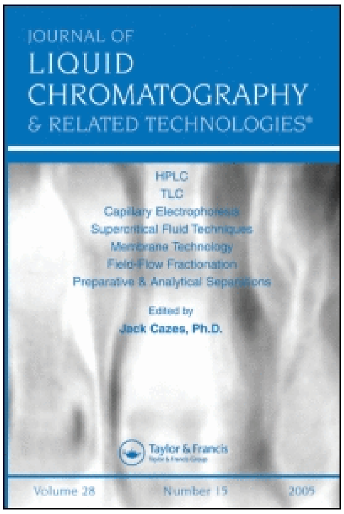

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Contribution of Size Exclusion Chromatography, Light Scattering, Viscometry, and Conductimetry to the Study of Solution and Gel Properties of a Cationic Polyelectrolyte

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Abstract: Solution properties of a cationic polyelectrolyte poly (acrylamide-co-diallyldimethylammonium) were studied by size exclusion chromatography with double detection (differential refractive index and light scattering), viscometry, and electrical conductimetry, in water containing different ionic salts. These techniques allow not only the determination of molecular weights, molecular dimensions, and scaling law coefficients, but also study the influence of the counterion on the unperturbed dimensions of the chain. Moreover, swelling properties of crosslinked gel samples of this copolymer, both in pure water and water containing ionic salts, were also studied. The swelling degree is also sensitive to the nature of the anion of the salt and there is a direct correlation between the solution properties of the linear samples and the swelling behaviour of their crosslinked counterparts. Thus, measurements of the polymer in aqueous solution can be used to anticipate the swelling behaviour of the corresponding hydrogel.

Keywords: Conductimetry, Hydrogels, On line light scattering, Poly(acrylamide-co-diallyldimethylammonium chloride), Polyelectrolytes, Size exclusion chromatography, Viscometry

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INTRODUCTION

Polyelectrolytes are a special class of polymers that are well known to play a central role in nature and technology. They have many applications related to modifying flow and stability properties of aqueous solutions and gels.[1–4] Polyelectrolytes bear ionizable groups that, when the polymer is dissolved, can remain either as electrically neutral groups or separate into electrically charged ions, depending on the chemical nature of the solvent and the thermodynamical conditions of the system. Thus, characterization of polyelectrolyte solutions by experimental techniques such as size exclusion chromatography (SEC) or viscometry is much more difficult than that of neutral polymers, because the interactions between electrical charges on the polymers and counterions contained in the solution strongly modify the conformational distribution of the polymer chain and, consequently, produce huge changes on the size and shape of the macromolecules.[5–7] As a consequence, magnitudes such as elution volume on SEC or viscosities are very sensitive to the ionic strength of the solution.

The use of SEC with double detection, i.e., combining a multiangle laser light scattering detector, MALS, which is sensitive to both molecular weight and radius of gyration of the eluting polymer and a refractive index detector, RI, which provides the concentration of the solution emerging from the column, has shown to be very helpful in the characterization of polymers.[8–14] In recent publications, we have made use of the technique SEC-MALS to look into the solution properties of some polyelectrolytes,[15,16] among them a cationic polyelectrolyte, poly(diallyldimethylammonium chloride), PDDA,[17,18] and we found that properties such as unperturbed molecular dimensions, scaling law parameters,[19,20] thermodynamical quality of the solvent, etc., are very different when the solvent is pure water than when aqueous solutions of ionic salts are employed as solvent. Furthermore, in this last case, noticeable differences are also found depending on the nature of the negative ions contained in the salt.

The polyelectrolyte used for this work is a copolymer of acrylamide and diallyldimethylammonium chloride,[21–24] broadly used in cosmetic formulations and water treatments. One of the aims of this work is to look at how the presence of neutral residues of acrylamide affect the characterization of the polyelectrolyte in different salt solutions.

On the other hand, polyacrylamide is an hydrophilic neutral polymer whose hydrogels have been widely studied in the literature.[25–30] Hydrogels are crosslinked, hydrophilic polymer networks, which can swell in water or aqueous solutions. This water sorption ability of hydrogels is an important characteristic of these materials and accounts for many of their applications in areas such as chemistry, pharmacy, agriculture or biotechnology.[2,31,32] The swelling degree of hydrogels depends not only on the crosslinking density, but also on the chemical nature of the polymer chains and the coexisting aqueous medium.

