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Synthesis and properties coming from the copolymerization of propene with α-olefins using different metallocene catalysts

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Abstract

Copolymerization of propene with two α-olefins (1-hexene and 1-octadecene) using iso- and syndioselective metallocene catalysts ($EtInd_2ZrCl_2$, $Et(2\text{-}MeInd)_2ZrCl_2$, $Me_2SiInd_2ZrCl_2$, $Ph_2CFluCpZrCl_2$ and $Me_2CFluCpZrCl_2$) activated with methylaluminoxane (MAO) is reported. The so-called comonomer effect was seen in the catalytic activity of the $Me_2SiInd_2ZrCl_2$/MAO system. Incorporation of syndiotactic copolymers was greater than that of isotactic copolymers. The molecular weight of the isotactic copolymers was not affected significantly by the presence of the comonomer, but the molecular weights of the copolymers obtained with the syndioselective catalysts decreased with increasing comonomer concentration in the medium. Tensile properties were studied. Syndiotactic copolymers with incorporation of the order of 6 mol% of 1-octadecene presented elastomeric properties.

Keywords: Propene/α-olefins copolymers; Metallocene catalysts; Polymer properties

1. Introduction

One of the efficient ways of modifying the properties of a polymer is the introduction of a second monomer into the main chain. In this relation, homo and copolymers of ethylene with α-olefins [1–6], cycloolefins [7–9], polar monomers [10] and dienes [11] obtained with metallocene catalysts have been studied extensively. The copolymers of propene and α-olefins, however, have received less attention.

Henschke et al. [12] studied the copolymerization of propene with different α-olefins (1-butene, 1-hexene, 1-octene, 1-dodecene and 1-hexadecene) using the $Et(Ind)_2HfCl_2$/MAO catalyst. Their results show that there is only a slight decrease in the reactivity of the comonomers as the length of the side-chain increases. On the other hand, the crystallinity of the material is affected substantially by the percentage of branching introduced in the chain. The above has a direct effect on the melting temperature, which decreases when going from a crystalline to a more amorphous material. However, size has no effect on this process, but rather the degree of incorporation [13–15].

The type of catalyst used and the polarity of the solvent affect the content of the comonomer inserted in the polymer chain. Mülhaupt and Schneider [16] showed that the incorporation of a benzene ring in the indenyl group increases the incorporation of 1-octene in copolymerizations with propene. On the other hand, Sacchi and co-workers [17], using the $Et(Ind)_2ZrCl_2$/MAO system in the copolymerization of propene and 1-hexene found that a

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gradual increase of CH_2Cl_2 in the CH_2Cl_2/toluene mixture used as solvent increased the catalytic activity and the incorporation of 1-hexene.

The objective of this work was to study the copolymerization of propene with two kinds of α-olefin (1-hexene and 1-octadecene), using iso and syndioselective metallocene catalysts (rac-$EtInd_2ZrCl_2$, rac-$Et(2\text{-}MeInd)_2ZrCl_2$, rac-$Me_2SiInd_2ZrCl_2$, $Ph_2CFluCpZrCl_2$ and $Me_2CFluCpZrCl_2$). Values of activity, molecular weight and mechanical properties will be evaluated.

2. Experimental

2.1. Materials

The solvent (commercial toluene) was purified by refluxing over metallic sodium, with benzophenone as indicator. The comonomers, 1-hexene and 1-octadecene, were purified by refluxing over metallic sodium for 3 h and then recovered by distillation, with that of 1-octadecene carried out under reduced pressure. Polymerization grade propylene (provided by Petroquim S.A.) was deoxygenated in a column containing BASF R3-11 catalyst, and then dried by passing it through a column of 4A molecular sieves. The methylaluminoxane (MAO) (from Witco) and the catalysts (provided by Boulder Scientific Company) were used without prior treatment. All the operations were carried out in an atmosphere of high purity N_2 (99.95%), using a dry box and the Schlenk technique for handling the metallocenes.

