

Titanium ketimide complexes as α -olefin homo- and copolymerisation catalysts. X-ray diffraction structures of $[\text{TiCp}'(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ ($\text{Cp}' = \text{Ind}, \text{Cp}^*$)

Alberto R. Dias, M. Teresa Duarte, Anabela C. Fernandes, Susete Fernandes, Maria M. Marques*, Ana M. Martins*, João F. da Silva, Sandra S. Rodrigues

Complexo I, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

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Abstract

The synthesis of $[\text{TiInd}(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ and the applications of $[\text{TiCp}'(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ ($\text{Cp}' = \text{Ind}, \text{Cp}^*, \text{Cp}$) as ethylene and propylene homopolymerisation catalysts, as well as its behaviour as catalysts of ethylene and 10-undecen-1-ol copolymerisation are described. The optimisation of the catalytic reactions showed that all compounds are very active homopolymerisation catalysts, particularly $[\text{TiInd}(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ that gives $123.37 \times 10^6 \text{ g}/(\text{molTi} [\text{E}] \text{ h})$ and $50.77 \times 10^6 \text{ g}/(\text{molTi} [\text{P}] \text{ h})$ of linear polyethylene and atactic polypropylene, respectively. The less active homopolymerisation catalyst, $[\text{TiCp}(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$, is the most effective ethylene/10-undecen-1-ol copolymerisation catalyst, leading to the highest degree of polar monomer incorporation. The polymers obtained were characterised by NMR and DSC. The molecular structures of $[\text{TiCp}'(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ ($\text{Cp}' = \text{Ind}, \text{Cp}^*$) were determined by X-ray diffraction studies.

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1. Introduction

Despite the vast developments in the field of olefin homo- and copolymerisation, the research in this area remains extremely active. The syntheses of new polymers and copolymers as well as the control of polymers stereochemistry are challenging problems that require not only a deep knowledge of the polymerisation reactions but also an expansion to new catalyst systems [1–5]. The post-metallocene period, initiated with constrained geometry catalysts [6], led to the extension of olefin polymerisation catalysts to diverse support ligands and metals with variable degrees of performance [7]. Among these, half-sandwich Group 4 ketimide complexes of general type $[\text{MCp}(\text{N}=\text{CR}_2)\text{Cl}_2]$ recently emerged as a new family of olefin polymerisation catalysts. Patents claiming the use of such compounds as catalysts for the

syntheses of ethylene–olefin and olefin–vinyl aromatic copolymers have been published [8–10]. Similar systems, where phosphinimides ($\text{N}=\text{PR}_3$) [11,12] and sterically protected η^1 -guanidinate type ligands ($\text{N}=\text{C}(\text{NR}_2)_2$) [13] were used as ancillary ligands also exhibit remarkable activities as ethylene polymerisation catalysts.

The work here presented focus on the behaviour of $[\text{TiCp}'(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ complexes ($\text{Cp}' = \text{C}_9\text{H}_7, \text{C}_5\text{Me}_5, \text{C}_5\text{H}_5$) as catalysts for ethylene and propylene polymerisation as well as ethylene–10-undecen-1-ol copolymerisation. The polymers obtained have been characterised by NMR and DSC.

2. Results and discussion

2.1. Syntheses and characterisation

The compounds $[\text{TiInd}(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ (**1**); $[\text{TiCp}^*(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ (**2**) and $[\text{TiCp}(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ (**3**) were prepared

* Corresponding authors. Tel.: +351218419172; fax: +351218464457.
E-mail address: ana.martins@ist.utl.pt (A.M. Martins).

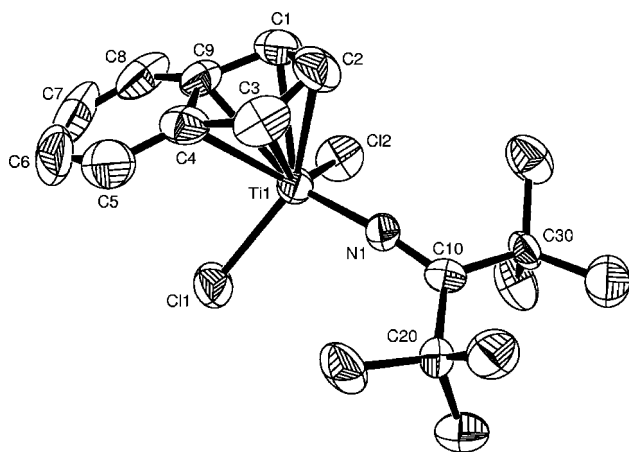


Fig. 1. Molecular structure of $[\text{Ti}(\eta^5\text{-Ind})(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ (**1**) (thermal ellipsoids at 40% probability level).

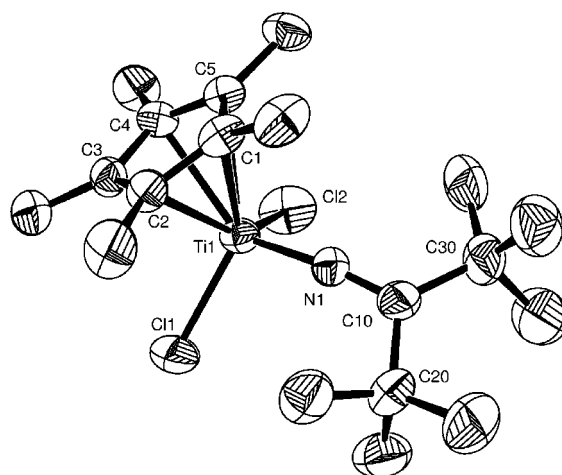


Fig. 2. Molecular structure of $[\text{Ti}(\eta^5\text{-Cp}^*)(\text{N}=\text{C}'\text{Bu}_2)\text{Cl}_2]$ (**2**) (thermal ellipsoids at 40% probability level).

