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Study of the polymerization of 1-octadecene with different metallocene catalysts

RAÚL QUIJADA[1*], **JUAN LUIS GUEVARA**[1], **MEHRDAD YAZDANI-PEDRAM**[2], **GRISELDA B. GALLAND**[3], **DANIEL RIBEIRO**[3].

[1]Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 2777 y Centro para la Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales (CIMAT). Santiago, Chile.

[2] Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile y Centro para la Investigación Multidisciplinaria Avanzada en Ciencias de los Materiales (CIMAT).

[3]Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500-91501-970 Porto Alegre-RS-Brazil.

E-mail: raquijad@cec.uchile.cl

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Summary

1-Octadecene (C18) was polymerized by using different metallocene catalysts. The rac-Et(Ind)$_2$ZrCl$_2$/MAO (I) and rac-Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO (III) presented the highest activity as compared with rac-Et(2-Me-Ind)$_2$ZrCl$_2$/MAO (II) and Ph$_2$C(Flu)(Cp)ZrCl$_2$/MAO (IV) catalysts. Catalyst IV produced polymers with highest molecular weights. The microstructure of the polymers was determined by ^{13}C-NMR spectroscopy. Catalyst systems I, II and III produced isotactic polymers while catalyst IV produced polymers with mainly syndiotactic structures but with large amount of stereoregular error.

Introduction

Copolymers of ethylene and/or propylene with long-chain α-olefins are commercially important materials since their development for different applications has been characterized them by their growing production and consumption in the last few years. In this context, the study of homopolymerization of long-chain α-olefins is very useful since very valuable information can be obtained that allows one to understand, in a complete form, the behavior of α-olefins when used as comonomers in copolymerizations with other olefins.

A number of investigations have demonstrated the possibility of synthesizing a large variety of poly (α-olefins) by using Ziegler-Natta and Metallocene catalysts [1-4]. Kim et. al. [5] reported that both monomer bulk and the lateral size of polymer influenced the activity of polymerization.

Recently, Landis and co-workers [6] reported a kinetic study of polymerization of 1-hexene by using the catalyst system (rac-Et(Ind)$_2$ZrMe)(MeB(C$_6$F$_5$)$_3$), and showed that the rate of propagation is first order with respect to monomer and to catalyst

The homopolymerization of 1-octadecene by using rac-Et(Ind)$_2$ZrCl$_2$/MAO (I) and Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO (III) as catalyst systems has been reported by our group [7-9] and thermal properties of poly (1-octadecene) synthesized by using system (I) catalyst, depended on the polymerization temperature.

The aim of this work is to complete the study of homopolymerization of 1-octadecene (C18) by using rac-Et(Ind)$_2$ZrCl$_2$/MAO (I), rac-Et(2-Me-Ind)$_2$ZrCl$_2$/MAO (II), rac-Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO (III) and Ph$_2$C(Flu)(Cp)ZrCl$_2$/MAO (IV). Specifically, the influence of the different type of interannular bridge (-CH$_2$-CH$_2$-; (CH$_3$)$_2$Si), the presence of substituents in the aromatic ring (catalyst systems I and II), and the type of stereo-selectivity on the microstructure and properties of the obtained polymers was studied. Catalytic activity as function of polymerization time and temperature was also investigated.

Experimental

Materials.

Toluene (Aldrich) was purified by refluxing over metallic sodium and using benzophenone as indicator. 1-Octadecene was purified by refluxing over metallic sodium and distilling under reduced pressure. Commercial methylaluminoxane (MAO) and the catalysts from Witco and Boulder Scientific Company respectively, were used as received.

Homopolymerization.

Reactions were carried out in a temperature controlled (±1°C) 250 mL glass reactor equipped with a mechanical stirrer. Reagents were introduced in to the reactor with syringes, in the following order: toluene, MAO, monomer and catalyst. The reaction was terminated by addition of 2 vol-% HCl/methanol and washing with acetone removed unreacted monomer.

Polymer characterization.

