NMR Study of Branched Polyethylenes Obtained with Combined Fe and Zr Catalysts

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ABSTRACT: The products obtained with the system $\{[(ArN{=}C(Me))_2C_5H_3N]FeCl_2\}$/MAO (Ar = 2-$C_6H_4$-(Et)) (**1**) and the ones obtained by the use of **1** in conjunction with $Me_2SiInd_2ZrCl_2$/MAO (**2**) or $EtInd_2ZrCl_2$/MAO (**3**) were completely characterized by ^1H NMR and ^{13}C NMR. Catalyst **1** gives mainly linear α-olefins of molecular weights close to 2000 g/mol and a low amount of alkanes. The use of **1** with **2** or **3** using only ethylene as monomer gives branched polyethylene with ethyl, butyl, and mainly long branches. Some amount of unreacted α-olefin was also found in some cases, especially in reactions where a high ratio Fe to Zr was used.

Introduction

Polyethylene copolymers such as linear low-density polyethylene (LLDPE) have grown in importance over the recent years. Estimates show that this development will continue, and polyolefins will displace some of the commercial plastics of today that are less easy to manufacture or pose more problems for recycling or waste disposal.[1] Many catalytic systems are used to produce polyethylene with different amounts and types of comonomers. Historically, heterogeneous polymerization catalysts (Ziegler−Natta) have been the workhorses of the polymer industry. During the past two decades an extraordinary amount of research has been directed toward the development of homogeneous, single-site polymerization catalysts.[2] Single-site catalysts have the advantage of producing homogeneous polyolefins with narrow distributions of molecular weight and comonomer. Metallocene catalysts, especially zirconocenes, treated with methylaluminoxane (MAO) have been used extensively to obtain polyethylene copolymers with different amounts and types of branching.[3−6] Branching in polyethylene directly affects many physical properties such as density, rigidity, hardness, permeability, and environmental stress crack resistance. In contrast to multisite catalysts, the metallocenes can incorporate vinyl-terminated oligo(ethene) produced by β-hydride elimination, to produce long-chain branches.[7] The effects of long-chain branching (LCB) on the mechanical and rheological properties of polymers are known to be quite remarkable. LCB polyethylene with a narrow molecular weight distribution provides an excellent combination of high mechanical strength and good processability.[8]

An alternative route for the synthesis of branched polyethylene at low pressure consists of using a catalytic system capable of simultaneously oligomerizing and copolymerizing ethylene. These catalytic systems which allow the synthesis of branched polyethylene have the main advantage of requiring only ethylene as a monomer in the feed. This system may be constituted by two active sites: one for oligomerization and other for copolymerization which are compatible between themselves and with the cocatalyst. That is, they should not interfere chemically when operating under certain reaction conditions: temperature, monomer pressure, or solvent.

Moreover, the activity of the component, which oligomerizes ethylene, must be such as to give rise to a sufficient concentration of comonomer for the formation of polyethylene with a given content of branches.

Recent reports on the use of combined catalysts for producing branched polyethylene from ethylene as the only monomer in the feed show the coordinated action of nickel catalysts which oligomerize ethylene to α-olefins and chromium, titanium, or metallocene catalysts for incorporating the α-olefins in the polymer chain.[9]

More recent examples include the use of boratobenzene catalysts such as $(C_5H_5)B{-}OEt)_2ZrCl_2$/MAO to oligomerize ethylene[10] with $[\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)]TiCl_2$/MAO[11,12] and systems such as $[(C_6H_5)_2PC_6H_4C(OB(C_6F_5)_3)O{-}K^2P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ with $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)]TiCH_3\}\{MeB((C_6F_5)_3\}$.[13] In the latter system the MAO is no longer required and offers more control over the polymer structure.

The correct analysis of branches in polyethylene is very important to correlate the molecular structure with physical properties. ^{13}C NMR is undoubtedly the best technique to investigate the microstructure of those materials, and it has been used extensively to characterize copolymers.[14−18] In a recent paper[19] we have shown a complete characterization of LLDPE obtained with a Brookhart type of catalyst. The presence of methyl, ethyl, propyl, butyl, and longer branches was completely assigned.

In this work we aim at using ^{13}C NMR to make an exhaustive characterization of LLDPE obtained with two catalyst systems used in conjunction: $\{[(ArN{=}C(Me))_2C_5H_3N]FeCl_2\}$/MAO (Ar = 2-$C_6H_4$(Et)) (**1**), with

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Table 1. 1-Decene ^{1}H NMR Chemical Shifts and Assignments

peak no.	chemical shift exptl (ppm)	multiplicity	assignments
1	0.80−0.85	t	$-C\mathbf{H}_3$
2	1.19−1.31	m	$-C\mathbf{H}_2-$
*	1.73	s	impurity
3	1.90−1.98	m	$-C\mathbf{H}_2-CH=$
4	4.84−4.97	m	$C\mathbf{H}_2=$
5	5.65−5.78	m	$C\mathbf{H}=$

the $Me_2SiInd_2ZrCl_2$/MAO (**2**) or $EtInd_2ZrCl_2$/MAO (**3**) systems.

