Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information for

Persistence Length of Polyelectrolytes with Precisely Located Charges

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Bending constant of the polyelectrolyte chain

Consider a chain with number of bonds *N*, bond length b and fraction of charged monomers α. Chain conformations are described by a set of the unit vectors $\vec{n}_i$ pointing along the chain bonds. The potential energy of a polyelectrolyte chain with the bending energy $k_B T K^0$ in a given conformation includes the bending energy and the electrostatic energy contributions

$$\frac{U_{PE}(\{\vec{n}_i\})}{k_B T} = \frac{K^0}{2}\sum_{i=0}^{N-2}(\vec{n}_i - \vec{n}_{i+1})^2 + \frac{l_B \alpha^2}{2}\sum_{i \neq j}^{N}\frac{\exp(-\kappa r_{ij})}{r_{ij}} \tag{S1}$$

, where r_{ij} is the distance between monomers *i* and *j* on the polymer backbone, κ^{-1} is the Debye screening length. In evaluating contribution of electrostatic interactions we will assume that a radius vector between monomers *i* and *j* along the polymer backbone does not deviate much from a straight line within the range of the exponential decay of the electrostatic potential. This allows us to expand the distance between two monomers as follows

$$r_{ij} = b\sqrt{\left(\sum_{s=i}^{j-1}\vec{n}_s\right)^2} \approx b l_{ij}\left(1 - \left(\frac{1}{4 l_{ij}^2}\sum_{s,s'}(\vec{n}_s - \vec{n}_{s'})^2\right)\right) \tag{S2}$$

where $l_{ij} = |j - i|$ is the number of bonds between *i-th* and *j-th* monomers along the polymer backbone. Using eq S2 we can expand the electrostatic potential energy about a rod-like conformation and obtain a correction to the electrostatic energy of a rod

$$\frac{\Delta U_{elec}(\{\vec{n}_i\})}{k_B T} \approx \frac{l_B \alpha^2}{4b}\sum_{i<j}^{N}\frac{\exp(-\kappa b l_{ij})}{l_{ij}^3}(1 + \kappa b l_{ij})\left(\sum_{s,s'=i}^{j-1}(\vec{n}_s - \vec{n}_{s'})^2\right) \tag{S3}$$

To proceed further we will introduce the normal coordinates for a set of the bond vectors $\{\vec{n}_i\}$

$$\vec{n}_s = \vec{a}_0 + 2\sum_{k=1}^{N-1} \vec{a}_k \cos\left(\frac{\pi k s}{N}\right) \tag{S4}$$

In this representation the n-dependent part of the chain's potential energy is a quadratic function of the mode amplitudes

$$\frac{\Delta U_{PE}(\{\vec{a}_k\})}{k_B T} \approx N\sum_{k=1}^{N-1}\left(K^0\left(\frac{k\pi}{N}\right)^2 + V\left(\frac{k\pi}{N}\right)\right)\vec{a}_k^2 \tag{S5}$$

where we defined

$$V(q) = \frac{2l_B\alpha^2}{b}\sum_{m=1}^{N}\left(1-\frac{m}{N}\right)\frac{\exp(-\kappa b m)}{m^3}(1+\kappa b m)\left(\sum_{s=1}^{m}(m-s)(1-\cos(qs))\right) \tag{S6}$$

We can perform summation over variable s in the r..h.s. of the eq S6 explicitly $\left(m^2 - (1-\cos(mq))/(1-\cos(q))\right)/2$. In the limit of small q, (q<<1) we can transform eq S6 as follows

$$V(q) \approx \frac{l_B\alpha^2 q^2}{12b}\sum_{m=1}^{N}\left(1-\frac{m}{N}\right)\exp(-\kappa b m)(1+\kappa b m)m \approx K_{el}q^2 \tag{S7}$$

Thus, the bending constant K of the polyelectrolyte chains is equal to

$$K = K^0 + K_{el} \approx K^0 + \frac{l_B\alpha^2}{12b}\sum_{m=1}^{N}\left(1-\frac{m}{N}\right)\exp(-\kappa b m)(1+\kappa b m)m \tag{S8}$$

