

Polyethersulfone supported titanium complexes as ethylene polymerization catalysts

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Polyethersulfone has been used as the support to anchor TiCl_4 or Cp_2TiCl_2 through dative 'O-Ti' bond. The supported complexes in combination with methylaluminoxane are effective ethylene polymerization catalysts. The polyethylene made by the supported catalysts, especially the titanocene-derived catalyst, has low polydispersity indicating single site character.

NOVEL catalysts for the manufacture of polyethylene are of great current research interest¹. While most of the commercial heterogeneous catalysts are based on silica-supported chromium, or magnesium chloride-supported titanium species, in recent years metallocene and non-metallocene transition metal complexes, the so-called single site catalysts, have attracted significant attention^{1,2}.

From the point of view of practical application anchoring of catalytically active titanium complexes onto a suitable support, by a simple synthetic procedure, and with minimum alteration of the ligand environments is a challenge^{3,4}. The supported catalyst at the molecular level must be well-defined and when used in polymerization reactions, should approximate single-site behaviour. TiCl_4 and Cp_2TiCl_2 are two of the most easily available and widely used precursors for magnesium chloride-supported Ziegler-Natta and single-site metallocene catalysts respectively. Thus from the point of view of potential application, it is highly desirable to find a polymer that without functionalization is capable of tethering TiCl_4 and titanium metallocene complexes through well-defined chemical bonds. Unlike other supported homogeneous catalysts, the purpose of anchoring is therefore not the easy separation of the catalyst, but to impart single site character to a supported catalyst. Furthermore such supported catalysts can be easily used in fluidized bed reactors.

In this communication we report that polyethersulfone (PES) is a versatile support material on which TiCl_4 and Cp_2TiCl_2 could be easily anchored through dative 'O-Ti' bond. The supported complexes in combination with methylaluminoxane (MAO) are effective ethylene polymerization catalysts. The polyethylene made by the supported catalysts, especially the titanocene-derived catalyst, has low polydispersity indicating single site character.

Triethylaluminum (AlEt_3) (Scherings, AG, Germany), titanium tetrachloride (TiCl_4) (Merck, Germany) and bis (cyclopentadiene) titanium dichloride (Cp_2TiCl_2) (Aldrich, USA) were used as received without further purification. Polyethersulfone (average $M_n \sim 20,000$) was a gift sample from Gharda Chemicals, India. All operations unless stated otherwise were carried out under an inert atmosphere of nitrogen or argon. GPC chromatograms (140°C, trichlorobenzene as solvent) were recorded on a Polymer Laboratory 220 instrument.

A solution of Cp_2TiCl_2 (1.7 GM) in dichloromethane (20 cm^3) is added drop wise under nitrogen to a dichloromethane (200 cm^3) solution of PES (5 GM) at 25°C and stirred for 2 h. Pale yellowish precipitate of **1** separates out from the clear solution, which is isolated by filtration and washed repeatedly with dichloromethane and stored under dry nitrogen. This material is used for all subsequent experiments with **1**.

Catalyst **2** is prepared and isolated by a similar procedure by using TiCl_4 (1.3 GM) and PES (5 GM). Catalyst **4** is prepared by mixing dichloromethane solutions (100 cm^3 each) of TiCl_4 (1.3 GM) and dimethyl sulfone (0.1 GM), stirring the solution for 4 h, removing the solvent under reduced pressure and washing the residue with toluene (1 ml) and hexane.

All polymerization experiments were carried out in a double-jacketed three-necked glass reactor of one-litre capacity, in toluene (200 ml) at 27°C for 60 min. In all the experiments the cocatalyst used was MAO (30%), the amount of

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catalyst used was between 0.05 to 0.5 GM and an Al:Ti molar ratio of 100:1 was maintained. For polymerization with **3**, the catalyst was prepared *in-situ* by mixing Cp_2TiCl_2 (0.37 GM) and Me_2SO_2 (0.09 GM) and allowing the solution to equilibrate for 2 h before initiating polymerization by the addition of MAO and ethylene.

Reactions of PES with Cp_2TiCl_2 and TiCl_4 lead to the formation of **1** and **2** respectively. The tentative formulations of the supported species (Scheme 1) are based on analytical and XPS data. By adjusting the relative amount of PES and the precursor titanium complex, the amount of titanium loading in the supported species could be controlled. Optimum catalytic activity is observed for titanium contents between 3 and 5%.

