



The Synthesis of a Superabsorbent Polymer

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PURPOSE OF THE EXPERIMENT Demonstrate free-radical polymerization by preparing crosslinked polyacrylic acid. Measure polymer absorbency under different conditions of ionic strength.

BACKGROUND REQUIRED You should be familiar with the use of microliter syringes or micropipets.

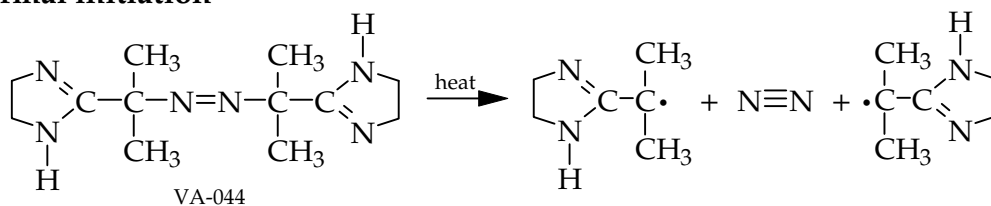
BACKGROUND INFORMATION Many alkenes can be polymerized under free-radical conditions. Polymerization occurs more readily when the alkene contains a functional group that stabilizes the radical intermediate. Acrylic acid is an example. The mechanism involves two major steps: thermal initiation and propagation, as shown in Figure 1 on the next page.

A small amount of a free-radical **initiator**, a compound that can be induced to form radicals, is included in the reaction to get it started. In this case, VA-044 is the initiator. The initiator radical adds to the carbon-carbon double bond of an alkene to form another radical. In this context, the alkene is called a **monomer**. The resulting radical adds to another alkene monomer to form a dimer, and so forth. The process can repeat itself many times, producing polyacrylic acid molecules containing up to millions of monomer units.

Very small amounts of initiator, enough to start only a relatively small number of chains, favor high molar mass products. If large amounts of initiator were used, many small chains would begin, leading to large numbers of short chains.

Despite being such a large molecule, polyacrylic acid is water-soluble. The polymer, however, is easily rendered water-insoluble by **crosslinking**, forming a chemical bridge between polymer chains. The chains are crosslinked during polymerization by including a **difunctional monomer**, a compound with two independent, polymerizable alkene functionalities. A common water-soluble crosslinking agent is N,N'-methylenebisacrylamide (MBA). The process is illustrated in Figure 2 later in this module. One end of the crosslinking agent acts as a monomer in the polymerization of one chain, while the other end of the crosslinking agent acts as a monomer in the polymerization of another chain. As a result, the two chains are linked together.

