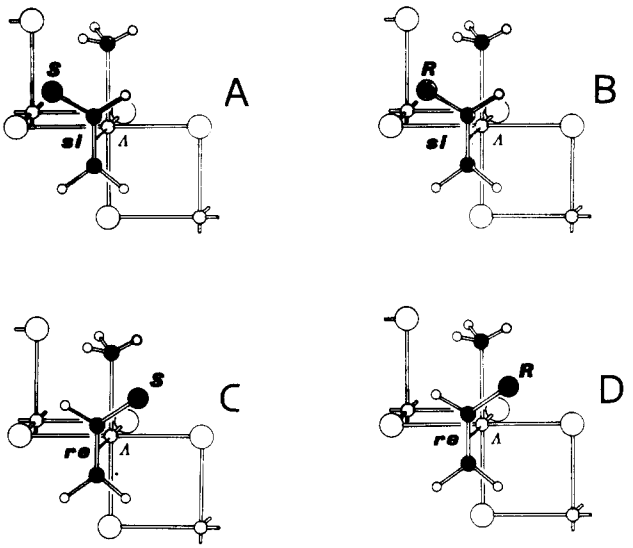

Figure 3. Diastereoisomeric situations on a model catalytic site of Λ chirality, after coordination of both enantiomers (*R* and *S*) of a chiral monomer with both prochiral faces (*si* and *re*), in the outward position; a methyl group is coordinated in the inward position.

our computations, without loss of generality, only Λ sites have been considered.

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. The local environment of the defective sites is well represented by the simple model shown in Figure 3.

In this paper the coordinations of a methyl group (the alkylating group in the considered initiation steps) in the inward position and of the C-3 branched monomers in the outward position have been considered (as shown for the two enantiomers of 3MP1 in Figure 3).

The method of calculation[14,16] and the parameters for the nonbonded potential functions[14] have been previously

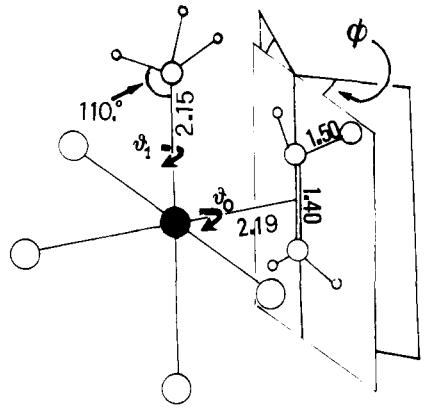

Figure 4. Model showing the coordination of the monomer and the methyl group at the same Ti atom and some of the dihedral angles that have been varied in our computations. The most relevant bond lengths (in angstroms) and valence angles (in degrees) are also reported. The depicted situation corresponds to $\vartheta_0 \simeq 0°$.

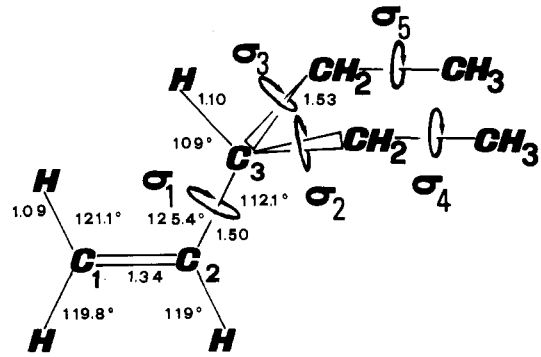

Figure 5. Model showing the most relevant bond lengths (in anstroms) and valence angles relative to the monomers, which have been assumed in our computations and the dihedral angles which have been varied.

described. The choice of such parameters, taken from ref 17, is due to the good agreement between some experimental and calculated values for energy differences which characterize the conformational analysis for 1-butene and 3MB1.[14]

Figure 4 shows the main structural parameter adopted and some of the dihedral angles varied in this study. The structural parameters are as in ref 2 (partially taken from ref 18), but the Ti–C distance of the methyl group is taken as 2.15 Å from recently described organometallic complexes.[19]

The dihedral angles are defined so that $\theta_0 = 0°$ corresponds to an orientation of the olefin suitable for primary insertion (while at $\theta_0 = 180°$ the olefin is oriented in a way suitable for secondary insertion); $\theta_1 \cong 0°$ corresponds to a C–H bond (of the methyl) cis to the line between the Ti and the center of the double bond; $\phi = 0°$ corresponds to the situation in which the plane, defined by the C1, C2, and C3 atoms of the olefins, is normal to the same line.

