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Dynamic Light Scattering Study of Polymer Chain Dimensions

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Adapted from handout by Agathe Robisson and Tracey Brommer

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 acetone
- 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,

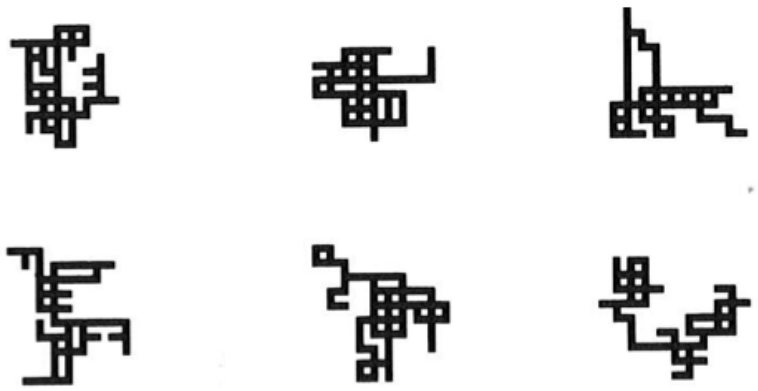

Figure 1: Realization of ideal random walk on square lattice – 100 step simulation [1].

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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

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

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

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

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

$$\langle R^2 \rangle^{1/2} \sim N^{3/5}$$

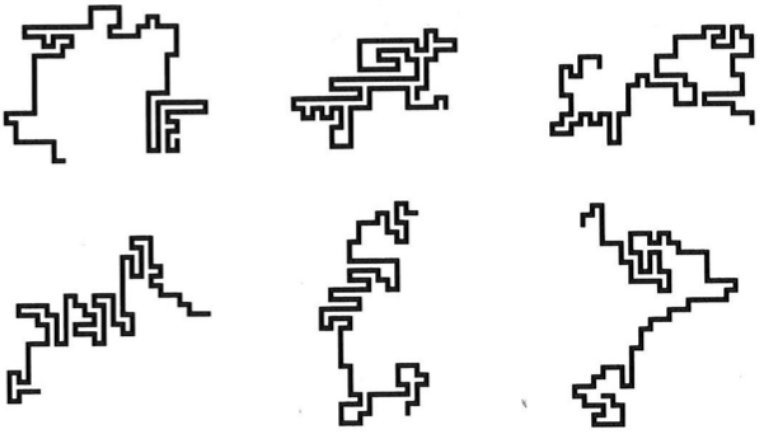


Figure 2: Realization of a self-avoiding random walk on a square lattice – 100 step simulation [1].

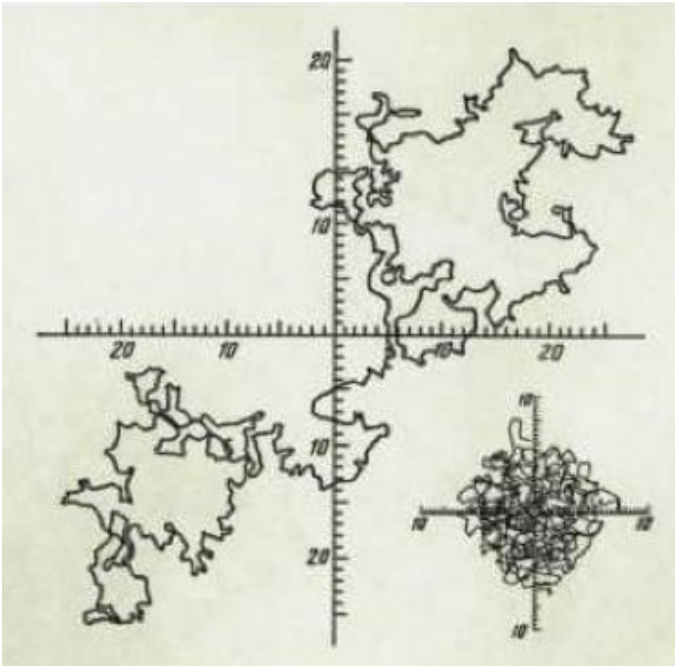


Figure 3: Monte Carlo simulation of swollen vs. globular states for $N = 626$ [3].

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:

$$R \sim N^n$$

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

Dynamic light scattering (DLS) measures the fluctuation in intensity of scattered light that occurs due to the random movements of particles in solution (Brownian motion). The intensity of scattered light fluctuates because the particles are constantly moving. The intensity fluctuates slower for large particles due to their slower diffusion rate, and fluctuates faster for smaller particles that diffuse quickly through solution. Thus, by measuring the velocity of fluctuations, the diffusion coefficient of the particles can be determined. The particle size can then be calculated using the Stokes-Einstein equation:

$$R_h = \frac{kT}{6\pi\eta_s D}$$

R_h is the hydrodynamic radius, k is the Boltzmann constant, T is the temperature in Kelvin, η_s is the viscosity of the solvent, and D is the diffusion coefficient.

DLS assumes that the particles in solution are perfect hard spheres. However, we know that polymers in good solvents are shaped like expanded coils. Thus, the radius calculated from DLS corresponds to the apparent size of the dissolved particle, or the *hydrodynamic radius* [4, 7]. The hydrodynamic radius is directly proportional to the rms end-to-end distance:

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

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]:

$\delta_{PS} = 18.5 \times 10^3 J^{1/2} m^{-3/2}$
$\delta_{THF} = 18.5 \times 10^3 J^{1/2} m^{-3/2}$
$\delta_{acetone} = 19.7 \times 10^3 J^{1/2} m^{-3/2}$

Thus, we expect THF to be a good solvent for polystyrene and acetone to be a worse solvent for polystyrene.

