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#26 Intrinsic Viscosity, Evaluating the Polymerization Pattern in Polyvinyl Alcohol

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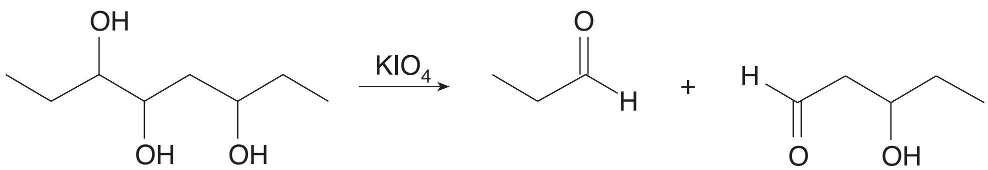
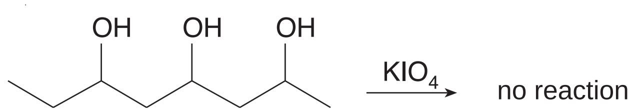
I. INTRODUCTION

Description

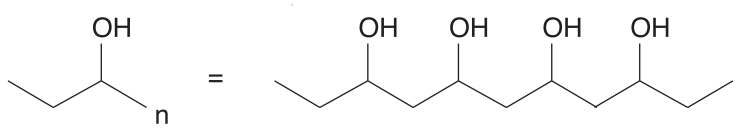
In this experiment, a high molecular weight polyvinyl alcohol polymer is treated with potassium periodate. Potassium periodate reacts with 1,2 (vicinal) glycols, cleaving the bond between the 1 and 2 carbons and producing two aldehydes.



Potassium periodate does not react with 1,3-glycols.



The regular repeating unit of polyvinyl alcohol is similar to a 1,3-glycol.



Polyvinyl alcohol is usually made by hydrolysis of polyvinyl acetate. Vinyl acetate normally polymerizes head to tail producing the alternating 1,3-acetate and, by hydrolysis, the alternating 1,3-alcohol.

Formation of a 1,2-glycol thus represents an abnormal head to head addition of monomer to the growing chain. Treatment of polyvinyl alcohol with periodate ion thus determines the number of abnormal head to head polymerizations.

In this experiment, the viscosity of polyvinyl alcohols of varying molecular weights will be measured. From a graph of viscosity versus molecular weight, the approximate molecular weight of the periodate treated polymer can be determined. The number of head to head polymerizations is estimated from the ratio of the average molecular weight of untreated polymer to the average molecular weight of periodate cleaved polymer.

Student Audience

Organic, polymer, or physical chemistry students. (Understanding the cleavage reaction used to probe the regularity of the polymer chain will be easier for students previously introduced to organic chemistry.)

Goals for the Experiment

By completing this investigation, students will:

- use an appropriate device to determine viscosity,
- experience viscosity as an intrinsic property of a solution or fluid,
- use a standard curve to determine an unknown molecular weight, and
- use a known organic reaction to determine the extent of the unusual head to head polymerization in a polymer that usually polymerizes head to tail.

Recommended Place in the Curriculum

This investigation can be used along with the discussion of any of the following:

- viscosity and viscosity determinations,
- polymerization reactions,
- molecular weight estimation, and
- reactions of glycols.

II . STUDENT HANDOUT

Intrinsic Viscosity, Evaluating the Polymerization Pattern in Polyvinyl Alcohol

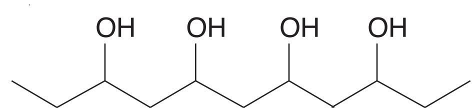
Scenario

Polyvinyl alcohol is used in the manufacture of hospital laundry bags. Contaminated laundry is placed in the bag and the bag and its contents are put directly into the washer. (This prevents exposure of the laundry personnel to the contaminated laundry.) The bag dissolves in the water and washes away. How easily the bag dissolves depends upon both the molecular weight of the polymers in the bag as well as the percent hydrolysis of the polyvinyl alcohol. A bag manufacturer has heard complaints of bits of undissolved bag being stuck to laundry. Since the polymer film supplier is not being very helpful as to the exact specifications of the polymer film, your supervisor assigns you to do an initial evaluation of the bag material for its molecular weight and polymer regularity.

