

# FTIR, $^{13}\text{C}$ NMR, and GPC Analysis of High-Propylene Content Co- and Terpolymers with Ethylene and Higher $\alpha$ -Olefins Synthesized with $\text{EtInd}_2\text{ZrCl}_2/\text{MAO}$

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**ABSTRACT:** This article reports the results of propylene/ $\alpha$ -olefin copolymerization and propylene/ethylene/ $\alpha$ -olefin terpolymerization using low concentrations (less than 5 mol %) of long  $\alpha$ -olefins such as 1-octene, 1-decene, and 1-dodecene. Kinetics data are presented and discussed. The highest activity was found with the longest  $\alpha$ -olefin studied (1-dodecene). A possible explanation is proposed for this and other characteristics of the polymers obtained. The effect of low-ethylene contents (4 mol % in the gas phase) on the copolymerization of propylene/ $\alpha$ -olefins was also examined. The polymers synthesized were characterized by  $^{13}\text{C}$  NMR, gel permeation chromatography, DSC, Fourier transform infrared spectroscopy, and wide-angle X-ray scattering. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 39: 2005–2018, 2001

**Keywords:** propylene copolymerization; propylene terpolymerization; metallocene; long-chain  $\alpha$ -olefins polymerization

## INTRODUCTION

Improvement in the Ziegler–Natta catalyst performance as a result of the presence of a longer  $\alpha$ -olefin is a well known effect of both technological and scientific interests. The aforementioned effect was observed under several of the following experimental conditions:<sup>1</sup>

1. Prepolymerization of  $\alpha$ -olefins followed by homopolymerization of ethylene.
2. Prepolymerization of  $\alpha$ -olefins followed by copolymerization with ethylene.
3. Copolymerization of  $\alpha$ -olefins and ethylene.

4. Ethylene polymerization stimulated by the consecutive introduction of an  $\alpha$ -olefin.
5. Prepolymerization of one  $\alpha$ -olefin followed by copolymerization of ethylene and a second  $\alpha$ -olefin.

The comonomer effect has been thoroughly investigated in industrial laboratories. However, most of the results are not available in the open literature. On the other hand, there have been few reports from academic research. Several conclusions were drawn from the experiments carried out to explain the comonomer effect using the following Ziegler–Natta catalysts:

1. Fracturing of the catalyst particles to expose new active sites (in case of supported catalysts).

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- Diffusion of ethylene and/or aluminum alkyl is slow for catalyst particles encapsulated in polyethylene. An increment in the diffusion was observed when the catalyst was encapsulated in poly-( $\alpha$ -olefins) as a result of its lower density and crystallinity.
- Activation of dormant sites.
- Formation of new active sites by reactions involving  $\alpha$ -olefin (but not ethylene).
- "Triggering" effect by an  $\alpha$ -olefin to increase the propagation constant ( $k_p$ ).
- Displacement of complexed molecules as Lewis bases from the active sites.
- Change in the distribution of the titanium oxidation states.
- Alteration of association state of the titanium.

Chien and Nozaki<sup>1</sup> concluded that  $\text{EtInd}_2\text{ZrCl}_2$ /methylaluminoxane (MAO) and  $\text{Cp}_2\text{ZrCl}_2$ /MAO present a "negative" effect at low  $\alpha$ -olefin (1-hexene) concentration; this means that lower activities are obtained when comonomer is added. On the other hand, other researchers reported different results: higher activities when comonomer is added.<sup>2-4</sup> In terpolymerization with the Ziegler-Natta catalysts, the addition of a short  $\alpha$ -olefin to an ethylene/long  $\alpha$ -olefin system commonly increases the amount of longer comonomer incorporated into the polymer backbone. However, for metallocenes this synergistic effect is almost unknown. The synergistic effect did not seem to work with the  $\text{Cp}_2\text{ZrCl}_2$  catalyst. Other copolymerizations showed that the syndiospecific catalyst  $\text{iPrFluoCpZrCl}_2$  inserts more  $\alpha$ -olefin than  $\text{Me}_2\text{SiInd}_2\text{ZrCl}_2$ , perhaps because of a broader coordination aperture between the  $\pi$  ligands.<sup>5,6</sup>

The synergistic effect of a long  $\alpha$ -olefin on propene was reported to be negative for ethylene/propylene/1-hexadecene using  $\text{EtInd}_2\text{ZrCl}_2$ /MAO.<sup>7</sup> However, the range of the studied second or third olefin is too small to generalize some conclusions. On the other hand, the effect of very low amounts of  $\alpha$ -olefins is not considered by that previous research. Herfert et al.<sup>6</sup> show that  $\alpha$ -olefins present an accelerating effect on the ethylene polymerization rate. They also surmise that the last two inserted monomers have an influence on the subsequent monomer inserted.

Although some co- and terpolymerizations based on ethylene have been done, the copolymerization of propylene with higher  $\alpha$ -olefins was less studied. Jüngling et al.<sup>8</sup> investigated the copoly-

merization of propene with 1-octene using several metallocenes, and they found a relatively high incorporation of  $\alpha$ -olefin. Recent reports on the copolymerization of propylene with 1-octene using a last-generation metallocene [ $\text{Me}_2\text{Si}(2\text{-Me-4,5-BenzInd})_2\text{ZrCl}_2$ ]/MAO at 30 °C in toluene) showed that at very low contents of 1-octene in the reaction media (less than 10 mol % in the liquid phase or 5 mol % of 1-octene in the copolymer) the catalytic activity increased by a factor of 2.<sup>9</sup>

The copolymerization of propene with high olefins such as 1-butene, 1-hexene, and cyclic olefins has also been described.<sup>10</sup> Only a few studies dealing with 4-methyl-1-pentene as comonomer in  $\alpha$ -olefin polymerization are found in the open literature.<sup>11,12</sup> Several groups have examined the copolymerization of higher  $\alpha$ -olefins. In a series of copolymerizations of propene with 1-butene, 1-hexene, 1-octene, 1-dodecene, and 1-octadecene with  $\text{EtInd}_2\text{HfCl}_2$ , the products obtained were random copolymers. The reactivity of the high  $\alpha$ -olefins in the copolymerization decreased only slightly when the length of the  $\alpha$ -olefin increased.<sup>13</sup>

A small amount of ethylene in propylene homopolymerization led to polymers with higher molecular weights (approximately twice) and only slightly lower mps. The increase in chain length was attributed to an activation of the catalytic sites by ethylene insertion, blocked by a preceding 2,1 insertion of propylene, which normally leads to a  $\beta$ -hydride elimination and chain termination. In ethylene-propylene copolymerization, bridged zirconocenes exhibit higher catalytic activities than the nonbridged analogues.<sup>14</sup>  $\text{EtInd}_2\text{ZrCl}_2$ /MAO produces copolymers having comonomer compositions similar to the feed composition, whereas nonbridged catalysts favor the incorporation of ethylene over propylene (or 1-hexene).<sup>15</sup>

The aim of the present work is to study the comonomer effect in the polymerization of propylene using  $\text{EtInd}_2\text{ZrCl}_2$  (EBI)/MAO. Results on the copolymerization of propylene with low amounts of 1-octene, 1-decene, and 1-dodecene (near 1 mol % of the total amount of olefins at the reaction media) are presented. The effect of the addition of 4 mol % of ethylene in the gas phase on the catalytic activity is also given to analyze the effect of a short olefin on propylene/ $\alpha$ -olefin copolymerization.

