Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 47 (2006) 2634–2642
polymer
www.elsevier.com/locate/polymer

^{13}Carbon nuclear magnetic resonance characterization of ethylene–propylene–1-octadecene terpolymers and comparison with ethylene–propylene–1-hexene and 1-decene terpolymers

Griselda Barrera Galland *, Fernanda F. Nunes Escher

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

Received 19 October 2005; received in revised form 18 January 2006; accepted 31 January 2006
Available online 10 March 2006

Abstract

In this paper, we report the complete ^{13}C NMR characterization of a set of ethylene–propylene–1-octadecene terpolymers obtained with the metallocenic system *rac*-ethylene bis-indenyl zirconium dichloride, using different comonomer ratios. A detailed study of ^{13}C NMR chemical shifts, triad sequence distributions, monomer average sequence lengths and reactivity ratios for these terpolymers is presented. The incorporations of 1-octadecene were superior of those obtained using 1-hexene and 1-decene in the same conditions. Catalytic activities of terpolymers of ethylene–propylene and α-olefins (α-olefins:1-hexene, 1-decene and 1-octadecene) were compared showing that they increase with the amount of propylene in the feed.

Keywords: Ethylene–propylene–1-octadecene terpolymers; ^{13}C NMR; Reactivity ratios

1. Introduction

Copolymers of ethylene or propylene with 1-octadecene are interesting materials due to the hexadecyl long branch that can improve some mechanical and rheological properties. In fact, the dynamic mechanical properties ethylene–1-octadecene copolymers have been studied and compared with that of other ethylene–1-olefin copolymers. The 1-octadecene comonomer showed to act as a more efficient plasticizer than 1-octene at 2 mol% of comonomer, but has higher stiffness at 9–10 mol% [1]. Modulus, yield stress, elongation at break and energy at break of ethylene–1-octadecene copolymers can be regulated by the increase of the comonomer content, going from a thermoplastic material to an elastomeric one [2]. Ethylene–1-octadecene copolymerizations have been studied with various metallocene catalysts [3–6]. In the copolymerization of ethylene and 1-octadecene using *rac*-Et[Ind]$_2$ZrCl$_2$/MAO the activity increases with the 1-octadecene concentration in the reaction medium until 0.35 M and the molecular weight decreases [4]. This copolymerization was also compared with the ethylene–1-hexene one, showing that the olefin with the longer chain has the highest activity [5]. Ethylene/1-octadecene copolymerizations were also carried out with unbridged metallocene catalysts such as (2-MeInd)$_2$ZrCl$_2$ and (2-BzInd)$_2$ZrCl$_2$ but the comonomer effect was not observed in this case. The reactivity ratios were similar with both catalysts and the melting temperature of the copolymers prepared with 1-octadecene decreased faster with increasing mole fraction of the α-olefin than with 1-hexene and 1-dodecene [6].

Propene copolymerization with 1-hexene and 1-octadecene using different metallocenes (Et[Ind]$_2$ZrCl, Me$_2$[Ind]$_2$ZrCl$_2$, Et[2-MeInd]$_2$ZrCl$_2$ and Ph$_2$CFluCpZrCl$_2$) was compared. The activities of the isoselective and syndioselective catalysts tend to decrease with the increment of the comonomer in the medium, except for the catalyst Me$_2$[Ind]$_2$ZrCl$_2$ where the comonomer effect was observed.

Tensile property measurements for propene–α-olefin copolymers coming from the catalyst Et[2-MeInd]$_2$ZrCl$_2$ and Ph$_2$CFluCpZrCl$_2$ indicate that the side chain length affects the stress values, 1-octadecene copolymers showing lower values than 1-hexene at similar degrees of incorporation [7]. Copolymerization of propene with 1-octene, 1-decene, 1-tetradecene and 1-octadecene with *rac*-Me$_2$Si(2-MeBenz[e]Ind)$_2$ZrCl$_2$ gave materials with high molecular weights (220,000–580,000 g/mol) and the yield decreased

---

* Corresponding author. Tel.: +55 51 3316 7317; fax: +55 51 3316 7304.
E-mail address: griselda@iq.ufrgs.br (G.B. Galland).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.01.094

with the increasing carbon number of the α-olefin. Crystallization temperature of these polymers decreased almost linearly with the α-olefin content and seemed to be independent on comonomer type [8].

Terpolymerization with 1-octadecene was fairly studied, however, it is possible to find a few cases in the literature. Terpolymerization ethylene–1-butene–1-octadecene with iPr[FluCp]$ZrCl_2$/MAO and $Me_2Si[Ind]_2ZrCl_2$ showed that the increase of 1-butene in the feed, decreases the 1-octadecene content in the terpolymer [9]. This effect was also noticed using Cp_2ZrCl_2 as catalyst and it is opposite to the traditional heterogeneous $MgCl_2$-supported titanium catalyst that showed a synergistic effect [3].

As the copolymers, terpolymers of ethylene–propylene–1-octadecene should be very interesting materials and they have not been studied yet. Following a series of works on terpolymers [10–12] here we report a detailed ^{13}C NMR study of ethylene–propylene–1-octadecene terpolymers, synthesized with the metallocene catalyst *rac*-ethylene bis-indenyl zirconium dichloride (*rac*-($Et[Ind]_2ZrCl_2$)) with different comonomer ratios. The results of incorporation and catalytic activities obtained with this system were compared with those obtained with ethylene–propylene–1-hexene and 1-decene terpolymers synthesized in the same conditions.

2. Experimental

2.1. Materials

The catalyst *rac*-$Et[Ind]_2ZrCl_2$ and the co-catalyst methylaluminoxane (MAO) (5.21 wt% in toluene) were provided by Witco and used as received. Analytical toluene was purified through refluxing over metalic sodium, with benzophenone as indicator, and was distilled under argon atmosphere. The polymerization grade ethylene and propylene were purified by conducting them through molecular sieve (4 Å) before feeding into the reactor. The α-olefin (Aldrich) was purified through refluxing over metalic sodium and distilled under argon atmosphere.

