

Fe(acac)₃-Bis(imino)pyridine/MAO: A New Catalytic System for Ethylene Polymerization

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ABSTRACT: New catalytic systems, composed of bis(imino)pyridine (2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine (A₁), methylene-bridged bis(imino)pyridine (A₂)), iron (III) acetylacetonate (Fe(acac)₃), and methylaluminoxane (MAO), are highly active for ethylene polymerization. The performance of this new catalytic system was evaluated with respect to catalytic activity and polymer properties. The highest catalytic activity of Fe(acac)₃-A₁/MAO (catA) system and Fe(acac)₃-A₂/MAO (catB) system at optimum condition reaches 10.5×10^6 g PE·(mol Fe h)⁻¹ and 17.3×10^6 g PE·(mol Fe h)⁻¹, respectively. The product viscosity-average molecular weight (M_v) of two catalytic systems range from 0.40 to 8.7

$\times 10^5$. GPC characterizations of PE obtained show that the PE has bimodal molecular weight distribution (MWD). ¹³C NMR and DSC analysis of PE sample indicates that the PE is highly linear and crystalline. Analysis of UV-vis absorption spectra, ethylene polymerization results, and prepared polyethylene structures indicate that Fe(acac)₃-bis(imino)pyridine/MAO catalytic system could generate same active species as bis(imino)pyridyliron catalytic systems. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 167–173, 2008

Key words: Fe(acac)₃; bis(imino)pyridine; polyethylene; methylaluminoxane; bimodal

INTRODUCTION

Numerous advances have been achieved in late transitional metal complexes for olefin polymerization in the last decade.^{1–3} One of the most important is iron complexes (Chart 1) based on bis(imino)pyridine ligand for ethylene polymerization, which have been reported by Brookhart et al.⁴ and Gibson and coworkers^{5,6} independently. This type of iron catalysts has attracted much attention in academia and in industry, for their high activity in ethylene polymerization and their remarkable selectivity for ethylene oligomerization to linear-olefins. Various modifications to the original bis(imino)pyridyl ligand framework have been reported, but have generally afforded less efficiency catalysts.^{7–15} For example, acetylacetonate containing cationic bis(imino)pyridyliron(II) complexes (Fe²⁺ in Chart 1), activated by methylaluminoxane (MAO), displayed high activity for ethylene polymerization at normal ethylene pressure.⁸ However, they only produced low-molecular weight PE with narrow molecular weight distribution (MWD).

As reported by literatures,^{16–18} Fe(acac)₃, AlR₃, and extra electron donors (such as nitrogen-containing and phosphorus compounds) were mainly used for the polymerization of conjugated diene. Recently, we observed that Fe(acac)₃-bis(imino)pyridine/MAO was another iron-based highly active catalytic system capable of polymerizing ethylene to high-molecular weight PE with broad MWD. In this catalytic system, active species can be formed in the “pot” (*in situ*) in which the ethylene polymerization takes place.^{19,20} In this case, there are two reasons that make this system attractive: one of them is that Fe(acac)₃ which is easy to handle, is a relatively cheap organic Fe compound and has been known not to polymerize ethylene when activated by MAO, the other reason is the *in situ* method can be used to conveniently investigate the properties of other nitrogen-containing compounds (e.g., α -diimine compound (DAD), pyridine) for the purpose of catalyzing ethylene polymerization. In this article, we present the catalytic performance of the system Fe(acac)₃-bis(imino)pyridine/MAO for ethylene polymerization.

EXPERIMENTAL PART

Materials

2,6-Diacetylpyridine were purchased from Aldrich (Milwaukee, WI). Polymerization grade ethylene was obtained from Jinshan Petrol-Chemical Co. (Shanghai,

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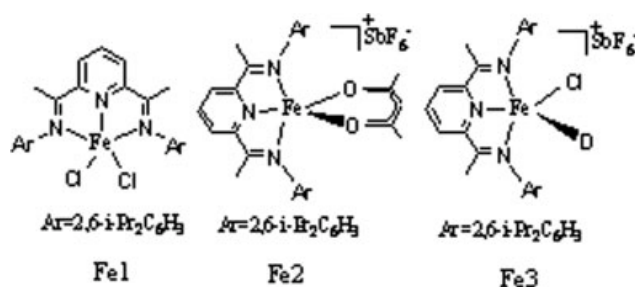


Chart 1. Bis(imino)pyridyliron complexes.

