Chain Length and Frequency of Reverse Linkages in a Polyvinyl Alcohol Polymer

Introduction

A <u>polymer</u> is a large molecule composed of similar or identical subunits, called <u>monomers</u>. Polymers may be <u>linear</u> (forming a single long chain of monomers) or <u>branched</u> (having several side chains of monomers attached to the main chain of the polymer). Examples of polymers include proteins (where the monomers are all amino acids, and which therefore have similar but not identical subunits), starch, natural and synthetic rubbers, plastics, and a variety of other materials. Polymer chemistry is interently interdisciplinary, making use of scientists from all of the subdisplines of chemistry, as well as scientists trained in related fields of science. Polymer chemistry is a major area of industrial chemistry. According to the Plastics Industry Trade Association [1], there were 940,000 jobs in the plastics industry in United States in 2015, with $ 427.3 billion dollars in sales.

A sample of polymer where the individual molecules making up the polymer are identical is called <u>monodisperse</u>. For monodisperse polymers, all of the polymer molecules will have the same chain length and molecular mass [2]. On the other hand, a polymer sample may be <u>polydisperse</u>, consisting of individual molecules of different chain length, and therefore different molecular mass. Synthetic polymers are often polydisperse.

One important property of a polymer is the average mass of the polymer molecules, defined as

$$M_{ave} = \frac{\sum_{i=1}^{\infty} M_i \, N_i}{\sum_{i=1}^{\infty} N_i} \qquad (1)$$

where N_i is the number of polymer molecules with mass M_i. The average chain length, or average number of monomers per polymer (N_{ave}), can also be defined, with

$$N_{ave} = \frac{\sum_{i=1}^{\infty} i \, N_i}{\sum_{i=1}^{\infty} N_i} \qquad (2)$$

For cases where the monomers making up the polymer are identical subunits, the average chain length of a polymer molecule is related to the average molecular mass of the polymer (M_{ave})

$$N_{ave} = M_{ave}/M_{mono} \qquad (3)$$

Many of the properties of a polydispase polymer, including the strength of the polymer, are related to the average chain length of the molecules making up the polymer.

<u>Polyvinyl alcohol</u>

Polyvinyl alcohol (PVOH) polymer consists of linear polymer molecules. In this polymer, the individual monomers have the formula - CH_2-$CHOH$ - [3], with M_{mono} = 44.0 g/mol. PVOH polymers are formed by the successive addition of monomers to a polymer radical ($R\cdot$)

$$R\cdot + M \rightarrow R - M\cdot \qquad (4)$$

Monomers usually add to the polymer in "head to tail" fashion, forming a chain with structure

$$- CH_2\text{-}CHOH - CH_2\text{-}CHOH - CH_2\text{-}CHOH - \ldots \qquad (5)$$

However, occasionally a monomer will add to the polymer radical in a "head to head" fashion

$$- CH_2\text{-}CHOH - CHOH\text{-}CH_2 - CH_2\text{-}CHOH - \ldots \qquad (6)$$

The linkage formed in 6 is called a <u>reverse linkage</u>, and, unlike the normal linkages in 5, can be broken by treatment of a solution of PVOH polymer by a strong oxidizing agent. Treatment of a solution containing PVOH polymer molecules with such an oxidizing agent will, by cleaving the reverse linkages, break the polymer into a larger number of small polymer molecules.

If the average molecular mass of a sample of PVOH polymer can be measured, the average number of reverse linkages per polymer molecule can be determined. This is done by measuring the average molecular mass of the PVOH polymer before (M_{ave}), and after (M_{ave}') treatment with oxidizing agent. The average number of reverse linkages per polymer molecule (Δ) is then [4]

$$\Delta_{ave} = (M_{ave}/M_{ave}') - 1 \tag{7}$$

Since the total number of linkages in the uncleaved polymer molecule (L) is [5]

$$L_{ave} = (M_{ave}/M_{mono}) - 1 \tag{8}$$

then the percentage of reverse linkages is

$$\% \text{ reverse linkages} = (\Delta_{ave}/L_{ave}) \times 100 \% \tag{9}$$

If it is possible to find the average mass PVOH polymer molecules, two important physical characteristics of the polymer, the average chain length and percentage of reverse linkages, can be found.

