

Available online at www.sciencedirect.com



Inorganica Chimica Acta

Inorganica Chimica Acta 361 (2008) 1843-1849

www.elsevier.com/locate/ica

Methylene bridged binuclear bis(imino)pyridyl iron(II) complexes and their use as catalysts together with Al(*i*-Bu)₃ for ethylene polymerization

Lincai Wang, Junquan Sun *

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China

Received 14 May 2007; received in revised form 18 July 2007; accepted 27 September 2007 Available online 5 October 2007

Abstract

Three novel methylene bridged binuclear iron(II) complexes: { $[2, 6-R_2-C_6H_3N=C(CH_3)C_5H_3N(CH_3)C=N(3, 5-R'_2)-C_6H_2-CH_2-(3, 5-R'_2)C_6H_2N=C(CH_3)C_5H_3N(CH_3)C=N(2, 6-R_2)C_6H_3]$ [FeCl₂₂(R,R' = *i*-C₃H₇ (6); R = *i*-C₃H₇, R' = CH₃ (7); R,R' = CH₃ (8))} have been synthesized. Activated by Al(*i*-Bu)₃, complex 6 shows very poor activity for the polymerization of ethylene at one bar ethylene pressure, whereas, 7 and 8 exhibit much higher activity than mononuclear iron catalysts {[ArN=C(Me)C_5H_3N-(Me)C=NAr']FeCl₂ (Ar,Ar' = 2,6-C_6H_3-*i*-Pr (9); Ar = 2,6-C_6H_3-*i*-Pr_2, Ar' = 2,6-C_6H_3-Me_2 (10); Ar,Ar' = 2,6-C_6H_3-Me_2 (11))}. The molecular weight (M_w) of PE produced by 7 and 8 are in the range 13.2–46.0 × 10⁴ and much higher than those produced by mononuclear iron catalysts 9 and 10. GPC results demonstrate that 7 and 8 yield PE with a broad/bimodal molecular weight distribution (MWD). In contrast, 9 and 10 yield PE with relatively narrow and unimodal MWD (4.26 and 3.55). Elevating the temperature and Al/Fe molar ratio will narrow the MWD of PE.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Iron; Binuclear catalysts; Bis(imino)pyridyl complexes; Bimodal polyethylene; Ethylene polymerization

1. Introduction

The production of polyethylene with high molecular weight and broad or bimodal molecular weight distribution has been of growing interest in recent years. Gibson and Brookhart independently reported in 1998 on the use of well-known bis(imino)pyridyl iron complexes as highly efficient catalysts [1–3], which activated by methylaluminoxane (MAO) [3] and some alkyaluminum compounds [4–9] produced low molecular weight PE with broad or bimodal MWD due to chain transfer reactions to aluminum. However, only PE with relatively narrow and unimodal MWD was obtained when Al(*i*-Bu)₃ was used as a cocatalyst. The

E-mail address: sunjunquan@zju.edu.cn (J. Sun).

reason maybe that $Al(i-Bu)_3$ does not force to chain transfer reactions like other alkyaluminum compounds [8,9].

As well known, catalyst structure is a key factor to influence catalytic activity and polymer properties (such as $M_{\rm w}$ and MWD). Recently, Li [10] reported on the macrocycle trinuclear bis(imino)pyridyliron catalyst 12 (Chart 1) which displays higher activity and produces much higher molecular weight PE than its analogue mononuclear iron catalyst 9 (Chart 1) in the presence of $Al(i-Bu)_3$. But also in this case, the MWD of PE obtained is still relatively narrow. Considerable attention has lately been focused on binuclear organometallic compounds, based on expectations that their catalytic behavior may significantly differ from that of analogous mononuclear compounds [11-13]. For binuclear catalysts, there maybe a cooperative effect between the two metal centers. The cooperative effect between closely adjacent metal centers could potentially modify catalytic performance or provide alternative means

^{*} Corresponding author. Tel.: +86 571 87953159; fax: +86 571 87951227.

^{0020-1693/\$ -} see front matter \odot 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2007.09.039



Chart 1. Mononuclear iron(II) catalysts 9–11 and macrocyclic trinuclear bis(imino)pyridyliron catalyst 12.

for substrate activation. In our previous work, the research on binuclear organometallic catalysts revealed that binuclear catalysts could broaden the MWD of the resulting PE [14-16].

