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Homo- and co-polymerization of styrene with ethylene by novel nickel catalysts

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Abstract

The homopolymerization of styrene has been studied by using catalysts based on bis(α-nitroacetophenonate)Nickel(II) [Ni(naph)$_2$] and bis(hexafluoroacetylacetonate)Nickel(II) [Ni(hfacac)$_2$] precursors and methylalumoxane (MAO) as co-catalyst. The former system displayed at room temperature a higher activity as compared with other previously reported nickel catalysts, giving rise to a substantially atactic polystyrene with a quite low molecular weight. The use of the basic and bulky tricyclohexylphosphine (PCy$_3$) as ancillary ligand allowed to increase both molecular weight (~20,000 Da) and isotacticity degree (~50%) of the polymer. On the contrary, the use of the less basic triphenylphosphine (PPh$_3$) caused a reduction of isotacticity degree. On increasing the reaction temperature at 70°C, even in absence of the phosphine ligand, both catalytic systems gave a polymer characterized by about 50% isotacticity degree. A significant further increase of isotacticity degree (65–70%) was obtained when a AlMe$_3$ free MAO was adopted in combination with the above nickel precursors. The GC/MS analysis of the oligomeric products allowed us to conclude that styrene insertion is mainly of secondary type. The above catalytic systems were found also to copolymerize ethylene with styrene, giving rise mainly to oligomeric products.

Keywords: Styrene polymerization; Styrene/ethylene copolymerization; Styrene/ethylene oligomerization

1. Introduction

It is well known that styrene may be polymerized to the isotactic polymer since the discovery of conventional Ziegler–Natta catalysts based on titanium chlorides and organoaluminium derivatives [1–3]. More recently, monocyclopentadienyl- and other titanium derivatives, combined either with methylalumoxane (MAO) or with pentafluorophenylborane and corresponding borates, were reported to give homogeneous catalysts active in the synthesis of syndiotactic poly(styrene) [4–9]. Organometallic nickel complexes have been also used in the polymerization of styrene. In particular, the cationic complex [η^3-methallyl)(η^4-cycloocta-1,5-dienyl) Ni(II)] hexafluorophosphate was reported to give low molecular weight isotactic poly(styrene) without the addition of any Lewis acid as co-catalyst [10]. The use of solvents with different polarity and phosphines as ancillary ligands for the above nickel complex allowed to markedly affect catalytic activity, molecular weight and microtacticity of the polymer [10,11]. More recently, several nickel complexes in combination with MAO have been proposed as catalysts for styrene polymerization [12–15]. However, when bis(acetylacetonate)Ni(II) [Ni(acac)$_2$]/MAO was adopted as catalyst, contradictory results concerning the microtacticity of the obtained poly(styrene) were reported. Subsequent studies evidenced that the stereoregularity of poly(styrene) is strongly dependent on the content of trimethylaluminium present in the MAO [16,17]. On the other hand, it is also known that MAO alone behaves as ionic initiator for some vinyl monomers [18]. When rather high Al/Ni molar ratios (60–90) were adopted, catalyst productivity was improved, but a detrimental effect on the polymer isotacticity degree was observed [16]. A detailed study of styrene polymerization with nickel derivatives/MAO catalysts allowed to conclude that Ni(acac)$_2$ and NiCl$_2$ were the best precursors, although quite low productivities (~220 mol of converted styrene/mol of Ni × h) and polymers with rather low molecular weight were obtained [19].

In this context, it appear very interesting to study the polymerization of styrene in the presence of novel catalytic systems based on α-nitroketonate nickel complexes which have been reported to be very versatile in the activation of

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ethylene [20,21]. Indeed, the behaviour of bis(α-nitroacetophenonate)nickel(II) [Ni(naph)$_2$] was similar to Ni(acac)$_2$ when allowed to react with organoaluminium compounds [20]. However, the higher acidity of naph [22], as compared with acac ligand [23] (p$K_a = 5.59$ and 8.8, respectively), would further decrease the electronic density on the metal centre in the Ni(naph)$_2$/MAO system, thus favouring the styrene coordination to the metal and hence its activation with respect to the Ni(acac)$_2$/MAO catalyst. In this regard, it appeared also appealing to check the activity of the bis(hexafluoroacetylacetonate)nickel(II) [Ni(hfacac)$_2$]/MAO system, considering that the pK_a of hfacac ligand is even lower (4.2) [23] than that of naph.

Finally, taking into account that the Ni(naph)$_2$/MAO catalyst was very efficient in promoting the activation of ethylene, the styrene/ethylene copolymerization by the above catalytic systems appeared also interesting to be investigated.

2. Experimental

2.1. 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 (4 Å).

Methanol (Carlo Erba), ethylene (Rivoira, >99%), tricyclohexylphosphine (PCy$_3$) (Aldrich), triphenylphosphine (PPh$_3$) (Aldrich), Ni(acac)$_2$ (Aldrich), Ni(hfacac)$_2$ (Aldrich), Ni(OAc)$_2$·4 H$_2$O (OAc = acetate) (Carlo Erba) and α-nitroacetophenone (naph) (Aldrich) were used as received.

MAO (Witco) was stored under dry argon and used either in toluene solution (4.5 M) as received, or after precipitation with anhydrous *n*-hexane for removing the impurities of trimethylaluminium.

