Experiment 1

Determination of 1,2-diols in poly(vinyl alcohol)

Introduction

Poly(vinyl alcohol) (PVOH) was discovered in 1924 by Herrmann and Haehnel, when they added alkali to an alcoholic solution of poly(vinyl acetate) (PVOAc) and obtained the ivory-coloured PVOH. Since that time, PVOH has become the largest volume, synthetic, water-soluble polymer resin produced in the world. The largest markets are in fibres, adhesives, emulsion polymerization, poly(vinyl butyral) production, and textile and paper sizing. PVOH is also receiving attention today because it is one of the few synthetic polymers which is completely biodegradable.

Since the vinyl alcohol monomer does not exist in the free state, PVOH must be manufactured in two steps. The most common method involves the polymerization of vinyl acetate to form PVOAc, followed by alcoholysis under basic conditions to form PVOH.

Vinyl acetate is polymerized by either batch or continuous processes. Batch polymerization is the preferred method when small quantities of several grades of PVOAc are required, while the continuous polymerization process is used when large quantities of a specific grade are needed. Both methods are essentially free-radical solution polymerizations. Typical reactor conditions in the continuous system are 55°C - 85 °C reflux temperatures and 0.1 - 0.5 MPa pressure. In order to suppress transesterification reactions between vinyl acetate and the solvent (which is usually an alcohol) prior to the first reaction vessel, small amounts of acid (2 - 50 ppm) are added to the vinyl acetate stream. This prevents the formation of acetaldelyde, which is a chain transfer agent and affects the color of the final product.

PVOAc can be converted into PVOH by direct hydrolysis, or by alcoholysis catalysed by a strong acid (sulfuric or hydrochloric acid) or strong base (sodium hydroxide, sodium alcoholates, or potassium hydroxide). A reaction scheme is shown below.



For large-scale industrial reactions, base-catalysed alcoholysis is preferred. The alcoholysis reaction is rarely taken to completion, as fully hydrolysed PVOAc is highly crystalline and difficult to dissolve in water. The degree of hydrolysis can be controlled by residence time in the reactor, catalyst concentration, temperature, and additives. So in essence, PVOH is actually a copolymer of vinyl acetate and vinyl alcohol, with a vinyl acetate content ranging from 0 - 30%.

Poly(vinyl alcohol) is a semi-crystalline polymer, and the degree of crystallinity has a pronounced effect on its solubility, water sensitivity, tensile strength, oxygen barrier properties, and thermoplastic properties. It is difficult to determine the melting point of PVOH because it begins to decompose at about 130 °C. Values for T_m range from 220 °C to 267 °C, for fully hydrolysed PVOH. A more accurate determination of T_m can be made by making use of diluents. The T_m can be measured at several diluent concentrations, and the curve is extrapolated to zero diluent concentration. This method gives a $T_m = 255$ °C - 267 °C for a commercial "superhydrolysed" grade of PVOH.

PVOH is one of the few polymers that are water soluble. The solubility is strongly dependent on the degree of hydrolysis. A fully hydrolysed grade is soluble only in hot to boiling water, but remains soluble once the solution is cooled. However, partially hydrolysed grades (70% - 80%) are only soluble between $10 \,^{\circ}$ C - $40 \,^{\circ}$ C. The PVOH precipitates above $40 \,^{\circ}$ C. An interesting aside is that aqueous solutions of highly hydrolysed grades of PVOH increase in viscosity on storage. This does not occur in solutions of partially hydrolysed grades of PVOH.

Typically, vinyl monomers add to the growing radical-ended polymer by the β -carbon of the vinyl group.



This is termed a "head-to-tail" addition. However, on occasion, a monomer unit will add through the α -carbon atom in a "head-to-head" fashion. In the case of PVOH, such a "head-to-head" linkage would yield a 1,2-diol in the polymer backbone as opposed to a 1,3-diol which is typically produced.



Head-to-tail addition is favoured over head-to-head addition on both steric and resonance grounds. From a steric stand point, approach of the vinyl group *via* the unsubstituted carbon (β -carbon) is sterically favoured over the α -carbon. On resonance grounds, the substituents on the α -carbon are able to stabilize the α -carbon radical, whereas they are not able to do this for the β -carbon radical. Therefore, for most vinyl polymers, especially poly(vinyl esters), there are typically fewer than 5% of head-to-head linkages.

For our purposes, the 1,2-diol linkages in PVOH are interesting in that they can be selectively cleaved by periodate ions.



The result, clearly, is that the polymer chain is broken into two shorter chains, and the molecular weight of the PVOH is decreased. It is this reduction in molecular weight that we will use to determine the number of head-to-head linkages in a commercial sample of PVOH.

The change in molecular weight of the PVOH upon cleavage of the 1,2-diol linkages will manifest itself in a reduction in the viscosity, of the polymer solution. We will employ a viscometer called an Ostwald viscometer (Figure 1) to determine this change in viscosity.



