

Ethylene polymerization with nickel complexes containing aminophosphine ligands

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Abstract

Bis(aminophosphines) were prepared by reaction of the corresponding diamines with chlorodiphenylphosphine. As phosphines are readily oxidized to pentavalent phosphorus forming P=O bonds, the analogous bis(aminophosphine oxide) were also synthesized. These bis(aminophosphines) and their products of air oxidation were employed to prepare the nickel complexes **I**, **II**, **III** and **IV** by reaction of dimethoxyethane nickel dibromide adduct and the bis(aminophosphorus) compounds in THF, at room temperature. The new Ni complexes activated by methylaluminumoxane (MAO) were active as catalysts for ethylene polymerization. The influences of Al/Ni ratio and polymerization temperature on the catalyst activity, as well as on the polymer microstructure, were investigated. Highest yield was obtained at Al/Ni ratio = 2000. The more flexible aminophosphine complex **II** showed the highest catalytic activity. The temperature influence on polymerization reaction present a peculiar behavior: at low temperatures the oligomer production was higher and yield of polymer was lower. At temperatures below zero, octene and/or its isomers were formed predominantly. The polyethylenes obtained by polymerization with aminophosphine complexes **I** and **II** presented molecular weight even higher than 200,000 as well as broad molecular weight distribution. ¹³C NMR analyses indicated that they were branched polymers with the melting temperature (T_m) in the range of 117–127 °C. The complexes containing the oxidized ligands (**III** and **IV**) produced more linear polyethylenes with T_m around 130 °C. © 2006 Published by Elsevier B.V.

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1. Introduction

Ethylene polymerization using diimine complex catalysts based on late transition metals such as nickel II and palladium II was reported by Brookhart and coworkers [1–11]. The bulky bidentate diimine ligands in those complexes are the key factor for the production of high molecular weight polymers. In addition, these catalysts are able to produce highly branched polyethylenes without using comonomers, such as 1-hexene or 1-octene. The Ni–nitrogen bond in the diimine complexes are stable enough to avoid removal of the bulky ligand during catalyst activation by the aluminum cocatalyst and the bulky aryl rings in the axial sites of the square plane Ni complex retard the rate of chain transfer, as result obtaining high molecular weight polyethylenes. Bidentate diphosphine compounds have tendency to form stable nickel complexes due to the following

characteristics: the donor effect of the electron pair of phosphorus atom and the use empty d orbital of the phosphorus atom to stabilize the metal–phosphorus bond, once the orbital 3p and 3d are close in the diagram of energy [12–16]. The literature has already reported examples in which complexes bearing bidentate phosphine ligands also produce branched polyethylenes in high yields, depending on the polymerization condition [17,18]. Thus, bidentate phosphorus-containing complexes can be potential ligands for good olefin polymerization catalysts if adequate steric hindrance is present around Ni atoms. Here we report the synthesis of Ni complexes with bis(aminophosphine) and bis(aminophosphine oxides) ligands and application of these compounds in ethylene polymerization.

2. Experimental

2.1. Materials and general conditions

4-(Dimethylamino)pyridine and chlorodiphenylphosphine were used as received. Tetrahydrofuran and *n*-pentane were

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purified by reflux with sodium/potassium alloy. Ethyl ether was purified by reflux with sodium/potassium alloy following LiAlH_4 treatment. Toluene was purified by treatment with P_2O_5 following by reflux with sodium/potassium alloy. Triethylamine and 1,2-ethylenediamine were purified by distillation. 1,2-Diaminebenzene was purified by sublimation. All the operations related to phosphorus complexes preparation were carried out under an argon atmosphere using standard Schlenk techniques. The complex was prepared according to literature [19]. The ligands were prepared modifying the methodology previous described in literature [20] as described below (Fig. 1).

