

Fe(acac)_n and Co(acac)_n Bearing Different Bis(imino)pyridine Ligands for Ethylene Polymerization and Oligomerization

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Received 5 August 2008; accepted 28 February 2009

DOI 10.1002/app.30350

Published online 27 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of iron and cobalt complexes ligated with different bis(imino)pyridyl ligands were synthesized and used in ethylene polymerization. The reaction temperature and Al/Fe ratio had a great influence on the activities and properties of the polymer in the iron system when methylaluminoxane was used as the cocatalyst. Bimodal polyethylene, unimodal polyethylene, and oligomers were achieved with ethylene polymerization according to the structures of the ligands and polymerization conditions. The cobalt sys-

tems showed low activities when bis(imino)pyridyl was used as the ligand in comparison with the iron system catalysts. Ethylene oligomerization was conducted, and the main products were 1-butylene and 1-hexene. A fast deactivation process was observed from the curve of the polymerization kinetics. The polymerization mechanism was examined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2378–2391, 2009

Key words: catalysts; oligomers; polyethylene (PE)

INTRODUCTION

Dramatic advances have been made in the development of polyolefins because of the invention of catalysts. In the past decade, significant progress has been achieved in the development of late-transition-metal catalysts. Some of the most important catalysts are iron complexes based on a bis(imino)pyridine ligand for ethylene polymerization, as reported by Brookhart et al.¹ and Gibson et al.² independently. These kinds of iron and cobalt catalysts have received more and more attention in both academia and industry^{3,4} because of their exceptionally high activity, remarkable selectivity for oligomerization, and potential commercial value. Various modifications of the original bis(imino)pyridine ligand framework have been made to study the influence of ligand structures on the properties of polymers.^{5–11} However, the obtained polyethylenes have had low molecular weight (M_w) values and narrow molecular weight distributions (MWDs).

Iron(III) acetylacetonate [Fe(acac)₃] is a relatively cheap organic compound. Some researchers have used Fe(acac)₃, AlR₃, and extra electron donors (e.g., nitrogen and phosphorous compounds) to polymerize the conjugated diene.^{12–14} Soga and coworkers^{15–17} studied tris(acetylacetonato)chromium supported on MgCl₂ for ethylene and propylene polymerization. Recently, Wang and Sun¹⁸ observed a novel iron-based system that contained Fe(acac)₃–bis(imino)pyridine/methylaluminoxane (MAO). This catalyst showed high activities for ethylene polymerization, and the obtained polyethylene had a high M_w value and a broad MWD.

To determine the influence of the steric hindrance of the ligand on the polymerization activities and polymer properties in the Fe(acac)₃–bis(imino)pyridine/MAO system, seven ligands with different structures were prepared in this study. The polymerization temperature and cocatalyst dosage were examined to study the catalyst properties. Subsequently, we tried to determine the relationship between the catalyst performance and the obtained polymers. The polymerization mechanism is discussed in this article.

EXPERIMENTAL

Materials

All manipulations involving air- or moisture-sensitive compounds were carried out under a nitrogen

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Contract grant sponsor: Major Project of the National Natural Science Foundation of China; contract grant numbers: 20776124, 20490205, 20736011.

Contract grant sponsor: National High Technology Research and Development Program of China; contract grant number: 2007AA030208.

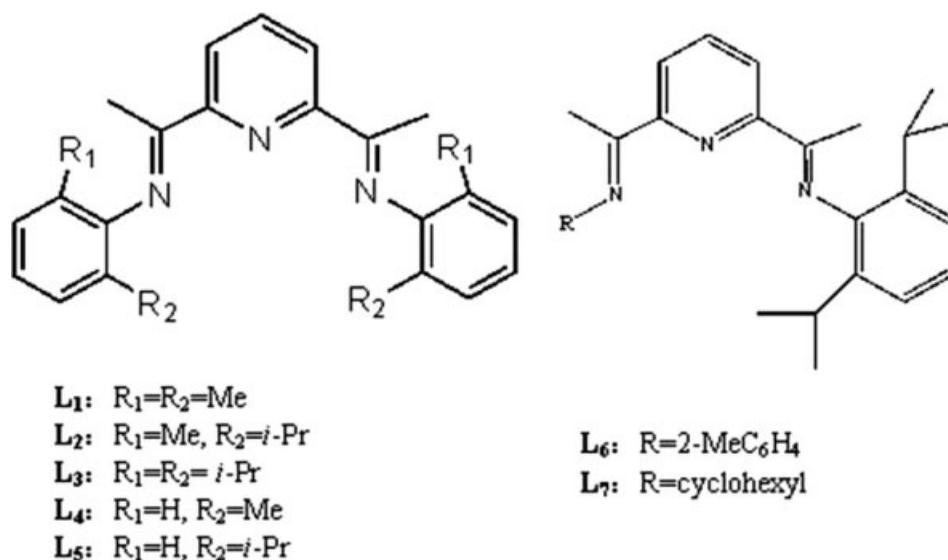


Figure 1 Structure of the bis(imino)pyridyl ligands.

atmosphere with a standard Schlenk technique. Fe(acac)₃ (99 wt %), Co(acac)₃ (99 wt %), and Co(acac)₂ (99 wt %) were purchased from J&K Chemical Corp. (Shanghai, China) and were used as received. Fe(acac)₂ (99 wt %) was purchased from Aldrich China (Shanghai, China). Toluene was dried over 4-Å molecular sieves for at least 10 days; it was then refluxed over sodium with benzophenone as the indicator and distilled under an argon atmosphere before use. MAO (10% solution in toluene) was purchased from Albermarle Chemical (Baton Rouge, LA). MAO-2 was prepared by the removal of Al(CH₃)₃ from commercial MAO with a vacuum and then dissolved in the desired amount of toluene. High-purity nitrogen and polymerization-grade ethylene were obtained from SINOPEC Shanghai Corp. (Shanghai, China) and purified by passage through Mn molecular sieves and 5-Å molecular sieves in turn. The systems of the α -diimine ligands were prepared according to the literature.^{1,19-21} The structure is shown in Figure 1.

Preparation of the ligands

Preparation of ligands L₁–L₅

For the preparation of ligands L₁–L₅, a 2,6-diacetylpyridine absolute ethanol solution was added to 2,6-dimethylaniline, 2-methyl-6-isopropylphenylimino, 2,6-diisopropylphenylimino, 2-(methylphenylimino) ethyl, and phenylamine. The solution was refluxed for 48 h after the addition of a few drops of glacial acetic acid. Upon cooling to room temperature, the solvent was removed by vacuum distillation. The product was crystallized at –18°C. The solid was dissolved in 25 mL of alcohol and crystallized at –18°C after filtration. Then, the solid was washed

with ethanol and dried in a vacuum oven. The structures of the ligands were as follows.

L₁. ¹H-NMR (CDCl₃, δ): 8.50 (d, 2, H_{pyr}), 7.93 (t, 1, H_{pyr}), 7.11 (d, 4, H_{aryl}), 6.96 (t, 2, H_{aryl}), 2.26 (s, 6, N=C–CH₃), 2.06 (s, 12, aryl-CH₃).

L₂. ¹H-NMR (CDCl₃, δ): 8.52 (d, 2, H_{pyr}), 7.95 (t, 1, H_{pyr}), 7.21 (d, 2, H_{aryl}), 7.11 (m, 4, H_{aryl}), 2.88 [sept, 2, CH–(CH₃)₂], 2.30 (s, 6, N=C–CH₃), 2.08 (s, 6, aryl-CH₃), 1.23 [d, 6, CH–(CH₃)(CH₃)], 1.20 [d, 6, CH–(CH₃)(CH₃)].

L₃. ¹H-NMR (CDCl₃, δ): 8.49 (d, 2, H_{pyr}), 7.94 (t, 1, H_{pyr}), 7.18 (d, 4, H_{aryl}), 7.13 (t, 2, H_{aryl}), 2.78 [sept, 4, CH–(CH₃)₂], 2.28 (s, 6, N=C–CH₃), 1.17 [d, 24, CH–(CH₃)₂].

L₄. ¹H-NMR (CDCl₃, δ): 8.40 (d, 2, H_{pyr}), 7.89 (t, 1, H_{pyr}), 7.22 (m, 4, H_{aryl}), 7.04 (t, 2, H_{aryl}), 6.70 (d, 2, H_{aryl}), 2.34 (s, 6, N=C–CH₃), 2.13 (s, 6, aryl-CH₃).

L₅. ¹H-NMR (CDCl₃, δ): 8.42 (d, 2, H_{pyr}), 7.91 (t, 1, H_{pyr}), 7.34 (d, 2, H_{aryl}), 7.22 (t, 2, H_{aryl}), 7.13 (t, 2, H_{aryl}), 6.68 (d, 2, H_{aryl}), 3.04 [sept, 2, CH–(CH₃)₂], 2.42 (s, 6, N=C–CH₃), 1.22 [d, 6, CH–(CH₃)₂].