2.2. Polymerization

The polymerizations were carried out in a 1-liter Büchi autoclave reactor equipped with a temperature and internal pressure control system, and with stirring. The reactor was coupled to a Brook model 5860E propene flowmeter, connected to data recording software to monitor the consumption of monomer during the course of the reaction.

The solvent was introduced in the reactor by nitrogen overpressure. The catalyst was dissolved in a given volume toluene. The required volumes of MAO, comonomer and catalyst were added using syringes. After evacuating the nitrogen from the reactor, the reaction was started by introducing the propylene until the desired pressure was reached. Reaction time was 30 min. The solvent volume was adjusted in such a way that the total volume inside the reactor was 500 mL.

The reaction was stopped by addition of a solution of methanol acidified with HCl (2%). The polymer was recovered by filtration and was washed with methanol and acetone to remove the unreacted comonomer. Finally, the product was dried in vacuum at 60 °C.

2.3. Characterization

2.3.1. Calorimetric analysis

A Perkin–Elmer DSC7 calorimeter connected to a cooling system and calibrated with different standards was used. Sample weight varied between 7 and 10 mg. The melting curves from the differential scanning calorimetry were recorded at a rate of 10 °C/min. Crystallization of the sample was done at the same rate. The melting curves obtained from the second heating were analyzed.

2.3.2. ^{13}C-NMR analysis

The ^{13}C-NMR spectra were obtained at 90 °C on a Varian Inova 300 spectrometer operated at 75 MHz. The samples were prepared by dissolving the polymer in *o*-dichlorobenzene and benzene-d_6 (20% v/v) in 5-mm sample tubes. The deuterated solvent was used to provide the internal lock signal. The chemical shift was referenced to TMS. The spectra were taken with a flip angle of 74°, an acquisition time of 1.5 s and a decay time of 4.0 s.

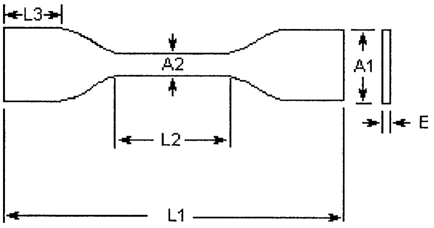
2.3.3. Molecular weights

Molecular weights were determined by GPC in a Waters Alliance 2000 system equipped with an optic differential refractometer. Three separation columns, HT6E, HT5 and HT3 were used, previously calibrated with narrow molecular weight distribution polystyrene standards. 1,2,4 Trichlorobenzene was used as solvent. The flow rate for analysis was 1 mL/min at 135 °C.

2.3.4. Tensile testing

The polymer obtained was placed in a stainless steel mold having the sizes shown in Scheme 1 and molded in an HP press under a pressure of 40 bar at the melting temperature of the material for 5 min. The sample was cooled with water at a rate of 15 °C/min.

After letting them rest and conditioning them for 24 h at



Dimensions (mm)	(mm)
L1: 80	A1: 13
L2: 50	A2: 10
L3: 10	E: 2

Scheme 1. Test sample used for tensile testing.

the temperature at which the test would be carried out, the samples were tested in a HP model D-500 dynamometer at a rate of 10 cm/min at room temperature.

3. Results and discussion

3.1. Catalytic activity

In the copolymerization of propene with α-olefins, the comonomer concentration and the type of catalyst were varied, keeping constant the other experimental variables (mol of catalyst, propene pressure, reaction temperature, and cocatalyst/catalyst ratio).

Figs. 1 and 2 show the results of the catalytic activity as a function of the initial concentration of 1-hexene and 1-octadecene, respectively. In general, a decrease of the catalytic activity is seen as comonomer concentration increases in the reaction medium. The insertion of a propene molecule or comonomer after to a comonomer insertion is much slower than a propene insertion followed for other propene insertion. The activity values of the copolymerization of propene and 1-hexene were greater than with 1-octadecene. The reason for this behavior can be attributed to steric hindrance caused by the larger size of the 1-octadecene branch.