2.2. Synthesis of ligands

2.2.1. Synthesis of N,N' -bis(diphenylphosphine)-1,2-phenylenediamine

To a solution of 1.45 g (0.013 mol) of 1,2-phenylenediamine, 3.7 ml of triethylamine and 100 mg of 4-(dimethylamino)pyridine in 50 ml of dry tetrahydrofuran were added dropwise to a solution containing 4.9 ml (0.0268 mol) of chlorodiphenylphosphine in 50 ml of tetrahydrofuran. After 3 h of intense stirring at room temperature, the solution was filtered through a sintered Schlenk and the residue washed with THF. The filtrate was evaporated and then the light brown oil was washed three times with 50 ml of diethyl ether, giving 2.75 g of a light brown powder (yield, 43%). Mp. 82–85 °C. IR (KBr disc, cm^{-1}) 905; 1098; 1292; 1433; 1493; 1594; 3067; 3335. NMR (CDCl_3) ^{31}P δ : 33.2; ^1H δ : 6.79–6.83 (m, 2H, CH arom); 7.06–7.09 (m, 2H, CH arom); 7.27–7.39 (m, 20H, CH arom); 4.27 (d, $J=7.75$ Hz, 2H, NH); ^{13}C δ : 131.2 (s, Car); 130.9 (s, Car); 128.9 (s, Car); 128.4 (s, Car); 121.9 (s, Car); 119.7 (s, Car); 119.5 (s, Car). Mass spectrum (m/z) 476 (M^+), 290 (100%), 213 (79%), 183 (81%), 137 (95%).

2.2.2. Synthesis of N,N' -bis(diphenylphosphine)-1,2-ethylenediamine

To a solution of 3.3 g (0.055 mol) of 1,2-ethylenediamine, 15.3 ml of distilled triethylamine and 100 mg de 4-(dimethylamino)pyridine in 50 ml of dry tetrahydrofuran were added dropwise to a solution containing 10 ml (0.055 mol) of chlorodiphenylphosphine in 100 ml of tetrahydrofuran. After 3 h of intense stirring, at room temperature, the solution was filtered and the solid residue washed with tetrahydrofuran. The filtrate was evaporated and the light brown oil was washed three

times with 50 ml of diethyl ether, giving of a white powder. IR (KBr disc, cm^{-1}) 835; 1108; 1433; 1480; 1602; 2857; 2921; 3047; 3288. NMR (CDCl_3) ^{31}P δ : 42.2; ^1H δ : 7.2–6.35 (m, 20H, arom); 2.96–2.99 (m, $J=7.5$, 4H, CH_2); 2.1 (s, 2H, NH); ^{13}C δ : 65.0 (s, Caliph); 68.0 (s, Caliph); 114.5 (s, Car); 128.2 (s, Car); 128.5 (s, Car); 131.1 (s, Car); 131.4 (s, Car); 174.0 (s, Car). Mass spectrum (m/z): 428 (M^+), 243 (61%), 230 (76%), 201 (100%).

2.2.3. Synthesis of N,N' -bis(diphenylphosphoryl)-1,2-phenylenediamine

To a solution of 12.25 g (0.020 mol) of 1,2-phenylenediamine, 3 ml of triethylamine and 100 mg of 4-(dimethylamino)pyridine in 50 ml of dry tetrahydrofuran were added dropwise to a solution containing 7.5 ml (0.04 mol) of chlorodiphenylphosphine in 50 ml of tetrahydrofuran. After 3 h of intense stirring at room temperature, the solution was filtered and the residue washed with tetrahydrofuran. The filtrate was evaporated and the light brown oil was washed three times with 50 ml of diethyl ether, giving a brown powder. IR (KBr disc, cm^{-1}) 899; 1114; 1161; 1436; 1479; 3244. NMR (CDCl_3) ^{31}P δ : 253.27; ^1H δ : 6.76–7.59 (m, 24H, CH arom); 4.3 (s, 2H, NH). Mass spectrum (m/z): 508 (M^+), 290 (100%), 201 (62%), 183 (55%).

2.2.4. Synthesis of

N,N' -bis(diphenylphosphoryl)-1,2-ethylenediamine

To a solution of 1.2 g (0.02 mol) of 1,2-ethylenediamine, 5.6 ml of triethylamine and 100 mg de 4-(dimethylamino)pyridine in 50 ml of dry tetrahydrofuran were added dropwise to a solution containing 7.3 ml (0.04 mol) of chlorodiphenylphosphine in 100 ml of tetrahydrofuran. After 3 h of intense stirring, at room temperature, the solution was filtered and the residue washed with tetrahydrofuran. The filtrate was evaporated and the light brown oil was washed three times with 50 ml of diethyl ether, giving a light yellow powder. IR (KBr disc, cm^{-1}) 886; 1090; 1124; 1185; 1436; 1479; 1586; 3225. NMR (CDCl_3) ^{31}P δ : 114.7; ^1H δ : 7.17–7.4 (m, 20H, arom); 3.5 (dd, $J=7.0$, 4H, CH_2); 3.1–3.2 (m, 1H, NH). Mass spectrum (m/z): 460 (M^+), 203 (48%), 201 (100%), 183 (48%).

