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Ethylene/hexene living copolymerization and ethylene/methyl 10-undecenoate copolymerization by titanium complexes bearing phenoxy-phosphine or thiophenoxy-phosphine ligands

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ABSTRACT

Several non-metallocene-type titanium(IV) complexes containing phenoxy-phosphine or thiophenoxy-phosphine ligands of type, (2-R_1-4-R_2-6-PPh_2-C_6H_2X)$_2$$TiCl_2$ (**2a**: $X = O$, $R_1 = R_2 =$ *t*-Bu; **2b**: $X = O$, $R_1 = R_2 =$ cumyl; **2c**: $X = S$, $R_1 = SiMe_3$, $R_2 = H$) have been synthesized by treating $TiCl_4$ with the corresponding ligands 2-R_1-4-R_2-6-PPh_2-C_6H_2XH in the presence of n-BuLi. The complexes **2a**–**c** were investigated as the catalysts for ethylene with 1-hexene and/or polar alkenes copolymerizations. The catalytic activity and the comonomer incorporation were highly dependent upon catalyst and reaction conditions employed. Among these complexes, **2a** can not only promote ethylene/1-hexene living copolymerization at room temperature, but also can utilize ethylene with methyl 10-undecenoate copolymerization.

1. Introduction

Linear low-density polyethylenes (LLDPE) produced via the copolymerization of ethylene with α-olefins (e.g. 1-butene, 1-hexene, and 1-octene) are important polymer materials due to their excellent performance [1–4]. Therefore, a great deal of academic and industrial research has been devoted to the efficient synthesis of LLDPE with controlled macromolecular structures. Living olefin polymerization is one of the most useful tools for the synthesis of precisely controlled polymers such as monodisperse polymers and block copolymers [5,6]. Recent advances in the design and synthesis of well defined transition-metal complexes have led to the advent of quite a few efficient catalysts for the living polymerization of ethylene, propylene, 1-hexene, or other olefins [5–16]. Nevertheless, successful examples concerning the controlled ethylene/α-olefins copolymerization by non-Cp transition-metal catalysts are limited so far.

In addition, the copolymerization of ethylene with polar alkenes catalyzed by transition-metal complexes is an attractive subject, because it provides easy and low-cost access to functional polyethylenes (PEs) with unique properties. Compared with late transition-metal catalysts, group IV compounds exhibits much oxophilicity. The catalytic species are poisoned by the polar alkene monomer and deactivate in most cases. Therefore, there are rare non-Cp group VI catalysts which exhibit high activity and incorporate polar monomers with good contents [17–21].

Recently, our group found that bis(phenoxy-phosphine) titanium complexes can mediate highly controlled, thermally robust living polymerization of ethylene with norbornene [22]. As part of our studies on the structure–reactivity relationship of the catalysts, we have explored olefin polymerization behaviors in a wide range. These investigations not only resulted in the development of living catalysts with high incorporation ability for higher α-olefins, but also carried out ethylene with polar alkene monomer copolymerization.

2. Experimental

2.1. General procedures and materials

All manipulation of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from MBraun solvent purification system (SPS). NMR data of the ligands were obtained on a Bruker 300 MHz spectrometer at ambient temperature with $CDCl_3$ as a solvent (dried by MS 4Å). NMR data of the copolymers were obtained on a Varian Unity-400 MHz

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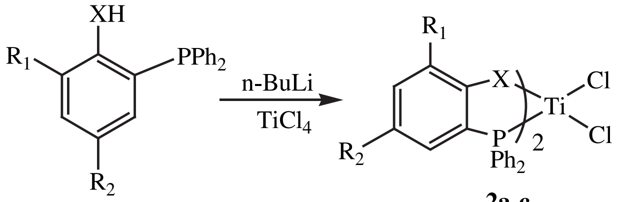
spectrometer at 135 °C, with o-$C_6D_4Cl_2$ as a solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. The molecular weights and the polydispersity indexes of polymer samples were determined at 135 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The 2.5 M n-BuLi solution in hexane was purchased from Acros. Commercial titanium tetrachloride ($TiCl_4$) was distilled prior to use. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Other reagents and solvents were commercially available.

