THE MOLECULAR WEIGHT OF A POLYMER

Introduction

A polymer is a macromolecule, composed of many repeated subunits, called monomers linked together by the process of polymerization. Many of the macromolecules found in nature are polymers. For example; proteins are polymers composed of amino acid monomers. Many of the plastics that we are familiar with are synthetic polymers. For example; polypropylene, used to make carpeting.

The properties of plastics depend on a number of factors such as the type of monomer subunits, their arrangement (straight chain or branched) and the degree of cross-linking in the polymer. These properties can be manipulated to produce plastics with different properties. For example, both plastic grocery bags and plastic soda bottles are made of polyethylene. Grocery bags are made from low density polyethylene (LDPE) while soda bottles are made from high density polyethylene (HDPE). LDPE and HDPE differ in the degree of branching in the polymer molecule. LDPE has more extensive branching and so is a less compact molecule (hence its lower density) while HDPE has less branching making it more compact (and higher density).

Polymers have a large molecular weight that depends on the number of monomer units that make up the polymer. A problem for polymer scientists is that in a sample of a particular polymer, there are many polymer molecules. Each polymer molecule in the sample can be made up of a different number of monomers so there is a range of molecular weights in the sample. For this reason, molecular weight is often expressed as an average of the different molecular weights in the sample. It is helpful for scientists to know the average molecular weight of a polymer sample as it is one variable that would need to be controlled in the experimental design when conducting research.

There are several methods for determining the molecular weight of a polymer. These include size exclusion chromatography (SEC) and dilute solution viscometry (DSV). In this experiment, we will use DSV which uses relatively simple and inexpensive equipment to determine the molecular weight of different samples of the polymer polyethylene glycol (PEG). PEG has many uses; it is used in toothpaste, as a lubricant, and as an ink solvent in printers. PEG with a
molecular weight of 3350 is used as a laxative and is sold at drug stores under several different brand names. As consumers of over-the-counter drugs we sometimes need to make a decision between the name brand of a drug and a less expensive store brand with the same active ingredient.

Quality control is very important in the pharmaceutical industry to ensure that drugs meet FDA standards, are safe and effective for the patient. For example, in 2012, a steroid injection, used to treat neck and back pain caused 15 deaths and almost 200 infections after it became tainted with bacteria that cause meningitis. In 2009, the FDA also took steps to improve monitoring of pharmaceuticals imported to the US from other countries after a tainted blood thinner killed three people and was suspected of more deaths. PEG is non-toxic, however, there are concerns that smaller toxic compounds, such as ethylene glycol or diethylene glycol, could be found as impurities in the manufacturing process of PEG 3350.

In this lab activity, your role will be that of a pharmacist comparing two bargain brands of PEG 3350 laxative that you are considering as replacements for a more expensive name brand of PEG 3350. You will use DSV to measure the viscosity of the name brand of PEG 3350 (the standard) at several dilutions, and graph the data in order to determine two constants (k’ and a) called the Mark-Houwink constants. After measuring the viscosity of the bargain brands (the unknowns), their molecular weights can be determined using the Mark-Houwink constants and equation. The results will be used to determine if the bargain brands of PEG 3350 are acceptable replacements for the more expensive name brand. You will also design an experiment to determine the concentration of an unknown PEG 3350 solution.

Pre-Lab Questions

1. PEG is made of repeating ethylene glycol units. Find the structure of ethylene glycol and show how four units of ethylene glycol can bond to form a PEG polymer by hydrolysis (loss of a water molecule).
2. Determine the molecular weight for one repeating unit of polyethylene oxide with the appropriate unit (remember that each polyethylene oxide unit has lost a molecule of water in the polymerization process). Use appropriate conversion factors (with units) to determine the number of repeating units in a PEG 3350 molecule.
3. Describe the types of intermolecular forces that might exist between PEG molecules. Explain where in the molecule these interactions might occur.

Materials

- MiraLax® 3350 laxative—10 % (mass/volume) aqueous solution (PEG standard)
- 10 % (mass/volume) aqueous solution of two store brands of PEG 3350 laxative
- Two discount store brands of PEG 3350 laxative
- Glass capillary tube viscometer (1.2 mm)
- Stopwatch
- 100 mL beaker
- 50 mL beakers (4)
- 25 mL measuring cylinder
- Ring stand and utility clamp
- Suction bulb

Safety

- Polyethylene glycol is non-toxic but should not be ingested due to its laxative properties.
- Use proper safety protocols for working with lab glassware
- Dispose of polyethylene glycol solution as instructed.

Procedure

1. Obtain about 80 mL of the 10 % aqueous solution of PEG standard in a 100 mL beaker
2. Using the 10 % standard PEG solution, prepare 25.0 mL aliquots of solutions with concentrations of 8 %, 6 %, 4 % and 2 % in separate 50 mL beakers. Mix each dilution well. Show your calculations for each dilution below.
3. Set up the capillary tube viscometer in the ring stand as demonstrated by the instructor.

