

Supporting Information

Optical control of alignment and patterning in an azobenzene liquid crystal photoresist

Gregory T. Carroll,^{*a†} Kyung Min Lee,^{b,c} Michael E. McConney^b and Harris J. Hall^a

^aAir Force Research Laboratory, Sensors Directorate, Wright-Patterson Air Force Base, OH, USA

^bAir Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, OH, USA

^cAzimuth Corporation, 2970 Presidential Drive, Beavercreek, OH, USA

[†]Present Address: Aerobiotix, Inc., Miamisburg, OH

Materials and Methods

4,4'-bis(6-acryloyloxyhexyloxy)azobenzene (**1**) was obtained from Alpha Micron. Irgacure 784 was obtained from BASF. 1,5-pentane dithiol, triethyl amine, trimethylolpropane tris(3-mercaptopropionate) and toluene were obtained from Aldrich. UV-Vis measurements were performed with a Carey UV-Vis spectrophotometer. Polarization measurements were performed by placing a Harrick polarizer between the light source of the spectrometer and the azobenzene thin film. The polarization angle could be selected by turning a dial on the polarizer. Photocuring was performed with a 532 nm laser set at an intensity of 4 W. Photoalignment was performed with a 455 nm laser at full intensity. Photoisomerization was performed with a 365 nm Omnicure LX500 LED lamp (Excelitas Technologies Corp.). The surface was held approximately 5 mm from the lamp head. Polychromatic visible light irradiation for non-polarized cis-trans photoisomerization was performed with a Gagne Light Box (Gagne, Inc.) containing white bulbs. Differential Scanning Calorimetry (DSC, Perkin Elmer) was performed under a nitrogen atmosphere at a scan rate of 5° C /min. Polarization microscopy (Nikon, Eclipse 50iPol) was performed with a heating/cooling stage (Mettler FP-90).

Preparation of formulation

The formulation containing **1** was prepared by adding .03517 g of **1**, .00331 g of 1,5-pentanedithiol and a drop of triethyl amine (typically .005-.01 g) to a small glass vial. The mixture was melted by heating with a heat gun until **1** melted. The resulting liquid was placed in a 65° C oven for 1 h. The vial was then allowed to cool in the dark before adding .35225 g toluene and .00814 g trimethylolpropane tris(3-mercaptopropionate).

Preparation of Films and Photopatterning

Films were cast by spin-coating. A few drops were applied and spread on the surface. The sample was then spun at 3000 RPM for 25 s. Samples were then immediately masked, placed on a black surface and irradiated with a 4 W 532 nm Verdi laser (Coherent, Inc.) for various amounts of time. Unless otherwise noted, samples were irradiated for 30 s. Films were immediately rinsed after photo-patterning with toluene. Films were further rinsed with acetone, methanol, isopropanol and water, however, only toluene is needed to remove unpolymerized material.

Photoalignment

Samples were first exposed to UV light for 3 s. After UV light exposure, samples were irradiated with a polarized 445 nm laser (Tiangreen) with an irradiance of ~35 mW/cm² for at least 10 min. In an alternative procedure, a

drop of toluene was placed on the film immediately before irradiation with the 445 nm laser. The wet sample was then irradiated for at least 10 min. as the toluene evaporated. Alignment was confirmed by placing the samples between crossed polarizers, illuminated with visible light and rotated to qualitatively monitor changes in brightness. Photoaligned samples show noticeable changes in brightness upon 45° rotation between crossed polarizers. Photoalignment was also confirmed with polarized UV-Vis spectroscopy. Absorption spectra of photoaligned films showed clear differences in intensity when analyzed with 0° and 90° polarized light in the spectrophotometer.

