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SYNTHESIS AND EVALUATION OF NEW BIS(IMINO) PYRIDINE BASED CATALYSTS FOR ETHYLENE POLYMERIZATION

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Abstract. Three-component catalytic systems based on 2,6-bis(imino) pyridine iron(II) chloride were synthesized from different ligands, which provided new alternative catalysts for polymerization of ethylene. The synthesized catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), and the lack of absorption bands was observed in the region related to the carbonyl, as well as the presence of bands in the region of imino groups corresponding to C=N bonds. Coordination with Fe was also carried out. The structure of the ligands and the new catalysts were confirmed by the elemental analysis (CHN), and ^{1}H- and ^{13}C-nuclear magnetic resonance spectroscopy. In ethylene polymerization with methylaluminoxane as a cocatalyst, the activity of catalyst C1 was high. Although this catalyst structure contains sterically bulky ligands, the metal center was not sufficiently protected allowing transfer reactions, producing polyethylene with a low molar mass and melting temperature.

Keywords: post-metallocene catalysts, bis(imino) pyridine ligands, ethylene polymerization.

1. Introduction

Great attention has been focused on the study of catalysts, in particular single site systems such as post-metallocene catalysts, which has been developed over the years and became capable of synthesizing polymers in larger amounts, with high performance and unique characteristics [1, 2]. Due to these studies, it is possible to proceed further advances in the architecture of the catalyst, which allows a wide range of variations in the ligand [3, 4], which may lead to an overall control of the microstructure of the polymer and, hence, the properties of the final product.

The new family of late-metal catalysts was independently discovered by Brookhart, Bennett and Gibson, the five-coordinate 2,6-bis(arylimino)pyridyl Fe(II) dihalide types, activated by MAO, are effective catalysts for the conversion of ethylene either to high-density polyethylene or to α-olefins with Schulz-Flory distribution [5]. Remarkably, the productivities were as high as those of most efficient metallocenes.

The advantages of these Fe catalysts over other types of single-site and Ziegler-Natta catalysts for ethylene homopolymerization (*e.g.*, metallocenes and constrained geometry complexes) are multiple, from the easiness of synthesis and the use of low-cost metals to low environmental impact. Another intriguing characteristic of bis(organylimino)pyridyl Fe(II) precursor is provided by the easy tuning of their polymerization activity by simple modification of the ligand architecture [6, 7].

Surrah *et al.* [8] describe the synthesis of complexes bearing ligands that contain bulky aromatic terminals such as pyrenyl, 2-benzylphenyl, and naphthyl where Fe(II) catalyst containing the ligand 2-benzylphenyl could convert ethylene to a linear polymer, while ligands pyrenyl and naphthyl produced branched polymers. In fact, it has been shown that the size, nature and regiochemistry of the substituents in the iminoaryl groups are extremely important in controlling the polymerization and oligomerization of ethylene [9, 10]. Iron complexes bearing small substituents at the 2-positions of the aryl groups proved to be excellent catalyst precursors for oligomerization of ethylene. These α-olefins are useful and industrially highly desired, such as for copolymerization reactions with ethylene to give linear low-density polyethylene (LLDPE) [11-13].

Due to its low cost and ready availability for using iron as a polymerization active centre, the objective of the present study was to develop new homogeneous catalytic systems comprehending iron complexes with different compounds based on bis(imino) pyridine ligands, functionalized for using in the future to polymerize ethylene by heterogeneous systems.

2. Experimental

All manipulations of air- and/or moisture-sensitive compounds were routinely performed under an inert atmosphere using a glove box and/or standard Schlenk techniques.

2.1. Materials

Methylaluminoxane (MAO) was purchased from Crompton Corporation, Germany, as 1.9 M toluene solution. Toluene (Ipiranga Petrochemical, commercial purity) was distilled over sodium/benzophenone ketyl prior to use. *n*-Butanol (P.A.) was dried over calcium hydride. Ethylene was supplied by White Martins Gases Industrial, purity 99.9 %, and eluted in columns 3A molecular sieve and copper catalyst. All other starting materials were commercially available and were used without further purification.

For the production of complexes we used the following reagents: 2,6-diacetylpyridine, bis(4-aminophenyl)-1,4-diisopropylbenzene, aniline, 2,6-diisopropylaniline, *p*-phenylenediamine. They were purchased from Sigma-Aldrich.

2.2. Synthesis of Ligands

Four different ligands (L1-L4) were prepared by the following methods.

2.2.1. Synthesis of L1 and L2 ligands

To a solution of 2,6-diacetylpyridine (18.4 mmol) in an absolute ethanol (30 ml), bis(4-aminophenyl)-1,4-diisopropylbenzene (L1) or aniline (L2) (53 mmol) was added. After the addition of a few drops of glacial acetic acid, the solution was refluxed for 40 h. Upon cooling to room temperature, the product was crystallized from ethanol. After filtration, the yellow solid (both L1 and L2) was washed with cold ethanol and dried under vacuum (5 Pa). The yield was 5.75 g (82 %).

This procedure was carried out according to the analogous method used by Britovsek *et al.* [14].

