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Polymer 44 (2003) 1995–2003

polymer

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Ethylene homopolymerization by novel Ziegler Natta-type catalytic systems obtained by oxidative addition of salicylaldimine ligands to bis(1,5-cyclooctadiene)nickel(0) and methylalumoxane

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Received 7 June 2002; received in revised form 20 December 2002; accepted 16 January 2003

Abstract

A new series of monochelate nickel(II) catalysts, obtained by oxidative addition of salicylaldimine ligands to bis(1,5-cyclooctadiene)nickel(0), was reported for the polymerization of ethylene (E). Almost stoichiometric amounts of MAO as co-catalyst were necessary in order to activate these systems, the productivity being dependent on the Al/Ni molar ratio.

The activity and the average molecular weight of the resulting PE were mainly influenced by the nature of the substituents on both the phenolate moiety and on the *N*-aryl ring. In particular, when two nitro groups are present on the 3,5-positions of phenolate moiety high activity (up to 120,000 g PE/(mol Ni × *h*)) was observed.

The obtained PE samples showed a high linearity and average molecular weight in the 100,000–500,000 Da range.

The obtained results seem to suggest that, at least for these catalysts based on salicylaldiminate ligands, the presence of electron withdrawing nitro groups on the phenoxy moiety plays a more important role with respect to the bulkiness of the substituents on both the ortho positions of the *N*-aryl group in order to prevent chain transfer and thus enhance the molecular weight of the polymer.

Keywords: Polyethylene; Oxidative addition; Salicylaldiminate nickel catalysts

1. Introduction

Quite recently Grubbs showed that neutral (aryl)(phosphino)nickel(II) mono-salicylaldiminate complexes (**I**), characterized by the presence of two bulky isopropyl groups on 2 and 6 positions of the *N*-aryl ring (Chart 1), when treated with a Ni(0) derivative as phosphine scavenger, are very active in the polymerization of ethylene (E) to give a substantially linear high molecular weight polyethylene (PE) [1].

However, when the phosphine was replaced by a more labile ligand, such as acetonitrile, no ligand scavenger was necessary for activating the system [2]. Moreover, it was found that the bulkiness of the R′ group and the electron withdrawing character of the X substituent, both on the phenolate fragment of the salicylaldiminate moiety, strongly affect the activity of the catalytic system [2,3].

It is also noteworthy that **I** do not need any organoaluminium co-catalyst for their activation, due to the presence of a nickel–carbon bond. However, the major drawback concerning the use of **I** as catalysts derives from the fact that they are obtained with a multi-step synthetic route.

Other monosalicylaldiminate nickel(II) complexes, usually activated by Lewis acid co-catalysts, have been claimed for E polymerization in some patents, although their catalytic activity was rather low [4,5].

Moreover, monosalycilaldiminate nickel(II) systems have been successfully employed for ethylene emulsion homopolymerization [6].

Very recently, we have reported that sterically hindered bis(salicylaldiminate)nickel(II) complexes, having the general structure **II** (Chart 2), when combined with an excess of methylalumoxane (MAO) (Al/Ni ≥ 100 mol/mol), are able to give extremely active catalysts in the oligomerization of E, only traces or a very low amount of PE being formed [7].

More recently we have also reported [8] that the above catalytic systems may co-activate E with methyl methacrylate (MMA) to give rather low molecular weight

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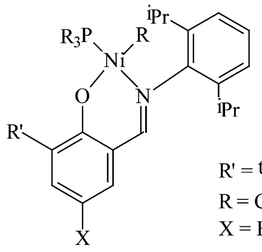
doi:10.1016/S0032-3861(03)00078-8



R' = ^{t}Bu, Ph, Phen, Anthr, H
R = CH_3, Ph
X = H, NO_2

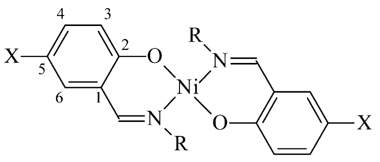
I

Chart 1.

($\bar{M}_n = 7-20 \times 10^3$ Da) copolymers containing 50–80 mol% of MMA co-units, without any formation of oligomeric products. On the other hand, the oxidative addition of different ligands (such as ylids, β-diketones, phosphino-carboxylic acids etc.) to $Ni(cod)_2$ is a well known route which allows one to obtain nickel catalysts active either in the oligomerization or in the polymerization of ethylene also in the absence of aluminium co-catalysts [9,10]. In this context, when one or two nitro groups were introduced on the phenolic moiety of the salicylaldimine ligand, the oxidative addition of the nitro-substituted ligands to a nickel(0) precursor, such $Ni(cod)_2$, gave salicylaldiminate(η^1,η^2-cyclooctenyl)nickel(II) complexes (**III**) [8,11] (Scheme 1).

Complexes **III** were able to promote the copolymerization of E with MMA to give high average molecular weight functionalized PE having 2–6 mol% of MMA co-units [8].

