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Titration of Poly(carboxylic acid)s in Methanol Solution. Polymer Chain Extension, Ionization Equilibria, and Conformational Mobility

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ABSTRACT: The titration of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) with $LiOCH_3$ and $NaOCH_3$ in methanol was studied by solution viscosity, potentiometry, and NMR spectroscopy. When titrating with $LiOCH_3$, the reduced viscosity (rv) first increased with an increasing degree of neutralization (α) but then decreased due to counterion condensation and the mutual attraction of the ion-pair dipoles. The earlier rv maximum and the steeper rv decline in the case of PMA were attributed to a lower local dielectric constant. The rise of the pK with α continued for PAA even after the onset of counterion condensation as judged by the rv reversal, although Manning's theory predicts that the polymer charge density should remain constant. The NMR spectra of PMA and PAA showed a significantly greater line broadening with increasing neutralization in methanol than in D_2O, indicating a sharp decrease of conformational mobility due to the energetic interactions between the polymer-bound ionic charges and ion-pair dipoles in the medium of low dielectric constant. When PAA or PMA was titrated with $NaOCH_3$, where the two polymers showed a similar behavior, the collapse of the polymer chain (as evidenced from both rv and NMR intensity) occurred at a much lower α than with lithium methoxide titration, and led to a rv much lower than that of the two unneutralized polymers. This was attributed to a much stronger tendency of Na ion-pairs than Li ion-pairs to dimerize.

Introduction

In 1984, Mandel and his collaborators published an extensive study of the titration of poly(acrylic acid) (PAA) in methanol finding some striking phenomena.[1] Unlike the titration in aqueous solution, which exhibits a very small dependence on the nature of univalent counterions,[2] the titration in methanol with $LiOCH_3$ and $NaOCH_3$ exhibited vastly different characteristics. With the Na^+ counterion, the reduced viscosity first increased steeply with increasing ionization but then dropped abruptly within the degrees of neutralization (α) of about 0.1 and 0.25 to values close to those corresponding to compact spheres. At this point the solution was opalescent, but no polymer precipitated up to full neutralization. The dependence of the pK on α was also unusual in that it exhibited a plateau in the range where the polymer collapsed, suggesting a phase transition. On the other hand, when Li^+ was the counterion, no such pK plateau was observed, and the decrease of the reduced viscosity was gradual, so that its value at full neutralization was similar to that of the unneutralized PAA.

A similar study was later reported for the titration of poly(methacrylic acid) (PMA) and PAA with $LiOCH_3$ in methanol,[3] and it was suggested that the gradual collapse of the chain is due to the mutual attraction of ion-pairs which are formed by the counterion condensation beyond a critical value of the charge density of the polymer chain, as predicted by Manning's theory.[4] Such a collapse due to ion-pair association is generally observed with ionomers in nonpolar media[5] as well as for polyelectrolyte gels in aqueous medium[6] and has been studied by molecular dynamics simulation.[7]

More recently, it was suggested on theoretical grounds[8] that polyelectrolytes assume in poor solvent media a "pearl-necklace structure" where sections of the polymer chain collapse into compact spherical globules which are connected by flexible chains. This prediction was verified by Aseyev et al.[9] in a study using dynamic light scattering to obtain the hydrodynamic radius of the polyelectrolyte and SANS to characterize the size of the globules. In a previous study in this laboratory[10] a different approach was used. Since the compact globules would not be expected to contribute to the solution high-resolution NMR spectrum, while the connecting sections of the chain would retain their conformational mobility, formation of the pearl necklace structure should lead to a reduction of the NMR spectral intensity with no diminution of the resolution of the spectrum. This was indeed the behavior of the sodium salts of poly(styrenesulfonic acid), PAA, and PMA when methanol was added to their aqueous solution close to the precipitation point. By contrast, such methanol addition to an aqueous solution of the uncharged polyacrylamide led to no change in the NMR spectrum.

