In-Plane Photoalignment of Liquid Crystals by Azobenzene-Polyelectrolyte Layer-by-Layer **Ultrathin Films**

Mi-Kyoung Park and Rigoberto C. Advincula*

Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294-1240

> Received December 31, 2001. In Final Form: March 19, 2002

Introduction

Photochromic moiety in polymers is very attractive due to the possibility of creating new light-sensitive materials and optical devices.^{1,2} Ultrathin films containing photoisomerizable moeities, e.g., azobenzene dyes, are excellent materials for holographic storage applications,^{3,4} photopatterning,⁵ and the photoalignment of liquid crystal (LC) molecules.^{6–13} Homeotropic or homogeneous photoalignment in LC systems involves reorientation of LC molecules as controlled by photoirradiation, i.e., resulting from the photogeneration of optical anisotropy of photochromic layers or films.⁶ Ichimura et al. have referred to these photochromic layers as "command surfaces", since a monolayer of azobenzene units on a substrate has been proven sufficient to regulate the long-range orientation of neighboring molecules up to 1×10^4 amplification.^{7,8}

In-plane homogeneous photoalignment of LC molecules has been observed with azobenzene-modified command surfaces using linearly polarized light.^{9–12} When linearly polarized UV light is used to irradiate a hybrid LC cell, the azimuthal or in-plane alignment of LCs becomes perpendicular to the electric vector of the linearly polarized light. The mechanism for azobenezene molecules has been previously reported to involve reorientation of the rodlike E-isomer photostationary states, acting as a "molecular rotor" for the LC molecules.⁹⁻¹² Furthermore, the alignment direction can be altered reversibly by rotating the electric vector of the light.¹³

There have been a variety of approaches toward the fabrication of azobenzene command surfaces, e.g., via spin coating of azo polymers,¹⁴ Langmuir-Blodgett (LB) tech-

- (1) Rochon, P.; Bissonnette, D.; Natansohn, A.; Xie, S. Appl. Opt. 1993, 32, 7277
 - (2) Natansohn, A.; Rochon, P. Adv. Mater. 1999, 11, 1387.
- (3) Andruzzi, L.; Altomare, A.; Ciardelli, F.; Solaro, R.; Hvilsted, S.; Ramanujam, P. S. Macromolecules 1999, 32, 448.
- (4) Wu, Y.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Zhang, Q. Polymer 1999, 40, 4787
- (5) Schonhoff, M.; Chi, L. F.; Fuchs, H.; Losche, M. Langmuir 1995, 11, 163.
- (6) Ichimura, K. Chem. Rev. 2000, 100, 1847.
- (7) Ichimura, K.; Suzuki, Y.; Seki, T.; Hosoki, A.; Aoki, K. Langmuir **1988**, *4*, 1214.
- (8) Seki, T.; Sukuragi, M.; Kawanishi, Y.; Suzuki, Y.; Tamaki, T.;
 Fukuda, R.; Ichimura, K. *Langmuir* **1993**, *9*, 211.
 (9) Ichimura, K.; Hayashi, Y.; Ishizuku, N. *Chem. Lett.* **1992**, 1063.
 (10) Ichimura, K.; Akiyama, H.; Kudo, K.; Ishizuki, N.; Yamamura,
- (10) Ichimura, K., Akiyama, H., Kudo, K., Ishizuki, N., Fahahihura, S. *Liq. Cryst.* **1996**, *20*, 423.
 (11) Ichimura, K.; Hayashi, Y.; Akiyama, H.; Ikeda, T.; Ishizuki, N. *Appl. Phys. Lett.* **1993**, *63*, 449.
 (12) Ichimura, K.; Hayashi, Y.; Akiyama, H.; Ishizuki, N. *Langmuir*
- 1993. 9. 3298.

(13) Ichimura, K. *Supramol. Sci.* **1996**, *3*, 67. (14) Ichimura, K.; Suzuki, Y.; Seki, T.; Kawanishi, Y.; Aoki, K. Makromol. Chem., Rapid Commun. 1989, 10, 5.

niques,¹⁵ and self-assembled monolayers (SAMs).^{11,12,16} Recently, several groups including ours have reported the fabrication of ultrathin molecular films by alternate electrostatic absorption of polyelectrolytes and low-molecular-weight azobenzene dyes.17 The fabrication of ultrathin molecular films by alternate electrostatic adsorption or layer-by-layer (LBL) deposition of oppositely charged polyelectrolytes from aqueous solutions has been reported by Decher et al. since the early 1990s.^{18,19} This multilayer film formation is simple and versatile, and applies to a broad range of charged species (e.g., polyelectrolytes, nanoparticles, proteins). The distinct advantages of this film preparation method have yet to be realized compared to LB and spin casting in terms of applications.