Preparation of ligands L₆ and L₇

The reaction was conducted with the protection of N₂; {2-acetyl-6-[1-(2,6-diisopropylphenylimino) ethyl]}pyridine and 2-methylaniline were added in turn, and the reaction occurred at 110°C for 48 h. Upon cooling to room temperature, the solvent was removed by vacuum distillation. The product was crystallized at –18°C. After filtration, the solid was dissolved in 10 mL of hot alcohol and crystallized at –18°C. Then, the solid was washed with ethanol and dried in a vacuum oven. For the preparation of L₇, instead of 2-methylaniline (used for preparing L₆), cyclohexylamine and toluene-4-sulfonate were

used; the rest of the process was the same as that for L_3 . The structures of L_6 and L_7 were as follows.

L_6 . $^1\text{H-NMR}$ (CDCl_3 , δ): 8.48 (d, 2, H_{pyr}), 7.93 (t, 1, H_{pyr}), 7.00–7.28 (m, 6, H_{aryl}), 6.72 (d, 1, H_{aryl}), 2.80 [m, 2, $\text{CH}-(\text{CH}_3)_2$], 2.37 (s, 3, $\text{N}=\text{C}-\text{CH}_3$), 2.30 (s, 3, $\text{N}=\text{C}-\text{CH}_3$), 2.16 (s, 3, aryl- CH_3), 1.18–1.97 [m, 12, $\text{CH}-(\text{CH}_3)_2$].

L_7 . $^1\text{H-NMR}$ (CDCl_3 , δ): 8.34 (d, 2, H_{pyr}), 7.82 (t, 1, H_{pyr}), 7.05–7.25 (m, 3, H_{aryl}), 3.55–3.70 (m, 1, CH), 2.75 [sept, 2, $\text{CH}-(\text{CH}_3)_2$], 2.46 (s, 3, $\text{N}=\text{C}-\text{CH}_3$), 2.27 (s, 3, $\text{N}=\text{C}-\text{CH}_3$), 1.24–1.96 (m, 10, CH_2), 1.15 [d, 12, $\text{CH}-(\text{CH}_3)_2$].

Ethylene polymerization

Normal ethylene pressure polymerization was carried out in a dried, 250-mL, three-necked flask with a stirring bar, which was purged with dry nitrogen three times and then with ethylene once. Toluene (100 mL) and a prescribed amount of MAO or another cocatalyst were injected into it, and the mixture was magnetically stirred at different temperatures. Ethylene monomer was continuously fed into it. Polymerization was started by the addition of the desired amount of a catalyst. The reaction was terminated by the addition of an ethanol–hydrochloride aqueous solution. The obtained polymer was dried *in vacuo* after it was filtered.

High-pressure polymerization was carried out in a 1-L Buchi stainless steel reactor. The reactor was filled with a toluene and MAO solution. The system was then saturated with a continuous flow of ethylene under atmospheric pressure. The polymerization was initiated by the injection of the catalyst and terminated with water. *n*-Heptane (1 mL) was added to the reactor and was used as the internal standard for analyzing the compositions by gas chromatography/mass spectrometry (GC–MS) analysis. Each sample was cooled at -18°C for 4 h and subjected to centrifugal separation. The liquid part was protected in a refrigerator, and the solid part was added to a 10% ethanol–hydrochloride aqueous solution and filtered. Then, the samples were dried in a vacuum oven.

Characterization

The synthesized polyethylene was characterized in terms of its MWD and molecular weight (M_w) with gel permeation chromatography (GPC). A PL-220 GPC (Polymer Laboratories, Darmstadt, Germany) assay was performed at 150°C with 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$ as the eluant.

Differential scanning calorimetry (DSC) was performed on a PerkinElmer (Waltham, MA) 7 series thermal analyzer with indium as the calibration standard. The nascent powder of the polymer was

heated to 160°C ($10^\circ\text{C}/\text{min}$), held at 160°C for 1 min, cooled to 25°C ($10^\circ\text{C}/\text{min}$), and held at 25°C for 1 min. Finally, the polymer was heated to 160°C ($10^\circ\text{C}/\text{min}$). The reported melting point was the peak value from the last heating.

Qualitative analysis of the oligomer composition was measured by GC–MS (HPGC6890/MS5973, Shanghai, China). Quantitative analysis was measured by GC (68090N, Agilent, Shanghai, China).

Ultraviolet–visible (UV–vis) spectra were recorded in 10-mm quartz glass cells on a PerkinElmer Lambda 20 spectrometer.

RESULTS AND DISCUSSION

Effect of the dosage of the ligand

Bis(imino)pyridyl ligands play an important role in iron and cobalt catalysts. Isolated $\text{Fe}(\text{acac})_3$ cannot show activity when MAO is used as the cocatalyst. Besides, the method of adding $\text{Fe}(\text{acac})_3$ and ligands one by one also leads to no activity. These catalyst systems can show activity only when the bis(imino)pyridyl ligands and $\text{Fe}(\text{acac})_3$ are premixed. Therefore, the molar ratio of the ligand to $\text{Fe}(\text{acac})_3$ definitely becomes the most important issue affecting the catalyst activity. The ligand L_3 was investigated because of the similar structures of the ligands. The results are shown in Figure 2. As the molar ratio increases, the activity first increases and then becomes stable when the ratio is greater than 1. Thus, equal molar amounts of $\text{Fe}(\text{acac})_3$ and the ligand are a suitable ratio for achieving the highest activity. The following experiments were conducted at this ratio.

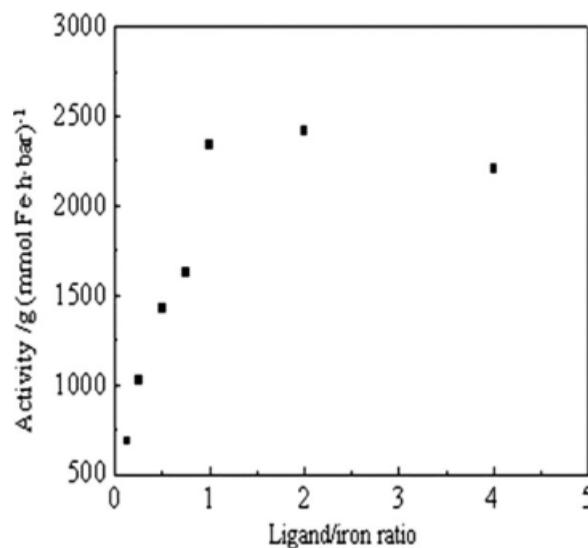


Figure 2 Effect of the $\text{Fe}(\text{acac})_3/L_3$ molar ratio on the activity in the $\text{Fe}(\text{acac})_3/L_3$ catalyst system ($\text{Al}/\text{Fe} = 1000$; pressure = 1 atm; temperature = 30°C).

TABLE I
Results of Ethylene Polymerization

Entry	Ligand	Al/Fe	Temperature (°C)	Activity (g mmol ⁻¹ h ⁻¹ bar ⁻¹)	M_w (kg/mol) ^a	M_n (kg/mol) ^a	M_{wpk} (kg/mol) ^a		M_w/M_n	T_m (°C) ^b
							Peak 1	Peak 2		
1	1	1000	0	136	—	—	—	—	—	—
2	1	1000	30	2593	25.4	3.29	2.40	46.4	7.72	128
3	1	1000	50	1105	2.37	1.57	2.37	—	1.51	122
4	1	1000	70	398	—	—	—	—	—	—
5	1	500	30	929	20.8	3.98	—	—	5.22	129
6	1	1500	30	4238	—	—	—	—	—	—
7	1	2000	30	3607	59.3	1.97	—	—	30.2	128
8	2	1000	0	1570	—	—	—	—	—	—
9	2	1000	30	2171	90.6	3.19	2.36	164	28.4	128
10	2	1000	50	926	2.35	1.63	2.35	—	1.44	122
11	2	1000	70	167	—	—	—	—	—	—
12	2	500	30	1124	65.7	10.5	—	—	6.27	132
13	2	1500	30	2695	—	—	—	—	—	—
14	2	2000	30	2752	81.4	1.87	—	—	43.6	126
15	3	1000	0	1325	383	9.31	—	—	41.1	136
16	3	1000	30	2337	164	2.65	3.72	762	62.0	131
17	3	1000	50	811	296	1.68	3.63	338	17.6	127
18	3	1000	70	438	—	—	—	—	—	—
19	3	500	30	631	65.1	15.2	—	—	4.28	133
20	3	1500	30	1742	—	—	—	—	—	—
21	3	2000	30	1520	155	2.03	—	—	76.7	130

Reaction conditions: [Fe(acac)₃] = [L_n] = 2 μmol; volume of toluene = 100 mL; ethylene pressure = 1 atm; run time = 30 min. M_n = number-average molecular weight; M_w = weight-average molecular weight; M_{wpk} = peak weight-average molecular weight; T_m = melting temperature.

^a Determined by GPC.

^b Determined by DSC (second heating run).

Results for the Fe(acac)₃/L₁, Fe(acac)₃/L₂, and Fe(acac)₃/L₃ systems

The polymerization results for the Fe(acac)₃/L₁, Fe(acac)₃/L₂, and Fe(acac)₃/L₃ catalyst systems are listed in Table I. The catalysts have acceptably high activity [10⁶ g (mol h bar)⁻¹].