Some of the factors that affect the hydrogel, swelling such as chain flexibility or interaction with water, also affect the dimensions that the linear (uncrosslinked) polymer chains adopt in solution. Thus, a second aim of the present work is to probe if the techniques of characterization of polyelectrolytes in solution can afford information about the swelling properties of the corresponding crosslinked polyelectrolyte hydrogels. Therefore, a linear sample of the copolymer was studied in pure water and/or in water containing different ionic salts by SEC with double detection, viscometry, and electrical conductimetry. On the other hand, swelling properties of crosslinked samples of this copolymer, both in pure water and water containing ionic salts, were also studied trying to correlate the properties of both kinds of samples, i.e., properties such as molecular dimensions or scaling law constants typical of linear samples, with the swelling behaviour characteristic of hydrogels.

EXPERIMENTAL

Materials

Poly(acrylamide-co-diallyldimethylammonium chloride) (CopolC) was a commercial sample (Aldrich). The chemical composition of the copolymer was determined by NMR using the procedures described in the literature.[21,33,34] The molar fraction of diallyl residues was 0.5. Poly (acrylamide-co-diallyldimethylammonium bromide) (CopolB) and poly (acrylamide-co-diallyldimethylammonium iodide) (CopolI), used in conductivity measurements, were obtained by ion exchange from poly (acrylamide-co-diallyldimethylammonium chloride) (CopolC). The copolymer copolC was dissolved in saturated salt solutions of either, NaBr or NaI, for obtaining copolB and copolI, respectively, the solutions were diluted with methanol (1:3) and added dropwise to acetone in the ratio of 1 volume of solution to 10 volumes of acetone. The precipitated polymer was collected, the procedure was repeated, and the final precipitate was vacuum dried at room temperature.

The salts used were NaCl, NaBr, and NaI (Scharlau). Water and the aqueous 0.5 M salt solutions used as eluents in SEC were filtered through a 0.2 μm mixed cellulose ester membrane (Millipore Co.) and degassed.

The crosslinked hydrogels were produced in an oxygen free aqueous solution, at 80°C, by radical polymerization of the monomers acrylamide (Across) and diallyldimethyl ammonium chloride (Aldrich), using N,N′-methylenebisacrylamide, MBA, (Aldich), as the crosslinking agent and hydrogen peroxide as initiator. Duplicate samples of the polymerization were carried out simultaneously, one with the crosslinking agent and another one, without the crosslinking agent. The linear sample obtained in this second polymerization was used for the determination of the chemical composition by NMR as described above.

The hydrogels thus obtained were divided into several samples. Part of the samples were washed with water and dried in vacuum to constant weight, whereas the other samples were used for swelling measurements. Thus, they were immersed in a large excess of water or aqueous salt solution during several days until the swelling equilibrium was reached. The degree of swelling was calculated as the ratio of the weight of the hydrogel swollen to equilibrium in the solvent (water or aqueous salt solution) to that of the dry gel.

Measurements

SEC measurements were carried out using equipment which consisted of a Waters Associates model 510 pump with a 0.1 μm on-line filter (Millipore), a U6K injector (Waters), and two different detectors: an Optilab Interferometric Refractometer (RI) operating at 632.8 nm and a Dawn DSP-F multiangle light scattering (MALS) photometer, equipped with a He-Ne laser ($\lambda_0 = 632.8\,\text{nm}$), both from Wyatt Technology Corp. The chromatographic columns used, Ultrahydrogel Linear 6–13 μm (Waters), were kept in an oven at 25°C. The flow rate was 0.5 mL/min. Repeated injections were made for each sample at different concentrations (<5 mg/mL) to ensure the reproducibility of the results.

The MALS photometer was calibrated with spectrometric grade toluene (Scharlau). The normalization of the detectors in the different aqueous solutions was performed with low molecular weight, standard samples of poly(ethylene oxide) and dextran. This detector simultaneously measures the excess Rayleigh ratio at different θ angles and allows calculating the weight average molecular weight, M_w, and the mean square radius of gyration, $<s^2>$, for each slice across a sample peak of the size exclusion chromatogram according to the basic equation:[8,35]

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{16\pi^2}{3\lambda^2} < s^2 > \sin^2\left(\frac{\theta}{2}\right) + \cdots\right) \tag{1}$$

where ΔR_θ is the excess Rayleigh ratio at angle of observation θ, λ the light wavelength in the solution, and K represents the optical constant that is related to the wavelength in vacuum, λ_0, the solvent refraction index, n, Avogadro's number, N_A, and refraction index increment, (dn/dc) by:

$$K = \frac{4\pi^2 n^2}{\lambda_0^4 N_A}\left(\frac{dn}{dc}\right)^2 \tag{2}$$

The differential refractive index increments (d*n*/d*c*) were determined, at 25.0 ± 0.1°C, with a Brice-Phoenix differential refractometer, at wavelengths of 436 and 546 nm and extrapolated to 632 nm using Cauchy relationship. The values thus obtained are collected in Table 1.

