Rodlike Behavior of Polyelectrolyte Brushes

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Spherical charged brushes are studied in the form of block copolymer micelles. These copolymers are diblocks made of one deuterated, highly charged block and of one protonated, hydrophobic block. Neutron scattering with contrast matching enables us to probe selectively the structure of the arms of the charged corona of the micelles. A near-perfect rodlike behavior (scattered intensity $\sim q^{-1}$) of the arms is observed at all salt concentrations above an onset in wave vector q_0, which increases with salt concentration above a threshold. Results are strikingly different from what is observed for linear polyelectrolytes, since charged brushes appear very weakly sensitive to the addition of salt. [S0031-9007(98)07484-5]

Many unresolved problems remain concerning charged polymers (polyelectrolytes) [1]. Among them are basic questions regarding the actual shape that a single linear polyelectrolyte chain adopts as the polymer concentration or the amount of added salt is varied. A fully charged chain is predicted [2] to adopt a rodlike conformation because of the electrostatic repulsion between monomers. This rodlike behavior crosses over to a more flexible conformation due to the screening of the interactions either by ions or monomers themselves above some characteristic length L_P, the persistence length. Analysis of previous experimental data [3] confirmed that poly(styrene-sulfonate) chains (fully ionized) adopt a rather extended structure in semidilute solutions with persistence lengths of about 65 Å. On the theoretical side, however [4], recent simulations do not show clear rodlike conformations at short spatial scales, even in the dilute or unscreened regime.

Situations where such charged chains are tethered to a surface by one end (in practice, grafted or adsorbed) are also of considerable interest [5]. In particular, polyelectrolyte brushes, where the typical distance between neighboring chains is less than the size of the chain in solution, have both fundamental and applied interests. Charged brushes are expected to efficiently protect colloids in polar media against flocculation owing both to charge and extended chain conformation. Additionally, it is predicted [5] that such charged structures are weakly sensitive to the addition of salt, a remarkable feature when compared to the sensitivity of charged bare surfaces to salt, as exemplified by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stabilization [6]. The main idea is that a charged brush is able to trap its own counterions, thus generating a large inner salinity, weakly sensitive to the addition of external salt. So far, few experimental studies have been performed since experimental systems are not so frequently encountered [7]. Tethered polyelectrolyte brushes of even modest density are difficult to create.

The theoretical predictions about the brush height as a function of added salt concentration rely on highly debated assumptions about polyelectrolytes, such as the behavior of the persistence length of a chain or the correct expression of the osmotic pressure for semidilute solutions of polyelectrolytes [1]. In this context, it is highly desirable to get more experimental insight at the microscopic level and to determine the conformation of chains within a charged brush. As shown in this study, for spherical geometries, the results are in agreement with chains having a strong rodlike behavior up to large spatial scales. These spherical brushes are formed by charged diblock copolymers associated as spherical micelles in solution [8,9], the charged brush being the corona of the micelle. When salt is added, we show that the conformation stays rodlike below a typical spatial scale q_0^{-1} which depends upon the addition of salt.

Association in water of charged diblock copolymers whose one moiety is long and fully charged and the other moiety is short and hydrophobic has been recently studied in detail by several groups [8–10]. We made use of a diblock neutral-charged copolymer of ordinary protonated poly(tert-butylstyrene) and deuterated sodium poly(styrene sulfonate) (PtBS-NaPSS) with a weight-average molecular weight of $M_W = 6880$ for the PtBS block and a $M_W = 1.26 \times 10^5$ for the NaPSS block. It was synthesized by anionic polymerization [11] with a sulfonation level of about 80% (polydispersity ratio of 1.03). Several solutions at different salinities (NaCl salt from Prolabo of analytical grade) were prepared in pure D_2O or in a mixture of D_2O (16% by volume) and de-ionized water (milli-Q system) of conductivity less than 18 M$\Omega \cdot$ cm^{-1}. The latter mixture was designed to yield a solvent whose contrast length

density is identical to that of the PtBS group. Small angle neutron scattering was performed at the Orphée reactor in Saclay on the PACE spectrometer at wavelengths of $\lambda = 0.65$ and 1.5 nm and sample to detector distances of 3.0 and 4.5 m, respectively. The sample cells were quartz cells of inner thickness 2 mm. The scattered intensities were corrected for the parasitic intensity scattered by the quartz cell by subtraction and normalization to the water-scattered intensity (in order to eliminate differences in the detector efficiency). The intensity scattered by the solvent was also subtracted. After this subtraction, the remaining signal is essentially all due to the coherent scattering of the polymer. The incoherent scattering due to the polymer itself was found negligible both by calculation and measurement $[(2-5) \times 10^{-4} \text{ cm}^{-1}]$.

