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Ethylene−Propylene Copolymerization with 2-Arylindene Zirconocenes

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ABSTRACT: Unbridged 2-arylindenylmetallocene complexes such as bis(2-phenylindenyl)zirconium dichloride in the presence of methylaluminoxane (MAO) are catalyst precursors for the synthesis of elastomeric polypropylenes. These catalysts are also active for the copolymerization of ethylene and propylene. Addition of small amounts of ethylene to a polymerization system derived from the 2-arylindene metallocenes results in a large and nonlinear increase in the polymerization rate. This increase in rate cannot be explained by the faster rate of ethylene insertion but is likely the result of the activation of dormant catalyst sites by ethylene. This “ethylene effect” is much larger for bis(2-phenylindenyl)zirconium dichloride/MAO ($(2PhInd)_2ZrCl_2$/MAO, **1**/MAO) and bis[2-(3′,5′-bis(trifluoromethyl)phenyl)indenyl]zirconium dichloride/MAO ($((CF_3)_2PhInd)_2ZrCl_2$/MAO, **2**/MAO) metallocene catalysts than for bridged *rac*-ethylene-bis(indenyl)zirconium dichloride/MAO ($EBIZrCl_2$/MAO, **3**/MAO) metallocene. Copolymerization parameters for **1**−**3**/MAO reveal that the unbridged 2-arylindene catalysts show a tendency toward random or slightly blocky incorporation of comonomers ($r_er_p = 1.0-1.9 \geq 1$), whereas the *ansa*-metallocene **3**/MAO exhibits a tendency toward alternating comonomer distribution ($r_er_p = 0.5 < 1$).

Introduction

Ethylene−α-olefin copolymers are of great practical importance. Copolymerization of ethylene with small amounts of 1-butene, 1-hexene, or 1-octene leads to the formation of linear low-density polyethylene (LLDPE), one of the largest volume polyolefin products.[1,2] Propylene polymers containing small amounts of ethylene exhibit lower crystallinity and higher impact strength than isotactic homopolypropylene.[3−5] Copolymerization of propylene with larger amounts of ethylene or their terpolymerization with a diene results in amorphous rubbery materials (ethylene−propylene or ethylene−propylene−diene rubbers), a rapidly growing class of elastomers.[2] Amorphous ethylene−propylene copolymers are also widely used as impact-strength modifiers in blends with isotactic polypropylene.[6−8]

The properties and performance of an olefin copolymer are determined by the comonomer content and, most importantly, by the comonomer distribution within and between single polymer chains. An amorphous polymer results if the comonomers are distributed randomly, whereas crystalline polymers could be obtained when the monomers are segregated into long sequences. Heterogeneous Ti-based and homogeneous V-based catalysts are used commercially for the production of olefin copolymers.[2] The development of metallocene catalysts, in combination with methylaluminoxane (MAO), for olefin polymerization has opened new opportunities for the synthesis of copolymers with controlled structure and properties.

First-order Markov statistics have been extensively applied to characterize the kinetics of olefin copolymerization.[9] In terms of this model, the reactivity of the two types of metal centers with a different last inserted monomer unit toward the two competing monomers is described by the reactivity ratios, r_1 and r_2, which are defined as $r_i = k_{ii}/k_{ij}$, the ratio of the rate constant for the homopropagation reaction (k_{ii}) to the rate constant for the cross-propagation reaction (k_{ij}). The product r_1r_2 is an indicator of the type of monomer distribution along the copolymer chain: $r_1r_2 = 1$ indicates a random distribution of comonomer units, $r_1r_2 < 1$ indicates a tendency of the catalyst to alternate the comonomers, and $r_1r_2 > 1$ indicates the tendency to form long sequences of at least one of the comonomers.[9] Examples of reactivity ratios (r_e and r_p) for ethylene−propylene (EP) copolymerization with a number of catalytic systems are given in Table 1. The product of the reactivity ratios for most heterogeneous titanium catalysts is typically greater than 1, which is consistent with the tendency of these types of catalysts to form long crystallizable ethylene sequences. Vanadium-based cata-