Effect of the polymerization temperature and Al/Fe molar ratio on the activity

The catalyst activity is strongly influenced by the polymerization temperature, as shown in Table I. The activity of each catalyst first increases and then decreases after reaching the maximum point at 30°C.

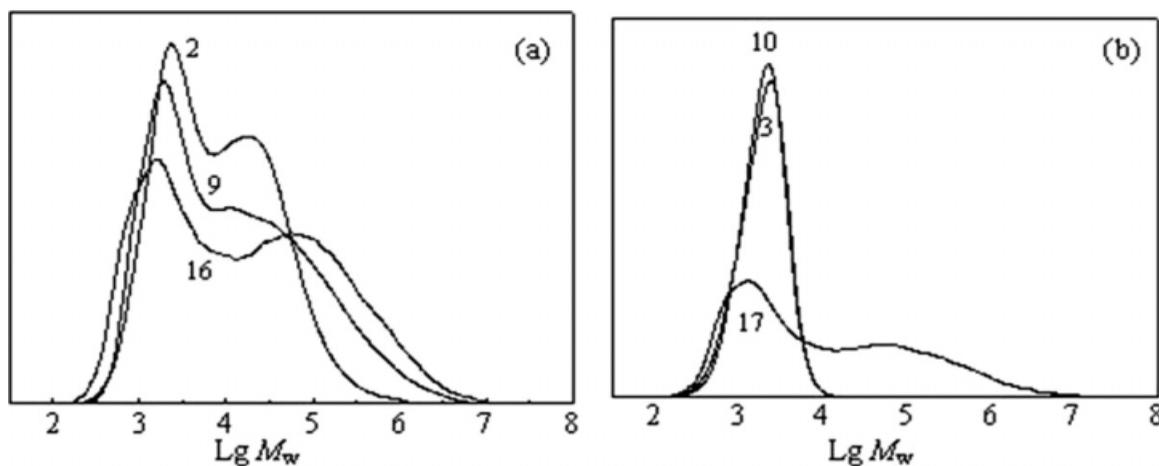


Figure 3 Effect of temperature on MWD in the Fe(acac)₃/L₁, Fe(acac)₃/L₂, and Fe(acac)₃/L₃ catalyst systems (Al/Fe = 1000; pressure = 1 atm): (a) 30 and (b) 50°C.

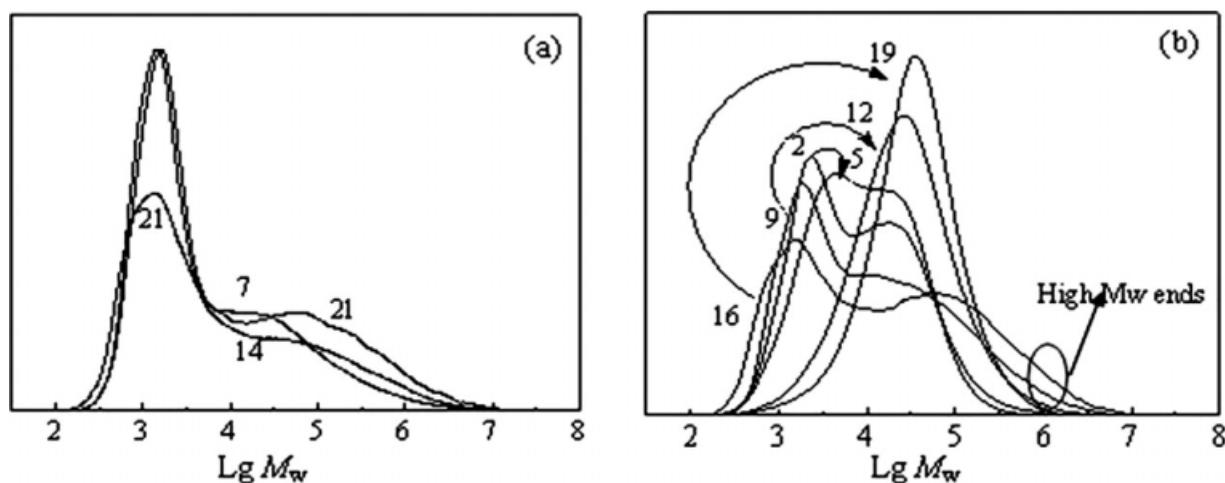


Figure 4 Effect of the Al/Fe molar ratio on MWD in the $\text{Fe}(\text{acac})_3/\text{L}_1$, $\text{Fe}(\text{acac})_3/\text{L}_2$, and $\text{Fe}(\text{acac})_3/\text{L}_3$ catalyst systems (pressure = 1 atm; temperature = 30°C): (a) Al/Fe = 2000 and (b) Al/Fe = 500 or 1000.

An increase in the polymerization temperature is expected to result in an overall enhanced propagation rate and therefore increased productivity. However, a decrease in ethylene solubility and an increase in catalyst deactivation at higher temperatures may result in a reduction of the activity.

Moreover, each catalyst system shows maximum activity at a different Al/Fe molar ratio when the

dosage of MAO is increased. Generally, more active species are formed when more MAO is added; however, superfluous MAO can deactivate the active center, especially the unstable active center, through the reaction with $\text{Al}(\text{CH}_3)_3$, which is found in commercial MAO. This is proved by the GPC results, which show that an increase in the Al/Fe molar ratio results in a decrease in MWD.^{22,23}

TABLE II
Ethylene Polymerization Results for the $\text{Fe}(\text{acac})_3/\text{L}_4$ and $\text{Fe}(\text{acac})_3/\text{L}_5$ Catalyst Systems

Entry	Ligand	Al/Fe	Temperature(°C)	Pressure (bar)	Total activity [g (mmol of Fe h bar) ⁻¹] ^a	K^b	M_w (g/mol) ^c	M_w/M_n^c	T_m (°C) ^d
1	L ₄	1000	0	1	5018	0.80	—	—	—
2	L ₄	1000	30	1	3577	0.77	827	1.68	76
3	L ₄	1000	50	1	2164	0.72	667	1.35	83
4	L ₄	500	30	1	2491	0.76	—	—	—
5	L ₄	2000	30	1	3967	0.76	589	1.35	78
6	L ₄	5000	30	1	5106	0.72	535	1.18	80
7	L ₄	4000	30	10	28971	0.70	1175	2.51	120
8	L ₅	1000	0	1	4935	0.86	—	—	—
9	L ₅	1000	30	1	2793	0.84	6863	5.19	124
10	L ₅	1000	50	1	1820	0.82	—	—	—
11	L ₅	1000	70	1	540	0.76	—	—	—
12	L ₅	500	30	1	1043	0.84	41146	20.6	127
13	L ₅	1500	30	1	2851	0.84	2129	3.05	—
14	L ₅	2000	30	1	2488	0.82	—	—	—

Reaction conditions: $[\text{Fe}(\text{acac})_3] = [\text{L}_n] = 2 \mu\text{mol}$; run time = 30 min. M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature.

^a The liquid fraction of the product was determined with GC and GC-MS.

^b Schulz-Flory parameter for the liquid fraction of the product: $K = \text{Rate of propagation}/(\text{Rate of propagation} + \text{Rate of chain transfer}) = \text{Moles of } C_{n+2}/\text{Moles of } C_n$. The K values were determined with the molar ratio of the C_{12} and C_{14} fractions.

^c Solid fraction (determined by GPC).

^d Solid fraction (determined by DSC; second heating run).

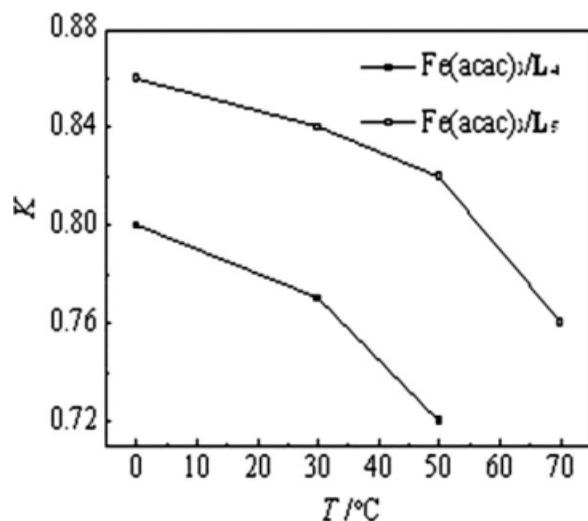


Figure 5 Effect of the reaction temperature (T) on K values in the $\text{Fe}(\text{acac})_3/\text{L}_4$ and $\text{Fe}(\text{acac})_3/\text{L}_5$ catalyst systems ($\text{Al}/\text{Fe} = 1000$; pressure = 1 atm).

