Quiz 10 Polymer Properties
April 1, 2016

1) Halperin, Kroger and Winnik wrote a review article on PNIPAM (Poly-n-isopropyl acryl amide)/water phase separation (*Angew. Chem. Int. Ed.* **54** 15342-15367 (2015)). Figures from that review are reproduced below.

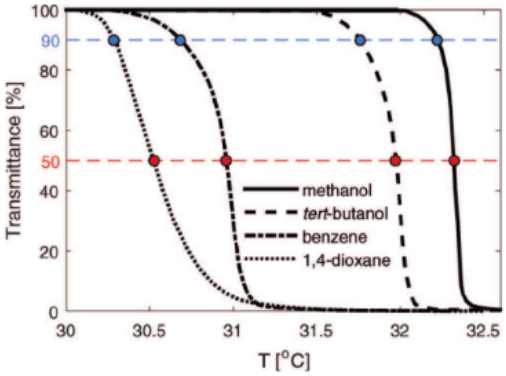
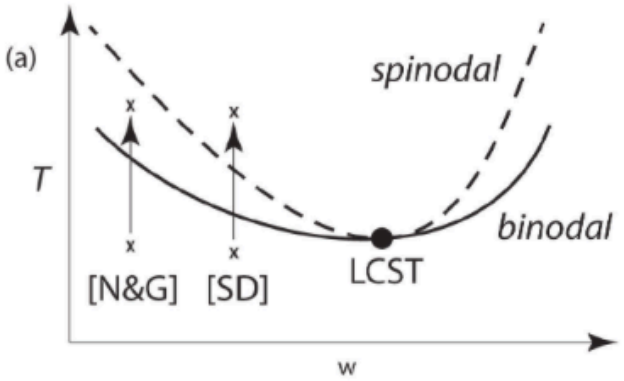
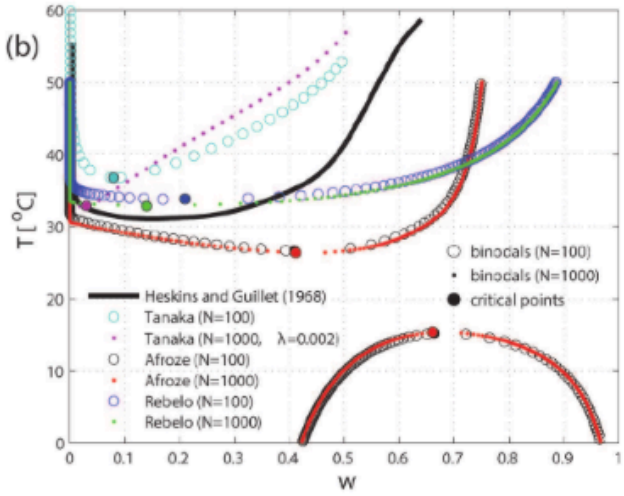
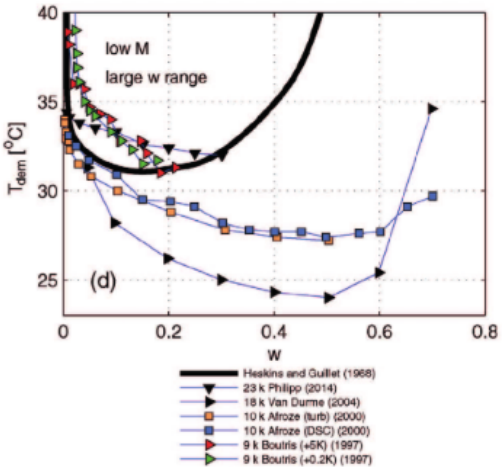


Figure 3. The relative transmittance curves obtained for PNIPAM samples of $M_w \simeq 50$ kDa and $w \simeq 0.05$ synthesized using AIBN in different solvents listed in brackets: $M_w = 6.45 \times 10^4$ (methanol); $M_w = 5.17 \times 10^4$ (*tert*-butanol); $M_w = 4.65 \times 10^4$ (benzene); $M_w = 5.18 \times 10^4$ (1,4-dioxane) redrawn after Figure 2 of Kawaguchi et al.[17] These authors identify T_{dem} with 10% reduction of the transmittance, i.e., 90% transmittance (blue circles). When the transmittance varies slowly with T the choice of criterion can have a significant effect as seen from the comparison to T_{dem} identified with 50% reduction (red circles).







a) Figure 3 shows a plot of light transmittance versus concentration PNIPAM in water. What is the purpose of this plot?
b) Explain what is shown in the figure below Figure 3. Curves are for different molecular weight polymers in water at weight fraction w.
c) The top figure on the right can be calculated from the Flory-Huggins equation from a single curve in Figure 3. Explain how this is done.
d) What are the two curves in the top right figure? How are they obtained from a plot of Gibbs free energy versus composition?
e) The bottom plot shows the results of theoretical calculations for PNIPAM/Water. What is the curve on the bottom right that has a gap? (This curve has a central critical point.)