Table 1
Selected bond lengths (Å) and angles (°) for **1** and **2**

	$[\text{TiInd}(\text{NC}'\text{Bu}_2)\text{Cl}_2]$		$[\text{TiCp}^*(\text{NC}'\text{Bu}_2)\text{Cl}_2]$
	1	1A	2
Ti(1)–N(1)	1.814(7)	1.826(7)	1.844(7)
Ti(1)–Cl(1)	2.255(4)	2.275(5)	2.299(3)
Ti(1)–Cl(2)	2.295(3)	2.280(3)	2.286(2)
Ti(1)–C(1)	2.336(10)	2.330(11)	2.385(8)
Ti(1)–C(2)	2.347(11)	2.313(11)	2.361(8)
Ti(1)–C(3)	2.325(11)	2.350(12)	2.382(8)
Ti(1)–C(4)	2.416(11)	2.424(10)	2.370(8)
Ti(1)–C(5)	–	–	2.371(8)
Ti(1)–C(9)	2.391(10)	2.406(10)	–
C(1)–C(2)	1.391(15)	1.391(15)	1.441(12)
C(2)–C(3)	1.383(17)	1.370(19)	1.433(11)
C(3)–C(4)	1.441(15)	1.397(15)	1.422(10)
C(4)–C(5)	1.381(18)	1.437(18)	1.388(12)
C(4)–C(9)	1.396(15)	1.420(14)	–
C(5)–C(6)	1.30(2)	1.32(2)	–
C(6)–C(7)	1.41(2)	1.38(2)	–
C(7)–C(8)	1.34(2)	1.31(2)	–
C(8)–C(9)	1.424(15)	1.409(16)	–
C(1)–C(9)	1.396(16)	1.419(17)	–
N(1)–C(10)	1.271(10)	1.262(10)	1.266(11)
C(10)–C(20)	1.546(14)	1.539(14)	1.576(13)
C(10)–C(30)	1.565(13)	1.545(14)	1.535(13)
N(1)–Ti(1)–Cl(1)	105.4(3)	104.0(3)	104.0(2)
N(1)–Ti(1)–Cl(2)	101.9(3)	102.6(3)	105.6(2)
Cl(1)–Ti(1)–Cl(2)	100.86(14)	100.59(14)	100.44(13)
C(10)–N(1)–Ti(1)	167.6(6)	166.1(6)	166.4(7)
N(1)–C(10)–C(20)	119.0(9)	117.6(9)	116.5(8)
N(1)–C(10)–C(30)	117.1(9)	117.6(9)	121.1(9)
C(20)–C(10)–C(30)	123.7(8)	124.8(8)	122.3(8)
(Cp')*–Ti(1)–N(1)	114.4(9)	114.5(9)	111.9(9)
(Cp')*–Ti(1)–Cl(1)	116.1(9)	116.4(9)	116.8(9)
(Cp')*–Ti(1)–Cl(2)	116.6(9)	116.4(9)	116.6(9)
Cl(1)–Ti(1)–N(1)–C(10)	52(4)	59(3)	56(3)
Cl(2)–Ti(1)–N(1)–C(10)	–53(4)	–45(3)	–50(3)
Ti(1)–N(1)–C(10)–C(20)	–92(4)	–101(3)	–84(3)
Ti(1)–N(1)–C(10)–C(30)	83(4)	77(3)	92(3)

by metathetical reactions of the corresponding [TiCp'₃Cl₃] (Cp' = C₉H₇, C₅Me₅, C₅H₅), with LiNC^tBu₂. This methodology has been reported before for the syntheses of **2** and **3** [14] and is detailed here for **1**. The NMR spectra of all complexes show the expected resonances for the *tert*-butyl and Cp' groups according to C_s symmetry. The quaternary carbons of the ketimide ligands appear at very low fields (δ 204.4 in **1**, 202.7 in **2** and 204.1 in **3**).

The molecular structures of complexes **1** (Fig. 1) and **2** (Fig. 2) have been determined by X-ray diffraction. Selected bond lengths and angles for both compounds are listed in Table 1.

Both complexes adopt piano-stool coordination geometries, with the angles (Cp')*-Ti-X larger than the X-Ti-X angles ((Cp')* represent the centroids of the aromatic rings and X denote chlorine and ketimide ligands). The bond distances between the titanium and the Cp' and Cl ligands in **1** and **2** are consistent with values observed in titanium (IV) complexes. The angles Ti-N-C (167.6(6)° for **1** and 166.4(7)° for **2**) are close to linearity due to the sp character of the nitrogen atom and together with the Ti-N bond lengths attest for the multiple nature of the titanium-nitrogen bonds. In fact, the dihedral angles defined between the least-square planes of Cp' and the Ti(1)-N(1)-C(10) planes (81.9(9)° in **1** and 85.5(9)° in **2**) also reflect the positioning of the ligand to allow the maximum overlap between the available titanium π -acceptor and nitrogen π -donor orbitals [15]. The metrical parameters registered for the ketimide ligands are similar to that found in other titanium ketimide complexes [16,17].

2.2. Polymerisation results

The titanium complexes **1–3** were examined as catalyst precursors in the polymerisation of ethylene and propylene as well as in the copolymerisation of ethylene with 10-undecen-1-ol.

2.2.1. Homopolymerisation of ethylene and propylene

The results obtained in the polymerisation of ethylene by using, as catalyst systems, the titanium complexes **1–3** activated by methylaluminoxane (MAO) are shown in Tables 2 and 3. The results in Table 2 show that a maximum activity is observed at 60 °C for all three systems. At 80 °C a reduction in the activity is observed. This reduction in the activity for temperatures higher than 60 °C may be due either to the effect of the temperature on the olefin coordination step or to some decomposition of the active species.