Therefore, it appeared interesting to check if the increased acidity of the phenol group in the salicylaldimine ligand, due to the presence of the electron withdrawing nitro groups, would be able to reduce the electron density on the metal thus favouring ethylene activation. However, in this picture also the role played by the bulky substituents either on the aromatic ring of the phenol moiety or on the *N*-ring of the salicylaldimine ligand appeared interesting to be studied. Therefore, in this paper the activation of ethylene will be studied in the presence of the catalytic systems obtained by the oxidative addition of 5-nitro- and 3,5-dinitro-*N*(2,6-diisopropylphenyl)salicylaldimine (NPS and DNPS, respectively) as well as of 3,5-dinitro-*N*-(phenyl) salicylaldimine (DNAS) and 3-phenyl-N(2,6-diisopropylphenyl)salicylaldimine (PPS) to $Ni(cod)_2$ and subsequent treatment with MAO, with the aim to obtain linear PE and possibly clarify mechanistic aspects of the polymerization process.



II

R = 2,6-diisopropyl-phenyl, X = H
R = 2,6-diisopropyl-cyclohexyl, X = H
R = isopropyl, X = H
R = tert-butyl, X = OCH_3

Chart 2.

2. Experimental

2.1. Materials

All manipulations were carried out under dry argon in Schlenk-type vessels, using anhydrous, air free reagents and solvents.

$Ni(cod)_2$ (Aldrich) was used as received and stored under dry argon at −20 °C.

Methylalumoxane (MAO) (Crompton GmbH), in toluene solution (4.5 M), was used as received and stored under dry argon.

Ethylene (Rivoira, >99%) was used as received.

5-nitro-*N*(2,6-diisopropylphenyl) salicylaldimine (NPS) and 3,5-dinitro-*N*(2,6-diisopropylphenyl) salicylaldimine (DNPS) were prepared according to the literature [12] by reacting 5-nitro- and 3,5-dinitro-salicylaldehyde (Aldrich) with freshly distilled 2,6-diisopropylaniline (Aldrich), (76 and 84% yield, respectively).

Characterization of NPS. ^1H NMR ($CDCl_3$) δ 14.35 (s, OH, 1H), 8.43 (d, HC=N, 1H), 8.38 (d, aromatic, 1H), 8.32 (d, aromatic, 1H), 7.25 (m, aromatic, 3H), 7.15 (s, aromatic, 1H), 2.97 (hept, $CH(CH_3)_2$, 2H), 1.22 (d, $CH(CH_3)_2$, 12H).

FT-IR $\nu_{C=N} = 1631\ cm^{-1}$. $T_m = 122-123$ °C.

Characterization of DNPS. ^1H NMR ($CDCl_3$): δ 16.38 (s, OH, 1H), 9.10 (d, aromatic, 1H), 8.58 (d, aromatic, 1H), 8.30 (d, HC=N, 1H), 7.35 (m, aromatic, 3H), 2.50 (hept, $C\mathit{H}(CH_3)_2$, 2H), 1.25 (d, $CH(C\mathit{H}_3)_2$, 12H) ppm.

FT-IR $\nu_{C=N} = 1639\ cm^{-1}$. $T_m = 145-146$ °C.

3-Phenyl-*N*(2,6-diisopropylphenyl)salicylaldimine (PPS) was prepared by reacting 2,6-diisopropylaniline with 3-phenyl-salicylaldehyde [12]. This last was synthesized in 47% yield by treating [(1,1′-biphenyl)-2-yl] diethylcarbamate with equimolar amounts of sec-BuLi and tetramethylenediamine and successively with an excess of *N*,*N*-dimethylformamide [13,14]. [(1,1′-biphenyl)-2-yl] diethylcarbamate was in turn prepared from 2-phenylphenol and *N*,*N*-diethylcarbamoyl chloride [13].

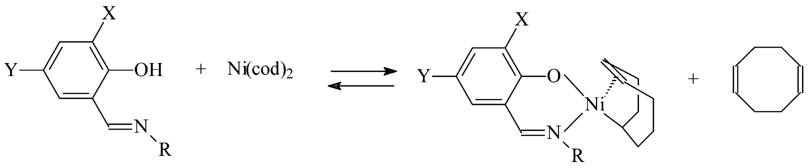
Characterization of PPS. ^1H NMR ($CDCl_3$): δ 13.65 (s, OH, 1H), 8.4 (d, HC=N, 1H), 7.7-7 (m, aromatic, 11H), 3.0 (hept, $C\mathit{H}(CH_3)_2$, 2H), 1.2 (d, $C\mathit{H}(CH_3)_2$, 12H).

FT-IR (KBr): $\nu_{C=N} = 1616\ cm^{-1}$. $T_m = 86-89$ °C.

3,5-Dinitro-*N*-phenyl-salicylaldimine (DNAS) was prepared [12] by reacting 3,5-dinitro-salicylaldehyde with freshly distilled aniline (Aldrich) in a 82% yield.

Characterization of DNAS. ^1H NMR ($CDCl_3$): δ 16.93 (s, OH, 1H), 9.06 (d, aromatic, 1H), 8.78 (d, aromatic, 1H), 8.62 (d, HC=N, 1H), 7.5 (m, aromatic, 5H).

