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SYNTHESIS AND EVALUATION OF ARYLIMINO PYRIDINE NICKEL(II) CATALYSTS: INFLUENCE OF SUBSTITUENTS ON POLYETHYLENE STRUCTURE

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Abstract. The asymmetric arylimino pyridine Ni(II) catalysts have been examined with different substituents including diisopropyl, diethyl, fluoro, and chloro groups. The influence of these substituents and variation of ethylene pressure on the catalytic activity, crystalline structure, as well as on thermal properties of polyethylene has been investigated. The result show that complexes with substituent alkyl groups, which provide the increased electron density on the metal center (*o*-diethyl and *o*-diisopropyl) exhibit higher activity, compared to those with electron acceptors substituents (*o*-fluoro and *o*-chloro).

Keywords: homogeneous catalyst, ethylene polymerization, asymmetric catalyst.

1. Introduction

The observations that K. Ziegler and coworkers (ethylene polymerization at ambient temperature and pressure) [1] and G. Natta and coworkers (preparation of stereospecific polymers from α -olefins) [2-4] reported in 1955 represented the starting point of a new era in polymer science and industry. Since then, we have witnessed the evolution of a new generation of catalysts and polyolefin materials which originate from studies on homogeneous, metallocene- and non-metallocene-based polymerization precursors [5-7]. After the studies of M. Brookhart and coworkers started in the 90s [8, 9], various types of nickel(II) catalysts for oligomerization and polymerization of olefins are known until now [10]. During the last years, investigations were mainly focused on α -diimine nickel(II) complexes as suitable catalysts in combination with methylaluminoxane (MAO) [11, 12].

In the past few years, late transition metal complexes became more and more interesting as catalyst

precursors for oligomerization and polymerization of olefins. In contrast to early metal systems, late metal catalysts most often dimerize or oligomerize olefins due to β -hydride elimination [13], which leads to a chain walking mechanism, producing alkyl branches of varying lengths randomly spaced along the polyethylene backbone [14]. This mechanism gives reasons for the formation of linear and branched polymers and short chain oligomers in the ethylene polymerization with nickel catalysts [10]. An important parameter of these catalysts is design and the ligand electronic structure, which has not been systematically investigated. Ligand electronic and steric effects have been observed in many catalytic systems [15].

In this paper we study the synthesis of asymmetric arylimino pyridine Ni(II) complexes as well as the polymerization of ethylene using these complexes as catalysts. We examined several aryl-substituted systems with variable ortho substituents, including diisopropyl, diethyl, fluoro, and chloro groups in attempt to observe the electronic and steric influence of these substituents on the final polymer. These complexes were highly capable of producing materials with highly variable structures and properties. The effect of ethylene pressure on activity and polymer microstructure will be presented.

2. Experimental

2.1. General

All manipulations of air-and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Commercial grade toluene was dried (refluxed 48 h under nitrogen atmosphere) over sodium and benzophenone before using. Polymerization grade ethylene was

purchased from White Martins Company and used without purification. The ligands and complexes were synthesized according to the literature [16]. The catalysts were evaluated in homogeneous polymerization of ethylene at different pressure values. The ligands and catalytic precursors were characterized by the melting point, elemental analysis (C, H, N), magnetic resonance spectroscopy of hydrogen ($^1\text{H-NMR}$), absorption spectroscopy in the infrared (Fourier transform infrared spectroscopy [FTIR]) and fluorescence microscopy. The obtained polyethylene was characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) to determine thermal properties, diffraction of X-ray spectroscopy (DRX) to determine degree of crystallinity (X_c). Eq. (1) was used:

$$W_c = \frac{A_c}{A_c + A_a} \quad (1)$$

where W_c – degree of crystallinity; A_c – crystallinity area; A_a – amorphous area.

Polymers were also evaluated according to their morphological stability. In the DSC the samples were maintained 15 min above the melting temperature and then they were cooled at 10 K/min to room temperature and heated again at the same rate to obtain T_m and T_c after annealing.

The catalytic activity was calculated using Eq. (2):

$$C.A. = \frac{Yield}{mmolNi \cdot pE \cdot t} \quad (2)$$

where $Yield$ – amount of obtained polymer, g; $mmolNi$ – amount of catalyst, mmol; pE – pressure of ethylene in the reaction, t – time of polymerization, h.

