Supporting Information

Precipitation Dominated Thin Films of Acetaminophen Fabricated by Meniscus Guided Coating

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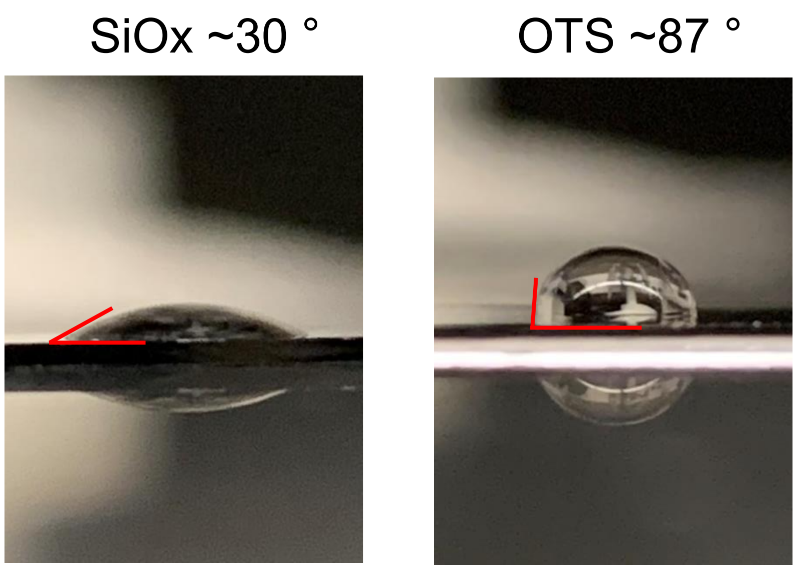
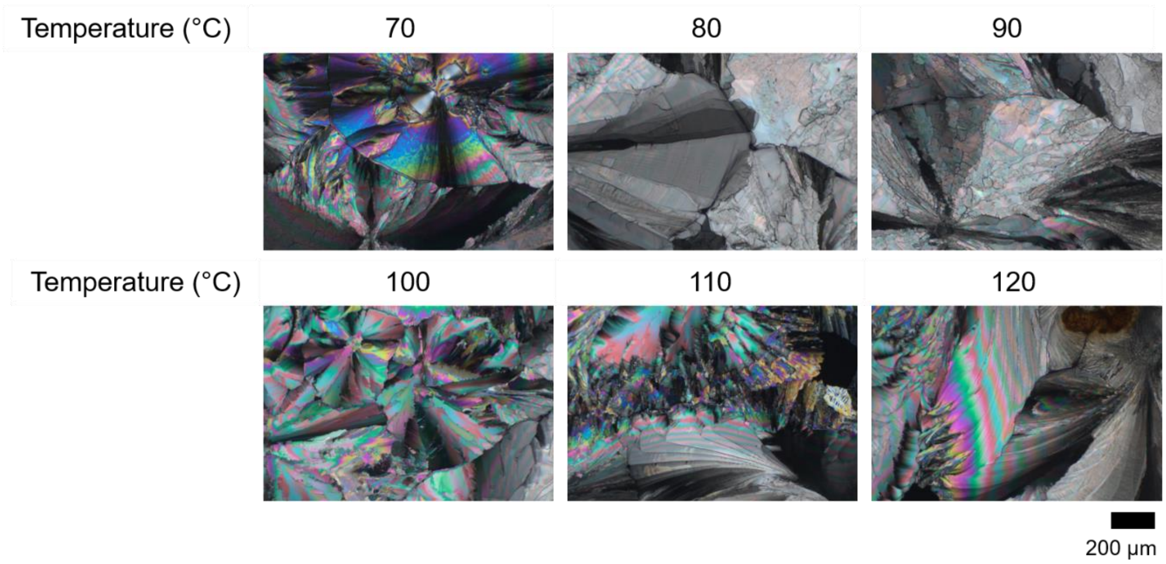
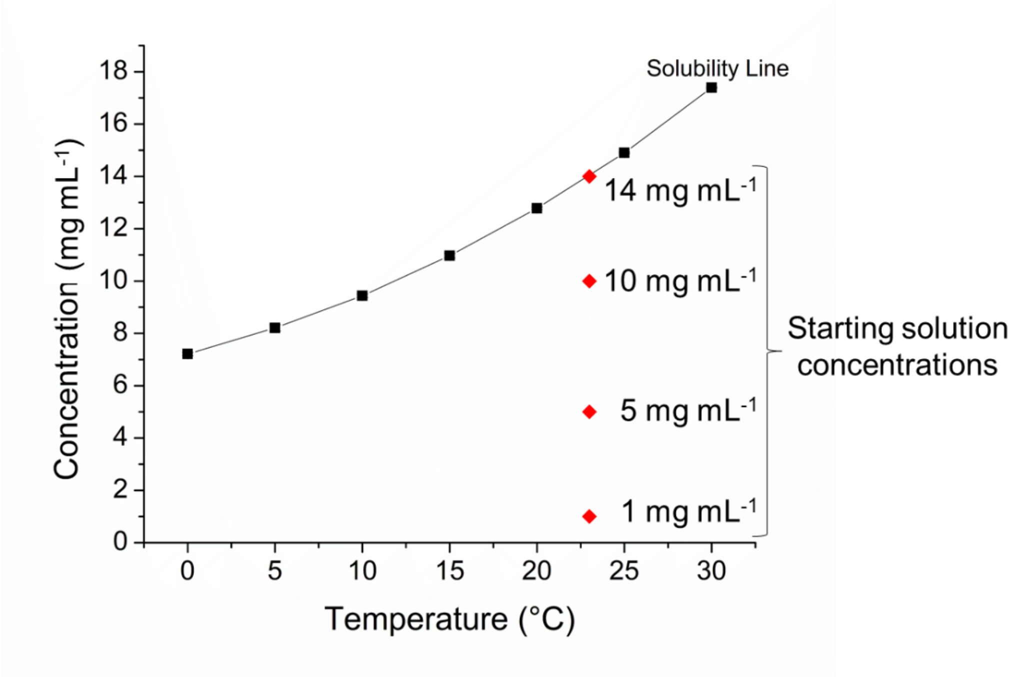


