Ethylene and hydrogen effects in propylene polymerization with 2-arylindenyl zirconocenes

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Abstract

Addition of small amounts of ethylene or hydrogen leads to significant productivity increase in propylene polymerization catalyzed by fluxional bis(2-arylindenyl)zirconocenes. To test if this phenomenon is related to the reactivation of dormant species formed as a result of regioirregular propylene insertions, we have reinvestigated the regioregularity of these catalysts. Approximately 0.1–0.3 mol% of 2,1-misinsertions were found in polymers synthesized by these catalysts. The presence of these regioirregular insertions could account for the ethylene and hydrogen effects observed but does not rule out formation of other catalyst dormant sites. © 2000 Elsevier Science B.V. All rights reserved.

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Unbridged 2-arylindenyl metallocenes generate elastomeric polypropylene when activated by MAO [1,2]. The proposed mechanism involves catalyst isomerization between a chiral *rac*-like and an achiral *meso*-like conformations during the growth of a single polymer chain resulting into formation of isotactic and atactic sequences, respectively (Fig. 1).

In the course of our studies of ethylene–propylene copolymerization with bis-(2-arylindenyl)zirconocenes, we discovered that the addition of small amounts of ethylene to the polymerization systems resulted in a significant increase in productivity [3]. Table 1 summarizes the results of these experiments. The poly-merization behavior of two unbridged 2-arylindenyl catalysts, $(2PhInd)_2ZrCl_2$ (**1**), and $(2-(3',5'-(CF_3)_2C_6H_3)Ind)_2ZrCl_2$ (**2**) as well as of the ethylene bridged bis-indenyl zirconocene, $EBIZrCl_2$ (**3**) was investigated. As shown in Table 1, all catalysts have higher productivities in E/P copolymerizations than in propylene homopolymerizations. For catalyst **2**, this effect is particularly striking: incorporation of 14 mol% ethylene results in a 7-fold increase in productivity.

The analysis of the productivity data is complicated by the fact that most metallocene catalysts insert ethylene faster than propylene. However, it is possible to account for the expected productivity increases for copolymerizations from first-order Markov copolymerization equations and ethylene and propylene reactivity ratios. This method of analysis led us to the definition of rate enhancement factors REF =

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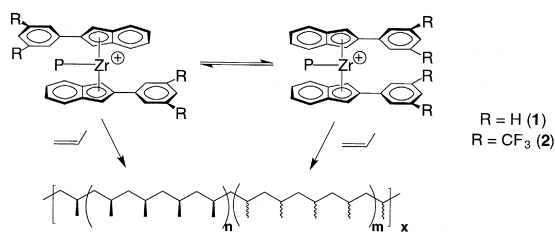
Fig. 1. Mechanism of stereoblock formation with bis-(2-arylindenyl)metallocenes.

$k_{pp}[M_p]/k_{pp}^h[M_p^h]$, the ratios of the rates of two consecutive propylene insertion in the presence and in the absence of ethylene[2], which allows for the comparison of the productivity data for different catalysts obtained under different conditions [3]. The REF values for the two unbridged catalysts **1** and **2** ranged between 1 and 8 while for the bridged metallocene **3** they did not exceed 2. These values indicate that for the 2-arylindenyl catalysts, the copolymerization productivity is up to a factor of 8 higher than would be expected from the propylene polymerization productivity and the E/P copolymerization parameters.

Studies of propylene polymerization in the presence of hydrogen reveal a measurable increase in productivity upon the addition of small amounts of hydrogen to propylene polymerizations catalyzed by unbridged **1**/MAO and **2**/MAO. In contrast, the productivity of **3**/MAO was not significantly influenced by added hydrogen (Fig. 2).