2.2. Polymerization conditions

All the polymers were obtained using *rac*-$Et[Ind]_2ZrCl_2$/MAO as catalytic system, an amount of catalyst of 2×10^{-5} mol and a [Al]/[Zr] ratio of 1500. The polymerization reactions were carried out in a 1-L glass reactor, equipped with a mechanical stirrer, at 40 °C at an olefin total pressure of 1.0 atm with continuous flow of ethylene and propylene. Ethylene and propylene flow were separately controlled with total gas flow of 0.66 L/min. The flow ratios of the gases were determined with mass flow meters. In the terpolymerization, α-olefin (1-hexene, 1-decene or 1-octadecene) was added to the reactor, under argon pressure, before feeding the monomer gases. Two different concentrations of α-olefin were used: 0.088 and 0.176 mol/L.

Toluene (300 mL), MAO and α-olefin were added to the reactor under argon, the reaction mixture was then saturated with the gas monomers. The reaction was started by the injection of the required amount of the catalyst solution. After a reaction time of 30 min, the gas monomer feed was interrupted and the reaction was stopped. The polymer solution was poured into the mixture of ethanol and hydrochloric acid and filtered. After filtration, the polymer was dried at room temperature until a constant weight. Each reaction was repeated three times to ensure reproducibility.

The gas mixture ratios were E/P = 100/0, 95/5, 90/10, 75/25, 50/50, 25/75, 10/90, 5/95 and 0/100. The concentration of ethylene in the solution was estimated by using the equation quoted by Kissin [13] and the concentration of propylene in toluene during the polymerization reaction was calculated using the correlation obtained by Villar and Ferreira [14] and described in detail in a previous work [10]. Under these conditions the monomer concentration in the liquid phase were C_E (mol/L)/C_P (mol/L) = 0.103/0.000; 0.098/0.016; 0.093/0.032; 0.078/0.079; 0.052/0.158; 0.026/0.237; 0.010/0.285; 0.005/0.301; 0.000/0.471.

2.3. Polymer characterization

The ^{13}C NMR spectra were recorded at 90 °C with an acquisition time of 1.5 s, pulse width of 74° and pulse delay of 4 s on a Varian Inova 300 spectrometer operating at 75 MHz. Sample solution of the polymers were prepared with *o*-diclorobenzene, benzene-d_6 (20% v/v) in a 5 mm sample tube. The deuterated solvent was used to provide the internal lock signal. The chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken as 30.00 ppm. The number of scans, 1800–10,000, depending on the sample, were enough to obtain good signal/noise ratios under these conditions the spectra are 90% quantitative, considering carbon atoms that have a relaxation time (T_1) shorter than 2.0 s [15,16].

3. Results and discussion

A set of ethylene–propylene–1-octadecene co- and terpolymers with ethylene–propylene gas flow ratios of E/P: 95/5, 90/10, 75/25, 50/50, 25/75, 10/90 and 5/95 and concentration of 1-octadecene in solution of 0.088 and 0.176 mol/L was prepared using the same catalytic system. Fig. 1 shows the ^{13}C NMR spectra of ethylene–1-octadecene, propylene–1-octadecene copolymers and three spectra of ethylene–propene–1-octadecene terpolymers with different amount of comonomers. The assignments were done using Lindeman and Adams [17], literature data [10,18,19] and ^{13}C NMR spectra of 1-octadecene and propylene homopolymers, ethylene–propylene, ethylene–1-octadecene and propylene–1-octadecene copolymers and ethylene–propylene–1-octadecene terpolymers with different amounts of comonomers, obtained in this work. Chemical shift assignments are shown in Table 1. Branches are named by xB_n, where n is the length of the branch and x is the carbon number starting with the methyl group as ‘1’ [20]. For the backbone carbons, Greek letters and ‘br’ are used instead of x for the methylenes and a branch point, respectively. For

