

A new iron catalyst for ethylene polymerization

Icaro S. Paulino, Ulf Schuchardt*

Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13084-971 Campinas, SP, Brazil

Received 10 June 2003; received in revised form 6 October 2003; accepted 6 October 2003

Abstract

The iron-based catalyst 2,6-bis[1-(4-bromo-2,6-dimethylphenylimino)ethyl]-pyridineiron(II) chloride, **1**, has been successfully synthesized and characterized. Its catalytic activity was evaluated for the polymerization of ethylene at different temperatures and Al/Fe ratios and compared with that of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride, **2**. The results show that the catalytic activity of catalyst **1** is highly dependent on the amount of MAO used in the polymerization of ethylene and presents a maximum value at about 20 °C.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Ethylene polymerization; Iron(II) complex; 2,6-Bis(imino)pyridyl ligand

1. Introduction

It has been shown that in the presence of methylaluminoxane (MAO) 2,6-bis(imino)pyridyliron(II) complexes catalyze the polymerization of ethylene with high activity [1,2]. These catalysts present great advantages since their dichloride derivatives can be easily prepared and isolated as air stable blue solids. Other advantages of these systems are their low cost and the ease with which they can be tailored. Indeed, the substitution pattern of the tridentate ligand is crucial in controlling the molar mass of the polymer, since the size of the aryl group is the main factor affecting olefin insertions, chain transfer reactions and catalytic activity.

For example, decreasing the size of the *ortho*-aryl substituents from isopropyl to methyl groups reduces the polyethylene molar mass [3]. In this way a range of linear polyethylene products can be synthesized by simple modification of the catalyst structure, as well as by changing the temperature and pressure of the polymerization.

Here we wish to report the synthesis of a new member of this family bearing a bulky *para*-bromo-aryl substituent. This catalyst is highly active in the polymerization of ethylene at low temperatures.

2. Experimental

The synthesis of the catalyst and the polymerization of ethylene were carried out under an argon atmosphere. Solvents (THF and toluene) were refluxed over an appropriate drying agent and distilled prior to use. Elementary analyses were performed with a Perkin-Elmer 2401 analyser. The mass spectra were obtained by electron impact at 70 eV and 10^{-5} bar, using a Shimadzu QP-5000 spectrometer, coupled to a direct inlet for solids, Shimadzu DI-50. 2,6-Diacetylpyridine, 4-bromo-2,6-dimethylaniline, 2,6-dimethylaniline and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from Aldrich; MAO was obtained from Witco and ethylene was obtained from Petroquímica União.

2.1. Synthesis of 2,6-bis[1-(4-bromo-2,6-dimethylphenylimino)ethyl]pyridine

2,6-Diacetylpyridine (9.2 mmol, 1.5 g) and 25 ml anhydrous ethanol were placed in a 50 ml flask fitted with a condenser. Under stirring, 4-bromo-2,6-dimethylaniline (18.6 mmol, 3.7 g) and a few drops of formic acid were added consecutively. The mixture was heated to 80 °C and kept at this temperature for 48 h. The yellow solid formed was then filtered and washed with cold methanol and dried under vacuum; the yield was 60%. Mass spectrum, m/z 525 [M^+]. Elemental analysis: Calculated: C, 56.9; H, 4.8; N, 8.0. Found: C, 56.3; H, 4.8; N, 8.2.

* Corresponding author. Tel.: +55-19-3788-3071/3099; fax: +55-19-3788-3023.

E-mail address: ulf@iqm.unicamp.br (U. Schuchardt).

2.2. Synthesis of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine

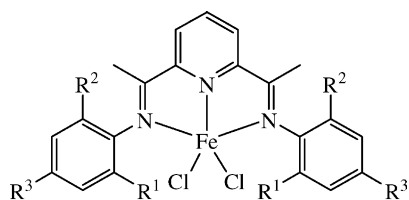
Using a procedure similar to that described above, this ligand was obtained from 2,6-diacetyl pyridine and 2,6-dimethylaniline as a yellow powder in 75% yield. Mass spectrum, m/z 369 [M^+]. Elemental analysis: Calculated: C, 81.6; H, 7.4; N, 11.4. Found: C, 80.2; H, 7.6; N, 11.2.