Figure 5 illustrates the main structural parameters relative to the isolated C-3 branched monomers assumed in our computations, taken from the CH_3-skew conformer of 1-butene,[20] and already assumed in the previous paper.[14] Energy changes for the minima less than 0.1 kcal/mol are obtained assuming the geometry of the CH_3-syn conformer. The C_{sp^3}–C_{sp^3}–C_{sp^3}, C_{sp^3}–C_{sp^3}–$H_{methylenic}$, and C_{sp^3}–C_{sp^3}–$H_{methylic}$ bond angles were assumed to be equal to 113°, 110.3°, and 108°, respectively. Upon coordination to the model site, such structural parameters are not changed, but the length of the double bond is increased from 1.34 to 1.40 Å.[18]

Figure 5 illustrates also the dihedral angles relative to the monomer varied in the reported calculations for the 3EP1. The dihedral angles for 3MP1 and 3MB1 are analogously named; the only difference is that in the first case σ_5 and in the second case σ_4 and σ_5 are not defined. The dihedral angles are defined according to the IUPAC rules,[21] but for the conformations relative to $\sigma_1(C_1,C_2,C_3,H)$ we have used the special names, previously adopted,[11,13,14] attributed to the following ranges of values: $\sigma_1 = 0° \pm 30°$ H-syn; $\sigma_1 = 120° \pm 30°$ H-skew +; $\sigma_1 = -120° \pm 30°$ H-skew –.

As zero energy we have assumed the energy of the H-syn conformation of 3MB1.

The populations of the complexes in which the considered monomers are *si* coordinated to a Λ site ($P_{si,X}$) have been assumed to be proportional to the corresponding conformational partition functions ($Q_{si,X}$); in such symbols, X may be R (for (*R*)-3MR1), S (for (*S*)-3MP1), B (for 3MB1), or P (for 3EP1). The relative populations have been evaluated by fixing $P_{si,R} = 1$ and by applying the equation

$$P_{si,X} = Q_{si,X}/Q_{si,R} \tag{1}$$

For instance, such a ratio for the two diastereoisomeric complexes, obtained by *si* coordination of (*S*)-3MP1 and (*R*)-3MP1, may be written as

$$Q_{si,S}/Q_{si,R} = \left\{\int \exp[-E_{si,S}(\theta_0,\theta_1,\phi,\sigma_1,\sigma_2,\sigma_3,\sigma_4)/RT]\, d\theta_0\, d\theta_1\, d\phi\, d\sigma_1\, d\sigma_2\, d\sigma_3\, d\sigma_4\right\} \Big/ \left\{\int \exp[-E_{si,R}(\theta_0, \theta_1, \phi, \sigma_1, \sigma_2, \sigma_3, \sigma_4)/RT]\, d\theta_0\, d\theta_2\, d\phi\, d\sigma_1\, d\sigma_2\, d\sigma_3\, d\sigma_4\right\} \tag{2}$$

In our computations such integrations were approximated by summations, and the partition functions were evaluated for fixed values of the dihedral angle ϕ

$$Q_{si,X}(\phi)/Q_{si,R}(\phi) = \left\{\sum_{\theta_0,\theta_1,\sigma_1,\sigma_2,\sigma_3,\sigma_4} \exp[-E_{si,S}(\theta_0,\theta_1,\sigma_1,\sigma_2,\sigma_3,\sigma_4)/RT]\right\} \Big/ \left\{\sum_{\theta_0,\theta_1,\sigma_1,\sigma_2,\sigma_3,\sigma_4} \exp[-E_{si,R}(\theta_2,\theta_1,\sigma_1,\sigma_2,\sigma_3,\sigma_4)/RT]\right\} \tag{3}$$

where θ_0 assumes values in the range (–15°, +15°) with increments of 5°; θ_1, σ_1, and σ_2 assume values in the range (0°, 360°) with increments of 10°; σ_3 and σ_4 (as well as σ_5 in the calculations for 3EP1) assume only values corresponding to all the staggered conformations.

