

Highly Regioselective Transition-Metal-Catalyzed 1-Alkene Polymerizations: A Simple Method for the Detection and Precise Determination of Regioirregular Monomer Enchainments

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Transition metal catalysts for the stereoselective polymerization of 1-alkenes are often exceedingly regioselective, 1,2 monomer insertion being largely predominant.^{1,2} As a matter of fact, it has been reported that regioirregular monomeric units are undetectable by ¹³C NMR in most polymers of practical interest, such as highly isotactic polypropylene produced with heterogeneous Ziegler–Natta systems,³ as well as syndiotactic polypropylene obtained in the presence of homogeneous catalysts derived from *C_s*-symmetric *ansa*-metallocenes of the fourth column.⁴

Even when the concentration of regioerrors exceeds, in principle, the limit for ¹³C NMR detectability (0.1–0.2 mol %, indicatively), their spectroscopic evaluation can be problematic. As an example, isotactic polypropylene samples prepared with *C₂*-symmetric *ansa*-metallocene catalysts^{2,5} typically contain 0.5–1 mol % of regioirregular enchainments, but these are often distributed among different structures:⁶ the misinserted units with 2,1 enchainment can be followed, e.g., by 1,2 units with opposite configurations (Charts 1 and 2) and/or rearrange to 3,1 units (Chart 3). This results in an increased number of resonances with correspondingly lower individual intensities.

On the other hand, accurate determinations of catalyst regioselectivities are of the utmost importance. Indeed, the kinetics of 1-alkene polymerizations can be strongly affected (and sometimes is actually dominated) by the occurrence of even traces of regioirregular monomer enchainments, due to the fact that the occasional 2,1 misinsertions, as a rule, strongly slow down chain propagation.^{7–10}

In particular, for isotactic propene polymerization promoted by *C₂*-symmetric metallocene catalysts, the ratio of specific rates k_{pp}/k_{sp} (Scheme 1; P = Polymeryl) has been estimated^{8b,d–f} to be in the range 10^2 – 10^3 ; a sterically hindered growing chain with a 2,1 last-inserted propene unit can thus be viewed as a "dormant" site, and the active species of such catalysts actually spend a relevant fraction of their life in this resting state.^{2,7–9} Recent results¹⁰ suggest that the same may apply to the last generations of MgCl₂-supported "high-yield" systems currently used for the industrial production of isotactic polypropylene.¹¹

On the other hand, a number of small molecules can easily react with the dormant sites. An extreme case is that of H₂, able to induce the transfer of growing poly-

Chart 1

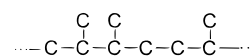


Chart 2

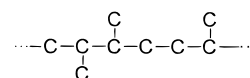
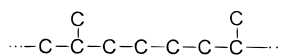
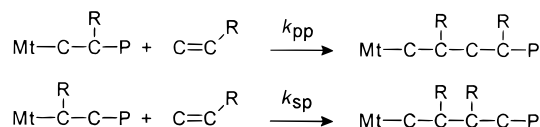


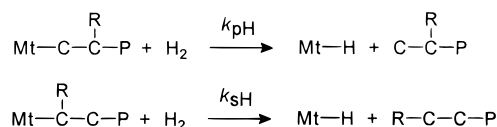
Chart 3



Scheme 1



Scheme 2



Scheme 3

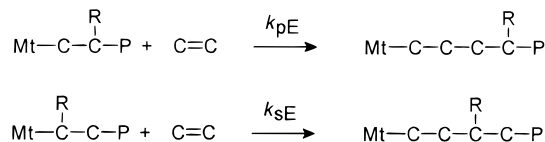
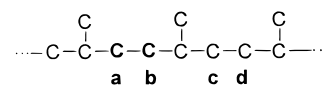


Chart 4

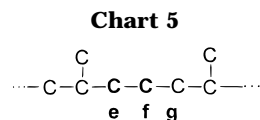


(1-alkene) chains with a 1,2 or a 2,1 last-inserted unit^{7,8} (Scheme 2) practically at the same rate; this accounts for the apparently awkward finding that a relatively large amount of the saturated polymer chains formed by H₂ transfer terminate with a 2,1 monomeric unit even when the polymerization is highly regioselective.^{7–10} It should also be noted that monomer insertion in a Mt–H bond is very fast, which can explain the observation that H₂ is often a catalyst activator.^{7–10}

Ethene shows a qualitatively similar behavior (Scheme 3); indeed, it has long been known¹² that, in ethene/1-alkene copolymerizations, this unsubstituted monomer inserts in a growing chain ending with a 2,1 1-alkene unit (much) faster than the bulkier 1-alkene comonomer.