2. Flory proposed the following equation for the osmotic pressure:

$$\Pi = \frac{kT}{V_c}\left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \ldots\right).$$

des Cloizeaux proposed use of the concentration blob model to account for deviations of the osmotic pressure from Flory's expression at high concentrations above Φ*. des Cloizeaux proposed an expression dependent on the first term in Flory's expression for osmotic pressure times $(\Phi/\Phi^*)^P$, where P can be determined under the condition that the osmotic pressure does not depend on the molecular weight of the chain, N, above the overlap concentration.

a) Find the power "P" in terms of the fractal dimension of the chain above the blob size.
b) What is the concentration scaling of osomtic pressure for $d_f = 5/3$? How does this compare with experimental observations?
c) What is the concentration scaling of osmotic pressure for $d_f = 2$? How does it compare with the Flory expression?
d) Does the des Cloizeaux approach really depend on the existance of a concentration blob? Explain your answer.
e) Vapor pressure osmometry can be used to measure molecular weight from changes in the vapor pressure of a solvent in a polymer solution. Do you think that this method would measure number average molecular weight? Why or why not?

ANSWERS: Quiz 10
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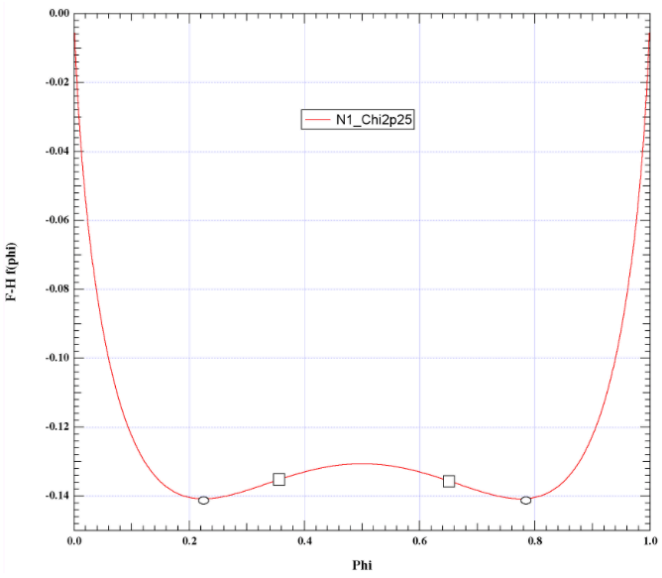
1) a) These are cloud point curves for measuring the bionodal temperature. The curves are shown for polymers synthesized under different conditions.
b) The figure below Figure 3 is a series of binodal curves obtained from the experiment in Figure 3.
c) For one binodal curve the cloud point temperature is equal to the first derivative of the free energy. Knowing the temperature and composition the interaction parameter can be obtained from this derivative since there is only one free parameter. Once the interaction parameter is obtained the Flory-Huggins equation can be used to calculate the binodal and spinodal curves and the critical point.
d)



This plot of Gibbs free energy from the Flory-Huggins Equation shows the first derivative equals 0 (binodal and circles) and the second derivative equals 0 (spinodal and squares) for one temperature. This is done for different temperatures in the two phase regime to obtain the plots shown in the right figure.
e) The bottom curve is a UCST binodal curve with a critical point at the top of the curve. This system can display an LCST and a UCST in different regions of the T-w space.

2) a) $\pi/(kT \Phi) = (1/N) (\Phi/\Phi^*)^P$ We have from earlier that $\Phi^* \sim N^{1-3/df}$, so if $\pi \sim N^0$, then $P(3/d_f-1) -1 = 0$, so $P = 1/(3/d_f-1)$.

b) $P = 5/4$ and $\pi \sim \Phi^{9/4}$. This matches experimental observations.

c) $P = 2$ and $\pi \sim \Phi^3$. This doesn't match the Flory prediction.

d) The des Cloizeaux approach relies on Φ/Φ^* being the basis of the concentration dependence. This is a kind of renormalization of the concentration that is common to the blob model. The assumption that the dimension is 5/3 above the overlap concentration is inherent to the concentration blob model.

e) Vapor pressure osmometry relies on Raoult's law which is a colligative law, depending on counting of molecular species. So it measures the number average molecular weight.