2.2. Synthesis of the Ligands and Catalysts

Ligands of the arylimino-pyridine type are synthesized by condensation reactions between carbonyl compounds and substituted anilines [17]. The ligands of this work were synthesized by reacting 25.7 mmol of R or R',R'- aniline derivatives with 25.70 mmol of 2-pyridinecarboxaldehyde in ethanol and allowed to reflux for 72 h. After this time, the ligands precipitate in the reaction medium, filtered and washed with cold ethanol. The molecular structures of the synthesized ligands can be found in Fig. 1.

The amount of 2 mmols of each synthesized ligand was reacted with 2 mmol of nickel(II) chloride in a mixture of acetonitrile and methanol (1: 3). After 72 h of reflux, the precipitates formed were washed with hexane and dried in vacuum. The molecular structures of the synthesized complexes can be found in Fig. 2.

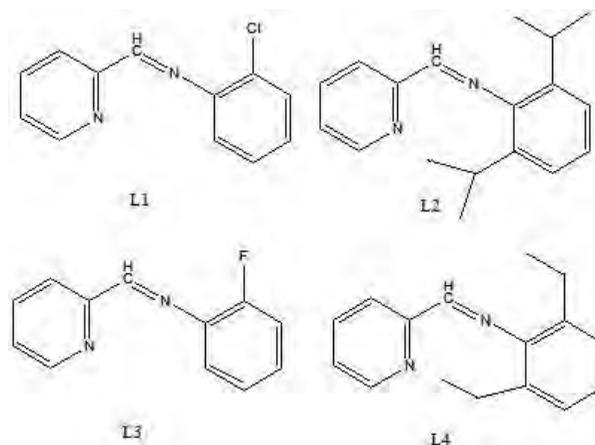


Fig. 1. Arylimino-pyridine synthesized ligands

2.2.1. Synthesis of the ligand L1

In a 100 ml flask containing 50 ml of ethanol 25.70 mmol (3.28 g; density: 1.210 g/ml) of 2-chloroaniline and 25.70 mmol (3.11 g; density: 0.984 g/ml) of 2-pyridinecarboxaldehyde were added. After the addition of 1 drop of glacial acetic acid, the system was refluxed for a period of 72 h. After this time, a brown precipitate was observed in the reaction medium. The precipitate was filtered and washed with cold ethanol (3x10 ml) and dried in vacuum. The solid (1.77 g, 28.76 %) was identified as **L1** on the basis of the following data. M.p. 330–332 K. CHN analysis, calc. for ($\text{C}_{12}\text{H}_9\text{N}_2\text{Cl}$): C, 66.51; H, 4.16; N, 12.93. Found: C, 66.80; H, 4.28; N, 12.79. i.r $\tilde{\nu}$ (cm^{-1}): 1595 ($\text{C}=\text{N}$ stretching). $^1\text{H-NMR}$ (CDCl_3): δ 7.02–7.31 (m, 4H, Ph), 7.36–7.40 (m, 1H), 7.79–7.85 (m, 1H, $J = 1.70$, 7.77 Hz), 8.30 (d, 1H, $J = 7.92$ Hz), 8.53 (s, 1H, $\text{CH}=\text{C}$), 8.70–8.72 (d, 1H, $J = 5.55$ Hz).

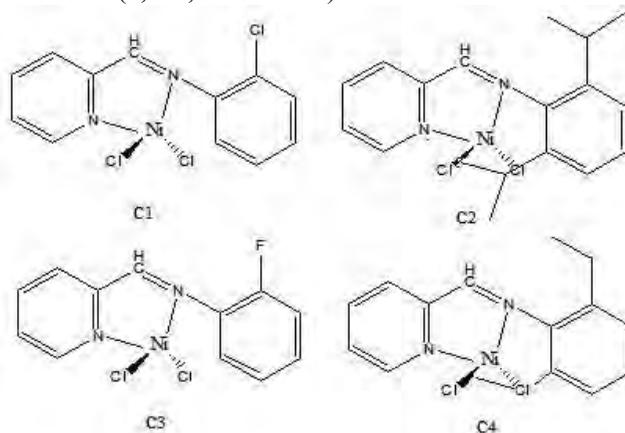


Fig. 2. Arylimino-pyridine nickel chloride complexes

2.2.2. Synthesis of the ligand L2

25.70 mmol (4.70 g; density 0.940 g/ml) of 2,6-diisopropylaniline and 25.70 mmol (3.11 g) of