Various phenoxy-phosphine or thiophenoxy-phosphine ligands containing different substituent on X, R_1 and R_2 positions, 2- R_1-4-R_2-6-PPh_2–C_6H_2OX (**1a**: $X = O$, $R_1 = R_2 = t$-Bu; **1b**: $X = O$, $R_1 = R_2 =$ cumyl; **1c**: $X = S$, $R_1 = SiMe_3$, $R_2 = H$) and complex **2a** were prepared according to literature procedures [23,24].

2.2. Synthesis of titanium complexes 2b–c

Bis(2,4-di-cumyl-6-diphenylphosphanyl-phenoxy)titanium dichloride (2b). Synthesis of **2b** was performed according to the same procedure as that of **2a**. To a stirred solution of compound **1b** (1.03 g, 2 mmol) in dried THF (30 mL) at − 78 °C, 2.5 M n-BuLi hexane solution (0.8 mL, 2 mmol) was added dropwise over 5 min. The mixture was stirred for 2.5 h, and then was added to $TiCl_4$ (0.19 g, 1 mmol) in dried THF (30 mL). The solution was warmed to room temperature and stirred overnight. The reaction mixture was then placed in a rotary evaporator to concentrate the reaction mixture under reduced pressure. The chilled solution placed in the freezer (− 30 °C) and afforded complex **2b** (0.74 g, 65% yield). ^1H NMR ($CDCl_3$): δ 1.10 (s, 3H, cumyl-Me), 1.41 (s, 3H, cumyl-Me), 1.50–1.53 (m, 12H, cumyl-Me), 1.76 (s, 3H, cumyl-Me), 2.01 (s, 3H, cumyl-Me), 6.31–6.62 (m, 4H, Ar–H), 6.71–6.83 (m, 3H, Ar–H), 6.85–7.37 (m, 34H, Ar–H), 7.60–7.71 (m, 3H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 28.1, 28.6, 29.3, 30.2, 30.8, 43.1, 125.6, 126.0, 126.7, 127.0, 127.2, 128.3, 128.4, 128.6, 130.0, 131.4, 133.0, 133.1, 133.8, 134.0, 145.2, 150.2. Anal. Calc. for $C_{72}H_{68}Cl_2O_2P_2Ti$: C, 75.46; H, 5.98. Found: C, 75.53; H, 5.90.

Bis(2-trimethylsilyl-6-diphenylphosphanyl-thiophenoxy)titanium dichloride (2c). Synthesis of **2c** was performed according to the same procedure as that of **2a**, except that 2-trimethylsilyl-6-diphenylphosphanyl-phenoxy (0.73 g, 2.0 mmol) was added slowly into a stirred THF solution containing $TiCl_4$ (0.19 g, 1.0 mmol). The chilled solution afforded red microcrystals (0.49 g, 58% yield). ^1H NMR ($CDCl_3$): δ 0.01 (s, 9H, $SiMe_3$–H), 0.35 (s, 9H, $SiMe_3$-H), 6.78–6.97 (m, 4H, Ar–H), 7.06–7.58 (m, 18H, Ar–H), 6.67–7.83 (m, 4H, Ar–H). ^{13}C NMR ($CDCl_3$): δ − 0.52, − 0.32, 123.4, 128.5, 129.2, 130.6, 131.3, 133.4, 133.9, 134.2, 134.6, 135.2, 138.1, 139.7, 143.2, 164.2. Anal. Calc. for $C_{42}H_{44}Cl_2S_2P_2Si_2Ti$: C, 59.36; H, 5.22. Found: C, 59.46; H, 5.13.



1a-c **2a-c**

a: $X = O$, $R_1 = R_2 = t$-Bu;
b: $X = O$, $R_1 = R_2 =$ Cumyl;
c: $X = S$, $R_1 = SiMe_3$, $R_2 = H$;

Scheme 1. General synthetic route of titanium complexes **2a**–**c**.

2.3. General procedure of copolymerization

The polymerization was carried out in a 150 mL Schlenk flask equipped with a mechanical stirrer. The flask was repeatedly evacuated and refilled with nitrogen, and finally filled with ethylene gas (atmospheric pressure) from a Schlenk line. Prescribed amount of toluene were added via a gastight syringe and the mixture was kept at a prescribed polymerization temperature. The monomer (in the case of the copolymerization) and MMAO were injected into the flask in sequence with vigorous stirring. And then a toluene solution of the titanium complex was added into the reactor to initiate the polymerization. Ethylene consumption was noted as a function of time from the gas burette. After prescribed time, ethanol containing 10% (v/v) hydrochloric acid was added to terminate the polymerization. The resulted polyethylenes were recovered by filtration, washed with ethanol, and dried in a vacuum oven at 60 °C.

