Experiment 1: Polymerization of acrylamide in water

Aim: (a) To polymerize acrylamide (monomer) in water to polyacrylamide (polymer) by free radical polymerization using a "redox" pair of initiators.

(b) To follow the kinetics of polymerization by monitoring the variation of temperature and viscosity (measured by using Stokes Law for falling spheres) with time.

Materials and Apparatus:

Solution I (Stock acrylamide solution): 30 wt/vol % acrylamide in water

Solution II (Dilution solution): 0.05 M $NaNO_3$ + 0.02 % NaN_3 in Milli Q water or equivalent.

Redox initiator AMPS (ammonium persulphate), granular solid, MW 232 g/mol

Redox initiator TEMED (tetramethylethylene diamine), liquid, density 1g/ml, MW 116 g/mol

Thermocouple set and read-out

250 ml Erlenmeyer flasks

Screw cap plastic test tubes (~ 5 " long)

Glass beads (3 mm)

Glass "wool" insulation

Parafilm

Stop watch

Electric balance

Helium or nitrogen tank with reducing valve (multiple outlets)
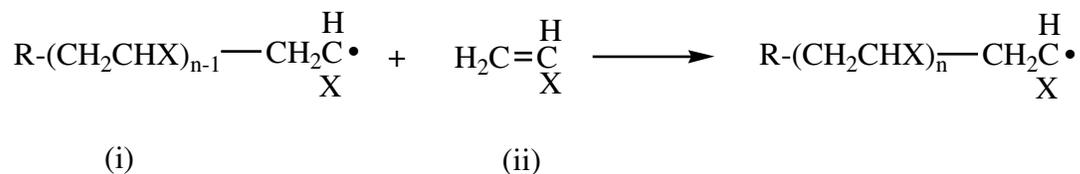
Sparge tips

Brief Background:

Free radical chain polymerization: (see handout from Rempp & Merrill, *Polymer Synthesis*, pp65-78)

Chain polymerization is the process by which a polymer chain grows by addition of monomers – single units – only; growth does not occur by addition of oligomers –multiunit segments. Free radical polymerization is one type of chain polymerization. Cationic and anionic polymerizations are other kinds of chain polymerization.

Free radical polymerization produces "linear" strings of monomer units by a chain reaction started by free radical initiators. Reaction I below shows the key reaction of propogation, that a chain initiated by a radical $\dot{R}$ already having n vinyl units (i) adds another

monomer (ii) to its active radical end, thereby making the added monomer the new active end.

R-(CH$_2$CHX)$_{n-1}$—CH$_2$$\overset{H}{\underset{X}{C}}$• + H$_2$C=$\overset{H}{\underset{X}{C}}$ $\longrightarrow$ R-(CH$_2$CHX)$_{n}$—CH$_2$$\overset{H}{\underset{X}{C}}$•

(i) (ii)

Reaction I

Kinetics of polymerization:

For homopolymerization and certain conditions, the conversion can be expressed as follows:

$$\text{Conversion} = \frac{([M_o] - [M])}{[M_o]} = 1 - e^{-Gt} \tag{1}$$

where,

M_o = Initial monomer concentration
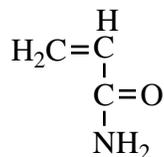
M = Monomer concentration at any time, t

G = "Group constant" which is a function of the rate constants involved in the reaction mechanism and the concentrations of the initiator. G need not be a constant.

Thus, as polymerization proceeds, conversion increases with time. If the polymerization process is exothermic then the increasing conversion results in the release of heat with time. In an adiabatic system, this heat realeased can be measured as a temperature increase and be used to monitor the kinetics of polymerization.

Also note that to a first approximation, the sum of monomer and polymer concentrations is constant. For example, 4 % monomer (4g/dl) solution has no polymer initially. At 50 % conversion, 2 g/dl of monomer and 2 g/dl of polymer coexist. At 100 % conversion, monomer has been completely depleted. Only 4 g/dl of polymer exists.
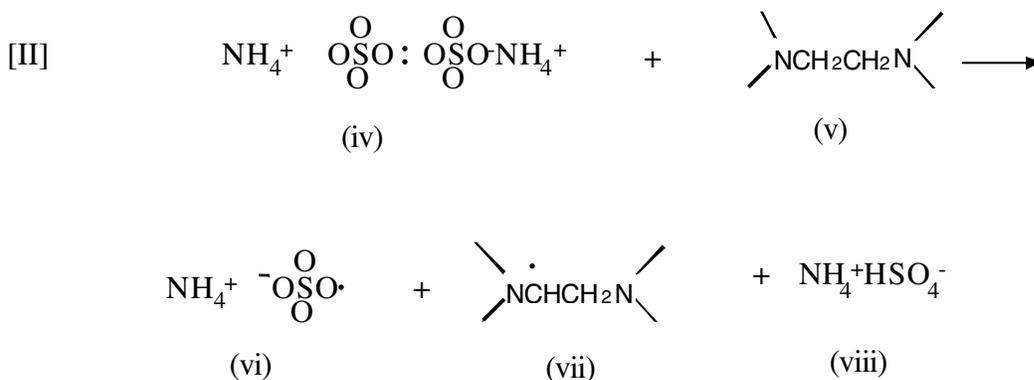
Free radical polymerization of acrylamide:

