Langmuir **2000,** *16,* 5227−5230

Self-Assembled Monolayers and Multilayered Stacks of Lyotropic Chromonic Liquid Crystalline Dyes with In-Plane Orientational Order

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Received January 19, 2000. In Final Form: April 14, 2000

A simple method to create large areas of in-plane *oriented* molecular mono- and multilayers is presented. The method is based on layer-by-layer adsorption of polyions and a lyotropic chromonic (nonamphiphilic) liquid crystal, which allows one to orient the molecules uniformly in the plane of deposition. The long-range in-plane orientation of the chromonic molecules determines the unique structural and optical properties of the films. Control of the orientational order allows one to use the films as polarizers, alignment layers, optical compensators, retarders, filters, etc.

Modern technologies of molecular self-assembly use noncovalent association of molecules into aggregates of nanometer size.[1] One of the proven strategies is layer-by-layer deposition of charged species that self-assemble by electrostatic interactions.[2] The technique allows one to assemble polyelectrolytes,[3] dye monolayers,[4] proteins,[5] SiO_2 nanoparticles,[6] etc. The layer thickness is often of the molecular (nanometer) size.[2,7]

One of the challenges of self-assembly techniques is controlling the in-plane orientation of the molecules. In this work, we propose a technique to obtain large-area films of molecular thickness with in-plane alignment. We use a layer-by-layer deposition of polyions and materials that belong to the class of so-called lyotropic chromonic liquid crystals (LCLCs).[8] The molecular structure and macrostructure of LCLC are markedly different from that of conventional lyotropic liquid crystals based on amphiphilic molecules (surfactants); the LCLC molecules are planklike rather than rodlike, rigid rather than flexible, and aromatic rather than aliphatic, Figure 1. The $\pi-\pi$ interaction of the aromatic cores is the main mechanism of molecular face-to-face stacking.[8] Hydrophilic ionic groups at the periphery of the molecules make the material water soluble. For our studies, we selected LCLC molecules with ionic groups at the opposite extremities. The corresponding electrostatic interactions fix the alternating stack of oppositely charged layers of polyions and LCLCs in the vertical direction. In the horizontal plane, stacking of aromatic cores of LCLC molecules provides the desired long-range orientational order.

Our technique is a sequence of the following steps. First, we prepare a liquid crystal composition by dissolving a sufficient amount of a chromonic material in water. Second, we prepare a substrate by covering it with a polyion. The polarity of the polyion is opposite to that of the charged chromonic molecules. Third, we deposit the LCLC on the substrate in a unidirectional manner. The direction can be set by shear during deposition, i.e., either the dye is sheared or the polyion is sheared, or both. Fourth, we reduce the macroscopically thick LCLC layer to a monomolecular film by rinsing off the excess of LCLC with water. The exposed layer of dye molecules is locked by electrostatic interactions with an underlying oppositely charged polyion. More importantly, this layer inherits the in-plane orientational order intrinsic to the liquid crystalline nature of the LCLC deposit. The procedure may be repeated many times until the desired number of alternating polyion and dye layers is produced.

The dye used in this experiment, Violet 20 (V20), is available from Optiva, Inc. In aqueous solutions, the end groups of the dye are negatively charged, Figure 1, as NH_4^+ dissociates in water. An 8% (wt) V20 aqueous solution was prepared such that the resulting LCLC was in the N-phase.[8] We used poly(diallyldimethylammonium chloride) (PDDA) from Aldrich, as a polyion. PDDA becomes positively charged in aqueous solution as Cl^- dissociates in water. Ultrapure water with a specific resistance of better than or equal to 18.1 MΩ cm was used in all cases of rinsing and mixing solutions.