2-pyridinecarboxaldehyde were added in a 100 ml flask containing 50 ml of ethanol. After the addition of 1 drop of glacial acetic acid, the system was refluxed for a period of 72 h. After this time, a caramel precipitate was observed in the reaction medium. The precipitate was filtered, washed with cold ethanol (3 x 10 ml) and dried in vacuum. The solid (5.01 g, 70.03 %) was identified as **L2** on the basis of the following data. M.p. 338–341 K. CHN analysis, calc. for (C₁₈H₂₂N₂): C, 81.20; H, 8.27; N, 10.52. Found: C, 82.04; H, 8.12; N, 11.74. i.r $\tilde{\nu}$ (cm⁻¹): 1629 (C=N stretching). ¹H-NMR (CDCl₃): δ 1.18 (d, 12H, J = 6.87 Hz, CH₃), 2.98 (heptet, 2H, J = 6.86 Hz, CHCH₃) 7.08–7.18 (m, 3H, J = 3.25, 5.34, 5.39 Hz, Ph), 7.38–7.42 (m, 1H, J = 1.22, 4.86, 7.51 Hz), 7.81–7.87 (m, 1H, J = 1.72, 7.77 Hz), 8.31 (s, 1H, CH=N), 8.26 (d, 1H, J = 8.83 Hz), 8.71–8.73 (d, 1H, J = 5.76 Hz).

2.2.3. Synthesis of the ligand L3

In a 100 ml flask containing 50 ml of ethanol 25.70 mmol (2.86 g; density 1.151 g/ml) of 2-fluoroaniline and 25.70 mmol (3.11 g) of 2-pyridinecarboxaldehyde were added. After the addition of 1 drop of glacial acetic acid, the system was refluxed for 72 h. After this period, a dark precipitate was observed in the reaction medium. The precipitate was washed with cold ethanol (3 x 10 ml) and dried in vacuum. The solid (4.78 g, 82.36 %) was identified as **L3** on the basis of the following data. M.p. 310–311 K. CHN analysis, calc. for (C₁₂H₉N₂F): C, 72.00; H, 4.5; N, 14.00. Found: C, 71.61; H, 4.14; N, 13.37. i.r $\tilde{\nu}$ (cm⁻¹): 1625 (C=N stretching). ¹H-NMR (CDCl₃): δ 7.13–7.25 (m, 4H, Ph), 7.36–7.40 (m, 1H, J = 1.23, 4.84, 7.53 Hz), 7.79–7.85 (m, 1H, J = 2.02, 8.04 Hz), 8.27 (d, 1H, J = 6.83 Hz), 8.67 (s, 1H, CH=C), 8.71–8.73 (d, 1H, J = 5.83 Hz).

2.2.4. Synthesis of the ligand L4

25.70 mmol (3.84 g; density 0.906 g/ml) of 2,6-diethylaniline and 25.70 mmol (3.11 g) of 2-pyridinecarboxaldehyde were added in a 100 ml flask containing 50 ml of ethanol. After the addition of 1 drop of glacial acetic acid, the system was refluxed for 72 h. After this period, a purple precipitate was observed in the reaction medium. The precipitate was washed with cold ethanol (3 x 10 ml) and dried in vacuum. The solid (4.40 g, 72.32 %) was identified as **L4** on the basis of the following data. M.p. 314–315 K. CHN analysis, calc. for (C₁₆H₁₈N₂): C, 80.67; H, 7.56; N, 11.76. Found: C, 80.90; H, 7.12; N, 12.24. i.r $\tilde{\nu}$ (cm⁻¹): 1641 (C=N stretching). ¹H-NMR (CDCl₃): δ 7.13–7.25 (m, 4H, Ph), 7.36–7.40 (m, 1H, J = 1.23, 4.84, 7.53 Hz), 7.79–7.85 (m, 1H, J = 2.02, 8.04 Hz), 8.27 (d, 1H, J = 6.83 Hz), 8.67 (s, 1H, CH=C), 8.71–8.73 (d, 1H, J = 5.83 Hz).

2.2.5. Synthesis of the complex C1

In a 100 ml flask containing 10 ml of acetonitrile and 20 ml of methanol 2 mmol of **L1** and 2 mmol of NiCl₂(DME) were added. The mixture was allowed to reflux for 72 h, after which the formation of a brown precipitate was observed. The solid was filtered and washed with 30 ml (3 x 10 ml) of hexane and dried in vacuum. The solid (0.61 g, 88.40 %) was identified as **C1** on the basis of the following data. M.p. > 573 K. CHN analysis, calc. for (C₁₂H₉N₂NiCl₃): C, 41.59; H, 2.60; N, 8.09. Found: C, 41.10; H, 2.49; N, 8.20. i.r $\tilde{\nu}$ (cm⁻¹): 1580 (C=N stretching).

