Supplementary Information for

Patterned crystal growth and heat wave generation in hydrogels

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S1. Supplementary video captions

Video S1. Crystallization of a metastable solution polymerized through a photomask. Sample was exposed to UV light in all areas outside the letter H, which was covered by a mask. Precursor solution composition: 2.8 M acrylamide, 26 mM N,N’-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM α-ketoglutaric acid. This video also demonstrates the procedure for crystallizing samples suspended in air; a paper grid supports the sample. Ruler shown for scale; numbered increments are centimeters. Video is shown in real time.

Video S2. Video microscopy (10x) through crossed linear polarizers showing progression of crystal growth along interface between masked and unmasked regions. Video shown at 10x magnification and 0.2x speed with automatic exposure. First frame shows faint phase boundary between masked (left) and unmasked (right) regions before growth front reaches field of view. Crystals grow rapidly through masked region with large, needle-like domains, then slowly outward through unmasked region where additives have been photopolymerized, forming small crystallites. Higher magnification view of unmasked region is shown in Figure S1; electron micrographs of similar samples are shown in Figure S2. After some time has passed, a secondary cascade of small crystallites engulfs the large needles in the masked region; this corresponds to the growth of bright white areas visible in Figure 4A and Video S4. Secondary crystallite growth appears to be restricted to masked areas. Precursor solution composition: 2.8 M acrylamide, 26 mM N,N’-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM α-ketoglutaric acid.

Video S3. Video microscopy (5x) through crossed linear polarizers showing progression of crystal growth along interface between masked and unmasked regions. Video shown at 5x magnification and 0.2x speed with automatic exposure. See caption from Video S2. This video also shows converging fronts and bubble formation, which is common in regions where fronts converge and hypothesized to be a result of gel contraction during crystallization due to the higher density of the solid phase.

Video S4. Visible, infrared, and threshold temperature videos of crystal growth in hydrogel polymerized through “hello” photomask. 10x speed; sample was crystallized on a Peltier cold plate held at 18˚C. Precursor solution composition: 2.8 M acrylamide, 13 mM N,N’-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM α-ketoglutaric acid. Threshold temperature shown: 34.5 ℃.

Video S5. Visible, infrared, and threshold temperature videos of crystal growth in hydrogel polymerized through hexagonal grid photomask. 10x speed; sample was crystallized while suspended in air on a paper grid, slowing heat dissipation in areas with converging fronts. Precursor solution composition: 2.8 M acrylamide, 13 mM N,N’-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM α-ketoglutaric acid. Threshold temperature shown: 42.5 ℃.

Video S6. Confocal Z-stack showing crystallization-induced wave of thermoresponsive gel contraction. 30x speed. Top-left is XZ plane (1.28 x 0.24 mm), bottom-left is XY plane (1.28 x 1.28 mm), bottom-right is YZ plane (0.24 x 1.28 mm). Film composition: N-isopropylacrylamide and Nile blue acrylamide cross-linked with polyethylene glycol diacrylate in water, frozen and thawed twice to induce microporosity and improve swelling kinetics. Fluorescence emission
appears in red ($\lambda_{ex} = 488$ nm); transmitted light appears in white and vanishes once crystals pass under sample. Metastable hydrogel precursor solution composition: 2.8 M acrylamide, 19.5 mM $N,N'$-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM $\alpha$-ketoglutaric acid; 2 mm spacer. Channel below area on screen was unmasked during polymerization.

**Video S7.** Confocal Z-stack showing crystallization-induced wave of thermoresponsive gel contraction. 35x speed. Top-left is XZ plane (2.56 x 0.26 mm), bottom-left is XY plane (2.56 x 2.56 mm), bottom-right is YZ plane (0.26 x 2.56 mm). Film composition: $N$-isopropylacrylamide and Nile blue acrylamide cross-linked with polyethylene glycol diacrylate in water, frozen and thawed twice to induce microporosity and improve swelling kinetics. Fluorescence emission appears in red ($\lambda_{ex} = 488$ nm). Metastable hydrogel precursor solution composition: 2.8 M acrylamide, 19.5 mM $N,N'$-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM $\alpha$-ketoglutaric acid; 2 mm spacer. Channel below area on screen was unmasked during polymerization.

