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^{13}C-Enriched End Groups of Isotactic Polypropylene and Poly(1-butene) Prepared in the Presence of Ethylenediindenyldimethyltitanium and Methylalumoxane

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ABSTRACT: Isotactic polypropylene and poly(1-butene) have been prepared in the presence of stereorigid chiral titanocenes and ^{13}C-enriched organoaluminum compounds. The polymers, carrying selectively ^{13}C-enriched end groups, have been analyzed by ^{13}C NMR. The structure of the enriched end groups confirms that the stereochemistry of the polyinsertion is controlled by the chiral titanium of the catalytic complexes. The mechanism of the steric control is very similar to that previously demonstrated for heterogeneous catalysts. Conversely, in the presence of achiral titanocenes, some isotactic steric control comes from the chirality of the last monomer unit of the growing chain end.

1. Introduction

Polymerization of propene and 1-butene to isotactic polymers, in the presence of homogeneous catalysts based on group IV (4)[18] transition metallocenes and methylalumoxane, has been reported by Ewen[1] and Kaminsky.[2] According to these authors, the stereochemical sequence of the configurations of the substituted carbons of the isotactic poly(α-olefins) obtained in the presence of stereorigid chiral titanocenes such as *rac*-ethylenediindenyl(X_2)titanium (where X may be halide, alkyl, aryl, etc.) is very much like that of isotactic polyolefins prepared in the presence of heterogeneous Ziegler–Natta catalysts and is in agreement with the "enantiomorphic sites" statistical model of the stereospecific propagation proposed by Shelden,[3] which implies that steric control is ultimately due to the chiral arrangement of the ligands of the transition-metal atoms of the catalytic complexes. The aim of this work is to investigate the mechanism of isotactic specific polymerization in the presence of the just-mentioned catalytic systems by determining the stereochemical structure of the ^{13}C-enriched end groups that result from initiation steps when polymerization is performed in the presence of ^{13}C-enriched aluminum alkyls. Similar research, concerning polymerization of α-olefins in the presence of heterogeneous catalytic systems and in the presence of soluble achiral titanocenes, has been reported in previous papers[4-6] and afforded considerable information about the mechanism of stereospecific insertion and regiospecificity.

2. Experimental Section

Ethylenediindenyldimethyltitanium (EITM) was prepared by allowing to react, under nitrogen atmosphere, ethylenediindenyltitanium dichloride, synthesized according to the literature,[7] with a slight excess of methyllithium dissolved in ethyl ether at $T = -20$ °C. After the temperature had raised to 0 °C, the reaction mixture was hydrolyzed with cold deaerated water. The organic layer was separated and dried over sodium sulfate, and the solvent was removed by distillation in vacuo to give the product as orange-red powder. Enriched $Al(CH_3)_3$ (TMA), $Al(CH_2CH_3)_3$ (TEA), and methylalumoxane were prepared according to the literature.[6,8] Polymerization-grade propene and 1-butene were purchased from Societá Ossigeno Napoli. Toluene was used after anhydrification and distillation over metallic sodium under nitrogen atmosphere. Polymerizations have been performed at −45 °C in a glass reactor as described previously.[6] The polymerization conditions and the yields are reported in Table I. In comparison with the results reported by Ewen,[1] the addition of $Al(C_2H_5)_3$ or $Zn(CH_3)_2$ greatly decreases the production of solid (i.e., insoluble in methanol) polymers.

The polymers were dissolved in 1,1,2,2-tetrachlorodideuterioethane containing hexamethyldisiloxane as internal chemical shift reference in 5-mm-o.d. tubes at 393 K. ^{13}C NMR spectra were obtained on a Bruker AM 250 spectrometer operating in the Fourier transform mode at 62.89 MHz. Spectral width, acquisition time, and data points were 3.5 kHz, 4.5 s, and 32 K, respectively. ^{13}C NMR spectra were performed with a 60° (2.5-μs) excitation pulse with a 1.5-s delay between pulses and broad-band decoupling mode to remove ^{1}H–^{13}C couplings. The relative amounts of the enriched carbons were confirmed by performing the spectrum of sample **2a** using inverse-gated mode of recording in order to obtain proton-decoupled ^{13}C spectra without NOE effect. Under this condition the areas of the peaks are proportional to the amounts of the different carbons. An 80° (3.5-μs) excitation pulse with 10 s of delay between pulses was used. All spectra were processed with a 1-Hz line-broadening function prior to transformation.

