# Isospecific Oligo-/Polymerization of Styrene with Soluble Cationic Nickel Complexes. The Influence of Phosphorus(III) Ligands

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ABSTRACT: The influence of several phosphorus(III) ligands upon the activity and the stereoregulation ability of the soluble organometallic complex $[Ni(\eta^3\text{-(2-methylallyl)})(\eta^4\text{-COD})]PF_6$ (COD = 1,5-cyclooctadiene), **1**, is studied. There is a general increase of the catalytic activity which can be associated with the P(III) ligand's lability. A detailed analysis of the mass distribution and microstructure is carried out by GPC and $^1$H and $^{13}$C NMR of the solvent-fractionated polymers. In the majority of cases, regioregular low molecular weight polymers with the structure $PhCH{=}CH_2[CH(Ph)CH_2]_nCH(Ph)CH_3$ are obtained. The addition of bulky phosphines, such as $P(o\text{-Tol})_3$ (*o*-Tol = *o*-tolyl) and $PCy_3$ (Cy = cyclohexyl), affords highly isotactic oligomers (≈90%). For the latter, the regioselectivity of the chain growth is broken during the insertion of the last monomer, which results in the formation of a tail-to-tail end group, $CH_2{=}C(C_6H_5)CH(C_6H_5)CH_2-$. The superimposed effects of $\eta^3$-coordination of the chain end and the large stereochemical influence of these ligands seem to be the reason for the observed isospecifity.

## Introduction

Over the past few years, there has been considerable interest in the polymerization of styrene using soluble catalytic systems. These are based mainly on metals lying in the extremities of the transition-metal block. In the early-transition side, compounds of the type $Cp_nMR_{4-n}$ ($n = 0$ or 1) together with a cationic generator cocatalyst ($AlR_3$, methylaluminoxane, $B(C_6F_5)_3$, or $[HNR_3][B(C_6F_5)_4]$) are very effective in the syndiospecific (M = Ti)[1,2] or nonstereospecific (M = Zr)[2,3] polymerization of styrene. In the late-transition end, nickel based systems such as $Ni(acac)_2$ + methylaluminoxane[1b] and neutral allyl dimer complexes alone[4] or modified by electron-deficient additives [*e.g.*, $CCl_3CHO$,[4b] $(CX_3)_2CO$ (X = Cl, F)[5]] are active nonstereospecific styrene polymerization catalysts.

In previous studies,[6] we reported the use of the aluminum-free cationic complex $[Ni(\eta^3\text{-(2-methylallyl)})(\eta^4\text{-(1,5-cyclooctadiene)})]PF_6$, **1**, as a very active homogeneous catalyst precursor for the low molecular weight polymerization of styrene. According to the classical work of Wilke and co-workers, the addition of phosphine and phosphite ligands to allyl nickel compounds strongly influences their activity and selectivity toward C−C bond formation reactions.[7] Particularly, in the case of **1** + $PCy_3$ (Cy = cyclohexyl), we reported the first case of isotactic polymerization of styrene performed in the homogeneous phase.[8] These results, together with the chemical isolation from a catalytic mixture of a cationic Ni complex containing an $\eta^3$-$CH(Me)C_6H_5$ ligand (the product of the insertion of styrene into a Ni−H bond), stressed the importance of this type of bonding in the growth of the polystyryl chain and ruled out a mechanism of simple cationic polymerization.[8,9] This has been confirmed by the activity and stereoselectivity exhibited by a series of cationic $\eta^3$-benzyl nickel complexes in the polymerization of styrene.[10] Besides heterogeneous Ziegler−Natta catalysts,[11] a homogeneous system based on $Ni(acac)_2$/methylaluminoxane/$NEt_3$ is known to produce isotactic and high molecular weight polystyrene.[12]

In this paper, we present a study of the influence of the nature and amount of a series of monophosphine ligands on the activity and stereospecificity of **1**. For the latter purpose, mass and microstructural analyses of the fractionated polymer samples are carried out. Attempted rationalization of those results in light of phosphine semiempirical data as the Tolman's electronic ($\chi$) and steric ($\theta$) parameters[13] is presented. Part of this work has been reported in preliminary form.[8]

## Experimental Section

**Materials.** All manipulations and reactions were carried out under an atmosphere of dinitrogen (<10 ppm oxygen or

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water) using standard Schlenk vessel and vacuum-line techniques.

All the solvents were predried over activated 4-Å molecular sieves and then distilled under an atmosphere of argon from sodium [tetrahydrofuran, toluene, light petroleum (bp 40−60 °C) and diethyl ether] or calcium hydride (dichloromethane). Styrene was predried, distilled under vacuum from calcium hydride, and collected under argon. The preparation of [Ni($\eta^3$-(2-methylallyl))($\eta^4$-COD)]$PF_6$, **1**, was carried out as described before.[6] NMR solvents were dried over 4-Å molecular sieves, degassed by freeze−pump−thaw cycles, and stored under argon. The phosphorus(III) compounds were purified by recrystallization from acetone ($PCy_3$, Aldrich) and methanol ($PPh_3$, Aldrich), distilled under vacuum ($PMe_3$, $P^nBu_3$, $P(OPh)_3$, Aldrich; $P^tBu_3$, Strem Chemicals), or used as received (P(*o*-Tol)$_3$, Pressure Chemical Co.). Phosphine purity was confirmed by $^{31}P$ NMR.

**Polymerization Reactions.** The polymerization reactions were carried out in Schlenk tubes or in stainless-steel autoclaves (for highly exothermic reactions) immersed in a thermostated water bath controlled to ±0.5 °C and with a stirring rate of 500 rpm. In a typical experiment, styrene (300 mmol) was introduced into the reaction vessel. Once thermal equilibrium has been reached, a thermostated solution of **1** (0.3 mmol) with a measured amount of phosphine was added immediately after preparation. After 2 h, the reaction was terminated by addition of methanol or by flushing the solution with air in order to decompose the catalyst. (In very fast and exothermic polymerizations, the reaction time was shorter since 100% conversion was attained in less than 2 h. In this case, the reaction temperature was monitored with a thermocouple and the time of reaction assigned to the maximum of the temperature peak. Total consumption of styrene was confirmed by GC.) The decomposed catalyst was removed from the reaction mixture by filtration on a silica gel bed. The solvent and unreacted styrene were evaporated to dryness under reduced pressure.

**Fractionation.** The resulting tacky polymers were exhaustively extracted with methanol at room temperature until complete reduction to powder was observed. After filtration and evaporation, a methanol-soluble fraction ($M_s$) of oligomers and a methanol insoluble fraction ($M_i$) of polymer were obtained. In selected samples, the methanol insoluble fractions were further fractionated by exhaustive extraction with boiling *n*-hexane. The resulting hexane-soluble ($H_s$) and hexane-insoluble ($H_i$) new fractions were evaporated and dried to constant weight.

