

Synthesis and characterization of titanium complexes bearing sulfoxide groups and their catalytic behaviors in ethylene homo- and copolymerization

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Received February 28, 2014; accepted March 21, 2014; published online July 1, 2014

Titanium complexes derived from 2,4-di-*tert*-butyl-6-((2-(arylsulfinyl)phenylimino)methyl)phenol are designed and synthesized. X-ray diffraction studies reveal that the complexes adopt distorted octahedral geometry with O(phenol), N(imine), and O(sulfoxide) coordinated with titanium. Combined with modified methylaluminoxane(MMAO), the complexes exhibit moderate to high activity to afford polyethylene even at 120 °C under 1 atm ethylene pressure. The complexes also show excellent capability in copolymerization of ethylene with either 1-hexene or norbornene. Results indicate that the introduction of sulfoxide groups could open the space around central metal and favors the insertion of bulky comonomers.

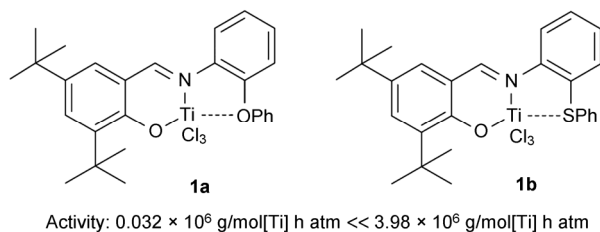
sulfoxide, catalyst, synthesis, ethylene polymerization, copolymerization

1 Introduction

Many efforts have been made to develop well-defined organometallic species as homogeneous olefin polymerization catalysts for the production of a variety of polymers that have novel uses and properties [1–21]. Of the catalysts developed, ligand scaffolds have shown significant influence in stabilizing polymerization-active metal centers and in controlling their behaviors of olefin polymerization [22–24]. For example, the introduction of bulky imine groups in α -diimine, salicylaldehyde, and pyridine diimine backbones allows the development of active late-transition metal catalysts [10–13]. In our previous study on olefin polymerization catalysts, we developed a family of [O⁻NX]titanium complexes based on regulation of the electronic and steric properties of the active species by introducing a pendant-coordination group (side-arm) into a simple ligand skeleton

[25–34]. In this system, strong side-arm effects on catalytic efficiency were observed. When the sidearm was –SR, SeR, or PPh₂, high activity could be obtained whereas low activity was always observed when OR was used as a sidearm (Scheme 1). However, a less-hindered R group enhanced activity levels as well as α -olefin incorporation [25, 26]. To understand the different effects of O-pendant and S-pendant groups on activity, we developed single-crystal titanium complexes **1a** and **1b**. As shown in Figure 1, the O atom in the pendant group of complex **1a** adopted sp² hybridization, whereas an sp³-hybridized S atom was observed in compound **1b**. The phenyl group in complex **1b** deviated from the [O⁻NS] plane, but the phenyl group of complex **1a** was at the [O⁻NO] plane (–177.6(5)° for N–Ti–O–C(22) compared to –107.51(13)° for N–Ti–S–C(22) in **1b**). Due to the hybridization pattern of the donor atom as well as the bond lengths of Ti–S and Ti–O1, the space around the titanium was much more open and favored the coordination and insertion of ethylene by replacement of the side-arm O-atom in compound **1a** with S-atom in compound **1b**.

Dedicated to Professor Qian Changtao on the occasion of his 80th birthday.
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Scheme 1 Activity comparison between complexes bearing $-\text{OPh}$ (**1a**) and $-\text{SPh}$ (**1b**) side-arm [26].

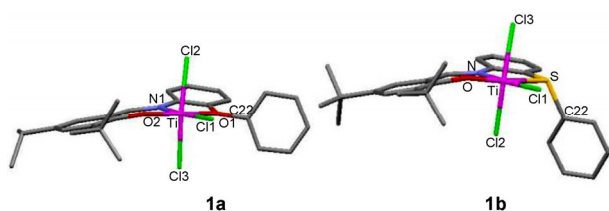


Figure 1 Molecular structures of complexes **1a** and **1b**.

In this work, we designed and synthesized ligand **7a**- and **7b**-bearing sulfoxide groups to further elaborate the influence of the electronic and steric properties of the pendant group on the catalyst behaviors during ethylene polymerization. The corresponding titanium complexes of **7b** showed good activity even at 120 °C upon activation with modified methyl aluminumoxane (MMAO). 1-Hexene and norbornene (NBE) could incorporate into polyethylene in more than 30 mol%.

