polymer reports

On the molecular weight dependence of the magnetic birefringence of polystyrene sulphonate at low ionic strength

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The molecular weight dependence of the magnetic birefringence of polystyrene sulphonate is reinterpreted. It arises from the dependence of the electrostatic contribution to the persistence length at $\kappa L < 25$.

(Keywords: polyelectrolytes; polystyrene sulphonate; persistence length; magnetic birefringence; molecular weight dependence)

We recently reported[1] that the concentration dependence of the magnetic birefringence of polystyrene sulphonate (PSS) solutions at low ionic strength is on the one hand molecular weight dependent and on the other much smaller than predicted from the dependence of the persistence length with ionic strength, the latter being calculated from the uncondensed counterions only. This result is in disagreement with that obtained on high molecular weight DNA solutions at the very low concentration of added salt required to avoid the melting of the double helical structure[2]. In that latter case the concentration dependence of the magnetic birefringence is satisfactorily predicted from the variation of the electrostatic persistence length[3]

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

where κ^{-1} is Debye's screening length and l_B Bjerrum's length. Considering the difference in intrinsic flexibility of the two polymers reflected by the bare persistence q_p which is 12 Å for PSS and 500 Å for DNA, we tentatively attributed the molecular weight dependence of PSS to electrostatic excluded volume effects and the reduction in the magnitude of the birefringence to an improper evaluation of the screening or to orientational correlation in semi-dilute solutions.

We realized that since formula (1) implies that the contour length L of the molecule is much larger than κ^{-1}, a condition which is fulfilled for a high molecular weight DNA ($L \sim 20\,000$ Å) but which is not fulfilled for our PSS samples with contour lengths 180 Å ($M = 15\,000$) 480 Å ($M = 140\,000$) and 1680 Å ($M = 140\,000$). The influence of finite length on the electrostatic contribution to the stiffness has been stressed by Hagerman[4] in relation to his measurements on short DNA fragments.

The complete formula can be written as[3]:

$$q_e = (4\kappa^2 l_B)^{-1}\left[1 - \frac{8}{3}y^{-1} + \frac{e^{-y}}{3}(y + 5 + 8y^{-1})\right] = q_{e,\infty} f(y) \qquad (2)$$

where $y = \kappa L$. Values of $f(\kappa L)$ are given in *Figure 1*. It appears that the correction factor remains substantially smaller than 1 up to the values of κL as large as 25. This provides a reasonable explanation for both the molecular weight dependence and the reduction in magnitude of the observed magnetic birefringence, as compared with that calculated using $q_e = q_{e,\infty}$.

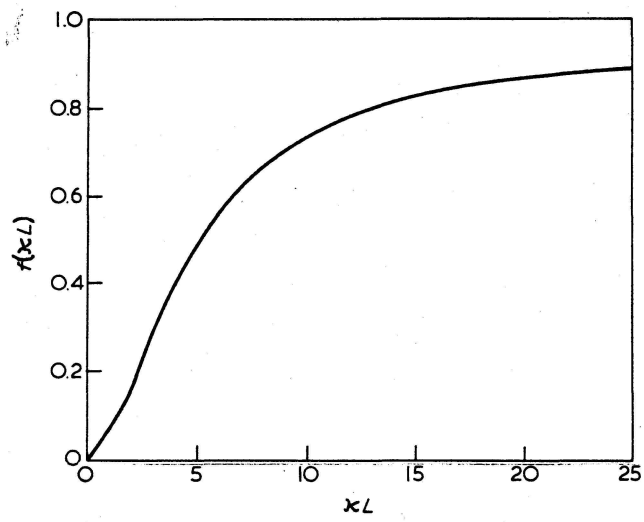

Figure 1 Correction factor for the calculation of the electrostatic persistence length at finite κL values (equation (2))

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Table 1 Comparison between the values of the electrostatic persistence length deduced from the magnetic birefringence $q_{e,obs}$ and calculated for two choices of the equivalent ionic strength $q_{e,calc}$

