conclusion in distinguishing a simple ionic core from a core–shell ionic aggregate. Therefore the origin of the ionic peak must be determined by considering the entire SAXS profile, in addition to information from other techniques.

Conclusions

The excess scattered intensity due to ions at very small scattering angles can be measured for the sulfonated polystyrene ionomers of sodium and zinc salts by subtracting the scattered intensity of either the corresponding polystyrene backbone or the ionomer in acid form from the scattered intensity of the ionomer salt. This approach simulates ASAXS,[12] because the metal ions dominate the SAXS curve. The Guinier approximation failed to yield a reasonable R_g value for the ionic aggregates. Both "intra" and "inter" models failed to explain the strong small-angle upturn. The correlation function approach, which was also used by Williams et al.[13] to explain their small-angle data in a study of telechelic ionomers, resulted in correlation lengths of 23 and ~15 nm respectively for the sodium and the zinc salts of S-PS. The small-angle upturn could therefore be attributed to the long-range inhomogeneity of the ions. Studies of SAXS profiles with changes in ion content, polstyrene polydispersity, and experimental temperature are under way.

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References and Notes

(1) MacKnight, W. J.; Earnest, T. R., Jr. *Macromol. Rev.* **1981**, *16*, 41.
(2) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871; *Polymer* **1985**, *26*, 371.
(3) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 45*, 113.
(4) Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 136; **1981**, *14*, 1309.
(5) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 299. See also: Brumberger, H.; Debye P. *J. Phys. Chem.* **1957**, *61*, 1623.
(6) Chu, B.; Creti, D. M. T. *J. Phys. Chem.* **1967**, *71*, 1943.
(7) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(8) Clough, S. B.; Cortelek, D.; Nagabhushanam, T.; Salamone, J. C.; Watterson, A. C. *Polym. Eng. Sci.* **1984**, *24*, 385.
(9) Chu, B.; Wu, D. Q.; MacKnight, W. J.; Wu, C.; Phillips, J. C.; LeGrand, A.; Lantman, C. W.; Lundberg, R. D. *Macromolecules* **1988**, *21*, 523.
(10) Chu, B.; Wu, D. Q.; Wu, C. *Rev. Sci. Instrum.* **1987**, *58*, 1158.
(11) Galambos, A. F.; Stockton, W. B.; Koberstein, J. T.; Sen, A.; Weiss, R. A.; Russell, T. P. *Macromolecules* **1988**, *20*, 3091.
(12) Cooper, S. L. *Bull. Am. Phys. Soc.* **1987**, *32*(3), 505.
(13) Williams, C. E.; Russel, T. P.; Jérôme, R.; Horrion, J. *Macromolecules* **1986**, *19*, 2877.

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^{23}Na NMR Study of Competitive Binding of Ions to Polyelectrolytes in Mixed Counterion Systems

CAIBAO QIAN, M. REZA ASDJODI,
H. GARTH SPENCER, and GEORGE B. SAVITSKY*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905. *Received April 6, 1988; Revised Manuscript Received August 1, 1988*

Introduction

Significant specificities in the interactions between polyions and counterions in solution have been known to exist for more than 2 decades.[1] Most of the studies on counterion-selective binding were carried out at high ionic strength by various experimental techniques. Thus, for example, Hen and Strauss[2] investigated the interactions of poly(vinylsulfonate) with hydrogen, silver, and selected alkali and alkaline-earth metal ions by dilatometry, dialysis equilibrium, and viscosity methods and found that the preference of this polyanion follows the order $Ag^+ > K^+ > Na^+ > H^+ \approx Li^+$ for the univalent cations and $Ba^{2+} > Mg^{2+}$ for the divalent cations. More recently, Mattai and Kwak[3] made use of a dye spectrophotometric method[4] to investigate polyion–counterion interactions in the mixed counterion system $M^{2+}/M^+/Cl^-$/polyion ($M^{2+} = Mg^{2+}$, Ca^{2+}; $M^+ = Na^+$, K^+; polyion = poly(styrenesulfonate), poly(galacturonate), and (carboxymethyl)cellulose). Their experiments were carried out in the presence of excess salt, and the results were compared with the prediction of Manning's two-variable theory.[5] This theory is applicable in the presence of excess salt and is formulated in terms of the dimensionless charge–density parameter, ξ, defined by