Thermal analyses of the samples were carried out with a Perkin-Elmer differential scanning calorimeter DSC-7. The ^{13}C-NMR spectra were obtained at 80° C on a Varian Inova 300 at 75 MHz. Sample solutions of polymer were prepared in o-dichlorobenzene and benzene-d6 (20% v/v) in a 5 –mm sample tube. Gel Permeation Chromatography (GPC) analysis was performed at 140 °C on a Waters 150C instrument equipped with a differential refractive index detector. The eluent was Trichlorobenzene at a flow rate of 1 mL/min. Calibration was done with polystyrene and polyethylene standards.

Results and discussion

Catalytic activity

Catalytic activities versus time for all the catalysts are presented in Figure 1. Catalysts I was slightly more active than III, as was observed in copolymerization of ethylene and 1-octadecene using these catalysts [8,9]. Catalyst II had lower activities than catalyst I, as was previously observed for polymerization of propene [10]. This probably is the result of steric effects generated by the CH_3- group of the indenyl ring, which hinders entrance of the olefin to the metallic center, thus decreasing the polymerization rate. On the other hand, Catalyst IV showed low activities.

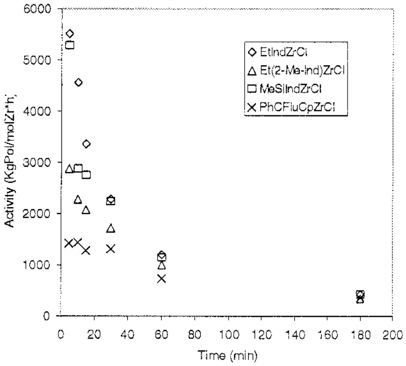
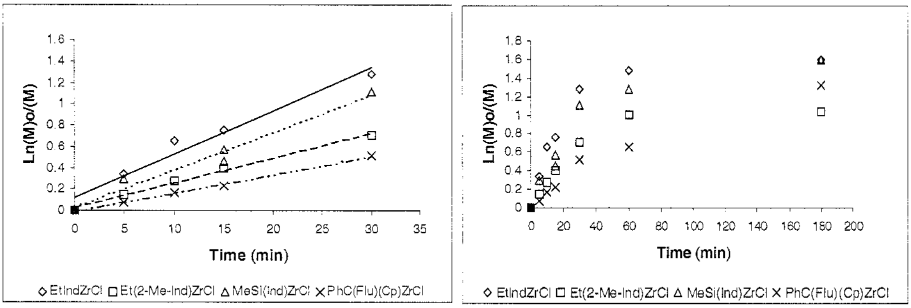


Figure 1: Influence of time on activities of the catalysts used in the study. Reaction Conditions: C_{18}: 7.89 g, n(Zr): 5x10^{-6} mol, n(Al)/n(Zr): 2000, Temperature: 70 °C, Solvent: 60 mL toluene, Reactor: 250 mL glass reactor, RPM 300.

Semi-logarithmic variations of the monomer concentration with respect to time for the polymerizations made with the studied catalysts are shown in figure 2a, and the linear relation indicates a first order dependency with respect to monomer. This result suggests, as was proposed by Landis [6] and Deffieux [11], that all the active species are formed quickly and that monomer concentration remains constant, in our case, up to 30 minutes.

For higher polymerization time, activity does not increase sharply, but rather, there is a small rate decrease after 60 minutes, which in principle would indicate deactivation of active species in our experimental conditions, Figure 2b.



(a) (b)

Figure 2: Semi-logarithmic variations of 1-octadecene conversion vs. polymerization time for the different catalysts. a) until 30 min; b) until 180 min. Reaction Conditions: C_{18}: 7.89 g, n(Zr): 5x10^{-6} mol, n(Al)/n(Zr): 2000, Temperature: 70 °C, Solvent: 60 mL toluene, Reactor: 250 mL glass reactor, RPM 300

As shown in Table 1, polymerization of 1-octadecene was performed at 30° C or 70° C. This was done, in order to analyze the effect of temperature on both, catalytic activity of metallocenes and properties of the polymers obtained with each catalyst system.

Table 1. Effect of the temperature on the catalyst activity and molecular weight for the polymerization of 1-octadecene using the Catalysts Systems I, II, III and IV.