**Table I.** Reaction Conditions

Mode	[Zr] (mol/L)	[Al] (mol/L)	Al/Zr	[Propylene] (mol/L)	<i>T</i> (°C)	<i>P</i> <sub>propylene</sub> (atm)	Time (min)
Semibatch	4.5 10 <sup>-6</sup> – 1.0 10 <sup>-5</sup>	0.015	3360	0.531	40	1.125	45
Continuous	1.0 10 <sup>-5</sup> – 1.2 10 <sup>-5</sup>	0.04	3400	0.402	40	0.825	90

## EXPERIMENTAL

### Materials

The catalyst EtInd<sub>2</sub>ZrCl<sub>2</sub> was obtained from Aldrich and manipulated in N<sub>2</sub> atmosphere, and the cocatalyst MAO (10 wt % in toluene) was provided by Witco. Propylene, polymerization grade, was purified using MnO/Al<sub>2</sub>O<sub>3</sub> and 13X molecular sieves to eliminate water and oxygen. 1-Octene (98% chemical purity), 1-decene (94% chemical purity), and 1-dodecene (95% chemical purity) were obtained from Aldrich and used as received. The impurities were *n*-alkanes and substituted  $\alpha$ -olefins in all cases. No internal olefins are present as impurities in longer  $\alpha$ -olefins. Toluene was JT Baker high-performance liquid chromatographic grade (water content less than 0.006%). It was dehydrated with 13X molecular sieves before use. Ethylene was used as received from Scott Specialty gases.

### Polymerization Conditions

Copolymerization and terpolymerization reactions were carried out in a stainless steel Parr reactor of 600 mL, with 200 and 300 mL of toluene for semibatch and continuous polymerizations, respectively.

### Propylene/High $\alpha$ -Olefins Copolymerization

Copolymerizations of propylene/1-octene, propylene/1-decene, and propylene/1-dodecene were carried out at 1.125 atm of propylene pressure in semibatch mode. The polymerization time was 45 min. We also studied the effect of increasing the amount of 1-decene added to the metallocene/MAO system to analyze the effect of  $\alpha$ -olefin concentration on catalyst activity. The kinetics of the different polymerizations are described. Propylene consumption to maintain a constant pressure was measured based on the propylene flow rate.

The concentration of propylene in the reaction media (toluene) was calculated using the following correlation:

$$[P] = p_P 7.67 \cdot 10^{-6} e^{3452.3/T} \quad (1)$$

where [P] is the concentration of propylene in the liquid phase (toluene) in moles per liter, *p<sub>P</sub>* is the partial pressure of propylene in atmospheres, and *T* is the absolute temperature. Eq 1 was obtained considering the data reported by Zambelli and Grassi.<sup>16</sup> In the calculation, we have taken into account the vapor pressure of toluene at 40 °C.

### Ethylene/Propylene Copolymerization and Ethylene/Propylene/High $\alpha$ -Olefins Terpolymerization

Copolymerizations and terpolymerizations were carried out at an olefin total pressure of 1.0 atm with a continuous flow of ethylene and propylene. Propylene and ethylene flows were separately controlled with a total gas monomer flow to the reactor of 0.35 L/min. In terpolymerizations, the higher  $\alpha$ -olefin (either 1-octene, 1-decene, or 1-dodecene) was added to the reactor before feeding the monomer gases batchwise under propylene or ethylene pressure. A concentration of 1 mol % of  $\alpha$ -olefin, based on the total amount of monomers in the liquid phase, was used with a concentration of ethylene in the gas phase of approximately 4 mol %. The polymerization time was 90 min.

The conditions used for the reactions were selected from the literature to avoid diffusional problems, and they are summarized in Table I. The reactor was purged with propylene or a mixture of ethylene/propylene at high flow for 15 min to remove the air. After that, dry toluene was added, and the polymerization temperature was achieved maintaining the highest speed of agitation possible. The solvent was then saturated with the gas monomers at the polymerization pressure. For terpolymerizations, the higher  $\alpha$ -olefin (1-octene, 1-decene, or 1-dodecene) was

**Table II.** Concentrations of Ethylene, Propylene, and Higher  $\alpha$ -Olefin in the Reaction Medium

Polymer	Gas Phase (mol %)		Liquid Phase (mol %)			
	Ethylene	Propylene	Ethylene	Propylene	Higher $\alpha$ -Olefin	Total Concentration (mol/L)
<b>PP4E</b>	4.1	95.9	1.4	98.6	—	
<b>PP4E1O</b>	4.1	95.9	1.3	97.4	1.3	0.119
<b>PP4E1D</b>	5.4	94.6	1.6	97.0	1.4	0.115
<b>PP4E1Do</b>	4.4	95.6	1.5	97.2	1.3	0.119

added as liquid by syringe methods. Metallocene catalyst and MAO were also introduced by syringe techniques: first MAO and then the zirconocene. Once the catalyst compounds were injected, the polymerization proceeded under the previously described conditions. The reaction was stopped by closing the gas monomer feed, and the polymerization medium was poured into a mixture of ethanol/hydrochloric acid and filtered. After filtration, the polymer was dried at room temperature until constant weight.

The ratio of ethylene concentration to propylene concentration in the liquid phase, at the reaction conditions, was calculated with the following equation:

$$\frac{[E]}{[P]} = \frac{p_E}{p_P} 16.946 e^{-1236.6/T} \quad (2)$$

where [E] is the concentration of ethylene in the liquid phase (toluene) in moles per liter, and  $p_E$  is the partial pressure of ethylene in atmospheres. The gas flows were related to the partial pressures, and the relation  $p_E/p_P$  was replaced by the gas flows.

Predictions of propylene and ethylene concentration in the liquid phase using eqs 1 and 2 were compared with experimental values obtained from the literature.<sup>16,17</sup> An error of less than 10% was found, indicating that the predictions are in good agreement with the reported experimental values.

The concentration of higher  $\alpha$ -olefin was calculated based on the added volume, taking into account the density and purity of the olefin as well as the volume of solvent (toluene).

