

Structural evidence of charge renormalization in semi-dilute solutions of highly charged polyelectrolytes

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Abstract. We show experimentally that Manning counterion condensation also leads to a renormalization of the charge density at high concentrations of highly charged, flexible, hydrophilic polyelectrolytes. Investigations by small angle neutron and X-ray scattering of semi-dilute solutions of poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonate) at different charge densities above the condensation threshold, show that the scattering function is invariant with the charge density.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.10.Eq X-ray scattering (including small-angle scattering) – 61.12.Ex Neutron scattering techniques (including small-angle scattering)

1 Introduction

Polyelectrolytes contain a variable proportion of ionizable monomers. In polar solvents such as water, the charges are dissociated; the charges of one sign are localized on the chain whereas the counterions, of opposite sign, are mobile in the solution. The linear charge density is an important parameter which regulates the behaviour of a polyelectrolyte chain. When the distance between charges along the chain, b , is such that the coulombic interaction is smaller than $k_B T$, entropic effects have to be taken into account. In the opposite limit, for highly charged polyelectrolytes, b is small and the solution behaviour is dominated by electrostatic interactions. This strong coupling regime starts at $b = l_B = e^2 / \epsilon k T$, where l_B is the Bjerrum length; in water at $T = 25$ °C, $l_B = 7.13$ Å. Thus for vinylic polymers it corresponds to a linear charge density f of about 0.36. Above that charge density the electrostatic potential at the chain becomes very large and some counterions are confined in a small volume around the chain in order to reduce the electrostatic interactions between monomers. Thus the chain has an effective charge density f_{eff} smaller than the nominal charge density f . The concept of counterion condensation [1, 2] has been first formalized by Manning who found that the effective charge is renormalized to a constant value such that $b = l_B$ above a condensa-

tion threshold [3]. A large body of experimental data have confirmed the validity of the model at sufficiently high dilution.

At higher concentrations the situation is less clear. Various calculations [4–6] have attempted to take into account the effects of finite concentration on charge renormalization, also including possible effects on the chain conformation and have predicted strong deviations from Manning’s model for the single chain. Attractive interactions have also been found between chains surrounded by their sheath of counterions. Measurement of the effective charge is difficult in that concentration range, mostly due to the complex structure of concentrated polyelectrolyte solutions which prevents the determination of the amount of free counterions by the usual techniques, *e.g.* osmometry, electrical conductivity or electrophoretic mobility.

The semi-dilute, salt-free solutions of intrinsically flexible, highly charged polyelectrolytes are well described by de Gennes’ isotropic model in which the entangled chains form an isotropic transient network [7, 8]. The mesh size of the network, also called correlation length ξ , is the most important feature of the model. On length scales smaller than ξ the portions of the chain are extended, similarly to their conformation in dilute solution. But on length scales larger than ξ the chain obeys random walk statistics. ξ is independent of the chain length N and is of the same order as (but not necessarily equal to [9]) the Debye-Hückel screening length $\kappa^{-1} = (\epsilon k T / 4 \pi c e^2)^{1/2}$ where c is the number of free counterions that are able to move in order to screen

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the electrostatic interactions in the solution. Hence measuring ξ provides a way of monitoring the amount of free (and therefore of condensed) counterions in the solution. Scattering techniques are most adequate to this end since they probe directly the monomer pair correlations at different length scales [10]. It is particularly easy to probe ξ in polyelectrolyte solutions since one signature of the model is the existence of a broad maximum in the light, X-ray and neutron small angle scattering intensity profiles whose position scales as ξ^{-1} [11–13].

Previous experiments have shown that *below* the condensation limit and at constant polymer concentration in the semi-dilute regime, the position of the peak was a function of the charge fraction f ; it scaled first as $f^{1/3}$ then leveled off slowly [14]. *Above* the condensation limit it remained constant [15]. In this paper we want to extend our previous measurements and give more evidence to the interpretation that a charge renormalization does indeed take place for highly charged chains *in semi-dilute solutions*, akin to Manning's condensation for single chains. This conclusion is reached not only by monitoring the position of the broad peak but also by showing the invariance of all those structural properties which depend only on electrostatic interaction, when the charge density is varied above the onset of Manning condensation for a single chain.