2.3. Ni complexes preparation

2.3.1. (N,N' -(Diphenylphosphoro)-1,2-phenylenediamine) NiBr_2 (I)

To a tetrahydrofuran solution containing 0.71 mmol of N,N' -(diphenylphosphine)-1,2-phenylenediamine was added to an equimolar amount of $\text{C}_4\text{H}_{10}\text{O}_2\text{NiBr}_2$. The reaction was maintained under stirring for 4 h at room temperature. The solvent was dried and the product was washed with pentane and dried under vacuum, giving a pink powder. IR (KBr disk, cm^{-1}) 911; 1100; 3210; 3327. Mass spectrum (m/z): 682 (M^+), 508 (10%), 308 (20%), 290 (100%), 262 (20%), 201 (30%), 183 (58%).

2.3.2. (N,N' -(Diphenylphosphoro)-1,2-ethylenediamine) NiBr_2 (II)

To a tetrahydrofuran solution containing 1.2 mmol of N,N' -(diphenylphosphine)-1,2-ethylenediamine was added to an

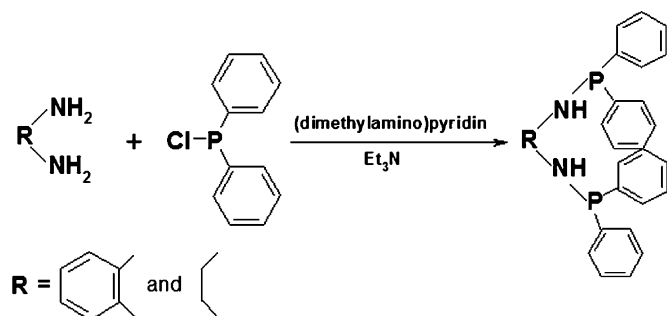


Fig. 1. Reaction for the synthesis of the aminophosphine ligands.

equimolar amount of $C_4H_{10}O_2NiBr_2$. The mixture was maintained under stirring for 4 h. The solvent was then removed under vacuum, the solid product was washed with pentane and dried under vacuum, giving a light green powder. IR (KBr disc, cm^{-1}) 744; 1101; 3333. Mass spectrum (m/z): 821 (M^+), 792 (10%), 765 (70%), 737 (100%), 736 (78%), 262 (58%), 121 (58%).

2.3.3. (*N,N'*-(Diphenylphosphoryl)-1,2-phenylenediamine) $NiBr_2$ (**III**)

To a tetrahydrofuran solution containing 0.65 mmol of *N,N'*-(diphenylphosphoryl)-1,2-phenylenediamine was added to an equimolar amount of $C_4H_{10}O_2NiBr_2$. The mixture was maintained under stirring for 4 h. The solvent was then removed under vacuum and the solid product was washed with pentane. After drying under vacuum, a green powder was obtained. Mass spectrum (m/e): 959 (M^+), 417 (10%), 308 (46%), 289 (100%), 213 (78%), 201 (38%), 183 (20%), 108 (100%).

2.3.4. (*N,N'*-(Diphenylphosphoryl)-1,2-ethylenediamine) $NiBr_2$ (**IV**)

To a tetrahydrofuran solution containing 0.65 mmol of *N,N'*-(diphenylphosphoryl)-1,2-ethylenediamine was added a equimolar amount of $C_4H_{10}O_2NiBr_2$. The mixture was maintained under stirring for 4 h. The solvent was then removed under vacuum and the solid product was washed with pentane. After drying under vacuum, a pink powder was obtained. IR (KBr disk, cm^{-1}) 749; 1180; 1125; 3327. Mass spectrum (m/z): 935 (M^+), 859 (10%), 611 (22%), 385 (100%), 308 (10%), 262 (22%), 185 (40%).

Fig. 2 shows the proposed structures of the complexes **I–IV**.

2.4. Polymerization

A solution of 10 mg of the Ni complex in 10 ml of dried toluene was prepared and kept under stirring in argon atmosphere. Methylaluminoxane (MAO) Witco purchased as a 10 wt% solution in toluene was then added to give the prescribed Al/Ni ratio. The Ni complex/MAO solution was dried

and the solid obtained was dispersed in dried pentane. The mixture was then submitted to ultrasound, generating a homogeneous suspension of catalyst to be used in the polymerization.

The polymerizations were performed in a 1000 ml dried and argon flushed Büchi glass autoclave. The pentane suspension of the catalyst was introduced into the reactor under slightly positive argon pressure and dried pentane was added until complete 500 ml. The reactor was kept at the desired temperature under stirring and ethylene was introduced to the reactor vessel, initiating the polymerization. All the reactions were carried out under pressure of 10 bar. After 1 h, the mixture was filtered under pressure and the solid fraction was washed several times with a dilute aqueous HCl solution in order to deactivate the catalyst system. The polymer was finely washed with water and methanol and dried under vacuum.

