Quiz 10 Polymer Properties November 1, 2013

- 1) Viscosity has a strong dependence on temperature following the Arrhenius relationship.
 - a) Give the Arrhenius function for the temperature dependence of viscosity (a thermally activated process).
 - b) How do you think the intrinsic viscosity would depend on temperature? How does this compare with your answer to part "a"?
 - c) Knowing the temperature dependence of the end-to-end vector, $\langle R^2 \rangle^{1/2}$ is given by Riowing the con-r $R^* = R_0^* \left(\frac{n^{1/2}V_0(1/2-\chi)}{b^3}\right)^{1/5}$, write a function for the temperature dependence of the intrinsic

- d) Give the molecular weight dependence of the intrinsic viscosity for a collapsed coil, a Gaussian chain, an expanded chain and a rod.
- e) How would the molecular weight depence of the intrinsic viscosity for the expanded coil be complicated by the temperature dependence you propose in part "c"?
- 2) Branching has a large effect on the intrinsic viscosity.
 - a) Consider two polymers of the same molar mass, one being a symmetric three arm star polymer and the other a linear polymer. Calculate the Gaussian radius of gyration for these two polymers.
 - b) Would you expect the hydrodynamic radius to show a similar difference?
 - c) Gel permeation chromatography (GPC) measures the hydrodynamic volume of a polymer by pumping the polymer through a nanoporous gel under high pressure (also called high pressure liquid chromatography or HPLC). Small polymers, having a smaller hydrodynamic volume, elute from the gel more slowly than large polymers. Would you expect the branched and linear polymers of this problem to elute at different times? Explain.
 - d) Modern GPC's couple a viscometer at the exit of the gel column so that the intrinsic viscosity of the elution can be obtained. Could a GPC system with a viscometer determine the extent of branching for the GPC elution fractions in a polydisperse polymer sample?
 - e) Would a light scattering detector, that measured R_g and M_w, be of any use in determining if the chains were branched?

1) a) $\eta_0 = A \exp\left(\frac{E}{k_B T}\right)$

b) The intrinsic viscosity is a specific volume for the coil, $[\eta] = \frac{V_H}{N} = \frac{4\pi/3}{N} \frac{R_H^3}{N}$ and RH has the following dependence:



c) If we assume that $R_{\rm H} \sim R_{\rm eted}$, and $\chi \sim B/T$ then $[\eta] \sim N^{\frac{4}{5}} (\frac{1}{2} - \frac{B}{T})^{3/5}$

d) $[\eta] = \frac{V_H}{N} = \frac{R_H^3}{N} = N^{3/df-1} = KN^a$ For collapsed coil $d_f = 3$ and a = 0. For Gaussian coil $d_f = 2$ and a = 0.5. For any and a = 2

 $d_f = 2$ and a = 0.5. For expanded coil $d_f = 5/3$ and a = 0.8. For a rod $d_f = 1$ and a = 2. e) The molecular weight dependence should remain at a = 0.8 for a given temperature. The intrinsic viscosity will increase with increasing temperature.

2) a) Linear $R_g = Nl^2/\sqrt{6}$. For the star each arm has a mass N/3 and a Rg of $R_g = Nl^2/(3\sqrt{6})$. The star has two arms across the star so that the star radius of gyration is $R_g = 2Nl^2/(3\sqrt{6})$. b) The hydrodynamic radius will have a similar difference. The star hydrodynamic radius will be smaller than that for the linear chain.

c) The branched star polymer would elute slower than the linear polymer since it has a smaller hydrodynamic volume.

d) The chains in a mixture are separated according to their hydrodynamic volume already so the measurement of intrinsic viscosity will not further distinguish the chains except to give an absolute calibration of the hydrodynamic volume.

e) Measurement of M_w would allow for the determination of the branch content since two fractions with the same molar mass would elute at different times if one were branched. The analysis of this data could become complex.