shapes reported in this work are very close to Lorentzian, which justifies use of eq 7 for the estimate of competitive binding at relatively low fields. The use of higher fields (comparable to the one used in ref 8) and T_1 measurements is being planned to investigate the effects, if any, of the presence of other ions on the correlation times, τ_c.

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Registry No. Mg^{2+}, 22537-22-0; Cs^+, 18459-37-5; Rb^+, 22537-38-8; K^+, 24203-36-9; Na^+, 17341-25-2; Li^+, 17341-24-1.

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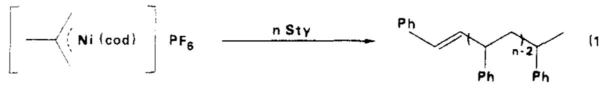
Communications to the Editor

Cationic η^3-Allyl Complexes. 16.[1] Isotactic Oligomerization of Styrene in the Presence of a Homogeneous Nickel(II) Catalyst

The mechanisms of polymerization of styrene into high isotactic polystyrenes with Ziegler–Natta catalysts, as well as into syndiotactic polystyrenes with soluble catalysts based on titanium and zirconium, have been recently investigated. Namely, the study by ^{13}C NMR of the regioselectivity of the initiation and propagation steps has demonstrated the primary insertion of styrene on metal–carbon bonds of the active sites of heterogeneous Ziegler–Natta isospecific catalysts.[2,3] On the other hand, secondary insertion of styrene was found for homogeneous catalysts like nonstereospecific tetrabenzylzirconium ($ZrBz_4$)[4] or $ZrBz_4$/triethylaluminum[5] and also syndiospecific ML_4 (M = Ti or Zr)/methylalumoxane.[6,7]

In a previous paper,[8] we described the nonstereospecific oligomerization of styrene by a very active cationic allylnickel catalyst, 1, [(η^3-methallyl)(η^4-cycloocta-1,5-diene)nickel(II)] hexafluorophosphate (eq 1). The ^{13}C NMR of the oligomeric fraction insoluble in methanol ($\bar{M}_n$ = 2350), 2, has shown the linearity of the olefinic chains as well as the secondary addition of styrene both in initiation and propagation steps of oligomerization. Furthermore, the presence of terminal unsaturated $-CH{=}CH(C_6H_5)$ groups indicated that the reaction of β-hydrogen elimination is the main-chain transfer process.



(1)

1 2

In this paper we report some studies on the mechanism of oligomerization of styrene to high isotactic oligomers ($\bar{M}_n$ = 1900) with the homogeneous nickel catalyst 3 composed by the organometallic complex 1 modified by the in situ addition of 1 equiv of tricyclohexylphosphine (PCy_3). This system is, as far as we know, the first monometallic catalyst having isospecific features in the oligomerization or polymerization of styrene.

The ^{13}C spectrum of the methanol-insoluble oligomeric fraction obtained with catalyst 3, in Figure 1, is characteristic of a high isotactic polystyrene oligomer. In effect, the main resonances of the aromatic C-1 carbons and of the methylenic carbons at δ 146.46 and δ 43.59 ppm correspond, respectively, to the isotactic pentads and tetrads of polystyrene.[9] The isotactic content of this fraction, determined by NMR, is 89%.

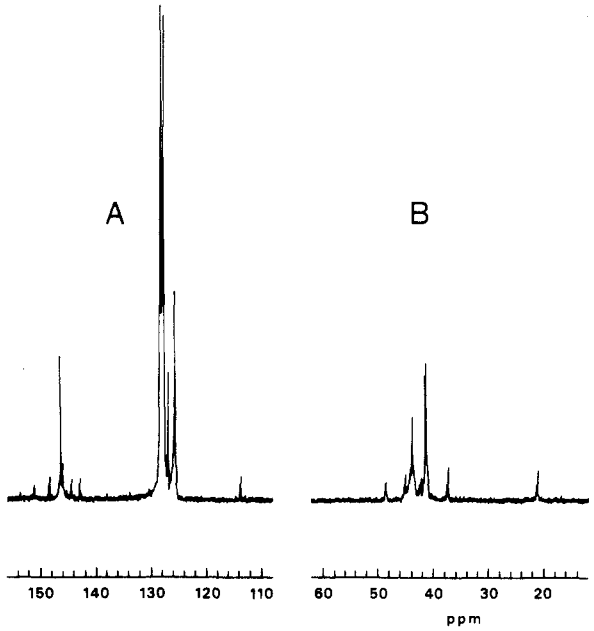


Figure 1. $^{13}C\{^1H\}$ spectrum of isotactic polystyrene: (A) aromatic region, (B) aliphatic region. The spectrum was obtained in tetrachlorodideuterioethane at 120 °C and 50.3 MHz. The pulse width was 3 μs (45°) and the number of scans 17 000.