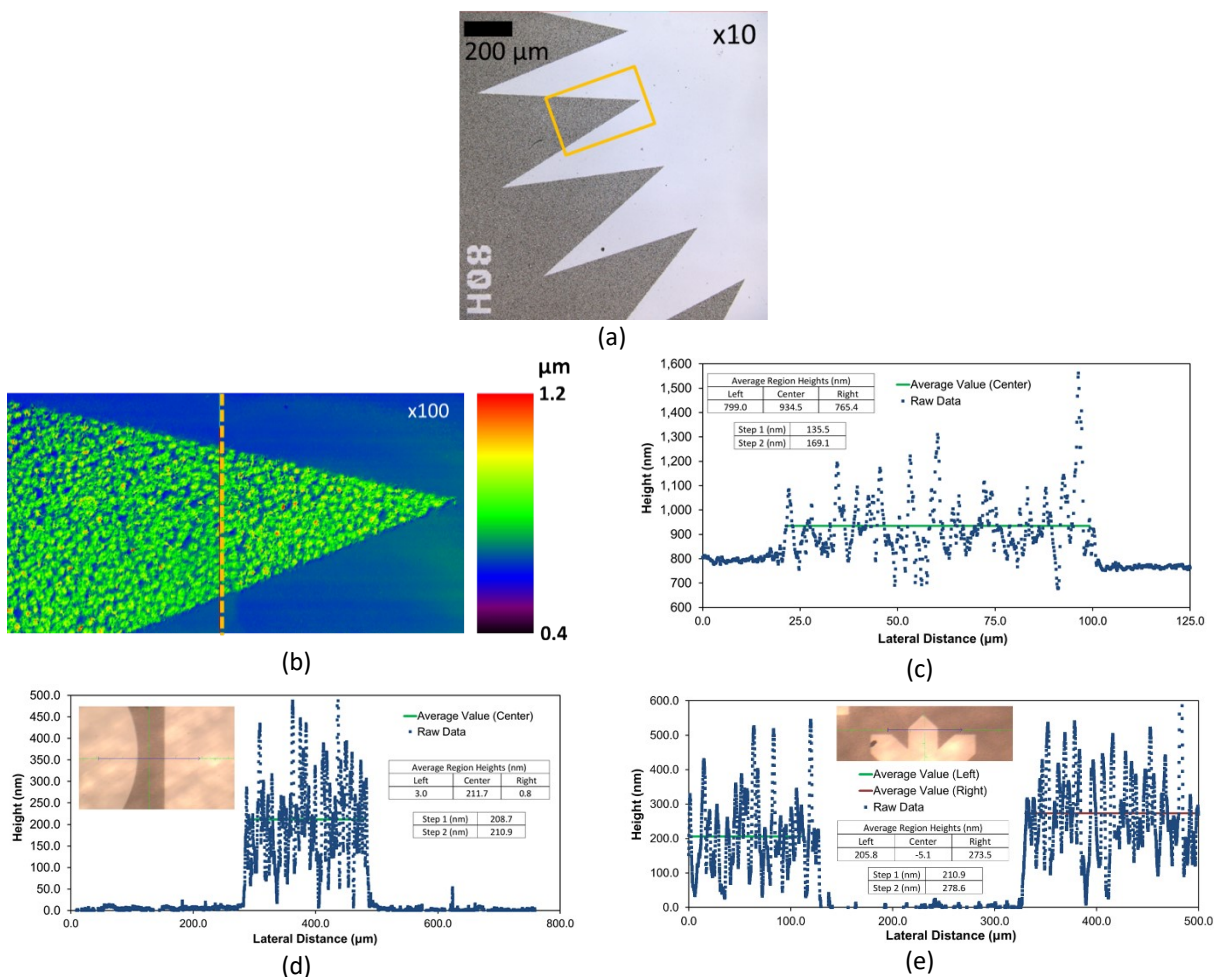


Fig. S1 Patterned liquid crystal elastomer imagery and profilometry data. (a) optical image of patterned feature at x10 magnification (b) surface height image of same feature from 3D confocal microscope at x100, dashed yellow line corresponds to height profile shown in (c) (d and e) show separate contact profilometry measurements on different patterned features with image and linear scan position shown inset.

