Experiment 3: Conversion of polyacrylamide to sodium polyacrylate salt and subsequent conversions to poly(acrylic acid).

Aim: (a) To convert PAM produced in Experiment #1 to sodium polyacrylate (NaPAA) and measure its intrinsic viscosity using an Ubbelohde capillary viscometer.

(b) To convert NaPAA solution to polyacrylic acid (PAA) powder.

(c) To precipitate NaPAA by converting it to the calcium salt of PAA using calcium chloride.

Materials and Apparatus:

Polyacrylamide synthesized in Experiment #1.

Water solution of NaOH (100g NaOH in a liter of solution)

Calcium chloride (1M)

HCl

0.05 M $NaNO_3$ + 0.02% NaN_3

Stoppered or capped flasks

Receiving flask

0.2 and 0.45 micron Millex syringe filter

Spatula

Aluminum weighing dishes

Vials

Small beakers (100 ml)

Hot plate with stirrer and stirring bars

Vacuum oven

Suction filtration stand

Brief Background:

Sythesis route - Conversion of PAM ---> NaPAA ---> PAA or CaPAA :

The polymer produced in experiment #1, polyacrylamide (PAM) is converted to a polymer having a different side group, without changing the degree of polymerization, by base hydrolysis shown in reaction III below.

$$—CH_2—\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle NH_2}{\overset{|}{C=O}}}{\underset{|}{C}}}— \quad + NaOH \quad \longrightarrow \quad —CH_2—\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle O^- Na^+}{\overset{|}{C=O}}}{\underset{|}{C}}}— \quad + \quad NH_3 \qquad [III]$$
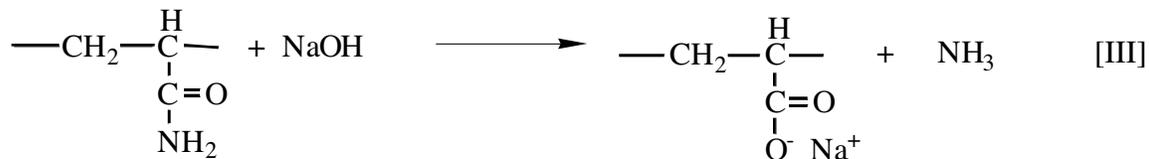
(ix)

Ammonia is detectable by its odor. The resulting polymer sodium polyacrylate, NaPAA, has the repeat unit shown in (ix). This polymer is a classical polyelectrolyte widely used in water treatment as a coagulant or flocculent.

The addition of calcium as $CaCl_2$, precipitates the polymer by bridging two carboxylate groups on neighboring polymer segments (reaction IV), leading to the non-ionized linkage (x).

(ix) $+ \ Ca^{2+} \longrightarrow$ (x)   IV
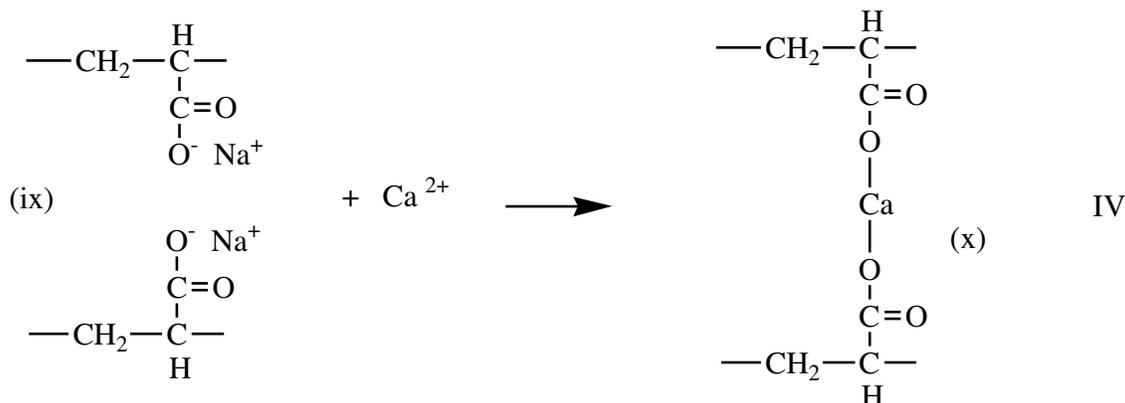
Treatment of the calcium salt form or the free acid form of the polymer by a strong base, e.g., NaOH, KOH, etc. regenerates the corresponding salt with monovalent cations (Na^+, K^+) and renders the polymer again soluble in water.

