Co- and Terpolymerization of Ethylene, Propylene, and Higher α-Olefins with High Propylene Contents Using Metallocene Catalysts

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ABSTRACT: The copolymerization of propylene/ethylene and terpolymerization of propylene/ethylene/α-olefins using long-chain α-olefins such as 1-octene and 1-decene have been carried out using EtInd₂ZrCl₂//methylaluminoxane. High concentrations of propylene and low concentrations of α-olefins (near 2 mol % of the total olefin concentration in the liquid phase) were used. The effect of the ethylene concentration in copolymerizations of propylene/α-olefins was studied at medium ethylene contents (12 and 40 mol % in the gas phase). The polymers were molecularly characterized by gel permeation chromatography-multiangle laser light scattering, wide-angle X-ray scattering, Fourier transform infrared spectroscopy, and DSC analyses. The shorter α-olefin studied (1-octene) produced the highest improvement of activity in terpolymerization at 12 mol % ethylene in the gas phase. About 2 mol % of 1-octene in the liquid phase increases the activity and decreases the molecular weight of terpolymers with respect to corresponding copolymers, whereas the mp is increased by almost 30 °C. The "termonomer effect" is less evident when higher amounts of ethylene are used. © 2001 John Wiley & Sons, Inc.
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INTRODUCTION

The copolymerization of ethylene with higher α-olefins using metallocene catalysts has been investigated.[1] A small amount of 1-butene, 1-hexene, or 1-octene leads to polymers with similar characteristics of linear low-density polyethylene, a product of high industrial interest. Attractive product properties are also stimulating interest in propylene copolymerization. Random copolymerization of propylene with ethylene and higher α-olefins can be a solution for low-temperature

applications because the glass-transition temperature (T_g) of polypropylene (PP) is relatively high (approximately 0 °C).[2] Propene and 1-octene have been copolymerized using different metallocenes.[3] The copolymerization of propylene with 1-butene, 1-hexene, or cyclic olefins using metallocenes has also been explored.[4] Recent reports show that the crystallization temperatures seem to be independent of the comonomer length.[5] However, there is little information on terpolymerizations of ethylene, propylene, and higher α-olefins aiming to obtain terpolymers with low contents of higher α-olefins (less than 2–5 mol %) and higher propylene contents. In this area, Kaminsky and Drogemuller[6] synthesized ethylene/propylene/diene elastomers using Cp₂ZrCl₂ and EtInd₂ZrCl₂ with a maximum diene incorporation

of 6–7 mol % of diene. To obtain functionalized polyolefins, Hackmann et al.[7] examined the results of the copolymerization of propylene with higher α-olefins using linear asymetrically substituted dienes. Other researchers studied the copolymerization of propylene with 1-octene, showing an important increase of activity in the range of 2–10 mol % of 1-octene in the liquid phase.[8]

In the mid-1980s Seppälä[9] noticed an enhanced enrichment of a higher α-olefin (1-decene or 1-dodecene) in its copolymerization with ethylene on a commercial $TiCl_3/AlEt_3$ catalyst when a short-chain α-olefin such as 1-butene was added. This phenomenon was called the "synergistic effect." The copolymerizability of a longer α-olefin with 1-butene or propylene should be higher than with ethylene, and 1-butene should be more reactive than higher α-olefins in its copolymerization with ethylene. This effect implies that 1-butene has a less sterically hindered structure in the growing chain end, allowing the longer α-olefin to react. However, this synergistic effect can be alternatively explained based on unsteady diffusion kinetics.[10] Owing to the lower diffusion coefficient and copolymerizability of a longer α-olefin, the attainment of its equilibrium concentration at the catalyst is more difficult. The presence of a lower α-olefin of a higher copolymerizability should lead to a considerable decrease in the crystallinity of polyethylene, facilitating the diffusion of the longer α-olefin as well as the attainment of its equilibrium concentration. Additionally, the incorporation of a small amount of ethylene into PP should destroy the regularity of PP chains and create the conditions for improved diffusion of a higher α-olefin. The extent of monomer-concentration increases at the catalyst surface for supported Ziegler–Natta copolymerization is in the following order: longer α-olefin > propylene > ethylene.

Other researchers have demonstrated that unsteady diffusion kinetics can predict that the reactivity of 1-hexadecene with propylene in a heterogeneous Ziegler–Natta copolymerization should increase by two to three times by adding a small amount of ethylene.[11] Those researchers had found that terpolymers with 2–10 mol % of 1-hexadecene as well as small amounts of ethylene incorporated (2–10 mol %) show both lower mps and crystallinity than corresponding copolymers (up to 5–10 °C in T_m and five to eight times in crystallinity values). Using Ziegler–Natta catalysts, they established that the addition of a small amount of ethylene in propylene/higher

α-olefin copolymerization is an excellent way for improving the copolymerizability of the higher α-olefin.

Seppälä et al.[12] studied the synthesis of co and terpolymers of ethylene with 1-butene and 1-decene using Cp_2ZrCl_2/methylaluminoxane (MAO). Those polymers were totally soluble in n-heptane, the solvent used as a polymerization medium. The enhancement of catalytic activity found can hardly be attributed to monomer diffusion. Furthermore, it has been proposed that in the case of this soluble system, virtually all the zirconium atoms form active sites for polymerization especially at high temperatures (70 °C). The molecular weight of ethylene/1-butene and ethylene/1-decene copolymers decreased, and the activity of the catalyst simultaneously increased. They concluded that the comonomer takes part in the activation of catalytic centers, decreasing the activation energy necessary for the insertion of monomer into an active metal–carbon bond, making propagation and chain-transfer reactions easier. Similar trends have been discovered for terpolymerizations: higher activity as well as lower molecular weights but no "synergistic effect" for the terpolymerization of ethylene with 1-butene and a longer α-olefin.