thermal initiation



propagation

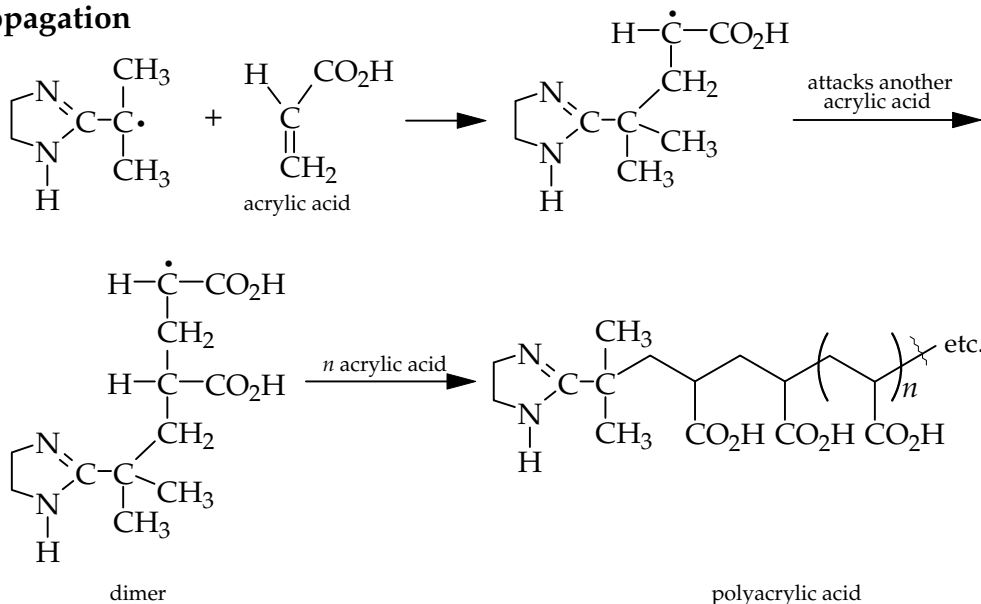


Figure 1 Thermal initiation and propagation of acrylic acid

High molar mass polyacrylic acid that is mostly neutralized and contains a small amount of crosslinking can absorb large amounts of water, yielding a gel. Such superabsorbent polymers are used to improve water retention for baby diapers and soil additives. The polymer must be of high molar mass. Low molar mass polymers, even if neutralized and lightly crosslinked, may be water-soluble.

In the acid form, the polymer material is extremely sticky and holds only a few times its mass in water. In contrast, the mostly neutralized form can absorb one thousand times or more of its mass in distilled water.

Reacting the acid polymer with sodium hydroxide (NaOH) neutralizes polyacrylic acid to form poly(sodium acrylate). The base converts most of the carboxylic acid groups (R-COOH) to carboxylate groups (R-COO⁻). In this case, the polymer has approximately 72 percent of its acid groups neutralized to carboxylate groups.

The absorbency of the polymer also depends on the degree of crosslinking. More crosslinking gives a more rigid, less absorbent material.

The ionic strength in the interior of the neutralized polymer is very high because a large concentration of ionic groups (R-COO⁻ Na⁺) is present. Thus, if the chains are not too tightly crosslinked, water will diffuse into the polymer to decrease the ionic strength inside the

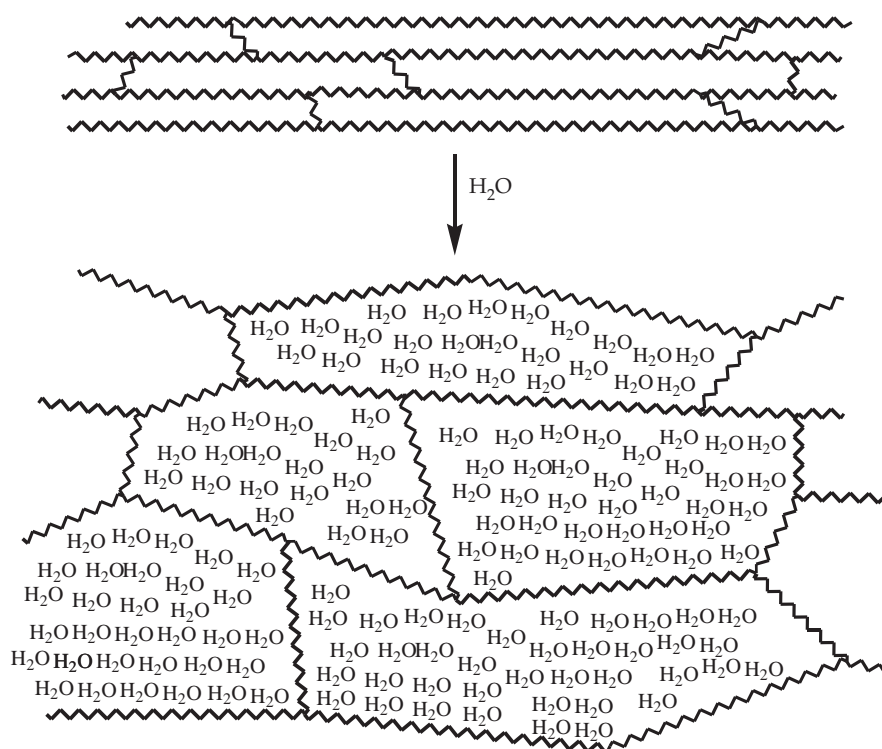


Figure 3 Poly(sodium acrylate) absorbing distilled water

Equipment

Laboratory Period One

marking pen
2 syringes, 50- μ L*
1-mL transfer pipet[†]

