

# Ethylene polymerization with homogeneous and heterogeneous catalysts based on bis(4-fluorophenyl)methyl-substituted bis(imino)pyridyliron complexes

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**ABSTRACT:** A series of bis(4-fluorophenyl)methyl-substituted bis(imino)pyridyliron chloride complexes were immobilized on oxide supports. The kinetics of ethylene polymerization by both homogeneous and heterogeneous systems was followed, the catalysts mostly demonstrating high activities. The effect of the ligands nature and reaction conditions on the catalytic activities and molecular weights of the resultant polyethylenes was examined. In contrast to homogeneous systems, the supported iron complexes were found to exhibit high and stable activity upon activation with triisobutyl aluminium, producing high-molecular-weight polyethylene with good morphology. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42674.

**KEYWORDS:** catalysts; kinetics; morphology; polyolefins; synthesis and processing

Received 12 March 2015; accepted 29 June 2015

DOI: 10.1002/app.42674

## INTRODUCTION

A milestone discovery of Gibson<sup>1–3</sup> and of Brookhart<sup>4</sup> was the introduction of the iron(II) 2,6-bis(imino)pyridyl complexes demonstrating high activities in ethylene polymerization in the presence of methylaluminoxane (MAO). In general, bis(imino)pyridyl iron complexes commonly produce highly linear polyethylene (PE).<sup>2,4–6</sup> The molecular weights (MW) and polydispersity (or molecular weight distribution, MWD) of the resultant polyethylenes could be precisely controlled by the nature of the ligands used. By finely tuning the ligand structure, one can obtain different ethylene products ranging from oligomers to high-molecular-weight polyethylene.<sup>1,4,7–9</sup> It was demonstrated that cheap and available aluminum trialkyls [AlMe<sub>3</sub>, Al(*i*-Bu)<sub>3</sub>, Al(*n*-Oct)<sub>3</sub>] could be used as activators for iron bis(imino)pyridyl complexes instead of MAO, thus broadening the research scope.<sup>10–12</sup>

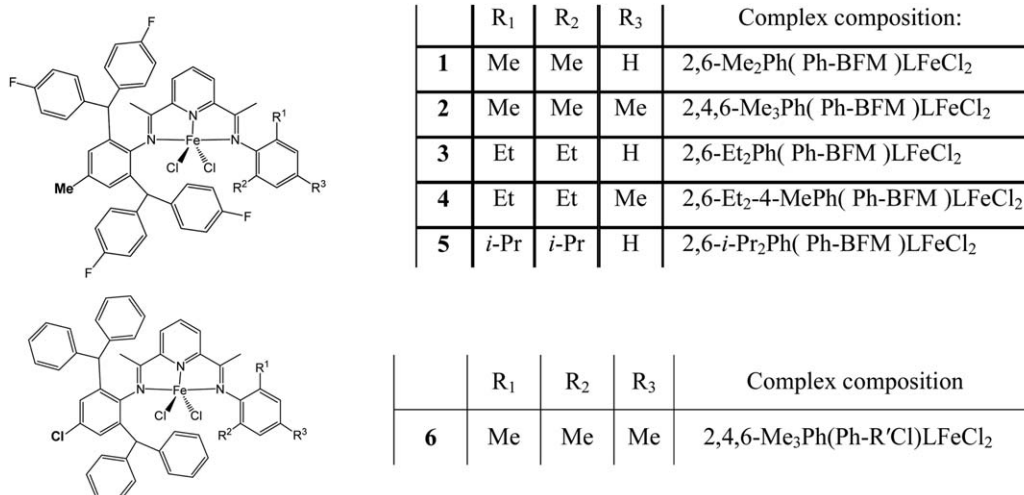
From an industrial perspective, a crucial drawback of bis(imino)pyridyl iron complexes is their low thermal stability, leading to deactivation at temperatures above 50°C. Therefore, the search for ligand structures ensuring higher thermal stability of iron catalysts and high activity at the same time is highly challenging. To this end, we screened various modified bis(imino)pyridine derivatives. High thermal stability of corresponding bis(imino)pyridyl

iron complexes was achieved by using bis(imino)pyridines with dibenzhydryl-<sup>13,14</sup> and bis(4-fluorophenyl)methyl-substituents.<sup>15,16</sup> The above catalysts displayed high apparent activities (recalculated from PE yields within 15 or 30 min) at temperatures up to 80°C upon the activation with MAO and MMAO, and the sophisticated ligand architectures provided rich opportunities for controlling the temperature stability, as well as molecular weights and polydispersities.<sup>13–16</sup>

For industrial use, especially in slurry and gas-phase processes, the use of immobilized catalysts is preferable. Earlier, we reported the immobilization of 2,6-bis(imino)pyridyliron complexes on the surface of the oxide supports (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) and MgCl<sub>2</sub>.<sup>10,17–19</sup> In this study, the bis(4-fluorophenyl)methyl-substituted bis(imino)pyridyl iron(II) chloride complexes<sup>15</sup> have been immobilized on different supports (silica, or Al-modified silica, or MgCl<sub>2</sub>). The ethylene polymerization activities and the polyethylene molecular weight characteristics achieved on supported as well as homogeneous catalysts are reported and discussed.

