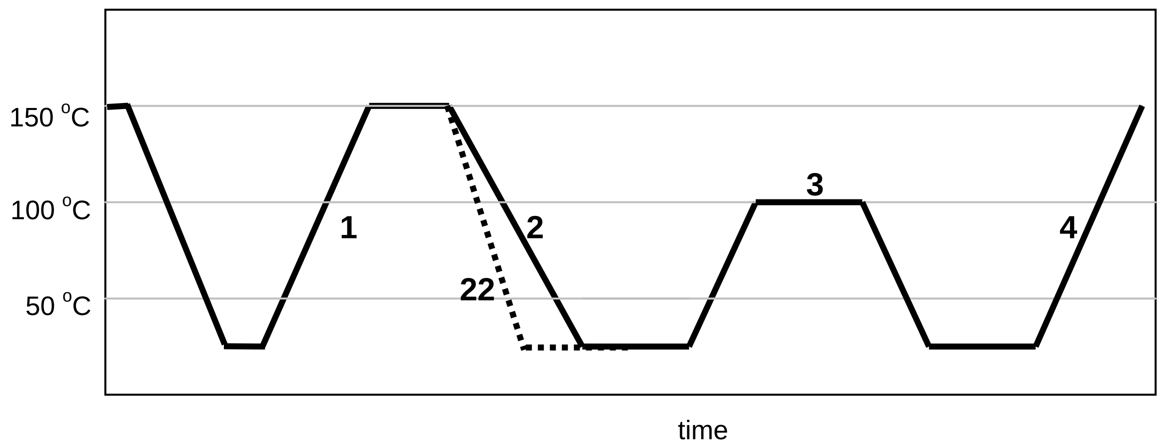
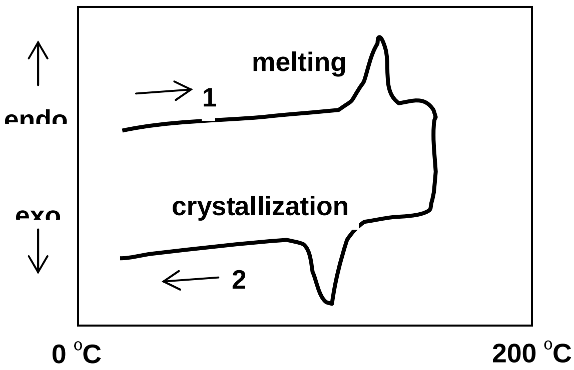
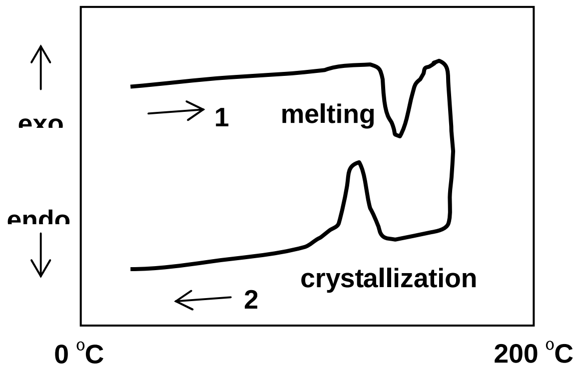
1. Comment on each of the following statements. Tell if the statement is true, true under some condition, or totally wrong. Give your reasoning also.
   (a) Polyethylene terephthalate, a semicrystalline polymer, does not form complete amorphous state.
      PET can form complete amorphous state if it is quenched.
   (b) There is no atactic vinyl polymer that can form semicrystalline state.
      Vinyl polymer with very small side group (OH of PVA) or long crystallizable side group (C8 or higher) can form semicrystalline state.
   (c) For a given polymer chain, its freely rotating chain is larger than the freely jointed chain.
      FRC is larger than FJC when bond angle is larger than 90 degree. The statement is true, since there is no bond angle smaller than 90 degree in reality.
   (d) For a given polymer chain, end-to-end distance calculated taking account of excluded volume effect is larger than that calculated by RIS model.
      It's true in that excluded volume effect gives larger end-to-end distance than RIS in calculation. In poor solvent end-to-end distance can be smaller than that calculated by RIS: If you call this an excluded volume effect, the statement is wrong.
   (e) A polymer chain in its amorphous state has the same dimension as in its unperturbed state.
      True. The dimension of a polymer chain in its amorphous state is not perturbed by excluded volume effect.

