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Original Citation:

Ultrahigh-Molecular-Weight Polyethylene by Using a Titanium Calix[4]arene Complex with High Thermal Stability under Polymerization Conditions / M. FREDIANI; D. SEMERIL; A. COMUCCI; L. BETTUCCI; P. FREDIANI; L. ROSI; D. MATT; L. TOUPET; W. KAMINSKY. - In: MACROMOLECULAR CHEMISTRY AND PHYSICS. - ISSN 1022-1352. - STAMPA. - 208:(2007), pp. 938-945. [10.1002/macp.200700075]

Availability:

The webpage <https://hdl.handle.net/2158/208983> of the repository was last updated on 2019-07-05T11:53:32Z

Published version:

DOI: 10.1002/macp.200700075

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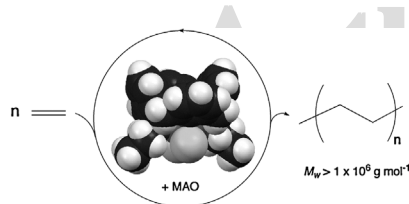
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macp.200700075C

Full Paper

 **Activation of [calix[4]arene-(O₂)-(OPrⁿ)₂]-TiCl₂ with methylalumoxane results in an efficient ethylene polymerization catalyst** suitable for the production of UHMWPE. The catalytic system displays remarkable high thermal stability due to the presence of two coordinating propyloxy side groups.



Ultrahigh-Molecular-Weight Polyethylene by Using a Titanium Calix[4]arene Complex with High Thermal Stability under Polymerization Conditions

M. Frediani,* D. Sémeril,* A. Comucci,
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Macromol. Chem. Phys. **2007**, *208*, 938–945

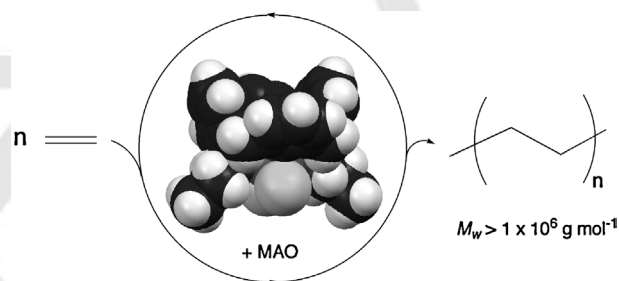

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macp.200700075

Ultrahigh-Molecular-Weight Polyethylene by Using a Titanium Calix[4]arene Complex with High Thermal Stability under Polymerization Conditions^a

Marco Frediani,* David Sémeril,* Alessandro Comucci, Lorenzo Bettucci, Piero Frediani, Luca Rosi, Dominique Matt, Loïc Toupet, Walter Kaminsky

The new complex 25,27-dipropoxy-26,28-dioxocalix[4]arene titanium (IV) dichloride (**1**) was evaluated as an ethylene polymerization catalyst. Activation with methylalumoxane resulted in an active system producing ultrahigh-molecular-weight polyethylene. As expected for a Ziegler-Natta catalyst, the polymerization reaction follows first-order kinetics. The most striking feature of the catalytic system (**1**/MAO) is its remarkably high thermal stability. This peculiarity probably relies on the electronic stabilization of the metal center by the two coordinating propoxy groups.



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^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mcp-journal.de>, or from the author.

Introduction

The design and synthesis of molecular complexes suitable for efficient Ziegler-Natta polymerization still constitutes an important challenge in both industrial and academic research. In this respect, the choice of the catalyst's first coordination sphere is critical for tuning the catalytic properties of the complex and notably for controlling the features of the outcoming polymer.

Most soluble Ziegler-Natta catalysts are very sensitive to high reaction temperatures and this represents a drawback for possible industrial applications. This defect is usually attributed to deactivation reactions, which lead to both a decrease in activity and a loss of selectivity. The molecular weight of polyethylene obtained with $[\text{Cp}_2\text{ZrCl}_2]$, for example, drops from 600 000 to 120 000 when the reaction temperature is raised from 20 to 70 °C.^[1,2]

Recently, several research groups have shown that various complexes of calixarenes and group IV or VI metals are able to promote the polymerization of α -olefins.^[3–5] Calixarenes are macrocyclic molecules consisting of phenol units linked via methylene bridges at the ortho positions of the phenol rings. They have found many applications in molecular and supramolecular chemistry, but surprisingly few studies have focused on the use of well defined calixarene complexes in ethylene polymerization.^[6]

The calix[4]arenes, i.e., those calixarenes containing four phenolic units, have several well-defined conformations but, in the so-called “cone”, they provide an O₄ donor-atom set able to function towards transition metals, in particular early transition metals, like a small oxo surface.^[7,8] In the present work we describe a complex derived from such a ligand, namely cone-25,27-dipropoxy-26,28-dioxocalix[4]arene titanium (IV) dichloride **1** (Figure 1), together with its catalytic properties in ethylene polymerization. A related complex has previously been reported, independently, by Floriani et al.^[9a] and by Radius et al.^[9b]