Comparison of X-ray and neutron scattering (SAXS and SANS) measurements allows one to obtain complementary information on the chains and the counterions since the origin of the contrast is different; both the chain and its counterions contribute to the X-ray intensity whereas the counterions are not seen by neutrons. The polymer is a random copolymer of acrylamide and sodium-2-acrylamido-2-methyl propane sulfonate, with a hydrophilic backbone so that the hydrophobic interactions which could alter the solution properties remain negligible [16]. It should be added that at the same nominal charge fractions as those investigated here, *i.e.* between 0.3 and 1, direct osmotic pressure measurements *at very low concentrations* have demonstrated that the effective charge is renormalized according to Manning's model for single chains [17]. In what follows, the effect of the charge fraction on the SAXS and SANS structural features will be analyzed at constant polymer concentration in the semi-dilute regime. Then for each charge fraction the effect of polymer concentration and added salt concentration will be investigated independently.

2 Experimental section

Poly(acrylamide-*co*-sodium-2-acrylamido-2-methylpropane sulfonate), abbreviated as AMAMPS, was synthesized by radical copolymerisation of acrylamide with acrylamido methyl propane sulfonic acid according to a standard procedure [18] which was optimized to obtain highly charged polyelectrolytes. The charge density was varied between 0.3 and 1, above the onset of Manning condensation for a single chain. The polymers had a $M_w = 670\,000$ and a polydispersity $M_w/M_n = 2.6$.

Semi-dilute solutions were prepared by dissolving the desired amount of dry polyelectrolyte in deionised H₂O (for SAXS) or D₂O (for SANS) with a conductivity of about 0.05 μS and let to rest for two days before investigation. All concentrations are expressed in monomole/l, using an average molecular weight for the monomers at each chain composition. For the SAXS measurements, the samples were enclosed in 1.2 mm thick cells with 50 μm kapton windows. For the SANS measurements, the samples were put in 5 mm thick cells with quartz windows. All measurements were performed at room temperature.

The structure of the solutions has been analysed by Small Angle X-ray Scattering (SAXS) and Small Angle Neutrons Scattering (SANS). SAXS measurements were performed on beam line D22 at LURE (Orsay, France) using the DCI synchrotron radiation source. The intense beam was monochromated with two Ge (111) parallel crystals to a wavelength $\lambda = 1.37 \text{ \AA}$ ($\Delta\lambda/\lambda =$ a few 10^{-3}) and collimated to $0.5 \times 0.5 \text{ mm}^2$ at the sample. The scattered X ray-photons were detected by a gas filled, one dimensional position sensitive detector with a resolution of 217 μm . The scattering vector q ($q = (4\pi/\lambda) \sin(\theta/2)$, where θ is the observation angle) was varied from 0.005 to 0.35 \AA^{-1} by using two sample-to-detector distances D of 930 mm and 1630 mm. The recorded intensity was corrected for incident beam intensity, sample thickness and transmission and a background scattering was subtracted. The scattering profiles are plotted as intensity $I(q)$ *versus* q , in relative units. Absolute measurements would require multiplying by a constant instrumental factor and by the chain/solvent contrast.

SANS measurements were performed on the PACE spectrometer, at the Orphée reactor, Laboratoire Léon Brillouin (Saclay, France). The wavelength was set by a velocity selector. To cover a q -range between 0.003 and 0.08 \AA^{-1} , two set-ups were used, characterized by $D = 5 \text{ m}$, $\lambda = 8 \text{ \AA}$ ($\Delta\lambda/\lambda = 0.1$) and $D = 2 \text{ m}$, $\lambda = 9.5 \text{ \AA}$. The scattered intensity was recorded by a multidetector with 30 concentric, 1 cm wide rings. The response of each ring was normalized to the (flat) incoherent scattering of water. The recorded intensity was corrected for sample thickness and transmission, incoherent and background scattering. Using direct beam measurements the intensities are obtained in absolute units of cross-section [19]; they are then divided by the contrast factor K^2 [20], to yield the structure factor $S(q)$. The SANS data are plotted as $S(q)$ *versus* q . For all profiles the peak position was determined as the centerpoint of the full width at half-maximum.