In this study we use NMR spectroscopy in addition to potentiometry and viscosimetry and take account more explicitly of counterion condensation and ion-pair interaction to interpret the behavior of PAA and PMA when they are neutralized in methanol solution with $LiOCH_3$ and $NaOCH_3$.

Experimental Section

5 mL of methacrylic acid in 20 mL of 1,4-dioxane containing 0.01 g of AIBN initiator was polymerized at 65 °C. 5 mL of acrylic acid in 15 mL of 1,4-dioxane containing 0.006 g of AIBN was polymerized at 65 °C. Both polymerization products were dissolved in water and purified by dialysis for 1 week, changing the dialyzate every day. Both product solutions were then dried by lyophilization. The molecular weights were determined from the intrinsic viscosity (for PMA in methanol at 26 °C, with Mark−Houwink constants[11] $K = 0.242$, $a = 0.51$, yielding $M_v = 325\,000$; for PAA in 2 M NaOH at 25 °C, with Mark−Houwink constants[12] $K = 0.0422$, $a = 0.64$, yielding $M_v = 224\,000$).

The potentiometric titrations were carried out using a Fisher Scientific accumet model 15 pH meter. As directed by Klooster et al.,[1] for pH measurements in methanol solution the glass electrode was kept in pure methanol overnight before a titration was started, and 2.34 was added to the value

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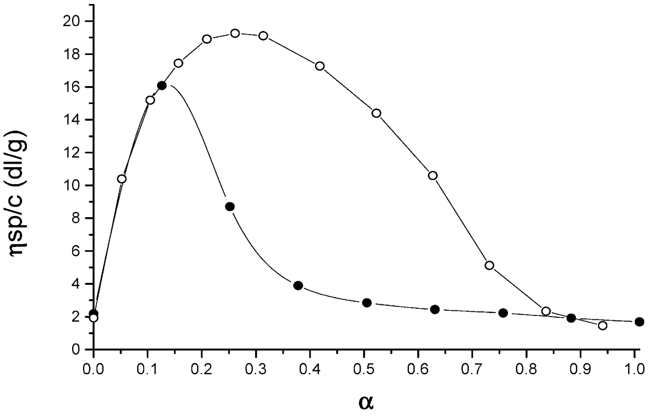

Figure 1. Reduced viscosity (η_{sp}/c) of 0.015 M PAA (○) and 0.015 M PMA (●) in methanol titrated with $LiOCH_3$.

indicated by the meter to account for the difference in the liquid junction potential in methanol and in water to obtain the true pH used in pK = pH + log [(1 − α)/α].

^1H NMR spectra were recorded on a Bruker 300 MHz spectrometer using D_2O and CD_3OD as solvents and TMS as a reference for chemical shifts.

Results and Discussion

Titration with $LiOCH_3$. Figure 1 shows the reduced viscosity of PAA and PMA as a function of α in methanol solution. It first exhibits a steep rise, passes through a maximum, and decreases at higher α to a value at full neutralization which is similar to that for the uncharged polymer. However, the detailed behavior of the two poly(carboxylic acid)s is strikingly different: For PMA the reduced viscosity maximum lies at α = 0.13, and the decline beyond that value is much steeper than with PAA, whose reduced viscosity maximum lies at α = 0.25.

It has been previously conjectured[1b,3,6] that the contraction of the poly(carboxylic acid)s at higher charge densities is due to the condensation of counterions, as predicted by Manning's theory,[4] and to the mutual attraction of the ion-pairs. Theory predicted that the maximum charge density which a polyelectrolyte can sustain is DkT/e, where D is the dielectric constant, kT has the usual meaning, and e is the charge of the electron. Since the charge density of the fully ionized polymer is e/d, where d is the distance between neighboring ionizable groups on the chain molecule, the critical degree of neutralization (α′) beyond which the counterion condensation keeps the charge density constant is $DkTd/e^2$. For PAA and PMA where d = 0.25 nm and for methanol with D = 31.4, this yields α′ = 0.13. This seems to agree remarkably with the reduced viscosity maximum for PMA, but why should this maximum occur at such different positions for PAA and PMA?

