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# Synthesis and characterization of titanium(IV) complexes bearing end functionalized biphenyl: Efficient catalysts for synthesizing high molecular weight polyethylene



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#### ABSTRACT

Two phenoxy-imine complexes **1d** and **2d** bearing bulky substituents were synthesized by introducing ethyl or vinyl substituted phenyl to the *para* position of *N*-aryl group and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. The X-ray crystallographic analysis revealed a distorted octahedral geometry of complex **2d**. When activated by dried MAO, two titanium complexes exhibited good to high activity (up to  $4.5 \times 10^6$  g mol<sup>-1</sup>(Ti) h<sup>-1</sup>) for ethylene polymerization. Using these two complexes, ultra-high molecular weight polyethylene (UHMWPE, M<sub>w</sub> > 1,000,000) can be prepared only by changing polymerization time in mild conditions.

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Ultra-high molecular weight polyethylene (UHMWPE), the polyethylene with molecular weight higher than 1,000,000 g/mol, shows an optimized mechanical properties, such as tensile strength, modulus, and abrasion resistance, which reach an extent that the polymer can be applied for special applications, including prostheses, additives for foaming resins, ropes for replacement of steel cables and bulletresistance armor [1]. Now, the industrial UHMWPE production is dominated by heterogeneous Ziegler-Natta and Philips catalysts and the resulted polymer exhibits broad molecular weight distribution (MWD) and chemical composition distribution (CCD), which directly result in inferior mechanical property of polymer [2]. However, with the advent of single site catalysts (SSC), the optimized control over molecular weight, specific tacticity and molecular weight distribution of UHMWPE becomes possible; thus, the research for industrial UHMWPE production by SSC attracts great attention from both academia and industry. Furthermore, the ultimate structural control over UHMWPE microstructure needs "living" catalysts, which can fine tune the molecular weight and keep a very narrow molecular weight distribution of polymer. This is just their uniqueness rather than common SSC [3].

Since 1997, the *ortho*-fluorinated FI catalysts were invented and gave a breakthrough to living coordination polymerization, which made controlled synthesis of UHMWPE possible. Pärssinen and Luhtanen [4] synthesized complex bis[*N*-(salicylidene)-2,6-difluoroanilinato]TiCl<sub>2</sub> and applied it for preparing UHMWPE ( $M_w = 1,540,000,PDI = 1.5$ ) in suitable conditions (10 bar of ethylene, 60 °C, 50 min). Severn and Chadwick [5] immobilized the complex bis[*N*-(3-t-butylsalic-ylidene)

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1387-7003/\$ - see front matter © 2014 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.inoche.2014.01.005 pentafluoroaniline  $|TiCl_2|$  to the support of MgCl<sub>2</sub>·0.24AlEt<sub>2.30</sub>(OEt)<sub>0.70</sub> and applied this heterogeneous catalyst for ethylene polymerization to prepare UHMWPE ( $M_w = 2152000$ , PDI = 3.1) under a slightly harsh condition (10 bar of ethylene, 50 °C, 2 h). Romano and Reyes [6] modified MAO solution with phenol to activate bis[*N*-(3-t-butylsalicylidene) pentafluoroaniline]TiCl<sub>2</sub> in ethylene polymerization and easily obtained UHMWPE ( $M_n = 1,800,000$ ) in mild conditions (1.1 bar, 30 °C). From the research of ethylene polymerization catalyzed by some FI-Zr complexes [7–11], a rule was disclosed that the molecular weight of resulted PE would increase by increasing the steric hindrance of orthosubstituents on the N-aryl group. However, increasing the bulk size of meta or para substituents on the N-aryl group would not result in the same change for these FI-Zr complexes. In this research, we introduce large substituents (4-ethylphenyl and 4-vinylphenyl) to para position of *N*-aryl group on titanium complexes and implement ethylene polymerization to initially explore the feasibility of synthesizing UHMWPE by using these two complexes in mild polymerization conditions. We report here the synthesis and structural characterization of complexes 1d and 2d bearing bulky substituents.

