

## Ethylene Polymerization with Novel Phenoxy-imine Catalysts Bearing 4-Vinylphenyl Group<sup>\*</sup>

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**Abstract** This contribution reports ethylene polymerization behavior of titanium complexes incorporating bis(phenoxy-imine) ligands. Six phenoxy-imine Ti(IV) complexes {6-R<sup>1</sup>-2-[CH=N(2,6-difluoro-3,5-diR<sup>2</sup>-4-R<sup>3</sup>Ph)]C<sub>6</sub>H<sub>3</sub>O}<sub>2</sub>TiCl<sub>2</sub> (**1**: R<sup>1</sup> = H, R<sup>2</sup> = H, R<sup>3</sup> = H; **2**: R<sup>1</sup> = H, R<sup>2</sup> = H, R<sup>3</sup> = 4-vinylphenyl; **3**: R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = H, R<sup>3</sup> = H; **4**: R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = H, R<sup>3</sup> = 4-vinylphenyl; **5**: R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = F, R<sup>3</sup> = H; **6**: R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = F, R<sup>3</sup> = 4-vinylphenyl) have been synthesized and evaluated for ethylene polymerization using dried MAO (simplified as DMAO) as cocatalyst. An obvious catalytic heterogeneity of Cat **2** (Complex **2**/DMAO) towards ethylene polymerization was observed, which was illustrated by decreased activity, multi-modal molecular weight distribution and partially improved particle morphology comparing with Cat **1**. Moreover, Cat **3** exhibits “living” characteristics in the process under certain conditions (25 °C, less than 20 min). Otherwise, the moderate to high ethylene polymerization activity of *ca.* 10<sup>5</sup>–10<sup>6</sup> g PE/(mol Ti·h) and high molecular weight (*M*<sub>w</sub> = 10<sup>5</sup>–10<sup>6</sup>) of polyethylene can be obtained by changing the skeleton structure of these complexes.

**Keywords:** Ethylene polymerization; Catalytic heterogeneity; “Living” polymerization; Phenoxy-imine ligand; 4-Vinylphenyl group.

### INTRODUCTION

The discovery of multi-site Ziegler-Natta catalysts opened a door to olefin coordination polymerization and greatly promoted polyolefin industry. Since metallocene catalyst was discovered by Sinn and Kaminsky in 1978<sup>[1–3]</sup>, a series of new polyolefins with unique microstructure such as syndiotactic PP, VLDPE, ULDPE and ethylene/propylene/diene elastomer (EPDM) were soon put into commercial production<sup>[4–9]</sup>. Inspired by the success of metallocene catalysts, people both from academia and industry have made great efforts to develop more well-defined single-site catalysts (SSC) for manufacturing high value added commodities. The most representative SSC after metallocene catalysts (named as post-metallocene catalysts) are  $\alpha$ -diimine ligated late-transition metal catalysts discovered by Brookhart in 1995<sup>[10, 11]</sup> and phenoxy-imine ligated early transition metal catalysts (named as FI catalysts) discovered by Mitsui Chemicals in 1997<sup>[12–14]</sup>.

For applying these homogeneous single-site catalysts to industrial scale process, it is necessary to transform them to heterogeneous ones. In slurry, bulk-monomer and gas-phase olefin polymerization processes, the corresponding products are usually of high density or high crystallinity (HDPE, *i*-PP), thus the catalysts needed to be insoluble in the dilute or fluidizing gas stream. If the catalysts are soluble, the polymer with bad

<sup>\*</sup> This work was financially supported by the National Natural Science Foundation of China (Nos. 20936006 and 20976152) and National Basic Research Program of China (2011CB606001). And Doctoral Program of Higher Education of China (No. 20100101110041) and Program for Changjiang Scholars and Innovative Research Team in Zhejiang University.

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Received September 29, 2013; Revised January 27, 2014; Accepted February 11, 2014

doi: 10.1007/s10118-014-1470-5

morphology would adhere to the reactor wall everywhere. Furthermore, in order to feed catalysts into reactor without clumping, the continuous process requires the industrial catalysts to have good particle morphology, which suggests that the solvent-soluble SSC must be “fixed” on insoluble supports in these processes<sup>[15]</sup>. Otherwise, in order to keep some unique catalytic characteristics of SSC, choosing suitable approaches and supports for immobilization turns to be a sophisticated but necessary work. Inorganic materials (such as silica and  $\text{MgCl}_2$ ) and polymer materials (such as polystyrene), have been successfully applied as supports for immobilizing SSC to produce polymers with high bulk density and relatively narrow molecular weight distribution.

