

Exploiting photopolymerization to modulate liquid crystalline networks actuation

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Supporting Information

Synthetic procedure

Synthesis of LCN-SH_x. Homogeneous mixtures were obtained by mixing RM257 (264 mg, 0.448 mmol, corresponding to 1 equivalent), BDMT (57 mg, 0.336 mmol corresponding to 0.75 equivalents for LCN-SH₇₅ and 38 mg, 0.224 mmol corresponding to 0.50 equivalents for LCN-SH₅₀), MHQ (1 mg, 0.008 mmol), DR1 (3 mg, 0.008 mmol) and the radical initiator Irgacure 369 (3 mg, 0.008 mmol) with some drops of dichloromethane. The mixtures were stirred at 75 °C for about 20 min then dried under vacuum. The mixtures were then infiltrated in LC cells made by two microscope glass slides opportunely coated with a PVA solution (5 % in weight in water), rubbed in one direction with a velvet cloth and kept separated by 20 µm glass beads (Duke Standards TM - Thermo Scientific). The infiltration step, which occurs for capillarity, was conducted by heating the mixtures at 120 °C, and then the filled cells were slowly cooled to room temperature (5 °/min). The samples were irradiated for 20 minutes with an LED UV lamp (Thorlabs M385L2-C4, 385 nm, 1.2 mW/cm²). The free-standing LCNs obtained were detached from the glass slides with a blade after 4 days of immersion in water.

Synthesis LCN-NH_{2x}. Homogeneous mixtures were obtained by mixing RM257 (78 mg, 0.132 mmol corresponding to 1 equivalent), DR1 (1 mg, 0.002 mmol) and the radical initiator Irgacure 369 (2.5 mg, 0.007 mmol) with some drops of dichloromethane. The mixtures were stirred at 75 °C for about 20 min and then dried under vacuum. 1-dodecylamine (18 mg, 0.1 mmol corresponding to 0.75 equivalents for LCN-NH₂₇₅ and 11 mg, 0.06 mmol corresponding to 0.50 equivalents for LCN-NH₂₅₀) was added and the mixture was stirred at 85 °C for 5 minutes. The mixtures were then infiltrated in LC cells made as previously described. The infiltration step was conducted by heating the mixtures at 85 °C, then the filled cells were cooled to 50 °C. After 20 hours the samples were irradiated for 20 minutes at 50 °C with a LED UV lamp (Thorlabs M385L2-C4, 385 nm, 1.2 mW/cm²). The free-standing LCNs obtained were detached from the glass slides with a blade after 4 days of immersion in water.

Synthesis LCN-Acrylate. A homogeneous mixture was obtained by mixing 4-Methoxybenzoic acid 4-(6-acryloyloxy-hexyloxy)phenyl ester (105 mg 0.264 mmol), RM257 (18 mg 0.03 mmol), DR1 (1 mg 0.003 mmol) and Irgacure 369 (1 mg 0.003 mmol) with some drops of DCM. The mixtures were

stirred at 65 °C for about 20 min and then exsiccated under vacuum. The mixture was infiltrated in LC cells made as previously described. The infiltration step was conducted by heating the mixture at 65 °C, then the filled cells were cooled to room temperature. The samples were irradiated firstly for 10 minutes at 45 °C then for another 10 minutes at 65 °C with an LED UV lamp (Thorlabs M385L2-C4, 385 nm, 1.2 mW/cm²). The free-standing LCNs obtained were detached from the glass slides with a blade after 1 day of immersion in water.

