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Langmuir Films of Flexible Polymers Transferred to Aqueous/ Liquid Crystal Interfaces Induce Uniform Azimuthal Alignment of the Liquid Crystal

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Abstract

We reported recently that amphiphilic polymers can be assembled at interfaces created between aqueous phases and thermotropic liquid crystals (LCs) in ways that (i) couple the organization of the polymer to the order of the LC and (ii) respond to changes in the properties of aqueous phases that can be characterized as changes in the optical appearance of the LC. This investigation sought to characterize the behavior of aqueous-LC interfaces decorated with uniaxially compressed thin films of polymers transferred by Langmuir-Schaefer (LS) transfer. Here, we report physicochemical characterization of interfaces created between aqueous phases and the thermotropic LC 4-cyano-4'-pentylbiphenyl (5CB) decorated with Langmuir films of a novel amphiphilic polymer (polymer **1**), synthesized by the addition of hydrophobic and hydrophilic side chains to poly(2-vinyl-4,4'-dimethylazlactone). Initial characterization of this system resulted in the unexpected observation of uniform azimuthal alignment of 5CB after LS transfer of the polymer films to aqueous-5CB interfaces. This paper describes characterization of Langmuir films of polymer **1** hosted at aqueous-5CB interfaces as well as the results of our investigations into the origins of the uniform ordering of the LC observed upon LS transfer. Our results, when combined, support the conclusion that uniform azimuthal alignment of 5CB is the result of long-range ordering of polymer chains in the Langmuir films (in a preferred direction orthogonal to the direction of compression) that is generated during uniaxial compression of the films prior to LS transfer. Although past studies of Langmuir films of polymers at aqueous-air interfaces have demonstrated that in-plane alignment of

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Supporting Information Available. Additional figures and other data showing: (i) surface pressure recorded during repeated compression and expansion of a Langmuir film of polymer **1**, (ii) a fluorescent micrograph of a film of 5CB after Langmuir-Schafer transfer of polymer **1**$_{TMR}$ to the aqueous-5CB interface, (iii) a representative AFM image of a film of polymer **1** transferred to an OTS-coated Si substrate, (iv) polarized light micrographs of a LC film after transfer of polymer **1** at an angle ~ 45° relative to the aqueous-air interface, (v) fractional transmittance of polarized light through polymer **1**-laden LC interfaces transferred at various angles relative to the direction of compression, (vi) representative π-A isotherms of Langmuir films of PMMA and PVS, (vii) polarized FT-IR spectra of PMMA films on CaF$_2$ substrates, (viii) and a description of the procedure for the synthesis of polymer **1**$_{TMR}$. This material is available free of charge via the Internet at http://pubs.acs.org.

polymer backbones can be induced by uniaxial compression, these past reports have generally made use of polymers with rigid backbones. One important outcome of this current study is thus the observation of anisotropy and long-range order in Langmuir films of a novel flexible polymer. A second important outcome is the observation that the existence, extent, and dynamics of this order can be identified and characterized optically by transfer of the Langmuir film to a thin film of LC. Additional characterization of Langmuir films of two other flexible polymers [poly(methyl methacrylate) and poly(vinyl stearate)] using this method also resulted in uniform azimuthal alignment of 5CB, suggesting that the generation of long-range order in uniaxially compressed Langmuir films of polymers may also occur more generally over a broader range of polymers with flexible backbones.

Keywords

Langmuir-Schaefer; Polymer; Liquid Crystals; Interfaces; Uniform Alignment

Introduction

Studies of the orientational ordering of liquid crystals (LCs) induced by contact with solid surfaces over the past several decades have led to substantial advances in our understanding of the fundamental basis of this interfacial phenomenon.[1,2] These studies have also contributed to the realization of a range of practical LC-based technologies (e.g., electro-optical devices). [1-3] In the course of these past studies, various approaches were developed to fabricate structured surfaces that can orient LCs, including mechanical rubbing of polymer-coated substrates,[4-7] physical vapor deposition of metals or metal oxides at oblique angles of incidence,[8-10] uniaxial stretching of polymer films,[11] and deposition of polymer films via the Langmuir-Blodgett method.[12,13] The key structural features of these surfaces and the associated mechanisms of alignment of the LCs have been largely elucidated through combined used of linear and non-linear optical methods as well as scanning probe microscopies.[14,15]

More recently, several studies have been reported on the ordering of LCs at aqueous interfaces of immiscible isotropic liquids. These studies have demonstrated that lipids,[16-19] surfactants, [20-25] polymers,[26,27] and proteins[16,28] can assemble at interfaces created between thermotropic LCs and aqueous phases, and that the orientational ordering of the LCs is coupled to the presence and organization of these species. In contrast to solid surfaces, where the lateral mobility of molecular assemblies is low, the mobility of molecules assembled at aqueous-LC interfaces is high, and thus aqueous-LC interfaces provide the basis of methods that can amplify dynamic phenomena that occur in aqueous phases or at these interfaces in real time (e.g., protein binding events[16] or enzymatic reactions[16,28]). It has also been demonstrated that the elastic properties of the LCs can be used to direct the interfacial assembly and organization of amphiphiles at these interfaces. For example, control of interfacial phase separation of lipids and surfactants at aqueous-LC interfaces has been reported.[29,30] We also note that, in contrast to solid-LC interfaces, that the interfaces formed between LCs and aqueous phases can be deformed out of the plane of the interface.[16] This combination of features makes the preparation and characterization of these interfaces substantially more challenging than for the solid surfaces used in the studies mentioned above.[16]

The work reported here is focused on the assembly of amphiphilic polymers at aqueous-LC interfaces as part of a general and versatile approach that we have been developing to tailor the structures and properties of these interfaces. We previously reported, for example, that appropriately designed amphiphilic polymers can assemble at aqueous-LC interfaces in a manner that couples the order of the LC to the organization of the polymers.[26,27] These studies suggest that the properties of LC interfaces can be tailored with multifunctional polymers to

render the LC responsive to external stimuli. In this specific context, we demonstrated that water-soluble polymers functionalized with side chains bearing both long aliphatic groups (as a means to couple the organization of the polymer with the order of the LCs) and pH-sensitive moieties (e.g., tertiary amines) can adsorb spontaneously from aqueous solution onto aqueous-LC interfaces in ways that permit reversible, pH-dependent control over the orientational order of the LCs.[26] In a separate study, we demonstrated that thin films of water-insoluble amphiphilic polyamines can be transferred to aqueous-LC interfaces from aqueous-air interfaces by Langmuir-Schaefer (LS) transfer, and that the resulting polymer-decorated aqueous-LC interfaces can trigger ordering transitions in the LCs upon exposure to anionic polymers (e.g., by *in situ* formation of polyelectrolyte complexes at the aqueous-LC interface). [27] This latter study also provided new insight into the structures and dynamics of interfacial polyelectrolyte complexes at aqueous-organic interfaces.

In the second of the two studies described above, amphiphilic polyamines were transferred to aqueous-LC interfaces by forming a Langmuir film of the polymer at the surface of an aqueous sub-phase followed by LS transfer of the Langmuir film of polymer to aqueous-LC interfaces. [17,27] The LS process is particularly useful in this context (e.g., as compared to methods for the adsorption of polymers from aqueous solutions) for two reasons: (i) it enables the transfer of films of water-insoluble polymers to LC interfaces and (ii) it allows the surface density of the polymers transferred to the LC to be defined by the surface density of the Langmuir film prior to LS transfer. We note that the surface density of polymer at the interface of the LC is a key parameter for the design of responsive, polymer-tailored LC interfaces.[27]

The study reported in this paper involves the investigation and characterization of amphiphilic polymer **1** at interfaces created between aqueous phases and the nematic phase of the thermotropic LC 4-cyano-4'-pentylbiphenyl (5CB). Our initial characterization of this system using methods similar to those used in our past studies resulted in the unexpected observation of uniform azimuthal alignment of 5CB after LS transfer of thin films of polymer **1** to aqueous-LC interfaces (LS transfer of the polymers used in our past studies lead to either homeotropic alignment or to non-uniform, azimuthally degenerate planar alignment, depending on the surface pressures used to compress the Langmuir films).[27] In this paper, we report the physicochemical characterization of Langmuir films of polymer **1** hosted at aqueous-5CB interfaces and the results of our investigation into the origins of the uniform ordering of the LC observed upon LS transfer. The results of these investigations, when combined, lead us to conclude that uniform azimuthal alignment of 5CB is the result of long-range ordering of the polymer chains in the Langmuir films that is generated during uniaxial compression of the films prior to LS transfer. Although past studies of Langmuir films of polymers at aqueous-air interfaces reported by other groups have demonstrated that in-plane alignment of polymer backbones can be induced by uniaxial compression, these past reports have generally been restricted to the characterization of rigid rod-type polymers,[31−35] polypeptides that form helical structures,[36−38] or piezochromic polysilanes[39] that are rigid and/or possess chromophores that facilitate characterization of the anisotropic nature of the Langmuir films (e.g., using methods such as polarized absorbance spectroscopy). One important outcome of this current study is thus the observation of anisotropy and long-range order in Langmuir films of a novel flexible polymer. A second important outcome is the observation that both the existence and the extent of this long-range order can be identified and characterized optically by simple transfer of the Langmuir film to a thin film of LC. Additional characterization of Langmuir films of two other flexible polymers [poly(methyl methacrylate) and poly(vinyl stearate)] using this method also resulted in uniform azimuthal alignment of 5CB, suggesting that the generation of long-range order in uniaxially compressed Langmuir films of polymers, previously identified using thin films created using polymers with more rigid backbones,[31−38] may occur more generally for a broader range of polymers with flexible backbones.

Materials and Methods

Materials

ᴅ-glucamine, *n*-decylamine, and poly(vinyl stearate) (PVS, MW = 90,000) were purchased from Sigma-Aldrich (St. Louis, MO). Poly(methyl methacrylate) (PMMA, MW = 126,000, 80% syndiotactic/16.5% isotactic/3.5% atactic) was obtained from Polysciences, Inc. (Warrington, PA). Poly(2-vinyl-4,4'-dimethylazlactone) (PVDMA, MW = 49,800 g/mol, PDI = 4.3) was a generous gift from Dr. Steven Heilmann (3M Corporation, St. Paul, MN). Tetramethylrhodamine cadaverine was purchased from Molecular Probes (Carlsbad, CA). The LC 4-cyano-4'-pentylbiphenyl (5CB) was obtained from EMD Chemicals (Hawthorne, NY). Sodium phosphate, sodium chloride, methanol, chloroform, octadecyltrichlorosilane (OTS), hydrogen peroxide, sulfuric acid, anhydrous ethanol, heptane, hexane, dimethyl sulfoxide (DMSO), dichloromethane, tetrahydrofuran (THF), carbon black, CaF_2 IR substrates, and Fisher's Finest glass microscope slides were purchased from Fisher Scientific (Pittsburgh, PA). Test-grade n-type silicon wafers were obtained from Si-Tech, Inc. (Topsfield, MA). Gold TEM grids (bars 20 µm thick, 55 µm wide, spaced 283 µm apart) were purchased from Electron Microscopy Sciences (Fort Washington, PA). Deionization of a distilled water source was performed using a Milli-Q system (Millipore, Bedford, MA) yielding water with a resistivity of 18.2 MΩ. All materials were used as received and without additional purification unless otherwise noted.