If the ionized (ion pair) NaPAA (ix) is neutralized by an acid, e.g., HCl, the free, nonionized carboxyl is produced, so that poly (acrylic acid), PAA, is produced (reaction V) of which the repeat unit is (xi).

$$—CH_2—\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle O^- Na^+}{\overset{|}{C=O}}}{\underset{|}{C}}}— \quad + \ H^+ \quad \longrightarrow \quad —CH_2—\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle OH}{\overset{|}{C=O}}}{\underset{|}{C}}}— \quad + Na^+ \qquad V$$

(ix)   (xi)
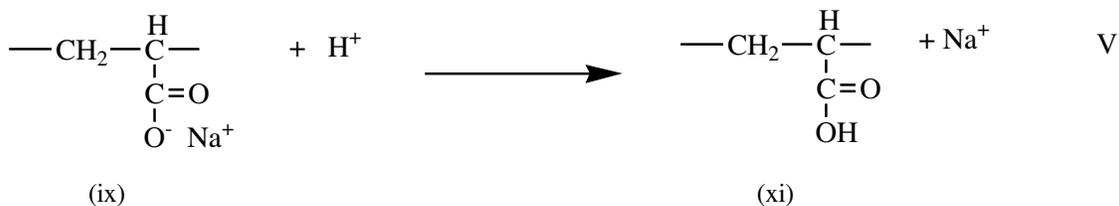
Extensive hydrogen bonding between carboxyl groups or neighboring polymer chains results in linkages like (xii). The water is no longer as effective a solvent for the polymer in the presence of this strongly H-bonded complex. The H-bonds form the basis of crystalline order, and the result is the immediate crystallization and its phase separation from aqueous solution.

$$-CH-H_2C-$$

$$OH \cdots O=C$$

$$C=O \cdots HO$$

$$-CH_2-C-$$

$$H$$

(xii)
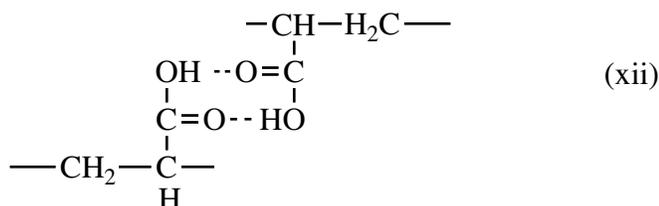
This is but one of many examples of producing polymers not by direct synthesis from monomer but by transformation of a previously synthesized polymer. Other important cases include:

poly (vinyl alcohol) from poly (vinyl acetate)

poly (vinyl butyral) from poly (vinyl alcohol)

acetate rayon from cellulose

poly (styrene sulfonate) from polystyrene.

The polyelectrolyte effect on intrinsic viscosity:

The molecular weight of NaPAA is followed by the same method of capillary viscometry used in Experiment #2. In water, a significant proportion of the carboxylic acid groups are dissociated, leaving negatively charged ions attached to the polymer chain. These anions repel each other, causing the molecular coil to expand. The counter ions in solution screen this repulsion, but as their concentration is made more dilute, the counter ions screen the repulsions less and less. Using ion free water to dilute the polyelectrolyte solution results in dilution of counter ions. For accurate results the polymer is diluted by a dilute ionic solution e.g., NaNO$_3$, or NaCl. Use the equation below to understand this effect.

$$[\eta] \sim M^{0.5} \, \alpha^3 \qquad\qquad (1)$$

where α is the expansion factor. (see handout from Rabek, *Experimental Methods in Polymer Science*, pp45-52.)

Polyelectrolytes:

Polyelectrolytes are polymers with incorporated ionic substituents along the polymer chain. Polyelectrolyte solutions show large ionic conductivities. It is the ionic nature of the polyelectrolyte, and its tendency to form complexes with other charged species and water soluble materials, that is exploited in applications such as the use of NaPAA as a coagulant in water treatment.

Precautions:

No special precautions.

Procedure:

A. Conversion of PAM to NaPAA:

1.   Use the PAM solution prepared at the end of Experiment #1: 100 ml of a 4% PAM solution treated with 150 ml of a solution of 100g NaOH / litre.

2.   Take 100 ml of the 4% PAM solution (**if you used the 6% solution, be sure to adjust all future calculations in this lab accordingly. You may dilute your solution if desired**) and add 112ml of the solution of 100g NaOH / litre. Let it stand in a stoppered or capped flask and keep warm (over 60 C) for 2 days (preferred method) **or** at room temperature for approximately 1 week. Over this period complete hydrolysis of AM units takes place to form an equal number of NaPAA units. (Question: If all AM units have been converted to NaPAA units, how many moles of NaOH remain unreacted? How many moles and grams of NaPAA units are there in the completely hydrolysed solution? Mol. wt. of NaPAA unit is 94 g/mol. What are the concentrations in g/ml and M of NaPAA, NaOH, $NaNO_3$ and NaN_3 in the 212 ml of completely hydrolysed solution? Mol. wt. of $NaNO_3$ = 85 g/mol and mol wt. of NaN_3 = 65 g/mol.) You should find the NaPAA concentration to be approximately 0.024 g/ml.

