

## Synthesis and Evaluation of Two New FI-Ti Catalysts for Living Polymerization of Ethylene

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**ABSTRACT:** Two new FI complexes, *bis*[*N*-(3-allylsalicylidene)-pentafluoroanilinato]titanium(IV) dichloride (**AFI**) and *bis*[*N*-(3-propylsalicylidene)-pentafluoroanilinato]titanium(IV) dichloride (**PFI**) were designed and synthesized as catalysts for living polymerization of ethylene. The two complexes were characterized by elemental analysis, spectroscopy and X-ray single diffraction. The catalysts were evaluated in ethylene polymerization under atmospheric pressure. It was found that both catalysts exhibited high activity and good livingness. The effects of temperature and *d*MAO/Ti molar ratio on the polymerization behavior of **AFI** were studied in detail. Elevating temperature increased self-immobilization of the **AFI** catalyst, which broadened the polymer molecular weight distribution.

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### INTRODUCTION

Living polymerization provides a powerful tool for precisely design and control of polymer chain microstructure, including a variety of homo-, co-, and block polymers,<sup>1</sup> for a broad range of targeted applications. In the past decade, there were numerous studies of catalysts for living polymerization of olefins at or above room temperature.<sup>2–24</sup> However, few supported catalysts were reported.<sup>25,26</sup>

Heterogeneous catalysts are preferred in industrial production of polyolefins. The advantages of heterogeneous catalysis are similar to those associated with gas phase and slurry processes, including *in situ* grain formation, no fouling on the reactor wall, and rapid heat dissipation. MgCl<sub>2</sub> and silica are commonly used to support catalysts. However, the inorganic supports generally reduce catalyst activity. Hence, the concept of heterogenizing homogeneous catalysts was proposed to preserve the activity of homogeneous catalysts and at the same time to achieve the advantages of heterogeneous polymerization.<sup>27</sup> This is accomplished by introducing an alkenyl group on the ligand. During polymerization, the catalyst center may become immobilized by incorporation into growing polymer chains while still remaining active. This kind of polymerization is also called self-immobilization.

There were several self-immobilized metallocene and half-metallocene catalysts reported.<sup>27–37</sup> Other types of self-immobilized Ti, Zr, and late-transition metal catalysts were also synthesized

and discussed in literatures.<sup>38–41</sup> However, we have not seen a self-immobilization technique for living polymerization of olefin. Living polymerization is also an ideal process for studying the influence of self-immobilization on polymer chain microstructure. Introduction of a functional alkenyl group provides flexibility to change catalyst structure and to investigate effects of the structure on polymerization behavior.

*N*-fluoroaryl FI-Ti catalysts are a well-known class of high-temperature catalysts for living polymerization of olefin, having high propagation rate and narrow molecular weight distribution.<sup>2–9</sup> In this work, two new FI-Ti catalyst precursors, *bis*[*N*-(3-allylsalicylidene)-pentafluoroanilinato]titanium(IV) dichloride (**AFI**) and *bis*[*N*-(3-propylsalicylidene)-pentafluoroanilinato]titanium(IV) dichloride (**PFI**), were synthesized and characterized for the living polymerization of ethylene. The effects of allyl group on polymerization were investigated with **AFI**. **PFI** was studied mainly for a comparison reason.

### EXPERIMENTAL

#### General Considerations

All manipulations were performed under a purified nitrogen atmosphere using Schlenk techniques. 3-Allyl-2-hydroxybenzaldehyde was purchased from J&K Scientific Company. Toluene (from TEDIA Company) and hexane (from Amethyst Chemicals) were distilled from potassium/benzophenone. Polymerization-grade

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**Table I.** Summary of the Crystallographic Data and Refinement Parameters for Complexes AFI and PFI

