Homogeneous Polymerization of Ethylene Using an Iron-Based Metal Catalyst System

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ABSTRACT: An iron-based catalyst of 2,6-*bis*-{1-(2-methyl-phenylimino)ethyl}pyridine iron dichloride was prepared. The ligand was prepared using 2,6-diacetylpyridine as the starting chemical under controlled conditions. The preparation procedure was followed using ^{13}C-NMR, ^{1}H-NMR, FT-IR, MS (mass spectroscopy), and elemental analysis methods. The homogeneous polymerization of ethylene was carried out using the prepared catalyst in toluene media. Methyl aluminoxane (MAO) was used as a cocatalyst. The effect of the [Al] : [Fe] molar ratio, polymerization temperature, and monomer pressure of 202,000 to 454,500 Pa on the polymerization behavior were studied. The highest activity of the catalyst was obtained at 30°C, the activity decreased with increasing temperature, while increasing pressure linearly increased its activity. The molecular weight distribution of the polyethylene obtained was 1.25 to 1.72. A weight average molecular weight of 7.1 $\times 10^4$ and 1.5×10^3 were obtained. The crystallinity of the polymer was about 19% and its melting point was about 65°C. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1517–1522, 2007

Key words: polymerization; polyethylene wax; iron catalyst; homogeneous catalyst

INTRODUCTION

Since the discovery of polyethylene in the 1930s, its polymerization has several major production procedures: (1) radical polymerization of the ethylene leading to LDPE; (2) Ziegler-Natta and Philips;[1] (3) metallocene catalysts;[2,3] (4) late metal catalysts;[4–6] and (5) phenoxy-imine (or amine) complex of Zr, Ti, or Hf (FI catalyst).[7–9] Each of these systems has its own academic and industrial advantages. Late-metal catalyst systems of Fe, Co, Ni, and Pd have developed since the mid-1990s.[4,5] They have the general formula of L_nMR, where L_n is an organic ligand bound to and modifying the reactivity of the active metal center (M). The advantage of these metals chelating with nitrogen-based ligands catalyst is their activity in the homopolymerization of ethylene and the copolymerization of ethylene with α-olefins and even polar comonomers.[6,10,11] The polymerization is expected in the cationic active centers of the metal; thus, the electrophilicty of the late metal center in these cationic complexes results in a rapid rate of olefin insertion. Although the use of bulky ligands favors insertion over chain transfer,[5] the polymers mainly obtained using the catalyst systems are oligomers.[12,13] The behavior indicates high chain transfer and termination reactions such as β-H elimination, which the bulky groups cannot reduce.[5]

The α-diimine ligands used in the late metal catalyst system can be easily varied steric and electronic properties of the catalytic active centers. Thus, they may play an important role in stabilizing the centers, while, due to better structural and morphological control of the polymer obtained, many of the industries employed polymerization catalysts that are heterogeneous. By tailoring the coordination environment of the metal center ''single-site'' catalyst of the homogeneous are now available that can control the molecular weight, molecular weight distribution, comonomer incorporation, end groups, polymer architectures and both the relative and absolute stereochemistry of a polymer in a way that is often impossible using conventional heterogeneous catalysts.[10,14] Certainly, heterogeneizing these systems using suitable support could produce its own advantages, such as reducing fouling of the polymerization reactor.

In the present work an iron-based catalyst was prepared and characterized. The polymerization of ethylene was carried out using different conditions. A polydispersity index of between 1 to 2 was an advantage of the polymer obtained. Low crystallinity, low melting point, and also low molecular weight of the polyethylene were achieved in compared with the
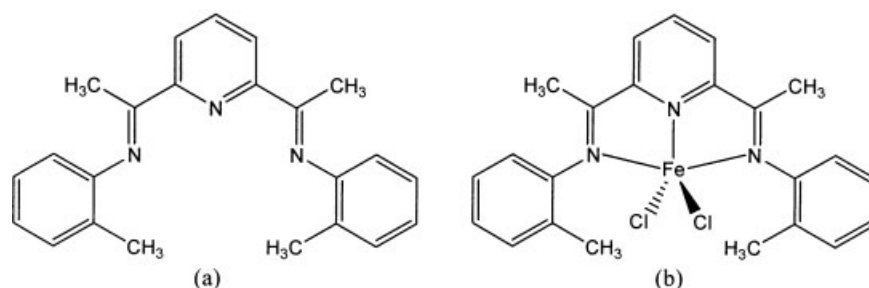
Figure 1 (a) Structure of the ligand, (b) structure of the iron complex catalyst.

polymer obtained using the Ziegler-Natta catalyst polymerization.

