



Deposited via The University of Sheffield.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/113045/>

Version: Supplemental Material

---

**Article:**

Alharbe, L.G., Register, R.A. and Hobbs, J.K. (2017) Orientation Control and Crystallization in a Soft Confined Phase Separated Block Copolymer. *Macromolecules*, 50 (3). pp. 987-996. ISSN: 0024-9297

<https://doi.org/10.1021/acs.macromol.6b02361>

---

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Macromolecules*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acs.macromol.6b02361>

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

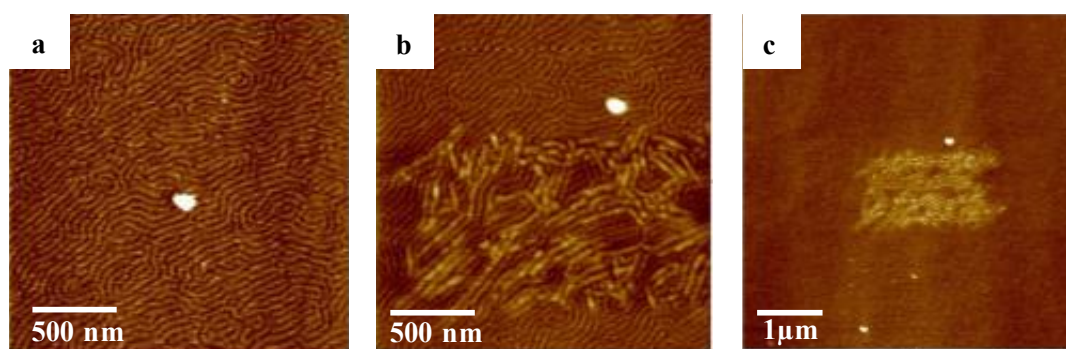
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

## Supporting Information (SI)

### Orientation Control and Crystallization in a Soft Confined Phase Separated Block Copolymer

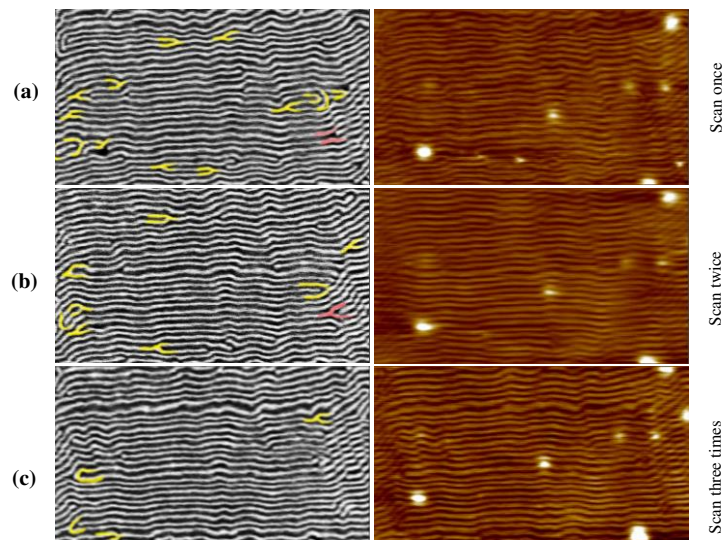
*Lamiaa G. Alharbe, Richard A. Register, Jamie K. Hobbs*

