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Regioirregular Propene Insertion in Polypropenes Synthesized with Unbridged Bis(2-aryl)indenyl Zirconium Dichloride Catalysts: Implications on Activity

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ABSTRACT: Catalysts of the type bis(2-(3,5-$R_2C_6H_3$)indenyl)zirconium dichloride/MAO (**2**, R = H; **3**, R = CF_3) were investigated for regioregularity of monomer insertion in bulk propene polymerization and compared to the isospecific catalyst *rac*-(ethene)bis(indenyl)zirconium dichloride/MAO (**1**). The amount of regioirregular propene insertions were in the range of 0.1−0.5 mol % and followed the trend **2** < **3** < **1**. Comparison of polymerizations in the presence and absence of hydrogen revealed a 4−10-fold increase in productivity for catalysts **2** and **3** in the presence of hydrogen but only a slight increase in productivity with **1**. For catalysts **2** and **3**, only 2,1-*erythro* internal regioerrors were observed, whereas **1** produced both 2,1-*erythro* and 2,1-*threo* misinsertions. Evidence for ethene insertion following a 2,1-regioerror was obtained by copolymerization of $^{13}C_2H_4$ with propene using catalyst **3**. The correlation between number of 2,1-misinsertions and catalyst activity is discussed.

Introduction

Metallocene catalysts polymerize α-olefins with high productivities and stereo- and regioselectivity for monomer insertion.[1] For propene, it is known that zirconium catalysts propagate the polymer chain with a 1,2-insertion mechanism through a primary metal−carbon bond (C_{12} of Scheme 1). However, regioirregular propene insertion does occur in some cases and has been implicated as a cause of deactivation of metallocene polymerization catalysts.[1−5] The sterically crowded secondary center that is formed by 2,1-insertion (C_{21} of Scheme 1) is thought to hinder subsequent monomer insertion. Calculations from hydrooligomerization experiments using *rac*-ethenebis(indenyl)zirconium dichloride (**1**) suggest that 90% of catalyst sites can be dormant due to regioerrors.[4] The experimentally observed increases in productivity of propene polymerizations with addition of small amounts of hydrogen can be attributed to these regioirregular insertions; reactivation of this dormant site can occur by chain transfer to hydrogen.[2−6]

The catalyst bis(2-phenylindenyl)zirconium dichloride (**2**) produces elastomeric polypropene. The proposed mechanism involves interconversion between aspecific and isospecific conformations of the catalyst through ligand rotation (Figure 1). For this catalyst, it was initially reported that propene insertion was highly regioregular.[7] However, results from copolymerizations of ethene and propene using catalyst **2** and its derivative, bis(2-(3,5-$(CF_3)_2C_6H_3$)zirconium dichloride (**3**), showed an increase in productivities over propene homopolymerizations on the order of 6−7-fold.[8] These results prompted a reexamination of the regioregularity of these unbridged catalysts to ascertain the origin of the ethene effect on productivity. As described below, these investigations provide evidence for regioerrors in polypropenes synthesized with 2-arylindenyl catalysts.

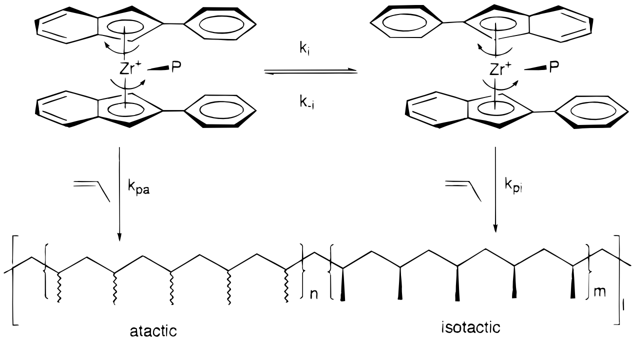

Figure 1. Proposed mechanism for the formation of elastomeric propene by catalysts **2**.

Results

Identification of Regioerrors. Regioerrors occurring both in internal propene sequences and at chain ends are identifiable and quantifiable by ^{13}C NMR.[9−11] Due to the low concentration of regioerrors found in polypropenes synthesized by unbridged catalysts **2** and **3**, detection of misinserted monomer units was enabled only by acquistion of 4000−8000 transients with 20-s delay between pulses on a large polymer sample (200−300 mg). Assignment of regioirregular structures were made according to literature values.[9−11] The possible regioerror and chain-end structures are shown in Figure 2. Structures A−C are internal regioerrors observed in polymers made by isospecific metallocenes.[12−14] Both structures A and B arise from 1,2-insertion of propene after a 2,1-insertion but in A the monomer insertion following a misinsertion occurs on the same enantioface as the previous 1,2-insertion; in B, the monomer is inserted with the opposite enantioface. Internal regioerror C results from rearrangement of A or B through β-hydride elimination followed by reinsertion. Structures D−F are end groups seen after regioregular propene insertion.[4,6,11,15] D is the chain end following chain transfer to monomer or β-hydride elimination, and E is the chain start from chains initiated after both chain-transfer events as well as chain transfer to hydrogen. Isobutyl group F is the product of chain transfer to hydrogen following a 1,2-insertion. Chain-transfer events after a regioirregular insertion result in structures G and H.[4,6,15] G is chain transfer to hydrogen, and H is chain transfer to monomer or β-H

