

Solution properties of poly(diallyldimethylammonium chloride) (PDDA)

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Abstract

Size exclusion chromatography (SEC) with dual detection, i.e. employing a refractive index (RI), concentration sensitive, detector together with a multiangle light scattering (MALS) detector which is sensitive to molecular size, has been applied to study the solution properties of poly(diallyldimethylammonium chloride) (PDDA) in water containing different electrolytes, namely: NaCl, NaBr and LiCl, at 25 °C. The analysis of a single highly polydisperse sample is enough for obtaining calibration curves for molecular weight and radius of gyration and the scaling law coefficients. The effect of the ionic strength on the conformational properties of the polymer can also be analyzed and unperturbed dimensions can be obtained by extrapolation of the values measured in a good solvent. The values of the characteristic ratio of the unperturbed dimensions thus obtained were: 17, 11 and 17, respectively, for NaCl, NaBr and LiCl solutions. Viscosity and conductivity measurements support the results obtained by SEC. Moreover, the experimental results are in good agreement with the theoretical calculations performed by combining molecular dynamics and Monte Carlo sampling procedures.

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1. Introduction

Size exclusion chromatography (SEC), coupled with molecular weight sensitive detectors, is the most widely used technique for determining the absolute molecular weight distribution (MWD) and averaged molecular weights of synthetic and natural polymers [1,2]. Light-scattering detectors are very useful since they provide absolute measurement of molecular weight, without requiring any calibration. Multiangle laser light scattering (MALS) offers an added advantage. The determination of the molecular dimensions of the polymer, in terms of the radius of gyration, from the angular dependence of the scattered light [3,4]. This combination of molecular weight and dimensions of the polymer chains, when applied to polydisperse samples of polymers, can be used to obtain the corresponding scaling laws and thus information about the size and shape of polymer chains in solution [5]. Moreover, the unperturbed dimensions can be obtained by extrapolating the results obtained in perturbed conditions [6,7].

The characterization of polyelectrolytes is much more difficult than neutral polymers since the interactions between the polymer charges and the counterions largely affect the dimensions of the chain. Thus the size of the polymer, and, therefore, the elution volume, changes with the ionic strength of the medium. Furthermore, the charged polymer may interact with the packing of the chromatographic column, thus modifying the exclusion mechanism in chromatography [8,9].

Poly(diallyldimethylammonium chloride) (PDDA), studied in the present work, is a cationic polyelectrolyte widely used, both in industrial applications and as a model for charged polymers behavior [10,11]. Dilute solution properties of PDDA have been studied by several methods [10,12–17]. Fractionated samples have been analyzed and branching has been reported for commercial samples of PDDA [10, 15]. Moreover, the effect of counterions on charged polyelectrolyte backbone is of crucial interest for understanding the solution properties of these systems [16,18–20]. In this paper we present the experimental results obtained by SEC-MALS for poly(diallyldimethylammonium chloride) (PDDA) in different salt solutions. Viscosity and conductivity measurements, which are also reported here, support the results obtained by chromatography.

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The comparison of experimental measurements and theoretical results obtained by simulation procedures is especially challenging and affords a deeper insight in the solution behavior and characterization of polymers [21]. A theoretical model describing the conformational properties of Poly(diallyldimethylammonium chloride) (PDDA) has been recently developed [22]. Molecular dynamics simulations were performed on dimers of PDDA. The results were employed to formulate a Rotational isomeric state model for these molecules and to evaluate a first estimation of the conformational energies and probabilities for the allowed conformations [23–26]. These probabilities were then employed to generate single chains of PDDA in vacuo according to standard Monte Carlo procedures and their main squared end to end distance $\langle r^2 \rangle$ were computed. The procedure was then repeated for two more realistic systems aimed to represent water solutions of PDDA, both in absence and in presence of NaCl as ionic salt. Thus, the first system contained a forty repeat units oligomer of PDDA together with their counterions and 500 water molecules packed into a cubic box with periodic boundary conditions providing a macroscopic density of ca. 1 g cm^{-3} . The last system differed from the former one just in the addition of 20 molecules of NaCl. The behavior of the three systems (i.e. the gas, pure water solution and a solution containing ionic salt) is noticeably different. In the present work, we extend the theoretical analysis to solutions containing either NaBr or LiCl instead of NaCl as ionic salts.

2. Experimental

2.1. Materials

The polymer poly(diallyldimethylammonium chloride) (PDDA) was a commercial sample (Aldrich). The salts used were NaCl, NaBr and LiCl (Scharlau). The water and the aqueous salt solutions used as eluents in SEC were filtered through a $0.2 \mu\text{m}$ cellulose membrane and degassed. The polymer precipitates in aqueous solution of NaI thus this solution cannot be used as solvent. Water is not a suitable eluent since the peak corresponding to the polymer is multinodal and presents tails. Different concentrations of salt were tested and, finally, a 0.5 M concentration was chosen for all the measurements, because increasing the concentration did not improve the appearance of peaks.

Table 1
Differential refractive indexes and scaling parameters for PDDA obtained at 25°C in the different eluents

Eluent/salts	$dn/dc \text{ ml g}^{-1}$	Q	q
NaCl	0.170	0.038	0.51
NaBr	0.145	0.268	0.35
LiCl	0.159	0.198	0.39

2.2. Measurements

SEC measurements were carried out using a Waters Associates equipment with a model 510 pump, a U6K injector and a differential refractive index detector model 410 (RI). Two Ultrahydrogel Linear 6–13 μm were the chromatographic columns used. The flow rate was 0.5 ml/min and the temperature 25°C . Typical initial polymer concentrations on the solutions injected were ca. $1\text{--}2 \text{ mg ml}^{-1}$. Repeated injections were made for each sample.

The multiangle light scattering detector (MALS) was a DAWN DSP-F laser photometer from Wyatt Technology Corp. The 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). The software used, ASTRA 4.73 from Wyatt Technology, allowed on-line data of molecular mass and radius of gyration collection as well as calculation of the distributions and averages.

The differential refractive index increments for the polymer in the different solvents used were measured with a Brice-Phoenix differential refractometer at $25 \pm 0.1^\circ\text{C}$ and are presented 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. The poly(diallyldimethylammonium bromide) (PDAAB), used in these measurements, was obtained by ion exchange from poly(diallyldimethylammonium chloride). The polymer solution was diluted with methanol (1:3) and added dropwise to acetone in the ratio of 1 volume of solution to 10 volumes of acetone. The precipitate was vacuum dried at room temperature.

