Mills equation for polydispersity gives eq 26, which adequately predicts the steady-state compliance for polydisperse polymers.

The present FEPs have very high molecular weights ($M_w/M_c = 29$–77) and are indeed found to verify the η_0 vs. M^3 relation predicted by the reptation theory. At lower molecular weights ($M_w/M_c = 1$–50), however, the empirical η_0 vs. $M_w^{3.4}$ relation holds. This is explained by the fluctuation of tube contour length (tube leakage). Consideration of the tube leakage effect in the reptation theory gives a relation that correctly predicts the molecular weight dependence of zero-shear viscosity over the entire molecular weight range ($M/M_c > 1$). That is, in the relation $\eta_0 = \eta_0(M_c)(M/M_c)^n$, $n = 4.1$ at $M = M_c$ and asymptotically decreases to $n = 3$ at $M \rightarrow \infty$.

Acknowledgment. The author thanks Dr. Howard W. Starkweather, Jr., for helpful discussions during the course of this work.

Registry No. Tetrafluoroethylene, 116-14-3; hexafluoropropylene, 116-15-4; (tetrafluoroethylene)·(hexafluoropropylene) (copolymer), 25067-11-2.

References and Notes

(1) Wu, S. *Polym. Eng. Sci.* **1985**, *25*, 122.

(2) Wu, S. In "Advances in Rheology, Volume 3. Polymers"; Mena, B., Garcia-Rejon, A., Rangel-Nafaile, C., Eds.; Universidad Nacional Autonoma de Mexico: Mexico, 1984; pp 359–366. Proceedings of IX International Congress of Rheology, Acapulco, Mexico, Oct. 1984.

(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818; **1979**, *75*, 38.

(4) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.

(5) McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: New York, 1967; pp 460–461.

(6) Ajroldi, G.; Garbuglio, C.; Ragazzini, M. *J. Appl. Polym. Sci.* **1970**, *14*, 79.

(7) Case, L. C. *Polym. Lett.* **1963**, *1*, 345; *J. Appl. Polym. Sci.* **1960**, *3*, 254.

(8) Tobolsky, A. V.; Katz, D.; Takahashi, M. *J. Polym. Sci., Part A* **1963**, *1*, 483.

(9) Nishioka, A.; Watanabe, M. *J. Polym. Sci.* **1957**, *24*, 298.

(10) Wu, S. "Polymer Interface and Adhesion"; Marcel Dekker: New York, 1982; pp 377–379.

(11) Nielsen, L. E. "Polymer Rheology"; Marcel Dekker: New York, 1977; pp 31–36.

(12) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.

(13) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.

(14) Onogi, S.; Masuda, T.; Kitagawa, K. *Macromolecules* **1970**, *3*, 109.

(15) Masuda, T.; Kitagawa, K.; Onogi, S. *Polym. J. (Tokyo)* **1970**, *1*, 418.

(16) Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1668.

(17) Elias, H.-G. "Macromolecules. I. Structure and Properties"; Plenum Press: New York, 1977; pp 287 ff.

(18) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.

(19) Mills, N. J. *Eur. Polym. J.* **1969**, *5*, 675.

(20) Zosel, A. *Rheol. Acta* **1971**, *10*, 215.

(21) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.

(22) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.

(23) Bernard, D. A.; Noolandi, J. *Macromolecules* **1982**, *15*, 1553.

(24) Friedman, E. M.; Porter, R. S. *Trans. Soc. Rheol.* **1975**, *19*, 493.

(25) Prest, W. M.; Porter, R. S. *Polym. J. (Tokyo)* **1973**, *4*, 154.

(26) Casale, A.; Porter, R. S.; Johnson, J. F. *J. Macromol. Sci., Rev. Macromol. Chem.* **1971**, *C5*, 387.

(27) Noolandi, J.; Bernard, D. A. *Can. J. Phys.* **1983**, *61*, 1035.

(28) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.

(29) Akovali, G. *J. Polym. Sci., Part A-2* **1967**, *5*, 875.

(30) Tobolsky, A. V.; Aklonis, J. J.; Akovali, G. *J. Chem. Phys.* **1965**, *42*, 723.

(31) Fox, T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 315; *J. Phys. Chem.* **1951**, *55*, 221.

New Model of the Origin of the Stereospecificity in the Synthesis of Syndiotactic Polypropylene

Paolo Corradini, Gaetano Guerra,* and Rachele Pucciariello

Dipartimento di Chimica, Università di Napoli, 80134 Napoli, Italy.

