

# High-Field $^{13}\text{C}$ NMR Characterization of Ethene-1- $^{13}\text{C}$ /Propene Copolymers Prepared with $C_s$ -Symmetric *ansa*-Metallocene Catalysts: A Deeper Insight into the Regio- and Stereoselectivity of Syndiotactic Propene Polymerization

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Received July 1, 1998; Revised Manuscript Received September 24, 1998

**ABSTRACT:** In this paper, we report the results of a 150 MHz  $^{13}\text{C}$  NMR characterization of ethene-1- $^{13}\text{C}$ /propene copolymers at low (<5 mol %) ethene content prepared in the presence of the syndiotactic-selective *ansa*-metallocene catalyst (Me)(Ph)C(cyclopentadienyl)(9-fluorenyl)ZrCl<sub>2</sub> (cocatalyst, MAO). In particular, from the fine structure of the resonances of the ethene-1- $^{13}\text{C}$  units we conclude that the enantioselectivity of 1,2-propene insertion is substantially lower and the probability of chain back-skip substantially higher after an ethene insertion than after a propene one. Moreover, we find that the regioirregular 2,1-propene units (whose concentration is higher than claimed in the literature) are also substantially stereoirregular.

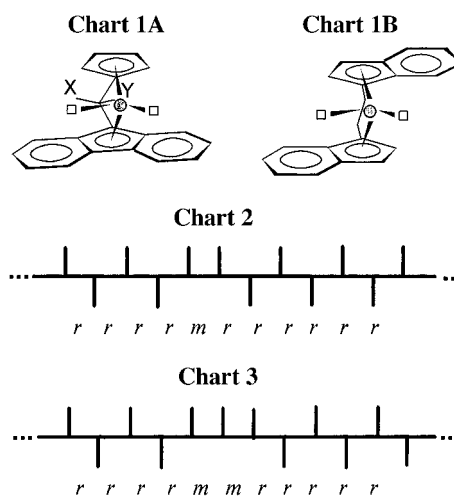
## Introduction

Highly syndiotactic polymers of 1-alkenes can be obtained in the presence of catalyst systems based on  $C_s$ -symmetric *ansa*-metallocenes of the fourth column (such as (X)(Y)C(cyclopentadienyl)(9-fluorenyl)ZrCl<sub>2</sub> with X and Y = methyl or phenyl (Chart 1A) in combination with methylaluminoxane (MAO).<sup>1,2</sup>

The stereoselectivity of such systems has been convincingly explained by Ewen and co-workers in terms of a chain migratory insertion mechanism,<sup>1a,b</sup> in which the growing polymer chain and the incoming monomer are assumed to exchange regularly their coordination to the two enantiotopic sites available at the transition metal.<sup>3</sup>

Consistent with the experimental finding, this mechanism predicts a fading of stereoselectivity with decreasing monomer concentration, resulting from an increased probability for the growing chain to skip back to its pristine coordination site between two consecutive monomer insertions, ending up with the formation of an ...*rrrrrmmrrrr*... stereodefekt (Chart 2).<sup>1b</sup>

Low amounts of ...*rrrrrmmrrrr*... stereodefekts (Chart 3), also observed in the polymers by  $^{13}\text{C}$  NMR,<sup>1</sup> can be ascribed instead (predominantly) to occasional monomer insertions with the less reactive enantioface. The concentration of such defects increases smoothly with increasing temperature but is substantially independent of monomer concentration;<sup>1b</sup> therefore, it appears that, different from the case of the isotactic-selective  $C_2$ -symmetric metallocenes<sup>4</sup> (Chart 1B), side reactions of growing chain epimerization<sup>5</sup> have very limited effects, if any, on the performance of  $C_s$ -symmetric metallocenes.<sup>6</sup> This is consistent with their remarkable stereoselectivity (under conditions of negligible chain



back-skip),<sup>1</sup> despite the relatively open steric environment of the active metal resulting from the short interannular bridge and the absence of substituents on the aromatic rings (Chart 1A).

