exercises during class

1.3. On a "chess-field" containing 64 squares, you distribute

a) 16 small solute molecules and 48 solvent molecules (which each use 1 square of space).

b) 1 polymer molecule of a length of 16 (each segment of the chain using 1 square of space) and 48 solvent molecules (using one square of space)

$k_B = 1.38 \times 10^{-23}$ J/K

What is the entropy of mixing in both cases? Which system has the higher entropy?

2.0: Experimental chain dimensions for poly(ethylene terephthalate) (PET) at 275°C are given by $\frac{\langle h^2\rangle_0}{M} \approx 0.90\text{Å}^2 mol/g$. Calculate C_∞, the statistical segment length, and the persistence length for this polymer. Based on these numbers, is PET a flexible polymer, or not? What would you expect based on the molecular structure?

2.3: The following data were obtained for different solutions of a polymer in a membrane osmometer:

c (g/L)	height difference measured (cm of solvent)
3.2	0.70
6.6	1.82
10.0	3.10
14.0	5.44
19.0	9.3

The temperature is 25 °C and the solvent density is 0.85 g/ml. Determine the molecular weight and second Virial coefficient of this polymer solution. How could you get the theta temperature for this polymer solvent system?

2.5: The following data were obtained for polystyrene solutions in butanone at 25 °C in viscosity measurements in an Ubbelohde viscosimeter

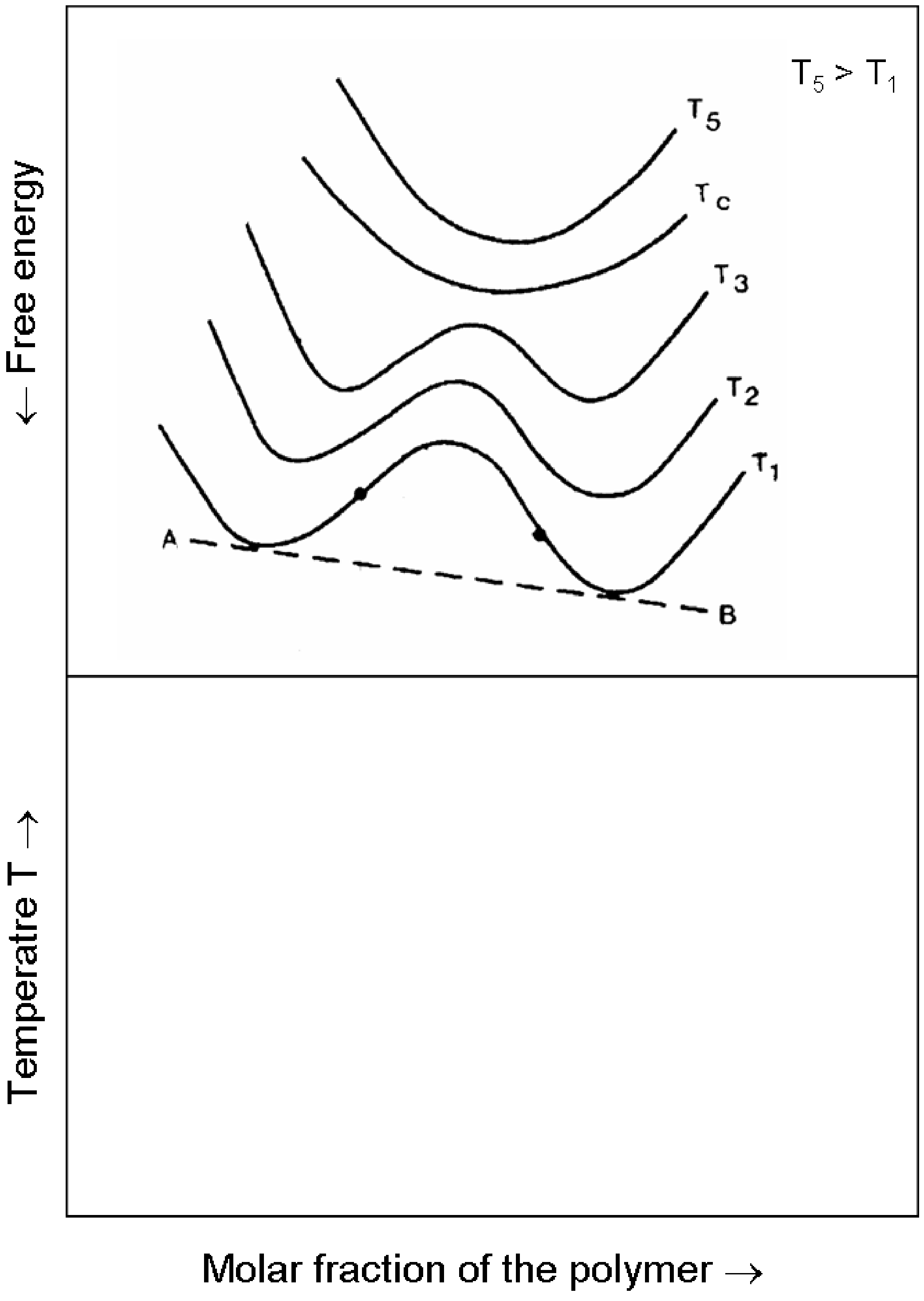
conc (g/dL)	t (sec)
0	65.8
0.54	101.2
1.08	144.3
1.62	194.6
2.16	257.0

Determine the intrinsic viscosity and the viscosity average molecular weight of the polymer knowing that K and a for this polymer are 0.039 $cm^3 \cdot mol^{1/2}/g^{3/2}$ and 0.58 respectively.