General Considerations

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC+ 300 spectrometer (300.135 MHz for proton; Billerica, MA). Chemical shift values are given in ppm and are referenced with respect to residual protons or carbon from solvent. Fourier Transform Infrared (FT-IR) spectra were collected in attenuated total reflectance (ATR) mode or transmission mode using a Bruker Tensor 27 spectrometer (Billerica, MA). Polarization of the IR radiation was achieved with a BaF_2 wire grid polarizer. Relative differences in peak intensities are reported as averages of three independent measurements of each sample prepared in triplicate (nine total measurements). Changes in the optical birefringence of the 5CB in TEM grids were characterized using plane-polarized light and an Olympus BX60 microscope equipped with crossed polarizers. Images were captured using a microscope-mounted digital camera (Olympus C-4000 Zoom). In cases where average gray-scale intensity was used to quantify changes in optical birefringence, conversion of color micrographs to gray-scale images was performed using Image J (National Institute of Health, Bethesda, MD); average intensities correspond to values measured over the entire grid area (including grid cross-bars and 5CB but excluding the circular rim of the TEM grid). Fractional transmittance was calculated by correcting for background intensity (light transmitted through OTS-coated glass with polarizers crossed) and normalizing relative to the intensity of light transmitted through OTS-coated glass with the polarizer and analyzer aligned parallel. The direction of azimuthal LC alignment was determined using a Berek compensator inserted between the LC film and the analyzer in the optical path. Fluorescence microscopy images were recorded using an Olympus IX71 inverted microscope equipped with a 100 W mercury lamp and filter cube with a 560 nm excitation filter and a 645 nm emission filter. Images were captured using a Hamamatsu 1394 ORCA-ER-CCD camera interfaced to a computer with an exposure time of 0.5 s. The optical thicknesses of films transferred onto OTS-silicon were determined using a Gaertner LSE ellipsometer (632.8 nm, incident angle = 70°). Data were processed using the Gaertner Ellipsometer Measurement Program assuming an average refractive of 1.577 for the polymer films. Atomic force microscopy (AFM) images were acquired in tapping mode on a Nanoscope Multimode atomic force microscope (Digital Instruments, Santa Barbara, CA), using scan rate of 10–20 µm/s. Silicon cantilevers with a spring constant of 40 N/m and a radius of curvature of less than 10 nm were used (model NSC15/NoAl MikroMasch USA, Inc., Portland, OR).

Height data were flattened using a second order fit. Root-mean-squared (RMS) roughness was calculated over the scan area using the Nanoscope IIIa software package (Digital Instruments). All experiments involving the use of 5CB were performed at ambient room temperature (~25 °C), well below the nematic/isotropic transition temperature of 5CB (33.5 °C) unless otherwise noted.

Synthesis of Polymer 1

PVDMA (0.1 g, 0.719 mmol) was added to a 20 mL glass, screw-capped vial equipped with a magnetic stir bar. DMSO (5 mL) was added and the solution was stirred to dissolve the polymer. D-glucamine (0.2 equiv, 0.0261 g, 0.143 mmol) was dissolved separately in 1 mL of DMSO and added to the PVDMA solution. The mixture was stirred at 50 °C. After 24 hours, *n*-decylamine (0.88 equiv, 124.4 μL, 0.633 mmol) was added and the reaction mixture was stirred for an additional 22 hours at 50 °C. Characterization of polymer **1** by FT-IR (ATR) spectroscopy confirmed the complete reaction of all azlactone functionality in PVDMA with the small-molecule amines as determined by the disappearance of the characteristic azlactone carbonyl peak at 1828 cm^{-1} (C=O).[40] The reaction solution was precipitated into a mixture of hexane and acetone (3:1, v/v). The resulting precipitate was redissolved in a mixture of dichloromethane and methanol (5:1, v/v) and precipitated twice more into a hexane/acetone mixture (4:1, v/v). The resulting white solid was dried and stored in a vacuum desiccator. ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 0.88 (br t, −NHCH$_2$(CH$_2$)$_8$C*H$_3$*), 1.26–1.47 (br m, −C*H$_2$*CH−, (−C*H$_3$*)$_2$, −NHCH$_2$(C*H$_2$*)$_8$CH$_3$), 2.23 (br s, −CH$_2$C*H*−), 2.92-3.17 (b m, -NHC*H$_2$*(CHOH)$_4$CH$_2$OH, −NHC*H$_2$*(CH$_2$)$_8$CH$_3$), 4.12 (b s, −NHCH$_2$(C*H*OH)$_4$C*H$_2$*OH).

Preparation of OTS-Coated Substrates and LC-Filled Grids

Glass slides were cleaned at ~80 °C for 1 hr in a piranha solution consisting of 30% (v/v) hydrogen peroxide and 70% sulfuric acid. (Warning: piranha reacts strongly with organic compounds and should be handled with extreme caution. Do not store in closed containers.) The slides were rinsed thoroughly with deionized water, methanol, and ethanol and dried for 12 hours at 120 °C. The glass slides were then functionalized with OTS according to published procedures.[21] Gold TEM grids were placed on a piece of OTS-coated glass (~5 × 20 mm) and filled with 5CB using methods published previously.[21] The grids confining the LC were examined by polarized light microscopy to confirm adequate filling of the gird pores with 5CB prior to use. Hydrophobic silicon substrates were prepared by cleaning, rinsing, and functionalizing silicon wafers with OTS using the same procedure as described for the glass slides.

Preparation of Langmuir Films and Langmuir-Schaefer Transfer

Spreading solutions of polymer **1** were prepared in a 19:1 chloroform/methanol mixture. Spreading solutions of PMMA and PVS were prepared in pure chloroform. All polymer solutions were used at a concentration of 2.0 mg/mL unless otherwise noted. Langmuir films were prepared on a Nima 602A film balance (Coventry, England) equipped with a filter paper Wilhelmy plate for surface pressure measurements. No significant surface pressure was observed upon complete compression of bare aqueous-air interfaces prior to spreading polymer solutions. A known volume of the solutions containing the polymers were deposited dropwise uniformly across the surface of phosphate-buffered saline (PBS) at pH 7.0 (25 mM sodium phosphate, 150 mM NaCl) and the spreading solvent was allowed to evaporate for 15 minutes before film compression was initiated. The temperature of the subphase was maintained at 25 °C by circulating water at a constant temperature beneath the trough. Symmetric compression of polymer films was performed at a constant rate of 50 cm^2/min (6.2 Å^2/min-repeat unit) unless otherwise noted. Once the desired surface density was reached, the LC-filled grids supported on OTS-treated glass (see above) were inverted and passed vertically through the

polymer-laden aqueous-air interface using tweezers as described previously (see Figure 2 for a schematic illustration of this process).[17] The OTS-treated glass and supported TEM grid were approximately parallel to the aqueous-air interface during the LS transfer unless otherwise noted. A homemade aluminum frame immersed in the sub-phase prior to spreading the polymer solution prevented the LC-filled grids from contacting the bottom of the trough. After LS transfer, the LC-filled grids were removed from the trough subphase and placed in a vial containing PBS for imaging. This transfer was performed such that the LC-filled grids remained immersed in the aqueous solution at all times. The alignment of 5CB was characterized by polarized optical microscopy, as described above under General Considerations. A similar procedure was used to transfer twelve layers of PMMA to a CaF_2 substrate for FT-IR characterization. A new Langmuir film was prepared for each layer and the CaF_2 substrate was handled to maintain a constant orientation relative to the direction of compression for each layer. As a control, films of PMMA were cast on CaF_2 substrates by immersing the substrate into a 2 mg/mL solution in chloroform for 5 minutes.

Powder Method for Characterization of Film Compression

A method for powder deposition based upon a previous report by Malcolm[41] was used to investigate the uniformity of Langmuir films of polymer **1** during compression of the films (see text). Briefly, a Langmuir film of polymer **1** (prepared as described above) was compressed partially to a surface density of 43 Å^2/monomer. Partial compression of the film prior to the application of powder (described below) was required to prevent the powder lines from drifting. A mask with slots ~1 mm wide was placed over the polymer film (without contacting the film) and carbon black powder was shaken over the mask. The mask was then removed and the process was repeated with another mask with slots oriented perpendicular the previously deposited lines. The polymer film was then compressed until the surface density reached 15 Å^2/monomer. The surface pressure did not change measurably when the carbon powder was placed on the film and the resulting π-A isotherm completely overlapped with isotherms collected in the absence of the powder grid. Images of the grid-laden Langmuir film were collected using a digital camera (Nikon Coolpix 4300).

Results and Discussion

Polymer Synthesis

Polymer **1** was synthesized in a modular fashion by reaction of amine-containing small molecules with the pendant azlactone functionality of poly(2-vinyl-4,4'-dimethylazlactone) (PVDMA, MW = 49,800 g/mol) using an approach similar to that described in our past study.[27] This approach provides a general method to incorporate a broad range of side chain functionality into the polymer at specific mole percentages.[40,42] For the work described here, we synthesized a polymer with 80 mol% hydrophobic alkane-functionalized side chains and 20 mol% hydrophilic carbohydrate-functionalized side chains. *N*-decylamine was used to introduce hydrophobic side chains into the structure of polymer **1** based on previous work demonstrating that interactions involving long aliphatic side chains can direct the ordering of LCs.[20,26,27,43] D-glucamine was used to impart non-ionic hydrophilic functionality to the polymer. These carbohydrate-functionalized side chains were also selected with a view to potential future studies involving the use of biological molecules, as past studies have demonstrated that D-glucamine, when presented on solid surfaces, can minimize or inhibit the non-specific adsorption of proteins.[44–46] (In future studies, for example, polymers with structures similar to polymer **1** could be used to design functional aqueous-LC interfaces that resist the non-specific adsorption of proteins.) Polymer **1** was characterized by ^{1}H NMR and ATR-IR spectroscopy (see Methods and Materials for additional details).

Characterization of Langmuir Films of Polymer 1

To characterize the behavior of polymer **1** at the aqueous-air interface, a solution of the polymer was spread on the surface of phosphate-buffered saline (PBS) confined within a Langmuir trough at a surface density of 58 Å^2/repeat unit. The resulting Langmuir film was compressed symmetrically at 50 cm^2/min (6.2 Å^2/min-repeat unit) by the movement of the two barriers of the trough. Figure 1 shows a representative π-A isotherm measured during compression of a Langmuir film of polymer **1**. The surface pressure increased continuously with no evidence of plateaus in the isotherm that would suggest first-order phase transitions during compression. Collapse of the film occurred at surface pressures in the range of 47–49 mN/m and a surface density of 14 Å^2/repeat unit. We note that the area per repeat unit at which film collapse occurred was smaller than the cross-sectional area of a single aliphatic chain (~18 Å^2), suggesting that the polymer may be partially desorbed into the subphase as loops or tails at this surface density. However, the optical thickness and AFM measurements of films of polymer **1** transferred to solid surfaces (discussed below) were consistent with the formation of a two-dimensional monolayer of polymer. Repeated compression and expansion of a single film of polymer **1** to areas below collapse produced similar π-A isotherms for each compression cycle with only small shifts in the isotherm (< 0.5 Å^2/repeat unit), suggesting that the films are stable and that compression is reversible (see Supporting Information).

Langmuir-Schaefer Transfer of Polymer 1 to Aqueous-5CB Interfaces

We performed an initial set of experiments to characterize the transfer of polymer **1** from aqueous-air interfaces to 5CB interfaces. For these experiments, we used Langmuir films compressed to a surface density of 15 Å^2/repeat unit. A 5CB-filled TEM grid supported on OTS-coated glass was inverted and vertically passed through a polymer-laden aqueous-air interface (the OTS-coated glass and TEM grid remained approximately parallel to the interface), using a procedure similar to that previously described[17,27] (see Figure 2 for a schematic illustration of the OTS-coated glass, TEM grid, 5CB, and LS transfer method). Figure 3 shows representative polarized light micrographs of a LC interface after passage through this polymer-laden aqueous-air interface (Figures 3A and 3B), as well as the result of a control experiment in which only solvent (no polymer) was spread at the aqueous-air interface (Figures 3D and 3E). Initial inspection of these images reveals a clear difference in the optical appearance of 5CB interfaces in the presence (Figures 3A and 3B) and absence (Figures 3D and 3E) of polymer **1** (interpretation of these differences will be discussed in further detail below) and suggests that the thin film of polymer was successfully transferred from the aqueous-air interface to the interface of the LC. Transfer of polymer was further verified by using an analog of polymer **1** fluorescently labeled with tetramethylrhodamine (polymer **1_{TMR}**). This labeled polymer was transferred to LC interfaces using the same LS procedure described above for polymer **1**. After transfer, uniform fluorescence intensity was observed across all grid squares confirming the transfer of the polymer to the LC interface (see Supporting Information for a representative micrograph). In a final experiment designed to verify transfer of polymer by the LS technique, a Langmuir film of polymer **1** was transferred directly to a silicon wafer hydrophobically modified by treatment with OTS. The optical thickness of films transferred in this manner measured by ellipsometry was 1.9 ± 0.3 nm. This result provides additional evidence that a Langmuir film of polymer **1** can be successfully transferred to a hydrophobic interface. These results are also consistent with the transfer of a film that is, on average, on the order of one or at most two monolayers thick (as described above). Additional characterization of the polymer **1** films transferred to OTS-coated silicon by AFM (see Supporting Information) revealed the films to be generally smooth and uniform on micrometer and nanometer scales (RMS roughness = 0.38 ± 0.07 nm) and provides additional support for the view that polymer **1** is transferred to the substrates as a monolayer and not a film of non-uniform thickness.