3. Results and Discussion

One sample of polypropylene (**1**) and one sample of poly(1-butene) (**2**) were prepared at −45 °C, as described in the experimental part with each of the following catalytic systems: (a) ethylenediindenyldimethyltitanium/methylalumoxane/^{13}C-enriched trimethylaluminum/dimethylzinc (samples **1a** and **2a**); (b) ethylenediindenyldimethyltitanium/methylalumoxane/triethylaluminum ^{13}C-enriched on the methylene carbons/dimethylzinc (samples **1b** and **2b**). The two samples of polypropylene prepared in the presence of catalytic systems a and b (**1a** and **1b**) and poly(1-butene) prepared in the presence of a (**2a**) were fractionated by stirring in the presence of heptane either at 25 °C (**1a** and **1b**) or at −20 °C (**2a**) and separating the soluble and the insoluble parts. The insoluble fractions of **1a**, **1b**, **2a** and poly(1-butene) prepared with system b (**2b**) were analyzed by ^{13}C NMR.

The spectra are reported in Figures 1 (samples **1a** and **2a**) and 2 (samples **1b** and **2b**). All the examined samples are highly isotactic. In fact the resonance of the *mmmm* methyl stereochemical pentads at 19.7_2 ppm of samples **1a** and **1b** and that of the *mmmm* methylene stereochemical pentads at 25.5_3 ppm of samples **2a** and **2b** are by far more intense than the resonances of any other stereochemical pentads.[9] Additional resonances due to the presence of ^{13}C-enriched end groups are observed at 20.5_2 and 21.7_4 ppm (sample **1a**), at 27.5_0 ppm (sample **1b**), at 17.7_1 and 18.0_1 ppm (sample **2a**), and at 24.2_0 ppm (sample **2b**) and are marked by stars in the spectra. The assignments of these resonances are reported in the literature[10-12] and include the stereochemical locations of the enriched carbons with respect to the alkyl substituents of the three neighboring monomer units. In Figure 3 are reported the observed chemical shifts and the Fisher projections of the corresponding end groups.[10,12]

The presence of enriched end groups can be easily understood by considering that (1) they are necessarily

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Table I
Polymerization Conditions[a]

sample	reagents: mol monomer	mL toluene	10^5 mol EITM	g MAO	10^3 mol TMA or TEA	10^3 mol $\mathrm{Zn(CH_3)_2}$	time, h	polymer yield,[b] g
1a	0.35	40	1.7	0.05	0.9	0.9	80	0.06
1b	0.45	40	1.7	0.05	0.9	0.9	130	0.04
2a	0.75	10	1.7	0.05	0.9	0.2	90	0.06
2b	0.75	10	1.7	0.1	0.9	0.2	130	0.07

[a] All the polymerizations have been performed at −45 °C. [b] Insoluble in methanol.