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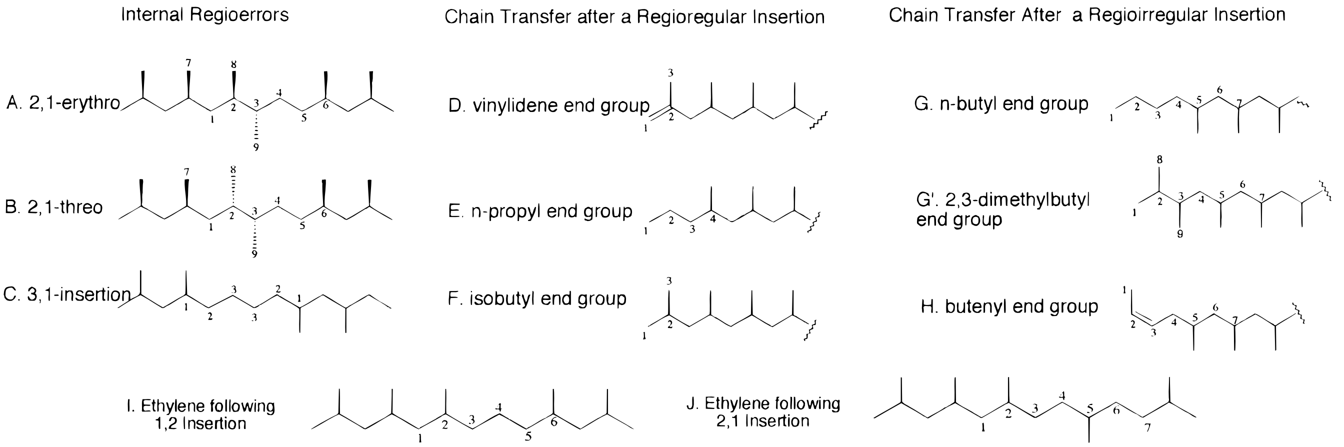
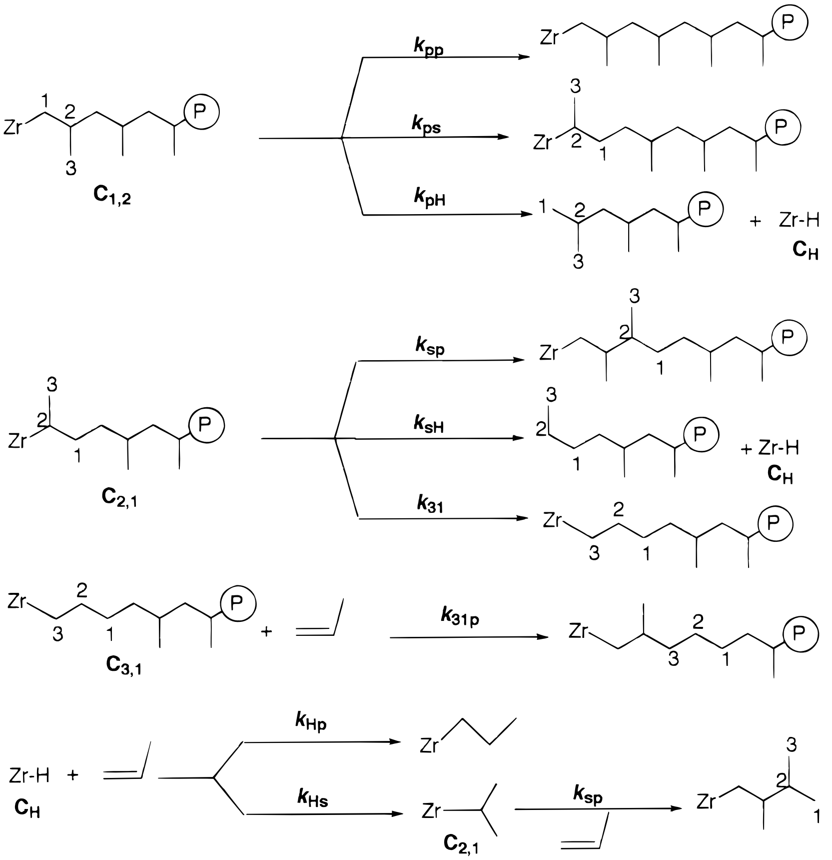


Figure 2. Internal regioirregular insertions and chain ends resulting from regioregular and regioirregular insertions.

Scheme 1. Possible Insertion, Isomerization, and Chain-Transfer Reactions Following a Regioregular or Regioirregular Propene Insertion in the Presence of Hydrogen



elimination. Structure G′ is a consequence of initial 2,1-misinsertion into a metal hydride followed by chain propagation via normal 1,2-insertion.[16] Figure 2 also shows the structures possible when ethene is incorporated into the polymers. Ethene insertion can occur following a normal 1,2-insertion (structure I) or after a 2,1-insertion (structure J).

Propene polymerizations were carried out at 20 °C in liquid propene using three different catalysts: *rac*-ethenebis(indenyl)$ZrCl_2$ (**1**), (2-phenylindenyl)$_2ZrCl_2$/MAO (**2**), and (2-(3,5-$(CF_3)_2C_6H_3$)Ind)$_2ZrCl_2$/MAO (**3**). Polymerizations with catalyst **3** were run at 0 and 20 °C to compare regioerror contents at the two temperatures. The productivity and molecular weights for polymers synthesized with catalysts **1**−**3** are listed in Table 1. Table 2 lists the regioerror contents of the polymers synthesized.[17] For bridged catalyst **1**, a total regioerror content of 0.4 mol % is observed. No 3,1-insertion is present at 20 °C although both 2,1-*erythro* (structure A) and 2,1-*threo* (structure B) misinsertions are evident. The two unbridged catalysts are more regioregular than **1**. For catalyst **2**, only trace amounts of 2,1-*erythro* insertion are observed, which accounts for the previous report that polypropene synthesized by this catalyst did not contain regioerrors.[7] For catalyst **3**, a temperature dependence on the amount of internal regioerrors is observed. At 0 °C only 0.1 mol % of 2,1-misinsertions is detected relative to the 0.2 mol % in polymers made at 20 °C. Analyzing the chemical shifts of these signals reveals that only 2,1-*erythro* insertions are present (Figure 2A). Some 3,1-insertions (0.1 mol %) are observed at 20 °C for polymerizations using **3**.