EXPERIMENTAL

Chemicals

Dichloromethane, methanol, ethanol, benzene, and iron dichloride were supplied by Merck Chemical (Darmstadt, Germany) and were used as received. Tetrahydrofuran and toluene (Merck Chemical) were prepared from distilling over sodium wire, benzophenon, and calcium hydride, respectively. The chemicals were stored over sodium wire and 13X and 4 Å activated molecular sieves. Nitrogen (purity 99.99%) was supplied by Roham (Tehran, Iran). Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical (Tehran, Iran). The gases were purified as explained elsewhere.[15,16] Aniline derivatives were supplied by Merck Chemical and vacuum-distilled before use. 2,6-Diacetylpyridine (purity > 99%) was prepared from Acros (Somerville, NJ). Methylaluminoxane (MAO) (10% solution in toluene) was pre-

pared by Aldrich Chemical (Steinheim, Germany). Catalyst component handling and polymerization procedures were carried out as previously described.[15–17] Toluene (500 mL) was used as diluent.

FT-NMR (80 MHz, Bruker, Billerica, MA, AC80), FT-IR (Shimadzu, Kyoto, Japan, FTIR-4300), Mass Spectrometer (5973), CHN analyzer (Thermo Finnegan, San Jose, CA, FLASH, EA, 1112 SERIES), differential scanning calorimetry (DSC) (Universal V4 IDTA) with a rate of 10°C/min, and gel permeation chromatography (GPC) (Waters, Milford, MA 2000) instruments were used for studying the catalyst preparation procedure and polymer characterization.

Preparation of 2,6-*bis*-[1-(2-methylphenylimino) ethyl]pyridine

The ligand was prepared using 2,6-diacetylpyridine and *o*-toluidine under controlled conditions. *o*-Toluidine was vacuum-distilled (18 mmHg, 90–105°C) just before use. 2,6-Diacetylpyridine (6.1 mmol) *o*-toluidine (28.1 mmol) was added to a 100-mL flask containing a magnetic stirrer bar and methylenechloride
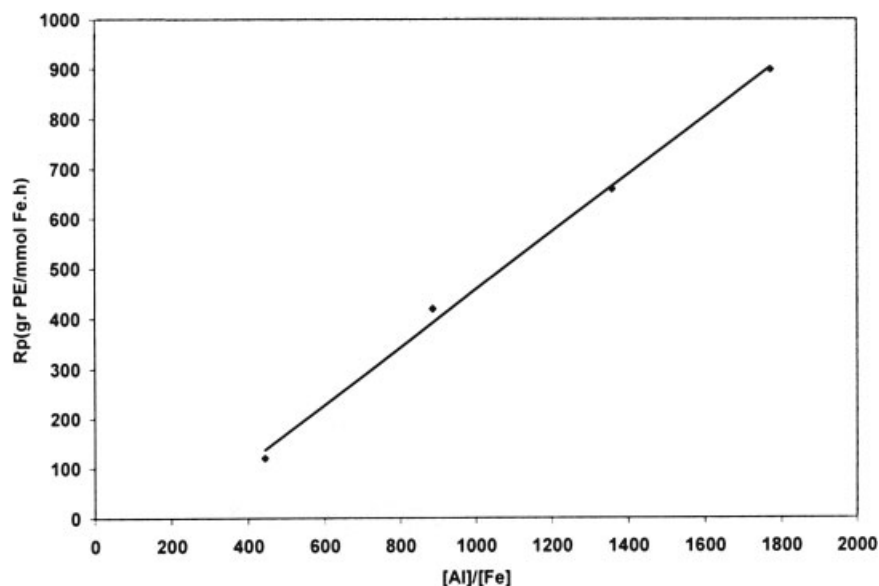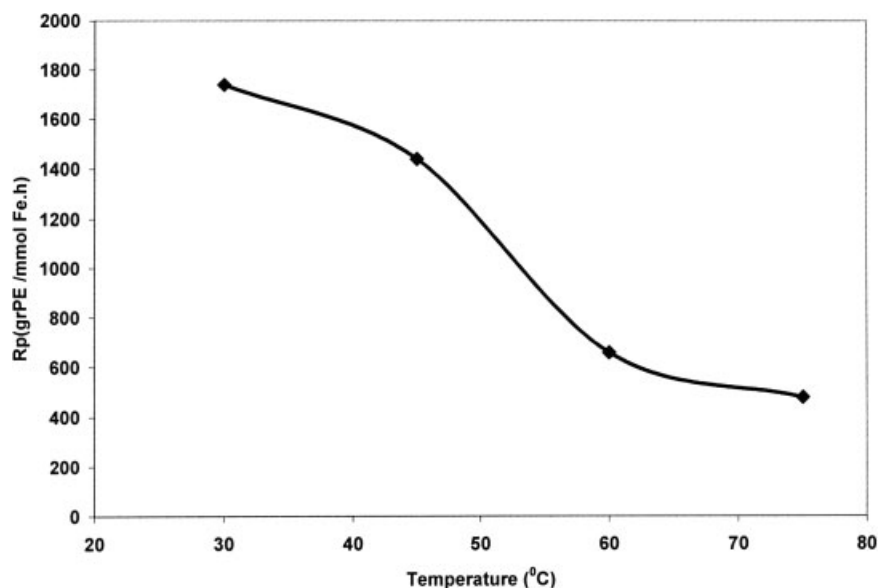

