

Supporting information

Directed Peptide Amphiphile Assembly Using Aqueous Liquid Crystal Templates in Magnetic Fields

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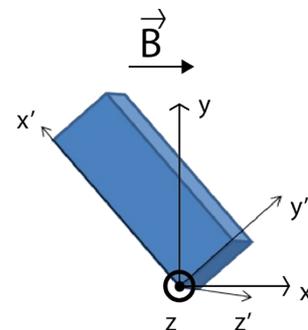
Materials

PA was synthesized according to a previous report.¹ DSCG was purchased from Sigma Aldrich and used as such.

The energy related to the magnetic moment of anisotropic molecules induced by an external magnetic field depends on the orientation of the molecules with respect to the magnetic field direction. The magnetic moment of a molecule induced by an applied magnetic field depends on the molar magnetic susceptibility, $\tilde{\chi}$:

$$\tilde{\chi} = \begin{pmatrix} \chi_{x'x'} & 0 & 0 \\ 0 & \chi_{y'y'} & 0 \\ 0 & 0 & \chi_{z'z'} \end{pmatrix}$$

where x' , y' and z' are the principle axes of the molecule (scheme right). The diamagnetic susceptibility of an organic molecule is given by the sum of all contributions of the different chemical groups². The susceptibility of most of the chemical groups is known and can be found in literature.² Based on this reference, we calculated the molar magnetic susceptibility of **DSCG** and found that it will align with their long axis in the plane parallel to the magnetic field since its susceptibility along the x -axis is higher than



Schematic representation of a molecule in a magnetic field. The x' , y' and z' are the principle molecular axes and x , y , z are the lab axes.

all the other directions ($\Delta\chi = \chi_{\parallel} - \chi_{\perp} \approx 1266 \cdot 10^{-12} \text{ m}^3 \text{ mol}^{-1}$ with $\chi_{\parallel} = \chi_{xx} = \chi_{yy}$ and $\chi_{\perp} = \chi_{zz}$).

The same calculations were carried out for **PA** monomers. The results show that **PA** monomers will be aligned perpendicular to the magnetic field direction because its susceptibility along the z-axis is higher than all the other directions ($\Delta\chi = \chi_{\parallel} - \chi_{\perp} \approx -611 \cdot 10^{-12} \text{ m}^3 \text{ mol}^{-1}$).

Glass cell preparation

Microscope glass slides (VWR) were cut into pieces 14 x 20 mm and 18 x 24 mm. After scrubbing the plates with a toothbrush and soap, they were rinsed with demiwater and sonicated in ethanol (99.8%) for 30 minutes. Subsequently, the glass plates were dried under nitrogen flow and additionally cleaned for 30 minutes using a Novascan PSD UV Surface Decontamination System. Cells were fabricated by sandwiching two plates with a 23 micron mylar spacer, after which the plates were glued on two opposing sides with two-component epoxy glue and dried for at least one hour before use.

Sample preparation

A solution of **PA** in milli-Q (0.03 wt%) was weighed in an empty eppendorf tube. The solution was homogenized with a vortex mixer and sealed with parafilm, after which the tube was wrapped in aluminum foil (to prevent premature photopolymerization of the PA by stray light) and fixated with parafilm. The solution was heated in a 50 °C water bath for 30 minutes after which the solution was sonicated at 50 °C for 15 minutes. After sonication, the mixture was heated to 90 °C for 1 minute, after which the mixture was cooled down to room temperature outside of the water bath. Using a 1 mL syringe, the solution was added on a weighing balance to solid DSCG with a HPLC filter (0.2 µm membrane size) in order to remove any large prepolymerized aggregates of **PA** present. The resulting suspension was heated to 90 °C to fully dissolve DSCG in the aqueous solution and completely disassemble **PA** to allow temperature induced assembly within the LCLC template during cooling the solution to room temperature.

Magnetic field application

After preparing the solution, the glass cells were filled. **PA** solutions in milli-Q and DSCG were inserted in the isotropic phase by capillary force in pre-constructed glass cells, which were preheated for 5 minutes at 50 °C and maintained at that temperature in a Linkam TMS 92 temperature controlled stage during filling. After filling, the cells were sealed with epoxy glue and dried for at least 1 hour after which the samples were placed in the magnetic field setup. After placing the glass cells in the magnetic field setup, the temperature was increased to 80 °C and maintained for 10 minutes. The magnetic field was applied and slowly over a period of 30 - 50 minutes, the sample was cooled down to room temperature. The sample was removed from the setup and investigated using optical microscopy.