Data	AFI	PFI
Formula	C <sub>32</sub> H <sub>18</sub> Cl <sub>2</sub> F <sub>10</sub> N <sub>2</sub> O <sub>2</sub> Ti	C <sub>32</sub> H <sub>22</sub> Cl <sub>2</sub> F <sub>10</sub> N <sub>2</sub> O <sub>2</sub> Ti
Formula weight	771.28	775.32
Temperature (K)	296(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
<i>a</i> (Å)	27.1030(13)	27.056(5)
<i>b</i> (Å)	8.5855(3)	8.7884(18)
<i>c</i> (Å)	14.0458(5)	14.002(3)
$\alpha$ (°)	90.00	90.00
$\beta$ (°)	102.024(4)	102.01(3)
$\gamma$ (°)	90.00	90.00
Volume (Å <sup>3</sup> )	3196.6(2)	3256.5(11)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.603	1.581
$\mu$ (mm <sup>-1</sup> )	0.527	0.518
<i>F</i> (000)	1544	1560
Crystal size (mm)	0.27 × 0.25 × 0.06	0.56 × 0.48 × 0.35
$\theta$ range (°)	3.04–27.48	3.00–27.45
Limiting indices	−35 ≤ <i>h</i> ≤ 35, −11 ≤ <i>k</i> ≤ 10, −18 ≤ <i>l</i> ≤ 18	−35 ≤ <i>h</i> ≤ 35, −11 ≤ <i>k</i> ≤ 10, −18 ≤ <i>l</i> ≤ 18
No. of rflns collected	30,436	48801
No. of unique rflns	7,304	7400
No. of obsd rflns [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2,577	4265
Completeness to $\theta$ (%)	99.6 ( $\theta = 27.48^\circ$ )	99.3 ( $\theta = 27.45^\circ$ )
Absorption correction	empirical	empirical
No. of parameters	442	442
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.973	1.149
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0791, <i>wR</i> <sub>2</sub> = 0.1567	<i>R</i> <sub>1</sub> = 0.0599, <i>wR</i> <sub>2</sub> = 0.1585
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.2327, <i>wR</i> <sub>2</sub> = 0.2167	<i>R</i> <sub>1</sub> = 0.1084, <i>wR</i> <sub>2</sub> = 0.2018
Largest diff. peak, hole (eÅ <sup>-3</sup> )	0.405, −0.316	0.456, −0.929

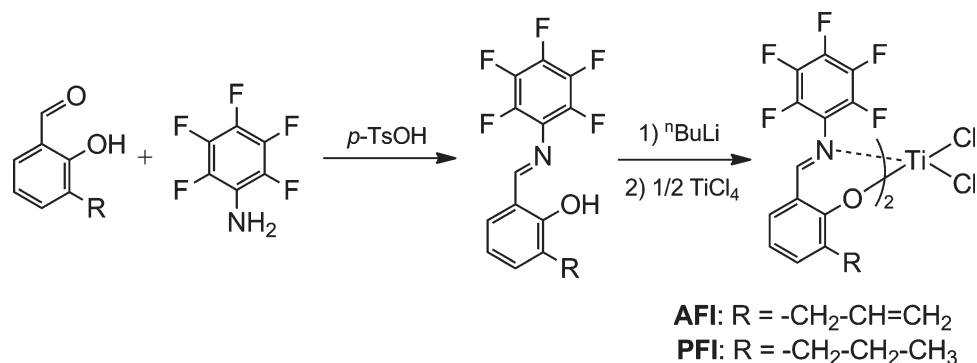
ethylene (99.99%) was purchased from TOPGRAND Petrification Industry Gas. Ltd. MAO (from Albemarle) was dried in *vacuo* to remove AlMe<sub>3</sub> and obtain *d*MAO (dried methylaluminoxane) as cocatalyst.

Molecular weight and distribution were measured at 150°C with a 1,2,4-trichlorobenzene PL-GPC 220. The polymer melting temperature was measured with Perkin-Elmer DSC 7 in standard mode. The polymer samples were first heated to 160°C at 10°C/min to eliminate thermal history and held constant for 2 min at 160°C. The samples were then cooled to 30°C at 10°C/min and held constant for 2 min at 30°C, before heated to 160°C at 10°C/min. FTIR spectra were recorded on a Nicolet5700 spectrometer using KBr disks in the range 4000–400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra was recorded on a Bruker DMX-400 or a Bruker DMX-500 NMR instrument. Element analysis data were collected using a Flash EA 1112 elemental analyzer. The morphology of polyethylene particle was determined with a Hitachi S-4700 SEM.