SI Figure 1: Silicon wafer (native oxide) and OTS functionalized wafer contact angles using 10 µL of water. Approximate angles found using the angle measure feature in ImageJ.



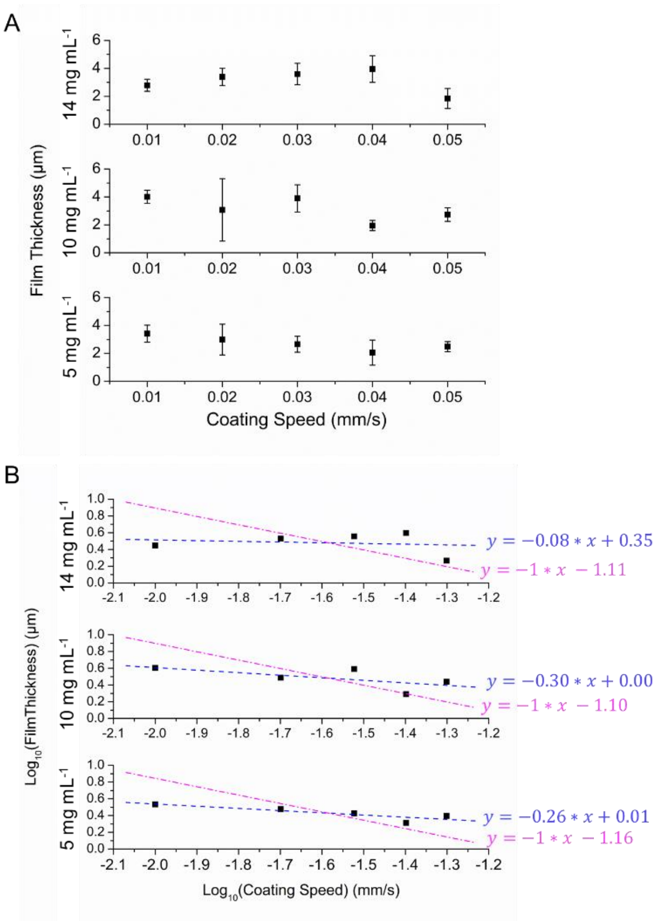
SI Figure 2: Dropcast samples created at different dropcast temperatures (70-120 °C). The coating regimes identified in the main text (Regions 1-3 in the processing diagram) show discrete crystal morphologies are isolated using MGC.