Styrene (Aldrich) was purified by distillation under vacuum after stirring for 4 h on CaH$_2$.

Ni(naph)$_2$ was prepared by heating under vacuum (150°C at 0.1 mmHg) Ni(naph)$_2$·2 EtOH, in turn obtained from Ni(OAc)$_2$·4 H$_2$O and naph [24].

^{1}H-NMR (C$_6$D$_6$): 7.2 (m, 5H, aromatic protons), 6.85 (s, 1H, CH kelate ring).

2.2. Styrene homopolymerization experiments

Polymerization experiments were carried out in a 50 ml Carius vessel under dry argon and magnetic stirring. In a typical procedure, the desired amount of nickel precursor dissolved in dry toluene (20 ml) at the reflux temperature, eventually in the presence of the suitable phosphine ancillary ligand, was transferred under dry argon into the reaction vessel. Then, an aliquote of styrene (1 ml) was introduced and the desired amount of MAO added at 50°C. After cooling at 25°C, the residual amount of styrene was added to reach the chosen monomer/Ni molar ratio. 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 analysed 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, weighted and finally characterized.

2.3. Styrene/ethylene copolymerization experiments

Copolymerization experiments were performed in a 150 ml rocking stainless steel autoclave. In a typical procedure the desired amount of nickel precursor was introduced in a Schlenk-type vessel, dissolved in anhydrous toluene under dry argon, eventually in the presence of the phosphine ancillary ligand, and then transferred with a syringe into the autoclave under ethylene atmosphere. Subsequently the suitable amount of MAO was added to the toluene solution of the nickel precursor and the desired amount of styrene was introduced in an open glass vial in the autoclave. Finally the autoclave was pressurized with ethylene and immediately stirred for contacting the catalyst solution also with styrene. The autoclave was immersed in a thermostatic oil-bath at the desired temperature. At the end of the experiment the reaction was stopped by fast cooling the autoclave and degassing unreacted ethylene through a trap cooled at −10°C, the condensed oligomeric products were added to the liquid reaction mixture which was collected, weighted and analysed by GC. Then the polymeric product was coagulated by pouring the reaction mixture in excess methanol containing 5% aq. HCl. The polymer was filtered, dried under vacuum, weighted and finally characterized.

2.4. 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. In this way it was possible to separate the co-dimers styrene(St)/ethylene(Et), co-trimers St/Et$_2$, co-tetramers St/Et$_3$, co-pentamers St/Et$_4$, co-trimers St$_2$/Et and co-tetramers St$_2$/Et$_2$.

The individual components were identified by GC/MS analysis on a HP 5995B spectrometer, equipped with a SE-52 capillary column, by using helium as transport gas and a HP 59970C ChemStation for data processing.

2.5. Physico-chemical measurements

The molecular weights of the polymers were determined by size exclusion chromatography (SEC) measurements,

Table 1
Homopolymerization of styrene by different nickel precursors activated by MAO, eventually in the presence of a phosphine ancillary ligand (styrene: 43.5 mmol (entries 1–5) and 80 mmol (entries 6–11); solvent: toluene (20 ml))

Entry	Nickel precursor		Al/Ni (mol/mol)	PR_3		Temp. (°C)	Time (min)	Conv. (%)	TF_t[a] (h^{-1})	TF_p[b] (h^{-1})
	Type	mmol		R	P/Ni[c]					
1	$Ni(naph)_2$	0.03	30	–	–	25	20	68	3600	2400
2	$Ni(naph)_2$	0.05	30	–	–	25	240	81	176	120
3	$Ni(naph)_2$	0.03	30	Cy	1	25	20	17	900	650
4	$Ni(naph)_2$	0.05	30	Cy	1	25	240	85	184	134
5	$Ni(naph)_2$	0.05	30	Ph	1	25	240	97	211	153
6	$Ni(naph)_2$	0.08	50	–	–	70	240	100	250	91
7	$Ni(hfacac)_2$	0.08	50	–	–	70	240	100	250	226
8	$Ni(acac)_2$	0.08	50	–	–	70	240	100	250	159
9[d]	$Ni(naph)_2$	0.08	50	–	–	70	240	97	243	95
10[d]	$Ni(hfacac)_2$	0.08	50	–	–	70	240	96	230	134
11[d]	$Ni(acac)_2$	0.08	50	–	–	70	240	92	240	141

[a] Turnover frequency, expressed as: (moles of converted styrene/moles of Ni × h) and related to the total amount of methanol soluble oligomers and methanol insoluble polymer.

[b] Turnover frequency, expressed as above indicated and related to the methanol insoluble polymer.

[c] Molar ratio.

[d] MAO was purified from Me_3Al by precipitation with *n*-hexane.

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 poly(styrene) samples having different molecular weights.

Polyethylene samples were examined by differential scanning calorimetry (DSC) on a Perkin–Elmer DSC 7 instrument equipped with a CCA 7 cooling and temperature control system. The instrument was interfaced to a computer PC uniTAC 7/DX.

^1H- 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. In particular, ^{13}C-NMR spectra of ethylene/styrene copolymers were carried out at 100°C in $C_2D_2Cl_4$ solution.

