Solution Behavior of the Poly[bis(carboxylatophenoxy)phosphazene] Polyelectrolyte

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ABSTRACT: The behavior of a high molecular weight sodium poly[bis(carboxylatophenoxy)phosphazene] (NaPCPP) polyelectrolyte sample in aqueous solution has been investigated by means of viscosity, conductivity, sodium counterion potentiometric "activity coefficient" (γ^+) measurements, and ^{23}Na-NMR experiments. The set of data clearly and consistently points out the peculiar polyelectrolytic behavior of NaPCPP in water. In our opinion, this is essentially due to the partial hydrophobic character of flexible NaPCPP chains which would easily "entangle" even at low concentrations in water and, in addition, would give rise to "entanglement collapse" with increasing solution temperature.

Introduction

The literature contains reports on the synthesis of different polyelectrolytes having in common a polyphosphazene backbone which appear to be of interest in view of their peculiar chemical structures.[1−6]

However, to our knowledge, no detailed physicochemical characterization of the solution properties of such species has been described. In our laboratory attention has been addressed to the case of the sodium salt of poly[bis(*p*-carboxylatophenoxy)phosphazene (NaPCPP) (Figure 1).[7] We wish to report here the results of a rather detailed study of the dilute solution properties of NaPCPP in water collected using different experimental approaches including viscosity, potentiometric sodium counterion "activity coefficients", conductivity, and ^{23}Na-NMR measurements.

Experimental Section

Synthesis. The synthetic route to obtain NaPCPP consists of the thermal ring opening polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene) (PDCP),[8,9] followed by the introduction of the side chain substituents by means of the reaction of PDCP with the sodium salt of *p*-(hydroxyethyl)benzoate.[10] The product of the nucleophilic substitution is poly[bis(*p*-(ethoxycarbonyl)phenoxyphosphazene] (EtPCPP). The complete substitution of chlorine atoms on the phosphazene backbone was confirmed by the presence of a sharp singlet in the ^{31}P-NMR spectrum of EtPCPP. EtPCPP was then subjected to complete alkaline hydrolysis (potassium *tert*-butoxide in tetrahydrofurane) to the corresponding potassium poly[bis(*p*-carboxylatophenoxy)phosphazene. The acid form of the polyelectrolyte, insoluble in water, was separated by addition of excess aqueous HCl. The polymer was transformed into the sodium salt form (NaPCPP) by addition of aqueous 0.01 M NaOH containing 0.1 M NaCl, exhaustively dialyzed against water (first distilled then double-distilled water), filtered through Millipore filters (8.0 and 0.8 μm), and finally freeze-dried. Prior to measurements, the pH of the NaPCPP solutions in water or in aqueous NaCl was controlled and, if necessary, brought to pH 8.5−9 by careful addition of dilute NaOH.

IR and ^{1}H-NMR spectra of both EtPCPP and NaPCPP are in agreement with those reported in the literature[10] with features consistent with linear chains devoid of branching.

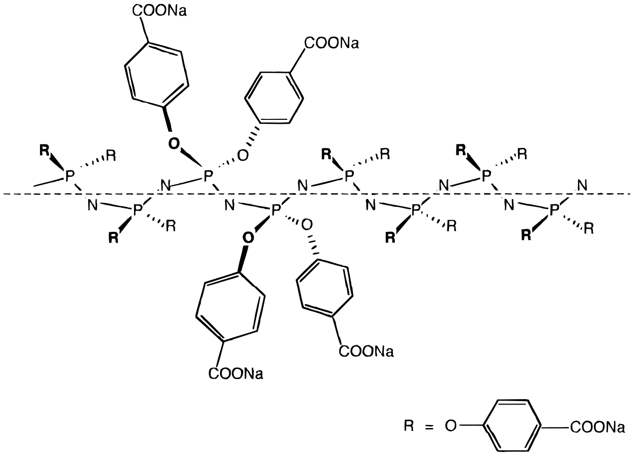

Figure 1. Chain portion of poly[bis(carboxylatophenoxy)phosphazene], sodium salt, NaPCPP. Bond length P-N = 0.159 nm; bond angle NPN = 117°; bond angle PNP = 130°.

