Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Photochemical Phase and Alignment Control of a Nematic Liquid Crystal in Core-Sheath Nanofibers

Matthew D. Thum[a†], Daniel Ratchford[a], Riccardo Casalini[a], Jakub Kołacz[b], Jeffrey G. Lundin[a]*

[a]Chemistry Division, Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, D.C. 20375

[b]Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, D.C. 20375

[†]American Society for Engineering Education Post-Doctoral Research Associate

*Corresponding author: **jeffrey.lundin@nrl.navy.mil**

Synthesis and Characterization.

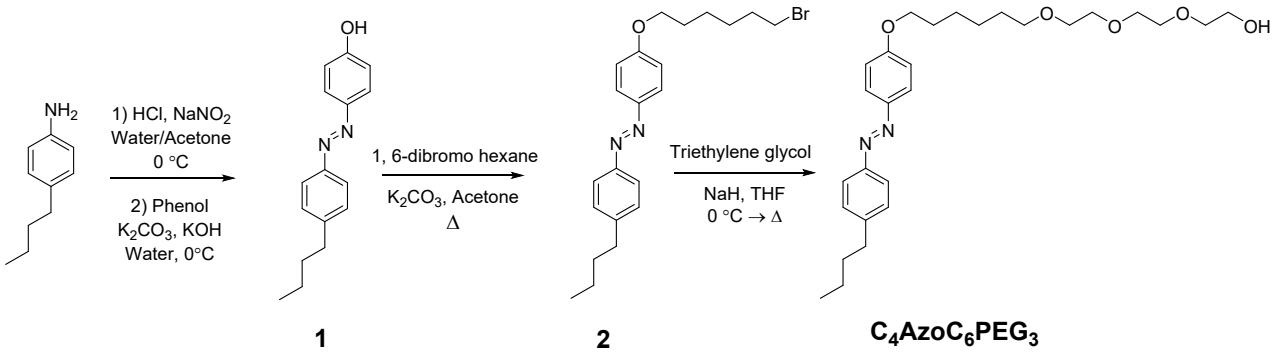

Figure S-1. Synthesis of **$C_4AzoC_6PEG_3$**

The synthesis of compounds **1** and **2** has been previously reported.[1]

(**$C_4AzoC_6PEG_3$**): In a 250 mL round bottom flask equipped with a stirrer, 1.13 g of triethylene glycol (7.55 mmol) was added along with 100 mL of dry THF. The components were stirred at room temperature under N_2 for 20 minutes before NaH (300 mg, 12.5 mmol) was added. The solution was stirred at room temperature under N_2 for 2 hours. After, a solution of **2** (1.59 g, 3.8 mmol) in 50 mL of dry THF was added dropwise via canula under N_2. After addition, the components were then refluxed under N_2 for 48 hours. The solvent was removed under reduced pressure and the residual solid was dissolved in chloroform where it was extracted with water (1 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure to give a red oil which was purified via. column chromatography (3:1 Hexanes/EtOAc) resulting in 1.015 g of **$C_4AzoC_6PEG_3$** in 55 % yield. The product was a red oil that solidified to an orange powder upon standing. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.90 (d, 2H), 7.8 (d, 2H), 7.31 (d, 2H), 7.00 (d, 2H), 4.05 (d, 2H), 3.75-3.59 (m, 12H), 3.49 (t, 2H), 1.91 (m, 2H), 1.63 (m, 5H), 1.47 – 1.26 (m, 6H), 0.95 (t, 3H) ;^{13}C NMR (400 MHz, $CDCl_3$) ^{13}C NMR (400 MHz, $CDCl_3$) δ, ppm: 161.5, 151.2, 147.1, 145.9, 129.4, 124.6, 122.6, 114.8, 72.6, 71.4, 70.7, 70.7, 70.5, 70.2, 68.3, 61.9, 35.6, 33.5, 29.6, 29.2, 26., 22.4, 14.0.

