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Ethylene polymerization with imine and phosphine nickel complexes containing isothiocyanate

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Three isothiocyanate complexes of nickel(II) containing diimine [ArN=C(Me)–C(Me)=NAr]Ni-(NCS)$_2$ (1), iminophosphine [Ph$_2$PC$_6$H$_4$CH=NAr]Ni(NCS)$_2$ (2), or diphosphine (dppe)Ni(NCS)$_2$ (3), [Ar = 2,6-^{i}Pr-C$_6$H$_3$; dppe = 1,2-bis(diphenylphosphine)ethane] were synthesized and examined for ethylene polymerization activated by methylaluminoxane (MAO). Their behavior was compared with those of the corresponding halide analogues [ArN=C(Me)–C(Me)=NAr]NiBr$_2$ (4), [Ph$_2$PC$_6$H$_4$CH=NAr]NiBr$_2$ (5), and (dppe)NiCl$_2$ (6). The diimines showed the highest polymerization activity. Replacement of the halide for the NCS pseudo halide affected the activity and decreased the molecular weight of the polymer formed. The highest molecular weights were obtained with the diimine complexes. Highly branched polyethylenes were obtained with the bulkier complexes 1 and 4. Replacement of the halide for NCS in the diimine complexes also caused an increase in the branching content, whereas the opposite occurs for the iminophosphine complexes. The different activities and behavior of the catalyst systems with halide versus NCS in the polymerization of ethylene and the characteristics of the final products suggest a modification in the active species caused by the non-chelating ligand. Polymer molecular weight and branching content is dependent on the MAO/Ni molar ratio and on the working temperature. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: nickel complexes; diimines; iminophosphines; diphosphines; ethylene polymerization; isothiocyanate complexes; catalysis; branched polyethylenes

INTRODUCTION

Polymerization of ethylene with late-transition-metal complexes has been a topic of significant interest. Since the discovery that nickel-diimine complexes are capable of polymerizing ethylene to high-molecular-weight branched polyethylenes,[1] efforts have been made to understand the mechanism and the factors controlling polymer formation with nickel catalysts. The branching number, distribution of branch types, and the molecular weight of these new polyethylenes seem to be determined mainly by the type of chelating ligand, but they are also markedly influenced by the polymerization conditions, including the cocatalyst type. There is much work about the influence of diimines in the polymerization of olefins,[1–7] but few are related to the influence of iminophosphines[3,8–11] and diphosphines.[3,12–14] The accepted mechanism for late-transition-metal-catalyzed polymerization involves a cationic organometallic species.[1,7,15] Thus, in the case of reactions cocatalyzed by alkylaluminum compounds, the counterion of the active species, produced from the interaction of the non-chelating ligand (usually a halide) with the alkyl aluminum activator, may also play an important role in the polymerization.[16] Nevertheless, the

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influence of the non-chelating ligand on the polymerization of olefins with nickel complexes has received less attention.[17,18]

We have investigated the preparation of nickel diimine and iminophosphine complexes containing isothiocyanate (NCS) as a non-chelating ligand. In this paper we discuss the synthesis of those complexes, as well as their effect on the polymerization of ethylene with methylaluminoxane (MAO) as cocatalyst, comparing their performance with that of the analogous halides and with that of the diphosphine complexes containing chlorine or NCS groups.

EXPERIMENTAL

Materials

The reactions were performed using standard Schlenk techniques. Nitrogen, argon and ethylene were purified by passage through columns of 3 Å molecular sieves and supported copper catalyst. Toluene was distilled with sodium and benzophenone under nitrogen. CH_2Cl_2 and MeCN were dried with CaH_2, distilled and used immediately. MAO (Witco) was purchased as a 10% toluene solution. 88% formic acid (Vetec), 97% 2,3-butanedione (Aldrich) and 90% 2,6-diisopropylaniline (Aldrich) were used as received. The synthesis and characterization of the $Ph_2PC_6H_4CH{=}NAr$ ligand[19] and the complexes $[Ph_2PC_6H_4CH{=}NAr]NiBr_2$ (**5**; Ar = 2,6-(^{i}Pr)$_2$-C_6H_3),[19] (dppe)Ni(NCS)$_2$ (**3**),[20] and (dppe)NiCl$_2$ (**6**),[20] dppe = 1,2-bis(diphenylphosphine)ethane, have been described elsewhere. The diimine and nickel complexes **1**, **2** and **4** were synthesized by the methods described below. IR data were obtained with an IR 760 Nicolet Magna spectrophotometer, using CsI pellets. Elemental analyses were performed on a Perkin Elmer 2400 CHN analyzer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 200 MHz instrument in CD_2Cl_2 (^{1}H NMR, δ 5.32) and $CDCl_3$ (^{13}C NMR, δ 77.2).