FT-IR (KBr): $\nu_{C=N} = 1623\ cm^{-1}$. $T_m = 210-211$ °C.



IIIa (Y = NO_2, X = H; R = 2,6-diisopropyl-phenyl)
IIIb (Y = X = NO_2; R = 2,6-diisopropyl-phenyl)
IIIc (Y = H, X = Ph; R = 2,6-diisopropyl-phenyl)
IIId (Y = X = NO_2; R = phenyl)

Scheme 1.

*2.2. Synthesis of (η^1,η^2-cycloocten-1-yl) salicylaldiminate nickel (II) complexex (**III**)*

The complexes **III** were prepared according to Scheme 1, by oxidative addition of the free salicylaldimine ligand to $Ni(cod)_2$ and structurally characterized after their isolation. As an example the detailed synthetic procedure is reported for the complex (η^1,η^2-cycloocten-1-yl)(3,5-dinitro-*N*-2,6-diisopropylphenyl-salicylaldiminate) nickel (II) (**IIIb**) deriving from DNPS ligand.

DNPS was added to an equimolar amount of $Ni(cod)_2$ in toluene solution under dry argon at 0 °C. During the slow addition of the ligand to the nickel(0) precursor it was possible to observe a progressive colour change of the solution from yellow to reddish-brown. GC quantitative analysis of the reaction mixture evidenced the release of 1 mol of free cod per mole of $Ni(cod)_2$, according to what is shown in Scheme 1. H^1 NMR analysis of the reaction product, isolated by precipitation in anhydrous *n*-hexane, showed the signals whose chemical shifts and relative intensity were consistent with the formation of the complex **IIIb** (Table 1).

Indeed, the analysis of the NMR spectrum allowed to exclude the presence of an allyl coordination of the C_8 ligand to the metal due to the absence of signals related to π-allyl protons [15]. In addition, the large high field shift of the H_p proton may be addressed to the strong magnetic shielding due to the presence of the metal center. Moreover, the IR spectrum of the reaction product showed a band at 1623 cm^{-1}, related to the symmetric stretching of the N=C group in the aldiminate ligand, which was shifted at lower frequency (16 cm^{-1}) with respect to that of the free DNPS, thus confirming the presence in **IIIb** of a salicylaldiminate ligand coordinated to the nickel through the *N*-aldimine moiety.

Analogous results were obtained for (η^1,η^2-cycloocten-1-yl)(5-nitro-*N*-2,6-diisopropylphenyl-salicylaldiminate)-nickel (II) (**IIIa**), for (η^1,η^2-cycloocten-1-yl)(3-phenyl-*N*(2,6-diisopropylphenyl-salicylaldiminate)nickel (II) (**IIIc**), and for (η^1,η^2-cycloocten-1-yl)(3,5-dinitro-*N*-phenyl-salicylaldiminate) nickel (II) (**IIId**).

2.3. Polymerization procedure

Catalytic batch experiments were carried out in a mechanically stirred 200 ml stainless steel autoclave. In a typical procedure the catalytic nickel precursor was previously obtained in a Schlenk-type vessel by oxidative addition of the salicylaldimine ligand (L) in toluene solution (5 ml) to the desired amount of $Ni(cod)_2$ (0.03–0.23 mmol) in toluene solution (15 ml) under argon (L/Ni = 0.5–2 mol/mol). Then the resulting nickel precursor was transferred into the autoclave under ethylene (E) atmosphere and MAO (Al/Ni = 5–100 mol/mol) subsequently added at room temperature. The autoclave was then pressurized with E at the proper pressure and maintained at the desired temperature (25–50 °C) by using a thermostatic oil bath. The pressure was manually held constant by repeated E feeds. In all cases the reaction was stopped by fast cooling the autoclave and degassing unreacted E through a trap cooled at −15 °C in order to recover eventually formed oligomeric products. When it was possible, a small amount of the liquid inside the autoclave was also collected, weighted and analyzed by gas-chromatography for determining eventual higher oligomers. The solid product was poured into an excess of methanol acidified with 5% HCl in order to purify the polymer. This was filtered, dried under vacuum, weighed and finally characterized.

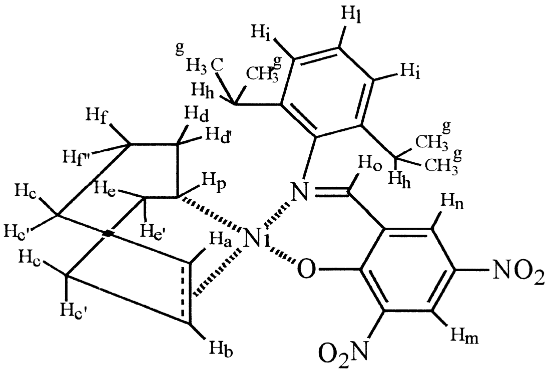
2.4. Structural characterization

Gas chromatography (GC) for the analysis of eventual oligomeric products was performed on a Hewlett-Packard 5890 equipped with a HP 3396 integrator and a flame ionization detector. A capillary column (50 m × 0.2 × 0.5 μm), based on poly(methyl-phenyl-siloxane) as stationary phase was adopted and nitrogen as carrier gas was used. The oven temperature program adopted was as follows: 25 °C for 45 min, then the temperature was increased by a 8 °C/min heating until 230 °C was reached and this value was maintained constant for further 40 min.