Effect of the polymerization temperature and Al/Fe ratio on the polymer properties

The GPC results show that M_w decreases as the polymerization temperature increases. Bimodal polyethylene can be obtained at different polymerization temperatures with an Al/Fe molar ratio of 1000, and MWD increases with the temperature increasing in the $\text{Fe}(\text{acac})_3/\text{L}_3$ catalyst. However, when the polymerization is conducted at 30°C, bimodal polyethylene can still be obtained with the $\text{Fe}(\text{acac})_3/\text{L}_1$ and $\text{Fe}(\text{acac})_3/\text{L}_2$ systems, but the high-molar-mass part disappears when the temperature increases to 50°C (Fig. 3). This was studied by Barabanoc et al.,²² who found that the active center in a homogeneous bis(imino)pyridine iron catalyst could be divided into two kinds of active centers: a less active one for preparing high-molar-mass polyethylene and a highly active one for preparing low-molar-mass polyethylene. However, two kinds of active centers can still be observed in our systems. The former active center has obviously been deactivated, and this leads to M_w decreasing with the polymerization temperature increasing. In addition, increasing the steric bulk of the ligand can stabilize the active center and reduce the chain termination. As a result, a high-molar-mass part in $\text{Fe}(\text{acac})_3/\text{L}_3$ can still be obtained, but the fraction of high-molar-mass polyethylene decreases in the obtained polyethylene.

Figure 4 reveals the dependence of M_w and MWD on the Al/Fe molar ratio. Increasing the Al/Fe molar ratio increases the fraction of the low-molar-mass part. The low-molecular-weight chains become the main part in the product when the Al/Fe molar ratio is 2000. This can be attributed to the fact that active centers are deactivated gradually and the chain termination rate increases with the dosage of MAO increas-

ing through the reaction with $\text{Al}(\text{CH}_3)_3$. However, a more highly steric ligand can stabilize the high-molar-weight active centers and decrease the chain-termination rate. Thus, higher M_w polymers can be obtained in more highly steric ligand systems.²³

Polymers have relatively high melting temperatures. Lower melting points for the obtained polymers can be achieved when the M_w is low.

Results for the $\text{Fe}(\text{acac})_3/\text{L}_4$ and $\text{Fe}(\text{acac})_3/\text{L}_5$ systems

The results for ethylene polymerization with the $\text{Fe}(\text{acac})_3/\text{L}_4$ and $\text{Fe}(\text{acac})_3/\text{L}_5$ catalyst systems are listed in Table II. The catalyst systems show relatively high activities. The main products are composed of the oligomer and polymer.

Effect of the polymerization temperature and Al/Fe molar ratio on the activities

The dependence of the catalyst activity on the temperature is the same with the last system, and this can be attributed to the same reason. However, the catalytic activity has a different dependence on the Al/Fe molar ratio. The catalyst activity increases when the Al/Fe molar ratio increases in the $\text{Fe}(\text{acac})_3/\text{L}_4$ catalyst system, whereas the curve of the activity variance with the Al/Fe molar ratio shows a maximum point in the $\text{Fe}(\text{acac})_3/\text{L}_5$ catalyst system. The reaction occurs more readily with a complex containing two CH_3 groups, which cannot provide sufficient protection to the central metal in comparison with the L_4 complex because of the enhanced ability of the electron donor.

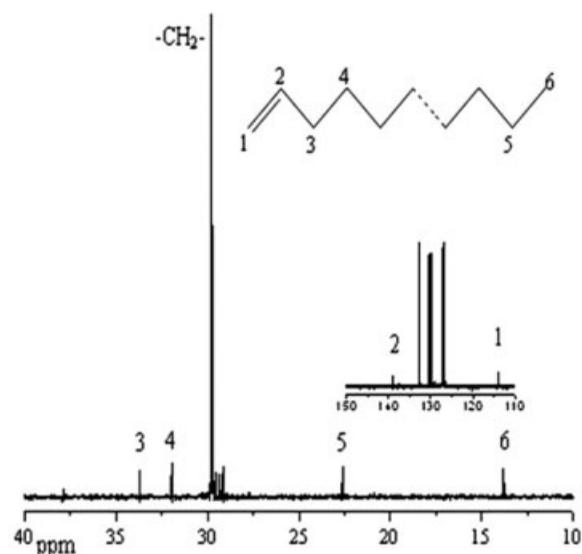


Figure 6 ^{13}C -NMR spectrum of the solid fraction obtained in the $\text{Fe}(\text{acac})_3/\text{L}_4$ catalyst system (temperature = 30°C; Al/Fe = 1000; pressure = 1 atm).

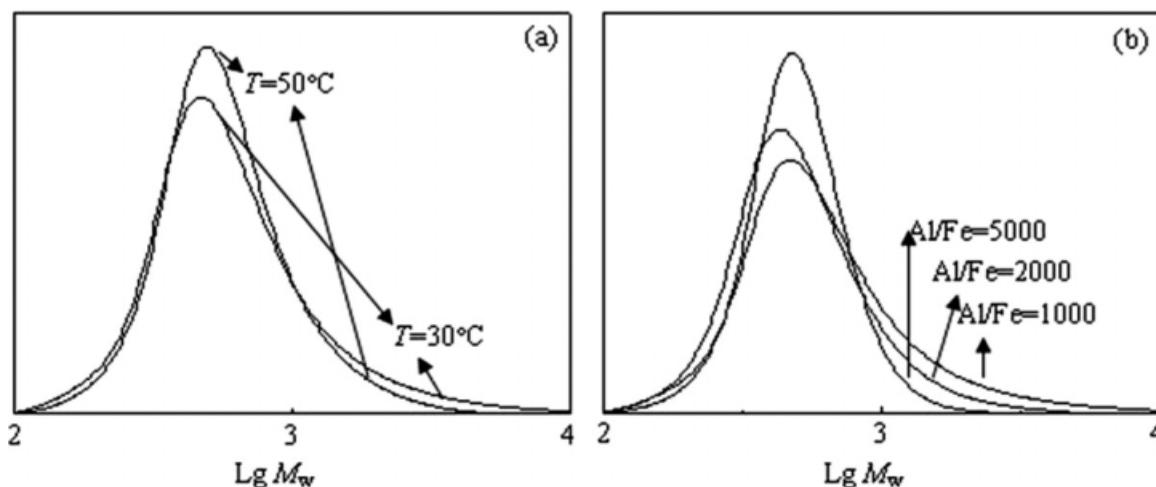


Figure 7 Effect of the Al/Fe molar ratio and temperature (T) on MWD in the $\text{Fe}(\text{acac})_3/\text{L}_4$ catalyst system: (a) Al/Fe = 1000 and (b) $T = 30^\circ\text{C}$.

Effect of the polymerization temperature and Al/Fe ratio on the polymer properties

Effect on the properties of the liquid part. The distribution of the obtained oligomer follows the Schulz–Flory rule, which can be characterized by the constant K , which represents the probability of chain propagation [$K = \text{Rate of propagation}/(\text{Rate of propagation} + \text{Rate of chain transfer}) = \text{Moles of } C_{14}/\text{Moles of } C_{12}$]. Figure 5 shows that as the reaction temperature increases, the value of K decreases, and this indicates that the content of the low-molar-mass part decreases. Increasing the reaction temperature will result in high overall transfer and propagation rates. The variance of K with temperature indicates that the rate of chain transfer increases more than the rate of chain propagation, which is expected to increase the mass fraction of lower M_w products. In addition, the product distribution is almost unchanged when the Al/Fe ratio is altered, as shown in Table II. This result is in good agreement with the results obtained by Zhang et al.²³

Effect on the properties of the solid part. The ^{13}C -NMR spectrum of the solid polymers obtained with $\text{Fe}(\text{acac})_3/\text{L}_4$ is shown in Figure 6. The assignments were determined according to the literature.^{24,25} The ^{13}C -NMR spectrum demonstrates that linear α -olefins absolutely predominate in the waxes. The single peaks at $\delta = 139.14$ ppm and $\delta = 114.17$ ppm show the property of a vinyl-unsaturated chain end. This indicates that β -H transfer is the main method of termination in this catalyst system.

When the ligand steric bulk is increased, chain transfer will be depressed, and this will lead to higher M_w values. The polymer obtained with the $\text{Fe}(\text{acac})_3/\text{L}_4$ catalyst shows a lower M_w , and M_w is

lower than 1000 g/mol. As the Al/Fe ratio and temperature increase, M_w decreases, as shown in Figure 7. The M_w values of the polymers obtained with $\text{Fe}(\text{acac})_3/\text{L}_5$ are higher, and bimodal curves of M_w can be obviously found with a low Al/Fe ratio (Fig. 8). Increasing the Al/Fe ratio increases the fraction of the low-molar-mass part and reduces the molar mass of the high-molecular-weight part. This can be attributed to the two kinds of active centers. One is sensitive to MAO, which is used to produce the low-molecular-weight part. The chain transfer to Al increases in this kind of active center when the dosage of MAO is increased. Thus, more and more low-molar-mass polyethylene is obtained. However, the active center for preparing the high-molar-mass part

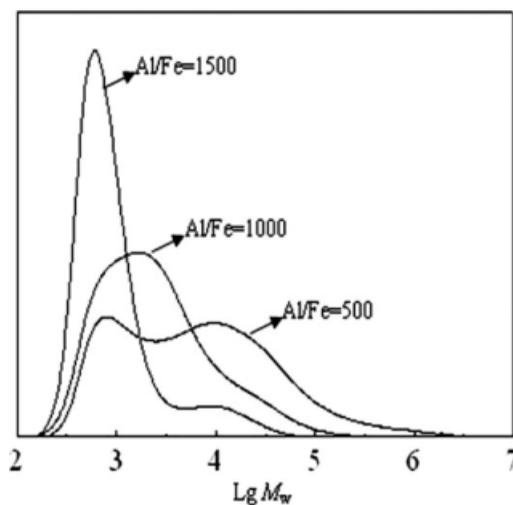


Figure 8 MWD of the solid fraction obtained in the $\text{Fe}(\text{acac})_3/\text{L}_5$ catalyst system (pressure = 1 atm; temperature = 30°C).