In the case of the polymerization of acrylamide to polyacrylamide, the monomer is (iii) given below:

$$H_2C=\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle NH_2}{\overset{|}{C}=O}}{\overset{|}{C}}}$$

(iii)

The polymerization of acrylamide in water solution is of interest because the rate constant k_p for the propogation reaction I is unusually large, the rate constant for termination relatively low, the so called transfer processes (to monomer, to solvent) very low. As a consequence very long chains (high degrees of polymerization) are created. Conversion of monomer to polymer is nearly complete within half an hour, not only because k_p is   large but also because the rate of generation of free radicals which start the copolymerization is made large by the use of a "redox" (reduction-oxidation) pair of initiators. One of this pair by itself would produce radicals at a much lower rate, and the other by itself would not generate any radicals. The redox pair we will use is AMPS (ammonium persulfate, (iv)) and TEMED (tetramethyl ethylene diamine, (v)). The reaction leading to radical production is shown in reaction II. The radicals are (vi) and (vii). Ammonium bisulfate (viii) is the inert by-product.

[II] NH_4^+ $O\overset{O}{\underset{O}{S}}O : O\overset{O}{\underset{O}{S}}O^-NH_4^+$ + $\diagdown NCH_2CH_2N \diagup$ $\longrightarrow$

(iv)   (v)

NH_4^+ $^-O\overset{O}{\underset{O}{S}}O\cdot$ + $\diagdown \overset{\cdot}{N}CHCH_2N \diagup$ + $NH_4^+HSO_4^-$

(vi)   (vii)   (viii)

Atmospheric oxygen is a dramatic inhibitor of polymerization. It can be removed by sparging the acrylamide solution with an inert gas like nitrogen, helium or argon.

The enthalpy of polymerization is around 15000 cal/mol (exothermic), thus around 225 cal/g of monomer polymerized. If this enthalpy is released adiabatically, the temperature rise will amount to several degrees, which can be monitored by us.

Degree of polymerization, molecular weight and viscosity: (See handout from Rabek, *Experimental Methods in Polymer Science*, Ch3 and Ch 9.)

As conversion increases, the polymer chains grow in length. The increase in length causes an increase in the viscosity of the polymer solution. This increase in viscosity can also be used to monitor the kinetics of polymerization. Some terms relating to the length of the polymer chain need to be defined:

The degree of polymerization is defined as the number of monomer units incorporated into the polymer chain during the lifetime of the chain.

The molecular weight of the chain is the degree of polymerization multiplied by the molecular weight of the repeat unit. (For the case of acrylamide, the molecular weight of the repeat unit is 3 C @ 12 g/mol + 1 O @ 16 g/mol + 1 N @ 14 g/mol + 5 H @ 1 g/mol = 71 g/mol.)

Typically, any polymerization produces chains of various molecular weights i.e., there is a distribution of molecular weights or degrees of polymerization. Hence, there is a need for measures of the average molecular weight and the spread of the distribution. The two most common averages of the distribution are the number average M_n and the weight average M_w. The spread of the distribution is measured by the polydispersity index (PDI) which is the ratio M_w/M_n.

As the molecular weight increases, the viscosity of the polymer solution increases. Typically, the "zero shear" viscosity varies with the molecular weight (M) and concentration (c) as follows;

$$\eta\,(0) \sim c^{2.5}\,M^{3.4} \qquad\qquad (2)$$

Viscosity measurement using Stokes Law: (See addendum on the Falling Ball Viscometer)

A solid sphere (of radius R and density ρ_s) falling through a liquid (of viscosity η and density ρ_L) under the action of gravitational forces (gravitational acceleration, g) acquires a steady terminal velocity V_t. Under these conditions, the viscosity of the liquid is given by the following equation:

$$\eta = \frac{2\,(\rho_S - \rho_L)R^2 g}{9\,V_t} \qquad\qquad (3)$$

Polyacrylamide:

Polyacrylamide solutions and variations of PAM solutions are widely used as model solutions for rheological studies on polymer solutions.

Precautions:

No special precautions. Follow general precautions.

Procedure:

For each of 3 runs:

1.   In preparation for the viscosity test, set aside a screw cap plastic test tube with a 3mm glass bead inside it.

2.   Mix Solution I and Solution II to produce a total of 200 ml, of x wt/vol %. Split the 200 ml into two approximately equal volumes of 100 ml each. Use 250 ml Erlenmeyer flasks.

3.   Add y grams of AMPS to one flask and z grams of TEMED to the other flask and then swirl each flask to dissolve the added redox initiator. Sparge each flask with helium or nitrogen for at least 10 minutes. Be sure to use clean sparge tips.

