Chemical Engineering 160/260  
Problem Set #3 Solutions:

1) Why do most polymers exhibit LCST rather than UCST behavior?

Consider an A B system. The appearance of UCST vs. LCST behavior can be determined by the sign of the enthalpy and entropy terms $\Delta H_{mix}$ and $\Delta S_{mix}$ in the free energy of mixing equation:

$$\Delta G_{mix}(\%A,T) = \Delta H_{mix} - T \Delta S_{mix},$$

assuming that the dominant temperature dependence of $\Delta G_{mix}$ is from the T term. If $\Delta G_{mix}$ is less than zero, the two components will form a single phase. If $\Delta G_{mix}$ is greater than zero the components will phase segregate. For most solutions $\Delta S_{mix}$ is greater than zero because mixing allows increased configurational entropy (more unique ways to arrange the two components A, B on a lattice). Consider a solution with concentration eg 0.5% A and 0.5% B. If $\Delta H_{mix}$ is also greater than zero for this system, (endothermic mixing) then at low temperatures $\Delta G_{mix}$ will be greater than zero, at some critical temperature $\Delta G_{mix}$ will be equal to zero and at higher temperatures $\Delta G_{mix}$ will be less than zero. Thus we will see UCST type behavior: a two phase region at low temperatures and a single phase region at high temperatures. If $\Delta H_{mix}$ is less than zero we see complete miscibility at all temperatures.

For polymers, as Sperling points out, $\Delta H_{mix}$ is usually less than zero and $\Delta S_{mix}$ is often greater than zero (the exact opposite of the UCST case). $\Delta S_{mix}$ is greater than zero because of densification, which leads to a loss of configurational entropy due to a loss of holes or lattice sites which would allow more microstates. Qualitatively, the chains are more locked into a given configuration when densification occurs. $\Delta H_{mix}$ is negative due to exothermic mixing. Both these terms are quite small, but the important point is their signs. For a given concentration, at low temperatures $\Delta G_{mix}$ is negative and a single phase exists. At higher temperatures $\Delta G_{mix}$ becomes positive and a two phase region exists.

2) We are asked to discuss the spheres which form when a poly(styrene-co-butadiene) block copolymer phase segregates. The polystyrene blocks have a molecular weight of 20,000 g/mol and the butadiene blocks have a molecular weight of 40,000 g/mol.

a) Size of spheres:
R = 1.33 $\alpha K M^{1/2}$  
$\alpha = 1.2$  
K = 670 E-3 A  
M = 20,000 g/mol  
Substituting in leads to $R = 151$ A: the spheres have a diameter of 302 Angstroms.

b) # blocks/sphere?  
There are two approaches one can think of to obtain this number. They are both estimates, but one is a better approach than the other.
Approach #1: Assume uniform density in the spheres, use bulk density of polystyrene to approximate the total mass within one sphere, and use the given molecular weight of polystyrene blocks to obtain the # blocks/sphere.

\[ V_{sphere} = \frac{4}{3} \pi R^3 = 1.442 \times 10^{-17} \text{ cm}^3 \]

\[ M_{sphere} = \rho V_{sphere} = 1.06 \text{ g/cm}^3 \times 1.442 \times 10^{-17} \text{ cm}^3 = 1.529 \times 10^{-17} \text{ g} \] [density from Table 3.2]

\[ \# \text{ blocks/sphere} = \frac{M_{sphere} \times N_A}{MW} = 1.529 \times 10^{-17} \text{ g} \times 6.023 \times 10^{23} \text{ blocks/mol} \div 20,000 \text{ g/mol} \]

\[ \# \text{ blocks/sphere} \approx 460 \]

Approach #2: Estimate the radius of gyration of the styrene block and divide the total sphere volume by this number.

