CHEMPHYSCHEM

Supporting Information

Macroscopic Control of Helix Orientation in Films Dried from Cholesteric Liquid-Crystalline Cellulose Nanocrystal Suspensions

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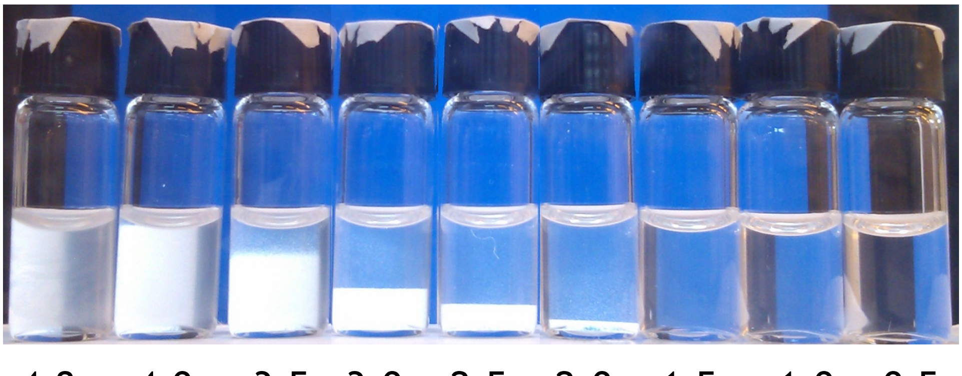
Supporting Information

SI 1.Movie of a suspension being dried on the orbital mixer. The PDMS mold holding the glass substrate is filled into a plastic Petri dish, and the suspension droplet has been placed on the glass. As the mixer is set in motion the liquid experiences a circular shear flow.

SI 2.Determination of the phase diagram of our CNC suspensions

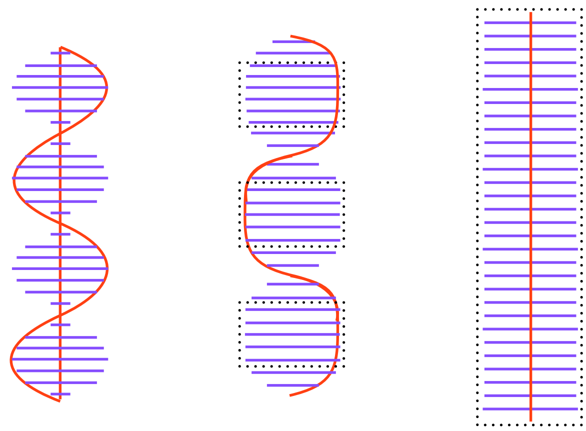
Following standard procedures for characterizing CNC phase behavior, we filled suspensions with varying concentration into identical vials and left them standing for one week at room temperature. They were then photographed between crossed polarizers, see below. In case of samples with coexisting liquid crystalline and isotropic phases, macroscopic phase separation took place over this time, with the lighter isotropic phase floating on top of the denser liquid crystalline phase. When no isotropic fraction could be detected at the top we drew the conclusion that the suspension was fully liquid crystalline, with the critical concentration being found to be 4.8 wt.-%. As discussed in the main text, this conclusion may not have been perfectly correct, but as no macroscopic phase separation could be detected in the experiment depicted below we can still assume that any isotropic phase is a minority. This assumption is substantiated by the experimental results on the 4.8% suspension presented in the paper, which reflect the behavior expected for a phase that is very close to fully liquid crystalline.