2.2.2. Synthesis of L3 and L4 ligands

To obtain the catalyst precursor, L4 was synthesized in two steps where in the first one the ligand L3 was produced. It was initiated by the reaction of a substituted cyclic amine (2,6-diisopropylaniline) and diketone (2,6 diacetyl pyridine) (as shown in Scheme 1), in equimolar amounts, with methanol and formic acid as a promoter to produce the keto-imine intermediates L3.

Then, in the second step, L4 was synthesized, initiated by the reaction that occurs between the product of the first reaction in equimolar amounts and diamine (*p*-phenylene diamine).

According to Bianchinni *et al.* [15], an important contribution to the selectivity of this reaction was made by the low solubility of the monoimine products (in methanol), which precipitated upon formation and so suppressed further condensation with aniline. However, the bis(imino) pyridine products were indeed obtained in low amounts (2–4 %), and so the crude reaction products were purified by repeated extraction of the (imino)pyridyl ketones with a boiling ethanol. Once purified, these products were treated with the appropriate neat primary amine at 373–383 K, in the presence neither of solvent nor of acid promoter, to give the expected 2,6-bis(imino) pyridyl ligands. Under these mild conditions, the bis(imino) compounds were obtained selectively.

2.3. Synthesis and Characterizations of Iron(II) Complexes

A suspension of the ligand in *n*-butanol was added dropwise at 353 K to a solution of $FeCl_2$ (1.89 mmol) in dried *n*-butanol (20 ml) to yield, in general, a blue solution. After being stirred at 353 K for 15 min, the reaction was allowed to cool to room temperature. The obtained material was concentrated, and diethyl ether (30 ml) was added to precipitate the product as a blue powder, which was subsequently washed 3 times with diethyl ether (3x10 ml); after this, it was filtered and dried [14].

The analysis of infrared absorption spectrometry with Fourier transform (FTIR) showed the absence of absorption band in ~1700 cm^{-1} of C=O group and the characteristic band of C=N indicating the formation of the ligand molecule bis(imino) pyridine at 1620–1640 cm^{-1}.

2.4. Polymerization Experiments

All polymerization reactions were performed in 1 l Büchi glass reactor equipped with a mechanical stirrer, connected to a thermostatic system. In a typical polymerization experiment, the autoclave was charged with 100 ml toluene and the system was fed with ethylene up to the desired pressure. The appropriate amount of the complex and MAO (mixed previously) was introduced at the temperature of 323 K. The mechanical stirrer was run with 600 rpm for all experiments to avoid diffusion controlled polymerization reactions. The molar ratios between Al/Fe (100, 200 or 2000) and ethylene pressures in the reaction medium (0.2 or 0.4 MPa) were the only parameters varied. Al/Fe was varied by decreasing the amount of Fe catalyst in the polymerization medium. After the desired polymerization time (60 min), the polymerization was stopped by quenching with ethanol containing 5% HCl. Polymers were dried overnight at 333 K, washed with 5% HCl in an ethanol solution and after with methanol for several times until total clean of the supernatant and dried again to a constant weight.

Catalytic activity was determined using Eq. (1):

$$C.A = \frac{Yield}{(molFe)\cdot(molE)\cdot t} \qquad (1)$$

where *Yield* – amount of obtained polyethylene, kg; (*molFe*) – amount of the catalyst in moles; (*molE*) – amount of ethylene in the reaction medium (0,2 MPa = 0.0135 mol); *t* – time of polymerization, h.

2.5. Polymer Characterization

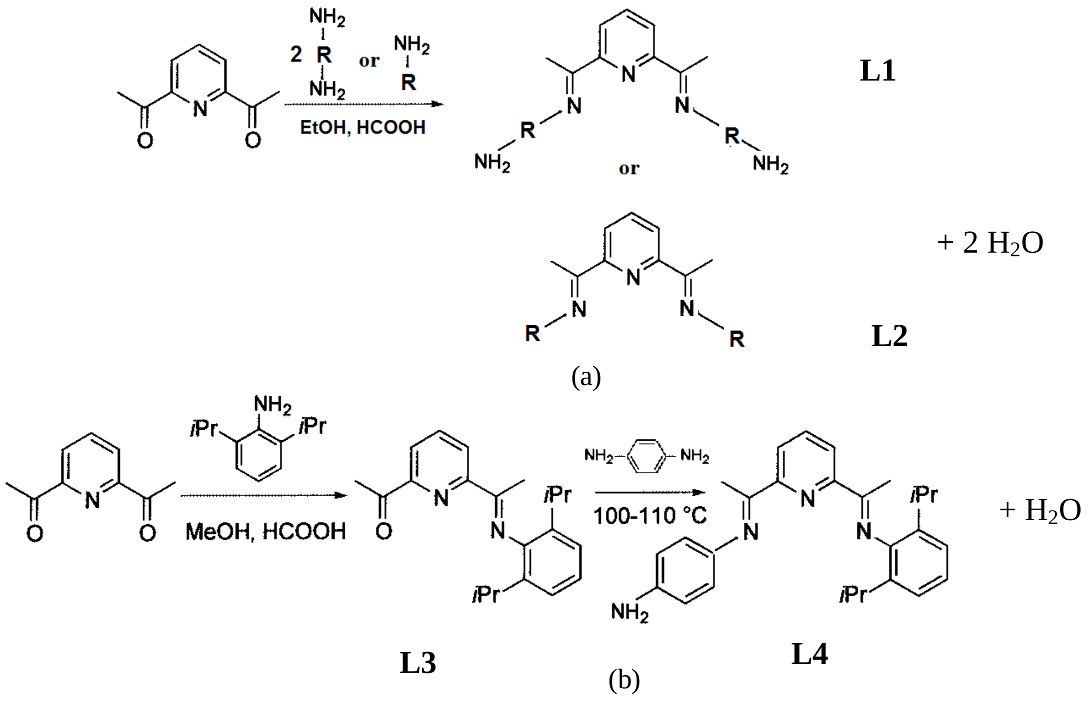
The X-ray diffractometer worked with a potential difference across the tube of 30 kV and 15 mA. The sweep was carried out in the range of 2θ from 2° to 40°, while the goniometer speed was 0.05°/min. The radiation used was CuK of λ = 1.5418 Å.

