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Structural Changes and Chain Conformation of Hydrophobic Polyelectrolytes

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A series of hydrophobic sodium poly(styrene-*co*-styrene sulfonate)'s of various charge fractions was studied by means of two combined techniques, static light scattering and small-angle X-rays scattering. The existence of structural changes as a function of the charge content was evidenced in the full scattering spectrum. By fitting the experimental data with some known models, we were able to show that these hydrophobic polyelectrolytes have a Gaussian shape at large scales. Moreover, the correlation between characteristic lengths of different scales suggests that the small angle upturn of the most hydrophobic polyelectrolytes could be related to the conformation of the chains.

Introduction

For the past five decades, polyelectrolytes have been the subject of intense research primarily because of their fundamental importance in biological and biophysical processes. Furthermore, because of their solubility in water, they are especially interesting in environment friendly applications. Polyelectrolytes are polymers containing ionizable groups. In a polar solvent such as water, these groups dissociate leaving a charged polymer chain and free counterions. Complete dissociation takes place only when the average distance between charged monomers, b , is bigger than the Bjerrum length $l_B = e^2/\epsilon k_B T$ (ϵ is the dielectric constant of the supporting solvent, e is the elementary charge, and $k_B T$ is the thermal energy). If b is smaller than l_B , the potential energy at the chain becomes prohibitively large and some counterions remain confined in a small volume around the chain in order to reduce the electrostatic interactions between monomers. This is the counterion condensation effect, first described by Oosawa and formalized by Manning for the case of an infinite line with constant charge density.¹ The Manning–Oosawa (MO) model predicts a renormalization of the effective charge of the chain to a constant value, above a condensation threshold at $b = l_B$. This model has been used to describe the experimental behavior of classic polyelectrolytes,² including osmotic pressure measurements,³ as well as structural properties.⁴ Although more elaborate models predict deviations,⁵ the conclusions remain qualitatively similar.

Hydrophobic polyelectrolytes are charged polymers with a bare backbone in very poor solvent conditions. As a consequence, a single chain experiences a series of local chain collapses, analogous to the Rayleigh instability found in a charged liquid droplet. This effect was first described by Kantor and Kardar⁶ for the case of polyampholytes (polyelectrolytes with alternated positive and negative charges). In the case of hydrophobic polyelectrolytes, the appearance of local globular regions (or pearls) was predicted by Dobrynin et al.⁷ Their pearl

necklace (PN) model consists of charged globules alternating with charged strings in a fully stretched configuration. As concentration increases, the extended chains keep the same conformation until they start overlapping at the concentration c^* , giving rise to a semidilute regime very similar to the hydrophilic polyelectrolyte regime as long as the size of the beads is small compared with the semidilute correlation length ξ . The situation at high concentrations when both lengths are of the same order of magnitude is more complex and still rather uncertain. It does not concern us at the concentrations considered here.⁷ Simulations also show pearl instabilities. The primitive model numerical simulations of Micka et al.⁸ investigated the pearl necklace conformations as concentration increases. They found that the model hydrophobic chains remain highly extended in the very dilute regime only; as soon as concentration increases, the conformation evolves to strongly collapsed, isolated, and charged chains thereby shifting the overlap concentration to much higher values. From an experimental point of view, hydrophobic polyelectrolytes are clearly different from hydrophilic ones. Measurements of thermodynamic properties such as osmotic pressure³ show a strong reduction of the amount of released counterions compared to the predictions of the MO model. Moreover, static light scattering (SLS) experiments in the thermodynamic limit⁹ revealed remarkable differences between hydrophobic polyelectrolytes of various charge contents. The discrepancies found in both techniques were interpreted as an evidence of the presence of drastic changes in the local structure due to hydrophobic effects. These experiments are in qualitative agreement with the theory and simulations that predict the appearance of globular structures and corroborate the findings of independent experiments of small-angle X-rays scattering (SAXS),^{10–12} small angle neutrons scattering (SANS),¹³ and fluorescence emission spectroscopy.¹² There is, however, a common feature to both hydrophilic and hydrophobic polyelectrolytes: a large excess of scattered intensity develops at the small angle (large distances) part of the spectrum. The puzzling presence of such large intensities has been the subject of controversies in the literature.^{14,15} A breakthrough was made recently by Ermi and Amis¹⁶ who analyzed the complete

