Supporting Information: Sub-5 nm structured films by hydrogen bonded siloxane liquid crystals and block copolymers.

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Materials & Methods

Heptasiloxane monohydride was obtained from the group of Meijer. All other solvents and standard chemicals were obtained from commercial sources and were used as received. Reactions with air or moisture sensitive reagents were performed under argon atmosphere with flame-dried glassware using standard Schlenk techniques. Nuclear magnetic resonance spectra (NMR spectra) were measured on a Varian Mercury 400Vx and a Bruker 400MR NMR apparatus at 300 K. Chemical shifts are indicated as δ values in parts per million (ppm) and are reported relative to $CHCl_3$. Mass spectra were measured on a Bruker ST-A2130 mass spectrometer with matrix-assisted laser desorption ionization and a time-of-flight analyzer (MALDI-TOF) using a 2 kHz laser. Depending on the measured substance, α-cyano-4-hydroxycinnamic acid (CHCA) or 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) in tetrahydrofuran (THF) were applied as matrices. Substances were detected with a Bruker Flash Detector. Polarized optical microscopy (POM) was performed with crossed polarizers using a Leica DM6000M equipped with a DFC420C camera and a Linkam THMS600 hot-stage for temperature control. For characterization of the LC textures, a small amount of LC material was placed between microscope slides, heated to the isotropic phase, and cooled (5 °C min^{-1}) to room temperature. Phase transition temperatures of the reactive mesogens were determined using a TA Instrument Q1000 differential scanning calorimeter (DSC). 3-4 mg of material was hermitically sealed in aluminum pans. The heating and cooling rate was 5 °C min^{-1} and the second cooling curve was used to determine the transition temperatures. X-ray scattering measurements were performed on a Ganesha lab instrument equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of $1x10^8$ phs^{-1}. Scattering patterns were collected using a Pilatus 300 K silicon pixel detector. The beam center and the q range were calibrated using the diffraction peaks of silver behenate. The sample to detector distance was 91 mm for wide-angle measurements, 441 mm for medium-angle measurements, and 1041 mm for small-angle measurements. The spectra were concatenated at q = 0.7 nm^{-1} and q = 5 nm^{-1}. Small-angle grazing incidence XRD was performed at the DUBBLE beamline at ESRF in Grenoble. Samples were measured at the critical angle (~ 0.18°). The AFM data were recorded in ambient conditions using a Dimension ICON atomic force microscope (Bruker Nano Inc., Santa Barbara, CA) fitted with an NCHV silicon probe (Bruker, spring constant 42 Nm^{-1} and a resonance

frequency 320 kHz). Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a FTS 6000 spectrometer from Bio-Rad equipped with Specac Golden gate diamond ATR and were signal-averaged over 50 scans at a resolution of 1 cm^{-1}. The degree of hydrogen bonding was generated using formula 1 with the inert FT-IR absorption at 1498 cm^{-1} as an internal reference.

Synthetic Procedures & Characterization

The synthetic scheme for the preparation of **LC** is shown in Scheme 1. Benzyl paraben was reacted with 11-bromoundec-1-ene in a Williamson ether synthesis to form intermediate **1**. Monodisperse heptasiloxane monohydride was received from the group of Meijer,[49] and coupled to **1** using Karstedt's catalyst to yield intermediate **2**. Finally, intermediate **2** was deprotected using catalytic hydrogenation with palladium on carbon to produce **LC**. The full synthetic procedure and characterization data are provided below.

