

Polymer Science 2024/25

Exercise 11

1. Use Origin or Excel for this question. The Flory-Huggins equation for a polymer-solvent system is

$$\Delta G_m = RT \left(\frac{\phi_1}{n_1} \ln(\phi_1) + \phi_2 \ln(\phi_2) + \chi \phi_1 \phi_2 \right)$$

where the effective degree of polymerization $n_1 = 20$ and the Flory-Huggins coefficient $\chi = 270/T$. T is the temperature in K and ϕ_i is the volume fraction of component i .

- (i) Show that:

$$\frac{d^2 \Delta G_m}{d\phi_1^2} = RT \left(\frac{1}{1 - \phi_1} + \frac{1}{n_1 \phi_1} - 2\chi \right)$$

- (ii) The spinodal curve is defined as the condition where the second derivative of the Gibbs free energy of mixing, $\Delta G_m''$, equals zero. Plot the spinodal curve of this system in the (T, ϕ_1) -space for the temperature range $-100 \leq T \leq 100$ °C.
- (iii) Plot ΔG_m as a function of ϕ_1 for several values of T between -100 and 100 °C. Using your plots, determine the binodal curve by identifying the points of common tangent.

Tip: the binodal represents the boundary of phase coexistence and is defined by the points of ϕ_1 at which the Gibbs free energy curve has a common tangent at a given temperature. These points correspond to the compositions of the two coexisting phases.

- (iv) You mix the polymer and the solvent at 150 °C and cool your mixture slowly. What phase separation mechanisms do you expect for $\phi_1 = 0.18$ and for $\phi_1 = 0.4$?
- (v) Phase separation will result in a polymer-rich phase and a solvent-rich phase. For $\phi_1 = 0.18$, estimate the compositions and volume fractions of these two phases at $T = 0$ °C.

- (vi) Suppose now that you start with a mixture of the solvent and a volume fraction $\phi_1 = 0.3$ of monomers of the polymer that you let react afterwards. At which value of n_1 (the degree of polymerization) will phase separation occur if the temperature is kept constant at 0 °C?
- (vii) Explain qualitatively why high molecular weight polymer blends are most often immiscible over wide ranges of composition below their degradation temperatures.
- (viii) How is it possible to improve the dispersion of an immiscible binary mixture of two polymers?