Table 1. Results of Polymerizations with Catalysts 1−3

entry	catalyst	T_p (°C)	H_2 (mmol)	productivity[a]	prod with H_2/ prod w/o H_2	M_n[b]	M_w[b]	M_w/M_n
1	1	20	0	40 600[c]		35 000[c]	69 000[c]	2.0[c]
2	1	20	3.9	38 000	0.94	18 000	37 000	2.2
3	1	20	19	38 000	0.94	17 000	75 000	4.4
4	1	20	56	61 000	1.5	10 000	22 000	2.2
5	2	20	0	18 000		130 000	430 000	3.3
6	2	20	2.6	39 000	2.2	12 000	28 000	2.3
7	2	20	3.9	11 1000	6.1	12 000	34 000	2.8
8	3	0	0	1 400		42 000	320 000	7.6
9	3	0	2.6	5 600	4.1	5 000	28 000	5.6
10	3	20	0	3 700[c]		68 000[c]	320 000[c]	4.7[c]
11	3	20	2.6	13 000	3.5	8 000	37 000	4.6
12	3	20	3.3	34 000	9.2	9 000	52 000	5.7
13	3	20	3.9	42 000	11	6 000	28 000	4.6
14	3	20	0	5 200		48 000	250 000	5.2
15	3	20	d	8 700	1.7	440 000	1 030 000	2.3

[a] kgPP/mol Zr/h. [b] Determined by high-temperature GPC versus polypropene standards. [c] Average values obtained from multiple polymerizations. [d] $^{13}C_2H_4$ dosed into reactor (ethene pressure 22 psig).

Table 2. Regioerror Content of Polymers Synthesized with Catalysts 1−3

entry	catalyst	T_p (°C)	H_2 (mmol)	[m]	[mmmm]	% 2.1 E[a] (mol %)	% 2.1 T[a] (mol %)	% 3.1[a] (mol %)	% ^{n}Bu[b] (mol %)	2,3-dimethyl (mol %)	total regioerror (mol %)
1	1	20	0	97	90	0.3	0.1	nd[c]	nd	nd	0.4
2	1	20	3.9	97	90	0.2	0.1	nd	0.1	trace	0.4
3	1	20	19	97	90	0.1	0.1	nd	0.2	trace	0.4
4	1	20	56	96	88	0.1	0.1	nd	0.3	0.1	0.6
5	2	20	0	80	51	trace	nd	nd	nd	nd	trace
6	2	20	3	67	28	0.10	nd	nd	nd	nd	0.1
7	2	20	4	65	25	nd	nd	nd	0.06	nd	0.1
8	3	0	0	87	68	0.1	nd	nd	nd	nd	0.1
9	3	0	2.6	88	71	nd	nd	nd	0.3	nd	0.3
10	3	20	0	88	70	0.1	nd	0.1	nd	nd	0.2
11	3	20	2.6	82	64	nd	nd	nd	0.2	nd	0.2
12	3	20	3.3	79	51	nd	nd	nd	0.2	nd	0.2
13	3	20	4.0	82	56	nd	nd	nd	0.3	nd	0.3

[a] Calculated according to ref 14. [b] Determined by intensity of ^{n}Bu methyl resonances versus total methyl resonances. [c] nd = not detected.