Experimental Part

The polymerization procedure has been described in detail in a previous work.[20]

The ^{13}C NMR spectra were obtained at 120° C. The equipment used was 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. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. Under these conditions the spectra are 90% quantitative if only carbon atoms that have a relaxation time (T_1) of less than 2.0 s are taken into account.[21]

Results and Discussion

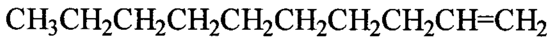
Polymerization of ethylene with **1** gives an insoluble fraction (75 wt %) and a minor product soluble fraction (25 wt %). Samples A1, A2, A3, A4, and A5 correspond to the insoluble fraction of the products recovered from two sets of homopolymerization with the Fe catalyst.

(a) Samples A1, A4, and A5 were obtained from reactions in which the role of MAO was examined by varying systematically the Al/Fe ratio from 460:1 to 2500:1. It was seen that as the ratio increases, the soluble fraction in the product also increases, with a slight decrease in the catalytic activity.

(b) Samples A2 and A3 were obtained from reactions at an Al/Fe ratio of 700, varying the temperature from 25 to 60 °C, respectively. It was seen that as the temperature increases, the soluble fraction in the product decreases, with a slight decrease in the catalytic activity.

Samples B1 and B2, corresponding to soluble fractions, were obtained from reactions at an Al/Fe ratio of 2000 and temperature of 60 °C.

To make an exhaustive characterization of linear α-olefins by ^{1}H NMR and ^{13}C NMR, 1-decene was used as model compound. ^{1}H NMR and ^{13}C NMR spectra of 1-decene are shown in Figures 1a and 2a and the corresponding assignments in Tables 1 and 2. Carbon 1 is the methyl carbon and the terminal vinylic carbon is 10, as shown in the following scheme:



$$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_2}\overset{7}{CH_2}\overset{8}{CH_2}\overset{9}{CH}=\overset{10}{CH_2}$$

1-decene

Theoretical ^{13}C chemical shifts of aliphatic carbons have been calculated using the Lindeman and Adams rules[22] and the shifts of vinyl and allyl carbons using the corresponding empirical additive rules for these types of compounds.[23,24] Carbon 4 (peak v, Table 2) was assigned at 29.58 ppm although its calculated chemical shift (29.71 ppm) was lower than those of C_7 (30.0 ppm) and C_6 (30.40 ppm) because it is also present in branched polyethylene and was identified at this shift as will be shown later.

Table 2. 1-Decene ^{13}C NMR Chemical Shifts and Assignments

peak no.	chemical shift exptl (ppm)	chemical shift calcd (ppm)	assignts
i	14.05	13.86	C_1
ii	22.86	22.65	C_2
iii	29.29	30.00	C_7
iv	29.42	30.40	C_6
v	29.58	29.71	C_4
vi	29.81	30.40	C_5
vii	32.16	32.40	C_3
viii	34.04	33.00	C_8
ix	114.20	115.1	C_{10}
x	139.11	139.60	C_9

Table 3. α-Olefin ^{1}H NMR Chemical Shifts and Assignments

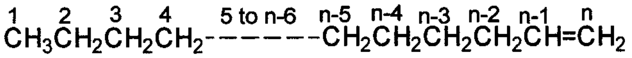
peak no.	chemical shift exptl (ppm)	multiplicity	assignts
1	0.825	m	$-C\mathbf{H}_3$
2	1.20−1.32	m	$-(C\mathbf{H}_2-)_n$
3	1.97	m	$-C\mathbf{H}_2-CH=$
4	4.84−4.99	m	$C\mathbf{H}_2=$
5	5.64−5.71	m	$C\mathbf{H}=$

Table 4. α-Olefin ^{13}C NMR Chemical Shifts and Assignments

peak no.	chemical shift exptl (ppm)	chemical shift calcd (ppm)	assignments
I	14.05	13.86	$1C_n$
II	22.86	22.65	$2C_n$
III	29.29	30.00	$(n-3)C_n$
IV	29.42	30.40	$(n-4)C_n$
V	29.58	29.71	$4C_n$
VI	29.70	30.40	$(n-5)C_n$
VII	30.00	29.96	5 to $(n-6)C_n$
VIII	32.17	32.40	$3C_n$
IX	33.93	33.00	$(n-2)C_n$
X	114.20	115.1	nC_n
XI	139.11	139.60	$(n-1)C_n$

Typical ^{1}H NMR and ^{13}C NMR spectra of the products obtained in the polymerization of ethylene with Fe catalyst (**1**) are shown in Figures1b (expanded), 1c, and 2b with the assignments in Tables 3 and 4.