Compared to the  $C_2$ -symmetric catalysts, the  $C_s$ -symmetric ones are also known to be more regioselective. In particular, isotactic polypropylene samples made with the former catalysts typically contain 0.2–1 mol % of isolated 2,1- and/or 3,1- misinserted units,<sup>4</sup> whereas no regioirregular enchainments are normally detected by  $^{13}\text{C}$  NMR in highly syndiotactic polypropylene samples.<sup>7,8</sup>

However, in a recent  $^{13}\text{C}$  NMR investigation<sup>9</sup> of ethene-1- $^{13}\text{C}$ /propene copolymers at low (<5 mol %) ethene content prepared with a representative  $C_s$ -symmetric metallocene catalyst (Chart 1A, with X = methyl, Y = phenyl<sup>2</sup>), we clearly observed ethene-1- $^{13}\text{C}$  units adjacent to regioirregular 2,1-propene units. From a quantitative evaluation of the spectra, we extrapo-

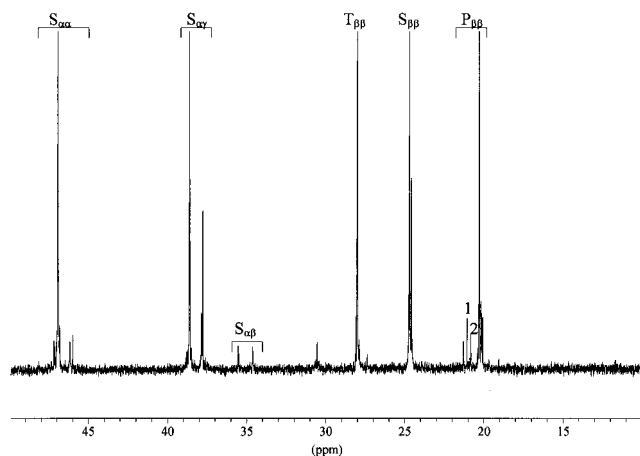
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**Table 1.** Preparation of Ethene-1-<sup>13</sup>C/Propene Copolymer Samples A, B, and C (See Text)

sample	<i>p</i> (bar) <sup>a</sup>	[E]/[P] × 10 <sup>3</sup> (liquid phase) <sup>b</sup>	<i>Q</i> <sub>E</sub> (mol %) <sup>c</sup>
A	1.0	3.72 ± 0.04	1.36 ± 0.02
B	1.0	7.80 ± 0.04	2.46 ± 0.03
C	0.3	2.98 ± 0.04	1.36 ± 0.05

<sup>a</sup> Total monomer pressure. <sup>b</sup> E = ethene, P = propene; estimated from the composition of the gas feed according to ref 22. <sup>c</sup> <sup>13</sup>C NMR mole fraction of ethene units in the copolymer. Other experimental conditions: [Zr] = 1 × 10<sup>-4</sup> M; [Al]/[Zr] = 1 × 10<sup>3</sup>; *T*<sub>p</sub> = 10 °C.



**Figure 1.** 150 MHz <sup>13</sup>C NMR spectrum of ethene-1-<sup>13</sup>C/propene copolymer sample B. Relevant peak attributions are explicitly indicated. In the *P*<sub>ββ</sub> region, peaks marked as 1 and 2 arise from *rrmrrr* and *rrrrrr* heptads, respectively.

lated<sup>9</sup> a fraction of 2,1-misinsertions in the propene homosequences (at 10 °C) as high as 0.08 mol %, that is just below <sup>13</sup>C NMR detectability in a homopolymer sample at natural <sup>13</sup>C abundance and at most 1 order of magnitude lower than that in isotactic polypropylene samples prepared with typical *C*<sub>2</sub>-symmetric metallocene catalysts at the same temperature.<sup>4</sup>

From the fine structure of the ethene-1-<sup>13</sup>C resonances in the 150 MHz <sup>13</sup>C NMR spectra of such copolymers, we have also obtained a deeper insight into the stereoselectivity of this important class of metallocene catalysts, as is discussed in the present paper.

## Results and Discussion

Three ethene-1-<sup>13</sup>C/propene copolymer samples at low ethene-1-<sup>13</sup>C content were synthesized in the presence of the catalyst system (Me)(Ph)C(cyclopentadienyl)(9-fluorenyl)ZrCl<sub>2</sub> (I)/MAO in toluene at 10 °C (Table 1). Samples A and B were prepared at the same total monomer pressure of 1.0 bar but at different comonomer feeding ratios, to result in ethene-1-<sup>13</sup>C incorporations of 1.4 and 2.5 mol %, respectively; sample C, with an ethene-1-<sup>13</sup>C content (1.4 mol %) coincident with that of sample A, was obtained instead at a total monomer pressure of 0.3 bar.