**Molecular Mass Analysis.** Most of the collected fractions were characterized by gel permeation chromatography (GPC) using three columns of Microstyragel (100, 500, and $10^4$ Å; 30 × 0.8 cm). THF was used as a solvent at a flow rate of 1 $cm^3$ $min^{-1}$, and the detection was made with a Waters R401 refractometer. Polymer average molecular weights ($\bar{M}_n$) were also calculated by determination of the end-group concentration by UV spectroscopy,[14] in a Perkin-Elmer Lambda 15 spectrophotometer.

**NMR Analysis.** The $^1H$ and $^{13}C$ NMR spectra of the polymer fractions in 1,2-tetrachloroethane-$d_2$ were run on a AM 200 Bruker spectrometer and on a Unity 300 Varian spectrometer at 120 °C. Hexamethyldisiloxane (HMDS) was used as internal reference ($\delta$ $^{13}C$ 2.0, $\delta$ $^1H$ 0.06 from TMS), and the chemical shifts were converted to the TMS scale. $^{31}P$ NMR spectra were referenced to external $H_3PO_4$ (85%). Nucleophilic substitutions of COD by P(*o*-Tol)$_3$ or $PCy_3$ in complex **1**, in $CD_2Cl_2$, were monitored by $^1H$, $^{13}C$, and $^{31}P$ variable-temperature NMR.

**DSC Analysis.** Differential scanning calorimetry measurements were performed in a DSC 101 from Setaram. The experiments were carried out in the range 20−250 °C, at a scanning rate of 10 °C $min^{-1}$.

## Results and Discussion

In general, the addition of phosphorus(III) ligands to complex **1** causes substitution of the weaker cyclooctadiene ligand. In the case of $PPh_3$, this substitution was studied by Souza[15] using $^1H$ and $^{31}P$ NMR. The $^1H$ studies reveal the addition of 1 equiv of $PPh_3$ to **1** results in the instantaneous formation of an approximately equimolar mixture of [Ni($\eta^3$-(2-methylallyl))($PPh_3$)$_2$]$PF_6$ [16] and unreacted **1**; the addition of 2 equiv of $PPh_3$ gives rise to the total conversion of **1** into the bis(phosphine) compound. In both cases, no species containing only one phosphine ligand are detected. This is confirmed in the $^{31}P$ NMR studies which, at room temperature, show a single resonance corresponding to the bis(phosphine) nickel complex, even upon the addition of large excesses of $PPh_3$ (*e.g.*, 10:1). The line shape and chemical shift of this resonance are invariant with $PPh_3$ concentration, and a second peak of free phosphine sharpens out progressively with decreasing temperature (room temperature to −60 °C). This behavior has been described by Tolman for $NiL_4$ compounds[17a] and is compatible with a “fast exchange and extensive dissociation” process of the type

$$[Ni(\eta^3\text{-(2-methylallyl))}(PPh_3)_2]^+ \leftrightarrows [Ni(\eta^3\text{-(2-methylallyl))}PPh_3]^+ + PPh_3 \quad (1)$$

Similarly, the formation of a bis(phosphine) complex [Ni($\eta^3$-(2-methylallyl))($PR_3$)$_2$]$PF_6$ is observed for all cases studied below,[18] and a dissociative behavior is also found for these species although involving different degrees of phosphine dissociation and exchange rates, which depend on the electronic and size features of each ligand.

The new phosphine-substituted catalytic precursors markedly affect the course of the reaction of oligo-/polymerization of styrene. The experimental results concerning the effect of the phosphorus(III) ligands on the activity of **1** and on the polymer microstructure are summarized in Table 1.

**Catalytic Activity.** The activity of the phosphine modified catalytic precursor is strongly dependent both on the nature of the *in situ* added ligand and on the $PR_3$/Ni ratio. Several phosphorus ligands covering a wide range of basicities and cone angles have been tested (Table 1, Figures 1 and 2). Plotting, as in Figure 1, the turnover frequency ($N_t$)[20] *vs* Tolman’s electronic parameter immediately separates the phosphines into families: the alkyl phosphines, the aryl phosphines, and a phosphite. The values of the $PR_3$ cone angles are indicated between parentheses.

The addition of 1 equiv of phosphorus ligand to precursor **1** generally increases the catalytic activity of this system. With the exceptions of $PCy_3$ and $P^tBu_3$, the activities of phosphine modified **1** are higher than those observed for unmodified precursor.

The most notorious case is that of $PPh_3$. At 10 °C (run 5), a turnover frequency of ≈ 17 $s^{-1}$ is measured, and at 25 °C, this system becomes so active that the reaction is immediately triggered when the first drop of catalyst solution contacts the thermostated styrene, giving rise to a very exothermic (thermally autoaccelerated) and almost instantaneous reaction. In the latter conditions, the measurement of an exact value of $N_t$ is almost impossible, although it can be estimated to be in the range of 100−150 $s^{-1}$. In contrast with pure, unmodified **1**,[6] this is a quite robust system since it is not deactivated by the high temperatures attained in the reaction vessel (≈130 °C). This enormous activity enhancement in relation to either unmodified **1** (run 1) or **1** modified with 2 equiv of $PPh_3$ (run 6) may be attributed to a higher effective concentration of a very reactive 14 electron monophosphine catalyst precursor species, [Ni($\eta^3$-(2-methylallyl))$PPh_3$]$^+$.

**Table 1. Influence of the *in Situ* Addition of Phosphorus Ligands on the Reaction of Polymerization of Styrene Catalyzed by 1 (Solvent, $CH_2Cl_2$, 10 $cm^3$; Catalyst, 0.3 mmol)**