A glass substrate is ultrasonically cleaned in an alkaline bath consisting of 5 g of KOH pellets, dissolved into 30 g of water, and 500 mL of 2-propanol for about an hour. This modifies the glass by etching the surface layer away and exposing a clean negatively charged surface. The substrate is rinsed for 30 s and then placed into a 2 mg/mL aqueous solution of (positively charged) PDDA for 20 min. Once a layer of PDDA is adsorbed, the substrate is rinsed for 30 s to remove excess polymer. We then adsorb the negatively charged LCLC V20. The nematic phase of V20 is sheared onto the substrate using a $^1/_4$-in. wire-wound wet-film applicator rod (no. 3, Paul N. Gardner Co., Inc.). We call the direction in which the rod moves in the plane of the substrate the “shear direction”. After 5 min, the excess of LCLC is rinsed off for 30 s.

To confirm that the dye was in fact adsorbed as a monolayer, the samples were examined with an atomic force microscope (AFM) NanoScope IIIa (Digital Instruments) in tapping mode. Three types of samples were

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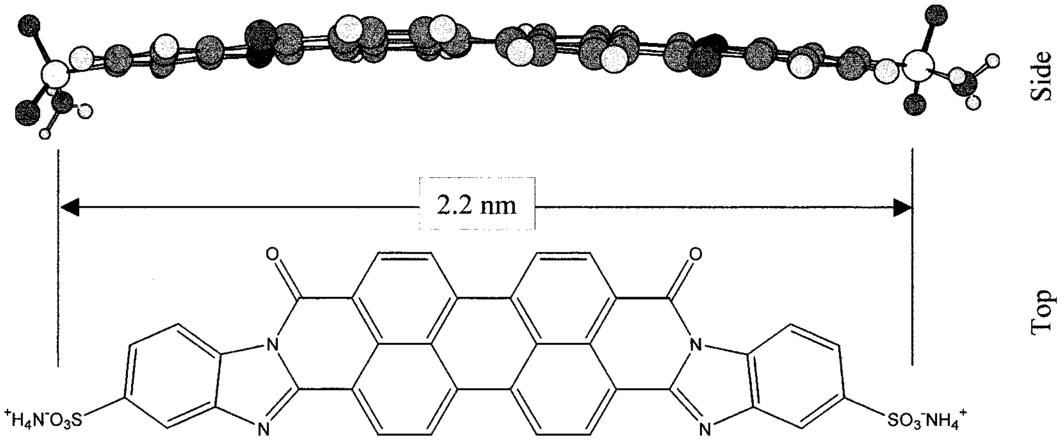

Figure 1. Structure of one of the common isomers of V20.

