MOHAWK

COLLEGE OF APPLIED ARTS AND TECHNOLOGY

CHEMICAL, ENVIRONMENTAL, AND BIOTECHNOLOGY DEPARTMENT

Polymers

by Professor David Cash

September, 2008

Contact information for Mohawk College will be found on the following page.

This Experiment is a 3 hour Organic Chemistry laboratory exercise. It is designed for students in the sixth term of a 3-year diploma program in Chemical Engineering Technology.

For Information or Assistance Contact:

MOHAWK COLLEGE
CHEMICAL, ENVIRONMENTAL, AND BIOTECHNOLOGY DEPARTMENT

Professor Cindy Mehlenbacher
cindy.mehlenbacher@mohawkcollege.ca
905-575-1212 ext. 3122

Bill Rolfe (Chief Technologist)
bill.rolfe@mohawkcollege.ca
905-575-2234

Experiment 3
Polymers

Brief Description

In this experiment you will synthesize and / or examine a variety of polymers: a polyester made from phthalic anhydride; an epoxy resin adhesive; a silly putty-like material made from carpenter's glue (polyvinyl alcohol); a polyacrylamide-sodium polyacrylate superabsorbing polymer; a superhigh molecular weight polyethylene oxide polymer.

References

1. **Wade**, 5th Edition, pages 352-357, 629-631 and 1182-1198; or 6th Edition, pages 363-367, 638-640 and 1184-1201.

2. **Shriner** and others, Systematic Identification of Organic Unknowns, 8th Edition, pages 306 and 308; or 7th Edition, pages 256 and 258.

3. CHEM CH602 Study Guide: Polymers - Supplementary Notes.

4. **Encyclopedia of Polymer Science and Technology** (library reference section).

5. **Kirk-Othmer Encyclopedia of Chemical Technology** (library reference section).

Documentation Reference (Not available in the Library Resource Centre)

Polymer Chemistry for High School, Workshop in Polymer Chemistry, Du Pont Experimental Station, June 1984, Du Pont Canada, Maitland, Ontario.

The Preparation Questions are on the Next Page →

Last Revised May 2008 by Professor David Cash

Experiment 3 Preparation Questions

Your Mohawk College I.D. number is **nnnnnnXYZ**.

1. An amount **0.8XY7 g** of **ethylene glycol** (**MW = 62.07**) is to be reacted with an **equimolar** amount (mol ratio 1:1) of **phthalic anhydride** (**MW = 148.12**).

   Calculate the mass of phthalic anhydride required. Show all calculations required.
   See the **Background and Theory** Section, page 3.

2. You are assigned the **dioic acid** in **Table 1** below having the same number as the **third last digit X** in your Mohawk College ID. You are assigned the **diamine** or **diol** in **Table 2** having the same number as the **second-last digit Y** in your Mohawk College ID.

   Draw yourself by hand or by using a draw program the structural formula of a **tetramer** (four monomers linked together) formed from your two monomers.

3. Identify **your polymer substance** in **Question 2** as a **polyester** or a **polyamide**, and locate on the structure the **characteristic bond** of the polymer.

   Indicate on the structure **one smallest repeat segment or unit** of your polymer.

Table 1: Some Dioic Acids

X	Dioic Acid
0, 5	propanedioic acid
1, 6	butanedioic acid
2, 7	pentanedioic acid
3, 8	hexanedioic acid
4, 9	heptanedioic acid

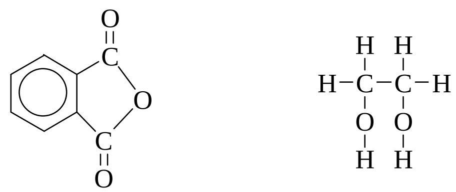
Table 2: Some Diamines and Diols

Y	Diamines	Y	Diols
9	propan-1,3-diamine	4	propan-1,3-diol
8	butan-1,4- diamine	3	butan-1,4-diol
7	pentan-1,5- diamine	2	pentan-1,5-diol
6	hexan-1,6- diamine	1	hexan-1,6-diol
5	heptan-1,7- diamine	0	heptan-1,7-diol

