

Quiz 8 XRD 5/18/01

Polymers crystallize into complex morphologies that display different structural features on different length scales. The hierarchical model for this structure is based on small scale features making up larger scale features just as bricks make up walls that make up buildings each with distinct structural features.

- a) **Explain** the hierarchical model for semi-crystalline polymers.

Begin with the crystal sketching the unit cell for PE,

Then the nano-scale structure indicating the direction of crystallographic axes in nano-scale structure.

Then the colloidal scale structure composed of stacked nano-scale features.

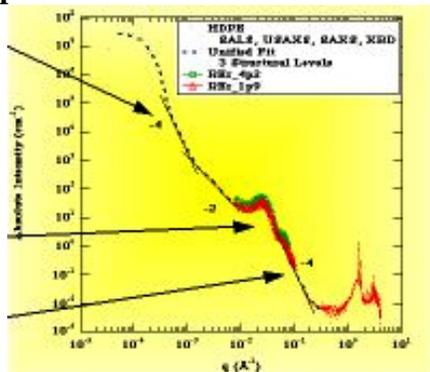
Then the micron (optical) scale feature indicating how the colloidal scale fits into the micron scale structure.

- b) **How** is the crystallographic c-axis related to the optical scale structure? (Use your hierarchical model to make this prediction).

How could this be verified using XRD and a micro-beam (diameter 1 μm) at a synchrotron?

- c) The following is a combined light scattering, Bonse-Hart SAXS, pinhole SAXS and XRD pattern for a piece of a milk jug (HDPE).

Explain the observed features in the scattering pattern based on your hierarchical model.



(log(Intensity cm^{-1}) versus log($q \text{ \AA}^{-1}$))

Begin with the XRD part (it has 2 components) then the nano-scale etc. just as you did in part a.

- d) **How does** the nano-scale size (observed in the lab using SAXS) relate to the temperature of crystallization?

Explain the equation that describes this behavior, i.e. what feature of the material leads to this behavior?

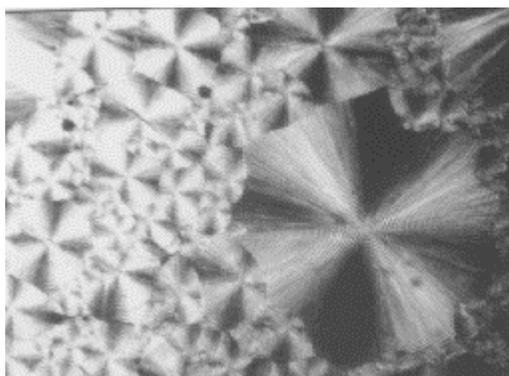
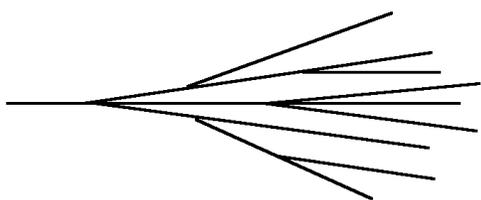
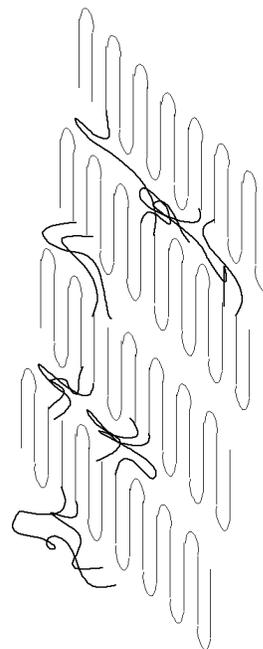
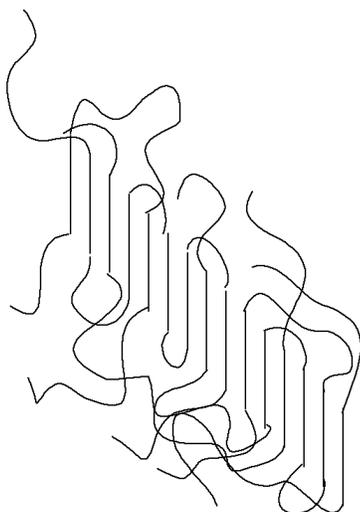
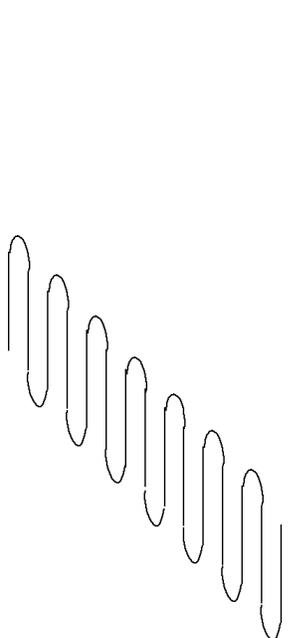
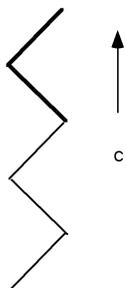
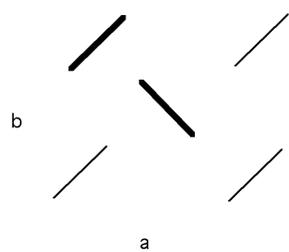
- e) The feature of part d can be measured using x-rays.

How is this size measured using SAXS?

How could this size be measured using XRD?

Answers: Quiz 8 XRD 5/18/01

a)



See web notes for description of these figures.

- b) The c-axis is normal to the lamellae. The lamellae normals are oriented radially in the spherulites. Micro-XRD using a 2-d detector would show that the c-axis is pointed radially.
- c) At highest q is the XRD pattern which displays an amorphous component (inter-lamellar) and the orthorhombic crystal structure. The peak in the small angle range is the repeat distance for the stacked lamellae (called the long period). At lower-q is scattering from the spherulites (light scattering range). This is the structure we observed in the first lab. As was seen in the first lab there can be some strikingly regular features to the spherulites that are related to twisting of fibrils as they radiate from the center of the spherulite (bands).
- d) The lamellar thickness is a function of the crystallization temperature from the Hoffman equation,

$$t = 2 \sigma_e T / (H_f (T_c - T_c^*))$$

The long period, $L = 2 \sigma_e / q^* = t / (\text{DOC})$ where DOC is the degree of crystallinity (from XRD). The Hoffmann equation relates the surface energy of the chain folds in the lamellae, to the bulk energy of fusion resulting in a size. The asymmetry of the crystals and the high surface area leads to this behavior.

- e) In SAXS the long period is measured from $L = 2 \sigma_e / q^*$. $t = \text{DOC} L$ if the amorphous is all interlamellar amorphous.

The size could also be measured from the peak breadth in XRD using the Scherrer equation, $t = 0.9 \lambda / (B \cos \theta)$