Macromolecules **2005,** *38,* 2559−2563

Ethylene Polymerization with a Highly Active and Long-Lifetime Macrocycle Trinuclear 2,6-Bis(imino)pyridyliron

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Received November 11, 2004; Revised Manuscript Received January 19, 2005

ABSTRACT: The synthesis, characterization, and ethylene polymerization behavior of a novel macrocycle trinuclear 2,6-bis(imino)pyridyliron precatalyst **2** are reported. The molecular model of **2** was predicted using the Insight II software package. The molecular simulation indicates that the center iron atoms of complex **2** are located inside the macrocycle ligand. This new precatalyst could restrain active iron center from deactivation and effectively control chain transfer reaction, such as β-H transfer to the metal or the monomer. Compared with its mononuclear analogue **1**, precatalyst **2** shows higher activity and longer lifetime for ethylene polymerization in the presence of modified methylalumoxane as a cocatalyst and produces much higher molecular weight polyethylenes with higher melting temperatures. Furthermore, higher molecular weight polymers with unimodel molecular weight distribution can be easily obtained using triisobutylaluminum as a cocatalyst.

Introduction

There is rapidly growing interest in the area of late-transition-metal catalysts for the polymerization of olefins because of their potential for tolerating heteroatomic functionalities, which may open up the possibility for copolymerization of olefins with polar monomers.[1−30] Recently, Brookhart and Gibson reported independently a type of very attractive iron catalysts bearing 2,6-bis(imino)pyridyl ligands for ethylene polymerization,[1−3] which possess much higher activity than the nickel and palladium catalysts.[4−6] However, iron catalysts produce highly linear polyethylene with low molecular weight and broad molecular weight distribution. Furthermore, the lifetime of the iron catalysts is relatively short with rapid deactivation during polymerization although the activity is high. In studies on polymerization behaviors of the iron catalysts, it is revealed that two chain transfer pathways, namely, β-H transfer to monomer or metal and chain transfer to aluminum, are controlled by not only reaction conditions but also catalyst structure.[3] We were attracted by the potential for using iron as an ethylene polymerization active center due to its low cost and high activity. The aim of our work is to develop the new ligand to protect the active center of iron catalyst and control the rates of two chain transfers so as to obtain higher activity and yield higher molecular weight polyethylene.

Here we describe a new macrocycle trinuclear 2,6-bis(imine)pyridyliron complex, in which central iron atoms are located inside the macrocycle ligand. The new complex displays higher activity for ethylene polymerization and longer lifetime and produces much higher molecular weight polymers than its mononuclear analogue.

Experimental Section

Materials. All manipulations of water and/or moisture sensitive compounds were performed by means of standard high-vacuum Schlenk and cannula techniques under a N_2 atmosphere. Toluene was refluxed and distilled from sodium/benzophenone under dry nitrogen. Modified methylaluminoxane (MMAO) (7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. The iron pyridinebisimine complex **1** was prepared according to a published procedure by Brookhart and co-workers.[1] All other chemicals were commercially available and used without further purification.

Measurements. The NMR data of the polymers were obtained on a Varian Unity-400 MHz spectrometer at 110 °C with o-$C_6D_4Cl_2$ as the solvent. Mass spectra were obtained using electron impact (EI-MS). Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. The molecular weights and the molecular weight distributions of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

Synthesis of Macrocycle Trinuclear Complex 2. Macrocycle ligand was synthesized by pseudo-high-dilution conditions. The 100 mL mixture containing di(2,6-diisopropyl-4-aminophenyl)methane (1.46 g, 4 mmol) and 2,6-diacetylpyridine (0.65 g, 4 mmol) was dropped to 1000 mL of toluene at a speed of 1 mL/h in the presence of p-toluenesulfonic acid (0.05 g); the solution was then refluxed for 24 h. The solvent was removed to yield an orange residue. The residue was purified via column chromatography (5% ethyl acetate/hexanes, 200 mm silica gel) to give cyclic ligand as a yellow powder (1.0 g, 51%). EI-MS: $m/z = 1481$ [M$^+$]. ^{1}H NMR ($CDCl_3$): $\delta = 8.45$ (d, Py−m-H), 7.94 (t, Py−p-H), 6.98 (s, Ar−H), 4.00 (s, $-CH_2-$), 2.78 (m, CHMe$_2$), 2.19 (s, N=CMe), 1.17−1.10 (m, CHMe_2). Anal. Calcd for $C_{102}H_{129}N_9$: C, 82.71; H, 8.78; N, 8.51%. Found: C, 82.65; H, 8.81; N, 8.54%.