TABLE III
Ethylene Polymerization Results for the Fe(acac)₃/L₆ and Fe(acac)₃/L₇ Catalyst Systems

Entry	Ligand	Al/Fe	Temperature (°C)	Activity [g (mmol of Fe h bar) ⁻¹] ^b	M _w (kg/mol) ^c	M _n (kg/mol) ^c	M _w /M _n	T _m (°C) ^d
1	L ₆ ^a	1000	0	2746	—	—	—	—
2	L ₆ ^a	1000	30	1182	45.9	2.06	22.3	127
3	L ₆ ^a	1000	50	568	1.47	0.97	1.51	115
4	L ₆ ^a	1000	70	383	—	—	—	—
5	L ₆ ^a	500	30	832	5.81	2.46	2.36	126
6	L ₆ ^a	1500	30	951	—	—	—	—
7	L ₆ ^a	2000	30	1032	16.9	0.98	17.3	122
8	L ₇ ^e	400	0	136	—	—	—	128
9	L ₇ ^e	400	30	360	133	39.3	3.39	134
10	L ₇ ^e	400	50	102	—	—	—	127
11	L ₇ ^e	200	30	49	—	—	—	136
12	L ₇ ^e	800	30	177	—	—	—	129

M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature.

^a Reaction conditions: [Fe(acac)₃] = [L_n] = 2 μmol; cocatalyst = MAO; volume of toluene = 100 mL; ethylene pressure = 1 atm; run time = 30 min.

^b A few oligomers were produced.

^c Determined by GPC.

^d Determined by DSC (second heating run).

^e Reaction conditions: [Fe(acac)₃] = [L_n] = 5 μmol; cocatalyst = MAO; volume of toluene = 100 mL; ethylene pressure = 1 atm; run time = 30 min.

is deactivated, and the rate of chain termination is increased by the superfluous MAO. As a result, the molar mass of the high-molar-mass part decreases with the MAO dosage increasing.

Results for the Fe(acac)₃/L₆ and Fe(acac)₃/L₇ catalyst systems

The Fe(acac)₃/L₆ and Fe(acac)₃/L₇ catalyst systems have asymmetric phenyl on the ligands. The obtained samples contained the oligomer and polymer. The polymerization results are shown in Table III.

Effect of the polymerization temperature and Al/Fe molar ratio on the catalyst activity. As the reaction temperature increases, the activity decreases much more. However, the Al/Fe ratio does not have a greater influence on the activity than the polymerization temperature in the Fe(acac)₃/L₆ system. Because of the cyclohexyl in L₇, the activity of the Fe(acac)₃/L₇ catalyst is low [10⁵ g (mmol of Fe h bar)⁻¹] in comparison with the other system. The same tendency of influencing the catalyst activity caused by the polymerization temperature and Al/Fe ratio can be observed.

Effect of the polymerization temperature and Al/Fe ratio on the polymer properties. Bimodal polyethylene is obtained when polymerization is conducted at 30°C, whereas only the low-molecular-weight part with a relatively narrow distribution occurs when polymerization occurs at 50°C in the Fe(acac)₃/L₆ catalyst system [Fig. 9(a)]. This change can be attributed to the same reason given for the Fe(acac)₃/L₁ case.

With the Al/Fe ratio increasing, the fraction of the low-molar-mass part increases, and the high-molecular-weight end is observed with the higher Al/Fe molar ratio. The bimodal shape of the curve is notable at higher Al/Fe ratios [1000 and 2000; Fig. 9(b)]. In our opinion, the reason is that when the Al/Fe molar ratio is increasing, the active center for preparing the high-molar-mass part is further activated, so the high-molecular-weight end can be obtained. Moreover, a further increase in the MAO dosage can promote chain transfer to Al(CH₃)₃ in the active center for preparing a low molar mass, which leads to a higher content of the low-molar-mass polyethylene in the obtained polymer. When the Al/Fe ratio is 400, the obtained polymer has a relatively high M_w, but the M_w value cannot be detected at a higher Al/Fe ratio because of the superhigh M_w in the Fe(acac)₃/L₇ catalyst. Fortunately, the melting temperature is really high. It decreases with the Al/Fe molar ratio increasing. This can be attributed to the fact that the chain termination can be definitely hindered by the highest steric bulk of the ligand in the Fe(acac)₃/L₇ system. Thus, a high-M_w polymer can be obtained.

Results for the Co(acac)_n (n = 2 or 3)/L₄ and Co(acac)_n (n = 2 or 3)/L₅ catalyst systems

The cobalt systems show low activity in comparison with the iron system catalysts. Ethylene polymerization can be conducted with Co(acac)_n (n = 2 or 3)/L₄ or Co(acac)_n (n = 2 or 3)/L₅ when MAO is used as the cocatalyst. The products are 1-butylene

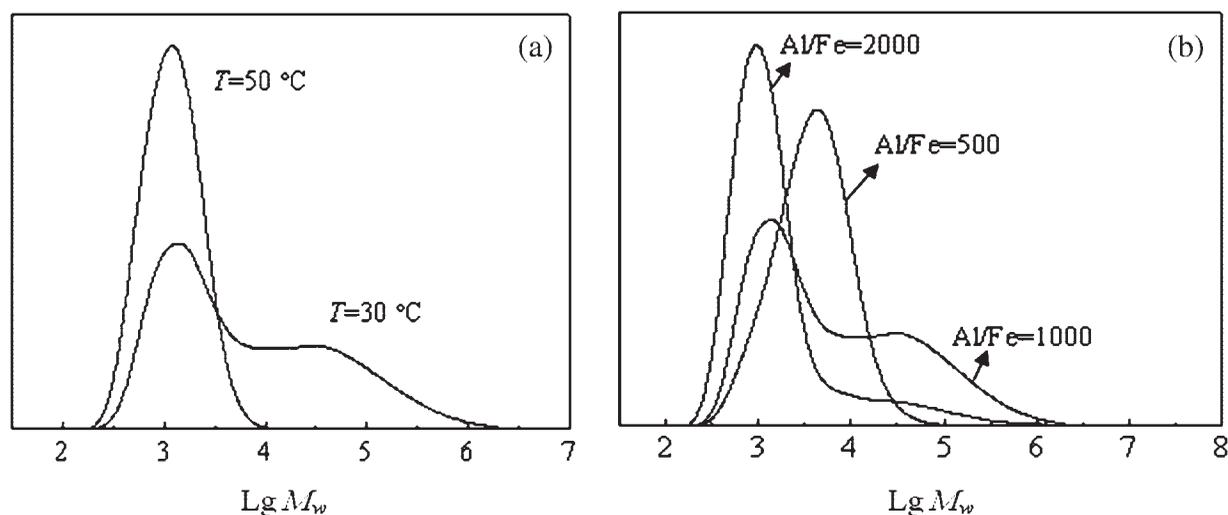


Figure 9 Effect of the Al/Fe molar ratio and temperature (T) on MWD in the Fe(acac)₃/L₆ catalyst system: (a) Al/Fe = 1000 (pressure = 1 atm) and (b) $T = 30^\circ\text{C}$ (pressure = 1 atm).

and 1-hexene. A high-molecular-weight polymer cannot be obtained with a cobalt system (Table IV).

Generally, the catalyst activity decreases when the steric bulk of the aniline group increases in the bis(imino)pyridyl cobalt complexes, but an increase in the steric bulk reduces the catalyst activity in our system; this is caused by the unstable active center of the L₄ system. The results of normal pressure polymerization show that the activities of the Co(acac)₃/L₄ and Co(acac)₂/L₄ systems can be kept for 5 min; however, the activity of the Co(acac)₃/L₅ and Co(acac)₂/L₅ systems can be maintained for 10 min at least. It is proved by high-pressure poly-

merization kinetics that the Co(acac)₂/L₄ system shows higher activity in the initial stage, and faster deactivation occurs in the following stage (Fig. 10).

