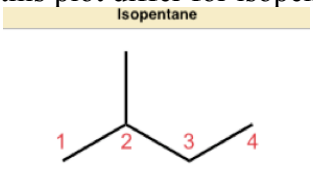
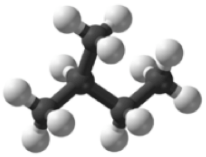
081024 Quiz 4 Morphology of Complex Materials

The physical primary unit of synthetic polymers (and any chain molecule in a random conformation) is the persistence length, l_p, or the Kuhn length, l_K ($l_K = 2\ l_p$). Chain persistence is controlled by what are termed "*short range interactions*" (SRI) referring to interactions that occur along a polymer chain with small differences in chain index (or residue number for a protein).

1) One type of SRI is the restriction in chain conformation associated with changes in energy on rotation of the carbon-carbon bond along the main chain of a vinyl polymer.
   a) Sketch a plot of energy versus bond rotation angle (0 to 360 degrees) for the central carbon-carbon bond of butane. Indicate the trans and gauche states using a Neumann projection.
   b) How would this plot differ for isopentane?



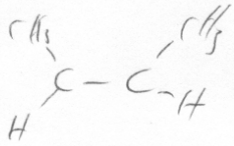


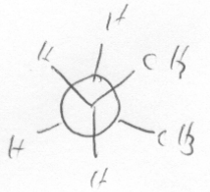
   c) Use the plot of part a to explain how temperature might effect the flexibility of a polymer chain.
   d) For a polyethylene chain sketch the trans configuration. Why is the trans configuration seen in crystals?
   e) Explain how the different energies associated with different rotational isomeric states could lead to a larger or smaller persistence length.

2) Another type of SRI involves the effect of tacticity and stereochemistry on the helicity of a vinyl polymer chain (a carbon main chain polymer).
   a) Define meso and racemic diads using polypropylene.
   b) Define the three types of triad tacticity.
   c) Define an atactic polymer.
   d) Why are polymers described in terms of triad tacticity? (You will need to briefly describe an NMR measurement in your answer.)
   e) Explain how tacticity could effect chain persistence.

3) Persistence can be described using two models.
   a,b) Describe these two models with the acronyms FJC and WLC.
   c) Derive an expression for the mean-square end-to-end size of a chain $\langle R^2 \rangle$ in terms of the number of Kuhn units, n, and the Kuhn length, l_K, for a random walk chain.
   d) How is the Kuhn length related to the length of a chemical unit?
   e) In the kinetic theory a gas atom (or other particle) displays a mean free path, *l*, which is the average distance a gas atom travels ballistically (in a straight line) before it collides with another gas atom. For a particle beam the mean free path is the inverse of the linear absorption coefficient, μ, (http://en.wikipedia.org/wiki/Mean_free_path). The linear absorption coefficient is defined by Beer's law ($I = I_0 \exp(-\mu x)$). Describe any similarity between the mean free path of a gas atom and the persistence length.

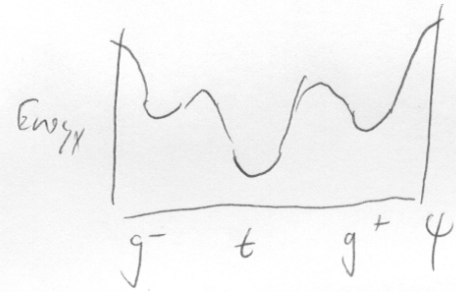
1) a) Butane



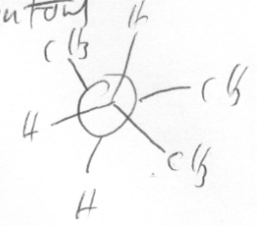


gauche "g"