Under an argon atmosphere, macrocycle ligand (0.35 g, 0.24 mmol) and ferrous chloride tetrahydrate (0.2 g, 1 mmol) were stirred with THF (20 mL) at room temperature for 6 h to give **2** as a blue powder in yield 85%. Anal. Calcd for $C_{102}H_{129}Cl_6Fe_3N_9$: C, 65.81; H, 6.99; N, 6.77; Fe, 9.02%. Found: C, 65.72; H, 6.94; N, 6.73%; Fe, 9.02%.

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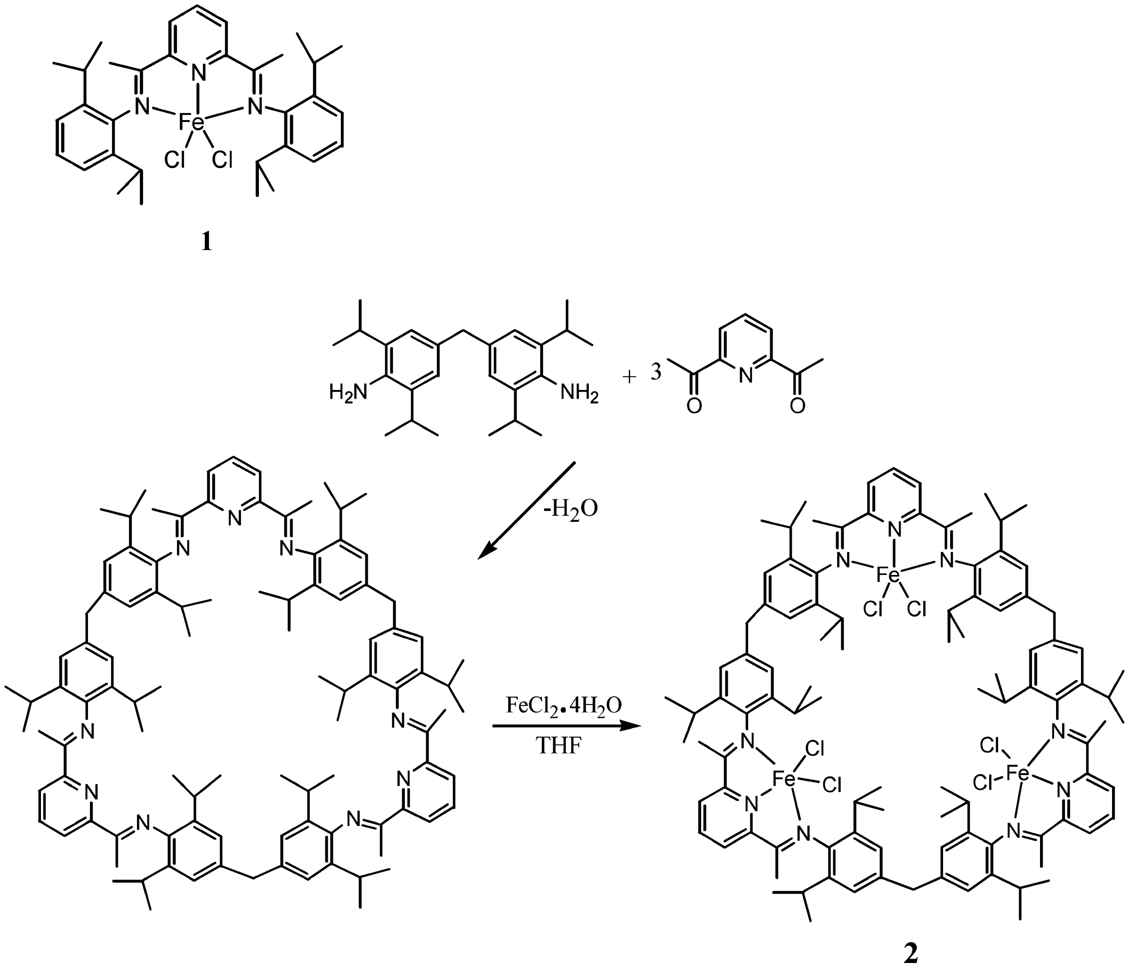
10.1021/ma047685y CCC: $30.25

