Multivalent counterions accumulate in star-like polyelectrolytes and collapse the polymer in spite of increasing its ionization.

Electronic Supplementary Information

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I. TITRATION CURVES

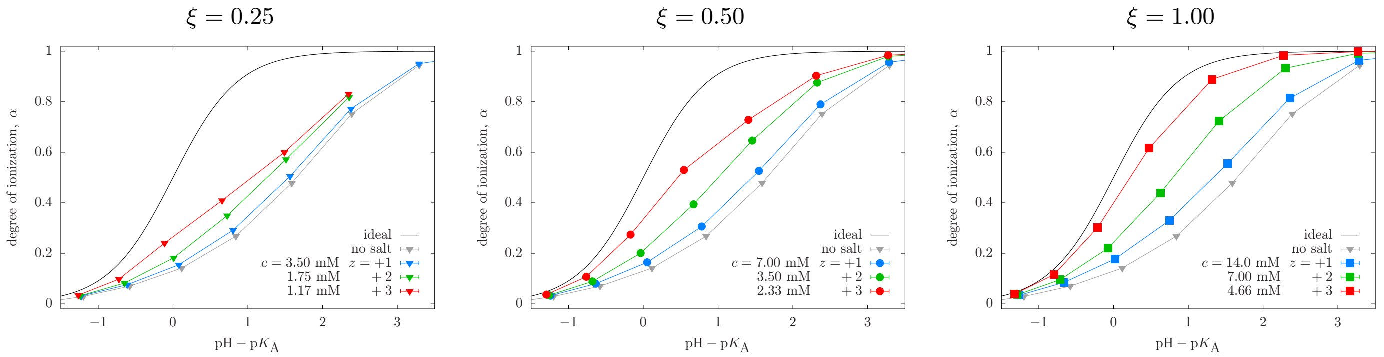

FIG. S1. Titration curves of 5 × 19 star-like weak polyelectrolyte in presence of salt at constant charged ratios.

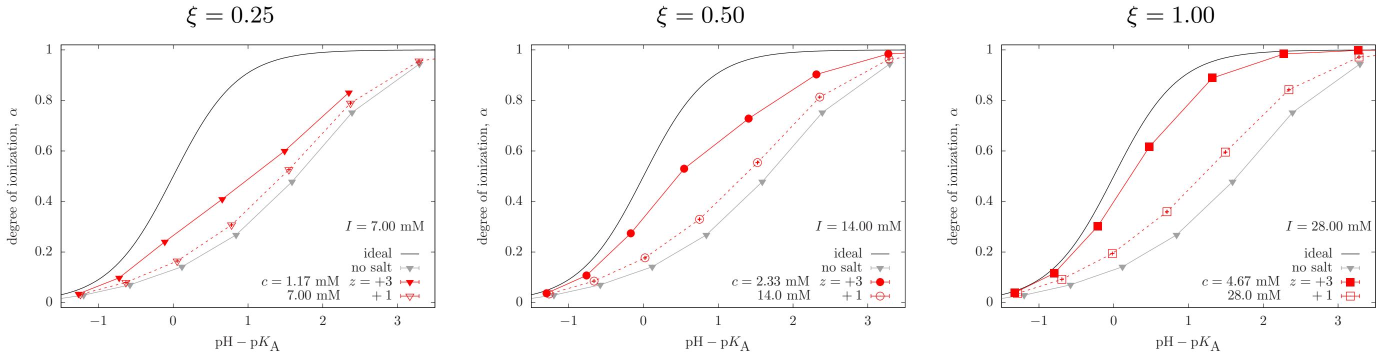

FIG. S2. Titration curves of 5 × 19 star-like weak polyelectrolyte in presence of trivalent salt at constant charged ratios compared to uni-uni counterion systems.