**Video S8.** Confocal Z-stack showing selective gel contraction over masked region of crystallizing sample. 13x speed. Top-left is XZ plane (2.56 x 0.30 mm), bottom-left is XY plane (2.56 x 2.56 mm), bottom-right is YZ plane (0.30 x 2.56 mm). Film composition: $N$-isopropylacrylamide and Nile blue acrylamide cross-linked with polyethylene glycol diacrylate in water, frozen and thawed twice to induce microporosity and improve swelling kinetics. Fluorescence emission appears in red ($\lambda_{ex} = 488$ nm). Metastable hydrogel precursor solution composition: 2.8 M acrylamide, 19.5 mM $N,N'$-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM $\alpha$-ketoglutaric acid; 2 mm spacer. Channel below area on screen was masked on left side during polymerization.

**Video S9.** Wax melting and wetting processes patterned using heat from crystal growth in hydrogel polymerized through “HOT” photomask. 10x speed. A layer of wax had been deposited onto the underside of the paper, which was attached using thermally conductive glue to the top of a channel bearing a patterned metastable hydrogel. Sample was crystallized on a Peltier cold plate held at 20°C. Wax composition: 1% (w/v) Oil Blue N in icosane. Hydrogel precursor solution composition: 2.8 M acrylamide, 19.5 mM $N,N'$-methylenebisacrylamide, 7.0 M sodium acetate, 2 mM $\alpha$-ketoglutaric acid.
S2. Precursor solution compositions by weight and molarity

When all components are fully dissolved, each solution has a final volume of 10 mL.

Table S1. Precursor solution compositions.

| Sample composition (molar) | deionized water (mL) | anhydrous sodium acetate (g) | Acrylamide (g) | N,N'-methylenedibisacrylamide (mg) |
|---------------------------|----------------------|-----------------------------|----------------|----------------------------------|
| 7.0 M NaAc                | 6.3                  | 5.75                        | --             | --                               |
| 7.0 M NaAc 0.7 M acrylamide | 5.9               | 5.75                        | 0.50           | --                               |
| 7.0 M NaAc 1.4 M acrylamide | 5.4                | 5.75                        | 1.0            | --                               |
| 7.0 M NaAc 2.1 M acrylamide | 4.9                | 5.75                        | 1.5            | --                               |
| 7.0 M NaAc 2.8 M acrylamide | 4.4                | 5.75                        | 2.0            | --                               |
| 7.0 M NaAc 2.8 M acrylamide 13 mM bis | 4.4            | 5.75                        | 2.0            | 20                               |

S3. Electron microscopy and crystal size characterization

Figure S1. Scanning electron micrographs of cured, crystallized sample containing 2.8 M acrylamide, 19.5 mM N,N'-methylenedibisacrylamide, 7.0 M sodium acetate, and 2 mM α-ketoglutaric acid. A. Boundary between masked (top) and unmasked (bottom) areas. B. Detail of unmasked area.
Figure S2. Scanning electron micrographs of cured, crystalline samples containing 7.0 M sodium acetate and varying concentrations of acrylamide polymerized with 2 mM α-ketoglutaric acid and without a cross-linker. Approximate domain sizes are aggregated in Table S2. A. No acrylamide. B. 0.7 M acrylamide. C. 1.4 M acrylamide (sectioned; corner visible). D. 2.1 M acrylamide (cross-section). E. 2.8 M acrylamide (cross-section; features clearly visible at this magnification are artifacts from sectioning). E. 2.8 M acrylamide (cross-section) at higher magnification.
Table S2. Approximate diameters of pores or crystalline domains in polymer solutions with a range of acrylamide concentrations. Extracted from SEM images such as those in Figure S2, plotted in Figure S3.

| Acrylamide concentration (M) | Crystal domain or pore diameter (µm) |
|------------------------------|-------------------------------------|
| 0                            | 80 - 200                            |
| 0.7                          | 20 - 120                            |
| 1.4                          | 10 - 40                             |
| 2.1                          | 0.5 - 5                             |
| 2.8                          | 0.1 - 1                             |

Figure S3. Crystal/pore size ranges from Table S2 fit with Equations S6 (red dotted line) and S8 (blue dashed line).