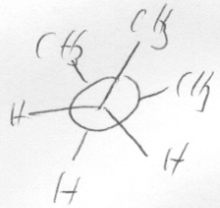
trans "t"



b) isopentane

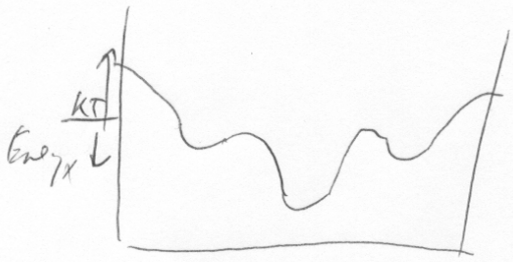


g H-CH3



t H-CH3

c)



q

As T increases kT will overcome barriers to bond rotation making the chain more flexible.

d)

S = 0

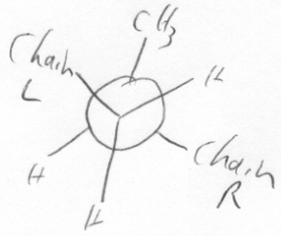
this is the most disordered structure as it is seen in crystals + has the lowest entropy.

e) The rotational energy barriers decide the local conformations of the chain. This combined with the interactions such as Hydrogen bonding lead to longer or smaller chain persistence.

2) a) ...  ...

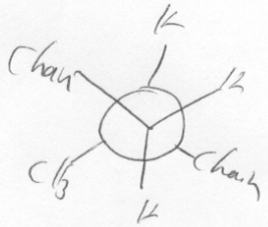
→

as you progress from left to right each α-carbon can have 2 stereochemical arrangements A or B



A

or



B

if the two neighbouring monomers show the same arrangement i.e. AA or BB then the diad is meso if they are different i.e. AB or BA then they are a racemic diad.

An Isotactic polymer would have 50% meso & 50% racemic diads.

b) For triads we can have 4 types

mm rr

mr rm

mm = isotactic

rr = syndiotactic

rm & mr = heterotactic

atactic would have 25% iso 25% synd.
& 50% heterotactic.

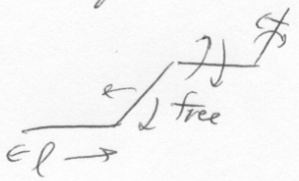
c) atactic = No preferred tacticity so
a random statistical distribution

For the most part atactic = Non Crystalline

d) We can only measure triads because NMR senses
the neighbourhood of the 2 Carbon in both directions
so it can only sense 3 mer units at a time
not 2.

c) Tacticity ⇒ helicity ⇒ increased chain persistence

3) a)
b) FJC
Freely Jointed chain
Chain is composed of steps of length ℓ that have free joints



overall there is an average length of persistence for these steps such that

$$\langle R^2 \rangle = n_k l_k^2$$

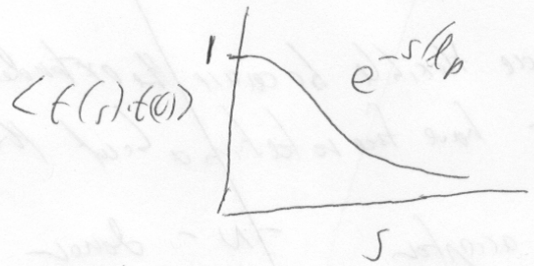
n_k: # of steps; l_k: Kuhn length

$$l_k = 2 l_p \leftarrow \text{persistence length}$$

WLC
Worm-like chain
Chain is a free path that has a tangent at any point $\vec{t}(s)$

The correlation function for the decay in direction for the chain is given by

$$\langle t(s) \cdot t(0) \rangle = e^{-s/l_p}$$



where l_p is the persistence length

(similar to the mean free path of a gas atom)

b) $\langle R^2 \rangle = \sum_i \sum_j (\underline{l}_i \cdot \underline{l}_j)$

for $i = j$ $\underline{l}_i \cdot \underline{l}_j = l^2$

for $i \neq j$ $\underline{l}_i \cdot \underline{l}_j = 0$

there are n cases where $i = j$

so

$$\langle R^2 \rangle = n_k l_k^2$$

d) l_k is not related to the length of a closed unit.

e) The definition of persistence length

$$\langle t(s) \cdot t(0) \rangle = e^{-s/l_p}$$

is identical to the kinetic theory formula

$$\frac{I}{I_0} \sim \exp(-\mu x) = \exp\left(-\frac{x}{\ell}\right)$$