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relevant scattering spectrum, extending over more than 2 orders of magnitude in wavevector, by using two complementary techniques, namely SLS and SANS. Ermi and Amis interpreted the scattered intensity upturn as due to domains of chains.¹⁶ In this paper, we present evidence that the small angle upturn in solutions of hydrophobic polyelectrolytes is not necessarily caused by domains of chains, but it could be related to the shape of single chains, at least in some specific cases. Using SLS and SAXS, we studied the complete scattering spectrum of a series of hydrophobic polyelectrolytes of various charge contents. Our study reveals that the different hydrophobic polyelectrolytes show deep structural changes in the full scattering spectrum. Additionally, for finite concentrations, the scattering profiles at low angles (large distances) have a Gaussian like shape at large distances, in agreement with experiments on hydrophilic polyelectrolytes.¹⁶ This investigation is an extension of previous studies which were performed in a more restricted wavevector range.^{10,11}

Experimental Setup

Our experimental system consisted of a series of hydrophobic sodium poly(styrene-*co*-styrene sulfonate) (noted for short as NaPSS) with variable charge content. Starting from neutral monodisperse polystyrene ($M_w = 6.7 \times 10^5$, $M_w/M_n = 1.11$, by Polymer Source Inc.), we produced a postsulfonation reaction that allows one to control the percentage of sulfonated monomers and thus the valence of the chain.^{9,17} After a thorough dialysis, the final product is recovered by freeze-drying. The charge fraction is then determined by chemical analysis (at Service Central d'Analyse of CNRS) to within a 5% error. It is important to mention that size exclusion chromatography studies show that the polydispersity of the parent polymer is not modified by the postsulfonation reaction.¹⁸ The clean and dry polymer is dissolved in ultrapure water of resistivity 18 M Ω cm. Polyelectrolyte solutions prepared in this way remain stable at room temperature for several months. Moreover, for the static properties reported in this work, identical results were obtained with freshly prepared solutions or previously stored ones. This behavior contrasts with a dependence on the preparation history observed in some dynamic properties.¹⁹

The solutions were filtered and contained in highly cleaned quartz cells for SLS and 2.5 mm glass capillaries for SAXS experiments. SLS experiments were performed with a Malvern 4700 light scattering goniometer, using an Ar-Kr laser operating at a wavelength of 4880 Å (Spinnaker 1161, by Spectra Physics). Most SLS results have been reported elsewhere.⁹ SAXS studies were performed on beam line BM-26B at the ESRF.²⁰ The X-rays wavelength, $\lambda_0 = 1.38$ Å, was set by a double-crystal monochromator with sagittal focusing followed by a meridional focusing mirror. We used a bidimensional position sensitive counter (512 \times 512 cells, Gabriel type detector, with a pixel size of 250 μ m). The distance between the sample and the detector was set to 7.43 m. While keeping constant the average number of monomers per chain (≈ 5800), our system was studied only as a function of the electrostatic charge and the number density of chains, ρ_1 . Values of the charged monomer fraction, f , were chosen to cover the whole range of NaPSS behavior in water. In other words, the lowest value of f was 0.47 which is very close to the limit of solubility for this polymer ($f = 0.42$). The highest value in study was 0.92, corresponding to a much more hydrophilic polymer (recall that at $f = 1$ the behavior is that of a fully hydrophilic polyelectrolyte). All of our experiments were carried out at room