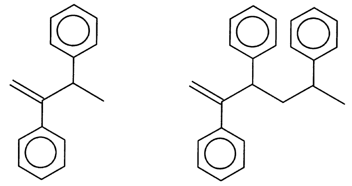
3. Results and discussion

3.1. Homopolymerization of styrene

Preliminary experiments (entries 1 and 2, Table 1) were carried out in the presence of the $Ni(naph)_2$/MAO catalyst by adopting the same conditions as previously reported for the $Ni(acac)_2$/MAO system [16] (molar ratio MAO/Ni = 30 and reaction temperature = 25°C).

As reported in entry 1, this new catalyst system displayed a quite good activity, a conversion of styrene of 68% being obtained after 20 min of reaction, corresponding to a turnover frequency to total products (oligomers + polymer) (TF_t) of 3600 h^{-1} and a turnover frequency to crude poly(styrene) (TF_p) equal to 2400 h^{-1}.

When the experiment was repeated by using a double amount of nickel precursor the same Al/Ni molar ratio and a longer reaction time (4 h), styrene was converted for 81% (entry 2). Under the above conditions TF_t and Tf_p were found to be much lower (176 and 120 h^{-1}, respectively) and the ratio between polymer and oligomers remained practically the same (about 2), TF_p being 2/3 of TF_t in both entries. This seems to indicate that no different active sites are responsible for the generation of oligomers and polymer. Indeed, if each of the above products would be generated by specific catalytic centres, these would be characterized by a different time stability and hence time evolution of their productivity, the ratio between oligomers and polymer being thus affected by the reaction time. SEC analysis of the methanol insoluble polymeric product of entries 1 and 2 showed a very low molecular weight (~1000 Da). The soluble methanol fraction in both cases, as determined by GC analysis, was characterized by the presence of dimers, trimers and tetramers. A fractional distillation allowed to isolate the dimeric (b.p.: 54–56°C/0.1 mmHg) and trimeric (72–74°C/0.1 mmHg) fractions which were characterized in more details by GC/MS and ^1H-NMR analyses. The MS spectrum of the dimeric product showed peaks at 208, 193, 115, 105, 91 and 77 *m*/*z* values, typical of 2,3-diphenyl-1-butene (DPB) (Chart 1)



DPB TPH

Chart 1.

Table 2
Fractional and characterization of poly(styrene)s obtained by different nickel precursor/MAO catalysts

Entry	Crude polymer		*n*-Hexane soluble fraction			*n*-Hexane insoluble fraction			
	M_n[a]	mmmm[b] (%)	wt-%	M_n[a]	mmmm[b] (%)	wt-%	M_n[a]	M_w/M_n[a,c]	mmmm[b] (%)
4[d]	5700	45	38	2200	36	62	19,800	3.9	48
5[e]	n.d.	20	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	500	49	61	300	42	39	14,000	1.5	50
7	6000	50	44	4000	42	56	9900	1.6	52
8	3700	40	46	2200	39	54	9000	1.4	43
9[f]	2500	50	50	1300	35	50	13,800	1.6	66
10[f]	4100	55	43	2200	40	57	11,200	1.9	70
11[f]	1900	44	59	1100	37	41	10,500	1.8	46

[a] Determined by SEC.
[b] Determined by ^{13}C-NMR analysis.
[c] Polydispersity index.
[d] PCy_3 was used as ancillary ligand.
[e] PPh_3 was used as ancillary ligand.
[f] Precipitated MAO was used as co-catalyst.

fragmentation. Accordingly, the ^1H-NMR spectrum showed, in addition to the aromatic protons in the 7–7.3 ppm region, two doublets centered at about 5.6 and 5.0 ppm, assignable to the vinylidenic protons, a multiplet at about 3.5 ppm, related to the methine group, and a doublet at about 1.3 ppm, connected with the methyl group. Analogously, the trimeric product showed a MS spectrum with peaks at 312, 207, 193, 115, 105, 91 and 77 *m/z* values, characteristic of 2,3,5-triphenyl-1-hexene (TPH) (Chart 1). Moreover, the ^1H-NMR spectrum of this product confirmed the proposed structure.

With the aim of having information about the tacticity of the polymeric products a ^{13}C-NMR analysis on the crude polymer obtained in entry 1 was performed. It is in fact known that the position of the signals of the quaternary aromatic protons of side-chain phenyl rings in poly(styrene) is related to the different configurational sequences of the monomeric units along the backbone [4,12,25]. In particular, isotactic poly(styrene) shows in the above spectral region a single peak at 146.2 ppm, connected with mmmm pentads, whereas the corresponding syndiotactic and atactic polymers display a single peak at 145.1 ppm and several peaks in the 147–145 ppm range, respectively. The ^{13}C-NMR analysis of the above mentioned polymer showed several peaks in the quaternary aromatic protons region with a content of mmmm pentads of about 30%, thus suggesting that the polymer is substantially atactic.

With the aim of verifying whether the presence of a phosphine ancillary ligand could affect the tacticity of polymer, the $Ni(naph)_2$/MAO system was modified by the presence of two different phosphines, such as PCy_3 (entries 3 and 4, Table 1) and PPh_3 (entry 5, Table 1), the former characterized by high basicity and bulkiness, the latter by a low basicity and comparable bulkiness [26,27]. Indeed, the catalytic performances of the same system when applied to ethylene activation were strongly influenced by the presence of an ancillary phosphine ligand [21].