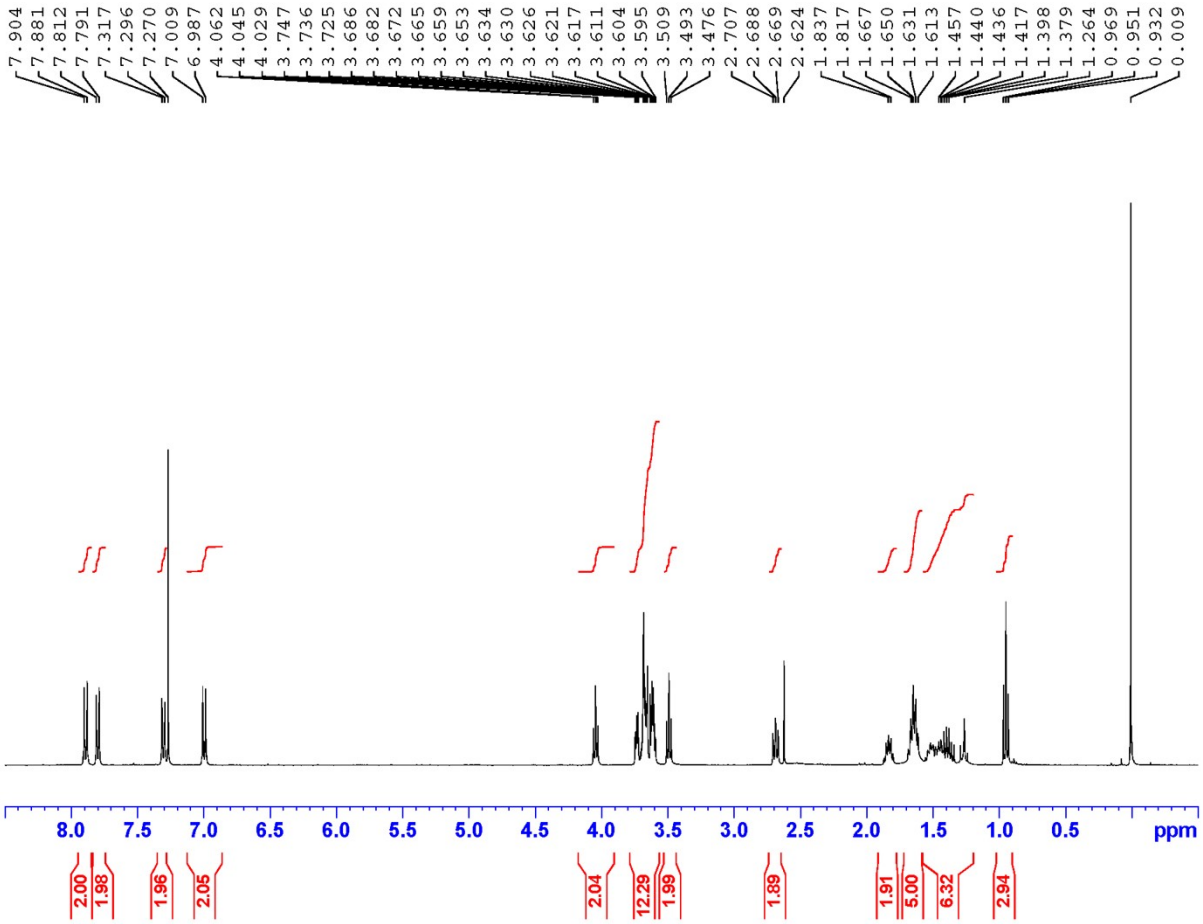

Figure S-2. ^{1}H NMR (400 MHz) of **$C_4AzoC_6PEG_3$** in $CDCl_3$

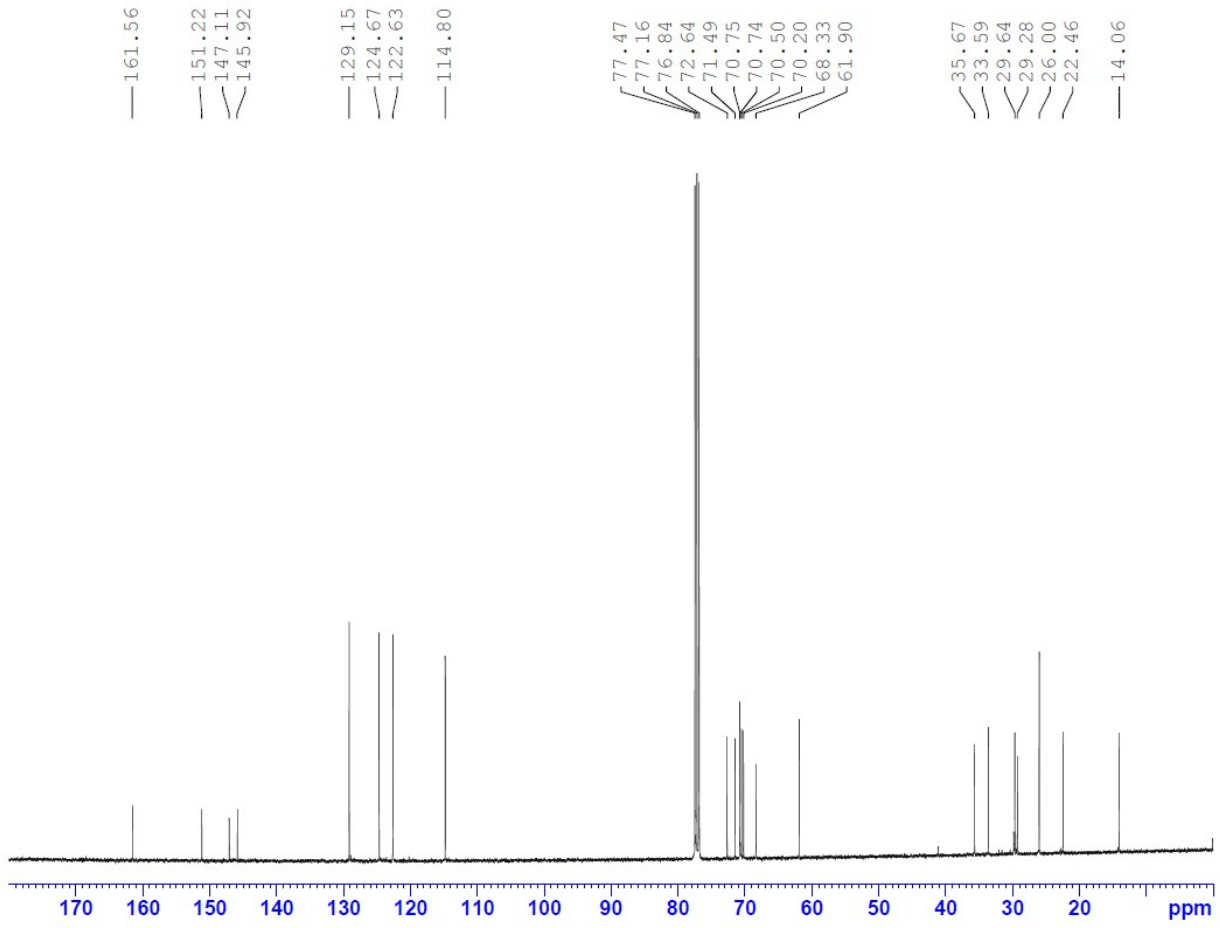

Figure S-3. ^{13}C NMR (400 MHz) of **$C_4AzoC_6PEG_3$** in $CDCl_3$

Monofilament fibers.

Monofilament fibers were electrospun from 12.5 wt. % PVP solutions in 90/10 ethanol/water mixtures containing up to 3.0 wt. % of **$C_4AzoC_6PEG_3$** and 0.05 wt. % NaCl. Uniform fibers were observed up to 3 wt. % of **$C_4AzoC_6PEG_3$**.