Background and Theory

Linear (1-D) Polyesters from Phthalic Anhydride

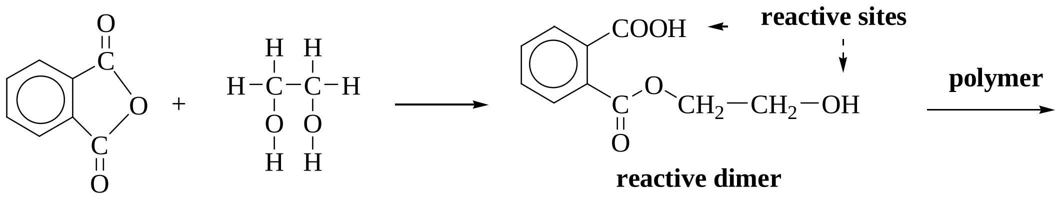
In this experiment, **phthalic anhydride** will be used as a reactant along with **ethylene glycol** to investigate the step reaction formation of a linear (1-D) polyester.



phthalic anhydride
MW = 148.12

ethylene glycol
MW = 62.07

The first step in a polymerization reaction of phthalic anhydride with ethylene glycol is shown. The dimer remains reactive at both ends.



The carboxylic acid end (-COOH) can react with another molecule of ethylene glycol or it can react with the alcohol functional group at the end of another dimer or growing polymer. In any case it will form a molecule of water (a condensation).

The alcohol end (-OH) can react with another molecule of phthalic anhydride or it can react with the carboxylic acid functional group at the end of another dimer or growing polymer. In the latter case it will form a molecule of water (a condensation).

The reaction proceeds, eventually forming linear (1-D) polymer molecules of high molecular mass. As discussed in the Supplementary Notes (Polymers) in the CHEM CH602 Study Guide, the average size of the molecules that will eventually form is critically dependant on the relative mol ratio of the two reactants.

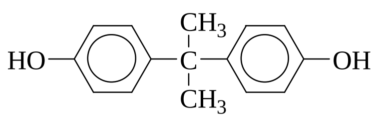
An excess of either of the two monomer reagents will cause the reaction to end without forming the very large molecules that are desired to give the required physical properties of the polymer mixture.

Epoxy Resin

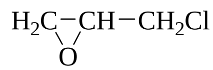
Reference: **Wade**, 5th Edition, pages 629-631; or 6th Edition, pages 653-655.

An **epoxy** resin adhesive results when two components, a **cement** and a **hardener** or **curing agent** are intimately mixed. The term epoxy refers to the chemical nature of the cement component.

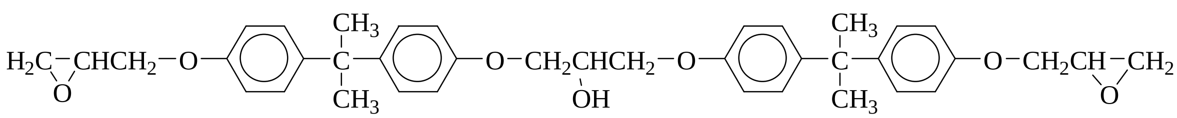
A typical epoxy cement is made from **bisphenol A** and **epichlorohydrin** by a step rection polymerization. The cement is made in a reaction in which there is a deliberate excess of epichlorohydrin, and the resulting polymer has a low average molecular mass, with terminal epoxide groups only. A low molecular mass polymer which has been made deliberately for further reaction is referred to as a **pre-polymer**.



bisphenol A



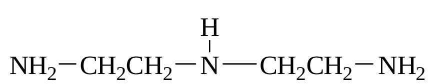
epichlorohydrin



a short segment of epoxy cement

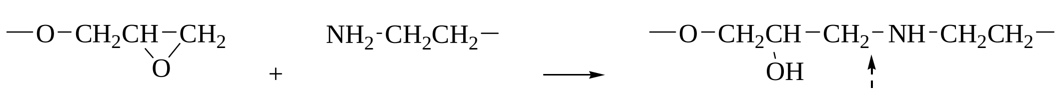
The terminal epoxide groups are very reactive to nucleophilic substitution. A variety of chemical types may be used as the **hardener**, sometimes called the **curing agent** or the **vulcanizing agent**.

