NIH Public Access
Author Manuscript
Small. Author manuscript; available in PMC 2014 August 26.

Published in final edited form as:
Small. 2013 August 26; 9(16): 2785–2784. doi:10.1002/smll.201202869.

Colloid-in-Liquid Crystal Gels that Respond to Biomolecular Interactions

Ankit Agarwal[$], **Sumyra Sidiq**[#], **Shilpa Setia**[#], **Emre Bukusoglu**[$], **Juan J. de Pablo**[$], **Santanu Kumar Pal**[*,#], and **Nicholas L. Abbott**[*,$]

Nicholas L. Abbott: abbott@engr.wisc.edu

[*]Department of Chemical and Biological Engineering, University of Wisconsin-Madison 1415 Engineering Drive, Madison, Wisconsin, 53706, USA

[*]Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, SAS Nagar, Mohali 140306, India

Department of Chemical and Biological Engineering, University of Wisconsin-Madison 1415 Engineering Drive, Madison, Wisconsin, 53706, USA

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, SAS Nagar, Mohali 140306, India

Abstract

This paper advances the design of stimuli-responsive materials based on colloidal particles dispersed in liquid crystals (LCs). Specifically, we report that thin films of colloid-in-liquid crystal (CLC) gels can undergo easily visualized ordering transitions in response to reversible and irreversible (enzymatic) biomolecular interactions occurring at aqueous interfaces of the gels. In particular, we demonstrate that LC ordering transitions can propagate across the entire thickness of the gels. We observe, however, that confinement of the LC to small domains with lateral sizes of ~10 μm does change the nature of the anchoring transitions, as compared to films of pure LC, due to the effects of confinement on the elastic energy stored in the LC. The effects of confinement are also observed to cause the response of individual domains of the LC within the CLC gel to vary significantly from one another, indicating that manipulation of LC domain size and shape can provide the basis of a general and facile method to tune the response of these LC-basedphysical gels to interfacial phenomena. Overall, the results presented in this paper establish that CLC gels offer a promising approach to the preparation of self-supporting, LC-based stimuli-responsive materials.

Keywords

Stimuli-Responsive Materials; Liquid Crystals; Gels; Colloids; Biomolecular Interfaces

Supporting Information is available on the WWW under http://www.small-journal.com or from the author.

NIH-PA Author Manuscript
NIH-PA Author Manuscript
NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

1. Introduction

Recent investigations of interfaces formed between thermotropic liquid crystals (LCs) and immiscible aqueous phases that are decorated with biomolecules and biomolecular fragments have revealed the orientational ordering of the LCs to be strongly coupled to the supramolecular organization of assemblies of biomolecules formed at these interfaces.[1–9] This phenomenon is providing new principles for manipulation of the interfacial phase state of biomolecules as well as the basis of facile approaches to the realization of new classes of stimuli-responsive materials.[1,10] In particular, when an aqueous phase forms an interface with a water-immiscible LC, interfacial events involving biomolecules can lead to surface-driven orientational transitions that propagate across micrometer-thick films of the LCs (so-called anchoring transitions), thus providing a particularly promising class of materials for engineering dynamic and stimuli-responsive interfaces between synthetic and biological systems.[11] Building from these past studies, herein we report that it is possible to prepare thin films of LC-based colloidal gels that are (i) stable under water and (ii) contain micrometer-sized domains of nematic LC that undergo surface-driven ordering transitions triggered by biological lipids and proteins.

The composite LC materials described in this paper are based on dispersions of colloids that form a network in the low molecular weight nematic LC called E7. Past reports have demonstrated that colloidal suspensions of microspheres, when dispersed in the isotropic phase of mesogens and then cooled below the isotropic-nematic transition temperature (T_{NI}), form a bulk birefringent waxy semi-solid (gel) with storage moduli (G') of 10^3–10^5Pa.[12] In this paper, we study thin films (thickness of ~4 μm) of CLC gels with nematic domains, confined by the colloidal network, that extend across the entire thickness of the gel.[13] We demonstrate that the thin films of CLC gel are stable under water, and can be driven through reversible anchoring transitions *via* the presence of adsorbates at the aqueous-CLC gel interface. We also find evidence that the adsorbate-driven anchoring transitions of the LC in the gel differ from those observed at the interface between a pure film of E7 and water, due to the confinement of the LC by the colloid-rich domain boundaries of the gel.

As noted above, a number of past studies have reported that the self-assembly of amphiphilic molecules at aqueous/LC interfaces can trigger ordering transitions in LCs.[1] These ordering transitions arise, at least in part, from coupling between the aliphatic chains of the adsorbed amphiphiles and the mesogens of the LCs. Consistent with this mechanism of interaction, the ordering transitions depend strongly on the length and structure of the aliphatic tails of the amphiphiles.[11,14] The majority of these studies were performed using nematic LC hosted within a gold-coated TEM-specimen grid that was immersed under an aqueous phase, while others used LC droplets or LC hosted within microfabricated structures such as micropillar arrays.[15] While these past studies demonstrate the promise of LC interfaces for reporting biomolecular interactions, the issue of how to integrate LCs within composite materials and microsystems to provide stable and robust "free" interfaces of LCs (as needed for stimuli-responsive materials) remains an open challenge.[16–20] The results of the study reported in this paper suggest that CLC gels may provide the basis of

NIH-PA Author Manuscript
NIH-PA Author Manuscript
NIH-PA Author Manuscript

technologically relevant approaches to the preparation of interfacially responsive LC-based materials.

In the study described below, we first demonstrate that it is possible to form stable thin films of CLC gels that can be immersed under water without dewetting the solid surface on which they are supported. We then demonstrate that the LC domains within the thin CLC films undergo surface-driven ordering transitions induced by contact with water and aqueous solutions of synthetic and biological amphiphiles. Significantly, we demonstrate that the anchoring transitions propagate across the thickness of the CLC films. Finally, we reveal that the aqueous interface of the CLC gel can be decorated with a biological lipid that serves as a substrate for an enzyme. Upon addition of the enzyme to the aqueous solution, the CLC gel is observed to undergo an anchoring transition that is consistent with the processing of the substrate by the enzyme at the interface of the CLC gel.

