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Articles

Synthesis of Branched Polyethylene from Ethylene by Tandem Action of Iron and Zirconium Single Site Catalysts

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ABSTRACT: The synthesis of low-density polyethylene from ethylene as the only monomer feed has been investigated as an alternative route to branched polyethylene and to obtain new materials with different properties, avoiding the need to feed 1-alkenes into the polymerization process. The details of the evaluation of two combination catalyst systems based on single site catalysts are discussed. The {[(2-ArN═C(Me))$_2$C$_5$H$_3$N]FeCl$_2$} (Ar = 2-C$_6$H$_4$(Et)) compound, designated as catalyst **1**, oligomerizes ethylene to produce linear α-olefins with high selectivity, and Me$_2$SiInd$_2$ZrCl$_2$ (**2**) or EtInd$_2$ZrCl$_2$ (**3**) are used as catalysts that incorporate the α-olefins in the polymer. For catalyst **1** in the presence of methylaluminoxane (MAO) and ethylene, a wide range of α-olefin products were found, both soluble and insoluble. Also, tandem catalyst combinations **1** and **2** or **1** and **3** in the presence of ethylene alone can readily produce branched polyethylene with levels of 1−4 branches per 100 units of ethylene. A change in activity was found for variations in the Fe/Zr ratio for both systems, with lower activity but higher frequency of branching in the polymer backbone for catalyst **2**. The final product obtained by the **1**/**3**/MAO systems, however, shows a more homogeneous structure as determined by DSC and GPC.

Introduction

Advances in the design of single site catalysts are providing an ever growing menu of metal−ligand combinations suitable for catalyzing the polymerization of olefins.[1] These catalysts enable control over the polymerization reaction and therefore of important bulk properties of the resulting polymer. An excellent body of mechanistic work also exists that provides insight into how the active site structure influences the elementary steps of the polymerization process. Overall, single site technology is making a considerable impact on the commercial processes that produce these commodity products.[2]

Modified polymerization catalysts are available that cleanly convert ethylene into 1-alkenes without loss of affinity toward the monomer.[3] It is of considerable interest to coordinate the action of these oligomerization reactions with polymerization catalysts that effectively incorporate 1-alkenes into the growing polyethylene chain. Coordination of this action should enable the synthesis of branched polyethylene from an ethylene feedstock, in particular using combinations of homogeneous nickel catalysts for α-olefin synthesis and chromium, titanium, or metallocene catalysts for α-olefin incorporation.[4] Other examples of the tandem approach to produce branched polyethylene include the use of the boratabenzene-based oligomerization catalyst (C$_5$H$_5$B−OEt)$_2$ZrCl$_2$/MAO[3] (MAO = methylaluminoxane) with [(η^5-C$_5$Me$_4$)SiMe$_2$(η^1-NCMe$_3$)]TiCl$_2$/MAO[5,6] and systems using [(C$_6$H$_5$)$_2$PC$_6$H$_4$C(OB(C$_6$F$_5$)$_3$)O-κ^2P,O]Ni(η^3-CH$_2$-CMeCH$_2$) with {[(η^5-C$_5$Me$_4$)SiMe$_2$(η^1-NCMe$_3$)]TiMe}-{MeB(C$_6$F$_5$)$_3$}.[7]

In view of the variety of performances achievable with single site catalysts, it would be of interest to elucidate the reactivity and structural attributes of catalysts that function as complementary pairs in a tandem polymerization reaction. In this contribution we present a study that probes how the iron catalyst {[(2-ArN═C(Me))$_2$C$_5$H$_3$N]FeCl$_2$}/MAO (**1**/MAO) can be coupled with the group 4 metallocene catalysts Me$_2$SiInd$_2$ZrCl$_2$/MAO (**2**/MAO) and EtInd$_2$ZrCl$_2$/MAO (**3**/MAO) to produce branched polyethylene. The **1**/MAO combination was chosen because it is known to be highly selective for the production of 1-alkenes and also because the distribution of the generated alkenes is independent of ethylene pressure.[8] The metallocenes **2** and **3** were chosen on the basis of our previous studies of their ability to copolymerize 1-octadecene and ethylene.[9]

Results and Discussion

Reactivity Profile of Individual Catalysts. The reactivities toward ethylene of compounds **1**, **2**, and **3** when activated using MAO have been reported in the literature.[8,9] In this section, however, we report on the performances obtained under our experimental condi-

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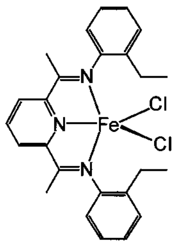