A substance commonly used as a hardener for epoxy is **diethylenetriamine**, a trifunctional amine. The nucleophilic nitrogen sites of this molecule can form bonds to the terminal carbons of the epoxide cement molecules. The terminal nitrogens of the diethylenetriamine can form two such bonds, the middle nitrogen one.



diethylenetriamine - epoxide hardener or curing agent

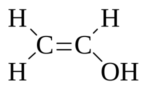
The result is a series of reactions which over time create giant molecules called a space-network or cross-linked or three-dimensional polymer. The rate of the process is dependant on temperature and the degree of mixing of the reagents.



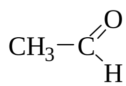
epoxy cement **hardener** **new linkage**

Polyvinyl Alcohol

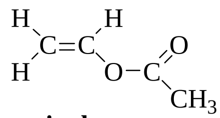
Carpenter's glue contains a water solution or suspension of a polymer which may be considered to be polyvinyl alcohol. It is possible to synthesize polyvinyl alcohol even though it is impossible to make vinyl alcohol. Vinyl alcohol is the enol form of acetaldehyde, an enol-keto tautomeric pair of structures. When you try to make vinyl alcohol, you get acetaldehyde instead.



vinyl alcohol



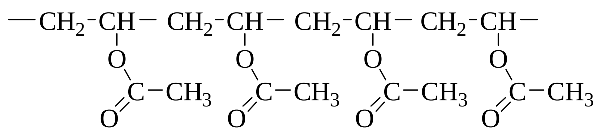
acetaldehyde



vinyl acetate

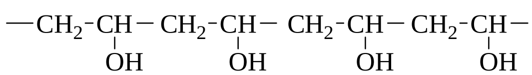
The industrial route to polyvinyl alcohol and its copolymers is through the synthesis and hydrolysis of **polyvinyl acetate**. The monomer vinyl acetate is produced on an industrial scale for use in a variety of polymers and copolymers.

Polyvinyl Acetate



Polyvinyl acetate or its copolymers may be hydrolysed partially or completely to produce the corresponding polyvinyl alcohol polymer or copolymer. Polyvinyl alcohol is water soluble. It is compatible with cellulose containing materials, and is used as a glue for wood or paper products, amongst many other uses.