When Pcy_3 was used, a strong reduction of activity was observed with respect to the experiments without phosphine (entry 3 vs entry 1 and entry 4 vs entry 2). Again, the catalyst productivity markedly decreased by increasing the reaction time. However, the ratio between TF_p and TF_t was substantially retained (about 2/3) and resulted quite similar to that observed for the previous experiments. The use of PPh_3 slightly increased the activity of the catalyst (entry 5 vs entry 2) whereas the ratio between oligomers and polymer remained substantially the same. The analysis of the oligomeric products gave the same results as that reported for the catalyst in absence of the phosphine ligand. The methanol insoluble crude polymeric products were extracted with *n*-hexane, in order to eliminate the trapped higher oligomers, and submitted to ^{13}C-NMR analysis for determining their microtacticity. The presence of PCy_3 (entry 4, Table 2) allowed to improve the isotacticity degree of the polymer from 30 to 48% of mmmm pentads, although still unsatisfactory. When PPh_3 was used as ancillary ligand the crude polymer showed a lower isotacticity degree (20% of mmm pentads) (entry 5, Table 2) as compared with that of the polymer obtained in absence of phosphine and therefore it was not further characterized. PCy_3 (entry 4, Table 2) allowed also to increase the molecular weight of the crude polymer, giving rise to a *n*-hexane insoluble polymer with about 20,000 Da. When the polymers obtained from experiments carried out at 70°C and with Al/Ni molar ratio equal to 50 were characterized, the $Ni(naph)_2$/MAO system gave a very low molecular weight crude product (entry 6, Table 2). However, even if with low yield (39%), a *n*-hexane insoluble poly(styrene) with a 14,000 Da molecular weight and 50% of mmmm pentads was obtained. When the $Ni(hfacac)_2$/MAO system was employed (entry 7, Table 2), the molecular weight of the crude polymer was increased to 6000 Da. However, the *n*-hexane insoluble polymer fraction was characterized by about 10,000 Da molecular weight and comparable microtacticity. Finally, the $Ni(acac)_2$/MAO catalyst, taken as a reference system, gave

Table 3
Copolymerization of styrene (St) with ethylene (Et) by different NiL_2/MAO catalysts (solvent: toluene (20 ml); reaction time: 1 h, if not otherwise specified)

Entry	NiL_2		MAO Al/Ni (mol/mol)	Temp. (°C)	P_{Et} (atm)	St in the feed		Conv. St (%)	Products[a]		
	L	mmol				mmol	mol%		Polymer (wt%)	TF_{Et}[b] (h^{-1})	TF_{St}[c] (h^{-1})
12	naph	0.10	30	25	60	65.2	15	98	0.3	2100	640
13	naph	0.10	30	25	50	43.5	13	98	0.7	1850	430
14	naph	0.10	30	25	80	65.2	12	97	1.5	2600	630
15[d]	naph	0.05	30	25	40	43.5	15	5	0	210	50
16	naph	0.10	100	25	80	65.2	12	99	0.1	3200	650
17	naph	0.03	100	0	80	65.2	12	86	0	6500	1900
18[e]	naph	0.08	50	70	70	80.0	15	100	2.0	4800	200
19[e]	hfacac	0.08	50	70	70	80.0	15	100	0.3	6400	200
20[e]	acac	0.08	50	70	70	80.0	15	100	0.2	6800	200

[a] Include oligomers and polymer.
[b] Turnover frequency expressed as: (moles of converted ethylene/moles of Ni × h) and related to the total amount of products (oligomers and polymer).
[c] Turnover frequency expressed as: (moles of converted styrene/moles of Ni × h) and related to the total amount of products (oligomers and polymer).
[d] PCy_3 was used as ancillary phosphine ligand (P/Ni = 1 mol/mol).
[e] Reaction time: 4 h.

even worse performances, both in terms of molecular weight and microtacticity (entry 8, Table 2). When MAO purified from Me_3Al was used with the same nickel precursors (entries 9–11, Table 2) a significant improvement of the polymer isotacticity degree was found, particularly in the case of $Ni(hfacac)_2$ where a 70% of mmmm pentads was achieved. This value, at our knowledge, is the best never obtained for poly(styrene) with homogeneous nickel based/MAO catalysts, even if a further improvement of both tacticity and molecular weight is required. Indeed, very recently highly isotactic poly(styrene) samples were obtained by Al_2O_3- or SiO_2-supported $Ni(acac)_2$/MAO catalysts [28]. The analysis of the oligomeric products for all the reported experiments (entries 5–11) showed the same results as described for entries 1–4, the dimeric and trimeric products being essentially constituted by DPB and TPH.