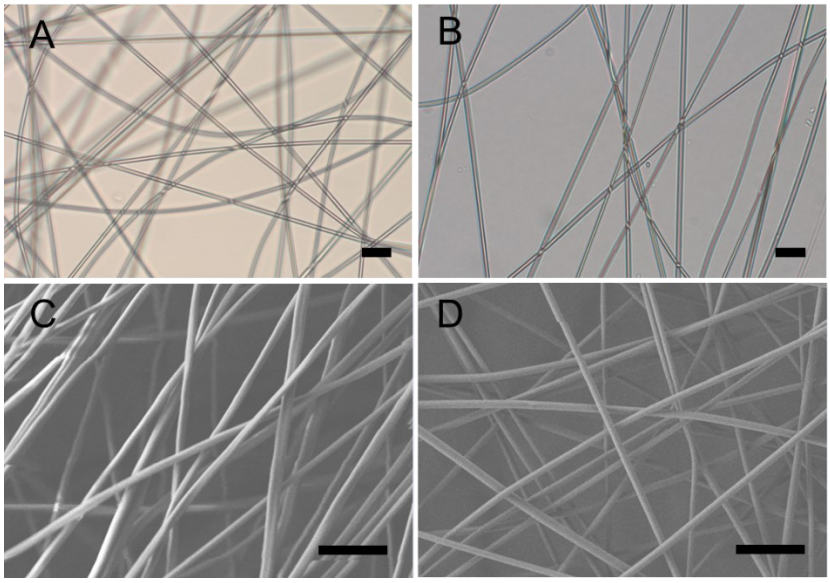

Figure S-4. POM and SEM Images detailing monofilament fibers made with varying concentration of **$C_4AzoC_6PEG_3$** in PVP (12.5 wt. %). 0 wt % (A,C) 3.0 wt. % (B,D). Fiber morphology does not significantly change with increasing concentration of **$C_4AzoC_6PEG_3$**.

UV/Vis. and Dark Recovery Kinetics.

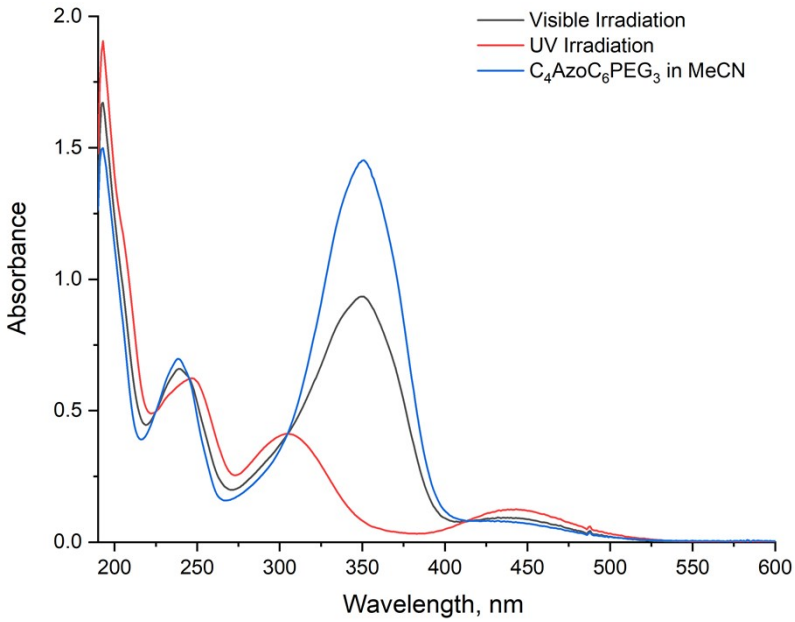

Figure S-5. UV/Vis absorption spectra of **$C_4AzoC_6PEG_3$** in MeCN before (Blue) and after (Red) irradiation with 365 nm light for 10 seconds. The spectra from visible light (400-500 nm) irradiation for 10 seconds of the *cis* isomer formed after UV irradiation.

A sample of **$C_4AzoC_6PEG_3$** was dissolved in acetonitrile and irradiated at 365 nm until the photostationary state was reached (ca. 10 seconds). The sample was kept in the sample holder of the UV/Vis and covered to keep out external light. The absorbance spectrum was collected every hour for 22 total hours to collect the data shown and perform the kinetic analysis in Figure S-6.