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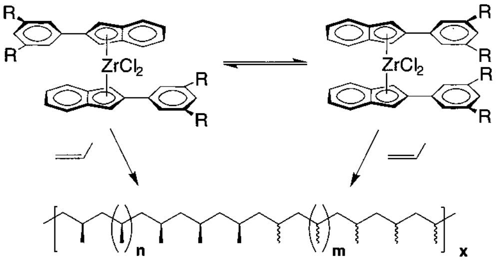
Table 1. Reactivity Ratios for Ethylene−Propylene Copolymerization

catalyst	T, °C	r_e	r_p	r_er_p	ref
δ-$TiCl_3$−$Al(C_2H_5)_2Cl$	70	11.6	0.35	4.1	10
δ-$TiCl_3$−$Al(C_2H_5)_3$	40	7.3	0.76	5.5	11
$MgCl_2/TiCl_4$/ethyl benzoate−$Al(C_2H_5)_3$	70	5.5	0.36	2.0	10
VCl_3−$Al(n\text{-}C_6H_{13})_3$	25	5.6	0.15	0.81	12
$VOCl_3$−$Al(n\text{-}C_6H_{13})_3$	25	18.0	0.07	1.2	12
Cp_2TiCl_2/MAO	30	15.7	0.009	0.14	13
$Cp_2Ti{=}CH_2$/MAO	50	24	0.0085	0.204	14
Cp_2ZrCl_2/MAO	30	16	0.025	0.4	13
Cp_2ZrCl_2/MAO	50	48	0.015	0.72	14
$Cp^*_2ZrCl_2$/MAO	50	250	0.002	0.5	14
$Me_2SiCp_2ZrCl_2$/MAO	50	24	0.029	0.7	14
Cp_2HfCl_2/MAO	30	20.6	0.074	1.5	13
$EBIZrCl_2$/MAO	50	6.61	0.06	0.4	15
$EBIZrCl_2$/MAO	25	6.26	0.11	0.69	15
$EBIZrCl_2$/MAO	0	5.2	0.14	0.73	16
$EBIZrCl_2$/MAO	50	2.6	0.39	1.0	13
$EBTHIZrCl_2$/MAO	50	2.9	0.28	0.81	13
$Me_2C(Cp)(Flu)ZrCl_2$/MAO	25	1.3	0.2	0.26	16

Scheme 1



lysts give a more random distribution of comonomers; r_er_p is close to unity in most cases. For most of the studied metallocene systems the product of the reactivity ratios is smaller than 1, indicating a tendency toward alternation of ethylene and propylene units.

We have recently reported a new strategy for the production of stereoblock polypropylene with nonbridged bis(2-arylindenyl)metallocenes.[17,18] These catalysts were designed to switch their coordination geometry from aspecific to isospecific during the course of polymerization in order to generate atactic and isotactic blocks (Scheme 1). Consistent with the stereoblock microstructure, polypropylene produced by a number of bis(2-arylindenyl) complexes activated by MAO was elastomeric.[19] This paper describes the behavior of these novel catalysts in ethylene−propylene copolymerization. The copolymerization behavior, reactivity ratios, and monomer sequence distribution for bis(2-phenylindenyl)zirconium dichloride/MAO, $(2PhInd)_2ZrCl_2$/MAO, **1**/MAO, and bis[2-(3′,5′-bis(trifluoromethyl)phenyl)indenyl]zirconium dichloride/MAO, $((CF_3)_2PhInd)_2ZrCl_2$/MAO, **2**/MAO, will be discussed and compared with those observed for a bridged metallocene *rac*-ethylenebis(indenyl)zirconium dichloride/MAO, $EBIZrCl_2$/MAO, **3**/MAO.