S4. Consideration of mechanisms for polymerization-induced crystal growth inhibition

Figure S4. Fits of various models described in this section to the data shown in Figure 2A.
A. Additive adsorption mechanisms

One possible mechanism by which additives might inhibit crystal growth more strongly when polymerized than as monomers in solution involves binding to the surface of the growing crystal, blocking its progression. We have fit our sodium acetate trihydrate crystal growth front velocity data in the presence of unpolymerized acrylamide to three leading models of crystal growth kinetics in the presence of adsorbing additives (Figure S4). These models differ slightly in their assumptions and functional forms as described below; an excellent overview of these models is provided in a monograph by Sangwal.\(^1\) Each model expresses the average linear step growth velocity in the presence of additives (\(v\)) normalized by the velocity in the absence of impurities (\(v_0\)) in terms of the additive concentration (\(c_{\text{add}}\)), the affinity of the additive for the surface (\(K\)), and an effectiveness factor (\(\alpha\)). The normalized average step velocity \(v/v_0\) is assumed to equal the normalized average face growth velocity via the Burton-Cabrera-Frank screw dislocation mechanism.\(^2\)

First, the model developed by Cabrera and Vermilyea\(^3\) (Equation S1) assumes that additive particles adsorb to the surface terrace and are immobile compared to the velocity of the step ledges. These particles prevent the progression of step growth when they are spaced close enough together to prevent a two-dimensional crystal nucleus of critical size from squeezing between them. A geometric mean of the step velocity is used. The effectiveness factor \(\alpha = \frac{r_{2D}^*}{\lambda} = \frac{a \gamma_1}{k_B T \lambda \sigma}\), where \(r_{2D}^*\) is the critical radius of a two-dimensional nucleus, \(\lambda\) is the average distance between adsorption sites on the surface, \(a\) is the diameter of a crystallizing molecule, \(\gamma_1\) is the linear edge free energy (related to the surface free energy \(\gamma\) by \(\gamma_1 = \gamma a^2\)), \(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(\sigma\) is the relative supersaturation of the crystallizing species. In this model, \(0 < \alpha < \infty\); additives with \(\alpha > 0.5\) can arrest crystal growth entirely at sufficient concentration. Using a Langmuir adsorption isotherm, the normalized velocity is expressed as Equation S1.

\[
\frac{v}{v_0} = \sqrt{1 - 2\alpha \frac{K c_{\text{add}}}{1 + K c_{\text{add}}}}
\]

(S1)

Next, a similar model developed by Kubota and Mullin\(^4\) instead uses an arithmetic mean of the step velocity; further analysis by Sangwal asserts that this model also applies in the case of mobile additives, which would adsorb preferentially to kinks in step ledges and block their further progression.\(^1\) The effectiveness factor takes the same form as the Cabrera-Vermilyea model: \(\alpha = \frac{r_{2D}^*}{x_0} = \frac{a \gamma_1}{k_B T x_0 \sigma}\), where \(x_0\) is the average distance between adsorption sites in the ledge (\(i.e.\) kinks). Again, \(0 < \alpha < \infty\); however, in this model, fully arresting growth requires that \(\alpha > 1\).

\[
\frac{v}{v_0} = 1 - \alpha \frac{K c_{\text{add}}}{1 + K c_{\text{add}}}
\]

(S2)

The earlier model developed by Bliznakov\(^5,6\) and refined by Chernov\(^7\) is also expressed using Equation S2, except that \(0 < \alpha < 1\), implying that crystal growth impeded by this mechanism can
never be fully arrested. This formulation eschews a consideration of critical nuclei; instead, $\alpha = \frac{v_0 - v_i}{v_0}$, where $v_i$ is the step growth rate in the presence of impurities at full coverage.

