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Styrene Polymerization by Ziegler-Natta Catalysts Based on Bis(salicylaldiminate)nickel(II) Complexes and Methyl Aluminoxane

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Summary: The homopolymerization of styrene by using different catalytic systems based on bis(salicylaldiminate)nickel(II) and methylaluminoxane was investigated. In particular, the effect on catalyst activity and polymer characteristics by electron withdrawing groups located on the phenolic moiety was studied. The influence of the bulkiness of the substituents on the N-aldimine ligand was also ascertained. Finally the catalytic performances were investigated as a function of the main reaction parameters, such as temperature, Al/Ni molar ratio and duration.

Keywords: addition polymerization; bis(salicylaldiminate)nickel complexes; methylaluminoxane; organometallic catalysts; styrene

Introduction

It is well established that isotactic poly(styrene) (i-PS) was obtained since the discovery of conventional Ziegler-Natta catalysts based on titanium chlorides and organoaluminium derivatives.[1-3] Quite recently, mono-cyclopentadienyl- and other titanium compounds, when combined with methylaluminoxane (MAO) or with tris(pentafluorophenyl)borane and corresponding borates were found to give in homogeneous phase syndiotactic poly(styrene) (s-PS).[4-9] Organometallic nickel complexes were also reported to be active in the polymerization of styrene. In particular, the cationic [(η^3-methallyl)(η^4-cycloocta-1,5-dienyl)Ni(II)] hexafluorophosphate complex was found to afford very low molecular weight i-PS without any addition of Lewis acids as co-catalysts.[10] When solvents with different polarity and phosphines as ancillary ligands were used in combination with the above nickel complex the catalytic activity and polymer characteristics were markedly affected.[10,11]

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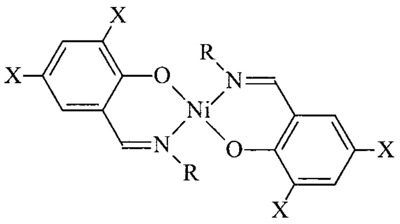
Neutral σ-acetylide nickel(II) complexes were found to be good initiators in chloroform solution for styrene polymerization, but a radical mechanism was proposed.[12] Recently, several nickel complexes, when combined with MAO, resulted active in the styrene polymerization.[13-16] In the presence of the bis(acetylacetonate)Ni(II) [Ni(acac)$_2$]/MAO catalyst, contradictory results concerning the PS microstructure were reported. Indeed, subsequent studies allowed to ascertain that the stereoregularity is strongly dependent on the content of trimethylaluminium (AlMe$_3$) present in MAO.[17,18] On the other hand, MAO alone behaves as ionic initiator for some vinyl monomers.[19] When Al/Ni molar ratios in the 60-90 range were adopted, catalyst activity was improved, but a detrimental effect on the PS stereoregularity was observed.[17] A detailed study of styrene polymerization with nickel derivatives/MAO catalysts allowed to conclude that Ni(acac)$_2$ and NiCl$_2$ resulted the best precursors, although rather low activities (~ 220 mol of converted styrene/mol of Ni × h) and molecular weights of the resulting polymers were obtained.[20] Moreover, the heterogenization of the aforementioned catalyst on SiO$_2$ allowed to improve the activity.[21] Novel nickel-based/MAO catalysts, prepared from bis(α-nitroacetophenonate)nickel(II) precursor were recently proposed by us for the polymerization of styrene.[22, 23] They displayed higher activity as compared with the Ni(acac)$_2$/MAO catalyst. However, the molecular weight of the obtained PS resulted rather low (< 20.000 Da) and significant amounts of oligomeric products were present. When AlMe$_3$ free MAO was used an increase of polymer isotacticity degree (up to 70%) was achieved. GC/MS analysis of oligomers allowed us to conclude that styrene insertion is mainly of secondary type. In this context it appeared very interesting to study the polymerization of styrene in the presence of novel catalytic systems based on bis(salicylaldiminate)nickel(II) complexes (Chart 1) which, in combination with MAO, have been found to be active in the polymerization of methyl methacrylate to a syndiotactic-rich polymer.[23,24]

In particular, the influence on the catalyst activity and polymer characteristics will be investigated by the insertion of electron withdrawing nitro groups on the phenol moiety as well as of bulky substituents on the N-aldimine moiety of the salicylaldiminate ligand.



