

SELF-PROPAGATING FRONTAL POLYMERIZATION IN WATER AT AMBIENT PRESSURE

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Introduction

Advances in polymer chemistry have led to the development of monomers and initiation agents that enable propagating free-radical polymerization fronts to exist. These fronts are driven by the exothermicity of the polymerization reaction and the transport of heat from the polymerized product to the reactant monomer/solvent/initiator solution. The thermal energy transported to the reactant solution causes the initiator to decompose, yielding free radicals, which start the free radical polymerization process as discussed in recent reviews^{1,2}. The use of polymerization processes based on propagating fronts has numerous applications. Perhaps the most important of these is that it enables rapid curing of polymers without external heating since the polymerization process itself provides the high temperatures necessary to initiate and sustain polymerization. This process also enables more uniform curing of arbitrarily thick samples³ since it does not rely on heat transfer from an external source, which will necessarily cause the temperature history of the sample to vary with distance from the surface according to a diffusion-like process. Frontal polymerization also enables filling and sealing of structures having cavities of arbitrary shape without having to externally heat the structure.

Water at atmospheric pressure is most convenient solvent to employ and the most important for practical applications (because of the cost and environmental issues associated with DMSO and other solvents). Nevertheless, to our knowledge, steady, self-propagating polymerization fronts have not been reported in water at atmospheric pressure. Currently, polymerization fronts require a high boiling point solvent (either water at high pressures or an alternative solvent such as dimethyl sulfoxide (DMSO) (boiling point 189°C at atmospheric pressure.) Early work on frontal polymerization⁴, employed pressures up to 5000 atm in order to avoid boiling of the monomer/solvent/initiator solution. High boiling point solutions are needed because in order to produce a propagating front, a high front temperature is needed to produce sufficiently rapid decomposition of the free radical initiator and subsequent free radical polymerization and heat release at a rate faster than heat losses remove thermal energy from the system. (While the conduction heat loss rate increases linearly with temperature, the free radical initiator decomposition is a high activation energy process whose rate increases much more rapidly than linearly with temperature, thus as the temperature decreases, the ratio of heat loss to heat generation increases, eventually leading to extinction of the front if the temperature is too low.)

In order to obtain atmospheric pressure frontal polymerization in water, it is necessary to identify a monomer/initiator combination that is water soluble and will not extinguish even when the peak temperature (T^*) is less than 100°C. In this work acrylic acid (AA) was chosen as the monomer because

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is it one of the most reactive monomers and can polymerize readily at low temperatures even without initiators. Ammonium persulfate (AP) was chosen as the initiator because it decomposes readily at low temperatures, produces relatively few bubbles and is commercially available. The propagation rates and extinction conditions of the fronts are studied for a range of AA and AP concentrations. Small amounts of fumed silica powder (Cab-o-sil, Cabot Corporation) were added to the solutions to inhibit buoyancy-induced convection in the solutions; future studies will investigate the effects of buoyant convection within the solutions.

Experiments

Experiments were conducted at ambient temperature ($22 \pm 2^\circ\text{C}$) using standard glass tubes of approximately 16 mm inside diameter, 1.1 mm wall thickness and 100 mm length. Acrylic acid (minimum purity 99%, inhibited with 200 ppm monomethyl ether hydroquinone to prevent spontaneous polymerization) and ammonium persulfate (98% minimum purity) were used as received from the suppliers. Solutions were prepared by making an AP-water mixture, mixing in Cab-o-sil, then finally adding the AA. This procedure minimized the time that AP and AA were mixed before the experiment was conducted, which in turn minimized the opportunity for pre-reaction. To verify that no significant pre-reaction was occurring, a few tests were conducted in which the mixed solutions were allowed to stand for periods of up to one hour before conducting the experiments. No significant change in the properties of the fronts was observed over this period. In contrast, a few tests performed using DMSO solvent rather than water did show substantial pre-reaction effects within a few minutes. Consequently, tests using DMSO solvent were not pursued further.