The EtPCPP molecular weight distribution, according to SEC measurements, was rather broad with a weight average molecular weight equal to 3×10^6. SEC data were collected using a HPLC Varian-5000 chromatograph with a Varian UV-50 detector ($\lambda = 234$ nm) and the elutions carried out using THF (Carlo Erba, HPLC grade) or THF/(TBA)Br (0.1 M) through Ultrastyragel comumns (10^4 and 10^6) at 303 K. All solutions and solvents were filtered through 0.45 μm Millipore filters immediately before use. A series of polystyrene standards (Shodex, SM-105 and SH-75) were employed for calibrating the instrument. In fact, it has been shown that the molecular weights measured by SEC for a series of phenoxyphosphazenes, relative to narrow molecular weight polystyrene standards, agree well (within ca. 20−30%) with the values determined by membrane osmometry.[11]

Calibration data and chromatograms were processed to obtain M_w and M_n.

The SEC measurements yielded the EtPCPP molecular weight and molecular weight distribution as the weight average molecular weight equal to 3×10^6 and the polydispersity (M_w/M_n) equal to 2.2.

The sodium content of the NaPCPP samples, determined by atomic absorption measurements on NaPCPP aqueous solutions and confirmed with ^{23}Na-NMR sodium quantitative analysis, is in very good agreement with the expected value (two equivalents of sodium per mole of polymer repeating unit). Thus, in what follows, the NaPCPP concentration (C_p) is given

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in millimolar units having taken 363 as the mass of the repeating unit.

Viscosity Measurements. The viscosity measurements were performed with a Ubbelohde viscosimeter ($r_{cap} = 0.46$ mm) in a AVS/G SCHOTT-GERATE apparatus equipped with a thermostatic bath (temperature control ± 0.1 K). Solvent flow times were always over 200 s. This justifies omission of the kinetic energy correction.

Activity Coefficient Measurements. The Na^+ counterions "activity coefficients" γ^+ (of the polyelectrolyte solutions in water) were determined using a Radiometer G502Na sodium selective glass electrode in conjunction with a reference calomel electrode (Radiometer K 401). Emf readings were taken using a Radiometer pHM 93 with an accuracy of ± 0.1 mV. All measurements were carried out in a water-jacketed titration cell at 298.15 ± 0.01 K. Reproducibility within ±0.1 mV was obtained. The calibration of the sodium electrode was frequently checked using standard NaCl solutions prepared by diluting a stock solution (0.10 NaCl). In the polymer concentration (C_p) range studied the slope of the emf (mV) vs a^+ calibration plots was close to 58 mV. In this range the γ^+ values were evaluated according to the equation

$$\gamma^+ = a^+/C_p \tag{1}$$

where a^+ (sodium activity) was evaluated from the calibration curve of standard NaCl solutions with the equation

$$\text{efm} = A + B \log a^+ \tag{2}$$

The pH measurements were carried out at 298.15 ± 0.01 K under N_2 flux with a Radiometer pHM 84 pH-meter using a combined glass/reference electrode (Radiometer GK2401C).

Conductivity Measurements. Conductivity measurements were carried out with a CDM3 Radiometer conductimeter equipped with a CDC 304 conductivity cell. The polymer solutions were thermostated at 298.15 ± 0.01 K and kept under constant nitrogen flux. The frequency dependence of the conductivities in the 10^2-10^4 Hz range was negligible, and hence all measurements were performed at 5×10^3 Hz. Solutions were prepared using deionized double-distilled water. The data have been found reproducible within 1%, approximately.

