Persistence Length for a PSSNa Polyion in Semidilute Solution as a Function of the Ionic Strength

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The persistence length of sodium sulfonated polystyrene (PSSNa) is measured by small angle neutron scattering in the semidilute regime for two polymer concentrations c as a function of the added salt concentration c_s. The results suggest that this persistence length l_p depends only on $c + 2c_s$. This questions the role of the counterion condensation at the nanometric scale. Moreover, a variation $l_p \sim (c + 2c_s)^{-1/3}$ is found. l_p could be simply related to the distance between ions, which is the relevant length for concentrated solutions. [S0031-9007(96)01895-9]

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We study polyelectrolyte solution [1,2] of sodium sulfonated polystyrene (PSSNa), where each monomer carries a group which dissociates in water. The resulting charged groups on the chain tend to make the polyion more rigid, i.e., to increase the persistence length. This quantity is determined here in the most direct way in semidilute solutions from the intrachain form factor $P(q)$ of a single chain. Two polymer concentrations c (the number of monomer per unit volume) are used, and salt (of concentration c_s) is progressively added. Our aim is to measure the corresponding effect on the values of the chain persistence length.

A straightforward effect is the screening of electrostatic repulsions due to the free ions. Its range is the screening length κ^{-1}. Usually its reference value is that calculated by Debye and Hückel [3] for a nearly perfect gas of ions:

$$\kappa_{\mathrm{DH}}{}^2 = 4\pi l_B I = 4\pi l_B c_f\,, \tag{1}$$

where l_B is the Bjerrum length equal to 7.1 Å at room temperature and I is the ionic strength of the free monovalent ions (of concentration c_f). Equation (1) is valid [4] for dilute solutions below a concentration $\tilde{c}_f$ at which $\kappa_{\mathrm{DH}}{}^{-1}$ becomes equal to the mean distance between free ions:

$$d(\tilde{c}_f) = 1/(\tilde{c}_f N_A)^{1/3} = (4\pi l_B N_A \tilde{c}_f)^{-1/2}, \tag{2}$$

where N_A is the Avogadro number.

In the polymer case, c_f may be strongly decreased by an effect of charge condensation on the polyion. The fraction of condensed ions is usually determined from osmotic pressure measurements of c_f at a macroscopic scale. It is of interest to see whether similar condensation effects are also observed on the persistence length value determined on the nanometric scale using SANS (small angle neutron scattering).

Several theoretical predictions of l_p have been made [2] in the semidilute regime. In the Odijk [5], Skolnick, and Fixman [6] (OSF) theory, considering a rigid chain and ignoring the others, l_p is assumed to vary like $\kappa_{\mathrm{DH}}{}^{-2}$. Earlier approaches [7,8], where l_p varies like $\kappa_{\mathrm{DH}}{}^{-1}$ have been reconsidered recently. For solutions where l_p would be greater than the mesh size ξ ($\xi \sim c^{-1/2}$), l_p should be reduced to ξ by deflection effects [9]. This corresponds to a strong coupling regime; it is even predicted that l_p should increase when salt is added, as deflection effects are screened. Experiments [10] with no added salt showed a crossover $\kappa_{\mathrm{DH}}{}^{-2}$-$\kappa_{\mathrm{DH}}{}^{-1}$ (c^{-1}-$c^{-1/2}$) in good agreement with the numerical result of Le Bret [11]. This is at variance with the variation of $q^*(c)$, the maximum position of the whole structure factor of the corresponding solutions which always varies [12] as $c^{1/2}$.

The measurements consist in determining $P(q)$ by SANS using the zero average contrast method: A mixture of hydrogenated and deuterated PSSNa with the same length and the same concentration $c/2$ is dispersed in a mixture of light and heavy water containing a D_2O volume fraction $x = 0.71$, so that the contrast length of the two kinds of chains relative to the solvent is opposite: $k_H = -k_D = k$. Under these conditions [13] the absolute measured intensity $i(q)$ is directly proportional to $P(q)$ without any influence of the interchain scattering:

$$i(q) = k^2 c N_w P(q)\,, \tag{3}$$

where N_w is the weight average number of monomer per chains, and c is the number of monomer per unit volume.

The value of l_p is extracted by fitting the curves to the Sharp and Bloomfield [14] scattering form factor $P(q)$ of a single finite wormlike chain of contour length L,

$$P(q) = \frac{2[\exp(-x) + x - 1]}{x^2} + \left[\frac{4}{15} + \frac{7}{15x} - \left(\frac{11}{15} + \frac{7}{15x}\right)\exp(-x)\right]\frac{2l_p}{L}\,, \tag{4}$$

with $x = \frac{Lq^2 l_p}{3}$. It is an approximation which is valid only for $L > 10 l_p$ in a q range $q l_p < 2$. For $q l_p = 2$, the values overlap [15] the curve rigorously obtained by des Cloizeaux [16] for chains of infinite length, which will be used for $q l_p > 2$.