Nonrelevant variations in the populations are obtained including in the computation also situations in which σ_3 or σ_4 or σ_5 are not exactly staggered, or considering lower increment values for the angles θ_0, θ_1, σ_1, σ_2.

Results

Stereoselectivity. The specific sections of the multidimensional energy surfaces $E(\sigma_1,\sigma_2,\sigma_3,\sigma_4)$, in which the dihedral angles σ_3 and σ_4 are assumed to be staggered, are reported in Figure 6, A and B for the isolated monomers (*R*)-3MP1 and (*S*)-3MP1, respectively.

The deepest energy minima correspond to the H-syn conformations ($\sigma_1 = 0°$), but energetic minima are also found for the conformations H-skew + and H-skew – ($\sigma_1 = \pm 120°$). However, the conformations H-skew + and H-skew – are not energetically equivalent; in particular for (*R*)-3MP1 ((*S*)-3MP1) the H-skew + (H-skew –) conformations, which present the methyl group in the syn position and the ethyl group in a skew position, are energetically favored.

Upon a *si* coordination of the monomers on the model catalytic site previously proposed (in the presence of a methyl group as indicated in Figure 3, A and B) for the

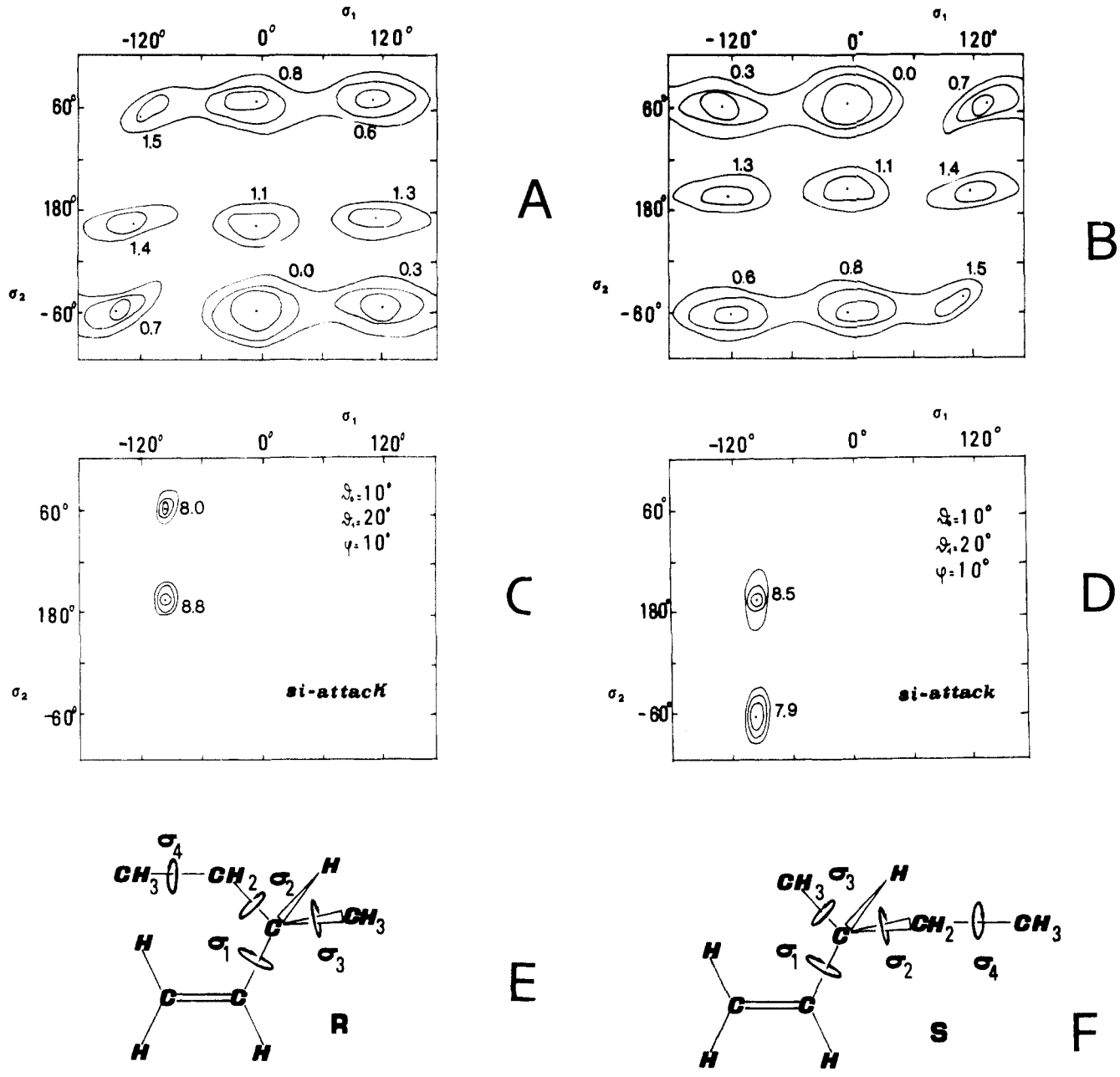

Figure 6. (A, B) Sections $E(\sigma_1,\sigma_2)$ of the multidimensional energy surfaces for the two isolated enantiomers of 3MP1. The dihedral angles σ_3 and σ_4 are assumed to be staggered; the isoenergetic curves correspond to 1, 2, and 3 kcal/mol. (C, D) Maps A and B after a *si* coordination of the monomers to the Λ model site; the indicated θ_0 and θ_1 values give rise to the deepest energetic minima; the assumed value for the dihedral angle ϕ is also indicated. The isoenergetic curves cooresponds to 9, 10, and 11 kcal/mol. (E, F) H-skew − conformations for (*R*)-3MP1 (E) and for (*S*)-3MP1 (F) are schematized.

