



Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcataEthylene homopolymerization and copolymerization with α -olefins catalyzed by titanium complexes bearing $[O^-NS^R]$ tridentate ligands

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ARTICLE INFO

Article history:

Received 29 April 2008

Received in revised form 12 June 2008

Accepted 15 June 2008

Available online 24 June 2008

Keywords:

Catalyst

Polymerization

Copolymerization

 α -Olefin

Titanium

ABSTRACT

A series of titanium complexes of the general formula $[N-(3,5\text{-di-}tert\text{-butylsalicylidene})\text{-}2\text{-alkylsulfanylanilinato}]\text{Ti(IV)Cl}_3$ (**5a**, **b**, **e** and **f**) exhibited very high catalytic activities in ethylene homo- and copolymerization with various α -olefins in the presence of modified methylaluminoxane (MMAO). The results showed that steric hindrance of the alkylthio groups in **5a–f** strongly influenced the polymerization behavior. An increase in the steric hindrance of these alkyl units led to the decrease in both catalytic activity and comonomer incorporation ratio. On the other hand, the amount of α -olefin incorporated into the copolymer chain depended on the molar ratio of the monomers in the polymerization reaction and was slightly influenced by the chain length of α -olefin. Comparisons between alkylthio and arylthio substituents on catalyst performance were also discussed in this article.

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1. Introduction

Exploring effective catalysts for olefin polymerization/copolymerization is always an attractive project for the great values in both basic research and industrial applications. In the past decades, a large amount of single-site catalysts including metallocenes [1] and non-metallocenes [1d, 2–9] has been synthesized for the production of new polyolefin materials. Among non-metallocene molecular catalysts [2–9], group 4 metal complexes containing phenoxy-imine ligands are the successful examples [4–9]. These bisligated complexes of the type $[\text{NO}]_2\text{-MCl}_2$ are excellent precatalysts for olefin polymerization including ethylene living polymerization [5,6], highly syndiospecific propene living polymerization [7], living copolymerization of ethylene with α -olefin [8], and the synthesis of functional and block copolymers of propylene [9].

On the basis of phenoxy-imine backbone [4–9] and the role of appended heteroatom groups in catalysis [10–12], we have devel-

oped a series of titanium complexes with tridentate $[O^-NX^{Ar}]$ ligands where X = O, S, Se, and P [13]. They exhibited a high activity for ethylene polymerization and copolymerization with α -olefin after activation with modified methylaluminoxane (MMAO), but a moderate activity for ethylene–norbornene copolymerization. Considering the steric/electronic nature of alkyl versus aryl substituents on the thio-sidearm, we recently communicated a new family of alkylthio-sidearmed complexes $[O^-NX^R]\text{TiCl}_3$ (R = alkyl) (**5a–f**) (Fig. 1) [14]. They were efficient catalysts for ethylene copolymerization with cycloolefins such as norbornene, cyclopentene and dicyclopentadiene in the presence of MMAO [14b]. The *n*-alkylthio complexes **5a**, **d–f** all exhibited better ethylene–cycloolefin copolymerization capabilities than the corresponding arylthio one **5g** (Fig. 2). In view of the potential applications of ethylene–higher- α -olefin copolymers in the production of elastomers and linear low-density polyethylene (LLDPE), we were interested in the catalytic properties of the aforementioned alkylthio-sidearmed complexes in ethylene polymerization and copolymerization with α -olefins. It was found that complexes **5a**, **b**, **d–f** were excellent catalysts for ethylene homo- and copolymerization with α -olefins including 1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-octadecene in the presence of MMAO. These results were reported in this article.

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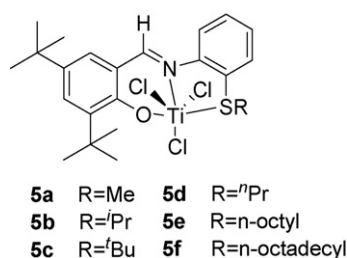


Fig. 1. Structure of titanium complexes $[O^-NS^{alkyl}]TiCl_3$ **5a–f**.

