120309 Quiz 6 Morphology of Complex Materials

1)   a) The diffraction pattern from a semi-crystalline polymer like polyethylene differs from that of a metal such as copper by three features mentioned in class. Sketch the diffraction pattern for these two materials and note the three differences.

b) In addition to these three features diffraction from processed polymers tends to show a high degree of orientation of the crystals. Explain why the differences in structure between copper and polyethylene could lead to more orientation in a processed polyethylene.

c) The following two graphics show different views of crystallization in polymers:
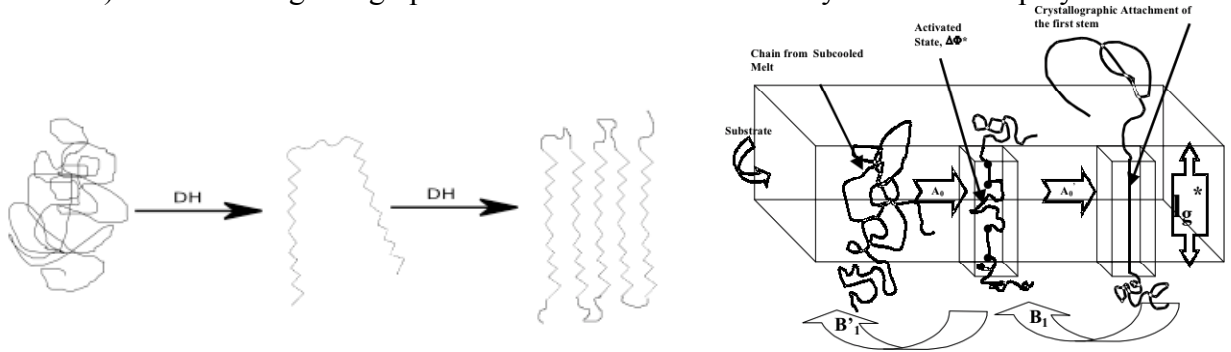
Explain these two models and comment on which of these seems most reasonable.

d) Teflon (PTFE) forms a 13/6 helix. Explain what this means. (How many monomers are in the c-axis direction of the unit cell along the a axis?)

e) Explain why the c-direction of polyethylene shows a linear thermal contraction while the a- and b-directions show non-linear thermal expansion.

2)   a) Describe the difference between the fringed micelle model and the chain folded model for polymer crystallization. (Mention a density problem at the fringed ends of the micelle and the energy required to fold a chain in an adjacent reentry folded chain structure.)

b) Describe the difference between polymer crystals grown in the melt and polymer crystals grown from dilute solution. What do you think might happen when polymers are crystallized in the semi-dilute regime?

c) Derive a relationship between the lamellar thickness and the depth of quench (crystallization temperature).

d) Would the function you propose for part c be applicable to copper nanocrystals?

e) What is the difference between a dendrite such as a snowflake and a spherulite?