2.2.6. Synthesis of the complex C2

In a 100 ml flask containing 10 ml of acetonitrile and 20 ml of methanol 2 mmol of **L2** and 2 mmol of NiCl₂(DME) were added. The mixture was allowed to reflux for 70 h, then the formation of an orange precipitate was observed. The solid was filtered and washed with 30 ml (3 x 10 ml) of hexane and dried in vacuum. The solid (0.76 g, 87.26 %) was identified as **C2** on the basis of the following data. M.p. > 573 K. CHN analysis, calc. for (C₁₈H₂₂N₂NiCl₂): C, 54.71; H, 5.57; N, 7.09. Found: C, 54.90; H, 5.20; N, 7.23. i.r $\tilde{\nu}$ (cm⁻¹): 1602 (C=N stretching).

2.2.7. Synthesis of the complex C3

2 mmol of **L3** and 2 mmol of NiCl₂(DME) were added in a 100 ml flask containing 10 ml of acetonitrile and 20 ml of methanol was added. The mixture was allowed to reflux for 72 h, after which the formation of an orange precipitate was observed. The dark solid was filtered and washed with 30 ml (3 x 10 ml) of hexane and dried in vacuum. The solid (0.46 g, 70 %) was identified as **C3** on the basis of the following data. M.p. > 573 K. CHN analysis, calc. for (C₁₂H₉N₂FNiCl₂): C, 43.79; H, 2.73; N, 8.51. Found: C, 43.20; H, 2.90; N, 8.78. i.r $\tilde{\nu}$ (cm⁻¹): 1600 (C=N stretching).

2.2.8. Synthesis of complex C4

In a 100 ml flask containing 10 ml of acetonitrile and 20 ml of methanol 2 mmol of **L4** and 2 mmol of NiCl₂(DME) were added. The mixture was allowed to reflux for 69 h, after which the formation of a violet precipitate was observed. The violet solid was filtered and washed with 30 ml (3 x 10 ml) of hexane and dried in vacuum. The solid (0.65 g, 88.43 %) was identified as **C4** on the basis of the following data. M.p. > 573 K. CHN analysis, calc. for (C₁₆H₁₈N₂NiCl₂): C, 52.34; H, 4.90; N, 7.63. Found: C, 52.82; H, 4.75; N, 8.02. i.r $\tilde{\nu}$ (cm⁻¹): 1620 (C=N stretching).

2.3. Ethylene Polymerization

Ethylene polymerizations were carried out in duplicate (error up to 13 % in yield) in a reactor Büchi 280 Glassuster BEP with a 1000 ml beaker, coupled with mechanical stirrer (maintained at 650 rpm during polymerization). The pressures used were 0.4 and 0.25 MPa. The reactions were performed at 323 K for 1 h.

3. Results and Discussion

3.1. Synthesis of the Ligands

The ligands were synthesized based on experiments in the literature [18] and their chemical structures can be seen in Fig. 1. All the synthesized ligands had a narrow melting point range which indicates high degrees of purity. The CHN elemental analysis corroborates the proposed structures as well as reaffirms the total purity of the compounds obtained. The infrared spectrum of the ligands showed complete disappearance of C=O vibrations aldehydic present in the starting material and the appearance of the intense stretching vibration of C=N bonds formed by condensation reactions. For the ligand **L1**, the stretching of the C=N bond is at 1595 cm⁻¹, in the region where the C=N vibrations are coupled with the C=C vibration of aromatic rings [19]. For the ligands **L2**, **L3** and **L4**, the vibrations of C=N can be found in 1629, 1625 and 1641 cm⁻¹, respectively, regions that are typical of C=C vibrations without coupling with vibrations of C=C on the aromatic rings. In all the obtained spectra it is possible to observe intense vibrations regions between 820–750 cm⁻¹ indicative of the presence of substituents on the aromatic rings. ¹H NMR spectra confirm the proposed structures. The chemical signals, as well as the coupling constants are in agreement with the literature [11].

