040604 Quiz 10 Polymer Properties

1) The Rouse model results in a proportionality between the viscosity and the molecular weight indicating additive contributions from each unit of a chain. The derivation of the Rouse model, however, uses Stokes law and a Gaussian assumption for the sphere radius, R, where R is the size of a Rouse unit. In view of these two statements, is the Rouse model a "draining" or a "non-draining" hydrodynamic model. (This is not a yes or no question.)

2) The Rouse model works well for oligomeric chains and for polymers in dilute solution. Explain what problems occur for higher molecular weights and at higher concentrations. (You will need to sketch log of the zero shear viscosity versus log of the molecular weight.)

3) What is a "mode" in the context of the Rouse model?

4) What does the 0'th order Rouse mode correspond to? Which mode dominates the dymanic response of a polymer chain?

5) Show that the dynamics of a "dumb bell" in the absence of inertial effects are described by an exponential decay. Define the relaxation time for such a model.

ANSWERS: 040604 Quiz 10 Polymer Properties

1) Stokes law using a Gaussian sphere radius assumes that the Rouse unit is non-draining. However, the result of the Rouse model indicates that the chain is completely draining. It appears that the basic assumption for a Rouse unit and the basic result of the Rouse model contradict each other. This issue could be "danced around" by considering that the size of a Rouse unit could be extremely small compared to the chain (but not so small that Gaussian statistics don't apply). The Rouse model, then, is a draining model down to the size scale of a Rouse unit where it is a non-draining model. This might be considered a type of partially draining system. However, since the size of a Rouse unit is treated as having no importance to the solution, then the Rouse model should be considered a draining model.

2) At high molecular weights (and concentrations) chains can entangle with each other leading to a gel-like network that can relax with time. Since this temporal network can percolate across the sample the viscosity increases geometrically. A log-log plot of the zero shear viscosity versus molecular weight shows a transition from a slope of 1 in the Rouse regime, to a slope of 3.4 in the entangled regime at the entanglement molecular weight which is usually around 10,000 g/mole.

3) For a vibrating chain the mode indicates the number of times the chain units (Rouse units) change the direction of motion along the chain axis. The 0'th order mode has no reversal of direction and refers to translational motion. The first order mode has a single reversal of direction at the center of the chain. Other modes follow in the same way up to the (N-1)'th order mode which is the highest order mode in the Rouse model, where N is the number of Rouse units in the chain.

4) The 0'th order mode refers to translational motion of the chain. The 1'st order mode dominates chain relaxation in the Rouse model since it accounts for 95% of the total amplitude of response for the chain.

5) For a dumb bell in the absence of inertia we have:

$$\xi \frac{dx}{dt} = kx$$

$$x = x_0 \exp\left(-\frac{t}{\tau}\right) \quad \textbf{where} \quad t = k/\xi$$

k is the spring constant for the dumb bell bar and x is the friction factor for the balls at the end of the dumb bell.