Thermogravimetric analysis (TA Instruments, TGA Q500) was performed under nitrogen, heating from room temperature to 973 K at 10 K/min. Differential scanning calorimetry (TA Instruments, DSC Q200) was carried out using 4 mg sample, heating from room temperature to 473 K at 10 K/min and cooling at the same rate. The second heating was performed to measure the melting temperature. Besides evaluating melting and crystallization temperatures, the degree of crystallinity of the polymer was also obtained from the melting enthalpy. The value adopted for the melting enthalpy of polyethylene 100% crystalline was 293 $J\cdot g^{-1}$.

Vinylene, vinyl and vinylidene unsaturations are originated at the end of the polymer chain by transfer reactions, through Hβ-elimination mechanism, and were used to determine the number-average molecular weight (M_n) of the copolymers. Molecular weights of standard polyethylenes were previously determined by gel permeation chromatography and their FTIR spectra were recorded, in order to build a calibration curve. The areas of vinylene (965 cm^{-1}), vinyl (908 cm^{-1}) and vinylidene (888 cm^{-1}) groups were calculated, resulting in a total area, which was normalized in relation to the film thickness of the sample. The calibration curve was then employed to determine the number-average molecular weight of the copolymers [16].

3. Results and Discussion

In the present work the bis(imino) compounds were obtained selectively according to Scheme 1.



Scheme 1. Synthesis of 2,6-bis[(phenylimino)]pyridine ligands L1 and L2 (a) and 2-(alkylimino)-6-(arylimino)pyridyl ligand–L4 (b)

Table 1

Structures of the ligands L1-L4

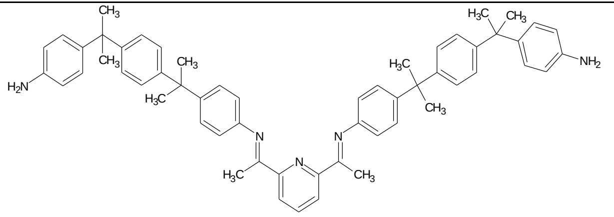
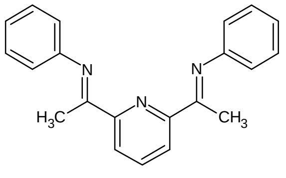
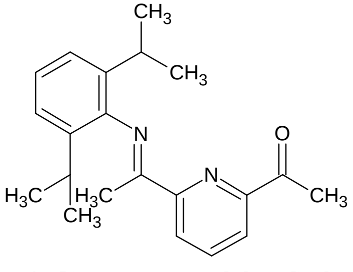
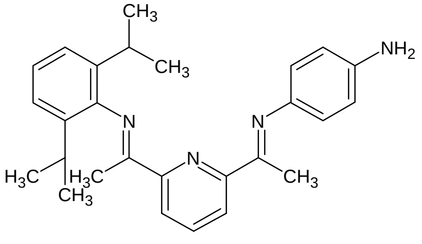
Code	Ligand
L1	 2,6–bis[bis(4-phenylimino)-1,4-diisopropylbenzyl]pyridine
L2	 2,6-bis[(1-phenylimino)ethyl]pyridine
L3	 1-{6-[(2,6-Diisopropylphenyl)ethanimidoyl]-2-pyridinyl}-1-ethanone
L4	 N-{1-[6-(aminophenyl-ethanimidoyl)-2-pyridinyl]ethylidene}-2,6-diisopropylaniline

Table 1 shows the structure of the synthesized ligands (L1-L4) for subsequent complexation reaction, except that the ligand L3 that was used only as a precursor for the synthesis of the ligand L4.

3.1. Characterization of Ligands and Complexes

The ligands and iron(II) complexes were characterized by elemental analysis, IR ^{1}H- and ^{13}C-NMR spectroscopy, as follows.

