"Seeing" the Stereoblock Junctions in Polypropylene Made with Oscillating Metallocene Catalysts

Vincenzo Busico,*,†,‡ Roberta Cipullo,‡ Anna Laura Segre,§ Giovanni Talarico,‡ Michele Vacatello,‡ and Valeria Van Axel Castelli†,‡

Dutch Polymer Institute and Dipartimento di Chimica, Università di Napoli "Federico II", Via Cintia, 80126 Napoli, Italy, and Servizio NMR, CNR, Area della Ricerca di Roma, 00016 Monterotondo, Stazione, Italy

Received June 28, 2001
Revised Manuscript Received September 25, 2001

A stereoblock nature has been claimed for polypropylenes made with a variety of transition-metal catalysts[1,2] but never proved directly and unambiguously by means of ^{13}C NMR. This can be traced to a number of reasons, the most trivial possibly being that the samples analyzed were rather (or mostly) physical blends of macromolecules with different stereostructures (which is often the case with heterogeneous catalysts). Alternatively, the stereoblocks may have been too long (hence, with a concentration of junctions too low for ^{13}C NMR) or too complicated (e.g., weakly tactic or atactic[3]). It should be added, however, that at least in some cases the naiveness and/or the poor quality of the ^{13}C NMR analysis represented an additional major limitation.

Recently, a conceptually simple synthetic route to isotactic/atactic stereoblock polypropylene, based on so-called "oscillating" metallocene catalysts of general formula (2-Ar-indenyl)$_2$ZrX$_2$ (Ar = aryl, X = halogen or alkyl), has received much attention. According to the literature,[2,4] the active species in solution would exist as an equilibrium mixture of two rotameric forms (Chart 1; adapted from ref 2; P = polymer chain): one with "*rac*-like" configuration (C_2 symmetry) and the other with "*meso*-like" configuration (C_s symmetry). Because of steric interference of the Ar substituents, the mutual rotation of the indenyl ligands would be slower than monomer insertion, although faster than chain transfer. As a result, the polymer chains would consist of blocks of monomeric units formed at *rac*-like and *meso*-like active species. Considering that the well-known stereorigid bis(1-indenyl) *ansa*-zirconocene catalysts with C_2 and *meso*-C_s symmetry[5] afford isotactic and atactic polypropylene, respectively, it seems plausible to predict[2] an isotactic/atactic stereoblock nature for polypropylene made with oscillating ones.

Consistent with such prediction, the polymer contains both isotactic and stereoirregular sequences (as shown by ^{13}C NMR), and the observed thermoplastic elastomeric properties have been taken as an indication that the two kinds of stereosequences are chemically bound, so that crystalline domains act as physical cross-links between amorphous ones.[2] On the other hand, by solvent extraction it is possible to isolate fractions widely differing in crystallinity,[2g,5b] from completely amorphous (but not purely atactic) to high melting (although not completely isotactic).

Table 1. Results of Boiling Solvent Fractionation of the Examined Polypropylene Sample and of the Characterization of All Fractions by Means of Solution Viscometry, DSC, and X-ray Diffraction

fraction[a]	wt %	$[\eta]^b$ (dL/g)	$T_m{}^{c,d}$ (°C)	$\Delta h_m{}^c$ (J/g)	X-ray cryst (%)
EE-soluble	78	1.1			0
EE-insoluble/C6-soluble	7	1.3	91	9	20
C6-insoluble/C7-soluble	8	2.1	132	59	42
C7-insoluble	7	2.1	148	76	50

[a] EE = diethyl ether; C6 = hexane; C7 = heptane. [b] Intrinsic viscosity in tetralin at 135°C. [c] On second heating scan. [d] Maximum of the DSC peak.

Literature ^{13}C NMR characterizations of raw samples and/or of fractions thereof[2] are—at most—at the level of the steric pentads, which is still the norm for polypropylene, but have been demonstrated to be inadequate for a conclusive microstructural description in complicated cases like the one under investigation.[2h,6−9]

In our laboratory, we have recently developed high-field ^{13}C NMR techniques aimed at improving the level of polypropylene configurational analysis.[7−9] We are pleased to report here the first clear high-field (150 MHz) ^{13}C NMR evidence of a stereoblock nature for a sample made with the most representative oscillating catalyst, i.e., (2-phenyl-indenyl)$_2$ZrCl$_2$[2a] (in combination with *N*,*N*-dimethylanilinium tetrakis(perfluorophenyl borate)/Al(isobutyl)$_3$[5a,10]).