## EXPERIMENTAL

Toluene was dried over molecular sieves (4Å), purified by refluxing over sodium metal and distilled in dry argon.



**Scheme 1.** Composition of the iron (II) bis(imino)pyridyl complexes used in the study.

Methylene chloride was dried over P<sub>2</sub>O<sub>5</sub> and distilled under vacuum. All solvents and prepared solutions were stored and handled in a vacuum. All experiments were carried out in sealed high vacuum systems using breakseal techniques.

Methylaluminoxane (MAO) was obtained from Crompton GmbH (Bergkamen) (toluene solution with total Al concentration 1.8 M). Modified methylaluminoxane [MAO, modified with Al(*i*-Bu)<sub>3</sub>, MMAO] was obtained from Akzo Nobel Corp. (heptane solution with total Al concentration 1.7 M). Commercial samples of Al(*i*-Bu)<sub>3</sub> and AlMe<sub>3</sub> were used as heptane solutions (0.2 M of Al).

Silica Davison 952 (surface area 260 m<sup>2</sup>/g) was calcined at 450°C for 3–4 h and dehydroxylated for 4 h under vacuum at 700°C. Silica, modified with alumina SiO<sub>2</sub>(Al) was prepared according to Ref. 20. Finely dispersed MgCl<sub>2</sub> (surface area 80 m<sup>2</sup>/g) was prepared as described in Ref. 21. Non-symmetrical bis(imino)pyridyl iron(II) complexes used in the study (Scheme 1) were prepared as described in Ref. 15. In polymerization experiments, the iron complexes were used as powders or as a solutions in CH<sub>2</sub>Cl<sub>2</sub> (1 μmol Fe/mL).

#### Preparation of Supported Catalysts

The weighed amount of support was stirred with calculated amount of iron complex solution in CH<sub>2</sub>Cl<sub>2</sub> (1 μmol Fe/mL) during 0.5 h at room temperature to provide the desired iron content in the catalyst. The liquid fraction was decanted; the solid part was washed with CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum. The iron content in the prepared catalysts was determined by AES-ICP.

#### Ethylene Polymerization

Ethylene polymerizations were performed in a 0.5 L steel reactor. A sealed glass ampoule with weighed amount of the examined catalyst sample (powdered iron complex, iron complex solution in CH<sub>2</sub>Cl<sub>2</sub> or supported catalyst) was placed into the reactor. The reactor was heated at 80°C in a vacuum for 1 h, then cooled to 25°C, and charged with the solution of co-catalyst in toluene (MAO: 1 mmol Al in 150 ml) or heptane (MMAO, Al(*i*-Bu)<sub>3</sub>, AlMe<sub>3</sub>; 1 mmol Al in 150 ml). After setting

up the desired polymerization temperature and ethylene pressure, the reaction was triggered by breaking the ampoule with the catalyst. During the reaction, ethylene pressure was maintained constant through automatic computer-controlled system for the ethylene feed, recording the ethylene consumption and providing the kinetic curve output both in the form of a table and as a graph. After a prescribed time the reactor was vented, the obtained solid product separated and dried at ambient conditions to constant weight. Detailed polymerization conditions (quantities, times, etc.) are provided in the footnotes of the tables.

#### PE Molecular Weight Measurements

GPC measurements were performed on a WATERS-150C High Temperature Chromatograph equipped with the 4 mixed bed TSK-gel columns set (GMHXL-HT, Tosoh Corp.). Run conditions used: 140°C; flow rate 1 cm<sup>3</sup>/min; 1,2,4-trichlorobenzene as a solvent. The data were collected and processed with a Viscotek GPC Software version 3.0. Conventional calibration was made using narrow PS standards and PE standards.

Molecular weights of high molecular mass polymers were characterized by the melt flow index values (MFI), measured at 190°C and loads of 5.0 and 21.6 kg according to the standard procedure (ASTM 1238-62T).

## RESULTS AND DISCUSSION

### Ethylene Polymerization with Non-Symmetrical Iron Bis(imino)pyridyl Complexes

To compare the polymerization properties of bis(4-fluorophenyl)methyl-substituted iminopyridyliron complexes (R<sub>n</sub>Ph(Ph-BFM)LFeCl<sub>2</sub>) with those of the previously studied bis(iminopyridyl)iron complexes ((R<sub>n</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub>), which are inactive at temperatures above 50°C,<sup>1–5,7,12</sup> complexes shown in the Scheme 1 were tested in the ethylene polymerization at 40°C. Data on the activity and melt flow indices (MFI) of the obtained polymers are summarized in Table I.

