

Magnetic birefringence of polystyrene sulphonate: Molecular weight and concentration dependence

G. Weill

Centre de Recherches sur les Macromolécules, CNRS, and Université L. Pasteur, Strasbourg, France

and G. Maret

Max Planck Institut Für Festkörper Forschung, Hochfeld Magnet Labor, Grenoble, France
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The specific Cotton–Mouton constant of water solutions of PSS–Na⁺ of different molecular weight have been measured at concentrations below 2% in the absence and presence of added salt. A bare persistence length $q = 12 \text{ \AA}$ is found from the high ionic-strength molecular weight and concentration independent value. The molecular weight and concentration dependence at low ionic-strength is discussed in terms of the electrostatic contribution to the persistence length and the structure of semi-dilute polyelectrolyte solutions.

Keywords Magnetic birefringence, polyelectrolytes; persistence length; polystyrene sulphonate; conformation; Cotton–Mouton effect

INTRODUCTION

The effect of long range coulombic interactions on the conformation of synthetic and natural flexible polyelectrolytes in solution and their progressive screening with the concentration or addition of simple salts has been known and qualitatively understood for a long time. Due to the dominant intermolecular interactions, scattering experiments, using light, X-rays or neutrons, fail, in the low ionic strength range, to give the molecular dimensions¹. Therefore most of our present experimental information relies on indirect hydrodynamic measurements such as intrinsic viscosity², flow birefringence or dichroism^{3,4} and relaxation of electro-optical effects⁵. Direct measurements of the intramolecular scattering factor from neutron scattering of mixtures or protonated and deuterated molecules, require difficult sample synthesis and experiments, as recently demonstrated⁶. It has been proposed that the amplitude of the magnetic birefringence is directly proportional to the persistence length and can be used to measure its variation with ionic strength⁷. The first experiments have been carried out with DNA which has a large persistence length and a high optical and magnetic anisotropy. They are presently extended and reinterpreted using a corrected relation for the magnetic birefringence of worm-like chains and measurements carried out at much lower concentrations and ionic strengths⁸. The improvements in sensitivity allows the technique to be applied to the much more flexible polystyrene sulphonate molecule. The effects of concentration and molecular weight have thus been investigated and are reported and discussed in this report.

EXPERIMENTAL METHODS

Polystyrene sulphonic acid has been prepared by sulphonation of anionically polymerized polystyrene using the method of Turbak⁹. Three samples (Na salt) of weight average molecular weight $M_w \sim 15\,000$, 40\,000 and

140\,000 have been used.

The magnetic birefringence set up has been already described¹⁰. Improvements in sensitivity resulted mainly from a reduction of the influence of the room temperature fluctuations on the base line, mechanical damping of the optical bench, and residual strain birefringence of the cell windows⁸.

RESULTS

The specific Cotton–Mouton constants of the three samples at different concentrations in polymer and added salt are given in *Table 1* as mean values with their mean-square deviation.

The results, with their actual dispersion, are reported in *Figure 1* as a function of the total equivalent ionic strength, i.e. a concentration of a simple salt which is supposed to give the same electrostatic screening as the ensemble of the polyion, counterions and co-ions. For that purpose, the contribution of the polyelectrolyte salt is either:

(a) taken as a concentration of fully dissociated monomers $[C_p]$ (*Figure 1a*).

(b) limited to the concentration of uncondensed counterions. According to Manning¹¹ this fraction is equal to $(z\lambda)^{-1}$ where z is the charge number of the counterion and λ the charging parameter of the polyion, i.e. the ratio of the Bjerrum length l_b to the mean distance b between charges along the chain axis. With $\lambda = 2.8$ for PSS and $z = 1$ the contribution of the polyelectrolyte is equal to that of a concentration $0.18 [C_p]$ of single salt (*Figure 1b*).

It is seen that at high ionic strength, the specific Cotton–Mouton constant is independent on molecular weight and concentration. At low concentration of polymer, in the absence of added salt, the Cotton–Mouton constant increases and becomes molecular weight dependent.