Scheme 1. Synthetic scheme for hydrogen bonding ODMS liquid crystal **LC**. The yields are indicated in brackets.
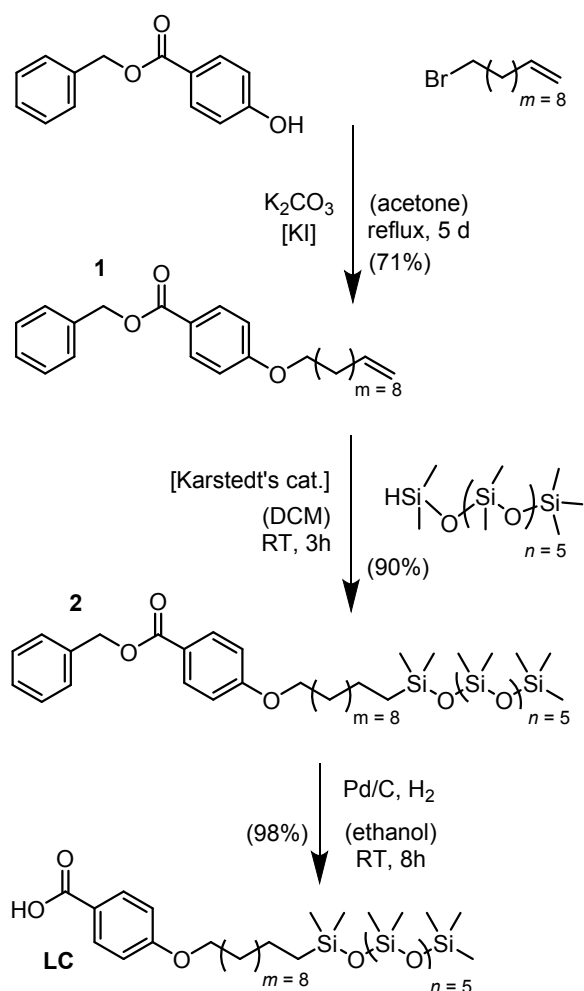
Benzyl 4-(undec-10-en-1-yloxy)benzoate (1)

A solution of 4.2 g of benzyl paraben (18.4 mmol, 1.0 eq.), 7.50 g of potassium carbonate (54.3 mmol, 2.95 eq.), 4.30g of 11-bromoundec-1-ene (18.8 mmol, 1.02 eq.), and 0.010 g of potassium iodide (0.06 mmol, 0.003 eq.) in 100 mL of acetone is stirred is refluxed under argon for 48h. The solution is washed with 1M NaOH and brine, and dried over magnesium sulfate. Column chromatography (heptane: ethyl acetate = 20:1, [UV]) was performed to give 71% of benzyl 4-(but-3-en-1-yloxy)benzoate (**1**) (4.95 g, 13.0 mmol) as a transparent liquid. ^{1}H-NMR (400 MHz, CDCl$_3$, 300 K): δ [ppm] = 8.02 (dd, J = 8.8, 1.7 Hz, 2H), 7.48 – 7.29 (m, 5H), 6.94 – 6.86 (m, 2H), 5.34 (s, 2H), 5.05 – 4.89 (m, 2H), 4.00 (t, J = 6.6 Hz, 2H), 2.10 – 1.99 (m, 2H), 1.79 (dt, J = 14.7, 6.6 Hz, 2H), 1.52 – 1.27 (m, 14H). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ [ppm] =166.20, 163.04, 139.17, 136.34, 131.70, 128.53, 128.07, 122.24, 114.12, 68.19, 66.33, 33.79, 29.47, 29.39, 29.32, 29.09, 28.91, 25.96. (MALDI-TOF): m/z = calculated (C$_{25}$H$_{32}$O$_3$): 403.23; found: 403.26 [M+Na]$^+$.

