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Syndiotactic-specific polymerization of propene with Nickel-based catalysts. 3. Polymer end-groups and regiochemistry of propagation

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Abstract

Low molecular weight prevailingly syndiotactic polypropylene samples have been synthesized under proper conditions with homogeneous catalytic systems based on Ni(II) diimine derivatives and methylaluminoxane. ^{13}C NMR analysis of the natural abundance end groups formed in both the initiation and termination steps suggests that the regiospecificity of propene insertion during the propagation is prevailingly 1,2. The effects of ligand variation at the Ni catalytic center on the regiospecificity of the polymerization is in agreement with 1,2 insertion as the main mode of propagation. © 1998 Elsevier Science B.V.

1. Introduction

Among the most recent advances in the development of homogeneous 'single-site' olefin polymerization catalysts, the disclosure of a novel class of catalysts based on Ni(II) or Pd(II) diimine compounds by Brookhart et al. [1] emerges as an important breakthrough. Compounds of the type (ArN=C(R)–C(R)=NAr)MX_2 (M = Ni or Pd; X = halogen or alkyl) were shown to efficiently promote olefin polymerization after activation with methylaluminoxane (or other ionizing co-catalysts analogous to those used in metallocene systems) affording cationic active species [1]. These systems polymerize ethylene to high molecular weight polymers, ranging from substantially linear to highly branched, and are the first late-transition metal catalysts to polymerize α-olefins, yielding amorphous polymers [1]. They have also been successfully used for the copolymerization of olefins and polar monomers, such as acrylates [2].

In this framework, we have recently reported that the homogeneous catalytic system (1,2-bis(2,6-diisopropylphenyl)ethylenediimine) nickel dibromide (**1**)–methylaluminoxane (MAO) at sub ambient temperatures (e.g. −78°C) affords a prevailingly syndiotactic crystalline polypropylene [3]. NMR analysis of the polymer microstructure showed the presence of isolated *m* dyads as the main stereodefects, thus suggesting that a 'chain-end' mechanism of steric control is operative in this system (i.e. the stereochemistry of the monomer insertion is controlled by the configuration of the methine carbon of the growing chain-end through *un-*

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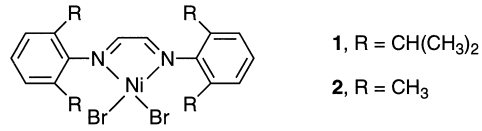
like-1,3 asymmetric induction) [4]. Moreover, a large content of regioirregularly arranged monomer units were observed [3]. These features are very similar to those of syndiotactic polypropylene produced with the classical vanadium-based catalysts, first disclosed by Natta et al. [5] On the contrary, Ewen's C_s-symmetric group 4 *ansa*-metallocene catalysts [6], such as [isopropylidene(cyclopentadienyl)(1-fluorenyl)]zirconium dichloride–MAO, produce syndiotactic polypropylene through an 'enantiomorphic site' mechanism of steric control, involving catalyst isomerization after each chain migratory insertion [7].

With the appealing goal to rationalize the steric requirements for designing stereospecific catalysts of this new class, we are investigating the relevant stereochemical features involved in the polymerization of propene promoted by these systems. Thus, in a previous study [8], we analyzed by NMR the ^{13}C-enriched end groups of polypropylene samples prepared using the catalytic system **1**–^{13}C-enriched MAO, and observed a largely prevailing 1,2 monomer insertion in the initiation step. However, since a significant amount of head-to-head and tail-to-tail enchainments are present, one cannot infer a 1,2 regiochemistry as the main mode of propagation. In fact, in the case of vanadium-based catalysts, only 1,2 insertion of propene occurs in the initiation step [9], but a largely prevailing 2,1 mode of insertion is involved during the propagation [10]. On the other hand, chain initiation via 1,2 insertion was shown to be stereoirregular for V-based systems [11] (in that case, syndiospecific chain-end control is operative only after 2,1 propene insertion) while in the case of the present Ni catalyst syndiospecific steric control was observed already in the second propagation step occurring through 1,2 monomer insertion (i.e., as soon as a chiral carbon is generated in the growing chain) [8].