2 Experimental

2.1 General information

All manipulations were carried out using standard Schlenk technique or glove-box under nitrogen or argon. Toluene, THF, hexane, and dichloromethane were purified by an MB SPS-800 (MBRAUN Company, Germany) prior to use. Modified methylaluminumoxane (MMAO) was purchased from Akzo Chemical (Holland) as heptane solution (1.88 M). Molecular weights (M_w and M_n) and molecular-weight distributions (M_w/M_n) of polymers were determined using a Waters Alliance GPC 2000 series (WATERS, USA) at 135 °C (using polystyrene calibration, 1,2,4-trichlorobenzene as solvent at a flow rate of 0.92 mL/min). ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz and Varian XL-400 MHz spectrometer (VARIAN, USA). Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). ^{13}C NMR data for polymers were obtained using CDCl_3 as the solvent at 25 °C. X-ray crystallographic data were collected at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The SADABS absorption correction was applied. The

structures were solved by direct methods and refined on F^2 by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program.

2.2 Synthesis of the ligands and complexes

(*E*)-2,4-di-*tert*-butyl-6-((2-(phenylsulfinyl)phenylimino)methyl)phenol (**7a**)

A mixture of the aniline **6a** (6.2 g, 28.5 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (6.7 g, 28.5 mmol) in ethanol (50 mL) in the presence of a catalytic amount of acetic acid (3 mL) was refluxed until the reaction was complete. The mixture was cooled to room temperature and the collected yellow solid was washed with cool ethanol to give pure product. Yield: 8.72 g (71%). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 12.81 (s, 1 H), 8.45 (s, 1 H), 8.16–8.17 (m, 1H), 7.68–7.12 (m, 10 H), 1.50 (s, 9 H), 1.31 (s, 9 H). ^{13}C NMR (300 MHz, CDCl_3): δ 165.1, 158.0, 145.7, 145.0, 140.9, 138.9, 137.2, 131.9, 131.1, 129.1, 129.1, 127.4, 127.4, 126.0, 124.5, 118.0, 117.8, 35.1, 34.1, 31.4, 29.3. Anal. calcd. for $\text{C}_{27}\text{H}_{31}\text{NO}_2\text{S}$: C 74.79, H 7.21, N 3.23. Found: C 74.40, H 7.22, N 3.01.

(*E*)-2,4-di-*tert*-butyl-6-((2-(2,6-diisopropylphenylsulfinyl)phenylimino)methyl)phenol (**7b**)

Using a similar procedure to **7a**, pure **7b** was obtained. Yield: 2.82 g (67%). ^1H NMR (300 MHz, CDCl_3 , δ ppm): δ 11.91 (s, 1 H), 7.96–7.98 (m, 2 H), 7.27–7.45 (m, 3 H), 7.00–7.09 (m, 2H), 6.85–6.91 (m, 2 H), 3.75–3.70 (m, 2 H), 1.42 (s, 9 H), 1.30 (s, 9 H), 0.96 (d, $J = 6.6 \text{ Hz}$, 12 H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.7, 157.7, 150.7, 147.8, 140.6, 136.9, 137.0, 132.0, 131.1, 128.6, 127.3, 126.4, 125.7, 124.7, 120.6, 117.9, 35.0, 34.0, 31.3, 29.4, 28.6, 24.4, 23.2. Anal. calcd. for $\text{C}_{33}\text{H}_{43}\text{NO}_2\text{S}$: C 76.55, H 8.37, N 2.71. Found: C 76.58, H 8.29, N 2.71.

[(*E*)-2,4-di-*tert*-butyl-6-((2-(phenylsulfinyl)phenylimino)methyl)phenol] Ti(IV)Cl₃ (**8a**)

To a solution of TiCl_4 (0.56 mL, 5.0 mmol) in toluene (30 mL) was added dropwise a solution of **7a** (2.0 g, 4.6 mmol) in toluene (30 mL) over 10 min at $-78 \text{ }^\circ\text{C}$. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. The generated dark-red solids were collected and washed with toluene ($3 \times 20 \text{ mL}$). Pure product was recrystallized in toluene at $-30 \text{ }^\circ\text{C}$. Yield: 2.0 g (74%). ^1H NMR (400 MHz, CDCl_3 , δ ppm): 8.46 (s, 1 H), 7.99–7.24 (m, 10 H), 6.48–6.46 (m, 1H), 1.61 (s, 9 H), 1.36 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): δ 168.1, 161.1, 150.1, 146.4, 137.0, 135.4, 134.5, 133.2, 133.1, 131.9, 130.6, 129.6, 128.2, 127.3, 126.1, 125.0, 35.4, 34.7, 31.2, 31.1, 29.8. Anal. calcd. for $\text{C}_{27}\text{H}_{30}\text{Cl}_3\text{NO}_2\text{STi}$:

C 55.26, H 5.15, N 2.39. Found: C 55.87, H 5.39, N 2.11.