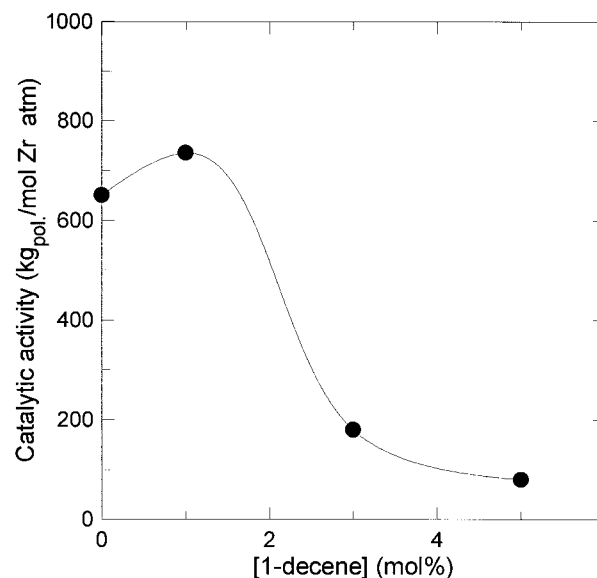
Table II shows the calculated concentrations of ethylene, propylene, and  $\alpha$ -olefins in the liquid phase in co- and terpolymerization reactions.

Two fractions of the final polymer were obtained in the copolymerization of propylene with

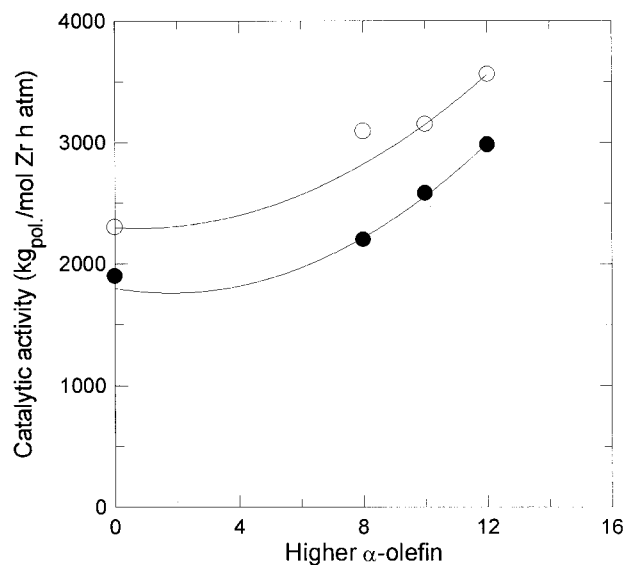
4 mol % of ethylene in the gas phase. One of the fractions precipitated in the alcoholic mixture (F1, insoluble), whereas the other was recovered by evaporating the solvent because it was soluble in the toluene/ethanol/HCl mixture (F2, soluble). Similar behavior was found in the terpolymerization of propylene with ethylene and 1-decene. The second fraction represented in both cases less than 10–12% of the total polymer.

#### Kinetics of Propylene/High $\alpha$ -Olefins Copolymerization

The copolymerization of propylene with different contents of 1-decene shows a maximum in catalytic activity at 1 mol % of long  $\alpha$ -olefin in the reaction medium (Fig. 1). The decrease in activity was drastic when more than 1 mol % of 1-decene



**Figure 1.** Catalytic activity as a function of 1-decene concentration in the liquid phase for the copolymerization of propylene/1-decene (reaction time = 20 min).



**Figure 2.** Catalytic activity for the co- and terpolymerization of propylene with 1-octene, 1-decene, and 1-dodecene [symbols: (●) propylene/ $\alpha$ -olefin copolymers and (○) ethylene/propylene/ $\alpha$ -olefin terpolymers; solid lines indicate data trend].

was added resulting in a deactivation of catalyst at approximately 20 min of reaction. Activity values for the copolymerization of propylene with different  $\alpha$ -olefins and terpolymerization with 4 mol % of ethylene in the gas phase are given in Figure 2. The catalytic activity increases, in all cases, in the presence of comonomers. The shape of the curve of propylene consumption changes when a long  $\alpha$ -olefin is present in the reaction medium, as can be seen in Figure 3. When 1-octene and 1-dodecene are added, the kinetic curve of propylene consumption is different compared with the curve obtained with 1-decene.

To analyze the effect of  $\alpha$ -olefin chain length on the catalytic activity, the amount of  $\alpha$ -olefin was kept constant in 1 mol % of the total olefin concentration.

### Polymer Characterization

The co- and terpolymers synthesized were explored by several analytical techniques such as gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), and DSC. Some of the obtained copolymers and terpolymers were also analyzed by  $^{13}\text{C}$  NMR and wide-angle X-ray scattering (WAXS).

### GPC and DSC

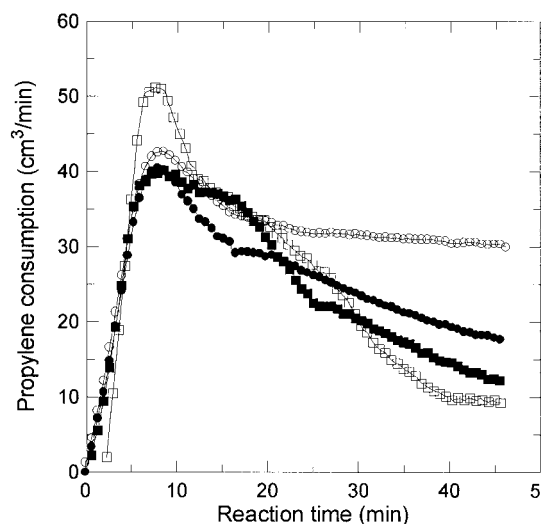
Average molecular weights and molecular weight distributions were obtained with GPC (Waters

150C) coupled with multiangle laser light scattering (Wyatt Dawn DSP). The GPC was equipped with three PLGEL columns of 500,  $10^4$ , and  $10^6$  Å. 1,2,4-Trichlorobenzene (TCB) was used as a solvent at a flow rate of 1 mL/min at 135 °C. The concentrations used were in the order of  $4 \times 10^{-3}$  g/mL. The TCB refractive index was taken as 1.502, and the specific refractive-index increment ( $dn/dc$ ) was taken as  $-0.104$ .<sup>18</sup> DSC measurements were performed on a PerkinElmer Pyris 1. Samples were heated at 10 °C/min from 30 to 160 °C, cooled at 10 °C/min from 160 to 30 °C, and then heated again from 30 to 160 °C at 10 °C/min. The peak melting temperature ( $T_{mp}$ ) and heat of fusion ( $\Delta H_f$ ) values were taken from the second heating curve.

### FTIR

FTIR spectra of the polymers in the solid state were obtained in a Nicolet 20 DXB. The films were prepared with a hydraulic hot press at temperatures lower than 150 °C. Solvent evaporation from a concentrated polymer solution on a NaCl window was an alternative method of films preparation.

An estimation of the propylene content in the copolymers using the FTIR information can be done using correlations given in the literature. Two of the following different expressions were



**Figure 3.** Kinetics of propylene/ $\alpha$ -olefin copolymerization. In all cases, a concentration of 1 mol % of the  $\alpha$ -olefin was used [symbols: (■) propylene homopolymer, (●) propylene/1-octene, (□) propylene/1-decene, and (○) propylene/1-dodecene copolymers].