The aim of our work is to develop new binuclear iron catalysts to obtain higher activity and yield higher molecular weight polyethylene with broad MWD. Here we report on three novel binuclear methylene bridged bis(imino)pyridyl iron(II) catalysts for ethylene polymerization with $Al(i-Bu)_3$ as cocatalyst. Except for $6/Al(i-Bu)_3$ system, these binuclear catalysts enhanced the catalytic activity and the molecular weight of PE compared with mononuclear iron(II) catalysts. At the same time, the MWD of PE obtained was also broadened. Effects of catalyst structure modification and polymerization parameters on catalysis behaviors were investigated in detail.

2. Experimental

All manipulations of air and/or moisture sensitive compounds were performed under an argon atmosphere with standard Schlenk techniques.

2.1. Materials

Toluene was refluxed and distilled from sodium/benzophenone under dry Ar. Triisobutylaluminum $(Al(i-Bu)_3)$ and triethylaluminum $(AlEt_3)$ were purchased from Roth company. All other chemicals including 4,4'-methylenebis(2,6-dimethylaniline) and 4,4'-methylene-bis(2,6-diisopropylaniline) were commercially available and used without further purification. The mononuclear 2,6-bis-(imino)pyridyl iron complexes **9**, **10** and **11** (Chart 1) [3,17], 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-thanone (**1**) [18] and 1-{6-[(2,6-dimethylphenyl)-ethanimidoyl]-2-pyridinyl}-1-ethanone (**2**) [18] were synthesized according to the known procedures.

2.2. Measurements

The ¹H NMR data of the ligands were obtained on Bruker Advance DMX400 instrument in DCCl₃ with TMS as standard. Mass spectra were recorded using ESI-MS on Esquire-LC 00075 and FAB-MS with High Resolution Mass Spectrometer (MAT95XP). The IR spectra were obtained on Nicolet E.S.P.560 FT-IR spectrometer. Elemental analyses were performed by Perkin Elmer240. The DSC measurements on $T_{\rm m}$ of PE were performed on a Q100 V9.5 Build 288 differential scanning calorimeter (DSC) from 30 °C to 160 °C at a rate of 10 °C/min. The molecular weights (M_w) and the molecular weight distributions (MWD) of the polymer samples were determined at 150 °C on a PL-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). The average viscosity molecular weight (M_n) was determined by the viscosity correlation method according to equation [19]: $[\eta] = 6.67 \times 10^{-4} M_n^{0.67} \,(\text{ml/g}).$

2.3. Preparation of methylene bridged bis(imino)pyridyl ligands and complexes

2.3.1. Preparation of ligands 3-5

Monoimine 1 (1.5 g, 4.65 mmol) was dissolved in 30 mL dry toluene, and p-toluenesulfonic acid (0.05 g) and 4,4'methylene-bis(2,6-diisopropylaniline) (0.85 g, 2.32 mmol) were added. The solution was stirred under reflux for 15 h. A Dean and Stark apparatus was used to remove the water generated during the reaction. The mixture was concentrated and cooled to give a yellow solid which was isolated by filtration and washed with ethanol several times. After drying a yellow powder was obtained in high yield (1.9 g, 83.7%). ESI-MS: m/z = 976.5 [M⁺]. ¹H NMR (400 MHz, DCCl₃): $\delta = 1.12 - 1.25$ (m, 48H, CH*Me*), 2.27 (s, 6H, N=CMe), 2.29 (s, 6H, N=CMe), 2.75 (m, 8H, CHMe₂), 4.02 (s, 2H, -CH₂-), 7.02-7.16 (m, 10H, Ar-H), 7.92 (t, J = 8.0 Hz, 2H, Py- H_p), 8.50 (d, J = 8.0 Hz, 4H, Py-H_m). Anal. Calc. for C₆₇H₈₆N₆ (975.4): C, 82.50; H, 8.89; N, 8.61. Found: C, 82.43; H, 8.91; N, 8.54%.