<u>Table</u>: Recipes

Variation	Run 1	Run 2	Run 3
Team A,D			
y & z	x=4% [0.56M]	x=4% [0.56M]	x=4% [0.56M]
	y=0.10g [$2.15X10^{-3}$M]	y=0.10g [$2.15X10^{-3}$M]	y=0.20g [$4.30X10^{-3}$M]
	z=0.05ml[$2.15X10^{-3}$M]	z=0.10ml[$4.30X10^{-3}$M]	z=0.10ml[$4.30X10^{-3}$M]
Team B,E			
x	x=2% [0.28M]	x=4% [0.56M]	x=6% [0.84M]
	y=0.10g [$2.15X10^{-3}$M]	y=0.10g [$2.15X10^{-3}$M]	y=0.10g [$2.15X10^{-3}$M]
	z=0.05ml[$2.15X10^{-3}$M]	z=0.05ml[$2.15X10^{-3}$M]	z=0.05ml[$2.15X10^{-3}$M]
Team C,F			
y & z	x=6% [0.84M]	x=6% [0.84M]	x=6% [0.84M]
(y=z)	y=0.05g [$1.08X10^{-3}$M]	y=0.10g [$2.15X10^{-3}$M]	y=0.20g [$4.30X10^{-3}$M]
	z=0.025ml[$1.08X10^{-3}$M]	z=0.05ml[$2.15X10^{-3}$M]	z=0.10ml[$4.30X10^{-3}$M]

4.   Add the contents of one flask into the other. Simultaneously, start the stop watch (This shall be time $= 0$ for both temperature and viscosity measurements). Mix the solution by swirling.

5.   Pour some of this solution to completely fill (to overflowing) the test tube set aside in step 1. Screw the cap on to the filled tube to exclude any bubbles of air. Every minute, invert the tube and estimate the time it takes for the glass bead to fall from the top to bottom.

6.   Set up the 250 ml Erlenmeyer flask with the remaining solution (approx. 200 ml), surrounded by glass fiber (glass "wool") as insulation. Inset a thermocouple probe through the parafilm or a stopper that excludes air.   Allow the remaining solution to polymerize. Record the temperature of the contents of the flask every minute.

7.   Store the resulting polyacrylamide for subsequent experiments. In anticipation of Experiment #3, place 100 ml of the polyacrylamide solution recovered at the end of step (6) in a 250 ml Erlenmeyer flask, add 112 ml of 10% wt/vol NaOH solution in water (provided by TA). Stopper and label "Sodium Polyacrlyate for Exp# 3" with your Team #). Note: Stir thoroughly to ensure complete hydrolysis, especially if viscous.   Use mild heat if necessary.

Observations and Calculations:

1.   For each recipe, tabulate:

Reaction time (min)	Temperature (C)	Bead falling time (sec)	Viscosity (cP)

2.   Show a sample calculation for viscosity. Specify units, illustrate unit conversions and give source of data.

3.   Plot (temperature) vs. (reaction time) and (bead falling time) vs. (reaction time) on same plot. Make one plot for each recipe. Legend should specify precise conditions for each recipe.

Discussion:

1.   To what degree can you tell when the reaction ceased by the two methods - temperature and viscosity? Do they agree?

2.   When did the reaction appear to begin?

3.   Do the results of your three runs, taken together, seem reasonable? (For example, was the reaction faster if the Redox concentration was increased?) If there is a trend, make a plot illustrating the trend.

4.   Find out if the data of another group with different recipes illustrated any other concepts/trends. Just state their result in one or two lines. Is that reasonable ?

Addendum: The Falling Ball Viscometer

This is a very simple device. A spherical bead is introduced into a column of liquid and its fall, if more dense than the liquid, or rise if the opposite is true, it then timed. The movement of the bead must occur in a laminar flow, and a steady velocity of fall (or rise) must be achieved. The bead cannot be near a wall of the container.

The bead has a radius R, a density ρ_s, and acquires a steady terminal velocity v_t.

The liquid has a density ρ_L and a viscosity η.

The net gravitational force acting on the bead is exactly balanced at equilibrium by the frictional force on the bead according to Stokes' law, i.e.:

$$(4/3)\pi R^3 (\rho_s - \rho_L) g = 6\pi R \eta v_t$$

Whence
$$\eta = \frac{2(\rho_s - \rho_L) R^2 g}{9 v_t}$$

Wherein g is the gravitational acceleration.

Thus, the terminal velocity is inversely proportional to viscosity.

In the CGS system (g, cm, sec, dyne) the dimensions of η are dyn•s/cm^{-2}. One dyn•s/cm^{-2} is called a "poise", in honor of Poiseuille. The viscosity of water at room temperature is about 1 centipoise, or 0.01 poise. In the SI system, the dimensions of η are pascal•sec. One milliPa•s is equal to 10 centipoise.

The falling ball viscometer is useful for the estimation of the viscosity of liquids that are Newtonian (viscosity independent of shear rate), transparent (so that the bead can be tracked), and of viscosity less than about 100 poise.