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Branched Polyethylene Produced by a Half-Titanocene Catalyst

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Introduction. Polymerization of ethylene by either the classical heterogeneous Ziegler−Natta or the new homogeneous "metallocene" catalysts affords highly linear polymers (high-density polyethylene). The production of "branched" low-density polyethylene (LLDPE) thus requires the copolymerization with a comonomer (usually 1-butene, 1-hexene, or 1-octene). In this respect, a recent technological advance involves the discovery of new half-metallocene catalysts in which the cyclopentadienyl ligand has a covalently attached donor group, which can either be anionic, e.g., an amido group ("constrained-geometry catalysts")[1], or neutral, e.g., an amino group ("low-valency catalysts").[2] These catalysts afford LLDPEs with narrow molecular weights and comonomer distributions without loss of processability and perform well even at high polymerization temperatures.

An alternative route to the synthesis of LLDPE from a simple ethylene feed involves the use of a dual-component catalytic system able to oligomerize ethylene to a suitable α-olefin and simultaneously copolymerize it with ethylene.[3] A major limitation to this approach comes from chemical interference between the two catalysts and different responses to the reaction conditions.

More recently, Brookhart et al.[4] disclosed a novel class of catalysts based on Ni(II) or Pd(II) diimine compounds which allow one to produce polyethylenes containing mainly methyl branches in variable amounts (tunable by proper selection of the reaction conditions and catalyst structure) via an alkyl chain isomerization mechanism.[4,5]

In this paper, we report the synthesis of polyethylenes containing significant amounts of almost exclusively butyl branches (i.e., having the structure of LLDPE achievable by copolymerizing ethylene and 1-hexene) from a simple ethylene feed by using the catalytic system Cp^*TiMe_3-$B(C_6F_5)_3$ ($Cp^* = \eta^5$-C_5Me_5). The mechanism of branching formation is also discussed.

Results and Discussion. We have previously reported that half-metallocene hydrocarbyls of formula $Cp'MR_3$ ($Cp' = C_5H_5$ or C_5Me_5, M = Ti or Zr, R = Me or CH_2Ph) activated by 1 equiv of $B(C_6F_5)_3$ are efficient catalysts for the polymerization of ethylene and propylene[6] and, for M = Ti, the syndiotactic-specific polymerization of styrene.[7] Subsequently, one of these catalysts, namely, Cp^*TiMe_3-$B(C_6F_5)_3$, has been extensively investigated by several authors in both the polymerization of olefins and styrene,[8] occurring via a Ziegler−Natta mechanism,[7b] and the polymerization of monomers such as vinyl ethers, *N*-vinyl carbazole and isobutene, occurring via a carbocationic mechanism.[9]

Table 1. Results of Ethylene Polymerizations with Cp^*TiMe_3-$B(C_6F_5)_3$[a]

run	polymerization temperature (°C)	yield (g)	branches per 1000 C[b]	T_m (°C)	M_n 10^{-3}	M_w/M_n
1	50	0.45	15	123	38	10.7
2	25	0.35	50	101[c]	39	15.4
3	0	0.30	32	118, 132[d]	156	5.0

[a] Polymerization conditions: Ti = B = 88 μmol, $AlMe_3$ = 0.1 mmol, toluene = 26 mL, ethylene = 1 atm, and time = 20 min. [b] In the main chain and evaluated from ^{13}C NMR. [c] Broad peak centered at 101 °C. [d] Two broad peaks centered around 118 and 132 °C.

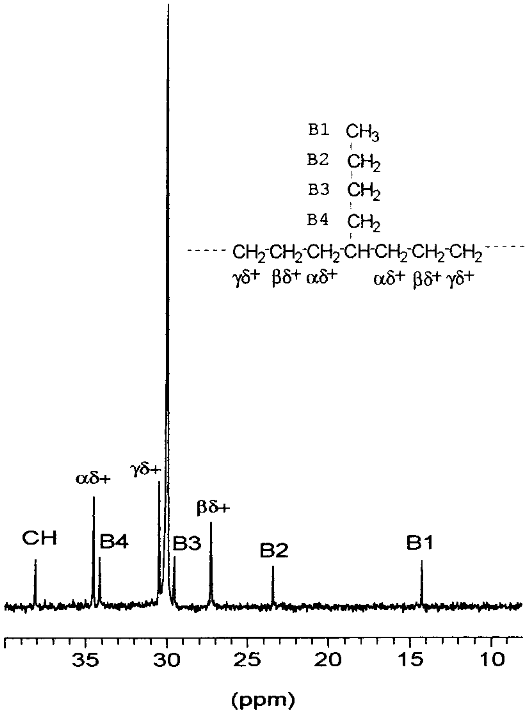

Figure 1. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 120 °C, δ in ppm from TMS) of a polyethylene sample prepared at 50 °C (sample 1). The resonances are assigned according to the scheme (see Soga et al.[10] for the nomenclature used to designate the different carbon types).