4. Pour 15.0 mL of distilled water into the viscometer. Use the suction bulb to draw the water into the bulb to above the highest line in the arm of the viscometer making sure that there are no bubbles in the liquid in the viscometer. Prepare the stopwatch.

5. Remove the suction bulb to allow the level of the water to drop. Start the stopwatch when the level of the water passes the highest line. Allow the water to drain, and stop the stopwatch when the water level passes the bottom line.

6. Record the time in the data table to the nearest 0.1 seconds (this is called the efflux time). Repeat two more times to obtain three trials. Carefully drain the liquid from the viscometer completely.

7. Repeat steps 4-6 using the 2 % PEG solution instead of water.

8. Repeat steps 4-6 using the 4 % PEG solution.

9. Repeat steps 4-6 using the 6 % PEG solution.

10. Repeat steps 4-6 using the 8 % PEG solution.

11. Repeat steps 4-6 using the 10 % PEG solution.

12. Discard the PEG solutions in the container designated by the instructor. Wash and dry the beakers.

13. Rinse the viscometer thoroughly with distilled water and drain completely.

14. For each set of trials, calculate the average efflux time.

15. Repeat steps 4-14 using the first discount store brand (unknown 1)

16. Repeat steps 4-14 using the second discount store brand (unknown 2)

**Data Table 1: Standard PEG Solution**

<table>
<thead>
<tr>
<th>EFFLUX TIME</th>
<th>TRIAL 1</th>
<th>TRIAL 2</th>
<th>TRIAL 3</th>
<th>AVERAGE TIME</th>
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<td>(sec)</td>
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<tr>
<td>Solvent (water)</td>
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<td>2 % PEG solution</td>
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<td>4 % PEG solution</td>
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<td>PEG Solution</td>
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<td>6% PEG</td>
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<td>8% PEG</td>
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<td>10% PEG</td>
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### Data Table 2: Unknown PEG Solution 1

<table>
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<tr>
<th></th>
<th>TRIAL 1</th>
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<th>TRIAL 3</th>
<th>AVERAGE TIME</th>
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<tr>
<td><strong>EFFLUX TIME</strong></td>
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<tr>
<td>2 % PEG solution</td>
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<td>4 % PEG solution</td>
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<td>6 % PEG solution</td>
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<td>8 % PEG solution</td>
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<td>10 % PEG solution</td>
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</table>

### Data Table 3: Unknown PEG Solution 2

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<tr>
<th></th>
<th>TRIAL 1</th>
<th>TRIAL 2</th>
<th>TRIAL 3</th>
<th>AVERAGE TIME</th>
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<tr>
<td><strong>EFFLUX TIME</strong></td>
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<td>10 % PEG solution</td>
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### Calculations

Use the formulas below to calculate each expression for viscosity using the average efflux times. Record the results in the table with units where appropriate:

- **Relative viscosity** ($n_r$) = \( \frac{\text{efflux time of PEG solution} \ (t)}{\text{efflux time of solvent} \ (t_0)} \)

- **Specific viscosity** ($n_{sp}$) = \( \frac{t - t_0}{t_0} \)

- **Reduced viscosity** ($n_{red}$) = \( \frac{n_{sp}}{\text{concentration}} \)
inherent viscosity \( n_{inh} \) = \( \frac{\ln (n_r)}{\text{concentration}} \)
<table>
<thead>
<tr>
<th></th>
<th>2 % PEG</th>
<th>4 % PEG</th>
<th>6 % PEG</th>
<th>8 % PEG</th>
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<tbody>
<tr>
<td><strong>CALCULATED VISCOSITIES-Standard PEG Solution</strong></td>
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<tr>
<td>Relative viscosity, $n_r$</td>
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<td>Specific viscosity $n_{sp}$</td>
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<td>Reduced viscosity, $n_{red}$</td>
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<td>Inherent viscosity, $n_{inh}$</td>
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<td><strong>CALCULATED VISCOSITIES-Unknown PEG Solution 1</strong></td>
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<tr>
<td>Relative viscosity, $n_r$</td>
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<td><strong>CALCULATED VISCOSITIES-Unknown PEG Solution 2</strong></td>
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<tr>
<td>Relative viscosity, $n_r$</td>
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<td>Specific viscosity $n_{sp}$</td>
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Graphs

Prepare three properly-labeled line graphs using the grids. One for the standard PEG solution, one for Unknown PEG solution 1 and one for Unknown PEG solution 2:

- Put concentration on the x-axis and both reduced viscosity and inherent viscosity on the y-axis.
- Plot each point for concentration vs reduced viscosity using an “x” and connect the points with a best fit line. Continue the line so that it intersects the y-axis.
- Plot each point for concentration vs inherent viscosity using an “●” on the same graph and connect the points with a best fit line. Continue the line so that it intersects the y-axis.
- NOTE: When you draw the two lines on the graph, they both should intersect the y-axis at the same point. The y-intercept is called the intrinsic viscosity $[\eta]$.
CONCENTRATION VS $n_{red}$ and $n_{inh}$ – STANDARD SOLUTION
CONCENTRATION VS $n_{red}$ and $n_{inh}$ – UNKNOWN PEG SOLUTION 1
CONCENTRATION VS $n_{\text{red}}$ and $n_{\text{inh}}$ – UNKNOWN PEG SOLUTION 2
Data Interpretation

1. The plot of concentration vs reduced viscosity ($n_{red}$) is described by a formula in slope intercept form:

\[ y = mx + b \]

\[ n_{red} = k'[n]^2 c + [n] \]

- The intrinsic viscosity, $[n]$ is the y-intercept and $k'$ is a constant.
- The slope of the line is given by: \( \text{slope} = k' [n]^2 \)

Use the slope and the y-intercept to calculate $k'$ for the standard PEG solution and the two unknown PEG solutions. Show work below:

2. The plot of concentration vs inherent viscosity ($n_{inh}$) is also described by a formula in slope intercept form:

\[ n_{inh} = k'' [n]^2 c + [n] \]

- The intrinsic viscosity, $[n]$ is the y-intercept and $k''$ is a constant.
- The slope of the line is given by: \( \text{slope} = k'' [n]^2 \)

Use the slope and the y-intercept to calculate $k''$ for the standard PEG solution and the two unknown PEG solutions. Show work below:
3. \( k' - k'' \) should be equal to 0.5. As a check on your work Calculate \( k' - k'' \). Is your value 0.5?

4. Once \( k' \) is calculated, the molecular weight of a polymer can be calculated using the Mark-Houwink equation:

\[
[n] = k' M^a
\]

- \([n]\) is the intrinsic viscosity (y-intercept in the graphs)
- M is the molecular weight
- \( a \) is a constant. In this experiment, you will calculate \( a \) for the standard solution which has a molecular weight of 3350 and use this value of \( a \) for the unknown PEG solutions.

Calculate the value of the constant \( a \) for the standard PEG solution. Show work below (If you need help solving for exponents in an equation, take a look at this website: [http://mathonweb.com/help_ebook/html/expolog_4.htm](http://mathonweb.com/help_ebook/html/expolog_4.htm))

5. Calculate the molecular weight for each of your unknown PEG solutions using the Mark-Houwink equation and the value of the constant, \( a \) for the standard PEG solution. Use the values of \( k' \) and \([n]\) that you calculated for each unknown PEG solution. Show your work below.
**Analysis and Conclusions**

1. Identify the independent variable and dependent variable in the experiment. Describe two controlled variables.

2. In the calculations, you determined relative viscosity, reduced viscosity and specific viscosity. Which of these viscosities have no units? For any of the viscosities that have units, show how the unit is derived.

3. The class results for molecular weights of PEG unknowns 1 and 2 will be shared with the class.
   a) Calculate the mean molecular weight and standard deviation for the class data for PEG unknown 1
b) Calculate the mean molecular weight and standard deviation for the class data for PEG unknown 2.

c) For each of the two unknowns subtract two standard deviations and add two standard deviations to the mean to get a range of values. Write your ranges below. It has been established that 3350 must fall within this range for the bargain brand PEG laxatives to be acceptable for patient use. Are the two bargain brands acceptable for use?

d) If we assume that the molecular weight of the standard PEG solution was determined by size exclusion chromatography (expressed as ‘weight average molecular weight’). Are your results for viscosity average molecular weights consistent with SEC based on the diagram below? Explain.
4. Using 3350 as the acceptable molecular weight value, calculate the percent error for your experimental molecular weights for Unknowns 1 and 2. Show your work.
5. You are given a sample of the standard PEG 3350 solution of unknown concentration.
   a) Use what you have learned in the lab to design an experiment that determines the
      concentration of PEG 3350 in the unknown in units of g/mL. Type up the procedure.
   b) Obtain a sample of the standard PEG solution of unknown concentration from the
      instructor and use your procedure to determine its concentration in g/mL using
      appropriate data tables.
   c) Convert units of g/mL for the concentration of the unknown to monomer units/L (you
      will need Avogadro’s number for this). Show your work.

References

1. Polymer Science Learning Center (2016), Molecular Weight. Retrieved from
   July 15, 2017
   meningitis-risk-from-tainted-drugs-feared.html on July 15th, 2017
4. Apoorva Mandavilli, (2008), The FDA Tackles Tainted Drugs From China, Discover