Mixed solutions were poured into the glass tube and ignited at the top using an electrically heated wire. The resulting downward propagating fronts were imaged using a standard video camera. From plots of front position vs. time, the instantaneous front speed could be determined. After an initial transient, either a steadily propagating front (constant propagation speed (S)) developed or the front extinguished. For some tests the front temperatures were measured using a type K thermocouple that was immersed in the solution with its junction about 30 mm from the bottom of the tube.

It was found that only a certain range of AA and AP concentrations produced steadily propagating fronts that neither extinguish due to too low peak temperatures nor bubble violently due to peak temperatures above the solution boiling point. Figure #1 shows these ranges. The limiting condition for bubbling depends mostly on the AA concentration and only weakly on the AP concentration. This is reasonable because the theoretical adiabatic front temperature (T_a) depends primarily on the heat release due to conversion of monomer to polymer, which in turn depends on AA concentration. AP concentration does have a slight effect on this limit, however, because, as discussed later, AP affects the front speed that in turn affects the ratio of heat loss to heat generation and thus affects the peak temperature, even for compositions with the same theoretical adiabatic T_a . The limiting condition for steadily propagating fronts that do not extinguish depends significantly on both AA and AP concentrations because, as discussed later, S is nearly constant at the limit and (as Figure #2 shows) S depends on both T_a (which depends mostly on AA concentration) as well as the initiator (AP) concentration.

Tests were also conducted in which the glass tube was immersed in a stirred water bath in order to obtain a nearly isothermal ambient wall temperature. For reasons suggested below, no conditions could be found for which the fronts were neither extinguished nor bubbling.

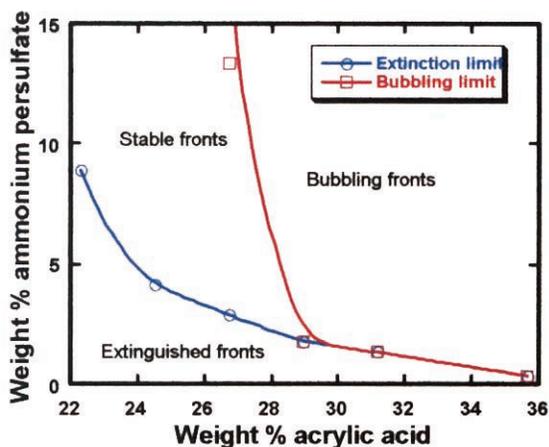


Figure 1. Effect of mass percent of AA on limits to steady and bubbling frontal polymerization in AA/AP/water solutions with 3.6 mass percent Cab-o-sil added to suppress buoyant convection.

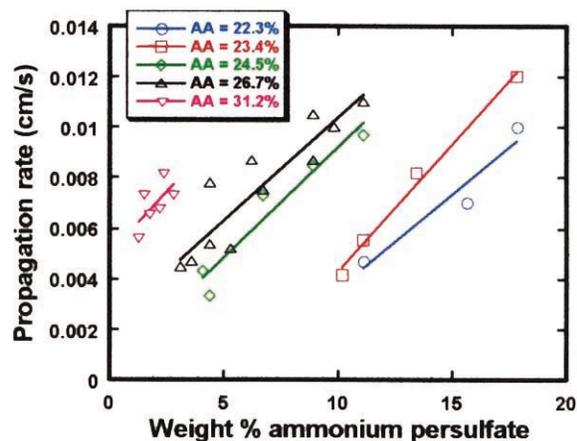


Figure 2. Effect of mass percent AP and AA on rates of steady frontal polymerization in AA/AP/water solutions with 3.6 mass percent Cab-o-sil.