The synergistic effect has also been found to be absent using bridged and unbridged soluble metallocene catalysts such as $iPrFluoCpZrCl_2$//MAO, $Me_2SiInd_2ZrCl_2$//MAO, and Cp_2ZrCl_2 in the terpolymerization of ethylene with 1-butene and 1-octadecene.[13,14]

Besides the lack of the synergistic effect, the following interesting conclusions have been conveyed:

1. $iPrFluoCpZrCl_2$//MAO was more favorable than $Me_2SiInd_2ZrCl_2$//MAO for the insertion of higher α-olefins in ethylene/α-olefins copolymerization because of the gap aperture between the π ligands.
2. No significant differences were observed between the r parameters obtained for the same catalyst system when 1-dodecene or 1-octadecene was used as a termonomer.
3. A long block of higher α-olefins at the end of a growing polymer chain forces the ligands into a more open arrangement, making the insertion of an α-olefin easier. Longer α-olefins open more of the zirconocene ligands than shorter ones.
4. Consumption of ethylene increased continuously with the addition of 1-butene al-

though the content of a longer α-olefin such as 1-octadecene decreased in the terpolymer. The ethylene consumption did not pass through a maximum as it does in the copolymerization of ethylene and 1-octadecene.

Previous research states that no comonomer effect can be expected for the ethylene/longer α-olefin copolymerization using the homogeneous catalyst EtInd$_2$ZrCl$_2$//MAO.[15] However, a very wide range was explored for the first point of longer α-olefin incorporation (from 0 to 13 mol %). A recent report on the co- and terpolymerization of ethylene and higher α-olefins with metallocenes concluded that the synergistic effect of longer α-olefins on propene was negative for (nBu)Cp$_2$ZrCl$_2$//MAO and EtInd$_2$ZrCl$_2$//MAO. In this case, the synthesized polymers were ethylene-rich (more than 85 mol % ethylene).[16]

Previous studies dealing with the copolymerization of ethylene and propylene using metallocenes have been published in the last decade.[17–19] Recent reports show reactivity ratio values and the effect of the structural fact of metallocenes on the copolymer structure.[20,21] The formation of sequences of ethylene and propylene could be correlated with the energy involved in the whole process that leads to the insertion of the comonomer, the approach to the catalytic center, and the following insertion into the metal–carbon bond. For those studies, it is evident that ethylene insertion is preferred when ethylene or propylene is the last inserted unit. However, the relative reactivity of propylene versus ethylene increases when propylene is the last inserted unit ($k_{22}/k_{21} > k_{12}/k_{11}$). It has been pointed out that these results could be explained considering steric effects, emphasizing that a correct interpretation should also take into account the role played by electronic effects. Electronic effects could be responsible for different values of r_1 and r_2 in the series of the racemic-substituted metallocenes. Ethylene and α-olefins differ from both the steric and the electronic point of view. In this sense, the copolymerization of ethylene with 1-hexene or 1-octene using EtInd$_2$ZrCl$_2$//MAO produces polymers with lower mps and viscosities as the amount of the incorporated higher α-olefin increases (up to 27 mol %).[22] Some researchers have proposed that a decrease in the copolymer molecular weight could be due to increasing chain-transfer reactions to the longer comonomer.[23] Electronic effects of substituents are becoming an important explanation of the results obtained with siloxy-substituted EtInd$_2$ZrCl$_2$ in the homo and copolymerization of ethylene and higher α-olefins.[24] The importance of electronic effects in metallocene chemistry can be visualized in several mechanistic problems that remain unsolved such as chain-termination reactions.[25] The electronic effect is evidently important when EtInd$_2$ZrCl$_2$ and EtInd$_2$HfCl$_2$//MAO are compared. The Hf catalyst presents lower activities than the Zr catalyst in ethylene polymerization and a higher dependence of comonomer concentration in the copolymerization with 1-butene. However, under the same conditions, the Hf catalyst has a higher capability of comonomer incorporation. Although Zr and Hf compounds show the same chemical properties, the nuclear charge is completely different. This is manifested in shorter bond lengths and stronger bonds strengths in organometallic Hf compounds. However, this fact does not explain why Hf compounds are more effective in the incorporation of higher α-olefins.[26] An alternative explanation may be the capability of a highly polarizable olefin to increase the positive charge at the Hf atom by coordination even further, as far as insertion is more probable than coordination for Hf with respect to Zr. Because both metallocenes show similar steric hindrances, the coordination of a longer olefin that is more basic and polarizable than ethylene would be preferred on Hf (more electrofilic) than on Zr. The Hf catalyst shows remarkably low r_1 parameters, and this is in agreement with the preceding idea. Another report on olefin polymerization using highly congested ansa-metallocenes under high pressure demonstrates that although Me$_2$Si(η^5-C$_5$Me$_4$)$_2$ZrCl$_2$ and Me$_2$Si(η^5-C$_5$Me$_4$)$_2$HfCl$_2$ have almost identical structures, they showed different activities and molecular weights for the polymerization of 1-octene and 1-hexene. In the polymerization of 1-hexene at 500 MPa, the zirconocene showed an activity 200 times higher than the value obtained at 0.1 MPa, whereas the hafnocene shows only a 25-fold higher activity. The molecular weight of poly(1-hexene) was 20-fold higher for the zirconocene and 22-fold higher for the hafnocene when values at 500 and 0.1 MPa were compared. This fact emphasizes that electronic effects are important for understanding the behavior in olefin polymerizations at high pressures.

The present article explores the results of co- and terpolymerization of ethylene, propylene, and a higher α-olefin using EtInd$_2$ZrCl$_2$//MAO. The

Table I.   Concentration and Composition of Monomers in the Gas and Liquid Phases

Polymer	Gas-Phase Composition (mol %)		Liquid-Phase Concentrations (mol/L)			Liquid-Phase Composition (mol %)		
	Ethylene	Propylene	Ethylene	Propylene	Higher α-Olefin	Ethylene	Propylene	Higher α-Olefin
PP	—	100	—		—	—	100.0	—
PP12E	11.2	88.8	0.0147	0.358	—	4.0	96.0	—
PP12E2O	11.8	88.2	0.0151	0.356	0.0085	4.0	93.8	2.2
PP12E2D	12.7	87.3	0.0167	0.352	0.0085	4.5	93.3	2.2
PP40E	40.8	59.3	0.0536	0.239	—	18.3	81.7	—
PP40E2O	40.0	60.0	0.0527	0.242	0.0068	17.5	80.3	2.2
PP40E2D	40.0	60.0	0.0527	0.242	0.0072	17.5	80.2	2.3

copolymers and terpolymers synthesized are rich in propylene (approximately 60–90 mol %). The effect of low concentrations of higher α-olefins in the reaction media, such as 1-octene and 1-decene, on product properties is also investigated.