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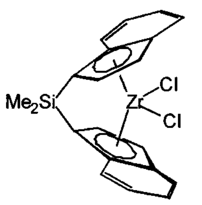

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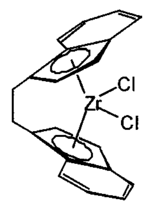

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tions. These measurements will provide a baseline measure when we examine the performance of dual catalyst systems. Consistent with previous reports **1**/MAO oligomerizes ethylene to linear α-olefins. Under our reaction conditions two fraction were obtained: 75 wt % of insoluble material and 25 wt % of soluble oils. Table 1 shows the results for two concentrations of catalyst **1**. Their evaluation showed an increase in the fraction of insoluble product at higher concentrations of Fe in the reactor and a decrease in the catalytic activity. The high reproducibility of the results should be pointed out.

During the 30 min of reaction time a noticeable decrease in the catalyst's activity was seen. It was also seen that this behavior is independent of the concentration of catalyst **1** in the reactor. Precipitation occurs after 5 min of reaction time, and changing the reaction temperature to 25 °C results in an increase of the soluble fraction, maintaining similar activity.

The products obtained by these catalysts were characterized by ^{1}H and ^{13}C NMR spectroscopy. Both fractions (insoluble and soluble) are made mainly of linear α-olefins as is shown in Figure 1, corresponding to sample RBFeN5: (a) insoluble fraction and (b) soluble fraction. On the other hand, considering that at an Al/Fe ratio of 2000 chain transfer can occur with the cocatalyst, and therefore saturated chains (alkanes) can be produced which could be found mainly in the lower molecular weight fraction (soluble fraction),[8b] an exhaustive characterization was also made of those samples using ^{1}H NMR. The results showed that under these conditions the soluble fraction is made up mainly of α-olefins with 20 wt % of alkanes. From Figure 1b was calculated the percentage of alkanes, taken the difference between the integrals of peaks 3, 4, and 5 corresponding to the allylic and vinylic protons of the α-olefin and the integral of peak 1 corresponding to the methyl protons (3H) of α-olefins as well as to the methyl protons (6H) of the alkanes. The number-average molecular weights (M_n) of both fractions were also determined using the same techniques (^{13}C and ^{1}H NMR) and were found to be about 2000 g/mol for the insoluble fractions and about 500 g/mol for the soluble ones, while the GPC analysis of the insoluble fraction, that is shown in Figure 2, revealed a molecular weight (M_w) of 11 000 and a polydispersity of 5.2. DSC analysis made to this sample showed a melting peak at 127 °C.

It is noteworthy that Brookhart reports that only soluble 1-alkenes are obtained when using MMAO (a modified version of MAO) with a lower Al/Fe ratio of 600−800 and more concentrated conditions (2.2×10^{-6} mol of Fe in 50 mL of toluene[8a]). The higher molecular weight fraction obtained under our conditions may be due to the different concentrations of **1** and to the different characteristics of the MAO used. Additionally, Gibson has shown that the molecular weights of the products obtained with this family of Fe catalysts are highly dependent on the Al/Fe ratios.[8b]

Conventional Copolymerizations. We have recently shown that the presence of comonomers such as 1-hexene or 1-octadecene increases the consumption of ethylene by **2**/MAO and **3**/MAO.[9] In Table 2 are presented the differences in catalytic activity and in comonomer content in the polymer chain obtained with these two catalysts.

Thus, for **3**/MAO under conditions similar to those of the reactions described above for the Fe catalyst, but in the presence of 1-octadecene at 0.06 and 0.33 M concentrations, activities of 32 000 and 62 000 kg of polymer (mol of Zr h bar)$^{-1}$, respectively, were obtained. Comonomer incorporation levels of 1.1 and 5.7 mol % as determined by ^{13}C NMR were found. In all cases, analysis by GPC and DSC shows that the molecular weight and the melting point of the material decreases with increasing 1-octadecene incorporation. In the case of **2**/MAO, at 1-octadecene concentrations of 0.06 and 0.33 M, activities of 24 000 and 29 000 kg of polymer (mol of Zr h bar)$^{-1}$, respectively, are obtained. These conditions lead to incorporation levels of 1.8 and 8.4 mol %. Therefore, relative to **2**/MAO, the **3**/MAO combination leads to greater consumption of ethylene but less efficient incorporation of 1-alkene.

