

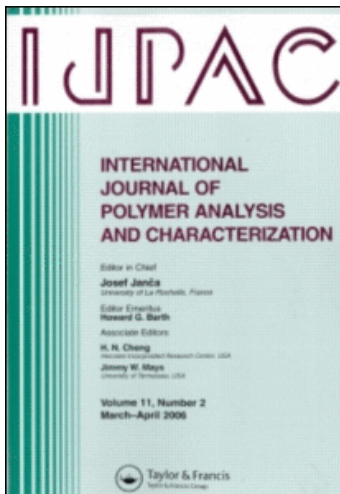
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# Measurements of the Persistence Length of Flexible Polyelectrolytes

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We review the experimental results concerning the dependence of the persistence length  $L_p$  of flexible polyelectrolytes on the ionic strength  $I$ , discussing, in particular, the case of sodium polystyrene sulfonate. In spite of the fact that some disagreement exists among results obtained by different authors and different techniques, the emerging trend is that the electrostatic part of  $L_p$  decreases, at large  $I$ , proportionally to the Debye-Hückel length, and saturates, at low  $I$ , at a value which depends on the contour length  $L$  and is much lower than  $L$ . The observed overall behavior of  $L_p$  versus  $I$  seems to disagree with the classical theory proposed by Odijk and by Skolnick and Fixman, and is in qualitative agreement with recent theoretical results.

**KEY WORDS** Persistence length, polyelectrolytes, sodium polystyrene sulfonate.

## INTRODUCTION

The electrostatic contribution to the rigidity of linear polyelectrolytes has been the subject of a number of theoretical and experimental studies in the recent past. One can define a rigidity parameter, the total persistence length  $L_p$ , in the following way: take a linear chain of contour length  $L$ , let  $\mathbf{R}(s)$  be the position of a point on the chain at the contour length  $s$ . The vector  $\mathbf{u}(s) = \partial\mathbf{R}/\partial s$  is a unit vector tangent to the chain. The straight rod corresponds to  $\mathbf{u}(s) = \text{constant}$ . If we call  $\theta(s)$  the angle formed between  $\mathbf{u}(0)$  and  $\mathbf{u}(s)$ , we can associate the flexibility of the chain with the ensemble average  $\langle \cos\theta \rangle = \langle \mathbf{u}(0) \cdot \mathbf{u}(s) \rangle$ . The quantity  $\langle \cos\theta \rangle$  decays with  $s$  according to an exponential law<sup>[1,2]</sup>:

$$\langle \cos\theta \rangle = \exp(-s/L_p) \quad (1)$$

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Equation 1 defines  $L_p$ . It should be noted that, in general,  $L_p$  is a function of  $L$  and becomes independent of  $L$  only for  $L_p \ll L$ . The presence of electrical charge on the polymer chain introduces long range repulsive forces between the monomers which make the chain more rigid. In the case of polyelectrolytes, the persistence length can be described as the sum of an intrinsic elastic contribution  $L_i$  plus an electrostatic part  $L_e$ . Clearly,  $L_e$  must be a decreasing function of the ionic strength  $I$  because the increase of  $I$  makes the screening of Coulomb forces more and more effective. Indeed, one would expect that, at high  $I$ , the chain behavior should be identical to that of a neutral polymer. Odijk[3], and Skolnick and Fixman[4] derived the following expression for  $L_e$ .

$$L_e^{OSF} = \frac{L_B}{4\kappa^2 L_o^2} F(\kappa L) \quad (2)$$

where  $L_o$  is the distance between two consecutive unit charges along the chain,  $L_B$  is the Bjerrum length,  $\kappa^{-1}$  is the Debye-Hückel length, and  $F(\kappa L)$  is a correction factor to the scaling behavior which takes into account finite size effects. We recall that the Bjerrum length is the distance between two electronic charges, immersed in a medium with relative dielectric constant  $\epsilon_r$ , at which the interaction energy equals  $k_B T$ :  $L_B = e^2 / (4\pi\epsilon_o\epsilon_r k_B T)$ . As an example, in water at room temperature,  $L_B = 0.72$  nm. The Debye-Hückel length depends on the ionic strength according to the law:  $\kappa^{-1} = (8\pi \times 10^{-3} L_B I N_A)^{-1/2}$ , where  $N_A$  is the Avogadro number,  $I$  is expressed in moles/liter, and the lengths  $\kappa^{-1}$  and  $L_B$  are in cm. The expression for  $F(\kappa L)$  is:

$$F(\kappa L) = 1 - \frac{8}{3\kappa L} + \frac{e^{-\kappa L}}{3} \left( \kappa L + 5 + \frac{8}{\kappa L} \right) \quad (3)$$