Apart from these conventional approaches, a convenient method<sup>[16]</sup> has been exploited by introducing unsaturated groups ( $\omega$ -alkenyl or  $\omega$ -alkyne) into complexes, so as to enhance the catalytic heterogeneity towards olefin polymerization. This method is called “self-immobilization” by Alt *et al.*, who think that the homogeneous SSCs will be transformed to heterogeneous ones by being copolymerized with  $\alpha$ -olefin in the process. It also has been proven that the proper size<sup>[17]</sup> of alkenyl (vinyl, allyl *etc.*) on complex is a key factor in terms of improving particle morphology and polymer processing performance (broadened MWD). Because the self-immobilization process removes the need of inorganic supports and keeps the catalytic characteristics of the non functionalized catalysts to some extent, it is regarded as being advantageous in catalytic productivity and product stereoselectivity. Although the underlying mechanism of “self immobilization” is still needed to be explored<sup>[15]</sup>, the simplicity and effectiveness of this method can be learned.

Searching for a flood of reviews and articles, there are few contributions about 4-vinylphenyl as functional group for heterogeneous SSC catalysis. For catalyst immobilization, 4-vinylphenyl is mostly used to construct polystyrene network *via* anionic or radical polymerization for preparing polymer immobilized SSCs; however, it is also a useful unsaturated group that can be directly used for heterogeneous SSCs in olefin coordination polymerization<sup>[18]</sup>. In this work, three FI catalysts bearing 4-vinylphenyl on the *para*-position of *N*-aryl group were synthesized and used to implement ethylene polymerization, and the effect of 4-vinylphenyl group on ethylene polymerization would be clarified by comparison with the polymerization behavior of the corresponding FI complexes just bearing H atom on the *para*-position of *N*-aryl group.

## EXPERIMENTAL

### *Solvents and Reagents*

Dried solvents (diethyl ether, tetrahydrofuran, toluene, dichloromethane and hexane) used for ligands and complexes synthesis were purchased from Hangzhou Chemical Reagents Company and refluxed over potassium using benzophenone as a water indicator under nitrogen atmosphere prior to use. 4-Vinylbenzeneboronic acid, tetrakis(triphenylphosphine) palladium were products of the Aldrich Chemical Company. Sodium carbonate was purchased from Alfa-Aesar and stored in an inert atmosphere glove box under nitrogen. 2,6-Difluoroaniline, 2,3,5,6-tetrafluoroaniline, salicylaldehyde and 3-methylsalicylaldehyde were purchased from Alfa-Aesar and used as received.  $\text{TiCl}_4$  (1 mol/L in  $\text{CH}_2\text{Cl}_2$ ) and *n*-BuLi (1.6 mol/L in hexane) were purchased from Tokyo Chemical Industry Co., Ltd and J&k Chemical Company, respectively. Polymerization-grade ethylene purchased from Yangzi Petrochemical Engineering Company was purified by passing it through  $\text{CuO}$ , ascarite and 0.5 nm molecular sieves. Methylaluminoxane (MAO, 1.4 mol/L in toluene) was purchased from Albemarle, and the remaining trimethylaluminum was evaporated in vacuo prior to use.

### *Ligand and Complex Analyses*

The NMR spectra were obtained on Bruker Advance DMX400 Instruments with TMS as internal standard. Elemental analyses were performed by using a Thermo Electron SPA EA1112.

### *Polymer Characterization*

DSC analysis was conducted using a DSC Q100 V9.5 Build 288 in the standard DSC mode. Ultra high pure  $\text{N}_2$  gas at a flow rate of 20 mL/min was purged through the calorimeter. The temperature and heat capacity of the instrument were initially calibrated with indium standard at the heating rate of 10 K/min. GPC was performed in

1,2,4-trichlorobenzene at 150 °C with three PL Waters Styragel columns (104, 103, and 500) and a refractive index (RI) detector. A calibration curve was established with polystyrene standards. SEM analysis was performed by a CrossBeam Workstation FIB-SEM. HT-<sup>13</sup>CNMR was performed on a Varian NMX300 Instrument with TMS as internal standard and 1,2-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> as deuterium reagent at 130 °C.

### Ligand Synthesis

In this research, two kinds of ligands were synthesized: three ligands containing 4-vinylphenyl group on the *para*-position of *N*-aryl group and the others only containing H atom on the *para*-position of *N*-aryl group while keeping the same ligand skeletons. The ligands (**b**, **d**, **f**) bearing 4-vinylphenyl group were prepared as the literature reported<sup>[19]</sup>. By the bromination of fluorinated aniline and Suzuki Coupling reaction, anilines containing 4-vinylphenyl group were obtained, which were reacted with the corresponding salicylaldehyde *via* Schiff base condensation reaction in ethanol to afford the corresponding ligands in 50%–90% yield. The ligands (**a**, **c**, **e**) without 4-vinylphenyl group were synthesized in *ca.* 81%–83% yields according to the literature<sup>[20]</sup>.