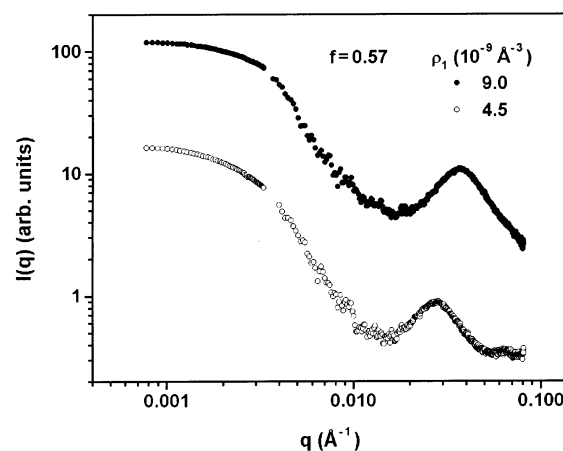


Figure 1. Full spectrum of scattered intensity, $I(q)$, plotted as a function of wavevector q for aqueous solutions of NaPSS. Keeping constant the charge content, $f = 0.57$, two different number densities are studied, 9.0 and $4.5 \times 10^{-9} \text{ \AA}^{-3}$ (corresponding to 15 and 7.5 g/L, respectively). The intensity curve corresponding to the most concentrate sample was multiplied by a factor of 3.

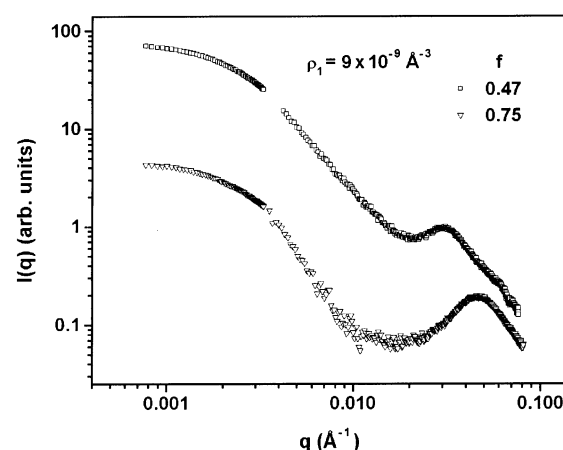


Figure 2. Scattered intensity, $I(q)$, as a function of q for polyelectrolyte solutions of two different charge contents, $f = 0.47$ (hydrophobic polymer) and $f = 0.75$ (hydrophilic one). The number density was kept constant ($\rho_1 = 9 \times 10^{-9} \text{ \AA}^{-3}$).

temperature without added salt. Figures 1 and 2 show scattered intensity spectra, $I(q)$, as a function of the wavevector magnitude q ($q = 4\pi n_s \sin(\theta/2)/\lambda_0$, with θ being the observation angle and n_s the solvent refractive index), for different polyelectrolyte systems. Intensity spectra combine previous SLS data⁹ (small wavevectors) and new SAXS data. SLS data were taken as a reference to join both techniques at their overlap point.

Results and Discussion

The combined measurements covered a q range of two decades, i.e., from 7.7×10^{-4} to 0.081 \AA^{-1} . Some general characteristics are present in these systems. A correlation peak can be noticed in the high wavevector part of the curves (see Figures 1 and 2). Such a peak is a distinctive feature of all polyelectrolyte systems at low ionic strength, either hydrophilic^{16,4} or hydrophobic.^{10,11} For lower q values ($q \lesssim 0.02 \text{ \AA}^{-1}$), a sharp upturn is developed for almost 2 orders of magnitude in scattered intensity. Let us first mention some known structural differences between hydrophilic and hydrophobic polyelectrolytes in this f range. For hydrophilic polyelectrolytes, the position q^* and the shape of the main peak remain unchanged for different values of f beyond the MO condensation threshold.⁴ For each f in the semidilute regime, q^* scales as ρ_1^α with $\alpha =$

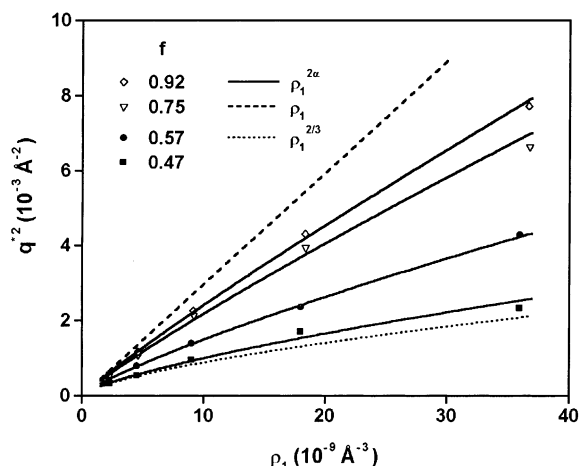


Figure 3. Square of the position of the main peak, q^{*2} , plotted versus ρ_1 for two hydrophobic polyelectrolytes ($f = 0.47$ and 0.57) and two hydrophilic ones ($f = 0.75$ and 0.92). Continuous lines are fits to the function $q^{*2} = A\rho_1^{2\alpha}$, with A and α being fitting parameters. Limiting functions $q^{*2} \sim \rho_1$ and $q^{*2} \sim \rho_1^{2/3}$ are plotted too (proportionality constants A were taken from the nearest cases).

