

THE BEHAVIOR OF HOMOGENEOUS IRON-BASED CATALYSTS BEARING PYRIDINE DIIMINE LIGANDS FOR ETHYLENE POLYMERIZATION*

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Abstract The polymerization of ethylene by two iron-based catalysts, {[2,6-ArN=C(Me)₂C₅H₃N]FeCl₂} (Ar = 2,6-C₆H₃-Me₂ I; 2,6-C₆H₃ (*i*-Pr)₂ II) has been investigated. Catalyst II produces higher molecular weight polyethylene (PE) and broadened polydispersities relative to catalyst I under analogous conditions and all polymers are linear. The kinetic profiles with iron catalysts showed a smooth pattern during both rate build-up and rate lowering, which are different from the metallocene catalysts. The polymerization activity increases with Al/Fe value and an optimum temperature range at 40–45 °C was observed. The molecular weight of PE decreases with the increase of Al/Fe ratio and rise of polymerization temperature.

Keywords Ethylene polymerization, Transition metal, Catalyst

INTRODUCTION

There is a fast growing interest in the area of late transition metal catalysts for polymerization of olefins. One particular recent breakthrough is the novel family of catalysts based on iron and cobalt reported by Brookhart and Gibson^[1–2]. Since iron has had no track record of being applied to olefin polymerization this finding demonstrates that new olefin catalysts should not be limited to the transition group IV metals^[3]. Generally speaking the late transition metal complexes are less oxophilic and easier to make than metallocenes^[4–5]. It was especially exciting that the new iron catalysts bearing tridentate pyridine-bis(imine) ligands were discovered to be also capable of producing isotactic polypropylene (*i*-PP) using modified methylaluminoxane (MMAO) as cocatalyst^[6]. The iron-based catalyst system shows a possibility of developing durable, low-cost and highly active catalysts for the polymerization of olefins to polymers with high molar mass. This work aims at revealing the behavior of 2,6-bis[1-(2,6-substituted phenylimino)ethyl]pyridineiron (II) chloride/MAO for ethylene polymerization including the effects of temperature and Al/Fe value. Until now no kinetic study on these new iron-based catalysts has been reported in the literature.

EXPERIMENTAL

Materials

2,6-Diacetylpyridine was purchased from Aldrich (USA) and 2,6-dimethylaniline and 2,6-diisopropylaniline were purchased from Acros (Belgium), anhydrous methanol and formic acid were purchased from Beijing Chemical Co. Ltd. (China), polymer grade ethylene was obtained from Yanshan Petro-Chemical Ltd. (China), and used without further purification. Methyl aluminoxane (MAO) solution in toluene was purchased from Albemarle Corp. (USA). Toluene and THF were distilled from sodium/benzophenone and were degassed.

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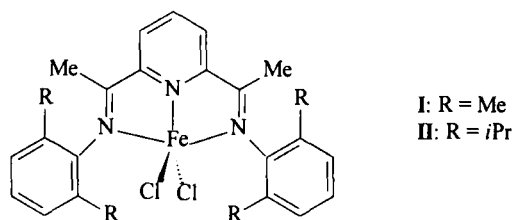
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Synthesis of Two Iron Complexes

Two iron catalysts shown in Scheme 1 were prepared according to the procedures described in Refs. [7, 8] with minor modification:

The general procedure for the preparation of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (ligand I) and 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine (ligand II): 254.4 mg 2,6-diacetylpyridine (1.56 mmol) and 50 mL anhydrous methyl alcohol were placed in a 100 mL three-necked flask fitted with a condenser. Under stirring 1.51 g 2,6-dimethylaniline (12.5 mmol, 8 eq.) or 2.4 mL of 2,6-diisopropylaniline (5 eq.) and then a few drops of formic acid were added successively. The mixture was heated at 45°C for 48 h. The mixture was filtered and the collected yellow powder was washed with methanol, and dried under vacuum. General yields are 60 % for ligand I and 80 % for ligand II, respectively.



Scheme 1

The structures of the two ligands were characterized by ¹H-NMR and MS: Ligand I: ¹H-NMR (300 MHz, CDCl₃, δ) 2.15 (s, 12H, —CH₃ on aryl), 2.25 (s, 6H, N=C—CH₃), 7.07 (t, 2H, H_{aryl}), 7.14 (d, 4H, H_{aryl}), 8.10 (t, 1H, H_{pyr}), 8.88 (d, 2H, H_{pyr}); MS (EI, 70 eV), 369.51 (calcd.), 369.48 (detd.) (C₂₅H₂₇N₃). Ligand II: ¹H-NMR (300 MHz, CDCl₃, δ) 1.20 (d, 24H, —CH—(CH₃)₂), 2.34 (s, 6H, N=C—CH₃), 2.76 (s, 4H, —CH—(CH₃)₂), 7.22 (m, 6H, H_{aryl}), 8.01 (t, 1H, H_{pyr}), 8.79 (d, 2H, H_{pyr}); MS (EI, 70 eV) 481.73 (calcd.), 481.69 (detd.) (C₃₃H₄₃N₃).