Figure 2 Effect of MAO concentration on average rate of polymerization. Polymerization conditions: [Fe] = 16.67 × 10^{-3} mmol, temp = 75°C, polymerization time = 30 min, monomer pressure = 202,000 Pa, toluene = 500 mL, stirrer speed = 800 rpm.

Figure 3 Effect of temperature on activity of the catalyst. Polymerization conditions: [Al]/[Fe] = 1359 : 1; other conditions as in Figure 2.

(20 mL). Formic acid (97%, 2–3 drops) was added until pH 4–6 was obtained. The content of the flask was stirred for 40 h at room temperature, then the solvent was evaporated. The content of the flask was cooled to −25°C and kept at that temperature for 4 days. The yellow solid crystal obtained was washed using cold methanol and recrystallized in the solvent. The solid ligand of 2,6-*bis*-[1-(2-methylphenylimino) ethyl]pyridine (1.24 g) was obtained. Figure 1 shows the structure of the ligand.[18]

Elemental analysis of the compound was N = 12.1%, C = 80.4%, and H = 6.8%. A molecular weight of Mw = 341 was obtained. Selected IR data (neat) was $v_{C=N}$ = 1643 cm^{-1}.^{1}H-NMR (CDCl$_3$): δ 8.41 (d,2, H$_{pyr}$), 7.90 (t,1,H$_{pyr}$), 7.10 (m,6,H$_{aryl}$), 6.69 (d,2,H$_{aryl}$), 2.34 (s, 6, N=C-CH$_3$), 2.13 (s,6,aryl-CH$_3$). The ^{13}C-NMR spectrum indicates 12 signals because of its symmetry plane.

Preparation of 2,6-*bis*-[1-(2-methylphenylimino) ethyl]pyridine iron dichloride catalyst