Each of these models fits well to our data from uncured solutions of acrylamide (Figure S4, Table S3). The models fit less well to the polymerized data sets; however, the free radical polymerization process used in this work produces a statistical distribution of molecular weights rather than monodisperse polymers. It may therefore be inappropriate to use the initial monomer concentration as $c_{add}$ in these models. However, polymerization can be reasonably expected to increase the binding affinity of an additive through cooperative effects, which is reflected in the fit parameters in Table S3.

### Table S3. Fitting parameters for additive adsorption models.

| Model                        | Unpolymerized samples | Polymerized samples |
|------------------------------|-----------------------|---------------------|
|                              | $\alpha$ | $K$ (M$^{-1}$) | $\alpha$ | $K$ (M$^{-1}$) |
| Cabrera-Vermilyea            | 0.688    | 0.283            | 0.514    | 5.68          |
| Kubota-Mullin                | 1.255    | 0.460            | 1.17     | 1.61          |
| Bliznakov-Chernov            | 0.982    | 0.796            | 0.991    | 5.14          |

#### B. Pore penetration mechanism

Another plausible mechanism by which polymeric additives may slow crystal growth requires considering the thermodynamics of crystallization in pores. When crystals are sufficiently small and have a high enough interfacial curvature ($\kappa$), the interfacial energy between the crystal and liquid phases, $\gamma$, contributes non-negligibly to the pressure inside the crystal $p_c$ according to $p_c = p_L + \gamma \kappa$, where $p_L$ is the pressure in the liquid. The normal melting point of a crystal, $T_m$, applies to infinitely large crystals with no curvature in contact with a liquid phase at its vapor pressure, $p_e$. The actual melting point $\tilde{T}_m$ of a crystal with finite curvature in a liquid whose pressure may deviate from $p_e$ is expressed by Equation S3; this curvature-related difference is known as the Gibbs-Thomson effect and is reviewed along with other thermodynamic considerations of crystallization in porous media by Scherer\textsuperscript{10,11} and more recently by Meldrum and O’Shaughnessy.\textsuperscript{12} In this formula, $v_L$ and $v_c$ are the partial molar volumes of the liquid and crystalline phases and $\Delta S_{fus,v}$ is the entropy of fusion of the crystal per unit volume.

$$\tilde{T}_m - T_m = \left(\frac{v_L - v_c}{v_c}\right) \frac{p_L - p_e}{\Delta S_{fus,v}} - \frac{\gamma \kappa}{\Delta S_{fus,v}}$$  \hspace{1cm} (S3)

To penetrate a pore of diameter $\xi$, a crystal must adopt a curvature $\kappa = \frac{2}{\xi}$; if $p_L = p_e$, then

$$\tilde{T}_m = T_m - \frac{2\gamma}{\xi \Delta S_{fus,v}}$$  \hspace{1cm} (S4)

This reduction in the melting point reduces the degree of supercooling ($\Delta T = \tilde{T}_m - T$) at room temperature, which is the driving force for crystallization in supercooled melts. This driving force is generally related to the crystal growth rate by a function of the form $v = k (\Delta T)^g$, where $k$ is a growth rate constant and $g$ is the “order” of the crystallization process (distinct from “order” in
chemical kinetics; here \( g \) has no obvious fundamental meaning) where \( 1 < g < 2.5 \). For constant \( T \), constructing a growth rate function in this way results in a function of the form:

\[
v = k((T_m - T) - \frac{2\gamma}{\xi \Delta S_{fus,p}})^g
\]

(S5)

The reduction of the driving force in porous media owing to the Gibbs-Thomson effect therefore lowers the crystal growth front velocity as the pore size is reduced.