SI Figure 3: Initial solution concentrations are below the solubility limit of acetaminophen in water. Solubility data is from Granberg et al.[1]

A

B



C

***Model* 1** (- - - - -): *regress* α *and* b *parameters*

$$\log_{10}(Film\ Thickness) = \boldsymbol{\alpha} * \log_{10}(Coating\ Speed) + \boldsymbol{b}$$

	α	b
14 mg /mL	-0.083 (0.270)	0.346 (0.433)
10 mg/mL	-0.304 (0.201)	0.000 (0.323)
5 mg/mL	-0.262 (0.085)	0.012 (0.137)

***Model* 2** (- · - · -): *Fix* $\boldsymbol{\alpha = -1}$, *regress for* $\boldsymbol{b}$

$$\log_{10}(Film\ Thickness) = \boldsymbol{-1} * \log_{10}(Coating\ Speed) + \boldsymbol{b}$$

	$\alpha = -1$	b
14 mg /mL	-1	-1.105 (0.127)
10 mg/mL	-1	-1.102 (0.096)
5 mg/mL	-1	-1.155 (0.093)

SI Figure 4: a) Film thickness as a function of coating speed and concentration. b) log transformed thickness and coating speeds with two linear fits. c) Model 1 (blue, --- line) presents a better fit to the data, while the evaporative regime model (model 2, pink -.- line) does not fit the data well.

SI Table 1: Microcrystal sizes for 5 mg mL^{-1} concentration

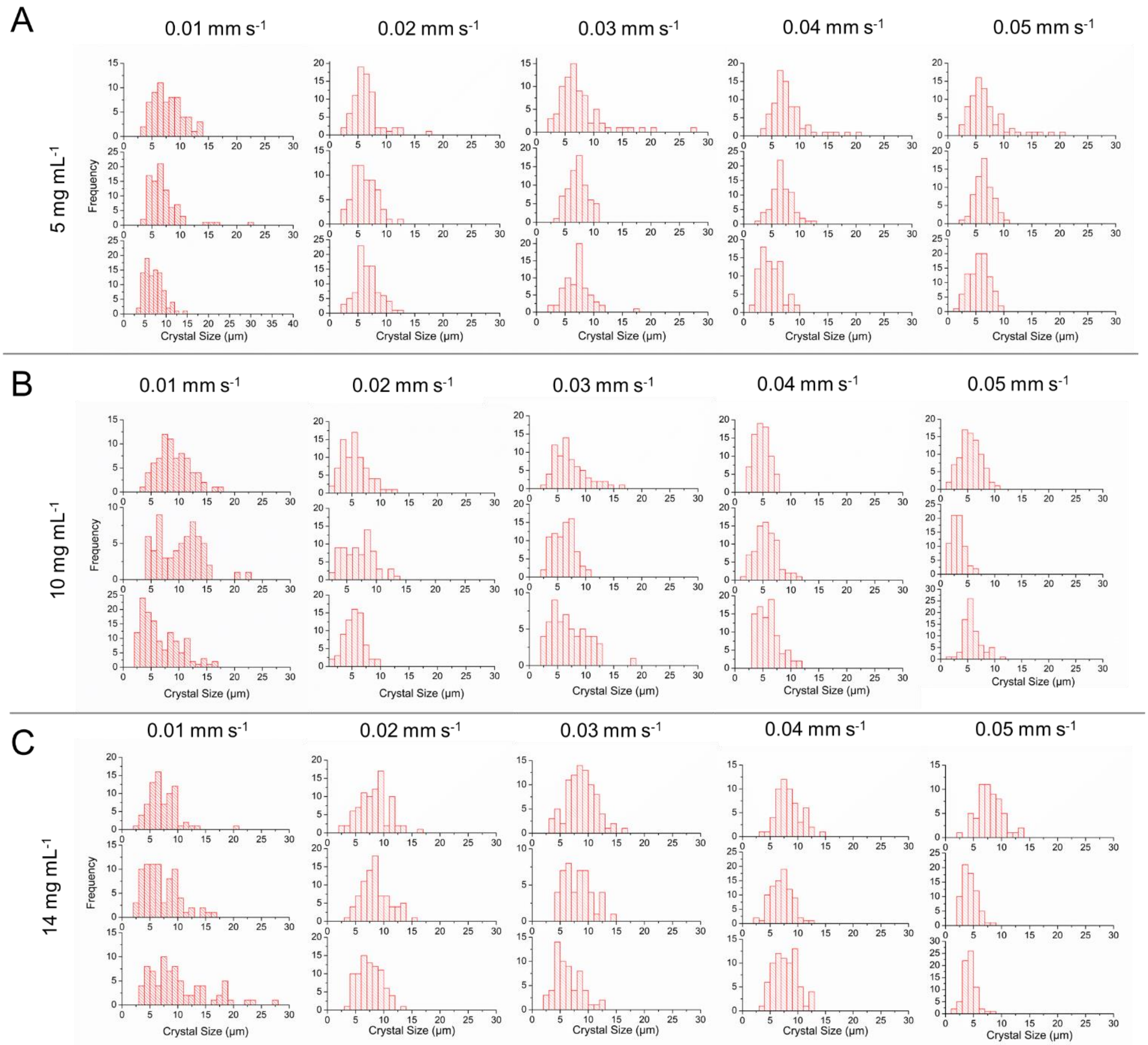
5 mg/mL				
Speed (mm s^{-1})		Average (µm)	Standard Deviation (µm)	PDI
0.01	Sample 1	7.02	2.13	0.09
0.01	Sample 2	7.02	2.82	0.16
0.01	Sample 3	7.80	2.58	0.11
0.02	Sample 1	6.66	1.97	0.09
0.02	Sample 2	6.14	2.03	0.11
0.02	Sample 3	6.37	2.41	0.14
0.03	Sample 1	7.20	2.34	0.11
0.03	Sample 2	7.21	1.71	0.06
0.03	Sample 3	7.61	4.15	0.30
0.04	Sample 1	4.87	1.86	0.15
0.04	Sample 2	6.92	1.83	0.07
0.04	Sample 3	7.90	3.10	0.15
0.05	Sample 1	5.62	1.70	0.09
0.05	Sample 2	6.46	1.62	0.06
0.05	Sample 3	6.84	3.52	0.27