In view of the above uncertainty, we have further investigated the structure of polypropylene samples prepared under different conditions either with catalyst **1** or the related system



Scheme 1.

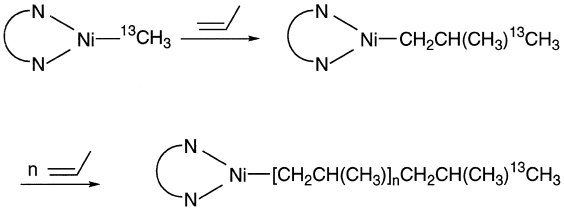
2 (Scheme 1) with the aim to establish the regiochemistry prevailing during the chain propagation.

2. Results and discussion

As mentioned in the introduction, in previous work we were able to observe by NMR the end groups of a syndiotactic polypropylene sample prepared at -45°C in the presence of **1** and MAO premixed with ^{13}C-enriched $Al(CH_3)_3$ [8]. These end groups originate from the insertion of propene into Ni–$^{13}CH_3$ bonds (generated in situ by reaction of **1** with the ^{13}C-enriched Al cocatalyst) in the initiation step (conventionally defined 'right' end groups) (Scheme 2).

In order to gain further insight in the polymerization regiochemistry, it would be of interest to characterize also the end groups formed in the termination step (the 'left' end groups), usually occurring either by β-hydrogen transfer or by hydrolysis of metal–polymer bonds.

^{13}C NMR analysis of polymer samples prepared under the previously used conditions [3,8] ($T = -45$°C or lower, [Ni] $\sim 6 \cdot 10^{-4}$ M; [propene] ~ 5 M) but without using ^{13}C-enriched cocatalyst does not reveal resonances attributable to any natural abundance end groups, owing to the high molecular weight. On the other hand, attempts to increase chain termina-



Scheme 2.

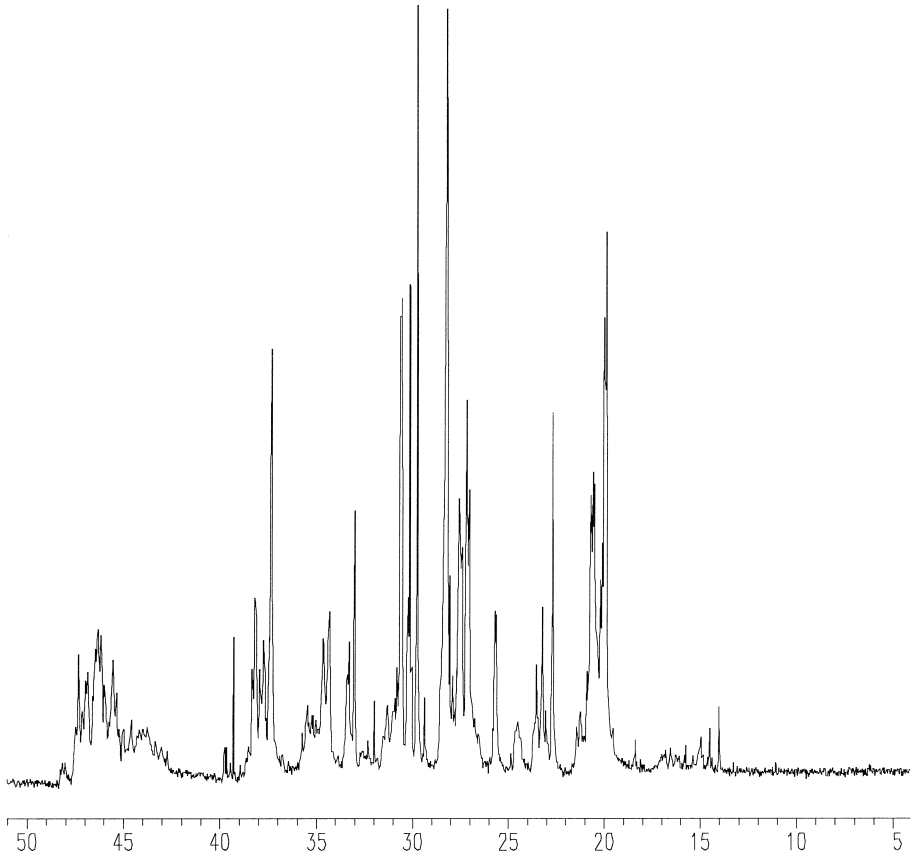


Fig. 1. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 120°C) of a polypropylene sample prepared with **1**–MAO at 50°C (sample 1). δ in ppm from TMS.