Alignment of LCs in Contact with Polymer Films

Inspection of the micrographs of polymer **1**-laden 5CB films shown in Figures 3A and 3B reveals that the optical appearance of the LC is either uniformly bright (Figure 3A) or uniformly dark (Figure 3B) depending on the orientation of the crossed polarizers (representative images at higher magnification are shown in Figures 5B and 5C). The bright regions near the grid edges in Figure 3B result from interactions between the gold grid and 5CB as described in past reports.[21] Rotation of the crossed polarizers while holding the polymer-laden LC film stationary (denoted as the angle ϕ, see Figure 3H for a schematic illustration of this rotation) resulted in periodic modulation in the intensity of the transmitted light every 90 degrees (Figure 3G, closed diamonds). No periodic extinction in the transmitted light was observed in the absence of polymer at the interface (e.g. Figure 3G, open circles; data obtained from polarized light micrographs shown in Figure 3D and 3E). Because the orientation of 5CB in immediate contact with OTS-coated glass is perpendicular to this surface (see the schematic in Figure 2), [21] we interpret this periodic modulation of polymer-laden 5CB films to indicate a continuous bend and splay in the LC director profile to an orientation that is parallel to the aqueous-LC interface and *uniformly* aligned in the azimuthal direction (e.g., Figure 3C). This conclusion is further supported by the lack of characteristic dark brushes, or Schlieren textures, in the images shown in Figures 3A and 3B. These Schleiren textures, which are indicative of *degenerate* planar alignment (e.g., Figure 3F) were observed in control experiments in which polymer was absent from the aqueous-LC interface (Figures 3D and 3E). Differences in the interference colors between the image shown in Figure 3A and images in Figures 3D and 3E are representative of variation between individual samples and are likely the result of small changes in the thickness of the film of 5CB.[47]

Origin of the Uniform Azimuthal Alignment of LC

The results of the experiments described above suggest that films of polymer **1** are organized or structured in a manner that templates or gives rise to uniform azimuthal alignment of the LCs. We designed a series of experiments to provide insight into the presence and/or origin of such organization or structure in the polymer films. We considered first the possibility that the compression of the Langmuir films of polymer **1** was not occurring in a uniaxial manner, but that it occurred in a manner that generated shear forces that could cause the alignment of polymer chains or side groups. For example, it has been demonstrated that the compression of some polymeric materials at aqueous-air interfaces can occur non-homogeneously, leading to in-plane flow of monolayer as well as shear forces that are perpendicular to the direction of compression.[38,48] Large-scale in-plane flows that occur during the compression of Langmuir films can be readily identified using a "powder grid" method described previously by Malcolm. [41] We used a slightly modified version of this method to deposit a grid of carbon powder onto the surface of a Langmuir film of polymer **1** (see Methods and Materials for additional details on the preparation of the powder grid). Figures 4A and 4B show images of the powder grid before and after compression of the film, respectively. Some deformation of the grid shape can be seen in the upper region of the image shown in Figure 4B where the film was near the edges of the trough, indicating that the polymer film was displaced in both vertical and horizontal directions in these regions during compression. However, in general, the vertical and horizontal lines of powder remain straight over the majority of the area of the film, suggesting that compression proceeded uniaxially without shear perpendicular to the direction of compression. (We note that the grid does not cover the entire film surface and hence does not appear symmetric because it was not applied to the lower region of the film. The location of the Wilhelmy plate on the film surface made application of the powder grid in this region difficult.) In the experiments performed to collect the images shown in Figures 3A and 3B, LS transfer was typically performed at a location in the center of the film, where the least non-uniaxial deformation of the powder grid was observed. However, varying the location of the transfer across the film, including within approximately 5 millimeters of the barrier and trough edges

(denoted by X's in Figure 4B), lead to similar alignment of the 5CB (e.g. as seen in Figures 3A and 3B) for all locations, even in regions where non-uniaxial deformation of the powder grid was observed (such as the upper regions of Figure 4B).

We also performed an additional series of experiments in which the rate of compression of the Langmuir films was varied from 200 cm^2/min (25 $Å^2$/min-repeat unit) to 10 cm^2/min (1.2 $Å^2$/min-repeat unit). Transfer of these films to LC interfaces produced results similar to those shown in Figures 3A and 3B, regardless of the compression rate (data not shown). Because it would be expected that the rate of compression would have an influence on the generation of shear stresses, these results provide further support for the view that shear stresses acting perpendicular to the direction of compression are unlikely to be responsible for the structuring of the polymer film that leads to the uniform azimuthal alignment of 5CB.

Past reports have demonstrated that when Langmuir films of polymers are transferred to solid substrates by vertically (as opposed to horizontally) passing the substrates through a Langmuir film (i.e., Langmuir-Blodgett transfer), shear stresses generated during the vertical movement of the substrate can produce a preferred orientation of the polymer backbone.[13,49–51] Although the Langmuir trough used in this study was not sufficiently deep to allow Langmuir-Blodgett transfer, we considered it possible that deviation from a horizontal orientation of the substrate during LS transfer was generating shear forces similar to those encountered during Langmuir-Blodgett transfer. To explore this possibility, we conducted experiments in which the 5CB-filled grids supported by OTS-treated glass were passed through films of polymer **1** at an angle of ~45° relative to the aqueous-air interface, and compared these samples to samples transferred horizontal to the aqueous-air interface. No significant difference in the alignment of the 5CB was observed for these two methods of transfer (see Supporting Information), suggesting that shear forces generated by deviations from horizontal transfer do not give rise to films that promote uniform azimuthal alignment of the LC.

Influence of Compression on Order Within the Polymer Films

In all of the experiments described above, care was taken to ensure that the OTS-coated glass substrates (~0.5 × 2 cm) supporting the TEM grids were passed through the polymer-laden aqueous-air interface such that the long axis of the glass (hereafter denoted as the y-axis of the glass slide, see Supporting Information for a schematic illustration) was approximately parallel to the edges of the movable barriers (perpendicular to the direction of compression). As seen in Figure 3G, this method of transfer resulted in the extinction of the polarized light when the crossed polarizers were oriented either 0° or 90° relative to the y-axis of the glass slide. This result indicates that the long axes of the rod-shaped 5CB mesogens were aligned, on average, in one of these two directions. Using a Berek compensator placed in the optical path of the polarized microscope between the sample and analyzer, we determined that the long axes of the 5CB mesogens were aligned parallel to the y-axis and, hence, perpendicular to the direction of compression.

To confirm that the alignment of 5CB was correlated to the direction of compression, and that it was not an artifact of the LS transfer process or our experimental set-up, we conducted experiments in which the angle (θ) of the y-axis of the glass slide was varied relative to the direction of compression. Langmuir films of polymer **1** were compressed to a surface density of 15 $Å^2$/monomer and OTS-coated glass slides supporting LC-filled grids were passed through the aqueous-air interface at angles of θ equaling 0°, 30°, or 60° relative to the direction of compression. A schematic illustrating this experimental geometry can be found in the (Supporting Information Figure S4A). After the LS transfer, the fractional transmittance of polarized light as the crossed polarizers were rotated relative to the y-axis of the glass slides (angle ϕ) was determined (see Supporting Information, Figure S4B). For each condition, the maximum extinction (minimum transmittance) occurred when the angle of LS transfer relative

to the direction of compression (θ) and the position of the crossed polarizers relative to the glass slides (ϕ) were equal. Likewise, the maximum transmittance occurred when the crossed polarizers were rotated 45° relative to the angle of transfer. This result demonstrates that the 5CB mesogens in each case were aligned in an identical direction relative to the direction of compression and the alignment was independent of the angle (θ) at which the LS transfer was performed.

The results described above demonstrate that the direction of uniform azimuthal alignment of 5CB in contact with polymer **1** films is correlated with the direction of uniaxial compression of the polymer films at the aqueous-air interface prior to transfer. To further explore the relationship between uniaxial compression and LC alignment, we conducted a series of experiments in which the polymer surface density (and hence degree of compression) was varied prior to LS transfer to aqueous-LC interfaces. For these experiments, Langmuir films of polymer **1** were compressed to surface densities that varied between 15 and 37 Å^2/repeat unit and transferred via the LS technique to the aqueous-5CB interface. Polarized micrographs of each polymer-laden 5CB film were captured with the crossed polarizers positioned for maximum or minimum transmittance of polarized light and the gray-scale intensities of these images were determined.

Figure 5A shows the ratio of these two values (denoted I_{45}/I_0, as maximum transmittance was measured when the polarizers are rotated 45° from the position of minimum transmittance) as a function of the surface density of polymer prior to LS transfer to aqueous-5CB interfaces. When polymer films were transferred to LC interfaces at low surface densities (>30 Å^2/repeat unit), the overall (meaning, when averaged over the entire grid) azimuthal alignment of 5CB was degenerate with little to no modulation of transmitted light upon rotation of the crossed polarizers, as indicated in Figure 5A by a value of I_{45}/I_0 near 1.0. Overall, degenerate alignment is evident in the corresponding polarized light micrographs (Figures 5F and 5G), which show the characteristic dark brushes of so-called Schlieren textures. Increasing the surface density of polymer **1** prior to LS transfer lead to an increase in the value of I_{45}/I_0, reaching a maximum at a surface density of 15 Å^2/ repeat unit. The optical appearances of LC films decorated with polymer **1** at this surface density were either uniformly dark (Figure 5B) or bright (Figure 5C), which indicates uniform azimuthal alignment of the LC. As discussed above, we observed variation in the interference colors both between independent samples and across grid squares within individual samples. We attribute this variation to small changes in the thickness of the LC films.[47] For example, the ring-like patterns that can be seen in Figure 5C suggest that the interface hosted within these grid squares is slightly curved (i.e., convex or concave, in contrast to the planar interface depicted in the illustration in Figure 2). At an intermediate surface density (20 Å^2/repeat unit), images of the LC films with the crossed polarizers positioned for maximum extinction (Figure 5D) still appeared dark relative to images collected with the crossed polarizers positioned for maximum transmission (Figure 5E). However, the contrast between these two images (Figures 5D and 5E) was diminished relative to films compressed to higher surface density (Figures 5B and 5C). These data suggest that the degree of uniform azimuthal alignment of 5CB laden with films of polymer **1** is correlated to the polymer surface density prior to LS transfer.

The experiments described above suggest that compression of the Langmuir films of polymer **1** is required to give rise to uniform azimuthal alignment of 5CB. To further explore this proposition, we conducted an experiment to compare a Langmuir film of polymer **1** spread directly at 15 Å^2/repeat unit (i.e., an uncompressed film) with a film spread at 58 Å^2/repeat unit and compressed to 15 Å^2/repeat unit (i.e., as described above). In this experiment, we sought to determine if polymer films prepared by the two methods would possess different surface pressures (if the polymers are at equilibrium, the surfaces pressures would be identical), and if the alignment of LCs in contact with polymer films prepared by the two methods would

be similar. Prior to spreading polymer **1** at the aqueous-air interface, the barriers of the Langmuir trough were moved to positions that would give rise to a surface density of 15 Å^2/ repeat unit if polymer were present at the interface. A sufficient mass of polymer **1** was then spread from solution onto this aqueous surface to reach a density of 15 Å^2/ repeat unit and the solvent was allowed to evaporate prior to LS transfer of this film to the aqueous-5CB interface. The surface pressure of this Langmuir film recorded after evaporation of the solvent (24–26 mN/m) was significantly lower than a Langmuir film that was compressed (44–47 mN/m), thus indicating that uniaxial compression of the film of polymer **1** does lead to states of the polymer film that reflect the processing of the polymer (and not an equilibrium state). Polarized light micrographs of 5CB films in contact with the interface of the polymer film spread at 15 Å^2/repeat unit are shown in Figure 6A and 6B and can be compared with a polymer film that did undergo compression (Figures 3A and 3B). These images were collected with the crossed polarizers at either 45° (Figure 6A) or 90° (Figure 6B) relative to the position of the barriers. Close inspection of the individual grid squares in Figures 6A and 6B (5CB in contact with a film of polymer **1** that did *not* undergo compression) reveal regions of uniform azimuthal alignment of 5CB. For example, the arrows in the upper right of Figures 6A and 6B designate an individual square that modulates between transmission (Figure 6A) and extinction (Figure 6B) of polarized light depending on the orientation the crossed polarizers. However, the direction of azimuthal alignment is not the same across the entire grid (i.e. there is significant variation both within and between individual grid squares), and thus contrasts to the overall uniform alignment seen with the compressed films. In a subsequent experiment, a single large piece of OTS-coated glass (2 × 5 cm) was prepared with eight 5CB-filled TEM grids spaced evenly across the glass (separated by approximately 1.5 centimeters). A compressed Langmuir film of polymer **1** was transferred to these LC interfaces and uniform azimuthal alignment of 5CB was observed in the same direction across all of these grids (data not shown), suggesting that the uniform structure or organization of the compressed films persists over length scales of tens of millimeters. We conclude on the basis of the above result that the processing (i.e., compression) of the film plays a critical role in organizing the Langmuir film of polymer **1** in a manner that leads to uniform azimuthal alignment of 5CB over large areas when transferred to LC interfaces.