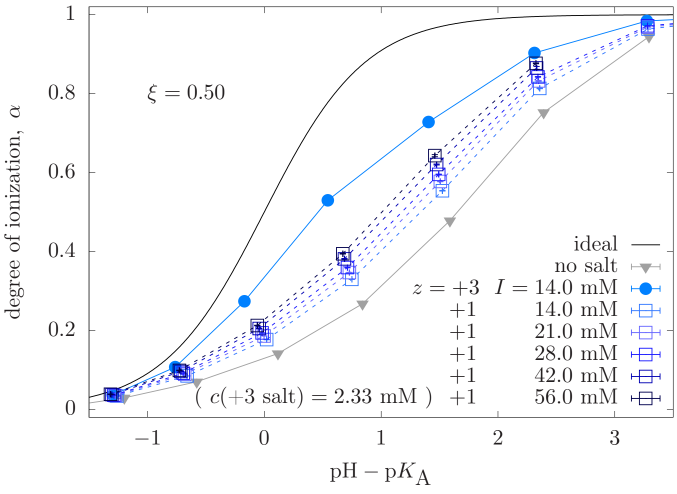

FIG. S3. Titration curves of 5 × 19 star-like weak polyelectrolyte in presence of multi- and monovalent salt. Charge ratio of solution with multivalent salt was held constant $\xi = 0.50$. Plots show also series of titration curves for monovalent salt of various ionic strengths to support that enforced ionization is not just a matter of ionic strength, but valency itself.

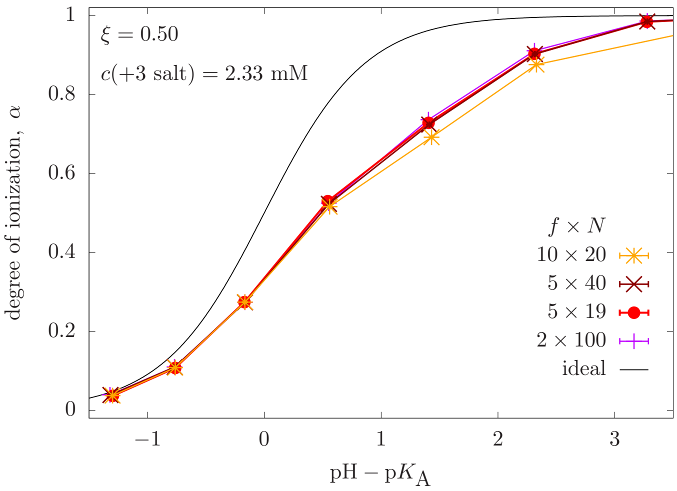

FIG. S4. Titration curves of star-like weak polyelectrolyte of different architectures in presence of multivalent salt. Charge ratio of solution with multivalent salt was held constant $\xi = 0.50$.

II. RADIUS OF GYRATION

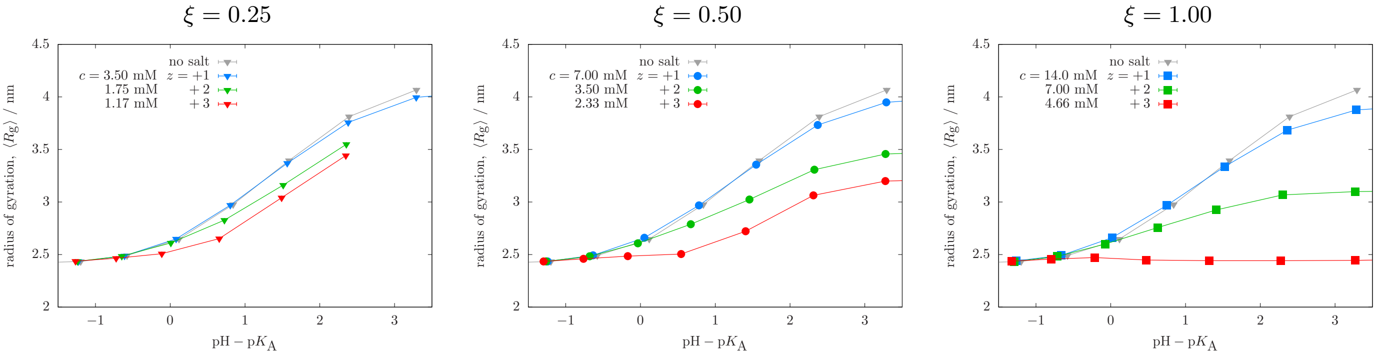

FIG. S5. Radius of gyration of 5 × 19 star-like weak polyelectrolyte in presence of salt at constant charged ratios.