2. A polyethylene sample is subjected to the thermal history given below, and a differential scanning calorimeter (DSC) recorded the heat flux.



   (a) Draw the schematic DSC thermogram for the process 1 and 2. Show exothermic and endothermic directions and name the peaks.

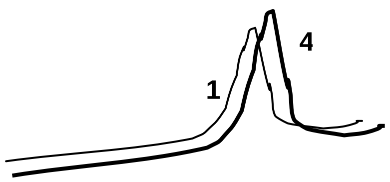




(b) What do you call the process 3? What happens to the semicrystalline structure during that process?

Annealing. Thicker (larger) crystal (lamella) and higher degree of crystallinity (larger portion of crystals)

(c) Draw the schematic DSC thermogram for the process 4 <u>in comparison</u> to the thermogram for the process 1.



Larger peak (area) due to higher crystallinity and higher peak temperature (T_m) due to thicker lamellae.

(d) If you follow the process 22 instead of process 2, what happens to the semicrystalline structure of the sample?

Thinner (smaller) crystal (lamella) and lower crystallinity

3. (a) It is usually found that a polymer of high heat stability is also of low flammability. How would you explain it?

Since the first step of burning is thermal degradation of polymer, polymers of high heat stability inflame at a high temperature. Also, char yield of heat-stable polymers is usually higher than unstable polymers.

(b) It is often found that the dielectric constant of one polymer (polymer A) is much lower than the other polymer (polymer B) at a high frequency, even though the dielectric constant of the two polymers were similar at a low frequency. How would you explain it?

Dipole of Polymer A is bound to slower-moving part like main chain of the polymer molecule, while dipole of polymer B is of faster-moving part like side chain of the polymer. At the low frequency both dipoles can orient, while, at the high frequency, only the dipole of polymer B can polarize to give higher dielectric constant.

4. Answer the following questions briefly.
   (a) Why is the temperature coefficient of chain dimension negative for polyethylene and positive for polyoxymethylene?
   For PE, portion of gauche conformation increases as temperature rise, which gives larger dimension. For POM, the other way.
   (b) Give the Miller index of the fold surface of a solution-grown polyethylene lamellar crystal. The plane is of the largest area of the lamella surfaces.
   (001), which is perpendicular to c-axis.
   (c) What would be the result of a high Keith-Padden structure parameter, $\delta = D/G$, in terms of structure of the spherulite?
   Dense (less impurity) spherulite, since the diffusion of impurity is fast and the growth of spherulite is slow.
   (d) Which of Rouse model or reptation model explains the dynamics of polymer chain in amorphous state better? Why?
   Reptation model, which takes the effect of neighbor chains (entanglement) into account. Rouse model describes the motion of a single chain.

5. A polymer specimen is subjected to a uniaxial tension of 20 MPa. Young's modulus and Poisson's ratio of the polymer is 2 GPa (2000 MPa) and 0.4, respectively.

   (a) Express the stress in a matrix form.

$$\boldsymbol{\sigma} = \begin{pmatrix} 20 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{(MPa)}$$

   (b) Calculate the volume strain. Assume that volume strain is the sum of normal strains.
   $\varepsilon_x = (1/2000)[20 – (0.4)(0+0)] = 0.01$
   $\varepsilon_y = \varepsilon_z = (1/2000)[0 – (0.4)(20+0)] = – 0.004$
   volume strain $= \varepsilon_x + \varepsilon_y + \varepsilon_z = 0.01 – 2(0.004) = 0.002$

   (c) Estimate bulk modulus of the polymer.
   mean normal stress, $\sigma_m = (1/3)[20 + 0 + 0]] = 20/3$ MPa
   $B = \sigma_m / \Delta V = (20/3)/0.002 = 20000/6$ MPa ~ 3.3 GPa
   or
   $B = E / (3)(1 – 2\nu) = 2 / 0.6$ GPa