060222 Quiz 6 Morphology of Complex Materials

1) Last week we considered dynamics using two dynamic hierarchical models associated with dilute and concentrated conditions, the Rouse and the reptation models respectively. Polymer crystallization also seems to display differences associated with concentration that may be linked to the differences seen in dynamics.

   a) Describe the structural hierarchy of polymer crystals grown from dilute conditions.

   b) Describe the structural hierarchy of polymer crystals grown from the melt.

   c) The micrographs below from Paul Ehrlich* in the 1990's shows polymer crystals grown in a semi-dilute solution. Comment on the hierarchy seen in these micrographs. How does it compare with "a" and "b" above?

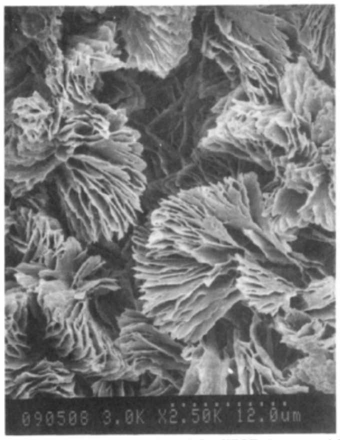


Figure 1. SEM micrograph of sample S-3, HDPE 1 (a commercial high density polyethylene with $\bar{M}_n = 7300$ and $\bar{M}_w = 43\,000$) (rapid cooling).

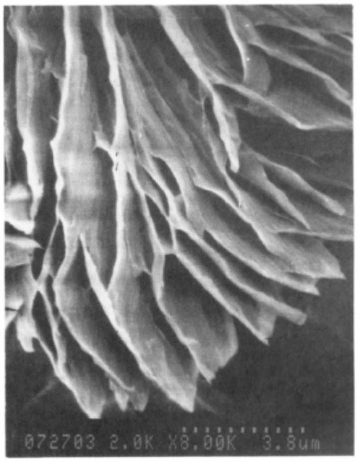


Figure 2. SEM micrograph of sample S-3, HDPE 1.

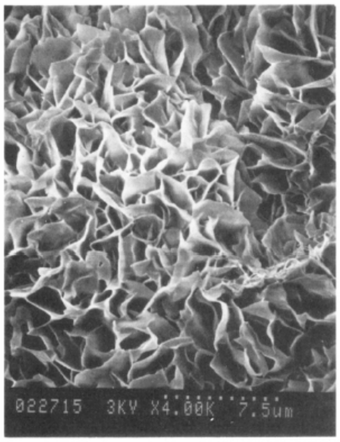


Figure 4. SEM micrograph of sample S-9, NBS 1475 (NIST standard reference linear polyethylene with $\bar{M}_n = 18\,310$ and $\bar{M}_w = 53\,070$; crystallized from a more concentrated solution).

   d) How does the dynamics hierarchy for dilute, semi-dilute and concentrated govern the structural hierarchy seen in your answers a to d?

   e) Explain how and why polymer spherulites differ from and how they are similar to dendrimers such as snow flakes.

2) The base structure seen in polymer crystals is a lamellar crystal.

   a) Obtain the Hoffman expression for lamellar thickness using the expression for the difference in the Gibbs free energy between the crystal and melt.

   b) Use the Hoffman expression to explain why polymer crystals are nanometer-sized crystals.

   c) Does the Hoffman expression work for the polymers shown in the Ehrlich micrographs above? Explain.

   d) Why are polymer crystals asymmetric (why is the lateral size larger than the thickness)?

   e) What governs the lateral size of polymer lamellae? (Define the Keith-Padden δ-parameter.)

Lamellar Structure and Organization in Polyethylene Gels Crystallized from Supercritical Solution in Propane.* Bush PJ, Pradhan D, Ehrlich P *Macromolecules* **24 1439-1440 (1991).

