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Linear low-density polyethylenes by co-polymerization of ethylene with 1-hexene in the presence of titanium precursors and organoaluminium co-catalysts

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Abstract

The co-polymerization of ethylene with 1-hexene has been performed with titanium precursors based on carboxylato ligands in the presence of organoaluminium compounds as activators to afford linear low-density polyethylenes (LLDPEs). The influence of the polymerization parameters was studied with particular reference to the type and amount of catalyst components, solvent, temperature, ethylene pressure, 1-hexene concentration. The chloro-substituted bis-carboxylato titanium complex resulted the most active precursor in the co-polymerization, allowing to obtain copolymers with modulable composition in the 1–5 mol% range of 1-hexene units. The obtained copolymers were characterized by thermal analysis, X-ray diffraction spectroscopy, FTIR and NMR techniques.

Keywords: Titanium(IV) bis-carboxylato precursors; Ethylene/1-hexene copolymers; Organoaluminium co-catalysts

1. Introduction

Ethylene/α-olefins copolymers, commercially known as linear low-density polyethylenes (LLDPEs), have received an increased attention in the recent years. Their commercial growth is expected to continue because polyolefins will displace other plastic materials which at present give some problems for recycling or waste disposal [1]. The main PE properties are in general affected by several structural and morphological parameters such as: nature, amount and distribution of the monomeric units derived from the higher α-olefin co-monomers, the extent of short and long chain branching as well as the average molecular weight of the macromolecules and its distribution. These in turn affect the crystallization degree, the melting temperature, the thermo-mechanical and optical properties of the resulting polymeric material [2]. Usually, the density of the material is a practical index for classifying these polymer characteristics [2]. Historically, the heterogeneous Ziegler/Natta multi-site catalysts have developed the polyolefins' industry. However, since the past two decades an extraordinary amount of research has been focused on the development of homogeneous, single-site catalysts (SSCs) for olefin polymerization [3–7]. In contrast to multi-site catalysts, the SSC systems offer the advantage to produce structurally homogeneous polyolefins in terms of narrow distributions of molecular weight and of a random insertion of the co-monomers in the backbone and hence of the branches.

However, the industry prefers to adopt processes characterized by a slurry or a gas–solid polymerization technology for the polyolefins production. Therefore, in the last years the research is going back to the study of new conventional Ziegler/Natta co-polymerization catalysts [8–13]. In this context, new catalytic systems based on titanium complexes with mono-carboxylato ligands, such as titanium(III)

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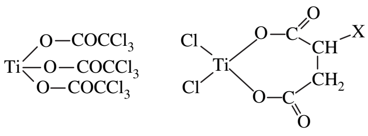

I **II** (X = H) **III** (X = Cl)

Chart 1.

tris(2,2,2-tri-chloroethanoato) (**I**) (Chart 1), combined with a reducing/chlorinating agent ($Et_3Al_2Cl_3$) and a trialkyl aluminium compound as co-catalyst, have been proposed for the co-polymerization of ethylene with higher α-olefins [14].

Therefore, the present article deals with homo- and co-polymerization of ethylene with 1-hexene in the presence of novel titanium catalytic systems based on bidentate chelate ligands, such as bis-carboxylates and chloro-substituted bis-carboxylates, when activated by $Et_3Al_2Cl_3$ and Al-^{i}Bu$_3$. In particular, titanium(IV)(dichloro)(1,4-butandionato) (**II**) and titanium(IV)(dichloro)(2-chloro-1,4-butandionato) (**III**) (Chart 1) will be employed as catalyst precursors for the co-polymerization of ethylene with 1-hexene.

The results, in terms of activity and characteristics of the resulting copolymers, will be compared with those obtained by **I**. Indeed, the presence of the chelate ligand would assure a more stability and rigidity to the complexes, favouring the formation of prevailing single-site catalysts, thus allowing to afford copolymers characterized by a narrower distribution of the molecular weights.

2. Experimental section

2.1. Materials

Manipulations of air-sensitive materials were carried out under dry argon atmosphere using Schlenk techniques. Toluene (Aldrich) and *n*-heptane (Aldrich) were refluxed over Na/K alloy and distilled under argon atmosphere. Chloroform (J. T. Baker) was dried on $CaCl_2$ and then distilled under dry argon. Ethylene and argon (≥99.9%, Rivoira) were used as received. 1-Hexene (Aldrich) was distilled under dry argon and stored in the refrigerator. 2,2,2-Trichloro-ethanoic acid (Aldrich), 1,4-butanedioic acid (Aldrich) and (*R*)(*S*)-2-chloro-1,4-butanedioic acid (Aldrich) were used as received. $TiCl_3$ (Aldrich) was used as received under dry atmosphere. $TiCl_4$ (Fluka) was used as received under dry argon and stored in the refrigerator. Ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, Aldrich), available in toluene solution (25 wt%), and tris-iso-butyl aluminium (Al-^{i}Bu$_3$) (Aldrich), available in *n*-hexane solution (1 M), were used as received under dry argon and stored in the refrigerator.