Experimental Part

General

All manipulations were carried out under a dry argon atmosphere using standard Schlenk tube techniques. The solvents were dried and distilled before use. Argon (99.998%) and ethylene (99.95%) were purchased by Air Liquide and used as received. 25,27-Dipropoxy-26,28-dihydroxycalix[4]arene was prepared according to a method reported in the literature.^[10] Solid methylaluminoxane (MAO) was obtained by removing toluene and AlMe₃ under vacuum at 50 °C from a commercially available toluene solution (10 wt.-% aluminum, Crompton GmbH). The resulting residue was heated further at 50 °C under vacuum overnight. A stock solution of MAO (100 mg · mL⁻¹) was prepared

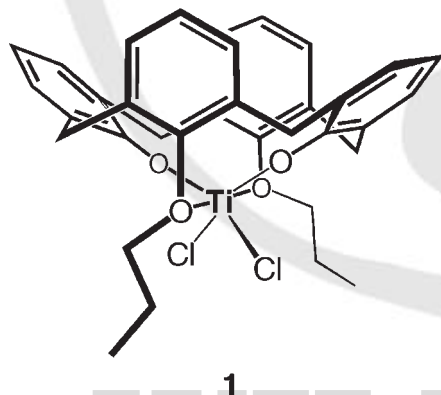


Figure 1. 25,27-Dipropoxy-26,28-dioxocalix[4]arene titanium (IV) dichloride. ■ Author: Figures were renumbered. Please check for consistency ■.

by dissolving the white solid in toluene. The solution was used within three weeks to avoid self-condensation effects of MAO. The ¹H and ¹³C NMR spectra were recorded on a Bruker Ultrashield 400 MHz instrument (400.0 MHz for ¹H and 100.6 MHz for ¹³C) and on a Varian Mercury 400 apparatus operating at 100 MHz in Fourier-transform mode at 298 K. ¹H NMR spectra were referenced to residual protonated solvents (7.26 ppm for CDCl₃ and 7.15 ppm for C₆D₆); ¹³C chemical shifts are reported relative to deuterated solvents (77.0 ppm for CDCl₃ and 128.0 ppm for C₆D₆).

Synthesis of the Titanium Complex 1

To a solution of 25,27-dipropoxy-26,28-dihydroxycalix[4]arene (1.000 g, 1.96 mmol) in toluene (100 mL) was added dropwise at room temperature a 1 M solution of TiCl₄ in CH₂Cl₂ (2.16 mmol, 1.1 equiv., 2.16 mL). The red solution was heated at 60 °C during 48 h, before being concentrated to ca. 15 mL. Addition of hexane (100 mL) afforded complex **1** as a red precipitate, which was filtered off and dried under vacuum. Yield: 1.030 g (84%).

¹H NMR (C₆D₆): δ = 6.96 (d, 4H, *m*-ArH, ³J = 7.3 Hz), 6.82 (dd, 2H, *p*-ArH, ³J = 7.6 Hz, ³J = 7.6 Hz), 6.53 (d, 4H, *m*-ArH, ³J = 7.6 Hz), 6.20 (t, 2H, *p*-ArH, ³J = 7.3 Hz), 4.85 (pseudo t, 4H, OCH₂, ³J = 8.6 Hz), 4.61 and 3.02 (AB spin system, 8H, ArCH₂Ar, ²J(AB) = 13.2 Hz), 1.88–1.78 (m, 4H, CH₂CH₃), 0.33 (t, 6H, CH₂CH₃, ³J = 7.4 Hz).

¹³C{¹H} NMR (CDCl₃): δ = 166.85 (s, C_qOTi), 157.43 (s, C_qOPr), 132.79–121.73 (arom. C's), 87.16 (s, OCH₂), 34.10 (s, ArCH₂Ar), 21.34 (CH₂CH₃), 9.07 (s, CH₂CH₃).

(C₃₄H₃₄O₄TiCl₂ · 0.25 toluene): Calcd. C 66.21, H 5.60; Found C 66.23; H 5.70.

Characterization of the Catalytic Species (1/MAO)

31 × 10⁻³ g (0.05 mmol) of complex **1** was dissolved in a solution (3 mL) of MAO in C₆D₆ ([MAO] = 100 mg · mL⁻¹). An aliquot (0.8 mL) of the resulting brown solution was used for NMR analysis.

¹H NMR (C₆D₆, 25 °C): δ = 6.99–6.97 (3H, CH arom), 6.96–6.95 (3H, CH arom), 6.38 (d, 4H, *m*-ArH, ³J = 7.6 Hz), 6.08 (t, 2H, *p*-ArH, ³J = 7.6 Hz), 4.24 (pseudo t, 4H, OCH₂, ³J = 8.2 Hz), 4.15 and 3.17 (AB spin system, 8H, ArCH₂Ar, ²J(AB) = 13.2 Hz), 2.66 (s, 3H, TiCH₃), 1.61–1.54 (m, 4H, CH₂CH₃), 0.76 (t, 6H, CH₂CH₃, ³J = 7.4 Hz). The signals corresponding to unreacted MAO appear in the range +0.4/–0.6 ppm.