2.3. Synthesis of 2,6-bis[1-(4-bromo-2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride (**1**)

The bromo ligand (0.24 mmol, 0.12 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.23 mmol, 0.046 g) were added to a Schlenk flask under argon. Then, 10 ml of *n*-butanol were added with a syringe. The mixture was magnetically stirred at 50 °C for 30 min and then filtered. The blue powder was collected, washed with ethyl ether and pentane and dried under vacuum; the yield was 95%. Mass spectrum, m/z 651 [M^+]. Elemental analysis: Calculated: C, 45.9; H, 3.9; N, 6.4. Found: C, 44.2; H, 4.0; N, 6.6.

2.4. Synthesis of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride (**2**)

Using the procedure described above, this catalyst was obtained from the unbrominated ligand as a dark blue powder in 85% yield. Mass spectrum, m/z 495 [M^+]. Elemental analysis: Calculated: C, 60.5; H, 5.5; N, 8.5. Found: C, 60.6; H, 5.8; N, 8.2.



1 $R^1=R^2= \text{Me}; R^3= \text{Br}$

2 $R^1=R^2= \text{Me}; R^3= \text{H}$

2.5. Polymerization

The polymerization experiments were carried out in a 1 l Büchi reactor varying the temperature from -5 °C up to 70 °C, the Al/Fe ratio from 1000 to 4000, and the pressure of ethylene from 2 to 5 bar, using 50 ml of toluene as solvent. After 30 min, the polymerization reactions were interrupted by the addition of ethanol. The polymers were filtered, washed with ethanol and dried in an oven at 60 °C for 4 h.

2.6. Determination of the melting point

The thermal characteristics of the polymers were examined using a DSC 4 instrument (Perkin-Elmer) with a heating rate of 10 °C/min, in the range from 50 to 200 °C. Melting points (m.p.) are related to the second heating cycle.

2.7. Determination of the molar masses

The intrinsic viscosity $[\eta]$ of a 0.1 g/dl polymer solution in decalin was determined using a Canon–Fenks viscosimeter at 135 °C and the one-point intrinsic viscosity method [4]. The viscosity–average molar masses (\bar{M}_v) of the polyethylenes were calculated using the Mark–Houwink equation [5]:

$$[\eta] = 62 \times 10^{-3} \bar{M}_v^{0.7}$$

3. Results and discussion

Complexes **1** and **2** were used in the homogeneous ethylene polymerization in order to investigate the effect of a *para*-bromo-aryl substituent on the catalytic properties of this compound, since it is very difficult to compare results obtained by different authors, as reaction conditions are usually different. The active catalysts were generated in situ in toluene by the addition of MAO. Typical results obtained in the polymerization reactions are shown in Table 1.

The results show that the variation of the *para* substituent at the aryl ring has a pronounced effect both on the catalytic activity and on the average molar mass of the resulting polymer. We observe that the replacement of the *para*-aryl hydrogen by a bromine results in an increase of the activity from 3750 to 5900 kg PE (mol Fe) $^{-1}$ bar $^{-1}$ h $^{-1}$ and a decrease in the average molar mass M_v from 65.4 to 49.6 kg/mol.

These results are interesting, since polymerization mechanisms of homogeneous Ziegler–Natta catalysts involve cationic intermediate species. In this way, steric and electronic ligand effects that make cationic species more stable or unstable can lead to the increase or decrease of catalytic activity. For catalysts **1** and **2** we can consider that the electronic effect is more important since a substitution in the *para* position is not expected to have a significant steric effect. The electronic effect of the *para*-bromo-aryl substituent probably accelerates the fundamental steps of the polymerization process (olefin insertion and chain termination), thus resulting in an increase in catalytic activity and a decrease of the polymer molar mass. This theory is plausible since the electron-withdrawing bromine increases the electrophilic character of the metallic center, thus accelerating ethylene coordination and chain transfer.

