Syndiospecific Polymerization of Propene Promoted by Bis(salicylaldiminato)titanium Catalysts: Regiochemistry of Monomer Insertion and Polymerization Mechanism

Marina Lamberti, Daniela Pappalardo, Adolfo Zambelli, and Claudio Pellecchia*

Dipartimento di Chimica, Università di Salerno, I-84081 Baronissi (SA), Italy

Received August 3, 2001

ABSTRACT: Syndiotactic polypropylene samples were synthesized under proper conditions using homogeneous catalytic systems based on bis(iminophenoxy)Ti(IV) derivatives and methylaluminoxane. ^{13}C NMR analysis of the natural abundance end groups suggests that the regiospecificity of propene insertion during the propagation is prevailingly 2,1, although 1,2 insertion is favored in the initiation step. A copolymer of propene with a small amount of 1-^{13}C-ethene was also prepared with one of the title catalysts, and its stereochemical structure was analyzed by NMR, confirming 2,1 monomer insertion as the main mode of propagation.

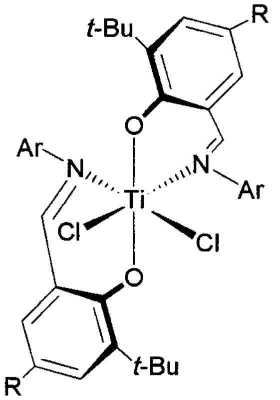
Introduction

One of the outcomes from the enormous development of the homogeneous Ziegler−Natta catalysis has been the expansion of stereospecific polymerizations.[1] Not only have new stereoregular polymers been synthesized from many different monomers, but also "*old*" polymers, such as syndiotactic polypropylene (s-PP), have experienced a renaissance. Syndiotactic-specific polymerization of propene was first achieved by Natta et al.[2] using a catalytic system consisting of VCl_4 (or other hydrocarbon-soluble vanadium compounds) and $Al(C_2H_5)_2Cl$. The V-based systems require subambient reaction temperature (e.g., −78 °C) to afford stereospecific polymerization; they were the only known syndiospecific catalysts until 1988, when Ewen et al.[3] disclosed C_s-symmetric group 4 *ansa*-metallocene catalysts able to produce highly syndiotactic polypropylene even at high temperature. The main mechanistic differences between these two classes of catalysts involve (i) the enantioface selectivity, dictated by the asymmetric configuration of the last unit of the reactive chain (*chain-end* mechanism) for V-catalysts and by the stereochemical structure of the active species (*enantiomorphic site* mechanism) for metallocene catalysts, and (ii) the prevailing mode of insertion of the monomer into the metal−carbon bonds of the propagating species, which is secondary (or 2,1) for V but primary (or 1,2) for metallocenes.[4]

Subsequently, other systems afforded s-PP, namely Brookhart's Ni α-diimine catalysts[5] and "constrained geometry" zirconium or titanium catalysts bearing *tert*-butyl(fluorenylsilyl)amido ligands.[6−8] For the former, a *chain-end* mechanism of steric control operates via 1,2 monomer insertion,[9,10] while for the latter some ambiguity remains in the literature concerning the origin of enantioselectivity,[11,12] which was claimed to be dictated by either a *chain-end*[7] or an *enantiomorphic site* control[8] on the basis of the microstructural analysis of the polymers;[12] the regiochemistry was 1,2.[7,8]

More recently, following the development of a new class of exceedingly active ethylene polymerization catalysts based on bis(salicylaldiminato) group 4 complexes by Fujita and co-workers,[13] the production of s-PP with low activity was achieved by Coates using a titanium catalyst of this class (**1**, Scheme 1 and Figure 1).[14] A moderately higher activity was then reported for related catalysts **3** and **4** (Scheme 1), which remarkably afford highly syndiospecific living polymerization of propene even at relatively high temperatures (0−25 °C).[15] A *chain-end* mechanism was suggested to be responsible for the enantioselectivity on the basis of the polymer microstructure.[14,15]

Scheme 1



Complex 1: R = *t*-Bu; Ar = C_6H_5

Complex 2: R = H; Ar = C_6H_5

Complex 3: R = H; Ar = C_6F_5

Complex 4: R = *t*-Bu; Ar = C_6F_5

In this paper we report a study concerning the regiochemistry and the stereochemistry of propene polyinsertion in the presence of the title catalysts via NMR end-group analysis and investigation of ethene-1-^{13}C/propene copolymers at low ethene content.