¹³C{¹H} NMR (C₆D₆, 25 °C): δ = 162.98 (s, C_qOTi), 144.11 (s, C_qOPr), 137.47–125.27 (arom. C's), 87.89 (s, OCH₂), 87.76 (s, TiCH₃), 32.38 (s, ArCH₂Ar), 22.07 (s, CH₂CH₃), 8.99 (s, CH₂CH₃). The ¹H NMR spectrum recorded at 100 °C is not significantly different from that obtained at room temperature.

General Catalytic Testing Procedure for Ethylene Polymerization

All polymerization reactions were performed in a 500 mL Brignole AU steel autoclave equipped with a magnetic stirrer. The autoclave was dried under vacuum at 95 °C for 1 h prior to use upon which it was cooled to room temperature under an argon

atmosphere. The ethylene pressure was kept constant during the catalytic run (semi batch process). The monomer concentrations were calculated using literature data.^[11] Toluene (200 mL) and MAO (100 mg · mL⁻¹) were introduced in the reactor kept at 30 °C. After thermal equilibration, a constant ethylene pressure was applied for a few minutes (until the solution was saturated with ethylene). The reactions were started by injection of 1 mL of a toluene stock solution of the precatalyst (4.2×10^{-3} M). The ethylene consumption was monitored with a digital mass flow meter (Bronkhorst High-Tech). After 2 h the reactions were quenched by injecting 1 mL of ethanol. The reaction mixture was poured into a solution (200 mL) containing ethanol (425 mL), HCl (37%, 200 mL), and water (1 450 mL) solution and stirred overnight. The polymers were filtered off, washed with water and ethanol, then dried at 60 °C under vacuum to constant weight.

Polymer Characterization

¹³C NMR spectra of the polymers were recorded on a Bruker 400-MHz instrument (100.6 MHz) at 100 °C using the waltz16 decoupling method. Polymer samples of 150–200 mg (10 mass %) were dissolved in a 4:1 (v/v) mixture of 1,2,4-trichlorobenzene and 1,1',2,2'-tetrachloroethane-*d*₂ (signal at $\delta = 74.24$ ppm) in 10 mm NMR tube: pulse angle 30 °; delay time 5 s; scan number 1 024. Melting temperatures (T_m) of the polymers were determined by DSC with a Mettler-Toledo DSC 821e instrument equipped with an intracooler and calibrated with the melting transition of indium (156.1 °C). The polymer sample mass was 10 mg and aluminum pans were used. The thermal history of the polymers was eliminated by heating the specimen at a rate of 20 to 200 °C · min⁻¹, then by cooling it at 20 to -100 °C · min⁻¹. The second scan was then recorded from -100 to +200 °C. The molecular weight (\overline{M}_w) and polydispersity index ($\overline{M}_w/\overline{M}_n$) of the polymers were determined, when possible, by gel permeation chromatography (GPC) with a Waters GPCV 2000 Alliance system equipped with a refractive index detector, viscosimetric detector, and a set of three columns, Styragel type (HT6, HT5, HT3). The analyses were performed at 140 °C using 1,2,4-trichlorobenzene as solvent, 2,6-di(*tert*-butyl)-4-methylphenol as thermostabilizer, with a flow rate of 1.0 mL · min⁻¹ and standard polystyrene as the reference. In the case of high molar mass polymers, the molecular weight was estimated by viscosimetric analysis. The samples were prepared by dissolving 10–15 mg

of polymer in 50 mL of decahydronaphthalene (Decalin) stabilized with 2,6-di(*tert*-butyl)-4-methylphenol (1 g · L⁻¹). The viscosity measurements were done at 135 °C using an Ubbelohde viscosimeter (Capillar 5300a, $K = 0.005$ mm² · s⁻²). The time was measured with a Viskoboy 2 analyzer. The solution was kept at 135 °C overnight and filtered at high temperature before the measurement. The capillary was cleaned up two times with the next polymer solution before measurement. The Mark-Houwink constants were taken from the literature.^[12]

Results and Discussion

Synthesis and Molecular Structure of **1**

The titanium (IV) complex **1** was obtained in 84% yield by reacting 25,27-dipropoxy-26,28-dihydroxycalix[4]arene with TiCl₄ at 60 °C in toluene. The ¹H and ¹³C NMR spectra of **1**, which reveal a C_{2v}-symmetrical structure, are consistent with a calixarene in the cone conformation (see Experimental Part). The molecular structure of **1** was determined by a single crystal X-ray diffraction study (Figure 2). The unit cell of **1** contains two molecules (**1a** and **1b**) which structurally differ only little. In both complexes the titanium atom is octahedrally coordinated to four

