Propagating Fronts of Polymerization in the Physical Chemistry Laboratory

3 AUTHORS, INCLUDING:

John Pojman
Louisiana State University

238 PUBLICATIONS **4,139** CITATIONS

Propagating Fronts of Polymerization in the Physical Chemistry Laboratory

John A. Pojman,* William W. West, and Jennifer Simmons
Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406

Many undergraduate laboratory experiences are a series of exercises devoted to the verification of a physical theory whose answer is well known. This often focuses students on explaining why they did not achieve the correct value, instead of on learning the more valuable process of applying mathematics, physics, and chemistry towards understanding a system. We believe that physical chemistry is less a series of topics to be covered or techniques to be learned than an approach in which mathematics and physics are applied to the understanding of chemical systems. Therefore, determining the "right" answer in a lab is less important than developing the ability to propose and test models of observed phenomena.

Previously, we reported a three-experiment module based on the Belousov–Zhabotinsky oscillating reaction (*1*) and on a unified approach based on oscillating reactions and traveling fronts (*2*). Students investigate the thermodynamics and kinetics of complex systems for which there are not simple "right" answers. Students are evaluated on their ability to develop models consistent with their chemical knowledge and the observed phenomena. As part of the unified lab, we investigate spatial self-organization in the spring semester, which includes Liesegang rings, propagating fronts, and B-Z waves.

Here we report a simple and inexpensive experiment with propagating fronts of addition polymerization that demonstrates a method of testing the steady-state model of polymerization and includes the effects of heat losses and gravity on a chemical reaction. The experiment involves a novel approach to synthesis of polymeric materials, and it requires no more than test tubes, two inexpensive chemicals, a ruler, and a stopwatch.

Traditionally, polymer chemistry plays little role in the physical chemistry lab, although it is arguably one of the most important areas of industrial chemistry. Historically, if polymers appear they do so in two experiments. The first utilizes viscometry to determine the fraction of head-to-head bonds in polyvinyl alcohol (*3*), and the second uses dilatometry to determine the rate of polymerization of styrene as a means to test the steady-state model of addition polymerization (*4, 5*).

In bench-top reactions the issues of heat loss and convection are often ignored, but these phenomena can play crucial roles in industrial-scale reactions. This experiment clearly illustrates that gravity and heat losses can significantly affect a chemical reaction. We contend that it is valuable to introduce these topics in the physical chemistry lab via an experiment that allows a simple macroscopic observation to reveal kinetic information and the importance of heat conductivity.

Propagating Fronts of Polymerization

An autocatalytic reaction in an unstirred vessel can support a constant-velocity wave front. The front is created by coupling the diffusion of the autocatalyst to the chemical reaction. This can occur in polymerization, but a more common example is a flame front. In both types of fronts,

heat is the autocatalyst diffusing into unreacted regions, stimulating reactions that produce more heat.

A propagating front is observed when a mixture of monomer and initiator is placed in a test tube and the reaction is started at the top by adding heat. Such fronts were first discovered in the former Soviet Union (*6–10*) and are currently studied in our lab (*11–15*). The narrow reaction zone travels down the tube with a constant velocity, creating hot, solid polymer as it progresses. The front propagates down the tube because the heat of polymerization diffuses into neighboring regions. This heat causes the decomposition of the initiator into radicals that initiate polymerization forming more polymer, releasing more heat, and so on; the reaction zone moves down the tube. Thus, there is a hot reaction zone (over 200 °C) with hot, solid polymer above it and a cold monomer/initiator mixture below.
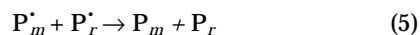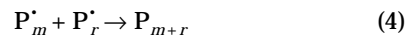
A propagating polymerization front can cause convection because of the large temperature and concentration gradients (*12*). Initiation from the bottom of the tube is often not possible owing to buoyancy-driven fluid motion from the hot front. (Pojman has discussed the role of buoyancy-driven convection in fronts [*16*]). If the tube is inverted in a descending front the reaction zone rises and cools, destroying the front. If the reaction tube is positioned at an angle to gravity, the front reorients perpendicular to the gravitational vector.

The fronts are also sensitive to heat loss. As the rate of heat loss increases, the front moves more slowly and will stop completely if heat is lost too quickly. For example, if the tube containing the reaction mixture is placed in a water bath at room temperature, a front started above the water line will stop when it reaches the water. In some instances, the airflow from a hood is enough to extinguish a front.