5-mL vial, wide-mouth, with
screw cap

*or adjustable micropipets

[†]if autopipet is not available for dispensing acrylic acid

Laboratory Period Two

3 beakers, 100-mL
forceps
10-mL graduated cylinder
50-mL graduated cylinder
labels

marking pen
plastic wrap or Parafilm
scissors
9-cm watch glass

Laboratory Period Three

50-mL graduated cylinder

1-mL transfer pipet

Reagents and Properties

<i>substance</i>	<i>quantity</i>	<i>molar mass</i> (g/mol)	<i>density</i> (g/mL)	<i>bp</i> (°C)
20% acrylic acid	1 mL	72.06	~ 1.0	~ 108
1M hydrochloric acid	1 mL			
methanol	30 mL	32.04	0.791	65
1% N,N'- methylenebisacrylamide (MBA)	35 μ L	154.17		> 300
0.2 % sodium chloride	50 mL	58.44	1.00	
0.5M sodium hydroxide	4 mL	40.00	~ 1.01	
1% VA-044	35 μ L	323		

*Preview***Laboratory Period One**

- Mix the acrylic acid, MBA, and VA-044 solutions
- Heat at 50 °C 3–24 hr or until Laboratory Period Two

Laboratory Period Two

- Neutralize the polymer and cut it into pieces
- Treat the polymer with methanol
- Dry the pieces for at least 1 hr at 80–85 °C
- Weigh two small polymer pieces; suspend one in excess distilled water and the other in 0.2% NaCl

Laboratory Period Three

- Weigh the swollen polymer pieces
- Treat the water-swollen polymer with 1M HCl and observe the effects

PROCEDURE **Caution:** Wear departmentally approved safety goggles at all times while in the chemistry laboratory.
Always use caution in the laboratory. Many chemicals are potentially harmful. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

Laboratory Period One

1. Preparing the Polymer
[NOTE 1]

NOTE 1: Part 1 will require approximately 15 min of laboratory time from the laboratory period preceding Parts 2–3.

Caution: 20% Acrylic acid is toxic and corrosive. 1% N,N'-Methylenebisacrylamide (MBA) and 1% VA-044 are toxic and irritating.

Transfer 1.0 mL of 20% acrylic acid to a 5-mL screw-cap vial. Use separate syringes or micropipets to add 35 μ L of freshly prepared 1% MBA and 35 μ L of 1% VA-044.

Cap the vial securely. Swirl the solution briefly to mix well.

Write your name on the vial. Place the vial into a 50 °C oven for 3–24 hr or until Laboratory Period Two for this experiment.

See Part 6. Cleaning Up

Laboratory Period Two

2. Neutralizing, Sizing, and Drying the Polymer

Caution: 0.5M NaOH is corrosive. Methanol is flammable and toxic. Use a *fume hood*.

Pour 4 mL of 0.5M NaOH into a small beaker.

Note that the polymer prepared in Part 1 is a stiff gel. *Do not touch the gel with your bare fingers.* Use forceps to transfer the gel from the vial to the beaker containing NaOH solution.

Use scissors to cut the gel into pieces about 3 mm across. Do not cut them too small. Allow the gel pieces to stand for about 10 min until *all* of the 0.5M NaOH is absorbed.

After the NaOH solution is absorbed, transfer the beaker to a *fume hood*.

Add 10 mL of methanol to the beaker. Swirl the beaker contents for 10 min. Note that the gel pieces contract.

Pour off the methanol. Repeat the methanol addition process two more times or until no further shrinkage is apparent.

Write your name on a watch glass. Weigh the watch glass and record its mass.