Polyvinyl Alcohol

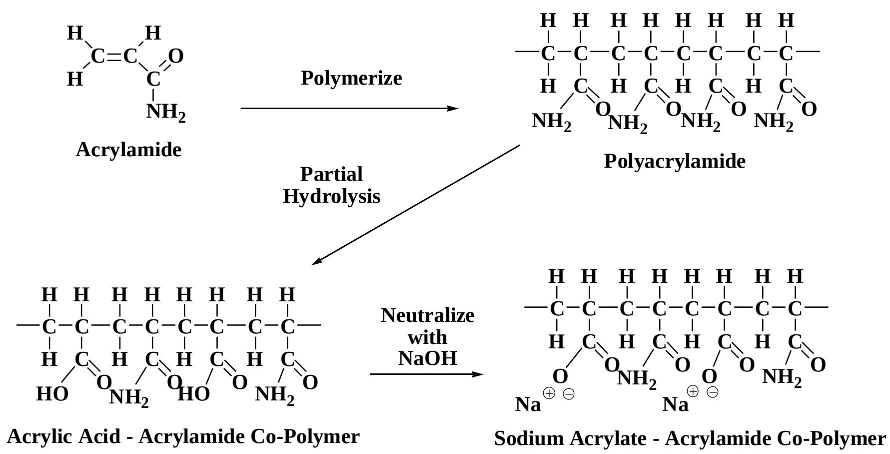


Water Gelling Superabsorbent Polymer

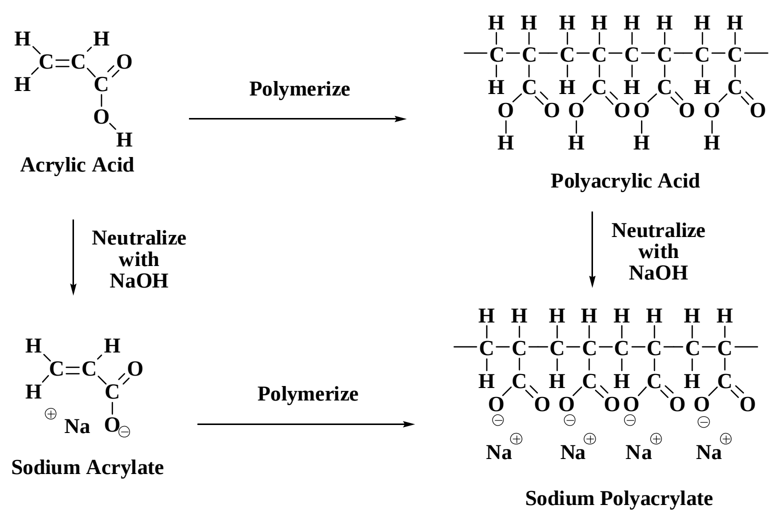
There are a number of types of water absorbent, gelling polymers. The first types were derivatives of cellulose. They were developed for use in horticulture and agriculture, to hold moisture which is very necessary for growing plants. The major use today (90 %) is in diapers.

Modern superabsorbent polymers are made from either acrylamide, or from acrylic acid or its sodium salt, as shown in the two graphics below. Diaper polymer is made from acrylic acid.

Graphic 1



Graphic 2



The polymers made from acrylamide are inherently more hazardous, because residues of the carcinogen acrylamide are difficult to remove from the final polymer.

Procedure The procedure is a long one. The partners should share the tasks equitably.

Use disposable 13 × 100 mm culture test tubes. Discard the used test tubes containing polymers.

A. A Linear (1-D) Polyester

A-1. Use a disposable test tube. If the test tube is not new, make sure it is clean and **dry**. Obtain a cork stopper for the tube.

A-2. Weigh the tube and its stopper on an **analytical balance**. Record the mass.

A-3. Add about **0.8 mL** of ethylene glycol to the tube. Stopper the tube immediately to avoid exposure to moisture.

A-4. Re-weigh the tube with its contents on the **analytical balance**. Record the mass.

A-5. Calculate the number of moles of ethylene glycol in the tube. Calculate the required mass of **phthalic anhydride** equal to the number of moles of ethylene glycol in the tube (mol ratio 1 to 1).

A-6. Add the calculated mass of phthalic anhydride to the tube as precisely as you can. Re-stopper and re-weigh the tube and its contents. Record the mass.

A-7. Add about **0.1 g** of solid **anhydrous sodium acetate** to the tube.

A-8. **Caution: use a fume hood**. Remove the cork. Heat the tube **gently** in a low burner flame until the mixture becomes liquid and appears to to boil very gently, and maintain it at an apparent gentle boil for at least **5 minutes**. **Do not allow the reagents to overheat or char**. Observe and note what happens in the tube.

A-9. After heating is finished, if possible, pour the product from the tube out onto parafilm backing-paper (not parafilm), paper, or wood. Otherwise, when cooled, remove the product for examination, by breaking the tube if necessary.

A-10. Note the hardness, viscosity and brittleness of the cooled liquid or solid product formed. Record all the observations.

A-11. If the product is solid, determine whether or not the product polymer can be melted without decomposition (**Caution: use a fume hood**).

A-12. If the product is liquid or melts, try to pull a sample out into the longest, thinest fibre you can. Test the fibre properties when cool. Is it fibrous (flexible but strong) or is it brittle (inflexible and easily fractured)? Record all of the observations.

