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Ethylene polymerization by novel highly active iron/acetyl(imino)pyridyl complex

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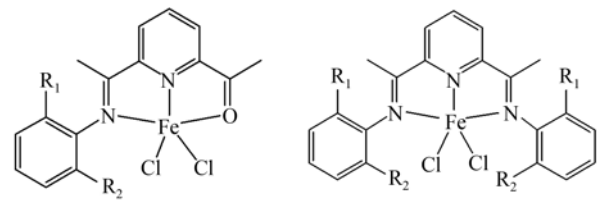
Abstract Novel iron-based complex and acetyl(imino)pyridine iron(II) chloride (**1** and **2**) have been successfully synthesized and characterized. The behavior of the complex/methylaluminoxane (MAO) for ethylene polymerization was investigated and compared with 2,6-Bis(imino)pyridyl iron(II) chloride (**3** and **4**)/MAO. The results show that the new acetyl(imino)pyridine iron(II) chloride/MAO catalytic systems were highly active for ethylene polymerization. Polyethylene from those polymerization systems has a bimodal molecular weight distribution (MWD).

Keywords: late transition metal, iron complex, catalyst, ethylene polymerization.

In recent years, significant developments have occurred in olefin polymerization with late-transition-metal catalyst systems, in particular, the discovery of exceptionally active catalysts based on penta-coordinate iron and cobalt bearing bis(imino)pyridyl tridentate ligands with substituted aryl groups, reported independently by the groups of Brookhart[1] and Gibson[2]. Following this discovery, a considerable amount of efforts have been dedicated to investigate the nature of the active species and to design new catalysts based on these types of ligands. More and more novel Fe(Ⅱ) and Co(Ⅱ) complexes have been synthesized and used in olefin polymerization. They are mainly variations on aromatic amine ligand, such as 1-naphthylamine[3], 1-aminopyrene[4], 2-benzylaniline[4], aniline[4], (-)-(*cis*)-myrtanylamine)[5], aminofluorene[5] and diphenylmethylamine[5]. Acetyliminopyridine ligand was synthesized by Bluhm group and used in ethylene oligomerization[6]. The other variations are centric atoms, such as ruthenium[7], chromium[8] and vanadium[9]. Different alkylaluminium compounds were used as co-catalysts for Fe(Ⅱ) and Co(Ⅱ) complex during olefin polymerization, such as trimethylaluminium (TMA), triethylaluminium (TEA), triisobutylaluminium (TiBA), trihexylaluminium (THA), trioctylaluminium (TOctA), MAO and $Ph_3C[B(C_6F_5)_4]$[10]. Supported Fe(Ⅱ) and Co(Ⅱ) complexes have been researched, and the supports used are SiO_2, $MgCl_2$ and Al_2O_3[11−14]. Novel ligands have been also synthesized and used in ethylene polymerization[15,16].

In this paper, we synthesize novel iron(II)-based complexes (**1** and **2**) bearing 2-acetyl-6-(imino)pyridyl ligands that contain bulky aromatic terminals such as 2,6-dimethylaniline and 2,6-diisopropylaniline. The behavior of **1** and **2** in polymerization of ethylene is investigated and compared with **3** and **4**. The properties of polyethylene are also compared (see Fig. 1).



1 R_1=R_2=CH_3
2 R_1=R_2=*i*–Pr
3 R_1=R_2=CH_3
4 R_1=R_2=*i*–Pr

Fig. 1. Mono and bis(imino)pyridine iron dichloride complexes.

1 Experiment

1.1 Materials

2,6-diacetylpyridine, 2,6-diisopropylaniline, and 2,6-dimethylaniline were purchased from Aldrich (USA). Polymerization grade ethylene was obtained from Daqing Petro-Chemical Ltd. (China). MAO solution (1.4 mol/L) in toluene was purchased from Albemarle Corp. (USA). Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone and degassed. All other chemicals were obtained commercially and used as received.

1.2 Preparation and characterization of ligands and complexes

(i) Preparation of 2-acetyl-6-[1-(2,6-dimethylphenylimino) ethyl]pyridine (**1**). 2,6-diacetylpyridine (1 g, 6.1 mmol), 25 mL anhydrous methyl alcohol and a few drops of formic acid were placed in a 100-mL

three-necked flask fitted with a condenser. Under stirring, the solution of 2,6-dimethylaniline (0.73 g, 6.0 mmol) in 25 mL methyl alcohol was dropped slowly. The solution was refluxed for 72 h. During this time, the water of the solution was removed using a Dean-Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuum and methanol was added to afford a yellow solid. The yellow solid (830 mg; 52%) was collected by filtration and dissolved in hot isopropyl alcohol to remove the diimine byproduct. The solution was refiltered, and the alcohol was removed to give 609 mg (38%) of the desired monoimine. EI-MS: *m*/*z* 266.3 [M^+]. ^{1}H NMR ($CDCl_3$, 300 MHz): 8.56 (d, Py-*m*-H), 8.12 (d, Py-*m*-H), 7.93 (t, Py-*p*-H), 6.89(s, Ar-*m*-H), 2.78 (s, Me), 2.29 (s, Me), 2.22 (s, Me). ^{13}C NMR ($CDCl_3$, 75.4 MHz): 199.9 (C=O), 166.7 (C=N), 155.6, 152.4, 145.9, 137.2, 132.3, 128.5, 125.2, 124.4, 122.5 (Py and Ar), 25.6, 20.6, 17.8, 16.2 (Me). $C_{17}H_{18}N_2O$: Calcd. C 76.66, H 6.81, N 10.52; Found: C 76.83, H 6.74, N 10.48.