### Complex Synthesis

All manipulations were performed with the exclusion of oxygen and moisture under nitrogen using standard Schlenk techniques. A little modified procedure for complexes synthesis followed the literature reported by Fujita *et al.*<sup>[21]</sup>. To a stirred solution of a phenoxy-imine ligand (4 mmol) in dry THF (20 mL) at –78 °C, a 1.6 mol/L *n*-butyllithium (2.5 mL) hexane solution was added dropwise over a 2 min period. The solution was allowed to warm to room temperature and stirred for 5 h, the resulting solution was added dropwise over a 20 min period to a stirred solution of TiCl<sub>4</sub> (2 mmol) in dry THF (10 mL) at –78°C. The mixture was allowed to warm to room temperature and stirred for 40 h. The resulting mixture was concentrated in vacuo to give a solid, to which dried dichloromethane (20 mL) was added, and the mixture was stirred for 5 min. The resultant mixture was filtered and the residue was washed with dry dichloromethane. The combined filtrates were concentrated in vacuo to afford the crude complex. To the crude complex, dried diethyl ether (10 mL) and dried hexane (15 mL) were added and stirred for 2 h. A titanium complex was collected by filtration, washed with dried hexane (5 mL) for 3 times and dried in vacuo.

#### *Bis*[*N*-(salicylidene)-2,6-difluoroanilinato]titanium(IV)dichloride (**1**)

Ligand **a**, *N*-(salicylidene)-2,6-difluoroaniline, was obtained as yellow crystals in 81% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 12.97 (s, 1H), 8.87 (s, 1H), 7.41 (dd, *J* = 10.7, 7.5 Hz, 2H), 7.20–7.09 (m, 1H), 7.07–6.90 (m, 4H).

Complex **1** was obtained as reddish brown powder in 70.4% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.24 (s, 2H), 7.38–6.42 (m, 14H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, δ): 171.20, 162.92, 156.80, 154.28, 137.28, 135.03, 127.71, 123.42, 121.64, 116.64, 112.06, 110.87. Elemental analysis for C<sub>26</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>F<sub>4</sub>TiCl<sub>2</sub> (%): Calcd.: C, 53.55; H, 2.77; N, 4.80; Found: C, 52.99; H, 2.81; N, 4.69.

#### *Bis*[*N*-(salicylidene)-2,6-difluoro-4-(4-vinylphenyl)anilinato]titanium(IV) dichloride (**2**)

Ligand **b**, *N*-(salicylidene)-2,6-difluoro-4-(4-vinylphenyl)aniline, was obtained as pale yellow crystals in 90% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ) 13.00 (s, 1H), 8.91 (s, 1H), 7.81–7.35 (m, 6H), 7.28–7.16 (m, 2H), 7.11–7.02 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.73 (m, 1H), 5.79 (t, *J* = 18.0 Hz, 1H), 5.28 (dd, *J* = 21.7, 11.2 Hz, 1H).

Complex **2** was obtained as reddish brown powder in 25.9% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.29 (s, 2H), 7.51–7.35 (m, 10H), 7.32 (m, 2H), 7.20 (d, *J* = 9.9 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.96 (m, 2H), 6.74 (dt, *J* = 23.6, 11.8 Hz, 3H), 6.66–6.37 (m, 2H), 5.82 (d, *J* = 17.7 Hz, 2H), 5.31 (m, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>, δ): 171.25, 162.99, 156.93, 154.65, 137.92, 137.35, 137.18, 136.17, 135.97, 135.08, 126.91, 123.45, 121.60, 116.75, 114.96, 114.19, 110.46, 109.11. Elemental analysis for C<sub>42</sub>H<sub>28</sub>O<sub>2</sub>N<sub>2</sub>F<sub>4</sub>TiCl<sub>2</sub> (%): Calcd.: C, 64.06; H, 3.58; N, 3.56; Found: C, 63.96; H, 3.61; N, 3.53.

#### *Bis*[*N*-(3-methylsalicylidene)-2,6-difluoroanilinato]titanium(IV) dichloride (**3**)

Ligand **c**, *N*-(3-methylsalicylidene)-2,6-difluoroaniline, was obtained as reddish yellow crystals in 83% yield.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.19 (s, 1H), 8.84 (s, 1H), 7.26 (d,  $J = 7.3$  Hz, 1H), 7.22 (d,  $J = 7.7$  Hz, 1H), 7.16–7.06 (m, 1H), 6.97 (t,  $J = 8.3$  Hz, 2H), 6.85 (t,  $J = 7.5$  Hz, 1H), 2.31 (s, 3H).

Complex **3** was obtained as reddish brown powder in 50.7% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.23 (s, 2H), 7.29 (d,  $J = 7.3$  Hz, 2H), 7.22 (d,  $J = 7.7$  Hz, 2H), 6.99 (d,  $J = 8.5$  Hz, 4H), 6.91–6.86 (m, 4H), 2.32 (s, 6H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 171.42, 161.58, 156.85, 138.01, 132.70, 127.37, 126.88, 123.10, 121.27, 112.31, 110.71, 15.25. Elemental analysis for  $\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{F}_4\text{N}_2\text{O}_2\text{Ti}$  (%): Calcd.: C, 55.02; H, 3.30; N, 4.58. Anal. found: C, 54.95; H, 3.39; N, 4.51.