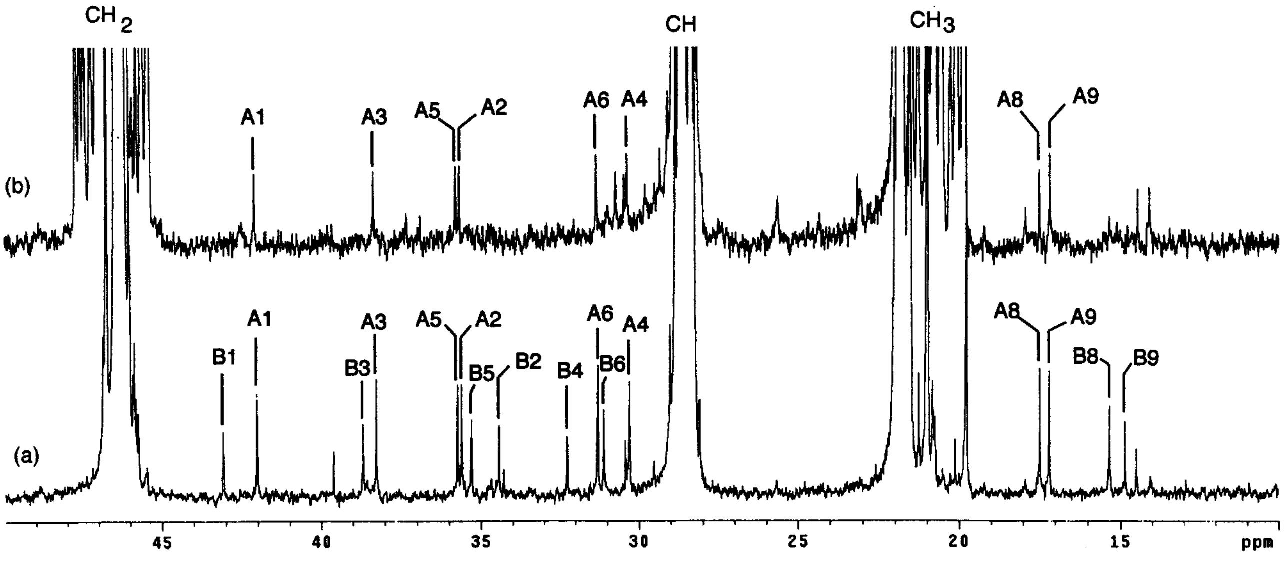


Figure 3. (a) ^{13}C NMR of polymer made by *rac*-(EBI)ZrCl$_2$/MAO (**1**). (b) ^{13}C NMR of polymer made by (2-(3,5-(CF$_3$)$_2$C$_6$H$_3$)Ind)$_2$-ZrCl$_2$/MAO (**3**).

There was no evidence for chain transfer following a 2,1-misinsertion (structure H) in any of the polymers studied.

Figure 3 compares the regioerror content of polymers made by **1** (Figure 3a) and **3** (Figure 3b). The absence of 2,1-*threo* misinsertions in polymers derived from catalyst **3** is evident in the lack of resonances for structure B.[18] The presence of only structure A in the polymer made by unbridged catalyst **3** is unexpected as this catalyst is less isospecific than *rac*-ethenebis(indenyl)zirconium dichloride ([mmmm] = 70% for **3** versus [mmmm] = 90% for **1**).

Propene Polymerizations with Hydrogen. Hydrogen was introduced into liquid propene polymerizations batchwise by pressurizing an injection tube with H_2 and then flushing the gas into the reactor with the

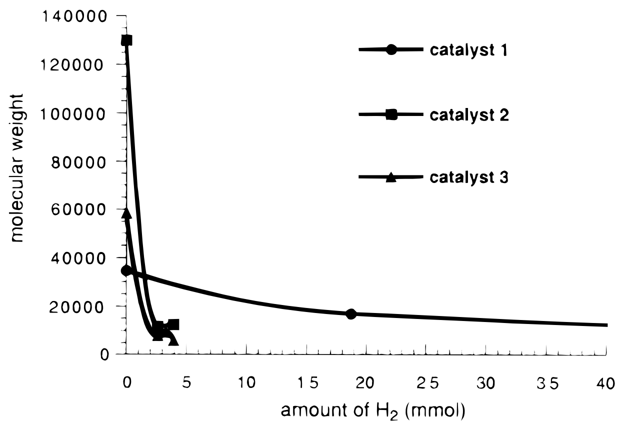


Figure 4. Effect of amount of hydrogen in polymerization on M_n for catalysts **1**−**3**.

liquid monomer. The productivity and molecular weights for polymers synthesized with catalysts **1**−**3** in the presence of hydrogen are listed in Table 1. Table 2 lists the regioerror contents of the corresponding polymers. Hydrogen acts as a chain-transfer agent in all polymerizations.[19] The reactivity of each catalyst to hydrogen as a chain-transfer agent was determined by plotting M_n versus the total amount of hydrogen (Figure 4). The extreme sensitivity of the unbridged catalysts to hydrogen can be seen in the 10-fold drop in M_n even when very small amounts of H_2 (4 mmol) are present. The molecular weights of polymers made by catalyst **1** even with large doses of H_2 (56 mmol) were reduced only by a factor of 3 in comparison.

The conversion of internal regioerrors to *n*-butyl chain ends with addition of hydrogen can be seen in the ^{13}C NMR spectra shown in Figure 5; the amounts of each type of misinsertion observed for catalysts **1**− **3** under varying hydrogen pressures is listed in Table 2. At the highest concentration of hydrogen employed, 1,2-propene insertion following a 2,1-misinsertion was still competitive with chain transfer to hydrogen in polymers made with catalyst **1**. For the unbridged catalysts **2** and **3**, all internal regioerrors were hydrogenated to yield *n*-butyl end groups even at the lowest amounts of hydrogen used.

In addition to the internal regioerrors observed at high hydrogen concentration with rac(EBI)$ZrCl_2$ (**1**), the presence of another type of misinsertion becomes evident in the ^{13}C NMR. Chain-end structure G′,[16,20] a 2,3-dimethylbutyl end group, arises from initial 2,1-insertion into a metal hydride followed by normal 1,2-insertion. The characteristic chemical shifts for G′ can be seen in the methyl region at δ 17.73 (G′8) and δ 16.27(G′9), the methine region at δ 36.41(G′3) and δ 31.86 (G′2), and the methylene region at δ 43.00 (G′4) near to the resonance from the B1 carbon of the 2,1-*threo* regioerror. Structure G′ is not observed in any of the polymers synthesized by unbridged catalysts **2** and **3**.

Increases in productivity for polymerizations with hydrogen versus polymerizations without hydrogen were on the order of 4−10-fold for the unbridged catalysts and less than 2-fold for the bridged catalyst. Furthermore, catalyst **1** showed little increase in productivity with addition of increasing amounts of hydrogen; both **2** and **3** produced increased amounts of polymer with increasing hydrogen concentration. This increase persisted even after all the regioerrors made by **2** and **3** were completely hydrogenated at the lowest hydrogen concentrations.