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.

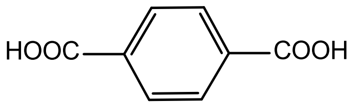
a.) Construct a phase diagram for the given polymer-solvent system from the curves of the free energy of mixing at different temperatures

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

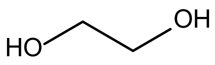


4.6: Di-n-ethylhexyl phthalate (DEHP) and related compounds are commonly used to plasticize poly(vinyl chloride) (PVC) to produce pliable material generically referred to as "vinyl". A good plasticizer is miscible with the polymer in question, does not crystallize itself, and has a very low vapor pressure. What fraction of DEHP should be added to PVC to bring T_g down below room temperature, say 293K, given that T_g for DEHP is about -86°C and for PVC 90°C respectively?

5.1: Polyethylene terephthalate (PET) is an important polymer for the production of synthetic fibers, foils and liquid containers (*e.g.* lemonade-bottles). It is produced by condensation of terephthalic acid with ethylene glycol (Fig. below). The raw material has a degree of crystallinity of up to 60%.



Terephthalic acid

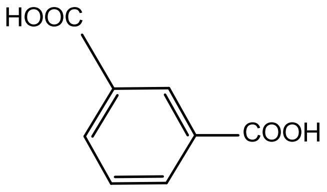


ethylene glycol

Depending how it is processed and thermally treated, it may exist both as an amorphous transparent or as a semi-crystalline material. The semi crystalline material might appear transparent or opaque and white depending on its crystal structure and crystal spherulite size.

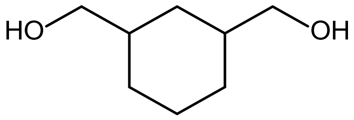
a.) Draw the structure of the polymer.

b.) You use 5% of isophthalic acid (Fig. a below) in the synthesis of your polymer. How does this influence the degree of crystallinity and the melting temperature of your polymer, compared to the unmodified polymer ? What happens if you use 5 % of cyclohexane-dimethanol (Fig. b below) instead of ethylene glykol in your synthesis?



Isophthalic acid

(a)



Cyclohexane dimethanol

(b)

c.) How would you process the homopolymer (from part a) in order to obtain a transparent product ?

d.) Calculate the density of the polymer, if its degree of crystallinity by weight is exactly 50%. Calculate the degree of crystallinity by volume.

Density amorphous ρ_a: 1370 kg/m^3
Density 100% crystalline ρ_c: 1455 kg/m^3

e.) What methods do you know to measure the degree of crystallinity of a polymer?

5.3: Chemical evidence for chain folding in polyethylene crystals is obtained by etching polymer crystals with fuming nitric acid, which cleaves the chain at the folded surface. The resulting chain fragments are separated chromatographically and their molecular weights determined by osmometry. The folded chain is pictured as crossing through the crystal, emerging and folding back, then reentering and recrossing the crystal, and so on. According to this picture, the shortest chain showing up in the chromatograms should equal the crystal thickness in length. The second shortest chain exceeds twice this value by same amount, which measures the length of the loop made by the chain outside the crystal. Molecular weights for the two shortest chain observed in an experiment of this sort were 1260 and 2530. Since the cleaved chains end in nitro and carboxyl groups, 60 should be subtracted from each of these molecular weights to give the polyethylene chain weight. Calculate the degree of polymerization of each molecule and the chain length (use the length of the unit cell along the chain axis, 2,53Å, as the distance per repeat unit). Compare the latter with the crystal thickness determined by x-ray diffraction, 105Å. What does the ratio of chain lengths for the first and second peaks suggest about the tightness of folding?

7.2: Use the Maxwell model analysis of stress relaxation to estimate the longest relaxation time for the highest molecular weight sample in the plot of the stress realxation modulus G(t) versus time t on page 3 of the lecture notes [$G = 3 \times 10^6$ dyn/cm^2 (plateau value) $M = 4.6 \times 10^5$ g/mol, $\eta = 5.5 \times 10^{11}$ P (= g/cm s)]

7.4: You are an engineer in charge of a polystyrene drinking cup manufacturing plant. Normally, you process the material at 160ºC, where the viscosity of the polymer melt is 1.5 x10^3 poises when $Z_w = 800$ (Note that $Z_{c,w}$ for polystyrene is 730). Today, your polystyrene has $Z_w = 950$. What change in processing temperature will bring down the viscosity to the initial value of 1.5 x10^3 poises? T_g for polystyrene is 100ºC. (Note: Use the universal constants for the Williams-Landel-Ferry equation $C_1 = 17.44$, $C_2 = 51.6$)

The following relationship exists between the melt viscosity of the polymer and its length:

$$\eta = K_H (Z_w)^{3.4}.$$

With Z the number of atoms along the polymer chain's backbone.

With $Z_{c,w}$ as critical entanglement chain length: weight average number of chain atoms in the polymer molecules