Photopolymerization

After the amphiphilic nanostructures were aligned within the LCLC template, they were photopolymerized by keeping them for a few hours uncovered on a lab table, exposed to sunlight and/or conventional lighting. Alternatively, 5 minutes of illumination (10 cm distance from the source) with a conventional UV light source was sufficient to polymerize **PA**. The bundled nanostructures turned blue due to the crosslinking of the diacetylene-functionalized backbones.

Cell opening & SEM imaging

The glass cells were opened by a 30-45 minute soaking procedure in dichloromethane. After this period, the softened epoxy glue was peeled of the glass by using a scalpel. The glass cells were pried open and the LCLC was removed by adding several drops of milli-Q on the glass plates, which were removed after 15 minutes by tilting the glass plate on a piece of KimWipe. Due to the presence of external (capillary) forces during the opening of the cells and washing/drying of the plates, the cells were opened only after a few days when polymerized **PA** bundles had grown several microns wide (due to time-dependent depletion forces of **PA** bundles in the DSCG template). Sub-micron thick **PA** bundles (with less interconnected physical crosslinks) might not be strong enough for the capillary forces present during the cell opening and washing procedure. For SEM imaging, plates were dried overnight and coated with gold/palladium using a Cressington 208HR sputter coater at 20mA for 10 seconds. SEM images were taken on a JEOL 6330 Cryo Field Emission Scanning Electron Microscope at 3 keV. TEM image was taken with a JEOL 1010.

(Polarized) optical microscopy

OM images in Figure 2b,c, 3, S6 were taken with a Leica DM-RX polarized optical microscope and a Leica DMC2900 camera. After taking the image, a background image was subtracted to remove any out of focus textures on the image due to dust or grease present on some parts of the microscope (e.g. on lenses, microscope slides).

POM images in Figure 2a, S1 and S12a were taken with a Olympus BX60 polarized optical microscope and a CoolSNAP-Pro camera. For determining the orientation of the LCLC stacks, a U-TP137 137nm retardation plate was used to determine the respective LCLC orientation within the sample cells. (P)OM images in Figure 5, S2, S3, S4, S5, S8, S9, S10, S11 and S12b are taken with a Carl Zeiss Jena polarized optical microscope and an AmScope MD900E camera. Photoshop CS5 (Levels tool) was used to enhance the contrast of the OM images in Figure 2b,c, 3, S2, S5, S6, S9, S11d and S12b in order to improve the visibility of the **PA** fibers.

