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Propene/Ethene-[1-^{13}C] Copolymerization as a Tool for Investigating Catalyst Regioselectivity. 1. Theory and Calibration

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ABSTRACT: In a previous letter, we proposed the synthesis and ^{13}C NMR characterization of propene/ethene-[1-^{13}C] copolymers at low ethene-[1-^{13}C] content as a convenient tool for measuring the regioselectivity of coordinated propene polyinsertion, in case ^{13}C NMR fails to detect the regiomistakes in propene homopolymers. In the present article, we introduce the foundations of the approach in more detail, and illustrate how its scope can be extended to the evaluation of catalyst "dormancy" due to regiochemical monomer inversion. The method was calibrated for two well-known C_2-symmetric *ansa*-metallocene catalysts (namely, *rac*-$Me_2Si(1\text{-indenyl})_2ZrCl_2$ and *rac*-$Me_2Si(2\text{-Me-4-phenyl-1-indenyl})_2ZrCl_2$), by means of a cross-check with results of a ^{13}C NMR characterization of samples of poly(propene-[3-^{13}C]) prepared under corresponding experimental conditions. In particular, it was proved that the fraction of consecutive 2,1 insertions in propene homopolymerization promoted by the quoted catalysts, although nonzero, is low enough not to invalidate the propene/ethene-[1-^{13}C] copolymerization approach.

Introduction

Propene polymerization promoted by most early transition metal catalysts (e.g., heterogeneous Ziegler−Natta[1] and homogeneous metallocene-based[2]) is highly regioselective in favor of 1,2 (primary) insertion.[1−3] As a matter of fact, ^{13}C NMR at natural isotopic abundance often fails to detect regioirregular enchainments in the polymers.[2,3]

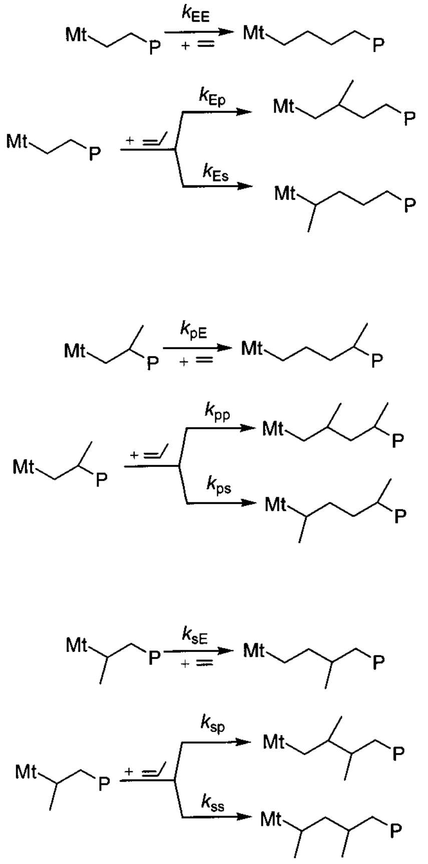
Neglecting the presence of minor amounts of *regio*-defects in polypropylenes with a (much) larger content of *stereo*defects may be acceptable as far as the relationship between microstructure and material properties is concerned,[3,4] but certainly not when one is interested in the polymerization kinetics. Indeed, a growing chain with a last-inserted 2,1 (secondary) monomeric unit has a comparatively poor reactivity, due to the high steric hindrance at the active metal.[2,5,6]

This is particularly well-documented for monomer insertion (Scheme 1; P = polymeryl). The specific rate k_{sp} has been measured to be—typically—from 100 to 1000 times lower than k_{pp}, and k_{ss} is usually even lower, which is already enough to justify the attribution of "dormant" frequently used for a $Mt-CH(CH_3)-CH_2-P$ species.[6] In this regard, an important point to keep in mind is that, under conditions of negligible chain tranfer and isomerization (vide infra), the fraction of dormant chains, C_s* is given by[6a]

$$C_s{}^* = (1 + k_{sp}/k_{ps})^{-1} \qquad (1)$$

which means that the extent to which the 2,1 regiomistakes slow-down chain propagation does *not* depend on how frequently they occur (i.e., on the ratio k_{ps}/k_{pp}) and that even traces can effectively inhibit a catalyst, whenever k_{sp}/k_{ps} is low enough ($C_s{}^* \rightarrow 1$ for $k_{sp}/k_{ps} \rightarrow 0$).

Scheme 1



Chain transfer at a dormant species also seems to be problematic. Some pathways, indeed, such as monomer-assisted β-H elimination and ligand exchange with the Al−alkyl cocatalyst, would benefit of more space at the active site than that left by a 2,1 last-inserted unit.[6b] This explains why, at least for catalysts with highly electrophilic metal centers, a competitive way-out from the dormant state can be the intramolecular isomerization of the 2,1 into a 3,1 enchainment, although this requires a first "expensive" β-H elimination event.[2,3,6c]

A number of molecules of small size, however, can easily react with dormant polypropylene chains. An

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extreme case, understandably, is that of molecular hydrogen, which “cuts” Mt−alkyl bonds almost independent of their nature.[5,6]

Due to its low steric hindrance, ethene also inserts in a dormant chain much faster ($>10^2$ times) than propene. This represents an *atout* for regiochemical studies; in fact, in a copolymerization, already at very low ethene/propene feeding ratio, most 2,1 propene insertions will be followed by an ethene one, and in the ^{13}C NMR spectrum of the resulting copolymer, the resonances of ethene units between two propene ones with opposite enchainments can be taken as markers of the propene regioerrors.[3,7] Of course, using ethene-[1-^{13}C] instead of ethene at natural isotopic abundance increases the sensitivity of ^{13}C NMR by a factor of 50, which means that the threshold for the detection of the regiodefects is lowered correspondingly (from ≈0.1−1 to ≈0.002−0.02 mol %, depending on the experimental setup and on the specific sample analyzed).

