If you find yourself without enough information, make and justify a reasonable approximation. Please answer all parts of a question! (This is good practice for an exam setting.)

1. This problem is from Painter and Coleman.

(a) The characteristic ratio $C_\infty$ for polyethylene is 6.8. What would be the root-mean-square end-to-end distance of a chain of degree of polymerization 100,000, if the chain is in a melt of other high molecular weight polyethylene chains? Use $\ell = 1.54$ Å for the carbon–carbon bond distance.

(b) What would be the radius of gyration in this circumstance?

(c) Assuming that all constants of proportionality cancel out, what is the ratio of the root-mean-square end-to-end distance of the same chain in a good solvent compared to that in the melt?

2. For the polyethylene chain in the previous problem, calculate its overlap concentration $c^*$ (units of g/cm$^3$ are fine) in a good solvent. Hint: use its radius of gyration and molecular weight, and assume a monodisperse sample. Then estimate the ratio by which the volume fraction of polymer will have to increase, compared to $\phi^*$ at the overlap concentration (i.e. calculate $\phi/\phi^*$) for the blob size $\xi$ to shrink from the size of the chain to the size of a monomer unit.

3. A common application of the Flory-Huggins model is interpreting phase equilibrium for the swelling of a polymer gel in a solvent. The net result is (see pp 412-413 in Hiemenz and Lodge)

$$\ln(1 - \phi_e) + \phi_e + \chi \phi_e^2 = \frac{\nu_e}{N_A V_0} \frac{\dot{V}_1}{V_0} \left( \frac{\phi_e}{2} - \phi_e^{1/3} \right)$$

in which the left side comes from the Flory-Huggins chemical potential for a solvent–polymer mixture and the right side comes from the free energy change of expanding the gel (essentially the entropy change of stretching the polymer chains as the gel swells). The extension ratio $\lambda$ that occurs during swelling is related to the final volume $V$ and unswollen polymer volume $V_0$ by $\lambda = (V/V_0)^{1/3}$, and $\phi_e = V_0/V$ is the equilibrium volume fraction of polymer in the swollen case. $\dot{V}_1$ is the molar volume of the solvent. The number of strands of polymer per unit volume ($\nu_e/V_0$) can be found from

$$\frac{\nu_e}{V_0} = \frac{\rho N_A \nu}{M_x} \left( 1 - \frac{2M_x}{M} \right)$$

and the ratio of (molecular weight between entanglements $M_x$ over molecular weight) is a correction factor for dangling ends.

With this background, do Hiemenz and Lodge 10.13 (copied in the next paragraph).

A rubber band made of a styrene–butadiene random copolymer is swollen to equilibrium in toluene; the volume increases by a factor of 5. Taking $\chi \approx 0.4$, estimate the number of strands per unit volume, and therefore the extent of cross-linking. Estimate Young’s modulus for both the dry and swollen rubber bands.

**Hint:** see the p 414 example.
4. A typical chemical bond has an energy of 350 kJ/mol. Even though that’s pretty strong, can you break a polymer chain with a pair of scissors?

Consider a single chain that has a molecular weight between entanglements of \(M_x = 10,000\) g/mol whose ends are caught in separate halves of the polymer as you cut it with the scissors. Use the uniaxial stress–extension relationship

\[
s = \frac{\rho RT}{M_x} \left(\lambda_x - 1/\lambda_x^2\right)
\]

to determine the stress required to stretch the chain. (Neglect the dangling ends correction factor for this problem.) Assume a reasonable value for the extension ratio \(\lambda\) ( = length / original length) and cross sectional area \(A\) over which the tensile stress \(s\) is applied. Recall that \(s = f/A\), and assume that the bond will break after enough force \(f\) is applied such that the integral of force times distance equals the bond energy.

5. Use the Sanchez-Lacombe equation of state to calculate the density of polystyrene at 1 atm and 50°C. Then calculate the pressure that is required for polystyrene to have this same density at 200°C. (This kind of pressure could arise in injection molding.)

6. The extensive Flory-Huggins free energy of mixing for a system of (1) solvent / (2) polymer A / (3) polymer B can be written as

\[
\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + (n_1 + n_2 M_2 + n_3 M_3) \left(\phi_1 \phi_2 \frac{\chi_{12}}{RT} + \phi_1 \phi_3 \frac{\chi_{13}}{RT} + \phi_2 \phi_3 \frac{\chi_{23}}{RT}\right)
\]

where \(n_i\) equals the moles of species \(i\), \(M_1 = 1\) is the size (in lattice units) of a solvent molecule, \(M_i\) is the size of polymer species \(i\) (i.e. its number of lattice units per chain). The volume of the system is \(V = (n_1 + n_2 M_2 + n_3 M_3)V_s\), where \(V_s\) is the volume of a solvent molecule, and the volume fraction is defined as

\[
\phi_i = \frac{n_i M_i}{n_1 + n_2 M_2 + n_3 M_3}
\]

Phase equilibria between two separate phases occurs when the chemical potential of each species \(i\) is equal in the two phases, i.e.

\[
\frac{(\mu_i - \mu_i^0)}{n_{tot}RT} = \frac{(\mu_i - \mu_i^0)}{n_{tot}RT} = \left(\frac{\partial \Delta G_m}{\partial n_i}\right)_{T,P,n_j}
\]

Derive the form of \((\mu_i - \mu_i^0)_{tot}/n_{tot}RT\) for each species \(i = 1, 2, 3\).

HINT(s): remember that the denominator of each \(\phi_j\) depends on each of the \(n_j\). Also check your answer against the 2 species solution for the case of \(n_3 = 0\).