Propagating fronts can be created with many monomers, including acrylamide, butyl acrylate, methacrylic acid, methyl methacrylate, and triethylene glycol dimethacrylate (TGDMA) (*11–15*). We have found that TGDMA is the safest monomer to use in these experiments; the others can cause the test tube to explode due to a buildup of pressure caused by the monomer vapor; TGDMA has a very low vapor pressure and will react before boiling.

Theory To Be Tested

This reaction scheme adequately describes many free radical addition polymerizations (*17*) :

$$I_2 \xrightarrow{\Delta} 2\, f I^{\bullet} \tag{1}$$

$$I^{\bullet} + M \rightarrow P^{\bullet} \tag{2}$$

$$P_n^{\bullet} + M \rightarrow P_{n+1}^{\bullet} \tag{3}$$

$$P_m^{\bullet} + P_r^{\bullet} \rightarrow P_{m+r} \tag{4}$$

$$P_m^{\bullet} + P_r^{\bullet} \rightarrow P_m + P_r \tag{5}$$

Reaction 1 yields two radicals from the thermal decomposition of the initiator. If the radical efficiency, *f*, is one, each radical can initiate polymerization by reacting with a monomer molecule. This yields polymer radicals (reaction 2) that reacts with monomers in the propagation step (re-

---

action 3) until the radicals terminate (reactions 4 and 5). Termination can occur by two mechanisms: combination (reaction 4) or disproportionation (reaction 5). In combination, two radicals react to form a single molecule. In disproportionation, one radical abstracts a hydrogen from another radical, creating a double bond in that molecule and leaving itself saturated.

Using this mechanism, we can derive a rate law for free-radical polymerization. The first assumption made is that the rate of initiation is equal to the rate of initiator decomposition:

$$R_i = R_d = 2fk_d[I] = k_i[I][M] \qquad (6)$$

where R_i is the rate of initiation, R_d is the rate of initiator decomposition, k_d is the decomposition rate constant, k_i is the initiation rate constant, and f is the mole fraction of initiator radicals that actually initiate polymerization.

Next, we consider termination and assume that both combination and disproportionation occur giving an effective rate constant, k_t:

$$R_t = 2k_t[M^\bullet]^2 \qquad (7)$$

The third assumption is that the rate of termination is equal to the rate of initiation, the so-called steady-state assumption.

$$d[M^\bullet]/dt = 0 \text{ and } R_i = R_t \qquad (8)$$

$$dfk_d[I] = dk_t[M^\bullet]^2 \qquad (9)$$

The steady-state model is very useful for many free-radical addition polymerizations. After some rearrangement, the polymerization rate is shown to be proportional to the square root of the initiator concentration and directly proportional to the monomer concentration (17).

$$\frac{d[M]}{dt} = \sqrt{\frac{fk_d[I]}{k_t}}\ k_p[M] \qquad (10)$$

If the rate of front propagation is directly proportional to the rate of polymerization, then the dependence of the front velocity on the initial initiator concentration can be used as test of the steady-state theory. We should note that the front velocity is also a function of the thermal diffusivity and other factors such as bubbles and convection (14).

Experimental Procedure

Six reactions are used in this experiment. Four are used to determine the dependence of the front velocity on the initiator concentration. The other two demonstrate the effects of convection and heat loss on the reaction.

SAFETY INFORMATION

• Benzoyl peroxide (BPO) should not be heated.

• Triethylene glycol dimethacrylate (TGDMA) should be kept cool.

• Dimethyl aniline (DMA) should be kept in the hood. Do not get this compound on the skin.

• Do not heat solutions of monomer and initiator, as they will polymerize very rapidly.

• Do not expose skin to either BPO or TGDMA. Gloves should be worn at all times. Safety glasses must be worn during this experiment. All reactions should be performed in a working fume hood.

• The test tubes containing the traveling front will be very hot—above 200 °C, so they should be allowed to cool at least an hour before handling.

Propagating Front Velocity

Three 100-mL solutions of BPO in TGDMA are prepared having molalities between 0.020 and 0.20 m. (This corresponds to 1–4 g/100 mL.) The solutions are stable at room temperature for a few hours and should be prepared and used in the same lab period. (Initiator/monomer solutions may be refrigerated for a day or two if necessary.) BPO is not very soluble in TGDMA at concentrations higher than than 4 g/100 mL and takes some time to prepare. **NOTE:** The solution should *not* be heated to speed dissolving because polymerization will occur.

Students should record the position of the front as a function of time. This can be done by either making centimeter markings on the test tube or placing a ruler beside the test tube. We use five 15 × 150-mm and one 22 × 150-mm test tubes in our experiments, although other sizes can be used. The size of the test tube does make a difference in the performance of the experiment, as it changes the amount of heat lost to the surroundings. If the tube is too small, then the heat losses will be excessive and no front can be sustained.