As a matter of fact, we have verified that, in ethene/propene copolymerizations promoted by a number of Ziegler–Natta and metallocene catalysts, the ratio of specific rates k_{sE}/k_{sp} (for definition, see Schemes 1 and 3) is of the order of 10^3 . It follows that, in the copolymers, already at very low ethene incorporation, nearly all 2,1 propene units are followed by an ethene unit (see Chart 4 for isotactic propagation).

Therefore, in the ¹³C NMR spectra of such copolymers, the resonances of isolated ethene units flanked by propene units with opposite enchainments, well



assigned^{6e,12,13} and free of overlaps with other peaks, can be taken as markers of the regioirregular propene units and analyzed alternatively to those of the regioirregular units themselves. *This is the key concept of this communication; indeed, if ethene-1-¹³C is used in the place of ethene at natural ¹³C abundance, the threshold for the spectroscopic detectability of the regioerrors is lowered by a factor of 50 with respect to that for a propene homopolymer (i.e., from 0.1–0.2 mol % to 0.002–0.004 mol %).*¹⁴

Although the use of ethene-1-¹³C in mechanistic studies of 1-alkene polymerizations dates back to the 1970s and has led to a number of fundamental achievements,^{1,12} to our knowledge it has never been aimed at systematic and quantitative measurements of regioselectivity.

In the following, the potentialities of this approach are illustrated for propene polymerization promoted by two well-known *ansa*-metallocene catalysts (cocatalyst: methylaluminoxane, MAO): the isotactic-specific *rac*-Me₂Si(1-indenyl)₂ZrCl₂¹⁵ (**I**), chosen as a reference for its relatively low regioselectivity (0.4–0.7 mol % of 2,1 misinsertions, depending on the temperature^{8e}), and (Me)(Ph)C(cyclopentadienyl)(9-fluorenyl)ZrCl₂^{16a} (**II**), belonging to a class of syndiotactic-specific catalysts¹⁶ reported⁴ to be exceedingly regioselective, no regioirregular units being normally detected by ¹³C NMR in the polypropylene produced.¹⁷

Figure 1A shows the ¹³C NMR spectrum of an isotactic polypropylene sample prepared with **I**/MAO at 10 °C (a temperature low enough to prevent the isomerization of 2,1 units to 3,1 units^{8e}). The two sets of weak resonances marked with the Roman numbers I and II, evident only at high vertical expansion, arise from sequences containing a regioirregular 2,1 propene unit in the two steric environments of Charts 1 and 2, respectively.^{6b,c,e} Although the spectrum was accumulated overnight using a concentrated polymer solution, the integration of such peaks is difficult since their signal-to-noise ratio is, at most, 4–5; by averaging over the normalized integrals of all peaks in each set, one obtains a fraction of 2,1 units of 0.32 ± 0.04 mol % in the structure of Chart 1 and of 0.1 ± 0.1 in that of Chart 2.

The ¹³C NMR spectrum of a copolymer of propene containing 2.9 mol % of ethene-1-¹³C, prepared with the same catalyst and under the same experimental conditions, is shown in Figure 1B. In addition to the main resonances of the propene units in the homosequences, four strong signals arising from the ¹³C-enriched ethene units are immediately evident: a first couple, at δ = 37.7 and 24.4 ppm, is due to the S_{αγ} and S_{ββ} C's¹⁸ of isolated ethene units between two propene units inserted with the same enchainment and enantioface^{12,13} (e and f in Chart 5); a second one, at δ = 34.6 and 34.4 ppm, to the S_{γαβδ}⁺ and S_{δαβδ} C's of ethene units flanked by two propene units inserted with opposite enchainments and enantiofaces^{6e,12d,e} (a and b in Chart 4).