^{23}Na-NMR. NMR experiments were performed on a Bruker AC-200 spectrometer operating on ^{23}Na at 52.9 MHz . Each aqueous sample contained 10% D_2O to provide a frequency lock. Longitudinal (T_1) and transverse (T_2) relaxation times were measured by the inversion−recovery and spin−echo (CPMG) methods, respectively. When a broad NMR signal is present and/or when the NMR line is not single, the CPMG method becomes unsuitable and T_2 was derived from the line width.

Longitudinal relaxation was fit using a single exponential function, since no indication of biexponential relaxation was found. Each T_1 value was the result of a least-squares fit of longitudinal magnetization vs delay time (t). Transverse relaxation data were interpolated with a single exponential curve. The fit procedure was extended to values of the magnetization (M) corresponding to about 20% of first echo. For both T_1 and T_2, experimental errors in the data reported are less than 10%.

In order to obtain T_1 the equation

$$M = A \exp(-t/T_1) + M_{\text{offset}} \tag{3}$$

was used, where M_{offset} is the mean value of the experimental noise.

The best fit of this equation was obtained using a program based on a Simplex algorithm.[12] The ^{23}Na NMR bands were deconvoluted using a full simulation program "GLINFIT";[13] this program can perform the deconvolution of overlapped lines with both Gaussian and Lorentzian shapes. Errors in the integrals are less than 10% of the reported values.

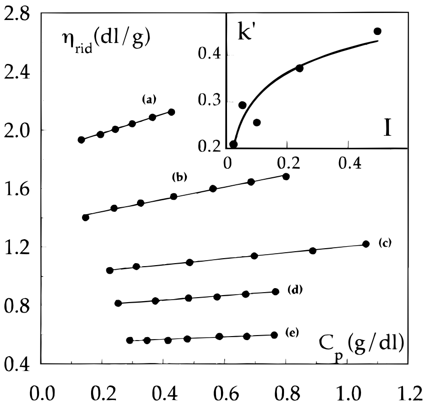

Figure 2. Specific reduced viscosity of NaPCPP in aqueous NaCl solutions at 298 K. Concentrations of NaCl (M) used were (a) 0.024, (b) 0.053, (c) 0.100, (d) 0.240, and (e) 0.495. The ionic strength dependence of the Huggins constant is shown in the inset.

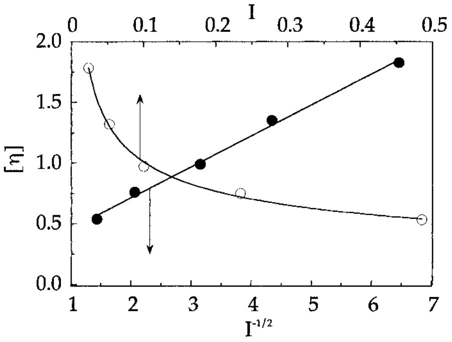

Figure 3. Dependence of NaPCPP intrinsic viscosity, [η], on ionic strength, I (○), and $I^{-1/2}$ (●) NaCl at 298 K. The slope of the linear plot leads to an estimate of the value for the stiffness parameter B (see text) of 0.26.

Results and Discussion

Viscosity Measurements. Viscosity measurements were carried out on aqueous polyphosphazene−sodium salt (NaPCPP) solutions as a function of NaCl concentration at 298 K as shown in Figures 2 and 3. In the full range of polymer concentration the reduced specific viscosity data display a normal behavior. The strong dependence of the intrinsic viscosity of NaPCPP on ionic strength, I (Figure 3), is typical of flexible polyelectrolyte chains which, due to the screening of fixed charges exerted by the added salt, markedly reduce their average dimensions with increasing I.

