# Quiz 3 Polymer Properties 4/17/01

The left figure below (from Strobl) is intended to demonstrate the existence of good solvent scaling. The right figure (from Doi) shows the behavior of $R_g$ and $R_H$ with temperature.

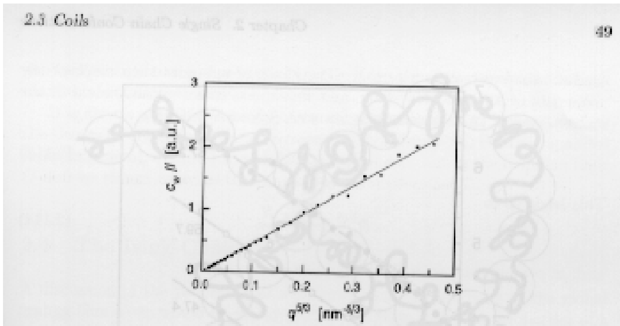


Fig. 2.18. Intensities obtained in a neutron scattering experiment on dilute solutions of (deuterated) PS ($\bar{M}_w = 1.1 \cdot 10^6$) in $CS_2$ ($c_w = 10^{-3}$ g · cm$^{-3}$). The straight line corresponds to the scattering law characteristic for expanded chains. Data from Farnoux [6].

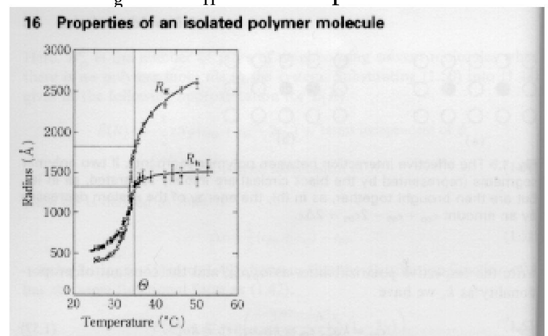


Fig. 1.6 The coil–globule transition in a solution of polystyrene in cyclohexane. The radius of gyration $R_g$ and the hydrodynamic radius $R_h$ of the polymer show a dramatic change as temperature passes through the $\Theta$ temperature. The hydrodynamic radius $R_h$ is defined by $R_h = k_B T/6\pi\eta D$, where $D$ is the diffusion constant of the polymer and $\eta$ is the viscosity of the solvent. (Sun, S.T., Nishio, I., Swislow, G., and Tanaka, T. (1980). J. Chem. Phys., 73, 5971, Fig.2.)

a) **-Explain** the axes on this plot. (You will need a scaling law and a generalized scattering law).

b) **-How can** the scaling law used in "a" be obtained from

$$(R/R_0)^5 - (R/R_0)^3 = (9\sqrt{6}/16)V_0\sqrt{N}/b^3 \qquad ?$$

c) **-What is $V_0$** in the equation in "b"?
**-Explain** the meaning.
**-Explain** how this term can be expanded to included enthalpic effects (give and equation).

d) **-Can the expanded** definition of V0 in "c" explain the Doi figure (right above)?
**-Explain** your answer.

e) The intrinsic viscosity [η] is proportional to 1/ρ, where ρ is the density of the polymer coil, $N_{coil}/V_{coil}$.
**-Show** that for a theta solvent [η] scales with $N^{1/2}$.
**-What** is the scaling for and expanded coil?
**-Explain** the values of "a" in the Mark-Houwink equation, $[\eta] = K N^a$, where "a" ranges from 0.5 to close to 1.
-Should [η] depend on $R_g$ or $R_H$ in the right figure above? Why?

**Answers: Quiz 3 Polymer Properties 4/17/01**

a) The plot reflects a curve such as described by a generalized OZ plot, $I(q) = K/(1 + (qR_g)^{df}/d_f)$, then 1/I is plotted versus $q^{df}$ and a line should result.

b) If R/R0 is big then the 5'th power term is much bigger than the 3'rd power term. Also $R_0$ scales with $N^{1/2}$ so,

$(R)^5 = (9\sqrt{6}/16)V_0\sqrt{N}/b^3\ (C\ N^{5/2}) = C\ N^{6/2}$

and

$R = C\ N^{3/5}$

c) V0 is the excluded volume. This reflects the volume of a single persistence unit in the original definition (hard core potential). It can be expanded in meaning by including a Boltzmann potential function under a lattice model to $V_0\ (1 - 2\chi)$, where $c = z\Delta\varepsilon/kT$.

d) The expanded definition of $V_0$ doesn't explain the behavior shown in the right graph since the function still predicts only two states, expanded and Gaussian.

e) $[\eta] = K/\rho = KR_F^3/N = K\ N^{3/2}/N = K\ N^{1/2}$.
For a good solvent coil, $R_F = C\ N^{3/5}$ so, $[\eta] = K\ N^{0.8}$
The MH equation doesn't explain blob behavior so can not completely explain the scaling behavior of real polymer coils. Numbers larger than 0.8 for a are generally associated with rod like behavior.
$[\eta]$ should depend on $R_H$ since the coil profile is the important feature and it is a dynamic measurement.