A (X = H, R = isopropyl)
B (X = H, R = 2,6-diisopropylphenyl)
C (X = NO_2, R = 2,6-diisopropylphenyl)
D (X = NO_2, R = phenyl)

Chart 1

Experimental Part

Materials

Anhydrous toluene (Baker) and *n*-hexane (Carlo Erba) were obtained by distillation on K/Na alloy under dry argon and stored on molecular sieves (4Å).

Methanol (Carlo Erba), $Ni(OAc)_2 \cdot 4\ H_2O$ (OAc = acetate) (Carlo Erba), methyl ethyl ketone (MEK) and 3,5-dinitro-salicylaldehyde (Aldrich) were used as received.

Methylaluminoxane (MAO) (Witco), containing about 30 wt-% of $AlMe_3$, was stored under dry argon and used in toluene solution (4.5 M) as received.

Styrene (Aldrich) was purified by distillation under vacuum after stirring for 4 h on CaH_2. It was stored under dry argon in a refrigerator.

2,6-diisopropylaniline (Aldrich), aniline (Aldrich), diisopropylamine (Aldrich) and salicylaldehyde (Carlo Erba) were distilled *in vacuo* (ca. 1 mm Hg) and stored under dry argon in the refrigerator.

Bis(salicyladiminate)nickel(II) complexes were prepared according to a general method.[25]

As an example the procedure is described for the synthesis of bis[(3,5-dinitro-N(2,6-diisopropylphenyl)]nickel(II) complex (**C**): 3,5-dinitro-salicylaldehyde was allowed to react with an equimolar amount of $Ni(OAc)_2 \cdot 4H_2O$ and 3 equivalents diisopropylamine in 100 ml of absolute ethanol at the refluxing temperature for 2 h. After cooling, the solid was filtered and crystallized from *n*-heptane.

C was thus obtained as yellow-green crystals.[24] ^1H-NMR ($CDCl_3$): δ: 9.5 (d, 2H, aromatic);

8.4 (d, 1H, HC=N); 7.5 (m, 6H, aromatic); 7.2 (t, 2H, aromatic); 3.8 [hept, 4H, $C\underline{H}(CH_3)_2$]; 1.44 [d, 24H, $CH(C\underline{H}_3)_2$] ppm.

FT-IR: 3089 ($\nu_{C\text{-}H}$ aromatic); 2965 ($\nu_{C\text{-}H}$ aliphatic); 1621 ($\nu_{s_{CH=N}}$) cm^{-1}. mp = > 270 °C.

Bis[3,5-dinitro-N(phenyl)salicylaldiminate]nickel(II) (**D**) was obtained as yellow crystals.[24]
^1H-NMR ($CDCl_3$): δ: 9.5 (s, 2H, aromatic); 8.4 (d, 1H, HC=N); 7.5 (m, 8H, aromatic); 7.2 (t, 2H, aromatic) ppm;

FT-IR: 3083 ($\nu_{C\text{-}H}$ aromatic); 1621 ($\nu_{s_{CH=N}}$) cm^{-1}. mp = > 270°C.

Bis(N-isopropylsalicylaldiminate)nickel(II) (**A**) was obtained as green crystals.[26]

FT-IR: 3053 ($\nu_{C\text{-}H}$ aromatic); 2970 ($\nu_{C\text{-}H}$ aliphatic); 1605 ($\nu_{s_{CH=N}}$) cm^{-1}. mp = 203°C.

Bis[(N-2,6-diisopropylphenyl)salicylaldiminate)]nickel(II) (**B**) was obtained as green crystals.[27]

FT-IR: 3059 ($\nu_{C\text{-}H}$ aromatic); 2960 ($\nu_{C\text{-}H}$ aliphatic); 1606 ($\nu_{s_{CH=N}}$) cm^{-1}. mp = >320°C.

Styrene Homopolymerization Experiments

Polymerization experiments were usually carried out at 25 °C in a 50 ml Carius vessel under dry argon and magnetic stirring. In a typical procedure, the desired amount of nickel precursor, dissolved at room temperature in dry toluene (15 ml), was transferred under dry argon into the reaction vessel. Then 5 ml of styrene (44 mmol) were introduced and the desired amount of MAO (Al/Ni = 30-100 mol/mol) was added. The reaction mixture was maintained, through a thermostated oil-bath, at the desired temperature for the chosen duration. At the end of the polymerization the reaction mixture was analyzed by gas-chromatography (GC) in order to determine styrene conversion and to check the presence of oligomeric products. After pouring the mixture in a large excess of 5% aq. HCl acidified methanol the coagulated polymer was filtered, dried under vacuum, weighed and finally characterized.