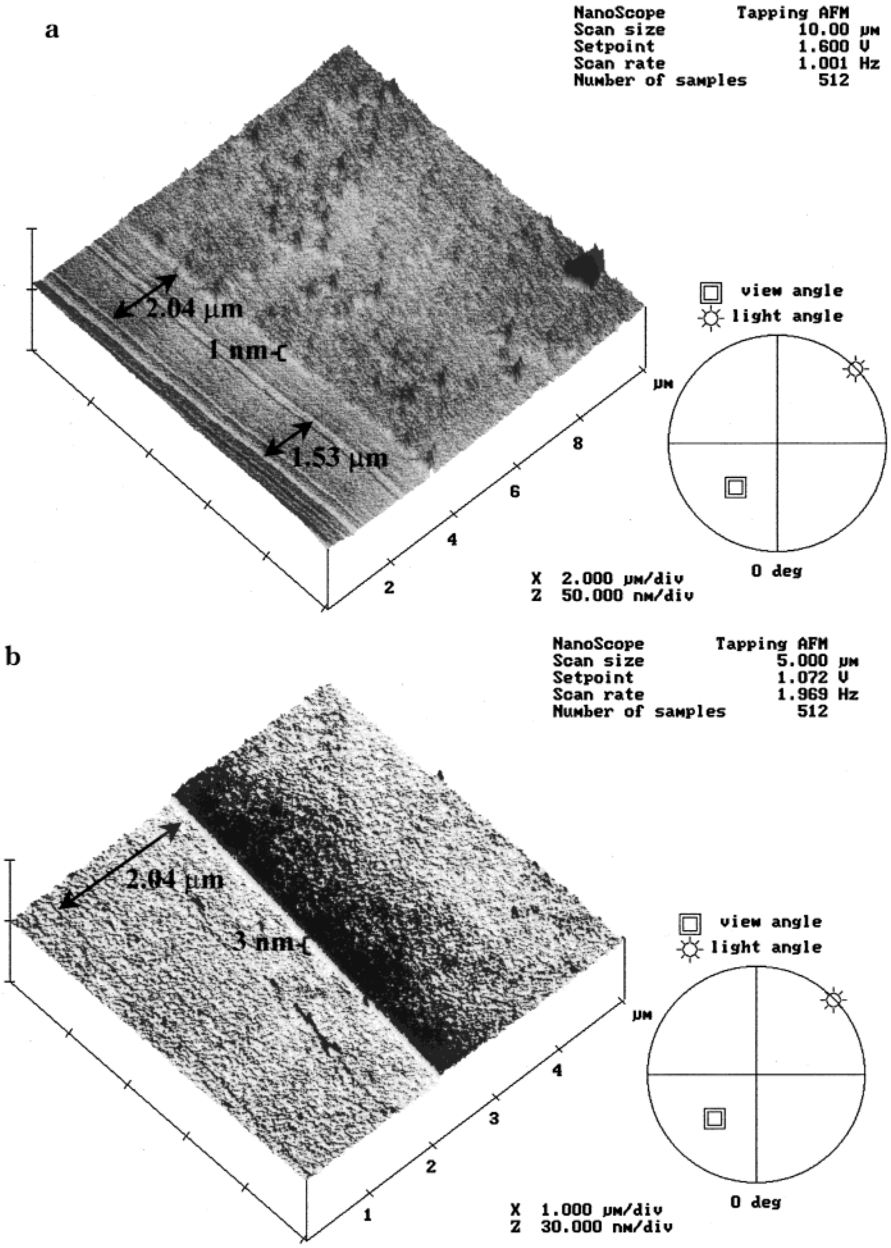

Figure 2. Tapping-mode AFM image of the (a) glass−PDDA sample, note the monolayer on the right ($x > 3.5$) that is ~1 nm high; (b) glass−PDDA−V20 sample, note the total deposit (of PDDA and V20) to the right of the characteristic scratch ($x > 2.5$) is ~3 nm high.

investigated: cleaned plain glass, glass−PDDA (Figure 2a), and glass−PDDA−V20 (Figure 2b). All samples were scratched with the same razor (to help in identification of the layers) and subsequently rinsed with deionized

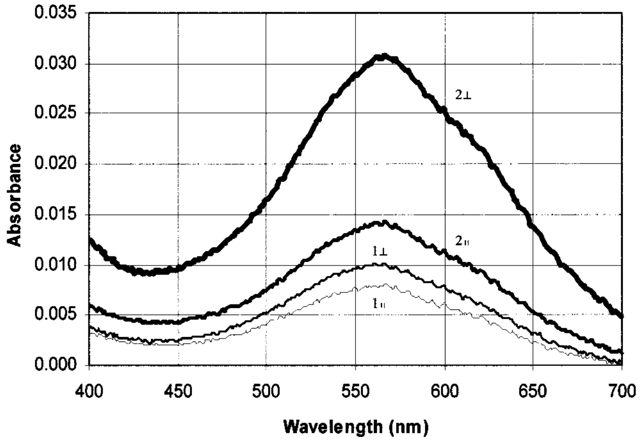

Figure 3. Anisotropy in the absorbance of light polarized parallel and perpendicular to the shearing direction of the dye indicating orientation within the dye monolayers. The number in the captions to the curves is the number of dye monolayers. The symbols ∥ and ⊥ indicate whether the light polarization is along or perpendicular to the shear direction.