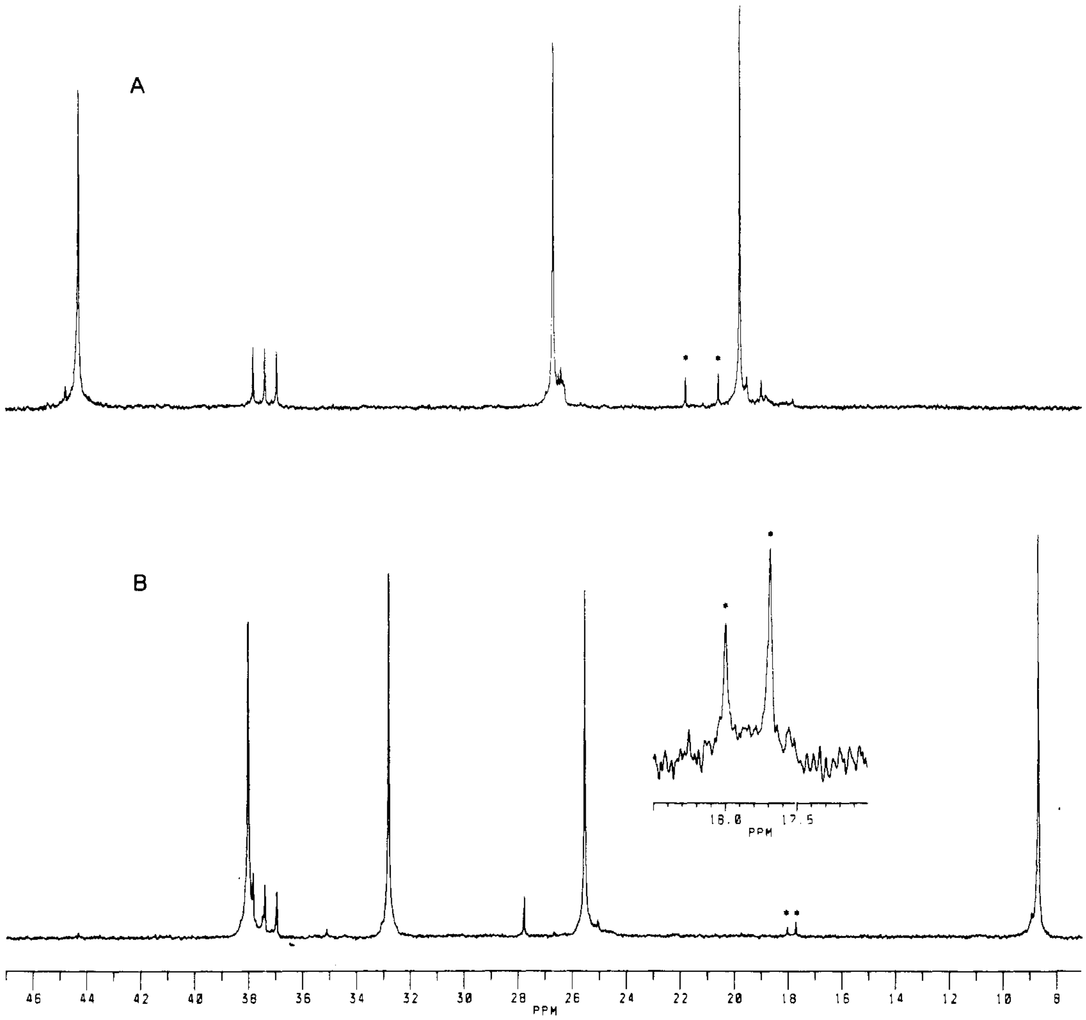

Figure 1. ^{13}C NMR spectra of sample **1a** (A) and sample **2a** (B). The triplet centered at 37.5 ppm is due to folded peaks of solvent.

formed in initiation reactions involving $\mathrm{Ti{-}^{13}CH_3}$ or $\mathrm{Ti{-}^{13}CH_2CH_3}$ bonds; (2) zinc alkyls are efficient chain-transfer agents[13] according to the scheme

$$\mathrm{Ti{-}P + ZnR_2 \rightarrow Ti{-}R + ZnRP}$$

(where P indicates polymer chain and R indicates ^{13}C-enriched alkyl); (3) a new chain starts growing on Ti–R after the chain-transfer process; (4) enriched Rs are quickly exchanged between aluminum alkyls and zinc alkyls.[4,13]

As shown in Figure 3, only some, among the possible diastereoisomeric enriched end groups, are actually detected in the four polymer samples. More precisely, two out of four possible placements of the enriched methyls are observed in the spectra of samples **1a** and **2a**. The other possible placements are absent or negligible.

