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Salt-induced contraction of polyelectrolyte brushes

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Abstract

We present an experimental study dedicated to understanding the behaviour of polyelectrolyte chains when salt goes into a polyelectrolyte brush. We use the ability of asymmetric neutral-charged diblock copolymers to anchor to a selective interface or to self-assemble in water, to examine polyelectrolyte brushes both in planar and in spherical geometries. Using neutron reflectivity, the monomer profile of planar brushes has been found to switch from a Gaussian profile to a parabolic profile, showing that at large spatial scale a salted planar brush behaves like a neutral one in good solvent. Using small angle neutron scattering, it is found that spherical brushes exhibit the same behaviour at a large spatial scale although polyelectrolyte chains remain rod-like at a small spatial scale whatever the salinity is. The charged chains inside a polyelectrolyte brush could be viewed as ‘surveyor’s chains’, which fold their rod-like segments of persistence length l_p . In the last part, spherical polyelectrolyte brushes in contact have been examined. Their behaviour is discussed in terms of interdigitation or contraction of the brushes.

(Some figures in this article are in colour only in the electronic version)

We dedicate this paper to the memory of Claudine Williams.

1. Introduction

Polyelectrolyte brushes made of dense polyelectrolyte chains tethered to an interface are of central interest in numerous fields. In applied processes, they can be used with a better efficiency than their neutral counterparts, for example, in colloidal stabilization and as

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lubricants. In life sciences, polyelectrolyte brushes are involved in cell adhesion as materials covering cells and as components of the extra-cellular matrix. The specific properties of the polyelectrolyte brushes are related to the presence of charges along the polymer backbone. In particular, the main features are the confinement of counterions within the brush and their distribution along the polymer backbone. Indeed, the global stretching of a polyelectrolyte brush is a balance between the osmotic pressure exerted by the counterions and the screened repulsion between the charged monomers.

For salt-free solutions in the dense chain regime, the monomer profile is predicted to follow a Gaussian law, whereas in salt, it should conform to a parabolic profile (neutral brush profile) whatever the density is (Zhulina *et al* 1992, Israëls *et al* 1994). Experimental results disagree with the theoretical predictions for the Gaussian profile and a more stratified profile has been found (Ahrens *et al* 1998, Tran *et al* 1999). However, this confirmation of the monomer profile in salt-free solution is still an open issue, due to the difficulties in achieving an ideal brush in practice. Indeed, the surface density must be fixed during each experiment, grafting or adsorbing charged chains onto a surface. Moreover, since the polymer backbone of polyelectrolyte chains is usually hydrophobic, interactions between the surface and the chains, which lead to parasitic adsorption (stratified profile), are difficult to avoid.

An exceptional feature of polyelectrolyte brushes is the weak dependence of the brush extension upon salt addition. This has been predicted theoretically from self-consistent field theory (Zhulina *et al* 1992) and scaling theory (Pincus 1991) and has been confirmed experimentally (Mays 1990, Guenoun *et al* 1996, Hariharan *et al* 1998, Balastre *et al* 2002). The addition of salt has no effect on the brush height as long as the added salt concentration, C_s , is less than the average ionic strength of the free counterions trapped in the brush. Above this threshold, the effect of added salt becomes significant. In the case of planar geometry and flexible chains, there seems to be an agreement on the scaling law $H \sim C_s^{-1/3}$, between theory (Zhulina *et al* 1992) and experiments (Guenoun *et al* 1995, Balastre *et al* 2002). In the case of spherical geometry, a scaling law $H \sim C_s^{-\beta}$ has been found with β varying from 0.11 to 0.18 for different block copolymer micelles (Guenoun *et al* 1996, van der Maarel *et al* 2000, Förster *et al* 2002, Muller *et al* 2004) or adsorbed chains on spherical colloids (Hariharan *et al* 1998). A quantitative comparison between these studies is difficult: the density of charges along the chains and the surface density are different as well as the average densities of the brushes. In addition, the surface density could change in some cases when salt enters the brush, inducing a change in the brush itself. Despite this considerable body of work, not much is known about the real statistics of the chains, in particular their local conformation.

