

Lab Week 1 – Module α_2

Polymer Conformation

**Lab. Instructor:
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OBJECTIVES

- ✓ Review random walk model for polymer chains
- ✓ Introduce dynamic light scattering as a technique to obtain dimensions of polymer chains in solution
- ✓ Investigate conformational differences between proteins and synthetic polymers

SUMMARY OF TASKS

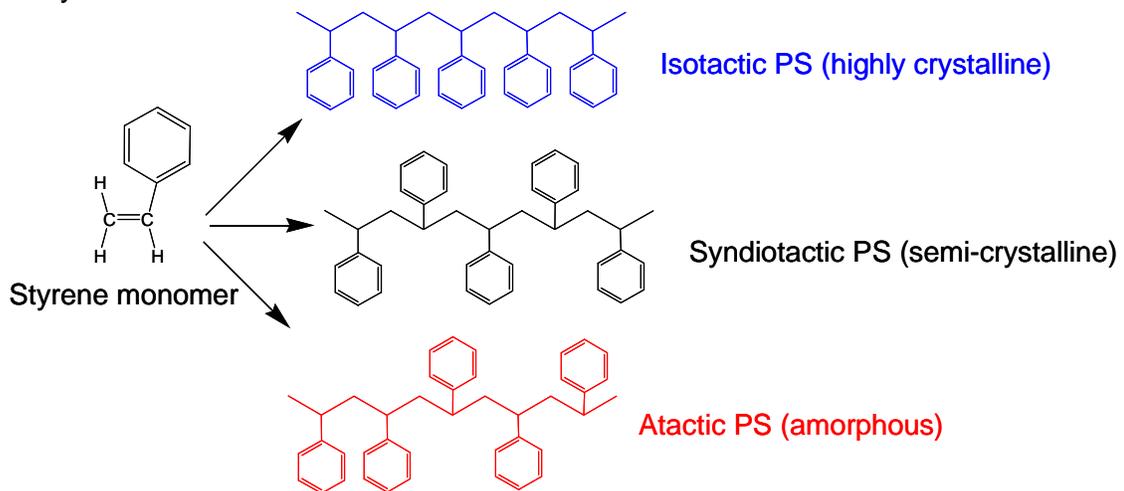
- 1) Prepare dilute polymer and protein solutions
- 2) Perform dynamic light scattering on all solutions to obtain hydrodynamic radius
- 3) Determine scaling relationship between radius and molecular weight for polymers and proteins
- 4) Investigate temperature effects on chain dimensions

BACKGROUND

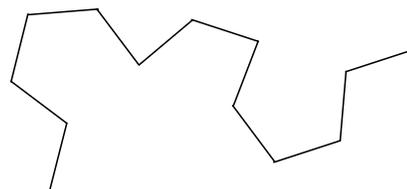
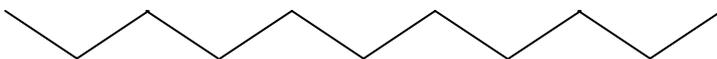
Polymer Conformations

Polymer Melts

Polymers are covalently bonded long chain molecules composed of repeating units, called monomers, comprised of carbon and hydrogen, and sometimes oxygen, nitrogen, sulfur, silicon and/or fluorine. The ability of polymer chains to pack into an ordered array depends strongly on the stereoregularity of their pendant groups. For example, depending on the method of polymerization, polystyrene may exhibit isotactic, syndiotactic or atactic structure. Atactic polystyrene, which is widely used commercially, is entirely amorphous due to the random arrangement of the pendant phenyl groups, while syndiotactic and isotactic polystyrene, having more regular structures, exhibit crystallinity.



Linear polymer chains in the amorphous (melt or glassy) state adopt conformations characteristic of a “random walk” due to the presence of both *gauche* and *trans* bond conformations along the backbone. A random walk denotes a path of successive steps in which the direction of each step is uncorrelated with, or independent of, previous steps—steps forward and backward, left and right, up and down are all equally probable.

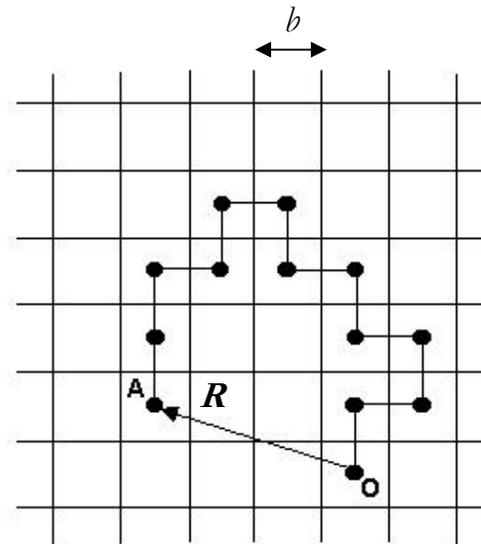


Because of the equal probability to step in opposite directions, the average end-to-end vector of a random walk of N steps, taken over many possible conformations, is identically zero.