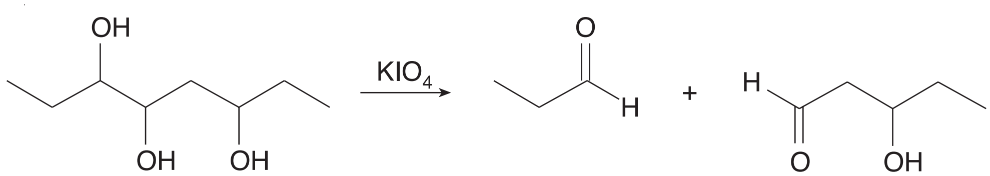
Introduction

Polyvinyl alcohol is a major commercial water soluble polymer. It can be used as a surfactant, adhesive, and thickener (contact lens wetting solution). Solutions of polyvinyl alcohol have different viscosities depending on their concentration and average molecular weight. Hence, a standard curve of viscosity versus average molecular weight might be constructed if different average molecular weight polyvinyl alcohols are available.

Polyvinyl alcohol is a regular repeating 1,3-glycol, coming from head-to-tail polymerization of vinyl acetate. (The polyvinyl acetate is hydrolyzed to yield polyvinyl alcohol.)



If abnormal head-to-head addition occurs, some 1,2-glycol units may be formed. Reaction with potassium periodate is one way to determine the extent of abnormal polymerization because periodate ion will cleave the 1,2 glycol to terminal aldehydes. This cuts the polymer in two or more pieces which have a much smaller average molecular weight.



The molecular weight of an polyvinyl alcohol sample will be determined as well as the number of abnormal (head to head) linkages in that sample.

Safety

- Goggles must be worn.
- Review the MSDS of any chemical used in the experiment.
- Potassium periodate is highly irritating to skin, eyes, and mucous membranes.
- Dispose of used reagents according to your teacher's instructions.

Materials

- one of the following
    - A size 100 Cannon-Fenske Viscometer with a 1000-mL beaker and a thermometer to maintain 25 °C
    - A homemade capillary viscometer constructed of a 10-mL polyethylene syringe barrel, with readable markings, plastic tubing connector, ultra micro pipet tip (this is a fairly reliable ready made plastic capillary), and a 10-mL graduated cylinder (or test tube in a test tube rack)
- one of the following
    - if preparing standard solutions
        - polyvinyl alcohol standards with different molecular weights
        - 100-mL volumetric flask
        - 5 150-mL beakers
    - if using teacher prepared standards
        - 1% solutions of each of the molecular weight standards in distilled water or in a 5% ethanol/distilled water solution
- polyvinyl alcohol
- a timer or stopwatch
- 50- or 100-mL graduated cylinder
- stirring rods or bars with magnetic heat and stir plates
- hot plate
- potassium periodate
- spatula
- balance which reads to 0.0001 or 0.001 grams
- distilled water
- (optional) 10% ethanol/distilled water solution
- (optional) funnel and filter paper (may be necessary for some solutions)

Procedure

Most accurate results will be obtained with the Cannon-Fenske Viscometer. Your instructor can demonstrate how to use it. The viscometer constant will be obtained using the density and viscosity of water at 25 °C so a large beaker where the water temperature is 25 °C works well as a bath for the viscometer. (Hot water may need to be incrementally added to the beaker bath to maintain it at 25 °C.)

If using the Cannon-Fenske Viscometer, it is recommended the polyvinyl alcohol samples be prepared with water. The viscometer must be carefully cleaned and dried between samples. Cleaning is best accomplished by at least 5 rinses with distilled water. Drying is most easily accomplished if the viscometer is rinsed with acetone followed by a stream of nitrogen or air. However, introducing acetone into a viscometer with traces of polyvinyl alcohol present on the walls of the capillary will glue that polyvinyl alcohol to the walls of the viscometer resulting in a sticky mess. Be sure that all the polyvinyl alcohol is removed before adding the acetone.