The liquid fraction obtained from the separation of the polymerization mixture was distilled at 50 °C in order to separate oligomers with higher boiling points from pentane. The remaining liquid was analyzed by gas chromatography.

2.5. Polymer characterization

^{13}C NMR spectra were obtained on a Varian Mercury 300 FT-NMR spectrometer. Polymers were analyzed in 1,2,4-trichlorobenzene (TCB)/benzene- d_6 solution. Branching number was evaluated according to literature [21]. Molecular weights of polymers were measured in TCB on a Waters plus 150CV plus chromatograph at 135 °C. Monodisperse polystyrene standards were used for calibration. Thermal analyses were performed on a Perkin-Elmer DSC7 differential scanning calorimeter at heating rate of 10 °C/min. The degree of crystallinity was calculated from the melting enthalpy (293 J/g was used for 100% crystalline polyethylene).

3. Results and discussion

The complexes were tested as catalyst in ethylene polymerization using MAO as activator at temperature range from –10 to 55 °C and Al/Ni ratio = 2000 (excepting entry 9). In all cases the production of oligomers were detected. The influence of temperature on polymer/oligomer production and polymer microstructure was investigated. Table 1 shows the results of polymerizations carried out in presence of the different Nickel complexes (**I–IV**) at different temperatures.

3.1. Catalyst activity

The results of Table 1 indicated that the polymer/oligomer production is highly dependent on the reaction temperature. Considering the polymerization at 30 °C (entries 2, 6, 10 and 11), the aminophosphine complexes **I** and **II** showed the highest catalytic activity, in terms of ethylene consumption, when compared to the aminophosphoryl complexes **III** and **IV**.

The influence of reaction temperature on polymer/oligomer production showed a peculiar behavior. At lower temperatures, the complexes showed highest activities, considering ethylene

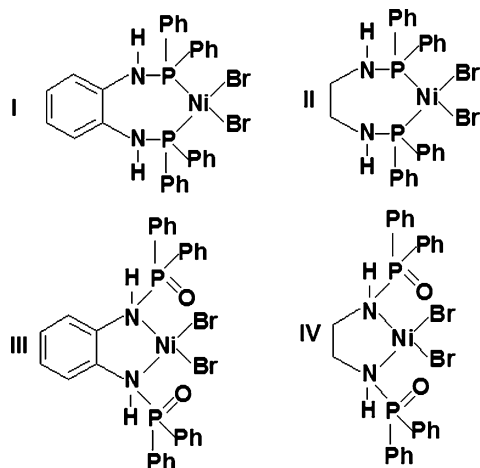


Fig. 2. Proposed structures for the nickel-aminophosphine and aminophosphine oxide complexes.

Table 1
Oligo/polymerization of ethylene with the nickel bis(aminophosphine)s and bis(aminophosphine oxides) complexes

Entry	Complex	Al/Ni ratio	Reaction temperature (°C)	Catalytic activity (g/mol Ni h bar)	M_n	M_w/M_n	T_m^a (°C)	T_c^b (°C)	X_c^c (%)	Branches (%)	Total ethylene consumption (l)
1	I	2000	55	20809	527500	3.2	124	111	7.7	6.13	18.0
2			30	3757	7639	19.4	125	112	9.0	7.89	83
3			5	2601	259100	6.9	127	112	28.0	4.21	15.0
4			–10	^d	–	–	–	–	–	–	–
5	II	2000	55	25268	384100	4.7	126	112	14.5	3.20	4.0
6			30	2149	36100	4.7	123	112	10.3	–	5.5
7			5	1612	1455	1.3	118	107	1.9	1.8	16
8			–10	1612	1360	1.7	122	109	20.6	2.43	60
9	III	1000	30	2189	–	–	127	114	6.87	1.12	0.5
10		2000	30	1250	86900	15.0	131	115	35.72	1.91	5.0
11	IV	2000	30	10156	35700	6.0	130	115	43.73	0.03	6.25

^a T_m : melting temperature.

^b T_c : crystallization temperature.

^c $\Delta H_m^\circ = 293$ J/g.

^d Only oligomers.

consumption, but as the temperature decreases the polymer productivity was reduced. It means the complexes presented high selectivity in forming, predominantly, oligomers at low temperature. This behavior can be well exemplified in entries 5–8. In general terms, the phosphine Nickel complexes (**I** and **II**) showed an increase in catalytic activity related to polymer production as temperature increases.