The activity of the systems **1**/MAO and **2**/MAO seems to be affected by the concentration of the catalyst precursor reaching a maximum for the lowest catalyst concentration studied [Ti] = 5 μ M (runs 115 and S3 in

Table 2
Homopolymerisation of ethylene catalysed by Ti systems. Effect of the temperature reaction on the polymerisation activity

Run No.	Catalyst	[E] (M)	T _p (°C)	Yield (g)	Activity $\times 10^3$ kg/(molTi [E] h)
112	LindTiCl ₂ (1)	0.44	0	0.46	4.17
113		0.37	21	0.38	40.95
111		0.31	40	0.45	68.52
115		0.24	60	0.87	123.37
114		0.17	80	0.45	90.76
93	LCp*TiCl ₂ (2)	0.43	1	0.06	0.19
99		0.37	20	0.14	1.33
12		0.31	40	0.30	2.63
91		0.24	60	1.68	24.15
94		0.18	78	1.00	7.33
117	LCpTiCl ₂ (3)	0.44	0	0.03	0.63
118		0.36	24	0.05	1.22
116		0.31	40	0.35	11.65
120		0.24	60	0.91	29.55
119		0.17	79	0.29	14.86

Experimental conditions: V = 50 ml toluene; cocatalyst MAO; P_E = 15 psi; Al/Ti = 2000; (**1**) [LindTiCl₂] = 5 μ M, t_p = 6 min; (**2**) [LCp*TiCl₂] = 70 μ M except for runs 93 and 94 for which [LCp*TiCl₂] = 160 μ M, t_p = 7 min; (**3**) [LCpTiCl₂] = 20 μ M, t_p = 6 min.

Table 3
Homopolymerisation of ethylene catalysed by Ti systems. Effect of catalyst concentration on the polymerisation activity

Run No.	Catalyst	[Ti] (μ M)	Yield (g)	Activity $\times 10^3$ kg/(molTi [E] h)
115	LindTiCl ₂ (1)	5	0.87	123.37
22		10	0.85	99.80
21		20	0.93	29.08
19 ^a		74	1.18	19.69
18 ^a		150	2.71	21.89
S3	LCp*TiCl ₂ (2)	5	0.42	80.09
95		20	0.87	18.42
92		35	0.94	19.45
91 ^a		70	1.68	24.15
11 ^a		140	3.60	10.20
S1	LCpTiCl ₂ (3)	5	0.12	21.68
69		20	0.93	22.56
66		40	0.92	13.87
65		80	0.74	8.96
5 ^a		170	2.48	8.23

Experimental conditions: V = 50 ml toluene; cocatalyst MAO; Al/Ti = 2000; T_p = 60 °C; [E] = 0.24–0.25 M; (**1**) t_p = 6 min; (**2**) t_p = 8 min; (**3**) t_p = 8 min.

^a Diffusion problems.

Table 3). However, for titanium concentrations higher than 20 μ M, the activity does not show any significant variation with the increase of the catalyst concentration in the range studied. The decrease observed for some runs are due to mass transport limitations resulting from high polymer concentrations inside the reactor. In the case of the system **3**/MAO the activity decreases slightly with the increase of catalyst concentration but

Table 4
Thermal properties of PE samples obtained with the Ti catalyst systems

Run No.	Catalyst	T_p (°C)	First heating run				Second heating run			
			T_{max}^f (°C)	T_{ons} (°C)	$\Delta T, T_f - T_i$	ΔH_f (J/g)	T_{max}^f (°C)	T_{ons} (°C)	$\Delta T, T_f - T_i$	ΔH_f (J/g)
77 ^a	LIndTiCl ₂ (1)	20	142.7	126.7	28.3	221.4	132.4	105.7	38.7	159.4
23 ^b		60	143.8	129.3	28.2	205.3	145.4	125.4	31.9	161.5
99 ^c	LCp*TiCl ₂ (2)	20	133.7	119.4	25.6	191.6	129.6	114.9	26.4	162.7
91 ^c		60	131.0	122.6	15.5	195.5	129.4	122.1	14.2	178.2
73 ^d	LCpTiCl ₂ (3)	20	140.1	124.0	30.4	206.6	133.3	123.7	26.9	190.1
69 ^e		60	137.0	123.1	31.3	199.4	133.5	124.5	17.4	176.5

Experimental conditions: $V = 50$ ml toluene; cocatalyst MAO; $P_E = 15$ psi; $t_p = 5$ – 10 min; Al/Ti = 2000.

^a [Ti] = 20 μ M.

^b [Ti] = 5 μ M.

^c [Ti] = 70 μ M.

^d [Ti] = 82 μ M.

^e [Ti] = 20 μ M.

^f The peak value of the melting endotherm (ideally taken as the temperature at which the largest and most perfect crystals are melting) is frequently assigned as the melting temperature, i.e., $T_m \equiv T_{max}$. The relative values of T_{ons} and T_{max} give an approximate idea of the melting range [45].

only for titanium concentrations higher than 20 μ M; the same activity is observed for titanium concentrations of 5 and 20 μ M (runs S1 and 69 in Table 3). The results in Table 3 also show that the catalyst system **1**/MAO is the most active one followed by the system **2**/MAO. In fact, the activity of **1**/MAO is about six times higher and the activity of **2**/MAO is about four times higher than that of the system **3**/MAO, which is the poorest catalyst system. Since it is widely accepted, based on both experimental [18–21] and theoretical studies [22–25], that the active species in transition-metal-catalysed polymerisation reactions is a metallic cation, this order of reactivity is very likely explained by the different ability of the ligands to stabilise the cationic active species (indenyl > Cp* > Cp). The increase in the activity observed when a Cp or Cp* ligand is substituted by the indenyl one has been reported in the literature for several catalyst systems [26–29]. However, the higher activity of the Cp* system as compared to the Cp one observed in our systems is not in agreement with other experimental results reported in the literature where, due to stereochemical constraints, the activities of the complexes bearing a Cp* ligand are usually lower than those of the Cp analogues [27]. Taking into consideration that the activity of an olefin polymerisation system depends (i) on the acidic properties of the metal centre, (ii) on the stabilisation of the cationic active species and (iii) on the stereochemical properties of the support ligand set, our data suggest that the stability of the cationic species is the governing factor of the catalyst reactivity when Cp* and Cp systems are compared, since the better electron donor ligand gives the better catalyst.

Compounds **1**–**3** display higher activities than the ketimide titanium complex [TiCp (NC^tBu)₂(CH₂Ph)₂] that, when activated by B(C₆F₅)₃ and $P_E = 5$ bar ([E] =

0.5899 M), show an activity in ethylene polymerisation at 80 °C ($A = 5.4 \times 10^5$ g/molTi h bar), one order of magnitude lower than that obtained for complex **3** activated by MAO at 60 °C [14]. The complex **3** shows an activity similar to that of the constrained geometry catalyst CGC ($A = 11.3$ kg/molTi h [E]) [30] and the other two, **1** and **2**, display activities one order of magnitude higher.