Received January 22, 1985

ABSTRACT: A new model is suggested for the origin of the syndiospecificity in the Ziegler–Natta polymerization of propene by homogeneous catalytic systems. Nonbonded energy calculations for possible diastereoisomeric situations at the proposed catalytic site are reported. In our model, the configuration of the last added monomeric unit influences directly the chirality (Λ or Δ) of an octahedral catalytic intermediate; such chirality, in turn, determines the configuration of the entering monomeric unit.

Introduction

The problem of the origin of syndiotactic stereoregulation in the polymerization of propene in the presence of homogeneous catalytic systems (e.g., VCl_4–AlR_2Cl or –$AlRCl_2$, where R = alkyl group) has been relatively little investigated up to now.

It has been established that the syndiotactic polymerization of propene is not completely regiospecific and that it must be formally considered as a binary copolymerization of head-to-tail and tail-to-head propene units;[1,2] moreover, the only syndiospecific step would be the insertion of the monomer into a metal–secondary carbon bond, with formation of a new secondary metal–carbon bond.[1-3]

All the proposed models for syndiotactic propagation suppose that the active center is a metal–carbon bond and that the monomer first coordinates to the metal atom; moreover, all of them attribute the stereospecificity to steric factors. However, different driving forces for the syndiospecificity have been proposed.

According to the model of Arlman and Cossee,[4] there are two adjacent accessible positions at the catalytic site, one for the growing chain and one for the incoming monomer. The two positions favor the coordination of the propene monomer with opposite prochiral faces; if the growing polymer chain alternates between the two positions at each insertion step, syndiotactic propagation is ensured. An analogous model has been proposed for the ring-opening polymerization of norbornene derivatives by $ReCl_5$, where the propagation species is a metallocarbene complex.[5]

Most of the authors[3,6,7] favored instead the hypothesis that the syndiotacticity is due to steric repulsions between the methyl group of the complexed propene and the last

0024-9297/85/2218-2030$01.50/0 © 1985 American Chemical Society

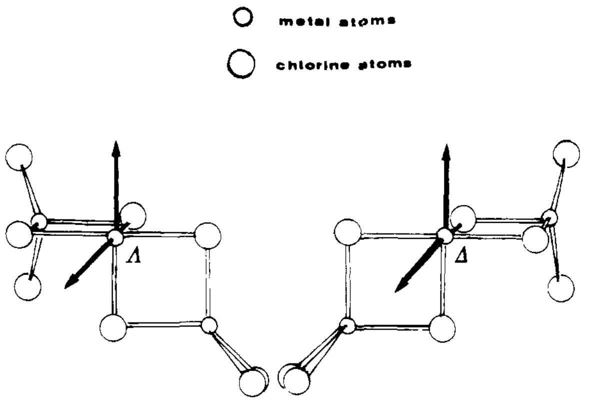


Figure 1. Model catalytic site and its chirality. The arrows indicate the two equivalent coordination positions accessible for the monomer and the growing chain.

unit of the growing chain. The idea that the configuration of the new inserted unit is influenced by the configuration of the previously inserted one seems to be supported by ^{13}C NMR studies of the structure of ethylene–propylene copolymers prepared with syndiospecific catalysts.[8]

The nonbonded interactions at a model catalytic site have been recently studied by Zambelli and Allegra.[9] Their proposed model accounts for several experimental observations concerning the homo- and copolymerization of propene and other olefins in the presence of the syndiospecific systems under consideration. However, Zambelli and Allegra pointed out that steric repulsions between the methyl group of the new coordinated propene and the last unit of the growing chain do not generate energy differences between diastereoisomeric situations in the hypothesized catalytic complex. In fact, even with the assumption of simultaneous coordination to the metal atom of the growing chain and of the monomer, it is not easy to conceive of a model in which the two chirality centers are able to influence each other in the secondary insertion step through direct nonbonded interactions. In the absence of stereospecificity in the catalytic complex, Zambelli and Allegra suggested that the syndiospecific control could arise from steric interferences with the growing chain during olefin approach to the catalyst.[9]

In the present paper a new model of the origin of the syndiospecificity is suggested. In this model the metal atom is assumed to be chiral; the chirality of the growing chain (the configuration of the last added unit) influences the chirality of the coordinated monomer (and hence the configuration of the successive inserted unit) by influencing directly the chirality of the metal atom.

