## 120426 Quiz 3 Polymer Properties

1) PNIPAAM (poly n-isopropyl acryl amide) displays a lower critical solution temperature (LCST) in water that is use to actuate artificial muscles and drug delivery devices. For a

polymer solution the interaction parameter is often expressed as  $\chi = A + \frac{B}{T}$ . What values of A and B would yield this type of phase behavior?

2) Bowling balls are manufactured with variable mass density distributions, for instance by hollowing out the core of a ball or by adding a denser material to the center.

a) Do you think that the radius of gyration for bowling balls is directly proportional to the diameter of the balls? Explain your answer.

b) Consider that you want to model the motion of a bowling ball as it rolls down the bowling alley using hollow spheres with the same mass as the ball. How would you calculate the radius of such a hollow sphere?

c) In bowling the ball is often released with a spin so that it slides down the alley and spins on an axis different than the natural rolling axis (the alley is covered with a lubricant that facilitates this (wax)). How would you expect the radius of gyration to effect the distance such a spinning ball will travel in a straight line? (Will a larger  $R_g$  lead to a higher, lower or the same straight-line distance? Why?)

d) How do you think the hydrodynamic radius would be effected for two bowling balls of the same diameter but with different mass distribution. Is  $R_h$  a better or worse measure of the size for a bowling ball?

e) When a figure skater spins she/he pulls her/his arms inwards to change the angular velocity. How does this effect  $R_g$  and why does the speed change?

3) The Einstein equation for the viscosity of a dilute suspension of spherical particles is given by  $\eta = \eta_0 (1 + 2.5\phi)$  where  $\eta$  is the solution viscosity,  $\eta_0$  is the solvent viscosity and  $\phi$  is the concentration of spherical particles.

a) What is the intrinsic viscosity for this suspension of spherical particles? (Include the units for the intrinsic viscosity.)

b) Give an expression for the molecular weight dependence of intrinsic viscosity and show that the molecular weight dependence you showed in part "a" agrees with your expression. (Remember that volume  $\sim R^3$  and  $R \sim M^{1/df}$ .)

c) DNA can form a helical conformation where the DNA particles are rod-like. DNA can also exist as a flexible chain in a good solvent (expanded coil). For a series of DNA of different molar mass how could you distinguish rods from coils using the intrinsic viscosity? (Use your answer to part "b".)

d) Polymer chains have a size of from 0.01 micron to 0.1 micron. In some cases dirt, or catalyst residue have a similar size so that it is impossible to filter these impurities from the polymer. How could you distinguish the presence of dirt in an intrinsic viscosity measurement?

## ANSWERS: 120426 Quiz 3 Polymer Properties



For an LCST the value of A is positive and larger than the combinatorial entropy term in the energy expression; the value of B is negative so that the system has a negative energy of mixing at low temperatures where the B/T term is larger than the A term minus the combinatorial entropy term. At high temperature B/T becomes smaller than the A term and the energy of mixing becomes positive favoring demixing. The LCST relies on 1) non-combinatorial entropy term that favors demixing; 2) specific interacitons that lead to a negative B; 3) a small combinatorial entropy term, as is common for connected systems like polymers, gels and networks where mixing leads to little dispersion of the monomer units since they are connected.

2) a) If the density of the balls were constant then  $R_g^2 = \frac{3}{5}R^2$  and the radius of gyration would be proportional to the radius, but sine the balls are not uniform in density then there is no such

proportional to the radius, but she the bans are not uniform in density then there is no such proportionality and an integration must be performed to obtain the radius of gyration. b) The radius of such a hollow sphere is the radius of gyration. This is obtained from the density as a function of radius  $\rho(r)$  by integration,

$$R_g^2 = \frac{\int\limits_0^{\infty} \rho(r)r^4 dr}{\int\limits_0^{R} \rho(r)r^2 dr}.$$

c) The larger the  $R_g$  the longer is the straight path since it will take the ball more time to correct its spin due to the higher momentum with larger  $R_g$ .

d) The hydrodynamic radius is related to the drag coefficient for the ball. This is defined by Stokes law,  $\xi = 6\pi R_{sphere}\eta_0$ . The hydrodynamic radius is only related to the external radius of

the ball and does not change with the mass distribution within the ball. In this case the hydrodynamic radius is a better measure of the ball size.

e) The skater decreases Rg when she/he pulls his or her arms in. This reduces the moment of inertia. Since the energy remains almost constant the angular velocity must increase.

 $Energy = \frac{MR_g^2 \omega^2}{2}$  where  $\omega$  is the angular velocity and M is the mass of the skater,  $\omega = \left(\frac{2E}{M}\right)^{1/2} \frac{1}{R}.$ 

3) a)  $\eta = \eta_0 (1 + [\eta]\phi)$  so for Einstein's spheres  $[\eta] = 2.5$ . The units are volume/mass, inverse to the units for  $\phi$ .

b) Intrinsic viscosity is a specific volume for the suspended object so

 $[\eta] = \frac{V_{object}}{M_{object}} \sim \frac{R_{object}^3}{M_{object}} = M_{object}^{\frac{3}{d_f}-1}.$  For a 3-d object like a sphere there is no mass dependence.

c) A rod has dimension 1;  $[\eta] \sim M^2$  and an expanded coil dimension 5/3;  $[\eta] \sim M^{0.8}$ . By

plotting the molecular weight dependence of the intrinsic viscosity we could distinguish between rods and expanded coils.

d) For a series of different molecular weight polymers the intrinsic viscosity would display two parts, one associated with 3-d objects and the other with a molecular weight dependence associated with expanded coils. So one might expect the intrinsic viscosity to follow a function such as,  $[\eta] = k_1 + k_2 M^{0.8}$  where  $k_1$  and  $k_2$  are constants.