3.2. Copolymerization of styrene with ethylene

The copolymerization of styrene with α-olefins by conventional Ziegler–Natta catalysts has been reported to occur with severe limitations [13,29–32]. Indeed, in most cases the incorporation of styrene units in the copolymer was below 1% and the molecular weight of the resulting polymeric products was too low. More recently, amido half-sandwich titanocenes and zirconocenes, activated by MAO, have been reported to give ethylene/styrene copolymers characterized by a content of St units up to 35% and higher molecular weights ($20–170 \times 10^3$ Da) [33–35]. Ethylene/styrene alternating copolymers were also obtained by using titanocene complexes based on an amido-fluorenyl ligand bridged by a dimethylsilylene group and activated by triphenylmethyl tetra(pentafluorophenyl)borate [36]. Finally, very recently, polyethylene with 4-phenyl-1-butyl branches was prepared by copolymerizing ethylene with styrene in the presence of half-titanocenes/$B(C_6F_5)_3$ catalysts [37]. The above results have been ascribed to the multi-site nature of the catalytic system which is supposed to contain species able to co-oligomerize ethylene and styrene to phenylhexenes and also species able to copolymerize the formed 6-phenyl-1-hexene with ethylene. However, at our best knowledge, the copolymerization of ethylene with styrene was never previously investigated by using nickel based catalytic systems. Therefore, $Ni(naph)_2$ as well as $Ni(acac)_2$ and $Ni(hfacac)_2$ in combination with MAO were checked in the ethylene/styrene co-activation.

When the $Ni(naph)_2$/MAO catalyst was employed, by using an Al/Ni molar ratio equal to 30 and 25°C as reaction temperature (entries 12–14, Table 3), despite the high activity of the catalytic system ($TF_{Et} = 1850–2600\ h^{-1}$) and an almost quantitative conversion of styrene with TF_{St} values in the 430–640 h^{-1} range, the most part of the reaction products consisted of oligomers (>98.5 wt%).

The use of PCy_3 as ancillary ligand for modifying the $Ni(naph)_2$/MAO catalyst (entry 15, Table 3) caused a drop of activity, TF_{Et} and TF_{st} being reduced to 210 and 50 h^{-1}, respectively. Moreover, styrene was converted only for 5% and no methanol insoluble polymeric product was detected. These results are in agreement with those previously obtained in styrene homopolymerization.

The increase of Al/Ni molar ratio from 30 to 100 for the same nickel-based catalyst, although caused a higher productivity related to both ethylene and styrene, further reduced the relative amount of the polymeric product (entry 16 vs entry 14, Table 3). The lowering of reaction temperature at 0°C (entry 17, Table 3) allowed to significantly improve the catalytic activity (TF_{Et} and $TF_{St} = 6500$ and 1900 h^{-1}, respectively) but it was accompanied by a detrimental effect on the yield of methanol insoluble polymeric product which was substantially absent.

Finally, when the reaction temperature was increased up to 70°C and an intermediate Al/Ni molar ratio (50) was used (entry 18, Table 3) a decrease of catalyst productivity was ascertained, although TF_{Et} and TF_{St}, owing to the increased

Table 4
Characterization of oligomeric and polymeric fractions of the products obtained in the co-polymerization of styrene with ethylene by different NiL_2/MAO catalysts

Entry	Homo- and co-oligomers distribution[a] (mol%)										Polymer Et-units[b]
	C_4	C_6	C_{8+}	C_{10+}	St–Et	St–Et_2	St–Et_3	St–Et_4	St_2-Et	St-$_2$-Et_2	(mol%)
12	37.0	8.0	2.3	1.1	41.4	7.3	0.6	0.0	2.0	0.3	75
13	26.3	19.2	10.8	2.8	23.0	11.7	3.4	0.6	1.6	0.6	74
14	47.9	13.2	4.6	2.6	20.4	7.0	1.6	0.7	1.8	0.2	0
15	51.1	9.7	3.0	1.6	26.7	7.9	0.0	0.0	0.0	0.0	–
16	32.3	13.2	7.0	4.2	28.9	11.6	1.6	0.4	0.7	0.1	100
17	29.1	12.7	4.5	2.3	39.0	10.5	1.0	0.2	0.6	0.1	–
18	21.9	10.3	7.1	6.1	28.1	13.5	4.2	1.1	4.0	3.7	100
19	29.9	20.4	7.3	6.3	19.3	9.2	3.5	0.9	1.3	1.9	49
20	33.7	25.1	8.7	7.5	9.5	6.8	3.3	1.6	1.4	2.4	82

[a] Determined by combining GC and GC/MS analyses.

[b] Determined by ^{1}H-NMR analysis of the methanol insoluble polymeric product.

reaction time (4 h) and the complete conversion of styrene, have to be considered as minimum values. However, under these adopted conditions the relative amount of polymeric product was increased (2 wt%), even if this appeared to be very unsatisfactory. The use of different nickel precursors, such as $Ni(hfacac)_2$ and $Ni(acac)_2$ in combination with MAO (entries 19 and 20, respectively, Table 3), under the same conditions as those adopted for entry 18, improved the catalytic performances only towards oligomeric products.

Therefore, all the reported data indicate that, even if the above systems are very active in the ethylene/styrene co-activation, they produce substantially only oligomeric products, particularly when an ancillary phosphine ligand is added.

However, it appeared interesting to characterize both oligomeric and polymeric products in order to have information on the mechanism of the co-activation process.

