071010 Quiz 3 Morphology of Complex Materials

1) Circular dichroism as a tool to quantify protein secondary structure.

a) Explain how a right-handed circularly polarized light beam can be obtained from two linearly polarized light beams.

b) Explain how a linearly polarized light beam is composed of two circularly polarized light beams.

c) When a linearly polarized light beam passes through a material displaying circular dichroism what is the state of polarization for the exiting beam?

d) When a linearly polarized light beam passes through a material displaying circular birefringence what is the state of polarization for the exiting beam?

e) Explain the terms ellipticity and optical rotation. Which is usually plotted in a UV circular dichroism measurement?

2) Tacticity and chirality.

a) Explain why an amino acid is a chiral molecule.

b) How does this chirality affect the properties of proteins?

c) If a polymer sample displays 50% syndiotactic traids and 50% isotactic triads from an NMR measurement can it be described as an atactic polymer in terms of diads?

d) Can it be atactic in terms of pentads? Explain why and give the arrangement of diads in the polymer of part c.

e) Why does tacticity affect the melting point of monosubstituted vinyl polymers but not the glass transition?

3) Synthetic polymer chain helicity and conformations.

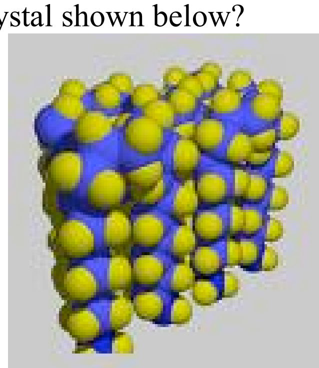
a) Explain the relationship between the β-sheet and planar zig-zag conformations in proteins and polyethylene respectively.

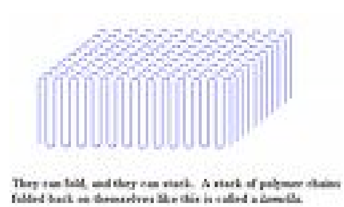
b) Sketch the unit cell for polyethylene on the (100) plane (normal to the c-axis).

c) Sketch an anti-parallel β-sheet structure.

d) Explain why the two polymers in b and c form different higher level structures despite the similarities between the chain conformations.

e) Would it be possible to crystallize a protein as a folded chain crystal similar to the polyethylene crystal shown below?

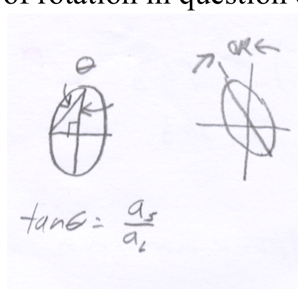




Folded Chain Crystals.

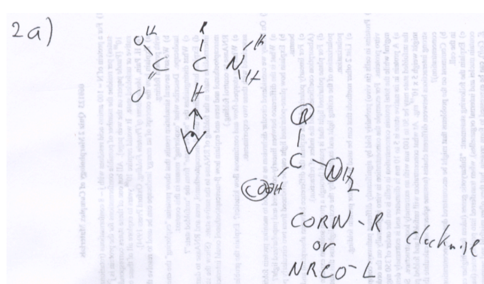
ANSWERS: ***071010 Quiz 3 Morphology of Complex Materials***

1) a) If the planes of polarization for the two beams are orthogonal and if the phase of the clockwise beam is delayed by 90° then a circularly polarized beam results.
b) A right-handed circularly polarized beam can be decomposed into two plane polarized beams, a vertically polarized beam and a horizontally polarized beam that is out of phase by 90°. A left-handed circularly polarized beam is composed of a vertically polarized beam and a horizontally polarized beam that is out of phase by -90°. If a left- and right-handed beam are added the vertical amplitude doubles but the horizontal amplitudes are out of phase by 180° so they cancel each other resulting in a vertically polarized beam. This can be done in reverse so a linear polarized beam can be decomposed into right- and a left-handed circular polarized beams.
c) Circular dichroism will lead to excess absorption of one of the two circular polarized beams that compose the linearly polarized beam leading to an elliptically polarized beam with no optical rotation (that is with the major axis of the ellipse on the vertical or horizontal axies).
d) Circular birefringence will lead to a phase shift in the left or right handed circularly polarized beams and cause a net optical rotation for the plane polarized beam but it will remain plane polarized.
e) Optical rotation (OR) is the angle of rotation in question d. The ellipicity is shown below as θ.



Ellipicity (or molar ellipicity) is usually plotted since optical rotation does not change with wavelength.

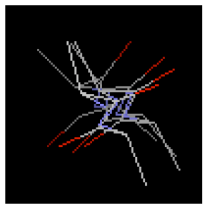
2) a)



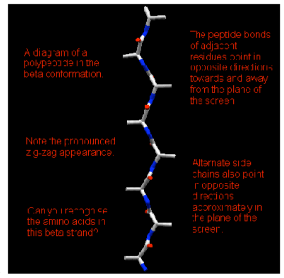
b) The chirality of naturally occurring residues is L allowing for regular secondary structure formation.
c) Isotactic triads are meso-meso units and syndiotactic are racemic-racemic. In order for a polymer to be 50% isotactic and 50% sydiotactic it would have to be a block copolymer of half isotactic and half syndiotactic or a mixture of chains that were pure isotactic and pure syndiotactic. In either case the polymer is atactic in terms of diads since it is 50% m and 50% r.
d) It can not be atactic in terms of pentads since this would require some significant population of mmrr groups for instance that can't exist in the block copolymer described above.

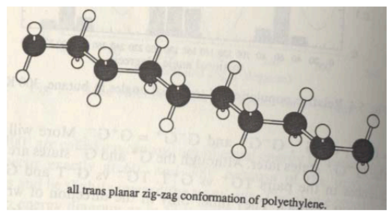
e) Tacticity affects the melting point because different helical forms are created with different tacticities. It doesn't affect the glass transition because the chain motion over 7 to 10 mer units is not affected.

3) a) The figure below shows that the β-sheet conformation is close to a planar zig-zag conformation. The β-sheet has a slight kink.

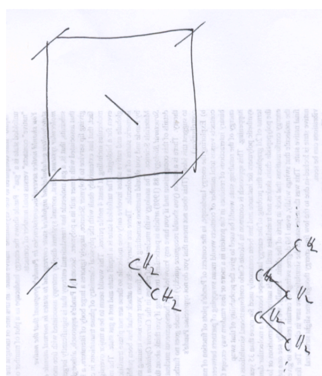


Beta Strand

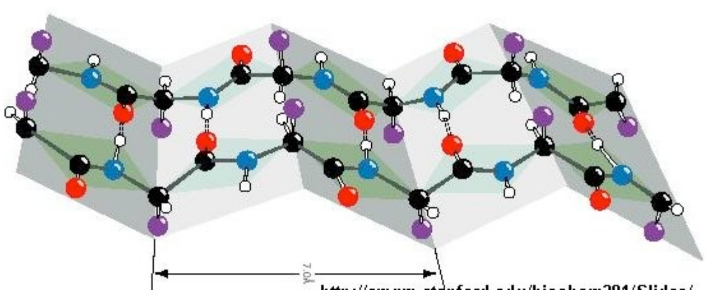




b)



c)



d) Hydrogen bonding in the β-sheet ensures a planar structure, the weak interchain bonding in PE allows for a 3-d structure. The different side groups in the protein chain do not allow for 3-d organization in a crystal similar to polyethylene. The difference is governed by the interchain bonding differences in the two systems and the variable side groups on the protein chain.
e) It would not be possible to crystallize a protein in a folded chain crystal since the structure isn't sufficiently regular.j