Viscosities were measured in a Schott Geräte automatic viscometer equipped with a thermostatic bath regulated to $25 \pm 0.1^\circ\text{C}$.

3. Theory

The basic light scattering equation [3] is:

$$\frac{Kc}{\Delta R} = \left(1 + \frac{16\pi^2}{3\lambda^2} \langle s^2 \rangle \sin^2(\theta/2) + \dots \right) \left(\frac{1}{M_w} + 2A_2c + \dots \right) \quad (1)$$

where R is the Rayleigh ratio, c is the concentration, λ is the wavelength of the incident light in the medium, θ is the scattering angle and K is the optical constant given by:

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

where λ_0 is the vacuum wavelength, n is the refractive

index, N_A is Avogadro's number, and dn/dc is the refractive index increment.

The first parentheses on Eq. (1) contains the terms of the particle form factor that takes into account the interferences among light scattered at different angles for large molecules, while the second parentheses include the non ideal terms arising from the polymer–polymer interactions. Since the concentrations employed in SEC-MALS are very small, and the solutions are further diluted while passing through the columns, Eq. (1) could be approximated by [3,4]:

$$\frac{Kc}{\Delta R} = \frac{1}{M_w} \left(1 + \frac{16\pi^2}{3\lambda^2} \langle s^2 \rangle \sin^2(\theta/2) + \dots \right) \quad (3)$$

The RI detector allows to measure the concentration of the polymer and the MALS detector measures simultaneously the excess Rayleigh ratio at different θ angles for each slice i of the chromatogram, which is assumed to be monodisperse both in composition and molecular mass. Hence, a plot of $Kc/\Delta R_\theta$ versus $\sin^2(\theta/2)$ affords to calculate the molecular mass M_i and the mean square radius of gyration $\langle s^2 \rangle_i$ for each slice across the chromatogram.

4. Results and discussion

4.1. Chromatograms

Figs. 1 and 2 show the RI and one of the MALS signals (at 90°), for the PDDA in the different salt solutions used as eluents. The light scattering signals are proportional to the product of molecular weight and concentration, so that they have a different shape than the RI signals that are proportional to concentration. The elution volume for the peak in the NaCl solution is slightly displaced towards higher elution volumes and also the profile is neater since the peaks in both the NaBr and the LiCl solutions present shoulders that disappear in the NaCl solution.

The corresponding calibration curves of molecular weight versus elution volume are also presented in Fig. 1

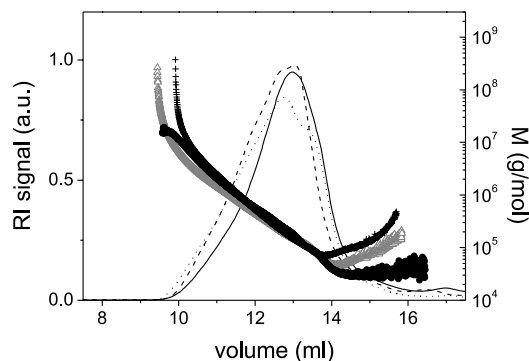


Fig. 1. Chromatograms showing the RI signal and logarithmic plots of molecular weight versus elution volume for PDDA in the different salt solutions: NaCl, (solid line and ●), NaBr (dashed line and +) and LiCl (dotted line and Δ).

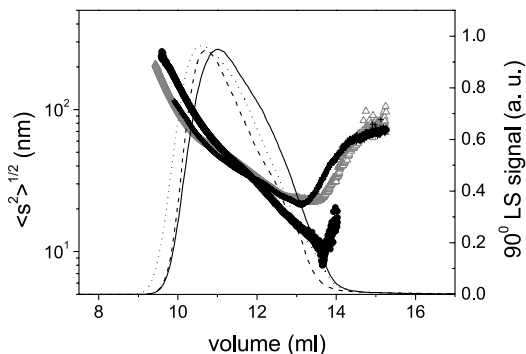


Fig. 2. Chromatogram showing the MALS signal at 90° and logarithmic plot of the root mean squared radius of gyration versus elution volume for PDDA in the different salt solutions. See legend for Fig. 1.

whereas the root mean squared radius of gyration versus elution volume is depicted in Fig. 2. The upward curvatures that appear at high elution volumes are characteristic of the presence of a small fraction of polymer molecules that are retarded through the column and elute later. The upturns, in M or R_g at large elution volumes, appear in the SEC-MALS of some polymers [27–30] and an accurate explanation of this behavior has not been found yet. The existence of a small fraction of very large molecules that are retarded in the column has been suggested as a possible explanation [29,30]. At small elution volumes, the molecules elute according to their hydrodynamic volume (normal SEC) whereas at higher elution volumes the normally eluting small molecules coelute with the retarded large molecules. The mechanism of the retardation is not clear, although it seems that molecular architecture plays an important role. However, it is important to realise that we do not use the values at low elution volumes for calculation of scaling parameters or unperturbed dimensions. Thus these magnitudes are not affected by the upturns. The NaCl solution seems to be the most suitable eluent for the measurements, since the calibration curve is the most linear as can be seen in Figs. 1 and 2. However, it should be pointed out that the existence of these anomalous curvatures do not affect the results of our analysis, since all the fittings employed in this work were performed within the limits of linear behavior.

4.2. Scaling laws

The scaling laws relating the size (radius of gyration) and the molecular weight $\langle s^2 \rangle^{1/2} = Q M^q$ provide information about shape and size of the polymer and the thermodynamical quality of the solvent [23,31]. Thus, for random coil polymers at theta conditions, $q=0.5$ and the unperturbed radius of gyration $\langle s^2 \rangle_0$ scales with M in the random walk manner. The exponent q increases with the quality of the solvent and reaches the value 0.6 for very good solvents. Below the theta conditions, the chains shrink avoiding the solvent molecules, q decreases and, in the limit, the polymer assumes a globular shape for which $q=1/3$.

The scaling laws for the polymer, in the three eluents, are presented in Fig. 3 and the values of the parameters are shown in columns three and four of Table 1. In the NaCl solution the plot is linear whereas the plots corresponding to the other two solvents, present a curvature due to the small fraction of molecules retarded in the column that was explained above. Dautzenberg et al. [10] found similar deviations of the scaling law for two samples of PDDA separated in about 15 fractions and characterized in 0.5 NaCl. The linear fit, for the whole range shown in Fig. 3, yields a value of 0.51 for the exponent q in aqueous NaCl solution. Dautzenberg et al. [10] obtained $q=0.48$ for the fractionated samples above mentioned when their radii of gyration were corrected for the polydispersity of the fractions and $q=0.52$ with uncorrected values of radii of gyration. Thus, our value, obtained with just one poly-disperse sample, is in very good agreement with their results. This value indicates that the polymer is a random coil slightly above theta conditions. The values of q obtained in the other two eluents, are lower than 0.5 (Table 1) which indicates that the polymer is below theta conditions in these solvents.

