Macromolecules **2004,** *37,* 2016−2020

Articles

High Selectivity in Polymerization of (*Z*)-1,3-Pentadiene, with the $CpTiCl_3$−MAO Catalytic System, Generated by Backbiting Coordinations of the Growing Polydienyl Chain

Chiara Costabile, Gaetano Guerra, Pasquale Longo,* and Stefania Pragliola

Dipartimento di Chimica, Universita' di Salerno, Via Salvador Allende,
I-84081 Baronissi, Salerno, Italy

Received December 12, 2003; Revised Manuscript Received January 21, 2004

ABSTRACT: Polymer microstructures obtained by copolymerizations of (*Z*)-1,3-pentadiene with ethene, conducted at different temperatures by the $CpTiCl_3$−MAO catalytic system, have been characterized by detailed ^{13}C NMR analyses. The observed microstructures indicate an essential role of the backbiting of the allyl-terminated growing chain on the occurrence of 1,2 syndiotactic and 1,4-cis high selectivities, which are observed for (*Z*)-1,3-pentadiene homopolymerizations at low and high temperatures, respectively. Molecular modeling studies suggest that the occurrence of 1,2-syndio and 1,4-cis stereoselectivities would be determined by the steric constrain (and stereorigidity) associated with the maintenance, in monomer bound intermediates, of the backbiting coordination of syn and anti allyl-terminated growing chains, respectively.

A puzzling open question relative to organometallic catalysis of polymerization is the high chemoselectivity and stereoselectivity, which can be easily achieved for diene monomer polymerizations, by catalytic systems whose stereocontrol is only dependent on the chirality of the growing chain end.[1] For olefin polymerizations, on the contrary, low stereoselectivities are generally observed when the stereocontrol is only determined by the chirality of the growing chain (see for instance ref 2), while high stereoselectivities can be achieved only in the presence of bulky and stereorigid additional ligands (like, e.g., for metallocenes).[3]

In this paper, we present experimental and molecular modeling results supporting the hypothesis that, at least for the widely studied $CpTiCl_3$−MAO catalytic system,[4] the occurrence of high stereoselectivities (both 1,2-syndio and 1,4-cis) for (*Z*)-1,3-pentadiene would be determined by the steric constraint (and stereorigidity) associated with the maintenance in monomer bound intermediates of the backbiting coordination of the growing polydienyl chain, which would be generally present in insertion products of conjugated dienes into a polydienyl chain.[4d,f,g,5−10]

In the presence of $CpTiCl_3$−MAO the chemoselectivity is generally low for monomers with low-energy s-cis η^4 coordination, like butadiene, isoprene and (*E*)-pentadiene, while the chemoselectivity and stereoselectivity can be very high for monomers with high energy s-cis η^4 coordination, like (*Z*)-1,3-pentadiene and 4-methyl-1,3-pentadiene. A comparison between chemoselectivity and stereoselectivity of this catalytic system with (*E*) and (*Z*) isomers of 1,3-pentadiene is particularly relevant. Actually, (*E*)-pentadiene affords at any temperature an irregular product containing substantial amounts of both 1,4-cis and 1,2 units, while (*Z*)-1,3-pentadiene is stereospecifically polymerized to 1,2 syndiotactic polymer at −20 °C or less[4b,c,e,g] and to 1,4-cis isotactic polymer at temperatures higher than 20 °C.[4a,b] As an example, the ^{13}C NMR spectra of poly(*Z*)-1,3-pentadiene samples obtained by polymerizations conducted at −20 and +20 °C are shown in parts A and B of Figure 1, respectively. (For polymerization conditions see Table 1, rows 1 and 2.)

Table 1. Homopolymerizations of (*Z*)-1,3-Pentadiene and Copolymerizations of Ethene and (*Z*)-1,3-Pentadiene in the Presence of the $CpTiCl_3$−MAO Catalytic System

run[a]	C_{ZP} (mol/L)	C_E (mol/L)	temp (°C)	time (h)	yield (mg)
1	0.55		−20	10	32
2	0.55		+20	10	99
3	0.63	0.83	−25	5	109
4	0.88	0.85	−20	12	170
5	0.55	0.62	+20	5	118
6	0.63	0.50	+40	5	120

[a] All polymerizations were carried out in 20 mL of toluene by using 3.5×10^{-5} mol of $CpTiCl_3$ and MAO/$CpTiCl_3$ = 500/1.