In this context, qualitative information on the stiffness of the NAPCPP chains can be obtained from the dependence of intrinsic viscosity on $I^{-1/2}$ in terms of the viscosity B parameter introduced by Smidsrod and Haug.[14]

The viscosity B parameter is obtained by the equation

$$B = \frac{S}{([\eta]_{0.1})^r} \tag{4}$$

where S is the angular coefficient of the curve obtained by the [η] (dL/g) vs $I^{-1/2}$ (equiv$^{-1/2}$L$^{1/2}$) plot, $[\eta]_{0.1}$ is the intrinsic viscosity (dL/g) measured at 0.1 equiv/L (ionic strength), and r is equal to 1.3.

The B parameter value calculated on the basis of data in Figure 3 is 0.26. This value is close to that obtained

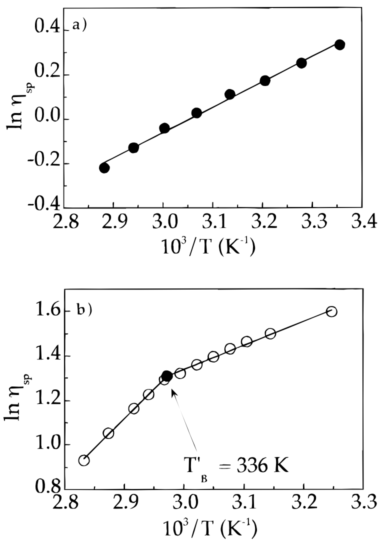

Figure 4. Temperature dependence of specific viscosity of aqueous solutions of NaPCPP at two different concentrations: (a) $C_p = 2.5$ mM; (b) $C_p = 12.5$ mM. $T'_B = 336$ K.

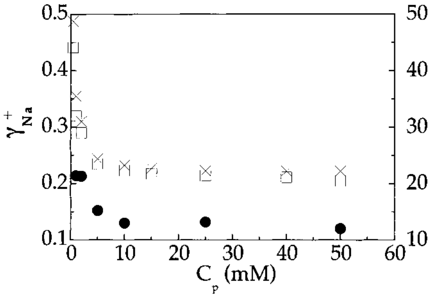

Figure 5. Sodium activity coefficient (☐) and conductivity (×) as a function of NaPCPP concentrations C_p (mM). For comparison, a plot of spin−lattice relaxation times T_1 (ms^{-1}) (●) in the same range of concentration is also reported. $T = 298$ K.

for polycarboxylates with a flexible backbone, such as polyacrylic acid for which $B = 0.23$. For relatively rigid, single stranded polycarboxylates, like the alginates, a much smaller value (e.g. $B = 0.04$) is reported.[14]

The temperature dependence of NaPCPP specific viscosity (η_{sp}) has been explored for two polyelectrolyte concentrations (2.5 mM and 12.5 mM) in water. Data from Figure 4 show that at the higher NaPCPP concentration there is a discontinuity in the trend of $\ln \eta_{sp}$ against $1/T$.

Discussion of this aspect will be resumed later in this section.

Activity Coefficient and Conductivity Measurements. The results of sodium counterions "activity coefficients" (γ^+) measurements in NaPCPP solutions without added salt are reported in Figure 5.

Whereas γ^+ shows almost no polymer concentration dependence over the C_p range 60−4 mM, it increases rather steeply below $C_p \approx 4$ mM.

Comparison between the average experimental value ($\gamma^+ = 0.22$, for $C_p > 5$ mM) and the γ^+ limiting value predicted by Manning's theory ($\gamma^+ = 0.10$) reveals that the latter is too low. In that theory[15−18] a basic parameter is the linear charge density, ξ, of the macroions given by $\xi = e^2/DkTb$, where e, D, k, T and b are, respectively, the elementary electric charge, the dielectric constant of the solvent, the Boltzmann constant, the absolute temperature, and the average axial spacing between charged groups on the polyions.

