030411 Quiz 2 Properties

Consider a polyethylene chain synthesized with 2000 ethylene units.

1) a) Calculate the root mean square (RMS) end-to-end distance if the carbon-carbon bond is 1.54 Å in length and the chain is considered a random walk of ethylene units.
b) Calculate the radius of gyration for this chain under this assumptions.
c) Why would radius of gyration be the preferred description of size for a branched chain?
d) Explain how R_g can be obtained from a neutron scattering measurement. (Sketch a typical data set and show the function that could be used to obtain R_g).

2) In a neutron scattering measurement using deuterated dichlorobenzene and a diluted solution of these polyethylene chains at 70°C the radius of gyration, R_g, was found to be 103 Å.
a) Calculate the characteristic ratio, C_{2000}, for this polymer at this temperature (or explain why you can't).
b) Calculate the statistical segment length for this polymer at this temperature (or explain why you can't).
c) Explain the physical meaning of the statistical segment length.
d) Calculate the persistence length for this polymer (or explain why you can't).

3) Criticize or support the following statement (first say if it is true or false):
"Local restrictions to bond rotation along the polymer chain lead to deviations from Gaussian scaling".

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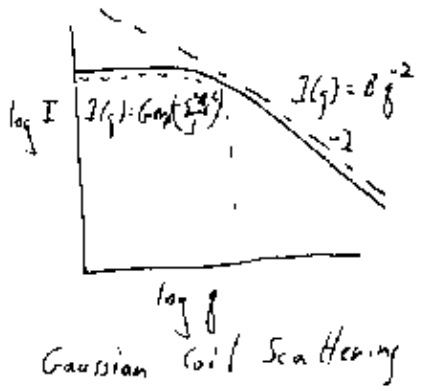
1) a) $\langle R^2 \rangle^{1/2} = (2\ DOP)^{1/2}\ l = (4000)^{1/2}\ 1.54\ Å = 97Å$

b) $97Å/(6)^{1/2} = 39.6Å$

c) End to end distance has no meaning for a branched polymer. Also, R_g is the quantity that is measured in scattering measurements.

d) R_g can be obtained from a fit of the data to the Guinier function, $I(q) = G \exp(-q^2 R_g^2/2)$ as shown below.



2 a) $C_{2000} = 6(103Å)^2/(97Å)^2 = 6.77$

b) $b_{ss} = (6\ R_g^2/4000)^{1/2} = 3.99Å$

c) The statistical segment length has no physical meaning. It is just a scaling factor to calculate the coil size from the chemical degree of polymerization.

d) The persistence length can not be calculated since it is independent of the coil radius of gyration and coil scaling. It must be measured in an independent measurement.

3) This statement is incorrect. Local restrictions to bond rotation do not effect chain scaling and this was demonstrated in class for a chain built on a lattice with no backward step. For the lattice model presented in class, with coordination number z, the net effect of restricting local bond direction was to lead to an effective step length,

$$b_{eff} = b\ (z/(z-2))^{1/2}$$

b_{eff} is always larger than b. Chain scaling remained Gaussian, that is the chain size was still related to the square root of the degree of polymerization or chain length. Only long range interactions effect chain scaling.