A relevant situation for lubrication is the case where the polyelectrolyte brushes are in contact. A high energy penalty has been predicted for the compression of two brushes (Pincus 1991). This is due to the overlap of the counterion clouds of each brush inducing a strong osmotic penalty and thus a strong repulsion. Recent predictions assume a contraction of the polyelectrolyte brush before overlap, possible interdigitation at high packing fraction, and relate the effective charge with the electrostatic screening (Borisov and Zhulina 1998, Jusufi *et al* 2002). From the experimental point of view, the extent to which polyelectrolyte brushes contract or interpenetrate is still an open question (Muller *et al* 2000, Korobko *et al* 2004).

In this paper, we report on the behaviour of polyelectrolyte chains when salt goes into a polyelectrolyte brush. We use the ability of asymmetric neutral-charged diblock copolymers to anchor to a selective interface or to self-assemble in water, to examine polyelectrolyte brushes both in planar and in spherical geometries. We examine the average monomer profile of a planar brush with and without salt. The brush is made from a Langmuir film of the copolymers spread on a water subphase and we use reflectivity measurements to determine the monomer profile. Then, we describe the behaviour of a spherical brush in terms of polyelectrolyte

conformation when salt goes into the brush using small angle neutron scattering in contrast matching conditions. Here, the brush is made from the corona of the copolymer micelles. Finally, we study the case of spherical brushes in contact and discuss their contraction or interpenetration.

2. Experimental details

An asymmetric neutral-charged diblock copolymer composed of 63 repeat units of poly(*tert*-butylstyrene) (PtBS) and of 356 repeat units of sodium poly(styrene sulfonate) (NaPSS) was used for the reflectivity studies. For the neutron scattering experiments, we used a neutral-charged diblock copolymer made of poly(ethylene-*alt*-propylene) (PEP) with 52 units and of deuterated sodium poly(styrene sulfonate) (NaPSS_d) with 251 units. Both diblocks were synthesized by anionic polymerization (Valint and Bock 1988, Yang and Mays 2002) with a sulfonation degree of 95% and of 90%, respectively, and a polydispersity ratio of 1.04. In the following the two diblocks will be called 63/356 and 52/251. All details about neutron reflectivity and small angle scattering measurements have been previously described (Romet-Lemonne *et al* 2004, Muller *et al* 2004).

3. Polyelectrolyte brushes in planar geometry

In order to deduce the monomer profile of polyelectrolyte brushes in planar geometry, we used Langmuir films of the 63/356 copolymer. The asymmetry of the copolymer used here ensures that the contribution to the pressure of the hydrophobic block is negligible compared to the pressure due to the polyelectrolyte block. The treatment and the analysis of reflectivity data were performed as follows. After normalization with respect to the plateau of total reflection and subtraction of the background signal, the reflectivity data were compared to the reflectivity of a multilayer, which can be computed exactly using Parrat's recursive method (Parrat 1954). The data are then fitted to a continuous scattering length density profile, without making any assumption regarding its analytical form, by modelling the monolayer as a set of n layers of equal thicknesses. The monomer profiles obtained by this treatment are shown in figure 1. The shape of the profile in pure water (figure 1) is in reasonable agreement with the theoretical result of self-consistent field computations (Zhulina *et al* 1992) for a planar polyelectrolyte brush in the osmotic regime which leads to a Gaussian profile. We believe that the somewhat better agreement with theoretical calculations and the disagreement with the previous experimental results (Ahrens *et al* 1998, Tran *et al* 1999) are due to the non-contributing anchor (small hydrophobic block). However some deviation from the Gaussian profile visible in figure 1 may be related to the slight expansion of the brush with surface density, an effect not predicted by theories leading to Gaussian profiles (Romet-Lemonne *et al* 2004). The profiles in 1 M salt are significantly different from those observed without salt (figure 1). In particular, the densities fall to zero abruptly at a certain distance from the interface. The profile is well adjusted by parabolic functions as predicted by self-consistent field computations. This shows that in the salted regime, the average monomer profile is similar to the neutral one in good solvent. However, an excess density is observed near the interface. This corresponds to about 7.5% of the observed copolymers for all molecular areas. This excess density suggests that a part of each polyelectrolyte chain adsorbs onto the interface. This stratified profile near the interface is caused by the reduction of the chain effective charge and the hydrophobicity of its backbone.