Titanium(III) tris(2,2,2-tri-chloroethanoato) ($Ti(OCOCCl_3)_3$) (**I**) was prepared in 54.3% yield from $TiCl_3$ and 2,2,2-trichloroethanoic acid as previously described [14]. The product was collected in sealed vials under dry argon.

^{13}C NMR (C_6D_6, δ, ppm): 163 (*C*OO), 90.4 (*C*Cl$_3$).

Fourier transform infrared spectroscopy (FTIR): $\nu_{as\ COO} = 1674\ cm^{-1}$; $\nu_{s\ COO} = 1395\ cm^{-1}$; $\nu_{C-Cl} = 740\ cm^{-1}$; mp = 100 °C.

Anal. Calcd for $C_6O_6Cl_9Ti$: C, 13.5; Cl, 59.6; O, 17.9; Ti, 8.9. Found: C, 13.9; O, 18.1; Cl, 59.2 (59.4 by Volhard titration); Ti, 8.5 (by SEM determination).

Titanium(IV)(dichloro)(1,4-butandionato) (**II**) was prepared in a 59% yield as previously reported [15], starting from 1,4-butanoic acid and $TiCl_4$ under dry argon. The product was stored in sealed glass vials under dry argon.

^{13}C NMR (DMSO-d_6, δ, ppm): 173.5 (*C*OO), 28.7 (*C*H$_2$).

^{1}H NMR (DMSO-d_6, δ, ppm): 3.33 (s, C*H*$_2$).

FTIR: $\nu_{as\ COO} = 1640\ cm^{-1}$; $\nu_{s\ COO} = 1436\ cm^{-1}$; mp = 190 °C.

Anal. Calcd for $C_4H_4O_4Cl_2Ti$: C, 20.5; H, 1.7; Cl, 30.2; O, 27.2; Ti, 20.4. Found: C, 20.9; O, 27.0; Cl, 29.6 (29.8 by Volhard titration); Ti, 20.9 (by SEM determination).

(*R*)(*S*)-Titanium(IV)(dichloro)(2-chloro-1,4-butandionato) (**III**) was synthesized for the first time adopting the following procedure: in a 1 l four-necked round-bottomed flask, equipped with a condenser, two dropping funnels and a thermometer, 5.1 g of 2-chloro-1,4-butanedioic acid (33.4 mmol) dissolved in 150 ml of $CHCl_3$ were introduced under dry argon. Then 3.67 ml of $TiCl_4$ (33.4 mmol) were added drop-wise while maintaining the temperature at 0 °C. After 30 min at 0 °C, the reaction mixture was heated for 24 h up to the boiling temperature of the solvent. After cooling at room temperature, the formed solid was filtered under dry argon, washed with anhydrous $CHCl_3$ and dried *in vacuo*. The pale yellow product obtained in an 83.3% yield was stored in sealed glass vials under dry argon. Several attempts to crystallize the product failed, thus enabling to obtain its structure by X-ray diffraction.

^{13}C NMR (DMSO-d_6, δ, ppm): 170.4 (*C*OO), 169.4 (CHCl—*C*OO); 64.1 (*C*HCl); 38.1 (*C*H$_2$).

^{1}H NMR (DMSO-d_6, δ, ppm): 4.6 (dd, C*H*Cl); 2.8 (d, C*H*$_2$).

FTIR: $\nu_{as\ COO} = 1532\ cm^{-1}$; $\nu_{s\ COO} = 1417\ cm^{-1}$; $\nu_{C-Cl} = 836\ cm^{-1}$; mp = 200 °C.

Anal. Calcd for $C_4H_3O_4Cl_3Ti$: C, 17.8; H, 1.1; Cl, 39.5; O, 23.8; Ti, 17.8. Found: C, 18.0; O, 23.5; Cl, 39.1; Ti 17.9 (by SEM determination).

The content of Cl bonded to Ti (calcd: 26.3) was confirmed by Volhard titration (found: 26.1).