Even in the absence of cross-linker, sufficiently concentrated “semi-dilute” polymer solutions have a characteristic mesh size. (“Semi-dilute,” in the parlance of polymer physics, indicates that the polymer fraction exceeds a threshold required for coils to overlap, but is much less than 1). The mesh size \( \xi \) of semi-dilute linear polymer coils in good solvent generally scales with the polymer fraction \( \Phi \) of the polymer according to \( \xi \cong a\Phi^{-3/4} \), where \( a \) is a constant, regardless of the degree of polymerization of the system. The molar concentration of acrylamide \( c \) is an approximately linear function of its mass fraction within the system (Supplementary Information Section S2), leading to Equation S6, which yields \( v(c) \) expressed by Equation S7:

\[
\xi = ac^{-3/4}
\]

(S6)

\[
v = k((T_m - T) - Ac^{3/4})^g
\]

(S7)

where \( A = \frac{2\gamma}{a\Delta S_{fus,p}} \).

Fitting Equation S7 to the rate data where polymers were present while setting \( T_m - T \) to 38 K and allowing \( k \), \( A \), and \( g \) to vary yields the red curve shown in Figure S4 and the parameters shown in Table S4. The resulting curve is very similar to the results of fitting the Kubota-Mullin model to the polymerized data.

### Table S4. Fitting parameters for pore penetration model using different methods of determining mesh size.

| Mesh size model       | \( k \)          | \( A \) | \( g \) |
|----------------------|------------------|--------|--------|
| Scaling (Eq. S6)     | \( 2.96 \times 10^{-4} \) | 12.4   | 2.49   |
| Empirical (Eq. S8)   | \( 1.58 \times 10^{-4} \) | 0.14   | 2.47   |

However, the trend in crystal and pore sizes observed via scanning electron microscopy (Figure S2,3, Table S2) as a function of acrylamide concentration is poorly fit by Equation S6 (Figure S3, red dotted line). The distribution is better described by the empirical relation in Equation S8 (Figure S3, blue dashed line):

\[
\xi \cong a \times 10^{-bc}
\]

(S8)

where \( a = 120 \mu m \) and \( b = 0.845 \).
Substituting Equation S8 into Equation S5 yields Equation S9:

\[ v = k((T_m - T) - A \times 10^{bc})^g \]  

(S9)

where \( A = \frac{2y}{aA_{fus,v}} \). Fitting Equation S9 to the rate data where polymers were present while setting \( T_m - T \) to 38 K, \( b \) to 0.845 (derived from the empirical fit above) and allowing \( k, A, \) and \( g \) to vary yields the blue curve shown in Figure S4 and the parameters shown in Table S4. The quality of this fit is noticeably worse than that of Equation S7; other functions that empirically fit the size data as a function of acrylamide concentration in Figure S3 and Table S2 well perform similarly poorly when substituted into Equation S5 and fit to the rate data.

Note that in this section we have considered salt hydrates as supercooled melts. Similar formulations exist for crystal growth from supersaturated solutions (e.g. \( v = k(\Delta c)^g \)), where the driving gradient is the degree of supersaturation. Salt hydrates such as sodium acetate trihydrate, in which solvating water co-crystallizes with the solute to form solid crystals that melt at 58˚C at standard pressure, may be fairly considered in either way; in this case, it is simpler to consider them as melts.

C. Growth arrest and stochastic nucleation mechanism

The descriptions above present means by which the growth rates of single crystals may be suppressed in the presence of polymers. However, Figures 1C, S2 and S3 make clear that polymerized samples form highly polycrystalline composites with a crystallite size range that decreases with increasing polymer concentration. A mechanism that takes this phenomenon into account may explain the observed growth rate trends.

