Highly Active and Easily Accessible Catalysts for Vinyl Polymerization of Norbornene Obtained by Oxidative Addition of Salicylaldimine Ligands to Bis(1,5-cyclooctadiene)nickel(0) and Methylaluminoxane

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ABSTRACT: Highly active, cheap, and easy to synthesize catalytic systems, obtained *in situ* by the oxidative addition of salicylaldimine ligands to bis(1,5-cyclooctadiene)nickel(0) and activated by methylaluminoxane (MAO), are now reported for the vinyl polymerization of norbornene. Their activity resulted mainly influenced by the nature of the substituents present both on the phenolate moiety and on the *N*-aryl ring as well as the content of free trimethylaluminum (TMA) present in the commercial MAO. In particular, the maximum activity, up to about 78,000 kg polynorbornene/mol Ni \times h, was ascertained when 3,5-dinitro-*N*-(2,6-diisopropylphenyl)salicylaldimine ligand was adopted in conjunction with Ni(cod)₂ and

INTRODUCTION Bicyclo[2.2.1]hept-2-ene, well known as norbornene (NB), can be polymerized by two basically different catalytic mechanisms: ring-opening metathesis polymerization (ROMP)¹ and vinyl or addition polymerization, as reviewed by Janiak et al.² Vinyl polymerization leaves intact the bicyclic structure, only opening the double bond, and the resulting polynorbornene (PNB) shows high chemical resistance, thermal stability, optical transparency, large refractive index, low birefringence, and unusual transport properties.³

Over the past decade, there has been an increasing interest in the use of late transition metal complexes, and in particular, nickel-based catalysts, for the vinyl polymerization of NB.^{4–12} Among the nickel-based precursors, neutral monoand/or bis-salicylaldiminate Ni(II) complexes bearing bulky substituents on the imino group were found to be active in the presence of a cocatalyst.^{13–15} However, these complexes have generally been obtained through tedious and multistep synthetic protocols.

Recently, we have developed a new simple synthetic approach for obtaining *in situ* N,O chelate nickel catalysts active in ethylene polymerization or oligomerization, which is based on the oxidative addition of a N,O-type ligand to bis(1,5-cyclooctadiene) nickel(0) [Ni(cod)₂] followed by the

TMA-depleted MAO. This remarkable performance, to the best of our knowledge, the highest never reported working in toluene instead of chlorinated aromatics, was reached adopting this more sustainable reaction medium. The influence of the main reaction parameters such as reaction time, temperature, monomer/Ni, and Al/Ni molar ratios on the catalytic performances and polymer characteristics was studied as well. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

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activation with methylaluminoxane (MAO).^{16–19} These catalytic systems resulted also active in the copolymerization of ethylene with polar monomers, such as vinyl ethers and methylmethacrylate.^{20,21} On the other hand, other nickel catalysts obtained by oxidative addition of ylids, β -diketones, and phosphino-carboxylic acids to Ni(cod)₂ are well known to be active either in the oligomerization or polymerization of ethylene even in the absence of aluminum cocatalysts.^{22,23} Nevertheless, to the best of our knowledge, NB polymerization catalysts synthesized via oxidative addition of different N,0-type ligands to Ni(cod)₂ are still unknown.

In this context, it appeared very interesting to investigate the homopolymerization of NB by catalytic systems obtained through the oxidative addition of different salicylaldimine ligands to Ni(cod)₂ with the aim of obtaining *in situ*, after treatment with MAO, novel really accessible catalytic systems for NB polymerization. This simple approach allows the big opportunity of easily modulating the electronic and steric properties of the ligand and thus of resulting nickel precatalyst.

Different ligands were tested [3,5-dinitro-*N*-(2,6-diisopropylphenyl)salicylaldimine (DNIPS), 3-nitro-*N*-(2,6-diisopropylphenyl)salicylaldimine (NIPS), *N*-(2,6-diisopropylphenyl)sali-

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SCHEME 1 Synthesis of the catalytic precursors I-V by oxidative addition.

cylaldimine (IPS), *N*-(phenyl)salicylaldimine (PS), and 3,5dinitro-*N*-(pentafluorophenyl)salicylaldimine (DNFPS)] in the oxidative addition (Scheme 1) to check if the presence of electron-withdrawing groups either on the phenol group or on the *N*-aryl moiety as well as of bulky substituents on this last would be able to influence the polymerization process.

