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Frontal Polymerization in Solution

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Received January 9, 1996

Frontal polymerization is a mode of converting monomer into polymer via a localized reaction zone that propagates, most often through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization reactions were first discovered in Russia by Chechilo and Enikolopyan in 1972.¹ They studied methyl methacrylate polymerization to determine the effect of initiator type and concentration on front velocity² and the effect of pressure.³ A great deal of work on the theory of frontal polymerization was performed.^{4–9} Work was also done with epoxy curing.¹⁰ The literature up to 1984 was reviewed by Davtyan et al.¹¹

Pojman and his co-workers demonstrated the feasibility of traveling fronts in solutions of thermal free-radical initiators in a variety of neat monomers at ambient pressure using liquid monomers that form polymers with melting points exceeding the reaction temperature of the front^{12–14} and a solid monomer.¹⁵ Unstable modes of propagation were found under some conditions.¹⁶ Recently Pojman et al. demonstrated that a thermochromic composite, that is, a material whose color is temperature dependent, could be prepared better via frontal polymerization than with traditional homogeneous methods because the rapid front prevented sedimentation.^{17,18}

Gusika considered a model of frontal polymerization through a suspension of monomer in a solvent,¹⁹ but no one has demonstrated a system in solution that would support fronts. Here we report the first example of frontal polymerization in solution, which expands the types of materials that can be prepared by this method. We have also found the first bubble-free frontal polymerization system at ambient pressure, which

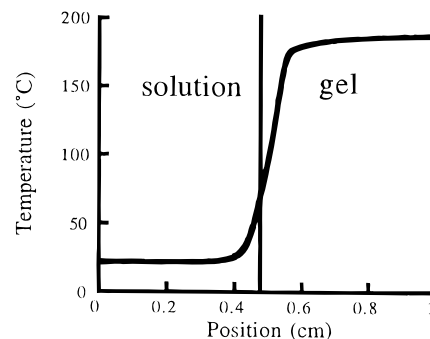


Figure 1. The temperature profile of a front with 1 g of acrylamide/1 mL of DMSO with potassium persulfate (0.02 M). The line indicates the transition from solution to gel, which occurs at 80 °C.

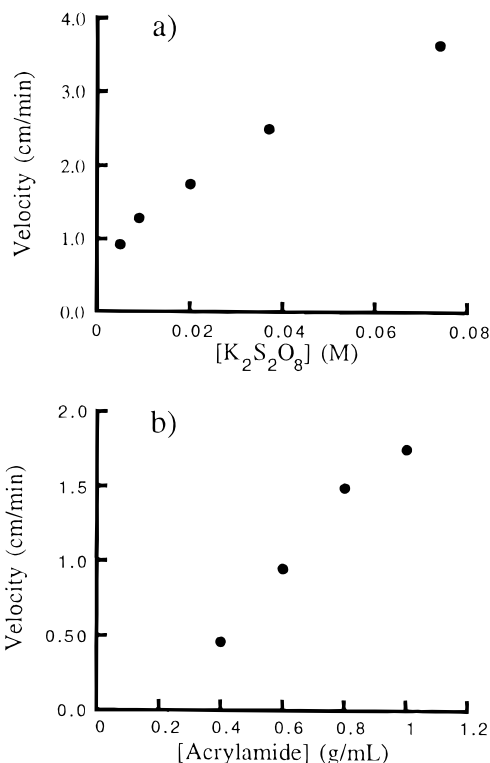


Figure 2. (a) The velocity dependence on initiator concentration with a fixed 20 g of acrylamide in 20 mL of DMSO solution. (b) The velocity dependence on acrylamide concentration (g/mL of DMSO) with a fixed persulfate concentration of 0.018 M (0.020 g/20 mL).

is essential for studying the convective and thermal stability of polymerization fronts.