EXPERIMENTAL

Materials

The catalyst $EtInd_2ZrCl_2$ was obtained from Aldrich and manipulated in N_2 atmosphere, and the co-catalyst MAO (10 wt % in toluene) was provided by Witco. The propylene polymerization grade was purified using MnO/Al_2O_3 and 13X molecular sieves to eliminate water and oxygen. 1-Octene (98% chemical purity) and 1-decene (94% chemical purity) were obtained from Aldrich and used as received. The impurities were n-alkanes and substituted α-olefins in all cases. No internal olefins exist as impurities in longer α-olefins. Toluene was obtained from JT Baker at a high-performance liquid chromatographic grade (water content less than 0.006%), and 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 at 40 °C 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 flow of gas monomer to the reactor of 0.35 L/min. In terpolymerizations the higher α-olefin (either 1-octene or 1-decene) was added to the reactor before feeding the monomer gases batchwise under propylene or ethylene pressure. A concentration of 2 mol % of 1-octene or 1-decene, based on total amounts of monomers in the liquid phase, was used. Two ethylene/propylene ratios were used for the gas monomers: 12/88 and 40/60 (on a molar basis). A zirconium concentration in the range of $1–1.3 \times 10^{-5}$ M was used for polymerizations carried out with 12 mol % of ethylene in the gas phase. The zirconium concentration was reduced to the range of $0.6–0.64 \times 10^{-5}$ M when a 40 mol % of ethylene was present in the gas phase. The Al/Zr molar ratio varies between 2000 and 2500, and the polymerization time was 60 min. The conditions used for the reactions were selected from the literature to avoid diffusional problems, and they are presented in Table I.

The reactor was purged with propylene or a mixture of ethylene/propylene at high flow rate for 15 min to remove the air. Next, 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 the terpolymerizations the higher α-olefin (1-octene or 1-decene) was added by syringe methods as liquid. Metallocene catalysts 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. On closing the gas monomer feed, the reaction was stopped, and the polymerization media were poured into a mixture of ethanol and hydrochloric acid and filtered. After filtration, the polymer was dried at room temperature until constant weight.

The concentration of propylene in toluene during the polymerization reaction was calculated using the following correlation:

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

where $[P]$ is the concentration of propylene in the liquid phase (toluene) in moles per liter, p_P is the partial pressure of propylene in atmospheres, and T is the absolute temperature. Eq 1 was obtained considering the data collected by Zambelli and Grassi.[27] In the calculation, we have taken into account the vapor pressure of toluene at 40 °C.

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

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

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 the propylene and ethylene concentration in the liquid phase using eqs 1 and 2 were compared with the experimental values obtained from the literature.[27,28] An error of less than 10% was obtained indicating that the predictions are in good agreement with the reported experimental values.

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

Polymer Characterization

Average molecular weights and molecular weight distributions were obtained with a gel permeation chromatograph (GPC) (Waters 150C) coupled with multi-angle laser light scattering (MALLS) (Wyatt Dawn DSP). The GPC was equipped with three photoluminescent gel columns of 500, 10^4, and 10^6. 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 to 5 10^{-3} g/mL. The TCB refractive index was taken as 1.502, and the specific refractive-index increment (dn/dc) was -0.104.[29] DSC measurements were performed on a PerkinElmer Pyris 1. Samples were cooled at -110 °C, heated at 10 °C/min from -110 to 140 °C, cooled at 10 °C/min from 140 to -110 °C, and then heated again from -110 to 140 °C at 10 °C/min. The T_g, the onset and peak melting temperatures (T_{monset} and T_{mpeak}, respectively), and the heat-of-fusion (ΔH_f) values were taken from the second heating curve.

Fourier transform infrared (FTIR) spectra of the polymers in solid state were obtained in a Nicolet 20 DXB. The films were prepared with a hydraulic hot press at temperatures lower than 120 °C. Solvent evaporation from a concentrated polymer solution on a NaCl window was an alternative method of film preparation.

An estimation of the propylene content in the copolymers using the FTIR information can be done using correlations provided in the literature. Two different expressions were used to obtain the molar percentage of propylene[30,31]

$$\text{mol }\%P_{COP} = -9.96 10^{-3} + 106X + 81X^2 - 166X^3$$
$$\div 78.8X^4 \qquad (3)$$

$$\text{mol }\%P_{COP} = \frac{1.59}{Y - 1.59} 100 \qquad (4)$$

where X and Y are defined based on the absorbance values at 720–730 cm^{-1} and 1160–1165 cm^{-1} by the following equations:

$$X = \frac{A_{1160}}{A_{720} + A_{1160}}$$

and

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

FTIR of the terpolymers show the changes produced when a low concentration of a higher α-olefin is incorporated. Differences with the respective copolymers can be observed in the 1600–1700 cm^{-1} and 500–1000 cm^{-1} zones.

Wide-angle X-ray scattering (WAXS) studies of copolymers and terpolymers, in the powder form, were done at room temperature with a diffractometer (Phillips, PW1710). A Cu tube anode at 45 kV and 30 mA was used. The 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).[32]

Table II.   Average Molecular Weights and Thermal Properties of Synthesized Polymers

Polymer	Productivity (kg Polymer/mol Zr h atm)	M_n (Da)	M_w (Da)	M_w/M_n	T_g (°C)	$T_{m_{onset}}$ (°C)	$T_{m_{peak}}$ (°C)	ΔH_f (J/g)
PP	1770	13,300	22,500	1.69	—	127.2	134.5	85.4
PP12E	2600	14,600	22,400	1.53	−35.2	57.3	74.0	19.9
PP12E2O	4500	9600	15,400	1.59	−19.9	85.0	100.4	44.5
PP12E2D	3480	10,300	17,900	1.72	−27.1	86.6	105.4	36.8
PP40E	4350	16,700	27,200	1.64	−42.2	58.1	71.1	14.4
PP40E2O	5190	9000	17,600	1.64	−42.6	66.3	84.3	19.8
PP40E2D	5240	13,000	23,900	1.84	−43.9	67.9	83.6	13.9

For polypropylene [Zr] = 4.46 10^{-6} M, Al/Zr = 3360, and T = 40 °C.[40]

The rheological characterization of the synthesized polymers was carried out in a rotational rheometer (Rheometrics Dynamics Analyzer RDA-II) at temperatures ranging from 110 to 180 °C. Shear flow was obtained by dynamic tests using 25-mm diameter parallel plates. The storage (elastic) modulus, G', and the loss (viscous) modulus, G'', were measured for frequencies ranging from 0.05 to 500 rad/s in the linear viscoelastic range of strain. The time–temperature superposition principle was used at a reference temperature (T_0) of 120 °C.