Note that the two peaks of each couple have an integral ratio close to 1:1, because the ¹³C-enriched methylene of an ethene-1-¹³C unit occupies randomly

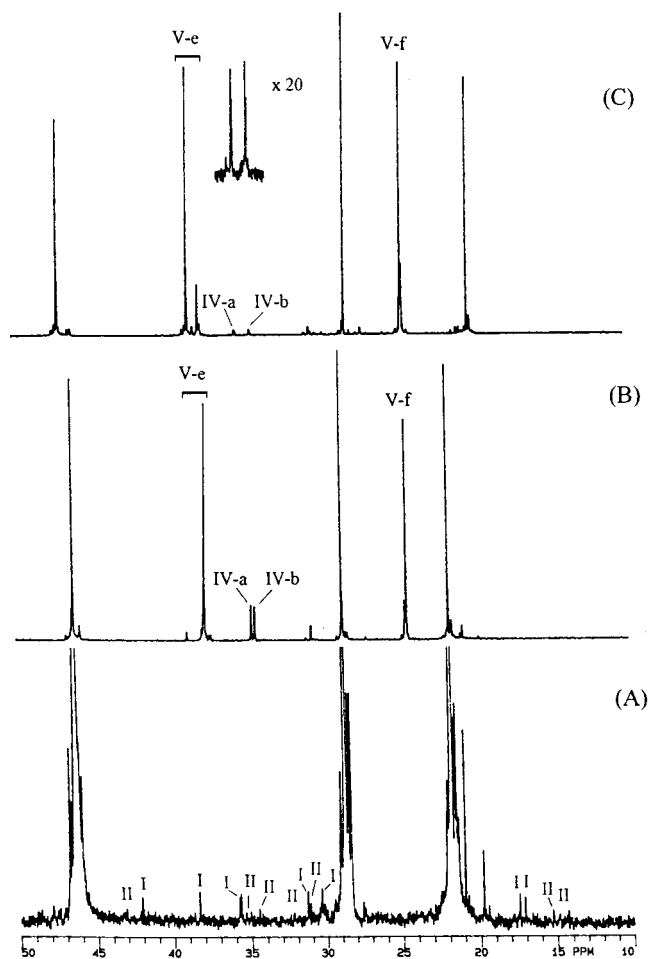


Figure 1. ¹³C NMR spectra of (A) a polypropylene sample prepared with **I**/MAO at 10 °C, (B) an ethene-1-¹³C/propene copolymer prepared with **I**/MAO (ethene content, 2.9 mol %; sample 6 of Table 1), (C) an ethene-1-¹³C/propene copolymer prepared with **II**/MAO (ethene content, 2.5 mol %; sample 12 of Table 1). The chemical shift scale is in ppm downfield of TMS. Relevant resonance attributions are explicitly indicated (see text and Charts 1, 2, 4, and 5).

the two possible locations in each structure, and the contributions of the unenriched C's c and d in Chart 4 and g in Chart 5 are negligible.

From the normalized integrals of the resonances at δ = 34.4 and 34.6 ppm, taking into account the ¹³C enrichment, it was trivial to evaluate¹³ a fraction of 2,1 regioerrors in the copolymer sample of 0.397 ± 0.005 mol %. This figure is expected to be virtually coincident with that in the propene homopolymer, and as a matter of fact, the two estimates based on the spectra of Figure 1A,B are in good agreement, although the former is affected by a much larger uncertainty.

However, a series of copolymerization experiments at variable ethene-1-¹³C/propene feeding ratios (Table 1) was carried out, to locate the value of ethene incorporation above which "all" 2,1 propene units are followed by an ethene one. From the results reported in Table 1 and diagrammed in Figure 2 (curve A), it can be immediately concluded that this occurs at around 3.0 mol % and that the plateau value of 0.40 ± 0.01 mol % does correspond to the previously reported estimate of regioerror concentration.

A similar series of ethene-1-¹³C/propene copolymerizations was then performed, at the same temperature of 10 °C, in the presence of the catalyst system **II**/

Table 1. Results of Ethene- $1^{13}C$ /Propene Copolymerizations at 10 °C in the Presence of the Catalyst Systems I/MAO and II/MAO (for Reaction Conditions, See Experimental Section)

