School of Engineering
Institute of Materials
Laboratory of Macromolecular
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Polymer Science 2025/26

Exercise 12

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

$$\Delta G_{\mathrm{m}} = \mathrm{R}T\left(\frac{\phi_1}{n_1}\ln(\phi_1) + \phi_2\ln(\phi_2) + \chi\phi_1\phi_2\right) \ ,$$

with 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:

$$\frac{\mathrm{d}^2\Delta G_{\mathrm{m}}}{\mathrm{d}\phi_1^2} = \mathrm{R}T\left(\frac{1}{1-\phi_1} + \frac{1}{n_1\phi_1} - 2\chi\right) \ .$$

(ii) The spinodal curve is defined as the condition where the second derivative of the Gibbs free energy of mixing, ΔG_{m}'', equals zero. Plot the spinodal curve of this system in the (T, ϕ_1)-space for the temperature range $-100 \le T \le 100$ °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.

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(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?

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