SI Table 2: Microcrystal sizes for 10 mg mL^{-1} concentration

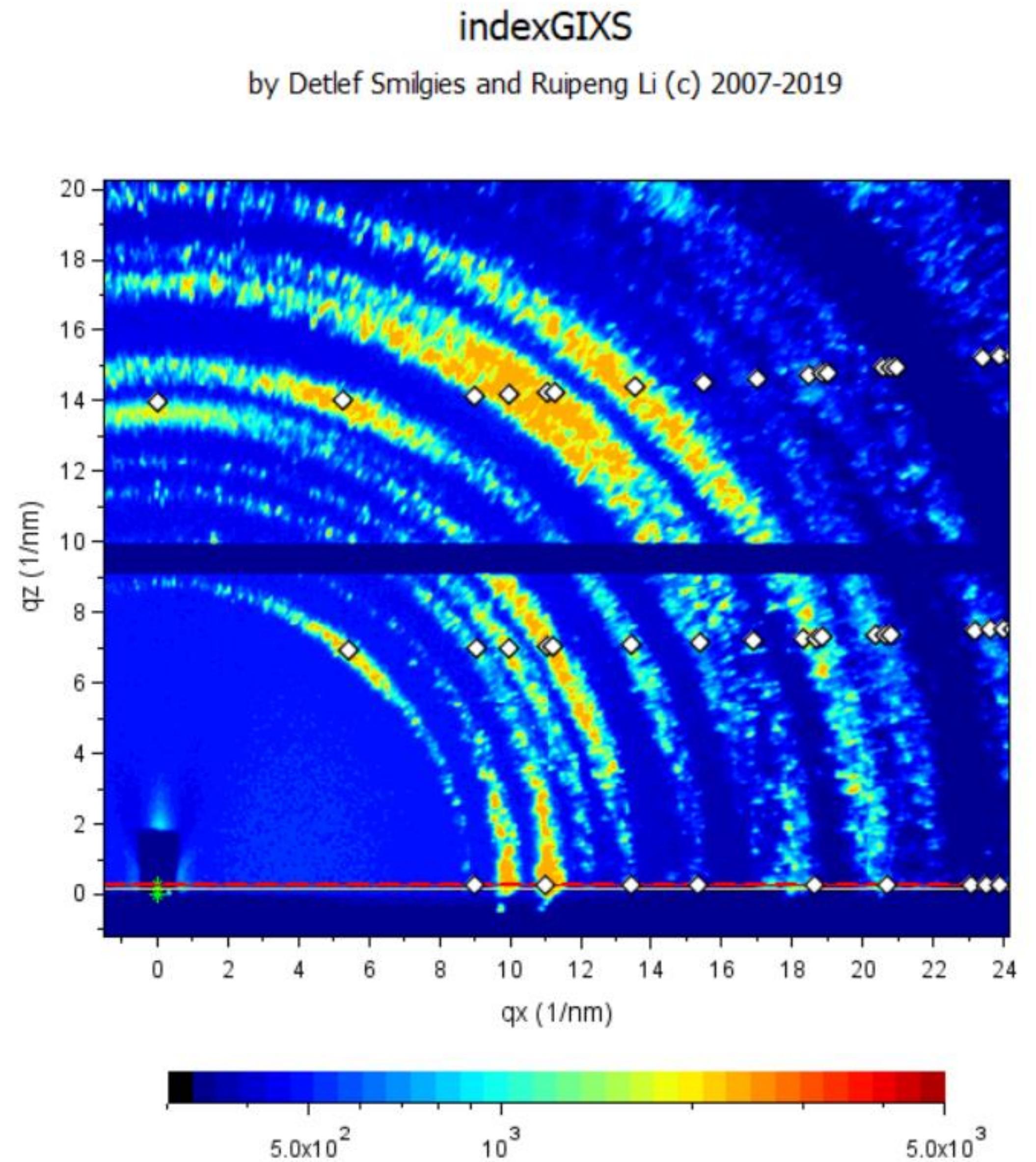
10 mg/ml				
Speed (mm s^{-1})		Average (µm)	Standard Deviation (µm)	PDI
0.01	Sample 1	6.68	3.42	0.26
0.01	Sample 2	10.19	3.93	0.15
0.01	Sample 3	9.09	2.91	0.10
0.02	Sample 1	5.38	1.62	0.09
0.02	Sample 2	7.05	2.59	0.14
0.02	Sample 3	5.49	2.29	0.17
0.03	Sample 1	7.13	3.32	0.22
0.03	Sample 2	6.09	1.87	0.09
0.03	Sample 3	7.23	2.85	0.16
0.04	Sample 1	5.95	1.97	0.11
0.04	Sample 2	5.69	2.03	0.13
0.04	Sample 3	4.80	1.34	0.08
0.05	Sample 1	5.83	1.76	0.09
0.05	Sample 2	3.26	1.17	0.13
0.05	Sample 3	5.50	1.93	0.12