The exception to this general behavior appears with the $Me_2SiInd_2ZrCl_2$/MAO system, which shows an increase of the polymerization rate compared to the propene homopolymerization. This synergistic effect (comonomer effect) has been reported for other systems, in copolymerizations of ethylene and propylene with α-olefins [17,18–21]. Fan et al. [20] it has also shown this synergistic effect in copolymerizations of propene and 1-octene with the $Me_2SiInd_2ZrCl_2$/MAO/TIBA system.

It has been proposed that occasional secondary insertions will lead the propagation chain to a dormant state and greatly reduce the polymerization rate [20,22]. The incorporation of the α-olefin to the main chain it would allow to reactivate the 'dormant sites', an explanation that applies quite well to our case. However, Landis et al., in a recent work [23], has demonstrated that the secondary insertions do not constitute a 'dormant site' in 1-alkene polymerizations. This new discovery makes necessary to analyze other possible explanations.

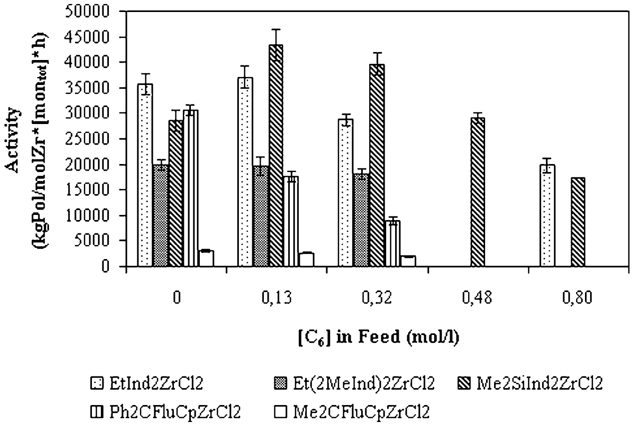


Fig. 1. Effect of initial concentration of 1-hexene on activity for the different catalytic systems in study. Activity = kgPol/molZr[mon_{tot}]h, were [mon_{tot}] is the total concentration of monomers ([propene] + [α-olefin]). Propene concentration was calculated in accord with Ref. [30].

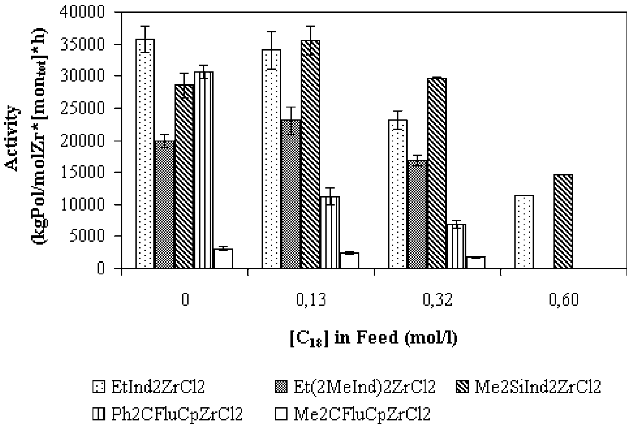


Fig. 2. Effect of initial concentration of 1-octadecene on activity for the different catalytic systems in study. Activity = kgPol/molZr[mon_{tot}]h, were [mon_{tot}] is the total concentration of monomers ([propene] + [α-olefin]). Propene concentration was calculated in accord with Ref. [30].

Copolymerizations with the syndioselective catalysts show a greater decrease of activity as the incorporation of α-olefin increases. The tacticity analysis indicates that the *mr* triad increases dramatically with the addition of comonomer, suggesting that site epimerization becomes a mechanism competitive with insertion. Recent work by Waymouth et al. [24] on the synthesis of syndiotactic polypropylenes using C_1 symmetry catalysts of the $Me_2C(Cp)(3\text{-}CH_2X\text{-}2R\text{-}Ind)MCl_2$ (M = Zr, Hf; R = H, Me; X = Me, $SiMe_3$) type also showed that an increase of backskip decreases the activity. The low activity shown by the $Me_2CFluCpZrCl_2$ catalyst can be attributed to active center deactivation caused by the highly electrophilic character of this complex [25].