A catalyst type of 2,6-*bis*-[1-(2-methylphenylimino) ethyl]pyridine iron dichloride was prepared using
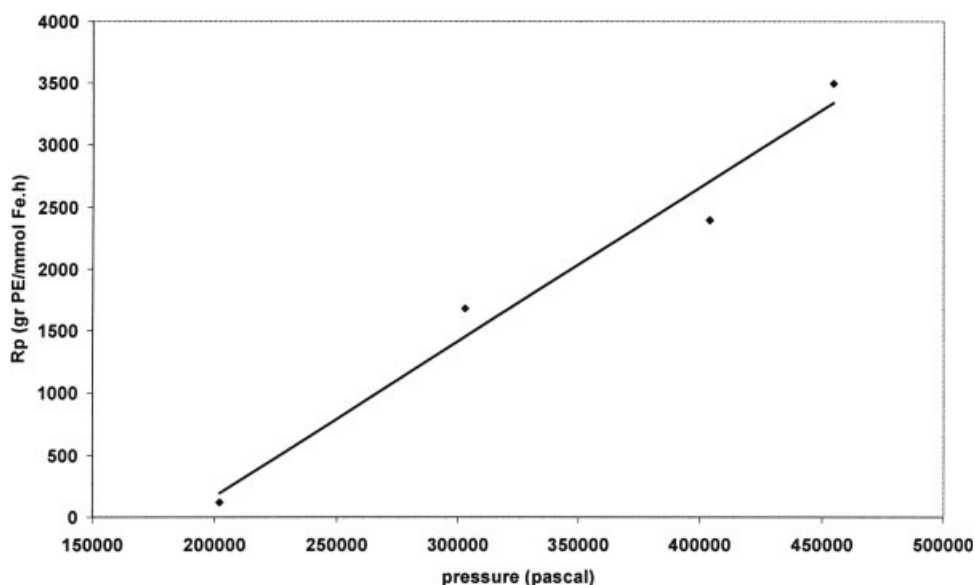
Figure 4 Effect of monomer pressure on rate of polymerization. Temperature = 75 ± 2°C; other conditions as in Figure 3.

TABLE I
Molecular Weight and Its Distribution of PE Obtained

Sample	Mn	Mw	Mp	Mz	Mz+1	Mw/Mn
1a	5.7×10^4	7.1×10^4	8.4×10^4	8.4×10^4	1.1×10^5	1.25
1b	1.0×10^3	1.6×10^3	0.4×10^3	2.8×10^3	4.1×10^3	1.60
2	0.9×10^3	1.5×10^3	–	3.4×10^3	6.5×10^3	1.74

[Al]/[Fe]=1359 : 1, monomer pressure for sample 1a and 1b = 20,2000 Pa and for sample 2 = 454,500 Pa, temperature = 35 °C, polymerization time = 30 min, toluene = 500 ml, stirrer speed = 800 rpm, Mp=the most possible molecular weight.

equimolar chemicals of the ligand and the iron dichloride compounds. The ligand (0.3 g) and iron dichloride (0.2 g) was mixed using a 50-mL flask containing THF (15 mL) under dried N_2 gas. The content of the reactor was stirred for 15 min. The solvent was evaporated using a vacuum. The solid catalyst (0.48 g) of the structure shown in Figure 1 was obtained.

RESULTS AND DISCUSSION

Catalyst activity

The activity of the catalyst, $R_p(average)$ is expressed as *g PE/(mmol Fe.h)*, which was determined after 30 min of polymerization for each run. The polymerization was studied at a constant concentration of the catalyst and various concentrations of MAO. The polymerization activity increased linearly with the addition of the [MAO]/[Fe] ratio (Fig. 2). The behavior is common for the catalyst with MAO used as the cocatalyst such as metallocene and late metal catalysts.[19] Due to the oligomeric nature of the MAO, the chemical is not able to deactivate or overreduce the catalytic active centers even at a very high concentration. The poly-

mer obtained was a waxy-like polyethylene. Due to the homogeneous nature of the polymerization, some fouling of the reactor was observed, which increased a bit with increasing the amount of MAO used.

The polymerization was carried out in the temperature range of 30–75°C (Fig. 3). The catalyst system showed polymerization activity over the entire temperature range studied. The maximum activity was observed from the beginning to about l0 min of polymerization. The highest activity of the catalyst was obtained at about 30°C. A higher temperature promotes easy transfer of the monomer to the active centers; meanwhile, the solubility of the monomer gas in the polymerization media decreases with increasing temperature.[19,20]