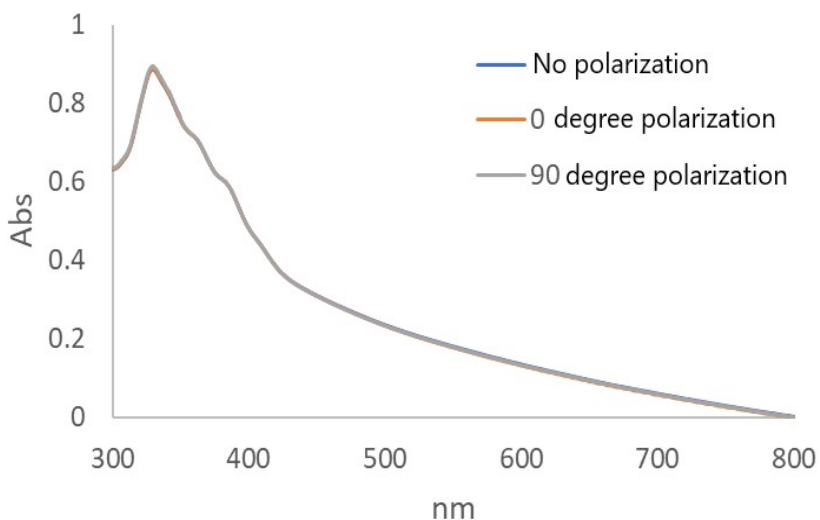


Fig. S2 Non-polarized UV-Vis of spin-coated film based on **1** after irradiating with green light (blue). Additionally, the UV-Vis spectra were taken with 0° (red) and 90° (grey) polarized light. The overlap of all three spectra indicate that the spin-coated and cured film shows no alignment of the azobenzene chromophores.

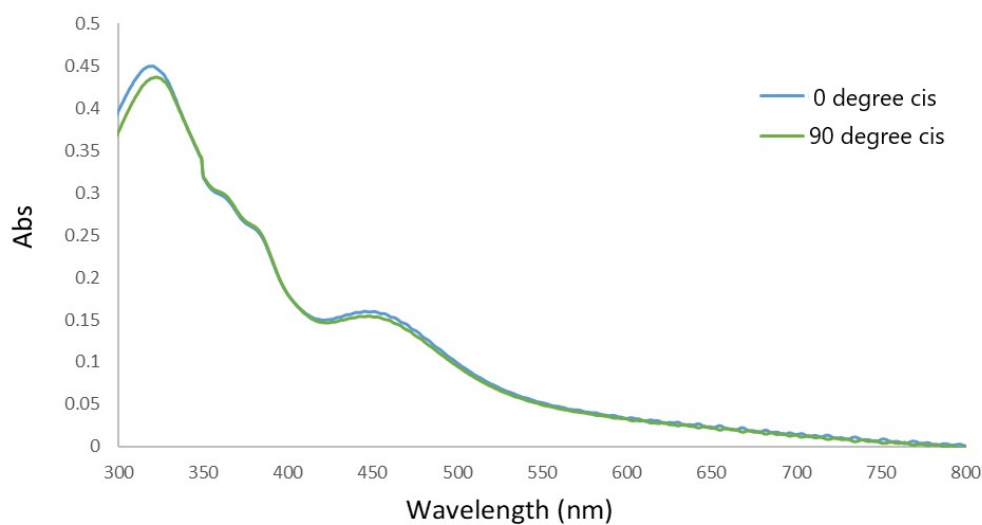


Fig. S3 Polarized UV-Vis spectra of spin-coated film after curing with green light and irradiating with UV light to generate the *cis* isomer. The slight reduction in intensity of the 90° polarized spectrum (green) in the visible region is due to the onset of thermal isomerization. Note that the intensity of the 90° polarized spectrum is slightly higher at some wavelengths in the UV region, which is indicative of thermal isomerization. The overlap of the 0° (blue) and 90° (green) spectra indicate that the chromophores are not aligned.