ANSWERS: 120309 Quiz 6 Morphology of Complex Materials

1) a) Large lattice size means low angles for peaks, nanocrystals mean broad peaks, semi-crystalline structure leads to the presence of an amorphous halo.
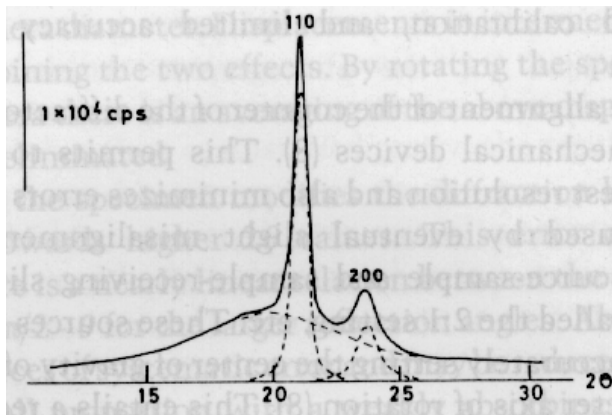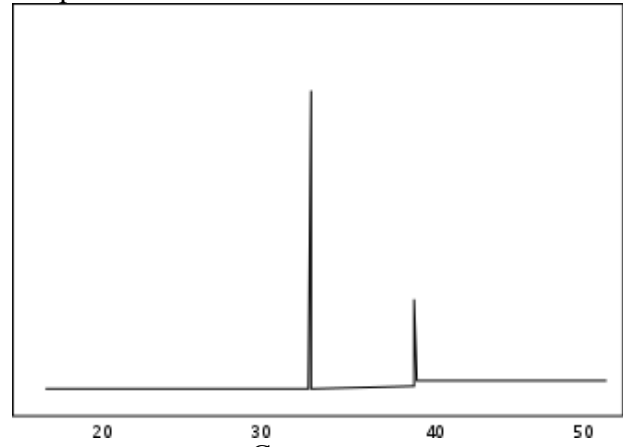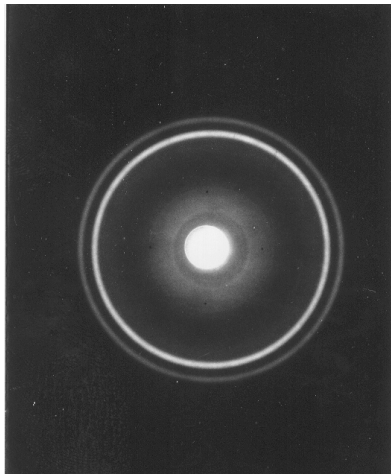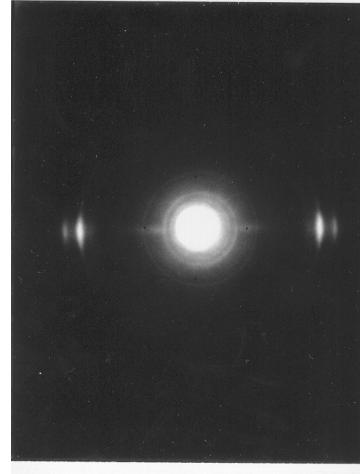

Polyethylene   Copper

b) Lamellar crystals in amorphous matrix allow for more orientation.

Unoriented PE   Oriented PE

http://www.eng.uc.edu/~gbeaucag/Classes/XRD/Labs/Lab2ImagesPionhole01.html

c) In the first cartoon the polymer forms a helix then the helix crystallizes. In the second cartoon the polymer attaches to a growth front on a crystal edge and then transforms into a helical chain while attached to the crystal.

There are advantages to both models. In the first model the helix can easily attach to the growing crystal or it could homogeneously nucleate as is shown. There are no space constraints to the attachment since the helix is the crystallizing structure. In the second model the space constraints at the growing surface would seem to interfere with the conformational changes shown.

A hybrid of these models probably occurs, more like a reeling-in process where the helix forms as the chain attaches to the crystallization front.

d) A 13/6 helix has 13 monomers for 6 turns of the helix returning to the repeated structure after these 13 monomers. So the c-axis of the crystal will have 13 monomers in it.
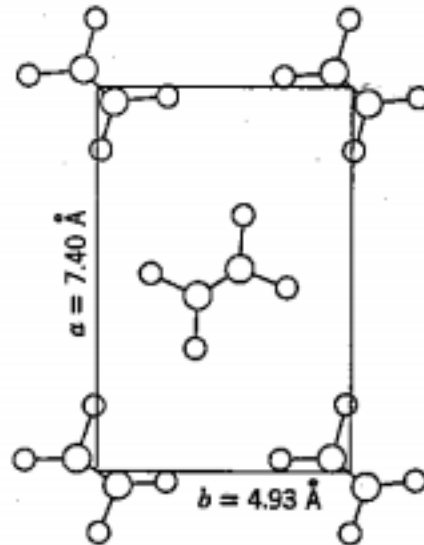
e)

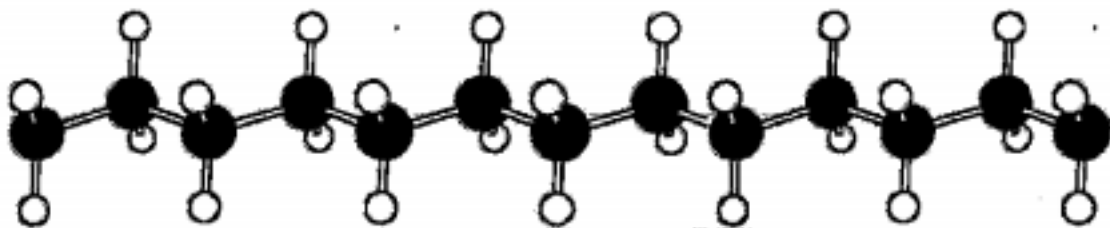Figure 6-40 Arrangement of the molecules of polyethylene in the c-projection. (Courtesy of E. S. Clark.)