Combined Action of Iron + Zirconium Catalysts. The efficient combination in a single reactor of oligomerization and copolymerization catalysts should lead to the formation of branched polyethylene from ethylene. The overall strategy for **1** + **2** or **1**+ **3** tandem catalyst systems is shown in Scheme 1.[6,7]

The reactions of ethylene with different catalyst combinations were carried out as follows: Stock solutions of **2** and **3** of specific concentration were made in toluene. Compound **1** showed poor solubility in aromatic solvents but could be dissolved in the MAO solutions, having an Al/Fe ratio on the order of 300. The appropriate volumes of stock solutions were then added to a glass reactor precharged with toluene and the rest of the MAO, which was thermostated and saturated under 2 bar of ethylene. The reaction was allowed to proceed for 30 min. The vessel was then depressurized, the solution quenched with aqueous base, and the polymer collected by filtration. After washing with acetone, the resulting polymers were dried under vacuum for 6 h at 60 °C.

A summary of the results obtained for the differents **1**/**2**/MAO/C_2H_4 and **1**/**3**/MAO/C_2H_4 combinations is given in Table 3 and Table 4, respectively.

Analyzing Table 3, it was found that, for a given concentration of Zr, increasing the Fe/Zr ratio leads to a reduction in the activity. Comparison of entries 1 and 4 shows that the activity decreases at higher total metal concentration and constant Fe/Zr ratio.

Polymerizations carried out with **1**/**3**/MAO/C_2H_4 combinations are summarized in Table 4. Relative to **1**/**2**/MAO combinations, a larger amount of ethylene was consumed. Additionally, the same trend was observed for this system with respect to catalyst content, which means that the increase in the Fe/Zr ratio decreases the activity, and when the total metal concentration is raised, a lower activity is observed.

Polymer Properties. a. Content of Branching. ^{13}C NMR data for the polymers obtained are consistent with a branched structure. For this combination, the percentage branching increases with increasing Fe/Zr ratio. A typical ^{13}C NMR spectrum, corresponding to

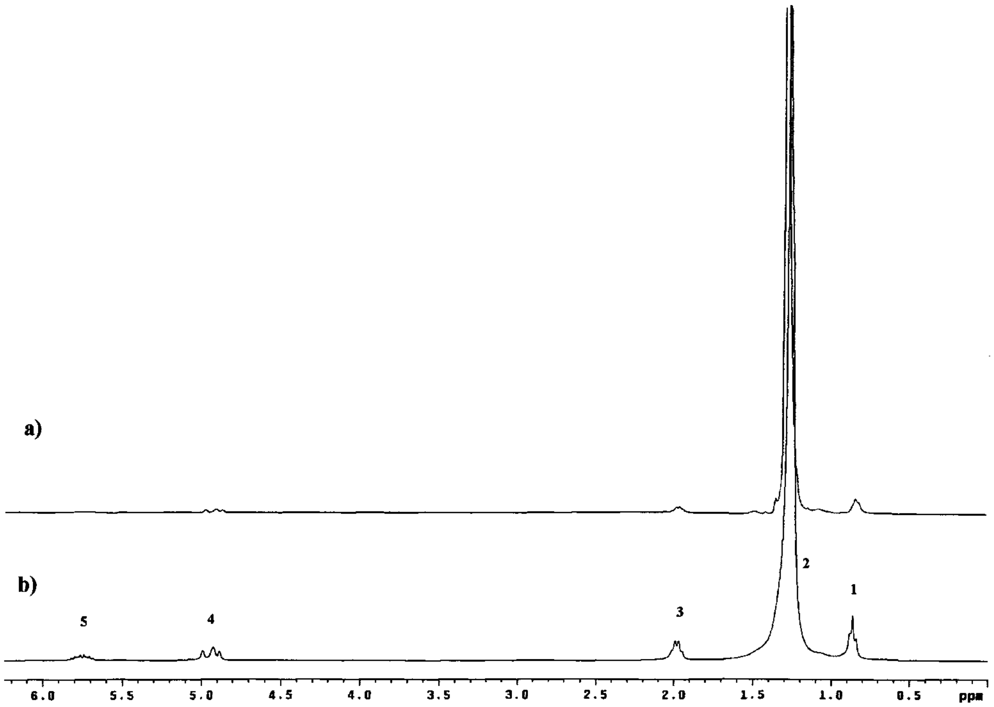

Figure 1. ^{1}H NMR spectrum of sample RbFeN5 obtained with catalyst **1**: insoluble fraction (a) and soluble fraction (b).

Table 1. Catalytic Behavior of Catalyst 1 in the Presence of MAO for Ethylene Polymerization[a]

sample	[Fe] (M × 10^6)	soluble fraction (g)	insoluble fraction (g)	activity [kg/(mol of Fe h bar)][b]
RBFeN3	1.56	6.5	19.30	16 538
RBFeN4	1.56	6.3	21.57	17 865
RBFeN5	2.53	6.7	27.62	13 565
RBFeN6	2.53	6.2	27.84	13 454

[a] Reaction conditions: Büchi reactor, 1 L; toluene, 500 mL; temperature, 60 °C; Al/Fe, 2000; ethylene pressure, 2 bar; stirrer rate, 500 rpm; polymerization time, 30 min. [b] Activity considering the soluble and insoluble fractions.