In the presence of MAO or MMAO the studied complexes showed high polymerization activity, close to that of the catalyst

**Table I.** Ethylene Polymerization on (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub> and 2,6-Me<sub>2</sub>Ph(Ph-BFM)LFeCl<sub>2</sub> with Different Activators

Entry	Complex	Activator	t, min	PE Yield, Kg PE/mol Fe bar	Average activity, Kg PE/mol Fe bar min	MFI (5), g/10 min <sup>2</sup>	MFI (21.6), g/10 min <sup>2</sup>
1 <sup>a</sup>	(2,6-Me <sub>2</sub> Ph) <sub>2</sub> LFeCl <sub>2</sub>	MAO	30	9100	303	>100	>100
2 <sup>a</sup>		MMAO	30	6800	226	2.3	>100
3 <sup>a</sup>		AlMe <sub>3</sub>	30	12,300	410	8.0	>100
4 <sup>a</sup>		Al( <i>i</i> -Bu) <sub>3</sub>	30	7600	250	2.7	>100
5	2,6-Me <sub>2</sub> Ph(Ph-BFM) LFeCl <sub>2</sub> ( <b>1</b> )	MAO	15	8400	560	0.1	1.5
6		MMAO	30	2450	90	0.1	5.4

Polymerization conditions: 40°C, P(C<sub>2</sub>H<sub>4</sub>) = 1 bar, 13.3 μmol Fe (as a powder), Al/Fe = 500, in toluene with MAO or in heptane with MMAO, AlMe<sub>3</sub> and Al(*i*-Bu)<sub>3</sub>.

<sup>a</sup>Data for the symmetrical complex (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub>, cited from Ref. 12.

<sup>b</sup>Melt flow index of PE determined at 190°C with 5 and 21.6 kg load.

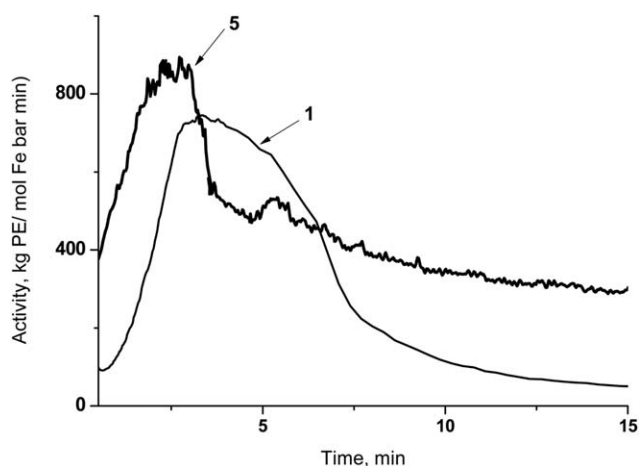
based on bis(iminopyridyl)iron complexes [(2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub>, Table I, entries 1, 2]. In contrast to iron complexes with symmetrical ligands, highly active upon the activation with aluminum trialkyls (Table I, entries 3 and 4 and Refs. 10,12), the studied complexes were inactive when AlMe<sub>3</sub> or Al(*i*-Bu)<sub>3</sub> were used as activators. In Refs. 22–24, it was shown that neutral heterobinuclear complexes [(R<sub>n</sub>Ph)<sub>2</sub>LFe(μ-R)<sub>2</sub>AlR<sub>2</sub>] dominate in (R<sub>n</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub> + AlR<sub>3</sub> systems, whereas upon interaction of bis(iminopyridyl)iron complexes with MAO, mainly heterobinuclear ion pairs [(R<sub>n</sub>Ph)<sub>2</sub>LFe(II)(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup>[M-MAO]<sup>-</sup> are formed. Both types of intermediates, however, afforded catalytically active sites. Apparently, for non-symmetrical complexes R<sub>n</sub>Ph(Ph-BFM)LFeCl<sub>2</sub>, only ion-pair intermediates are responsible for generating the active centers of these systems.