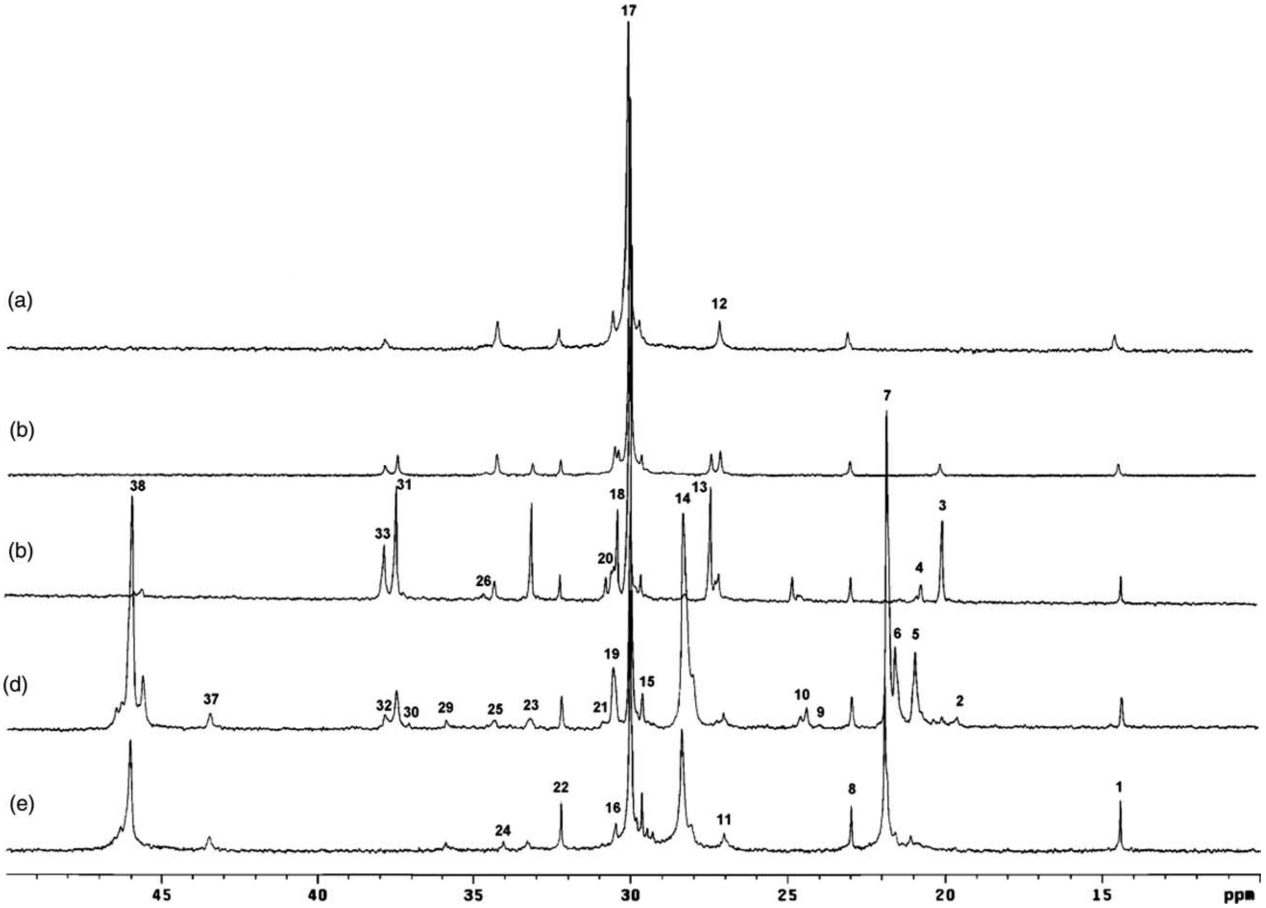

Fig. 1. ^{13}C NMR spectra of: (a) copolymer ethylene–1-octadecene EO 56 (E=90.9 mol%, O=9.1 mol%), (b) EPO 58 (E=91.4 mol%, P=4.2 mol%, O=4.4 mol%), (c) EPO 62 (E=65.8 mol%, P=29.1 mol%, O=5.1 mol%), (d) EPO 70 (E=9.4 mol%, P=86.8 mol%, O=3.8 mol%), (e) copolymer propylene–1-octadecene PO 73 (P=87.0 mol%, O=13.0 mol%).

methylenes between equal branches, two Greek letters are used (e.g. $xy\mathrm{B}_n$) and between different branches, the carbon is named $xy\mathrm{B}_n\mathrm{B}_m$. Fig. 2 shows an example of carbon-atom identification. The carbon atom assignments shown in the fifth column of Table 1 refer always to the central carbon of the triads listed in the fourth column of the same table.

The difference in the assignments for the terpolymers with the 1-octadecene in relation to the terpolymers with 1-decene [10] is in the contribution of the carbons of the branch in the region of 29.91–30.00 ppm, that for 1-decene corresponds to one carbon and for 1-octadecene to nine carbons (5-13B_{16}). Propylene–1-octadecene copolymers and ethylene–propylene–1-octadecene terpolymers with high amount of propylene present two resonances for carbons 5-13B_{16} in OOO, POP and POO+OOP triads, for terpolymers with low amount of propylene peak 16 is not present, as it can be seen in Fig. 3. As the catalyst used gives mainly isotactic sequences (see the propene region 19.4–21.7 ppm) the major peak at 30.00 ppm (peak 17) can be attributed to the isotactic sequences (mm) and the minor peak at 29.91 ppm (peak 16) to the heterotactic (mr) ones. Others attributions such as those of resonances 9,10, 12 and 13 where already discussed in a previous paper [10].

From Table 1 it is possible to establish correspondences between some peaks and monomer sequences, and to relate them with the resonance integrals (I_x, being x the peak number).

The quantitative analysis was, thus, obtained using the equations listed in Table 2. In all cases we used carbon atoms from the carbon chain or from the branch, closed to the branch point that have T_1 inferior to 2 s [21,22]. The only case that we used a carbon atom with longer T_1 was carbon 3B_{16} (peak 22) because there were no other possibility of isolate resonance to estimate the triads centered in 1-octadecene, so the equations containing this resonance can have some error, but we believe that this does not change significantly the results obtained.

The monomer sequence distributions calculated by the equations above are shown in Tables 3 and 4. The EO 56 and EO 57 are ethylene–1-octadecene copolymers with concentration of 1-octadecene in the liquid phase of 0.088 and 0.176 mol/L, respectively. The PO 72 and PO 73 are propylene–1-octadecene copolymers with concentration of 1-octadecene in the liquid phase of 0.088 and 0.176 mol/L, respectively.

The amount of 1-octadecene incorporated in the terpolymer has the tendency to decrease when the amount of propylene in the feed increases, for the two 1-octadecene concentration studied. This fact was already observed for ethylene–propylene–1-decene terpolymers [10], ethylene–propylene–1-

Table 1
Calculated and observed carbon 13 chemical shifts and assignments for ethylene–propylene and 1-octadecene terpolymers