#### SI 1: Crystallization Induced by AFM Tip



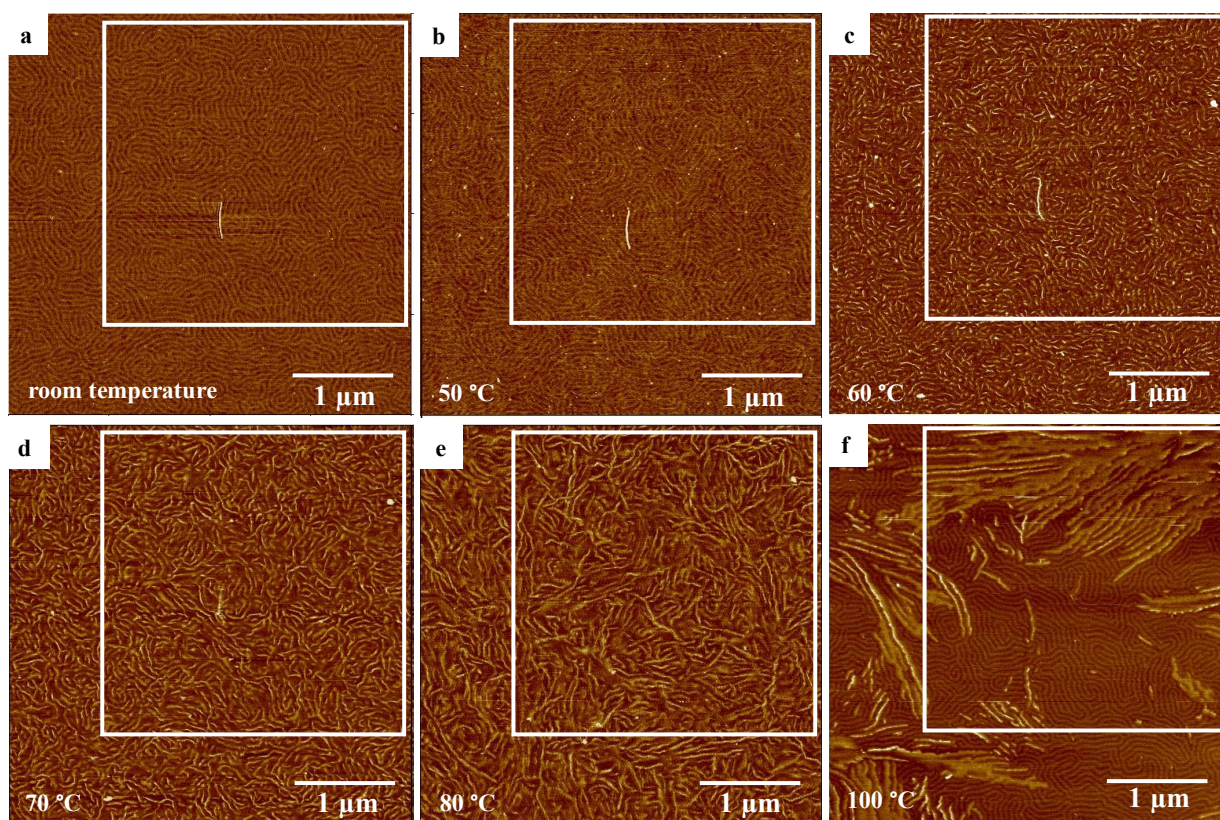
**Figure S1:** AFM phase images showing the crystallization induced by the AFM tip during the aligning of the cylinders at 110 °C: **(a)** before dropping the amplitude setpoint (i.e. increasing the tapping force) and **(b, c)** after that, when the crystallization was induced.

