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Dynamic Ordering Transitions of Liquid Crystals Driven by Interfacial Complexes Formed Between Polyanions and Amphiphilic Polyamines

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Abstract

We report the design of an amphiphilic polyamine based on poly(2-alkenyl azlactone) (polymer **1**) that strongly couples the formation of polyelectrolyte complexes at aqueous/liquid crystal (LC) interfaces to ordering transitions in the LC. We demonstrate that the addition of a strong anionic polyelectrolyte to aqueous solutions in contact with polymer **1**-laden LC interfaces (prepared by Langmuir-Schaefer transfer of monolayers of polymer **1** onto micrometer-thick films of nematic LC) triggers ordering transitions in the LCs. We further demonstrate that changes in the ordering of the LCs (i) are driven by electrostatic interactions between the polyelectrolytes, (ii) involve multivalent interactions between the polyelectrolytes, and (iii) are triggered by reorganization of the hydrophobic side chains of amphiphilic polymer **1** upon formation of the interfacial complexes. The results presented in this paper lead us to conclude that ordering transitions in LCs can be used to provide insights into the structure and dynamics of interfacial complexes formed between polyelectrolytes.

Recent studies have demonstrated that assemblies of surfactants,^{1–7} lipids,^{8–12} or polymers^{13–17} formed at interfaces between aqueous phases and thin films of water-immiscible, thermotropic liquid crystals (LCs) can exert a substantial influence over the ordering of the LCs. These past studies have also demonstrated that suitably tailored aqueous/LC interfaces can respond to events such as protein binding,^{8,11} the enzymatic processing of substrates,^{3,8,11,14} or changes in solution conditions (e.g., pH)¹³ in ways that trigger ordering transitions in the LCs and associated changes in the transmission of polarized light. While these past studies illustrate the potential utility of LCs as amplifiers of interfacial phenomena, the scope of interfacial events that can be coupled to ordering transitions in LCs has not yet been established. In this paper, we report a new class of molecular interactions that can be coupled to ordering transitions in LCs – the formation of complexes between polyanions and LC interfaces decorated with amphiphilic polymers.

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Supporting Information Available: Details of experimental protocols and polymer synthesis and characterization. Figures illustrating the effect of surface density of Langmuir films of polymer **1** on the alignment of 5CB after LS transfer to aqueous/LC interfaces and fluorescence micrographs of a polymer laden-LC interface before and after contact with solutions of SPS. Description and additional discussion regarding experiments designed to find evidence of complexes formed between polymer **1** and SPS within the bulk of the aqueous solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The amphiphilic polymers used in our study were synthesized by the reaction of amine-containing molecules and the pendent azlactone groups of poly(2-vinyl-4,4'-dimethylazlactone) (PVDMA, Scheme 1). This synthetic approach is modular and provides a general method to introduce a broad range of functionalized side chains (including cationic, hydrophobic, and hydrophilic groups) to a non-degradable polymer backbone.^{18–20} Amphiphilic polymer **1** was synthesized by the sequential addition of *n*-decylamine and 3-(dimethylamino)propylamine to PVDMA. *n*-Decylamine was used to introduce hydrophobic side chains based on past reports demonstrating that molecules with long aliphatic chains can assemble at aqueous/LC interfaces and strongly influence the ordering of LCs.^{1,2,13} 3-(Dimethylamino)propylamine was selected to introduce hydrophilic, tertiary amine-functionalized side chains that can be protonated in aqueous environments. The synthetic approach shown in Scheme 1 permits the synthesis of polymers having a range of different mole percentages of hydrophobic and hydrophilic side chains. For the work described below, we synthesized a polymer containing 40 mol% hydrophobic side chains and 60 mol % hydrophilic side chains (see Supporting Information for additional details of polymer synthesis and characterization).