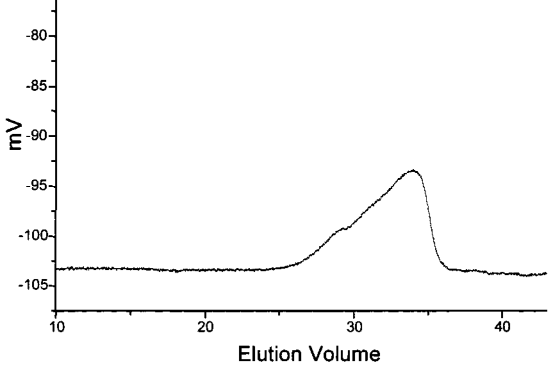

Figure 2. GPC trace of the insoluble product obtained by **1**/MAO.

products coming from Tables 3 and 4, entries 4 and 2, respectively, is shown in Figure 3. The signals due to branching (ethyl, butyl, and longer) are well-defined, and their intensity increases with increasing Fe content. The last column of Tables 3 and 4 contains the percentage of branching calculated by using a published method;[10] more details with respect to the particular study will be given in a forthcoming paper.[11]

The presence of ethyl branches is confirmed by resonances at 11.13, 26.59, and 39.56 ppm, corresponding to carbon atoms $1B_2$, $2B_2$, and brB_2. The presence of butyl branches is confirmed by the peak at 23.37 ppm, corresponding to carbon $2B_4$. The presence of long branches can be detected by the signals at 14.05, 32.16, and 38.10 ppm, corresponding to carbon atoms $1B_n$, $3B_n$, and brB_n. The first and last signals are superposed to the signals of carbons $1B_4$ and brB_4 from butyl branches. It is possible to identify the presence of long branches comparing the integrals of those peaks with that of the peak at 23.37 ppm corresponding to carbon $2B_4$ from butyl branches. The $1B_n$, $2B_n$, and $3B_n$ signals are also characteristic of α-olefins that are not incorporated. It was also possible to determine the presence of α-olefins in the product by evaluating the integral of the signals at 29.29 and 29.42 ppm marked in Figure 3b (entry 4, Table 3), which are not present in the spectrum of Figure 3a, corresponding to (entry 2, Table 4). These signals correspond to aliphatic carbons two and three bonds away from the olefinic carbon atom, respectively.

b. Molecular Weight Distribution. The polymers produced by **1**/**2**/MAO/C_2H_4 combinations are characterized by a broad and bimodal molecular weight distribution centered at M_w 70 000 and 1500 (Figure 4). The low molecular weight fraction becomes more pronounced as the Fe/Zr ratio increases, giving compositions similar to those of the product obtained with the Fe catalyst. These data indicate that a significant fraction of the products coming from the iron site are not incorporated into the growing polyethylene chain governed by the zirconium site. These systems also showed difficulties of controlling certain properties of the polymers, since the production of long-chain α-olefins is favored. Figure 5 shows the GPC traces for the polymers obtained with the **1**/**3**/MAO/C_2H_4 system. Comparing with the product obtained using **1**/**2**/MAO/C_2H_4 systems, these are characterized by presenting a monomodal narrow molecular weight, in all cases centered at M_w of 60 000. The branching of the backbone, which increases with increasing concentration of catalyst **1**, and the monomodal weight distribution strongly support the formation of branched polyethylene and an efficient conversion of the

Table 2. Effect of Comonomer Concentration on the Catalytic Activity and Content of 1-Octadecene and 1-Hexene in Ethylene Copolymers[a]

		$Et(Ind)_2ZrCl_2$		$Me_2Si(Ind)_2ZrCl_2$	
	[comonomer] (mol/L)	activity × 10^{-3} (kg/(mol of Zr h bar))	comonomer incorporated (mol %)	activity × 10^{-3} (kg/(mol of Zr h bar))	comonomer incorporated (mol %)
1-octadecene	0	18.4	0	17.1	0
	0.06	32.3	1.1	24.0	1.8
	0.12	48.2	2.0	33.9	4.0
	0.23	56.6	4.7		
	0.33	61.6	5.7	28.9	8.4
1-hexene	0.16	35.1	8.0	18.0	6.2
	0.31	48.9	9.1	30.9	8.7
	0.45	42.0	12.0		
	0.59	28.1	14.3	18.9	14.9

[a] Reaction conditions: solvent, toluene; *n*(Zr), 1.9×10^{-6} mol; Al/Zr, 2620; temperature, 60 °C; polymerization time, 30 min; ethylene pressure, 1.6 bar.