3 Results

In order to investigate the effect of the chain charge content on the overall structure of the solution, the polymer concentration and the concentration of added salt have been varied systematically for each charge fraction in a range between 0.3 and 1. The main features of the scattering profiles of semi-dilute solutions of flexible polyelectrolytes have been described at length previously ([21] and

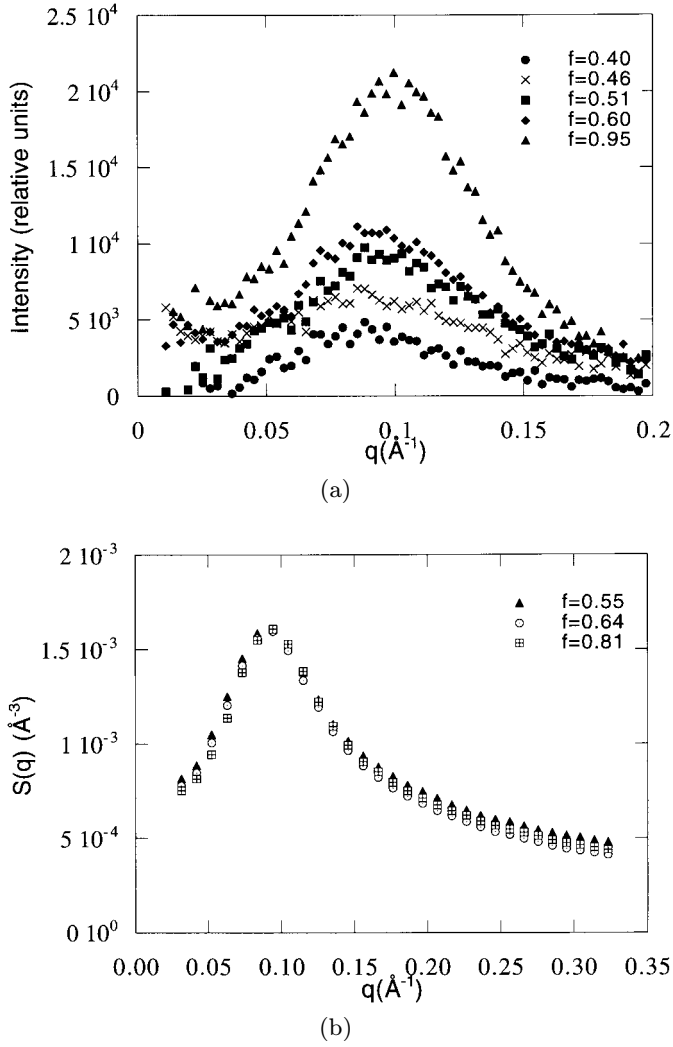


Fig. 1. (a) Evolution of the SAXS profiles as a function of the charge density f ($f = 0.4, 0.46, 0.51, 0.6, 0.95$) for AMAMPS solutions at a monomer concentration of 0.32 M/l. (b) Absolute SANS structure function $S(q)$ as a function of q at various charge fractions f ($f = 0.55, 0.64$ and 0.81) of AMAMPS solutions at a concentration of 0.32 M/l.

references therein). Here we only focus on the variation of those features with f .

The evolution of the SAXS and SANS profiles as a function of the charge density f , at a constant monomer concentration $c_p = 0.32$ monomol/l, are shown in Figures 1a and 1b, respectively. The characteristic low intensity, broad maximum appears in all samples. At all charge densities above the condensation limit, its position q^* is independent of f for both SAXS and SANS within experimental precision, except for the largest charge content where there is a slight difference (Fig. 2). In SAXS the relative peak width at half maximum $\Delta q/q^*$ stays constant at about 0.9 and the intensity increases as f increases. The variation of intensity in SAXS deserves some comments, since both the chains (*via* the SO_3 groups) and the sodium counterions contribute to the scattering [22,23]. Thus the

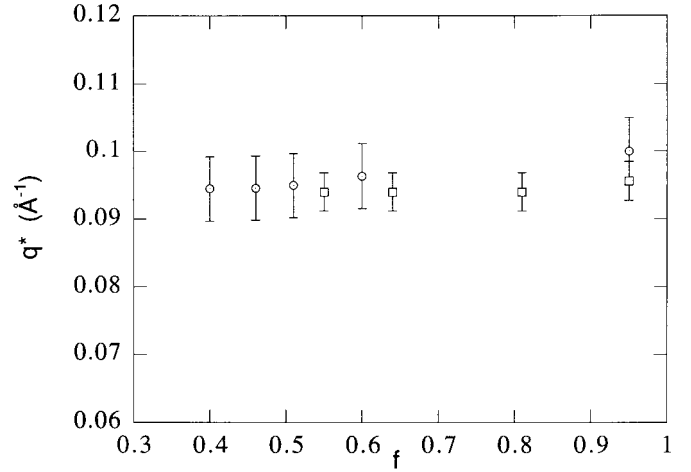


Fig. 2. Position of the maximum of $S(q)$, q^* , as a function of charge fraction f at a monomer concentration of 0.32 M/l, from SAXS (circles) and SANS (squares) data.