(ii) Synthesis of complex **1.** Under an Argon atmosphere, 53.2 mg ligand 1(0.2 mmol) and 38.0 mg ferrous chloride tetrahydrate (0.19 mmol) were stirred with 5 mL THF at 25℃ for 2 h. Pentane was added to precipitate 1, which was obtained as a deep blue powder, and was subsequently washed with diethyl ether, filtered and dried (yield: 68%). EI-MS: *m/z* 393[M^+], 357.1[M^+-Cl], 266.1[M^+-$FeCl_2$]. $C_{17}H_{18}N_2OFeCl_2$: Calcd. C 51.94, H 4.62, N 7.13; Found: C 51.83, H 4.64, N 7.45.

(iii) Preparation of 2-acetyl-6-[1-(2,6-diisopropylphenyl-imino)ethyl]pyridine (**2**). 2,6-diacetylpyridine (1 g, 6.1 mmol), 25 mL anhydrous methyl alcohol and a few drops of formic acid were placed in a 100 mL three-necked flask fitted with a condenser. Under stirring, the solution of 2,6-diisopropylaniline (1.06 g, 6.0 mmol) in 25 mL methyl alcohol was dropped slowly. The solution was refluxed for 72 h. During this time, the water of the solution was removed using a Dean-Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuum and methanol was added to afford a yellow solid. The yellow solid (801 mg; 41.4%) was collected by filtration and dissolved in hot isopropyl alcohol to remove the diimine byproduct. The solution was refiltered, and the alcohol was removed to give 653 mg (33.7%) of the desired monoimine. EI-MS: *m*/*z* 322.2 [M^+]. ^{1}H NMR ($CDCl_3$, 300 MHz): 8.56 (d, Py-*m*-H), 8.19 (d, Py-*m*-H), 7.93 (t, Py-*p*-H), 7.18(q, Ar-*m*-H), 7.08(q, Ar-*m*-H), 7.01(q, Ar-*p*-H), 4.47(q, 2H), 2.78 (m, 2H), 2.29 (s, 3H), 1.45 (t, 3H), 1.35 (t, 12H). $C_{21}H_{26}N_2O$: Calcd. C 78.22, H 8.13, N 8.69; Found: C 78.16, H 8.21, N 8.78.

(iv) Synthesis of complex **2.** Under an argon atmosphere, 64.4 mg ligand **2** (0.2 mmol) and 38.0 mg ferrous chloride tetrahydrate (0.19 mmol) were stirred with 5 mL THF at 25℃ for 2 h. Pentane was added to precipitate **2**, which was obtained as a deep blue powder, and was subsequently washed with diethyl ether, filtered and dried (yield: 75%). EI-MS: *m/z* 448[M^+], 412.1[M^+-Cl], 321.1[M^+-$FeCl_2$]. $C_{17}H_{18}N_2OFeCl_2$: Calcd. C 56.15, H 5.83, N 6.24; Found: C 56.23, H 5.64, N 6.25.

Complexes **3** and **4** were synthesized according to the methods described in ref. [2]. The results of analysis confirmed their structure.

1.3 Ethylene polymerization

A dried three-necked flask with a stir-bar was backfilled with N_2 three times, once with ethylene, and then charged with 50 mL of toluene. MAO was added via syringe while stirring. After 5 min, the catalyst, dissolved in toluene, was added via syringe. Polymerization was quenched with acidified ethanol. The polymer was isolated by filtration, washed with ethanol and then dried at 50℃ in a vacuum oven.

2 Results and discussion

The results of ethylene polymerization catalyzed by **1**, **2**, **3** and **4** using MAO as a cocatalyst and the characters of polymer are summarized in Table 1. There are obvious different results from catalysts **1** and **2** compared with **3** and **4**. The activity of acetyl-(imino) pyridyl iron complex is lower than that of bis-(imino)pyridyl iron complex. The molecular weights of polymer obtained from **1** and **2** are lower than those obtained from **3** and **4**. It shows that the ligand environment around the metal center has a profound effect on catalyst productivity and product molecular weight. Changing the ligand environment from bis-(imino)pyridyl to acetyl-(imino)pyridyl, results generally in a slight drop in productivity and in a decrease in the molecular weight. These results suggest that, for acetyl-(imino)pyridyl catalysts, the rate of propagation is decreased more than the rate of β-H transfer, resulting in lower productivities and lower molecular weights. It shows that the conjugation and steric protection of the metal center are crucial for high activity tridentate ligand Fe(Ⅱ) complex catalyst for olefin