Association of the polymer was checked by neutron scattering on solutions in D_2O where only the cores of the micelles are visible. An average value of the radius of gyration of the cores is found to be $R_G = 33$ Å ± 2, giving an aggregation number of about 25. Dynamic light scattering on dilute solutions (0.02 wt %) confirms the association and also provides a hydrodynamic radius of the whole micelle of about 120 nm. Results of the neutron scattering experiments on solution in the mixed solvent are shown in Fig. 1 for a polymer concentration of 1 wt % and several salinities. The $I(q)$ versus q (log-log representation) where q is the wave vector and $I(q)$ the scattered intensity demonstrates the asymptotic behavior in q^{-1} of the intensity. This is the signature of the diffraction by a rod for $qL > 1$ where L is the contour length of the rod (number of monomers × monomer size). The q^{-1} behavior extends down to some lower limit q_0 in q which depends upon the addition of salt. This limit has a threshold in salt concentration S_0. For salt concentrations below S_0, the limit q_0 is constant, whereas above S_0 the value of q_0 slowly increases with salt concentration.

How can these results be interpreted with respect to the intramolecular structure of chains in a spherical brush? The concentration of 1 wt %, mainly used in this study, is the lowest one compatible with an acceptable signal to noise ratio. This concentration is such that intermicellar or intramicellar interactions between arms of the corona may both contribute to the scattering signal. The arms may either interpenetrate or contract as the micelle volume fills space on increasing concentration [9]. However, scattering curves for three different samples of polymer concentrations of 1, 2, and 3 wt % nicely superimpose in the range of wave vectors $0.1 < q < 1$ nm^{-1} (Fig. 2). This indicates that, at this spatial scale q^{-1}, the scattered signal mainly probes the intramicellar conformation and not the intermicellar interactions. Moreover the inset of Fig. 2 shows that the q^{-1} behavior extends up to 2 nm^{-1}, a range where the interactions between arms cannot be responsible for the signal. The q^{-1} behavior therefore originates from the statistics of the chains in the corona.

The scattered signal depicted above $q = 0.1$ nm^{-1} in Fig. 2 is typical of a single star. Between $q = 0.1$ nm^{-1} and $q = 0.2$ nm^{-1}, the signal is mainly due to the average profile of monomer in the corona, giving rise to a rather sharp decrease [12]. Above $q = 0.2$ nm^{-1} the signal is, on the contrary, mainly due to the fluctuations of the monomer profile, thus revealing the statistics of the individual chains [13] which is here rodlike ($\sim q^{-1}$). The above behavior can be seen clearly in a calculation of the particle scattering function of a shell of symmetrically arranged rods [14]. Such an illustrative, scattering function is shown in Fig. 3 for 20 rods of length 116 nm, symmetrically arranged around a sphere of radius 43 Å (representing the micellar core). In a log-log representation, the asymptotic behavior clearly exhibits a q^{-1} behavior originating from the rodlike statistics.
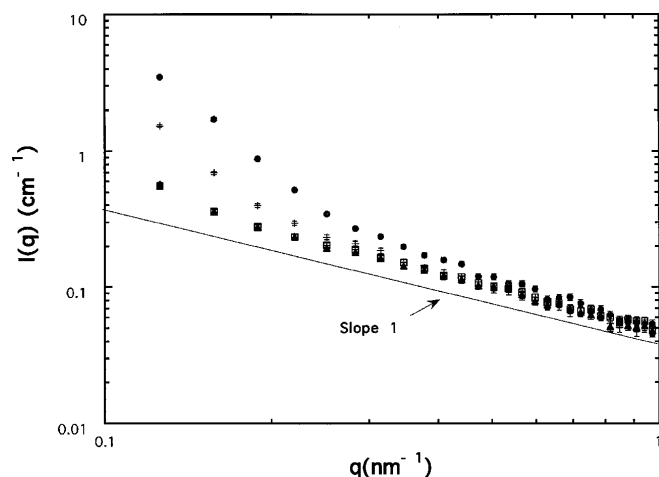