A study of the nonbonded energies at the proposed catalytic site, analogous to that previously effected for heterogeneous catalytic site models,[10,11] is reported.

Catalytic Model, Notation, and Computation Method

The model for the syndiospecific catalytic complex assumed by us consists of a hexacoordinated metal (vanadium) atom surrounded by four chlorine atoms, one secondary carbon atom (i.e., the last atom of the growing chain), and a π-coordinated propene molecule. As in previously proposed models,[9,12,13] the vanadium atom is considered to be in oxidation state 3, and the chlorine ligands are assumed to belong to bridge bonds with other metal atoms, for instance aluminum atoms (Figure 1); the other ligands of the aluminum atoms could be chlorine atoms or alkyl groups, but, for the sake of simplicity, in our calculations only chlorine atoms were considered. In such a hypothesis the two accessible positions for the monomer and the growing chain, indicated by arrows in Figure 1, are equivalent.

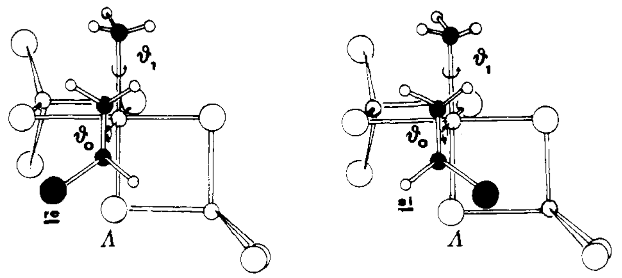


Figure 2. *re* and *si* coordination of the propene on the proposed catalytic site; the growing chain is simulated by a methyl group. The main dihedral angles varied in our computations are also shown.

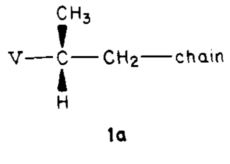
Such a catalytic site is chiral, and the chirality can be labeled by the symbols Λ and Δ, defined for octahedral coordination compounds, in which an atom is bonded to at least two bidentate chelating agents,[14] and already used by us for the heterogeneous polymerization catalytic sites.[10,11] Unlike the heterogeneous model site, interconversion between enantiomeric complexes is assumed to be possible for such a syndiospecific model site. The interconversion would be possible after each insertion step, when the metal atom is pentacoordinated (a coordination vacancy for the incoming monomer being available) and its rate would be higher than the rate of the monomer insertion (roughly evaluated by us, using kinetic literature data on polymerizations at −78 °C of 40 g of propylene in 50 mL of *n*-heptane,[15] as ≅10 insertions per minute). The hypothesis of high interconversion rates for pentacoordinated complexes having two bidentate ligands does not seem to be unreasonable.[16]

We have assumed, as in previously proposed models[3,7,9] and as pointed out by kinetic studies on some vanadium-based catalytic systems,[17] that the propagation reaction occurs through a two-stage mechanism: coordination of the olefin and its subsequent insertion into the metal–polymer bond.

It has been shown that, upon coordination, a prochiral olefin such as propylene may give rise to nonsuperposable *re* or *si* coordinations[18] (Figure 2). The formation of a syndiotactic polymer according to all the proposed mechanisms,[3–7,9] as well as in the present mechanism, implies that successive monomer insertions correspond to coordinations of opposite chirality.

As far as the coordination of the olefin is concerned, placements with the double bond perpendicular to the plane containing the V–olefin and V–chain bonds are to be considered as unfavorable for the successive insertion reaction.[19] If the olefin is unable to reorient itself with the double bond nearly parallel to the V–chain bond, as in Figure 2, no reaction can occur and eventually the olefin abandons the coordination site. Moreover, we assume, as established for the case of the catalytic system VCl_4–Al$(C_2H_5)_2Cl$–anisole at −78 °C,[20] that the polymerization occurs through a cis opening of the double bond of the olefin.