All the polymers obtained are linear polyethylenes. The ¹³C NMR spectra of the samples show only one peak at 30ppm.

The thermal properties of the polymers are shown in Table 4. T_{ons} and T_{max} represent the onset and maximum temperatures of the melting peaks, respectively, and ΔH_f is the enthalpy of fusion. The results show that the crystallisation is more effective when performed from solution (1st heating run) than from the melt (2nd heating run), in spite of the low cooling rate used. The melting temperatures and enthalpies of fusion of the polyethylenes, prepared with different catalyst systems, are very close to each other, showing degrees of crystallinity ranging from 67% to 77%,¹ if the 1st heating run is considered. These values of crystallinity are characteristic of high-density polyethylene. The polymers obtained with the system **1**/MAO have a T_m and a ΔH_f slightly higher than the others. Thus, the indenyl ligand not only confers higher activity to the catalyst system but also induces higher crystallinity in the polymers obtained. In contrast, comparison of samples subjected to similar thermal histories (2nd heating run)

¹ The degree of crystallinity was determined by using the expression: D.C. = $\frac{\Delta H_f}{\Delta H_f^0} \times 100\%$, where ΔH_f is the fusion enthalpy of the polyethylene sample and ΔH_f^0 is the fusion enthalpy of a 100% crystalline polyethylene sample. $\Delta H_f^0 = 285.98$ J/g according to B. Wunderlich and Cromier, J. Polym. Sci. A-2 5 (1967) 987.

reveals that the system **1**/MAO has the lowest degree of crystallinity (56%) and the largest melting range, ΔT , defined as the difference between the endset and the onset of melting. This decrease in crystallinity suggests the presence of a high molecular weight polymer. The observed reduction in crystallinity is also associated with a large melting range and melting point depression, which is characteristic of a broad mixture of morphological units.

The differences observed in the thermal properties of polymers obtained with the same catalyst, but at a different temperature, are not significant, except for the system **1**/MAO. The melting point depression observed in the 2nd heating run, for a polymerisation temperature, T_p , of 20 °C, is not observed when $T_p = 60$ °C. This result is in accordance with the usual observation that a higher T_p does not favour the growth of polymer chains. The topological constraints that caused the decrease in crystallinity and in the melting point, when $T_p = 20$ °C, are not present at $T_p = 60$ °C.

Complexes **1–3** activated by MAO were also studied in the polymerisation of propylene (Table 5). Again, the most active system was shown to be the system **1**/MAO. However, complex **3** that was the poorest catalyst precursor in the polymerisation of ethylene now shows better activities at 0 and 20 °C than the precursor **2**. The order of activities observed in the polymerisation of propylene for these systems, **1** > **3** > **2**, is the same as that reported for the zirconocene ones [31]. This differ-

ent behaviour in the polymerisation of ethylene and propylene observed for complex **2** is probably due to a higher steric hindrance to the approach of propylene caused by the Cp* ligand and in such case the catalyst activity is ruled by stereochemical factors.

The temperature, although at different extents, affects the activity of all the systems in the polymerisation of propylene. No polymer could be obtained at 60 °C no matter which catalyst system was used and the best activities are observed either at 0 or 20 °C. The drop in the activity observed for the system **1**/MAO with the increase of the temperature is much less severe than that observed for the other two systems. In fact, while at $T_p = 40$ °C the activity is zero in the case of the system **3**/MAO, and only a reduction of around 15% is observed (compared to the highest value observed at $T_p = 0$ °C) in the case of the system **1**/MAO. The reduction in the activity with the increase of temperature in the range 0–40 °C is around 85% for the system **2**/MAO.

The activity of the systems **1**/MAO and **3**/MAO increases with the Al/Ti ratio up to 1000 and 1500, respectively. Above these values the activity remains constant. The activity of the system **2**/MAO seems not to be affected by the Al/Ti ratio in the range studied (250–2000). All the polymers obtained showed to be atactic polypropylene. Fig. 3 shows a typical ^{13}C NMR spectrum of the polymers obtained with these catalyst systems.

Table 5

Homopolymerisation of propylene catalysed by Ti systems. Effect of T_p and Al/Ti ratio on the polymerisation activity

Run No.	Catalyst	[P] (M)	Al/Ti	T_p (°C)	Yield (g)	Activity $\times 10^3$ kg/(molTi [P] h)
79	LindTiCl ₂ (1)	0.98	2000	0	1.98	50.77
26		0.70	2000	20	1.47	43.82
25		0.44	2000	40	0.78	42.64
28		0.22	2000	60	0	–
33		0.70	400	20	0.84	23.6
32		0.70	1000	20	1.59	44.7
80		0.70	4000	20	1.71	41.6
83 ^(a)		LCp*TiCl ₂ (2)	0.93	1000	0	0.22
82 ^(a)	0.70		1000	20	0.10	0.78
85 ^(a)	0.45		1000	40	0.02	0.16
81 ^(a)	0.22		1000	60	0	–
89 ^(b)	0.70		250	20	0.26	0.94
88 ^(b)	0.70		500	20	0.23	0.84
90 ^(b)	0.70		2000	20	0.23	0.73
54	LcpTiCl ₂ (3)	0.89	800	0	1.88	8.08
55		0.67	800	20	1.82	10.42
53		0.44	800	40	0	–
57		0.20	800	60	0	–
61		0.67	400	20	1.07	9.09
60		0.67	1500	20	1.78	19.16
62		0.67	3000	20	1.92	17.79

Experimental conditions: $V = 50$ ml toluene; cocatalyst MAO; (**1**) [LindTiCl₂] = 10 μM , $t_p = 6$ min. (**2**) ^(a)[LCp*TiCl₂] = 35 μM ; ^(b)[LCp*TiCl₂] = 69 μM , $t_p = 7$ min; (**3**) [LcpTiCl₂] = 29 μM , $t_p = 7$ min.