FIG. 1. Neutron-scattered intensity in the representation $I(q)$ versus q for a polymer concentration of 1 wt % at various salinities: $S = 8.5 \times 10^{-4}M$ (open squares), $S = 10^{-2}M$ (triangles), $S = 0.16M$ (crosses), and $S = 1M$ (full dots).
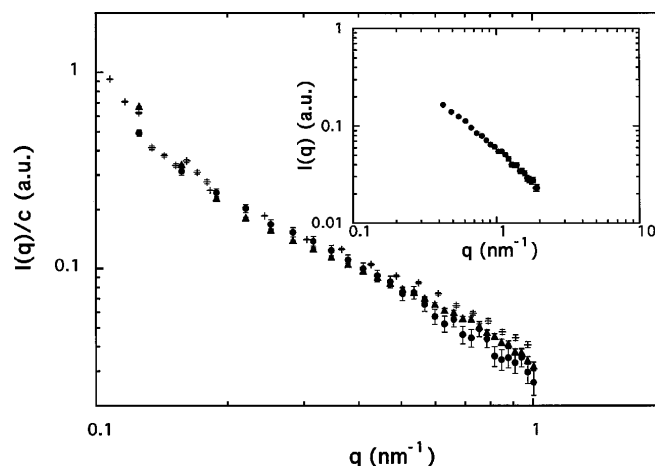

FIG. 2. Neutron-scattered intensity $I(q)/c$ versus q without added salt at three different polymer concentrations: 1 wt % (dots), 2 wt % (crosses), and 3 wt % (triangles). The inset depicts how the q^{-1} behavior extends over such a large range of q that interarms interactions cannot induce this behavior (1 wt % solution).
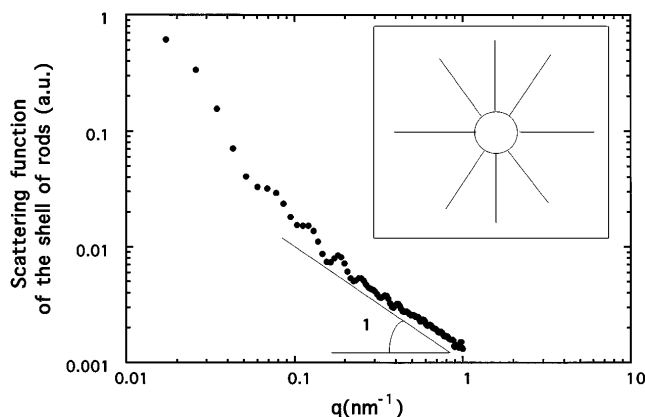
FIG. 3. Particle scattering function of a shell of symmetrically arranged rods (see inset) around a sphere. A q^{-1} regime is evidenced at high wave vectors. The inset depicts the scattering object made of rods (of number 20) of length 116 nm arranged around a sphere (of zero contrast) of radius 43 Å as depicted in Ref. [14].