3. Results and discussion

3.1. Synthesis of complexes (2-R_1-4-R_2-6-PPh_2-C_6H_2X)$_2TiCl_2$

Various titanium complexes employed in this study (2-R_1-4-R_2-6-PPh_2-C_6H_2X)$_2TiCl_2$ (**2a**: $X = O$, $R_1 = R_2 = t$-Bu; **2b**: $X = O$,

Table 1
Ethylene Copolymerization with Hexene or Methyl 10-undecenoate.[a]

Entry	Catalyst (μmol)	Comonomer (mol/L)	Temperature (°C)	Al/Ti	Yield (mg)	Activity [b]	M_w [c] (10^4)	M_w/M_n [c]	Monomer incorp.[d]
1	**2a**(2)	Hexene (0.49)	25	2000	223	669	10	1.25	6.5
2	**2a**(2)	Hexene (1.15)	25	2000	165	495	5.6	1.17	12.3
3	**2a**(2)	Hexene (1.15)	50	2000	225	675	8.5	1.45	17.1
4	**2a**(2)	Hexene (1.15)	75	2000	112	336	3.0	1.67	26.1
5	**2a**(5)	Methyl 10-undecenoate (0.022)	25	2000	195	234	4.0	2.1	0.5
6	**2a**(5)	Methyl 10-Undecenoates (0.044)	25	2000	75	90	3.6	2.8	0.7
7	**2a**(5)	Methyl 10-undecenoate (0.044)	25	3000	110	132	3.0	2.5	1.0
8	**2a**(5)	Methyl 10-undecenoate (0.044)	25	4000	185	222	2.1	2.3	0.9
9	**2a**(5)	Methyl 10-undecenoate (0.044)	50	3000	–	–	–	–	–
10	**2b**(2)	Hexene (1.15)	25	2000	43	129	7.6	1.27	11.8
11	**2b**(5)	Methyl 10-undecenoate (0.044)	25	3000	95	114	4.1	3.3	0.8

[a] Conditions: $V_{total} = 50$ ml, 10 min, 1 ethylene pressure.
[b] Activity in kg/mol$_{Ti}$·bar·h.
[c] GPC data in trichlorobenzene vs polystyrene standards.
[d] Hexene incorporation determined by ^{13}C NMR and Methyl 10-undecenoate incorporation determined by ^1H NMR.

$R_1 = R_2 =$ cumyl; **2c**: $X = S, R_1 = \mathrm{SiMe_3}, R_2 = H$) are shown in Scheme 1, which were synthesized either according to published procedures or in a similar manner via the reaction of $TiCl_4$ with the lithium salt of the corresponding phenoxy-phosphine or thiophenoxy-phosphine ligand [22–24]. The complexes were identified by ^{1}H and ^{13}C NMR and elemental analysis.

3.2. Ligand effects in ethylene/1-hexene copolymerization

We explored ethylene/1-hexene copolymerization with above titanium complexes in presence of modified methylaluminoxane (MMAO) under the different conditions. The typical data for the copolymerizations are summarized in Table 1. It was revealed that the copolymerization with 1-hexene by complex **2a** took place. The catalytic activity of complex **2a** decreased upon increasing the 1-hexene concentration (entries 1–2). The resultant products were poly(ethylene-*co*-1-hexene)s confirmed by ^{13}C NMR spectra, and the copolymer possessed high molecular weight with unimodal molecular weight distributions. Narrow M_w/M_n values ($M_w/M_n = 1.17–1.25$) suggested that the complex **2a**/MMAO catalyst system may possess the characteristic of incorporating 1-hexene into polymer chains in a living fashion. In an attempt to confirm the living nature of the copolymerization, M_n and M_w/M_n values were monitored as a function of polymerization time. A plot of M_n and M_w/M_n values *vs* polymerization time is shown in Fig. 1. The M_n value increased proportionally with polymerization time, and the narrow M_w/M_n value was retained for each run ($M_w/M_n = 1.15–1.20$), suggesting that the system is indeed living.