China). MAO solution (10 wt %) in toluene was purchased from Albemarle Co. (USA). Toluene is distilled from sodium/benzophenone and degassed. 2,6-Bis[1-(2,6-diisopropylphenylimino) ethyl] pyridine (A_1), DAD, and $\text{Fe}(\text{acac})_3$ were prepared according to the known procedure, respectively.^{6,21,22}

Characterization

^1H NMR spectra were recorded on a Bruker Advance 400 instrument at room temperature, ^{13}C NMR spectra were recorded on a Bruker Advance 300 instrument at 120°C , elemental analysis was conducted on a Perkin-Elmer 240 elemental analyzer. UV-vis spectra were recorded in 10-mm quartz glass cells on a Perkin Elmer Lambda 20 spectrometer. The viscosity-average molecular weight (M_η) was measured in decahydronaphthalene at 135°C by a modified Ubbelohde-type viscometer according to $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$ (mL g^{-1}). The melting points (T_m) of polyethylene were determined by means of differential scanning calorimetry (DSC) using a DSC Q100 V9.5 Build 288, operating at a heating rate of $10^\circ\text{C min}^{-1}$ from 20 to 160°C . The MWD of some PE samples with ortho-dichlorobenzene as solvents were determined by gel-permeation chromatography (GPC, waters 150, 135°C) using polystyrene columns as a standard.

Synthesis of $\{[2,6\text{-R}_2\text{-C}_6\text{H}_3\text{N}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_3\text{N}(\text{CH}_3)\text{C}=\text{N}(3,5\text{-R}'_2)\text{C}_6\text{H}_2\text{-CH}_2\text{-}(3,5\text{-R}'_2)\text{C}_6\text{H}_2\text{N}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_3\text{N}(\text{CH}_3)\text{C}=\text{N}(2,6\text{-R}_2)\text{C}_6\text{H}_3]\text{(R} = \text{R}' = \text{isopropyl)}\}$ (A_2) (Scheme 1)

To a methanol solution of 2,6-diacetylpyridine (0.9 g, 5.52 mmol), 2,6-di-isopropylaniline (0.99 g, 5.52 mmol) and formic acid (0.5 mL) were added and stirred at room temperature for 2 days. The monocondensation yellow product (1.63 g, 5.06 mmol 91.0%) was collected by filtration and washed with cold methanol. This monoimine (1.5 g, 4.65 mmol) was dissolved in 30-mL purified toluene, followed by addition of a 0.05 g *p*-toluenesulfonic acid and di(2,6-diisopropyl-4-aminophenyl) methane 0.85 g (2.33 mmol). The solution was stirred and refluxed for 15 h. During the reaction, a Dean and Stark ap-

paratus was used to remove the water. The mixture was concentrated and cooled to give yellow solid. The solid was washed with cold methanol to give A_2 (1.9 g, 83.7%). ESI-MS: $m/z = 976.5$ [M^+]. ^1H NMR(400 MHz, DCCl_3): $\delta = 1.12\text{--}1.25$ (m, 48H, CHMe), 2.27 (s, 6H, N=CMe), 2.29 (s, 6H, N=CMe), 2.75 (m, 8H, CHMe₂), 4.12 (s, 2H, $-\text{CH}_2-$), 7.02–7.16 (m, 10H, Ar-H), 7.92 (t, 2H, Py- H_p), 8.50 (d, 4H, Py- H_m). $\text{C}_{67}\text{H}_{86}\text{N}_6$ (%): Calcd. C 82.50, H 8.89, N 8.61, found: C 82.43, H 8.91, N 8.54.

Homogeneous ethylene polymerization

The catalytic systems were prepared by mixing bis(imino)pyridyl compounds and $\text{Fe}(\text{acac})_3$ with suitable molar ratio ($A_1 : \text{Fe}(\text{acac})_3 = 1 : 1$, $A_2 : \text{Fe}(\text{acac})_3 = 0.5 : 1$) previously, and then dissolved in proper amount of toluene.

Normal ethylene pressure polymerization was carried out in a 50-mL glass reactor. High-pressure polymerization was carried out in a 100-mL stainless steel reactor. The reactor was filled with a proper amount of toluene and MAO solution. The system was then saturated with a continuous flow of ethylene under atmospheric pressure. The polymerization was initiated by injection of the above mixture solution. After the reaction, the resulting polyethylene were precipitated in acidified ethanol, filtered, and dried under vacuum to constant weight.