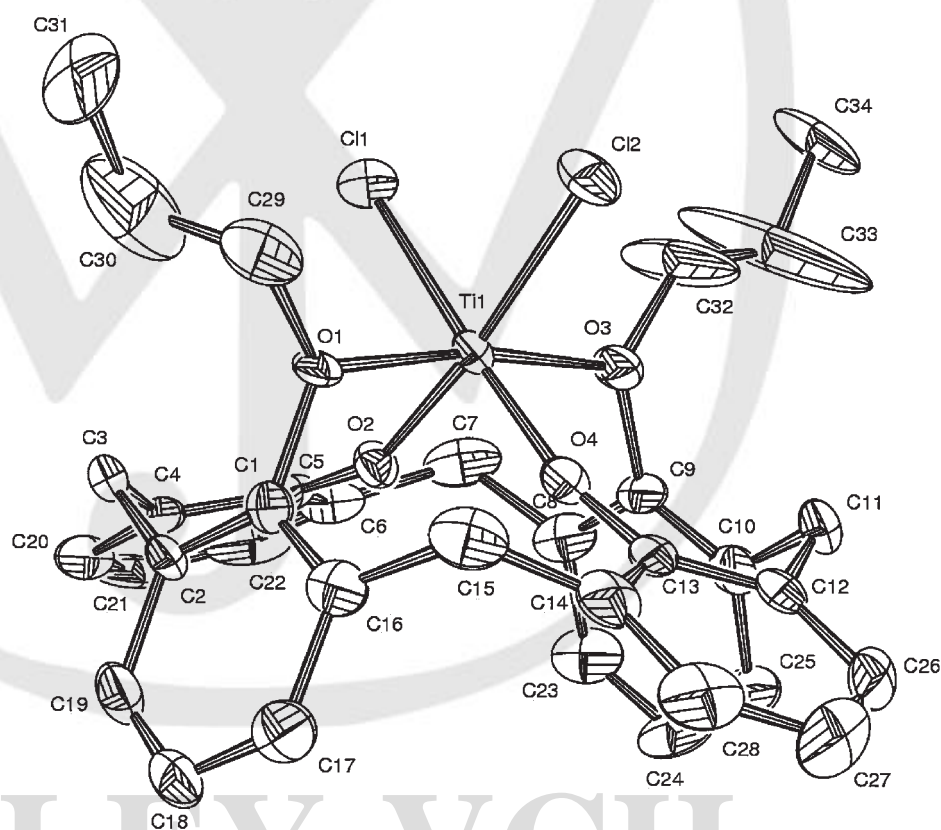


Figure 2. Molecular structure of **1** (only one of the two molecules of the unit cell is shown). The molecules of solvation, dichloromethane, and water, have been omitted for clarity.

Table 1. Polymerization of ethylene at different temperatures in the presence of a calix[4]arene-Ti catalyst. Experimental conditions: $[Ti] = 2.1 \times 10^{-5} \text{ M}$; $[Al]/[Ti] = 1440$; toluene 200 mL; polymerization time = 2 h; $[ethylene] = 0.5 \text{ M}$.

Run	T	$P_{ethylene}$	Isolated yield	Activity	T_m	$M_n^a)$	$M_w^b)$	$M_w/M_n^c)$
	°C	bar			°C	$10^6 \text{ g} \cdot \text{mol}^{-1}$	$10^6 \text{ g} \cdot \text{mol}^{-1}$	
1	45	5.3	0.089	10.6	135.8	3.98	—	—
2	60	6.1	0.252	29.8	136.9	3.44	—	—
3	75	7.0	0.367	43.7	137.0	2.56	—	—
4	90	7.9	0.504	60.0	134.2	0.96	1.11	1.5
5	105	8.8	0.458	54.5	137.0	0.73	0.99	1.4
6	120	9.6	0.227	27.0	135.5	0.60	0.74	1.3

^{a)}Viscosimetric average molar mass; ^{b)}Weight-average molar mass measured by GPC with light scattering online and expressed in $\text{g} \cdot \text{mol}^{-1}$; ^{c)}Polydispersity index.

oxygen and two chlorine atoms, the two propylated oxygen atoms occupying *trans* positions. In keeping with the fact that the phenolate oxygen atoms are the better oxygen donors, the Ti–O (phenolate) bonds (aver. 1.79 in **1a**; 1.80 Å in **1b**) are significantly shorter than the other Ti–O bonds (aver. 2.11 Å in **1a**; 2.11 Å in **1b**). The calixarene core adopts a flattened cone conformation, with dihedral angles between the symmetrically sited phenoxy rings of 122 (average) and 42° (average), respectively. A similar distortion has been observed by Radius et al. in the related complex $[\text{calix[4]arene-(O}_2\text{)-(OMe)}_2\text{TiCl}_2]$.^[9b]