Manning's theory assumes that the dielectric constant D, which controls the counterion condensation, is the bulk value of the solvent medium. However, a study of the ratio of the first and second ionization constant of dicarboxylic acids, K_1/K_2, has shown that the effective dielectric constant in the neighborhood of an organic molecule is much lower than its bulk value.[13] Muthukumar also stated that the effective dielectric constant in the vicinity of the polyion should be different than that of the bulk solvent.[14] Moreover, when Eberson studied a series of succinic acids, he found that alkyl substituents increased dramatically the K_1/K_2 ratio, i.e., decreased the effective local D.[15] We may then conclude that the methyl substituents of PMA lower the effective dielectric constant in the neighborhood of the chain molecule below that in PAA, leading to an earlier onset of the counterion condensation and a stronger attraction between the ion-pair dipoles as evidenced by the steeper decline of the rv with an increasing degree of neutralization.

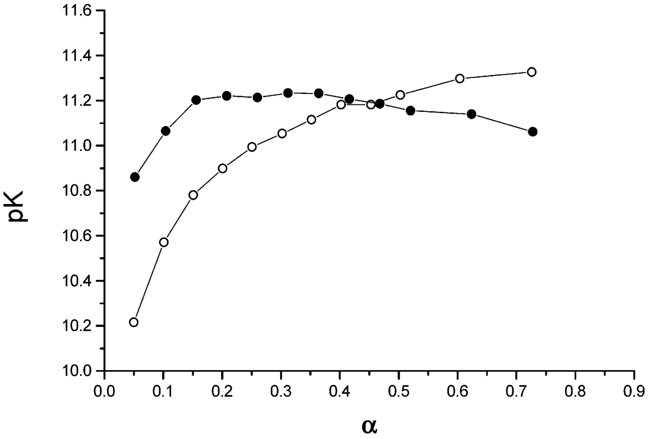

Figure 2. pK of 0.015 M PAA (○) and 0.015 M PMA (●) titrated with $LiOCH_3$ in methanol.

When the concentrations of PMA and PAA were reduced from 0.015 to 0.0075 M, the rv increased (as expected for polyelectrolytes due to the decreasing shielding of the polyion charges by counterions) and the rv maxima increased from 16 to 21 for PMA and from 19 to 26 for PAA. Also, these maxima now occurred at lower α values, shifting from α = 0.13 to α = 0.10 for PMA and from α = 0.25 to α = 0.20 for PAA. This feature was unexpected since theory predicts the onset of counterion condensation to be independent of the polyelectrolyte concentration.[4b]

Since the rise of the pK of poly(carboxylic acid) with increasing α is due to the increasing free energy $\Delta G_{el}(\alpha)$ required to separate a proton from the polymer charge, i.e.

$$pK = pK^\circ + \Delta G_{el}(\alpha)/kT$$

where pK° characterizes a monocarboxylic analogue of the polymer, one might have expected the pK of the polymer to level off at the start of the counterion condensation beyond which the polymer charge density is theoretically predicted[4] to remain constant.

Yet, as shown in Figure 2, no such leveling off was observed with PAA titrated in methanol with $LiOCH_3$. Previous studies of the titration of PAA in water also exhibited no pK leveling at the point where counterion condensation would have been expected,[2] and Mandel found that the pK of PAA could be fitted to a quadratic function of α.[16] Manning has formulated a theory which concludes that the pK should keep increasing even as counterion condensation keeps the net charge of the polymer domain constant.[17] In his model the counterions are territorially bound rather than forming ion-pairs. However, this would not lead to a collapse of the polyion, which suggests energetic interactions between ion-pairs. There is, however, one feature of the physical situation which the theory does not deal with: after the onset of counterion condensation, un-ionized carboxyls find themselves increasingly in the vicinity of ion-pairs. Their dipoles should affect $\Delta G_{el}(\alpha)$ depending on their mutual orientation in a manner which is difficult to predict but