When polymerization is conducted at 0 or 30 °C, the Co(acac)₃ system has lower activity, but when the reaction temperature is 50 or 70 °C, the two systems show similar activities in comparison with the Co(acac)₂ system. This may be because different active intermediates are generated at different temperatures in the Co(acac)₃ catalyst system. At a low temperature, the formation of an active center from an active intermediate needs more activation energy in the Co(acac)₃ system, and this results in lower

TABLE IV
Ethylene Oligomerization Results for the Cobalt Catalyst Systems

Entry	Ligand	Co(acac) _n	Amount (μmol)	MAO (equiv)	Temperature (°C)	Activity [g (mmol Co h bar) ⁻¹] ^a	Hexane selectivity (%) ^a
1	—	Co(acac) ₃	10	300	30	28	0
2	L ₄	Co(acac) ₃	10	300	0	34	4.70
3	L ₄	Co(acac) ₃	10	300	30	24	5.85
4	L ₄	Co(acac) ₃	10	300	50	80	5.90
5	L ₄	Co(acac) ₃	10	300	70	30	5.59
6	L ₄	Co(acac) ₂	10	300	0	192	4.53
7	L ₄	Co(acac) ₂	10	300	30	126	5.43
8	L ₄	Co(acac) ₂	10	300	50	94	5.66
9	L ₄	Co(acac) ₂	10	300	70	35	5.95
10	L ₅	Co(acac) ₃	10	300	0	164	16.4
11	L ₅	Co(acac) ₃	10	300	30	169	20.4
12	L ₅	Co(acac) ₃	10	300	50	374	21.4
13	L ₅	Co(acac) ₃	10	300	70	168	22.1
14	L ₅	Co(acac) ₂	10	300	0	652	15.1
15	L ₅	Co(acac) ₂	10	300	30	417	19.0
16	L ₅	Co(acac) ₂	10	300	50	391	20.7
17	L ₅	Co(acac) ₂	10	300	70	191	22.4

Reaction condition: run time = 15 min.

^a Determined by GC and GC-MS.

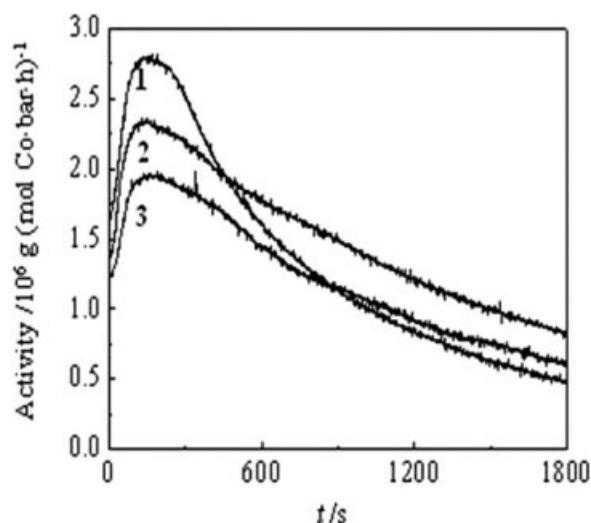


Figure 10 Catalytic oligomerization rate of the Co catalyst system: (1) $\text{Co}(\text{acac})_2/\text{L}_4$, (2) $\text{Co}(\text{acac})_2/\text{L}_5$, and (3) $\text{Co}(\text{acac})_3/\text{L}_5$ (pressure = 3 atm; temperature = 30°C ; volume of toluene = 100 mL; amount of the catalyst = 10 μmol ; Al/Co = 300).

oligomerization activity. However, the activation energy can be relatively overcome at a high temperature. As a result, the activity is similar for each system.

The steric bulk has a great influence on the distribution of products. A higher steric bulk has higher hexane selectivity because of the higher chain propagation rate in the $\text{Co}(\text{acac})_3/\text{L}_5$ and $\text{Co}(\text{acac})_2/\text{L}_5$ catalyst systems.

Active centers

The bis(imino)pyridyl iron complexes can be detected when they are used as catalyst precursors because of the easy separation and purification; however, the structures of the samples cannot be

measured clearly when the catalyst precursor reacts with MAO. UV-vis studies of MAO-activated olefin polymerization systems were carried out previously for bis(imino)pyridyl iron catalysts.^{26,27} UV-vis was used to study the possible existence of active centers when MAO was added in our work. The results agree with the literature^{27,28} (Fig. 11). $\text{Fe}(\text{acac})_3/\text{L}_3$ and $\text{Fe}(\text{acac})_3$ have the same characteristic adsorption peak at 445 nm before MAO is added; however, when MAO is added, the peak of $\text{Fe}(\text{acac})_3/\text{L}_3$ at 445 nm disappears, and a new peak is generated between 500 and 600 nm because of the interaction between the catalyst systems and MAO.

Multiactive centers and chain transfer

From the polymerization results, it can be found that the bis(imino)pyridyl iron complexes can produce bimodal distribution polyethylene when the dosage of MAO is high. Gibson et al.²⁸ observed that the end groups of the low-molar-mass part of polyethylene obtained by bis(imino)pyridyl iron complexes were almost saturated. Britovsek and coworkers^{29,30} added an effective chain-transfer agent to the bis(imino)pyridyl iron complexes. When ZnEt_2 was added, the low-molar-mass part of polyethylene was mainly prepared by chain transfer to ZnEt_2 . Thus, the low-molecular-weight part of polyethylene was formed by chain transfer to $\text{Al}(\text{CH}_3)_3$. These standpoints can explain the formation of bimodal polyethylene, but chain transfer to Al cannot clearly explain the variation of the GPC curve in our catalyst system; the main problems are as follows.

First, when the Al/Fe ratio is 1000, M_w of the low-molecular-weight part of polyethylene obtained with $\text{Fe}(\text{acac})_3/\text{L}_n$ ($n = 1, 2, \text{ or } 3$) systems is lower than what is obtained at a lower Al/Fe ratio, but as shown in Figure 4, all the polyethylene contains a

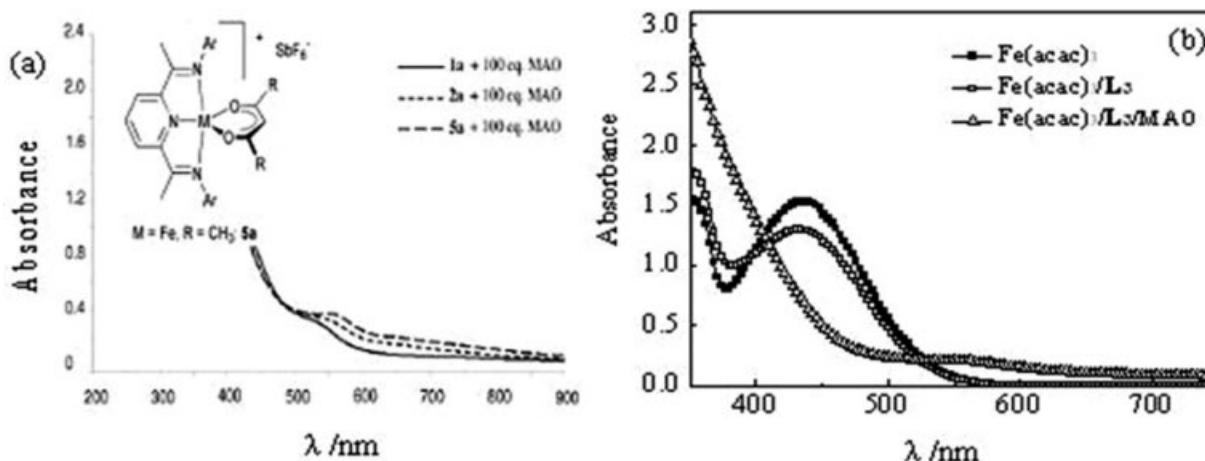


Figure 11 UV-vis spectra of (a) the iron catalyst reported in the literature and (b) $\text{Fe}(\text{acac})_3$, $\text{Fe}(\text{acac})_3/\text{L}_3$, and $\text{Fe}(\text{acac})_3/\text{L}_3/\text{MAO}$.

TABLE V
Ethylene Polymerization Results for the Fe(acac)₃/L₁ Catalyst System

Entry	Cocatalyst	Al/Fe	Activity [g (mmol of Fe h bar) ⁻¹]	M _w (kg/mol) ^a	M _n (kg/mol) ^a	M _w /M _n	T _m (°C) ^b
1	MAO	500	929	20.8	3.98	5.22	129
2	MAO	1000	2593	25.4	3.29	7.72	128
3	MAO	1500	4238	—	—	—	—
4	MAO	2000	3607	59.3	1.97	30.2	128
5	MAO-2	500	2256	23.8	4.44	5.35	129
6	MAO-2	1000	3773	39.7	4.35	9.13	129
7	MAO-2	2000	2791	—	—	—	124

Reaction conditions: [Fe(acac)₃] = [L₁] = 2 μmol; temperature = 30°C; volume of toluene = 100 mL; ethylene pressure = 1 atm; run time = 30 min. M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature.

^a Determined by GPC.

^b Determined by DSC (second heating run).

higher M_w end part in comparison with the lower Al/Fe ratio case.