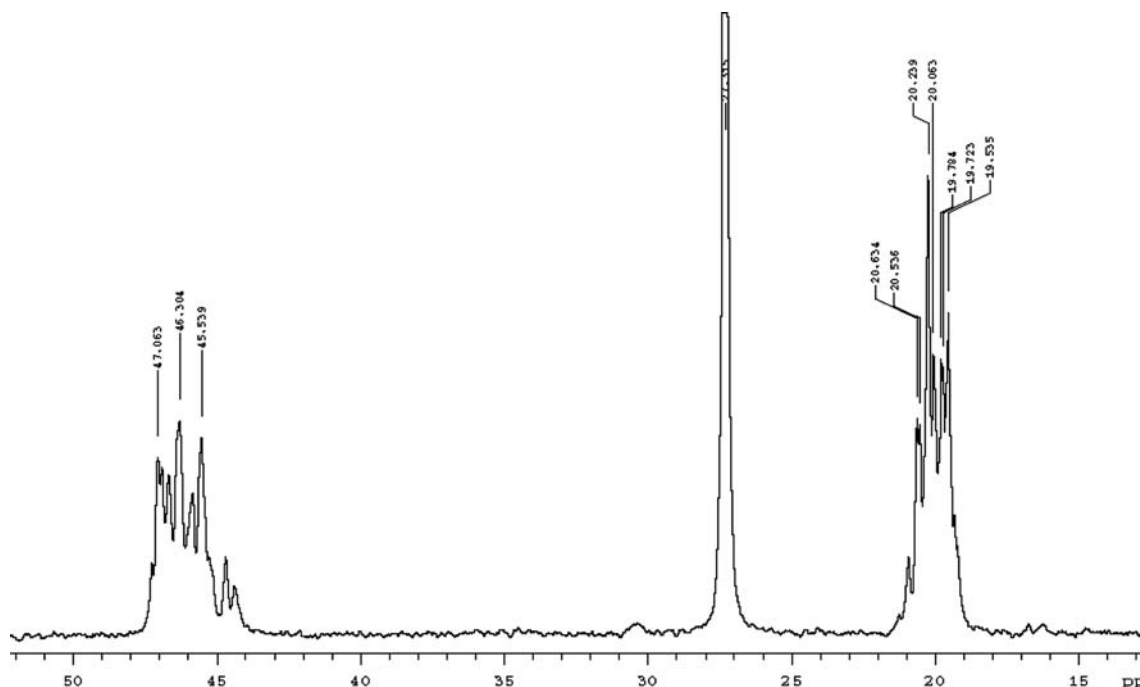


Fig. 3. Typical ^{13}C NMR spectrum of atactic polypropylene. Catalyst system $\text{LIndTiCl}_2/\text{MAO}$; $T_p = 20^\circ\text{C}$ (run #26).

2.2.2. Copolymerisation of Ethylene with 10-undecen-1-ol (U)

The three titanium complexes **1–3** were used as catalyst precursors in copolymerisation reactions of ethylene with a polar comonomer. The comonomer studied in these reactions was a α,ω -unsaturated alcohol, namely the 10-undecen-1-ol (U). Following a methodology developed previously [32,33] the polar comonomer was protected by an alkylaluminium in the reaction medium and MAO was used as cocatalyst. All the attempts made in order to obtain homopolyundecenol using the titanium systems **1–3**/MAO failed. No polymer

could be obtained when only 10-undecen-1-ol was used as monomer. However, the results in Table 6 show that all the three catalyst precursors **1–3** are able to incorporate the polar comonomer in the polyethylene chain. As expected, the catalyst system **3**/MAO leads to copolymers with the highest polar monomer incorporation levels while the system **1**/MAO leads to the lowest levels of polar monomer incorporation. In fact, the rate of polymerisation of the polar monomer is expected to be much lower than that of the ethylene and the closer the two rates are, the higher the level of incorporation of the comonomer will be. Thus, the least active system in

Table 6
Copolymerisation of ethylene with 10-undecen-1-ol (U) catalysed by Ti systems

Run No.	Catalyst	[U] (mM)	Yield (g)	Activity $\times 10^3$ kg/(molTi [E] h)	Polymer OH (mol%)
77	LIndTiCl_2 (1)	–	1.33	34.97	–
74		50	1.82	4.79	0.7
75		100	1.10	2.90	2.0
76		200	0.39	1.03	4.8
99	$\text{LCp}^*\text{TiCl}_2$ (2)	–	0.14	1.33	–
96		50	0.67	0.53	1.8
97		100	0.59	0.47	3.5
98		200	0.02	0.02	6.2
73	LCpTiCl_2 (3)	–	0.43	2.93	–
70		50	2.86	1.95	1.6
71		100	1.15	0.78	4.7
72		200	0.51	0.35	9.5

Experimental conditions: $V = 50$ ml toluene; $T_p = \text{RT}$; $t_p = 1$ h, except for runs 73, 77 and 99 for which $t_p = 6$ min; $\text{Al/Ti} = 2000$; U was treated with TMA (1/1) in situ; $[\text{E}] = 0.360.37$ M; $[\text{LCpTiCl}_2] = 82$ μM ; $[\text{LCp}^*\text{TiCl}_2] = 69$ μM ; $[\text{LIndTiCl}_2] = 21$ μM .

the polymerisation of ethylene will be the best one regarding the copolymerisation reaction, i.e., will lead to the highest comonomer incorporation and the most active one will lead to the lowest incorporation levels.