Polymer **1** was determined to be sparingly soluble in water, and thus aqueous/LC interfaces decorated with this material were prepared by transfer of monolayers of the polymer from the surface of water (i.e., a Langmuir film) onto aqueous interfaces of thin films of the LCs¹⁰ (so-called Langmuir-Shafer transfer²¹). To this end, polymer **1** was dissolved in chloroform and spread onto the surface of aqueous phosphate-buffered saline (PBS, 25 mM sodium phosphate, 150 mM NaCl, pH 5.0) between the barriers of a Langmuir trough, and the chloroform was allowed to evaporate. The Langmuir film of polymer **1** was then compressed symmetrically by moving the barriers of the trough until a surface density corresponding to 15.3 Å²/repeat unit of the polymer was achieved. As seen in the π -A isotherm shown in Figure 1A (black curve), a continuous rise in surface pressure was recorded during the compression of polymer **1**. Below, we return to discuss the observations that lead to this choice of surface density of polymer. The Langmuir films of polymer **1** were transferred to approximately planar surfaces of thin films of nematic 4-cyano-4'-pentylbiphenyl (5CB) prepared by hosting the LC in the pores of a gold grid (thickness 20 μ m) supported on an octadecyltrichlorosilane (OTS)-functionalized glass slide. LS transfer was achieved by inverting the 5CB-filled grid and then passing it through the polymer **1**-laden aqueous/air interface while maintaining a horizontal orientation of the grid (as illustrated in Figure 1B and 1C).¹⁰

Figure 1D shows a representative polarized light micrograph (transmission mode; viewed through crossed polarizers) of an LC film hosted within a TEM grid after the LS transfer of polymer **1** onto the aqueous interface of the LC. The dark optical appearance of the LC within each square of the grid is consistent with perpendicular (homeotropic) alignment of 5CB (Figure 1E). The bright lines evident at the edge of each grid square are a consequence of interactions between the 5CB and the vertical surfaces of the grids, as discussed in past studies.^{1,2,13} For comparison, Figure 1F shows an image of a LC-filled grid that was passed through an air/water interface onto which only chloroform was spread (no polymer). The bright appearance of the LC in Figure 1F is indicative of parallel (or planar) alignment of 5CB at the aqueous/LC interface; this boundary condition leads to so-called hybrid anchoring of the LC in which the LC undergoes a continuous splay and bend distortion from an orientation that is perpendicular at the OTS-treated lower surface to a parallel orientation at the aqueous interface (Figure 1G).²² The homeotropic alignment of the LC at the aqueous interface in the presence of polymer **1** (Figures 1D and 1E) is similar to that observed at polymer-laden aqueous/5CB interfaces prepared in a past study by the adsorption of amphiphilic polymers from solution,¹³ and suggests that (i) LS transfer results in the

deposition of polymer **1** at the aqueous/LC interface, and (ii) that the presence of polymer **1** at the interface influences the ordering of the 5CB.

As discussed above, when polymer **1** was transferred from the surface of water to the aqueous-LC interface at a surface density of $15.3 \text{ \AA}^2/\text{repeat unit}$ (equivalent to $\sim 38 \text{ \AA}^2/\text{aliphatic group}$), the LC assumed a homeotropic orientation. In contrast, when the surface density of polymer **1** was decreased to $16\text{--}19 \text{ \AA}^2/\text{repeat unit}$ (or $40\text{--}48 \text{ \AA}^2/\text{aliphatic group}$), the orientation of the LC was observed to tilt away from the surface normal. At still lower interfacial densities of polymer **1** ($>21 \text{ \AA}^2/\text{repeat unit}$ or $52 \text{ \AA}^2/\text{aliphatic group}$), the LC assumed an orientation that was parallel to the interface (see Supporting Information, Figure S1). This progression in orientation of the LC as a function of the density of polymer **1** is similar to that observed in past studies of the adsorption of low molecular weight surfactants at the aqueous-LC interface.^{1,2,23,24} Those studies concluded that the interfacial density of aliphatic groups played a central role in determining the orientation assumed by the LCs.^{2,7-11} The results described above with polymer **1** also, therefore, suggest that interactions of the decyl chains of polymer **1** play a central role in dictating the orientations of the LC. In the experiments described below, we prepared interfaces of LC laden with interfacial densities of polymer **1** that were sufficient to cause homeotropic alignment of the LC ($15.3 \text{ \AA}^2/\text{repeat unit}$).