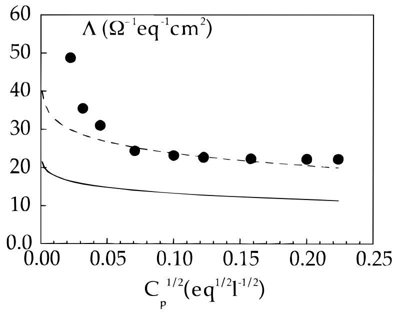

Figure 6. Equivalent conductivity as a function of the square root of the normality of NaPCPP at 298 K. Full and dashed lines are the theoretical predictions based on Manning theory corresponding, respectively, to a charge density parameter ξ equal to 6.3 and 3.4.

Simple calculations[19] lead to an estimate of $b = 0.113$ nm for the NaPCPP chains in the fully extended state (Figure 1), which corresponds (298 K in water) to $\xi = 0.715/b = 6.3$ and hence to $\gamma^+ = 0.10$ (in fact: $\ln \gamma^+ = -\frac{1}{2} - \ln \xi$; $\xi > 1.0$[15−18]). To reproduce the experimental γ^+ value (for the higher C_p values), one should impose $\xi = 3.0$

For the same experimental conditions, the equivalent conductivity Λ of salt-free aqueous solutions of NaPCPP has been measured for different polymer concentrations (see Figure 5). The contribution of free OH$^-$ ions to the measured total conductivity has been neglected since the pH values of the solutions exceeded only slightly 9.5. The experimental Λ values can be compared with theoretical ones (full line in Figure 6) according to the equations[20,21]

$$\Lambda = f(\lambda_p + \lambda_c^0); \quad f = 0.866\xi^{-1} \tag{5}$$

where λ_p is the equivalent conductivity of the polyions, λ_c^0 is the equivalent conductivity of counterions at infinite dilution ($\lambda_c^0 = 50.1\ \Omega^{-1}$ eq^{-1} cm^2, at 298 K), and f is the fraction of uncondensed counterions. The equivalent conductivity of polyion, λ_p, in water at 298 K is written in the following form:[21]

$$\lambda_p = \frac{22.37|\ln \kappa a|}{1 + 3.467(\lambda_c^0)^{-1}|\ln \kappa a|} \tag{6}$$

Here

$$\kappa = \left[\left(\frac{4\pi e^2}{\epsilon kT}\right)\frac{C_p}{\xi}\right] \tag{7}$$

a is the radius of the polyion rod ($a = 7.4$ Å), e is the protonic charge, ϵ is the bulk dielectric constant, and kT is the Boltzmann factor.

In the present study, assuming $\xi = 6.3$, λ_p varies from 111.93 to 305.18 Ω^{-1} equiv^{-1} cm^2.

As shown in Figure 6, the agreement between experiment and theory assuming $\xi = 6.3$ and $f = 0.13$ is rather poor. In fact, to partially superimpose the theoretical curve (dotted curve in Figure 6) and the experimental data, one must use $\xi = 3.4$, qualitatively consistent with what was found for the counterion activity coefficients.

The rather sharp rise of both the activity coefficient and the conductance at low C_p is a phenomenon which will be discussed in the following section.

^{23}Na-NMR Measurements. The ^{23}Na-NMR line width has been studied as a function of NaPCPP concentration, C_p, in water. For $C_p > 25$ mM, a single

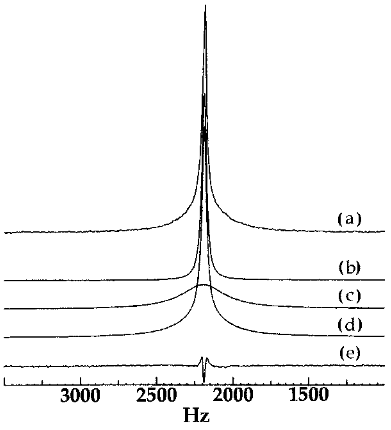

Figure 7. ^{23}Na-NMR spectrum of a 1.0 mM solution of NaPCPP in H_2O/ D_2O (90/10) (a) and single components of the deconvoluted spectrum (b) and (c). The difference between the experimental (a) and simulated spectrum (d) is shown in part e.