RESULTS AND DISCUSSION

Productivity

The concentration of zirconium used in the polymerization reactions was similar to those utilized for propylene homopolymerization because the co- and terpolymers are propylene- rich. In all cases, [Zr] was low to avoid diffusional and temperature problems. Productivity values obtained for each reaction are shown in Table I. An increase in productivity is observed when a higher α-olefin (1-octene or 1-decene) is present in the reaction media. The ethylene concentration also affects the productivity. For terpolymers obtained with 40 mol % of ethylene in the gas phase, both 1-octene and 1-decene have almost the same effects. However, for terpolymers synthesized with 12 mol % of ethylene in the gas phase, 1-octene is more effective than 1-decene, taking into account the increment in productivity.

GPC-MALLS

In both series, the molecular weight distribution of terpolymers is shifted to lower molecular

weights with respect to the corresponding copolymer, although the activity increases. The decrease in molecular weight is higher for terpolymers prepared with 1-octene compared with those obtained with 1-decene. Polymers prepared with higher ethylene contents (40 mol % in the gas phase) show higher polydispersity values compared with those obtained with 12 mol % of ethylene. A shoulder of molecules with a higher molecular weight (lower elution volume) can be observed in the molecular weight distribution of polymers containing higher ethylene contents. Number and weight average molecular weights as well as polydispersity values of synthesized polymers are shown in Table II.

DSC Analysis

The T_g value of copolymers decreases as the ethylene content increases. The influence of higher α-olefins on T_g values is different for both series. Terpolymers prepared with the lower concentration of ethylene show a stronger influence than those obtained with a higher concentration of ethylene. For the **PP40E** series, all polymers show T_g values from −42 to −44 °C. On the other hand, the **PP12E** series shows a maximum T_g value for the terpolymer obtained with 1-octene. The melting temperature and melting enthalpy show important differences when copolymers and terpolymers are compared. In both series, the terpolymers present melting temperatures that are 10–30 °C higher than corresponding copolymers. Melting enthalpies also show similar trends in Table II. Terpolymers synthesized with 1-octene have a higher melting temperature as well as a higher degree of crystallinity than those obtained with 1-decene.

Table III. FTIR Characterization of Synthesized Polymers

Polymer	A_{998}/A_{973}	A_{720}/A_{900}	A_{720}/A_{1160}	$A_{720}/A_{720} + A_{1160}$	mol % P from eq 3	mol % P from eq 4
PP12E	0.64 ± 0.02	0.78 ± 0.01	0.35 ± 0.11	0.78 ± 0.01	82.2 ± 0.2	85.1 ± 0.3
PP12E2O	0.75 ± 0.04	0.80 ± 0.17	0.40 ± 0.14	0.72 ± 0.07	77.4 ± 6.0	80.2 ± 5.7
PP12E2D	0.71 ± 0.01	1.01 ± 0.01	0.57 ± 0.01	0.64 ± 0.01	70.5 ± 0.2	73.6 ± 0.2
PP40E	0.47 ± 0.07	1.37 ± 0.10	0.48 ± 0.03	0.68 ± 0.01	73.8 ± 1.1	76.8 ± 1.0
PP40E2O	0.76 ± 0.26	0.92 ± 0.04	0.52 ± 0.20	0.66 ± 0.08	72.6 ± 7.4	75.4 ± 7.2
PP40E2D	0.94 ± 0.01	0.97 ± 0.01	0.85 ± 0.01	0.54 ± 0.01	61.6 ± 0.2	65.1 ± 0.2

FTIR Spectra

FTIR results are used only in a qualitative way to evaluate major changes in the spectra. Copolymers show only one important band in 732 cm^{-1} (PP12E) and 728 cm^{-1} (PP40E) in the 600–800 cm^{-1} zone. Principal differences with respect to the corresponding copolymers can be observed in the 1600–1700 and 500–1000 cm^{-1} zones. Terpolymer PP12E2O (2 mol % of 1-octene) presents only one band at 732 cm^{-1}, whereas terpolymer PP12E2D (2 mol % of 1-decene) shows two bands: one at 723 cm^{-1} and a second one at 733 cm^{-1}. The IR band for isolated ethylene units containing three CH$_2$ groups appears at 732.5 cm^{-1}. On the other hand, if there are ethylene units with five or more CH$_2$ groups, a band at 720 cm^{-1} can be found.[33]

Copolymer PP40E shows a band in 732 cm^{-1}. The terpolymer containing 1-octene (PP40E2O) presents two bands at 725 and 732 cm^{-1}, and the terpolymer with 1-decene (PP40E2D) also shows two bands located at 723 and 733 cm^{-1}.

Copolymers of ethylene/propylene show one band in the 1600–1700 cm^{-1} zone. It is located at 1648 cm^{-1} in the copolymer PP12E and at 1651 cm^{-1} for the copolymer PP40E. Terpolymers belonging to the PP12E series show several additional bands (as shoulders). On the other hand, terpolymers prepared with 40 mol % ethylene in the gas phase (PP40E series) present only one band at 1650 cm^{-1}.

In the copolymer with 40 mol % of ethylene, several bands at 1028 and 1078 cm^{-1} appear. The bands of terminal vinyl (910 cm^{-1}) and transvinylene (965 cm^{-1}) are present only as shoulders in the spectra. The band at 888 cm^{-1} (vinylidene) is more important than the band at 900 cm^{-1} in PP12E and PP40E as well as the terpolymers with a high ethylene content (PP40E2O and PP40E2D) and decreases in PP12E2O and PP12E2D.

Table III summarizes the FTIR results. Although several films were prepared, differences arise mainly in the samples with higher ethylene contents. This fact can be correlated to some inhomogeneities in the structure of these copolymers. A_{998}/A_{973} have been included in Table III because this absorbance ratio can be taken as a measure of the regularity of the PP blocks.