The kinetic curve for polymerization run with **1** is shown in Figure 1. In the presence of MAO, the catalyst exhibited high initial activity which subsequently decreased with polymerization time (Figure 1, curve 5). Similar unsteady kinetics was previously observed for the (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub> catalyst<sup>10,12,25</sup> (Figure 1, curve 1). As compared to (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub>/MAO, the catalyst **1**/MAO deactivates slower, indicating higher stability of the active centers, formed upon the activation of **1** with MAO. The catalyst system **1**/MMAO showed lower activity than **1**/MAO (Table I, entry 6). The initial increase of the activity of the **1**/MMAO system was considerably smaller than that observed in the **1**/MAO system, and subsequent decline of the polymerization rate was steeper. MW of highly linear polymers obtained with R<sub>n</sub>Ph(Ph-BFM)LFeCl<sub>2</sub> was too high to be evaluated by GPC, instead, data on the melt flow index (MFI) were used for comparison of the obtained polymers. MW of polyethylene samples produced by complex **1** with both MAO and MMAO was noticeably higher (MFI values lower) than that of polymers, obtained with the catalysts based on (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub> (Table I). The results of polymerizations on complexes R<sub>n</sub>-Ph(Ph-BFM)LFeCl<sub>2</sub> bearing different substituents R<sub>n</sub> at the phenyl group (complexes 2-5) are collected in Table II. All studied complexes proved to be highly active in the presence of MAO and MMAO and exhibited no activity when aluminum trialkyls were used as activators. Like for the catalysts

based on the complex **1** and (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub>, the rate of ethylene polymerization with complexes 2-5 was nonstationary, with high initial activity that decreased with reaction time.

At a low polymerization temperature (40°C), complexes 2-5, activated with MAO and MMAO, produced PE with high MW (low values of MFI at high load (21.6 kg)) (Table II). In line with earlier observations for catalysts based on symmetrical iron complexes,<sup>1,4,7-9</sup> the molecular weight of the polymer increases (MFI value decreases) with the increase of the size of the alkyl substituents at the phenyl group (R<sub>n</sub>Ph). Thus, in spite of the presence of a very bulky (Ph-BFM) moiety in the structure of the ligand, the substituents in the group (R<sub>n</sub>Ph) retain their influence upon the molecular mass of the produced polymer (cf. data for complexes 3 and 5). Polymers obtained on the R<sub>n</sub>Ph(Ph-BFM)LFeCl<sub>2</sub> complexes in the presence of MMAO, had somewhat lower MW (higher MFI values) (Table II, entries 2 and 5).

Substituents at the other, bulky aniline group of the ligand was also found to affect the polymerization properties of iron



**Figure 1.** Ethylene polymerization rate vs. time for (2,6-Me<sub>2</sub>Ph)<sub>2</sub>LFeCl<sub>2</sub> (curve 1) and 2,6-Me<sub>2</sub>Ph(Ph-BFM)LFeCl<sub>2</sub> (curve 5) in the presence of MAO at 40°C. Numbers of the curves correspond to the entry numbers in Table I.

**Table II.** Effect of R<sub>n</sub>Ph Group on Catalysts Activity and MW of Polymers

Entry	R <sub>n</sub> Ph	Activator	t, min	PE Yield, Kg PE/mol Fe bar	Average activity, Kg PE/mol Fe bar min	MFI (21.6) g/10 min <sup>a</sup>
1	2,4,6-Me <sub>3</sub> Ph (complex <b>2</b> )	MAO	15	8250	550	1.4
2		MMAO	30	5150	170	2.1
3	2,6-Et <sub>2</sub> Ph (complex <b>3</b> )	MAO	15	7150	450	3.4
4	2,6-Et <sub>2</sub> -4-MePh (complex <b>4</b> )	MAO	30	9750	325	2.7
5		MMAO	15	3950	260	3.8
6	2,6- <i>i</i> Pr <sub>2</sub> Ph (complex <b>5</b> )	MAO	15	6900	460	0.6

Polymerization conditions: 40°C, P(C<sub>2</sub>H<sub>4</sub>)= 1 bar, 13.3 μmol Fe (as a powder), Al/Fe = 500, in toluene with MAO or in heptane with MMAO.  
<sup>a</sup>Melt flow index of PE determined at 190°C with 21.6 kg load.

**Table III.** Ethylene Polymerization on Me<sub>3</sub>Ph(Ph-BFM)LF<sub>2</sub>Cl<sub>2</sub> (**2**) and Me<sub>3</sub>Ph(Ph-R'Cl)LF<sub>2</sub>Cl<sub>2</sub> (**6**) with Different Activators

Entry	Complex	Activator	t, min	T, °C	PE Yield, Kg PE/mol Fe bar	Average activity, Kg PE/mol Fe bar min	MFI (21.6) g/10 min <sup>a</sup>
1	<b>2</b>	MAO	15	40	8250	550	1.4
2		MMAO	30	40	5150	170	2.1
3		MMAO	30	70	3580	180	2.7
4	<b>6</b>	MAO	15	40	9010	600	0.1
5		MMAO	30	40	4800	160	1.3
6		MMAO	30	70	3450	115	0.3

