

Copolymerization of Ethylene with Cyclopentene or 2-Butene with Half Titanocenes-Based Catalysts

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ABSTRACT: Half titanocenes ($\text{CpCH}_2\text{CH}_2\text{O}$)/ TiCl_2 (1), ($\text{CpCH}_2\text{CH}_2\text{OCH}_3$)/ TiCl_3 (2), and CpTiCl_3 (3), activated by methylaluminoxane (MAO) were tested in copolymerization of ethylene with internal olefins such as cyclopentene. All the catalysts were able to give incorporation of cyclopentene in polyethylene matrix. ^{13}C NMR analysis of obtained copolymers showed that the catalytic systems have low regiospecificity. In fact, in ethylene–cyclopentene copolymers, cyclic olefin inserts with both 1,2 and 1,3-enchainment. X-ray powder diffraction analysis of these copolymers confirmed that 1,2 inserted cyclopentene units are excluded from crystalline phase, whereas 1,3-cyclopentene units are included, giving rise to expansion of unit cell of crystalline polyethylene. Titanium-based catalysts were investigated also in the copolymerization of ethylene with *E* and *Z*-2-butene. Only complex (1) was able to give copolymers and ^{13}C NMR analysis of products showed 2-3, 1-3, and 1-2 insertion of 2-butene. Differential scanning calorimetry analysis displayed that ethylene–cyclopentene, as well as ethylene-2-butene, copolymers are crystalline and their melting point decreases by increasing the comonomer content. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 4725–4733, 2008

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INTRODUCTION

Cyclopentene and other internal olefins, for example, *E* and *Z*-2-butene can be copolymerized with ethylene in the presence of several Ziegler–Natta catalysts.^{1–15} At first, Natta reported about the copolymerization of ethylene with cyclopentene or 2-butene (both *E* or *Z*) using vanadium-based catalysts that produced, although with low-activity, alternating copolymers.^{1,2}

More recently, Kaminsky reported that zirconocene catalysts are able to give 1,2-insertion of cyclopentene³ and Müller and coworkers, using specific zirconocene catalyst (rac-dimethylsilylene(ferrocene) [2,3] indenyl cyclopentadienyl zir-

conium dichloride) detected 1,3-cyclopentene in resulting copolymer.⁴ As reported by Naga and coworkers, usually, zirconocene-based catalysts show very high-activity, but, frequently, low regioselectivity. In fact, cyclopentene is inserted in the polymer chain both with 1,2- and 1,3-enchainment.^{5–7} *Ansa*-zirconocenes activate by methylaluminoxane (MAO) are also active in the copolymerization of *E* and *Z* isomers of 2-butene with ethylene, giving growing chain isomerization dependent on the configuration (*E* or *Z*) of 2-butene, and independent from metallocene symmetry.^{8,9}

Differently from zirconocenes, nickel- and titanium-based catalysts show higher regiospecificity.

In fact, 1,3-insertion of cyclopentene, in ethylene–cyclopentene copolymers, as reported by Brookhart et al., is selectively obtained by α -diimine nickel(II) complexes.¹⁰

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Instead, Wang et al. using half titanocene catalysts obtained ethylene–cyclopentene copolymers having cyclopentene inserted only with 1,2 enchainment.¹¹ Copolymerization of ethylene and cycloolefins with series of constrained geometry titanium catalysts,^{12–14} was investigated by Waymouth and Shiono, while Fujita and Coates performed this copolymerization in the presence of bis(phenoxyimine) titanium catalysts. These titanium complexes also gave 1,2-enchainment of cycloolefin.¹⁵

The polymerization of 2-butene and its copolymerization with ethylene was investigated using dichlorobis(β -diketonato)titanium complexes and $[\text{ArN}(\text{CH}_2)_3\text{NAr}]\text{TiCl}_2$. The obtained copolymers displayed incorporation of 2-butene units, and *E*-isomer showed a higher copolymerization rate than *Z*-2-butene.¹⁶

Herein, we report the results of ethylene–cyclopentene copolymerization performed in the presence of three half-titanocene based catalysts: $(\text{CpCH}_2\text{CH}_2\text{O})\text{TiCl}_2$ (**1**), $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$ (**2**), and CpTiCl_3 (**3**) to study the behavior of three titanium complexes having different ancillary ligands: cyclopentadienyl-ethylen-oxy (dianionic and bidentate ligand), cyclopentadienyl-ethylen-metoxo (mono-anionic and bidentate ligand), and monocyclopentadienyl (monoanionic and monodentate ligand). Because of the differences between these three ligands, the corresponding metal center show different electrophilicity and steric hindrance. The copolymerization results of ethylene with *E* and *Z*-2-butene, with catalyst (**1–3**) will be also reported.