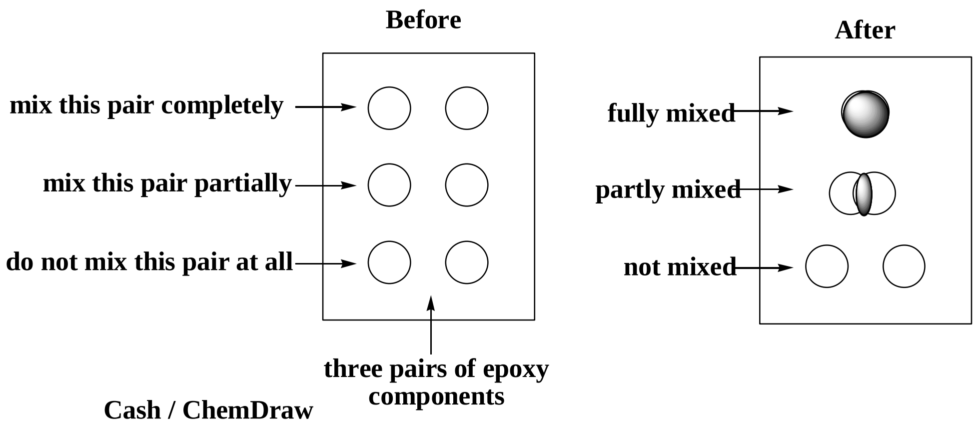
B. An Epoxy Resin

If possible, use a two-component, equal volume type epoxy product for this procedure.

B-1. If the epoxy resin product has labels, make a note of any pertinent chemical information.

B-2. Onto a piece of wax paper or parafilm, squeeze out or dispense three sets of **small** (**0.5 mL**) portions of each of the two components of the epoxy resin, as illustrated.

However, pay attention to the epoxy instructions: some epoxy products required equal volumes of the two components; other products use unequal volumes of the two components.



B-3. Mix one pair completely; mix the second pair slightly; leave the third pair unmixed. Use disposable stirring sticks or toothpicks to avoid cross-contaminations.

B-4. Test the physical rigidity and properties of each of the pairs after **five minutes**, after **ten minutes**, and after **one hour**. Record all of your observations.

C. A Silly Putty-Like Material - Carpenter's Gluep*

(*Cherkas, Cherkas and Cherkas, Chem 13 News, November 1994, page 3)

C-1. If the glue product (Elmer's Carpenter's Glue™ or a similar commercial glue) has a label, record any informative data.

C-2. Pour **50 mL** of saturated borax solution into a beaker or a disposable plastic cup.

C-3. Stir with a stirring rod or a disposable stir-stick. While stirring, squeeze a thin stream of the glue into the borax solution. Add no more than **25 mL** of the glue solution. Stir for another **2 minutes**.

C-4. A blob of a putty-like material should form. Remove it from the solution. If it is sticky, place it in some fresh borax solution for **10 seconds**, then remove it. Dry it on some paper towel. Record all the observations.

C-5. Examine the material. Squeeze it. Stretch it. Roll it into a ball shape and bounce it. **Not in the laboratory please.** Use it to remove the print from a freshly printed newspaper. Record all the observations.

C-6. Store the product solid in a Ziplock™ (or other) sealable bag for future use if desired. **Caution: Hazardous and not suitable for children below age 5 years.**

D. A Water-Gelling Superabsorbent Polymer

A package of "Stiffy-Stuff" **superabsorbent** polymer powder should be available.

D-1. **Caution: Wear gloves and do not inhale any dust**. Divide the polymer powder into five (5) approximately equal portions.

D-2. Add one portion of the powder to about **50 mL** of cold distilled water in a small beaker. Mix well. Record all the observations.

D-3. Repeat with a second portion of the powder and distilled water, but the second time, add the water to the dry powder in a beaker. Is there any difference in the result?

D-4. Repeat with fresh samples of the powder with: hot distilled water; cold vinegar or dilute acetic acid; cold saline solution (**0.9 % NaCl**). Record all the observations.

D-5. The gels may be safely discarded into the municipal waste container (garbage).