Examples of activation of propylene polymerization systems by ethylene and hydrogen were previously reported for other catalysts [4–6]. One of the possible explanations for this

phenomenon is the reactivation of the dormant sites formed as a result of 2,1-propylene misinsertions [7–9]. The ethylene and hydrogen effects described prompted us to reinvestigate the regioregularity of bis(2-arylindenyl) catalysts since we had previously reported that catalyst **1** was highly regioregular [1].

Acquisition of at least 4000 transients on concentrated samples allowed us to observe and quantify propylene misinsertions in ^{13}C NMR spectra of polypropylenes generated with catalysts **1**–**3**/MAO. The bridged catalyst **3**/MAO generated 0.4–0.6 mol% misinsertions of both 2,1-*erythro* and 2,1-*threo* types whereas unbridged catalysts **1**/MAO and **2**/MAO showed only 2,1-*erythro* misinsertions (0.1–0.2 mol%). In addition, catalyst **2**/MAO generated some 3,1-misinsertions at room temperature [10–12].[3] The absence of 2,1-*threo* regioerrors in polypropylenes produced with the unbridged catalysts suggested that regioerrors occur only in the isotactic sequences and are produced by isospecific sites.

Addition of hydrogen to propylene polymerization catalyzed by **1**/MAO and **2**/MAO rapidly converted the internal regioerrors into *n*-butyl chain-ends. For **3**/MAO, some internal regioerrors were still observed even at the highest concentrations of hydrogen employed. These results suggest that for **3**/MAO, propylene insertion into a metal–polymer bond containing a regioerror is competitive with chain transfer to hydrogen. In contrast, for **2**/MAO hydrogen transfer is much faster than propylene insertion into a regioerror.

We also detected ethylene insertions after 2,1-propylene misinsertions in the ^{13}C NMR spectra of ethylene–propylene copolymers gen-

Table 1
Productivity enhancement in ethylene–propylene copolymerizations

Catalyst[a]	T (°C)	[E]/[P] in feed[b]	%E in polymer[c]	Productivity[d]	REF[e]	$M_w \cdot 10^{-3f}$
(2PhInd)$_2$ZrCl$_2$	0	0	0	11,920	n/a	838
1	0	0.11	30	25,560	1.0	2230
	19	0	0	13,200	n/a	549
	19	0.065	25	69,280	3.2	1789
(2-(3′,5′-(CF$_3$)$_2$C$_6$H$_3$)Ind)$_2$-ZrCl$_2$	0	0	0	6000	n/a	756
2	1	0.082	18	64,540	7.8	2386
	19	0	0	8300	n/a	621
	19	0.048	14	58,260	5.3	1776
EBIZrCl$_2$	0	0	0	19,100	n/a	98.8
3	1	0.082	40	106,230	1.7	75.5
	20	0	0	86,400	n/a	70.6
	20	0.048	39	243,240	1	67.2

[a]MAO used as co-catalyst.
[b]See Ref. [3] for the method of determination of the monomer ratio [E]/[P] in the feed.
[c]Determined by quantitative ^{13}C NMR.
[d](kg PP)/mol Zr h.
[e]Rate enhancement factor, for definition see footnote 2.
[f]Determined by high temperature GPC vs. polypropylene calibration standards.