Nuclear magnetic resonance spectroscopy (NMR) was carried out on a Varian Gemini 200 spectrometer operating at 200 (^1H) and 50 (^{13}C) MHz. The spectra of PE were performed in 1,2,4-trichlorobenzene at 140 °C, using as internal standard 1,1,2,2-d_2-tetrachloroethane, whereas those of ligands and **III** intermediates were carried out in $CDCl_3$.

Table 1

Structural characterization by ^{1}H NMR analysis of the **IIIb** complex resulting from the oxidative addition of DNPS to $Ni(cod)_2$ under dry argon, after isolation by precipitation in *n*-hexane



IIIb

Proton assignment	Relative intensity	Chemical shift (ppm)	Multiplicity
H_m	1	8.9	dd
H_n	1	7.9	d
H_o	1	7.5	d
H_i, H_l	3	7.3	m
H_a, H_b	2	5.5	m
H_c, $H_{c'}$, H_h	6	2.4	m
H_d, $H_{d'}$, H_e, $H_{e'}$, H_f, $H_{f'}$, H_g	18	1.3–0.6	m
H_p	1	−0.5	m

FT-IR spectra were usually performed on KBr pellets by using a Perkin–Elmer Spectrum One spectrophotometer. When polymer samples were analyzed the above spectrophotometer was equipped with an attenuated total reflectance (ATR) apparatus.

Intrinsic viscosity ($[\eta]$) measurements on polymeric samples were performed by using a Desreaux–Bischoff dilution viscometer in decalin solution at 135 °C. The viscometric average molecular weight ($\bar{M}_v$) was then determined according to the equation $[\eta] = 2.3 \times 10^{-5}\bar{M}_v^{0.82}$ reported for PE [16].

Differential scanning calorimetry (DSC) analysis was performed on a Perkin–Elmer DSC7 instrument equipped with a CCA 7 temperature control system and interfaced with an uniTac 7/DX personal computer.

3. Results and discussion

3.1. Ethylene polymerization by catalytic systems obtained in situ by oxidative addition of 5-nitro-N(2,6-diisopropylphenyl)salicylaldimine (NPS) to $Ni(cod)_2$

Preliminary ethylene homopolymerization experiments, carried out by using NPS as ligand for the oxidative addition to $Ni(cod)_2$ without the subsequent treatment with MAO (entries 1 and 2, Table 2), allowed to confirm that, even in the presence of E high pressure (50 atm), the resulting catalytic system was inactive for both poly- and oligomerization of the olefin, probably due to olefin incapability, even at rather high temperature (60 °C), to remove the η^1,η^2-cyclooctenyl ligand from the intermediate **IIIa**, (here not isolated but the structure of which has been determined after precipitation (Section 2)).

Therefore in the other experiments MAO was added to the above intermediate and the effect of the Al/Ni molar ratio was studied. Indeed, when MAO was added at room temperature in a slight excess (Al/Ni = 5 mol/mol) and E was charged up to 50 atm (entry 3, Table 2) the resulting catalytic system gave, a high molecular weight PE ($\bar{M}_v \sim 100{,}000$ Da) with a rather fair activity, productivity (P) being 15,200 g of PE/(mol Ni × *h*). The IR spectrum and ^{13}C NMR analysis of the obtained PE showed a high linearity of the polymer. The above results seem to suggest that the combination of MAO with E is able to release the η^1,η^2-cyclooctenyl ligand from the intermediate **IIIa** complex, giving rise to a supposed alkyl active species (Scheme 2), responsible for the polymerization process.

However, when the molar ratio Al/Ni was increased up to 15 and 50 (entries 5 and 6, Table 2, respectively,) a decrease of catalyst productivity was observed, *P* decreasing to 8400 and 2200, in that order. The above data, contrary to what reported for α-diimine nickel catalysts [4,17], suggest not only that an almost stoichiometric amount of MAO suffices

Table 2
Ethylene homopolymerization by nickel catalysts obtained 'in situ' by oxidative addition of NPS to Ni(cod)$_2$

Entry	Ni(cod)$_2$ (mmol)	NPS/Ni (mol/mol)	MAO Al/Ni (mol/mol)	Reaction temp. (°C)	Time (h)	Polymeric product[a]		
						wt (g)	$\bar{M}_v$[b]	P[c]
1	0.17	1	0	25	8	0	–	–
2	0.15	1	0	60	8	0	–	–
3	0.20	1	5	25	8	24.30	98,000	15,200
4	0.08	1	5	25	1	0.35	90,000	4400
5	0.20	1	15	25	8	13.40	106,000	8400
6	0.23	1	50	25	1	0.51	110,000	2200
7	0.13	1	5	50	1	0.73	85,000	5600
8[d]	0.33	0.5	15	25	1	0.41	109,000	1250
9	0.10	2	15	25	1	2.60	76,000	26,000

Experiments carried out in a rocking 150 ml stainless steel autoclave; solvent (toluene): 20 ml; $P_{\mathrm{C_2H_4}} = 50$ atm.