| run | ligand ($PR_3$) | $[PR_3]/[Ni]$ | styrene, mmol | $T$, °C | time, min | convsn, % | $N_t$,[a] $min^{-1}$ | $M_i$ fraction, % | $\bar{M}_n$[b,c] | $\bar{M}_w/\bar{M}_n$[d] | $P_m$[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | 300 | 10 | 120 | 11 | 0.9 | 91 | 1400 | 1.7 | 0.65 |
| 2 | | | 300 | 25 | 120 | 26 | 2.2 | 69 | 1200 | 1.5 | |
| 3 | $P(OPh)_3$ | 1 | 311 | 10 | 120 | 95 | 8.2 | 93 | 1000 | 1.5 | 0.69 |
| 4 | $P(OPh)_3$ | 1 | 304 | 25[f] | 5.5 | 100 | 189 | 79 | 820 | 1.7 | |
| 5 | $PPh_3$ | 1 | 304 | 10[f] | 1 | 100 | 1013 | 84 | 740 | 1.4 | 0.62 |
| 6 | $PPh_3$ | 2 | 292 | 10 | 120 | 84 | 6.8 | 81 | 710 | 1.4 | 0.66 |
| 7 | $P(o\text{-Tol})_3$ | 1 | 304 | 10 | 120 | 79 | 6.7 | 89 | 840[g] | 2.0 | 0.75 |
| 8 | $P(o\text{-Tol})_3$ | 2 | 306 | 10 | 120 | 86 | 7.3 | 83 | 1100[g] | 1.7 | 0.78 |
| 9 | $P(o\text{-Tol})_3$ | 5 | 295 | 10 | 129 | 95 | 7.8 | 90 | 1200[g] | 1.7 | 0.76 |
| 10 | $PMe_3$ | 1 | 302 | 10[f] | 48 | 100 | 48 | 18[h] | 320[h] | 1.6 | |
| 11 | $PMe_3$ | 2 | 307 | 10[f] | 35 | 100 | 35 | 26[h] | 303[h] | 1.6 | |
| 12 | $P^nBu_3$ | 1 | 314 | 10[f] | 31 | 100 | 34 | >99.5 | 860 | 1.5 | 0.77 |
| 13 | $P^nBu_3$ | 1 | 297 | 25[f] | 2.75 | 100 | 360 | 74 | 730 | 1.6 | |
| 14 | $P^nBu_3$ | 2 | 299 | 25 | 120 | 2 | 0.2 | | | | |
| 15 | $PCy_3$ | 1 | 298 | 10 | 120 | 11 | 0.9 | 58 | 1700 | 1.5 | 0.90 |
| 16 | $PCy_3$ | 2 | 302 | 10 | 120 | 9 | 0.8 | 48 | 1800 | 1.6 | 0.89 |
| 17 | $PCy_3$ | 5 | 300 | 10 | 120 | 9 | 0.8 | 46 | 1700 | 1.6 | 0.87 |
| 18 | $PCy_3$ | 1 | 296 | 25 | 120 | 22 | 1.8 | 80 | 980 | 1.4 | |
| 19 | $P^tBu_3$ | 1 | 301 | 10 | 120 | 3 | 0.3 | 69 | 1700[j] | 3.5 | 0.61 |
| 20 | $P^tBu_3$ | 1 | 298 | 25[i] | 120 | 6 | 0.5 | 61 | 2000 | 2.0 | 0.51 |

[a] Turnover frequency. [b] Methanol-insoluble fraction. [c] UV. [d] GPC. [e] $^{13}C$ NMR. [f] Exothermic reaction. [g] Bimodal distribution. [h] Methanol-soluble fraction. [i] Catalyst decomposition. [j] Multimodal distribution.

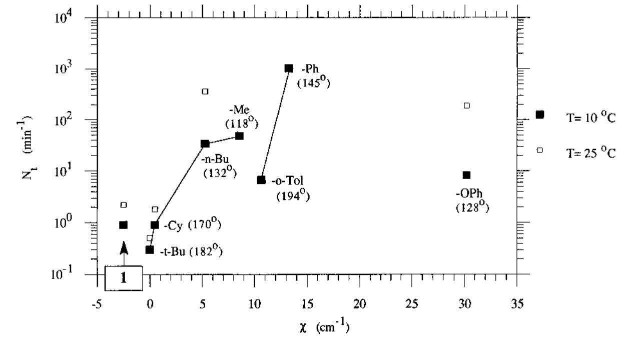


**Figure 1.** Plot of the turnover frequency ($N_t$) *vs* Tolman's electronic parameters ($\chi$) of the $PR_3$ ligands added in the oligo-/polymerization of styrene with complex **1** ($[PR_3]/[Ni] = 1$), at 10 and 25 °C. The corresponding Tolman's cone angles are indicated between parentheses.

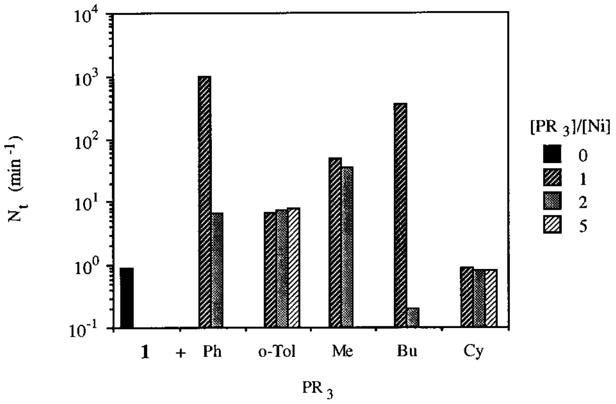


**Figure 2.** Influence of the $[PR_3]/[Ni]$ ratio on the turnover frequency ($N_t$) of complex **1** ($P^nBu_3$, 25 °C; others at 10 °C).

The activity measured upon the addition of 1 equiv of $P(o\text{-Tol})_3$ is substantially smaller (run 7; $N_t = 6.7$ $min^{-1}$). Taking into consideration that the basicity of $P(o\text{-Tol})_3$ is similar to that of $PPh_3$ but with a much higher steric demand (194° *vs* 145°) one can conclude the important role of the steric factor in the determination the reaction rate.

A similar conclusion is obtained in the case of the trialkylphosphine family: the activities decrease with increasing cone angles ($PMe_3 > P^nBu_3 \gg PCy_3 > P^tBu_3$). Besides the large sizes of $PCy_3$ (170°) and $P^tBu_3$ (182°), one has to consider their very good donor properties which originate strong dissociation bond energies for the corresponding Ni–P bond.[13b] In fact, it is observed that these coordinated phosphines do not exchange appreciably with free ligand in solution, unlike the other more labile members of the family.[17b,18] This exchange process has to be borne in mind when considering the catalytic conditions where the styrene competes with the phosphorus ligand for the same coordination positions.

In the specific case of $P^tBu_3$ (runs 19 and 20), the polymerization mixture does not acquire the characteristic deep red color of the Ni($\eta^3$-benzyl) complexes,[8-10] meaning the steric hindrance of the ligand prevents $\eta^3$-stabilization of the polystyryl chain and originates subsequent decomposition of the system (radical or other). This is confirmed 3-fold: (a) visual decomposition of the catalytic system, with precipitation of colloidal nickel, at 25 °C, (b) multimodal mass distribution (not common in this system); and (c) very atactic samples when compared to the other cases.