It can be seen that these spectra are similar to that of 1-decene, except for the main peak corresponding to the ethylene chain (peak 2 in the ^{1}H NMR and peak VII in the ^{13}C NMR spectra) corresponding to the central methylene (C_5 to C_{n-6}) as shown in the following scheme:



$$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\text{-}\overset{5\text{ to }n\text{-}6}{------}\text{-}\overset{n\text{-}5}{CH_2}\overset{n\text{-}4}{CH_2}\overset{n\text{-}3}{CH_2}\overset{n\text{-}2}{CH_2}\overset{n\text{-}1}{CH}=\overset{n}{CH_2}$$

α–olefin

Besides the presence of linear α-olefins as a result of *β*-hydride transfer reactions, it is reasonable to assume, as was already reported,[25] the presence of alkanes as a result of chain transfer to aluminum (MAO). The long-chain alkanes formed should have resonances superposed on peaks 1 and 2 in the ^{1}H NMR spectrum (Table 3) and on peaks I, II, V, VII, and VIII in the ^{13}C NMR spectrum (Table 4). It is possible to determine alkanes

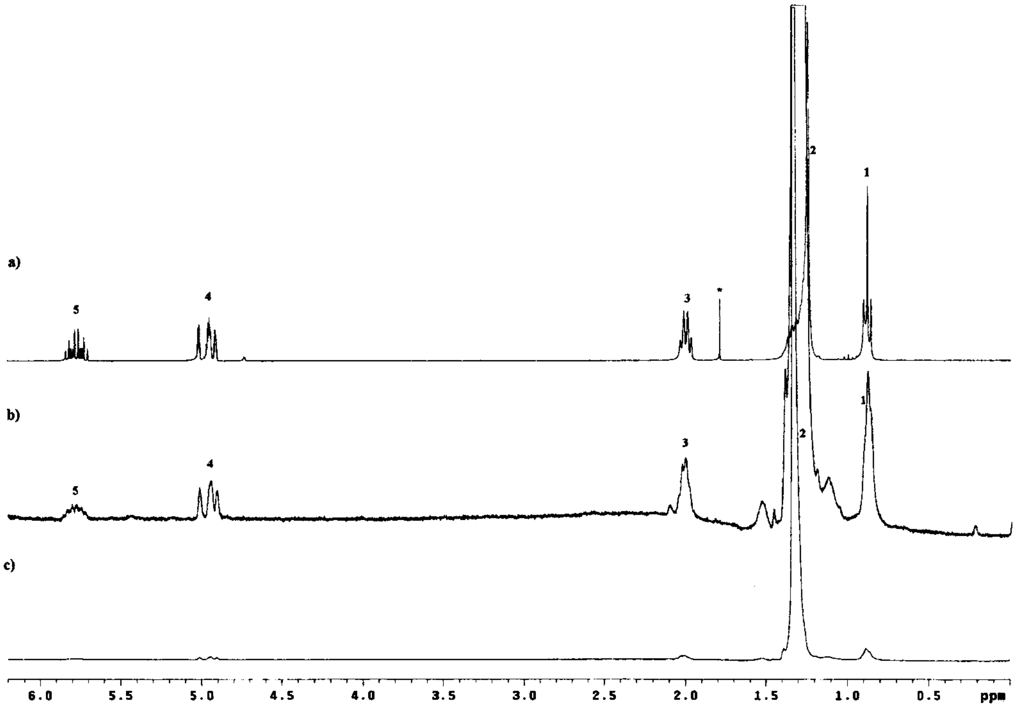


Figure 1. ^{1}H NMR spectrum of (a) 1-decene, (b) α-olefin A2 obtained with catalyst 1 (expanded), and (c) α-olefin A2 obtained with catalyst **1** (normal spectrum).

Table 5. Molecular Weights of α-Olefins and Alkanes Percentage Obtained by NMR

sample	M_n obtained by ^{1}H NMR	M_n obtained by ^{13}C NMR	alkanes (mol %)
A1	2050		2
A2	1700	2100	3
A3	1700	2100	12
A4	1800	1600	
A5	2300	2500	10
B1	600	500	25
B2	500	450	16

percentage relative to α-olefin by ^{1}H NMR using the following relationships:

$$I_{\mathrm{H\alpha-olefin}} = (I_3/2 + I_4/2 + I_5)/3$$

$$I_{\mathrm{Halkane}} = (I_1 - 3I_{\mathrm{H\alpha-olefin}})/6$$

$$\%\ \mathrm{alkane} = 100 \times I_{\mathrm{Halkane}}/(I_{\mathrm{Halkane}} + I_{\mathrm{H\alpha-olefin}})$$

I being the resonance integrals and the subscripted numbers referring to the peak numbers, as shown in Table 3.

The amount of alkanes in samples A1–A5 and B1, B2 was quantified in this manner (Table 5).

Number-average molecular weights (M_n) of α-olefins have been calculated by ^{1}H NMR and ^{13}C NMR.

M_n from ^{1}H NMR. Molecular weights from ^{1}H NMR spectra (Figure 1b and Table 3) were obtained using the average of integrals corresponding to one proton of α-olefin ($I_{\mathrm{H\alpha-olefin}}$) as was shown above.

The integral corresponding to the total H (backbone + terminals) is given by the main peak protons integral (I_2) and the 8 H that are separate from this peak, corresponding to resonances 1, 3, 4, and 5.

$$I_{\mathrm{TotalH}} = I_2 + 8I_{\mathrm{H\alpha-olefin}}$$

$I_{\mathrm{TotalH}}/I_{\mathrm{H\alpha-olefin}}$ correspond to the α-olefin total number of protons. The molecular weight of the α-olefin can be obtained from the product of the number of CH_2 present and the CH_2 mass (14 g). As there are 2 H in each CH_2, to obtain the number of methylene units present, the total number of protons must be divided by 2. Thus, the number-average molecular weight (M_n) is

$$M_n = (I_{\mathrm{TotalH}}/I_{\mathrm{H\alpha-olefin}})/2 \times 14$$

In the cases where alkanes are present, I_2 must be recalculated taking into account the percentage of alkanes.