2. Results and Discussion

The CLC gels were prepared, as described in Methods, using polystyrene (PS) microspheres (diameter of 1 μm with surface sulfate groups) dispersed in E7. E7 is a mixture of four alkoxycyanobiphenyls (*n*CBs) with different aliphatic chain lengths: 51 wt% 4-cyano-4‘-n-pentyl-biphenyl (5CB), 25 wt% 4-cyano-4’-*n*-heptyl-biphenyl (7CB), 16 wt% 4-cyano-4’-*n*-oxyoctyl-biphenyl (8OCB), and 8 wt% 4-cyano-4’-*n*-pentyl-p-terphenyl (5CT). Upon cooling to room temperature, the colloidal particles form a percolating network that contributes to the strength to the composite material (Figure 1). In the experiments reported in this paper, the thicknesses of the CLC gels were determined (see Materials and method for details) to be approximately 4 μm (i.e., a thickness that is approximately 4 times the diameter of the polystyrene particles used to form the gels).[13] In a previous study, CLC gels prepared with E7 with thicknesses of >12 μm were reported to be stable when immersed under water and to possess mechanical properties that permitted the attachment and proliferation of mammalian cells on their surfaces (in contrast, E7 alone, was found to be too soft to permit cell attachment and spreading).[12] These previously prepared CLC gels, however, were sufficiently thick that the LC domains within the gel did not extend across the thickness of the gel. In the first experiments reported in this paper, we sought to determine if thin films of CLC gels (thicknesses of ~4 μm) would be stable when immersed under water (i.e., not dewet the chemically functionalized glass substrates). Here we note that films of pure E7 (not gel) supported on either DMOAP- or OTS-coated glass do dewet these surfaces upon immersion into water[2] (if not confined with a TEM grid).

Figure 2 shows polarized light (crossed polars, Figure 2A) and bright-field (Figure 2B) micrographs of a thin film of CLC gel supported on a glass microscope slide treated with OTS (which, as noted above, anchors the LC at the LC-glass interface in a homeotropic orientation). We note that the polarized light microscopy provides information regarding the orientation of the LC within the LC-rich domain whereas bright field microscopy reveals the CLC domain structure. The top surface of the film of CLC gel was in contact with air. The dark optical appearance of the CLC gel in Figure 2A (which was invariant to rotation between crossed polars) is consistent with most of the LC within the film having a homeotropic orientation (or near homeotropic orientation, see below for additional

NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

comments) of the LC across the entire gel. Figure 2B, obtained with bright field microscopy, reveals the CLC domain structure, with a median lateral size of LC-rich domains corresponding to ~10 μm. Because the thickness of the CLC gel is ~4 μm (less than the characteristic lateral size of the LC domains), we predicted that the LC-rich domains would span the CLC gel (as illustrated in the sketch in Figure 2C). This prediction is consistent with the observation of a near-uniform homeotropic orientation of LC within the CLC gel (as both surfaces confining the CLC gel promoted homeotropic anchoring).

Next, we immersed the thin film of CLC gel supported on the OTS-treated glass under water to determine if the CLC would dewet the surface. Inspection of the polarized light micrograph of the CLC film in Figure 2D reveals that, upon immersion in water, the CLC film immediately assumed a bright optical appearance between crossed polars. The domain structure of the CLC gel, as evident in Figure 2E, however, was not perturbed/destroyed (and the gel did not dewet the OTS-treated glass) upon contact with water. We observed the CLC gels to be stable under water over the time periods for which we used the gels in the experiments reported in this paper (hours to a day). The bright optical appearance of the CLC gel in Figure 2D is consistent with a change from homeotropic anchoring when the free interface of the CLC gel was in contact with air to a planar orientation after immersion under water (see Figure 2F for a schematic illustration). We note that some of the LC-rich domains of the CLC gel appear dark in water when viewed under cross-polars. This arises because the azimuthal alignment of the LC is largely parallel to either the analyzer or polarizer (further evidence to support this interpretation is presented below). These results, when combined with quantitative measurements of optical retardance of the LC films reported below, provides further confirmation that the LC-rich domains extend across the thickness of the CLC film. As described below, we also observe changes in the orientation of the LC at the aqueous interface that are caused by adsorbates to propagate across the thickness of the LC-rich domains within the CLC film.

To the aqueous solution covering the CLC gel, we next added the biological amphiphile LPS. Also called endotoxin, this amphiphile, which is found in the outer membrane of gram-negative bacteria, comprises a lipid with 6 tails (called lipid A) and a polysaccharide headgroup. In our initial experiments, we sought to determine if the CLC gel would be stable in the presence of LPS, and if adsorption of LPS to the aqueous interface of the CLC gel would lead to an anchoring transition within the LC-rich domains of the gel.

Inspection of Figure 3A reveals that, following the addition of 20 μg/mL of LPS to the aqueous solution in contact with the CLC gel, the CLC gel remained stable and the optical appearance of the CLC gel changed from bright to dark (a few bright domains remain evident after 25 min – see below for additional comment). The change in optical appearance of the CLC gel is indeed consistent with an adsorbate-driven anchoring transition of the LC (to a homeotropic orientation) at the LC-aqueous interface of the LC-rich domains of the gel (Figure 3C). This result is consistent with prior reports of homeotropic anchoring of nematic LCs at LPS-decorated interfaces.[19] Quantification of the intensity of light transmitted through a macroscopic region of the CLC gel, as shown in Figure 3B, reveals that the anchoring transition occurred over approximately 15 min following the addition of the LPS. While the macroscopic appearance of the CLC gel changed continuously over time

NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

following the addition of the LPS, we wish to make three additional observations regarding the ordering of the LC-rich domains of the gel. First, the extinction of light between crossed polars, in the presence of LPS (see right most image in Figure 3A), is incomplete. We note that some of the LC-rich domains of the CLC gel do not exhibit a dark appearance in the presence of LPS. Many of these domains appear to be small (lateral size of ~2–3 μm), and thus the interaction of the LC with the surrounding colloids likely prevents the orientation of the LC in those domains from responding to the adsorbate at the aqueous-LC interface. In addition, given their small size, it is also possible that these LC domains do not span the entire thickness of the film of the CLC gel and thus the orientation of the LC is not under control of the external surfaces of the CLC gel. This conclusion is consistent with our observation that the CLC gels, when viewed in air, also exhibit LC-rich domains that are not extinct between crossed-polars (see Figure 2A). Second, careful analysis of time-lapse images of the CLC gel revealed that the LC domains that possessed a dark optical appearance prior to contact with LPS (see above), underwent a transient change in optical appearance and birefringence upon contact with the LPS solution. This result supports our conclusion that these domains appeared dark prior to contact with LPS because the azimuthal orientation of the LC within the domains was aligned with one of the polars. Third, an analysis of the change in optical appearance of individual domains of LC within the gel, lead us to conclude that, at the single-domain level, the LPS-triggered change in optical appearance of the LC differed substantially from one domain to the next (see Figure S1 of Supporting Information). For example, the time at which the anchoring transitions started and ended varied greatly between domains, and some domains exhibited a non-monotonic change in brightness (presumably due to interference effects associated with the white-light illumination). This heterogeneity in the response of the domains likely reflects variation in the sizes and shapes of the LC-rich domains in the gel, and thus differences in elastic and surface anchoring energies for each domain. It also suggests that manipulation of the sizes and shapes of the LC domains may provide a means to rationally tune the response of CLC gels to interfacial adsorbates.

The results shown in Figure 4 demonstrate that synthetic surfactants, in addition to biological lipids such as LPS (Figure 3), can trigger anchoring transitions in the LC-rich domains of the CLC films (the results also show that the CLC gels are stable in the presence of synthetic surfactant solutions). Similar to LPS, the influence of SDS on the anchoring of the LC is to promote homeotropic anchoring of the nematic E7 at the LC-aqueous interface.[2] As shown in Figure 4A, with increasing concentration of SDS, we observed the equilibrium orientation of the LC domains to undergo a continuous change in optical appearance, indicative of a continuous change in the orientation of the LC at the aqueous interface of the LC-rich domains of the CLC gel as a function of increasing surfactant concentration. We also note that this change in optical appearance of the LC by SDS was reversible (data not shown), consistent with the known reversible adsorption of SDS at aqueous-LC interfaces.[2]

Measurements of the optical retardance of the LC within the LC-rich domains of the CLC gel were used to quantify the tilt of the LC at the LC-aqueous interface, as a function of the concentration of SDS in solution. The results are shown in Figure 4B, both for a CLC gel and for nematic E7 (free of colloids) hosted within a TEM grid. We note that the tilt of the

NIH-PA Author Manuscript NIH-PA Author Manuscript NIH-PA Author Manuscript

LC is calculated to change continuously as a function of increasing SDS concentration in both of the geometries. We also note that this tilt angle is calculated assuming the anchoring of the LC at the OTS-treated glass remains homeotropic during the entire experiment (i.e., strong anchoring at the OTS-treated glass). Inspection of Figure 4B reveals that the sensitivity of the LC to SDS is greater when E7 is hosted within the CLC gel as compared to E7 hosted in a TEM grid. This difference in response of the LC is, we believe, due to the difference in thicknesses of the E7 domains in the CLC gel (approximately 4 μm) and the TEM grid (approximately 20μm). Past studies have demonstrated that the elastic energy stored within the strained state of a LC, which increases as D^{-1} where D is the thickness of the LC domain, can predispose the LC to an adsorbate-induced change in ordering.[11] More generally, the result in Figure 4B suggests that the elasticity of the LC in the LC-rich domains of the CLC gel influences the response of the gel to adsorbates, and provides further evidence that control of the LC domain size within a CLC gel can be used to tune the response of the LC within the LC-rich domains to the concentration of adsorbate.

Finally, we demonstrate that CLC gels can be used to report the activity of enzymes, when the substrates for the enzymes decorate the aqueous interface of the CLC gel. In this experiment, we first incubated a CLC gel against an aqueous solution of L-DLPC (Figure 5A). Inspection of Figure 5A shows that the LC-rich domains within the CLC gel undergo an anchoring transition in the presence of L-DLPC, consistent with formation of a monolayer of L-DLPC at the aqueous interface of the LC[1] (and thus homeotropic anchoring, Figure 5A). Next, we removed the residual L-DLPC from the aqueous solution and introduced the enzyme phospholipase A_2 (PLA_2). PLA_2 is known to catalyze the hydrolysis of L-DLPC in the presence of Ca^{2+}, thus resulting in the formation of the lysophospholipid and the corresponding fatty acid. We note also that our previous studies have demonstrated that PLA_2, in the absence of Ca^{2+}, does not perturb the anchoring of LCs at LC-aqueous interfaces.[1] As shown in Figure 5B, during the 1 h period following the addition of 10nM of PLA_2 into the aqueous phase, the LC rich domains of CLC gel were observed to undergo an ordering transition. The change in optical appearance of the gel from dark to bright over a period of 60 min is consistent with past studies of hydrolysis of L-DLPC by PLA_2 (the anchoring transition is caused bydesorption of the hydrolysis products of the enzymatic reaction from the interface).[1] We make two additional observations regarding this result. First, we note that the interference colors generated by the CLC gel (under white-light illumination) after hydrolysis of L-DLPC by PLA_2 are almost identical to those observed prior to adsorption of L-DLPC on the surface of the CLC gel. This observation confirms that LC-rich domains of CLC films can be driven through reversible anchoring transitions *via* the introduction and removal of adsorbates at the aqueous-CLC gel interface. This result also suggests that the extent of hydrolysis of the L-DLPC on the interface of the LC is sufficiently high to recover planar anchoring. Second, we note that our past observations of enzymatic hydrolysis of L-DLPC at interfaces of LCs hosted in TEM grids have revealed the formation of patterned orientations of the LC consistent with the presence of domains of lipid on the interface with lateral dimensions of tens of micrometers.[1] In contrast, presumably due to the compartmentalization of the interface of the LC within the CLC gel (the LC-rich domains shown in Figure 5B have lateral sizes of

~5μm), we observe no evidence of domain formation during the enzymatic hydrolysis of the L-DLPC.