$$\xi = \frac{e^2}{4\pi k T l \epsilon_0 \epsilon_r} \qquad (1)$$

where e is the elementary charge, l the projection of the intercharge distance when polyelectrolyte is considered as a cylinder, k Boltzmann's constant, T the Kelvin temperature, ϵ_0 permittivity in vacuum, and ϵ_r the dielectric constant of the solvent. These authors found that their results were in agreement with the two-variable theory in the case of sulfonated or sulfated polyions, but were in disagreement with the theoretical predictions in the case of carboxylated polyions.

According to Manning's model,[6] the charge fraction of the polyion—that is, the charge per ionic group of the polyelectrolyte—equals the constant value of $(z\xi)^{-1}$, z being the valence (without sign) of a given counterion. Thus, the number of counterions associated with or "atmospherically condensed" onto the polyanion per unit charge, P_b, is given by

$$P_b = 1 - (z\xi)^{-1} \qquad (2)$$

and is independent of concentration, excess salt, and radial dimension of the polyelectrolyte.

Although considerable experimental evidence[7] supports the validity of eq 2 in concentrated solutions and in the presence of salts, it is no longer valid at low concentrations and in the absence of excess salts. This was clearly demonstrated by the ^{23}Na NMR studies of sodium poly(galacturonate), poly(mannuronate), and poly(galuronate) in aqueous solutions by Grasdalen and Kvam.[8] These authors extracted the correlation times, τ_c, from the spectral line shapes which become distinctly non-Lorentzian for τ_c exceeding 0.5 ns. Using the concentration dependence of τ_c, they showed that the data were consistent with the Poisson–Boltzmann (PB) model[9] and a theory developed by Halle et al.[10] for the quadrupolar relaxation of counterions, as testified by the relative constancy of the ^{23}Na quadrupolar coupling constant at different polyelectrolyte concentrations, the latter being calculated from the mathematical formulation of this model. It occurred to us that the study of competitive binding of counterions in the absence of salts using ^{23}Na NMR would be of interest for several reasons. In the absence of salts, a direct and simple method for studying competitive binding is available, and such a study would compliment other studies in the presence of salts. As will be shown below, our results indicate that some polyanions behave "ideally" with respect

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Table I
Theoretical Values of $P_{b,M}$ in Aqueous Solutions of Neutral Salts of PGM and PSSM at Two Concentrations at 298 K

		$P_{b,M}$			
		MPG		MPSS	
M	Δ, nm	c_m = 50 mM	c_m = 5 mM	c_m = 50 mM	c_m = 5 mM
Li^+	0.76	0.37	0.27	0.52	0.47
Na^+	0.72	0.36	0.26	0.51	0.46
K^+	0.66	0.34	0.25	0.50	0.45
Rb^+	(0.66)[a]	0.34	0.25	0.50	0.45
Cs^+	0.66	0.34	0.25	0.50	0.45
Mg^{2+}	0.86	0.62	0.56	0.74	0.65

[a] Interpolated value.

to the PB model as far as their competitive binding is concerned and some do not. Thus, a "nonideal" competitive behavior for any given polyelectrolyte may indicate specific site binding, in addition to territorial binding. In the case of "ideal" binding, the PB model in the absence of salt results in the explicit formulation of P_b for a single counterion of valence z:

$$P_b = 1 - \frac{1}{z\xi}\left[1 - \frac{1 - s \tan\left[s \ln \dfrac{R}{a + \Delta}\right]}{1 + (1/s) \tan\left[s \ln \dfrac{R}{a + \Delta}\right]}\right] \qquad (3)$$