Although the polar comonomer was protected by an alkylaluminium, its presence in the reaction medium lowers the activity of the systems. The decrease in the

activity is much higher in the case of the most active system **1**/MAO, around 7 times for a comonomer concentration in the feed of 50mM, than it is in the case of the other two less active systems **2**/MAO and **3**/MAO which show decreases in the activity of 2.5 and 1.5, respectively, for the same comonomer concentration. Further increase of the polar monomer concentration in

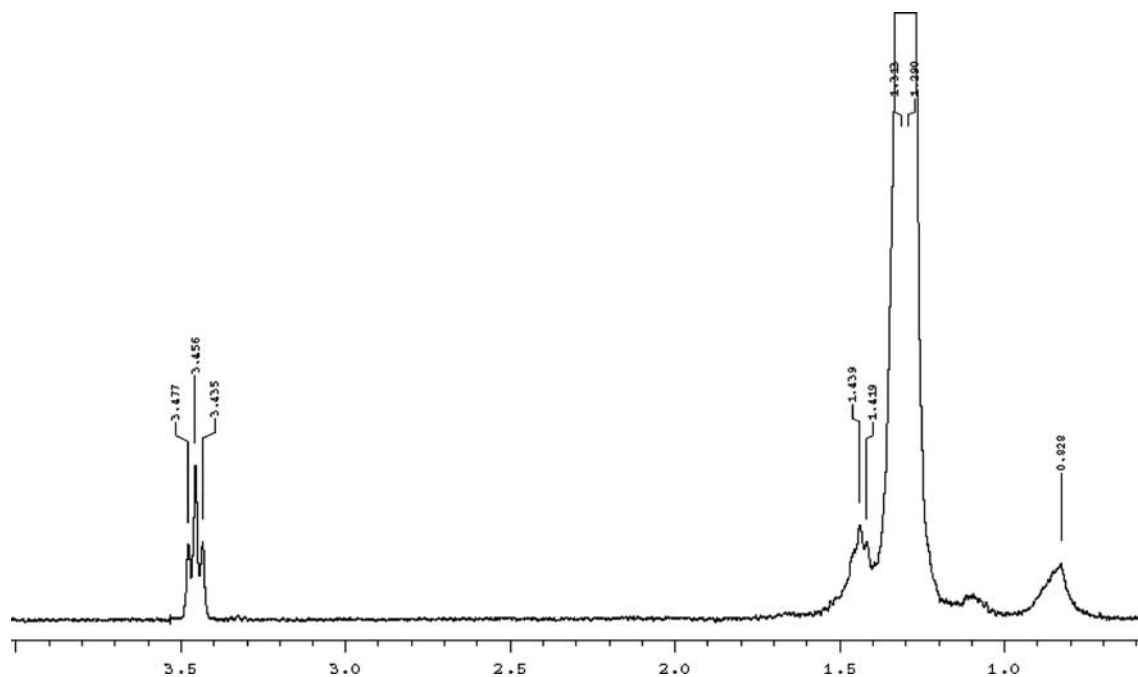


Fig. 4. Typical ^1H NMR spectrum of ethylene/10-undecen-1-ol copolymer. Catalyst system $\text{LCp}^*\text{TiCl}_2/\text{MAO}$; $[\text{U}] = 200 \mu\text{M}$; $T_p = 20^\circ\text{C}$ (runs #98).

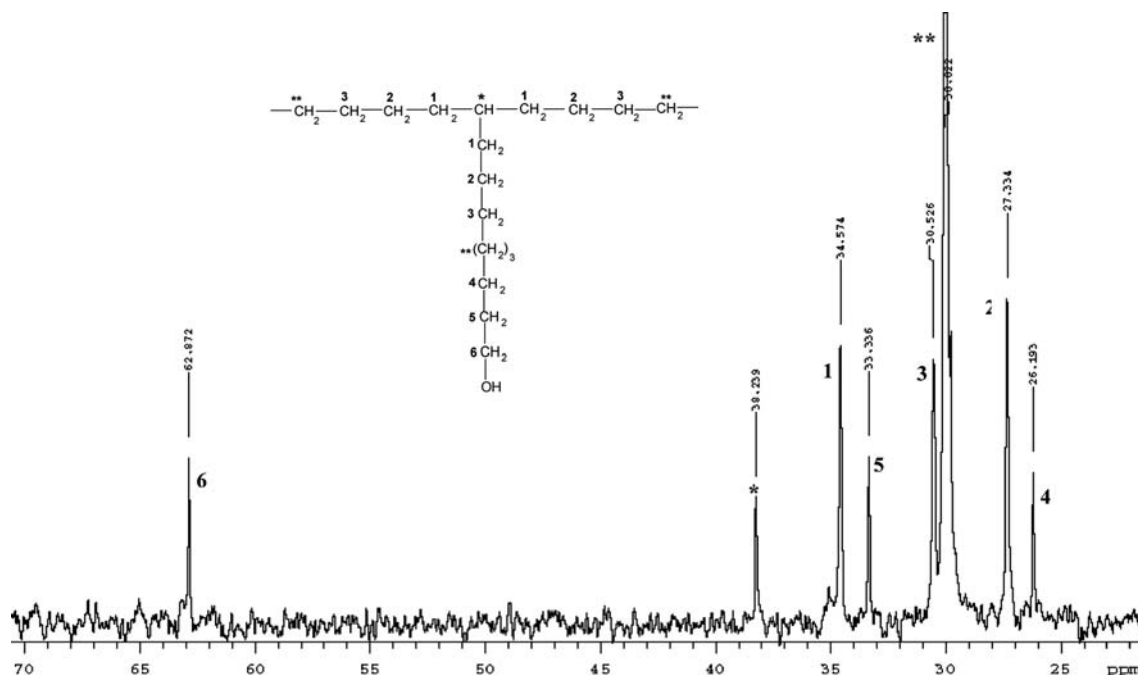


Fig. 5. Typical ^{13}C NMR spectrum of ethylene/10-undecen-1-ol copolymer. Catalyst system $\text{LCp}^*\text{TiCl}_2/\text{MAO}$; $[\text{U}] = 200 \mu\text{M}$; $T_p = 20^\circ\text{C}$ (runs #98).

Table 7
Thermal properties of E/U copolymers obtained with the Ti catalyst systems

Run No.	Catalyst	[U] (mM)	First heating run				Second heating run			
			T_{\max} (°C)	T_{ons} (°C)	ΔT , $T_f - T_i$	ΔH_f (J/g)	T_{\max} (°C)	T_{ons} (°C)	ΔT , $T_f - T_i$	ΔH_f (J/g)
74	LindTiCl ₂ (1)	50	131.6	117.6	60.6 ^a	157.4	120.3	104.2	28.3	89.6
75		100	117.7	106.1	58.1 ^a	137.9	111.7	76.8	50.7	79.7
76		200	103.3	81.6	34.0	86.2	145.4	74.3	38.8	58.2
96	LCp*TiCl ₂ (2)	50	120.2	102.3	46.3 ^a	138.9	114.4	89.9	35.7	86.1
97		100	104.4	85.5	44.5 ^a	94.4	97.3	65.3	47.2	35.7
98		200	75.0	63.8	22.5	Nd	122.7	107.5	26.9	10.8
			127.5	119.1	16.5	22.6				
70	LCpTiCl ₂ (3)	50	125.4	107.9	56.0 ^a	132.4	120.0	92.6	41.8	84.8
71		100	110.8	95.2	34.8	86.7	104.6	83.9	42.3	64.8
72		200	85.6	76.3	21.8	Nd	115.4	107.0	14.9	3.18
			118.1	112.7	12.0	5.9				

Experimental conditions are those of Table 6; nd, not determined.

