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Syndiotactic-Specific Polymerization of Propene with Nickel-Based Catalysts. 2. Regiochemistry and Stereochemistry of the Initiation Steps

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ABSTRACT: A homogeneous catalytic system based on a suitable Ni(II) diimine derivative and methylaluminoxane affords predominantly syndiotactic polypropylene at subambient temperatures. The polymer microstructure is that expected for a "chain-end" mechanism of steric control. NMR analysis of polymer samples carrying selectively ^{13}C-enriched end groups indicates a largely prevailing 1,2 regiochemistry for the insertion of propene into Ni−$^{13}CH_3$ bonds in the initiation step and a syndiotactic steric control already effective in the second propagation step.

Introduction

Syndiotactic-specific polymerization of propene was first achieved by Natta *et al.*[1] using a catalytic system consisting of VCl_4 (or other hydrocarbon-soluble vanadium compounds) and $Al(C_2H_5)_2Cl$ operating at low temperatures (e.g. −78 °C). The polymerization mechanism involved in these V-based catalysts has been extensively studied.[2] In the present discussion, the most relevant stereochemical features are (i) the prevailingly secondary (2,1) mode of insertion of the monomer into the V−C bonds of the propagating species[3] and (ii) the steric control arising from the asymmetric configuration of the last unit of the reactive chain[4] (chain-end mechanism of steric control).[5]

The above-mentioned V-based systems have long been the only known syndiospecific catalysts for propene polymerization. In 1988, Ewen *et al.*[6] disclosed C_s-symmetric *ansa*-metallocene catalysts, such as [isopropylidene(cyclopentadienyl)(1-fluorenyl)]zirconium dichloride−methylaluminoxane (MAO), able to produce highly syndiotactic polypropylene even at high temperature. In this case, the stereochemical reaction mechanism was shown[7] to involve (i) prevailingly primary (1,2) monomer insertion and (ii) steric control dictated by the catalyst stereochemical structure ("enantiomorphic site" mechanism of steric control).[8]

More recently, a report by Brookhart *et al.*[9] disclosed novel catalysts based on Ni(II) or Pd(II) diimine derivatives which, after activation with MAO or other ionizing reagents, efficiently promote ethylene polymerization and are the first late-metal systems able to produce high molecular weight poly(α-olefins). This finding, which represents a breakthrough for the development of a new class of catalysts based on late transition metal derivatives, prompted us to investigate the possibility to achieve stereospecific polymerization. In fact, as reported in a preliminary communication,[10] polymerization of propene at −78 °C in the presence of the homogeneous catalytic system (1,2-bis(2,6-diisopropylphenyl)ethylenediimine)nickel dibromide (**1**)−MAO afforded prevailingly syndiotactic crystalline polypropylene (rr triad content ∼ 80%). ^{13}C NMR analysis of the polymer microstructure suggested a "chain-end" mechanism of steric control. In order to provide further insight into the stereochemical mechanism involved in these new systems, we report here a study concerning the stereochemical structure of the ^{13}C-enriched end groups resulting from initiation steps when the polymerization is performed in the presence of suitably ^{13}C-enriched catalytic systems. Similar investigations concerning both heterogeneous[11] and homogeneous[12] Ziegler−Natta catalytic systems have been proved to afford valuable mechanistic information.