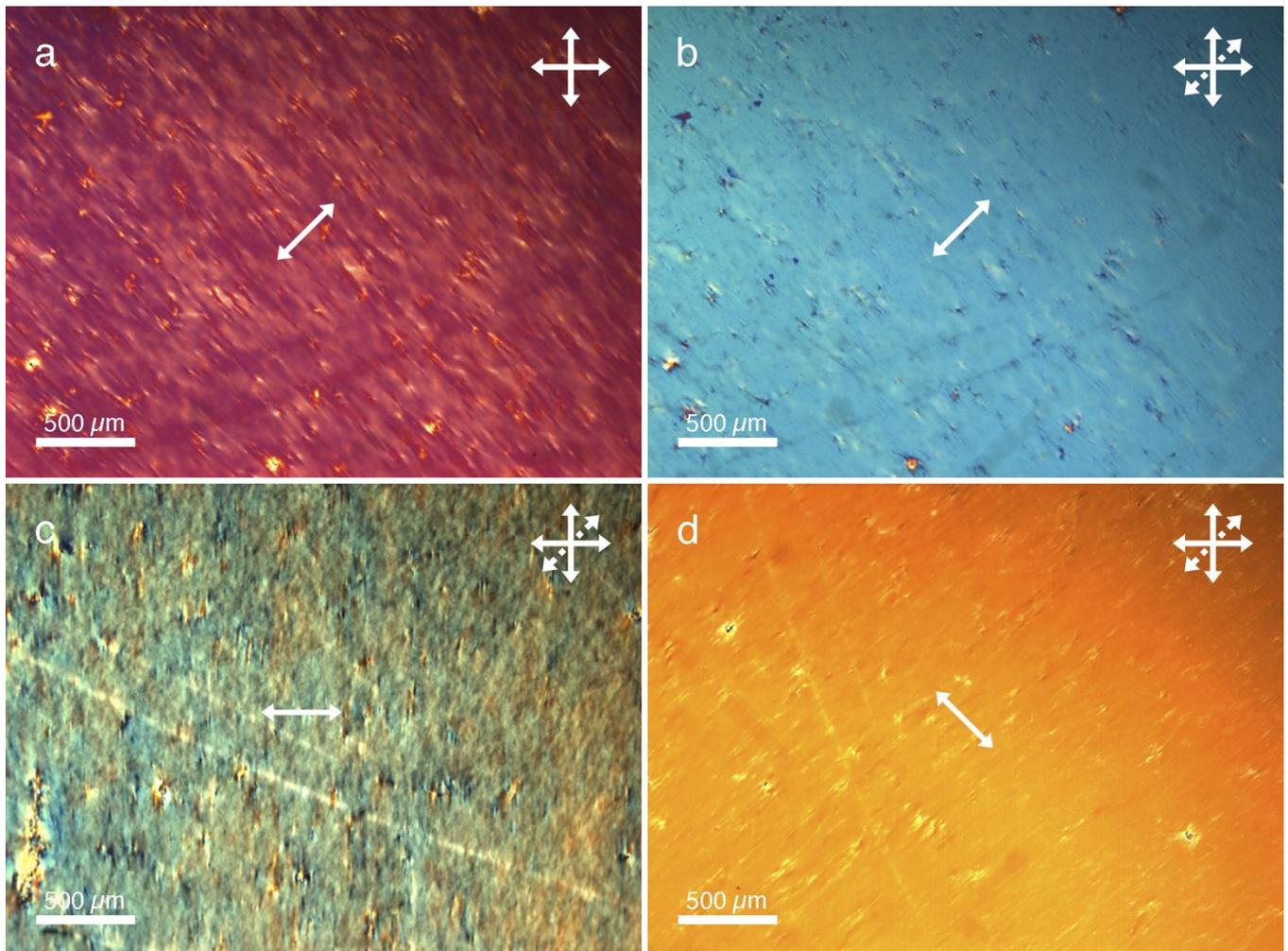


Figure S1. Determination of LCLC alignment direction after 2 Tesla magnetic field application. POM image of a mixture of PA (0.026 wt%), DSCG (13.7 wt%), showing a unidirectionally aligned DSCG domain without (a) and with (b,c,d) a quarter waveplate inserted between analyzer and sample. The central white double-sided arrows indicate the magnetic field direction. DSCG is negatively birefringent as it forms elongated aggregates due to π - π stacking of individual stacked plank shaped molecules. The stacked aggregates in the domain which show a higher order (blue) interference color (b) are aligned with their long axis parallel to the slow axis of the quarter waveplate. When rotating the sample 90° (d), the interference color changes to (lower order) orange, indicating the LCLC stacks are aligned parallel to the fast axis of the quarter waveplate and thus perpendicular to the direction of the magnetic field.

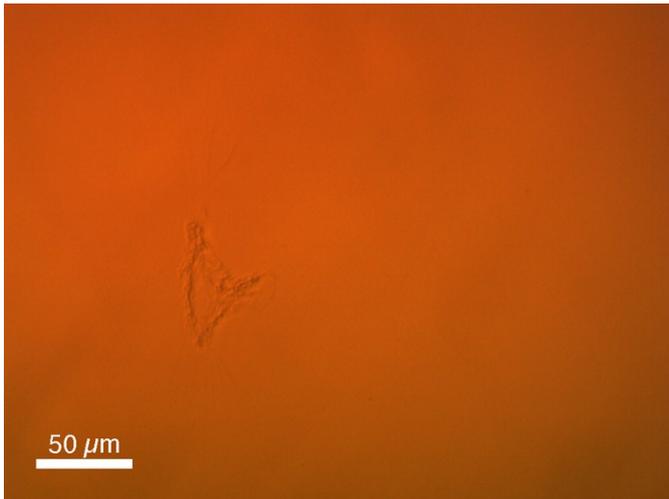


Figure S2. OM image of **PA** (0.015 wt% in water) at room temperature after cooling down from 80 °C (0.6 °C/min) in the absence of a magnetic field. The OM image shows an aggregate of **PA** fibers without any preferential unidirectional alignment.