Analytical Procedures

Oligomers analysis was performed by GC on a Hewlett Packard 5890 chromatograph equipped with a flame ionization detector, a SE-52 capillary column (50 m × 0.2 mm × 0.33

μm) and a Hewlett-Packard (HP) 3396 integrator. The following temperature program of the oven was adopted: 100 °C for 5 min, then the temperature was increased by a 15 °C/min heating until 250 °C was reached; this value was maintained constant for further 60 min. The oligomeric products were finally analyzed by GC/MS employing a HP 5973 Mass Selective Detector an a HP 6890 series GC System.[22] In this way it was possible to separate and identify in the oligomeric mixtures 2,3-diphenyl butene (DPB) (m/z values: 208, 193, 115, 105, 91 and 77) and 2,3,5-triphenyl-1-hexene (TPH) (m/z values: 312, 207, 193, 115, 105, 91, and 77).

Physico-chemical Measurements

The molecular weights of PS samples were determined by size exclusion chromatography (SEC) measurements, performed on a Perkin-Elmer Series 10 instrument, equipped with a Jasco 830-RI refractive index detector and an UV-VIS Perkin-Elmer LC-25 model working at 270 nm wavelength, by using a HPLC PL gel 5 μm MIXED-C column and chloroform as eluent. Calibration curve was obtained by using several monodisperse PS samples having different molecular weights.

^{1}H- and ^{13}C-NMR spectra were performed on a FT Varian Gemini 200, working at 200 and 50 MHz, respectively, by using tetramethylsilane (TMS) as internal standard.

FT-IR spectra were performed on powdered samples by using a Perkin Elmer Spectrum One spectrophotometer, equipped with an Attenuated Total Reflectance (ATR) apparatus.

Results and Discussion

Polymerization of styrene by bis[(N-substituted)salicylaldiminate]nickel(II)/MAO catalytic systems

The experiments were preliminarily carried out by using as catalyst precursors bis(salicylaldiminate)nickel(II) characterized by the absence of substituents on the phenoxy moiety and by the presence of groups with different steric hindrance directly bound to the aldimine nitrogen.

Therefore, complexes **A** and **B** have been tested in combination with MAO for the polymerization of styrene. Both complexes were previously employed by us in the activation of ethylene but they substantially resulted oligomerization catalysts.[26] However, when used in the polymerization of styrene in the presence of MAO (Table 1), they resulted appreciably active, although rather low molecular weight PS samples were formed.

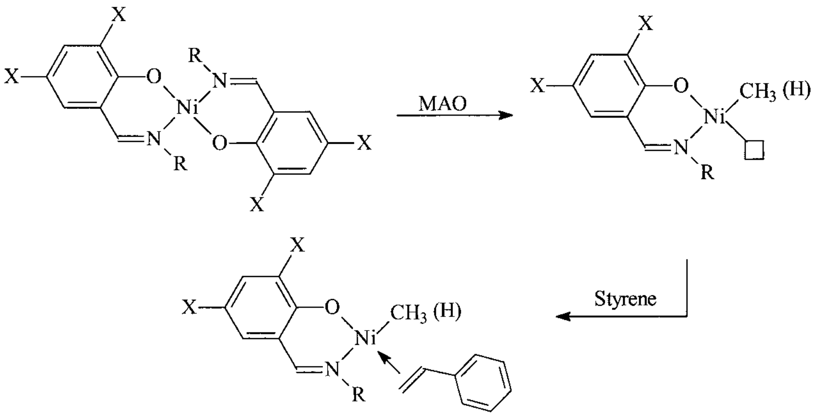
Table 1. Styrene polymerization by **A** or **B**/MAO catalytic systems. Polymerization conditions: Nickel complex, 0.04 mmol; solvent (toluene), 15 ml; styrene (5 ml), 44 mmol; $T = 25°C$; time, 1 h.

Entry	Nickel complex	Al/Ni mol/mol	Crude polymeric product				$A^{a)}$
			g	Yield (%)	$M_w{}^{b)}$ (x 10^{-3})	$PDI^{b,c)}$	
1	**A**	30	0.90	20	10	2.2	22.5
2	**A**	50	1.00	22	10	2.3	25.0
3	**A**	100	0.70	15	14	2.4	17.5
4	**B**	30	0.50	11	22	2.0	12.5
5	**B**	50	0.70	15	22	1.9	17.5
6	**B**	100	1.55	34	27	1.8	38.8

a) Activity expressed as: Kg of PS /(mol of Ni x h).
b) Determined by SEC.
c) Polydispersity index, M_w/M_n.

