

Supporting Information:

A Surprisingly Gentle Approach to Cavity Containing Spherocylindrical Microparticles from Ordinary Polymer Dispersions in Flow

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S1. Experimental Details

S1.1 Materials

Styrene (STY), ethyl methacrylate (EMA), and methyl methacrylate (MMA) were obtained from Acros Organics and were each purified by passing through a column packed with alumina adsorption powder (Fisher Scientific) and then stored at -8 °C prior to use. Glycidyl methacrylate (GMA; 96% Acros Organics), potassium persulfate (KPS; Acros Organics), sodium dodecyl sulfate (SDS; Acros Organics), ethylene diamine (EDA; 99% Acros Organics), azobisisobutyronitrile (AIBN; 98% Sigma Aldrich), polyvinylpyrrolidone (Mw = 360,000) (PVP360; Sigma Aldrich), ethanol (Pharmco Products) and Dowex Marathon MR-3 mixed bed ion-exchange resin (Sigma Aldrich) were used as received.

S1.2 Dispersion Polymerization

The recipe used for the dispersion polymerizations (e.g. Figure 1a) is listed in Table S-1. PVP360 and ethanol were added in a 250 ml glass reactor under stirring. After dissolving PVP360 (~30 min), the remaining components were added to the reactor at room temperature. The reactor was then flushed with nitrogen, sealed, and suspended in an oil bath set at 70 °C and allowed to react over 24 hours. After cooling, the serum phase (including free PVP360) was replaced with deionized (DI) water by multiple centrifugation-redispersion cycles. This process also removed particles smaller than 5 μm .

Table S-1. Recipe for dispersion polymerization to produce poly(STY-co-GMA) particles.

Ingredients	Amount
Ethanol	112.50 g
PVP360	0.60 g
Styrene (STY)	19.69 g
GMA, EMA, or MMA	6.56 g
AIBN	0.69 g

S1.2.1 Glass Transition Characterization of poly(STY-co-EMA) and poly(STY-co-MMA)

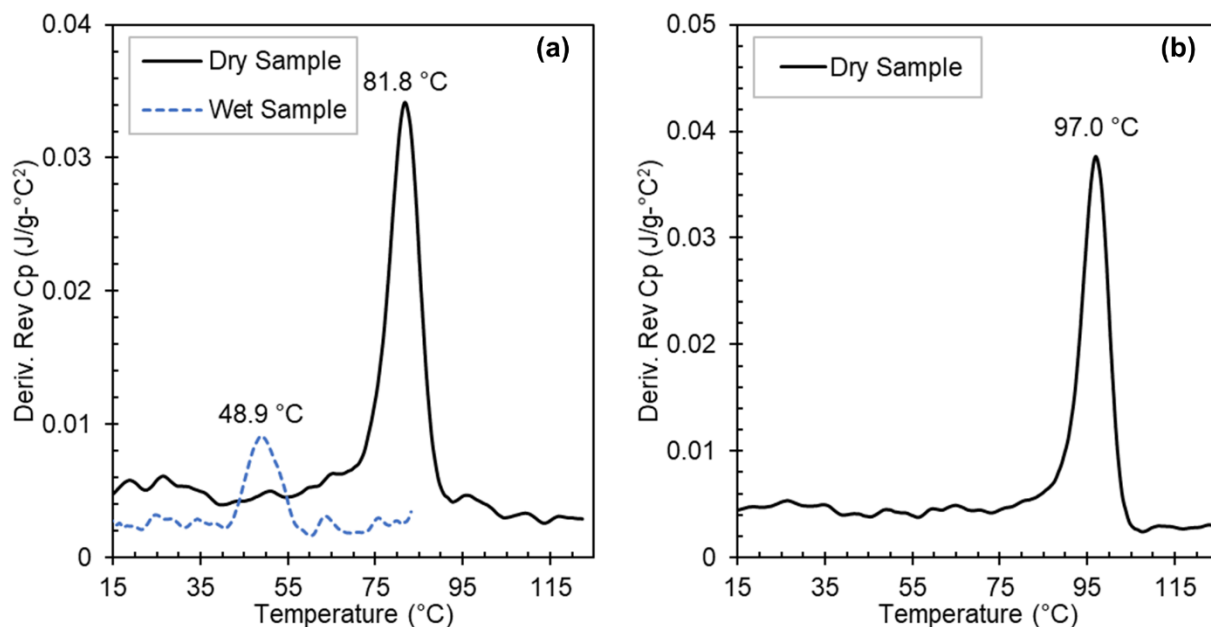


Figure S1. Differential scanning calorimetric analysis of glass transitions for a) poly(STY-co-EMA) (dry and wet sample) and b) poly(STY-co-MMA) (dry sample).