Place the moist gel onto the watch glass. Dry the gel in an 80–85 °C oven for at least 1 hr.

Remove the gel from the oven. Cool the gel to room temperature.

Weigh the gel and record its mass.

In your laboratory notebook, write a description of the gel's appearance.

3. Setting Up the Absorbency Label two 100-mL beakers "water" and "NaCl", respectively. Weigh each beaker and record its mass.

Pour 50 mL of distilled or deionized water into the water beaker. Select a piece of dried gel that weighs about 10 mg. Weigh the piece and record its mass. Place the gel in the water beaker.

Pour 50 mL of 0.2% NaCl into the NaCl beaker. Select a second piece of dried gel that weighs about 10 mg. Weigh the piece and record its mass. Place the gel in the NaCl beaker.

Seal both beakers with plastic wrap or Parafilm to prevent evaporation. Leave the beakers in your laboratory drawer until the next laboratory period.

See Part 6. Cleaning Up

Laboratory Period Three

4. Analyzing the Absorbency

[NOTE 2]

NOTE 2: Parts 4–5 will require approximately 15 min of laboratory time at the *beginning* of the laboratory period following Parts 2–3. Periodic observations will be required throughout the laboratory period.

Pour off the excess liquid from the gel in the water beaker. Weigh the beaker and gel and record the mass.

In the same way, pour off the excess liquid from the gel in the NaCl beaker. Weigh the beaker and gel and record the mass.

In your laboratory notebook, write a description of each gel's appearance.

5. Observing the Effects of Acidification

Caution: 1M HCl is toxic and corrosive.

Pour 50 mL of distilled or deionized water into the water beaker containing the swollen gel piece. Add approximately 1 mL of 1M HCl. Swirl to mix.

Occasionally observe the gel for the remainder of the laboratory period. Record your observations.

6. Cleaning Up

Use the labeled collection containers provided by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

- Post-Laboratory Questions**
- What percent yield of dry polymer did you obtain? Assume the polymer consists of 72% sodium acrylate and 28% acrylic acid, with an average monomer molecular mass of 87.9 g/mol.
 - If your percent yield is greater than 100%, what might be responsible? [Note: for these purposes, the amounts of VA-044 and MBA are negligible.]
 - Calculate the percent increase in mass of the polymer in both distilled water and in 0.2% NaCl by completing the table below.

	<i>mass of dry polymer, g</i>	<i>mass of swollen polymer, g</i>	<i>percent increase</i> $\left(\frac{\text{swollen} - \text{dry, g}}{\text{dry, g}}\right)(100\%)$
in distilled water			
in 0.2% NaCl			

- Describe the appearance of the gel pieces when
 - dry
 - in water
 - in 0.2% NaCl
 - after treatment with 1M HCl
- Explain why it is important that the polymer be
 - crosslinked, but only to a small extent?
 - mostly neutralized?
- How do you suppose the gel properties would have differed if you had used
 - no MBA in the reaction?
 - a lot more MBA?
 - a lot more VA-044?
- It has been observed that the presence of divalent metal salts (for example, Ca^{2+} or Mg^{2+}) greatly reduces the absorbency of the polymer. Can you postulate a reason for this? What does this imply about the absorbency of this material toward tap water?

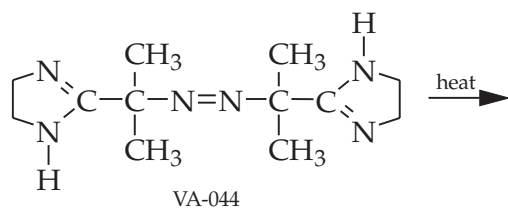
NAME _____

SECTION _____

DATE _____

*SYNT 739/The Synthesis of a Superabsorbent Polymer***Pre-Laboratory Assignment**

1. What hazards are associated with
 - (a) acrylic acid?
 - (b) methanol?
2. Complete the equation below to show how VA-044 forms radicals when heated.



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