2.2. Polymerization experiments

In a general procedure the titanium precursor was contacted for 30 min at room temperature in an Schlenk-type vessel under dry argon with $Et_3Al_2Cl_3$ in 10 ml of anhydrous toluene. Then Al-^{i}Bu$_3$, dissolved in 50 ml of anhydrous *n*-heptane, was added. When this catalytic system was used either in the homo- or in the co-polymerization of ethylene with 1-hexene under pressure, it was transferred into a 200 ml stainless-steel reactor under ethylene atmosphere. After the eventual addition of the proper amount of the comonomer, the reactor was closed, pressurized with ethylene up to the chosen pressure. Then, under magnetic stirring, the reaction mixture was maintained at the desired temperature by a thermo-stated oil-bath for the programmed time, manually charging ethylene during the polymerization experiment. In the co-polymerization experiments the composition of the feed was roughly evaluated by considering the amount of 1-hexene used and the starting amount of ethylene charged, taking into account its solubility in the reaction medium at the adopted ethylene pressure [16,17]. The polymerization was stopped by fast cooling of the reactor at 0 °C and slowly degassing the unreacted ethylene through a trap cooled at −15 °C to collect any eventually formed low oligomeric product. The reactor was opened and the reaction mixture (solid and liquid) was weighed; then a small amount of the liquid was collected with a syringe and analyzed by gas chromatography (GC) for determining the eventual presence of higher oligomers. The reaction product was poured into a large excess of methanol acidified with aqueous 5% HCl to completely precipitate the polymer and purify it from the catalyst residues. The crude polymer was filtered, washed with fresh methanol, dried *in vacuo*, weighed, and finally characterized. In the case of either 1-hexene homo-polymerization or in its co-polymerization with ethylene at 0.1 MPa pressure the experiments were carried out into a two-necked 250 ml round-bottomed flask where the catalytic system was directly prepared with the same procedure as previously described. The recovery of the crude polymer and its purification were performed according to the experimental approach above mentioned.

2.3. Physico-chemical measurements and analytical procedures

Intrinsic viscosity measurements on PE samples and on the ethylene/1-hexene (E/H) copolymers were performed with a Desreaux-Bischoff dilution viscometer in decalin solution at 135 °C. Taking into account the high content of ethylene co-units in the copolymers, the viscometric average molecular weight (M_v) was determined assuming valid the equation reported for PE under the above conditions [intrinsic viscosity ($[\eta]) = 2.3 \times 10^{-5} M_v^{0.82}$] [18].

In a limited number of PE and E/H copolymer samples the molecular weight and its distribution were determined at the Istituto Guido Donegani – EniTecnologie by SEC analysis at 135 °C performed in trichlorobenzene, with a Waters 150C chromatograph equipped with a refractive index detector. The universal calibration method was applied to evaluate molecular weights, by using narrow distribution poly(styrene) standards.

^{1}H NMR spectra were performed on a FT Varian Gemini 200 spectrometer at 200 MHz, by using tetramethylsilane (TMS) as an internal standard. The NMR spectra of E/H copolymers were performed in 1,2,4-trichlorobenzene at 140 °C, operating at 200 (^{1}H) and 50 (^{13}C) MHz, using 1,1,2,2-d_2-tetrachloroethane as an internal standard [19–21].

In a limited number of E/H copolymer samples the ^{13}C NMR determination of sequences' distribution was performed by using a Bruker AM-270 spectrometer working at 67.89 MHz on 1,1,2,2-d_2-tetrachloroethane solutions at 103 °C. Hexamethyldisiloxane was employed as an internal standard. The triads' determinations were accomplished according to the literature [22].

FTIR spectra were carried out on a Perkin–Elmer Spectrum One spectrophotometer equipped with an attenuated total reflectance apparatus. Data elaboration was performed by a Spectrum V 3.2 Perkin–Elmer program. In the case of E/H copolymers, the IR spectra were also performed on thin films obtained by die-casting at 170 °C through an Autoimage Perkin–Elmer Microscope combined with a Spectrum GX Perkin–Elmer spectrophotometer. The spectra have been registered in the 1400–1265 cm^{-1} region, where the bands typical of CH_3 bending (1380 cm^{-1}) and CH_2 wagging (1370 cm^{-1}) display absorption values which obey to the Lambert–Beer law [23–25]. The calibration curve was determined by using E/H copolymer standards of known composition as determined by ^{13}C NMR analysis, kindly supplied by Polimeri Europa, EniTecnologie S.p.A.

The thermal behaviour of polyethylene and E/H copolymers was examined with a Perkin–Elmer Pyris Diamond DSC at standard heating/cooling rate of 10 °C/min, under nitrogen flow. The samples were first melted to 180 °C (1st scan) and kept at this temperature for 3 min, then cooled to 50 °C and again heated up to the melting with the same heating rate (2nd scan). The reported melting temperature values are referred to the second heating scan. Temperatures and heats of phase transitions were determined, respectively, from the maxima and areas of the crystallization and melting peaks.

It is well known that the melting enthalpy (ΔH_m) of an E/α-olefin copolymer decreases with increasing the content of the comonomer [26], the insertion of the α-olefin reducing both the degree of crystallinity and the melting temperature of the copolymer [27,28]. Randall evidenced that for E/α-olefin copolymers including E/H copolymers the density of the sample decreases with increasing the comonomer content [29,30]. In this context, it was possible to relate ΔH_m (J/g) to the density (d, g/ml) of the copolymer through the following semi-empirical equation: $d = (2195 + \Delta H_m)/2500$ [31]. Finally, using standards of known composition, a linear correlation between sample density and its content in terms of 1-hexene co-units was found, at least in the 0.915–0.94 g/ml density range [31]. Therefore, this is a very simple method for evaluating the content of 1-hexene co-units from a DSC measurement in order to compare the results with those obtained from FTIR microscopy.