In an effort to prepare photochromic azobenzene polymer ultrathin films using the LBL approach, we investigated the combination of poly{1-[4-(3-carboxy-4hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium solt} (PAZO) with the polycation poly(diallyldimethylammonium chloride) (PDADMAC) at various layer thicknesses. Previous investigations showed the preparation of well-defined multilayers of PAZO/PDADMAC, capable of forming various thicknesses, layer ordering, and photoisomerization.²⁰ To investigate azimuthal photoalignment in LC molecules, we utilized polarized visible light to induce photoorientation of these ultrathin films in a hybrid LC cell configuration. While a large number of these studies have been reported with Langmuir monolayers, LB films, and SAMs, to the best of our knowledge our work reports one of the first details on the use of LBL polyelectrolyte films for azimuthal in-plane photoalignment.²¹ The results reveal interesting orientational properties unique to LBL films with read/write capabilities and stability that is thickness dependent. This is significant in that a number of parameters available for the LBL deposition can be used to optimize new optical and data storage thin film materials, which are not available for other ultrathin film preparation methods.⁶

Experimental Section

Materials. The polyanion PAZO and polycation PDADMAC (MW 100 000-200 000) were purchased from Aldrich and used without further purification. The nematic (N-35 °C-I) 5CB LC molecules (4-pentyl-4'-cyanobiphenyl) were purchased from Roche. The molecular structures for PDADMAC and PAZO are shown in Figure 1. Aqueous solutions (Milli-Q water with 18.2

- (18) Decher, G.; Hong, J. Makromol. Chem., Macromol. Symp. 1991, 46.321
- (19) Decher, G. Science 1997, 277, 1232.

(20) Dante, S.; Advincula, R.; Frank, C.; Stroeve, P. Langmuir 1999, 15. 193.

(21) (a) Advincula, R.; Baba, A.; Kaneko, F. *MRS Proceedings, Spring* 1999 Meeting—Liquid Crystal Materials and devices, Bunning, T., Chen, S., Chien, L., et al., Eds.; 1999; Vol. 559, pp 195–200. (b) Baba, A.; Kaneko, F.; Shinbo, K.; Kato, K.; Kobayashi, S.; Advincula, R. *Mol. Cryst. Liq. Cryst.* **2000**, *347*, 259.

10.1021/la015771a CCC: \$22.00 © 2002 American Chemical Society Published on Web 05/02/2002

^{*} Corresponding author. Telephone: (205) 934-8286. Fax: (205) 934-2543. E-mail: gobet@uab.edu.

^{(15) (}a) Katayama, N.; Ozaki, Y.; Seki, T.; Tamaki, T.; Iriyama, K. Langmuir 1994, 10, 1898. (b) Seki, T.; Sakuragi, M.; Kawanishi, Y.; Suzuki, Y.; Tamaki, T.; Fukuda, R.; Ichimura, K. Langmuir 1993, 9, 211.

⁽¹⁶⁾ Evans, S.; Johnson, S.; Ringsdorf, H.; Williams, L.; Wolf, H. Langmuir 1998, 14, 6436.

^{(17) (}a) Ariga, K.; Lvov, Y.; Kunitake, T. J. Am. Chem. Soc. 1997, *19*, 2224. (b) Cooper, T.; Campbell, A.; Crane, R. *Langmuir* **1995**, *11*, 2713. (c) Yoo, D.; Wu, A.; Lee, J.; Rubner, M. *Synth. Met.* **1997**, *85*, 1425. (d) Advincula, R.; Fells, E.; Park, M. K. Chem. Mater. 2001, 13, 2870. (e) Advincula, R. In Handbook of Polyelectrolytes and their Applications; Tripathy, S. K., Kumar, J., Nalwa, H. S., Eds.; American Scientific Publishers: in press.



Figure 1. Chemical structure of poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt} (PAZO) and poly(diallyldimethylammonium chloride) (PDADMAC). UV-vis absorbance of PDADMAC/PAZO films as a function of increasing number of bilayers (10-100 bilayers). The inset shows the increase of absorbances at 373 nm with the number of bilayers.

