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Classification

Physics Abstracts

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Conformation and order in polyelectrolyte solutions

Gilbert Weill

Institut C. Sadron (CRM-EAHP), (CNRS-ULP), 6 rue Boussingault, 67083 Strasbourg Cedex, France

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Résumé. — Le pic existant dans le facteur de diffusion d'une solution de polyélectrolytes en l'absence de sel ajouté et dont la position q_m varie comme $C^{1/2}$ est parfois interprété comme résultant d'un ordre orientationnel local. Le fait que cette variation soit observée à travers plusieurs régimes de concentration conduit à évaluer les théories formulées en terme de trous de corrélation, et les autres évidences expérimentales de l'absence d'ordre orientationnel. La diffusion anisotrope de la lumière, les temps de relaxation de la biréfringence électrique et la grandeur de la biréfringence magnétique ne présentent aucune anomalie interprétable en terme de corrélation orientationnelle entre les chaînes.

Abstract. — The scattering factor of polyelectrolyte solutions in the absence of added salt presents a peak at a scattering vector q_m which varies like $C^{1/2}$. This has been sometimes interpreted in terms of a local orientational order of cylinders. The variation holds however through many concentration regimes, and other explanations in term of correlation holes have been proposed. We evaluate the different models together with the other possible evidences for the lack of orientational order. Anisotropic light scattering, electric birefringence relaxation and the magnitude of magnetic birefringence show no evidence for orientational order between single chain conformation.

While the existence of colloidal crystals in salt free solutions of charged latex [1] is now well documented, the existence of similar ordered arrays of rod like particles in very low concentration solutions of flexible polyelectrolytes remain largely hypothetical. Theoretical predictions based on simplified intermolecular potentials lead to ambiguous answers [2]. The claim for possible long range attractive forces advocated by Sogami and Ise [3] has been shown by Overbeck [4] to be non valid. The contribution of dispersion forces due to the large fluctuations in the counterion distribution which is responsible of the high dielectric increment of polyelectrolyte solutions and to high ionic polarisability anisotropy responsible for their easy orientation in an electric field [5, 6] is nevertheless not taken in account. It should favour a parallel arrangement and perhaps modify the arguments against the formation of nematic order when the polyions are intrinsically flexible [7]. From an experimental point of view the interpretation of the peak in the total X-ray and neutron scattering [8, 9] and of the $C^{1/2}$ dependence (C = monomolar concentration in polymer) of its position q_m (q scattering vector) in terms of a 2 dimensional parallel order of rod like segments is

made questionable by the very fact that this concentration dependence holds over a range covering many concentration regimes [10].

Our present view of these regimes takes in account the gradual change of conformation of the polymeric chains with the reduction of the screening upon dilution. It is now generally accepted that the effect of coulombic interactions on flexible chain conformations can be divided into a short range stiffening described by an electrostatic contribution L_e to the total persistence length L_T [11, 12] ($L_T = L_e + L_p$, $L_p = kT/E$, E being the Young modulus of the uncharged semi flexible macromolecule) and a longer range contribution to the excluded volume [13]. When including Manning's condensation model [14] in its simplest form

$$L_e = \frac{1}{4 \kappa^2 l_B} F(\kappa l) \quad (1)$$

for monovalent counterions [15]. κ^{-1} is the Debye screening length, l_B the Bjerrum length : $e^2/\epsilon kT$ and l the contour length of the polyelectrolyte. The functions $F(\kappa l)$ tends to one for $\kappa l \gg 1$.

In the absence of added salt, a simple prescription for the calculation of κ is to assume that the

screening is due to the fraction of osmotically free counterions b/l_B where b is the distance between charges along the chain

$$\kappa^2 = 8 \pi l_B \left(\frac{1}{2} \frac{b}{l_B} n \right) = 4 \pi \mathcal{N} b c \quad (2)$$

n is the number of monomers per unit volume.

Direct observations of the pure intramolecular scattering factor from a series of measurements on mixtures of protonated and deuterated polyelectrolyte molecules at constant total concentration [16, 17, 18] have semi quantitatively substantiated relations (1) and (2). It has however been proposed [19] on the basis of a collective model designed to interpret the concentration dependence of the reduced viscosity [20] that the stiffening in the semi dilute range should be reduced by the presence of the other chains.