The areas of the two resonances of the enriched methyls of the 2,4,6-trimethylheptyl end groups observed in sample **1a** (polypropylene) are equal. The area of the resonance of the δt ζt[14] enriched methyls of the 2,4-diethyl-6-methyloctyl end groups of sample **2a** (poly(1-butene)) is twice as large as that of the δe ζe ones. The enriched methylenes of the 2,4,6-triethyloctyl end groups of sample **2b** (poly(1-butene)) have almost all δt ζt placement. The whole picture is similar to that previously observed for the enriched end groups of isotactic polypropylene and poly(1-butene) prepared in the presence of $\delta\mathrm{TiCl_3{-}Al(^{13}CH_3)_3}$ and $\delta\mathrm{TiCl_3{-}Al(^{13}CH_2CH_3)_3}$ catalysts.[4,15,16] The unique stereochemical placement of the enriched methylenes of sample **2b** unequivocally shows that the stereochemistry of the insertion is controlled by the asymmetric environment of the titanium of the catalytic complexes. In fact, as previously discussed,[4,6,16] neither the chain initiation step

$$\mathrm{Ti^{13}CH_2CH_3 \rightarrow TiCH_2CH(C_2H_5)^{13}CH_2CH_3}$$

nor the subsequent insertion step (first propagation step)

$$\mathrm{TiCH_2CH(C_2H_5)^{13}CH_2CH_3 \rightarrow TiCH_2CH(C_2H_5)CH_2CH(C_2H_5)^{13}CH_2CH_3}$$

