

SYNTHESIS AND PROPERTIES OF HOMOPOLYMER AND COPOLYMERS
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Abstract Studies related to the behavior of different metallocene catalysts for the homopolymerization of 1-octadecene and its copolymerization with ethylene will be presented. The metallocenes: *rac*-Et(Ind)₂ZrCl₂, *rac*-Me₂Si(Ind)₂ZrCl₂ and Ph₂C(Flu)(Cp)ZrCl₂ were chosen for the homopolymerization study. They show important differences in catalytic activity at high temperatures ($\geq 70^\circ\text{C}$), with *rac*-Et(Ind)₂ZrCl₂ showing the highest activity. At lower temperatures ($\leq 30^\circ\text{C}$) the differences are negligible. For the copolymerization of ethylene with 1-octadecene only the catalysts *rac*-Et(Ind)₂ZrCl₂ and *rac*-Me₂Si(Ind)₂ZrCl₂ were studied. The results show that their catalytic activity is just like that for the homopolymerization of 1-octadecene, with higher activity for the metallocene with the Et-bridged catalyst. ¹³C-NMR analysis shows that the composition of the copolymerization products depends on the catalytic systems. Copolymers obtained with *rac*-Me₂Si(Ind)₂ZrCl₂ have greater comonomer incorporation. Thermal analysis shows that poly-1-octadecene synthesized with the catalyst *rac*-Et(Ind)₂ZrCl₂ is very dependent on the polymerization temperature. The homopolymer obtained at 70°C presents two endothermal peaks at 41°C and 53°C, as compared with the one obtained at 30°C which presents one wider peak with a maximum at 67°C. For the catalyst *rac*-Me₂Si(Ind)₂ZrCl₂ this trend is not observed. The type of metallocene and the reaction time do not significantly change the intrinsic viscosity, but the polymerization temperature changes it drastically, giving higher values at lower temperature. Viscosity measurements on the copolymers show that an increase of comonomer concentration in the feed reduces the molecular weight of the copolymer, and it was also found that for homopolymer, the molecular weight is independent of the catalytic systems.

Keywords Homopolymerization, Copolymerization, Metallocene, Catalytic activity, Poly-1-octadecene

INTRODUCTION

The discovery that metallocene catalysts can polymerize different monomers at a very high rate and make it possible to obtain *homo*- and *co*-polymers with well defined structures, has introduced new alternatives for producing a wide variety of polymer materials which show attractive properties. In contrast to conventional multisite Ziegler-Natta catalysts, the metallocene based catalysts produce very uniform *homo*- and *co*-polymers. The presence of an aromatic planar ring, steric and electronic effects, and the bridge group that restricts the mobility of the metallocene, play an important role in the control of stereochemistry, molecular mass and incorporation of α -olefin comonomer^[1, 2].

Recently, much attention has been paid to the preparation of *homo*- and *co*-poly(α -olefins) with novel interesting properties using well-known metallocene catalysts. These poly(α -olefins) can be tailor-made for specific applications by introducing long chain or well defined functional groups in the hydrophobic main chain, or at the end of each polymer chain. Our earlier investigations have shown that several metallocene catalysts

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promote the copolymerization of ethylene with α olefins^[3, 4].

In recent years, theoretical models obtained with *ab-initio* and semiempirical methods have been used to understand the experimental behavior in metallocene-catalyzed olefinic systems, and also to predict the behavior of similar new catalytic systems. Using these methods, several phenomena have been studied^[5]. Among them are the tacticity of the resulting polymer, the reaction mechanism and the influence of agostic interactions (where the C—H bond of the growing polymer chain acts as a ligand to the metallic center forming a C—H metal bond)^[6–8]. Other studies make use of molecular mechanics to characterize, from a geometry-optimized standpoint, catalyst molecules for obtaining ring dihedral angles, for observing the influence of ring substituents on the catalytic properties, and for determining possible steric hindrances affecting polymer chain structure^[9, 10].