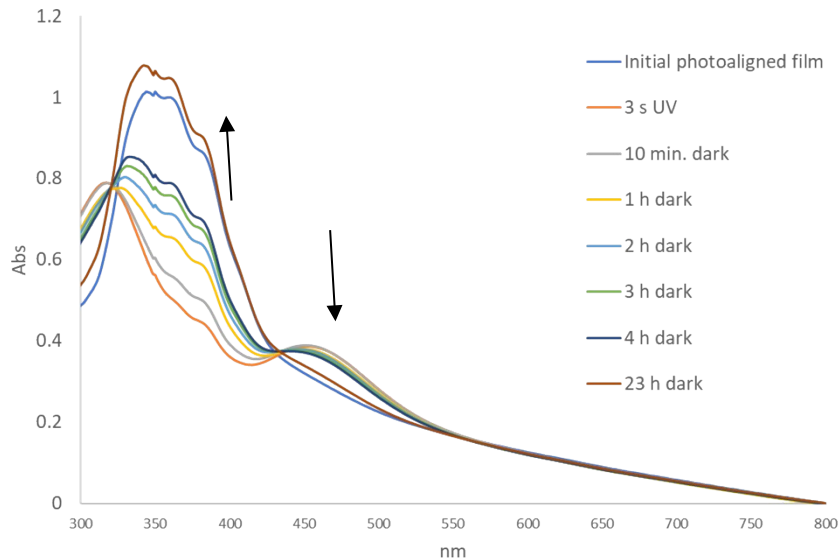


Fig. S4 A photo-aligned film (blue) was exposed to UV light for 3 s to generate a *cis* enriched film (orange). Thermal isomerization of the film was followed for a period of 23 h. The sample was stored in the dark and spectra were taken at various times as indicated on the graph. After 23 h the intensity in the visible region associated with the *cis* isomer has almost fully attenuated. The peak in the UV region associated with the *trans* isomer has surpassed the intensity of the original spectrum.

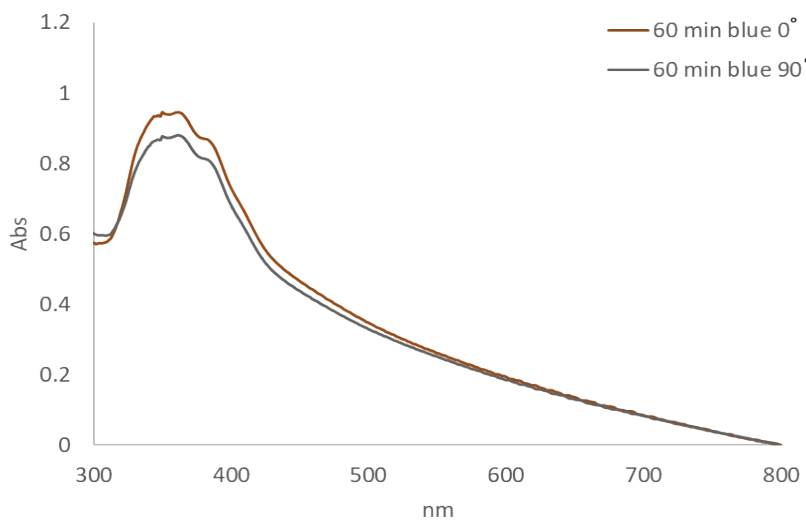


Fig. S5 Exposure to blue light for 60 minutes, without first irradiating with UV light shows a much smaller absorbance difference between 0° (red) and 90° (black) polarized light compared to a sample that was irradiated with UV light prior to blue light exposure. The dichroic ratio is 1.08 at 342 nm.

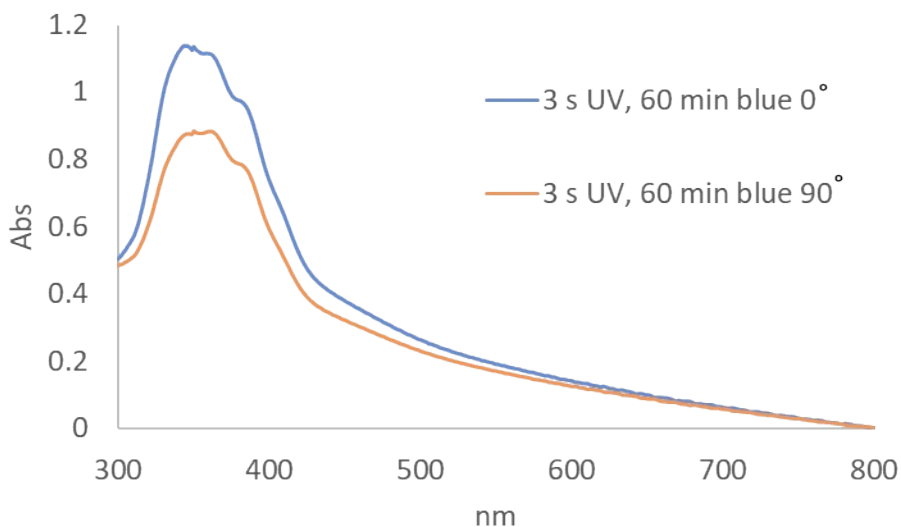


Fig. S6 When the same spot that was irradiated and analyzed in S4 is then exposed to UV light for 3 s followed by blue light for 60 min., the dichroic ratio increases from 1.08 to 1.31 at 342 nm, indicating a considerable enhancement in photoalignment when samples are first irradiated with UV light.