Both PSSNa samples were prepared by sulfonating polystyrene following Vink's method [17], which leads to totally charged macroions. For the hydrogenated PSSNa, SEC-LS (size exclusion chromatography with on line light scattering) measurements give $M_{wH} = 150\,000$, and a polydispersity $M_w/M_n = 1.12$. For the deuterated one, $M_{wD} = 170\,000$ and $M_w/M_n = 1.20$. The added salt used was NaBr. The solutions are semidilute since c is always greater than $300c^*$ where c^* is the overlap concentration of the totally extended polymer. For each polyion concentration c, four salt concentrations were made. For $c = 0.34$ M (mol/l), c_s was taken equal to 0, 0.34, 1.5, and 3 M. For $c = 0.17$ M, c_s was 0, 0.85, 1.5, and 3 M. All samples were filtered through membranes of porosity 0.2μ, in order to eliminate aggregates.

The experiments were performed at the Orphée reactor (LLB, Saclay), using the spectrometers PACE and PAXY, with configurations allowing us to explore the q range [5×10^{-3}–4.2×10^{-1} Å^{-1}]. Absolute values of $i(q)$ were obtained from the determination of the neutron flux in the incident beam [15]. The incoherent scattering was subtracted from the corresponding brine solution alone, since the incoherent background of polyelectrolytes is negligible in the mixture of H and D solvents.

We will now describe the procedure used to determine l_p: the eight curves $i(q)$ allow us to determine N_w from $i(q = 0)$ [cf. Eq. (3)]. The best value obtained, $N_w = 850$, is in good agreement with that of $N_{wH} = 820$ or $N_{wD} = 890$ obtained by SEC-LS. Then $i(0)$ is maintained constant and each of the eight curves is fitted with Eq. (3), giving eight couples of values of the parameters L and l_p. We obtain a distribution of L values; most of them lie around $L = 1750$. This value is adopted since, in addition, the mean value $N_n = 710$ obtained from SEC-LS measurement corresponds to a monomer length $a = L/N_n = 2.46$ Å very close to that of a C-C bond 2.54 Å. Finally, $i(0)$ and L are fixed and the eight l_p values are obtained. The consistency of the l_p values is confirmed from the representation $Ll_pq^2P(q)$ versus ql_p of des Cloizeaux, giving a universal curve for an infinite wormlike chain [16] (see Fig. 1). The agreement is very good since all the data superimpose in the range $qR_g > 1$, and the absolute values are close to the des Cloizeaux predictions. This leads us to be confident in the wormlike chain model and in the l_p values for all the salt concentrations c_s included in the range 0–3 M.

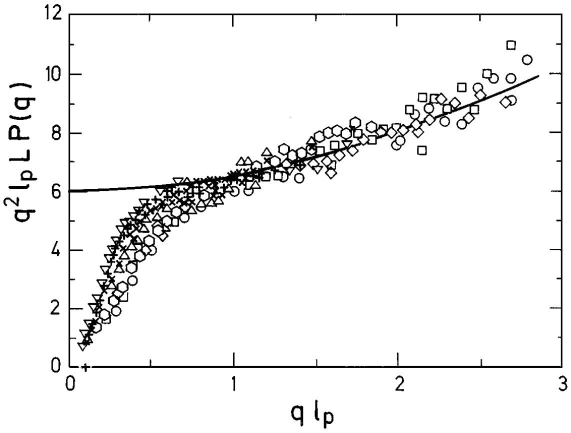

FIG. 1. Dimensionless representation $Ll_pq^2P(q)$ of the form factor as a function of ql_p, where L is the contour length of the polyion, l_p its persistence length, and q is the scattering vector. The eight curves correspond to the following value of the monomer concentration $c = 0.34$ M, and the salt concentration (◇) $c_s = 0$ M, (⬡) $c_s = 0.34$ M, (×) $c_s = 1.5$ M, (+) $c_s = 3$ M, and to $c = 0.17$ M and (○) $c_s = 0$ M, (□) $c_s = 0.085$ M, (△) $c_s = 1.5$ M, (▽) $c_s = 3$ M. The full curve is the form factor of des Cloizeaux for an infinite wormlike chain [16].

The l_p values are given in Table I. First, with no added salt, l_p decreases when c increases. This has already been observed [10,18]. Second, l_p decreases with adding salt. Thus we are not in a strong coupling regime [9] (i.e., there is no screening of deflections leading to an increase of l_p).