The influence of monomer pressure from 202,000 to 454,500 Pa was studied. The polymerization behavior is shown in Figure 4. The polymerization was carried out at [Al]/[Fe] = 1359 : 1 and a temperature of 35°C. The activity of the catalyst in terms of *g PE/(mmol Fe.h)* was linearly increased with the monomer pressure. The increase was mainly due to the higher concentration of the monomer close to the active centers. Due to the exothermic nature of the reaction, a sudden
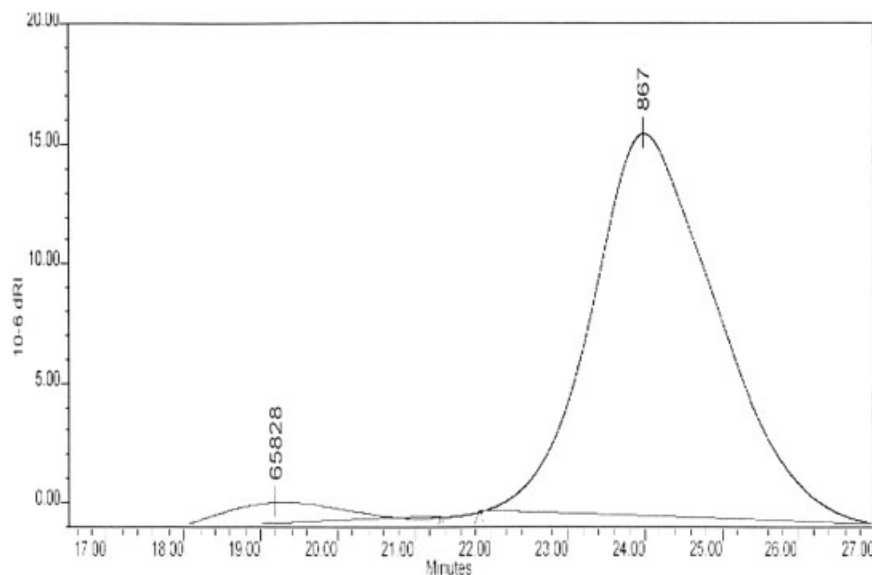
Figure 5 GPC graph of the polyethylene obtained.
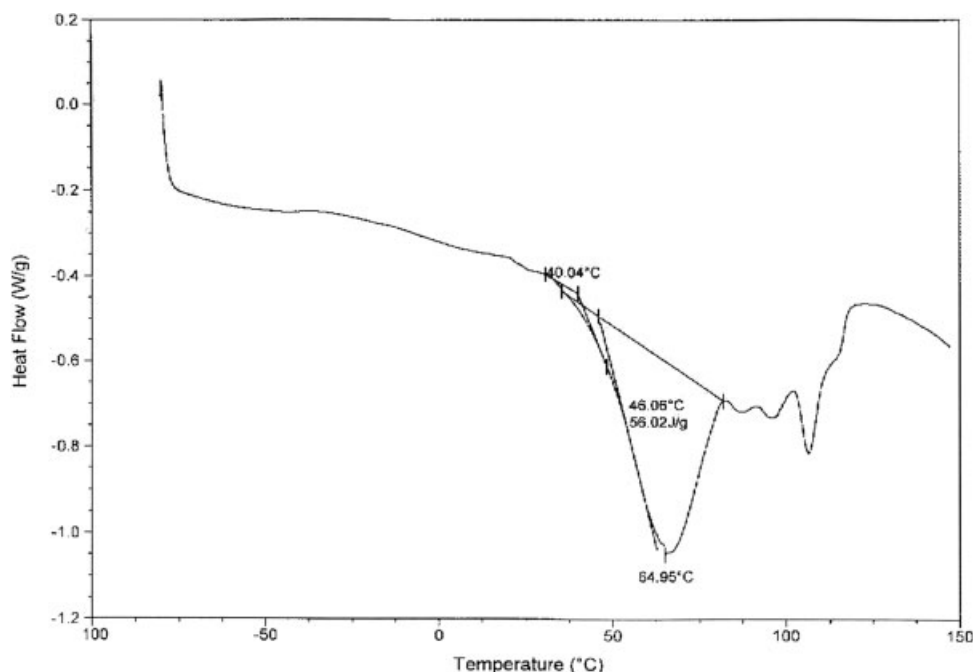
Figure 6 DSC of a polyethylene sample obtained, at a polymerization temperature and pressure of 45°C and 202,000 Pa, respectively.

increase in temperature, particularly at the beginning, was observed. The increase is very difficult at higher pressures of the monomer, which could destroy the active center structure of the catalyst.

Polymer characterization

The molecular weight and molecular weight distribution of some polyethylene samples were determined using the GPC method. Table I shows the results obtained. Figure 5 shows a GPC thermogram obtained that shows a sign of bimodal character.