Scheme 1

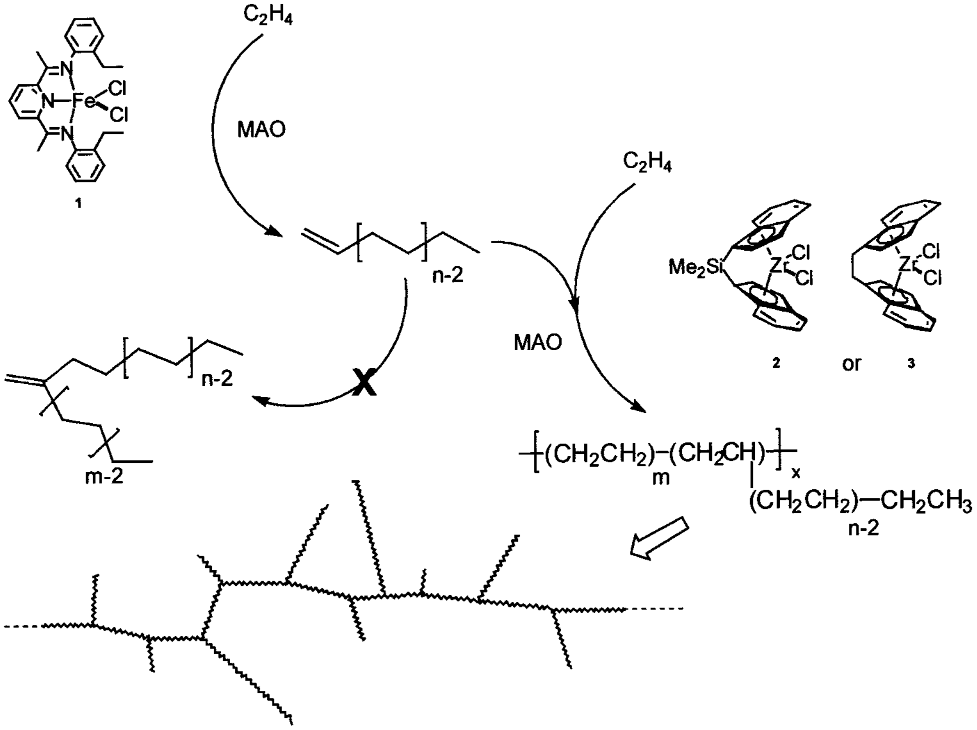

Table 3. Olefin Polymerization Date 1/2/MAO

	reaction conditions[a]				polymer properties				
entry	Al/Zr	[Fe] (M × 10^6)	[Zr] (M × 10^7)	Fe/Zr	activity[b]	T_m (°C)[c]	$M_w \times 10^{-3}$	M_w/M_n	branching (mol %)[d]
1	7800	1.03	2.3	4.5	20 933	107, 123	55.9	16.1	2.4
2	17230	2.21	2.3	10	9 850	108, 125	29.9	13.2	3
3	5200	1.6	5.7	2.9	19 455	100, 121	83.9	15.6	2.9
4	5840	2.55	5.7	4.5	12 090	101, 124	57.3	15.2	4
5	3350	1.6	8.1	2	12 675	110, 120	80.5	9.1	2.3

[a] Reaction conditions: solvent, toluene; polymerization time, 30 min; stirrer rate, 500 rpm; pressure, 2 bar; temperature, 60 °C; Al/Fe, 2000. [b] In kg of polymer/(mol of Zr + mol of Fe h bar). [c] Melting point determined by DSC, two transitions present. [d] In mol of branching per 100 ethylene units.

monomer to polymeric material.

c. Thermal Properties. DSC analysis reveals that the products obtained from different metal combinations possess different thermal properties. Figure 6 shows that for polymers obtained with **1**/**2**/MAO two peaks were present. In contrast, the polymers from **1**/**3**/MAO show only a single transition (Figure 7), consistent with a more homogeneous product structure. Furthermore, the melting temperature of the materials from the **1**/**3**/MAO reactions decreases as the Fe/Zr ratio increases. Thus, the thermal properties are consistent with the NMR and GPC data and show that the properties of the materials can be controlled by simply adjusting the ratio of the catalysts (Fe/Zr).