Finally, Figure 5D and E show that the adsorption of L-DLPC as well as the enzymatic removal of L-DLPC from the interface of the CLC gel can also be conveniently quantified by measurement of the intensity of light transmitted through the CLC gel (crossed polars). As noted above, because the CLC gel was imaged with white light, we observed interference phenomena to cause non-monotonic changes in the gray-scale brightness of the images (not the initial rise in brightness in Figure 5D and the transient dip in brightness in Figure 5E). We note also that the overall rate of response of the E7 to enzymatic activity of PLA_2 is greater when the E7 is hosted within a CLC gel as opposed to a TEM grid (see Figure S2). This difference, as noted above, is likely related to the difference in the thickness of the LC in the domains of the CLC gel and the TEM grid, and thus the influence of the elastic energy of the LC on the orientation of the LC.

3. Conclusions

The key result reported in this paper is that thin films of CLC gels, specifically, CLC gels with LC-rich domains that span the thickness of the gel, are stable under water and can be used to report adsorption of biological and synthetic amphiphiles at LC interfaces as well as the processing of a substrate of an enzyme. We observe, however, that the confinement of the LC to small domains with lateral sizes of ~10 μm does change the nature of the anchoring transitions, as compared to LCs hosted within TEM grids. We also observed that the response of individual domains of the LC within the CLC gel to vary significantly, suggesting that manipulation of domain size and shape may provide the basis of a general and facile method to tune the response of these LC composite materials to interfacial phenomena. Overall, we conclude the CLC gels offer a general and facile approach to the preparation of “free interfaces” of LCs suitable for design of LC-based stimuli-responsive materials.

4. Experimental Section

4.1. Materials

Lipopolysaccharides (LPS) (from *E. coli* 0111:B4), N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP), octadecyltrichlorosilane (OTS), and sodiumdodecylsulfate (SDS) were purchased from Sigma-Aldrich (St. Louis, MO). 1,2-dilauroyl-sn-glycero-3-phosphocholine (L-DLPC) was purchased from Avanti Polar Lipids Inc. Phospholipase A_2 from *naja mossambica mossambica* was purchased from Sigma-Aldrich (St. Louis, MO). Sulfuric acid and hydrogen peroxide (30% w/v) were purchased from Merck (Mumbai, India). Ethanol was obtained from Jebsen & Jenssen GmbH and Co., Germany (s d. fine–chem limited). E7 was obtained from EMD chemicals. Sulfate-coated PS microspheres (#S37498) with diameters of 1 μm were obtained from Invitrogen. Deionization of a distilled water source was performed using a Milli-Q-system (Millipore, Bedford, MA). Fisher's Finest Premium Grade glass microscopic slides and cover glass were obtained from Fischer Scientific (Pittsburgh, PA). Gold TEM-specimen grids (20 μm

NIH-PA Author Manuscript NIH-PA Author Manuscript NIH-PA Author Manuscript

thickness, 50 μm wide bars, 283 μm grid spacing) were obtained from Electron Microscopy Sciences (Fort Washington, PA).

4.2. Cleaning of glass substrates

Glass microscope slides were cleaned using 'piranha' solution [70:30 (% v/v) H_2SO_4:H_2O_2 (30%)], as described in detail elsewhere.[12] Briefly, the glass slides were immersed in a piranha bath at 100 °C for at least 1h and then rinsed in Milli-Q water for 5–10 min. Finally, the slides were rinsed sequentially in ethanol and then dried under a stream of nitrogen. The clean slides were stored overnight in an oven at 100 °C. All other glassware was cleaned prior to use.

4.3. CLC gels

The methods used to prepare CLC gels have been described in detail elsewhere.[12] Briefly, sulfate-coated PS microspheres, 1 μm in diameter, were washed three times with Milli-Q water in Eppendorf tubes by centrifugation for 5 min at 9000 rpm and then resuspended in Milli-Q water (using sonication and vortexing). Next, the microspheres were washed and suspended in ethanol (200 μL)and dried in air for several days. Dried PS microspheres were weighed and suspended in E7 in an Eppendorf tube at room temperature to obtain the desired wt% of PS microspheres in the mixture. The suspension was heated above the T_{NI} of E7 (~59 °C) in an oven and vortexed and sonicated vigorously with extensive shaking and tumbling for several hours to ensure formation of a homogeneous dispersion of colloids in the isotropic E7. The suspension was then cooled to room temperature in an oven, where it formed a CLC gel. To prepare thin films of CLC gels, a small piece of CLC gel prepared as described above was placed on a clean glass slide (chemically functionalized with DMOAP or OTS) and then heated above the T_{NI} of E7 (~59°C) in an oven. After the composite formed a transparent suspension, another pre-warmed glass slide was placed on top of the suspension. Mylar spacers with a thickness of ~1.5 μm were used to prevent the two slides from coming into contact. The slides were clamped with binder clips and cooled at a fixed rate (~0.2 °C/min) to room temperature. After cooling to room temperature, the top glass slide was removed using forceps to create a thin film of CLC gel with a free interface (gel-air interface) that was supported on a glass substrate.

4.4. Preparation of DMOAP- and OTS-coated glass slides

Clean glass slides (see above) were dipped into DMOAP solutions (0.1% v/v) in Milli-Q water for 5 min at room temperature and then rinsed with Milli-Q water to remove unreacted DMOAP from the surface. The DMOAP-coated glass slides were dried under a stream of nitrogen gas and baked in an oven at 100 °C for 3h to allow crosslinking of DMOAP.

OTS-coated glass slides were prepared by incubation of clean glass slides in OTS solution in heptane (10 mM) for 30 min. The slides were then rinsed with dichloromethane and dried under a stream of nitrogen gas.