Note that  $F(\kappa L)$  becomes equal to 1 for large  $\kappa L$ , and equal to  $(\kappa L)^2/18$  for small  $\kappa L$ .

The theory of counterion condensation [5] predicts that the effective linear charge density can never be larger than one charge per Bjerrum length. Therefore, in the case  $L_o \leq L_B$ , Equation 2 should be replaced by:

$$L_e^{OSF} = \frac{1}{4\kappa^2 L_B} F(\kappa L) \quad (4)$$

The derivation of Equation 2 is based on a perturbation approach which is valid if  $L_e \ll L_i$  and  $\kappa^{-1} \ll L_p$ . Further investigations were later performed by Le Bret and by Fixman [6] by numerically solving the Poisson-Boltzmann equation for particular geometries. While they find a dependence of  $L_e$  on the ionic strength  $I$  significantly different from  $I^{-1}$  for  $I$  larger than a few millimolar, they both conclude that Equation 4 should retain its validity in the limit of vanishing  $I$ .

A few experimental studies have been performed with polyelectrolytes having large intrinsic rigidity, like DNA [7]. Some data [7a] seem to be in reasonable agreement with the Odijk-Skolnick-Fixman (OSF) theory, but other data [7b] suggest a weaker dependence of  $L_e$  on  $I$ .

Several measurements of  $L_p$  for polyelectrolytes with high intrinsic flexibility, obtained with a variety of techniques, are reported in the literature [8–15]. There is a set of results [8–12] which seems to suggest the following conclusions: i)  $L_e$  is proportional to  $\kappa^{-1}$  at

large ionic strength, in disagreement with Reference 3 and 4, but consistently with the numerical results of Le Bret [6] and with the calculations of Koyama [16]; ii)  $L_c$  does not diverge at vanishing ionic strength, but rather reaches a maximum value that depends on  $L$  and may be much smaller than the polymer extended length. It is interesting to note that very recent theoretical treatments [17–19] which go beyond the approximations used in Reference 1 seem to agree with these conclusions. It should however be recalled that other authors (see, for instance, Ref. 20) have developed theories which are consistent with the OSF approach. Also concerning the experimental data the situation is somewhat controversial because some authors present experimental results which do not disagree with the OSF theory [13] or could be brought into agreement once various correction factors are taken into account [14,15].

It is difficult to perform experiments on polyelectrolytes at low ionic strength in the dilute regime: most of the techniques require significant polymer concentrations, so that the lowest accessible ionic strength is in practice determined by the concentration of polymer counterions. In most cases, experiments in no-salt solutions concern the semidilute regime where interchain interactions are expected to play a significant role.

The aim of this paper is to discuss the experimental methods used to obtain  $L_p$  and the available data, focussing attention on investigations dealing with flexible polyelectrolytes. In particular, we compare the data obtained with a variety of techniques on the persistence length of sodium polystyrene sulfonate, a polyelectrolyte studied by several investigators.

## EXPERIMENTAL METHODS

A method which measures directly  $L_p$  according to the definition given in Equation 1 is the direct visualization of the chain configuration. A recent experiment was performed by Ott et al. [21] by using fluorescence microscopy on labeled actin chains. The measured correlation function is presented in Figure 1. We note that the behavior is indeed exponential, so that  $L_p$  can be derived from the slope in the semilogarithmic plot. Of course, such a technique is applicable only for chains presenting a value of  $L_p$  larger than the resolution of the microscope.

