

Supplementary Information

Experimental details for frontal polymerization set-up

Acrylamide monomer (> 99%, Sigma-Aldrich) is dissolved in dimethyl sulfoxide (DMSO, Fisher) with potassium persulfate (Sigma-Aldrich) acting as the reaction initiator. Trace amounts of hydroquinone (Acros, 25 µg/ml of hydroquinone in DMSO) are used as an inhibitor to eliminate spontaneous polymerization thus to achieve a better control of the polymerization process. For all the experiments, 1g/ml of acrylamide in DMSO and 1:750 ratio of initiator to monomer (by moles) is used. The reaction chamber consists of a home-built rectangular Teflon jacket sandwiched between two thick (≈6 mm) borosilicate glass plates (McMaster Carr, 75 mm x 25 mm). The thickness of the Teflon jacket (lateral dimensions 60 mm x 15 mm) is varied from 0.4 to 5 mm to achieve different degrees of vertical confinement in the reaction chamber. The system is ignited by holding a rectangular soldering iron (≈200°C) in contact with one of the narrower edges of the reaction chamber. Snapshots of the propagating front are taken at regular time intervals with a Canon Rebel iX camera (Canon). Thermal images of the propagating front are captured using a FLIR A325sc infrared camera (FLIR). An hour after the ignition, the system is dismantled and the reaction is quenched by dunking the chamber into liquid nitrogen. Polymer samples are taken at equispaced intervals (1 cm) successively from the heat source for size exclusion chromatography (SEC) characterization. The samples are dissolved in 0.1 M sodium nitrate (Sigma-Aldrich) aqueous solution (HPLC grade water, Fisher) to prepare 1µg/ml solutions. Those are passed through SEC columns (Waters) in an aqueous medium (eluent: 0.1 M sodium nitrate solution) and subsequently characterized using light-scattering (Wyatt) and differential refractive index (Waters) detectors.

Calculating the rate of initiation using Differential Scanning Calorimetry (DSC)

The thermal decomposition of potassium persulfate leads to formation of free radicals that initiate the polymerization process. The kinetics of the thermal decomposition of the initiator was characterized using differential scanning calorimetry (Q2000 differential scanning calorimeter, TA Instruments). The DSC trace of potassium persulfate is shown in **Figure S1a**. The Arrhenius constants for the initiator decomposition were obtained as following. The heat of

reaction ΔH_{tot} is evaluated by integrating the dH/dt curve (zeroed to the baseline value) with respect to temperature and dividing by the heating rate ($^{\circ}\text{C}/\text{min}$) [1]. Then the reaction conversion $x(T)$ at each temperature is calculated by integrating the heat evolved up to the temperature of interest (ΔH_i) and dividing by the total heat of reaction (ΔH_{tot}). The rate constant k_d of initiator decomposition, assuming a first order reaction, is given by:

$$k_d(T) = \frac{\Delta H}{\Delta T} \frac{1}{\Delta H_{tot}(1 - x(T))}$$

In order to calculate k_d values for each temperature, we generate an Arrhenius plot in the form of $\ln k_d$ vs. $1/T(\text{K})$. The linear portion of the plot, typically the values between 1% and 50% of initiator conversion, is fitted to a line, and the slope and intercept of the best-fitting line are used to determine the activation energy and the pre-exponential factor, respectively. **Figure S1b** shows the Arrhenius plot derived from the DSC trace for potassium persulfate. The activation energy was determined to be ≈ 134 kJ/mol, and the pre-exponential factor $\approx 10^{18} \text{ s}^{-1}$.

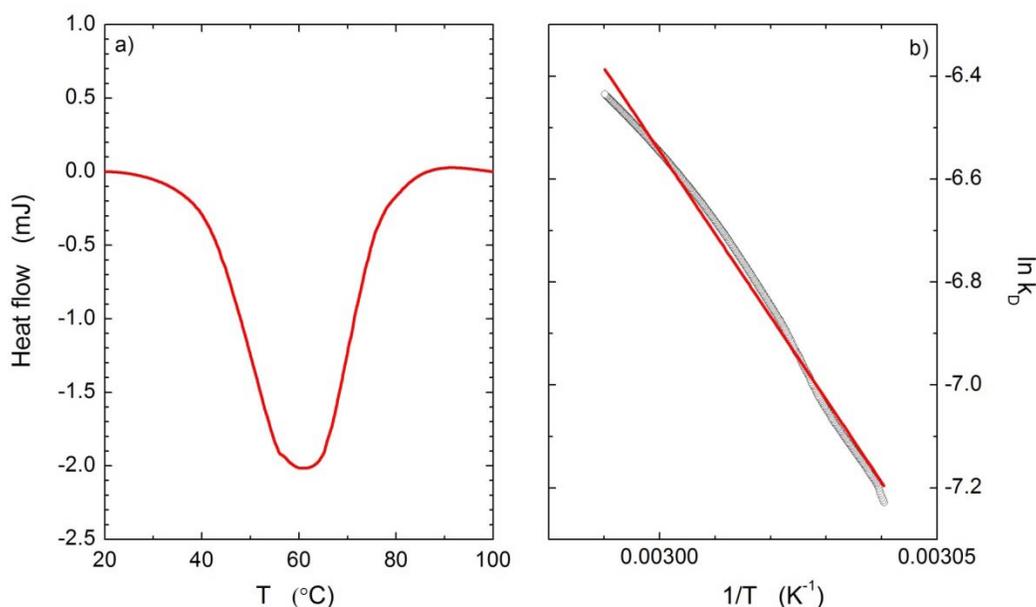


Figure S1. a) DSC trace of potassium persulfate at 5°C heating rate. b) Linear portion of Arrhenius plot derived from DSC trace in **Figure S1a**.