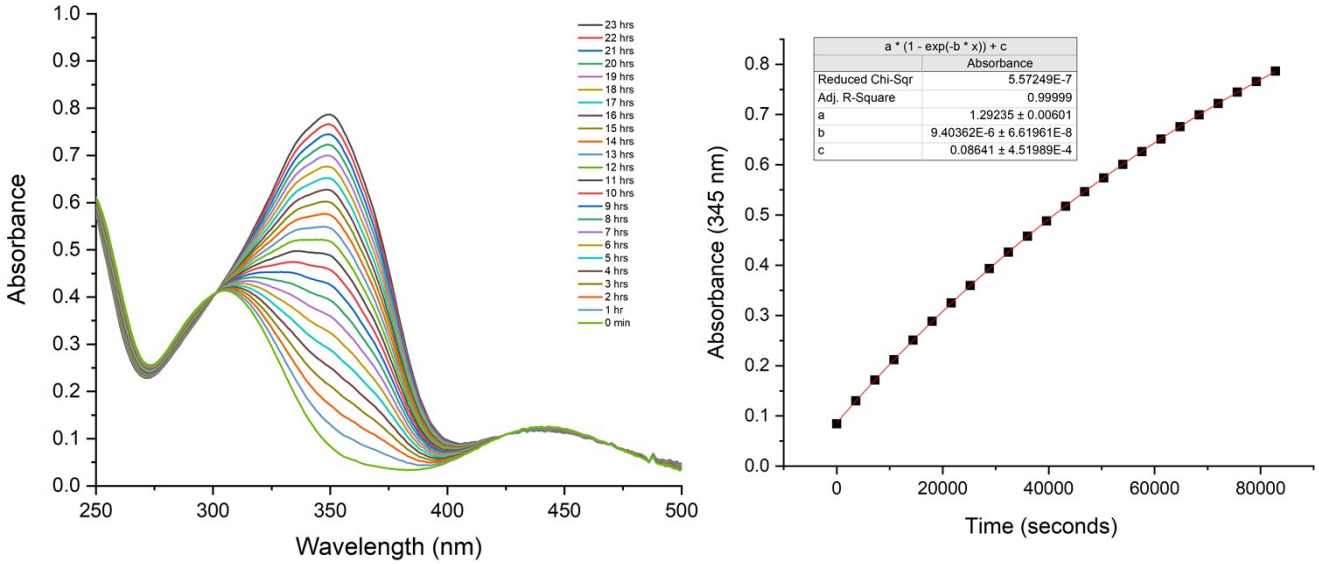

Figure S-6. Thermal *cis-trans* isomerization of **$C_4AzoC_6PEG_3$** in the dark at room temperature. *Left*: UV/Vis spectra showing the thermal recovery of *trans*-**$C_4AzoC_6PEG_3$** in the dark at room temperature. *Right*: The absorbance of **C_4AzoC_6 PEG_3** at 345 nm vs time. The data was fit to a first order model using the kinetics tool in OriginLab 2018.

Additional Quarter Wave Retardation Plate Images.

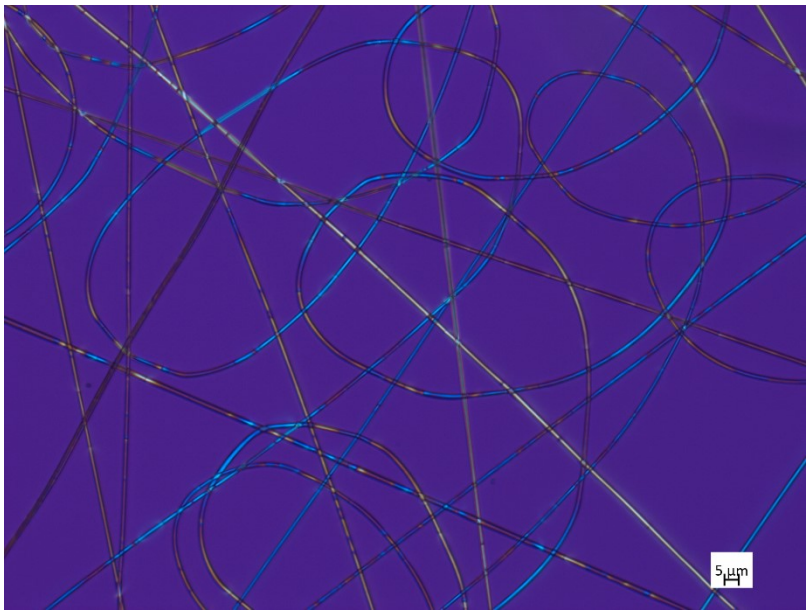

Figure S-7. Crossed POM images with a quarter wave retardation plate of fibers formed with 2.0 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core.

Fatigue Resistance.

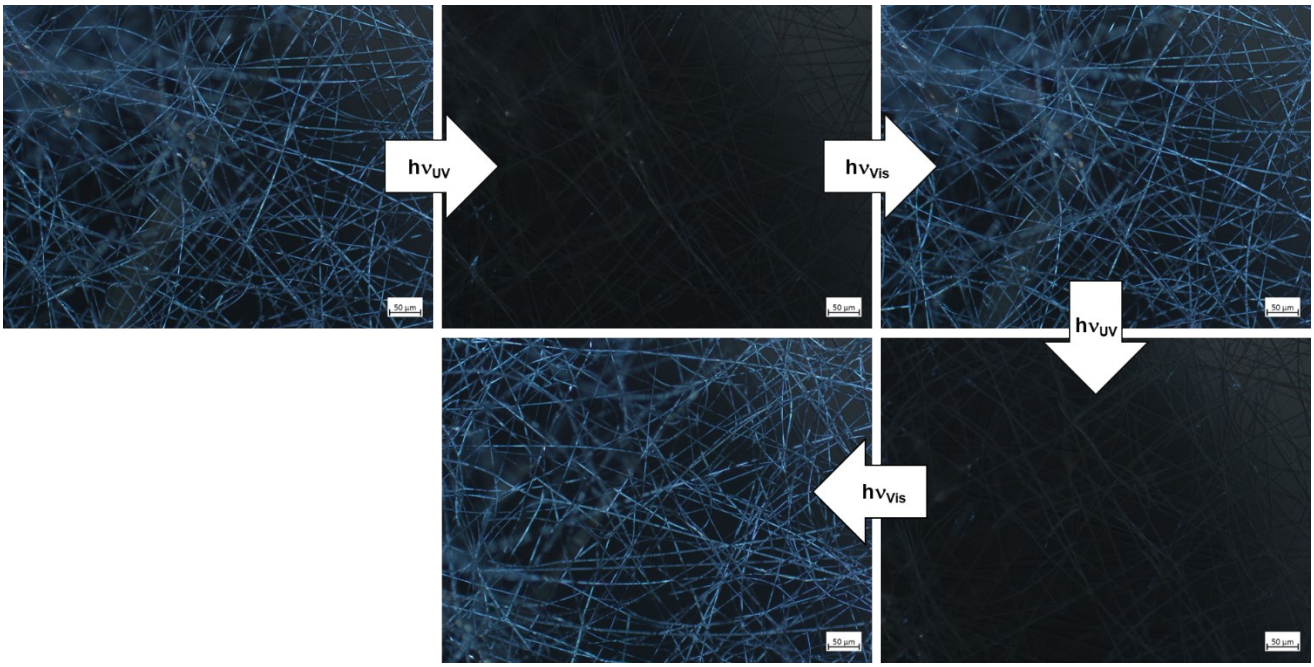

Figure S-8. Crossed POM images showing "On"/"Off" Cycles at 29 °C for 1.5 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core.

Thermal Phase Control.