## SI 2: Reducing the Number of Defects



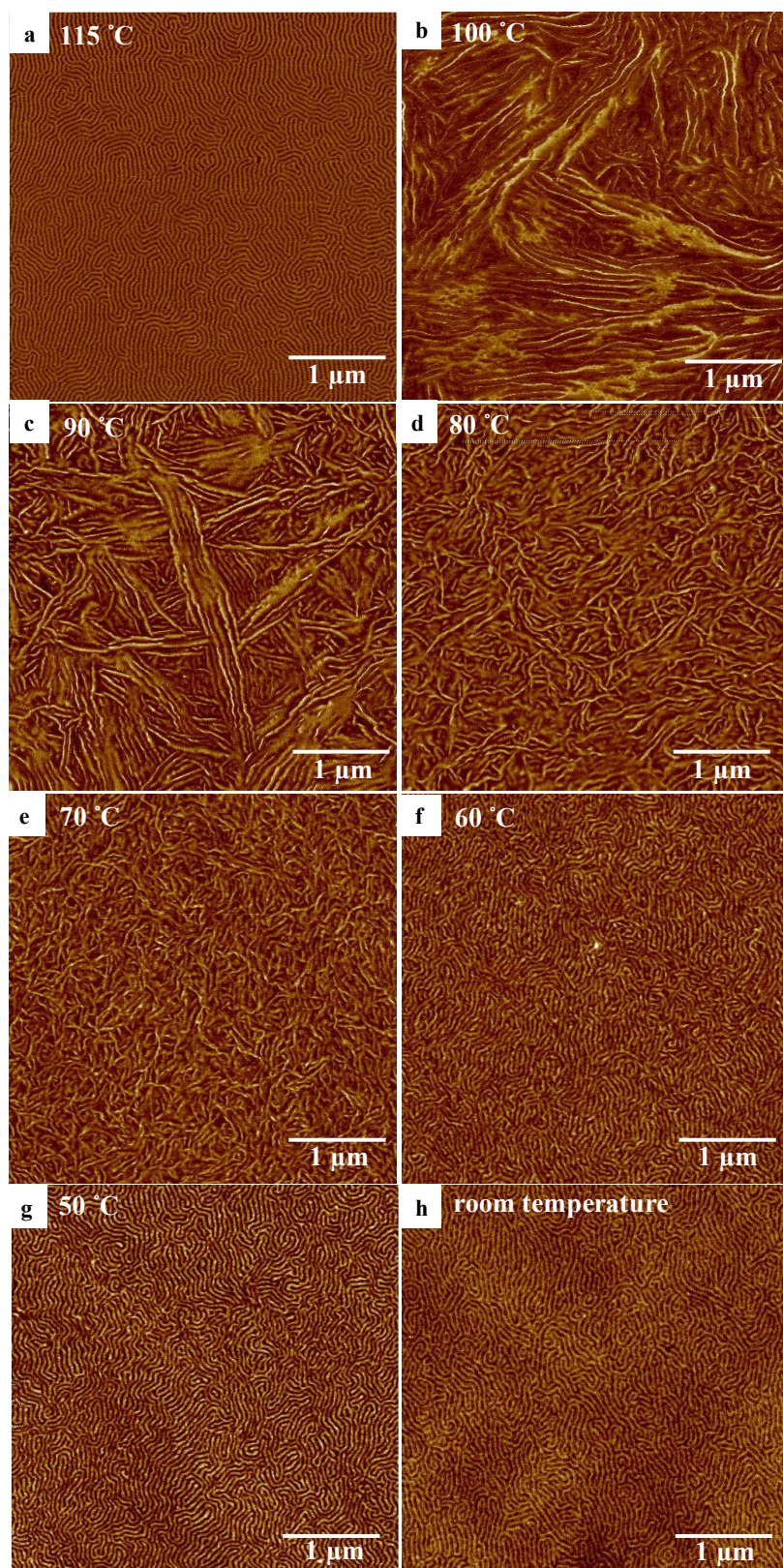
**Figure S2:** AFM phase (the left column) and height (the right column) images showing the effect of the number of orienting scans on the defects per unit area, **(a)-(c)** 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> scan, respectively with relatively high tapping force (lower amplitude and lower  $r_{sp} \approx 0.1$ ) at 115 °C. The defects are highlighted to aid the reader to follow the reduction as a function of the number of scans. The region highlighted in red shows an example of producing a new defect with the same scanning conditions but where the overall number of defects is still reduced. The image size is  $3 \times 1.5 \mu\text{m}$  and the black to white scale  $12^\circ$ .