Subsequent experiments revealed that the homeotropic ordering of 5CB at polymer **1**-laden aqueous/5CB interfaces was perturbed substantially upon introduction of a strong anionic polyelectrolyte into the aqueous PBS. Figure 2A–C presents a series of optical micrographs showing changes in the optical appearance of the LC upon the addition of sodium poly(styrene sulfonate) (SPS) into the aqueous phase ($[\text{SPS}] = 200 \text{ \mu M}$, based on repeat unit molecular weight). Inspection of these images reveals that the optical appearance of the LC began to change from dark to bright within 15 minutes after the addition of SPS. After 30 minutes, the appearance of the 5CB became bright across the entire grid (Figure 2C), indicating a change in the alignment of 5CB from homeotropic to a planar/tilted orientation. Control experiments in which polymer **1**-laden 5CB interfaces were incubated in PBS in the absence of SPS remained uniformly dark (indicating homeotropic orientation of the LC) for at least 4 days (data not shown).

We considered the possibility that the changes in the orientation of 5CB observed in Figure 2A–C were caused by SPS-driven displacement of polymer **1** from these interfaces. The high resolution polarized light micrograph (crossed polars, transmission mode) shown in Figure 2G, however, does not support the proposition that polymer **1** is largely displaced from the interface. Figure 2G reveals that the introduction of SPS into the aqueous PBS in contact with the polymer **1**-laden aqueous/LC interface led to the formation of a high density of disclination (defect) lines in the LC. These line defects, which varied in density across the sample, are also evident in the corresponding bright field image shown in Figure 2H because they strongly scatter light. In contrast, the introduction of SPS into aqueous phases above LC interfaces that were free of polymer **1** (Figure 2I) did not lead to the appearance of defects of the type evident in Figure 2G. The dark brushes, or Schlieren textures observed in Figure 2I indicate degenerate planar alignment of the LC at this polymer-free interface.²² The variation in the interference colors within the grid squares of Figures 2G and 2I results from slight variation in the thickness of the LC film. We conclude on the basis of these results that the optical textures of the LC evident in Figures 2A–C are characteristic of complexes of SPS and polymer **1** that form at the aqueous/5CB interface.

To provide additional insight into the possibility of SPS-driven displacement of polymer **1** from the LC interface, we prepared Langmuir films from mixtures of polymer **1** and a derivative of polymer **1** labeled with the fluorescent dye tetramethylrhodamine (polymer

1_{TMR}) and transferred these mixed monolayers to the aqueous-LC interface using the LS method. A representative fluorescence micrograph of a polymer-laden aqueous/5CB interface imaged immediately after the LS transfer can be found in the Supporting Information (Figure S2A). The fluorescence intensity of the image was uniform across each grid square and confirms the successful and uniform transfer of the polymer film (as inferred above from changes in the LC order upon LS transfer). The same polymer-laden interface was contacted with a solution of SPS (200 μ M) for one hour and imaged by fluorescence microscopy (see Supporting Information, Figure S2B). A comparison of these images (Figures S2A and S2B) reveals that the intensity of the fluorescence did not change significantly after the addition of SPS; the average intensities of fluorescence from images collected before and after the addition of SPS were 105 ± 5 A.U. and 107 ± 6 A.U., respectively (relative to a background level of 36 ± 0.4 A.U., corresponding to a polymer **1**-free interface). However, the corresponding optical appearance of the LC viewed between crossed polarizers after the addition of SPS was bright and similar in appearance to that of the image shown in Figure 2G (data not shown). The constant intensity of fluorescence from polymer **1**_{TMR} at the LC interface before and after the LC ordering transition provides further evidence that SPS does not drive the displacement or loss of polymer **1** from the LC interface. This conclusion is reinforced by fluorescence, surface pressure and light scattering measurements, all of which yielded no evidence of complexes formed between polymer **1** and SPS within the bulk of the aqueous solution (see Supporting Information for details)..

