121031 Quiz 8 Polymer Properties

1) Kirkwood proposed the following equation for the hydrodynamic radius,

$$\frac{1}{R_{H}} = \frac{1}{2N^{2}} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \frac{1}{|r_{i} - r_{j}|} \right\rangle$$
(1)

Kirkwood J. Polym. Sci. 12 1 (1953).

a) Compare equation (1) with a similar expression for the radius of gyration by writing the radius of gyration summation.

b) Can the Gaussian function $R^2 = nl^2$ be used to simplify the Kirkwood equation for a Gaussian chain?

c) The Stokes-Einstein equation is $D = \frac{k_B T}{6\pi\eta R_H}$. Can this be used to explain the form of

the Kirkwood equation?

2) a) Write an power series (virial) expansion for solution viscosity in terms of the concentration and show how the Martin Equation can be obtained from this expression.

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \phi[\eta] \exp(K_M \phi[\eta])$$

(2)

Utracki and Jamieson "Polymer Physics from Suspensions to Nanocomposites and Beyond" Chapter 1 (2010).

b) Explain the behavior seen in the following graph (differnce between curves and shape of curves).



Fig. 5.3. Reduced viscosity η_{red} as a function of the concentration *c* for a poly(acryl-amide) (PAAm) in the solvents H₂O, formamide and ethylene glycol at *T*=25 °C. Data from [89, 90]. The intrinsic viscosity (intersection with the Y-axis) rises with the solvent quality

c) The following sketch shows the flow lines in capillary flow.



What happens when the fluid displays shear thinning (power law fluid)? Is the Poiseuille equation $(t \sim \eta)$ appropriate under these conditions?

3) In figure (a) below the packing fraction (fraction of space occupied by particles) is calculated for randomly-arranged, rod-shaped particles of variable aspect ration, A_f. Also show are the behavior for platelets, fibers and spheres.

a) Explain why the packing fraction drops dramatically with aspect ratio for randomlyarranged, asymmetric particles. How is the packing fraction related to c*?



FIG. 9. Semiempirical estimate for the maximum packing volume fraction Φ_m of randomly dispersed cylindrical particles. $A_f = \text{height/diameter}$ for fibers and thickness/ diameter for platelets. For comparison, Φ_m for spheres and geometrical percolation threshold p_c for ellipsoids with biaxial symmetry are also shown. Note that Φ_m is calculated directly for cylindrical fibers, but estimated for cylindrical platelets with a scaling relation based on p_c values for ellipsoids.





FIG. 14. Maximum packing volume fraction Φ^* . Calculated from Eq. 10 at a given temperature as a function of the shear rate, for cylindrical platelets of $A_f = 0.01$, dispersed in the Newtonian fluid (curve labeled "Eqn 10 using Eqn 12") and in the polymer melt (curve labeled "Eqn 10 using Eqn 11") indicated in Fig. 13.

(b)

Bicerano, Douglas, Brune J. Macromol. Sci. Rev. Macromol. Chem. Phys. 39 561 (1999).

b) Figure (b) shows how the packing fraction changes with the shear rate for two models involving platelets. How would this plot appear for spheres?

c) Explain why the packing fraction shows a fairly discrete (sharp) transition in shear rate. What occurs at the transition shear rate?

d) How would the intrinsic viscosity relate to the packing fraction?

ANSWERS: 121031 Quiz 8 Polymer Properties

1) a)
$$\frac{1}{R_H} = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N \left\langle \frac{1}{|r_i - r_j|} \right\rangle \qquad R_g^2 = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N \left\langle (r_i - r_j)^2 \right\rangle$$

The equations are similar in terms of the matrix summation.

b) The Gaussian substitution could be made for $|r_i - r_j|$. This is done for the Rouse model for instance.

c) The Kirkwood equation can be seen as a summation of diffusion coefficients for different subunits of the chain.

2) a)

$$\eta = \eta_0 \left(1 + c[\eta] + k_1 c^2 [\eta]^2 + k_2 c^3 [\eta]^3 + \dots + k_{n-1} c^n [\eta]^n \right)$$

$$= \eta_0 \left(1 + c[\eta] \left(1 + k_1 c[\eta] + k_2 c^2 [\eta]^2 + \dots + k_{n-1} c^n [\eta]^n \right) \right)$$

$$\exp(\mathbf{x}) = 1 + \mathbf{x} + \mathbf{x}^2 / 2! + \mathbf{x}^3 / 3! + \dots$$

substitute $x = Kc[\eta]$

$$\frac{\eta}{\eta_0} = \eta_r = \left(1 + c[\eta] \exp(Kc[\eta])\right)$$

b) The upper curves show linear behavior (dashed lines) that deviates at high concentration above ~c*. c* changes with solvent quality. For the glycol solvent the sample is in a collapsed condition so $d_f = 3$ and $[\eta]$ (slope) is small. Solvent quality increases in foramide ($d_f \sim 2$) and is best in water ($d_f \sim 5/3$). The intrinsic viscosity increases (slope increases) and the overlap concentration (cutoff for linear regime) decreases, $c^* \sim M^{3/df-1}$.

c) In shear thinning the viscosity drops, often with a power-law decay.



The areas of high shear, at the edges of the capillary, experience lower viscosity so flow is enhanced and the low shear regions at the center have a high viscosity so flow is suppressed. The net effect is that the flow become like a plug flow (flat flow profile). In this case the

$$\frac{Volume}{time} = \frac{\pi R^4 \Delta p}{8\eta l}$$

Poiseuille equation is not appropriate, $\Delta p = \rho g h$

$$\dot{\gamma}_{Max} = \frac{4Volume}{\pi R^3 time}$$

3 a) The packing fraction is like a particle density at the overlap concentration, packing fraction $\sim c^* \sim volume/mass$ for the randomly arranged particles. The higher the aspect ratio the lower the density of packing if the particles are randomly arranged.

b) The plot would have no transition for spheres, the packing factor does not change with spheres since spheres can not be oriented.

c) At the transition point the forces/energy acting on the platelets are stronger/larger than the energy associated with randomization of the platelets, k_BT , so $F^*R/k_BT \sim 1$. Above the transition the shear forces align the platelets and they can pack much more tightly. Below the transition the platelets are randomly arranged.

d) The intrinsic viscosity is directly related, proportional, to the packing fraction since they both measure the effective specific volume of the particles.