^aShoulder.

the feed leads to a decrease in the activity in a much smoother way. The comonomer incorporation level in the polymers increases almost linearly with the comonomer concentration in the feed for all the three catalyst systems studied. The copolymers were characterised by ¹H and ¹³C NMR spectroscopy and by DSC. ¹H NMR spectroscopy was used to determine the amount of comonomer incorporated in the polymer. Fig. 4 shows a typical ¹H NMR spectrum of these copolymers. The ¹³C NMR spectrum in Fig. 5 shows that true random copolymers were obtained. The assignment of the peaks was done according to Aaltonen et al. [34,35]. The resonance of the tertiary carbon (*) appears at 38.25 ppm and those of the secondary carbons $\alpha(1)$, $\beta(2)$ and $\gamma(3)$ show up at 34.57, 27.33 and 30.52 ppm, respectively. The signal at 62.97 ppm refers to the carbon bonded to the OH group (6) and those at 26.19 and 33.33 ppm refer to carbons labelled numbers 4 and 5, respectively (Fig. 5). The main resonance at 30.02 ppm is due to the secondary carbons (***) far from any branch or polar group ($S\delta$, $\delta+$).

The results of DSC analysis are shown in Table 7. The copolymers E/U obtained with the titanium systems show generally lower melting temperatures and fusion enthalpies than the homopolymers of ethylene. This is the expected result since the presence of the polar comonomer introduces some disorder in the polymer chains. In fact, the higher the comonomer incorporation, the lower the fusion enthalpy is. It should be mentioned that, for high comonomer concentrations, two separate peaks are observed in the first heating run, at temperatures lower and close to the melting temperature of PE. However, we do not believe that a mixture of PE and comonomer E/U has been obtained. Instead, we think that two copolymer fractions with different morphological units, showing different degrees of crystallinity, are present. This assumption is based on two

observations. First, in the second heating run the two peaks overlap and only one peak is observed. Secondly, no PE could be isolated by solvent extraction of the product of the reaction.

3. Conclusions

The titanium complexes **1–3** activated by MAO show quite high activities in the polymerisation of ethylene ($A = 10^7\text{--}10^8$ g/molTi [E] h) and propylene ($A = 10^6\text{--}10^7$ g/molTi [E] h). All the systems give rise to linear polyethylenes and atactic polypropylenes. The DSC results of the polyethylene samples show typical melting temperatures of high-density polyethylene. The systems **1–3**/MAO show also good ability to promote copolymerisation reactions of ethylene with unsaturated alcohols. These reactions could be achieved with quite good activities ($A = 10^5\text{--}10^6$ g/molTi [E] h) and comonomer incorporation levels ($\text{OH}_{\text{in polymer}} = 1\text{--}10\%$). These results are similar to those obtained with the systems [(Ind)₂ZrCl₂/MAO [32,34,35] and [Cp*Si(Me)₂N-*t*-Bu]TiCl₂/MAO [32] and slightly better than those obtained with the system (Benzind)₂ZrCl₂/MAO [32]. The thermal properties of the copolymers show that the polar comonomer incorporated in the chain causes, as expected, a decrease in the crystallinity of the polymers.

4. Experimental

4.1. General procedures

All manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk techniques. Literature methods were used to prepare [TiIndCl₃] [36], [TiCp*Cl₃] [37], [TiCpCl₃] [38], [TiCp*(NC^{*t*}Bu₂)Cl₂], [TiCp(NC^{*t*}Bu₂)Cl₂] [14], and LiNC^{*t*}Bu₂ [39], 10-unde-

cen-1-ol (U) and trimethylaluminum (TMA) were purchased from Aldrich. The polar monomer was used without any previous purification except degassing. Methylaluminoxane (MAO) was supplied by Akzo Chemical Co. Ethylene and propylene were supplied by Ar Liquido and passed over molecular sieves before used in polymerisation. NMR spectra were recorded on a Varian Unity 300 instrument at room temperature and referenced to the residual proton and carbon resonances of the solvents (^1H , δ 7.15 (C_6D_6), 7.24 (CDCl_3); ^{13}C δ 128.0 (C_6D_6), 77.0 (CDCl_3)). Mass spectra were recorded on a Finnegan MAT System 8200 spectrometer and elemental analyses were performed on a Fisons Instruments 1108 device.

[TiInd(NC'Bu₂)Cl₂] (**1**). A solution of LiNC'Bu₂ (0.51 g, 3.45 mmol) in toluene (20 ml) was added dropwise, at -50°C , to a solution of [TiIndCl₃] (0.93 g, 3.45 mmol) in the same solvent (30 ml). The temperature was allowed to rise to room temperature while stirring overnight. The precipitate of LiCl was filtered-off and the solution was concentrated to half of its volume. Cooling to -20°C gave dark red crystals of **1** that were separated by filtration (1.08 g, 96% yield). ^1H NMR (C_6D_6): δ 7.30 (m, $^3J_{\text{H}_5\text{H}_6} = 6.6$, $^4J_{\text{H}_5\text{H}_7} = 2.7$, 2H, H₅, H₈), 6.90 (m, $^3J_{\text{H}_6\text{H}_5} = 6.6$, $^4J_{\text{H}_6\text{H}_8} = 2.7$, 2H, H₆, H₇), 6.48 (d, $^3J_{\text{H}_1\text{H}_2} = 3.3$, 2H, H₁, H₃), 6.42 (t, $^3J_{\text{H}_2\text{H}_1} = 3.3$ Hz, 1H, H₂), 1.00 (s, 18H, NC{C(H₃)₃}₂). ^{13}C - ^1H

