DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
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Dynamic Light Scattering Study of Polymer Chain Dimensions

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Objectives:

- Introduce random walk model and self-avoiding walk model for polymer chains
- Prepare dilute solutions of polystyrene in tetrahydrofuran (THF) and a mixture of THF and methane
- Perform dynamic light scattering to obtain hydrodynamic radius of polymer chains in solution
- Determine scaling relationship between radius and molecular weight of polymers
- Investigate influence of solvent choice on polymer coil dimensions

1 Introduction

Polymers are long chain molecules composed of covalently bonded repeating units, called monomers, and generally comprised of carbon and hydrogen, and sometimes oxygen, nitrogen, sulfur, silicon, and/or fluorine. The number of monomers in the chain is called the *degree of polymerization.* Typically, this value varies from 500 to 10,000.

1.1 Physical models of polymers in solution

The long, string-like nature of polymers causes them to take on a variety of complex, coiled *conformations.* The conformations of polymers in solution depend on three characteristics: 1) the chain flexibility (some chains are stiff like piano wires, others are flexible like silk thread, depending on bond stiffness), 2) interactions between monomers in the chains (attractive or repulsive), and 3) interactions between monomers and the solvent. These conformations can be modeled using *random walk statistics.*

An ideal random walk denotes a path of successive steps in which the direction of each step is uncorrelated with or independent of the previous steps: steps forward and backward, left and right, up and down are all equally probable (Figure 1). In the ideal random walk, the root mean squared (rms) end-to-end distance characterizes the average spacial dimension traversed. Given a step length of l, the rms end-to-end distance is shown to be

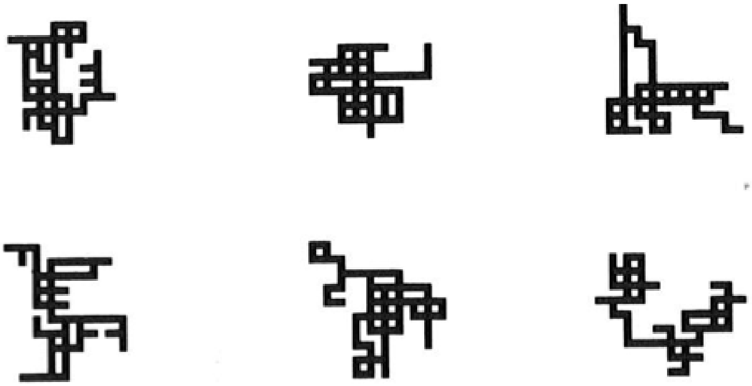

Figure 1: Realization of ideal random walk on square lattice – 100 step simulation [1].

$$< R^2 >^{1/2} = N^{1/2} l$$

for a random walk with N steps [2].

This model is valid for freely jointed chains. In most typical polymers, restrictions on bond angles occur. Thus, a *characteristic ratio*, C_∞, must be introduced. The rms end-to-end distance for a polymer chain with restrictions on bond angle is given by

$$< R^2 >^{1/2} = N^{1/2} C_\infty^{1/2} l$$

C_∞ depends on the polymer. For polystyrene, the polymer used in this experiment, C_∞ is ~ 10.8 at room temperature [1].

If interactions between the monomers and solvent were equally favorable – that is, the interaction energy of monomers with other monomers and with the solvent were exactly the same – then the conformation would be close to an ideal random walk. However, whereas a random walk is able to cross its own trajectory, a physical polymer molecule is prohibited from doing so. Thus, polymer chains are said to follow a "self-avoiding walk" (SAW) and have "excluded volume," which gives rise to an effective swelling (Figure 2).

Polymers in solution can be exposed to a variety of solvents. Good solvents, in which the monomer-solvent interactions are more favorable than monomer-monomer interactions, cause the polymer to swell in order to maximize the interactions between the polymer and solvent. In a good solvent, the rms end-to-end distance is thus

$$< R^2 >^{1/2} \sim N^{3/5}$$

If the polymer is in a poor solvent – that is, monomer-monomer interactions are more favorable than monomer-solvent interactions – the chain will collapse (Figure 3).