In a similar method described for **3**, ligand **4** was prepared using monoimine **1** (1.5 g, 4.65 mmol) and 4,4'-methylene-bis(2,6-dimethylaniline) (0.58 g, 2.32 mmol) as a yellow powder. Yield: 1.74 g (87.0%). ESI-MS: $m/z = 864.3 \text{ [M^+]}$. ¹H NMR (400 MHz, DCCl₃): $\delta = 1.12$ – 1.26 (m, 24H, CHMe), 2.04 (s, 12H, Ar-Me), 2.27 (s, 12H, N=CMe), 2.78 (m, 4H, CHMe₂), 3.88 (s, 2H, -CH₂-), 6.94–7.12 (m, 10H, Ar-H), 7.92 (t, J = 10.8 Hz, 2H, Py-H_p), 8.50 (m, 4H, Py-H_m). Anal. Calc. for C₅₉H₇₀N₆ (863.2): C, 82.09; H, 8.17; N, 9.74. Found: C, 81.89; H, 8.23; N, 9.63%.

In a similar method described for ligand **3**, ligand **5** was prepared using monoimine **2** (1.5 g, 5.63 mmol) and 4,4′methylene-bis(2,6-dimethylaniline) (0.72 g, 2.81 mmol) as a yellow powder. Yield: 1.75 g (83.0%). ESI-MS: m/z = 751.5 [M⁺]. ¹H NMR (400 MHz, DCCl₃): $\delta = 2.04$ (m, 24H, Ar-Me), 2.27 (m, 12H, N=CMe), 3.88 (s, 2H, -CH₂-), 6.95-7.09 (m, 10H, Ar-H), 7.92 (t, J = 10.0 Hz, 2H, Py- H_p), 8.50 (d, J = 8.4 Hz, 4H, Py- H_m). Anal. Calc. for $C_{51}H_{54}N_6$ (750.4): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.48; H, 7.19; N, 11.25%.

2.3.2. Preparation of complexes 6–8

Under an argon atmosphere, a solution of ligand 3 (1.00 g, 1.03 mmol) in THF was added dropwise to a solution of $FeCl_2 \cdot 4H_2O(0.41 \text{ g}, 2.06 \text{ mmol})$ in THF to yield a blue solution. After stirring under reflux for 10 min, the reaction was allowed to cool to room temperature and then stirred overnight. The reaction volume was concentrated, and diethyl ether (30 mL) was added to precipitate the product as a blue powder, which was subsequently washed with diethyl ether $(3 \times 20 \text{ mL})$, filtered, and dried to afford complex 6 as a blue powder. Yield: 1.18 g (93.6%). NMR: not recorded due to the paramagnetic character of the complex. IR (KBr, disk, cm⁻¹): 3065w, 2962vs, 2923w, 2867m, 1617w (v_{C=N}), 1582s, 1458s, 1371s, 1267s, 1215s, 1178w, 1102s, 1057w, 935w, 813s, 777m, 739w, 717w. MS (FAB): m/z 1229 [M⁺], 1192 [M⁺-Cl], 1103 [M⁺-FeCl₂], 976 $[M^+-2FeCl_2]$. Anal. Calc. for C₆₇H₈₆Cl₄Fe₂N₆ (1228.9): C, 65.48; H, 7.05; N, 6.84. Found: C, 65.38; H, 6.96; N, 6.79%.

According to the same procedure described above, using ligand **4** (1.0 g, 1.16 mmol) and FeCl₂ · 4H₂O (0.46 g, 2.32 mmol) yielded complex **7** as a blue powder. Yield: 1.17 g (90.2%). NMR: not recorded due to the paramagnetic character of the complex. IR (KBr, disk, cm⁻¹): 3064w, 2962vs, 2927w, 2867m, 1619w ($v_{C=N}$), 1582s, 1463s, 1368s, 1264s, 1210s, 1173w, 1101s, 1042w, 935w, 803s, 773m, 739w, 717w. MS (FAB): *m/z* 1118 [M⁺], 1081 [M⁺-Cl], 954 [M⁺-FeCl₂]. *Anal.* Calc. for C₅₉H₇₀Cl₄Fe₂N₆ (1117.3): C, 63.46; H, 6.32; N, 7.53. Found: C, 63.40; H, 6.28; N, 7.50%.