**Table III.** Results for the Semibatch Copolymerization of Propylene and Higher  $\alpha$ -Olefins

Polymer	Activity <sup>c</sup> (kg polymer/mol Zr)	$M_n$ (Da)	$M_w$ (Da)	$M_w/M_n$	$T_{mp}$ (°C)	$\Delta H_m$ (J/g)	$X_c$ (%)
<b>PP</b>	730	16,300	30,900	1.90	134.3	83.7	40.0
<b>PP1O</b>	735	12,800	22,000	1.72	129.5	82.7	39.6
<b>PP1D</b>	860	15,800	27,100	1.72	132.0	82.8	39.6
<b>PP3D<sup>a</sup></b>	200	15,100	27,300	1.81	116.6	47.1	22.5
<b>PP5D<sup>b</sup></b>	90	15,200	29,300	1.93	112.6	45.6	21.8
<b>PP1Do</b>	990	9250	16,200	1.75	128.1	81.5	39.0

<sup>a</sup> [1-decene] liquid phase = 3 mol %.<sup>b</sup> [1-decene] liquid phase = 5 mol %.<sup>c</sup> Calculated at 20 min of reaction time.

used to obtain the molar percentage of propylene:  
19,20

$$\text{mol \% P}_{\text{COP}} = \frac{13.7}{X + 13.7} 100 \quad (3)$$

$$\text{mol \% P}_{\text{COP}} = \frac{1.59}{Y + 1.59} 100 \quad (4)$$

where  $X$  and  $Y$  in eqs 3 and 4 are defined, based on absorbance values at 720–730, 900, and 1155–1165  $\text{cm}^{-1}$ , by

$$X = \frac{A_{720-730}}{A_{900}}$$

and

$$Y = \frac{A_{720-730}}{A_{1155-1165}}$$

### <sup>13</sup>C NMR

The <sup>13</sup>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*<sub>6</sub> (20% v/v) in 5-mm sample tubes. The deuterated solvent was used to provide the internal lock signal. The chemical shifts were referenced to Me<sub>4</sub>Si. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay time of 4.0 s. Under these conditions the spectra are 90% quantitative, considering carbon atoms that have a relaxation time ( $T_1$ ) shorter than 2.0 s.<sup>21</sup>

### WAXS

WAXS studies of copolymers and terpolymers, in the powder form, were performed at room temperature with a diffractometer (Phillips, PW1710). A Cu tube anode at 45 kV and 30 mA was used. Crystal size was estimated using Scherrer's equation where the reported size is the average dimension of the crystallites normal to the diffraction planes ( $hkl$ ).<sup>22</sup>

## RESULTS AND DISCUSSION

### GPC and DSC

Table III lists the results for the semibatch copolymerization of propylene/1-decene. The catalytic activity decreases with an increase in the concentration of 1-decene. The molecular weight of the copolymers obtained is similar to the polypropylene homopolymer, but the peak mp ( $T_{mp}$ ) and crystallinity ( $X_c$ ) decreased when the concentration of 1-decene in the reaction medium increased.

The results of the semibatch copolymerization of propylene with 1 mol % of  $\alpha$ -olefins of different lengths are also shown in Table III. The catalytic activity increases with an increase in the length of the  $\alpha$ -olefin. A similar trend is observed in the terpolymerization with 4 mol % of ethylene in the gas phase (Table IV).

The terpolymers showed lower molecular weights than the polypropylene obtained in the same conditions, and the polydispersity index ( $M_w/M_n$ ) increased with an increase in the length of the  $\alpha$ -olefin. Both the copolymer and terpolymer containing 1-decene showed the highest mo-

**Table IV.** Results of Continuous Co- and Terpolymerization of Propylene and  $\alpha$ -Olefin

Polymer	Activity (kg polymer/ mol Zr h atm)	$M_n$ (Da)	$M_w$ (Da)	$M_w/M_n$	$T_{m_p}$ (°C)	$\Delta H_m$ (J/g)	$X_c$ (%)
<b>PP</b>	1700	12,500	22,500	1.69	134.5	85.4	40.8
<b>PP4E</b> (F1) ~ 90 wt %	2300	9600	16,800	1.76	111.0	51.6	24.7
<b>PP4E</b> (F2) ~ 10 wt %	—	—	—	—	112.2	44.7	21.4
<b>PP4E1O</b>	3090	8800	15,200	1.73	113.7	63.8	30.5
<b>PP4E1D</b> (F1) ~ 88.2 wt %	3150	10,100	19,400	1.85	110.1	49.1	23.5
<b>PP4E1D</b> (F2) ~ 12.8 wt %	—	—	—	—	70.5	24.3	11.6
<b>PP4E1Do</b>	3560	6000	14,600	2.45	116.0	64.5	30.9

lecular weight of the series with values similar to the corresponding polypropylene.

Copolymer crystallinity was similar to the value obtained for polypropylene, whereas terpolymers showed lower values than the respective copolymers. The copolymerization of propylene with 4 mol % of ethylene in the gas phase gives a material with a lower crystallinity and mp than propylene. The presence of a low concentration of a high  $\alpha$ -olefin in the reaction media gives terpolymers with higher crystallinities and mps than the corresponding copolymer. The length of the  $\alpha$ -olefin seems to influence the crystallinity more than the melting temperature. Terpolymer containing 1-decene shows the lowest crystallinity and mp in the series.

### FTIR

The ethylene content in the polymers was estimated by FTIR. Table V summarizes the values obtained. It is known that the long  $\alpha$ -olefins present a band at 720  $\text{cm}^{-1}$ ; therefore, the apparent amount of incorporated propylene in the terpolymers would be lower than the real ones and the ethylene content overestimated.

The FTIR spectra of the terpolymers present the bands at 720–730  $\text{cm}^{-1}$  characteristic of ethylene/high  $\alpha$ -olefins copolymers [(CH<sub>2</sub>)<sub>4</sub> sequences] and changes (new bands) in the 1600–1700  $\text{cm}^{-1}$  zone, corresponding to C=CHR. The FTIR spectrum of terpolymer containing 1-dodecene (**PP4E1Do**) shows bands at 667–695  $\text{cm}^{-1}$  and increased intensity in the bands near 1600–1650  $\text{cm}^{-1}$ , when compared to terpolymers obtained with 1-octene and 1-decene. It is clear that there is a contribution of the dodecene chain to the 720- $\text{cm}^{-1}$  band; therefore, the FTIR results using eq 3 are incorrect considering the higher amount of long olefin incorporated as it was observed by <sup>13</sup>C NMR. On the other hand, eq 4 could not be applied to this polymer for the same reason mentioned previously.