The general procedure for the preparation of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron (II) chloride (cat. I) and 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridineiron(II) chloride (cat. II): 0.25 mmol of the respective ligands obtained as above and 43.5 mg hydrous ferrous chloride (0.218 mmol) were placed in a 50 mL round-bottom flask with a magnetic stirrer. Under argon atmosphere, 5 mL THF was added with a syringe. The mixture was stirred at room temperature for 2~3 h and was then filtered. The blue solid product was collected, washed with methanol and then dried under vacuum. Elemental analysis: (% , calcd./detd.) for cat. I: C 60.51/60.80, H 5.48/5.77, N 8.47/8.03; for cat. II, C 65.14/65.06, H 7.12/7.43, N 6.92/6.08.

Polymerization

A 250 mL three-necked flask fitted with a N₂ inlet was purged with N₂ three times and with ethylene once. Then 50 mL toluene and the required amount of MAO were charged. After stirring for about five min, the required amount of catalyst dissolved in toluene was added with a syringe under the protection of ethylene. The polymerization was quenched with ethanol containing 10% (V/V) hydrogen chloride. The resulted polyethylene was washed with ethanol and dried under vacuum.

Characterization

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 300 spectrometer. MS was measured by a Kratos AEI MS-50 instrument. Elemental analysis was carried out using Carlo Erba 1106 and ST02 systems. The T_m (melting temperature) of PE was determined with a Perkin-Elmer DSC-7 system and the samples were heated from 20°C to 150°C at a heating rate of 20 K/min (double-scanned). M_w, M_n and MWD of the polymer were measured at 135°C with Waters 150C instrument using polystyrene as standard. Intrinsic viscosity of the polymers in decalin was measured at 135°C with an AVS300 viscometer and the viscosity-average molecular weight, M_v, was calculated by Staudinger's viscosity equation $[\eta] = 2.3 \times 10^{-4} M_v^{0.82}$ given in Ref. [9].

RESULTS AND DISCUSSION

The general results of ethylene polymerization with iron-based complexes **I** and **II** at room temperature are illustrated in Table 1. Besides the high activities reported by Brookhart and Gibson^[1, 2] it is notable that cat. **II** produces higher molecular weight PE and broadened polydispersity relative to cat. **I** under similar conditions. This is further proof that the steric factor of these pentacoordinated iron complexes frame is extremely important for controlling the molecular weight. Polyethylene in entry 1 is highly linear (characterized by ¹³C-NMR for one sample) as shown in Fig.1 and has a high density (HDPE) of about 0.96.

Table 1. Results of ethylene polymerization by iron catalyst **I** and **II**

Entry	Catalyst	Al/Fe	Yield (g)	Activity (10 ⁶ g PE/mol Fe h)	<i>T_m</i> (°C)	<i>M_w</i> (× 10 ⁴)	<i>M_w/M_n</i>
1	I	500	1.76	1.68	134.74	6.96	3.84
2	I	1000	3.36	3.20	133.57	-	-
3	I	2000	5.22	4.97	131.40	4.42	3.67
4	I	3000	5.88	5.60	130.61	-	-
5	I	4000	8.81	8.39	130.16	2.98	3.11
6	II	500	1.90	2.38	135.59	17.93	11.39
7	II	1000	2.89	3.61	132.60	-	-
8	II	2000	3.40	4.26	130.04	8.33	8.97
9	II	3000	3.31	4.14	128.08	-	-
10	II	4000	3.34	4.18	129.09	4.18	5.89

General conditions: all catalysts were activated with MAO; polymerization temperature = 25°C; polymerization time = 30 min; *P*(C₂H₄) = 1.03 × 10⁵ Pa

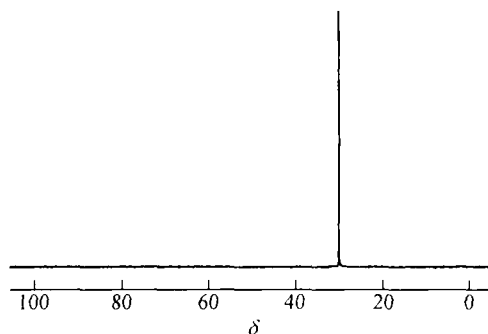


Fig. 1 ¹³C-NMR spectrum of polyethylene polymerized with cat. **I** (entry 1)

Kinetic Profiles for Ethylene Polymerization by Iron-Based Catalysts

Typical ethylene polymerization profiles for iron catalysts/MAO are shown in Fig. 2. The variation of rate of polymerization, *R_p*, with time is followed by manometric measurement of monomer consumption. The period of rate build-up in the iron complex systems was between 5 to 10 min, which seems to be a little longer than that in metallocene catalyst systems^[10, 11]. It also demonstrates that the curves attenuate smoothly as Ziegler-Natta and metallocene catalysts do.