Peak no.	Chemical shift exp. (ppm)	Chemical shift calcd (ppm)	Triad	Assignments
1	14.13	13.86	EOE EOO/OOE OOO POP POO/OOP	$1B_{16}$
2	19.40–20.30	20.61	PPP (rr)	$1B_1$
	19.58		PPP(mrrm)	
3	19.87	19.63	EPE	$1B_1$
4	20.55	20.12	EPP + PPE	$1B_1$
5	20.30–21.00	20.61	PPP(mr + rm)	$1B_1$
	20.9		PPP (mmrr)	
6	21.00–21.50	20.61	PPP(mmmr + rmmm + rmmr)	$1B_1$
	21.4		PPP(mmmr + rmmm)	
7	21.71	20.61	PPP(mmmm) OPO PPO + OPP	$1B_1$
8	22.88	22.65	EOE EOO/OOE OOO POP POO/OOP	$2B_{16}$
9	24.3	25.08	OEO	$\beta\beta B_{16}$
10	24.35–24–85	24.58	PEP	$\beta\beta B_1$
10a	24.4		PPEPP	
10b	24.57		EPEPE(m)	
10c	24.63		PPEPE + EPEPP	
10d	24.8		EPEPE(r)	
11	26.9–27.1	27.52	POP POO + OOP OOO	$15B_{16}$
11a	26.97		POP(mr)	
11b	27.03		POP(mm)	
12	27.038	27.52	EOE EOO + OOE	$15B_{16}$
			OEE + EEO	βB_{16}
13	27.18–27.43	27.27	EEP + PEE	βB_1
13a	27.18		PPEE + EEPP(r)	
13b	27.24		PPEE + EEPP(m)	
13c	27.41		EPEE + EEPE	
14	28.16–28.53	28.38	PPP OPO OPP + PPO	brB_1
15	29.2–29.6	29.71	EOE EOO + OOE OOO POP POO + OPP	$4B_{16}$
16	29.91	29.96	OOO POP POO + OOP (mr)	$5–13B_{16}$
17	30.00	29.96	EEE	$\delta\delta$
			OOO EOE EOO + OOE POP POO + OOP (mm)	$5–13B_{16}$
18	30.36	30.21	EEP	γB_1
19	30.48–30.58	30.21	EOE EOO + OOE OOO	$14B_{16}$
			EEO + OEE	γB_{16}
			POO + OOP POP	$16B_{16}$
20	30.68	30.45	EPP + PPE	brB_1
21	30.72–31.03	30.46	OEEO	$\gamma\gamma B_{16}$
			PEEP	$\gamma\gamma B_{16}$
22	32.15	32.4	EOE EOO + OOE OOO POP POO + OOP	$3B_{16}$
23	33.11	32.52	EPE	brB_1
24	33.52	32.91	OOO POP POO + OOP	brB_{16}
25	34.3	34.47	EOE	$16B_{16}$
			EOE OEE	αB_{16}
26	34.64	34.98	EOO + OOE	brB_{16}
27	34.78	34.72	OEO	$\alpha\gamma B_{16}$
			EOO	αB_{16}
			EOO + OOE	$16B_{16}$
28	35.54	34.97	OOEOO	$\alpha\gamma B_{16}$
29	35.96	34.97	POP POO + OOP OOO	$16B_{16}$
30	37.21	37.41	PPEPP	$\alpha\gamma B_1$
			PEPP(EP)	
31	37.45	36.91	EPE PEE	αB_1
32	37.80	37.16	EPEPE	$\alpha\gamma B_1$
			EPP	αB_1
33	37.94	37.05	EOE	brB_{16}
34	39.36	39.48	POO + OOP	$\alpha\alpha B_1B_{16}$
35	39.78	38.98	OOE + EOO	$\alpha\alpha B_{16}$
36	41.00	39.48	OOO	$\alpha\alpha B_{16}$
37	43.54	41.92	POP POO + OOP	$\alpha\alpha B_1B_{16}$
			OPO OPP + PPO	$\alpha\alpha B_1B_{16}$
38	45.6–46.7	43.86	PPE EPPE	$\alpha\alpha B_1$
		44.11	PP*P*E + EP*P*P	$\alpha\alpha B_1$
		44.36	PPPP PPO	$\alpha\alpha B_1$

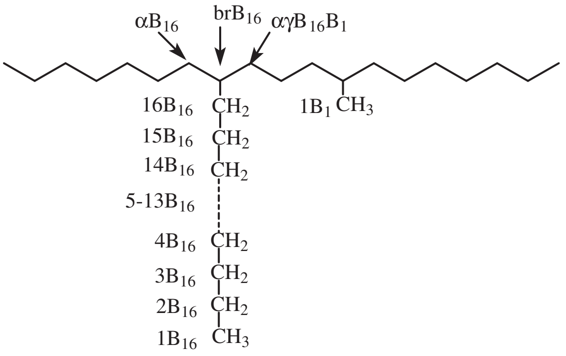

Fig. 2. Carbon atom nomenclature.

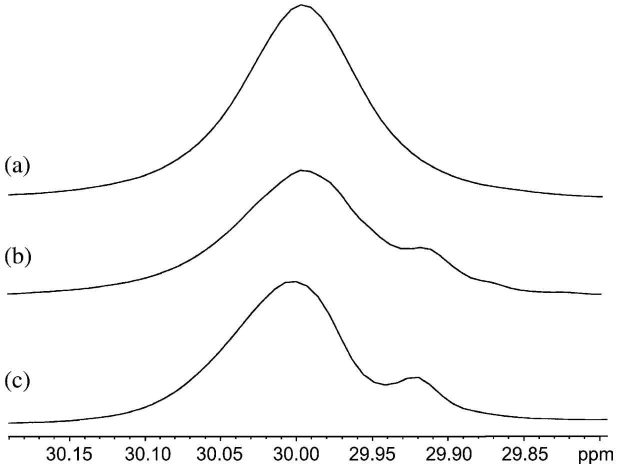

Fig. 3. ^{13}C NMR spectra expansion of 29.8–30.2 ppm region: (a) ethylene–propylene–1-octadecene terpolymer (E = 88.5 mol%, P = 3.3 mol%, O = 8.2 mol%), (b) ethylene–propylene–1-octadecene terpolymer (E = 17.9 mol%, P = 77.7 mol%, O = 4.4 mol%), (c) propylene–1-octadecene copolymer (P = 92.0 mol%, O = 8.0 mol%).

hexene terpolymers [11] and with other metallocenes using 1-butene instead of propene [9]. There is a competition for the active site between the propylene and the 1-octadecene and being propylene the smaller monomer, its incorporation is favored. For very high amounts of propylene (> 84 mol%) and low amounts of ethylene (< 9 mol%) in the terpolymer (EPO 70 and 71) the amount of 1-octadecene incorporated increases again. In this case, 1-octadecene competes with ethylene for the active site, being ethylene in very low concentration the amount of 1-octadecene in the terpolymer increases.

Table 5 shows the mol percentages of ethylene, propylene and 1-octadecene in the feed and in the terpolymers. The percentages are ordered by decreasing amounts of ethylene for the two concentrations of 1-octadecene 0.088 M (on the top) and 0.176 M (on the bottom).

The number average sequence lengths, n_{XY} (e.g. n_{EP} means: number average of ethylene sequences between propene sequences) in terpolymers and the reactivity ratios, r_{XY} (e.g. $r_{EP}=k_{EE}/k_{EP}$, where k_{EP} is the rate constant for the insertion of monomer P into a growing chain terminated by E unit), were evaluated using relationships already published in a previous paper [10].