The characterization of oligomers by combined GC, GC/MS and ^{1}H-NMR analyses allowed to identify the individual components and their quantitative distribution. As reported in Table 4, in all cases the oligomeric products consist of ethylene homo- and co-oligomers, no homo-oligomers of styrene being present. Moreover the ethylene homo-oligomers usually prevail in the reaction products, but this occurrence is particularly enhanced when the $Ni(naph)_2$/MAO catalyst was used at room temperature (entries 13–16, Table 4).

This is even more evident when Pcy_3 was added as ancillary phosphine ligand (entry 15). Indeed, the presence of the phosphine drastically reduced the catalytic activity, TF values for both ethylene and styrene being reduced of about one order of magnitude. In particular, only 5% of styrene was converted and no polymer at all was formed. Moreover, almost ethylene homo- and co-dimers and trimers were obtained, thus confirming that the phosphine ligand strongly modifies the characteristics of nickel sites, orienting the reaction essentially toward oligomeric products. When the reaction temperature was increased to 70°C, the catalytic systems, almost independently from the nickel precursor used, gave products whose distribution was shifted towards higher oligomers. The $Ni(naph)_2$/MAO catalyst gave (entries 12 and 13) a polymeric product with a content of styrene units, as determined by ^{1}H-NMR analysis, of about 25 mol% (Table 4), according to an arrichment with respect to comonomers feed (styrene $\leq$ 15 mol%). However, in entries 16 and 18 the small amount of polymer obtained was essentially polyethylene (Table 4). Indeed, the polymers did not show any IR band associated with side chain phenyl rings of styrene co-units and exhibited a doublet near 720 cm^{-1}, typical of polyethylene. Accordingly, DSC spectrum of the polymer obtained in entry 18 showed a melting point at 124.5°C.

When $Ni(hfacac)_2$/MAO and $Ni(acac)_2$/MAO catalysts used (entries 19 and 20, respectively, Table 4) polymeric products with 51 and 18 mol% of styrene units were obtained, respectively.

The copolymeric samples were characterized by ^{13}C-NMR analysis in $C_2D_2Cl_4$ at 100°C, in order to have information on the distribution of the co-monomeric units along the backbone.

The ^{13}C-NMR spectrum (Fig. 1a) of the polymeric product obtained with the $Ni(naph)_2$/MAO catalyst (entry 13), in addition to an intense signal at 29.7 ppm, due to methylene groups embedded in long polymethylene sequences [36], as expected on the basis of a 74 mol% content of ethylene co-units, showed also signals at 27.2 and 37 ppm. The former is assignable [32] to methylene groups in β-position to the main chain tertiary carbon atom of an adjacent styrene unit ($-CH(Ph)-CH_2-\mathit{C}H_2-(CH_2)_n-$), and the latter may be related [32] to a methylene group in α-position to the same styrene moiety ($-CH(Ph)-\mathit{C}H_2-(CH_2)_n-$), both situations being diagnostic of styrene units adjacent to polymethylene sequences. Moreover, signals centered at 40.4 and 43 ppm were present at lower fields, assignable to main chain tertiary carbon atoms of styrene units and to methylene groups in $-CH(Ph)-CH_2-$