The specific conductivities were measured in a conductometer Metrohm, model 712. The molar conductivity was calculated dividing the specific conductivity by the molar concentration.

Viscosities were measured in a Schott Gerate automatic viscometer equipped with a thermostatic bath regulated to 25.0 ± 0.1°C.

RESULTS AND DISCUSSION

Chromatograms and Scaling laws

Figures 1 and 2 show the RI signal and one of the MALS signals (at 90°), respectively, for CopolC in aqueous NaCl, NaBr, and NaI 0.5 M solutions as eluents. Weight averaged molecular weights obtained with the Astra software are presented in Table 1. The logarithmic plots of molecular weight and the root mean squared radii of gyration versus elution volume are also presented in Figures 1 and 2, respectively. Both, chromatogram traces and plots are rather similar, although there is a slight displacement of the chromatogram traces towards lower elution volumes as the size of the anion increases. Plots of radius of gyration seem to indicate that the size of the polymer decreases as the anion size increases. However, the differences in the chromatograms are not enough to get definite conclusions, and thus, it is worthwhile to determine polymer scaling laws and unperturbed dimensions in order to obtain additional information.

Table 1. Differential refractive indexes, weight averaged molecular weights, scaling law parameters, unperturbed dimensions, characteristic ratios and intrinsic viscosities for copolC obtained at 25°C in the different eluents

Eluent/salt	dn/dc ($mL\ g^{-1}$)	$10^5 M_w$ (g/mol)	Q	q	$10^3 <s^2>_0/M$ ($nm^2\ mol\ g^{-1}$)	C_N	$[\eta]$ ($dL\ g^{-1}$)
NaCl	0.17	1.24	0.015	0.59	1.90	19	2.13
NaBr	0.16	1.36	0.268	0.61	1.40	17	2.05
NaI	0.14	1.63	0.198	0.60	1.20	10	1.81

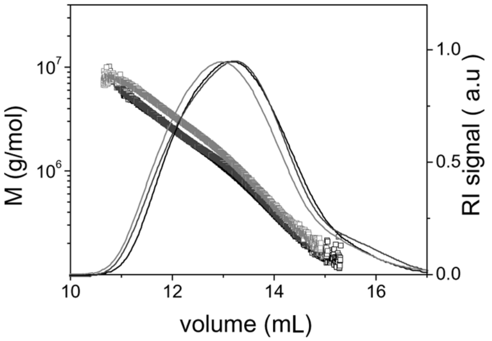

Figure 1. Refractive index signal (in arbitrary units) and molecular weight versus elution volume for copolC in 0.5 M aqueous solution of NaCl (black squares), NaBr dark gray squares), and NaI (gray squares).

The scaling laws $<s^2>^{1/2} = Q\ M^q$ relating to the size (root mean squared radius of gyration), $<s^2>^{1/2}$, and the molecular weight provide information about shape and size of the polymer and, if the polymer is in random coil, of the thermodynamic quality of the solvent.[19,20] Thus, for random coil polymers at theta conditions, $q = 0.5$ and the unperturbed radius of gyration $<s^2>_0$ scales with M in the random walk manner. The exponent q increases with the quality of the solvent and reaches the value of 0.6 for very good solvents.

The scaling laws obtained in NaCl, NaBr, and NaI aqueous solutions are linear and are depicted in Figure 3, while the values of the q and Q parameters are collected in Table 1. The q coefficients are close to 0.6 and indicate that the three salt solutions are very good solvents for the

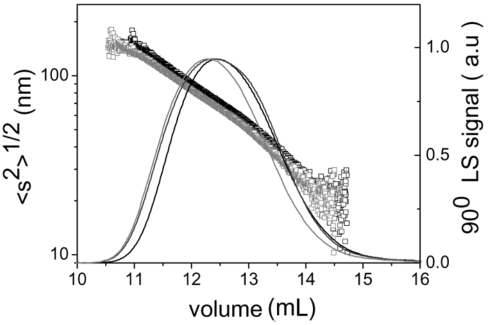

Figure 2. Light scattering at 90° signal (in arbitrary units) and radius of gyration versus elution volume for copolC in 0.5 M aqueous solution of NaCl, NaBr, and NaI. See legend for Figure 1.

