On the Distribution of Hydrophilic Polyelectrolytes and their Counterions around Zwitterionic Micelles: the Possible Impact on the Charge Density in Solution

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Compared to the $\mathcal{L}(1,60)$ cases, for $\mathcal{LS}(1,60)$ systems the monomers distributions (top panel in Figure 1) display a lower peak and a marked shoulder due to the star-like structure that keeps the majority of the monomers distant from the micellar corona. A shorter tail is also displayed by $\mathcal{S}(6,10,\mathrm{SBS})$. The average properties shown suggest a lower propensity for the star-like species to be adsorbed onto the micelles, together with a lower value for the osmotic coefficient that is typical of this denser species[1].

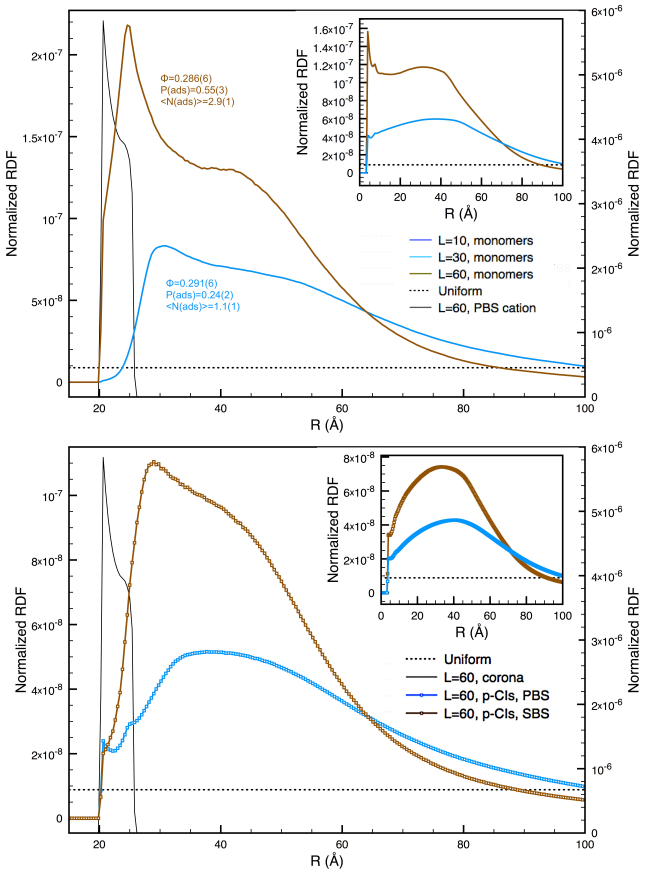

Figure S1: Radial and pair distribution functions for $\mathcal{S}(6,10,\mathrm{SBS})$ and $\mathcal{S}(6,10,\mathrm{PBS})$. The dashed line represent the distributions for uniformly distributed species; the right axis related to the zwitterion anion distributions. Top: distributions from the micelle centre for the charged monomers, together with the results for the osmotic coefficient Φ, the probability of polyelectrolyte adsorption, and the average number of adsorbed monomers; the distributions for the monomer/cationic moiety pairs are also shown in the inset. For the isolated $\mathcal{S}(6,10)$, $\Phi = 0.32(2)$. Bottom: distributions from the micelle centre for the p-CIs; the distributions for the p-CIs/$\mathrm{A_{SBS}}$ pairs are also shown in the inset.