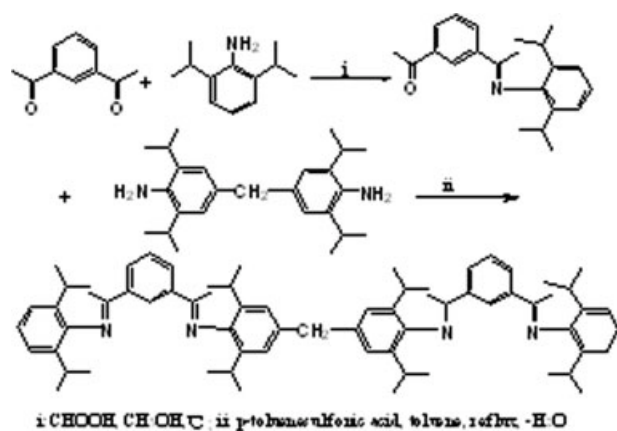
RESULTS AND DISCUSSION

Synthesis of methylene bridged bis(imino)pyridine (A_2)

Condensation of 2,6-diacetylpyridine and 2,6-diisopropylaniline with equivalent molar ratio gave the monoimine which could further react with the primary diamine to form the methylene-bridged bis(imino)pyridyl compound (A_2) (Scheme 1) with high yield. In the first step, formic acid was used to catalyze the condensation reaction. But the second step was difficult to carry out and needed stronger catalyst. So that *p*-toluenesulfonic acid was added. In addition, the water generated in the second step was removed to accelerate the reaction. ESI-MS, ^1H NMR, and element analysis proved A_2 to be the desired compound.

Homopolymerization of ethylene

In the polymerization of conjugated diene, iron-based catalytic systems have been widely investigated.^{16,17,23,24} The binary system iron-compound/alkylaluminum has very low activity for conjugated diene polymerization, and accordingly, an additional electron donor is needed to achieve reasonable activity. Most of the electron donors used for the iron-



Scheme 1 Synthesis route for bis(imino)pyridyl ligand A₂.

based catalyst system are bidentate nitrogen-containing compounds, which will complex (coordinate) with the low valence iron.^{18,23,24} In this case, Fe(acac)₃/MAO could not catalyze the polymerization of ethylene. When bis(imino)pyridine was added as a third component, Fe(acac)₃/MAO catalytic system displayed high activity for ethylene polymerization. The results confirm that bis(imino)pyridine as an electron donor is effective to stabilize the active species from over-reduction by complexing (coordinating) with lower valence iron.^{16,23}

These catalytic systems do not show any induction period, the exotherm is generally observed immediately. This phenomenon was also observed by Gibson and coworkers⁶ using FeI/MAO system. To investigate the effects of various conditions on polymerization reaction, polymerization experiments were carried out on the molar ratio of Al/Fe, reaction temperature, ethylene pressure, time, the molar ratio of bis(imino)pyridine/Fe(acac)₃, different nitrogen-containing compounds and mixing order of catalyst composites.

Effect of methylaluminumoxane

Figure 1 reveals that the molar ratio of Al/Fe has a great influence on catalytic activity. As shown in Figure 1, both the catalytic activity and the M_n of polyethylene increase first and then decreases with Al/Fe molar ratio increasing. It may be ascribed to the excess MAO, which leads to a balance between chain propagation and chain transfer reaction during polymerization process. In addition, the viscosity-average molecular weight of PE produced by catA and catB is very high and reaches 10^5 .

Effect of temperature

Figure 2 demonstrates the influence of the polymerization temperature on the catalytic activity and the

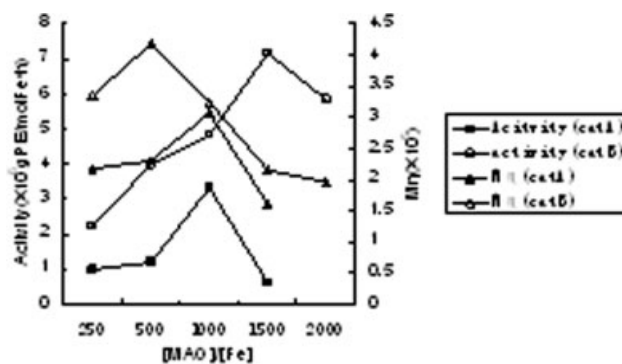


Figure 1 Influence of the [MAO]/[Fe] molar ratio on catalytic activity and molecular weight of polyethylene. Polymerization conditions: [Fe] = 0.4×10^{-4} mol L⁻¹, T_p = 20°C, t_p = 20 min, P_e = 1 bar, V_{toluene} = 25 mL.

M_n of polyethylene. It is clear that an increase in temperature results in large decreases in catalytic activity and the M_n of PE obtained. Generally, higher temperature will result in higher chain-propagation and chain-transfer rates, which would be expected to increase the catalyst activity and decrease the molecular weight. However, the decreasing solubility of ethylene in toluene and the increasing rate of catalyst deactivation may occur at higher temperature. A combination of these effects is likely to account for the dependence of catalytic activity and polymer properties on temperature. Furthermore, catA is more sensitive to the polymerization temperature than catB. It maybe due to the methylene-bridged bis(imino)pyridyl ligand structure of A₂, which might be able to retard the deactivation.

