120912 Quiz 2 Polymer Properties

1) We often refer to a Gaussian chain when discussing a polymer in the theta-state.

a) What is the Gaussian function and how does it relate to a polymer in the theta-state?b) Show how the Gaussian function can be used to determine the most probable chain end-to-end distance.

c) How can the Gaussian function be used to calculate $\langle R^2 \rangle$? (Just outline the method to solve for $\langle R^2 \rangle$ using the Gaussian probability.)

d) Show how the Gaussian probability can be used to quantify the energy associated with extension of a theta-chain.

e) Obtain an expression for the spring constant for a theta-chain.

2) Macromolecules can display a variety of topologies ranging form linear strands to highly branched networks and dendritic structures. Consider a dimensional analysis of such structures.

a) Both a disk and a polymer coil in the theta-state display a mass-fractal dimension of 2. Explain how these two different objects can both be two-dimensional and how they can be distinguished using scaling dimensions.

b) Calculate the connectivity dimension for a cyclic chain by estimating p as a function of n.

c) Calculate the connectivity dimension for a 4 arm (f = 4) symmetric star polymer (arms of equal mass z_{arm}). How does this compare with a cyclic? Can you find a general formula for the connectivity dimension of symmetric stars of functionality (number of arms) f?

d) Calculate the average connectivity dimension for a sample of high density polyethylene that has one long chain branch in 30,000 carbons so that for chains of 140,000 g/mole average molecular weight one chain in 3 has a branch of equal length to half of the linear chain length.

(First calculate then number of carbons in an average chain, use this for z, then the number of chains that have branches, this will be less than 1 branch per chain. Calculate the average number of carbons in a linear chain, use this for p and then use p and z to calculate c, $p^c = z$).

e) Graphene is a sheet structure composed of conjugated carbon atoms so that over the conjugated path the structure is highly conductive. Defects in the structure lead to a break in conjugation and a loss in conductivity. Defects also make the sheet structure crumpled. For a graphene sheet of 10,000 carbon atoms with two defects per 100 carbon atoms (defects shared by 2 planar segments) calculate the connectivity dimension, c, and the minimum path, p. What would be needed to calculate the minimum dimension, d_{min}?

ANSWERS: 120912 Quiz 2 Polymer Properties

1) a) The Gaussian function is $P(R) = Kexp(-3R^2/(2n_k l_k^2))$. In the theta-state the chain adopts a Gaussian conformation displaying a mass fractal dimension of 2.

b) The most probable end-to-end distance, R*, can be obtained by taking the derivative of $d(R^2P(R))/dR$ which yeilds $(R^*)^2 = 2/3 nl^2$ for the Gaussian distribution function. The most probable end-to-end distance also scales with $n^{1/2}$ so it reflects a 2-dimensional chain.

c)
$$\langle R^2 \rangle = \frac{\int_{-\infty}^{\infty} R^2 P(R) dR}{\int_{-\infty}^{\infty} P(R) dR}$$

d) The entropy can be obtained from $S = ln(P(R)) \sim -3R^2/(2n_k l_k^2)$ and the chain energy can be obtained from $E = -k_BT S = 3 k_BT R^2/(2n_k l_k^2)$ for chains with no enthalpic interactions (athermal chains).

e) For extension the change in energy, dE, with estension is equal to the applied force, F, times the change in end-to-end distance, dR, $dE/dR = F = (3 k_B T/(n_k l_k^2)) R = k_{spr} R$.

2) a) For the Gaussian chain $\langle R^2 \rangle = n_k l_k^2$ so the size to the power 2 scales with the mass. The power of size is the mass fractal dimension, d_f . Similarly for a disk Mass $\sim R^2$.

b) For a cyclic chain of molecular weight z the minimum path p is z/2. Since $p^c = z$ we have c = ln(z)/ln(p) = ln(z)/(ln(z) - ln(2)) or 1/c = 1 - ln(2)/ln(z) so large cyclics (large z) behave like linear chains (c =>1) in terms of the connectivity.

c) For f = 4 p = z/2 so, $1/c = 1 - \ln(2)/\ln(z)$ identical to the cyclic. (R_g for the star is smaller than R_g for a cyclic of the same z.) In general for symmetric stars $1/c = 1 - \ln(f/2)/\ln(z)$.

d) Each chain contains about 10,000 carbons (140,000 g/mole/14 g/mole for CH₂). With one branch per 30,000 carbons there is one branch per three chains. We have 7 half linear chains for 30,000 carbons so 2*30,000/7 = 8570 is p. $c = \ln(z)/\ln(p) = 1.02$.

e) For a sheet structure c = 2. For the graphene sheet p is $(10,000)^{1/2} = 100$. To calculate the minimum dimension either d_f or the size of the sheet, R, would be needed.