Titration of polypeptoids with precisely placed charged side chains

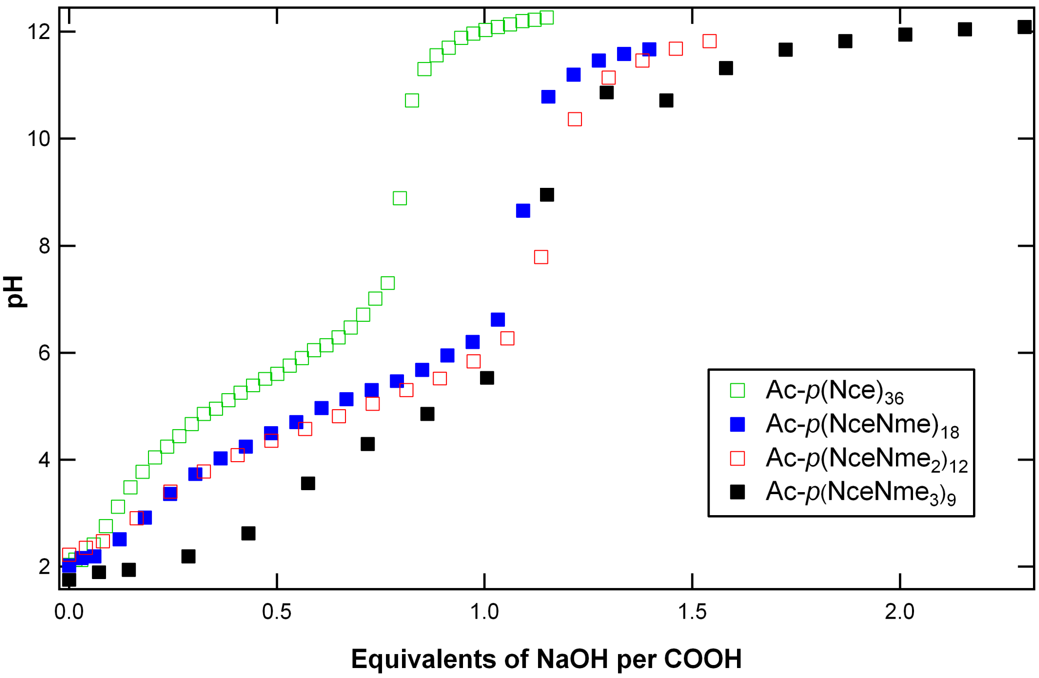

Figure S1. The charge state of each molecule was probed through titrations with sodium hydroxide (NaOH). Sodium hydroxide (0.5 M) was added in increments of 10 μL to each solution (10 mg/mL peptoid in water) while stirring. The solutions were allowed to stabilize for at least one hour before the pH was measured. All titration curves collapse onto the same curve except for Ac-*p*$(Nce)_{36}$.

SANS I vs. q plots

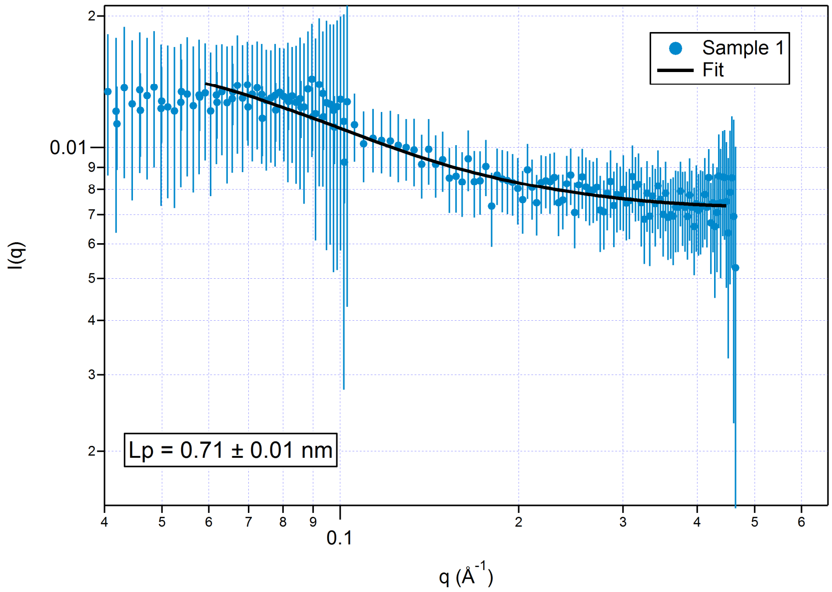

Figure S2. I vs q plot for Ac-*p*(Nce)$_{36}$ with 1x equivalent NaOH in water.