EXPERIMENTAL

General Procedure

Polymerization grade ethylene was purchased from Società Ossigeno Napoli and used without further purification. Cyclopentene, *E* and *Z*-2-butene were purchased from Aldrich. MAO was purchased from Witco and used as a solid after distillation of solvent.

Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. Half-titanocenes $(\text{CpCH}_2\text{CH}_2\text{O})\text{TiCl}_2$ (**1**), $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$ (**2**), and CpTiCl_3 (**3**) were synthesized according to the literature.^{17–19}

Cyclopentene Homopolymerization

Run 1

Polymerization of cyclopentene was carried out by introducing sequentially in a 100-mL glass

flask, equipped with a magnetic stirrer, toluene (13 mL), MAO (340 mg, 6.0×10^{-3} mol based on Al), and cyclopentene (3 mL). The reactor was thermostated at reaction temperature, and the run was started by introducing the titanocene complex (**1**) (1.3×10^{-5} mol) dissolved in toluene (2 mL). The polymerization conditions are specified in Table 1. Polymerization was stopped by introducing a few milliliters of methanol, and the mixture was poured into acidified ethanol. The polymer was recovered by filtration, washed with fresh ethanol, and dried in vacuum at 60 °C.

Ethylene Homopolymerization

Run 2

Polymerization of ethylene was performed by introducing dry toluene (18 mL) and MAO (340 mg, 6.0×10^{-3} mol based on Al) into 100-mL glass flask equipped with magnetic stirrer. The inert gas was removed and the flask was feed with constant pressure of 1 atm of ethylene. The polymerization was started by injecting titanocene (**1**) (1.3×10^{-5} mol) dissolved in toluene (2 mL). Polyethylene was recovered as usual.

Ethylene–Cyclopentene Copolymerizations

Runs 3–14

Copolymerizations were carried out by the following general procedure: in a 100 mL glass-flask, equipped with a magnetic stirrer, were introduced sequentially dry toluene, cyclopentene, MAO (340 mg, 6×10^{-3} mol), and half-titanocene (**1–3**) (1.3×10^{-5} mol) dissolved in 2 mL of toluene, as reported in the Table 1. The flask was feed with a constant over-pressure of ethylene of 10 cm of paraffin-oil. The copolymer was recovered as usual.

Ethylene-2-Butene Copolymerizations

Runs 15–18

Copolymerizations were performed by introducing dry toluene (18 mL) and MAO (340 mg, 6.0×10^{-3} mol based on Al) into 100 mL glass flasks equipped with magnetic stirred. The flasks were cooled with liquid nitrogen and the inert gas was evacuated. 2-butene (the amount are reported in Table 2) was condensed into the flasks, then the reactors were quickly thermostated at the reaction temperature and was introduced the titanocene complex (**1**) (1.3×10^{-5} mol) dissolved in toluene (2 mL). The flasks

Table 1. Polymerization of Ethylene and Cyclopentene in the Presence of (1), (2), (3) Based Catalysts

Run ^a	Cat	[CP] ^b (mol/L)	<i>t</i> (h)	Yield (mg)	Activity ^c	X _{CP} ^d (%)	<i>f</i> _{1,2-<i>cis</i>} ^e	<i>f</i> _{1,3-<i>cis</i>} ^e	<i>f</i> _{1,3-<i>trans</i>} ^e	<i>T</i> _m ^f (°C)	<i>M</i> _w ^g (Dalton × 10 ⁴)	<i>M</i> _w / <i>M</i> _n ^g
1	1	2.3	65	25	27	100	–	100	–	–	n.d.	n.d.
2	1	–	1	350	14 × 10 ⁴	–	–	–	–	135	33.0	1.8
3	1	1.1	65	232	275	2.8	17.4	65.2	17.4	122	9.7	1.7
4	1	2.5	65	130	154	2.3	33.3	55.6	11.1	120	9.2	1.8
5	1	3.2	65	110	130	3.3	46.1	38.4	15.4	116	9.5	2.4
6	1	6.2	65	30	36	5.0	37.8	45.9	16.2	110	4.5	1.6
7	2	1.1	115	60	40	1.1	56.0	44.0	–	126	20.0	1.8
8	2	2.5	115	50	33	1.3	50.0	50.0	–	125	15.0	2.0
9	2	3.2	115	50	33	1.8	48.0	55.0	–	123	9.3	2.1
10	2	3.8	115	20	14	2.5	15.0	72.5	12.5	122	6.5	1.8
11	3	1.1	115	90	60	3.3	–	71.4	18.6	118	3.5	1.8
12	3	2.5	115	70	47	4.0	7.7	86.5	5.8	113	3.3	2.0
13	3	3.2	115	50	33	4.2	–	85.7	14.3	110	2.5	1.8
14	3	6.2	115	20	14	5.9	–	100	–	100	2.0	1.9

^a All polymerizations were carried out at 25 °C in dry toluene at *V*_{tot} = 18 mL by using 1.3 × 10^{−5} mol of precatalyst and 6.0 × 10^{−3} mol MAO (based on Al), with a constant ethylene concentration of 3.6 × 10^{−4} mol/L for the runs 1, 3–14, and 0.19 mol/L for the run 2.