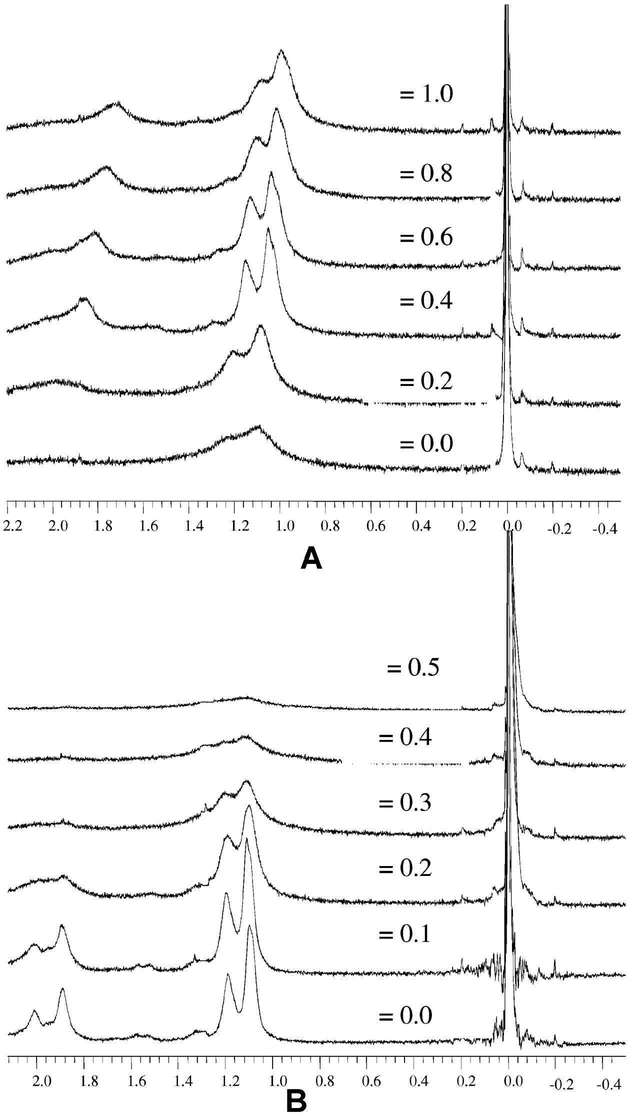

Figure 3. NMR spectra of 0.015 M PMA as a function of α: (A) solution in D_2O titrated with NaOH; (B) solution in CD_3OD titrated with $LiOCH_3$.

should depend on the structure of the polyion. This may explain why the p*K* of PAA increased after the onset of counterion condensation but that of PMA did not.

Figure 3 compares the ^1H NMR spectra of PMA when titrated in D_2O and in methanol. There is a dramatic difference in the effect of ionization on the NMR spectra in the two solvent media. In D_2O the α-methyl peak is broad in the un-ionized PMA and is only resolved on ionization to peaks which may be deconvoluted to indicate that the polymer contains 59% syndiotactic, 33% heterotactic, and 8% isotactic triads, characteristic of PMA produced by free radical polymerization. The NMR peaks first narrow with increasing α and then slightly broaden. A similar behavior was observed by Kay et al.,[18] who concluded that the breadth of the α-CH_3 peak (and the absence of methylene peaks) indicated a steric restriction in the un-ionized PMA, whereas the sharpening of the methyl peaks at moderate α values reflected the local conformational transition responsible for the p*K* plateau during the PMA titration.[19] The broadening of the methyl peaks at higher degrees of ionization may be ascribed to a decreased conformational mobility due to the repulsion between polymer-bound ionic charges. In methanol the peaks corresponding to heterotactic and syndiotactic triads are resolved in the un-ionized PMA, suggesting that the breadth of the methyl peak of un-ionized PMA in D_2O may be related to various anomalous properties of PMA in aqueous solution at low pH, such as the tendency of the polymer to encapsulate aromatic solutes.[20] A striking broadening of the methyl peaks is observed in methanol between $\alpha = 0.2$ and $\alpha = 0.3$, the range corresponding to the collapse of the polyion. At high degrees of ionization the NMR spectra disappear entirely, indicating a sharp decrease of conformational mobility due to the repulsion between ionic charges and the attraction between ion-pairs in different sections of the polyion in the low dielectric constant medium.