The chirality of the first carbon atom of the chain can be R or S. In particular the R chirality



$$\mathrm{V{-}\overset{CH_3}{\underset{H}{C}}{-}CH_2{-}chain}$$

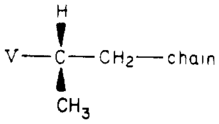
1a

Table I

	bond length, Å	ref
V-Cl	2.45	22
Al-Cl_b[a]	2.25	23
Al-Cl_t[b]	2.05	23
C-H	1.10	9
=C-C	1.50	9
C-C	1.54	9
C=C	1.42	9
	bond angle, deg	**ref**
C=C-H	120.5	9
C=C-C	120.5	9
C-C-H	109	9
V-C-H		
C-C-C	112	9
V-C-C		
H-C(olefin)-H		
H-C(olefin)-C	114.6	9

[a] Cl_b stands for bridged chlorine atom. [b] Cl_t stands for terminal chlorine atom.

is obtained by a cis secondary insertion of a *re*-coordinated propene, and the *S* chirality



1b

is obtained by a cis secondary insertion of an *si*-coordinated propene. For this reason, models **1a** and **1b** will be named here after *re*-ending model chain (or more briefly *re* chain) and *si*-ending model chain (or more briefly *si* chain), respectively.

As far as the orientation of the polymeric chain is concerned, as already assumed for the isospecific polymerization catalytic models,[10,11,19] the second carbon atom of the polymeric chain should be as near as possible to the olefin, compatibly with steric repulsions, in order that the insertion occurs through the "least nuclear motion".[21] In particular, it is assumed that the first carbon–carbon bond of the growing chain, for a possible insertion of the monomer, has to be nearly perpendicular to the already cited plane defined by the V–chain and V–olefin bonds.

The main internal coordinates, which have been varied in the performed calculations, are shown in Figure 2. They are the dihedral angle θ_0 to be associated with the rotation of the olefin around the axis connecting the metal to the center of the double bond and the internal rotation angle θ_1 around the bond between the metal and the first carbon atom of the chain. At $\theta_0 = 0°$ the olefin is oriented in a way suitable for primary insertion, while $\theta_0 = 180°$ corresponds to an orientation suitable for secondary insertion.

Two different alkyl groups are considered in our computations as models for the growing chain: the methyl group and the isopropyl group. In this paper the dihedral angle θ_1 will be referred to an H atom of the alkyl group and for this reason will be indicated explicitly as θ_{1H}. $\theta_{1H} = 0°$ corresponds to the V–C–H moiety cis to the olefin.

The main structural parameters assumed in our computations are listed in Table I, together with the relevant references. The bond angles Cl–V–Cl for the chlorine atoms bridge bonded to the same aluminum were set equal to 85°; in fact, values in the range 80–90° are generally observed.[24-26]

The bond length V–C(alkyl) was set equal to 2.05 Å and the bond length V–C(olefin) was set to 2.10 Å on the basis of metal–carbon distances found in complexes of other transition metals,[27-32,33] taking into account the different values for the covalent radii. However, we have verified that small variations of such distances (±0.10 Å) do change the numerical results but not the general conclusions that can be drawn.

We were not able to fix in an accurate way the bond angle Cl–Al–Cl for the terminal chlorine atoms (hereafter indicated as τ). Such a geometrical parameter has a relevant influence on the results and hence has been varied in our computations.

The method of calculation of the nonbonded potential energies has been previously described.[31] Two different sets of parameters in the potential functions have been used: the parameters proposed by Flory[35] and those reported by Hopfinger,[36] previously used by us also for the isospecific model sites.[37,38]

The torsional potential 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 so for θ_0. Since our comparisons of energy will be made at θ_0 constant, the conclusions may be taken as reasonably sound. The torsional potentials for the other rotation angles (methyl group rotations) are included. For single C–C bonds not adjacent to a double bond we applied the equation

$$E_t = (E_0'/2)(1 + \cos 3\theta) \qquad (1)$$

while for single bonds adjacent to a double bond we applied the equation

$$E_t = (E_0''/2)(1 - \cos 3\theta) \qquad (2)$$

with $E_0' = 2.8$ kcal/mol and $E_0'' = 2.0$ kcal/mol.

Results and Discussion

The possible diastereoisomeric catalytic intermediates are originated by the different combinations of the three cited elements of chirality: (i) the Λ or Δ chirality of the site, (ii) the *si* or *re* chirality of the coordinated α-olefin, and (iii) the chirality of the tertiary carbon atom of the growing chain nearest the metal atom (*si* or *re* chain).

As already established,[9] the chirality elements (ii) and (iii) are not able to influence each other, by nonbonded interactions, in the catalytic complexes having conformations suitable for secondary insertion. For this reason we have simplified the analysis by considering only catalytic intermediates having as a maximum two elements of chirality at a time.