In a previous letter to this journal,[7] we illustrated in a preliminary and compact form how the above concepts can be turned into a quantitative method for measuring the regioselectivity of a coordination catalyst. The application protocol requires the synthesis and ^{13}C NMR characterization of a series of propene/ethene-[1-^{13}C] copolymers with increasing ethene-[1-^{13}C] content (typically, up to 5 mol %). Plotting the mole fraction of ethene-[1-^{13}C] units found to be adjacent to a 2,1 propene unit (Q_{sE}) against the total ethene-[1-^{13}C] mole fraction (Q_{E}) gives an asymptotic curve, and the limit for $Q_{\mathrm{E}} \rightarrow 1$ can be plausibly assumed to coincide with the fraction of 2,1 insertions in propene homopolymerization (i.e., with the ratio $k_{\mathrm{ps}}/k_{\mathrm{pp}}$, Scheme 1). In the present article, we present the method in more detail and show how it can be extended to estimate catalyst dormancy as well.

One possible objection to the approach is that the presence of ethene, even in small amounts, perturbs the homopolyinsertion of propene and that investigating the latter in terms of copolymerization data is conceptually incorrect. In particular, a major concern can be that, even for metallocene and Ti-based Ziegler−Natta catalysts, the specific rate k_{ss} is not truly negligible and that adding ethene prevents the formation of consecutive 2,1 propene units, which would ultimately lead to overestimate the regioselectivity.

This concern is not unbased; indeed, apart from the low rate, propene insertion in a dormant chain is “anomalous” also with respect to its regio- and stereochemistry. The incoming monomer has actually to choose whether to restore the “normal” 1,2 mode, and thus undergo the repulsive interactions with the last monomeric unit inherent in the formation of a head-to-head enchainment, or to iterate the 2,1 insertion, which brings instead the methyl group in direct steric contact with the ancillary ligand(s) of the transition metal (and is also disfavored for electronic reasons). The solution to this dilemma is not trivial: although for most catalysts the 2,1 insertions tend to remain isolated,[2,3] a few cases have also been documented in which, on the other hand, blocks of 2,1 units are formed.[3,8,9]

Quantum mechanical calculations carried out in our own group[10] on a number of model metallocene active species (such as Cp_2TiR^+, Cp_2ZrR^+, and $H_2SiCp_2ZrR^+$) pointed out that the preference of propene for the 1,2 insertion mode, which is large (3−5 kcal/mol) at a Mt−CH$_2$−R bond, reduces to about 1 kcal/mol at a Mt−CH(CH$_3$)−R bond. Also in view of the fact that the uncertainty on such calculations is on the order of 1 kcal/mol (at least), we are the first to admit that assuming serendipitously that $k_{\mathrm{ss}} \approx 0$ is hazardous.

Therefore, we considered it worthwhile to address this aspect in depth for two representative C_2-symmetric *ansa*-zirconocene catalysts—the archetypical *rac*-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$[11] (**I**) and the much more efficient *rac*-Me$_2$Si(2-Me-4-phenyl-1-indenyl)$_2$ZrCl$_2$[12] (**II**)—with a regioselectivity low enough to measure precisely the fraction of isolated and consecutive 2,1 units in propene *homo*polymers, provided that these are ^{13}C-enriched. As we shall see, the results lend full support to the propene/ethene-[1-^{13}C] copolymerization approach, and represent at the same time an excellent calibration in view of future applications to catalysts of higher regioselectivity.

Results and Discussion

(i) Measurements of Regioregularity on Poly(propene-[3-^{13}C]). Propene homopolymers at natural ^{13}C abundance prepared with catalyst **I** contain ^{13}C NMR detectable amounts of regioirregular enchainments. These can be in the form of 2,1 and 3,1 units,[2,3,6c] which complicates somewhat the microstructural analysis. The proportion of 3,1 units, however, decreases with increasing propene concentration and with decreasing polymerization temperature (T_{p}),[2,3,6c] and for $T_{\mathrm{p}} < 20$ °C (indicatively), it becomes negligible, unless the polymerization is carried out at vanishingly low [C_3H_6].

Figure 1 shows a quantitative ^{13}C NMR spectrum of a polypropylene sample obtained with **I**/MAO (MAO = methylalumoxane) at $T_{\mathrm{p}} = 10$ °C and [C_3H_6] = 0.9 M. Apart from the main resonances arising from fully regioregular, predominantly isotactic sequences, minor peaks are also present, due to various kinds of chain-ends and to regioirregular sequences. The latter contain exclusively 2,1 units, and occur in the two stereochemical arrangements shown in Chart 1, which confirms that 2,1 insertion at the quoted catalyst is fully enantioselective (the reactive enantioface being opposite to that favored in 1,2 insertion), whereas a subsequent 1,2 insertion is only weakly so.[2,3,6c,13]

From peak integration, it can be safely concluded that the 2,1 units (0.3 mol % in the stereostructure of Chart 1A, and 0.1 mol % in that of Chart 1B) are *mostly* isolated; indeed, the areas of the $P_{\alpha\beta}$ ($\delta = 17.54$ and 15.44 ppm) and $P_{\alpha\gamma}$ ($\delta = 17.32$ and 14.89 ppm) peaks[14] are equal within the experimental error, whereas an excess of $P_{\alpha\beta}$ relative to $P_{\alpha\gamma}$ is expected in case of consecutive 2,1 units (Chart 2). However, from the figure it can be seen that, for all said peaks, the signal-to-noise ratio is—at most—5 (despite a 24 h accumulation); this means that the possible occurrence of consecutive 2,1 units at a fraction up to 25% of their total amount cannot be ruled out, which is not acceptable for our purpose.