The test tube is arranged in a hood so that the markings (or ruler) can be easily seen. Then, one of the solutions is poured into the test tube. The tube is clamped to a ring stand and a small portion (~1–2 mL) of dimethyl aniline (DMA) is added to the top of the tube. (DMA reacts with BPO via a redox process and produces free radicals, which initiate polymerization, releasing heat.) The DMA is mixed with the first centimeter of solution and a reaction should be observed almost immediately. A common soldering iron can be substituted for DMA. The hot iron must be inserted into the first centimeter of solution to initiate the reaction. Those using a soldering iron should take care that it is not too hot, as the solution can spatter out of the test tube. Figure 1 shows the simple apparatus and a propagating front.

Once the reaction has begun, it is allowed to proceed for about two or three centimeters down the tube. This allows enough time for the front to stabilize. Then the time at which the front reaches each centimeter mark is recorded, and a plot of position vs. time is made for each of the three solutions.

Heat Loss

The effect of heat transfer on the front is investigated in two ways. In the first, the tube size is changed from 16 × 150 mm to the larger 22 × 150-mm size. In the second, the smaller tube is placed in a water bath. The first method changes the surface-to-volume ratio, whereas the latter changes the heat transfer coefficient between the tube and the surroundings.

Because the polymer formed is cross-linked, the effect of initiator concentration on molecular weight distribution can not be studied. Other monomers (methacrylic acid, bu-
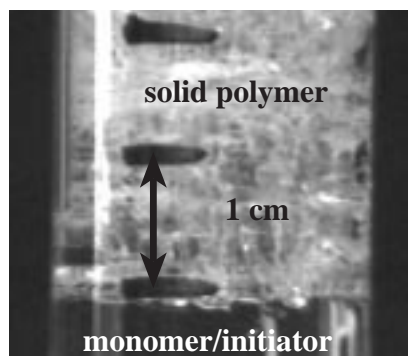

Figure 1. A TGDMA front propagating downward in a 2.2-cm (i.d.) test tube with 1% m/v BPO.

tyl acrylate) can be used for such a study, but they require additional techniques and equipment. See references *14* and *18* for more information.

Typical Results

The front velocity is the slope of a linear regression of front position vs. time. This plot is prepared for each concentration and the data are used in the comparison with the predictions of the steady-state model. The students observe that as the initiator concentration increases the velocity of the front increases. To determine if the steady-state model applies to this system, they plot velocity as a function of initiator concentration. If the steady-state model applies, then the students should find that velocity increases linearly with the square root of increasing initiator concentration. This can be determined by preparing a power function fit to a plot of velocity vs. initiator concentration. A linear regression of a plot of front velocity vs. $\sqrt{I}$ would also test the validity of the steady-state theory, but would not give the general functional dependence of the front on initiator. We also wish to expose students to nonlinear data fitting. Typical results from a student experiment are shown in Figures 2 and 3.

Students will find that the steady-state theory does not apply to front velocities. This can be attributed to at least two factors. The steady-state theory applies to homogeneous reactions and not to fronts, which are functions not only of the rate of polymerization but also of transport processes such as thermal diffusion and convection. Secondly, the conditions in a front are not isothermal, as assumed in the steady-state analysis.

Heat losses in a propagating front have a significant effect upon the front velocity. This is related to two factors: the size of the tube, which affects the surface-to-volume ratio, and the medium outside the tube, which affects the rate of heat conduction. If the tube diameter is decreased, the front travels slower. In tubes of the size we have used, the polymerization front stops when the vessel is placed in room-temperature water. This is because water conducts heat more effectively than air.

Changing the orientation of the test tube gives a clear example of the effects of gravity on the front. If a well-established front is inverted, the hot reaction zone rises quickly to the top of the mixture, and the front may be extinguished, depending on viscosity and the tube diameter. If the tube is tilted, the front reorients so that it is perpendicular to the gravitational vector (Fig. 4). These effects occur because the hot liquid reaction zone is trapped between cold, dense monomer below and solid polymer above. Buoyancy forces the reaction zone to remain above the monomer layer.

Conclusions

Using a propagating front of polymerization, students can rapidly, easily, and inexpensively observe the effect of initiator concentration on the rate of polymerization. They also gain insight into transport processes (convection and heat conduction) that are traditionally not addressed in the physical chemistry laboratory.

