Quiz 3 Polymer Properties February 5, 2016

1) Elli, Ganazzoli, Timoshenko, Kuznetsov and Connolly

(Citation: J. Chem. Phys. 120, 6257 (2004); doi: 10.1063/1.1651052) proposed the following equation to describe the molecular weight dependence, n_b , of the persistence length for linear chains, $l_{per} = an_b^{\xi}$

and

$$l_{per}^{branched} / l_{per}^{linear} = A + B\left(1 - \exp\left(-\frac{n_b}{C}\right)\right)$$

for branched chains.



a) Does this approach agree with the simulation results shown below? Explain why.

b) Consider the high and low n_b -limits of the power-law equation for linear chains. Do these limits make sense? Does the function agree with what was observed in class?

c) The parameter A reflects how the persistence length for a chain of large n_b increases with branching. What does the parameter B reflect? (Consider this in the context of the unbranched chain power-law equation.)

d) Consider the data of Yethiraj below. What is the conceptual basis for plotting the data in this way. (Citation: J. Chem. Phys. 125, 204901 (2006); doi: 10.1063/1.2374884)



e) Explain why the following plot is more linear.



2) Weakly charged polyelectrolytes are characterized by three size scales that govern whether the charge has an effect on the persistence length.

a) What is the difference between a weakly charged polyelectrolyte and a strongly charged polyelectrolyte. Give an example of each.

b) What three sizes are important to polyelectrolytes.

c) Define each of these sizes with equations as best you can.

d) When polyelectrolytes are mixed with surfactants of opposite charge the phase behavior shown in Figure 4 below is observed (SDS is an amphiphilic surfactant molecule). Sketch a polyelectrolyte chain and show what structures might be expected in the different concentration regimes, such as shown in Figure 2 below.

e) Explain how you think the persistence length would change across this series.



Figure 4. Photograph showing the different observed phase behaviors. From the left, the first photograph is one-phase mixture, and the next two are two-phase samples. The last sample is a one-phase mixture.

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Figure 2. Phase diagram for SDBS/JR 400 and SDES/JR 400 mixtures. Solid outline with white background: two-phase region of SDBS/JR 400 mixtures; dashed outline with gray background: two-phase region of both SDBS/JR 400 and SDES/JR 400 mixtures.

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ANSWERS: Quiz 3 Polymer Properties February 5, 2016

1) a) The simulation results show a power-law relationship for the linear chains and a modified power-law relationship for the branched chains. (In a log-log plot a power-law relationship is a straight line.) The modified behavior could be explained with an exponential function (or many other functions such as a simple Taylor series).

b) At high n_b the persistence length would be extremely large, and at low n_b , extremely small. It was noted in class that we expect a plateau molecular weight at high n_b but this function doesn't produce such a plateau, it continues to infinity. The exponential correction seems to make little sense. Why would the exponential change in the branching effect disappear at large n_b ? I just seems to happen to fit the results at low n_b values.

c) The parameter B reflects the degree to which the function deviates from a power-law at low n_b.

d) This plot follows a classic end group effect where we expect the fraction of the chain occupied by end groups to be proportional to 2 $(1/n_b)$, 2 for the two ends which are diluted in the chain of size n_b . So we expect $l_p(n_b) = l_p(n_b=\infty)+K_1/n_b$.

e) The feature that should be modeled is the chain stiffness not the persistence where the chain stiffness is proportional to $1/l_p$. Then the functional form is: $1/l_p(n_b) = 1/l_p(n_b=>\infty)+K_2/n_b$.

2) a) Strongly charged polyelectrolytes have a charge on each monomer, like sulfonated polystyrene, weakly charge polyelectrolytes do not, such as polyacrylic acid.

b) persistence length, l_p , separation distance of charges, a, and the Debye screening length, λ_D .

c) l_p is defined in terms of the exponential correlation function for chain tangent orientation, $< t(s) \cdot t(s') >= exp(-(s-s')/l_p)$

The Debye screening length, λ_D , is defined in terms of the exponential decay function for screening of binary coulomb interactions, U(r), with concentration of counter ions, n, site charge, e, and temperature, T,

 $\lambda_{\rm D} = (-kT\epsilon/(4\pi ne^2))^{1/2}$

$$U(r) = (e^2/(\epsilon r))exp(-r/\lambda_D)$$

The spacing of charges, a, is just the distance between charges on the chain.

d) See drawing below.

e) At low concentration, below the critical aggregation concentration, some of the charges are balanced by the surfactant molecules so the persistence length should drop in this regime. At the CAC the chain should have a bare persistence length with no charge.

Above the CAC the chain should have a larger persistence length since some charges are free of micelles such as in a grape vine structure.

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