Propene Polymerization with C_2H_4. Figure 6a shows the ^{13}C NMR spectrum of a copolymer of propene with a small amount of ethene made with catalyst **3**.[21] This polymer contains ethene inserted after a normal 1,2-insertion (structure I) as can be seen from the prominent $S_{\alpha\gamma}$ and $S_{\beta\beta}$ peaks at 37.7 ppm (I3 and I5) and 24.4 ppm (I4), respectively. The weaker signals at 34.4 and 34.6 ppm are due to $S_{\alpha\beta}$ resonances arising from ethene insertion following a 2,1-misinsertion (structure J, carbons 3, 4, 6, and 7) which are very sharp in comparison to the $S_{\alpha\gamma}$ and $S_{\beta\beta}$ peaks. The chemical shifts of the $S_{\alpha\beta}$ carbons are identical to those of $S_{\alpha\beta}$ carbons in polypropenes synthesized with rac(EBI)$_2ZrCl_2$ (**1**), providing further evidence that regioerrors are formed preferentially at isospecific sites.

To better observe ethene insertion following a 2,1-misinsertion for an unbridged catalyst, $^{13}C_2H_4$ was mixed with liquid propene at 20 °C and polymerized with catalyst **3**. The quantitative[22] ^{13}C NMR spectrum of the polymer obtained is shown in Figure 6b. The polymer contained 2.40 mol % ethene, 92% of which was inserted following a normal 1,2-insertion (structure I). The prominent $S_{\alpha\gamma}$ and $S_{\beta\beta}$ peaks now exhibit a $^{13}C-^{13}C$ coupling of 34.5 Hz; the accompanying smaller peaks are due to different stereochemical configurations around the ethene unit. The remainder of the labeled ethene (8%) is incorporated adjacent to 2,1-misinsertions (the

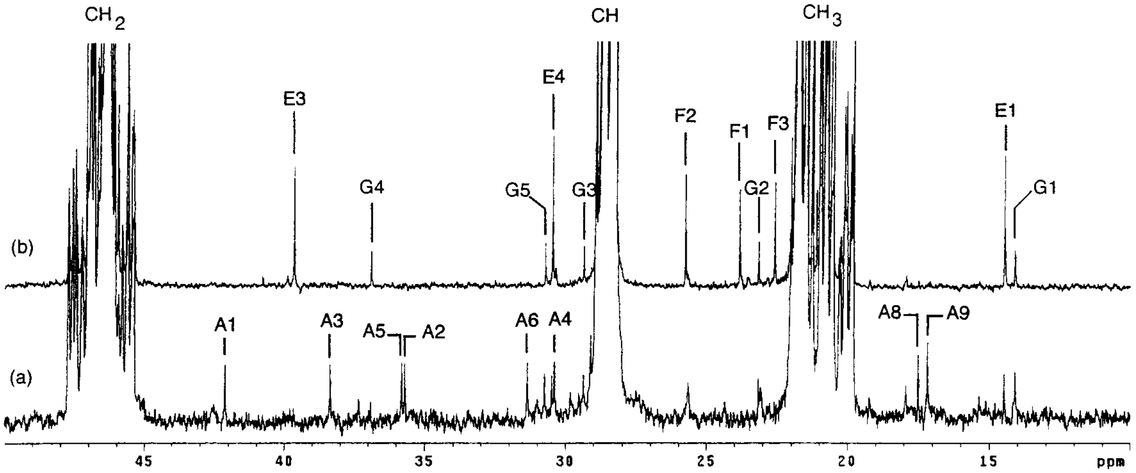


Figure 5. ^{13}C NMR of polymer made by (2-(3,5-$(CF_3)_2C_6H_3$)Ind)$_2ZrCl_2$/MAO (**3**): (a) without H_2 and (b) with H_2.

