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Isotactic Polymerization of α-Olefins: Stereoregulation for Different Reactive Chain Ends

As reported in a previous paper,[1] ^{13}C-enriched methyls have been detected by ^{13}C NMR on the isobutyl end groups of isotactic polypropylene (sample a) produced in the presence of the catalytic system δ-$TiCl_3$[2]–$Al(^{13}CH_3)_2I$ (system I).

The stereochemical placement of the enriched carbon is mostly threo (or syndiotactic) with respect to the methyl substituent lying four bonds apart (δ methyl).

The stereospecific enrichment of the end groups, albeit lower than the average stereoregularity of the polymer, called for a sort of isotactic steric control of the polymerization, coming from stereospecific nonbonded interactions of the incoming monomer with the chiral ligand environment of the active site.[1] We have observed similarly enriched end groups in isotactic polypropylene (sample b) produced in the presence of the catalytic system δ-$TiCl_3$–$Al(^{13}CH_3)_3$–$Zn(^{13}CH_3)_2$ (system II), but in this case, the placement of the enriched methyl carbon is stereoirregular. Actually, in the ^{13}C NMR spectrum of the just-mentioned sample (Figure 1b) one can observe, in addition to the usual resonances for isotactic polypropylene, two more peaks, having very close intensities, at 21.6_4 and 21.7_3 ppm from hexamethyldisiloxane. As previously reported,[1,4] these resonances are expected for methyl carbons of isobutyl end groups in erythro (21.7_3 ppm) and threo (20.6_4 ppm) placement with respect to a further δ methyl.

It has also been previously reported[5] that the chemical shift of the quoted methyls is affected by the stereochemical placement of further methyl substituents up to 6 bonds distant. In fact, four resonances, instead of two, have been detected for the enriched methyl of isobutyl end groups of stereoirregular poly[(3-^{13}C)propylene].

The complete assignment of these resonances is reported in Table I according to the literature.[4,5]

On the matter it is worthwhile to observe that for both samples a and b (the spectrum of a is reported in Figure 1a) the resonances at 21.5_4 and 20.8_7 ppm are negligible in comparison with those at 21.7_3 and 20.6_4 ppm. Therefore, on inspection of Figure 1 and Table I, one can conclude that for both samples the stereochemical placement of the δ and ζ methyls relative to each other is isotactic to an extent comparable with the average stereoregularity of the whole polymer.

In isotactic polypropylene prepared with the catalytic system δ-$TiCl_3$–$Al(^{13}CH_3)_2Cl$ a stereochemical placement of the enriched methyls like that of sample b[6] was observed.

In the spectrum of isotactic poly(1-butene) (Figure 1d) produced in the presence of catalytic system II, two sharp resonances having very close intensities are detected at 18.1_3 and 17.8_4 ppm together with the usual resonances of the carbons of the inner monomer units[7] (see Figure 1d). Comparison with the spectrum of 2,4,6-trimethyloctane reported elsewhere[5] allows one to assign the quoted resonances to the enriched carbon of (2-^{13}C)-2-methylbutyl end groups in erythro (18.1_3 ppm) and threo (17.8_4 ppm) placement with respect to the inner (δ) ethyl substituent: $...CH_2CH(C_2H_5)CH_2CH(^{13}CH_3)C_2H_5$.

Finally, predominant threo placement of enriched methylene carbon is detected for (3-^{13}C)-2-methylbutyl end groups in isotactic polypropylene (sample c) produced in the presence of the catalytic system δ-$TiCl_3$–$Al(^{13}CH_2CH_3)_3$–$Zn(^{13}CH_2CH_3)_2$ (system IV) (see Figure 1c). In fact, the resonances at 27.7_2 and 28.8_2 ppm of the spectrum of Figure 1c are due to the enriched C_3 of the 2-methylbutyl groups threo and erythro, respectively, with regard to the δ and ζ methyls: $...CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)^{13}CH_2CH_3$. Here again the assignment is achieved by comparison with the spectrum of suitable model compounds reported previously.[5]