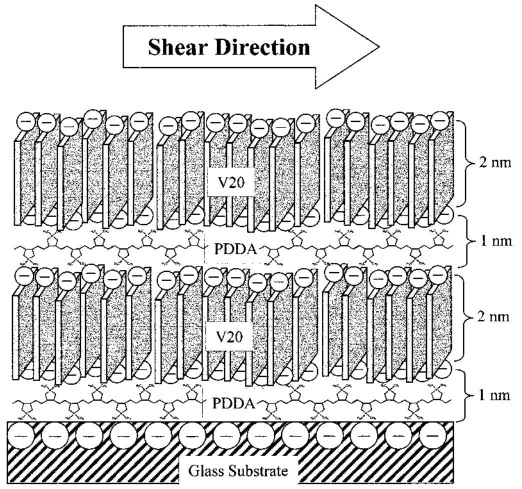

Figure 4. Plausible geometry of the assembled polyion−dye multilayered structure.

water. The razor leaves two characteristic scratches 1.53 μm apart where the distance from the leftmost scratch to the unscratched film is 2.04 μm, Figure 2. The thickness of the PDDA layer, as measured by the AFM in Figure 2a, is about 1 nm, which coincides with the reported results of independent studies.[9] The measured total PDDA−V20 layer thickness in Figure 2b is about 3 nm. This implies