4.8 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 wt%

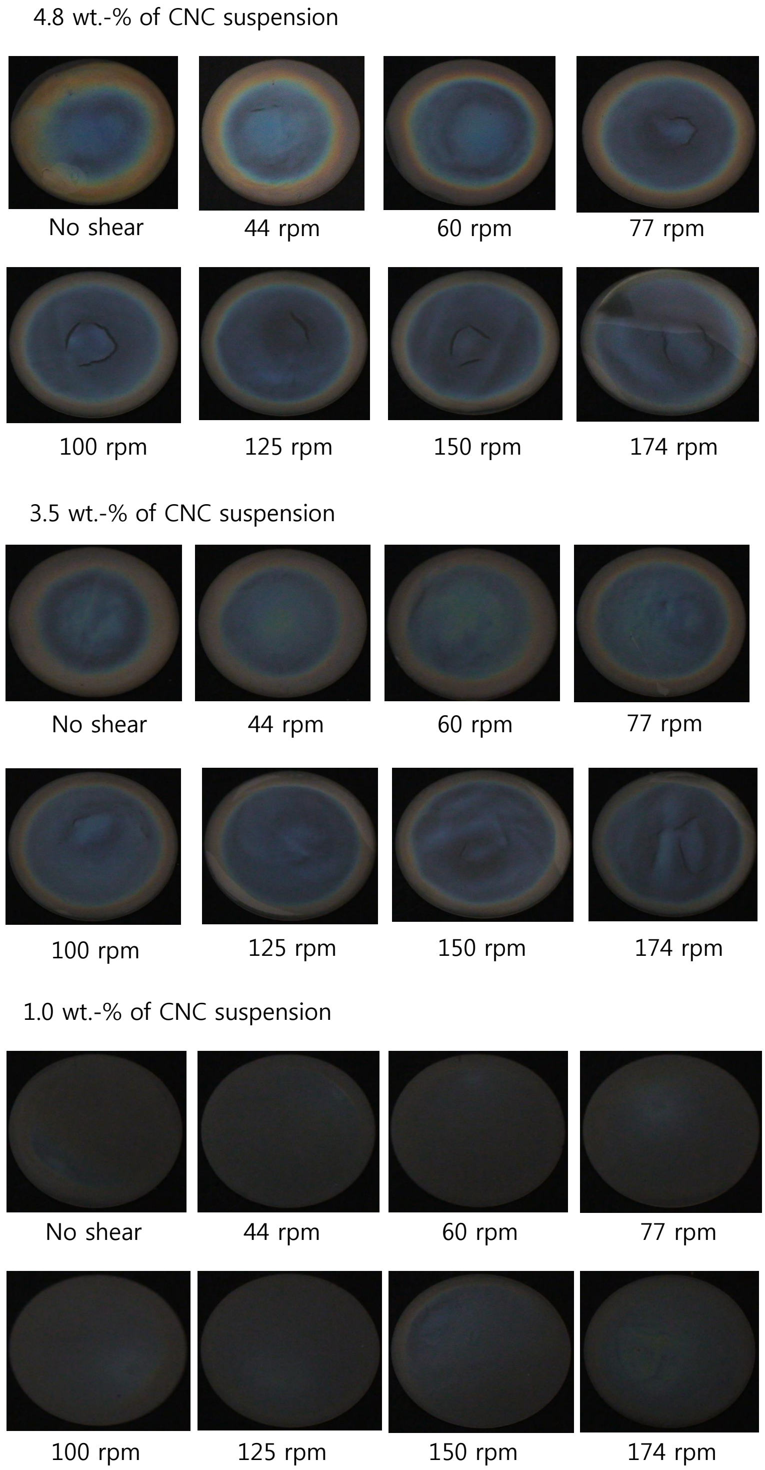
SI3. Shear-induced distortion of the helix.

When exposed to shear flow a nematic liquid crystal phase tends to orient with its director along the shear direction, since this minimizes the viscosity. In a chiral nematic (cholesteric) phase, however, this alignment trend competes with the helical modulation, which promotes a continuous rotation of the director. As shown in the schematic figure below, an intermediate shear flow will thus only expand the regions with director along the shear flow while the regions connecting two adjacent uniform regions will contain a compressed 180° twist of the director (middle case). Once a threshold shear strength is reached the helix is fully unwound (right case). As witnessed by the stratified internal structure revealed by SEM in our study, it seems we did not reach this final state at any shear flow investigated. However, for the strongest shear flow we must have created a strongly distorted state, similar to the middle structure in the figure below, giving rise to the strong birefringence.



no shear | shear strength below unwinding threshold | shear strength above unwinding threshold

SI 4. Macroscopic photos of films prepared from three different starting concentrations and without or with shear flow, at varying speed.