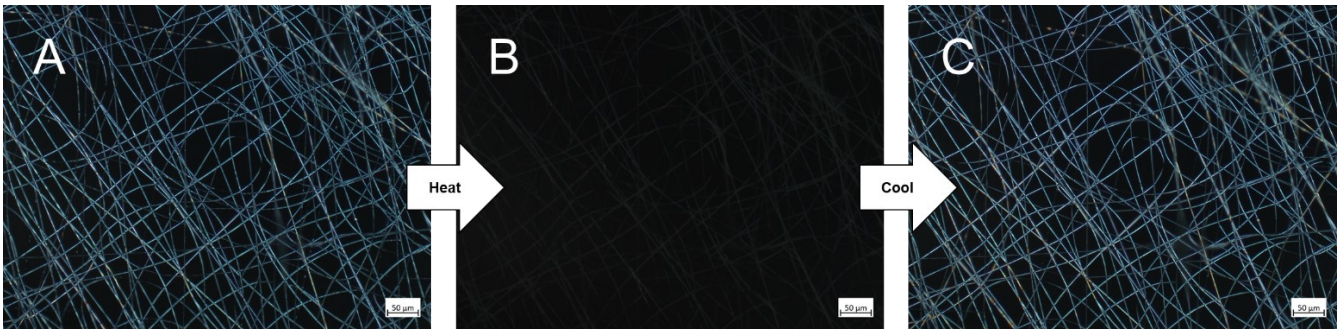

Figure S-9. Crossed POM images showing 1.0 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core with heating from 25 °C (*A*) to 37 °C (*B*) and cooling back to 25 °C (*C*).

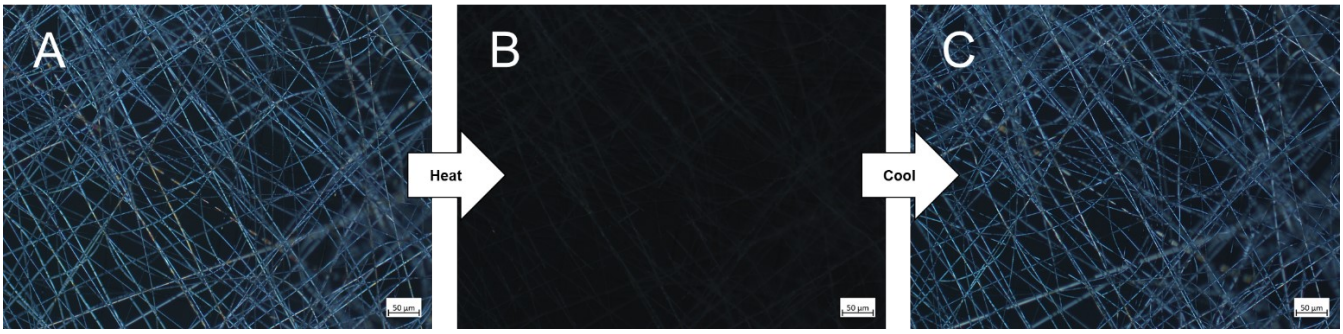

Figure S-10. Crossed POM images showing 1.5 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core with heating from 25 °C (*A*) to 37 °C (*B*) and cooling back to 25 °C (*C*).

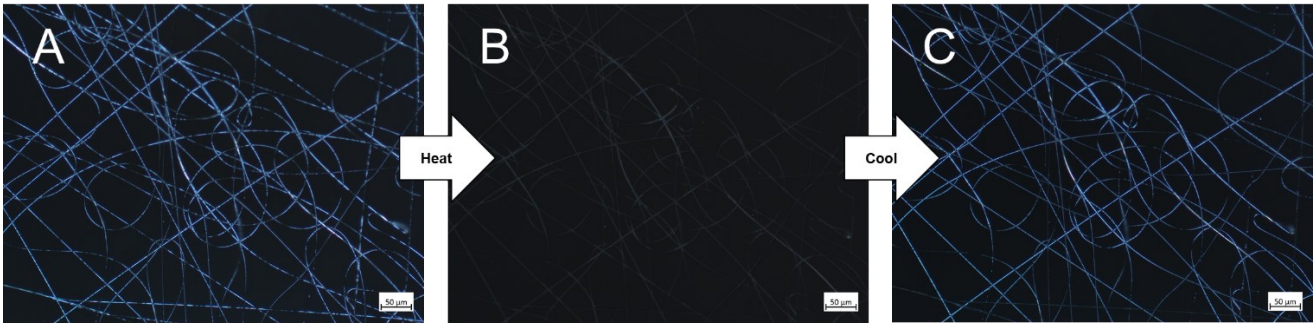

Figure S-11. Crossed POM images showing 2.0 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core with heating from 25 °C (*A*) to 37 °C (*B*) and cooling back to 25 °C (*C*).

Photochemical Phase Control.

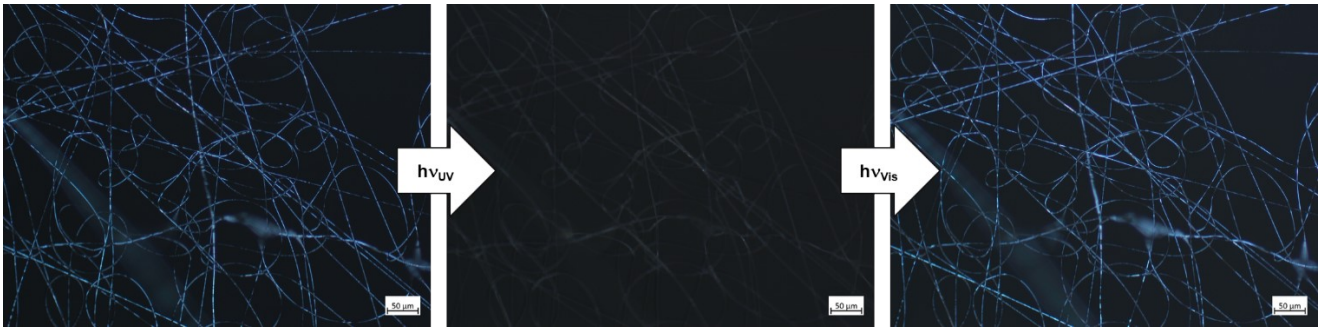

Figure S-12. Crossed POM images showing 2.0 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core at 27 °C before, and after 5 seconds of UV irradiation and after 5 seconds of visible light irradiation.