Table 1 Specific Cotton–Mouton constants C_M/c of aqueous solutions of PSS NA without and with added salt

PSS concentration c g/100 cc	C_p monomol.	NaCl C_s molar	C_M/c (10^{-13} cm ² Oe ⁻² g ⁻¹)		
			15000	40000	140000
2	$9.6 \cdot 10^{-2}$	—	5.9 ± 0.2	6.1 ± 0.2	7 ± 0.2
1	$4.8 \cdot 10^{-2}$	—	7 ± 0.2	7.6 ± 0.2	9.2 ± 0.9
0.5	$2.4 \cdot 10^{-2}$	—	9 ± 0.5	12.1 ± 0.3	12.8 ± 1.1
0.25	$1.2 \cdot 10^{-2}$	—	13 ± 1.3	15.8 ± 1.3	19.5 ± 1.2
0.20	$0.96 \cdot 10^{-2}$	—	14 ± 1.6	17.5 ± 2.0	23.8 ± 4.5
0.125	$0.6 \cdot 10^{-2}$	—	17 ± 2.0	17.5 ± 2.0	31 ± 2.5
0.100	$0.48 \cdot 10^{-2}$	—			39 ± 4.0
2	$9.6 \cdot 10^{-2}$	0.08	3.4		4.1 ± 0.2
2	$9.6 \cdot 10^{-2}$	0.1		3.6 ± 0.2	
2	$9.6 \cdot 10^{-2}$	0.25			2.8 ± 0.2
2	$9.6 \cdot 10^{-2}$	0.5	3.4 ± 0.2	2.7 ± 0.3	2.85 ± 0.2
2	$9.6 \cdot 10^{-2}$	2	2.65	2.7 ± 0.2	2.75 ± 0.2
1	$4.8 \cdot 10^{-2}$	0.5	2.45		
0.2	$0.96 \cdot 10^{-2}$	$0.73 \cdot 10^{-2}$			8.5 ± 1.8

When indicated the errors are standard deviations over a series of measurements

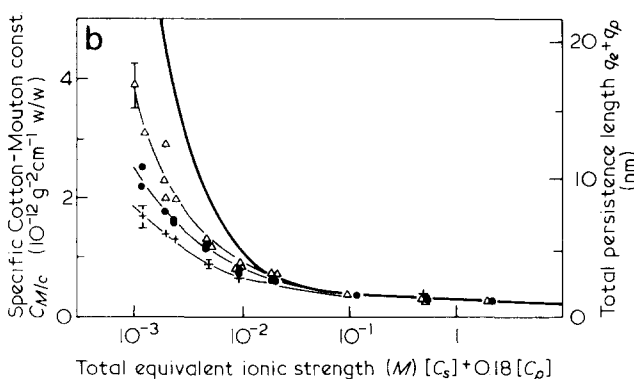
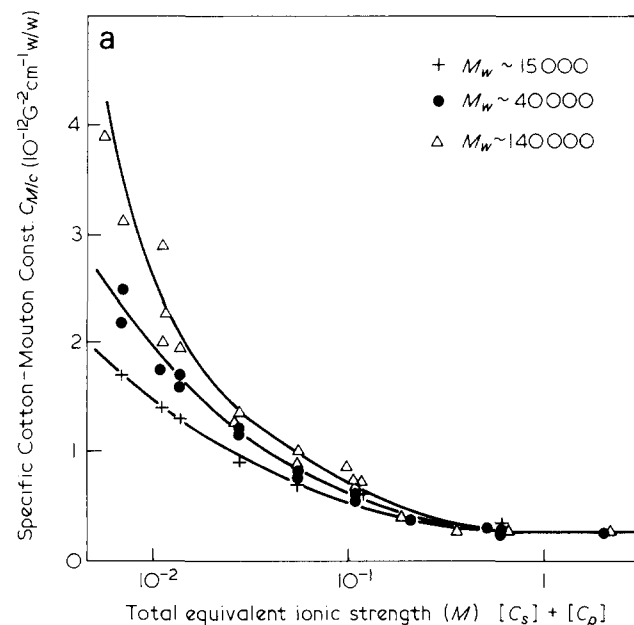


Figure 1 Specific Cotton–Mouton constant of PSS Na⁺ as a function of the ionic strength: (a) calculated from the total monomolar concentration in polyion and salt; (b) calculated with only the uncondensed counterions. The heavy line has been calculated assuming a change in electrostatic persistence length according to refs. 16 and 17

