

# Highly Active Ethylene/Hydroxyl Comonomers Copolymerization Using Metallocene Catalysts

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**ABSTRACT:** Ethylene was copolymerized with 10-undecen-1-ol and 5-hexen-1-ol using stereorigid [*rac*-ethylene(Ind)<sub>2</sub>ZrCl<sub>2</sub>], [*rac*-ethylene(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>], and the new catalyst systems [*rac*-norbornane(Ind)<sub>2</sub>TiCl<sub>2</sub>] and [mesonorbornane(Ind)<sub>2</sub>TiCl<sub>2</sub>], activated with methylaluminoxane. The characterization of the copolymers by <sup>13</sup>C NMR spectroscopy revealed that the polymerization products were copolymers and that the conversion of the polar comonomer was strongly favored in the case of the

zirconocene precursors. Very high catalytic activity values, nearly independent on the amount of comonomer in the feed, and comonomer incorporations up to 25.4%-weight have been found for 10-undecen-1-ol comonomer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1529–1534, 2008

**Key words:** metallocene catalyst; copolymerization; functionalization of polymers

## INTRODUCTION

The preparation of functionalized polyolefins by direct copolymerization of  $\alpha$ -olefins with comonomers containing polar groups (hydroxyl, ester, etc.) is an area of growing scientific interest, since the presence of reactive groups in otherwise inert materials may extend their final properties, applications, and uses.<sup>1–4</sup> The interest of the use of single-site catalysts for the polymerization of this type of materials lies on the interest of a controlled molecular architecture, i.e., polymer composition, molecular weight, and distribution, which allows the direct study of the relationships between molecular features, physical properties, and processing.<sup>5</sup> Nevertheless, these copolymerization methodologies suffer from a low catalytic activity due to the trend of the polar functional groups to deactivate the catalyst centers. This deactivation is caused by the presence of molecules that contain oxygen atoms, the acid/base Lewis coordination, or a protonolysis reaction. To avoid deactivation it is necessary (a) to increase the steric

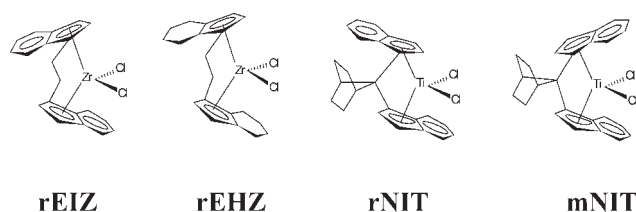
hindrance of comonomer heteroatom, protecting it with trialkylaluminum (TMA, TEA, TIBA, ...) or alkylaluminoxane (MAO) compounds, (b) to reduce the electron-donor ability of the functional group; or (c) to choose catalyst components inert to the functional groups.<sup>4,6–8</sup> Other approach to improve the activity in these processes is to increase the distance between the double bond and the heteroatom of the functional group in the polar comonomer by introducing a spacer segment between them (aliphatic chain).<sup>1,9,10</sup> Aaltonen et al.<sup>1,2</sup> performed very interesting studies concerning the conditions for copolymerization of ethylene and polar monomers, including temperature, pretreatment of the polar comonomer, the metal/MAO ratio, and the chemical structure of the catalyst. They found that the pretreatment of the polar monomer with the cocatalyst (MAO), and a bridge connecting the ligands in the structure of the catalytic precursor strongly favored the copolymerization with ethylene and propylene.

The synthesis of functionalized ethylene copolymers using different methodologies and the characterization of the copolymers are both valuable areas of current interest.<sup>11–14</sup> Continuing with our investigations on the computer simulation of the performance of single-site catalyst systems,<sup>15–23</sup> the synthesis of polyolefins and the evaluation of the properties,<sup>24–26</sup> the study of the relationship between molecular architecture, rheological properties and processing,<sup>27–31</sup> and the combination of experimental

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**Figure 1** Structures of the metallocene catalysts precursors used in the copolymerizations.