Table 1 Data for the polymerization of ethylene and characterize of polyethylene [a)]

Entry	Catalyst	Al/Fe (mol/mol)	Temp (℃)	Activity [b)]	*M*w (10^{-4})	*M*w/*M*n
1	**1**	2000	20	1.243	3.93	18.02
2	**1**	2000	40	2.436	2.45	16.25
3	**2**	2000	20	1.379	10.67	19.25
4	**2**	2000	40	0.247	8.92	17.36
5	**3**	2000	20	4.85	4.61	3.67
6	**3**	2000	40	5.10	3.44	7.32
7	**4**	2000	20	4.22	13.05	8.33
8	**4**	2000	40	4.56	9.25	4.38

a) All runs were done using 1.013 bar pressure of ethylene and 50 mL toluene with MAO as the cocatalyst. Each polymerization was run for 30 min. b) 10^6 g PE·mol^{-1} · Fe · h^{-1} · bar^{-1}.

polymerization.

The curves of MWD are given in Fig. 2. The GPC analysis indicates that the obtained polyethylene has a relatively low molecular weight, with the *M*n value in the range of 1500—20000. As shown by the GPC traces in Fig. 2, the PE samples obtained from complexes **1** and **2** display bimodal molecular weight distribution. The observed bimodal distribution is attributed to the formation of the different types of active species when the complexes are activated by MAO and the rate difference between chain transfer and chain propagation of these active species. The *M*w values of the PE produced by complexes **3** and **4** are much higher than those obtained from complexes **1** and **2**, which is in accord with previous reports[1,17], demonstrating a higher molecular weight for PE produced with a ligand of greater steric bulk.

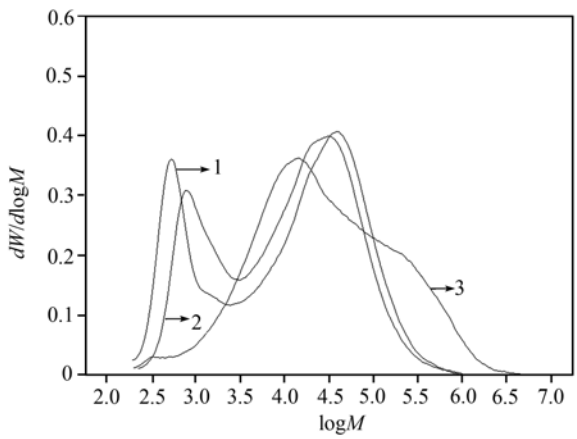


Fig. 2. GPC curves of PE prepared with catalyst systems **1**, **2** and **3**/MAO. 1, PE prepared with catalyst systems 1/MAO; 2, PE prepared with catalyst system 2/MAO; 3, PE prepared with catalyst systems, **3**/MAO.

High temperature ^{13}C NMR spectroscopy for the PE sample listed in entry 2 of Table 1 was also performed (Fig. 3). The NMR spectrum of polyethylene presented in Fig. 3 is in good agreement with a highly linear polyethylene. Indeed, the signals detected at 14.0, 22.8 and 32.1 ppm are only due to chain ends. Their relatively high intensity is due to low molar masses[18,19]. Furthermore, the IR spectroscopic analysis of the obtained PE confirms the presence of end vinyl groups, which implies that chain termination occurs with β-H elimination for the polymerization of α-olefin. Further work is in progress on this series of catalysts, including different substitutions at aryl amine for ethylene oligomerization, polymerization and copolymerization.

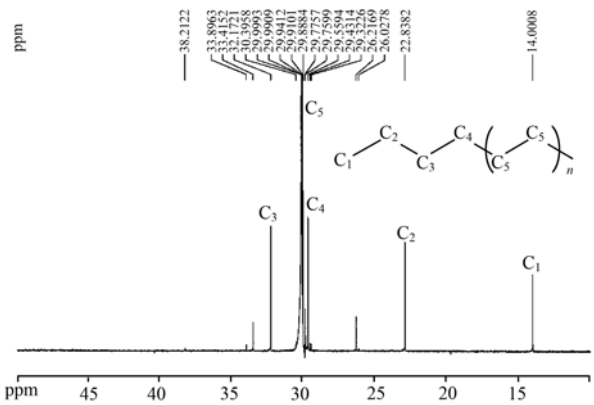


Fig. 3. ^{13}C NMR spectra of PE prepared with catalyst system **1**/MAO.

3 Conclusion

The modification of a ligand from bis-(imino)pyridyl to acetyl-(imino)pyridyl greatly enhanced the MWD of the PE, which is the result from the formation of the different types of active species when the complexes are activated by MAO and the rate difference between chain transfer and chain propagation of these active

species. In addition, decreasing molecular weights could be attributed to the decreasing steric bulk of the ligand. Decreasing the activity of the catalyst for ethylene polymerization could be derived from the decreasing of the conjugation and steric protection of the metal center.

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