Table 1. ^{23}NaNMR Transverse Relaxation Rates, $R_2{}^{*f}$ and $R_2{}^{*s}$, Estimated Correlation Times, τ_c, of Bound Na^+, Longitudinal Relaxation Time, T_1, Activity Coefficient, γ^+, Conductivity, Λ, Fraction of Bound Na^+ Ions, and P_b, in Salt-Free D_2O Solutions of NaPCPP at Different Polymer Concentrations, C_p (mM), at 298 K

C_p (mM)	$R_2{}^{*f}$ (Hz)	$R_2{}^{*s}$ (Hz)	τ_c (ns)	T_1 (ms)	γ^+	Λ (Ω^{-1} equiv^{-1} cm^2)	P_b
50	151			12.0	0.206	22.2	
40					0.211	22.2	
25	138	484	4.9	13.2	0.214	22.3	0.67
15					0.217	22.7	
10	122	477	5.3	13.0	0.223	23.2	0.67
5	100	653	7.6	15.2	0.235	24.4	0.67
2	91	672	8.2	21.3	0.290	31.0	0.60
1	82	732	9.2	21.4	0.320	35.5	0.53
0.5					0.441	48.7	

Lorentzian line is observed. Upon lowering the concentration, two Lorentzian components, centered at about the same chemical shift but with different line widths, contribute to the resulting line shape. The ^{23}Na NMR spectrum of a 1 mM solution of NaPCPP in H_2O/ D_2O (90/10) is shown in Figure 7a. Single components of the deconvoluted spectrum are shown in Figure 7b and in Figure 7c; in Figure 7d the calculated spectrum is reported. In Figure 7e the difference between the experimental (Figure 7a) and the calculated spectrum (Figure 7d) is shown.

The presence of two observable resonances can be attributed to a slow equilibrium existing between free and bound sodium ions: when the polyelectrolyte concentration is increased, the exchange rate increases and only one component can be detected.

By performing a careful simulation[13] of the ^{23}Na-NMR spectrum in the C_p range in which two components are observed, the line widths resulting from the deconvolution with their relative weight have been calculated. The two overlapped Lorentzian lines are due respectively to unbound Na^+, the sharp (s) component, and to bound Na^+ ions, the broad (b) component. Thus, from the line width data two relaxation rates can be obtained:

$$R_2{}^{*f} = \pi\Delta\nu_{\mathrm{sharp}} \qquad R_2{}^{*s} = \pi\Delta\nu_{\mathrm{broad}} \tag{8}$$

The fast and slow relaxation rates at different C_p values are reported in Table 1.

Correlation times, τ_c, are calculated from the relaxation rates ratio with the equation

$$\frac{R_2{}^{*f}}{R_2{}^{*s}} = \frac{1 + 1/(1 + \omega^2\tau_c{}^2)}{1/(1 + \omega^2\tau_c{}^2) + 1/(1 + 4\omega^2\tau_c{}^2)} \tag{9}$$

where ω is the resonance frequency, are listed in Table 1. The resulting quadrupolar coupling constant value[22] is 220 ± 20 KHz.

These values can be compared with the corresponding data obtained for polyelectrolytes of similar chain flexibility.[22] For instance, in the case of polyacrylate assuming χ = 220 KHz, experimental values for the amount of bound sodium counterions are well reproduced[22] assuming "counterion condensation" driven essentially by electrostatic interactions.

The analysis of correlation times reported in Table 1 has been done according to the arguments developed by van Rijin et al.[23-25] in their ^{23}Na-NMR and ^{2}H-NMR studies of flexible chain polyelectrolytes in solution. It has been recognized that the more important contributions to the experimental correlation times come from segmental motions and counterion axial diffusion. In this fashion, the increase of τ_c with dilution is mostly due to a concomitant increase of the chains total persistence length. Accordingly, the trend with C_p of correlation times listed in Table 1 is consistent with a notable expansion of NaPCPP chains upon dilution in water.