The number average sequence length and the reactivity ratio values are shown in Table 6. For the terpolymers with high ethylene concentrations in the polymer (Table 5) (EPO 58, 59, 60, 61, 62 and 64), the formation of ethylene blocks is observed among units of propylene ($n_{EP}=2$–22 and $n_{PE}=1$–1.6). When the amount of propene is much superior to the amount of ethylene in the feed (EPO 68, 69, 70, 71), propylene blocks are formed among ethylene units (n_{PE} 12–35). The values of reactivity ratios r_{EP} are all much larger than r_{PE}, showing that in all of the cases the homopolymerization of ethylene is favored in relation to copolymerization with propene. In all of the cases the 1-octadecene is incorporated as isolated units among ethylene blocks ($n_{EO}>18$ and $n_{OE}=1.0$) or propylene blocks ($n_{PO}>21$ and $n_{OP}=1$). The homopolymerization of ethylene and propylene is always favored over the copolymerization with the 1-octadecene ($r_{EO}>27$ and $r_{OE}=0$ and $r_{PO}>25$ and $r_{OP}=0$).

It was verified that the three superior α-olefins studied (ethylene–propylene–α-olefin:α-olefin:1-hexene [11], 1-decene [10] and 1-octadecene) were incorporated in the polymeric chain and, in most of the comonomer ratios, the α-olefin that incorporated the best was the 1-octadecene in the two concentrations of termonomers (Table 7). This behavior was unexpected once the 1-octadecene, for having a very long chain, should have a higher steric hindrance that should reduce its incorporation in the chain.

However, previous studies [9,23], proposed that long branched α-olefins force the π ligands into a more open arrangement reducing the steric hindrance, providing a larger incorporation of big monomers in the chain.

We observed that the incorporation of the superior α-olefins is unfavored when there is more propene in the medium, this behavior was also observed in the terpolymerization of ethylene–1-butene–1-octadecene with Cp_2ZrCl_2 [3,4]. These authors [9] explained that the higher the 1-butene concentration is, the more there are [R-(1-butene)-cat] active centers which favor the addition of ethylene and 1-butene rather

Table 2
Equations for the quantitative analysis of ethylene–propylene–1-octadecene terpolymers

$[EEE]=k\,(I_{16}+I_{17}-9I_{22})/2$	$[EPE]=kI_{23}$	$[POP]=k(I_{29}-I_{34}-I_{36})$
$[EEP+PEE]=kI_{13}$	$[EPP+PPE]=kI_{20}$	$[OOO]=kI_{36}$
$[PEP]=kI_{10}$	$[PPP]=k(I_{14}-I_{37}+I_{29}-I_{36})$	$[OOP+POO]=kI_{34}$
$[EEO+OEE]=k(I_{12}-I_{22}+I_{11})$	$[OPP+PPO]+[OPO]=k(I_{37}-I_{29}+I_{36})$	$[EOE]=k(I_{22}-I_{35}-I_{29}-I_{36})$
$[OEO]=kI_9$		$[EOO+OOE]=kI_{35}$

k, normalization constant.

Table 3
Triad sequence distribution of the terpolymers obtained by ^{13}C NMR with a 1-octadecene concentration in the feed of 0.088 M

Triad	Samples								
	EO 56	EPO 58	EPO 60	EPO 62	EPO 64	EPO 66	EPO 68	EPO 70	PO 72
[EEE]	81.7	74.1	63.2	23.7	35.5	11.3	2.7	1.2	0.0
[EEP+PEE]	0.0	9.4	18.0	30.5	22.0	11.2	4.3	2.5	0.0
[PEP]	0.0	0.0	1.3	7.4	4.0	22.6	8.2	5.7	0.0
[EEO+OEE]	9.2	7.9	5.7	4.3	3.7	0.0	0.0	0.0	0.0
[OEO]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[EPE]	0.0	4.2	9.7	20.2	13.2	8.3	2.0	2.9	0.0
[EPP+PPE]	0.0	0.0	0.0	4.7	14.2	11.3	2.6	1.3	0.0
[PPP]	0.0	0.0	0.0	4.2	4.7	31.2	77.0	80.4	94.9
[OPP+PPO]+[OPO]	0.0	0.0	0.0	0.0	0.0	0.0	2.1	2.3	0.9
[POP]	0.0	0.0	0.0	0.0	0.0	0.0	0.2	1.5	3.6
[OOO]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[OOP+POO]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[EOE]	9.1	4.4	2.1	5.1	2.7	4.1	0.9	2.3	0.5
[EOO+OOE]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[E]	90.9	91.4	88.3	65.8	65.1	45.1	15.2	9.4	0.0
[P]	0.0	4.2	9.7	29.1	32.1	50.8	83.7	86.8	95.8
[O]	9.1	4.4	2.1	5.1	2.7	4.1	1.1	3.8	4.2

than 1-octadecene. The same explanation can be applied in our case.

This behavior can also be related with the polarity and basicity effects of the olefin. Ferreira [23] proposed that the system *rac*-Et[Ind]$_2$ZrCl$_2$/MAO can present two coordination positions, one polymerizable and other nonpolymerizable. When there is more propene in the medium, this olefin, for being more basic than the others, will coordinate in the nonpolymerizable position causing an increase in the positive charge of the zirconium, and, consequently, an increase in the propagation constant of the olefin coordinated at the polymerizable position. As propene and ethylene are more reactives than 1-octadecene, they will incorporate faster and the incorporation of the superior α-olefin will be hindered. When there is more ethylene in the medium, the coordination of this monomer in the nonpolymerizable position will not cause significant changes in the propagation constant of the olefin coordinated at the polymerizable position, allowing the superior olefins to compete in a more favorable way with the smaller monomers, thus, being more incorporated in the chain. When there is a very small concentration of ethylene in the medium (E/P = 5/95) the incorporation of the superior α-olefin increases again because its concentration is much superior to the ethylene.