The purpose of this work is to present some results obtained from the homopolymerization of 1-octadecene and the copolymerization of ethylene with 1-octadecene, using some racemic and nonracemic catalytic systems. For homopolymerization, the yield, catalytic activity and viscosity will be related to the metallocene structure. For the copolymerizations, the study is based on the observation of how the comonomer concentration influences the system's catalytic activity and the viscosity of the polymer. DSC analysis shows that the type of metallocene and polymerization temperature influence the final structure formed.

EXPERIMENTAL

Materials

Commercial toluene was purified by refluxing over metallic sodium, using benzophenone as an indicator. The 1-octadecene comonomer (Aldrich) was purified by distilling over metallic sodium. Polymerization grade ethylene was deoxygenated and dried by passage through columns of BASF R3-11 catalyst and 0.4 nm molecular sieves. Commercial methylaluminoxane (MAO) and the catalysts *rac*-Et(Ind)₂ZrCl₂ and *rac*-(CH₃)₂Si(Ind)₂ZrCl₂ from Witco and Boulder Scientific Company, were used without further refinement. All manipulations were carried out in an inert nitrogen atmosphere.

Homopolymerization of 1-Octadecene

Reactions were carried out in a 250 mL flask and 500 mL glass reactor using toluene as solvent at a reaction temperature of 70°C and 30°C. The reagents were introduced into the reactor in the following order: toluene, MAO, monomer and the catalyst. The reaction was terminated by the addition of a 2 vol% of HCl/methanol solution and then washed with acetone to remove all the unreacted monomer.

Copolymerization

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

Characterization

The amount of comonomer incorporated was measured by ¹³C nuclear magnetic resonance spectroscopy. Measurements were performed at 80 °C on a Varian XL-200 or XL-300 spectrometer. The samples were dissolved in *o*-dichlorobenzene. Benzene-*d*₄ (20%) was used as an internal lock, and chromium(III) triacetylacetonate as paramagnetic substance to reduce the relaxation time. The intrinsic viscosities were determined in decahydronaphthalene (decalin) at 135°C using a Viscosimatic-Sofica viscometer.

For poly-1-octadecene, calorimetric analyses were carried out in a Perkin-Elmer DSC7 calorimeter, connected to a cooling system and calibrated with different standards. The sample weights ranged from 7 to 10 mg. The DSC melting curves were recorded at a heating rate of 10 K/min, after crystallization from the melt at

10 K/min.

RESULTS AND DISCUSSION

Homopolymerization of 1-Octadecene: Activity

Table 1 shows the results of the catalytic activity for the homopolymerization of ethylene (C₂) and 1-octadecene (C₁₈), obtained with different metallocene catalysts: *rac*-Et(Ind)₂ZrCl₂, *rac*-Me₂Si(Ind)₂ZrCl₂ and Ph₂C(Flu)(Cp)ZrCl₂. In the homopolymerization of ethylene, the catalysts do not show any really marked difference, but for the homopolymerization of 1-octadecene, the *rac*-Et(Ind)₂ZrCl₂ catalyst presents the highest activity. Under the reaction conditions (closed reaction vessel with the same starting amount of 1-octadecene), it was observed that after 30 min the activity of the polymer produced by *rac*-Et(Ind)₂ZrCl₂ relative to *rac*-Me₂Si(Ind)₂ZrCl₂ was approximately 3 times higher. This result is consistent with the findings from theoretical studies where the electronic charge on the Me₂Si-bridged compound is more positive than on the Et-bridged catalyst, and the monomer linked more times to the active center^[5]. These results are also consistent with a recent study reported by Brintzinger on the correlation between charge density and dissociation free energy^[11].

In order to verify the thermal properties of the poly-1-octadecene, syntheses at different temperatures were carried out in a different reactor (500 mL), characterized by having an excellent control of temperature and stirring. Table 2 shows the results of the catalytic activity at different temperatures for the two main catalysts, *rac*-Et(Ind)₂ZrCl₂ and *rac*-Me₂Si(Ind)₂ZrCl₂.