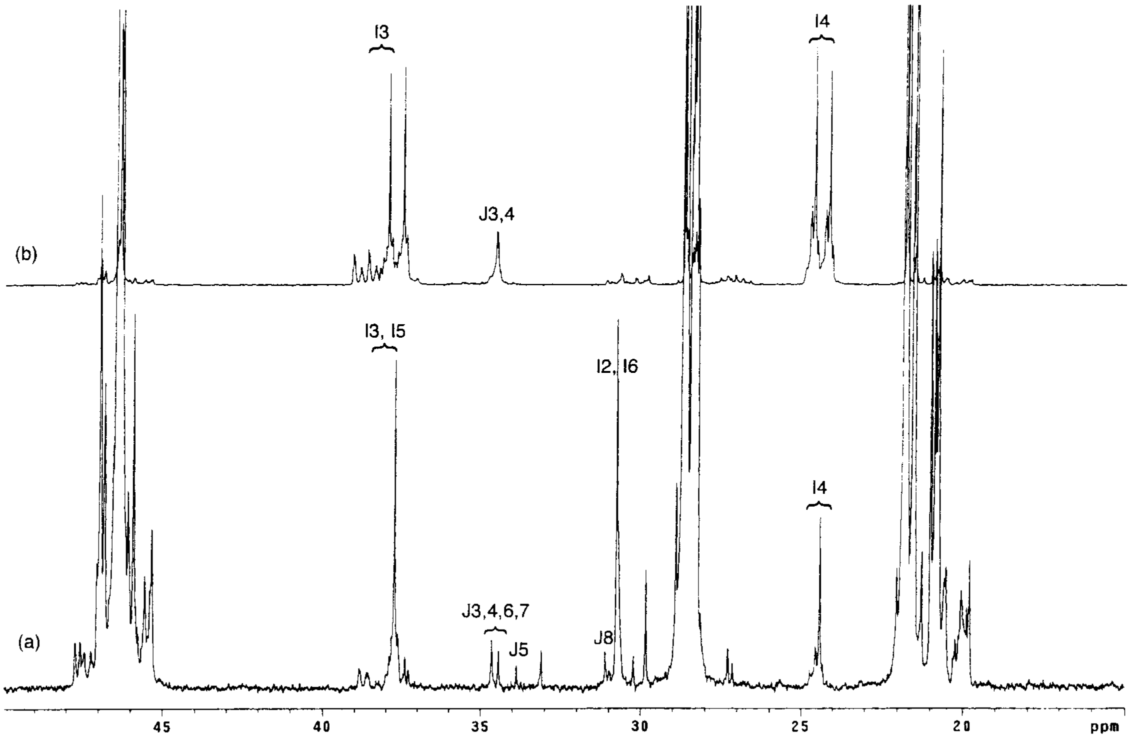


Figure 6. ^{13}C NMR of copolymer of propene and (a) $^{12}C_2H_4$ or (b) $^{13}C_2H_4$ using catalyst **3**.

Table 3. Polymer Characterization of PP1 and Solvent Fractions

entry	solvent fraction	wt %	T_p (°C)	[mmmm]	% 2.1 E^a (mol %)	% 2.1 T^a (mol %)	% 3.1^a (mol %)	M_n (10^3 g/mol)	M_w (10^3 g/mol)	M_w/M_n
1	whole		20		trace	nd	nd^b	166	476	2.9
2	ether soluble	48	20	19	nd	nd	nd	141	333	2.4
3	heptane soluble	32	20	40	nd	nd	nd	167	432	2.6
4	heptane insoluble	20	20	59	0.30	nd	0.07	244	678	3.0

^{a} Calculated according to ref 14. ^{b} nd = not detected.

$S_{\alpha\beta}$ resonances at 34.5 ppm). The small difference in chemical shifts between J3 and J4 and the large ^{13}C-^{13}C coupling constant result in an AB splitting pattern. From the integration, the amount of 2,1-misinserted units is ~0.2 mol % which is in agreement with the regioerror contents measured using hydrogen for catalyst **3**.

Discussion

Investigation of unbridged catalysts **2** and **3** show that while both catalysts are more regioregular than *rac*-ethenebis(indenyl)zirconium dichloride (**1**), they are not completely regioselective for propene polymerization. Small amounts of misinserted units are observed within the polymer chains (0.1−0.2 mol %) while some fraction of hydrogenated chain ends arise from chain transfer after a regioerror (up to 0.3 mol %). The trend in the number of regioerrors made (**2** < **3** < **1**) is identical to the observed trend in isospecificities for these three catalysts and agrees with the correlation between catalyst isospecificity and occurrence of regioerrors recently proposed.[23]

Stereocontrol of 1,2-insertion of propene following a 2,1-misinsertion has been reported in the literature for a variety of bridged catalysts.[5,24,25] The high stereoselectivity of 2,1-misinsertions found in polypropene synthesized by **2** and **3** relative to **1** is surprising given that the unbridged catalysts produce polymers of lower isotacticity. The appearance of only 2,1-*erythro* insertions suggest that the regioerrors are being made only in the isotactic sequences of polymer. This in turn implies that only isotactic sites are responsible for misinsertions.[26] The absence of other stereochemical configurations about the 2,1-misinsertions and 3,1-misinsertions as calculated and observed by Cheng[11] is in agreement with the observed *meso* relationship of the two methyl groups before an *n*-butyl end group (structure G, carbon 4) in polymers made by **3** in the presence of hydrogen.

To show that regioirregular propene insertion is occurring in the isotactic blocks of polymer, ^{13}C NMR spectra were recorded of three solvent fractions of polymer PP1 which was synthesized by catalyst **2**. This polymer has been previously studied extensively.[27] The characterization of the whole sample and each of the fractions are shown in Table 3. The most isotactic fraction, the heptane insoluble fraction, contains 2,1-*erythro* insertions (0.3 mol %) and 3,1-misinsertions (0.07 mol %), whereas the least isotactic fraction (ether-soluble) contains no regioirregular insertions. Further evidence for regioerrors arising from isospecific catalyst sites was found in examining polypropenes synthesized by the *rac* and *meso* dimethylsilyl-bridged analogues of (2-phenylindenyl)$_2$ZrCl$_2$ (**2**).[28] The *meso* catalyst made no misinsertions, whereas the *rac* catalyst contained trace quantities of 3,1-insertions.

The effect of hydrogen on the molecular weights of the polymers synthesized by the bridged catalyst **1** and the unbridged catalysts **2** and **3** differed in that catalyst **1** was relatively insensitive to hydrogen. These differences can be attributed to the larger rate of monomer insertion (Scheme 1, k_{pp}) versus chain transfer (k_{pH}) for the bridged catalyst. There appeared to be no trend in polydispersity versus hydrogen concentration for any of the catalysts. However, a careful study of the effect of hydrogen on molecular weight distributions would require a more precise and reproducible method of introducing hydrogen into the polymerization rather than batchwise.[29]

Insertion of ethene after a 2,1-misinsertion has been previously observed in polypropenes synthesized by metallocenes.[6,30−32] Recently, ^{13}C-1-ethene was used in propene polymerizations as a means of more precisely quantifying regioerrors.[33] The $S_{\alpha\beta}$ peaks for ethene inserted in polypropenes prepared from catalyst **3** are identical with those seen in isotactic polymers made with **1**, providing further evidence for stereospecific placement of regioerrors.