At first glance, an odd behavior could be attributed to $P(OPh)_3$ (runs 3 and 4), the most acidic ($\chi = 30.20$ $cm^{-1}$) and one of the less sterically demanding ($\theta = 128°$) of the ligands studied. In this case, the activity is lower than with most of the more basic and bulky phosphines. However, this can be explained by the better $\pi$ acceptor properties of the phosphites in relation to phosphines, which are able to accommodate metal back-donated electron density through their P–O $\sigma^*$ molecular orbitals. In the case of late-transition metals like Ni, this results in higher bond dissociation energies for $M{-}P(OR)_3$.[13b]

In conclusion, the influence of these ligands is not straightforward if one uses a single criterion of basicity or size. Nevertheless, bearing in mind that we only investigated a limited number of ligands, one can say that *within* each structural family (*e.g.* trialkyl-, triarylphosphines), the cone angle seems to control the activity. For instance, in the case of the trialkylphosphine family, one can notice a steric threshold for the activity in the polymerization of styrene lying around 180°. Comparing the activities *between* families, it

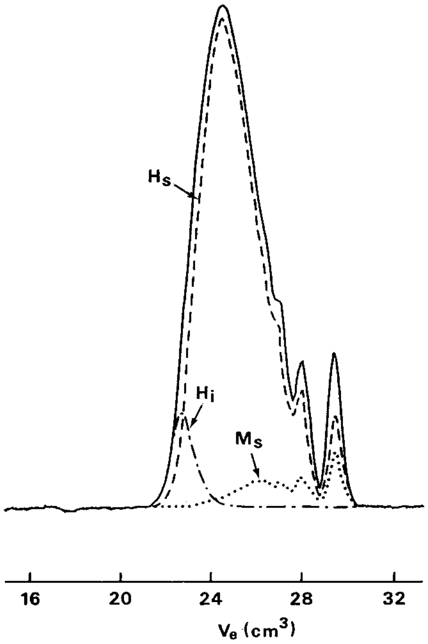


**Figure 3.** GPC curves of polystyrene from run 3 [10 °C, with 1 equiv of $P(OPh)_3$]. The peaks in the right correspond to the styrene dimer, trimer, and tetramer (shoulder), respectively. The nonfractionated sample (—) has been fractionated into 7% of a methanol-soluble fraction ($M_s$; $\bar{M}_n = 420$; $\bar{M}_w/\bar{M}_n = 1.37$), 86% of a hexane soluble/methanol-insoluble fraction ($H_s$; $\bar{M}_n = 960$; $\bar{M}_w/\bar{M}_n = 1.47$; $P_m = 0.69$), and 7% of a hexane insoluble fraction ($H_i$; $\bar{M}_n = 3500$; $\bar{M}_w/\bar{M}_n = 1.13$; $P_m = 0.74$).

seems that, for similar $\theta$ values, the dissociation capacity of the ligand in the bis(phosphine) species controls the activity. The higher this capacity, the higher the catalytic activity.

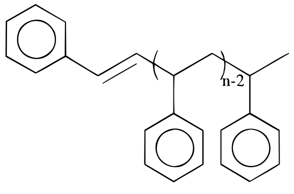
The polystyrene molecular weights vary in an inverse order to that observed for the turnover frequency. In general, the value of $\bar{M}_n$ rises with increasing size, while for similar cone angles the most dissociative ligand gives lower $\bar{M}_n$ values. Both situations are a consequence of a less crowded coordination sphere, in which positions for the chain-transfer process by $\beta$-hydrogen elimination are more readily available.

The addition of a second equivalent of donor ligand to complex **1** generally produces a decrease in the activity, but its values still remain higher than those obtained for unmodified phosphine-free **1** (Figure 2). With the smaller $PMe_3$, this reduction is not as dramatic as with $PPh_3$ or $P^nBu_3$. A different situation is observed for both $P(o\text{-Tol})_3$ and $PCy_3$ where the addition of 1, 2, or 5 equiv affects the activities only to a small extent. As a consequence of the large size of these ligands, the Ni center will be less accessible to styrene even when coordinating a single phosphine (see discussion below).

**Polymer Fractionation and Structural Characterization.** In order to account for microstructural heterogeneities, all the samples were fractionated with methanol into a soluble oligomeric fraction, $M_s$, and an insoluble polymeric fraction, $M_i$. In a few selected samples, the latter was further fractionated with *n*-hexane into a soluble, $H_s$, and an insoluble fraction, $H_i$ (see Experimental Section).

**1. The Cases of $P(OPh)_3$, $PPh_3$, $PMe_3$, and $P^nBu_3$.** The case of $P(OPh)_3$ was chosen as an example for complete fractionation. The GPC chromatograms in Figure 3 show that this procedure gave a large $H_s$ fraction. The $H_i$ fraction has a monodisperse character ($\bar{M}_w/\bar{M}_n = 1.13$) and also has higher isotactic content (0.74 *vs* 0.69 for $H_s$), which indicates that the fractionation did not occur only by a molecular weight effect. This $H_i$ polystyrene fraction still has an amorphous behavior ($T_g = 69$ °C) close to that obtained for the corresponding fraction of a polystyrene synthesized in the absence of phosphorus(III) ligands ($\bar{M}_n = 3200$; $\bar{M}_w/\bar{M}_n = 1.26$; $P_m = 0.68$; $T_g = 69$ °C).

In the presence of any of the title ligands, complex **1** promotes the formation of polystyrenes with unimodal mass distributions, essentially reflecting the presence of a single type of active center. These polymers have a structure of type A, similar to that obtained with unmodified **1**.[6] Indeed, $^1H$ and $^{13}C$ NMR spectra clearly show the presence of vinyl and methyl terminal groups and a head-to-tail regioregular enchainment.



A

This structure indicates a secondary addition (Ni → $C_2$) of styrene monomer both in initiation (eq 2) and propagation (eq 3) steps of the polymerization. The presence of terminal unsaturated $CH(C_6H_5){=}CH-$ groups points to the occurrence of a chain-transfer process either by $\beta$-hydrogen elimination to the metal with regeneration of a cationic nickel hydride species (eq 4)[6]

$$[Ni]^+H + CH(C_6H_5){=}CH_2 \rightarrow [Ni]^+CH(C_6H_5)CH_3 \quad (2)$$

$$[Ni]^+CH(C_6H_5)CH_3 \xrightarrow{(n-1)Sty} [Ni]^+CH(C_6H_5)CH_2[CH(C_6H_5)CH_2]_{n-2}CH(C_6H_5)CH_3 \quad (3)$$

$$[Ni]^+CH(C_6H_5)CH_2[CH(C_6H_5)CH_2]_{n-2}CH(C_6H_5)CH_3 \rightarrow [Ni]^+H + CH(C_6H_5){=}CH[CH(C_6H_5)CH_2]_{n-2}CH(C_6H_5)CH_3 \quad (4)$$

or by direct transfer to the monomer (eq 5):

$$[Ni]^+CH(C_6H_5)CH_2[CH(C_6H_5)CH_2]_{n-2}CH(C_6H_5)CH_3 + CH(C_6H_5){=}CH_2 \rightarrow [Ni]^+CH(C_6H_5)CH_3 + CH(C_6H_5){=}CH[CH(C_6H_5)CH_2]_{n-2}CH(C_6H_5)CH_3 \quad (5)$$

**2. The Case of $P(o\text{-Tol})_3$.** This bulky ligand ($\theta = 194°$), with electron donor/acceptor features lying close to those of $PPh_3$, gives rise to bimodal molecular weight distributions. This is clearly seen in Figure 4 where the curve distribution of the nonfractionated polystyrene sample has a shoulder in the region of the high molecular weights (left). This shoulder corresponds to the $H_i$ fraction and can be separated from the sample by fractionation with *n*-hexane.