Invoking an argument first presented by Chernov,7 Asenath-Smith et al.15 have proposed that crystals growing into polymer fibers may experience an abrupt increase in resistance to mass transport to the interface. As sodium acetate crystals grow in a needle shape, the active growth face has a small area; small crystallites in particular may be fully occluded upon contact with the polymer mesh and halt their lengthwise growth completely. In such a case, the growth front would proceed only due to the continuous stochastic secondary nucleation of new crystallites.

We have simulated this scenario using MATLAB. To initialize the simulation, a predetermined polymer volume fraction is distributed across random voxels throughout a sample volume and initial crystal “seeds” are planted at one end. A loop of timesteps follows; during each timestep, a) each active crystal grows by a length unit, b) each crystal that has collided with a polymer, another crystal, or the sample volume boundary is rendered inactive, and c) each voxel occupied by a crystal has a set probability of nucleating a new crystal with a random orientation. A snapshot of a simulated volume containing polymers (red) and crystals (blue) is shown in Figure S5A. At each timestep, the position is recorded of the farthest plane from the starting point in which a threshold percentage of the voxels have been converted to crystal; thresholds of 10%, 1%, 0.1%, 0.01% are shown in black. By inspection, after a sufficient induction time has passed, the average rate of progression of these threshold planes is constant and equal to one another regardless of the threshold percentage (Figure S5B). Induction times increase with increased threshold percentage; the velocities of higher threshold planes over time fluctuate less than in lower thresholds.
to analyze front velocity trends, we tracked the velocity of the 1% threshold plane during the final half of growth simulations which ran for more than twice this induction time. We used a 100 x 100 x (variable length) sample volume; 25 initial seeds were evenly placed along the initial plane during initialization and randomly oriented at angles of more than 45˚ from the direction of front progression. We ran 3 simulations for each set of parameters.

**Figure S5.** Simulations of growth arrest and stochastic nucleation mechanism. **A.** Snapshot of simulation with a polymer volume fraction of 0.022125 and a nucleation probability per timestep of 0.00125. Red voxels are polymer, blue voxels are crystal, and black voxels indicate various threshold planes. **B.** Progress of threshold planes over time in the simulation shown in A. **C.** Simulated crystal growth front velocities at different polymer volume fraction and nucleation probability per timestep values overlaid with experimental rate data. Error bars show s.e.m., $N = 3$ for all values.

The two variables that affect the growth rate in simulated systems containing polymers relative to simulated systems without polymers are the polymer volume fraction and the probability of nucleation per timestep. The effects of these parameters on front velocity are shown in **Figure S5C.** Growth front rates are depressed at increased polymer volume fraction; this dependence is reduced as nucleation rates are raised. **Figure S5C** is overlaid with experimental data from **Figure 2A** (assuming 100% polymerization and that the density of polyacrylamide in solution is the same as that of solid acrylamide monomers). While no one parameter set fits the experimental data perfectly, the overall trend of a monotonically decreasing front velocity with increasing polymer concentration is captured.
D. Viscous mechanism

Finally, polymerizing the acrylamide in a solution drastically increases its viscosity (captured in the denominator of the parameter $k$ in Equation S5). The various mass transfer processes involved in crystal growth (e.g. diffusion and orientation of solute ions) may be slower in a more viscous solution, slowing the velocity of the growth front. However, polymer solutions are complex fluids in which viscous interactions are dependent on both length and time scales;\textsuperscript{16} untangling this contribution to crystal growth inhibition is non-straightforward. It may be that the processes involved in crystal growth take place on small enough characteristic length scales to be unaffected by the polymers’ contribution to the viscous environment; a past analysis of ice growth in hydrocolloid suspensions discarded viscosity as the main driver of inhibition.\textsuperscript{17}