According to the same procedure described above, using ligand **5** (1.0 g, 1.33 mmol) and FeCl₂ · 4H₂O (0.53 g, 2.66 mmol) yielded **8** as a blue powder. Yield: 1.23 g (92.1%). NMR: not recorded due to the paramagnetic character of the complex. IR (KBr, disk, cm⁻¹): 3074w, 2962s, 2920s, 2867w, 1625w ($v_{C=N}$), 1587s, 1473s, 1372s, 1263s, 1218s, 1170w, 1095s, 1037s 812s, 773s, 740w, 717w. FAB MS: m/z 1005 [M⁺], 1004 [M], 843 [M⁺-FeCl₂-Cl]. *Anal.* Calc. for C₅₁H₅₄Cl₄Fe₂N₆ (1004.5): C, 60.98; H, 5.42; N, 8.37. Found: C, 60.85; H, 5.39; N, 8.29%.

2.4. General procedure for ethylene polymerization

The polymerization was carried out in a 50 ml glass reactor. The reactor was filled with a proper amount of toluene, $Al(i-Bu)_3(AlEt_3)$ solution and saturated with a continuous flow of ethylene under one bar ethylene pressure. The polymerization was initiated by injection of the catalyst solution. The total volume of the solution is 25 mL. The reaction mixture was stirred for an appropriate period at the desired temperature. It was quenched by addition of acidified ethanol containing 10% HCl. The precipitated PE

was then filtered, washed repeatedly with ethanol and dried in vacuum at $60 \,^{\circ}$ C to a constant weight.

2.5. Results and discussion

2.5.1. Synthesis of new ligands and iron complexes

Methylene bridged bis(imino)pyridyl ligands 3-5 were prepared by the reaction of bridged diamines with 1-{6-[(2,6-diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1ethanone (1) and $1-\{6-[(2,6-dimethylphenyl)-ethanimi$ doyl]-2-pyridinyl}-1-ethanone (2) according to the known procedure as shown in Scheme 1. During the reaction, ptoluenesulfonic acid was added as catalyst and a Dean and Stark apparatus was used to remove the water to accelerate the reaction. The reaction of the new ligands 3-5 with iron(II) dichloride results in the formation of the blue complexes 6-8 in nearly quantitative yields. The paramagnetic character of the resulting catalyst makes NMR analysis impossible. These three binuclear complexes 6-8 are characterized by FT-IR spectra. The absorptions of C=N bands at ca. 1617-1627 cm⁻¹ are present in all the derivatives, which appear together with the other one intense absorption in the range 1590–1580 cm⁻¹. Their composition could be proved by FAB-MS spectra as well as by elemental analysis. The mass spectrometric data (FAB-MS) reveal the molecule ion in all the cases and the fragments after the loss of one chloride atom for 6 and 7. The fragmentation pattern with halide loss has been shown to occur for analogue compounds 9 and 11 [3].

2.5.2. Comparison of the catalytic behavior with that of corresponding catalysts 9–12

Table 1 demonstrates a dramatic change in the catalytic activity of the new binuclear iron complexes 6-8 compared with that of the mononuclear iron(II) complexes 9–11. We observed that, compared with the corresponding mononuclear iron(II) catalysts, the binuclear iron(II) catalysts except for the inactive catalyst 6 exhibited much higher catalytic activity and produced much higher molecular weight PE in the presence of $Al(i-Bu)_3$. It is obviously due to the introduction of the methylene bridge between the phenyl groups of ligands in the structure of the catalysts, which might lead to coorperative effect between the closely adjacent metal centers. Generally, it is believed that electronic and steric ligand effects that make cationic active species more stable or unstable can lead to the increase or decrease of catalytic activity. For the binuclear iron catalysts 7 and 8, the electronic effect is taken into account for the modification on catalytic performance. Such binuclear catalysts have two similar parts around the central methylene group. Each part together with the CH₂ group can be considered as a big para-substituent of the other phenyl group. The big *para*-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 [20]. In this case, special substituents (containing one metal center) at the para-position makes the phenyl ring more electron riched



Scheme 1. The route for the preparation of ligands 3–5 and complexes 6–8.