^b Cyclopentene concentration in the feed.

^c For runs 1 and 2: Activity = g of homopolymer/mol of precatalyst × time in h × monomer concentration in mol/L; for runs 3–14: Activity = g of copolymer/mol of precatalysts × time in h.

^d Percent molar fraction of cyclopentene units in the polymer chains.

^e Fraction of cyclopentene leading to 1,2-*cis* units (*f*_{1,2-*cis*}), 1,3-*cis* units (*f*_{1,3-*cis*}) and 1,3-*trans* units (*f*_{1,3-*trans*}).

^f Melting temperature.

^g Molecular weight and polydispersity index (*M*_w/*M*_n) determined by gel permeation chromatography versus polystyrene standards.

were feed with a constant over-pressure of ethylene of 10 cm of paraffin-oil. The copolymers were recovered as usual.

Measurements

¹³C NMR Analysis

¹³C NMR spectra were recorded on an AV 300 Bruker spectrometer operating at 75 MHz, using

these acquisition parameters: acquisition time AQ = 1.2 s, pulse delay D1 = 4 s, and pulse angle P1 = 8.25 μs (90°). The samples were prepared by dissolving polymer sample (40 mg) into tetrachloro-dideuterio-ethane (0.5 mL). The spectra were recorded at 100 °C using hexamethyldisiloxane (HMDS) as internal chemical shift reference. Sample 1 was prepared by dissolving polymer (30 mg) into CDCl₃ (0.5 mL).

Table 2. Polymerization of Ethylene and 2-Butene in the Presence of (1) Based Catalysts

Run ^a	<i>E</i> ^b (mol/L × 10 ^{−4})	Comonomer ^c (mol/L)	X _B ^d	Activity (g _{pol} /mol _{Ti} h)	<i>f</i> _{2,3-<i>erythro</i>} ^e	<i>f</i> _{2,3-<i>threo</i>} ^e	<i>f</i> _{1,2} ^e	<i>f</i> _{1,3} ^e	<i>T</i> _m ^f (°C)
15	3.6	Z-2-butene (2.1)	0.8	115	0.66	–	0.33	–	130
16 ^g	3.6	Z-2-butene (4.0)	4.0	77	0.73	–	0.07	0.20	118
17	2.5	E-2-butene (2.1)	3.1	96	–	0.33	0.66	–	124
18 ^h	3.6	E-2-butene (4.1)	3.5	77	–	0.20	0.80	–	120

^a All polymerizations were carried out for 40 h at 25 °C in dry toluene at *V*_{tot} = 18 mL by using 1.3 × 10^{−5} mol of precatalyst and 6.0 × 10^{−3} mol MAO (based on Al).

^b Ethylene concentration in the feed.

^c 2-Butene concentration in the feed.

^d Percent molar fraction of 2-butene units in the polymer chains.

^e Fraction of 2-butene leading to 2,3-*erythro* units (*f*_{2,3-*erythro*}), 2,3-*threo* units (*f*_{2,3-*threo*}), 1,2 units (*f*_{1,2}), and 1,3 units (*f*_{1,3}).

^f Melting temperature.

^g Numeral molecular weight *M*_n = 2.6 × 10⁴ evaluated by ¹³C NMR analysis.

^h Numeral molecular weight *M*_n = 1.5 × 10⁴ evaluated by ¹³C NMR analysis.

The spectrum was recorded at room temperature using tetramethylsilane (TMS) as internal chemical shift reference.

The resonances were assigned on the base of the data reported in the literature for carbons in similar environments,^{4,5,20–22} of the distortionless enhancement by polarization transfer ¹³C NMR experiments (DEPT)^{23,24} and on additivity Grant and Paul rules.²⁵

The molar fraction of ethylene and cyclopentene (X_E and X_{CP}) and the fractions of inserted cyclopentene leading to 1,2-*cis*, 1,3-*cis*, and 1,3-*trans* units ($f_{1,2-cis}$, $f_{1,3-cis}$, $f_{1,3-trans}$, respectively) were calculated by the following equations using area of the ¹³C NMR signals (C_i) as labeled in Figure 1.

$$E = 1/2 (\Sigma C_s - 5CP)$$

$$CP = C_{1,16} + C_7 + 1/3 C_{12,13}$$

$$X_E = E/(E + CP)$$

$$X_{CP} = CP/(E + CP)$$

$$f_{1,2-cis} = C_{1,16}/CP$$

$$f_{1,3-cis} = C_7/CP$$

$$f_{1,3-trans} = 1/3 C_{12,13}/CP$$

The molar fraction of ethylene and 2-butene (X_E and X_B) and the fractions of inserted 2-butene leading to 2,3 (*erythro* and *threo*), 1,3 and 1,2 units ($f_{2,3-erythro}$, $f_{2,3-threo}$, $f_{1,2}$, $f_{1,3}$, respectively) were calculated by the following equations using area of the ¹³C NMR signals (C_i) as labeled in Figure 5.