*Bis[N-(3-methylsalicylidene)-2,6-difluoro-4-(4-vinylphenyl)anilinato]titanium(IV) dichloride (4)*

Ligand **d**, N-(3-methylsalicylidene)-2,6-difluoro-4-(4-vinylphenyl)aniline, was obtained as yellow crystals in 85% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 13.10 (s, 1H), 8.93 (s, 1H), 7.52 (q,  $J = 8.4$  Hz, 3H), 7.45 (s, 1H), 7.34–7.19 (m, 4H), 6.87 (t,  $J = 7.5$  Hz, 1H), 6.76 (dd,  $J = 17.6, 10.8$  Hz, 1H), 5.80 (t,  $J = 18.4$  Hz, 1H), 5.29 (dd,  $J = 21.6, 10.9$  Hz, 1H), 2.33 (s, 3H).

Complex **4** was obtained as reddish brown powder in 79.3% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.30 (s, 2H), 7.50 (d,  $J = 7.7$  Hz, 4H), 7.45 (s, 2H), 7.37 (d,  $J = 7.7$  Hz, 2H), 7.30–7.14 (m, 6H), 6.95–6.85 (m, 2H), 6.81–6.72 (m, 2H), 6.58 (s, 2H), 5.83 (d,  $J = 17.6$  Hz, 2H), 5.34 (d,  $J = 10.7$  Hz, 2H), 1.88 (d,  $J = 24.4$  Hz, 6H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 171.42, 161.66, 156.79, 154.41, 137.96, 135.98, 132.76, 126.76, 126.44, 123.18, 121.28, 114.97, 110.35, 108.88, 15.24. Elemental analysis for  $\text{C}_{44}\text{H}_{32}\text{O}_2\text{N}_2\text{F}_4\text{TiCl}_2$  (%): Calcd.: C, 64.80; H, 3.96; N, 3.44. Found: C, 64.78; H, 3.98; N, 3.41.

*Bis[N-(3-methylsalicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride (5)*

Ligand **e**, N-(3-methylsalicylidene)-2,3,5,6-tetrafluoroaniline, was obtained as yellow crystals in 50% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 12.59 (s, 1H), 8.82 (s, 1H), 7.33 (d,  $J = 7.3$  Hz, 1H), 7.25 (s, 1H), 7.00–6.84 (m, 2H), 2.32 (s, 3H).

Complex **5** was obtained as reddish brown powder in 41.0% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.25 (s, 2H), 7.42 (d,  $J = 7.3$  Hz, 2H), 7.28 (s, 2H), 6.96 (t,  $J = 7.6$  Hz, 2H), 6.83 (s, 2H), 2.03 (s, 6H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 171.05, 160.63, 138.04, 132.18, 125.55, 121.60, 120.83, 102.59, 102.37, 102.48, 14.08. Elemental analysis for  $\text{C}_{28}\text{H}_{16}\text{O}_2\text{N}_2\text{F}_8\text{TiCl}_2$  (%): Calcd.: C, 49.22; H, 2.36; N, 4.10; Found: C, 48.97; H, 2.49; N, 3.92.

*Bis[N-(3-methylsalicylidene)-2,3,5,6-tetrafluoro-4-(4-vinylphenyl)anilinato]titanium(IV) dichloride (6)*

Ligand **f**, N-(3-methylsalicylidene)-2,3,5,6-tetrafluoro-4-(4-vinylphenyl)aniline, was obtained as yellow crystals in 50% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 12.67 (s, 1H), 8.90 (s, 1H), 7.54 (d,  $J = 8.3$  Hz, 2H), 7.47 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 7.3$  Hz, 1H), 7.28 (d,  $J = 7.8$  Hz, 1H), 6.90 (t,  $J = 7.5$  Hz, 1H), 6.78 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.83 (t,  $J = 17.5$  Hz, 1H), 5.33 (dd,  $J = 18.9, 10.9$  Hz, 1H), 2.34 (s, 3H).

Complex **6** was obtained as reddish brown powder in 52.0% yield.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.34 (s, 2H), 7.75–7.28 (m, 12H), 7.06–6.92 (m, 2H), 6.76 (dt,  $J = 21.9, 10.9$  Hz, 2H), 5.86 (d,  $J = 17.6$  Hz, 2H), 5.37 (d,  $J = 10.8$  Hz, 2H), 2.09 (s, 6H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 172.14, 161.73, 155.66, 153.12, 139.10, 135.99, 133.32, 130.13, 126.47, 125.84, 122.79, 121.84, 121.08, 115.62, 15.14. Elemental analysis for  $\text{C}_{44}\text{H}_{28}\text{O}_2\text{N}_2\text{F}_8\text{TiCl}_2$  (%): Calcd.: C, 59.55; H, 3.18; N, 3.16; Found: C, 59.51; H, 3.24; N, 3.12.