The results shown in Figure 2A–C lead to several insights into the nature of the polyelectrolyte complexes formed at the interfaces of the LCs. First, as mentioned above, previous studies have shown that interactions involving the aliphatic moieties of amphiphilic molecules at aqueous/LC interfaces are largely responsible for the ordering of the LCs at amphiphile-decorated interfaces.^{23,24} Events that lead to reorganization of the amphiphilic molecules at these interfaces, and hence reorganization of aliphatic tails, lead to ordering transitions in the LC. The fact that we observe an ordering transition in the LC upon the formation of interfacial complexes between SPS and polymer **1** indicates that changes in the organization of the aliphatic side chains of polymer **1** accompany the formation of these interfacial complexes. In this respect, LCs are useful as probes of the organization of aliphatic side chains within polyelectrolyte complexes. Second, polarized light micrographs of the LC films used in our study can be interpreted to provide spatial and temporal information regarding the processes that lead to formation of the interfacial complexes between polymer **1** and SPS. In particular, several past studies have noted that changes in the lateral organization of molecules at LC-aqueous interfaces are readily identified via patterned orientational behaviors of LCs.^{6,8,9,23,24} For example, a recent study by Price and Schwartz has revealed that complexes formed between cationic amphiphiles and DNA lead to the formation of micrometer-sized domains at the aqueous-LC interface.⁶ Interestingly, in our study of complexes formed between two polyelectrolytes, we observed no evidence of domains during or after formation of the interfacial complexes (see Figure 2A–C, G). The ordering transitions that we observed in the LC occurred uniformly across the interface without the appearance of domains. This result suggests that the polymeric nature of the cationic amphiphiles used in our study does not permit lateral reorganization of the complexes formed at the interface over spatial scales (micrometers) that lead to patterned orientations of the LCs. Third, because the orientations of the LCs relax within the thin films over ~ 100 ms, it is possible to use the dynamic response of the LCs shown in Figure 2A–C to characterize the rates of formation of organized interfacial complexes of polyelectrolytes. For example, when polymer **1**-laden LC films are contacted with SPS solutions containing 150 mM NaCl, the ordering transition is relatively rapid (~ 15 – 30 mins). Below we show that solutions containing 1 M NaCl slow the rate of the ordering transition (such that it occurs over ~ 10 hrs).

To investigate the influence of ionic strength of the aqueous solution on the orientational response of the LC to the formation of complexes between SPS and polymer **1**, polymer **1**-laden interfaces of 5CB, prepared as described above, were transferred from the PBS buffer used during the LS transfer into PBS buffer adjusted to 1.0 M NaCl. This high salt concentration did not perturb the ordering of 5CB at the polymer **1**-laden interface away from the homeotropic orientation. When SPS (at a concentration of 200 μM) was added, the optical appearance of the LC changed in the manner shown in Figure 3B. For comparison, the response of the system to the addition of SPS in 150 mM NaCl is also shown (Figure 3A). Inspection of Figure 3A and 3B reveals that while ionic strength strongly influences the dynamics of the LC ordering transition driven by addition of SPS, both samples are undergoing an ordering transition that involves the tilting of the director away from the surface normal and the appearance of disclination lines within the LC film. From this experiment, we conclude that the characteristics of the equilibrium complexes formed between polymer **1** and SPS at the LC interface that lead to loss of homeotropic ordering of the LC are tolerant to variations in ionic strength. In particular, it is evident from the response of the LC that the formation of complexes between SPS and polymer **1** at the interface is not prevented even at ionic strengths as high as 1.0 M, at which electrostatic interactions are substantially screened. However, we note that the influence of high salt concentrations on complexes formed in bulk solution and at interfaces between polyelectrolytes of opposite charge is varied, as the presence of a high salt concentration can not only screen electrostatic interactions but also promote other associative interactions mediated, for example, by hydrophobic effects.^{25–28}

