**071107  Quiz 6  Morphology of Complex Materials**

1)  The dynamics of a high molecular weight polymer chain in dilute solution, $c \ll c^*$, is similar to the dynamics of a low molecular weight polymer chain, $M < M_c$, in the melt.
   a)  What is $c^*$?
   b)  What is $M_c$?
   c)  Why would polymer chains in these two conditions behave in a similar manner?
   d)  The plateau modulus can be obtained from a dynamic mechanical measurement of log of the elastic modulus versus log of the frequency.  Sketch this plot and show how the plateau modulus is measured.
   e)  Give an equation that relates the plateau modulus to the entanglement molecular weight and explain the origin of this equation briefly.

2)  The tube model is used to describe chains above $M_c$ in molecular weight or above $c^*$ in concentration.
   a)  Explain the source of the "tube".
   b)  How is the Rouse model incorporated in the tube model?
   c)  Show how the scaling of relaxation time with molecular weight is obtained in the tube model.
   d)  How is the scaling of the diffusion coefficient obtained?
   e)  If the tube obeyed good solvent scaling (while within the tube Gaussian scaling was retained) such as in a thermal blob how would the scaling of the diffusion coefficient change?

3)  Polymers crystallize forming a hierarchical structure.
   a)  Describe the levels of structural hierarchy in polymer crystals.
   b)  Sketch the crystallite thickness versus molecular weight for low molecular weight linear alkanes (waxes) to polyethylene of high molecular weight.
   c)  Why do linear alkanes crystallize into asymmetric crystallites?
   d)  From a kinetic/topological perspective, why doesn't polyethylene crystallize as an extended chain crystal?  Give several reasons and draw a few cartoons showing possible kinetic barriers to an extended chain structure.
   e)  From a thermodynamic perspective give some reasons why an extended chain crystal might be unlikely.

**ANSWERS: 071107 Quiz 6 Morphology of Complex Materials**

1) a) $M/R_0^3$ M is the polymer molar mass and $R_0$ is the coil end-to-end distance.
b) $M_c$ is the transition molecular weight between Rouse scaling of viscosity and the scaling associated with entanglements.
c) In both cases the chains are not entangled.
d) At low frequency a power 2, moderate frequency a plateau and high frequency a power ½. The plateau modulus is the value of the modulus in the plateau region.
e) $G_0 \sim 3kT/M_{elK}^2$ arising from rubber elasticity using the entanglement molecular weight as the molecular weight between crosslinks.

2) a) The tube is created from the other chains in the melt or concentrated solution. These chains serve to confine the chain within a primitive path which is Gaussian.
b) The chain, at sizes smaller than the tube diameter or Rouse size, behaves as a Rouse chain.
c) The diffusion coefficient for diffusion within the tube is given by the Einstein Fluctuation Dissipation Theroem $D \sim kT/\xi$. Where $\xi$ is the Rouse friction factor for the chain $\xi_R N_R$. The distance of the tube is $L_{pr} = N_R a_R$. The relaxation time is the square of the distance diffused divided by the diffusion coefficient so the relaxation time scales with $N_R^3$.
d) The distance diffused in the sample space is the end to end distance of the tube, $N_R^{1/2} a_R$. The relaxation time for this distance of motion scales with $N_R^3$ and we can write $L^2 = D \tau$, so $D \sim N_R^{-2}$.
e) The distance diffused would scale with $N_R^{3/5} a_R$, so $D \sim N_R^{6/5-3} = N_R^{-9/5}$

3) a) For a melt crystal: Chemical structure => Helix structure => Lamallae => Stacked Lamellae => Fibers => Spherulites.
b)
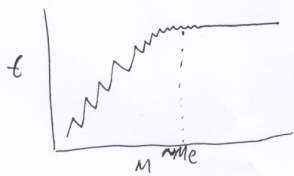


c) Linear alkanes crystallize with extended chains. The ends of the chains do not fit in the crystals so the ends are clustered at the surface making thin lamellar crystals that give rise to a waxy feel to the material.
d) Long chain polymers would have to diffuses long distances to form an extended chain crystal. The chains cluster locally during crystallization which further hinders translation to from extended chain crystals. Chain entanglements also prevent formation of extended chain crystals. Since chains are not of the same length it would be impossible to fit all chains into a single, extended chain crystal. Significant motion of the chains in the crystal would be required to align all chain ends.
e) At a low temperatures (deep quenches) it is possible to overcome the energy penalty in creating large surface areas. With chain folding the conformational entropy loss associated with crystallization is minimized since the chain, crystallized from a melt, retains the same overall radius of gyration. Local chain conformational entropy is lost but globally entropy is retained.