4.5. Preparation of aqueous solutions of LPS and L-DLPC

Powdered LPS (endotoxin) was dissolved in Milli-Q water at room temperature to obtain the required concentration. The resulting solutions were then sonicated for 5 min and vortexed

NIH-PA Author Manuscript NIH-PA Author Manuscript NIH-PA Author Manuscript

NIH-PA Author Manuscript
NIH-PA Author Manuscript
NIH-PA Author Manuscript

for 10 min at room temperature. Aqueous dispersions of L-DLPC were prepared by evaporation of a solution of L-DLPC in chloroform within a glass vial using a stream of nitrogen. Milli-Q water was added to the dried L-DLPC in the vial. The resulting solutions were then sonicated for 10 min to prepare vesicles.

4.6. Preparation of LC films in TEM grids

Gold-coated, specimen grids (typically used for TEM) were cleaned by washing with ethanol, methanol and acetone, and then dried under nitrogen at 100 °C overnight. The grids were then placed on OTS-coated glass slides and E7 (~0.2 μL) was dispensed onto grids. Excess LC was removed from the grid using a syringe to produce an approximately planar interface, as described elsewhere.[2]

4.7. Optical characterization of LC films in aqueous solutions

The LC films formed within TEM grids (as mentioned above) were immersed into the aqueous solution. The orientational ordering of E7 was then determined using an Olympus BX60 microscope with an objective power of 4X and cross polars. Orthoscopic examinations were performed with the source light intensity set to 50% of full illumination and the aperture set to 0.55 (50X) in order to collimate the incident light. In-plane birefringence was indicated by the presence of brush textures, typically four–brush textures when the sample was viewed between cross polars. All images were captured using a Q-imaging camera.

4.8. Surface-induced ordering transitions of CLC gels in presence of LPS, SDS, L-DLPC and PLA_2

As described above, CLC films were prepared on OTS-functionalized glass slides that provided homeotropic alignment of the LC at the CLC gel-treated glass interface. The CLC films were then immersed into aqueous solution and the optical appearance was observed under cross-polars. Specified volumes of concentrated solutions of either LPS, SDS, L-DLPC or PLA_2 were added to the aqueous solutions into which CLC films supported on OTS-functionalized glass slides were immersed to achieve the desired concentration. The resulting changes in optical appearance of the CLC films were characterized using a polarizing optical microscope (as detailed above).

4.9. Determination of thickness of CLC gels

The methods used to measure the thickness of CLC gels have been described in detail elsewhere.[13] Briefly, thin film of the CLC gel was dissolved into a known volume of ethanol and the UV absorbance of the solutions was measured with a Cary 1E UV-Vis spectrophotometer (Varian Instruments, Sugar Land, TX). The absorbance spectra of five standard solutions of 5CB in ethanol were used to determine the mass of 5CB in the ethanol solution.

4.10. Tilt Angle Measurements

The optical retardance of the nematic domains within the CLC gels were measured using a CRI PolScope (CRI, Woburn, MA) (a retardance mapping instrument that can measure the

optical retardance with a precision of up to ± 0.2 nm). The retardance values reported in this paper are averages obtained over three measurements within a single LC-rich domain of the CLC-gel film. For a thin film of nematic LC with strong homeotropic anchoring ($\Theta_1 = 0°$) at the OTS-treated glass interface and a tilt angle of Θ_s away from the surface normal at the aqueous-LC interface, the tilt of the LC across the film varies linearly with position so as to minimize the elastic energy of the LC film (assuming splay and bend elastic constants of the LCs to be equal). This result permits the establishment of a relationship between optical retardance (r) of the film of LC and the tilt of the director at the aqueous-LC interface (Θ_S), namely

$$\Delta r \approx \int_0^d \left(\frac{n_0 n_e}{\sqrt{n_e^2 \sin^2\left(\frac{z}{d}\theta_s\right) + n_o^2 \cos^2\left(\frac{z}{d}\theta_s\right)}} - n_e \right) dz \quad (1)$$

where n_e and n_o are the indices of refraction parallel (so-called extraordinary refractive index) and perpendicular (ordinary refractive index) to the optical axis of the LCs, respectively. The retardance values obtained from the PolScope were used to calculate the tilt angle of the LC at the aqueous-LC interface by numerically solving equation (1). The indices of refraction of E7 were taken to be $n_e = 1.74$ and $n_o = 1.52$.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The studies of the CLC gels described in this paper were supported by the Department of Energy, Basic Energy Sciences, Biomaterials Program (DESC0004025), the NSF through DMR-1121288 (Materials Research Science and Engineering Center), the Army Research Office (W911NF-07-1-0446 and W911NF-06-1-0314), and the National Institutes of Health (CA108467and CA105730). S. Sidiq acknowledges the receipt of a graduate fellowship from IISER Mohali.

References

1. Brake JM, Daschner MK, Luk YY, Abbott NL. Science. 2003; 302:2094. [PubMed: 14684814]
2. Brake JM, Abbott NL. Langmuir. 2002; 18:6101.
3. Kinsinger MI, Sun B, Abbott NL, Lynn DM. Adv. Mater. 2007; 19:4208.
4. Lockwood NA, Gupta JK, Abbott NL. Surf. Sci. Rep. 2008; 63:255.
5. Bi X, Hartono D, Yang KL. Adv. Funct. Mater. 2009; 19:3760.
6. Hartono D, Lai SL, Yang KL, Yung LYL. Biosens. Bioelectron. 2009; 24:2289. [PubMed: 19162466]
7. Hartono D, Xue CY, Yang KL, Yung LYL. Adv. Funct. Mater. 2009; 19:3574.
8. Xue CY, Khan SA, Yang KL. Adv. Mater. 2009; 21:198.
9. Seo JM, Khan W, Park SY. Soft Matter. 2012; 8:198.
10. Lai SL, Huang S, Bi X, Yang KL. Langmuir. 2009; 25:311. [PubMed: 19067505]
11. Bai Y, Abbott NL. Langmuir. 2011; 27:5719. [PubMed: 21090596]
12. Agarwal A, Huang E, Palecek S, Abbott NL. Adv. Mater. 2008; 20:4804.
13. Pal SK, Agarwal A, Abbott NL. Small. 2009; 5:2589. [PubMed: 19777464]
14. Lowe AM, Abbott NL. Chem. Mater. 2012; 24:746. [PubMed: 22563142]