The increase of polymerization temperature resulted in a slight delay of the time at which *R_p* reaches its maximum but the duration does not exceed 10 min. It was observed in our study that the shape of kinetic profiles is more dependent on the ratio of iron catalyst to MAO than on temperature. As shown in Fig. 3 the time to reach the maximum of *R_p* became longer when the Al/Fe value was increased. The overall polymerization activities were enhanced as the Al/Fe value was increased. The so-called “steady state” of the polymerization catalyzed by these iron complexes was reached usually between 20 to 30 min because the lowering of *R_p* was slower than that found for metallocene catalysts.

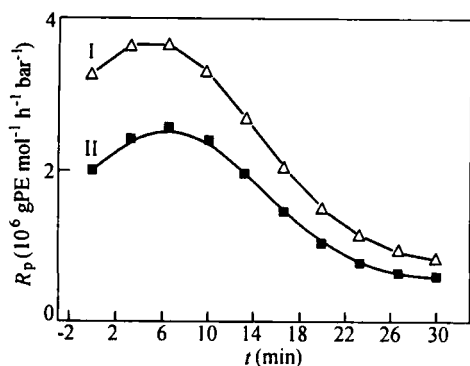


Fig. 2 Rate of polymerization versus time curves for cat. I/MAO and II/MAO
 $\text{Al/Fe} = 500$, $T = 25^\circ\text{C}$, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$

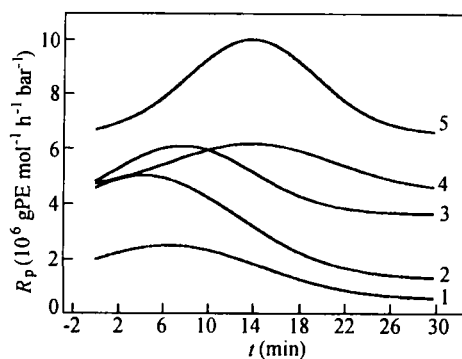


Fig. 3 Kinetic profiles for ethylene polymerized with Cat. I/MAO
 $T = 25^\circ\text{C}$, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$
 Al/Fe : 1) 500; 2) 1000; 3) 2000; 4) 3000; 5) 4000

Effect of Al/Fe Value

The Al/Fe value mainly influences the catalyst activity, the molecular weight of polymers and kinetic profile of polymerization. The effect of Al/Fe value on the overall activity of both catalysts is demonstrated in Fig. 4. The activity of cat. I increases with increasing Al/Fe ratio. For cat. II its activity almost reaches a maximum at $\text{Al/Fe} = 2000$ and then remains at the same level.

The molecular weight of PE is decreases with increasing Al/Fe ratio (see Table 1) for both cat. I and cat. II. The same trend was also observed for the melting point of the polymer. It is not surprised from the results obtained from the study of metallocene systems that the chain transfer to aluminum alkyl, the dominant transfer process for the classical Ziegler-Natta catalysts, occurs readily in the iron catalyzed process. It was also noticed that increasing the Al/Fe ratio resulted in the occurrence of bimodal behavior on the GPC trace (Fig. 5). The bimodal behavior showed of entries 3,6,8,10 extents to a certain range but not for entries 1 and 5 in as shown Table 1.

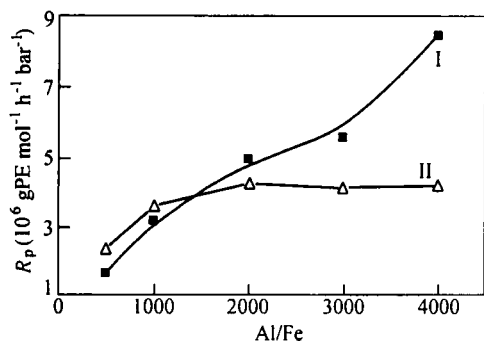


Fig. 4 Effect of Al/Fe on polymerization rate
 $T = 25^\circ\text{C}$, Time = 30 min, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$

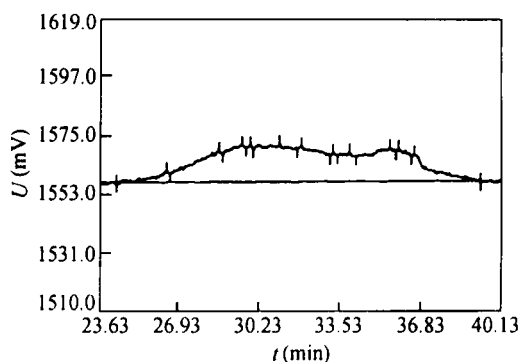


Fig. 5 GPC elution curve of polyethylene
Cat I, $\text{Al/Fe} = 2000$, $T = 25^\circ\text{C}$, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$

Effect of Polymerization Temperature

Temperature plays an important role in ethylene polymerization with late transition metal catalysts. It influences mainly the catalyst activity and the molecular weight of polymer. As with Ziegler-Natta catalysts there is an optimum temperature range for maximum activity, below or above which the activity decreases (Fig. 6). From our experiments the optimum temperatures for both cat. I and cat. II are found to be between 40 and 45°C .