Effect of ethylene pressure

Figure 3 shows the dependence of catalytic activity and the M_n of PE on ethylene pressure. Both the cat-

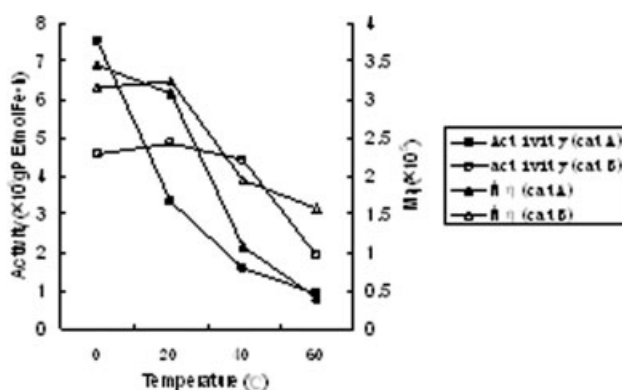


Figure 2 Influence of the polymerization temperature on catalytic activity and molecular weight of polyethylene. Polymerization conditions: [Fe] = 0.4×10^{-4} mol L⁻¹, [MAO]/[Fe] = 1000, t_p = 20 min, P_e = 1 bar, V_{toluene} = 25 mL.

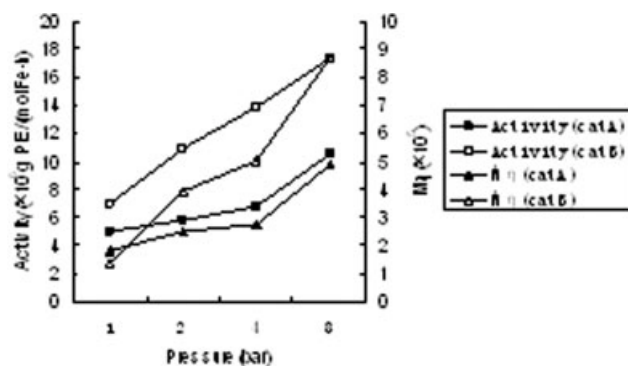


Figure 3 Influence of ethylene pressure on catalytic activity and molecular weight of polyethylene. Polymerization conditions: $[\text{Fe}] = 0.4 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{MAO}]/[\text{Fe}] = 1000$, $t_p = 10 \text{ min}$, $T = 20^\circ\text{C}$, $V_{\text{toluene}} = 50 \text{ mL}$.

alytic activity and the molecular weight of PE increase with elevating ethylene pressure. Effect of the ethylene pressure on catalytic activity is in accordance with the results observed by Gibson and coworkers⁶ using Fe1/MAO catalytic system. Additionally, the highest molecular weight of PE reached 8.68×10^5 because of less chain transfer reaction under higher ethylene pressure.⁶

Effect of reaction time

The reaction time has significant effect on catalytic activity and polymer characteristics. The influence of the polymerization time on ethylene polymerization is shown in Figure 4. It is clear that the catalytic activity of two catalytic system decreases with reaction time prolonging, because of the deactivation of the catalyst. However, as the reaction time increases from 10 to 60 min, the molecular weight of PE obtained by two catalytic systems is always increasing. The changing trend was similar with Fe1/MAO catalytic system.⁶

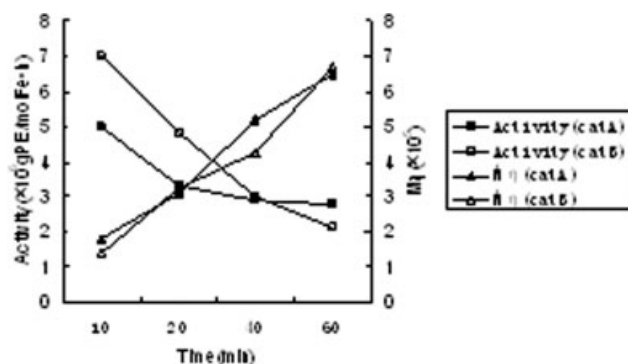


Figure 4 Influence of the polymerization time on catalytic activity and molecular weight of polyethylene. Polymerization conditions: $[\text{Fe}] = 0.4 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{MAO}]/[\text{Fe}] = 1000$, $T_p = 20^\circ\text{C}$, $P_e = 1 \text{ bar}$, $V_{\text{toluene}} = 25 \text{ mL}$.