All the other methods measure some property of the polyelectrolyte solution which is related to  $L_p$  by using some model. The usual model is the Kratky-Porod wormlike chain model<sup>22</sup> which describes the chain as a continuous line with elastic energy for bending. According to this model the mean-square end-to-end distance is:

$$\langle R^2 \rangle = 2LL_p - 2L_p^2(1 - e^{-L/L_p}) \quad (5)$$

and the square of the radius of gyration is:

$$R_g^2 = \frac{LL_p}{3} - L_p^2 + 2\frac{L_p^3}{L} - 2\frac{L_p^4}{L^2}(1 - e^{-L/L_p}) \quad (6)$$

Note that Equations 5 and 6 describe a rigid rod in the limit  $L \ll L_p$ , and a random coil in the opposite limit. The ratio between  $\langle R^2 \rangle$  and  $R_g^2$  is 6 for a random coil, 12 for a rigid rod, and takes intermediate values for a wormlike chain.

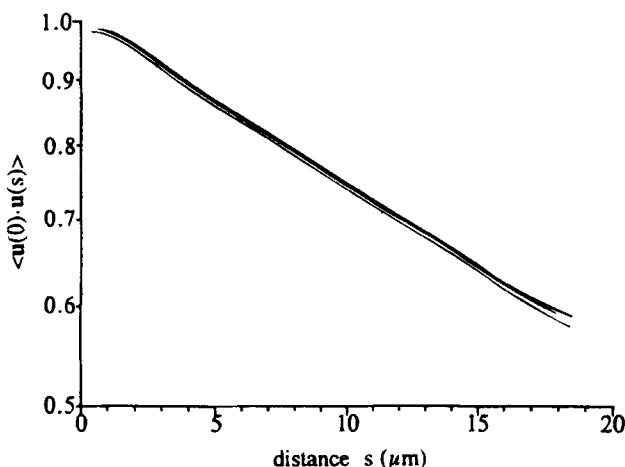


FIGURE 1 Correlation function of the monomer orientation within an actine chain (dilute solution). Different curves correspond to different digitization procedures of the microscope pictures. (Reproduced from Phys. Rev. E, 48, 1642 (1993, with permission.)

Equations 5 and 6 do not contain any excluded volume effect, that is, they do not take into account that chain segments cannot interpenetrate. In the case of a neutral chain, calculations including excluded volume predict that  $\langle R^2 \rangle^{1/2}$  and  $R_g$  scale, for large  $L$ , as  $L^x$ , with  $x \approx 0.6$  instead of the value 0.5 predicted by Equations 5 and 6 [23]. In the case of a charged chain, calculation are more complex because electrostatic repulsions become more important than steric repulsions [3,4].

Static light scattering (SLS) experiments measure the scattered intensity  $I(q)$  as a function of the scattering wavevector  $q$ . Under the assumption that interchain interactions are negligible, one can derive from  $I(q)$  the radius of gyration [11,14,15]. As discussed in detail in Reference 11, interactions are negligible if the concentration of added monovalent salt  $c_s$  is somewhat larger than the unimolar polymer concentration  $c_p$ . By further assuming that the chain can be treated as a wormlike chain, one can calculate  $L_p$  by using Equation 6, provided that the ratio  $L/L_p$  is not so large to make necessary the inclusion of excluded volume effects.

Dynamic light scattering experiments allow to derive the translational diffusion coefficient  $D$  of the polymer chain. Under the assumption that interchain interactions are negligible,  $D$  is related to the hydrodynamic radius  $R_h$  of the chain by the Einstein-Stokes relation. Calculations including hydrodynamic interactions among the polymer segments predict that  $R_h = 0.665R_g$ . However, some authors have questioned the validity of this latter relation for polyelectrolytes at low ionic strength [14].

Small-angle neutron scattering (SANS) measures  $I(q)$ , similarly to SLS. SANS is usually less sensitive than SLS, so that larger polymer concentrations are needed. This makes more difficult to conduct experiments in the dilute solution limit. However, SANS provides a range of  $q$  values much larger than that of SLS. Furthermore, the possibility of using isotope labelling allows the separation of intrachain from interchain contributions, so that the form factor  $S(q)$  of the individual chain can be obtained from SANS measurements performed on semidilute solutions [9].  $L_p$  is derived from the measured  $S(q)$  by a fitting procedure which uses the theoretical expression of  $S(q)$  for a wormlike chain [9].

