Polymer Course – HW #3 Due date: **Monday, Oct. 20th, 2008**

(Most problems from Chapter 7 of Lodge.)

1. Estimate the configurational entropy change ΔS_m (in J/K) that occurs when

   a) 25 g of toluene (T) (M_T = 92 g/mol) are mixed with 25 g of styrene (S) monomer (M_S = 104 g/mol).

   b) 25 g of toluene are mixed with 25 g of polystyrene (PS), M_n = 100,000 g/mol.

   c) 25 g of polystyrene (PS), M_n = 100,000 g/mol are mixed with 25 g of polyphenylene oxide (PPO), M_n = 150,000. (This is one of the rare cases where two high molecular weight polymers are soluble with each other.)

   Note that I'm looking for the entropy change of the *whole mixture* (i.e., for 25 g worth of each component). You may also find it easier to work in mole fractions x_i rather than volume fractions ϕ_i, even for the polymer.

2. Problem 7.5 (Remember Flory-Huggins counts pair wise interactions.)

3. Problem 7.4
   - Note that there are three different fractions of PS, meaning there are three different samples with different molecular weights. Each fraction (i.e., sample) will need their own graph of Π/cRT versus c to identify M_n for that fraction from the toluene and MEK data.
   - Be careful of your units. 1 dyn = 1 g cm/s^2 = 10^{-5} N
   - To get reasonable intercepts you may want to consider "a more sophisticated analysis" by including another term in your virial expansion.

4. Problem 7.8
   - Start by considering the impact of changing the temperature on the free energy of mixing and make generalizations about UCST or LCST for when $\alpha > 0$ and $\alpha < 0$.
   - To consider the impact of β, keep in mind that $\chi_c \approx ½$ for high MW polymer solutions, meaning that you need $\chi > ½$ for phase separation to occur.

5. Problem 7.18
   - For a high MW polymer blend, the Gibbs free energy of mixing is $\Delta G_m/kT = \phi_A/N_A \ln \phi_A + \phi_B/N_B \ln \phi_B + \chi \phi_A \phi_B$
   - The second and third derivatives of ΔG_m with respect to ϕ set to zero can be solved to obtain the critical point $\chi_c = (N_A^{½} + N_B^{½})^2 / (2N_AN_B)$, which for high MW polymer is simply $\chi_c \approx 0$. (For $N_A = N_B = N$, $\chi_c = 2/N \rightarrow 0$ for large N.)
   - Note that for polymer blends the entropy of mixing ΔS_m is so tiny as to be basically zero, so miscibility is entirely determined by the sign of χ.

6. Problem 7.2