<u>Viscosity</u>

<u>Viscosity</u> is the resistance of a fluid to flow. The viscosity of a pure liquid or liquid solution is given in terms of the <u>viscosity coefficient</u> (η). Highly viscous liquids, such as a syrup, will have a large value for their viscosity coefficient, and flow more slowly than liquids with a small value of viscosity coefficient, such as pure water.

There are a variety of methods that can be used to measure the viscosity of a liquid. One common method is use of a glass device called an Ostwald viscometer, as shown in Figure 1. The viscometer has two reservoirs, with the bottom reservoir connected to a sample chamber by a long, narrow diameter tube. The relative viscosity of a liquid is determined by measuring the time it takes for the level of liquid to move from the high to the low mark on the viscometer. This elapsed time is related to the viscosity coefficient of the liquid by the expression

$$\frac{\eta}{\rho} = Bt \tag{10}$$

where ρ is the density of the liquid and B is the apparatus constant for the viscometer. The value for B depends on the length and diameter of the tube connecting the sample chamber to the reservoirs. By measurements of the elapsed time for a liquid whose viscosity coefficient is known, the value for B can be found. Since water is the solvent in this experiment, it is used to find the viscometer constant.

For a solution of PVOH in water, the specific viscosity of the solution (η_{sp}) is defined as

$$\eta_{sp} = (\eta/\eta_0) - 1 \tag{11}$$

where η is the viscosity coefficient of the solution and η_0 is the viscosity coefficient of the pure solvent.

The viscosity coefficient for a liquid depends strongly on temperature. Table 1 gives the viscosity coefficient for pure water at several different temperatures, and can be used to find the viscosity coefficient for the temperature used in the experiment (by interpolation, if necessary). However, note that if all of your measurements are carried out at the same temperature, and the density of the polymer solutions is assumed to be the same as the density of the pure solvent, (as expected for a dilute solution), inserting eq 10 into the expression for η_{sp} gives

$$\eta_{sp} = (t/t_0) - 1 \tag{12}$$

where t is the time it takes for the solution to flow through the viscometer, relative to t_0, the elapsed time for the solvent to pass through. It is convenient to do all of the experimental measurements at the same temperature so that eq 12, rather than eq 10 and 11, can be used in the data analysis.

Table 1. Viscosity coefficient of water as a function of temperature.

T (°C)	η (cP)	T (°C)	η (cP)
15.0	1.139	23.0	0.9317
17.0	1.081	25.0	0.8909
19.0	1.027	27.0	0.8525
21.0	0.9779		

The viscosity coefficient is often given in units of cP (centipoise). $1\ P = 0.1\ Nt \cdot s/m^2$. $1\ cP = 0.01\ P$.
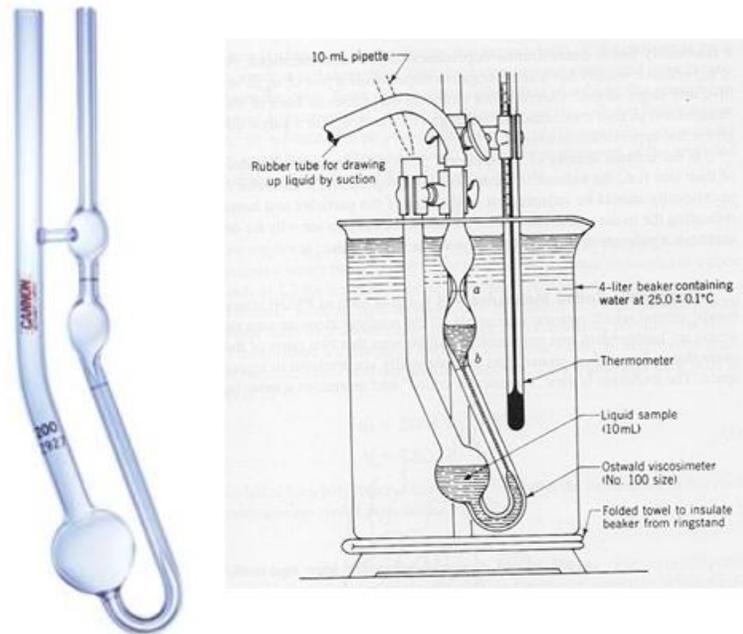

Figure 1. Left – Ostwald viscometer. Right – Experimental apparatus, including the Ostwald viscometer.