Figure 1: Viscometer Arrangement (beaker will be replaced by a thermostatted bath).

The time, *t*, taken for the meniscus of the solution to pass from mark a to mark b is measured, and the relative viscosity (η/η_o) is calculated from

$$\frac{\mathbf{h}}{\mathbf{h}_{o}} = \frac{t}{t_{o}} \tag{1}$$

where t and t_o are the flow times in the viscometer for the solution and the solvent, respectively.

The intrinsic viscosity is defined as the ratio of the specific viscosity to the concentration, in the limit of zero concentration.

$$[\mathbf{h}] = \lim_{c \to 0} \left[\frac{\mathbf{h}_{sp}}{c} \right] = \lim_{c \to 0} \left[\frac{1}{c} \times \frac{\mathbf{h} - \mathbf{h}_o}{\mathbf{h}_o} \right]$$
(2)

Here, *c* is defined as the concentration in grams per 100 mL of solution, giving units of dLg⁻¹ for $[\eta]$. The specific viscosity, η_{sp} , is given by $(\eta/\eta_o) - 1$, which becomes $(t/t_o) - 1$ in combination with equation (1). A plots of η_{sp}/c against *c* yields a straight line at low concentrations, and can be used to determine $[\eta]$.

$$[\mathbf{h}] = K M V^{a} \tag{3}$$

In CHEM 470, you learned the Mark-Houwink-Sakurada equation, where \overline{M}_v is the viscosity-average molecular weight, and *K* and *a* are the Mark-Houwink-Sakurada constants, which depend on polymer type, solvent, and solution temperature. Flory and Leutner have found that for aqueous solutions of PVOH, $K = 2 \times 10^{-4}$, and a = 0.76 at 25EC for poly(vinyl alcohol) polymers with a molecular weight range of 30,000 - 70,000 g.mol⁻¹.

In this experiment, we wish to calculate the ratio, Δ , of head-to-head linkages to the total number of monomer units. It is equal to the increase in the number of molecules present in the system, divided by the total number of monomer units represented by all molecules in the system.

$$\Delta = \frac{H - H \, linkages}{total \, monomerunits} \tag{4}$$

The total number of monomer units in a polymer chain is equal to \overline{X}_n , the total number of head-to-

head linkages in a polymer chain is equal to the number of new segments formed $\left(\frac{\overline{X}_n}{\overline{X}_{n'}}\right)$ less one,

where $\overline{X}_{n'}$ is the total number of monomer units in the cleaved polymer chain; therefore, for all the molecules in the system (N_o), equation (4) becomes

$$\Delta = \frac{N_o \left(\frac{\overline{X}_n}{\overline{X'}_n} - 1\right)}{N_o \overline{X}_n} \tag{5}$$

This simplifies to become

$$\Delta = \frac{\overline{X}_n}{\overline{X}_n} - 1 \tag{6}$$

which can be rewritten in terms of molecular weights, bearing in mind that $\overline{M}_n = \overline{X}_n M_o$;

$$\Delta = M_o \left[\frac{1}{\overline{M}_n} - \frac{1}{\overline{M'}_n} \right] \tag{7}$$

where \overline{M}_n and $\overline{M}_{n'}$ are the number-average molecular weights before and after degradation, and M_o is the monomer weight (44 g/mol). Flory and Leutner also showed that $\overline{M}_v / \overline{M}_n = 1.89$.

Hence, we can write

$$\Delta = 83 \left[\frac{1}{\overline{M'_{\nu}}} - \frac{1}{\overline{M}_{\nu}} \right] \tag{8}$$

which permits us to use viscosity average molecular weights directly.

Experimental

One partner should prepare the stock solution, while the other begins to clean the viscometer and determine the flow time for the solvent, water.

Clean the viscometer with a sulfochromic acid cleaning solution (solutions of sulfochromic acid are extremely toxic and must be handled with labcoat, gloves and goggles), rinse copiously with distilled water, and dry with acetone and air. Immerse in a 25° C bath to equilibrate. Place a small flask of distilled water (~100 mL) in the bath.

Preparation of the **STOCK** solution: (Note: This will take considerable time and care, so be prepared to exercise your patience!) Weigh out accurately on a watch glass 4.0 to 4.5 g of the dry polymer. Add it slowly, with stirring (use a stir bar, and a stirrer/hotplate), to about 200 mL of distilled water in a beaker. When adding the polymer, **CAREFULLY** sift the powder onto the surface and stir gently so as not to entrain bubbles or produce foam. When all the polymer has been added, stir for an additional 10-15 minutes, and then increase the temperature to about 95°C to dissolve the PVOH. Let the solution cool and transfer it carefully and quantitatively into a 250-mL volumetric flask. Avoid foaming as much as possible by letting the solution run down the side of the flask. Make the solution up to the mark and mix by slowly inverting a few times.