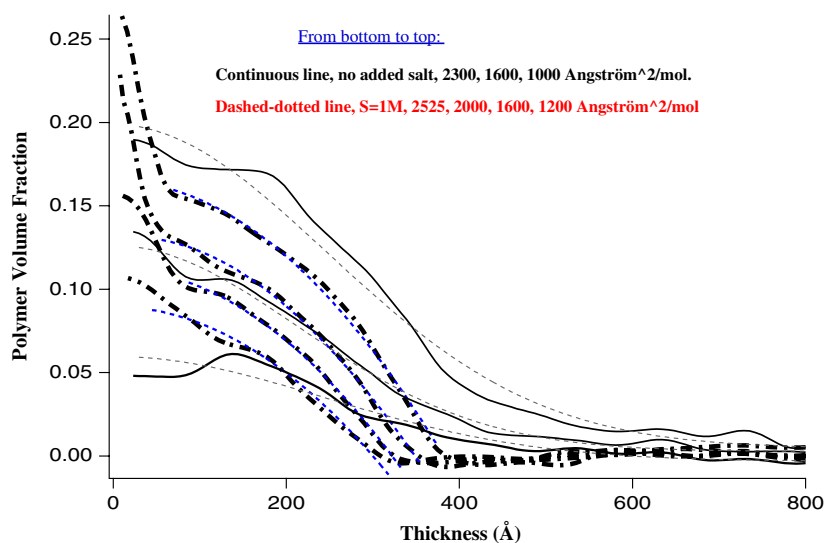


Figure 1. Monomer profiles deduced from reflectivity measurements for a pure water subphase (continuous lines) at 1000, 1600, 2300 Å² per molecule from top to bottom, and for a salted subphase at 1 M (dashed-dotted lines) at 1200, 1600, 2000, 2525 Å² per molecule from top to bottom. The dashed lines represent the fits as described in the text. This shows clearly the contraction of the brush and the spectacular change in shape of the monomer profile.

4. Polyelectrolyte brushes in spherical geometry

In previous experiments, the 52/251 copolymer has been found to self-assemble as spherical micelles (Muller *et al* 2000), a self-assembly due to the large counterion condensation within the micelle (Huang *et al* 1997, Muller *et al* 2001). Moreover, using contrast matching, we have demonstrated that the core radius (made of the hydrophobic block) is insensitive to the concentration (Muller *et al* 2000) and to the addition of NaCl (Muller *et al* 2004). This allows us to test how a spherical charged brush evolves with salt concentration at a fixed grafting density. For small angle neutron scattering, the solvent was chosen to match the core scattering length. The scattering spectra obtained without and at different salt concentrations are given in figure 2. At low scattering wavevectors (average profile) a significant change in scattering profile is shown whereas at high scattering wavevectors a q^{-1} signal characteristic of a rod-like form factor is evidenced (Guenoun *et al* 1998) whatever the salinity is.

As a first approach, we have restricted our analysis to low scattering wavevectors where the q^{-1} profile contribution is negligible in the scattering signal. Thus the average profile can be written as $P_a(q) = (1 - \frac{1}{p}) \times |F_{ave}(q, R_m, R_c, \alpha)|^2$ where p is the aggregation number, R_m the micelle radius, R_c the core radius and α the exponent describing the centrosymmetric density profile of the corona given by $\rho(r) \sim r^{-\alpha}$ (the function $F_{ave}(x)$ is given in Muller *et al* (2004)). The exponent α is related to the effective Flory exponent ν by $\alpha = \frac{3\nu-1}{\nu}$. The parameters p and R_c are known from the core signal analysis. Therefore, the average profile can be fitted using two adjustable parameters R_m and α . The fit results are not shown in figure 2 for reasons of clarity and only the results will be discussed. As the salt concentration increases, the radius R_m diminishes showing that the micelle contracts. Assuming that the height of the polyelectrolyte shell is $R_s = R_m - R_c$, the brush thickness is found to be essentially constant at the lowest salt concentrations, and a significant contraction is only observed above an added salt

