ChE 529 Polymer Experimental Methods University of Rhode Island
Professor Greenfield Fall 2008

Lab 1, Introduction to Chain Shape and Physical Properties
September 9, 2008

Objective: The goal of this lab is to become more familar with the shapes of polymer chains and properties of polymer systems.

Safety:

The most important consideration in the polymer lab (or any lab) is to conduct the experiment safely. This means using a method that minimizes (and hopefully eliminates) both short-term and long-term hazards. This first experiment is expected to be conducted before all students have taken the required URI safety training or the refresher course. Thus it strives to demonstrate the key principles using materials that can be found around a house.

There are specific risks for these experiments:

- You will be dropping items off a high surface and having them fall to the floor. Look before dropping to make sure that there aren't people in the way. Be careful to watch above you as you retrieve what you dropped.
- Boiling water will be used to heat some of the polymer samples. This water can cause burns. Use gloves or a mitt to protect your hands and safety glasses to protect your eyes in cases of splashes.

Experiment A: Shape of a polymer chain

The goal of this experiment is to simulate the statistical shape of a polymer chain by using a string. The different shapes taken by the string are an approximation of the shapes taken on by a polymer in a solution or melt. Measurements will be made on the chain using a ruler that are analogous to the measurements made using actual polymer equipment later in the semester.

You will be provided two pieces of string that are approximately 2 to 4 ft long. First, record the fully extended length of each piece of string. Next, drop them (from as high a place as possible; a balcony over a stairwell is great, such as in the senior lab) onto a flat surface 20 times. Each time for both strings, measure two distances:

1. The end-to-end distance r, where r equals the distance between the two ends of the piece of string,
2. The maximum distance between two parts of the string. There is no typical symbol for this quantity, so we'll label it $\natural$ in order to prevent nomenclature conflicts later. This distance is serving as a stand-in for the radius of gyration (s or r_g).

Record the raw data for each piece of string and include them in your lab report.

Data Analysis

The intent of the 20 measurements for each string is to measure the distribution of sizes found in your samples. For a real polymer, the distribution is expressed by the sizes taken on by a mole of polymer chains. (In comparison to 10^{23}, using 20 measurements is getting off easy.) To determine the distribution, calculate $\langle r^2 \rangle^{1/2}$ (the square root of the average of the square of the end-to-end distance, also called the "root-mean-square" or RMS) for each of your measured data. (The shorthand "r" will be used below for $(r^2)^{1/2}$.) Then calculate and plot the measured distribution $P(r)$. In other words, how many string measurements had r values within each range of r values? (See also note below.) Repeat the calculations for the lengths $\natural$.

In your lab report, compare your results with the shape prediction based on a statistical "random walk":

$$P(r, n)dr = \frac{2}{n\ell^2} r \exp\left(-\frac{r^2}{n\ell^2}\right) dr \tag{1}$$

This equation corresponds to a polymer chain in two-dimensions, i.e. constrained to a flat surface. For the parameter combination $n\ell^2$ in this equation, use the fact that the average mean-squared distance is $\langle r^2 \rangle = n\ell^2$ for this model, as in one and three dimensions. (That means that you set $n\ell^2$ equal to the value of $\langle r^2 \rangle$ that you measured.)

How did $\langle r^2 \rangle^{1/2}$ compare with the fully extended length? How do your results compare for the two different lengths of string? Why? (Hint: think about how they are more or less stiff.)

Notes on how to plot a distribution: to calculate values of $P(r)$ from your data, divide up all the possible r's into domains, such as $a < r < b$. Then figure out the fraction of measured r's that fall into each domain. The value of $P(r)$ equals this fraction, DIVIDED BY the width of the domain, $(b - a)$. This division may seem artificial, but it's actually necessary. As an example, think about if you were guessing real numbers that fell between 0 and 10. Say you tried two bin sizes, either 1 or 2 wide (i.e. 10 or 5 bins). In the first case, you'd expect each bin to have 1/10 of the numbers. In the second case, you'd expect each bin to have 1/5 of the numbers, or twice as many per bin! Since these are both the same distribution, the way to compensate for the "extra" bin width in the second case is to divide each bin by its width, leading to (1/10) / 1 compared to (1/5) / 2 = 1/10.

If you'd rather think about it in terms of math, consider it this way. The normalization has to be

$$1 = \int P(r)dr \approx \sum_{\text{bins } i} P_i \Delta r_i = \sum_{\text{bins } i} \text{fraction in bin } i$$

where Δr_i is the width of bin i. (Not all bin widths have to be the same.) Comparing the individual terms in each of the last two sums,

$$P_i \Delta r_i = \text{fraction in bin } i$$

so

$$P_i = (\text{fraction in bin } i)/\Delta r_i$$

as described in words above.

Experiment B: Thermal effects on polymer properties

The goal of this experiment is to compare (qualitatively) the mechanical properties of different polymers and how they vary with temperature.

Your sample kit should contain several household polymers:

- a beverage container

- a clear food produce container (dates, most likely)
- a yogurt cup
- a regular plastic bag ("Staples")
- a biodegradable plastic bag (green, probably made of poly(lactic acid), or PLA)
- Silly Putty, a toy made of polydimethylsiloxane
- a few sets of rubber spheres

From day-to-day experience, you likely know that these polymers exhibit different properties. But how is that a result of our day-to-day experience occurring near 25°C? Answering that question is the point of this experiment.

In one set of experiments, compare the "bounce" of these systems:

- room temperature silly putty, warm silly putty, cold silly putty
- room temperature rubber spheres, warm rubber spheres, cold rubber spheres

The cold samples should be available from a freezer (ask Prof. Greenfield). Warm the room temperature samples by immersing them in boiling (or hot) water.

How would you rank the "bounciness" of these samples? Which bounces the most? Which bounces the least? How do changes in temperature affect the bouncing?

In another experiment, begin by noting what polymer was used to make each sample. (Do this first! It is much easier to do before conducting the rest of the experiment.) Then qualitatively compare the force (i.e. effort) it takes to bend the polymer containers. Press them down against a lab table or floor, for instance. First try this for the samples at room temperature. Then press the sample down while at least part of it is immersed in the boiling/hot water.

In your lab report, answer the following questions:

- What happens (if anything) when the sample is immersed in the boiling water? Describe.
- How does the modulus (see below) compare for the same material under room temperature and 100°C conditions?
- How does the modulus compare for these different samples and/or different polymers?

Experiment C: Sorption of liquid water

The goal of this experiment is to compare the effect of water on different household polymers. You will use two different polymers: part of a disposable diaper and a blob of hair gel.

Add water a few drops at a time to the disposable diaper. How much water can it absorb, and what do you observe as you add water?

Use a balance to measure the initial mass and the mass as you add water. Place some paper towel underneath the polymer in order to keep the scale clean.

The balance is in the second room off of the senior lab (next to the small shop room).

Qualitatively compare the effects of adding water to hair gel. **Do not do this on the balance.** Also compare the effect of adding salt to hair gel and to the polymer from the diaper.