If using the homemade viscometer, it is recommended the solutions are 1% polymer in 5% ethanol/distilled water. The polyethylene syringe barrel does not wet like the glass viscometer and surface tension effects may be less pronounced with the ethanol solutions. Also, the viscosity of the solutions may be more stable over time in the 5% ethanol/water solutions. This is more important for the previously prepared polymer solutions.

Preparation of the 1% Polyvinyl Alcohol Solutions

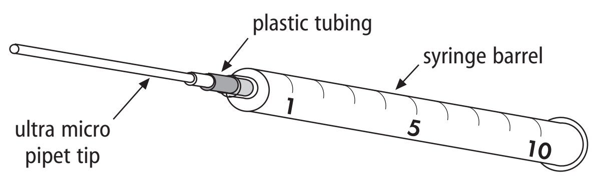
1. Weigh 1.000 grams of each sample into a 150-mL beaker. Add 40 to 45 mL hot distilled water to each sample, heat, and stir to dissolve. Best results will be obtained if the temperature is kept just below boiling. Try to avoid whipping a lot of air into the solutions while stirring to dissolve the polyvinyl alcohol.
2. When the polyvinyl alcohol sample is dissolved in about 40 mL hot distilled water, it may be poured into the 100-mL volumetric flask. Dilute with water to the mark if preparing water only solutions or add 50 mL of a 10% ethanol/distilled water solution and then dilute to the mark with water. Mix well by inverting the volumetric flask repeatedly. The solutions may be transferred to a labeled sample bottle or returned to the labeled beaker.
3. Prepared a 1% solution of the polyvinyl alcohol laundry bag in the same way as steps 1 and 2 above. Label this solution as well.
4. Weigh 0.0625 grams of potassium periodate into another beaker, add 25 mL of the polyvinyl alcohol bag solution (step 3 above) to it and stir to dissolve. Label this solution as well.

Determination of the Viscosity of the 1% Polyvinyl Alcohol Solution

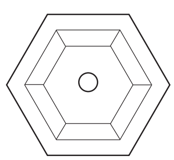
1. Measure the time each solution drains in the viscometer 4 or 5 times. Determine the average. If solutions clog, they may need to be filtered. If using the Cannon-Fenske Viscometer, follow the instructor's guidelines for its use.

   If using the homemade capillary viscometer, follow the instructor's guidelines as well. Some hints for its successful operation include:

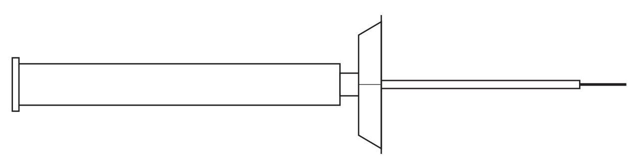
a. Attach the ultra micro pipet tip to the barrel of the 10-mL syringe with a very small piece of plastic tubing.



A small plastic weighing boat may be attached to the bottom of the barrel of the syringe to function as a stabilizer when the syringe is rested on top of 10-mL graduated cylinder or test tube.



top view of weighing boat with hole



homemade capillary viscomenter with weighing boat attached

b. Fill the syringe barrel to above the 10 mL line. Place the syringe, pipet tip down, on top of the 10-mL graduated cylinder or test tube.

c. Begin timing on the timer or stopwatch when the solution reaches the 10 mL line on the syringe barrel.

d. Stop timing when the solution has drained to the 5 mL line on the syringe barrel. Record this time as the drain time.

e. Return the solution in the graduated cylinder or test tube to the syringe barrel and repeat the procedure several times.

2. Be sure to determine the viscosity of each solution as well as water and 5% ethanol water (if you use the latter). The determination of the viscosity of water only is important with both methods because the viscometer constant is determined from water where the viscosity is known. Thus the drain times of the solutions can be converted to comparative viscosities and a graph of viscosity versus molecular weight can be generated.