#### Preparation of Bis[*N*-(3-allylsalicylidene)-pentafluoroanilinato]titanium(IV) dichloride (AFI)

**Synthesis of Ligand.** 3-Allyl-2-hydroxybenzaldehyde (10 mmol) and 2,3,4,5,6-pentafluoroaniline (10 mmol) were added to 10 mL ethanol with *p*-toluenesulfonic acid as a catalyst, refluxed under 80°C for 12 h, and then recrystallized. Yellow crystals were obtained in 81.6% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.50 (d, 2H, *J* = 6.5 Hz, Ar—CH<sub>2</sub>—), 5.13 (m, 2H, =CH<sub>2</sub>), 6.05 (m, 1H, —CH=), 6.95 (t, 1H, *J* = 7.5 Hz, aromatic-H), 7.30 (d, 1H, *J* = 7.5 Hz, aromatic-H), 7.36 (d, 1H, *J* = 7.5 Hz, aromatic-H), 8.83 (s, 1H, CH=N), 12.53 (s, 1H, Ar—OH). FTIR (KBr disk, cm<sup>-1</sup>): 3448 ( $\nu_{\text{O—H}}$ ), 2912, 1649 ( $\nu_{\text{C=N}}$ ), 1637 ( $\nu_{\text{C=C}}$ ), 1604, 1578, 1519, 1509, 1480, 1444, 1426, 1367, 1307, 1271, 1240, 1225, 1162, 1105, 1074, 1022, 996, 973, 914, 829, 756. Anal. found: N 4.33, C 58.86, H 3.05. Calcd. for C<sub>16</sub>H<sub>10</sub>NOF<sub>5</sub>: N 4.28, C 58.67, H 3.06.

**Synthesis of Complex.** *n*-BuLi/*n*-hexane solution of 1.3 mL (1.6M, 2.07 mmol) was added dropwise to a stirred solution of



**Scheme 1.** Synthesis route of complexes AFI and PFI.

*N*-(3-allylsalicylidene)-pentafluoroaniline (2.07 mmol) in 20 mL of dried ether at  $-78^\circ\text{C}$ . The solution was warmed to room temperature and stirred for 3 h. The obtained solution was slowly poured into a stirred solution of  $\text{TiCl}_4/\text{CH}_2\text{Cl}_2$  (1M, 1.04 mmol) in 15 mL dried ether at  $-78^\circ\text{C}$  for 5 min. The vessel containing Li salt was washed twice with 5 mL dried ether. The solution was warmed to room temperature and stirred for 42 h. The solvent was evacuated and an additional 30 mL of extra dry  $\text{CH}_2\text{Cl}_2$  was added. The solution was stirred for 15 min and then filtered through diatomite. The residue was washed with 10 mL  $\text{CH}_2\text{Cl}_2$ . The solvent was evacuated and the resulting solid was then washed twice with 15 mL dried *n*-hexane before drying in vacuo. Finally, 0.67 g reddish brown solid was obtained in 84.0% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.04 (q, 2H, Ar- $\text{CH}_2$ -), 3.30 (q, 2H, Ar- $\text{CH}_2$ -), 5.02–5.13 (m, 4H,  $=\text{CH}_2$ ), 5.78 (m, 2H,  $-\text{CH}=\text{}$ ), 6.97 (t, 2H,  $J = 7.8$  Hz, aromatic-H), 7.24 (d, 2H,  $J = 7.5$  Hz, aromatic-H), 7.43 (d, 2H,  $J = 7.5$  Hz, aromatic-H), 8.18 (s, 2H,  $\text{CH}=\text{N}$ ). Anal. found: N 3.42, C 48.57, H 2.55. Calcd. for  $\text{TiC}_{32}\text{H}_{18}\text{N}_2\text{O}_2\text{F}_{10}\text{Cl}_2 \cdot 1/3\text{CH}_2\text{Cl}_2$ : N 3.50, C 48.54, H 2.35.

#### Preparation of Bis[*N*-(3-propylsalicylidene)-pentafluoroanilinato]titanium(IV) dichloride (PFI)

**Synthesis of Ligand.** 3-Propyl-2-hydroxybenzaldehyde was synthesized according to the literature procedures.<sup>42</sup> The following