3.2. Synthesis of the Complexes

Four synthesized complexes had their chemical structures and purities confirmed by CHN elemental analysis, as can be seen in the Experimental Section. The purity of these complexes is of fundamental importance to its activities as catalysts for olefin polymerization reactions [16]. The comparison between infrared spectra of ligands and complexes indicate the successful synthesis of the complexes. The main feature observed was the shift vibration of C=N in the spectra of the free ligands to regions of lower energy in the spectra of the complexes [20]. In the **L1** spectrum, there is a C=N stretch at 1595 cm⁻¹, whereas the **C1** complex spectrum with the same ligand, the vibration is shifted to 1580 cm⁻¹. The same behavior was observed in the spectra of the complexes **C2**, **C3** and **C4**, wherein the vibrations related to C=N stretching move from 1625 to 1601 cm⁻¹ for **C2**, 1625 to 1600 cm⁻¹ for **C3** and 1641 to 1620 cm⁻¹ for **C4**. In complexes using nickel as a metal center, it takes a tetrahedral geometry corresponding to *sp*³ hybridization with two unpaired electrons. Thus, these compounds are paramagnetic and do not allow NMR analysis. The chemical structures of the synthesized complexes can be found in Fig. 2.

3.3. Ethylene Homogeneous Polymerization

The study of ethylene polymerization employing the synthesized complexes presented in this article is based on observations on the activation and deactivation of the catalysts, the crystalline structure and evaluation of the thermal behavior of polymeric material obtained. Table 1 presents the results of the ethylene polymerization.

Table 1

Polymerization results for the complexes C1-C4

Complex	Pressure, MPa	Yield, g	Activity, Kg-PE/(mol-Ni.atm.h) ⁻¹
C1	4	0.109	5.5
C1	2.5	0.068	5.4
C2	4	0.910	45.5
C2	2.5	0.110	8.8
C3	4	0.139	7.0
C3	2.5	0.118	9.5
C4	4	0.556	27.8
C4	2.5	0.550	44.0

Note: polymerization conditions: Cat = 0.005 mmol; MMAO= 4.5 mmol; solvent (toluene) = 100 ml; T = 298 K; time of polymerization = 1 h.

3.4. Influence of the Pressure on the Ethylene Polymerization

Ethylene was polymerized at 0.25 and 0.4 MPa applying catalysts **C1-C4/MAO**. As expected, the increase of pressure results in a higher ethylene yields, since this is a higher concentration of monomer. However, calculating the catalytic activity and tacking into account the ethylene pressure (in Kg-PE/mol-Ni.atm.h), it can be seen that, except for the **C2** complex system, all the others do not increase the catalytic activity at higher ethylene pressure. In general, increasing the ethylene concentration tends to facilitate insertion and reduce the walking chain, reducing the number of branches and thus increasing the degree of crystallinity of polyethylene [21, 22].

3.5. Influence of the Crystalline Structure on the Ethylene Polymerization

The profiles of X-ray diffraction of the polymers synthesized under 0.25 and 0.4 MPa pressure are shown in Figs. 3-6, where the crystalline peaks appear thinner PE synthesized at the lower pressure (0.25 MPa). For most samples, the peaks at $2\theta = 21.3^\circ$ and $2\theta = 23.7^\circ$ are designated (110) and (200) equivalent structures to the crystallographic planes of the orthorhombic unit cell polyethylene with the d_{110} possessing higher intensity [21].