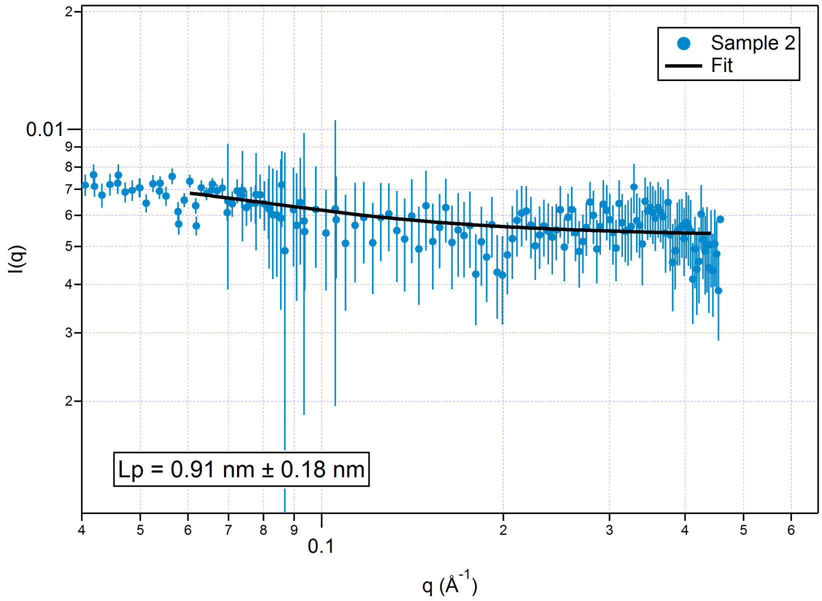

Figure S3. I vs q plot for Ac-*p*(Nce)$_{36}$ with 3x equivalent NaOH in water.

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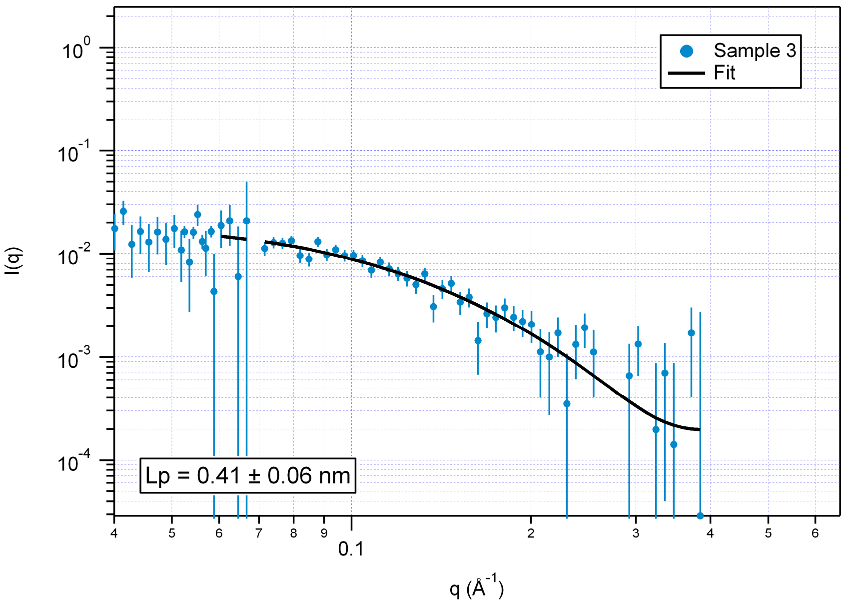

Figure S4. I vs q plot for Ac-*p*(Nce)$_{36}$ with 10x equivalent NaOH in water.