The mentioned behavior can be explained taking into consideration the process of chain termination. At low temperatures, the catalysts are probably more stable. However, it seems that at these lower temperatures the occurrence of β -hydrogen elimination is increased, resulting in formation of oligomers. Thus, one possible explanation could be that, at low temperature, molecular spinning of phenyl rings, which is one of the main sources of steric hindrance around nickel in these complexes, are restricted. This may increase the frequency of β -agostic hydrogen interaction that is the main step for chain termination by β -hydrogen elimination.

The more flexible aliphatic aminophosphine complex **II** showed the highest catalytic activity at low temperature (entry 8). At temperatures below zero, octene and/or its isomers were formed predominantly. The results obtained may be explained by the stability of phosphorus–nickel bond, once the 3-substituted phosphine shows a strong bond with nickel, due to the donor effect of the electron pair of phosphorus atom and the empty d orbital of the metal ion. On the other hand, 5-substituted phosphorus acquires a very high stability after bonding to oxygen (130 kcal/mol), once phosphorus has completed the eight electrons around its nucleus. In this case, the metal–ligand bond does not occur at the phosphorus atoms and only the oxygen or nitrogen is able to bond to the metal. P–Ni bonds probably do not allow rupture after addition of the cocatalyst. At the same time, may generate active species with useful life time, once permits the production of seven-membered ring, which contributes to the complex stability. N–Ni bonds are theoretically less stable than P–Ni bonds but in this case it is possible to produce five-membered ring which also contribute to the stability of the

complex. These preliminary polymerization results showed that both catalysts (aminophosphines and aminophosphine oxides) have satisfactory activity.

The effect of Al/Ni ratio on catalytic activity is considered in entries 9 and 10 of Table 1. From the table, it is possible to conclude that, in terms of total ethylene consumption, at Al/Ni = 2000 higher catalytic activity was obtained, but higher production of polyethylene was achieved at Al/Ni = 1000.

3.2. Polymer molecular weight

All the complexes produced polymers with high molecular weight and broad molecular weight distribution depending on the polymerization condition. Polyethylenes formed by the aminophosphine complexes **I** and **II** presented molecular weight even higher than 200,000. While GPC analyses reveal that the polymer obtained at 55 °C with **I** and **II** presented only one peak (Fig. 3a), the polyethylenes produced at –10, 5 and 30 °C showed two or three peaks. Fig. 3b and c present typical GPC curves of the polymers obtained with complexes **II** and **III** at 30 °C, respectively. The polymers obtained at 30, 5 and –10 °C are probably a mixture of polyethylenes of different molecular weights from high oligomers to very high molecular weight polymers. The maximum of these peaks appear at retention volumes equal to 20, 23 and 28 ml which corresponds approximately to a molecular weights $M_p = 10^6$, 10^5 and 10^3 , respectively. The peak intensities were highly dependent on the reaction temperature.

The multimodal molecular weight distribution showed by the GPC curves indicates that there are at least three types of active species performing ethylene polymerization in the mentioned conditions. In this case these polymerization sites contribute for the simultaneous production of significantly different polymers, broadening the polymer molecular weight distribution.

The increase in temperature from 30 to 55 °C probably deactivate the less stable species, favoring the most stable one which

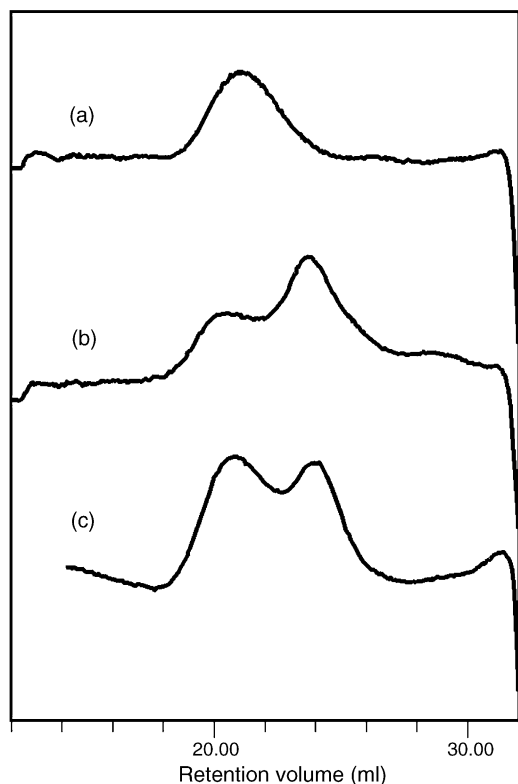


Fig. 3. GPC curves for the polyethylenes produced with nickel-aminophosphine catalyst: (a) catalyst **I** at 55 °C and (b) catalyst **II** at 30 °C, and aminophosphine oxide: (c) catalyst **III** at 30 °C.

produces single broad GPC peak. It is also possible that if the species which generates low MW polymers are still active at this temperature (55 °C) the differences of kinetics of each species are small.