results with computer simulations,<sup>32,33</sup> we have further investigated the capability of two bridged metallocene catalyst systems, not reported previously, for the copolymerization of ethylene with polar monomers (10-undecen-1-ol and 5-hexen-1-ol). The catalyst systems are the commercial [*rac*-ethylene(Ind)<sub>2</sub>ZrCl<sub>2</sub>] and [*rac*-ethylene(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>], and the [norbornane(Ind)<sub>2</sub>TiCl<sub>2</sub>], the latter was synthesized by our group.<sup>25</sup> These catalysts have proven to be very active in the ethylene copolymerization with another comonomer type such as styrene.<sup>18,24–26</sup>

## EXPERIMENTAL

The structures of the catalytic precursors used in the copolymerizations are shown in Figure 1. All operations were performed under nitrogen using a glovebox or Schlenk techniques. The reactions were carried out in a 1-L glass autoclave (Büchi). The reactor was filled with toluene (Scharlau Chemie, Barcelona, Spain, 600 mL), and the required amount of MAO (Albemarle, USA, 30 wt % MAO in toluene). After thermostating the reactor at the polymerization temperature (60°C), the polar comonomer (Sigma-Aldrich, Dorset, UK, molar ratio comonomer/MAO = 0.25) was added. Then, the reaction mixture was saturated with ethylene (1.6 bar). Finally, the catalyst (8.3 μM) was injected into the reactor. During copolymerizations, the ethylene pressure was kept constant. The reactions were stopped (after a maximum period of time of 45 min) by degassing the reactor to the atmosphere and by adding a solution of acidic methanol (Scharlau, Chime, Barcelona, Spain, 20 mL, containing 5% HCl). Finally, the reaction products were washed in plenty of acidic methanol and acetone (Scharlau, Chemie, Barcelona, Spain), filtered and dried at 60°C under vacuum to constant weight.

It can be presumed that some of the generated copolymer chains are crosslinked over their OH-groups to the oligomer MAO in solution.<sup>34</sup> The samples have been purified to obtain the molecular features once the insoluble fraction and MAO impurities were recovered by filtration. SEC traces have been obtained in a 150CV Waters GPC coupled with refractive index and viscosity detectors. The solvent used for the analysis was 1,2,4-trichlorobenzene

(TCB), the flow rate was 1.0 mL/min, and the temperature was 145°C. The SEC-viscosity system was calibrated using polystyrene standards.

All the samples were analyzed by <sup>13</sup>C NMR spectroscopy. Spectra were recorded at 100°C on a Bruker DRX 500 spectrometer operating at 75 MHz. The samples were dissolved in hot TCB and d<sup>6</sup>-benzene. Carbon signals and comonomer contents (Tables I and II) were assigned according to the literature.<sup>2</sup>

Melting temperatures (*T*<sub>m</sub>) and crystallinities (α) were determined with a Perkin–Elmer DSC7 differential scanning calorimeter (a value of 288.4 J/g was used as the reference melting enthalpy for 100% crystalline polyethylene). Indium was used for the calibration of the temperature scale. Melting features were measured upon the second heating of the samples from 25 to 160°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

Table I shows the details of the ethylene/10-undecen-1-ol copolymerizations using [*rac*-ethylene(Ind)<sub>2</sub>ZrCl<sub>2</sub>] (rEIZ), [*rac*-ethylene(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>] (rEHZ), and [mesonorbornane(Ind)<sub>2</sub>TiCl<sub>2</sub>] (mNIT) as catalytic precursors. Surprisingly, for the zirconocene precursors, rEIZ and rEHZ, an increased concentration of polar comonomer in the reactor feed does not

**TABLE I**  
Copolymerization of Ethylene with 10-Undecen-1-ol by Different Catalysts and Under Different Comonomer Concentration in the Feed