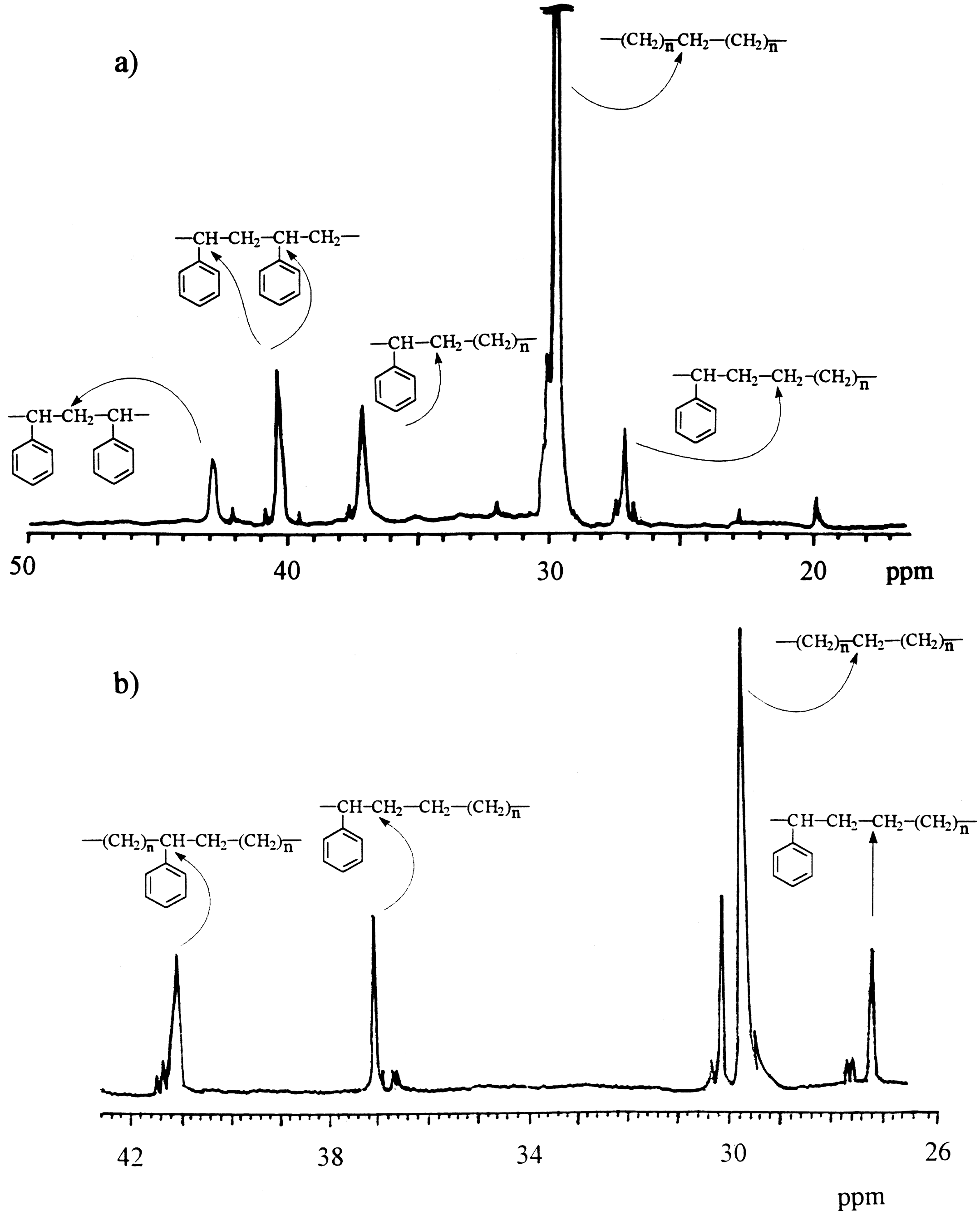


Fig. 1. ^{13}C-NMR spectra in $C_2D_2Cl_4$ solution at 100°C of ethylene/styrene copolymers: (a) with 26 mol% of styrene co-units and prepared with the Ni(naph)$_2$/MAO system (entry 13); (b) with 18 mol% of styrene co-units and prepared with the Ni(acac)$_2$/MAO system (entry 20).

CH(Ph)– sequences, respectively. Taking into account that resonances centered around 25 and 45 ppm, typical of alternating ethylene/styrene sequences [36], are not present in the above spectrum, it is reasonable to conclude that this polymeric product is substantially constituted by a blocky distribution of the two co-units. The polymeric product prepared by the Ni(hfacac)$_2$/MAO catalyst (entry 19), containing 51 mol% of styrene units, is also characterized by a blocky structure, according to the ^{13}C-NMR spectrum, substantially equal to that of the above described sample. This was also confirmed by DSC analysis which showed a T_g at 65°C and a melting point at 121°C, related to blocks of styrene and ethylene co-units, respectively (Fig. 2). Finally, the polymer prepared by the Ni(acac)$_2$/MAO system (entry 20) and containing 18 mol% of styrene units was examined by ^{13}C-NMR spectrometry. The spectrum (Fig. 1b) showed resonances at 29.7 ppm, related to methylene groups embedded in a polymethylene sequence, at 27.2 and 37 ppm, belonging to methylene groups in β and α position to an adjacent styrene unit, respectively, and at about

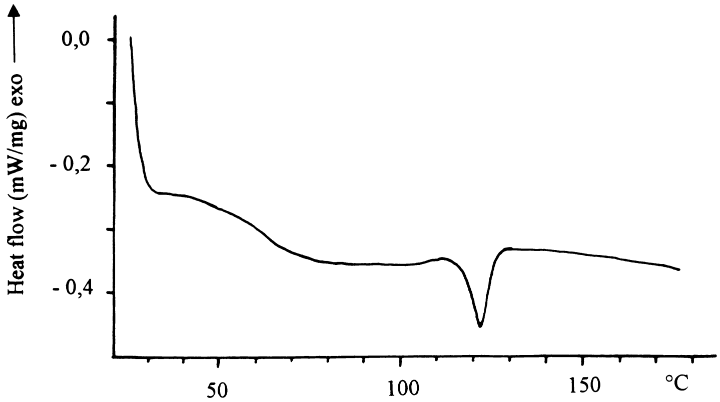


Fig. 2. DSC trace of the ethylene/styrene copolymer containing 51 mol% of styrene co-units prepared by the Ni(hfacac)$_2$/MAO system (entry 19). Heating rate = 10°C/min.

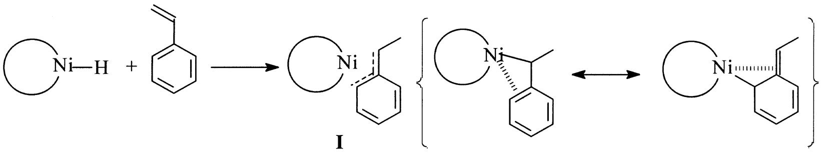
41 ppm, typical of main chain tertiary carbon atoms of styrene co-units adjacent to long blocks of ethylene units, thus suggesting that this polymeric product is characterized by substantially isolated styrene units.

Therefore, despite the very low amount of polymeric products obtained in all copolymerization experiments, the characteristics of the obtained copolymers appear to be interesting because, changing the type of nickel precursor and reaction conditions, it is possible to vary in a wide range both copolymer composition and co-units distribution.