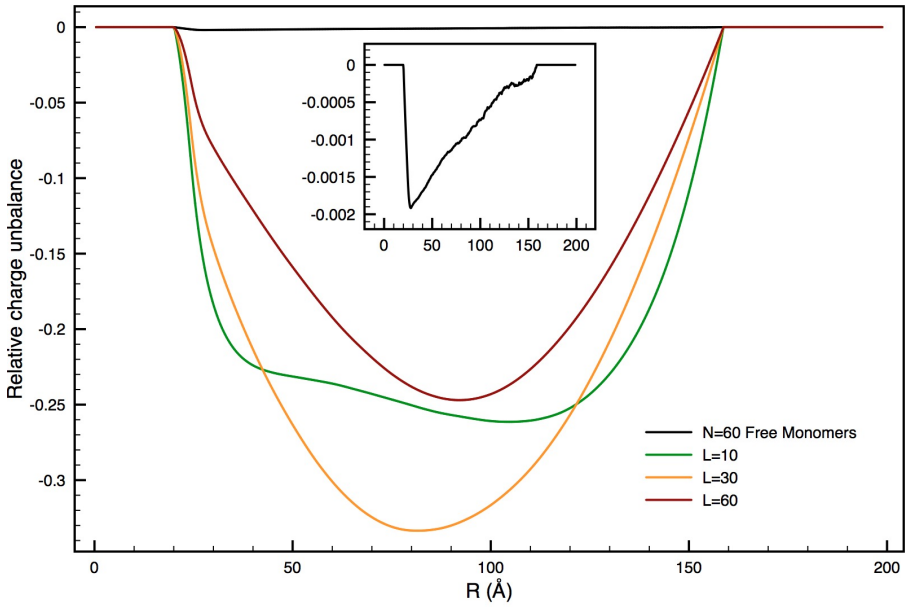

Figure S2: Relative charge unbalance within a distance R from the micelle center, $(4\pi \int_0^R [\rho_+(r) - \rho_-(r)]r^2 \mathrm{d}r)/N_{\mathrm{mono}}$, for the $\mathcal{L}(1, L, \mathrm{SBS})$ and free monomers cases discussed in the main text. Here, $\rho(r)$'s are the local concentrations of polyanion monomers and p-CIs. Notice the two orders of magnitude difference in this quantity for the polymeric and simple ion (also in the inset) systems. The presence of a substantially non-compensated negative charge in the vicinity of the micelle when the polyanions visit the corona region is made clearly evident by the behaviour at short R values.

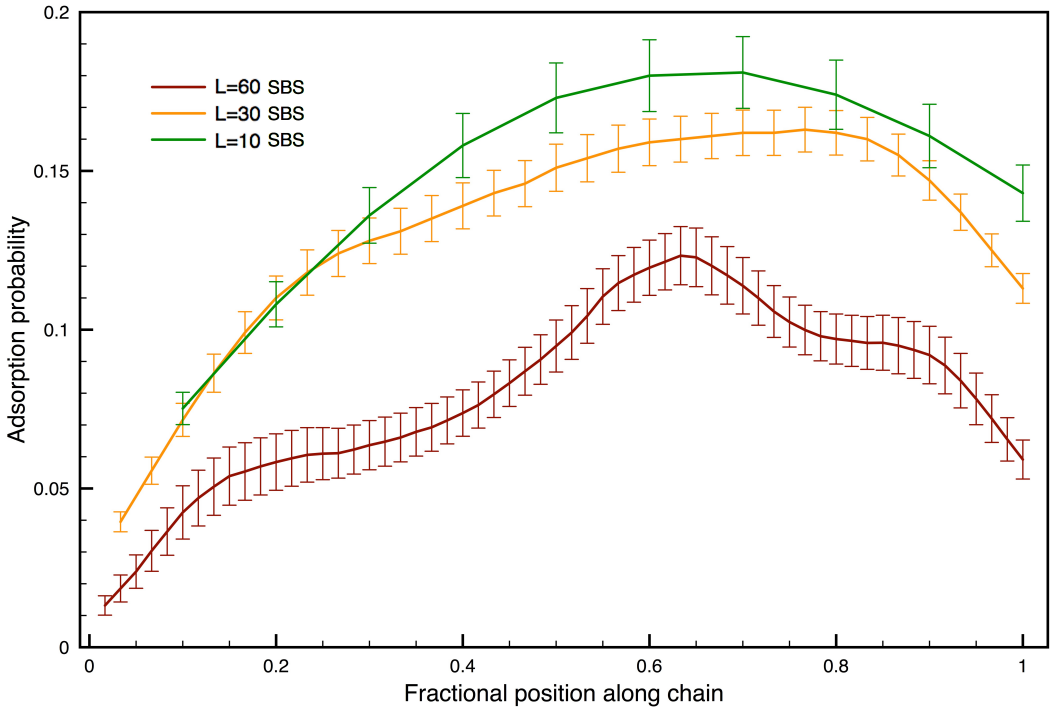

Figure S3: Adsorption probability on SBS micelles for anionic monomers versus their fractional position along linear chains with $L = 10$, 30, and 60.