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* Corresponding author. Fax 39 089 965296; e-mail pellecchia@chem.unisa.it.

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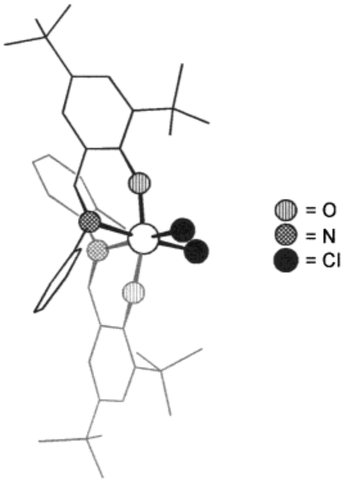


Figure 1. Structure of bis(iminophenoxy) complex **1**.

Table 1. Polymerization Conditions and Results[a]

run	catalyst	reaction time, h	polymer yield, g	activity[b]	[rr], %
1	**1**	6	0.49	0.30	85
2	**2**	6	0.34	0.21	81
3[c]	**2**	1.25	0.09	0.27	87
4[d]	**2**	6	0.78	0.48	62
5[e]	**3**	2	0.24	1.20	94
6[d,e]	**3**	2	0.23	1.15	87

[a] General conditions: toluene = 150 mL; Ti precatalyst = 100 μmol; cocatalyst: MAO = 15 mmol; $T = 20$ °C; propene pressure = 2.7 atm. [b] In $\mathrm{kg_{(PP)}\ mol_{(Ti)}^{-1}\ h^{-1}\ atm^{-1}}$. [c] Terminated by injecting a 2:1 mixture of CH_3CH_2OD and CF_3CH_2OD. [d] Solvent: heptane = 150 mL, cocatalyst: MMAO 15 mmol. [e] Propene pressure = 1 atm.

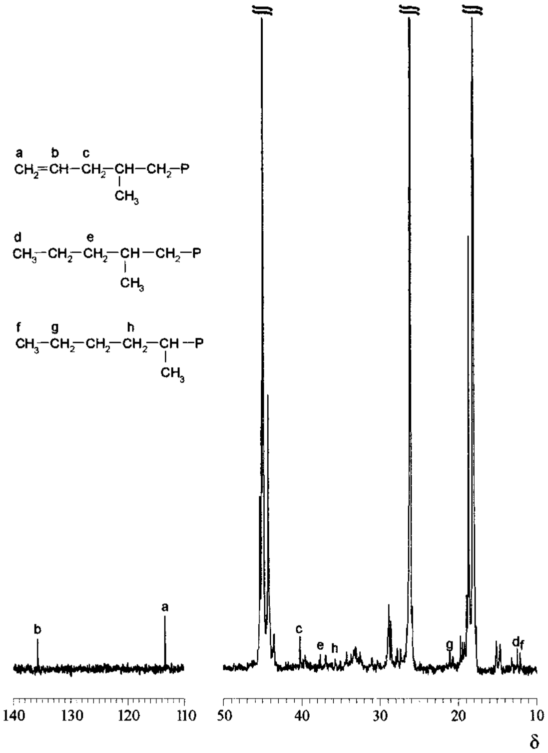
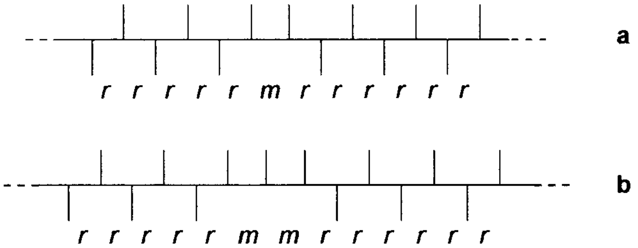


Figure 2. The 62.9 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a polypropylene sample prepared with **2**-MAO (run 2). δ in ppm from hexamethyldisiloxane.

