Polymer Properties Quiz 3 February 1, 2017

Murnen HK; Rosales AM; Dobrynin AV; Zuckermann RN; Segalman RA (*Soft Matter* **9** 90-8 (2013)) explored the impact of charge density on chain stiffness using polypeptoids (like a polypeptide but with the R group on the nitrogen) with 100% or 50% alternating carbolylic acid groups. They measured the persistence length with SANS.

a) Murnen summarizes the study:

"The results show that at low ionic strength, a polypeptoid in which every monomer contains an ionizable group has a higher persistence length than a polypeptoid in which ionizable and hydrophilic monomers alternate. At high ionic strength, this difference is far smaller, and both polypeptoids show a decrease in persistence length." Explain this behavior based on changes in the Debye screening length with counter ion concentration and the three sizes associated with polyelectrolyte persistence.

b) Murnen further states that: "It is shown that the persistence length has a quadratic dependence on the Debye screening length." $(l_p \sim r_D^2)$. Is this consistent with the functionality described in class for the OSE theory?

Is this consistent with the functionality described in class for the OSF theory?

c) The two polypeptoids studied are shown below with the subscript reflecting the number of monomer units. Comment on these samples with regards to the simulation studies of chain persistence that we looked at last week.



d) Murnen gives the following expression for the chain persistence length as it relates to the "chain bending constant" K,

$$L_{\rm p} = \frac{b}{2} \frac{1 + \coth K - K^{-1}}{1 - \coth K + K^{-1}} \approx \begin{cases} bK, & \text{for } K \gg 1\\ b/2, & \text{for } K \ll 1 \end{cases}$$
(4)

and K is given by,

$$K \approx K^0 + \frac{l_B \alpha^2}{12b} \sum_{m=1}^N \left(1 - \frac{m}{N}\right) \exp(-\kappa bm)(1 + \kappa bm)m \qquad (3)$$

 K^0 is the bare chain bending rigidity in the absence of charge. Some of the terms use standard nomenclature. For instance what are l_B , and $\kappa?$

e) α is f from the class discussion, b is the bond length, and m is the chain index. Does the exponential term look familiar? Compare the second term in (3) to the Debye potential.

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a) Polyelectrolytes are governed by three lengths: a, the length between charge groups. This is varied directly in this experiment. r_D the Debye screening length given by

$$\mathbf{r}_D = \left(\frac{\varepsilon kT}{4\pi ne^2}\right)^{\frac{1}{2}}$$

which is varied with counter ion concentration, n. l_{p0} the bare persistence length with no potential. Here a << l_p and the charge has a potential effect on persistence. At low ionic strength $r_D >>$ a and the charges contribute to persistence. At high ionic strength $r_D \sim$ a and there is less impact of charge on persistence, the two chains have similar persistence length approaching l_{p0} . When a is smaller there is a greater impact on the persistence length since the potential between charge groups follows the

$$U(r) = \frac{e^2}{\varepsilon r} \exp\left(-\frac{r}{r_{\rm D}}\right)$$

Debye potential: $r = (r_p)$ where r is the separation distance for the charges and the potential is greatest at short distances or small "a".

b) It is exactly what is predicted,

$$l_{\mathrm{p}} \approx l_{0} + l_{\mathrm{p}}^{\mathrm{OSF}} \approx l_{0} + rac{l_{\mathrm{B}}f^{2}}{4(\kappa b)^{2}}$$

- c) There are only 18 or 36 monomers so we do not expect to see a plateau in the persistence length for these shot chains according to the simulation results we saw earlier.
- d) l_B is the Bjerrium length, the length where the Coulombic potential equals kT, $l_B = e^{2/\epsilon k_B T}$. κ is the inverse of the Debye screening length.

 $U(r) = \frac{e^2}{\varepsilon r} \exp\left(-\frac{r}{r_D}\right)$ The Debye potential has the same argument with r replaced by bm, the length of a series of m bonds. The prefactor is 1/b, similar to 1/r in the Debye potential. So the second term is based on the Debye potential. The summation sums interaction potential between chain units, bm being the variable separation distance between charged groups. If you combine 1/b and 1-m/N you get (N-m)/(bN), bN is the maximum r for two charge groups, but there is a weighting that decreases this contribution the further the two groups are apart (N-m). With time you could sort out the entire expression.