S1.2.2 Additional SEM Characterization of poly(STY-co-MMA)

Figure 2 in the main text showed images after 120 hours of stirring for best comparison to Figure 4, yet here in Figure S2 we show an image from a poly(STY-co-MMA) sample after only 24 hours of stirring at room temperature. With significantly larger particles in the size distribution, particle rupture is clearly observed even after this shorter timeframe. Figure S2b and S2c highlight the rupture occurring predominantly at the equatorial region of the cylinder with open “caps” of each side visible for certain particles.

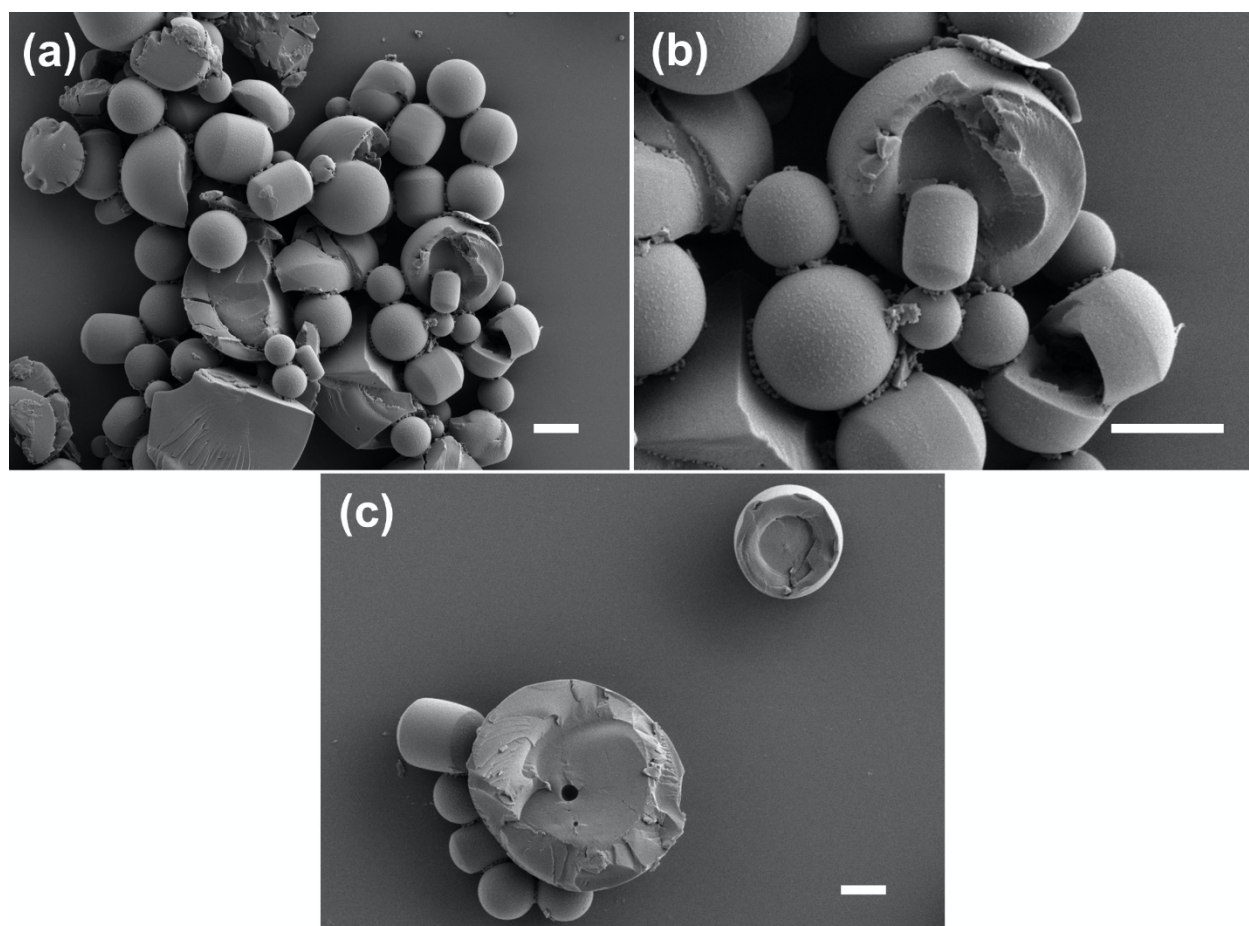


Figure S2. (a) Scanning electron microscopy (SEM) image of poly(STY-co-MMA) particles after exchanging ethanol for water, removing excess PVP, and stirring at RT for 24 hours, (b) zoomed image of a few ruptured particles and (c) image of a remaining 'cap' after full rupture. All scale bars are 5 μm .