The polymer, prepared at 20 °C in bulk propene (see Experimental Section), was fractionated by sequential exhaustive Kumagawa extraction in boiling diethyl ether (EE), hexane (C6), and heptane (C7). The results are given in Table 1, along with those of a differential scanning calorimetric (DSC) and powder X-ray diffractometric characterization. Almost 80 wt % of the sample dissolved in EE and turned out to be completely amorphous; on the other hand, 7 wt % was insoluble even in boiling C7 and melted at around 150 °C.

All fractions were examined by means of 150 MHz ^{13}C NMR. The spectra always indicated the copresence of predominantly isotactic and poorly stereoregular sequences. Full resonance assignment (Figure 1) was based on our previous work on model polypropylenes.[7a,b] Peaks arising from chain ends or regioirregular units were either below detectability or weak enough not to interfere with the microtacticity measurements.

The stereosequence distributions, determined precisely at pentad/heptad level by full simulation of quantitative spectra (see, e.g., the data in Table 2, which refer to the EE-insoluble/C6-soluble fraction), were subjected to statistical analysis in terms of suitable stochastic models, with matrix multiplication codes already described elsewhere.[8,9] The results are summarized in Table 3.

Quite unexpectedly, for the EE-soluble and the EE-insoluble/C6-soluble fraction, that together represent 85 wt % of the sample, models combining enantiomorphic-site-controlled isotactic and truly atactic sequences, either as a physical mixture (second column of Table 3) or in the form of stereoblocks in agreement with the mechanistic proposal of Chart 1[2] (third column of Table 3), resulted in very poor fits of the experimental configuration, with unacceptably high values of the reduced-χ^2 function.

† Dutch Polymer Institute.
‡ Università di Napoli "Federico II".
§ Servizio NMR, CNR.
* Corresponding author. E-mail: busico@chemistry.unina.it.

10.1021/ma011107p CCC: $20.00
Published on Web 10/26/2001

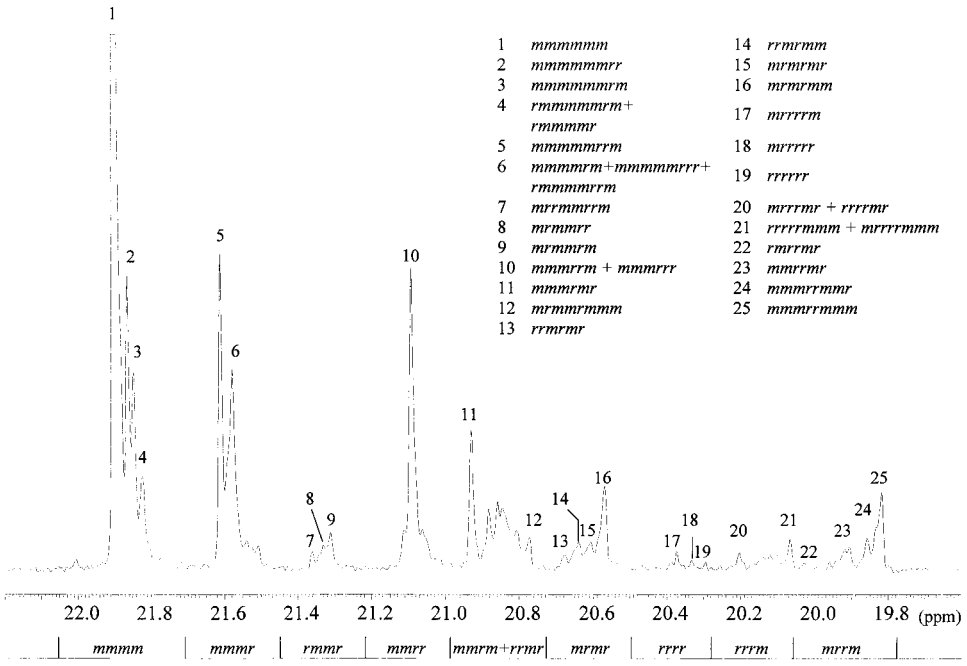
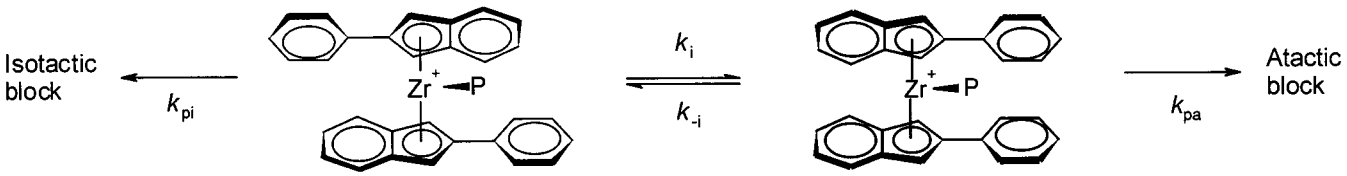