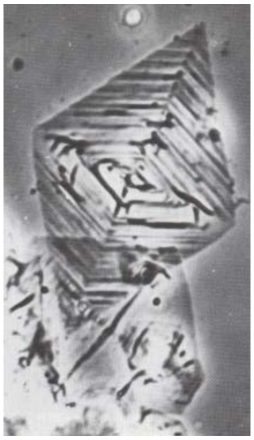
3) Chains in polymer lamellae are not normal to the lamellar surface but display a significant tilt in the lamellar crystal.

a) Sketch a cross section of a polymer lamellae showing the chains and the crystalline unit cell and indicating the c-axis.

b-e) Explain how chain tilt can be used to describe the following morphologies from Bassett and Ehrlich:

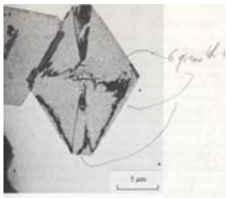
Figure 4. Axialite with dishing. HDPE 1 at 23.7% w/v, run S-3.

b)



c)

d)

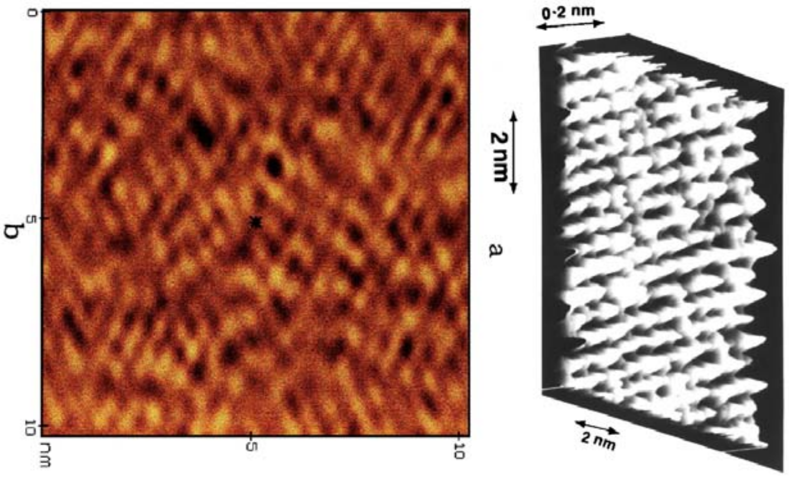


g. 3.8. Six sectors in a truncated polyethylene lozenge revealed in d
From Bassett, Frank & Keller, 1959.)

e)

ANSWERS: 060222 Quiz 6 Morphology of Complex Materials

1) a) Persistence => Helix => Lamellae (i. Thickness and ii. Lateral) => Stacking/Folding
b) Persistence => Helix => Lamellae => Stacks of Lamellae in Fibers =>Low Angle Branching => Spherulitic
c) In some sense the semi-dilute solution crystals are intermediate between spherulitic crystals and single lozenge shaped crystals. Individual lamellae are seen but the do not form pyramid shapes but rather bend slowly similar to spherulitic lamellaeThe lamellae are loosely stacked and show some degree of branching but the branching is not space filling. I would appear that there is a fairly rich morphological continuum from dilute to melt crystallization. Ehrlich didn't really understand the morphological importance of his samples and he saw semi-dilute solution crystallization as a route to high surface area polymer foams for applications like gas storage.
d) The dynamic hierarchy we looked at last has implications for crystallization. The most obvious effect involves entanglements. Dilute solution single crystals do not display tie molecules and there are no entanglements. Chains fold tightly with adjacent reentry as has been shown in AFM micrographs such as that shown below (Reneker) and this is largely due to the absence of entanglements and high mobility of polymer chains in dilute solution. In the melt chains must reptate and the reptation time is generally several orders of magnitude longer than the time required to crystallize. Entanglements are trapped and chains must span several crystals. As crystallization proceeds crystals are reeled in together since the chains are pulled into the crystals. This leads to tight stacking, switch board type reentry and dense crystalline regions. The semi-dilute samples of Ehrlich show intermediate behavior.



e) Dendrimers differ from spherulites in that dendrimers display high-angle branching along crystallographic directions (hexagonal directions for ice for instance). Spherulites display low angle branching due to twinning and epitaxial branching. Both dentrimers and spherulits grow by a fibrous motif. This is governed in both cases by a parameter like the Keith Padden δ parameter, $\delta \sim D/G$. The faster the growth rate, G, the finer the structure and the faster the transport of impurities the coarser the structure. The mechanism involving transport of impurities or thermal transfer from the crystallization front ensures low dimensional growth (non space filling).