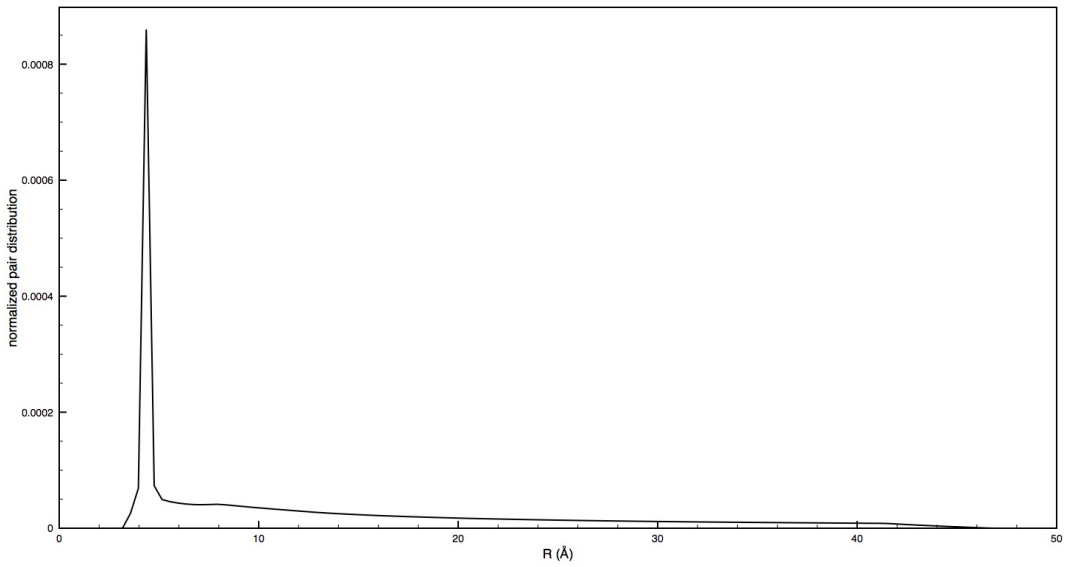

Figure S4: Normalized pair distribution function for the A_{SBS}/C_{SBS} couple when external electrolytes were absent. Notice the intense peak at short R values representative of the pair interaction strength, which remains unchanged even after adding 60 monomer/p-CI pairs.