Figure 1. Methyl region of the 150 MHz ^{13}C NMR spectrum of the EE-insoluble/C6-soluble fraction (in tetrachloroethane-*1,2-d*$_2$ at 90 °C; δ scale in ppm downfield of TMS).

Chart 1



For the former fraction, a satisfactory fit ($\chi_r^2 = 0.9$) was obtained when the enantiomorphic-sites statistics[9,11] (describing well the Bernoullian distribution of configurations in the isotactic part) was linearly combined with a first-order Markov statistics[9,12,13] for the stereoirregular part, which turned out to contain a slight but appreciable excess of *meso* (*m*) over *racemo* (*r*) diads (conditional probabilities of diad formation: $P_{RS} = P_{SR} = P_r < P_{RR} = P_{SS} = P_m \approx 0.58$; Table 3, fourth column). In principle, one may invoke a weak chain-end control (1,3-*like* asymmetric induction)[9,12] at the *meso*-like catalytic species of Chart 1, but that would be unprecedented for bis(indenyl)-type zirconocenes.[5] An alternative, more plausible mechanistic explanation, involving the direct interconversion between the two enantiomorphous forms of the *rac*-like active species, at a frequency only slightly lower than that of monomer insertion, is proposed in an independent paper.[14]

A nearly equivalent fit was achieved under the assumption that the (predominantly) isotactic and the (quasi-)atactic sequences are chemically bound;[15] this, however, is neither surprising nor significant. Indeed, isotactic sequences (blocks) occurring in an EE extract must be *completely* unable to crystallize and therefore *highly* stereodefective and/or *very* short. It is easy to realize that the microstructural modeling of such sequences in mixture with (quasi-)atactic ones is intrinsically ambiguous, irrespective of the resolution of the ^{13}C NMR data.

The configurational analysis of the semicrystalline EE-insoluble/C6-soluble fraction, instead, was much more demanding and revealing. Already on inspection, the ^{13}C NMR spectrum shows an anomalous intensity of some resonances that can be diagnostic for chemical junctions between isotactic and stereoirregular blocks (see, e.g., the strong and well-resolved peaks of the *mmmrmr* and *mmrmrm* heptads in the methyl region; no. 11 and 16 in Figure 1). This visual impression found a dramatic validation by quantitative statistical analysis (Table 2 and last two columns of Table 3); indeed, the reduced-χ^2 function dropped vertically from $\chi_r^2 = 4.0$ for the physical blend model down to $\chi_r^2 = 0.3$ for the stereoblock one. The reason is a general improvement of the fit, although for a few key stereosequences, such as the cited *mmmrmr* and *mmrmrm* heptads, the effect is particularly impressive.

Similar results were obtained also for the C6-insoluble/C7-soluble and the C7-insoluble fraction (see again Table 3), although the lower content of (quasi-)atactic blocks prevented a precise evaluation of their configuration.

It is important to note that the stereoregularity of the isotactic part turned out to be almost complete in all three semicrystalline fractions. If one considers also the fairly high average molecular masses, one has to conclude that the largely different solubilities and values of melting temperature and enthalpy (Table 1) should rather be traced to differences in the average isotactic block length, which can be desumed from the conditional probabilities of switch between isotactic and (quasi-)atactic propagation. As a matter of fact, according to our ^{13}C NMR analysis (Table 3, fifth column), in the EE-insoluble/C6-soluble fraction the number-average length of the enantiomorphic-site-controlled