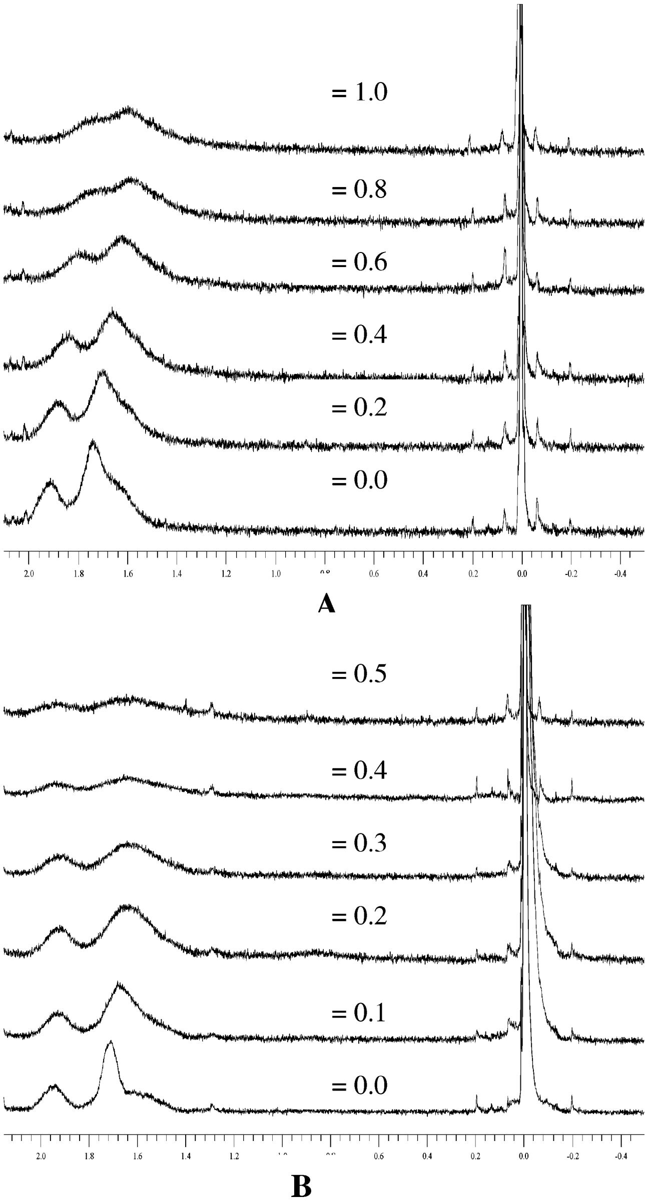

Figure 4. NMR spectra of 0.015 M PAA as a function of α: (A) solution in D_2O titrated with NaOH; (B) solution in CD_3OD titrated with $LiOCH_3$.

For PAA the difference in the NMR spectra in D_2O and methanol (Figure 4) is less pronounced, but even here it is clearly evident that the NMR peaks in methanol rapidly disappear as the decrease in the rv with increasing α indicates counterion condensation and polyion collapse.

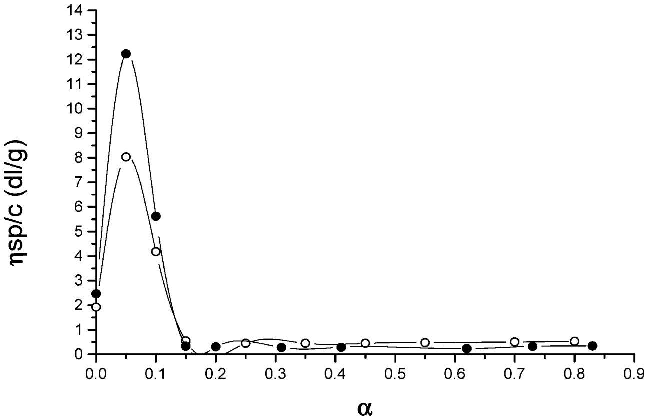

Figure 5. Reduced viscosity (η_{sp}/c) of 0.015 M PAA (○) and 0.015 M PMA (●) in methanol titrated with $NaOCH_3$.