Changes in the polymer configuration influence the viscosity of a polymer solution, so that viscosity measurements can be used to derive the persistence length. In practice, the interpretation of the experimental data is simple only in the situation of excess salt solutions [8]. The relationship between the intrinsic viscosity and the persistence length was calculated by Yamakawa and Fujii [24] for wormlike chains, and extensively applied by Tricot [8] to analyze many literature data.

Magnetic birefringence (MB) is due to the orientation of molecules which are both magnetically and optically anisotropic by a strong magnetic field  $B$ . The steady-state induced birefringence  $\Delta n$  can be expressed as:  $\Delta n = K_{CM} c_p \lambda B^2$ , where  $c_p$  is the polymer concentration,  $\lambda$  is the wavelength of the light beam used to measure  $\Delta n$ , and  $K_{CM}$  is the specific Cotton-Mouton constant. Since  $K_{CM}$  is related to configuration of the polymer chain, by measuring  $K_{CM}$  one could derive  $L_p$  [13]. However, in practice, there is a considerable uncertainty on the absolute calibration of MB data.

Electric birefringence is induced by orienting molecules with an electric field  $E$ . In a way analogous to that of magnetic birefringence, one can define the specific Kerr constant as  $K = \Delta n / (c_p \lambda E^2)$ . In principle, one should be able to derive  $L_p$  from  $K$ , but no explicit formula is presently available. Instead of using the steady-state response, it is possible to exploit the transient response. The transient electric birefringence (TEB) experiment consists in applying a rectangular voltage pulse to the solution, and in observing the relaxation of the induced birefringence after the electric field is switched off [12]. The birefringence relaxation time  $\tau$  can be simply considered as the rotational time of the macromolecule. From  $\tau$  one can derive  $L_p$ , by using the expression for the rotational relaxation time of a wormlike chain of given persistence length obtained in Reference 25:

$$\tau(x) = \tau_{rod} [x + (e^{-2x} - 1)/2]^{1.5} [1 + 0.54 \ln(1 + x)]/x^3 \quad (7)$$

where  $\tau_{rod}$  is the rotational time of a rigid rod of length  $L$ , and  $x = L/2L_p$ . A similar formula is given in Reference 26.

TEB allows to perform experiments at very low polyelectrolyte and salt concentration, the limiting polymer concentration and ionic strength being practically determined by the solvent contribution to the signal and by the residual ionic impurities.

It should be recalled that the birefringence dynamics of long polyelectrolyte chains in moderate ionic strength is strongly nonexponential, and is quite well described by a stretched exponential response [27]:

$$R(t) = \exp[-(t/\tau_1)^\alpha] \quad (8)$$

where  $0 \leq \alpha \leq 1$ . The time constant  $\tau_1$  coincides with the rotational decay time only if  $\alpha$  is close to 1, that is, when the birefringence relaxation does not differ too much from a simple exponential law. We recall that  $\alpha$  equals 1 for short chains at low  $I$  and has the limiting value of about 0.44 for a random coil (long chain at high  $I$ ) [27]. Therefore, in order to give a simple interpretation of the experimental data and unambiguously derive the persistence length as a function of  $I$  and of the molecular weight  $M$ , it is better to work with molecular weights and ionic strengths low enough to remain in the exponential relaxation regime.

A problem in the comparison between theory and experiment is the knowledge of the value of the ionic strength. The ionic strength of a solution containing a molar concentra-

tion of univalent salt  $c_s$  and a unimolar concentration of polymer  $c_p$  should be given by  $I = c_s + 0.5c_p$ . However, if the theory of counterion condensation [5] applies, a part of the polymer counterions are not free to move and do not contribute to screening. Therefore, the formula for  $I$  should read [28]:

$$I = c_s + 0.5\beta c_p \quad (9)$$

where  $\beta$  is the fraction of uncondensed counterions which takes the value  $\beta = 1$  for  $L_0 \geq L_B$ , and  $\beta = L_0/L_B$  for  $L_0 \leq L_B$ . It should be noted that direct experimental tests of the theory of counterion condensation are lacking, and that it is not known whether  $\beta$  depends on the nature of the polyelectrolyte and of the counterion, and on the concentration of polyelectrolyte and added salt. This means that an unambiguous assignment of  $I$  can be made only for experiments performed in excess salt.