S5. Derivation and fitting of temperature profiles

The following derivation takes as its starting point the formulation that Hopper and Uhlmann (1973) solved for the one-dimensional temperature distribution around the moving crystal-solution interface during crystal growth at a constant velocity.\textsuperscript{18} These authors found a steady state solution for the temperature profile within the liquid phase, but none exists for the temperature profile in the solid phase under the conditions they describe, which includes no heat transfer outside the system. This result is consistent with our observations of crystallizing systems suspended in air (Figure S6), in which temperatures at and behind the moving front rise over time. However, we observed that crystallizing systems on a cold plate held to a constant temperature quickly reach a temperature profile around the solid-liquid interface that remains stable over time (Figure 3A,B). When formulating the heat transfer problem under these conditions, we include a dissipation term representing conductive heat transfer to the cold plate (normal to the direction of crystal growth) that was absent in Hopper and Uhlmann’s analysis; this addition gives rise to a steady state solution (Equations S17 and S18).

![Figure S6](image_url). Spatial temperature profiles at 5-second intervals resulting from growth of sodium acetate trihydrate crystals through aqueous solutions of unpolymerized (A) and polymerized (B) additives in samples suspended in the air. Precursor solution composition for all samples: 7.0 M sodium acetate, 2.8 M acrylamide, 13 mM $N,N'$-methylenebisacrylamide, 2 mM $\alpha$-ketoglutaric acid in water. Profiles do not reach a steady state, contrasting with Figure 3A,B.
In this analysis, we derive the one-dimensional temperature distributions in the solid and liquid phase \( T_s(x), T_l(x) \) in a crystallizing supercooled system on a cold plate held at temperature \( T_\infty \) with a frame of reference centered around a solid-liquid boundary \( (x = 0) \) moving with constant velocity \( v \) (Figure S7). The system is solid in the negative domain \((-\infty < x < 0)\) and liquid in the positive domain \((0 < x < \infty)\). Equations S10 and S11 quantify heat conduction, equations S12-S14 are boundary conditions, and equation S15 is a heat balance at the interface. In the equations below, \( \alpha (m^2 s^{-1}) \) is the thermal diffusivity, \( \beta (K) \) is the latent heat scaled by specific heat capacity, and \( \gamma (s^{-1}) \) is the thermal contact conductance of the interface between the system and the cold plate scaled by heat capacity; for simplicity, these parameters are assumed to be identical between the solid and liquid states.

\[
\begin{align*}
\alpha \frac{d^2 T_s}{dx^2} + \gamma (T_s - T_0) &= v \frac{dT_s}{dx} \quad \text{S10} \\
\alpha \frac{d^2 T_l}{dx^2} + \gamma (T_l - T_0) &= v \frac{dT_l}{dx} \quad \text{S11} \\
T_s(-\infty) &= T_\infty \quad \text{S12} \\
T_l(\infty) &= T_\infty \quad \text{S13} \\
T_s(0) &= T_l(0) \quad \text{S14} \\
\frac{dT_s}{dx}\bigg|_{x=0} - \frac{dT_l}{dx}\bigg|_{x=0} &= \frac{\beta}{\alpha} \quad \text{S15}
\end{align*}
\]

Equations S10 and S11 each have solutions of the form shown in S16 where \( C_1 \) and \( C_2 \) are constants:

\[
T(x) = T_\infty + C_1 e^{-\frac{v}{2\alpha} \left(1 + \sqrt{1 + 4\alpha \gamma v^2}\right) x} + C_2 e^{-\frac{v}{2\alpha} \left(1 - \sqrt{1 + 4\alpha \gamma v^2}\right) x} \quad \text{S16}
\]

After applying boundary conditions S12-S15, equations S17 and S18 emerge as solutions:

\[
T_s(x) = T_\infty + \frac{\beta}{\sqrt{1 + 4\alpha \gamma v^2}} e^{-\frac{v}{2\alpha} \left(1 - \sqrt{1 + 4\alpha \gamma v^2}\right) x}, \quad (-\infty < x < 0) \quad \text{S17}
\]

\[
T_l(x) = T_\infty - \frac{\beta}{\sqrt{1 + 4\alpha \gamma v^2}} e^{-\frac{v}{2\alpha} \left(1 + \sqrt{1 + 4\alpha \gamma v^2}\right) x}, \quad (0 < x < \infty) \quad \text{S18}
\]
$$T(x) = T_\infty + \frac{\beta}{\sqrt{1 + 4 a^2 \frac{v}{v^2}}} e^{-\frac{v}{2 \sqrt{1 + 4 a^2 \frac{v}{v^2}}} x}, \quad 0 < x < \infty$$  \hspace{1cm} (S18)