Both 1,4-cis and 1,2-syndiotactic selectivities, achieved for (*Z*)-1,3-pentadiene homopolymerizations at high and low temperatures, respectively, are lost for copolymerization with ethylene. Just as an example, the ^{13}C NMR spectra of copolymers of (*Z*)-1,3-pentadiene with an ethene content close to 80 mol %, which have been obtained at −20 and +20 °C, are shown in parts A′ and B′ of Figure 1, respectively.

A more detailed ^{13}C NMR analysis has been carried out on two copolymer samples obtained at −25 and +40 °C. (For polymerization conditions see Table 1, rows 3 and 6.) For both copolymers, the 115−140 ppm chemical shift range is reported in the upper part of Figure 2,

10.1021/ma035892c CCC: $27.50

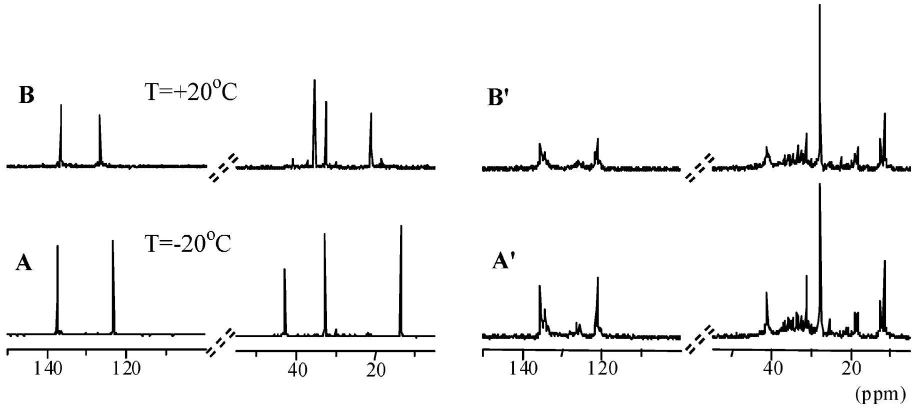


Figure 1. ^{13}C NMR spectra of polymer samples obtained by the CpTiCl$_3$−MAO catalytic system at −20 °C (A and A′) and +20 °C (B and B′): (A) syndiotactic 1,2-poly(*Z*)-1,3-pentadiene; (B) 1,4-*cis*-poly(*Z*)pentadiene; (A′ and B′) copolymers of (*Z*)-1,3-pentadiene with nearly 80 mol % of ethene.

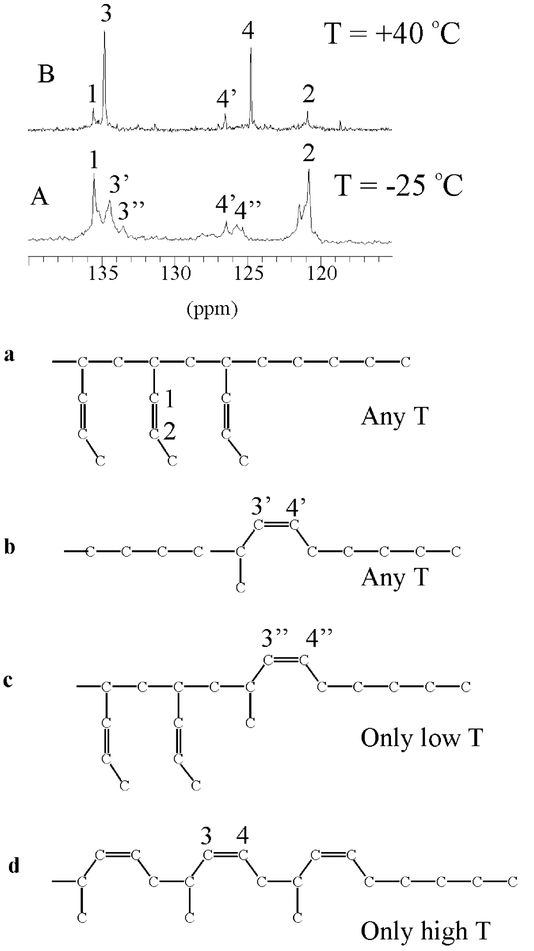
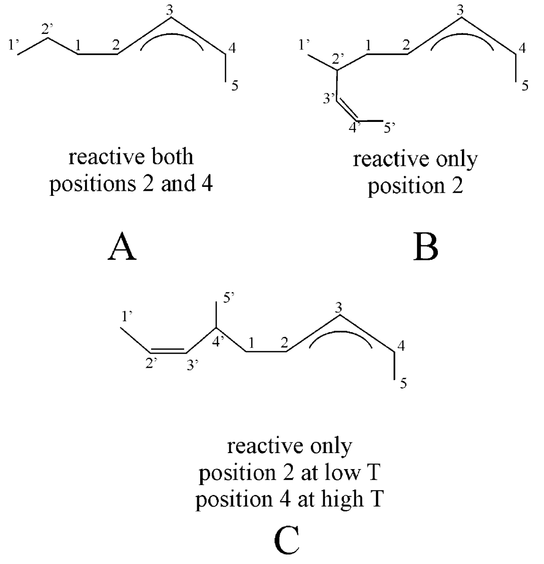