Scheme 1. Route of Synthesis of Precatalyst 2



Procedure for Ethylene Polymerization. Polymerization was carried out in a 200 mL Schlenk flask equipped with a magnetic stirrer. The flask was repeatedly evacuated and refilled with nitrogen and finally filled with ethylene gas (ambient pressure) from a Schlenk line. MMAO and toluene were added via a gastight syringe. The catalyst, dissolved in toluene under a dry nitrogen atmosphere, was transferred into the Schlenk flask to initiate the polymerization. Ethylene consumption was noted as a function of time from the gas buret. The polymerization was carried out with 1 μmol of iron complex **2** (3 μmol of Fe) or 3 μmol of iron complex **1** and quenched with ethanol containing 10% (v/v) hydrochloric acid. The resulted polyethylene was isolated by filtration, washed with ethanol, and dried in a vacuum oven at 60 °C.

High-pressure polymerization was carried out in a 200 mL stainless steel reactor equipped with a mechanical stirrer and internal cooling water coils. The reactor was baked under nitrogen flow for 24 h at 150 °C, subsequently cooled to the desired reaction temperature, and then purged by ethylene for three times. Reagents and toluene were transferred to the reactor via a gastight syringe. Ethylene was introduced into the reactor, and pressure was maintained at 5 atm throughout the polymerization run by continuously feeding ethylene gas. After proceeding for 10 min, the polymerization was stopped by turning the ethylene off and relieving the pressure. The reaction mixture was poured into a solution of HCl/ethanol (10 vol %). The polymer was isolated by filtration, washed with ethanol, and dried under vacuum.

Results and Discussion

The route of macrocycle trinuclear 2,6-bis(imino)-pyridyliron(II) complex **2** is shown in Scheme 1. Macrocycle ligand was synthesized by condensation of 2,6-diacetylpyridine with di(2,6-diisopropyl-4-amidophenyl)methane using *p*-toluenesulfonic acid as a catalyst under pseudo-high-dilution conditions and purified by column chromatography. Complex **2** was synthesized at high yield by the reaction of the macrocycle ligand with iron dichloride hydride in tetrahydrofuran. Molecular model of complex **2** was built on Origin 3900 workstation by using the Insight II software package (Figure 1). Molecular mechanism (MM) calculations were performed to predict the structure of complex **2**. The ESFF (the extensible systematic force field) was employed in the energy minimization and the molecular dynamical calculation. The conformation with the lowest energy

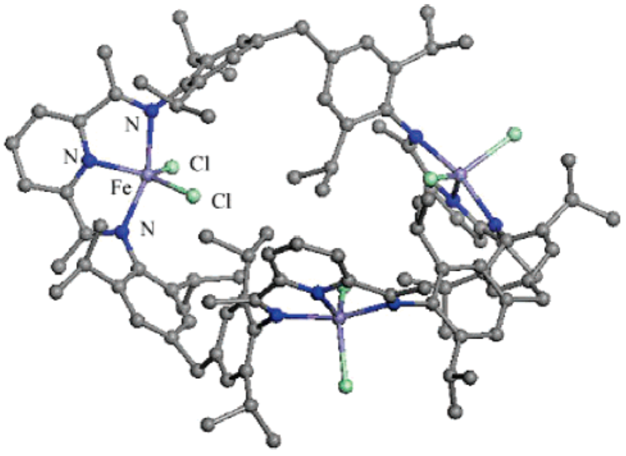


Figure 1. Molecular structure of precatalyst **2**.