For this expression, ξ has the same meaning as in eq 1, a is the radius of the cylinder approximating the polymer itself, and R is the radius of a cylindrical cell whose dimensions are chosen so as to give the correct overall concentration of polymer, c_m molar (on a monomer basis), and is given by

$$R = [(\pi l c_m N)1000]^{-1/2} \qquad (4)$$

where N is Avogradro's number and l has been previously defined. The parameter s in eq 3 is dimensionless and is the solution to the transcendental equation:

$$z\xi = \frac{1 + s^2}{1 + s \cot\,[s \ln\,(R/a)]} \qquad (5)$$

The remaining variable, Δ, in eq 3 is the thickness of the region where the ions are supposed to be "bound" to the polymer and is usually chosen to be the diameter of the hydrated ion in question.

Equation 3 predicts that the valence has a large effect on P_b but that the latter is not sensitive to the value of Δ, as has been pointed out by Grasdalen and Kvam.[8] This is an important point since in the "ideal" behavior, i.e., if there is no specific ion binding but only territorial binding obeying PB model, the ions of the same valence should not exhibit any significant competitive behavior.

Listed in Table I are the $P_{b,M}$'s which we have calculated by using eq 3 (with M = Li^+,Na^+,K^+,Rb^+,Cs^+,Mg^{2+}) for the neutral salts of poly(galacturonate) (MPG) and poly(styrenesulfonate) (MPSS) in aqueous solution and at two different concentrations, c_m. In these calculations, we have used the same parameters as previously estimated in the literature,[8,10] except that instead of taking Δ to be uniformly 0.5 nm for all ions we have used the literature estimates of the diameter of hydrated ions, as compiled by Israelachvili.[11]

If $P_{b,m}$ is to be taken as a measure of the binding capacity for a given ion M, the competitive binding between the monovalent alkali ions in a territorial sense is hardly significant, whereas it should strongly favor the divalent ion when pitted against any monovalent alkali ion. Thus, in a mixed neutral salt of a polyanion containing a one-to-one equivalent ratio of ion M to sodium ion, the actual mole fraction of territorially bound sodium ion, X_B(M/Na), will be very close to its mole fraction bound in the pure neutral salt of sodium, X_B(Na), at the same concentration if M is another alkali ion and will be significantly lower than X_B(Na) if M is a divalent ion.

In what follows we shall denote the ratio of X_B(M/Na) to that of X_B(Na) by Γ_M:

$$\Gamma_M = \frac{X_B(M/Na)}{X_B(Na)} \qquad (6)$$

Stated otherwise, Γ_M should be close to unity if M is an alkali ion, and Γ_M should be less than unity if M is a divalent ion in the absence of any specific interactions for which the PB model does not account.

Now, Γ_M can be readily determined by measuring the ^{23}Na NMR line widths at half height using the relation[8,12]

$$\Delta\nu_{1/2} = (1 - X_B)\Delta\nu_{1/2,F} + X_B\Delta\nu_{1/2,B} \qquad (7)$$

where $\Delta\nu_{1/2,F}$ and $\Delta\nu_{1/2,B}$ are the line widths which characterize the free and the bound states, respectively, and X_B is the mole fraction of bound sodium ions, while $\Delta\nu_{1/2}$ is the experimentally observed line width. Assuming that the presence of a competing ion does not affect the value of $\Delta\nu_{1/2,B}$ for any given concentration, by measuring $\Delta\nu_{1/2}$ for a mixed salt of the polyion which we shall denote by $\Delta\nu'$ and the corresponding $\Delta\nu_{1/2}$ for the pure salt of it at the same concentration, $\Delta\nu$, one can determine Γ_M by combining eq 6 with eq 7

$$\Gamma_M = \frac{\Delta\nu' - \Delta\nu_{1/2,F}}{\Delta\nu - \Delta\nu_{1/2,F}} \qquad (8)$$

and estimating $\Delta\nu_{1/2,F}$ from a salt of NaCl in aqueous solution, at the same temperature.