LS Transfer of Other Polymers

Our next experiments sought to determine whether the uniform azimuthal alignment of 5CB promoted by LS transfer of thin films was unique to films of polymer **1** or whether films of other polymers could orient LCs in a similar manner. For these experiments, we selected two polymers to investigate: (i) poly(methyl methacrylate) (PMMA) because it has been one of the most widely studied polymers at the aqueous-air interface and (ii) poly(vinyl stearate) (PVS) because it contains long aliphatic chains, similar to polymer **1**. The π-A isotherms measured during compression of these polymers at the aqueous-air interface are similar to previous reports[52–55] and can be found in the (Supporting Information Figure S5). Langmuir films of PMMA and PVS were compressed to surface pressures below film collapse (6.7 and 13.3 Å^2/ monomer, respectively) and the polymer films were transferred to the 5CB interface using the LS procedure used to transfer films of polymer **1**. Representative polarized light micrographs of these polymer-laden 5CB films are shown in Figure 7. As seen in these images, the transmittance of polarized light modulated from bright (Figures 7A and 7C) to dark (Figures 7B and 7D) as the crossed polarizers were rotated. This modulation in the intensity of transmitted light indicates that the 5CB mesogens were uniformly aligned at the aqueous-LC interface in the azimuthal direction, similar to the films of polymer **1**. This observation suggests that anisotropy or molecular-level organization may also exist in compressed Langmuir films of these two other flexible polymers, and that the behavior observed above in experiments conducted using polymer **1** may occur more generally for Langmuir films of a broader range of flexible polymers (we address this issue in further detail below).

Polarized FT-IR of Polymer Films

As discussed in the introduction, past reports have demonstrated that uniaxial compression of rigid-rod type polymers generates molecular-scale orientation of polymer chains at aqueous-air interfaces.[31–38] The results described in this current study using polymer **1**, PMMA, and PVS suggest that this behavior also occurs in compressed Langmuir films of polymers with flexible backbones. We note here, however, that the alignment of LCs near surfaces and interfaces is sensitive to order and structure on a wide range of length scales (e.g., extending from oriented molecular chains to micrometer-scale topographical features).[1,2,56–58] In this context, it is possible that the films used in our current studies could have topographical features on the micrometer or nanometer length scale that could direct and account for the observed orientation of the LCs. However, as discussed above, characterization of films of polymer **1** transferred to silicon substrates by AFM did not reveal the presence of significant microscale or nanoscale features (RMS roughness $= 0.38 \pm 0.07$ nm, see Supporting Information). This result suggests a mechanism for the uniform azimuthal alignment of 5CB that is instead based on the molecular-level ordering or anisotropy of the orientation of the polymer chains within the compressed films. To investigate this possibility, we characterized films of PMMA transferred to solid substrates by the LS method using Fourier Transform Infrared (FT-IR) spectroscopy. We selected PMMA for these studies, rather than polymer **1**, because the structure of PMMA is relatively simple compared to that of polymer **1** and provides a more readily interpretable IR spectrum. Films of PMMA were deposited on a CaF_2 substrate under one of three different conditions: (i) LS transfer from aqueous-air interfaces at a density of 6.7 $Å^2$/repeat unit (analogous to methods described above for transfer of polymers to 5CB interfaces), (ii) LS transfer at a density of 12.4 $Å^2$/repeat unit (a surface density that did not give rise to uniform azimuthal alignment of 5CB, data not shown), or (iii) dip coating the substrate using a solution of PMMA dissolved in chloroform. For samples prepared by the LS method, 12 layers were transferred to the same substrate in order to achieve a film thick enough to produce sufficient signal above the background absorbance. In order to characterize anisotropy within the polymer films, transmission FT-IR spectra of the samples were collected with a polarizing grid inserted between the IR source and sample. For these experiments, IR radiation was polarized either parallel ($\theta = 0°$) or perpendicular ($\theta = 90°$) relative to the direction of compression.

Comparison of the spectra collected from films prepared by LS transfer at 6.7 $Å^2$/repeat unit revealed a small but measurable difference in absorbance depending on the angle of polarization. Most notably, we observed a stronger absorption band at 1730 cm^{-1} (C=O symmetric stretching) when the source was polarized parallel to the direction of compression (see Supporting Information, Figure S4, for FT-IR spectra). To quantify this difference in adsorption, we calculated the percent difference of the peak intensity at 1730 cm^{-1} when the IR beam was polarized either parallel or perpendicular relative to the direction of film compression (see Materials and Methods). These values are listed in Table 1. When the LS transfer of PMMA multilayers was performed at 12.4 $Å^2$/repeat unit, we observed the anisotropy in the IR spectra to be reduced relative to films prepared at 6.7 $Å^2$/repeat unit. A reduction in the anisotropy of the IR spectra correlates with the absence of uniform azimuthal alignment of 5CB observed when Langmuir films of PMMA were transferred to LC interfaces at 12.4 $Å^2$/repeat, and suggests that a threshold level of molecular anisotropy is required to give rise to uniform azimuthal alignment of 5CB. Films prepared by dip coating the CaF_2 substrate in a solution of PMMA revealed no difference between the IR spectra collected at $\theta = 0°$ or 90° within the error of the measurement. This result suggests that the anisotropy reported above for films prepared by LS transfer is not an artifact of the IR measurement.

The dependence of IR transmission on the polarization of the IR source suggests that there is a degree of structural order on the molecular-scale in the PMMA films transferred to surfaces

at 6.7 Å^2/repeat unit by the LS method. These results also support the view that the uniform alignment of 5CB in contact with these films is a consequence of this molecular-scale structure or organization. This is consistent with previous studies demonstrating that the observation of uniform LC alignment on mechanically rubbed polymer films is the result of the alignment of polymer chains induced by the rubbing process.[5–7] The difference between IR transmission of PMMA films prepared by the LS transfer method when the source was polarized perpendicular or parallel to the direction of compression was small but reproducible for measurements of three different locations on three independent samples. Ito et al. demonstrated in a past study that a small degree of anisotropy in the molecular organization of polyimide films can lead to alignment of LCs when transferred to solid substrates using the Langmuir-Blodgett method (as characterized by polarized fluorescence adsorption).[13] In that study, the polymers were observed to be oriented only slightly (the second moment of orientation was between 0.54 and 0.58 on a scale of 0.5 to 1.0, with a value of 1.0 indicating perfect uniaxial orientation), and when LC was placed in the space between two polyimide films, uniform alignment of the LC was observed in the direction of dipping.[13] The results of our current experiments are consistent with the results of this past study and suggest that LCs can unmask and amplify a small degree of molecular anisotropy present in the polymer films.

Dynamics of Polymer Films at LC Interfaces

The results of experiments described above (e.g., the results presented in Figure 6) hint that the molecular-level, anisotropic organization of the polymer films that gives rise to uniform alignment of 5CB is not an equilibrium condition. In all of the experiments discussed above, the alignment of 5CB was characterized within five minutes after LS transfer of polymer films. In a final series of experiments, we sought to characterize further the dynamics of the films of polymer **1** after transfer to LC interfaces. To this end, polymer **1**-laden LC films were prepared by the LS method, as described above, and maintained at 25 °C or 32 °C (the temperature of the aqueous subphase was 25 °C during film compression). The latter temperature is just below the nematic/isotropic transition temperature of 5CB (33.5 °C). Polarized light micrographs of the LC films were periodically collected over a period of 20 hours. Inspection of the images of the 5CB interfaces maintained at 25 °C (Figures 8A and 8B) indicate that the initial uniform alignment of 5CB was generally maintained over a period of several hours. Initially, there was a distinct contrast between a uniformly dark (Figure 8A) or a uniformly bright (Figure 8B) optical appearance of the LC films depending on the orientation of the crossed polarizers. Over several hours, this contrast became less defined in a manner that is most apparent as an increase in the brightness near the grid edges in the series of images shown in Figure 8A. This suggests that some loss of the uniform azimuthal alignment of 5CB occurred in these regions. Incubating the polymer **1**-laden 5CB films in aqueous solutions at 32 °C increased the rate at which the uniform azimuthal LC alignment degraded. After two hours, Schlieren textures, indicative of degenerate azimuthal alignment, were readily apparent in the optical micrographs (Figures 8C and 8D). After 20 hours, no modulation in the intensity of light was observed as the crossed polarizers were rotated (data not shown). The change in LC alignment over time indicates the presence of time-dependent changes in the organization of the thin film of polymer **1**. The results shown in Figure 8 suggest that the films of polymer **1** exist in an initial, well-ordered state, but that they relax to a more disordered state over time in a temperature-dependent manner. This provides additional evidence that the processing of the Langmuir films by uniaxial compression leads to an unstable, kinetic organization of the polymer within the films. Additionally, these results illustrate methods in which LCs can report on dynamic changes in the structure or organization of ultrathin polymer films at LC interfaces and the effects that environmental conditions (e.g., temperature) can have on these processes.

Mechanism for LC Alignment

The results presented in this paper, when combined, demonstrate that uniaxial compression of the Langmuir films of polymers leads to anisotropic orientations of the polymer chains within the films, and that the LS transfer of these films onto interfaces of 5CB leads to uniform azimuthal alignment of the LC. The existence of molecular-level anisotropy in the polymer films is supported by the results of polarized FT-IR experiments (Table 1). Characterization of polymer films transferred onto solid substrates using AFM suggests that the uniform alignment of the LC is not likely to be promoted by micrometer- or nanometer-scale topographical features on the surfaces of the films. The results of our experiments demonstrate that uniaxial compression of the Langmuir films is required to give rise to long-range uniform alignment (e.g., as shown in Figure 5 and Figure 6). These results suggest that as Langmuir films of polymer are compressed symmetrically in a uniaxial direction, the polymer chains are forced into a configuration with an average orientation perpendicular to the direction of the uniaxial compression (represented schematically in Figure 9) and, when these films are transferred to 5CB interfaces, this average orientation of the polymer chains promotes uniform azimuthal alignment of the LCs in a preferred direction that is orthogonal to the direction of uniaxial compression. Alternative schemes for the ordering of polymer chains based on non-uniaxial compression or shear stresses generated during the LS transfer are not supported by the results or our experiments (e.g., images shown in Figure 5).

Deterioration or loss of the uniform alignment of LC over time (e.g., as shown in Figure 8) suggests that the organization of the polymer film generated by compression does not correspond to an equilibrium condition, but that the rate of film compression is greater than the rate at which the polymers can relax over the duration of the experiments reported in this paper. This notion is consistent with past studies by Peng and Barnes, who reported gradients in the surface pressure across compressed Langmuir films of PMMA and PVS.[54,55] The authors attributed these gradients to the slow diffusion and rearrangement of the polymers at the surface relative to the rate of compression employed. Future studies that make use of non-traditional Langmuir trough designs that allow for omni-directional compression or that permit the compression of polymers at rates that are orders of magnitude slower than those used in this study may provide additional insights into the structure or organization of polymers induced by film compression.