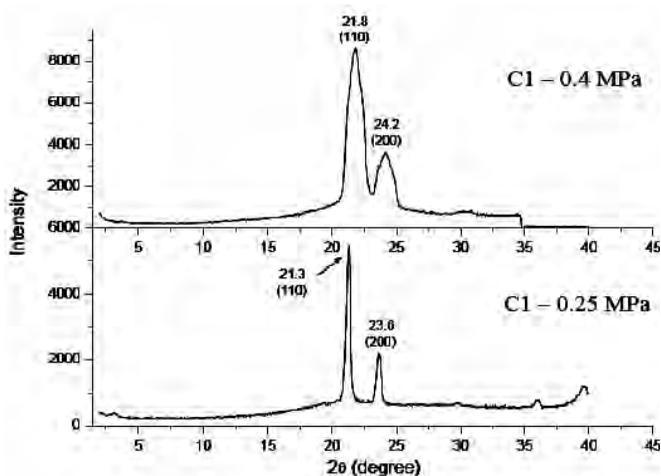


Fig. 3. X-ray data of the polyethylene obtained from complex C1

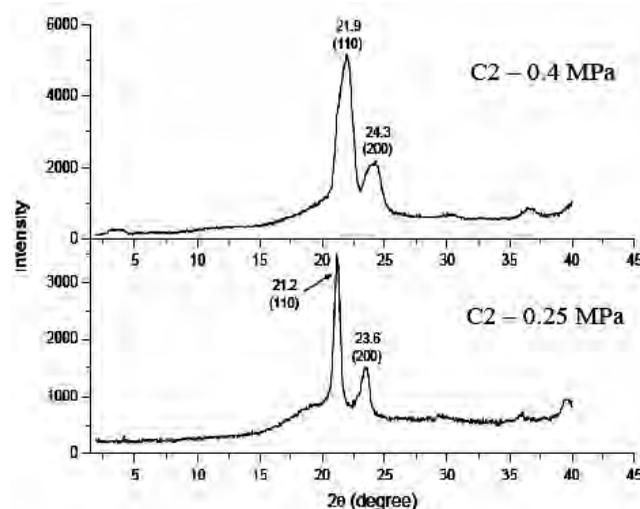


Fig. 4. X-ray data of the polyethylene obtained from complex C2

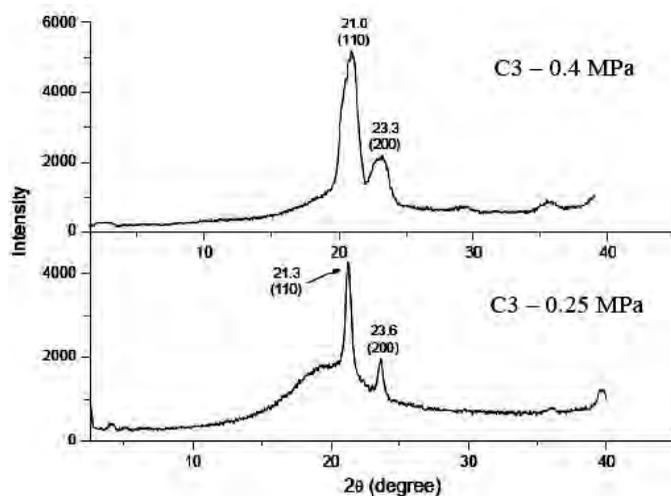


Fig. 5. X-ray data of the polyethylene obtained from complex C3

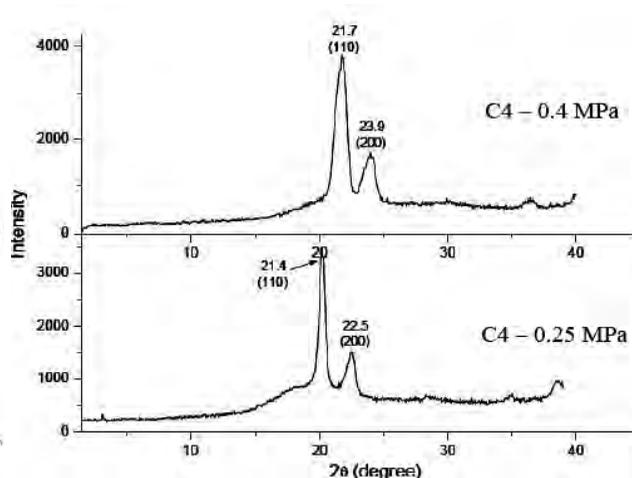


Fig. 6. X-ray data of the polyethylene obtained from complex C4

Table 2

Degree of crystallinity results from X-ray measurements

Complex	Pressure, MPa	XRD X_c , %
C1	0.4	72
C1	0.25	78
C2	0.4	56
C2	0.25	55
C3	0.4	50
C3	0.25	23
C4	0.4	61
C4	0.25	64

Table 3

Values of initial temperature of mass loss (T_{onset}) and temperature of maximum rate of mass loss (T_{peak}) on the ethylene polymerization

Complex	Pressure, MPa	Weight loss, % at 973 K	T_{onset} , K	T_{peak} , K
C1	0.4	98	478/818	531/838
C1	0.25	nd*	nd*	nd*
C2	0.4	97	704	731
C2	0.25	nd*	nd*	nd*
C3	0.4	99	442/715	nd*
C3	0.25	99	422/713	nd*
C4	0.4	95	666	723
C4	0.25	99	655	720

Note: nd*= not detected.