3.1.1. Ligand L1 and catalyst C1

Yield 5.21 g (55 %). Anal. calc. for $C_{49}H_{45}N_5$ (%): C, 83.60; H, 6.44; N, 9.94. Found: C, 83.93; H, 6.38; N, 10.04. M.p. 425–426 K. ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) = 1.68 (s, 12H, CMe_2), 1.73 (s, 12H, CMe_2), 2.64 (s, 6H, Me-C=N), 6.58 (d, 6.84 Hz, 4H, p-Ar-H), 7.01(d, 6.84 Hz, 16H, C=N-Ar-H_o), 7.27 (d, 6.84 Hz, 4H, o-$Ar_{Aniline}$-H), 7.34 (t, 1H, Py-Hp), 8.12 (d, 2H, Py-Hm). ^{13}C-NMR (75 MHz, $CDCl_3$): (δ ppm) = 170.15 (Ar-N=C), 159.32 (Ar-NH_2), 151.95 (Py-Co), 144.65 (N-Ar-C_o), 142.86 ($Ar_{aniline}$-Co), 140.85 (Ar-C_m), 128.40 ($Ar_{aniline}$-Cm), 127.49 (Ar-Cq), 126.36 (Py-Cm), 125.51 (Py-Cp), 115.33 (N=C-Me), 45.88 (C_q-Me_2), 30.33 (CH_3-C=N), 21.97 (CH_{3isop}).

By FTIR analysis of the ligand L1 and its respective catalyst (C1), according to Fig. 1 it can be observed the absence of peak at about 1700 cm^{-1}, indicating the absence of the carbonyl group, contributing to synthesis of the ligand.

It is still possible to observe a shift of the band characteristic of the C=N bond of the ligand in the complex, since after the complexation reaction, there is a shift toward lower wave number (1635–1599 cm^{-1}) corresponding to the peak of C=N bond, indicating that the complexation reaction was successfully performed.

3.1.2. Ligand L2 and Catalyst C2

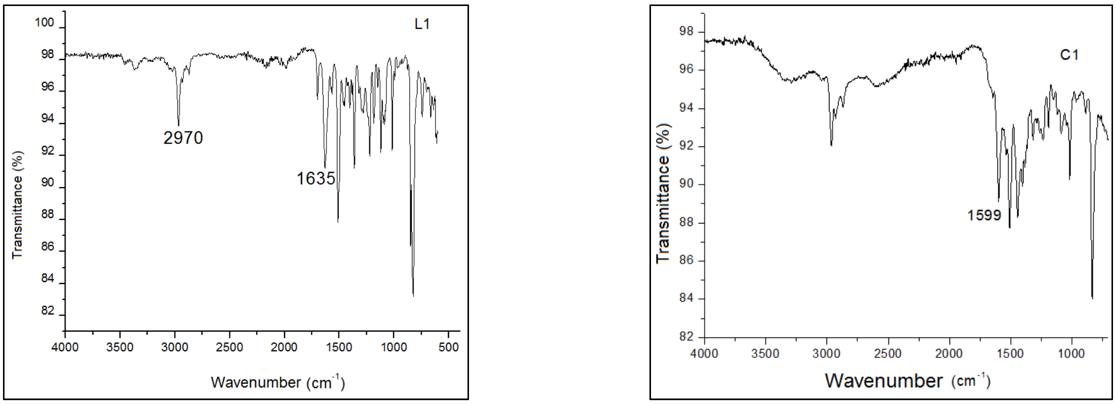
Yield 0.635 g (66 %). Anal. Calc. for $C_{21}H_{19}N_3$ (%): C, 80.48; H, 6.11; N, 13.40. Found: C, 79.98; H, 6.29; N, 13.06%. M.p. 431–433 K. ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) = 2.42 [s, 6H, $C(CH_3)(CH_3)$], 7.07 (dd, J = 7.7, 1.2 Hz, 2 H, CH Ar), 7.25-7.30 (m, 4 H, CHAr), 7.32-7.37 (m, 4 H, CHAr), 7.79-7.82 (dd, J = 6.7, 1.2 Hz, 2 H, CH Ar), 7.92 (d, J = 7.7, 1.2 Hz,1 H, CH Ar). ^{13}C-NMR (75 MHz, $CDCl_3$): δ(ppm) = 167.92 (N=C-Me), 159.33 (Py-Co), 148.36 (C_{Ar}-N), 128.73 (C_m-Ar), 123.63 (Cp-Ar), 120.64 (Co-Ar), 125.81 (Py-C_p), 124.68 (Py-C_m), 22.01 (CH_3-C=N).

By means of FTIR analysis shown in Fig. 2 the same behavior (L1/C1) was identified for L2/C2.