## RESULTS AND DISCUSSION

We will discuss in detail the results concerning aqueous solutions of a flexible polyelectrolyte, sodium polystyrene sulfonate (NaPSS), which is commercially available in reasonably monodisperse form. We recall that, for NaPSS, the molecular weight of the monomer is  $M_0 = 206$  and the monomer length is  $L_0 = 0.25$  nm.

Many experiments have been performed on NaPSS solutions, using, in most cases, either light scattering [29] or electric birefringence [12,27,30,31]. In this article we discuss only the investigations which have been explicitly aimed at the measurement of the persistence length.

We have reported in Figure 2 the values of  $L_e$  derived by Tricot [8] who analyzed viscosity data [32] by a fitting procedure based on the Fujii-Yamakawa relation [24], and found, by extrapolating  $L_p$  to infinite ionic strength, an intrinsic persistence length for NaPSS equal to  $L_i = 1.4$  nm. The range of investigated molecular weights was  $M = 3.9 \times 10^5$  to  $23 \times 10^6$ . The ionic strength was controlled by addition of NaCl in the concentration range 0.005–0.5 M. The solutions were prepared in conditions of excess salt ( $c_s \gg c_p$ ).

We have also reported in Figure 2 the data obtained by Nierlich et al. [9] by using SANS. They investigated NaPSS solutions with  $M = 8 \times 10^4$  at four polymer concentrations without adding salt. The value of  $I$  is entirely due to the polymer counterions, and is calculated by taking  $\beta = 0.36$ . The agreement between viscosity and SANS data is excellent. Both data are consistent with a power law dependence of the type  $L_e \approx I^{-1/2}$ .

Figure 2 also shows the TEB data [12]. The molecular weights used are:  $M = 7.4 \times 10^4$ ,  $10^5$  and  $2 \times 10^5$ , corresponding to  $L = 90$ , 121, and 243 nm, respectively. Except for the lowest ionic strength, the solutions are in excess salt, so that the ionic strength is mainly determined by the concentration of added NaCl. The range of investigated ionic strengths is:  $I = 5 \times 10^{-5} - 2 \times 10^{-3}$  M. The TEB data, therefore, concern very low ionic strengths which are not accessible to viscosity and SANS measurements.

A new feature which emerges from the low ionic strength results is the dependence of  $L_e$  on the molecular weight of the polymer. The observed dependence of  $L_e$  on  $M$  becomes weaker, and tends to disappear, when the ionic strength  $I$  is larger than a few mM. The TEB data seem to extrapolate nicely to the viscosity and SANS data. A second interesting feature of the TEB data is the trend of the persistence length to reach, at very low ionic strength, a limiting value which depends on the extended chain length  $L$ , but is much

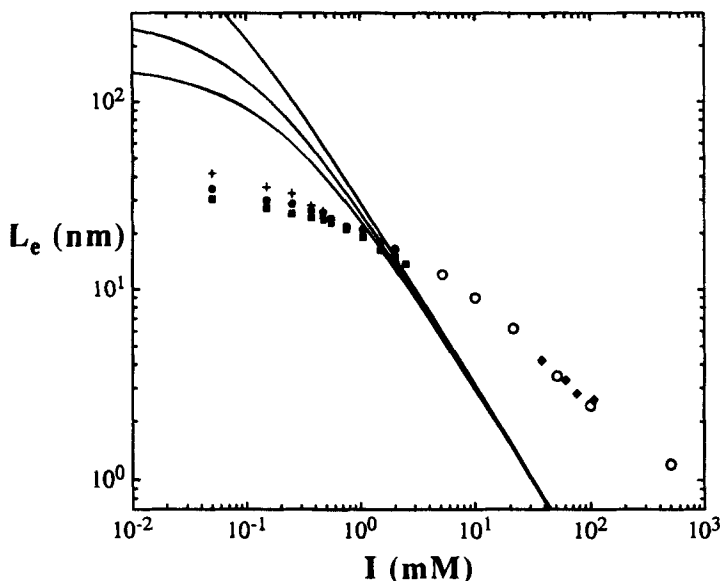


FIGURE 2 Electrostatic persistence length of NaPSS measured as a function of the ionic strength: TEB data for  $M = 74000$  ( $\nabla$ ),  $M = 100000$  ( $\bullet$ ),  $M = 200000$  (+), SANS data ( $\blacklozenge$ ) [Ref.9], viscosity data ( $\circ$ ) [Ref.8]. The full lines represents the predictions of Eq.2 for the three values of  $M$  used in the TEB experiment.