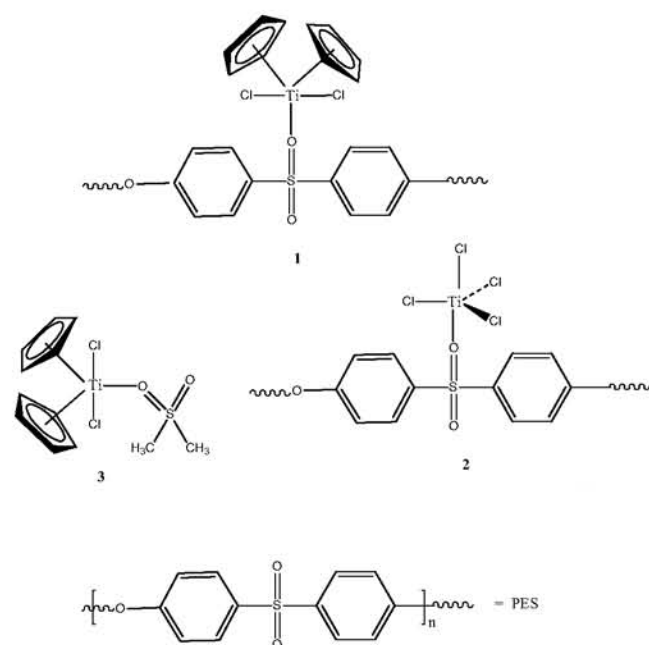
In **1** and **2** the Ti:Cl molar ratios are found to be 1:2 and 1:4 respectively. In PES the XPS signal corresponding to sulfur 2p (spin-orbit unresolved) is observed as a broad feature centered at ~ 170 eV (Au $4f_{7/2}$ as reference at 84.0 eV). However, in both **1** and **2** the sulfur peak could be deconvoluted into two peaks (spin-orbit unresolved) of binding energies 173.5 and 170 eV. It is reasonable to ascribe the peak of binding energy 173.5 eV to the sulfur atoms of those sulfone groups that have oxygen atoms co-ordinated to Ti^{4+} . For **2**, the titanium spin-orbit doublet, $2p_{3/2}$ and $2p_{1/2}$ appear at 458.5 and 465.5 eV, while the peak due to chlorine 2p appears at 200 eV. These values are close to that of the literature reported data⁵ for TiCl_4 on MgCl_2 .

By reacting Cp_2TiCl_2 and TiCl_4 with molar amounts of Me_2SO_2 we attempted the syntheses and isolation of the model complexes $\text{Cp}_2\text{TiCl}_2(\text{Me}_2\text{SO}_2)$ **3**, and $\text{TiCl}_4 \cdot \text{Me}_2\text{SO}_2$ **4**, respectively. While the addition of Me_2SO_2 to an orange

solution of Cp_2TiCl_2 does lead to a slight colour change, all attempts to isolate **3** as a solid have been unsuccessful. At the end of the reaction, unreacted Cp_2TiCl_2 and Me_2SO_2 are recovered. This indicates that **3** is stable in solution, and its isolation as a solid is not possible due to the labile bonding of Me_2SO_2 with Cp_2TiCl_2 . In contrast, complex **4** can be isolated as a moisture and air-sensitive orange yellow microcrystalline solid. The analytical data (Ti, Cl, C, H) of **4** are consistent with the proposed formulation. In **4** the 935 cm^{-1} band of dimethylsulfone is replaced with a band at $\sim 900\text{ cm}^{-1}$. The electrospray ionization mass spectrum of **4** has a molecular ion peak at 284 mass number.

Attempts to grow single crystals of **4** for X-ray structure determination have so far been unsuccessful. However, as shown in Figure 1a, on the basis of density functional (DFT) calculations at B3LYP/LANL2DZ level, the minimum energy structure of **4** is expected to be a slightly distorted trigonal bipyramid. Examples of co-ordination complexes where DMSO as one of the ligands co-ordinates either through oxygen or sulfur atom are known⁶. In the DFT predicted structure, dimethylsulfone co-ordinates through an oxygen atom and acts as a monodentate ligand. Preliminary DFT calculations predict a similar structure and co-ordination environment also for **3**.

The catalytic activities of **1–4** have been evaluated for ethylene polymerization (Table 1), and not for any co-polymerization reactions involving other 1-alkenes. The



Scheme 1. Proposed formulations of **1**, **2** and **3**. DFT based structure of **4** is given in Figure 1a.