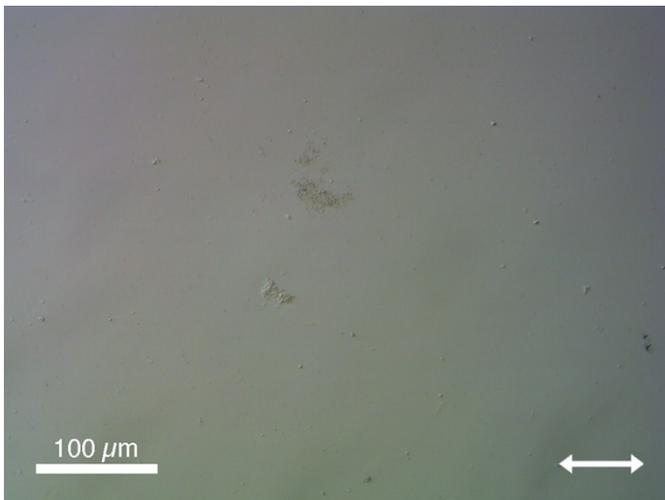


Figure S3. OM image of **PA** (0.03 wt%) water after 2 T magnetic field alignment and photopolymerization. No aligned fiber formation can be observed, only clustered aggregates, which is similar to a situation of **PA** assembled in water on rubbed polyimide surfaces.³

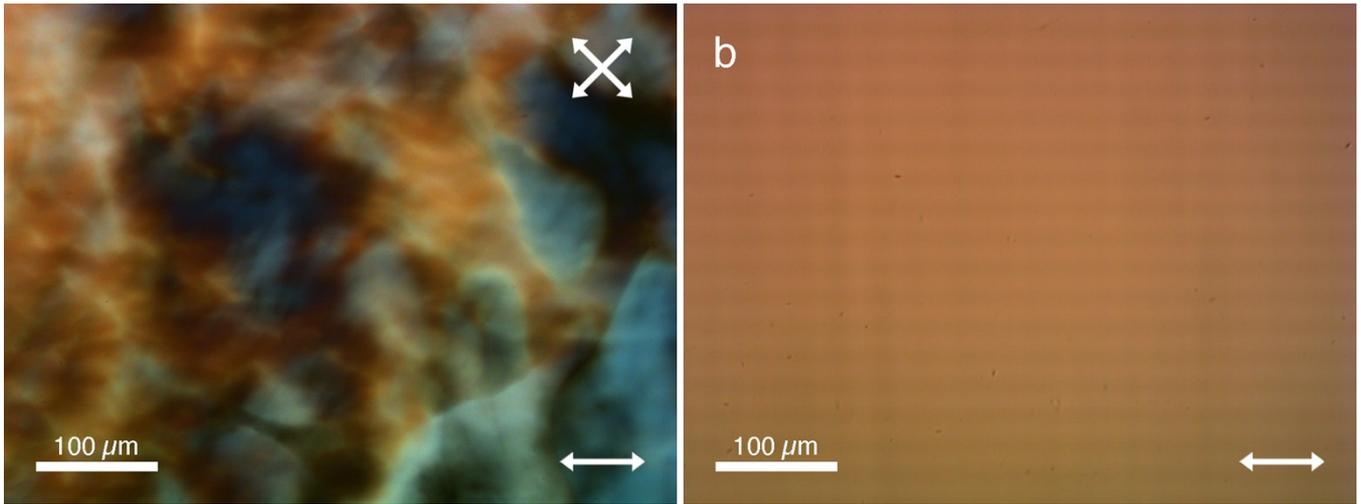


Figure S4. POM (a) and OM (b) image of a mixture of **PA** (0.026 wt%), DSCG (13.7 wt%) in the absence of a magnetic field. POM image (a) shows random in-plane orientation of DSCG. When removing the polarizer and analyzer (b) only tiny PA fibers can be observed organized isotropically. The horizontal stripes in the background in image (b) are present due to interference of the light with the camera of the OM.

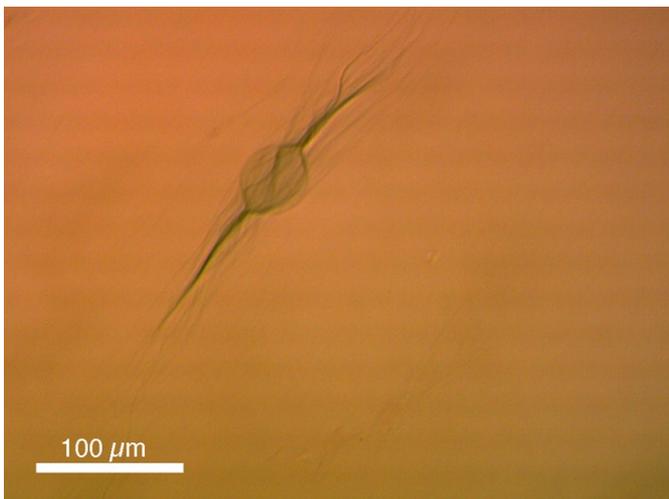


Figure S5. OM image of DSCG (13.4 wt%) and **PA** (0.015 wt%) at room temperature after cooling down from 80 °C (0.6 °C/min) and photopolymerization. No magnetic field was applied during the cooling down process. The OM image shows a photopolymerized spindle-like assembly of **PA** fibers similar in morphology to the assemblies annealed in a 2 T magnetic field (Figure 2).