### SI 3: Crystal Morphology as a Function of Temperature



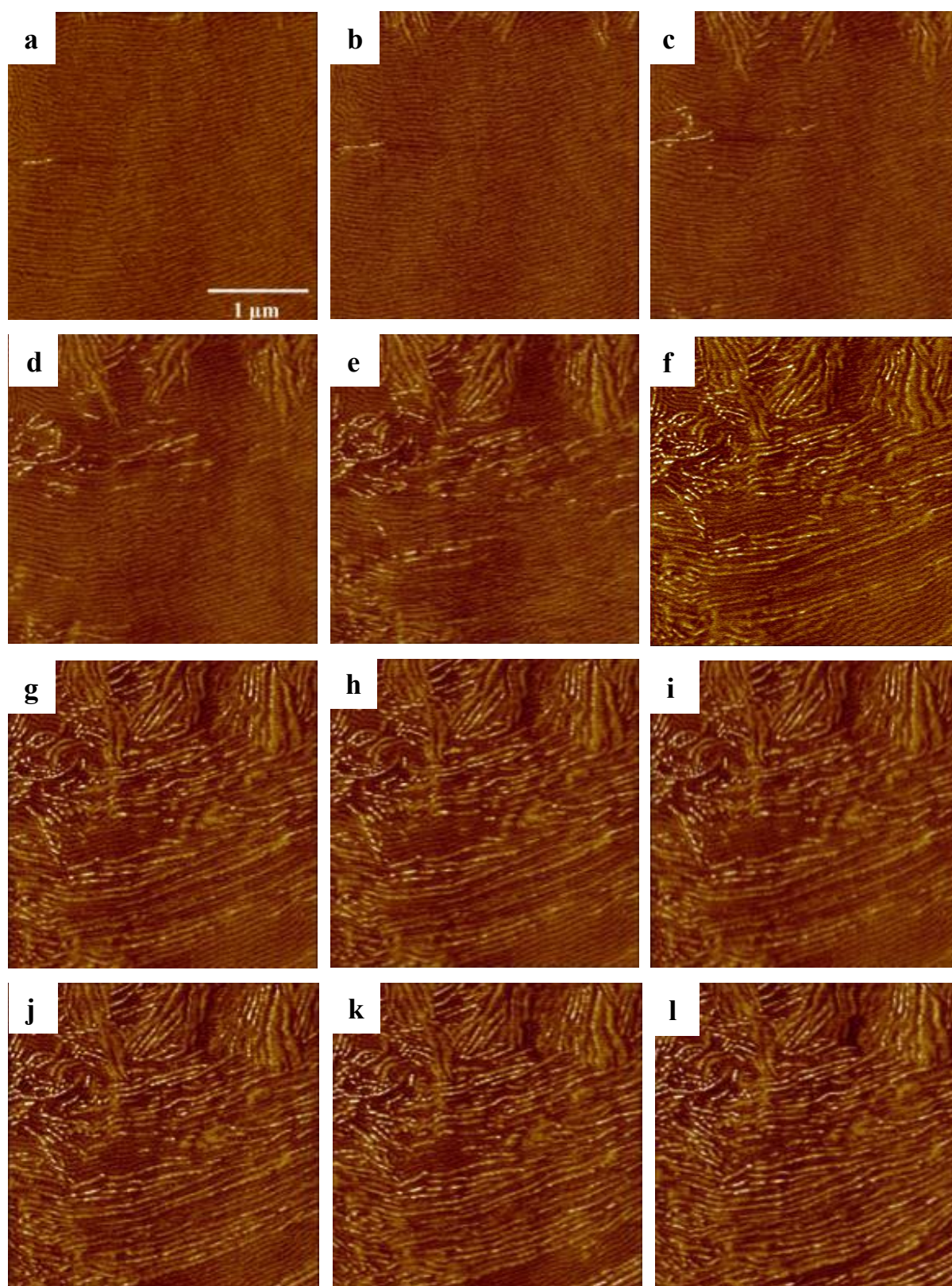
**Figure S3:** AFM phase images of crystallized E/MB after isothermal crystallization (the same area) at: (a) room temperature, (b) 50 °C, (c) 60 °C, (d) 70 °C, (e) 80 °C and (f) 100 °C (unoriented cylinders). The white squares illustrate the magnified area in **Figure 5** in the main text.

Another example of morphology formation from unoriented cylindrical microdomains (random) is shown in Figure S4.



**Figure S4:** AFM phase image of (a) melt phase E/MB at 115 °C and (b-h) crystallized E/MB after isothermal crystallization at (b) 100 °C, (c) 90 °C, (d) 80 °C, (e) 70 °C, (f) 60 °C, (g) 50 °C and (h) room temperature (unoriented cylinders).