steps are the same as those given for the ligand of AFI. Yellow crystal was obtained in 79.8% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.00 (t, 3H,  $J = 7.4$  Hz,  $-\text{CH}_3$ ), 1.70 (m, 2H,  $-\text{CH}_2-$ ), 2.71 (t, 2H,  $J = 7.6$  Hz, Ar- $\text{CH}_2-$ ), 6.93 (t, 1H,  $J = 7.6$  Hz, aromatic-H), 7.28 (d, 1H,  $J = 8.0$  Hz, aromatic-H), 7.34 (d, 1H,  $J = 7.2$  Hz, aromatic-H), 8.83 (s, 1H,  $\text{CH}=\text{N}$ ), 12.51 (s, 1H,  $-\text{OH}$ ). FTIR (KBr disk,  $\text{cm}^{-1}$ ): 3448 ( $\nu_{\text{O-H}}$ ), 2960, 1650 ( $\nu_{\text{C-N}}$ ), 1604, 1578, 1519, 1508, 1480, 1445, 1426, 1370, 1307, 1268, 1244, 1164, 1096, 1071, 1016, 971, 823, 753. Anal. found: N 4.29, C 58.55, H 3.68. Calcd. for  $\text{C}_{16}\text{H}_{12}\text{NOF}_5$ : N 4.28, C 58.67, H 3.67.

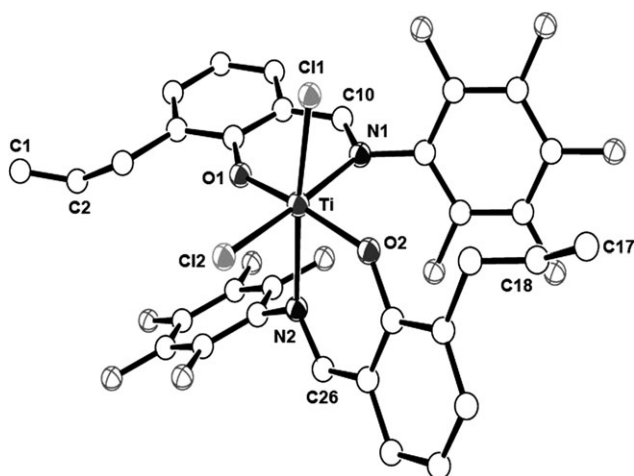
**Synthesis of Complex.** The steps to synthesize PFI were the same as AFI. Reddish brown solid was obtained in 76.8% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.98 (t, 6H,  $J = 7.2$  Hz,  $-\text{CH}_3$ ), 1.54–1.67 (m, 4H,  $-\text{CH}_2-$ ), 2.24 (m, 2H, Ar- $\text{CH}_2-$ ), 2.52 (m, 2H, Ar- $\text{CH}_2-$ ), 7.01 (t, 2H,  $J = 7.6$  Hz, aromatic-H), 7.30 (d, 2H,  $J = 8.0$  Hz, aromatic-H), 7.47 (d, 2H,  $J = 7.6$  Hz, aromatic-H), 8.25 (s, 2H,  $\text{CH}=\text{N}$ ). Anal. found: N 3.25, C 47.57, H 3.10. Calcd. for  $\text{TiC}_{32}\text{H}_{22}\text{N}_2\text{O}_2\text{F}_{10}\text{Cl}_2 \cdot 1/2\text{CH}_2\text{Cl}_2$ : N 3.42, C 47.71, H 2.81.

#### Ethylene Polymerization

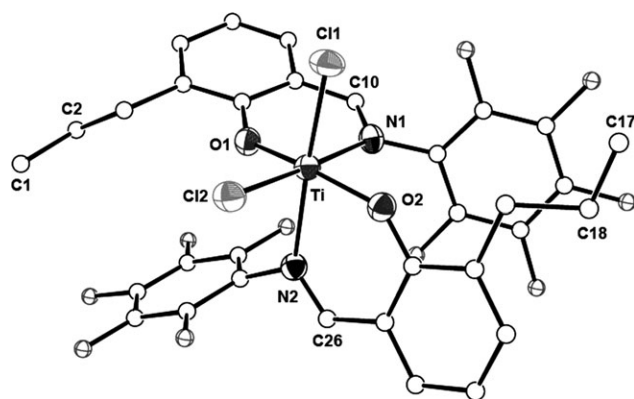
Ethylene polymerization was carried out in 250 mL glass reactor under atmospheric pressure. Before the polymerization, the reactor was vacuum dried with  $600^\circ\text{C}$  heat Gun and it was purged 3 times with nitrogen replaced twice with ethylene. Toluene of 150 mL was introduced into the reactor stirred 600 rpm. The solution of *d*MAO in toluene was injected. Subsequently 3  $\mu\text{mol}$  of catalysts/toluene solution was injected after sonication. After a preset time, 10 mL 1 wt % HCl/ethanol solution was injected into the reactor to terminate the polymerization. Hundred milliliter of 1 wt % HCl/ethanol solution was added to the mixture. The polymer yield was filtered, washed by ethanol, and dried overnight in a vacuum oven at  $60^\circ\text{C}$ .