Catalyst	Run	10-Undecen-1-ol in feed		Yield (g)	Activity [kg h/(mol <sub>M</sub> bar)]	<i>X</i> <sub>com</sub> (mol %)
		(mmol)	Time (h)			
rEIZ (60°C)	1	0.0	0.35	22.4	29,743	0.0
	3	7.5	0.75	28.2	14,135	0.5
	4	15.0	0.75	25.2	11,912	0.9
	5	20.0	0.75	36.0	16,454	1.0
	6	30.0	0.75	19.0	8,182	2.5
	7	50.0	0.42	16.0	10,982	3.1
	8	75.0	0.42	19.6	11,560	5.4
	9	0.0	0.25	30.7	47,969	0.0
rEHZ (60°C)	10	7.5	0.75	27.4	13,600	0.3
	11	15.0	0.75	44.3	20,940	0.4
	12	30.0	0.75	33.1	14,254	1.0
	13	40.0	0.75	30.8	12,555	1.7
	14	50.0	0.75	36.6	14,068	2.3
	15	0.0	0.75	6.9	3,594	0.0
mNIT (60°C)	16	7.5	0.75	4.0	1,989	n.d.
	17	15.0	0.75	2.1	993	n.d.
	18	0.0	0.75	3.8	4,123	0.0
mNIT (35°C)	19	7.5	0.75	6.0	2,984	n.d.
	20	15.0	0.75	8.3	3,923	n.d.
	21	30.0	0.75	7.7	3,316	n.d.
	22	50.0	0.75	6.6	2,537	n.d.
	23	75.0	0.75	0.8	983	1.0

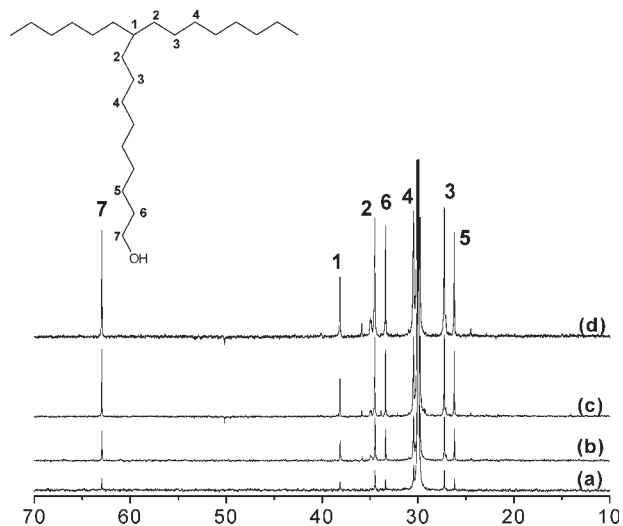
**TABLE II**  
Copolymerization of Ethylene with 5-Hexen-1-ol by Different Catalysts and Under Different Comonomer Concentration in the Feed

Catalyst	Run	5-Hexen-1-ol in feed (mmol)	T (h)	Yield (g)	Activity [kg h/(mol <sub>M</sub> bar)]	X <sub>com</sub> (mol %)
rEIZ (60°C)	24	0.0	0.25	21.0	32,813	0.0
	25	7.5	0.75	11.8	5,868	0.1
	26	15.0	0.75	9.9	4,680	0.5
	27	15.0	0.75	18.2	8,603	n.d.
	28	20.0	0.75	18.6	8,535	n.d.
	29	30.0	0.75	30.0	12,919	n.d.
	30	30.0	0.75	12.2	5,254	1.1
rEHZ (60°C)	31	50.0	0.58	11.3	5,637	1.2
	32	0.0	0.25	30.7	47,969	0.0
	33	7.5	0.75	33.1	16,460	0.0
	34	15.0	0.75	39.7	18,766	0.0