Table 4
Triad sequence distribution of the terpolymers obtained by ^{13}C NMR with a 1-octadecene concentration in the feed of 0.176 M

Triad	Samples							
	EO 57	EPO 59	EPO 61	EPO 63	EPO 65	EPO 69	EPO 71	PO 73
[EEE]	75.6	69.3	56.3	19.2	12.2	5.8	0.0	0.0
[EEP+PEE]	0.0	7.1	17.6	27.3	28.9	5.0	1.9	0.0
[PEP]	0.0	0.0	0.0	8.4	15.0	7.1	5.4	0.0
[EEO+OEE]	14.2	10.8	7.1	5.2	0.5	0.0	0.0	0.0
[OEO]	0.0	1.4	0.0	0.0	0.0	0.0	0.0	0.0
[EPE]	0.0	3.3	10.3	18.8	22.3	4.7	1.7	0.0
[EPP+PPE]	0.0	0.0	0.0	9.3	9.3	1.9	1.2	0.0
[PPP]	0.0	0.0	0.0	3.9	8.1	64.6	76.5	84.0
[OPP+PPO]+[OPO]	0.0	0.0	0.0	0.0	0.0	6.6	4.9	3.0
[POP]	0.0	0.0	0.0	0.0	0.0	3.7	5.1	4.4
[OOO]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[OOP+POO]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[EOE]	10.2	8.2	8.7	8.2	3.7	0.7	3.3	8.6
[EOO+OOE]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
[E]	89.8	88.5	81.0	59.9	56.6	17.9	7.3	0.0
[P]	0.0	3.3	10.3	31.9	39.7	77.7	84.2	87.0
[O]	10.2	8.2	8.7	8.2	3.7	4.4	8.4	13.0

Table 5
Molar percentages of ethylene, propylene, and 1-octadecene in the feed and in the terpolymers

	In the feed (mol%)			In the polymer (mol%)		
	E	P	O	E	P	O
[O] = 0.088 M in liquid phase						
EO 56	54.0	0.0	46.0	90.9	0.0	9.1
EPO 58	48.6	7.8	43.6	91.4	4.2	4.4
EPO 60	43.7	14.9	41.4	88.3	9.7	2.1
EPO 62	31.7	32.3	36.0	65.8	29.1	5.1
EPO 64	17.3	53.1	29.5	65.1	32.1	2.7
EPO 66	7.4	67.6	25.1	45.1	50.8	4.1
EPO 68	2.7	74.3	23.0	15.2	83.7	1.1
EPO 70	1.3	76.3	22.3	9.4	86.8	3.8
PO 72	0.0	84.2	15.8	0.0	95.8	4.2
[O] = 0.176 M in liquid phase						
EO 57	37.0	0.0	63.0	89.8	0.0	10.2
EPO 59	33.9	5.5	60.7	88.5	3.3	8.2
EPO 61	30.9	10.5	58.5	81.0	10.3	8.7
EPO 63	23.3	23.8	52.9	59.9	31.9	8.2
EPO 65	13.4	41.0	45.6	56.6	39.7	3.7
EPO 69	2.2	60.5	37.4	17.9	77.7	4.4
EPO 71	1.1	62.4	36.5	7.3	84.2	8.4
PO 73	0.0	72.8	27.2	0.0	87.0	13.0

Table 6
Comonomer average sequence lengths (n_{XY}) and reactivity ratios (r_{XY}) calculated by ^{13}C NMR

	n_{EP}	n_{PE}	r_{EP}	r_{PE}	$r_{EP}r_{PE}$	n_{EO}	n_{OE}	r_{EO}	r_{OE}	$r_{EO}r_{OE}$	n_{PO}	n_{OP}	r_{PO}	r_{OP}	$r_{PO}r_{OP}$
[H] = 0.088 M in th liquid phase															
O 56	–	–	–	–	–	39.3	1.0	31.8	0.0	0.0	–	–	–	–	–
EPO 58	17.8	1.0	5.4	0.0	0.0	41.7	1.0	35.7	0.0	0.0	–	–	–	–	–
EPO 60	8.0	1.0	4.8	0.0	0.0	48.1	1.0	43.7	0.0	0.0	–	–	–	–	–
EPO 62	2.7	1.3	3.5	0.6	2.0	26.3	1.0	27.5	0.0	0.0	–	–	–	–	–
EPO 64	4.1	1.6	19.0	0.4	7.2	42.5	1.0	69.0	0.0	0.0	–	–	–	–	–
EPO 66	1.6	3.6	11.0	0.6	6.3	–	–	–	–	–	–	–	–	–	–
EPO 68	1.5	25.1	26.0	1.7	45.6	–	–	–	–	–	74.3	1.0	45.4	0.0	0.0
EPO 70	1.	24.1	40.8	0.8	32.2	–	–	–	–	–	73.4	1.0	42.3	0.0	0.0
PO 72	–	–	–	–	–	–	–	–	–	–	207.8	1.0	77.6	0.0	0.0
[H] = 0.176 M in th liquid phase															
EO 57	–	–	–	–	–	25.3	1.0	39.6	0.0	0.0	–	–	–	–	–
EPO 59	21.6	1.0	6.7	0.0	0.0	24.1	1.0	39.6	0.0	0.0	–	–	–	–	–
EPO 61	8.4	1.0	5.0	0.0	0.0	35.7	1.0	63.9	0.0	0.0	–	–	–	–	–
EPO 63	2.5	1.4	3.0	0.7	2.2	18.8	1.0	38.2	0.0	0.0	–	–	–	–	–
EPO 65	1.9	1.5	5.5	0.3	1.7	–	–	–	–	–	–	–	–	–	–
EPO 69	1.9	12.6	47.5	0.8	40.2	–	–	–	–	–	21.6	1.0	25.4	0.0	0.0
EPO 71	1.1	35.2	16.9	1.2	20.4	–	–	–	–	–	33.0	1.0	37.5	0.0	0.0
PO 73	–	–	–	–	–	–	–	–	–	–	57.3	1.0	42.1	0.0	0.0

3.1. Catalytic activity

The study of the copolymerization of ethylene–propylene and terpolymerizations of ethylene–propylene-α-olefins (α-olefins: 1-hexene, 1-decene and 1-octadecene) showed that the catalytic activities increase with the increase of the amount of propylene in the feed. Tables 8 and 9 show the catalytic activities of the ethylene–propylene (EP), ethylene-α-olefin and propylene–α-olefin copolymers and ethylene–propylene–α-olefins terpolymers of 1-hexene (EPH), 1-decene (EPD) and 1-octadecene (EPO) for different ethylene/propylene (E/P) gas mixtures and two different α-olefin concentration in the medium (0.088 and 0.176 M).