Summary and Conclusions

Under the reaction conditions in which this study was carried out with Fe catalyst, the main products are 1-alkenes. We have shown that it is possible to incorporate the 1-alkenes produced by the **1**/MAO/C_2H_4

Table 4. Olefin Polymerization Date 1/3/MAO

	reaction conditions[a]				polymer properties				
entry	Al/Zr	[Fe] (M × 10^6)	[Zr] (M × 10^7)	Fe/Zr	activity[b]	T_m (°C)[c]	$M_w \times 10^{-3}$	M_w/M_n	branching (mol %)[d]
1	7300	1.05	2.3	4.6	34 060	124	81.2	1.68	2
2	15400	2.19	2.3	9.3	16 850	112	65.1	1.65	2.8
3	3730	1.03	5.3	1.9	27 884	119	74.6	1.56	1.8
4	6460	1.59	5.3	3.1	18 259	119	81.8	1.61	2.2
5	8000	2.5	5.3	4.7	16 180	117	68.7	1.68	2.5
6	6200	1.66	8.1	2	20 850	121	81.1	1.91	1.8

[a] Reaction conditions: solvent, toluene; polymerization time, 30 min; stirrer rate, 500 rpm; pressure, 2 bar; temperature, 60 °C; Al/Fe, 2000. [b] In kg of polymer/(mol of Zr + mol of Fe h bar). [c] Melting point determined by DSC. [d] In mol of branching per 100 ethylene units.

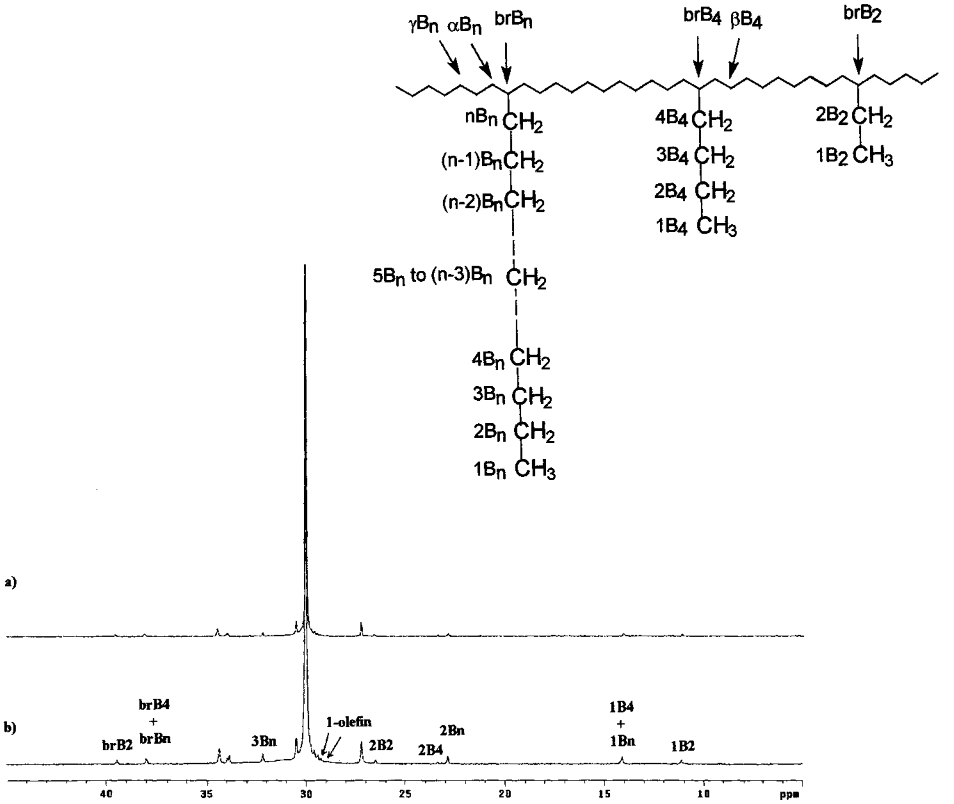

Figure 3. Branched polyethylene ^{13}C NMR spectrum: entry 2, Table 4a; entry 4, Table 3.

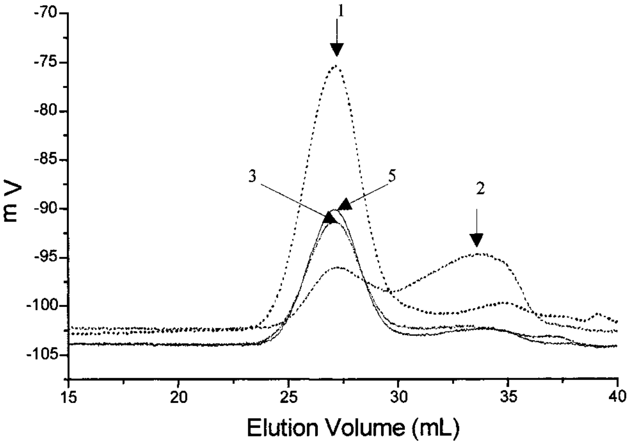

Figure 4. GPC Traces of the product obtained with **1**/**2**/MAO/C_2H_4, entries: 1 (• • •); 2 (- - -); 3 (— • • —); 5 (—).