total intensity is a function of all partial structure factors, namely monomer-monomer, S_{mm} , monomer-counterion, S_{mc} and counterion-counterion, S_{cc} [24,25]. Contrast variation effects using anomalous X-ray scattering with a caesium counterion were too weak to provide even qualitative information about the counterion dependent structure factors. Another problem comes from the fact that the partial volume, hence the scattering length of the sodium counterion depends very much of its state: bound to the chain (ionic radius of 0.97 Å) or solvated with about five hydration molecules; it is not clear which state a condensed counterion is in [26]. Therefore, because of all these uncertainties, we did not correct the SAXS intensities for contrast. In SANS on the other hand, the contribution of the counterions is negligible [23,27] and absolute intensities may be obtained with a good precision. After correcting for chain/solvent contrast, it is found that the SANS structure function $S(q)$, equivalent to S_{mm} , is independent of the charge f . This implies that the monomer-monomer correlations and therefore the conformation of the chains and their interactions are invariant with the charge f . Returning to the SAXS profiles, one can qualitatively conclude that the contribution of the monomer-counterion and the counterion-counterion correlations increase as f increases.

Another more direct measurement of the amount of free counterions is to obtain $S(q \rightarrow 0)$ which is related to the osmotic compressibility $\partial c_p / \partial \Pi$ by:

$$S(q \rightarrow 0) = kT c_p \frac{\partial c_p}{\partial \Pi}. \quad (1)$$

Although the limited range of the SANS data at small q 's does not allow an extrapolation to $q = 0$, it is remarkable that the intensity at $q < 0.03 \text{ \AA}^{-1}$ is independent of f at constant polymer concentration [28]. Thus the osmotic compressibility appears constant with f , as estimated at that concentration. In the semi-dilute range both the free counterions and the chains contribute to Π (kT per counterion and kT per correlation volume, respectively). Since

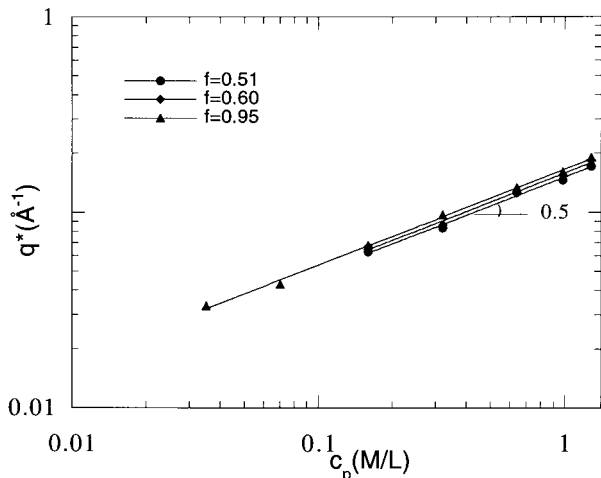


Fig. 3. Evolution of q^* as a function of polymer concentration c_p , for $f = 0.51, 0.60$ and 0.95 , obtained from SAXS and SANS measurements. The line indicates a slope of $1/2$.

the monomer correlations have been shown to be independent of f (superposable scattering profiles), the contribution of the free counterions is independent of f .

The effect of *polymer concentration* c_p was studied by SAXS and SANS in a range between 0.035 and 1.5 monomol/l. The same evolution was observed at each f as c_p increases: (i) the relative intensity per monomer at the maximum $I(q^*)$ decreases; (ii) the relative peak width $\Delta q/q^*$ increases and (iii) the peak position q^* shifts to higher q and scales as $c_p^{1/2}$ for all f , as seen in Figure 3 which also includes some SANS data. These features indicate a decrease of monomer concentration fluctuations, a loss of structural organization in the solution and a decrease of the correlation length, respectively. They are characteristic of all flexible, hydrophilic, highly charged polyelectrolytes in semi-dilute solutions [11,13] and verify rather well the scaling predictions for highly charged polyelectrolytes [7,8]. Note that the high- q tail of the intensity profiles does not show the q^{-1} dependence expected for locally rod-like segments and due to the unscreened electrostatic repulsion between neighbour charges, for any charge fraction or polymer concentration. Figure 4 shows a typical $qI(q)$ versus q representation for SAXS data where a horizontal plateau would be the signature of a rodlike conformation. A similar representation is obtained for SANS data. Although the q^{-1} behaviour could be masked by the very wide peaks and the poor signal-to-noise ratio in that q -range, it can also reflect the findings of molecular dynamics simulations which show that the stretched chains still retain some local flexibility [29].