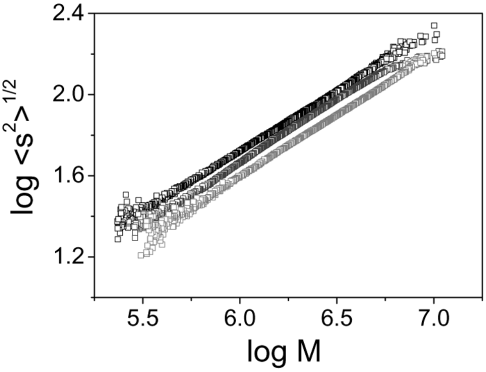

Figure 3. Scaling laws for copolC in 0.5 M aqueous solution of NaCl (black), NaBr (dark gray), and NaI (gray).

copolymer. It is worthwhile to compare these results with those reported in the literature for the corresponding homopolymers, namely the parent polyelectrolyte, poly(diallyl-dimethylammonium chloride), PDDA, and the neutral polymer poly(acrylamide). The solution behaviour of PDDA strongly depends on the kind of anion contained in the salt added to the water, since the aqueous solution of NaCl is a solvent close to θ conditions with $q = 0.51$, whereas NaBr solution is a much poorer solvent, $q = 0.37$, and finally, the polymer is not soluble in NaI solutions.[36,37] On the other hand, the behaviour of polyacrylamide is similar in water and in the different aqueous salt solutions; all of them are very good solvents with q values very close to 0.6.[38,39] Thus, the presence of acrylamide residues favors the expansion of polyelectrolyte chains in all salt solutions and enhances their solubility. This improvement of the quality of the solvent masks the dependence, if any, of solution properties on the kind of anion used, and prevents us from obtaining further conclusions about the influence of the counterion based exclusively on the scaling law parameters. However, extrapolation of the results to unperturbed dimensions, i.e., theta conditions will afford further information on solution properties.

Unperturbed Dimensions

The sets of values of radii of gyration versus molecular weight (scaling laws) for each sample can be used to obtain the unperturbed dimensions of the chain. The dimensions of a polymer chain in a given solvent are related to the dimensions that the same chain would adopt at unperturbed (i.e., theta) conditions by:[19]

$$<s^2> = \alpha <s^2>_0 \tag{3}$$

where the expansion factor, α, depends on the thermodynamic quality of the solvent and the molecular weight of the polymer chain. The expansion factor becomes unity in two circumstances: First, at theta conditions when the interactions polymer-polymer counterbalance those of polymer solvent and the dimension of the chain reaches the unperturbed value, and second, at the limit of such a low molecular weight that the interactions between segments of the same chain are not possible. The dependence of the expansion factor on molecular weight M can be used to extrapolate results obtained in perturbed condition to theta conditions. For polymers in good solvents, a widely used expression is the Fixman extrapolation,[40] defined in equation 4:

$$\frac{<s^2>}{M} = \frac{<s^2>_0}{M} + 0.0299B\left(\frac{<s^2>_0}{M}\right)^{-1/2} M^{1/2} \tag{4}$$

In this equation B represents the extent of the solvent-polymer interaction[19] and provides $<s^2>_0/M$ as the intercept.

The length of a polymeric chain is customarily represented by the characteristic ratio C_N, defined as the ratio of the unperturbed dimensions of the real chain to the dimensions of a freely jointed chain containing the same number of skeletal bond N:[19]

$$C_N = \frac{<r^2>_0}{Nl^2} = \frac{6M_0}{nl^2}\frac{<s^2>_0}{M} \tag{5}$$

where $<r^2>_0$ is the unperturbed value of the mean square end to end distance, which for flexible chains can be obtained as $<r^2>_0 = 6<s^2>_0$, M_0 is the molecular weight of the repeating unit, which depends on the chemical composition, n is the number of skeletal bonds of the repeating unit, i.e., 2 for acrylamide residues and 4 for diallyldimethylammonium residues, and l the length of these bonds, i.e., $l = 0.153$ nm for a single C–C bond.