tion via β-hydrogen elimination performing the polymerization at higher temperatures, e.g. +50°C, failed to give polymers carrying detectable unsaturated end groups, but resulted in polypropylene samples having a substantially stereoirregular and regioirregular structure, with a large content of polymethylene sequences of different lengths (see, e.g., the ^{13}C NMR spectrum of sample 1, displayed in Fig. 1). This finding is in agreement with Brookhart's mechanism involving slow associative displacement of unsaturated polymer chains after β-H elimination in comparison with the rate of reinsertion either with the same or the opposite regiochemistry [1].

However, when the polymerization was carried out, as reported in the Experimental section, at −45°C using a higher catalyst concentration ([Ni] ~ $3 \cdot 10^{-3}$ M) and low monomer concentration ([propene] ~ 0.2 M), a low molecular weight polypropylene (sample 2, $\overline{M}_n = 1500$, $\overline{M}_w/\overline{M}_n = 4.7$) suitable for end group analysis was obtained. The ^{13}C NMR spectrum of sample 2 (see Fig. 2) is similar to those previously reported [3,8], indicating a prevailing syndiotactic structure and a significant content of regioinversions (~ 72% of rr triads and ~ 13% of head-to head and tail-to-tail enchainments [1]). In addition to the main resonances due

[1] Evaluation of the triad content was made by neglecting the presence of regioinversions and is to be considered just an estimate (see the Experimental section for further details). A more detailed NMR analysis of the polymer microstructure is in progress and will be reported in due time.

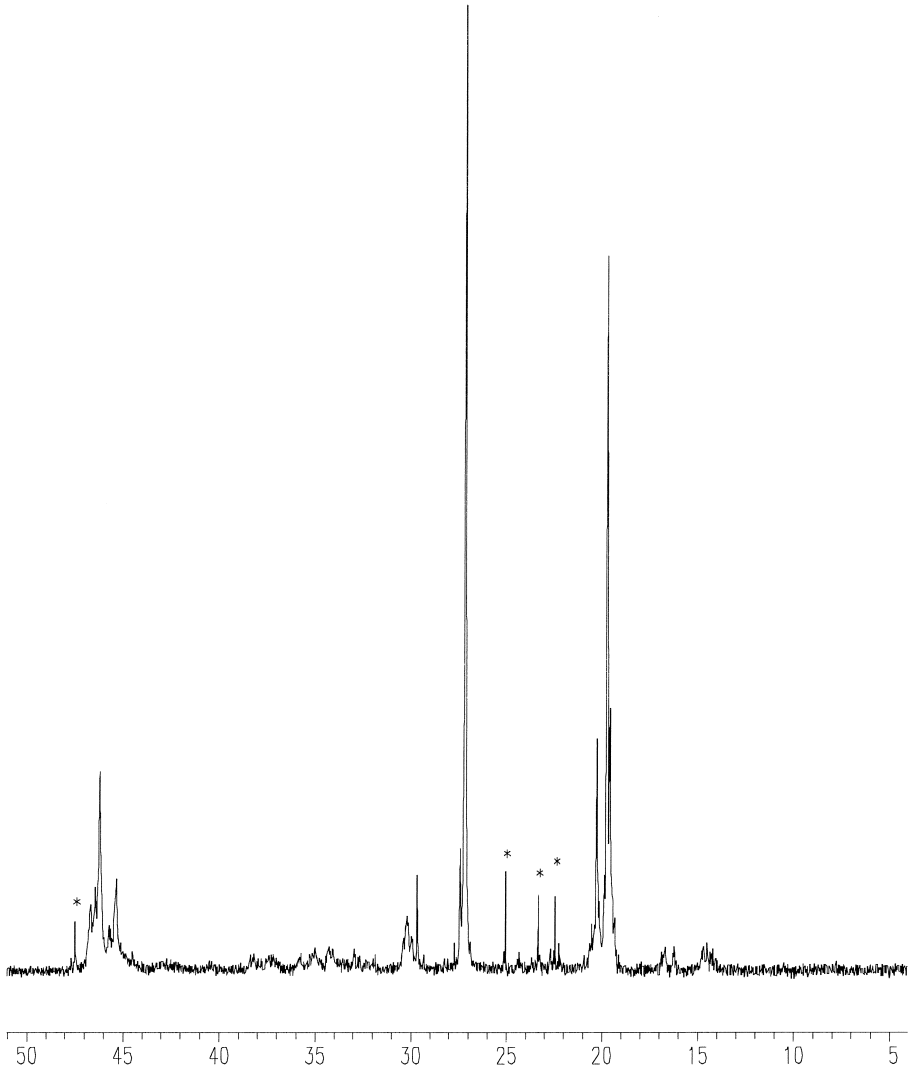
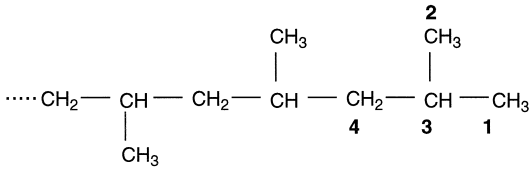