θ_0 and θ_1 values which give rise to the deepest energetic minima and imposing for instance a value of 10° for the dihedral angle ϕ the maps of Figure 6, A and B, are changed into the maps of Figure 6, C and D.

Only minima in the H-skew − regions are still present and only the corresponding conformations may be thought of as reactive, in agreement with the hypothesis formulated by Zambelli et al.,[13] only on the basis of the reactivity ratios of the monomer faces. In other words, upon *si* coordination, only the methyl-syn conformation should be accessible for (*S*)-3MP1 (Figure 6F) and only the ethyl-syn conformation for (*R*)-3MP1 (Figure 6E), and this fact would favor the *si* attack of the *S* enantiomer with respect to the same attack of the *R* enantiomer, independently of the chirality of the catalytic site. It is worth noting that conformations in the region of the H-syn minimum are present (instead) in the tetracoordinated planar complexes of chiral α-olefins with platinum.[22,23]

The relative stability of the two diastereoisomeric complexes (schematically represented in Figure 3, A and B) expressed by eq 2 has been evaluated by the approximation of eq 3, using energetic maps analogous to those of Figure 6, C and D.

Assuming for the dihedral angle ϕ the values 5°, 10°, and 15°, such calculated ratio results equal 2.2, 1.9, and 1.4, respectively. Such data are in a good agreement with the observed reactivity ratio between the two *si* attacks of the enantiomers in the initiation step (~1.9[11]).