Second, in general, increasing the steric bulk of a ligand decreases the rate of β-H chain transfer; thus, the influence of chain transfer to Al turns out to be more obvious in ligands with a higher steric bulk. The previous results agree with this tendency. However, when polymerization is conducted with Fe(acac)₃/L_n (n = 1, 2, or 6), as the reaction temperature increases from 30 to 50°C, the high molar mass disappears, but the bimodal polyethylene is still obtained with the Fe(acac)₃/L₃ catalyst systems. If the low-M_w part is made by chain transfer to Al, the whole M_w will decrease as the temperature increases according to this hypothesis. L₃ has the largest steric bulk of the four ligands, so it should have the biggest variance depending on the reaction temperature. However, the polymerization temperature shows a great influence on the polyethylene M_w values; when Fe(acac)₃/L₁ and Fe(acac)₃/L₂ are used, the smallest variance is shown by the Fe(acac)₃/L₃ catalyst system.

Another view of the active centers of bis(imino)pyridyl iron complexes considers bimodal polyethylene to be made of two kinds of catalyst active centers.^{21,30} Kissin et al.³¹ fitted the GPC curves of bimodal polyethylene obtained with bis(imino)pyridyl iron catalysts; the fitting results showed that multi-active centers existed in that catalyst system. The combined influence on the polymerization results, contributed by multi-active centers and chain transfer to Al, can clearly explain the tendency in our catalyst systems. The multi-active centers are made of two parts: one is used to prepare high-M_w chains that will appear under certain reaction conditions, and the other is used to produce a low-M_w part that shows a strong correlation with chain transfer to MAO. As the temperature increases, the part of the active center that is used to make high-M_w chains cannot steadily exist, and this results in

the disappearance of the high-molar-mass part in Fe(acac)₃/L_n (n = 1, 2, or 6) systems; however, this kind of active center is stable in the Fe(acac)₃/L₃ catalyst system. Thus, the bimodal polyethylene can still be obtained.

As the steric bulk increases, β-H transfer decreases in Fe(acac)₃/L₁, Fe(acac)₃/L₂, and Fe(acac)₃/L₃ catalyst systems. Thus, the chain transfer to Al is relatively enhanced, and this indicates that the influence of the Al/Fe ratio on the MWD will be magnified. However, as the Al/Fe ratio increases from 500 to 1000, the active center used to prepare the high-M_w part is generated in these catalyst systems; thus, the high-M_w chain end is prepared. The results for Fe(acac)₃/L_n (n = 4–7) can be explained with the same reasoning.

Effects of the different cocatalysts and catalyst active center precursors

To obtain further knowledge on producing bimodal polyethylene, different cocatalysts were used for ethylene polymerization; moreover, Fe(acac)₂ and Fe(acac)₃ were used as the catalyst active center precursors.

Different cocatalysts

Al(CH₃)₃ in the commercial MAO was removed with a vacuum and was named MAO-2; it was used for studying the influence of chain transfer to Al.

The results for Fe(acac)₃/L₁ catalyst polymerization conducted with MAO and MAO-2 are listed in Table V. When the Al/Fe ratio is 500 or 1000, the activity of the MAO-2 system is higher. However, it is lower than that of the MAO system when the Al/Fe ratio is 2000. The influence of cocatalysts MAO and MAO-2 on the activities of the Fe(acac)₃/L₃ system is shown in Table VI. When MAO is used as the cocatalyst, the activity reaches the maximum when

TABLE VI
Ethylene Polymerization Results for the Fe(acac)₃/L₃ Catalyst System

Entry	Cocatalyst	Al/Fe	Activity [g (mmol of Fe h bar) ⁻¹]	<i>M_w</i> (kg/mol) ^a	<i>M_n</i> (kg/mol) ^a	<i>M_w</i> / <i>M_n</i>	<i>T_m</i> (°C) ^b
1	MAO	500	631	65.1	15.2	4.28	133
2	MAO	1000	2337	164	2.65	62.0	131
3	MAO	1500	1742	—	—	—	—
4	MAO	2000	1520	155	2.03	76.7	130
5	MAO-2	500	1946	79.9	2.36	33.9	130
6	MAO-2	1000	2020	35.6	2.79	12.7	129
7	MAO-2	1500	2181	74.8	3.60	20.8	—
8	MAO-2	2000	2486	105	7.20	14.6	126

Reaction conditions: [Fe(acac)₃] = [L₃] = 2 μmol; temperature = 30°C; volume of toluene = 100 mL; ethylene pressure = 1 atm; run time = 30 min. *M_n* = number-average molecular weight; *M_w* = weight-average molecular weight; *T_m* = melting temperature.

^a Determined by GPC.

^b Determined by DSC (second heating run).

the ratio is 1000. However, when MAO-2 is used as the cocatalyst, increased activity is observed with the Al/Fe molar ratio increasing.

M_w decreases as the Al/Fe ratio increases, and a high-molecular-weight chain end is obtained in the MAO case (Fig. 4). Because of the low steric bulk in L₁, β-H transfer is the main method in comparison with chain transfer to Al. As the content of Al(CH₃)₃ in MAO-2 is lower, chain transfer to Al is further lowered in the MAO-2 system, and the result is that increasing the Al/Fe ratio increases *M_w*. In addition, both high-molecular-weight ends are observed at the higher Al/Fe ratio in these two systems [Fig. 12(a)]. This indicates that the active center for preparing the high-molar-mass part has less dependence on the amount of Al(CH₃)₃ in the cocatalyst.

The steric bulk is high in the L₃ system. Thus, the effect of β-H transfer is lower. As a result, the cocatalyst has a great influence on the properties of the obtained polymer. As the Al/Fe ratio increases, *M_w* decreases when MAO is used as the cocatalyst. The bimodal polyethylene and high-molecular-weight chain end are not obtained with the Al/Fe molar ratio of 500 [Fig. 4(b)]. As the Al/Fe ratio increases, *M_w* of the polymer and *M_w* of the low-*M_w* part increase with MAO-2. Bimodal polyethylene is obtained with each Al/Fe ratio [Fig. 12(b)]. All these results prove the existence of multi-active centers in the catalyst active centers; the active center for preparing the low-molar-mass part is sensitive to Al(CH₃)₃, and the active center for preparing the high-molar-mass part has less dependence on the dosage of Al(CH₃)₃.

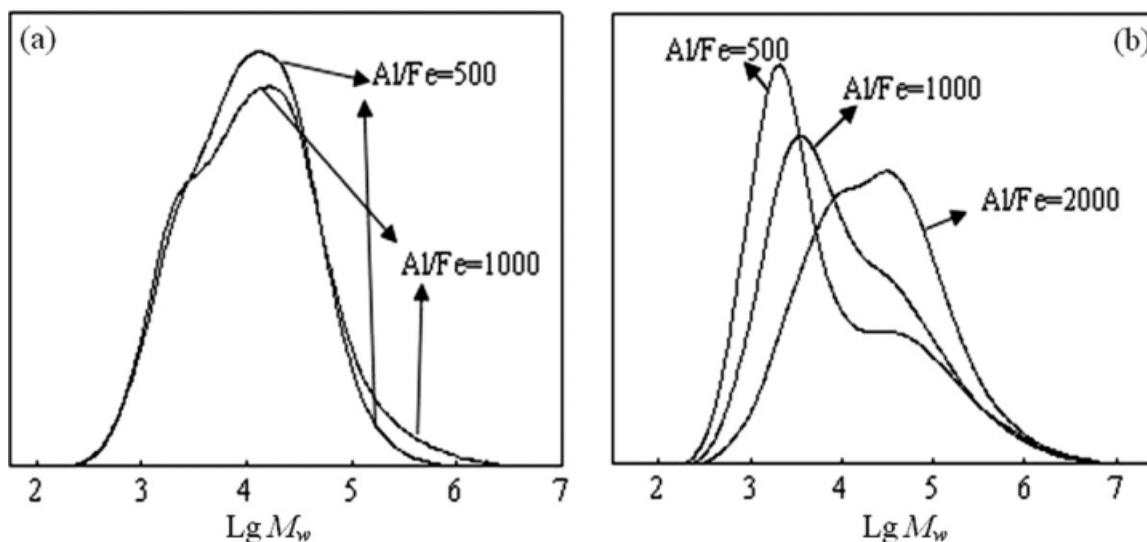


Figure 12 GPC results for (a) the Fe(acac)₃/L₁ catalyst system and (b) the Fe(acac)₃/L₃ catalyst system when MAO-2 was used as the cocatalyst.

TABLE VII
Ethylene Polymerization Results for the Fe(acac)_n/L₃ Catalyst Systems

Entry	Fe(acac) _n	Al/Fe	Activity [g (mmol of Fe h bar) ⁻¹]	M _w (kg/mol) ^a	M _n (kg/mol) ^a	M _w /M _n	T _m (°C) ^b
1	Fe(acac) ₃	500	631	65.1	15.2	4.28	133
2	Fe(acac) ₃	1000	2337	164	2.65	62.0	131
3	Fe(acac) ₂	500	150	10.3	1.35	7.59	56
4	Fe(acac) ₂	1000	279	5.75	1.04	5.52	57

Reaction conditions: [Fe(acac)_n] = [L₃] = 2 μmol; temperature = 30°C; cocatalyst = MAO; volume of toluene = 100 mL; ethylene pressure = 1 atm; run time = 30 min. M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature.