So far, the reported data have been obtained in salt free solutions. *Addition of a 1-1 electrolyte, namely NaCl*, to the polyelectrolyte solutions is expected to screen the coulombic interactions. Indeed it is found that the scattered intensity at very small angles, up to the position of the maximum, increases with c_s reflecting larger long-range polymer fluctuations. Figure 5 shows the evolution for $f = 1$ which is representative of all f 's; the peak shifts

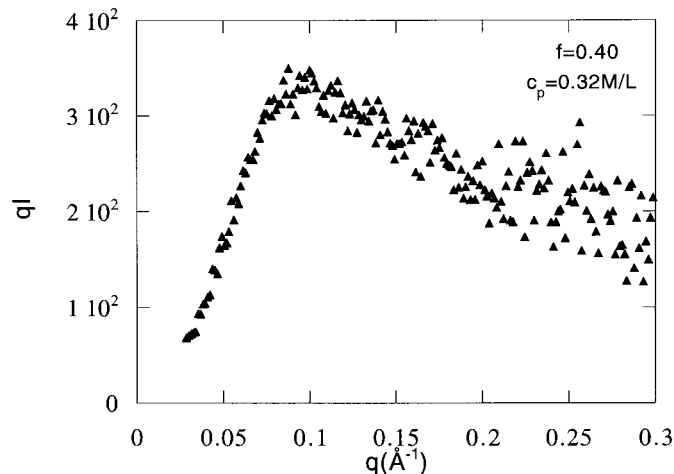


Fig. 4. High- q behaviour of the SAXS profile of AMAMPS solution ($f = 0.4, c_p = 0.32$ M/l) in a qI versus q plot.

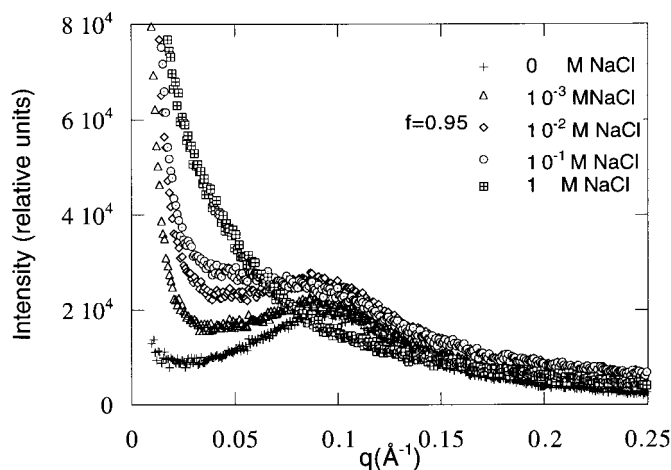


Fig. 5. Effect of added NaCl at concentrations c_s of 0, 10^{-3} , 10^{-2} , 10^{-1} and 1 M, for a sample of AMAMPS 0.95 at $c_p = 0.32$ M/l (SAXS).

slightly to smaller q 's as c_s increases in qualitative agreement with the model of Dobrynin *et al.*; then it becomes less visible until it completely vanishes at a salt concentration c_s^* which does not depend on f . It is found that the ratio of the number of free counterions from the polymer $c_p f_{\text{eff}}$ to the number of coions c_s^* is of the order of 0.1 where f_{eff} is the effective charge of the chain in dilute solution as measured by osmometry [16,17]. Eventually at sufficiently high c_s the scattering profile resembles that of a neutral polymer as is commonly observed. A detailed discussion of the effect of salt on polyelectrolyte solutions is outside the scope of this paper and will be published elsewhere.