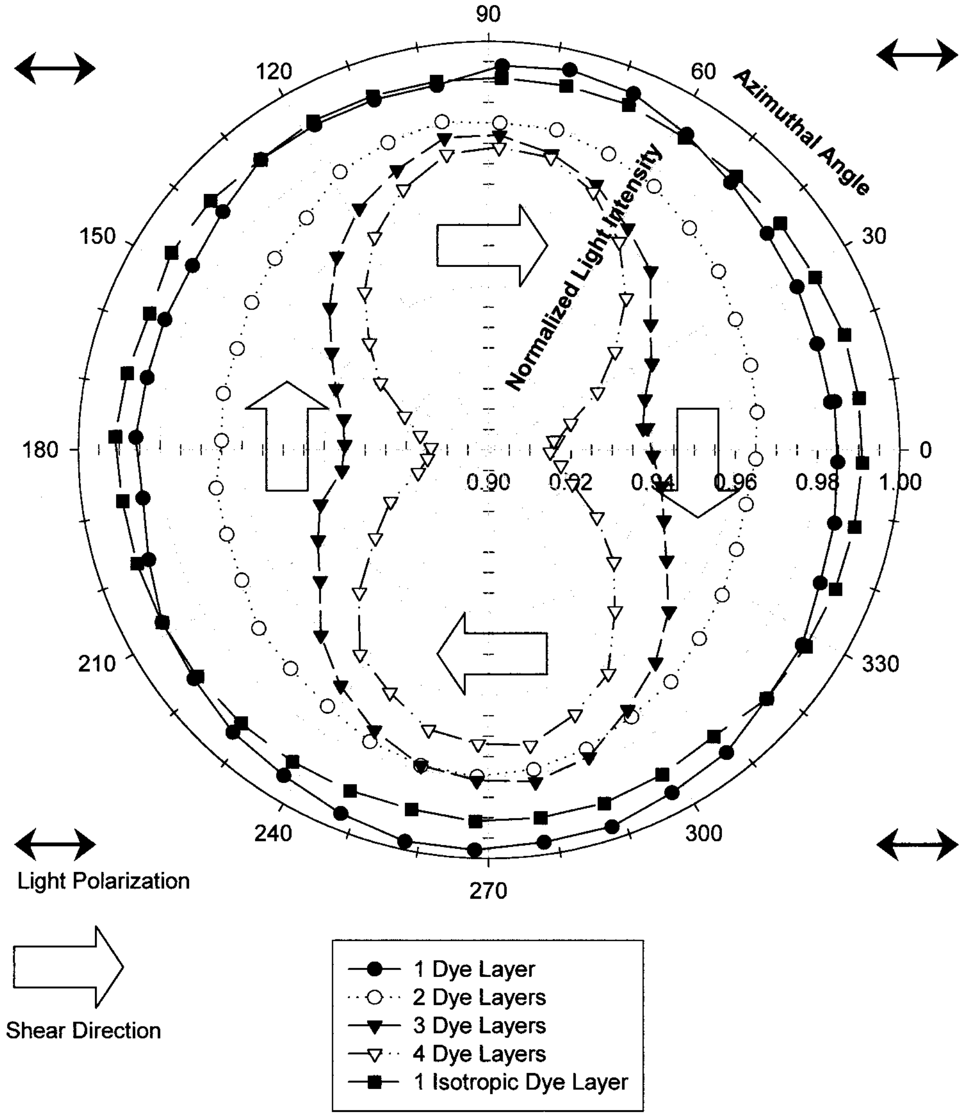

Figure 5. Intensity of polarized light transmitted by multilayer stacks of increasing thickness as the sample is rotated with respect to the polarization of the incident light: normal incidence; wavelength 567 nm that corresponds to the maximum of absorbance.

that the thickness of the V20 layer is about 2 nm, which agrees with the estimate of the molecular model in Figure 1: the distance between two charged extremities of V20 molecules is approximately 2 nm.

To prove the in-plane alignment of the dye monolayers, we performed spectroscopic measurements (Perkin-Elmer Lambda 18 spectrometer) with the incident light linearly polarized parallel and perpendicular to the shear direction, Figure 3. Light absorption is strongest for the polarization perpendicular to the shear direction. Since the absorption axes are in the plane of the molecular core, the result suggests that, on average, the long axes of the planklike molecules are perpendicular to the shear direction, Figure 4. The whole structure of the dye monolayer is thus biaxial: the electrostatic interactions of charged extremities of the dye molecules control the vertical order, while the face-to-face stacking of aromatic planklike cores controls the in-plane order. The in-plane order should manifest itself in the dependence of light adsorption on the in-plane (azimuthal) angle between the polarization of normally incident light and, say, the shear direction. This is exactly what is observed in Figure 5, which correlates with the results in Figure 3. The symmetry of the pattern corresponds to a uniaxial in-plane orientational order.

Our experiments show that the liquid crystalline state of the dye is crucial for the in-plane order of the films. If one uses an isotropic solution (less than 5% of dye), no anisotropy in the absorption of light is observed (see Figure 5). Furthermore, when the solution is in the liquid crystalline phase, it can be oriented even without shearing during the deposition: one can simply prealign the polyion layer by shear and then coat it with the LCLC solutions by dipping.

To conclude, we have developed a simple technique of *in-plane* orientation of *mono*- and *multilayers* of anisometric molecules by using alternate adsorption of polyions and lyotropic chromonic liquid crystals. The liquid crystalline order is responsible for the in-plane orientation of the resulting monolayers. The stability of monolayers after rinsing off the excess material is assured by electrostatic interactions with the underlying polyionic substrate. Note that not only dyes but potentially many other organic materials can be oriented by the described technique: it suffices to supplement the corresponding molecules with zwitterionic groups to make them soluble in water and capable of mesomorphism. Using this technique, one can create films with a variety of useful properties, for example, polarizers,[10] alignment layers, optical compensators, retarders, filters, etc.

Acknowledgment. This work was supported by the National Science Foundation Science and Technology Center for Advanced Liquid Crystalline Optical Materials (ALCOM) under Contract DMR 89-20147 and partially by grants from the 3M Company, No. GI01343, and the Ohio Board of Regents Research Challenge Fund. We thank L. C. Chien, J. Kelly, P. Lazarev, Y. Lvov, and S. V. Shiyanovskii for fruitful discussions, J. C. Lee, Y. Nastishyn, and T. Sergan for experimental help, and T. Gardner for providing us with the chemical structures.

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