The synthesis of phenoxyimine ligands and complexes was summarized in Scheme 1. The starting material **a** (substituted aniline) for ligand synthesis was prepared by Suzuki coupling reaction of 4-bromo-2,3,5,6-tetrafluoroaniline and 4-vinylphenylboronic acid at 85 °C and purified by column chromatography prior to use. Ligand **b** was prepared by the condensation reaction of 3-tertbutylsalicylaldehhyde and the bulky aniline **a** in ethanol at 80 °C, then purified by recrystallization. The hydrogenation of ligand **b** using HSi(OEt)<sub>3</sub> as H donor and Pt catalyst afforded the formation of ligand **c**. The addition of ether solution of lithium salts of ligand **b** or **c** to 0.5 equiv. of TiCl<sub>4</sub> in ether gave bis(phenoxyimine) titanium complexes **1d** and **2d** in moderate to

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Scheme 1. Synthesis of complex 1d and 2d.

high yield. The <sup>1</sup>H NMR spectra of complex **1d** reveal that the chemical shift of protons on end group (CH=CH<sub>2</sub>) appear at 5.36 ppm (=CH<sub>2</sub>), 5.84 ppm (=CH<sub>2</sub>), and 6.76 ppm (CH=), respectively, while the chemical shifts of CH<sub>2</sub>CH<sub>3</sub> on complex **2d** shift to 1.30 ppm (CH<sub>3</sub>), and 2.72 ppm (CH<sub>2</sub>). The carbon chemical shifts of both benzene rings and side groups also show up in the <sup>13</sup>C NMR spectra of complexes **1d** and **2d**. The elemental analysis reveals a high purity of the complexes.

The structure of complex **2d** was determined by single-crystal X-ray diffraction analysis (Fig. 1), which shows that the geometry around the titanium center can be described as distorted octahedral with

*cis*-N/*trans*-O/*cis*-Cl and two ligands take a  $C_2$  symmetry. The two *cis* components N1 – Ti1 – N2 and Cl2 – Ti1 – Cl1 exhibit the angle values of 96.45(6)° and 90.25(12)°, respectively, and the *trans* component O2 – Ti1 – O1 exhibits angle values of 164.02(13)°. Both of Ti1 – N1 (2.256(3) Å) and Ti1 – N2 (2.246(3) Å) bonds are longer than those of pentafluorinated FI titanium complex (2.217–2.234 Å), [1,12] indicating a decreased interaction between ligand and metal center when replacing the F atom with 4-ethylphenyl group. The Ti1 – O2 (1.843(3) Å), Ti1 – O1 (1.849(3) Å) and Ti1 – Cl2 (2.2708(14) Å), Ti1 – Cl1 (2.2775(14) Å) bonds are nearly the same as those of pentafluorinated FI titanium



**Fig. 1.** Molecular structure of complex **2d**. Thermal ellipsoids are shown at 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ti1 – O2 1.843(3), Ti1 – O1 1.849(3), Ti1 – N1 2.256(3), Ti1 – N2 2.246(3), Ti1 – Cl2 2.2708(14), Ti1 – Cl1 2.2775(14) and O2 – Ti1 – O1 164.02(13), O2 – Ti1 – N1 87.27(12), O1 – Ti1 – N1 80.22(12), O2 – Ti1 – N2 80.92(11), O1 – Ti1 – N2 89.16(12), N1 – Ti1 – N2 90.25(12), O2 – Ti1 – Cl2 96.34(10), O1 – Ti1 – Cl2 95.40(10), N1 – Ti1 – Cl2 174.16(10), N2 – Ti1 – Cl2 85.81(9), O2 – Ti1 – Cl1 94.11(9), O1 – Ti1 – Cl1 95.32(10), N1 – Ti1 – Cl1 87.85(9), N2 – Ti1 – Cl1 174.76(10), Cl2 – Ti1 – Cl1 96.45(6).

## Table 1 Result of ethylene polymerization of complex 1d and 2d with dried MAO.

|                    | -   |          |                | -                |                           |                   |             |                       |               |
|--------------------|-----|----------|----------------|------------------|---------------------------|-------------------|-------------|-----------------------|---------------|
| Entry <sup>a</sup> | Cat | Time/min | A <sup>b</sup> | $M_n{}^c\!/10^4$ | $M_w{}^{\text{c}}\!/10^4$ | $M_w\!/\!M_n{}^c$ | $T_m^{d}/C$ | $\Delta H^{\text{e}}$ | $\chi^{f}/\%$ |
| 1                  | 1d  | 2        | 1.299          | 27.14            | 33.63                     | 1.24              | 139.6       | 234.0                 | 80.4          |
| 2                  | 2d  | 2        | 4.348          | 21.28            | 25.15                     | 1.18              | 139.2       | 237.5                 | 82.7          |
| 3                  | 1d  | 10       | 1.211          | 49.79            | 85.85                     | 1.74              | 140.8       | 238.2                 | 82.9          |
| 4                  | 2d  | 10       | 3.380          | 52.13            | 78.33                     | 1.50              | 142.8       | 238.1                 | 82.9          |
| 5                  | 1d  | 30       | 0.962          | 53.17            | 110.54                    | 2.08              | 141.1       | 243.3                 | 84.7          |
| 6                  | 2d  | 30       | 2.839          | 88.02            | 150.79                    | 1.71              | 142.0       | 238.7                 | 83.1          |
| 7                  | 1d  | 60       | 0.773          | 121.68           | 191.88                    | 1.58              | 141.1       | 238.5                 | 83.0          |
| 8                  | 2d  | 60       | 4.498          | 69.9             | 130.73                    | 1.87              | 143.3       | 199.1                 | 69.3          |