Finally, we note again that, in general, the observation of anisotropy in uniaxially compressed Langmuir films of polymers is not itself new. As described in the introduction, several past studies have demonstrated that in-plane alignment of polymer backbones can be induced by uniaxial compression of Langmuir films of polymers at aqueous-air interfaces.[31−39] We note further, however, that these past reports have generally made use of polymers with rigid structures and/or other properties that facilitated characterization of the anisotropic nature of the Langmuir films. One important outcome of this current study is therefore the observation of anisotropy and long-range order in Langmuir films of three different polymers with flexible backbones. A second significant outcome that goes beyond the scope of these past studies is the observation that the existence, extent, and dynamics of the long-range order in these films can be identified and characterized optically simply by the LS transfer of compressed Langmuir films of these polymers to thin films of LC. In these two particular contexts, it is important to note that such long-range order can only be unmasked readily by the LC if the Langmuir films orient the LC in a planar orientation relative to the aqueous/LC interface (i.e., an orientation that results in bright optical images, as seen in Figure 3A, when viewed under crossed polarizers). In a past study, we reported that LS transfer of Langmuir films of a polymer similar in several respects to polymer **1** to aqueous-LC interfaces lead to either azimuthally degenerate planar alignment (for films compressed to low surface pressures) or uniform *homeotropic* alignment (for films compressed to higher surface pressures similar to those that lead to planar

alignment in this current study).[27] Although it seems likely that the polymers in the compressed films used in this past study could also possess some degree of in-plane alignment, this alignment was not revealed by visual inspection of optical images of the LC because homeotropic alignment of the LC yielded uniformly dark images when viewed under crossed polarizers.[27]

Summary and Conclusions

We have demonstrated that Langmuir films of polymers transferred to aqueous/LC interfaces induce long-range, uniform azimuthal alignment of the LC. The results of experiments using a novel amphiphilic polymer (polymer **1**) demonstrate that the uniform azimuthal alignment of the LC is the consequence of non-equilibrium, molecular-level organization of polymer chains in the film that is generated (in a preferred direction orthogonal to the direction of compression) during uniaxial compression of the polymer films at the aqueous-air interface. Our results also demonstrate that uniform azimuthal alignment of the LC can be made to extend over distances on the scale of centimeters, and that the polymer relaxes over time. Past studies demonstrating the in-plane alignment of polymer backbones induced by uniaxial compression have generally been restricted to the use of polymers with rigid structures and/or other intrinsic properties that allow characterization of the anisotropic order within the Langmuir films. Two important results of this investigation are therefore (i) the identification of long-range anisotropic order in Langmuir films of a novel flexible polymer, and (ii) that the existence, the degree, and the dynamics of this order can be unmasked and characterized using optical techniques that simply involve the transfer the Langmuir film of polymer to a thin film of a LC. Finally, our results demonstrate the LS transfer of thin films of two other flexible polymers (PMMA and PVS) also resulted in uniform azimuthal alignment of the LC. These results suggest that uniaxial compression may generate long-range order in Langmuir films formed from a broad range of other flexible polymers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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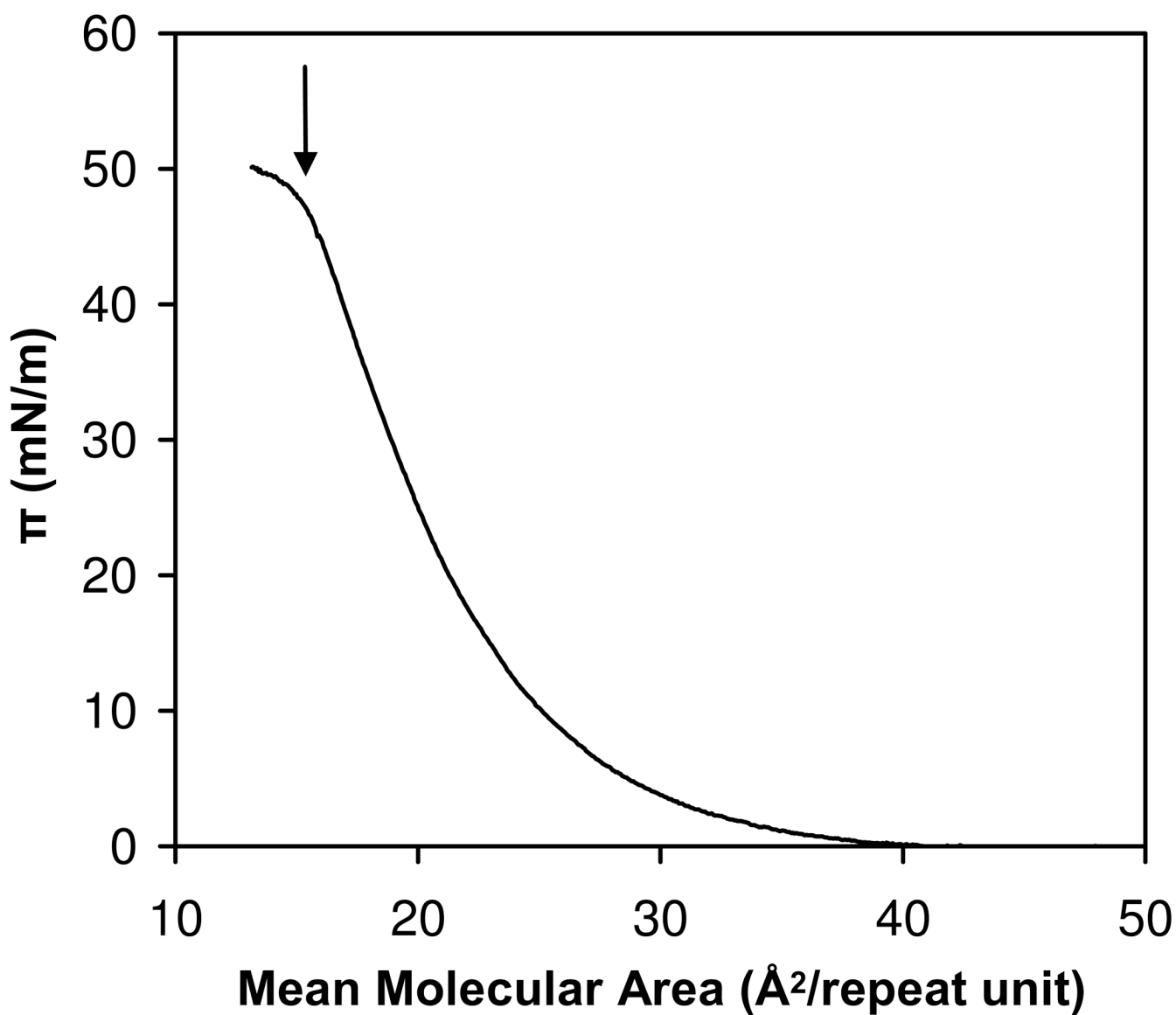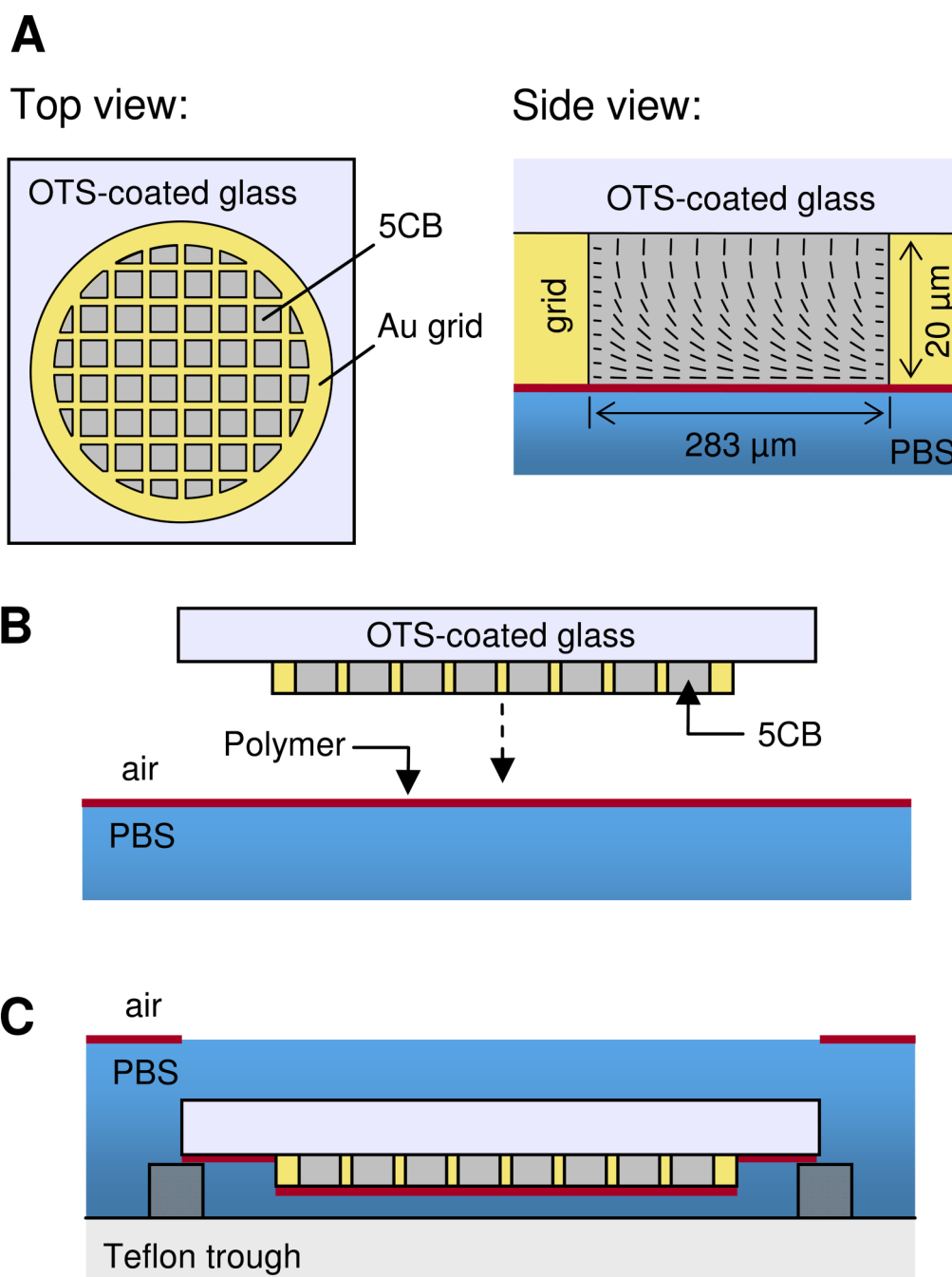58. Wolff U, Greubel W, Kruger H. Mol. Cryst. Liq. Cryst 1973;23:187.

Figure 1.
π-A isotherm of polymer **1** at 25°C spread on a PBS surface and compressed symmetrically between movable barriers. The arrow indicates the surface density at which LS transfer of polymer **1** to the aqueous-5CB interface was performed (see text).

A

Top view:

Side view:

B

C

Figure 2.
A) Schematic illustration of experimental set-up used in this study as viewed from the top and side (not drawn to scale). B) Schematic illustration of the configuration used for Langmuir-Schaefer transfer of polymer **1** (represented by the red bar) from the PBS surface to the aqueous-5CB interfaces B) before and C) after transfer.