NIH-PA Author Manuscript NIH-PA Author Manuscript NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

15. Cheng D, Sridharamurthy SS, Hunter JT, Park JS, Abbott NL, Jiang H. J. Microelectromech. Syst. 2009; 18:973.
16. Gupta JK, Sivakumar S, Caruso F, Abbott NL. Angew. Chem. Int. Ed. 2009; 48:1652.
17. Clegg PS, Birgeneau RJ, Park S, Garland CW, Iannacchione GS, Lehency RL, Neubert ME. Phys. Rev. E Stat. Nonlin. Soft Matter Phys. 2003; 68:031706/1. [PubMed: 14524787]
18. Tong X, Chung JW, Park SY, Zhao Y. Langmuir. 2009; 25:8532. [PubMed: 19199711]
19. Lin IH, Miller DS, Bertics PJ, Murphy CJ, de Pablo JJ, Abbott NL. Science. 2011; 332:1297. [PubMed: 21596951]
20. Wood TA, Lintuvuori JS, Schofield AB, Marenduzzo D, Poon WCK. Science. 2011; 334:79. [PubMed: 21980107]

NIH-PA Author Manuscript
NIH-PA Author Manuscript
NIH-PA Author Manuscript

Figure 1.
Schematic illustration of the formation of a film of CLC gel between glass substrates. The LC-rich domains of the CLC gel span the thickness of the gels.

NIH-PA Author Manuscript
NIH-PA Author Manuscript
NIH-PA Author Manuscript

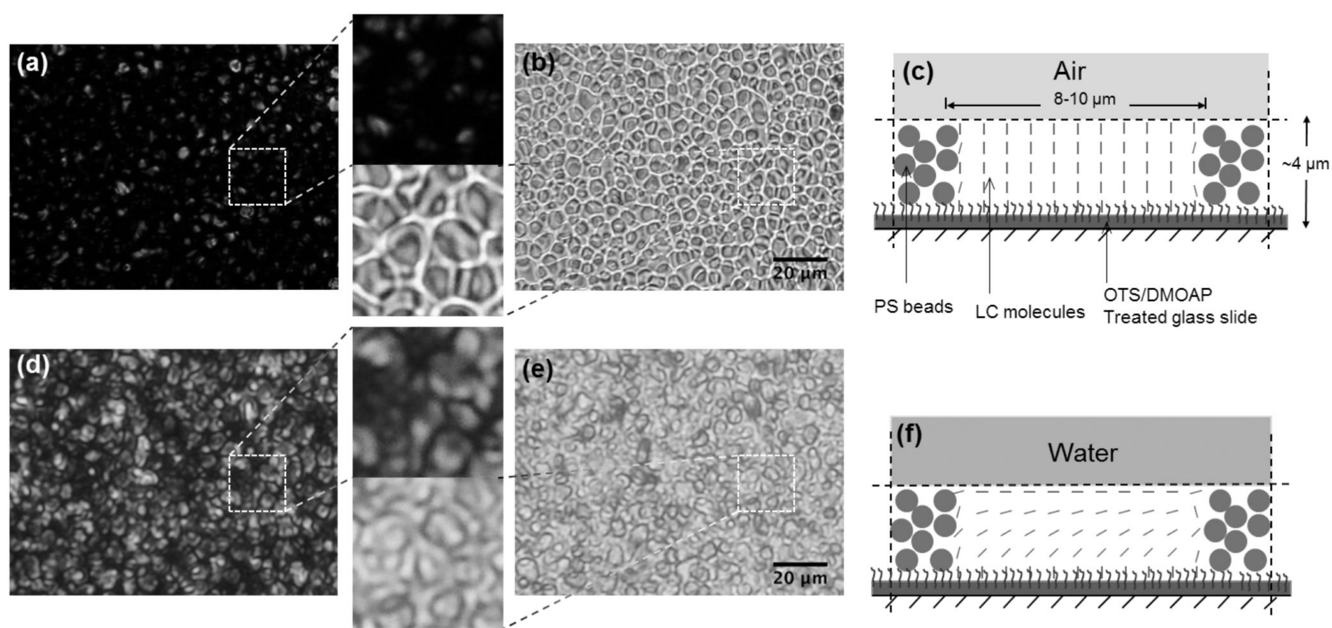

Figure 2.

(**a**) Polarized light (crossed-polars) and (**b**) bright field micrographs of thin CLC gels cast on OTS-functionalized glass slides exposed to air at room temperature. (Dashed squares show magnified regions of the film) (**c**) Sketch of the orientation of LC within one LC-rich domain of CLC gel shown in (a) and (b). (**d**) and (**e**) show the corresponding images of the thin film of CLC gel when immersed under water (the brightness of the image in Figure 2d was increased 30% by image processing) (**f**) Sketch of the orientation of LC within one LC-rich domain of CLC gel shown in (d) and (e).