Experimental Section

Poly(styrenesulfonic acid) (M_w = 70000), poly(galacturonic acid) (M_w = 30000), and poly(acrylic acid) (M_w = 5000) were obtained from Polysciences, Inc. To obtain their sodium salts, these polyacids were neutralized with NaOH solution, and to prepare their mixed salts, they were half-neutralized with NaOH and half-neutralized with the corresponding bases (aqueous solutions of alkali hydroxides and solid MgO).

The ^{23}Na NMR were recorded with a Bruker ACP-200 spectrometer (52.939 MHz) using optimized pulse angle and repetition time. Temperature was controlled within ±0.1 deg. The line width for free sodium $\Delta\nu_{1/2F}$, was estimated from a 0.05 M solution of NaCl, and each individual run consisting of a complete set of measurements (e.g., all mixed salts of a given polyacid at one particular concentration) was carried out under identical instrumental settings. The estimated error in the reported Γ_M is on the order of 1% or 2% for the poly(galacturonates) (large line widths in the range 120–140 Hz) and on the order of 4% or 5% for the poly(styrenesulfonates) (small line widths in the range 8.5–10.5 Hz).

Results and Discussion

Listed in Table II are the experimentally determined Γ_M values in the mixed neutral salts (M/Na) of poly(galacturonate) and poly(styrenesulfonate). In the case of poly(galacturonates), Γ_M is equal to unity within experimental error for all the alkali ions and lower than unity for Mg^{2+}, which is consistent with the prediction of the PB model. On the other hand, in the case of the mixed salts of poly(styrenesulfonate), Γ_M for alkali ions is significantly different from unity. In the case of Li^+, Γ_M is actually greater than unity, indicating that the fraction of bound sodium is higher in the presence of Li^+ than in the absence

Table II
Experimentally Obtained Γ_M Values at 293 K in Aqueous Solutions of the Mixed Salts (M/Na)PG and (M/Na)PSS at 50 mM Concentration

M	Γ_M	
	(M/Na)PG	(M/Na)PSS
Li^+	1.0	1.1
K^+	1.0	0.88
Rb^+	1.0	0.76
Cs^+	1.0	0.66
Mg^{2+}	0.86	0.44

Table III
Experimentally Obtained Γ_{Mg} in Mixed (Mg/Na)PG, and Theoretically Calculated $P_{b,Na}$ and $P_{b,Mg}$ in Pure MgPG and NaPG and Their Ratios (κ) at Different Concentrations (c_m)

c_m, mM	Γ_{Mg}	$P_{b,Mg}$	$P_{b,Na}$	κ
50	0.86	0.609	0.356	1.71
25	0.76	0.583	0.317	1.84
16.7	0.69	0.570	0.300	1.90
8.3	0.61	0.555	0.274	2.03
4.2	0.55	0.544	0.253	2.15

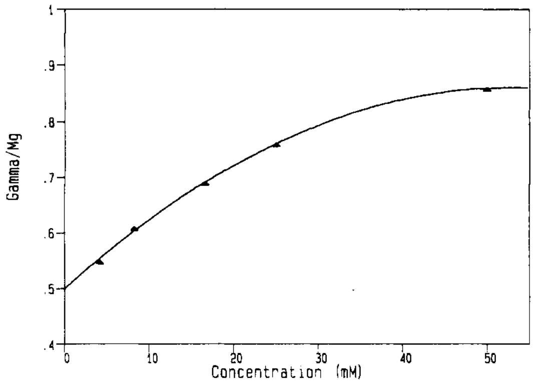

Figure 1. Dependence of the ratio of the amount of Na^+ territorially bound in a mixed neutral salt of poly(galacturonate) containing Na^+ and Mg^{2+} in equal equivalent amounts to the Na^+ bound in pure sodium poly(galacturonate) at the same concentration, Γ_{Mg} (as defined by eq 6), on the poly(galacturonate) concentration, c_m.