### <sup>13</sup>C NMR

<sup>13</sup>C NMR chemical shifts, carbon, and sequence assignments for propylene/ethylene/long-chain  $\alpha$ -olefin (1-octene, 1-decene, and 1-dodecene) are shown in Table VI. Theoretical chemical shifts were calculated by Lindeman's and Adams's<sup>23</sup> additive rules and on previous assignments.<sup>24</sup> The

**Table V.** Results of FTIR Characterization

Polymer	Gas-Phase Composition (mol %)		Polymer Composition (mol %)		
	Ethylene	Propylene	Ethylene	Propylene (Eq 3)	Propylene (Eq 4)
<b>PP4E</b>	4.1	95.9	3.0–5.1	97.0	94.9
<b>PP4E1O</b>	4.1	95.9	4.0	96.0–	—
<b>PP4E1D</b> (F1)	5.4	94.6	4.3	95.7	88.7
<b>PP4E1D</b> (F2)	5.4	94.6	—	—	75.6
<b>PP4E1Do</b>	4.4	95.6	4.7	95.3	—

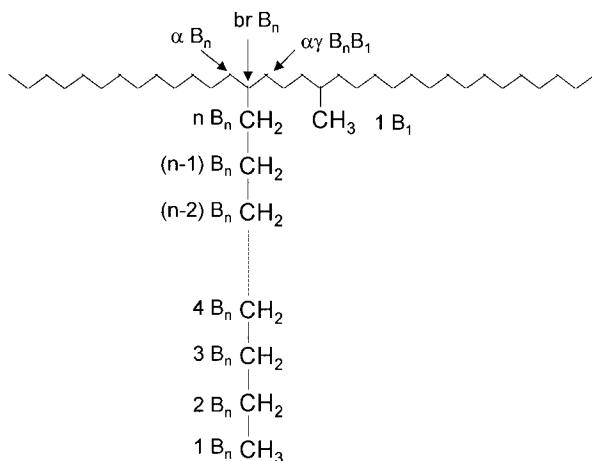
**Table VI.**  $^{13}\text{C}$  NMR Characterization of Synthesized Polymers: Experimental and Theoretical Chemical Shifts, Triads, and Carbon Assignments

Signal Number	Chemical Shifts Experimented (ppm)	Chemical Shifts Calculated (ppm)	Triads	Carbon	$N^\circ$ of C
1	14.03	13.86	PTP	1B $n$	1
2	19.64	20.61	PPP(rr)	1B1	1
3	20.80	20.12	EPP + PPE	1B1	2
4	20.91	20.61	PPP(mr)	1B1	1
5	21.43	20.61	PPP(mm)	1B1	1
6	21.72	20.61	PPP(mm)	1B1	1
			TPP + PPT	1B1	2
7	22.82	22.65	TPT	1B1	1
			PTP	2B $n$	1
8	24.45	24.58	PEP	$\beta\beta\text{B}1$	1
9	24.62	24.58	TET	$\beta\beta\text{B}n$	1
10	27.03	27.52	PTP	7B $n$	1
11	27.36	27.27	EEP + PEE	$\beta\delta\text{B}n$	2
			PPP	brB1	1
12	28.60	28.38	TPP + PPT	brB1	2
			TPT	brB1	1
13	29.52	29.71	PTP	4B $n \geq 8$	1
			PTP	5 to $(n - 5)\text{B}n > 8$	
14	29.87	29.96		4B6	
			EEE	—CH2—	1
15	30.40	30.21	PTP	$(n - 2)\text{B}n \geq 8$	1
16	30.72	30.45	PPE + EPP	brB1	2
17	32.10	32.40	PTP	3B $n$	1
18	33.10	32.91	PTP	brB $n$	1
19	34.46	34.97	PTP	nB $n$	1
			(P)PEP(P)	$\alpha\gamma\text{B}1$	1
20	37.66	37.41	(P)EPP + PPE(P)	$\alpha\gamma\text{B}1$	1
21	37.84	37.41	TET	$\alpha\gamma\text{B}n$	2
			TTP + PTT	$\alpha\alpha\text{B}1\text{B}n$	2
22	43.71	41.92	PTP	$\alpha\alpha\text{B}1\text{B}n$	1
			TPP + PPT	$\alpha\alpha\text{B}1\text{B}n$	2
23	45.82	44.11	TPT	$\alpha\alpha\text{B}1\text{B}n$	1
			(P)EPP + PPE(P)	$\alpha\alpha\text{B}1$	2
24	46.24		(E)PPP(E)	$\alpha\alpha\text{B}1$	2
25	46.71	44.36	(P)PPP(P)	$\alpha\alpha\text{B}1$	2

nomenclature used for carbon atoms is that of Usami and Takayama<sup>25</sup> for isolated branches. Branches are named by  $x\text{B}n$ , where  $n$  is the length of the branch (e.g.,  $n = 6$  for the hexyl branch), and  $x$  is the carbon number starting with 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. For methylenes between equal branches, two Greek letters are used (e.g.,  $xy\text{B}n$ ), and between different branches, the carbon is named  $xy\text{B}n\text{B}m$ . Figure 4 shows an example of carbon-atom identification.

The spectrum corresponding to the terpolymer of propylene/ethylene/1-decene is shown in Figure 5. The terpolymer of propylene/ethylene/1-octene does not have peaks 13 and 15 because these resonances are only present in terpolymers with  $\alpha$ -olefin branches with  $n \geq 8$ , but it has the carbon atom 4B $_6$  at peak 14 in the place of carbon-atom resonance  $[5 - (n - 5)]\text{B}n$  present only in branches with  $n \geq 8$ . Quantitative analysis (Table VII) was achieved using the same integral resonances for the three terpolymers with differences in triad EEE. Because 1-dodecene has two more carbon atoms than





**Figure 4.** Representation of carbon atom identification for  $^{13}\text{C}$  NMR.

1-decene, the following relationship must be used for this triad:  $(I_{14} - 3 I_{17})/2$ .

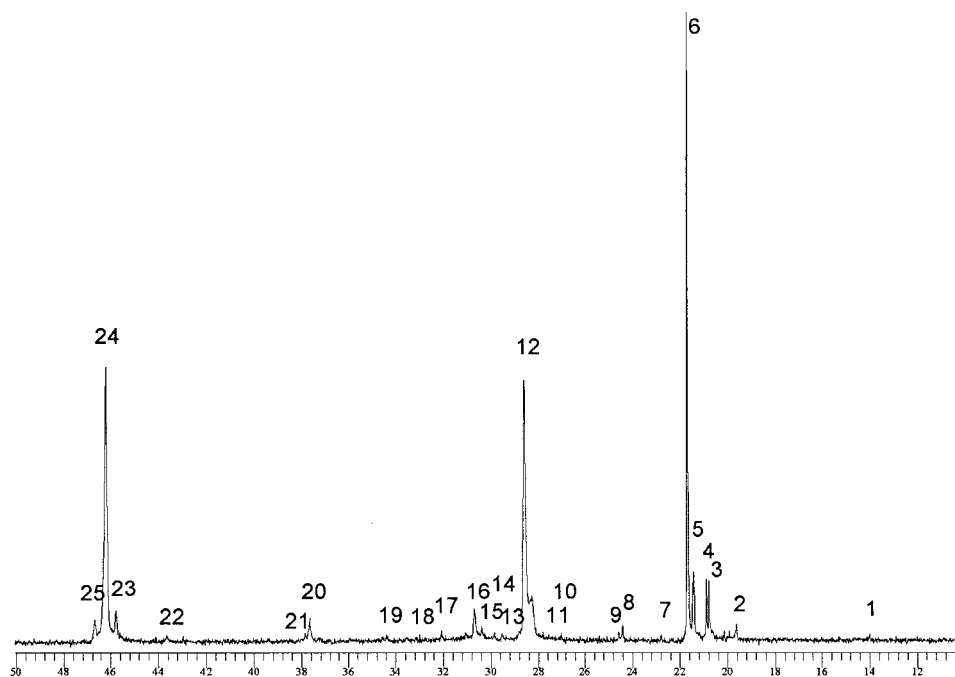
The triads [EEP+PEE], [EET+TEE], [EPE], [TTT]+[TTP+PTT], [ETE], and [ETT+TTE] (T = 1-octene, 1-decene, or 1-dodecene) are set to 0 in all terpolymers because there is no evidence of these peaks in the spectra.