$$E = 1/2 (\Sigma C_s - 4B)$$

$$B = 1/2 C_1 + C_2 + C_3 + 1/2 C_4$$

$$X_E = E/(E + B)$$

$$X_B = B/(E + B)$$

$$f_{2,3-erythro} = 1/2 C_1/B$$

$$f_{1,3} = C_2/B$$

$$f_{1,2} = C_3/B$$

$$f_{2,3-threo} = 1/2 C_4/B$$

Gel Permeation Chromatography Analysis

The analysis of the samples were performed at 135 °C by Waters instrument GPCV 2000 equipped with refractive index and viscosimeter detectors, using four PSS columns set consisting of, 10⁵, 10⁴, 10³, 10² Å (pore size) and 10 μm (particle size). *o*-dichlorobenzene was the carrier solvent used with a flow rate of 1.0 mL/min. The

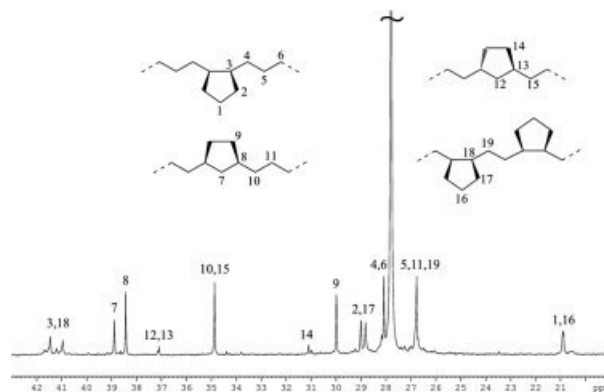


Figure 1. ¹³C NMR spectrum of sample 4 and resonance assignments of ethylene–cyclopentene copolymers.

calibration curve was established with polystyrene standards.

Differential Scanning Calorimetry Analysis

Calorimetric measurements have been carried out on DSC 2920 apparatus manufactured by TA Instruments, calibrated against an indium standard ($T_m = 156.6$ °C), with heating scans from –10 to 200 °C, at a 10 °C/min heating rate, under a flowing nitrogen atmosphere. Specimens were sealed in aluminum pans.

X-ray Powder Diffraction Analysis

Wide-angle X-ray powder diffraction profiles were collected at room temperature, with automatic 1710 Philips diffractometer using Ni-filtered Cu K α radiation ($\lambda = 1.5418$ Å) and scans in the 2θ range 4–40°.

RESULTS AND DISCUSSION

(1–3)-based catalysts activated by MAO were utilized in homopolymerization of cyclopentene. Only catalyst (1) produced polycyclopentene, however, its activity was 10⁴ times lower than observed in the polymerization of ethylene (see runs 1 and 2 in Table 1).

Therefore, ethylene–cyclopentene copolymerizations were carried out using a low concentration of ethylene (3.6×10^{-4} mol/L), obtained by overpressure of 10 cm of vaseline oil (see experimental part).

Data reported in Table 1 show the results of copolymerization performed in the presence of titanium compounds (1–3) activated by MAO,

using constant concentration of catalyst (runs 3–14).

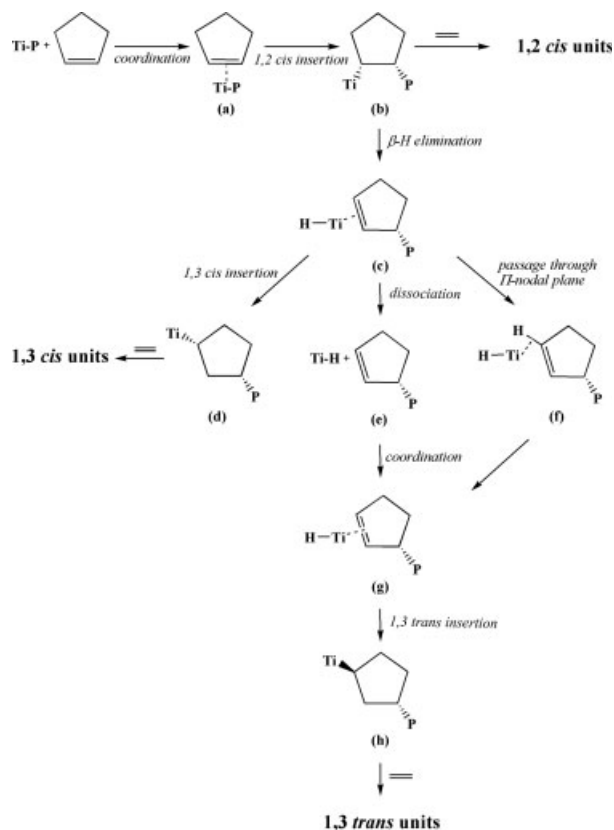
Comparison of the results obtained by different catalysts reveals that half titanocene catalyst (**1**) was the most active and its activity decrease with increasing the amount of cyclopentene in the feed (runs 3–6). Copolymers with a range of cyclopentene molar fraction values (X_{CP}), evaluated by ^{13}C NMR analysis, included between about 2% and 5%, were achieved.