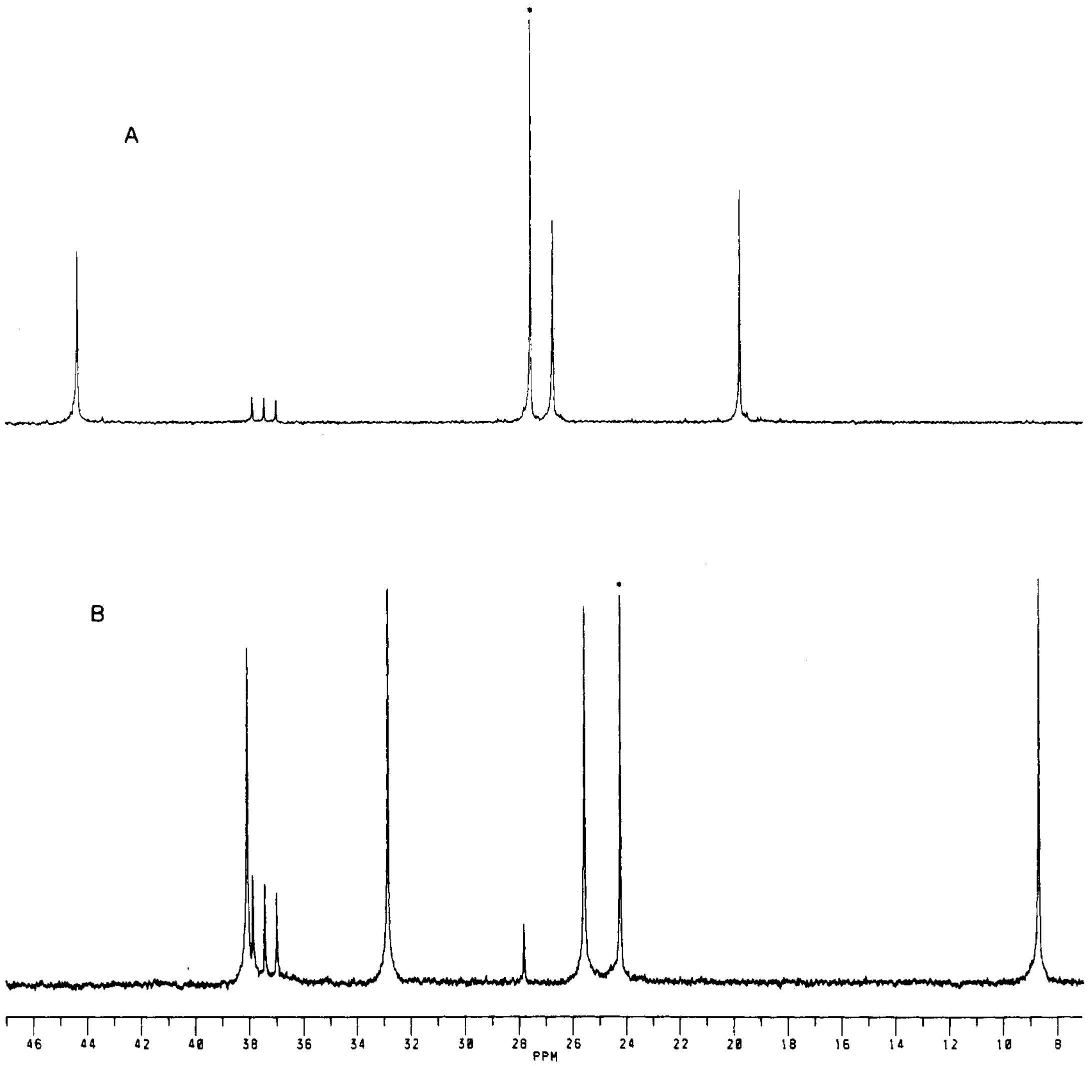

Figure 2. ^{13}C NMR spectra of sample **1b** (A) and sample **2b** (B). The triplet centered at 37.5 ppm is due to folded peaks of solvent.

involves the participation of any chemically asymmetric carbons at the alkyl moiety of the catalytic complexes. Despite that, it turns out that the unenriched ethyls of the resulting 2,4,6-triethyloctyl end groups are in e (or isotactic) arrangement to each other (and, of course, the enriched methylene is in t, or syndiotactic, arrangement with respect to the 2- and 4-ethyls). Therefore the first and the second monomer units entered into the chain did experience the same enantioselective steric control as the third one entered. The presence of such enantioselective control of the insertion before any chiral carbon is involved implies that there must be a chiral center at the titanium moiety of the catalytic complexes and that the steric control depends on this asymmetric center.[4,15,16] A unique stereochemical placement of the enriched methylenes is also observed on the 2,4,6-trimethyloctyl end groups of sample **1b**. Consideration of the subsequent insertions leading to the these end groups leads to the conclusion that even in this case the insertion of all the first three monomer units is highly enantioselective (isotactic). The presence of a chiral carbon at the alkyl moiety of the catalytic complexes soon after the insertion of the first monomer unit (initiation step)

$$Ti^{13}CH_2CH_3 \rightarrow TiCH_2CH(CH_3)^{13}CH_2CH_3$$

does not seem to play a necessary role in determining the steric control.

Equal amounts of δt ζt and δe ζe enriched methyls are observed on the 2,4,6-trimethylhexyl end groups of sample **1a**. This seems to show that chirality of the titanium moiety is not effective in controlling the stereochemistry of the insertion when both the alkyl moiety of the catalytic complexes and the alkyl substituent of the monomer are CH_3. The same behavior was observed in the presence of heterogeneous catalysts based on $\delta TiCl_3-Al(^{13}CH_3)_3$. Both δt ζt and δe ζe enriched methyl carbons have been detected on the 2,4-diethyl-6-methyloctyl end groups of sample **2a** (poly(1-butene)). In this case, however, the area of the resonance of the δt ζt enriched methyls is twice as large as that of the δe ζe ones. This means that the presence of an ethyl substituent on the monomer is sufficient for partial enantioselective control by the asymmetric titanium moiety. In a previous paper a larger amount of δe ζe methyls than δt ζt methyls was detected in poly(1-butene) prepared in the presence of alumoxane and achiral Cp_2TiX_2.[6] As previously discussed,[6] in the presence of these achiral complexes, steric control is ensured, although to a smaller degree, by the presence of chiral carbons on the alkyl moiety of the catalytic complexes.

Of course the structure of the enriched end groups also confirms that, at least for the first steps, the insertion of the monomer is primary (or metal to C1).