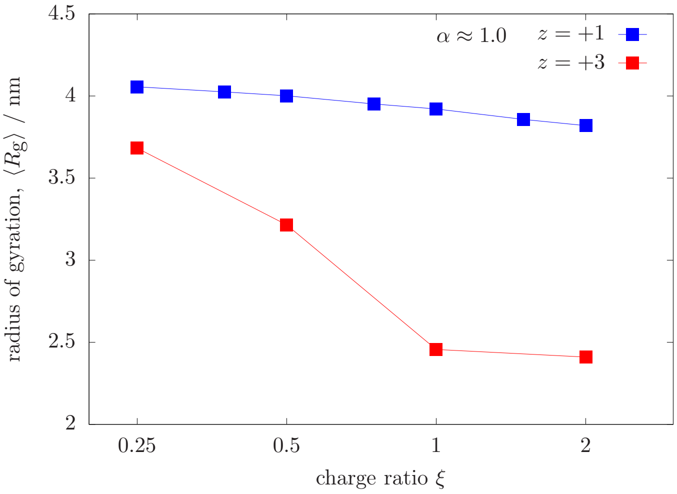

FIG. S6. Radius of gyration of 5 × 19 star-like weak polyelectrolyte at full ionization, as a function of charge ratio between the polyelectrolyte and the additional ions. This representation demonstrates the agreement of our observations with the experiments by Mei et.al. [1].

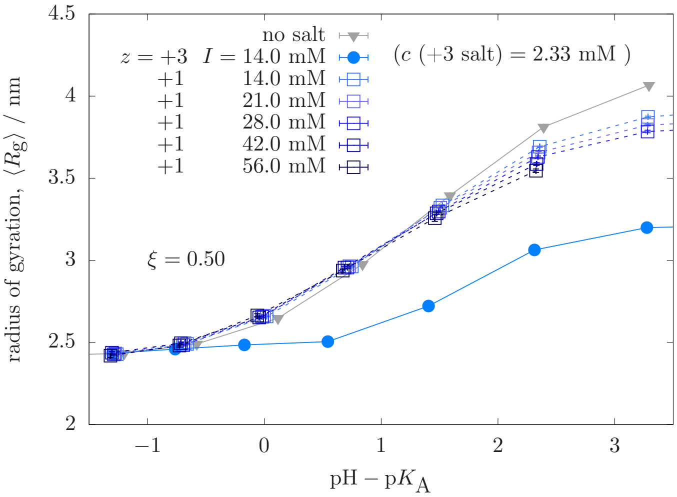

FIG. S7. Radius of gyration of 5 × 19 star-like weak polyelectrolyte in presence of multi- and monovalent salt. Charge ratio of solution with multivalent salt was held constant $\xi = 0.50$. Plots show also series of curves for monovalent salt of different ionic various to support that conformational changes are not just a matter of ionic strength, but valency itself.

III. DENSITY PROFILES

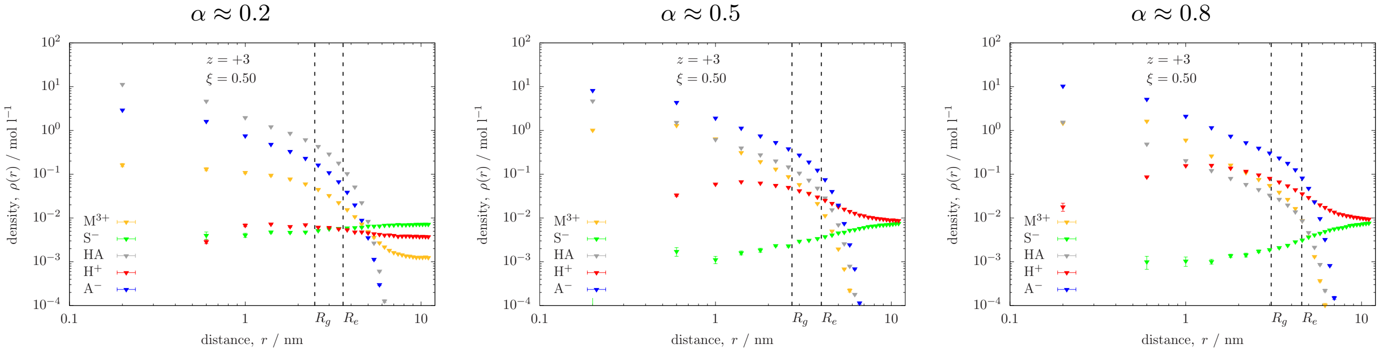

FIG. S8. Density profiles of individual entities from the center of the 5 × 19 star-like weak polyelectrolyte in trivalent salt solution of charge ratio of $\xi = 0.50$ compared at three different degrees of ionization, α.