DISCUSSION

For an isolated worm-like chain in the absence of excluded volume effects, the specific Cotton–Mouton constant $\frac{C_M}{c}$ is related to the chain properties (i.e. the monomer length l_0 , monomer molecular weight m_0 , with optical and magnetic anisotropies $\Delta\alpha$ and $\Delta\chi$ with respect to the chain axis, the persistence length q and the total contour length L) through^{12,13}

$$\frac{C_M}{c} = \left(\frac{\Delta n}{\lambda c H^2} \right)_{CGS} = \frac{4\pi}{45} \frac{1}{n_0 \lambda} \frac{N}{kT} \frac{\Delta\alpha \Delta\chi}{m_0 l_0} q \left[1 - \frac{q}{3L} \left(1 - \exp\left\{ -\frac{3L}{q} \right\} \right) \right] \quad (1)$$

where Δn is the magnetic birefringence at field H , λ the wave length, n_0 the solution index of refraction, N Avogadro's number and kT the usual Boltzmann factor.

The variation of C_M/c should therefore reflect directly the change in persistence length. When $L \gg q$ the last bracket is equal to 1 and C_M/c should be molecular weight independent as is the case for PSS at high ionic strength.

From the value $\frac{C_M}{c} = 2.7 \cdot 10^{-13}$ cm² Oe⁻² g⁻¹, a value of q can be calculated if the product $\Delta\alpha \Delta\chi$ is known. We have derived a value of $\Delta\alpha$ from the electric birefringence of PSS at high fields as measured by Kikuchi and Yoshioka¹⁴. Extrapolation of these data to an infinite field, i.e. full orientation of the molecules gives $(\Delta n/\lambda c)_{E \rightarrow \infty} = 10^3$ cm² g⁻¹. Using $\lambda = 5.46 \cdot 10^{-5}$ cm, $m_0 = 209$, $n_0 = 1.33$ one derives the optical anisotropy:

$$\Delta\alpha = \frac{(\Delta n)}{c} \frac{n_0 m_0}{E \rightarrow \infty} \frac{1}{2\pi N} = 4.10^{-24} \text{ cm}^3$$

This value is 2/3 of that of benzene, a plausible value considering that the anisotropy arises mainly from the aromatic side group, the plane of which is not strictly perpendicular to the main chain and which has a limited rotational freedom. We therefore assume similarly:

$$\Delta\chi = \frac{2}{3}\Delta\chi_{\text{Benzene}} = 39.8 \cdot 10^{-6} \text{ cm}^3 \text{ mol}^{-1} = 6.6 \cdot 10^{-29} \text{ erg/Oe}$$

Inserting these values in relation (1) with $l_0 = 2.5 \cdot 10^{-8}$ cm one gets $q = 12 \text{ \AA}$. This value can be compared with that calculated from the unperturbed radius of gyration of a PSS K^+ sample of $M_w = 10^6$ given by Takahashi¹⁵ $\langle R^2 \rangle = \frac{Lq}{3} = 3.6 \cdot 10^{-12} \text{ cm}^2$; $q = 9.5 \text{ \AA}$. The agreement is fair.

The molecular weight effect observed on the concentration dependence of the Cotton–Mouton constant at lower ionic strength precludes its interpretation in terms of a simple change in persistence length. Indeed, the highest Cotton–Mouton constant observed for each molecular weight would correspond to values of $q \ll L$ so that the bracketted term in relation (1) should remain close to 1 and molecular weight independent. The molecular weight dependence might indicate that long range correlations affect the tensorial averaging performed to obtain relation (1), where excluded volume effects have been neglected. Although in most of the concentration range practically available, the solutions are not in the dilute regime, we discuss first the possible excluded volume effect on single chains magnetic birefringence. We shall then discuss the influence of additional screenings and correlations in the semi-dilute regime on single chain behaviour.