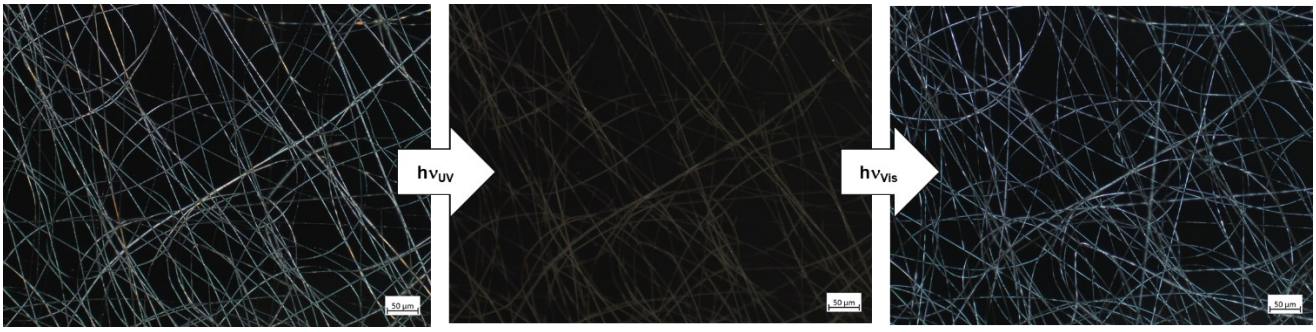

Figure S-13. Crossed POM images showing 1.0 wt % **$C_4AzoC_6PEG_3$** sheath and a neat 5CB core at 32.5 °C before, and after 5 seconds of UV irradiation and after 5 seconds of visible light irradiation.

Fiber Morphology.

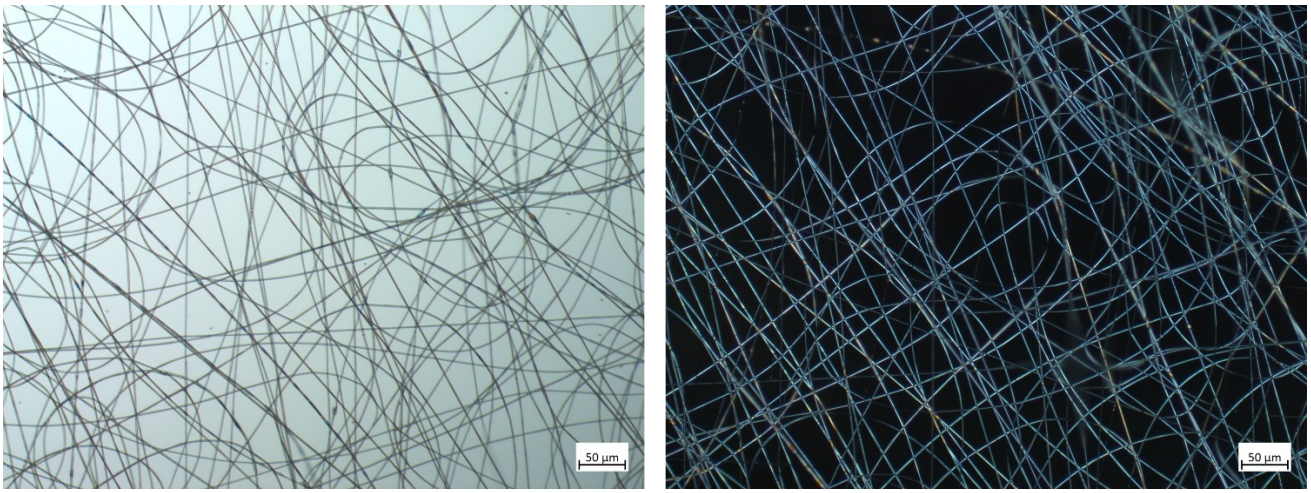

Figure S-14. POM Images of fibers made with 1.0 wt % **$C_4AzoC_6PEG_3$**.

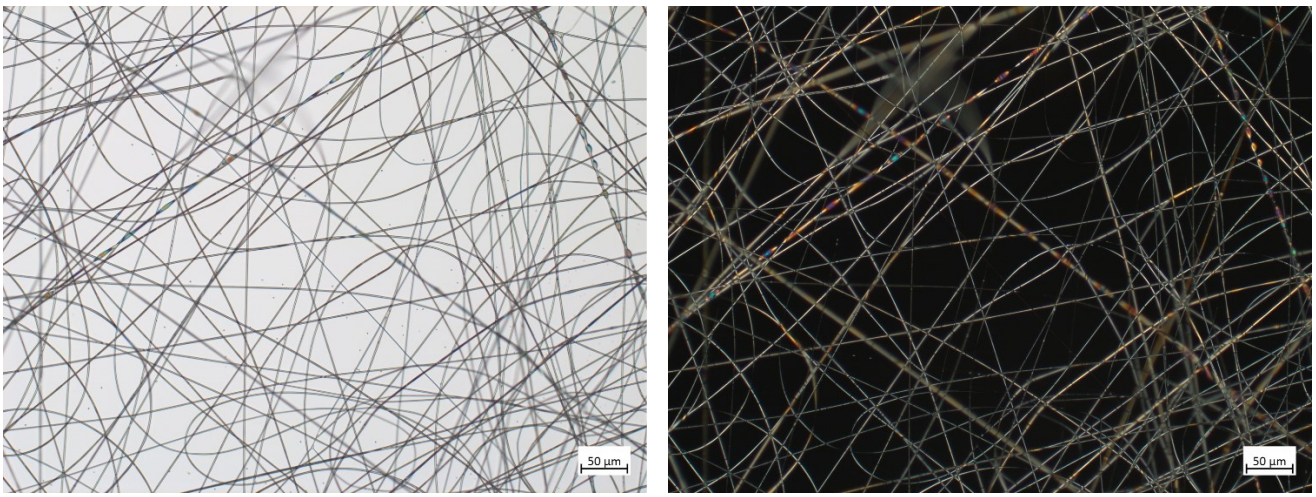

Figure S-15. Figure S-12. POM Images of fibers made with 1.5 wt % **$C_4AzoC_6PEG_3$**.