2 Experimental Procedure

2.1 Lab Safety

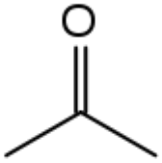
Acetone and tetrahydrofuran (THF) are both extremely flammable. Additionally, THF is moderately reactive, causes irritation to skin, eyes, and respiratory systems, and affects the central nervous system. Solvents should only be handled within a fume hood. Additionally, the following safety equipment should be worn when handling chemicals:

- Long pants, closed-toed shoes
- Lab coat
- Goggles
- Heavy (blue) nitrile gloves

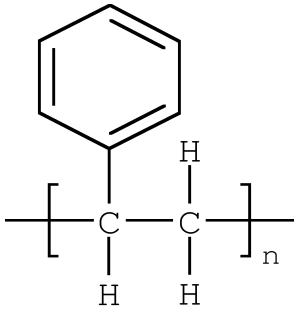
2.2 Materials

- Tetrahydrofuran (THF)

- Acetone



- Polystyrene in a variety of molecular weights (see procedure)



- Empty vials
- Cuvettes
- 1mL pipettor and pipette tips
- 10mL syringes and needles
- 0.2μm syringe filters

- Spatula
- Microbalance
- Vortexer
- Three waste beakers: small (sharps waste), medium (liquid waste), and large (solid waste)

2.3 General lab practice

- Label waste beakers
- Avoid contaminating solvent supply – use a clean pipette tip if you have to
- Clean spatula between each polystyrene sample

2.4 Procedure

Solutions to be prepared:

Polystyrene M_w (g/mol)	**Target Concentration** (g/mL)	**Solvent**
90,000	0.01	THF & THF/Acetone
152,000	0.009	THF
200,000	0.007	THF & THF/Acetone
390,000	0.006	THF
575,000	0.004	THF & THF/Acetone
900,000	0.003	THF
2,000,000	0.001	THF

All solutions will be 5mL, so you will need to calculate the appropriate amount of polymer to use.

1. Create polymer solutions:

- Put clean vial on microbalance
- Zero balance
- **Remove vial from balance**, then use clean spatula to add enough polystyrene to the vial to create a 5mL solution. Place vial on balance periodically to check mass.
- In the fume hood, use pipettor to add 5mL of solvent (either pure THF, or 40% Acetone and 60% THF)
- Dispose of used pipette in waste beaker
- Cap the vial and mix with vortexer for 2 minutes or until dissolved

2. Filter solutions to avoid dust:

- Attach long needle to 10mL syringe
- Fill syringe with polymer solution. You will have to tilt the vial with one hand and use the syringe with the other.
- Turn syringe upside down and remove needle

- Keeping the syringe upside down, discard needle in sharps beaker
- Attach 0.2μm filter to syringe and use light pressure to transfer filtered polymer to cuvette. Stop a few millimeters below the top of the cuvette to avoid over-filling.
- Place cap on cuvette
- Transfer the remaining solution to the liquid waste beaker
- Disassemble syringe and place in solid waste beaker
- Label the top of the cuvette with tape
- Clean sides of cuvette using a kimwipe and acetone

3. Measure particle size with DLS:

- Take cuvettes to room 8-206
- Remove sample pedestal
- Open Brookhaven Instruments software, Particle Sizing program (this turns on the laser; turn it off when done!)
- Under the *File* menu, select *Database*, then the class folder, and click "Open file"
- Load cuvette into DLS machine, put on black cap, and close lid
- Input parameters:

  Tetrahydrofuran:
  - Viscosity: 0.46 cP at 25°C
  - Refractive index: 1.408

  Acetone:
  - Viscosity: 0.32 cP at 25°C
  - Refractive index: 1.359

  Polystyrene:
  - Refractive index: 1.55
- Set machine to do 3 runs, 1 minute per run
- Record the *mean* and *combined* hydrodynamic radius values

4. Clean up:

- Pour liquid waste into hazardous waste container
- Wait for solid waste to dry in fume hood, then dispose of plastic in sharps disposal, broken glass bin, and trash can as appropriate
- Rinse cuvettes twice in THF and let dry in fume hood
- Once dry, clean waste containers with a bit of isopropanol and kimwipes

References

[1] Allen, S.M., and E.L. Thomas. The Structure of Materials. New York: John Wiley and Sons, 1999 p.51-60.

[2] Flory. Principles of Polymer Chemistry. Cornell UP, 1953.

[3] Grosberg, A.Y., and A.R. Khokhlov. Statistical Physics of Macromolecules. New York: AIP, 1994 p.86.

[4] Young, R.J., and P.A. Lovell. Introduction to Polymers, 2nd ed. Cheltenham: Stanley Thornes, UK, 2000 p.150-164.

[5] Ed: Brandrup, J., Immergut, E.H., Grulke, E.A., Abe, Akihiro, and D.R. Bloch. Polymer Handbook, 4th ed. John Wiley & Sons, 2005.

[6] A.F.M. Barton. Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press, 1983.

[7] Rubinstein, M., and R.H. Colby. Polymer Physics. New York: Oxford UP, 2003 p. 8, 49-54, 345-347.