shorter than  $L$ . To be more precise, the extrapolation of  $L_e$  to  $I = 0$  gives 32, 37, and 48 nm for  $M = 7.4 \times 10^4$ ,  $10^5$  and  $2 \times 10^5$ , respectively.

It should be noted that the data of Reference 12 are really probing single chain properties because they are taken at polymer concentrations smaller than the entanglement concentration  $c^*$ , where  $c^*$  is calculated, very conservatively, by assuming fully stretched chains. Moreover, all the investigated solutions satisfy the criterion that the average inter-chain distance is larger than  $\kappa^{-1}$ . It is known, in any case, that  $\tau$  is only moderately influenced by interactions [30], unless one goes into the strong interaction regime.

The full lines in Figure 2 represent the predictions of Equation 4 for the three values of  $M$  investigated in the TEB experiment. At low ionic strength the OSF theory predicts values of  $L_e$  larger than those observed experimentally, whereas, at high ionic strength, theoretical values scale as  $\kappa^{-2}$  and are much smaller than the experimental ones which scale as  $\kappa^{-1}$ . It appears that there is a crossover between theory and experiment at a ionic strength around 2 mM.

It should be added that viscosity [8] and SLS [11] data taken on other flexible polyelectrolytes follow the same trend shown in Figure 2 by the NaPSS data. However, there are also results which do not fit into the picture. We report in Figure 3 the MB results of Reference 7 which were obtained with three different molecular weights of NaPSS,  $M = 1.5 \times 10^4$ ,  $4 \times 10^4$  and  $1.4 \times 10^5$ , without adding salt to the solution. The equivalent ionic strength is calculated also in this case by taking  $\beta = 0.36$ . The full curves are the theoretical predictions, as calculated from Equation 5, for the three different molecular weights. We see that the MB data show an agreement with the OSF theory which is more satisfactory than that shown by the data of Figure 2.

Measurements of the persistence length were performed by SLS on NaPSS with  $M = 7.8 \times 10^5$  with added NaCl in the range 0.0015-1 M [33]. The dashed line in Figure 3 is



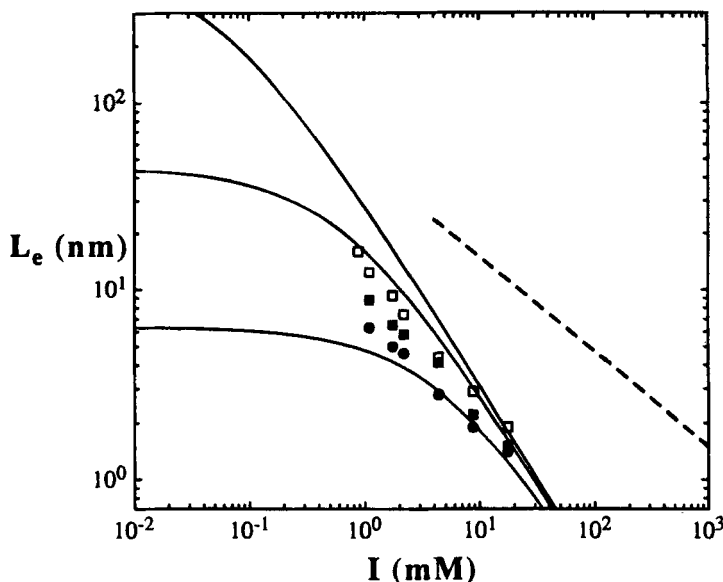


FIGURE 3 Electrostatic persistence length of NaPSS measured by MB as a function of the ionic strength for  $M = 15000$  (●),  $M = 140000$  (■),  $M = 140000$  (□) [Ref.9]. The dashed line interpolates the persistence length data obtained by SLS [Ref. 33]. The full lines represents the predictions of Eq.2 for the three values of  $M$  used in the MB experiment.

drawn according to the law  $L_e = 47.2I^{-0.5}$  (with  $L_e$  expressed in nm and  $I$  in mM), which according to the authors of Reference 33, interpolates the data. The obtained values of  $L_e$  are larger than those found by the other techniques.