C

uniform

F

degenerate

G

H

transmitted light
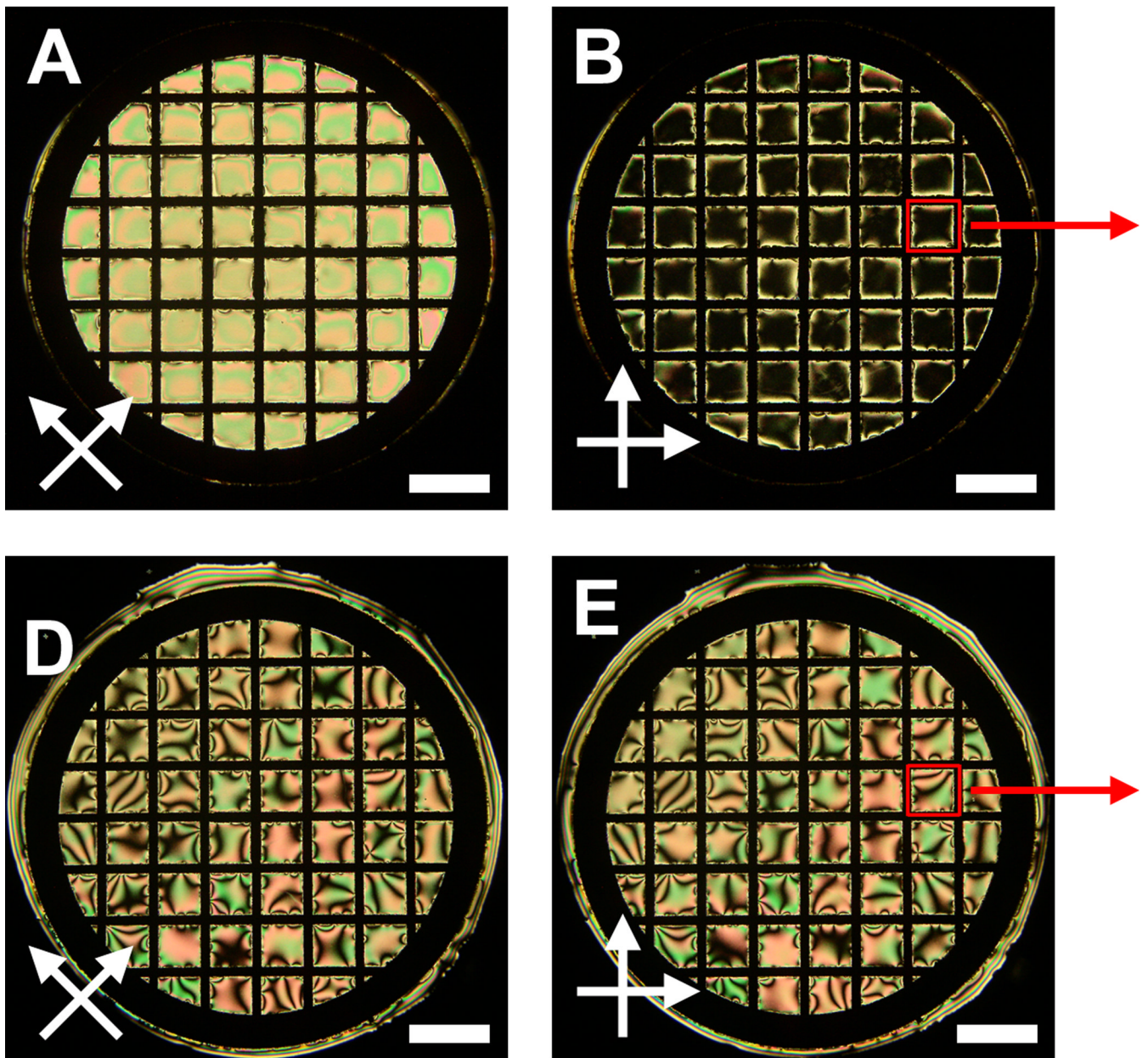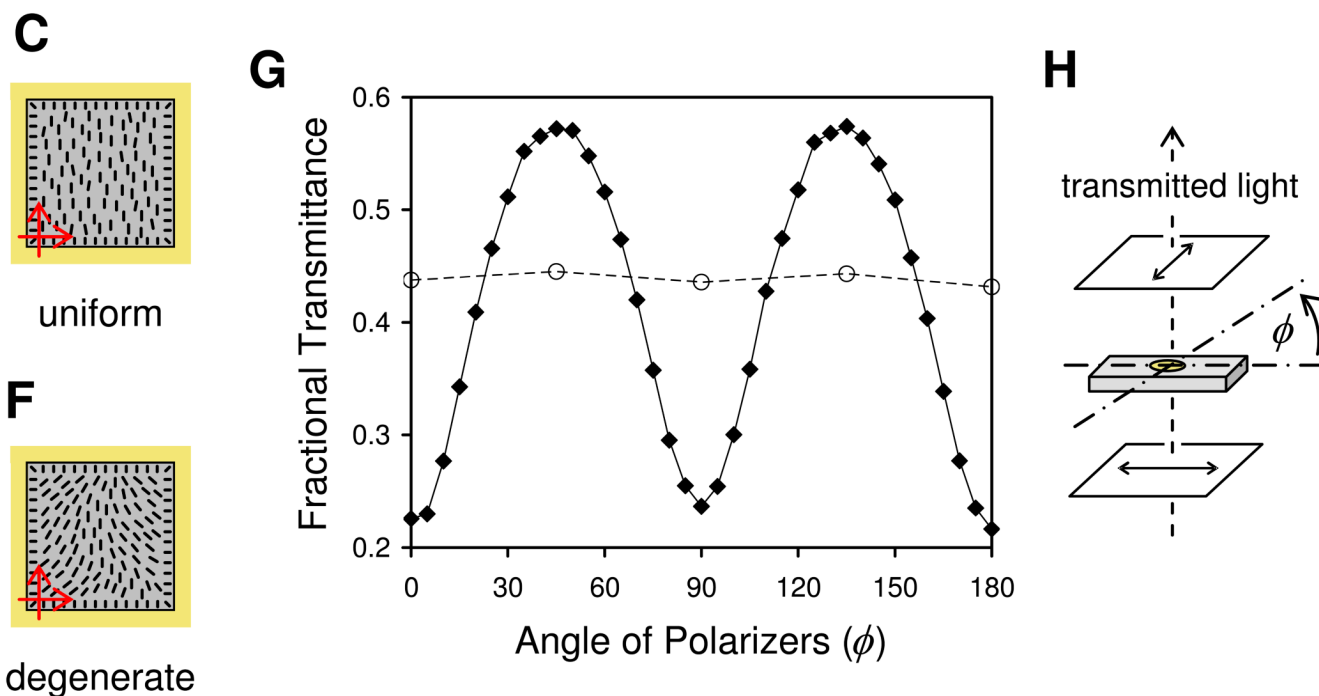
Figure 3.
(A and B) Polarized light micrographs of an aqueous-5CB interface after LS transfer of polymer **1** from the aqueous-air interface. (D and E) Polarized light micrographs of an aqueous-5CB interface after passage through aqueous-air surfaces in the absence of polymer. Micrographs were captured with the crossed polarizers at (A, D) 45° or (B, E) 0° relative to the LC optical cells (indicated by the arrows). Scale bars correspond to 500 µm. Schematic illustrations of example director fields for 5CB as views from above for C) uniform and F) degenerate planar alignment. G) Fractional transmittance of light between crossed polarizers as a function of the angle between the optical cells and polarizer for a 5CB film (♦) laden with polymer **1** and (○) in the absence of polymer. Fractional transmittance is the intensity of light transmitted through the polymer-laden LC interfaces relative to light transmitted through OTS-coated glass under parallel polarizers (See Methods and Materials). Solid and dashed lines are included to guide the eye. H) Schematic representation of the angle (ϕ) between the LC optical cells and crossed polarizers.
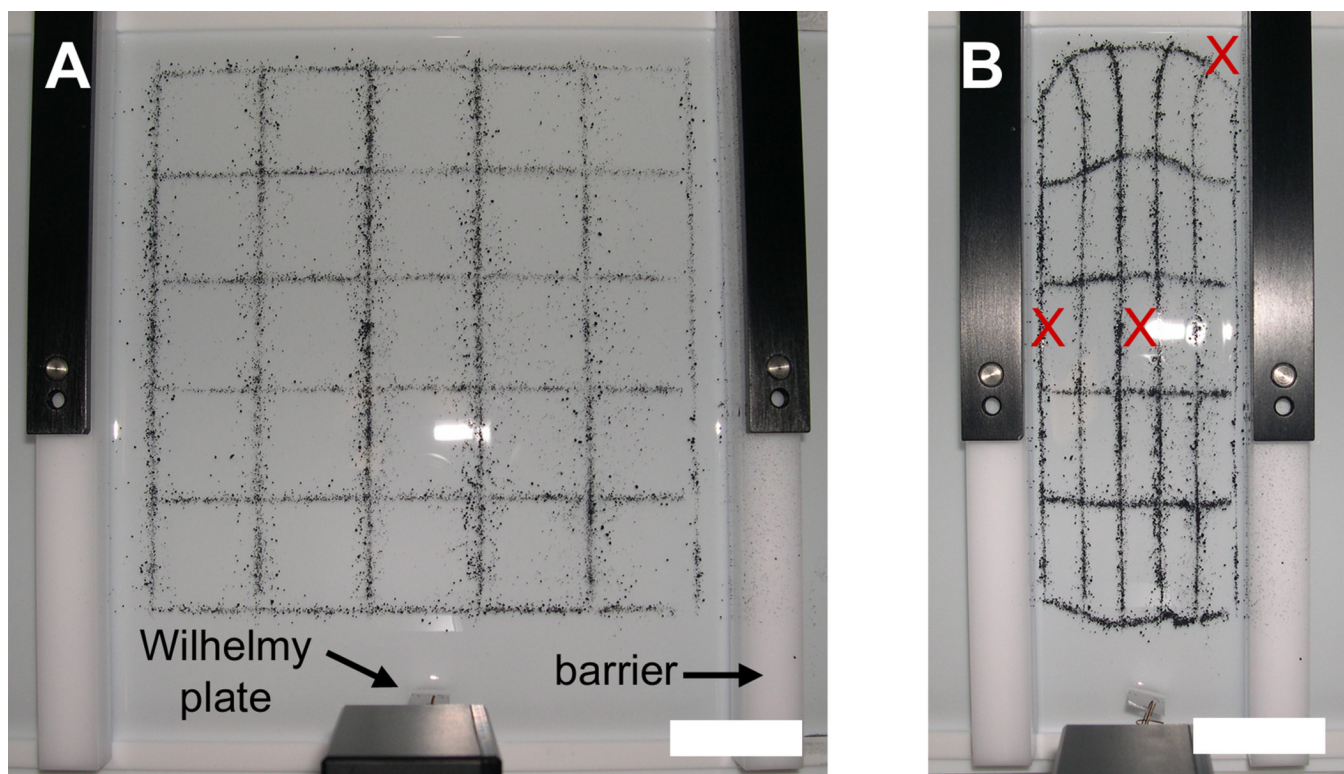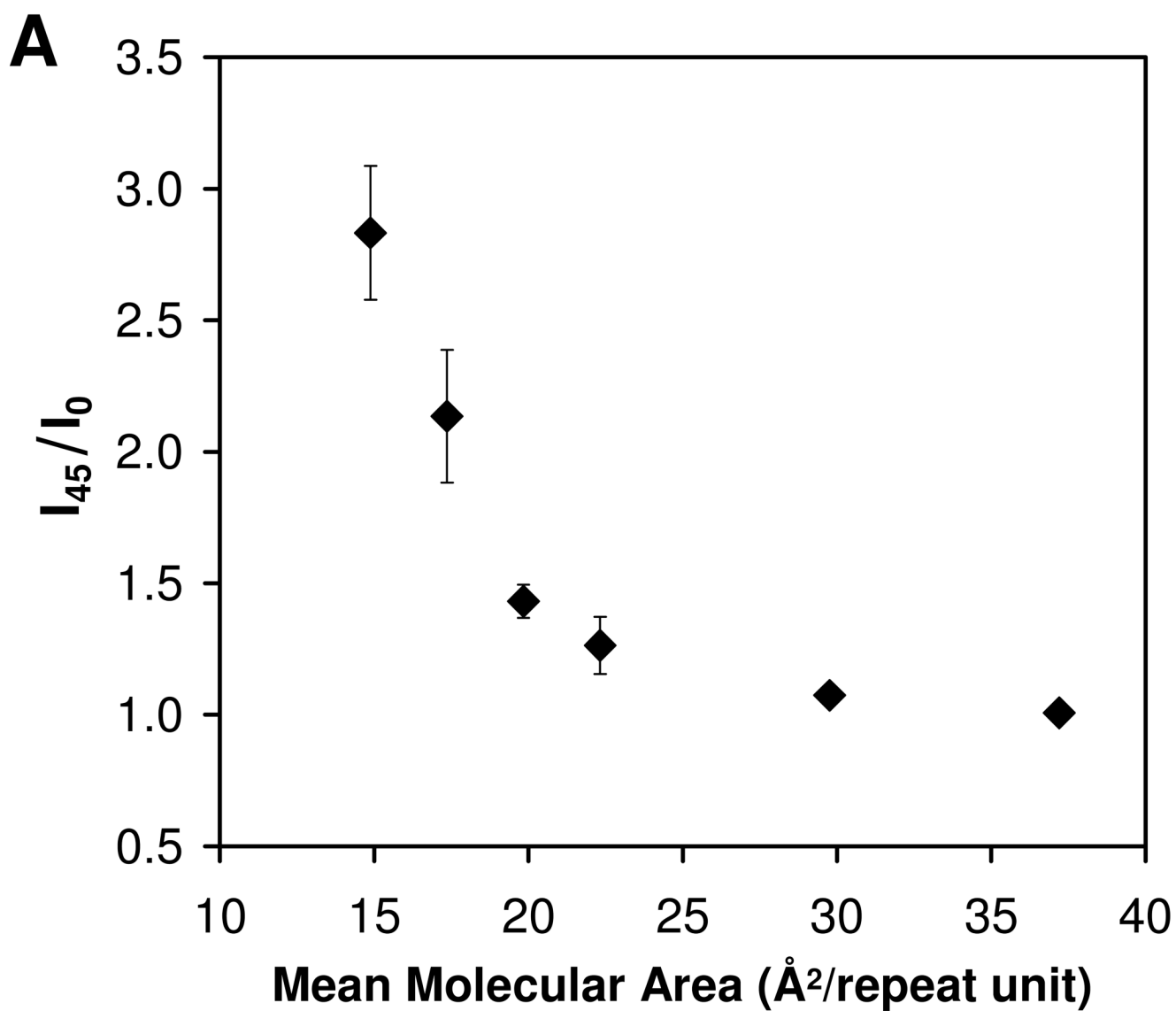
Figure 4.
Images of a Langmuir film of polymer **1** captured from above the Langmuir trough A) before and B) after compression to 15 $Å^2$/repeat unit. The grid of carbon powder was initially applied to the surface of the Langmuir film at 43 $Å^2$/ repeat unit. The red X's in B correspond to approximate locations where LS transfer of polymer 1 to aqueous-5CB interfaces was performed during experiments designed to investigate the influence of transfer location on the alignment of the LC (see text). The bright white spots near the center of the images are an artifact of the imaging method. Scale bars correspond to 3 cm.