M_n from ^{13}C NMR. Using the α-olefin ^{13}C NMR spectra (Figure 2b and Table 4), the integral corresponding to one carbon can be obtained using the isolated signals II, VIII, and IX, corresponding to carbons atoms $2C_n$, $3C_n$, and allyl carbon $(n - 2)C_n$.

$$I_{1C} = (I_{\mathrm{II}} + I_{\mathrm{VIII}} + I_{\mathrm{IX}})/3$$

Carbon atom $1C_n$ is not used because terminal carbons have long relaxation times and the delay used to let all carbons return to the equilibrium state is insufficient. Carbon atoms III to V could be used, but their signals are not sufficiently isolated to have reliable integrals.

The integral corresponding to the total C (backbone + terminals) is given by the sum of integrals I_{III}, I_{IV}, I_{V}, I_{VI}, and I_{VII} (main peak), the integrals of the four aliphatic carbons out of the main peak, and the integrals of the two olefinic carbon atoms. The integral of this last six carbon atoms is equivalent to 6 I_{1C} (I_{1C} was calculated above)

$$I_{\mathrm{Total}} = (I_{\mathrm{III}} + I_{\mathrm{IV}} + I_{\mathrm{V}} + I_{\mathrm{VI}} + I_{\mathrm{VII}}) + 6I_{1C}$$

$$\alpha\text{-olefin total number of carbons} = N^{\mathrm{o}}_{\mathrm{C}} = I_{\mathrm{Total}}/I_{1C}$$

$$M_n = N^{\mathrm{o}}_{\mathrm{C}} PM_{\mathrm{CH_2}} = I_{\mathrm{Total}}/I_{1C} \times 14$$