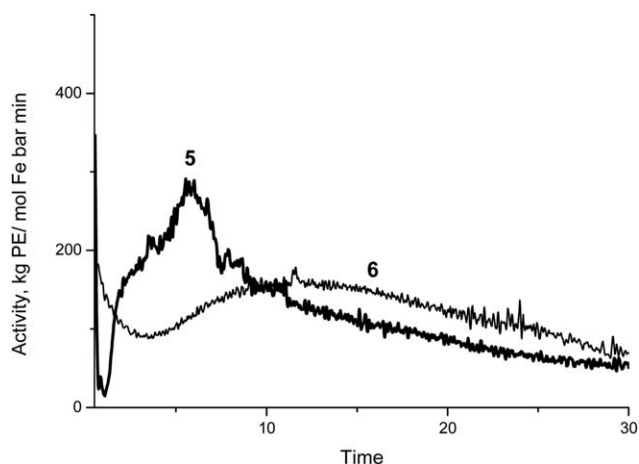
Polymerization conditions: P(C<sub>2</sub>H<sub>4</sub>)= 1 bar, 13.3 μmol Fe (as a powder), Al/Fe=500, in toluene with MAO or in heptane with MMAO.  
<sup>a</sup>Melt flow index of PE determined at 190°C with 21.6 kg load

bis(imino)pyridyl complexes. At 40°C, when activated with MAO or MMAO, complexes **2** and **6** with different composition of the bulky moiety (Scheme 1) displayed similar unsteady kinetics and close activities (Table III, entries 1 and 4, 2 and 5), while molecular weights of polymers obtained with complex **6** were noticeably higher (MFI values lower).

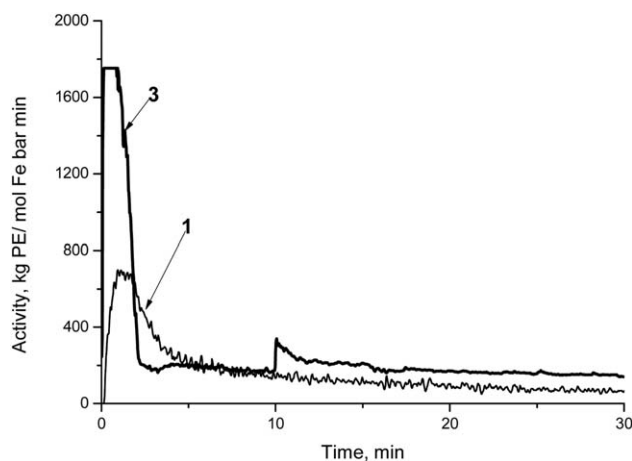
Raising the polymerization temperature from 40 up to 70°C resulted in the decrease of the observed catalytic activities of both catalysts (entries 3 and 6). For entry 6 of Table III, there was no initial increase of the activity and the kinetic curve was more stable (Figure 2, curve 6). We hypothesize that the initially formed active sites in the system **6**/MMAO are less thermally stable than those present in the system **2**/MMAO, and rapidly disappear at high temperature. At the same time, another type of more thermally stable sites appear in this system, producing PE with substantially higher molecular weight as compared to PE obtained at 40°C (Table III, entry 6 vs. entry 5).

Complexes of the type R<sub>n</sub>Ph(Ph-BFM)LF<sub>2</sub>Cl<sub>2</sub> are poorly soluble in aliphatic solvents and toluene. To avoid the solubility problems in the course of their interaction with activator, polymerizations using solutions of iron complexes in CH<sub>2</sub>Cl<sub>2</sub> were conducted. Reduction of the catalyst concentration gives an opportunity to conduct the reaction at a higher ethylene pressure (5 bar). The results obtained for complexes **2** and **6** in the presence of MMAO are collected in Table IV. When complex **2** was used as solution in CH<sub>2</sub>Cl<sub>2</sub>, the reaction started with high

activity that rapidly (within 3 min) dropped by a factor of 8 (Figure 3, curve 3). The value of the initial activity increases with the decrease in complex concentration (Table IV), probably due to the increase in MMAO/iron complex ratio. When the solution of complex **6** was used for polymerization, the activity time profile at a high polymerization temperature was similar



**Figure 2.** Ethylene polymerization rate vs. time at different polymerization temperatures for the catalyst system **6**/MMAO at 40°C (curve 5) and at 70°C (curve 6). Numbers of the curves correspond to the entry numbers in Table III.



**Figure 3.** Ethylene polymerization rate vs. time for the catalyst system **2**/MMAO at different concentrations of iron complex: 13.3  $\mu\text{mol Fe}$  (curve 1) and 2.5  $\mu\text{mol Fe}$  (curve 3) at 70°C. Numbers of the curves correspond to the entry numbers in Table IV.

to that of the catalyst **2**/MMAO (Figure 3), albeit with a lower initial activity value.