erated with **2**/MAO (structure B, carbons 3, 4, 6, 7, Fig. 3a). To better observe this type of insertions, we prepared a propylene copolymer with a small amount of ^{13}C$_2$H$_4$. Fig. 3b shows a quantitative ^{13}C NMR spectrum of this sample. The polymer contained 2.4 mol% ethylene, 0.2 mol% of which followed 2,1-propylene regioerrors (signals B3, 4, Fig. 3b). The latter number is in a good agreement with the regioerror content measured for polypropylenes generated with **2**/MAO.
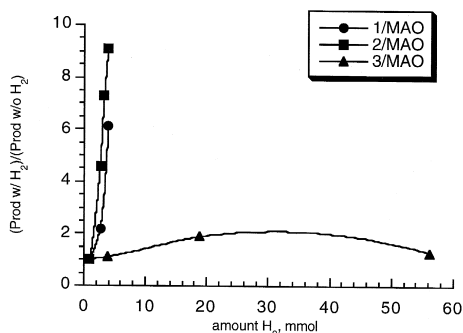
In summary, polypropylenes generated with the unbridged bis(2-arylindenyl) catalysts contain small amounts of 2,1-propylene misinsertions (0.1–0.3 mol%). Our NMR experiments suggest that these regioerrors occur only in the isotactic sequences. Copolymerization of ^{13}C$_2$H$_4$ with propylene provided evidence for ethylene insertions after 2,1-regioerrors. Addition of hydrogen to propylene polymerization catalyzed by bis(2-arylindenyl)zirconocenes eliminates 2,1-sites by chain transfer to hydrogen. These results provide strong evidence that regiochemical misinsertions produce dormant sites, which can be reactivated in the presence of small amounts of hydrogen or ethylene [13–15].[4]

Fig. 2. Effect of hydrogen on propylene polymerization productivity.

[4] Some reports have suggested that other species, such as allyl groups or unsaturated chain branches, may also lead to dormant sites in propylene polymerization.

1. Experimental

Unbridged catalysts (2-PhInd)$_2$ZrCl$_2$ (**1**) and (2-(3′,5′-(CF$_3$)$_2$PhInd)$_2$ZrCl$_2$ (**2**) were prepared as previously described [1,2]. *rac*(Ethylen-ebisindenyl)zirconium dichloride (**3**) was purchased from Witco and used without further purification. Type IV methylalumoxane (MAO) was purchased from Akzo in a toluene solution and dried in vacuo to yield a solid before use. ^{13}C$_2$H$_4$ was purchased from Cambridge Isotope Laboratories and used as received.

Propylene homo- and copolymerizations with ethylene were conducted as previously described [3]. Hydrogen was dosed into the reactor by pressurizing an injection tube with gas and flushing liquid propylene through the tube into the reactor. For polymerization with ^{13}C$_2$H$_4$, the reactor was directly pressurized with ethylene before filling with liquid propylene.