WAXS Data

Jones et al.[34] claimed that the γ-phase of PP is characterized by five strong X-ray reflections of d-spacing at 6.37 (100), 5.29 (74), 4.415 (85), 4.19 (40), and 4.05 Å (63%). Four of these reflections lie very close to four of the reflection characteristics of the α-phase with d-spacing at 6.26, 5.19, 4.77, 4.19, and 4.04 Å. From those values, the reflection at 4.77 Å can be taken as distinctive of the α-phase, whereas the peak at 4.415 Å is indicative of the γ-phase.[35,36] Figures 1 and 2 show the WAXS profiles of PP40E and PP12E2O as well as PP40E2O, respectively.

Table IV shows the relative intensities of different reflections in the WAXS difractograms.
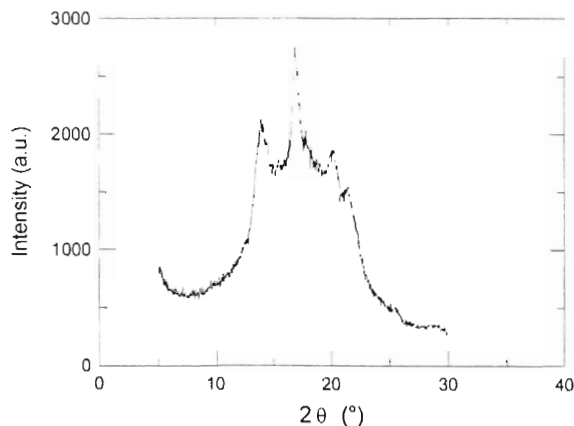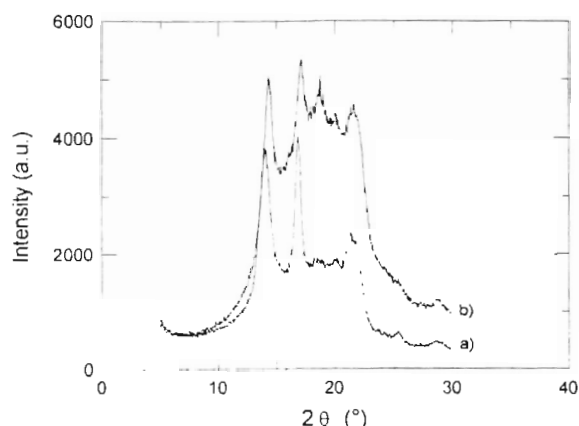

Figure 1. WAXS spectra of copolymer PP40E.

Figure 2. WAXS spectra of terpolymer containing 1-octene as termonomer: (a) **PP12E2O** and (b) **PP40E2O**.

Figure 3. Master curves of viscosity (η') as a function of frequency (ω) at 120 °C [symbols: (λ) **PP12E**, (σ) **PP12E2O**, and (ν) **PP12E2D**].

Polyethylene presents several crystalline forms. In the β form, there are two peaks in the zone analyzed in these polymers: at 4.6 (30) and 4.1 Å (100%). The other reflections lie at angles 2θ higher than 35°.

Rheological Studies

Figures 3 and 4 show the melt viscosities of the polymers synthesized with 12 mol % (**PP12E** series) and 40 mol % (**PP40E** series) of ethylene in the gas phase, respectively. All the samples obtained behave as thermorheologically simple materials. In both series, terpolymers show viscosity values lower than the corresponding copolymers. This can be attributed to the average molecular weight because all polymers present similar polydispersity values. Terpolymers containing 1-octene present the lowest viscosity, whereas those containing 1-decene show values closer to those obtained with the copolymers.
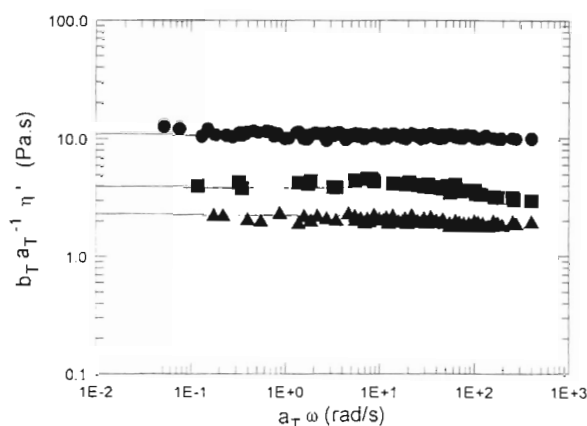
When all polymers analyzed obey the time–temperature principle, then curves of G' (ω) and G'' (ω) measured at different temperatures can be superposed by shifting along the frequency axis using a temperature shift factor (a_T). For the set of polymers studied in the present work, a value of 49.0 kJ/mol was found for the flow activation energy in an Arrhenius-type dependency of a_T with temperature.[37] The value found in this work is in good agreement with the values reported by Ferry[37] and Llinas et al.[38] for an ethylene/propylene copolymer containing 16 mol % of ethylene as well as PP obtained with a metallocene catalyst, respectively.

General Discussion

Increasing the ethylene content in the gas phase gives an increment in the activity because of its minor steric hindrance with respect to propylene. A decrease in the melting temperature is also ob-

Table IV. Relative Intensity of the Main Reflections, Crystal Size, and Crystallinity of Synthesized Polymers from WAXS Data