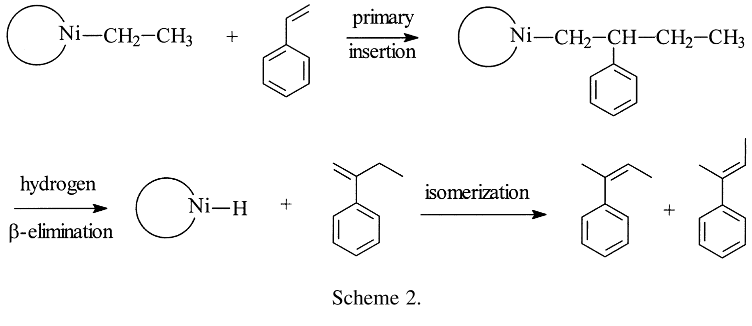
3.3. Mechanistic implications

As previously mentioned in styrene homopolymerization experiments, the accurate analysis of the oligomeric products has allowed to ascertain that the dimeric and trimeric products are essentially constituted by DPB and TPH (Chart 1). The formation of these products is readily explained by assuming that either one or two secondary styrene insertions on a pristine nickel hydride species occur, respectively, followed by a final primary styrene insertion. Indeed, a secondary insertion of styrene stabilizes the resulting intermediate species (**I**) by a π-benzylic resonance (Scheme 1), analogously to what previously proposed [10]. The same mechanism is still valid for explaining the formation of polystyrene. In fact, the macromolecular chain growing proceeds through many subsequent secondary styrene insertions until a primary styrene insertion causes chain termination. Indeed, when a primary styrene insertion occurs, the nickel intermediate species is no more stabilized by π-benzylic resonance and chain termination is favoured by a hydrogen β-elimination mechanism, a nickel-hydride species still active for continuing the process being formed.

When the oligomeric products of styrene/ethylene co-activation were examined in detail by ^{1}H-NMR and GC/MS analyses, it was possible to verify that the co-dimers are mainly constituted by 2-phenyl-1-butene and a *trans*-/*cis*-2-phenyl-2-butene mixture. This occurrence may be rationalized according to the above-mentioned mechanism (Scheme 2), where isomerization to internal olefins is metal-assisted through a secondary insertion of the vinylidenic olefin followed by β-hydrogen elimination.



Scheme 1.



Scheme 2.

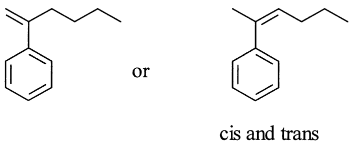


Chart 2.

Moreover, as far as the components of co-trimer, co-tetramer and co-pentamer fractions containing two styrene units and variable amounts of ethylene co-units are concerned, the GC/MS analysis, combined with ^{1}H-NMR spectrometry, gave useful indications about the sequences of the two types of monomeric units in the above co-oligomers. In particular, the St–Et$_2$ fraction is mainly constituted by unsaturated isomers which may be structurally referred to the saturated skeletal of 2-phenylhexane (Chart 2).

Moreover, it was observed that in the co-oligomeric mixture containing at least two styrene units are mainly present as 2,3-diphenylbutenyl end-groups (Chart 3).

Therefore, when styrene is activated in the presence of ethylene, the same mechanism reported for its homopolymerization is valid; however, now ethylene competes with styrene and, considering that hydrogen β-elimination is quite easy in polymethylene growing chain on nickel sites, the prevalence of oligomeric products in the ethylene/styrene co-activation may be explained. However, after a secondary styrene insertion, due to energetic reasons, a subsequent styrene insertion of the same type is favoured with respect to a primary one, even in the presence of ethylene in the feed, and this can explain the tendency of the nickel catalyst to give copolymers with a blocky structure, although in low yield.

4. Conclusions

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

1. Bis(α-nitroacetophenonate)Ni(II) precursors, when combined with MAO as co-catalyst, displayed a much higher activity as compared with previous reported nickel based catalysts in styrene activation. Moreover, the structural characteristics of polystyrene may be easily modulated by varying the kelate ligand on the nickel centre as well as reaction parameters, such as temperature, presence of an ancillary phosphine ligand and type of aluminium co-catalyst. In particular, when Me$_3$Al was removed from MAO, a remarkable improvement of molecular weight and isotacticity degree (up to 70%) was obtained.
2. The same catalytic systems were also active in the copolymerization of styrene with ethylene, although oligomeric products were mainly obtained. Once again, by changing reaction conditions and nature of the nickel precursor it was possible to affect not only the copolymer composition but also its structural characteristics, thus obtaining block copolymers in the 50–75 mol% range of ethylene units and copolymers with substantially isolated styrene co-units containing more than 80 mol% of ethylene moieties.
3. Finally, the structural characterization of oligomeric products allowed to clear the reaction mechanism, thus indicating that secondary styrene insertions are favoured in both homo- and co-polymeric products, primary insertion favouring β-hydrogen elimination.

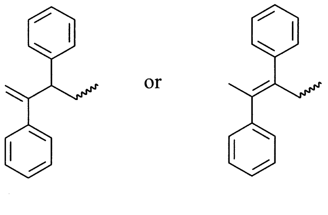


Chart 3.

Acknowledgements

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