[a] No oligomeric products were found, unless otherwise specified.

[b] Determined in decalin at 135°C.

[c] Productivity calculated as: g PE/(mol Ni × h).

[d] 0.5 g of oligomeric products were also obtained.

to activate the system, but also that a large excess of MAO is detrimental. When the experiment as in entry 3 was repeated with a shorter reaction time (1 h) (entry 4, Table 2) a significant reduction of productivity was observed ($P = 4400$), thus indicating that the formation of the active species needs a certain induction period. Accordingly, the increase of the reaction temperature up to 50 °C (entry 7, Table 2) produced an improvement of activity ($P = 5600$) as compared with entry 4.

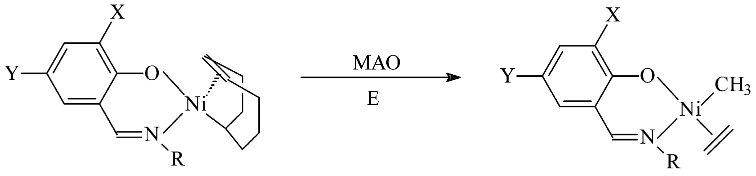
The effect of the NPS/Ni molar ratio was also studied. When a deficit of salicylaldimine ligand was used as compared with the Ni(cod)$_2$ (entry 8, Table 2) a significant reduction of catalytic activity (compare entry 8 with entry 5) was observed, much more than that expected on the basis of the shorter reaction time adopted (1 h against 8 h), due to the induction period. It is noteworthy that in this case oligomeric products were also obtained, differently from the preceding experiments, the excess of Ni(cod)$_2$ reacting with MAO to give an olefin oligomerization catalyst, as previously reported [18]. On the contrary, when an excess of salicylaldimine ligand was used (NPS/Ni = 2) (entry 9, Table 2) a large improvement of productivity was observed ($P = 26{,}000$), thus suggesting that an equilibrium probably exists in the reaction of Scheme 1 affording the **IIIa** species.

All the obtained data strongly support the fact that the acidity of the salicylaldimine ligand plays a key role in promoting the formation of active species via oxidative addition and the subsequent ethylene polymerization. In this context, the use of 3,5-dinitro-*N*(2,6-diisopropylphenyl) salicylaldimine (DNPS), a more acid ligand with respect to NPS, would further increase the activity of the system in ethylene polymerization.

3.2. Ethylene polymerization by catalytic systems obtained in situ by oxidative addition of 3,5-dinitro-N(2,6-diisopropylphenyl)salicylaldimine (DNPS) to Ni(cod)$_2$

The first three experiments (entries 10–12, Table 3) were performed at room temperature by using a DNPS/Ni(cod)$_2$ molar ratio equal to 2, taking into account the best results obtained in the previous experiments where NPS was adopted as ligand. Moreover, the MAO/Ni molar ratio was changed in the 15–100 range.

The results obtained indicate that again an increase of the Al/Ni molar ratio is detrimental for the catalyst activity, P varying from 42,400 g PE/(mol Ni × h) for Al/Ni = 15 (entry 10) to 1400 for Al/Ni = 100 (entry 12). In all cases a linear high molecular weight ($\bar{M}_v \sim 100{,}000$ Da) PE was obtained, as evidenced by FT-IR and ^{13}C NMR analyses as well as viscometric measurements. A comparison of entry 10 with entry 9 of Table 2, where the same ligand/Ni(2) and Al/Ni(15) molar ratios were adopted, confirms that the higher acidity of DNPS with respect to NPS causes a significant improvement of catalyst activity. However, contrary to what observed in the preceding experiments series, a DPNS/Ni molar ratio equal to 1 instead of 2, caused



III

Scheme 2.

Table 3
Ethylene homopolymerization by nickel catalysts obtained “in situ” by oxidative addition of DNPS to $Ni(cod)_2$ and subsequent treatment with MAO

Entry	$Ni(cod)_2$ (mmol)	DNPS/Ni (mol/mol)	MAO Al/Ni (mol/mol)	Reaction temp. (°C)	$P_{C_2H_4}$ (atm)	Time (h)	Polymeric product[a]		
							wt (g)	$\bar{M}_v$[b]	P[c]
10	0.05	2	15	25	50	5	10.6	108,000	42,400
11	0.03	2	50	25	50	5	2.6	107,000	17,300
12	0.07	2	100	25	50	5	0.5	95,000	1400
13	0.14	1	0	25	50	5	–	–	–
14	0.10	1	15	25	50	5	35.2	320,000	72,000
15	0.14	1	5	25	50	5	28.1	205,000	40,100
16	0.07	1	5	25	10	3	5.3	95,000	25,200
17	0.21	1	5	25	1	0.25	0.3	125,000	5700
18	0.08	1	5	50	50	3	28.7	510,000	119,600

Experiments carried out in a mechanically stirred 200 ml stainless steel autoclave; solvent (toluene): 20 ml.