3.1.3. Ligand L3

Yield 0.456 g (83 %). Anal.calc. for $C_{21}H_{26}N_2O$ (%): C 78.22, H 8.13, N 8.69. Found: C 78.38, H 8.16, N 8.74. M.p. 435–437 K. IR: ν(C=N) 1648 cm^{-1}, ν(C=O) 1698 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) = 1.23 [d, J = 6.9 Hz, 6H, $CH(CH_3)(CH_3)$], 1.25 [d, J = 6.9 Hz, 6 H, $CH(CH_3)(CH_3)$], 2.45 [s, 3 H, $C(NAr)CH_3$], 3.22 [sept, J = 6.9 Hz, 2 H,$CH(CH_3)(CH_3)$], 2.42 [s, 3 H, $C(O)CH_3$], 7.17-7.20 (m, 3 H, CHAr), 7.40 (t, J = 7.8 Hz, 1 H, CH Ar), 7.86 (dd, J = 7.7, 1.2 Hz,1 H, CH Ar), 7.98 (dd, J = 7.9, 1.2 Hz, 1 H, CH Ar). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 199.8 [1 C, $C(O)CH_3$], 166.34 [1 C, $C(NAr)CH_3$], 158.72(1 C, C Ar), 146.29 (1 C, C Ar), 137.74 (1 C, CH Ar), 135.69 (2 C, C Ar), 124.92 (1 C, CH Ar), 124.04 (1 C, CH Ar), 122.97 (2 C, CHAr), 123.2 (1 C, CH Ar), 28.30 [2 C, $CH(CH_3)(CH_3)$], 26.24 [1 C, $C(O)CH_3$], 23.29 [2 C, $CH(CH_3)(CH_3)$], 23.05 [2 C,$CH(CH_3)(CH_3)$], 22.85 [1 C, $C(NAr)CH_3$].

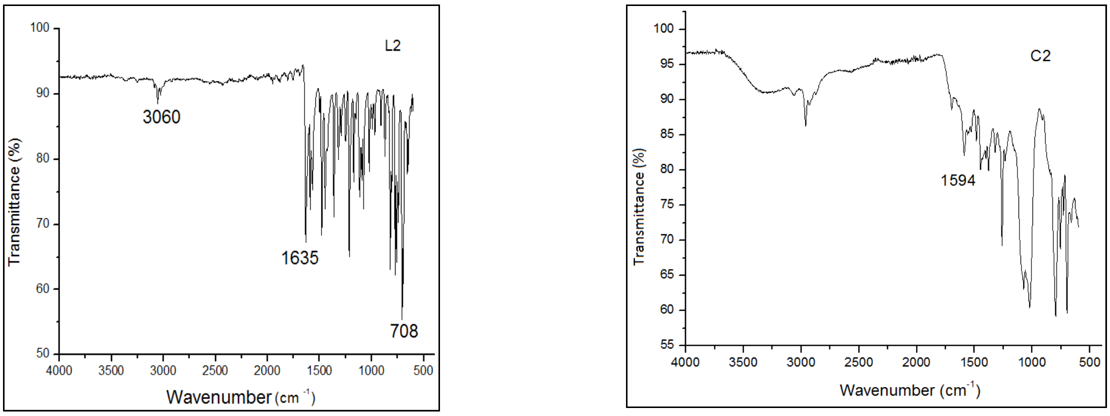
All results are according to the literature [15].



a)

b)

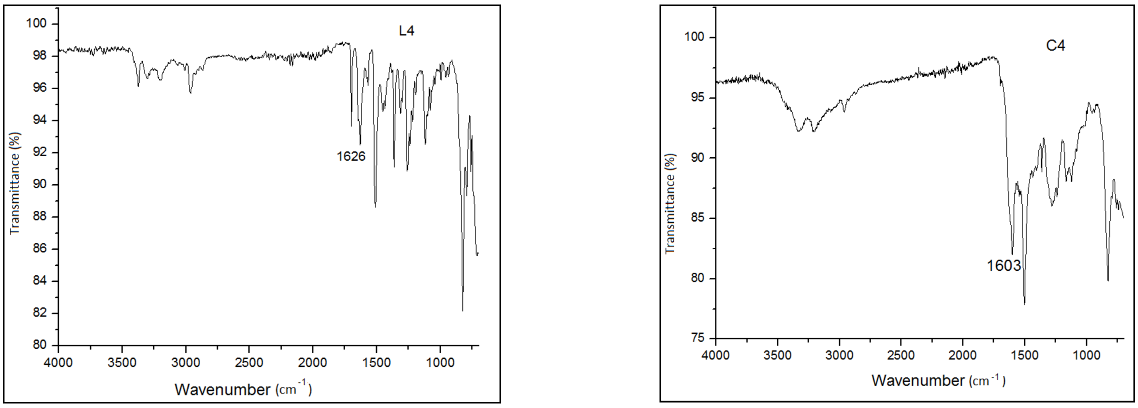
Fig. 1. FTIR analysis of the ligand L1 (a) and its respective catalyst C1 (b)



a)

b)

Fig. 2. FTIR analysis of the ligand L2 (a) and its respective catalyst C2 (b)



a) b)

Fig. 3. FTIR analysis of the ligand L4 (a) and its respective catalyst C4 (b)