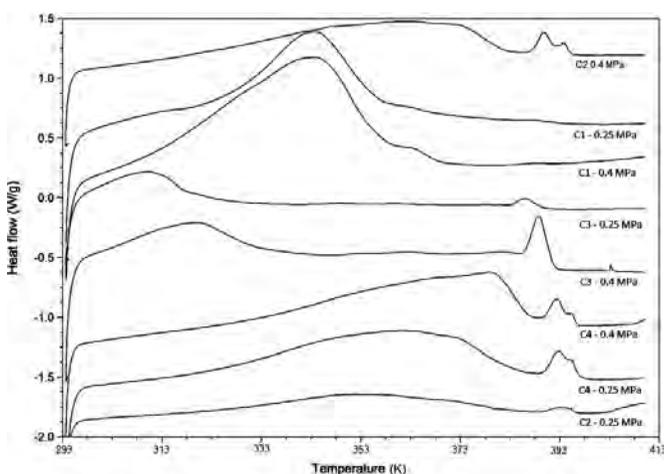


Fig. 7. DSC curves measured on heating (T_m) of polyethylene. Heating rate of 10 K/min

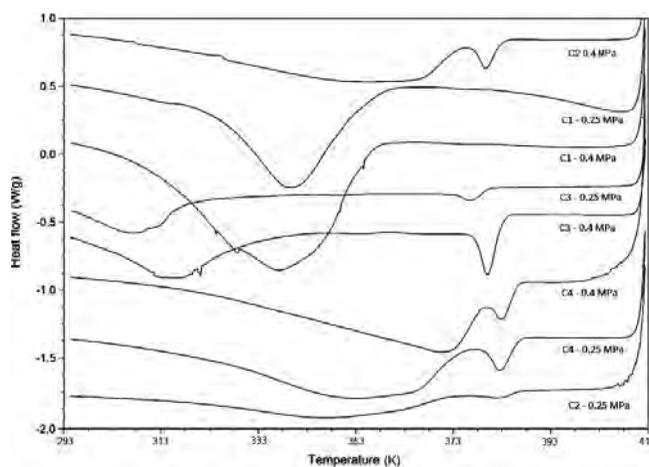


Fig. 8. DSC curves measured on cooling (T_c) of polyethylene. Cooling rate of 10 K/min 4

According to the results presented in Table 2 for the PE synthesized with the complex **C3**, a great increase in the degree of crystallinity with increasing monomer pressure can be noticed. However, for PE synthesized with complexes **C1** and **C4**, the opposite situation is observed. In general, increasing the ethylene concentration tends to facilitate monomer insertion reducing the chain walking, and then the number of branches, thus increasing the degree of crystallinity of polyethylene.

It is possible that polymer precipitation occurred during polymerization, so that the catalyst may have been covered by a layer of insoluble polymer, causing problems of mass transfer or the monomer cannot reach the active site.

This problem of barrier between the catalytic site surrounded by polymer and monomer could also have affected the degree of crystallinity of the polymer. The complex **C1** produced PE with the highest X_c between the catalyst evaluated, followed by complexes **C4**, **C2** and **C3**.

Table 4

Values of T_m and T_c and crystallinity obtained from X-ray data

Complex	Pressure, MPa	T_m , K	T_c , K	XRD X_c , %
C1	0.4	343/364	337/354	72
C1	0.25	343/363	339/355	78
C2	0.4	361/390	354/382	56
C2	0.25	352/393	347/386	55
C3	0.4	320/388	314/383	50
C3	0.25	310/386	307/376	23
C4	0.4	378/392	370/386	61
C4	0.25	360/392	353/382	64

Table 5

Molecular mass of the polymers calculated by the integration of the peaks in the infrared spectra

Complex	Pressure, MPa	Molecular mass	Integrated peaks		
			Vinylene (965 cm^{-1})	Vinyl (909 cm^{-1})	Vinylidene (890 cm^{-1})
C2	0.4	91000	1.941	1.721	0.042
C2	0.25	529	1.777	1.576	0.048
C4	0.25	642	2.249	1.411	0.078
C1	0.4	178	3.134	13.526	0.116

3.6. Influence of the Complex Structure on the Ethylene Polymerization

The results of the polymerizations of ethylene with the complex using diethyl substituent on the aromatic ring show that the PE obtained presented a higher degree of crystallinity compared to the polymer synthesized with complex diisopropyl substituent group. Ethyl groups have a lower steric volume than isopropyl groups and then it is possible to observe that complex that leaves the most exposed nickel atom produces polymers with a higher crystalline fraction, while bulkier substituents provide greater ease of transfer reactions. Moreover, the higher steric hindrance the more difficult the chain termination by associative displacement transfer ($H\beta$) [23].

The catalyst activity also appears to be related to its structure. Substituent groups (*o*-diisopropyl and *o*-diethyl) which provide increased electron density on the metal center have higher activities when compared with substituents electron acceptors (*o*-chloro and *o*-fluoro).

3.7. Thermal Characterization of the Obtained Polyethylene

For better understanding of the thermal properties of the polymers, they were characterized by a thermogravimetric analysis and differential scanning calorimetry.