The  $^{13}\text{C}$  NMR of terpolymers containing 1-octene and 1-decene (Table VIII) reveal that although the amount of terpolymer incorporated is nearly the same (0.77 mol % for 1-octene and 0.74 mol % for

1-decene), the amount of ethylene incorporated is lower in the case of 1-octene (3.98 vs 3.69 mol %). The [EEE] sequence is lower when 1-decene is present (F1, insoluble), whereas the termonomer–ethylene–termonomer sequence [TET] is higher (0.83 vs 1.15 mol %). The copolymers of propylene/high  $\alpha$ -olefins show no incorporation of long  $\alpha$ -olefin at the detection level of  $^{13}\text{C}$  NMR (Fig. 6). No significant difference in the tacticity of the polymers was observed by  $^{13}\text{C}$  NMR (Table IX).

## WAXS

WAXS data demonstrate that the incorporation of low amounts of high  $\alpha$ -olefins do not change the profile of polypropylene homopolymer. In the copolymer and terpolymers containing approximately 4 mol % of ethylene, the results show changes in the relative importance of different planes (Table X), especially the signal at  $17^\circ$  [(040) plane of PP]. In the terpolymer containing 1-octene (**PP4E1O**), this signal is increased from 75.5 to 90.9% and to 95% for the terpolymer containing 1-decene. On the other hand, the signal at  $21.4^\circ$  changes from 46 up to 73.3%. These changes entail different implications of these planes, induced by the presence of the termonomer. WAXS crystallinity of terpolymers decreases with an increasing length of the added termonomer (Table X).



**Figure 5.**  $^{13}\text{C}$  NMR spectra of the terpolymer propylene/ethylene/1-decene (F1).

**Table VII.** Equations for Quantitative Analysis of Terpolymer Propylene (P)-Ethylene (E)-Long-Chain  $\alpha$ -Olefins (1-Octene, 1-Decene, and 1-Dodecene) (T) Sequences

$[EEE]^a = (I_{14} - I_{17})/2$	
$[EEP + PEE] = I_{11}$	
$[PEP] = I_8$	$[E] = (I_{14} - I_{17})/2 + I_{11} + I_8 + I_9$
$[EET + TEE] = 0$	
$[TET] = I_9$	
$[EPE] = 0$	
$[EPP + PPE] = I_{16}/2$	$[P] = I_{16}/2 + I_{12}$
$[PPP] + [TPP + PPT + TPT] = I_{12}$	
$[PTP] = I_{17}$	
$[TTT] + [TTP + PTT] = 0$	$[T] = I_{17}$
$[ETE] = 0$	
$[ETT + TTE] = 0$	

<sup>a</sup>  $[EEE] = (I_{14} - 3 I_{17})/2$  for propylene-ethylene-1-dodecene terpolymers.

### General Discussion

A concentration of 1-decene higher than 1 mol % drastically decreases the productivity using EtInd<sub>2</sub>ZrCl<sub>2</sub>/MAO, as can be observed in Figure 1. On the other hand, for a constant amount of  $\alpha$ -olefin in the reaction medium (such as 1 mol %) the catalytic activity increases with the length of the higher  $\alpha$ -olefin (Fig. 2). The increase of catalytic activity with the length of the  $\alpha$ -olefin is not easy to understand, but several researchers have reported this performance at low  $\alpha$ -olefin concentrations. Some of them pointed out that the catalytic activity of ethylene/1-octadecene is similar to that of ethylene/1-dodecene and higher than ethylene/1-hexene copolymerization.<sup>2,5</sup> The effect of low quantities of  $\alpha$ -olefin remains unexplained because almost all of the preceding studies focused

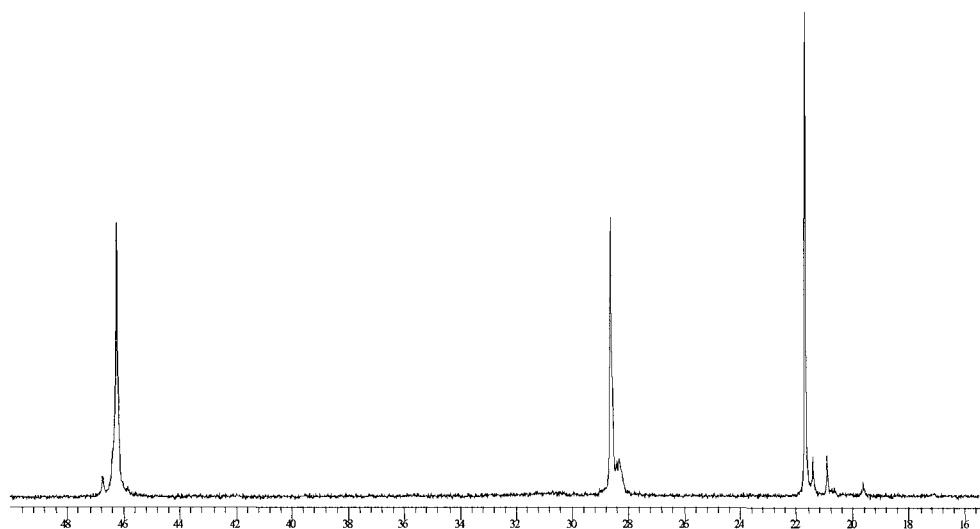
on the effect of high amounts of  $\alpha$ -olefin in the polymerization media. This effect in activity improvement when low quantities of  $\alpha$ -olefin are added (less than 3 mol %) could be important when supported catalysts are used in propylene polymerization.<sup>26</sup> However, the amount of  $\alpha$ -olefin that becomes a poison to the catalyst activity varies with the particular zirconocene.