N,N′-Bis(2,6-diisopropylphenyl)-2,3-butanediimine, $ArN{=}C(CH_3){-}C(CH_3){=}NAr$ (Ar = 2,6-(^{i}Pr)$_2$-C_6H_3)

Formic acid (0.5 ml, 11.5 mmol) was added to a solution of butanedione (2.0 ml, 22.1 mmol) in CH_2Cl_2 (50 ml), containing freshly dehydrated sodium sulfate (25 g). 2,6-Diisopropylaniline (9.4 ml, 44.9 mmol) was added to the vigorously stirred mixture. After 5 min, additional sodium sulfate (25 g) was added. The reaction mixture was stirred for 24 h at room temperature, filtered, washed with CH_2Cl_2 and the solvent removed *in vacuo*. MeOH (30 ml) was added to the residue, giving a yellow precipitate and a dark solution. This mixture was cooled at −20 °C overnight and then filtered off. The yellow solid was washed with cold MeOH and dried *in vacuo* (51%). M.p. 100 °C (lit.[21] m.p. 99 °C). ^{1}H NMR (CD_2Cl_2, 200.13 MHz): δ 7.05–7.21 (m, 6H, C_6H_3), 2.74 (sept, $^3J_{HH} = 6.9$ Hz, 4H, $CH{-}(CH_3)_2$), 2.07 (s, 6H, $N{=}C(CH_3)$), 1.21 (d, $^3J_{HH} = 6.9$ Hz, 12H, $CH{-}(CH_3)_2$), 1.17 (d, $^3J_{HH} = 6.9$ Hz, 12H, $CH{-}(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 50.75 MHz): δ 168.4 ($C{=}N$), 146.4 (Ph *ipso*-C), 135.3 (Ph *o*-C), 123.9 (Ph *p*-C), 123.2 (Ph *m*-C), 28.7 ($CH{-}(CH_3)CH_3$), 23.2 ($CH{-}(CH_3)CH_3$), 22.9 ($CH{-}(CH_3)CH_3$), 16.8 ($CH_3{-}C{=}N$); IR (CsI, cm^{-1}): 1636 (vs, C=N).

N,N′-Bis(2,6-diisopropylphenyl)-2,3-butanediimine(diisothiocyanate)nickel(II), $[ArN{=}C(Me){-}C(Me){=}NAr]Ni(NCS)_2$ (1)

$Ni(NCS)_2$ (310 mg, 1.77 mmol), dried at 150 °C for 1 h, was dispersed in 50 ml of MeCN. $ArN{=}C(CH_3){-}C(CH_3){=}NAr$ (800 mg, 1.98 mmol) was added and the mixture was refluxed for 2 h. The brown solution was filtered and the solvent removed *in vacuo*. A red precipitate was obtained and washed with 5 × 10 ml of hexane and dried *in vacuo*. Yield 96%. M.p. 220 °C dec. Anal. Found: C, 61.48; H, 6.80; N, 9.56. Calc. for $C_{30}H_{40}N_4NiS_2$: C, 62.18; H, 6.96; N, 9.67%. IR (CsI, cm^{-1}): 2108, 2093 (vs, C=N of NCS), 1621 (w, C=N of diimine).