[(*E*)-2,4-di-*tert*-butyl-6-((2-(2,6-diisopropylphenylsulfanyl)-phenylimino)methyl)phenol] Ti(IV)Cl₃ (**8b**)

By employing a similar procedure to that of **8a**, **8b** was obtained as dark-red solid. Pure product was obtained from recrystallization in CH₂Cl₂. Yield: 2.0 g (77%). ¹H NMR (300 MHz, CDCl₃, δ ppm): δ 8.45 (s, 1 H), 7.26–7.77 (m, 8 H), 6.80–6.84 (m, 1H), 3.61–3.66 (m, 1 H), 3.48–3.52 (m, 1 H), 1.61 (s, 9 H), 1.42 (d, *J* = 3.9 Hz, 3 H), 1.40 (d, *J* = 4.8 Hz, 3H), 1.35 (s, 9 H), 1.17 (d, *J* = 5.4 Hz, 3 H), 0.98 (d, *J* = 5.1 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): δ 167.9, 161.7, 155.2, 152.9, 150.4, 145.9, 136.8, 135.7, 134.3, 133.0, 130.5, 130.0, 128.7, 128.0, 127.0, 126.99, 125.5, 125.1, 124.1, 35.4, 34.6, 31.2, 31.0, 30.6, 29.8, 25.9, 25.2, 23.6, 22.6 ppm. Anal. calcd. for C₃₃H₄₂Cl₃NO₂STi: C 59.07, H 6.31, N 2.09. Found: C 59.30, H 6.28, N 1.82.

2.3 General procedure of ethylene (co)polymerization

A flame-dried Schlenk flask was charged with ethylene and placed in an oil bath at the polymerization temperature. The desired amount of freshly distilled dry toluene was transferred into the flask and saturated with ethylene, followed by a comonomer in the case of copolymerization. MMAO was injected into the flask via a syringe and the mixture was stirred for 5 min. Then the catalyst precursor in toluene was added. After the polymerization was quenched with acidified ethanol, the mixture was poured into acidified ethanol (300 mL, 10 vol% HCl in ethanol). The precipitated polymer was collected, washed with ethanol, and dried at 50 °C under vacuum until it maintained a constant weight.

3 Results and discussion

3.1 Synthesis and characterization of ligands and complexes

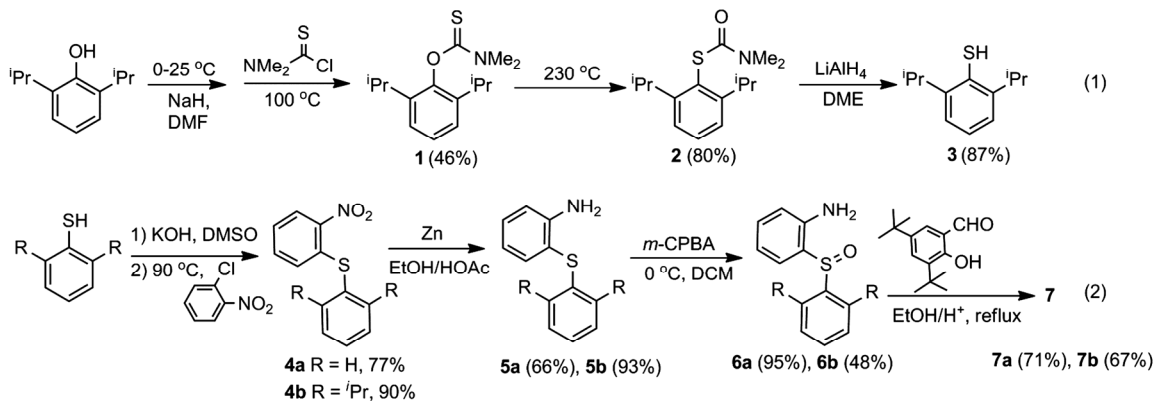
The synthesis of ligands and complexes is summarized in Scheme 2. Thioether **5a** and **5b** were readily available from

benzenethiol **3a** and **3b**, which were prepared according to the procedures in literature [26]. Oxidation of **5** readily generated 2-(phenylsulfanyl)aniline **6**. Refluxing the mixture of **6** and the aldehyde for several hours in ethanol resulted in the formation of **7**, which was recrystallized from cool EtOH to give the pure product as yellow solid. Complexes **8a** and **8b** were obtained by treating ligand **7** with TiCl₄ in toluene as dark-red solid, which was purified from recrystallization in toluene or CH₂Cl₂ at –30 °C (Scheme 3).