The three copolymers were characterized by 150 MHz <sup>13</sup>C NMR (the spectrum of sample B is shown in Figure 1). The main results obtained are summarized in Table 2.

The resonances of the *P*<sub>ββ</sub>, *T*<sub>ββ</sub>, and *S*<sub>αα</sub> C's<sup>10</sup> of the propene units in prevalingly syndiotactic homosequences are observed in the ranges of  $\delta = 19.6$ – $21.4$ ,  $28.1$ – $28.5$ , and  $46.6$ – $47.6$  ppm (downfield of TMS), respectively. Tacticity splittings are very evident; the methyl resonance, in particular, is resolved at the

**Table 2.** Main Results of the 150 MHz <sup>13</sup>C NMR Characterization of Ethene-1-<sup>13</sup>C/Propene Copolymer Samples A, B, and C

sample	<i>rrmrrr</i> (%) <sup>a</sup>	<i>rrrrrr</i> (%) <sup>a</sup>	<i>P</i> <sub>err</sub> <sup>b</sup>	<i>P</i> <sub>sk</sub> <sup>c</sup>	[ <i>r</i> ]/[ <i>m</i> ] <sup>d</sup>	<i>I</i> ( <i>r</i> - <i>S</i> <sub>αγ</sub> )/ <i>I</i> ( <i>m</i> - <i>S</i> <sub>αγ</sub> ) <sup>e</sup>	<i>Q</i> <sub>E</sub> (mol %) <sup>f</sup>
A	2.4	1.8	0.014	0.010	26	3.45 ± 0.06	0.054 ± 0.005
B	2.4	2.1	0.014	0.012	25	3.31 ± 0.04	0.072 ± 0.005
C	2.5	4.2	0.015	0.026	18	3.37 ± 0.04	0.039 ± 0.005

<sup>a</sup> Fractional abundance in the propene homosequences. <sup>b</sup> Probability of monomer insertion with the less reactive enantioface at each of the two enantiotopic active sites. <sup>c</sup> Probability of "skipped" monomer insertion. <sup>d</sup> Ratio between *r* and *m* diads in the propene homosequences. <sup>e</sup> Integral ratio of the *r*-*S*<sub>αγ</sub> and *m*-*S*<sub>αγ</sub> resonances. <sup>f</sup> <sup>13</sup>C NMR mole fraction of 2,1-propene units followed by ethene units (referred to the total propene unit content).

Chart 4

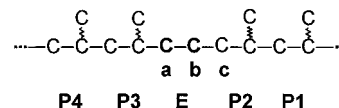
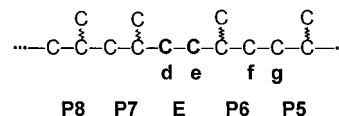


Chart 5



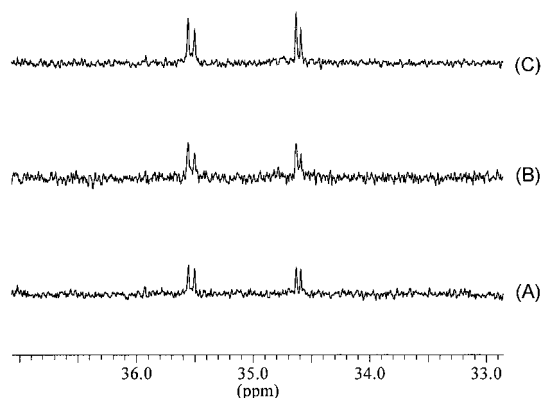
heptad level. From the normalized integrals of the well-separated peaks corresponding to the *rrmrrr* ( $\delta = 20.87$  ppm) and *rrrrrr* ( $\delta = 21.05$  ppm) heptads,<sup>11</sup> we evaluated (Table 2, columns 2–5) the concentrations of stereodeflects associated with skipped insertions (Chart 2) or wrong enantioface selections (Chart 3). In line with the expectation,<sup>1</sup> the latter was found to occur in equal amounts (1.4–1.5 mol %) in all three samples, whereas the former turned out to be more abundant in sample C (2.6 mol %), prepared at a lower monomer concentration, than in samples A and B (1.0 and 1.2 mol %, respectively).