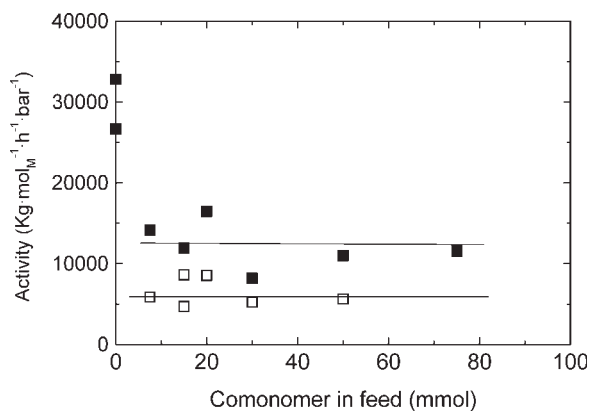
affect the catalytic activity, which remains almost constant within the comonomer feed range studied (Table I, runs 1 to 14). Other results in the literature pointed out an important decrease and moderate activities of the catalysts with the addition of the polar monomer, including both metallocene<sup>2,6,34</sup> and nonmetallocene<sup>35</sup> precursors. When using the new mNIT catalyst, it is observed that the catalytic activity (i) is lower than the obtained with the zirconocene complexes, and (ii) it sharply decreases as the comonomer concentration increases. These facts can be explained since the titanium center is more susceptible to undergo changes in its oxidation state (titanium species with +4 or +2 oxidation states may exist in the reaction medium). In contrast, for the zirconium species, the more stable oxidation state is +4. Our group has recently carried out theoretical studies about the influence of the metal type in the copolymerization of ethylene with  $\alpha$ -olefins, and demonstrated that the formation of the  $\pi$ -complex with an ethylene or comonomer molecule is less feasible in titanium catalysts than in the case of zirconium catalysts due to the great steric hindrance around titanium atom. Moreover, in the titanium systems, the comonomer secondary insertion process leads to more stable structures in the termination step than in the propagation reaction.<sup>18</sup> These facts, applied to the present results with polar comonomers, could explain the low activity and comonomer incorporation when titanium complexes are used. To increase the activity of the titanium complexes (mNIT), the copolymerization reaction have been carried out at a lower temperature (35°C). As expected, the reduced temperature causes an important increase in activity values, as it is observed in Table I (runs 18–23).

Figure 2 provides the <sup>13</sup>C NMR spectra obtained for some of the ethylene/10-undecen-1-ol copolymers synthesized with rEIZ catalyst. For the rest of the samples the recorded spectra are very similar, independently of the type of comonomer. The signal

due to the branching carbon appears at  $\delta = 38.1$  ppm (labeled as number 1 in the scheme of Fig. 2). The peaks observed at  $\delta = 34.5, 27.2, 30.5$  ppm are assigned to S <sub>$\alpha$</sub>  $\delta$ , S <sub>$\beta$</sub>  $\delta$ , and S <sub>$\gamma$</sub>  $\delta$  (labeled as numbers 2, 3 and 4 in the scheme of Fig. 2). The resonances at  $\delta = 26.2, 33.4, \text{ and } 62.8$  ppm are attributed to the carbons settle in the chain of the alcohol branch (labeled as such as 5, 6, and 7 in the scheme of Fig. 2). In general, for all the catalysts used in this study, an increase of the 10-undecen-1-ol concentration causes a higher concentration of the polar monomer in the copolymer, as it can be observed in Table I. Nevertheless, it is possible to observe some differences regarding the comonomer incorporation ability. On one hand, the catalyst rEHZ allows the preparation of copolymers with a slightly higher amount of comonomer than the rEIZ complex (Table I, runs 1–14). On the other hand, these two zirconocene catalysts are more effective than the titanocene precursor



**Figure 2** <sup>13</sup>C NMR spectra of ethylene/10-undecen-1-ol copolymers (rEIZ catalysts) solutions in TCB and d<sup>6</sup>-benzene: (a) 1.0, (b) 2.5, (c) 3.1, and (d) 5.4 mol % hydroxyl contents.

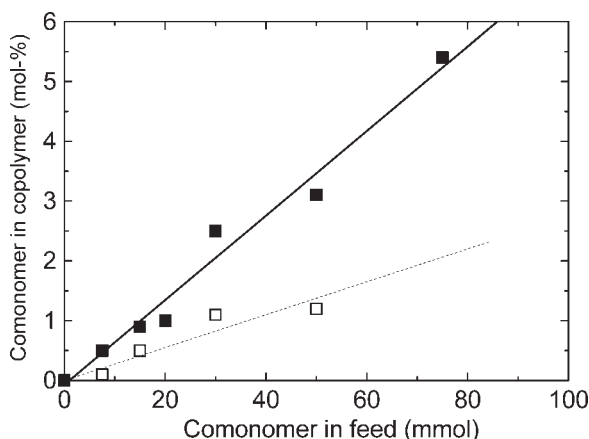


**Figure 3** Effect of the comonomer feed concentration on the activity of the catalyst rEIZ: (■) 10-undecen-1-ol and (□) 5-hexen-1-ol.

sors (Table I, run 8 versus run 23). This fact may be due to the size of titanium atom, which is smaller than zirconium, so the comonomer approximation to the active center is disabled.