Table 8 shows that in the homopolymerization of ethylene, the system *rac*-Et[Ind]$_2$ZrCl$_2$/MAO has a catalytic activity of 1.5×10^6 g/mol Zr.h.atm. In the copolymerization with the α-olefins, there was an increase of the activity (line 1), this effect it is also called the comonomer effect and it has been observed in many copolymerizations [4,24–29]. The positive comonomer effect has been attributed to the activation of dormant sites by the comonomer, to the formation of new types of catalytic sites or to the increase of solubility in the medium favoring the monomer diffusion [28].

It is also verified that the best activities were presented by the ethylene–1-decene copolymerization. In the homopolymerization of propylene (line 9) the system is three times more active than in the ethylene polymerization, presenting an activity of 4.9×10^6 g/mol Zr.h.atm. In the copolymerization of propylene with 1-hexene and 1-octadecene there is a decrease of the catalytic activity or a negative effect of the comonomer. However, with 1-decene the effect of the comonomer is positive (line 9). The homopolymer and copolymers of propylene showed better activities than the homo and copolymers of ethylene (compare line 1 and 9). A possible explanation to this fact it may be related with the polymerization temperature. Ethylene presents a better activity at higher temperatures (60 °C) [30] on the other hand propylene presents a better performance at 40 °C [13,31], the temperature in which these reactions were done.

Table 8 also shows that the increase of propylene in the feed from 5 to 95% with respect to ethylene causes an increase in the catalytic activity for the copolymers of ethylene–propylene (column EP lines 2–8) as for the terpolymers with 1-hexene (column EPH, lines 2–8). For the terpolymers with 1-decene, there is a decrease in the catalytic activity till 50% of propene in the feed (column EPD, lines 2–5). Two factors can influence this behavior: the temperature and the steric hindrance. At the temperature of this reaction (40 °C) ethylene has a poor reactivity so at high amounts of this monomer the activity is lower than at high amounts of propylene. On the other hand, 1-decene presents a long chain causing a higher steric hindrance for the coordination and insertion in the polymer chain, decreasing the catalytic activity. However, when the amount of propylene is high (more than 50%) the activity starts to increase (column EPD, line 6–8). The insertion of propylene is favored at this temperature increasing the insertion rate

Table 7
Incorporation of α-olefin (H = 1-hexene; D = 1-decene; O = 1-octadecene), in ethylene–propylene–α-olefin terpolymers for the same amounts of monomers in the medium

Gás mixture ratios (E/P)	Amount of α-olefin in the terpolymer (mol%)		
	H[a]	D[b]	O
[α-Olefin] = 0.088 M in the liquid phase			
100/0	9.5	7.1	9.1
95/5	3.4	5.5	4.4
90/10	3.4	3.8	2.1
75/25	1.7	3.4	5.1
50/50	1.6	1.1	2.7
25/75	1.6	0.5	4.1
10/90	1.3	1.3	1.1
5/95	2.4	1.2	3.8
0/100	3.1	4.4	4.2
[α-olefin] = 0.176 M in the liquid phase			
100/0	10.0	14.4	10.2
95/5	8.4	8.4	8.2
90/10	6.1	6.9	8.7
75/25	3.8	5.4	8.2
50/50	3.1	7.0	3.7
25/75	1.1	2.6	–
10/90	2.5	0.8	4.4
5/95	4.5	2.3	8.4
0/100	6.5	4.9	13.0

[a] Data already published in Ref. [11].

[b] Data already published in Ref. [10].

and thus the catalytic activity. The behavior of the terpolymers of 1-octadecene is similar to those of 1-decene, nevertheless the catalytic activities are inferior. This fact can be associated to the higher steric hindrance of 1-octadecene.

The concentration of α-olefins in the feed was duplicated and the results are shown in Table 9. The catalytic activity of the copolymerizations of ethylene with the α-olefins was not significant modified by the duplication of the amount of α-olefin in the feed (line 1). In the copolymerization of propylene with α-olefins (compare line 9 of Tables 8 and 9) there is a significant increase of the activity when the concentrations of 1-hexene and 1-decene were doubled in the reaction medium and a decrease with 1-octadecene.

Table 8
Catalytic activity of EP, EPH, EPD and EPO vs the propene ratio in the feed for the termonomer concentration of 0.088 M

Line	E/P ratio in the feed	Catalytic activity $\times 10^{-6}$ (g pol/mol Zr.h.atm)			
		EP	EPH	EPD	EPO
1	100/0	1.5	2.3	3.9	2.5
2	95/5	2.0	1.6	3.8	3.2
3	90/10	3.3	1.8	3.3	3.1
4	75/25	3.4	2.1	3.2	2.3
5	50/50	3.7	2.2	3.2	0.5
6	25/75	4.2	2.3	3.3	2.0
7	10/90	3.6	2.3	3.6	2.4
8	5/95	4.7	3.1	4.2	2.6
9	0/100	4.9	4.1	5.1	3.1

$[Zr] = 2\times10^{-5}$ mol, Al/Zr = 1500, $T = 40$ °C, P = atm.

Table 9
Catalytic activity of EP, EPH, EPD and EPO vs the propene ratio in the feed for the termonomer concentration of 0.176 M

Line	E/P ratio in the feed	Catalytic activity $\times 10^{-6}$ (g pol/mol Zr.h.atm)			
		EP	EPH	EPD	EPO
1	100/0	1.5	2.0	3.8	2.1
2	95/5	2.0	1.6	3.4	3.7
3	90/10	3.3	2.4	3.5	3.3
4	75/25	3.4	2.6	3.1	1.1
5	50/50	3.7	2.6	3.3	1.1
6	25/75	4.2	2.9	3.4	0.1
7	10/90	3.6	2.6	3.5	0.8
8	5/95	4.7	3.5	5.9	1.1
9	0/100	4.9	4.9	6.2	1.2

$[Zr] = 2\times10^{-5}$ mol, Al/Zr = 1500, $T = 40$ °C, P = atm.