Diisothiocyanate{*N*-[2-(diphenylphosphino)-benzylidene]-2,6-diisopropylaniline-k^{2}N,P}-nickel(II), $[Ph_2PC_6H_4CH{=}NAr]Ni(NCS)_2$ (2)

$Ni(NCS)_2$ (116 mg, 0.67 mmol), dried at 150 °C for 1 h, was dispersed in 10 ml of MeCN. A solution of the ligand $Ph_2PC_6H_4CH{=}NAr$ (315 mg, 0.70 mmol) in 30 ml of dichloromethane was added and refluxed for 3 days. The reddish solution was filtered and the solvent removed *in vacuo*. A red solid was obtained and washed with 5 × 10 ml of hexane and dried *in vacuo*. Yield 87%. M.p. 122 °C dec. Anal. Found: C, 64.44; H, 5.47; N, 6.62. Calc. for $C_{33}H_{32}N_3NiPS_2$: C, 63.47; H, 5.17; N, 6.73%. IR (CsI, cm^{-1}): 2096 (vs, C=N of NCS), 1611 (w, C=N of iminophosphine).

Dibromo[*N,N′*-bis(2,6-diisopropylphenyl)-2,3-butanediimine]nickel (II), $(ArN,{=}C(H){-}C(H){=}NAr)NiBr_2$ (4)

Anhydrous $NiBr_2$ (0.88 g, 4.0 mmol) and MeCN (30 ml) were maintained under reflux for 30 min until complete dissolution of the nickel halide, and then the solvent was removed *in vacuo* to give a yellow solid. $ArN{=}C(CH_3){-}C(CH_3){=}NAr$ (1.8 g, 4.4 mmol) was added to a dispersion of the yellow solid in 30 ml of CH_2Cl_2 and refluxed for 2 h. A brown precipitate was formed and the solvent was removed *in vacuo*. The product was washed with 5 × 10 ml of hexane and dried *in vacuo* (95%). M.p. 305 °C dec. Anal. Found: C, 53.72; H, 6.46; N, 4.52. Calc. for $C_{28}H_{40}Br_2N_2Ni$: C, 53.97; H, 6.47; N, 4.50%. IR (CsI, cm^{-1}): 1639 (w, C=N), 266 (s, Ni–Br).

Polymerization

Polymerizations were performed in a previously dried and nitrogen-flushed 250 ml Büchi glass autoclave coupled with an in-line Brooks flowmeter. The reactor temperature was adjusted by a thermostatic bath. Toluene and a measured amount of MAO were charged into the reactor. Nitrogen was replaced by ethylene and the reactor saturated with the monomer under pressure. After saturation, a fresh catalyst solution was charged into the reactor under pressure, starting the polymerization. The reactions were terminated after 1 h by quenching the mixture with a dilute HCl–ethanol solution. The polymers were precipitated in ethanol, filtered and washed with plenty of ethanol, and dried under vacuum at 50 °C overnight before characterization.

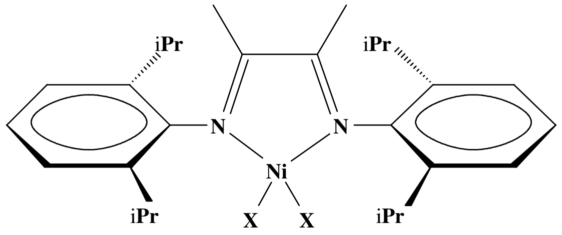
Polymer characterization

^{13}C NMR spectra were obtained from a Varian Mercury 300 FT-NMR spectrometer. Polymers were analyzed in 1,2,4-trichlorobenzene (TCB)–benzene-d_6 solution. Evaluation of branching content was calculated according to the literature.[22] The molecular weights of the polymers were measured in TCB on a Waters 150CV plus chromatograph at 135 °C. Polystyrene standards were used for calibration. Thermal analyses were performed on a Perkin Elmer DSC7 differential scanning calorimeter at a heating rate of 10 °C min^{-1}. The degree of crystallinity was calculated from the enthalpy of fusion, taking the value 293 J g^{-1} for 100% crystalline polyethylene.