EXPERIMENTAL

Materials

Manipulations of sensitive materials were carried out under a dry argon atmosphere using Schlenk techniques. Toluene (Aldrich) was refluxed over a Na/K alloy and distilled under a dry argon atmosphere. MAO was purchased from Witco as a 10 wt % solution in toluene and was used as received. Trimethylaluminum (TMA)-depleted MAO (DMAO) was prepared from MAO as a solid residue by high-vacuum distillation as previously reported.²⁴ NB (Aldrich) was distilled from CaH₂ and then dissolved in dried toluene in appropriate concentrations. Ni(cod)₂ (Aldrich) was used as received and stored in the refrigerator in sealed vials under dry argon. Phenoxyimine ligands (DNIPS, NIPS, IPS, and PS) were prepared by the Schiff base condensation of the appropriate aniline and salicylaldehyde derivatives as previously described.^{25–28}

DNFPS was synthesized by reacting pentafluoroaniline with 3,5-dinitrosalicylaldehyde in absolute ethanol according to the general procedure (75% yield).²⁵

Characterization of DNFPS

¹H NMR (200 MHz, CDCl₃, δ , ppm): 14.55 (s, 1H, OH), 9.57 (d, 1H, Ar H), 9.06 (d, 1H, Ar H), 8.98 (d, 1H, HC=N); ¹³C NMR (50 MHz, CDCl₃, δ , ppm): 169.05 (C=O), 121.60-159.79 (Ar); ¹⁹F NMR (CDCl₃, δ , ppm): -164.54 (m, 2F, *meta*), -158.28 (q, 1F, *para*), -152.20 (m, 2F, *ortho*).

Polymerization Procedure

NB polymerization was carried out in a 100-mL two-necked round-bottomed flask equipped with a magnetic stirrer and a dropping funnel. In a typical procedure, the nickel precursor was obtained by oxidative addition of desired N,O ligand dissolved in toluene (5 mL), which was added dropwise to the proper amount of Ni(cod)₂ dissolved in toluene (15 mL), working under argon at 0 °C. The formation of the desired nickel precursors **I–V** and the release of 1 mol of free cod per mole of Ni(cod)₂ were confirmed by ¹H NMR on the resulting solution, as previously reported.¹⁷ The resulting solution was allowed to reach room temperature, and then the desired amounts of monomer and cocatalyst were added into the flask in that order and the polymerization was allowed to proceed. When the polymerization experiment was carried out at a higher temperature than room temperature, the flask was immersed in a thermostatic oil bath at the chosen temperature. The polymerization was stopped by the addition of a large excess of methanol acidified with 5% aqueous HCl to purify the polymer from catalyst residues. The precipitated polymer was washed with fresh methanol, filtered, dried *in vacuo*, weighed, and finally structurally characterized.

Physicochemical Measurements

IR spectra were performed with a PerkinElmer Spectrum One Fourier transform infrared (FTIR) spectrophotometer equipped with an attenuated total reflectance apparatus. Data elaboration was performed with a Spectrum V 3.2 PerkinElmer program. NMR measurements were recorded on Varian Gemini 200BB instrument at 293 K. The chemical shifts for ¹H and ¹³C were referenced to the nondeuterated aliquot of the solvent, whereas the chemical shifts for ¹⁹F NMR spectra were referenced to CFCl₃. The NMR spectra of PNB samples were performed in the mixture of chlorobenzene and $1,1,2,2-d_2$ -tetrachloroethane. Size exclusion chromatography (SEC) measurements were carried out with a HPLC pump equipped with a 50- μ m Rheodyne loop, a Waters 515 oven at 35 °C, and a Waters 2410 refractive index detector. A PL 5- μ m gel MIXED-C column was used. Chlorobenzene and 1 mL/min were used as the eluent and the elution rate, respectively. Monodispersed polystyrene samples were used for the calibration curve.

Differential scanning calorimetry (DSC) analysis of the PNB samples was performed on a Perkin-Elmer Pyris Diamond DSC instrument. Thermogravimetric analysis of the PNB samples was performed on a Mettler TG50 thermobalance and Mettler TC11 processor, with a dry nitrogen purge and a scanning rate of 10 $^\circ$ C/min.