3.2. Molecular weight

From the results shown in Table 1, no significant influence of the comonomer on molecular weight is seen when polymerization takes place with the isoselective catalysts. On the contrary, the molecular weight of the copolymers obtained with the syndioselective catalysts decreased as the comonomer concentration increased. There are an almost linear correlation between the activity and the molecular weight (remember that these catalysts showed a dramatic decrease of activity when increasing the concentration of the comonomer). The larger spacing between the Cp rings allows a better approach of the long-chain α-olefin, giving rise to chain transfer to the

Table 1
Effect of the comonomer on the molecular weight of the copolymers

Catalyst	[α-Olefin] in the feed (mol/L)	$M_w \times 10^{-3}$ (g/mol)		M_w/M_n	
		C_6	C_{18}	C_6	C_{18}
$EtInd_2ZrCl_2$	0.13	29	28	2.0	1.9
	0.32	29	30	2.0	1.8
	0.6	–	32	–	1.8
	0.8	32	–	1.8	–
$Me_2SiInd_2ZrCl_2$	0.13	56	56	2.1	2.0
	0.32	54	54	2.1	2.0
	0.6	–	52	–	1.8
	0.8	49	–	1.8	–
$Et(2MeInd)_2ZrCl_2$	0.13	68	66	2.1	2.1
	0.32	67	67	2.0	1.9
$Ph_2CFluCpZrCl_2$	0.13	358	388	2.0	1.8
	0.32	322	374	1.9	1.7
$(CH_3)_2CFluCpZrCl_2$	0.13	–	120	–	2.0
	0.32	–	117	–	1.8

comonomer, a process that is enhanced by the slower insertion of propene. The above is supported by the fact that the molecular weight of the copolymers with 1-hexene are lower than those with 1-octadecene. The smaller size of the former allows a better approach to the active center.

In all cases, the molecular weight distribution (M_w/M_n) is around 2, a value characteristic of metallocene systems.

3.3. Incorporation of α-olefin and tacticity

Calculation of the amount of comonomer incorporated into the copolymer was made by ^{13}C-NMR. Figs. 3 and 4 show the spectra of copolymers of propene with 1-octadecene and 1-hexene, respectively, obtained with different initial comonomer concentrations.

Assignments of the ^{13}C-NMR spectra of the copolymers of propene-α-olefin were made using the rules of Linderman

Table 2
Chemical shifts measured in the spectra of propene-1-octadecene copolymers

Signal (No.)	Carbon	Chem. shift (ppm)
1	$1B_{16}$	13.86
2	$1B_1$	20.61
3	$2B_{16}$	22.65
4	$15B_{16}$	27.52
5	brB_1	28.38
6	$4B_{16}$	29.71
7	$5\text{–}13B_{16}$	29.96
8	$14B_{16}$	30.21
9	$3B_{16}$	32.40
10	brB_{16}	32.91
11	$16B_{16}$	34.97
12	$\alpha\alpha B_{16}B_{16}$	39.48
13	$\alpha\alpha B_1B_{16}$	41.92
14	$\alpha\alpha B_1$	44.36