Similar results were obtained from the microstructural characterization of polypropylene samples prepared with **II**/MAO. Compared with **I**, catalyst **II** has a lower propensity to isomerize 2,1 last-inserted units into 3,1; as a matter of fact, we could operate at T_{p} as high as 40 °C and down to [C_3H_6] = 0.1 M and still obtain a polymer without detectable 3,1 enchainments. Under the said conditions, we measured a total 2,1 unit content of 0.3 mol %, all in the stereostructure of Chart 1A (which indicates that a high enantioselectivity of 1,2 insertion is maintained even after a 2,1 regiomistake,

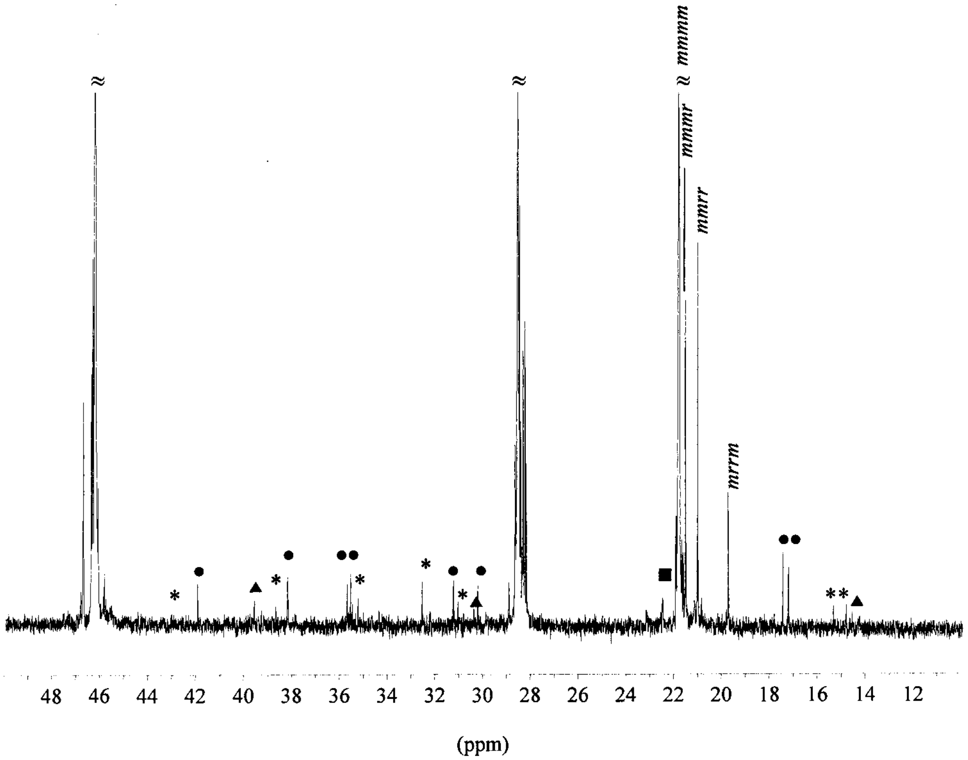


Figure 1. 100 MHz ^{13}C NMR spectrum (recorded in tetrachloroethane-1,2-d_2 at 110 °C; δ scale in ppm downfield of TMS) of a polypropylene sample prepared with catalyst system **I**/MAO at 10 °C, $[C_3H_6] = 0.9$ mol/L. In the methyl region, the resonances of the four main pentads in regioregular sequences are explicitly assigned. Minor peaks arising from regioirregular sequences containing (mostly isolated) 2,1 units in the two stereochemical arrangements of Chart 1A (●) and 1B (∗), as well as from *n*-propyl (▲) and vinylidene (■) end groups, are also indicated.

Chart 1

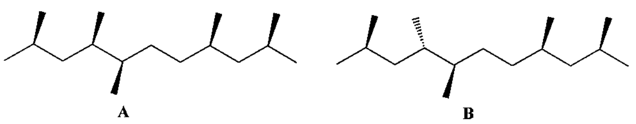
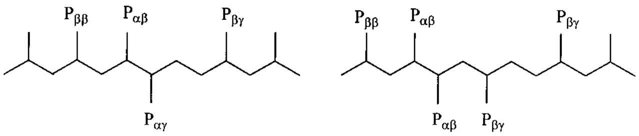


Chart 2



probably due to the more hindered steric environment of the active metal compared with **I**). In this case too, we could only conclude that consecutive 2,1 units, if present, were below 25%.

To improve the sensitivity of our ^{13}C NMR analysis we prepared, for each catalyst system, a sample of ^{13}C-enriched polypropylene, under conditions identical to those already described for the polymerization of unlabeled propene. We chose to label selectively the methyl C only, to minimize ^{13}C$-$^{13}C coupling, in view of the fact that our main purpose was an accurate integration of the $P_{\alpha\beta}$ and $P_{\alpha\gamma}$ peaks. Due to the prohibitevely high cost of propene-[3-^{13}C], we used it in mixture with unlabeled propene at a 15/85 ratio, which was enough to increase the signal-to-noise ratio for the peaks of interest up to ≈50, as can be seen from the detail of the methyl region in the spectrum of the poly(propene-[3-^{13}C]) sample prepared with **I**/MAO (Figure 2).