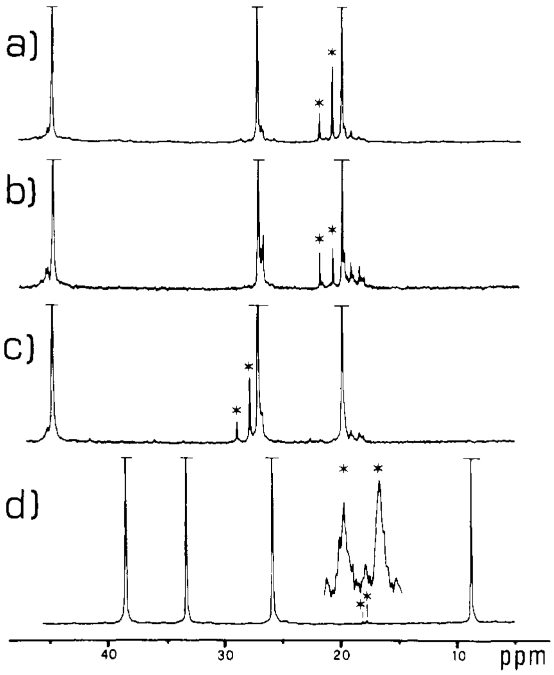

Figure 1. ^{13}C NMR spectra of boiling-heptane-soluble, boiling-pentane-insoluble fractions of samples a–c and of the fraction insoluble in boiling diethyl ether of sample d. The resonances of the methyl and methylene ^{13}C-enriched carbons of the end groups are marked by a star. Chemical shifts are in ppm downfield from HMDS. A 32-fold vertical expansion on a 0.1 ppm/cm scale of the enriched methyl end groups is also reported in the spectrum of high molecular weight poly(1-butene). The spectra of the heptane-soluble fractions are reported instead of those of the residues because the low molecular weight enhances the resonances of the end groups. From the spectra it can be appreciated that the stereoregularity of the fractions is very high (comparable with that of the residues). The unusual solubility in boiling heptane comes from the low molecular weight and not from a lack in stereoregularity.

Table I
Chemical Shifts of the Methyl Carbons of Isobutyl End Groups of Polypropylene as a Function of the Configurational Relationships with the Methyls Four δ and Six ζ Bonds Distant[a]

shift, ppm	config relationship	
21.7_6	δ e	ζ e
21.5_4	δ e	ζ t
20.8_7	δ t	ζ e
20.6_9	δ t	ζ t

[a] e = erythro; t = threo.

These puzzling experimental facts concerning the stereochemical placement of enriched carbon on the end groups of isotactic polymers can be rationalized as follows:

(1) The stereochemical placement of the enriched carbon observed in isotactic polymers b–d comes from the fact that insertion of the monomer undergoes steric control whenever it occurs on primary alkyl groups larger than methyl. Steric control is ultimately due to the chiral structure of the active sites (see below).

The possibility that the placement of the enriched carbon may be due to the occurrence of stereospecific insertion of the monomer only after the appearance of a

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Table II
Polymerization Runs Performed in the Presence of Different ^{13}C-Enriched Aluminum Alkyls[a]

						fractionation of the crude polymer					
sample	catalytic system[c]	aluminum alkyl	monomer	time, h	polym yield, g	ether ext, %	$\bar{M}_V$	n-heptane ext, %	$\bar{M}_V$	residue, %	$\bar{M}_V$
a	I	$Al(^{13}CH_3)_2I$	C_3H_6	2	7.5	0.8	nd	3.4	<20 000	95.8	375 000
b[b]	II	$Al(^{13}CH_3)_3$	C_3H_6	22	9.4	8.9	nd	10.2	<20 000	80.9	>500 000
c[b]	III	$Al(^{13}CH_2CH_3)_3$	C_3H_6	48	8.4	5.3	nd	8.2	<20 000	86.5	>500 000
d[b]	II	$Al(^{13}CH_3)_3$	C_4H_8	3	5.7	13.0	nd	87.0	182 000		