Data on the molecular weights and, MWD characteristics of polymers obtained with catalysts **2** and **6** (at 70°C and 5 bar ethylene pressure) are collected in Table V and Figure 4. Both complexes produce PE with close values of  $M_w$  and broad polydispersity ( $M_w/M_n = 8.3$  and 9.1 for **2** and **6**, respectively), indicating multisite nature of the catalysts. The PE obtained on **6**/MMAO system contains two noticeable fractions – the major one with higher MW and a shoulder with lower MW (Figure 4, curve 2), indicating that this system contains two types of active sites, producing PEs with drastically differing MW. The obtained PE sample contained mainly terminal  $\text{CH}_3$ -groups (IRS data), verifying participation of alkyl aluminium compounds in the chain termination reactions in polymerization with this system.

#### Ethylene Polymerization with Supported Catalysts Based on $\text{Me}_3\text{Ph}(\text{Ph-BFM})\text{LFeCl}_2$

Supporting iron(II) bis(imino)pyridyl complexes on the surface of inorganic materials (silica, alumina,  $\text{MgCl}_2$ ) results in the formation of highly active and stable catalysts.<sup>10,17–19,26,27</sup> In this work, supported catalysts were prepared by adsorption of complex **2** on the surface of silica, alumina-modified silica, and

**Table V.** Data on the Molecular Weight and Molecular Weights Distribution of Polymers Produced with Complexes **2** and **6**

Entry	Complex	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w/M_n$
1	<b>2</b>	36	300	8.3
2	<b>6</b>	32	290	9.1

Polymerization conditions: 70°C,  $\text{P}(\text{C}_2\text{H}_4)$  5 bar,  $[\text{Fe}]$  2.5  $\mu\text{mol/L}$ , in heptane (200 ml), MMAO as activator (1 mmol), for 15 min.

$\text{MgCl}_2$ , and were tested in ethylene polymerization. The data on the composition of the catalysts and the polymerization results are provided in Table VI. For comparison, polymerization data for the homogeneous system **2**/MMAO (Table VI, entry 1), and for supported catalysts based on bis(imino)pyridyl complex  $(2,6\text{-Me}_2\text{Ph})_2\text{LFeCl}_2$  (entry 6)<sup>17</sup> are given. The kinetic curves for polymerization over homogeneous and supported complex **2** are compared in Figure 5. In contrast to homogeneous systems, supported catalyst **2** exhibited rather high and stable activity at polymerization temperature of 80°C in the presence of  $\text{Al}(i\text{-Bu})_3$  as co-catalyst. The average activity of supported **2** was lower than that of the homogeneous system but the former was very stable, providing high polyethylene yield (Table VI, entry 5).

Bis(imino)pyridyl complexes of iron are strongly bound to the support surface and do not desorb in the course of polymerization, ensuring the formation of PE with good morphology, corresponding to the morphology of the support (the effect of replication) (Figure 6), and high bulk density (0.35  $\text{g/cm}^3$ , Table VI).

The nature of the support affects the amount of immobilized iron complex. Like for the iron complexes with symmetrical substituents  $(2,6\text{-Me}_2\text{Ph})_2\text{LFeCl}_2$ ,<sup>10,17</sup> only a small amount of complex **2** can be adsorbed on dehydroxylated silica (Table VI, entry 3), resulting in the formation of catalyst with very low activity. When alumina-modified silica  $[\text{SiO}_2(\text{Al})]$  was used for the catalyst preparation, higher content of the active component was achieved, apparently due to the interaction of iron complex with both surface hydroxyl groups and Lewis acidic sites.<sup>28</sup> The catalysts prepared by adsorption of **2** on  $\text{SiO}_2(\text{Al})$  provide high yield of PE (Table VI, entry 5), comparable with that for the catalyst  $(2,6\text{-Me}_2\text{Ph})_2\text{LFeCl}_2/\text{SiO}_2(\text{Al})$  (entry 4).  $\text{MgCl}_2$  proved to be a very effective support for anchoring  $(2,6\text{-Me}_2\text{Ph})_2\text{LFeCl}_2$ ,<sup>18</sup> assuring the formation of the most active supported

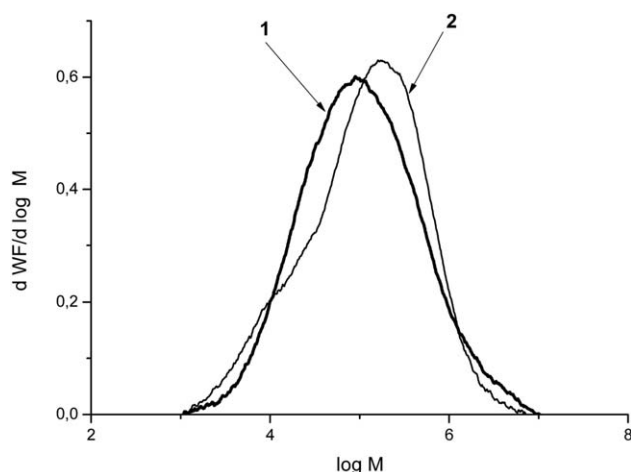
**Table IV.** Effect of Catalyst Concentration of Ethylene Polymerization Activity

Entry	Complex	$[\text{Fe}] \mu\text{mol/L}^a$	$\text{P}_{\text{C}_2\text{H}_4}$ , bar	Average activity Kg PE/mol Fe bar min	Maximum activity, Kg PE/mol Fe bar min <sup>b</sup>
1	<b>(2)</b>	13.3	1	80	700
2		2.5	5	180	1800
3	<b>(6)</b>	13.3	1	160	155
4		2.5	5	221	650

Polymerization conditions: 70°C, in heptane (200 ml), activator: MMAO (1 mmol), polymerization time 30 min.