4-((11-(Pentadecamethylheptasiloxanyl)undecyl)oxy)benzoate (2)

A flame-dried Schlenk flask is charged with 704 mg of compound **1** (1.85 mmol, 1.00 eq.), 988 mg of 1,1,1,3,3,5,5,7,7,9,9,11,11,13,13-pentadecamethylheptasiloxane (1.90 mmol, 1.03 eq.) and one drop of Karstedt's catalyst (2% Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene) in 3 mL of dry dichloromethane under argon. The reaction mixture is stirred at room temperature for 3 hours under argon and then quenched with 40 mL of methanol. The solvents are removed under vacuum. Chromatography (heptane : ethyl acetate 20:1, [UV]) was performed to give 90% benzyl 4-(4-(pentadecamethylheptasiloxanyl)butoxy)benzoate (**2**) (1.50 g, 1.67 mmol) as a colourless oil.^{1}H-NMR (400 MHz, CDCl$_3$, 300 K): δ [ppm] = δ 8.08 – 7.96 (m, 2H), 7.51 – 7.29 (m, 5H), 6.99 – 6.80 (m, 2H), 5.33 (s, 2H), 3.99 (t, J = 6.4 Hz, 2H), 1.79 (m, 2H), 1.52 – 1.27 (m, 16H), 0.53 (dd, J = 9.5, 5.7 Hz, 2H), 0.14 – 0.02 (m, 45H).^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ [ppm] = 166.21, 163.05, 136.33, 131.69, 128.53, 128.06, 122.22, 114.05, 68.21, 66.32, 33.45, 29.62, 29.58, 29.56, 29.38, 29.10, 25.98, 23.21, 18.25, 1.78, 1.14, 1.05, 0.18. (MALDI-TOF): m/z = calculated (C$_{40}$H$_{78}$O$_9$Si$_7$): 898.40; found: 921.42 [M+Na]$^+$.

4-((11-(Pentadecamethylheptasiloxanyl)undecyl)oxy)benzoic acid (LC)