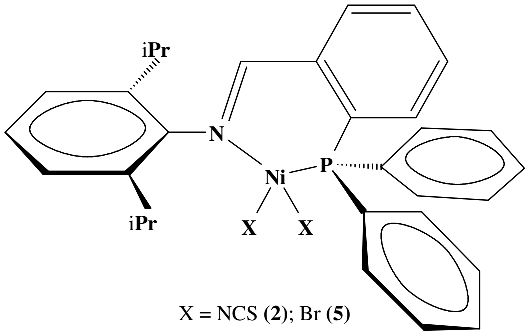
RESULTS AND DISCUSSION

The diimine ligand coordinated to the nickel salt shows a considerable frequency shift in its IR absorptions, relative to the free ligand. The characteristic absorption at 1636 cm^{-1} is shifted to 1621 cm^{-1} in **1** and to 1639 cm^{-1} in **4**. In complex **2**, the absorption attributed to the C=N bond of the ligand is seen at 1611 cm^{-1}, compared with 1630 cm^{-1} in the free ligand. The complexes with the pseudo halide show absorptions characteristic of the CN, at 2108 and 2093 cm^{-1} in **1** and at 2096 cm^{-1} in **2**. It was not possible to observe the CS absorptions, owing to the organic ligand skeletal vibrations present in the same region. However, the CN absorptions are consistent with those of nitrogen-bonded nickel isothiocyanate complexes,[23] in which the 'hard' Ni^{II} metal center binds preferentially to the 'hard' nitrogen end of the NCS ligand. Elemental analyses of the complexes are in accordance with the structures proposed in Fig 1. ^{1}H NMR spectroscopy in deuterated acetonitrile of **1** and **2** reveals that these complexes are paramagnetic, indicating that their geometries are not square planar. Usually, the diimine nickel (II) dibromide is prepared by the reaction of (DME)NiBr$_2$ (DME = dimethoxyethane) with the diimine.[21] We hereby report a new procedure to prepare this type of compound. The first step is the formation of an adduct of NiBr$_2$ with acetonitrile. The reaction of diimine with the adduct leads to the desired compound in high yield.

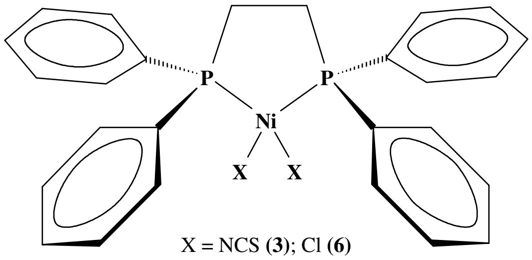
Polymerization of ethylene was carried out at 25 °C using complexes **1**–**6**/MAO, under a monomer pressure of 1 bar for 60 min. The results are reported in Table 1. It is evident that, of all the complexes, **1** and **4** give the highest amount of polyethylene compared with the other complexes. The catalyst activity in the polymerization of ethylene



X = NCS (**1**); Br (**4**)



X = NCS (**2**); Br (**5**)



X = NCS (**3**); Cl (**6**)

Figure 1. Structures of **1**–**6** complexes.

Table 1. Ethylene polymerization[a] using **1**–**6** nickel complexes activated by MAO

Complex	Activity (g PE/ (g cat. h))	M_n[b] ($\times 10^{-4}$)	M_w/ M_n[b]	T_m[c] (°C)	Branches[d] (mol%)
1	1244	8.33	2.7	—	51.0
2	30	5.47	3.3	126	
3[e]	0	—	—	—	
4	532	33.3	1.9	—	31.6
5	8	5.31	13[f]	117	
6	1	6.98	2.2		

[a] Polymerization condition: [Ni], 0.016 mmol/100 ml in toluene; polymerization time, 1 h; $T_p = 25$ °C; monomer pressure, 1 bar; MAO/Ni = 100.

[b] M_n and M_w determined by GPC at 135 °C in TCB.

[c] Determined by differential scanning calorimetry.

[d] Estimated.[22]

[e] High ethylene consumption and production of volatile addition compounds detected by gas chromatography.