SI.3 Polystyrene seed preparation

The polystyrene seed (for seeded dispersion polymerizations) was prepared by emulsion polymerization using the recipe listed in Table S-2. All ingredients were added to a 250 ml 3-neck jacketed reactor under stirring at room temperature and allowed to equilibrate for 30 minutes under nitrogen flush and condenser. After 30 minutes, the temperature was raised to 70 °C and the batch reaction was performed for 5 hours. The particle size was estimated as 123 nm using capillary hydrodynamic fractionization with a CHDF2000 (Matec).

In order to use these poly(STY) particles for seeded dispersion polymerization, the latex was cleaned to remove serum-phase ionic compounds (such as residual KPS, SDS and water-soluble oligomers) using a mixed-bed ion-exchange resin. Approximately 25% (by weight) of the ion exchange resin was added to the poly(STY) latex (~10% solid content) and stirred overnight. Cleaned poly(STY) latex was obtained by filtering through cheesecloth.

Table S-2. Recipe for batch emulsion polymerization to produce polystyrene seed particles.

Ingredients	Amount
DI Water	162.10 g
SDS	0.19 g
KPS	0.45 g
Styrene (STY)	17.50 g

SI.4 Seeded dispersion polymerization

Seeded dispersion polymerization to produce more uniformly sized poly(STY-co-GMA) particles using small (~120 nm) poly(STY) seed particles was done using the recipe shown in Table S-3. PVP360 and ethanol were added into a 100 mL reactor at room temperature and stirred (~30 mins) to dissolve the PVP360. Once homogeneous, the cleaned poly(STY) seed latex was added while stirring. The AIBN and monomer mixture was then added to the reactor, flushed with nitrogen for 5 minutes, sealed and then suspended in an oil bath at 70 °C. The reaction was held under these conditions for 22 hours. After cooling, the serum phase (including free PVP360) was replaced with DI water by multiple centrifugation-redispersion cycles.

Table S-3. Recipe for seeded dispersion polymerization to produce poly(STY-co-GMA) particles.

Ingredients	Amount
poly(STY) seed (0.017% solid content)	0.492 g
Ethanol	48.71 g
PVP360	0.324 g
AIBN	0.324 g
Styrene	8.10 g
GMA	2.70 g

S1.5 Characterization

S1.5.1 Differential Scanning Calorimetry (DSC)

The polymer samples were characterized via modulated-DSC (TA Instruments Q2000 modulated DSC). Dried samples were analyzed at a heating rate of 3 °C/min (modulation amplitude of ± 2 °C and a period of 60 s) from -20 °C to 150 °C. The derivative of the reversing heat capacity is plotted to more clearly reveal both the glass transition temperature as well as the width of the transition.^{S1} For the wet samples, the dispersion was first concentrated by centrifugation and then pipetted into hermetically sealed DSC pans. The DSC conditions were similar to that for the dry sample, except the maximum temperature for analysis was limited to 90 °C due to the presence of water.^{S2}

S1.5.2 Scanning Electron Microscope (SEM)

The polymer particles were analyzed by SEM using a Tescan Lyra3 GMU with a GaFIB column. The samples were dried on glass coverslips mounted onto a SEM stub. The dried samples were

then coated with Au/Pd (~15 nm thick layer) using a Hummer V Sputter (Anatech). SEM was performed at an acceleration voltage of 5 kV primarily with imaging from the secondary electron detector. For focused ion beam (FIB) conditions (e.g. Figure 1d or Figure 3), the same samples were ablated within the SEM using 30 keV Ga⁺ ions.

S1.5.3 Optical Images

The optical images were obtained from a Nikon Ti2 microscope using a Nikon DS-Ri2 camera.