 $M\Omega$ resistivity) of the polymers, with a concentration of 1 mg/ mL, were freshly prepared for each experiment at pH 5.7. A self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APS; from Aldrich) was used to form a uniformly charged substrate in Si wafer and glass. All solvents were spectroscopic grade and obtained from Fisher Scientific.

Film Fabrication. Si wafers or glass slides were immersed in piranha solution ($v/v = 1:3.30\% H_2O_2/98\% H_2SO_4$) for 1 h and carefully washed with deionized water and dried. SAM treatment with APS (sonicating procedure in 0.001 M toluene) was done followed by 0.1 M HCl solution to render a positively charged surface. The substrates were then alternately immersed in aqueous solutions of PAZO and PDADMAC for 15 min each, with water rinsing between each deposition.¹⁹ The last deposition is always done with PAZO (outermost layer). The procedure was automatically carried out using an HMS Series Programmable Slide Stainer apparatus (Carl Zeiss, Inc).

Cell Fabrication. A hybird LC cell was fabricated with the dye/polymer deposited substrate and a glass substrate modified with a monolayer of stearic acid deposited by the LB technique.^{7,8} This was done by sandwiching the nematic LC (5CB) material between the modified substrates and separation by a Mylar spacer (16 μ m). A homeotropic alignment was induced with this initial arrangement from the stearic acid side of the cell (Figure 2).

Instrumentation and Measurements. UV–visible absorption spectra were obtained using a Perkin-Elmer Lambda 20 spectrophotometer. The ellipsometric measurements were carried out with a Microphotonics SE400 ellipsometer (632.8 nm, 70° angle of incidence). The LC cell was illuminated with a 150 W Xe lamp with color filter (<430 nm) and a sheet polarizer. The irradiation intensity based on the distance, area, and intensity of the lamp was calculated at 185 mW/cm² on the sample.

The transmittance through the LC cell was monitored by following the intensity of the transmitted He–Ne laser beam through the hybrid LC cell (rotated) and a mounted polarizer/



Hybrid LC cell structure

Figure 2. Experimental setup for measurement of the photoinduced birefringence of the cell. Hybrid LC cell structure and actinic light exposure conditions at defined angles. (The cell axis is defined as the direction of the longer sides of the rectangular cell, and the polarization plane angle (θ) contained by the cell axis and the polarization plane of actinic light.)

analyzer, i.e., as a function of the rotation angle. This is essentially a crossed-polarizer experiment where the polarizer properties of the hybrid LC cell can be quantified. The experimental setup and interpretation have been previously reported^{7,8} as illustrated in Figure 2 (see Supporting Information).²²

Results and Discussion

Layer-by-Layer Deposition (LBL). The layer-bylayer deposition of the polyelectrolyte pair layers were investigated by UV-vis absorption spectroscopic and ellipsometric measurements. In general, a linear trend in thickness increase with sequential deposition of polyelectrolytes was observed consistent with previous results.²⁰ The average thickness is 2.4 nm/bilayer for PDADMAC/PAZO at a concentration of 1 mg/mL (see Supporting Information). Figure 1 shows the UV-vis absorption spectra of PDADMAC/PAZO films on glass slides with increasing number of bilayers. The absorbance at 373 nm of PDADMAC/PAZO bilayer (Figure 1 inset) increases in proportion to the number of bilayers, indicating regular growth of the PDADMAC/PAZO layers. The maximum absorbance, λ_{max} , at ~373 nm is due to the $\pi - \pi^*$ transition of the trans-azobenzene isomer. The small shoulder at \sim 460 nm is assigned to the n- π^* transition. Aqueous solutions of PAZO have $\lambda_{max} = 366$ nm indicating a red shift with respect to the film. This suggests that the PAZO azobenzene dyes are J-aggregated, consistent with previously reported results.²⁰ Thus these results indicate the formation of uniform PAZO/PDADMAC ultrathin films suitable for our photoalignment studies.

In-plane Photoalignment. The photoisomerization behavior and kinetics of these films have been previously reported.²⁰ The kinetics of the photoalignment process for the PAZO/PDADMAC films is reported in the Supporting

⁽²²⁾ The $\theta = 0$ axis is defined by the direction of the longer side of the 25 mm \times 75 mm cell, where θ is the polarized irradiation angle of the actinic light as illustrated in Figure 2. The polarization birefringence was then monitored by following the intensity of transmitted linearly polarized He–Ne laser beam though the cell and the polarizer (analyzer). The cell is then rotated with respect to the fixed analyzer as a function of the rotation angle (ϕ). The transmission behavior is then plotted as a function of the rotation angle (ϕ) and the transmission intensity.