Results

Copolymerization Procedure. Ethylene−propylene copolymerizations were conducted in liquid propylene under a constant head pressure of ethylene.[20] The copolymerization behavior of three catalysts $(2PhInd)_2ZrCl_2$/MAO (**1**/MAO), $((CF_3)_2PhInd)_2ZrCl_2$ (**2**/MAO) and $EBIZrCl_2$ (**3**/MAO) was studied at two temperatures: 20 ± 1 °C and 1 ± 1 °C. In all experiments used for the reactivity ratio determination, the consumption of propylene did not exceed 3.0 g (6% conversion) for catalysts **1**- and **2**/MAO and 4.8 g (10% conversion) for **3**/MAO. To avoid strong exothermic effects, we used low catalyst concentrations (1−2 μM). At the same time, at least 50 mg of MAO had to be used in the reaction for reproducible results. The above requirements for the catalyst and MAO concentrations resulted in high [Al]:[Zr] ratios (up to 10 000). The ratio of mole fractions of ethylene and propylene in the liquid phase, X_e/X_p, was determined using fugacity diagrams (for details see Supporting Information).[21]

Monomer diad distribution obtained from quantitative ^{13}C NMR spectroscopy (gated decoupling mode and 13 s pulse repetition intervals) was used for the reactivity ratio determination.[22] To test the reproducibility of our results, we conducted five copolymerizations at both temperatures with each of the catalysts except for **3**/MAO. For **3**/MAO, only one run was conducted at 20 °C. The average reactivity ratios and standard deviations calculated on the basis of the series of copolymerizations are summarized in Table 2.

At both copolymerization temperatures the following order of the reactivity ratios for ethylene was observed: **1**/MAO < **2**/MAO < **3**/MAO. The order of the propylene reactivity ratios was found to be **3**/MAO < **1**/MAO < **2**/MAO. For all three catalysts, the reactivity ratio for ethylene increased slightly with temperature but the propylene reactivity ratios did not vary with temperature significantly. The product of the reactivity ratios was not very temperature sensitive for **3**/MAO and increased slightly with temperature for **1**- and **2**/MAO.

Shown in Figure 1 is the comparison of triad distributions for samples of similar composition (42−43% ethylene) prepared with all three catalysts at 1 ± 1 °C. Both **1**- and **2**/MAO generated more of PPP triads and EEE triads than **3**/MAO. At the same time the ratio of the alternating EPE and PEP triads was greater in the samples prepared with **3**/MAO than in those generated with **1**- and **2**/MAO. These differences were reproduced in copolymer samples with lower ethylene content (21%).

The unbridged bis(2-arylindenyl) catalysts, **1**- and **2**/MAO, incorporated more propylene into a copolymer

Table 2. Copolymerization Parameters for 1−3/MAO Determined on the Basis of Copolymerizations in Liquid Propylene

catalyst	T, °C	N_{exp}[a]	X_e/X_p in feed[b]	%E in polymer[c]	r_er_p[d]	r_e[d]	r_p[d]	r_p/r_e
1/MAO	1 ± 1	5	0.06−0.22	21−44	0.92 ± 0.08	3.8 ± 0.3	0.25 ± 0.01	0.066
	20 ± 1	5	0.06−0.16	23−45	1.3 ± 0.2	5.4 ± 0.9	0.24 ± 0.04	0.044
2/MAO	1 ± 1	5	0.07−0.25	18−43	1.3 ± 0.1	4.2 ± 0.7	0.31 ± 0.03	0.074
	20 ± 1	5	0.05−0.08	14−22	1.9 ± 0.1	6.0 ± 0.2	0.33 ± 0.03	0.055
3/MAO	1 ± 1	5	0.04−0.18	23−54	0.49 ± 0.03	5.4 ± 0.6	0.09 ± 0.01	0.017
	20 ± 1	1	0.07	42[e]	0.50[e]	7.1[e]	0.07[e]	0.010[e]

[a] Number of experiments used for determination of the average reactivity ratios. [b] The range of the ratios of the mole fractions of ethylene (X_e) and propylene (X_p). [c] The range of mole % E in copolymers determined using ^{13}C NMR. [d] Determined using ^{13}C NMR. [e] One experiment was used for the reactivity ratio determination under these conditions; see text.