It is important to make a numerical comparison among the available data. As an example, at  $I = 10$  mM, the value of  $L_e$  derived from viscosity data is 9 nm, that derived from SLS is 14.9 nm, and that derived from MB, considering the longest chain at a unimolar polymer concentration  $c_p \approx (10/0.18)$  mM, is 2.9 nm. The discrepancies are enormous. In the case of MB data, the discrepancy is reduced if one assumes that no counterion condensation occurs [13] (the value  $I = 10$  mM would be attained at  $c_p = 20$  mM, giving the interpolated value of  $L_e = 5.4$  nm), but deviations from the other data are still large. It is possible that some problem exists about the absolute calibration of the data. In the case of the SLS data of Reference 33, the authors point out the relevance of the excluded volume effect which swells  $R_g$ , and gives, therefore, through the use of Equation 6, an apparent persistent length larger than the true one. This, however, does not explain the discrepancies with the results obtained by different techniques, because all the results reported in Figures 2 and 3 were derived neglecting excluded volume effects. It should be noted that excluded volume effects are more important when  $L/L_p$  is large, that is, when the polymer has a high molecular weight and the ionic strength is large: this means that such effects should be smaller for the TEB, SANS and MB data than for the viscosity and SLS data. An evaluation of the importance of excluded volume effect could perhaps be obtained by extending the SLS data also at lower molecular weights.

A very interesting TEB investigation of NaPSS in solutions without salt was performed by Krämer and Hoffmann [30]. Although these authors do not derive values of  $L_e$  from their data, it is appropriate to recall that they have observed in the dilute regime relaxation

times faster than those expected for fully stretched rods. They suggest that the “ground state” configuration of the polyelectrolyte may not correspond to the all-trans configuration but could include some rotations which would make the chain shorter. A similar concept was suggested to us by Odijk [34].

The fact that the comparison between data taken in excess salt and data taken in solutions without salt is not straightforward is illustrated also by the TEB results presented in Figure 2 of Reference 12, where the measured rotational time  $\tau$  is given as a function of  $c_p$  for the polymer with  $M = 74000$ . The obtained data did not agree with those obtained in excess salt if the equivalent ionic strength is calculated with  $\beta = 0.36$ . A better agreement was obtained with the assumption  $\beta = 1$ .

As a final comment to this Section, we want to stress that the body of experimental data concerning the persistence length of polyelectrolytes is very wide, so that it may be possible that some relevant contribution has inadvertently escaped our attention. All the data we have selected are, we believe, accurate. Internal discrepancies arise because of the difficulty of deriving  $L_p$  from the direct experimental data.

## CONCLUSIONS

Although several aspects have still to be clarified, we tend to believe that the data shown in Figure 2 represent the effective behavior of  $L_e$  as a function of  $I$ . Such a conclusion seems to be supported by recent theories which are qualitatively in agreement with the trend shown in Figure 2.

In particular, Stevens and Kremer [19] have performed molecular dynamics simulations on a salt-free system consisting of several flexible chains with full Coulomb interactions of monomers and counterions treated explicitly. They have calculated the ratio  $r = \langle R^2 \rangle / R_g^2$  which is shown in Figure 4 as a function of the unimolar polymer concentration. Even in the dilute limit some flexibility persists, resulting in a saturation of  $r$  at a value smaller than the rigid rod limit  $r = 12$ . Note that the saturation behavior is strongly dependent on the chain length. In Figure 5 the microscopically calculated persistence length is reported versus the polymer concentration. This is the full  $L_p$  and not  $L_e$ , so that the high density limit is 1 and not 0. Figure 5 presents a striking similarity with Figure 2. The work of Reference 19 indicates the importance of performing simulation with a system of many chains, since the results are considerably different from those obtained in previous single-chain simulations [35].