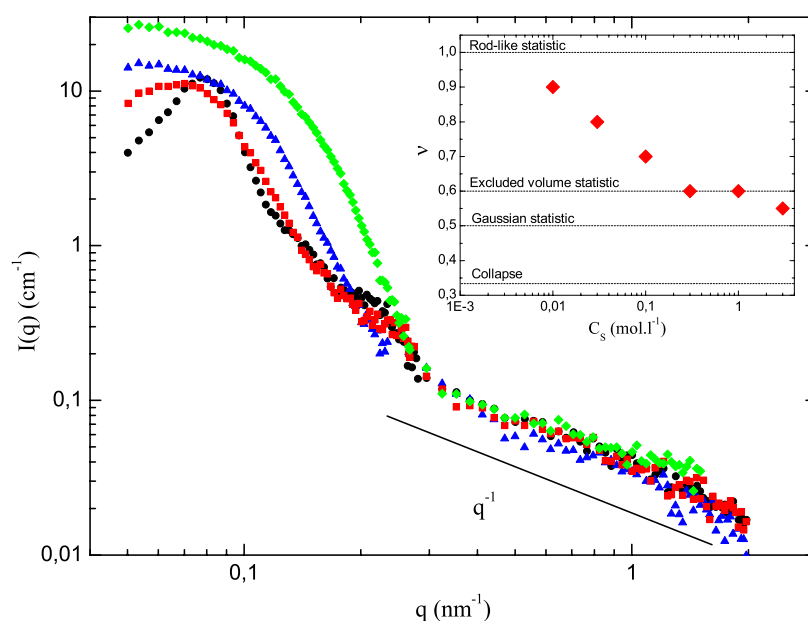


Figure 2. Absolute neutron intensities scattered by the polyelectrolyte shell of the 52/251 copolymer micelles in dilute samples ($C_p = 0.5$ wt%) at different NaCl concentrations: $C_s = 0$ M (circles), $C_s = 0.01$ M (squares), $C_s = 0.1$ M (triangles), $C_s = 1$ M (diamonds). A q^{-1} dependence is clearly observed whatever the salinity is. In the inset, the effective Flory exponent as a function of NaCl concentrations (linear–log representation) deduced by fitting the low wavevector contribution of the scattered intensities (average profile) is shown.

concentration of about 2×10^{-2} M. This threshold has been previously shown to correspond to the average ionic strength of the free counterions in the brush, I_0 (Muller *et al* 2004). Above the threshold, the brush height follows a scaling law $R_s \sim C_s^{-0.2}$. This result is consistent to some extent with the data in the literature (Guenoun *et al* 1996, Hariharan *et al* 1998, van der Maarel *et al* 2000, Förster *et al* 2002). The values of ν deduced from the parameter α are shown in the inset of figure 2, indicating that ν tends to a constant which corresponds to an excluded volume statistics ($\nu = 3/5$). This demonstrates that a spherical polyelectrolyte brush resembles on average a planar brush.

Surprisingly, it is clear from the spectra that the q^{-1} part at large scattering wavevectors remains identical to the salt-free solution spectrum (figure 2). This q^{-1} dependence means that the chains remain rod-like at a small spatial scale at high salt concentrations. Moreover, the constancy of the absolute intensity at large scattering wavevectors from 0 to 1 M added salt shows that one measures the mass per unit contour length in this range. This is characteristic of worm-like chains (des Cloizeaux 1973). The charged chains inside a polyelectrolyte brush could be viewed as ‘surveyor’s chains’, which fold their rod-like segments of persistence length l_p . Of course this must be viewed as a qualitative picture since, in particular, the persistence length l_p has no reason to stay constant along the radial distance from the core.

5. Polyelectrolyte brushes in close contact: local order and contraction

Spherical polyelectrolyte brushes in contact can be obtained by using frozen micellar solutions above the close packing concentration c^* . In previous work (Muller *et al* 2000) it has been

