# 061117 Quiz 8 XRD

This week we covered polymer crystal structure and determination of the degree of crystallinity using x-ray diffraction.

1) Starting with an expression for the difference in Gibbs free energy between a lamellar crystal and the melt (including bulk and surface terms) derive the Hoffmann-Lauritzen expression for the lamellar thickness, $t = 2\sigma T_0/(\Delta H_f\ (T_0 - T))$. List the assumptions you need to make. (You will need to associated $\Delta S_f$ with $T_0$ and $\Delta H_f$ by setting the free energy to 0 at the equilibrium melting point, $T_0$.)

2) Polymer crystals can display various polymorphs (different crystalline structures). List one polymer that displays polymorphs and explain the conditions under which polymorphs might be formed.

3) List three differences between polymer diffraction patterns and a metal powder pattern in 2D.

4) How is the degree of crystallinity determined from a polymer diffraction pattern?

5) Other than sperulites, what other types of crystalline forms are observed in polymers (list at least two others).

**ANSWERS: 061117 Quiz 8 XRD**

1) First an expression for the Gibbs free energy difference between a lamellar crystal of volume V and surface area 2A and the melt at equilibrium temperature T is written:

$\Delta G_f = 0 = V(\Delta H_f - T\ \Delta S_f) - 2\ \sigma\ A = tA(\Delta H_f - T\ \Delta S_f) - 2\ \sigma\ A$

so

$t = 2\ \sigma/(\Delta H_f - T\ \Delta S_f)$ (1)

also, at $T_0$ the crystal is of infinite thickness so it has no surface and,

$\Delta G_f = 0 = V(\Delta H_f - T_0\ \Delta S_f) = tA(\Delta H_f - T_0\ \Delta S_f)$

so

$\Delta S_f = \Delta H_f / T_0$ (2)

and substituting this in equation (1),

$t = 2\ \sigma/(\Delta H_f(1 - T/T_0)) = 2\ \sigma\ T_0/(\Delta H_f(T_0 - T))$.

2) Polypropylene or Nylon, The polymorphs form under different conditions of pressure and shear

3) Broad Peaks; High degree of orientation of patterns; Presence of amorphous Halo.

4) Plot $Iq^2$ vs q and determine the area under the crystalline peaks C and under the amorphous halo (A). The fraction crystallinity is C/(C+A) and the degree of crystallinity is 100*C/(C+A).

5) Lozenge-shaped single crystals, stacked single crystals, axialites, shish kebabs, fibrils and fibers.