Globally fitting these equations to the profiles at the final timepoints shown in Figure 3A, B with \(v\) fixed to the recorded front velocities (In Figure 3A, \(v = v_{unpoly} = 0.896 \text{ mm s}^{-1}\); in Figure 3B, \(v = v_{poly} = 0.131 \text{ mm s}^{-1}\)) and \(\alpha, \beta, \gamma\) allowed to vary (but shared between data sets) yielded the dashed curves in the figures and fitting parameter values listed in Table S5, which displayed reasonable agreement with literature values (which were calculated based on parameters collected for sodium acetate trihydrate in somewhat different conditions, making some discrepancy unavoidable; see Table S6). Profiles for a variety of velocities with \(\alpha, \beta, \gamma\) fixed to the fit values are shown in Figure 3C. The sharp peak present in the model fit is blunted in the experimental data for the unpolymerized sample; this may be explained by a rough (non-discrete in \(x\)) advancing front or the diffusion of this steep gradient within the thickness of the cover glass between the crystallizing solution and the infrared camera.

**Table S5:** Fitting parameter values from global fits of curves from Figure 3 A, B. See Table S6 for calculation of reference values from literature parameters.

| Parameter | Value from fit | Reference value |
|-----------|----------------|-----------------|
| \(\alpha\) | \(4.2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}\) | \(2.2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}\) |
| \(\beta\) | 34 K | 45 K |
| \(\gamma\) | 0.175 s\(^{-1}\) | |

**Table S6:** Calculation of reference values from Table S5 using literature parameters. Below, \(k\) is thermal conductivity, \(\rho\) is density, \(C_p\) is specific heat capacity at constant pressure, and \(\Delta H_{fus}\) is enthalpy of fusion.

| Parameter | Formula | Literature values |
|-----------|---------|-------------------|
| \(\alpha\) | \(\alpha = \frac{k}{\rho C_p}\) | \(k = 0.67 \text{ W m}^{-1} \text{ K}^{-1}\) (45.3 mass\% sodium acetate, solid, at 300 K)\(^{19}\) \(\rho = 1372 \text{ kg m}^{-3}\) (pure)\(^{20}\) \(C_p = 2.2 \text{ kJ kg}^{-1} \text{ K}^{-1}\) (54.3 mass\% sodium acetate, solid, at 303 K)\(^{19}\) |
| \(\beta\) | \(\beta = \frac{\Delta H_{fus}}{C_p}\) | \(C_p\) as above; \(\Delta H_{fus} = 100 \text{ kJ kg}^{-1}\) (47.5 mass\%, 303 K)\(^{19}\) |

It is clear that varying the crystal growth front velocity alone – which can be achieved by varying the composition and polymerization state of the additives to the solution – can be responsible for large changes in the temperature profile of the system. The maximum temperature can be expressed as a function of crystal growth front velocity using Equation S19. This is plotted in Figure S8; it can be observed that \(\lim_{v \to \infty} T_{max} = T_\infty + \beta = 55^\circ\text{C}\). Based on prior reports of crystallization in metastable sodium acetate solutions diluted beyond a 1:3 salt:water stoichiometric mixture,\(^{21,22}\) we expect this temperature to approach but never reach sodium acetate trihydrate’s melting point of 58 °C, which agrees with this result.
\[ T_{\text{max}} = T_s(0) = T_l(0) = T_\infty + \frac{\beta}{\sqrt{1 + \frac{4\alpha y}{\nu^2}}} \]  

(S19)

**Figure S8.** Maximum temperature varies as a function of crystal growth front velocity.

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