The minor ^{13}C resonances on the aromatic and aliphatic regions of the spectrum in Figure 1 correspond to the terminal groups of the oligomers. A quantitative ^{13}C spectrum has revealed that they have the same relative intensity, corresponding to one carbon.

The methyl and methine resonances at δ 21.07 and δ 37.06 ppm are characteristic of a $-CH(C_6H_5)CH_3$ terminal group.[10] Furthermore, the presence of this type of groups indicates a secondary mode of addition of styrene into the Ni–H bond of the active sites in the chain-initiation step.

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

The regioselectivity of this step is maintained throughout the propagation steps, as no resonances corresponding

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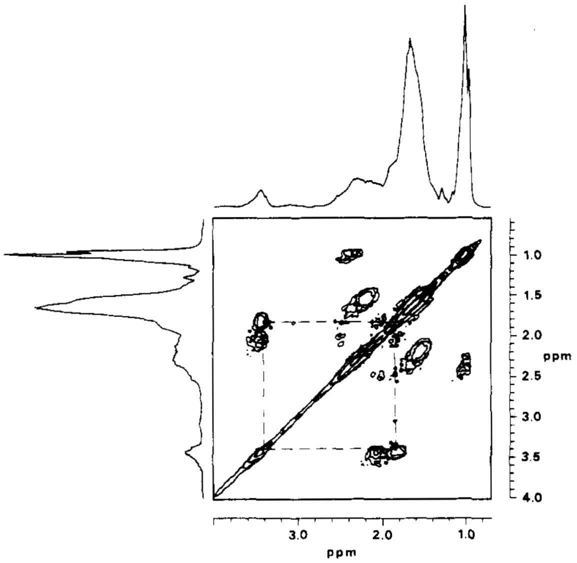
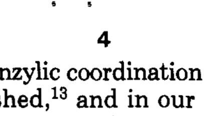


Figure 2. *J*-correlated 2D ^1H spectrum of isotactic polystyrene, at 120 °C, in tetrachlorodideuterioethane. The spectrum corresponds to 100 scans and was obtained with the sequence COSY using a mixing pulse $\theta = 90°$. The correlation between the methine proton and its vicinal methylenic protons of the $CH_2{=}C(Ph)CH(Ph)CH_2—$ terminal group is indicated by dotted lines.

to irregular styrene tail-to-tail or head-to-head additions in the middle of the chain were observed.[11]

This regioregularity is, however, broken in the last insertion of a styrene molecule occurring before chain termination by β-hydrogen elimination. This conclusion is based on the NMR (^{13}C and ^1H) identification of the other terminal group as $CH_2{=}C(C_6H_5)CH(C_6H_5)CH_2—$. In fact, the ^{13}C resonances of this group were found at 113.66 and 142.91 ppm for the vinylic carbons and at 48.29 ppm for the methine carbon. These shifts are quite close to the ones found by us in the styrene tail-to-tail dimer,[8] $CH_2{=}C(C_6H_5)CH(C_6H_5)CH_3$, $\delta_{CH_2=}$ 112.90, $\delta_{=C(Ph)-}$ 142.15 and $\delta_{-CH(Ph)-}$ 44.13 ppm. Further confirmation of this terminal structure is provided by the *J*-correlated 2D ^1H spectrum of this fraction (Figure 2), which shows the methine proton resonance at 3.48 ppm to be coupled to its vicinal methylenic protons at about 1.9 ppm. Some correlation is also observed with minor methylenic resonances at 2.05 ppm probably belonging to traces of light styrene oligomers still present in the fraction.