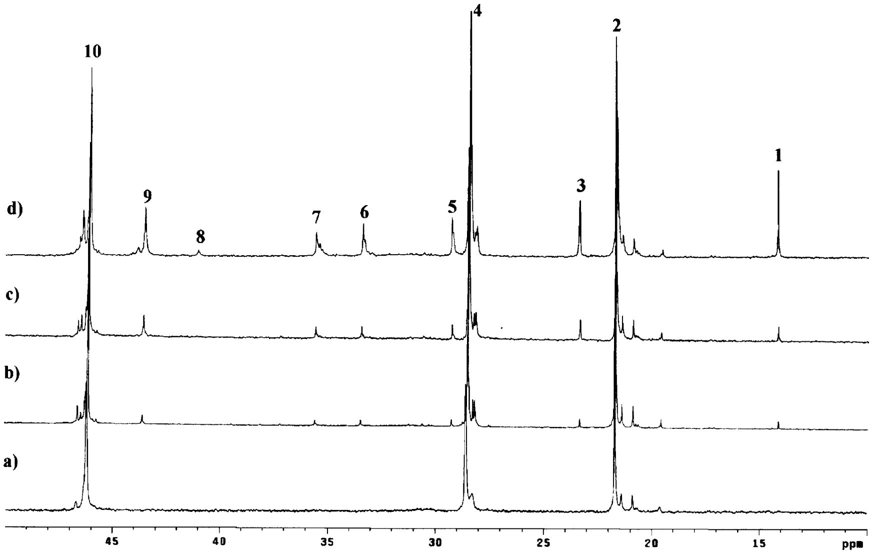


Fig. 3. ^{13}C-NMR spectra of copolymers of propene-1-octadecene obtained with catalyst $EtInd_2ZrCl_2$. (a) Propene homopolymer, (b) 0.12 M of 1-octadecene, (c) 0.32 M, (d) 0.6 M of 1-hexene.

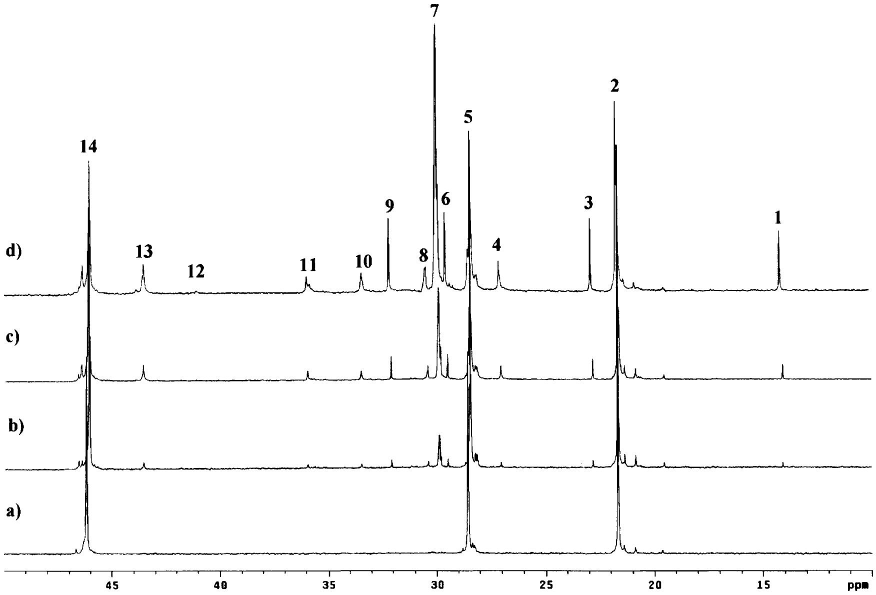


Fig. 4. ^{13}C-NMR spectra of copolymers of propene-1-hexene obtained with catalyst $EtInd_2ZrCl_2$. (a) Propene homopolymer, (b) 0.12 M of 1-hexene, (c) 0.32 M, (d) 0.8 M of 1-hexene.

and Adams and data from the literature [13,14,16,20]. They are given in Tables 2 and 3. The nomenclature used is that of Usami [26], according to Fig. 5.

The percentages of comonomer incorporation are shown in Table 4. The isotactic copolymers have similar percentages of comonomer inserted in the chain. No important differences are seen in the incorporation of 1-hexene and 1-octadecene. Neither the methyl group located at position 2 of the aromatic ring nor the kind of bridge affected the incorporation of the comonomer. The syndiotactic copolymers show greater incorporation of α-olefin than their isotactic homologues. As mentioned earlier, the syndioselective catalysts have larger opening angles between the Cp rings, facilitating the insertion of the α-olefin.

As the concentration of comonomer increases in the reaction medium, the percentage of incorporation in the polymer chain also increases.

The average number of consecutive propene units (n_p) (calculated in accord with Ref. [27]) decreases with the increase of α-olefin incorporated, as expected. The average number of consecutive comonomer units is 1 in all cases. All these values indicate a tendency for the α-olefin to form isolated units between blocks of propene.