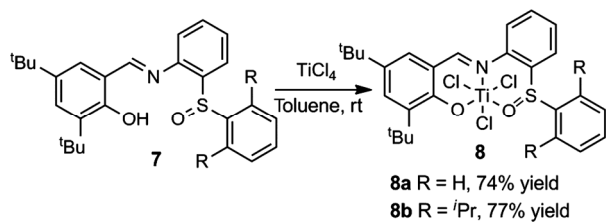
Complexes **8a** and **8b** were characterized by ¹H and ¹³C NMR and elemental analysis. Crystals of **8a** and **8b** were developed from toluene/CH₂Cl₂ for X-ray structure determination. As shown in Figures 2 and 3, complexes **8a** and **8b** adopted a distorted octahedral coordination around the titanium, similar to the parental complexes in **1** [26]. Three chlorines appeared in a mer-position, which could facilitate olefin insertion. Phenolate, imine, and sulfoxide fragment in the ligands coordinated with titanium in both cases. The Ti–O1 bond in complex **8a** (2.013(4) Å) was significantly shortened compared with the corresponding complex **1a** bearing ether appending group (2.249(5) Å) [26]. Bond lengths of Ti–O2 and Ti–N1 in **8a** were 1.793(4) and 2.236(5) Å, respectively. The bond angle of O1–Ti–O2 in **8a** was larger than in the corresponding complex **1a** that bore ether appending group (163.66(18) vs. 158.32(17) [26]. In the molecular structure of **8b**, similar bond lengths and bond angles to those of **8a** were observed.

3.2 Ethylene homo-polymerization

Complex **8a** was first used as a model to investigate the ethylene polymerization in the presence of modified methyl aluminoxane (MMAO) for optimizing the conditions. It is worthwhile to note that **8a** showed good thermostability. As shown in Table 1, the highest activity of 5.3×10^5 g/mol[Ti] h atm was achieved at 60 °C when **8a**/MMAO polymerized ethylene in toluene (entry 3). This activity was influenced by the polymerization temperature. At 30 °C, the activity was 1.9×10^5 g/mol[Ti] h atm, which increased to 4.9×10^5 g/mol[Ti] h atm at 80 °C (entry 6). Decalin was also a



Scheme 2 Synthesis of ligand 7.



Scheme 3 Synthesis of titanium(IV) complexes **8**.

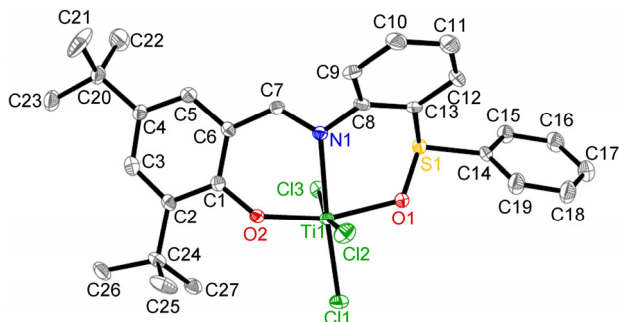


Figure 2 Molecular structure of **8a**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1–O1, 2.013(4); Ti1–O2, 1.793(4); O1–S1, 1.542(4); Ti1–N1, 2.236(5); O2–Ti–O11, 63.66(18); C13–S1–C14, 102.9(3).