Let us now consider the variation of l_p as a function of the global free ion concentration. As the polyion is fully charged (one dissociable group per monomer, or about three per Bjerrum length), condensation could occur. From osmotic pressure measurements, the number of free ions $c_f = fc + 2c_s$ is measured and gives values of f, the free counterion fraction. For the PSSNa, f is known [19] to be close to 0.2 in this concentration range. From SANS measurements, the striking result is that the same l_p is observed for different couples of c and c_s, giving the same $c + 2c_s$ (see Table I). Now plotting all values of l_p versus $fc + 2c_s$, the best value of f for which all data lie on a single curve is $f = 1$. In this case our results are even consistent with two other sets of data obtained from earlier experiments [10,18] observing the effect of the variation of c with no salt added (see Fig. 2).

This would mean that in contrast to the osmotic pressure ($f = 0.2$), SANS measurements are not sensitive to

TABLE I. Values of the persistence length l_p for different concentrations of polymer c and salt c_s. They can be compared to the bare persistence length of 9.2 Å [15] of the nonsulfonated polystyrene. Note that the couples of l_p values similarly underlined are obtained for different couples of c and c_s values, providing that $c + 2c_s$ remains constant.

c_s (M)	0	0	0.085	0.34	1.5	1.5	3	3
c (M)	0.17	0.34	0.17	0.34	0.17	0.34	0.17	0.34
$c + 2c_s$	0.17	0.34	0.34	1.02	3.17	3.34	6.17	6.34
l_p (Å)	60 ± 5	46 ± 2	48 ± 4	32 ± 4	22 ± 3	22 ± 2	15 ± 1	14 ± 1

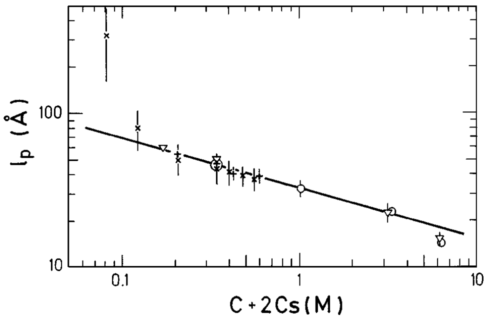

FIG. 2. Persistence length l_p (Å) as a function of the concentration of counterions and salt ions $c + 2cs(M)$. (○) $c = 0.34$ M; (▽) $c = 0.17$ M; (×) values extracted from Ref. [10]; (+) values extracted from Ref. [18]. The straight line corresponds to a fit which gives a slope equal to -0.33 ± 0.03. It does not take into account the points at the lowest and the largest values of the abscissa axis at either extremity.

counterion condensation. Apart from condensation, the activity of ions could also depart from the nominal concentration $2c_s$ for very large salt concentrations (typically superior to 0.1 M [20]). This does not modify anymore the $c + 2c_s$ superposition of Fig. 2. This result leads us to two remarks. On one hand, if l_p depends directly on screening, all counterions and coions contribute to the screening length. On the other hand, repulsions along the polyion depend on its number of effective charges. Then the $c + 2c_s$ dependence implies no partial neutralization of the polyion. Such a high number of charges would explain the large values of the observed persistence lengths, greater that the distance between ions (20 to 6 Å), which may be considered as the screening length (see below). Both effects suggest that ions are all located beyond a certain distance from the chain. This distance has to be short enough to remain imperceptible by osmotic pressure and conductivity coefficient measurements.

The data of Fig. 2 show that the persistence length l_p is found to vary like $(c + 2c_s)^{-0.33\pm0.03}$. The exponent is quite different from that of $\frac{1}{2}$ usually predicted. This difference is not due to the use of the value $f = 1$ since with a smaller value ($f = 0.2$), we find a smaller exponent: $l_p \sim (0.2c + 2c_s)^{-0.19\pm0.05}$, with data much more dispersed in the log-log representation. We could obtain an exponent closer to $\frac{1}{2}$ by assuming, as in the OSF theory, that the persistence length is the sum of the bare persistence length l_0 (here [15] $l_0 = 9.2$ Å) and the electrostatic one l_e. Under this condition, one finds $l_p - l_0 \sim (c + 2c_s)^{-0.45\pm0.05}$, thus an exponent near $\frac{1}{2}$. However, the OSF additivity assumption is established for intrinsically rigid chains, which is not the case for PSSNa, well known for its low stiffness. We are therefore tempted to assume that l_p is directly proportional to κ^{-1} as soon as l_p is greater than l_0. This would then imply that κ^{-1} does not vary as $(c + 2c_s)^{-1/2}$ but as $(c + 2c_s)^{-1/3}$. This is an expected behavior since the concentrations used here are really higher than the value $\tilde{c}_f \sim 2 \times 10^{-3}$ M [see Eq. (2)] above which the expression of the Debye-Hückel screening length is no longer valid. Thus it is the distance between ions which is relevant. This is also consistent with $f = 1$.

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