A 100 mL flask is charged with 1.47 g (1.63 mmol) of compound 2b, and 2 mL of ethyl acetate. To this is added 100 mg Pd/C 30% in 6 mL of ethanol. The flask is fitted with a rubber stopper and stirred overnight under H$_2$ atmosphere. The solution is filtered over celite and solvents are removed under vacuum to yield 98% of **LC** (1.29 g, 1.60 mmol) as a transparent paste.^{1}H-NMR (400 MHz, CDCl$_3$, 300 K): δ [ppm] = δ 8.05 (m, 2H), 6.93 (m, 2H), 4.02 (t, J = 6.4 Hz, 2H), 1.81 (m, 2H), 1.52 – 1.27 (m, 16H), 0.54 (dd, J = 9.5, 5.7 Hz, 2H), 0.14 – 0.02 (m, 45H).^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ [ppm] = 171.91, 163.66, 132.30, 121.40, 114.15, 68.27, 33.45, 29.59, 29.39, 29.09, 25.98, 23.22, 18.26, 1.77, 1.16, 1.05, 0.18. (MALDI-TOF): m/z = calculated (C$_{33}$H$_{72}$O$_9$Si$_7$): 831.35; found: 831.35 [M+Na]$^+$.
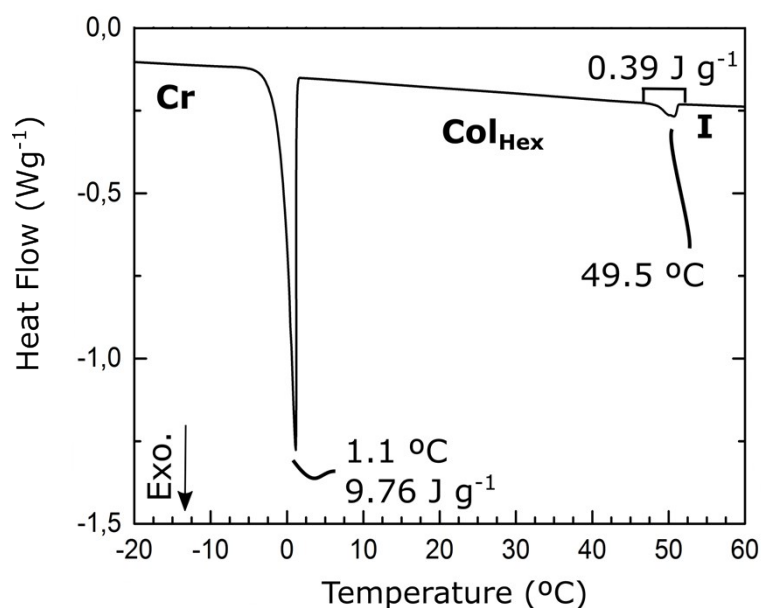
Fig S1. DSC thermographs of the hydrogen bonding ODMS liquid crystal **LC**, obtained on second cooling of the compound (10 °C/min). **LC** shows a phase transition at 49 °C, with an associated enthalpy of 0.4 J g^{-1}, and an additional phase transition at 1 °C, with an associated enthalpy of 9.8 J g^{-1}.
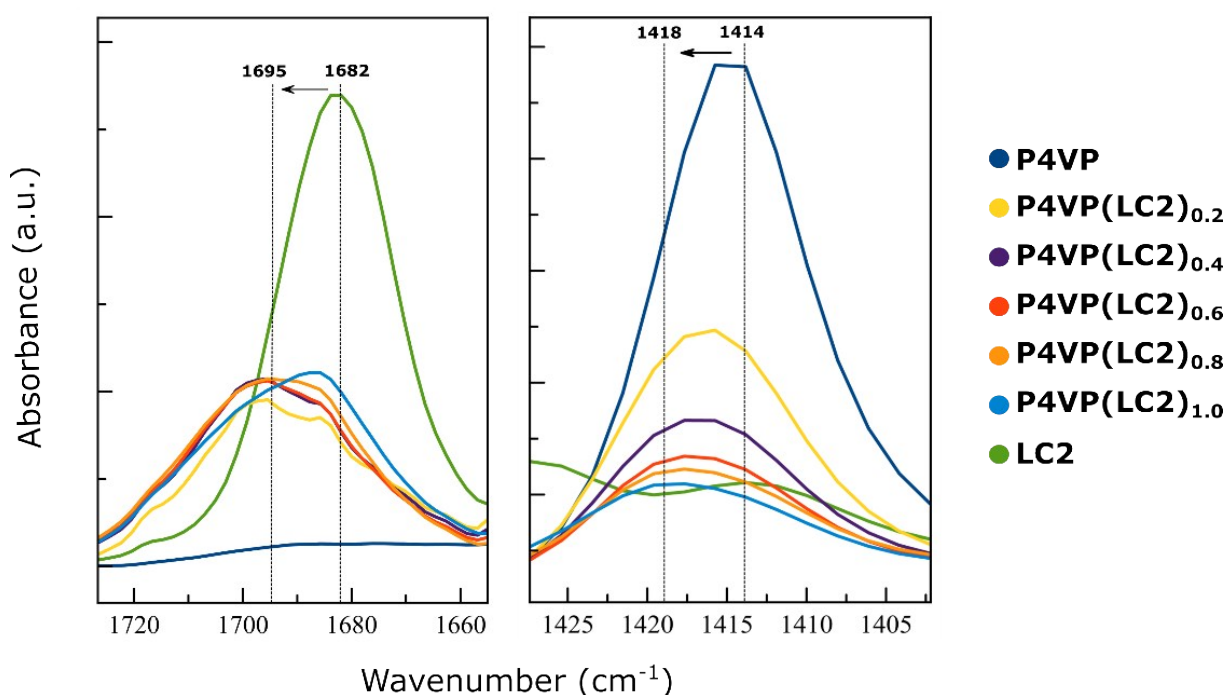