Fig. 2. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 25°C) of a low molecular weight polypropylene sample prepared with **1**–MAO at −45°C (sample 2). Resonances of the isobutyl end groups are marked by stars. δ in ppm from TMS.

to the backbone carbons, minor resonances having comparable intensities attributable to the natural abundance end groups are detected at δ 22.4, 23.3, 25.0, 47.4 ppm from TMS [2]. Comparison with literature data [8,9,11,12] and DEPT experiments indicate that they are due to the methyl, methine and methylene carbons, respectively, of the isobutyl end groups. More precisely, they are attributable to C1, C2, C3 and C4, respectively, of the diastereoisomeric 2,4,6-trimethylheptyl end group (Scheme 3) which is expected for a syndiotactic polymer [8]. No resonances attributable to different saturated end groups, i.e. *sec*-butyl or *n*-propyl end groups are detected. In the unsaturated region of

[2] Many literature data are based on NMR spectra recorded at high temperature (e.g. 120°C) and referenced vs. hexamethyldisiloxane, while the chemical shifts reported in the text are those observed at room temperature and thus differ from literature values. NMR analysis of sample 2 at 120°C showed resonances at δ 46.1_5, 23.6_5, 21.4_6, 20.7_5 from hexamethyldisiloxane, which are coincident with previously reported values, see, e.g. Refs. [8,12].



Scheme 3.

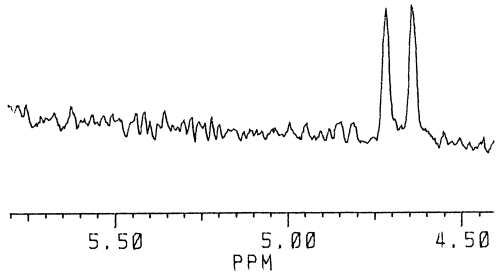


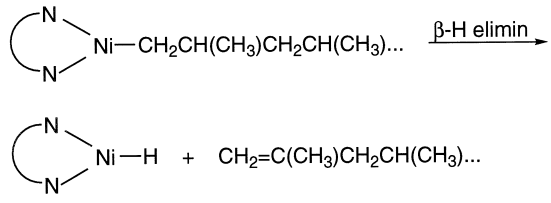
Fig. 3. Unsaturated region of the ^{1}H NMR spectrum ($C_2D_2Cl_4$, 25°C) of sample 2.

the ^{13}C NMR spectrum of sample 2, weaker resonances (with intensity ~ 1/6 of the just mentioned ones) at δ 111.2 and 144.9 are observed. They are attributable to the methylene and quaternary carbons, respectively, of vinylidene end groups. The ^{1}H NMR spectrum confirms this attribution (see Fig. 3), showing resonances at δ 4.6_4 and 4.7_1 ppm due to the unsaturated methylene protons of the vinylidene end groups. The latter arise from the termination reaction of Scheme 4.

