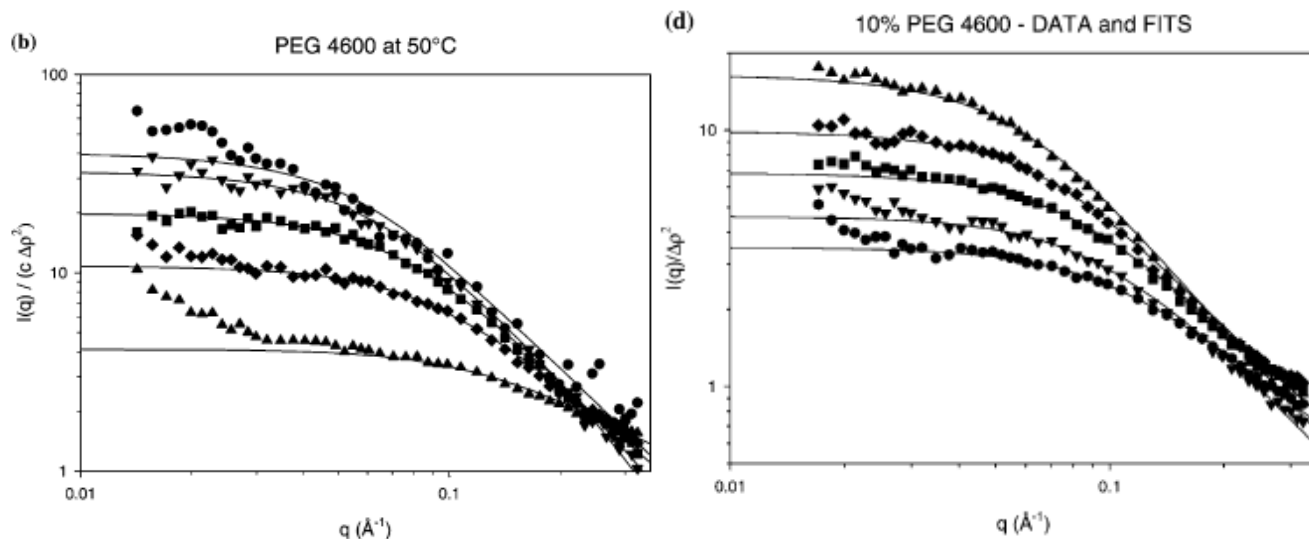# Quiz 8 Polymer Properties October 17, 2013

A plot of scattered x-ray intensity versus q for polyethylene oxide in water is shown for variable concentrations (left, b), and for variable temperatures (right, d) (Pedersen JS and Sommers C *Prog. Colloid Polym. Sci.* **130** 70-78 (2005)).

1, 2, 5, 10, 20% from top to bottom in the left plot; and 100, 80, 60, 40, 20 °C from top to bottom in the right plot.

a) For the most dilute curve in the left plot, where on the plot would R_g be determined? Explain how it could be determined from this plot. Why do the left curves drop with c while the right curves increase in intensity with T?

b) On the scale given in these plots, what range of q would be used for visible light scattering? Explain why it involves this range in comparison to the range shown.

c) 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 from light scattering. R is the Rayleigh ratio, which is proportional to the scattered intensity, c is the concentration of polymer and K is a constant.
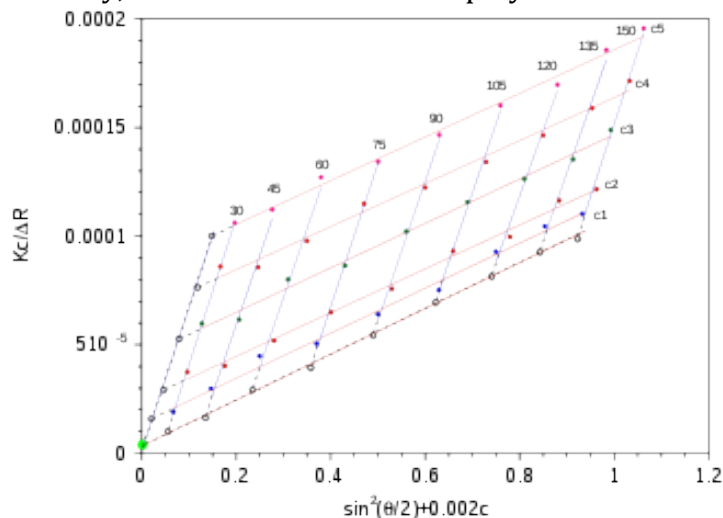
How is this plot related to the two plots shown at the top of this quiz? (You will

need to write Guinier's Law and an expansion, as well as the second virial expansion term.)

d) What can be obtained from the left most point on the y-axis of this plot? What is the slope of the curves as a function of concentration at fixed q, and the slope as a function of q at fixed concentration? Use the left plot at the top to explain which of the concentration curves you would use to determine R_g and the plot at the right to explain which of the temperature curves you would use to determine A_2.