4.3. The reciprocal scattering function $P(\theta)^{-1}$

The lowest value of the q parameter for PDDA is obtained in 0.5 M aqueous NaBr solution, and since it is close to that expected for spheres, it is worthy to investigate the values of the scattering function $P(\theta)$ in order to determine the shape of the polymer and to discriminate among random coil and globular conformations.

The reciprocal scattering function can be written as [3]:

$$\lim_{\theta \rightarrow 0} P(\theta)^{-1} = 1 + \frac{h^2 \langle s^2 \rangle}{3} = 1 + \frac{16\pi^2}{3\lambda^2} \langle s^2 \rangle \sin^2(\theta/2) \quad (4)$$

where h represents the scattering vector, which is related to the scattering angle θ , and the wavelength of light λ .

The scattering function, $P(\theta)$, for spheres of diameter D

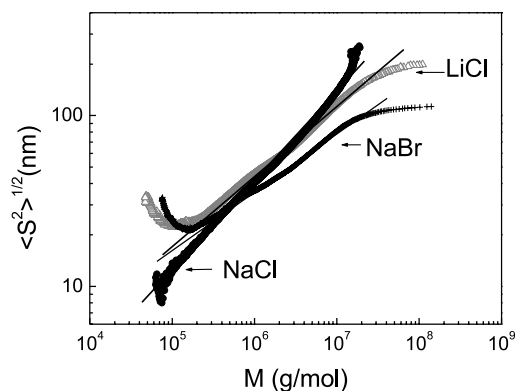


Fig. 3. Log–log plot of root mean squared radius of gyration versus molecular weight for PDDA in the different salt solutions. See legend for Fig. 1.

can be calculated as [3]:

$$P(\theta) = \left\{ \frac{3}{\mu^3} [\sin(\mu) - \mu \cos(\mu)] \right\}^2 \quad (5)$$

where $\mu = (2\pi D/\lambda) \sin(\theta/2)$.

The diameter can be easily obtained from the value of $\langle s^2 \rangle$, using the geometrical relationship for spheres $\langle s^2 \rangle = 3D^2/20$.

The reciprocal function can be obtained from the measured light-scattering data for each slice of the chromatogram as:

$$P(\theta)^{-1} = \frac{\Delta R_{\theta=0}}{\Delta R_{\theta}} = \frac{KcM_w}{\Delta R_{\theta}} \quad (6)$$

Fig. 4 presents the experimental values of $P(\theta)^{-1}$ as a function of $h^2 \langle s^2 \rangle$ for three slices (Table 2). The solid line represents the curve that fits the values of $P(\theta)^{-1}$ calculated for an sphere according to Eq. (5). The differences between experimental values of $P(\theta)^{-1}$ and those obtained with Eq. (5) are significant and suggest that the chain behaves as a random coil despite being below theta conditions.

4.4. Zimm plot

The value of the q parameter obtained at 25 °C for PDDA in NaCl 0.5 M water solution indicates that this system is close to unperturbed conditions. This point could be confirmed by off line measurements of scattered light as function of both concentration and scattering angle. The Zimm plot [32] thus obtained is shown in Fig. 5. The second virial coefficient, A_2 , is obtained from the slope of the extrapolation to zero concentration and provides information about the thermodynamic conditions of the system. The value obtained, $A_2 = (2.6 \pm 0.2) 10^{-4} \text{ mol ml g}^{-2}$, is positive and small, which supports the affirmation that the polymer is in a good solvent although relatively close to theta conditions.

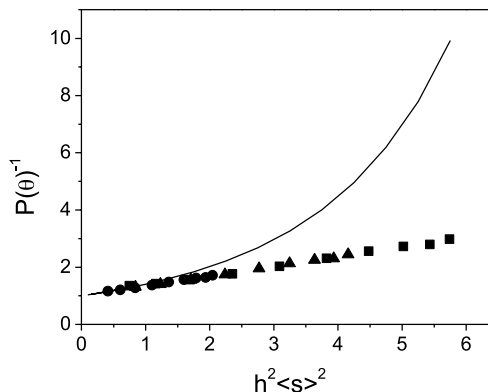


Fig. 4. Reciprocal of the form factor for three slices of PDDA in the NaBr solution (see Table 2). Circles (slice 1), triangles (slice 2) and squares (slice 3). The solid line represents the values calculated for an sphere according to Eq. (5).

Table 2

Elution volume, molecular weight and averaged root mean square radii of gyration for three slices of the chromatogram obtained with the NaBr eluent whose reciprocal form factors are represented in Fig. 4

Slice	$V_e(\text{ml})$	$10^{-6} M_w$	$\langle s^2 \rangle_z^{1/2}(\text{nm})$
1	10.725	3.9	56
2	10.283	9.5	80
3	10.113	16.6	94

4.5. Unperturbed dimensions

The relationship between the dimensions of a polymer in a given solvent and the dimensions at theta conditions is given by:

$$\langle s^2 \rangle = \alpha^2 \langle s^2 \rangle_0 \quad (7)$$

where the expansion factor, α , depends on the 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 dimension of the chain reaches the unperturbed value, and second at the limit of such a low molecular weight that the interaction among segments of the same chain is not possible. The dependence of the expansion factor on molecular weight M can be used to extrapolate results obtained in perturbed condition to θ conditions. However, the dependence is complex and several theoretical and empirical expressions can be found in the literature. For polymers in good solvents, such as PDDA in water solution containing NaCl at 25 °C, a widely used expression is the Fixman extrapolation [33], defined in Eq. (8), which provides $\langle s^2 \rangle_0/M$ as the intercept:

$$\frac{\langle s^2 \rangle}{M} = \frac{\langle s^2 \rangle_0}{M} + 0.0299B \left(\frac{\langle s^2 \rangle_0}{M} \right)^{-1/2} M^{1/2} \quad (8)$$

However, the scaling laws in the case of PDDA solutions containing either LiCl or NaBr salts indicate that these