Peak integration was carried out by means of full spectral simulation. From the measured fraction of 2,1 units, we estimated the values of k_{ps}/k_{pp} in the first row of Table 1; these agree, within the experimental error, with those evaluated on polymers at natural ^{13}C abundance, although—understandably—the accuracy is much higher now. Importantly, in both cases the $P_{\alpha\beta}/P_{\alpha\gamma}$ integral ratio turned out to be 1.06 ± 0.02, which means that the fraction of consecutive 2,1 units is on the order of 5% of the total 2,1 unit content. Although nonzero, in agreement with the predictions of our quantum-mechanical calculations,[10] this is low enough not to invalidate the propene/ethene-[1-^{13}C] copolymerization method.

(ii) Measurements of Catalyst Regioselectivity via Propene/Ethene-[1-^{13}C] Copolymerization. Two sets of propene/ethene-[1-^{13}C] copolymers at low (<5 mol %) ethene-[1-^{13}C] content, prepared with catalyst systems **I**/MAO at $T_p = 10$ °C[7] and **II**/MAO at $T_p = 40$ °C, were characterized by means of ^{13}C NMR. For all copolymers, Table 2 reports the total mole fraction of incorporated ethene-[1-^{13}C] units (Q_E), and the mole fraction of such units between propene units with opposite enchainments (Q_{sE}), along with the comonomer mole ratio in the feed ([E]/[P] in the liquid phase).

Plots of Q_{sE} vs Q_E (see Introduction) are shown in Figure 3. For both copolymer sets, the experimental points have the expected asymptotic behavior,[7] and are well-fitted by a standard saturation function:

$$Q_{sE} = k_1 Q_E/(k_2 + Q_E) \qquad (2)$$

The best-fit values of $k_1 = k_{ps}/k_{pp}$ are (0.59 ± 0.03)% for **I**/MAO and (0.35 ± 0.03)% for **II**/MAO, in perfect agreement with the estimates based on propene-[3-^{13}C] homopolymerization (compare rows 1 and 2 in Table 1).[15]

In the Introduction, we noted that knowing how many 2,1 regiodefects are formed in a polyinsertion process

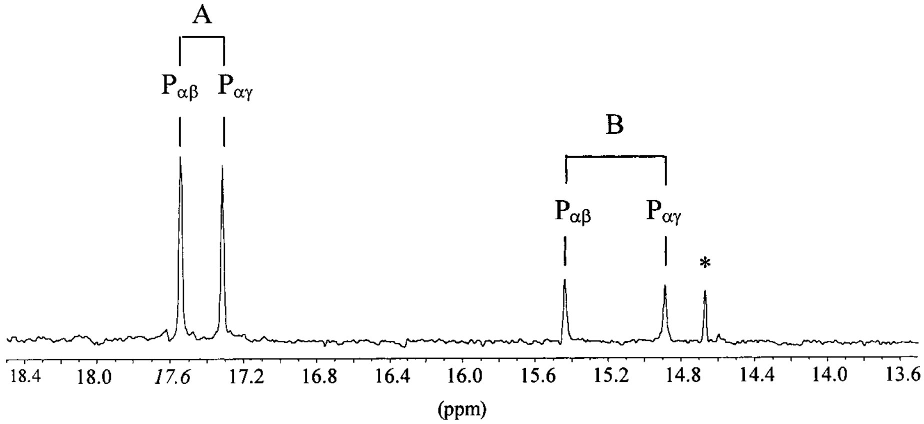


Figure 2. Detail of the methyl region of the 100 MHz ^{13}C NMR spectrum (recorded in tetrachloroethane-1,2-d_2 at 110 °C; δ scale in ppm downfield of TMS) of a polypropylene-[3-^{13}C] sample prepared at 10 °C in the presence of catalyst system **I**/MAO. For peak attributions, see Charts 1 and 2. The peak marked with an asterisk (*) is due to the methyl C of *n*-propyl end groups.

Table 1. Estimates of *Chemo*- and *Regio*selectivity, Based on Results of Propene-[3-^{13}C] Homopolymerization and Propene/Ethene-[1-^{13}C] Copolymerization, for Catalyst Systems I/MAO (at 10 °C) and II/MAO (at 40 °C)

	I/MAO	**II**/MAO
$k_{ps}/k_{pp} \times 10^2$ [a]	0.62 ± 0.01	0.31 ± 0.02
$k_{ps}/k_{pp} \times 10^2$ [b]	0.59 ± 0.03	0.35 ± 0.03
$k_{pE}/k_{ps} \times 10^{-3}$	1.19 ± 0.04	0.76 ± 0.05
$(k_{pE}/k_{sE})(k_{sp}/k_{ps})$	1.44 ± 0.08	4.4 ± 0.2
k_{pE}/k_{pp}	7.0 ± 0.3	2.7 ± 0.3
$k_{sE}/k_{sp} \times 10^{-2}$	8.3 ± 0.5	1.7 ± 0.14

[a] From the ^{13}C NMR characterization of poly(propene-[3-^{13}C])
[b] From data of propene/ethene-[1-^{13}C] copolymerization