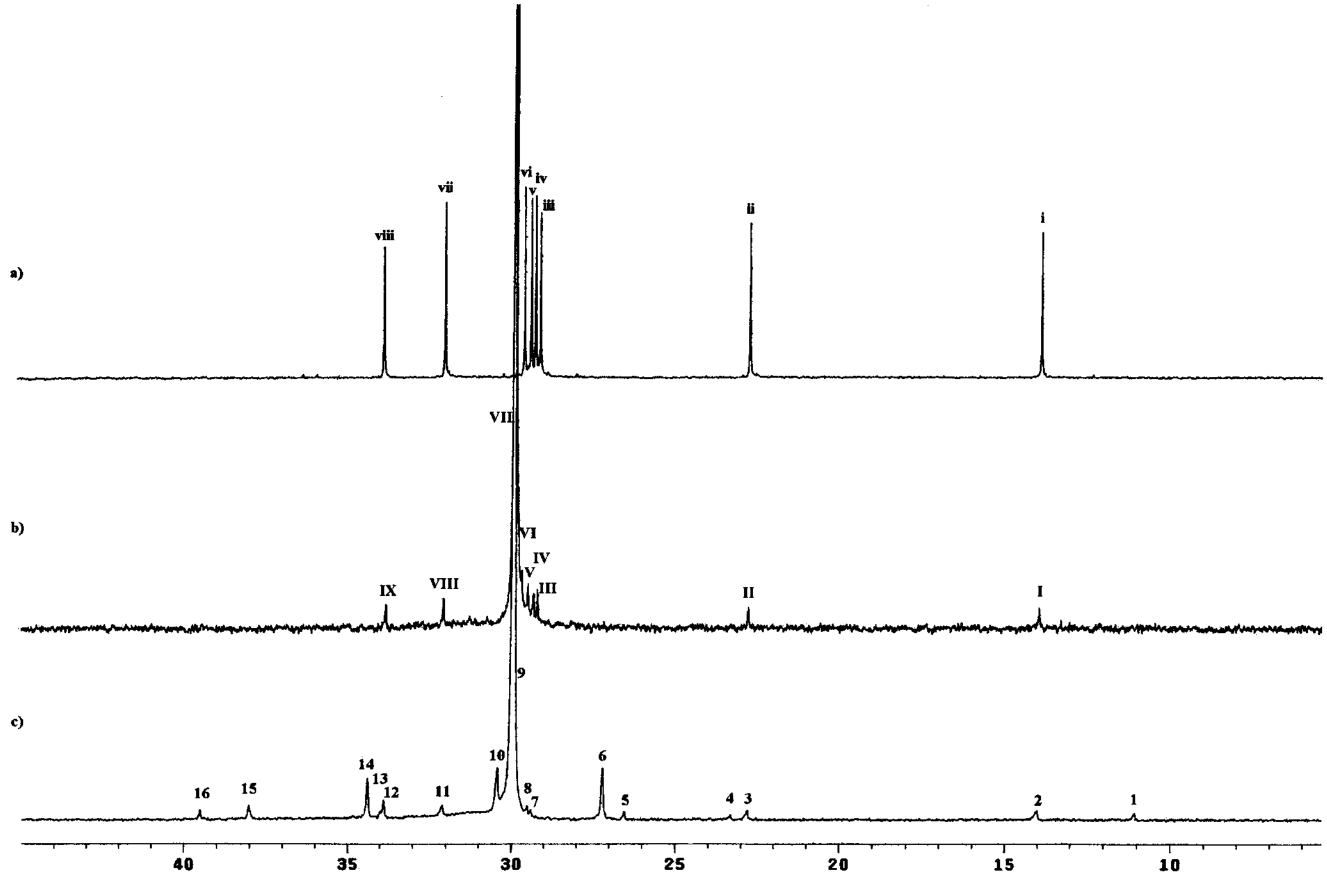


Figure 2. ^{13}C NMR spectra of (a) 1-decene, (b) the α-olefin obtained with catalyst **1** (A2), and (c) branched polyethylene obtained with the mixture of catalysts **1** and **3** (C5).

Table 6. Experimental Condition and Amount of Unreacted α-Olefin in the Branched PE[a]

entry[b]	sample	[Fe] (mol × 10^6)	[Fe]/[Zr]	unreacted α-olefin (%)
1	C1	1.03	4.5	27
2	C2	2.21	10	91
3	C3	1.6	2.9	0
4	C4	2.55	4.5	26
	C5	3.49	6.1	11
5	C6	1.6	2.0	0
1	D1	1.05	4.6	0
2	D2	2.19	9.3	13
3	D3	1.03	1.9	0
4	D4	1.59	3.1	14
5	D5	2.5	4.7	5
6	D6	1.66	2.0	0
	D7	1.59	6.8	38
	D8	2.0	8.9	4

[a] Reaction conditions: solvent = toluene; polymerization time = 30 min; stirrer rate = 500 rpm; pressure = 2 bar; temperature = 60 °C; [Al]/[Fe] = 2000. [b] Referred to numbers used in ref 20.

Table 5 shows the number-average molecular weight calculated by ^{1}H NMR and ^{13}C NMR. The results from both spectra agree reasonably well and the values are all close to 2000 g/mol for the insoluble fraction and to 500 g/mol for the soluble ones. These values are in accordance with GPC results shown in ref 20.

Study of Branched Polyethylene. Branched polyethylene obtained from ethylene as the only monomer feed through the coordinated action of **1** and **2** or **3** in the presence of MAO as cocatalyst, under the conditions given in a recent publication,[20] have been considered here for a detailed study of the branch type and content.

The names of the samples considered in this study correspond to two types: the C samples, which correspond to copolymers obtained with the **1**/**2**/MAO/C_2H_4 system and the D samples, which denote copolymers obtained with the **1**/**3**/MAO/C_2H_4 system. The reaction conditions used to obtain the polymer samples are listed in Table 6.

The nomenclature used in this work is that of Usami and Takayama[26] for isolated branches. Branches are named as xB_n, where n is the length of the branch and x is the carbon number starting from the methyl group as "1". For branch point carbons, "br" is used instead of x and the methylenes of the backbone are labeled with Greek letters.

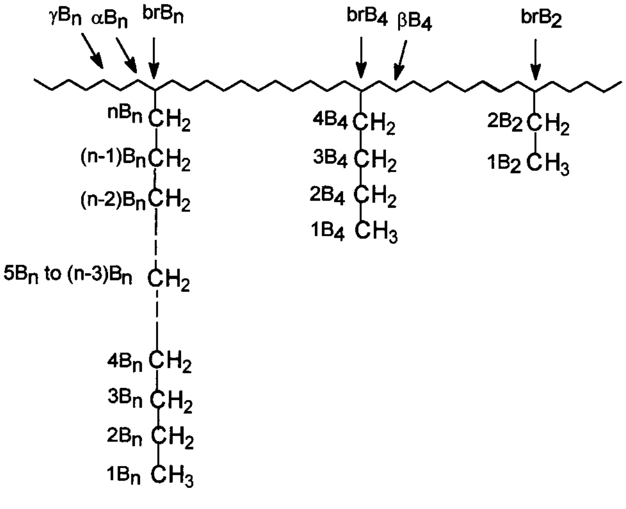


Table 7. Calculated and Observed Carbon-13 Chemical Shifts and Assignments

peak no.	chem shift exptl (ppm)	chem shift calcd[22] (ppm)	assignments
1	11.13	11.36	$1B_2$
2	14.05	13.86	$1B_4$, $1B_n$,
3	22.86	22.65	$2B_n$
4	23.37	22.90	$2B_4$
5	26.59	27.16	$2B_2$
6	27.26	27.52	βB_2 βB_4, βB_n, $(n-1)B_n$,
7	29.47	29.96	$3B_4$
8	29.58	29.71	$4B_n$
9	30.00	29.96	$\delta\delta CH_2$ (main chain) $5B_n$ to$(n-3)B_n$
10	30.48	30.21	γB_2,, γB_4, γB_n, $(n-2)B_n$
11	32.16	32.40	$3B_n$
12	33.95	34.22	αB_2
13	34.04	34.22	$4B_4$
14	34.45	34.47	αB_4 αB_n, nB_n
15	38.10	37.05	brB_4 brB_n
16	39.56	39.12	brB_2

A ^{13}C NMR spectrum of branched PE is shown in Figure 2c, and assignments are listed in Table 7.