3.7.1. Thermogravimetric analysis

From Table 3 it is possible to observe the typical representation of the polyethylene decomposition, which typically occurs within 719–773 K [24].

3.7.2. Differential scanning calorimetry analysis

The DSC analyses of the prepared polyolefins indicate that the highest melting temperature and the crystallization of the PE have been obtained with the catalysts **C2** and **C4**.

Fig. 7 presents the endothermic melting of the PE, while Fig. 8 shows the cooling curves with crystallization of the PE.

It is important to note the DSC thermograms presented (Figs. 7 and 8) that the melting and crystallization peaks are broad and multimodal indicating coexistence of different crystal sizes. It is suggested that these polyolefins show a structure with different types of branching with side chains of different lengths from short to very long branches.

Table 4 shows that complexes **C2** and **C4** produced PE with higher values of T_m and T_c although they have higher values of X_c . This indicates that the increase in the lamellar thickness of the polyethylene cannot be directly related to the increasing degree of crystallinity, so that the polymers produced by these complexes that presented higher degree of crystallinity have less crystallites dispersed in the amorphous matrix. Possibly these polyethylene chains contain lower levels of branches [25].

3.8. Infrared Spectroscopy of the Obtained Polymers

The polymer synthesized at 0.4 MPa using the complex **C2** shows higher molecular weight (91000), followed by PE synthesized at 0.25 MPa, obtained with

the complex **C4**. The results show that the polymer with the lowest molecular weight is synthesized at 0.4 MPa through the complex **C1**.

Apparently, the complex produced the highest molecular weight polymer due to the structure of the complex **C2** which is the most voluminous, promoting greater steric hindrance, and thus avoiding greater degree in the chain transfer reactions. The complex **C1** produced lower molecular weight polymer, most probably due to the presence of a strong electron leaving group bonded to the ring in the *ortho*-position. All polymers show the vinylene group with main group termination, except for the polymer obtained by the catalyst **C1**, in which it is presented as the main group of the terminal vinyl group. Table 5 shows the molecular mass of the polymers calculated by the integration of the peaks in the infrared spectra.

4. Conclusions

In this paper various aspects of ethylene polymerization produced were evaluated using nickel(II) complexes activated by MAO, from the synthesis of the ligands and catalysts precursors to the structures of the polymers in the solid state.

It was observed that the structure of the nickel complexes used has a strong influence on the structure of polyethylene produced. Complexes with substituent groups which provide increased electron density on the metal center (*o*-diethyl and *o*-diisopropyl) showed higher activity compared to complexes with electron acceptors substituents (*o*-fluoro and *o*-chloro). It is possible to correlate direct effect of these substituents on the electron density of the metal center.

The increase of the pressure favors the synthesis of more crystalline polymers except for the polymer produced with the catalyst **C4**. By DSC analysis, it was observed that the melting and crystallization peaks were broad and multimodal, indicating the coexistence of crystals with different sizes. This means that these polyolefins show structures with different sizes of branches, and the XRD study allowed the observation signals identified as planes (110) and (200) of the orthorhombic structure of polyethylene, confirming the lamellar structure of PE.

The polymer synthesized at 0.4 MPa using the complex **C2** showed higher molecular weight (91000), followed by the polymer synthesized at 0.25 MPa, obtained with the complex **C4**. Apparently, the complex produced the highest molecular weight polymer due to the structure of the complex **C2**, which is the most voluminous, promoting greater steric hindrance, and thus avoiding greater degree in the chain transfer reactions.

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СИНТЕЗ І ХАРАКТЕРИСТИКА НІКЕЛЬ(II) АРИЛІМІНО ПІРИДИНОВИХ КАТАЛІЗАТОРІВ: ВПЛИВ ЗАМІСНИКІВ НА СТРУКТУРУ ПОЛІЕТИЛЕНУ

Анотація. Досліджені асиметричні ариліміно піридин Ni(II) каталізатори з різними замісниками, включаючи діізопропіл-, діетил-, флуоро- і хлор-замісники. Досліджено вплив цих замісників і тиску етилену на каталітичну активність, кристалічну структуру, і термічні властивості поліетилену. Показано, що комплекси із заміщеними алкільними групами, які забезпечують підвищену електронну щільність на центрі металу (*o*-діетил і *o*-діізопропіл), більш активні в порівнянні з комплексами з електрон-акцепторними замісниками (*o*-флуоро і *o*-хлор).

Ключові слова: гомогенний каталізатор, полімеризація етилену, асиметричний каталізатор.