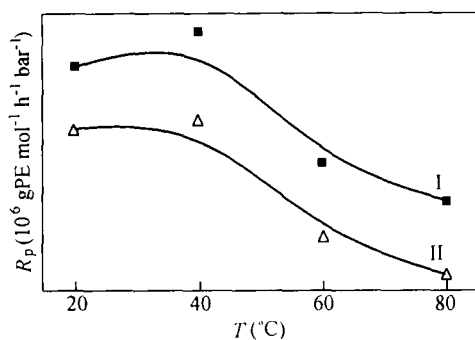


Fig. 6 Effect of temperature on polymerization rate
Al/Fe = 1000, $T = 25^{\circ}\text{C}$, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$

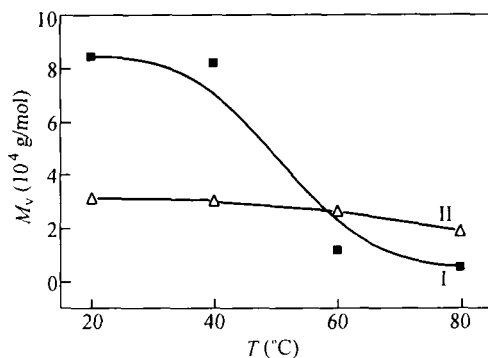


Fig. 7 Effect of temperature on molecular weight of polymer
Al/Fe = 1000, $T = 25^{\circ}\text{C}$, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$

Table 2. Summary of temperature effect on ethylene polymerization by iron catalyst **I** and **II**^a

Cat.	$T (^{\circ}\text{C})$	Activity ($10^6 \text{ g/mol Fe} \cdot \text{h}$)	M_v (10^4 g/mol)	$T_m (^{\circ}\text{C})$	$\Delta H_f (\text{J/g})$	$X_c (\%)$
I	20	5.11	3.14	133.2	133.19	48.05
	40	5.84	3.00	133.06	132.97	48.00
	60	3.04	2.59	128.69	191.74	69.17
	80	2.19	1.87	126.6	229.04	82.63
II	20	3.78	8.47	132.27	187.76	67.7
	40	3.96	8.23	132.89	188.37	68.0
	60	1.40	1.18	132.39	98.34	35.5
	80	0.59	0.51	108.88	136.06	49.1

^a Al/Fe = 2000, $t_p = 30 \text{ min}$, $P(\text{C}_2\text{H}_4) = 1.03 \times 10^5 \text{ Pa}$

The variation of molecular weight with temperature is shown in Fig. 7 and it decreases monotonically with increasing temperature for both catalysts. In the case of cat. **I** the molecular weight of the polymer drops dramatically after 50°C but it changes slowly for cat. **II**.

REFERENCES

- Small, B.L., Brookhart, M. and Bennett, A.M.A., *J. Am. Chem. Soc.*, 1998, 120: 4049
- Britovsek, G.J.P., Gibson, V.C., Kimberley, B.S., Maddox, P.J., Mctavish, S., Solan, J.G.A., White, A.J.P. and Williams, D.J., *Chem. Commun.*, 1998, 849
- Freeantle, M., *C & EN*, 1998, April 13: 11
- Johnson, L.K., Mecking, S. and Brookhart, M., *J. Am. Chem. Soc.*, 1996, 118: 267
- Killian, C.M., Tempel, D.J., Johnson, L.K. and Brookhart, M., *J. Am. Chem. Soc.*, 1996, 118: 11664
- Small, B.L. and Brookhart, M., *Macromolecules*, 1999, 32: 2120
- Brookhart, M. and Small, B.L., E.I. Du Pont & University of North Carolina-Chapel Hill, Invs., 1998, WO 98/30612
- Killian, C.M. and Brookhart, M., *J. Am. Chem. Soc.*, 1995, 117: 6414
- Chien, J.C.W. and Bres, P.L., *J. Polym. Sci., Part A: Polym. Chem.*, 1986, 24: 2483
- Chien, J.C.W. and Ranzavi, A., *J. Polym. Sci., Part A: Polym. Chem.*, 1988, 26: 2369
- Reddy, S.S. and Sivaram, S., *Prog. Polym. Sci.*, 1995, 20: 309