Fig. 2.1. The steric structure of PE. Rotations about the C–C bonds result in a change in the conformation

The c-axis is the chain direction. With increase in temperature the retractive force increases following rubber elasticity. That is, the planar zig-zag structure represents a fully extended chain which entropically desires to become randomized. This results in a retractive force that is related to the rubber elasticity force, $F = 3kT/(nl^2)$ c, where c is the c-axis unit cell parameter. Then the c-axis might be expected to contract linearly with temperature in response to this retractive force.

In the a- and b-directions the crystal is held together by van der Waals interactions. These are weak interactions that follow a $1/r^2$ rule in terms of strength (http://en.wikipedia.org/wiki/Van_der_Waals_force) so that we expect a non-linear decay in the interaction with thermal expansion, i.e. a non-linear thermal expansion.

2) a) The fringed micelle model proposes that chains align in certain regions forming helical conformations that simply line up. At the ends of the micelles the structure requires a density

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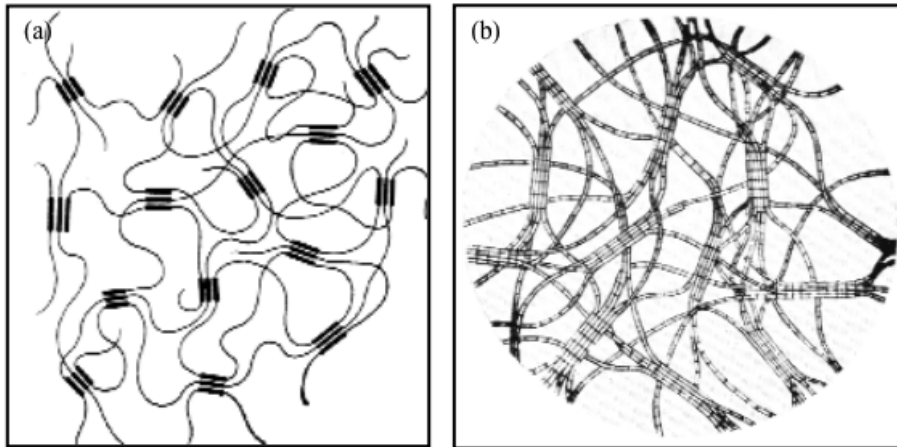change from crystalline density to amorphous density in a gradient. This interface would be difficult to create.

Figure 2.5 Fringed micelle model (a) Model of crystallization as might be visualized in a thermoreversible gel (Keller et al[10].) (b) Hermann and Gerngross model[15] for a semicrystalline polymer. Similar schematics illustrate the general molecular picture in fringed micellar crystallization.

The chain-folding model involves a knitting of the polymer chains in a helical conformation into lamellar crystals. The tight folding of adjacent reentry of the chain would require a significant energy barrier to formation of such a chain folded structure. The folded chain crystal resolves the end interface issue of the fringed micelle model.
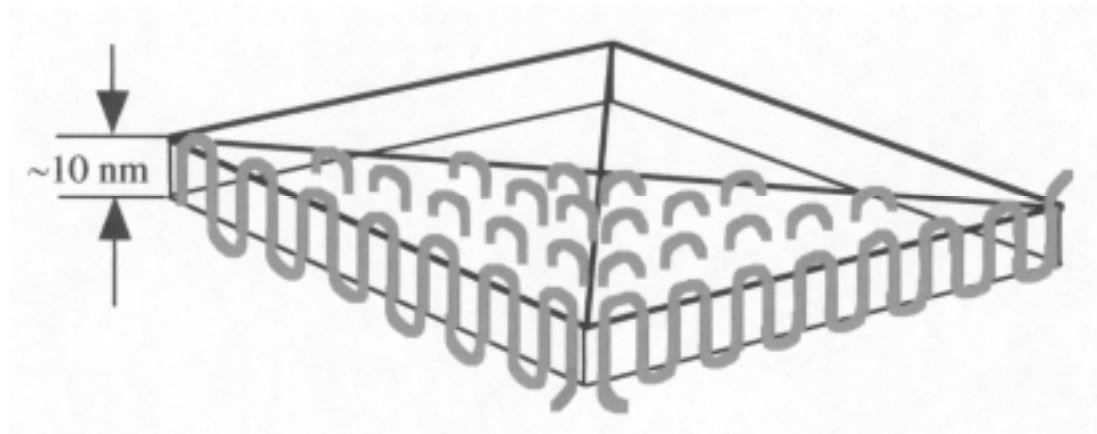