A
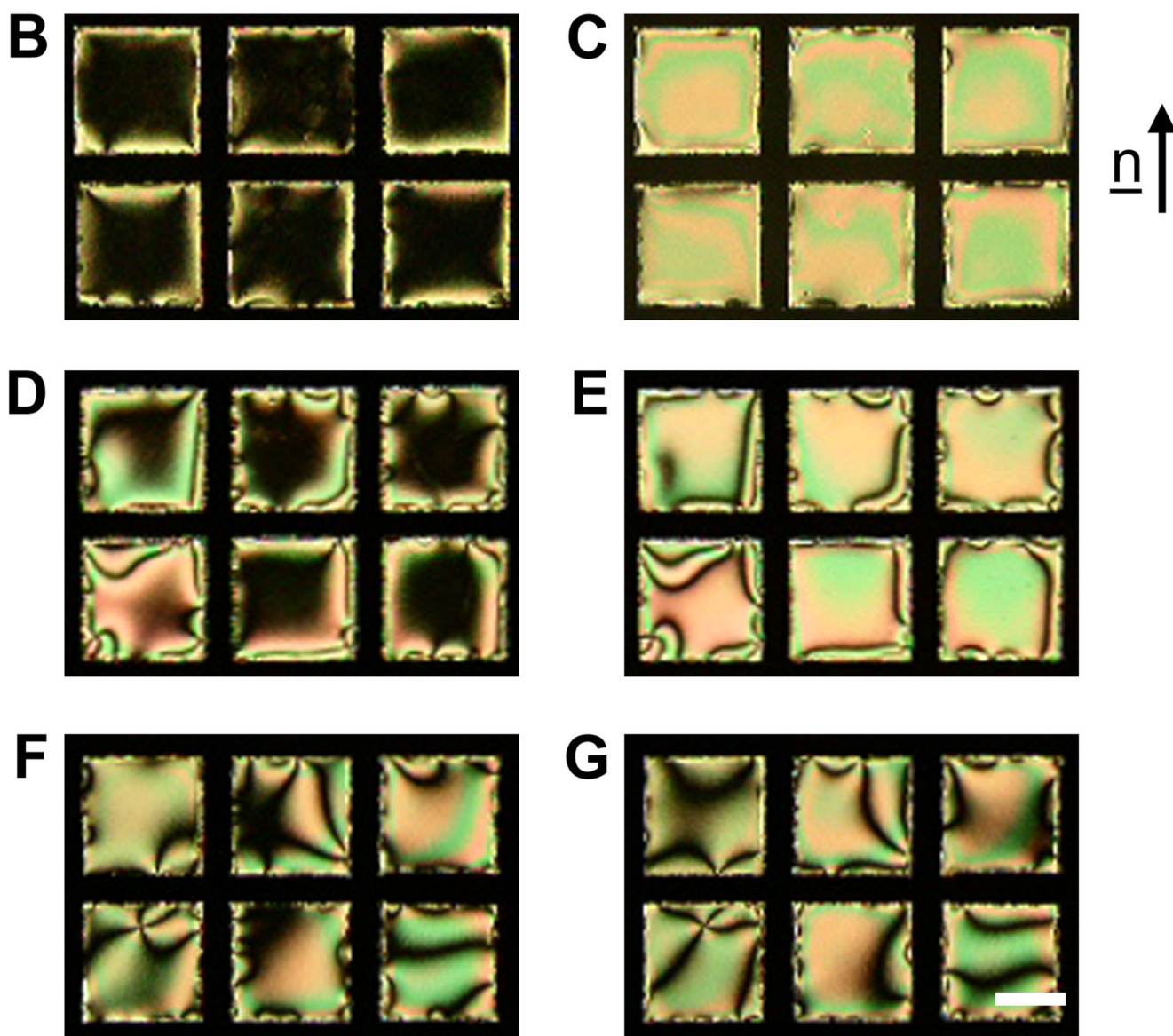
Figure 5.
A) I_{45}/I_0 ratio (see text for description) of transmitted light through 5CB films laden with polymer **1** as a function of the surface density to which the Langmuir films of polymer **1** were compressed prior to LS transfer. Representative polarized light micrographs of aqueous-5CB interfaces after LS transfer of films of polymer **1** at B, C) 15, D, E) 20, and F, G) 30 $Å^2$/repeat unit. The crossed polarizers were positioned for B, D, F) maximum extinction or C, E, G) maximum transmission of polarized light. Scale bar corresponds to 150 µm. The direction of 5CB alignment is indicated by the arrow.
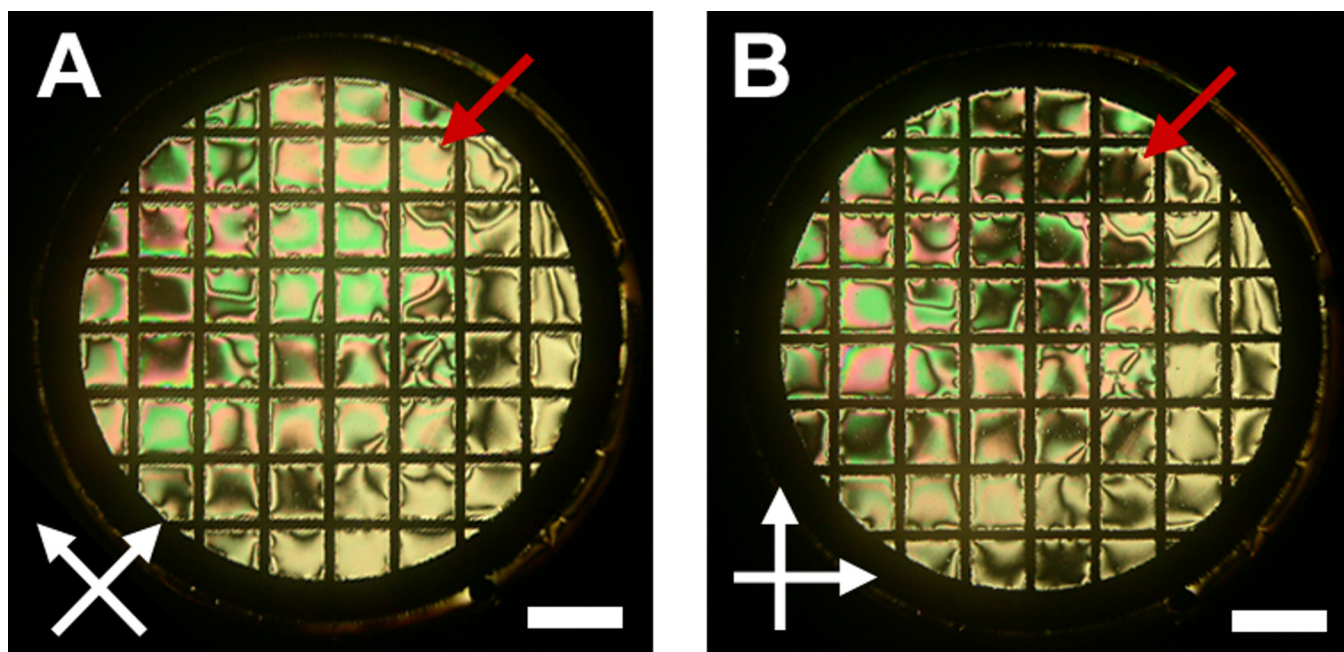
Figure 6.
Polarized light micrographs of an aqueous-5CB interface after LS transfer of polymer **1** spread at the aqueous-air surface at a density of 15 Å^2/repeat unit (i.e., an uncompressed film). The surface density of polymer **1** at the aqueous-air interface was identical to the micrographs in Figure 3A and B although surface pressure was not identical. Images were collected with the crossed polarizers at A) 45° and B) 0° relative to the direction of the barrier movement. Scale bars correspond to 500 µm.
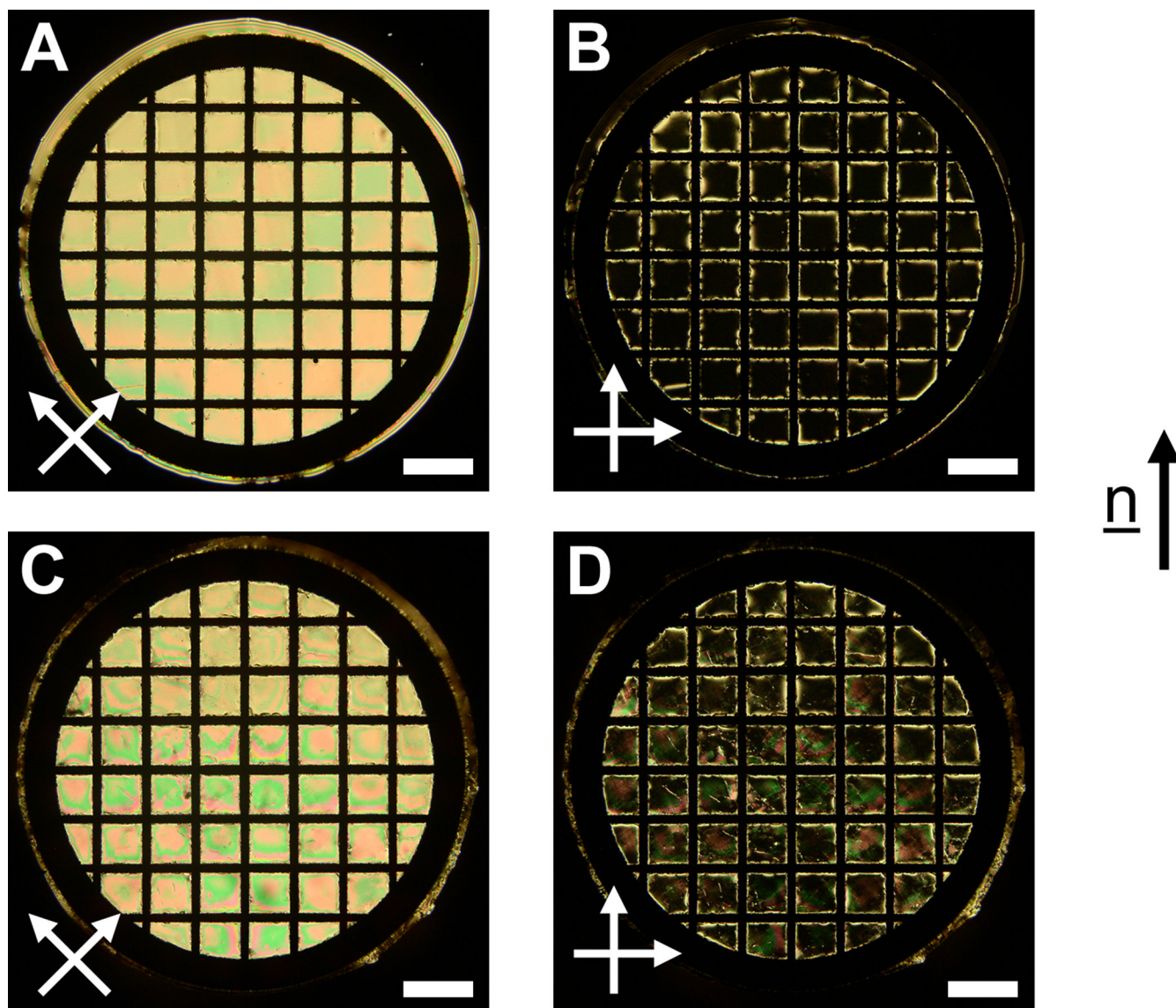
Figure 7.