Chart 1

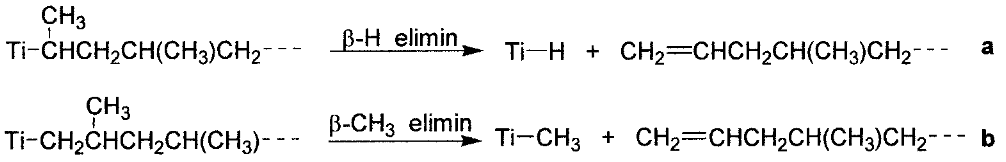


Results and Discussion

Propene was polymerized in the presence of precatalysts **1**−**3** activated by methylaluminoxane (MAO) at 20 °C, as described in the Experimental Section. The relevant results are summarized in Table 1. All of the activities are rather low and range from 0.2 to 1.2 kg of polymer/($\mathrm{mol_{(Ti)}}$ h atm) at Al/Ti ratio 150 and monomer pressures 1−3 atm, with the perfluorinated arylimino complex **3** being more active than the hydrogenated analogue **2**, in agreement with previous results.[14,15] In the case of precatalyst **2,** polymerization in heptane rather than in toluene, using modified methylaluminoxane (MMAO) instead of MAO, results in a significant increase of polymer productivity (cf. runs 2 and 4). The polypropylene samples were analyzed by ^{13}C NMR and found to be prevailingly syndiotactic, with rr triad contents ranging between 62 and 94%, again with precatalyst **3** being the most stereospecific. The polymer samples produced in heptane as the solvent are less stereoregular than those produced in toluene (cf. runs 2 vs 4 and 5 vs 6). The ^{13}C NMR spectrum of sample 2, obtained in run 2, is displayed in Figure 2; the relative intensities of the main methyl resonances in the region between 17.7 and 20.1 ppm from hexamethyldisiloxane (HMDS) confirm that the polymer is prevailingly syndiotactic, the content of rr triads being 81%. Pentad analysis shows that the most intense resonances detected in addition to the rrrr signal (18.1_8 ppm) are those due to the rrmr (18.7_1 ppm) and the rrrm (18.0_4 ppm) sequences, in approximately 1:1 ratio, while the remaining pentad resonances are much less intense. The polymer microstructure therefore mainly consists of blocks of r dyads bridged by *isolated* m dyads, as already reported[14,15] (Chart 1a). This microstructure is that expected for a "*chain-end*" mechanism of steric control, as opposed to an *enantiomorphic site* mechanism of steric control, for which the microstructure of Chart 1b would be anticipated.[4,12]

Further analysis of the spectrum shows the presence of a few regioirregularly arranged monomer units (<2%), as indicated, e.g., by the methyl resonances of the tail-to-tail units observed between 12.6 and 15.2 ppm. In addition to the main resonances due to the backbone carbons (δ 18.1_8, 26.1_1, 44.9_4 ppm), minor resonances having comparable intensities, attributable to the natural abundance end groups, are observed (vide infra). In the unsaturated region resonances at δ 135.7_8 and 113.4_6 ppm from HMDS are present. On the basis of literature assignments,[16] they are attributable to the methine and methylene carbons, respectively, of allyl end groups (Figure 2, carbons b and a). The resonance for the methylene adjacent to the double bond of the mentioned end groups (Figure 2, carbon c) is found at δ 40.2_6, as expected when allyl groups are flanked by an rr triad (carbon c is sensitive to the stereochemical arrangement of the neighboring monomer units),[16] while the resonance of the next methine, expected around 28.6, is obscured by the resonances due to the methine carbons of the regioirregular sequences. The ^{1}H NMR