Polarised Optical Microscopy Analysis

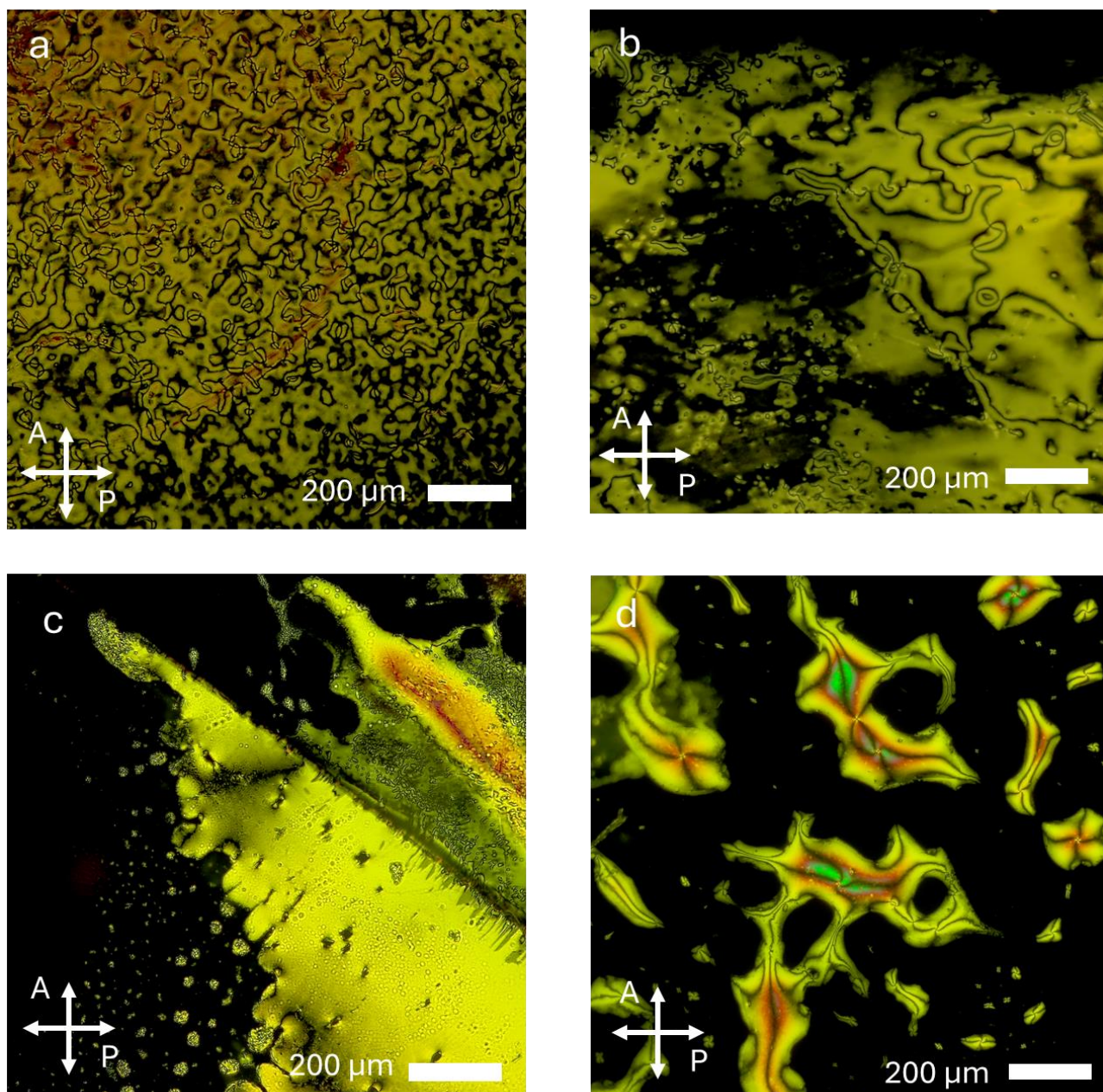


Figure S1. Polarised optical microscope (POM) images of a) LCN-NH₂50 monomeric mixture b) LCN-SH50 monomeric mixture c) LCN-NH₂50 oligomerized mixture d) LCN-NH₂75 oligomerized mixture. The scale labels are 200 μm. The mixtures and the oligomers show Schlieren textures with twofold and fourfold brushes typical of the nematic mesophase.