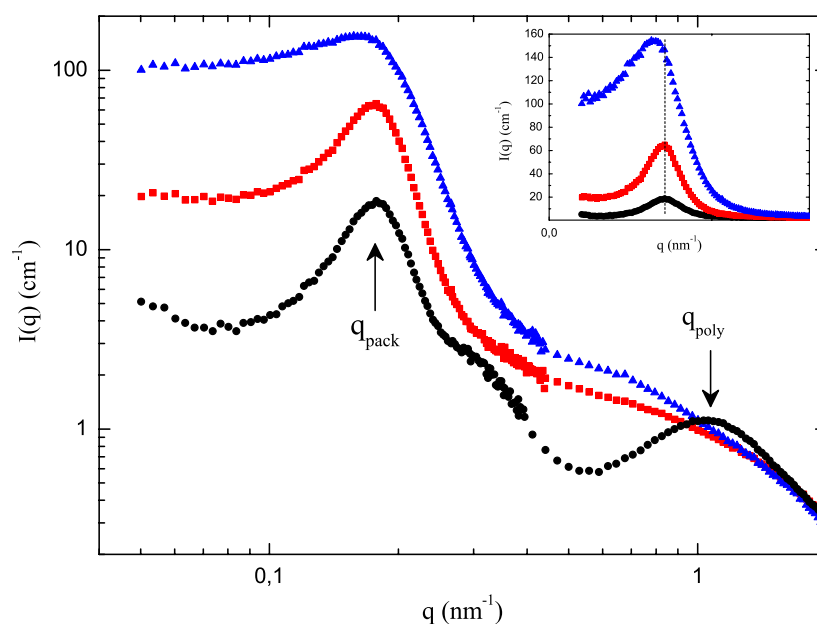


Figure 3. Absolute neutron intensities scattered by the polyelectrolyte shell of the 52/251 copolymer micelles in concentrated samples ($C_p = 10$ wt%) at different NaCl concentrations: $C_s = 0$ M (circles), $C_s = 0.5$ M (squares), $C_s = 2$ M (triangles). The polyelectrolyte peak (q_{poly}) clearly vanishes when salt is added while the packing order (q_{pack}) still exists. In the inset, a zoom on the packing peak (linear-linear representation) is shown. The dashed line represents the position of q_{pack} at $C_s = 0$ M.

shown from the scattered intensities that for $c \gg c^*$ a polyelectrolyte peak appears ($q_{\text{poly}} \sim c^{1/2}$) at large scattering wavevectors corresponding to polyelectrolyte chains in the semi-dilute regime while a packing order peak is present ($q_{\text{pack}} \sim c^{1/3}$). In figure 3, we present scattering intensities obtained when salt is added to a copolymer solution of concentration 10 wt%. This shows that the polyelectrolyte peak q_{poly} vanishes when salt is added. This corresponds to the screening of the charges at the local scale. The distance between micelles seems to slightly increase at high salt concentration as illustrated in the inset of figure 3 but the change in the form factor of the shells could be responsible for such a moderate shift.

The packing order clearly persists up to a concentration of 10 wt% which can be estimated to be about $6c^*$ for micelles with no added salt and about $1.4c^*$ and $1c^*$ for added salt values of 0.5 and 2 M respectively. The value of c^* is calculated knowing the micelle radius (Muller *et al* 2004) and taking into account a packing coefficient of micellar spheres of 0.6 (random packing). In the context of lubrication by charged brushes, it is worth deducing from the above results whether brushes interpenetrate or contract.

In the hypothesis of interpenetration, the persistence of the packing order peak far above c^* for unsalted micelles is markedly different from what is obtained for neutral star polymers of similar density (Grest *et al* 1996). This could be accounted for by the additional repulsion coming either from counterions or screened Coulomb repulsion though it has been shown that a hard sphere potential could reasonably describe micellar interactions (Romet-Lemonne *et al* 2005). The polyelectrolyte peak originates from the semi-dilute polyelectrolyte solution created by the interpenetration of coronae. For salted micelles, the order observed is compatible with what is measured for neutral stars but, surprisingly, the order is very different (see the

inset in figure 3) between 0.5 M and 2 M whose polymer concentrations are both in the neighbourhood of c^* . This seems contrary to the observation (Grest *et al* 1996) for neutral stars. The polyelectrolyte peak disappears because of screening.

In the hypothesis of contraction, the micelles contract in order to keep the concentration locked at c^* . Now, the polyelectrolyte peak comes from the contracted denser shell of each micelle. In this framework, the ordering peak can persist up to high concentrations ($6c^*$) and the nature of the order could be modified between 0.5 and 2 M by a transition from a mostly non-interpenetrated contracted state (highly repulsive) to a progressively interpenetrated one (less repulsive).

Scattering data, both with or without added salt, may not be clear-cut enough for experiments to distinguish between interdigitation and contraction of polyelectrolyte brushes. A cross-checking by other techniques, using rheology for example, may be needed to really distinguish between the two scenarios.

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