Communications to the Editor

Formation of Quaternary Carbon Centers in Ethylene Polymerization with *meso*-Isopropylidenebis(1-indenyl)zirconium Dichloride Activated by MAO

Lorella Izzo, Francesco De Riccardis, Caterina Alfano, Lucia Caporaso, and Leone Oliva*

Dipartimento di Chimica, Università di Salerno, I-84081 Baronissi, Italy

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Incorporation of alkyl branches into the polyethylene chain giving rise to so-called “linear low-density polyethylene”, LLDPE, is usually obtained by ethylene copolymerization with 1-alkenes. In principle, such a result can be also gained by chain growing isomerization during ethylene homopolymerization.

A few evidences have been reported in the literature indicating the presence of some amount of branches in polyethylene produced by homopolymerization with a variety of homogeneous catalysts. The significant formation of about 2 mol % ethyl branches has been recently found by some of us[1] using the *meso* isomer of the ethylenebis(1-indenyl)zirconium dichloride (EBI-$ZrCl_2$) while a not specified amount of the same branching was found by Wang et al.[2] in polyethylene obtained with other asymmetric zirconocenes. An isomerization mechanism for the ethyl branches formation has been proposed involving β-hydrogen transfer to the incoming monomer. This reaction should be in competition with the back skip when the growing chain is in the inward site, where the conformation suitable for insertion should have higher energy, according to the calculations of Guerra et al.[3] for the propene polymerization with *meso*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl) ligands. On the basis of this hypothesis, the branching mechanism should be more or less active depending on the constraints of the *meso* ligands' environment.

In the investigation of several *meso*-zirconocene-based catalysts, we have found the remarkable behavior of the title zirconocene, which has been isolated from the *meso*−*racemic* mixture[4] by crystallization from toluene and characterized by ^{1}H NMR.[5] Actually the ^{13}C NMR spectrum of polyethylene synthesized at 50 °C and 1 atm monomer pressure shows a complex series of peaks in addition to the signal of polymethylene sequence at 29.9 ppm and to the signals of ethyl branches. The sample obtained at lower polymerization temperature (20 °C) shows a simplified NMR spectrum with resonances assigned to ethyl branches (11.2, 26.6, 27.2, 30.3, 33.8, and 39.5 ppm), to *n*-alkane chain end (14.1, 22.8, and 32.1 ppm), to vinylidene chain end (12.7, 28.3, 29.1, 36.5, 107.8, and 152.1 ppm), and with the unprecedented pattern of signals at 7.9, 23.4, 28.8, 31.0, 36.4,and 37.6 ppm.[6] In Figure 1 is reported the ^{13}C NMR spectrum of the polyethylene[7] obtained at 0 °C where all the above signals are present. The relative intensities of the signals of the unprecedented pattern increase with decreasing the polymerization temperature. In the polymer produced at −20 °C they become the more intense signals besides the peak of polymethylene sequence. To identify the structural feature accountable for the unassigned pattern of resonances, oligomeric products have been isolated from the reaction mixture at −20 °C and analyzed by GC mass and NMR. The oligomers mixture has the general formula $(C_2H_4)_n$, with *n* ranging from 7 to 14, and the ^{13}C NMR spectrum is substantially identical to that of the polymer but for reduced intensity of the signal of polymethylene sequence. The ^{1}H NMR spectrum, in $CDCl_3$ at 25 °C, shows resonances at $\delta = 0.72$ t, 0.86 t, 1.02 t, 1.10 bs, 1.18 q, 1.26 s, 1.40 m, and 2.01 m.

Extensive ^{1}H and ^{13}C NMR chemical shift assignments have been carried out using a combination of mono- (DEPT) and two-dimensional (COSY-DQF,[8] HSQC,[9] and HMBC[10]) experiments. In particular, the connectivities at the branching point were deduced through unambiguous rationalization of the key crosspeaks observed in the HMBC experiment. Correlation between the signals at $\delta = 0.72$ (CH_3, t) and 1.18 (CH_2, q) with that belonging to the quaternary carbon, resonating at 37.3 ppm, strongly suggests a bis-ethyl branched hydrocarbon chain. This conclusion is also corroborated by comparing the ^{13}C NMR chemical shift values of our double branched polyethylene chain with those calculated using the known additivity rules.[11] The ^{13}C NMR chemical shifts assignment is reported in Figure 2. On the basis of the relative intensities of the above-described patterns of resonances, a structure can be hypothesized with a *n*-alkyl chain end arising from initiation through ethylene insertion into the Zr−H bond, a vinylidene chain end arising from termination (detachment of unsaturated chain from the metal), the ethyl branching, and the typical double branching in the inner part of the chain.