GPC peaks of the resultant copolymers shifted to the higher molecular weight region with an increase in polymerization time, while the unimodal shape was maintained and no shoulder peak and/or no low molecular weight tail was detected during the course of the polymerization (Fig. 2). These results clearly indicate that the complex **2a**/MMAO catalyst system initiates highly controlled living ethylene/1-hexene copolymerization.

An enhancement in polymerization temperature from 25 to 50 °C led to an increase in the catalytic activity (entry 2, 495 kg/mol$_{Ti}$·h·atm; entry 3, 675 kg/mol$_{Ti}$·h·atm) and 1-hexene incorporation (from 12.3 to 17.1%) as well as in the molecular weight of the resultant copolymer. A significant decrease in the activity and molecular weight was found if the copolymerization was conducted at 75 °C (entry 4 in Table 1), and the level of 1-hexene incorporation approached 26.1 mol% in the resultant copolymer. However, the living nature was lost at higher temperature as a result of a common increase of chain transfer reactions (entries 3–4).

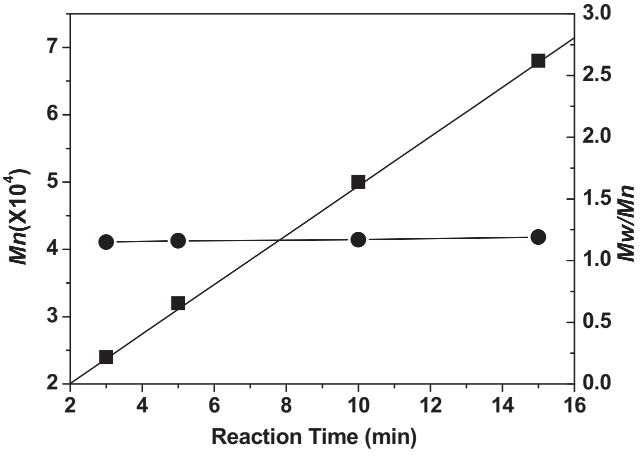


Fig. 1. Plots of the number-average molecular weights and the polydispersity indexes of the poly(ethylene-*co*-1-hexene)s *vs* reaction time (catalyst **2a** 2 μmol, Al/Ti molar ratio = 2000:1, 25 °C, atmospheric pressure, V_{total} = 50 mL, Hexene = 1.15 mol/L).

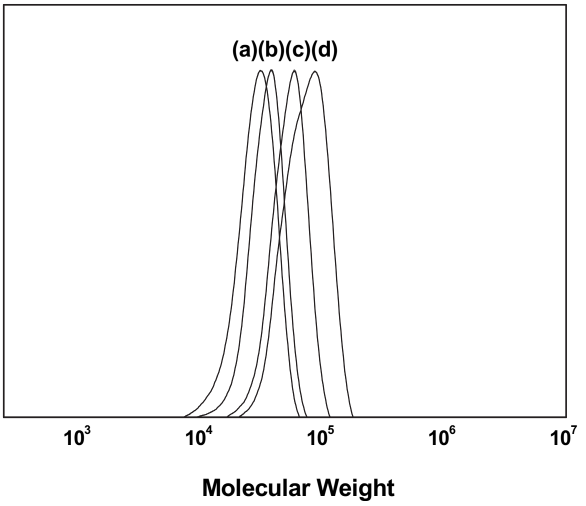


Fig. 2. GPC profiles of Ethylene/Hexene copolymer. (1): 3 min, M_n 2.4 × 10^4, M_w/M_n 1.15; (2): 5 min, M_n 3.2 × 10^4, M_w/M_n 1.16; (3): 10 min, M_n 5.0 × 10^4, M_w/M_n 1.17; (4): 15 min, M_n 6.8 × 10^4, M_w/M_n 1.20.

The steric bulk of the substituent and the co-ordinational donors in the ligand significantly affected the copolymerization behaviors. Complex **2b** has bulky substituent at *ortho*-position, which disfavored the insertion of ethylene into metal-carbon bond. Therefore, **2b** showed much lower catalytic activity for ethylene/1-hexane copolymerization than **2a** under the same condition (entry 10). Complex **2c** containing the soft sulfur and phosphorous donors was inactive catalyst system for ethylene/1-hexene copolymerization.