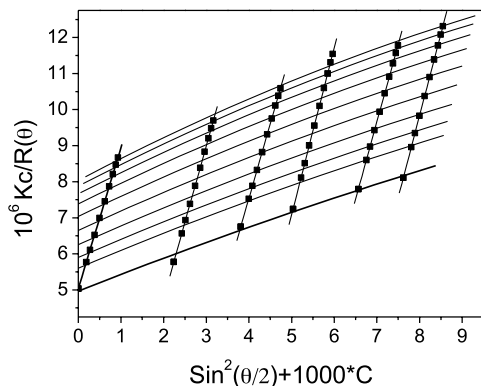


Fig. 5. Zimm plot of PDDA in the NaCl solution. Measured angles (from top to bottom) θ (in degrees) = 149, 139, 129, 117, 104, 90, 76, 63 and 51. Measured concentrations (from left to right) c (g/l) = 1.959, 3.334, 4.406, 5.746 and 6.608.

systems are below theta conditions and, in these cases, the dependence of α on molecular weight is better expressed according to the two parameters theory [34]:

$$\alpha^2 = (1 + 1.276z - 2.082z^2 + \dots) \quad (9)$$

where z is a parameter proportional to $M^{1/2}$ and to the excluded volume interaction energy of the polymer system, which is negative when the system is below theta conditions. Thus, the values of $\langle s^2 \rangle/M$ versus $M^{1/2}$ should fit a relationship:

$$\frac{\langle s^2 \rangle}{M} = \frac{\langle s^2 \rangle_0}{M} (1 + AM^{1/2} + BM + \dots) \quad (10)$$

and with the omission of the z^2 and higher terms the relationship is linear, exhibits a negative slope and provides $\langle s^2 \rangle_0/M$ as the independent term. Fig. 6 shows the experimental values of $\langle s^2 \rangle/M$ versus $M^{1/2}$ for the polymer. The upwards curvature exhibited by the extrapolation is a straight consequence of the under theta conditions of the system. Thus, the value of α should decrease below unity and the ratio $\langle s^2 \rangle/M$ will increase with decreasing M . Extrapolation of the linear parts of the curves shown in Fig. 6 provides the values of $\langle s^2 \rangle_0/M$ collected on the second column of Table 3.

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 rotating chain containing the same number of skeletal bond N :

$$C_N = \frac{\langle r^2 \rangle_0}{Nl^2} = \frac{6M_0}{4l^2} \frac{\langle s^2 \rangle_0}{M} \quad (11)$$

where M_0 is the molecular weight of the repeating unit, and $\langle r^2 \rangle_0$ the unperturbed value of the mean square end to end distance, which for flexible chains can be obtained as $\langle r^2 \rangle_0 = 6\langle s^2 \rangle_0$. The values of C_N computed according to Eq. (11) with the extrapolations obtained from Fig. 6 are shown in the third column of Table 3.

Although the definition of C_N is quite straightforward,

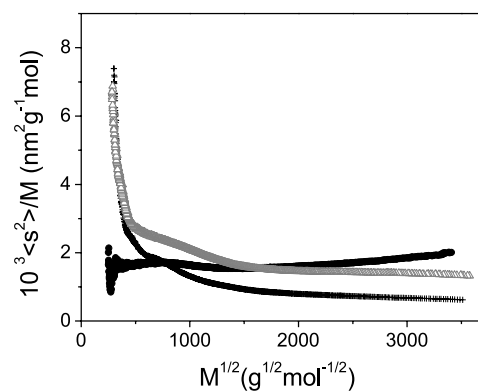


Fig. 6. Extrapolations to unperturbed dimensions for PDDA in the different salt solutions. See legend for Fig. 1.

Table 3

Unperturbed dimensions, characteristic ratio, intrinsic viscosity and Huggins and Kraemer coefficients obtained for PDDA in the different eluents

Eluent	$10^3 \langle r^2 \rangle_0 / M$ ($\text{nm}^2 \text{ mol g}^{-1}$)	C_N	$[\eta]$ (dl/g)	k_H	k_K
NaCl	1.63	17	1.11	0.46	0.17
NaBr	1.09	11	0.78	0.30	0.05
LiCl	1.67	17	1.15	0.47	0.19

comparison of the results reported by different authors could be risky because different approaches might be used while defining the units of the freely jointed chain. Thus, we represent each repeat unit of the real chain by four freely jointed C–C bonds, each one of them having a length $l = 0.154$ nm. Consequently, the term nl^2 appearing on Eq. (11) amounts to 0.095 nm^2 . However, Dautzenberg et al. [10] represent each unit by a single bond of length 0.55 nm and, therefore, the term nl^2 amounts to 0.3025 nm^2 in their case. Thus, our results of C_N should be divided by a factor of 3.1 before comparison. Moreover, values of persistence length a or the length of equivalent Kuhn segment l_K are often employed instead of C_N . The relationship among these magnitudes is [23]:

$$C_N = \frac{\langle r^2 \rangle_0}{Nl^2} = \frac{l_K}{l} - 1 = \frac{2a}{l} - 1 \quad (12)$$

Employing a single bond of 0.55 nm for each unit, our results provide values of $l_K = 2.5$ – 3.6 nm, which are between the values of 5 and 1.4 nm reported by Dautzenberg et al. [10] from measurements of light scattering and viscosity, respectively.

It seems that addition of NaCl to water produces a nearly theta solvent for PDDA at 25°C . Replacement of NaCl by LiCl decreases the thermodynamical quality of the solvent, as it is evidenced by the lower value of the q parameter, and the polymer adopts more compact conformations. However, extrapolation to unperturbed conditions produces the same value of the characteristic ratio for both systems. When the

anion of the salt is replaced, employing either NaBr or NaI, the situation seems to be different. The, NaI produces a precipitation of the polymer that precludes any further experimental measurement, as it was indicated in the experimental section. On the other hand, NaBr decreases the quality of the solvent modifying even the value of the extrapolated unperturbed dimensions.

One possible reason for this different effect of the anion and the cation of the added salt is that PDDA is a polycation, i.e. the polymer chain contains neat positive charges. Consequently, the anions could get closer to the polymeric chain and might have a larger incidence on its behavior than the cations.

However, it might be argued that the different behavior of the three systems presented above could be, at least in part, produced by experimental uncertainties which become larger in the case of systems below theta conditions. For this reason we have performed measurements of viscosity and electrical conductivity of these systems seeking for additional support of the differences observed in SEC measurements.