SI 4: Following Crystallization in Pre-Oriented Domains *in Situ*



**Figure S5:** AFM phase images showing the crystallization in E/MB from the aligned melt structure at 99 °C, taken at (a) 0 s, (b) 149 s, (c) 298 s, (d) 596 s, (e) 894 s, (f) 1192 s, (g) 1341 s, (h) 1490 s, (i) 1639 s, (j) 1788 s, (k) 2086 and (l) 2980 s. Dark to bright represents a variation in phase of 7°.

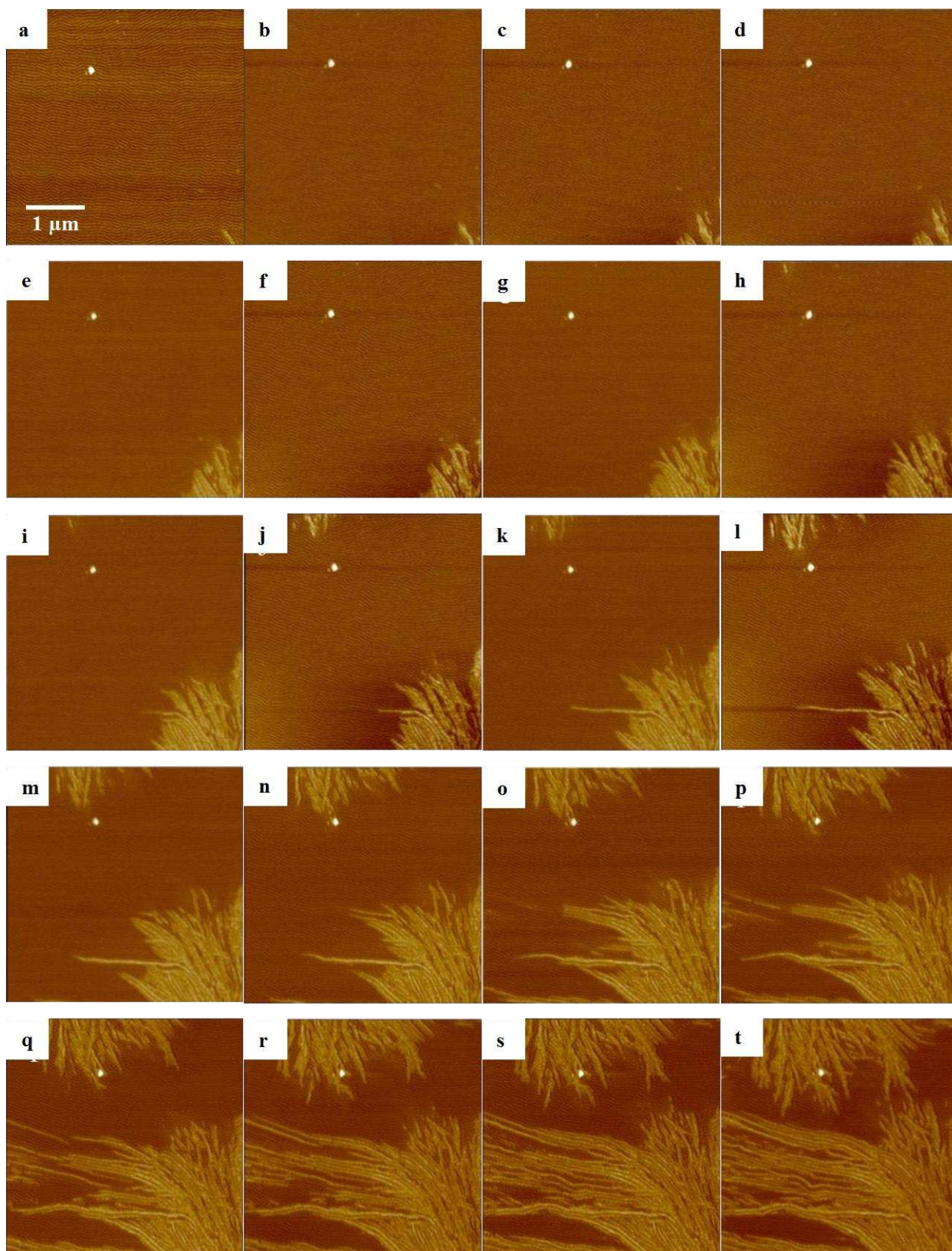
## SI 5: Growth Rates & Ratio of Parallel and Perpendicular Crystals