Another hypothesis to be considered to explain both the multimodal molecular weight distribution and the single peak at high temperature is the occurrence of oligomer reinsertion during the polymerization. The energy associated with each polymerization temperature may indicate this behavior, once the high temperature could induce reinsertion of oligomers with double bond end group, producing higher molecular weight polymers and a monomodal GPC curve.

At 55 °C the catalysts produced molecular weight over 500,000 and at –10 °C mainly oligomers were produced. Another hypothesis to explain this dramatic difference in the molecular weight with temperature is based on the nature of the ligands. At low temperatures phenyl ring rotation and/or vibration of the bulky phosphine ligands around the nickel may be considerably decreased, favoring β -agostic interactions and subsequent chain termination by β -hydrogen abstraction as illustrated in Fig. 4. On the other hand, at high temperatures increasing rotation and vibration of the bulky phosphine ligands may occur, increasing steric hindrance and avoiding chain transfer involving the chain β -hydrogen.

3.3. Polymer structure

According to ^{13}C NMR and DSC analyses some of the polyethylenes produced with these catalysts are considerable branched, showing T_m in the range of 118–130 °C. The complexes containing the oxidized ligand (**III** and **IV**) produced more linear polyethylenes with T_m around 130 °C.

The branch content was evaluated by ^{13}C NMR using the methodology reported by Galland et al. [21]. Values of branch percentage between 0.03 and 7.9% (Table 1) were obtained and these polyethylenes can be considered as low branched polymers

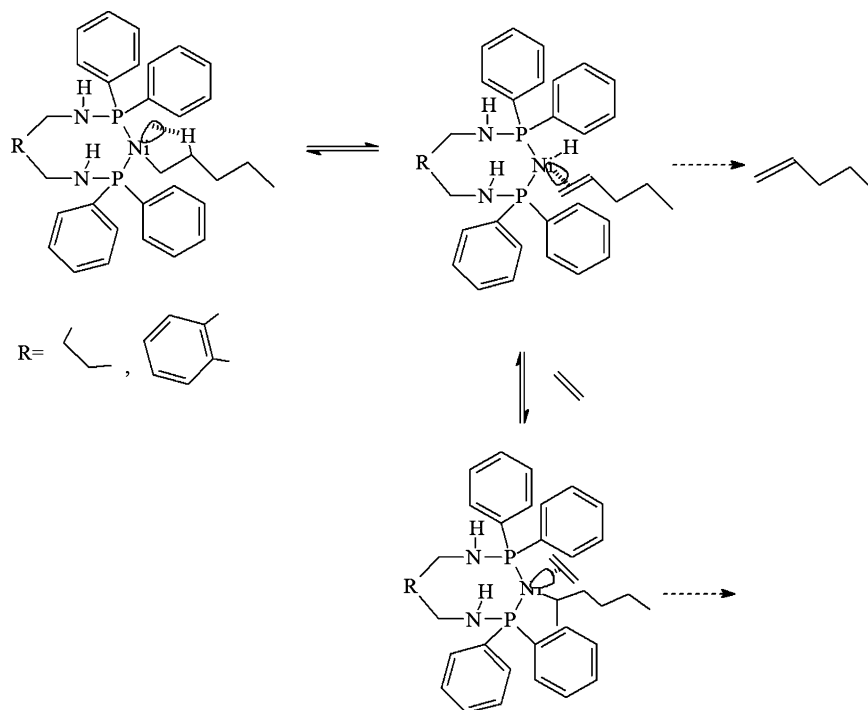


Fig. 4. Proposed scheme for oligomer formation by β -hydrogen elimination and branching in addition-catalyzed reactions with aminophosphine complexes.



Fig. 5. ^{13}C NMR of polyethylenes produced with: (a) aminophosphine complex **II** at 55 °C and (b) aminophosphine oxide complex **IV** at 30 °C.

(Fig. 5a and b). The branches affect the polymer properties such as processability and crystallinity. For instance, long branches increase the melt flow index and improve polymer processability, while the increase in the content of short branches decreases the polymer crystallinity and T_m .