NIH-PA Author Manuscript NIH-PA Author Manuscript NIH-PA Author Manuscript

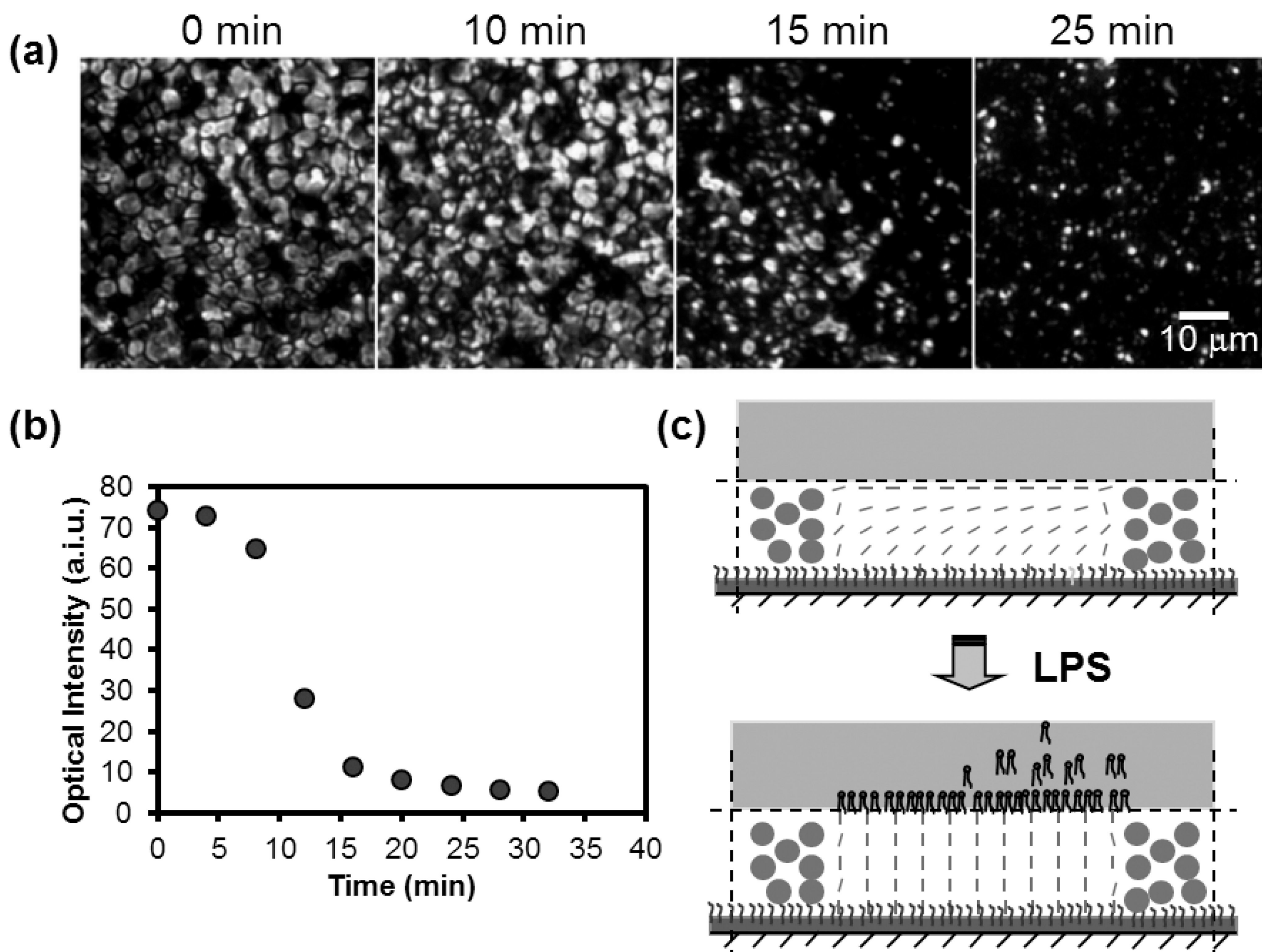

Figure 3.

(**a**) Time-lapse polarized light micrographs (crossed-polars) of a thin CLC gel (15% by wt PS) film cast on a DMOAP- treated glass slide following contact with 20 μg/mL aqueous LPS. (**b**) Optical intensity of the polarized-light images of the thin film of CLC-gel shown in A. (**c**) Schematic representation of the orientation of the LC within an LC-rich domain of the CLC gel before (top) and after (bottom) exposure to the aqueous LPS solution.

NIH-PA Author Manuscript
NIH-PA Author Manuscript
NIH-PA Author Manuscript

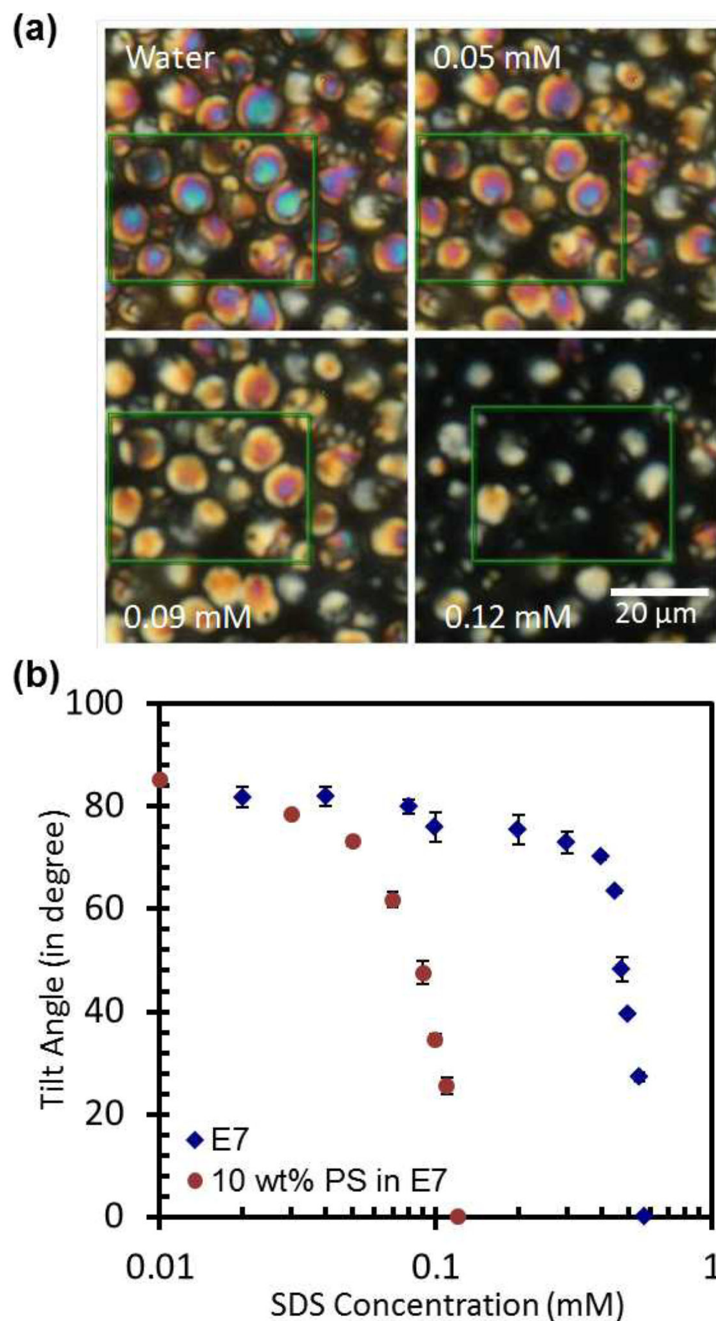

Figure 4.