Table 1. Results of Ethylene Polymerization by Iron Catalysts Activated with MMAO or TIBA

entry	catalyst (μmol)	cocatalyst	Al/Fe (molar ratio)	pressure (atm)	temp (°C)	yield (g)	activity (kg PE/(mol$_{Fe}$ h bar))	T_m[c] (°C)	$\bar{M}_w$[d] (kg/mol)	$\bar{M}_w/\bar{M}_n$[d]
1[a]	**1** (3.0)	MMAO	1000	1	0	1.15	2300	127.1	74.3	40.5
2[a]	**1** (3.0)	MMAO	1000	1	30	0.82	1640	126.8	47.2	32.4
3[a]	**2** (1.0)	MMAO	1000	1	0	2.15	4300	139.0	401.3	66.7
4[a]	**2** (1.0)	MMAO	1000	1	30	1.37	2740	138.1	213.4	51.2
5[a]	**1** (3.0)	TIBA	1200	1	0	0.81	1620	126.4	36.6	4.11
6[a]	**1** (3.0)	TIBA	1200	1	30	0.68	1360	126.1	28.3	3.61
7[a]	**2** (1.0)	TIBA	1200	1	0	1.10	2200	139.9	219.1	3.96
8[a]	**2** (1.0)	TIBA	1200	1	30	0.97	1940	138.2	200.7	3.71
9[b]	**1** (0.6)	MMAO	1000	5	30	0.90	1800	127.0	61.6	13.9
10[b]	**2** (0.2)	MMAO	1000	5	30	1.64	3280	139.3	421.0	10.6
11[b,e]	**1** (3.0)	MMAO	1000	5	30	4.30	1720	126.9	59.8	15.7
12[b,e]	**2** (1.0)	MMAO	1000	5	30	7.35	2940	138.8	364.9	12.2

[a] 1 atm ethylene pressure, toluene 50 mL, reaction for 10 min. [b] 5 atm ethylene pressure, toluene 100 mL, reaction for 10 min. [c] T_m, melting temperatures were determined by means of DSC with a heating rate of 10 °C/min in nitrogen. [d] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined by GPC vs polystyrene standards, uncorrected. [e] Mass transport limitations may have occurred.

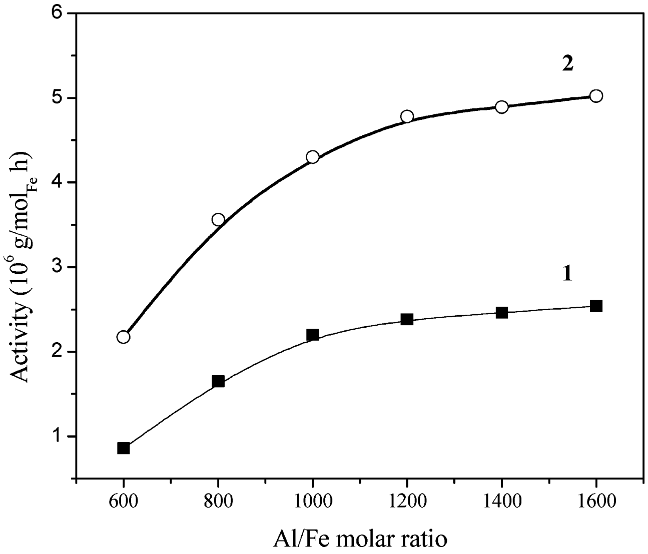


Figure 2. Effect of the Al/Fe ratio on the catalytic activity of precatalysts **1** (■) and **2** (○). Pressure of ethylene, 1 atm; time of polymerization, 10 min; temperature, 0 °C; cocatalyst, MMAO.