The signals arising from the <sup>13</sup>C-enriched ethene units indicate that these are practically all isolated (which is fairly obvious, due to their low concentration), and are located in the two different constitutional environments of Charts 4 and 5.<sup>12</sup> It is important to note, for the following discussion, that propene insertion is predominantly of the 1,2-type,<sup>1,13</sup> which implies that the active end of the growing chain is at the left-hand side of each structure.

The structure of Chart 4 is fully regioregular; however, the spectra indicate deviations of the stereochemistry from that of the highly stereoregular propene homosequences. Indeed, the resonances of the *S*<sub>αγ</sub> C-a and *S*<sub>ββ</sub> C-b of the ethene-1-<sup>13</sup>C unit (in 1:1 integral ratio since the <sup>13</sup>C-enriched methylene occupies randomly the two locations and the contribution of the unenriched *S*<sub>αγ</sub> C-c belonging to the propene unit P2 is negligible) occur as multiplets (Figure 1) due to the occurrence due to the presence of different stereostructures.

In particular, the *S*<sub>αγ</sub> resonance (see expansions in Figure 2 A–C) is split into two doublets, at  $\delta \approx 38.6$  and 37.8 ppm, which can be assigned to sequences in which the ethene-1-<sup>13</sup>C unit is followed by two propene units (P3 and P4 in Chart 4) in racemic (*r*) or meso (*m*) arrangement, respectively (Chart 4A and 4B).<sup>14</sup> The integral ratio *I*(*r*-*S*<sub>αγ</sub>)/*I*(*m*-*S*<sub>αγ</sub>) was found to be independent of the monomer concentration and as low as 3.3–3.4 (Table 2, column 7), whereas the average [*r*]/[*m*] ratio measured in the propene homosequences is 26 for





**Figure 3.** Expansion of the 150 MHz  $^{13}\text{C}$  NMR spectra of ethene-1- $^{13}\text{C}$ /propene copolymer samples A, B, and C in the region of the  $S_{\alpha\beta}$  resonance.

Let us consider now the structure of Chart 5. This is the result of ethene insertion after an occasional regioirregular 2,1 propene enchainment (unit P6), after which the correct 1,2-propene enchainment is restored. In fact, propene insertion in a  $\text{Zr}-\text{CH}(\text{CH}_3)-\text{CH}_2(\text{P}_n)$  bond ( $\text{P}_n$  = polymeryl) is exceedingly slow,<sup>18,19</sup> so that, even at the low ethene/propene feeding ratios used in this investigation, a 2,1-last-inserted propene unit tends to be followed by an ethene one.<sup>9</sup>

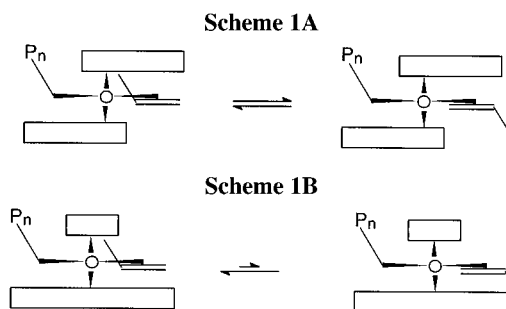
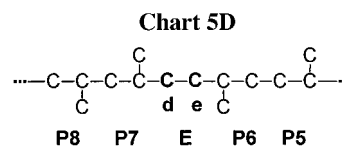
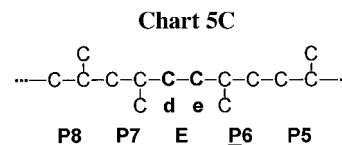
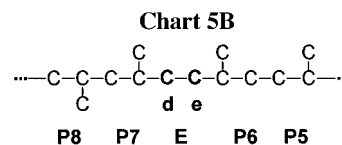
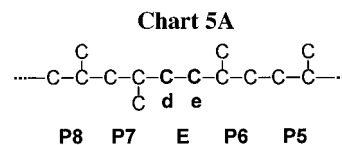
This structure is detectable by  $^{13}\text{C}$  NMR only because of the  $^{13}\text{C}$  enrichment of the ethene unit: as a matter of fact, only the signals of the  $S_{\alpha\beta}$  C's d and e of Chart 5 (in 1:1 integral ratio since the  $^{13}\text{C}$ -enriched methylene of ethene-1- $^{13}\text{C}$  occupies randomly the two locations) were observed. From such signals, we evaluated (last column of Table 2) a fraction of regioirregular propene units of  $0.054 \pm 0.05$  mol % in sample A,  $0.072 \pm 0.05$  mol % in sample B, and  $0.039 \pm 0.05$  mol % in sample C (i.e., in all cases lower than the "saturation" value of 0.08 mol %, which is reached at a higher ethene content<sup>9</sup>).