The degree of crystallinity X_c of PE and its copolymers was calculated from the ratio between the values of melting enthalpy, ΔH_m (as calculated from the second heating scan) and the heat of fusion of 100% crystalline PE taken as $\Delta H_m^0 = 293$ J/g [32].

The morphology of the polymeric samples was examined on the surfaces of samples freeze-fractured in liquid nitrogen; the samples were sputter-coated with a fine layer of gold in an Edward Sputter Coater and analyzed with Jeol T300 and JEOL JSM-5600LV electron scanning microscopes. Wide-angle X-ray diffraction (WAXD) analysis was carried out on a Siemens 810 apparatus working at 40 kV and 30 mA and using the Cu Kα radiation ($\lambda = 0.1546$ nm) in the 5°–40° 2θ range with a scanning step of 0.01° in the reflection geometry.

Gas chromatography (GC) for the analysis of oligomeric products was performed on a Series II Hewlett–Packard 5890, equipped with a HP 3396 integrator, as previously reported [33]. GC/mass spectrometry (MS) analysis was carried out employing a HP5973 Mass Selective Detector and a HP6890 Series GC system, equipped with a HP5-MS crosslinked 5% phenylmethylsiloxane column (30 m × 0.25 mm × 0.25 μm).

Elemental analysis was carried out at the EniTechnologies Laboratory (San Donato Milanese).

The content of titanium in the catalytic precursors has been determined by scanning electron microscopy (SEM) by a Jeol JFSM-5600LV apparatus, equipped with a microanalysis system EDS Oxford Inca Energy 400, which allows to obtain semi-quantitative analysis of the heavy metals directly on the solid sample [34,35].

The determination of the ionic Cl content in the catalytic titanium precursors was also performed by titration by the well known Volhard method [36–38].

3. Results and discussion

3.1. Ethylene homo-polymerization

A preliminary experiment (run 1, Table 1) was carried out by using **I** as catalytic precursor and adopting the best conditions claimed for ethylene/propylene co-polymerizations [14]. Because the ascertained catalytic activity was rather low, successively the reaction conditions were changed, in terms of ethylene pressure and duration, in order to verify how these parameters could affect the catalyst performances (runs 2–5, Table 1).

On the basis of the obtained results, the increase of ethylene pressure caused a remarkable improvement of the productivity up to 145 kg PE/mol Ti × h. When the duration was triplicated, the catalyst performances markedly improved in terms of productivity (compare run 3 with run 1), thus suggesting that the catalytic system is characterized by an induction period for the formation of the active sites.

When the catalytic system based on the bidentate **II** precursor was employed (runs 6–8, Table 1) a very low productivity was observed. Moreover, the prolongation of the reaction time, in contrast to what occurred for the precursor **I**, was detrimental in terms of productivity. This seems to suggest that, in the presence of the chelate ligand not containing a chlorine substituent, low activity catalytic sites are rapidly formed, but they are also characterized by a fast deactivation. However, the molecular weight of the resulting PE samples reaches high values ($M_v > 300{,}000$ Da) and it seems to be unaffected by the reaction conditions.

Finally, when the chloro-substituted chelate **III** was employed as catalytic precursor (runs 9 and 10, Table 1) a higher productivity was obtained in comparison with the catalysts based on **I** and **II** under similar reaction conditions (Fig. 1).

When a reference conventional catalyst, based on $TiCl_4$, was adopted (run A, Table 1) under the same conditions as in run 9 lower activity was ascertained to give a high molecular weight PE with a lower crystallinity degree (37%).

The **I**–**III** catalytic systems give rise to the formation of highly linear PE samples, as shown by their high T_m (~140 °C) and crystallinity degree (~50%), as determined by DSC measurements. FTIR spectra confirm the extreme linearity of all the PE samples. As an example the IR and DSC spectra of a PE sample, obtained by the catalyst based on **III** (run 9), are reported in Figs. 2 and 3, respectively.