Polymerization Studies

The polymerization runs were carried out in toluene in the presence of methylalumoxane (MAO) as activator applying a constant pressure of ethylene (semi-batch process). Mixing complex **1** with 1400 equiv. of MAO at 45 °C under 5.3 bar of ethylene produced an active catalyst (Table 1, run 1). Its catalytic performance was first optimized by studying the influence of the temperature in the range 45–120 °C, the ethylene concentration being kept constant

(0.5 M)^[11] (Table 1 and Figure 3). The highest activity was found at 90 °C $[65.9 \text{ kg}(\text{polym.}) \text{ mol}^{-1}(\text{Ti}) \text{ h}^{-1}]$. The GPC analysis revealed the formation of high molecular weight polymers ($M_w = 1.11 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$ at 90 °C), a result that was rather unexpected for such high temperatures. It is noteworthy that the M_w/M_n ratios were all smaller than 2, which is typical for a single-site catalyst. Polymerization runs carried out at temperatures below 90 °C even led to much higher molar masses (up to $4 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$, see Table 1). For the latter experiments, the measurements were done by viscosimetric analysis. Overall, complex **1** is suitable for the production of ultrahigh-molecular-weight polyethylene (UHMWPE).

The DSC thermogram of the polymers showed only one melting temperature (T_m), which is consistent with the

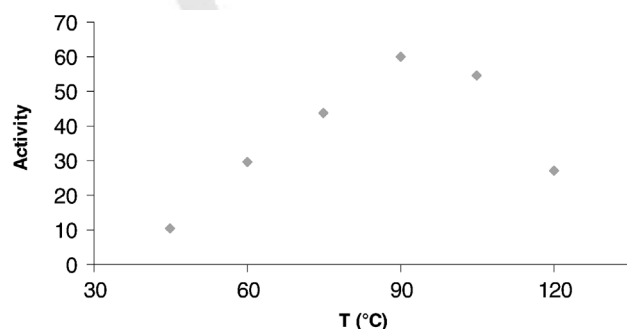


Figure 3. Polyethylene yield at different temperatures with: $[1] = 2.1 \times 10^{-5} \text{ M}$; $[Al]/[1] = 1440$; toluene 200 mL; polymerization time: 2 h; $[ethylene] = 0.5 \text{ M}$ (see also Table 1). Activity in $\text{kg}(\text{polym.}) \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}$.

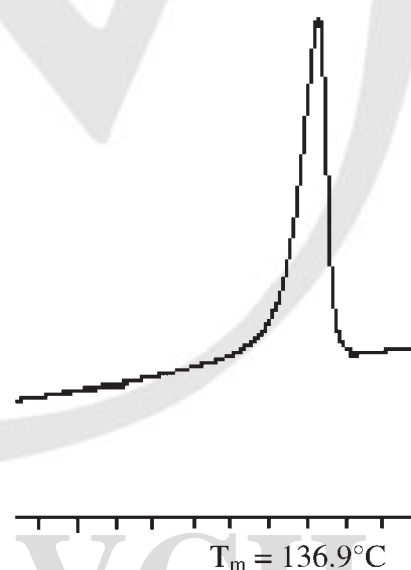
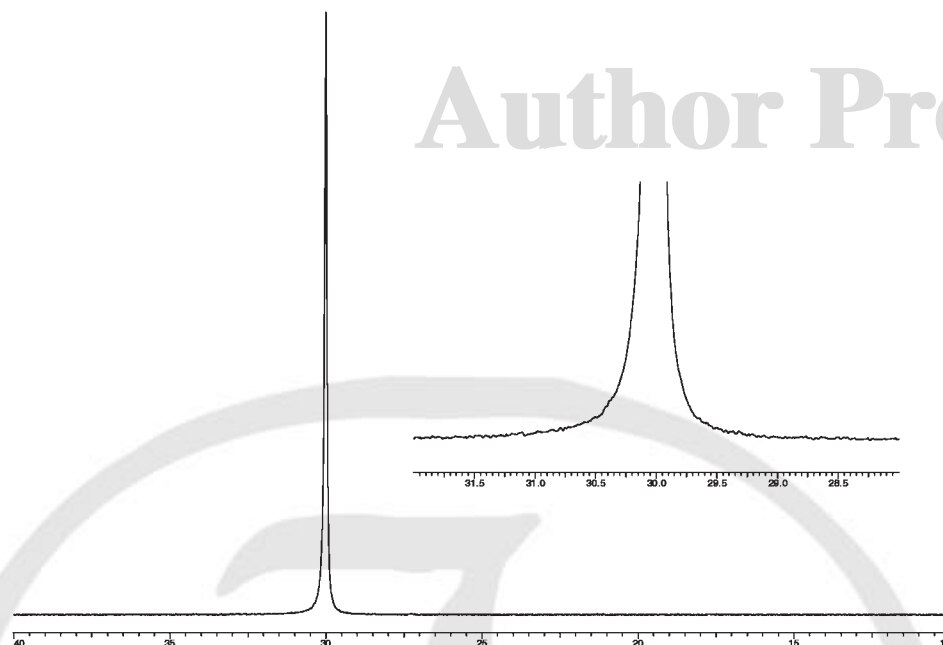


Figure 4. DSC spectrum of polyethylene obtained at 60 °C in the presence of **1**/MAO (Table 1, run 2).