The derivation of relation (1) involves a double summation over all pairs of monomers i and j

$$\frac{1}{N} \sum_i \sum_j \left\langle \frac{3\cos^2\theta_{ij} - 1}{2} \right\rangle \quad (2)$$

where θ_{ij} is the angle between the axis of the segments of the polymer i and j . Excluded volume interactions introduce additional long range correlations which make the double sum molecular weight dependent. This is easily seen in the analogous calculation of the end to end distance

$$\langle h^2 \rangle = l_0^2 \sum_i \sum_j \langle \cos \theta_{ij} \rangle = 2Lq \alpha^2 \quad (3)$$

$\alpha > 1$ reflects the swelling due to excluded volume interaction. It is known to depend upon the molecular weight as:

$$\begin{aligned} \alpha &= 1\alpha M^{1/2} \text{ for small excluded volume} \\ \alpha &= \alpha M^{0.1} \text{ for large excluded volume} \end{aligned}$$

No explicit calculation of the excluded volume effect in summation (2) has been reported so far. A log–log plot of the Cotton–Mouton constant as a function of M indicates a molecular weight dependence close to $M^{0.2}$ at low concentration (Figure 2). This gives some confidence to the qualitative argument that the averaged sum over the second Legendre polynomial $P_2(\cos \theta_{ij})$ could have, for small values, the same functional dependence on

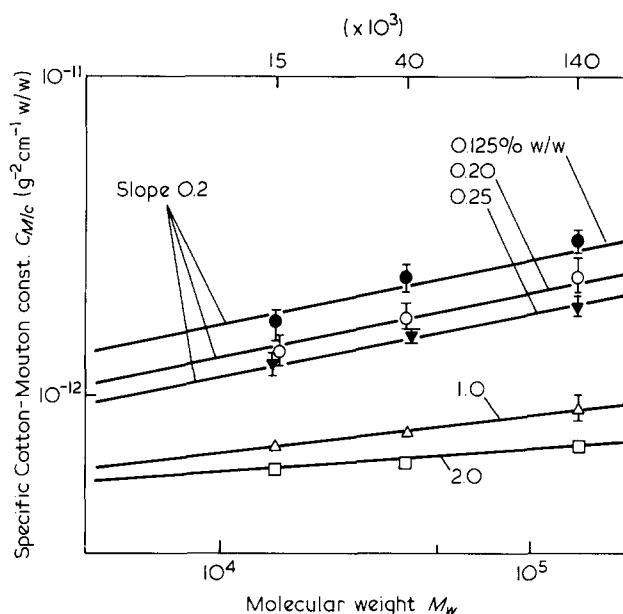


Figure 2 Log–log plot of the molecular weight dependence of the specific Cotton–Mouton constant of PSS Na^+ in the low concentration range in the absence of added salt

molecular weight as the sum over the first Legendre polynomial $P_1(\cos \theta_{ij})$.

In any case, in this single chain picture, the dependence observed with the lower molecular weight sample PSS 15.000 should reflect at best the true dependence of the persistence length.

Theoretical expressions for the electrostatic contribution to the persistence length have been published by Odijk¹⁶ and Skolnick and Fixman¹⁷. The total persistence length is:

$$q = q_p + q_e \quad (4)$$

where q_p is the ‘bare’ high ionic strength persistence length and

$$q_e = (4\kappa^2 l_B)^{-1} \quad (5)$$

is the ‘electrostatic persistence length’ for highly charged polyions, where the concept of counterion condensation applies; κ^{-1} is the Debye screening length.

Relations (4) and (5) seem to hold in the case of DNA for concentration in salt C_s of the order of C_p , if κ is calculated from an equivalent ionic strength ($[C_s] + (2z\lambda)^{-1}[C_p]$) according to the above scheme (b). Therefore here we calculate:

$$q_e = 0.32(0.18[C_p] + [C_s])^{-1}$$

Using this value with $q_p = 12 \text{ \AA}$ in relations (4) and (1) we find the theoretical rise of the specific Cotton–Mouton constant at low ionic strength which is drawn on Figure 1b. It is much steeper than the experimental data for PSS 15.000.

This deviation is possibly related to the fact that the experiments in the absence of added salt are not carried out in the dilute regime so that we grossly underestimate the screening of the electrostatic interactions. It must be

noted however that the value of C_M/c of PSS 140.000 at $[C_p]=9.6 \cdot 10^{-2}$ M in the presence of $7.3 \cdot 10^{-3}$ M NaCl drops roughly to the value observed with $[C_p]=4.8 \cdot 10^{-2}$ M in the absence of added salt, as expected from our calculation of the total equivalent ionic strength. Due to the low accuracy achieved at low $[C_p]$, especially in the presence of salt, it is not possible at present to pursue this comparison over a large range of $[C_p]$ and $[c_s]$ values.