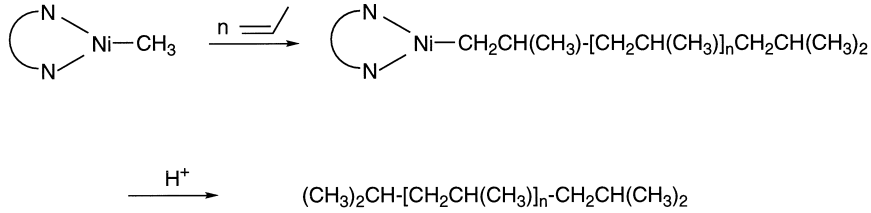
Since the amount of unsaturated end groups is much lower than that of the saturated ones, the above findings suggest that isobutyl end groups are formed both in the initiation and the termination steps, according to Scheme 5.

In order to confirm the formation of isobutyl 'left' end-groups, we attempted to introduce a deuterium label on the latter by quenching several polymerization runs with mixtures of CH_3CH_2OD and CF_3COOD, under different conditions. When the polymerization mixture was poured into ethanol a short time after the addition of the deuteriated compounds, the ^{13}C NMR spectra of the polymer did not contain detectable resonances attributable to deuterium incorporation. On the other hand, when the reaction mixture was allowed to slowly warm up to room temperature in the presence of the deuteriated compounds, a sample containing comparable amounts of vinylidene and isobutyl end groups (with no detectable deuterium incorporation) was obtained. These findings suggest that hydrolysis of the Ni-polymer bonds is very slow at −45°C, while at higher temperatures β-H elimination compete favorably with hydrolysis. Based on that, one run was quenched in ethanol after stirring the polymerization mixture with the deuteriated compounds 20 h at −45°C. The obtained polymer (sample 3, $M_n = 7900$, $M_w/M_n = 2.1$) was analyzed by ^{13}C NMR at 100°C as described in Section 3. The methyl and methine region of the isobutyl end groups of sample 3 is displayed in Fig. 4. In addition to the previously observed resonances, a new resonance 0.07 ppm upfield from that of the methine of the non-deuteriated end group is detected. Also, a new triplet resonance with a coupling constant of 19 Hz (a typical J_{C-D} value) is detectable near the resonance of one of the methyl groups. Similar spectra were observed for the model compound 1-deuterio-2,4,6-trimethylheptane [13], as well as for deuteriated isobutyl end groups of isotactic polypropylene [14]. These additional resonances can be attributed to the diastereoisomeric deuteriated ('left') end group displayed in Scheme 6. The above reported results clearly indicate that the preferred mode of propene insertion is 1,2 both in the initiation and the termination steps.

A polypropylene sample was prepared under similar conditions using **2**–MAO as the catalyst



Scheme 4.



Scheme 5.

(sample 4). The ^{13}C NMR spectrum of sample 4 (see Fig. 5) indicates that the polymer is significantly less stereoregular and regioregular than sample 2 ($\sim$56% of rr triads and $\sim$23% of head-to-head and tail-to-tail enchainments). The above mentioned resonances of the isobutyl end groups are still observed, although minor peaks due to other diastereoisomeric 2,4,6-trimethylheptyl end groups are more intense with respect to sample 2, owing to the lower stereoregularity. Interestingly, additional resonances of slightly lower intensities are detected at δ 14.2, 22.7, 31.8 ppm. Based on literature data and DEPT experiments, the latter can be attributed to C1, C2, C3 of a polymethylene chain-end (Scheme 7). Resonances attributable to $S_{\delta^+\delta^+}$ carbons are also detected at δ 29.7 [1,8].