ATR Analysis

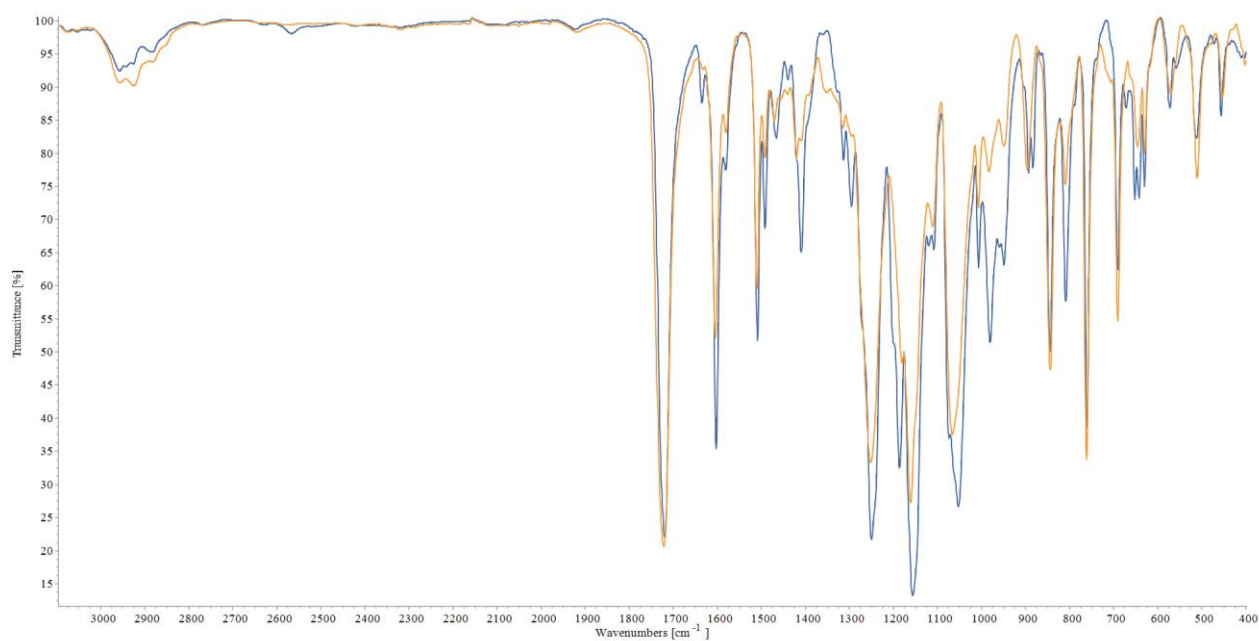


Figure S2. ATR spectra of LCN-SH75 mixture (in blue) and LCN-SH75 after photopolymerization (yellow). The reaction was monitored observing the disappearance of the band at 1410 cm^{-1} relative to the C=C double bond in the acrylate group and the characteristic band relative to the =CH₂ (811 cm^{-1}) and the disappearance of the band at 2500 cm^{-1} relative to the -SH group.