TABLE I
Effect of Different Molar Ratio of Bis(imino)pyridine/
 $\text{Fe}(\text{acac})_3$ and Different Nitrogen-Containing
Compounds^a

Entry	$\text{Fe}(\text{acac})_3$ (μmol)	Bis(imino)pyridyl compound (μmol)	Activity ^b	M_n (10^{-5})
1	1	0.5 (A_1)	2.35	3.04
2	1	1 (A_1)	3.31	3.07
3	1	2 (A_1)	1.96	3.15
4	1	0.25 (A_2)	3.35	3.54
5	1	0.5 (A_2)	4.85	3.23
6	1	1 (A_2)	2.86	2.97
7	3	1 (DAD)	0.051	0.288
8	3	3 (Pyridine)	0.003	0.279

^a Polymerization conditions: solvent = toluene (25 mL), polymerization pressure = 1 bar, MAO/Fe = 1000, polymerization time = 20 min, temperature = 20°C .

^b $10^6 \text{ g PE} \cdot (\text{mol} \cdot \text{Fe} \cdot \text{h})^{-1}$.

Effect of different molar ratio of bis(imino)pyridine/ $\text{Fe}(\text{acac})_3$ and different nitrogen-containing compounds

As pointed out by the literature,^{5,6} the structurally bulky bis(imino)pyridine is an essential component in the catalytic system, offering necessary steric hindrance around the metal center. The polymerization results in Table I reveal that there is one optimum molar ratio of bis(imino)pyridine/ $\text{Fe}(\text{acac})_3$ for the highest catalytic activity to be achieved. In addition, DAD and pyridine have also been used with $\text{Fe}(\text{acac})_3$ to catalyze ethylene polymerization. Comparing to bis(imino)pyridyl compounds, these two compounds can not stabilize the metal center and display lower activity for ethylene polymerization. These results indicate that bis(imino)pyridyl ligands added as electron donors are more favorable for stabilizing active centers than DAD and pyridine.

As well known, bulky substituents on the imino nitrogen donors were found to play a pivotal role in preventing the formation of bis-chelate complexes and controlling the rates of propagation and chain termination, thus influencing both activity and molecular weight of the resultant polymer.¹⁵ Comparing with A_1 , A_2 have two similar parts around the cen-

TABLE II
Effect of Catalyst Preparation Methods on Ethylene
Polymerization with $\text{Fe}(\text{acac})_3$ - A_1 /MAO Catalyst

Mixing order	Activity ^a	M_n ^b
(Fe+Al)+ A_1	—	—
(A_1 +Al)+Fe	0.89	21.5
(A_1 +Fe)+Al	3.31	30.7

Polymerization conditions: $[\text{Fe}] = 0.4 \times 10^{-4} \text{ mol L}^{-1}$, Al/Fe = 1000, $T = 20^\circ\text{C}$, $t = 20 \text{ min}$, $V_{\text{toluene}} = 25 \text{ mL}$, ethylene pressure = 1 bar.

^a $10^6 \text{ g PE} \cdot (\text{mol} \cdot \text{Fe} \cdot \text{h})^{-1}$.

^b 10^4 g mol^{-1} .

TABLE III
GPC and DSC Results of PE Samples Produced by catA and catB^a

Entry	Cat (μmol)	Al/Fe	T ($^{\circ}\text{C}$)	t (min)	M_w	M_n	M_w/M_n	M_{pk}		T_m ($^{\circ}\text{C}$)
								Peak 1	Peak 2	
1	1 (catA)	1000	0	20	382,998	9310	41.1	16,149	762,218	133.1
2	1 (catA)	1000	20	20	212,307	3554	59.7	2741	151,110	132.4
3	1 (catA)	1000	20	60	667,009	12022	55.5	1959	815,592	134.0
4	1 (catB)	1000	0	20	412,056	7968	51.7	1658	171,246	134.1
5	1 (catB)	1000	20	20	288,474	4031	71.6	560	106,922	133.4

^a Polymerization conditions: $V_{\text{toluene}} = 25$ mL, ethylene pressure = 1 bar, MAO/Fe = 1000.

tral methylene group. Each part together with the CH_2 group can be considered as a *para*-substituent of the other phenyl group. The substituent in the ligand backbone is quite remote from the active site but still within range to influence the activity and selectivity of the active center.¹⁵ In this case, special substituents at *para*-position make the phenyl ring more electron rich,²⁵ which probably influences the fundamental steps of the polymerization process (olefin insertion and chain termination) by modifying the coordination environment of the metal center,²⁶ thus resulting in an increase in catalytic activity and molecular weight.