NMR (C_6D_6): δ 204.4 (N(C'Bu₂), 127.2 (C₄, C₉), 127.2 (C₆, C₇), 125.8 (C₅, C₈), 119.3 (C₂), 109.1 (C₁, C₃), 47.2 (NC{C(CH₃)₃}₂), 30.2 (NC{C(CH₃)₃}₂). MS (EI, m/z): 373 (M⁺), 338 ({M-Cl}⁺), 316 ({M-'Bu}⁺), 281 ({M-'Bu-Cl}⁺), 233 ({Ti(C₉H₇)Cl₂}⁺), 198 ({Ti(C₉H₇)Cl}⁺), 115 ({C₉H₇}⁺). Anal. Calc. for C₁₈H₂₅Cl₂NTi: C, 57.77; H, 6.73; N, 3.74. Found: C, 57.82; H, 6.76; N, 3.66%.

4.2. Crystal structure determination of compounds **1** and **2**

Crystallographic and experimental details of the crystal structure determinations are given in Table 8. Suitable crystals of complexes **1** and **2** were mounted on a MACH3 Nonius diffractometer equipped with Mo radiation ($\lambda = 0.71069 \text{ \AA}$) and on a TURBO CAD4 with a Cu rotating anode ($\lambda = 1.54180 \text{ \AA}$), respectively. Data were collected at room temperature. Solution and refinement were made using SIR97 [40] and SHELXL [41] included in the package of programs WINGX-Version 1.64.03b [42]. For both complexes all nonhydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealised positions riding in the parent C atom. Complex **1** crystallises in a noncentrosymmetrical space group, $P2_1$, with two molecules which have a pseudo-centrosymmetrical relationship. Refinement was tried in both $P2_1/m$, $P2_1/c$ and other centrosymmetrical groups (like $C2/c$) but refinement always

Table 8
Crystal data and structure refinement details for **1** and **2**

Compound	1	2
Empirical formula	C ₃₆ H ₅₀ Cl ₄ N ₂ Ti ₂	C ₁₉ H ₃₃ Cl ₂ NTi
Formula weight	748.38	394.26
Temperature	293(2) K	293(2) K
Wavelength	0.71069 Å	1.54180 Å
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$Pbc21$
Unit cell dimensions	$a = 6.515(3) \text{ \AA}$, $b = 27.591(6) \text{ \AA}$, $c = 10.431(3) \text{ \AA}$ $\beta = 90.22(3) \text{ deg}$	$a = 9.354(1) \text{ \AA}$, $b = 16.630(2) \text{ \AA}$, $c = 13.865(4) \text{ \AA}$
Volume	1875.0(11) Å ³	2156.8(7) Å ³
Z	2 (2 molecules)	4
Calculated density	1.326 Mg/m ³	1.214 Mg/m ³
Absorption coefficient	0.738 mm ⁻¹	5.616 mm ⁻¹
$F(000)$	784	840
Crystal size	1.4 × 0.1 × 0.1 mm	1.2 × 0.1 × 0.1 mm
Crystal morphology	Needle	Needle
Colour	Dark red	Orange
θ range for data collection	1.95°–26.96°	4.73°–66.91°
Limiting indices	$-8 \leq h \leq 0$, $0 \leq k \leq 35$, $-13 \leq l \leq 13$	$0 \leq h \leq 11$; $-19 \leq k \leq 0$; $-16 \leq l \leq 15$
Reflections collected/unique	4518/4161 [$R_{\text{int}} = 0.0662$]	3762/3762 [$R_{\text{int}} = 0.0000$]
Completeness to theta	99.7% ($\theta = 26.96$)	100.0% ($\theta = 66.91$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4161/1/398	3762/1/209
Goodness-of-fit on F^2	0.950	1.002
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0679$, $wR2 = 0.1157$	$R1 = 0.0867$, $wR2 = 0.2045$
R indices (all data)	$R1 = 0.1650$, $wR2 = 0.1397$	$R1 = 0.1241$, $wR2 = 0.2398$
Absolute structure parameter	0.18(8)	0.00(2)
Extinction coefficient	0.0009(5)	0.0004(3)
Largest diff. peak and hole	0.335 and $-0.399 \text{ e \AA}^{-3}$	0.384 and $-0.460 \text{ e \AA}^{-3}$

resulted in higher R values and a residual electron density of about $5\text{--}6\text{ e \AA}^{-3}$. Due to the low β -value, refinement was tried in orthorhombic space group $P2_12_12_1$ and the same residual electron density was always found.

The molecular structures were made with ORTEP3 [43]. Data were deposited in CCDC under the deposit numbers 215,719 for **1** and 215,720 for **2**.

4.3. Polymerisation studies

The polymerisation apparatus and polymer work up were described in previous papers [32,33,44]. The polymerisation mixture was quenched with acidic methanol (1% HCl) and the precipitated polymer was filtered, washed with methanol and dried in a vacuum oven at $60\text{ }^\circ\text{C}$ during three days.

^1H NMR and ^{13}C NMR spectra were obtained on samples dissolved in either a mixture of 1,3,5-trichlorobenzene with 30% C_6D_6 at $110\text{ }^\circ\text{C}$ (the spectra were referenced internally using hexamethyldisiloxane δ_{H} 0.058, δ_{C} 1.9 relative to tetramethylsilane, TMS) or CDCl_3 at room temperature. The amount of α -olefin (U) incorporated in copolymers was determined by ^1H NMR.

A differential scanning calorimeter, DSC121 from Setaram, was used to determine the thermal properties of the polymers. In order to minimise the differences in the thermal history of the samples, the polymers were subjected to a heating/cooling/heating cycle, between 30 and $200\text{ }^\circ\text{C}$ using a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ and a cooling rate less than $10\text{ }^\circ\text{C}/\text{min}$. After the first heating scan the samples remained at $200\text{ }^\circ\text{C}$ for 10 min. The results obtained in the first and second heating runs were registered and are presented. During the experiments the sample holder was continuously purged with argon.

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