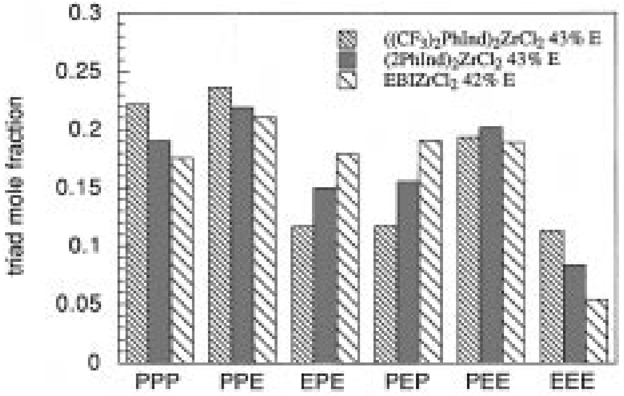


Figure 1. Triad distribution for copolymers containing 42−43 mol % ethylene.

than the bridged catalyst, **3**/MAO, at both polymerization temperatures. For example, at 20 ± 1 °C and the ratio of monomer mole fractions $[X_e]/[X_p] = 0.06-0.07$ in the feed, the mole percent propylene incorporated into a copolymer was 76% for **1**/MAO, 81% for **2**/MAO, and only 60% for **3**/MAO.

Effect of Ethylene on M_w and Productivity. Table 3 summarizes polymer molecular weights and productivities for propylene homopolymerizations and propylene copolymerizations with ethylene conducted under similar conditions. Addition of 5−10% ethylene into the reaction feed did not have a measurable effect on molecular weights and molecular weight distributions (MWD's) of polymers generated with the bridged catalyst **3**/MAO. However, in the case of the unbridged 2-arylindene catalysts **1-** and **2**/MAO, the molecular weights of EP copolymers increased by a factor of 2.2−3.3 relative to the propylene homopolymers. For catalysts **1-** and **2**/MAO incorporation of over 18% ethylene into a polymer resulted in narrower molecular weight distributions.

Since most polymerization catalysts are more active for ethylene than for propylene homopolymerization, a higher overall polymerization productivity would be expected for EP copolymerization than for propylene homopolymerization. However, the unusually high increase in polymerization productivity observed for catalysts **1-** and **2**/MAO in the presence of even less than 1% ethylene in the reaction feed[23] prompted us to investigate this phenomenon in more detail. As shown below, from the copolymerization equations and the ethylene and propylene reactivity ratios it is possible to discriminate between the linear polymerization productivity increase due to the higher rate of ethylene insertion and the "nonlinear" increase in the rate of propylene−propylene insertions in the presence of ethylene.

The first order Markov model is described by the following four equations:

$$M_e + E \xrightarrow{k_{ee}} M_e \qquad (1)$$

$$M_e + P \xrightarrow{k_{ep}} M_p \qquad (2)$$

$$M_p + P \xrightarrow{k_{pp}} M_p \qquad (3)$$

$$M_p + E \xrightarrow{k_{pe}} M_e \qquad (4)$$

where M_e and M_p are the active centers with the last ethylene and propylene inserted units, respectively. Then the rate of copolymerization, R_{ep}, can be expressed as

$$R_{ep} = k_{ee}[M_e][E] + k_{pe}[M_p][E] + k_{ep}[M_e][P] + k_{pp}[M_p][P]$$

Under steady-state conditions the concentrations of all active species must remain constant, which means that the rates of interconversion of M_e into M_p and of M_p into M_e are equal:

$$k_{pe}[M_p][E] = k_{ep}[M_e][P]$$

and we can express $[M_e]$ through $[M_p]$

$$R_{ep} = k_{ee}(k_{pe}/k_{ep})[M_p][E][E]/[P] + 2k_{pe}[M_p][E] + k_{pp}[M_p][P]$$