It is noteworthy to mention that, although different reaction conditions were adopted, the polydispersity of the PE sample obtained in run 9 by using **III** as catalyst precursor, was significantly narrower than that of PE sample resulting from the **I** precursor (run 5). These results could suggest that the chelate

Table 1
Ethylene homo-polymerization by titanium carboxylato precursors (**I**–**III**) activated by $Et_3Al_2Cl_3$ and Al-$^iBu_3$[a]

Run	Titanium precursor type (μmol)	$P_{C_2H_4}$ (MPa)	Time (h)	PE (g)	P[b]	M_v[c]	PDI[d]	T_m[e] (°C)	d[f] (g/ml)	X_c[g] (%)
1	**I** (21)	1	1	0.35	16.7	83,000				
2	**I** (13)	1	1	0.28	21.5	45,000				
3	**I** (22)	1	3	1.40	23.3	243,000		137.4	0.94	48
4	**I** (26)	2	1	2.70	103.8	419,000				
5	**I** (20)	4	1	2.90	145.0	115,000	17.4			
6	**II** (48)	1	3	0.20	1.4	340,000		142.1	0.96	45
7	**II** (54)	2	1	0.20	4.0	303,000				
8	**II** (54)	2	6	0.20	0.6	320,000				
9	**III** (102)	1	5	24.3	47.7	194,000	4.3	134.7	0.94	51.5
10	**III** (55)	0.5	5	0.50	1.8	190,000				
A	**$TiCl_4$** (102)	1	5	3.70	7.2	443,000		134.4	0.92	37

[a] Reaction conditions: T – 30 °C; solvent – toluene (10 ml), n-heptane (50 ml); $Et_3Al_2Cl_3$/Ti – 3 mol/mol; Al-$^iBu_3$/Ti – 50 mol/mol.

[b] Productivity expressed as kg PE/mol Ti × h.

[c] Average viscometric molecular weight.

[d] Polydispersity index, evaluated as M_w/M_n, and determined by SEC analysis.

[e] Melting temperature determined by DSC analysis.

[f] PE density determined according to the equation: $d = (2195 + \Delta H_m)/2500$.

[g] Crystallinity degree determined according to the equation: $(\Delta H_m/\Delta H_m^0) \times 100$, assuming $\Delta H_m^0 = 293$ J/g.

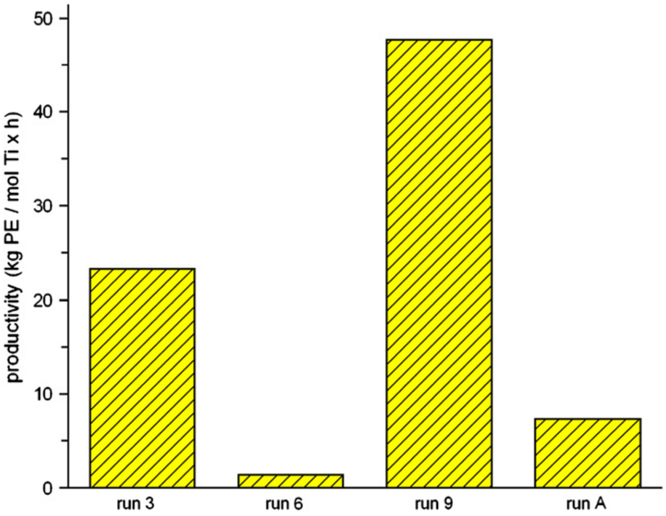

Fig. 1. Catalysts' productivity in ethylene homo-polymerization as a function of the type of titanium precursor.

ligand favours the formation of a more limited number of active sites with respect to monodentate ligands. On the other hand the presence of a chloro-substituent on the chelate ligand in **III** significantly improves the activity of the resulting catalyst, due to the increased electron deficiency of the metal centers which are more reactive toward ethylene coordination [39,40]. Although no evidence can be reported about the nature of the active sites, the clear influence of the steric and electronic characteristics of the chelate ligand on the catalyst performances suggests that this ligand remains in the coordination sphere of the metal.

3.2. Homo- and co-polymerization of 1-hexene with ethylene

1-Hexene homo-polymerization experiments, carried out under the same conditions as previously reported for ethylene ($T = 30\ ^\circ$C; solvent = toluene/n-heptane (10/50 ml); $Et_3Al_2Cl_3$/Ti = 3 mol/mol; Al-^{i}Bu$_3$/Ti = 50 mol/mol), gave, independently from the titanium precursor adopted (**I**–**III**), only traces of polymeric products, even prolonging the reaction time up to a week.

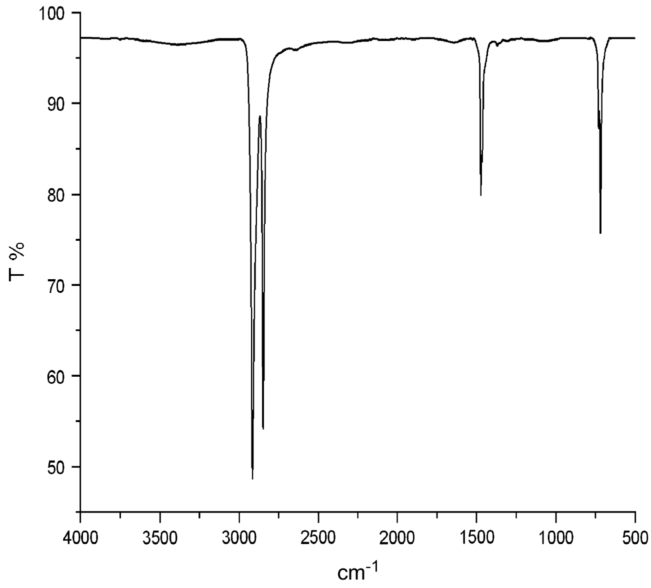

Fig. 2. IR spectrum of PE resulting from run 9.