Increases in productivity for polymerizations with hydrogen versus polymerizations without hydrogen were on the order of 4−10-fold for the unbridged catalysts and 2-fold for the bridged catalyst. One possible origin of this increase is the reactivation of sites derived from regioerrors which are slow to insert propene. If we assume that the total number of metal sites available is constant, eq 1 expresses catalyst productivity, R_p, in terms of all the propagating species in solution. From the number of regioerrors made by catalysts **1**−**3**, we know k_{pp}/k_{ps} can be estimated to be on the order of 10^2 so we can neglect the contribution of k_{ps} to the first term of eq 1 (where rate constants are as defined in Scheme 1). If we make two simplifying assumptions: (1) that $[C_H]$ is small due to k_{Hp} being large (monomer insertion into a metal hydride is expected to be facile in liquid monomer); (2) the concentration of C_{31} can be assumed to be ~0 since k_{31} is on the same order of magnitude as $k_{sp}[M]$ and k_{31p} is likely to be similar to k_{pp}, then R_p can be reduced to eq 2 where C_{12}, C_{21}, and all rate constants are as defined in Scheme 1 and [M] is propene concentration.

$$R_p = (k_{pp} + k_{ps})[C_{12}][M] + k_{sp}[C_{21}][M] + k_{31p}[C_{31}][M] + k_{Hp}[C_H][M] \quad (1)$$

$$R_p = k_{pp}[C_{12}][M] + k_{sp}[C_{21}][M] \quad (2)$$

If the total number of metal sites is a constant $[C_T] = [C_{12}] + [C_{21}]$, then eq 2 can be rewritten in terms of $[C_{12}]$ and $[C_T]$:

$$R_p = k_{pp}[C_{12}][M] + k_{sp}([C_T] - [C_{12}])[M] \quad (3)$$

The relationship between C_{12} and C_{21} in the presence of $[H_2]$ can be expressed using the steady-state assumption in C_{21} (eq 4). For catalyst **3**, chain-transfer events after a 2,1-misinsertion were not observed in the absence of hydrogen and so are not included in eq 4:

$$d[C_{21}]/dt = k_{ps}[C_{12}][M] - k_{sp}[C_{21}][M] - k_{31}[C_{21}] - k_{sH}[C_{21}][H_2] = 0 \quad (4)$$

Equation 4 can be further simplified by considering the case of the unbridged catalysts **2** and **3**. In the presence of hydrogen, no internal regioerrors are evident which suggests that the terms $k_{sp}[M]$ and k_{31} can be neglected as their rates are insignificant compared to $k_{sH}[H_2]$. Equation 4 can then be rearranged to give

$$\frac{[C_{21}]}{[C_{12}]} = \frac{k_{ps}[M]}{k_{sH}[H_2]} \quad (5)$$

Since the total number of catalyst sites is constant, eq 5 can be rearranged to give $[C_{12}]$ in terms of $[C_T]$:

$$[C_{12}] = \frac{[C_T]}{\left(\frac{k_{ps}[M]}{k_{sH}[H_2]} + 1\right)} \quad (6)$$

Equation 6 can now be substituted into eq 3 to give the expression for productivity in terms of $[C_T]$:

$$R_p = \frac{k_{pp}[C_T][M]}{\left(\frac{k_{ps}[M]}{k_{sH}[H_2]} + 1\right)} + k_{sp}[M]\left([C_T] - \frac{[C_T]}{\left(\frac{k_{ps}[M]}{k_{sH}[H_2]} + 1\right)}\right) \quad (7)$$

Equations 6 and 7 predict that when $k_{sH}[H_2] \gg k_{ps}[M]$, $[C_{12}] = [C_T]$ and R_p will be at a maximum. The data in Tables 1 and 2 can be examined to see if this behavior is manifested as $[H_2]$ is increased. For rac-(EBI)ZrCl$_2$ (**1**), the productivity increases slightly with hydrogen concentration but addition of more H_2 does not result in a larger productivity (entries 2 and 3). For unbridged catalysts **2**, productivity increases with H_2 whereas for catalyst **3**, productivity increases and then decreases. Unfortunately, attempts to more rigorously correlate productivities with hydrogen concentration were complicated by experimental difficulties. Nevertheless, the data in Table 1 show an increase in productivity with addition of up to 4 mmol of hydrogen.

At very low hydrogen concentration, internal regioerrors are no longer evident in the polymers made by **3** and yet the productivities continue to increase with added hydrogen. The disappearance of internal regioerrors indicates the point at which $k_{sH}[H_2] \gg k_{sp}[M]$. However, a fraction of C_T may still exist as C_{21} since as seen from eq 5, C_{21} approaches zero only when $k_{ps}[M]/k_{sH}[H_2]$ approaches zero. From entry 13 in Tables 1 and 2, we estimate that $k_{ps}[M]/k_{sH}[H_2]$ is on the order of 0.5.[34] From eq 5, this implies that at steady-state, $[C_{21}]$ is approximately 33% of $[C_T]$. This is consistent with our results indicating that productivity of catalyst **3** continues to increases with addition of hydrogen even when no internal regioerrors are evident in the polymer.

The analysis just presented assumes that 2,1-sites are produced exclusively from regioirregular propene insertion into a metal−carbon bond. The occurrence of 2,3-dimethylbutyl end groups (structure G′) with bridged catalyst **1** suggests that 2,1-sites might also be generated from regioirregular insertion into metal−hydride bonds. The absence of structure G′ from polymers made with the unbridged catalysts does not rule out initial 2,1-misinsertion; this only indicates that propagation from such a metal center is not competitive with chain transfer to hydrogen. The presence of this additional pathway to C_{21} sites may help explain the highly variable influences on productivity that have been attributed to the hydrogen effect with a variety of metallocene catalysts.