Figure #2 shows propagation speeds for the full range of AA and AP concentrations for which steady values of S could be measured. This includes some conditions at higher AA concentrations for which bubbling was observed but was not so substantial that steady values of S could not be determined. It is interesting to note that

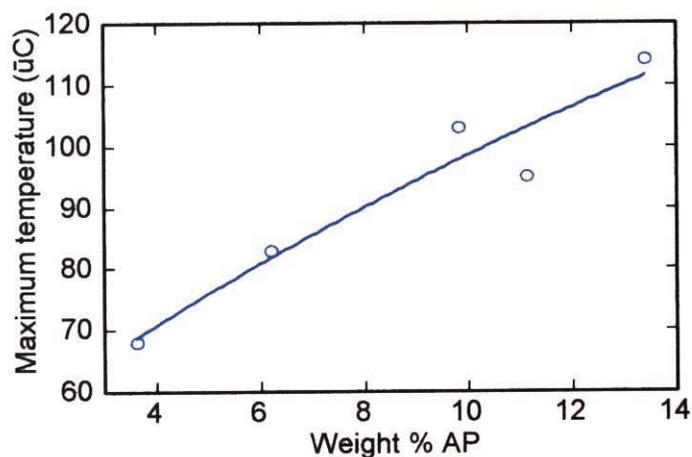


Figure 3. Effect of mass percent AP on the maximum temperature of steady frontal polymerization in AA/AP/water solutions with 26.7 mass percent AA and 3.6 mass percent Cab-o-sil.

the minimum steady value of S (*i.e.*, at the extinction limit) is nearly the same for each mass fraction of AA. The mean value of S at the extinction limit is 0.0048 cm/s with a standard deviation that is 13% of the mean. The corresponding Peclet number at the limit ($= Sd/\alpha_s$, where α_s is the thermal diffusivity of the solution (approximated as water for the purpose of estimating thermal properties) and d the tube diameter), which has a mean value of $(0.0048 \text{ cm/s})(1.6 \text{ cm})/(0.0015 \text{ cm}^2/\text{s}) = 5.1$, where α_s (and all subsequently required thermal properties) will be based on the average of the ambient temperature and the peak temperature T^* .

Figure #3 shows the measured values of T^* during front passage for one value of AA mass fraction (0.267) and several values of the AP mass fraction. Note that except for the point on this plot corresponding to the highest AP concentration, values of T^* are close to or below 100°C . Consistent with this information, Figure #1 shows that only the highest point exhibited bubbling.

Discussion

Following standard combustion theory (Williams, 1985), a theoretical value of the Peclet number at the extinction limit is estimated by determining the value of Pe for which the ratio of heat loss rate across the front thickness to heat generation rate is of the order $1/\beta$, where $\beta \equiv E/RT^*$ is the non-dimensional activation energy, E is the apparent overall activation energy for the chemical reaction and R is the gas constant. The slope of a plot of $\ln(S)$ vs. $1/T^*$, where T^* must be on an absolute scale, is $-E/2R$. From this plot (not shown), a value of $E \approx 13.5$ kcal/mole is inferred. For the limit mixture at 0.267 mass fraction AA, whose peak temperature is 68°C , $\beta = 19.9$ can then be estimated.

