

8. (a) What do you mean by thermoplastic and thermosetting, respectively?

Thermoplastic ~ deformable (plastic deformation) upon heating

Thermosetting ~ not deformable upon heating

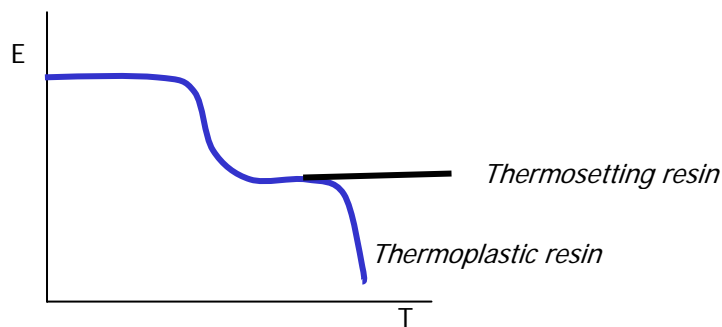
(b) Why is a thermosetting resin not soluble in a solvent?

In thermosetting resins, the polymer chains are crosslinked and are not separable by solvent to make solutions

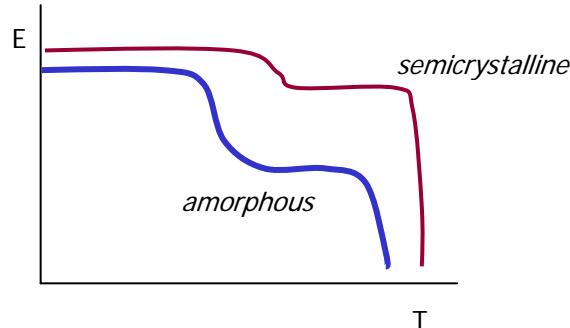
(c) Why is a semicrystalline polymer not soluble in a solvent?

For a semicrystalline polymer to be soluble, the crystals have to be first collapsed, which needs energy (heat of fusion). The heat of fusion plus heat of mixing is too large for the entropy of mixing to overcome.

(d) Draw a modulus (E, on y-axis) – temperature (T, on x-axis) curve for a thermosetting resin in comparison with a thermoplastic resin.



(e) Draw a modulus (E, on y-axis) – temperature (T, on x-axis) curve for a semicrystalline polymer in comparison with an amorphous polymer.



9. (a) Does the *conformation* of a polymer chain change by varying the temperature? If yes, explain how. If no, explain why not. You may use an example.

Yes. The conformation is determined by the rotation of bonds in the polymer chain, which changes with varying temperature. For example, trans to gauche transition in polyethylene with increasing temperature.

(b) Does the *configuration* of a polymer chain change by varying the temperature? If yes, explain how. If no, explain why not. You may use an example.

No. For the configuration to be changed the bonds in the polymer has to be broken and recombined, which does not occur by varying the temperature. For example, tacticity of a polymer does not change by varying temperature. If you think of the rearrangement of bonds at excessively high temperatures, the answer can be yes.

10. (a) Yes. [1]  $\Delta S > 0$ ;  $\Delta H = 0$ ;  $\Delta G < 0$ .

(b) No, not always. [1]  $\Delta S > 0$ ;  $\Delta H > 0$ ; soluble only when  $\Delta H < T\Delta S$ .

(c) Not ordinarily. A solution is ideal when solute molecule is identical to solvent molecule in size, shape and forces. A polymer molecule is too much larger than solvent molecules to give an ideal solution.

But possible in dilute solution, when excess free energy of mixing becomes zero. At theta condition, the solution behaves ideally.

11. (a) 10 molecules with M of 10E4 and 1 molecule with M of 10E5.  $M_z = 92000$   
 (b)  $0.5 < a < 0.8$ .  $M_v$  is between 43000 ( $a=0.5$ ) and 50500 ( $a=0.8$ )  
 Taking K value of 0.001,  $[\eta]$  is between 0.2 dL/g ( $a=0.5$ ) and 5.8 dL/g ( $a=0.8$ ).