Fig S2. FTIR spectra of **LC**, **P4VP**, and **PV4P(LC)$_x$** samples. **LC** exhibits a carbonyl stretch vibration at 1682 cm^{-1} which is characteristic for the formation of hydrogen bonded benzoic acid dimers.[49,50] In the supramolecular assemblies **P4VP(LC)$_x$**, the band shifts to 1695 cm^{-1}, because the C=O groups are no longer involved in hydrogen bonding .[33,51] The characteristic band at 1414 cm^{-1} corresponds to the stretching mode of the free pyridine ring on pristine **P4VP**. The vibrational mode is perturbed due to the formation of hydrogen bonds, causing a decreased absorption intensity and a shift to 1418 cm^{-1}.[49]
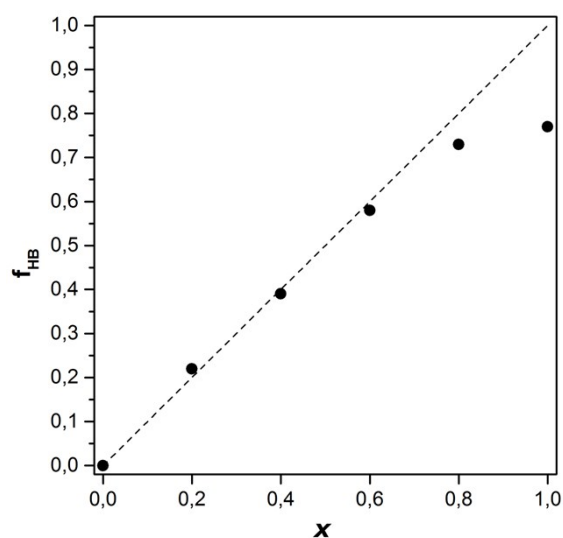
Fig S3. Fraction of hydrogen-bonded pyridines (f_{HB}) as a function of molar ratio x (LC:P4VP) for the **P4VP(LC)$_x$** supramolecular assemblies. The fraction of hydrogen-bonded 4-vinylpyridines (f_{HB}) was estimated by deconvolution of the data in Fig S2.[37]
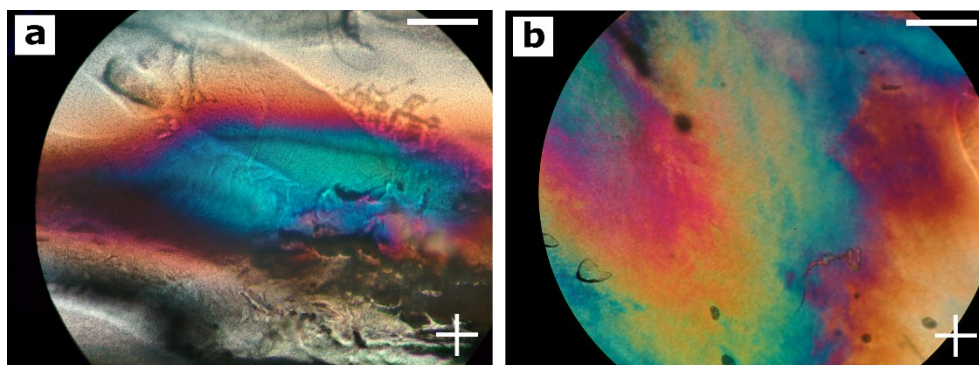