Figure 2. ^{13}C NMR spectra of the ethene/(*Z*)-1,3-pentadiene copolymer samples obtained by the CpTiCl$_3$−MAO catalytic system at −25 (A) and +40 °C (B), for the 115−140 ppm chemical shift range. The major peaks have been assigned to the microstructures **a**−**d** shown below.

and the signals have been attributed to the microstructures, which are shown in the lower part of Figure 2.

As for the low-temperature copolymer, signals relative to 1,2 homosequence (**a**) ($\delta_{C1} = 135.5_3$ ppm; $\delta_{C2} = 120.9_3$ ppm) are prevailing while well-defined signals corresponding to the isolated 1,4 unit between ethylene units (**b**) ($\delta_{C3'} = 134.5_9$ ppm; $\delta_{C4'} = 126.9_3$ ppm) and to the 1,4 unit between 1,2 and ethylene sequences (**c**) ($\delta_{C3''} = 133.4_8$ ppm; $\delta_{C4''} = 125.7_8$ ppm) are clearly present. As for the high-temperature copolymer, signals relative to 1,4 homosequence (**d**) ($\delta_{C3} = 134.7_7$ ppm; $\delta_{C4} = 124.7_4$ ppm) are prevailing while well-defined signals corresponding to sequences **a** and **b** are also present.