<sup>a</sup>At concentration 13.3  $\mu\text{mol/L}$ , Fe complex was used as a powder, at concentration 2.5  $\mu\text{mol/L}$ , Fe as solution in  $\text{CH}_2\text{Cl}_2$  (1  $\mu\text{mol/ml}$ ).

<sup>b</sup>Calculated from PE yield for 1 min of polymerization.

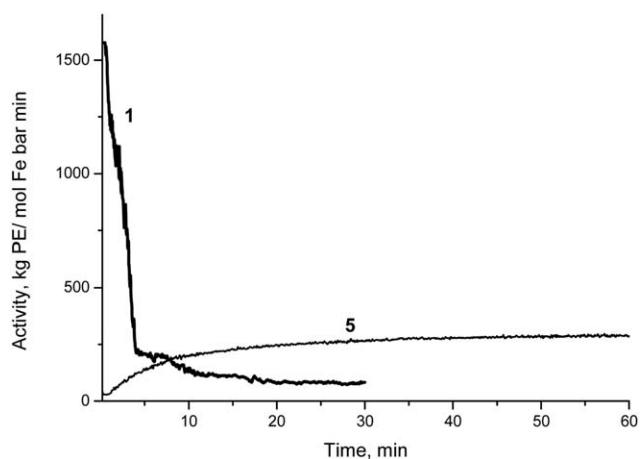


**Figure 4.** Molecular weight distribution of PE produced with catalyst systems **2**/MMAO (curve 1) and **6**/MMAO (curve 2). Numbers of the curves correspond to the entry numbers in Table V.

catalysts (Table VI, exp. 6). In contrast to this, the activity of the catalysts prepared by adsorption of **2** on the surface of  $\text{MgCl}_2$  was noticeably lower than that of the catalysts ( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2/\text{SiO}_2(\text{Al})$  (entry 7).

Catalysts based on the immobilized **2** produced linear PE with much higher molecular weight (lower MFI values) than those for polymers, obtained on homogeneous catalysts (Table VI, entries 1 and 5), and higher than MW of PE obtained on supported ( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2$  (entry 4).

In earlier studies, it was found that the presence of hydrogen noticeably enhances the activity of supported catalysts based on ( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2$ .<sup>17,18</sup> In Ref. 29 this “effect of hydrogen” was attributed to reactivation of “dormant” active centers, formed due to the 2,1-insertion of low-molecular-weight products ( $\text{RCH}=\text{CH}_2$ ) into the growing polymer chain. In the case of supported complex **2**, the introduction of hydrogen into the polymerization medium had negligible effect on the polymerization activity and molecular weight of PE. Apparently, polymers produced by supported complex **2** have high molecular weight



**Figure 5.** Ethylene polymerization rate vs. time for the homogeneous system **2**/MMAO (curve 1) and for the heterogeneous system **2**/SiO<sub>2</sub>(Al)/Al(*i*-Bu)<sub>3</sub> (curve 5). Numbers of the curves correspond to the entry numbers in Table VI.

and low content of terminal vinyl groups and are not able to form the “dormant” active centers by 2,1-insertion.

## CONCLUSIONS

In conclusion, ethylene polymerization properties of non-symmetrical bis(4-fluorophenyl)methyl-substituted bis(imino)pyridyl iron(II) complexes, both homogeneous and supported, have been investigated. The size of the substituents  $R_n$  in the small moiety of the ligand affect the polymer molecular weight, the latter increasing in the following order:  $i\text{-Pr} > \text{Et} > \text{Me}$ . Substituents at the bulky group of the ligand also affect the activity and stability of homogeneous catalysts based on  $R_n\text{Ph}(\text{Ph-BFM})\text{LFeCl}_2$ .