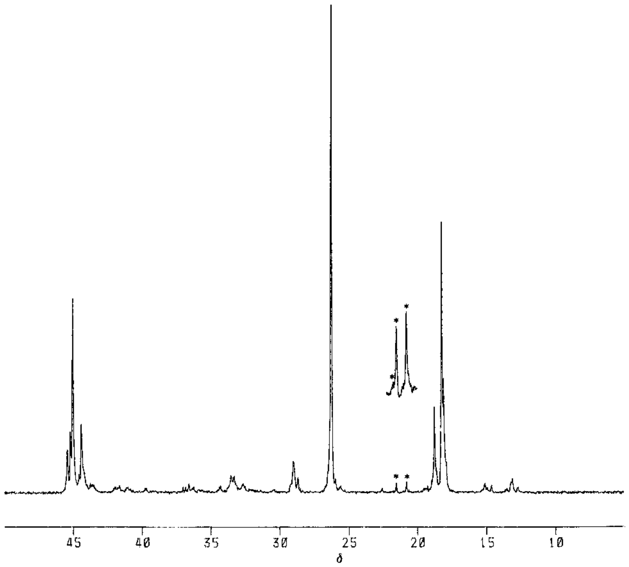

Figure 1. ^{13}C NMR spectrum of a polypropylene sample prepared with **1**−MAO−Al($^{13}CH_3$)$_3$ at −45 °C (sample 1). The resonances of the ^{13}C-enriched end groups are marked by stars and are displayed in the vertical expansion. δ in ppm from hexamethyldisiloxane.

Results and Discussion

A polypropylene sample (sample 1) was prepared at −45 °C in the presence of **1** and MAO premixed with ^{13}C-enriched $Al(CH_3)_3$, as described in the Experimental Section. The ^{13}C NMR spectrum of sample 1 (see Figure 1) is similar to the previously reported spectrum of a PP sample prepared at −78 °C.[10] The polymer has a prevailingly syndiotactic structure, with a content of rr triads of 74% and a microstructure consistent with the Bernoullian statistical model proposed by Bovey[5] for a

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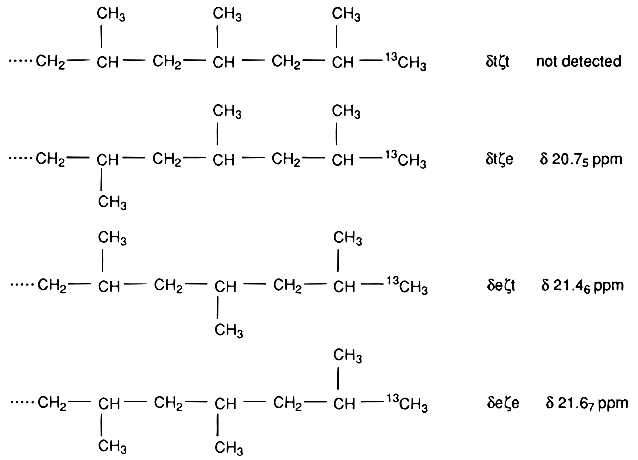


Figure 2. Fischer projections of the four possible diastereomeric [7-^{13}C]-2,4,6-trimethylheptyl end groups, with the chemical shifts observed for the enriched methyl carbons. The diastereotopic placements of $^{13}CH_3$ are indicated, as in previous papers,[11,12] by using Greek letters to denote the number of bonds between the enriched CH_3 and the methyl backbone substituents, followed by the symbol e (erythro) or t (threo), giving the steric relationship between the same methyl carbons.

"chain-end" mechanism of steric control, with $P_r = 0.86$ and $P_m = 1 - P_r$ (P_r and P_m are the probabilities of syndiotactic (r) and isotactic (m) placements, respectively).[13] A significant amount (~12%) of regioirregularly arranged monomer units is present, as indicated, e.g., by the methyl resonances of the tail-to-tail units observed between 12.6 and 15.0 ppm from hexamethyldisiloxane (HMDS).[3c,14] Some sequences of three and four CH_2's (resonances at δ ~22.6, 25.6, and 35–37 from HMDS)[4a] are also detected.[15] Except for the last finding, the whole picture is very similar to that outlined for syndiotactic polypropylene obtained in the presence of the above-mentioned homogeneous catalysts based on vanadium derivatives.