3.1.4. Ligand L4 and catalyst C4

Yield 0.456 g (83 %). Anal. calc. for $C_{27}H_{32}N_4$ (%): C 79.4, H 7.76, N 13.6. Found: C 78.25, H 7.51, N 14.12. ^{1}H-NMR (300 MHz, CDCl3): δ(ppm) =1.35 [d,12 H, (CH(CH3)(CH3)$_2$)], 2.59 [sept, J = 6.9 Hz, 2H, CH(CH3)(CH3)], 3.40 [s, 3H, C(NAr)CH3], 3.46 [s, 3H, C(NAr)CH3], 3.89 (s, 4H, NH_2), 6.57 (d, 2H_m-$Ar_{Aniline}$), 6.60 (d, 2H_o-$Ar_{Aniline}$), 7.17 (m, 3H, Ar-H), 7.27 (t, 1H, Py-Hp), 8.10 (d, 2H, Py-Hm). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.15 ($Ar_{Aniline}$-N=C), 169.25 (Ar-N=C), 159.32 (Ar-NH_2), 145.63 (Py-Co), 143.59 ($Ar_{aniline}$-Co), 142.40 ($Ar_{aniline}$-Cm), 140.46 (Ar-C_o), 133.20 (Ar-C_p), 125.99 (Py-C_m), 124.77 (Py-Cp), 123.50 (Ar- C_m), 115.03 (N=C-Me), 22.94 (CH_3-C=N), 30.69 ($CHMe_2$), 21.97 (CH_{3isop}).

FTIR analysis shown in Fig. 3 presents the same behavior of L1/C1 and L2/C2 for the system L4/C4.

3.2. Results of Ethylene Polymerization

In this work, three catalysts were evaluated where the first (C1) contains ligands with a bulky *ortho*-alkyl substituent, the second one (C2), existing in the literature, has the unsubstituted binder and the less bulky moieties; and finally the third one (C4) has an asymmetric ligand, which has intermediate bulkiness with only one side of its face, containing *ortho*-alkyl substituent.

These differences in a catalyst structure and the reaction conditions were presented in Table 2, where the obtained yield of ethylene polymerization and the catalytic activity using the homogeneous catalysts 1, 2 and 4 are also presented.

For each catalyst studied in homogeneous systems, polymerizations were performed in order to evaluate the effect of the Al/Me molar ratio in a catalytic activity.

3.2.1. Influence of ratio [Al]/[Fe]and structure of the ligands

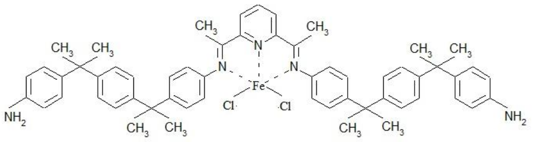
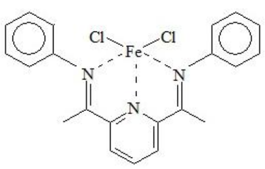
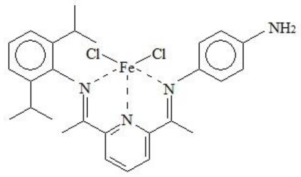
Regarding the results obtained in polymerizations using the unprecedented catalyst C1 based on bis[(phenylimino)]pyridine iron, it can be observed that the catalytic activity increases with increasing Al/Fe molar ratio (the ratio between the concentrations of cocatalyst (MAO) and the catalytic iron complex see Table 2). This result is consistent with that reported in the literature [14]. It is suggested that, for bulky catalysts larger amounts of MAO should be required.

Therefore, for the catalyst C1, the presence of a bulky group substituted in the *ortho*-position of the aromatic ring would provide huge steric effect, which could inhibit the β-hydride elimination and benefit the propagation of polymer chain. However, as in the catalysts C2, the rotation of C-N bond is free and it was observed that there was low contribution to protect the active site [17].

Polymerizations results with the catalyst C4 at different Al/metal molar ratios (100, 200, 2000) also show that the highest activity was achieved in the reaction using the highest Al/metal ratio (run 9). The same behavior aforementioned was observed, this is, the catalytic activity tends to increase with increasing Al /metal ratio in the reaction medium. The presence of higher amounts of MAO in the reaction medium provides elimination of impurities in the polymerization system and better performance of the cocatalyst as a counterion in these catalysts systems that contain less bulky groups. Moreover, the structure of C4 has an isopropyl substituent in ortho-position of one aniline ring, which provided hindrance to termination reactions. Further studies should be conducted to report the effect of the structure with NH_2 group on the catalytic activity but it is believed that this group, which contains pairs of free electrons, may be negatively influencing, for example, the activity of the catalyst C4.

Table 2

Polymerizations performed with catalysts 1, 2 and 4 in homogeneous systems

Run	Structure of catalyst	Polymer samples	Fe, mmol	[Al]/[Me][a]	Yield, g	[b]Catalytic activity
1	 C1	P1 0.1	0.1	100	traces	–
2		P1 0.05	0.05	200	2.390	3541
3		P1 0.005	0.005	2000	0.258	3822
4	 C2	P2 0.1	0.1	100	2.218	1643
5		P2 0.05	0.05	200	1.661	2461
6		P2 0.005	0.005	2000	traces	–
7	 C4	P4 0.1	0.1	100	1.433	1061
8		P4 0.05	0.05	200	0.029	43
9		P4 0.005	0.005	2000	1.768	26192

Notes: [a]concentration of cocatalyst methylaluminoxane is constant and concentrations of metal are 0.1, 0.05 and 0.005 mmol; [b]catalytic activity: kg/molFe·molE·h. Polymerization conditions: 100 ml toluene, cocatalyst methylaluminoxane, 323 K, ethylene pressure 0.2 MPa.