$1/2$, as predicted by the isotropic model of de Gennes et al.²¹ This power law has been extensively verified for flexible hydrophilic polyelectrolyte solutions.²² However, the same scaling law is observed as well in the case of entangled charged rod systems.²³ For the case of very dilute polyelectrolyte or rod systems²³ and also in colloids, the known scaling exponent is $\alpha \approx 1/3$, related to a simple 3D dilution of scattering objects. On the other hand, hydrophobic polyelectrolytes, like NaPSS, have a completely different behavior. Essafi et al.^{10,11} first observed that α increases from $1/3$ to $1/2$ as f increases. A NaPSS of molecular weight 2.5×10^5 with a rather high polydispersity ($M_w/M_n \approx 2$) was used. In our experiments, with a monodisperse polymer of a higher molecular weight (6.7×10^5), we confirm the continuous variation of the scaling exponent α as a function of f . The highest value of α is 0.46 , corresponding to $f = 0.92$, whereas the lowest is 0.36 , and it belongs to the most hydrophobic polymer in study, $f = 0.47$. In Figure 3, we plot q^{*2} (to enhance differences) as a function of ρ_1 for polyelectrolytes of four representative charge contents (0.47 , 0.57 , 0.75 , and 0.92), together with the corresponding fit curves $q^{*2} \sim \rho_1^{2\alpha}$. As a comparison, we also plot the limiting curves $q^{*2} \sim \rho_1$ and $q^{*2} \sim \rho_1^{2/3}$. In the same figure, it can be noticed that for a fixed value of ρ_1 , q^{*2} (and then q^*) is smaller for lower values of f . This result can be characterized in terms of a correlation length $\xi \equiv 2\pi/q^*$, which indicates that correlated objects are farther away when the system becomes more hydrophobic. All previous evidences^{3,9,10,11,13} indicate that this effect is not only due to simple electrostatic interactions but it is also related to changes in the local configuration of the chains. Let us recall a relevant finding from our previous work.⁹ Despite the expected small numerical value of the low wavevector static structure factor, there is an important scattered intensity in the same limit ($q \rightarrow 0$). Furthermore, there is a huge difference in scattered intensity between polymers of various charge contents. In agreement with the PN model, our results were interpreted in terms of the presence of globular instabilities or pearls, whose size depends on the degree of hydrophobicity. Structural changes such as these should then be noticeable in the full spectrum. Thus, the effect of changes in number density and charge content have been analyzed in a broader wavevector range. As a reference, in Figure 1, we present the scattering intensity curves of a polymer of charge content $f = 0.57$, for two chain number

