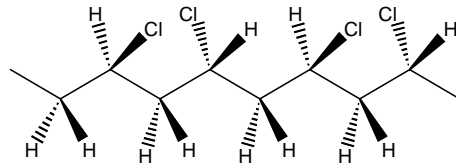


1. (a) Draw the structure of syndiotactic poly(vinyl chloride).



- (b) Would the glass transition temperature of syndiotactic PVC be lower than, the same to, or higher than atactic PVC? Explain your answer.  
 Higher. Segmental motion of chains in amorphous region of semicrystalline syndiotactic PVC is somewhat restricted by the crystals.
- (c) If atactic PVC is crosslinked somehow, would the glass transition temperature be lower than, the same to, or higher than linear (uncrosslinked) PVC? Explain your answer.  
 Higher. Crosslinking point restricts the segmental motion just like crystals does.
- (d) Polyethylene terephthalate (PET) is prepared from ethylene glycol (HO-CH<sub>2</sub>-CH<sub>2</sub>-OH) and terephthalic acid (HOOC-Ph-COOH). Draw the structure of PET.  
 -[O-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-Ph-CO-]-
- (e) PET is not soluble in organic solvent, and is soluble only in pretty strong acid like trifluoroacetic acid or phenol. Explain.  
 The fact that PET is not soluble in organic solvent means it is a (semi)crystalline polymer. ΔH for solution of semicrystalline polymers is larger than that of amorphous polymers due to (positive) heat of fusion. PET is soluble in an acid through forming hydrogen bonding, which results in negative heat of solution.
- (f) Cellulose acetate is soluble in either acetic acid or pyridine, but is not soluble in a mixture of the two. Explain.  
 Cellulose acetate must be soluble to the two solvents through some interaction, whether it is dispersion, dipole, or H-bonding (actually, H-bonding). However, the interaction (actually an acid-base reaction) between the amine and the acid is stronger than interaction between the polymer and the solvents.

2. In Flory-Huggins lattice theory for polymer solutions, the entropy of mixing is given as:

$$\Delta S_m = k \ln [\Omega_{12}/\Omega_1\Omega_2].$$

- (a) What are  $\Omega_{12}$ ,  $\Omega_1$ , and  $\Omega_2$ , respectively? Answer in your own words. No equations.  
 $\Omega_{12}$  ~ the number of ways to fill  $N_1$  solvent molecules and  $N_2$  polymer molecules in  $N_1 + xN_2$  cells, where  $x$  is the number of mers in polymer  
 $\Omega_1$  ~ the number of ways to fill  $N_1$  solvent molecules in  $N_1$  cells  
 $\Omega_2$  ~ the number of ways to fill  $N_2$  solvent molecules in  $xN_2$  cells
- (b) Is  $\Omega_2$  larger, the same, or smaller than  $\Omega_1$ ? Why?  
 $\Omega_2 \gg \Omega_1$ .  $\Omega_1 = 1$  and  $\Omega_2 \gg 1$ , since the mers in polymer are connected.

3. Answer the following questions for  $\chi$ .

(a) What is it called?

(Flory-Huggins) interaction parameter

(b) How is the polymer/solvent system with higher  $\chi$  compared to the system with lower  $\chi$ ?

High  $\chi$  is related to high  $\Delta H_m$  and high  $(\delta_1 - \delta_2)$ , both of which indicate low solubility.

The polymer/solvent with higher  $\chi$  is less soluble to each other than that with lower  $\chi$  is.

(c) What does it mean by  $\chi = 0.5$ ?

When  $\chi = 0.5$ , excess free energy of mixing becomes 0 (zero).

In this condition the solution behaves ideally (ideal solution), and is in theta condition.

(d) If a polymer/solvent system has negative  $\chi$  value, what does it mean?

A negative  $\chi$  gives a negative  $\Delta H_m$ . Negative heat of mixing is possible when there exists a specific interaction like H-bonding between solvent and solute.

(e)  $\chi$  of polystyrene in toluene at 25 °C is 0.37. Would  $\chi$  at 40 °C be higher than, lower than, or the same to 0.37? Why?

Lower. With positive heat and entropy of mixing in this system, the solution becomes more soluble as temp increases, and  $\chi$  decreases.

(f) Would  $\chi$  of polystyrene in acetone at 25 °C be higher than, lower than, or the same to 0.37? Why?

Higher. Considering the chemical structures and polarities of toluene and acetone (more polar), polystyrene should be more soluble in toluene than in acetone.  $\chi$  of less soluble solution is higher.

4. [10 points] You want to determine the theta temperature of a polymer in a certain solvent. You are given with the polymer samples with a few different known molecular weights and the solvent.

Design and explain your experiment that determines the theta temperature.

Theta condition is the borderline between good and poor solvent, and in theta condition the infinitely high molecular weight fraction just precipitates (p135, Textbook)..

You make dilute (should be dilute, since theta condition is defined only in dilute solution) solutions of the samples of different molecular weights given. You raise the temperature, if some of the solution is not clear, until you get the clear solution. Then you lower the temperature very slowly, and take the temperature where the first precipitation is observed. The theta temperature is given by extrapolating to the infinite molecular weight.

5. (a) Name the methods, as many as you can, that can be used in the molecular weight determination of polymers.

end-group analysis, ebulliometry, cryoscopy, MO, VPO, LS, DSV, GPC

(b) Categorize the methods of your answer to (a) into three groups; methods measuring  $M_n$ ,  $M_w$ , and molecular size.

$M_n$  ~ end-group analysis, ebulliometry, cryoscopy, MO, VPO

$M_w$  ~ LS

size ~ DSV, GPC

6. Using the table given below, answer the following questions.

- (a) For a polystyrene solution in cyclohexane at 34.5 °C, a relative viscosity of 1.60 was measured at the concentration of 1.0 g/dL. Estimate the viscosity average molecular weight of the polymer.

The solution is in theta condition; you need just one concentration.

$$[\eta] = \eta_{sp}/c = (1.6 - 1)/1.0 \text{ dL/g} = 60 \text{ mL/g} = K M_v^a = (84.6 \times 10^{-3} \text{ mL/g}) M_v^{0.5}$$

$$M_v = 5 \times 10^5$$

- (b) The use of ‘universal calibration’ in GPC is based on the observation that the hydrodynamic volume is the same for all the polymers at the same retention volume. If a monodisperse cis-polybutadiene standard with molecular weight of 100000 eluted at the retention volume of 100 mL in the GPC experiment with benzene at 30 °C, what would be the molecular weight of the fraction of polyvinyl acetate eluted at the same retention volume at the same condition?

From the definition of intrinsic viscosity, hydrodynamic volume  $\sim [\eta] M = K M^{a+1}$

Using K and a values of the two polymers, M of PVAc fraction =  $2 \times 10^5$

**Table 3.10 Selected intrinsic viscosity–molecular weight relationship**

Polymer	Solvent	$T(^{\circ}\text{C})$	$K \times 10^{3a}$	$a^b$
<i>cis</i> -Polybutadiene	Benzene	30	33.7	0.715
<i>it</i> -Polypropylene	1-Chloronaphthalene	139	21.5	0.67
Poly(ethyl acrylate)	Acetone	25	51	0.59
Poly(methyl methacrylate)	Acetone	20	5.5	0.73
Poly(vinyl acetate)	Benzene	30	22	0.65
Polystyrene	Butanone	25	39	0.58
Polystyrene	Cyclohexane	34.5	84.6	0.50
Polytetrahydrofuran	Toluene	28	25.1	0.78
Polytetrahydrofuran	Ethyl acetate hexane	31.8	206	0.49

<sup>a</sup> K in mL/g