catalyst	sample no.	[E]/[P] × 10 ³ (liquid phase) ^a	¹³ C enrichment (%) ^b	Q _E (mol %) ^c	Q _{SE} (mol %) ^d
I	1	0.17 ± 0.02	100	0.12 ± 0.01	0.044 ± 0.004
	2	0.63 ± 0.02	100	0.41 ± 0.01	0.130 ± 0.004
	3	1.33 ± 0.02	100	0.92 ± 0.01	0.226 ± 0.005
	4	1.99 ± 0.05	41	1.68 ± 0.01	0.334 ± 0.005
	5	3.23 ± 0.03	30	2.35 ± 0.01	0.384 ± 0.005
	6	4.02 ± 0.06	100	2.93 ± 0.02	0.397 ± 0.005
	7	4.52 ± 0.05	20	3.2 ± 0.1	0.40 ± 0.01
	8	8.56 ± 0.05	16	5.9 ± 0.1	0.40 ± 0.01
II	9	0.58 ± 0.05	100	0.17 ± 0.01	0.015 ± 0.005
	10	1.48 ± 0.04	100	0.42 ± 0.01	0.028 ± 0.005
	11	3.72 ± 0.04	100	1.36 ± 0.02	0.054 ± 0.005
	12	7.80 ± 0.04	100	2.46 ± 0.03	0.072 ± 0.005
	13	14.22 ± 0.03	30	4.3 ± 0.1	0.08 ± 0.01

^a E = ethene, P = propene; estimated from the composition of the gas feed according to ref 21. ^b At C-1 of ethene. 100% corresponds to ethene- $1^{13}C$ (Isotec Inc., 99+% isotopic purity) used as received; lower enrichments were achieved by dilution with ethene at natural ^{13}C abundance (see Experimental section). ^c ^{13}C NMR mole fraction of ethene units in the copolymer. ^d ^{13}C NMR mole fraction of 2,1 propene units followed by ethene units (referred to the total propene unit content).

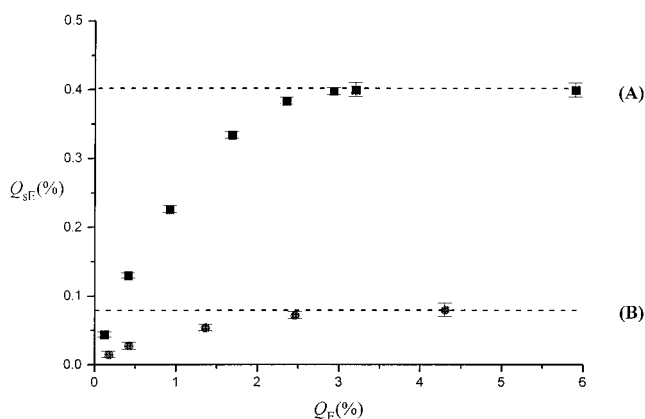


Figure 2. Mole fraction of 2,1 propene units followed by ethene units (Q_{SE}) vs ethene content (Q_E) in ethene- $1^{13}C$ /propene copolymers prepared with the catalyst systems I/MAO (curve A) and II/MAO (curve B) at 10 °C (data taken from Table 1).

MAO. The results are also given in Table 1 and Figure 2 (curve B).

Despite the higher regioselectivity, regioirregular sequences were clearly detected by ^{13}C NMR also in the copolymers prepared with this catalyst. As an example, Figure 1C shows the spectrum of a copolymer with a 2.5 mol % content of ethene- $1^{13}C$; the resonances of the ^{13}C nuclei labeled as a and b in Chart 4 and e and f in Chart 5 occur at $\delta = 35.5$ and 34.5 ppm and at $\delta = 37.8$ –38.5 and 24.5 ppm, respectively, as expected from the literature¹³ (the stereochemistry of the ethene-containing sequences is not trivial and will be commented on in a separate paper).

From Figure 2, in particular, it can be concluded, practically on inspection of curve B, that the fraction of 2,1 regioerrors in propene polymerization promoted by catalyst II in the used conditions is 0.08 ± 0.01 mol % (i.e., just below ^{13}C NMR detectability in a homopolymer and only 5 times lower than that in polypropylene prepared with catalyst I).

The above procedure for measuring catalyst regioselectivities in 1-alkene polymerization is more simple and more general than the one based on 1-alkene hydro-oligomerization experiments,⁸ introduced by our research group a few years ago. In particular, it does not require the use of H_2 at high pressure (with its practical and conceptual drawbacks) and the interpretation of the

results is immediate. Moreover, ethene- $1^{13}C$ is a commercial monomer and, at the low incorporations needed, it is inexpensive and does not alter too much the physical properties of the copolymers with respect to those of the corresponding 1-alkene homopolymers.¹⁹ The latter point is highly important when the method is applied to multisite catalysts; indeed, differently from the case of hydro-oligomers,⁸ the solvent fractionation of ethene/1-alkene copolymers at very low ethene content is controlled, at least in part, by the tacticity of the 1-alkene homosequences,²⁰ so that the results of the spectroscopic characterization of the fractions can be referred to classes of active species with different types and/or degrees of stereocontrol.