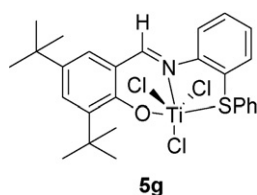


Fig. 2. Structure of titanium complex $[O^-NS^{Ph}]TiCl_3$ **5g**.

2. Experimental

2.1. Materials

Modified methylaluminoxane was purchased from Akzo Chemical as a 7-wt.% solution in toluene. Polymerization-grade ethylene was purified before use. Complexes **5a–f** [14] and **5g** [13b] were prepared according to our previously published methods.

2.2. General procedure of ethylene homo- and copolymerization

A flame-dried Schlenk flask was charged with ethylene and placed in an oil bath at a desired temperature. The desired amount of freshly distilled toluene was transferred into the flask, and saturated with ethylene. The comonomers (in the case of the copolymerization) and MMAO were injected into the flask in sequence *via* a syringe, and the mixture was stirred for 5 min. The polymerization was started by adding a catalyst precursor solution in toluene *via* a syringe. After a desired time, the polymerization was quenched with acidified ethanol, and poured into a large amount of acidified ethanol (300 mL, 10 vol.% HCl in ethanol). The precipitated polymer was filtered off, washed with ethanol, and then dried at 50 °C under vacuum till a constant weight.

2.3. Copolymer characterization

The copolymer samples for 1H and ^{13}C NMR spectra were prepared by dissolving the copolymer in 1,2-dichlorobenzene at 110 °C. Molecular weights (M_w and M_n) and polydispersities were determined by a Waters high-temperature GPC 2000 at 135 °C using polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min. Transition melting temperatures (T_m) of the copolymers were determined by DSC with a Perkin-Elmer Pyris 1 differential scanning calorimeter, measured upon reheating the copolymer samples from 50 to 200 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Ethylene polymerization

In the presence of MMAO, complexes **5a**, **b**, **d–f** exhibited a very high catalytic activity for ethylene polymerization. The

Table 1

Results of ethylene polymerization catalyzed by **5d**/MMAO^a

Entry	Al/Ti	T (°C)	Time (min)	Yield (g)	Activity ^b
1	100	50	15	0.573	0.57
2	500	50	15	1.122	1.12
3	1000	50	15	1.393	1.39
4	1500	50	15	1.351	1.35
5	2000	50	15	1.309	1.31
6	1000	10	15	0.240	0.24
7	1000	30	15	0.734	0.73
8	1000	70	15	0.815	0.82
9	1000	50	5	0.707	2.12
10	1000	50	10	1.293	1.94
11	1000	50	20	1.502	1.13
12	1000	50	30	1.674	0.84
13 ^c	1000	50	60	2.276	0.57

^a Polymerization conditions: ethylene pressure, 0.1 MPa; toluene, 30 mL; catalyst **5d**, 4 μ mol.

^b 10^6 g polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹.

^c Toluene, 40 mL.

results were compiled in Tables 1 and 2. Detailed polymerization conditions were consulted on the activity of **5d** (Table 1). Even if the cocatalyst/catalyst molar ratio (Al/Ti ratio) was as low as 100, the activity of **5d** was still very good (0.57×10^6 g PE (mol Ti)⁻¹ h⁻¹ atm⁻¹; Table 1, entry 1). The activity was increased to 1.39×10^6 g PE (mol Ti)⁻¹ h⁻¹ atm⁻¹ as the Al/Ti ratio was raised to 1000 (Table 1, entries 1–3). Further increase in the Al/Ti ratio from 1000 to 2000 led to a small variation in the activity (Table 1, entries 3–5). After the examination of temperature effect in the range 10–70 °C, a maximum activity of **5d** was achieved at 50 °C (Table 1, entries 3 and 6–8). The activity gradually decreased as the polymerization time increased (Table 1, entries 3 and 9–13).