Scheme 2



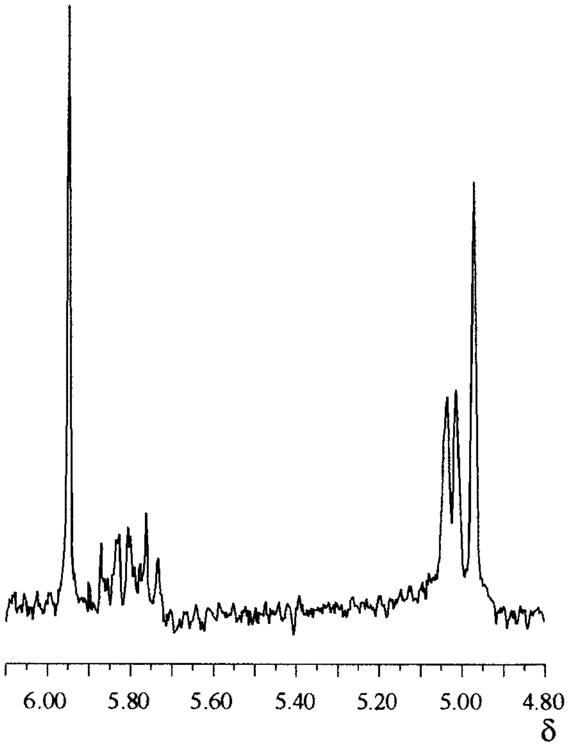


Figure 3. Unsaturated region of the 250 MHz ^{1}H NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a polypropylene sample prepared with **2**-MAO (run 2).

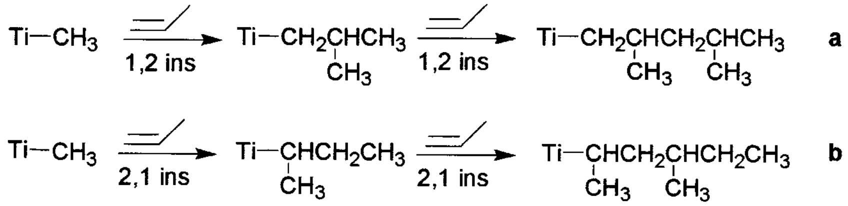
spectrum confirms the presence of allyl end groups[17] (Figure 3). Allyl end groups could in principle originate (Scheme 2) from either (a) β-hydrogen elimination at the methyl of the growing chain-end after a 2,1 insertion or (b) β-methyl elimination after a 1,2 insertion (which has been observed in the polymerization of propene with sterically hindered metallocene catalysts).[16] In the former case, most of the chains would initiate by insertion into Ti−H bonds, while in the latter case, initiation would occur prevailingly on Ti−CH_3 bonds.

In the saturated region of the spectrum, no resonances attributable to isobutyl or *sec*-butyl end groups are observed, thus excluding the presence of end groups deriving from propene insertion into Ti−CH_3 bonds with either 1,2 or 2,1 regiochemistry (see Scheme 3) and ruling out β-methyl elimination as the main termination step. On the contrary, a resonance of intensity comparable to those of the unsaturated end groups is observed at δ 12.4$_5$, which can be attributed to the methyl of *n*-propyl end groups (Figure 2, carbon d).[16] The latter would originate from (at least two) consecutive 1,2 monomer insertions into Ti−H bonds (Scheme 4a). Another resonance attributable to *n*-proyl end groups is observed at δ 38.5$_1$ (Figure 2, carbon e); the intensity of this peak is somewhat lower than that of carbon d, because methylene e is sensitive to the stereochemical arrangement of the neighboring monomer units. (Minor resonances are actually observed around δ 37.7.) According to the literature,[16−19] the lower field resonance is diagnostic of an rr arrangement of the subsequent monomer units. Another less intense high-field methyl resonance is observed at δ 12.1$_1$, which can be attributed to *n*-butyl end groups (Figure 2, carbon f);[18] other resonances of comparable intensity attributable to *n*-butyl end groups are observed at δ 21.1$_0$ (carbon g) and at δ 35.7$_6$ (carbon h), although these regions of the spectrum are not easily interpreted because of the presence of additional resonances due to regioinversions. *n*-Butyl end groups would originate from 1,2 monomer insertion into Ti−H bonds, followed by an insertion with opposed (2,1) regiochemistry (see Scheme 4b).