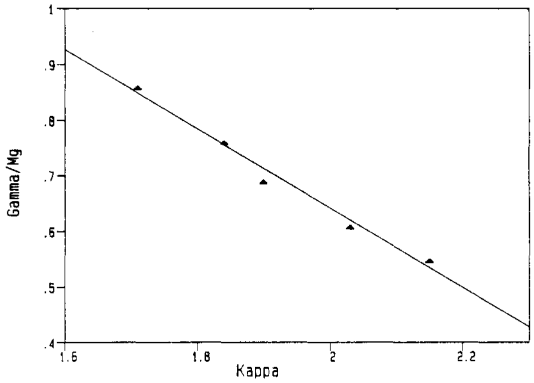

Figure 2. Γ_{Mg}, defined by eq 6 and in the caption of Figure 1, versus the ratio $\kappa = P_{b,Mg}/P_{b,Na}$, where $P_{b,Mg}$ and $P_{b,Na}$ are the numbers of counterions per unit charge calculated by eq 3 bound in pure magnesium and sodium poly(galacturonate), respectively, at the same concentrations.

of any competing ions. Thus, the preference of this polyanion follows the order $Mg^{2+} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. In the case of the alkali metals, this is the order from higher to lower atomic numbers in the periodic chart and from lower to higher hydration numbers (1–2 for Cs^+, 3–4 for K^+, 4–5 for Na^+, 5–6 for Li^+).[11]

It is evident from these results that poly(styrenesulfonate) in the absence of excess salts does not behave "ideally"; i.e., there are specific interactions of different alkali ions with this polyanion. It is noteworthy that Manning[7] referred to this particular polyanion as an example of the "extreme" or special conditions which result in the breakdown of the condensation rule, based on the ultrasonic absorption measurements by Tondre et al.,[13] and ascribed this to overriding hydrophobic interactions between the polyion and tetraalkylammonium ions. Thus, a simple test for the conformity with the ideal behavior of a given polyanion may be that of measuring the ^{23}Na NMR line width of the sodium salt and of the mixed salts with other alkalis. If the line width in pure sodium salt is the same as in the mixed alkali salts, the result is consistent with the PB model and inconsistent otherwise.

We have repeated the same experiment with the mixed salts of poly(acrylate) and found their line widths to be also identical within experimental error. Both poly(galacturonate) and poly(acrylate) passed the same test over the range of concentrations from 5 to 50 mM. Thus, contrary to the findings of Mattai et al.,[3] who used a dye spectrophotometric method in the presence of excess salts, in the absence of excess salt it is the two carboxylated polyions which are consistent with ideal behavior and it is the sulfonated polyion that demonstrates nonideal behavior. Of course, by nonideal behavior we do not imply that PB theory is invalid or not operational, but that superposed on the mechanism of territorial binding or atmospheric condensation there is also some degree of specific site bonding which shows as a deviation in the P_b values predicted by eq 3.

With regard to competition of a divalent ion with a monovalent one in binding to the polyanion in the absence of salts, the PB theory predicts that there would be a lowering of Γ_M in a mixed salt in which M is a divalent ion. We have made a study of the concentration dependence of Γ_{Mg} in a mixed (Mg/Na) PG system. The results of these studies are listed in Table III. The same table lists the $P_{b,Mg}$ and $P_{b,Na}$ values calculated for pure neutral magnesium and sodium poly(galacturonate), respectively, at each corresponding concentration, c_m, as well as their ratio, κ:

$$\kappa = \frac{P_{b,Mg}}{P_{b,Na}} \qquad (9)$$

A plot of Γ_{Mg} versus c_m shown in Figure 1 indicates that there is a monotonic decrease of Γ_{Mg} with the decrease in concentration; i.e., Mg^{2+} competes better with Na^+ at lower concentrations. We thought that a qualitative explanation for this can be made in terms of the calculated values of $P_{b,Mg}$ and $P_{b,Na}$. The latter should reflect separately bonding affinities of Mg^{2+} and Na^+. We note that they both decrease with decreasing concentrations but that the decrease in $P_{b,Na}$ values is percentagewise greater than the corresponding decrease in $P_{b,Mg}$. Thus, the ratio, κ, progressively increases with decreasing c_m. If κ is to be viewed as the measure of the extent to which Mg^{2+} competes for bonding with Na^+, one would expect the lowering of Γ_{Mg} with the increasing κ. In fact, the plot of Γ_{Mg} versus κ shown in Figure 2 does not only substantiate thie expectation but results in a linear relationship in the interval of concentrations studied. Whether this linear relationship is common to other systems in which both monovalent and divalent ions bind in agreement with the PB model is presently under investigation.