■ Figure 5. ^{13}C NMR spectrum of polyethylene obtained at 60°C in the presence of **1**/MAO (Table 1, run 2).

formation of a homogeneous material (Figure 4). The T_m values lie in the range 135.5 – 145.0°C , a range which is typical for high-density polyethylene (HDPE) as well as UHMWPE.^[13]

The linearity of the polymers was easily deduced from the ^{13}C NMR spectra, which displayed a unique peak at 30.0 ppm ($-\text{CH}_2-$ groups) (Figure 5). No ethylene branching^{Q1} was detected by ^{13}C NMR analysis on the polymer formed under these polymerization conditions. In spite of its moderate activity compared to that of Cp_2ZrCl_2 [the latter typically leads to activities as high as 3×10^4 kg(polym.) $\text{mol}^{-1}(\text{Zr}) \text{ h}^{-1}$], complex **1** gave polyethylenes with higher molecular weights when operating at high temperatures. The polydispersities obtained with **1** were also remark-

able, the $\overline{M}_w/\overline{M}_n$ ratios being all smaller than 2. These results strongly contrast with those recently obtained for some *ansa*-zirconocenes leading also to high molecular weight polyethylene, but with considerable higher polydispersity index (>5).^[14]

The remarkable property of precatalyst **1** to polymerize ethylene at high temperatures is possibly due to the presence of the two propyloxy groups capable of stabilizing by coordination catalytic intermediates. Clearly, the calixarene core serves as pre-organizing unit that maintains the two ether arms close to the metal center.

The influence of the ethylene concentration on the reactivity was also studied. In these experiments the following conditions were applied: $T = 60^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 1440$ (Table 1 run 2 and Table 2). The catalytic

■ Table 2. Influence of $[\text{ethylene}]/[\text{Ti}]$ ratio on the polymerization yield of polyethylenes synthesized with **1** as catalyst precursor. Experimental conditions: $[\text{Ti}] = 2.1 \times 10^{-5} \text{ M}$; $[\text{Al}]/[\text{Ti}] = 1440$; toluene 200 mL ; $T = 60^\circ\text{C}$; polymerization time = 2 h .

Run	[Ethylene]	P_{ethylene}	Isolated yield	Activity	T_m	$\overline{M}_n^{\text{a)Q2}}$
	$\text{mol} \cdot \text{L}^{-1}$	Bar	g	$\text{kg}(\text{polym.}) \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}$	$^\circ\text{C}$	$10^6 \text{ g} \cdot \text{mol}^{-1}$
7	0.25	3.0	0.082	9.8	138.3	3.24
8	0.50	6.1	0.252	29.8	136.9	3.44
9	0.75	9.1	0.452	53.8	137.8	3.53
10	1.00	12.1	0.692	82.4	138.3	4.22

^{a)}Viscosimetric average molar mass.

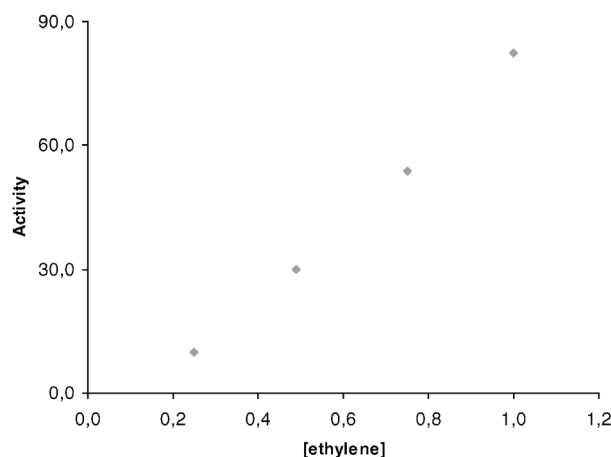


Figure 6. Influence of the ethylene concentration on the activity $[\text{kg}(\text{polym.}) \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}]$ with: $[\mathbf{1}] = 2.1 \times 10^{-5} \text{ M}$; $[\text{Al}]/[\mathbf{1}] = 1.440$; toluene 200 mL; $T = 60^\circ\text{C}$; polymerization time: 2 h (data from Table 2).

activity followed a linear trend (Figure 6), the production reaching $82.4 \text{ kg}(\text{polym.}) \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}$ for a 1 M solution of ethylene. Such a linear variation is typical for Ziegler-Natta catalytic systems.