Spectra of materials obtained by polymerization of ethylene with **1** and **2** or **3** catalysts in tandem exhibit ethyl, butyl, and long ($n \geq 6$) branches. Considering that the Zr catalyst homopolymerizes ethylene to linear polymers, shows high reactivity toward long chain α-olefins, and that the Fe catalyst produces α-olefins with molecular weights close to 2000 g/mol, it is reasonable to assume that a copolymerization occurs between ethylene and the α-olefins produced by Fe, at the Zr site. The presence of more than 40% of long branches (vide infra) with respect to the total branching confirms this copolymerization. The presence of some ethyl and butyl branches may be due to the formation of small amounts of 1-butene and 1-hexene with the Fe catalyst. Small comonomers are much more reactive than high α-olefins and therefore are incorporated more easily even if they are only present in small quantities.

Characterization of the branched polyethylene was carried out as described in ref 19, with some modifications.

A list of the number of branches corresponding to each peak is summarized below, k being the normalization constant. The symbols N_E, N_B, and N_L represent the branch content of ethyl, butyl, and longer ($n \geq 6$) branches, respectively.

$I_1 = kN_E$, $I_2 = k(N_B + N_L)$, $I_3 = kN_L$, $I_4 = kN_B$, $I_5 = kN_E$, $I_6 = k(2N_E + 2N_B + 3N_L)$, $I_7 = k(N_B)$, $I_8 = k(N_L)$, I_9 = main chain ($\delta\delta CH_2$) + $5B_n$ to $(n-3)B_n$, $I_{10} = k(2N_E + 2N_B + 3N_L)$, $I_{11} = kN_L$, $I_{12} = k2N_E$, $I_{13} = kN_B$, $I_{14} = k(2N_B + 3N_L)$, $I_{15} = k(N_B + N_L)$, and $I_{16} = kN_E$. From these equations it is possible to obtain the following relations directly (with $k = 1$): $N_E = (I_5 + I_{16})/2$, $N_B = I_4$, and $N_L = I_{15} - I_4$.

To quantify ethyl branches, the relationship $N_E = (I_5 + I_{16})/2$ was used instead of $N_E = (I_5 + I_{12}/2 + I_{16})/3$ used in ref 19, because the integral of peak 12 corresponding to carbon atom αB_2 at 33.95 ppm is obscured due to the presence (in certain cases) of unreacted α-olefin with a resonance at 33.93 ppm due to the $(n-2)C_n$ carbon atom. For the same reasons, $N_B = I_4$ corresponding to carbon atom $2B_4$ was used instead of $N_B = (I_4 + I_{13})/2$ (because I_{13} corresponding to $4B_4$ is coincident at 34.04 ppm with $(n-2)C_n$ in the presence of unreacted α-olefin).

The integrals used to calculate long chain branching (N_L) were also modified $N_L = I_{15} - I_4$ instead of $N_L = I_{11}$, as the same carbon atom $3B_n$ (I_{11}) is present in both long branches and the α-olefin. I_{15} at 38.10 ppm is due to the resonances of brB_4, brB_5, and brB_n,[19] but the spectra confirm the absence of amyl branches, so in this case I_{15} is due only to brB_4 and brB_n from butyl and long branches, respectively. I_4 corresponding to $2B_4$ can be subtracted from I_{15} to obtain the brB_n integral.

Besides the presence of unreacted α-olefin, it is possible to have some long-chain alkanes due to the chain transfer to the cocatalyst (MAO). These alkanes would present five signals in ^{13}C NMR, at the same resonance as $1B_n$, $2B_n$, $3B_n$, $4B_n$, and $\delta\delta CH_2$. To detect the presence of these alkanes, the integrals I_3, I_{11}, and $(I_{14} - 2I_4)/3$ corresponding to resonances of carbon atoms $2B_n$, $3B_n$, and nB_n were compared with $N_L = I_{15} - I_4$ corresponding to brB_n, existing only in branched PE. If the integral of the first three carbons is greater than that of the brB_n, it means that there is unreacted α-olefin or alkanes. When the amount of unreacted α-olefin was calculated by the method below, it could be seen that this difference was only due to the unreacted α-olefin.

The presence of unreacted α-olefin is not easy to detect, as most of the α-olefin resonances are superposed by peaks 2, 3, 8, 9, and 11 of the branched PE corresponding to carbons $1B_n$, $2B_n$, $4B_n$, $\delta\delta CH_2$, and $3B_n$ respectively. The allylic α-olefin carbon at 33.93 ppm $(n-2)C_n$ is too close to resonances 12 and 13 (corresponding to αB_2 at 33.95 ppm and $4B_4$ at 34.04 ppm, respectively) in branched PE to determine the correct integral value.