<sup>a</sup> Conditions: 100 ml toluene, 1 atm ethylene pressure, 30 °C, 5 µmol complex, 10 mmol Al.
 <sup>b</sup> Activity, 10<sup>6</sup> g PE/(mol Ti·h).

<sup>c</sup> Determined by GPC using polystyrene calibration.

<sup>d</sup> Measured by DSC.

<sup>e</sup> Unit, J/g.

<sup>f</sup> On the basis of polyethylene fully crystallization  $\Delta H_{f}^{0} = 287.3 \text{ J/g.}$ 

complex (1.841–1.845 Å for Ti1–O and 2.2578–2.2876 Å for Ti1–O) [1,12]. For complex **2d**, the phenol plane (Ph1) and the phenyl (Ph2) on *para* position of the aniline orient themselves tilt to the phenyl ring of the aniline moiety (Ph3) with dihedral angle as 66.1° and 55.3°, respectively. The Ti1–O1–Ph1–C15–N1 combination of complex **2d** is almost coplanar with an average deviation from the mean plane of 0.12 Å. The Cl1–Ti1–Cl2 angle is 96.45° and the *cis*-location of chlorine atoms around the metal center in the complex indicates its potential as catalyst precursor for olefin polymerization [12–14].

Upon activation with excess of dried MAO (Al/Ti = 2000), complexes **1d** and **2d** turned to be active catalysts for ethylene polymerization. The complexes **1d** and **2d** possess high activity and ability to synthesize UHMWPE in specified time and the results are summarized in Table 1.

Complex **2d** exhibits much higher catalytic activity than that of complex **1d** under the same polymerization conditions (Fig. 2). The great difference in catalytic activity can be only attributed to the subtle structural difference of the two complexes. The catalytic activity was undermined when the end group changes from ethyl to vinyl group, which was probably ascribed that the vinyl group in **1d** was possibly inclined to coordinate to the metal center and occupied the active site for ethylene insertion, resulting in a decreased activity [15–17].

Complex **1d** possessed a higher potential in synthesizing UHMWPE when prolonging the polymerization time in mild conditions (Fig. 3). Complex **1d** exhibited quasi living characteristic that the molecular weight of resultant PEs increased from  $33.6 \times 10^4$  at 2 min (PDI = 1.24) period to  $191.88 \times 10^4$  at 60 min (PDI = 1.58). In the whole



Fig. 2. Comparison for catalytic activity with time between complexes 1d and 2d.



Fig. 3. Variation of M<sub>w</sub> with polymerization time for complexes 1d and 2d.

process, the polymer chain is consistently propagating with a suppressed chain transfer. However, complex **2d** is inferior to **1d** in terms of controlling the molecular weight of PEs. For complex **2d**, chain transfer has an advantage over chain propagation in longer polymerization time, which could be observed by the decreased  $M_w$  of PEs from  $150.79 \times 10^4$  (30 min) to  $130.73 \times 10^4$  (60 min). It is probable that the inactive species (caused by the coordination of Ti center with double bond) in **1d** would impose a larger steric hindrance around Ti center than that in **2d**, which would suppress both the chain transfer and chain propagation. All the PEs synthesized by these two complexes exhibit high melting points (139–144 °C) and high crystallinity (70–85%), which are consistent with the typical HDPE.

In summary, two phenoxy-imine titanium complexes bearing end functionalized phenyl on para position of *N*-aryl group were synthesized and characterized. The complexes exhibit good to high activity upon activation with dried MAO. Only by changing polymerization time, UHMWPE (Mw > 1,000,000) can be synthesized in mild conditions. But for complex **2d**, with polymerization time increasing, there is a tendency to decrease the molecular weight of the resulted UHMWPE when chain transfer turned to be serious.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.inoche.2014.01.005.

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