Table 3
Chemical shifts measured in the spectra of propene-1-hexene copolymers

Signal (No.)	Carbon	Chem. shift (ppm)
1	$1B_4$	13.86
2	$1B_1$	20.61
3	$2B_4$	22.90
4	brB_1	28.38
5	$3B_4$	29.96
6	brB_4	32.91
7	$4B_4$	34.72
8	$\alpha\alpha B_4B_4$	39.48
9	$\alpha\alpha B_1B_4$	41.92
10	$\alpha\alpha B_1$	44.36

The tacticity of the copolymers at the triad level is shown in Tables 5 and 6. The isotacticity of the copolymers obtained with the isoselective catalysts increases as the percentage of incorporated comonomer

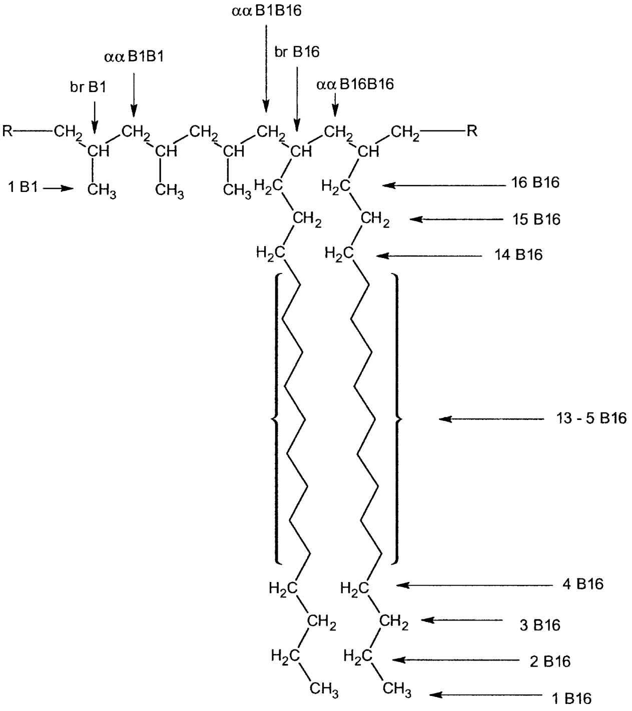


Fig. 5. Nomenclature used by Usami [26] to identify the different types of carbon.

Table 4
Percentage of comonomer incorporation, and mean number of consecutive units of propene (n_p) as a function of the initial concentration of α-olefin

Catalyst	[α-Olefin] in the feed (mol/L)	Incorporation (mol%)		n_p[a]	
		C_6	C_{18}	C_6	C_{18}
$EtInd_2ZrCl_2$	0.13	2.1	2.3	65	70
	0.32	4.7	4.3	30	25
	0.6	–	9.9	–	4
	0.8	12.3	–	8	–
$Me_2SiInd_2ZrCl_2$	0.13	1.8	2.5	106	70
	0.32	4.2	4.3	30	28
	0.6	–	9.6	–	9
	0.8	12.5	–	8	–
$Et(2MeInd)_2ZrCl_2$	0.13	2.1	1.5	61	80
	0.32	5.5	4.7	23	27
$Ph_2CFluCpZrCl_2$	0.13	2.9	2.2	61	50
	0.32	8	6.3	15	18
$(Me)_2CFluCpZrCl_2$	0.13	3.1	3.2	–	39
	0.32	–	9.5	–	15

[a] Calculated in accord with Ref. [27].

is increased. This suggests that the rotation undergone by the chain in the epimerization mechanism is hindered by the branching.

The syndiotactic copolymers, on the other hand, show a dramatic increase of stereoerrors. The constant values of the *mm* triad indicate that the backskip mechanism is responsible for the loss of stereoregularity. A decrease in insertion rates following comonomer incorporation makes that the chain back skip be a more competitive process.

Melting temperature decreases as comonomer incorporation increases. As the α-olefin content increases, the material becomes more amorphous due to the difficulty to form crystalline zones. The copolymers with 1-octadecene have lower melting temperatures than those with 1-hexene. For the syndiotactic copolymers the greater number of stereoerrors also contributes to enrichment in the amorphous phase.