Fig S4. POM images of the **P4VP(LC)$_x$** supramolecular assemblies. a) x = 0.4. b) x = 0.6. The POM images were obtained under crossed polarizers just under the isotropization temperature (polarizer axes are indicated in the images with a cross). All scale bars: 500 μm
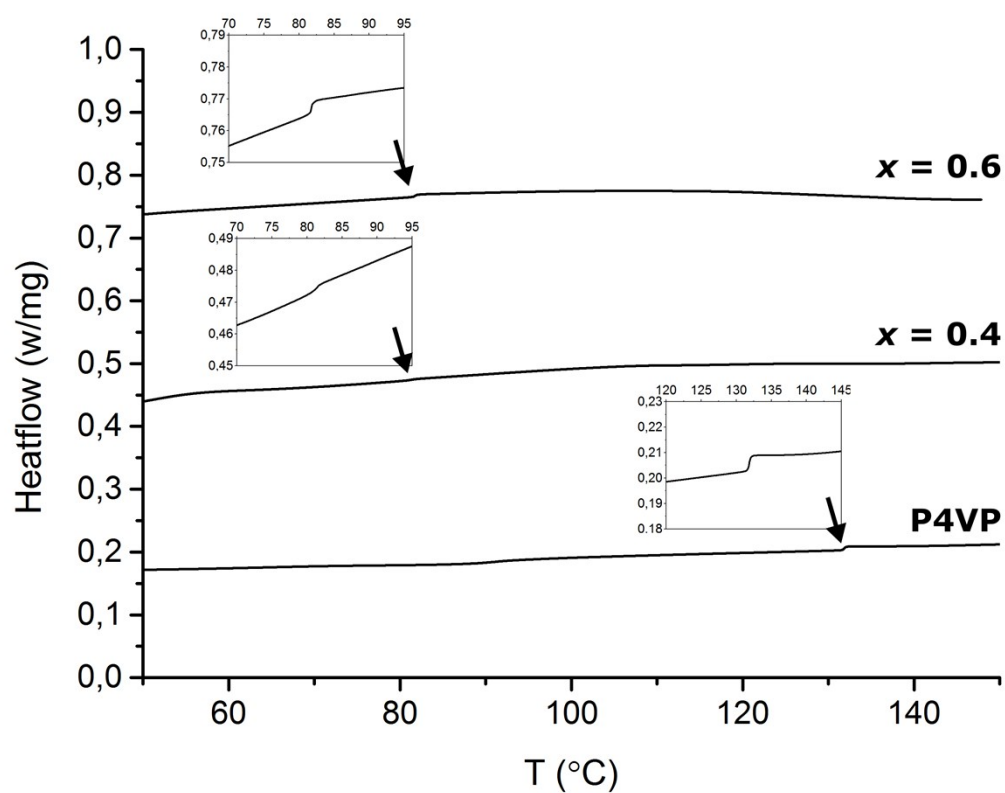
Fig S5. DSC spectra of P4VP and the **P4VP(LC)$_x$** supramolecular assemblies where x = 0.4. and x = 0.6.
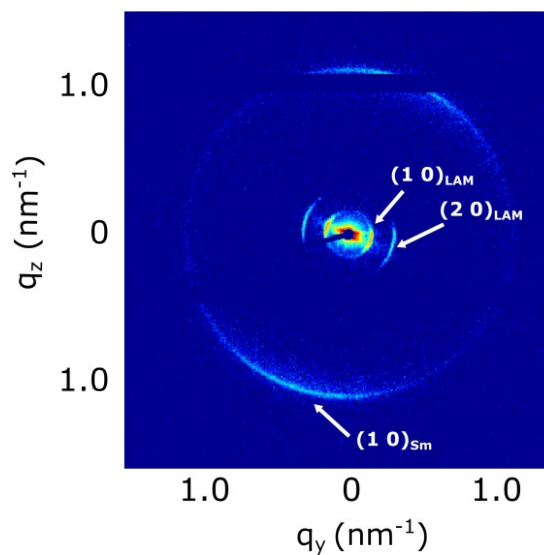