In addition to the natural-abundance carbon resonances, two resonances due to ^{13}C-enriched end groups having comparable intensities[16] are observed at δ 20.7_5 and 21.4_6; a much less intense resonance is also detected at δ 21.6_7. These resonances have been attributed in previous papers[11,12] to the enriched CH_3's of the diastereomeric [7-^{13}C]-2,4,6-trimethylheptyl end groups deriving from the primary insertion of one propene molecule into the Mt–$^{13}CH_3$ (Mt = metal) bonds of the active species (initiation step), followed by further primary insertion of two monomer units (first and second propagation steps, respectively):

$$\mathrm{Ni{-}^{13}CH_3} \xrightarrow[\text{1,2 ins}]{C_3H_6} \mathrm{Ni{-}CH_2CH(CH_3)^{13}CH_3} \xrightarrow[\text{1,2 ins}]{C_3H_6}$$

$$\mathrm{Ni{-}CH_2CH(CH_3)CH_2CH(CH_3)^{13}CH_3} \xrightarrow[\text{1,2 ins}]{C_3H_6}$$

$$\mathrm{Ni{-}CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)^{13}CH_3}$$

and, more precisely, to the $^{13}CH_3$ stereochemical locations δtζe, δeζt, and δeζe, at decreasing field (see Figure 2). The resonance of the δtζt end group, expected around 20.6 ppm, is not detected, possibly because it is obscured by the rather broad resonance centered at 20.7_5 ppm.[16] Of course, the Ni–$^{13}CH_3$ bonds are generated *in situ* by reaction of **1** with the ^{13}C-enriched Al cocatalyst.

No peak is observed in the region between 9.1 and 9.3 ppm, where the resonances of the *sec*-butyl end groups which would arise from secondary insertion of propene into the Ni–$^{13}CH_3$ bonds are expected.[17]

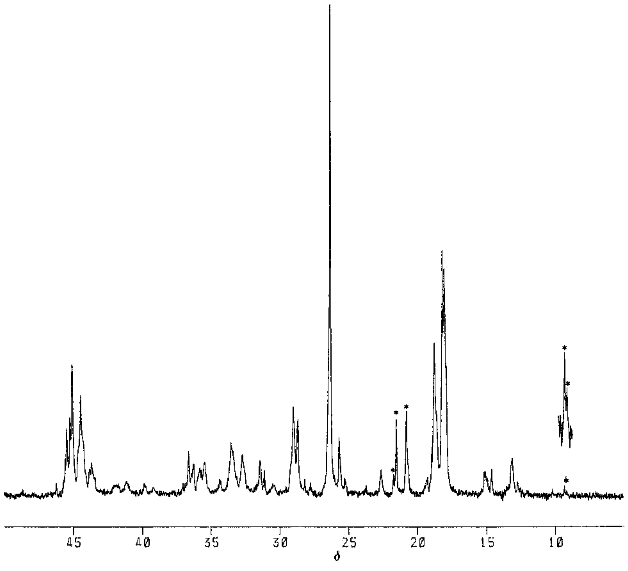


Figure 3. ^{13}C NMR spectrum of a polypropylene sample prepared with **1**–MAO–Al($^{13}CH_3$)$_3$ at 0 °C (sample 2). The resonances of the ^{13}C-enriched end groups are marked by stars. The low-intensity resonances due to the ^{13}C-enriched end groups deriving from secondary monomer insertion (see Figure 4) are displayed in the vertical expansion. δ in ppm from hexamethyldisiloxane.

These experimental findings indicate unambiguously a 1,2 regiochemistry for the insertion of propene into Ni–CH_3 bonds in the initiation step. The same behavior was observed for the syndiospecific polymerization promoted by V-based catalysts.[12a] In the latter case, however, four different resonances with comparable intensities were observed for the enriched CH_3's of the four possible diastereomeric [7-^{13}C]-2,4,6-trimethylheptyl end groups (see Figure 2). This finding indicated that primary insertion of the monomer in the initiation and the first two propagation steps is stereoirregular: in fact, in the case of V catalysts, syndiotactic steric control requires that propene insertion turns from 1,2 to 2,1.[2-4] On the contrary, in the present case, two major resonances attributable to δtζe and δeζt enriched methyls of the above-mentioned end groups are observed. As previously discussed,[11,12] this finding indicates that the insertion of the third monomer unit (second propagation step) is syndiotactic; i.e., the third propene unit incorporated into the chain has a configuration opposite to the second one. The ratio between the area of the resonance of the δeζt enriched methyl and that of the δeζe one is ~8:1 (cf. the value of $P_r = 0.86$, meaning that, in the polymer chain, [r]/[m] = 6.2), thus indicating that the second propagation step is at least as stereospecific as the following propagation steps. Of course, no stereospecificity is expected in the initiation and the first propagation steps for a chain-end mechanism of steric control, due to the lack of any chiral carbon in the growing chain.