^a Determined by GPC.

^b Determined by DSC (second heating run).

In addition, normal pressure polymerization can be conducted with Fe(acac)₃/L₃ with Al(*i*-Bu)₃ as the cocatalyst. When the reaction temperature is 30°C and the Al/Fe ratio is 1000, the catalyst activity is extremely low [124 g (mmol of Fe h bar)⁻¹]; M_w is 16.8 kg/mol, and MWD is 4.2. In addition, the Fe(acac)₃/L₁ and Fe(acac)₃/L₃ systems do not show activity when Al(Et)₃ is used as the cocatalyst during the polymerization.

Catalyst active center precursors

The activity of the Fe(acac)₃/L₃ catalyst system can reach 10³ g (mmol of Fe h bar)⁻¹; however, the activity is only 10² g (mmol of Fe h bar)⁻¹ in the Fe(acac)₂/L₃ catalyst system. Furthermore, with an increase in the Al/Fe ratio, the activity is still low (Table VII). In addition, no activity of the catalyst is achieved when polymerization is conducted at 0°C.

The polymer obtained with Fe(acac)₃/L₃ has a higher content of high-molecular-weight chains in comparison with the polyethylene obtained with Fe(acac)₂/L₃ (Fig. 13). This is because the active center of the Fe(acac)₂/L₃ system is formed by the interaction with MAO, but the active center used to prepare the high-M_w part is difficult to form. Accordingly, the number of active centers for a high M_w value is less. This results in a lower content of the high-M_w part, and the high-molecular-weight end can be observed only when the dosage of MAO reaches a certain amount.

CONCLUSIONS

A series of iron and cobalt acetylacetonate complexes bearing bis(imino)pyridyl ligands of different structures were synthesized and used for ethylene polymerization. The active center was formed by coordination between equal amounts of the iron acetylacetonate complexes and ligands. Broad bimodal polyethylenes and oligomers could be obtained with

these catalyst systems. Bis(imino)pyridyl ligands showed a great influence on the catalyst systems. High-M_w polyethylene was obtained with the Fe(acac)₃/L₁, Fe(acac)₃/L₂, and Fe(acac)₃/L₃ systems. The main products were made of the oligomer and polymer in the Fe(acac)₃/L₄ and Fe(acac)₃/L₅ systems. However, the polymer was the predominant product with the Fe(acac)₃/L₆ and Fe(acac)₃/L₇ catalyst systems, and there was a comparatively small amount of the oligomer. The main products were 1-butylene and 1-hexene, and no polymer was obtained with the Co(acac)₃/L₄ and Co(acac)₃/L₅ systems. The polymerization results showed that increasing the reaction temperature could make the M_w lower. With decreased steric bulk, the number of active centers for preparing high-M_w polyethylene decreased, and the effect of temperature on the MWD of the products became much more notable. The effect of the Al/Fe ratio on the polymer properties was sensitive to the steric bulk. When Al(CH₃)₃ in the commercial MAO was removed and the Al/Fe ratio was increased, higher M_w polyethylene was

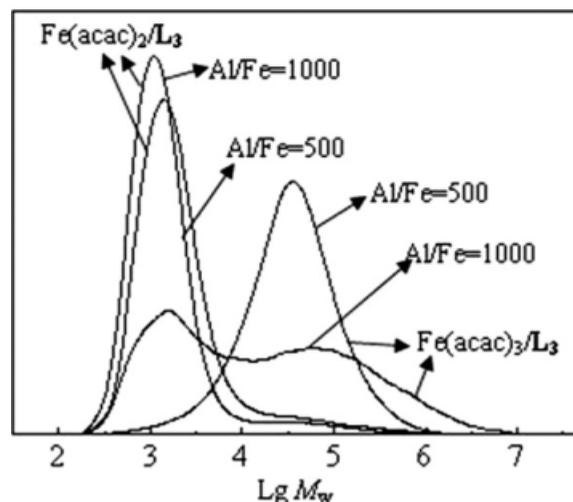


Figure 13 Effect of the pre-catalyst on MWD when polymerization was conducted at 30°C.

obtained, and the M_w value of the low- M_w part was increased. We suppose that two kinds of active centers were shown in the catalyst. One used for preparing the low-molar-mass part was sensitive to $\text{Al}(\text{CH}_3)_3$, and the other used for preparing the high-molar-mass part was less dependent on $\text{Al}(\text{CH}_3)_3$. The latter one needed more activation energy to form in comparison with the former active center. As a result, the combination interaction between the multi-active centers and chain transfer could clearly explain the results of the polymerizations conducted with our novel $\text{Fe}(\text{acac})_3/\text{L}_n$ ($n = 1-7$) catalyst systems.

References

1. Small, B. L.; Brookhart, M.; Bennett, A. M. *J Am Chem Soc* 1998, 120, 4049.
2. 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. *Chem Commun* 1998, 849.
3. Gibson, V. C.; Wass, D. F. *Chem Bri* 1999, 35, 20.
4. Bennett, A. M. A. *CHEMTECH* 1999, 7, 24.
5. Britovsek, G. J. P.; Gibson, V. C.; Mastroianni, S.; Oakes, D. C. H.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur J Inorg Chem* 2001, 2001, 431.
6. Matsunaga, P. T. *Chem Abstr* 1999, 131, 351802.
7. Benna, S. A.; Sarsfield, M. J.; Pett, M. T.; Ormsby, D. L.; Maddox, P. J.; Bres, P.; Bochmann, M. *J Chem Soc Dalton Trans* 2000, 23, 4247.
8. Dawson, D. M.; Walker, D. A.; Pett, M. T.; Bochmann, M. *J Chem Soc Dalton Trans* 2000, 4, 459.
9. Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A.; Barrett, A. G. M.; Smith, T. W.; Pearson, J. C. *World Pat. WO 00/50470* (2000).
10. Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A.; Barrett, A. G. M.; Smith, T. W.; Pearson, J. C. *Chem Abstr* 2000, 133, 208316.
11. Engehausen, R.; Nentwig, W.; Schertl, P.; Rosenau, M. A.; Pyrlik, O.; Guillemot, M. *Chem Abstr* 2000, 133, 310282.
12. Swift, H. E.; Bozik, J. E.; Wu, C. Y. *J Mol Catal* 1970, 17, 331.
13. Zhang, Z. Y.; Zhang, H. J.; Ma, H. M.; Wu, Y. *J Mol Catal* 1982, 17, 65.
14. Sun, Q.; Wang, F. *Acta Polym Sinica* 1988, 2, 145.
15. Kaji, E.; Uozumi, T.; Jin, J.; Sano, T.; Soga, K. *J Polym Sci Part A: Polym Chem* 1998, 36, 2735.
16. Takawaki, K.; Uozumi, T.; Ahn, C. H.; Sano, T.; Soga, K. *Macromol Chem Phys* 2000, 201, 1279.
17. Takawaki, K.; Uozumi, T.; Ahn, C. H.; Tian, G. L.; Sano, T.; Soga, K. *Macromol Chem Phys* 2000, 200, 1605.
18. Wang, L. C.; Sun, J. Q. *J Appl Polym Sci* 2008, 108, 167.
19. Small, B. L.; Brookhart, M. *J Am Chem Soc* 1998, 120, 7143.
20. Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Zanolini, F.; Laschi, F.; Sommazzi, A. *Eur J Inorg Chem* 2003, 8, 1620.
21. Bianchini, C.; Giambastiani, G.; Guerrero, I. R.; Meli, A.; Passaglia, E.; Gragnoli, T. *Organometallics* 2004, 23, 6087.
22. Barabanoc, A. A.; Bukatov, G. D.; Zakharov, V. A.; Semikoleniva, N. S.; Echevskaja, L. G.; Matsko, M. A. *Macromol Chem Phys* 2005, 206, 2292.
23. Zhang, Z. C.; Chen, S. T.; Zhang, X. F.; Li, H. Y.; Ke, Y. C.; Lu, Y. Y.; Hu, Y. L. *J Mol Catal A* 2005, 230, 1.
24. Galland, G. B.; Souza, D.; Mauler, R. F.; Nunes, R. S. *Macromolecules* 1999, 32, 1620.
25. Galland, G. B.; Quijada, R.; Rojas, R.; Bazan, G. C.; Komon, Z. J. A. *Macromolecules* 2002, 35, 339.
26. Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellmann, K. P.; White, A. J. P.; Williams, D. J. *J Chem Soc Dalton Trans* 2002, 6, 1159.
27. Wang, S. B.; Liu, D. B.; Huang, R. B.; Zhang, Y. D.; Mao, B. Q. *J Mol Catal A* 2006, 245, 122.
28. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; Mctavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J Am Chem Soc* 1999, 121, 8728.
29. Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Meurs, M. *J Am Chem Soc* 2004, 126, 10701.
30. Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Maddox, P. J.; Meurs, M. *Angew Chem Int Ed* 2002, 41, 489.
31. Kissin, Y. V.; Qian, C. T.; Xie, G. Y.; Chen, Y. F. *J Polym Sci Part A: Polym Chem* 2006, 44, 6159.