121017   Quiz 6 Polymer Properties

1) The following plot (left) shows the behavior of R_g (and R_h) as a function of temperature for polystyrene in cyclohexane. The plot to the right shows a schematic phase diagram of a polymer solution displaying UCST behavior near the overlap concentration, c*.

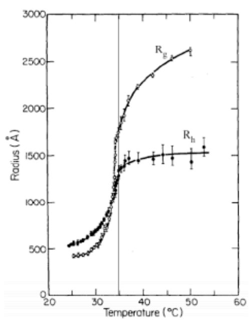

Figure 3. Radius of gyration, R_g, and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].

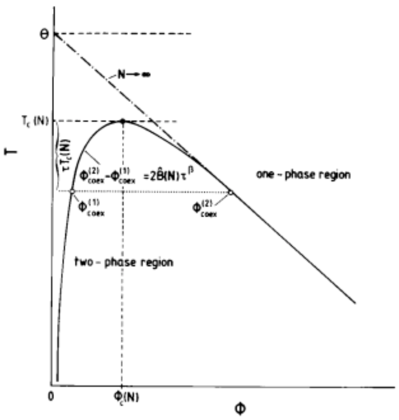

FIG. 1. Schematic phase diagram of a polymer solution in the space of the temperature T and the volume fraction ϕ. The coexistence curve separates a dilute solution of collapsed chains [at $\phi^{(1)}_{coex}$] from a semidilute solution of overlapping chains [at $\phi^{(2)}_{coex}$]. These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N\rightarrow\infty$ the critical point merges with the Θ point of a dilute polymer solution [$T_c(N\rightarrow\infty)\rightarrow\Theta$, $\phi_c(N\rightarrow\infty)\rightarrow 0$] and the unmixing transition has a tricritical character. At $T=\Theta$, the chain conÆgurations are ideal Gaussian coils, while their structure at $T_c(N)$ is nontrivial.

Figure 1. (a) (b)

a) At what composition on the right plot would the behavior seen in the left plot be observed? Why.

b) How would the left plot differ if a concentration to the right side of the right plot were used?

c) Define c*.

d) At the lowest concentrations on the right plot the phase boundary is physically not achievable. Explain what happens to the right plot at very low concentrations if c* is accounted for.

e) Explain why the theta temperature is the critical point (critical temperature) for an infinite molecular weight polymer. At what composition does the critical point for an infinite molecular weight polymer occur? In the context of c* is it possible to achieve this critical point?

2) The following equation is the Flory-Krigbaum expression for the free energy of an isolated coil: $E(R) = kT\left(\frac{3R^2}{2nl^2} + \frac{n^2 V_c\left(\frac{1}{2}-\chi\right)}{R^3}\right)$.

a) Rewrite this expression as a function of the coil expansion factor, α, then take the derivative of this free energy as a function of α and solve for the scaling of coil size with molecular weight at the minimum of free energy. (use α = R/R_0)

b) The following cartoon introduces the concept of blobs that are used to describe coil collapse (Fig. 1a below 34.5°C),

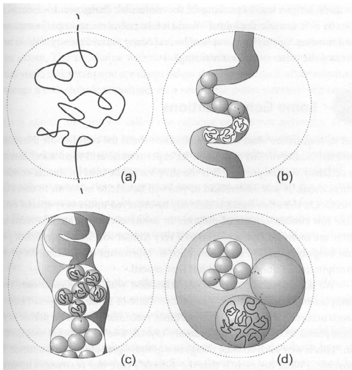

FIGURE 8.6
A few initial stages of the coil-globule transition. This looks self-similar! (Compare with what we write about self-similarity in Chapter 10). *Source:* Courtesy of S. Nechaev.

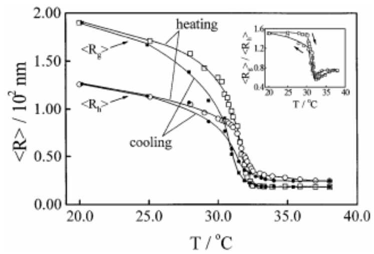

FIG. 2. Temperature dependence of the average radius of gyration $\langle R_g \rangle$ and the average hydrodynamic radius $\langle R_h \rangle$, respectively, in the coil-to-globule (heating) and the globule-to-coil (cooling) processes, where each point was obtained at least 2 h after the solution reached the thermal equilibrium to ensure that the polymer chains were thermodynamically stable. The inset shows the temperature dependence of $\langle R_g \rangle / \langle R_h \rangle$ in the heating and the cooling processes.

Figure 2. (a) (b)
Wu, C. and Wang, X. *PRL* **80** 4092-4 (1998).

How are the number of blobs related to the mass of a blob, "g", and the mass of a chain, "z"? If the coil size at the theta state $R_0^2 \sim z$ and in the collapsed state for the largest value of g*, $R^2 \sim g^*$, assuming Gaussian statistics. Each blob contributes kT to the entropic part of the free energy, explain why the entropy of the collapsed coil has the form $kT\left(\alpha^2 + \alpha^{-2}\right)$, where the first term is from the Flory-Krigbaum expression.

c) Explain the origin of the last term in the following expression:

$$F(\alpha) \sim kT\left(\alpha^2 + \alpha^{-2}\right) + \frac{kTBz^{1/2}}{2\alpha^3 l^3} + \frac{kTC}{\alpha^6 l^6} \qquad (10).$$

d) Explain the following graph based on the equation,

$$\alpha^5 - \alpha = x + y\alpha^{-3} \qquad (11)$$

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FIGURE 8.3
The dependence $\alpha(x)$ given by equation (8.7) for different values of y; from top to bottom, the curves correspond to the following values of y: 10, 1, 0.1, 1/60, 0.01, 0.001, 0.0001.