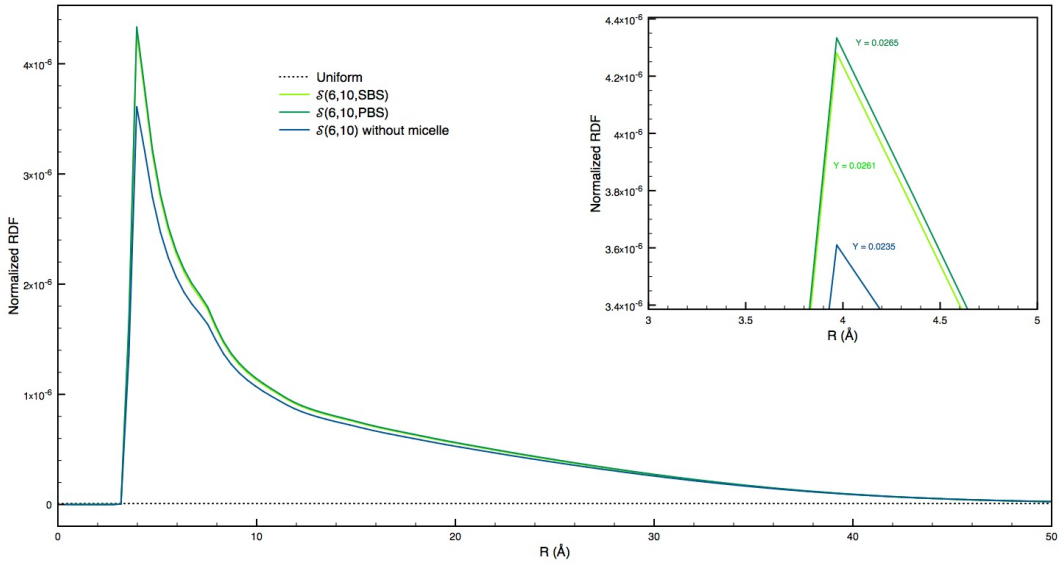

Figure S5: Normalized distributions for the monomers/p-CIs pairs ($\lambda(r)$) obtained simulating $\mathcal{S}(6, 10, \mathrm{SBS})$ and $\mathcal{S}(6, 10, \mathrm{PBS})$ systems and the isolated polyelectrolytes $\mathcal{S}(6, 10)$ (noM). The inset shows a magnificated view of the peak region; the "condensation index" γ for each case is also provided in the vicinity of the appropriate distributions with matching colors.

In agreement with the results in Figure 1, the condensation index γ appears higher than the one for $\mathcal{L}(1, 60)$. Apart from this, a lower Φ (roughly 10%) is found for the micelle/polyelectrolyte complexes than for the isolated polyelectrolytes; this agrees well with the relative γ values and suggests some form of synergy between micelles and polyelectrolyte in maintaining p-CIs localized on polymer arms.