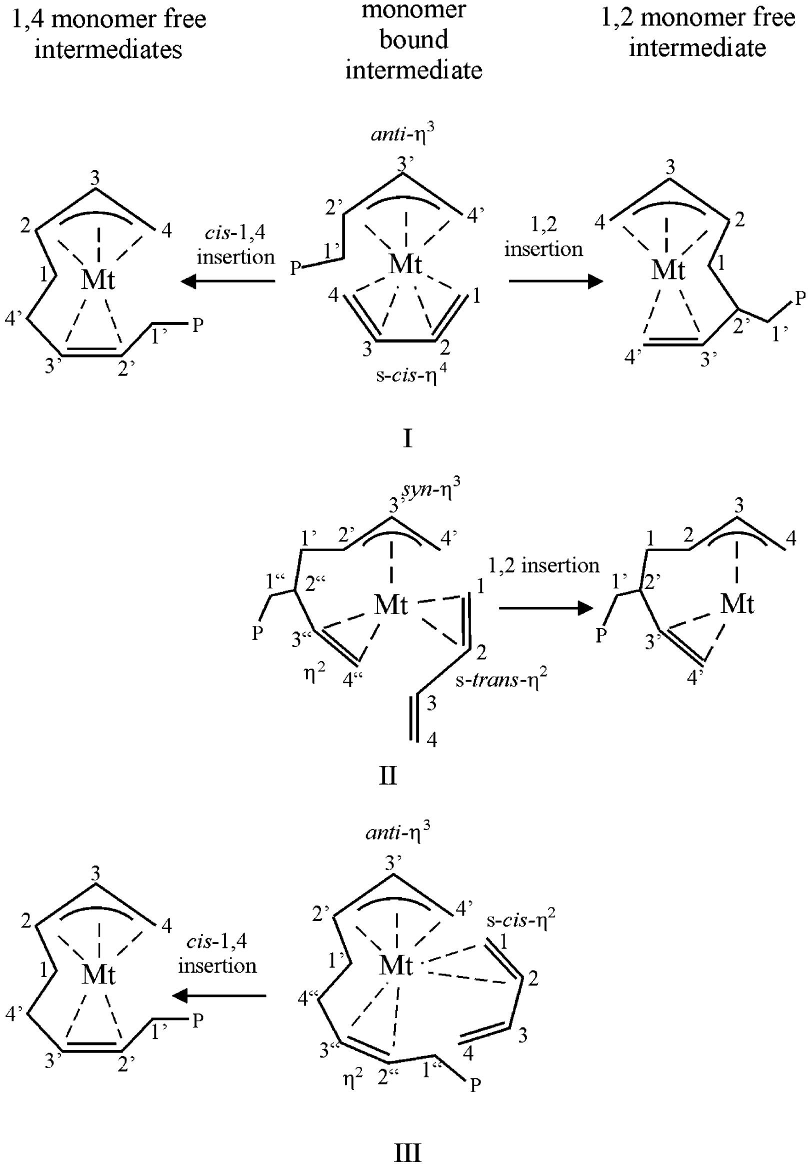
Scheme 1



It is worth noting that the achievement of microstructure **a** for (*Z*)-1,3-pentadiene−ethene copolymerization also at high temperature is not surprising. In fact, (*Z*)-1,3-pentadiene when copolymerized with styrene[11a] or with 4-methyl-1,3-pentadiene[11b] at either low or high temperature affords products mostly containing 1,2-pentadiene units with blocky sequences of comonomers.

In the framework of the well-established π-allyl polymerization mechanism,[1,5−10] the microstructures of Figure 2 indicate the following: (i) The allylic intermediate which is obtained after a (*Z*)-1,3-pentadiene insertion following an ethene insertion (Scheme 1A), independently of the polymerization temperature, is not selective as for the formation of the new diene constitutional unit. In fact, it can react with the following monomer molecule with the allyl carbon 4, leading to 1,4 insertion (as shown by microstructures **b** and **c** for low *T* and microstructures **b** and **d** at high *T*) or with the allyl carbon 2, leading to 1,2 insertion (as shown by microstructure **a** for all *T*). (ii) The allylic intermediate which is obtained after (*Z*)-1,3-pentadiene insertion following a 1,2 inserted pentadiene unit (Scheme 1B) reacts with the following pentadiene monomer molecule prevailingly with the allyl carbon 2, leading to 1,2

Scheme 2



insertion (as shown by microstructure **a** for all *T*). (iii) The allylic intermediate which is obtained after (*Z*)-1,3-pentadiene insertion following a 1,4 inserted pentadiene unit (Scheme 1C) reacts with the following pentadiene monomer molecule prevailingly with the allyl carbon 2, leading to 1,2 insertion at low temperatures (as shown by microstructure **c**) or with the allyl carbon 4, leading to 1,4 insertion at high temperatures (as shown by microstructure **d**).

These results clearly indicate that the especially relevant role of the microstructure of growing chain end in determining chemoselectivity, which was already suggested for 1,2-syndiotactic polymerization,[4b,c,e,g] holds also for 1,4-cis polymerization. In particular, these results suggest that the backbiting coordination of the closest double bond of the allyl terminal of the growing polydienic chain, which is feasible when the penultimate inserted unit is a diene (Scheme 1B,C) and unfeasible when the penultimate unit is ethene (Scheme 1A), can be essential to the high 1,4-cis and 1,2-syndiotactic selectivities of (*Z*)-1,3-pentadiene homopolymerizations.

More in detail, it is possible to speculate that the usual mechanism, involving a monomer bound intermediate with a s-cis-η^4 coordinated diene monomer as well as an anti-η^3 coordinated allyl terminal of the growing chain (I in Scheme 2),[1h,i] for which a backbiting coordination of the allyl growing chain is energetically unfeasible, generally would be poorly chemoselective. This is in good agreement with the poor chemoselectivity of polymerization of butadiene, isoprene, and (*E*)-1,3-pentadiene. The poorly chemoselective intermediate I would be unsuitable for (*Z*)-1,3-pentadiene homopolymerization due to the high energy of s-cis-η^4 coordination of this monomer. In principle, it is possible to hypothesize two alternative monomer bound intermediates (II and III in Scheme 2) which present an η^2 coordination of (*Z*)-1,3-pentadiene[4b,c] (being s-trans and s-cis) and a backbiting allyl terminal of the growing chain (syn-η^3 and anti-η^3, respectively). These monomer bound intermediates could be stabilized by the reduced bulkiness of η^2 diene coordination, which could allow the maintenance of the backbiting coordination of the growing chain typical of monomer free intermediates.[12]