The $^1H$ and $^{13}C$ NMR spectra demonstrate that the three resulting fractions also have a type A structure. The $^{13}C$ NMR spectrum of the aromatic ipso (C1) carbon (Figure 5A) shows a very isotactic $H_i$ fraction ($P_m = 0.88$), with the most intense *mmmm* isotactic pentad resonance at $\delta$ 146.6. In this fraction, the isotactic blocks are separated by ..*mr*.. stereodefects. In contrast, the corresponding $^{13}C$ spectrum of fraction $H_s$ (Figure 5B) reveals a much lower isotactic content ($P_m = 0.73$)

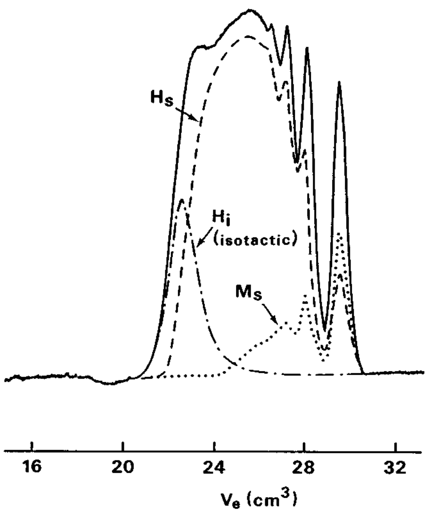


**Figure 4.** GPC curves of polystyrene from run 7 [10 °C, with 1 equiv of P(*o*-Tol)$_3$]. The peaks in the right correspond to the styrene dimer, trimer, and tetramer (shoulder), respectively. The nonfractionated sample (—) has been separated into 11% of a methanol-soluble fraction ($M_s$; $\bar{M}_n = 380$; $\bar{M}_w/\bar{M}_n = 1.27$), 76% of a hexane soluble/methanol-insoluble fraction ($H_s$; $\bar{M}_n = 750$; $\bar{M}_w/\bar{M}_n = 1.62$; $P_m = 0.73$), and 13% of a hexane-insoluble fraction ($H_i$; $\bar{M}_n = 3500$; $\bar{M}_w/\bar{M}_n = 1.30$; $P_m = 0.88$). The nonfractionated sample curve is bimodal in the high molecular weights side (left). The left shoulder nearly coincides with the isotactic $H_i$ fraction.

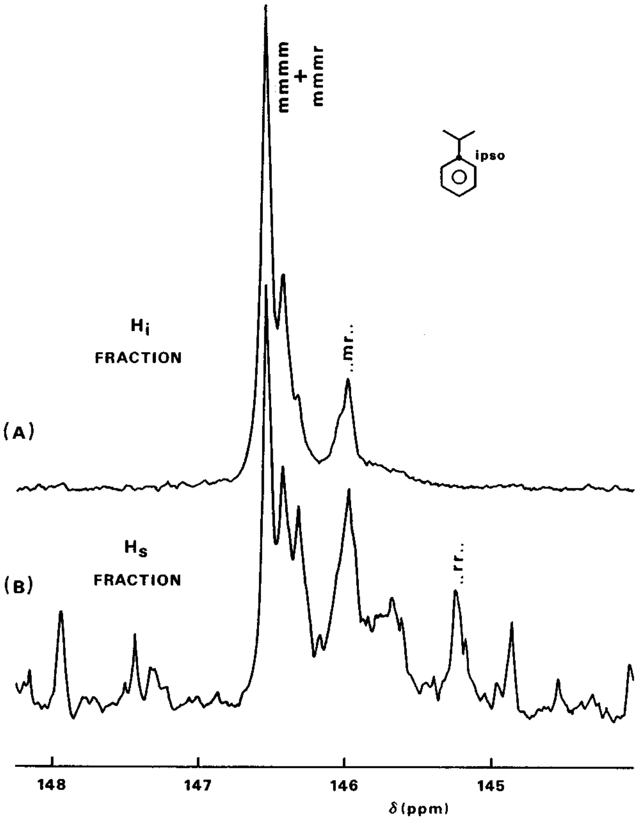


**Figure 5.** $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_2CDCl_2$, 120 °C) spectra of the aromatic ipso carbon of the (A) hexane-insoluble/methanol-insoluble fraction ($H_s$) and (B) hexane-insoluble fraction ($H_i$) of the polymer obtained in run 7 [10 °C, with 1 equiv of P(*o*-Tol)$_3$]. The upper spectrum corresponds to an isotactic polystyrene sample. Minor resonances are assigned to terminal groups.

and the presence of *..rr..* and larger syndiosequences (Table 2). In the $^{13}C$ spectrum, minor resonances are observed for the $CH(C_6H_5)$=$CHCH(C_6H_5)CH_2$− terminal group at $\delta_{CH(Ph)=}$ 130.5, $\delta_{=CH}$ 133.0, and $\delta_{CH(Ph)}$ 46.5 and the aromatic C1 resonances at δ 130.1 for CH(*Ph*)= and 145.2 for −CH(*Ph*)−. In the other terminal group $CH(C_6H_5)CH_3$, the methyl resonances were assigned at δ 21.2, the methine at δ 37.2, and the C1 aromatic carbon at δ 148.2. No $^{13}C$ resonances corresponding to anomalous styrene−styrene additions (tail-to-tail or head-to-head) were observed.[21]

**Table 2. Influence of the Amount of P(*o*-Tol)$_3$ Added to Complex 1 in the Tacticity and Molecular Weight of the $H_s$ and $H_i$ Polystyrene Fractions**

| | 1 equiv | | 2 equiv | | 5 equiv | |
|---|---|---|---|---|---|---|
| | $H_s$ | $H_i$ | $H_s$ | $H_i$ | $H_s$ | $H_i$ |
| $mm^a$ | 0.52 | 0.76 | 0.57 | 0.80 | 0.55 | 0.81 |
| $mr^a$ | 0.41 | 0.24 | 0.33 | 0.20 | 0.37 | 0.19 |
| $rr^a$ | 0.07 | 0 | 0.10 | 0 | 0.08 | 0 |
| $P_m{}^b$ | 0.73 | 0.88 | 0.74 | 0.90 | 0.74 | 0.91 |
| $\bar{n}_m{}^c$ | 3.5 | 7.3 | 4.5 | 8.0 | 4.0 | 9.5 |
| $\bar{n}_r{}^d$ | 1.3 | 1.0 | 1.6 | 1.0 | 1.4 | 1.0 |
| $\bar{M}_n$ | 750 | 3500 | 1000 | 3600 | 980 | 3800 |

[a] From $^{13}C$ NMR pentad analysis of the aromatic ipso carbon pattern. [b] $P_m = (m) = (mm) + [(mr)/2]$. [c] Average length of *m* blocks $= 1 + [2(mm)/(mr)]$. [d] Average length of *r* blocks $= 1 + [2(rr)/(mr)]$.