The polymers produced with the aminophosphine complexes **I** and **II** presented lower T_m (118–128 °C) than those obtained with the aminophosphine oxide complexes **III** and **IV** (130–131 °C). This indicates presence of higher branch content in the polymers produced by the aminophosphine catalysts. The melt temperatures indicate that the polymers produced with these nickel-aminophosphine catalysts showed a behavior which is intermediate between LDPE (105–115 °C) and HDPE (133–138 °C).

All the DSC traces showed broad peaks in the first heating, indicating the existence of broad distribution of crystal sizes in the produced polymer. In the second heating, the peaks became narrowest, but still broad. Typical DSC traces of these polyethylenes showing the melting (second heating) and crystallization peaks are presented in Fig. 6.

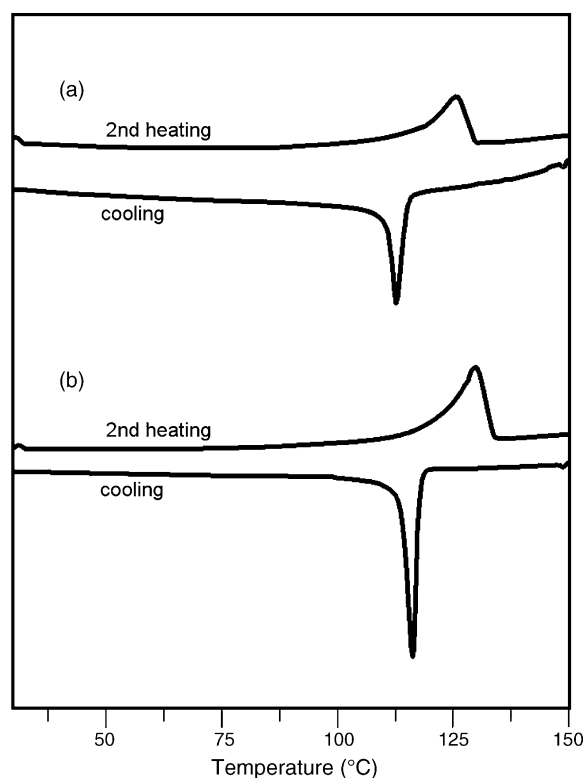


Fig. 6. DSC traces of polyethylenes produced with: (a) aminophosphine complex **II** at 55 °C and (b) aminophosphine oxide complex **IV** at 30 °C.

Polyethylenes with low degree of crystallinity (X_c) were obtained, once the DSC analysis presented X_c results from 2 to 43%. The differences in X_c observed among the polyethylenes produced from the four catalysts are probably due to the different and broad molecular weight distribution generated at the different polymerization temperatures.

3.4. Oligomer analysis and characterization

Polymerization experiments produced not only polymers but also retrievable fractions of oligomers obtained after solvent (pentane) distillation. For some catalysts tested and in specific experimental conditions, mainly oligomers were produced. The distilled fractions were submitted to gas chromatography. Table 2 presents the results of the analysis.

Oligomers with up to eight carbons, including the solvent used in the polymerization were identified. The data were compared to a standard sample of pentane:1-hexene:1-octene = 1:1:1 (volume). By comparison with the retention times of the standard sample, components of the standard as well as its isomers were identified as reaction products.

Liquid oligomers recovered from the polymerizations at 55 °C showed a small fraction of octenes and a considerable percentage of oligomers with retention time between hexenes and octenes (12–15%). These intermediate fractions were ascribed to branched octenes, once the branches reduce the boiling point of hydrocarbons.

For the catalyst **II**, the behavior at 30 °C was similar to that observed at 55 °C. On the other hand, the catalyst **I** produced

Table 2
Gas chromatography analysis of oligomers generated by the nickel catalysts

Complex	Reaction temperature (°C)	Gas chromatography (area%)			
		Hexenes	Fraction with t_R between C6 and C8 ^b	Octenes	Solvents + higher molecular weight fractions
I	55	23.5	11.7	4.25	58.8
	30	32.4	14.9	7.1	44.1
	5	36.6	24.9	11.6	25.1
	–10	13	40.9	2.3	43
II	55	18.9	14.7	8.7	55.4
	30	22.9	11	4.3	59.7
	5	45.1	9.3	17.5	28.5
	–10	44.3	6.95	24.09	20.6
III	30	28.0	10.0	0.4	61.2
III^a	30	10.46	13.4	2	74.0
IV	30	44.3	11.0	22.3	22.2

^a Al/Ni = 1000.