densities, 9.0 and $4.5 \times 10^{-9} \text{ \AA}^{-3}$. Both curves have clear similarities and some small differences that can be quantified. First, the position of the peak, q^* , is slightly shifted as a function of the decreasing number density, i.e., 0.0373 and 0.0283 \AA^{-1} . There is a relative difference of 32% between both values. On the other hand, the ratio $I(0)/\rho_1 I(q^*)$ is a distinctive feature of each spectrum, relating information of the scattered intensity at different scales, namely, the thermodynamic limit ($q = 0$) and the correlation peak. For the systems of Figure 1, the $I(0)/\rho_1 I(q^*)$ values are very close, i.e., 19.4 and 22.8 , corresponding to the chain number densities 9.0 and $4.5 \times 10^{-9} \text{ \AA}^{-3}$, respectively. Figure 2 differs drastically from Figure 1. Here, keeping fixed ρ_1 , we compare two polyelectrolytes of different charge contents, $f = 0.47$ and 0.75 . Even if both curves have common features, their shape is certainly not alike. The value of q^* equals 0.0309 \AA^{-1} for the 0.47 polymer and 0.0462 \AA^{-1} for the 0.75 case. The relative difference of 50% between these two peak positions contrasts with the 32% difference of the systems of Figure 1. Moreover, the ratio $I(0)/\rho_1 I(q^*)$ is 81.5 for the most hydrophobic polyelectrolyte (0.47) and only 24.3 for the hydrophilic one (0.75). Note that, in both figures, the change of ionic strength is similar. From the comparison between these two figures, it becomes clear that the ratio $I(0)/\rho_1 I(q^*)$, as well as the rest of the spectrum, strongly depend on f and weakly on the density. Summarizing all of the evidences just discussed, it is possible to say that there are important changes in the structure of hydrophobic polyelectrolytes as a function of the charge content. As expected, such changes are noticeable in all regions of the scattering spectrum. Quantities such as α , ξ , and the previously measured $I(0)$ point out that the most hydrophobic polyelectrolyte has a closer behavior to a globular system, whereas the most hydrophilic one should be similar to the classic polyelectrolyte solution. The remaining polyelectrolytes must have an intermediate behavior between these two extreme situations. Previous SAXS and SANS measurements performed in a limited wavevector range pointed to similar conclusions.^{10,11,13} Let us now provide some insights into the shape of hydrophobic polyelectrolytes. To determine the organization of the solutions, we performed a fit to the first 10 or 12 experimental points (in the low wavevector region) with a limited general expansion. This fit allowed us to obtain an apparent radius of gyration, R_g^{app} , which is closely related to the effective radius of gyration, R_g^{eff} , of our previous work.²⁴ R_g^{app} is then used as an input parameter in three known models that might describe the system,²⁵ namely, the Debye function for a Gaussian shape, i.e., $I_D(q) \sim 2/y^2[e^{-y} - 1 + y]$ with $y = (qR_g^{\text{app}})^2$. The form factor of a rigid rod, $I_r(q) \sim 2/x \int_0^x 1/\eta \sin \eta d\eta - [2/x \sin(x/2)]^2$ with $x = \sqrt{12}qR_g^{\text{app}}$, and the same for a sphere, $I_s(q) \sim 9/v^6(\sin v - v \cos v)^2$ with $v = \sqrt{(5/3)qR_g^{\text{app}}}$. In Figure 4, we present a comparison of the three fit models to the experimental data of two polymers of different charge contents (0.47 and 0.75). Clearly, for intermediate wavevectors, $I_s(q)$ and $I_r(q)$ are very far from the experimental data. On the other hand, both cases seem to be properly described by the Debye function with small differences probably because of many body effects. Our results are consistent with the experimental results of Ermi and Amis,¹⁶ who also found a Gaussian shape for the case of strictly hydrophilic polyelectrolytes. The complete scattering profile allowed us to determine two characteristic lengths. At low angles, R_g^{eff} (or R_g^{app}) is extracted, whereas ξ comes from the wider angles pattern. An important finding is that R_g^{eff} and the correlation length ξ are closely related for the most hydrophobic systems in study. As shown in Table 1, for three markedly hydrophobic polymers ($f = 0.47$, 0.50 , and 0.57),

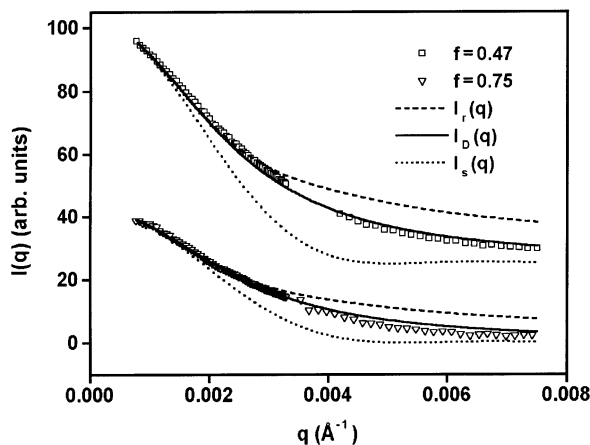


Figure 4. Scattered intensity, $I(q)$, plotted as a function of q for two different charge contents, $f = 0.47$ and 0.75 , and a constant number density ($\rho_1 = 9 \times 10^{-9} \text{ Å}^{-3}$). As a comparison, three different models are plotted too, namely, the Debye function, $I_D(q)$, and the functions describing a rigid rod, $I_r(q)$, and a sphere, $I_s(q)$ (see text).