Copolymerizations performed in the presence of (**2**) and (**3**) based catalysts, runs 7–10 and 11–14, respectively, in Table 1, displayed that (**3**)/MAO system give products containing amount of cyclopentene inserted units very close to that obtained in the presence of (**1**), whereas (**2**)/MAO catalyst provide copolymers with a lower molar fraction of inserted cyclopentene.

^{13}C NMR analysis allow to determinate the microstructure of copolymers, which was achieved by full attribution of resonances done on the basis of the data reported in the literature for carbon in similar environments,^{4,5,20–22} of the distortionless enhancement by polarization transfer ^{13}C NMR experiments (DEPT)^{23,24} and of the additivity rules.²⁵ Figure 1 shows ^{13}C NMR spectrum of sample 4.

In the spectrum, besides the resonances at 27.8 ppm due to ethylene units, signals attributable to *cis*-1,2 and both *cis*- and *trans*-1,3 inserted cyclopentene units are explained (resonances are labeled according to inset of Fig. 1). In fact, one can observe the resonances: (i) at 40.8–41.9 ppm, due to methine carbons 3 and 18, at 28.7–29.2 ppm attributable to methylene carbons 2 and 17 and at 20.9 ppm assigned to methylene carbons 1 and 16 of *cis*-1,2-enriched cyclopentene; (ii) at 38.9 ppm, conferred to methylene carbon 7, at 38.4 ppm attributable to methine carbon 8 and at 30.0 ppm due to methylene carbon 9 of isolated *cis*-1,3-enriched cyclopentene; (iii) at 37.1 ppm, assigned to methylene carbon 12 and to methine carbon 13 and at 31.1 ppm attributable to methylene carbon 14 of isolated *trans*-1,3-enriched cyclopentene. Cyclopentene homosequences were, practically, not detected in the copolymers, denoting difficult insertion of cyclopentene on metal-cyclopentene chain end, as it is also deducible observing the homopolymerization results.

The molar fraction of ethylene and cyclopentene (X_E and X_{CP}) and the relative amounts of 1,2-*cis*, 1,3-*cis*, and 1,3-*trans* ($f_{1,2-cis}$, $f_{1,3-cis}$ and $f_{1,3-trans}$, respectively) inserted cyclopentene



Scheme 1. Mechanism of formation of inserted cyclopentene units.

units were calculated by means of equations reported in experimental part.

As shown in Table 1, catalytic systems based on precursors (**1**) and (**2**) produce copolymers having both 1,2 and 1,3 inserted cyclopentene units. The ratio of amount 1,2 versus 1,3 is quite variable, ranging between about 1.3–0.2 (see runs 7 and 10); thus, randomness amount of both possible units, suggest that the catalysts have a low regiospecificity. Instead, they have a fair stereospecificity, because all the achieved samples present 1,2-inserted cyclopentene units with *cis* configuration and 1,3-insertion occur, preferentially, with *cis* arrangement, being the fraction of 1,3-*cis* configuration $\geq 70\%$.

(**3**)-based catalyst, instead, seems to have both regioselectivity and stereoselectivity higher with respect to (**1**) and (**2**), because the 1,2-cyclopentene units are almost absent in copolymer samples and the fraction of 1,3-*cis* configuration is $\geq 80\%$.

The formation mechanism of different cyclopentene units is sketched in Scheme 1. Accord-

ing to this reaction scheme, 1,2-*cis* units are due to the mode of addition of the growing chain-end to the double bond of the incoming cyclopentene (pathway (a), (b) in Scheme 1), that should be *cis*, as already reported to occur with, for example, propylene and styrene.^{26,27} 1,3-*cis* units, reasonably, can arise from isomerization reaction, which take place as consequence of 1,2-insertion followed from β -hydride abstraction and re-insertion (pathway (a)–(d) in Scheme 1).^{28,29} This is analogous to the well-known 3,1 isomerization reaction observed, as effect of secondary monomer insertion, for propene polymerization with several metallocene-based catalytic systems.³⁰ Instead, the occurrence of 1,3-*trans* insertion of cyclopentene could be explained considering that the hydride complex (c), produced by β -hydride elimination, could undergo dissociation of cyclopentene-polymer-chain-ending, which could bind to the same or to another metal center with its opposite faces, determining a 1,3-*trans* stereo relationship between the two substituents of cyclopentene: the metal and the polymer chain (pathway (a)–(c), (e), (g), and (h) in Scheme 1).^{28,29} An alternative mechanism involve the intramolecular metal passage through the π nodal plane without dissociation, exploiting carbon-hydrogen σ -complex (pathway (a)–(c), (f)–(h) in Scheme 1).³¹