Manipulating the Data

For the commercial viscometer, the following equation approximately describes the flow of the solution through a capillary due to gravity. In the equation, h is the coefficient of viscosity [for water = 0.8937 centipoise (cP)], r is the density of water (0.997 g cm^{-3} at 25°C), B is the viscometer constant, and t is the measured time of flow (in seconds).

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

1. Use your data for water to determine B, the viscometer constant for the viscometer you used.
2. After calculating B, use it, along with the drain times, to determine the coefficient of viscosity for each solution. Assume that the densities are the same.
3. Graph the coefficient of viscosity versus the molecular weight for each known polymer.
4. Determine the approximate molecular weight of the polyvinyl alcohol laundry bag from its coefficient of viscosity and the graph.
5. Determine the approximate molecular weight of the potassium periodate treated polyvinyl alcohol solution.
6. Determine the approximate number of head-to-head polymerizations by dividing the molecular weight of the untreated polymer by the molecular weight of the periodate treated polymer.

Questions

1. Is the polyvinyl alcohol film of the laundry bag low (~ 25,000), medium (~ 66,000), or high (~97,000) molecular weight material? Is there evidence of many head-to-head linkages due to abnormal polymerizations? Explain your answers to both questions.
2. (optional) If you prepared the polyvinyl alcohol solutions that you tested, is your answer to question 1 (above) reasonable in light of the dissolving behavior of the other polymer samples?
3. Would a laundry bag that was slow to dissolve be out of specification because of too low an average molecular weight or because of too high an average molecular weight? Explain your answer.
4. Why does the molecular weight of the polymer influence the viscosity of the solution?
5. Why is it important to keep the temperature of the bath constant?

6. What happens to h when you increase/decrease the concentration of polymer?

References

Howe-Grant, M. Editor, *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 21,* 4th Edition**,** “Rheological Measurements,” Wiley-Interscience, 1997.

Howe-Grant, M. Editor, *Kirk-Othmer Encyclopedia of Chemical Technology, Volume 24,* 4th Edition, “Vinyl Polymers,” Wiley-Interscience, 1997.

III. INSTRUCTOR NOTES

Intrinsic Viscosity, Evaluating the Polymerization Pattern in Polyvinyl Alcohol

Purpose

The purpose of this investigation is to determine the approximate average molecular weight of a polymer by comparing its viscosity with the viscosity of known average molecular weight polyvinyl alcohol. The average number of abnormal polymerizations in a sample can be estimated from the determination of the molecular weight after treatment with potassium periodate.

Time Required

This investigation will take a 3 hour laboratory period if the students prepare the solutions. The time is less than 2 hours if the polymer solutions are prepared in advance. Use of a Cannon-Fenske Viscometer might necessitate that students share some data for the different molecular weight standards due to the relatively long time it takes to clean the viscometer.

Suggested Group Size

We recommend that students work in pairs. In larger groups, it would be difficult for all students to be actively involved. Different pairs might do different standards as well as the unknown.

Materials

- one of the following
  - A size 100 Cannon-Fenske Viscometer with a 1000-mL beaker and a thermometer to maintain 25°C. Cannon-Fenske Viscometers are available and routinely used in industry. They cost approximately $100 each. (A local industry might lend or donate one or more.)
  - A homemade capillary viscometer constructed of a 10-mL polyethylene syringe barrel with readable markings, plastic tubing connector, ultra micro pipet tip (this is a fairly reliable ready made plastic capillary), and a 10-mL graduated cylinder (or test tube in a test tube rack) The Ultra Micro Pipet Tip is available in the automatic pipet section of the Fisher Catalog as well as from other suppliers. (Fisher Cat. No. 21-197 2F)
- polyvinyl alcohol samples with different molecular weights (Different average molecular weight polyvinyl alcohol samples are available from Aldrich Chemical Company. Recommended molecular weight samples are 31,000–50,000, 85,000–146,000, and 124,000–186,000.)
- a timer or stopwatch which measures seconds
- 100-mL volumetric flask
- 5 150-mL beakers
- 50- or 100-mL graduated cylinder
- stirring rods or bars with magnetic heat and stir plates
- hot plate
- potassium periodate
- spatula
- balance which reads to 0.0001 or 0.001 grams
- distilled water
- (optional) 10% ethanol/distilled water solution
- (optional) funnel and filter paper (may be necessary for some solutions)