As noted above, the ordering transitions of the LC shown in Figure 3 provide access to information regarding the rates of formation of the SPS-polymer **1** interfacial complexes. In particular, it is evident that the ordering transition in the presence of 150 mM NaCl occurred over a few tens of minutes whereas the ordering transition in the presence of 1.0 M NaCl occurred over ten hours. This former time scale (tens of minutes) is similar to past studies of the adsorption kinetics of SPS to charged surfaces.^{29–32} For example, by using a quartz crystal microbalance, Lvov and coworkers reported that adsorption of SPS to a solid surface coated with poly(allylamine) (PAH) is essentially complete after 10 minutes.²⁹ In separate study, Lvov and coworkers concluded that the adsorption of poly(vinyl sulfate) to PAH-coated surfaces was largely complete within 15 to 30 minutes.³³ In this latter study, the authors noted that the adsorption of poly(vinyl sulfate) was not limited by diffusion but rather by reorganization of the interface (although, we note the concentration of polyanion used by Lvov et al was significantly higher [20 mM] compared to the concentrations used in the studies reported herein [200 μM]). Past studies have established that polyelectrolyte adsorption generally occurs in stages – the transport of material to the interface followed by a slow rearrangement of the polymer layer.^{25,34} Because we observe the ordering transitions in Figure 3 to occur over time periods as long as ten hours, we propose that the kinetics of these ordering transitions do not reflect the transport of SPS to the interface but rather the slow reorganization of polymer **1** at the LC interface. Our results suggest the background electrolyte concentration has a strong influence on this reorganization process.

To provide further insight into the role of electrostatic interactions underlying the formation of interfacial complexes between polymer **1** and SPS at aqueous interfaces of nematic 5CB, we performed a series of experiments similar to those described above in which we substituted the SPS for a non-ionic polymer [poly(ethylene glycol)] or a strong polycation [poly(diallyldimethylammonium chloride)] (at concentrations of 200 μM based on the molecular weights of the repeat units of these polymers). After 48 hours of contact, no change from the initial polymer **1**-dictated homeotropic alignment of the LC was observed (data not shown). In addition, we prepared aqueous/5CB interfaces using thin films of polymer **2**, which is an analog of polymer **1** that contained 60 mol% of a non-ionic

oligo(ethylene glycol) side chain functionality. Polymer **2** lacks the protonatable tertiary amine side-chain functionality of polymer **1**. A Langmuir film of polymer **2** was prepared and compressed symmetrically to a surface density of $18.5 \text{ \AA}^2/\text{repeat unit}$ (identical mass density as the experiments described above utilizing polymer **1**; see Figure 1A (grey curve) for a representative π -A isotherm). LS transfer of polymer **2** from aqueous/air interfaces to aqueous/5CB interfaces resulted in homeotropic alignment of the 5CB similar to the results shown in Figure 1D. However, incubation of polymer **2**-laden aqueous/5CB interfaces with PBS solutions of 200 \mu M SPS did not trigger an ordering transition in the LC for up to 48 hours (data not shown). These results support our conclusion that the complexes that form between SPS and polymer **1** and lead to the orientational transitions of the LC shown in Figures 2A–C arise from electrostatic interactions between SPS and polymer **1**.

We performed a final series of experiments to determine whether the polymeric nature of SPS was required to trigger the ordering transitions shown in Figures 2A–C. These experiments were conducted by introducing sodium ethylbenzenesulfonate (SEBS) into the aqueous phases contacting polymer **1**-laden aqueous/5CB interfaces (at a concentration of 200 \mu M). SEBS is a low molecular weight, monovalent salt with a structure representative of the constitutional repeat unit of SPS. This small-molecule salt is thus capable of associating with polymer **1** through electrostatic interactions, but the interactions of multiple molecules of SEBS with polymer **1** cannot be coupled with (or correlated to) each other in the manner that they are in complexes formed between polymer **1** and polymeric SPS. After the addition of SEBS to the aqueous phase, we observed no change in ordering of the 5CB for periods of up to 24 hours (Figures 2D–F). Past studies of electrostatically-driven association of molecules in bulk solution and at interfaces have reported that a minimum number of repeat units (typically 4–6 units) is required to promote the formation of stable complexes.^{27,35} It is generally believed that the cooperative effects of multiple points of interaction promote the formation of these stable complexes.^{27,35} Our observations of ordering transitions of 5CB at interfaces decorated with complexes formed by electrostatic association are consistent with this proposition. In particular, our measurements reveal that the polymeric nature of SPS is required to trigger the LC ordering transitions shown in Figures 2A–C.