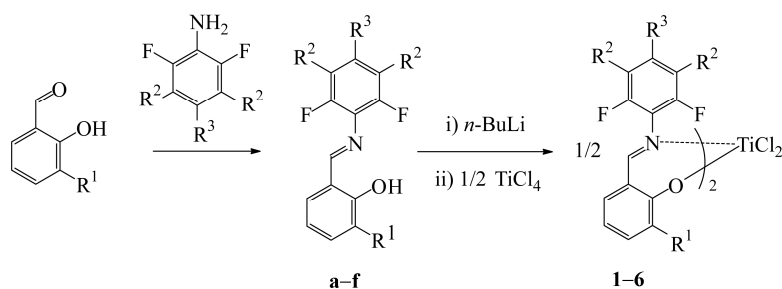
**Ethylene Polymerization**

Ethylene polymerization was carried out under atmospheric pressure in toluene using a 500 mL glass reactor equipped with a mechanical stirrer. The reactor was charged and evacuated with nitrogen (3 times) and ethylene (twice). Toluene (250 mL) was introduced into the ethylene-purged reactor and stirred vigorously (600 r/min). Then the polymerization was initiated by injecting toluene solution of DMAO followed by toluene solution of complex into the reactor with vigorous stirring (600 r/min). After a certain polymerization time, 4 mL acidic ethanol (10 mL HCl dissolved in 1000 mL ethanol) was added to terminate the polymerization, and then large amount of acidic ethanol was added to the resulted mixture. The polyethylene was isolated by filtration, washed with ethanol for several times, and dried in vacuo to constant weight (60 °C, vacuum oven).

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Ligands and Complexes

The synthesis of ligand **a** and complex **1** was previously reported<sup>[22]</sup>. Phenoxy-imine ligands **b**, **c**, **d**, **e** and **f** were easily prepared in high yield (85%–90%) by the Schiff base condensation reaction of salicylaldehyde and corresponding aniline. Complexes **2**, **3**, **4**, **5**, and **6** were synthesized in low to high yield (25.9%–79.3%) by treating  $\text{TiCl}_4$  with two equivalents of lithium salts of corresponding ligands (Scheme 1).



Ligand **a**/Complex **1**:  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ;  
 Ligand **b**/Complex **2**:  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = 4\text{-vinylphenyl}$ ;  
 Ligand **c**/Complex **3**:  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ;  
 Ligand **d**/Complex **4**:  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{H}$ ,  $\text{R}^3 = 4\text{-vinylphenyl}$ ;  
 Ligand **e**/Complex **5**:  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{F}$ ,  $\text{R}^3 = \text{H}$ ;  
 Ligand **f**/Complex **6**:  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{F}$ ,  $\text{R}^3 = 4\text{-vinylphenyl}$ ;

**Scheme 1** Synthetic route of titanium complexes

### Catalytic Ethylene Polymerization Behavior

#### The effect of some substituents on the ethylene polymerization

DMAO was used as cocatalyst to activate complexes **1–6** for ethylene polymerization in toluene during 30 min under atmospheric pressure. The effect of  $\text{R}^1$ ,  $\text{R}^3$  and  $\text{R}^2$  (fluorine or hydrogen atom) groups on ethylene polymerization has been disclosed in this research (Table 1).

**Table 1.** Results of ethylene polymerization with complexes **1–6**/DMAO<sup>a</sup>

| Entry | Complex  | Activity <sup>b</sup> | $T_m$ (°C) | $M_w (\times 10^4)^c$ | $M_w/M_n^c$ |
|-------|----------|-----------------------|------------|-----------------------|-------------|
| 1     | <b>1</b> | 151                   | 135.2      | 20.6                  | 2.64        |
| 2     | <b>2</b> | 106                   | 132.3      | 53.7                  | 6.74        |
| 3     | <b>3</b> | 561                   | 134.9      | 31.8                  | 1.19        |
| 4     | <b>4</b> | 160                   | 133.2      | 31.9                  | 2.26        |
| 5     | <b>5</b> | 869                   | 134.3      | 100.3                 | 1.80        |
| 6     | <b>6</b> | 529                   | 134.4      | 140.8                 | 1.43        |

<sup>a</sup> Reaction conditions: 0.1 MPa, polymerization temperature 25 °C, 250 mL of toluene, stirring rate: 600 r/min, DMAO as cocatalyst (10 mmol), 5  $\mu\text{mol}$  of complex, 30 min;

<sup>b</sup> Unit, kg PE/(mol Ti·h);

<sup>c</sup>  $M_w$  and MWD of the polymers were determined at 150 °C using polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent at a flow rate of 1 mL/min.

These data disclosed that the steric bulk of the  $\text{R}^1$  substituent affects catalytic activity and molecular weight of resultant PEs. Complex **1** having a H atom at the  $\text{R}^1$  position produced polyethylene with a  $M_w$  of 206000, displaying a moderate activity of 151 kg PE/(mol Ti·h). Under the same conditions, complex **3** bearing a sterically hindered methyl at the  $\text{R}^1$  position, gave much higher molecular weight polyethylene ( $M_w = 318000$ ) with a considerably enhanced activity of 561 kg PE/(mol Ti·h). Likewise, a similar but a little different conclusion can be drawn from the comparison of complex **2** and complex **4**: the molecular weight of polyethylene produced by complex **2** is higher than that by complex **4** (concerning the wider MWD of PE

produced by complex **2**, number average molecular weight  $M_n$  by complex **2** is lower than that by complex **4**), while catalytic activity followed the same trend. According to Vyboishchikov's conclusion<sup>[23]</sup>, the increase of activity can be attributed to the fact that bulky  $R^1$  substituents can enhance the dissociation of unexpected coordination species (formed by metal center coordination with competitors such as L donors, counteranions, alkylaluminums, and so on) and shift the equilibrium to the olefin-coordination species.