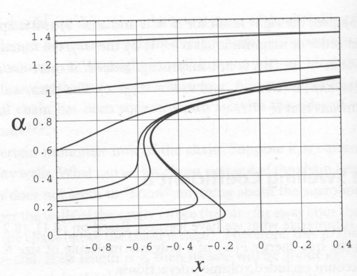

Figure 3.

e) In Figure 3) b) above (top of page) Wu and Wang show that PNIPAM displays hysteresis in the coil collapse behavior (different behavior on heating and cooling). Use the model in Figure 3) (a) to explain why hysteresis might be expected in a first order transition but not in a second order transition of coil collapse (coil to globule versus globule to coil transitions).

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1) a) The left plot is for a single coil going through the collapse transition. This occurs at concentrations below the overlap concentration and presumably below the critical composition (peak value on the miscibility limit curve in figure 1) b. So the behavior would be seen to the far left of the right plot.

b) In more concentrated conditions the coils would overlap (above c*) so that interactions would be screened at large scales. This means that a different mechanism for coil collapse would be observed. At large scales the coils would be in the theta state at all temperatures, at small scales we would observe coil collapse. The situation would be complex. On reaching the miscibility limit the system would separate into two distinct phases with the less dense phase on the top, like oil and water.

c) c* is the concentration where polymer coils (or other structures) just begin to overlap. It is the mass of the molecule divided by the volume of the molecule z/R^3. For a mass fractal object $z \sim R^{df}$ so $c^* = z/R^3 \sim z^{1-3/df}$.

d) Below c* the coil can not be diluted further since it maintains a concentration of c* within the coil. Under these conditions the miscibility limit is frozen at the c* value and the phase diagram would have a horizontal line to lower concentrations. That is, coil collapse would happen at the same temperature for all compositions more dilute than c*.

e) The critical point on the phase diagram follows .

$$T_c(N) = \Theta/(1+1/\sqrt{N})^2 \approx \Theta - 2\Theta/\sqrt{N}, \quad N \to \infty, \qquad (1)$$

$$\phi_c(N) = 1/(1+\sqrt{N}) \approx 1/\sqrt{N}, \quad N \to \infty. \qquad (2)$$

so as $N \Rightarrow \infty$ $T_c \Rightarrow \theta$ and $\Phi_c \Rightarrow 0$. It is not possible to reach this critical concentration since we are limited to concentrations above c*. However, as we approach $N \Rightarrow \infty$, $c^* \Rightarrow 0$ so in the limit of an infinite chain we can reach this critical composition.

2) a)

The Flory Krigbaum expression for the free energy of a self-avoiding chain is given by,

$$F(R) = \frac{z^2 V_0 (1-2\chi) kT}{2R^3} + \frac{3R^2 kT}{2zl^2} = U(R) - TS(R) \qquad (1)$$

Equation (1) can be rewritten using the coil expansion coefficient, α,

$$\alpha^2 = \frac{R^2}{R_\theta^2} = \frac{R^2}{zl^2} \qquad (2)$$

$$F(\alpha) = \frac{z^{1/2} BkT}{2\alpha^3 l^3} + \frac{3\alpha^2 kT}{2} = U(\alpha) - TS(\alpha) \qquad (3)$$

where B is the second virial coefficient,

$$B = V_0(1-2\chi) \qquad (4)$$

Finding the minimum in the free energy expression, equation (3), yields the most probable value for α,

$$\alpha \sim \left(\frac{z^{1/2} B}{l^3}\right)^{1/5} \qquad (5)$$

.

b) The first term is from the Flory Krigbaum expression, second term of equation 3 in the answer to 2a. The second term is related to the idea that for each blob one kT is added to the entropy so with N blobs we have NkT contributed and $N = z/g^* = R_0^2/R^2 = \alpha^{-2}$.

c) The last term arises from the third virial coefficient which has a prefactor of the density cubed for ternary interactions. The density is z/R^3 so this results in a term of α^{-9} . In the Flory Krigbaum expression we multiply by the volume of the coil or R^3 so the term has a dependence on α of α^{-6} .

The virial expansion of the enthalpic interactions is given by,

$$U(\alpha) = V_{Coil} kT \left[n^2 B + n^3 C + \ldots \right] \approx V_{Coil} kT n^2 B \sim \frac{kTR^3 B z^2}{R^6} = \frac{z^{1/2} BkT}{2\alpha^3 l^3} \qquad (6)$$

where n is the segmental density in the coil and V_{Coil} is the volume of the coil. The second virial coefficient describes binary interactions and the third virial coefficient describes ternary interactions. In dilute conditions we can ignore the higher order interactions and use only the second virial coefficient.

d) The equation is based on setting the derivative of the free energy expression in 2c to 0 to find the optimium R and α. The result is that there are two regimes in x. x correlates with the second virial coefficient and with temperature. As temperature drops the coil collapses so α drops. At large y (large third virial coefficient) a continuous transition is observed, second order similar to synthetic polymers, while at smaller y (smaller third virial coefficient) a discrete transition is observed, first order similar to biopolymers.

e) The sequence of events that are shown in Figure 3 a can only occur on coil collapse since once the polymer forms a solid 3-d globule it is unlikely to revert to a blob situation. There is no driving force for a transition from a globule to a blob structure. For a first order transition we expect this to be strongly the case. For a second order transition the collapse of the coil is less well defined so a reversible transition might be expected.