Figure 3. Radial plot showing angular (ϕ) dependence of transmittance of monitoring He–Ne laser beam through the cell upon exposure to linearly polarized light (>430 nm) with $\theta = 0^{\circ}$ as a function of exposure time.

Information. Following the hybrid LC cell assembly procedure as described in the Experimental Section, the fabricated cells were irradiated with linearly polarized light (>430 nm) for $n-\pi^*$ excitation (E-isomer) at defined polarization angle, θ . The $n-\pi^*$ excitation with linearly polarized visible light causes reorientation of the rodlike E-isomer photostationary states to become oriented perpendicular to θ . The E-isomer acts as a "molecular rotor" causing azimuthal reorientation of the LCs.¹² An alternative mechanism has been suggested for this photoorientation involving thermal dissipation of the electronic excitation energy in oriented aggregates.²³

The polar plot (extended 180° range) in Figure 3 shows the time evolution of light transmittance through the cell with rotation angle (ϕ) when the cell was irradiated with linearly polarized light filtered > 430 nm at the polarization plane, $\theta = 0^{\circ}$. A 50 bilayer PDADMAC/PAZO film was used as one side of the cell. We observed that, before irradiation, some degree of alignment existed due to the initial effect of loading the LC molecules.¹² The maximum transmittances are approximately located at 45° \pm 90° \times *n*, indicating that the director (S) of the LC molecules exists perpendicular to the polarization plane. The 80% transmittance was reached after 20 min irradiation and 86% after 60 min irradiation. The transmittance through a hybrid LC cell with a 90 bilayer PDADMAC/PAZO was also examined (data not shown). It was found that the maximum transmittance was \sim 56% (after 60 min) and the process of alignment of LC was slower than that for the 50 bilayer PDADMAC/PAZO cell. On the other hand, for a 10 bilayer film, 90% transmittance was reached at 20 min. In our previous studies, the kinetics of photoisomerization of PDADMAC/PAZO film was influenced by the thickness of the samples; i.e., the isomerization is slower for the thicker samples.²⁰

Since the homogeneous alignment of LC molecules is controlled by the photorientation of azobenzenes in PDADMAC/PAZO films, it is clear that the alignment kinetics of the LC molecules can be influenced by the *thickness* of PDAMAC/PAZO film. This indicates that LC reorientation may not simply be a function of the immediate azobenzene layer in contact with the LC molecules,¹³ but is influenced by the overall layer ordering and photoisomerization of the film. This photoalignment behavior is found to be distinct for LBL films in contrast to monolayers and Langmuir-Blodgett films, where the monolayer largely influences the LC alignment behavior.^{9–12} In fact, the addition of more LB multilayers tends to repress azimuthal photoalignment and reorientation.¹⁵ It is well-known that dipole forces, polarity, surface energy, and topological factors influence the surface anchoring energy of LC molecules²⁴ and has been modeled.²⁵ Important differences in the orientation and aggregation of the azobenzene molecules may play an important role. Recent second harmonic generation (SHG) studies of PAZO LBL films suggests thicknessdependent orientation and aggregation where the azobenzene dyes are tilted 20° with respect to the surface normal and with a large degree of interpenetration between layers.²⁶ The LBL PAZO/PDADMAC films are J-aggregated in contrast to most azobenzene molecules in LB films, which tend to be tightly packed and H-aggregated.¹⁵ An important comparison should also be made with spincoated films in which the azobenzene dyes are largely isotropic and also aggregated.27 Thus, there is a need to strongly correlate the ordering on these photoalignment layers and their LC photoorientation behavior.

Phase Shift. To examine azimuthal photoalignment control of the LC molecules in LBL films further, we irradiated uniformly preirradiated cells by linearly polarized light at various axes (θ). Figure 4a shows the *shift* of the transmittance as a function of time when the cell was subsequently irradiated with linearly polarized light from $\theta = 0^{\circ}$ to $\theta = 30^{\circ}$ polarization plane. Before the experiment, the cell was preirradiated with linearly polarized light at $\theta = 0^{\circ}$ for 40 min. After 90 min of irradiation, the full transformation of the molecular axis of the azobenzene to perpendicular to the electric vector of the second light was achieved. Figure 4b shows the transmittance curves after irradiation with the actinic visible light (>430 nm) at $\theta = 30^{\circ}$ and 45°. The results clearly show that the direction of in-plane alignment can be controlled kinetically by changing the angle of the linearly polarized light, θ , resulting primarily in a *phase shift* of the transmittance curves in the polar plot. The transmittance maximum appears periodically at $\theta + \pi/4$ $+ \pi/2 \times n$ (*n* = integral numbers), confirming a homogeneous alignment perpendicular to the polarization plane of the irradiation light.