4.6. Viscosity

Fig. 7a shows the plot of reduced viscosity η_s/c as a function of concentration for PDDA in water solution. The plot shows the characteristic behavior of a polyelectrolyte solution, that the reduced viscosity increases with decreasing concentration [35]. On the contrary, measurements performed employing as solvent the same eluents used in SEC show the ordinary shape, as can be seen in Fig. 7b. Intrinsic viscosities were obtained by a simultaneous extrapolation of the viscosity measurements to zero concentration using the well known equations of Huggins [36] and Kraemer [37] and the values are collected in Table 3 together with the Huggins, k_H , and Kraemer, k_K , constants. As can be seen in Fig. 7b, the viscosities obtained in the NaBr solution are systematically lower than that those measured in the NaCl and LiCl counterparts. This result could indicate that the polymer adopts a much more compact conformation in presence of NaBr than in the cases of NaCl or LiCl, as the SEC measurements suggest.

4.7. Electrical conductivities

The solution behavior of the polymer chain can be further

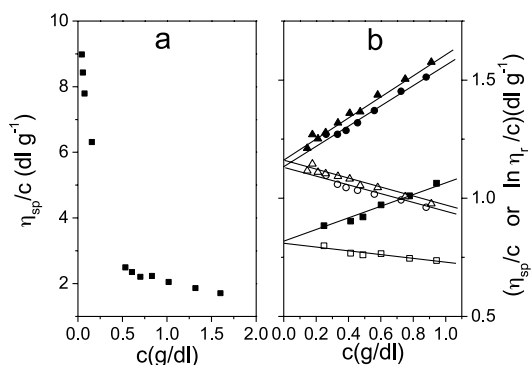


Fig. 7. (a) Dependence on concentration of the reduced viscosity of water solutions of PDDA. (b) Huggins (filled symbols) and Kraemer (hollow symbols) plots for PDDA in the different salt solutions: NaCl (circles), LiCl (triangles) and NaBr (squares).

investigated by studying the dependence of the electrical conductivity of the polymer solution on concentration. Measurements were performed for water solutions of PDDA (i.e. polymer chain with Cl^- as counterions) and PDDAB (i.e. polymer chain in which the Cl^- counterions were replaced by Br^- as explained in the experimental section).

The theoretical values of molar conductivity of polyelectrolytes can be expressed by the equation [38]:

$$\Lambda = f(\lambda_c^0 + \lambda_p) \quad (13)$$

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 [38,39] 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^- and Br^- are very close [40], namely 76.31 and 78.1 in $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$, respectively, similar values of molar conductivity should be expected for solutions of PDDA and PDDAB of the same concentration. However, the plots of conductivity versus concentration of diluted solutions of both polymers are very different as can be noticed in Fig. 8 which indicates that the conductivity is smaller with Br^- than with Cl^- counterions. This fact can be qualitatively explained assuming, as Nagaya et al. [41] pointed out, that the conductivity may be conformation dependent, and is a straight consequence of the different interactions between the polyion and the Cl^- and Br^- anions that have been evidenced in the SEC measurements in NaCl and NaBr solutions. The uncondensed counterions fraction f according to Manning's theory [38,39] depends on the inverse of charge density parameter ξ

$$\xi = e^2/\epsilon kTb \quad (14)$$

where e is the proton charge, ϵ the bulk dielectric constant of medium, k the Boltzmann constant, T the

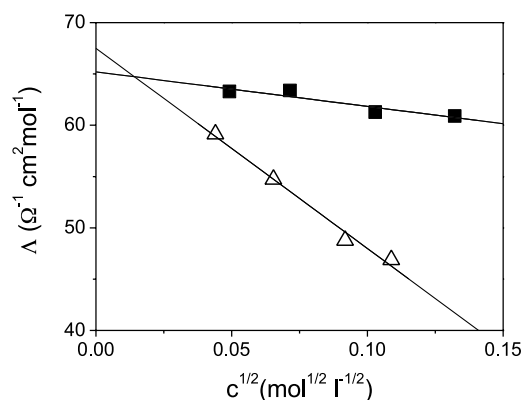


Fig. 8. Molar conductivities of PDDA (filled squares) and PDDAB (hollow triangles) versus concentration.

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 Fig. 8, b decreases when Cl^- counterions are replaced by Br^- . Then, assuming that the b parameter follows the same trend than molecular dimensions, the results of conductivities would suggest that molecular dimensions should be smaller in the presence of Br^- than with Cl^- counterions, which is exactly what we have obtained (Table 1 for values of the q parameter and Table 3 for unperturbed dimensions).

5. Theoretical calculation of the molecular dimensions

Fig. 9 represents a dimer of the PDDA chain. Two configurations, namely cis and trans, are allowed to the skeletal $\text{CH}-\text{CH}$ bond of each cycle. Consecutive cycles along the chain are connected through three rotatable bonds which are labeled ϕ_1 , ϕ_2 and ϕ_3 .

In a recent paper [22] we have presented a conformational model for PDDA. Thus, Molecular dynamics procedures employing the Amber force field [42] were applied to simulate oligomers of this chain, both in vacuo and in solution. Both pure water and water containing NaCl salt were simulated as solvents in this last case. Analysis of the MD trajectories shows three preferred rotational states, namely negative gauche (g^- for $\phi \approx 70^\circ$), trans (t for $\phi \approx 180^\circ$) and gauche (g for $\phi \approx -70^\circ$), for each rotatable bond of the chain and allows the formulation of a simple rotational isomeric state model. Writing the states in the order g^-, t, g , the statistical weight matrices for each one of the three rotatable bonds on a dimer could be represented as [22]:

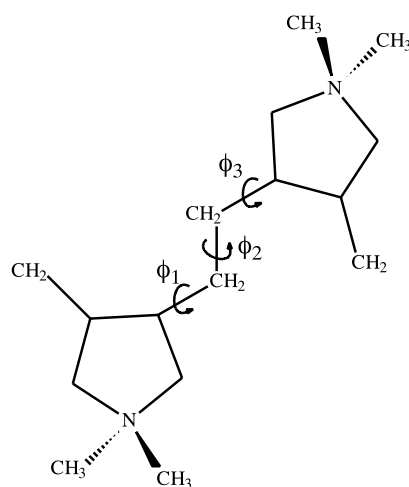


Fig. 9. Schematic representation of a dimer of PDDA showing its three rotational angles. Two configurations (i.e. cis and trans) are allowed to each skeletal $\text{CH}-\text{CH}$ bond within the cycles.