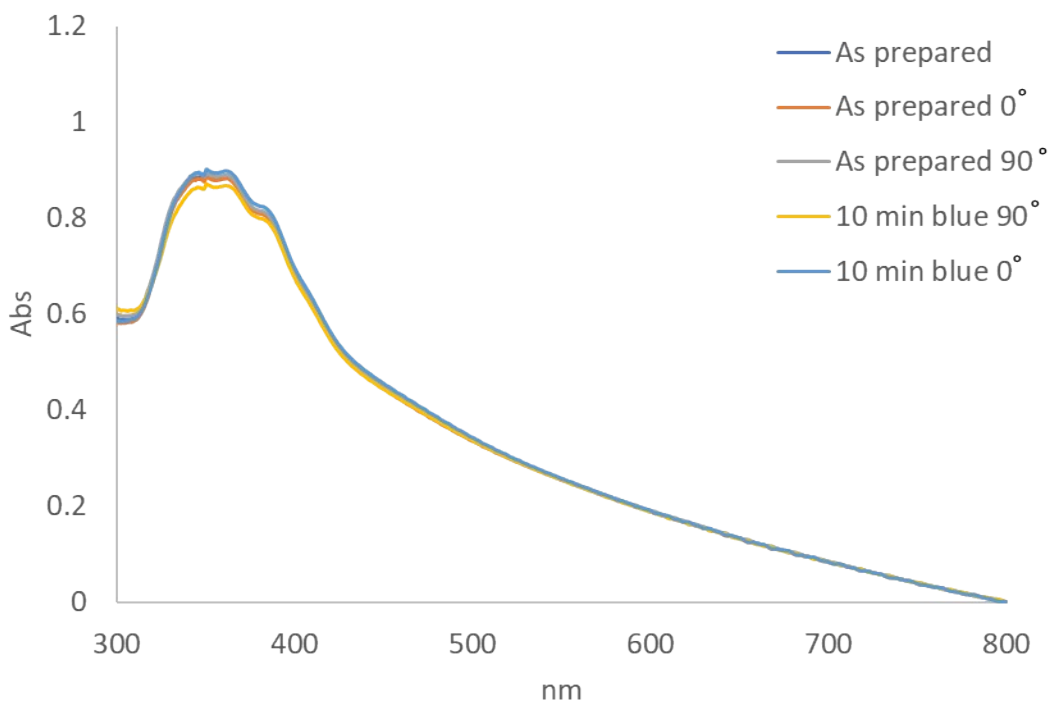


Fig. S7 10 minutes of exposure to blue light without prior exposure to UV light shows no dichroism. The polarized spectra of the film after curing with green light are overlaid with polarized spectra (0° and 90°) of the film after exposure to blue light for 10 min. Additionally, the non-polarized spectrum of the film after curing is included. All spectra essentially overlap. The dichroic ratio after irradiation with blue light is 1.03, indicating that essentially little to no change occurs upon irradiation with blue light when the sample is not irradiated with UV light prior to exposure to polarized blue light.

