

## 081205 Quiz 9 Morphology of Complex Materials

- 1) Polymers crystallize into structures that have an aspect ratio similar to a sheet of paper.
  - a) Describe how low molecular weight alkanes (waxes crystallize). Do these materials form sheet-like crystals? What is the degree of crystallization (final fraction of crystal versus amorphous).
  - b) Describe how proteins crystallize. Do these materials form sheet-like crystals? What is the degree of crystallization?
  - c) Explain the differences between crystals in a synthetic polymer and the materials of question a and b in terms of the ability to form chain-folded, sheet-like crystals. Why is the degree of crystallinity not 100% for polymers?
  - d) Monodisperse, linear polyethylene can be produced by hydrogenation of anionically polymerized polybutadiene. This polymer has no stereochemical defects and could completely form a planar zig-zag conformation. Do you expect such polyethylene's to form chain folded lamellar crystals or extended chain crystals from the quiescent melt? Explain your answer.
  - e) Metallocene-polymerized copolymers of polybutene and polyethylene have short branches of two carbon units that are regularly spaced at any interval that is desired. What effect do you think these *controlled* short-chain branches would have on the lamellar crystalline structure and on the degree of crystallinity for polyethylene copolymers?
  
- 2) Polymer crystal thickness,  $t$ , varies with the temperature of crystallization,  $T_c$ , following the functionality  $1/t \sim (T_\infty - T_c)$ .
  - a) Why do you think deeper quenches would lead to smaller crystals (in your answer consider that small crystals are non-equilibrium structures, that is, an infinite crystal is the equilibrium structure).
  - b) Write a pseudo-equilibrium expression for the free energy of a nano-crystal that displays lamellar structure.
  - c) From this free energy expression write an expression for  $1/t$  as a function of  $T_c$ .
  - d) What parameters are needed to calculate the lamellar thickness  $t$  as a function of  $T_c$ . Which of these parameters is most difficult to obtain? Why?
  - e) Explain how these parameters could be measured using SAXS or TEM.
  
- 3) The Avrami equation is used to describe the growth of crystals in terms of the geometry of crystal growth.
  - a) Sketch a plot of the fraction crystallinity versus time for a typical isothermal crystallization of a polymer.
  - b) Give the Avrami equation and sketch a plot associated with this equation.
  - c) Describe the two parameters needed for the Avrami Equation and give their values for 2d growth with spontaneous nucleation.
  - d) Could the Avrami equation be used to describe dendritic growth of ice on a car windshield? Explain.
  - e) How would you expect the Avrami exponent  $n$  to vary if 2-d crystal growth with spontaneous nucleation were augmented with secondary crystalline growth (crystalline growth within a crystallite nucleated on the initial crystallographic skeleton)?

## Answers: 081205 Quiz 9 Morphology of Complex Materials

- 1) a) Low molecular weight alkanes crystallize as extended chain crystals. The degree of crystallinity is 100%. They form sheet-like crystals which gives rise to their “waxy” feel as sheets slide against each other.
- b) Proteins crystallize in their native state with a collapsed native state protein at each unit cell site perfectly oriented in registry with other identical native state collapsed structures. Proteins do not form lamellar crystals. The degree of crystallinity is 100%.
- c) Synthetic polymers form chain-folded sheet-like crystals. The degree of crystallinity is less than 100% since the fold surface is amorphous and there is a region between lamellae with material that can not crystallize due to defects and chain folding itself. Polymers are polydisperse and form disordered collapsed structures so a collapsed chain, protein-like crystal is not possible. The chain can not easily form extended-chain crystals like low-molecular weight alkanes due to the loss in conformational entropy as well as entanglements in the melt among other reasons.
- d) Such polyethylene’s form chain folded crystals. This is due to the entropy difference between an extended chain crystal and a chain folded crystal.
- e) Short branches can not be included in polymer crystals so the lamellar thickness can be controlled to some extent by inclusion of regularly spaced short chain branches. This lowers the melting point of the crystals following the Hoffman-Lauritzen function. Short chain branches also dramatically decrease the degree of crystallinity leading to thermoplastic elastomer materials. These are elastomers that can be melted and processed in injection molding and extrusion equipment.

2) a) Small crystals are non-equilibrium structures and are formed far from the equilibrium point (equilibrium melting point), that is, at deep quenches.

b) For a lamellar crystal with dimensions  $a \times b \times t$  and where  $t \ll a \sim b$  we have,

$-2ab\gamma + abt\Delta f_m = 0$  at pseudo equilibrium. Also,  $\Delta f_m = \Delta H(1-T/T_\infty)$  so,

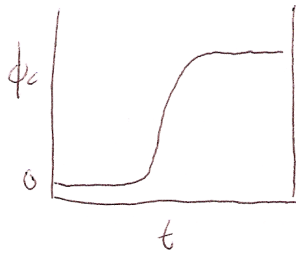
$$t = 2\gamma T_\infty / (\Delta H(T_\infty - T))$$

c)  $1/t = (\Delta H / (2\gamma T_\infty))(T_\infty - T)$

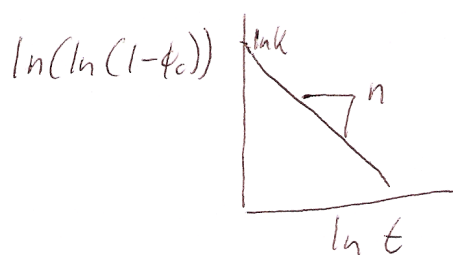
d) You need  $\gamma$ ,  $T_\infty$ , and  $\Delta H$ .  $\gamma$  is the most difficult to obtain because the exact nature of the chain fold surface is not known.

e) If  $t$  can be measured a plot of  $T$  versus  $1/t$  yields  $T_\infty$  as the intercept and the other parameters from the slope.

3) a) b)



$$\phi_c = 1 - \exp(-k t^n)$$



$$\ln(\ln(1-\phi_c)) = -n \ln t + \ln k$$

- c)  $n$  is the Avrami exponent and it reflects the dimension of growth and the type of nucleation (spontaneous or sporadic).  $k$  is the Avrami prefactor and it reflects the details of growth. For 2d growth and spontaneous nucleation  $n$  is 2 and  $k$  is  $\pi N(\text{dr}/\text{dt})^2$ .
- d) Yes it could be used to describe 2d spontaneous nucleation of ice dendrites.
- e) If crystallization were augmented by secondary crystallization the Avrami exponent would be slightly larger than 2.