$$\begin{array}{l}
 \text{Trans – Trans : } U_1 = \begin{bmatrix} \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \end{bmatrix} \quad U_2 = \begin{bmatrix} \sigma_2\omega' & 1 & \sigma_2 \\ \sigma_2\omega' & 1 & \sigma_2 \\ \sigma_2\omega' & 1 & \sigma_2 \end{bmatrix} \quad U_3 = \begin{bmatrix} \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \end{bmatrix} \\
 \text{Cis – Cis : } U_1 = \begin{bmatrix} \sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega'' \end{bmatrix} \quad U_2 = \begin{bmatrix} \sigma_4 & 1 & \sigma_4 \\ \sigma_4 & 1 & \sigma_4 \\ \sigma_4 & 1 & \sigma_4 \end{bmatrix} \quad U_3 = \begin{bmatrix} \sigma_3\omega'' & 1 & \sigma_3 \\ \sigma_3\omega'' & 1 & \sigma_3 \\ \sigma_3\omega'' & 1 & \sigma_3 \end{bmatrix} \\
 \text{Cis – Trans : } U_1 = \begin{bmatrix} \sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega'' \\ \sigma_3 & 1 & \sigma_3\omega'' \end{bmatrix} \quad U_2 = \begin{bmatrix} \sigma_5 & 1 & \sigma_5 \\ \sigma_5 & 1 & \sigma_5 \\ \sigma_5 & 1 & \sigma_5 \end{bmatrix} \quad U_3 = \begin{bmatrix} \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \\ \sigma_1 & 1 & \sigma_1\omega \end{bmatrix}
 \end{array} \quad (15)$$

The trans-cis configuration of a dimer is equivalent to the cis-trans with reversal of angles, i.e. reading them from right to left.

These matrices can be employed [23–26] to compute a priori probabilities for any combination of conformational states allowed to the polymer. For instance, the probability for the three bonds of a dimer being at conformational state i,j,k (with i,j,k representing one of the allowed rotational isomers) is given by:

$$\begin{aligned}
 P_{123}(i,j,k) &= \frac{1}{Z_{123}} \\
 &\times (1 \ 0 \ 0) U_1^0(i) U_2^0(j) U_3^0(k) \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} Z_{123} \\
 &= (1 \ 0 \ 0) U_1 U_2 U_3 \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}
 \end{aligned} \quad (16)$$

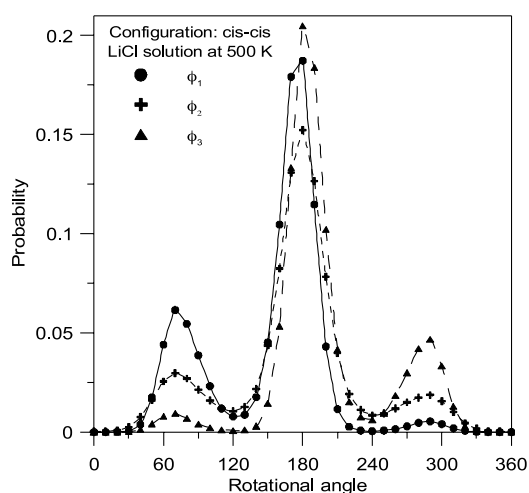


Fig. 10. Probability distribution for independent orientations of the three rotational angles of a cis-cis dimer of PDDA in the LiCl solution obtained from a MD simulation performed at 500 K.

where the $U^0(i)$ matrices are obtained from the corresponding U by replacing all their elements by zero except those of column i which are left unchanged.

These probabilities could also be obtained from the MD simulation just by counting how many times a given combination of values of the rotational angles appears along the trajectory. Comparison of probabilities obtained from MD and computed according to Eq. (16) (or its equivalent for two bonds instead of three) could be used to determine the values of conformational energies appearing in Eq. (15).

Molecular dimensions of the polymeric chains were calculated [22] by standard procedures of Monte Carlo sampling that were employed to generate chains containing different number x of repeat units up to $x=200$. Each chain was generated 1,000 times with a predetermined fraction of trans units (p_t) and random placement of cis and trans cycles and 1,000 conformations were generated for each configuration according to the probabilities for simultaneous placements of the three rotatable bonds of each repeat unit obtained from MD simulations. Values of the squared end to end distance thus obtained were averaged over the 10^6 simulations performed for each chain and transformed into characteristic ratios C_N . Standard errors of the averages were smaller than 1% and the computed values of C_N reached the asymptotic limit for infinite chains at $x \approx 80$ units, so that values computed with $x=200$ are a good approximation for high molecular weight polymers.

In the present work we have performed the same calculation for systems representing water solutions of PDDA in presence of either NaBr or LiCl salts. Thus, MD procedures were applied to simulate the time evolution of systems containing a forty units oligomer of PDDA with their corresponding counterions (either Br^- or Cl^-), 500 water molecules and 20 molecules of either NaBr or LiCl salt [43]. The side length of the PBC boxes were adjusted as to reproduce macroscopic densities of ca. 1 g cm^{-3} (i.e. $L=30.8$ and 30.0 \AA , respectively, for NaBr and LiCl).

However, we encountered the inconvenience that standard tabulations of the parameters for the Amber force field [42] do not contain the non bonded parameters for the Br^- ion. We have devised a procedure for obtaining, at

Table 4

Averaged locations of rotational states and probabilities for simultaneous orientations of the three rotatable bonds within a PDDA dimer obtained from MD simulations performed at 500 K. Only the more probable states, among the 27 allowed, are collected in the table. Probabilities at 300 K collected in the last column were calculated from those at 500 K by assuming that the ratio between the probability of any state i , p_i and that of all trans, p_{tt} , is given by $p_i/p_{\text{tt}} = \exp(-E_i/RT)$ at any temperature