[f] Bimodal peak.

decreased according the order: diimines ≫ iminophosphines > diphosphines. In the case of the nickel diimine complexes, increase in the bulk of ortho substituents in the phenyl groups of the chelating ligands results in an increase in catalyst activity.[5] Among the complexes used in this work, those with bulk ortho substituents are **1** and **4**, which could explain their high activities. Lower polymerization activity was shown by complex **3** with no *ortho*-alkyl substituent in the phenyl rings of the ligand. Bulk ligands around the nickel atom are also a key factor in the generation of high-molecular-weight polymers in nickel (II)-catalyzed polymerizations.[1] The highest molecular weights were obtained with the diimine complexes. The replacement of the halide ligands for the NCS pseudo halide changed the catalyst activity and decreased the molecular weight of the polymers. The decrease in molecular weight caused by the presence of isothiocyanate was more dramatic with the diphosphine complexes. Even considering that aryl groups in the diphosphine ligands have no substituents, a relatively high molecular weight could be obtained for the chloride complex **6**. Changing the halide for the NCS pseudo halide, complex **3**, caused such a drastic reduction in the molecular weight of the addition products that no solid could be recovered after 1 h of reaction. Vacuum evaporation of the solvents after reaction termination did not yield non-volatile oligomers. Gas chromatography of the liquid phase revealed the presence of several peaks of volatile products, indicating that complex **3** has a high capacity to convert ethylene into low-molecular-weight hydrocarbons. The consumption of ethylene in the reaction with **6**/MAO was not much different from that of **3**/MAO, in spite of the different polymerization capacities of the two systems (Fig 2). Except for the iminophosphine complex **5**, which generate polymers with broad molecular weight distribution and bimodal gel-permeation chromatography (GPC) peaks, the other polymerization-active complexes, **1**, **2**, **4** and **6**, produced polyethylenes with polydispersities close to two.

Highly branched polyethylenes were obtained with the bulkier complexes **1** and **4**. The ^{13}C NMR spectra of these polymers are presented in Fig 3. Changing chlorine for NCS causes different effects on the branching number when one compares the diimine complexes **1** and **4** with each other, or also the iminophosphine complexes **2** and **5** with each other. In the case of **1** and **4**, replacement of halide for NCS led to an increase in the branching number, whereas for complexes **2** and **5** the opposite behavior was observed, as indicated by T_m values of 126 °C and 117 °C respectively. The highly branched polyethylenes obtained from **1** and **4** did not present any crystalline melting transition when the reaction was performed at room temperature.

According to the accepted mechanism of polymerization catalyzed by a nickel complex/MAO system, the non-chelating ligands are removed by the cocatalyst to form a cationic active species. However, replacement of halide for isothiocyanate produced significant changes in the polymerization behavior and polymer structure. The results in Table 1 are an indication that isothiocyanate affects the active site in a different manner than the halide. This can be due to an influence on the degree of interaction between the nickel cationic center and its counterion, which is likely to contain the non-chelating fragments (Scheme 1).

The effect of the MAO/Ni molar ratio on the ethylene polymerization with the highly active **1**/MAO catalyst system is presented in Table 2. An increase of the Al/Ni ratio from 100 to 500 caused a slight increase in the polymer molecular weight. At an Al/Ni ratio of 50, instead of a rubber-like material, a higher molecular weight, less-branched polyethylene was obtained in powder form. The activity of the **1**/MAO system presents a maximum when the Al/Ni ratio is near 100. Figure 4 shows the consumption of ethylene with time in several polymerizations with different Al/Ni ratios. The drop in ethylene consumption in the reaction with Al/Ni 500 can be attributed to the higher viscosity of the solution and to the catalyst deactivation. The higher molecular weight of the polymer in solution is responsible for the higher viscosity, which leads to a more difficult mass transfer of the monomer from the gas phase to the solution, decreasing the monomer consumption. Otherwise, MAO is a powerful reduction agent, and increasing its concentration in the reaction medium could increase the deactivation of the catalyst.