The Fixman extrapolations obtained in NaCl, NaBr, and NaI solutions are depicted in Figure 4, and unperturbed dimensions and characteristic ratios are collected in Table 1. The dependence of these magnitudes on the kind of anion is evident. The characteristic ratio, C_N, diminish as the anion size increases. Thus, the unperturbed dimensions obtained in the three salt solutions show a marked dependence of the polyelectrolyte chain expansion on the type of counterion present. This dependence can not be attributed to the different thermodynamic compatibility between

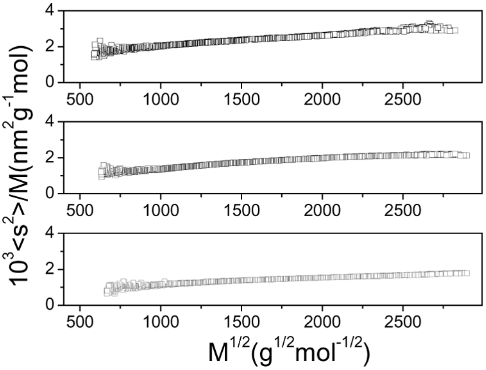

Figure 4. Extrapolations to unperturbed conditions for copolC in 0.5 M aqueous solutions of NaCl, NaBr, and NaI.

the copolymer and the solvent, since the results have been extrapolated to unperturbed conditions. Thus, it must be due to the higher screening effect, which reduces the electrostatic repulsion of similar charges, promoting changes to less extended conformations.

We have performed measurements of viscosity and electrical conductivity of these systems seeking for additional support of the differences observed in dimensions obtained by SEC measurements.

Viscosity

Figure 5 shows the plot of reduced viscosity η_s/c as a function of concentration for copolC in the three different salt solutions. The plot shows that the reduced viscosity decreases with decreasing concentration of

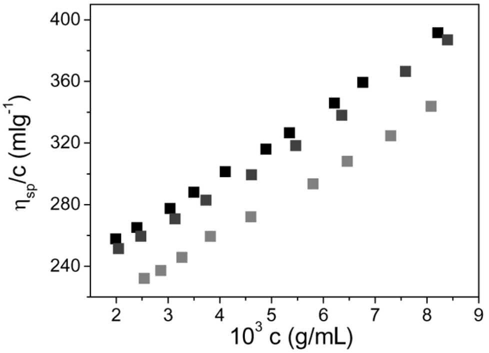

Figure 5. Dependence on concentration of the reduced viscosity of copolC in 0.5 M aqueous solution of NaCl (black squares), NaBr (dark gray squares), and NaI (gray squares).

copolymer. Moreover, at the same concentrations of copolymer, the viscosity diminishes as the size of the anion increases. Intrinsic viscosities were obtained by extrapolation to zero concentration using Huggins equation and the values are collected in Table 1. The decrease in the viscosity values as the size of anion increases is similar to the results obtained for the parent homopolyelectrolyte PDDA,[37] and suggests that the polymer adopts a much more compact conformation as the Cl^- is replaced by Br^- and this anion by I^-, which perfectly agrees with the variation of the values of characteristic ratio obtained in these solvents.

Electrical Conductivities

The solution behavior of the polymer chain can be further investigated by studying the electrical conductivity of the polymer solutions.[41] The dependence of the molar conductivity on the type of anion has been studied, comparing copolC with copolB and copolI for which the anion has been replaced by Br^- and I^-, respectively, (as explained in the experimental section) and is depicted in Figure 6. The theoretical values of molar conductivity of polyelectrolytes can be expressed by the equation:[42]

$$\Lambda = f(\lambda_c^0 + \lambda_p) \tag{5}$$

where f is the fraction of free counterions, i.e., the fraction of counterions that have not condensed on the polyion. The molar conductivity of the polyion residue λ_p, depends on the nature of counterion through both its charge $|z_c|$ and molar conductivity at infinite dilution λ_c^0. Since the molar conductivities at infinite dilution, λ_c^0, of counter anions Cl^-, Br^-,

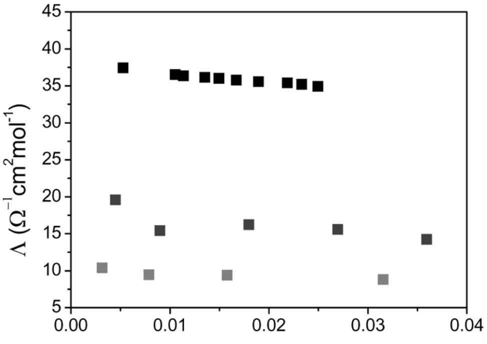

Figure 6. Molar conductivities of copolC (black squares), copolB (dark gray squares), and copolI (gray squares) in water versus polymer concentration.