4 Interpretive discussion

The striking feature of these data is the invariance of all structural characteristics as the fraction of charged

monomers is varied between 0.3 and 1, all other parameters being constant. We believe that this behaviour can be related to a renormalization of the charge fraction mediated by condensation of the counterions, as shown by the fact that:

- (i) the position of the peak does not vary with f : when the structure of the solution is dominated by the electrostatic interactions as is the case here (highly charged polyelectrolytes) the position of the peak is related to the inverse of the correlation length of the network of entangled chains, which is proportional to κ^{-1} , the Debye-Hückel screening length [7,8]. The invariance of q^* shows that the number of mobile charges that participate in the screening is constant. Although the contribution of the condensed counterions and polyions to the screening is not known, we believe more likely, as usually assumed, that most of the screening comes from the free counterions. Thus the number of dissociated monomers is also constant. However because the factor relating κ^{-1} to q^* is not known by scaling theory, the absolute value of the number of free charges is not known. It is important to recall that at low charge fractions, the peak has been found to vary as $f^{1/3}$ [14];
- (ii) the SANS intensity at low q 's has the same constant value at a fixed concentration. Although in a strict sense, neutron scattering does not extend to the very low q regime, and the presence of an upturn at very low angle may make extrapolation misleading, this could show that the osmotic compressibility of the solution does not depend on f . This implies a constant osmotic pressure. In the semi-dilute range, the free counterions and each correlation blob contributes to it [8]. The invariance of the neutron profiles imply that the former contribution should not vary with f ;
- (iii) the SANS intensity of the peak when suitably corrected for contrast, remains constant and therefore so does the number of monomers per correlation blob; the chain configuration does not change with f ;
- (iv) the variation of intensity in SAXS is partially due to an increase in the monomer-counterion and counterion-counterion correlations; although we can not rule out other effects, this can be qualitatively explained by an increase of the number of condensed counterions;
- (v) the same amount of simple electrolyte (salt) had to be added to screen completely the electrostatic interactions (disappearance of a peak) and thus increase the polymer density fluctuations.

These findings extend to a more concentrated range the validity of Manning's condensation model and complement previous results in dilute solutions of the same polyelectrolytes, which verified by direct osmotic pressure measurements that the effective charge of the chains remained constant as the chemical charge f was varied above a condensation threshold [17]. It also validates the assumption made in the theoretical models for semi-dilute solutions.

On the other hand, it has been shown that, for each chemical charge content f , the behaviour of the semi-dilute solutions as a function of polymer concentration

and added electrolyte was that of a "classic" hydrophilic polyelectrolyte. For instance, it has been found that in salt free solutions the peak position q^* scales as $c_p^{1/2}$ over a large concentration range at all f . This implies that the condensed counterions do not affect the structural properties of the chains since the experiments probe chains with a large variation in the amount of condensed counterions. Note that this criterion is rather sensitive. For instance, it has been shown that for polyelectrolytes with an hydrophobic backbone the change of chain conformation induced by increasing hydrophobicity, *i.e.* by the presence of non electrostatic interactions, results in a change of exponent from 1/2 to 1/3 [15,16].

5 Conclusion

SAXS and SANS experiments on semi-dilute solutions of linear, hydrophilic polyelectrolyte (AMAMPS) show that a charge renormalization also exists at high concentrations for charge fractions between 0.3 and 1, akin to the Manning-Oosawa counterion condensation for isolated chains. At all charge densities f , the structural features are independent of f . Furthermore, at each charge density, there is a good agreement with the predictions of the Dobrynin *et al.* model [8], as an extension of de Gennes [7] isotropic model. It is important to stress that the invariance with f of the structural properties of semi-dilute solutions holds for hydrophilic polymers but that it breaks down when the uncharged chain is hydrophobic, as will be discussed in a forthcoming paper.

All experiments reported here have been performed at LURE (Synchrotron radiation) and LLB (neutrons) which are joint CNRS, CEA, MEN laboratories. The authors would like to thank Dr J.-P. Cotton, their local contact at the LLB for his constant helpful concern during the SANS experiments.

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 20. In scattering experiments the contrast is given by the square of the apparent scattering length K where $K = b_{\text{AMAMPS}(f, f_{\text{eff}})} - b_s \frac{V_{\text{AMAMPS}(f, f_{\text{eff}})}}{V_s}$; $b_{\text{AMAMPS}(f, f_{\text{eff}})}$ is the scattering length of the AMAMPS at a charge density f and taking into account the presence of the fraction $(f - f_{\text{eff}})$ of the condensed counterions around the chains, b_s is the scattering length of the solvent, $V_{\text{AMAMPS}(f, f_{\text{eff}})}$ is the partial molar volume of the AMAMPS of a charge density f and a fraction $(f - f_{\text{eff}})$ of condensed counterions and V_s is the partial molar volume of the solvent. f_{eff} is taken as the value for dilute solutions.
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