12. When a polymer solution behaves like an ideal solution thermodynamically, i.e., when excess free energy change of mixing ( $\Delta G^{ES}$ ) is zero (0), it is said that the solution is in theta ( $\theta$ ) condition. In this condition, concentration is low (low, medium, or high), interaction parameter is 1/2, and second virial coefficient ( $A_2$ ) in the virial equation for osmotic pressure is zero (0).

13.

(a) Solubility parameter 용해도상수

(b)  $\delta^2 = \delta_D^2 + \delta_P^2 + \delta_{HB}^2$

The higher the polarity, the larger the  $\delta$ . Acetone is of higher polarity than decane is.

(c)  $\Delta\delta < 1.0 \text{ cal/cm}^3$  ( $2.0 \text{ MPa}^{1/2}$ );  $8.45 < \delta(\text{solvent}) < 10.45$

acetone, benzene, carbon tetrachloride, 1,4-dioxane, toluene

(d) Would you expect polystyrene be soluble in poly(methyl methacrylate)? Why or why not?

No;  $\Delta\delta$  must be much smaller for polymer/polymer solution ( $< 0.1$ ) due to high mol wt and resulting small  $\Delta S$ .  $\Delta\delta$  of 0.35 is too big.

(e) PE is a (semi)crystalline polymer, which requires overcoming of positive heat of fusion to be soluble.  $\delta$  given in the table is for amorphous PE at 25 °C.

(f) Heating. For a semicrystalline polymer to be soluble, there needs high temperature (to make  $T\Delta S$  large enough) or specific interaction between solvent and polymer. Since no specific interaction is expected for PE due to the absence of functional group, heating the mixture is the only resolution.

(g) Atactic; iso- and syndiotactic PS is semicrystalline due to its regular structure.

(h) Lower. The higher the  $\Delta\delta$ , the larger the  $\chi$ .  $\Delta\delta$  for toluene/PS is smaller than that for toluene/PMMA.

14.

concentration (g/dL)	0.00	0.25	0.50	0.75	1.00
elution time (s)	250	325	412	513	625
relative viscosity		1.30	1.648	2.052	2.50
specific viscosity		0.30	0.648	1.052	1.50
$\eta_{sp}/c$		1.20	1.296	1.403	1.50

(a)  $\eta_{sp} = \eta_{rel} - 1 = (t/t_0) - 1 = 0.648$

(b)  $[\eta] = 1.10 \text{ (dL/g)}$  from the plot

(c) From Table 3.10,  $K = 5.5 \times 10^{-3} \text{ mL/g}$  and  $a = 0.73$ .  $[\eta] = 110 \text{ mL/g}$   
 $M_v = ([\eta]/K)^{1/a} = 772876 \sim 772000$

(d)  $M_v$  is smaller than  $M_w$  (when  $a = 1$ ).  $M_w$  is smaller than  $M_z$ . Then by syllogism.

(e) Yes. The plot  $\eta_{sp}/c$  vs  $c$  is linear. When the solution is not dilute enough it becomes non-Newtonian and the plot is not linear.

- (f) In theta condition the plot should be independent of concentration, i.e., the slope is zero. Since it is not the case, the solution is not in theta condition.
  - (g) Polystyrene in cyclohexane at 34.5 °C (and polytetrahydrofurane in ethyl acetate hexane at 34.5 °C) is (are) in theta condition, for which the parameter  $a$  is 0.5.
15. (a) Molecular 'weight' cannot be measured directly. Measures only the molecular size and converts it to the weight.
- (b) Assumptions: equivalent (volume) sphere, Poiseulli flow ( $\text{time} \propto \text{viscosity}$ )  
Conditions: dilute solution, laminar flow, controlled temperature
  - (c) Universal calibration. Converts retention volume (size) to molecular weight using a calibration curve that is constructed with standards.