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Branched Polyethylene by Ethylene Homopolymerization with *meso*-Zirconocene Catalyst

Lorella Izzo,* Lucia Caporaso, Gerardo Senatore, and Leone Oliva

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

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ABSTRACT: The polyethylene obtained in the presence of the catalyst constituted by the meso isomer of the prototypical zirconocene complex (ethylene)bis(1-indenyl)zirconium dichloride activated by methylalumoxane is characterized by the presence of ethyl branches. The intensities of the ^{13}C NMR signals associated with these branches indicate that there are about 1−2 ethyl groups per 100 monomer units. As a consequence, the melting temperature is 10−15 °C lower than the linear polyethylene obtained with the rac mixture of the same zirconocene complex. On the basis of kinetic evidence, a branching mechanism that involves a β-H transfer to the coordinated ethylene is proposed.

Introduction

The traditional polyinsertion processes as well as the more recent homogeneous Ziegler−Natta catalysts promote ethylene polymerization to linear high-density polyethylene (HDPE). The substantial absence of defects allows these polyethylene chains to organize themselves into stable crystalline lattices with melting points around 135 °C. Aimed at reducing this melting temperature and the size of the crystals, some industrial processes employ 1-alkenes as comonomers which introduce short branches in the polyethylene chain (LLDPE). The discovery of catalysts based on late-transition metal compounds disclosed the possibility of obtaining branched polyethylene by ethylene homopolymerization. As a matter of fact, methyl branches are present, e.g., in the polyethylene obtained by Brookhart with Ni-based catalysts,[1] whereas more recently, small amounts of long branching together with methyl branches have been detected in the polyethylene synthesized at high temperatures with a constrained geometry catalyst.[2] On the contrary, little information is available on the synthesis of ethyl branched polyethylene with metallocene-based catalysts.[3]

Results and Discussion

In Figure 1 is reported the ^{13}C NMR spectrum of the polyethylene obtained in the presence of *meso*-(ethylene)bis(1-indenyl)zirconium dichloride (meso-1) activated by methylalumoxane (MAO) at 20 °C and 1 atm of ethylene. In addition to the resonance of the polymethylene sequence ($S_{\delta+\delta+}$) at 27.8 ppm (HMDS scale), the spectrum shows a pattern of weak signals, as reported in Table 1, which can be assigned to ethyl branches in the polymeric chain.[4] The spectrum does not show relevant signals of other kind of branches. The amount of ethyl branches can be evaluated from the relative areas of the methylene carbon resonances associated with the branching, e.g., through the following relationship:

$$\%\ \text{branches} = 100[A_e/A_{TOT}] \qquad (1)$$

and it results in 1.3 mol %, on the basis of monomer units.

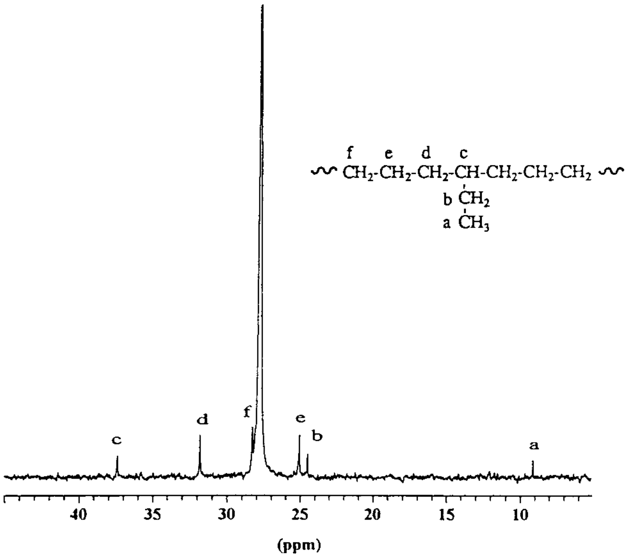

Figure 1. ^{13}C NMR spectrum of the polyethylene obtained in the presence of *meso*-(ethylene)bis(1-indenyl)zirconium dichloride at 20 °C and 1 atm of ethylene.