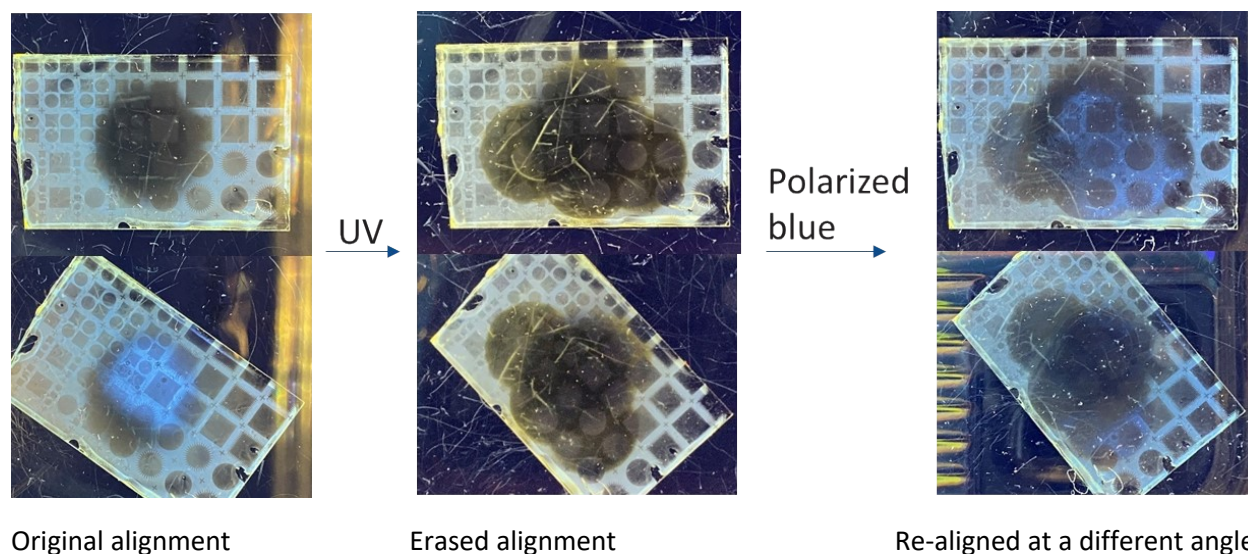


Fig. S8 The birefringence of a photoaligned sample can be erased by exposure to UV light. Birefringence can be regenerated by exposure to polarized blue light. Note that in the sample shown, the alignment was regenerated with the sample placed at a 45° angle relative to the initial placement of the sample during the initial photoalignment. This shows that the alignment direction of a previously aligned film can be manipulated by changing the angle of the polarized light relative to the substrate.

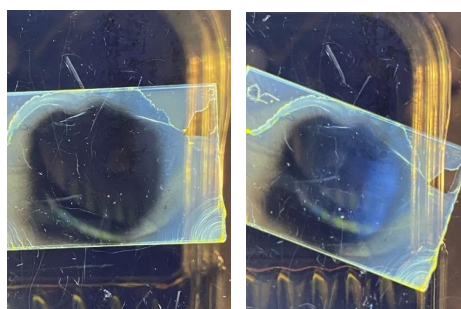


Fig. S9 Drying a drop of the formulation containing **1** under a polarized blue laser results in birefringent material. This shows that enhanced mobility that gradually becomes frozen due to solvent evaporation during irradiation enhances the propensity to photoalign.

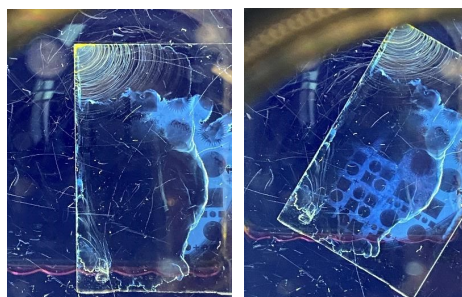
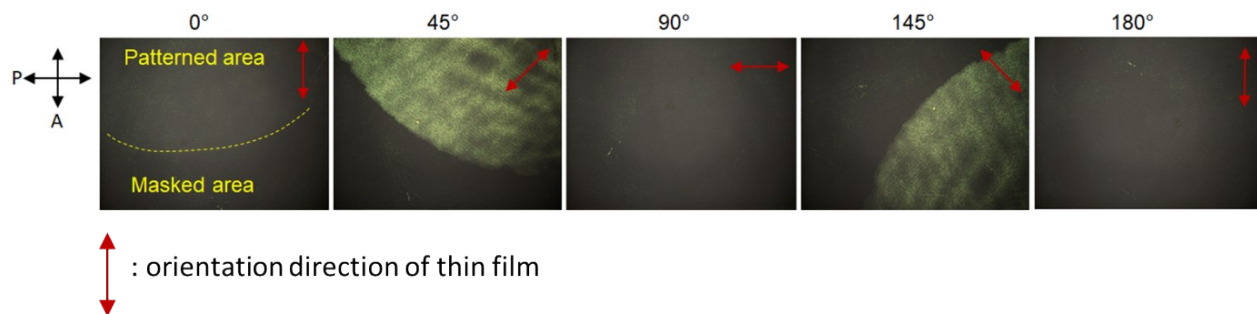
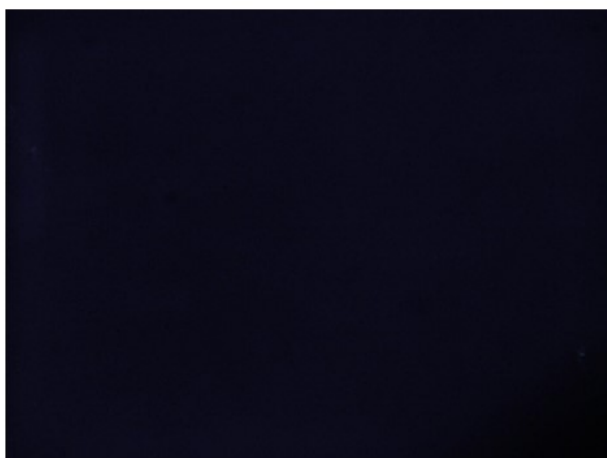