Effect of mixing order of catalyst composites

For this type of three-component catalytic system, it is worth mentioning that the mixing order is essential. Table II shows the ethylene polymerization results of different mixing orders. For instance, adding bis(imino)pyridine to a toluene solution containing $\text{Fe}(\text{acac})_3$ and MAO resulted in a brown solution which displayed a very low activity. When $\text{Fe}(\text{acac})_3$

and MAO aged first, inactive Fe^0 species is very easily produced because of over-reduction by aluminum compound,^{16,23} resulting in much less active species formed by the complexing of bis(imino)pyridine with the metal center.¹⁷ And this is probably one of the reasons why extra electron donor, such as bis(imino)pyridine, which is assumed to stabilize (by complexing) active species, is a prerequisite for the system.

GPC and DSC result of sample PE

As shown in Table III, PE with a bimodal MWD was obtained in the case of catA and catB. However, the high-molecular weight fraction is dominant in the PE produced by catA and catB (Fig. 5). The results in Table III reveal that increasing temperature will broaden the MWD. Additionally, the molecular weight of PE produced with catA and catB reached 10^5 for less β -H elimination in chain growth and lower chain transfer rate during polymerization process.⁶ As a result, the melting temperatures are all above 132°C , which indicates that the PE are highly linear and highly crystalline. Furthermore, the ^{13}C NMR analysis (Fig. 6) of the polymers produced with catA shows only one strong signal at 29–30 ppm for methylene. Since polymers having the same structural characteristics are produced, it might be suggested that the similar active metal centers are generated in these different catalytic systems con-

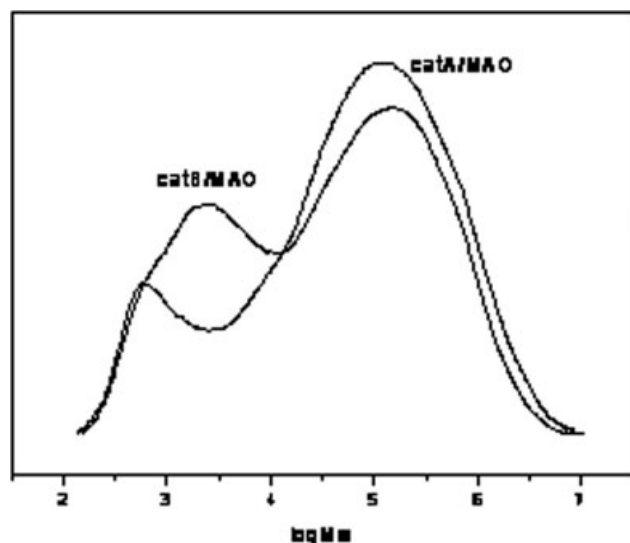


Figure 5 GPC characterization of PE samples. Conditions: $[\text{Fe}] = 0.4 \times 10^{-4}$ mol L^{-1} , Al/Fe = 1000, 20°C , 20 min, 1 bar.

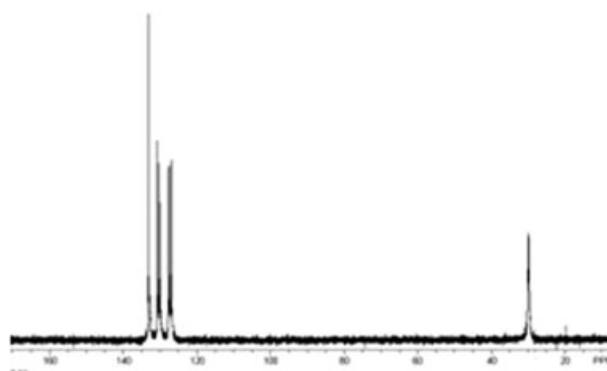


Figure 6 ^{13}C NMR analysis of PE sample with catA.