$$\langle \mathbf{R} \rangle = 0$$

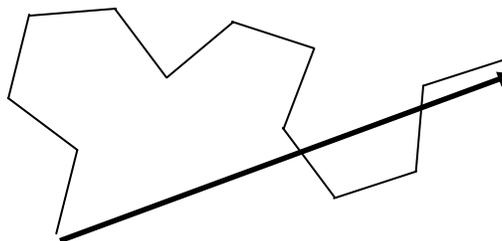
The root-mean-square (rms) end-to-end distance, however, is finite, and characterizes the average spatial dimension traversed. If the length of each step is b , the rms end-to-end distance can be shown to be^{1,2}:

$$\langle \mathbf{R}^2 \rangle^{1/2} = N^{1/2} b$$



For a polymer chain of N monomer segments, restrictions on available bond angles lead to an “effective” step size b , that is larger than the actual bond length l (l is $\sim 1.54 \text{ \AA}$ for a C-C bond). The rms end-to-end distance for the polymer chain of N monomers is given by²:

$$\langle \mathbf{R}^2 \rangle^{1/2} = R_0 = N^{1/2} C_\infty^{1/2} l$$



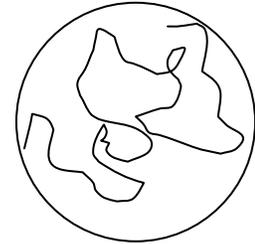
where C_∞ is called the characteristic ratio, which depends on the particular polymer. For polystyrene, C_∞ is ~ 10.8 at room temperature.² A polystyrene chain of $N = 1000$ would be expected to have a dimension $R_0 \sim 160 \text{ \AA}$ in the melt or glassy state.

An important feature of this result is that the polymer chain has a characteristic size which scales with the number of monomers in the chain to the one-half power: $R_o \sim N^{1/2}$. The average volume occupied by the coil is therefore much greater than the volume of the chain itself, so that in the melt or glassy state, many other chains will be found intermingled with a single chain. This is very different than the case of small molecule systems, and leads to the unique rheological and mechanical properties polymers exhibit.

$$V_{\text{coil}} \approx R_o^3 \sim N^{3/2}$$

$$V_{\text{chain}} = Nv_{\text{mer}} \sim N$$

$$V_{\text{coil}}/V_{\text{chain}} \sim N^{1/2} = \text{approx. \# of chains that fit in a single coil volume}$$



Polymers in solution

When polymers are dissolved in good solvents, the chains similarly take on coil-like conformations, but often are somewhat swelled, as a result of interactions between the monomer and solvent. The conformations of polymer chains in dilute solutions are well described as “self-avoiding” random walks (SAWs). Whereas a random walk is able to cross its own trajectory, a SAW disallows such configurations—the chain is said to have “excluded volume”.^{1,2} This gives rise to an effective swelling, so that:

$$R_{\text{SAW}} \sim N^{3/5}$$

Note that the degree of swelling is also a function of the solution temperature—raising the temperature typically causes the

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Monte Carlo simulation of swollen vs. globular states for $N = 626$ (from A.Y. Grosberg and A.R. Khokhlov, *Statistical Physics of Macromolecules*, AIP, NY, 1994, pg. 86)

chain dimensions to expand, while at low temperatures, chains can collapse into a dense, “globular” state, before precipitating out of solution.³

Measurement of Coil Dimensions by Dynamic Light Scattering

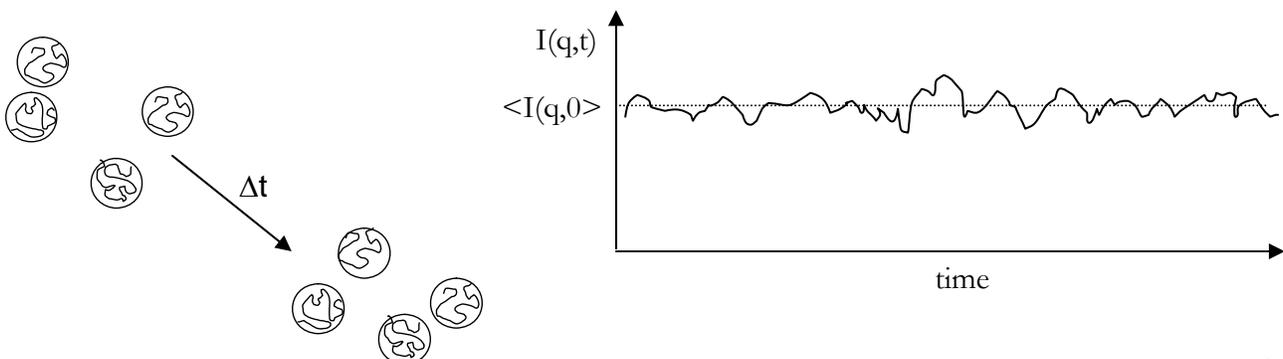
There are a number of experimental techniques by which the coil dimensions for a polymer chain can be measured. From dynamic light scattering (DLS) measurements, for instance, one can determine the hydrodynamic radius R_h of a polymer chain in dilute solution,³⁻⁵ which is directly proportional to the rms end-to-end distance for linear chains:

$$R_h = \text{const} \langle \mathbf{R}^2 \rangle^{1/2}$$

In a dynamic light scattering experiment, incident light that scatters from many individual polymer coils within a measured volume of polymer solution are detected at a fixed angle from the incident beam. Constructive and destructive interferences between scattered electromagnetic waves give rise to an average measured intensity. Because the polymer coils are moving in solution, the path length of the scattered light from a given chain within the measured volume will change as a function of time, causing the scattered intensity to fluctuate around its time-averaged mean value $\langle I(q,0) \rangle$. By observing the decay of these fluctuations, we can obtain information about the rate at which the polymer chains diffuse through the solution, which is inversely related to their size, through the Stokes-Einstein relation:

$$R_h = \frac{kT}{6\pi\eta_s D} \quad [1]$$

where D is the diffusion coefficient, η_s is the solvent viscosity, k is Boltzmann’s constant, and T is temperature in Kelvin.



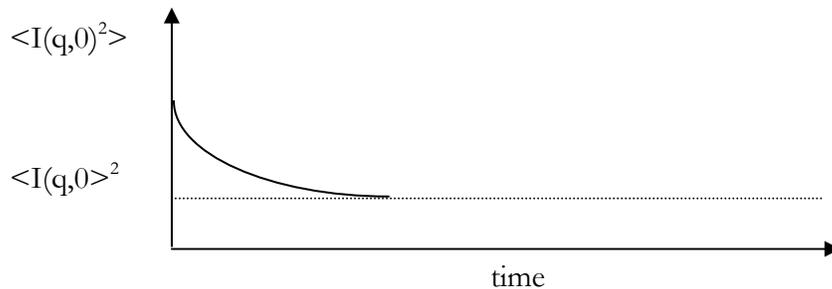
In DLS experiments, the measured intensity fluctuations in $I(q,t)$ depend on rearrangements of molecules in solution on length scale of $1/q$, where q is the scattering vector defined by:

$$q = \frac{4\pi}{\lambda} n_s \sin \theta \quad [2]$$

where θ is the scattering angle (90°), λ is the radiation wavelength (657 nm), and n_s is the refractive index of the solvent. The decay of fluctuations can be quantified by measuring the time auto-correlation function $\langle I(q,0)I(q,t) \rangle$. For a dilute monodisperse solution of coils⁴:

$$\langle I(q,0)I(q,t) \rangle = \langle I(q,0) \rangle^2 + [\langle I(q,0)^2 \rangle - \langle I(q,0) \rangle^2] \exp\left(\frac{-t}{\tau}\right) \quad [3]$$

From this expression, we observe the auto-correlation function takes an initial value of $\langle I(q,0)^2 \rangle$, but decays to $\langle I(q,0) \rangle^2$ for times much larger than the characteristic correlation time τ . Physically, the memory of the initial location of chains in the measured volume at $t=0$ is “lost” for times $t \gg \tau$, when most chains have diffused out of the scattering volume.



Because the chains behave as Brownian particles, the correlation time τ is related to the distance traveled ($1/q$) by⁴:

$$\frac{1}{q} = \sqrt{2D\tau} \quad [4]$$

where D is the diffusion coefficient for the coil in solution.

Experimentally, the autocorrelation function is measured, and fit to an expression of the form^{3,4}:

$$\langle I(q,0)I(q,t) \rangle = A + B \exp\left(\frac{-t}{\tau}\right) \quad [5]$$

In order to determine the correlation time τ , or similarly, the characteristic decay rate $\Gamma = 1/(2\tau)$.⁵ This value is used to calculate D from [4], which in turn can be related to the hydrodynamic radius R_h through [1], knowing the viscosity of the solvent.

Experimental

Materials to be investigated:

Polystyrenes of several molecular weights

Solvents:

Tetrahydrofuran

$$\eta_{THF} = 5.88 \cdot 10^{-5} T^2 - 7.95 \cdot 10^{-3} T + 6.11 \cdot 10^{-1} \text{ in centipoise}$$

$$n_{THF} = 1.405$$

REFERENCES

1. S.M. Allen and E.L. Thomas, *The Structure of Materials*, John Wiley & Sons: New York, 1999, pp. 51-60 (class handout)
2. R.J. Young and P.A. Lovell, *Introduction to Polymers*, 2nd ed., Stanley Thornes Ltd: Cheltenham, UK, 1991, pp. 151-164 (class handout)
3. E. Serhatli, M. Serhatli, B.M. Baysal, F.E. Karasz, Coil-globule transition studies of sodium poly(styrene sulfonate) by dynamic light scattering, *Polymer* **42**, 5439-5445 (2002)
4. M. Rubinstein and R.H. Colby, *Polymer Physics*, Oxford Univ. Press, New York, 2003, pp. 345-347 (class handout)
5. 3. R.J. Young and P.A. Lovell, pp. 189-193 (class handout)