#### Crystal Structure Determination

The single-crystal data for AFI and PFI were collected using a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters were determined by global refinement of the positions of all collected reflections. The X-ray intensities were corrected for Lorentz, polarization and empirical absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  with all nonhydrogen atoms anisotropically. All the



**Figure 1.** Molecular structure of complex AFI (all hydrogen atoms have been omitted for clarity).



**Figure 2.** Molecular structure of complex **PFI** (all hydrogen atoms have been omitted for clarity).

hydrogen atoms were included on calculated positions. Structure solution and refinement were performed using the *SHELXL-97* Package.<sup>43</sup> Table I summarizes the crystallographic data and processing parameters for complexes **AFI** and **PFI**.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of **AFI** and **PFI** Complexes

Scheme 1 shows the synthesis routes of the complexes **AFI** and **PFI**, which mainly followed the open literature.<sup>3</sup> Comparing with the ligand (3.50 ppm), the <sup>1</sup>H NMR chemical shifts of the Ar-methylene methylene groups in **AFI** complex apparently moved to higher fields and separated into two quartet peaks (3.04 and 3.30 ppm), indicating that the two Ar-methylene groups and the four hydrogen atoms on them

**Table II.** Selected Bond Lengths (Å) and Angles (°) of Complexes **AFI** and **PFI**

	<b>AFI</b>	<b>PFI</b>
Bond lengths		
Ti–Cl1	2.262(18)	2.300(12)
Ti–Cl2	2.283(17)	2.273(12)
Ti–O1	1.820(4)	1.851(2)
Ti–O2	1.842(4)	1.846(2)
Ti–N1	2.214(5)	2.261(3)
Ti–N2	2.240(5)	2.236(3)
C10–N1	1.289(7)	1.299(5)
C26–N2	1.295(6)	1.308(4)
C1–C2	1.287(5)	1.512(7)
C17–C18	1.293(5)	1.379(10)
Bond angles		
O1–Ti–O2	161.73(17)	160.98(12)
N1–Ti–N2	91.92(16)	93.09(11)
Cl1–Ti–Cl2	94.43(7)	94.44(4)

are in different environments. So do the Ar-methylene groups of **PFI**. The unambiguous structures of **AFI** and **PFI** complexes were further confirmed by single crystal X-ray diffraction analysis.

### Crystal Structure of **AFI** and **PFI**

The single crystals of the **AFI** and **PFI** complexes suitable for X-ray diffraction analysis were obtained by slow diffusion of

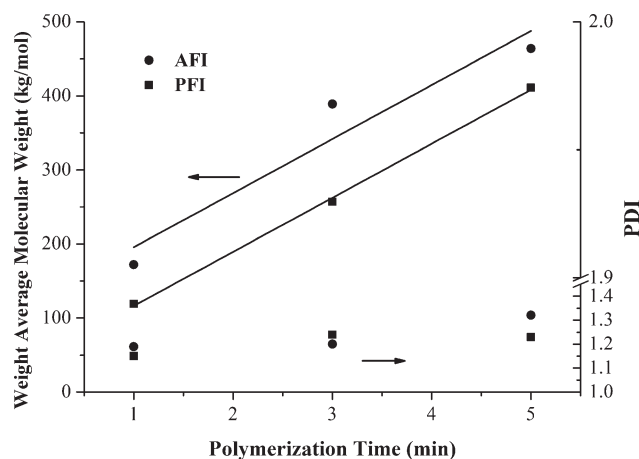
**Table III.** Results of Ethylene Polymerization with **AFI** and **PFI**

Run	Al/Ti	Temp (°C)	Time (min)	Yield (g)	$M_n$ (kg/mol)	$M_w$ (kg/mol)	PDI <sup>b</sup>	Num. of polymer chains (μmol)	$T_m$ (°C)	$X_c^c$ (%)
<b>AFI</b>										
1	500	25	5	0.41	153	238	1.56	2.68	135.0	56.8
2	1000	25	5	1.25	310	423	1.37	4.03	135.0	39.4
3	2000	25	5	1.20	352	464	1.32	3.41	136.4	47.2
4	2000	25	1	0.36	145	172	1.19	2.48	137.0	58.0
5	2000	25	3	0.96	322	389	1.20	2.99	134.0	27.2
6	2000	25	15	3.13	483	801	1.66	6.48	135.9	41.9
7	2000	0	5	0.90	252	394	1.56	3.57	135.4	49.8
8	2000	50	5	1.32	284	415	1.46	4.65	135.9	46.8
<b>PFI</b>										
9	2000	0	5	0.49	209	284	1.36	2.34	136.8	54.2
10	2000	25	5	0.74	333	411	1.23	2.22	135.2	48.0
11	2000	25	1	0.20	104	119	1.15	1.92	134.0	55.7
12	2000	25	3	0.53	207	257	1.24	2.56	134.7	48.6
13	2000	50	5	0.85	332	409	1.23	2.56	135.5	45.5
14	2000	25	15	1.38	590	905	1.53	2.34	136.0	41.7