Polymers were precipitated in methanol/HCl and dried in vacuo at 40°C. High temperature GPC measurements of polymers were performed at Amoco Chemical using a Watts 150C
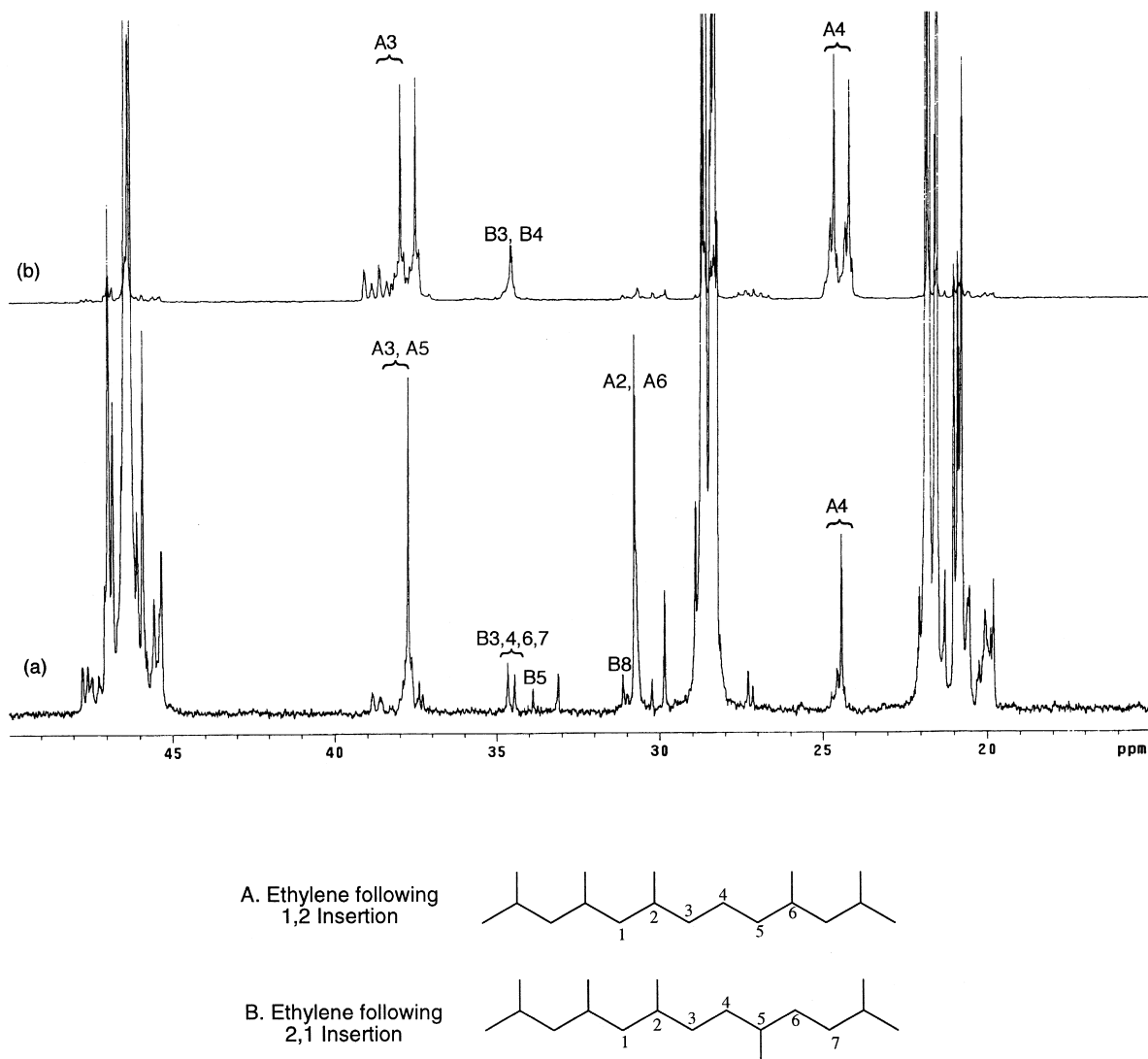

Fig. 3. ^{13}C NMR spectra of ethylene–propylene copolymers generated with **2**/MAO: (a) 5 mol% C$_2$H$_4$; (b) 2.4 mol% ^{13}C$_2$H$_4$.

GPC at 100°C in dichlorobenzene and referenced to polypropylene standards. Solution ^{13}C NMR spectra were run at 75 MHz on a Varian Inova-300 NMR spectrometer equipped with a 10-mm broad-band probe. Samples were run as solutions in $C_2D_2Cl_4$ at 100°C. Quantitative spectra were acquired with 3500–7000 transients, a 90° pulse width and a 20-s delay between pulses. Decoupling was always on during acquisition so that NOE was present except for $^{13}C_2H_4$/propylene copolymer, which was run with gated decoupling. Regioerrors were identified according to chemical shifts reported in Refs. [16–18]. The percentage of regioerrors was calculated as described by Resconi et al. [12] or, in the case of *n*-butyl end groups, by integration of methyl resonances.

Percentage ^{13}C-1,2-ethylene incorporation was determined by the following procedure which accounts for the natural abundance of ^{13}C in the $S_{\alpha\alpha}$ carbons (see Fig. 3 for identification of carbons numbers A and B):

$$\text{Total CH}_2 \text{ units} = (S_{\alpha\alpha}/0.011) + A3 + A4$$
$$+ B3 + B4$$

$$\% \; ^{13}C - 1,2 - \text{ethylene incorporation}$$
$$= [(A3 + A4 + B3 + B4)/2]$$
$$/[\text{Total CH}_2 \text{ units}]^* 100$$

Acknowledgements

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