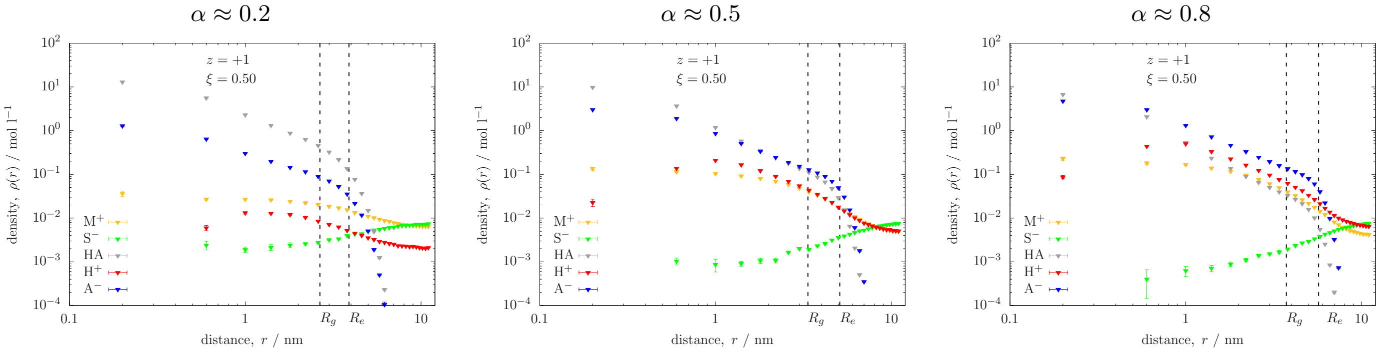

FIG. S9. Density profiles of individual entities from the center of the 5 × 19 star-like weak polyelectrolyte in monovalent salt solution of charge ratio of $\xi = 0.50$ compared at three different degrees of ionization, α.

IV. PARTITION COEFFICIENTS

To obtain the partition coefficients, we defined concentrations inside and outside the star, c^{in} and c^{out}, by integrating the density profile from the centre of the star up to the average end-to-end distance of its arms, R_{e}, that defines the volume that we consider as interior of the star

$$c^{\mathrm{in}} = \frac{1}{V^{\mathrm{in}}} \int_0^{R_{\mathrm{e}}} \rho(r) 4\pi r^2 \mathrm{d}r \tag{S1}$$

$$c^{\mathrm{out}} = \frac{1}{V^{\mathrm{out}}} \left(cL^3 - c^{\mathrm{in}} V^{\mathrm{in}} \right) \tag{S2}$$

where c is the total concentration of the given species in the simulation box of size L; V^{in} and V^{out} are the corresponding volume of the interior and exterior of the star, defined as

$$V^{\mathrm{in}} = \frac{4\pi R_{\mathrm{e}}^3}{3} \qquad V^{\mathrm{out}} = L^3 - V^{\mathrm{in}} \tag{S3}$$

$$\tag{S4}$$

We also tested different definitions of the interior of the star, within a reasonable range around R_{e}, and obtained qualitatively similar results for the ion partitioning (data not shown).

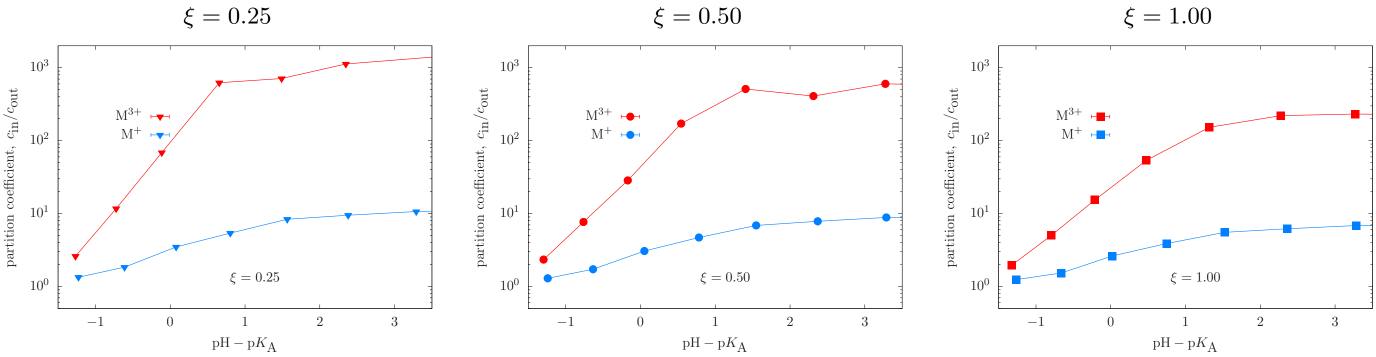

FIG. S10. Partition coefficient of counterions of 5 × 19 star-like weak polyelectrolyte in presence of salt at constant charged ratios.