The ratio of the rate of copolymerization, R_{ep}, to the rate of propylene homopolymerization, R_{pp}, is

$$\frac{R_{ep}}{R_{pp}} = \frac{k_{ee}k_{pe}[M_p][E][E]}{k_{ep}k_{pp}{}^{h}[M_p{}^{h}][P][P^h]}\frac{k_{pp}}{k_{pp}} + \frac{2k_{pe}[M_p][E]}{k_{pp}{}^{h}[M_p{}^{h}][P^h]}\frac{k_{pp}}{k_{pp}} + \frac{k_{pp}[M_p][P]}{k_{pp}{}^{h}[M_p{}^{h}][P^h]}$$

where $k_{pp}{}^{h}$, $M_p{}^{h}$, P^h signify the values for propylene homopolymerization. At ethylene concentrations in the feed below 10% the mole fraction of propylene in the reaction feed, [P], would be expected to change very little as compared to propylene homopolymerization, and we can assume that $[P] = [P^h]$. The expression can be simplified even further by taking into account that $k_{ee}/k_{ep} = r_e$ and $k_{pp}/k_{pe} = r_p$:

$$\frac{R_{ep}}{R_{pp}} = \frac{r_e[E]^2}{r_p[P]^2}\frac{k_{pp}[M_p]}{k_{pp}{}^{h}[M_p{}^{h}]} + \frac{2[E]}{r_p[P]}\frac{k_{pp}[M_p]}{k_{pp}{}^{h}[M_p{}^{h}]} + \frac{k_{pp}[M_p]}{k_{pp}{}^{h}[M_p{}^{h}]} = \frac{k_{pp}[M_p]}{k_{pp}{}^{h}[M_p{}^{h}]}\left(\frac{r_e[E]^2}{r_p[P]^2} + \frac{2[E]}{r_p[P]} + 1\right)$$

The ratio of the rates of co- and homopolymerization can be estimated from the ratio of the corresponding productivities, P_{ep} and P_{pp}:

$$\frac{R_{ep}}{R_{pp}} = \frac{P_{ep}}{P_{pp}} = \frac{k_{pp}[M_p]}{k_{pp}{}^{h}[M_p{}^{h}]}(r_e[E]^2/r_p[P]^2 + 2[E]/(r_p[P]) + 1) \qquad (5)$$

In eq 5 the increase of polymerization productivity due to the faster rate of ethylene insertion is described by the expression $(r_e[E]^2/r_p[P]^2 + 2[E]/(r_p[P]) + 1)$. The expression $k_{pp}[M_p]/k_{pp}{}^{h}[M_p{}^{h}]$ describes the ratio of the rate of consecutive propylene−propylene insertions in the presence of ethylene as compared to the rate in the absence of ethylene:

Table 3. Effect of Ethylene on Polymer Molecular Weights and Polymerization Productivity[a]

catalyst	T, °C	[E]/[P] in feed	%E in polymer[b]	productivity[c]	$M_w \times 10^{-3}$ [d]	MWD[d]	$k_{pp}[Mp]/k_{pp}{}^h[M_p{}^h]$ [e]
1/MAO	0	0	0	11 920	838	5.40	n/a
	0	0.084	30	25 560	2230	3.00	1.0
	19	0	0	13 200	549	3.49	n/a
	19	0.065	25	69 280	1789	2.62	3.2
2/MAO	0	0	0	6 000	756	5.70	n/a
	3	0.102	30	75 970	2159	2.99	6.7
	1	0.082	18	64 540	2386	3.41	7.8
	19	0	0	8 300	621	4.58	n/a
	19	0.048	14	58 260	1776	5.60	5.3
3/MAO	0	0	0	19 100	98.3	2.13	n/a
	1	0.082	40	106 230	75.5	1.96	1.7
	20	0	0	86 400	70.6	1.98	n/a
	20	0.048	39	243 240	67.2	2.03	1
	22	0.055	46	286 600	70.3	1.97	1

[a] $[Zr] = 1 \times 10^{-6}$ M, [Zr]:[Al] = 1:10 000, t_{rxn} = 25−30 min. [b] Mole %E in the polymer determined by ^{13}C NMR. [c] kg·polymer/(mol·Zr·h). [d] Determined by GPC. [e] For definition see text.

$$\frac{k_{pp}[M_p]}{k_{pp}{}^h[M_p{}^h]} = \frac{P_{ep}}{P_{pp}}(r_e[E]^2/r_p[P]^2 + 2[E]/(r_p[P]) + 1)^{-1}$$

If there is no change in the intrinsic rate of propylene−propylene insertions ($k_{pp} = k_{pp}{}^h$) and/or the concentration of the active centers with the last inserted propylene unit ($[M_p] = [M_p{}^h]$) in copolymerization as compared to homopolymerization, $k_{pp}[M_p]/(k_{pp}{}^h[M_p{}^h])$ should be equal to unity.