In Table 1 we also observe that an increase of the polymerization pressure (entries 1 and 2) results in an increased yield, but in a decrease in catalytic activity. Furthermore, the polymerization pressure does not have an influence on

Table 1
Results obtained in the ethylene polymerization using catalysts **1** and **2**

Entry	Catalyst	Al/Fe ^a	Polymerization Conditions	Activity (kg PE (mol Fe) ⁻¹ bar ⁻¹ h ⁻¹)	Yield (g)	\bar{M}_v (kg/mol)	m.p. (°C)
1	1	1000	Fe = 2.0 μ mol, 50 °C, 5 bar	1300	6.5	16.7	129.6
2	1	1000	Fe = 2.0 μ mol, 50 °C, 2 bar	2350	4.7	16.7	129.7
3	1	1000	Fe = 2.0 μ mol, 30 °C, 2 bar	3580	6.0	25.4	131.4
4	1	2000	Fe = 2.0 μ mol, 30 °C, 2 bar	5900	11.8	49.6	134.8
5	2	1000	Fe = 2.0 μ mol, 30 °C, 2 bar	2150	4.3	38.5	134.1
6	2	2000	Fe = 2.0 μ mol, 30 °C, 2 bar	3750	8.0	65.4	135.1

^a Al/Fe ratio during polymerization.

the average molar mass or melting point of the polymers obtained.

In order to investigate the effects of the Al/Fe ratio on the catalytic activity, polymerizations of ethylene were performed with **1** and **2** at 30 °C, varying the Al/Fe ratio from 1000 to 4000. Fig. 1 shows the results for the polymerizations of ethylene at different concentrations of MAO. When we used catalyst **1** at an Al/Fe ratio of 1000, the catalytic activity was 3580 kg PE (mol Fe)⁻¹ bar⁻¹ h⁻¹, while using an Al/Fe ratio of 4000, the catalytic activity was 9550 kg PE (mol Fe)⁻¹ bar⁻¹ h⁻¹. These results show that the catalytic activity of catalyst **1** is highly dependent on the amount of MAO used in the polymerization process. Additionally, we observed an increase of the average molar mass with an increase of the Al/Fe ratio, indicating that the MAO concentration has little influence on the chain termination process, independent of the Al/Fe ratio used.

A similar behavior was observed for catalyst **2** for an increase of the Al/Fe ratio from 1000 to 4000, however, the catalyst activity was smaller for all Al/Fe ratio used and the molar mass of the polyethylene always higher for the reasons already explained before.

Several studies were carried out to determine the effect of the temperature on the catalytic activity. Fig. 2 shows the results of these experiments in a temperature range of -5 to 70 °C, using catalysts **1** and **2**.

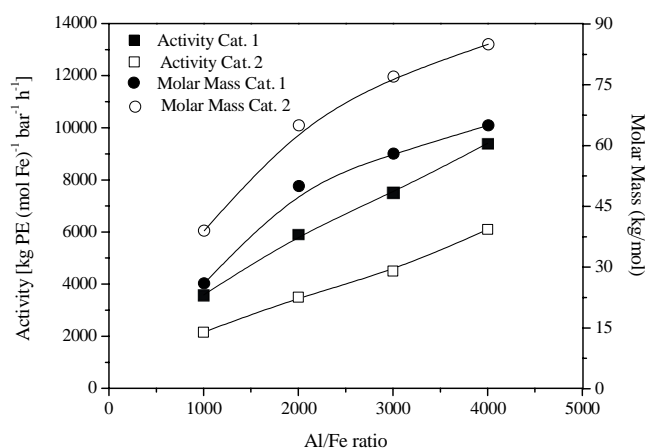


Fig. 1. Effect of the Al/Fe ratio on the catalytic activity of catalyst **1** and **2**. Ethylene pressure, 2 bar; polymerization time, 0.5 h; temperature, 30 °C.