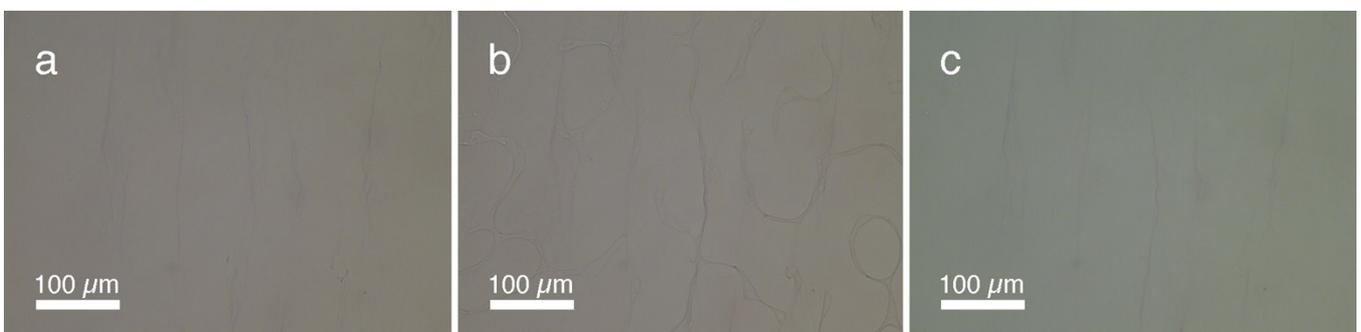


Figure S6. Effect of temperature on photopolymerized **PA** (0.026 wt%) and DSCG (13.7 wt%) in a 2 T magnetic field aligned LCLC template. OM image shows aligned photopolymerized bundles at room temperature (a), during heating

to the isotropic phase (b) and at 65 °C (c). The cells were also heated at 90 °C for at least 10 minutes, during which the overall appearance of the fibrous assemblies of **PA** hardly changed (besides that bundles of **PA** become slightly more reddish in color).

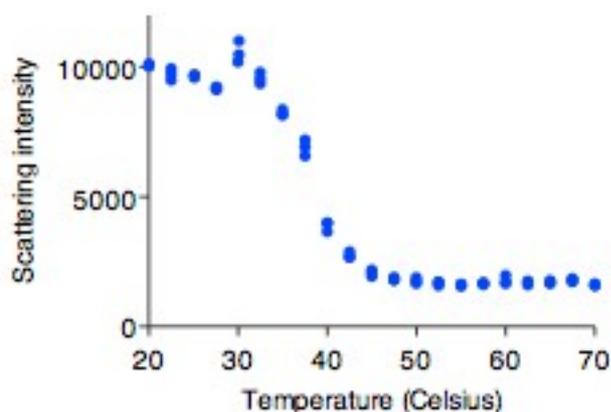


Figure S7. Dynamic light scattering (DLS) plot of **PA** (0.1 wt% in water) during cooling down procedure. When the sample is cooled down, at roughly 50° C, the overall scattering starts to increase, indicating the onset of **PA** assembly formation. DLS investigations of **PA** in DSCG was impossible due to the large scattering of nematic DSCG and its high concentration relative to **PA**.