In the unsaturated region of the ^{1}H NMR spectrum (see Fig. 6) very weak resonances attributable to vinylidene and allyl end groups are detected [12]. Allyl end group could in principle originate either from β-hydrogen elimination from the methyl of growing chain-end after a 2,1 insertion, or from β-methyl elimination after a 1,2 insertion. The former reaction has been implicated by Brookhart [1] in

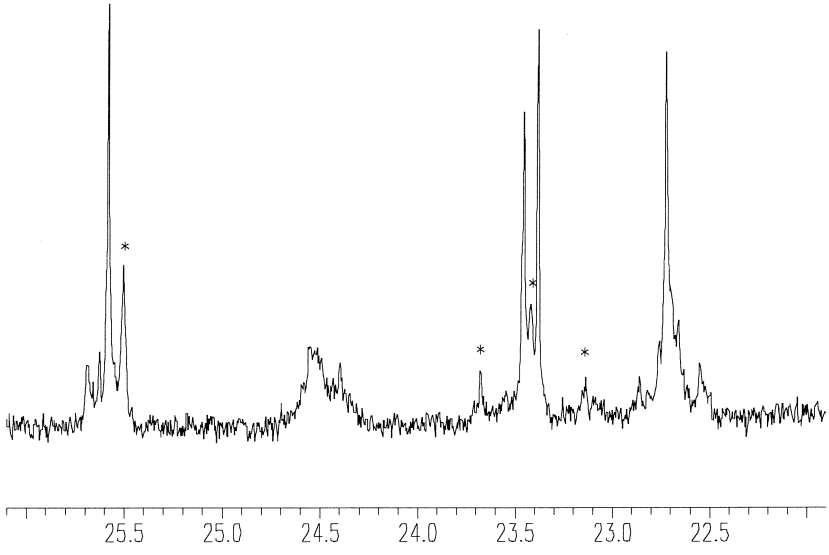


Fig. 4. ^{13}C NMR spectrum in the methyl and methine region of the isobutyl end groups ($C_2D_2Cl_4$, 100°C) of a low molecular weight polypropylene sample prepared with **1**–MAO at −45°C and quenched with CH_3CH_2OD (sample 3). Resonances due to the deuteriated end groups are marked by stars. The presence of a double peak between 23.3 and 23.5 ppm can be due either to an impurity or to some long range effect. δ in ppm from TMS.

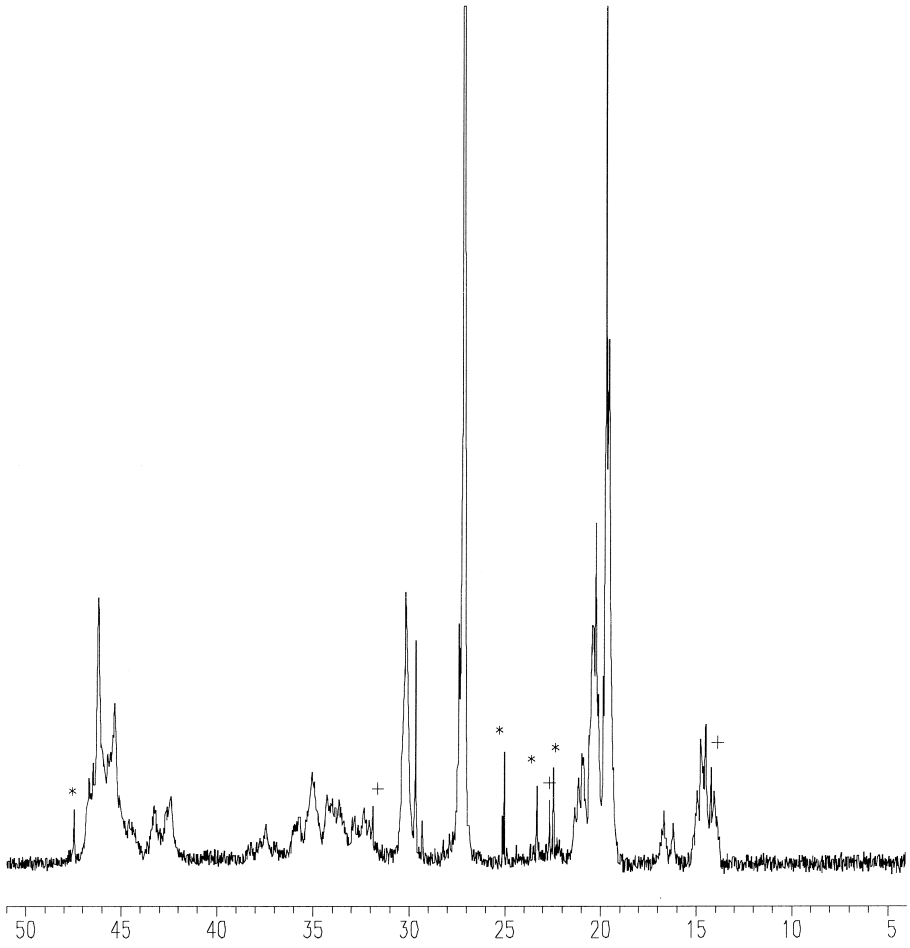
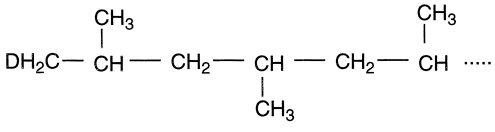
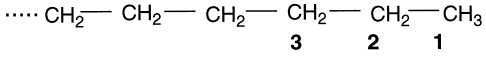


