040429 Quiz 5 Polymer Properties

In class we discussed a discrepancy between the Flory-Krigbaum result and measurements of the radius of gyration for isolated, dilute polymer coils as a function of temperature.

a) Describe this discrepancy by making a graph of R_g versus temperature. Briefly explain the FK prediction.

b) The blob concept can be used to accommodate both the FK prediction and the experimental observation of "a". Describe this blob model. Give scaling relationships defining R_B, the blob size, in terms of the number of persistence units in a blob, n_B, as well as in terms of the interaction parameter, χ.

c) We also discussed a "new" thermodynamics where size-scale dependence to the entropy can lead to unexpected thermodynamic accommodations for long chain molecules. Use this concept to explain how a polymer chain in a very good solvent responds to a reduction in temperature through the theta temperature to the collapsed state. (First describe with a sketch the very good solvent condition. Then describe local chain contraction following the blob model. Then describe the rapid approach to theta conditions. Finally describe the limit of intra-chain accommodation and the coil/globule transition.)

d) Describe the overlap concentration and give the molecular weight dependence of the overlap concentration. (Make a sketch showing the approach to overlap concentration for a polymer solution.)

e) Sketch the neutron scattering pattern for a dilute polymer solution in the theta, very good solvent and good solvent conditions (indicate the direction of increasing temperature). Make a second sketch showing the behavior of a dilute polymer solution in a very good solvent in the region of the overlap concentration as the concentration varies from dilute to concentrated (indicate the direction of increasing concentration).

Answers: 040429 Quiz 5 Polymer Properties

a) The FK prediction is that there is a discrete transition from the theta state to the good-solvent condition with no rounding of the R_g curve as is seen in the experimental data. The experimental data indicates a continuous transition.

16 Properties of an isolated polymer molecule

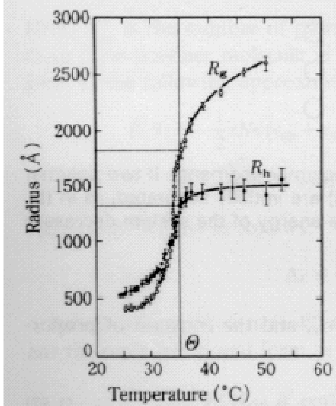


Fig. 1.6 The coil–globule transition in a solution of polystyrene in cyclohexane. The radius of gyration R_g and the hydrodynamic radius R_h of the polymer show a dramatic change as temperature passes through the Θ temperature. The hydrodynamic radius R_h is defined by $R_h = k_B T/6\pi\eta D$, where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

b) $R_{BT} \sim n_B^{1/2} l_P \sim \dfrac{l_P}{(1-2\chi)}$

The thermal blob model renormalizes the chain into sub-chains with dimension 2 called thermal blobs. N_B of these blobs form the chain with a dimension 5/3 for good solvent scaling. The blob size changes continuously with temperature since $\chi \sim 1/T$ in the equation given above. Then the thermal blob model can accommodate both the FK discrete transition in scaling and the experimental evidence of a continuous transition in size. The thermal blob model has been experimentally verified directly in neutron scattering measurements.

c) As discussed in class:

1) The coil in a very good solvent (high T) is fully expanded, $d_f = 5/3$, meaning that the thermal blob size is fixed at the persistence length and $N_B = N$.

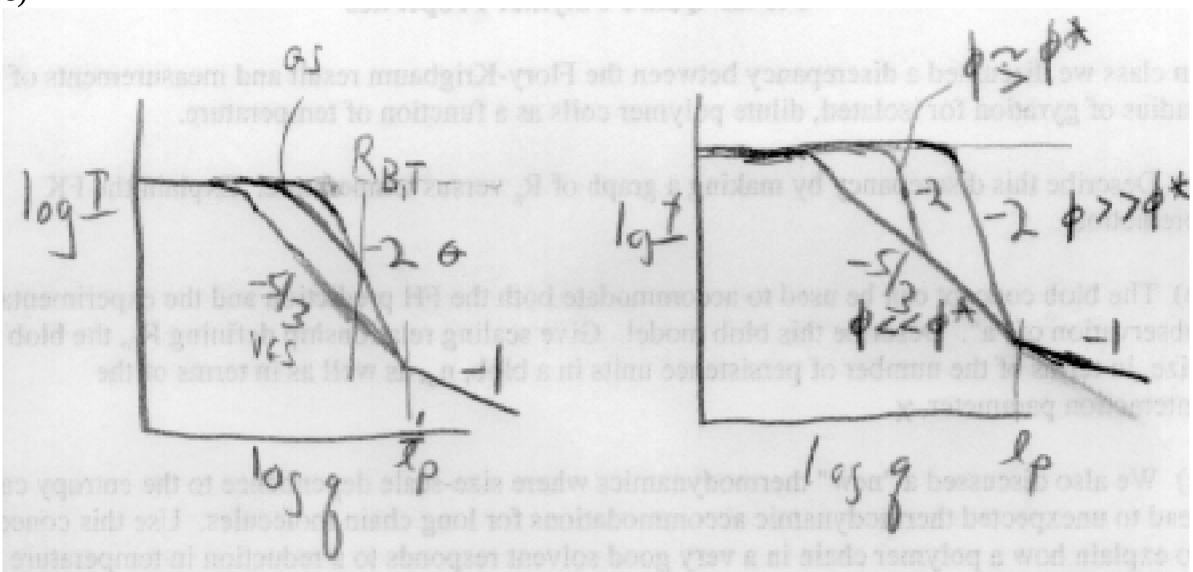
2) As the temperature drops the chain collapses to the theta condition locally, at small scales, by changing the short distance scaling to $d_f = 2$. This makes the chain smaller overall since some part of the chain has a higher dimension. Small scales collapse first since the entropy at small scales is lower than at large scales so large scales can accommodate poorer solvation conditions.

3) The coil rapidly approaches the theta-condition where the entire chain is Gaussian, as seen in the figure in question "a" and as predicted by the equation for R_B in question "b".

4) If the temperature drops below the theta condition the coil can no longer accommodate changes in solvation internally and must collapse into a globule. Then the theta-temperature is the overall miscibility limit for the coil.

d) The overlap concentration occurs when the solution concentration equals the concentration within a coil, $\varphi^* \sim N^{1-3/df}$. At the overlap concentration coils, on average, just begin to touch each other.

e)



In the left graph (thermal blob) higher T is towards the left. In the right graph, concentration blob, higher concentration is towards the right