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,

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

(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 Zimm plot shown above.

1) a) For the most dilute curve in the left plot, where on the plot would R_g be determined? Explain how it could be determined from this plot. Why do the left curves drop with c while the right curves increase in intensity with T?

The curve is composed of a power-law decay at high-q and a knee shaped region at low-q. The knee-region follows Guinier's law, $I(q) = G \exp(-q^2 R_g^2/3)$. R_g is determined from a fit to the low-q region of the knee.

The left curves drop with concentration due to screening of the scattering associated with the second virial coefficient, $A_2 = 1-2\chi$. The Zimm equation can be written:

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

so as the conentratin increases the second virial term increase and $1/I(q)$ increases or $I(q)$ decreases.

The right curve increases with T because the system is approaching phase separation, that is it is a lower-critical solution that phase separates on heating. For these systems $\chi = A + B/T$ and A is positive, B is negative so that increasing temperature reduces the negative term and makes χ approach ½ for phase separation.

b) Light scattering occurs for 1e-6 to 1e-4 Å^{-1}, in the micron range. This is to the far left off the scale of these plots. In this range the intensity is essentially constant in q. It changes slightly, sufficiently to measure R_g. The range is determined by $1/\lambda$. λ for light is close to one micron and for x-ray is close to one Ångstrom.

c) The Zimm plot contains the information from the top two plots. As concentration changes in the left plot the intensity drops due to screening that is associated with A_2. The inverse of Intensity increases in concentration in the Zimm plot (c1, c2, c3, c4, c5 to the right). As q increases the intensity decays in both plots, so 1/I increases with q at constant concentration. So the Zimm plot is a compact presentation of some of the information shown in the top two plots, particularly those features involved in an extrapolation to zero concentration and to zero q. This plot is a manifestation of the Zimm equation:

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

where the second term is an expansion of $1/\text{Guinier'sLaw} = (1/G) \exp(+q^2 R_g^2/3)$ $\sim (1 + q^2 R_g^2/3)$. The first term is a virial expansion of $I(q=>0)$ as will be discussed later.

d). The Zimm plot yields 1/N at the left most point on the y-axis. The slope in concentration at fixed angle is the second virial coefficient. The slope in q at fixed composition is $R_g^2/3$. In the top two plots you would use the lowest concentration plot to estimate Rg since there is less or no screening at low concentration (the second virial coefficient has little effect). You would use the highest temperature plot (for an LCST system) to determine A_2 since this is where A_2 has the largest signal. Actually, any curve would yield A_2, A_2 depends on T so you want the temperature dependence to predict the critical point (phase-separation temperature).

e) The equation from Zhou is from the RPA equation for a polymer solution that we will discuss later. The equation from Zimm is empirical. Zimm's equation is only useful in extrapolation while the RPA equation can be used at finite q and concentration. In extrapolation the Zimm and RPA approaches are identical so either on can be used to describe the Zimm plots extrapolation. They differ in that the Zimm expression has a finite q dependence to the enthalpy. Thermodynamic parameters such as enthalpy cannot have a size dependence by definition so the Zimm equation fails at non-zero q values. Pedersen and Sommer use the following modification of the equation used by Zhou et al. (the left term is the scattered intensity and P(q) is the Guinier expansion or an expression that is more complicated and can handle the power-law regime also),

$$\frac{d\sigma(q)}{d\Omega} = cM_w \Delta\rho_m^2 \frac{P(q)}{1 + vP(q)} \tag{1}$$

where c is the concentration in g/mL, M_w is the weight-average molecular mass, and $\Delta\rho_m$ is the excess scattering length per unit mass of polymer. $P(q)$ is the single chain form factor and v is a parameter depending on the reduced concentration c/c^* and the

$$v = \eta \frac{V_{PEG}}{V_{H2O}} \left[\frac{1}{1-\eta} - 2\chi \right] \tag{3}$$

where η is the polymer volume fraction, V_{PEG} is the PEG molecular volume, V_{H2O} is the volume of a water molecule, and χ is the temperature dependent Flory-Huggins interaction parameter. For