SI Table 3: Microcrystal sizes for 14 mg mL^{-1} concentration

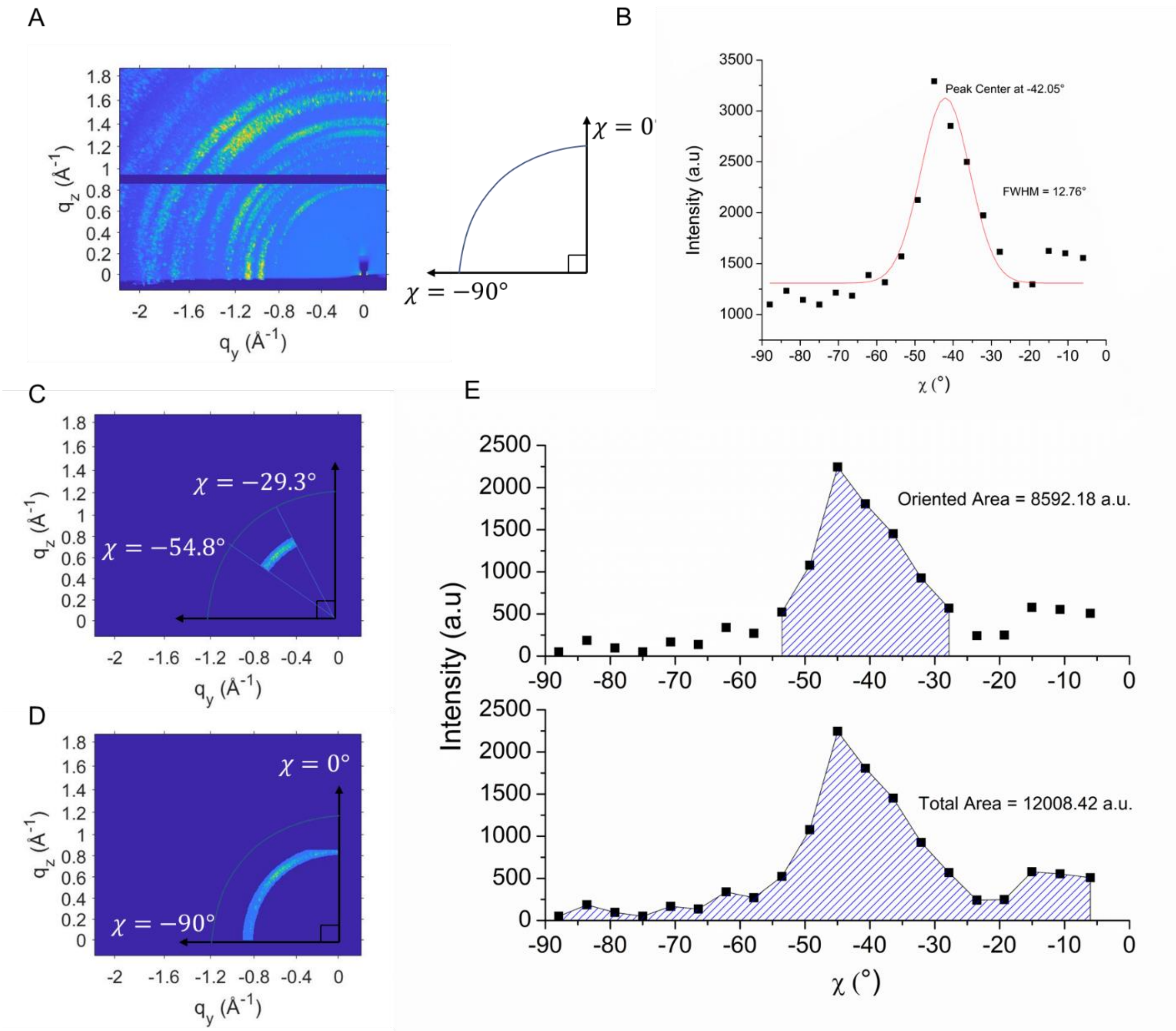
14 mg/ml				
Speed (mm s^{-1})		Average (μm)	Standard Deviation (μm)	PDI
0.01	Sample 1	10.03	5.27	0.28
0.01	Sample 2	7.09	3.11	0.19
0.01	Sample 3	7.32	2.71	0.14
0.02	Sample 1	7.52	2.11	0.08
0.02	Sample 2	8.51	2.52	0.09
0.02	Sample 3	8.21	2.65	0.10
0.03	Sample 1	6.28	2.35	0.14
0.03	Sample 2	8.14	2.45	0.09
0.03	Sample 3	8.78	2.56	0.09
0.04	Sample 1	7.80	2.20	0.08
0.04	Sample 2	7.03	1.94	0.08
0.04	Sample 3	8.37	2.14	0.07
0.05	Sample 1	4.28	1.19	0.08
0.05	Sample 2	4.29	1.29	0.09
0.05	Sample 3	7.81	2.20	0.08



SI Figure 5: Histograms of crystal size distributions for a) 5 mg mL^{-1} b) 10 mg mL^{-1} and c) 14 mg mL^{-1} solution concentrations