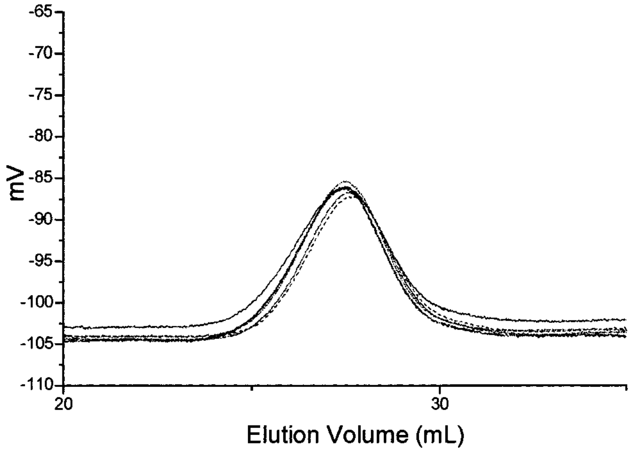

Figure 5. GPC Trace of the product obtained with **1**/**3**/MAO/C_2H_4, for different sets of Fe/Zr ratios, entries: 1 (• • •); 2 (- - -); 3 (— • • —); 5 (— • —); 6 (—).

system into a growing polyethylene chain at a group 4 metallocene site. Higher activity but less incorporation was observed with **1**/**3**/MAO compared to **1**/**2**/MAO. This is in agreement with what is found in traditional copolymerization of ethylene and α-olefins (1-hexene, 1-octadecene, etc.) using only **2**/MAO or **3**/MAO catalysts. However, the **1**/**3**/MAO systems which give less

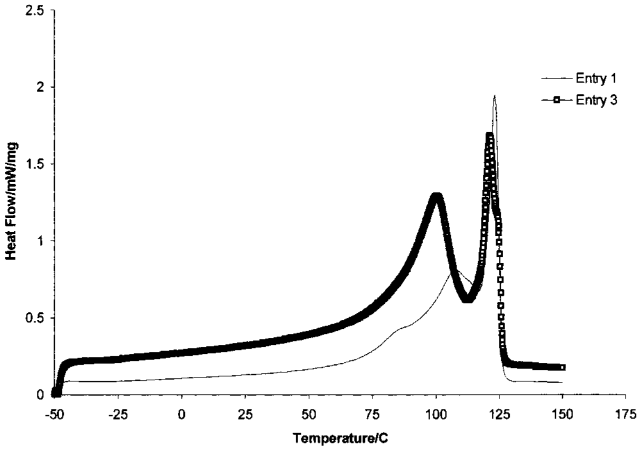

Figure 6. DSC of polymer obtained with **1**/**2**/MAO/C_2H_4.

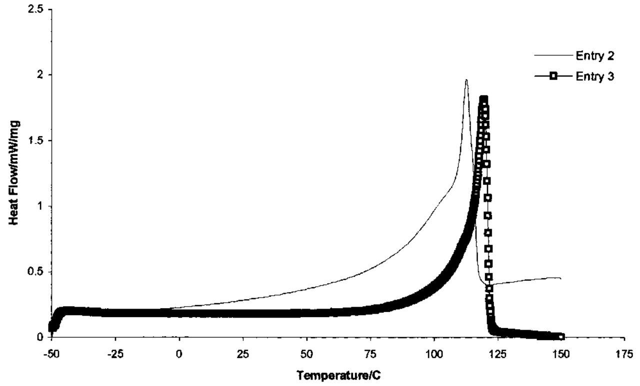

Figure 7. DSC of product obtained with **1**/**3**/MAO/C_2H_4.

branching in the product lead to more homogeneous materials. Thermal, GPC, and ^{13}C NMR spectroscopy analysis of the polymers produced by these systems are consistent with the characteristics already mentioned. The presence of a heterogeneous product when **1**/**2**/MAO/C_2H_4 systems was used can be associated with incomplete incorporation of the α-olefins produced by the Fe catalysts.