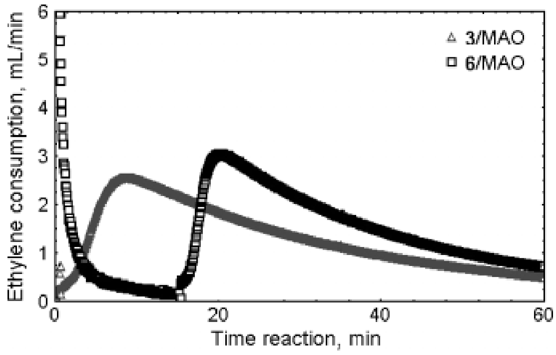
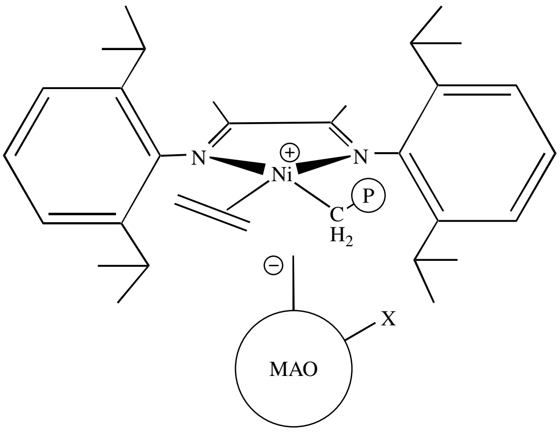


Figure 2. Curves of ethylene consumption for **3**/MAO and **6**/MAO.



Scheme 1.

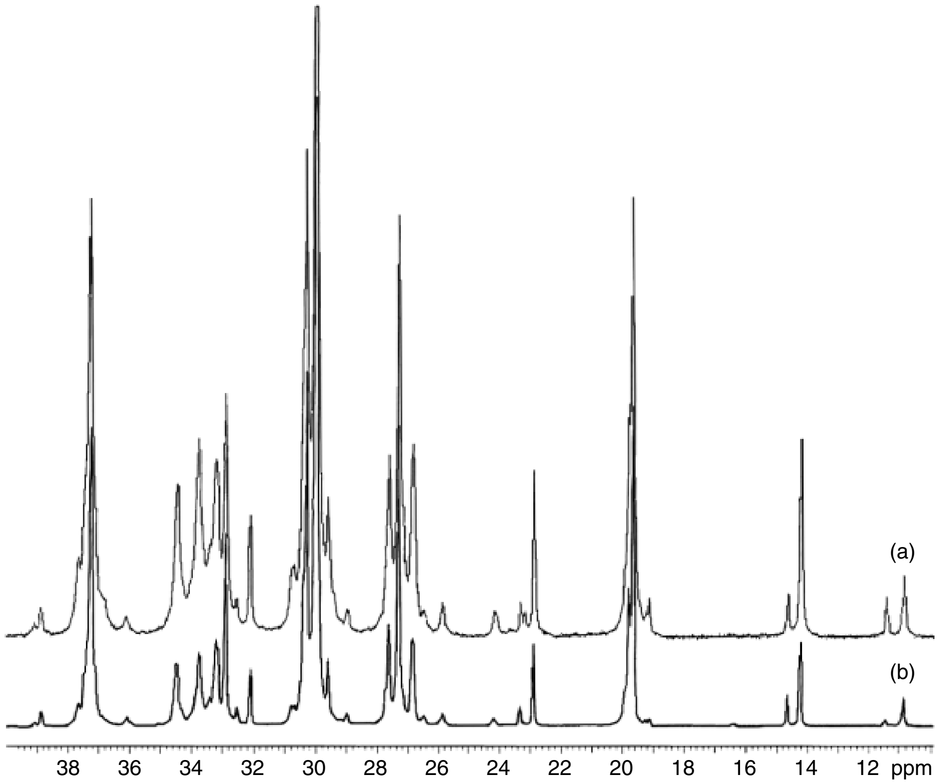


Figure 3. ^{13}C NMR spectra of a highly branched polyethylene produced with (a) **1**/MAO and (b) **4**/MAO at 25 °C, Al/Ni 100.

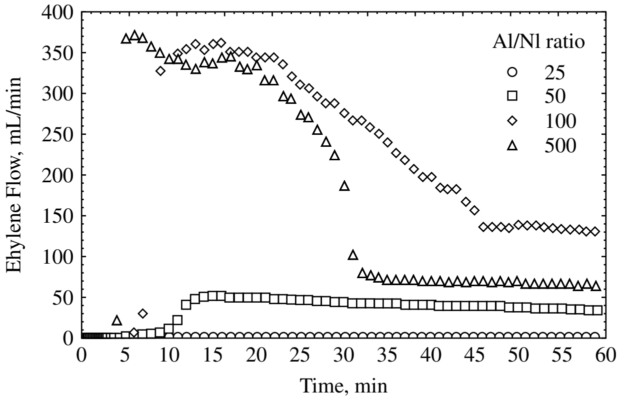


Figure 4. Curves of ethylene consumption for **1**/MAO at 25 °C and different Al/Ni molar ratios.