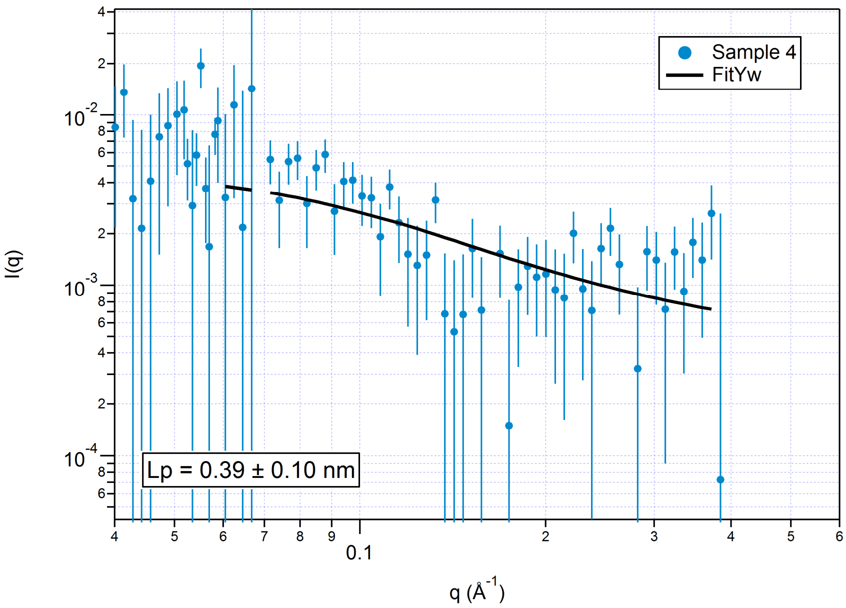

Figure S5. I vs q plot for Ac-*p*(Nce)$_{36}$ with 30x equivalent NaOH in water.

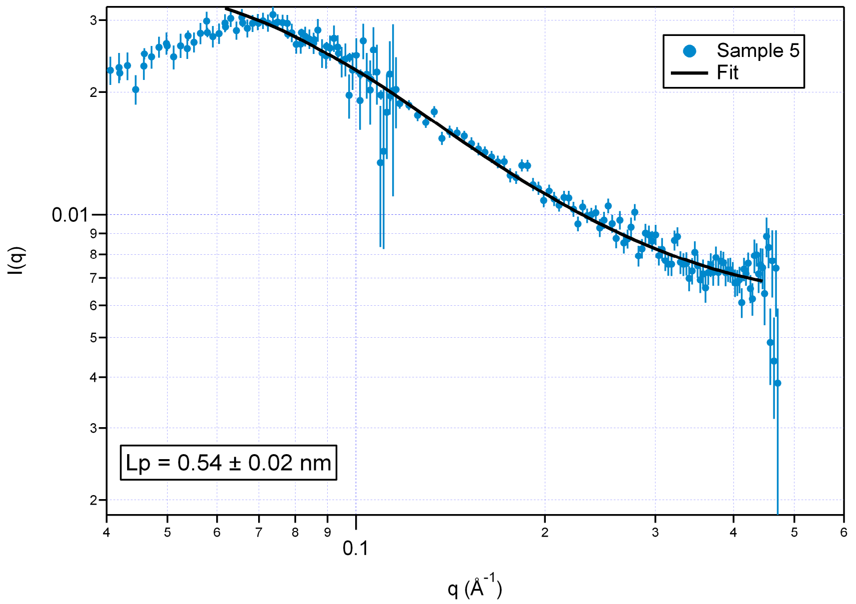

Figure S6. I vs q plot for Ac-*p*(NmeNce)$_{18}$ with 1x equivalent NaOH in water.

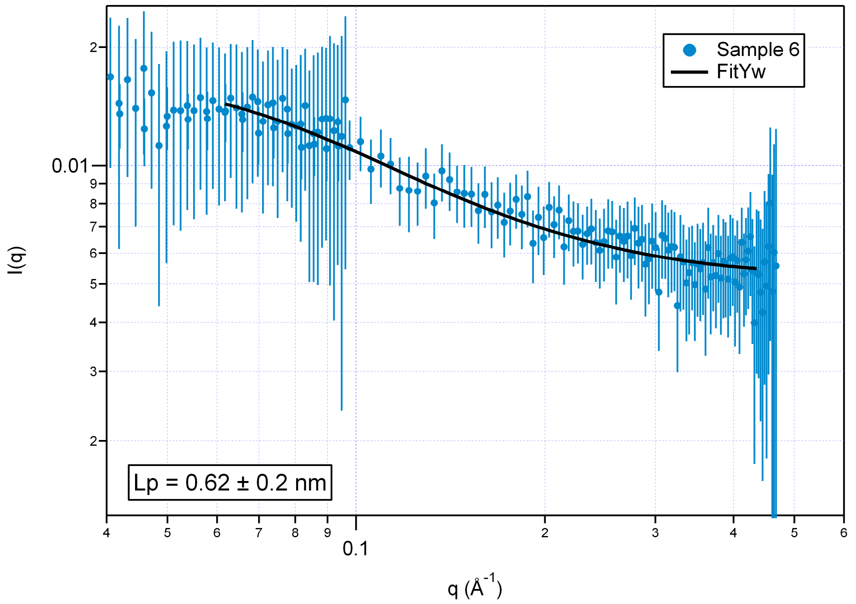

Figure S7. I vs q plot for Ac-*p*(NmeNce)$_{18}$ with 3x equivalent NaOH in water.