Gel permeation chromatography analysis carried out on the copolymeric samples showed the molecular weight (M_w) included between 2.0×10^4 and 2.0×10^5 Da, monomodal and quite narrow molecular weight distribution ($M_w/M_n \approx 2$), indicating that polymerization reaction occur on single site catalyst. Catalyst-based on complex (**3**) produced polymers having the lowest molecular weight. A likely explanation arise considering that one of the most relevant chain termination take place via β -hydride elimination, which can occur when a vacant coordination site on the metal is present. Therefore, with this catalyst, which has ancillary ligand monoanionic and monodentate, termination reaction, supported by agostic interaction between metal and a hydrogen on β -carbon of the chain-end, occur easier respect to catalysts (**1**) and (**2**) having bidentate ligands, dianionic, and mono-anionic, respectively.

Characterization of thermal properties of copolymer samples by means differential scanning calorimetry (DSC) showed single melting points, indicating even distribution of copolymer composition, and, as reported in Table 1, melting tem-

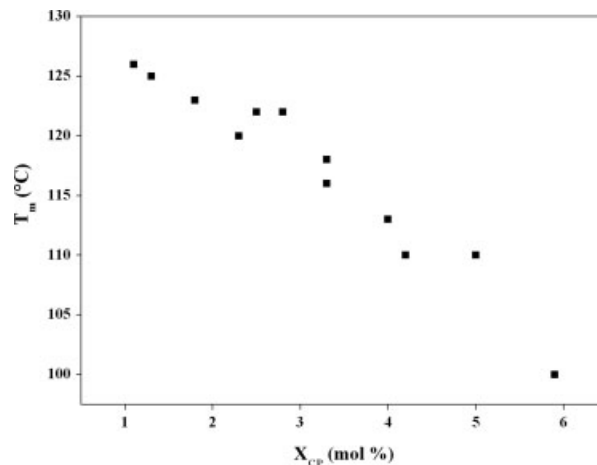


Figure 2. Dependence of melting temperature from cyclopentene content in polymer chains.

perature varies between 135 °C for polyethylene (run 2 of Table 1) and 100 °C for copolymer containing 5.9 mol % cyclopentene (run 14 of Table 1). Obviously, melting enthalpies reduce with increasing of X_{CB} , reflecting lowering crystallinity due to cyclopentene incorporation. In Figure 2, the relationship between the comonomer content and the melting point is reported.

Moreover, the crystalline structure of ethylene-cyclopentene copolymers was investigated by wide-angle X-ray diffraction (WAXD). Naga et al. previously explained with wealth of detail, how cyclopentene units, incorporated in polyethylene matrix, influence the crystalline structure.⁶ They recognized that 1,2-cyclopentene units are excluded from the crystalline phase of polyethylene, determining decreasing of the intensity of reflection peaks, whereas 1,3-cyclopentene units are incorporated in the crystalline phase and expanded the unit cell of crystalline polyethylene. Thus, when only 1,3-inserted cyclopentene units are present in the copolymers (see samples 11, 13, and 14 in Table 1), we observed expansion of unit cell of polyethylene. In fact, increasing the content of cyclopentene in the copolymers, the reflection peaks due to (110) and (200) crystal planes (peaks observed at $2\theta = 21^\circ$ and 23.5° for polyethylene, respectively) are shifted to lower angles and the intensity of (200) reflection peak decrease respect to that of polyethylene (see Fig. 3). When both 1,2- and 1,3-units are included in the polyethylene matrix, we obtained structures which present decreasing of the intensity of reflection peaks and expanded unit cell of crystalline polyethylene with increasing of cyclopentene contents as showed by dif-