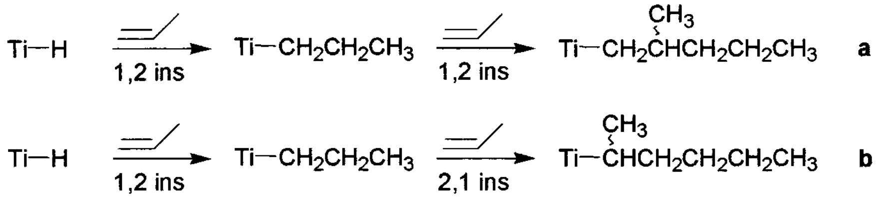
The whole picture suggests that initiation occurs via 1,2 monomer insertion into Ti−H bonds, followed, either immediately or after a few insertion steps, by inversion of the regiochemistry to 2,1, the latter being substantially retained until β-H abstraction occurs in the termination step. (Note that the amount of regioinversions is comparable to the end groups.)

The assumption that the saturated *n*-propyl and *n*-butyl end groups are formed essentially in the initiation step, rather than by hydrolysis of polymer chains bound either to Ti or Al in the termination step, is corroborated by analysis of a polypropylene sample produced under similar conditions (run 3) but terminating the polymerization by adding a mixture of C_2H_5OD and CF_3CH_2OD. No incorporation of deuterium in the polymer was observed by either ^{13}C or ^{2}H NMR analysis, in contrast to similar experiments reported in the literature for other catalysts affording s-PP,[10a,20] such as the previously mentioned V- and Ni-based systems. In summary, 1,2 insertion is favored only in the initiation step, while syndiospecific propagation proceeds via 2,1 monomer insertion, and chain termination occurs mainly via β-hydrogen elimination, while chain transfer with MAO is infrequent, at least under the above conditions. A similar picture was previously observed for the classical V-based catalysts, although the latter are stereospecific only at subambient temperature, mainly due to thermal instability of the active species, at which temperature chain termina-

Scheme 3



Scheme 4



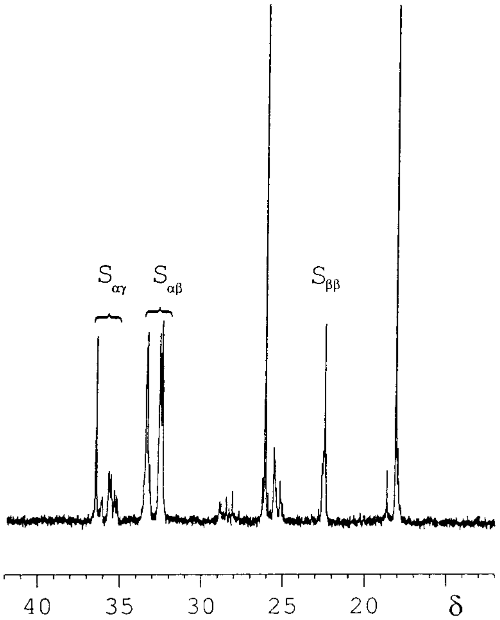
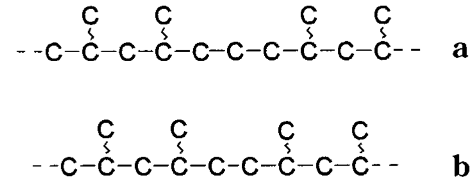


Figure 4. Aliphatic region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propene with a little amount of 1-^{13}C-ethene prepared with **3**-MAO (run 7). δ in ppm from hexamethyldisiloxane.

Chart 2



tion is disfavored ("living" polymerization).[21]