QM models corresponding to these hypothesized monomer bound intermediates for (*Z*)-1,3-pentadiene polymerization are shown in Figure 3, together with the relative energies. It is apparent that the intermediate II is of minimum energy while the higher energy

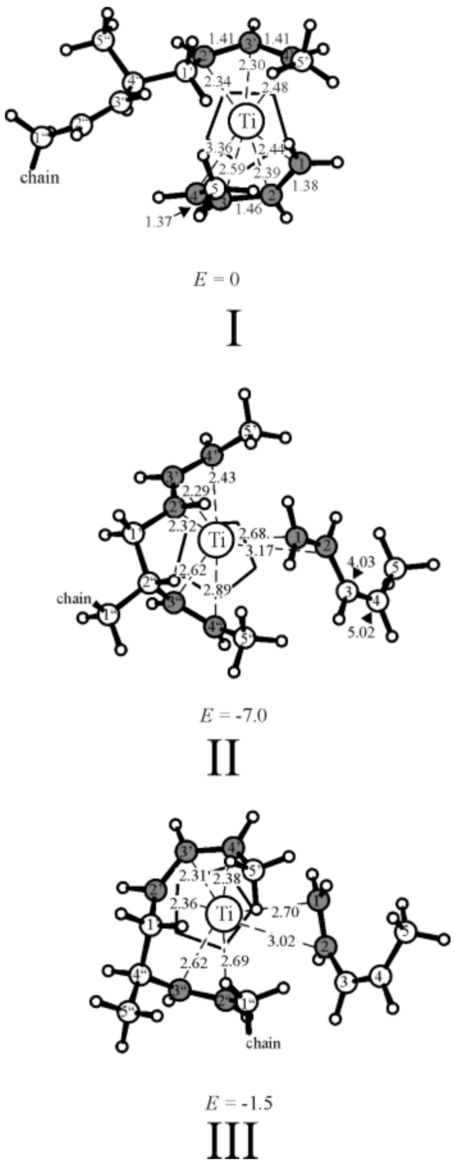


Figure 3. Minimum-energy geometries and relative energies of the hypothesized monomer bound intermediates for (*Z*)-1,3-pentadiene polymerization: I (s-cis η^4 coordinated (*Z*)-1,3-pentadiene and anti-η^3 poly(*Z*)-pentadienyl chain), II (s-trans η^2 coordinated (*Z*)-1,3-pentadiene and backbiting syn η^3 poly(*Z*)-pentadienyl chain), and III (s-cis η^2 coordinated (*Z*)-1,3-pentadiene and backbiting anti-η^3 poly(*Z*)-pentadienyl chain). Distances are in Å and energies are in kcal/mol.

intermediate III anyway presents an energy lower than for the usual monomer bound intermediate I. Already on inspection of the models of Figure 3, it is apparent that, due to the geometrical constraint associated with the backbiting coordination of the allyl growing chain, the monomer bound intermediates II and III should be highly chemoselective. In fact, intermediates II and III of Figure 3 present the reactive terminal carbon atom 1 of the diene with orientation and proximity preferably suitable for reaction with the allyl carbons 2 and 4, respectively. Preliminary molecular modeling studies of the complete insertion reactions indicate that the preferred reaction routes for the intermediates II and III of Figure 3 lead to 1,2 and 1,4 insertions, respectively (as shown in the simplified sketches of Scheme 2).

Hence, the molecular modeling analysis suggests that the high selectivities in favor of 1,2-syndiotactic or 1,4-cis (*Z*)-1,3-pentadiene polymerization at low and high temperatures would be due to the formation of intermediates II and III, respectively. The switch with increasing temperature between mechanisms involving intermediates II or III could be due to some entropic effect.