This behavior in catalytic activity at low concentrations of longer  $\alpha$ -olefins was also found for other metallocenes. A complex metallocene such as Me<sub>2</sub>Si(2-Metilbenz-Indenyl)<sub>2</sub>ZrCl<sub>2</sub> shows a similar behavior, but the catalytic activity decreases when 10 mol % of 1-octene is present.<sup>9</sup> Then it is possible to obtain a higher catalytic activity maintaining the percentage of long  $\alpha$ -olefin near 1 mol % of the total olefin concentration

**Table VIII.** Monomer-Sequence Distribution of Polypropylene 4% Ethylene 1% Higher  $\alpha$ -Olefins in Molar Percentages

Polymer	[EEE]	[EEP] + [PEE]	[PEP]	[TET]	[EPP] + [PPE]	[PPP] + [TPP] + [PPT] + [TPT]	[PTP]	E (mol %)	P (mol %)	T (mol %)
<b>PP4E1O</b>	1.01	0.00	2.14	0.83	3.92	91.30	0.77	3.98	95.25	0.77
<b>PP4E1D</b> (F1)	0.58	0.00	1.96	1.15	3.69	91.90	0.74	3.69	95.57	0.74
<b>PP4E1D</b> (F2)	1.48	1.08	1.49	0.97	4.90	87.80	2.24	5.00	92.80	2.20
<b>PP4E1Do</b>	0.00	1.56	0.00	0.00	2.26	94.40	1.80	1.60	96.60	1.80

$[EET] + [TEE] = 0.0$  and  $[EPE] = 0.0$ .



**Figure 6.**  $^{13}\text{C}$  NMR spectra of the copolymer propylene/1-dodecene.

using EBI/MAO. This behavior was also found in the presence of ethylene where the effect is more pronounced (almost 25% of catalytic activity increase). Another point to be considered is the diffusional problem. Wang et al.<sup>27</sup> have proposed that in the copolymerization of ethylene and  $\alpha$ -olefins, which results in a lower crystallinity material, the monomer reaches the equilibrium concentration more easily at an increased diffusion rate. It is apparent that a slight decrease in crystallinity would bring about a remarkable increase in the diffusion coefficient. On the basis of unsteady diffusion kinetics, an interesting speculation about the addition of a small amount of ethylene should also facilitate a higher incorporation of a long-chain  $\alpha$ -olefin such as 1-hexadecene. This was verified in the copolymerization with propylene for the Ziegler–Natta catalysts.<sup>27</sup> For these researchers, in the terpolymerization of ethylene/propylene/1-hexadecene the diffusion coefficient of monomer is in the following order: ethylene > propylene > 1-hexadecene. Then, the extent of the increase in monomer concentration, if it is not in equilibrium, will be 1-hexadecene > propylene > ethylene.<sup>28</sup>

**Table IX.** Tacticity of Copolymers Propylene/High  $\alpha$ -Olefins

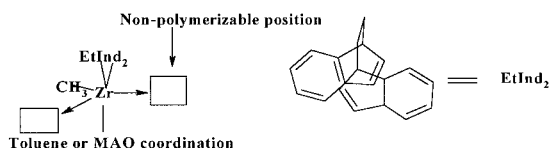
Polymer	mm	mr	rr	m	r
<b>PP1O</b>	0.88	0.10	0.02	0.93	0.07
<b>PP1D</b>	0.89	0.09	0.03	0.93	0.07
<b>PP1Do</b>	0.90	0.08	0.02	0.94	0.06

With Ziegler–Natta catalysts, the conversion of 1-hexadecene is raised from 10 to above 20–40% when small amounts of ethylene are added. On the other hand, when metallocene catalysts were considered the situation was not the same. In terpolymerizations of 1-butene, ethylene, and 1-hexadecene with  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ , an increase in 1-butene concentration gave a decrease in the consumption of both long-chain  $\alpha$ -olefin and ethylene.  $\text{MgCl}_2$ -supported Ti catalysts incorporated higher amounts of 1-decene or 1-hexadecene into the polymer in the presence of 1-butene in ethylene/1-butene/1-decene (1-hexadecene) terpolymerization with respect to the corresponding copolymerization.<sup>2</sup>

The unsteady diffusion kinetics is not an important fact in the terpolymerization with metallocenes. Chemical interactions must be considered to explain the obtained results. Data reported by Kaminsky and Drogemuller<sup>29</sup> show that the catalytic activity of ethylene/propylene/

**Table X.** Crystal Size and Crystallinity by WAXS of Selected Co- and Terpolymers

Polymer	Crystal Size 14° (Å)	Crystal Size 17° (Å)	Crystallinity (%)
<b>PP1O</b>	146	235	50.3
<b>PP1D</b>	146	180	51.3
<b>PP4E</b>	137	236	44.8
<b>PP4E1O</b>	122	296	38.8
<b>PP4E1D</b>	122	195	33.4



Scheme 1

1,5-hexadiene terpolymerization using  $\text{EtInd}_2\text{-ZrCl}_2$  varies considerably. Catalytic activity increases with the concentration of 1,5-hexadiene at low amounts of ethylene (12 mol %) and decreases at higher amounts. Other systems analyzed were the terpolymerizations of ethylene/propylene/*p*-methylstyrene and ethylene/1-octene/*p*-methylstyrene using metallocene catalysts with constrained ligand geometry.<sup>30</sup> A recent work reports that 1-hexene or 1-octene can be polymerized to high molecular weight products at high pressures (100–1000 MPa) with permethylated zirconocenes.<sup>31</sup> Zirconocenes and hafnocenes with the same steric structure showed quite different high-pressure effects, giving support to the idea that electronic effects are more important than steric ones in these conditions. Homo- and copolymerization of ethylene and long  $\alpha$ -olefins under high pressures using 1 and 2 siloxy-substituted EBI also indicates the importance of electronic and steric effects.<sup>32</sup> When different comonomers are interacting in the reaction medium, the formation of new kinds of active sites could be a possible explanation for electronic and steric effects. It seems that the presence of high  $\alpha$ -olefins other than propylene induces the formation of a more active site for propylene polymerization, whereas the same situation occurs in terpolymerization, where the higher  $\alpha$ -olefin seems to increase the activity of both ethylene and propylene. Ethylene also increases the catalytic activity in copolymerizations. This effect is easier to understand considering that ethylene has a higher propagation constant ( $k_p$ ), a lower steric hindrance, and a possible reactivating effect to dormant sites by 2,1 insertion of propylene.

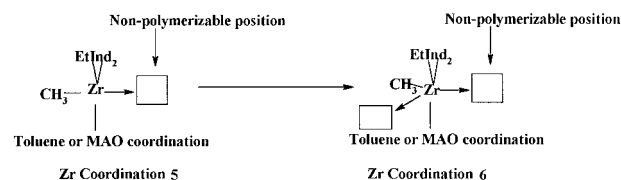
Considering two active positions for olefin coordination (Scheme 1)—one to polymerize and a second one to stabilize the zirconium ion—it is possible to explain the results obtained for propylene/ $\alpha$ -olefin polymerizations. If long  $\alpha$ -olefin displaces propylene, as a result of its higher polarizability, from the nonpolymerizable position, the propagation constant of propylene will be higher. On the other hand, because  $\beta$ -H elimination is the predominant termination reaction in

propylene polymerization, a low concentration of a longer  $\alpha$ -olefin will not change the ratio of propagation/termination constants.

