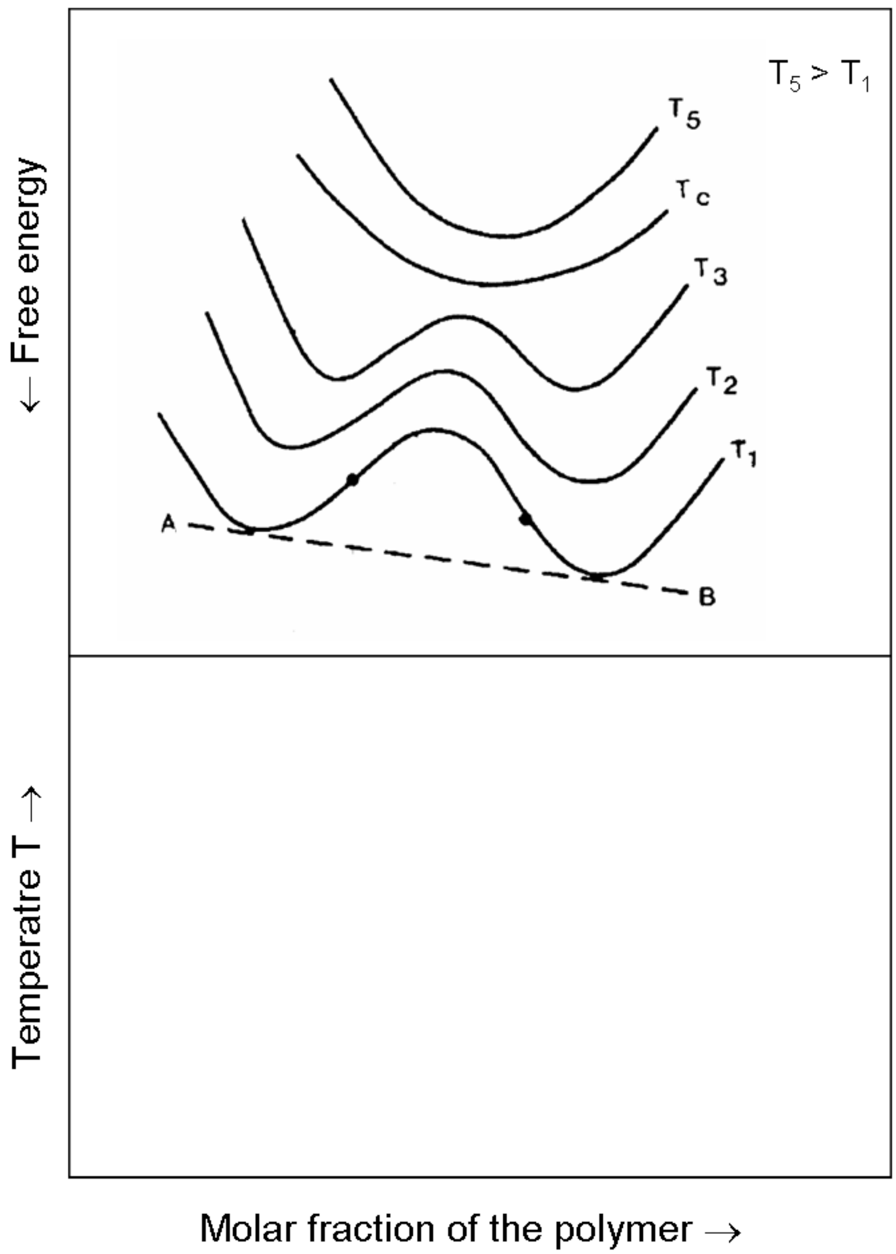
Exercises 3: Concentrated Solution and Phase Behavior

3.1: The upper part in the following diagram shows a plot of the free-energy of mixing as a function of the concentration for a given polymer-solvent system.

a.) Construct a phase diagram for the given polymer-solvent system from the curves of the free energy of mixing at different temperatures

b.) Does this polymer show a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) in the given solvent?



3.2: The following relationship can be obtained between the critical temperature T_c for phase separation and the degree of polymerization n (Flory-Krigbaum-Equation)

$$\frac{1}{T_c} = \frac{1}{\theta}\left[1 + \frac{1}{\Psi}\left(\frac{1}{\sqrt{n}} + \frac{1}{2n}\right)\right]$$

The following critical temperatures were obtained for polyisobutylene [- CH_2 – $C(CH_3)_2$-]$_n$, M = 56 g/mol, in diisobutylketone:

M [g.mol^{-1}]	22700	285000	6000000
T_c [°C]	18.2	45.9	56.2

Calculate Θ, ψ and χ at 298K for polyisobutylene in diisobutylketone.

Use: $\frac{1}{2} - \chi = \psi(1 - \frac{\Theta}{T})$ to calculate χ

3.3:
(a) The Flory-Huggins theory may be extended to a binary mixture of different polymers, i.e., an A/B blend. The resulting free energy of mixing can be written as

$$\Delta G_m = kT \left\{ (\phi_A/ N_A) \ln \phi_A + (\phi_B/N_B) \ln \phi_B + \chi\phi_A\phi_B \right\}$$

where N_A and N_B are the respective degrees of polymerization. Find the critical point (χ_c and ϕ_c) in terms of N_A and N_B. Show that your results reduce to the solution case when N_B --> 1. Compare the solution and symmetric blend (i.e. $N_A = N_B$) results in the limit of infinite molecular weight; what is the crucial difference?

(b) If you have a blend of polystyrene and polybutadiene, at what critical temperature would you expect to find a homogeneously mixed system for all polymer fractions if the molecular weight of the PS is 10^5 g/mol and PB is 10^4 g/mol.
M_{mon} (PS) = 104 g/mol, M_{mon} (PB) = 52 g/mol.
As we discussed a way to calculate is to use the Hildebrand approach:

$$\chi = \frac{v_0}{k_B T}(\delta_1 - \delta_2)^2$$

For this system take: v_0= 100 Å^3, δ_{PS} = 1.87x10^4 $J^{1/2}$ $m^{-3/2}$, and δ_{PB} = 1.62x10^4 $J^{1/2}$ $m^{-3/2}$