While polymerization of ethylene by the above catalyst was previously reported to afford linear polymers,[8a] we have now unexpectedly found that polyethylene samples containing up to 5% branches are obtained at temperatures ranging between 0 and 50 °C under 1 atm of monomer pressure using high Ti concentrations (~3.5 mM). The main polymerization conditions and results are reported in Table 1. The ^{13}C NMR spectrum of a polyethylene prepared at 50 °C (sample 1) is displayed in Figure 1. In addition to the main peak at δ 30.0 ppm due to the $S_{\delta+\delta+}$ carbons of the polymethylene sequences, minor resonances are observed at δ 14.2, 23.4, 27.3, 29.6, 30.5, 34.2, 34.6, and 38.2 ppm. On the basis of the literature data[10] and distortionless enhancement by polarization transfer experiments, they are attributed according to the scheme of Figure 1 to the carbon atoms of a *n*-butyl side group and to the main chain methine and $\alpha\delta^+$, $\beta\delta^+$, and $\gamma\delta^+$ methylene carbons.[10] In other words, sample 1 is identical to an ethylene (E)-1-hexene (H) copolymer containing 1.5%

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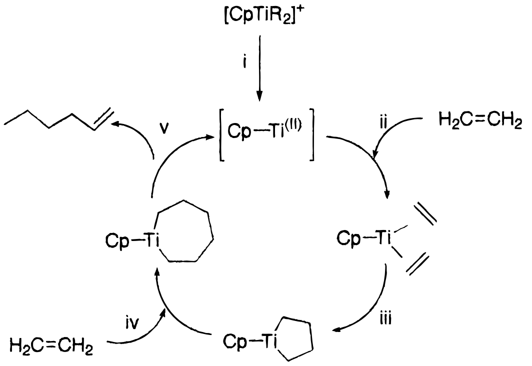
Scheme 1. Mechanism for the Formation of 1-Hexene[a]



[a] All of the titanium complexes in the catalytic cycle have a +1 overall charge.

isolated comonomer units (...EEHEE...). Samples 2 and 3, prepared at 25 and 0 °C, respectively, have similar spectra, but the amount of butyl branches is higher and some lower intensity resonances due to HEEH and EHEH sequences,[10] as well as to unidentified different branches, are detected. No resonances attributable to ethyl or hexyl branches are observed.

The most reasonable mechanism accounting for the observed butyl branching would involve the in situ formation of 1-hexene and its subsequent copolymerization with ethylene, although alternative mechanisms, involving e.g., C−H activation of the growing chain via σ-bond metathesis, have been proposed to explain related findings.[11] In the present case, GC analysis of the polymerization mixtures actually showed the presence of 1-hexene, which was unambiguously identified by mass spectroscopy and ^1H NMR.

1-Hexene is reasonably produced by a catalytic species, formed in situ from the precursors, able to selectively trimerize ethylene. As a matter of fact, strong evidence is reported in the literature pointing to a multisite nature of the catalytic system Cp^*TiMe_3-$B(C_6F_5)_3$.[12] In fact, the $[Cp^*TiMe_2]^+$ cationic complex, which is the primary reaction product, has been shown to decompose to lower oxidation species, including the Ti(III) $[Cp^*TiMe]^+$ complex.[12b,c] In this particular catalytic system, the $[Cp^*TiMe_2]^+$ cation is believed to be active in the polymerization of ethylene and α-olefins, while the Ti(III) cation has been shown to be the catalyst producing syndiotactic polystyrene.[12b,c] Moreover, dimeric methyl-bridged Ti complexes, as well as Ti-μ-Me-B zwitterions have been identified.[12c,13] Related MAO-activated half-sandwich catalysts have also been shown to be multisite systems, containing Ti(IV), Ti(III), and Ti(II) species.[14]