We are presently investigating a number of highly regioselective catalysts (e.g., homogeneous catalysts based on C_{2v} -symmetric metallocenes^{2,4} and heterogeneous $MgCl_2$ -supported catalysts modified with different types of internal and external donors,^{10,11} most of which are suspected of being highly dormant in propene polymerization). The results will be reported in due course.

Experimental Section. Reagents and Catalysts. *rac*-Me₂Si(1-indenyl)₂ZrCl₂ (**I**) and MAO (10 wt % solution in toluene) were provided by Witco GmbH (Bergkamen, FRG). A sample of (Me)(Ph)C(cyclopentadienyl)-(9-fluorenyl)ZrCl₂ (**II**) was obtained from Dr. C. J. Schaverien (Shell Research and Technology Centre, Amsterdam). Ethene- $1^{13}C$ (Isotec Inc., 99+% isotopic purity) and propene (Società Ossigeno Napoli, polymerization grade) were used as received.

Polymerization Procedures. All copolymerizations were run at 10 °C, in a 100 mL Pyrex reactor containing a toluene solution (20 mL) of catalyst ($[Zr] = 5 \times 10^{-5}$ M for **I**, 1×10^{-4} M for **II**) and MAO (Al/Zr mole ratio = 5×10^3 for I/MAO, 1×10^3 for II/MAO). Gas mixtures of ethene- $1^{13}C$ and propene at the appropriate composition, prepared with vacuum line techniques and analyzed by gas chromatography, were bubbled through the liquid phase at atmospheric pressure and a flow rate of 0.10 L/min. Under such conditions, total monomer conversions were lower than 5%, thus ensuring a nearly constant comonomer feeding ratio. The copolymers were coagulated with excess methanol acidified with HCl (aqueous, concentrated), filtered, washed with additional methanol, and vacuum-dried. Typical yields were 0.4–0.5 g in 30 min reaction time.

For copolymers at relatively high ethene contents (indicatively, >1 mol % for I/MAO; >3 mol % for II/MAO), it proved unnecessary to use pure ethene- I - ^{13}C in order to obtain well detectable ethene resonances in the ^{13}C NMR spectra. Therefore, for the synthesis of such copolymers, ethene- I - ^{13}C was conveniently diluted with ethene at natural ^{13}C abundance; mixtures at suitable compositions were prepared using vacuum line techniques and analyzed by ion cyclotron resonance fourier transform mass spectrometry (ICR/FT-MS).

The sample of polypropylene prepared with catalyst system I/MAO at 10 °C was obtained by feeding pure propene at atmospheric pressure under conditions otherwise identical to those of the corresponding copolymers.

^{13}C NMR Characterizations of Homo- and Copolymers. The spectra were recorded with a Varian XL-200 spectrometer operating at 50.3 MHz, on 10% w/v polymer solutions in tetrachloroethane- $1,2-d_2$ (also used as internal standard) at 125 °C. Conditions: 5 mm probe; 90° pulse; acquisition time, 1.2 s; relaxation delay, 1.3 s; 15K–30K transients. The fractional abundances of the various constitutional and configurational sequences in the samples were evaluated according to the literature.^{6,13}

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- (17) Resonances indicative of regioirregular enchainments just above detectability have been noted in the ^{13}C NMR spectrum of a syndiotactic polypropylene sample prepared with the catalyst system Me₂C(cyclopentadienyl)(9-fluorenyl)ZrCl₂/MAO at 80 °C; see ref 16c, Figure 7.
- (18) For the nomenclature of the magnetic C's, see: Carman, C. J.; Wilkes, C. E. *Rubber Chem. Technol.* **1971**, *44*, 781.
- (19) In principle, homopolymers of selectively ^{13}C -enriched 1-alkenes (e.g., propene- 3 - ^{13}C) might be prepared and characterized alternatively to ethene- I - ^{13}C /1-alkene copolymers. However, the monomers would need to be synthesized on purpose and used in much higher amounts compared to the case of ethene- I - ^{13}C . Moreover, the ^{13}C NMR characterization of the copolymers is much more informative (see, e.g. ref 12).
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