It is very important to be meticulous about **promptly and very thoroughly** rinsing glassware that has been in contact with polymer solution, for once the polymer has dried on the glass surface it is quite difficult to remove.

Pipette 50 mL of the STOCK solution into a 100-mL volumetric flask, and make up to the mark with distilled water. Mix, and place in the 25EC bath to equilibrate. Rinse the pipette very thoroughly with water and dry with acetone and air. Call this sample **"UNCLEAVED A"**.

To cleave the polymer, pipette 100 mL of the **STOCK** solution into a 250-mL Erlenmeyer flask and add up 0.50 g of solid KIO₄. Warm the flask to about 70 °C (on a hotplate), and stir until all the salt is dissolved. Clamp the flask in a thermostated bath and stir until the solution is at 25 °C. Transfer quantitatively to a 100-mL volumetric flask. Place in the 25 °C bath to equilibrate. Call this sample "**CLEAVED A**". (This operation can be carried out while viscosity measurements are carried out on the uncleaved polymer.)

At this point, two solutions have been prepared: 100 mL of each of two aqueous polymer solutions, one with a concentration of uncleaved polymer ~0.9 g/100 mL (UNCLEAVED A), and one with a concentration of ~1.8g/100mL of polymer cleaved with periodate (CLEAVED A). To obtain a second concentration of each material, pipette 50 mL of the "A" solutions into 100-mL volumetric flasks and make up to the mark with distilled water (UNCLEAVED B and CLEAVED B). And now make a third concentration of each polymer solution by pipetting 50 mL of the "B" solutions (~0.45 g/100 mL) into 100-mL volumetric flasks and make up to the mark with distilled water (UNCLEAVED B to the mark with distilled water (UNCLEAVED C and CLEAVED C). Place all solutions in the thermostat bath to equilibrate. The viscosity of all three solutions of each polymer (six in total, uncleaved and cleaved) should be determined.

The recommended procedure for measuring the viscosity is as follows:

- The viscometer should be mounted vertically in a constant-temperature bath so that both reference marks are visible below the water level. The temperature should be maintained within (25 ± 0.1)°C during a run.
- 2. Pipette the required amount of solution (or water) into the viscometer. Immediately rinse the pipette with copious amounts of distilled water, and dry it with acetone and air before using again.
- 3. Using a pipette bulb, draw the solution up to a point above the upper reference mark. Release the suction and measure the flow time between the upper and lower marks with a stopwatch. Obtain two or more runs with the same filling of the viscometer. Three runs agreeing within about 0.5

second should suffice.

4. Each time the viscometer is emptied, rinse it very thoroughly with distilled water, then dry with acetone and air. Be sure to remove all polymer with water before adding acetone.

Calculations

For each of the polymer solutions studied, tabulate t/t_o and the concentration c in grams of polymer per 100 mL of solution. Then calculate η_{sp}/c . Plot η_{sp}/c versus c and extrapolate linearly to c = 0 to obtain [η] for the original and degraded polymer.

Calculate \overline{M}_{v} for both the original polymer and the degraded polymer, and obtain a value for Δ .

Discussion

In your discussion of this experiment and the results that you obtained, pay attention also to the following points:

- 1. List a number of factors that would give an under- or over-estimated value of Δ .
- 2. Discuss and explain the solubility of PVOH as presented in the introduction. Why does the solubility decrease as the drying temperature is increased for highly-hydrolysed grades of PVOH? Why does the viscosity of solutions of highly-hydrolysed grades of PVOH increase with time?
- 3. Why is it not possible to prepare PVOH directly from vinyl alcohol?

Some useful references:

Polymer encyclopedia article, page 167 - 198.

D.P. Shoemaker, C.W. Garland, and J.W. Nibler, Experiments in Physical Chemistry, 6th edition, McGraw-Hill, New York, 1996, pp 317-326.

- P.J. Flory and F.S. Leutner, J. Polym. Sci., 3, 880 (1948); 5, 267 (1950).
- P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y. (1953).
- A. Einstein, Investigations on the Theory of Brownian Motion, chap. III, Dover, New York (1956).

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J.R. Schaefgen and P.J. Flory, J. Am. Chem. Soc., 70, 2709 (1948).

<u>Apparatus</u>

Water bath (25EC)	1
pipette bulb	1
Ostwald viscometer	1
stirrer/hotplate	1
50-mL pipette	1
125 mL Erlenmeyer flasks	2
250 mL beaker	1
250 mL volumetric flask	1
100 mL volumetric flasks	6
thermometer	1
funnel	1
glass wool	1
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<u>Chemicals</u> Poly(vinyl alcohol) (M.W. ~ 60,000 - 80,000 g/mol) KIO₄ (1 g) chromic acid cleaning solution (50 mL).