One explanation for this behavior can be associated with the lower total conversion of ethylene (less activity) to polymer shown by **1**/**2**/MAO/C_2H_4; this was also observed in the copolymerization reactions of ethylene with 1-hexene and 1-octadecene, as was shown in Table 2, when comparing catalysts **2** and **3**. We assume that, even though there is no chemical interference that could lead to the generation of new active sites, the two active sites may compete for ethylene, favoring the formation of α-olefins in the presence of metallocene catalyst **2** (**1**/**2**/MAO/C_2H_4) as compared to the **1**/**3**/MAO system which showed higher activity, doing that the total amount of α-olefins generated must be less, and therefore, all the α-olefins produced have been incorporated.

Finally, we can confirm that, for these tandem homogeneous catalysts to work in a predictable manner, there must be negligible interference between the catalytic centers.

Experimental Section

General Details. Toluene was purified by refluxing over metallic sodium, using benzophenone as an indicator. Polymerization grade ethylene was deoxygenated and dried by passing though columns of BASF R3-11 catalyst and 4 Å molecular sieves. The cocatalyst 10% methylaluminoxane (MAO) in toluene was obtained from Witco. $\{[(2\text{-ArN}{=}C(CH_3))_2{-}C_5H_3N]FeCl_2\}$ (Ar = 2-C_6H_4(Et)) (**1**) was synthesized using procedures from the literature.[8a] The *rac*-$EtInd_2ZrCl_2$ (**2**) and *rac*-$(CH_3)_2SiInd_2ZrCl_2$ (**3**) compounds were supplied by Boulder Scientific Company and used as received.

Homopolymerization. The polymerization was carried out in a 1 L Buchi autoclave reactor. Toluene (500 mL) and MAO were introduced into the reactor under an inert nitrogen atmosphere. The reactor was partially evacuated and then purged with ethylene. Mechanical stirring was kept constant at 500 rpm, and the ethylene pressure was adjusted to 2 bar for 5 min before introducing the catalyst. 2.55×10^{-6} mol of catalyst **1** dissolved in toluene in the presence of MAO (Al/Fe = 400) was pumped into the reactor to initiate the polymerization. Ethylene pressure and reactor temperature (60 °C) were monitored and kept constant throughout the polymerization. Consumption of ethylene was followed continuously using a mass flow controller connected to a computer.

Turning the ethylene feed off and relieving the pressure stopped the polymerization. The reaction mixture was poured into a solution of NaOH/methanol (2 vol %). The insoluble polymer product was recovered by filtration and washed with NaOH/methanol solution and then with acetone. The soluble product in the solution phase was isolated by removal of the solvent in vacuo.

Polymerizations using **2** and **3** were carried out in a similar way using 2.3×10^{-7} mol of Zr previously dissolved in toluene in the absence of MAO, and a similar procedure was followed for the synthesis of the polymers.

Conventional Copolymerization. All copolymerizations were carried out in a 500 mL glass reactor with toluene as solvent at a reaction temperature of 60 °C. The reagents were introduced in the reactor in the following order: toluene, comonomer, MAO, and the required amount of catalyst solution. The reaction mixture was degassed, and then ethylene was introduced until a pressure of 1.6 bar was reached. After 30 min the polymerization was stopped by addition of 2 vol % of HCl/methanol solution. The polymer was recovered by filtration, washed first with HCl/methanol solution and then with acetone until removal of all the unreacted comononer, and finally dried in a vacuum at 60 °C.

Copolymerization of Ethylene with Catalyst Mixtures. A procedure similar to that of the homopolymerization described above was carried out. The Fe and Zr (Fe/Zr: 10 to 2 ratios) mixtures were introduced into the reactor at the same time.

Polymer Characterization. ^{13}C NMR spectra were obtained at 120 °C on a Varian Inova 300, operating at 75 MHz. Sample solutions of the polymer were prepared in *o*-dichlorobenzene and benzene-d_6 (20% v/v) in a 5 mm sample tube. The deuterated solvent was used to provide the internal lock signal. The chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken as 30.00 ppm from Me_4Si. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. Under those conditions the spectra are 90% quantitative if only carbon atoms that have a relaxation time (T_1) of less than 2.0 are taken into account.[12]

Gel permeation chromatography (GPC) was carried out on a Waters model 150 C instrument equipped with a refractive index detector and a set of three columns, Styragel HT type (HT3, HT4, HT6). 1,2,4-Trichlorobenzene was used as solvent. The analyses were performed at 140 °C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene, polypropylene, and polyethylene.

The calorimetric analyses were carried out on a Perkin-Elmer DSC7 calorimeter, connected to a cooling system, and calibrated with different standards. The sample mass ranged from 7 to 10 mg. Differential scanning calorimetry (DSC) melting curves were recorded at a rate of 10 °C/min. The melting temperature (T_m) value reported in Tables 3 and 4 was obtained from the second heating curve.

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