## Quiz 5 Polymer Properties February 19, 2016

1) In class we obtained an expression for the energy of a polymer chain subject to enthalpic interactions between chain units as a function of chain end to end distance, R.

- a) The virial expansion of the ideal gas law expresses energy in terms enthalpic and entropic contributions. Write the virial expansion up to the second virial coefficient.
- b) Virendra U, Rajiah A, and Prasad DHL [*Chem. Eng. J.* **56** 73 (1995)] proposed the expression for the second virial coefficient for non-polar substances,  $B_2(T) = 0.125 0.305/(T_r 0.345)$  where  $T_r$  is the reduced temperature,  $T/T_c$  and  $T_c$  is the critical temperature (plotted in Fig. 1 (a)). Virendra et al. show that this empirical expression is a good representation for 30 pure fluids. Use this expression to explain which parts of the virial expansion are entropic and which parts are enthalpic.
- c) The second virial coefficient, B<sub>2</sub>, represents binary interactions. Does it contain an entropic part? Why would this be the case?
- d) The expression for polymer chain energy has some similarities to the virial expansion. Write this expression including an expansion of the  $\chi$ -parameter and compare it with the virial expansion using Virendra's expression for B<sub>2</sub>(T).
- e) Explain how the chain energy expression has entropic and enthalpic components. Explain the two types of entropic terms in this expression.

2) Figure 1 a) shows experimental data for coil size, b) shows the predicted behavior of the Flory Kirgbaum theory.



*Figure 1. a)B2 from* Virendra. B) *Coil size versus temperature for polystyrene/toluene. c) Flory-Krigbaum results.* 

- a) What is "Rg" in Figure 1 b). Explain how it is measured.
- b) Does the Flory Krigbaum equation match the experimental data? Use Figure 1 b) and c).
- c) Identify the two regimes of coil scaling predicted in the Flory-Krigbaum equation in Figure 1 b).
- d) Can you explain the structural changes that occur with temperature based on the Flory-Krigbaum equation? Can you make a sketch of the structural changes?
- e) Give a description of what occurs in Figure 1 b) below 35°C.

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1) a)  $P = \rho kT + \rho^2 B_2(T)$ 

b) Entropic parts of the expression are temperature dependent. The plot in Figure 1a) shows that the Virendra expression has an enthalpic part that is about 1 at low temperatures and an approximately exponentially increasing part that is entropic that enhances the pressure at high temperatures. The second term in Virendra's expression can be approximated as  $(-1.131+0.305 T_r)^{-1}$  for small Tr this becomes  $[-(1/1.131)exp(-0.270T_r)]^{-1}$  or  $-1.131 exp(+0.270T_r)$  so his expression would be  $B_2(T) = -0.125 + 1.131 exp(+0.270T_r)$  for low  $T_r$ . The expression approaches -1 at low  $T_r$  and exponentially increases with  $T_r$  as can be seen in figure 1 (a). Part of B2 is enthalpic since it does not depend on temperature and part is entropic. For gasses this is dominated by the repulsive interaction that leads to a higher pressure with temperature. c) The enthalpic part of B2 describes the organization of the material due to binary interactions such as organization in a crystal structure during the enthalpically driven process of crystallization.

d)  $E(R) = kT (3R^2/(2nl^2) + n2Vc(1/2-z\Delta\epsilon/(kT)/R^3))$ 

There are some similarities between the two expressions. Both have enthalpic and entropic contributions to the binary interaction energy and an entropic part for ideal conditions. e) The first term is purely entropic, having to do with the kinetic motion of the Kuhn units with kT. The second term has an entropic term associated with organization of Kuhn units related to binary interactions. There is also an enthalpic term associated with energetic associations between Kuhn units.

2) a) Rg is the radius of gyration. It is measured by modeling the scattering from a polymer solution as a bell shaped curve in  $q = 4\pi/\lambda \sin(\theta/2)$  about q = 0. For a Gaussian curve  $I(q) = G \exp(-q^2/2\sigma^2) = G\exp(-q^2R_g^2/3)$  where G is a constant having to do with the square of the contrast and the number of polymer coils in the scattering volume. R<sub>g</sub> is directly proportional to the chain end-to-end distance for a Gaussian chain,  $\sqrt{6} R_g = R_{eted}$ .

b) Figure 1 b and c show that the FK equation matches the experimental curve almost exactly from high temperature to the theta temperature. This can be seen by comparing the fifth root of the excluded volume to the  $R_g$  curve.

c) The theta state is the vertical line in Figure 1 b and c. The points to the right of this line are the expanded coil state.

d) The Flory-Krigbaum expression give no clue as to what happens to the chain structurally as it cools from the expanded coil state to the theta state. The coil size prediction is excellent but there is no explanation for how this could physically occur. This is a major problem that was later explained by the French researchers lead by de Gennes in the 1980's.

e) Below 35°C the coil collapses, like protein folding. This is local coil phase separation below c\*.