SI Figure 6: Microcrystal film diffraction pattern with simulated 010 oriented Form I peak positions marked (◊). This demonstrates the preferential 010 orientation (the 010 plane lies parallel to the substrate). Figure created using indexGIXS.[2]



$$\frac{Oriented\ Area}{Total\ Area} = \frac{8592.18}{12008.4} = 0.71$$

SI Figure 7: a) Full diffraction pattern for microcrystal thin film and axis definition for χ (0° pointing up and -90° to the left). b) integrated diffraction intensity for the (011) plane with gaussian fit, peak center and FWHM. c) Masked diffraction pattern isolating the oriented region associated with the (011) plane and d) masked diffraction pattern isolating the full signal associated with the (011) plane. e) 1D integration of the oriented and full 011 diffraction signals after background subtraction and calculation of preferential orientation =0.71.

Additional comments on Degree of Preferential Orientation:

$$Degree\ of\ Preferential\ Orientation = \frac{\int_{\chi=-29.3^\circ}^{\chi=-54.8^\circ} I_{110}(\chi)\,d\chi}{\int_{\chi=0^\circ}^{\chi=-90^\circ} I_{110}(\chi)\,d\chi}$$

The theoretical limits of this measure fall between 0 and 1, with 1 corresponding to a highly oriented sample (all diffraction is observed between $-29.3^\circ < \chi < -54.8$. A value of 0 would indicate that none of the diffraction occurs between $-29.3^\circ < \chi < -54.8$. However, an isotropic sample, where the diffraction occurs evenly across the interval (observed as Debye Scherrer rings around the origin) would result in a value of 0.28, as intensity (I) is a constant.

$$Degree\ of\ Preferential\ Orientation\ for\ an\ isotropic\ (powder\ texture)\ sample$$

$$\frac{\int_{\chi=-29.3^\circ}^{\chi=-54.8^\circ} I_{110}(\chi)\,d\chi}{\int_{\chi=0^\circ}^{\chi=-90^\circ} I_{110}(\chi)\,d\chi} = \frac{I_{110} * (-54.8 + 29.3)}{I_{110} * (-90 - 0)} = -\frac{-25.5}{-90} = 0.28$$

Therefore, while the theoretical range of this descriptor of orientation is 0 - 1, the expected functional limits are 0.28 – 1.

SI Table 4: Sample conditions and calculated degree of preferential orientation using the method described in **SI Figure 7** for microcrystal thin films (region 3 of processing diagram). Data corresponds to main text **Figure 6c**.

Films with microcrystal morphology		
Temperature (°C)	Coating Speed (mm s^{-1})	Preferential Orientation
120	0.03	0.71
120	0.05	0.66
120	0.08	0.82
120	0.03	0.89
120	0.05	0.57
110	0.03	0.69
110	0.05	0.81
	Average (n=7)	0.74
	Standard Deviation	0.11

SI Table 5: Sample conditions and calculated degree of preferential orientation using the method described in **SI Figure 7** for non-uniform thin films (region 2 of processing diagram). Data corresponds to main text **Figure 6c**.

Films with non-uniform morphology		
Temperature (°C)	Coating Speed (mm s^{-1})	Preferential Orientation
110	0.08	0.42
100	0.03	0.25
100	0.05	0.43
100	0.08	0.56
90	0.03	0.40
90	0.05	0.44
90	0.08	0.35
80	0.03	0.22
80	0.05	0.28
80	0.08	0.33
70	0.03	0.25
70	0.05	0.23
100	0.03	0.19
100	0.05	0.36
100	0.08	0.55
90	0.03	0.35
90	0.05	0.15
90	0.08	0.21
80	0.03	0.27
80	0.05	0.25
80	0.08	0.45
70	0.03	0.28
	Average (n=22)	0.33
	Standard Deviation	0.11

References

1. Granberg, R. A. & Rasmuson, Å. C. Solubility of paracetamol in pure solvents. *J. Chem. Eng. Data* (1999) doi:10.1021/je990124v.

2. Smilgies, D. M. & Blasini, D. R. Indexation scheme for oriented molecular thin films studied with grazing-incidence reciprocal-space mapping. *J. Appl. Crystallogr.* **40**, 716–718 (2007).