Polymer	(111) γ-PP (110) α-PP near 6.3 Å	(115) γ-PP (040) α-PP near 5.2 Å	(130) α-PP near 4.8 Å	(120 ó 117) γ-PP near 4.4 Å	(202) γ-PP (111) α-PP near 4.2 Å	(026) γ-PP (041) α-PP near 4.0 Å	Crystal-Size 14° (Å)	Crystal Size 17° (Å)	% X_c
PP12E	86.5	100	—	36.0	38.8	24.0	91	224	29.4
PP12E2O	90.3	90–100	33.3	34.3	52.0	44.4	86	200	32.4
PP12E2D	76.3	100	40.6	41.8	60.6	45.1	91	256	32.0
PP40E	60.6	100	—	34.9	19.7	—	129	200	14.1
PP40E2O	94.7	100	87.7	72.4	63.1	—	113	200	15.8
PP40E2D	85.0	100	—	22.2	38.9	—	51	164	14.1
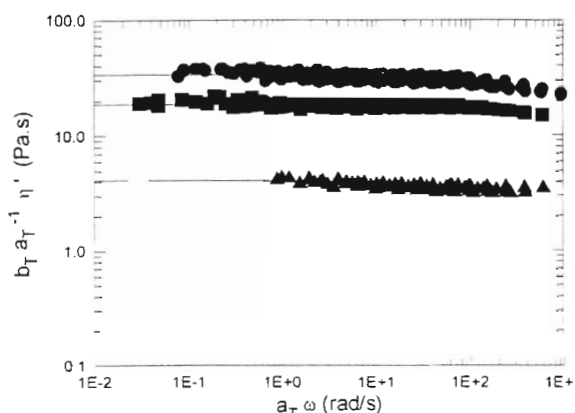
Figure 4. Master curves of viscosity (η') as a function of frequency (ω) at 120 °C [symbols: (λ) **PP40E**, (σ) **PP40E2O**, and (ν) **PP40E2D**].

Figure 5. Representation of the catalytic site formation coordinated with two ethylene molecules.

served because the incorporation of ethylene destroys the regularity of the propylene blocks. This effect is stronger when higher amounts of ethylene are incorporated, as can be seen in Table IV [relative intensity of (111) and (202) γ PP planes]. The T_g is also lower at higher ethylene incorporations (Table II). Although this trend is clear in copolymers. the terpolymers show interesting properties. The terpolymerization total activities are all higher than those corresponding to copolymerization. In both series, terpolymers synthesized with 1-octene (**PP12E2O** and **PP40E2O**) show higher crystallinity than corresponding copolymers (**PP12E** and **PP40E**). The melting temperature increases by approximately 25 °C for **PP12E2O** and 13 °C for **PP40E2O** with respect to the corresponding copolymers. **PP12E2O** shows a higher T_g value than **PP12E**, whereas a similar T_g value is found for **PP40E2O** and **PP40E**. When 1-decene is used as a termonomer, a similar trend is observed.

Our recent data[39,40] proposed that the active site in EtInd$_2$ZrCl$_2$//MAO (which can be extended to other metallocenes//MAO soluble systems) can be schematically visualized as the structure shown in Figure 5. In this representation, there are two positions for olefin coordination: one is polymerizable, and the other is not. The olefin at the nonpolymerizable position interacts directly with the cationic metal. The electronic effect on the Zr electrophilicity would depend on polarizability, basicity (in terms of the inductive effect of substituent R of C=C), and steric hindrance of the coordinated olefin. No changes in the coordination number of Zr take place in this situation: an empty vacancy is occupied. The order of the polarizability is ethylene < propylene < 1-octene
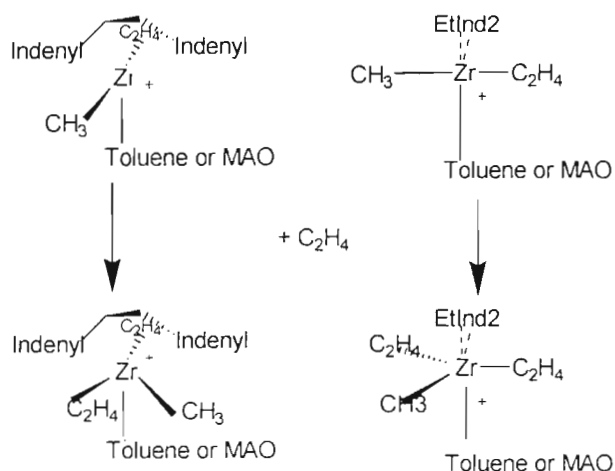
< 1-decene—just the same of increasing steric hindrance. The basicity in terms of the inductive effect of the R substituent would be propylene > 1-octene > 1-decene > ethylene.

The steric hindrance would be the most important fact to be considered when the olefin is coordinated at the polymerizable position (bottom representation of Fig. 5). The coordination number of Zr changes (in -1 unit) when the olefin is coordinated in the polymerizable position. Generally, this change in the coordination number implies a decrease in the transition metal charge. Figure 6 shows the lateral and upper views of the active-site structure coordinated with two ethylene molecules.

The electronic effect must be considered to evaluate the changes produced when different olefins are coordinated at the nonpolymerizable position. Based on recent reports on the calcula-
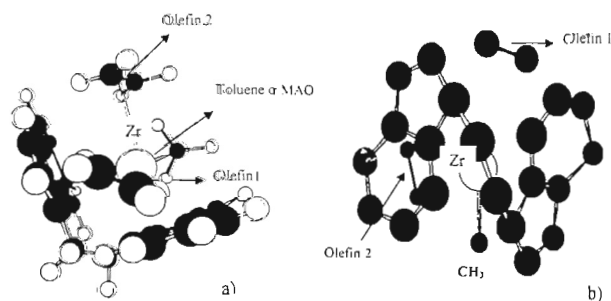

Figure 6. Lateral (a) and upper (b) views of the active site structure coordinated with two ethylene molecules [symbols: (dark circles) carbon atoms and (open circles) hydrogen atoms; toluene or MAO and hydrogen atoms are not shown in the upper view].