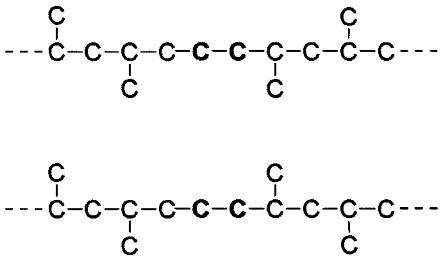
In the ^{13}C NMR spectrum of a polypropylene sample prepared by using precatalyst **3** under the conditions reported in Table 1 (run 5), no natural abundance end groups are detected, in agreement with the living nature of this system.[15] To confirm the proposed regiochemistry and to obtain a deeper insight in the stereochemical polymerization mechanism, we prepared a copolymer of propene containing a very small amount (<2 mol %) of ethene 99% ^{13}C-enriched on C1 (run 7, see the Experimental Section for details). The ^{13}C NMR spectrum of this sample is displayed in Figure 4. Under the conditions used, all ethene units are isolated; i.e., they are flanked on both sides by blocks of propene units and are located in two different environments (see Chart 2), leading to either a three-methylene sequence (Chart 2a) or a two-methylene sequence (Chart 2b). Because of the enrichment of ethene-1-^{13}C, the contribution of unenriched carbons to the resonances of the mentioned sequences is negligible, and of course, the ^{13}C-enriched methylene occupies randomly two locations. The first noticeable finding is the fact that the methylene pairs outnumber the three-methylene sequences, as can be easily deduced by comparing the area of the resonances of the $S_{\alpha\beta}$ carbons (two multiplets centered at δ 32.5 and 33.3 ppm from hexamethyldisiloxane) with the area of the resonances of the $S_{\alpha\gamma}$ carbons (peaks between 35.2 and 36.6 ppm) and of the $S_{\beta\beta}$ carbons (multiplet centered at δ 22.5). In other words, ethene units more often bridge blocks of propene units with opposite regiochemistry than blocks of regioregularly arranged propene units. This agrees with the previous discussion concerning the regiochemistry of monomer insertion based on end-group analysis; 2,1 insertion of propene is favored during the "*normal*" propagation, but 1,2 insertion becomes preferred after the insertion of an ethene unit, which generates a metal–primary carbon bond, and is often followed by a few primary insertions of propene until a 2,1 insertion restores the predominant secondary regiochemistry.

The second relevant aspect is the spreading of the resonances of the $S_{\alpha\beta}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ carbons, indicating a stereoirregular arrangement of the propylene units flanking enriched ethene units. The resonances of the m-$S_{\alpha\beta}$ (the lower field multiplet)[4,22] have substantially the same intensity of the r-$S_{\alpha\beta}$ (the actual r/m ratio is 1.2). This indicates a loss of enantioselectivity after the insertion of an ethene unit followed by propene units with opposed (1,2) regiochemistry. A similar result was obtained for V-based catalysts.[4,22] The fine structure of the $S_{\alpha\gamma}$ resonances is somewhat different from that observed in the case of V-based catalysts: in the latter case,[4,22] the amounts of $S_{\alpha\gamma}$ carbons flanked by r propene dyads (peak at lower field) and of $S_{\alpha\gamma}$ carbons flanked by m propene dyads (peak at higher field) are comparable, suggesting that the three methylene sequences are due prevailingly to enriched ethylene spanning nonstereoregular blocks of 1,2 inserted propene units. In the present case, the r-$S_{\alpha\gamma}$ resonance is more intense than the m-$S_{\alpha\gamma}$; this may be due to the fact that in this case the probability of a 2,1 insertion after an intervening ethene unit is higher than in the case of V-catalysts (i.e., the three methylene sequences are due also to enriched ethylene spanning stereoregular blocks of 2,1 inserted propene units). Finally, the fine structure of the $S_{\beta\beta}$ resonances consists of a sharp peak in addition to some less intense broad peaks; this pattern is somewhat different from that observed for V-based catalyst, requiring further investigation.[23] However, recent results from our laboratory[23] indicate that, under our experimental conditions, the $S_{\beta\beta}$ resonances for the stereochemical sequences of Chart 3, which are diagnostic of the mechanism of steric control, accidentally coincide within the limit of resolution of the spectra, not providing any firm additional information on the origin of the enantioselectivity.