Table 1. ^{13}C NMR Chemical Shift Assignments for the Ethyl Branches

type of carbon	chemical shift (ppm)	no. of carbons
a	9.11	1
b	24.49	1
e	25.07	2
f	28.20	2
d	31.70	2
c	37.40	1

On the contrary, in the ^{13}C NMR spectrum of the polyethylene obtained in the same experimental conditions with the *rac*-(ethylene)bis(1-indenyl)zirconium dichloride (rac-1) activated by MAO, other signals besides the $S_{\delta+\delta+}$ were not detected. The difference between the polymers obtained with the two catalytic systems is also evidenced by differential scanning calorimetry (DSC) analysis. In Figure 2 are reported the thermograms of the polyethylene synthesized with meso-1/MAO (a) and with rac-1/MAO (b). Although the melting temperature indicated by curve b is that expected for HDPE, the melting temperature of the

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* E-mail: izzo@chem.unisa.it.

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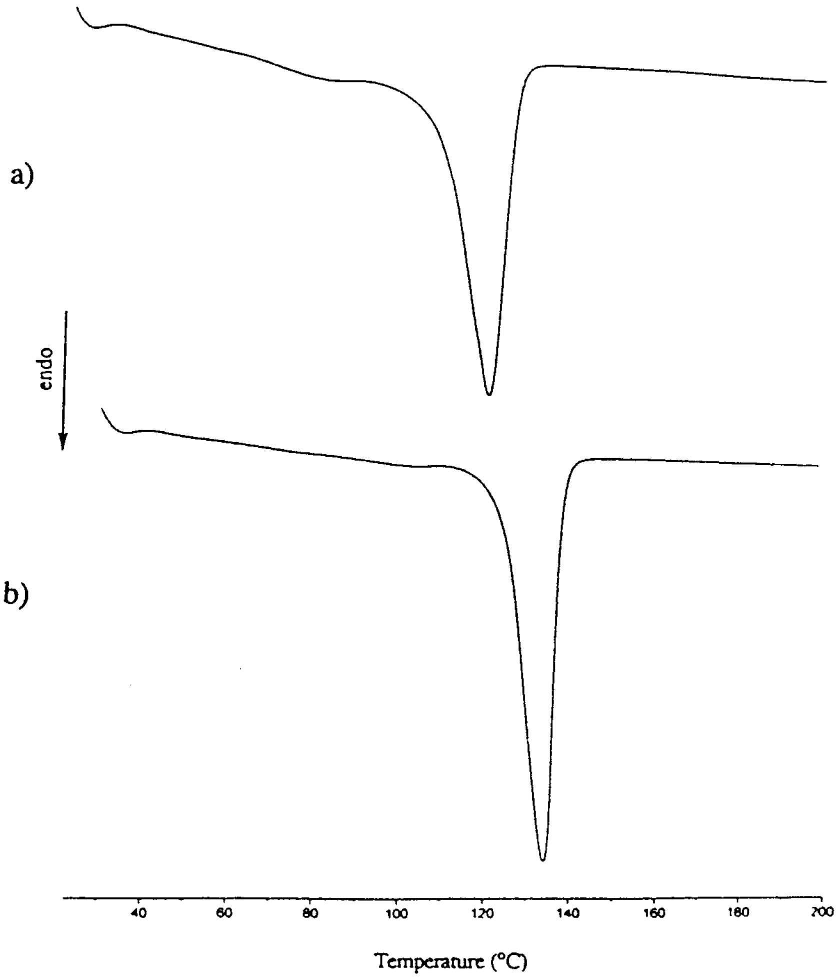

Figure 2. DSC diagrams of the polyethylenes obtained with meso-1 (T_m = 123 °C) (a) and rac-1 (T_m = 135 °C) (b) at 20 °C and 1 atm of ethylene.

polymer obtained with the meso-1/MAO is in the range of the values expected for LLDPE.[5]

Any proposed mechanism must account for the observed ethyl branching and for the absence of any other branching. In the Scheme 1 are reported three possible mechanisms: (I) Formation of 1-butene by ethylene dimerization followed by copolymerization. (II) Growing chain isomerization through γ-hydrogen abstraction followed by chain rearrangement, according to the mechanism involved in the formation of stereoerrors in propene polymerization.[6] (III) Growing chain isomerization through β-hydrogen transfer to the coordinated monomer with formation of a zirconium−ethyl bond followed by insertion of the unsaturated chain end into this bond.[7]

In the GC analysis of the low-boiling components of the polymerization mixture, 1-butene was not detected. This result suggests that 1-butene even if produced by meso-1/MAO is not enough to form the ethyl branches through mechanism I, which therefore can be discarded.