Metallocene	Sample	Temp. (°C)	Conv. (%)	Activity (kg Pol/mol Zr*h)	Mw (g/mol)	Mw/Mn
(I)	2	70	77	1,200	6,300	1.6
	13	30	28	472	22,700	1.8
(II)	5	70	63	1,004	5,400	1.6
	14	30	25	400	22,100	1.7
(III)	8	70	33	530	9,900	1.5
	15	30	25	408	25,000	1.7
(IV)	11	70	47	730	19,100	1.6
	16	30	7	112	37,700	2.2

Reaction Conditions: C_{18}: 7.89 g, n(Zr): 5x10^{-6} mol, n(Al)/n(Zr): 2000, Time: 1 h, Solvent: 60 mL toluene, Reactor: 250 mL glass reactor, RPM: 300.

All catalytic activities decrease when polymerizations were performed at 30° C, with similar activities for catalyst systems I, II and III. Catalyst system IV showed the lowest activity at 30° C by a factor of 6.5 times lower for polymerizations at 30° C as compared with those at 70° C.

Polymer properties

Molecular weights

The effect of temperature on molecular weight and its distribution is shown in Table 1. Molecular weights increase considerably on decreasing the polymerization temperature but the molecular weight distribution increases slightly. The polymer obtained by using catalyst system IV at 30° C has the highest molecular weight. All other polymers show similar molecular weights.

Effects of both catalyst type and polymerization time on molecular weights and molecular weight distributions of the polymers are shown in Table 2. Molecular weights decrease slightly on increasing polymerization times as expected because almost all the monomer is consumed after three hours. Molecular weights of polymers produced by using catalysts I and II are low, as compared with other polymers obtained in this study. The polymers obtained have narrow molecular weight distributions (1.5-1.7) which are similar to the obtained by Schneider et.al. [12] M_w/M_n=1.8 and by Henschke and co-workers [13] M_w/M_n=1.85, when catalyst III was used for polymerizations of 1-octene and 1-octadecene respectively.

The molar mass of the polymer obtained in this work, are lower than that obtained by Henschke [13] using the catalyst rac-$Me_2Si(Ind)_2ZrCl_2$, where they found a value of 68,000 g/mol. The large difference between these two results, could be due to the different reaction conditions that they used [13] (reaction temperature was 10 °C and the monomer concentration was 1 mol/L). These lower values can also be due to the nature of the catalysts, as for example, when it is compared with the one used by Brüll [4] where the catalysts was rac-$Me_2Si(2\text{-methylbenz[e]indenyl})_2ZrCl_2$. They discussed their results and compared them with those reported by other workers in terms of the molar masses of the polymers produced at 20 °C. They showed that the values are significantly higher than those of various higher poly-α-olefins synthesized with other zirconium-based metallocenes under similar conditions.

Table 2. Yield, polymerization time, catalyst activity, molecular weights and molecular weight distributions of poly (1-octadecene) samples prepared by using the Catalysts Systems I, II, III and IV.

Metallocene	Sample	Reaction Time (h)	Yield (g)	Conv. (%)	Activity (kg Pol/mol Zr*h)	Mw (g/mol)	Mw/Mn
(I)	1	0.5	5.7	72	2280	6,700	1.6
	2	1	6.1	77	1,200	6,300	1.6
	3	3	6.3	80	420	6,100	1.6
(II)	4	0.5	4,3	54	1720	6,400	1.5
	5	1	5.0	63	1,004	5,500	1.6
	6	3	5.1	64	337	4,700	1.5
(III)	7	0.5	5,6	71	2240	9,400	1.7
	8	1	2.6	33	530	9,943	1.5
	9	3	6.3	80	417	9,156	1.6
(IV)	10	0.5	3,3	41	1320	21,600	1.7
	11	1	3.8	47	730	19,100	1.6
	12	3	5.8	74	357	13,700	1.7

Reaction Conditions: C_{18}: 7.89 g, n(Zr): 5×10^{-6} mol, n(Al)/n(Zr): 2000, Temperature: 70 °C, Solvent: 60 mL toluene, Reactor: 250 mL glass reactor, RPM 300.