Stability. The stability of the LC cell was examined against unpolarized light and heat treatment. After the photoirradiated LC cell was exposed to unpolarized light for up to 60 min (Figure 4c), the maximum transmittance was observed to decrease to about 45%. The transmittance curves of the preirradiated cell after 1 h heating at 100 °C was also investigated (Figure 4d). The maximum transmittance was also observed to decrease to 48%. These results are in contrast to the stability of azobenzene SAM induced photoalignment, which is very stable to heat and unpolarized light.¹¹ This clearly shows a unique aspect of LC alignment in LBL films in that stability is dependent on the overall thermal stability of the azobenzene–polyelectrolyte film toward maintaining high anisotropy.

⁽²³⁾ Schonhoff, M.; Mertesdorf, M.; Losche, M. J. Phys. Chem. 1996, 100, 7558.

^{(24) (}a) de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*;
Clarendon Press: Oxford, 1993. (b) Chandrasekhar, S. *Liquid Crystals*,
2nd ed.; Cambridge University Press: Cambridge, UK, 1992.
(25) Palto, S.; Barberi, R.; Iovane, M.; Lazarev, V.; Blinov, L. *Mol.*

⁽²⁵⁾ Parto, S.; Barberi, K.; Iovane, M.; Lazarev, V.; Bilnov, L. *Mol. Mater.* **1999**, *11*, 277. (26) (c) Coscon L: Wang H: Poherts, L: Parikh A: Pohinson L:

^{(26) (}a) Casson, J.; Wang, H.; Roberts, J.; Parikh, A.; Robinson, J.; Johal, M. J. Phys. Chem. B **2002**, 106, 1697. (b) Lvov, Y.; Yamada, S.; Kunitake, T. Thin Solid Films **1997**, 300, 107.

⁽²⁷⁾ Gibbons, W.; Shannon, P.; Sun, S.; Swetlin, A. B. *Nature* **1991**, *351*, 49.



Figure 4. Radial plots at 180° showing (a) shift of angular dependence of transmittance from $\theta = 0^{\circ}$ to 30° as a function of exposure time, (b) LC alignment phase shift properties of irradiated hybrid cell at different angular positions ($\theta = 0^{\circ}$, $\theta = 30^{\circ}$, and $\theta = 40^{\circ}$), (c) angular (ϕ) dependence of transmittance of monitoring He–Ne laser beam through the cell upon exposure to unpolarized light (>430 nm) as a function of exposure time, and (d) transmittance before and after heating at 100 °C for 1 h. The cell is irradiated with linearly polarized light ($\theta = 0^{\circ}$) in advance.

Based on the thickness-dependent photoalignment behavior, the stability should also be correlated with thickness.

Conclusions

In this work, we have demonstrated the utility of PAZO/ PDADMAC LBL films for controlling LC azimuthal alignment. Irradiation of a hybrid LC cell with linearly polarized light resulted in in-plane homogeneous LC alignment, which is dependent on the thickness, irradiation time, orientation, and stability of the films. The director of the LC molecules was found to be perpendicular to the polarization plane θ and can be reoriented. In the future, it will be interesting to focus on any unique mechanism of photoalignment for this type of films. The parameters for LBL film preparation and polyelectrolyte design can be optimized for the photoalignment process and even allow patterning.

Acknowledgment. We thank Dr. Akira Baba (MPI-P) for his help during the setup of the photoinduced birefringence experiment. We also acknowledge collaborations with the groups of Prof. Kaneko from Niigata University (Dr. Kato and Dr. Shinbo). Funding from ACS-PRF, PRF-35036-G7, is gratefully acknowledged.

Supporting Information Available: Ellipsometry measurements, details of the retardation measurement setup, procedure for conversion of X-Y charts to polar plots, and kinetics of the photoalignment process. This material is available free of charge via the Internet at http://pubs.acs.org.

LA015771A