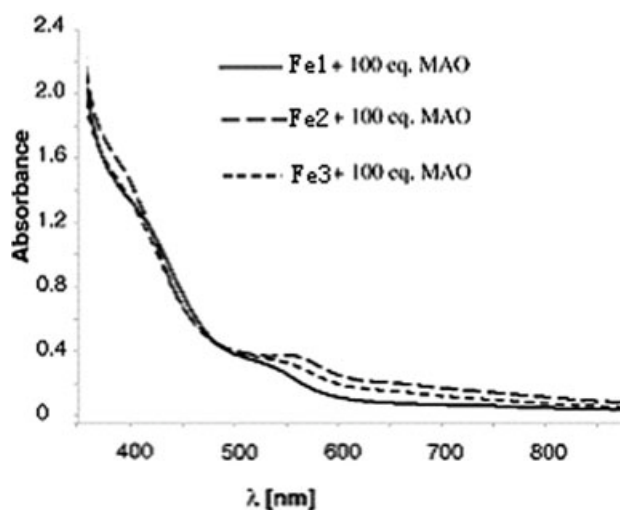


Figure 7 UV-vis spectra of Fe1-Fe3 catalytic system.⁸

taining bis(imino)pyridine but by different initiation pathways.^{8,20}

UV-vis studies on the catalytic system

UV-vis studies of MAO-activated olefin polymerization systems have been carried out previously for bis(imino)pyridyl iron catalysts.^{8,27,28} UV-vis studies showed that Fe1 and Fe2 (Chart 1) had broad absorption at 700 nm and 500–600 nm, respectively. When MAO was added, Fe1 and Fe2 system display similar UV-vis spectrum (Fig. 7), suggesting that the same active species are being generated.⁸ As shown in Figure 8, Fe(acac)₃+A₁(a) has no absorption at 700 nm and 500–600 nm (Fig. 8a). After controlled amount of MAO was added, the red solution of Fe(acac)₃+A₁ immediately turned orange-yellow.

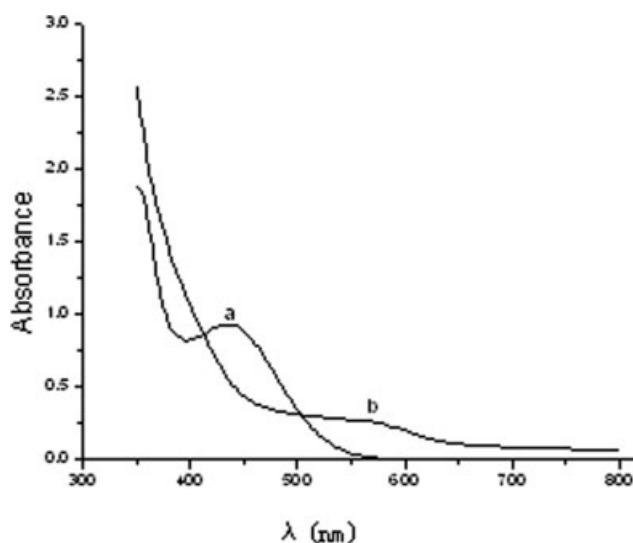
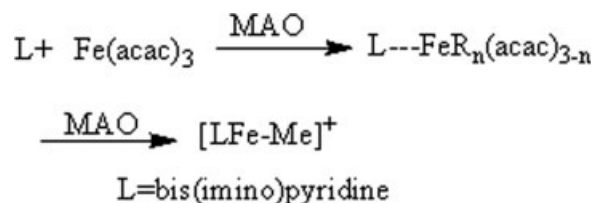


Figure 8 UV-vis spectra of the catalytic system: Fe(acac)₃+A₁ (a), Fe(acac)₃+A₁ + 1000 equiv. MAO (b).



Scheme 2 Possible activation process.

The addition of MAO leads to broad absorption at 500–600 nm (Fig. 8b). The solution of Fe(acac)₃+A₁+MAO displayed a similar UV-vis spectrum with Fe1+MAO and Fe2+MAO systems, which showed that irrespective of the catalytic system employed, the same active species appeared to be generated. In addition, Fe(acac)₃-bis(imino)pyridine/MAO exhibited similar catalytic activity for ethylene polymerization with Fe1 and Fe2 catalytic system.^{6,8} The polyethylene properties were also comparable. The polymerization results also suggest that there are same active species in Fe(acac)₃-bis(imino)pyridine/MAO and iron complexes (Chart 1)/MAO catalytic systems.

As pointed by the literature,²⁰ the involvement of MAO causes the acac ligand to be replaced by DAD, finally resulting in the active Ni(II) species complexed (coordinated) with DAD, when Ni(acac)₂-DAD/MAO catalytic system was employed. For Fe(acac)₃, positively charged Fe(III) is strongly bound to three bidentate anionic ligand acac. Fe(acac)₃ does not react with bis(imino)pyridine in the absence of other reagent, indicating that MAO does participate in the process of ligand substitution. On the basis of our experimental results and the literature,^{8,16,17,20,23} a possible activation process of Fe(acac)₃-bis(imino)pyridine/MAO catalytic system is illustrated in Scheme 2. First Fe(acac)₃ is reduced and alkylated by MAO to give Fe(acac)Me.¹⁶ The reduced state of iron immediately complexed (coordinated) with the bis(imino)pyridine compound to give an intermediate products like LFe(acac)Me,¹⁶ whereafter the acac group is abstracted by the strong lewis acid-MAO to form the final catalytic species [LFeMe]⁺ (L = bis(imino)pyridine) which could initiate the polymerization of ethylene.⁸