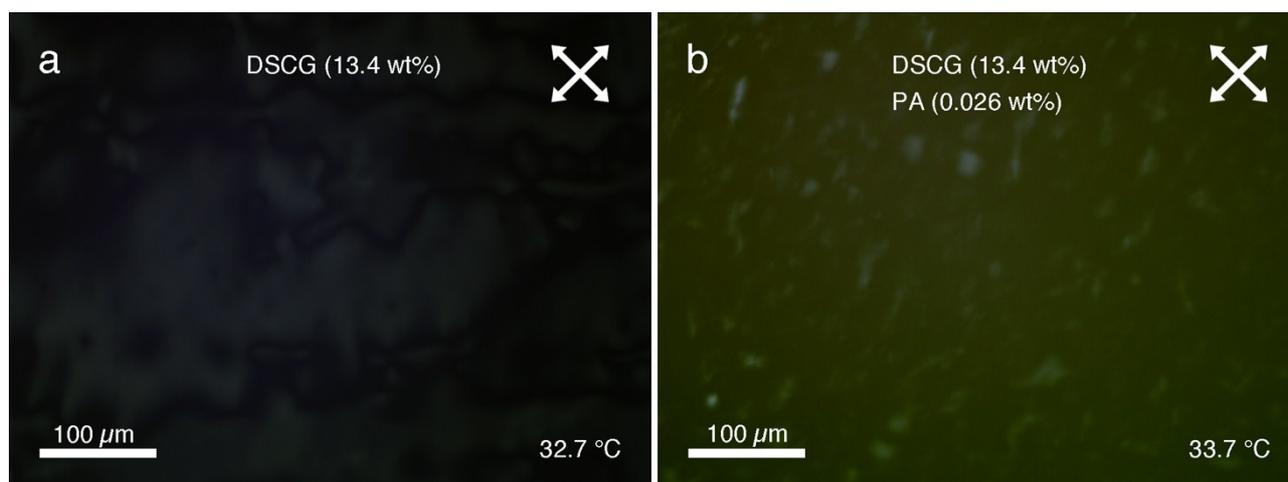


Figure S8. POM images of (a) DSCG (13.4 wt%) and (b) DSCG (13.4 wt%) and PA (0.026 wt%) during an annealing procedure from 80 °C (0.6 °C/min) in the absence of a magnetic field. Both POM images show the onset of birefringence (lightly colored structures emerging from the dark background) arising from nematic domain formation of the LCLC. The presence of **PA** (b) may facilitate the onset of nematic DSCG formation due to the slightly higher isotropic to nematic transition temperature (33.7 °C compared to 32.7 °C).

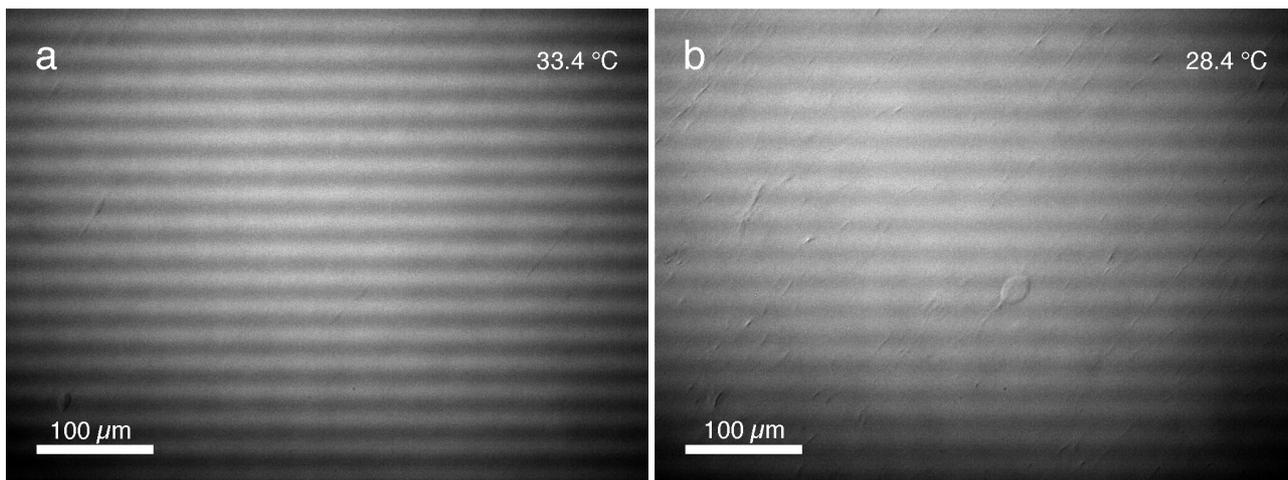


Figure S9. OM images of DSCG (13.4 wt%) and PA (0.026 wt%) during an annealing procedure from 80 °C (0.6 °C/min) in the absence of a magnetic field. At a 33.4 °C (a) a few PA bundles can be observed, which during cooling down (b) have grown substantially, while also other bundles have emerged which are large enough to be observed with the OM. The contrast was enhanced in this image using Photoshop (Levels tool) and the OM image was converted to greyscale in order to increase the visibility of the bundles. The horizontal stripes in the background in both images are a result of interference of the light with the camera of the OM.