The  $R^3$  substituent, a VPY group, also has an important influence on the catalytic performance of complexes distinguished from  $R^1$  substituent. Complex **2**, having a VPY at the  $R^3$  position, exhibits a lower activity of 106 kg PE/(mol Ti·h) and a higher  $M_w$  (537000) of produced polyethylene than complex **1**. In general, the introduction of VPY to  $N$ -aryl group increases product molecular weight at the expense of catalytic activity (except for complexes **4** and **3**, the molecular weight of PEs produced by them are nearly the same). The VPY effect on ethylene polymerization is similar to the catalytic performance of some FI complexes to which certain substituents are introduced to the *ortho*-position of  $N$ -aryl groups<sup>[12, 24]</sup>, however, to excavate the intrinsic reason, fussy molecular structure calculation are needed.

Alternatively, the effect of *meta*-F atoms on the catalytic activity and molecular weight of resultant PEs is also prominent. Complex **6** bearing *meta*-F atoms on  $N$ -aryl group exhibited much higher catalytic activity (529 kg PE/(mol Ti·h)) and the ability to synthesize higher molecular weight PE ( $M_w = 1408000$ ) than complex **4**. Similarly, the effect of F atoms also occurred on complex **5** and complex **3**. Therefore, the introduction of fluorine to *meta*-position of  $N$ -aryl group can result in the increase of both catalytic activity and molecular weight. The same conclusion can be found in some related literatures<sup>[25, 26]</sup>. However, there is a striking difference between two kinds of catalysts in terms of the effect of *meta*-fluorine on the control of molecular weight distribution of resultant PEs. For complex **3**, the "living" characteristics would be damaged by introducing F atoms to *meta*-position of  $N$ -aryl group, which is in accordance with the fact observed by Fujita<sup>[26]</sup>. However, the introduction of *meta*-F atoms to  $N$ -aryl of complex **4** would result in more uniform chain structure of PE. The difference between these two kinds of catalysts may be attributed to a strong interaction between bulky VPY group and *meta*-fluorine, that is, the existence of VPY group can undermine the damaging effect on "living" characteristics by *meta*-fluorine.

#### "Living" polymerization of complex **3**/DMAO

Searching for an industrially applicable living catalyst for olefin coordination polymerization is a limitless pursuit from both academia and industry. Precise control over polymer structure by living olefin polymerization would lead to the advent of some unique materials, such as controlled polyolefin-based block copolymers and chain end-functionalized polymers<sup>[27]</sup>. The appearance of fluorinated phenoxy-imine titanium complexes (FI catalysts) made "living" polymerization at room temperature or higher (no more than 50 °C) possible and set off a research boom<sup>[28]</sup>. Among these six catalysts, only complex **3** showed "living" characteristics upon activation with dried MAO.

To investigate the "living" characteristics of complex **3**/DMAO system,  $M_n$  and  $M_w/M_n$  values versus polymer yield were performed under room temperature (25 °C). As a result, a linear relationship between  $M_n$  and polymer yield, as well as almost constant PDI values ( $M_w/M_n = 1.07$ – $1.15$ ), were found (Table 2 and Fig. 1).

**Table 2.** "Living" ethylene polymerization with complex **3**/DMAO<sup>a</sup>

| Time (min) | Polymer yield (g) | $M_n (\times 10^4)^b$ | $M_w/M_n^b$ |
|------------|-------------------|-----------------------|-------------|
| 1          | 0.07              | 1.6                   | 1.07        |
| 5          | 0.30              | 6.0                   | 1.11        |
| 10         | 0.62              | 11.0                  | 1.14        |
| 20         | 1.20              | 20.7                  | 1.15        |

<sup>a</sup> Reaction conditions: 0.1 MPa, polymerization temperature 25 °C, 250 mL of toluene, stirring rate: 600 r/min, DMAO as cocatalyst (10 mmol), 5  $\mu$ mol of complex;

<sup>b</sup>  $M_n$  and MWD of the polymers were determined at 150 °C using polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent at a flow rate of 1 mL/min.