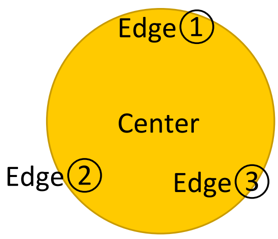
All photos were taken under identical exposure conditions, with diffuse illumination from the opposite side of the film with respect to the camera. The low thickness of the films prepared from 1.0% CNC suspension makes the selective reflection difficult to see macroscopically, but it is easily detectable in the microscope, yielding textures very similar to those in Fig. 2 and Fig. 6 in the main article.

SI 5. Thickness measurements from all films.

Since the CNC film cannot be removed from the hydrophilic glass without breaking, we measured the thickness of CNC film + glass substrate using a micrometer screw, see table below. Data were taken at the center and at three edge points of each sample. Subtracting the average glass substrate thickness and doing appropriate averaging, we find that films prepared from an isotropic suspension were about 4 μm thick at the center and 6 μm at the edge, those from a biphasic suspension were about 16 μm at the center and 34 μm at the edge, whereas those from a fully liquid crystalline suspension were about 22 μm at the center and 42 μm at the edge.

Thickness of CNC films on cover glass (unit: μm; average thickness of cover glass : 150 ± 5μm)

Rotation speed (rpm)	LC phase (4.8%)				Bi-phase (3.5%)				Isotropic (1%)			
	Center	Edge1	Edge2	Edge3	Center	Edge1	Edge2	Edge3	Center	Edge1	Edge2	Edge3
0	178	187	190	183	167	187	183	183	147	151	157	153
40	172	192	192	192	166	179	182	188	154	157	159	161
59	173	193	193	193	164	182	174	192	147	155	152	148
77	168	194	189	191	166	182	188	184	160	158	158	160
104	169	191	193	182	164	180	180	176	154	154	154	153
125	173	200	211	196	164	189	179	192	153	153	150	152
149	172	192	194	204	167	183	189	186	156	161	160	154
174	172	186	184		168	185	186	177	158	160	160	158



SI 6. Color versions of figures.

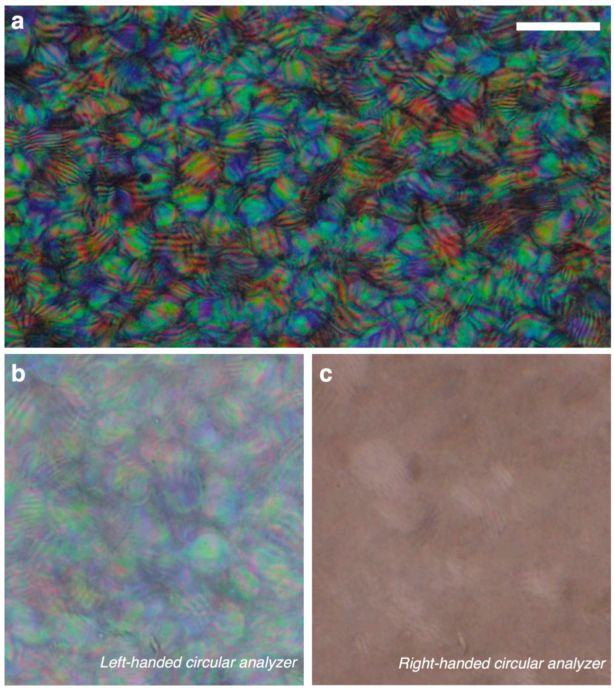


Figure 2: Example of the mosaic-like polydomain texture that is seen in dried CNC films produced following the standard protocol. An isotropic suspension (0.37 wt.-% CNC) was left to dry without any motion. In (a) the film is viewed in reflection between crossed polarizers, while in (b-c) a quarter wave plate is inserted in the light path, giving us an analyzer for circular light. The analyzer is set for left-handed light in (b) and right-handed in (c). The scale bar is 50 μm.