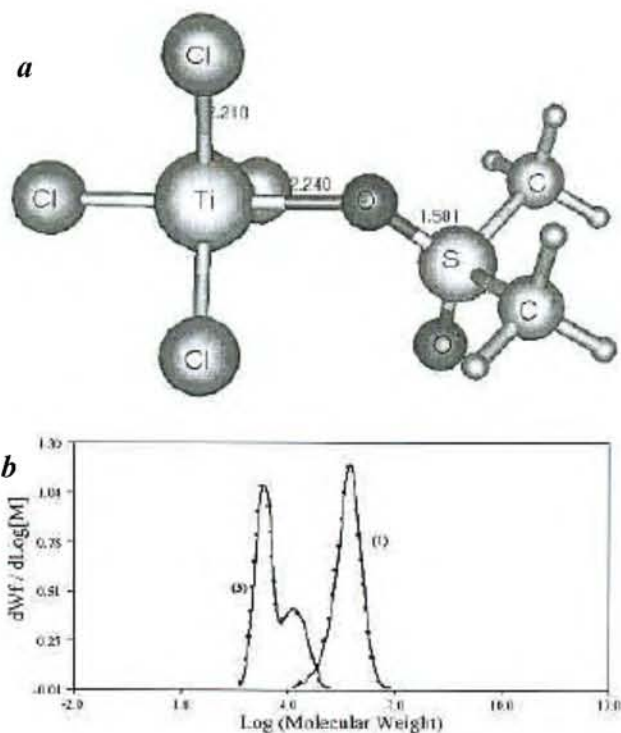


Figure 1. a, DFT (B3LYP/LANL2DZ) predicted structure of **4**; b, Molecular weight distribution of polyethylene obtained by using **1** and **3** as the catalysts.

Table 1. Evaluation of **1–4** as polyethylene catalysts and polymer properties

| Catalyst | Activity* (kg PE/moleTi/h/bar) | M _n ** (× 10 ⁵) | Polydispersity** |
|----------|-----------------------------------|---|------------------|
| 1 | 1600 | 3.1 | 2.1 |
| 2 | 40 | 2.7 | 4.5 |
| 3 | 25.9 | 0.27 | Bimodal |
| 4 | 11.5 | 0.33 | 22.7 |

*All catalytic runs carried out in toluene (200 ml) at 298 K under 1 bar ethylene for 1 h with MAO as the cocatalyst (Al : Ti is 100 : 1).

**Measured by high temperature GPC with polyethylene as standard.

number of average molecular weights of polyethylene obtained with **1** and **2** is approximately one order of magnitude higher than those obtained with **3** and **4**. There is a notable reduction in the polydispersity of the polymers obtained with **1** and **2** as the catalysts, compared to those obtained by using **3** and **4**. As shown in Figure 1b, a broad and distinctly bimodal molecular weight distribution function, a characteristic feature of many multisite catalysts is obtained for **3**. However with **1**, a narrow unimodal molecular weight distribution function is obtained.

When combined with the cocatalyst, complexes **3** and **4** like the well-established first generation Ziegler–Natta system are expected to give rise to *multisite colloidal* catalysts resulting in the formation of polymers with high polydispersity. On the other hand, majority of the surface catalytic sites in the supported catalysts have identical structures. These species are therefore expected to behave more as single site catalysts giving polymers of comparatively low polydispersity^{2b,7}.

Polymerization reactions where MAO is used as the co-catalyst have been reported to involve the cleavage of metal alkoxide bonds⁸. It is very likely that with **1** and **2**, cleavage of some of the dative Ti–O bonds does take place and as the reaction proceeds some of the anchored titanium species are leached out of the support. However, the leached out dissolved species, as well as **2**, **3** and **4** probably undergo quick deactivation. In contrast, the diffusion barrier between the solution and the insoluble support, and the steric crowding in Cp₂TiCl₂ make the supported catalytic species of **1** resistant towards deactivation. This would explain why the molecular weight of polymer obtained with **1** is notably higher than that of all the others.

In conclusion, we have shown that PES is versatile support material for polymerization catalysts. Complexes Cp₂TiCl₂ and TiCl₄ can be supported on PES through dative O–Ti bonds. The supported materials in combination with MAO give polymers of low polydispersity indicating single site behaviour.

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ACKNOWLEDGEMENTS. Experimental assistance of M. V. Birajdar and B. J. Modi, useful discussions with Dr S. Kulkarni, constructive comments from the referee and financial assistance from Reliance Industries Limited, are gratefully acknowledged.

Received 12 October 2004; revised accepted 19 January 2005