Polarized light micrographs of aqueous-5CB interfaces laden with thin films of (A and B) PMMA and (C and D) PVS. Micrographs were captured with the crossed polarizers positioned for (A, C) maximum transmittance or (B, D) maximum extinction of polarized light through the 5CB films as indicated by the arrows. Scale bars correspond to 500 µm. The direction of 5CB alignment is indicated by the arrow.
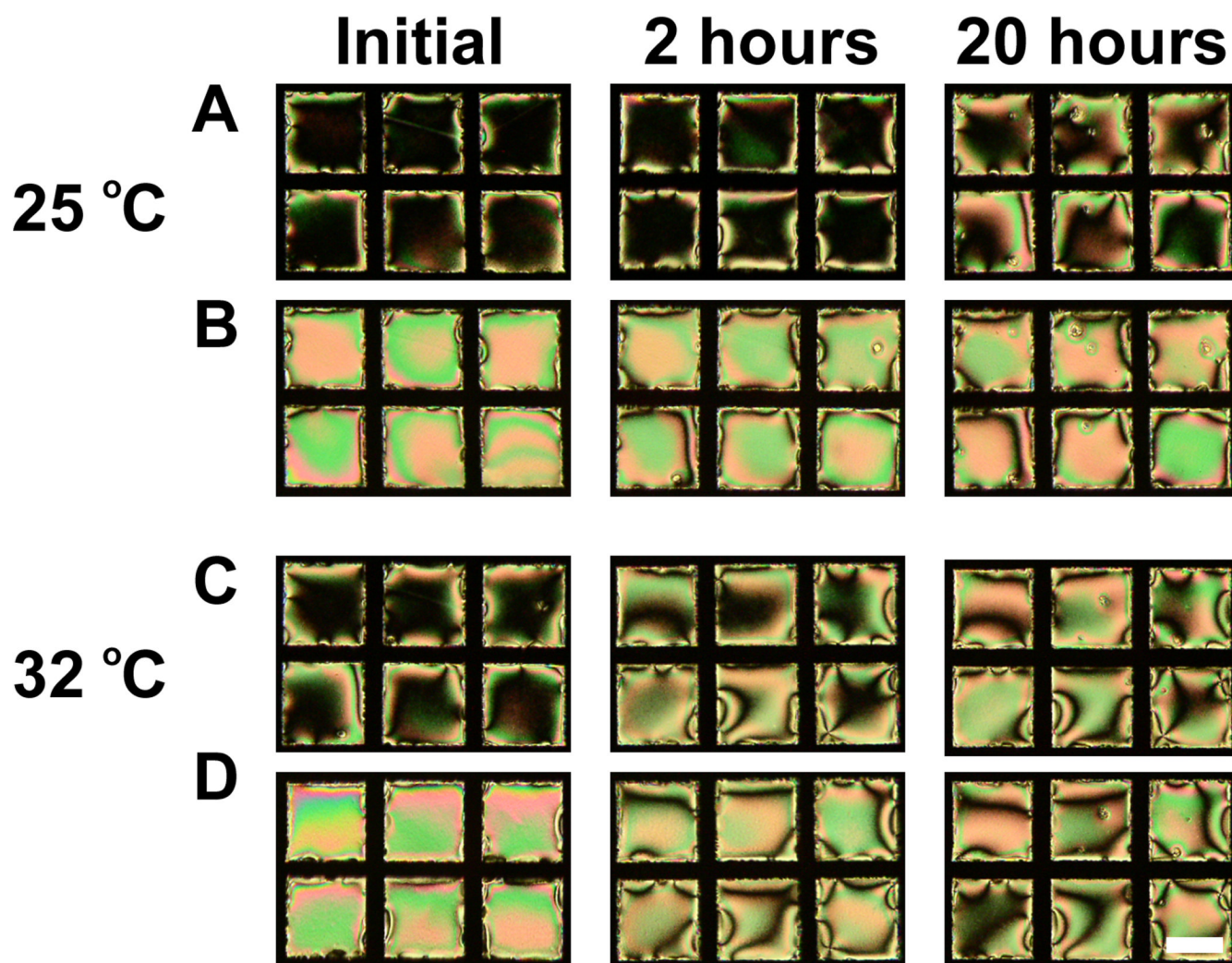
Figure 8.
Representative polarized light micrographs collected over time of polymer **1**-laden 5CB films incubated at (A and B) 25 °C or (C and D) 32 °C. The crossed polarizers were positioned for maximum extinction (A and C) or maximum transmission (B and D). Scale bar corresponds to 200 µm.
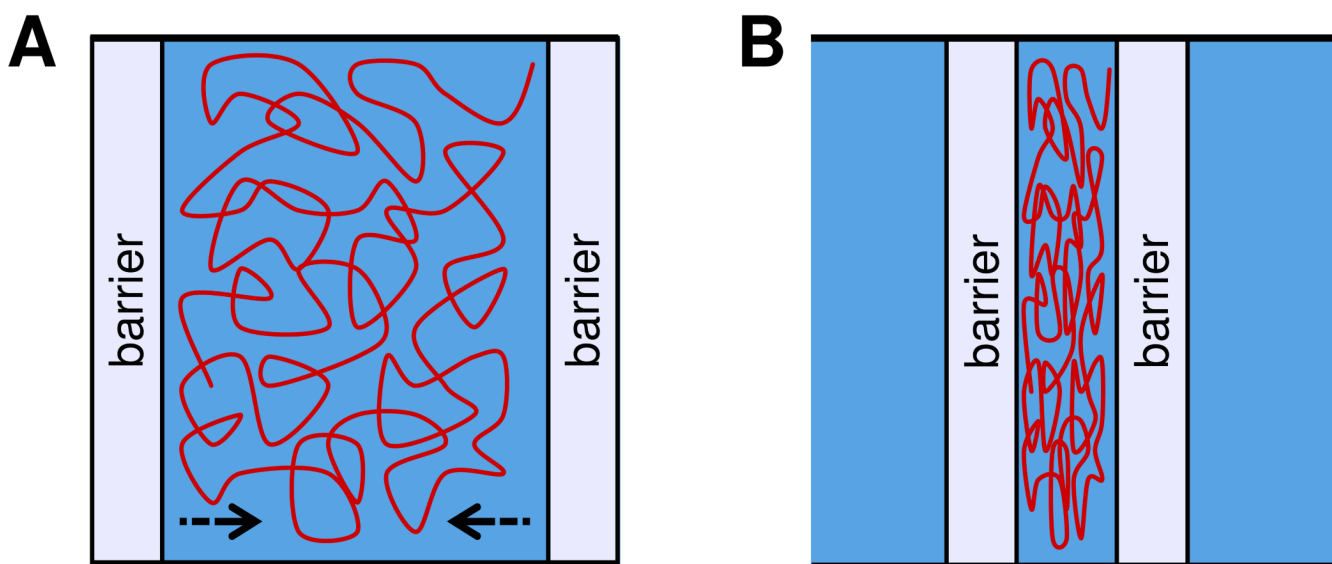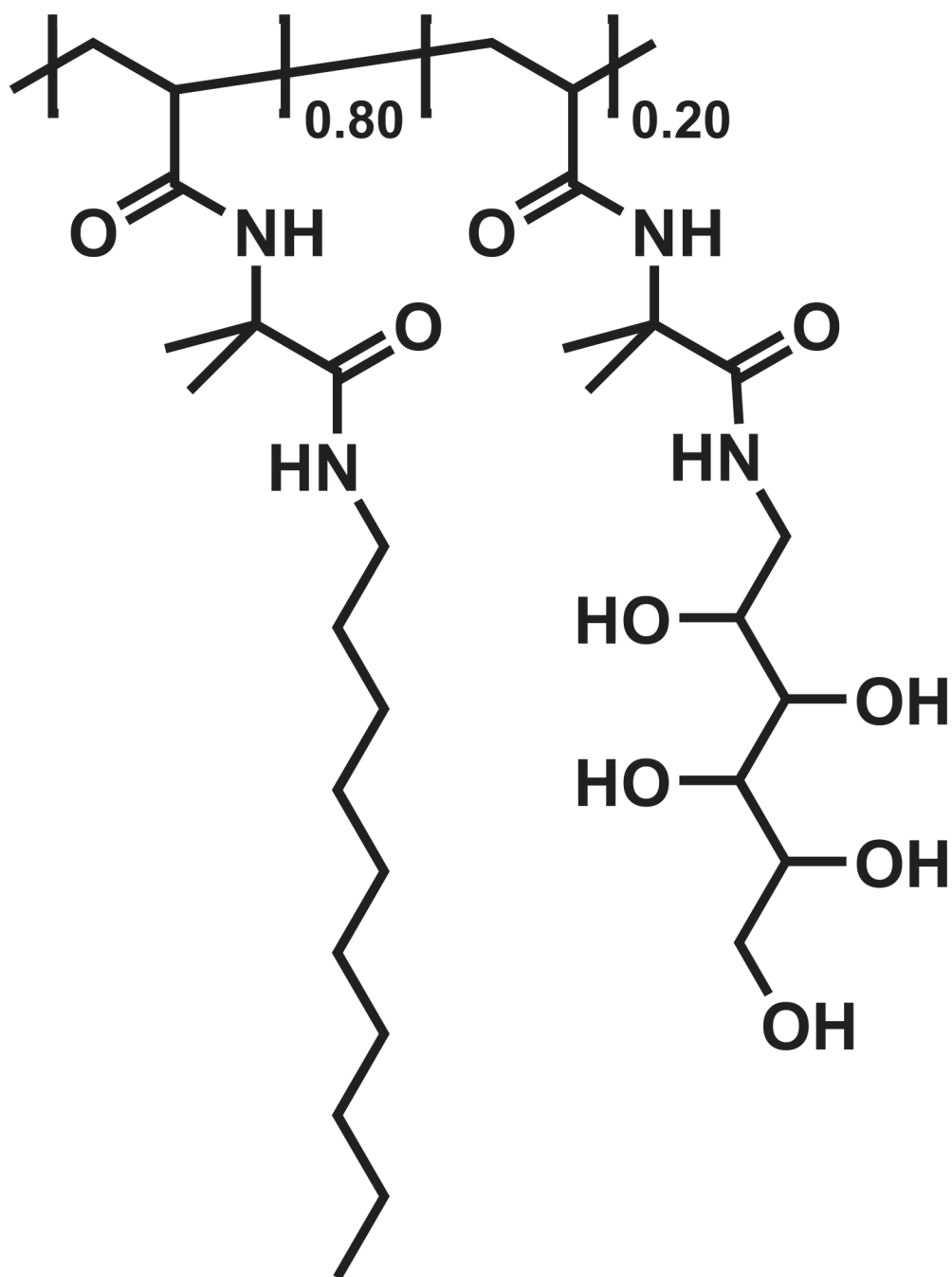
Figure 9.
Schematic illustration (view from above) of the conformation of polymers (red line) at the aqueous-air surface A) as spread and B) after uniaxial compression. The direction of compression is indicated by the arrows. Not drawn to scale.

Structure-Polymer 1.

Table 1

Anisotropy of IR transmission of thin films of PMMA prepared under various conditions.

Surface Density at LS Transfer	Average Difference in Peak Intensity at 1730 cm^{-1}[*]
6.7 Å2/repeat unit	6.0 ± 0.4 %
12.4 Å2/repeat unit	2.2 ± 0.9 %
Dip coat	0.4 ± 0.8 %

[*] Average of three independent samples for each condition.