Microstructure

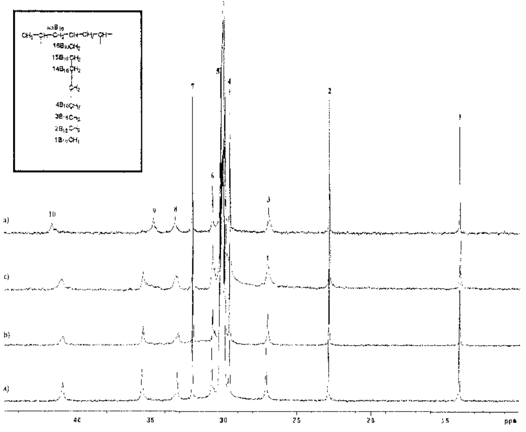


Figure 3: ^{13}C-NMR spectra of poly-1-octadecene samples a) 13, b) 8, c) 6 and d) 16 obtained at 70 °C and 30 °C with catalysts I-IV.

Table 3. Experimental and calculated chemical shift assignments for poly (1-octadecene) samples

Peak n°	Chemical Shift Calculated (ppm)	Chemical Shift Sample 8 (ppm)	Chemical Shift Sample 12(ppm)	Assignments
1	13.86	14.09	14.09	$1B_{16}$
2	22.65	22.85	22.85	$2B_{16}$
3	27.52	27.02	26.3-27.5	$15B_{16}$
4	29.71	29.58	29.58	$4B_{16}$
5	29.96	29.93-30.23	29.93-30.23	$-(CH_2)_9-$
6	30.21	30.74	30.77	$14B_{16}$
7	32.4	32.14	32.14	$3B_{16}$
8	32.91	33.13	32.9-33.8	brB_{16}
9	34.97	35.56	34.2-35.8	$16B_{16}$
10	39.48	40.99	40.3-42.0	$\alpha\alpha B_{16}$

The ^{13}C-NMR spectra of polymers obtained by using catalyst systems I-IV, for polymerizations at 30° C or 70° C, are shown in figure 3. Assignments for differents carbons followed the rules of Linderman and Adams [14]. These assignments, and the experimental chemical shifs, are in table 3 where Usami [15] nomenclature is used as in figure 3. There was good agreement between experimental and calculated values by Linderman and Adams rules.

As shown in figure 3 and table 3 differences in chemical shifts of the polymers appear in peaks 3 ($15B_{16}$), 8 (brB_{16}), 9 ($16B_{16}$) and 10 ($\alpha\alpha B_{16}$), which are affected by the tacticity. The signal appearing around 35 ppm was used to estimate the degree of stereoregularity of the polymer samples as reported for α-olefins with long linear side chains [16,17]. Asakura et al.[18] reported the tacticity assignment by ^{13}C NMR spectra of a series of polyolefins with long linear side chains on the basis of the ^{13}C NMR effect and application of the rotational isomeric state (RIS) model. Based on these data, the spectra signals at 34.2 – 35.8 ppm and the spectra of an atactic poly-1-octadecene obtained with the aspecific catalyst, Cp_2ZrCl_2, approximate assignments were made.

To make a comparative study of tacticity of the polymers, triads and dyads were used. The normalized integral of the region 35.80 – 35.20 ppm was taken as the isotactic triad mm, even thought this region may have a slight contribution of the atactic pentad mmrr (18). The region 35.20 – 34.88 ppm was taken as the atactic mr triad and at 34.88– 34.20 ppm as the syndiotactic triad rr. The diads r and m were obtained from the triads as already published [19]. Table 4 summarizes the tacticity data obtained for the polymers. The tacticities shown in table 4 are not definitive values, there still exist doubts about the chemical shifts of each pentad but they are presented for comparative purposes.