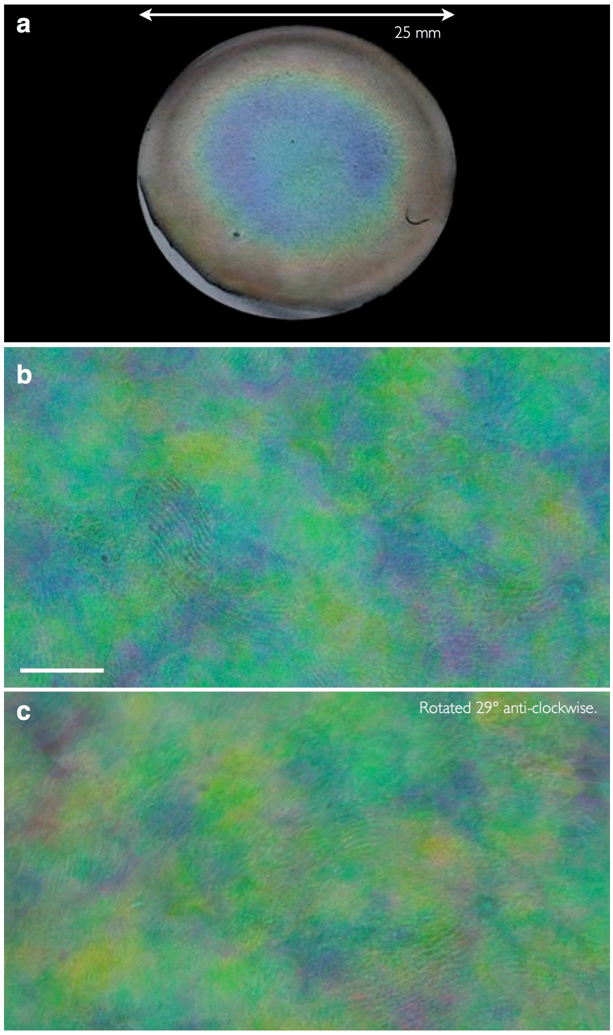


Figure 3. A film dried on a 25 mm diameter glass slide from a 4.8 wt.-% CNC suspension (macroscopic appearance fully liquid crystalline). Photo (a) shows the complete film, revealing the radial variation in color from green at the center, blue in the intermediate range, and red along the periphery. Photos (b-c) show crossed polarizer reflection microscopy images of an area close to the center of the film (scale bar: 50 μm), with (c) rotated 29° compared to (b). Sections of these images have previously been shown in reference [2].

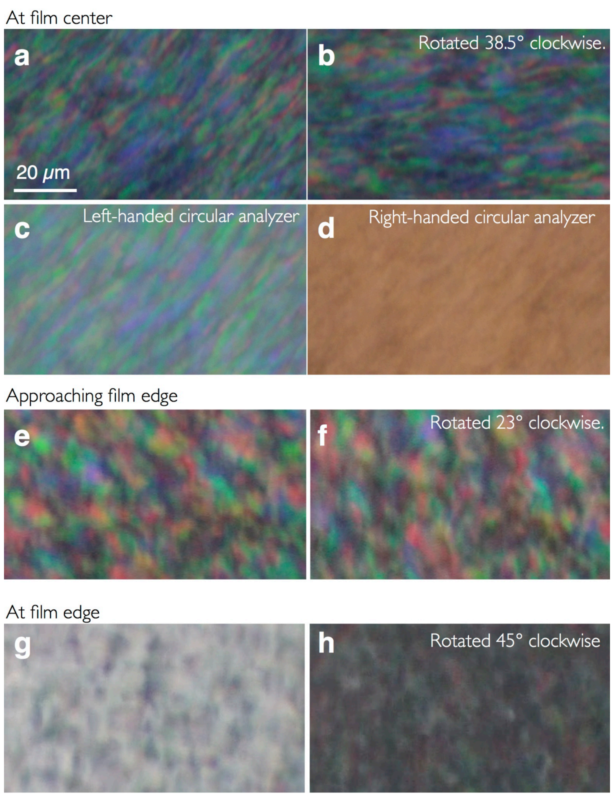


Figure 6. Reflection polarizing microscopy images of a film prepared by drying an isotropic CNC suspension (0.48 wt.-%) under a left-handed circular shear flow. The central portion of the film shows reflection in the blue-green regime, with colors unaffected by sample rotation (a-b), and insertion of a quarter wave plate confirms that the reflected light is left-handed circular polarized (c-d), as expected for CNC N* Bragg reflection. Further away from the center (e-f) the color is less uniform and there is a general red shift, but the appearance is still essentially insensitive to rotation, confirming that the colors are due to selective reflection and not birefringence. In contrast, at the edge (g-h) the shear flow was strong enough to strongly distort the helix, leading to almost no selective reflection but strong birefringence, yielding a clear variation in intensity upon sample rotation.