Let us consider the Arrhenius Eq. (1) where k is the kinetic constant, and K a pre-exponential factor.^[15] Assuming that k represents the activity of the catalyst expressed in $\text{kg}(\text{polym.}) \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}$, the Arrhenius equation was found to be valid over the range of temperatures $45\text{--}90^\circ\text{C}$ (Table 1, Figure 7):

$$\ln k = \ln K - E_a/RT \quad (1)$$

The calculated activation energy for the system was $E_a = 36.1 \text{ kJ} \cdot \text{mol}^{-1}$. The linear relation between $\ln(\text{activity})$ versus $1/T$ is in line with the remarkable stability of the catalytic species at high temperature. Moreover, the occurrence of side reactions such as the formation of bimetallic species may be ruled out in these conditions for the Ti complex **1**. The latter would result in a non-linear relation of the Arrhenius plot, as found for polymerizations carried out at higher temperature ($T > 90^\circ\text{C}$).^[16]

In order to get some insight into the nature of the catalytically active species, ^1H and ^{13}C NMR spectra of mixtures containing **1** and an excess

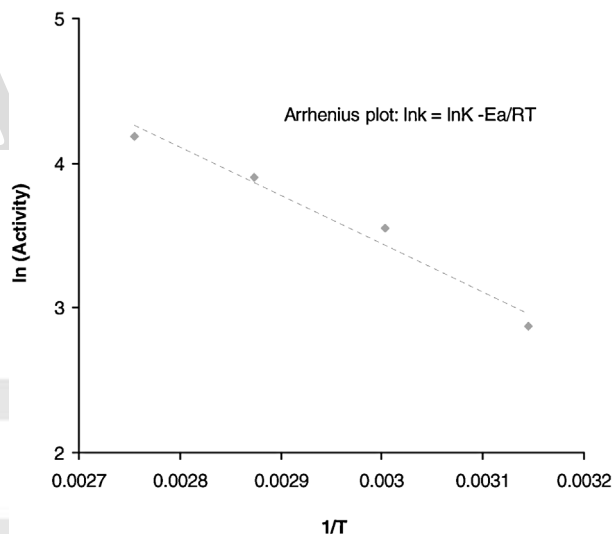


Figure 7. Arrhenius plot of the activity $[\text{kg}(\text{polym.}) \cdot \text{mol}^{-1}(\text{Ti}) \cdot \text{h}^{-1}]$ of the catalytic system **1**/MAO in the polymerization of ethylene with: $[\mathbf{1}] = 2.1 \times 10^{-5} \text{ M}$; $[\text{Al}]/[\mathbf{1}] = 1.440$; toluene 200 mL; polymerization time: 2 h; $[\text{ethylene}] = 0.5 \text{ M}$ (see also Table 1).

of MAO were run (all spectra in C_6D_6). NMR assignments were made in combination with ^1H - ^1H COSY (Figure 8), ^1H - ^{13}C gHSQC analysis (Figure 9) and DEPT (see Figure S2, Supporting Information). The ^1H NMR spectrum reveals a singlet at 2.66 ppm corresponding to a TiMe fragment (Figure 10). Integration shows a Me/Calixarene ratio of 1:1. This observation is in keeping with the general faith that