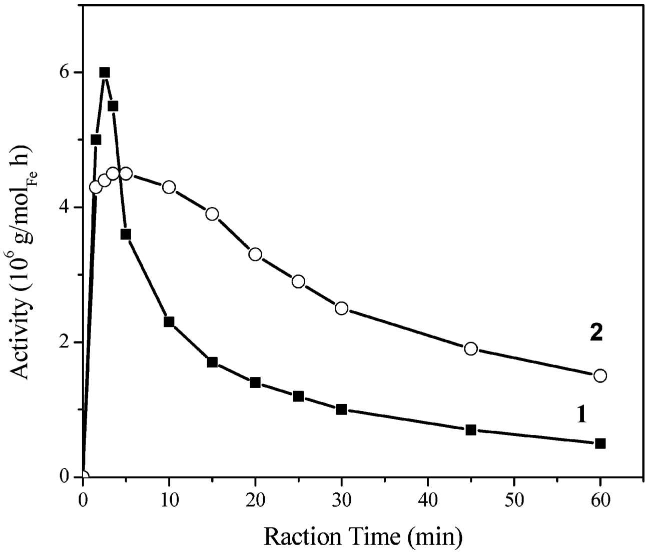


Figure 3. Kinetic profiles of ethylene polymerization using precatalysts **1** (■) and **2** (○). Pressure of ethylene, 1 atm; temperature, 0 °C; Al/Fe ratio, 1000; cocatalyst, MMAO.

was chosen as the final model. Complex **2** is composed of three parts, and each part is similar to its mother analogue **1**. The three parts are distorted to three different orientations due to the existence of flexible CH_2 spacer. The molecular simulation indicates that the centeral iron atoms of complex **2** are located inside the macrocycle ligand.

Macrocycle trinuclear iron complex **2** as a precatalyst was used to promote ethylene polymerization in the presence of modified methylaluminoxane (MMAO) as a cocatalyst. The polymerizations were carried out under low catalyst concentration, such as 1 μmol of precatalayst **2** (3 μmol of Fe) or 3 μmol of precatalyst **1**, to avoid the occurrence of mass transport limitations.[31] Reaction temperature had a significant influence on catalyst activity and polymer characteristics. The catalytic activity had a maximum value at 0 °C. The molecular weight and melting point of the polymer decreased with the increase of temperature (Table 1). To investigate the effects of the Al/Fe ratio on the catalytic activity, polymerizations of ethylene were performed with precatalysts **1** and **2** at 0 °C, varying the Al/Fe ratio from 600 to 1600. Figure 2 shows the results for the polymerization of ethylene at different concentrations of MMAO. We can see precatalyst **2** displays higher activity than precatalyst **1**. Representative data for ethylene polymerizations are summarized in Table 1. Entries 1−4 show that a structure modification from mononuclear precatalyst **1** to macrocycle trinuclear analogue **2** results in an enhancement in catalytic activity from 2300 and 1640 to 4300 and 2740 kg PE/(mol$_{Fe}$ h) at 0 and 30 °C, respectively. Furthermore, in contrast to precatalyst **1**, precatalyst **2** affords a 5-fold increased molecular weight, and as a result, the melting temperature (T_m) is elevated by 10−12 °C. Clearly, steric protection of the metal center is a crucial factor in controlling molecular weight.

The kinetic profiles of ethylene polymerization using precatalysts **1** and **2** are shown in Figure 3. The rate profile of precatalyst **1** exhibits typical decay kinetics with a very high initial rate followed by a rapid decay. Although precatalyst **1** displays higher activity than precatalyst **2** at initial stage, the attenuation rate of the catalytic activity (or deactivation rate) of precatalyst **1** is much faster than that of precatalyst **2**. The activity of precatalyst **2** is found to keep constant up to 10 min and followed by a laggard attenuation. Hence, precatalyst **2** exhibits much higher catalytic activity than precatalyst **1** with polymerization time, which indicates that the macrocycle ligand can restrain the iron catalytic active center from deactivation. Besides the variation in catalytic activity, changes in molecular weights