DO NOT DISCARD INTO THE SINK (WHY NOT?)

E. WonderVase® (Coloured Plastic Material)

Wear gloves. The material has "new car" smell, which may indicate the presence of plasticizers.

E-1. Follow the manufacturer's instructions for the "WonderVase® - The amazing vase you can shape!". Note the feel of the cold plastic.

E-2. Fill the WonderVase with warm or hot water. Warm tap water may not be warm enough.

E-3. Hand form the vase into any desired shape. Note the feel of the warm plastic.

E-4. Empty out the warm water and re-fill the vase with cool water.

E-5. Place flowers in vase! (Optional!)

E-6. Empty the vase.

E-7. Rinse the vase in warm water; smooth flat. Dry off the plastic.

E-8. Record a description of the physical state of the vase material (soft, hard, stiff, flexible, etc.) at each stage of the process.

F. Self-Siphoning Properties of a Superhigh Molecular Weight Polyethylene Oxide (PEO) Material

The polyethylene oxide used in the procedure has an average molecular mass of approximately 4 million.

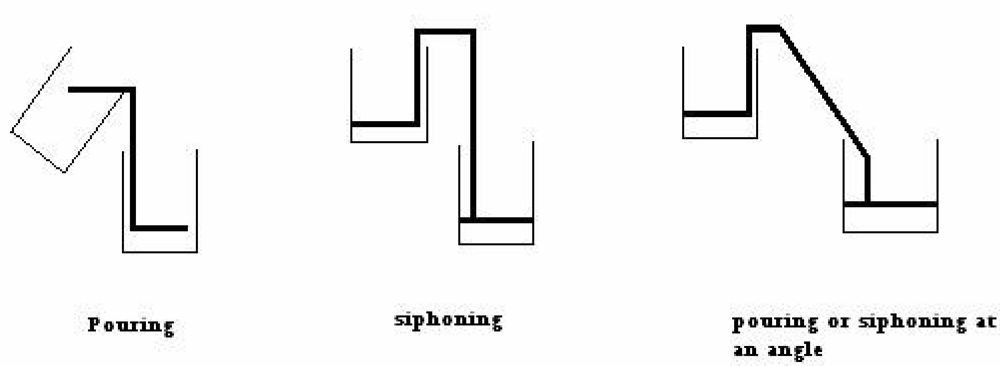
F-1. In a clean, **dry 100 mL** beaker, mix **2** to **3 mL** of a **dry** alcohol (methyl alcohol or isopropyl alcohol) with **0.3** to **0.4 g** of the polyethylene oxide resin. Swirl well to completely coat the resin with the alcohol.

F-2. Put **20 mL** of distilled water into a second **100 mL** beaker. In one pour, add the water to the resin in the first beaker. Pour back and forth between the two beakers until the resin has **gelled**.

F-3. A few drops of a food dye solution may be added to the gel to make it more easily visible.

F-4. Pour the gel back and forth between two beakers. The gel can be made to siphon by raising one beaker above the other while gradually pouring. Once the gel begins to pull, separate the two beakers and return the upper beaker to a vertical position.

F-5. While pouring between the beakers, move the upper beaker away and see how the gel moves between the beakers at an angle to the vertical (see the illustration).



F-6. Add **10 mL** of water to the empty beaker. Pour the gel into the water, then back. Observe the siphoning and pouring properties of the diluted gel.

F-7. Record all of your observations. The gel may be safely discarded into the municipal waste container (garbage).

Report Instructions

A Linear (1-D) Polyester

R-1. Report your mass measurements. Calculate the number of mol of each reactant and the mol ratio of the phthalic anhydride to ethylene glycol from the actual masses used in the reaction. Show your calculations.

R-2. Determine which of the two monomer rreagents is in excess according to the calculation?

R-3. Tabulate all of the observations made during the polymerization and during the physical property testing.

R-4. Draw a partial (but representative) structural formula of the polymer formed by the reaction between **ethylene glycol** and **phthalic anhydride**. Show at least 4 monomers linked together.