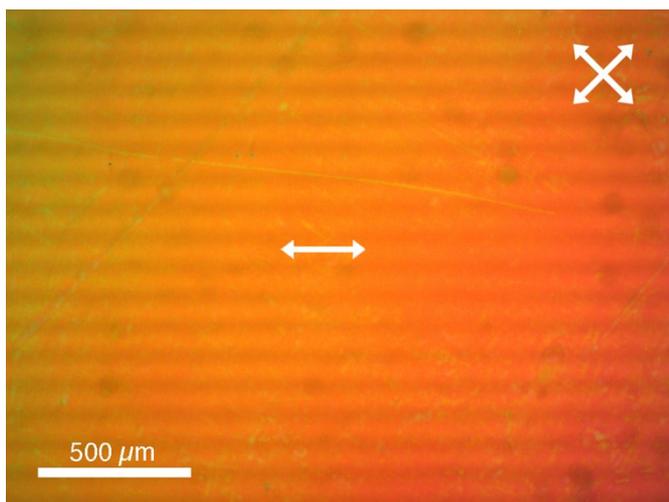


Figure S10. POM image DSCG (13.7 wt%) after 20 T magnetic field alignment. Double white-sided arrow indicates magnetic field direction. The horizontal stripes in the background in image (b) are present due to interference of the light with the camera of the OM. The variation in color relates to a small difference in local thicknesses of the cell.