Table 1 Results of ethylene polymerization by iron catalysts 6-11 activated with Al(*i*-Bu)₃

Run	Cat	Al/Fe	Yield (g)	Activity ^d	$M_{ m w}/10^{4}$	$M_{\rm n}/10^4$	MWD	$T_{\rm m}/^{\circ}{\rm C}$
1	6	1000	trace					
2 ^a	6	200	1.77	5.32	29.3	0.50	58.0	131.3
3	7	1000	1.79	5.36	46.0	1.07	43.2	132.2
4	7	2000	2.08	6.24	21.7	0.76	28.7	131.1
5 ^b	7	1000	0.69	2.07	13.2	0.45	29.4	130.5
6	8	1000	2.19	6.57	20.3	0.50	40.9	131.5
7	9	1000	0.42	1.26	4.15	0.97	4.26	127.1
8	10	1000	0.23	069	3.21	0.90	3.55	126.5
9	11	1000	trace					
10 [10] ^c	12	1200	1.10	2.20	21.9	5.53	3.96	

Polymerization conditions: $[Fe] = 0.4 \times 10^{-4} \text{ mol/L}, 0 \,^{\circ}\text{C}, 20 \text{ min}, 1 \text{ bar ethylene pressure, } 25 \text{ mL toluene.}$

^a AlEt₃ as cocatalyst, Al/Fe = 200, 20 °C.

^b Obtained at 40 °C.

^c [10] [Fe] = 0.6×10^{-4} mol/L, Al/Fe = 1200, 0 °C, 1 bar ethylene pressure, 10 min.

^d 10^6 g PE/(mol Fe · h).

[21] and strengthens the coordination bond between N–Fe to some extent, which probably influences the fundamental steps of the polymerization process (olefin insertion and chain termination) by modifying the coordination environment of the metal center, thus resulting in an increase in catalytic activity and molecular weight [22].

Besides the electronic effects, steric effects also cause an important influence on the catalytic activity of the bridged binuclear iron catalytic systems. In view of the catalytic behaviors of the mononuclear iron catalyst 9 and macrocyclic trinuclear iron catalyst 12 [10], binuclear iron(II) catalyst 6 containing the same substituents (isopropyl) on the phenyl rings is expected to exhibit high catalytic activity for ethylene polymerization. However, the experimental results showed that there is no doubt that only 6 is inactive

(Run1) in the presence of TIBA. To investigate the potential catalytic performance of **6**, one polymerization experiment was carried out, in which **6** was found to be an effective catalyst for the polymerization of ethylene in the presence of AlEt₃. The explanation for this phenomenon may be that the steric bulk around the active iron atoms formed by **6** and Al(i-Bu)₃ is too big so that the insertion of ethylene monomer is prohibited. In addition, the results also indicate that the introduction of methylene bridge into the catalyst structure might increase the steric bulk around the metal center. The combination of electronic and steric effects maybe the reason for the different catalytic activities of the binuclear iron(II) catalysts **6** and **7** and the mononuclear iron(II) catalysts **9–11**, even if they had similar substituents.

2.5.3. Effects of polymerization conditions on ethylene polymerization

Polymerization conditions have a great influence on the activity of the catalytic system employed and the nature of the PE produced. A series of experiments under various conditions were carried out to study these effects with the catalytic system 7/TIBA. The results of ethylene polymerization using various temperatures are displayed in Fig. 1.

As shown in Fig. 1, the catalytic system 7/TIBA is highly sensitive to the polymerization temperature. The activity decreases from 5.38×10^6 g PE/(molFe \cdot h) at 0 °C with an Al/Fe molar ratio of 1000:1 to 2.53×10^6 g PE/(molFe \cdot h) after raising the temperature to 20 °C. Above 0 °C, a higher deactivation rate of the catalytic centers and a lower solubility of ethylene in toluene result in low activity of the catalytic system. The molecular weight of PE also decreases with rising polymerization temperature, slowly between 0 and 20 °C and more drastically between 20 and 40 °C.