(**a**) Polarized light micrographs (crossed-polars) of thin films of CLC gel (10% by wt PS) cast on OTS-functionalized glass slides following equilibration against aqueous sodium-dodecyl sulfate (SDS) solutions at the indicated concentrations. (**b**) Graph showing the change in tilt angle of the LC at the aqueous interface of the LC-rich domains of the CLC gel, measured relative to surface normal. Also shown is the tilt of the LC at the aqueous interface of the LC housed in a TEM specimen-grid (282 µm square grid size; 20 µm depth, scale bar = 10 µm).

NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript

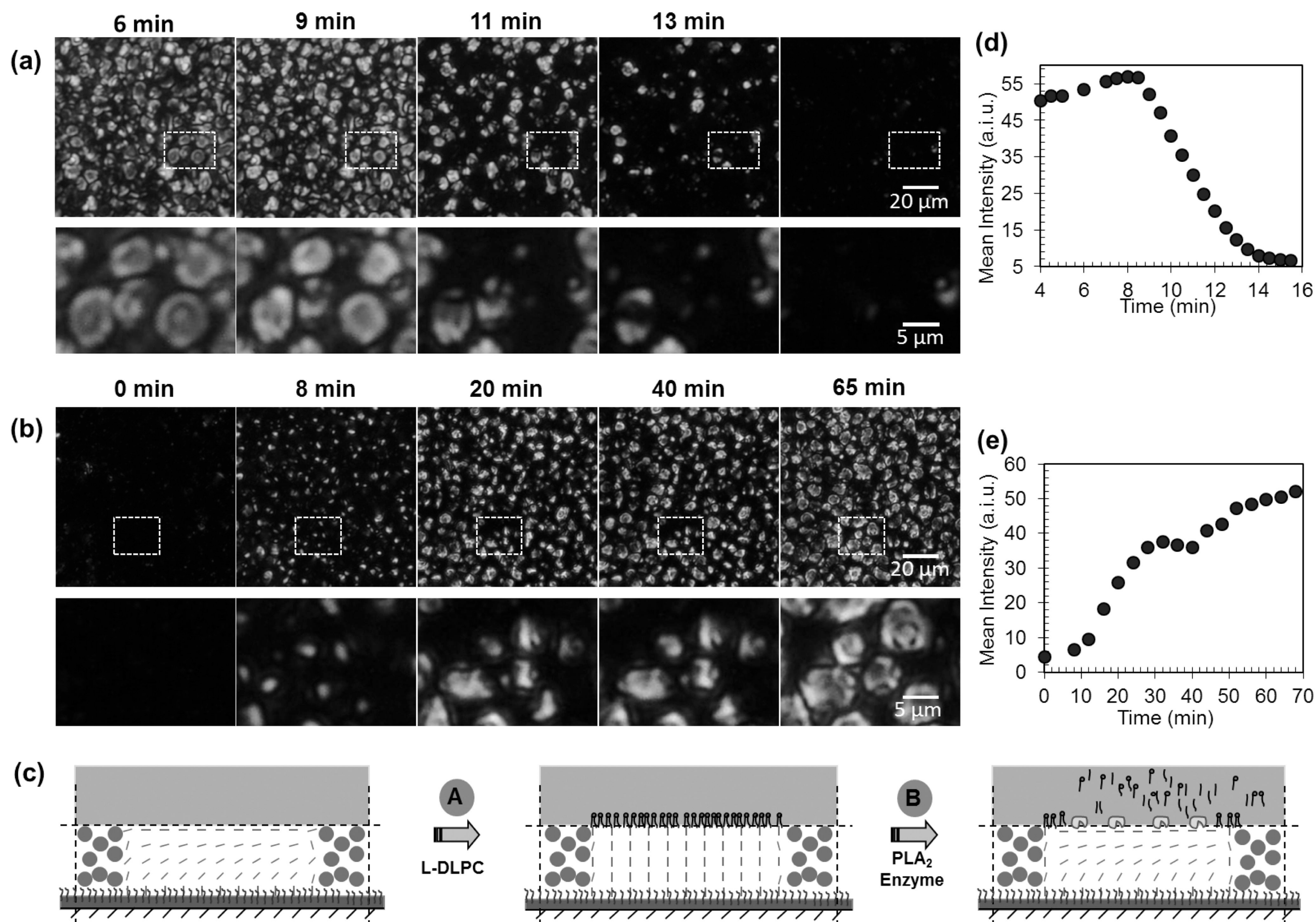

Figure 5.

(**a**) Time-lapse polarized light micrographs of a thin CLC gel film cast on an OTS-treated glass slide following exposure to 20 μg/mL L-DLPC. The change in optical intensity of the polarized-light images of the CLC-gel films as a function of time following incubation with aqueous 20 μg/mL L-DLPC is plotted in the graph. (brightness of micrographs increased by 30% for the ease of visualization) (**b**) Optical micrographs (between crossed-polars) of a CLC gel thin film on OTS-functionalized glass, with L-DLPC absorbed on the aqueous/LC surface, at successive time points after incubating against 10 nM PLA_2. The change in optical intensity of the polarized-light images of the CLC-gel films as a function of time following incubation with aqueous 10 nM PLA_2 is plotted in the graph.(brightness of micrographs increased by 30% for the ease of visualization). (**c**) Schematic representation of the expected orientational change of LC molecules confined in LC-rich domains of CLC gels exposed to aqueous L-DLPC solution followed by PLA_2 enzyme treatment.(**d** and **e**) The measured intensity of light transmitted through the CLC gel (crossed polars), corresponding to images (a) and (b), respectively.