System	Configuration	$\langle\phi_1\rangle$	$\langle\phi_2\rangle$	$\langle\phi_3\rangle$	Prob. (500 K)	Prob. (300 K)
NaCl	Trans–Trans	178.9	183.7	178.8	0.267	0.518
		183.1	295.5	181.9	0.136	0.168
		176.4	183.7	297.3	0.075	0.062
		297.4	181.5	175.1	0.069	0.055
		174.3	172.3	72.6	0.064	0.048
		70.9	167.6	71.2	0.052	0.034
	Cis–Cis	175.3	179.7	183.8	0.361	0.646
		79.2	173.5	184.5	0.125	0.111
		175.6	186.2	280.5	0.090	0.064
		179.	285.1	197.0	0.075	0.047
		167.8	84.2	180.5	0.072	0.044
		74.8	70.1	180.6	0.063	0.036
	Cis–Trans	177.7	181.3	181.0	0.331	0.623
		182.2	292.0	184.7	0.122	0.117
		177.5	187.2	287.7	0.103	0.089
		178.5	180.1	78.1	0.066	0.043
80.9		183.1	182.9	0.066	0.043	
288.5		173.5	175.4	0.053	0.029	
NaBr	Trans–Trans	178.4	185.3	178.2	0.265	0.496
		182.2	294.5	180.2	0.138	0.167
		72.6	172.8	174.0	0.085	0.075
		175.3	173.8	73.1	0.084	0.073
		300.4	183.8	177.9	0.076	0.062
		177.3	184.0	299.1	0.066	0.049
	Cis–Cis	175.8	178.6	183.5	0.353	0.650
		78.0	172.1	184.9	0.101	0.081
		164.1	76.3	181.1	0.081	0.056
		74.8	66.7	180.1	0.079	0.054
		173.4	182.8	282.2	0.076	0.050
		76.7	182.3	283.5	0.056	0.030
	Cis–Trans	176.9	181.7	181.0	0.351	0.677
		179.4	290.8	185.2	0.115	0.106
		76.3	176.5	182.5	0.077	0.054
		175.0	182.2	289.0	0.063	0.039
177.8		179.6	76.6	0.053	0.029	
74.0		176.1	290.3	0.047	0.024	
LiCl	Trans–Trans	177.7	185.4	177.8	0.280	0.552
		74.2	176.8	177.0	0.094	0.090
		176.4	175.6	74.6	0.088	0.081
		176.4	181.6	298.1	0.079	0.067
		179.8	293.7	182.3	0.077	0.064
		300.3	185.5	178.6	0.060	0.043
	Cis–Cis	175.6	179.7	183.6	0.353	0.623
		76.6	176.2	184.9	0.130	0.118
		175.3	183.7	283.4	0.107	0.085
		164.7	78.2	180.6	0.090	0.063
		178.6	280.6	194.6	0.062	0.034
		74.0	68.3	179.4	0.060	0.032
	Cis–Trans	177.3	182.1	180.7	0.282	0.544
		180.8	292.1	186.1	0.124	0.138
		176.0	185.3	288.5	0.091	0.082
		75.3	174.3	182.1	0.074	0.058
176.4		179.5	75.3	0.067	0.050	
163.9		77.2	176.8	0.053	0.034	

least, a reasonable estimation of these values. Thus, the Amber force field computes coulombic and non bonded interactions between species i and j separated a distance r as:

$$E_{\text{coul}}(i,j) = 332 \frac{q(i)q(j)}{\epsilon r} \quad E_{\text{nb}} = [\sigma(i)\sigma(j)]^{1/2} \left[\left(\frac{r^0(i) + r^0(j)}{r} \right)^{12} - 2 \left(\frac{r^0(i) + r^0(j)}{r} \right)^6 \right] \quad (17)$$

with q , σ and r^0 representing the partial charge, polarizability and van der Waals radius of corresponding specie, ϵ is the dielectrical constant of the medium and the numerical constant 332 transforms the units so that the energy is obtained in kcal/mol when the distances are measured in Å and the charges in electrons.

We have performed calculations for NaBr and KBr molecules in vacuo and adjusted the $\sigma(\text{Br}^-)$ and $r^0(\text{Br}^-)$ parameters in such a way that the sum of $E_{\text{coul}} + E_{\text{nb}}$ interactions presented a minimum at a value matching the experimental interatomic distance [44] for the corresponding salt (i.e. $r = 2.64 \pm 0.01$ Å for NaBr and $r = 2.94 \pm 0.03$ for KBr), while employing tabulated values of the parameters for K and Na ions. Thus we obtained $\sigma(\text{Br}^-) = 0.105$ kcal/mol, $r^0(\text{Br}^-) = 2.582$ Å that produce minima at $r_{\text{min}} = 2.66$ and 2.92 Å, respectively, for NaBr and KBr. The same procedure applied to determine the parameters for the Cl^- from experimental interatomic distances of NaCl and KCl produce values which are in close agreement with those tabulated in the Amber field. Consequently we have employed the values indicated above for the Br^- ion in the present work.

Fig. 10 shows, as an example of MD results, the probability distribution for the three rotatable bonds on the repeat unit of the polymer, taken as independent of all neighbors, obtained for the system having LiCl salt and cis-cis configuration on the cycles. This figure is very similar to

its counterpart for the NaCl system [22]. Table 4 summarizes the preferred combinations for simultaneous orientations of the three rotatable bonds for the three salts (NaCl taken from Ref. [22]). As Table 4 indicates, all trans is by far the preferred conformation for all the systems, followed by the combinations in which two bonds are trans and one in either g or g^- , with combinations that place two or more bonds in any combination of g^\pm states being highly disfavored. Table 4 also shows that the results for three salts are quite similar. The similarity could be better observed in Table 5 which summarizes the values of the conformational energies optimized by comparison of probabilities for simultaneous orientations of pairs of bonds obtained by MD simulation and those computed with the statistical weight matrices given in Eq. (15).

Characteristic ratios of the unperturbed dimensions, calculated at 300 K with the procedure indicated above with a fraction of trans units $p_t \approx 0.84$ (similar to that of the measured sample), amount to 16.5, 13.9 and 14.4, respectively, for the systems having NaCl, NaBr and LiCl. Agreement with experimental values summarized in Table 3 is excellent in the case of NaCl and reasonable for the other two salts. Theoretical values seem to confirm the experimental results in the sense that the NaBr system exhibits the lowest dimensions, although the differences are rather small. It might be just a coincidence, but it is interesting to notice that the best agreement is obtained in the case of NaCl which has been measured closer to unperturbed conditions than the other two and, therefore, it should provide a more reliable extrapolation to unperturbed dimensions.