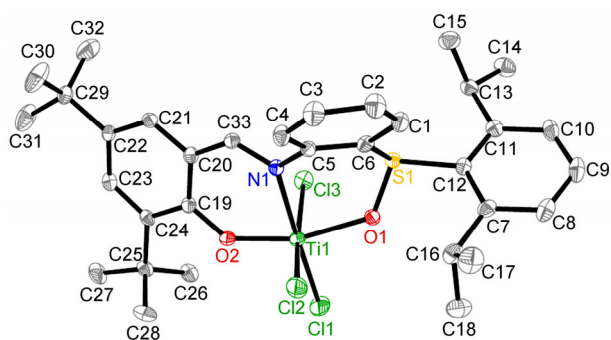


Figure 3 Molecular structure of **8b**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1–O1, 2.004(3); Ti1–O2, 1.813(3); O1–S1, 1.542(3); Ti1–N1, 2.244(3); O2–Ti–O1, 163.36(12); C6–S1–C12, 102.56(19).

suitable solvent for the polymerization. For example, an activity of 8.0×10^5 g/mol[Ti] h atm was achieved at 80 °C (entry 10) and was still very active even when the temperature was increased to 120 °C (2.2×10^5 g/mol[Ti] h atm, entry 12) under 1 atm of ethylene pressure (in spite of the reduced solubility of ethylene at 120 °C). The polymer yield was increased when the polymerization time was prolonged to 1 h, which indicated good catalyst thermostability (Figure 4).

The molecular weight of the polymer reduced sharply when temperature was increased. For example, M_w in toluene decreased from 20.2×10^4 g/mol at 30 °C to 3.2×10^4 g/mol at 80 °C. When the polymerization proceeded in decalin at above 100 °C, the molecular weights were below

Table 1 Effect of reaction temperature on ethylene polymerization results using catalyst **8a** in toluene^{a)}

Entry	T^b (°C)	Solvent	Time (min)	Activity ^{c)}	$M_w^{d,e)}$	$M_w/M_n^e)$
1	30	toluene	10	1.9	20.2	2.0
2	50	toluene	10	4.6	9.5	1.6
3	60	toluene	10	5.3	7.8	1.7
4 ^{d)}	60	toluene	10	2.7	19.8	2.9
5	70	toluene	10	4.8	5.6	1.5
6	80	toluene	10	4.9	3.2	1.7
7	60	toluene	20	3.2	3.8	1.7
8	60	toluene	30	3.2	4.7	1.8
9	60	toluene	60	2.4	6.5	2.0
10	80	decalin	10	8.0	1.8	2.7
11	100	decalin	10	5.0	0.7	1.9
12	120	decalin	10	2.2	0.5	1.7

a) Conditions: **8a** (3 μ mol) in 30 mL solvent; ethylene pressure, 0.1 MPa; reaction time, 10 min; cocatalyst, MMAO 3.2 mL (1.88 mmol/mL in heptane). b) Temperature of the bath. c) 10^5 g/mol[Ti] h atm. d) 10^4 g/mol. e) Determined by GPC. f) **8b** (3 μ mol) was used instead of **8a**.

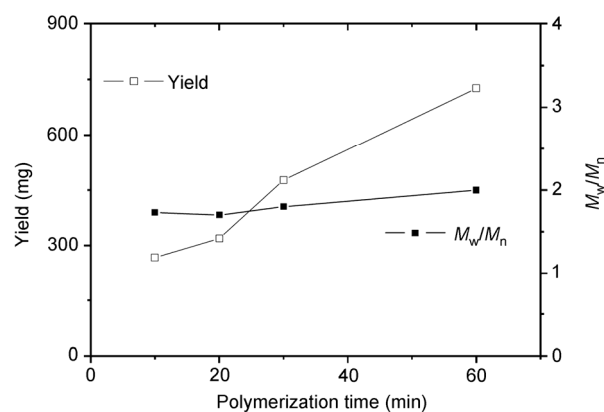


Figure 4 The ethylene polymerization character of **8a**/MMAO. Conditions: 3 μ mol of catalyst **8a** in 30 mL solvent; ethylene pressure, 0.1 MPa; cocatalyst, MMAO 3.2 mL (1.9 mmol/mL in heptane).

10000, probably due to rapid chain transfer during polymerization process at high temperature [35]. As shown in Table 1, the molecular weight distribution was narrow, similar to that of a single-site catalyst. Under the same polymerization conditions, the activity of **8b** was halved relative to **8a** and the molecular weight of the resulting polymer from **8b**/MMAO was almost doubled. These results could be ascribed to steric effects.

The cocatalyst/catalyst molar ratio (Al/Ti ratio) had little effect on the polymerization activity (Table 2). For example, reducing the Al/Ti ratio to 1000, the activity was nearly maintained (5.3×10^5 vs. 4.5×10^5 g/mol[Ti] h atm, entries 2 and 4). The activity was 4.1×10^5 g/mol[Ti] h atm when the ratio was further reduced to 500 (entry 1).