The terpolymers show the same behavior presented with the lower concentration of α-olefin with the increase of propylene in the feed from 5 to 95%. The catalytic activities of the terpolymers with 1-hexene and 1-decene are slightly higher than those obtained with lower amount of α-olefin. For the 1-octadecene terpolymers the increase of the concentration of the termonomer decreases the catalytic activity.

The behavior with the terpolymers is peculiar because the addition of 1-decene causes a more significant increase in the activity than the addition of 1-hexene. As the 1-decene has a longer side chain than 1-hexene, it should be expected to have a higher steric hindrance and thus a lower rate of propagation reducing the catalytic activity (this behavior is observed with 1-octadecene).

This fact can also be explained by the presence in a catalyst as *rac*-Et[Ind]$_2$ZrCl$_2$ of two coordinating sites [23]. The more polarizable the olefin the more increases the positive charge on the Zr, increasing the propagation constant of the olefin coordinated at the polymerizable position. The biggest α-olefins are more polarizables, this effect is compensated by the steric hindrance that slows down their insertion in the polymer chain. The more polarizable α-olefin among those studied is 1-octadecene but its effect in the Zr charge may be compensated by its bigger size. The good results in catalytic activity of 1-decene can be attributed to the fact of being more polarizable than 1-hexene and not as big as 1-octadecene.

4. Conclusions

Terpolymers of ethylene–propylene–1-octadecene have been completely characterized by ^{13}C NMR. The amount of 1-octadecene incorporated in the terpolymer decreases when the amount of propylene in the feed increases showing a competition for the active site between these two monomers. Compared with other α-olefins such as 1-hexene and 1-decene, 1-octadecene has the best incorporation in the terpolymer at the same conditions, however, the terpolymerization with this monomer presented the lowest catalytic activities. The properties of these terpolymers will be published in a following paper.

Acknowledgements

The authors thank CAPES, CNPq and FAPERGS for their financial support and Ipiranga Petroquímica for the supply of some raw materials.

References

[1] Clas SD, McFaddin DC, Russell KE. J Polym Sci, Part B: Polym Phys 1987;25:1069.

[2] Benavente R, Pérez E, Quijada R. J Polym Sci, Part B: Polym Phys 2001; 39:277.

[3] Koivumäki J, Seppälä JV. Macromolecules 1994;27:2008.

[4] Quijada R, Narváez A, Rojas R, Rabagliati FM, Galland GB, Mauler RS, et al. Macromol Chem Phys 1999;200(6):1306.

[5] Quijada R, Retuert J, Guevara JL, Rojas R, Valle M, Saavedra P, et al. Macromol Symp 2002;189:111.

[6] Yoon J-S, Lee D-H, Park E-S, Lee I-M, Park D-K, Jung S-O. J Appl Polym Sci 2000;75:928.

[7] Quijada R, Guevara JL, Galland GB, Rabagliati FM, Lopez-Majada JM. Polymer 2005;46:1567.

[8] Van Reenen AJ, Brull R, Wahner U, Pasch H. Polym Prepr 2000;41(1): 496.

[9] Koivumäki J, Fink G, Seppälä JV. Macromolecules 1994;27:6254.

[10] Escher FFN, Galland GB, Ferreira M. J Polym Sci, Part A: Polym Chem 2003;41:2531.

[11] Escher FFN, Galland GB. J Polym Sci, Part A: Polym Chem 2004;42: 2474.

[12] Silva FAA, Galland GB. J Appl Polym Sci 2001;80:1880.

[13] Kissin YV. Isoespecific polymerization of olefins with heterogeneous Ziegler–Natta catalysts. New York: Spinger; 1985 p. 3.

[14] Villar MA, Ferreira ML. J Polym Sci, Part A: Polym Chem 2001;39:1136.

[15] Traficante DD. Concepts Magn Reson 1994;6:131.

[16] Galland GB, De Souza RF, Mauler RS, Nunes F. Macromolecules 1999; 32:1620.

[17] Lindeman LP, Adams JQ. Anal Chem 1973;43:1245.

[18] (a) Hsieh ET, Randalll JC. Macromolecules 1982;15:353.
(b) Randall JC. Rev Macromol Chem Phys 1989;29:201.

[19] Busico V, Cipullo R, Segre AL. Macromol Chem Phys 2002;203: 1403.

[20] Usami T, Takayama S. Macromolecules 1984;17:1756.

[21] Adriaensens PJ, Karssenberg FG, Gelan JM, Mathot VBF. Polymer 2003; 44:3483.

[22] Pham QT. Etude de la microstructure des polymers par RMN ^{1}H–^{13}C ‘Liquide’. Annales dês Composites, Techiques Analytiques et Caractérisation dês Materiaux Macromoléculaires, Paris 16–17. vol. 49; 1985.

[23] Ferreira ML, Galland GB, Damiani DE, Villar MA. J Polym Sci, Part A: Polym Chem 2001;39:2005.

[24] Quijada R, Scipioni RB, Mauler RS, Galland GB, Miranda MSL. Polym Bull 1995;35:299.

[25] Quijada R, Dupont J, Miranda MSL, Scipioni RB, Galland GB. Macromol Chem Phys 1995;196:3991.

[26] Arnold M, Bornemann S, Koller F, Menke T, Kressler J. Macromol Chem Phys 1998;199:2647.

[27] Köppl A, Babel AI, Alt HG. J Mol Catal A: Chem 2000;153:109.

[28] Herfert N, Montag G, Fink P. Makromol Chem 1993;194:3167.

[29] Chien JCW, Nozaki T. J Polym Sci, Part A: Polym Chem 1993;31:227.

[30] (a) Lehtinen C, Löfgren B. Eur Polym 1997;33:115.
(b) Lehtinen C, Starck P, Löfgren B. J Polym Sci, Polym Chem 1997;35: 307.

[31] Graef S, Wahner UM, Van Reenen AJ, Brüll R, Sanderson RD. J Polym Sci, Polym Chem 2002;40:128.