4. Conclusions

The results reported in section 3 concerning the structure of the enriched end groups of isotactic polypropylene and poly(1-butene) prepared in the presence of homogeneous catalysts based on ethylenediindenyl(X_2)titanium

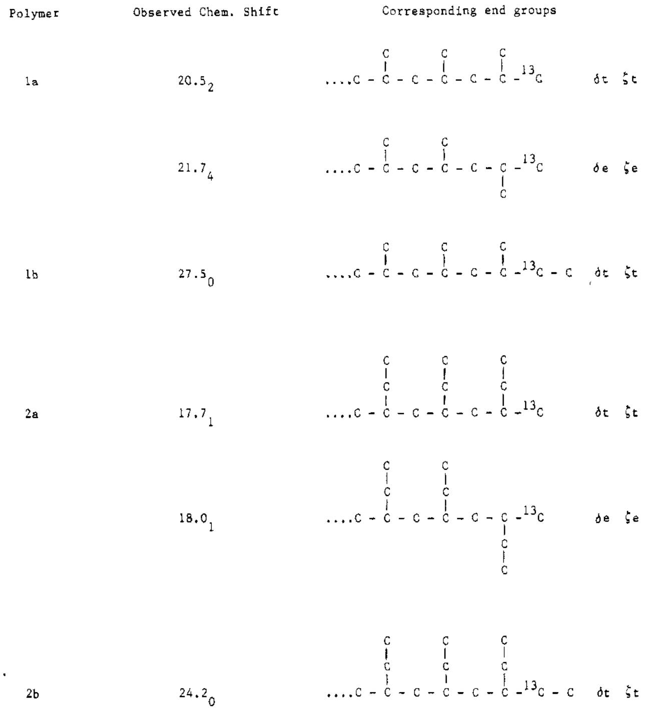

Figure 3. Stereochemical structure of the enriched end groups detected in samples **1a**, **1b**, **2a** and **2b**.[14]

and enriched organometallic cocatalysts are similar to those previously obtained by performing polymerizations in the presence of heterogeneous catalytic systems based on $\delta TiCl_3$ and $Al(^{13}CH_3)_3$ or $Al(^{13}CH_2CH_3)_3$. In both cases isotactic polymerization seems to be due to the fact that the chiral environment of the titanium moiety of the catalytic complexes ensures enantioselective polyinsertion. The presence of chiral carbon at the growing chain end seems to have little or no relevance in view of the steric control. These results are on line with the mechanism of the steric control suggested by Ewen for these homogeneous catalysts.[1] Insertion on a titanium–C_2H_5 bond of both propene and 1-butene is more enantioselective than it was previously observed in the presence of heterogeneous catalysts.[4] This could be simply due to the lower reaction temperature (−45 °C instead of +50 °C). Insertion of 1-butene on a Ti–CH_3 bond is partially enantioselective; insertion of propene on titanium–methyl does not seem enantioselective at all. This suggests that insertion is appreciably enantioselective when the steric hindrance of the alkyl group bonded to the titanium and/or that of the alkyl substituent of the monomer is larger than that of CH_3. The size of the alkyl moiety of the catalytic complexes is more critical than that of the alkyl substituent of the monomer. As a matter of fact, insertion of propene on Ti–C_2H_5 is much more enantioselective than insertion of 1-butene on Ti–CH_3.

Similar conclusions have been previously achieved concerning the mechanism of the steric control in the presence of heterogeneous catalysts.[4,15-17]

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Registry No. TEA, 97-93-8; TMA, 75-24-1; $Zn(CH_3)_2$, 544-97-8; $H_2C{=}CHCH_3$, 115-07-1; $H_2C{=}CHCH_2CH_3$, 106-98-9; isotactic polypropylene, 25085-53-4; poly(1-butene), 9003-28-5; ethylenediindenyldimethyltitanium, 107455-10-7.

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(14) Hereinafter the stereochemical structure of the enriched end groups and the placement of the enriched carbon will be reported according to the notation of ref 10 and 11 (see also Figure 3), i.e., by using (1) a Greek letter denoting the number of bonds between the enriched carbon and the methyl (or ethyl) substituents along the backbone and (2) either the symbol e (erythro) or t (threo), which give the steric relationship between the enriched carbon and the indicated methyl (or ethyl) substituent.
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(18) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)