

Experimental:

Chemicals:

E7 is composed of n-cyanobiphenyls. The chiral dopant used in the monomer mixture was R811, which is R-octan-2-yl 4-((4-(hexyloxy)benzoyl)oxy)benzoate. The achiral diacrylate, R257, contains a single component, 4-(3-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenylene ester. RM691 is a chiral monomer mixture containing both monoacrylates and diacrylates, specifically it contains: 4-(3-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenylene ester, 4-(6-acryloyloxyhexyloxy)-benzoic acid-(4-methoxyphenylester), 2-methyl-1,4-phenylene-bis[4-(6-acryloyloxyhexyloxy)benzoate], 4-(6-acryloyloxyhexyloxy)benzoic acid (4-(trans-4-propylcyclohexyl) phenyl ester), 4-(6-acryloyloxyhexyloxy)-benzoic acid (4-cyanophenyl ester). The initiator, I-369, is a single component, specifically 1-Butanone, 2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-2-(phenylmethyl)-(9Cl) (CAS:119313-12-1).

Cell Preparation

Polyimide solution was prepared by thoroughly mixing 8mL of PI2555 polyimide (HD Microsystems), 32.5 mL of N-methyl prolidone and 9.1 mL of 1-methoxy-2propanol. After filtering the mixture with a 0.45um filter (Pall, Acrodisc PSF syringe filter). The polyimide solution was spin coated on a glass substrate at 2000 rpm for 1 minute. The coated glass was baked at 200°C for 30 minutes. A polyimide-initiator solution was prepared by mixing 99% by weight of the originally prepared polyimide solution with 1% by weight Irgacure 369 (Ciba). A glass substrate was coated with this polyimide-initiator solution under identical spin-coating conditions. This coated glass was also baked at 200°C for 30 minutes. Then the films were rubbed to achieve a planar oriented anchoring layer. Then the glass pieces were glued together with 30um spacers to form an empty cell.

Polymeric Scaffold Preparation:

All the cells were filled with a 19.5% chiral monomer RM691 (Merck), 8.5% chiral dopant R811(Merck), and 3.5 % achiral diacrylate RM257(Merck), and 68.5% achiral nematic E7(Merck), except cells used for the photo-tuning experiments (all percentages are weight percentages). The mixture for the photo-tuning experiments was slightly adjusted to red shift the notch so that during phototuning the tuning notch from bulk photo-sensitive mixture could be seen between the azo-absorbance and the notch due the polymer templated LC, so that the dynamics of the notch tuning could be tracked better. For photo-tuning experiments the cells were filled with a mixture of 16% RM691, 8% R811, 2.8% RM257 and 73.2% E7. The cells were exposed to 1.1 mW/cm² of UV light (Exfo Omnicure S1000, 300-500 nm) for 30 minutes to initiate polymerization. While the polymer side was exposed to the UV first, we found that the exposure side made little difference. Upon polymerization, the cells were immersed in cyclohexane for at least 7 days, until the cell color was homogenous and did not change with time. Then the cell was dried under light-vacuum. The dried polymer has a very faint reflection, as shown in the transmission spectra below. When the cell is broken open this polymer layer is attached only to the side with the initiator doped polyimide. Dried cells were capillary filled with their respective mixtures (as described in the manuscript) and then heated to 60-70°C to help fully swell the polymer.

Transmission Spectrometer Measurements

Transmission spectra were taken with an ocean optics USB2000+ vis-NIR spectrometer. Measurements were made by passing unpolarized light through the sample and then passing it through a Fresnel-Rhomb which broke the light into the left circularly polarized component and the right circularly polarized component. A split fiber was used to send both the right-CPL and left-CPL to the ocean optics USB2000+ vis-NIR spectrometer. Right-CPL measurements were performed by blocking the fiber entrance to the left-CPL component of the split fiber and left-CPL measurements were performed by blocking the right-CPL component of the split fiber. The unpolarized measurements were performed by combining the left-CPL and right-CPL channels of the Fresnel Rhomb with the split fiber. For photo-tuning experiments samples were exposed to UV-light with an Exfo Novacure 2100 with a peak at ~365 nm and subsequently exposed to green laser light from an argon ion laser (National Laser Co.) with a 514 nm filter.