Steric hindrance of the alkylthio group was proved to strongly influence the polymerization behavior of the catalysts. As steric hindrance of the alkyl substituents on sulfur atom was increased from methyl to isopropyl to *tert*-butyl, the catalytic activity of the catalysts was dramatically decreased, and the molecular weight (M_w) of polymer was largely increased (Table 2, entries 1–3). This is understandable since the bulkier group made both ethylene coordination and chain transfer more difficult. On the other hand, complexes **5a**, **d–f** containing a linear alkyl chain exhibited similar high activities (1.26 – 1.42×10^6 g PE (mol Ti)⁻¹ h⁻¹ atm⁻¹; Table 2, entries 1 and 4–6) in ethylene polymerization.

The molecular weight distributions of polymers produced by these catalysts were in the range 2.13–2.38, which was similar to those generated by single-site catalysts [15]. The melting points (T_m) of the polymers fell in between 129.3 and 132.4 °C, which

Table 2

Results of ethylene polymerization catalyzed by **5a–g**/MMAO^a

Entry	Precatalysts	Yield (g)	Activity ^b	M_w ^{c,d}	M_w/M_n ^c	T_m ^e (°C)
1	5a	1.260	1.26	1.46	2.32	129.3
2	5b	1.099	1.10	4.59	2.14	132.1
3	5c	0.025	0.03	10.96	2.13	132.4
4	5d	1.393	1.39	2.01	2.38	130.7
5	5e	1.419	1.42	1.74	2.34	129.9
6	5f	1.361	1.36	1.72	2.26	130.1
7	5g	1.424	1.42	4.05	2.85	130.8

^a Polymerization condition: ethylene pressure, 0.1 MPa; toluene, 30 mL; [Al]/[Ti] = 1000; catalyst, 4 μ mol; polymerization temperature, 50 °C; reaction time, 15 min.

^b 10^6 g polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹.

^c Determined by GPC.

^d $\times 10^{-4}$.

^e Determined by DSC.

Table 3
Results of copolymerization of ethylene with 1-octene and 1-decene catalyzed by **5d**/MMAO^a

Entry	Comonomer (mmol)	T (°C)	Yield (g)	Activity ^b	Incorporation (mol%) ^c	$M_w^{d,e}$	M_w/M_n^d	T_m^f (°C)
1	1-Octene (10)	25	1.394	1.39	7.5	7.71	2.39	105.0
2	1-Octene (20)	25	1.643	1.64	11.7	7.08	2.39	101.2
3	1-Octene (40)	25	1.472	1.47	15.0	9.64	2.34	87.2
4	1-Octene (80)	25	0.915	0.92	19.1	8.67	2.25	^g
5	1-Octene (0)	25	0.426	0.43	–	8.69	3.02	136.2
6	1-Octene (10)	10	0.871	0.87	6.6	19.52	2.23	104.0
7	1-Octene (10)	50	1.716	1.72	8.3	2.47	2.35	108.4
8	1-Decene (10)	25	1.476	1.48	9.6	5.28	2.44	99.5
9	1-Decene (20)	25	1.693	1.69	8.6	6.41	2.92	95.5
10	1-Decene (40)	25	1.626	1.63	11.3	8.27	2.34	86.0
11	1-Decene (0)	25	0.426	0.43	–	8.69	3.02	136.2
12	1-Decene (10)	10	0.801	0.80	9.8	12.98	2.42	104.2
13	1-Decene (10)	50	1.677	1.68	10.3	1.81	1.98	105.1

^a Polymerization condition: ethylene pressure, 0.1 MPa; toluene, 30 mL; [Al]/[Ti] = 1000; catalyst, 4 μ mol; reaction time, 15 min.^b 10^6 g polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹.^c Determined by ¹³C NMR.^d Determined by GPC.^e $\times 10^{-4}$.^f Determined by DSC.^g T_m cannot be determined.

was slightly lower than the typical T_m (133 °C) for high-density polyethylene (HDPE). The ¹³C NMR studies on the polyethylenes showed that they were highly linear polymers with no detectable branches.