Fig. 2 shows the influence of the Al/Fe molar ratio on the catalytic activity and molecular weight of PE. It is clear that the catalytic activity is higher with increasing amounts of $Al(i-Bu)_3$ in the range studied. The low activity of the catalytic system at low Al/Fe ratio might result from insufficient activation of the catalyst. When the Al/Fe molar ratio is increased from 500 to 4000, the color of the polymerization system turned from orange-yellow to pink, indicating there might be different kinds of active species generated at different Al/Fe molar ratios [23,24]. Furthermore, the pink color does not disappear within the polymerization time. These results reveal that Al(i-Bu)₃ as a cocatalyst can not only activate iron centers but also stabilize active iron centers effectively. In addition, a high Al/Fe molar ratio will lead to such more active species formed that are responsible for the preparation of low molecular weight PE [24], which is also confirmed by the GPC characterization of the PE sample.

The effect of reaction time on ethylene polymerization is illustrated in Fig. 3. The activity of catalyst 7 keeps con-



Fig. 1. Effects of reaction temperature on catalytic activity and M_{η} of PE. Polymerization conditions: [Fe] = 0.4×10^{-4} mol/L, Al/Fe = 1000, 20 min, 1 bar ethylene pressure, 25 mL toluene.



Fig. 2. Effects of Al/Fe molar ratio on catalytic activity and M_{η} of PE. Polymerization conditions: [Fe] = 0.4×10^{-4} mol/L, 0 °C, 20 min, 1 bar ethylene pressure, 25 mL toluene.



Fig. 3. Effects of reaction time on catalytic activity and M_{η} of PE. Polymerization conditions: [Fe] = 0.4×10^{-4} mol/L, 0 °C, Al/Fe = 1000, 1 bar ethylene pressure, 25 mL toluene.

stant up to 20 min and decreases gradually with the prolonging polymerization time. However, catalyst 9 displays a very high activity in the initial stage followed by a rapid decay [5,10]. This behavior indicates that the methylene bridged ligand in 7 could effectively restrain the active center from deactivation [10]. Additionally, the molecular weight of PE always increases with prolonged reaction time. This trend is in accordance with the literature [24].

2.5.4. Characterization of resultant PE

The molecular weight and MWD of the resultant PE were determined by the GPC method and listed in Table 1. The results demonstrate that **7** and **8** produce PE with higher molecular weight than those of PE produced by the mononuclear iron(II) catalysts **9** and **10**. Fig. 4 shows the GPC plots of PE samples prepared by different iron catalysts with TIBA as cocatalyst. The molecular weight distributions of PE prepared by **7** and **8** are very broad, with the bimodal character in the case of **8**. In contrast, the mononuclear iron catalysts **9** and **10** yield PE with relatively narrow MWDs (4.26 and 3.55) as a result of a missing chain transfer to aluminum in those iron/TIBA systems. But the possible chain transfer reaction to aluminum



Fig. 4. GPC curves of PE samples produced with 7–10/TIBA systems. (numbers of the curves correspond to runs in Table 1) Polymerization conditions: $[Fe] = 0.4 \times 10^{-4} \text{ mol/L}$, 20 min, 0 °C, 1 bar ethylene pressure, 25 mL toluene.

num in the case of the catalytic active systems 7 and 8 can not explain the bimodal behavior of the resulting PE. A possible explanation for this maybe the existence of two different kinds of catalytic active species, $[LFe(II)Cl(\mu-R)_2AlR_2]$ (a) and $[LFe(II)R(\mu-R)_2AlR_2]$ (b) (L =bis(imino)pyridyl ligand, $R = CH_2CH(CH_3)$) in the bridged binuclear iron complexes [24,25]. Elevating the temperature and the Al/Fe molar ratio will benefit the formation of b, which mainly produces PE with low molecular weight [24]. Therefore, changing the reaction temperature and the Al/Fe molar ratio could increase or decrease the high molecular weight fraction as shown in Fig. 5 (see Chart 2).

Additionally, the last column of Table 1 shows that the melting temperatures of the PE samples produced by the binuclear iron(II) catalysts 7 and 8 are higher (above 130 °C) than that of the PE produced by the mononuclear



Fig. 5. GPC curves of PE samples produced with 7/TIBA systems under different polymerization conditions (numbers of the curves correspond to runs in Table 1). Polymerization conditions: $[Fe] = 0.4 \times 10^{-4} \text{ mol/L}$, 20 min, 1 bar ethylene pressure, 25 mL toluene; 2: 0 °C, Al/Fe = 1000; 3: 0 °C, Al/Fe = 2000; 4: 20 °C, Al/Fe = 1000.