Starting from the chain conformation a number of concentration regimes have been postulated [15] schematically depicted in figure 1. The limiting concentrations are given by the following cross over :

— dilute to semi dilute : $n \sim (l^3)^{-1}$ or expressed in molar concentration of monomer $C_1 = (\mathcal{N} N^2 b^3)^{-1}$ where N is the number of monomers in the chain ($l = N b$) ;

— rod like to semi flexible

$$L_T \sim L_e = l \quad [15] \quad (3)$$

$$C_2 \sim (16 \pi \mathcal{N} N b^2 l_B)^{-1} . \quad (4)$$

This value is overestimated for small l since at C_2

$$\kappa l \sim 2 l^{1/2} l_B^{-1/2} \quad \text{and} \quad F(\kappa l) < 1$$

— semi flexible to flexible disordered at $\kappa l_B \sim 0.1$ [12]

$$C_3 \sim (32 \pi^2 \mathcal{N} l_B^2 b)^{-1} . \quad (5)$$

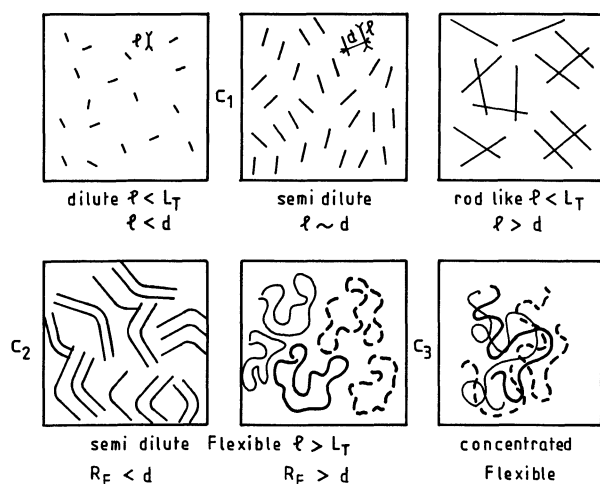


Fig. 1. — Schematic representation of the different concentration regimes.

It must be stressed that under the assumption of local parallel ordering, since both κ^{-1} and d are proportional to $C^{-1/2}$, $\kappa d = \text{cst.} \sim 4$ and one should expect an ordered array in the C_1 - C_3 range.

Typical values of C_1 , C_2 , C_3 for the typical vinylic polyelectrolytes are given in table I together with the values in g/l for sodium polystyrene sulfonate of varying molecular weights in a range corresponding to the large body of experiments reported on this polymer.

Table I. — Cross over concentrations in salt free fully ionized vinylic polyelectrolyte solutions.

	C_1	C_2	C_3
$C_{\text{monomolar}}$	$\frac{106}{N^2}$	$\frac{0.74}{N}$	4×10^{-2}
C g/l			
PSS Na $M = 15\,000$	4	2	8
75 000	0.16	0.4	8
150 000	0.04	0.2	8
750 000	0.0016	0.01	8

The idea of a 2 D parallel ordering underlying this description was originally inspired by thermodynamic considerations on the concentration dependence of the counterions activity [21] as well by success of the so called cellular model [22]. In this model the regular arrangement of parallel rods was however assumed as a pure mathematical convenience. It retains the cylindrical symmetry for the calculation of the counterion distribution around each rod using Poisson-Boltzmann equation with suitable boundary conditions. Therefore the simple arguments for a 2 D quasi crystalline ordering being at the origin of the $C^{-1/2}$ dependence of the position q_m of the peak [23] have to be quantitatively compared to those attributing the peak in the scattering to a simple liquid like correlation grossly described in terms of the exclusion of the segments of other macromolecules in a volume (the correlation hole) around each segment of one macromolecule [24].

1. The scattering of salt free polyelectrolyte solutions.

It is clear that all of the X-rays and neutron scattering experiments [8, 9, 16, 17, 18] have been carried out at concentration $> C_3$. There is only one set of experiments carried out by light scattering in the C_1 - C_2 range where q_m can be observed in a much lower q region. q_m has been claimed [7] to obey the same $C^{1/2}$ law throughout the whole concentration range and the distance d derived from the Bragg relation $2 \pi q_m^{-1} \approx d$ to fit the predicted value $\pi d^2 b = c^{-1}$. Care must however be exercised con-

sidering that q_m has been found molecular weight dependent [25] above C_3 .