3.2. Ethylene copolymerization with α -olefin

Except for **5c**, complexes **5a–f** were also very good catalysts for ethylene copolymerization with α -olefins including 1-hexene,

Table 4
Results of copolymerization of ethylene with α -olefin catalyzed by **5a–g**/MMAO^a

Entry	Precatalysts	Comonomer	Yield (g)	Activity ^b	Incorporation (mol%) ^c	$M_w^{d,e}$	M_w/M_n^d	T_m^f (°C)
1	5a	1-Hexene	1.996	2.00	12.1	5.37	1.97	101.6
2	5b	1-Hexene	0.600	0.60	3.6	18.95	2.48	105.7
3	5c	1-Hexene	Trace	–	–	–	–	–
4	5d	1-Hexene	1.469	1.47	7.8	7.29	2.22	108.5
5	5d ^g	1-Hexene	2.316	1.16	– ^h	7.68	3.24	– ^h
6	5e	1-Hexene	1.276	1.28	9.2	6.47	2.34	101.4
7	5f	1-Hexene	1.247	1.25	6.6	8.81	2.30	106.1
8	5g	1-Hexene	1.025	1.03	12.2	7.16	2.18	111.6
9	5a	1-Octene	2.326	2.33	10.2	5.39	2.34	100.9
10	5b	1-octene	0.662	0.66	4.7	18.43	2.49	104.7
11	5c	1-Octene	Trace	–	–	–	–	–
12	5d	1-Octene	1.394	1.39	7.5	7.71	2.39	105.0
13	5e	1-Octene	1.450	1.45	7.1	9.55	2.34	101.4
14	5f	1-Octene	1.476	1.48	9.1	7.79	2.21	100.5
15	5g	1-Octene	1.454	1.45	11.0	7.59	2.30	–
16	5a	1-Decene	2.137	2.14	9.6	6.42	1.95	98.4
17	5b	1-Decene	0.562	0.56	0.45	25.40	2.84	111.8
18	5d	1-Decene	1.476	1.48	9.6	5.28	2.44	99.5
19	5e	1-Decene	1.569	1.57	7.6	7.03	2.23	99.9
20	5f	1-Decene	1.474	1.47	7.0	8.41	2.30	102.2
21	5g	1-Decene	1.334	1.33	8.5	9.11	2.61	–
22	5a	1-Dodecene	2.039	2.04	9.8	5.75	2.16	98.1
23	5b	1-Dodecene	0.627	0.63	0.53	23.30	2.67	109.2
24	5d	1-Dodecene	1.240	1.24	9.4	6.29	2.24	102.1
25	5e	1-Dodecene	1.658	1.66	6.7	6.94	2.16	102.2
26	5f	1-Dodecene	1.684	1.68	6.4	7.84	2.20	100.4
27	5a	1-Octadecene	2.535	2.54	7.4	5.59	1.98	96.6
28	5b	1-Octadecene	0.664	0.66	1.8	23.11	2.25	110.1
29	5d	1-Octadecene	1.540	1.54	6.9	6.59	2.14	102.9
30	5e	1-Octadecene	2.053	2.05	5.0	8.42	2.09	100.4
31	5f	1-Octadecene	1.945	1.95	8.3	6.27	2.34	98.3

^a Polymerization condition: ethylene pressure, 0.1 MPa; toluene, 30 mL; comonomer, 10 mmol; [Al]/[Ti] = 1000; catalyst, 4 μ mol; polymerization temperature, 25 °C; reaction time, 15 min.^b 10^6 g polymer (mol Ti)⁻¹ h⁻¹ atm⁻¹.^c Determined by ¹³C NMR.^d Determined by GPC.^e $\times 10^{-4}$.^f Determined by DSC.^g Reaction time, 30 min.^h Not determined.