Upon a *re* coordination of the enantiomers on the same model site, two other diastereoisomeric situations are obtained (sketched in Figure 3, C and D, and briefly indicated by (*re*,Λ,*R*) and (*re*,Λ,*S*)) for which only energy minima in the H-skew + region are still present. However, the diastereoisomeric complexes (*re*,Λ,*R*) and (*re*,Λ,*S*) are energetically equivalent to the complexes (*si*,Λ,*S*) and (*si*,Λ,*R*), respectively, even if such situations are not enantiomeric.

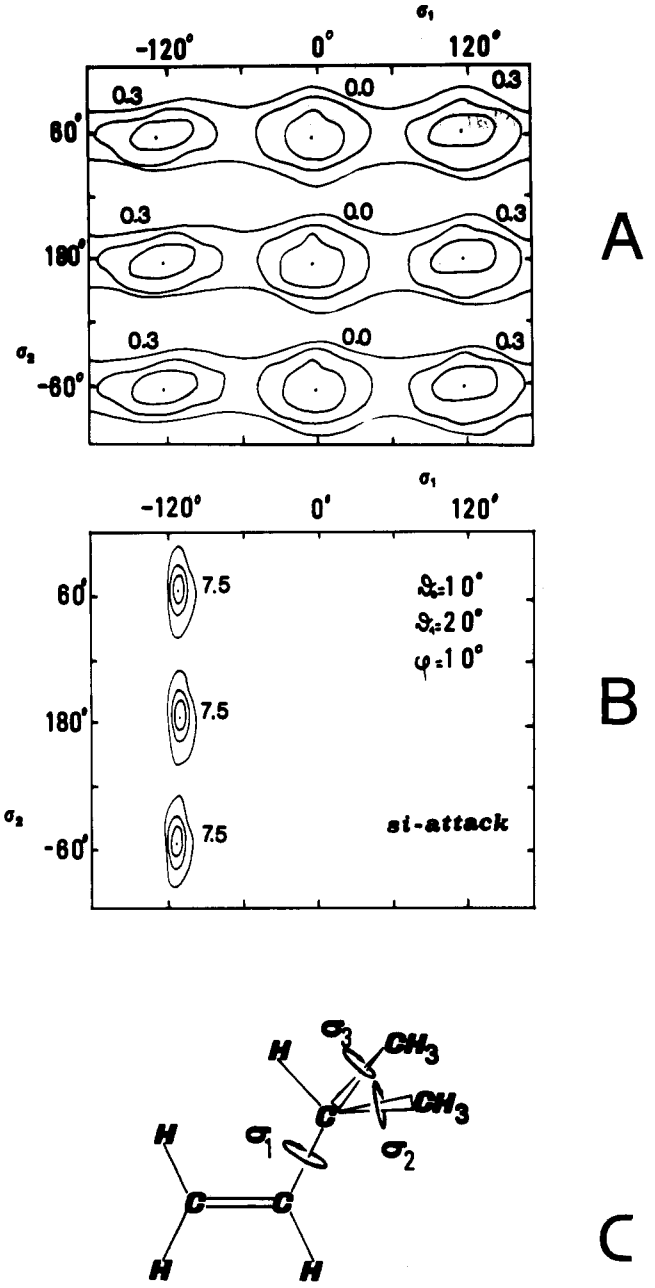

Figure 7. (A) Map $E(\sigma_1,\sigma_2)$ for 3MB1 where σ_3 is assumed to be staggered. The isoenergetic curves correspond to 1, 2, and 3 kcal/mol. (B) Map A after a *si* coordination of the monomer to the model site. The θ_0, θ_1, and ϕ values are as in Figure 6. The isoenergetic curves correspond to 8, 9, and 10 kcal/mol. (C) Schematic drawing of the monomer 3MB1.

This result accounts for the absence of enantioface discrimination, that is, the equal reactivity of *si* and *re* faces, of the initiation step of the isospecific polymerization of 3MP1, when the starting alkyl group is a methyl[11] (as happens for the propene monomer[3,6]).

During the propagation steps, according to our model, the chirality of the catalytic site (for instance, of kind Λ) imposes the chirality of the coordination of the α-olefin (*si* coordination), which in turn sensibly favors the coordination and then the insertion of one enantiomer (*S* enantiomer as it happens in the initiation step).