On the basis of mechanism II, the rate of branch formation must be independent of the monomer concentration, and as a consequence, one should expect a decrease of the branch content with increases in the monomer concentration in the feed, due to the corresponding increase of the propagation rate. The results of a series of polymerizations carried out at different monomer pressures and temperatures in the presence of meso-1/MAO are reported in Table 2. One can observe that the branch content is substantially constant. As a consequence, it seems reasonable to affirm that the kinetics of both chain propagation and branch formation are dependent on the ethylene concentration in the polymerization mixture, in agreement with mechanism III.

It is worthwhile to observe that the absence of ^{13}C NMR signals relative to the unsaturated chain end seems to indicate that practically all of the β-H transfers with formation of a chain end unsaturated polyethylene evolves toward reinsertion into the zirconium−ethyl bond. That suggests a concerted mechanism of β-H abstraction and insertion of unsaturated chain end into zirconium−ethyl bond.

The proposed mechanism for ethyl branch formation is indirectly supported by the behavior of the more hindered catalyst, *meso*-(ethylene)bis(4,7-dimethyl-1-indenyl)zirconium dichloride/MAO. This catalyst, which has been reported to scarcely be prone to the β-H abstraction in the propene polymerization,[8] polymerizes ethylene to highly linear polyethylene.[9]

There is necessarily a correlation between the spatial position of the two indenyl ligands in the meso-1 and the microstructure of the obtained polyethylene. A molecular mechanics analysis on model complexes based on the analogous *meso*-(ethylene)bis(4,5,6,7-tetrahydro-1-indenyl) ligand as a possible intermediate for the propene polymerization was reported by Guerra et al.[10]

Scheme 1

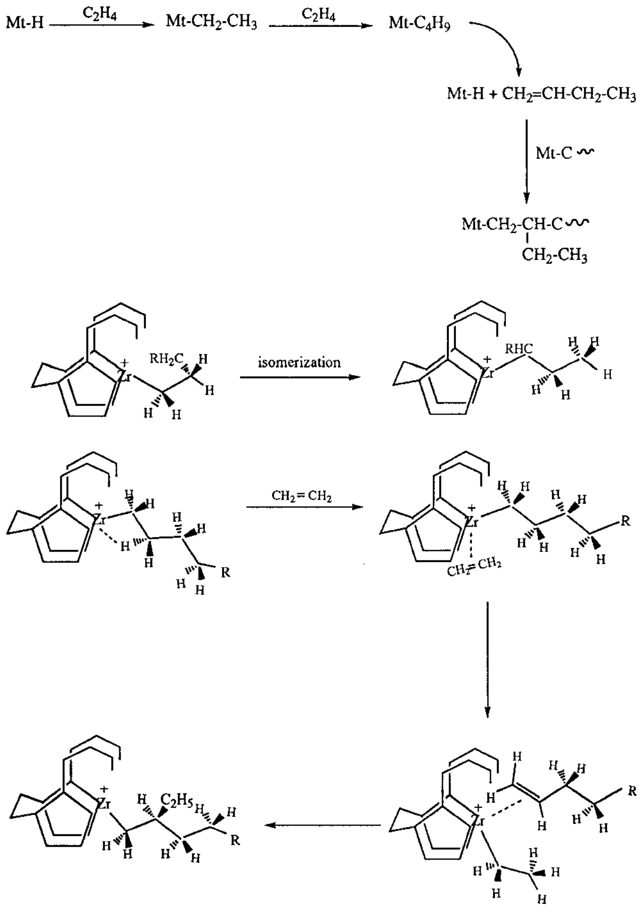

Table 2. Percentage of Ethyl Branches and Melting Point for Polyethylenes Obtained at Different Monomer Concentrations and at Different Temperatures in the Presence of *meso*-1/MAO

T (°C)	P (atm)	$[E]_{feed}$	% branches[a]	T_m (°C)
20	0.3	0.07	1.5	121
20	1	0.2	1.3	123
20	2	0.5	1.4	122
20	5	1.4	1.1	122
0	1	0.3	1.6	122
−25	1	0.6	1.8	121

[a] Calculated according to the eq 1 (see the text).

In that paper, the β-H transfer to the coordinated olefin rather than the monomer insertion was supposed for the growing chain in the more crowded ("inward") site.

Experimental Section

Materials. All manipulations of air-sensitive materials were performed under a nitrogen atmosphere using either standard Schlenk-type techniques or a Braun drybox. Polymerization-grade ethylene was purchased from Società Ossigeno Napoli and used without further purification. Toluene was refluxed for 48 h over metallic sodium and distilled under a nitrogen atmosphere. Methylaluminoxane (MAO), 30% toluene solution from Witco, was used as dry solid after toluene was removed by distillation in vacuo.