Chart 2. Possible active species.

iron(II) catalysts **9** and **10**, which indicates that the PE produced is highly linear and highly crystalline [8,9].

3. Conclusions

Three novel methylene bridged binuclear iron(II) catalysts were synthesized and successfully used to catalyze ethylene polymerization in the presence of TIBA. Compared with mononuclear iron(II) catalysts 9–11, binuclear iron(II) catalysts demonstrate quite different catalytic performance due to the combined electronic and steric effects from the structure of the complexes. High molecular weight PE with broad/bimodal MWD was easily obtained using methylene bridged binuclear iron(II) catalysts 7 and 8.

Acknowledgements

The research was supported by the National Natural Science Foundation of China (20374043). We thank Prof. H. Schumann for helpful discussion.

References

- G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. 7 (1998) 849.
- [2] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
- [3] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.
- [4] S.T. Babik, G. Fink, J. Mol. Catal. A: Chem. 188 (2002) 245.
- [5] K.R. Kumar, S. Sivaram, Macromol. Chem. Phys. 201 (2000) 1513.
- [6] E.P. Talsi, D.E. Babushkin, N.V. Semikolenova, V.N. Zudin, V.N. Panchenko, V.A. Zakharov, Macromol. Chem. Phys. 202 (2001) 2046.
- [7] N.V. Semikolenova, V.A. Zakharov, E.P. Talsi, D.E. Babushki, A.P. Sobolev, J. Mol. Catal. A: Chem. 182–183 (2002) 283.
- [8] Q. Wang, H.X. Yang, Z.Q. Fan, Macromol. Rapid. Commun. 23 (2002) 639.
- [9] K. Radhakrishnan, H. Cramail, A. Deffieux, P. Francois, A. Momtaz, Macromol. Rapid. Commun. 24 (2003) 251.
- [10] J.Y. Liu, Y.S. Li, J.Y. Liu, Z.S. Li, Macromolecules 38 (2005) 2559.
- [11] H. Li, L. Li, T.J. Marks, Angew. Chem., Int. Ed. 43 (2004) 4937.
- [12] Q.H. Chen, J. Yu, J.J. Huang, Organometallics 26 (2007) 617.
- [13] J.Q. Sun, H.Y. Zhang, X.J. Liu, X.H. Xiao, F. Lin, Eur. Polym. J. 42 (2006) 1259.

- [14] F. Lin, J.Q. Sun, X.J. Liu, W.K. Lang, X.H. Xiao, J. Appl. Polym. Sci. 101 (2006) 3317.
- [15] X.H. Xiao, B.C. Zhu, X.T. Zhao, Y.G. Wang, J.Q. Sun, Inorg. Chim. Acta 360 (2007) 2432.
- [16] X.H. Xiao, J.Q. Sun, X. Li, H.F. Li, Y.G. Wang, J. Mol. Catal. A: Chem. 267 (2007) 86.
- [17] C. Bianchini, G. Giambastiani, I.R. Guerrero, A. Meli, E. Passaglia, T. Gragnoli, Organometallics 23 (2004) 6087.
- [18] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Zanobini, F. Laschi, A. Sommazzi, Eur. J. Inorg. Chem. 8 (2003) 1620.
- [19] P.S. Francis, R.C.J. Cooke, J.H. Elliott, J. Polym. Sci. 31 (1958) 453.

- [20] V.C. Gibson, N.J. Long, P.J. Oxford, A.J.P. White, D.J. Williams, Organometallics 25 (2006) 1932.
- [21] H.K. Luo, H. Schumann, J. Mol. Catal. A: Chem. 227 (2005) 153.
- [22] I.S. Paulino, U. Schuchardt, J. Mol. Catal. A: Chem. 211 (2004) 55.
- [23] K.P. Bryliakov, N.V. Semikolenova, V.N. Zudin, V.A. Zakharov, E.P. Talsi, Catal. Commun. 5 (2004) 45.
- [24] S.B. Wang, D.B. Liu, Y.D. Zhang, B.Q. Mao, J. Mol. Catal. A: Chem. 245 (2006) 122.
- [25] K.P. Bryliakov, N.V. Semikolenova, V.A. Zakharov, E.P. Talsi, Organometallics 23 (2004) 5375.