Frontal polymerization of several reactive monomers can be performed in high boiling point solvents. Acrylamide polymerization will propagate in water (with some vapor formation), in dimethyl sulfoxide (DMSO), and in dimethylformamide (DMF) with several initiators, including sodium persulfate, potassium persulfate, ammonium persulfate, and benzoyl peroxide. Several other monomers also work in these solvents, including acrylic acid, sodium methacrylate, and zinc dimethacrylate.

Interestingly, no gas bubbles are observed with acrylamide/persulfate in DMSO at ambient pressure; the only system we have found with this feature. (The persulfates do not produce volatile side products.) Bubbles can interfere with front velocity measurements¹⁴ and can affect the stability of the front.²⁰

Because of the density difference between the polymer and monomer, a descending front can be subject to double-diffusive and/or Taylor instabilities that manifest themselves as descend-

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ing "fingers".¹³ Fronts of acrylamide in DMSO (1:1) do not exhibit extensive fingering because the polyacrylamide gels. However, acrylic acid, which does not gel in DMSO, exhibits rampant fingering and will not propagate without the addition of a few percent of bis(acrylamide) (a difunctional monomer), which produces a cross-linked gel. The same is true for acrylamide in DMF.

To suppress fingering, all experiments were performed with 1% (w/w) of bis(acrylamide), with respect to the acrylamide. With DMSO as the solvent, a rubbery polymer was produced. Because the front temperature exceeds the boiling point of water for some concentrations of acrylamide (used as received from Aldrich), all experiments in this work were performed in degassed DMSO (Fisher) with potassium persulfate (Aldrich) as the initiator. The solutions were poured into a 15 × 16 mm test tube and the fronts initiated from the top with a soldering iron. Frontal polymerization occurs as a solution-to-gel transition that propagates down the tube with a constant velocity. Because simple convection can occur with an ascending or horizontally propagating front, which will alter the propagation velocity, all measurements were performed with descending fronts.

Acrylamide with persulfate is unstable at ambient temperature because of oxygen-induced decomposition and initiation of polymerization. Addition of 0.25 g/L of hydroquinone can suppress the homogeneous reaction for about an hour. This amount of hydroquinone did not significantly affect the front velocities.

We measured the temperature profile of the front with 1:1 (w/v) acrylamide, which is shown in Figure 1. The temperature increased 165 °C over 3 mm, and the solution-to-gel transition occurred at about 80 °C. This corresponds to the reaction at each point in the solution occurring in less than 10 s!

Using a ΔH of polymerization in DMSO of 59 kJ/mol and taking the heat capacity of the solution to be 2 J/mL, we estimate the conversion to be above 80%.²¹ In fronts with powdered acrylamide, Pojman et al. reported conversions from 60% to 90%, depending on the initiator concentration.¹⁵

We determined the velocity as a function of persulfate concentration for fixed acrylamide concentration (Figure 2a). We make two observations. First, the dependence on the initiator concentration could not be fit to a power function, as has been observed for frontal polymerization with pure monomers.^{1,2,14} We are not sure of the causes of this different velocity, but the initiator is unusual (peroxides and nitriles were used in other works), and a solvent is present. Secondly, the front velocities are several times greater than fronts with neat methacrylic acid, methyl methacrylate, or tri(ethylene glycol) dimethacrylate^{1,14} but comparable to fronts with powdered acrylamide.¹⁵

Unlike neat monomer systems, the concentration of monomer can be varied to change the propagation velocity. Figure 2b shows the velocity dependence on the initial monomer concentration with fixed initiator concentration. Below 0.4 g/mL, no front would propagate.

The ability to perform frontal polymerization with many different monomers in several high boiling point solvents greatly increases the systems that can be studied and types of materials that can be prepared. The lack of bubbles means that the thermal and convective stability of polymerization fronts can be studied readily at ambient pressure.

Acknowledgment. This work was supported by the National Science Foundation (CTS-9319175) and the Air Force Office of Scientific Research. We thank Terry Myers for helpful discussions.

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