Titration with $NaOCH_3$ in Methanol. Both PAA and PMA exhibit a strikingly different behavior with Li^+ and Na^+ counterions (compare Figure 1 with Figure 5). As seen in Figure 5, with Na^+ counterions the rv reaches its maximum at $\alpha = 0.05$ and drops at $\alpha = 0.15$ to a value well below that for the unneutralized polymers. Yet, as pointed out for PAA,[1] although this indicates that the polymer chains collapse to slightly solvated globules, no phase separation occurs even at full neutralization. This may be accounted for by the ionic charges at the surface of the globules, which would inhibit their aggregation. As would be expected, the slightly solvated globules exhibit no high-resolution solution NMR spectrum (see Figure 6) which disappears at $\alpha = 0.25$.

In searching for an explanation of the dramatic dependence of the behavior of PAA and PMA on the nature of singly charged counterions, we record the observation[21] that ionomers carrying alkali naphthyl carboxylate residues exhibit two fluorescence peaks which could be assigned to the naphthyl carboxylate ion-pair and to its intramolecular dimer. In toluene solution the dimerization of the Li naphthyl carboxylate is more pronounced than that of the Na ion-pair. However, Chabanel and Wang,[22] who studied Li and Na isothiocyanates in the polar medium THF, $D = 7.52$, found that the equilibrium constant for the dimerization of the ion-pair was 2 orders of magnitude higher for the Na salt due to the higher energy required for the desolvation of the Li isothiocyanate. We may then conjecture that in methanol Na ion-pairs also dimerize much more than Li ion-pairs and that this accounts for the difference in the behavior of PAA and PMA with these counterions.

This investigation should be supplemented by the use of ^7Li and ^{23}Na NMR. ^7Li has been shown to yield quantitative data on the formation of ion-pairs of Li^+ with ionized carboxyls[23] and would provide more detail of how such ion-pair formation is responsible for the collapse of PAA and PMA. Also, solutions of sodium isothiocyanate should be studied with ^{23}Na NMR to see whether the dimerization of the ion-pair observed by Chabanel and Wang[22] leads to a characteristic shift in the ^{23}Na NMR peak. If so, this can be used to see whether our proposal that the behavior of poly(carboxylic acid)s titrated with $NaOCH_3$ in methanol solution is due to ion-pair dimerization is correct.

Concluding Remarks

As a result of this study the following points may be emphasized:

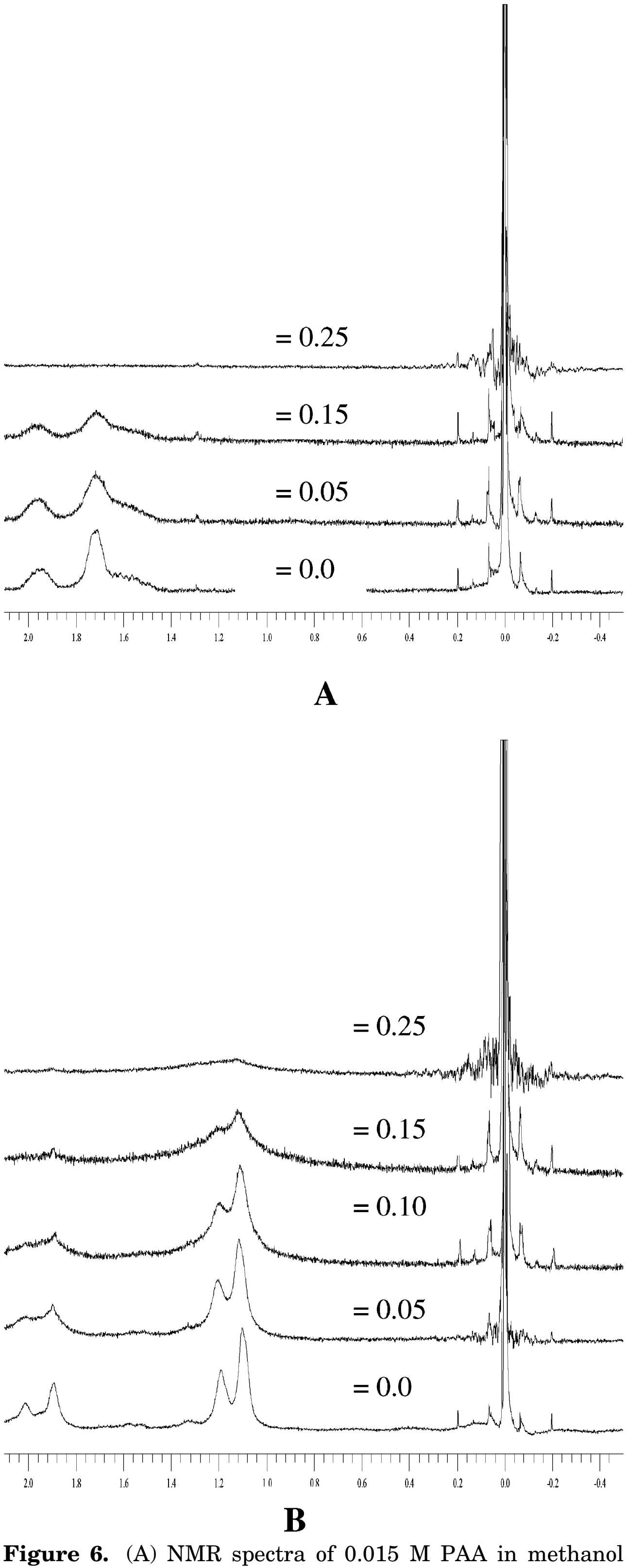

Figure 6. (A) NMR spectra of 0.015 M PAA in methanol titrated with $NaOCH_3$. (B) NMR spectra of 0.015 M PMA in methanol titrated with $NaOCH_3$.

(1) Manning's theory of counterion condensation assumes that the phenomenon depends on the density of the polymer bound ionic charges projected on the axis of the polyion and the bulk dielectric constant of the solvent medium. Both these assumptions may be liable to some correction. As mentioned above, there is convincing evidence[11,12] that the effective dielectric constant

in the vicinity of an organic solute is much lower than in bulk water; this should increase counterion condensation and may account for the difference in the behavior of PAA and PMA. (Manning's theory involves no assumption of an effect of the chemical nature of the polyion on the effective dielectric constant in its vicinity.[4b]) But counterion condensation should also depend to some extent on the physical distance between neighboring ionic charges carried by the polyion, although Manning has argued that this would be negligible at low ionic strength where this distance would be small compared to the Debye screening length. The distance between polymer-bound charges assumed by the theory corresponds to an isotactic polymer in the all-trans conformation but is, in fact, substantially increased by a racemic placement of neighboring carboxyl groups and gauche bonds in the chain backbone. This should lead to a decrease in counterion binding. We conjecture that the two effects described above approximately cancel each other, thus accounting for any agreement of Manning's theory with experimental data.[4]

(2) We have argued previously[10] that, in comparing the NMR spectrum of a polyelectrolyte in water and in poor solvent, the pearl necklace model would imply a decrease in the spectral intensity (since the "pearls" would not contribute to the spectrum) but no change in the resolution of the spectrum (since the chain segments connecting the "pearls" would retain their conformational mobility). In the present study we show that in methanol solution the repulsion between the polymer-bound ionic charges leads to an inhibition of conformational mobility and to a disappearance of the NMR spectrum at full ionization, so that we can make no inference as to the validity of the pearl necklace model. Of course, the proposal of the pearl necklace model does not consider a possible effect of the nature of univalent counterions.

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