Table 2. 150 MHz ^{13}C NMR Stereosequence Distribution for the EE-Insoluble/C6-Soluble Fraction and Best-Fit Calculated One in Terms of Three Different Stochastic Models (See Text)[a]

	normalized fraction			
		calculated		
stereosequence	experimental	ES + atactic, physical blend[12]	ES+M1, physical blend[12]	ES/M1 stereoblocks[14]
mmmm	0.4854(63)	0.4648	0.4833	0.4875
mmmmmm	0.3808(66)	0.3792	0.3832	0.3752
mmmr	0.1453(20)	0.1199	0.1437	0.1446
mmmmrr	0.0716(39)	0.0776	0.0705	0.0724
rmmr	0.0212(20)	0.0236	0.0236	0.0197
mmrr	0.0990(20)	0.1199	0.1022	0.0989
mmrm+rmrr	0.1096(20)	0.0942	0.1149	0.1098
mmmrmr	0.0330(20)	0.0159	0.0226	0.0324
rmrm	0.0521(20)	0.0471	0.0472	0.0504
mrmrmm	0.0288(20)	0.0159	0.0226	0.0306
rrrr	0.0093(20)	0.0236	0.0078	0.0089
rrrrrm	0.0030(20)	0.0104	0.0027	0.0030
rrrrrr	0.0012(10)	0.0052	0.0008	0.0009
rrrm	0.0278(20)	0.0471	0.0262	0.0285
rmrrmr	0.0030(20)	0.0052	0.0025	0.0019
mmrrmr	0.0128(20)	0.0159	0.0133	0.0121
mmrrmm	0.0345(20)	0.0388	0.0353	0.0336
		$\chi_r^2 = 43$	$\chi_r^2 = 4.0$	$\chi_r^2 = 0.3$
		$\sigma = 0.916(10)$	$\sigma = 0.930(3)$	$\sigma = 0.997(3)$
			$P_m = 0.664(10)$	$P_m = 0.580(5)$
		$w(\mathrm{ES}) = 0.690(43)$	$w(\mathrm{ES}) = 0.575(12)$	$P_{12} = 0.192(6)$
				$P_{21} = 0.335(7)$

[a] ES = enantiomorphic sites; M1 = first-order Markov. σ = conditional probability of selecting a given monomer enantioface at an active species of given chirality, according to the ES statistics.[10] P_m = conditional probability of generating a *meso* diad, according to the M1 statistics.[11] w(ES) = weight fraction of sample following the ES statistics. P_{12} = conditional probability of switching from ES to M1 statistics. P_{21} = conditional probability of switching from M1 to ES statistics.

Table 3. Best-Fit Values of the Adjustable Parameters and of the χ_r^2 Function in the 150 MHz ^{13}C NMR Configurational Analysis of the Four Polymer Fractions, According to Various Stochastic Models (See Text)[a]

fraction	ES + atactic, physical blend[12]	ES/atactic stereoblocks[14]	ES + M1, physical blend[12]	ES/M1 stereoblocks[14]
EE-soluble	$\sigma = 0.819(34)$	$\sigma = 0.991(9)$	$\sigma = 0.891(6)$	
			$P_m = 0.577(2)$	
		$P_{12} = 0.319(26)$		
		$P_{21} = 0.135(16)$		
	$w(\mathrm{ES}) = 0.373(90)$	[w(ES) = 0.297]	$w(\mathrm{ES}) = 0.153(7)$	
	$\chi_r^2 = 40$	$\chi_r^2 = 10$	$\chi_r^2 = 0.9$	
EE-insoluble/C6-soluble	$\sigma = 0.916(10)$	$\sigma = 0.999(2)$	$\sigma = 0.930(3)$	$\sigma = 0.997(3)$
			$P_m = 0.664(10)$	$P_m = 0.580(5)$
		$P_{12} = 0.162(6)$		$P_{12} = 0.192(6)$
		$P_{21} = 0.301(14)$		$P_{21} = 0.335(7)$
	$w(\mathrm{ES}) = 0.688(41)$	[w(ES) = 0.650]	$w(\mathrm{ES}) = 0.575(12)$	[w(ES) = 0.636]
	$\chi_r^2 = 43$	$\chi_r^2 = 4.6$	$\chi_r^2 = 4.0$	$\chi_r^2 = 0.3$
C6-insoluble/C7-soluble	$\sigma = 0.968(3)$	$\sigma = 0.999(1)$	$\sigma = 0.973(1)$	$\sigma = 0.996(4)$
			$P_m = 0.662(14)$	$P_m = 0.536(14)$
		$P_{12} = 0.067(3)$		$P_{12} = 0.065(7)$
		$P_{21} = 0.319(15)$		$P_{21} = 0.310(26)$
	$w(\mathrm{ES}) = 0.832(17)$	[w(ES) = 0.826]	$w(\mathrm{ES}) = 0.785(8)$	[w(ES) = 0.827]
	$\chi_r^2 = 15$	$\chi_r^2 = 1.3$	$\chi_r^2 = 3.0$	$\chi_r^2 = 1.1$
C7-insoluble	$\sigma = 0.981(3)$	$\sigma = 0.998(2)$	$\sigma = 0.981(3)$	$\sigma = 0.999(2)$
			$P_m = 0.650(47)$	$P_m = 0.479(34)$
		$P_{12} = 0.049(6)$		$P_{12} = 0.049(5)$
		$P_{21} = 0.268(35)$		$P_{21} = 0.268(30)$
	$w(\mathrm{ES}) = 0.830(16)$	[w(ES) = 0.845]	$w(\mathrm{ES}) = 0.808(15)$	[w(ES) = 0.845]
	$\chi_r^2 = 3.4$	$\chi_r^2 = 1.5$	$\chi_r^2 = 2.9$	$\chi_r^2 = 1.7$