This is more easily understood in terms of a correlation hole effect. Qualitatively the total scattering is known to be ~ 0 at $q = 0$ due to the osmotic incompressibility. At large $q \gg d^{-1}$ it should reduce to the single scattering factor. A peak must therefore exist and the simplest form for the total scattering function can be written [24]

$$\frac{I(q)}{nN} \propto NP(q) \frac{q^2 \xi^2}{1 + q^2 \xi^2} \quad (6)$$

where $P(q)$ is the single particle scattering factor and ξ a correlation length for segmental interaction. Assuming $\xi < L_T$, as it should for $C > C_3$ one expects $P(q)$ in the region of q_m to reflect the rod like behaviour and if in first approximation $P(q) \sim (qN)^{-1}$, $q_m = \xi^{-1}$. The $C^{1/2}$ dependence would reflect the relation between ξ and κ^{-1} ; the peak amplitude then also decreases as $\xi \sim C^{-1/2}$ in fair agreement with the experimental results [8]. The small molecular weight dependence can then arise from the fact that in the high concentration range $C \geq C_3$, ξ and L_T are of the same order of magnitude so that $P(q)$ has not exactly a q^{-1} dependence around the maximum [22]. Writing the total scattering

$$I(q) \sim nNP^2(q) + Q(q) \quad (7)$$

where $P(q)$ is the intramolecular scattering factor and $Q(q)$ the intermolecular scattering factor, one can extend for not too rigid molecules the derivation of $S(q)$ carried out by Benoît [26] for semi dilute solution of polymers with an excluded volume

$$v = \int [g(r_{ij}) - 1] 4 \pi r^2 dr = v \delta(r_{ij}) \quad (8)$$

to the case where the excluded volume factor has a q dependence. In the absence of orientational correlation

$$v(q) = 4 \pi \int r^2 [g(r_{ij}) - 1] \frac{\sin qr}{qr} dr. \quad (9)$$

Replacing in $v(q)$, $[g(r) - 1]$ by the direct correlation function $c(r)$ and assuming Ornstein-Zernicke relation

$$\frac{I(q)}{nN^2} \propto P(q) \frac{1}{1 + nN^2 v(q) P(q)}$$

or

$$\frac{nN^2}{I(q)} = \frac{1}{P(q)} + nN^2 v(q) \quad (10)$$

Jannink [27] has used $c(r) = \frac{1}{r} e^{-\kappa r}$ and found that q_m does not vary as $C^{1/2}$.

Benmouna and Grimson [28] have used an approximation to the one component plasma [28] and again q_m is found to vary more closely to $C^{1/3}$.

Koyama [29] has used directly $g(r) = 1 - \exp - \frac{r^2}{R_0^2}$ therefore not using the Ornstein-Zernicke formula. This leads to

$$\frac{I(q)}{nN} \propto NP(q) \left[1 - \pi^{3/2} nNbR_0^2 \exp - \frac{q^2 r^2}{4} \right]. \quad (11)$$

Assuming $I(0) \sim 0$ i.e. $R_0^2 n = \text{cst.}$ this leads to $R_0 \propto C^{1/2}$ and a maximum at $qn^{-1/2} = 8.36 \text{ \AA}^{-1}$ if $P(q) \sim (qN)^{-1}$. But this result is clearly dependent upon the somewhat arbitrary choice of a gaussian function for $g(r) - 1$. Making $C(r) = 0$ for $R < R_0$ and 1 for $R > R_0$ would not reproduce the $C^{1/2}$ dependence of q_m [28, 30]. There is a need for more exact derivations of the structure factor for interacting rods, taking in account orientational correlation. A first attempt, limited to extremely diluted solutions, has recently been made in this direction [31].

We therefore look below for other possible evidences for orientational correlations in polyelectrolytes.

2. Depolarized light scattering.

It is well known that the part of the scattering by liquids which is due to their molecular anisotropy does not suffer the drastic reduction that the part due to the mean polarisability suffers as compared to the gaseous state [32]. A formulation based on the use of a correlation function $g(r, \omega)$ for the relative positions and orientation in the liquid state has been given [33]. The isotropic part of the V_v polarized component of the scattering is reduced according to the isothermal compressibility while the anisotropic part of V_v and the whole of H_v are only multiplied by

$$\begin{aligned} \frac{N}{V} \iint \frac{3 \cos^2 \varnothing - 1}{2} [g(r, \omega) - 1] d^3r d\omega = \\ = 1 + Z \frac{3 \langle \cos^2 \varnothing \rangle - 1}{2} \end{aligned} \quad (12)$$