Table 1. Yield, activity and viscosity values at different times for the homopolymerization of C₂ and C₁₈ using *rac*-Et(Ind)₂ZrCl₂, *rac*-Me₂Si(Ind)₂ZrCl₂ and Ph₂C(Flu)(Cp)ZrCl₂ catalysts

Metallocene type	Monomer	[Zr]×10 ⁵ (mol/L)	<i>t</i> (h)	Yield (g)	Activity (kg pol/mol Zr h)	Viscosity (dL/g)
<i>rac</i> -Et(Ind) ₂ ZrCl ₂	C ₂ ^a	0.76	0.5	27.9	18,400	2.71
	C ₁₈ ^b	6.4	0.5	4.5	1,765	–
	C ₁₈	6.4	1	6.1	1,200	0.63
	C ₁₈	6.3	3	6.3	420	0.73
<i>rac</i> -Me ₂ Si(Ind) ₂ ZrCl ₂	C ₂	0.76	0.5	25.9	17,100	3.73
	C ₁₈	6.6	0.5	1.5	580	–
	C ₁₈	6.6	1	2.6	530	0.62
	C ₁₈	6.6	3	6.3	417	0.72
Ph ₂ C(Flu)(Cp)ZrCl ₂	C ₁₈	6.5	3	5.8	357	0.96

Reaction conditions: a) ethylene, C₂: *n*(Zr) = 1.9 × 10^{−6} mol; *n*(Al)/*n*(Zr) = 2,620; *T* = 60 °C; solvent = 250 mL toluene; *t* = 30 min; ethylene pressure = 1.6; b) 1-octadecene: C₁₈ = 7.89g; *n*(Zr) = 5 × 10^{−6} mol; *n*(Al)/*n*(Zr) = 2,000; *T* = 70 °C; solvent = 60 mL toluene, reactor = 250 mL flask

Table 2. Yield, activity and viscosity values at different temperatures for the homopolymerization of C₁₈ using *rac*-Et(Ind)₂ZrCl₂ and *rac*-Me₂Si(Ind)₂ZrCl₂

Metallocene type	[Zr]×10 ⁵ (mol/L)	<i>T</i> (°C)	Yield (g)	Activity (kg pol/mol Zr h)	Viscosity (dL/g)
<i>rac</i> -Et(Ind) ₂ ZrCl ₂	5.8	70	9.2	1,102	0.63
	6.2	30	3.8	472	1.26
<i>rac</i> -Me ₂ Si(Ind) ₂ ZrCl ₂	5.9	70	5.1	609	0.62
	5.8	30	3.4	408	1.26

Reaction conditions: C₁₈ = 13.4 g, *n*(Zr) = 8 × 10^{−6} mol; *n*(Al)/*n*(Zr) = 2,000; solvent = 100 mL toluene, RPM = 300, *t* = 1 h, reactor = 500mL

The catalytic activity of the *rac*-Et(Ind)₂ZrCl₂ shows a great decrease. This can be due to the steric effect related to the loss of mobility of the aromatic ring linked to the zirconium atoms. This make it difficult for the olefin to be inserted, affecting the catalytic behavior of the metallocene. On the other hand, the *rac*-

$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ has a more rigid structure and the temperature does not change the interaction too much.

Copolymerization of Ethylene with 1-Octadecene: Activity

Table 3 shows the catalytic behavior of a system in the presence of comonomer for two different catalysts, $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$, respectively. Here it is clear that the increase of the comonomer fraction causes an increase in the catalytic activity until a maximum value is reached. Several explanations have been given^[4], of which the more consistent could be the following two: on the one hand, the presence of the comonomer and its incorporation increase the solubility of the monomer in the liquid phase, thus increasing its insertion rate; and on the other hand, the comonomer activates new catalyst sites by an increased affinity for the metallocene.