Concerning the stereochemistry of this structure, we note that the resonances of the  $S_{\gamma\alpha\beta\delta^+}$  C-d and  $S_{\delta\alpha\beta\delta}$  C-e appear as two doublets, at  $\delta = 35.50\text{--}35.55$  and  $34.59\text{--}34.625$  ppm respectively (see expansions in Figure 3A–C), whose components are not far from a 1:1 integral ratio, independent of the comonomer feeding ratio and total monomer concentration.

The  $\delta$  value of the  $^{13}\text{C}$ -enriched  $S_{\gamma\alpha\beta\delta^+}$  C-d proves that the propene diad P7-P8 is (predominantly) in *r* arrangement.<sup>14</sup> However, on the basis of literature  $^{13}\text{C}$  NMR data on ethene/propene copolymers<sup>14</sup> and on model alkanes,<sup>15</sup> from the discussed fine structure of the  $S_{\gamma\alpha\beta\delta^+}$  and  $S_{\delta\alpha\beta\delta}$  resonances it can be concluded that the sequence P6–E–P7 is configurationally disordered, in the sense that the cumulative fraction of the two structures of Charts 5A and 5B is comparable with that of the two structures of Charts 5C and 5D.

*The above implies that, in syndiotactic polypropylene samples prepared in the presence of the catalyst under investigation, the regioirregularly inserted 2,1-propene units are also substantially stereoirregular.*

This is at variance with what is known to happen in the presence of  $C_2$ -symmetric metallocene catalysts, for which both 1,2- and 2,1-propene insertions are highly enantioselective, and occur with opposite enantiofaces.<sup>20,21</sup> According to recent molecular mechanics calculations on models of metallocene catalysts,<sup>7</sup> the origin of this inverse correlation can be traced to the fact that



whenever a propene molecule approaches the transition metal with the "wrong" enantioface for 1,2-insertion, rotation around the coordination bond followed by 2,1-insertion can represent a viable alternative to a stereoirregular 1,2-insertion (Scheme 1A).

This would not be the case at a  $C_s$ -symmetric active species like that of Chart 1A, due to nonbonded contacts between the methyl substituent of the monomer and one of the  $C_6$  rings of the fluorenyl moiety (Scheme 1B).<sup>7</sup>

Our results indicate that this conclusion has some validity, although it appears that the steric effects presiding over the regioselectivity of  $C_s$ -symmetric metallocenes have been overestimated and/or that electronic effects are able to balance in part such effects.

## Conclusions

In this paper, we have reported the results of a 150 MHz  $^{13}\text{C}$  NMR characterization of ethene-1- $^{13}\text{C}$ /propene copolymers at low (<5 mol %) ethene content prepared in the presence of the syndiotactic-selective *ansa*-metallocene catalyst (Me)(Ph)C(cyclopentadienyl)(9-fluorenyl)ZrCl<sub>2</sub> (cocatalyst, MAO).<sup>1,2</sup>

In particular, from the fine structure of the resonances of the ethene-1- $^{13}\text{C}$  units we have pointed out that the enantioselectivity of 1,2-propene insertion is substantially lower and the probability of chain back-skip is substantially higher after an ethene insertion than after a propene one. These findings can be rationalized in terms of a lower steric hindrance and of a higher conformational mobility of the growing polymer chain (respectively) in the former case.