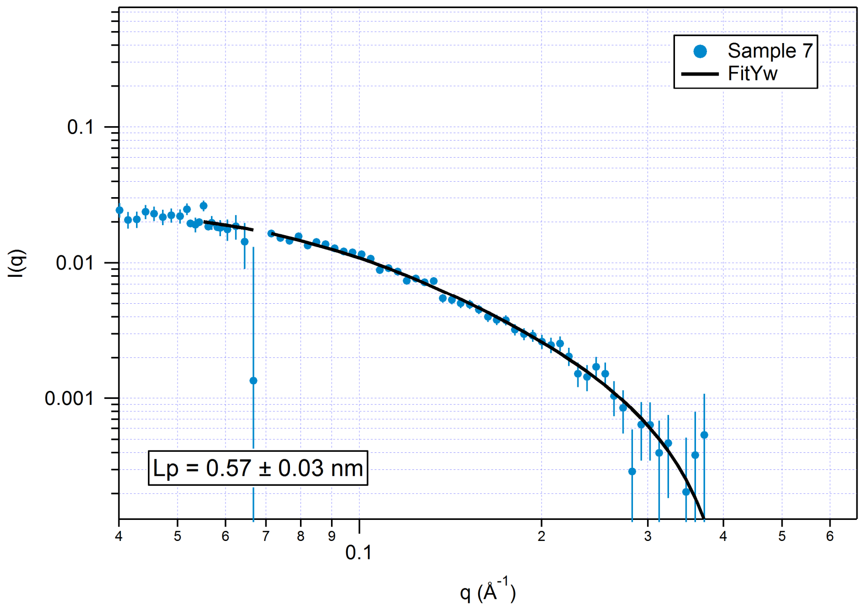

Figure S8. I vs q plot for Ac-*p*(NmeNce)$_{18}$ with 10x equivalent NaOH in water.

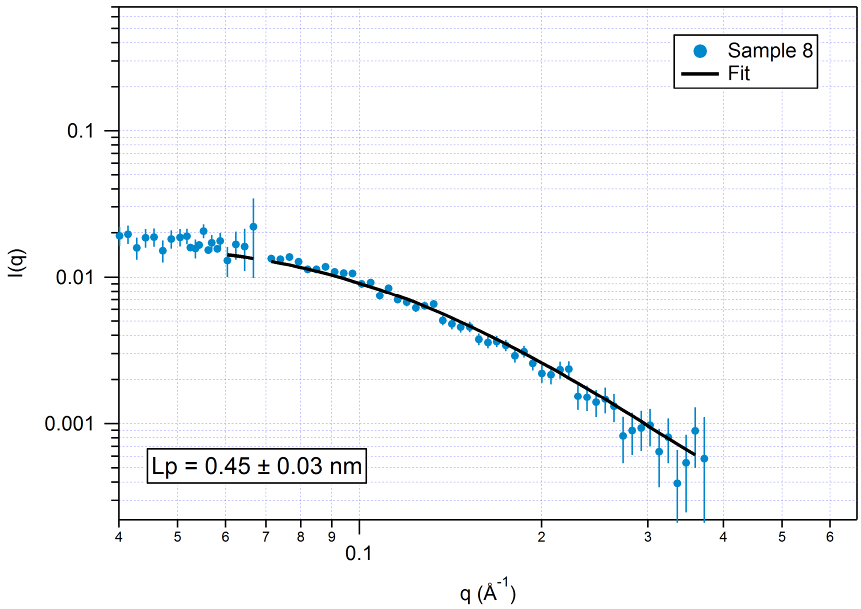

Figure S9. I vs q plot for Ac-*p*(NmeNce)$_{18}$ with 30x equivalent NaOH in water.