S2. Volume Estimation of Spherocylindrical Particles

The volume of spherocylindrical particles was estimated directly via the SEM images. A spherocylinder can be visualized as a combination of 1 cylinder and 2 spherical caps. In order to estimate full dimensions of such particles from SEM, only particles who appear to be clearly laying prone on the SEM stub were selected. For each such particle, coordinates of 6 points (P1 ... P6) on the particle were estimated using ImageJ v1.52p (<https://imagej.nih.gov/ij>) as shown in Figure S3. The coordinate of each point is represented as (x_i, y_i) for point P_i and the distance between point P_i and P_j is represented as L_{ij} .

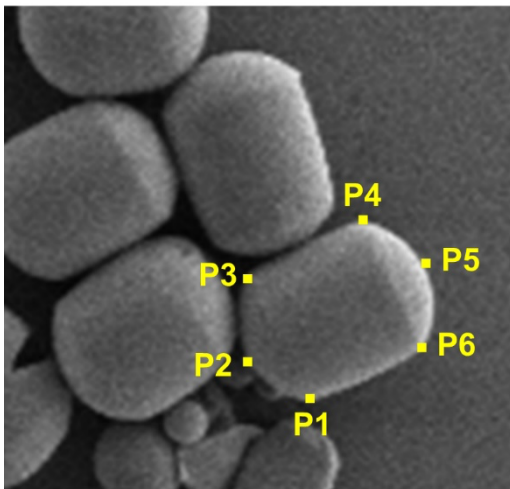


Figure S3. Identifying 6 points on a spherocylindrical particle for estimation of particle volume

The volume of the cylindrical portion (P₁.P₃.P₄.P₆) is estimated using the average dimensions for length and circular base as

$$V_{cyl} = \left(\frac{\pi}{4}\right) \left(\frac{L_{13} + L_{46}}{2}\right)^2 \left(\frac{L_{16} + L_{34}}{2}\right) \quad (S1)$$

The volume of the spherical cap can be estimated using the cap height (h) and radius of the circular base (a) as^{S3}

$$V_{sphCap} = \left(\frac{\pi}{6}\right) h(3a^2 + h^2) \quad (S2)$$

The radius of the circular base for each spherical cap was estimated as $L_{13}/2$ and $L_{46}/2$, respectively, for spherical cap P₁.P₂.P₃ and P₄.P₅.P₆. The cap height for each spherical cap was estimated, for example, for spherical cap P₁.P₂.P₃ as the perpendicular distance from point P₂ to line P₁.P₃.

S3. Additional DSC Analysis

Figure 6 in the main text shows both the dried polymer T_g analysis as well as the effective T_g, considering all aspects of plasticization potentially present in the sample. Water is an effective and known plasticizer, yet any residual PVP stabilizer that is grafted and phase-mixed with some portion of the polymer can also serve as a plasticizer. A depression in the T_g from the dried state is clearly evident, with the “wet T_g” shown to be observed at 72 °C. One challenge with measuring thermal properties of polymers in the hydrated state is the enthalpy associated with phase transitions such as melting of water during heating, which are fairly dramatic in scale compared to the glass transition of the small portion of plasticized polymer in the total sample. Here in Figure S4, we show the full temperature scale on the x-axis for the analysis shown in Figure 6, where the

heating started at $-20\text{ }^{\circ}\text{C}$. On the heat flow y-axis, one can clearly see the melting transition for the water present and the derivative of the associated heating profile specific to the reversing heat capacity on the right axis. The inset zooms in, relative to the right axis scale, to show the relation to Figure 6. Clearly, there are no other observable polymer related transitions other than the primary peak discussed in the text.