V. POTENTIALS OF MEAN FORCE

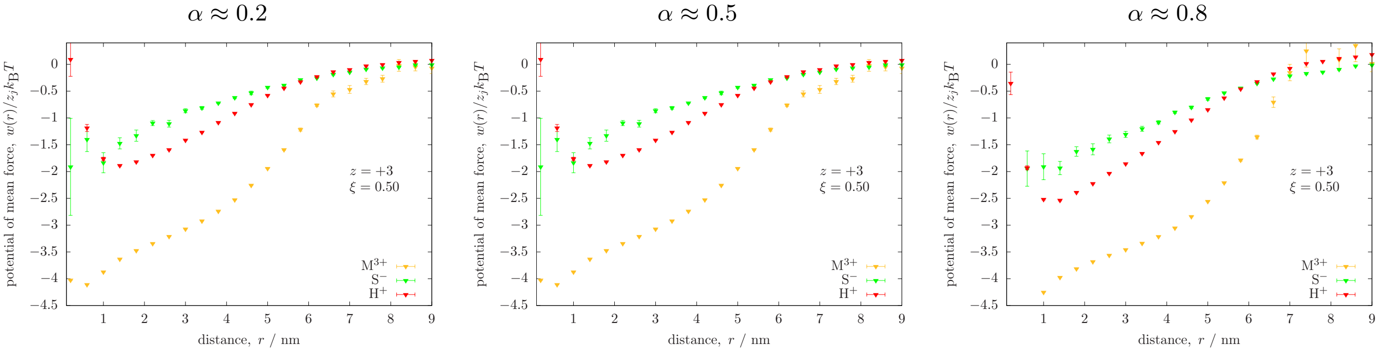

FIG. S11. Potential of mean force felt by coions and counterions as a function of distance, r, from the center of the 5×19 star-like weak polyelectrolyte in trivalent salt solution of charge ratio of $\xi = 0.50$ compared at three different degrees of ionization, α.

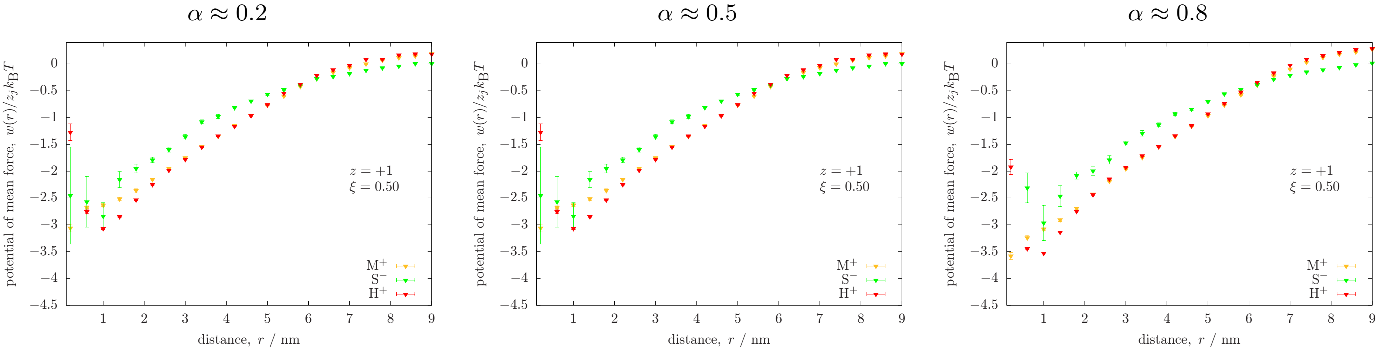

FIG. S12. Potential of mean force felt by coions and counterions as a function of distance, r, from the center of the 5×19 star-like weak polyelectrolyte in monovalent salt solution of charge ratio of $\xi = 0.50$ compared at three different degrees of ionization, α.

[1] Y. Mei, K. Lauterbach, M. Hoffmann, O. V. Borisov, M. Ballauff, and A. Jusufi, Physical Review Letters **97**, 158301 (2006).