The above theories can be generalized into a universal power law in which n is the scaling exponent:

$$R \sim N^n$$

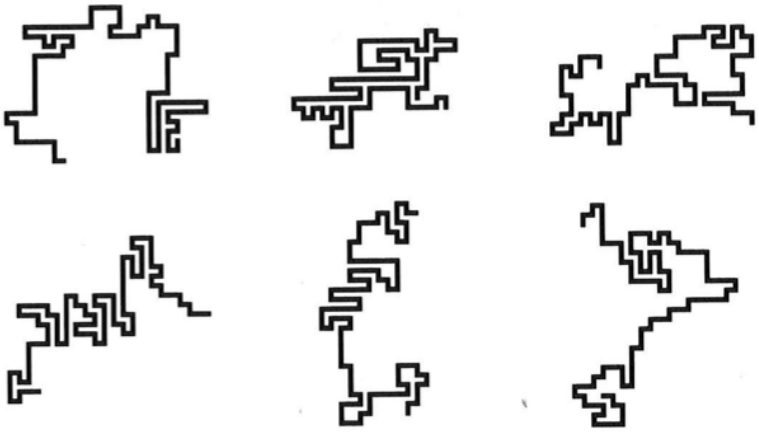

Figure 2: Realization of a self-avoiding random walk on a square lattice – 100 step simulation [1].

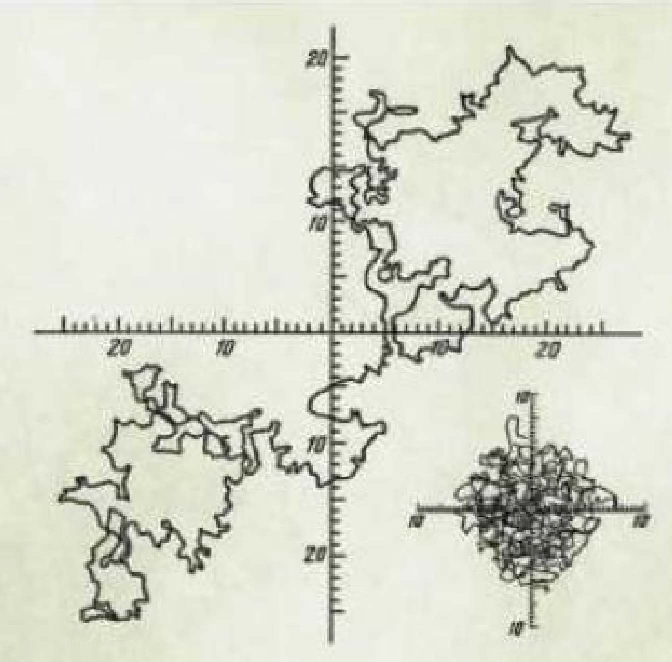

Figure 3: Monte Carlo simulation of swollen vs. globular states for $N = 626$ [3].

A value of $n = 3/5$ indicates a good solvent (though any value of $n > 1/2$ indicates that monomer-solvent interactions are more favorable than monomer-monomer interactions), while $n < 1/2$ indicates a poor solvent. A solvent that gives $n = 1/2$ approximates the ideal random walk and is known as a "theta solvent."

1.2 Dynamic Light Scattering

[todo]

1.3 Choice of solvent

In this experiment, we will mostly work with polystyrene in a good solvent. To determine which solvent should be used, we look at a result developed by Hildebrand that relates the enthalpy of mixing to the solubility parameters of the two components, δ_1 and δ_2 [4]:

$$\Delta H_m \sim (\delta_1 - \delta_2)^2$$

A low value of ΔH_m predicts favorable mixing and thus a good solvent, while a higher value of ΔH_m predicts less favorable mixing.

The solubility parameters of the polymers and solvents used in this experiment are [5, 6]:

$\delta_P S = 18.5 \times 10^3 J^{1/2} m^{-3/2}$
$\delta_T HF = 18.5 \times 10^3 J^{1/2} m^{-3/2}$
$\delta_M ethane = 29.7 \times 10^3 J^{1/2} m^{-3/2}$

Thus, we expect THF to be a good solvent for polystyrene and a mixture of THF and methanol to be a worse solvent for polystyrene.

2 Experimental Procedure

[todo – copy over from Lab 1 Procedure document]

References

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