A polypropylene sample has also been prepared with **1**–MAO–Al($^{13}CH_3$)$_3$ at 0 °C (sample 2). The ^{13}C NMR spectrum of sample 2 (see Figure 3) shows that the polymer is much less stereoregular (~65% of rr triad) and regioregular (~16% of regioinversion) and contains a much higher amount of sequences of three and four CH_2's with respect to sample 1. Strong resonances due to ^{13}C-enriched end groups are detected at the same chemical shifts observed in the spectrum of sample 1.

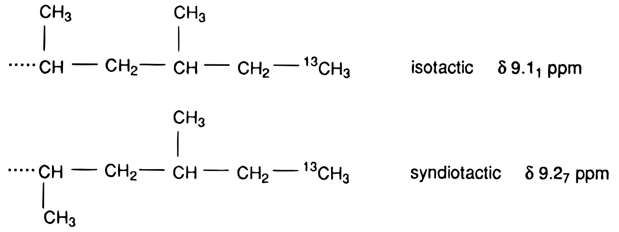


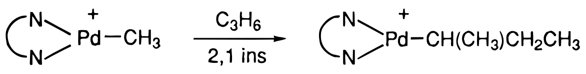
Figure 4. Fischer projections of the two possible diastereomeric [5-^{13}C]-1,3-dimethylpentyl end groups, with the chemical shifts observed for the enriched methyl carbons, assigned on the basis of a model compound reported in the literature.[17]

Also in this case, the ratio between the area of the resonance of the $\delta e\zeta t$ enriched methyl and that of the $\delta e\zeta e$ one shows that the second propagation step is at least as stereospecific as the following propagation steps. However, at variance with sample 1, additional resonances of much lower intensity are detected at 9.1_1 and 9.2_9 ppm from HMDS. These resonances are attributable, on the basis of model compounds reported in the literature,[17] to the two diastereomeric end groups (see Figure 4) deriving from 2,1 insertion of two propene units into Ni-^{13}CH$_3$ bonds:

$$\mathrm{Ni{-}{}^{13}CH_3} \xrightarrow[\text{2,1 ins}]{\mathrm{C_3H_6}} \mathrm{Ni{-}CH(CH_3)CH_2{}^{13}CH_3} \xrightarrow[\text{2,1 ins}]{\mathrm{C_3H_6}} \mathrm{Ni{-}CH(CH_3)CH_2CH(CH_3)CH_2{}^{13}CH_3}$$

The resonance at 9.2_7 ppm (attributable to the syndiotactic end group) is more intense than that at 9.1_1 ppm (attributable to the isotactic one): this seems to indicate that the first propagation step through 2,1 insertion is also partially syndiotactic-specific.

It is worth noting that for a closely related catalytic system based on a Pd(II) diimine derivative, Brookhart[9] suggested a 2,1 regiochemistry for propylene insertion in the initiation step, on the basis of the detection by NMR monitoring of a *sec*-butyl Pd complex, deriving from secondary monomer insertion into the Pd−CH$_3$ bond, according to the reaction:



Of course, the different results obtained in the present investigation can be due to a different reactivity of the Ni and Pd catalytically active complexes, which were shown to be cationic diimine alkyl olefin complexes of formula $[(N{-}N)\mathrm{Mt(R)}(\eta^2\text{-olefin})]^+$,[9] possibly resulting from the larger ionic radius of Pd^{2+}. Alternatively, it is possible that the Pd single-insertion adduct detected by Brookhart is not the true propagating complex, but, e.g., a resting catalyst state or a less reactive species.