Fig S6. Small-angle XRD data of **PS-P4VP(LC)$_{0.3}$** complex**.** The assigned miller indices are indicated in the Fig. The BCP and LC scattering peaks are perpendicular to each other, thereby validating the schematic representation of the lattices shown in 3b.
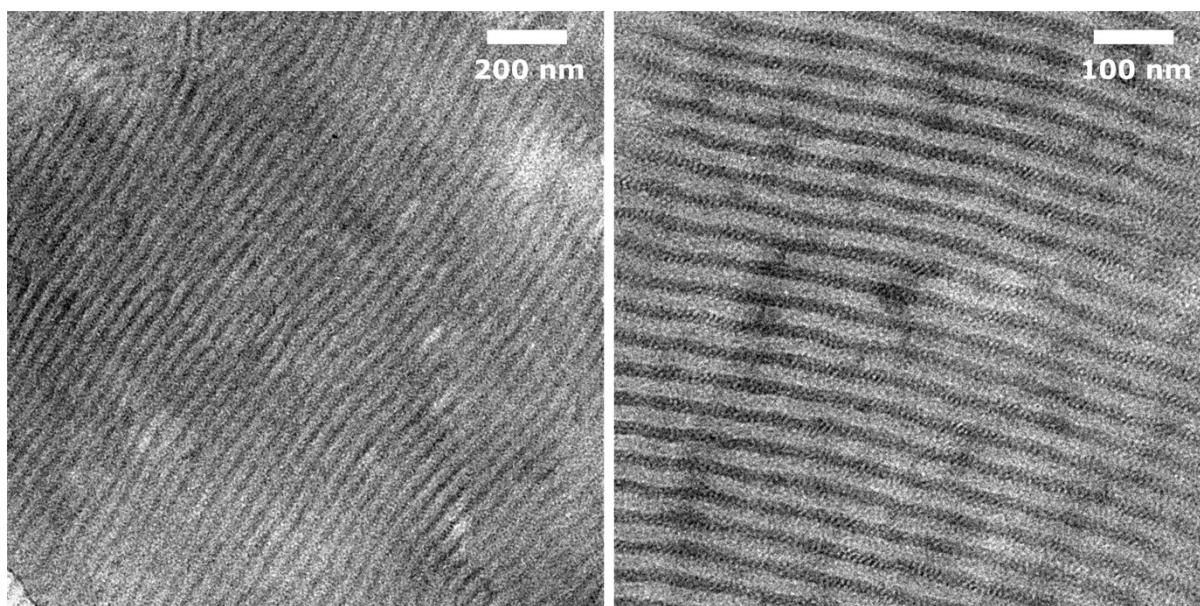
Fig S7. Large area transmission electron micrographs of **PS$_{33k}$-b-P4VP$_{4k}$(LC)$_{0.5}$** on an epoxy substrate. PS lamellae are light; ODMS side chains are dark.