Analogously to what was proposed in the case of ethylene activation with the same systems,[26] bis(salicylaldiminate)nickel(II) precursors can react with MAO giving rise to a pristine monochelate methyl nickel species characterized by the presence of a vacancy able to coordinate styrene and initiate its polymerization (Scheme). These active sites are supposed to evolve into intermediate hydride species due to the growing chain termination step; in any case, they are characterized by the presence of a residual salicylaldiminate ligand whose electronic and steric requirements may significantly influence catalyst performances.[28]

Independently from the type of catalyst precursor adopted, the polydispersity index (PDI), of the resulting PS samples, as determined by the M_w/M_n ratio, was found to be near to 2. The relatively higher activity of **B** as compared with **A** and the different behaviour of the two systems in terms of activity as a function of Al/Ni molar ratio may be addressed not only to the different steric constraints around the metal sites in **A** and **B** precursors[29,30] but also to the different basic character of the aldimine nitrogen when either an alkyl group or a



Scheme

substituted phenyl ring is directly bound to it. It is noteworthy that when **A** complex was used as catalyst precursor a very low amount (yield: up to 2 %) of oligomeric products containing ca. 85 % of dimers, was formed in addition to PS. When **A** was replaced by **B** only traces of oligomeric products were obtained. However, in both cases the GC/MS analysis allowed to establish that the dimeric product was essentially constituted by 2,3-diphenyl-1-butene (DPB) and the trimeric one by 2,3,5-triphenyl-1-hexene (TPH) (Chart 2). No detectable amount of tetramers and higher oligomers was ascertained even by SEC analysis.

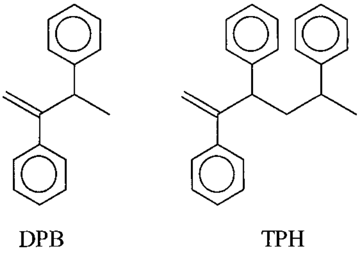


Chart 2

This occurrence is in agreement with a mechanism of oligomers formation via styrene secondary insertion which stabilizes the resulting nickel species through an equilibrium between η_1 and η_3 species, analogously to what was previously proposed.[10,22,23,31-33] In fact, the formation of these oligomers is readily explained by assuming that either one or two secondary styrene insertions on a pristine nickel hydride species occur, followed by a final primary insertion. The crude polymers were also fractionated by extraction with boiling solvents using *n*-hexane, MEK and toluene in that order. The first solvent was adopted for extracting a very low molecular weight polymer fraction, whereas the other solvents were used for dissolving a-PS and i-PS, respectively. When the crude PS samples were subjected to fractionation (Table 2), the **A**/MAO catalyst gave a higher percentage of very low molecular weight polymer in agreement with the larger oligomerization capability of this system. In all cases, the polymers were completely soluble in MEK, thus indicating that a-PS was formed, as confirmed by ^{13}C-NMR analysis.

Table 2. Characterization of the polymer fractions obtained by extraction with boiling solvents of the crude PS obtained by **A**/MAO (entry 2) or **B**/MAO (entry 6) catalysts.

Polymer fraction[a)]	Entry 2			Entry 6		
	wt.%	M_w[b)] (x 10^{-3})	PDI[b,c)]	wt.%	M_w[b)] (x 10^{-3})	PDI[b,c)]
1	23.0	3.7	1.5	4.9	5.2	1.8
2	77.0	10.0	2.2	95.1	23.8	1.9
3	0.0	-	-	0.0	-	-

[a)] 1 *n*-Hexane soluble fraction; 2 *n*-Hexane insoluble, MEK soluble fraction; 3 MEK insoluble, toluene soluble fraction.
[b)] Determined by SEC analysis.
[c)] Polydispersity index.

Polymerization of Styrene by bis[3,5-dinitro-N(substituted)salicylaldiminate]Nickel(II)/ MAO Catalytic Systems

With the aim to improve the catalytic activity two electron withdrawing substituents, such as nitro groups, were introduced on the phenoxy moiety of the salicylaldiminate ligands bound to the nickel(II). Indeed, this structural situation should reduce the electron density on the metal center and hence increase its propensity to the coordination by an electron-rich monomer, such as styrene. Moreover, the influence on catalytic performances by the bulkiness of the substituents on the N-aryl moiety of the ligand was checked. Therefore, **C** and **D** complexes were tested as catalyst precursors in combination with MAO (Table 3). On the basis of the obtained results we may conclude that the presence of the two electron withdrawing nitro groups on the ligands caused a large improvement of catalyst activity (up to 255 Kg of PS/mol Ni x h). Moreover, also the molecular weight of the resulting PS samples was significantly increased. However, when **C** was replaced by the less hindered **D** (entries 12-15, Table 3) despite a substantially similar activity, a decrease of the molecular weights was achieved, thus confirming that also steric factors around the metal play an important role in determining the competition between chain growth and termination steps.[28]

Table 3. Styrene polymerization by **C** or **D**/MAO catalytic systems. Polymerization conditions: Nickel complex, 0.04 mmol; solvent (toluene), 15 ml; styrene (5 ml), 44 mmol.