In summary, the reported experimental results indicate an essential role of the backbiting of the allyl-terminated growing chain on the occurrence of both 1,2 syndiotactic and 1,4-cis high selectivities for (*Z*)-1,3-pentadiene polymerization, at least for the $CpTiCl_3$−MAO catalytic system. Molecular modeling results allow an easy rationalization of these experimental data. The low-temperature 1,2-syndiotactic selectivity and the high-temperature 1,4-cis selectivity would occur through two different mechanisms, both involving a η^2 coordination of (*Z*)-1,3-pentadiene and maintaining into the monomer bound intermediate the backbiting coordination of the growing chain, typical of monomer free intermediates. The main difference between the mechanisms leading to 1,2 or 1,4 selectivities would be the syn or anti coordination of the allyl terminal of the backbiting polydienyl chain, respectively.

Experimental Part

General Procedure. All the operations were performed under a nitrogen atmosphere by using conventional Schlenk line techniques. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. Ethylene was purchased from Società Ossigeno Napoli (SON) and used without further purification. (*Z*)-1,3-Pentadiene was purchased from Sigma Aldrich and used after distillation on methylalumoxane. Methylalumoxane was purchased by Witco and used as a solid after distillation of solvent. Cyclopentadienyltitanium trichloride ($CpTiCl_3$) was purchased from Sigma Aldrich and used without further purification.

(*Z*)-1,3-Pentadiene Homopolymerization. Polymerizations were carried out by introducing in the reactor 20 mL of dry toluene, 2,5 $\times$ 10^{-3} mol of MAO, and 5 $\times$ 10^{-6} mol of $CpTiCl_3$. The solution was maintained at 50 °C for 15 min and then cooled at the reaction temperature, and the polymerization was finally started by introducing 1 $\times$ 10^{-2} mol of monomer. All the polymers were recovered by precipitation with ethanol/HCl, washed several times with fresh ethanol, and dried under reduced pressure at room temperature.

(*Z*)-1,3-Pentadiene−Ethene Copolymerization. In a 100 mL glass flask equipped with a magnetic stirrer were introduced 10 mL of toluene, 1.0 $\times$ 10^{-3} mol of MAO, and 1 mL of (*Z*)-1,3-pentadiene. The reactor was cooled by liquid nitrogen, and the inert gas was evacuated. The mixture was thermostated at the reaction temperature and then was fed with ethene at a costant pressure of 1 atm. Polymerization was initiated by introducing in the reactor at the reaction temperature a solution of 10 mL of toluene, 1,5 $\times$ 10^{-3} mol of MAO, and 5 $\times$ 10^{-6} mol of $CpTiCl_3$ previosly maintained at 50 °C for 15 min. All the polymers were recovered by precipitation with ethanol/HCl, washed several times with fresh ethanol, and dried under reduced pressure at room temperature.

NMR Analysis. NMR spectra were recorded on an Avance 300 Bruker spectrometer operating at 75.47 MHz at 373 K. The samples were prepared by dissolving 40 mg of polymer in 0.5 mL of tetrachlorodideuterioethane. Hexamethyldisiloxane was used as the internal chemical shift reference.

Computational Details. Stationary points on the potential energy surface were calculated with the Amsterdam Density Functional (ADF) program system developed by Baerends et al.[13,14] The electronic configurations of the molecular systems were described by a triple-ζ STO basis set on Ti for 3s, 3p, 3d, 4s, and 4p. Double-ζ STO basis sets were used for C (2s, 2p) and H (1s). The basis sets on C is augmented with a single 3d polarization function except for H, where a 2p function was used. The $1s^22s^22p^6$ configuration on titanium and $1s^2$ configuration on carbon were assigned to the core and treated within the frozen core approximation. Energetics and geometries were evaluated by using the local exchange-correlation potential by Vosko et al.[15] augmented in a self-consistent manner with Becke's[16] exchange gradient correction and Perdew's[17] correlation gradient correction. First-order scalar relativistic corrections were added to the total energy, since a perturbative relativistic approach is sufficient for 3d metals. Because of the open-shell character of the systems under study, an unrestricted formalism has been used.

Geometry optimizations were terminated if the largest component of the Cartesian gradient was smaller than 0.002 au.

Acknowledgment. We thank Prof. Adolfo Zambelli, Prof. Luigi Cavallo, and Dr. Giuseppe Milano of the University of Salerno for useful discussions and Dr. Patrizia Oliva for technical assistance. This work was supported by the Italian National Research Council (CNR) and by the Ministry of University of Italy (Grant PRIN-2002, FISR).