3.3. Ligand effects in ethylene/methyl 10-undecenoate copolymerization

Copolymerizations of ethylene with methyl 10-undecenoate by complexes **2a**–**c** were also investigated under the similar conditions. The catalytic activity and the monomer incorporation were highly dependent upon catalyst and reaction conditions employed. The typical results are summarized in Table 1. **2a**/MMAO catalyst system displayed moderate catalytic activity for copolymerization with methyl 10-undecenoate, and the activity decreased with increasing comonomer content in the feed (entries 5–6).

The incorporations of methyl 10-undecenoate into the copolymers have been characterized with ^{1}H NMR (Fig. 3). The existence of the polar comonomer can be determined by the signal of methyl protons of -COO*Me* at 3.55 ppm. The relative integrated intensity ratio of the chemical shift at 3.55 ppm and the chemical shifts between 1 and 1.6 ppm, as well as the number of protons that both chemical shifts represent, determines the incorporation of methyl 10-undecenoate into the copolymer.

The copolymerization reactions carried out with different Al/Ti ratios by **2a** are also listed in Table 1. The increase in Al/Ti molar ratio caused significant change both in the catalytic activity and the molecular weight for the resultant copolymers (entries 6–8). However, monomer incorporation was independent of the Al/Ti molar ratio. The resultant copolymer possessed high molecular weight with unimodal molecular weight distribution, suggesting that the copolymerization took place with single catalytically active

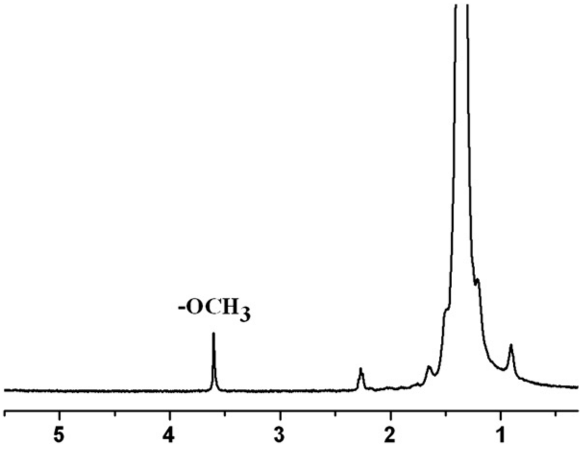


Fig. 3. ^{1}H NMR spectrum of poly(ethylene-*co*-methyl 10-undecenoate) prepared by **2a**/MMAO catalytic system (Table 1, entry 7).

species. A significant decrease in the activity was found if the copolymerization was conducted at 50 °C (entry 9). Catalyst **2b** displayed low catalytic activity for copolymerization with methyl 10-undecenoate (entry 11). Complex **2c** was inactive catalyst system for above copolymerization.

Without being masked with Lewis acids, methyl 10-undecenoate can be easily incorporated into the copolymer chain by **2a**/MMAO system under the mild conditions, leaving a polar group which offers easy access to functionalized PEs. These results indicated that the titanium complexes containing the softer second-row donor incorporated [O,P] ligands displayed good tolerance to polar group.

4. Conclusions

Ethylene with 1-hexene and/or methyl 10-undecenoate copolymerizations were investigated using non-metallocene-type titanium(IV) complexes containing phenoxy-phosphine or thiophenoxy-phosphine ligands of type, $(2\text{-}R_1\text{-}4\text{-}R_2\text{-}6\text{-}PPh_2\text{-}C_6H_2X)_2TiCl_2$ (**2a**: $X = O, R_1 = R_2 = t$-Bu; **2b**: $X = O, R_1 = R_2 =$ cumyl; **2c**: $X = S, R_1 = SiMe_3, R_2 = H$) as the catalysts in the presence of MMAO. The steric bulk of the substituent and the co-ordinational donor in the ligands have significant influence on the copolymerization behaviors. Complex **2a** was able to carry out ethylene/1-hexene living copolymerization at room temperature. Furthermore, it displayed some extent tolerance to functional groups, thus promoting the copolymerization of ethylene with polar alkenes. To the best of our knowledge, this is the first example of copolymerization ethylene with methyl 10-undecenoate using non-Cp titanium catalyst.

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