An intense melting peak at 131 °C ($T_m$) in the DSC thermogram shows a highly crystalline isotactic $H_i$ fraction. In this thermogram, a glass transition temperature is also observed at $T_g = 70$ °C and is due to a small percentage of amorphous $H_s$-like polymer that comes from the not fully separated and interpenetrating $H_s$ and $H_i$ distribution curves.

The influence of the amount of P(*o*-Tol)$_3$ in the polystyrene microstructure and molecular weight was studied. The results (Table 2) show that the addition of 1, 2, or 5 equiv of this phosphine produces $H_s$ and $H_i$ fractions with almost invariant $P_m$ values. A constant value of 5.8 min$^{-1}$ for the atactic fraction turnover frequencies and slightly increasing values (0.9, 1.5, and 2.0 min$^{-1}$, respectively) for the isotactic fraction are obtained. This increase suggests that the phosphine excess is responsible for the formation of a higher concentration of a more stereoselective catalyst center. However, a simple interpretation of these trends is not possible. In fact, the COD replacement in the percursor **1** is *immediately* observed upon mixing only in the case of a 5-fold excess of P(*o*-Tol)$_3$. For the other two cases, a slow COD substitution rate originates nonequilibrium concentrations of **1**, $\{Ni(\eta^3\text{-(2-methylallyl)})[P(o\text{-Tol})_3]_2\}^+$, and free P(*o*-Tol)$_3$.[22] In this mixture, one also has to consider the further dissociative equilibrium giving rise to a monophosphine species.

With this situation in mind, one could put forward the existence of a process where the most stereoselective nickel site has two coordinated phosphines, producing the higher molecular weight isotactic fraction $H_i$; on the other hand, the species bearing a single phosphine (the most active one) along with the unconverted less active phosphine-free **1** gives rise to the heterotactic $H_s$ fraction (Scheme 1).

**3. The Case of PCy$_3$.** In contrast with the preceding case, the addition of $PCy_3$ to complex **1** gives rise to polystyrenes with unimodal and narrow mass distributions (Figure 6). All three samples generated by fractionation in methanol and *n*-hexane possess a highly isotactic microstructure ($P_m = 0.91$ and 0.89 for $H_s$ and $H_i$, respectively). The $^{13}C$ NMR aromatic ipso carbon patterns for both fractions (Figure 7) are very similar. Like in the P(*o*-Tol)$_3$ hexane insoluble fraction, these polymers only contain *..mr..* stereodefects. Their structure may be schematically represented as in Chart 1.

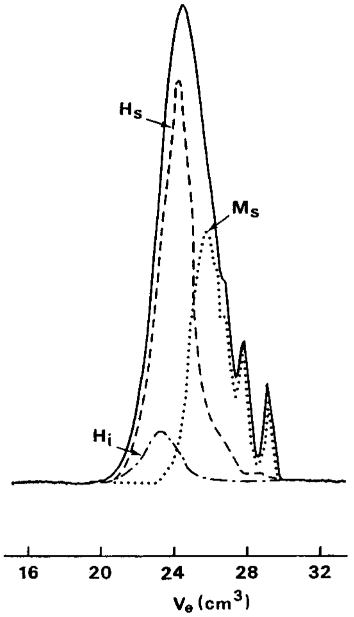
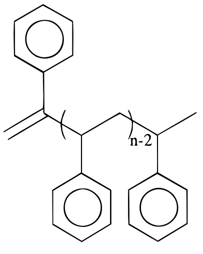


**Figure 6.** GPC curves of run 15 polystyrene (10 °C, with 1 equiv of $PCy_3$). The peaks in the right correspond to the styrene dimer, trimer, and tetramer (shoulder), respectively. The nonfractionated sample (—) has been separated into 42% of a methanol-soluble fraction ($M_s$; $\bar{M}_n = 640$; $\bar{M}_w/\bar{M}_n = 1.23$), 52% of a hexane-soluble/methanol-insoluble fraction ($H_s$; $\bar{M}_n = 1700$; $\bar{M}_w/\bar{M}_n = 1.32$; $P_m = 0.91$), and 6% of a hexane-insoluble fraction ($H_i$; $\bar{M}_n = 4100$; $\bar{M}_w/\bar{M}_n = 1.53$; $P_m = 0.89$).

As described below, the NMR data are consistent with a polymer in which the great majority of chains have a structure of the type B, differing from A in one of the terminal groups.



B

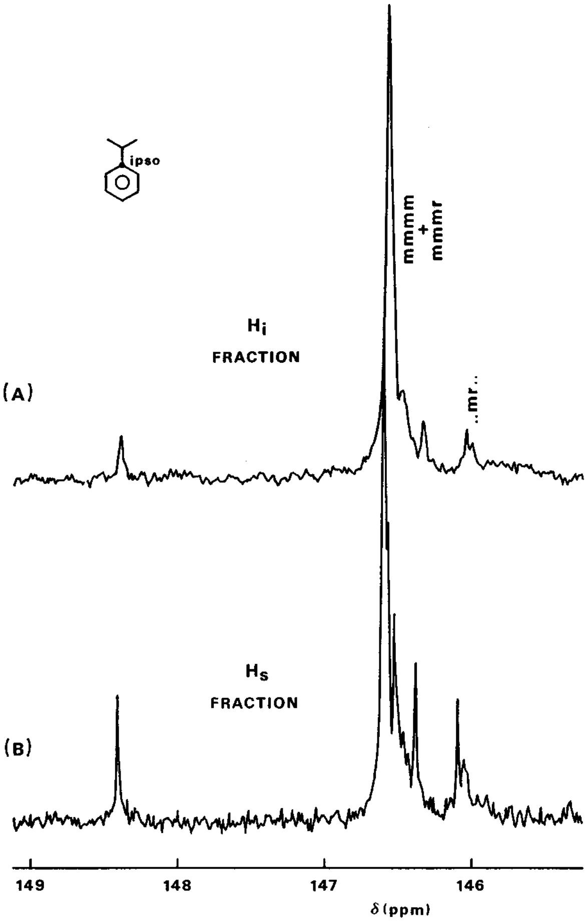
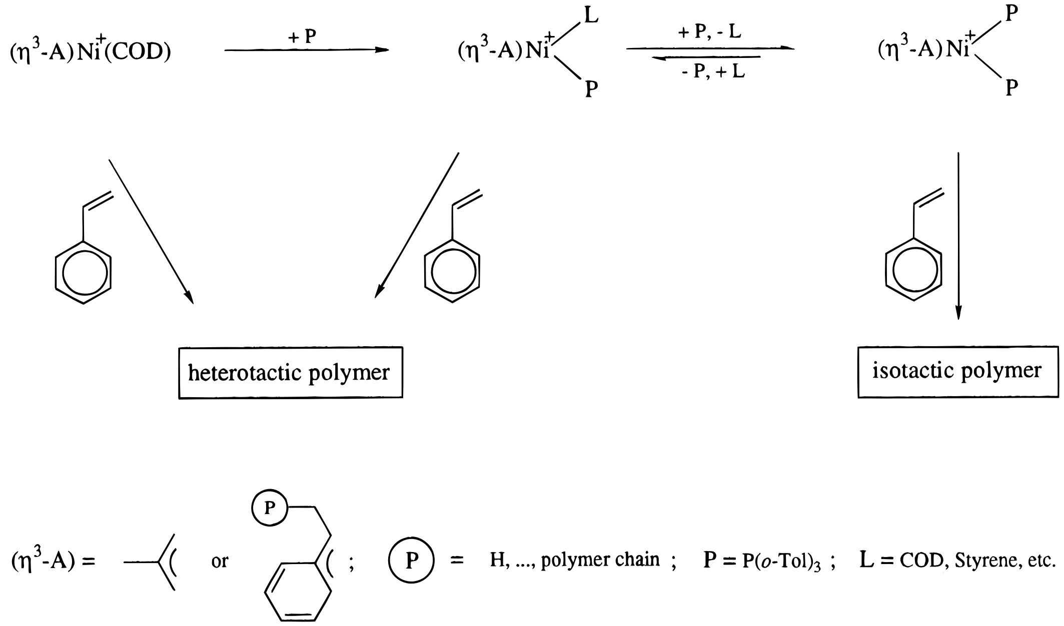