We have also shown that the regioirregular 2,1-propene units (whose concentration is higher than that claimed in the literature<sup>7</sup>) are also substantially stereoirregular, at variance with what is known to happen with typical isotactic-selective  $C_2$ -symmetric *ansa*-metallocene catalysts.<sup>4,20,21</sup>

## Experimental Section

**Catalyst and Reagents.** (Me)(Ph)C(cyclopentadienyl)(9-fluorenyl)ZrCl<sub>2</sub> (**I**) was prepared according to the literature.<sup>2</sup> MAO (10 wt % solution in toluene) was provided by Witco GmbH (Bergkamen, FRG). Ethene-1-<sup>13</sup>C (Isotec Inc., 99+% isotopic purity) and propene (Società Ossigeno Napoli, polymerization grade) were used as received.

**Copolymerization Procedure.** All copolymerizations were run at 10 °C, in a 100-mL Pyrex reactor containing a toluene solution (20 mL) of catalyst **I** ( $[Zr] = 1 \times 10^{-4}$  M) and MAO (Al/Zr mole ratio =  $1 \times 10^3$ ). Gas mixtures of ethene-1-<sup>13</sup>C and propene (preparation of copolymer samples A and B) or of ethene-1-<sup>13</sup>C, propene, and N<sub>2</sub> (preparation of copolymer sample C) at the appropriate composition (Table 1), prepared with vacuum line techniques and analyzed by gas chromatography, were bubbled through the liquid phase at atmospheric pressure and a flow of 0.10 L/min for 30 min. Under such conditions, total monomer conversions were lower than 5%, this ensuring a nearly constant comonomer feeding ratio. The copolymers were coagulated with excess methanol acidified with HCl (aqueous, concentrated), filtered, washed with more methanol, and vacuum-dried. Yields: 0.5 g for samples A and B and 0.2 g for sample C.

**<sup>13</sup>C NMR Characterizations of the Copolymers.** The spectra were recorded with a Bruker AMX 600 spectrometer operating at 150 MHz, on 1% w/v copolymer solutions in tetrachloroethane-1,2-*d*<sub>2</sub> (also used as the internal standard) at 70 °C. Conditions: 5-mm probe; 45° pulse; acquisition time, 2.3 s; relaxation delay, 2.0 s; 64 K points; 15 K transients. Fourier transformation was performed either without any correction or, for resonance assignment only, after the application of a weak resolution-enhancing Gaussian function. The assignment of the various constitutional and configurational sequences in the samples and the measurement of their fractional abundances were made according to the literature.<sup>11,14,15</sup>