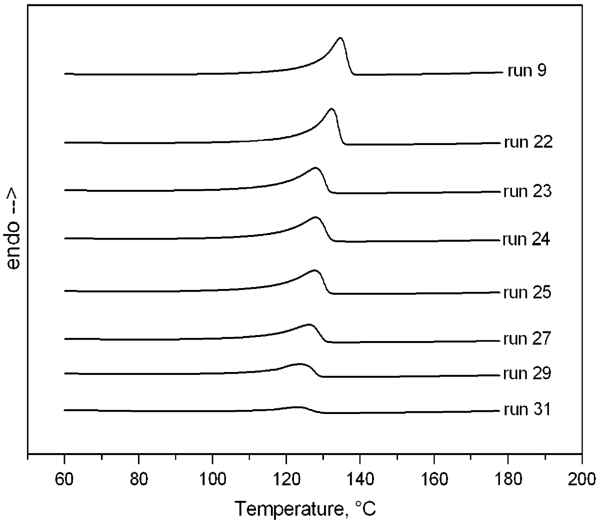

Fig. 3. DSC traces of PE (run 9) and E/H copolymers with an increasing content of 1-hexene co-units (runs 22–31).

When **I** was employed for ethylene/1-hexene co-polymerization under similar conditions (run 11, Table 2), as those adopted for ethylene homo-polymerization (run 3, Table 1) but in the presence of 1-hexene (concentration in the feed: 52 mol%), only traces of polymeric product were obtained. However, when the experiment was repeated (run 12, Table 2) with a reaction time of 24 h a high molecular weight (M_v = 187,000 Da) polymeric product with 1 mol% of 1-hexene co-units was obtained, although the productivity of the process was much lower than in the case of ethylene homo-polymerization. When **I** was replaced by **II** and a higher concentration of catalyst was adopted together with a prolonged reaction time (24 h) (runs 15 and 16, Table 2) polymeric products with similar characteristics in terms of density and composition as in run 12 were obtained. The higher T_m ($\sim$140 °C) suggests that an even more linear polymeric product was obtained in these cases. A further increase of the relative amount of 1-hexene (run 17, Table 2) reduced the productivity and the polymer molecular weight, without improving the content of 1-hexene co-units. The attempt to increase this last by reducing the ethylene pressure (run 18, Table 2) failed, the only effect being a reduction of the molecular weight and of T_m. The very low catalytic activity and mainly the scarce modulation of the polymer characteristics as a function of the reaction parameters forced us to abandon **II** as precursor. When **III** was adopted as catalyst precursor, under analogous reaction conditions as those used in run 11 (run 19, Table 2), a much higher productivity was obtained (P = 20.9), the resulting crude polymeric product containing 1 mol% of 1-hexene units. The increase of the relative amount of 1-hexene in the feed (run 20, Table 2) allowed to slightly improve the content of 1-hexene units in the obtained polymer (1.5 mol%). However,

Table 2
Ethylene/1-hexene co-polymerization by titanium carboxylato precursors (**I**–**III**) activated by $Et_3Al_2Cl_3$ and Al-^{i}Bu$_3$[a]