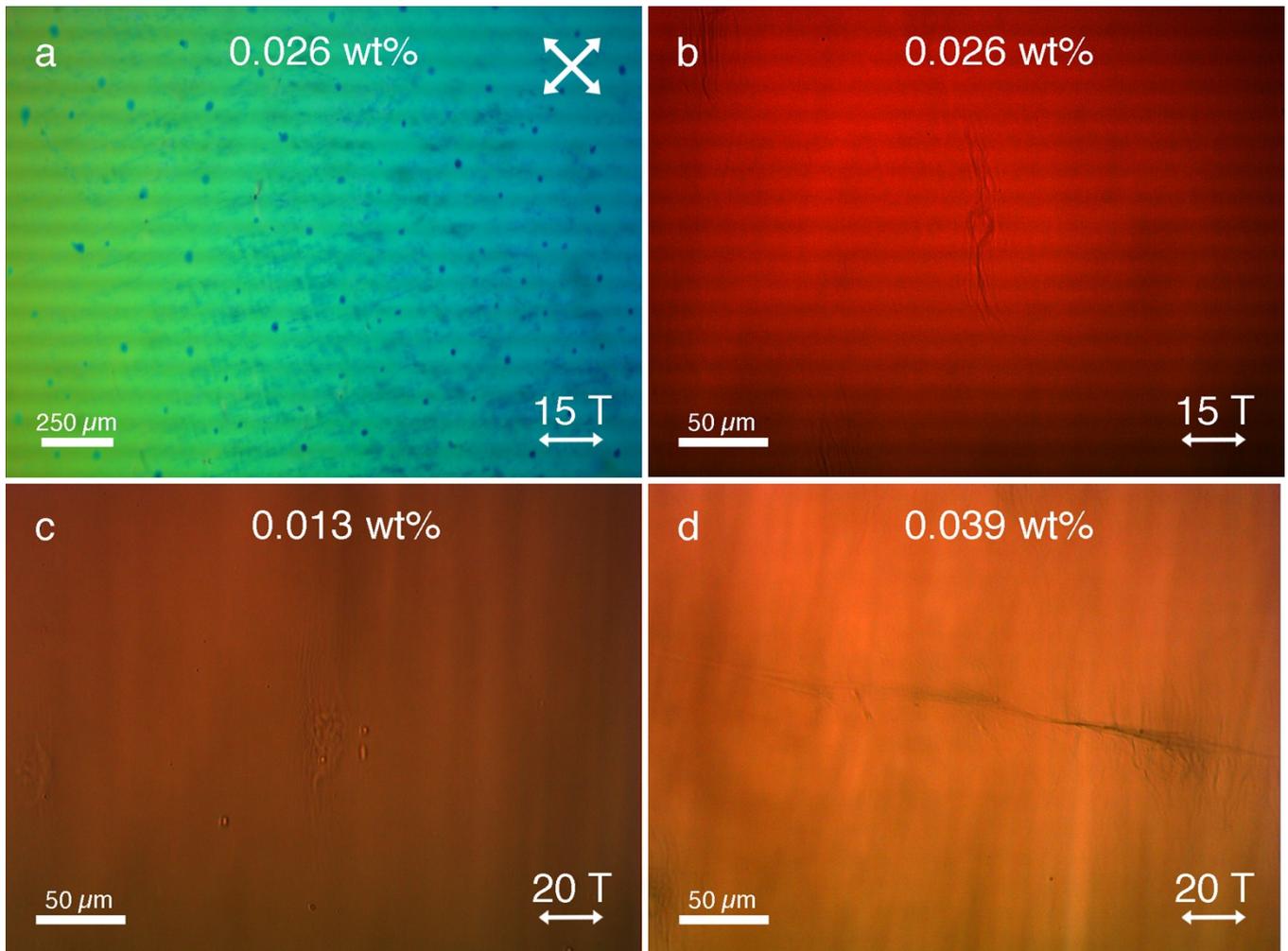


Figure S11. (P)OM images of **PA** assembled in nematic DSCG (13.7 wt%) after magnetic field alignment. POM image (a) shows a DSCG monodomain after the sample was cooled at 15 T. OM image (b) shows the presence of similar spindle-like aggregates as in the 2 T experiment (Figure 2). OM images (c) shows spindle-like **PA** (0.013 wt%) aggregate after cooling down in nematic DSCG (13.7 wt%) in a 20 T magnetic field aligned. When the **PA** concentration is increased to 0.039 wt% (d), similar structures (assembled in nematic DSCG (13.7 wt%) and in a 20 T magnetic field) emerge compared to the ones in Figure 5 and 6.

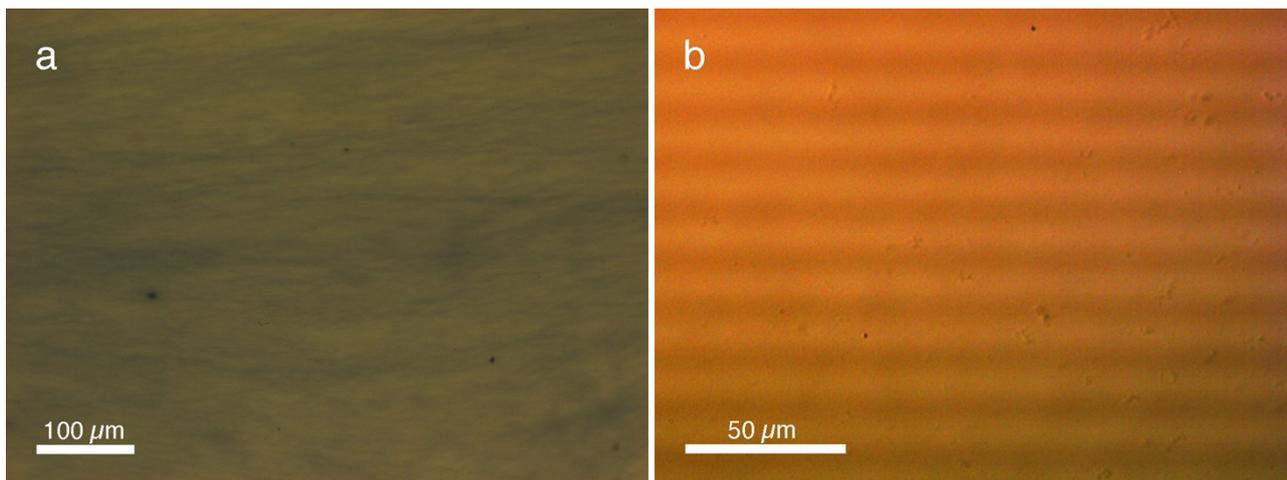


Figure S12. OM images of (a) PA (0.1 wt% in water) and (b) PA (0.015 wt%) after cooling down to room temperature in a 20 T magnetic field (horizontal direction) and subsequent photopolymerization. At a high PA concentration of 0.1 wt% (a), macroscopic fiber bundle alignment can be observed while at a lower concentration (0.015 wt%) only isotropic aggregates are present which do not align along the magnetic field.

References

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2. R. R. Gupta, K. H. Hellwege, A. M. Hellwege *Diamagnetische Suszeptibilität*, Landolt Börnstein. Gruppe II, Atom- und Molekularphysik, Vol. 16, Springer, Berlin, Germany **1986**.
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