The model is hence also able to account for (at least qualitatively) the stereospecificity and the stereoselectivity of the propagation steps of the polymerization reaction.

Reactivity. Sections $E(\sigma_1,\sigma_2)$ of the multidimensional energy surfaces, in which the dihedral angles σ_3, σ_4, and σ_5 (or only σ_3 for 3MB1) are assumed to be staggered, are reported in Figures 7A and 8A for the isolated monomers 3MB1 and 3EP1, respectively. Upon a *si* coordination of the monomers on the previous model site, under conditions analogous to those described for 3MP1, the maps of the Figures 7a and 8A are changed into the maps of Figures 7B and 8B.

As well as for the chiral monomer, for such achiral monomers only minima in the H-skew – region are still present, again in agreement with the hypothesis by Zambelli et al.[13] Again, as for 3MP1, the model does not present enantioface discrimination in the initiation step. In fact, for both 3MB1 and 3EP1, the diastereoisomeric complexes (*re*,Λ) and (*si*,Λ), in the presence of a methyl as alkyl group, are energetically equivalent.

The populations of the complexes in which the C-3 branched monomers are *si* coordinated to a Λ site have been evaluated from eq 1, using four sets of energetic maps analogous to those of Figures 6C,D, 7B, and 8B. The calculated values are reported in Table I, for three different values of the dihedral angle ϕ; in the calculation was made the assumption that only the nonbonded and torsional contributions to the coordination energy are relevant in determining the relative stability of the complexes.

Such calculated data of populations of the catalytic complexes may be compared to the relative reactivities of the *si* faces of (*R*)-3MP1, (*S*)-3MP1, 3MB1, and 3EP1, in the initiation step taken from ref 13 and reported in Table II.

A fairly good agreement between the experimental reactivities and the calculated complex populations is pointed out, as would be expected in the assumption that the energetic differences in the transition states would be only slightly different from those in the catalytic complexes.

The agreement is better than the one obtained by simply comparing the populations of the H-skew – conformers of the uncoordinated monomers with the experimental relative reactivities of the monomer faces.[14]

Table I
Relative Populations Calculated for the Complexes in Which (*R*)-3MP1, (*S*)-3MP1, 3MB1, and 3EP1 Are *si* Coordinated to a Λ Site, for Three Values of the Dihedral Angle ϕ

	ϕ = 5°	ϕ = 10°	ϕ = 15°
$P_{si,R}$	1	1	1
$P_{si,S}$	2.2	1.9	1.4
$P_{si,B}$	5.4	5.2	3.6
$P_{si,P}$	0.07	0.11	0.11

Table II
Relative Reactivities of the *si* Faces of (*R*)-3MP1, (*S*)-3MP1, 3MB1, and 3EP1 in the Initiation Steps, Defined in Figure 1 and Taken from Ref 13

$K_{si,R}/K_{si,R} = 1$	$K_{si,B}/K_{si,R} = 2.3$
$K_{si,S}/K_{si,R} = 1.9$	$K_{si,P}/K_{si,R} = 0.3$

Conclusions

The proposed model for the catalytic site, for the Ziegler–Natta polymerization of the α-olefins, which account for the observed isospecific behavior, seems also to be useful in the study of the factors which determine the stereoselectivity of the reaction.