	PSS conc (g/100 cc)	2	1	0.5	0.25	0.20	0.125	0.100
$q_{e,obs}$ (Å)	M = 140 000	19 ∓ 3	29 ∓ 4	44 ∓ 6	74 ∓ 9	93 ∓ 12	124 ∓ 15	160 ∓ 15
	M = 40 000	15 ∓ 2	22 ∓ 3	41 ∓ 6	58 ∓ 8	65 ∓ 12	88 ∓ 16	–
	M = 15 000	14 ∓ 2	19 ∓ 3	28 ∓ 4	46 ∓ 6	50 ∓ 10	63 ∓ 12	–
$[C_S] = 0.18\ [C_p]$	κ^{-1} (Å)	24	34	48	68	76	96	108
	$q_{e,\infty}$ (Å)	20	40	80	160	220	320	400
$q_{e,calc}$ (Å)	M = 140 000	19	38	74	140	176	270	330
	M = 40 000	17	32	58	100	130	157	–
	M = 15 000	13	20	30	40	48	48	–
$[C_S] = 0.36\ [C_p]$	κ^{-1} (Å)	17	24	34	48	54	68	76
	$q_{e,\infty}$ (Å)	10	20	40	80	110	160	200
$q_{e,calc}$ (Å)	M = 140 000	10	19	38	74	91	144	176
	M = 40 000	9	17	32	58	70	100	176
	M = 15 000	7.5	13	18	22	32	38	–

A quantitative test is given in *Table 1*. The experimental values of q_e for each molecular weight and PSS concentration in the absence of added salt have been derived from the specific Cotton–Mouton constants from ref. 1, using for the bare persistence length at high ionic strength $q_p = 12$ Å corresponding to $C_M/C = 2.7\ 10^{-13}$ cm^2 Oe^{-2} g^{-1}. The theoretical values have been calculated for two estimates of the equivalent ionic strength $[C_S]$ required for the evaluation of κ^{-1} to be used in the calculation of both $q_{e,\infty}$ and κL. The first value corresponds to the contribution of the uncondensed counterions only $[C_S] = 0.18\ [C_p]$. Since, for the higher molecular weight, κL remains higher than 15, and therefore, $f(\kappa L) > 0.8$, this cannot explain the twofold difference between q_e and $q_{e,\infty}$ visible for that sample in *Figure 1* or in ref. 1. However, it gives a satisfactory agreement for the lower molecular weight sample. Using a value twice as large, i.e. $[C_S] = 0.36\ [C_p]$, brings the high molecular weight results into fair agreement at the expense of the agreement for the low molecular weight sample.

Considering the magnitude and variation of $f(\kappa L)$ up to large values of κL, a more elaborate analysis on the relation between $[C_S]$ and $[C_p]$ would require careful control of the polydispersity.

At the present stage, our reinterpretation of the data indicates that excluded volume effects and orientational correlations are certainly of minor importance in semi-dilute polyelectrolyte solutions. It reconciles the PSS and the DNA results and gives a strong support to the calculation of the electrostatic persistence length at arbitrary values of κL.

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Studies on the structure of poly(vinyl chloride)/poly(acrylonitrile-co-butadiene) blends

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The structures of poly(vinyl chloride)/poly(acrylonitrile-co-butadiene) blends cast from tetrahydrofuran solutions were studied by various methods. Evidence was found for the two-phase nature of blends. A fairly regular two-phase structure having a periodicity of 1.36 μm was found in a blend of PVC and poly(acrylonitrile-co-butadiene).

(Keywords: blend; two-phase nature; poly(vinyl chloride)/poly(acrylonitrile); radiothermoluminescence; light scattering; X-ray diffraction)

INTRODUCTION

More than thirty years ago, the blend of poly(vinyl chloride) (PVC) with poly(acrylonitrile-co-butadiene) NBR) was recognized as a compatible polymer pair[1]. The pair historically represented the initial observation that a polymer–polymer mixture was possible. The single phase structure in the blend was suggested by a single glass transition observed in dynamic mechanical[2] and differential scanning calorimetry (d.s.c.) studies[3]. Gas permeation studies have also shown the single phase nature of the blend[4]. However, the two-phase structure in the blend has

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