3.2.2. Characterizations of polyethylene by XRD analysis

It was shown in Fig. 4 the X-ray diffractograms of the polymer P1-run 2, P2-run5 and P4-run8, where the presence of peaks at 2*q* at about 21 and 24 degrees is characteristic of the crystal structure of polyethylene, which is marked as crystallographic planes (110) and (200), respectively. These planes identify the orthorhombic unit cells of polyethylene.

It is also possible to observe that the amorphous halo of polyethylene P1 seems to be higher than for the polymer P2, which is in agreement with the results of DSC, which showed higher values of T_m and T_c for P2 (Table 3).

The diffractogram of the polymer P4 has two PE crystal diffractions, but with lower intensity compared to P1 and P2 polymers. As the activity of this catalyst was very low, it is shown that the polymer contains high amounts of catalyst residue, which is confirmed by the thermogravimetric analysis also presented in Table 3.

3.2.3. Characterizations of polyethylene by DSC and TGA

DSC analyses of the polyethylenes were performed and values of crystallization temperature (T_c), melting temperature (T_m) and crystallinity degree (X_c) of samples P1 and P2 are shown in Table 3. For P1, the T_m and T_c are smaller than for the polymer obtained with the catalyst C2 (P2), and this indicates that P1 polyethylene crystals are smaller and more defective, probably due to difficulties in organizing polymer chains into crystals. This indicates that the polyethylene obtained by the catalyst C1 is more branched.

The degree of crystallinity of P1 and P2 calculated based on the melting enthalpy of polyethylene, showed very similar levels of crystallinity. It was unable to analyze P4 by DSC due to the low yield obtained.

The thermograms of DSC of polymers P1 and P2 are shown in Fig. 5.

The endotherm of P1 presents a large monomodal peak, differing from the profile obtained for P2, which is bimodal, indicating the presence of very different crystallites sizes.

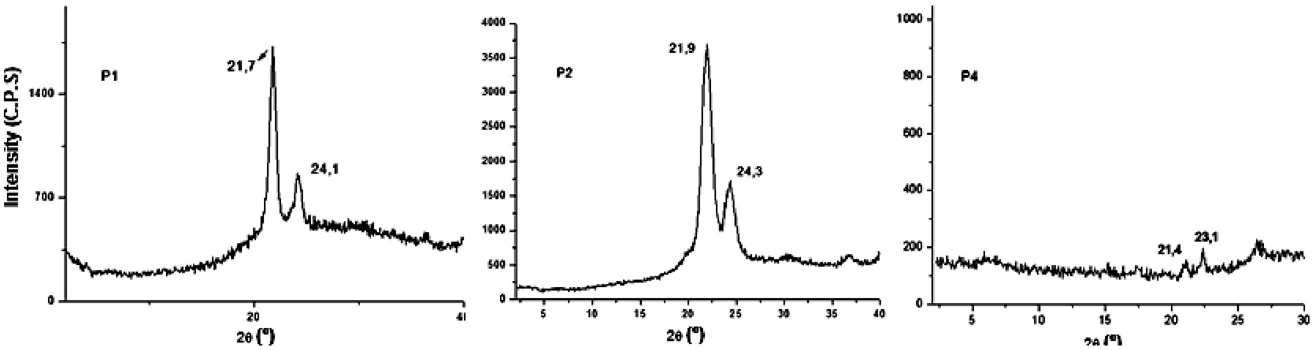


Fig. 4. X-ray diffractograms of the polyethylene sample P1 (run 2), P2 (run 5) and P4 (run 8)