B. Dilution and intrinsic viscosity measurement:

1.   Take 5 ml of NaPAA solution and make a 10 fold dilution with distilled water. You will need to add 45 ml of distilled water. You need not take exactly 5 ml or 5g but you must know what you took to the second decimal place. (Calculate the concentrations for the appropriate quantity taken.) You will obtain a solution with NaPAA concentration of approx. 0.0024 g/ml and NaOH concentration of 0.1056 M.

2.   Filter this dilute solution through a 0.2 micron Millex Syringe into a clean flask.

3.   Use an Ubbelhode viscometer (see "Procedure" section of Experiment #2 for details) to determine the flow times for

        a) the dilution solution "solvent" i.e., 0.05M $NaNO_3$ + 0.02% NaN_3 water.

        b) the filtered solution: NaPAA concentration of approximately 0.0024 g/ml

c) the filtered solution diluted 1:1 with the dilution solution "solvent": NaPAA concentration of approximately 0.0012 g/ml

d) the filtered solution diluted 1:2 with the dilution solution "solvent": NaPAA concentration of approximately 0.0008 g/ml.

4.   Demonstration of the polyelectrolyte effect:

a) Take some of the original solution (NaPAA concentration of 0.0024 g/ml) and dilute 1:7 with <u>distilled water</u>, so as to reduce polymer concentration and NaOH concentration by a factor of 8 giving NaPAA concentration of approximately 0.0003g/ml and NaOH concentration of 0.0132M. Now use the Ubbelhode viscometer to determine the flow time for this solution.

b) Prepare another solution of NaPAA concentration of 0.0003 g/ml but this time use the dilution solution (0.05 M $NaNO_3$ + 0.02%NaN_3) for dilution. Again determine the flow time in the Ubbelhode viscometer.

<u>C. Conversion of NaPAA solution to PAA powder:</u>

1.   Set up a 100 ml beaker with a stirring bar on a magnetic stirrer. Add about 50 ml of 0.5 M HCl solution. Set the stirrer speed so as to produce a vortex. Drop-wise add 20 ml of the original NaPAA solution of which the polymer concentration is about 0.024 g/ml (presuming use of the original 4% PAM solution).

2.   A precipitate of finely divided PAA will form. Cease stirring. Let the precipitate settle. Decant and discard the clear supernatant, but do not let the precipitate escape.

3.   Add now about 40 ml of distilled water. Stir the precipitate, then let it settle. Decant and discard the water. Transfer by spatula as quantitatively as possible the damp precipitate into the aluminum (or plastic) weighing dish. Place in vacuum oven operating at about 60 C. When dry, weigh the residue (now as PAA) and check how closely the material balance closes.

4.   Save the dried powder (PAA) in a labelled vial.

<u>D. Precipitation of NaPAA by Calcium Chloride:</u> 1.   Take 10ml of the NaPAA solution of concentration 0.024 g/ml. Add 20 ml of 1M $CaCl_2$ solution. A small beaker or an aluminum weighing dish would be appropriate.

2.   Pre-weigh a 0.45 micron dry filter. Install this on a suction filtration stand. Transfer the precipitate onto the filter. Filter off the solution into the receiving flask. Under suction rinse with about 40 ml of distilled water (to remove NaCl and excess $CaCl_2$).

3.   Dry the filter plus precipitate on a hot plate at low heat, or in a vacuum oven, to constant weight. Determine the net weight of the precipitate and report whether the weight

observed, relative to the weight of the initial NaPAA is in accord with the differences in molecular weights of NaPAA and CaPAA.

Observations and Calculations:

1.   Answer questions and perform the calculations in the "Procedure" section as you go along.

2.   Tabulate all necessary Ubblehode data and weight measurements in the lab note book.

3.   Present the Huggins plot of the Ubbelhode data and from it calculate the Huggins constants, intrinsic viscosity and molecular weight (using the Mark-Houwink relationship and the constant given in "Brief Background" section of experiment 2). Indicate the conditions of polymerization of your PAM from which NaPAA was made as a legend.

4.   Report the material balance closure on NaPAA --> PAA. (We know that this will be at best an estimate, and with certain groups, impossible.) Indicate the conditions of polymerization of your PAM from which NaPAA was made as a legend.

5.   Report the material balance closure on NaPAA --> CaPAA. (We know that this will be at best an estimate, and with certain groups, impossible.) Indicate the conditions of polymerization of your PAM from which NaPAA was made as a legend.

Discussion:

1.   When 0.05 M $NaNO_3$ is used as diluent, is the Huggin's plot reasonable (i.e., do the Huggins constants have proper values, and do the two curves have a common intercept)?

2.   Is the value of molecular weight calculated (using the Mark-Houwink relationship) for your NaPAA consistent with what would be expected from the molecular weight you calculated on your PAM samples in experiment #2?

3.   Discuss the polyelectrolyte effect.

4.   How can you improve the accuracy of material balance closures?

5.   You may find more CaPAA than expected from the NaPAA amount. What are some possible reasons?