[a] ES = enantiomorphic sites; M1 = first-order Markov; EE = diethyl ether; C6 = hexane; C7 = heptane. σ = conditional probability of selecting a given monomer enantioface at an active species of given chirality, according to the ES statistics.[10] P_m = conditional probability of generating a *meso* diad, according to the M1 statistics.[11] w(ES) = weight fraction of sample following the ES statistics. P_{12} = conditional probability of switching from ES to M1 statistics. P_{21} = conditional probability of switching from M1 to ES statistics.

(ES) strands is $\langle L_n(\mathrm{ES})\rangle \approx 1/P_{12} \approx 5$ monomeric units, and only ≈20 wt % corresponds to m_n sequences with $n \geq 11$ (which is considered to be the threshold for crystallization[1b]). On the other hand, for the C6-insoluble/C7-soluble fraction the calculated values of $\langle L_n(\mathrm{ES})\rangle$ and $[m_{n\geq 11}]$ are ≈15 and ≈50%, respectively. Finally, for the C7 residue we find $\langle L_n(\mathrm{ES})\rangle \approx 20$ and $[m_{n\geq 11}] \approx 60\%$. Such estimates are in very nice agreement with the DSC and X-ray diffraction results of Table 1.

In forthcoming papers, we will report in more detail on the microstructural and physicochemical characterization of polypropylene samples prepared with a num-

ber of oscillating metallocene catalysts, along with a mechanism of stereocontrol in agreement with the observed polymer configuration.

Experimental Section. The polypropylene sample was prepared in a 2 L stainless steel reactor (Brignole, model AU-2), equipped with a magnetic stirrer (1000 rpm) and a glass vial holder−breaker. The reactor was charged with 50 mL of dry toluene containing 1.0 mL of Al(isobutyl)$_3$ (Witco GmbH) and 240 g of propene (SON, polymerization grade) and thermostated at 20 °C. The reaction was started by breaking a glass vial containing 6.1 mg of the catalyst (prepared according to the literature[2a]) and 24 mg of *N*,*N*-dimethylanilinium tetrakis(perfluorophenyl borate) and stopped after 1.0 h by monomer degassing. The polymer was coagulated in methanol (1.0 L) added with 20 mL of HCl(aq,conc), filtered off, and vacuum-dried; yield, 5.1 g.

The sample was fractionated by sequential exhaustive Kumagawa extractions with boiling diethyl ether, hexane, and heptane. All fractions were then characterized by solution viscometry, DSC, X-ray diffraction, and ^{13}C NMR. Intrinsic viscosities were measured in tetralin at 135 °C with a single-point technique.[16] DSC curves were recorded with a Perkin-Elmer DSC-7 apparatus, at the scanning rate of 10 deg/min, in flowing nitrogen. Powder X-ray diffraction spectra were obtained with a Philips PW-1830 automatic diffractometer, using Ni-filtered Cu Kα radiation.

Quantitative ^{13}C NMR spectra were recorded with a Bruker AMX-600 spectrometer operating at 150 MHz in the FT mode, on polymer solutions in tetrachloroethane-*1,2*-d_2 (10 mg/mL) at 70−120 °C, as already described.[7] The spectra were fully simulated using the SHAPE-2000 program.[17] The statistical analysis of the stereosequence distribution was carried out with the CONFSTAT suite (version 2.3 for Windows).[18] For each stochastic model, the confidence intervals on the adjustable parameters were estimated using the Monte Carlo simulation routine of CONFSTAT, accepting all solutions with a value of the χ_r^2 function up to 1.2 times that at the absolute minimum.