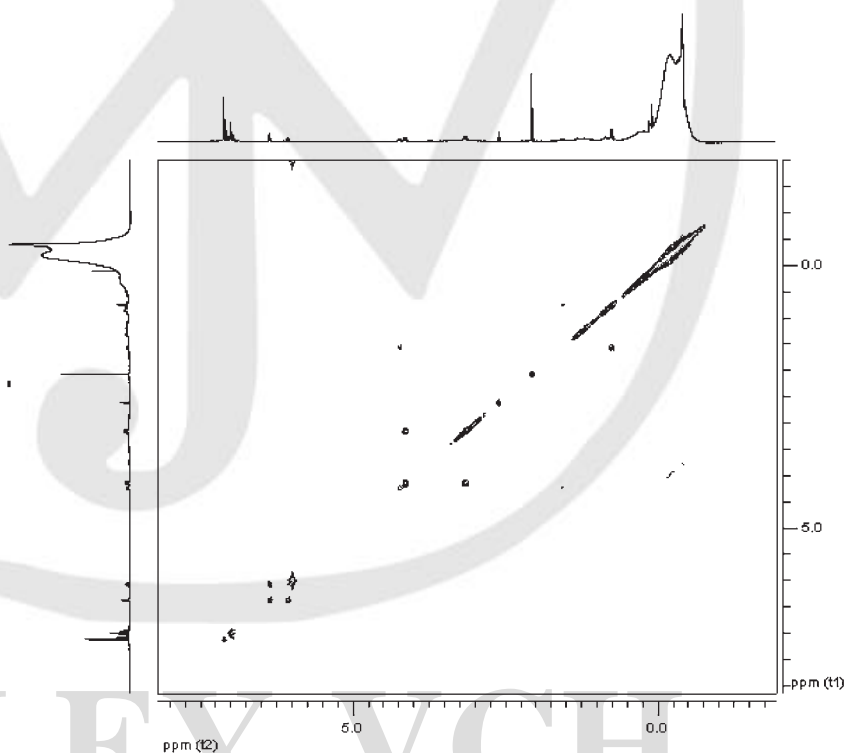
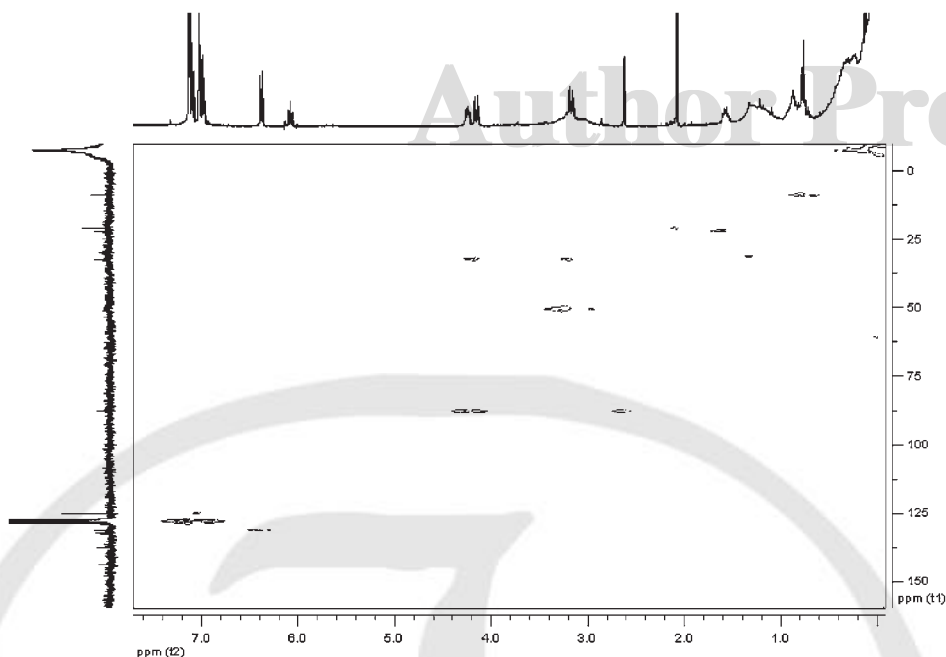


Figure 8. ^1H - ^1H COSY spectrum of **1**/MAO in C_6D_6 at 400 MHz.

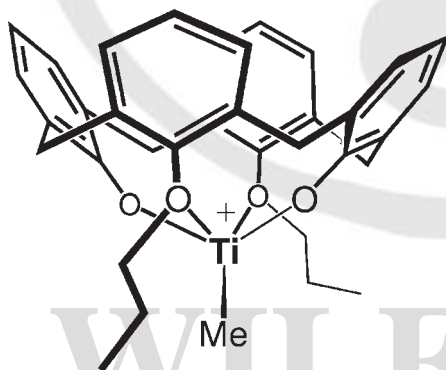


■ Figure 9. ^1H - ^{13}C gHSQC (b) spectrum of **1**/MAO in C_6D_6 at 400 MHz.

treatment with MAO of complexes with the general formula L_nMX_2 result in a cationic, monoalkylation product.^[17,18]

It is also noteworthy that the NMR spectra are consistent with a C_{2v} -symmetrical structure. This finding suggests that the titanium center adopts a pentacoordinate square pyramidal coordination geometry (with the Me group in apical position), as found by Floriani et al. in [calix[4]arene-(O_3)-(OMe)]Ti(*p*-MeC₆H₅).^[9a]

In the NMR spectrum, the ArCH₂ groups appear as an AB pattern with an AB separation of 0.98 ppm, versus 1.59 ppm for **1**, which indicates that the calixarene has undergone some flattening with respect to the calixarene core of **1**.^[19]



■ Figure 10. TiMe fragment revealed by NMR spectrum.

Finally, we found that this cationic species was stable in solution at room temperature during several days. Introduced in an autoclave after standing for three days, the solution displayed activity in ethylene polymerization comparable to that of a catalyst prepared in situ.

Conclusion

The present work has shown that calixarene **1** provides, in its deprotonated form, an "O₄-surface" suitable for the stabilization of a TiCl₂ unit. Combined with MAO, complex **1** reacts with ethylene to give UHMWPE at high temperatures. As unambiguously inferred from an NMR study, the catalytically active species is a titanium-alkyl complex containing one methyl group per calixarene fragment. Its remarkably high thermal stability makes it interesting for possible industrial applications. Further studies will concentrate on variants of complex **1**, with the aim of improving the activity of the catalyst.

Acknowledgements: The authors are grateful to the *University of Florence*, the *Italian MIUR* (PRIN 2004 project, prot. 2004030719) and the *COST action D30-WG1* for financial support.

Received: February 8, 2007; Accepted: February 19, 2007; DOI: 10.1002/macp.200700075

Keywords: calix[4]arene; catalysis; methylalumoxane (MAO); NMR; titanium; ultrahigh-molecular-weight polyethylene (UHMWPE); Ziegler-Natta

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