The two possible diastereoisomeric situations for a Λ catalytic site when the growing chain is substituted by a methyl group are sketched in Figure 2. As already pointed out by the sketch, for the orientation of the propene suitable for a secondary insertion ($\theta_0 \cong 180°$) an energy minimum is present only for the *re* coordination of the olefin (energy differences of at least 50 kcal/mol are involved); such a result is independent of the choice of the geometrical parameters. Hence on a Λ site (Δ site) only the insertion of a *re* coordinated (*si* coordinated) propene would be possible in a secondary insertion.

Energy calculations have been performed also for the catalytic model when an ethylene monomer is coordinated (and hence the coordination is achiral) and the growing chain is simulated by an isopropyl group.

The energy values (minimized with respect to the rotation of the methyl groups) for both the sets of the potential function parameters are reported vs. θ_{1H} in Figure 3 for $\theta_0 = 0° = 180°$ and for $\tau = 118°$. Two energy minima are present, roughly in the regions $\theta_{1H} \cong +30°$ and $\theta_{1H} \cong -30°$.

The energy differences between the two minima (ΔE) favor the minimum at $\theta_{1H} \cong +30°$, and its value is strongly

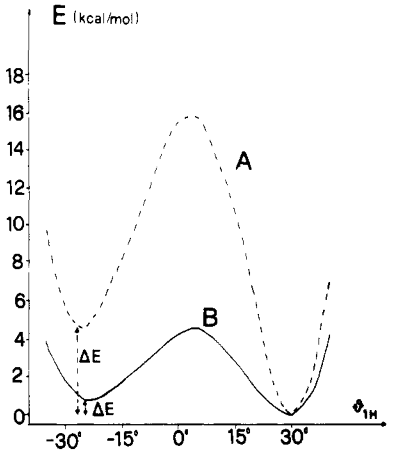


Figure 3. Calculated potential energies (E) (minimized with respect to the rotations of the methyl groups) reported vs. θ_{1H} of the isopropyl group for $\theta_0 = 180°$ and $\tau = 118°$ for a Λ site: (A) calculations using Flory's parameters (dotted line); (B) calculations using Hopfinger's parameters (heavy line).

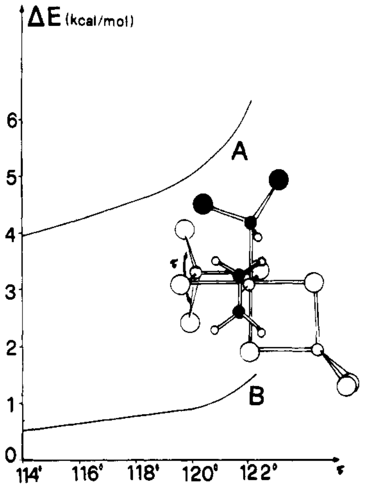


Figure 4. Energy difference between the two minima of the kind of Figure 3 (ΔE) vs. the bond angle τ: (A) calculations using Flory's parameters; (B) calculations using Hopfinger's parameters. The definition of the τ parameter is also visualized in the figure.

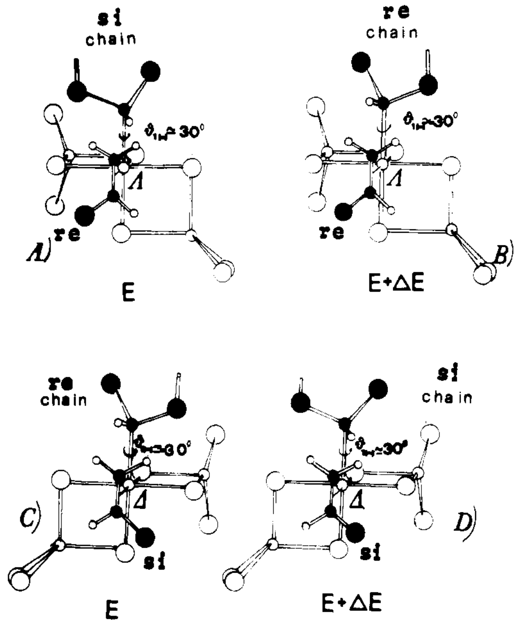


Figure 5. Possible diastereoisomeric catalytic complexes presenting suitable orientation of the growing chain ($\theta_{1H} \cong +30°$ for the *si* chain and $\theta_{1H} \cong -30°$ for the *re* chain) and of the olefin ($\theta_0 = 180°$); only complexes having *re* coordination of the monomer on a Λ site or *si* coordination on a Δ site are sketched (see text). The corresponding minimum energies are indicated on the bottom of the models.