CONCLUSIONS

Fe(acac)₃-bis(imino)pyridine/MAO catalytic system displays high activity for ethylene polymerization and produce linear high-molecular weight PE with bimodal MWD and high melting temperature. Comparing to bis(imino)pyridyl compounds, DAD compound and pyridine could not stabilize the metal center, resulting in very low catalytic activity. The polymerization results, combined with UV-vis stud-

ies, suggest that Fe(acac)₃-bis(imino)pyridine/MAO system could generate same active species as bis(imino)pyridyliron/MAO catalytic system. MAO is proposed to participate in the ligand exchange process. To the best of our knowledge, this is the first reported iron(III) acetylacetonate catalytic system for ethylene polymerization.

References

1. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem Rev* 2000, 100, 1169.
2. Boffa, L. S.; Novak, B. M. *Chem Rev* 2000, 100, 1479.
3. Gibson, V. C.; Spitzmesser, S. K. *Chem Rev* 2003, 103, 283.
4. Small, B. L.; Brookhart, M.; Bennett, A. M. *J Am Chem Soc* 1998, 120, 4049.
5. Britovsek, G. P. J.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mctavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem Commun* 1998, 849.
6. Britovsek, G. P. J.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; Mctavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J Am Chem Soc* 1999, 121, 8728.
7. Abu-Surrah, A. S.; Kristian, L.; Ulla, P.; Petri, L.; Timo, R.; Markku, L. *J Organomet Chem* 2002, 648, 55.
8. Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellmann, K. P. *J Chem Soc Dalton Trans* 2002, 6, 1159.
9. Schmidt, R.; Welch, M. B.; Palackal, S. J.; Alt, H. G. *J Mol Catal A: Chem* 2002, 155, 179.
10. Qiu, J. M.; Li, Y. F.; Hu, Y. L. *Polym Int* 2000, 49, 5.
11. Ma, Z.; Wang, H. J.; Qiu, M.; Xu, D. M.; Hu, Y. L. *Macromol Rapid Commun* 2001, 22, 1280.
12. Kolb, P.; Demuth, D.; Newsam, J. M.; Smith, M. A.; Sundermann, A.; Schunk, S. A.; Bettonvill, S.; Breulet, J.; Francois, P. *Macromol Rapid Commun* 2002, 25, 280.
13. Liu, J. Y.; Li, Y. S.; Liu, J. Y.; Li, Z. S. *Macromolecules* 2005, 38, 2559.
14. Sun, W. H.; Jie, S. Y.; Zhang, S.; Song, Y. X.; Ma, H. W. *Organometallics* 2006, 25, 666.
15. Gibson, V. C.; Long, N. J.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *Organometallics* 2006, 25, 1932.
16. Swift, H. E.; Bozik, J. E.; Wu, C. Y. *J Mol Catal* 1970, 17, 331.
17. Zhang, Z. Y.; Zhang, H. J.; Ma, H. M.; Wu, Y. *J Mol Catal* 1982, 17, 65.
18. Sun, Q.; Wang, F. *Acta Polym Sinica* 1988, 2, 145.
19. Johnson, L. K.; Killian, M. C.; Arthur, S. D. W.O. Pat. 96/23,010 (1996).
20. Zeng, X. F.; *Macromol Z. K. Chem Phys* 1998, 199, 2677.
21. Dieck, H.; Svoboda, M.; Grieser, T. *Z Naturforsch B* 1981, 36, 823.
22. Fang, J. H.; Huang, S. L.; Ge, C. X.; Zhang, Z. Y. *Acta Polym Sinica* 1999, 4, 465.
23. Zhang, Z. Y.; Qu, S. H.; Wu, Y. *Sci China (Series B)* 1985, 9, 785.
24. Lu, J.; Hu, Y. M.; Zhang, X. Q.; Bi, J. F.; Dong, W. M.; Jiang, L. S.; Huang, B. T. *J Appl Polym Sci* 2006, 100, 4265.
25. Luo, H. K.; Schumann, H. *J Mol Catal A: Chem* 2005, 227, 153.
26. Paulino, I. S.; Schuchardt, U. *J Mol Catal A: Chem* 2004, 211, 55.
27. Luo, H. K.; Yang, Z. H.; Mao, B. Q.; Yu, D. S.; Tang, R. G. *J Mol Catal A: Chem* 2002, 177, 195.
28. Wang, S. B.; Liu, D. B.; Huang, R. B.; Zhang, Y. D.; Mao, B. Q. *J Mol Catal A: Chem* 2006, 245, 122.