Several past studies have reported on the formation of polyelectrolyte complexes at interfaces between aqueous phases and LCs.^{6,15–17} In particular, it was demonstrated recently that the sequential contact of aqueous-LC interfaces with aqueous solutions of SPS and PAH leads to the formation of polyelectrolyte multilayers with properties that can be surprisingly similar to multilayers formed by the adsorption of these same polyelectrolytes at the surfaces of solids.¹⁵ These studies also revealed, however, that neither the adsorption of the initial SPS layer nor the subsequent deposition of additional polyelectrolyte layers resulted in ordering transitions of the LC when in contact with aqueous phases. In addition, no change in the orientation of the LC was observed even when the LC interface was seeded with dilauroylethylphosphatidylcholine, a double-tailed cationic phospholipid. These results further support the proposition that multiple points of interaction between two polymers are required to induce ordering transitions in LCs.

In conclusion, we have reported that LC interfaces laden with amphiphilic polyamines strongly couple the formation of polyelectrolyte complexes to the ordering transitions in the LCs. In particular, these ordering transitions, which are driven by electrostatic interactions, require (i) that the interacting molecules are of opposite charge and (ii) that both molecules are polymeric in structure, allowing for multiple points of interaction. Because the aliphatic side-chains of polymer **1** are responsible for the ordering of the mesogens at aqueous/LC interfaces, we interpret changes in LC orientation to indicate reorganization of the polymer-laden LC interface upon formation of the polymer **1**/SPS complexes. Our results suggest the

basis of general and facile methods to couple the orientation of the LCs with hydrophobically-modified polyelectrolytes and provide new insights into the formation and structure of polyelectrolyte complexes at interfaces.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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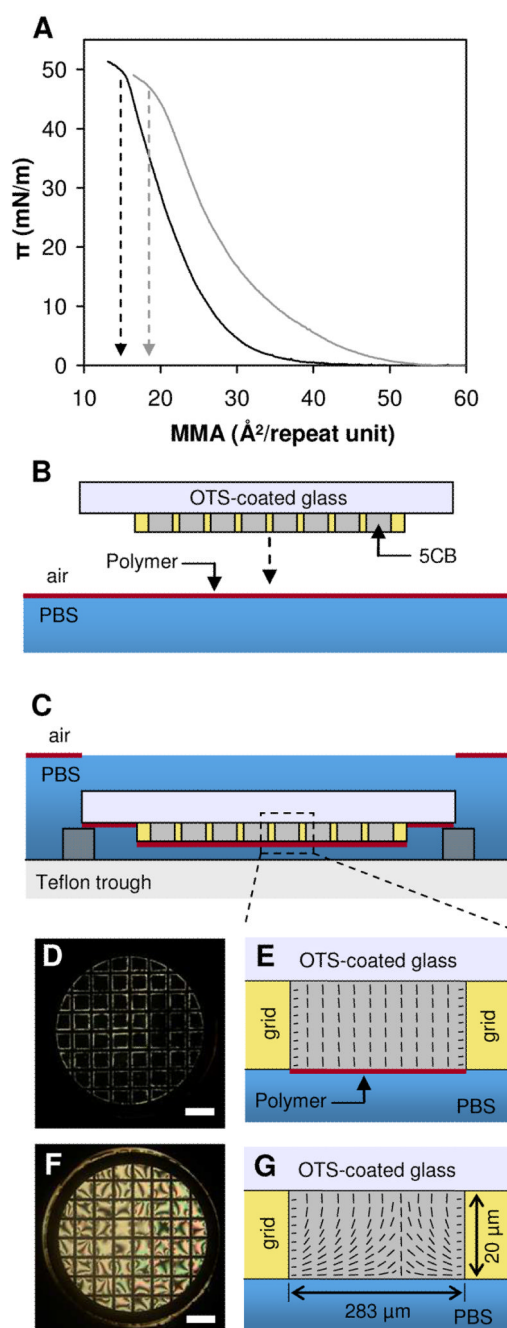


Figure 1.