<sup>a</sup>Polymerization conditions: 3 μmol catalyst, 150 mL toluene, 600 rpm mechanical stir, 1 atm.

<sup>b</sup>PDI =  $M_w/M_n$ .

<sup>c</sup>The heat of fusion of completely crystalline PE is 290 J/g.<sup>44</sup>



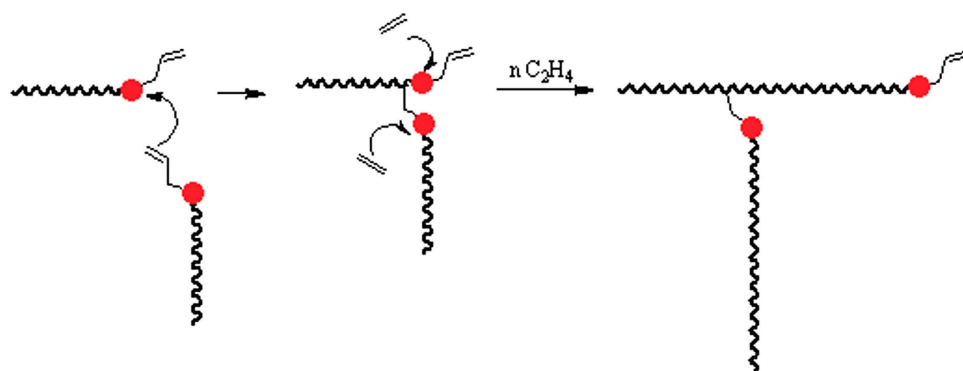
**Figure 3.** Molecular weight and distribution index versus polymerization time in the presence of AFI and PFI catalysts at 25°C.

*n*-hexane to their corresponding solutions in dichloromethane, respectively. Figures 1 and 2 show their molecular structures with selected bond lengths and angles listed in Table II.

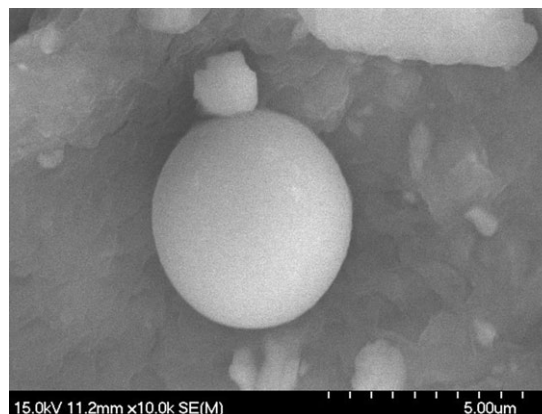
The AFI and PFI complexes display distorted octahedral geometries around the titanium centers, in which the titanium atom is bound to two *cis*-coordinated phenoxy-imine [O,N] chelating ligands. The oxygen atoms are situated in *trans* positions with O1—Ti—O2 bond angles: 161.73(17)° for AFI and 160.98(12)° for PFI, respectively; whereas the two nitrogen atoms and two chlorine atoms are located in *cis* positions. All the bond lengths and bond angles around the titanium centers are similar to the phenoxy-imine titanium complex with *tert*-butyl group in the phenoxy benzene ring and pentafluorophenyl.<sup>2,3</sup>

### Ethylene Polymerization

Table III reports the ethylene polymerization results of AFI and PFI. Both catalysts exhibited high activities, in the order of 10<sup>6</sup> g PE/(mol Ti h bar). The activity and molecule weight obviously increased with increasing the *d*MAO/Ti ratio from 500 to 1000. When the *d*MAO/Ti ratio was increased to 2000, the molecular weight increased slightly and the PDI became narrower (Run 1–3). On the basis of these, all the other experiments were carried out by using the *d*MAO/Ti ratio of 2000.