tions of the quantum mechanics (QM) methods, a second coordinated ethylene molecule increases the positive charge at the Zr atom.[41] This increase would be higher when either propylene or a higher α-olefin is coordinated in the nonpolymerizable position. The polarizability seems to be more important than the basicity for changes in the electrophilicity of transition metal. Our recent results indicate that the copolymerization of propylene with 1 mol % of 1-octene, 1-decene, or 1-dodecene increases the consumption of propylene. Longer α-olefins produce higher increments in propylene consumption. However, no evidence of the incorporation of longer α-olefin was found by ^{13}C NMR.[42] Propylene polymerization kinetics changes because higher polarizabilities of coordinated α-olefin (no copolymerizable) imply higher Zr positive charges and, therefore, higher propagation constants of the polymerizable coordinated olefin. On the other hand, the low concentration of longer α-olefin makes the coordination less probable in the polymerizable position. For copolymers of propylene with low concentrations of longer α-olefins, the termination constant also increases, and the molecular weight is almost unchanged. An increase in the propagation constant is possible if the steric hindrance is not a problem. Olefins like ethylene and propylene would have a positive effect in the presence of low concentrations of longer α-olefins. There are two important points to be considered: the steric effect and the basicity-polarizability effects. First, the coordinated longer α-olefin in the polymerizable position can open the zirconocene ligands, diminishing the steric effect for insertion. Second, considering the basicity, 1-octene can displace ethylene from the nonpolymerizable position, increasing the positive charge on the zirconium atom, but it cannot displace propylene. The sites coordinated with 1-octene will have higher propagation constants for ethylene and propylene, and, therefore, the productivity will be increased especially at 12 mol % of ethylene in the gas phase (near 4 mol % in the liquid phase). The increment is not so high with 1 decene because the basicities of ethylene and 1-decene are similar. The polarizabilities also play a role; the final result obtained will be a compromise between both properties (basicity and polarizability) in the competition for this vacancy. Koivumäki and Seppälä[14] have published similar r_2 parameters for the copolymerization of ethylene with 1-dodecene and 1-octadecene. On the other hand, we found an increase of propylene polymerization with added longer olefins, although the comonomers were not detected by ^{13}C NMR. The basicity remains almost unchanged after a length of 10 C of the pendant chain R. The effect is not so evident when higher amounts of ethylene are present because of the lower relative concentration of sites coordinated with longer α-olefins. On the other hand, it would be almost absent when higher amounts of longer α-olefins are present because of the steric hindrance of the copolymerizable olefin insertion. These ideas are in good agreement with the data reported by Galland et al.[43] They found that for a given zirconocene, the α-olefin size (such as 1-hexene or 1-octene) did not affect neither its reactivity toward ethylene nor its comonomer incorporation in the ethylene/long α-olefin copolymerization. On the other hand, a linear relationship between the concentration of the comonomer incorporated in the copolymer and its concentration in the liquid phase was found.

The trend to decrease the molecular weight in the terpolymers with respect to the corresponding copolymer can be related to an additional chain transfer, in this case to the comonomer. When ethylene is added, the molecular weight decreases because it is possible that a chain transfer to the ethylene monomer exists besides the β-H elimination of the propylene polymerization. In this sense, the chain transfer seems to improve when 1-octene is present. The decrease in the 888-cm^{-1} band (terminal vinylidene) as well as the increase in the definition of the 965-cm^{-1} band (transvinylene) are evidence of additional transfers to the comonomer or termination after 2,1 insertion of the higher α-olefins. The ethylene can probably reactivate these deactivated sites, and chain transfer to propylene, after a secondary insertion, is negligible at low monomer concentrations but becomes more relevant above 0.8 mol/L (pressures higher than 2.0 atm).[44] This fact correlates well with the diminished molecular weight of the terpolymers (Figs. 7 and 8). However, FTIR and WAXS results show that the comonomer increases the regularity and length of the PP blocks (Table III) especially with added 1-octene, where the peak of the α-phase appears with increased importance. Arnold et al.[8] pointed out that a strong influence of the olefin structure on the catalyst was found when 1-octene was copolymerized with propylene. However, only a small difference in the incorporation behavior of the olefin in the polymer chain was detected. Depending on comonomers, the content with a very different ratio of the α-phase to the γ-phase can be ob-
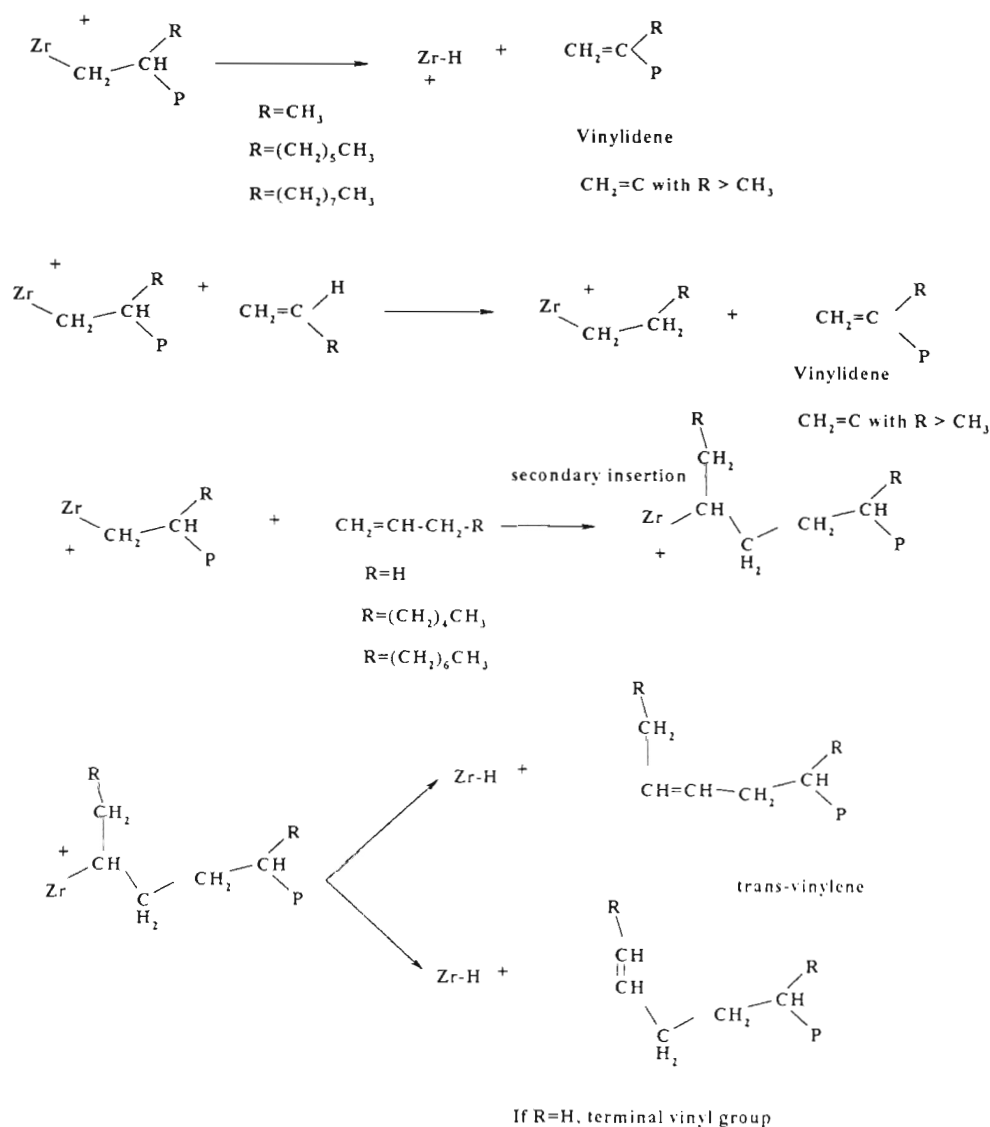
Figure 7. Representation of termination reactions giving vinylidene and transvinylene groups.