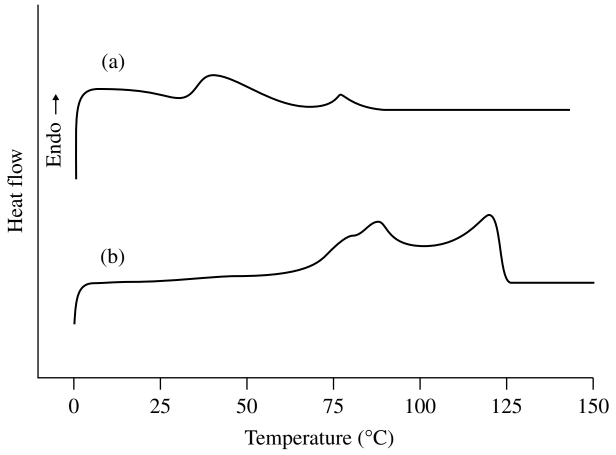


Figure 5. Differential scanning calorimetry traces (first heating run) of polyethylenes obtained with **1**/MAO at (a) 10 °C and (b) 0 °C.

Ethylene polymerization with **1**/MAO was also carried out at sub-room temperatures (10 °C and 0 °C). The results are presented in Table 2. Lowering the reaction temperature caused a considerable decrease in the branching number, and the molecular weight increased. In the reaction at 0 °C, precipitation of the polymer was observed, and the solution was not viscous, which could explain the high activity of the catalytic system under this condition. At those low temperatures, the polymers presented melting transitions that appeared as broad bimodal endotherms at low temperatures in a first heating run at 10 °C min^{-1} (Fig 5). After cooling at 10 °C min^{-1}, both polymers showed exothermic crystallization transitions, but in the polymer obtained at 10 °C the crystallization was very low. After a second heating at 10 °C min^{-1}, the branched polyethylenes obtained at 0 and 10 °C showed T_m values of 93 °C and 42 °C respectively and degrees of crystallinity X_c of 3% and 18% respectively.

Table 2. Ethylene polymerization[a] with the catalytic system **1**/MAO. The effect of the Al/Ni ratio and the temperature

Al/Ni ratio	T (°C)	Activity (g PE/(g cat. h))	M_n[b] (×10^{-4})	M_w/M_n[b]	Branches[c] (mol%)	T_m (°C)	X_c (%)
25	25	0	—	—	—	—	—
50	25	227	16.8	2.35	33.1	—	—
100	25	1244	8.33	2.65	51.0	—	—
200	25	1157	9.39	2.52	49.8	—	—
500	25	918	10.9	2.67	49.9	—	—
100	10	667	26.1	2.11	22.9	41	0.6
100	0	1177	36.3	3.40	9.0	88	18.2

[a] Polymerization conditions: [Ni], 0.016 mmol/100 ml of toluene; polymerization time, 1 h; monomer pressure, 1 bar.
[b] M_n and M_w determined by GPC at 135 °C in TCB.
[c] Estimated.[22]

CONCLUSIONS

New precursor catalysts for the polymerization and oligomerization of ethylene are presented. The activity and characteristics of the polymer formed depend upon the structure of the chelating ligand and upon the reaction conditions. Comparison of the complexes containing the NCS pseudo halide group as a non-chelating ligand with their analogous halide counterparts shows that complex activity and polymer characteristics also vary with this type of ligand. This can be explained by considering that the active site is an ionic pair formed by the metal cation and the counterion made up by MAO and the abstracted ligand (Scheme 1). The type of ligand modifies the interaction of the counterion with the metal center. The **1**/MAO system proved to be by far the most active system in ethylene polymerization in this work.

Acknowledgements

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