^b t_R : retention time.

higher octene fractions, although the intermediate C6–C8 fraction was still considerable. At 5 °C both complexes showed higher percent of octenes, but complex **I** showed a tendency of producing the 2.7 min retention time (t_R) product, identified as a intermediate C6–C8.

At –10 °C, mainly fractions higher than hexenes were produced. The catalyst **II** generated several fractions with close retention times, near the octene retention time, which may suggest the production of 1-octene isomers. On the other hand, the catalyst **I** produced preferentially a high intensity peak product with retention time 2.7 min, already observed at 5 °C.

Catalysts **I** and **II** showed different behavior under the experimental polymerization conditions. While catalyst **I** produced mainly one product as the temperature decreased ($t_R = 2.7$ min, intermediate between C6 and C8), catalyst **II** produced several peaks with close retention times, near the octene t_R , which may be octene isomers.

Catalysts **III** and **IV** produced considerable quantity of intermediate C6–C8 fractions, however catalyst **IV** generated hexenes and octenes in high yields.

Catalysts **I**, **II** and **IV** showed potential to produce liquid oligomers under specific conditions. This behavior is interesting because liquid oligomers may be used as comonomers for branched polyethylene production using the metallocene technology. In fact, reinsertion of these oligomers is one of the possibility that cannot be neglected for explain the branched nature of the polymers obtained in this work.

4. Conclusion

Ni complexes containing aminophosphine and aminophosphine oxide as ligands are able to be activated by MAO generating active catalysts for ethylene polymerization. These Ni catalysts produced a mixture of high molecular weight branched polymers and oligomers of ethylene, indicating that during the catalyzed-addition reaction of the monomer, more than one type of active species were generated.

Among the four catalysts used in this work, aminophosphine catalysts present the highest activity, consuming up to 60 l/h of the monomer at 10 bar. In general, these catalysts had similar behavior concerning polymers molecular weight distribution with broad multimodal GPC curves at lower temperatures and unimodal curves at 50 °C. The more flexible complex **II** containing the aliphatic aminophosphine ligand showed the highest catalytic activity. As polymerization temperature decreases, the amount of oligomer generated increases while polyethylene yield decreased. Low temperatures favors oligomer production, mainly C6–C8.

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References

- [1] L.K. Johnson, C.M. Kilian, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414.
- [2] C.M. Killian, L.K. Johnson, M. Brookhart, *Organometallics* 16 (1997) 2005.
- [3] L.K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* 118 (1998) 267.
- [4] S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* 120 (1998) 888.
- [5] B.L. Small, M. Brookhart, A.M.A. Bennett, *J. Am. Chem. Soc.* 120 (1998) 4049.
- [6] A.C. Gottfried, M. Brookhart, *Macromolecules* 34 (2001) 1140.
- [7] D.P. Gates, S.A. Svejda, E. Oñate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, *Macromolecules* 33 (2000) 2320.
- [8] M.J. Rachita, R.L. Huff, L.J. Bennett, M. Brookhart, *J. Polym. Sci., Polym. Chem.* 38 (2000) 4627.

- [9] B.L. Small, M. Brookhart, *J. Am. Chem. Soc.* 120 (1998) 7143.
- [10] E.L. Dias, M. Brookhart, P.S. White, *Organometallics* 19 (2000) 4995.
- [11] S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (2000) 1169.
- [12] H. Zeiss, *Organometallic Chemistry*, American Chemical Society, Reinhold Pub. Co., 1960.
- [13] T.Q. Ly, J.D. Woolins, *Coord. Chem. Rev.* 176 (1998) 451.
- [14] W. Keim, R.P. Schulz, *J. Mol. Catal.* 92 (1994) 21.
- [15] K. Kurtev, A. Tomov, *J. Mol. Catal. A: Chem.* 88 (1994) 141.
- [16] A. Tomov, K. Kurtev, *J. Mol. Catal. A: Chem.* 103 (1995) 95.
- [17] N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen, P.G. Pringle, *Organometallics* 20 (2001) 4769.
- [18] M. Sauthier, F. Leca, R.F. Souza, K. Bernardo-Gusmão, L.F.T. Queiroz, L. Toupet, R. Réau, *New J. Chem.* 26 (2002) 63.
- [19] O. Daugulis, M. Brookhart, *Organometallics* 21 (2002) 5926.
- [20] T.Q. Ly, A.M.Z. Slawin, J.D. Wooling, *J. Chem. Soc., Dalton Trans.* (1997) 1611–1616.
- [21] G.B. Galland, R.F. Souza, R.S. Mauler, F.F. Nunes, *Macromolecules* 32 (1999) 1620.