Quiz 4 Polymer Properties September 20, 2013

1) In considering restrictions on the freely jointed chain model, we considered in class 1) a total avoidance of the previous step in a lattice model; 2) the freely rotating chain model and 3) a rotating chain model that considered the energies of bond rotation in the trans, gauche+ and gauche- positions. These were found to have an increasing characteristic ratio in the series 1.22; 1.4; 3.4. The polyethylene chain displays $C_\infty$ of 6.7, which is higher than any of these models, and a bond length of 1.54Å.

a) Why is the value of the characteristic ratio for polyethylene larger than 3.4? Would you expect any polymer to have a smaller characteristic ratio than 3.4?

b) For a 2d lattice model would the characteristic ratio be higher or lower than that for a 3d lattice? Why?

c) Polydimethyl siloxane (PDMS) is composed of a backbond of $-\text{Si}-\text{O}-$ units that have a bond angle of 142.5° and a bond length of 1.64Å. The Si-O bond is rotationally flexible similar to the C-O bond. Calculate the characteristic ratio for polydimethyl siloxane assuming a freely rotating chain and give a value for the Kuhn-length.

d) If the oxygens in PDMS were replaced by CH$_2$ would you expect the characteristic ratio to be larger or smaller? Why?

e) Do you expect $C_n$ for polyethylene (having a finite molecular weight) to be larger or smaller than 6.7? Why?

2) Elli et al. (J. Chem. Phys. 120 6257(2004)) proposed the equation

\[ l_p = \left( a n_b^k \right) \left[ A + B \left\{ 1 - \exp \left( -n_b/C \right) \right\} \right] \]

to describe the functionality of persistence length with backbone molar mass, $n_b$, for bottle brush polymers that they simulated. This equation is used to fit the data shown in the figure where HD chains have a branch on every monomer and LD chains have a branch on every other monomer (linear have no branches).

a) For the HD chains do you think that the proposed function is unique, that is, are there other functions with the same number of parameters that could fit this data? (Give an example if yes.)

b) If you were studying the molecular weight dependence of persistence length what value would you want to predict from these simulated values? Can the proposed function predict this value?

c) In class it was shown that the bottle brush simulation results follow the function

\[ \frac{1}{l_p} = \left( \frac{1}{l_{p,\infty}} \right) + \left( \frac{2K}{M} \right) \]

which indicates that the chain flexibility varies linearly with the number of end groups. Why do you think that “flexibility”, inverse persistence length, is linear in the fraction of the chain composed of end groups rather than the persistence length itself?

\[ l_K = l_{K,0} + kM_{sc}^2 \]

where \( l_K \) is the Kuhn length of the brush, \( l_{K,0} \) is the Kuhn length for the main chain with no side chains, \( k \) is a constant and \( M_{sc} \) is the molecular weight of the side chain. Explain why the Kuhn length would increase with molecular weight of the side chain. Why do you think \( M_{sc} \) is squared in this expression?

e) Experimentally an exponent of 1.79 is found in good solvents and 1.42 in close to theta solvents by Zhang et al. *Macro.* 39 8440 (2004). Why would the exponent of \( M_{sc} \) change with the quality of the solvent?
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1) a) Polyethylene has a larger characteristic ratio because there exist higher level interactions beyond just bond rotational isomeric states. These include steric interference between local chain groups for tight curvatures. Chains with a smaller bond angle than polyethylene and with more flexible bonds would have a lower characteristic ratio.

b) For a 3d lattice the coordination number is 6 and for a 2d lattice z is 4. The characteristic ratio is \( \sqrt{\frac{z}{z-2}} \) so 1.22 for 3d and 1.41 for 2d.

c) \( C_\infty = \sqrt{\frac{(1+\cos(180-142.5))}{(1-\cos(180-142.5))}} = 2.94 \) and \( l_K = 4.83 \text{ Å} \). PDMS has a characteristic ratio of 5.2 from the Polymer Handbook.

d) The characteristic ratio would be higher since the carbon bond is less rotationally flexible than the oxygen bond.

e) For a finite molecular weight we expect a lower characteristic ratio due to the end group effect.

2) a) HD has 5 data points and the proposed function has 5 free parameters so this represents the maximum number of parameters a function could have that describes this data. There are many 5 parameter functions that could equally describe this data, for instance \( l_p = a + b \ n_b + c \ n_b^2 + d \ n_b^3 + e \ n_b^4 \).

b) \( l_{p,\infty} \), the persistence length at infinite molecular weight should be a constant value that could be obtained from this data. The proposed function at large \( n_b \) is a power-law in \( n_b \). Such a power-law does not reach a plateau value at high \( n_b \). The proposed function cannot be used to obtain \( l_{p,\infty} \).

c) Increasing the fraction of the chain composed of end groups by decreasing the molecular weight directly changes the chain flexibility. We would expect the flexibility of the chain to increase in a simple fashion with the fraction of the chain composed of end groups. Persistence length is a derived parameter rather than a direct measure of chain properties. Flexibility is similar to chain bending modulus.

d) As the side chain length increases the side chains sterically interfere with each other leading to a straightening out of the chain. The volume of the side chain is proportional to \( M^{3/2} \) since \( (R/l)^2 \sim M \). Binary interaction of these volumes would lead to a higher power-law dependence for instance \( M^3 \). \( M^2 \) is obtained by considering an energy balance for the chain by Subbotin.

e) The side chain coil expands with goodness of the solvent so there should be a higher exponent for better solvents as is seen. The power 1.42 (close to 1.5) might indicate a direct dependence on the volume of a side chain.