Fig. 5. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 25°C) of a low molecular weight polypropylene sample prepared with **2**–MAO at −45°C (sample 4). Resonances of the isobutyl end groups are marked by stars, while those of the *n*-alkyl end groups are marked by crosses. δ in ppm from TMS.

the formation of polymethylene sequences in the polymerization of propene with Ni diimine catalysts at higher temperatures, while the latter has been observed in the polymerization of propene with sterically hindered metallocene catalysts [12,15]. The above findings are compatible with a lower regiospecificity of initiation and/or termination steps, paralleling a lower regiospecificity of propagation, which could also favor the formation of polymethylene sequences. In fact, according to Brookhart [1], polymethylene sequences would result after β-hydrogen abstraction in growing polymer chains ending with a 2,1-inserted propene unit, followed by reinsertion of the resulting α-olefin with opposite regiochemistry.



Scheme 6.



Scheme 7.

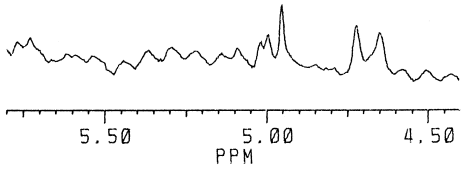


Fig. 6. Unsaturated region of the ^{1}H NMR spectrum ($C_2D_2Cl_4$, 25°C) of sample 4.

Finally, the very fact that turning from catalyst **1** to **2** (i.e. introducing a less steric demanding ligand) the amount of regioirregularities increases is in agreement with 1,2 monomer insertion as the 'normal' mode of propagation and 2,1 insertion as the 'wrong' one, since the latter is reasonably favored by a less hindered coordination sphere.

In conclusion, the above reported results indicate that with these new Ni(II) diimine catalysts the preferred mode of propene insertion is 1,2 both in the initiation and the termination steps, thus suggesting that the same regiochemistry is prevailing during the propagation. Accordingly, decrease of the steric bulk of the ligand environment at the Ni center results in an increase of regioirregularities in both the polymer backbone and the end-groups.

3. Experimental section

All the operation and manipulations were carried out under a dry nitrogen atmosphere using Schlenk or glove-box techniques.

3.1. Materials

{Ar–N=C(H)C(H)=N–Ar}$NiBr_2$ (Ar = 2,6-(i-C_3H_7)$_2$$C_6H_3$, **1**; Ar = 2,6-($CH_3$)$_2$$C_6H_3$, **2**) were prepared according to the literature [16]. MAO (Witco) was used as 30 wt% solution in toluene. Polymerization grade propene (SON) was distilled over Al(i-Bu)$_3$ before use. Toluene (Carlo Erba) was refluxed over metallic sodium and distilled under a nitrogen atmosphere before use.