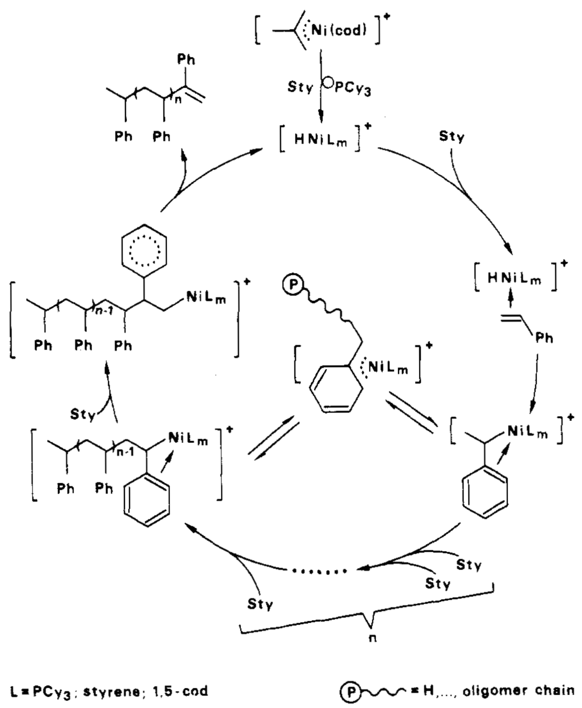
In order to understand the mechanism of the reaction, we attempted the isolation of nickel complexes present in a catalytic reaction performed with unmodified catalyst **1**. Low-temperature evaporation of the mixture after 30 min of reaction in the usual conditions[8] and extraction with toluene left a solid residue stable below −10 °C. After careful washing and reprecipitation from CH_2Cl_2, the resulting red-orange solid was analyzed by ^1H NMR. Besides unreacted **1**, the other component of this mixture is complex **4**. Though L_m has not yet been unambiguously assigned, the presence of an η^3-benzylic ligand is very clear.[12]



4

This type of η^3-benzylic coordination in nickel complexes is now well established,[13] and in our case, it is probably obtained from the reaction of a molecule of styrene with a nickel hydride species arising from some transformation on complex **1**. Further insertions of styrene molecules will occur, originating an oligomer chain that is stabilized in a secondary way by the η^3-benzyl–nickel bond, until β elimination occurs through a $\eta^3 \leftrightarrow \eta^1$ isomerization process. Such a species should explain the regioselectivity of the oligomerization of styrene in the presence of **1** alone or modified by less bulky and less basic phosphines than PCy_3.[8]

Scheme I



However, with the use of catalyst **3**, the coordination sphere of nickel becomes more crowded and the increase of steric interactions with the growing polymer chain may determine an inversion of the styrene mode of addition from secondary to primary. Once the primary addition occurs, the π-benzylic stabilization is no longer possible and the β-elimination reaction terminates the chain, leaving the 2,3-diphenylbuten-3-yl end group and regenerating the nickel hydride active species (Scheme I).

In conclusion, we are led to think that a (π-benzyl)nickel species plays an important role in determining the secondary insertion of styrene in the initiation and propagation steps. The added effects of a π-benzylic coordination of the growing chain and the presence of the basic and bulky PCy_3, giving origin to a very crowded nickel coordination sphere, are believed to be responsible for a high isotactic content and for the irregular tail-to-tail chain transfer through β-hydrogen elimination.

Experimental Section. Preparation of **1** as well as the oligomerization run ($T = 10$ °C) was carried out according to ref 8. A solution of the catalyst precursor **3** (0.3 mmol) in 10 mL of dichloromethane is added to 316 mmol of styrene. After 2 h, the reaction is quenched by addition of methanol and the reaction mixture is filtered through a silica gel bed. The clear solution is evaporated to dryness. After redissolution in dichloromethane, methanol is added to precipitate the heavier oligomer fraction which is collected by filtration, thoroughly washed with methanol, and dried under vacuum. Yield: 4.0 g. Lighter oligomers are recovered by evaporation of the dichloromethane/methanol washings to give 1.1 g. Total styrene conversion: 15.5%. Number average molecular weight ($\bar{M}_n$) of the heavier oligomer fraction was determined by comparing the intensities of the in-chain protons with those of the terminal groups and found to be $\bar{M}_n = 1900$. ^{1}H NMR characterization of 4 was performed in CD_2Cl_2, at −20 °C, on a WM 250 Bruker spectrometer. ^{1}H and ^{13}C NMR spectra of oligomer samples were run on an AM 200 Bruker spectrometer at 120 °C in a solution of $CDCl_2CDCl_2$. Hexamethyldisiloxane (HMDS) was used as an internal reference (δ ^{13}C 2.0 ppm and δ ^{1}H 0.06 ppm), and the chemical shifts were converted to the TMS scale. For selection of the ^{13}C resonances, the sequence DEPT with a pulse angle $\theta = 135°$ was used. Minor ^{13}C resonances appear as follows: quaternary carbons downfield 140 ppm; methinic resonances at 48.29 and 37.06 ppm; methylenic resonances at 113.66, 44.91, 44.12, and 42.05 ppm; a methyl resonance at 21.07 ppm. The *J*-correlated 2D ^{1}H spectrum was obtained with the pulse sequence COSY, using a 90° mixing pulse.