**Acknowledgment.** We thank Witco GmbH (Bergkamen, FRG) for providing free samples of the MAO solution in toluene.

## References and Notes

- (1) (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.; Kodansha: Tokyo, 1990; pp 439–482. (c) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117. (d) Razavi, A.; Peters, L.; Nafpliotis, L.; Atwood, J. L. In *Catalyst Design for Tailor-Made Polyolefins*; Soga, K., Terano, M., Eds.; Kodansha: Tokyo, 1994; Supplement.
- (2) Winter, A.; Rohrmann, J.; Antberg, M.; Dolle, V.; Spaleck, W. German Patent 3,907,965, Sep 13, 1990, to Hoechst AG; *Chem. Abstr.* **1991**, *114*, 165103w.
- (3) For a molecular mechanics study of this mechanism, see: Cavallo, L.; Guerra, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1991**, *24*, 1784.
- (4) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907, and refs therein.
- (5) (a) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329. (b) Busico, V.; Cipullo, R. *Macromol. Symp.* **1995**, *89*, 277. (c) Busico, V.; Cipullo, R. *J. Organomet. Chem.* **1995**, *497*, 113. (d) Leclerc, M.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (e) Resconi, L.; Fait, A.; Piemontesi, F.; Colonna, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667. (f) Busico, V.; Caporaso, L.; Cipullo, R.; Landriani, L.; Angelini, G.; Margonelli, A.; Segre, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 2105. (g) Leclerc, M.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024. (h) Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971. (i) Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal., Part A (Chem.)* **1998**, *128*, 53.
- (6) In line with this conclusion, we found that, in poly(propene-2-*d*) samples prepared at 80 °C and low monomer concentration in the presence of the investigated catalyst system, the fraction of monomeric units with the D label migrated to position 1 or 3 as a result of growing chain epimerization is <2 mol %.
- (7) Guerra, G.; Longo, P.; Cavallo, L.; Corradini, P.; Resconi, L. *J. Am. Chem. Soc.* **1997**, *119*, 4394.
- (8) Resonances indicative of regioirregular enchainments just above detectability have been noted in the <sup>13</sup>C NMR spectrum of a syndiotactic polypropylene sample prepared with the catalyst system Me<sub>2</sub>C(cyclopentadienyl)(9-fluorenyl)ZrCl<sub>2</sub>/MAO at 80 °C; see ref 1b, Figure 7.
- (9) Busico, V.; Cipullo, R.; Talarico, G.; Caporaso, L. *Macromolecules* **1998**, *31*, 2387.
- (10) For the nomenclature of the magnetic C's, see: Carman, C. J.; Wilkes, C. E. *Rubber Chem. Technol.* **1971**, *44*, 781.
- (11) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M.; Segre, A. L. *Macromolecules* **1997**, *30*, 6251.
- (12) In the adapted Fischer notations of Charts 4 and 5, the waving bond indicates that the configuration of the tertiary C is not specified.
- (13) Longo, P.; Proto, A.; Grassi, A.; Ammendola, P. *Macromolecules* **1991**, *24*, 4624.
- (14) Cheng, H. N. *Macromolecules* **1984**, *17*, 1950.
- (15) Bajo, G.; Rigamonti, E.; Zambelli, A. *Makromol. Chem.* **1978**, *179*, 1249.
- (16) (a) Corradini, P.; Guerra, G. *Prog. Polym. Sci.* **1991**, *16*, 239. (b) Corradini, P.; Busico, V.; Cavallo, L.; Guerra, G.; Vacatello, M.; Venditto, V. *J. Mol. Catal.* **1992**, *74*, 433, and references therein.
- (17) (a) Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Rigamonti, E. *Macromolecules* **1980**, *13*, 798. (b) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, E. *Macromolecules* **1982**, *15*, 211. (c) Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Tritto, I. *Macromolecules* **1982**, *15*, 831. (d) Sacchi, M. C.; Locatelli, P.; Tritto, I.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 661. (e) Tritto, I.; Sacchi, M. C.; Locatelli, P. *Makromol. Chem.* **1986**, *187*, 2145. (f) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo, P.; Proto, A. *Macromolecules* **1986**, *19*, 2703. (g) Longo, P.; Grassi, A.; Pellicchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015. (h) Sacchi, M. C.; Locatelli, P.; Tritto, I. *Makromol. Chem.* **1989**, *190*, 139. (i) Sacchi, M. C.; Barsties, E.; Tritto, I.; Locatelli, P.; Brintzinger, H. H.; Stehling, U. *Macromolecules* **1997**, *30*, 3955.
- (18) (a) Tsutsui, T.; Kashiwa, N.; Mizuno, A. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 565. (b) Kashiwa, N.; Kioka, M. *Polym. Mater. Sci. Eng.* **1991**, *64*, 43. (c) Kioka, M.; Mizuno, A.; Tsutsui, T.; Kashiwa, N. In *Catalysis in Polymer Synthesis*; Vandenberg, E. J., Salamone, J. C., Eds.; American Chemical Society: Washington, D.C., 1992; p 72.
- (19) (a) Busico, V.; Cipullo, R.; Corradini, P. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 97. (b) Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538. (c) Busico, V.; Cipullo, R. *J. Organomet. Chem.* **1995**, *497*, 113.
- (20) (a) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617. (b) Tsutsui, T.; Ishimaru, N.; Mizuno, A.; Toyota, A.; Kashiwa, N. *Polymer* **1989**, *30*, 1350. (c) Mizuno, A.; Tsutsui, T.; Kashiwa, N. *Polymer* **1992**, *33*, 254.
- (21) Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M.; Corradini, P. *J. Am. Chem. Soc.* **1994**, *116*, 2988.
- (22) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985; p 3.

MA9810417