Table 2. ^{13}C NMR Mole Fraction of Ethene-[1-^{13}C] Units Following a 2,1 Propene Unit (Q_{sE}), as a Function of Total Ethene-[1-^{13}C] Mole Fraction (Q_E), for Propene/Ethene-[1-^{13}C] Copolymers Prepared with Catalyst Systems I/MAO at 10 °C, and II/MAO at 40 °C

catalyst system	$[E]/[P] \times 10^3$ (liquid phase)[a]	Q_E (mol %)	Q_{sE} (mol %)
I/MAO[b]	0.17 ± 0.02	0.12 ± 0.01	0.044 ± 0.004
	0.63 ± 0.02	0.41 ± 0.01	0.130 ± 0.004
	1.33 ± 0.02	0.92 ± 0.01	0.226 ± 0.005
	1.99 ± 0.05	1.68 ± 0.01	0.334 ± 0.005
	3.23 ± 0.03	2.35 ± 0.01	0.384 ± 0.005
	4.02 ± 0.06	2.93 ± 0.02	0.397 ± 0.005
	4.52 ± 0.05	3.2 ± 0.1	0.40 ± 0.01
II/MAO	0.17 ± 0.02	0.052 ± 0.005	0.0097 ± 0.0009
	0.45 ± 0.02	0.106 ± 0.006	0.0189 ± 0.0011
	1.14 ± 0.02	0.314 ± 0.007	0.0460 ± 0.0012
	3.58 ± 0.02	0.897 ± 0.007	0.106 ± 0.0013
	5.49 ± 0.03	1.34 ± 0.012	0.137 ± 0.002
	9.80 ± 0.04	2.83 ± 0.04	0.226 ± 0.012

[a] E = ethene-[1-^{13}C], P = propene. [b] Data from ref 7.

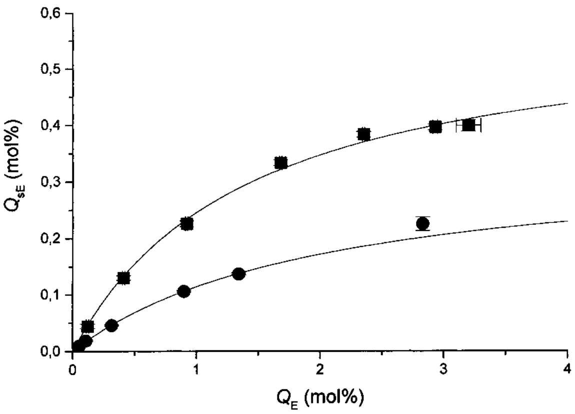


Figure 3. Mole fraction of ethene-[1-^{13}C] units adjacent to a 2,1 propene unit (Q_{sE}) vs total ethene-[1-^{13}C] content (Q_E), for propene/ethene-[1-^{13}C] copolymers prepared with catalyst systems **I**/MAO at 10 °C (■) and **II**/MAO at 40 °C (●) (data from Table 2).

(i.e., the value of the k_{ps}/k_{pp} ratio) is not informative on the dormancy of the catalytic species, which depends instead on the k_{sp}/k_{ps} ratio only (eq 1). The copolymerization data in Table 2, however, can also be used to extract some information on the latter ratio.

Scheme 1 shows all possible chain propagation steps in a propene/ethene copolymerization, under the plausible assumptions that (i) the copolymerization statistics is first-order Markovian, (ii) chain configuration (when the last inserted unit is a propene one) does not affect the insertion rates, and (iii) chain transfer and isomerization processes can be neglected.

Let us define now the following variables:

$C^*_{n,p}$ = concentration of growing chains with degree of polymerization *n*, in which the last inserted monomeric unit is a 1,2 propene one.

$C^*_{n,s}$ = concentration of growing chains with degree of polymerization *n*, in which the last inserted monomeric unit is a 2,1 propene one.

$C^*_{n,E}$ = concentration of growing chains with degree of polymerization *n*, in which the last inserted monomeric unit is an ethene one.

Under the assumption of stationary state and in the hypothesis that the reaction order with respect to all monomers (1,2 propene, 2,1 propene and ethene) is 1, it is straightforward to derive the equations below:

$$dC^*_{n,p}/dt = 0 = k_{pp}C^*_{(n-1),p}[P] + k_{sp}C^*_{(n-1),s}[P] + k_{Ep}C^*_{(n-1),E}[P] - k_{pp}C^*_{n,p}[P] - k_{ps}C^*_{n,p}[P] - k_{pE}C^*_{n,p}[E] \quad (3)$$

$$dC^*_{n,s}/dt = 0 = k_{ps}C^*_{(n-1),p}[P] + k_{ss}C^*_{(n-1),s}[P] + k_{Es}C^*_{(n-1),E}[P] - k_{sp}C^*_{n,s}[P] - k_{ss}C^*_{n,s}[P] - k_{sE}C^*_{n,s}[E] \quad (4)$$

where [P] ([E]) = concentration of propene (ethene) in the reaction phase.