Using data from Table 3.9 in Sperling, we can obtain \( <R_g^2> = 6.6 \times 10^{-12} \text{ cm}^2 \) at 34.2° C (theta temperature) for polystyrene with a molecular weight of \( M_w = 7.65 \times 10^5 \text{ g/mol} \). We can assume to first approximation that the blocks in the spheres are in a theta solvent because they are mostly surrounded by blocks of the same chemical structure. To be more accurate we would have to consider boundary effects. Since the ratio \( <R_g^2>/M_w \) should be roughly constant for a given molecular weight of the same polymer in the same solvent we can estimate \( R_g \) for the block with molecular weight 20,000 g/mol as

\[ <R_g^2>^{1/2} = \left[ 6.6 \times 10^{-12} \text{ cm}^2 \times \left( \frac{20,000 \text{ g/mol}}{7.65 \times 10^5 \text{ g/mol}} \right) \right]^{1/2} = 4.15 \times 10^{-7} \text{ cm} \]

\( R_g \approx 41.5 \text{ Angstroms} \)

\[ \# \text{ blocks/sphere} \approx \frac{V_{sphere}}{V_{block}} = (R_{block}/R_g)^3 = (151/40)^3 = 48 \]

I think that the first approach will give a more accurate number, because the second assumes that no other blocks can penetrate into the volume \( \frac{4}{3} \pi R^3 \) assigned to one block. In fact we know that there is a great deal of interpenetration.

c) \# spheres/cm³?

Here we need to take into account the fact that much of the space in a cubic centimeter will be filled by the matrix butadiene. The volume of butadiene required for each sphere to satisfy the stoichiometry of the block copolymer can be determined using the given molecular weights of each block in conjunction with the bulk densities of each polymer, again assuming as in approach #1 that these values are valid here.

\[ \rho_{polystyrene} = 1.06 \text{ g/cm}^3 \]
\[ \rho_{butadiene} = 1.01 \text{ g/cm}^3 \]

The volume ratio of butadiene to polystyrene is thus given by
80,000 g/mol ÷ 20,000 g/mol * ρ_{polystyrene} ÷ ρ_{butadiene} = 4.198

So for every sphere of polystyrene with volume $V_{\text{sphere}}$, we must account for $4.198V_{\text{sphere}}$ volume for the matrix. Thus the number spheres per cm$^3$ is $[(1+4.198)V_{\text{sphere}}]^{-1} = 1.334 \times 10^{16}$ spheres/cm$^3$.

3) What is the analytical expression for $X_{\text{blend}}$ for the system of two copolymers $A_x B_{1-x} n / (C_y D_{1-y}) n'$?

$X_{\text{blend}} = \sum c_{ij} X_{ij}$. This can be solved by inspection using $X_{\text{blend}}$ for the $A/(C_x D_{1-x})_n$ as given in Sperling. The result is:

$$X_{\text{blend}} = xyX_{AC} + x(1-y)X_{AD} + (1-x)yX_{BC} + (1-x)(1-y)X_{BD} - x(1-x)X_{AB} - y(1-y)X_{CD}$$

4) We are given an equation for the enthalpy of vaporization at 25°C, the boiling point at one atmosphere pressure, density, and molecular weight of toluene and asked to calculate its solubility parameter at 25°C.

-The solubility parameter can be calculated from the equation $\delta = (\Delta E/V)^{1/2}$ where $V$ is the molar volume and $\Delta E$ is the change in internal energy of the material on going from liquid to gas states.

-Substituting in $T_b$ to the given $\Delta H_{\text{vaporization}}$ gives $\Delta H(25^\circ C) = 9083$ cal/mol

-To relate $\Delta H$ to $\Delta E$, consider the definition of enthalpy:

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

The third term is usually negligible because any pressure change occurring would be very small. There is however a significant molar volume change on vaporization so the second term is not negligible. We can approximate $dV \approx V_{\text{vapor}}$ since $V_{\text{vapor}} >> V_{\text{liquid}}$. We can further assume the vapor behaves ideally so that from the ideal gas law

$$PV_{\text{vap}} = RT$$. So

$$dH \sim dE + PV_{\text{vap}} = dE + RT$$

$$\Delta E = \Delta H - RT = 9083 - 1.987(298) = 8283 \text{ cal/mol}$$

The molar volume can be found from the density and molecular weight given as

$$V = \frac{MW}{\rho} = 105.7 \text{ cm}^3/\text{mol}$$

$$\delta = (\Delta E/V)^{1/2} = (8283 \text{ cal/mol} ÷ 105.7 \text{ cm}^3/\text{mol})^{1/2} \sim 8.9 \left(\frac{\text{cal}}{\text{cm}^3}\right)^{1/2}$$