[a] No oligomeric products were found.

[b] Determined in decalin at 135 °C.

[c] Productivity calculated as: g PE/(mol Ni × *h*).

a remarkably higher productivity, as evidenced in entry 14, Table 2, where a Al/Ni = 15 mol/mol was used (compare entry 14 with entry 5, Table 2). This occurrence may be rationalized considering that, due to the higher acidity of the dinitro-substituted ligand as compared with the corresponding mononitro, one equivalent of DNPS is sufficient to shift the equilibrium towards the formation of the intermediate species **IIIb**, the addition of a second equivalent of the ligand probably competing with the coordination of the olefin on the metal site. It is noteworthy that a remarkable increase of the average molecular weight was obtained in the resulting PE ($\bar{M}_v = 320,000$ Da). Moreover, the characterization of the obtained PE by FT-IR (Fig. 1) and ^{13}C NMR spectroscopy as well as by DSC (Fig. 2) indicated that the polymer is highly linear with a T_m equal to 133.6 °C.

Again, in absence of MAO the oxidative reaction product of DNPS to $Ni(cod)_2$ did not show any catalytic activity (entry 13, Table 3). Moreover, when the Al/Ni molar ratio was further reduced (5) the catalyst gave a PE with a high average molecular weight ($\bar{M}_v = 205,000$ Da), although a lower productivity was observed ($P \sim 40,000$) (see entry 15, Table 3). This seems to suggest that, depending on the acidity of the ligand, a proper Al/Ni molar ratio exists in order to obtain a maximum of activity. Indeed, it is confirmed that only a slight excess of MAO with respect to the stoichiometric amount is necessary for obtaining the best catalytic performances. When ethylene pressure was reduced from 50 to 10 and finally to 1 atm (entries 16 and 17, Table 3) the productivity of the catalyst, as expected, decreased, but it remained still significant ($P = 25,200$ and

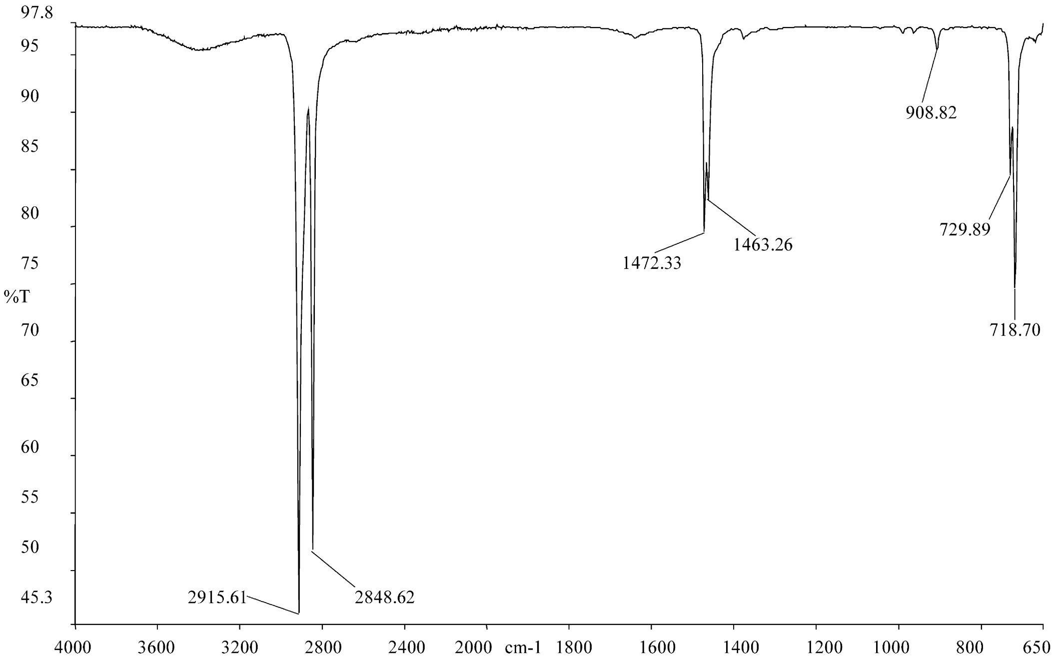


Fig. 1. FT-IR (ATR) spectrum of the polyethylene sample obtained in entry 14.