The strong temperature dependence of the catalytic activity is a common characteristic of Ziegler–Natta catalysts due to the high activation energy required for the polymerization process. However, for different kinds of catalysts, we can observe maximum values at different temperatures. When the temperature is increased, the catalytic activity is gradually increased up to a maximum value and then begins to decrease. This behavior is intrinsically related to the stability of the catalyst at higher polymerization temperatures. For example, for zirconocene catalysts the catalytic activity increases with temperature up to 80 °C and then decreases [6]. The same behavior was observed for the bis(salicylaldiminato)titanium catalysts, which shows maximum activity at 40 °C [7]. We observed the same tendency for the 2,6-bis[1-(4-bromo-2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride catalyst **1**, since the catalytic activity increases up to 20 °C and then decreases quickly, due to deactivation of the catalyst. For catalyst **2** the highest activity was observed at 10 °C, however, the activity was always lower than that observed for catalyst **1** at similar temperatures.

The temperature also shows a significant influence on the average molar mass of the polyethylene obtained with catalyst **1**, which decreases quickly as the temperature increases.

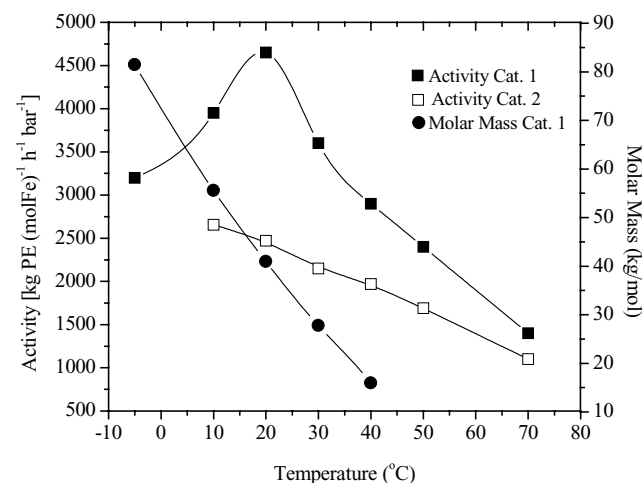


Fig. 2. Effect of temperature on the performance of catalyst **1** and **2**. Pressure of ethylene, 2 bar; time of polymerization, 0.5 h; Al/Fe ratio, 1000.

This can be attributed to an increase of chain transfer processes with increasing polymerization temperatures, since chain length is determined by the relative rates of propagation (insertion) and chain termination (by chain transfer) [8]. At lower temperatures the chain transfer rates are lower and polymers with higher molar mass can be obtained.

4. Conclusions

We have shown that 2,6-bis(iminoethyl)pyridine iron complexes, bearing bulky *para*-bromo substituted aryl groups, present high catalytic activity for the polymerization of ethylene, mainly when the reactions are carried out around 20 °C. The electronic effect of the *para*-bromo-aryl groups results in an increase of activity and a decrease of the molar mass. Furthermore, we observed that only at low polymerization temperatures can polyethylene with a higher molar mass be obtained. Increasing the Al/Fe ratio gives polyethylene with higher yields and higher molar mass while the variation of the ethylene pressure does not change the properties of the polymer.

Acknowledgements

The authors would like to thank FAPESP and CNPq for financial support and Petroquímica União and Witco for supplying the starting materials.

References

- [1] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049–4050.
- [2] 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. (1998) 849–850.
- [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) 8728–8740.
- [4] J.H. Elliott, K.H. Horowitz, T. Hoddock, J. Appl. Polym. Sci. 19 (1970) 2947–2963.
- [5] R. Chiang, J. Polym. Sci. 36 (1959) 91–103.
- [6] J.C.W. Chien, B.P. Wang, J. Polym. Sci. Part A 26 (1988) 3089–3102.
- [7] S. Matsui, T. Fujita, Catal. Today 66 (2001) 63–73.
- [8] S.S. Reddy, S. Sivaram, Prog. Polym. Sci. 20 (1995) 309–367.