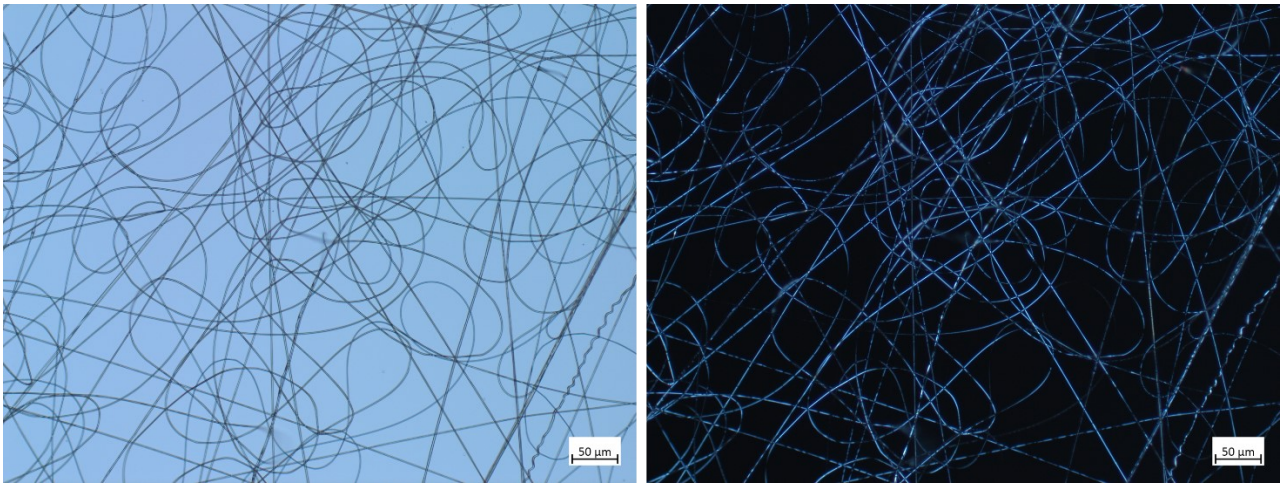

Figure S-16. Figure S-12. POM Images of fibers made with 2.0 wt % **$C_4AzoC_6PEG_3$**.

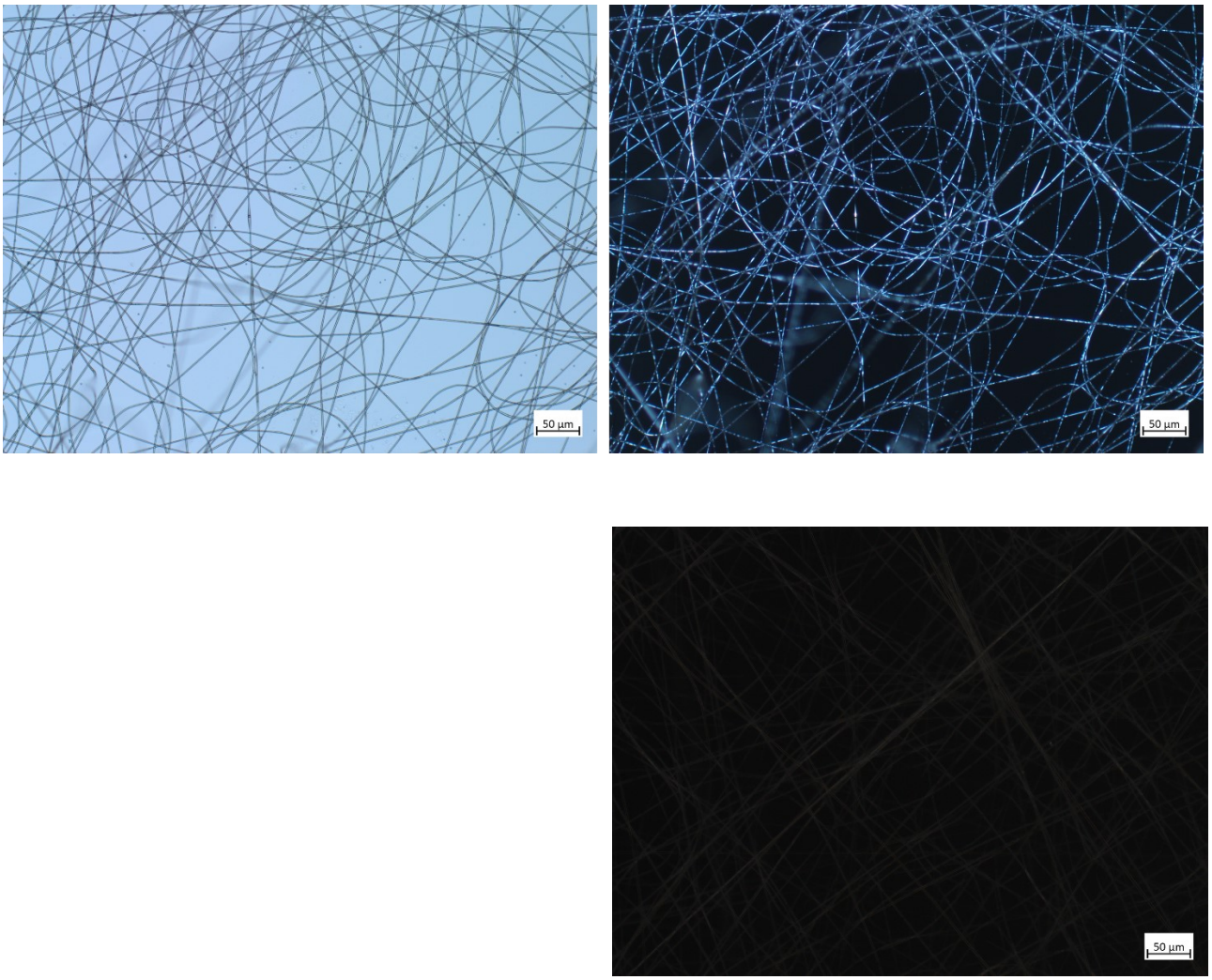

Figure S-17. POM Images of fibers made with 3.0 wt % **$C_4AzoC_6PEG_3$**.