Table 3. The effect of comonomer concentration on the catalytic activity, content of 1-octadecene and viscosity in ethylene copolymers, with $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$

Metalloocene type	[comonomer] feed (mol/L)	Activity 10^{-3} (kg/mol Zr h bar)	Comonomer incorporated (mol%)	Viscosity (dL/g)
<i>rac</i> - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$	0	18.4	0	2.71
	0.06	62.3	1.1	1.98
	0.012	48.2	2.0	1.80
	0.23	56.6	4.7	1.47
	0.33	61.6	5.7	1.20
<i>rac</i> - $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$	0	17.1	0	3.73
	0.06	24.0	1.8	2.36
	0.12	33.9	4.0	1.87
	0.23	-	-	-
	0.33	28.9	8.4	1.42

Reaction conditions: $n(\text{Zr}) = 1.9 \times 10^{-6}$ mol; $n(\text{Al})/n(\text{Zr}) = 2,620$; $T = 60^\circ\text{C}$; $t = 30$ min; ethylene pressure = 1.6 bar

In Table 3, it is shown that the catalytic activity of the Et-bridged catalyst is higher than that of the Me_2Si -bridged catalyst. As mentioned before, this is consistent with the findings from theoretical studies where the electronic charge in the Me_2Si -bridged compound is more positive than that on the Et-bridged catalyst, and the monomer is linked more times to the active center^[5].

Comonomer Incorporation.

As shown in Table 3, the amount of comonomer incorporated in the copolymer increases with the increase of 1-octadecene concentration of the reaction medium.

For the copolymerization with other comonomers with shorter chains, such as 1-hexene^[5], it has been found that the percentage of comonomer incorporation is independent of the catalytic systems. Nevertheless, in the presence of 1-octadecene some significant differences are observed, the $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$ system incorporates more comonomer than the $[\text{Et}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$ system (8.4 mol% for the former, and 5.7 mol% for the latter, for a starting concentration of 0.33 mol/L). This behavior can be explained based on the theoretical analysis already discussed^[5]: the approach of a 1-octadecene chain to the metallic center finds less opposition in $[\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$ than in $[\text{Et}(\text{Ind})_2\text{ZrCH}_3^+ \text{Cl}_2\text{MAO}^-]$, and therefore the metallic center is more favorable in the first catalyst than in the second.

With respect to the percentage of incorporation as a function of the type of comonomer, it was found that there is a lower incorporation for those of larger size such as 1-octadecene, and this is what was expected due to the steric effects of the larger groups^[4, 5].

POLYMER PROPERTIES

Homopolymer of 1-Octadecene: Crystallinity and Viscosity

For the 1-octadecene homopolymer obtained with the three catalysts, the DSC melting curve shows very interesting results which are presented in Figs. 1, 2 and 3. Figure 1 shows the DSC curves for poly-1-octadecene

obtained with $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ catalyst at 70 and 30 °C, respectively. For the 70 °C curve there are two endothermic peaks at 41 and 53 °C, and for the 30 °C curve the peaks are at 46 and 67 °C, in inverse proportion to the peaks at 70 °C. The presence of these two peaks may be due to the presence of two types of crystalline phases resulting from isotactic and atactic structures. The endotherms at 53 °C and 67 °C are due to the presence of crystalline regions in the isotactic poly-1-octadecene. The peaks at lower temperatures could result from the disordered regions of the chains, but which present certain crystallinity due to some partial order of the lateral chain of poly-1-octadecene. The inversion of the intensity of the peaks may be due to the increase in mobility of the structure of the catalyst when it is polymerized at 70 °C, affecting the stereoselectivity. When the temperature is lowered to 30 °C the inverse phenomenon is observed. Figure 2 shows the melting curves of the synthesized poly-1-octadecene with the $rac\text{-Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$ catalyst at 70 and 30 °C. It is possible to observe a similar melting curve with differences only in the melting point. The curve of the synthesized homopolymer at 70 °C shows two endothermic peaks at 40 and 57 °C, and the one synthesized at 30 °C presents a peak at 67 °C. Clearly, lowering the temperature implies an increased rigidity in the metallocene structure, allowing a better stereoselectivity control.