Safety, Handling, and Disposal

- Goggles must be worn.
- Review the MSDS of any chemical used in the experiment.
- The shelf life of polyvinyl alcohol solutions can be short due to growth of mold.
- Potassium periodate is an oxidant, although not considered strong.
- Dispose of used reagents according to local ordinances.

Points to Cover in Pre-Lab

- Since the materials in this experiment are relatively safe to work with, the emphasis is on experimental design. Correct use of the viscometer should be stressed. If the homemade modified polyethylene version of the viscometer is used, the way it mimics the official version should be discussed. (For example, by timing the flow between 10 and 5 mL on the syringe one is working in a relatively constant flow section of the syringe just as is used in the Cannon-Fenske Viscometer.
- A cup viscometer such as timing the flow from 5 mL to 0 mL on the syringe suffers from very decreased flow rates as the syringe empties. It is also prone to significantly more clogging.
- Define viscosity ([η]; the internal friction or resistance to flow of a liquid; the constant ratio of shear stress to shear rate) and hydrodynamic volume (the volume of a polymer coil when it is in solution).

Procedural Tips and Suggestions

- The viscometer is probably best taught individually if the class is small enough to allow this. For a large class, directions will need to be more specific. If a Cannon-Fenske Viscometer and the homemade modified polyethylene viscometer are both used, the students may be confused by the results. Since the polyethylene does not wet, the surface tension effects of water are large. Polyvinyl alcohol is a surfactant in water and hence the polymer solutions decrease the surface effects in the homemade viscometer. Use of the 5% ethanol/distilled water solutions of the polymers seems to make the surface effects less troublesome but a value of the viscosity of the 5% ethanol/water solution wasn't known for its use as the viscometer constant.

Sample Results

<u>Size 100 Cannon-Fenske Viscometer</u>

Water
63.6 sec
60.6 sec
64.0 sec
61.3 sec average 62.3 sec with h = .8937 cP

1% PVOH average molecular weight 85,000–146,000
139.1 sec
136.2 sec
137.4 sec average 137.6 sec with h = 2.81 cP

1% PVOH average molecular weight 124,000–186,000
180.7 sec

181.4 sec
171.7 sec
178.6 sec average 178.1 sec with h = 3.64cP

1% PVOH laundry bag
128.2 sec
130.3 sec
132.1 sec
130.8 sec average 130.4 sec with η = 2.66 cP Average molecular weight from graph about 75,000

1% PVOH laundry bag plus KIO_4
81.8 sec
82.8 sec
82.4 sec
82.8 sec average 82.5 sec with η = 1.68 cP Average molecular weight from graph about 15,000

Abnormal head to head polymerization

75,000/15,000 or 5 head to head linkages

1% PVOH "SLIME" 93,500 average molecular weight
154.9 sec
144.0 sec
146.5 sec
145.3 sec
145.5 sec average 147.2 sec with η = 3.01 cP

1% PVOH "SLIME" 93,500 plus KIO_4
67.7 sec
68.4 sec
70.3 sec
70.6 sec
71.2 sec
70 2 sec
71.7 sec average 70.0 sec with η = 1.43 cP Average molecular weight about 15,000

Abnormal head to head polymerization

93,500/15,000 is about 6 head to head linkages. (5 is a typical value.)