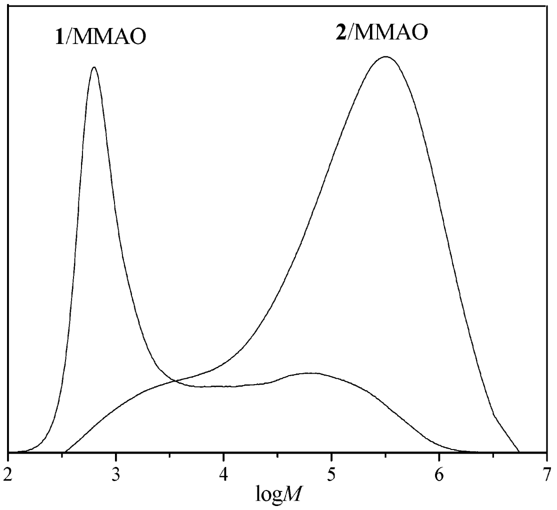


Figure 4. GPC curves of the polyethylene prepared with precatalysts **1** and **2**. **1**/MMAO: entry 1 in Table 1; **2**/MMAO: entry 3 in Table 1.

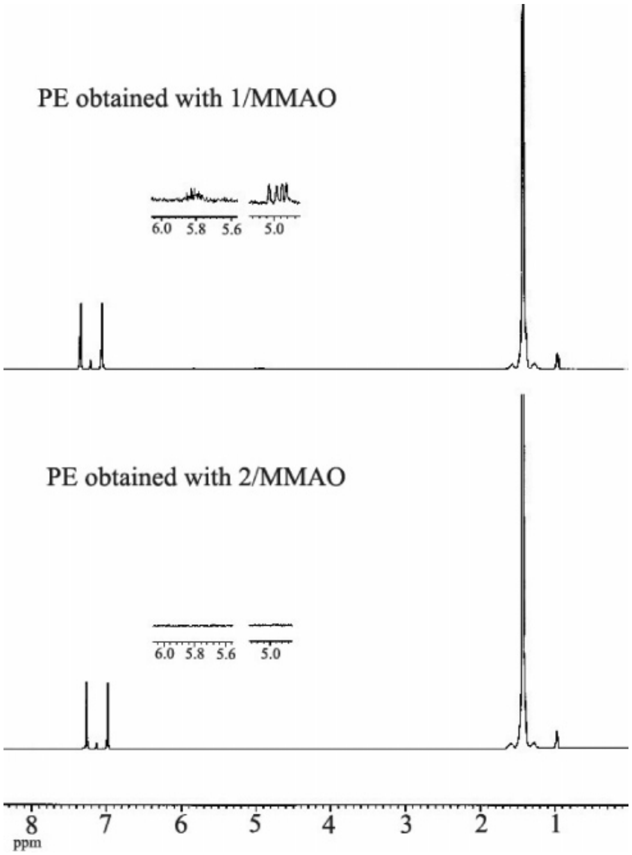


Figure 5. ^{1}H NMR spectra of PE obtained.

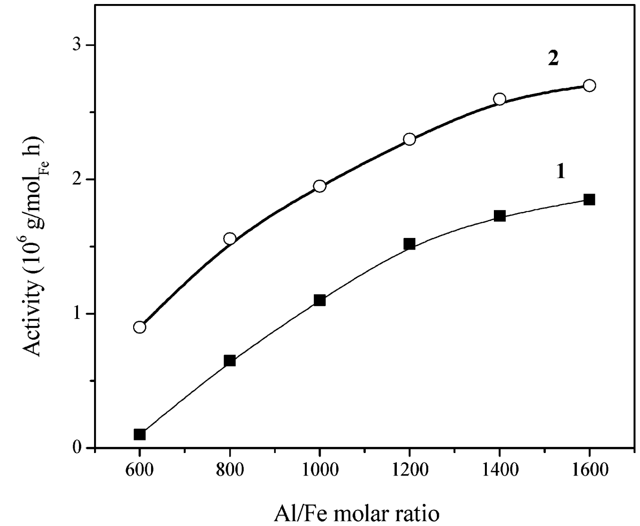


Figure 6. Effect of the Al/Fe ratio on the catalytic activity of precatalysts **1** (■) and **2** (○). Pressure of ethylene, 1 atm; time of polymerization, 10 min; temperature, 0 °C; cocatalyst, TIBA.