For the catalysts considered here, $k_{pp} \gg k_{ps}$ and $k_{sp} \gg k_{ss}$. Moreover, in our reaction conditions, due to the very low [E]/[P] mole ratio in the feed (Table 2), it is also $k_{pE}[E] \ll k_{pp}[P]$. Therefore, eqs 3 and 4 can be approximated as follows:

$$\mathrm{d}C^*_{n,\mathrm{p}}/\mathrm{d}t = 0 \approx k_{\mathrm{pp}}C^*_{(n-1),\mathrm{p}}[\mathrm{P}] + k_{\mathrm{Ep}}C^*_{(n-1),\mathrm{E}}[\mathrm{P}] - k_{\mathrm{pp}}C^*_{n,\mathrm{p}}[\mathrm{P}] \tag{5}$$

$$\mathrm{d}C^*_{n,\mathrm{s}}/\mathrm{d}t = 0 \approx k_{\mathrm{ps}}C^*_{(n-1),\mathrm{p}}[\mathrm{P}] + k_{\mathrm{Es}}C^*_{(n-1),\mathrm{E}}[\mathrm{P}] - k_{\mathrm{sp}}C^*_{n,\mathrm{s}}[\mathrm{P}] - k_{\mathrm{sE}}C^*_{n,\mathrm{s}}[\mathrm{E}] \tag{6}$$

Solving them for $C^*_{n,\mathrm{p}}$ and $C^*_{n,\mathrm{s}}$ gives

$$C^*_{n,\mathrm{p}} \approx (k_{\mathrm{pp}}C^*_{(n-1),\mathrm{p}}[\mathrm{P}] + k_{\mathrm{Ep}}C^*_{(n-1),\mathrm{E}}[\mathrm{P}])/k_{\mathrm{pp}}[\mathrm{P}] \tag{7}$$

$$C^*_{n,\mathrm{s}} \approx (k_{\mathrm{ps}}C^*_{(n-1),\mathrm{p}}[\mathrm{P}] + k_{\mathrm{Es}}C^*_{(n-1),\mathrm{E}}[\mathrm{P}])/(k_{\mathrm{sp}}[\mathrm{P}] + k_{\mathrm{sE}}[\mathrm{E}]) \tag{8}$$

If one admits that $k_{\mathrm{Ep}} \approx k_{\mathrm{pp}}$ and $k_{\mathrm{Es}} \approx k_{\mathrm{ps}}$, dividing eq 7 by eq 8 leads to

$$C^*_{n,\mathrm{p}}/C^*_{n,\mathrm{s}} \approx (k_{\mathrm{sp}}[\mathrm{P}]+k_{\mathrm{sE}}[\mathrm{E}])/k_{\mathrm{ps}}[\mathrm{P}] \tag{9}$$

Finally, considering that the ratio $Q_{\mathrm{pE}}/Q_{\mathrm{sE}}$ between the amounts of ethene units inserted after a 1,2 or a 2,1 propene unit, respectively, is given by

$$Q_{\mathrm{pE}}/Q_{\mathrm{sE}} \approx (k_{\mathrm{pE}}C^*_{n,\mathrm{p}})/(k_{\mathrm{sE}}C^*_{n,\mathrm{s}}) \tag{10}$$

and combining eqs 9 and 10, one obtains

$$Q_{\mathrm{pE}}/Q_{\mathrm{sE}} \approx (k_{\mathrm{pE}}/k_{\mathrm{sE}})(k_{\mathrm{sp}}/k_{\mathrm{ps}}) + (k_{\mathrm{pE}}/k_{\mathrm{ps}})[\mathrm{E}]/[\mathrm{P}] \tag{11}$$

Experimental plots of $Q_{\mathrm{pE}}/Q_{\mathrm{sE}}$ vs[E]/[P] for the two catalyst systems **I**/MAO and **II**/MAO, based on the data in Table 2 ($Q_{\mathrm{pE}} = Q_{\mathrm{E}} - Q_{\mathrm{sE}}$), are shown in Figure 4. The linear dependence predicted by eq 11 is nicely verified. A linear regression gave the best-fit values of $k_{\mathrm{pE}}/k_{\mathrm{ps}}$ and $(k_{\mathrm{pE}}/k_{\mathrm{sE}})(k_{\mathrm{sp}}/k_{\mathrm{ps}})$ reported in rows 3 and 4 of Table 1. From the former ratio, and the previously determined $k_{\mathrm{ps}}/k_{\mathrm{pp}}$, one can immediately derive $k_{\mathrm{pE}}/k_{\mathrm{pp}}$, which gives the preference for ethene over 1,2 propene to insert after a previous 1,2 propene unit. Dividing $k_{\mathrm{pE}}/k_{\mathrm{ps}}$ by $(k_{\mathrm{pE}}/k_{\mathrm{sE}})(k_{\mathrm{sp}}/k_{\mathrm{ps}})$ gives the same preference after an occasional 2,1 propene insertion, i.e., the ratio $k_{\mathrm{sE}}/k_{\mathrm{sp}}$. The results, also given in Table 1 (rows 5 and 6), confirm the assumptions behind the method and—in particular—that ethene inserts much faster than propene at a chain with a 2,1 last-inserted propene unit ($k_{\mathrm{sE}}/k_{\mathrm{sp}} > 1.5 \times 10^2$).

Let us consider now the product $(k_{\mathrm{pE}}/k_{\mathrm{sE}})(k_{\mathrm{sp}}/k_{\mathrm{ps}})$. Unfortunately, there is no experimental way to measure separately the two factors $k_{\mathrm{sp}}/k_{\mathrm{ps}}$ and $k_{\mathrm{pE}}/k_{\mathrm{sE}}$. However, quantum mechanical calculations on a number of model metallocene cations[10] indicated that ethene has almost no preference for insertion into a Mt$-$CH$_2$$-$R or a Mt$-$CH(CH$_3$)$-$R bond, which suggests that the ratio $k_{\mathrm{pE}}/k_{\mathrm{sE}}$ should be close to 1.