The effect of the presence of other ions on the shapes of ^{23}Na NMR spectral lines could not be estimated with accuracy because the strength of the field at which the measurements were made is not high enough for the systems studied. Thus, within experimental error, all the 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.

References and Notes

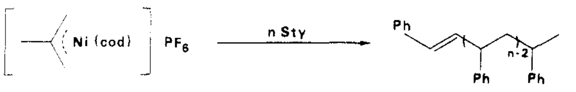
(1) Armstrong, R. W.; Strauss, U. P. Polyelectrolytes. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Gaylord, N. G., Bikales, N. M., Ed.; Wiley-Interscience: New York, 1969; Vol. 10, pp 781–861.
(2) Hen, J.; Strauss, U. P. *J. Phys. Chem.* **1974**, *78*, 1013.
(3) Mattai, J.; Kwak, J. C. T. *Macromolecules* **1986**, *19*, 1663.
(4) Kwak, J. C. T.; Joshi, Y. M. *Biophys. Chem.* **1981**, *14*, 55.
(5) Manning, G. S. *Rev. Biophys.* **1978**, *8*, 179.
(6) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(7) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443.
(8) Grasdalen, H.; Kvam, B. J. *Macromolecules* **1986**, *19*, 1913.
(9) Fuoss, R.; Katchalsky, A.; Litson, S. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 579.
(10) Halle, B.; Wennerstrom, H.; Piculell, L. *J. Phys. Chem.* **1984**, *88*, 2482.
(11) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic: London, 1985.
(12) Anderson, C. F.; Record, M. T., Jr. *Biophys. Chem.* **1978**, *7*, 301.
(13) Tondre, C.; Kale, K. M.; Zana, R. *Eur. Polym. J.* **1978**, *14*, 139.

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%.

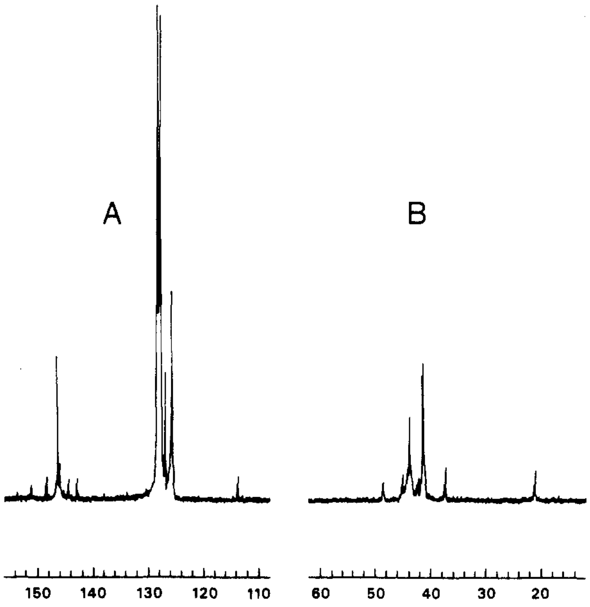


Figure 1. $^{13}C\{^1H\}$ spectrum of isotactic polystyrene: (A) aromatic region, (B) aliphatic region. The spectrum was obtained in tetrachlorodideuterioethane at 120 °C and 50.3 MHz. The pulse width was 3 μs (45°) and the number of scans 17 000.

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.

$$\text{Ni—H} + \text{CH}(C_6H_5)\text{═CH}_2 \rightarrow \text{Ni—CH}(C_6H_5)\text{—CH}_3 \quad (2)$$

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

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