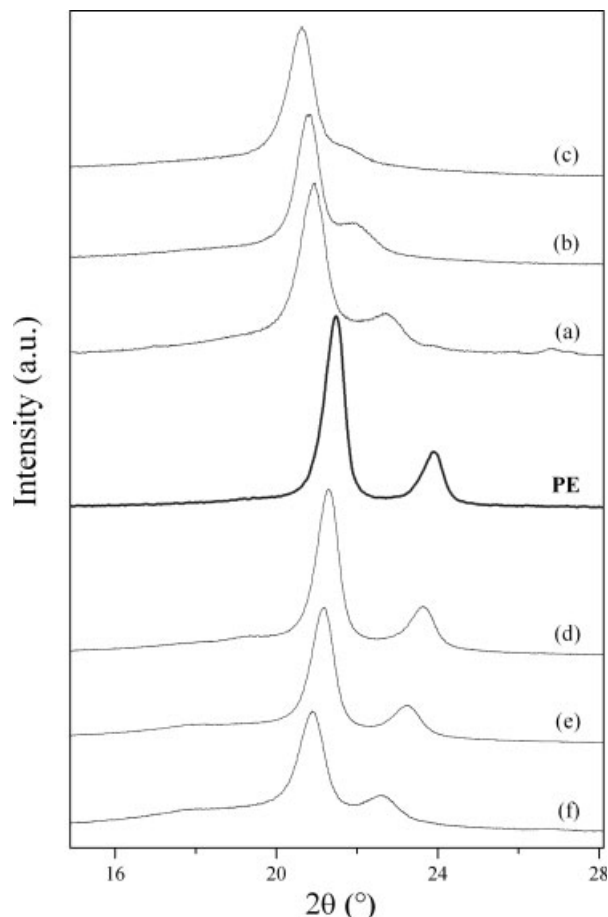


Figure 3. X-ray diffraction profiles of samples 2 (PE), 11 (a), 13 (b), 14 (c), 7 (d), 5 (e), and 6 (f).

fraction profile of, for example, samples 7, 5, and 6 reported in Figure 3.

In Figure 4 are reported the relationship between both a and b -axial length of units cell and comonomer content assuming orthorhombic crystal for copolymers. As one can note b -axial length is unaffected by content of cyclopentene units. Instead, a -axial length increases almost linearly with increasing cyclopentene contents. Moreover, observing the a -axial length of samples 5 and 11 having same molar fraction of cyclopentene ($\approx 3.3\%$) it is possible note that the a -axial length of sample 11 is higher than sample 5, being fraction of 1,3- inserted cyclopentene higher for the former than for the latter.

Instead, samples 13 and 14 having different content of cyclopentene unit (4.2 and 5.9, respectively) present the same a -axial length because they include the same molar fraction of 1,3- inserted cyclopentene units.

These data confirm that practically 1,2- inserted cyclopentene units do not influence the

a -axial length, whereas 1,3 units strongly produce expansion of the unit cell of crystalline polyethylene.

Thus, the three half-titanocene ($\text{CpCH}_2\text{-CH}_2\text{O}$) TiCl_2 (1), ($\text{CpCH}_2\text{CH}_2\text{OCH}_3$) TiCl_3 (2), and CpTiCl_3 (3), activated by MAO are all able to give copolymerization of ethylene with cyclopentene. They were also tested in copolymerization of ethylene with other internal olefins, that is, *E*-2-butene and *Z*-2-butene. Only complex (1) was able to give copolymers, although with very low-activity. With each monomer, two runs were carried out using two different concentration and the copolymerization results are summarized in Table 2.

Under conditions reported in Table 2, the productivities were modest. However, the obtained copolymers contain from 0.1 to 4 mol % of inserted comonomer, estimated by ^{13}C NMR analysis. Figure 5 reports ^{13}C NMR spectra of sample 16 and 18. The copolymers display lower melting point than that polyethylene (see run 2 of Table 1).

Spectrum of sample 16 obtained with *Z*-2-butene [Fig. 5(a)] disclose that this monomer give rise to prevalingly 2,3-insertion. In fact, in addition to signals at 27.8 ppm, due to ethylene sequences, in the spectrum were present signals at 15.0 ppm attributable to methyl carbon, in *erythro* position, placed on neighboring methine (C_1 in Fig. 5). Signal at 18.1 ppm assigned to isolated methyl carbon in methylene sequences, derived of 1,3-insertion of 2-butene (C_2 in Fig. 5) was also, detected. Moreover, signal of lower intensity at 9.2 ppm attributable to methyl carbon

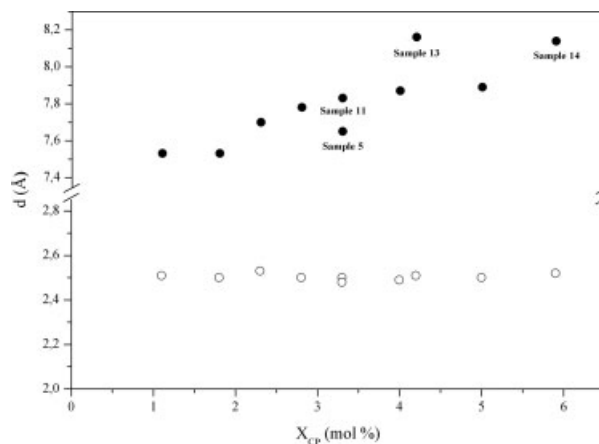


Figure 4. Relationship between cyclopentene content with a -axial length (●) and b -axial length (○) of units cell of ethylene-cyclopentene copolymers.