References and Notes

(1) (a) Porri, L.; Natta, G.; Gallazzi, M. C. *Chim. Ind. (Milan)* **1964**, *46*, 428. (b) Natta, G.; Porri, L.; Carbonaro, A.; Greco, A. *Makromol. Chem.* **1964**, *71*, 207. (c) Wilke, G.; Bogdanovich, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kromer, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151. (d) Marconi, W. In *Stereochemistry of Macromolecules*; Ketley, A. D., Ed.; Dekker: New York, 1967; Vol. 1, p 239. (e) Natta, G.; Porri, L. In *Polymer Chemistry of Synthetic Elastomers*; Kennedy, J. P., Tornquist, E., Eds.; Wiley-Interscience: New York, 1969; Part II, p 597. (f) Teyssie, P.; Dawans, F. *The Stereo Rubbers*; Saltman, W. M., Ed.; Wiley: New York, 1977; p 79. (g) Porri, L. In *Structural Order in Polymers*; Ciardelli, F., Giusti, P., Eds.; Pergamon Press: Oxford, UK, 1981; p 51. (h) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, UK, 1989; Vol. 4, Part II, p 53. (i) Porri, L.; Giarrusso, A.; Ricci, G. *Prog. Polym. Sci.* **1991**, *16*, 405. (j) Taube, R.; Windisch, H.; Maiwald, S. *Macromol. Symp.* **1995**, *89*, 393.

(2) (a) Resconi, L.; Abis, L.; Franciscono, G. *Macromolecules* **1992**, *25*, 6814. (b) Erker, G.; Fritze, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412.

(3) (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (b) Corradini, P.; Cavallo, L.; Guerra, G. In *Metallocene-based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: New York, 2000; Vol. 2, pp 1−36.

(4) (a) Oliva, L.; Longo, P.; Grassi, A.; Ammendola, P.; Pellecchia, C. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 519. (b) Ricci, G.; Italia, S.; Porri, L. *Macromolecules* **1994**, *27*, 868. (c) Ricci, G.; Porri, L.; Giarrusso, A. *Macromol. Symp.* **1995**, *89*, 383. (d) Longo, P.; Proto, A.; Oliva, P.; Zambelli, A. *Macromolecules* **1996**, *29*, 5500. (e) Longo, P.; Oliva, P.; Proto, A.; Zambelli, A. *Gazz. Chim. Ital.* **1996**, *126*, 377. (f) Longo, P.; Grisi, F.; Proto, A.; Zambelli, A. *Macromol. Rapid Commun.* **1997**, *18*, 183. (g) Longo, P. Guerra, G.; Grisi, F.; Pizzuti, S.; Zambelli, A. *Macromol. Chem. Phys.* **1998**, *199*, 149.

(5) (a) Guerra, G.; Cavallo, L.; Corradini, P.; Fusco, R. *Macromolecules* **1997**, *30*, 677. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.

(6) Tobish, S.; Bögel, H.; Taube, R. *Organometallics* **1996**, *15*, 3563.

(7) Tobisch, S.; Bogel, H.; Taube, R. *Organometallics* **1998**, *17*, 1177.

(8) Tobisch, S.; Taube, R. *Organometallics* **1999**, *18*, 5204.

(9) (a) Tobisch, S.; Taube, R. *Organometallics* **1999**, *18*, 3045. (b) Tobisch, S. *Acc. Chem. Res* **2002**, *35*, 96.

(10) Costabile, C.; Milano, G.; Cavallo, L.; Guerra, G. *Macromolecules* **2001**, *23*, 7952.

(11) (a) Longo, P.; Proto, A.; Oliva, P.; Sessa, I.; Zambelli, A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2697. (b) Ricci, G.; Porri, L. *Macromol. Chem. Phys.* **1997**, *198*, 3647.

(12) Costabile, C.; Milano, G.; Cavallo, L.; Longo, P.; Guerra, G.; Zambelli, A. *Polymer* **2004**, *45*, 485.

(13) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(14) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 52.

(15) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(16) Becke, A. D. *Phys. Rev. B* **1986**, *34*, 7406.

(17) Perdew, J. P. *Phys. Rev. B* **1988**, *38*, 3098.

MA035892C