3.2. Polymerizations

The polymerization runs were carried out in 100 ml, magnetically stirred glass flasks, which were charged under nitrogen sequentially with toluene, MAO, propene, and Ni precatalyst. Runs 1, 2, and 4 were stopped by pouring the reaction mixture into acidified ethanol, and the precipitated polymers were recovered by filtration, dried, dissolved in petroleum ether, filtered through silica, and dried in vacuo at 70°C. Run 1 was carried out at 50°C under 1 atm of propene by using 30 ml of toluene, 7.5 mmol MAO, 59 mg of **1**; time 2 min, yield 0.05 g (sample 1). Run 2 was carried out at −45°C by using 30 ml of toluene, 10 mmol of MAO, 200 ml of gaseous propene (20°C, 1 atm), 61 mg of **1**; time 2 h, yield 0.2 g (sample 2). Run 4 was carried out at −45°C by using 30 ml of toluene, 10 mmol of MAO, 500 ml of gaseous propene (20°C, 1 atm), 48 mg of **2**; time 5 h, yield 0.2 g (sample 4). Run 3 was carried out at −45°C by using 30 ml of toluene, 10 mmol of MAO, 500 ml of gaseous propene (20°C, 1 atm), 63 mg of **1**; after 5 h, 3 ml of a 2:1 mixture of C_2H_5OD and CF_3COOD was injected, the polymerization mixture was stirred 20 h at −45°C, and then poured into ethanol. The precipitated polymer was recovered as above; yield 0.9 g (sample 3).

3.3. Analysis of the polymers

Samples 1,2 and 4 were analyzed on an AM 250 Bruker spectrometer, as ~10% w/v solutions in 1,1,2,2-tetrachlorodideuterioethane in 5 mm o.d. tubes at 120°C (sample 1) or 25°C (samples 2, 4). In all measurements, a broadband noise decoupling was used, the pulse angle was 65°, the acquisition time was 0.69 s, the delay between pulses was 1 s; the FID's (~30 000 scans) were stored in 32 K data points by using a spectral width of 12 000 Hz. Sample 3 was analyzed on an AM 270 Bruker NMR instrument, as ~10% w/v solution in 1,1,2,2-tetrachlorodideuterioethane in a 10 mm o.d. tube

at 100°C, using a 90° pulse angle, a 6.6 s acquisition time, a 19 s relaxation delay, and Waltz 16 pulse sequence for decoupling; the FID's ($\sim$ 9000 scans) were stored in 64 K data points using a spectral window of 5000 Hz.

The rr triad contents of samples 2 and 4 were evaluated by neglecting the regioinversions. Since the resonances of the $P_{\beta\gamma}$ carbons overlap with those of the $P_{\beta\beta}$ carbons used for the measurement of the triads, and their chemical shifts are largely dependent on tacticity effects [17,18] a more precise triad evaluation would require a complete microstructural analysis taking into account also the tacticity of the regioirregular sequences. However, one can easily estimate the upper limit of the correction to be introduced. In fact, since $P_{\alpha\beta}$ and $P_{\alpha\gamma}$ carbons resonate in the region 14–17 ppm, and since the amount of $P_{\beta\gamma}$ carbons is equal to that of $P\alpha_{\beta}$ ones, the upper limit of $P_{\beta\gamma}$ (assuming $P_{\alpha\gamma} = 0$) can be evaluated from the area of the mentioned resonances between 14–17 ppm. This value is the maximum amount to be subtracted from the area of the rr triad region (in the hypothesis that all the $P_{\beta\gamma}$ carbon resonances overlap with the rr $P_{\beta\beta}$ ones). Such a calculation, e.g. in the case of sample 2, results in a change of the rr content from 72% to 68%. Of course, the real value is comprised in between these two values. The amount of regioinversions was evaluated from the ratio between the area of the $P_{\alpha\beta} + P_{\alpha\gamma}$ carbons and the total area of the methyl carbons.

Molecular weight data for samples 2 and 3 were obtained from GPC analysis performed in 1,2-dichlorobenzene at 135°C on a Waters 150C instrument.

Acknowledgements

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