In trying to understand in what measure the single chain magnetic birefringence can be affected in semi-dilute polyelectrolyte solutions, one should remember that they have a very complicated behaviour with four characteristic lengths L, q, κ^{-1} and ξ , the mean distance of contacts between different chains. These lengths define at least four domains of concentration^{18,19} the existence of which find some experimental confirmation in some recent quasi elastic light scattering measurements of the diffusion coefficients²⁰. In our experimental conditions we are dealing with three different concentration regimes.

At high salt concentration, the radius of gyration $\langle R^2 \rangle = \frac{1}{3} L q_p$ and the overlap concentration $C^* \sim M/4R^3 N$ is 10% for the highest molecular weight sample. Our experiments deal essentially with Gaussian isolated chains.

In the absence of added salt $C^* \sim M/L^3 N$ and all our solutions are in the semi-dilute regime, which can be divided into several subregimes according to the relative ratios of ξ/q and q/L . For $q \ll \xi \ll L$ corresponding to $c \gg 1 \text{ g cm}^{-3}$ each molecule can be considered as a Gaussian chain of blobs of size ξ inside of which electrostatic interactions are still operative. In this region relations (4) and (5) should apply to each blob and the magnetic birefringence should be molecular weight independent. At lower concentrations q and ξ increase as different powers of c , which can be roughly taken as $q \sim C_p^{-1}$ and $\xi \sim C_p^{-1/2}$. The cross over concentration has been evaluated at $C \sim 1 \text{ g cm}^{-3}$.²⁰ Below this concentration, despite the fact that $q > \xi$ it has been shown that the cooperative diffusion coefficient scales like $C^{0.5} \propto \xi^{-1}$. Its molecular weight independence has however not been

checked. Orientational correlation extends however over distances $> \xi$. It is in this region that we find a molecular weight dependence of the magnetic birefringence. This suggests that in this region of progressive overlap of chains with decreasing stiffness and swelling, C_M is not very sensitive to intermolecular penetration. But the assumption that κ^{-1} can be calculated from the uncondensed counterions alone is probably no more valid and an increased electrostatic screening may account for the small observed variation of q_c and consequently C_M with concentration.

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REFERENCES

- Oosawa, F. 'Polyelectrolytes', M. Dekker, NY (1971)
- Wolff, C. *J. de Phys.* 1978, **39**, C-2, 169
- Harrington, R. E. *Biopolymers* 1978, **17**, 919
- Rizzo, V. and Schellmann, J. *Biopolymers* 1981, **20**, 2143
- Hagerman, P. J. *Biopolymers* 1981, **20**, 1503
- Williams, C. E., Nierlich, M., Cotton, J. P., Jannink, G., Boue, F., Daoud, M., Farnoux, B., Picot, C., de Gennes, P. G., Rinaudo, M., Moan, M. and Wolff, C. *J. Polym. Sci. Polym. Lett. Edn.* 1979, **17**, 379
- Maret, G. and Dransfeld, K. *Physica* 1977, **86/88 B**, 1077
- Maret, G. and Weill, G. in preparation
- Turbak, A.F., C.A. (1973) 58, 13851 C
- Torbet, J. and Maret, G. *Biopolymers* 1981, **20**, 2657
- Manning, G. S. *J. Chem. Phys.* 1969, **51**, 924
- Wilson, R. W. *Biopolymers* 1978, **17**, 1811
- Weill, G. in 'Molecular Electrooptics', (Ed. S. Krause), Plenum Press (1981) p. 473
- Kikuchi, K. and Yoshioka, K. *J. Phys. Chem.* 1973, **77**, 2101
- Takahashi, A., Kato, T. and Nagasawa, M. *J. Phys. Chem.* 1967, **71**, 2001
- Odiijk, T. and Houwart, A. C. *J. Polym. Sci. Polym. Phys. Edn.* 1978, **16**, 627
- Skolnick, J. and Fixmann, M. *Macromolecules* 1977, **10**, 944
- Odiijk, T. *Macromolecules* 1979, **12**, 688
- De Gennes, P. G., Pincus, P., Velasco, R. M. and Brochard, F. *J. de Phys.* 1976, **37**, 1461
- Grüner, F., Lehmann, W. P., Fahlbusch, H. and Weber, R. *J. de Phys. A. Math. Génér.* 1981, **14**, 307