A) π -A isotherm of polymer **1** (black line) and polymer **2** (gray line) at 25 °C. Dashed lines indicate the surface density at which Langmuir-Schaefer transfer was performed (see text). Schematic illustration of the configuration used for Langmuir-Schaefer transfer of polymer **1** from the PBS surface to the aqueous/LC interface B) before and C) after transfer. The dark red bar represents a thin film of polymer **1** (not drawn to scale). Images in D and F are polarized light micrographs showing D) perpendicular (or homeotropic) alignment of LC after transferring polymer **1** to the aqueous/LC interface (illustrated by E) and F) planar alignment of LC in contact with PBS (illustrated by G). Scale bars = 500 μ m.

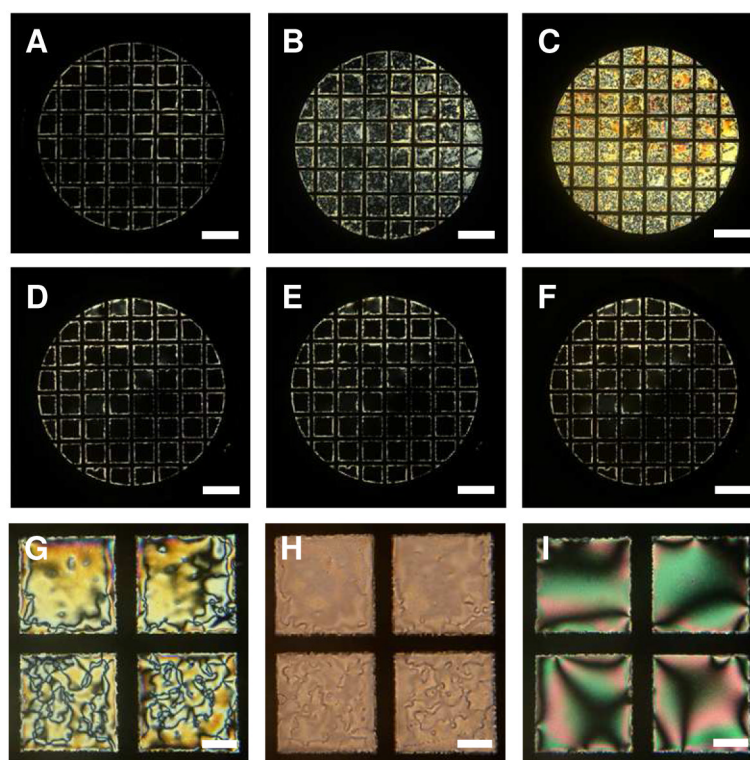


Figure 2. (A–H) Polarized light micrographs of aqueous/5CB interfaces functionalized with a thin film of polymer **1**. The 5CB interfaces were contacted with aqueous solutions of 200 μM SPS (A–C) or 200 μM sodium ethylbenzene sulfonate (D–F). Images were acquired 5 minutes (A and D), 15 minutes (B and E), 30 minutes (C), or 24 hours (F) after contact with solutions of SPS or sodium ethylbenzene sulfonate. The high magnification images (G–I) are polarized light (G and I) and brightfield (H) micrographs of aqueous/5CB interfaces contacted with SPS for 1 hour. The images in G and H correspond to polymer-laden interfaces; the image in I corresponds to a polymer-free interface. Scale bars in A–F = 500 μm and G–H = 100 μm .

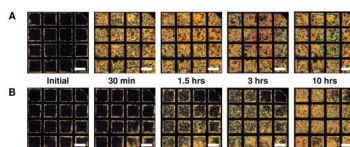


Figure 3. Polarized light micrographs of aqueous/5CB interfaces laden with polymer **1** and contacted with 200 μM SPS in 25 mM sodium phosphate buffer solutions containing A) 150 mM or B) 1.0 M NaCl. The optical appearance of the polymer-**1** laden 5CB interface before the addition of SPS but after increasing the ionic strength of the aqueous solution (see text) is denoted as “initial.” Scale bars = 300 μm .