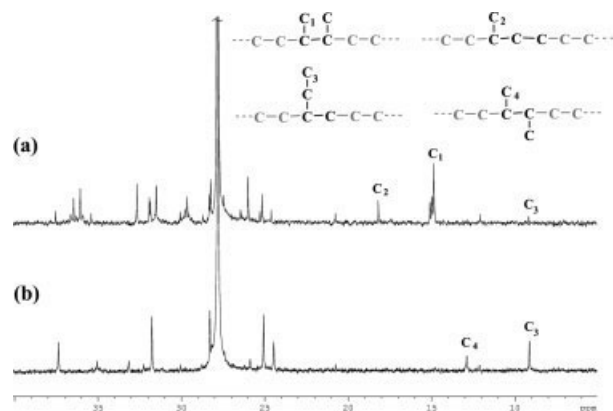


Figure 5. ^{13}C NMR spectra of sample 16 (a) and sample 18 (b).

of ethyl branching was pointed (C_3 in Fig. 5). This signal are due to inserted 1-butene units arising from isomerization of 2-butene.^{8,9}

^{13}C NMR analysis of sample 18 obtained with *E*-2-butene [Fig. 5(b)] showed that this olefin insert prevalingly with 1,2-enchainment, in fact resonance at 9.2 ppm attributable to 1,2-insertion of butene can be detected.^{8,9} Moreover, signal at 13.8 ppm attributable to methyl carbon, in *threo* position, placed on adjacent methine (C_4 in Fig. 5), derived of 2,3-insertion was present.^{9,16}

Thus, in the presence of (1)-based catalyst, 2,3-inclusion of comonomers in the polymer chain can occur either with *Z* and *E* 2-butene, and, due to *cis* outbreak of double bond,^{26,27} it produces *erythro* and *threo* configuration of vicinal methyls, respectively. In addition, both monomers can give isomerization, when they are the last inserted units, producing 1,3 and 1,2 insertion. These isomerization were already observed in the copolymerization of ethylene with 2-butene in the presence of zirconocene-based catalysts, and isomerization mechanisms involving intermediates with metal-allyl bonds were suggested.^{8,9}

CONCLUSIONS

Half-titanocenes (1–3) activated by MAO were able to copolymerize ethylene with internal olefins. Among the three used complex, the most active in the polymerization of internal olefins was (1). The different reactivity of titanium compounds could be due to the differences between the three ligands. (1) has ancillary ligand dia-

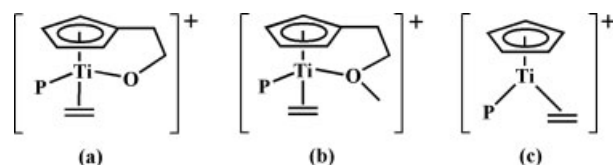
nylic and bidentate, therefore, presumably, the catalytic alkyl cation formed after reaction with MAO, should have oxidation state equal to 4 [see Scheme 2(a)]. Instead (2) and (3), having monoanionic and bidentate and monoanionic and monodentate ligand, respectively, could reduce their oxidation state to 3, by reaction with MAO, as already reported for complex (3) in several paper,^{32–34} and consequently to have lower electrophilicity than (1) and therefore lower reactivity [see Scheme 2(b,c)].

On the other hand, as reported by Wang et al.¹¹ (substituted cyclopentadienyl)(aryloxo)titanium-dichloride based catalysts display higher activity respect to catalysts (1–3), probably, because the catalytic sites have a higher electrophilicity, being the basicity of aryloxo ligand lower than alchoxy ligand.

^{13}C NMR analysis of the obtained samples, show that all utilized catalysts are able to insert cyclopentene in polyethylene matrix either with 1,2 and 1,3 constitutional units, therefore, they have a low regiospecificity, nevertheless they are quite stereospecific. ^{13}C NMR spectra, substantially, do not show resonances attributable to cyclopentene homosequences, so, for catalysts based on (1–3) titanium complexes follow that the insertion of cyclopentene on metal-cyclopentene is tricky.

All the obtained copolymers are crystalline and the degree of crystallinity is related to the amount of cyclopentene incorporated in the polyethylene matrix. This finding was pointed out observing the relationship between the comonomer content and the melting point. Moreover, X-ray powder diffraction unequivocally confirmed that 1,3 cyclopentene units are incorporated in the crystalline cell of polyethylene producing its enlargement, whereas 1,2 cyclopentene units are excluded from crystalline phase giving lowering of crystallinity.

Catalyst-based on titanium compound (1) was also able to copolymerize ethylene with *E* or *Z*-2-butene, producing copolymers having methyls placed on vicinal methines in *erythro* and *threo*



Scheme 2. Possible preinsertion intermediates for catalysts based on (1), (2), and (3) titanium complexes.

configuration, respectively. Moreover, 2-butene can give partial isomerization producing 1,3 or 1,2 inserted units.

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