Conclusions

Many features of the stereochemical polymerization mechanism operating in these new Ni-based catalysts are similar to those previously found for the classical V-based catalysts, in particular the chain-end mechanism of steric control and the poor regiospecificity. The above-reported results concerning the analysis of ^{13}C-enriched end groups of polypropylene samples prepared using a suitably enriched Ni-based catalyst confirm the analogies between the two systems but also point out some significant differences. In fact, a 1,2 regiochemistry has been observed for the insertion of the monomer into Mt−^{13}CH$_3$ bonds in the initiation step in both cases. However, chain propagation via 1,2 insertion was shown to be stereoirregular for V-based systems, while for the present Ni catalyst, syndiotactic steric control has been observed already in the second propagation step occurring through 1,2 monomer insertion. In view of that, further investigation is needed to establish the regiochemistry prevailing during the chain propagation, i.e. to ascertain if the monomer insertion is still mainly primary or if it turns to predominantly secondary, as observed in the case of V catalysts.

Experimental Section

All operations and manipulations were carried out under a dry nitrogen atmosphere using Schlenk or glovebox techniques.

Materials. $\{2,6\text{-}(i\text{-}\mathrm{C_3H_7})_2\mathrm{C_6H_3N{=}C(H)C(H){=}N\text{-}2,6\text{-}C_6H_3}(i\text{-}\mathrm{C_3H_7})_2\}\mathrm{NiBr_2}$ (**1**) was prepared according to the literature.[18] ^{13}C-enriched Al(CH$_3$)$_3$ was synthesized by reaction of ^{13}CH$_3$Li and AlBr$_3$ as previously reported.[12b] MAO, purchased from Witco as a 30 wt % solution in toluene, was recovered as a white solid after distilling off the solvent and stored in a glovebox. Polymerization grade propene (SON) was distilled over Al(*i*-Bu)$_3$ before use. Toluene (Carlo Erba) was refluxed over metallic sodium and distilled under a nitrogen atmosphere before use.

Polymerizations. The polymerization runs were carried out in 100-mL, magnetically stirred glass flasks, which were charged under nitrogen sequentially with toluene, Ni precatalyst **1**, propene, and a toluene solution of MAO premixed with 80% ^{13}C-enriched Al(CH$_3$)$_3$. Run 1 was carried out at −45 °C by using 20 mL of solvent, 10 mL of liquid propene, 12 mg of Ni precatalyst, 230 mg of MAO, and 0.4 mmol of Al(^{13}CH$_3$)$_3$; the run was stopped after 3 h by pouring the reaction mixture into acidified methanol, and the precipitated polymer was recovered by filtration, washed with fresh methanol, and dried in vacuo; yield 0.3 g (sample 1). Run 2 was carried out at 0 °C under a continuous feed of propene at atmospheric pressure, by using 30 mL of solvent, 10 mg of Ni precatalyst, 100 mg of MAO, and 0.2 mmol of Al(^{13}CH$_3$)$_3$. The run was stopped after 40 min and the polymer was recovered as above; yield 0.2 g (sample 2).

Analysis of the Polymers. The polymer samples were analyzed on an AM 250 Bruker spectrometer operating in the Fourier transform mode at 62.89 MHz for ^{13}C. The spectra were recorded in C$_2$D$_2$Cl$_4$ at a temperature of 120 °C using hexamethyldisiloxane as an internal chemical shift reference.

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(15) The presence of such sequences in polypropylene samples prepared at higher temperatures was previously observed by Brookhart *et al.*[9] and was explained on the basis of a reaction mechanism involving β-hydride elimination of growing polymer chains ending with a 2,1 propene unit followed by reinsertion of the resulting α-olefin with opposite regiochemistry.

(16) The resonance at δ 20.7_5 is actually slightly more intense and broader than that at δ 21.4_6. This could be due to the presence of some regioinversions already in the first propagation step: in fact, the enriched methyl resonance for the end group resulting from 1,2 propene insertion followed by a 2,1 propene insertion is expected around 20.7 ppm.[12a]

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