R-5. Name the linkage type of this polymer and locate one example of that linkage on the structure you have drawn.

R-6. Is any water formed during the reaction? **Explain** your answer.

R-7. According to your answer to **R-2** above, which functional group would be at both ends of all of the polymer chains when the reaction terminates? **Explain** your answer.

An Epoxy Resin

R-8. Report any chemically useful information from the product tube labels.

R-9. Tabulate all of the observations.

R-10 Draw a partial but representative structural formula of a final cured (hardened) epoxy polymer, assuming it to have the structure suggested in **Wade** and in the Background Section of this experiment.

Reference: **Wade**, 5th Edition, pages 629-631; or 6th Edition, pages 653-655.

R-11. How do the physical properties of the hardened, fully cured final product of epoxy resin correlate to the structure you have drawn?

The Report Instructions Continue on the Next Page →

Report Instructions (Cont.)

A Silly Putty-Like Material - Carpenter's Gluep*

R-12. Report any chemically useful data available from the product labelling.

R-13. Tabulate the observations made.

R-14. Draw a partial (but representative) structural formula of a **polyvinyl acetate - polyvinyl alcohol copolymer** such as is present in the Carpenter's glue, assuming it to be a 100 % linear, but **random copolymer**, in a ratio of 1 to 4.

R-15. Compare the water solubility and the physical properties of the Carpenter's Gluep product solid polymer to the original polymer in the glue solution.

A Water Gelling Superabsorbent Polymer

R-16. Tabulate the observations made.

WonderVase® (Coloured Plastic Material)

R-17 Report your observations on the vase material at cold and warm temperatures.

Self-Siphoning Properties of a Superhigh Molecular Weight Polyethylene Oxide (PEO) Material

R-18. List all of the observations made on the PEO sample and the gel solutions prepared and examined.

R-19. Draw labelled sketches to illustrate the pouring properties.

R-20. Draw a partial (but representative) structural formula of the polyethylene oxide polymer.

R-21. If a single polyethylene oxide molecule has a molecular mass of **4, 000, 000** how many units of ethylene oxide are contained in the molecule? Show your calculation.

Post-Laboratory Questions

1. There is a discussion in the Supplementary Notes (Polymers) of the CHEM CH602 Study Guide describing how an excess of one of the monomers in a step reaction polymerization will prevent the formation of any product molecules of high molecular mass.

   In the reaction of **phthalic anhydride** and **ethylene glycol**:

   a. If there is an excess of ethylene glycol, draw the structural formula of a **pentamer** molecule with terminal alcohol groups

   b. Describe how the physical nature of a mixture of low molecular mass product molecules will differ from that of a mixture of high molecular mass product molecules (e.g. - M. Pt., viscosity, etc.). Why is this an important matter when synthesizing polymer products?

2. Assume that **borax** reacts with hydroxy groups as shown in **Shriner**, but that these hydroxy groups may be on different polymer chains of the polyvinyl alcohol in the glue solution.

   Reference: **Shriner**, 8th Edition, pages 306 and 308; or 7th Edition, pages 256 and 258.

   a. Draw a simplified partial (but representative) structural formula for the final product of the **gelled** Carpenter's Gluep polymer substance. The polymer structure you have drawn should be **a space-network (cross-linked or 3-D) polymer** with cross-linking of chains.

   b. Explain how the physical properties of the final product relate to the polymer structure.

Bonus Questions

1. Explain the unusual properties of the superhigh molecular weight PEO polymer – water gel. Give a reference. Give some examples of the industrial or consumer uses of this polymer.

2. The polymer substance of the shape-changing vase (WonderVase) has a $\mathbf{T_g}$ value above room temperature, but below the temperature of hot water.

   a. List some polymers having such a $\mathbf{T_g}$ value (quote source of data).
   Could you determine the identity of the vase material experimentally? Explain how.

   b. Explain in simple terms the phenomenon of the glass transition point.

   c. For use in the WonderVase, should the polymer contain plasticizers?
   Explain your answer.