The mechanism responsible for the formation of such a branching could be the simple prolongation of the process previously proposed[1] for the formation of ethyl branches. In Figure 3 where the overall pathway is reported is shown the intermediate **4** with the branched chain in the inward site transferring the β-hydrogen to the incoming monomer. Then the unsaturated chain end should give insertion through ethyl migration from the outward site to form the quaternary carbon.

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* Corresponding author. E-mail oliva@chem.unisa.it.

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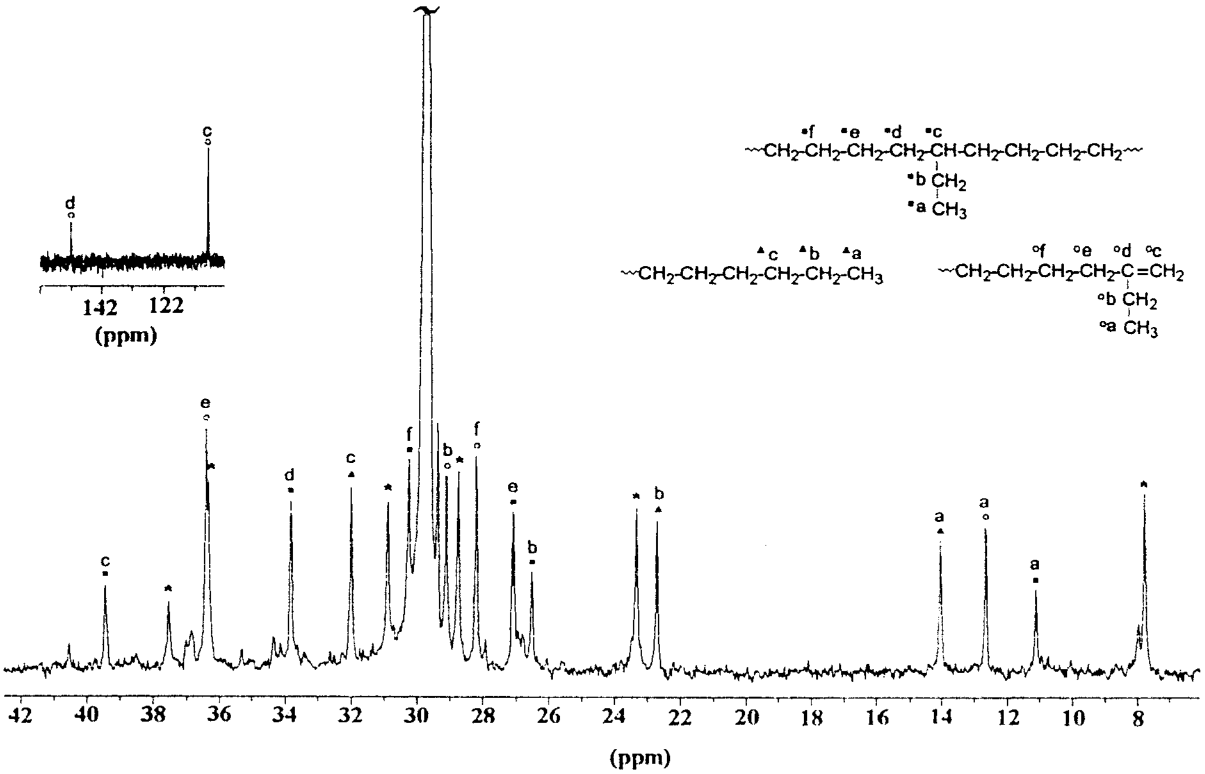
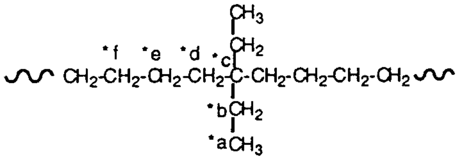


Figure 1. ^{13}C NMR spectrum of the polyethylene prepared at 0 °C (see text and note 6). The lines indicated by asterisks are the unprecedented resonances.



carbon type	chemical shifts (ppm)
a	7.9
b	28.8
c	37.6
d	36.4
e	23.4
f	31.0

Figure 2. Chemical shift assignment of the unprecedented pattern of resonances.