The increase in productivity with the addition of small amounts of ethene may be considered in a similar kinetic scheme as Scheme 1 with removal of C_{21} sites by C_2H_4 insertion instead of chain transfer to hydrogen. In that case, an analogous equation to eq 5 may be derived:

$$\frac{[C_{21}]}{[C_{12}]} = \frac{k_{ps}[M]}{k_{sE}[C_2H_4]} \tag{8}$$

where k_{sE} is the rate of ethene insertion after a 2,1-misinsertion and $[C_2H_4]$ is the concentration of ethene. On the basis of entries 14 and 15 in Table 1, we can only say that addition of ethene does increase the productivity and results in ethene insertion following all 2,1-misinsertions. A study of productivity increase with addition of ethene is complicated by the necessity of factoring out the faster insertion of ethene over propene by the catalyst and the complicated copolymerization behavior that arises at higher ethene concentrations.[8]

The data obtained in this study points to regioerrors being responsible for some of the productivity increase with addition of hydrogen and ethene. The trends in productivity increasing with hydrogen concentration are supported when considering the simple kinetic picture outlined in Scheme 1. A model which includes formation of C_{21} sites from metal hydrides, as seen with catalyst **1**, may complicate the relationship between regioerrors and productivity. This study does not rule out the possibility of some mechanism other than regioerrors playing a part in the hydrogen effect. Other researchers have concluded that other species, such as allyl groups or unsaturated chain branches, may also lead to dormant species in propene polymerization.[5,35,36]

Conclusion

Unbridged catalysts (2-phenylindenyl)$_2$ZrCl$_2$ and (2-(3,5-(CF$_3$)$_2$C$_6$H$_3$)indenyl)$_2$ZrCl$_2$ produce 0.1−0.3 mol % 2,1-inserted units during propene polymerization. These regioerrors occur only in the isotactic sections of polymer which suggests that the catalysts are in a *rac*-like conformation. ^{13}C NMR analysis of solvent fractionated polymers made by catalyst **2** revealed that regioerrors occurred in the most highly isotactic fraction. In polymers made with low ethene content, ethene is inserted preferentially into isotactic segments as well and all 2,1-misinsertions are followed by insertion of ethene. Further studies are being conducted on the effect of regioerrors on polymer crystallization. A detailed kinetic study of the effect of hydrogen on catalyst activity is planned.

Experimental Section

rac-(Ethenebisindenyl)zirconium dichloride (**1**) was commercially available from Witco and used without further purification. Unbridged catalysts (2-phenylindenyl)$_2$ZrCl$_2$ (**2**) and (2-(3,5-(CF$_3$)$_2$C$_6$H$_3$)indenyl)$_2$ZrCl$_2$ (**3**) were prepared as previously described. [7,37,38] Type IV methylalumoxane (MAO) was purchased from Akzo in a toluene solution and dried before use. $^{13}C_2H_4$ was purchased from Cambridge Isotope Laboratories and used as received.

Polymerizations were conducted in 100 mL liquid propene using 5×10^{-6} M concentration of catalyst and Al/Zr ≈ 3000. Hydrogen was dosed into the reactor by pressurizing an injection tube with gas and flushing liquid propene through the tube into the reactor. For polymerization with $^{13}C_2H_4$, the reactor was directly pressurized with ethene before filling with liquid propene.

The polymers synthesized were precipitated in methanol/HCl and dried. High-temperature GPC measurements of polymers were performed at Amoco Chemical Co. using a Watts 150C GPC at 100 °C in dichlorobenzene and referenced to polypropene 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 the nuclear Overhauser enhancement was present except for $^{13}C_2H_4$/propene copolymer which was run with inverse gated decoupling. Regioerrors were identified according to chemical shifts reported in the literature.[9−11] The percentage of regioerrors were calculated as described by Resconi[14] or, in the case of *n*-butyl end groups, by integration of methyl resonances.

Percentage ^{13}C-1,2-ethene incorporation was determined by the following procedure which accounts for the natural abundance of ^{13}C in the $S_{\alpha\alpha}$ carbons (see Figure 2 for identification of carbons numbers I and J):

$$\text{total CH}_2\text{ units} = (S_{\alpha\alpha}/0.011) + \text{I3} + \text{I4} + \text{J3} + \text{J4}$$

$$\%\ ^{13}\text{C-1,2-ethene incorporation} = [(\text{I3} + \text{I4} + \text{J3} + \text{J4})/2]/[\text{total CH}_2\text{ units}] \times 100$$

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(18) The unmarked resonances at δ 14−15 ppm and δ 29−33 ppm in Figure 3 are due to structures which could not be identified.

(19) MAO can also act as a chain-transfer agent in propylene polymerizations. The Al/Zr ratio = 3000 for all polymerizations in this study.

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$$P_n = \frac{k_{pp}[C][M]}{k_{pH}[C][H_2]} \tag{9}$$

For entry 13, M_n = 5900 g/mol and so P_n = 140. Assuming $k_{pH} \cong k_{sH}$[39] and using $k_{pp} \cong 300k_{ps}$ from the total number of regioerrors observed for catalyst **3**, eq 9 can be written as follows:

$$\frac{k_{ps}[M]}{k_{sH}[H_2]} = \frac{P_n}{300} = 0.47 \tag{10}$$

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