i.e. are only sensitive to the orientational correlations. This formulation has not been quantitatively used in liquids owing to the difficulties arising from the anisotropy of the internal field [34] but it should hold for solutions of rodlike particles in the domain $q < l^{-1}$. This qualitative assumption has been recently confirmed by a more exact calculation of the structure factor S_{H_v} for a solution of interacting rods [35]. In the case of charged rods, the reduction in the isotropic part of the component V_v can be in first approximation related to the number of osmotically free counterions, i.e. divided by $b/l_B N$ [36]. Then the excess scattering of the solution

$$\Delta V_v = V_v - V_{v0} \propto \frac{l_B}{bN} (\bar{\alpha} - \bar{\alpha}_0)^2 + \frac{4}{45} (\alpha - \beta)^2 \left[1 + Z \frac{3 \langle \cos^2 \varnothing \rangle - 1}{2} \right]$$

$$\Delta H_v = H_v - H_{v0} \propto \frac{3}{45} (\alpha - \beta)^2 \times \left[1 + Z \frac{3 \langle \cos^2 \varnothing \rangle - 1}{2} \right] \quad (13)$$

where $\bar{\alpha}_0$ is the mean polarizability of a volume of solvent equal to the molecular volume. In terms of the molecular anisotropy δ of the rods, identical to that of the monomer

$$\Delta V_v = \frac{l_B}{b \cdot N} \left(\frac{\bar{\alpha} - \bar{\alpha}_0}{3 \bar{\alpha}} \right)^2 + \frac{4}{5} \delta^2 \left[1 + Z \frac{3 \langle \cos^2 \varnothing \rangle - 1}{2} \right]$$

$$\Delta H_v = \frac{3}{5} \delta^2 \left[1 + Z \frac{3 \langle \cos^2 \varnothing \rangle - 1}{2} \right]. \quad (14)$$

For PSSNa one can evaluate $(\alpha - \beta) \sim 4 \times 10^{-24} \text{ cm}^3$; $(\alpha + 2\beta) \sim 36 \times 10^{-24} \text{ cm}^3$; $\delta^2 \sim 12 \times 10^{-3}$ and $(\bar{\alpha} - \bar{\alpha}_0)/\bar{\alpha} \sim \frac{n^2 - n_0^2}{n_0^2 - 1} \sim 0.5$. ΔH_v becomes

of the order of ΔV_v for $N \sim 100$, $l \sim 250 \text{ \AA}$ where the condition $q < l^{-1}$ holds even for backward light scattering. But the concentration must be kept smaller than $C_2 \sim 10^{-2} \text{ M} \sim 2 \text{ g/l}$ to maintain $L_T > 1$ even with the κl correction. This implies that the anisotropic scattering ΔH_v remains a small fraction of the water V_v (the control of the polarisation is very important) and still of the order of the water H_v (the cleaning of water from dust becomes a major problem) unless the orientational correlation factor is large. We have not yet succeeded to observe significant values of ΔH_v which implies that the orientational correlation factor is small.

3. Electro optical and magneto-optical effects.

Due to the high sensitivity of birefringence measurements, the use of orientation in an electric field to characterize the conformation and possible orientation of flexible polyelectrolytes in very dilute solutions is very old [37]. The steady state birefringence results from an optical and an electrical factor, the latter being related to the mechanism of orientation. In polyelectrolytes it results from the very large ionic polarisability originating in the easy displacement of counterions along the molecular axis [3]. We have however up to now no real model to evaluate its dependence upon length, flexibility, field strength, concentration in salt free solution and in presence of added salt [38, 39, 40]. It remains therefore a qualitative tool to detect small changes.

Recent results [41] on the concentration and molecular weight dependence of the electrical birefringence of a series of PSS at very low concentration show clearly the existence of a molecular weight dependent concentration below which the birefringence at a fixed electric field becomes independent of the concentration. The value fits very well with C_2 . Since the optical factor can be calculated from the extrapolation of the birefringence at very high fields, the orientation factor can be measured. But since the electrical polarisability anisotropy of a single molecule is not available theoretically, no information whether it corresponds to the alignment of single molecules or to clusters of elongated molecules with a strong correlation in orientation can be derived. Such an information can be obtained from a comparison of the orientational correlation time with that of a single elongated molecule, or from the study of the magnetic birefringence where the orientational mechanism is related to the molecular magnetic susceptibility anisotropy which can be measured or evaluated with a rather good accuracy.