RESULTS AND DISCUSSION

A preliminary NB polymerization experiment was carried out by using DNIPS as ligand for the oxidative addition to JOURNAL OF Polymer POLYMER SCIENCE Chemistry

TABLE 1 Vinyl Polymerization of Norbornene by Using I/MAO Catalytic System^a

Run	Ni(cod) ₂ (µmol)	Al/Ni (mol/mol)	NB/Ni (mol/mol)	7 ^b (°C)	Time (min)	Yield (g)	A ^c	$M_{\rm w}{}^{ m d}$ (Da)	PDI ^e
1	30	-	2,000	25	60	-	-	-	-
2	30	500	2,000	25	60	2.8	93	201,000	3.4
3	30	500	2,000	25	15	2.1	280	253,000	5.6
4	30	500	2,000	0	15	0.9	120	292,000	3.4
5	30	500	2,000	50	15	4.1	547	165,000	3.8
6	30	250	2,000	50	15	3.8	507	159,000	3.8
7	30	50	2,000	50	15	2.5	333	116,000	3.6
8 ^f	30	500	2,000	50	5	3.6	1,440	345,000	5.2
9 ^f	15	500	4,000	50	5	3.7	2,960	301,000	5.5
10 ^f	5	500	12,000	50	5	1.2	2,880	301,000	5.4
11 ^f	15	500	8,000	50	1	7.5	30,000	252,000	6.2
12 ^f	15	1,000	10,000	50	0.5	9.8	78,400	387,000	7.6

 a Total volume of toluene = 20 mL; cocatalyst = MAO; ligand/Ni = 1 (mol/mol).

^b Reaction temperature.

^c Activity (kg of PNB/mol Ni \times h).

 $Ni(cod)_2$ to give I without its subsequent treatment with MAO (run 1, Table 1). The complete absence of activity allowed to confirm that the catalytic system I was inactive for the polymerization of NB in the absence of cocatalyst.

This result can be related to NB incapability to remove the η^1 , η^2 -cyclooctenyl ligand from the intermediate I, thus giving rise to the supposed methyl nickel active species characterized by the presence of a vacancy able to coordinate NB and initiate its polymerization.^{5(e)} An analogous behavior had been previously ascertained for the precursor I in ethylene homopolymerization: even at high pressures of ethylene, the addition of MAO became necessary to obtain an appreciable activity.¹⁷

THREFore, in the successive experiments (runs 2–7, Table 1) commercial MAO was always used as cocatalyst adopting different reaction conditions, in terms of reaction time, MAO concentration, and temperature.

Indeed, when the precursor was treated with MAO at room temperature for 1 h of reaction time (run 2, Table 1), the resulting catalytic system gave high-molecular-weight PNB ($M_w = 201,000$ Da) having large polydispersity with a moderate activity, activity being 93 kg of PNB/mol Ni × h. The high polydispersity of the PNB can be ascribed to diffusion phenomena, taking into account that the viscosity of the medium gradually increased during the polymerization. The coexistence, under the reaction condition, of different active species could also be responsible of this high polydispersity; research is in progress to clarify the nature of active species.

As expected, the decrease of the reaction time to 15 min (run 3) caused a significant improvement in the catalyst activity, up to 280 kg PNB/mol Ni \times h. On the other hand, when the polymer yield reached in this run (2.1 g) was compared with that obtained in run 2 (2.8 g), where the duration was four times longer, it is evident that a certain deacti-

^d Determined by SEC analysis.

^e Polydispersity index, determined as $M_{\rm w}/M_{\rm n}$.

^f DMAO was used as cocatalyst.

vation of the catalyst takes place with time. As a consequence, when short durations are adopted to work under the same conditions reported in the literature for other Ni systems, it is evident that overestimated performances can be obtained, which cannot be maintained after longer reaction times, when the viscosity becomes very high, PNB precipitation takes place, and monomer concentration is reduced.

The reaction temperature dramatically influenced catalytic behavior and molecular weights of resultant polymers. Polymerization at 0 °C caused, as expected, a remarkable decrease of activity (P = 120 kg PNB/mol Ni × h), whereas, when the reaction temperature was increased to 50 °C (run 5, Table 1), an increase of activity (P = 547 kg PNB/mol Ni × h) was observed, and the resulting PNB displayed a relatively lower molecular weight ($M_w = 165,000$ Da). The temperature of 50 °C was adopted for the successive catalytic runs, metal deposition and partial deactivation being ascertained at higher temperatures.

Variation of the Al/Ni molar ratio in the range of 50–500 evidenced the significant influence of MAO concentration on polymer yield and molecular weight (runs 5–7, Table 1). When the Al/Ni molar ratio progressively decreased, lower polymer yields were ascertained, thus suggesting that at lower molar ratios of Al/Ni, the precatalyst cannot be fully activated by MAO.