The ^{13}C-NMR spectra of polymers synthesized by using catalysts systems I, II and III, show signals in the mm triad region (35.80-35.20 ppm). Integration of this peak gave percentage of isotacticity values between 67-92% depending on the temperature employed for the polymerization. These values indicate that the metallocene catalysts used have capacities of maintaining their isospecificity in polymerization of α-olefins with long linear side chains such as 1-octadecene, but that stereoregularity always decreases with temperature. For polymers obtained by using the system IV catalyst, the most intense signal was in the region of the rr triads (34.88-34.20 ppm). Integration of this signal gave values between 59-75%. This means that the polymer is mainly syndiotactic, but with extensive stereorregular errors. In accordance with the mechanism proposed for syndiospecific polymerization, it is necessary that the polymer chain migrates to the position previously occupied by coordinated monomer after monomer insertion has taken place. From this point of view, the loss of syndioselectivity with the system IV catalyst could be attributed to slow monomer insertion as the consequence of the steric effects caused by the long side chain of the monomer, the growing polymer chain should then migrate before the monomer could insert (back-skip mechanism [20]). In the case of isoselective polymerization, the slow monomer insertion would not affect isoselectivity since coordination sites are homotopic. This is probably the reason that catalysts systems I, II and III do not loss their isoselective characters. The polymers obtained at 30° C by using these catalysts show an important increase of isotacticity which is consistent with results previously obtained for polymerization of propene [21]. The poly (1-octadecene) synthesized by using catalyst system IV also shows changes in its microstructure when polymerizations are performed at 30° C.

Table 4. Signal integration of the amplified region of the ^{13}C-MNR spectra shown in Fig. 3.

Metallocene	Sample	mm	mr	rr	m (%)	r (%)
(I)	2	0.71	0.13	0.16	77.9	22.1
	13	0.91	0.05	0.03	93.9	6.1
(II)	5	0.67	0.16	0.17	74.9	25.1
	14	0.86	0.08	0.06	90.3	9.7
	6	0.67	0.15	0.18	74.3	25.7
(III)	8	0.81	0.09	0.10	85.6	14.4
	15	0.92	0.05	0.03	94.8	5.2
	9	0.79	0.08	0.13	83.3	16.7
(IV)	11	0.14	0.25	0.60	26.9	73.1
	16	0.08	0.17	0.75	16.7	83.3
	12	0.16	0.25	0.59	28.4	71.6

mm: 35.80 – 35.20 ppm,; mr: 35.20– 34.88 ppm; rr: 34.88 – 34.20 ppm

Thermal Analysis

The DSC melting curves of the polymers synthesized by using systems I and III catalysts have been already reported [7-9]. The DSC melting curves of the polymers prepared at 30° C or 70° C, by using catalysts systems II and IV are presented in Figure 5 and 6 respectively

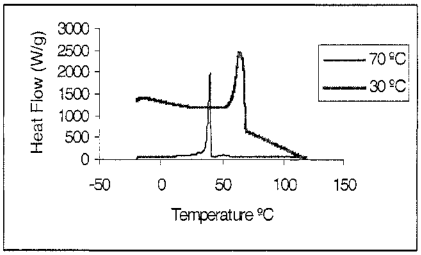


Figure 5: DSC melting curves of the poly-1-octadecenes obtained at 70 °C and 30 °C with catalyst system II

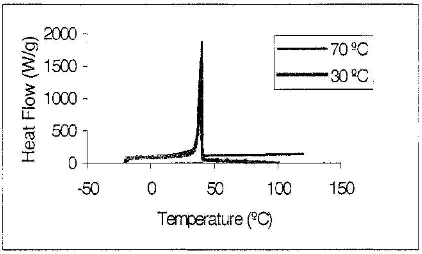


Figure 6: DSC melting curves of the poly-1-octadecenes obtained at 70 °C and 30 °C with catalyst system IV.

In the DSC melting curve of the polymer synthesized at 70° C by using catalyst system II, there are two endotherms at 40° C and at 50° C. When polymerization with this catalyst was carried out at 30° C, there was only one melting endotherm peak at 65° C. The DSC thermograms of the polymer synthesized by using catalyst system IV showed only one melting peak at 40° C. The melting endotherm observed at 40° C could be associated with crystallization of the syndiotactic segments.

Conclusions

The catalyst systems I and III showed higher catalytic activities than systems II and IV. Catalyst III produced polymers with higher isotacticity than those obtained with Catalysts I and II. Catalyst system IV produced syndiotactic structures but with large amounts of stereorregular error.

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