

Kinetics: Thermal Frontal Polymerization

Background Reading:

- 1) Class notes (Kinetics, Genchem review and "Free Radical Polymerization" handout)
Related material is the difference between an instantaneous and average front and the mechanism of free-radical polymerization
- 2) "Introduction to a Proposal Written on IFP"
Related material is the definition of a thermal frontal polymerization reaction (TFP not IFP) and how one can compare it to a burning cigarette. The reaction literally moves through the test tube like a wave or flame.
- 3) Lewis, L. L.; DeBisschop, C. S.; Pojman, J. A.; Volpert, V. A. "Isothermal Frontal Polymerization: Confirmation of the Mechanism and Determination of Factors Affecting Front Velocity, Front Shape, and Propagation Distance with Comparison to Mathematical Modeling," *J. Poly. Sci. A*, **2005**, 43, 5774.
Related material is the definition of a thermal frontal polymerization reaction (TFP not IFP) and its uses and background (introduction), experimental methods (source of chemicals and their purity—first paragraph),
- 4) **Pojman, J. A.; West, W. W.; Simmons, J. "Propagating Fronts of Polymerization in the Physical Chemistry Laboratory," *J. Chem. Edu.*, **1997**, 6, 727.
Related material is the majority of the paper.

Goals of the Experiment:

- To determine if we produce a self-sustaining frontal polymerization reaction
- To determine the velocity (rate) of each polymer front (each sample) run for all teams
- To determine the behavior (e.g. linear, exponential) of these velocities
- To determine average and standard deviation of the velocities of a single monomer
- To determine if there are trends present between the different monomers used, e.g. does one monomer's front travel faster than another monomer's front based on steric hindrance, etc.

Strategy: By running thermal polymer fronts (traveling polymer reactions) and noting their position with respect to time, we can plot their position with respect to time and find the slope of these samples. These slopes will be the fronts' velocities. We will determine the velocities' behavior (e.g. linear, exponential), the average and standard deviation of the velocities of all runs of a single monomer (e.g. methyl methacrylate), and any trends present between different monomers.

Assignment: You will perform this lab with your lab group over a one week period during pchem lab. All groups will share data. Each student will write a formal lab report due at the stipulated due date after the lab is performed. This report should adhere to the guidelines outlined in your lab syllabus addendum (handout and on class web page). One rewrite will be allowed. (The final grade will be the average of the first draft and the final draft.)

Procedure

I. Supplies Needed

Hot plate, three capped test tubes, silica, designated monomer, spatula, AIBN (2,2'-azobisisobutyronitrile, the initiator)

WEAR SAFETY GLASSES OR GOGGLES AT ALL TIMES WHILE IN THE LAB!

II. Experimental Procedure

1. Make one 50-mL solution of each of the following: 40 mM AIBN in MMA, 60 mM AIBN in MMA, and 80 mM AIBN in MMA.
2. For each solution:
 - a. Under the fume hood, fill one tube $\frac{3}{4}$ full of one solution. Add enough powdered silica (one spatula at a time, vortexing after each spatula) to produce a solution that has the consistency of Vaseline. If the test tube is not full, pack enough powdered silica into the top until the test tube is full.
 - b. Mark the test tube with centimeter markings. Prepare to monitor the movement of the polymerization reaction as it travels through the test tube. (The monomer and silica gel have a grayish appearance, and the color turns white upon polymerizing.) You will need a stopwatch of some sort.
 - c. Position the test tube upside down (to minimize convection) holding the capped surface on the surface of the hood. Have one student hold the test tube, while another student holds a heat source (that is already hot) on the bottom of the test tube (the test tube is inverted, and thus, "bottom" means the real bottom of the test tube, not the capped end). Soon, you should see the portion closest to the hot source polymerizing, as indicated by its white appearance. At this point attempt to take away the heat source and determine if the polymer reaction will continue on its own. (You'll see the white portion move down the test tube.) If this does not occur, reapply the heat source leaving it on top of the test tube. In either case, please start timing the behavior of the front when it reaches the 1.0 cm mark.
 - d. Note if samples were self-supporting or not.
3. Clean up all materials used disposing of them in the fashion indicated by the professor.

III. Analysis

- a. To answer our previously stated goals...
 - i. Collect data from all lab groups.

The following steps should be performed in Excel.
 - ii. Zero the data for each sample. (Subtract the numerical value of the position at 1.0 cm from each position's value.)
 - iii. Plot each sample as (y,x) (or (position, zeroed time)) using a line-scatter graph.

Analyze the appearance of the graph.

Questions to ask...

1. Is the slope linear? What is the R^2 factor if a linear trend line is fit to the data?
 2. Is the slope curved? If so, is the front slowing down or speeding up and how do we know? Can we use a different fit to this data, e.g. exponential or polynomial? What is the R^2 for this curve fit?
- iv. Plot all samples and repeat the analysis.
- v. Questions to ask and answer about the group of samples
For an individual monomer (e.g. methyl methacrylate)...
1. If the slope is constant (e.g. linear or polynomial fit), average the slopes of all MMA samples and determine the standard deviation.
 2. If the slope is not constant (R^2 factor for any trendline fit is nowhere near one), determine an average slope (velocity) (versus an instantaneous slope) according to the procedure on p. 8 of our Kinetics class notes. Determine the average and standard deviation of all slopes.
Repeat steps 1 and 2 for the second monomer
Now, let's compare both monomers to one another...
 3. How does the average velocity of methyl methacrylate compare to benzyl methacrylate? (Faster or Slower or the same.) Can we explain why this behavior occurs?
- IV.** Following the guidelines in the syllabus addendum on the class web page, please write a formal lab report including the following points.
- a. Address/answer each goal stated on page one of this procedure.
(How do I answer each goal? Where does this goal fit within my report? How do these goals and their answers fit together with one another?)
 - b. In the introduction, please be sure to include...
 - i. What is a thermal front?
 - ii. How does a thermal front work?
 - iii. What are its practical uses in the chemical world? Why is it important to study these?
 - c. In the results and discussion, please be sure to include all necessary graphs and tables. Please also make sure that all graphs' axes are labeled.
- V.** Please let me know if you have any questions! We can have a study session where we discuss how to analyze the data and what the results mean.