tained. Then, modifications in the crystalline phase can be tailored via the copolymer composition. The appearance of a second band in FTIR at 730–735 cm^{-1} could result from an increased crystallinity of the polyethylene sequences. The increased band near 720 cm^{-1} could result from longer ethylene sequences and/or the appearance of terminal alkyl groups in the polymer (Fig. 7). When a longer α-olefin is added, a second band of crystalline polyethylene appears in the FTIR spectra. In **PP40E2D** a band near 750 cm^{-1} appears that could be assigned to $(CH_2)_4$ sequences.[45] Although the molecular weight of the terpolymer is lower than the corresponding copolymers, the crystallinity is higher as can be ob-

served in the WAXS and DSC results. This fact can be related to higher propagation constants that can be corroborated by productivity values. Because the crystallinity increases in the terpolymers at a low termonomer content (Table II), the diffusional explanations cannot be applied. Herfert et al.[46] reported that α-olefins show an accelerating effect on the ethylene polymerization rate during copolymerization, whereas norbornene shows an exclusively decreased rate effect. The acceleration effect can be explained by an increase in the concentration of active sites and/or an increase of the rate of the ethylene insertion constant. In copolymers with a high content of longer α-olefins, the last two monomers have an
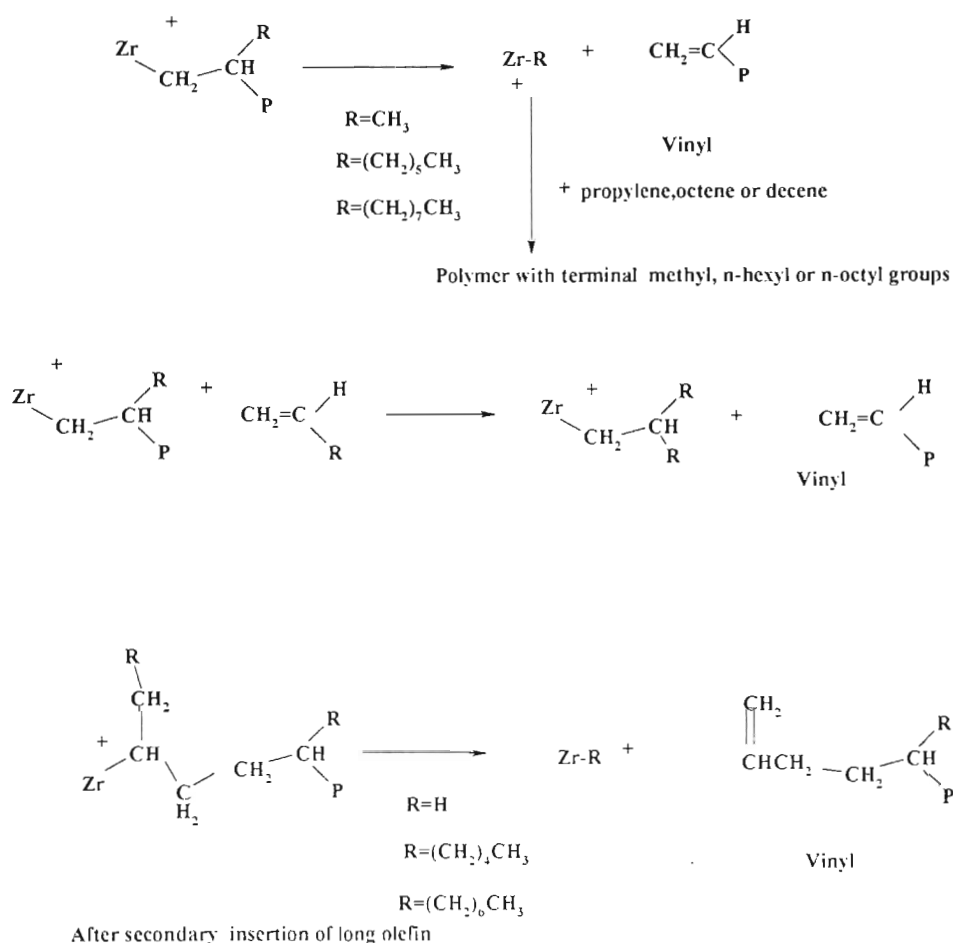
Figure 8. Representation of termination reactions for vinyl group formation.

influence on the insertion of the subsequent monomer. However, the reactivity parameters show only a small dependence on the chain length. Chien and He[47] showed that terpolymers of ethylene, propylene, and ethylidene norbornene have higher mps than the corresponding copolymers (12–13 °C higher) as well as T_g's near −40 °C (the same T_g found in the present work with 40 mol % of ethylene in the gas phase). To obtain the materials, the researchers used SiO_2-supported $EtInd_2ZrCl_2//MAO$, and the activities decreased with the added olefin.

CONCLUSION

A "termonomer effect" was found using $EtInd_2ZrCl_2//MAO$ in terpolymerizations of propylene with ethylene and longer α-olefins when the amount of ethylene in the gas phase was near 12 mol % and a low concentration of longer α-ole-

fin (near 2 mol %) was added. This effect increases the activity and decreases the molecular weight, whereas the mp is increased near 30 °C. Higher ethylene concentrations such as 40 mol % in the gas phase dilute this effect. Steric and electronic considerations can explain this behavior. The longer α-olefin at low concentrations seems to increase the polymerization propagation constant of ethylene and propylene, whereas at the same time, it introduces additional chain-transfer reactions and/or affects the termination constants.

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