TABLE 1: Comparison of the Effective Radius of Gyration, R_g^{eff} , and the Correlation Length, $\xi \equiv 2\pi/q^*$, for Three Different Hydrophobic Polyelectrolytes ($f = 0.47, 0.50$, and 0.58)^a

ρ_1 (10^{-9} Å^{-3})	$f = 0.47$		$f = 0.50$		$f = 0.57$	
	R_g^{eff} (Å)	R_g^{eff}/ξ	R_g^{eff} (Å)	R_g^{eff}/ξ	R_g^{eff} (Å)	R_g^{eff}/ξ
9.0	659	3.2 ± 0.2	529	2.8 ± 0.2	411	2.4 ± 0.1
4.5	812	3.1 ± 0.2	672	2.8 ± 0.3	545	2.4 ± 0.1
2.3	1006	3.0 ± 0.2	793	2.5 ± 0.2	780	2.6 ± 0.1

^a In each case, the comparison is done for three different number densities.

TABLE 2: Same as Table 1 for the Case of the Three Most Hydrophobic Polyelectrolytes in the Study ($f = 0.72, 0.75$, and 0.92)

ρ_1 (10^{-9} Å^{-3})	$f = 0.72$		$f = 0.75$		$f = 0.92$	
	R_g^{eff} (Å)	R_g^{eff}/ξ	R_g^{eff} (Å)	R_g^{eff}/ξ	R_g^{eff} (Å)	R_g^{eff}/ξ
9.0	434	3.1 ± 0.1	655	4.7 ± 0.3	755	5.7 ± 0.2
4.5	572	3.0 ± 0.1	561	2.9 ± 0.2	784	4.3 ± 0.3
2.3	611	2.4 ± 0.1	719	2.8 ± 0.1		

the ratio R_g^{eff}/ξ remains constant as a function of ρ_1 , within experimental errors. On the other hand, for three hydrophilic polyelectrolytes ($f = 0.72, 0.75$, and 0.92) the ratio R_g^{eff}/ξ varies in a systematic way with molecular parameters. As the charge content f increases to the saturation value 1, R_g^{eff}/ξ progressively becomes different from a constant value, see Table 2. For the most hydrophilic polyelectrolyte ($f = 0.92$), we recover a result found by Ermi and Amis,¹⁶ where R_g^{eff} is now a constant as a function of ρ_1 , whereas ξ has a scaling exponent close to $1/2$. As a reference, the contour length of our polymers is $L \approx 14500 \text{ Å}$, according to the degree of polymerization. The Debye–Hückel screening length $\kappa^{-1} \equiv (4\pi l_B \rho_2)^{-1/2}$ (ρ_2 is the counterion number density⁹) takes values between 38 and 120 Å , for all of the systems in the study. Even if it is clear that polyelectrolyte solutions (either hydrophilic or hydrophobic) adopt a Gaussian organization at large distances, it is not possible to provide a definitive description of the behavior of individual chains. Let us mention that, based on general arguments, Diamant and Andelman²⁶ proposed that a charged polymer chain should be described by Gaussian statistics if it develops intrachain aggregates (pearls, in our case). This is the so-called partial collapse conjecture which has been verified in other systems.²⁶ For the systems in study, we extracted an