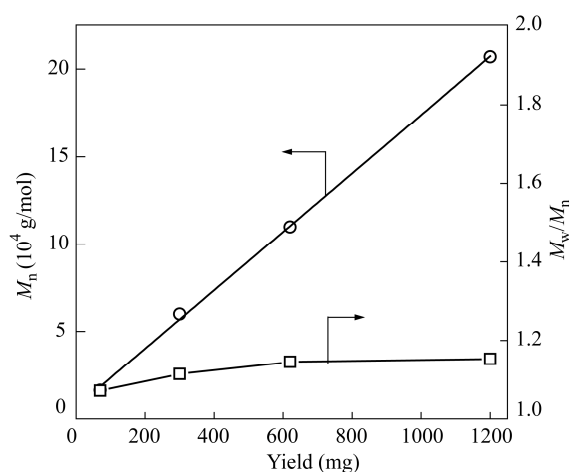


**Fig. 1** Plots of  $M_n$  and  $M_w/M_n$  versus polymer yield for polyethylene produced with complex **3**/DMAO at 25 °C

In terms of the reason for “living” nature of *ortho*-fluorinated (on N-aryl) FI catalyst, Fujita<sup>[29]</sup> proposed a rationale by DFT calculation that there is an probable attractive and electrostatic interaction between the negatively charged *ortho*-F and positively charged  $\beta$ -H, this interaction causes an electronic stable  $\beta$ -agostic state which is a intermediate for  $\beta$ -H chain transfer reactions. To some extent, this theory accounts for the livingness of catalyst **3** in spite of there being academical disputes between Fujita and Coates<sup>[12, 30]</sup>.

#### Polyethylene morphology

Like some self-immobilized catalysts<sup>[31–34]</sup>, catalytic performance of catalyst **2** possessed catalytic heterogeneity towards ethylene polymerization. Catalyst **2** bearing VPY substituent exhibited an ethylene polymerization activity of 106 kg PE/(mol Ti·h) with PDI value of 6.74 (Table 1, Fig. 2). However, catalyst **1**, having no VPY group, exhibited a higher activity of 151 kg PE/(mol Ti·h) with less PDI value of 2.64 under the same conditions. The similar effect also happened on catalyst **4**, however, the little PDI value (2.26) and fractured PE morphology (Fig. 3) exhibits that there is not so intense heterogeneous nature of this catalyst as catalyst **2**. In addition, the single-site catalyst **6** exhibited a highly catalytic homogeneity towards ethylene polymerization. Therefore, in this system, the catalytic heterogeneity caused by VPY group follows the order: **2** > **4** > **6**.

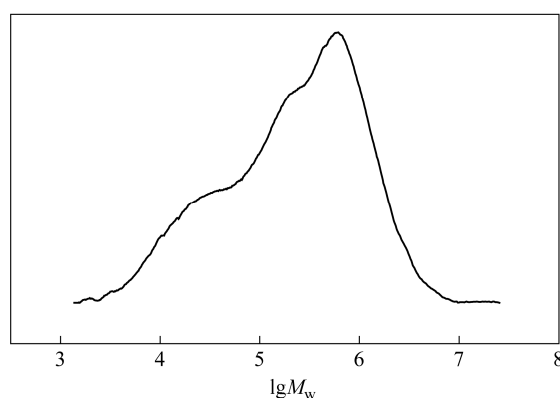


**Fig. 2** Multimodal MWD of PE produced by Cat **2** at 25 °C

Comparing SEM images of resulted polymers (Fig. 3), the polymer produced by catalyst **1** has a block shape with several gouges inside it, indicating an amorphous morphology caused by typically homogeneous catalysis. However, from the SEM image of the PE produced by catalyst **2**, a large amount of round

nanoparticles (1–50 nm) aggregate into spherical microparticles (1–5  $\mu\text{m}$ ) and distribute on the polyethylene matrix, and this partially improved particle morphology relieved the “fouling” of glass reactor.

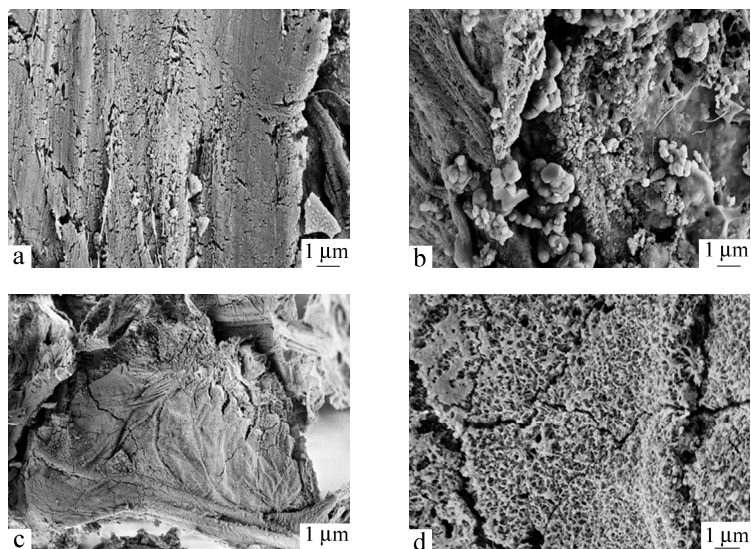


**Fig. 3** The SEM images of polymer morphology: (a) PE produced by complex **1**/DMAO, (b) PE produced by complex **2**/DMAO, (c) PE produced by complex **4**/DMAO and (d) magnified image of PE produced by complex **4**/DMAO