Acknowledgment. This study was funded by the Dutch Polymer Institute (DPI Project #100). V.V.A.C. acknowledges the DPI for a postdoctoral fellowship. V.B. and R.C. are grateful to the Italian Ministry for University (PRIN 2000) for financial assistance. The authors thank Ms. Valentina Langella for sample preparation and fractionation.

References and Notes

(1) (a) Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Muelhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851. (b) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858. (c) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.-H.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030. (d) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 8569. (e) Babu, G. N.; Newmark, R. A.; Cheng, H. N.; Llinas, G. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 7400. (f) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242. (g) Lieber, S.; Brintzinger, H. H. *Macromolecules* **2000**, *33*, 9192.

(2) (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217. (b) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586. (c) Kravchenko, R.; Masood, A.; Waymouth, R. M. *Organometallics* **1997**, *16*, 3635. (d) Maciejewski Petoff, J. L.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909. (e) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174. (f) Maciejewski Petoff, J. L.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316. (g) Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908. (h) Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707. (i) Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147. (j) Nele, M.; Collins, S.; Pinto, J. C.; Dias, M. L.; Lin, S.; Waymouth, R. M. *Macromolecules* **2000**, *33*, 7249.

(3) Stereoblock fractions are present also in polypropylenes produced with classical Ziegler−Natta catalysts (see, e.g.: (a) Natta, G.; Mazzanti, G.; Crespi, G.; Moraglio, G. *Chim. Ind. (Milan)* **1957**, *39*, 275. (b) Busico, V.; Corradini, P.; De Biasio, R.; Landriani, L.; Segre, A. L. *Macromolecules* **1994**, *27*, 4521). However, because of the extreme complexity of such polymers, the ^{13}C NMR microstructural evidence of a true stereoblock nature cannot be taken as conclusive.

(4) (a) Pietsch, M. A.; Rappé, A. K. *J. Am. Chem. Soc.* **1996**, *118*, 10908. (b) Cavallo, L.; Guerra, G.; Corradini, P. *Gazz. Chim. Ital.* **1996**, *126*, 463. (c) Maiti, A.; Sierka, M.; Andzelm, J.; Golab, J.; Sauer, J. *J. Phys. Chem. A* **2000**, *104*, 10932.

(5) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(6) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779.

(7) (a) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M.; Segre, A. L. *Macromolecules*, **1997**, *30*, 6251. (b) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M.; Bella, J.; Segre, A. L. *Macromolecules* **1998**, *31*, 8713. (c) Busico, V.; Cipullo, R.; Monaco, G.; Talarico, G.; Vacatello, M.; Chadwick, J. C.; Segre, A. L.; Sudmeijer, O. *Macromolecules* **1999**, *32*, 4173.

(8) Busico, V.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. *Macromolecules* **1995**, *28*, 1887.

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

(10) We activated the catalyst with *N*,*N*-dimethylanilinium tetrakis(perfluorophenyl borate) rather than with methylalumoxane, because with the latter polymers of lower average molecular mass were obtained (due to chain transfer to AlMe$_3$). This is undesirable for two main reasons: (i) the fractionation behavior is not controlled any more by sample tacticity "only"; (ii) the ^{13}C NMR microstructural characterization becomes more complicated, due to the nonnegligible presence of resonances arising from chain end groups.

(11) Shelden, R. A.; Fueno, T.; Tsunetsugu, T.; Furukawa, J. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 23.

(12) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.

(13) Doi, Y. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 635.

(14) Busico, V.; Cipullo, R.; Kretschmer, W.; Talarico, G.; Vacatello, M.; Van Axel Castelli, V., submitted to *Angew. Chem.*

(15) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.

(16) Ram Mohan Rao, M. V.; Yaseen, M. *J. Appl. Polym. Sci.* **1986**, *31*, 2501.

(17) SHAPE-2000, by Michele Vacatello, University of Naples "Federico II" (e-mail vacatello@chemistry.unina.it).

(18) CONFSTAT (Ver. 2.3), by Michele Vacatello, University of Naples "Federico II" (e-mail vacatello@chemistry.unina.it).

MA011107P