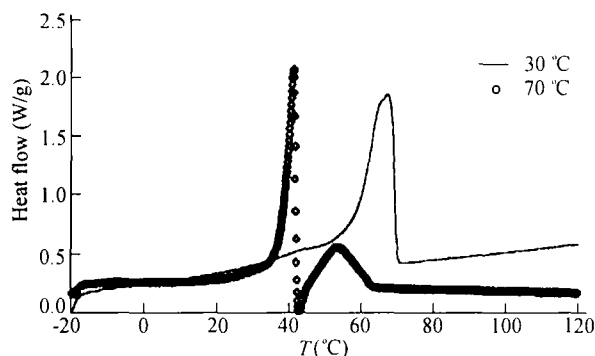


Fig. 1 DSC melting curve of 1-polyoctadecene obtained with $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ at 70 °C and 30 °C

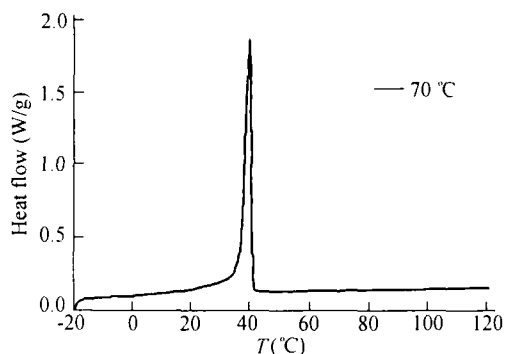


Fig. 2 DSC melting curve of 1-polyoctadecene obtained with $rac\text{-Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$ at 70 °C and 30 °C

As it can be seen in Fig. 3, for the polymer obtained with $\text{Ph}_2\text{C(Flu)(Cp)ZrCl}_2$ catalysts there is only one peak at 37 °C, which can be attributed to the syndiotactic order for the chain of poly-1-octadecene, presenting one crystalline phase.

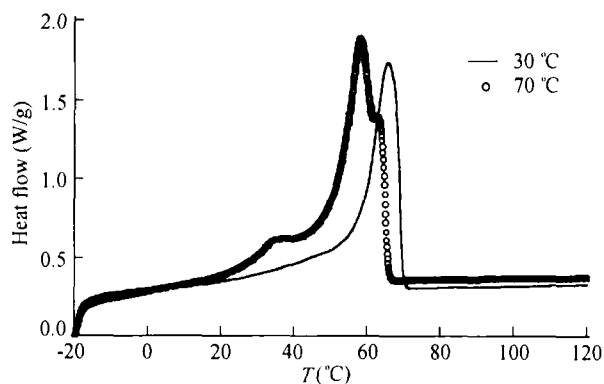


Fig. 3 DSC melting curve of 1-polyoctadecene obtained with $\text{Ph}_2\text{C(Flu)(Cp)ZrCl}_2$ at 70 °C

The viscosity values show no great changes due to the metallocene involved; The higher value found for the $\text{Ph}_2\text{C(Flu)(Cp)ZrCl}_2$ could be due to the lower reactivity of the active center with the monomer, decreasing transfer and β -elimination reactions. When the temperature is decreased, an increase in viscosity values was found. This is in agreement with this type of catalytic reactions where the termination rate constant decreases

with the decrease of temperature.

Copolymer of Ethylene -1-Octadecene: Viscosity

In Table 3 it is shown that an increase in the comonomer concentration in the reaction medium decreases the intrinsic viscosity and therefore the weight average molecular weight of the polymer. This can be explainedly assuming that the ratio of propagation rate to the termination rate is decreased by the presence of comonomer, due to β -type terminations. This is attributed to the fact that the α -olefin favors the stabilization of the four-center intermediary, thereby allowing more time for interaction with the active site and making it possible for β -elimination or monomer transfer reactions to occur^[4].

It was also noticed that the variation in the molecular weight is independent of the catalytic system, as was found for the homopolymerization of 1-octadecene.

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