Homemade Modified Polyethylene Capillary Viscometer

Water
47.6 sec
46.0 sec
45.9 sec
45.2 sec
45.6 sec average 46.1 sec with η = 0.8937 cP

5% Ethanol/Water
40.7 sec
41.3 sec
41.0 sec
41.6 sec average 41.2 sec with η = 0.803 cP

1% PVOH 5% Ethanol/Water average molecular weight 31,000–50,000
47.6 sec
51.2 sec
47.2 sec
47.2 sec average 48.3 sec with η = 0.937 cP

1% PVOH 5% Ethanol/Water average molecular weight 85.000–146,000
54.2 sec
54.1 sec
53.9 sec
53.5 sec average 53.9 sec with η = 1.05 cP

1% PVOH 5% Ethanol/Water average molecular weight 124,000–186,000
55.6 sec
57.0 sec
54.5 sec
60.0 sec average 58.4 sec with h = 1.132 cP

1% PVOH 5% Ethanol/Water average molecular weight 86,000
52.7 sec
51.6 sec
53.6 sec
53.2 sec average 52.8 sec with η = 1.02 cP

1% Laundry Bag 5% Ethanol/Water
47.3 sec
47.6 sec
48.0 sec
48.4 sec
49.6 sec
48.9 sec average 48.3 sec with h = 0.937 cP Average molecular weight about 50,000–60,000

1% Laundry Bag 5% Ethanol/Water plus KIO4
43.3 sec
43.5 sec
44.0 sec
45.1 sec average 44.0 sec with η = 0.853 cP Average molecular weight about 15,000

Abnormal head to head polymerization

55,000/15,000 is an average of 3–4 head to head linkages

1% PVOH "SLIME" 5% Ethanol/Water Average molecular weight 93,500
49.9 sec
54.2 sec
54.3 sec
53.6 sec
53.5 sec average 53.1 sec with η = 1.03 cP

1% PVOH "SLIME" 5% Ethanol/Water plus KIO_4
43.2 sec
42.9 sec
43.9 sec
43.9 sec average 43.4 sec with η = 0.842 cP Average molecular weight about 15,000

Abnormal head to head polymerization

93,500/15,000 is about 6 head to head linkages (5 is a typical value)

Plausible Answers to Questions

1. Is the polyvinyl alcohol film of the laundry bag low (~ 25,000), medium (~ 66,000), or high (~97,000) molecular weight material? Is there evidence of many head to head linkages due to abnormal polymerizations? Explain your answers to both questions.

A: The viscosity data suggests the laundry bag is of relatively low molecular weight with few abnormal head to head polymerizations. The bag behaves like the lower to medium molecular weight material with respect to viscosity which changed only a little with potassium iodate treatment.

2. (optional) If you prepared the polyvinyl alcohol solutions that you tested, is your answer to question 1 (above) reasonable in light of the dissolving behavior of the other polymer samples?

A: The laundry bag dissolved relatively quickly, as expected; the higher molecular weight polyvinyl alcohols took much longer to dissolve, so it fits that the bag materials are low in molecular weight.

3. Would a laundry bag that was slow to dissolve be out of specification because of too low an average molecular weight or because of too high an average molecular weight? Explain your answer.

A: Based upon molecular weight variability only, a bag that was slow to dissolve would probably be made of polyvinyl alcohol of too high an average molecular weight. In this study, the viscosity and solubility difficulties both increase with increasing molecular weight.

4. Why does the molecular weight of the polymer influence the viscosity of the solution?

A: Viscosity is the result of the interaction of the polymer chains with the solvent. Longer chains (higher molecular weight) interact with more solvent, creating more viscous drag and thus a higher viscosity.

5. Why is it important to keep the temperature of the bath constant?

A: The coefficient of viscosity, η, decreases as the temperature increases.

6. What happens to h when you increase/decrease the concentration of polymer?

A: η will increase with increase in polymer concentration.

References

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Shoemaker, D.P., Garland, C.W., Nibler, J.W., *Experiments in Physical Chemistry,* 6th Edition, The McGraw Hill Companies, Inc., New York, 1996, 317–326.

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