Using our experimental data, we estimated the rate enhancement factors, $k_{pp}[M_p]/(k_{pp}{}^h[M_p{}^h])$, for catalysts **1**−**3**/MAO (Table 3). The rate enhancement factor for **3**/MAO was 1.7 at 0 °C and 1 (no propylene polymerization rate enhancement) at 20 °C. In the case of catalysts **1**- and **2**/MAO, greater rate enhancement factors were observed: from 3.2 for **1**/MAO at room temperature to 7.8 for **2**/MAO at 0 °C.

Discussion

Experimental Procedure. To minimize the change in the feed composition, we adopted an experimental procedure which involved the use of excess propylene as both monomer and solvent and a continuous supply of ethylene. In all of our experiments, propylene conversion did not exceed 10% and the feed composition could be considered nearly constant. We based our determination of the reactivity ratios on the monomer sequence distribution obtained from quantitative ^{13}C NMR spectra of copolymers.[22] For **1**- and **2**/MAO at both temperatures and for **3**/MAO at 1 °C we averaged the NMR-based reactivity ratios over five experiments conducted at slightly different feed compositions (Table 2). For **3**/MAO at 20 °C, due to its very high activity under these conditions, only one of the runs, in which propylene conversion was less than 10%, was used for the reactivity ratio determination.

Copolymerization Parameters. The reactivity ratios determined for **3**/MAO at 1 and 20 °C are in a fair agreement with those reported by Zambelli et al. and by Kaminsky et al. for the corresponding conditions (Table 1).[15,16]

While copolymerization parameters reported in the literature vary (Table 1), most studied metallocenes have values for $r_er_p \leq 1.0$. The copolymerization parameters for the unbridged 2-arylindene catalysts **1**/MAO (r_er_p = 0.9−1.3) and **2**/MAO (r_er_p = 1.3−1.9) reveal that these catalysts tend to give less alternating polymers than those derived from most metallocenes. A direct comparison of monomer sequence distributions in copolymers generated with bis(2-arylindenyl) catalysts and those generated with **3**/MAO (r_er_p = 0.5) shows that **3**/MAO generates a higher fraction of the alternating EPE and PEP triads than **1**/MAO and **2**/MAO (Figure 1). Two other examples of $r_er_p > 1$ for metallocenes include Chien's report of r_er_p = 1.5 for Cp_2HfCl_2[13] and Lehtinen and Löfgren's recent report of r_er_p = 2.51−2.75 for Ind_2ZrCl_2/MAO.[24] In contrast to **1**/MAO (r_e = 3.8−5.4) and **2**/MAO (r_e = 4.2−6.0), both of these systems have relatively high values for r_e (r_e = 13 and 20, respectively), indicating a tendency to incorporate longer ethylene sequences.

For **1**/MAO r_er_p is approximately 1, both at 1 and 20 °C, which formally corresponds to a random comonomer distribution. However, the monomer sequence distributions in copolymers generated with **1**/MAO are not completely Bernoullian since the relationships between certain triad fractions do not hold.[25]

The relatively low values of r_e (r_e = 3.8−6.0) and the larger values of r_er_p = 0.9−1.9 for the unbridged catalysts **1**/MAO and **2**/MAO indicate that these catalysts incorporate propylene readily. The ability of the catalysts **1**−**3**/MAO to incorporate propylene into ethylene−propylene copolymers can be correlated with the ratio of the corresponding reactivity ratios $r_p/r_e = k_{pp}k_{ep}/(k_{ee}k_{pe})$ (Table 2), greater numbers corresponding to higher ability to incorporate propylene. While it was previously found that unbridged catalysts are less efficient for propylene incorporation into EP copolymers than bridged ones,[24] we find that the unbridged bis(2-arylindenyl) catalysts **1**- and **2**/MAO incorporate more propylene into copolymers than the ethylene-bridged bis(indenyl) catalyst **3**/MAO.