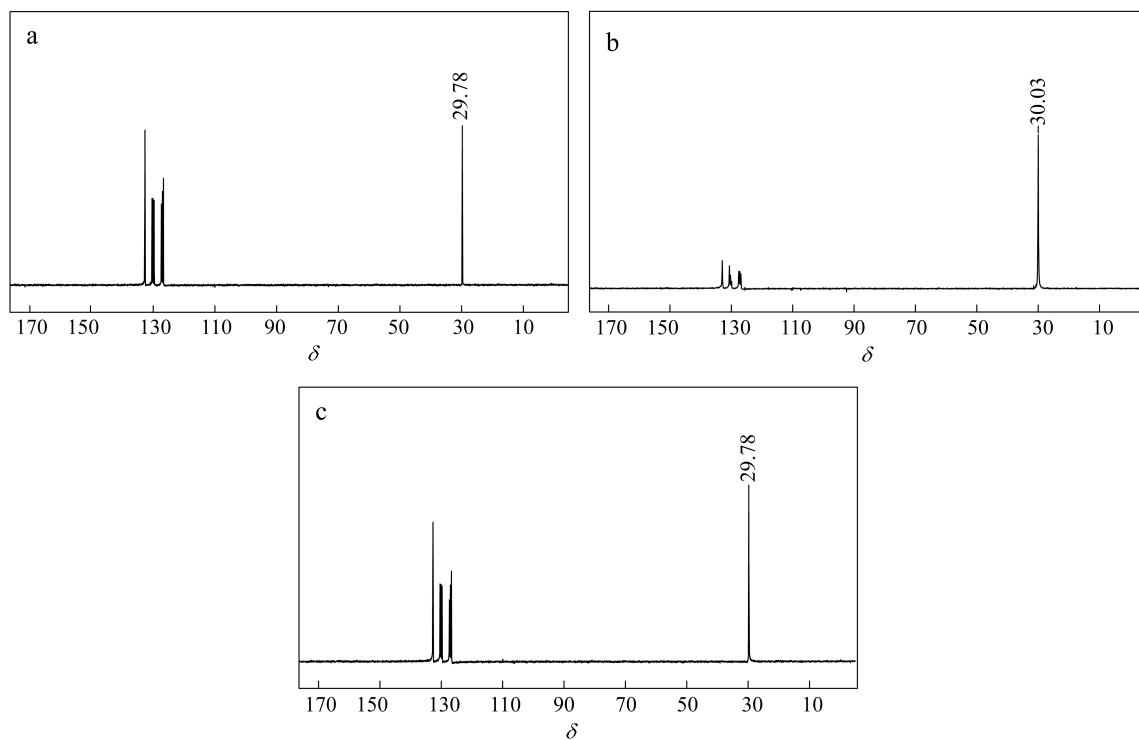


**Fig. 4** The  $^{13}\text{C}$ -NMR spectra of PE produced by complex **2** (a), complex **4** (b) and complex **6** (c) ( $1,2\text{-C}_6\text{D}_4\text{Cl}_2$  was used as solvent,  $130^\circ\text{C}$ .)

In order to find out the reason for the effect of VPY, the microstructure of PEs produced by complex **2**, **4** and **6** are characterized by  $^{13}\text{C}$ -NMR (Fig. 4). The spectra show the main peaks around  $\delta = 30$ , indicating the linear characteristics of the PEs. There are no signals for aromatic compounds in the  $\delta$  range of 15–175, which proves that the ligands cannot be incorporated in the polymer chain in terms of self immobilization effect.

The reason for the catalytic heterogeneity of catalysts **2** and **4** can be probably attributed to the coordination effect of vinyl group with active species which would impose large steric hindrance on metal center, thus causing a decreased catalytic activity and broad molecular weight distribution. For catalyst **2**, the steric hindrance for vinyl group reaching to active species is much weaker than that for catalyst **4**, thus the steric hindrance around metal center will become larger, leading to a more intense catalytic heterogeneity of catalyst **2** than that of catalyst **4**. However, the strong interaction between *meta*-F atoms and VPY group protects catalyst **6** from catalytic heterogeneity in ethylene polymerization.

## CONCLUSIONS

In summary, the catalytic heterogeneity of ethylene polymerization is enhanced by introducing VPY to *N*-aryl groups of FI catalysts. For the structure difference, the three complexes bearing VPY group exhibit catalytic heterogeneity towards ethylene polymerization at different extents, which follows the order of **2** > **4** > **6**. The catalytic ethylene polymerization behavior of the three parent complexes without VPY substituent on *N*-aryl groups has successfully clarified the VPY effects: One, to markedly undermine the catalytic activity; the other, to intensify catalytic heterogeneity towards ethylene polymerization. However, the interaction between VPY group and *meta*-fluorine endows catalyst **6** with a single-site characteristics. The  $^{13}\text{C}$ -NMR analysis of polyethylene produced by catalysts **2**, **4** and **6** reveals that the complexes can't be incorporated in the polymer chains and the catalytic heterogeneity are not caused by self-immobilization effect. Furthermore, the "living" characteristics of catalyst **3** is disclosed.

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