The catalytic model proposed is indeed able to account for the diastereoselectivity (discrimination between the (*S*-*si*) and (*R*-*si*) attacks) and nonenantioselectivity (equal reactivity of *si* and *re* faces) of the initiation step of the isospecific polymerization, when the starting alkyl group is a methyl. The model is also able to account (at least qualitatively) for the stereospecificity and the stereose-

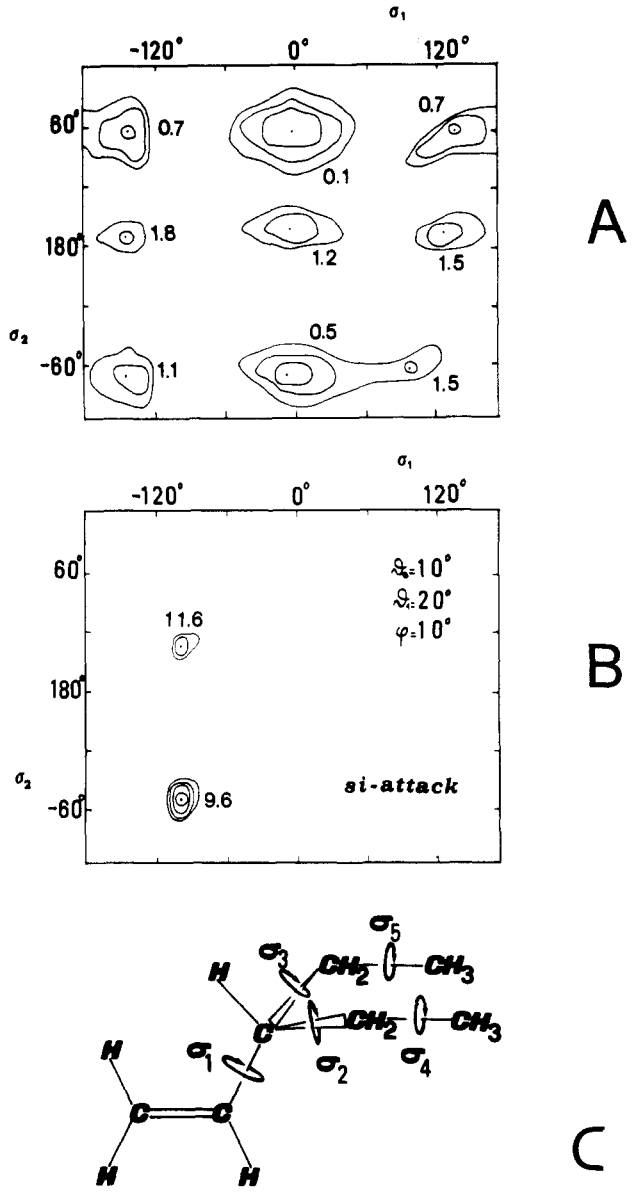

Figure 8. (A) Map $E(\sigma_1,\sigma_2)$ for 3EP1, where σ_3, σ_4, and σ_5 are assumed to be staggered (in particular $\sigma_3 = -60°$). The isoenergetic curves correspond to 1, 2, and 3 kcal/mol. (B) Map A after a *si* coordination of the monomer to the model site. The θ_0, θ_1, and ϕ values are as in Figure 6. The isoenergetic curves correspond to 10, 11, 12, and 13 kcal/mol. (C) Schematic drawing of the monomer 3EP1.

lectivity of the propagation steps of such reaction.

According to our model the main factor in determining the stereoselectivity of the polymerization reaction is the fact that only H-skew − (H-skew +) conformations, which are energetically favored in (*S*)-3MP1 ((*R*)-3MP1), are accessible upon a *si* (*re*) coordination of the C-3 branched monomers. For this reason on a Λ site (Δ site) which would favor the *si* attack (*re* attack) of the α-olefins, the insertion of the *S* enantiomer (*R* enantiomer) would be favored.

This result is in perfect agreement with the previous hypothesis of Zambelli et al.,[13] formulated only on the basis of the reactivity ratios of the monomer faces, for which the *si* (*re*) attacks of the α-olefins should be possible only from the H-skew − (H-skew +) conformations.[13]

Moreover, the coordination of the C-3 branched monomers (chiral and achiral) to the model catalytic site allows us to see that the experimental relative reactivities of the monomer faces in the initiation step[13] are consistent with the calculated catalytic complex populations.

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Registry No. 3MB1, 563-45-1; (*R*)-3MP1, 39914-58-4; (*S*)-3MP1, 5026-95-9; 3EP1, 4038-04-4.

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