3.4. Mechanical properties

Stress–strain tests were carried out on the propene-α-olefin copolymers with the purpose of studying the influence of the kind and percentage of comonomer on their mechanical behavior. Since all the samples were prepared in the same way and the testing conditions were the same for all of them, the influence of the method of crystallization and of the testing conditions can be disregarded.

Figs. 6 and 7 show the stress–strain curves of iso and syndiotactic higher molecular weight propene-α-olefin copolymers having different percentages of comonomer incorporation. The stress values given were calculated based on the initial size of the test mold.

The stress–strain curves obtained for each copolymer show that as the percentage of incorporation increases there is a decrease in the stress, as well as less well defined flows, indicating that the response of the materials is affected by its

Table 5
Tacticity and melting temperature of propene 1-hexene copolymers

Catalyst	[α-Olefin] in the feed (mol/L)	[α-Olefin] incorporated (mol%)	T_m (°C)	Tacticity		
				mm	*mr*	*rr*
$EtInd_2ZrCl_2$	0	0	127	0.85	0.11	0.06
	0.13	2.1	111	0.87	0.10	0.04
	0.32	4.7	97	0.89	0.08	0.03
	0.8	12.3	66–40	0.90	0.08	0.03
$Me_2SiInd_2ZrCl_2$	0	0	140	0.87	0.09	0.05
	0.13	1.8	129	0.94	0.05	0.01
	0.32	4.2	117	0.93	0.06	0.02
	0.8	12.5	87	0.92	0.06	0.02
$Et(2MeInd)_2ZrCl_2$	0	0	126	0.84	0.12	0.05
	0.13	2.1	108	0.86	0.10	0.04
	0.32	5.5	88	0.85	0.11	0.04
$Ph_2CFluCpZrCl_2$	0	0	118–126	0.02	0.04	0.93
	0.13	2.9	103	0.02	0.13	0.85
	0.32	8	52–84	0.02	0.22	0.76

Table 6
Tacticity and melting temperature of propene 1-octadecene copolymers

Catalyst	[α-Olefin] in the feed (mol/L)	[α-Olefin] Incorporated (mol%)	T_m (°C)	Tacticity		
				mm	*mr*	*rr*
EtInd$_2$ZrCl$_2$	0	0	127	0.85	0.11	0.06
	0.13	2.3	108	0.84	0.11	0.05
	0.32	4.3	87	0.89	0.08	0.03
	0.6	9.9	np[a]	0.88	0.10	0.03
Me$_2$SiInd$_2$ZrCl$_2$	0	0	140	0.87	0.09	0.05
	0.13	2.5	120	0.92	0.06	0.02
	0.32	4.3	96	0.92	0.06	0.03
	0.6	9.6	52	0.90	0.07	0.04
Et(2MeInd)$_2$ZrCl$_2$	0	0	126	0.84	0.12	0.05
	0.13	1.5	105	0.85	0.10	0.05
	0.32	4.7	82	0.87	0.09	0.05
Ph$_2$CFluCpZrCl$_2$	0	0	118–126	0.02	0.04	0.93
	0.13	1.5	98	0.02	0.13	0.85
	0.32	4.7	np[a]	0.02	0.23	0.75
(Me)$_2$-CFluCpZrCl$_2$	0	0	115–129	–	–	–
	0.13	3.2	94	0.02	0.16	0.81
	0.32	9.5	np[a]	0.03	0.22	0.75

[a] Not present.

crystallinity. An increase in the number of comonomer units in the chain produces a decrease in the crystallinity, as can be inferred by the decrease of the melting temperature as the percentage of comonomer incorporation increases.

At present it is accepted that the characteristic crystallization mode of polymers (from the melt) is of the lamellar type [28]. The random introduction of noncrystallizable co-units in the chain causes a gradual deterioration of the lamellar structure by restricting the incorporation of chain segments within the crystal [29].