1H NMR Analysis

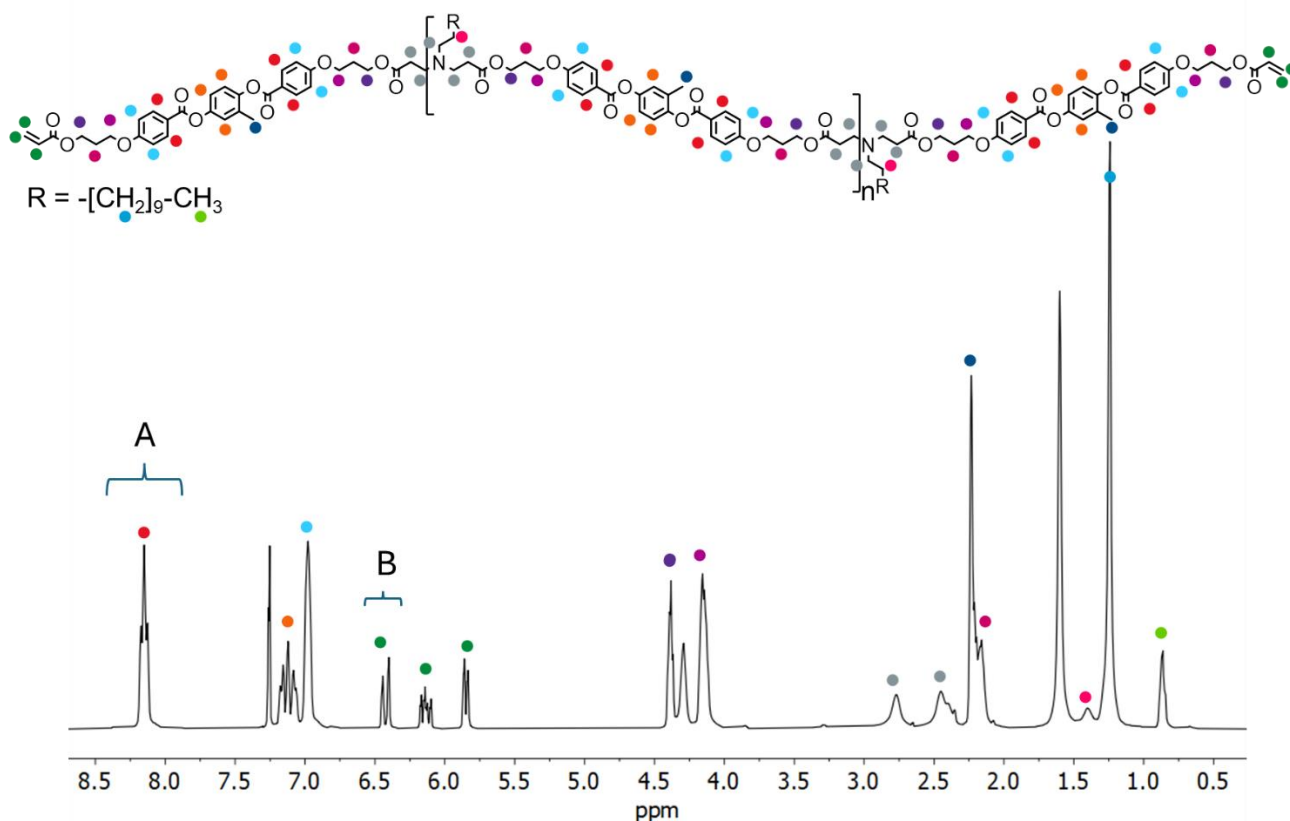


Figure S3. ¹H NMR of LCN-NH₂50 oligomer and peak assignment.

The average number of RM257 units in the oligomers was calculated through equation 1 where A is the subtended area at the peak at 8.2 ppm and B is the subtended area at the peak at 6.4 ppm.

$$RM257 \text{ units} = \frac{\frac{B}{2}}{\frac{A}{4}} \quad \text{Equation 1}$$

Consequently, the number of repeating units (*n*) is calculated through equation 2.

$$n = \frac{\frac{B}{2}}{\frac{A}{4}} - 2 \quad \text{Equation 2}$$

The repeating units were 0 and 1 respectively for LCN-NH₂50 and LCN-NH₂75 oligomers.

Additional experimental methods for LCN characterization

Order Parameter

The alignment degree of the materials was evaluated by calculating an order parameter (S) starting from the film's absorption of linear polarised light. S was calculated through equation 3, where A_{\parallel} is the absorbance of the film (at 500 nm) with its director oriented parallel to the plane of polarisation of light and A_{\perp} is the absorbance of the film with its director oriented perpendicular to the plane of polarisation of light

$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \quad \text{Equation 3}$$

Crosslinking density

The crosslinking density for the LCN films was calculated through equation 4 where E'_{rubbery} is the storage modulus 50 °C above T_g , R is the gas constant and T is the temperature

$$\nu_c = \frac{E'_{\text{rubbery}}}{3RT} \quad \text{Equation 4}$$

Light actuation

The tension developed under illumination by the LCNs was recorded in a custom-made setup composed by a force transducer WPI SI-KG4 connected to a force transducer amplifier SI-BAM21-LC. Two LED lamps Thorlabs M470L5 emitting blue light (470 nm) to irradiate the materials simultaneously on both sides were employed. LCN samples of 12x1 mm² were clamped in isometric conditions and the sample was shined with a frequency of 0.1 Hz and illumination time of 5 s with intensity between 1.25 and 8.45 mW/mm². The LEDs control and the force recording were effectuated by a LabVIEW program with a multichannel driver. The forces measured were normalised per the cross-section of each specimen obtaining tension values. The rate of actuation was calculated as the slope of the tangent at the first 200 ms of the tension trace.