Synthesis of the Zirconocene Compounds. The *meso*-ethylenebis(1-indenyl)zirconium dichloride was synthesized through the reaction between the *syn*-1,2-bis(3-(trimethylsilyl)-inden-1-yl)ethane and $ZrCl_4$.[11] The syn-ligand isomer, in fact, leads to the *meso*-zirconocene, whereas the anti-ligand isomer leads to the *rac*-zirconocene. The syn ligand was synthesized as reported by Nifant'ev[11] for the analogue anti isomer, by adding dropwise at −40 °C 6.5 mL of Me_3SiCl (52 mmol) to a suspension of 6 g (23.2 mmol) of dilithio-1,2-bis(indenyl)-ethane[12a,b] in 120 mL of Et_2O anhydrous. The solution was filtered, and the solvent was removed in vacuo. The yellow residue was recrystallized from anhydrous pentane. Yield: 3.7 g (40%). ^1H NMR in C_6D_6: δ 7.52 (d, 2H), 7.46 (d, 2H), 7.30 (t, 2H), 7.23 (t, 2H), 6.33 (d, 2H, $=CH-$), 3.29 (bs, 2H, C_5 ring), 3.10 (bm, 4H, $-CH_2-CH_2-$), −0.060 (s, 18H, $-SiMe_3$). The *meso*-(ethylene)bis(4,7-dimethyl-1-indenyl)zirconium dichloride was synthesized according to the literature procedure.[8]

Polymerization Procedure. Ethylene polymerizations at atmosphere pressure were carried out in a 100 mL glass flask charged under nitrogen atmosphere with 27 mL of a freshly prepared MAO solution (15.2 mg/mL) obtained by dissolving dry solid MAO in toluene. The mixture was magnetically stirred and thermostated at +20, 0, or −25 °C. The inert atmosphere was replaced by ethylene at 1 atm (or by a 0.3/0.7 ethylene/nitrogen gaseous mixture at 1 atm), and then, 3 mL of a toluene solution of *meso*-ethylenebis(1-indenyl)-zirconium dichloride (1 mg/mL) was introduced (Al/Zr in mol = 1000). After 1 h, the reaction mixture was poured into 100 mL of acidified ethanol. The product was recovered by filtration and dried in a vacuum.

Polyethylene at higher pressure was prepared in a Büchi glass autoclave previously evacuated and thermostated at +20 °C and then filled with 80 mL of an anhydrous toluene solution containing 7.1 mmol of MAO and 7.1×10^{-6} mol of *meso*-ethylenebis(1-indenyl)zirconium dichloride (Al/Zr in mol = 1000). The ethylene was quickly introduced at the desired pressure (2.0 or 5.0 atm). Temperature, pressure, and stirring rate (1000 rpm) were kept constant during the experiment. After 20 min, the ethylene was vented, and the mixture was discharged into 200 mL of ethanol acidified with HCl. The polyethylene was recovered by filtration and dried under vacuum.

The ethylene composition in the liquid phase was calculated by Lewis and Luke's equation[13a] in conjunction with fugacity function chart as reported in the literature.[13b]

^{13}C NMR Analysis. The spectra of the polymers were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode. The results were obtained at 120 °C using a delay time of 1.0 s; any change in the relative carbon intensity has been observed with a delay time of 4 s. A pulse width of 2.0 μs, corresponding to a 90° flip angle, was used. The proton decoupler remained on for the complete cycle.

The samples were prepared by introducing 30 mg of polymer with 0.5 mL of tetrachloro-1,2-dideuterioethane into a tube (5 mm outer diameter). Hexamethyldisiloxane (HMDS) was used as an internal reference.

DSC Analysis. The thermal measurements were carried out in a Du Pont 2920 differential scanning calorimeter at heating rate of 10 °C/min on about 10 mg of sample. The instrument was calibrated by the measurement of the melting point of indium.

GPC analysis. The GPC of the copolymers were recorded on a Waters 150-C gel-permeation chromatography with four polystyrene gel columns (10^4 Å pore size) in dichlorobenzene at 120 °C and calibrated with polystyrene. The M_w were in the range between 6.2×10^4 and 1.0×10^5, with $M_w/M_n = 1.9-2.1$.

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