120924 Quiz 3 Polymer Properties

1) In a computer simulation it was found that the Kuhn length is 1 for a random walk but is 1.2 for a chain that does not take a back step and is 1.4 for a chain with fixed bond angle.
   a) Show that the absence of a back step leads to $l_k = 1.22$.
   b) Show that a restricted bond angle of 109º leads to $l_k = 1.4$.
   c) Experimental measurement for polyethylene finds $C_\infty = 6.7$. What is l_k?
   d) Why is this value for l_k larger than $1.4\ l_0$?
   e) Do you expect C_n for polyethylene (finite molecular weight) to be larger or smaller than 6.7? Why?

2) Under certain conditions of salt content and concentration soap can form worm-like micellar (WLM) chains that display a high degree of persistence.

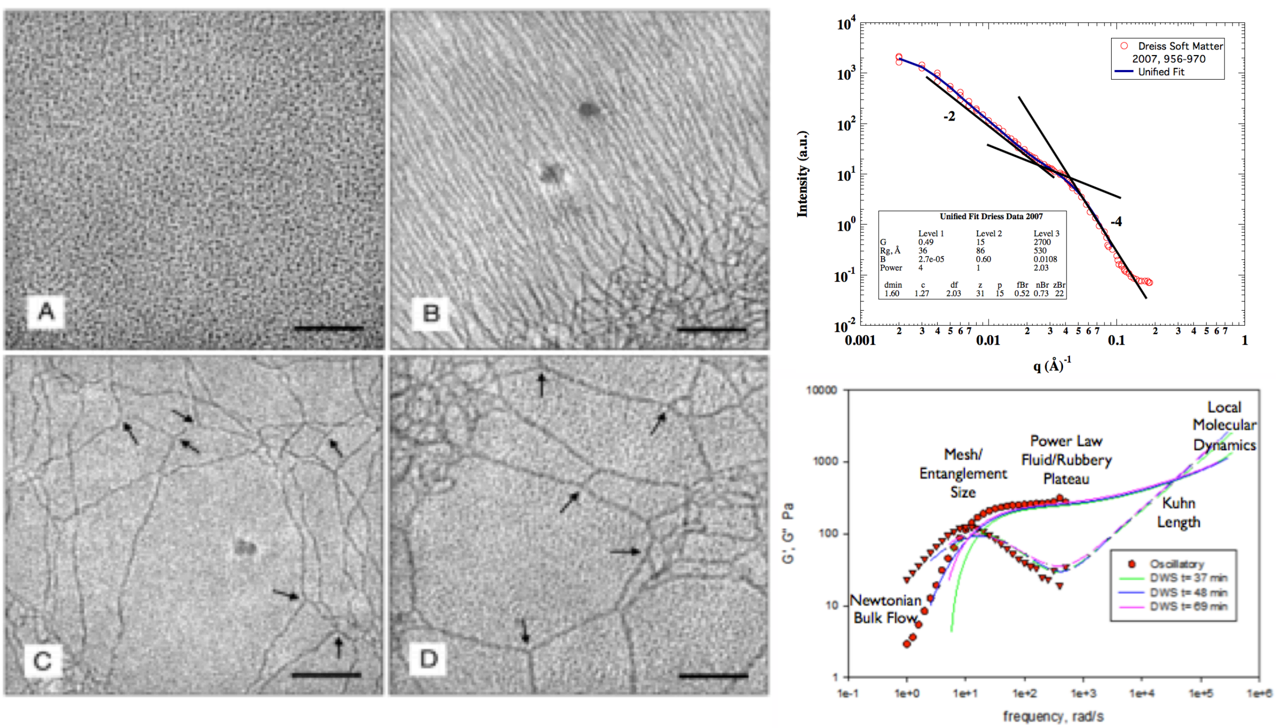

*Figure showing the control of micellar topology by addition of salt [1]. Cryo-TEM of WLM's using EHAC with (A) no KCl, (B) 2 wt% KCl, (C) 6 wt% KCl, and (D) 12 wt % KCl. Bar is 100 nm. [1 Croce V, Cosgrove T, Maitland G, Hughes T, Karlsson G Langmuir **19** 8536-41 (2003).] Graphs show neutron scattering, log intensity versus log q and dynamic mechanical measurements, log storage and loss modulus versus log frequency from WLM chains.*