Thickness Measurements

The thickness studies were performed on samples that were drained and dried as described as above. A dried templated cell was split open. The thickness of the dried polymer on the templated glass surface was measured with white light interferometry (Veeco, Santa Barbara). The thickness was measured as the difference between the height of the dry polymer and the polyimide surface (with added initiator). Then a drop of nematic LC, E7, was deposited onto the surface, two wetting regimes could clearly be seen. Essentially an LC drop with a clear contact angle at the polymer template surface and the drop was surrounded by a rim of LC that wet and swelled the polymer template without a discernable contact angle. The fact that an inner contact angle can be clearly seen, it is safe to interpret this outer wet rim as a uniform swollen polymer. Then the sample was briefly heated to to totally swell the polymer. The reflectivity was checked to ensure the sample was properly swollen. The sample was allowed to reach equilibrium for 20 minutes. Then the thickness difference between the the swollen polymer and the dried polymer was measured. The total thickness of the swollen polymer was taken as the thickness of the dried polymer plus the thickness difference between the swollen polymer and dried polymer. This approach was used instead of measuring the thickness difference between the swollen polymer and the polyimide film because of the possibility that the polymer-polyimide edge may effect the swelling of the polymer. Data analysis was performed on slice plots, see supporting material. The slice plots of the polymeric regions, swollen and unswollen, show a relatively rough surface with a clear discernable top layer. This top layer was used as a measure of the thickness and the error associated was used to estimate the chosen as 1 μm , in order to estimate the innacuracy caused by the surface roughness.

Video Description

The video labeled tune movie 450uW_cm-2 shows the photo-tuning when the sample was exposed to 450uW/cm². The video labeled 300uw-cm-green-return-19 min shows the photo-tuning when the sample was exposed to 300uW/cm² for roughly 19 minutes, then the sample is exposed to a 5mW/cm² green laser (the light can be seen in the spectrum at 514 nm) to blue-tune the notch back. In the end of

this video, the right and left notches are left overlapping and that is because that is the photo-stationary state from the green exposure.

Surface localized Polymerization Description:

The polymerization of the monomer is an acrylate-based radical polymerization. The attachment mechanism of the formed polymer to the polyimide surface will be the subject of further investigation, but preliminary experiments indicate that the formed polymer is attached through chain entanglement with the surface. Unfortunately, the polyimide, PI2555, is a commercial product whose chemical structure is proprietary and thus a simple analysis of the chemical structure is not possible. The polyimide surface can still be dissolved after the photo-polymerization reaction (even with 10% initiator in the polyimide), indicating that the polyimide is not significantly cross-linked. While the adhesion mechanism is likely only chain entanglement and not grafting, the adhesion is still strong. In fact a typical qualitative adhesion tape test leads to the entire film, including the polyimide to delaminate from the glass.

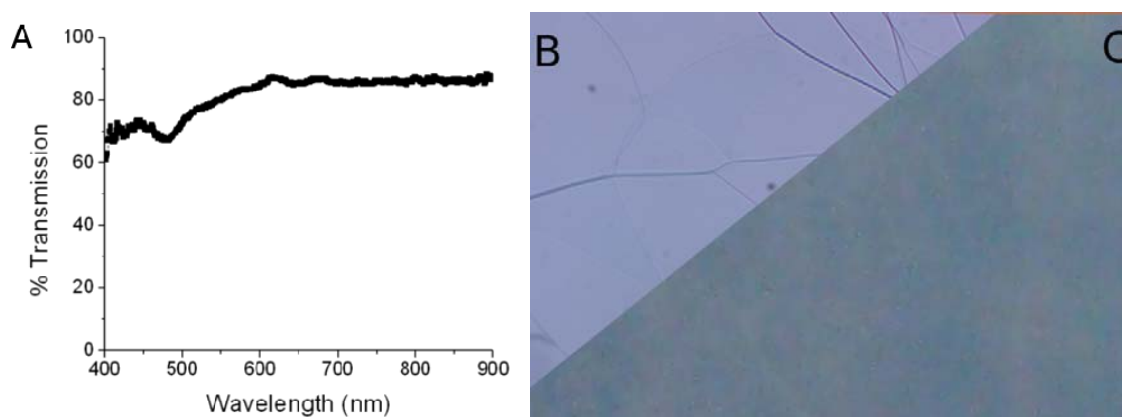


Figure ESI 1: A) A transmission spectra of a dried cell. B) An optical micrograph of the Grandjean texture of a dried cell, which is present in the polymer region of the cell throughout the whole process, including refilling. C) An photograph of a dried cell showing the weak blue color of the dried cell.

The resulting polymer (after cell draining) does have weak photonic properties, but because the birefringence is weak it is difficult to see. Figure ESI 1A, shows the transmission spectra of a dried cell. Figure ESI 1C shows an optical photograph of a dried cell, notice the blue color. Furthermore, after the polymerization the texture of the initial CLC monomer mixture is locked in and seen in the dried state (Figure ESI 1B). This Grandjean texture is seen even when the cell is reswollen with a nematic liquid crystal. it should The texture of the region without polymer takes on the texture of the filling mixture.