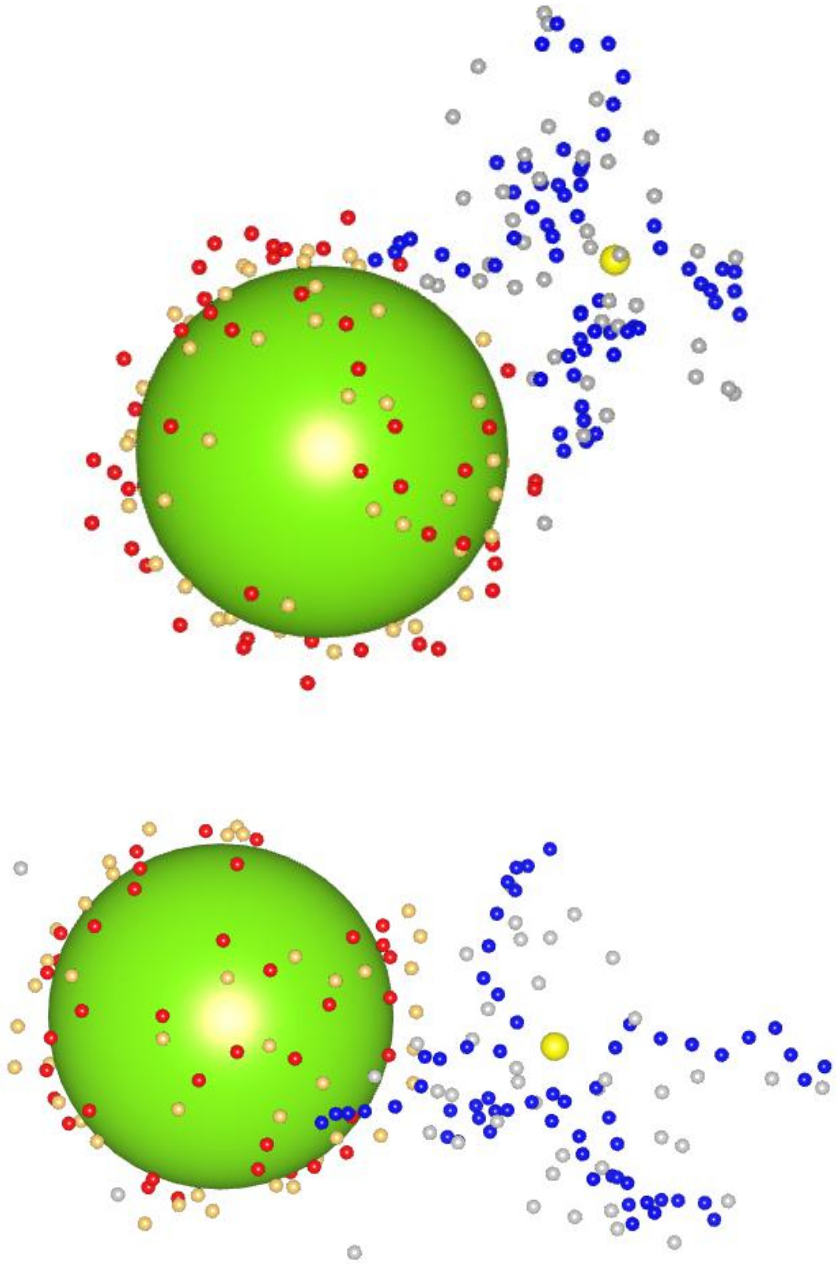

Figure S6: Adsorbed configurations sampled for the $\mathcal{S}(6, 10, \mathrm{SBS})$ (top) and $\mathcal{S}(1, 60, \mathrm{PBS})$ (bottom) systems. Color coding: light blue, negative monomers; silver, p-CIs; red, SBS and PBS negative moieties; light orange, SBS and PBS positive moieties; yellow, neutral nucleus. The impenetrable micellar core is depicted in green.

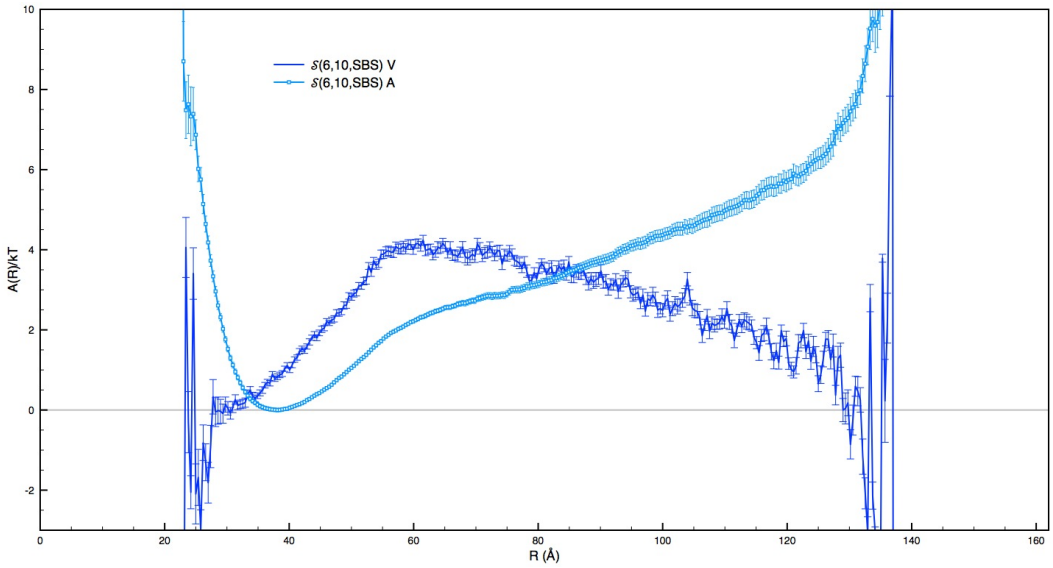

Figure S7: Helmholtz ($A(R)$) and potential ($\bar{V}(R)$) energy profiles along the P/M centers of mass distance for $\mathcal{S}(6, 10, \mathrm{SBS})$ system.

References

1. M. Mella, A. Tagliabue, L. Mollica, and L. Izzo, J. Colloid Interf. Sci. **560**, 667 (2020), ISSN 0021-9797, URL `http://www.sciencedirect.com/science/article/pii/S0021979719312317`.