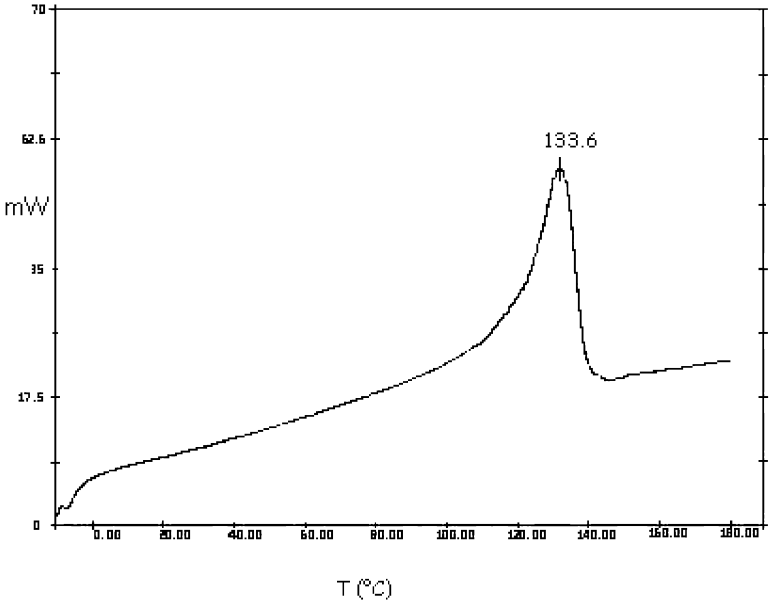


Fig. 2. DSC of the polyethylene sample obtained in entry 14.

5700, respectively) and no oligomeric products were ascertained. It is noteworthy that, even at low E pressure, the average molecular weight of the resulting PE was high ($\bar{M}_v = 125{,}000$ Da). Finally, when the reaction temperature was increased to 50 °C (entry 18, Table 3) not only the catalyst exhibited an extremely high productivity ($P = 119{,}600$) but also the resulting PE displayed a very high average molecular weight ($\bar{M}_v = 510{,}000$ Da) and rather high T_m (129.5 °C). All these data confirm that the electronic situation of the metal, at least for nickel catalysts based on salicylaldimine chelate ligands, is more important than steric constraints around the metal for promoting E polymerization. In fact, sterically hindered bis(salicyladiminate)nickel/MAO catalysts, when no electron withdrawing nitro groups are present on the aromatic moiety of the phenolic group, are unable to polymerize E, although they are excellent oligomerization catalysts [7]. The fact that the last catalysts are able to copolymerize E with MMA without any formation of oligomeric products [8] could be explained assuming that MMA may interact through the ester group with both MAO and the active sites, thus changing the electronic situation around the metal.

On the other hand, as mentioned in the introduction, sterically hindered salicylaldiminate nickel(II) complexes having structure **I** (Chart 1), when activated by $Ni(cod)_2$, changed dramatically their catalytic activity depending on the bulkiness of the substituent R′ in ortho position to the phenolic group of the salicylaldimine moiety, an increase of the bulkiness improving the activity and the molecular weight of the obtained PE [1,2]. In this context, it appeared of interest to check if the presence of a phenyl substituent on the 3 position of the salicylaldimine ligand, in absence of electron withdrawing nitro groups, could equally promote ethylene polymerization. Therefore, 3-phenyl-*N*(2,6-diisopropylphenyl)salicylaldimine (PPS) was prepared and employed in the oxidative addition to $Ni(cod)_2$ to give, after treatment with MAO, a potential E polymerization catalyst. Finally, as in nickel based catalysts the bulkiness of the two isopropyl groups in ortho, ortho′ positions with respect to the nitrogen of imine [19–21] or diazene [22] moieties has been claimed as necessary in order to ‘protect’ the metal center, lowering the propensity towards chain transfer reactions, DNAS was used for the oxidative addition. In fact this ligand, containing two nitro groups on the phenolic ring, but not the bulky isopropyl groups on the imine moiety, would better clarify the role played by steric and electronic effects in the reaction.

3.3. Mechanistic considerations

When PPS was used as salicylaldimine ligand, the experiments (entries 19 and 20, Table 4) were carried out by using a PPS/Ni molar ratio equal to 2 in order to shift the equilibrium of the oxidative addition to the nickel(0) complex towards the species **IIIc** (Scheme 1), considering the lower acidity of PPS with respect to NPS and DNPS. However, as reported in Table 4, notwithstanding the use of an excess of salicylaldimine ligand with respect to $Ni(cod)_2$ the resulting catalytic system after MAO addition was mainly active in the oligomerization of ethylene rather than in its polymerization. Indeed, only a small amount of PE was obtained, although characterized by a high molecular weight ($\bar{M}_v > 150{,}000$ Da).