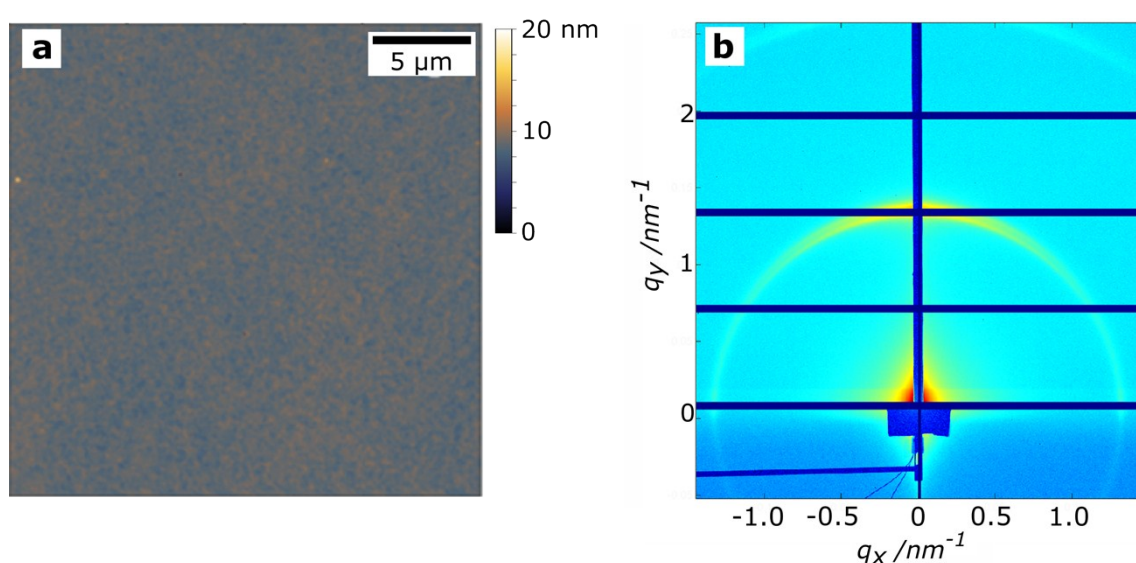**Fig S8.** Thin film characterization of as-cast PSA thin film of thickness *ca.* 80 nm of **P4VP$_{15k}$(LC)$_{0.4}$**. a) Atomic force microscopy height image showing a grainy multidomain surface. b) Grazing-incidence x-ray diffraction data in small-angle configuration, measured around the critical angle, showing a broad distribution of domain orientations.
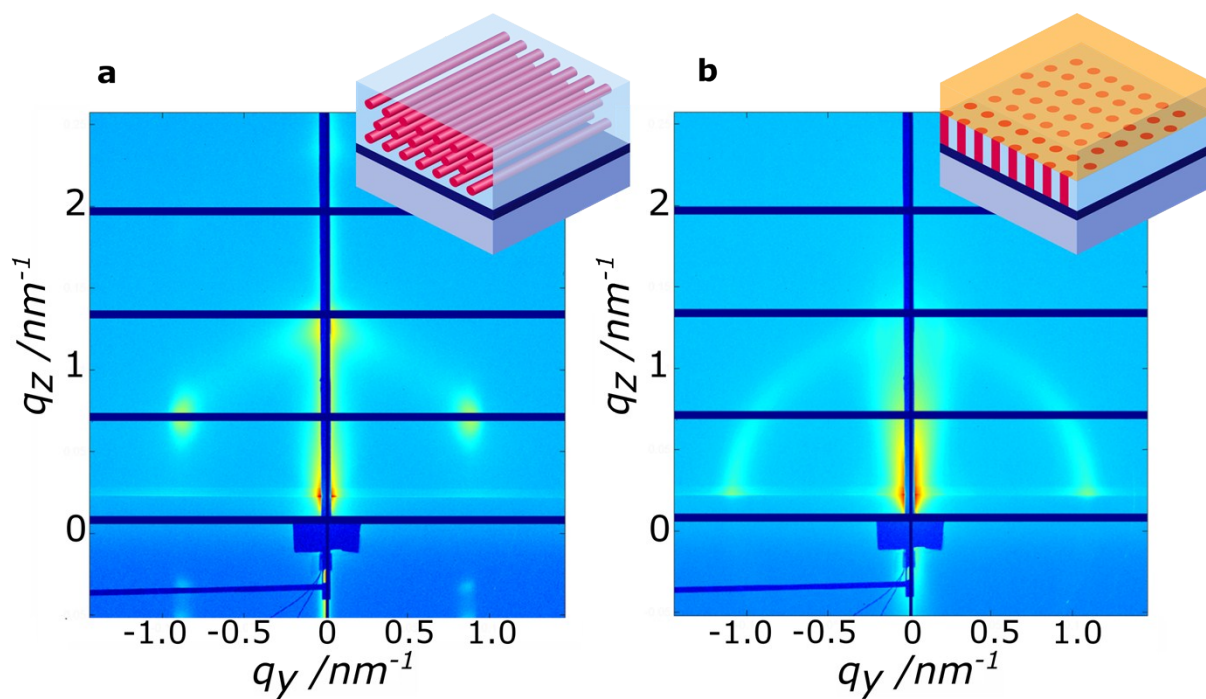
Fig S9. Grazing-incidence x-ray diffraction data in small-angle configuration for PSA thin films of thickness ~ 80 nm, measured around the critical angle. For a) **P4VP(LC)$_{0.6}$** the scattering data is fitted with a Col$_{Hex}$ phase (a = 6.8 nm) in which the cylinders are oriented planar to the substrate. For b) **PS-P4VP(LC)$_{0.5}$**, the primary scattering peak is oriented normal to the surface.