[a] See experimental part. [b] Performed in the presence of dialkylzinc ([Al]/[Zn] ≃ 1.5). [c] See text.

chiral carbon on the growing chain end has to be ruled out since it is conflicting with the stereoirregular placement of the enriched carbon in isotactic poly(1-butene) (Figure 1d). In fact, both the insertion of C_3H_6 on $Mt{-}^{13}CH_2CH_3$ and the insertion of C_4H_8 on $Mt{-}^{13}CH_3$ produce a chiral 2-methylbutyl group:

$$Mt{-}^{13}CH_2CH_3 \xrightarrow{C_3H_6} Mt{-}CH_2CH(CH_3)^{13}CH_2CH_3$$

$$Mt{-}^{13}CH_3 \xrightarrow{C_4H_8} Mt{-}CH_2CH(^{13}CH_3)CH_2CH_3$$

If the steric control of the insertion of the following unit were connected with the chirality of the alkyl group, stereospecific placement of the enriched carbon would be observed not only in sample c but also in sample d.

(2) Excepting sample a, the presence on the active site of an alkyl group larger than methyl seems to be a necessary condition for the occurrence of stereospecific insertion of the monomer.[8]

As to sample a it must be mentioned that the isotactic specificity of the catalytic systems consisting of δ-$TiCl_3$ and alkylaluminum iodide is exceedingly high.[9] Doi et al. showed[10] that it is due to partial I–Cl exchange between the surface of δ-$TiCl_3$ and the alkylaluminum iodide. According to these authors such halide exchange should increase the asymmetry of the active sites, causing an additional driving force for isotactic steric control. The presence of halides of different size on the same chiral active site could cause additional stereospecific nonbonded interactions with the incoming monomer and explain the partially stereospecific placement of the enriched carbon even in sample a.[8]

Experimental Section. Reagents. δ-$TiCl_3$ (HRA Stauffer) was purified by extraction with boiling toluene.[9]

Enriched 50% $Al(^{13}CH_3)_3$ was prepared starting from aluminum turnings and enriched $^{13}CH_3I$ according to the literature.[11] $Al(^{13}CH_3)_2Cl$ was prepared by exchange of $Al(^{13}CH_3)_3$ with $AlCl_3$. Enriched 60% $Al(^{13}CH_2CH_3)_3$ was prepared via Grignard reagent and $AlCl_3$[12] starting from enriched $CH_3{}^{13}CH_2I$.

$Zn(CH_3)_2$ and $Zn(C_2H_5)_2$ were prepared from the corresponding trialkylaluminum compounds and $ZnCl_2$.[13] Due to the fast exchange between dialkylzinc and aluminum compounds,[14] enrichment of $Zn(CH_3)_2$ and $Zn(C_2H_5)_2$ was achieved simply by mixing with enriched $Al(^{13}CH_3)_3$ and $Al(^{13}CH_2CH_3)_3$, respectively.

Sample a was prepared in an autoclave at 75 °C and $p(C_3H_6)$ = 2.5 atm as described in a previous paper.[1] Samples b–d were prepared at atmospheric monomer pressure and room temperature in a three-necked flask provided with a magnetic stirrer in the presence of δ-$TiCl_3$ (1 g), heptane (100 mL), and enriched organometallic compound (see Table II), with a 2/1 Al/Ti molar ratio.

The fractionation of polymers with boiling solvents and the determination of the viscosimetric-average molecular weight of the fractions were performed according to the literature.[15,16]

^{13}C NMR analysis of the polymers dissolved in 1,2,4-trichlorobenzene containing 1% of hexamethyldisiloxane (HMDS) as an internal standard was carried out at 140 °C in the PFT mode on a Bruker HX-90 spectrometer operating at 22.63 MHz.[17]

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