The only α-olefin resonances distinguishable from the branched PE are the ones corresponding to peaks III and IV in Table 4 and in Figure 3a,b, which are the carbons close to the double bond, $(n-3)C_n$ at 29.29 ppm and $(n-4)C_n$ at 29.42 ppm. These carbons can be used to detect the presence of unreacted α-olefin. The main problem in using these peaks is that they are close to the intense $\delta\delta CH_2$ carbon resonance of the main carbon chain, and the integrals of these peaks may not be very precise. As the signal at 29.29 ppm is farthest from the main peak it was chosen to measure the percentage of α-olefin present. Thus, the integral of resonance at 29.29 ppm (I_{III}) corresponds to 1 C of an α-olefin chain. The fraction of unreacted α-olefin is

$$X_{\text{unreacted }\alpha-\text{olefin}} = [I_{III}]/([I_{III}] + I_{\text{Total branching}})$$

$$I_{\text{Total branching}} = N_E + N_B + N_L$$

Table 6 shows the results of this analysis. The amount of unreacted α-olefin is proportional to the amount of Fe catalyst used. For high iron-to-zirconium ratio ([Fe]/[Zr] = 10, sample C2) the amount of unreacted α-olefin is very high (91%) and for a low iron-to-zirconium ratio ([Fe]/[Zr] = 2.9, sample C3) unreacted α-olefin was not detected.

As was already mentioned, these results are an approximation due to the imprecision of the I_{III} integral.

Quantitative Study of Branching. Main peak I_9 (Figure 2c) corresponds to the two $\delta\delta CH_2$ carbons of the ethylene units from the branched PE (backbone + long branches $\delta\delta CH_2$ carbons) and also from carbon 5 to $(n-6)C_n$ of unreacted α-olefin. The percentage of unre-

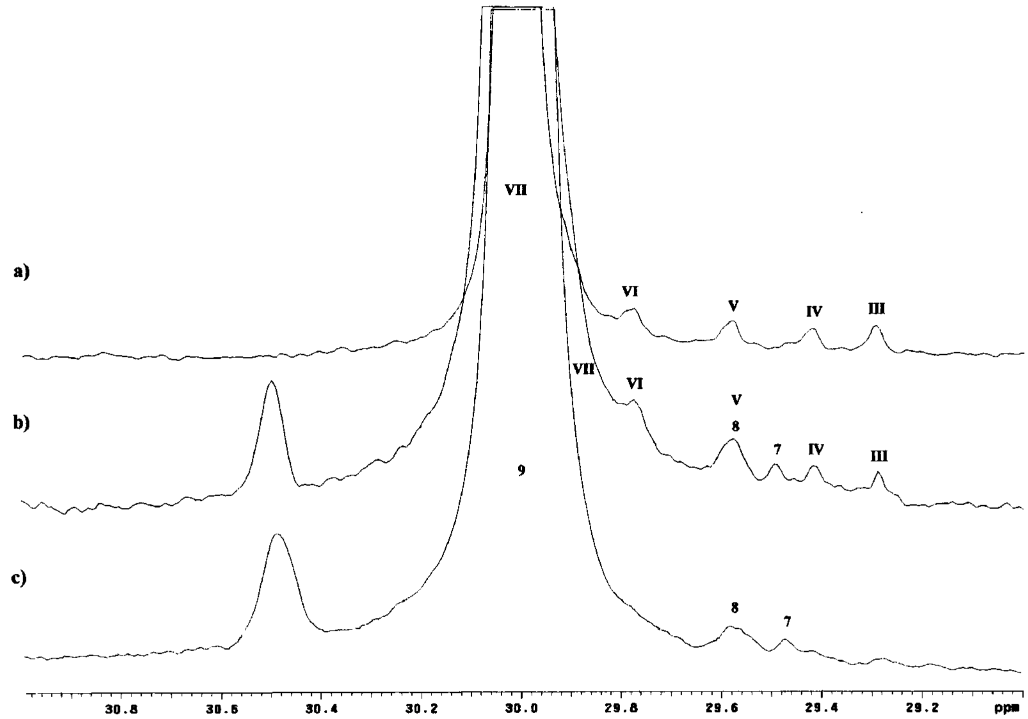


Figure 3. ^{13}C NMR spectra of (a) the α-olefin obtained with catalyst **1**, (b) sample C1 of branched polyethylene obtained with the mixture of catalysts **1** and **2** showing the presence of unreacted α-olefin, and (c) sample C3 of branched polyethylene obtained with the mixture of catalysts **1** and **2** without the presence of unreacted α-olefin.

Table 8. Amount of Branching in Branched Polyethylene

	branching with respect to total			branching with respect to total [E] units				
sample	N_E' (%)	N_B' (%)	N_L' (%)	N_E'' (%)	N_B'' (%)	N_L'' (%)	R (%)	branch/1000 C
C1	26.0	0	74.0	0.64	0	1.8	2.4	12
C2	0	0	100	0	0	3.0	3.0	15
C3	30.5	17.9	51.6	0.90	0.53	1.5	2.9	14.5
C4	34.3	23.2	42.5	1.4	0.95	1.7	4.0	20
C5	31.3	20.2	48.5	1.3	0.83	2.0	4.1	20.5
C6	33.3	9.6	57.1	0.75	0.22	1.3	2.3	11.5
D1	45.5	0	54.5	0.9	0	1.1	2.0	10
D2	36.2	0	63.8	1.0	0	1.8	2.8	14
D3	37.5	0	62.5	0.65	0	1.1	1.8	9
D4	22.6	20.8	56.6	0.37	0.34	0.92	1.6	8
D5	27.0	30.1	42.9	0.42	0.47	0.67	1.6	8
D6	0	0	100	0	0	1.8	1.8	9
D7	22.5	25.6	51.9	0.55	0.63	1.3	2.5	12.5
D8	37.8	17.8	44.4	1.1	0.52	1.3	2.9	14.5

acted α-olefin ($X_{\text{unreacted α-olefin}}$) was used to calculate the part of the main chain integral (I_9) corresponding only to branched PE.