Unlike the symmetrical bis(imino)pyridyl iron(II) complex ( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2$ , non-symmetrical bis(imino)pyridyl iron(II) complexes of the type  $R_n\text{Ph}(\text{Ph-BFM})\text{LFeCl}_2$  cannot be activated with aluminum trialkyls in the homogeneous systems. When activated with MAO, the latter catalysts are more active

**Table VI.** Effect of Catalysts Composition on Ethylene Polymerization over Supported Catalysts Based on Iron(II) Bis(imino)pyridine Complexes with Symmetrical and Nonsymmetrical Ligands

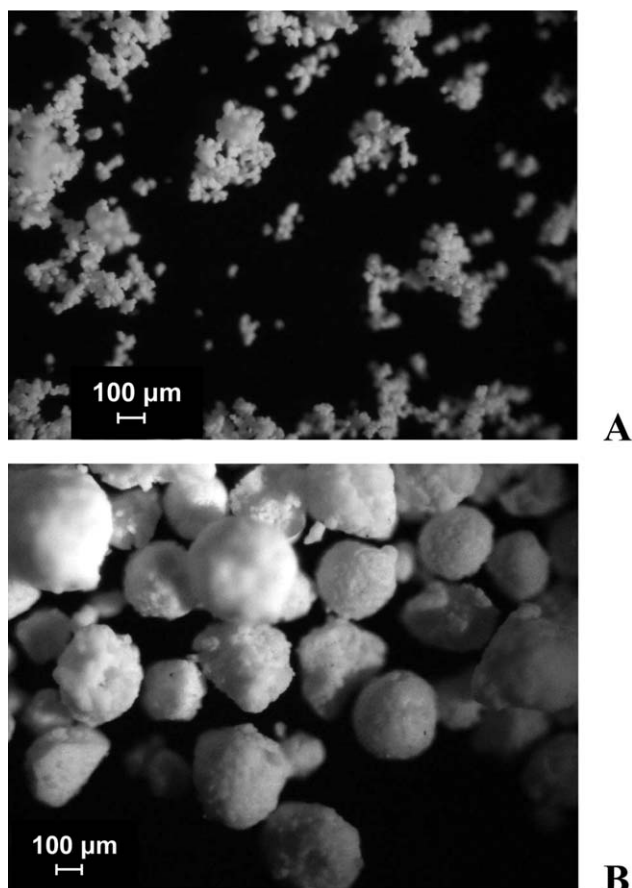
Entry	Support	Complex	Content of Fe, % wt.	PE Yield g PE/g cat	Activity, kg PE/g Fe bar h	MFI <sup>b</sup> g/10 min	Bulk density, g/cm <sup>3</sup>
1	-	<b>2</b> /MMAO (homogeneous) <sup>a</sup>	-	-	180	4.4	0.093
2	SiO <sub>2</sub>	( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2$ <sup>c</sup>	0.07	143	40	1.9	-
3		<b>2</b>	0.05	15	6	-	-
4	SiO <sub>2</sub> (Al)	( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2$ <sup>c</sup>	0.30	1105	75	1.8	-
5		<b>2</b>	0.35	1074	60	0.03	0.350
6	MgCl <sub>2</sub>	( $2,6\text{-Me}_2\text{Ph}$ ) $_2\text{LFeCl}_2$ <sup>c</sup>	0.35	2600	150	2.0	-
7		<b>2</b>	0.30	333	25	<0.01	-

Polymerization conditions: 80°C,  $\text{P}(\text{C}_2\text{H}_4) = 5$  bar, co-catalyst: Al(*i*-Bu)<sub>3</sub> in heptane, polymerization time 1 h.

<sup>a</sup>Entry 3 of Table IV.

<sup>b</sup>Melt flow index of PE determined at 190°C with 21.6 kg load.

<sup>c</sup>From Ref. 17.



**Figure 6.** Microphotographs of PE samples obtained on the homogeneous system 2/MMAO (A) and on supported catalyst  $2\text{SiO}_2(\text{Al}) + \text{Al}(i\text{-Bu})_3$  (B).

and stable [as compared to  $(2,6\text{-Me}_2\text{Ph})_2\text{LFeCl}_2$ ] at low polymerization temperatures ( $35\text{--}40^\circ\text{C}$ ), and highly active at higher temperatures (up to  $80^\circ\text{C}$ ), producing polymers with higher MW and broad bimodal MWD.

In contrast to homogeneous systems, supported (on  $\text{MgCl}_2$  or  $\text{SiO}_2(\text{Al})$ ) non-symmetrical iron complexes were found to exhibit high and stable activity upon the activation with  $\text{Al}(i\text{-Bu})_3$ , producing high-molecular-weight polyethylene with good morphology, corresponding to the morphology of the support, and high bulk density ( $0.35\text{ g/cm}^3$ ).

#### ACKNOWLEDGMENTS

This study was jointly supported by the Russian Foundation for Basic Research and the National Natural Science Foundation of China (Grant no. 14-03-91153/51411130208), and partially supported by the Ministry of Education and Science of the Russian Federation, unique identification RFMEFI60714X0046. The authors thank Dr. I. E. Soshnikov for the synthesis of one of the iron complexes, and Dr. M. A. Matsko for the GPC measurements.

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