It should be emphasized that the carbon NMR spectra of copolymers contain information only on the average composition and monomer sequence distribution but not on their variation among different polymer chains. Generally, ethylene−α-olefin copolymers produced by metallocene catalysts are much more homogeneous in their composition than those produced by conventional heterogeneous Ziegler−Natta catalysts.[26,27] However, the fact that the molecular weight distributions of copolymers generated with bis(2-arylindenyl) catalysts **1**- and **2**/MAO (MWD = 2.5−5) are broader than for those generated with **3**/MAO (MWD < 2.5) raises the question of whether the broadening of the MWD's may be accompanied by an increase in compositional heterogeneity. Further studies are underway to address this question. Nevertheless, the average kinetic parameters determined using the simple first order Markov model are useful for the description and comparison of the trends in the monomer sequence distribution for all three catalysts.

Effect of Ethylene on M_w and Productivity. It has been previously reported that for bis(tetrahydroindenyl)zirconocene catalyst there is no significant change in copolymer molecular weights as compared to homopolypropylene for ethylene contents below 40%, while for ethylene incorporation above 40% the molecular weights of copolymers increase.[28] In contrast, Naga reports a continuous increase in M_w for $EBIZrCl_2$ with increasing ethylene concentration in the polymer,[29] and Ziegler observes a significant molecular weight increase for EP copolymer generated with ethylenebis(4,7-dimethylindenyl) metallocene upon incorporation of as little as 4 wt % ethylene.[30] In this study we observe little effect of ethylene on the molecular weight of copolymers generated with **3**/MAO for ethylene contents up to 55%. However, a striking increase is observed in molecular weights of polymers generated with **1**- and **2**/MAO for ethylene incorporation of only 14 mol % (Table 3).

We have also observed a dramatic increase in polymerization productivity for catalysts **1**- and **2**/MAO upon addition of ethylene as compared to *propylene homopolymerization*. This increase cannot be accounted for by the faster rate of ethylene insertion relative to propylene and is more pronounced in the case of bis(2-arylindenyl) catalysts **1**- and **2**/MAO than in the case of bridged metallocene **3**/MAO. Similar activation of propylene polymerization systems with ethylene has been previously observed for supported Ti-based[31,32] and homogeneous V-based catalysts.[33] In addition, many examples of propylene polymerization activation with hydrogen have been reported.[34] One of the explanations for the hydrogen effect is the reactivation of the dormant sites resulting from 2,1-propylene misinsertions.[35−37] It is possible that ethylene and hydrogen effects are mechanistically related in that ethylene might insert easily after propylene regioerrors reactivating them for further propagation. This notion is further supported by the copolymer microstructure studies by Zeigler where he observed a high level of ethylene insertions adjacent to 2,1-propylene misinsertions.[30]

Another type of activation effect has been observed for *ethylene polymerization* upon addition of small amounts of an α-olefin comonomer. Several explanations have been forwarded to explain this phenomenon, usually referred to as a “comonomer effect”, including the “trigger” mechanism,[29] and improved rates of diffusion due to the solubilization of active centers by incorporation of comonomer.[38]

Our observation of rate enhancement factors $k_{pp}[M_p]/(k_{pp}^h[M_p^h])$ greater than unity indicates that the rate of propylene consumption is higher in the presence of ethylene than in the absence of ethylene. This could be explained either by an increase in the rate constant k_{pp} or by an increase in the number of the active centers $[M_p]$ in the presence of ethylene. Since polypropylenes generated with **1**- and **2**/MAO are only partially isotactic and should be sufficiently soluble in the reaction medium, we do not believe that the increase in k_{pp} and/or $[M_p]$ is caused by solubilization of active centers due to ethylene incorporation. Besides, no significant rate enhancement is observed for **3**/MAO which in propylene polymerization produces a highly isotactic crystalline polymer.[39] However, in view of the hydrogen and ethylene effect studies outlined above, it is possible that ethylene increases the number of the active centers $[M_p]$ by reactivating dormant 2,1-propylene sites. We had previously reported that we could not detect regioerrors in polypropylenes produced with $(2PhInd)_2ZrCl_2$.[17] More recent studies revealed the presence of detectable amounts of 2,1-misinsertions in polypropylenes generated with catalysts **1**- and **2**/MAO.[40] Further studies are underway to determine if the occurrence of 2,1-regioerrors in propylene polymers produced with 2-arylindenyl catalysts could account for the ethylene rate enhancement factors observed in this work.