On the other hand, in previous papers,[6] we have shown that propene hydro-oligomerization gives access to the product $(k_{\mathrm{pH}}/k_{\mathrm{sH}})(k_{\mathrm{sp}}/k_{\mathrm{ps}})$ (where k_{pH} and k_{sH} are the specific rates of hydrogen transfer at a propagating and dormant polypropylene chain, respectively). The ratio $(k_{\mathrm{pH}}/k_{\mathrm{sH}})$ has also been suggested to be close to 1, in view of the small size of the H$_2$ molecule.[6]

In due time, for **I**/MAO we measured $(k_{\mathrm{pH}}/k_{\mathrm{sH}})(k_{\mathrm{sp}}/k_{\mathrm{ps}}) \approx 0.35$ at 60 °C.[6c] We considered it worthwhile to carry out a set of propene hydro-oligomerization experiments for **II**/MAO as well, at the same temperature (40 °C) of the propene/ethene-[1-^{13}*C*] copolymerizations; from the results, given in Table 3, we extrapolated—with the procedure illustrated in ref 6a—a value of $(k_{\mathrm{pH}}/k_{\mathrm{sH}})(k_{\mathrm{sp}}/k_{\mathrm{ps}}) \approx 0.8$.

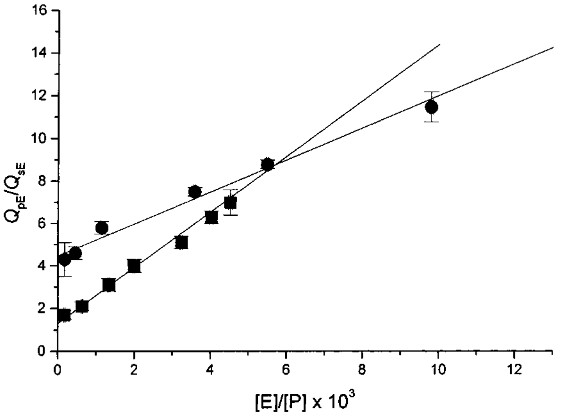


Figure 4. Ratio between ethene-[1-^{13}*C*] units following a 1,2 or a 2,1 propene unit ($Q_{\mathrm{pE}}/Q_{\mathrm{sE}}$) vs ethene-[1-^{13}*C*]/propene feeding ratio in the liquid phase ([E]/[P]), for propene/ethene-[1-^{13}*C*] copolymers prepared with catalyst systems **I**/MAO at 10 °C (■) and **II**/MAO at 40 °C (●) (data from Table 2).

Table 3. Results of Propene Hydro-Oligomerization for Catalyst System II/MAO at 40 °C

sample no.	p(H$_2$) (bar)	X_n[a]	$Q_{\mathrm{pH}}/Q_{\mathrm{sH}}$[b]
1	1.0	260 ± 70	1.8 ± 0.3
2	2.0	216 ± 30	2.2 ± 0.5
3	3.0	117 ± 10	3.4 ± 0.6
4	6.0	69 ± 5	6.0 ± 1.4

[a] Number average degree of polymerization, determined by means of ^{13}C NMR. [b] ^{13}C NMR mole ratio between isobutyl and *n*-butyl chain ends in the hydro-oligomer.

The fact that, for both catalysts investigated here, it turned out that $(k_{\mathrm{pE}}/k_{\mathrm{sE}})(k_{\mathrm{sp}}/k_{\mathrm{ps}}) \approx 5(k_{\mathrm{pH}}/k_{\mathrm{sH}})(k_{\mathrm{sp}}/k_{\mathrm{ps}})$ and hence that $k_{\mathrm{pE}}/k_{\mathrm{sE}} \approx 5k_{\mathrm{pH}}/k_{\mathrm{sH}}$ can be taken as a proof that the latter ratios are indeed not far from unity, but it also indicates that at least one of the two is not "exactly" 1. A quantum mechanical investigation of the hydrogenolysis of Zr$-$ethyl and Zr$-$(isopropyl) bonds at zirconocene model cations[16] suggests that the ratio $k_{\mathrm{pH}}/k_{\mathrm{sH}}$ is slightly <1, but once again the error on such calculations is too high to be conclusive in this sense.

Therefore, it is probably wise to assume that the "true" value of C_{s}^* is within a range whose extremes are the estimates based on propene hydro-oligomerization and propene/ethene-[1-^{13}*C*] copolymerization taking $k_{\mathrm{pH}}/k_{\mathrm{sH}} = 1$ and $k_{\mathrm{pE}}/k_{\mathrm{sE}} = 1$, respectively. Such a range would be $0.4 < C_{\mathrm{s}}^* < 0.8$ for **I**/MAO and $0.2 < C_{\mathrm{s}}^* < 0.6$ for **II**/MAO. This is enough to state that the fraction of dormant chains is nonnegligible for both catalysts, and also that catalyst **I** is somewhat more dormant than **II**, which can be one of the reasons for its lower (average) productivity.[2,11,12]

In conclusion, we can confirm our previous suggestion[7] that propene/ethene-[1-^{13}*C*] data can be conveniently and confidently used to measure the regioselectivity of propene polymerization promoted by coordination catalysts which favor the 1,2 insertion mode,[1-3] whenever the fraction of regiomistakes is too low for a simple ^{13}C NMR analysis on propene homopolymers at natural ^{13}C abundance. The method also allows one to estimate catalyst dormancy due to regiochemical monomer inversion,[2,3,5,6] although with a relatively large margin of uncertainty, which can be reduced somewhat when propene/ethene-[1-^{13}*C*] copolymerization is combined with propene hydro-oligomerization.[6] Applications to a number of highly regioselective heterogeneous Ziegler–Natta and homogeneous metallocene and post-metallocene catalysts will be reported in forthcoming papers of this series.