1-octene, 1-decene, 1-dodecene, and 1-octadecene. Table 3 summarized the results of copolymerization of ethylene with 1-octene and 1-decene catalyzed by **5d**/MMAO. As the initial amount of 1-octene fed was increased from 10 to 80 mmol while the ethylene pressure remained constant of 1 atm, 1-octene incorporation ratio was increased (Table 3, entries 1–4) [16]. However, the copolymerization activity was first increased and then decreased (Table 3, entries 1–4). The highest activity (1.64×10^6 g polymer $(\text{mol Ti})^{-1} \text{h}^{-1} \text{atm}^{-1}$; Table 3, entry 2) was observed when 20 mmol of 1-octene was fed. A similar trend was also observed for the copolymerization of ethylene with 1-decene (Table 3, entries 8–10) [17]. These results showed that **5d**/MMAO exhibited a higher activity in copolymerization than that in ethylene homopolymerization (Table 3, entries 1–4 vs. 5 and entries 8–10 vs. 11). As the copolymerization temperature was raised from 10 to 50 °C, both the catalytic activity and the comonomer incorporation ratio were increased (Table 3, entries 1, 6–8, 12, and 13). However, the M_w of copolymers were greatly decreased, indicating that the rate of chain transfer increased with raising polymerization temperatures. The melting points (T_m) of the copolymers were decreased with the higher comonomer incorporation ratio (Table 3, entries 1–4 and 8–10).

The results of copolymerization of ethylene with α -olefins such as 1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-octadecene catalyzed by **5a–g**/MMAO were summarized in Table 4. Steric factors again played a very important role in catalysts performance. Bulkier alkyl substituent on sulfur resulted in a decrease in both catalyst activity and comonomer incorporation ratio (Table 4, entries 1–3 and 8–10). Among **5a–f**, complex **5a** exhibited the highest activity and capability in copolymerization of ethylene with α -olefin, probably due to steric reasons. Complexes **5b**, **d–f** displayed similar catalytic activities. The results also showed that the chain length of the α -olefin has a little effect on the catalyst activity and comonomer incorporation ratio. Noticeably, the activity of methylthio complex **5a** was two times higher than that of phenylthio one **5g**. The molecular weight distribution of the copolymers produced from **5a**, **b**, **d–f** was relatively narrow, between 2.0 and 3.0. The T_m of copolymers fell in the range 97–112 °C.

4. Conclusions

In the presence of MMAO, a family of $[\text{O}^-\text{NS}^R]\text{TiCl}_3$ complexes containing phenoxyimine ligands with appended alkylthio groups (except for **5c**) was very efficient precatalysts for ethylene homo- and copolymerization with various α -olefins such as 1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-octadecene. Steric hindrance of the alkyl substituents on the sulfur atom in the precatalysts was proved to strongly influence the polymerization behavior. An increase in steric hindrance of the alkyl units led to the decrease in both catalyst activity and comonomer incorporation ratio. Complex **5a** (with a MeS-moiety) exhibited the highest activity and capability in copolymerization. Complexes **5d–f** bearing linear alkyl groups showed similar activities, which was almost independent of the chain length of the alkyl moieties. Their catalytic activities were very comparable to those containing appended arylthio groups [13b,c]. The experimental results also indicated that the chain length of the α -olefin has a very little effect on the catalyst activity and comonomer incorporation ratio.

Acknowledgements

We are grateful for the financial supports from the National Natural Science Foundation of China (NSFC), the Major State Basic Research Development Program (Grant No. 2006CB806105), The Chinese Academy of Sciences, the Science and Technology Commis-

sion of Shanghai Municipality, and NSFC/RGC of Hong Kong Joint Research Scheme (Grant No. 20710011 To YT and N.CUHK446/06 to ZX).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.06.006.

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