Conclusions

The sterochemical mechanism of syndiospecific polymerization of propene promoted by Fujita's bis(salicylaldiminato)titanium(IV) catalysts,[13] first reported by

Chart 3



Coates and co-workers,[14] has been investigated. End-group NMR analysis of suitable s-PP samples suggests that the regiochemistry of monomer insertion is prevailingly 2,1 during chain growth, although 1,2 insertion is observed in the initiation step occurring into Ti−H bonds. Analysis of the structure of ethene-1-^{13}C/propene copolymers at low ethene content confirms this picture and provides evidence that the steric control is lost after the insertion of an ethene unit, which is mostly followed by stereoirregular blocks of propene units with opposed (1,2) regiochemistry. All of these stereochemical features are very similar to those involved in syndiospecific polymerization of propene promoted by the classical V-based catalysts. Although the exact structure of the active species involved in the latter catalysts remains poorly defined, most of the experimental features of the polymerization were well accounted for by a theoretical study by Guerra et al.,[24] assuming as the active site an octahedral chiral C_2-symmetric V atom surrounded by four Cl atoms (bridging two dialkylaluminum moieties), a secondary growing chain, and the coordinated monomer.[25] In this model, the configuration of the last added monomer unit influences directly the chirality (Λ or Δ) of the octahedral catalytic intermediate: the site chirality, which inverts at each insertion step, in turn dictates the configuration of the incoming propene unit. A QM/MM theoretical study by Guerra and co-workers is in progress[26] to investigate whether a similar mechanism could also explain the syndiotactic-specific polymerization of propene promoted by bis(salicylaldiminato)titanium catalysts.

Experimental Section

Materials. Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk or glovebox techniques. Polymerization grade propylene (SON, 99%) was used without further purification. Toluene and heptane were refluxed over metallic sodium and distilled under a nitrogen atmosphere. Methylaluminoxane (MAO, Aldrich) was purchased as a 10 wt % solution in toluene and used as received. Modified methylaluminoxane (MMAO-3A, Akzo Nobel) was purchased as a 7 wt % solution in heptane and used as received.

Polymerizations. The polymerization conditions and results are detailed in Table 1. As an example, run 2 was carried out in a 500 mL, magnetically stirred, glass autoclave, which was conditioned under dynamic vacuum and thermostated at 20 °C and then charged sequentially with a solution containing toluene (150 mL), MAO (9 mL of a 10 wt % solution in toluene), and **2** (62 mg, 100 μmol). Propene was fed continuously at a pressure of 2.7 atm; after 6 h, the autoclave was vented and the polymerization mixture was poured into acidified ethanol. The precipitated polymer was recovered by filtration and dried under reduced pressure at 80 °C. Yield 0.34 g; $\bar{M}_n = 3.8 \times 10^3$ (evaluated from NMR); see the text for detailed NMR characterization. Runs 5 and 6 were performed similarly, but in 250 mL glass flasks under 1 atm of monomer pressure. Run 3 was terminated by injecting a mixture of CH_3CH_2OD (3 mL) and CF_3CH_2OD (1.5 mL); the polymerization mixture was stirred 1 h and then poured into acidified methanol. Run 7 was carried out at 20 °C in a 250 mL glass flask charged with toluene (150 mL) and MAO (15 mmol); nitrogen was replaced by propene at atmospheric pressure and a solution containing 100 μmol of precatalyst **3** was injected; then a gas mixture of propene and 1-^{13}C-ethene (99% enriched, 0.4 mol %) was bubbled through the solution for 5 h. The run was terminated by pouring the reaction mixture into methanol and the copolymer (0.36 g) recovered as above.

Analysis of the Polymers. The polymers obtained in runs 1−6 were analyzed by NMR on an AM 250 Bruker spectrometer operating in the Fourier transform mode. The ^{13}C NMR spectrum of the copolymer sample prepared in run 7 was recorded on a Bruker Advance 400 MHz spectrometer. The spectra were recorded in $C_2D_2Cl_4$ at a temperature of 100 °C and referenced vs hexamethyldisiloxane (HMDS).

Acknowledgment. We thank Professor G. Guerra for valuable discussions. This work was supported by the Italian Ministry of University and Research (MURST, PRIN 2000) and by the Italian National Research Council (CNR).

References and Notes

(1) For recent collections of reviews on homogeneous olefin polymerization catalysts, see: (a) *Chem. Rev.* **2000**, *100* (4). (b) *Top. Catal.* **1999**, *7* (1−4). (c) *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, UK, 2000.