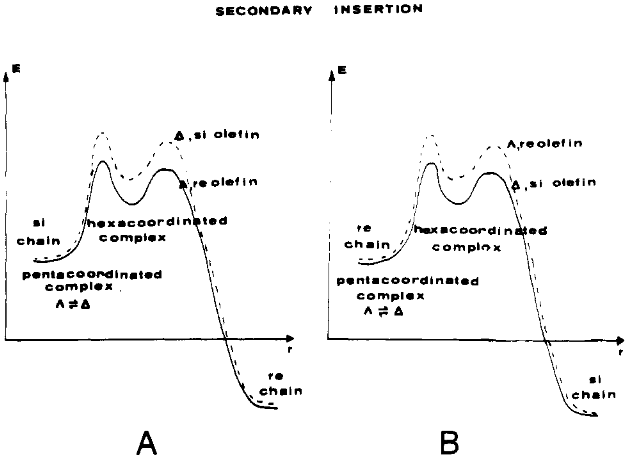


Figure 6. Possible reaction profile for the syndiospecific polymerization of propene. The reagents are chains containing n monomeric units, and the products are chains containing $n + 1$ monomeric units. The reaction pathways indicated by full lines (dashed lines) correspond to syndiotactic (isotactic) enchainments. Our calculations and the reported energy differences (ΔE) of Figures 3 and 4 refer to the intermediate hexacoordinated complexes.

dependent on the set of the energetical parameters and on the selected value for the geometrical parameter τ (as shown in Figure 4).

For the Δ site, of course, results corresponding to the opposite chirality are obtained and the energy differences ΔE favor the region with $\theta_{1H} \cong -30°$.

The only orientation of an *si* chain (*re* chain) suitable for the monomer insertion according to the least nuclear motion corresponds to the energy minimum with $\theta_{1H} \cong +30°$ ($\theta_{1H} \cong -30°$) (see previous section). As a consequence, according to our model, the insertion of an olefin monomer in an *si* chain (*re* chain) would be easier on a Λ site (Δ site), ΔE being the energy difference in the intermediate complexes.

The possible diastereoisomeric intermediates presenting suitable orientations of the growing chain and of the olefin are sketched in Figure 5; the high-energy intermediates having *si* coordination of the olefin on a Λ site or *re* coordination on a Δ site have been excluded. The two diastereoisomeric models of Figure 5A,C present equal minimum energies (E) lower than the minimum energies of the intermediates of Figure 5B,D ($E + \Delta E$). The situations presenting minimum energies correspond to the coordination to the catalytic site of *si* chain and *re* olefin or *re* chain and *si* olefin.

A possible reaction profile, according to our catalytic model, is depicted in Figure 6. The profile starts from a pentacoordinated catalytic complex at which, for instance, an *si* chain is coordinated (Figure 6A) and for which the interconversion between complexes of Λ or Δ chirality is assumed to be fast with respect to the insertion rate. Two possible reaction pathways would be possible, leading to the two hexacoordinated intermediate complexes sketched in Figure 5A,D. The insertion of a new monomer would be slightly favored on a Λ site (for the *si* chain), which in turn, for the monomer orientation suitable for secondary insertion, would allow only the *re* coordination of the propene monomer. If one assumes that an energy difference of the order of magnitude of that (ΔE) calculated in the supposed intermediate complexes is present in the transition state of the rate-determining step, the model is syndiospecific.

Acknowledgment. We acknowledge Prof. Adolfo Zambelli for useful discussions. We thank the National Research Council (CNR) "Progetto Finalizzato Chimica Fine e Secondaria" and the Ministry of Public Education (Italy) for financial support.

Registry No. Propene, 115-07-1.