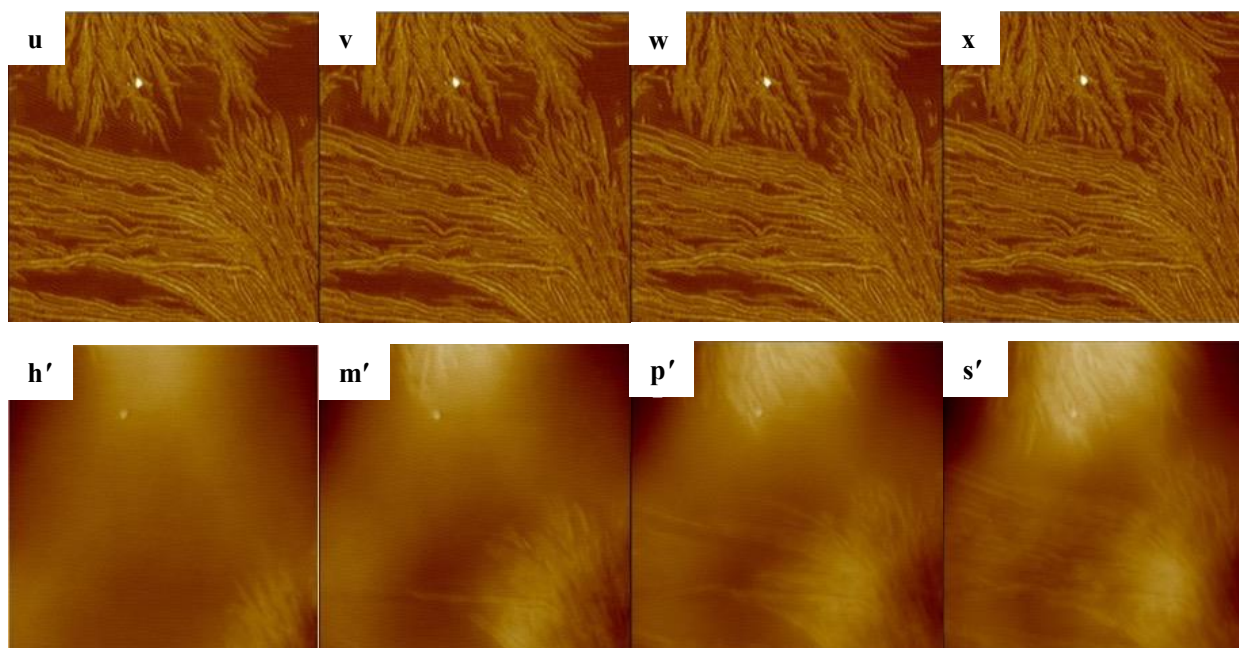
The measurement of the difference in the growth rates of the crystals growing parallel to the cylinders and perpendicular to the cylinders is summarized in the below table (See the corresponding graphs of these values in the main text).

**Table S1:** The ratios and overall average growth rates of a number of crystals growing along the cylinder axis and the growth rate perpendicular to the cylinder axis at temperatures of 97 °C–100 °C.

Crystallization temperature (°C)	Average growth rate (nms <sup>-1</sup> )		Ratio of growth rates
	Parallel to cylinders	Perpendicular to cylinders	
100	0.916	0.19	4.8
99	1.46	0.28	5.2
98	2.1	0.35	6
97	3.4	0.425	8

## SI 6: The Transition from 'Breakout' to 'Templated' Growth





**Figure S6:** A full series of AFM phase images showing E/MB crystallization at 101 °C. The last bottom row (images **h'**, **m'**, **p'**, and **s'**) are the corresponding height images of **h**, **m**, **p**, and **s** image. Each image was captured in 128 s. Dark-bright represents a variation in phase of 25° and the height scale is 120 nm.