   a) In synthetic polymers persistence is displayed because the chain is composed of linear bonds with bond angle/rotation restrictions. What do you think governs the existence of persistence in WLM chains?
   b) The micrographs show WLM chains. From such a micrograph how would you estimate the chain persistence? (Estimate the persistence length from these micrographs.)
   c) The scattering graph shows three power-law regimes $I \sim q^{-df}$. What is the slope for the central regime and estimate the persistence length from this plot.
   d) The dynamic mechanical plot shows a point where G' (circles, solid line) and G" (triangles and dashed line) cross as indicative of the Kuhn (per.) length. Explain this.
   e) Why would the Kuhn length be observed at high frequency while entanglements are observed at low frequency?

ANSWERS: 120924 Quiz 3 Polymer Properties

1) a)

$$\langle r_{i+1} \rangle = \sum_{k=1}^{k=z} b_k = 0$$

For exclusion of the previous step this sum does not equal 0

$$\langle r_{i+1} \rangle_{Random} = \sum_{k=1}^{k=z} b_k = 0 = (z-1)\langle r_{i+1} \rangle_{ShortRangeInteraction} - r_i$$

so

$$\langle r_{i+1} \rangle_{ShortRangeInteraction} = \frac{r_i}{(z-1)}$$

$$\langle r_i \bullet r_j \rangle = \frac{b^2}{(z-1)^{|i-j|}}$$

and

$$\langle R^2 \rangle = \sum_{i=1}^{n}\sum_{j=1}^{n} \langle r_i \bullet r_j \rangle \cong \sum_{i=1}^{n}\sum_{k=-\infty}^{\infty} \frac{b^2}{(z-1)^{|k|}} = nb^2 \frac{z}{z-2} = nb^2_{effective}$$

The second to the last equality is the result of the Sum of Geometric Progression Rule,
lim n->∞ of a + ar + ar^2 +... = a/(1-r)
substituting x=1/(z-1) results in 2/(1-x) - 1 = 2(z-1)/(z-2) - 1 = z/(z-2)

For Cartesian simulation z = 6 and b_{eff} is 1.22 b so about a 25% increase for one step self-avoidance.

b) Use same approach as in (a) replacing 1/(z-1) with cos(71º). The final equation is $nb^2(1+\cos(71^o)/(1-\cos(71^o))) = 2\ nb^2$. So b_{eff} = 1.4 b.

c) l_k = 1.54 Å* 6.7 = 10.3 Å.

d) It is larger due to bond rotation restrictions and higher order restrictions to chain flexibility.

e) C_n should be smaller due to end group effects that serve to reduce persistence due to a higher degree of flexibility for chain ends. In class we suggested an end-group functionality, $\frac{1}{C_n} = \frac{1}{C_\infty} - \frac{2K}{M_n}$.

2) a) The micelles begin as columnar micelles so have some tendency to form rods. This is due to packing constraints on the surfactant molecules. Charge of the head groups will encourage persistence in these chains.

b) The persistence length for a worm like chain is defined by the function

$$\langle t(s) \bullet t(0) \rangle = e^{-s/l_p} \quad (3)$$

. When the percent of chain path in the direction of the starting point is 1/e or about 1/3 (a turn of about 70º) we have reached the persistence length. The black bar is 100 nm so the chains in the micrographs have a large persistence of perhaps 300 nm.

c) Slope is -1 for a rod structure. the smallest q reflects the length of the rod, 2π/0.02 = 314 Å

d) The curves show an increase in G"/G' with frequency in the range where the Kuhn length is observed. At shorter times or higher frequency more of the energy that is applied to the sample produces heat and less is associated with an elastic response. This is because the motion of the Kuhn units occur on short time scales and the diffusive motion of these rod like units is easier at higher frequencies. When G" = G' the rod motion begins to dominate the mechanical properties of the material.

e) Smaller object move at shorter times so the relaxation time for the Kuhn units is at a higher frequency compared to the larger entangled chain lengths.