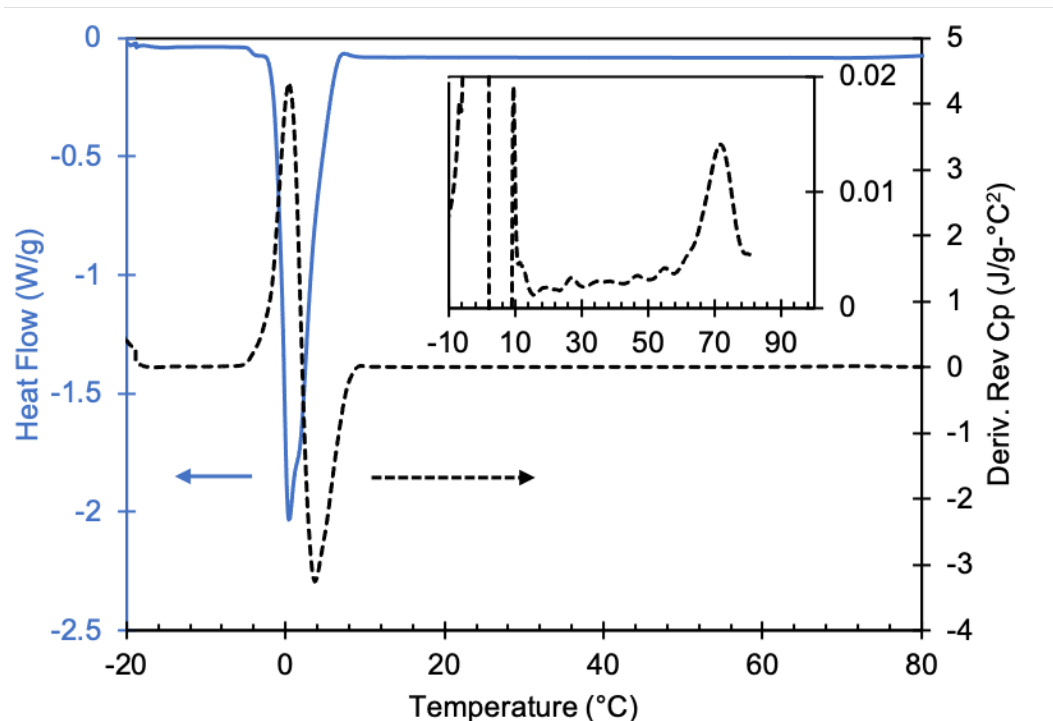


Figure S4. Full Scale of DSC Characterization shown in Figure 6

S4. Impact of Primary Particle Size, Particle T_g, and Stabilizer Type

Primary particle size, the viscosity of the particle relative to the continuous phase (vis-à-vis effective particle T_g), and even the stabilizer type are deemed important variables influencing whether or not a system will elongate to spherocylinders or not. We were able to reproduce the conditions for spherocylinders for a smaller 1.5 micron particle size homopolymer of poly(styrene) with PVP as the stabilizer, and with a PVP solution added after synthesis (conditions similar to

Minami et al. Figure 3a^{S4}). After 48 hours of stirring at room temp a small fraction of spherocylinders were observed (Figure S5).

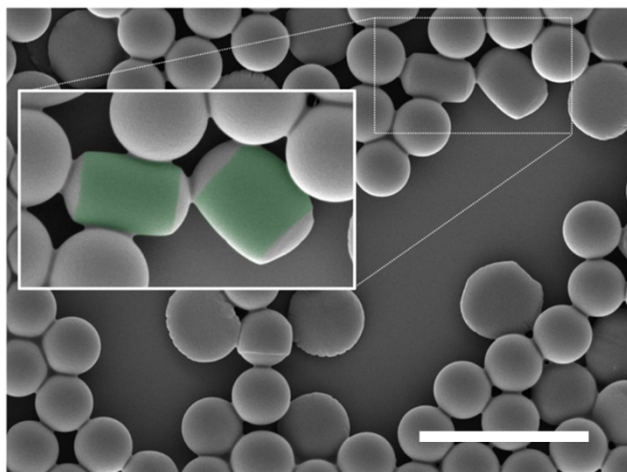


Figure S5. Reproduction of Minami et al.^{S4} for 1.5 micron poly(STY) particles with 1 wt% PVP (Mw 58k) added after synthesis. The scale bar is 5 μm .

However, contrary to the claims of that paper, we indeed were able to generate a significant fraction of spherocylinders without any PVP stabilizer present. Interestingly, the morphological transformation for a poly(STY-co-GMA) system stabilized with PAA (Mw 50k) during synthesis, and fully cleaned and exchanged to have DI water as the continuous phase, proceeded nicely but only for particle sizes larger than around 5 microns. The system as-prepared was quite polydisperse (Figure S6 a,b), which allows us to observe the impact of the process conditions as a function of particle size. Smaller particles remained spherical even after nearly 120 hrs (Figure S6 c,d).