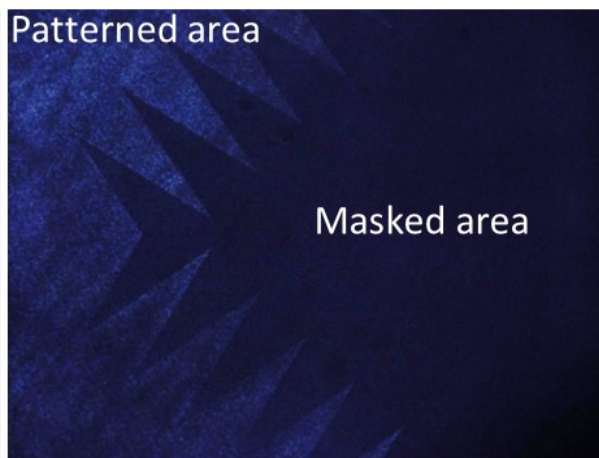
Fig. S10 Patterned films can be photoaligned by irradiating with a polarized blue laser while a drop of solvent spreads on the film and evaporates. Sections of the pattern that were in contact with toluene for some amount of time during the irradiation become birefringent upon exposure to blue polarized light while the toluene evaporates. Sections that were not in contact with toluene or possibly not in contact for a long enough time are not birefringent.



Polarized OM, 0°



Polarized OM, 45°



Patterned area in the thin film (spin-coated)

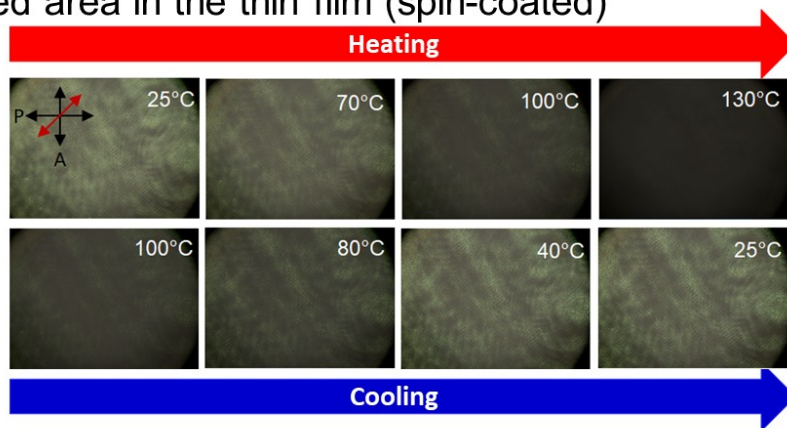


Figure S11: Polarized optical microscopy (POM) images of patterned film. The masked area shows no birefringence. The irradiated area of the pattern shows birefringence. The temperature dependence of the birefringence is shown.

A video of a photoaligned pattern rotated between crossed polarizers is included.