6. Conclusions

Application of SEC techniques with dual detection to the study of water solutions of a single polydisperse sample of PDDA at 25 °C allows a full analysis of the conformational properties of this polymer and permit the evaluation of absolute molecular weight distributions, scaling laws coefficients, molecular dimensions, shape of the chains, etc. Pure water is not a suitable solvent for these measurements, but addition of NaCl to concentrations of ca. 0.5 M produces a roughly theta solvent. Replacement of the NaCl salt by either LiCl or NaBr decreases the thermodynamical quality of the solvent and the chains adopt more compact conformations, although they still behave as random coil. Despite the difference in the thermodynamical quality of the solvent, the systems with NaCl and LiCl extrapolate to the same values of unperturbed conditions, while the system having NaBr produce noticeably lower unperturbed dimensions. Measurements of viscosity and electrical conductivities of these solutions seem to support the conclusions obtained in the SEC analysis. Theoretical calculations of the molecular dimensions performed by a combination of Molecular

Table 5
Conformational energies (in kcal/mol) obtained through comparison of a priori probabilities adjacent pairs of bonds obtained from MD simulations performed at 500 K and computed by matrix multiplication scheme. Statistical weights are taken to be single Boltman's factors of their corresponding energies, for instance, $\omega = \exp(-E_\omega/RT)$

Parameter	Conformational energies		
	Added salt		
	NaCl	NaBr	LiCl
σ_1	1.09	1.17	0.97
σ_2	1.14	1.13	1.72
σ_3	1.21	1.15	1.14
σ_4	1.62	1.51	1.66
σ_5	1.64	1.63	1.43
ω	0.21	0.29	0.36
ω'	0.99	1.56	1.94
ω''	1.68	1.72	1.97

dynamics and Monte Carlo sampling procedures produce results that are in excellent agreement with the experimental values obtained in the NaCl and seem to confirm that the NaBr salt produces small molecular dimensions, although the differences are smaller than those obtained in experimental measurements.

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References

- [1] Potschka M, Dubin PL, editors. *Strategies in size exclusion chromatography*. Washington DC: American Chemical Society; 1996.
- [2] Trathnigg B. *Prog Polym Sci* 1995;20:615–50.
- [3] Huglin MB, editor. *Light scattering from polymer solutions*. London: Academic Press; 1972.
- [4] Wyatt PJ. *Anal Chim Acta* 1993;272:1.
- [5] Laguna MTR, Medrano R, Plana MP, Tarazona MP. *J Chromatogr A* 2001;919:13–19.
- [6] Búrdalo J, Medrano R, Saiz E, Tarazona MP. *Polymer* 2000;41:1615–20.
- [7] Laguna MTR, Gallego J, Mendicuti F, Saiz E, Tarazona MP. *Macromolecules* 2002;35:7782.
- [8] Potschka M. *J Chromatogr* 1988;441:239–60.
- [9] García R, Porcar I, Campos A, Soria V, Figueruelo JE. *J Chromatogr A* 1994;662:61–9.
- [10] Dautzenberg H, Görnitz E, Jaeger W. *Macromol Chem Phys Ed* 1998;199:1561–71.
- [11] Matsumoto A. *Prog Polym Sci* 2001;26:189–257.
- [12] Bowman LM, Cha CY. *J Polym Sci, Polym Lett* 1979;17:167–73.
- [13] Burkhardt CW, McCarthy KJ, Parazak DP. *J Polym Sci, Part C. Polym Lett* 1987;25:209–13.
- [14] Wandrey Ch, Görnitz E. *Acta Polym* 1992;43:320–6.
- [15] Xia J, Dubin PL, Edwards S, Havel H. *J Polym Sci, Part B: Polym Phys* 1995;33:1117–22.
- [16] Dautzenberg H, Karibyants N. *Macromol Chem Phys* 1999;200:118–25.
- [17] Trzcíński S, Vårum KM, Staszewska DU, Smidsrød O, Bohdanecký M. *Carbohydr Polym* 2002;48:171–8.
- [18] Reed WF. Chapter 2 in Ref. 1.
- [19] Dautzenberg H, Rother G. *Macromol Chem Phys* 2004;205:114–21.
- [20] Hinderberger D, Jeschke G, Spiess HW. *Macromolecules* 2002;35:9698–706.
- [21] Tarazona MP, Saiz EJ. *Biochem Biophys Methods* 2003;56:95–116.
- [22] Marcelo G, Tarazona MP, Saiz E. *Polymer* 2004;45:1321–30.
- [23] Flory PJ. *Statistical mechanics of chain molecules*. New York: Wiley; 1969.
- [24] Flory PJ. *Macromolecules* 1974;7:381.
- [25] Riande E, Saiz E. *Curr Trends Polym Sci* 1997;2:1.
- [26] Mattice WL, Suter UW. *Conformational theory of large molecules*. New York: Wiley; 1994.
- [27] Laguna MTR, Tarazona MP, Carriedo GA, Alonso FJG, Fidalgo JI, Saiz E. *Macromolecules* 2002;35:7505.
- [28] Laguna MTR, Tarazona MP, Saiz E. *J Chem Phys* 2003;119:1148.
- [29] Percec V, Ahn CH, Cho WD, Jamieson AM, Kim J, Leman T, et al. *J Am Chem Soc* 1998;120:8619.
- [30] Gerle M, Fischer K, Roos S, Müller AHE, Schmidt M. *Macromolecules* 1999;32:2629.
- [31] De Gennes PG. *Scaling concepts in polymer physics*. Ithaca, NY: Cornell University Press; 1979.
- [32] Zimm BH. *J Chem Phys* 1948;16:1093.
- [33] Fixman MJ. *J Chem Phys* 1955;23:1656.
- [34] Yamakawa H. *Modern theory of polymer solution*. New York: Haper and Row; 1971.
- [35] Nishida K, Kaji K, Kanaya T, Fanjat N. *Polymer* 2002;43:1295–300.
- [36] Huggins ML. *J Am Chem Soc* 1942;64:2716.
- [37] Kraemer EO. *Ind Eng Chem* 1938;30:1200.
- [38] Manning GS. *J Phys Chem* 1971;75:1691.
- [39] Manning GS. *J Phys Chem* 1975;79:262–5.
- [40] Lide DL. (Ed. in Chief). *CRC Handbook of Chemistry and Physics*. 76th ed. Boca Raton: CRC Press; 1995.
- [41] Nagaya J, Minakata A, Tanioka A. *Colloids Surfaces A. Physico-chemical Eng Aspects* 1999;148:163–9.
- [42] <http://www.amber.ucsf.edu/amber/amber.html>; <http://www.amber.ucsf.edu/amber/dbase.html>; <http://pharmacy.man.ac.uk/amber/>
- [43] The number of added salt molecules should be large enough as to produce a noticeable effect in the calculation and yet low enough as to represent a reasonable macroscopic concentration. A number of ca. 20 molecules (producing a macroscopic concentration of 2M) compromise
- [44] Sutton LE, editor. *Tables of interatomic distances and configuration in molecules and ions*. Chem Soc Special Pub no 11, London. Supplement Chem. Soc. Special Pub. No 18, London; 1965.