b) In dilute solution polymers crystallized into lozenge shaped single crystals that contain only a few chains with no entanglements between lamellar crystals. The lamellae are isolated but follow the Hoffman-Lauritzen equation for crystal thickness as a function of crystallization temperature.
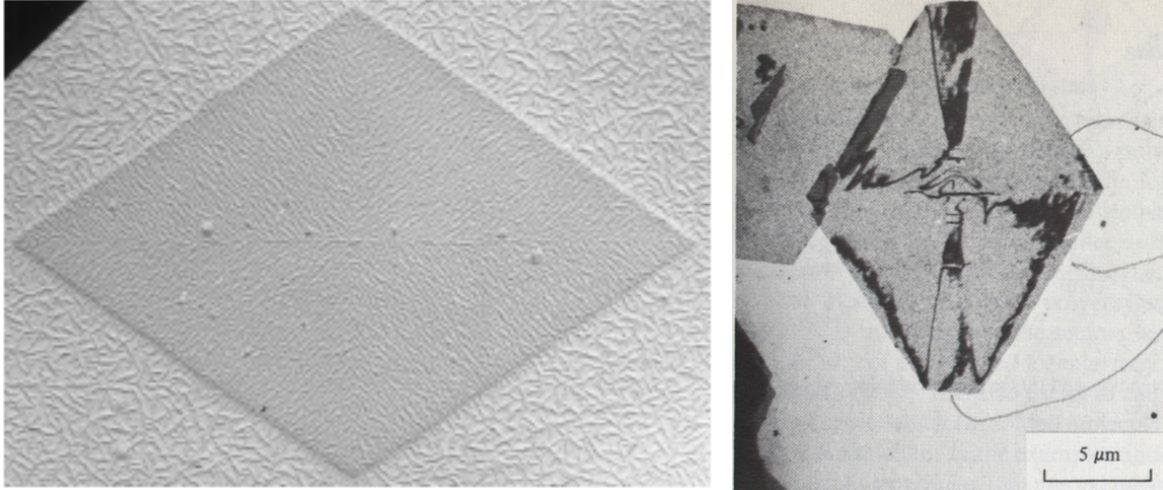
In the melt lamellae are also formed but they are stacked and radiate out from a nucleation's site forming a spherulite or if crystallzation occurs near a surface or under shear the lamellar stacks can form other structures.

Figure 19. Transmission electron micrograph of a shadowed carbon replica of permangani- cally etched linear polyethylene showing ridged crystals. The specimen ($M_w = 37\,000$, $M_n = 29\,000$) had been crystallised at 130 °C for 7.5 days followed by 30 min at 125 °C prior to a cold-water quench. (Bassett and Hodge, unpublished work. Photograph supplied by D C Bassett.)
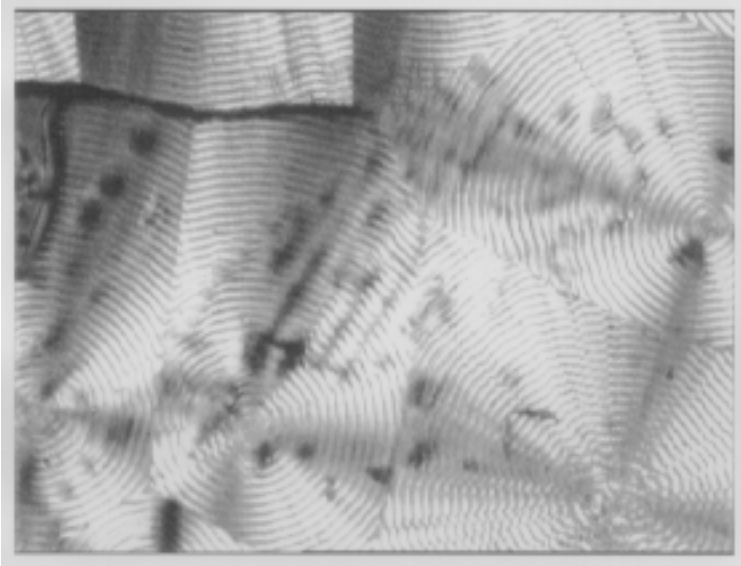
In the semi-dilute regime a gradient in structure for lamellar interaction can be found as observed by Ehrlich (see below for an intermediate structure).