Run	Ti precursor type (μmol)	Feed		Time (h)	Crude polymer							P[b]
		$P_{C_2H_4}$ (MPa)	H ml (mol%)		(g)	H[c] (mol%)	M_v[d] ($\times 10^{-3}$)	PDI[e]	T_m[f] (°C)	d[g] (g/ml)	X_c[h] (%)	
11	**I** (43)	1	5 (52)	5	Traces							
12	**I** (23)	1	5 (52)	24	1.17	1	187	2.0	130.7	0.97		2.6
13	**I** (28)	0.1	5 (93)	5	Traces							
14	**I** (36)	0.1	7.5 (94)	5	Traces							
15	**II** (67)	1	5 (52)	24	2.00	1	68		138.6	0.97		1.2
16	**II** (86)	1	7.5 (62)	24	1.17	1	382		141.8	0.96		0.6
17	**II** (59)	1	10 (68)	24	0.14	1	169		140.9	0.96		0.1
18	**II** (53)	0.5	7.5 (77)	24	0.5	1	117		131.0	0.97		0.4
19	**III** (99)	1	5 (52)	5	10.3	1	382		133.0	0.96		20.9
20	**III** (50)	1	10 (68)	5	1.41	1.5	283		131.5	0.97		5.6
21[i]	**III** (76)	0.5	7.5 (84)	5	7.30	1	230		133.0	0.96		19.1
22[i]	**III** (79)	0.5	10 (92)	5	7.20	1	267		132.3	0.97	41.0	18.3
23[i]	**III** (82)	0.5	20 (93)	5	6.5	1.5	30		127.9	0.94	36.8	15.9
24[i]	**III** (100)	0.5	30 (94)	5	4.4	2	35	2.8	127.9	0.95	37.1	8.8
25[i,j]	**III** (78)	0.5	20 (92)	5	3.6	2	28		127.8	0.94	37.1	9.2
26[i,j]	**III** (78)	0.5	30 (93)	5	3.2	2	27		129.1	0.94		8.2
27[i]	**III** (67)	0.1	7.5 (94)	5	0.54	2.5	400		126.2	0.92	33.4	1.6
28[i]	**III** (112)	0.1	10 (95)	5	1.60	3.5	220	15.1	125.5	0.92		2.9
29[i]	**III** (91)	0.1	15 (96)	5	0.5	3.5	194		123.8	0.92	23.9	1.1
30[i]	**III** (89)	0.1	20 (97)	5	0.67	3.5	135.5		124.6	0.92		1.5
31[i]	**III** (116)	0.1	30 (98)	5	1.45	5	28	17	123.4	0.91	9.1	1.8
B[i]	**$TiCl_4$** (116)	0.1	30 (98)	5	4.74	40.2[k]	1.460[l]	22	Amorphous			8.2

[a] $T = 30$ °C, if not otherwise specified; solvent: toluene/n-heptane (10/50 ml), if not otherwise specified; $Et_3Al_2Cl_3$/Ti: 3 mol/mol; Al-^{i}Bu$_3$/Ti: 50 mol/mol.
[b] Productivity expressed as kg copolymer/mol Ti × h.
[c] Content of 1-hexene co-units in the copolymer, as determined by FTIR microscopy and DSC measurements (both methods give substantially the same results).
[d] Average viscometric molecular weight.
[e] Polydispersity index, evaluated as M_w/M_n, and determined by SEC analysis.
[f] Melting temperature determined by DSC analysis.
[g] Copolymer density determined according to the semi-empirical equation: $d = (2195 + \Delta H_m)/2500$.
[h] Crystallinity degree determined according to the equation: $(\Delta H_m/\Delta H_m^0) \times 100$, assuming $\Delta H_m^0 = 293$ J/g.
[i] Solvent: toluene (10 ml).
[j] $T = 50$ °C.
[k] Determined at 80 °C by ^{1}H NMR in 1,1,2,2-d_2-tetrachloroethane.
[l] M_w as determined by SEC analysis.

the increase of 1-hexene concentration in the feed caused a drop of productivity ($P = 5.6$), although it remained higher than in all the experiments performed with **I** and **II** precursors. When toluene alone was used as solvent and in minor amount (10 ml) with respect to the toluene/n-heptane mixture (60 ml), thus allowing to increase the concentration of 1-hexene in the

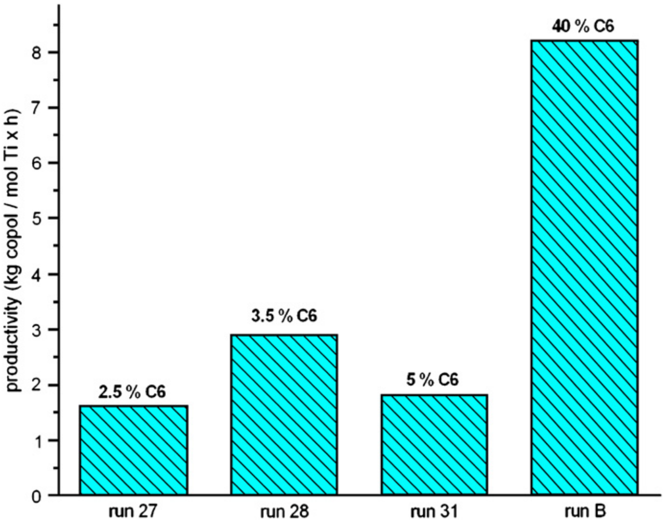

Fig. 4. Catalysts' productivity in ethylene/1-hexene co-polymerization as a function of the type of the titanium precursor.