Experimental Part

Catalysts and Monomers. *rac*-$Me_2Si(1\text{-indenyl})_2ZrCl_2$ (**I**) and MAO (10 wt % solution in toluene) were provided by Witco GmbH; *rac*-$Me_2Si(2\text{-Me-4-phenyl-1-indenyl})_2ZrCl_2$ (**II**) was purchased from Boulder Scientific Co. Ethene and propene at natural ^{13}C abundance (Società Ossigeno Napoli, polymerization grade), ethene-[1-^{13}C], and propene-[3-^{13}C] (Isotec Inc., 99+% isotopic purity), were used as received.

Propene/Ethene-[1-^{13}C] Copolymerizations. All propene/ethene-[1-^{13}C] copolymerizations were run in a 50 mL Pyrex reactor, equipped with a thermostatic jacket, a magnetic stirrer, a silicone rubber septum, and a gas inlet/outlet, with the following procedure. The reactor, charged under nitrogen with 20–25 mL of dry toluene (Aldrich) and MAO (Al/Zr mole ratio $= 5 \times 10^3$ for **I**/MAO, 3×10^4 for **II**/MAO), was thermostated at the chosen polymerization temperature (10 °C for **I**/MAO; 40 °C for **II**/MAO). A gaseous mixture of propene and ethene-[1-^{13}C] at the appropriate composition, prepared with vacuum line techniques and standardized by gas chromatography, was bubbled through the liquid phase at atmospheric pressure and a flow rate of 0.10 L/min, until the gas/liquid equilibrium was attained. The reaction was then started by injecting through the rubber septum the metallocene catalyst (1.0 μmol for **I**, 0.075 μmol for **II**), previously dissolved in 1.0 mL of dry toluene, and allowed to proceed for 30 min, during which the comonomer mixture was kept flowing through the liquid phase. Under the said conditions, total monomer conversions were lower than 10%, which ensured a nearly constant comonomer feeding ratio. After the reaction was quenched with 5 mL of methanol/HCl (aqueous, concentrated) (95/5 v/v), the copolymer was coagulated with excess methanol/HCl, filtered, washed with more methanol, and vacuum-dried.

Propene-[3-^{13}C] Polymerizations. Propene-[3-^{13}C], in a 15/85 mixture with unlabeled propene, was homopolymerized in the same reactor used for the copolymerization experiments, according to the procedure which follows. 20–25 mL of dry toluene (Aldrich) and MAO (Al/Zr mole ratio $= 7 \times 10^2$ for **I**/MAO, 2×10^4 for **II**/MAO) were introduced in the reactor, which was thermostated at the desidered temperature (10 °C for **I**/MAO, 40 °C for **II**/MAO) and pressurized with the propene mixture at a partial pressure of 0.25 bar. The reaction was started by injecting through the rubber septum the appropriate amount of catalyst (4.0 μmol of **I**, 0.10 μmol of **II**) previously dissolved in 1.0 mL of dry toluene and allowed to proceed at constant monomer pressure for 30 min, after which it was quenched with 5 mL of methanol/HCl (aqueous, concentrated) (95/5 v/v). The polymer was then coagulated with excess methanol/HCl, filtered, washed with more methanol, and vacuum-dried.

Propene Hydro-Oligomerizations. Propene hydro-oligomerizations in the presence of catalyst system **II**/MAO at 40 °C were carried out in a 2 L magnetically stirred stainless steel reactor (Brignole AU-2), equipped with a glass vial holder-breaker. In a typical experiment, the reactor was charged under nitrogen with 500 mL of dry toluene containing 8 mL of MAO solution and saturated with hydrogen at an appropriate partial pressure ($p(H_2) = 1.0–6.0$ bar) and propene at a partial pressure of 1.5 bar. The reaction was started by breaking a glass vial containing 1.0 μmol of **II** (previously sealed under argon in a Vacuum-Atmospheres glovebox), allowed to proceed at constant propene pressure, and stopped after 30 min by quickly venting the reactor. Under the said conditions, we checked that the consumption of hydrogen due to the chain transfer reaction was negligible. The hydro-oligomer was coagulated with 1 L of methanol/HCl (aqueous, concentrated) (95/5 v/v), filtered, and vacuum-dried.

^{13}C NMR Polymer Characterizations. Quantitative ^{13}C NMR spectra of all propene/ethene-[1-^{13}C] copolymers were recorded with a Varian VXR 200 spectrometer operating at 50.3 MHz, on 100 mg/mL solutions in tetrachloroethane-1,2-d_2 at 120 °C. Conditions: 5 mm probe; 76° pulse; acquisition time, 1.2 s; relaxation delay, 1.2 s; 36K transients.

Polypropylene samples, either at natural isotopic abundance or ^{13}C-enriched at C-3, were characterized with a Bruker DRX 400 Avance spectrometer, operating at 100.6 MHz, on 10 mg/mL solutions in tetrachloroethane-1,2-d_2 at 110 °C. Conditions: 5 mm probe; 90° pulse; acquisition time, 1.2 s; relaxation delay, 1.2 s; 36K transients.

Finally, quantitative spectra of propene hydro-oligomers were recorded with a Bruker AM 500 spectrometer operating at 125.77 MHz, on 100 mg/mL solutions in a 90/10 (w/w) mixture of 1,2,4-trichlorobenzene and 1,4-dichlorobenzene-d_4 at 120 °C. Conditions: 10 mm probe; 60° pulse; acquisition time, 1.3 s; relaxation delay, 15.5 s; 3K transients.

Full simulation of the spectra was performed with the SHAPE2000 software package.[17]

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