It is worth noting that no evidence of the presence of this double branch was found by analyzing the polyethylene obtained with *meso*-(EBIZrCl_2). The comparison between the behavior of the two zirconocenes suggests that the β-branched growing chain (intermediate **4**) evolves toward insertion with the more crowded EBIZrCl_2 whereas either insertion or β-hydrogen transfer occurs with the title zirconocene. In this picture the monomer insertion occurs possibly after skip of the β branched growing chain to the outward site. The frequency of such a skip should decrease with decreasing the temperature and correspondingly should increase the β-hydrogen transfer and the quaternary carbon centers formation.

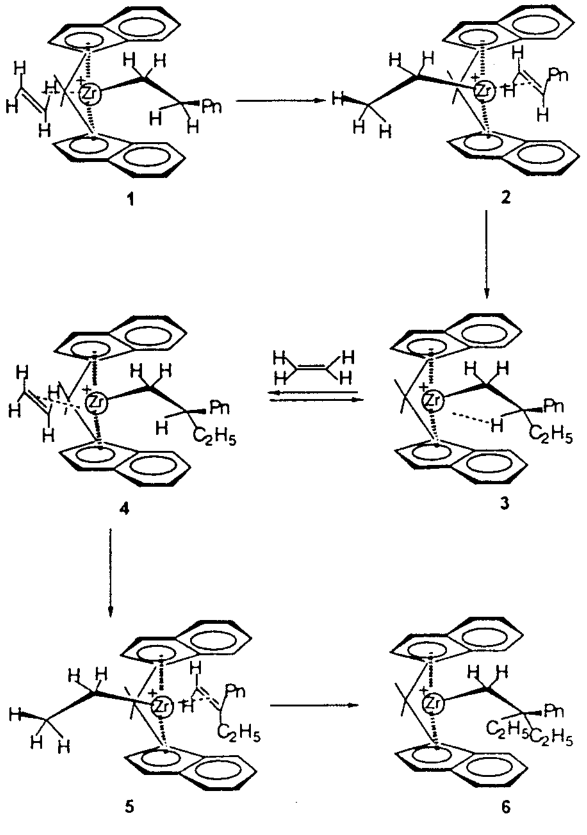


Figure 3. Proposed mechanism for the formation of the quaternary carbon.

As a final remark we would like to stress that from the above-described isomerization arises a kind of branching lacking in chemically vulnerable tertiary carbons and as a consequence a LLDPE with higher stability toward oxidative degradation.

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References and Notes

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(5) δ = 7.34 (2H, d, J 8.8 Hz), 7.18 (2H, d, J 7.5 Hz), 6.84 (2H, dd, J 7.5, 7.0 Hz), 6.57 (2H, dd, J 8.8, 7.0 Hz), 6.53 (2H, d, J 3.4 Hz), 5.53 (2H, d, J 3.4 Hz), 2.01 (3H, s), 1.51 (3H, s) at 25 °C in C_6D_6.

(6) The NMR spectra of the polymers were recorded at 105 °C in tetrachlorodideuterioethane on an AM 250 Bruker spectrometer. The chemical shifts are referred to $C_2D_2Cl_4$ used as internal reference at $\delta = 74.26$ ppm. For the assignment of the vinylidene chain end see: Rossi, A.; Zhang, J.; Odian, G. *Macromolecules* **1996**, *29*, 2331.

(7) The polymerization was carried out in a 100 cm^3 glass flask charged under a nitrogen atmosphere with 27 cm^3 of toluene and 400 mg of solid MAO. The mixture was magnetically stirred, thermostated at 0 °C, and inert atmosphere was replaced by ethylene at 1 atm; then 3 cm^3 of the toluene solution of *meso*-isopropylidenebis(1-indenyl)zirconium dichloride (1 mg cm^{-3}) was introduced. The flask was fed with constant monomer pressure, and after 2 h the reaction was stopped by injecting methanol. The mixture was poured into acidified methanol, and the polymer was recovered by filtration, was washed with fresh methanol, and dried in a vacuum. Yield 1.6 g, mp 121 °C. A M_n value around 2000 Da has been calculated from the NMR spectrum. The level of saturated quaternary carbon centers is around 2 mol % on the basis of monomer units.

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