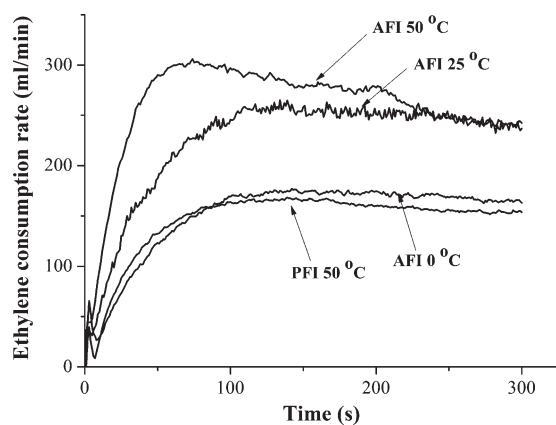
**Scheme 2.** Proposed mechanism of self-immobilization in ethylene polymerization with AFI. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** The SEM photo of polyethylene particle for Run 8.

Figure 3 shows that the ethylene polymerization with both catalysts preceded in a living manner at 25°C in the first 5 min. AFI gave a faster rate than PFI, whereas the rate slowed down with growing chains for AFI. During all the polymerizations, the solution became slurry, which should be attributed to the precipitation of the polymer from the solvent. The polyethylene prepared with AFI had slightly broader molecular weight distribution than that with PFI. However, the MWD could become much broader in a prolonged time of polymerization with both AFI and PFI. After 15 min (Runs 6 and 14), the number of polymer chains doubled the catalyst amount for AFI, but not for PFI. It suggested the occurrence of chain transfer reactions, which could be attributed to self-immobilization of the AFI complex rather than the precipitation of polymer.

The self-immobilization as a side reaction was dependent on the reaction temperature and became severe at an elevated temperature (50°C, Run 8). Chain transfer happened with broader PDI because the number of the polymer chains reached about 1.5 times the amount of AFI. However, there was no sign that chain transfer happened with PFI at 50°C (Run 13). This indicated that chain transfer was caused by self-immobilization rather than the rise in temperature. The SEM photo of polyethylene particle with self-immobilized catalyst AFI for Run 8 was shown as Figure 4. Lowering temperature would normally suppress the  $\beta$ -hydrogen



**Figure 5.** Ethylene consumption curves in the presence of AFI and PFI catalysts.

transfer reaction and thus improve the polymerization livingness and narrow the MWD. However, the  $\beta$ -hydrogen transfer reaction has already been well inhibited for *N*-fluoroaryl FI-Ti catalyst at room temperature.<sup>2–9</sup> It should be noted again that the prepared PE samples had  $T_m$ 's all above 135°C, suggesting high-density polyethylene that cannot be dissolved in toluene at the experimental temperatures in Table III. At lower temperatures, the growing chains could more easily precipitate and this precipitation would also broaden the MWD without chain transfer. This explained the broader PDIs at 0°C (Run 7 and Run 9). The two factors of self-immobilization and precipitation worked against each other in determining the polymer MWD, with temperature played a dominant role in balancing the two.

Scheme 2 presents a proposed mechanism of self-immobilization during the living polymerization of ethylene. When an active site inserts into another living chain, its ligand is linked to the chain. Since, the linked position is close to the titanium center of AFI, an increased steric hindrance makes the monomer insertion difficult and the propagation rate reduced.

Figure 5 shows the polymerization kinetic behavior of AFI and PFI. In the first 5 min ethylene polymerization at 50°C, PFI maintained nearly constant activity after the max rate. However, the ethylene consumption rate with AFI clearly decreased after reaching its max, because of the occurrence of self-immobilization.

## CONCLUSIONS

A new type of FI type catalyst precursor AFI was designed and synthesized for living polymerization of ethylene. This catalyst became supported during polymerization through self-immobilization. The heterogeneous catalyst was compared to a homogeneous counterpart PFI, having a similar structure. Both showed living feature in the 5 min polymerization under atmospheric pressure. The rate of ethylene insertion for AFI was higher than that for PFI. However, at a prolonged period of time, AFI started to produce polymer having a broad molecular weight distribution. Elevating temperature favored self-immobilization that facilitated catalyst supporting but it also broadened

the polymer molecular weight distribution because of induced chain transfer reactions.

## ACKNOWLEDGMENTS

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