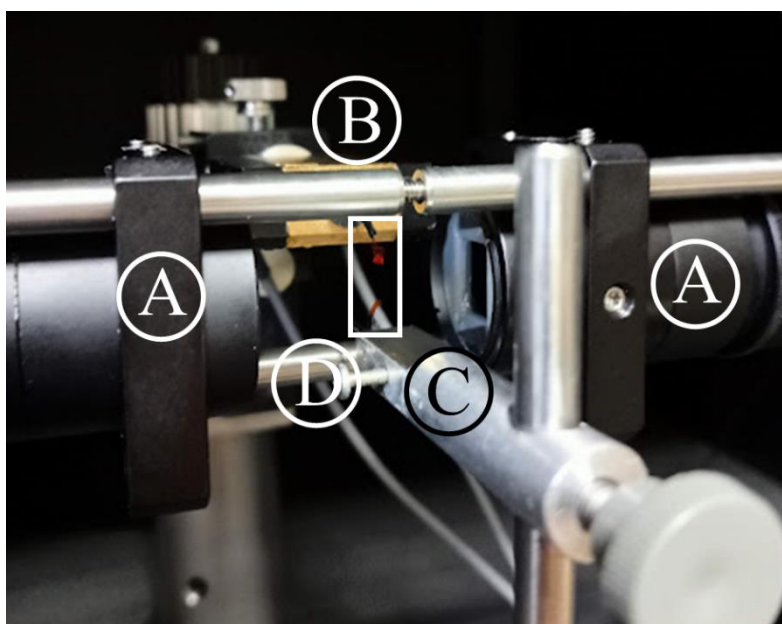


Figure S4. The photo shows the set-up used for the experiment of photo actuation. The letter A marks the two LED lamps. The letter B marks the force transducer while the letter C marks the metallic bar to hold the sample. The letter D and the white rectangle highlight a mounted broken sample.

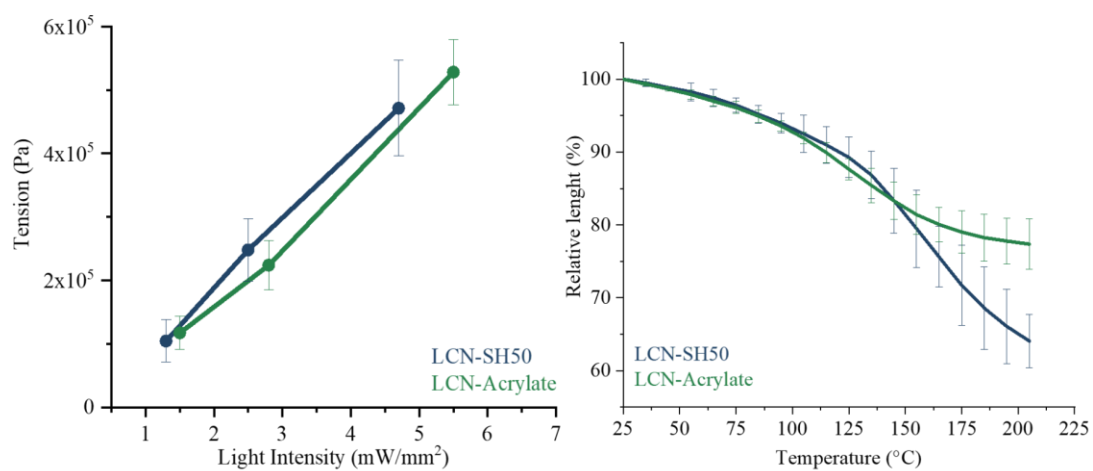


Figure S5. a) Average of the maximum tension developed by the materials vs intensity of light for LCN-SH50 compared with LCN-Acrylate. b) Thermal actuation in free standing conditions for LCN-SH50 compared with LCN-Acrylate.

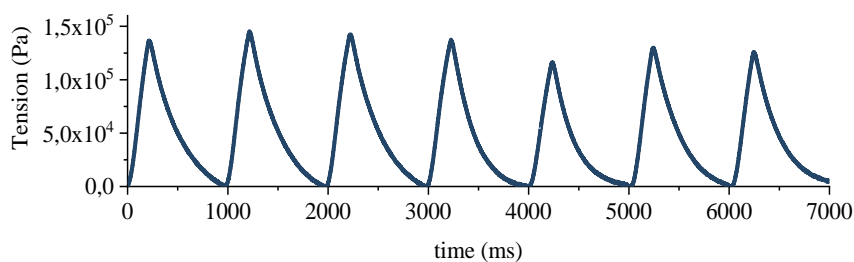


Figure S6. Tension traces of LCN-SH50. Frequency 1 Hz and time of illumination of 250 ms.