2) a)

$$\Delta G = \Delta H - T\Delta S \text{ so at } T_\infty \text{ where } \Delta G = 0 \text{ we have } \Delta S = \frac{\Delta H}{T_\infty}$$

and for a real crystal with a finite thickness, t,

$$(\Delta G)V = abt\Delta H\left(1 - \frac{T}{T_\infty}\right) - 2\sigma_e ab - 2\sigma_a bt - 2\sigma_b at = 0$$

where the last quality is for pseudo equlibrium and we ignore the a and b surface energies so,

$$t\Delta H\left(1 - \frac{T}{T_\infty}\right) = 2\sigma_e \text{ or } t = \frac{[2\sigma_e/\Delta H]}{\left(1 - \frac{T}{T_\infty}\right)}$$

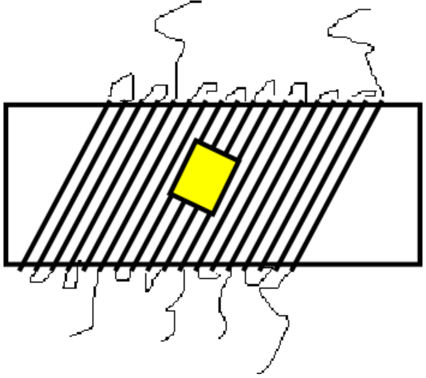
b) The numerator indicates low surface energy leads to small crystals and the denominator indicates that low temperature crystallizations lead to small crystals.

c) Hoffman works for all polymer crystals.

d) Asymmetry is due to the difference in the surface energy.

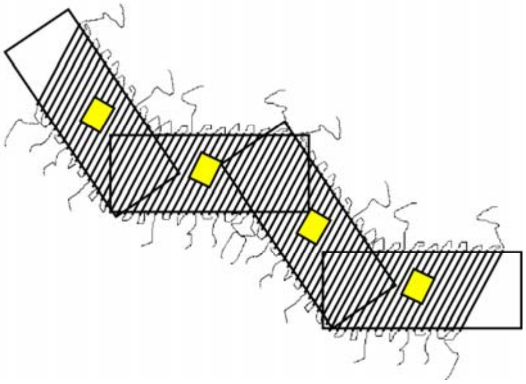
e) Keith-Padden del parameter governs lateral size due to a balance between transport of impurities and growth rate.

3) a) Box is the unit cell. c-axis is in the chain direction.



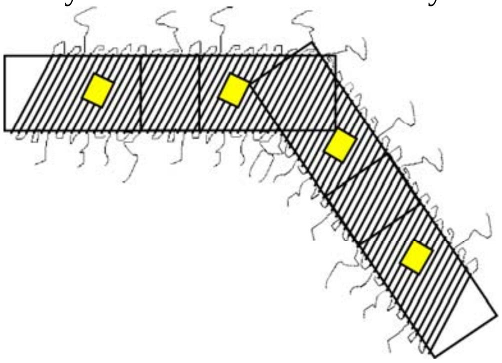
b) Chain tilt leads to a tension in the surface of the lamellae that can be relieved by bending of the lamellae if they do not have a significant lateral extent. b and d show such a bending.

c) shows a zig-zag structure which is another way the strain can be reduced.



d) Figure d shows spherulitic growth where the width is small and the length is long. Here twisting can be effective at relieving stress.

e) For pyramid lozenge shaped crystals the stress is relieved by an edge.



The edge is usually crushed out in dried samples leading to prominent crease.