The selective trimerization of ethylene to 1-hexene by a homogeneous chromium catalyst was previously reported by Briggs,[15] who proposed a mechanism involving metallacycle intermediates. This mechanism was later supported by the synthesis and the reactivity of chromacyclopentane and chromacycloheptane derivatives.[16] By analogy, a possible mechanism accounting for the selective formation of 1-hexene in our case could involve (see Scheme 1) five steps: (i) reductive elimination in a $[Cp^*TiR_2]^+$ cation (R = alkyl or H), affording a cationic Ti(II) species; (ii) coordination of two ethylene molecules to the latter; (iii) oxidative addition to form a cationic Ti(IV) metallacyclopentane; (iv) further insertion of ethylene to give a metallacycloheptane; (v) followed by reductive elimination of 1-hexene, possibly via an intermediate hexenyl hydride species. The selective formation of 1-hexene would be due to the relative stabilities of the different metallacycles with respect to further monomer insertion or β-H abstraction preceding the reductive elimination. Metallacyclopentane intermediates have been previously observed in olefin dimerization.[17] The formed 1-hexene would then easily be copolymerized with ethylene by the $[Cp^*TiR_2]^+$ complex, which efficiently incorporates the bulkier α-olefin because of its rather open coordination sphere. Although at this moment the mechanism is tentative and requires further support, several features, such as the absence of ethyl branches in the polymer and of 1-butene in the oligomeric fraction, favor the metallacycle route versus a more conventional insertion/β-H-elimination oligomerization mechanism.

The degree and the type of polymer branching are reasonably connected to a variety of factors which are diversely affected by the polymerization conditions, e.g., the competitive formation of the different organometallic species derived from the catalyst precursors, the relative rates of ethylene oligomerization and polymerization, and the reactivity ratios of the competitive incorporation of ethylene and 1-hexene. In this framework, one can explain the effect of the polymerization temperature on the resulting polymer, as well as the fact that only linear polyethylene was previously obtained under different conditions.

In conclusion, a butyl-branched polyethylene having the features of LLDPE has been synthesized from an ethylene feed without any added comonomer by using the Cp^*TiMe_3-$B(C_6F_5)_3$ catalytic system. This unexpected result has been rationalized by detecting the in situ formation of 1-hexene. The latter would be selectively produced by a cationic Ti(II) active species through a mechanism involving metallacycle intermediates, and subsequently, it would be copolymerized with ethylene by a different organometallic species, namely, the $[Cp^*TiR_2]^+$ complex. Work is in progress in order to identify or synthesize Ti(II) species able to oligomerize ethylene.

Experimental Section. Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk or glovebox techniques. Polymerization grade ethylene was used without further purification. Toluene was refluxed over metallic sodium and distilled under a nitrogen atmosphere. Cp^*TiMe_3[18] and $B(C_6F_5)_3$[19] were prepared according to the literature.

The polymerization runs were carried out in 100-mL glass flasks provided with a magnetic stirrer and thermostated at the proper temperature. The reactor was charged under nitrogen introducing 26 mL of toluene and 0.1 mmol of $AlMe_3$ (as a scavenger); nitrogen was replaced with ethylene at atmospheric pressure, and the run was initiated by injecting simultaneously 88 μmol of Cp^*TiMe_3 and 88 μmol of $B(C_6F_5)_3$ in toluene solutions (1 mL each). The run was stopped with methanol after 20 min, the reaction mixture was poured into acidified methanol, and the precipitated polymer was collected and dried under vacuum at 90 °C. The main polymerization results are reported in Table 1. To check for the presence of 1-hexene in the polymerization mixture, some runs were carried out as above, but at the end of the polymerization, a few milliliters of the reaction mixture were distilled and analyzed by GC-MS and ^{1}H NMR, both revealing the presence of 1-hexene.

The obtained polymers were analyzed by NMR on an AM 250 Bruker spectrometer operating in the Fourier transform mode. The spectra were recorded in $C_2D_2Cl_4$ at a temperature of 120 °C and referenced versus TMS using the resonance of the $S_{\delta+\delta+}$ carbons of the polymethylene sequences ($\delta = 30.0$ ppm) as a secondary standard. DSC analyses were carried out with a DuPont 9900 instrument with a heating rate of 10 °C/min. DSC thermograms of samples 2 and 3 showed very broad peaks, probably as a consequence of inhomogeneous 1-hexene incorporation into the polymers. Molecular weights were measured versus atactic polystyrene by GPC on a Waters 150-C instrument operating at 120 °C in *o*-dichlorobenzene.

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