This is consistent with the trend of specific reduced viscosity with C_p in water without added salt (data not reported in this paper). NaPCPP specific reduced viscosity, as observed in general for polyelectrolytes, increases by increasing the dilution. This is due to the progressive release of sodium counterions from the polyion domains as the polyelectrolyte concentration is decreased. The reduced screening of negative charges on macroion promotes the expansion of the polymer, increasing the reduced viscosity.

From the same deconvolutions (simulated spectra of Figure 7) it is also possible to evaluate the amount of the broad component, A_b, and the amount of the sharp component, A_s. Here $p_b = A_b/(A_b + A_s)$ corresponds to the mole fraction of bound sodium counterions, as reported in Table 1.

The sodium NMR spin–lattice relaxation times, T_1, have been measured at different C_p values. When C_p is lowered, T_1 increases from 12 to 21 ms (see Table 1). It is worth noticing that the dependence on C_p of T_1, a microscopic parameter, is qualitatively correlated with those of the activity coefficient (γ^+) and the equivalent conductivity (Λ), both macroscopic parameters (see Figure 5).

Finally, the temperature dependence of the ^{23}Na-NMR line widths was investigated at three NaPCPP concentrations, namely, C_{pA} = 2.5 mM, C_{pB} = 12.5 mM, and C_{pC} = 25.0 mM. The results are reported in Figure 8.

When the temperature is increased, the exchange rate between bound and free sodium ions increases and only one resonance in the high-resolution NMR spectrum becomes detectable for C_{pA} and C_{pB} in the T range considered.

Note that at C_{pA}, a linear dependence of the line width on $1/T$ can be observed (Figure 8a), while for both C_{pB} and C_{pC} two different regions characterized by different slopes exist (see Figure 8b,c). The temperatures at which the change in the slope occurs are, approximately, T_B (326 K) and T_C (315 K). These results find a counterpart, at least qualitative, in the viscosity results collected for NaPCPP concentrations equal to C_{pA} and

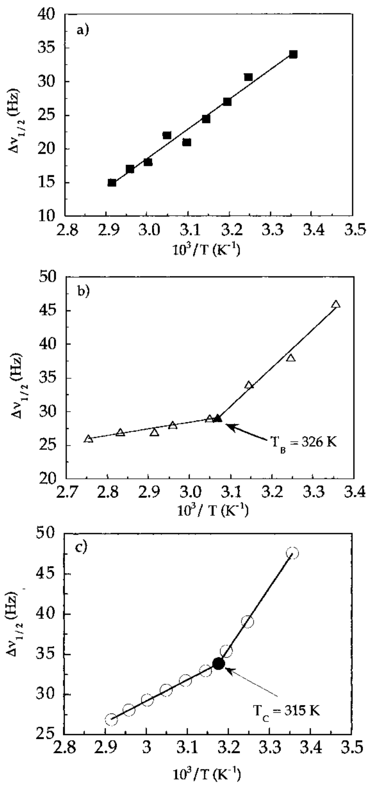

Figure 8. Temperature dependence of the ^{23}Na-NMR line width of aqueous solutions of NaPCPP in H_2O/ D_2O (90/10) at 52.9 Mhz. Key: (a) $C_p = 2.5$ mM; (b) $C_p = 12.5$ mM; (c) $C_p = 25.0$ mM. $T_B = 326$ K; $T_C = 315$ K.

C_{pB} and illustrated in Figure 4. In fact, for C_{pB} but not for C_{pA} a discontinuity in the viscosity vs temperature plot is observable near $T'_B = 336$ K.

We believe that, despite the $T'_B - T_B$ difference (beyond experimental errors), the two types of experiments, one dynamic and one static in nature, point out the occurrence of the same phenomenon.

Concluding Remarks

Viscosity data at 298 K measured for different ionic strengths (NaCl) suggest that NaPCPP chains are rather flexible.