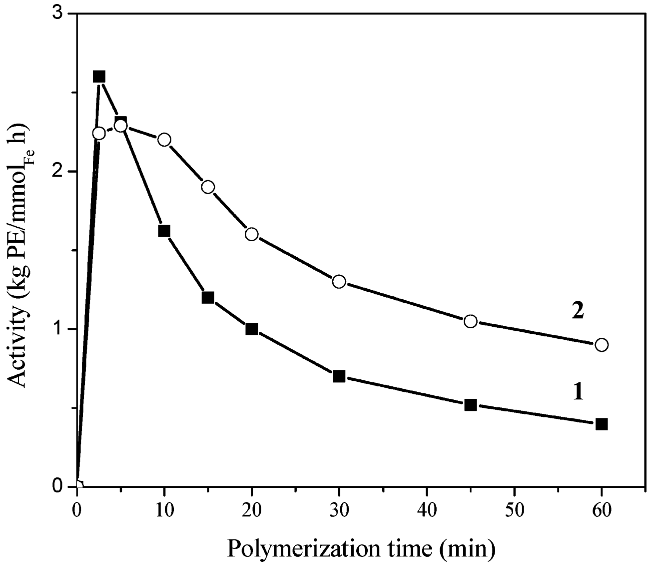


Figure 7. Kinetic profiles of ethylene polymerization using precatalysts **1** (■) and **2** (○). Pressure of ethylene, 1 atm; temperature, 0 °C; Al/Fe ratio, 1200; cocatalyst, TIBA.

(MWs) and molecular weight distributions (MWDs) of the resulting polymers could be observed in Figure 4, which shows two GPC traces for polymerization tests of precatalysts **1** and **2** under different conditions. Using precatalyst **1**/MMAO (entry 1), the MWD of PE displays clearly bimodal distribution and the low molecular weight fraction is dominant. In contrast, using precatalyst **2**/MMAO (entry 3), we obtain high molecular weight polymer with a *M*pk at 401.3 kg/mol in combination with a lower molecular weight shoulder. As well-known, β-H-transfer reaction, to the metal or the monomer, gives one unsaturated chain end per polymer chain (vinyl end group), whereas chain transfer to aluminum results in almost completely saturated polymer chains.[3] ^{1}H NMR analysis of the polymers produced with precatalyst **1** reveals both saturated and unsaturated chain ends, as shown in Figure 5. However, it is very difficult to observe the unsaturated chain ends for the polymers produced with precatalyst **2** due to higher molecular weight and less β-H-transfer reaction. These results indicate that the macrocycle 2,6-bis(imine)pyridyl ligand could restrain active iron center from deactivation and control chain transfer reaction.

To further evaluate the performance of the macrocycle precatalyst **2**, triisobutylaluminum (TIBA) was also used as an activator for precatalysts **2** and **1**. In general, the activity decreases using TIBA as a cocatalyst compared with MMAO (Figure 6). The rate profiles also show typical decay type kinetics (Figure 7). However, several features listed in Table 1 are noteworthy. First, the activity of precatalyst **2** is much higher than that of precatalyst **1** in both cases (from 1620 to 2200 kg PE/(mol$_{Fe}$ h) at 0 °C; from 1360 to 1940 kg PE/(mol$_{Fe}$ h) at 30 °C). Second, MW and T_m of the resulting polyethyl-