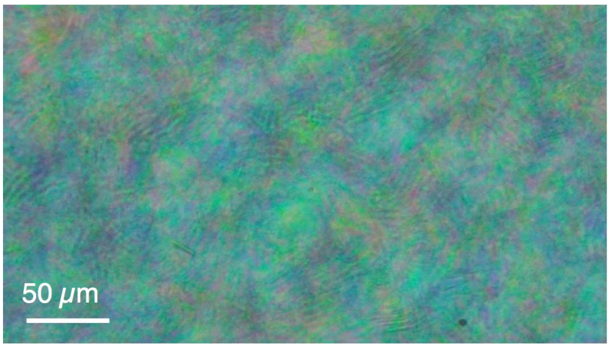


Figure 7. Reflection polarizing microscopy image of a film prepared by drying a suspension with 3.5 wt.-% CNC, exhibiting coexistence of isotropic and N* phases, under a left-handed circular shear flow.

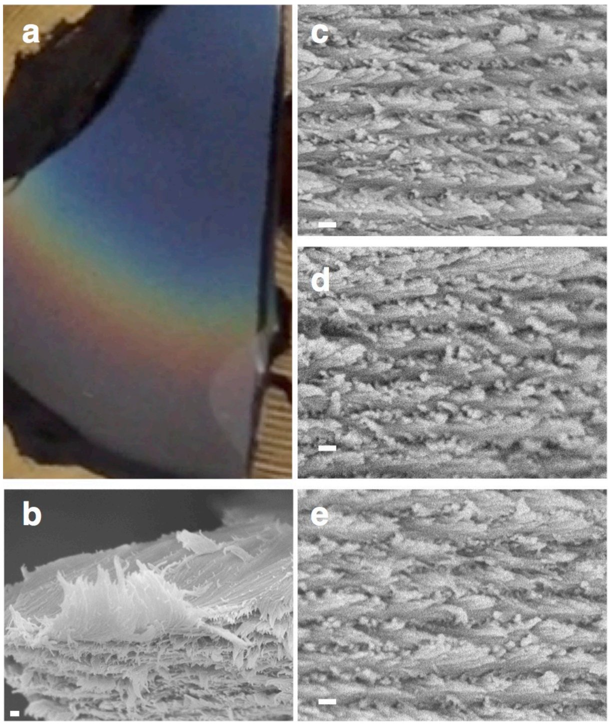


Figure 8. Macroscopic optical appearance (a) and scanning electron microscopy images (b-e) of a CNC film prepared by drying a 4.8 wt.-% suspension with 40 rpm circular shear flow. The SEM images depict the fracture surface along the right side of the film in (a), with image (b) obtained near the red-reflecting edge and images (c-e) near the blue reflecting center. The latter images are obtained from the same region of the sample, near the air surface (c), in the film bulk (d) and near the glass surface (e). Scale bar in b-e is 100 nm.

Figure 9. A film prepared by drying a 4.8 wt.-% liquid crystalline CNC suspension under 174 rpm circular shear flow, imaged by polarizing microscopy and by SEM of the internal surface exposed by fracturing the film. The center of the film is viewed between crossed polarizers in reflection in (a) and in transmission in (b). In (c) a first order wave plate is inserted with its optic axis from lower left to upper right, confirming tangential director alignment. The SEM images were obtained near the center of the film, in the bulk (d), close to the air interface (e) and close to the glass substrate (f). Circular polarization analysis reveals an unusual reflection behaviour, confirming the presence of a left-handed chiral structure in the film (g-h). All optical images have the same scale as in (a).