(2) Natta, G.; Pasquon, I.; Zambelli, A. *J. Am. Chem. Soc.* **1962**, *84*, 1488.

(3) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (b) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Curtis, S.; Cheng, H. N. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1990; p 271.

(4) For a recent review on syndiotactic polymerization of propene promoted by different catalysts, see: Zambelli, A.; Sessa, I.; Grisi, F.; Fusco, R.; Accomazzi, P. *Macromol. Rapid Commun.* **2001**, *22*, 297.

(5) (a) Pellecchia, C.; Zambelli, A. *Macromol. Rapid Commun.* **1996**, *17*, 333. (b) For a review on nickel α-diimine catalysts, see: Ittel, S. D.; Johnson, L. K.; Brookhart, M. In ref 1a, p 1169.

(6) Turner, H. W.; Hlatky, G. G.; Canich, J. A. M. PCT Int. Appl. WO 9319103, 1993.

(7) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1997**, *30*, 4783.

(8) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184.

(9) Pellecchia, C.; Zambelli, A.; Oliva, L.; Pappalardo, D. *Macromolecules* **1996**, *29*, 6990.

(10) (a) Pellecchia, C.; Zambelli, A.; Mazzeo, M.; Pappalardo, D. *J. Mol. Catal. A: Chem.* **1998**, *128*, 229. (b) Milano, G.; Guerra, G.; Pellecchia, C.; Cavallo, L. *Organometallics* **2000**, *19*, 1343.

(11) McKnight, A. L.; Masood, M. A.; Waymouth, R. M.; Straus, D. A. *Organometallics* **1997**, *16*, 2879.

(12) Busico, V.; Cipullo, R. *Prog. Polym. Sci.* **2001**, *26*, 443.

(13) (a) Fujita, T.; Tohi, Y.; Mitani, M.; Matsui, S.; Saito, J.; Nitabaru, M.; Sugi, K.; Makio, H.; Tsutsui, T. Eur. Pat. EP 0874005, 1998 (Mitsui Chemical); *Chem. Abstr.* 129:331166. (b) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, 1065. (c) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, 1263. (d) Matsui, S.; Mitani, M.; Saito, J.; Matsukawa, N.; Tanaka, H.; Nakano, T.; Fujita, T. *Chem. Lett.* **2000**, 554. (e) Matsukawa, N.; Matsui, S.; Mitani, M.; Saito, J.; Tsuru, K.; Kashiwa, N.; Fujita, T. *J. Mol. Catal. A* **2001**, *169*, 99. (f) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847.

(14) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626.

(15) (a) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134. (b) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Nashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576.
(16) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.
(17) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.
(18) Hayashi, T.; Inoue, Y.; Chujo, R.; Asakura, T. *Macromolecules* **1988**, *21*, 2675.
(19) Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 3356.
(20) Zambelli, A.; Longo, P.; Terenghi, S.; Recupero, D.; Zannoni, G. *J. Mol. Catal. A* **2000**, *152*, 25.
(21) Doi, Y.; Nozawa, F.; Murata, M.; Suzuki, S.; Soga, K. *Makromol. Chem.* **1985**, *186*, 1825.
(22) (a) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249. (b) Grassi, A.; Ammendola, P.; Longo, P.; Albizzati, E.; Resconi, L.; Mazzocchi, R. *Gazz. Chim. Ital.* **1988**, *118*, 539. (c) Ammendola, P.; Xiao, S.; Grassi, A.; Zambelli, A. *Gazz. Chim. Ital.* **1988**, *118*, 769.
(23) A detailed reinvestigation of ethene-1-^{13}C/propene copolymers at low ethene content produced by different catalysts is in progress and will be reported shortly.
(24) Corradini, P.; Guerra, G.; Pucciariello, R. *Macromolecules* **1985**, *18*, 2030.
(25) Zambelli, A.; Pasquon, I.; Signorini, R.; Natta, G. *Makromol. Chem.* **1968**, *112*, 160.
(26) Guerra, G. Personal communication.

MA011389T