**Figure 7.** $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_2CDCl_2$, 120 °C) spectra of the aromatic ipso carbon of the (A) hexane-insoluble/methanol-insoluble fraction, $H_s$, and (B) hexane-insoluble fraction, $H_i$, of the polymer obtained in run 15 (10 °C, with 1 equiv of $PCy_3$). Both fractions correspond to highly isotactic polystyrene samples. Minor resonances are assigned to terminal groups.

The $^1H$ NMR spectra of these samples show different features in relation to the previous cases. In the spectrum of the $H_i$ fraction, two resonances at $\delta$ 5.19 and 4.87 are assigned to the *trans* and *cis* protons of a new $CH_2{=}C(C_6H_5)CH(C_6H_5)CH_2-$ inverted terminal

**Scheme 1**



**Scheme 2**

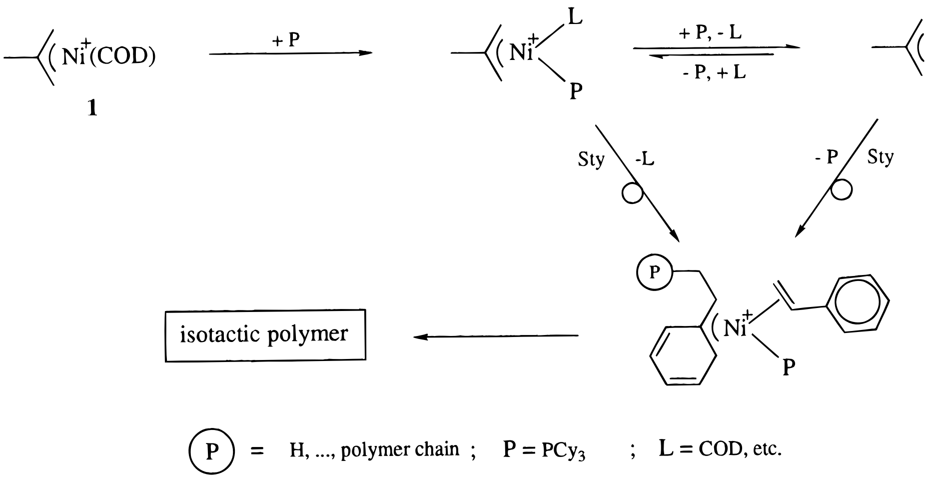
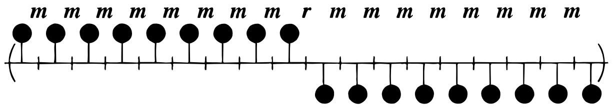


**Chart 1**



group. A COSY spectrum assigns the quartet observed at $\delta$ 3.43 to the allylic proton, showing it to be coupled to each of the adjacent methylenic protons at $\delta$ 1.83 and 2.07 which are hidden underneath the in-chain methylenic and methinic protons. The nonequivalence of these two methylene protons reflects the isotactic nature of the polystyrene chains. In the other end group, $-CH(C_6H_5)CH_3$, the methyl doublet at $\delta$ 0.97 correlates to the adjacent methine proton at $\delta$ 2.4, hidden underneath the in-chain methine envelope.

The $^{13}C$ NMR spectra of the $H_s$ and $H_i$ fractions have essentially the same characteristic features of the spectrum described in a previous communication[8] for the methanol insoluble fraction and confirm the linearity of the polystyrene chains obtained with these isotactic Ni catalyst precursors. The methyl resonances at 21.1 ppm and the methine resonances at 37.0 ppm are assigned to the $-CH(C_6H_5)CH_3$ terminal group. The first value traces a highly isospecific secondary insertion of styrene into a $Ni^+-H$ bond for the initiation step.[23] The regioselectivity of this step is maintained throughout the propagation steps as confirmed by the absence of head-to-head or tail-to-tail in-chain defects. The $^{13}C$ resonances characteristic of the inverted terminal group $CH_2{=}C(C_6H_5)CH(C_6H_5)CH_2-$, are observed at $\delta_{CH2=}$ 113.7 and $\delta_{=C(Ph)}$ 143.0.

The DSC thermogram of the $H_i$ fraction is consistent with a highly isotactic crystalline polystyrene. The melting range begins at 143.5 °C and contains two peaks: the broadest one with a maximum at 159 °C is partially superimposed on the most intense and narrowest peak with a maximum at 168 °C. These two peaks are likely to correspond to different crystalline phases of the polymer.

The influence of the amount of $PCy_3$ added to complex **1** in the tacticity and molecular weight is illustrated in Table 3, for the methanol-insoluble ($M_i$) polystyrene fractions. A very slight decrease of tacticity is observed with increasing amount of $PCy_3$. However, this can be explained by the presence of tiny amounts of high molecular weight atactic polymer in the case of the addition of 2 and 5 equiv, which can be induced by some radical decomposition of the catalytic system.[10] The average molecular weights and the turnover frequencies (Table 1) do not change appreciably.