072706 2.0K X1.00K 30um

c)

$$V\Delta G_{Crystallization} = V\Delta H_{Crystallization} - VT\Delta S_{Crystallization} - S\sigma$$

For an infinite crystal V/S is very large and we can ignore the surface
At the equilibrium melting point ΔG = 0 so:

$$T_\infty = \frac{\Delta H_{Crystallization}}{\Delta S_{Crystallization}}$$

substituting in the first equation,

$$V\Delta G_{Crystallization} = V\Delta H_{Crystallization}\left(\frac{T_\infty - T}{T_\infty}\right) - S\sigma$$

For a lamellar crystal S is $2R^2$ and V is tR^2

At a pseudo-equilibrium point where the crystal has a finite thickness of t and a depressed
melting point, T

$$0 = t\Delta H_{Crystallization}\left(\frac{T_\infty - T}{T_\infty}\right) - 2\sigma$$

$$t = \frac{2\sigma T_\infty}{\Delta H_{Crystallization}\Delta T}$$

d) For a copper nanocrystal there are 6 sides rather than 2 (for a cubic nano-crystal). So $S = 6R^2$
and $V = R^3$. This results in:

$$R = \frac{6\sigma T_\infty}{\Delta H_{Crystallization}\Delta T}$$

which is a form of the Gibbs-Thompson Equation.

e) Dendrites grow by crystallographic branching so that they lead to more open and more regular structures when compared with sphereulites that display low angle, non-crystallographic branching.
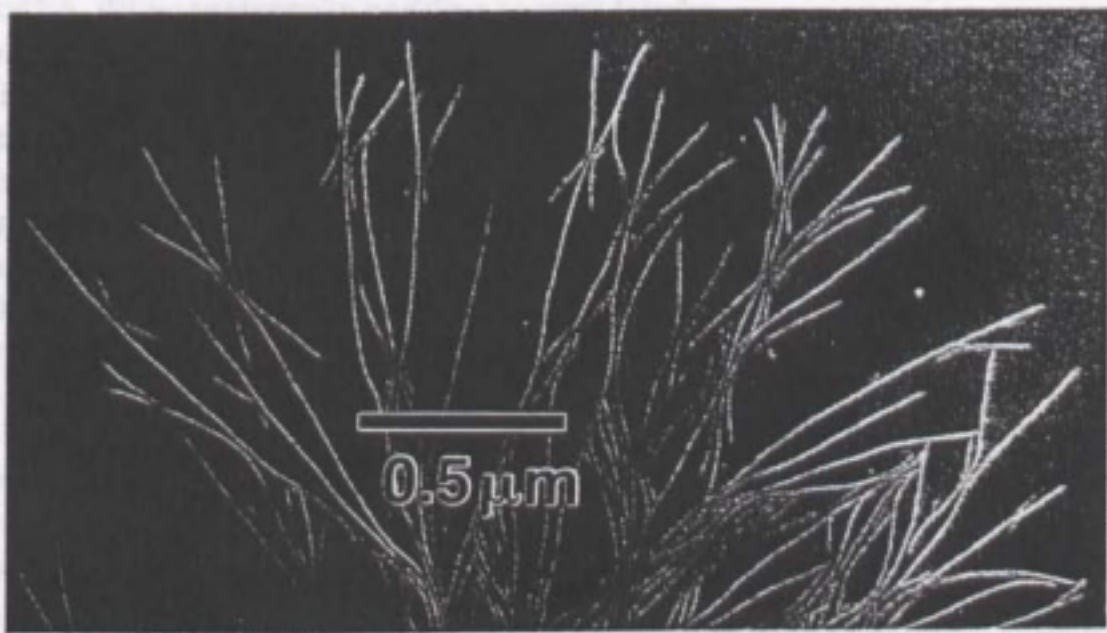

Fig. 29. Non-crystallographic branching in cis-polyisoprene crystallized at −15°C.

Snow Flake