A behavior qualitatively similar to that of Figure 2 was found in Reference 11 by a numerical calculation which minimizes the total free energy of a wormlike chain. Furthermore, Qian and Kholodenko [36] have performed calculations of  $L_e$  by using a variational method, and found a behavior in agreement with the data analyzed by Tricot [8].

Barrat and Joanny [18] have proposed a distinction between rigid chains and flexible chains. The persistence length of intrinsically rigid chains is described satisfactorily by the OSF theory, whereas, for flexible chains, their variational approach predicts that  $L_e$  is proportional to  $\kappa^{-1}$ , in contrast with OSF theory, but in agreement with the results presented in Figure 2.

Note added in proof: a recent paper [37] suggests that the calibration used in Ref. 13 for the MB data is not correct. The re-calculated values are considerably larger than those given in Ref 13.

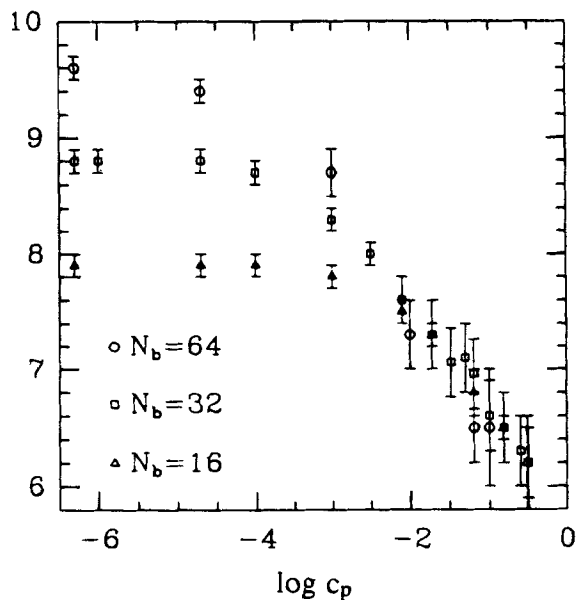


FIGURE 4 The ratio  $r$  between the mean-square end-to-end distance and the square of the gyration radius plotted versus the unimolar concentration  $c_p$  for three different values of the chain length  $N_b$  expressed in number of monomers.  $r = 12$  correspond to a rigid rod and  $r = 6$  correspond to a neutral chain in a dense solution (random walk). (Reproduced Phys. Rev. Lett., 71, 2228 (1993) with permission.)

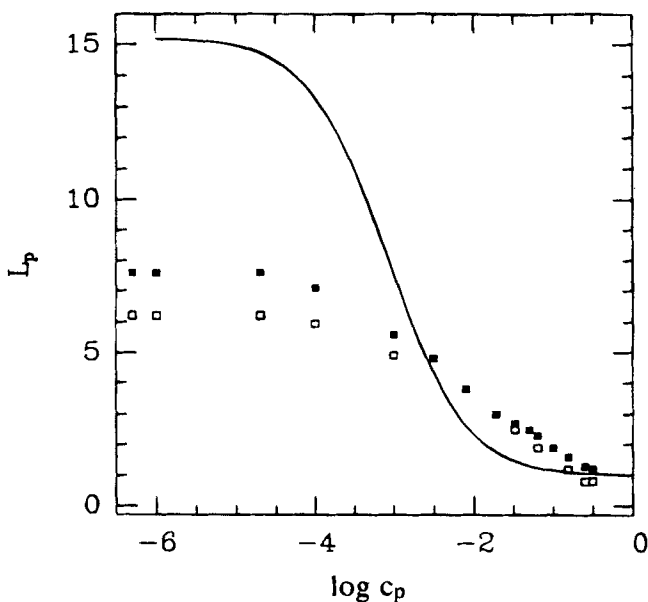


FIGURE 5 The persistence length of a chain composed by 32 monomers calculated assuming a wormlike chain ( $\square$ ) and using the microscopic definition ( $\blacksquare$ ). The line gives  $L_p$  from Odijk's complete expression including finite size corrections. (Reproduced from Phys. Rev. Lett., 71, 2228 (1993) with permission.)

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