Because it is well established that the relative amount of free TMA in the commercial MAO largely affects the catalytic performances of nickel catalysts based on N,O ligands in ethylene polymerization,^{29,30} MAO was replaced by DMAO as cocatalyst and a 5-min polymerization time was adopted (run 8, Table 1). The catalytic activity resulted highly improved and an activity of 1440 kg PNB/mol Ni \times h was ascertained. The lower activity in the presence of MAO with



TABLE 2 Vinyl Polymerization of Norbornene by Using II-V/DMAO Catalytic Systems^a

Run	Catalyst	Al/Ni (mol/mol)	NB/Ni (mol/mol)	Time (min)	Yield (g)	A^{b}	M _w ^c (Da)	PDI ^d
13	II	500	8,000	1	5.7	22,800	361,000	5.2
14	III	500	8,000	1	2.3	9,200	343,000	4.8
15	IV	500	8,000	1	3.1	12,400	355,000	4.9
16	V	500	2,000	1	0.8	2,900	201,000	4.3
17	V	500	8,000	1	7.0	28,000	256,000	5.9
18	V	1,000	10,000	0.5	9.1	73,000	305,000	6.7
19	Ni(cod) ₂	1,000	10,000	30	0.5	66	n.d	n.d
20	DNFPS	1,000 ^e	10,000	30	Traces	_	_	_

 a Ni(cod)₂: 15 μ mol; total volume of toluene = 20 mL; T= 50 °C; ligand/ Ni (mol/mol) = 1.

^b Activity (kg of PNB/mol Ni \times h).

^c Determined by SEC analysis.

^d Polydispersity index, determined as M_w/M_n .

e Al/DNFPS molar ratio.

respect to DMAO is probably due to the deactivating interaction of free TMA present in MAO with the catalytically active species, as previously observed for chelated and nonchelated Ni(II) precursors.^{2,31,32} The absence of free TMA also caused a significant increase of the PNB molecular weight; this observation can be ascribed to the chain transfer to free TMA.

Taking into account that the NB concentration had been reported to exert a large influence on the catalyst performances,³³ run 8 was repeated by progressively increasing the NB/Ni molar ratio up to 8000, using a halved amount of Ni precursor (runs 9 and 10, Table 1). When a NB/Ni molar ratio equal to 8000 was adopted, an activity of 30,000 kg PNB/mol Ni \times h was ascertained. When the reaction time decreased to 0.5 min to minimize the possible effects of diffusion-caused deceleration at high conversions and the Al/Ni molar ratio increased to 1000 mol/mol, the remarkable activity of 78,000 kg PNB/mol Ni \times h was reached (run 12, Table 1). This value is, to the best of our knowledge, the highest never reported for nickel precursors under similar reaction conditions, adopting very short reaction times and toluene as sustainable reaction medium instead of the classic high boiling chlorinated aromatic solvents, and much higher with respect to the best performance obtained with the corresponding bis(salicylaldiminato)Ni(II) complex in toluene (145 kg PNB/mol Ni \times h).¹⁵ This result is remarkable because it has been reported for highly active nonchelated nickel precursors³² and also for cobalt catalysts³⁴ that the addition of small amounts of toluene to 1,2-dichlorobenzene causes a drop of the activity. This generally ascertained negative effect of toluene has been ascribed to the better solvent effect of chlorinated hydrocarbons, in which PNB is soluble, and also to the formation of tight or contact ion pairs in nonpolar solvent and of solvated ion pair in polar solvent.32

The polydispersity was significantly enhanced when the yield and viscosity increased (PDI 7.6 for run 12), thus confirming the determinant role of diffusion phenomena in toluene.

When NIPS, presenting only one nitro group on the *ortho* position of the phenoxy moiety, was used as salicylaldimine ligand in the place of DNIPS under the same conditions of

run 11 (run 13, Table 2), the activity of the resulting precursor II slightly decreased up to 22,800 kg PNB/mol Ni \times h.

On the other hand, when IPS, not containing any nitro group but retaining steric hindrance on the chelate ligand, was used for the *in situ* preparation of catalytic system **III** (run 14, Table 2), a considerable reduction in activity (ca. 9200 kg PNB/mol Ni × h) was observed when compared with DNIPS- and NIPS-based systems. This result confirmed that NB coordination on the metal center is favored by the presence of electron-withdrawing groups on the salicylaldimine moiety. In fact, it is well known that these ligands influence the electrophilicity of the metal center, and a relatively positive nickel center will exhibit high activities for NB polymerization.^{5(e)} On the other hand, for this type of precursors, the acidity of the salicylaldimine ligand also plays a key role in promoting the preliminary formation of the active species via oxidative addition.^{17,35}