and I^- are very close,[43] namely 76.31, 78.1, and 76.8 in $cm^2\ \Omega^{-1}\ mol^{-1}$, respectively, similar values of molar conductivity should be expected for the three copolymer solutions at the same concentration. However, the plots of conductivity versus concentration of diluted solutions of the three polymers are very different as can be noticed in Figure 6, which indicates that the conductivity is smaller with I^- and Br^- than with Cl^- counterions. The fact that the conductivity may be dependent of the different interactions between the polyion and the Cl^-, Br^-, and I^- anions has been reported.[44,45] The uncondensed counterions fraction f according to Manning's theory[46,47] depends on the inverse of charge density parameter ξ:

$$\xi = e^2/\varepsilon kTb \tag{6}$$

where e is the proton charge, ε the bulk dielectric constant of medium, k the Boltzmann constant, T the absolute temperature, and b the averaged distance taken along the chain, between the charged groups of the polyion. Therefore, the molar conductivity Λ should be proportional to b and consequently, according to the results presented in Figure 6, it decreases when Cl^- counterions are replaced by Br^- and I^-. Then, assuming that the b parameter follows the same trend of molecular dimensions, the results of conductivities would suggest that molecular dimensions should diminish as the Cl^- counterion are replaced by Br^- and I^-, which is exactly what we have obtained from the other two techniques, namely: SEC with on line multiple angle light scattering and viscometry.

Swelling Behaviour

The swelling behaviour of a crosslinked gel sample of poly(acrylamide-co-diallyldimethyl ammonium chloride) in pure water and in water solutions of NaCl, NaBr, and NaI was also investigated in order to find possible correlations between solution and gel properties. The samples were swollen in the same solutions used as eluents in SEC measurements, until the equilibrium was reached, and then the degrees of swelling were determined (see experimental section). The values of the swelling degree thus obtained were 247, 73, 27, and 24, respectively, for pure water, water/NaCl, water/NaBr, and water/NaI. As expected, the swelling is much higher in pure water than in water containing ionic salts, and in this second case, decreases with increasing size of the anion contained in the salt. It seems then, that unperturbed dimensions and swelling properties follow a similar trend. The unperturbed dimensions obtained in solution are similar to the dimensions in the amorphous solid polymer.[19] Thus, a relationship between the behaviour of polymer in solution and in gel form is not surprising.

The degree of swelling of hydrogels is important with regard to the use of these materials. However, swelling measurements of crosslinked hydrogels are time consuming since equilibrium has to be reached and this can take several days. Although more experiments have to be done, the correlation between unperturbed dimensions that can be obtained by SEC coupled with on line multiple angle light scattering, would afford obtaining straight away information relative to the swelling of a crosslinked hydrogel in different media.

CONCLUSIONS

The characterization of a polyelectrolyte, poly(acrylamide-co-diallyldimethyl ammonium chloride), has been accomplished by size exclusion chromatography with multiple angle light scattering. Moreover, the dependence of solution properties of the polymer on the kind of counterion, chloride, bromide, or iodide can be inferred from the scaling laws and especially from the unperturbed dimensions. An increase of the anion size, results in a contraction of polyelectrolyte chains. These results are in very good agreement with those obtained by viscosity and conductivity measurements of the polymer solutions.

Compared to the parental homopolyelectrolyte, PDDA, the acrylamide residues favour the solution in aqueous salt solutions. However the behaviour of the copolymer with respect to the anion present in the salt is similar to the polyelectrolyte poly(diallyldimethylammonium chloride) homopolymer and not to the neutral poly(acrylamide).

The variation of the swelling properties for hydrogels, obtained from crosslinked poly(acrylamide-co-diallyldimethylammonium chloride), with the kind of salt have also been investigated. The results show that the swellability of the gel is related to the unperturbed dimensions of its corresponding linear copolymer. The swelling degree is different when determined in pure water or in water containing ionic salts and, in this last case, it is also sensitive to the negative ion of the salt. The good correlation, reported in this paper, between unperturbed dimensions of linear samples, that can be determined by SEC-MALS and swelling of their corresponding hydrogels, whose determination requires a much longer time, could be used to anticipate the hydrogel behaviour of different systems.

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