According to the Table I, the polyethylene obtained is of low molecular weight; however, it is not an oligomer, as reported for a late metal catalyst polymerization of ethylene. The higher molecular weight obtained could be due to the high steric effect of the ligand used, which increases the rate of insertion of the monomer more than the rate of chain transfer reaction. Of course, for the Fe-based catalyst a higher molecular weight has been reported than for the other late metal catalysts.[5] The behavior is a result of a β-H elimination reaction, which bulky groups were not able to reduce.

The melting point (T_m) and crystallinity of the polyethylene sample was determined using the DSC technique (Fig. 6). The chosen sample was obtained at a polymerization temperature of 35°C, monomer pressure = 454,500 Pa, and [Al]/[Fe] = 1359 : 1. The crystallinity was determined according to Kong and Hay,[21] which was about 19%, and the T_m of the polymer was about 65°C.

CONCLUSIONS

The conclusions obtained for the polymerization of ethylene using the 2,6-*bis*-[1-(2-methylphenylimino) ethyl]pyridine iron dichloride/MAO catalyst system are as follows:

1. The iron-based catalyst polymerize ethylene to a low molecular weight, waxy-like polymer.
2. The polymer obtained has a low melting point of about 65°C and low crystallinity of about 19%.
3. The highest activity of the catalyst was obtained at 30°C in the range studied (30–75°C).
4. The activity of the catalyst increased linearly with increasing MAO, the cocatalyst concentration, and monomer pressure.
5. A molecular weight distribution of 1.25–1.72 was obtained under the polymerization condition used. The behavior indicates the potential of the catalyst to produce a narrow molecular weight distribution.

References

1. Peacock, A. N. Handbook of Polyethylene; Marcel Dekker: New York, 2000.
2. Hlatky, G. G. Chem Rev 2000, 100, 1347.
3. Kaminsky, W., Ed. Metalorganic Catalysts for Synthesis and Polymerization; Springer: Heidelberg, 1999.
4. Brookhart, M.; Johnson, L. K.; Ittel, S. D. Chem Rev 2000, 100, 1169.
5. Ittel, S. D.; Johnson, L. K. Chem Rev 2000, 100, 1169.

6. Bernhard, B.; Bugh, L. S.; Kacer, S.; Strieghdr, S. Late Transition Metal Polymerization Catalysis; Wiley-VCH: New York, 2003.
7. Terunori, F.; Yasuhi, T. Mitsui Chemical (Japan), EP 0874005 A1, 1998.
8. Matsukawa, N; Matsui, S.; Mitan, M.; Saito, J.; Tsuru, K.; Kashiwa, N.; Fujita, T. J. Mole Cat A Chemical, 2001, 169, 99.
9. Bott, R. K. J.; Hughes, D. L.; Schormann, M.; Bochmann, M.; Lancaster, S. J. Organometallic Chem 2003, 665, 135.
10. Coates, G. W. J. Chem Soc Dalton Trans 2002, 467.
11. Schnerder, M. G.; Schafer, R. Polymer 1997, 38, 2455.
12. Soya, K.; Naito, Y. Jpn. Pat. 02 182706 (1989).
13. Ketley, A. D. U.S. Pat. 35 35302 (1968).
14. Coates, G. W. Chem Rev 2000, 100, 1223.
15. Zohuri, G. H.; Azimfar, F.: Jamjah, R.; Ahmadjo, S. J Appl Polym Sci 2003, 89, 1177.
16. Zohuri, G. H.; Ahmadjo, S.; Jamjah, R.; Nekoomanesh, M. Iran Polym J 2001, 10, 149.
17. Zohuri, G. H.; Jamjah, R.; Ahmadjo, S. Iran Polym J 2005, 14, 111.
18. Small, B. L.; Brookhart, M. J Am Chem Soc (Communication) 1998, 120, 7143.
19. Justino, J.; Romao Dias, A.; Ascenso, J.; Marcues, M.; Tait P. J. T. Polym Int 1997, 44, 407,18.
20. Tsai, W. M.; Chien, J. C. W. J Polym Sci 1994, 32, 179.
21. Kong, Y.; Hay, J. N. Polymer 2002, 43, 3873.