The specific viscosity of a solution of polymer is related to the intrinsic viscosity of the polymer ([η]) by the relationship

$$[\,\eta\,] = \lim_{c \to 0} \eta_{sp}/c \tag{13}$$

In the above expression c is the solute concentration in units of grams of solute per 100 mL of solution [6]. The value for [η] can be found by plotting η_{sp}/c vs c and extrapolating to c = 0. By expressing c in units of g/100 mL the units for [η] are then $10^2\ cm^3/g$.

The value for M_{ave} for a polymer is related to the average molecular mass of the polymer and the shape of the polymer in the solution. For PVOH polymers in water, this relationship has been determined experimentally [7], and is

$$M_{ave} = 4.0 \text{x } 10^4 \, [\, \eta \,]^{1.32} \qquad\qquad (14)$$

where M_{ave} is in units of g/mol.

Experimental

<u>Polymer solution preparation</u>

A stock solution of polymer is prepared by dissolving approximately 3.0 g of polymer into about 200 mL of hot deionized water. The polymer will dissolve slowly. Stir the solution gently to promote dissolving the polymer, while trying to avoid any foaming of the solution. When the polymer has completely dissolved, let the solution cool, and then carefully transfer the solution into a 250. mL volumetric flask. If there appears to be a small amount of undissolved polymer, the solution can be transferred by filtering through a small piece of glass wool inserted into the bottom of a funnel. Fill the flask with water to the mark. This solution represents a stock polymer solution.

Pipette 50. mL of the stock polymer solution into a 100 mL volumetric flask and add deionized water. Mix the solution. This will represent the first solution of uncleaved polymer.

To prepare the first solution of cleaved polymer (at the same concentration as the above solution of uncleaved polymer), pipette 50 mL of stock polymer solution into a flask, and add up to 25 mL of water and 0.25 g of solid potassium periodate (KIO_4), a strong oxidizing agent. Warm this solution to ~ 70 °C and stir until all of the KIO_4 has dissolved. Let the solution gradually cool to room temperature with stirring. Transfer the solution into a 100 mL volumetric flask and fill the flask to mark by adding additional deionized water. This represents the first solution of cleaved polymer.

At this point you will have two polymer solutions, one cleaved and one uncleaved, at the same concentration of polymer (which will be approximately 0.6 g/100 mL). A second solution of cleaved and uncleaved polymer can be obtained by pipetting 50 mL of the first solution into a 100 mL volumetric flask, and then filling the flask to mark by adding deionized water.

<u>Measurement of viscosity</u>

<u>Thoroughly clean the viscometer before use, and also after every measurement of the viscosity of a polymer solution</u>. This is to prevent polymer solution from drying inside the viscometer, which will clog the connecting tubes in the viscometer. To make a measurement, the viscometer should be filled with 10.0 mL of solution, and then placed in the temperature bath, as shown in Figure 1. The temperature of the bath should be slightly higher than room temperature, and should be kept constant. A temperature in the range 25-30 °C is usually a good choice. Temperatures significantly higher than this can give poor results. After placing the filled viscometer in the water bath let it equilibrate for at least 10 minutes, so that it is at the same temperature as the bath. Use a pipette bulb to suction liquid above the first mark between the two reservoirs. Let the liquid drain, and begin timing when the level of liquid passes the upper mark on the viscometer. When the liquid passes the second mark, stop the timing. The time you measure represents the elapsed time for that liquid.

Calibrate the viscometer by measuring the elapsed time for deionized water to flow through the viscometer. Do this measurement at least two times (do more trials if possible). Your individual measurements for pure water should have elapsed times within a few seconds of one another. Then make measurements of the elapsed time for each of the two uncleaved polymer solutions and cleaved polymer solutions. At least one measurement of each is needed, but two measurements are recommended to evaluate consistency. During the taking of all the measurements, the bath temperature should be recorded to a precision of ± 0.1 °C at 15 minute intervals. This is because the viscosity is highly dependent on temperature, and so fluctuations in bath temperature are one source of error in this experiment.