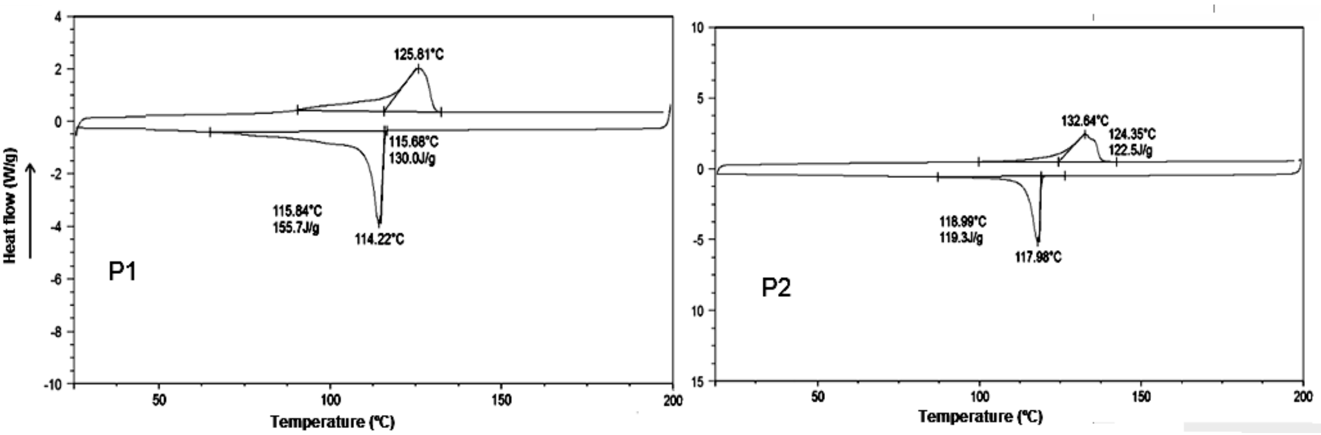


Fig. 5. DSC thermogram of the polyethylene sample P1 (run 2), P2 (run 5)

Table 3

Thermal properties of polyethylenes synthesized with catalysts 1, 2 and 4

PE	DSC			TGA			FTIR
	T_c, K	T_m, K	X_c, %	T_{onset}, K	$T_{\max}$, K	Residue, %	M_n, g/mol
P1	389	399	44.4	729	751	1.7	$7.1 \cdot 10^3$
P2	392	406	41.8	731	750	3.6	$7.5 \cdot 10^3$
P4	–	–	–	699	738	20.1	–

The TGA profiles of P1, P2 and P4 are characteristics of the polyethylene decomposition, which generally occurs from 703 to 773 K. It was possible to observe that polymer P4 showed significant amounts of residue (approximately 20 %). This residue is arising from the presence of catalyst residue and the formation of aluminum hydroxide by the hydrolysis reaction of the MAO solution used to precipitate the polymer, which was obtained in low yield. These residues may have accelerated the degradation of the polymer resulting in the decrease at degradation temperatures.

3.2.4. Characterizations of polyethylene by FTIR

The polymers were analyzed by FTIR in order to observe the presence of vinylene, vinyl and vinylidene end-groups that appear after the active site undergoes chain transfer reactions.

Polyethylenes P1 and P2 have an average molar mass (M_n) next to 7,000 g/mol. This value is considered low and it is possibly caused by the absence of stereo-hindrance in the ortho position on the aniline moieties of the catalyst skeleton, which causes the increase in chain termination reactions forming more terminal groups, especially vinyl groups, with relatively high absorption in the region of 908 cm^{-1}, due to β H transfer reaction. As reported in the literature [18], bulky substituents in the ortho-position suppress the chain migration process and also the chain termination reactions.

Catalyst C1 contains sterically bulky ligands, although the coordination sphere with the metal center is not sufficiently protected in order to reduce the transfer reactions. In this case, the two aromatic rings near the metal must be perpendicular to the pyridine ring, leaving the active sites free to side reactions.

4. Conclusions

The 2,6-bis[bis(4-phenylimino)-1,4-diisopropylbenzyl]pyridine and N-{1-[6-(aminophenyl-ethanimidoyl)-2-pyridinyl]ethylidene}-2,6-diisopropylaniline ligands were prepared and reacted with iron chloride to form the title complexes, sharing the similar framework as complexes containing 2,6-bis(imino) pyridines. The new iron complexes exhibited high activities for ethylene polymerization in the presence of MAO. The higher activities were at 323 K, and Al/Me molar ratio was 2000 with the pressure of ethylene of 0.2 MPa. Unit cells of polyethylene were identify as orthorhombic, the melting temperature was low, 399 K, and the degradation T_{onset} was 729 K.

It is useful to highlight the performance of a new catalyst C1, which has the high catalytic activity in homogeneous systems.

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СИНТЕЗ І ОЦІНКА НОВИХ КАТАЛІЗАТОРІВ ПОЛІМЕРИЗАЦІЇ ЕТИЛЕНУ НА ОСНОВІ БІС(ІМІНО)ПІРИДИНУ

Анотація. *З використанням різноманітних лігандів синтезовані нові трикомпонентні каталітичні системи на основі 2,6-біс(іміно)піридин хлориду заліза(II), які можуть бути альтернативними каталізаторами полімеризації етилену. За допомогою Фур'є-спектроскопії проведено аналіз синтезованих каталізаторів. Виявлено відсутність смуг поглинання в області карбонільних груп, і наявність смуг в області іміногрупи, що відповідає C=N зв'язкам. Встановлено відповідність з Fe. Структура лігандів і нових каталізаторів підтверджена за допомогою елементного аналізу, 1Н- та 13С-ЯМР спектроскопії. При полімеризації етилену з метилалюмоксаном як співкаталізатором, встановлено високу активність каталізатора С1. Незважаючи на те, що каталізатор містить стерично об'ємні ліганди, металевий центр не є достатньо захищеним і тому мають місце реакції перенесення, внаслідок чого отримується поліетилен з низькою молекулярною масою і температурою плавлення.*

Ключові слова: *пост-металоценовий каталізатор, біс(іміно) піридинові ліганди, полімеризація етилену.*