Unlike gas combustion theory, it is inappropriate to presume ambient wall temperature in order to estimate the rate of heat loss. Instead, for the polymerization fronts (whose solutions have much higher thermal conductivity than fuel-air mixtures), it can easily be shown that the main source of thermal resistance is between the wall of the tube and ambient air, rather than between the hot products and the tube wall itself. In this case the heat loss rate is given by $Nu(k_g/d)A\Delta T$, where Nu is the Nusselt number for buoyant convection heat transfer from the tube wall to ambient, k_g the gas thermal conductivity, d the tube diameter, A the area exposed to heat transfer (in this case the flame thickness multiplied by the perimeter of the tube $= \pi d$), and ΔT the temperature difference between the tube wall and ambient. The rate of heat generation is $\rho C_p S A' \Delta T$, where ρ is the solution density, C_p its specific heat, and A' the cross-sectional area of the tube $= \pi d^2/4$. The ratio of the heat loss to heat generation is then $4Nu(k_g/k_s)Pe^2$, where k_s is the thermal conductivity of the solution. If this ratio is $1/\beta$ at extinction, then Pe at extinction is given by $[4\beta Nu(k_g/k_s)]^{1/2}$. To estimate the Nusselt number we assume buoyant convection on a vertical wall in air whose height is the flame thickness δ ($\delta = \alpha/S = (0.0015 \text{ cm}^2/\text{s})/(0.0048 \text{ cm/s}) = 0.31 \text{ cm}$) and width is πd . The corresponding Rayleigh number (Ra) is $g(\Delta\rho/\rho)d^3/\nu\alpha$ where $\Delta\rho/\rho$ is the fractional density change (estimated as 0.22 based on the measured limit temperature and the ideal gas law) and ν the kinematic viscosity of air. Thus (again using temperature-averaged properties) $Ra \approx (981 \text{ cm/s}^2)(0.22)(0.31 \text{ cm})^3/(.17 \text{ cm}^2/\text{s})(.25 \text{ cm}^2/\text{s}) = 150$. For a vertical plate in air with $Ra = 150$, $Nu \approx 3.3$. Using $Nu = 3.3$, $\beta = 19.9$, $k_s = 0.63 \text{ W/mK}$ (taken as that of water), $k_a = 0.028 \text{ W/mK}$, we obtain $Pe = 3.4$ at the extinction limit. Despite the simplicity of the model employed, this value is reasonably close to that seen experimentally and suggests that heat loss to ambient via buoyant convection is the mechanism of extinction for the data shown in Figure #1.

For the isothermal tube walls (corresponding to our experiments in which the tubes were placed in a stirred water bath), the same type of analysis as that presented in the previous paragraph can be used to predict that the limit Peclet number would be $[4\beta Nu]^{1/2} \approx 17$, where in this case $Nu = 3.75$ is the value for convective heat transfer for laminar pipe flow with isothermal walls. In a 16 mm diameter tube, this value of limit Pe would require $S \geq 0.016 \text{ cm/s}$. With $E = 13.5$ kcal/mole and $S = 0.0048 \text{ cm/s}$ at $T^* = 68^\circ\text{C}$, we can infer that $T^* \geq 115^\circ\text{C}$ would be required to obtain $S \geq 0.016 \text{ cm/s}$. Thus, for a 16 mm diameter tube with isothermal, ambient temperature walls, bubbling would always be expected at atmospheric pressure for any solution having a high enough value of S to avoid extinction. Another means to avoid extinction is by using larger diameter tubes that would allow lower S for the same Pe . According to our estimate of activation energy,

a value of T^* of 100°C corresponds to $S \approx 0.010$ cm/s. For a limit Pe of 17, the corresponding d is about 25 mm. Thus, for sufficiently large tubes, it should be possible to obtain solutions that do not extinguish nor bubble even for isothermal, ambient temperature wall boundary conditions.

Summary and conclusions

Frontal polymerization at ambient pressure using water as the solvent has been demonstrated by using a very reactive monomer (AA) and free-radical initiator (AP) that enabled self-propagating free-radical polymerization fronts to occur at temperatures below 100°C . The range of AA and AP concentrations producing polymerization fronts is limited by extinguishments via heat losses at low AA and AP concentrations, and boiling at high concentrations. The heat losses leading to extinction appear to be due to buoyant convection from the tube wall to ambient air. When the wall condition is isothermal, the range of compositions exhibiting propagating fronts is much smaller and no AA and AP concentrations exhibited non-bubbling fronts. It is shown, however, that with sufficiently large tubes, non-bubbling propagating fronts could probably be obtained. It is suggested that frontal polymerization in water at ambient pressure could lead to new practical applications because of the cost and environmental issues associated with solvents other than water and the inconvenience of using pressures higher than atmospheric to avoid boiling.

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