Figure 2 gives a typical plot of η_{sp}/c vs c for the data from this experiment. The y-intercept of the plot is equal to $[\eta]$, the intrinsic viscosity. Based on theoretical considerations, the slope of the plot should be approximately zero. However, examination of the figure shows that this is not observed. This is due to experimental error [7]. **Therefore, to find the value for $[\eta]$, average the two experimental values for η_{sp}/c (which corresponds to using the horizontal line in Figure 2).** Do this for both the uncleaved and the cleaved polymer data. As a check, your value for $[\eta]$ is expected to be in the range 0.5 – 1.5 for the uncleaved polymer, and 0.1 – 0.5 for the cleaved polymer. If your values fall outside of these ranges check your calculations and then talk with your instructor.
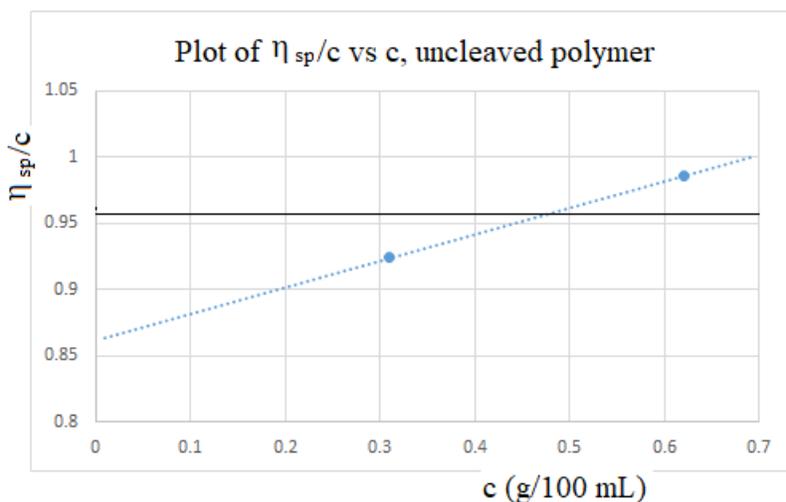

Figure 2. A plot of specific viscosity/concentration (η_{sp}/c) vs concentration for the uncleaved polymer solution.

Lab Report

Your laboratory report should include the following:

1) The experimental measurements for the elapsed time for draining the viscometer for deionized water and each of the polymer solutions (uncleaved and cleaved), along with the concentration of each polymer solution.

2) The calculations for the specific viscosity for each solution (eq 12), and the determination of the intrinsic viscosity for the uncleaved and cleaved polymer solution.

3) The average molecular mass of the polymer before cleavage (eq 14), the average molecular mass after cleavage (eq 14), and the average number of monomers per polymer before and after cleavage (eq 3).

4) The average number of reverse linkages per polymer molecule and the percentage of reverse linkages per polymer molecule (eq 7 – 9).

5) Because you only obtain a small amount of data in this experiment it is not possible to do a rigorous analysis of error. You should, however, be able to identify the major sources of error in the experiment and estimate their effect on your final results.

6) Since the values for average molecular mass for the uncleaved and cleaved polymer are unique to this particular batch of polymer, there are no literature values for the properties of the polymer.

References

1. Plastics Industry Trade Association, <u>Size and Impact of the Plastics Industry on the U. S. Economy</u>, December 2015 http://www.plasticsindustry.org/sites/plastics.dev/files/U.S.%20Size%20and%20Impact%202015.pdf

2. Aside from small differences due to random differences in the isotopic composition of the atoms making up the polymer molecules.

3. Other than the terminal molecules of the polymer, which will have an extra H atom to satisfy the bonding requirements for the terminal carbon atom.

4. This result can be derived as follows. If there were no reverse linkages than M_{ave}' would be equal to M_{ave}. If there were one reverse linkage per polymer then M_{ave}' would be equal to $M_{ave}/2$. In the general case, if the number of reverse linkages is Δ, then $M_{ave}' = M_{ave}/\Delta$, from which follows eq 7.

5. Eq 8 is derived in a manner similar to the derivation of eq 7.

6. For example, a solution containing 3.55 g of solute per liter of solution would have c = 0.355 g/100 mL.

7. This is more important for the cleaved polymer than for the uncleaved polymer. The elapsed time for draining the viscometer for the cleaved polymer solutions is usually only a few seconds longer that the elapsed time for pure water, and so the value for η_{sp}/c has a lot of uncertainty. In fact, in some cases a plot of η_{sp}/c vs c leads to a negative value for the intrinsic viscosity, a physically unrealistic result. It is therefore better to find the value for $[\eta]$ by the averaging method than by graphical extrapolation.
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