Conclusions

Unbridged 2-arylindene metallocenes are capable of homopolymerizing propylene to yield elastomeric polypropylenes. These catalysts are also active catalysts for ethylene−propylene copolymerizations. The distribution of comonomers in the EP copolymers produced conform to first-order Markov statistics. These catalysts show less of a tendency toward alternation of comomers than most metallocenes and incorporate propylene quite efficiently.

We have also observed a significant comonomer effect, where the rate of propene polymerization in the presence of ethylene is significantly higher than the rate in the absence of ethylene. This rate enhancement is likely a consequence of the higher number of active centers in the presence of ethylene.

Experimental Section

General Considerations. All manipulations with organometallic compounds were conducted using standard Schlenk and drybox techniques. Complexes $(2PhInd)_2ZrCl_2$ (**1**),[17] $((CF_3)_2PhInd)_2ZrCl_2$ (**2**),[18] and $EBIZrCl_2$ (**3**)[41] were synthesized according to the literature procedures. Toluene was passed through two purification columns packed with activated alumina and supported copper catalyst.[42] Polymerization grade ethylene and propylene gases were purchased from Matheson, and liquid propylene was obtained from Amoco. Both monomers were further purified by passage through two columns packed with activated alumina and supported copper catalyst. Methylaluminoxane (MAO), type 3A, purchased from Akzo, was dried *in vacuo* prior to use.

Ethylene−Propylene Copolymerization. A 300-mL stainless steel Parr reactor equipped with a mechanical stirrer was evacuated, purged 4−5 times with gaseous propylene by pressurizing and venting, and charged with liquid propylene (100 mL). Propylene was cooled to the reaction temperature and overpressurized with ethylene to a certain total pressure. The monomer mixture was equlibrated at the reaction temperature under constant ethylene pressure for at least 20 min. Immediately prior to the catalyst injection, the ethylene line was disconnected and the reactor was cooled to 2−3 °C below the reaction temperature to compensate for the exothermic effect upon initiation. In a nitrogen filled drybox a 50-mL pressure tube was charged with zirconocene/MAO solution in toluene (20 mL) and outside the box immediately pressurized with argon (30 mL × 250 psig). In the case of polymerizations at 0−2 °C the catalyst was cooled in an ice bath prior to being injected. The reaction was started by catalyst injection. *CAUTION: the reaction can be very exothermic leading to a significant pressure buildup. Reliable temperature control is required!* After the catalyst injection the ethylene line was reconnected and the reaction was run for 25−30 min at constant total pressure and temperature. The reaction was quenched by injecting MeOH (20 mL); the reactor was slowly vented and opened. The polymer was precipitated in acidified

MeOH (5% HCl), filtered, washed with MeOH, and dried in a vacuum oven at 40 °C to constant weight.

Propylene Polymerization. Procedures for reactor preparation, catalyst injection, and polymer workup were the same as those for copolymerizations in liquid propylene.

Polymer Characterization. Polymer molecular weights and molecular weight distributions were determined by high-temperature gel permeation chromatography using polypropylene for GPC calibration. A Varian UI 300 spectrometer was used to perform ^{13}C NMR measurements; 180−350 mg of each sample was dissolved in 2.5 mL of *o*-dichlorobenzene/10 vol % benzene-d_6 in a 10 mm tube. The spectra were measured at 135 °C using acquisition times of 1 s, 12 s additional delays, and gated proton decoupling.

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Supporting Information Available: Text detailing the procedure for the monomer feed composition determination (3 pages). Ordering information is given on any current masthead page.

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