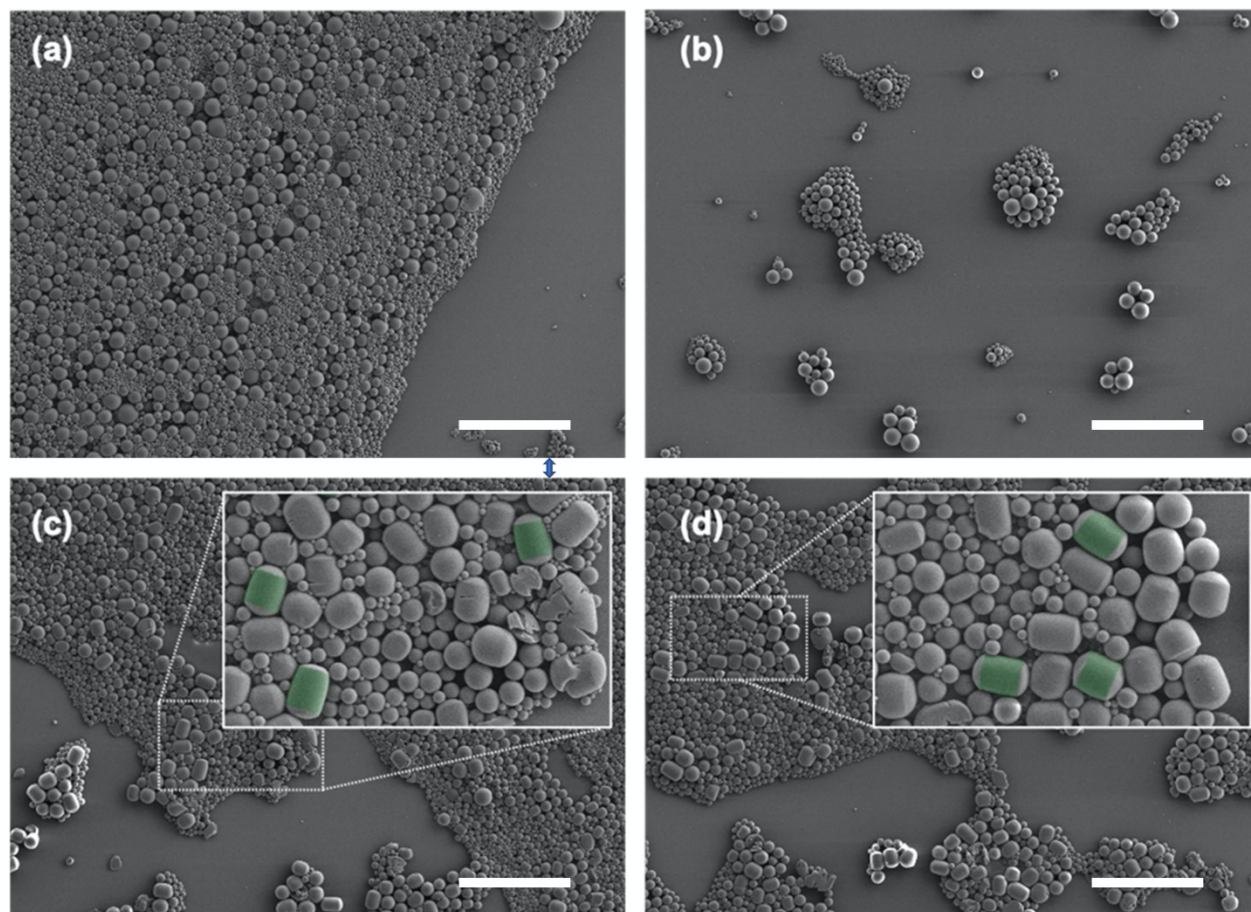


Figure S6. Highly polydisperse poly(STY-co-GMA) particles, stabilized by PAA (Mw 50k) during synthesis (**a**, **b**) and their transformation to spherocylinders after cleaning and exchanging the continuous phase for DI water and stirred at room temperature for 117 hours (**c**, **d**). The scale bar is 50 μm .

Supplemental Information References

S1 A.K. Tripathi, J.G. Tsavalas, and D.C. Sundberg, *Thermochim. Acta*, 2013, **568**, 20.

S2 B. Jiang, J.G. Tsavalas, and D.C. Sundberg, *Langmuir*, 2010, **26**, 9408.

S3 E.W. Weisstein, "Spherical Cap." From *MathWorld* - A Wolfram Web Resource. <https://mathworld.wolfram.com/SphericalCap.html>

S4 W. Li, T. Suzuki, and H. Minami, *Angew. Chemie - Int. Ed.*, 2018, **57**, 9936.