On the contrary, when DNAS was used as salicylaldimine ligand (entry 21–25, Table 4), an equimolar DNAS/Ni ratio was always employed in order to obtain the species **IIId** (Scheme 1), the acidity of this ligand being similar to that of DNPS. However, the use of a slight excess of MAO

Table 4
Ethylene homopolymerization by nickel catalysts obtained ‘in situ’ by oxidative addition of either PPS or DNAS to $Ni(cod)_2$ and subsequent treatment with MAO

Entry	Ligand (L)	$Ni(cod)_2$ (mmol)	L/Ni (mol/mol)	MAO Al/Ni (mol/mol)	Oligomeric products			Polymeric product		
					wt (g)	$C_4/C_6/C_8$ (mol%)	P^a	wt (g)	$\bar{M}_v{}^b$	P^c
19	PPS	0.05	2	15	7.0	74/23/3	17,500	0.13	155,000	320
20	PPS	0.03	2	50	9.2	70/23/7	38,300	0.44	173,000	1800
21	DNAS	0.07	1	5	0.0	–	0	traces	–	–
22	DNAS	0.07	1	10	0.0	–	0	11.6	357,000	21,000
23	DNAS	0.05	1	15	0.0	–	0	1.70	340,000	6000
24	DNAS	0.06	1	30	0.0	–	0	2.20	202,000	4600
25^d	DNAS	0.07	1	15	0.0	–	0	5.25	230,000	9300

Reaction conditions: temperature: 25 °C; time: 8 h; solvent (toluene): 20 ml; $P_{C_2H_4} = 50$ atm.

[a] Productivity calculated as: g oligomeric products/(mol Ni × *h*).

[b] Determined in decalin at 135 °C.

[c] Productivity calculated as: g PE/(mol Ni × *h*).

[d] Reaction temperature: 50 °C.

(Al/Ni = 5 mol/mol) caused an almost complete inactivation of the catalytic system (entry 21, Table 4). The successive experiment, carried out in the presence of a double amount of co-catalyst evidenced an appreciable productivity ($P = 22{,}000$) to give linear PE without the contemporary formation of oligomers (entry 22, Table 4). The progressive increase of the MAO/Ni molar ratio in the range 15–30 evidenced a progressive decrease of the catalytic activity (entries 23–24, Table 4), analogously to what observed with the more active **IIIb** system. When the reaction temperature was increased to 50 °C (run 25, Table 4) a productivity enhancement was ascertained (compare entry 25 with entry 23), once again in complete agreement with the catalytic behaviour of the DNPS-based system. Despite the absence of bulky alkyl groups in ortho, ortho′ positions to the *N*-moiety of the salicylaldiminate ligand, in all the above experiments a high molecular weight linear PE was obtained ($200{,}000 < \bar{M}_v < 350{,}000$ Da) without any formation of oligomeric products, although the activity of the catalyst resulted lower than that observed when DNPS was correspondingly used. These data nicely confirm the hypothesis that the driving force of the chain growing of the alkyl group bound to the metal, at least in the case of these nickel catalysts, is mainly influenced by the acidity of the ligand rather than by the steric hindrance around the metal site. Indeed, this situation should imply a more effective retention of the electron density on the chelate system, thus increasing the positive charge on the metal site and hence its olefin affinity. The reduced electron density on the metal would therefore promote the coordination of the olefin and the subsequent insertion on the carbon–metal bond against β-hydrogen elimination and/or monomer transfer, thus favouring propagation versus termination and chain transfer steps. In fact, despite the presence of a bulky phenyl ring on the 3-position of the salicyl moiety as well as of two isopropyl groups on the ortho, ortho′ positions of the *N*-ring of the PPS ligand, the contemporary absence of an electron withdrawing nitro group seems to play a prevalent role in the formation of oligomeric products.

A further support to this hypothesis is offered by the fact that the DNAS ligand, which does not contain any bulky isopropyl group on the *N*-moiety but retains two nitro groups on the phenolic ring, showed a complete selectivity towards polymerization affording a very high molecular weight PE.

4. Conclusions

On the basis of the obtained data the following conclusions can be drawn:

1. For the preparation of E polymerization nickel catalysts a new approach has been successfully applied consisting in the oxidative addition of a free nitro-substituted salicylaldimine ligand to a nickel(0) precursor.
2. The catalytic systems may be activated by using an almost stoichiometric amount of MAO with respect to the metal.
3. The obtained catalysts are able to afford a high molecular weight linear PE.
4. The activity of catalysts based on the 3,5-dinitro-*N*(2,6-diisopropylphenyl)salicylaldimine is significantly higher than that obtained with catalysts prepared with the mono-substituted 5-nitro-*N*(2,6-diisopropylphenyl)salicylaldimine, according to the higher acidity of the former ligand.
5. From the selectivity point of view, in terms of polymerization capability against oligomerization, the steric constraints around the metal due to the bulkiness of the two isopropyl groups in ortho, ortho′ positions on the *N*-ring do not seem to play a determinant role, in contrast to what proposed on the basis of DFT calculations [23] and very recently emphasized for anilinotropone-based neutral nickel(II) catalysts for E polymerization [21]. In

fact, high molecular weight linear PE was obtained in the presence of 3,5-dinitro-*N*-phenyl-salicylaldimine as ligand. Work is in progress in order to computationally investigate and clarify the role of the electronic and steric factors governing the catalytic process in these nickel systems.

Acknowledgements

The financial support from MIUR through the Research Project of National Interest (PRIN) 2000: 'New strategies for controlling reactions: interactions of molecular fragments with metal sites in non-conventional species' is gratefully acknowledged.

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