Results of counterion "activity coefficient" and conductivity measurements consistently show that for concentrations higher than about 5−10 mM, NaPCPP in water behaves as a "normal" polyelectrolyte in that both type of results depend little on polymer concentration (in the limited range investigated). Comparison with predictions based on Manning theory indicate that in order to reproduce the experimental data in said range the linear charge density of the NaPCPP chains has to be taken to be about half that calculated for the structural model of the fully expanded polyphosphazene chain. For concentrations lower than 5−10 mM, both the activity coefficient and the conductivity start to rise.

The picture emerging from the ^{23}Na-NMR data collected at 298 K is fully consistent with observations mentioned above.

With increasing temperature, however, a discontinuous trend can be clearly detected in the viscosity and ^{23}Na-NMR data for polymer concentrations higher than about 5−10 mM. Such a phenomenon cannot be rationalized in terms of conventional polyelectrolyte theories.

In our opinion, the unusual complex behavior observed working at C_p greater than about 7 mM, e.g., C_p* (roughly estimated by equation $C_p^*[\eta] \approx 1$ using the intrinsic viscosity at 4×10^{-3} M ionic strength) can be traced both to chain overlap and to partial aggregation phenomena mainly due to the hydrophobic character of the NaPCPP skeleton.

At higher concentrations ($C_p \gg C_p$*), in the overlap concentration regime, the mean electrostatic field within the polyion "lattice" would be practically invariant with concentration and, as a consequence, also the fraction of counterions "bound" would be nearly constant, as observed.

Lowering the NaPCPP concentration further promotes progressive free chain expansion and the release of sodium counterions from the polyion domains.

However, the chain flickering "lattice" would start to collapse above a critical temperature (e.g. T_B).

This interpretation appears consistent with all the experimental evidence obtained.

Above the overlap concentration, where the mean electrostatic field is practically invariant, activity coefficients, conductivities, and line widths change only a little with diluition. If the concentration is then lowered below the critical overlap limit, the individual chains become progressively separated so that distinct regions containing no polymer chains will appear. The loss of counterions from the polymer chains becomes greater and, as a result, activity coefficients, conductivities, and line widths increase.

The temperature dependence of viscosity and line width is consistently explained when the effect of intermolecular association is properly taken into account. In the presence of singly dispersed chains, e.g., at $C_p < C_p$*, a linear dependence of the line width and of ln η_{sp} on $1/T$ is observed (see Figures 4a and 8a). At higher temperatures, the hydrophobicity of polyelectrolyte chains becomes dominant and induces the intermolecular association of polyions. The intermolecular association may cause a reduction in polyelectrolyte size, since the observed η_{sp} at higher temperatures is smaller than expected from the linear extrapolation of η_{sp} from the lower temperature regime.

The effects on Δv are qualitatively consistent with those on η_{sp}. At concentrations higher than the critical overlap concentration, with the mean electrostatic field practically invariant with concentration, the exchange rate is fast; that is, the activation energy of the process is low. Consistently, in this concentration range and at temperatures lower than the discontinuity, the higher the polymer concentration the higher the slope of the linear region. This means that the activation energy decreases. With an increase in the temperature above the discontinuity, the intermolecular association will cause the polyions "lattice" to collapse. The mean electrostatic field is no longer invariant in the solution domain, and the activation energy increases with respect to the low-temperature region. The fact that $T_C < T_B$ (see above) is consistent with our interpretation in as much as higher NaPCPP concentrations should facilitate hydrophobic chain interactions.

In the context it is interesting to mention that even limited protonation of the polyphosphazene polyelectrolyte (about 20%) in dilute aqueous solution promotes phase separation. Different is the behavior of NaPCPP in the presence of uniunivalent salts, among which hydrophobic tetralkylammonium salts as well as cationic dyes (e.g. methylene blue) exhibit a peculiar affinity for the polyelectrolyte chains. These features should be reported elsewhere.[26]

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