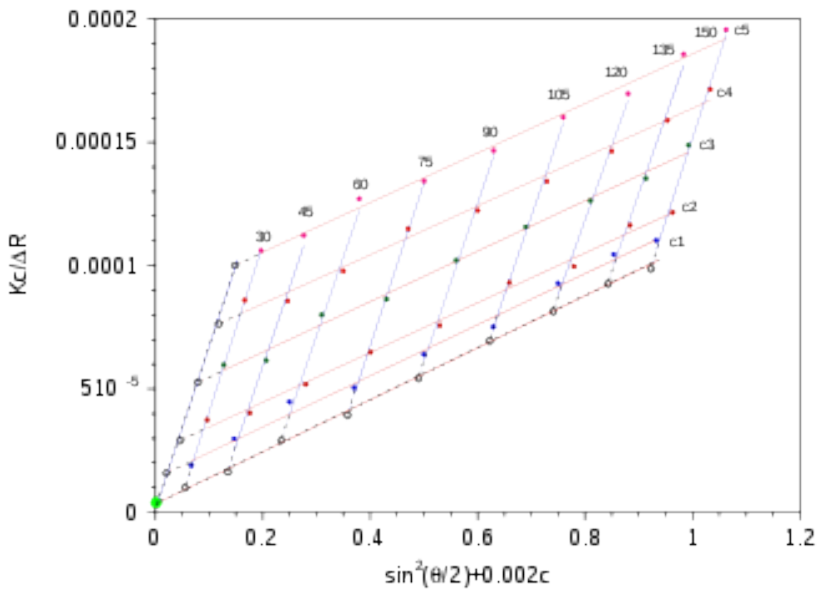
Quiz 8 Polymer Properties October 18, 2013

1) In class the relationship between the radius of gyration and the end to end distance for a polymer chain was obtained.
   a) Give this relationship and the assumptions that are associated with it. Does it apply to an expanded coil?
   b) Sketch a plot of the radius of gyration and the hydrodynamic radius versus temperature for a polymer in dilute solution. Why do the values differ?
   c) How is the radius of gyration measured?
   d) Calculate the radius of gyration for a sphere.
   e) What is the moment of inertia and how is it related to the radius of gyration?

2) The following plot is used to obtain the radius of gyration, the interaction parameter and the weight average molecular weight for a polymer in dilute solution. R is the Rayleigh ratio, which is proportional to the scattered intensity, c is the concentration of polymer and K is a constant.



   a) The x-axis contains a term $\sin^2(\theta/2)$. Explain why this is chosen for the x-axis.
   b) The plot shows a series of almost horizontal lines and a series of almost vertical lines. What does the slope of these lines correspond to?
   c) The two extrapolated lines at c = 0 and at q = 0 intersect at a point on the y-axis. What does this point correspond with?
   d) Why is it necessary to extrapolate to 0 concentration and q = 0 in this plot?
   e) Zhou et al. (Macro. **41** 8927 (2008)) give the following equation for solution scattering from a polymer,

$$\frac{KC}{R_{vv}(q)} \simeq \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^{\,2}\rangle q^2\right) + 2A_2C \qquad (1)$$

   while Zimm gave the equation,

$$\frac{\phi}{S(qR_g << 1)} = \left(\frac{1}{N} + (1-2\chi)\phi\right)\left(1 + \frac{q^2R_g^2}{3}\right) \qquad (6).$$

(1) P. Doty, B. H. Zimm, and H. Mark, *J. Chem. Phys.*, **12**, 144 (1944); **13**, 159 (1945).

   Explain how or if these two equations would differ in the plot shown above.

ANSWERS: **Quiz 8 Polymer Properties October 18, 2013**

1) a) $R_g^2 = R_{eted}^2/6$ This relies on the assumption of a Gaussian chain (theta condition).
b)

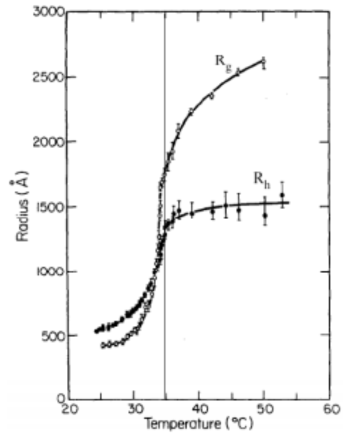


***Figure 3.** Radius of gyration, R_g, and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].*

The radius of gyration is a direct measure of the structure and is based on the location of the mass in 3d space. The hydrodynamic radius is the radius of a sphere with the same drag coefficient as the object. For instance, a rod would align with flow and have a very low hydrodynamic radius $R_g/R_h = 1.732$ while a Gaussian coil has a higher hydrodynamic radius especially if the solvent is non-draining, $R_g/R_h = 1.5$.

c) The radius of gyration is measured using light scattering or other scattering methods (neutrons or x-rays) and Guinier's Law, $I(q) = I_e N n_e^2 \exp\left(-R_g^2 q^2 / 3\right)$.

d) The probability function for mass in a sphere using spherical coordinates is $P(r) = 4\pi r^2$.

The radius of gyration is calculated from, $R_g^2 = \dfrac{\int_0^R r^2 P(r)\,dr}{\int_0^R P(r)\,dr} = 3/5R^2$.

e) The moment of inertia has the same definition as the radius of gyration but it uses mass as the weighting factor rather than index of refraction or electron density or neutron cross section.

2) a) Guinier's Law, $I(q) = I_e N n_e^2 \exp\left(-R_g^2 q^2 / 3\right)$ is linearized at low-q by $\dfrac{G}{I(q)} = \left(1 + \dfrac{R_g^2}{3} q^2\right)$ which suggests a plot of 1/I versus q^2. $q = \dfrac{4\pi}{\lambda}\sin\left(\dfrac{\theta}{2}\right)$ so the sin squared term is the angular dependent part of q.

b) The almost horizontal lines are at constant q and variable concentration, the almost vertical lines are at constant concentration and variable q. The slope of the almost vertical lines is $R_g^2/3$ and that of the almost horizontal is $(1-2\chi)$.

c) The intercept on the y-axis is $1/N^2$ where N is the weight average moleculare weight.

d) It is necessary to extrapolate because the Zimm function is an approximation both in q (and expansion of the exponential function) and in concentration (the first two terms of the virial expansion). Also, the form of the Zimm equation is an approximate form, the exact form is given in question (e).
e) In extrapolation the two equations are identical. The shape of the curve at moderate concentration and moderate q would be different. A_2 is $(1-2\chi)$.