We also examined **8a** in the ethylene/1-hexene copolymerization (Table 3) and good activities were observed in all cases. The 1-hexene incorporation proved to be influenced by its initial concentration. For example, the copolymerization produced copolymer in an activity of 3.2×10^5

g/mol[Ti] h atm with 16.6 mol% incorporation in the case of 1.5 mL of 1-hexene. However, when 10 mL of 1-hexene was added, the activity of 1.6×10^5 g/mol[Ti] h atm and 38.8 mol% incorporation was achieved (entries 3 vs. 4). **8b**/MMAO was also active in the ethylene/1-hexene copolymerization but with low incorporation compared to **8a** (entry 5).

Complex **8a** also proved to be suitable for ethylene/norbornene (NBE) copolymerization although NBE was a steric comonomer (Table 4). As summarized in Table 4, moderate activity and high NBE incorporation (25–32 mol%) could be obtained under the optimized conditions (entries 1–4). The copolymerization behaviors of the catalysts and the chain structures of the copolymers were affected by both the initial concentration of NBE and reaction time. Higher initial NBE concentration favored the incorporation (entries 3 and 4). The incorporation of NBE had little influence when the reaction time was prolonged from 10 to 60 min.

Table 2 Effect of Al/Ti ratio on ethylene polymerization results using catalyst **8a**^{a)}

Entry	Al/Ti ^{b)}	PE (mg)	Activity ^{c)}	M_w ^{d,e)}	M_w/M_n ^{e)}
1	500	208	4.1	11.3	1.8
2	1000	225	4.5	7.6	1.7
3	1500	215	4.3	6.7	1.6
4	2000	267	5.3	7.8	1.7

a) Conditions: **8a** (3 μ mol) in 30 mL toluene; ethylene pressure, 0.1 MPa; reaction time, 10 min; temperature of the bath, 60 °C. b) Cocatalyst, MMAO (1.88 mmol/mL in heptane). c) 10^5 g/mol[Ti] h atm. d) 10^4 g/mol. e) Determined by GPC.

Table 3 Results of ethylene/1-hexene copolymerization using catalyst **8a**^{a)}

Entry	1-Hexene (mL)	t ^{b)} (min)	Incorp. (mol%) ^{c)}	Activity ^{d)}	M_w ^{e,f)}	M_w/M_n ^{f)}
1	1.5	60	11.0	1.0	7.9	2.0
2	1.5	30	13.1	1.3	10.1	1.8
3	1.5	10	16.6	3.2	16.3	3.7
4	10	10	38.8	1.6	9.0	3.3
5 ^{g)}	1.5	10	0.6	2.2	14.3	3.8

a) Conditions: **8a** (3 μ mol) in 30 mL toluene; ethylene pressure, 0.1 MPa; temperature of the bath, 50 °C; cocatalyst, MMAO 3.2 mL (1.88 mmol/mL in heptane); b) Reaction time. c) Determined by 13 C NMR spectroscopy, mol%. d) 10^5 g/mol[Ti] h atm. e) 10^4 g/mol. f) Determined by GPC. g) **8b** (3 μ mol) in 30 mL of toluene.

Table 4 Results of ethylene/NBE copolymerization using catalyst **8a**^{a)}

Entry	NBE (mmol)	t (min) ^{b)}	Incorp. (mol%) ^{c)}	Activity ^{d)}	M_w ^{e,f)}	M_w/M_n ^{f)}
1	10	60	22.2	3.6	3.3	3.0
2	10	30	23.4	3.6	5.4	3.8
3	10	10	20.7	6.0	7.7	3.0
4	20	10	30.4	8.0	5.4	4.2

a) Conditions: **8a** (12 μ mol) in 30 mL toluene; ethylene pressure, 0.1 MPa; temperature of the bath, 50 °C; cocatalyst, MMAO 6.4 mL (1.88 mmol/mL in heptane); b) Reaction time. c) Determined by 13 C NMR spectroscopy, mol%. d) 10^4 g/mol[Ti] h atm. e) 10^4 g/mol. f) Determined by GPC.

4 Conclusions

In summary, titanium complexes bearing sulfoxide as side-arm were synthesized and fully characterized. In the presence of MMAO, the complexes exhibited good activity in the polymerization of ethylene and copolymerization of ethylene/1-hexene, ethylene/NBE, which was different than the corresponding titanium complexes **1a** bearing an ether side-arm. Future study will focus on exploring the hereoatom effects.

This work was supported by the National Natural Sciences Foundation of China (21174159, 21121062), the Science and Technology Commission of Shanghai Municipality, and the Chinese Academy of Sciences.

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