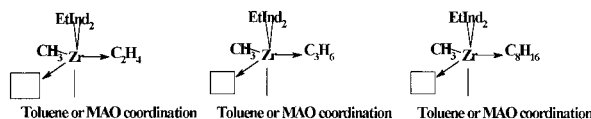
No incorporation of longer  $\alpha$ -olefin was observed by  $^{13}\text{C}$  NMR when 1 mol % of  $\alpha$ -olefin was present in the reaction medium. If the longer  $\alpha$ -olefins are mainly coordinated at the nonpolymerizable position, the net effect is an increase in the activity for propylene polymerization. On the other hand, the coordination of the second olefin to the polymerizable position depends on both concentration and steric effects. A change in the coordination number of the Zr atom (from 5 to 6) is needed to coordinate the second olefin in the polymerizable position; then the coordination of propylene is favored (Scheme 2).

The  $^{13}\text{C}$  NMR analyses indicate that the incorporation of a longer  $\alpha$ -olefin is achieved by a reduction of ethylene incorporation, especially for 1-dodecene (Table VIII). The diffusional explanations cannot be applied here because the crystallinity of the terpolymers with a low content of a long  $\alpha$ -olefin increases when compared with corresponding values of the copolymer (Tables III and IV). It seems that a “long  $\alpha$ -olefin effect” is present at low concentrations of ethylene and longer  $\alpha$ -olefin, especially when the  $\alpha$ -olefin has more than 10 carbon atoms in the backbone.

The FTIR spectra of copolymers with low amounts of long  $\alpha$ -olefins can be explained considering both the transfer reaction to comonomer as an additional chain-transfer reaction (with increasing of C=C bonds) and a higher probability of 1,3 insertion of propylene because of the increased electrophilicity of the Zr atom. However, considering that molecular weight is almost constant and catalytic activity decreases in the copolymerization of propylene with different amounts of 1-decene, a more complex explanation must be formulated. It seems that a lower amount of sites is functioning when the concentration of 1-decene in the reaction medium increases. However, those sites must have a higher propagation constant because of the coordination of 1-decene in the nonpolymerizable position. On the other hand, an



Scheme 2



Scheme 3

irreversible deactivation by 2,1 insertion of 1-decene must also be possible.

In the terpolymerization reactions, different sites could be formed when ethylene, propylene, or a longer  $\alpha$ -olefin is coordinated in the nonpolymerizable position (Scheme 3).

The three olefins shown in Scheme 3 will produce different catalytic sites because electronic properties (such as polarizability and basicity) are different. Looking at Table VIII, the [EEE] content decreases from 1.01 (**PP4E1O**) to 0 (**PP4E1Do**). On the other hand, the [EEP]+[PEE] sequences increase their concentration from 0 to 1.56%. Whereas the ability to insert terpolymer increases (see changes in [PTP] sequences), the ability to insert ethylene in the majority fraction decreases and to insert propylene increases, especially when comparing **PP4E1O** and **PP4E1Do**. The order of polarizability is ethylene < propylene < 1-octene < 1-decene < 1-dodecene and the basicity, in terms of the inductive effect of the methyl group, would be propylene > 1-octene > 1-decene > 1-dodecene > ethylene.

Considering the hyperconjugation, the effect of increased negative charge on the C1 of the olefin is higher for propylene (three hyperconjugable H atoms) and lower for the higher  $\alpha$ -olefins (only two hyperconjugable H atoms). Ethylene does not have hyperconjugable H atoms. Therefore, the hyperconjugation effect will be in the order of ethylene  $\ll$  1-octene, 1-decene, and 1-dodecene < propylene.

If we now considered some selection for coordination in the polymerizable position in terms of the Pearson theory of acids and bases, the higher the Zr electrophilicity the higher the tendency to coordinate propylene and termonomer in the polymerizable position. This selection would explain the lack of [EEE] sequences when 1-dodecene is present in the reaction medium. Because the concentrations of ethylene and termonomer are similar (Table II), termonomer or propylene can displace ethylene from the polymerizable position. This effect would be more notorious when the length of the higher  $\alpha$ -olefin increases, if the polarizability is taken into account.

The increased incorporation of ethylene and 1-decene in the minority fraction (F2) points out that the final result is a combination of the different effects previously mentioned. In this case, ethylene is incorporated in such a way that the concentration of sequences [PEP] is close to the concentration of sequences [TET]. It seems that 1-decene can displace, in some sites, propylene from the nonpolymerizable position. Therefore, the coordination of ethylene and 1-decene is favored in the polymerizable position. Two different reactivity ratios for ethylene/1-decene copolymerization have been reported. Values of  $r_E = 200$  and 80 were found for copolymers of ethylene/1-decene when the content of 1-decene in the copolymer was lower and higher than 2.1 mol %, respectively.<sup>33</sup> This difference in the  $r_E$  values can explain the different fractions obtained in the terpolymers prepared with 1-decene. On the other hand, this fact is also in line with our <sup>13</sup>C NMR results (Table VIII). The second fraction (F2) of terpolymer **PP4E1D** shows a higher amount of ethylene (5 vs 3.69%) and a three-times-higher content of 1-decene (2.2 vs 0.74%) than the majority fraction (F1). This is indirect evidence of more than one kind of site structure in the EBI/MAO system.

Because the mp of terpolymers remains almost constant for different  $\alpha$ -olefins with respect to the value obtained for the ethylene/propylene copolymer, the diffusional explanation is not applicable. The decrease in the mp for the second fraction of terpolymer containing 1-decene [**PP4E1D** (F2)] can be explained considering the higher amount of ethylene and 1-decene incorporated.

A severe steric hindrance to insertion using EtInd<sub>2</sub>ZrCl<sub>2</sub> can be observed in the copolymerization of propylene when the concentration of long  $\alpha$ -olefin is higher than 1 mol %. It has been reported that the coordination of a polymerizable olefin decreases the metal charge, depending on its polarizability. Then, the coordination of an  $\alpha$ -olefin in the polymerizable position has a deactivating effect because of the high steric hindrance and the low Zr electrophilicity. The drastic change in catalytic activity when higher amounts of a longer  $\alpha$ -olefin such as 1-decene is present in the reaction medium can be explained based on previous considerations.

When ethylene is added, a new termination reaction (transfer to ethylene monomer) must be considered. Therefore, changes in the molecular weights and FTIR spectrum become relevant. In this case, the incorporation of longer  $\alpha$ -olefin is

detected resembling some kind of effect, at least in certain active sites. The increase in catalytic activity observed for terpolymers can be related to a reactivation of dormant sites of 2,1 insertion of propylene and an increase in the electrophilicity of the Zr atom as a result of the coordination of a longer  $\alpha$ -olefin at the nonpolymerizable position, in some active sites. The increase in electrophilicity as a result of the presence of different olefins in the nonpolymerizable position can explain the higher catalytic activity and the improved chain-transfer reactions, mainly the  $\beta$ -H elimination. The increase in the polydispersity index of the polymers obtained is also evidence of the possibility of different kinds of active sites.

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