$$\text{amount of } \delta\delta\text{CH}_2 \text{ from branched PE} = X_{\delta\delta\text{CH2PE}} = \{(1 - X_{\alpha\text{-olefin}}) \times I_9\}/2$$

The percentage of each type of branching with respect to the total branching can be obtained from the following relationships:

$$N_E' = N_E/(N_E + N_B + N_L)$$

$$N_B' = N_B/(N_E + N_B + N_L)$$

$$N_L' = N_L/(N_E + N_B + N_L)$$

Branching (% R) can be calculated with respect to the total ethylene units $X_{\delta\delta\text{CH2PE}}$ present in the polymer:

$$\%\ \text{R} = N_E + N_B + N_L/N_E + N_B + N_L + X_{\delta\delta\text{CH2PE}}$$

or each type of branching:

$$N_E'' = N_E/(N_E + N_B + N_L + X_{\delta\delta\text{CH2PE}})$$

$$N_B'' = N_B/(N_E + N_B + N_L + X_{\delta\delta\text{CH2PE}})$$

$$N_L'' = N_L/(N_E + N_B + N_L + X_{\delta\delta\text{CH2PE}})$$

The results of these calculations are given in Table 8, which shows that all branched PE samples have more than 40% long branches, ethyl branches accounting for 22−45%, and butyl branches for 10−30% in the cases in which all three types of branches exist. In samples D3, D1, D2, and C1 only ethyl and long branches exist, and in samples D6 and C2 there are only long branches. Branching with respect to total ethylene units in sample D4 means that there is 0.37 C of ethyl branches, 0.34 C from butyl branches, and 0.92 C of long branches per 100 units of ethylene. It is possible to calculate the number of branches/1000C multiplying by 5.

The ethylene units (E) are not only derived from the main carbon chain ($\delta\delta$CH$_2$) but also from the long chains

($5B_n$ to ($n - 3$)Bn). To distinguish the amount of main resonance peak (I_9) that is due to main chain or to long branches, it is necessary to know the size of the branch. Based on the study of the polymerization of ethylene with catalyst **1**, the α-olefins produced (main fraction) have an average molecular weight of about 2000 g/mol. We made the assumption that each long branch corresponds to 143 carbon atoms (2000/14). (This is an approximation and is believed to carry over to the tandem system but cannot be proven.) Since the branching carbon atom corresponding to long chains is N_L, the carbon atoms due only to the main chain can be calculated subtracting $143N_L$ from the main peak integral (I_9). To obtain the integral corresponding to 1 C of the main carbon chain, it is necessary to divide this quantity by 2:

$$\text{ethylene backbone} = \text{EB} = (I_9 - 143N_L)/2$$

or in a general form

$$(I_9 - M_n/14N_L)/2$$

Branching can be recalculated, obtaining in this way the moles of branching per 100 mol of polymer:

$$\text{ethyl branches (mol \%)} = N_E/(N_E + N_B + N_L + \text{EB})$$

$$\text{butyl branches (mol \%)} = N_B/(N_E + N_B + N_L + \text{EB})$$

$$\text{long branches (mol \%)} = N_L/(N_E + N_B + N_L + \text{EB})$$

As an example, if it is assumed that sample D4 has long branches of $M_n = 2000$, it will have 1.1 mol % of ethyl branches (N_E), 1.0 mol % of butyl branches (N_B), and 2.7 mol % of long branches (N_L) per 100 mol of polymer.

Conclusions

A complete characterization of the products obtained with catalyst **1** and its combination with catalysts **2** and **3** was done by NMR. It was proved that the Fe catalyst produces linear α-olefins with number molecular weight centered mainly at 2000 g/mol with a minor fraction (about 25 wt %) centered at $M_n = 500$ g/mol. Their bimodal distribution of molecular weights is probably due to the presence of more than one active site in this type of catalyst mixture. Previous GPC studies had shown a polydispersity of 5.2 for the insoluble fraction.[20] The presence of a low amount of alkane from chain transfer to Al was also detected, mainly in the soluble fraction. Metallocene catalysts **2** and **3** copolymerized ethylene with α-olefins produced with the Fe catalyst, giving branched PE with ethyl, butyl, and long branches. In some cases the presence of ethyl or butyl branches was not detected. When high [Fe]/[Zr] ratios were used, the presence of unreacted α-olefin was detected.

Catalyst **2** gave higher amount of branching than catalyst **3** as was already reported for 1-octadecene/ethylene copolymerization.[6]

NMR has been shown to be, once again, a very powerful tool and the only technique that permits elucidation of, with some accuracy, the presence of different branches, unreacted α-olefin, and the presence of alkanes.

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