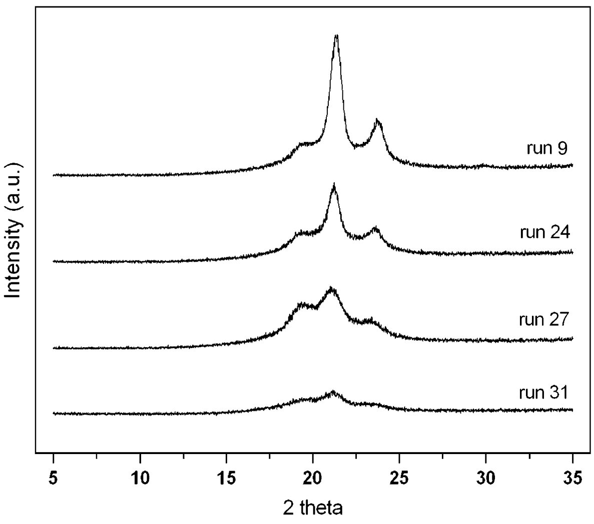

Fig. 5. X-ray diffraction spectra of PE (run 9) and E/H copolymers with an increasing content of 1-hexene co-units (runs 24–31).

Table 3
Diads' and triads' distributions for E/H copolymers obtained by catalysts based on **III** precursor, as determined by ^{13}C NMR analysis

Run	H (mol%)	Dyads (%)			Triads (%)					
		HH	HE	EE	HHH	HHE	EHE	HEH	EEH	EEE
24	1.6[a]	0.00	3.09	96.91	0.00	0.00	2.34	0.00	3.24	94.42
27	2.3[a]	0.00	4.52	95.48	0.00	0.00	2.92	0.00	3.84	93.24
31	5.5[a]	Traces	11.00	89.00	0.00	1.31	4.28	1.05	8.56	84.79

[a] Determined by ^{13}C NMR analysis.

feed (runs 21 and 22, Table 2), analogous productivities as in run 19 were obtained, notwithstanding a lower ethylene pressure (0.5 MPa). A further increase of 1-hexene concentration in the feed (runs 23 and 24, Table 2) allowed to reach in the polymer samples a 2 mol% of 1-hexene units together with lower density and T_m values, without a marked reduction of the productivity. On the other hand, a dramatic reduction of the molecular weight was ascertained. The reduction of ethylene pressure (0.1 MPa) in the presence of a progressive increase of 1-hexene concentration (runs 27–31, Table 2) made possible to modulate the content of 1-hexene units in the polymers up to 5 mol%, although with a significant decrease of the productivity (Fig. 4).

The polymeric products were characterized by rather high molecular weight, which dropped only in the case of the polymer containing 5 mol% of 1-hexene units. When run 31 was repeated for comparison, employing a conventional catalyst based on $TiCl_4$ (run B, Table 2), a completely different behaviour was ascertained. Indeed, a rubbery amorphous polymeric product very rich in 1-hexene units (>40%) and characterized by a broad polydispersity was obtained. These results suggest a very high affinity toward 1-hexene with respect to the catalyst based on the chelate **III** precursor.

It is worth noting that the molecular weight polydispersity increases with increasing the content of 1-hexene in the LLDPE, thus suggesting that the insertion of higher α-olefin co-monomers favours transfer and termination reactions. Moreover, the degree of crystallinity of the copolymer samples, as determined by thermal measurements, substantially showed a monotonic decrease with increasing the content of 1-hexene co-units and at the same time a progressive decrease of T_m, at least in the 1–5 mol% range (Fig. 3).

Accordingly, X-ray diffraction spectra showed, going from PE to E/H copolymers with an increasing content of H co-units, a progressive decrease of the peaks' intensity (Fig. 5).

These above results indicate that, when **III** is adopted as catalyst precursor, it is possible to modulate the characteristics of the resulting LLDPE samples.

Preliminary experiments on ^{13}C NMR determination of the sequences' distribution of the two co-units along the backbone are reported in Table 3.

It is interesting to underline that the composition of the examined copolymers, as determined by NMR analysis, is in a substantial agreement with that obtained by FTIR and DSC analyses. Moreover, as expected on the basis of the compositions, only isolated H co-units were practically ascertained, thus confirming that the obtained polymers are really copolymers.

4. Conclusions

In this article we have reported the use of titanium(IV) precursors **II** and **III**, based on bidentate carboxylato ligands, in the homo- and co-polymerization of ethylene and 1-hexene, in the presence of organoaluminium co-catalysts. Precursor **III** based catalytic systems are much more active than those derived from **II** to afford LLDPE with modulable composition (1–5 mol% of H co-units) as a function of the adopted reaction conditions. The main characteristics of the E/H copolymers (density, melting point and crystallinity degree) are dependent on the functionalization extent. The ^{13}C NMR analysis of selected polymeric products has allowed to conclude that these LLDPE samples are really copolymers where isolated H units are inserted in long ethylene sequences. Further optimization of the reaction parameters, in terms of both type and relative amounts of organoaluminium co-catalysts with respect to **III**, is in due course.

Finally, work is also in progress on a full thermal and structural characterizations of the copolymers.

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