**Table 3. Influence of the Amount of $PCy_3$ Added to Complex 1 in the Tacticity and Molecular Weight of the Methanol-Insoluble ($M_i$) Polystyrene Fractions (See Table 2 for Additional Notes)**

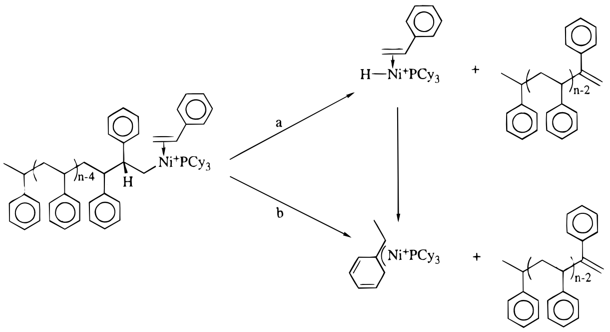
| | 1 equiv | 2 equiv | 5 equiv |
|---|---|---|---|
| $mm^a$ | 0.81 | 0.77 | 0.73 |
| $mr^a$ | 0.19 | 0.23 | 0.27 |
| $rr^a$ | 0 | 0 | 0 |
| $P_m$ | 0.90 | $0.89^b$ | $0.87^b$ |
| $\bar{n}_m$ | 9.5 | 7.7 | 6.4 |
| $\bar{n}_r$ | 1 | 1 | 1 |
| $\bar{M}_n$ | 1700 | 1800 | 1800 |

[a] From $^{13}C$ NMR pentad analysis of the aromatic ipso carbon pattern. [b] Slightly contaminated with an atactic polystyrene high $\bar{M}_n$ (~50 000) fraction.

These results demonstrate that the structure of the Ni active center is invariant with the number of equivalents of $PCy_3$ added. On the other hand, no cationic benzyl Ni complexes containing two $PCy_3$ ligands could be isolated so far,[10] but neutral monophosphine complexes of the type $[Ni(\eta^3\text{-}CH_2C_6H_5)(PCy_3)X]$ ($X = Cl, Br$) are well characterized.[24] These facts suggest the coordination of only one $PCy_3$ ligand to the catalytic active metal center (Scheme 2). This highly donor phosphine is very likely to be firmly bound to the $Ni-\eta^3$-polystyryl center, having a short Ni–P distance and, therefore, exerting all its bulkiness ($\theta = 170°$) to prevent coordination of a second $PCy_3$ ligand. Due to the same reasons, it will induce regio- and isospecific secondary insertion ($Ni \rightarrow C_2$) of styrene in the initiation and propagation steps. After a certain growth extent, the coordination sphere becomes crowded, and a less sterically demanding primary ($Ni \rightarrow C_1$) insertion will occur. On the basis of the proposed mechanism,[8] this last inserted unit cannot become stabilized by $\eta^3$-coordination and a chain transfer reaction immediately occurs by $\beta$-hydrogen elimination. This reaction regenerates the cationic nickel hydride active species and gives rise to the inverted terminal group (Scheme 3, route a). Alternatively to the formation of a nickel hydride species, a direct chain-transfer reaction to the monomer can be considered (Scheme 3, route b).

However, a closer inspection of the NMR data of these fractions shows that besides this inverted tail-to-tail terminal group, there is a small percentage (*ca.* 10%) of type A polymer chains. A more detailed work on the origin of regio- and stereocontrol will be presented in a future publication.[25]

**Scheme 3**



## Conclusions

The addition of phosphorus(III) ligands strongly influences the polymerization of styrene catalyzed by $\{Ni[\eta^3\text{-}CH_2C(CH_3)CH_2](\eta^4\text{-}COD)\}PF_6$, **1**.

Most of the P(III) ligands added act as activity promoters, giving rise to regioregular head-to-tail low molecular weight polymers. This activity enhancement seems to be related to the dual capacity of the ligand to stabilize the active species (cationic nickel hydride) and dynamically dissociate from its coordination sphere. The average degree of polymerization varies from 3 to 45 according to the type and amount of added P(III) ligand and to the used fractionation procedure. A control over the stereoselectivity can be achieved by employing sterically demanding phosphines. With $P(o\text{-}Tol)_3$ ($\theta = 194°$) and $PCy_3$ ($\theta = 170°$), highly isotactic polymers ($P_m \approx 0.9$) are obtained which bear a different inverted tail-to-tail terminal group, $CH_2{=}C(C_6H_5)CH(C_6H_5)CH_2-$. According to these obervations, the previously proposed[8] stereoregulation mechanism by superimposed effects of a $\eta^3$-benzylic asymmetric coordination of the growing chain and a high steric influence of a bulky ligand is reaffirmed.

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(18) For example, with $PCy_3$, the formation of the complex $\{Ni[\eta^3\text{-}CH_2C(CH_3)CH_2](PCy_3)_2\}PF_6$ is evident: $^1H$ NMR (300 MHz, $CD_2Cl_2$, 20 °C) $\delta$ 3.87 (br s, 2 H, *syn*-$H$HCC(Me)CH$H$), 2.40 (s, 2 H, *anti*-H$H$CC(Me)C$H$H), 1.95 (s, 3 H, $H_2CC(CH_3)$-$CH_2$), 0.8−2.6 ($PCy_3$ protons); $^{13}C\{^1H\}$ NMR (75.42 MHz, $CD_2Cl_2$, 20 °C) $\delta$ 125.0 ($H_2CC(Me)CH_2$), 65.3 ($H_2CC(Me)CH_2$), 25−38 ($PCy_3$ carbons), 22.3 ($H_2CC(CH_3)CH_2$); $^{31}P$ NMR (121.42 MHz, $CD_2Cl_2$, 20 °C) $\delta$ 30.3 (2 P), −143.7 (sept, $^1J_{PF} = 711.5$ Hz, $PF_6^-$). Below *ca.* −35 °C, the allyl ligand becomes asymmetric due to the slow intermeshing of the two $PCy_3$ groups.[19] $^1H$ NMR (300 MHz, $CD_2Cl_2$, −70 °C) $\delta$ 4.07 (br s, 1 H, *syn*-$H_a$HCC(Me)CH$_2$), 3.61 (br s, 1 H, *syn*-$H_2CC(Me)$-$CHH_d$), 2.62 (br s, 1 H, *anti*-$HH_bCC(Me)CH_2$), 2.29 (br s, 1 H, *anti*-$H_2CC(Me)CH_cH$), 2.02 (s, 3 H, $H_2CC(CH_3)CH_2$), 0.8−2.6 ($PCy_3$ protons); $^{31}P$ NMR (121.42 MHz, $CD_2Cl_2$, −70 °C) $\delta$ 30.0 (br, 1 P), 29.3 (br, 1 P), −143.7 (sept, $^1J_{PF} = 711.5$ Hz, $PF_6^-$). For $[PCy_3]/[Ni] > 2$ the excess free phosphine resonance is also observed at room temperature, indicating a slow-exchange process.

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(22) In a $[P(o\text{-}Tol)_3]/[Ni] = 1$, the $^1H$ (300 MHz, $CD_2Cl_2$: $\delta$ 7.25, 7.07, 6.71, 2.37) or $^{31}P\{^1H\}$ (121.42 MHz, $CD_2Cl_2$: $\delta$ −29.5) resonances due to free ligand only disappeared after *ca.* 4 h. In a $[P(o\text{-}Tol)_3]/[Ni] = 2$, the full COD substitution in **1** occurs in less than 2 h.

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