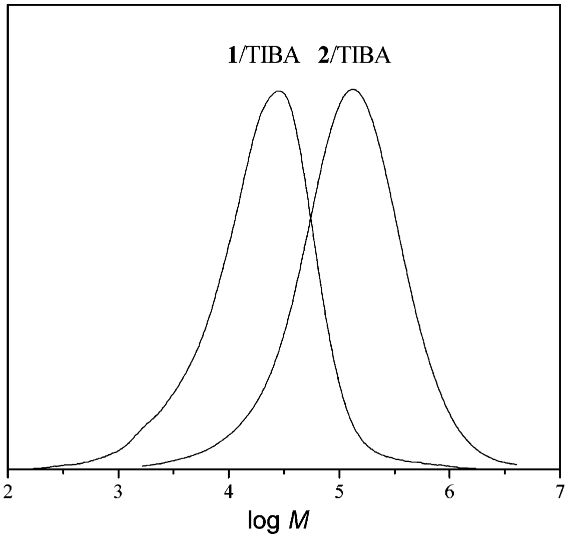


Figure 8. GPC curves of the polyethylene prepared with precatalysts **1** and **2**. **1**/TIBA: entry 6 in Table 1; **2**/TIBA: entry 8 in Table 1.

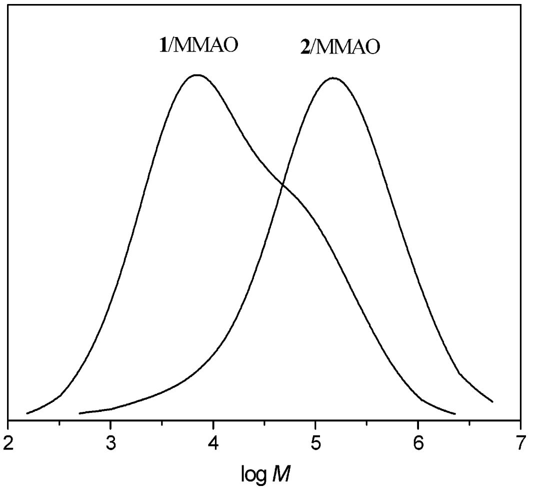


Figure 9. GPC curves of the polyethylene prepared with precatalysts **1** and **2**. **1**/MMAO: entry 9 in Table 1; **2**/MMAO: entry 10 in Table 1.

enes are dramatically increased. For example, the MW values range from 28.3 (entry 6) to 200.7 kg/mol (entry 8), and T_m values range from 126.1 (entry 6) to 138.2 °C (entry 8) when precatalyst **2** substitutes precatalyst **1** at 30 °C. Third, MWD changes little despite extremely high molecular weight polymers obtained, as shown in Figure 8. This shows the macrocycle trinuclear complex **2** is a more promising precatalyst for ethylene polymerization than its mononuclear analogue **1**.

A series of high-pressure polymerization experiments were carried out to further evaluate the performance of the macrocycle precatalyst **2**. Some representative results are listed in Table 1 (entries 9−12). Precatalyst **2** still displays much higher catalytic activity toward ethylene polymerization than precatalyst **1** under 5 atm. As shown in Figure 9, moreover, the polyethylenes with higher molecular weight and unimodal distribution can be obtained using precatalyst **2** due to the less chain transfer reaction, while the lower molecular weight and boarder distribution polymers with a *M*pk at 6800 and a big shoulder around 61 000 were observed when prectatlyst **1** was used under the same conditions.

In conclusion, we have prepared a macrocycle trinuclear iron precatalyst based on (2,6-diisopropylanil)-$FeCl_2$. The precatalyst displays much higher activity and longer lifetime for ethylene polymerization than the corresponding mother precatalyst, and high molecular weight polyethylene can be easily obtained using it. To the best of our knowledge, this is the first reported macrocycle polynuclear late transition catalyst for olefin polymerization.

Acknowledgment. The authors are grateful for the financial support by the National Natural Science Foundation of China and SINOPEC (Nos. 20334030 and 20174041).

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(31) Experiments run under identical conditions with 0.2 and 1 μmol of **2** produced essential activities, indicating mass transport limitation is not an issue with this system.

MA047685Y