A striking result of this study is that, although screened by large amounts of salt, charged arms in a brush still adopt an extended conformation at high q. A better inspection of this behavior can be done by plotting the same results on a $q^2 I(q)$ versus q representation (Fig. 4) to reveal the departure from the q^{-1} dependence. Increasing the salt concentration, the shift towards high q values of the relative minimum q_0 of the curves represents the shift of the beginning of the q^{-1} regime. A threshold ($S_0 \approx 10^{-2}M$) in added salt concentration S can be determined below which no detectable shift occurs (Fig. 5). The existence of such a threshold in salt S_0 confirms that the added salt concentration must be larger than the inner concentration in order to have any influence [5,7]. This effect can be viewed alternatively as a result of the higher osmotic pressure of the inner counterions with respect to the osmotic pressure of the added counterions in the bulk. The inner
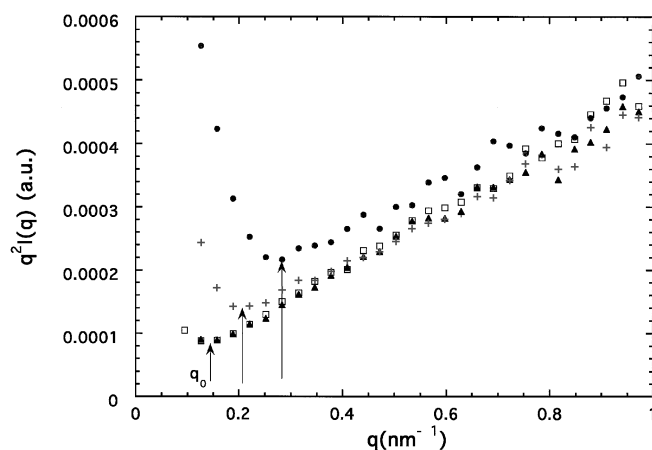
concentration of counterions can be estimated at 1 wt % as $5 \times 10^{-2}M$, where the latter value corresponds to the polystyrene sulfonate monomer concentration. In a first approximation, if we assume that the counterion condensation follows the Manning model for linear polyelectrolytes [15], the concentration of free counterions, which are those contributing to the osmotic pressure, is less than the above value by a factor $l_b/a = 2.8$ where l_b is the Bjerrum length (7 Å) and a the monomer size (2.5 Å). This provides a threshold value of $1.8 \times 10^{-2}M$, in excellent agreement with the value determined in Fig. 5. Above the threshold, the change in conformation with salt concentration is of very small amplitude and could be approximated by a power law behavior with a weak exponent 0.13. This behavior has to be contrasted with those encountered in the description of linear polyelectrolytes where the persistence length L_P, which delimits a regime where the chain has a rodlike shape ($L < L_P$) from one where the chain is Gaussian ($L > L_P$), varies as S^1 or $S^{0.5}$ according to the authors [1]. Although q_0 cannot be strictly equated to a persistence length, the weak variation of this quantity with added salt raises the question of whether the statistics of a chain within a charged brush may be described by such a single length.

In any case this variation, in excellent agreement with the small overall contraction of charged polymeric micelles or charged stars upon addition of salt [8,16], demonstrates the weak influence of added salt on charged brushes at the microscopic level. We believe these results in spherical geometry to be of direct relevance for the area of colloids in polar media. A natural extension of this work is to determine the form factor of a single chain within the micelle in an attempt to define more correctly if the notion of a true persistence length is applicable. Such an extension is in progress.

FIG. 4. Scattered intensity in a $q^2 I$ versus q representation for a 1 wt % polymer concentration at different salinities (symbols are as in Fig. 1). The threshold q_0 of the q^{-1} regime is the minimum (indicated on the plot by arrows).
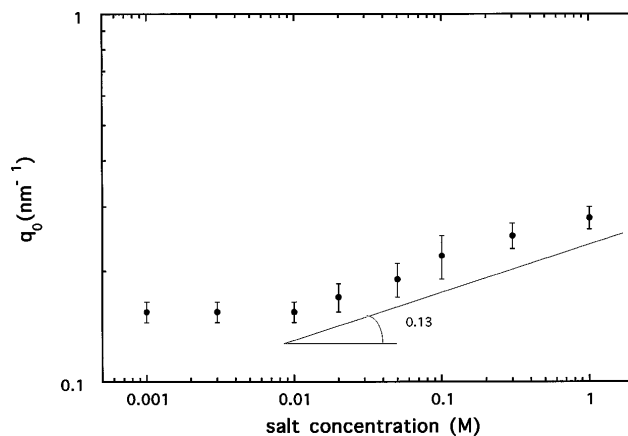

FIG. 5. Behavior of the onset of the rodlike regime, q_0, versus the concentration in added salt. A minimum amount of about $S_0 = 10^{-2}M$ has to be added to detect a noticeable shift.

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