Molecular Weight calculations using Gillespie's Stochastic Simulation Algorithm (GSSA)

The temperature at a specific location inside the frontal polymerization system is a function of time after initiation and distance from the heat source. Since the polymer chain lengths depend on by the rates of initiation and propagation, which are inherently temperature-dependent, the molecular weight of the polymerization products is a function of the location (distance from heat source) and the time elapsed after initiation. We discretize the system by dividing it into equally spaced bins and assume the temperature of each bin to be uniform within a specific time interval. The glass-air top-surface temperature of each bin at a specific time is obtained from a line of best-fit to the experimental temperature profiles corresponding to a specific channel height (from the IR images). We assume conductive heat transfer from the interior of the bin to the top glass surface, across polyacrylamide and glass layers, in order to calculate temperature inside each bin. We use a stochastic Monte Carlo scheme based on Gillespie's algorithm to simulate bulk free radical polymerization (FRP) in each of the discrete bins for a specific time-interval. The Gillespie's algorithm has been previously implemented in a bulk FRP set-up by Bain *et al.* [2]. It evaluates reaction probabilities using empirical kinetic parameters and models the time dependence of reactions, resulting in significantly accurate predictions of reaction kinetics. The GSSA method considers each reacting species independently, allowing calculation of the distributions of molecular weight and sequence distribution for polymerized chains. The program calculates bulk rate constants at the reaction temperature according to the kinetic equations for acrylamide polymerization in DMSO reported in literature [3,4]. We keep count of the number of polymers generated, the average molecular weight, the number of monomers, the number of initiators and the monomer concentration in each bin after each discrete time interval. Since the radicals are short-lived, we rightly assume that the polymer chains generated in each time interval are dead at the end of the simulation run. The unconverted monomer and initiator concentrations at the end of each run serves as the input parameters for the simulation for the next time interval. At the end of the entire simulation run, we calculate the weighted average molecular weight in each bin by summing over all the discrete time intervals. The overall molecular weight of the polymer product is then calculated by summing over all the bins with appropriate weightage. The molecular weight distributions corresponding to different distances from heating source and the overall average molecular weight of the polymerization products

calculated at the end of the consecutive runs corresponding to a channel height of 0.4 mm are shown in **Figure S2**.

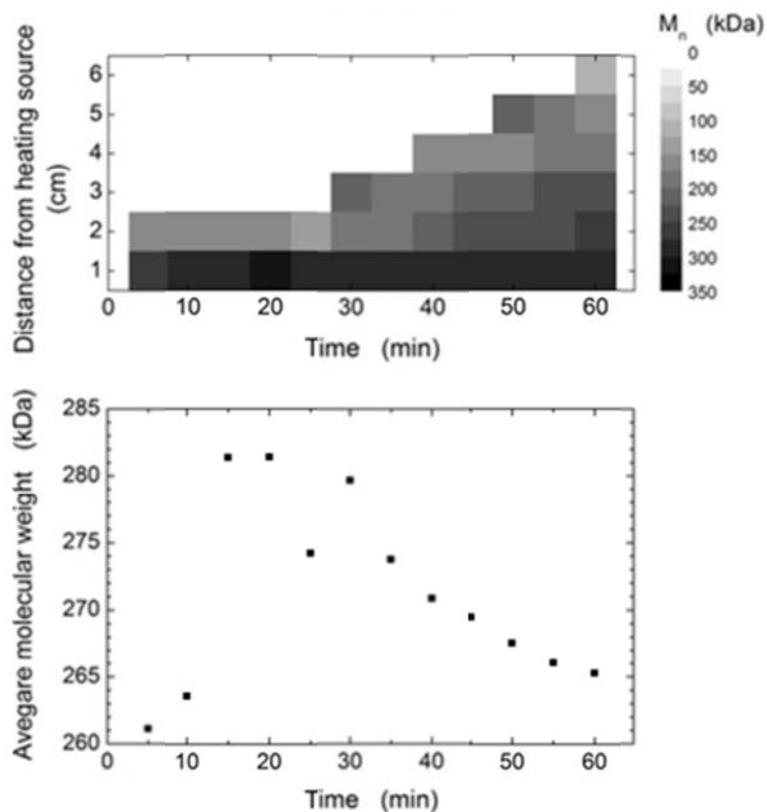


Figure S2. (top) Molecular weight distribution of polymer at different distances from the heat source at the end of consecutive runs. (bottom) Variation of overall average molecular weight of the polymer with time after initiation for channel height of 0.4 mm.

References

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