In the study of the orientational correlation time, care must be taken of the influence of polydispersity which makes the decay highly non exponential [42]. Non exponentiality can also arise from residual bending. Another effect, directly reflected by an increase of the birefringence upon electric field reverseal has been recently described [41]. It is interpreted as due to the coiling of the extremities of the molecule where the accumulation of counterions displaced by the electric field increases the screening and reduces locally the electrostatic persistence length. It can be eliminated by using a train of reversed pulses with a duration smaller than the coiling time. In these conditions sufficiently high fields can be used to measure sizeable birefringence at concentrations between C_1 and C_2 . Relaxation times τ are then measured which are independent of C and very close to τ_R for the totally stretched molecule [43]

$$\tau_R = \frac{\pi \eta_0 l^3}{3 kT} \left[\text{Ln} \frac{l}{r_0} - 1,57 \left[\frac{7}{\text{Ln} \frac{l}{r_0}} - 0,28 \right]^2 \right] \quad (15)$$

where r_0 is the radius of the cylinder (see table II).

Table II. — *Experimental electrooptical relaxation time τ at C_2 and computed rotational correlation time τ_R of fully stretched PSS molecules (from [38]).*

10^{-3} M	70	210	290	390	570	750	1 100
$\tau \text{ } \mu\text{s}$	7	56	350	790	1 400	3 500	6 700
$\tau_R \text{ } \mu\text{s}$	7	145	360	820	2 400	5 200	13 000

Further evidence for an orientation of individual molecules can be found from the absolute value of the magnetic birefringence. We have calculated [44] the specific Cotton-Mouton constant for a solution of non interacting worm like chains

$$\frac{\Delta n}{CH^2} = \frac{4\pi N}{45} \frac{1}{n} \frac{\Delta\alpha \Delta\chi}{kT l_0 m_0} \times \left[1 - \frac{L_T}{3l} \left(1 - \exp - \frac{3l}{L_T} \right) \right] \quad (16)$$

where $\Delta\alpha$, $\Delta\chi$, l_0 , m_0 are respectively the optical anisotropy, magnetic anisotropy, length and molecular weight of a repeat unit.

The values [45, 46] measured on solutions of PSS have been compared to those calculated introducing in (16) for L_T and κ the values calculated from relation (2) and (3) as shown in figure 2. Slightly different parameters have been used as compared to the original publication. In particular the product $\Delta\alpha \Delta\chi$ has been adjusted to give the measured specific Cotton-Mouton constant at high added salt content (2 M) using L_p deduced from the radius of gyration measured by light scattering with an excess of salt such as $A_2 = 0$ ($L_p = 10 \text{ \AA}$) [47]. The predicted values are in general higher than the observed ones. Since the sensitivity of the experiment allows only measurements in the C_2 - C_3 range, it may well be due to the fact that the screening calculated according to relation (2) is underestimated. Such low values preclude however any strong parallel ordering which would result in a much higher specific magnetic birefringence, roughly multiplied by the number of molecules in an ordered array.

4. Conclusion.

We are then led to the conclusion that no strong orientational correlations with a parallel array of rod

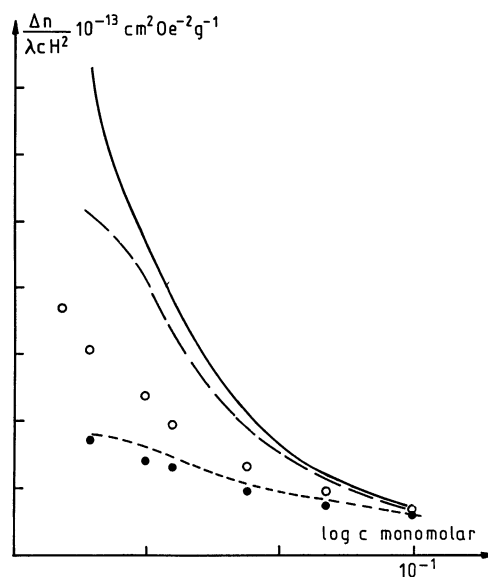


Fig. 2. — Specific magnetic birefringence of PSS solutions as a function of concentration: $M = 15,000$ (●), $M = 140,000$ (○). Full curves are calculated for $M = 15,000$, $140,000$ and ∞ .

like molecules exist in the C_1 - C_3 concentration range. Interpretations based on such an ordered array should be considered with care. The isotropic model of polyelectrolyte solutions with a liquid like correlation function should hold. The shape of $v(q)$ should then be safely obtained from the application of relation (10) to the total intensity $I(q)$ measured by neutron scattering, using the theoretical expression of $P(q)$ for worm like chains [48]. There is a good hope to derive from such a systematic investigation [49] a general form of $c(r)$ and its dependence on charge density, concentration and added salt which will explain the dependence of the position of the scattering peak.

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