The behavior of the two diastereoisomers, *rac*- and *meso*- forms of NIT precursor, have also been compared. The *rac*- isomer is not active in the presence of polar comonomer. This result may be due to the great steric hindrance caused by aromatic ligands disposition in the *rac*- isomer, in such a way that either hinders the bulkier comonomer approximation (10-undecen-1-ol) or does not allow the evolution from the steady state with  $\alpha$ -agostic interactions to the double bond insertion of the polar comonomer into  $\sigma$  Ti—CH<sub>3</sub> bond of the growth polymer (the step where the region of stereoselectivity is produced).

To study the influence of the distance between the double bond and the hydroxyl group in the comonomer, we have also carried out copolymerizations with ethylene/5-hexen-1-ol. The features of the polymerizations are listed in Table II when the zirconocene precursors, rEIZ and rEHZ, are used. As it has



**Figure 4** Comonomer content in the copolymers at different comonomer concentration in the feed obtained with the catalyst rEIZ: (■) 10-undecen-1-ol and (□) 5-hexen-1-ol.

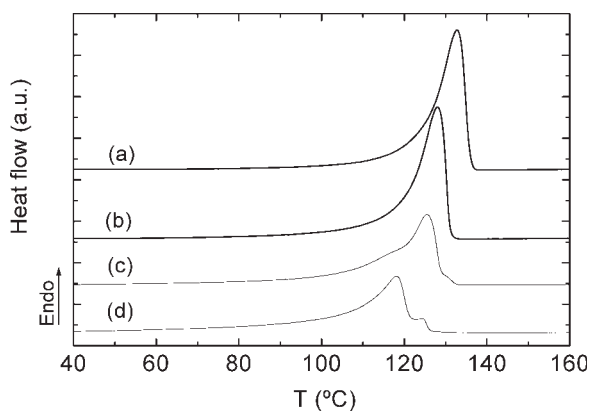
been indicated in previous lines for 10-undecen-1-ol, the catalytic activity of the copolymerizations also remains constant within the studied interval of comonomer feed concentration (Table II, runs 24–31). Concerning the 5-hexen-1-ol incorporation, the most outstanding result is related to the rEHZ catalyst (Table II, runs 33 and 34), which is not able to incorporate this polar comonomer, contrary to the result observed in the case of the rEIZ precursor. In addition, the analysis of the performance of the rEIZ catalyst with both polar species gives rise to the following observations: (i) the activity is two times greater when the 10-undecen-1-ol is used (Fig. 3), and (ii) this longer comonomer incorporates better to the growth polymer chain (Fig. 4). The results in Figure 4 allow us to calculate the reactivity ratios using the Finemann-Ross method<sup>36</sup> for both ethylene/10-undecen-1-ol and ethylene/5-hexen-1-ol copolymerization reactions. These values are  $r_E = k_{EE}/k_{E-undOH} = 4.0 \pm 0.7$  and  $r_{undOH} = k_{undOH-undOH}/k_{undOH-E} = 4.0 \pm 0.2$  for the ethylene/10-undecen-1-ol copolymerization, and  $r_E = k_{EE}/k_{E-hexOH} = 5.1 \pm 0.8$  and  $r_{hexOH} = k_{hexOH-hexOH}/k_{hexOH-E} = 2.5 \pm 0.9$  for the ethylene/5-hexen-1-ol copolymerization. These values for the reactivity ratios show a higher preference to incorporate 10-undecen-1-ol in the copolymers.