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Registry No. 1, 78002-90-1; PCy_3, 2622-14-2; $C_6H_5CH{=}CH_2$, 100-42-5.

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(12) Benzyl moiety ^{1}H NMR assignments, at −20 °C, performed by selective irradiations: δ 0.82 (d, 3 $H^{(1)}$, $^2J_{H^{(1)}H^{(2)}} = 7$ Hz), 3.08 (m, $H^{(2)}$), 6.28 (d, $H^{(4)}$, $^2J_{H^{(4)}H^{(6)}} = 7$ Hz), 7.58 (m, $H^{(5)}$), 7.74 (m, $H^{(7)}$ and $H^{(8)}$), 7.98 (m, $H^{(6)}$).
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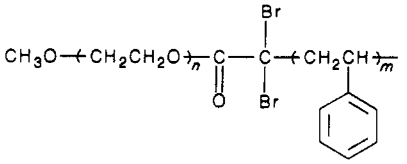
Reversible Interpolymer Complexation between Poly(oxyethylene)-Based Amphiphilic Block Polymer and Poly(acrylic acid) at the Air–Water Interface

The present paper describes the results of a study on surface monolayer properties and reversible interpolymer complexation at the air–water interface for the amphiphilic block polymer 1, poly(oxyethylene-*block*-styrene). The interpolymer complexation between 1 and poly(acrylic acid) in the subphase is reversibly controllable by varying pH in the subphase; at the lower pH (<5) the formation of an interpolymer complex is observed, whereas such a complex is deformed at pH >5.



1: n = 10; m = 14, 20, 113

We have reported that amphiphilic block polymers consisting of poly(acrylic acid) (PAA) and poly(styrene) (PSt), prepared by using the catalytic system[1,2] of halo-terminated polymer and manganese carbonyl ($Mn_2(CO)_{10}$), can form stable monolayers at the air–water interface and that they are readily transferred on a quartz plate at each downward and upward dip (Y-type deposition)[3] by using the Langmuir–Blodgett method.[4]

In the present study, we prepared amphiphilic block polymers composed of poly(oxyethylene) (POE) and PSt and studied the effect of addition of PAA in the subphase on the monolayer behavior by using surface pressure (Π)–area (A) isotherm measurements at various pHs in order to obtain information regarding the polymer–polymer interaction at the air–water interface. Polyion complexations from bilayer-forming amphiphiles and oppositely charged polyions at the air–water interface have been reported to be useful for stabilization and facilitated deposition of surface monolayers.[5,6] It is well-known that an interpolymer complex is formed between PAA and POE through hydrogen bonding in an aqueous medium.[7–9] However, the polymer–polymer interaction at the air–water interface has not yet been established.

Amphiphilic block polymers 1 with different hydrophobic chain length were prepared according to Scheme I. Macroinitiator 2 was prepared by the reaction of sodium ω-methoxypoly(oxyethylene) (M_n = 480; Japan Catalytic Chemical Industry Co., Ltd.) with tribromoacetyl chloride.[10] Block polymerizations of styrene (St) as a second monomer with macroinitiator 2 were carried out in bulk with $Mn_2(CO)_{10}$. We have already established that well-defined block copolymers with controlled chain length of blocking are prepared by varying the conversion of the second monomer and the feed composition of macroinitiator and second monomer in such catalytic system.[1–3] Resulting amphiphilic block copolymers were characterized to consist of a POE chain (n = 9.7) as the hydrophilic part and a PSt chain (m = 14, 20, and 113) as the hydrophobic part on the basis of the structural analyses.[11]

Spreading experiments of 1 were performed on a microprocessor-controlled film balance (San-esu Keisoku Co., Ltd.). A series of 1 was spread from benzene. The concentrations of the spreading solutions were about 1.5 mg/mL. The surface pressure (Π)–area (A) isotherm measurements for 1 on pure water showed that well-behaved monolayers were formed and the limiting area trended toward expanding with increasing m similar to the case of PAA-*block*-PSt as described before:[3] i.e., when m

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