Entry	Nickel complex	Al/Ni mol/mol	Temp. °C	Time h	Crude polymeric product g	Yield (%)	M_w [b] (x 10^{-3})	PDI[b,c]	A[a]
7	**C**	30	25	1	1.90	43	121	10.7	47
8	**C**	100	25	1	3.45	78	103	10.8	86
9	**C**	100	25	4	4.00	89	99	6.0	25
10	**C**	100	25	0.33	3.40	77	37	3.5	255
11	**C**	100	70	4	3.30	74	31	2.3	18
12	**D**	30	25	1	3.31	72	51	2.8	83
13	**D**	50	25	1	3.34	74	52	3.0	85
14	**D**	100	25	1	3.65	80	28	1.8	91
15	**D**	100	25	0.33	3.40	77	23	2.2	255

[a] Activity expressed as: Kg of PS /(mol of Ni x h).
[b] Determined by SEC.
[c] Polydispersity index, M_w/M_n.

The polymers obtained in entries 9 and 13 were also fractionated with the same series of boiling solvents employed in the preceding section. As shown in Table 4, the crude polymers prepared with **C** or **D**/MAO catalysts, differently from those obtained with nickel precursors without nitro substituents, were characterized by the presence of a small amount (8-10%) of a largely polydispersed (PDI ca. 10) high molecular weight (M_w = ca. 400000 Da) MEK insoluble fraction which should be constituted by i-PS. Indeed, the ^{13}C-NMR analysis of these last fractions allowed to determine a content of mmmm pentads in the 60-70% range.

In order to elucidate the polymerization mechanism, the polymer end-chain structure of low molecular weight *n*-hexane soluble fractions of PS obtained from entry 2 and 9 was analyzed by ^{13}C-NMR.

Table 4. Characterization of the polymer fractions obtained by extraction with boiling solvents of the crude PSt obtained by **C**/MAO (entry 9) or **D**/MAO (entry 13) catalysts.

Polymer fraction[a)]	Entry 9			Entry 13		
	wt.%	M_w[b] (x 10^{-3})	PDI[b,c)]	wt.%	M_w[b] (x 10^{-3})	PDI[b,c]
1	8.1	3.7	2.0	2.5	5.2	1.8
2	82.1	44.4	3.7	89.5	29.3	2.0
3	9.8	359	10.1	8.0	413	10.3

[a)] 1 *n*-Hexane soluble fraction; 2 *n*-Hexane insoluble, MEK soluble fraction; 3 MEK insoluble, toluene soluble fraction.

[b)] Determined by SEC analysis.

[c)] Polydispersity index.

In both cases signals at 37.8 and 20.9, as well as at 36.7 and 21.5 ppm, assignable respectively to erythro and threo 2,4-diphenylbutyl end groups,[22] were detected, suggesting a secondary styrene insertion on a nickel hydride bond in the initial chain growth step. Moreover, signals at 128.4 and 133.2 ppm were present and assignable to 1,3-diphenyl-1-butenyl end-groups[14] deriving by β-hydrogen elimination from the ultimate inserted styrene secondary unit. Indeed, no detectable regioirregular arrangement of styrene units due to primary insertions was observed in the PS samples. The above data support a polymerization mechanism different from that proposed for the oligomerization, this last probably occurring at a very low extent on different catalytic species.

Conclusions

On the basis of the obtained results the following concluding remarks can be drawn:

1. Bis(salicylaldiminate)nickel(II)/MAO catalysts resulted active in the styrene

polymerization. The catalytic performances, in terms of activity and polymer characteristics, are significantly affected by the structure of the nickel precursor and by the reaction parameters.

2. The presence of electron withdrawing nitro groups on the phenoxy moiety of the ligand markedly enhanced the activity of the catalytic system. The average molecular weight of the polymer was also influenced by the bulkiness of the substituents on the N-aryl moiety.
3. The analysis of oligomeric and polymeric products suggested that they are probably derived from different catalytic species.

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