On the contrary, when PS, once again not containing any nitro group and also without hindered substituents on the *N*-aryl moiety, was used as salicylaldimine ligand (run 15, Table 2), a modest enhancement in the activity was achieved with respect to that ascertained in the presence of the precursor **III** (ca. 12,400 vs. 9200 kg PNB/mol Ni \times h). This



FIGURE 1 Influence of the ligand structure on norbornene polymerization with precatalysts **I–V**.

result can be related to a moderate deactivating effect of the *ortho* isopropyl substituents due to steric reasons. 36

To enhance the positive character of the nickel center, the ligand DNFPS, having two nitro groups on the phenoxy moiety and a perfluorinated *N*-aryl moiety, was tested (runs 16–18, Table 2). The precatalyst **V** evidenced catalytic performances similar to those of **I**, giving PNB with analogous characteristics, thus confirming the determinant role of the presence of two nitro groups on the phenol ring for achieving remarkable productivities. In this respect, the optimized results, summarized in Figure 1, evidence that for **I–V** nickel catalysts the electronic situation on the metal center is more striking than steric constraints around the nickel itself for promoting NB polymerization.

Finally, two blank runs (runs 19 and 20, Table 2) were carried out under the optimized conditions of run 18 but for a longer reaction time, in order to ascertain also a scarce activity. The first one was carried out in the absence of the salicylaldimine ligand and evidenced the negligible activity of the system Ni(cod)₂/MAO. The second blank run (run 20, Table 2) was carried out in the absence of Ni(cod)₂ and allowed to exclude the catalytic activity of salicylaldiminate aluminum species, which could be generated *in situ* by addition of the free salicylaldimine ligand DNFPS to MAO.³⁷ These results indicate that the ascertained catalytic performances are exclusively due to the Ni precatalyst obtained *in situ* by reaction of Ni(cod)₂ with the ligand.

FTIR, ¹H and ¹³C NMR spectra of all the obtained PNB samples were typical of a vinyl-type structure. There are no absorptions around 960 and 735 cm⁻¹, assigned to the *trans* and *cis* form of double bonds, respectively, which are characteristic of the ROMP structure of PNB. No resonances are displayed at about 5.2 and 5.3 ppm in the ¹H NMR spectrum of the PNB, assigned to the *cis* and *trans* form of the double bonds. The ¹³C NMR spectra of all the obtained PNB samples confirmed a nonstereoregular vinyl-type structure, with no traces of double bonds being present.^{1,11} These data indicate that the PNB obtained with the aforementioned catalysts was an addition-type (2,3-linked) product.

Our attempts to determine $T_{\rm g}$ of the PNB samples failed, the DSC spectra not evidencing well-defined endothermic signals upon heating up to the decomposition temperature, as previously reported for vinyl-type PNB.^{33,38}

CONCLUSIONS

The catalytic activity of N,O chelate nickel (II)/MAO catalysts, obtained by simple oxidative addition of the free salicylaldimine ligand to Ni(cod)₂, has been studied for the first time in the vinyl polymerization of NB using toluene as reaction medium. This approach is very fast and sustainable, because of the remarkable simplicity of the ligand syntheses and the great opportunities of fine tuning of their electronic and steric properties.

The presence of nitro groups on the phenol moiety of the chelate ligand significantly increases the activity. On the con-

trary, the presence of bulky alkyl substituents on the *N*-aryl moiety of the ligand does not appreciably affect the catalyst activity and the molecular weight of the resulting polymer. The catalytic performances can be enhanced by the optimization of the reaction parameters. In particular, TMA depleted MAO results in a better polymerization activator with respect to commercial MAO. Moreover, very short reaction times (min), high NB/Ni and Al/Ni molar ratios are crucial for improving the catalytic performances. The maximum ascertained activity, about 78,000 kg PNB/mol Ni \times h, to the best of our knowledge, is the highest never reported for Ni(II)/ MAO systems adopting in toluene as reaction medium and short polymerization times. On the other hand, it must be borne in mind that when short durations are adopted overestimated performances can be obtained, which cannot be maintained after longer reaction times.

Remarkable performances and therefore a low content of nickel in the obtained polymers are required because of the well-known toxicity of this metal, whose use is widening in modern technologies. The accumulation of nickel in the environment can cause not only skin allergies but also cardiovascular system poisoning and stimulation of neoplastic transformation.³⁹

The obtained polymers are characterized by high molecular weights and broad molecular weight distributions as well as nonstereoregular vinyl-type structure.

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