Because of all these reasons, we have not carried out copolymerizations of ethylene and 5-hexen-1-ol using the NIT precursors, since these catalysts also show lower activity and comonomer incorporation than zirconocene precursors when 10-undecen-1-ol is used. The length and flexibility of the spacer between the double bond and the polar group in the comonomer could influence the conformers population for which the polar group comes into the proximity of the double bond, i.e., when this distance is longer the polar group can reduce the probability of  $\pi$ -complex formation with the metal center. Ahjopalo et al.<sup>10</sup> found by molecular dynamics simulation that not only the number of conformers was larger in the 10-undecen-1-ol, but also that in most of the low-energy conformers, the distance between the groups was larger than in the case of 5-hexen-1-ol. Therefore, it can be expected that under similar polymer-

**TABLE III**  
Copolymerization of Ethylene with 1-Undecen-1-ol with the rEIZ Precursor

Run	$M_w$ (kg/mol)	$M_w/M_n$	$X_{com}$ (mol %)	$T_m$ (°C)	$\alpha$ (%)
1	545.5	5.0	0.0	133.0	0.63
3	246.4	5.3	0.5	128.1	0.57
4	207.4	4.5	0.9	122.8	0.50
5	164.6	4.5	1.0	125.4	0.46
6	138.4	4.5	2.5	118.1	0.42
7	n.d.	n.d.	3.1	n.d.	n.d.
8	138.4	4.0	5.4	n.d.	n.d.





**Figure 5** DSC melting thermograms of ethylene/10-undecen-1-ol copolymers with different comonomer contents produced with the catalyst rEIZ: (a) 0.0 mol %, (b) 0.5 mol %, (c) 1.0 mol %, and (d) 2.5 mol %.

ization conditions, the comonomer incorporation will be larger in the case of 10-undecen-ol.

The preliminary study of the melting behavior of selected samples of the ethylene/10-undecen-1-ol copolymers obtained with the rEIZ catalyst (see Table III) supports the results obtained by  $^{13}\text{C}$  NMR spectroscopy. The melting endotherms of some of the copolymers are shown in Figure 5. The results obtained are in agreement with the expected behavior of polyolefins with side chain branches. The melting endotherm of the pure polyethylene sample appeared at the characteristic value of  $133^\circ\text{C}$ , which with the addition of 10-undecen-1-ol in the feed decreased below  $120^\circ\text{C}$  for a comonomer content in the copolymer of 2.5%-mol. An increase in the comonomer content in the copolymer produces both a decreased crystallinity and melting temperature peak, as it is expected for side-branched polyolefins in which the branches are excluded from the crystalline phase (see Table III). It can also be seen that the shape of the melting thermograms are influenced by the amount of 10-undecen-1-ol in the copolymer. Figure 5 shows certain degree of heterogeneity in the samples with the highest comonomer content, as it has been observed in other copolymers obtained with single-site catalyst systems.<sup>26</sup>

## CONCLUSIONS

The results obtained in this work clearly indicate that the catalyst chemical structure plays a principal role on copolymerization parameters like the activity and the ability to incorporate polar comonomers. For similar steric environment around the metal center, a change in the electronic features of the ligands can produce variations on the comonomer insertion step ( $\text{H}_4\text{Ind}$  versus  $\text{Ind}$ ). When the catalytic complexes chemical structure is the same, the arrangement of the

ligands (*meso* versus *rac*) can induce that the metal species to be active or not in the presence of a polar comonomer. Furthermore, the bridge length (one or two carbon atoms) and the type of metal (zirconium or titanium) modulate the catalyst performance. The polar comonomer structure, and more specifically the flexibility of the side branch containing the hydroxyl group (10-undecen-1-ol versus 5-hexen-1-ol), which is the length of the spacer between the double bond and the polar group, contributes to the insertion and the incorporation of the comonomer units to the growing polymeric chains. The results obtained in the case of commercial zirconocene precursors are also very interesting, as both show a similar performance for the copolymerization of ethylene with polar monomers, independently of the comonomer feed in the reactor medium. It is possible to obtain with these catalysts polymers with a high 10-undecen-1-ol content (with weight content up to 25%).

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