Acknowledgments

Literature Cited

1. Pojman, J. A.; Craven, R.; Leard, D. *J. Chem. Educ.* **1994,** *71,* 84–90.
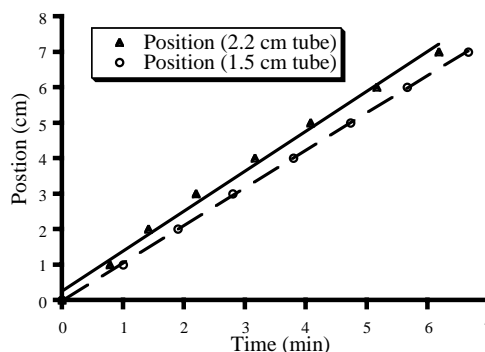2. Pojman, J. A.; West, W. W. *J. Chem. Educ.* **1996,** *73,* 35.

Figure 2. Plot of front position vs. time for two fronts showing the effect of tube diameter. In the front run in a 15 × 150 mm tube, the velocity is 1.06 cm/min with an initiator concentration of 0.10 m. In the front run in a 22 × 150 mm tube, velocity is 1.12 cm/min with an initiator concentration of 0.10 m.
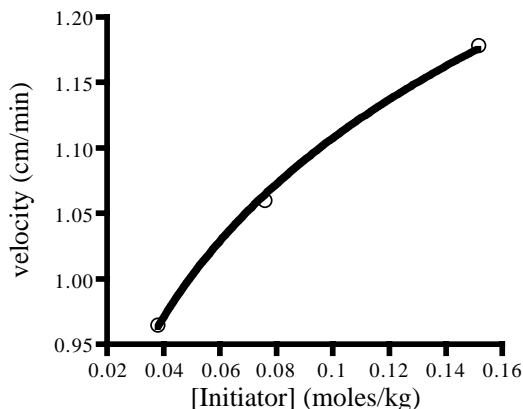

Figure 3. Velocity as a function of initiator concentration. Power fit indicates that velocity $\propto [I]^{0.14}$ The number of points can be increased to give a more accurate fit, but the results of the comparison to the steady-state model will not change.
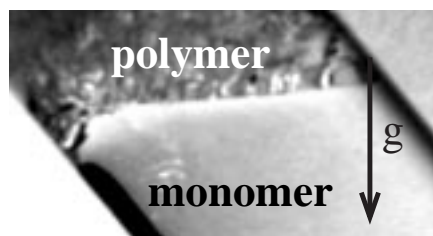

Figure 4. Picture of a front showing the effect of gravity on front orientation. When the tube is tilted, the downward propagating front reorients so that it is perpendicular to the plane of gravity. The TGDMA front is propagating in a 2.2 cm (i.d.) tube with 1% BPO.

3. Schoemaker, D. P.; Garland, C. W.; Steinfeld, J. I.; Nibler, J. W. *Experiments in Physical Chemistry*; McGraw-Hill: New York, 1981.
4. Collins, E. A. *Experiments in Polymer Science*; Wiley: New York, 1973.
5. Pearce, E. M. *Laboratory Experiments in Polymer Synthesis and Characterization*; Educational Modules for Materials Science and Engineering Project, Materials Research Laboratory, Pennsylvania State University: University Park, 1982.
6. Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. *Dokl. Akad. Nauk SSSR* **1972,** *204,* 1180–1181.
7. Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1974,** *214,* 174–176.
8. Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1975,** *221,* 392–394.
9. Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1976,** *230,* 840–843.

10. Davtyan, S. P.; Zhirkov, P. V.; Vol'fson, S. A. *Russ. Chem. Rev.* **1984,** *53,* 150–163.
11. Pojman, J. A. *J. Am. Chem. Soc.* **1991,** *113,* 6284–6286.
12. Pojman, J. A.; Craven, R.; Khan, A.; West, W. *J. Phys. Chem.* **1992,** *96,* 7466–7472.
13. Pojman, J. A.; Nagy, I. P.; Salter, C. *J. Am. Chem. Soc.* **1993,** *115,* 11044–11045.
14. Pojman, J. A.; Willis, J.; Fortenberry, D.; Ilyashenko, V.; Khan, A. *J. Polym. Sci. A: Polym. Chem.* **1995,** *33,* 643–652.
15. Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *Physica D* **1995,** *84,* 260–268.
16. Pojman, J. A. *J. Chem. Educ.* **1990,** *67,* 792–794.
17. Odian, G. *Principles of Polymerization*; Wiley: New York, 1981.
18. Pojman, J. A.; Willis, J. R.; Khan, A. M.; West, W. W. *J. Polym. Sci. A: Polym. Chem.* in press.