The length of the branches also affects the stress values, with the 1-octadecene copolymers showing lower values than those of 1-hexene at similar degrees of incorporation. The syndiotactic copolymers with 8.8 and 6.3 mol% incorporation of 1-hexene and 1-octadecene, respectively, showed an elastomeric behavior.

4. Conclusion

Propene copolymerization has been studied with 1-olefins of long chain using different metallocene catalysts. The results indicate that the activities of the isoselective catalysts tend to diminish with the increment of the comonomer in the medium. With the catalyst Me$_2$SiInd$_2$ ZrCl$_2$ the denominated comonomer effect was observed. With the syndioselective catalysts an important decrease was observed for the activity when the comonomer concentration is increased. As it was expected the comonomer incorporations in the polymer increase with the increment of the concentration of the 1-olefins of long chain in the reaction system. Significant differences are not observed in the incorporation values of the isoselectives systems. Contrary to the above-mentioned, in the

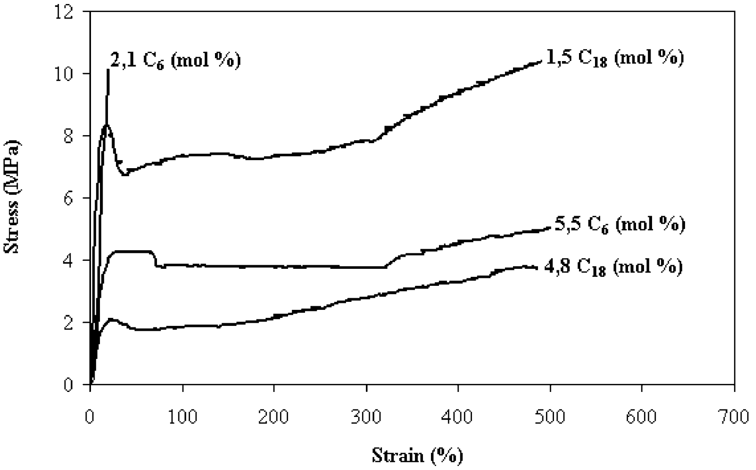


Fig. 6. Stress–strain curves of the copolymers obtained with the Et(2Me-Ind)$_2$ZrCl$_2$ catalyst.

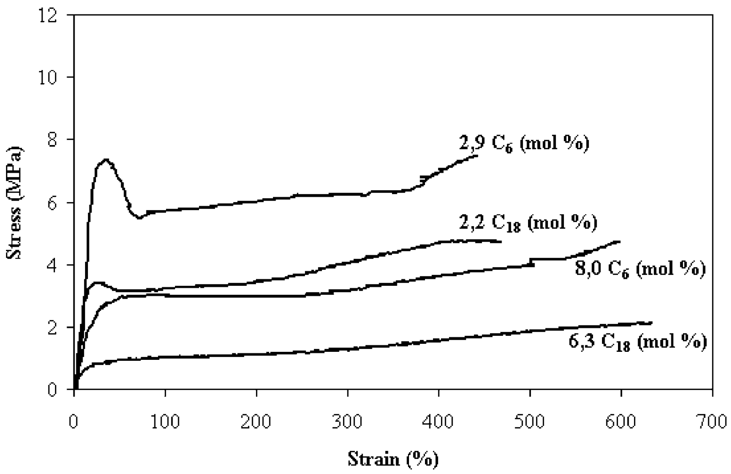


Fig. 7. Stress–strain curves of the copolymers obtained with the $Ph_2CFluCpZrCl_2$ catalyst.

syndiotactic copolymers, an important increment in the incorporation is observed when the concentrations of comonomer is 0.32 M. In a similar way to that found for the incorporations, the molecular weight of the isotactic copolymers do not show to be influenced by the comonomer concentration. A contrary behavior was observed for the syndiotactic copolymers.

Tensiles properties was measured for copolymers coming from the catalysts $Et(2\text{-}MeInd)_2ZrCl_2$ and $Ph_2CFluCpZrCl_2$. The results indicate that the side chain length favours the formation of materials with elastic properties.

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