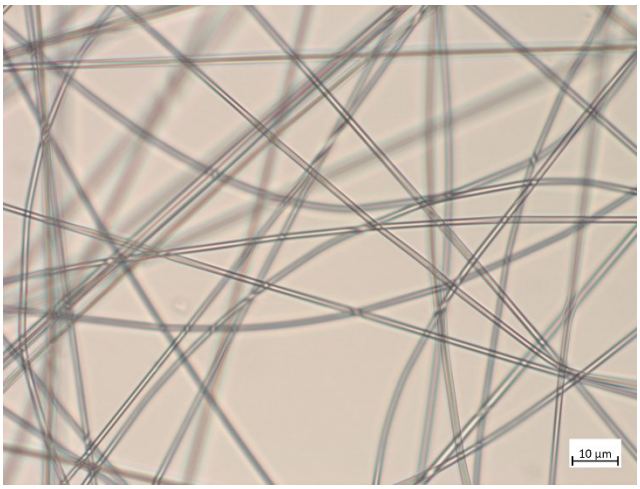

Figure S-18. POM images of PVP nanofibers without a LC core showing a lack of birefringence when viewed under crossed polarizers (*right*).

Differential Scanning Calorimetry (DSC)

TA Instruments Discovery DSC (New Castle, DE) was employed to investigate the phase transitions of the core-sheath fibers. Samples were cut from the electrospun mat and placed into Tzero Pans (TA Instruments). The DSC equilibrated at 5 °C before a temperature ramp to 60 °C at a rate of 5 °C·min^{-1}. The sample was then cooled at a rate of 5 °C·min^{-1} to 10 °C. This process was repeated three times. Results were analyzed using TA Instruments TRIOS software.

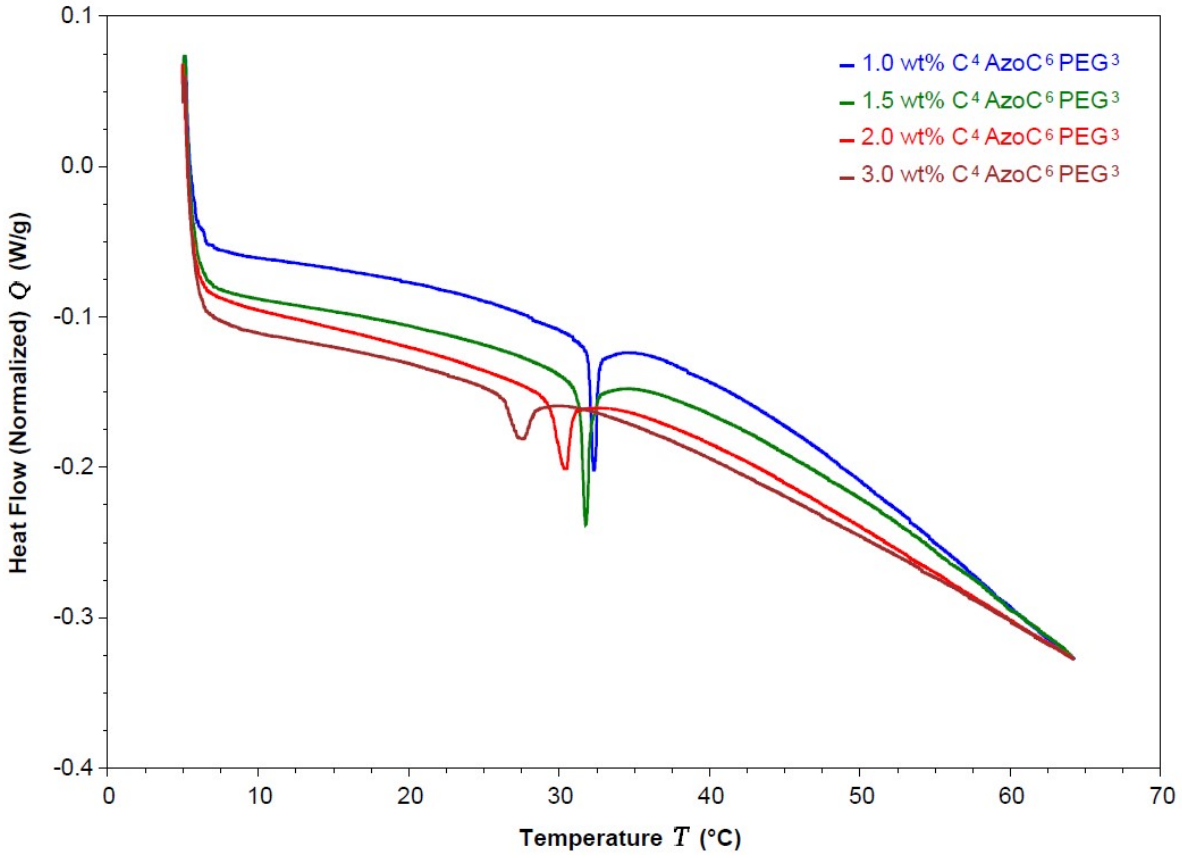

Figure S-19. DSC scans showing the nematic to isotropic transition of **5CB** within the electrospun nanofibers. The data is represented with respect to the concentration of **$C_4AzoC_6PEG_3$** in the PCP sheath solution before spinning. With increasing concentration of azobenzene, the nematic to isotropic transition broadens and shifts to lower temperatures which is consistent with the LC ordering and phase transitions as measured by POM. Results shown are for the first of three scans.

References.

1. Thum, M. D.; Ratchford, D. C.; Casalini, R.; Wynne, J. H.; Lundin, J. G., Azobenzene-Doped Liquid Crystals in Electrospun Nanofibrous Mats for Photochemical Phase Control. *ACS Applied Nano Materials* **2021,** *4* (1), 297-304.