effective total persistence length, l_t , from the equation,²⁷ $(R_g^{\text{eff}})^2 = l_t^2[2(\exp(-L/l_t) - 1 + L/l_t)(L/l_t)^{-2} - 1 + L/3l_t]$ and the values of R_g^{eff} of Table 1. In all cases, l_t is at least ~ 70 times (almost 2 orders of magnitude) smaller than L . This result indicates the possible existence of individual chains of Gaussian shape. The problem is still the determination of the degree of entanglement between polymers of different charge contents. On one hand, the numerical simulations of Micka et al.⁸ point out that, at least for much smaller polyelectrolyte chains in poor solvent conditions, the agglomeration of two chains is unfavorable. This effect is related to the significant presence of excluded volume interactions. From the experimental point of view, Essafi¹¹ showed that only very hydrophobic NaPSS chains ($f = 0.27$) close to the solubility limit can be treated as completely isolated, colloid-like particles. In our experiments, an interpretation of R_g^{eff} as the physical size of polymer chains is possible only for the most hydrophobic ones, as explained in the following lines. In a recent publication, Nishida et al.²⁸ found that the electrostatic persistence length of flexible polyelectrolytes can be described by means of a master curve. Such a curve results from putting together a collection of experimental data obtained through different techniques. As a result, these authors proposed that l_e^{mc} (in Å) and the ionic strength I (in mol/L), are related by the empirical equation $l_e^{\text{mc}} = 7.5(\rho_2 + 2 \times 10^{-4})^{-1/2}$ (in our case, $I = \rho_2$). The total persistence length is then $l_t^{\text{mc}} = l_e^{\text{mc}} + l_0$, with l_0 being the intrinsic persistence length ($l_0 \approx 10 \text{ Å}$, for polystyrene). We found a quite good agreement between l_t^{mc} and l_t only for the most hydrophobic and dilute systems (e.g., if $f = 0.47$, $l_t^{\text{mc}} = 208$, and $l_t = 219 \text{ Å}$, for $\rho_1 = 2.3 \times 10^{-9} \text{ Å}^{-3}$; $l_t^{\text{mc}} = 155$ and $l_t = 140 \text{ Å}$, for $\rho_1 = 4.5 \times 10^{-9} \text{ Å}^{-3}$). The agreement progressively deteriorates when f or ρ_1 are increased. There is still an important point that has to be clarified. If the polymer chains of the most hydrophobic and dilute systems are isolated (or just slightly entangled), the mean distance between centers of mass of neighbor polyelectrolytes (denoted as d) should correspond to the correlation length ξ . This supposition turns out to be incorrect. Taking $d \equiv \rho_1^{-1/3}$, such distance is clearly larger than ξ (more than two times). On the other hand, the constant ratio R_g^{eff}/ξ suggests that ξ comes from a prevailing contribution of intrachain correlations due to the presence of highly correlated objects (charged pearls and strings) inside the chains. For $f = 0.47$ (see Table 1), the increasing values of R_g^{eff} , as a function of the decreasing number densities, seem to be in the right direction. In other words, as the screening decreases, the interaction becomes longer ranged and thus the chain is more stretched. For the most hydrophilic polymers in the study (see Table 2), the excluded volume interactions are weaker because the hydrophobic domains (or pearls) are much smaller.⁹ Such polyelectrolytes are certainly more entangled with a more important contribution of interchain correlations (for the $f = 0.92$ case, R_g^{eff} is now a constant as a function of number density). For the most hydrophilic polyelectrolytes, a further interpretation of the experimental results seems unrealistic for the moment.

Conclusions

We have shown experimental evidence that hydrophobic polyelectrolytes of different charge contents exhibit structural changes in all relevant regions of the scattering spectrum. Such changes are related to the appearance of pearl-like structures which depend on the degree of hydrophobicity of the chain. By fitting our experimental data with some known form factor functions, we were able to conclude that the different polyelec-

trolyte solutions have a Gaussian shape, at least at large distances. We also studied the behavior of two characteristic lengths extracted from the full relevant spectrum, i.e., the effective radius of gyration R_g^{eff} and the correlation length ξ (obtained from the position of the correlation peak). For the most hydrophobic polymers, the ratio R_g^{eff}/ξ remained constant as a function of the chain number density, up to experimental errors. Taking into account excluded volume effects, this result suggests that the hydrophobic chains are mainly isolated. This result is consistent with a total persistence length determined in two different ways. On the other hand, the ratio R_g^{eff}/ξ is no longer a constant for the most hydrophilic polyelectrolytes in study. This property should be a consequence of the fact that such polyelectrolytes are more likely to overlap in comparison with the most hydrophobic ones, for a given number density. Finally, we can say that the whole spectrum of scattered intensity is not due to artifacts but it reflects the physical properties of the system.

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