References and Notes

(1) (a) F. A. Bovey, M. C. Sacchi, and A. Zambelli, *Macromolecules* 7, 752 (1974); (b) A. Zambelli, G. Bajo, and E. Rigamonti, *Makromol. Chem.*, **178**, 1249 (1978).
(2) T. Asakura, I. Ando, A. Nishioka, Y. Doi, and T. Keii, *Makromol. Chem.*, **178**, 791 (1977).
(3) (a) A. Zambelli, C. Tosi, and M. C. Sacchi, *Macromolecules*, **5**, 575 (1969); (b) A. Zambelli and C. Tosi, *Adv. Polym. Sci.*, **15**, 31 (1974).
(4) E. J. Arlman and P. Cossee, *J. Catal.*, **3**, 103 (1964).
(5) (a) H. H. Thoi, K. J. Ivin, and J. J. Rooney, *Makromol. Chem.*, **183**, 1629 (1982); (b) J. G. Hamilton, K. J. Ivin, J. J. Rooney, and L. C. Waring, *J. Chem. Soc., Chem. Commun.*, 159 (1983); (c) J. G. Hamilton, K. J. Ivin, and J. J. Rooney, *J. Mol. Catal.*, **28**, 255 (1985).
(6) J. Boor and E. A. Youngman, *J. Polym. Sci., Part A-1*, **4**, 1861 (1966).
(7) T. Suzuki and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **43**, 1484 (1970).
(8) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).
(9) A. Zambelli and G. Allegra, *Macromolecules*, **13**, 42 (1980).
(10) P. Corradini, G. Guerra, R. Fusco, and V. Barone, *Eur. Polym. J.*, **16**, 835 (1980).
(11) P. Corradini, V. Barone, R. Fusco, and G. Guerra, *J. Catal.*, **77**, 32 (1982).
(12) A. Zambelli, I. Pasquon, R. Signorini, and G. Natta, *Makromol. Chem.*, **112**, 160 (1968).
(13) I. Pasquon, *Pure Appl. Chem.*, **15**, 465 (1967).
(14) Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, **28** (1971).
(15) A Zambelli, G. Natta, I. Pasquon, and R. Signorini, *J. Polym. Sci., Part C*, **16**, 2485 (1967).
(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1966, Part 1, p 172.
(17) Y. Doi, S. Veki, S. Tamura, S. Nagahara, and T. Keii, *Polymer*, **23**, 258 (1982).
(18) K. R. Hanson, *J. Am. Chem. soc.*, **88**, 2731 (1966).
(19) P. Cossee, in "The Stereochemistry of Macromolecules", A. D. Ketley, Ed., Marcel Dekker, New York, 1967, Vol. 1, Chapter 3.
(20) A. Zambelli, M. G. Giongo, and G. Natta, *Makromol. Chem.*, **112**, 183 (1968).
(21) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *Adv. Phys. Org. Chem.*, **15**, 1 (1977).
(22) Von K. P. Lörcher, J. Strähle, and I. Walker, *Z. Anorg. Allg. Chem.*, **452**, 123 (1979).
(23) G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).
(24) J. C. Bart, I. W. Bassi, M. Calcaterra, E. Albizzati, U. Giannini, and S. Parodi, *Z. Anorg. Allg. Chem.*, **482**, 121 (1981).
(25) N. Serpone, P. H. Bird, A. Samogyvary, and D. G. Bickley, *Inorg. Chem.*, **16**, 2381 (1977).
(26) G. J. Olthof, *J. Organomet. Chem.*, **128**, 367 (1977).
(27) I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chiocciola, *J. Am. Chem. Soc.*, **93**, 3787 (1971).
(28) M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, **250**, 395 (1983).
(29) M. R. Shaw, J. McDonald, F. Basolo, and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 2526 (1972).
(30) N. A. Bailey, C. J. Jones, B. L. Shaw, and E. Singleton, *Chem. Commun.*, 1051 (1967).
(31) P. G. H. Troughton and A. C. Shapskii, *Chem. Commun.*, 575 (1968).
(32) M. Calligaris, D. Minichilli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, 2720 (1971).
(33) J. C. Bailor, H. J. Emeleus, R. Myholm, and A. F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry"; Pergamon Press, New York, 1973, Vol. 4, p 829.
(34) V. Petroccone, B. Pirozzi, A. Frasci, and P. Corradini, *Eur. Polym. J.*, **12**, 323 (1976).
(35) U. W. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975).
(36) A. J. Hopfinger, in "Conformational Properties of Macromolecules", Academic Press, New York, 1973.
(37) P. Corradini, G. Guerra, and V. Barone, *Eur. Polym. J.*, **20**, 1177 (1984).
(38) P. Ammendola, G. Guerra, and V. Villani, *Makromol. Chem.*, **185**, 2599 (1984).